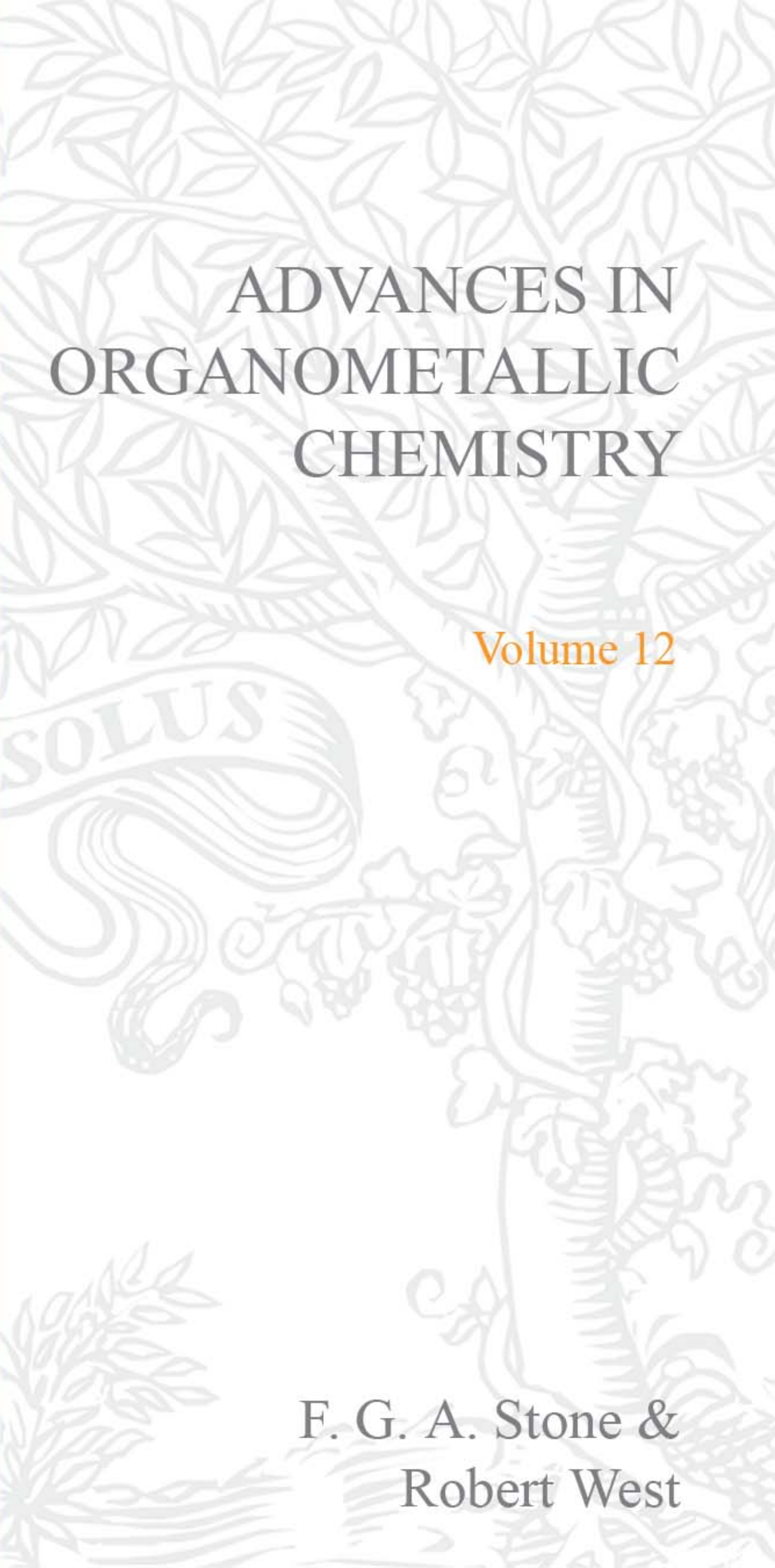

ADVANCES IN ORGANOMETALLIC CHEMISTRY

Volume 12

F. G. A. Stone &
Robert West

Advances in

ORGANOMETALLIC CHEMISTRY

VOLUME 12

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Advances in Organometallic Chemistry

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The Literature of Organo-Transition Metal Chemistry 1972

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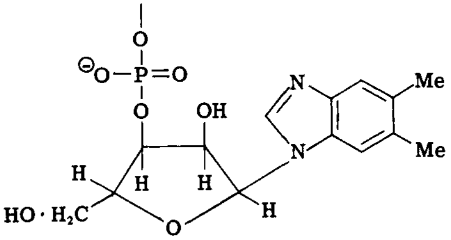
Erratum

Volume II

Page 93. The sentence starting on line 3 under Eq. (13) should be changed to read:

For example, the reaction in Eq. (14) is followed by the elimination of CO from the acyl as shown in Eq. (15) (*219*).

Page 337, bottom of page. The following structure should appear next to structure (IIIa):



(IIIb)

The Organic and Hydride Chemistry of Transition Metals

JOSEPH CHATT

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I am grateful to the Editors of *Advances in Organometallic Chemistry* for their invitation to describe the development of organo-transition metal chemistry in my laboratory as I saw it. The year 1937, when I graduated from Cambridge, provides a suitable starting point, although my interest in organometallic compounds and chemical bonding had roots dating back to my school days.

During the past 35 years many threads of thought and experiment, from a great number of laboratories, have contributed to our present relatively vast but still rapidly growing knowledge of organo-transition metal chemistry. Textbooks and reviews provide sufficient summary of this chemistry as it developed, and it is not my remit to produce a digest of it. This article is a subjective account of how I saw developments originating in my laboratory. It is subjective because the results of one's own research are learnt first and one's thoughts and future experiments are shaped largely by them. Nor do I intend to dwell on detailed chemistry; it is mostly published. I propose to emphasize highlights, initiation, and motives. All good research raises as many or more problems than it solves. It provides a number of parallel lines all pointing to the same general goal and a choice must be made between them. The goal is necessary to provide the direction needed to make a substantial and unique advance in any subject. My general goals were, in order:

1. To understand more thoroughly the nature of the coordinate bond and to apply this knowledge to determine the nature of the bonding of simple unsaturated hydrocarbons to the metal in their complexes.
2. To find the reason for the instability of simple transition metal alkyl, aryl, and hydride derivatives.
3. To discover a means of activating dinitrogen in a catalytic manner on transition metal ions.

The latter is outside the scope of organometallic chemistry, but within the first two topics the work involved three main themes: olefin and acetylene complexes, alkyl and aryl complexes, and hydride complexes. As continuous subsidiary themes throughout ran the complex chemistry of tertiary phosphines and such ligands, the nature of the trans effect, and the nature of the coordinate bond. All the work from 1947 to 1969 was carried out in the Butterwick Research Laboratories, later renamed Akers Research Laboratories, of Imperial Chemical Industries Ltd., and I am indebted to that Company and particularly to Mr. R. M. Winter, the Company's Controller of Research, and Sir Wallace Akers, its Director of Research, who in 1947, made available to me the opportunity to develop my research in my own way, in those laboratories.

I

PRELIMINARIES

It must be very difficult for anyone graduating now to realize how little was known about organo-transition metal chemistry in 1937. We were taught the extraction of the metals from their ores, the properties of their oxides and simple salts in terms of the Periodic Law, and a very little complex chemistry. Although Departments of Physical Chemistry were well established, they were still young, and physical methods other than electrolytic methods found very little application in the study of complicated organic or inorganic compounds. Infrared spectrometers were sophisticated and temperamental instruments, applied mainly to the study of spectroscopy as such and to simple molecules such as HCl and NH_3. They had not yet become tools of the preparative chemist. Visible and ultraviolet spectroscopy was then rarely used and mainly to identify and determine quantitatively substances whose spectra were known. Magnetic spectroscopy was unknown. Elemental analysis was done on a microscale using 0.3 mg rather than the 0.1 gram scale which had been used only a decade earlier. Electrolytic conductivity, magnetic moments, and dipole moments might be used by preparative chemists in departments where the equipment was available, but such equipment was not available commercially and usually had to be assembled by the potential user. For these reasons physical methods were rarely applied. Melting points were the main criteria of identity and purity, and these were determined in capillary tubes closed at one end and attached to the bulb of a thermometer by the surface tension of the concentrated sulfuric acid or oil used as the fluid which was warmed to melt the specimen. There was little money for research and I remember a certain feeling of elation when we were able to obtain £10 for the purchase of an electric, copper-block melting-point apparatus. Research students, at least in theory and often in practice, bought their own chemicals and paid for any apparatus they broke. The laboratory benches in Cambridge were lighted by gas, and the gas ring and Bunsen burner were the only forms of heating for chemical reactions and distillations. Interchangeable ground glass joints were newly introduced and expensive, and kept for especially difficult preparations such as that of trialkylphosphines; normally rubber bungs sufficed.

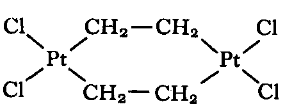
The organic chemistry of the Main Group elements had reached a fairly advanced stage. It was known that the halides of most of the Main Groups elements, on treatment with organomercury compounds or Grignard reagents, would yield simple organic derivatives of the general formula R_nMX_{m-n} (m = the valency of the metal M, and X = halogen). The reactions of organomercury compounds had been extensively studied, and Grignard reagents were important reagents in organic chemistry. Lithium reagents were in their infancy, and dialkylzinc compounds as reagents in organic chemistry had long passed out of use.

The chemists who had taken part in the development of the organic chemistry of the Main Group elements over the past 75 years had tried to prepare similar organo-transition metal derivatives analogously. They had achieved remarkably little; the only extensive and apparently simple organo-transition metal chemistry being that of chromium, developed by Hein from 1919 (*50*). He had reported pentaphenylchromium salts, tetraphenylchromium salts, and triphenylchromium and its salts, but others had had difficulty in repeating his work. His compounds were finally reformulated in 1954 as sandwich compounds, containing hexahaptobenzene and hexahaptobiphenyl as ligands (*73*).

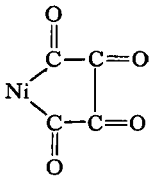
Between 1928 and 1937 A. E. Goddard's four books on "Organometallic Chemistry" were published (*50*). They gave, in 1449 pages of text, a detailed account of the organometallic compounds known at that time. The organometallic compounds of boron, silicon, phosphorus, and selenium as well as those of the more metallic elements were all included. There were 457 pages on arsenic alone, and mercury occupied 190 pages; yet all the transition metals together, from the scandium to the copper groups, occupied only 12 pages, ½ a page to copper and silver, 1 page to gold, 1½ pages to platinum, and 9 pages to chromium. It is not surprising that the chemists of the day believed that transition metals had no organic chemistry of any consequence.

Olefin complexes and metal carbonyls were not considered to be organometallic compounds, any more than were the complex cyanides. Very few olefin complexes were known, the only firmly established ones being those of palladium(II), e.g., $[Pd_2Cl_4(C_2H_4)_2]$; platinum(II), e.g., $K[PtCl_3(C_2H_4)]$ and $[Pt_2Cl_4(C_2H_4)_2]$; copper(I), e.g., $CuCl(C_2H_4)$; and silver(I), e.g., $[Ag(olefin)aq.]NO_3$. There was considerable mystery concerning the bonding of the olefin to the metal. Only the platinum complexes were sufficiently stable for detailed study and these were often formulated as containing platinum(IV) substituted into ethane, sometimes to form a three-membered ring, sometimes to form a six-membered ring, e.g., (I). The binary carbonyls were mysterious substances with no definite place in either organic or inorganic chemistry. They were usually mentioned in books on inorganic chemistry in connection with Mond process for the refining of nickel. They were even formulated as organic compounds with ring structures, such as (II) for $Ni(CO)_4$, which structure illustrates well the confusion which existed between "oxidation state" and "valency." The explosive "potassium carbonyl" was then known to be the potassium salt of hexahydroxybenzene.

Professor Hieber has described the early development of the chemistry



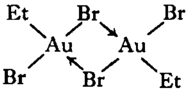
(I)



(II)

of the metal carbonyls (*52*). Because these substances appeared to be exotic they had very little influence on the early development of organo-transition metal chemistry. Carbon monoxide was also known to form complexes with metal halides, e.g., $[PtCl_2(CO)_2]$, and in these it was recognized to be a ligand exactly equivalent to ammonia in the corresponding platinum(II) ammines. Many chemists also recognized that ethylene in Zeize's salt, $K[PtCl_3(C_2H_4)]H_2O$, which had been discovered in 1827, was behaving like a molecule of ammonia in a platinum(II) complex salt, although ethylene would not fit into the lone-pair theory of coordination.

In common with everyone else at that time, I believed that the transition metals formed no alkyl or aryl derivatives, except perhaps analogs of the mysterious phenylchromium compounds, and the alkylbromogold compounds, e.g., $AuEt_2Br$ and $AuEtBr_2$, which had been formulated as halogen-bridged compounds (III or IV) (*47*).



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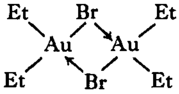
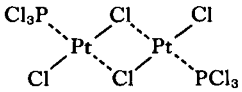


(IV)

Even the halogen bridge was a subject of controversy, although chemists from Werner's school had formulated halogen-bridged compounds, e.g., Schützenberger's $[Pt_2Cl_4(PCl_3)_2]$, as (V) in 1923.



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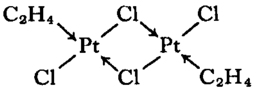


(VI)

Such formulations were not universally accepted because of the fixed idea in many chemists' minds that chlorine in metal salts should always be monovalent, i.e., form one bond. However, in the middle 1930s the existence of halogen bridges was established beyond doubt by X-rays

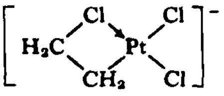
(*10*). The only problem remaining in formulating say, ethylene platinous chloride (VI), was how the olefin attached itself to the transition metal atom. There were reports of ill-defined zinc- and aluminum-olefin complexes, and most chemists, if they thought of them at all, believed that olefin compounds, though much less stable and less numerous than the ammines, occurred just as widely.

My research for the Ph.D. degree was conducted with Dr. F. G. Mann. Although this work was not concerned with organo-transition metal compounds, it involved the preparation of tertiary alkylphosphines and arsines and their use as ligands to produce halogen-bridged compounds of palladium. These were soluble in organic solvents, and this facilitated the study of the reactions of the halogen bridge. After this I made an incursion into the preparation of diarsines and some of their complex compounds having asymmetric centers. In this way I acquired a background of techniques in the organometallic field and a knowledge of coordination chemistry, which was usually taught only cursorily in undergraduate courses. The knowledge of complex chemistry proved to be vital for the preparation and study of stable hydride, alkyl, aryl, and other organo-transition metal compounds.

II

OLEFIN AND ACETYLENE COMPLEXES

My first incursion into organo-transition metal chemistry occurred because of my interest in chemical bonding. How did olefins with no lone pair of electrons form coordinate bonds to metal atoms? The position in 1941 can be read in Keller's review on olefin complexes (*54*). During the war years I was able to assemble a card index of all references to olefin complexes and I convinced myself that they should be formulated as chelate complexes of, for example, structure (VII) for Zeise's ion; if chlorine could bridge metal atoms why should it not bridge carbon to a metal? *Nature* rejected my letter on this topic as being



(VII)

"too speculative." My evidence was mainly taken from the properties of the products of the reaction of olefins with mercuric salts, e.g., $HgCl(OH)(C_2H_4)$ from ethylene and $HgCl_2$ in aqueous solution, now known to be $HOCH_2CH_2HgCl$. At that time there was some slight controversy about the nature of these organomercurials because they readily regenerated the olefin on treatment with halogen acid, and regenerated a *cis*-olefin when a *cis*-olefin was used in their preparation. A thorough examination of the literature, and a few experiments, convinced me that *Nature*'s referee was right. I never attempted to publish the experiments but the literature survey appeared as a review (*15*).

Some attempts which I had made in 1946 to obtain $PtPh_2$ or $[PtPh_4]^{2-}$ from the reaction of phenylmagnesium bromide with $[\{PtCl_2(C_2H_4)_2\}_2]$ in ether had yielded biphenyl as the only pure solid product, and this served to confirm in my mind the belief that transition metals had no "normal" organometallic chemistry. I decided then to concentrate on the platinum(II)-olefin complexes. The first question was whether the olefin–metal bond used the *d* electrons normally involved in the oxidation of platinum(II) to platinum(IV) (valence *d* electrons) to bind the olefin, as required by such structures as (I), or whether, as was then generally believed, they were olefin coordination compounds formed independently of the presence of *d* electrons, even by Main Group element ions.

The bridged compound $[Pt_2Cl_4(C_2H_4)_2]$ (VI) has rather poor solubility in cold organic solvents, except in ethanol and acetone in which it is not very stable, and I attempted to obtain more soluble platinum(II)-ethylene complexes by introducing trialkylphosphines according to Eq. (1). In fact ethylene was lost and $[Pt_2Cl_4(PR_3)_2]$ was obtained instead.

$$[Pt_2Cl_4(C_2H_4)_2] + 2PR_3 \longrightarrow 2[(PtCl_2(C_2H_4)(PR_3)] \qquad (1)$$

Halogen-bridged platinum(II) complexes of the tertiary phosphines, arsines, etc., were then unknown and they had properties well worth studying for comparison with those of their palladium analogs. Also, they could be oxidized to platinum(IV)-bridged species, and these showed marked instability compared with their platinum(II) analogs. This led me to speculate that the electrons in the *d*-orbitals of platinum(II) in some way stabilized the halogen-bridged $Pt^{II}Cl_2Pt^{II}$ ring relative to the $Pt^{IV}Cl_2Pt^{IV}$ ring. It is noteworthy that the most stable halogen-bridged species are those where the metal is in a low oxidation state and I thought that electron donation from the filled *d* orbitals of the less positively charged metal played an essential part in stabilizing the ring (*13*). This led to a general study of sulfur-bridged platinum(II) species which are particularly stable and eventually to diphenylphosphide-bridged species, both of which show properties which suggest that the ring is more than a simple σ-bonded four-atom system (*21*). It also led to a general study of tertiary phosphine complexes of platinum(II) halides and related species to determine qualitatively the affinities of such ligands as the tertiary phosphines, arsines, stibines, and bismuthines, and also the ethers and organic sulfides, sellenides, and tellurides for platinum(II), all in connection with elucidating the nature of the coordinate bond and the possible role of the filled metal *d* orbitals in the bonding. This culminated in a review of the relative affinities of ligand atoms for acceptor molecules and ions. In it an attempt was made to explain the differences between the coordinating powers of the transition metal ions in their low oxidation states as compared with their higher oxidation states and with the Main Group metals in terms of the availability of electrons from the *d* orbitals in the former to contribute to the strength of the coordinate bond (*5*).

In 1947 Walsh (*68*) proposed that because the ionization potential of the π electrons in ethylene and of the lone pair in ammonia are both around 10.5 eV, the π electrons in the olefins should be equally capable of donation to acceptor centers. This implied that olefin complexes should be much more widespread than they were.

I decided that the reaction of ethylene with trimethylborane would provide a very good test of Walsh's idea because Brown was then showing that trimethylborane produced a great number of nonvolatile adducts by direct addition to Lewis bases (*9*). The formation of those adducts required no activation energy and so occurred readily at low temperatures. A freezing point curve of the liquid mixtures of trimethylborane and ethylene should demonstrate complex formation unequivocally if such occurred, but no complex, $Me_3B \cdot C_2H_4$, was found. From this I concluded that the two valence *d* electrons in platinum(II) and similar atoms which form olefin complexes were probably necessary in the bonding of the olefin to the metal (*12*). If they were, they would impose an absolute limit of one olefin molecule to one metal atom—as had always been observed. However, our discovery of dichlorobis(ethylene)-platinum (*38*) indicated that something more subtle than the use of the two valence *d* electrons was involved.

Olefin complexes had been extensively studied by Gel'man in Moscow and her review (*45*), which reached me in the late 1940s, introduced me to the Russian literature and the trans effect. Olefins, like carbon monoxide, had a high trans effect. Anderson (*6*) had earlier drawn attention to the fact that the olefin complexes of platinum(II) chloride resembled the carbonyl complexes, and my experience of palladium(II) and platinum(II) tertiary phosphine and arsine complexes indicated to me that they also had some similarity. This raised the question as to what these three types of ligands, CO, C_2H_4, and PR_3, had in common. Did they all involve *d* electrons from the metal in bonding to the metal? Pauling (*63*) supplied a possible answer, as did a paper by Phillips, Hunter, and Sutton (*64*). Pauling had noticed that in the structures of the metal carbonyls which had now been determined, the metal-to-carbon bond was rather shorter than the sum of the covalent single bond radii, and he suggested that the nonbonding *d* electrons were used in forming a double bond from the metal to the carbon monoxide ligand. Phillips, Hunter, and Sutton had similarly explained the low dipole moments and short intratomic distances in such substances as the phosphine oxides as evidence for the formation of double bonds between oxygen and phosphorus. This would now involve the donation of *p* electrons from oxygen into the *d* orbitals of the phosphorus. Could it be that in the tertiary phosphine complexes of platinum(II) there was similarly a double bond between the platinum and phosphorus with electron drift from the *d* orbitals of the platinum into the *d* orbitals of the phosphorus (Fig. 1)? R. S. Nyholm, lately come from Australia, whom I had met in 1947, had very similar ideas concerning coordinate bonding

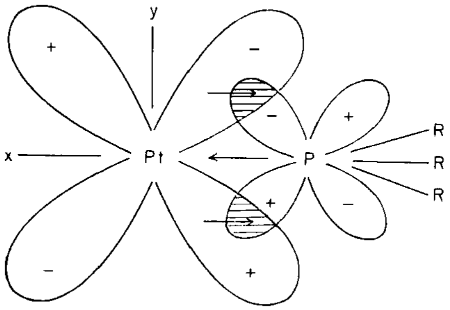


FIG. 1. Schematic molecular orbital representation of the dative π-type bond.

in tertiary arsine complexes, and from that time he and I kept in close touch with each other and with Dr. L. E. Sutton in Oxford.

Concentrating my attention on platinum(II) chemistry, I sought ways to enhance the strength of double bonding between phosphorus and platinum, if it existed. The π-type bond could be visualized as being formed by the overlap of the filled d_{xy} orbitals of the phosphorus to form a π-type bond (Fig. 1). Equivalent d orbitals are available in planes at right angles (d_{xz}) and the Pt—P bond would be essentially a triple bond. Since the electrons are provided entirely by the platinum atom it seemed that the more electronegative the group R, the greater would be the electron drift to the phosphorus and the stronger the π-type bonds. This led me naturally to try phosphorus trifluoride as an exceptionally electronegative phosphine. It was soon shown to have no affinity at all for trimethylborane; in this respect it appeared to be in the same class as ethylene and carbon monoxide. However, if bonding of the type visualized in (Fig. 1) occurred it might form very stable complexes with platinum(II). You can imagine the excitement when, on passing phosphorus trifluoride through a plug of platinum(II) chloride at 200°C, I (*14*) observed the production of a colorless complex $[PtCl_2(PF_3)_2]$ and an orange complex $[Pt_2Cl_4(PF_3)_2]$, subliming out in exactly the same way as Schützenberger (*66*) had described in his preparation of the corresponding carbon monoxide complexes. The production of these compounds and the fact that PF_3 would not combine with trimethylborane, was entirely consistent with a bond of the type (Fig. 1) which I dubbed a dative π bond (*14*). This π-type bonding is now more generally known as π-bonding or back-bonding, but then the problem was how to apply this particular type of bonding to explain the olefin-platinum(II) bond, and would such bonding provide an explanation of the trans effect?

A characteristic feature of the carbonyl, ethylene, and phosphorus trifluoride complexes of platinum(II) chloride was the easy formation of the halogen-bridged complexes $[Pt_2Cl_4L_2]$ ($L = Co$, C_2H_4, or PF_3) from the simple complexes $[PtCl_2L_2]$, in marked contrast to the difficulty experienced when $L = PR_3$ or AsR_3. This could be explained if those three ligands had a very high trans effect, so labilizing the group in the trans position to themselves and facilitating the condensation of the mononuclear species to form bridged species. For this reason it became important to find out whether there was any relation between dative π-bonding and the trans effect, and also to apply the idea of dative

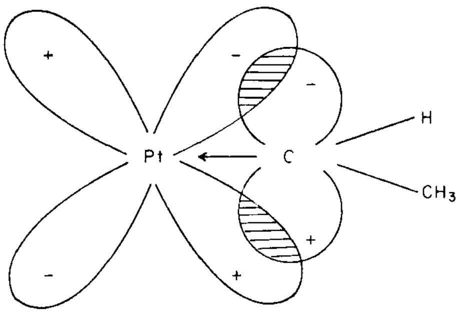


FIG. 2. Schematic molecular orbital representation of the ethylidene structure.

π-bonding to formulate a molecular orbital picture of the Pt–olefin coordinate bond.

Anderson (*6*) had noted that the platinum-ethylene complexes in boiling water produced acetaldehyde, and Schützenberger (*66*) had noted the extreme sensitivity of the carbonyl complexes of platinum(II) to moisture, with which they reacted to form carbon dioxide. It seemed to me that these two reactions were equivalent and that the ethylene complexes might be formulated as ethylidine complexes (*16*) (methylcarbene complexes) (Fig. 2), analogous to Pauling's formulation of the M—CO bond in the carbonyls. Some considerable evidence was educed in favor of that structure but all attempts to produce 1,1′-dichloroethane by chlorination showed that $[Pt_2Cl_4(C_2H_4)_2]$ had a remarkable resistance to complete chlorination and when the chlorination was forced it produced 1,2-dichloroethane and none of the 1,1′-isomer. In the meantime Dewar (*43*) had produced a structure for the silver-olefin complexes, essentially Pitzer's (*65*) argentated double bond modified by back-donation of electrons from the *d* orbitals of the silver ion into the antibonding orbitals of the olefin. This structure was easily applicable to the platinum(II)-olefin complexes, leading to the well-known structure (Fig. 3). Infrared spectroscopy had now become established as a tool of the organic chemist, and I was joined by Dr. L. A. Duncanson who was an expert in this technique. Some four years earlier I had attempted an infrared investigation of ethylene-platinum(II) complexes but had obtained no useful spectra or information. Now the infrared spectra, much better resolved, showed definitely that the ethylene in the platinous complex was essentially unchanged, as required by the structure (Fig. 3), and the study of the dipole moments of certain ethylene complexes

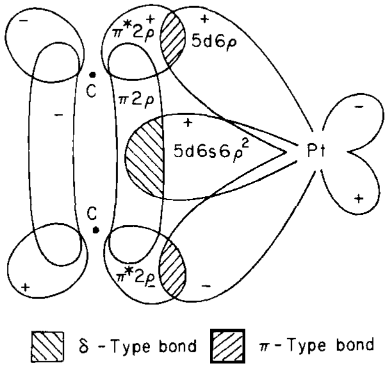


FIG. 3. Schematic molecular orbital representation of the ethylene-platinum bond. Reproduced from J. Chatt and L. A. Duncanson, *J. Chem. Soc.* 2939 (1953), by permission of the Chemical Society.

indicated that the platinum–olefin bond had a probable bond order of about 1.3.

An interesting observation for the history of organo-transition metal chemistry was that of Gel'man and Gorushkina (*46*), who had observed that the reaction of methylmagnesium iodide and Zeise's ion $[PtCl_3(C_2H_4)]^-$ produced trimethylplatinum iodide. They had presented this as evidence that the platinum was quadrivalent. I repeated their work exactly, and also using Na_2PtCl_4 as an indisputable source of platinum(II), and still obtained trimethylplatinum iodide. This product obviously resulted because they had used a large excess of methyl iodide in preparing the Grignard reagent. Evidently dimethylplatinum(II) had been produced as a sufficiently stable intermediate to allow methyl iodide to form trimethylplatinum(IV) iodide by a reaction now known as oxidative addition. This set me considering how to stabilize the dimethylplatinum, and it led eventually, in 1954, in collaboration with Dr. M. E. Foss, to the production of the first tertiary phosphine ligand-stabilized alkyl complex of the Group VIII metals. It was not published until 1959 because the dative π bond occupied my attention and the 1954 attempts to extend the series to phenyls and higher alkyls showed little promise.

It is obvious that two ligand atoms with a very strong tendency to form dative π bonds could not both bond strongly to the platinum if they were in mutually trans positions, because they would be competing for electrons from the same *d* orbitals to form the multiple bond. On the other hand, if they were in cis positions they would interact with different *d* orbitals and stronger back-bonding would be expected. Since dative π-bonding appeared essential for holding carbon monoxide and phosphorus trifluoride to the platinum, one would expect to find that trans isomers of the composition $[PtCl_2L_2]$ ($L = CO$ or PF_3), if they existed at all, would be unstable substances. Therefore the two colorless substances of those compositions which are obtained on passing the appropriate gases over hot platinum(II) chloride should be cis isomers, confirmed by measuring their dipole moments. Furthermore, the dipole moments were only about half those of *cis*-$[PtCl_2L_2]$ ($L = PR_3$ or AsR_3); not only had the compounds a cis configuration as required, but the back-donation of electrons in the dative π bond was sufficient to have neutralized almost completely the dipole moment of the σ-donor bond from the CO or PF_3 to the platinum (*41*). The relative stabilities of the isomers of $[PtCl_2(C_2H_4)_2]$ were also in accord with the above (*38*).

It was still a question as to whether the trialkylphosphines and -arsines formed weak double bonds with platinum(II). If they did then one might expect that the isomers, *cis*-$[PtCl_2(QR_3)_2]$ ($Q = P$, As, or Sb), would be stabilized relative to the corresponding trans isomers. With Dr. R. G. Wilkins, equilibria between cis and trans isomers were measured and, interestingly, the indications were that the phosphine and stibine complexes probably gained more in metal-to-ligand atom bond strength by double bonding than did the corresponding trialkylarsine complexes (*39*). This accords very nicely with the existence of phosphorus and antimony pentachlorides and absence of arsenic pentachloride. The *d* orbitals of arsenic are evidently less forthcoming for either π-type or σ-bonding than are those of phosphorus or of antimony. Nevertheless it seemed that double bonding in all the QR_3 platinum(II) complexes was relatively slight as compared with that found in the carbonyl, olefin, and phosphorus trifluoride complexes.

Out of the study of the dative π bond there developed an attempt to explain directing effects in platinum(II) substitution reactions in terms of dative π-bonding. This work has little to do with organometallic chemistry and will not be described here. It is enough to say that the double-bonding hypothesis was invoked to explain the strong trans-directing effect of olefins and such ligands. This was rationalized in terms of a bimolecular mechanism whereby the displacing ligand attacked the platinum atom on the side trans to the olefin, from which the *d* electrons had been withdrawn by the olefin, and so displaced the trans ligand (*26*). This hypothesis, independently proposed by L. E. Orgel (*60*), stood until ligands such as H^- and CH_3^-, which could not form dative π bonds, were found to have very high trans effects (see Section III).

A brief incursion into nontransition organometallic chemistry, apart from the preparation of organophosphines and such ligands, occurred in an attempt to determine whether back-bonding from platinum(II) to the tertiary phosphines, arsines, or stibines was likely to be strong by looking for analogs in terms of more familiar molecular systems. The aromatic system seemed a possible model for the platinum(II) atom, the π system of the benzene ring being an analog for this purpose of the *d* orbital system of the metal. The trans-directing effects of ligands in the substitution reactions of platinum(II) complexes resemble superficially the directing effects in aromatic chemistry, ligands of high trans effect corresponding to strongly *ortho–para*-directing substituents. In a series of analogous acids p-R_3MC_6COOH (R = Me or Et, M = C, Si, Ge, or Sn) one would expect, in the absence of any $d\pi$–p_π-bonding between the atom M and the aromatic ring, that the acid strengths would fall in the order of decreasing electronegativity of M (i.e., C $\gg$ Si $>$ Ge $>$ Sn). On the other hand, if dative π-bonding occurred, the mesomeric release from the ring into the *d* orbitals of the elements M, possible only when M = Si, Ge, or Sn, would raise the strengths of those acids relative to the carbon acid. The above three acids were found to be stronger than the carbon acid, and so indicated that the heavier atoms did receive electron density from the π system of the aromatic ring. The differences in strength were not great, but by analogy provided a *prime facie* case for the existence of weak dative π-bonding in the closed-shell transition metal complexes of tertiary phosphines, arsines, and stibines (*42*). Although this interpretation has since been challenged (*72*) the acid strengths are so close as to preclude any strong dative π-bonding from the aromatic system to silicon, and also by analogy from platinum(II) to phosphorus.

It was somewhat puzzling that while olefin compounds of platinum(II) were well established, acetylene complexes were virtually unknown. Acetylene gives red intractable materials on reaction with potassium chloroplatinate(II) in aqueous solution, presumably acetylides; and dimethylacetylene does not react, in marked contrast to ethylene, which forms $[PtCl_3(C_2H_4)]^-$. However, Gel'man, Bukhovets, and Meilakh (*44*) had been able to obtain stable acetylene complexes from the acetylenic glycol, e.g., $HOCMe_2C{\equiv}CCMe_2OH$ (ac), which formed a Zeise-type salt $K[PtCl_3(ac)]$, and *cis*-$[PtCl_2(ac)(NH_3)]$ by the methods commonly used to prepare the corresponding olefin complexes. With R. G. Guy, I set out to find whether the OH groups were necessary for the stability of those acetylene complexes. Much to our surprise we found that di-*t*-butylacetylene also formed stable acetylene complexes and indeed any mono-*t*-butylacetylene except *t*-butylacetylene itself, of those we tried, gave complexes sufficiently stable to isolate. It seemed necessary to have at least one bulky group in the acetylene. Presumably the acetylene complexes were stabilized by sterically preventing solvent-assisted dissociation of the complex. Generally the acetylene complexes isolated (*25*) had similar properties to those of their olefin analogs and will not be discussed further.

III

ALKYL AND ARYL COMPLEXES

A. *Formed by Reaction of Complex Halides with Grignard and Lithium Reagents*

The platinum(II) methyls discovered in 1954 in collaboration with Dr. M. E. Foss (Section II) had then been shown to add methyl iodide to form the platinum(IV) $[PtIMe_3(PR_3)_2]$ type of derivative, so confirming the view that Gel'man and Gorushkina (*46*) had obtained trimethylplatinum iodide from dimethylplatinum(II) by the oxidative addition of methyl iodide. The thought behind attempts to stabilize the platinum(II) alkyls arose because we now knew that dimethylplatinum, although too unstable to isolate, had sufficient life to react with methyl iodide, whereas gold in the next group formed reasonably stable and easily isolated ethyls, e.g. $[(EtAuBr_2)_2]$ and $[(Et_2AuBr)_2]$, and mercury from the next group again gave relatively very stable alkyls, e.g., $[Hg(CH_3)_2]$. The only change as one passes along that period from platinum(II) to mercury(II) is the lowering of *d*-orbital energy as one leaves the transition metal series. The problem was how to make platinum(II) behave like mercury(II). Evidently one must lower the *d*-electron energy level. After all the work on dative π-bonding there seemed no better method than to use a ligand atom such as phosphorus which, by draining some electronic charge from the *d* orbitals to form the dative π bond, would lower the energy level of the electrons in those orbitals. This, one realized later, is the equivalent of using ligands of high ligand-field strength and certainly the experiments based on that argument worked beyond all expectation.

In general Dr. B. L. Shaw, who joined me at this stage, found that mono- and dimethyl derivatives were obtained by the reaction of methylmagnesium halide with either *cis*- or *trans*-$[PtX_2(PR_3)_2]$ (X = Cl or Br; PR = tertiary phosphine) and these methyl derivatives, like mercury dimethyl, were not hydrolyzed by dilute acids nor oxidized in air. They appeared to be stable indefinitely. *cis*-$[PtMe_2(PEt_3)_2]$ could be distilled at 85°C in a high vacuum in very marked contrast to the transient $PtMe_2$ itself. The higher alkyl platinum complexes were less stable because of the elimination of olefin with formation of a platinum hydride complex, but this was only discovered years later (*20*); the platinum hydride complexes had not even been thought of when the methyls were isolated. The platinum aryl derivatives were also surprisingly stable. A great number of alkyl and aryl platinum compounds were prepared and studied, and also the oxidative addition of methyl iodide to some of them (*31*).

The formation of the analogous palladium derivatives was less successful because the compounds were less stable. When we learned that Professor G. E. Coates was doing similar work and had prepared more palladium derivatives than we, we turned to the corresponding nickel compounds. Extrapolating stability from platinum through palladium we did not expect to find any stable organonickel analogs. The first experiments came up to this expectation. Methyl nickel derivatives, e.g., $[NiMe_2(PEt_3)_2]$, were undoubtedly formed at low temperatures by reaction of MeMgBr on $[NiBr_2(PEt_3)_2]$, but decomposed during attempted isolation. The diphenyls $[NiPh_2(PR_2)_2]$ were obtained crystalline but impure, spontaneously breaking down to give biphenyl. We then attempted again to apply our principle of lowering the *d*-electron energy level of the metal. For this we needed to increase electron withdrawal from the phenyl groups and decided to try *p*-chlorophenyl. At the time, however, *p*-bromochlorobenzene was not immediately available to make the *p*-chlorophenylmagnesium bromide and Dr. F. A. Hart who was preparing *o*-chlorophenylmagnesium bromide as an intermediate on the way to *o*-phenylenebis(diethylphosphine) said "Why not try my

Grignard?" We did, and it worked surprisingly well. The very stable d^8 planar bis(*o*-chlorophenyl)bis(diethylphenylphosphine)nickel compound resulted. The principle of lowering *d*-orbital energy levels was working beyond expectation, or so it seemed, but when the *p*-chlorophenyl analog was finally prepared it was found to be no more stable than the unsubstituted phenyl derivative. The stabilization was a simple steric effect of the *o*-chloro substituent, and indeed any ortho substituent, whether electron-withdrawing or not, was sufficient to stabilize the nickel complexes of the types $[NiRCl(PR'_3)_2]$ and $[NiR_2(PR'_3)_2]$ (R = *o*-substituted phenyl). A number of such derivatives were made and those with two ortho substituents, for example, the mesityl and pentachlorophenyl derivatives, were particularly stable. We then attributed the stabilizing effect of the ortho substituent to its preventing rotation of the phenyl about the Ni–C bond, so that its π system interacted solely with the highest energy nonbonding *d* orbital to lower its energy (*32*). Success with nickel encouraged us to try cobalt and iron analogs (*33*). No cobalt complexes, $[CoCl(aryl)(PR_3)_2]$, were stable. The $[Co(aryl)_2(PR_3)_2]$ type required one large or two small ortho substituents for stability and the compound $[Co(mesityl)_2(PEt_2Ph)_2]$ was particularly stable. Its structure (by X-ray) showed its molecule to be highly congested around the cobalt atom; the ortho substituents introduced such steric strain that the molecule bent at the aryl carbon atoms attached to the cobalt atom in such a way that the methyl groups were able to lie side by side over the cobalt atom (*62*). Evidently the main effect of the ortho substituent is to prevent the attack of reagents or solvent at the metal atom, or the rearrangement of ligand atoms from the planar to the tetrahedral configuration. Such rearrangement would have lowered the ligand-field splitting by the ligands and so destabilized the organo complex. The bis(pentachlorophenyl) complex $[Co(o\text{-}C_6Cl_5)_2(PEt_2Ph)_2]$ was exceptionally stable, and the corresponding iron complex, $[Fe(C_6Cl_5)_2(PEt_2Ph)_2]$, was the only stable iron complex obtained. This is a most unusual iron(II) complex, being four-coordinate and planar with two unpaired electrons. It seemed that for stability one needed everything one could give the metal: a highly congested complex to prevent attack at the metal, and as many electronegative substituents as possible in the phenyl ring to bring down as far as possible *d*-orbital energy level on the metal.

An interesting point which arose in connection with the cobalt and iron complexes was that the complex compounds $[MCl_2(PR_3)_2]$ (M = Ni, Co, or Fe) are sufficiently unstable to smell of the phosphine if it is volatile. Nevertheless the organic derivatives $[MR_2(PR'_3)_2]$ do not have the phosphine smell. It was evident that not only did the phosphines stabilize the M—C bond, but that the carbon radicals themselves with their high ligand-field strengths (*28*) stabilized the M—P bonds. Thus the whole complex was tightened up.

This suggested that if all the halogen atoms in the complex compounds of the transition metals could be replaced by hydrocarbon radicals, the resultant complex, for example, K_2PtR_4, should be stable. The main problem is to find a method of synthesis whereby one does not go through an unstable $[PtR_2Cl_2]^{2-}$ type of intermediate on the way, and we have not been able to achieve this.

The series of phosphine-stabilized alkyl and aryl complexes was extended to include those of octahedral configuration, and organo derivatives of rhodium, ruthenium, osmium, and rhenium were obtained (*35*). Generally they were more difficult to obtain because of the more inert character of the highly congested d^6-halogeno(tertiary phosphine) complexes used as starting materials, and they showed no startlingly new chemistry.

B. Formed by Splitting a C—H Bond

Two important reactions [Eqs. (2) and (3)] which resulted in the production of a transition metal–carbon bond were discovered incidentally in successful attempts with R. H. Watson to stabilize metals in low oxidation states using only tertiary phosphines as ligands (*19*, *40*). Sodium-naphthalene in tetrahydrofuran was used as reductant, and from $[RuCl_2(Me_2PCH_2CH_2PMe_2)_2]$ we produced a metal hydride complex, instead of the expected metal(0) complex, as shown by a "hydride band" in its IR spectrum. The study of this complex was taken up with J. M. Davidson and found to be really very difficult (*22*). It appeared to be a naphthalene hydrido complex $[MH(C_{10}H_8)(Me_2PCH_2CH_2PMe_2)_2]$ because on warming *in vacuo* naphthalene could be sublimed from it, still leaving the hydride complex with the hydride band only slightly shifted. The complexes were, of course, very sensitive to air and moisture and difficult to handle. With halogen (HI$_2$), the dihalide, $[MHI_2(Me_2PCH_2CH_2PMe_2)_2]$ and naphthalene were obtained, but no HHI. Finally the problem was solved in terms of two tautomeric equilibria involving the breaking of carbon–hydrogen bonds and the formation of metal–carbon bonds [Eqs. (2) and (3)]. In the solid state the naphthalene-derived product was (VIIIb) and the material obtained on subliming out the naphthalene was (IXb), hence the retention of a "hydride band" in the IR spectrum after the loss of naphthalene. In solution both compounds existed in equilibrium with their metal(0) tautomers (VIIIa) and (IXa), respectively, and these being the more chemically reactive, their reactions dominated the chemistry.

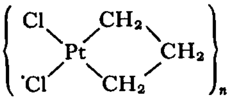
$$\underset{\text{(VIIIa)}}{[\mathrm{Ru(C_{10}H_8)(Me_2PCH_2CH_2PMe_2)_2}]} \rightleftharpoons \underset{\text{(VIIIb)}}{[\mathrm{RuH(\beta{-}C_{10}H_7)(Me_2PCH_2CH_2PMe_2)_2}]} \quad (2)$$

$$\underset{\text{(IXa)}}{[\mathrm{Ru(Me_2PCH_2CH_2PMe_2)_2}]} \rightleftharpoons \underset{\text{(IXb)}}{[\mathrm{RuH(CH_2PCH_2CH_2PMe_2)(Me_2PCH_2CH_2PMe_2)}]} \quad (3)$$

Now there are many examples of the formation of metal–carbon bonds by the splitting of carbon–hydrogen bonds in complexes of transition metals in low oxidation states with aromatic or unsaturated hydrocarbon moieties, but only one other example has been discovered of the splitting of a saturated aliphatic carbon–hydrogen bond. The fact that an aliphatic carbon–hydrogen bond can be split at all holds out hope that at some time a system may be discovered capable of reacting under mild conditions with saturated hydrocarbons, with all its implications for the petrochemical industry.

C. Formed by Splitting a C—C Bond

Following suggestions by Walsh (*69*) that there is considerable delocalization of electrons in the cyclopropane ring, Tipper (*67*) prepared a substance "cyclopropaneplatinous chloride," of formula $PtCl_2(C_3H_6)$, from which cyclopropane was regenerated on reaction with potassium cyanide. He proposed that it was an analog of $[Pt_2Cl_4(C_2H_4)_2]$, "ethylene platinous chloride." However, it gave a pyridine derivative $[PtCl_2(py)_2(C_3H_6)_2]$ whose stereo-chemistry is not in accord with platinum(II) chemistry. This prompted reinvestigation (*3*) which showed it to be a platinacyclobutane(IV) derivative (X), converted to a mononuclear octahedral complex $[PtCl_2(\text{—}CH_2\text{—}CH_2\text{—}CH_2\text{—})(py)_2]$ on reaction with pyridine. It provided the first of the very few complexes where a metal–carbon σ bond is formed by splitting of a C—C bond,

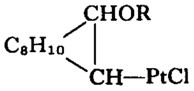


(X)

albeit in a very strained system. This ring structure has since been confirmed by X-rays (*48*).

D. Formed by Reaction of an Olefin Complex

Hofmann and von Narbutt (*53*) in 1908 described some compounds formed by the reaction of aqueous potassium chloroplatinate(II) in aqueous alcohols (ROH) with dicyclopentadiene. They formulated them as (XI) in which ROPtCl had added across one of the double bonds of the diene. This formulation could not be correct because it



(XI)

leaves platinum in an unsatisfactory coordination state and reinvestigation was undertaken in collaboration with L. M. Vallerino and L. M. Venanzi. Hofmann and von Narbutt were almost correct. The compounds, which were the archetypes of many more which we prepared from that and other dienes are dimeric substances of the general structural type shown in Fig. 4, which are platinum(II) complexes containing

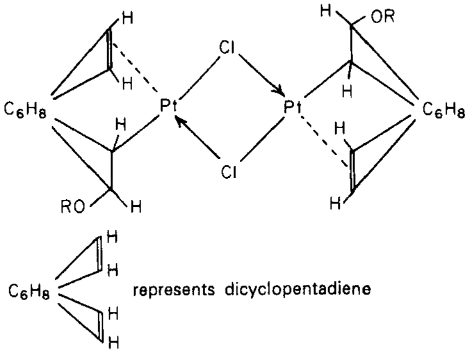


FIG. 4. Structure of the product formed by the reaction of dicyclopentadiene with K_2PtCl_4 in aqueous alcohols.

metal–carbon σ bonds (*37*). They provided one of the first examples of the activation of a double bond to a relatively inert reagent (ROH) by coordination to a metal, and also showed that the first platinum(II) σ-bonded organo compounds were prepared as early as 1908 without, not surprisingly, their significance having been realized.

IV

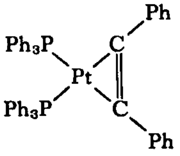
HYDRIDE COMPLEXES

Looking back it seems obvious that having found the surprisingly stable complexes $[PtClMe(PR_3)_2]$ and $[PtMe_2(PR_3)_2]$, one should try to produce the corresponding hydrides, e.g., $[PtClH(PR_3)_2]$. In the middle of the 1950s the only transition metal hydride complexes definitely identified were those containing carbon ligands in addition to the hydride ligand. They were the newly discovered $[Re(cp)_2H]$ (*71*) and the long known transition metal carbonyl hydrides, e.g., $[Co(CO)_4H]$ (*51*), and Weichselfelder's hydrides (*70*). There was plenty of scope for the development of transition metal hydride complexes, but chemists generally believed them to be too unstable to isolate, as in the case of the alkyl and aryl complexes. In addition, there was no method of detecting the hydride ligand in the presence of hydrogen-containing ligands. Infrared spectroscopy had failed to demonstrate its presence in the metal carbonyl hydrides and NMR spectroscopy was just beginning. Our discovery of $[PtClH(PEt_3)_2]$ did not follow logically from the discovery of alkyl complexes, but was found entirely by accident.

Longuet-Higgins and Orgel in 1956 (*55*) predicted that cyclobutadiene might be stabilized as a ligand on a metal ion such as nickel. Around 1955, L. E. Orgel frequently visited the Akers Research Laboratories and he suggested that I try to make substituted cyclobutadiene complexes by the reaction of acetylenes with nickel, palladium, or platinum salts. Diphenylacetylene was readily available for such experiments. Nickel(II) showed no promise, but this did not surprise us as nickel(II) does not react with olefins. A solution of sodium tetrachloropalladate(II) in acetone, where it dissolves with loss of some sodium chloride, reacted to give hexaphenylbenzene. This reaction was never published by us, but the fact of its occurrence provides a very interesting example of the one which got away. Had I chosen ethanol as solvent we would have obtained the ethoxytetra(phenyl)cyclobutenylpalladium(II) chloride complex, found a few years later by Malatesta *et al.* (*59*), which on reaction with hydrochloric acid eliminated ethanol to give the tetraphenylcyclobutadiene complex $[PdCl_2(C_4Ph_4)]$ which we had sought, and which, in the hands of P. Maitlis (*56*), has opened the way to other C_4Ph_4 complexes. All this development was delayed many years because of the wrong choice of solvent for the reaction of diphenylacetylene with sodium tetrachloropalladate(II). Nevertheless, at that time platinum(II) seemed the obvious choice for the production of a stable cyclobutadiene complex because of its great affinity for olefins, and we set about trying to produce a substance, $[Pt(C_4Ph_4)(PPh_3)_2]$. Since Malatesta and Angoletta (*58*) had obtained $[Pt(PPh_3)_4]$ by reaction (4), it seemed

$$cis\text{-}[PtCl_2(PPh_3)_2] + PPh_3 + N_2H_4 \xrightarrow{EtOH} [Pt(PPh_3)_4] + N_2H_5Cl + N_2 \qquad (4)$$

logical to substitute C_2Ph_2 for PPh_3 in that reaction. G. A. Rowe, who did these experiments, obtained a beautifully crystalline product which turned out to have the formula $[Pt(C_2Ph_2)(PPh_3)_2]$, a new type of acetylene complex whose general properties including the dipole moments of substituted derivatives suggested that the structure was nearer to (XII)

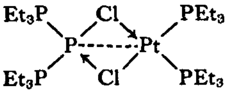

(XII)

than to that of a three-coordinate platinum(0) complex. These new complexes took our interest away from the C_4Ph_4 complexes. Great numbers were made from a variety of acetylenes, and their reactions examined, but for various reasons they were never published, except for the preliminary announcement (*30*) and what has appeared in lectures (*17*). It was also found that olefins give corresponding but much less stable complexes (*36*).

All of the above acetylene compounds contained triphenylphosphine and were obtained by reaction (5). An attempt to prepare the triethylphosphine analogs by the same reaction failed. Nevertheless, the reaction

$$cis\text{-}[PtCl_2(PPh_3)_2] + C_2R_2 + N_2H_2 \xrightarrow{EtOH} [(Ph_3P)_2Pt(C_2R_2)] \qquad (5)$$

product was interesting because it did not deposit metallic platinum even on boiling the reaction medium with an excess of hydrazine. Dr. B. L. Shaw took up the work at this point and showed that the product was an oil which would not crystallize and that the acetylene had no part in its production. I had expected that the linear platinum(0) complexes of type $[Pt(PR_3)_2]$ isoelectronic with R_3PAuCl might be prepared in this way (*19*) and felt certain that our product was $[Pt(PEt_3)_2]$. Because such complexes as $[PtMe_2(PEt_3)_2]$ can be sublimed in high vacuum, we tried to sublime our oily, supposed platinum(0), product, and indeed an off-white crystalline solid sublimed out of the oil. However, it analyzed as $[PtCl(PEt_3)_2]$ and was diamagnetic. First we formulated it as (XIII) but its molecular weight showed it to be monomeric. Finally we were forced to the conclusion that it must contain an additional hydrogen atom, presumably on the metal. Up to this time no hydrogenic vibrations had been identified in the infrared spectra of the metal carbonyl hydrides, which were the only transition metal hydrido complexes known. It was generally believed that the proton in some way tunnelled through the π-orbital system associated with the metal and carbon atoms. We thought that the existence of dative π-bonding from phosphorus to platinum might provide a similar environment for the hydrogen atom in our newly discovered platinum complex now formulated $[PtClH(PEt_3)_2]$. I did not expect to find any hydrogenic vibration associated with the Pt—H bond in its IR spectrum but Duncanson was confident, and found it as a sharp, strong Pt—H stretching absorption. It was the first strong clearly resolved transition metal hydride band to be recognized and gave us a means to detect M—H and so develop the area of transition metal hydride complexes (*24*). This assignment was confirmed by replacing the hydrogen by deuterium. In the meantime, Wilkinson (*71*) had shown that NMR spectroscopy (not then available to us) gave an even more valuable diagnostic test for hydrogen bonded to a transition metal, and NMR spectroscopy was used eventually to confirm the presence of the hydride ligand in our platinum complex. It also confirmed the trans configuration which



(XIII)

had been determined previously by dipole moments. In this way the hydride arose from attempts to prepare cyclobutadiene complexes. Its surprising stability and resistance to oxidation took us completely by surprise. It seemed very peculiar that a substance $[PtClH(PEt_3)_2]$ which we expected to reach a stable electronic state, $[Pt(PEt_3)_2]$, by loss of hydrogen chloride from a noble metal should hold hydrogen chloride so tenaciously that it could be sublimed unchanged in vacuum.

As soon as solid material, $[PtClH(PEt_3)_2]$, was obtained it became obvious that we should prepare it in aqueous solution, and we found that an aqueous suspension of *cis*-$[PtCl_2(PEt_3)_2]$ on warming with a few drops of hydrazine hydrate, evolved dinitrogen and precipitated the almost pure *trans*-$[PtClH(PEt_3)_2]$. This solid hydride offered the first opportunity to determine by X-rays the structure of a transition metal hydride complex and Owston, Partridge, and Rowe (*61*) showed that *trans*-$[PtBrH(PEt_3)_2]$ was a normal planar platinum(II) complex.

These platinum hydride complexes immediately alerted us to the possibility of preparing other similar complexes. Within a decade a great number were obtained from the Group VIII metals (*49*) and even now the series is being extended to include the early transition metal groups (*8*).

The hydride complexes by their sharp M—H stretching bands in the infrared spectrum offered an excellent method of measuring the trans influence of ligands which could be put in trans position to the hydrogen. In this way the trans influence of a number of anions was shown to increase along the series $NO_3 < Cl < Br < I < NO_2 < SCN < CN$ (*23*), and found to be essentially in the same sequence as that of the trans effect series established by relative rates of ligand substitution by Russian workers (see *41*). We extended this study by exploring the effect of various anions on the Pt—C stretching frequency in a number of platinum methyls and again found the same trans-influence series (*4*). Evidently the trans effects of the anions in the above series operated mainly by trans bond weakening, as Russian workers had always maintained.

These early studies of the effect of various anionic ligands on ν(M—H) alerted us to the possibility that ν(M—Cl) would provide a much more generally applicable method of finding relative trans influences if we could determine the stretching frequencies of metal–halogen vibrations. L. A. Duncanson, followed by D. M. Adams, proceeded to develop a long-wave infrared spectrometer (*1*), but it only came into doing useful work after we had obtained some interesting kinetic data concerning the magnitude of the trans effect of hydride ligand and of organic groups by study of the replacement of chloride ion by pyridine according to reaction (6) (7). The experimentalists involved in this work were H. B. Gray and B. L. Shaw. As everyone now knows, both are excellent chemists; they had a synergic interaction which got them through the work in double quick time. The collaboration arose from my meeting Fred Basolo when we discussed the trans effect of hydride and carbon ligands, which preliminary ν(Pt—Cl) frequency measurements in the *trans*-$[PtClR(PEt_3)_2]$ (R = H or organic group) complexes had shown might be high. He offered to do the measurements if we provided the compounds. Before long the compounds and results of measurements sped in opposite directions across the Atlantic so quickly that Shaw complained, "That man Gray must be an absolute glutton for work. I did not know it was possible to do kinetics so fast, as soon as I get a compound out of the lab the result is in and he is waiting for another. I cannot keep up with him," and he redoubled efforts to do just that. When I met Fred Basolo at our next conference he said "That guy Shaw's a worker. He nearly drove Harry Gray mad the compounds came in so fast, as soon as he had done one the next compound was waiting."

$$\textit{trans}\text{-}[PtClX(PEt_3)_2] + py \longrightarrow \textit{trans}\text{-}[PtX(py)(PEt_3)_2]^+ + Cl^- \qquad (6)$$

Their experiments showed that the chloride ligand trans to hydride was eliminated some 10^6 times faster, and trans to methyl some 10^4 times faster, than when it was trans to chlorine. The high trans effect of the methyl and hydride ligands could only be inductive, thus leading to the conclusion that there were two electronic mechanisms for causing a strong trans effect: (1) by electron release in the σ bond from the trans-directing ligand and (2) by electron withdrawal in the dative π bond to the trans-directing ligand, the former enhancing an S_N1 and the latter an S_N2 mechanism of substitution. Hydride ion and ethylene provided examples of ligands with high trans effects promoted mainly by mechanisms (1) and (2), respectively. Physical measurements since that time appear to have confirmed this general conclusion and the strongest trans influence comes from one of the most strongly electropositive ligand atoms, silicon, as observed in the compounds *trans*-$[PtCl(SiR_nR'_{3-n})(PR_mR'_{3-m})_2]$ (R = R' = alkyl or aryl radicals), which show the lowest Pt—Cl stretching frequencies in platinum(II) chemistry (*27*). A chloride ion trans to an olefin normally shows relatively high Pt—Cl stretching frequencies in accord with a mesomeric rather than an inductive origin of the olefinic trans effect (*2*). The mainly ν(M—Cl) stretching vibration is rarely a pure stretching mode and so is only a rough guide to relative trans influences (*27*).

The early work on hydride complexes stabilized by tertiary phosphines was summarized in my Tilden Lecture (*18*). As their chemistry developed one became more and more surprised at their stability, variety of types, and ease of formation. Even "alcoholic potash," well-known reagent of the early chemists, is sufficiently reducing to form them in variety, and we prepared many by treating tertiary phosphine Group VIII metal halide complexes with alkaline ethanol (*34*). Undoubtedly some must have been made by the earlier chemists, probably even in the last century, but never identified because there was no means of detecting the hydride ligand.

It is interesting, too, that when I started work in my chosen field many of my older chemist friends thought I was entering a quiet backwater, and so it seemed for a decade. It was only when, around 1955, the transition metals were shown to have an organic and hydride chemistry that interest started to grow. The petrochemical industry began to realize that such compounds lay at the basis of many of their catalytic processes, some already known, e.g., the hydrocarbonylation of olefins, and other newly discovered or on the verge of discovery, e.g., Ziegler-Natta polymerization of olefins and the Hoechst-Wacker oxidation of olefins. Money then became available for organo-transition metal chemical research on a large scale; now it is doubtful whether any chemist or small group of chemists can make a unique, spectacular advance within the subject. Its growth has become so enormous during the past ten years that palladium, whose organic chemistry got no mention in Goddard's books in 1928–1937 (*50*) now occupies a complete 319-page volume on its own (*57*), and the interest of organo-transition metal chemistry to industry is obvious (*11*). The interactions of dihydrogen, aromatics, olefins, and other unsaturated organic compounds with transition metal ions and complexes are now well known, reasonably understood, and much studied. Two great areas of related chemistry remain relatively unexplored and still intractable. These are the reactions of dinitrogen and of saturated hydrocarbons carried out catalytically under mild, i.e., ambient, reaction conditions. The former shows every promise of leading eventually to as rich a field of chemistry as the study of olefin and hydride complexes has done already (29), the latter is still in a very embryo stage waiting for the first real breakthrough. It is not only the approach to the goal itself which gives interest and excitement to chemical research, it is the unexpected and fascinating pieces of chemistry one finds along the way which provide the fun.

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Insertion Reactions of Transition Metal–Carbon σ-Bonded Compounds
II. Sulfur Dioxide and Other Molecules

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List of Abbreviations

The following abbreviations, listed alphabetically, will be used in the text and in the tables:

bae	*N,N′*-Ethylenebis(acetylacetonyliminato)
n-Bu	*n*-Butyl
Cp	h^5-Cyclopentadienyl (but not h^1-C_5H_5)
Cpr	Cyclopropyl
dipy	2,2′-Bipyridine
DMF	*N,N*-Dimethylformamide
dmgH	Dimethylglyoximato
Et	Ethyl
Ind	h^5-Indenyl
isoquin	Isoquinoline
L	Monodentate ligand (usually nonionic)
M	Metal (sometimes with ancillary ligands)
Me	Methyl
Me_xCp	*x*-Methyl-substituted h^5-cyclopentadienyl
Naph	Naphthyl
Ph	Phenyl
o-phen	1,10-Phenanthroline
Pr	Propyl
py	Pyridine
R,R′,R″	Hydrocarbon radicals
R'_xCp	h^5-Cyclopentadienyl with *x* substituents R′
salen	*N,N′*-Ethylenebis(salicylaldiminato)
salophen	*N,N′*-Phenylenebis (salicylaldiminato)
THF	Tetrahydrofuran
X	Halogen, pseudohalogen, or a similar group

I

INTRODUCTION

This is the second chapter of a two-part review concerned with insertion reactions of transition metal–carbon σ-bonded compounds. The first chapter, which appeared in Volume 11 of this series (*137*), provided a broad introduction to the subject of insertion reactions in general and a detailed treatment of the carbon monoxide insertion and decarbonylation. Presented herein are the insertion and elimination reactions of sulfur dioxide and of a few other unsaturated molecules. The reactions of sulfur dioxide are accorded a complete literature coverage, whereas those of the other inserting species are treated selectively. Metal–carbon σ-bonded compounds of the main group elements are discussed only in the context of comparisons with their transition metal analogs.

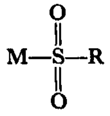
II

SULFUR DIOXIDE INSERTION. GENERAL CONSIDERATIONS AND BACKGROUND

Sulfur dioxide insertion reactions may be represented by the equation

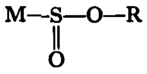
$$\mathrm{M{-}R + SO_2 \longrightarrow M{-}(SO_2){-}R} \qquad (1)$$

where M stands for a metal together with its ancillary ligands and R is an alkyl or a related σ-bonded carbon group. In sharp contrast to the behavior of CO, such interposition of SO_2 can, in principle, generate several types of structure for the M—(SO_2)—R moiety. The resulting linkages which particularly require consideration are an *S*-sulfinate (I), an *O*-alkyl-*S*-sulfoxylate[1] (II), an *O*-sulfinate (III), and *O*,*O*′-sulfinate (IV). In addition, various dinuclear and polynuclear structures are possible with



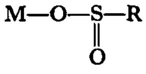
$$\mathrm{M{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}{-}R}$$

(I)



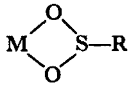
$$\mathrm{M{-}\underset{\underset{O}{\|}}{S}{-}O{-}R}$$

(II)



$$\mathrm{M{-}O{-}\underset{\underset{O}{\|}}{S}{-}R}$$

(III)



(IV)

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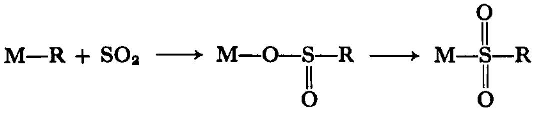
[1] Named as a derivative of sulfoxylic acid, $S(OH)_2$; this name is thought to be superior to *S*-alkoxysulfenate, used previously (*54*, *73*).

bridging RSO_2 ligands (*39*). However, the latter are of little relevance to the insertion itself and will not be considered here.

Assignment of a structure to the SO_2 insertion products is generally made on the basis of infrared and proton NMR spectroscopic criteria. Structure (I) usually exhibits the sulfur–oxygen stretching frequencies $\nu_{as}(SO_2)$ and $\nu_s(SO_2)$ in the ranges 1250–1100 cm^{-1} and 1100–1000 cm^{-1}, which are to be compared with the absorptions at 1085–1050 cm^{-1} and 1000–820 cm^{-1} (or even lower) for structures (II)–(IV) (e.g., *38*, *40*, *54*, *68*, *128*). The latter three structures are normally difficult to distinguish. Under favorable conditions, the chiral sulfur center in (II) and (III) will render adjacent methylene protons magnetically nonequivalent in the NMR spectra. Such behavior has been observed for $CpFe(CO)_2OS(O)CH_2Ph$, $CpMo(CO)_3OS(O)CH_2Ph$, and $PhCH_2S(O)OMn(CO)_5$ (*72*, *73*). In contrast, $PhCH_2Hg(SO_2)CH_2Ph$, of presumed structure (III), shows magnetic equivalence of the sulfinate CH_2 protons, perhaps owing to rapid, although slight, ionization (*106*) or to linkage isomerization (*37a*). Structures (III) and (IV) can sometimes be distinguished on the basis of a much greater separation between the two $\nu(SO_2)$ modes in the former than in the latter (*40*). Additionally, structure (IV) is very improbable for products derived from SO_2 insertion into metal–carbon bonds of coordinatively saturated complexes, since the central metal would exceed a stable 18-electron configuration. The NMR spectra of a limited number of authentic examples of (II) seem to suggest that it may be possible to differentiate these groupings from the isomeric (III) by the position of their α-carbon proton signals (*73*). Accordingly, $MeOS(O)Ir(CO)(PMePh_2)_2Cl_2$ absorbs at a lower field than $MeS(O)_2Ir(CO)(PMePh_2)_2Cl_2$ (*54*); in contrast, a number of *O*-sulfinates of $CpFe(CO)_2$, $CpMo(CO)_3$, $Mn(CO)_5$, and $Re(CO)_5$ show resonances at higher fields than the corresponding *S*-sulfinates (*73*).

Structures of several transition metal sulfinates, *viz.*, $(Me_5Cp)Fe(CO)_2S(O)_2CH_2CH{=}CHPh$ (*24*), $CpFe(CO)_2S(O)_2C_6F_5$ (*17*), $MeS(O)_2Mn(CO)_3dipy$ (*122*), and $Cu(H_2O)_4[OS(O)C_6H_4Me\text{-}p]_2$ (*89*), have been determined by X-ray crystallography. In each case, the mode of metal–sulfinate bonding is that inferred from spectroscopic data (*110*, *43*, *68*, *39*, respectively). Recently, the structure of polymeric, oxygen-bridged $[Me_3SnOS(O)CH_2C{\equiv}CH]_n$ was also elucidated crystallographically (*56a*).

Products isolated from the insertion of SO_2 into transition metal–carbon bonds have been shown to adopt structures (I), (III), and possibly, (IV). The first mode of bonding, expected of class "b" (*1a*) or soft metals (*105*), is by far the most common one encountered. In fact, oxygen-bonded insertion products have been isolated only for titanium and zirconium (*131*, *132*). However, recent spectroscopic studies have demonstrated that (III) is the kinetic product of the insertion with a number of metal carbonyl alkyls and aryls; it then isomerizes to (I) (*72*, *73*):



$$\text{M—R} + \text{SO}_2 \longrightarrow \text{M—O—}\underset{\underset{\text{O}}{\|}}{\text{S}}\text{—R} \longrightarrow \text{M—}\overset{\overset{\text{O}}{\|}}{\underset{\underset{\text{O}}{\|}}{\text{S}}}\text{—R} \qquad (2)$$

This aspect of the SO_2 insertion will be considered in detail in Section III, B.

Sulfur dioxide insertions can be either intermolecular or intramolecular. For example, in the reaction (3) (*73*) precoordination of the inserting

$$\text{CpFe(CO)}_2\text{Me} + \text{SO}_2 \longrightarrow \text{CpFe(CO)}_2\text{OS(O)Me} \qquad (3)$$

SO_2 is not likely. Thus the process appears to be almost certainly intermolecular. However, for coordinatively unsaturated alkyl complexes, e.g., *trans*-$Pt(PEt_3)_2(Ph)Cl$, the insertion, shown in Eq. (4) (*46*), may proceed intramolecularly via a five-coordinate intermediate, $PhPt(SO_2)(PEt_3)_2Cl$.

$$\textit{trans}\text{-Pt(PEt}_3)_2\text{(Ph)Cl} + \text{SO}_2 \longrightarrow \textit{trans}\text{-Pt(PEt}_3)_2\text{[S(O)}_2\text{Ph]Cl} \qquad (4)$$

Although SO_2 insertion is a clean reaction for many metal–carbon complexes, some metal alkyls, e.g., $PhCH_2Cr(H_2O)_5^{2+}$ (*4*), decompose rapidly to unidentified materials upon treatment with sulfur dioxide. At the other end of the reactivity scale, a number of metal–carbon σ-bonded compounds are inert to SO_2. These include, in particular, perfluoroalkyls and -aryls such as $CF_3Mn(CO)_5$ (*66*) and $CpFe(CO)_2C_6F_5$ (*13*), as well as other complexes with electron-withdrawing substituents in the σ-bonded carbon fragment (*71*).

Besides the insertion, three distinct types of behavior of SO_2 toward metal–carbon systems have been noted.

1. Sulfur dioxide adds to the metal. In general, this has been observed for coordinatively unsaturated complexes containing strong metal–carbon bonds (*16*, *139*), e.g. (*16*),

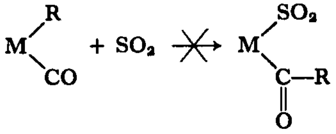
$$\mathrm{MeC{\equiv}CIr(CO)(PPh_3)_2 + SO_2 \longrightarrow MeC{\equiv}CIr(CO)(SO_2)(PPh_3)_2} \qquad (5)$$

2. Sulfur dioxide adds to another coordinated ligand. Equation (6) (*115*) illustrates this type of behavior. Here SO_2 acts as an acid toward coordinated iodide.

$$\mathrm{MePt(PPh_3)_2I + SO_2 \longrightarrow MePt(PPh_3)_2(I{-}SO_2)} \qquad (6)$$

3. Sulfur dioxide undergoes cycloaddition to the hydrocarbon fragment. The formation of $\mathrm{CpFe(CO)_2\overline{C{=}C(Me)S(O)OC}H_2}$ from $\mathrm{CpFe(CO)_2CH_2C{\equiv}CMe}$ and SO_2 (*25*, *124*) provides a typical example. This general behavior is discussed in Section V.

Finally, it is of interest to note that no reactions have been reported in which SO_2 effects CO insertion [Eq. (7)] in a manner typical of many Lewis bases (*137*).



$$\mathrm{M}\begin{matrix}\nearrow R\\ \searrow CO\end{matrix} + \mathrm{SO_2} \not\longrightarrow \mathrm{M}\begin{matrix}\nearrow SO_2\\ \searrow C(=O){-}R\end{matrix} \qquad (7)$$

Sulfur dioxide insertion is not limited to metal–carbon σ bonds, although M—C is by far the most common substrate involved. Reactions have been reported which lead to insertion of SO_2 into metal–carbon π (or *polyhapto*) bonds (*26*, *102*, *130–132*), as well as transition metal–transition metal (*112*), transition metal–Group IVB metal (*14*, *19*), and metal–oxygen (*9*, *58*) linkages. Moreover, reaction (8) (*91*) where M = Rh

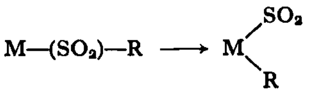
$$\mathrm{HM(CO)(PPh_3)_2 + SO_2 \longrightarrow HM(CO)(SO_2)(PPh_3)_2 \rightleftharpoons HS(O)_2M(CO)(PPh_3)_2} \qquad (8)$$

or Ir leads to what may be an equilibrium mixture of SO_2-containing tautomers. Thus is appears to represent SO_2 insertion into an M—H bond.

The desulfination (*84*) [also called desulfonation (*88*), desulfonylation

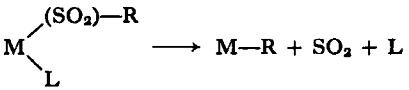
(*136*), and desulfurylation (e.g., *13*)], shown in Eqs. (9) and (10),[2] bears close analogy to the decarbonylation of metal-acyl complexes (*137*). In

$$M{-}(SO_2){-}R \longrightarrow M{-}R + SO_2 \tag{9}$$

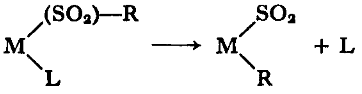


$$M{-}(SO_2){-}R \longrightarrow M\begin{array}{l} SO_2 \\ R \end{array} \tag{10}$$

some cases it is accompanied by loss of another ligand, L, such as a phosphine [Eqs. (11) and (12)] (*15*), thus suggesting that a vacant coordination position may be required for the fragmentation of RSO_2. In general, elimination of SO_2 from transition metal sulfinates is not



$$M\begin{array}{l} (SO_2){-}R \\ L \end{array} \longrightarrow M{-}R + SO_2 + L \tag{11}$$



$$M\begin{array}{l} (SO_2){-}R \\ L \end{array} \longrightarrow M\begin{array}{l} SO_2 \\ R \end{array} + L \tag{12}$$

as common as elimination of CO from the corresponding acyls. The reactions represented by Eqs. (9) and (11) have been effected only for a limited number of complexes (Section IV). Furthermore, whereas some mercury and bismuth aryl compounds reversibly insert SO_2 (*37a*, *40*), among transition metal systems only $CpMo(CO)_3CH_2Ph$ and its *S*-sulfinate have been reported to undergo insertion–elimination (*57*).

This chapter covers kinetic and stereochemical results and mechanistic interpretations of the sulfur dioxide insertion (Section III) and the desulfination (Section IV). Reactions of SO_2 with metal-σ-allyl, -propargyl (or -2-alkynyl), -cyclopropyl, and -cyclopropylmethyl complexes are treated in Section V, whereas a comprehensive survey of reactions of SO_2 with transition metal–carbon σ-bonded compounds, arranged by the triads, is the subject of Section VI. Sulfur dioxide insertion reactions were reviewed during 1970–1971 by Kitching and Fong (*84*), Vitzthum and Lindner (*128*), Otsuka and Tatsuno (*103a*), and by the author of this chapter (*136*). The first two reviews include also metal–carbon compounds of the main group elements, and the second review treats metal sulfinates in general.

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[2] To systematize the nomenclature of these processes, the eliminations of SO_2 and SO_3 are termed *desulfination* (from sulfinate) and *desulfonation* (from sulfonate), respectively.

III

KINETICS AND MECHANISM OF SULFUR DIOXIDE INSERTION

A. Scope

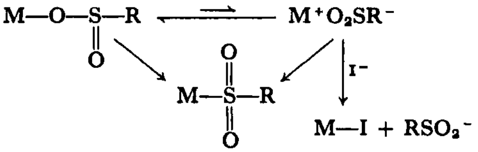
Kinetic studies on the sulfur dioxide insertion have been few and most have utilized liquid SO_2 as the reaction medium. The most exhaustive investigation in neat SO_2 was conducted on the systems $CpFe(CO)_2R$ and various $(R'_xCp)Fe(CO)_2R$ (*71*, *74*, *75*); studied cursorily were $CpMo(CO)_3R$, $CpRu(CO)_2R$, $RMn(CO)_5$, and $RRe(CO)_5$ (*71*, *76*). Kinetic studies in organic solvents have been confined to a few $CpFe(CO)_2R$ complexes (*71*, *77*). Of the many SO_2 reactions of the main group metal–carbon systems, only those involving some Me_3SnR aryl and benzyl compounds were examined kinetically (*51*, *52*, *99*).

Likewise, stereochemical data on the insertion are rather limited. The reported investigations have been concerned with changes occurring either at the metal or at α carbon in $CpFe(CO)_2R$ (*2*, *133*, *134*) $(R'R''Cp)Fe(CO)LR$ (*7*), $CpMo(CO)_2LR$ (*57*), $RMn(CO)_5$ (*109*), and $RMn(CO)_4L$ (*68*) during the formation of the corresponding isolable *S*-sulfinates. Stereochemical data have been obtained also for the reactions of SO_2 with some metal-σ-allyl complexes; this will be taken up in Section V, B. Finally, supplementing the foregoing investigations are studies on the detection and characterization of the insertion reaction intermediate (*72*, *73*), as well as qualitative observations on the relative reactivities from various literature sources.

B. Reaction Intermediate

Examination of solutions of $CpFe(CO)_2R$ (R = Me and CH_2Ph), $CpMo(CO)_3CH_2Ph$, $RMn(CO)_5$ (R = Me and CH_2Ph), and $MeRe(CO)_5$ in neat SO_2 by NMR and infrared spectroscopy has revealed the presence of a species which rearranges to the isolable *S*-sulfinate (*72*, *73*). This intermediate has been assigned an *O*-sulfinato structure. The infrared spectrum also implicates such an intermediate in the insertion with $CpFe(CO)_2(p\text{-}C_6H_4Me)$, thus suggesting common features in the reactions of both the alkyls and the aryls. Finally, the formation of the *O*-bonded sulfinates extends to SO_2 insertion in organic solvents, as demonstrated for $CpFe(CO)_2(i\text{-}Pr)$ and $MeRe(CO)_5$.

Further studies on these systems have shown that the *S*-sulfinate is probably formed by the pathways depicted in Eq. (13) (*73*). This has



(13)

been suggested because the amount of MI [generally, $CpFe(CO)_2I$], resulting from addition of KI to MOS(O)R in liquid SO_2, does not increase in proportion to the added iodide. Additionally, the species $M^+O_2SR^-$ needs to be invoked for stereochemical reasons in the formation of MOS(O)R from the metal alkyls (MR) and neat SO_2 (Section III, I). Its identity is not certain, but a reasonable formulation would be an ion pair present in concentrations too low to be detectable by spectroscopic techniques. Rates of the *O*-sulfinate-to-*S*-sulfinate isomerization have not yet been measured for the above systems. However, qualitative observations show that the methyl complexes rearrange much more slowly than their benzyl counterparts. This led to attempts at isolation of $CpFe(CO)_2OS(O)Me$ and $MeS(O)ORe(CO)_5$ which, however, proved unsuccessful. A rapid isomerization occurred upon removal of the last traces of sulfur dioxide.

From the evidence cited above it has been assumed that the formation of the *O*-sulfinates is a common feature of the insertion reactions of coordinatively saturated transition metal alkyls and aryls. The kinetic studies discussed in Section III refer to the scission of the M—R bond which yields the appropriate metal sulfinate.

It needs to be emphasized that the reaction picture presented herein may not apply to various coordinatively unsaturated metal alkyls and aryls. In fact, recent isolations of $CHF_2CF_2Rh(CO)(SO_2)(PPh_3)_2$ (*139*) and $RC{\equiv}CIr(CO)(SO_2)(PPh_3)_2$ (*16*) from the appropriate four-coordinate complexes and SO_2 suggest that the insertion with $RPtL_2Cl$ (*46*) proceeds through a five-coordinate intermediate, $RPt(SO_2)L_2Cl$. Similarly, $Cp_2Ti(Me)Cl$ (*131*) may adopt a different reaction route, perhaps via initial coordination of SO_2 to yield $Cp_2Ti(OSO)(Me)Cl$.

C. *Effect of Alkyl and Aryl Groups*

The nature of R exerts a very profound effect on the reactivity of the alkyls and aryls of a given system MR toward sulfur dioxide. Kinetic data on reactions of various $\mathrm{CpFe(CO)_2R}$ alkyls with neat SO_2, which were monitored by infrared spectroscopy (*71*, *74*, *75*), are presented in Table I. The insertion obeys the rate law

$$-\frac{d[\mathrm{CpFe(CO)_2R}]}{dt} = k_{\mathrm{obs}}[\mathrm{CpFe(CO)_2R}] \qquad (14)$$

with the dependence on the concentration of SO_2 being indeterminable.

The data show that in those cases where steric effects are unimportant, e.g., for several $\mathrm{CpFe(CO)_2R}$ with R = CH_2X, the reactivity increases with an increase in the electron-releasing tendency of X. Accordingly, R = $CH_2C_6F_5$ (*11*) ≪ CH_2Ph < $CH_2C_6H_4OMe$-*p*, and R = CH_2CN < CH_2OMe < Me (*71*, *75*). For such complexes there is a reasonable

TABLE I

RATES OF INSERTION OF SOME $\mathrm{CpFe(CO)_2R}$ ALKYLS IN LIQUID SO_2[a]

R	Temp. (°C)	k_{obs} (sec^{-1})	Rel. k_{obs}	Taft σ^*	ν(CO) in cyclohexane (cm^{-1})
CH_2SiMe_3	−65	very fast	—	−0.26	2012, 1961
i-Pr	−65	very fast	—	−0.19	2004, 1950
Et	−65	very fast	—	−0.10	2010, 1956
Me	−65	1.1×10^{-3}	—	0.00	2014, 1960
	−40	2.8×10^{-3}[b]	340	—	—
$CH_2C_6H_4OMe$-*p*	−61	1.8×10^{-4}	—	—	2007, 1955
	−40	3.8×10^{-4}[b]	46	—	—
CH(Me)Ph	−30	3.4×10^{-4}	—	—	2004, 1952
	−40	2.5×10^{-4}[b]	30	—	—
CH_2Ph	−40	1.6×10^{-4}	19	+0.22	2010, 1959
CH_2OMe	−40	8.3×10^{-6}	1	+0.64	2017, 1961
CH_2CHMe_2	−10	~75% completion in 2 hr	—	—	2008, 1955
$CH_2CH_2CMe_3$	−10	~40% completion in 2 hr	—	—	2008, 1955
CH_2CMe_3	−10	~22% completion in 30 hr	—	−0.16	2005, 1950
CMe_3	−10	~10% completion in 30 hr	—	−0.30	2003, 1948
CH_2CN	25	no product observed in 60 hr	—	+1.30	2030, 1981

[a] From Jacobson (*71*).

[b] Calculated.

correlation between (1) the rate constants, k_{obs}, and Taft polar substituent constants σ^* (*123*) or (2) the rate constants and the values of ν(CO), which reflect the electron density at the iron and, therefore, show indirectly the electron-donating ability of R. These relationships become less valid as steric properties of R gain importance. The relative rates R = Me > CH_2CHMe_2 > $CH_2CH_2CMe_3$ > CH_2CMe_3 > CMe_3 appear to be governed substantially by robust features of R near the metal.

Other investigations have established that complexes containing R groups which can engage in π-bonding with the metal generally appear to be inert to the insertion. Accordingly, $CpFe(CO)_2R$ with R = $CH{=}CH_2$, $CH{=}C{=}CH_2$, $CH{=}C{=}CHMe$, $C{\equiv}CMe$ (*124*), C(O)Me, and C(O)Ph (*13*) do not react with neat SO_2 at temperatures up to −10°C.

The above-mentioned trends indicate an electrophilic nature of the insertion of SO_2 into metal–carbon bonds. Furthermore, the reactivity dependence on the steric properties of R is consistent with a backside approach of the sulfur dioxide electrophile (e.g., *78*).

Although other metal alkyl systems have not been studied nearly as exhaustively as $CpFe(CO)_2R$, they seem to manifest a parallel behavior. Thus, for $CpMo(CO)_3R$, the reactivity toward neat SO_2 at −48°C to −40°C decreases with R in the order Et (4) > Me (1) ~ CH_2Ph (~1) ≫ CF_3 (no reaction) (*57*, *71*, *76*); for $RMn(CO)_5$, R = Me (4) > CH_2Ph (1) ≫ CF_3 (no reaction) in liquid SO_2 at −18°C (*66*, *71*, *76*). However, SO_2 insertion proceeds faster with $MeCo(dmgH)_2py$ than with (*i*-Pr)$Co(dmgH)_2py$ (*82*), in contrast to the relative reactivities of the two $CpFe(CO)_2R$ counterparts. It is of interest that whereas carbon monoxide insertion of $CpFe(CO)_2R$ follows the order R = *i*-Pr > Me (*60*), the electrophilic cleavage by mercury(II) of the M—C bond in both $CpFe(CO)_2R$ and the cobaloximes shows the opposite behavior (*1*, *42*).

Appreciably less information is available for the insertion with $CpFe(CO)_2R$ in organic solvents. Both in isopropyl alcohol and in chloroform (Table II), the rate constants decrease in the order R = *i*-Pr > CH_2CMe_3 ~ CH_2SiMe_3 > Me (*71*, *77*). This sequence is significantly different from that obtained by using neat SO_2 (see Table I). In particular, the reactivity of $CpFe(CO)_2Me$ has been substantially repressed, and that of $CpFe(CO)_2CH_2CMe_3$ enhanced, relative to those of the other complexes. The order is no longer in harmony with a backside attack of

TABLE II

RATES OF SO_2 INSERTION OF SOME $CpFe(CO)_2R$ ALKYLS IN CHLOROFORM[a]

R	k_2 ($M^{-1}sec^{-1}$)	Rel. k_2
i-Pr	5.2×10^{-4}	460
CH_2CMe_3	3.6×10^{-5}	32
CH_2SiMe_3	3.1×10^{-5}	27
Me	1.2×10^{-6}	1
CH_2Ph	very slow	—
CMe_3	very slow	—

[a] At 26°C; from Jacobson (*71*).

sulfur dioxide; instead, it best reflects the relative stabilities (in the experimental context) of the metal alkyls.

The effect of the aryl group on the rate of the insertion has been investigated only for $CpFe(CO)_2R$ in neat SO_2 (*71*, *74*, *75*). As shown in Table III, a good correlation exists between k_{obs} and modified Hammett σ^+ values (*116*), supporting electrophilic cleavage of the iron–carbon bond. The value of ρ (-4.3) reflects moderate sensitivity of the reaction to substituent effects. That the differences in the rate constants are best ascribed to the relative stabilities of the respective transition states rather than the ground states receives support from the virtual identity of the

TABLE III

RATES OF INSERTION OF SOME $CpFe(CO)_2R$ ARYLS IN LIQUID SO_2[a]

R	Temp. (°C)	k_{obs}	Rel. k_{obs}	σ^+	ν(CO) in cyclohexane (cm^{-1})
p-C_6H_4OMe	-40	1.4×10^{-3}	700	-0.78	2027, 1971
o-C_6H_4Me	-40	2.9×10^{-4}	150	—	2024, 1968
p-C_6H_4Me	-40	6.6×10^{-5}	33	-0.31	2027, 1971
m-C_6H_4Me	-23	1.9×10^{-5}	—	—	—
	-40	1.4×10^{-6}[b]	~1	-0.07	2027, 1970
Ph	-40	2.0×10^{-6}	1	0.00	2023, 1972

[a] From Jacobson (*71*).

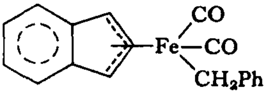
[b] Calculated.

values of ν(CO) for these substituted metal aryls. The enthalpies of activation, $\Delta H^{\ddagger}$, for the aryl complexes are generally higher than those for the analogous metal alkyls (Section III, G).

D. *Effect of Ancillary Ligands*

Replacement of carbon monoxide (or another attendant ligand) with a stronger base invariably enhances the rate of SO_2 insertion of a metal alkyl. Accordingly, $CpFe(CO)(PPh_3)CH_2Ph$ reacts very rapidly with SO_2 in chloroform solution (*59*) whereas the parent $CpFe(CO)_2CH_2Ph$ is inert under comparable conditions (Table II). Similarly, $CpFe(CO)(PPh_3)Me$ and $CpFe(CO)[P(n\text{-}Bu)_3]Me$ very rapidly ($t_{1/2} < 3$ min) insert SO_2 in chloroform solution at room temperature (*59*), in contrast with the much slower reaction of the dicarbonyl $CpFe(CO)_2Me$ (Table II). The first-mentioned methyl complex even reacts with gaseous SO_2 in the solid. Further examples of this general reactivity pattern include $CpMo(CO)_2(PPh_3)Me$ and Cp_2TiMe_2, which insert SO_2 much more rapidly than do $CpMo(CO)_3Me$ and $Cp_2Ti(Me)Cl$, respectively (*57*, *131*).

A similar acceleration in the rate of the insertion can be effected by increasing the degree of methyl substitution on the h^5-cyclopentadienyl ring of $(Me_xCp)Fe(CO)_2R$. Thus, in liquid SO_2 at −40°C, the following reactivity order was established: $CpFe(CO)_2CH_2Ph$ (1) < $(MeCp)Fe(CO)_2CH_2Ph$ (8) ≪ $(Me_5Cp)Fe(CO)_2CH_2Ph$ (very fast at −60°C) (*71*, *75*). By way of contrast however, $(Me_5Cp)Fe(CO)_2Ph$ < $CpFe(CO)_2Ph$, perhaps owing to stabilization of the Fe—C linkage in the former via π-bonding. It is noteworthy that $IndFe(CO)_2CH_2Ph$, in which iron can vacate an orbital for attack by SO_2 [see (V)], reacts with neat SO_2 (−40°C) at about the same rate as does $CpFe(CO)_2CH_2Ph$. This contrasts with the higher reactivity of $IndMo(CO)_3Me$ than $CpMo(CO)_3Me$ toward P-donor ligands in the carbon monoxide insertion (*62*).



(V)

The enhancement of the rate of SO_2 insertion as the base strength of ancillary ligands increases is consistent with an electrophilic nature of this reaction. Both replacement of CO by PR_3 and progressive substitution of Me for H on the h^5-cyclopentadienyl ring place a higher negative charge at the metal. This, in turn, should result in a greater carbanionic character of R, thus promoting its reaction with SO_2.

E. *Effect of Solvent*

Sulfur dioxide has been employed as the solvent in most of the investigations of its insertion reactions. The presence of moisture in SO_2 was reported markedly to accelerate the rate of the insertion with $MeCo(dmgH)_2py$ (*82*); on the other hand, added water had no effect on the reaction of $CpFe(CO)_2CH_2Ph$ (*71*, *75*).

The reactions which proceed very rapidly and often exothermally in liquid SO_2 can be controlled by the use of an organic solvent. Although advantage has been frequently taken of this procedure in synthesis (e.g., *57*, *131*), little information is available on the relative reactivities of the metal alkyls toward SO_2 in various solvents. This is because of the slow and sluggish reactions of the more stable complexes with SO_2 in dilute solution. The use of concentrated solutions, possible since SO_2 is highly soluble in organic solvents [e.g., 127.5 gm of SO_2 in 1 liter of its saturated benzene solution at 30°C (*113*)], can markedly alter the medium polarity and dielectric. Therefore, it no longer casts information on the solvent itself.

The only complex whose kinetic behavior toward the insertion has been examined closely in several solvents is $CpFe(CO)_2(i\text{-Pr})$. In solutions containing a 100-to-200-fold excess of SO_2 the relative second-order rate constants at 26°C were found to vary with the solvent in the order C_6H_6 (1) < $CHCl_3$ (7) < *i*-PrOH (8) (*71*, *77*). The dielectric constant of these solvents increases in a parallel manner: 2.28, 4.81, and 18.3. The increase in the rate constant on going from benzene to isopropyl alcohol is rather modest and indicates a more polar nature of the transition state than of the ground state. Three other $CpFe(CO)_2R$ alkyls were examined, but only cursorily, in organic solvents. The reactivity is greater in *i*-PrOH than in $CHCl_3$ when R = Me (18 times) and CH_2SiMe_3 (2 times), but slightly lower in *i*-PrOH than in $CHCl_3$ when R = CH_2CMe_3.

F. Intratriad Trends

Limited information is available on how the reactivity toward SO_2 varies within a given triad, all other factors being constant. The SO_2 insertion, like the CO insertion (*137*), proceeds much faster with $CpMo(CO)_3R$ than with $CpW(CO)_3R$ (*57*, *87*). Furthermore, the complexes $CpFe(CO)_2R$ (R = Me and CH_2Ph) react with SO_2 more rapidly than do their $CpRu(CO)_2R$ counterparts (*71*, *76*). Based on the above comparisons, the observed reactivity order $MeRe(CO)_5 > MeMn(CO)_5$ (*71*, *76*) comes as a surprise. It would be desirable to correlate the rates of SO_2 insertion with the relative M—C bond strengths; unfortunately, the latter data are not available.

G. Comparison of Various Systems

Compared in this section are the activation parameters and the relative reactivities toward SO_2 of the various types of transition metal alkyl and aryl complexes. As shown in Table IV, the values of $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ range from −63 to −43 e.u. and from 2.7 to 8.7 kcal/mole, respectively. These entropies of activation are more negative than those for the solvent-assisted carbon monoxide insertion [−33 to −17 e.u. (*137*)] or for the SO_2 insertion into the Sn—R (R = Ph and CH_2Ph)

TABLE IV

ACTIVATION PARAMETERS FOR SO_2 INSERTION REACTIONS[a]

Complex	Solvent	$\Delta H^{\ddagger}$ (kcal/mole)	$\Delta S^{\ddagger}$ (e.u.)
$CpFe(CO)_2(i\text{-}Pr)$	$CHCl_3$	8.7	−46
$CpFe(CO)_2CH_2Ph$	SO_2	2.9	−62
$(MeCp)Fe(CO)_2CH_2Ph$	SO_2	5.2	−52
$IndFe(CO)_2CH_2Ph$	SO_2	5.0	−54
$CpMo(CO)_3Me$	SO_2	2.7	−63
$CpFe(CO)_2Ph$	SO_2	7.3	−52
$CpFe(CO)_2(p\text{-}C_6H_4OMe)$	SO_2	3.5	−55
$CpFe(CO)_2(p\text{-}C_6H_4Me)$	SO_2	7.8	−43
$CpFe(CO)_2(o\text{-}C_6H_4Me)$	SO_2	3.4	−59

[a] From Jacobson (*71*).

bonds of Me_3SnR in MeOH solution [−43 and −40 e.u., respectively (*51*, *52*, *99*)]. However, oxidative addition reactions of some square-planar rhodium(I) and iridium(I) complexes are known to proceed with $\Delta S^‡ = -50$ to -40 e.u. (*21*, *29*). The extremely large and negative $\Delta S^‡$ for the SO_2 insertion may result from the following features: (1) strong solvation, (2) a marked increase in polarity on going from the reactants to the transition state, and (3) stringent stereochemical restrictions in the transition state. Some support for the solvation by SO_2 of the *O*-sulfinato intermediate was given in Section III, B. The enthalpies of activation in Table IV are substantially lower than those for the solvent-assisted CO insertion [12 to 18 kcal/mole (*137*)], and somewhat lower than those for the SO_2 insertion into the Sn—R bonds [7.4 and 9.6 kcal/mole (*51*, *52*, *59*)]. For the insertion in neat SO_2, the metal aryls generally show a higher $\Delta H^‡$ than the metal alkyls. This may in part reflect the stronger Fe—C bond in the former.

The reactivity of the various methyl complexes investigated follows the sequence $CpFe(CO)_2Me$ (15) > $MeRe(CO)_5$ (4) > $CpRu(CO)_2Me$ (2) ~ $MeMn(CO)_5$ (2) > $CpMo(CO)_3Me$ (1) ≫ $CpW(CO)_3Me$ (very slow), and that of the benzyl complexes $CpCr(NO)_2CH_2Ph$ (very fast) ≫ $CpMo(CO)_3CH_2Ph$ (2) > $CpFe(CO)_2CH_2Ph$ (~2) > $PhCH_2Mn(CO)_5$ (1) > $CpRu(CO)_2CH_2Ph$ > $CpW(CO)_3CH_2Ph$ (very slow), both series being compared in neat SO_2 at −18°C (*76*). Two points warrant comment. First, the order here differs considerably from the sequence $MeMn(CO)_5$ > $CpMo(CO)_3Me$ > $CpFe(CO)_2Me$ noted for the CO insertion (*137*). Second, apart from the very reactive $CpCr(NO)_2R$ and the very unreactive $CpW(CO)_3R$, there generally does not appear to be much of a spread in the relative rate constants for a given R.

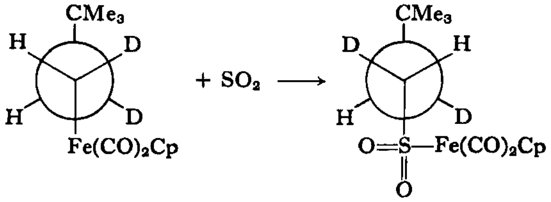
A comparison of the isoelectronic $CpFe(CO)_2R$ and $CpCr(NO)_2R$ is also noteworthy. When R = CH_2Ph or Ph, the latter system inserts SO_2 much more rapidly than the former (*61*, *71*). This may be a result of the lower formal oxidation state of chromium(0) than of iron(II) and is consistent with an electrophilic nature of the insertion.

H. Stereochemistry

Gross stereochemical changes occurring in the SO_2 insertion have been noted for *trans*-$CpMo(CO)_2(PPh_3)Me$ (*57*) and *cis*-$MeMn(CO)_4$-PPh_3 (*68*). These reactions yield *trans*- $CpMo(CO)_2(PPh_3)S(O)_2Me$ and *cis*-$MeS(O)_2Mn(CO)_4PPh_3$ as the isolable products; however, structures of the respective *O*-sulfinato intermediates have not been determined. One cannot therefore rule out possible changes in geometry around the metal in two of the steps comprising the overall process. That rearrangements may have occurred is suggested by the reaction of SO_2 with *cis*-$MeMn(CO)_4{}^{13}CO$ which yields substantial *trans*-$MeS(O)_2Mn(CO)_4$-${}^{13}CO$ in addition to the cis isomer (*109*).

The most definitive stereochemical studies have concerned configurational changes at the α carbon. Alexander *et al.* (*2*, *138*) showed that $(+)_{546}$-$CpFe(CO)_2CH(Me)Ph$ reacts with neat SO_2 at −60° or −10°C, or with SO_2 in saturated pentane at 27°C, to give the corresponding *S*-sulfinate. The specific rotation of the product, $[\alpha]_{546}$, varied somewhat with the method of synthesis (−186°, −176°, and −158°, respectively). It was concluded that the insertion is a substantially stereospecific process, but whether it involves retention or inversion could not be determined.

More recently, the reaction shown in Eq. (15) was examined by NMR

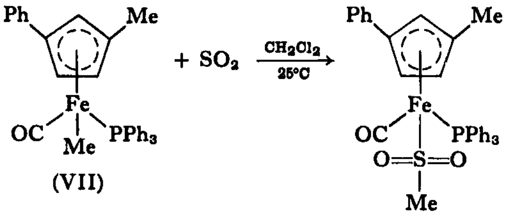


(VI)

(15)

spectroscopy. Initial experiments, conducted in neat SO_2 at −50°C, showed that the *threo*-alkyl complex affords ~80% *erythro*-*S*-sulfinate (*134*). Subsequently it was demonstrated that the insertion is highly stereospecific. The *S*-sulfinate formed in neat SO_2 at −10°C, as well as in a saturated solution of SO_2 (42 psi pressure of SO_2) in pentane, $CHCl_3$, MeOH, or DMF is >95% erythro (*133*). Thus, in these media at least, the insertion proceeds virtually completely with inversion at α carbon.

Stereochemical changes occurring at the metal have been investigated for the iron alkyl (VII). The reaction shown in Eq. (16) was carried out with each of the two diastereomerically related pairs of enantiomers (i.e., *RR*—*SS* and *RS*—*SR*) (*7*). Complete (>95%) stereospecificity, corresponding to either inversion or retention at iron, was noted from the NMR spectra of (VIII). In neat SO_2 at $-60°C$ this same reaction is $\sim 80\%$ stereospecific. Very recently it was shown by NMR and circular dichroism spectroscopy that the insertion of SO_2 into the Fe—C bond of $CpFe(CO)(PPh_3)CH_2C(O)OC_{10}H_{19}$ [$C_{10}H_{19}O$ = (−)-mentholate] in liquid SO_2 at $-10°C$ proceeds with $>90\%$ retention of configuration at iron (*48a*).



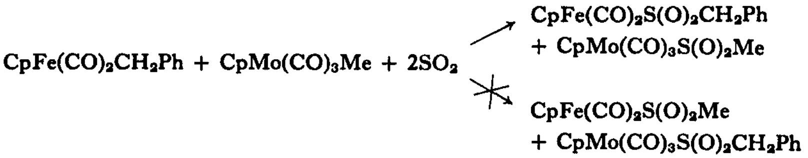
(VII) (VIII)

(16)

I. Mechanism

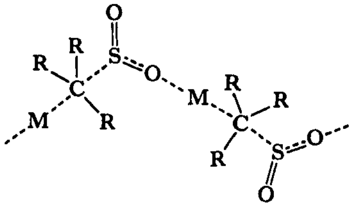
Presented here are mechanistic conclusions derived from the data discussed in the preceding parts of this section. They apply to $CpFe(CO)_2R$ and related coordinatively saturated systems.

Considering first the reactions of the metal alkyls with neat SO_2, the dependence of the rate on the nature of both R and ancillary ligands implicates electrophilic cleavage of the M—C bond. The rate profile for $CpFe(CO)_2R$, e.g., $R = Me \gg CH_2CMe_3$ and $R = CH_2CHMe_2$, $CH_2CH_2CMe_3 > CH_2CMe_3$ (*71*, *75*), is consistent with an S_E2 backside (*79*) attack of sulfur on α carbon. This is corroborated by the observed inversion of configuration at α carbon in the SO_2 insertion of *threo*-$CpFe(CO)_2CHDCHDCMe_3$ (*133*, *134*). Lack of any detectable change in the rate upon addition of a free-radical scavenger, 2,2-diphenyl-1-picrylhydrazyl, to a solution of $CpFe(CO)_2CH_2Ph$ in SO_2 (*71*, *75*) accords with the above mechanism. That SO_2 rather than, e.g., SO^{2+} is the interacting species receives support from a virtual insensitivity of the rate of the insertion with $CpFe(CO)_2CH_2Ph$ to addition of $S_2O_5^{2-}$ [SO_3^{2-} and SO_2 (*90*)]. Finally, absence of the *S*-sulfinato cross-products in the reaction represented by Eq. (17) as well as in the analogous reaction of SO_2 with $CpFe(CO)_2CH_2Ph$ and $MeMn(CO)_5$, precludes



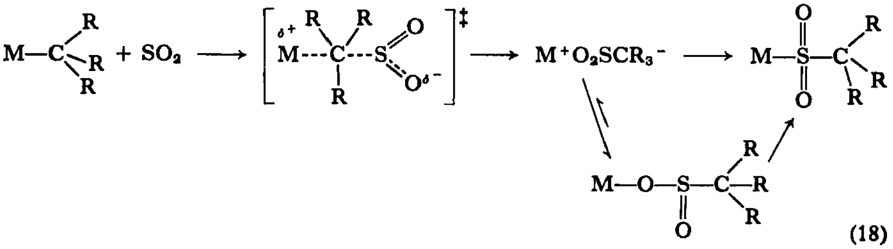
$$\mathrm{CpFe(CO)_2CH_2Ph + CpMo(CO)_3Me + 2SO_2}\ \begin{array}{l} \nearrow\ \mathrm{CpFe(CO)_2S(O)_2CH_2Ph} \\ \qquad \mathrm{+\ CpMo(CO)_3S(O)_2Me} \\ \not\searrow\ \mathrm{CpFe(CO)_2S(O)_2Me} \\ \qquad \mathrm{+\ CpMo(CO)_3S(O)_2CH_2Ph} \end{array} \qquad (17)$$

intermolecular interactions of a general type (IX) or random recombination of ions in the insertion (*71*, *75*).



(IX)

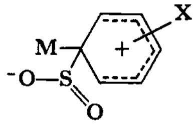
A mechanism consistent with these results is depicted in Eq. (18). The species $M^+O_2SCR_3^-$, most likely a contact ion pair, is invoked for steric and chemical (see Section III, B) reasons. It arises from the metal alkyl and SO_2 in the rate-determining step and then very rapidly affords $MOS(O)CR_3$. An irreversible formation of the *S*-sulfinate from both $M^+O_2SCR_3^-$ and $MOS(O)CR_3$ completes the reaction.



(18)

The insertion with $CpFe(CO)_2R$ in organic solvents follows second-order kinetics, first order in both the alkyl complex and the SO_2. However, the rate profile, i.e., R = *i*-Pr > CH_2CMe_3 > Me (*71*, *77*), is not that expected for a backside approach of SO_2. Such an attack would be suggested by the observation of inversion at α carbon in the insertion with $CpFe(CO)_2CHDCHDCMe_3$ in various solvents (*133*). However, this stereochemical result cannot be unambiguously applied to the mechanistic problem in question because extremely concentrated SO_2 solutions were employed. A similar difficulty exists with the insertion involving $(+)_{546}$-$CpFe(CO)_2CH(Me)Ph$ in pentane (*2*, *138*) (see Section III, H). Since a radical pathway for the solution reactions appears unlikely (*71*, *77*), either a four-center S_Ei or frontside S_E2 mechanism (*79*) may be operative in leading to the formation of the *O*-sulfinato intermediate. Of course, such a mechanism would be in discord with the observed (albeit not unambiguously) stereochemical change at carbon. Clearly, additional studies are needed to provide a more definitive picture.

Sulfur dioxide insertion with the aryl complexes also proceeds initially to the corresponding *O*-sulfinates. A moderate ρ value of -4.3 is to be compared with $\rho = -1.87$ for SO_2 insertion into the Sn—R bonds of Me_3SnR (*51*, *52*). It reflects some stabilization by the substituent X of the positive charge developing on the ring during the reaction. A transition state approximating (X) (or a corresponding closed structure), similar to the classical σ complex of electrophilic aromatic substitution reactions (*103*), seems reasonable on this basis.



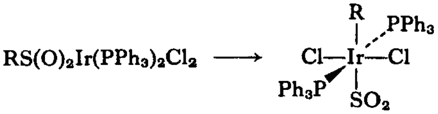
(X)

IV

KINETICS AND MECHANISM OF DESULFINATION

In contrast with the behavior of a number of arenesulfinates of mercury (*33*, *40*) and bismuth (*38*), transition metal sulfinates generally do not lose SO_2. Examples of the desulfination among the latter are limited to $CpFe(CO)_2S(O)_2C_6F_5$ (*43*), $CpMo(CO)_3S(O)_2CH_2Ph$ (*57*), and a few complexes of rhodium(III) (*15*, *41*, *45*), iridium(III) (*15*, *30*, *88*), palladium(II) (*53a*), and platinum(II) (*20*, *31*). Several of these, including four-coordinate platinum(II), have a vacant metal orbital which can provide a pathway for migration of R from $MS(O)_2R$. However, most of the sulfinates, especially the *S*-sulfinato carbonyls, lack this feature. Absence of a vacant coordination site, or a difficulty in making it available through ligand dissociation, very likely prevents facile desulfination. Use of vigorous experimental conditions, on the other hand, often leads to a substantial, if not complete, decomposition. Attempts to circumvent this by employing photochemical techniques (e.g., *13*, *57*, *66*) or by using $Rh(PPh_3)_3Cl$ to abstract coordinated CO (*3*) and thus furnish a vacant site on the metal have both been generally unsuccessful. In agreement with these observations, mass spectral studies on $RS(O)_2M(CO)_5$ (M = Mn and Re) (*81*, *97*) and $RS(O)_2Co(salen)(H_2O)_x$ (*36*) show that elimination of SO_2 from the parent ions represents only a minor fragmentation path. Loss of R is the major process.

The only kinetic study was that conducted on the reaction shown in Eq. (19) (*88*) where the isolated product is sometimes the dinuclear



(19)

(XI)

$[RIr(PPh_3)_2Cl_2]_2SO_2$ rather than (XI). Kinetic data for this reaction are presented in Table V. With the *p*-substituted aryl complexes, electron-withdrawing groups enhance the rate of the desulfination. When R = C_6F_5, the rearrangement is thought to be very rapid, since $C_6F_5S(O)_2Ir(PPh_3)_2Cl_2$ could be neither isolated nor detected during the reaction of $Ir(N_2)(PPh_3)_2Cl_2$ with $C_6F_5SO_2Cl$. Only $C_6F_5Ir(SO_2)(PPh_3)_2Cl_2$ was obtained. The desulfination is much slower for the metal alkyls than for the metal aryls and follows the order R = Me > Et > *n*-Pr. Solvent appears to have a modest effect on the rate: A twofold-to-threefold increase was observed for the metal aryls on going from benzene to THF. The relative velocity constants for the different complexes may

TABLE V

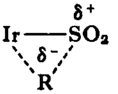
KINETIC DATA FOR DESULFINATION

$RS(O)_2Ir(PPh_3)_2Cl_2 \rightarrow RIr(SO_2)(PPh_3)_2Cl_2$[a]

R	Temp. (°C)	$k \times 10^3$ (sec^{-1})	$\Delta H^\ddagger$ (kcal/mole)	$\Delta S^\ddagger$ (e.u.)
p-$C_6H_4NO_2$	25.0	26.0	—	—
p-C_6H_4Cl	35.0	7.5	7.5	−44
Ph	35.0	4.3	16.3	−17
p-C_6H_4Me	35.0	3.5	15.3	−20
p-C_6H_4OMe	35.0	2.8	14.1	−25
Me	35.0	0.014	—	—
Et	35.0	0.009	—	—
n-Pr	35.0	0.006	—	—

[a] In THF; from Kubota and Loeffler (*88*).

indicate significant contributions of the carbanionic characteristics of R in the transition state, i.e., (XII). The kinetic cis product obtained in this manner would then undergo isomerization to (XI).



(XII)

V

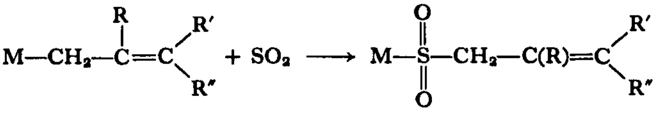
REACTIONS OF SULFUR DIOXIDE WITH σ-ALLYL, PROPARGYL, CYCLOPROPYL, AND CYCLOPROPYLMETHYL COMPLEXES OF TRANSITION METALS

A. Introduction

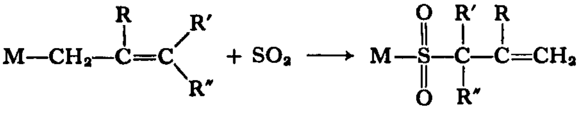
Three classes of transition metal–carbon σ-bonded compounds exhibit a behavior toward SO_2 which is different from that discussed in Section III. They are (1) allyl, (2) propargyl, and (3) cyclopropyl and cyclopropylmethyl complexes. Their reactions with SO_2 will be considered in this same order.

B. Metal-σ-Allyl Complexes

Two general types of *S*-sulfinate have been isolated from reactions of metal-σ-allyl complexes with SO_2: (1) that derived from insertion of SO_2 into the original M—C bond [Eq. (20)] and (2) that resulting from


$$\text{M—CH}_2\text{—C(R)=C}\begin{smallmatrix}\text{R}'\\\text{R}''\end{smallmatrix} + \text{SO}_2 \longrightarrow \text{M—}\overset{\text{O}}{\underset{\text{O}}{\overset{\|}{\underset{\|}{\text{S}}}}}\text{—CH}_2\text{—C(R)=C}\begin{smallmatrix}\text{R}'\\\text{R}''\end{smallmatrix} \qquad (20)$$

the insertion with rearrangement of the allylic moiety [Eq. (21)]. In several cases where both isomers were obtained, interconversion between

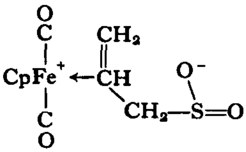

$$\text{M—CH}_2\text{—C(R)=C}\begin{smallmatrix}\text{R}'\\\text{R}''\end{smallmatrix} + \text{SO}_2 \longrightarrow \text{M—}\overset{\text{O}}{\underset{\text{O}}{\overset{\|}{\underset{\|}{\text{S}}}}}\text{—}\overset{\text{R}'}{\underset{\text{R}''}{\overset{|}{\underset{|}{\text{C}}}}}\text{—}\overset{\text{R}}{\overset{|}{\text{C}}}\text{=CH}_2 \qquad (21)$$

them was shown not to occur under the experimental conditions for the insertion (*32*, *43*). Some representative reactions are summarized in Table VI.

Several generalizations are possible from these data.

1. The nature of the metal together with its ancillary ligands plays a major role in determining whether the insertion occurs with or without rearrangement (e.g., Table VI, reactions 2, 4, 6, 16, and 18).
2. An increasing bulk of substitution at carbon-3 of the allyl group favors the unrearranged product (e.g., Table VI, reactions 1, 2, and 3 or 5, 6, and 9).
3. Electron-releasing Me substituents on the Cp ring promote formation of the unrearranged product (Table VI, reactions 6 and 11 or 9 and 14).
4. In neat SO_2, the relative amount of the rearranged *S*-sulfinate increases as the temperatures decreases (Table VI, reactions 6 and 7 or 11 and 12).
5. An inert solvent such as hexane promotes formation of the rearranged product when compared with neat SO_2 (Table VI, reactions 6 and 8 or 11 and 13).

It was shown recently that dissolution of $CpFe(CO)_2CH_2CH{=}CH_2$ in liquid SO_2 very rapidly affords a reaction intermediate which is formulated as zwitterionic (XIII) (*117*). The allyl $CpMo(CO)_3CH_2CH{=}CH_2$ behaves similarly. The olefin complex (XIII) rearranges during



(XIII)

attempts at isolation or, gradually, upon storage in neat SO_2 to yield $CpFe(CO)_2S(O)_2CH_2CH{=}CH_2$ and another $CpFe(CO)_2(C_3H_5SO_2)$ product. The latter has not yet been satisfactorily characterized, although spectroscopic evidence implicates an Fe—C σ bond, as well as an organic sulfone group, therein. Both products are stable with respect to interconversion. In contrast with the above behavior, $CpFe(CO)_2CH_2C(Me)$

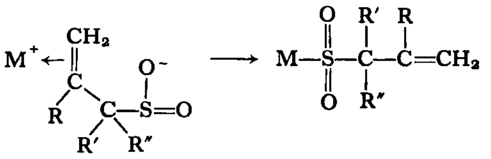
TABLE VI

Representative Data for $\mathrm{SO_2}$ Insertion of Various σ-Allyl Complexes

Reaction No.	Complex	Reaction conditions	Relative % of sulfinate		Reference
			Rearranged allyl group	Unrearranged allyl group	
1	$\mathrm{MeCH{=}CHCH_2Mn(CO)_5}$	$\mathrm{SO_2}$ at reflux	100	—	(*67*)
2	$\mathrm{Me_2C{=}CHCH_2Mn(CO)_5}$	$\mathrm{SO_2}$ at reflux	100	—	(*67*)
3	$\mathrm{PhCH{=}CHCH_2Mn(CO)_5}$	$\mathrm{SO_2}$ at reflux or neat $\mathrm{SO_2}$ at −70°C	—	100	(*67*)
4	$\mathrm{Me_2C{=}CHCH_2Re(CO)_5}$	$\mathrm{SO_2}$ at reflux	100	—	(*67*)
5	$\mathrm{CpFe(CO)_2CH_2CH{=}CHMe}$	$\mathrm{SO_2}$ at reflux	100	—	(*43,98*)
6	$\mathrm{CpFe(CO)_2CH_2CH{=}CMe_2}$	$\mathrm{SO_2}$ at reflux	25	75	(*43*)
7	$\mathrm{CpFe(CO)_2CH_2CH{=}CMe_2}$	Neat $\mathrm{SO_2}$ at −60°C	85	15	(*43*)
8	$\mathrm{CpFe(CO)_2CH_2CH{=}CMe_2}$	$\mathrm{SO_2}$-saturated hexane solution at 27°C	93	7	(*43*)
9	$\mathrm{CpFe(CO)_2CH_2CH{=}CHPh}$	$\mathrm{SO_2}$ at reflux	20	80	(*43*)
10	$\mathrm{(Me_5Cp)Fe(CO)_2CH_2CH{=}CHMe}$	$\mathrm{SO_2}$ at reflux	100	—	(*110*)
11	$\mathrm{(Me_5Cp)Fe(CO)_2CH_2CH{=}CMe_2}$	$\mathrm{SO_2}$ at reflux	—	100	(*110*)
12	$\mathrm{(Me_5Cp)Fe(CO)_2CH_2CH{=}CMe_2}$	Neat $\mathrm{SO_2}$ at −50°C	40	60	(*110*)
13	$\mathrm{(Me_5Cp)Fe(CO)_2CH_2CH{=}CMe_2}$	$\mathrm{SO_2}$-saturated hexane solution at 27°C	10	90	(*110*)
14	$\mathrm{(Me_5Cp)Fe(CO)_2CH_2CH{=}CHPh}$	$\mathrm{SO_2}$ at reflux	—	100	(*110*)
15	$\mathrm{CpMo(CO)_3CH_2CH{=}CHMe}$	$\mathrm{SO_2}$ at reflux	~90	~10	(*43*)
16	$\mathrm{CpMo(CO)_3CH_2CH{=}CMe_2}$	$\mathrm{SO_2}$ at reflux	—	100	(*43*)
17	$\mathrm{MeCH{=}CHCH_2Co(dmgH)_2py}$	Neat $\mathrm{SO_2}$ at −75° to 25°C	100	—	(*32*)
18	$\mathrm{Me_2C{=}CHCH_2Co(dmgH)_2py}$	Neat $\mathrm{SO_2}$ at −75° to 25°C	—	100	(*32*)
19	$\mathrm{PhCH{=}CHCH_2Co(dmgH)_2py}$	Neat $\mathrm{SO_2}$ at −75° to 25°C	—	100	(*32*)

$=CH_2$ and $CpFe(CO)_2CH_2CH{=}CHMe$ afford only the respective *S*-sulfinates, there being no evidence for Fe—C σ-bonded species.

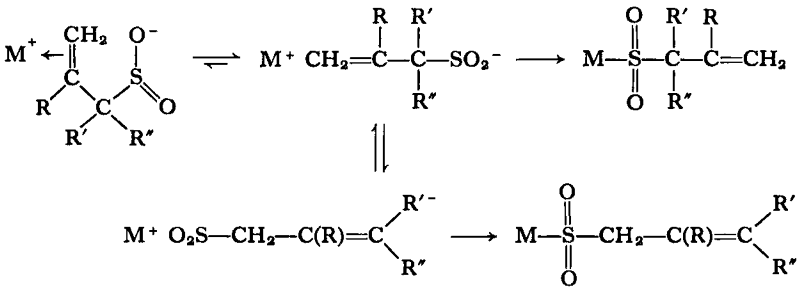
The above results may reflect on the relative stabilities of the zwitterionic olefin complexes, with the least alkyl-substituted olefin, *viz.* (XIII), affording the most stable intermediate. Displacement of the olefinic C=C from the metal by the anionic terminus of the ligand furnishes the *S*-sulfinate, possibly via its *O*-bonded isomer. If this substitution occurs in a concerted fashion, then the product most likely will contain a rearranged allylic fragment [Eq. (22)]. An alternative mode of collapse



(22)

of the zwitterionic intermediate is through attack of the oxygen (or sulfur) at the $CH_2{=}C(R)$. This would be expected to occur with the more stable olefin complexes such as (XIII); it accounts satisfactorily for the formation of the Fe—C σ-bonded $CpFe(CO)_2(C_3H_5SO_2)$ species therefrom.

The pathway which gives rise to the unrearranged *S*-sulfinates [see Eq. (20)] is not obvious. A reasonable mechanism comprises dissociation of the olefin intermediate, rearrangement of the allylsulfinate anion, and then recombination of the ions [Eq. (23)]. Such a scheme accords with



(23)

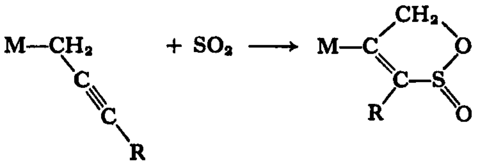
generalizations (1)–(5) made earlier in this section concerning the mode of the insertion with the various metal allyl systems. Nevertheless, the above observations can also be satisfactorily accommodated by assuming a "direct insertion" into the M—C bond such as that proposed for the alkyl complexes (Section III, I). The latter would then compete with an "olefin-complex intermediate" pathway which leads to rearrangement.

Allyl complexes of formula $RR'C{=}CHCH_2Co(dmgH)_2py$ also yield the rearranged as well as the unrearranged sulfinates when treated with SO_2 (Table VI, reactions 17–19) (*32*). It has been suggested that these reactions involve a free-radical mechanism initiated by homolysis of the Co—C bond. Whereas this appears to be a reasonable proposal for the complexes in question, its applicability to the metal allyl carbonyl systems is doubtful. It would seem highly improbable that $CpFe(CO)_2CH_2CH{=}CH_2$ and $CpMo(CO)_3CH_2CH{=}CH_2$, which form zwitterionic olefin complexes, should react by a mechanism different from that of their substituted analogs.

No desulfination has been reported for metal *S*-sulfinates containing an allyl grouping.

C. Metal-Propargyl Complexes

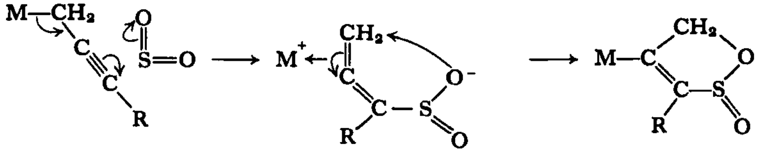
Virtually all of the transition metal–propargyl complexes investigated react readily with either neat SO_2 or SO_2 in organic solvents according to Eq. (24), where M = $CpFe(CO)_2$ (*111*, *124*), $CpMo(CO)_3$ (*111*, *124*),



(24)

$CpMo(CO)_2L$ (*124*), $CpW(CO)_3$ (*87*), $Mn(CO)_5$ (*92*, *93*, *124*, *125*), or $Mn(CO)_4L$ (*8*), and R = Me, Ph, $CH_2Fe(CO)_2Cp$, or H. Insertion into the M—CH_2 bond has not been observed in these reactions, and only $HC{\equiv}CCH_2Mn(CO)_3(PPh_3)_2$ was found to be inert toward SO_2 (*8*). The structure of a representative product, $CpFe(CO)_2\overline{C{=}C(Me)S(O)OC}H_2$, was elucidated by X-ray crystallography (*23*, *25*).

The above reactions are thought to proceed as shown in Eq. (25) (*8*, *92*). Consistent with this general scheme, the 3-alkynyl complex $CpFe(CO)_2CH_2CH_2C{\equiv}CMe$ affords the corresponding *S*-sulfinate when treated with sulfur dioxide (*124*).

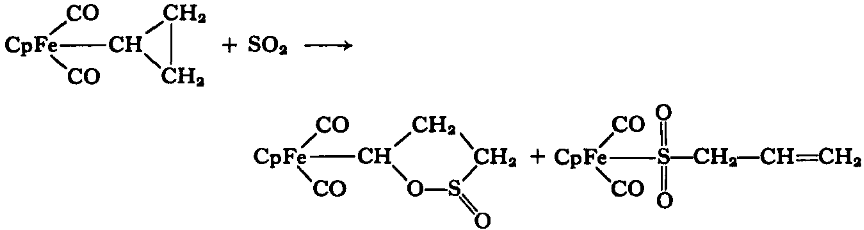


(25)

The desulfination of the metal-vinyl products containing a sultine ring has been effected for CpFe(CO)$_2$C=C(Me)S(O)OCH$_2$ and CH$_2$OS(O)CH=CMn(CO)$_5$ (*124*). The parent propargyl complex was isolated in each case.

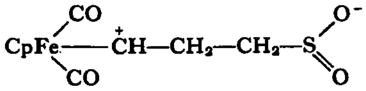
D. *Metal-Cyclopropyl and Metal-Cyclopropylmethyl Complexes*

Rosenblum and co-workers (*37*) synthesized CpFe(CO)$_2$Cpr and investigated its reaction with SO$_2$ [Eq. (26)]. The formation of both (XIV) and, in small amounts, CpFe(CO)$_2$S(O)$_2$CH$_2$CH=CH$_2$ is believed to involve the intermediacy of the dipolar carbene complex (XV), which results from electrophilic attack of SO$_2$ at the cyclopropyl ring.

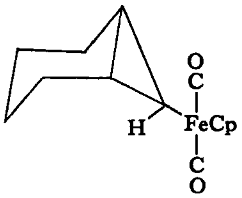


(26)

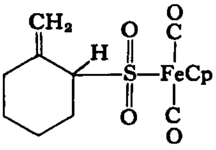
(XIV)



(XV)



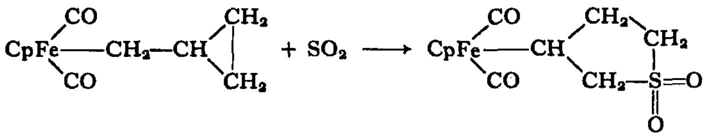
(XVI)



(XVII)

The reaction of SO_2 with the norcarane complex (XVI) yields only the *S*-sulfinate (XVII) for stereochemical reasons.

The cyclopropylmethyl derivative $CpFe(CO)_2CH_2Cpr$ reacts with SO_2 according to Eq. (27) (*56*). The product rearranges to $CpFe(CO)_2$-$S(O)_2CH_2CH_2CH{=}CH_2$ on heating at 125°–130°C.

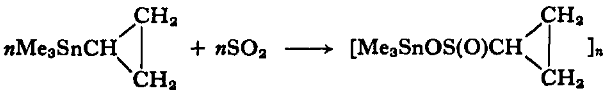

(27)

E. Comparisons and Conclusion

Most of the SO_2 reactions presented in this section, especially those of the propargyl and cyclopropyl complexes, contrast sharply with the reactions of the corresponding tin–carbon compounds. Representative examples of the latter are provided in Eqs. (28)–(30) (*49*, *50*). It is

$$n\mathrm{Ph_3SnCH_2CH{=}CHMe} + n\mathrm{SO_2} \longrightarrow [\mathrm{Ph_3SnOS(O)CH(Me)CH{=}CH_2}]_n \tag{28}$$

$$n\mathrm{Me_3SnCH_2C{\equiv}CH} + n\mathrm{SO_2} \longrightarrow [\mathrm{Me_3SnOS(O)CH{=}C{=}CH_2}]_n \tag{29}$$


(30)

noteworthy that the interposition of SO_2 always occurs with rearrangement of the allyl and propargyl fragments, and that the cyclopropyl ring remains intact in the insertion.

The foregoing product differences may be ascribed to the propensity of a transition metal to participate in ligand rearrangements and to stabilize certain organic species through coordination. Accordingly, the occurrence of $\sigma \rightleftharpoons \pi$ (or *monohapto* $\rightleftharpoons$ *dihapto*) rearrangements such as those depicted in Eq. (25), as well as formation of metal–carbene intermediates, represent pathways which are accessible to the metal–carbon systems of the transition elements but not the main group elements.

VI

SURVEY OF REACTIONS INVOLVING SULFUR DIOXIDE

Surveyed in this section are known SO_2 insertion and desulfination reactions. Kinetic and stereochemical results already discussed in Sections III–V, as well as the cycloaddition processes treated in Section V, have been given a cursory mention for the sake of completeness. The insertion reactions involving bonds other than M—C are omitted. Also excluded are all aspects of the chemistry of metal sulfinate complexes except sulfur dioxide insertion and desulfination. Readers interested in alternative methods of synthesis and in the physical and chemical properties of these and related compounds are referred to a recent review (*128*).

A. Titanium Triad

1. *Titanium*

The complex Cp_2TiMe_2 reacts with SO_2 in CH_2Cl_2 or petroleum ether at −78°C to afford $Cp_2Ti(O_2SMe)_2$ (*131*). A similar diinsertion was carried out with Cp_2TiPh_2 at room temperature. The monomethyl compound $Cp_2Ti(Me)Cl$ is less reactive than Cp_2TiMe_2; with neat SO_2 it gives $Cp_2Ti(O_2SMe)Cl$ which appears to be a mixture of two isomers, possibly *O*- and *O,O′*-sulfinates. The synthesis of $Cp_2Ti(O_2SPh)_2$ and $Cp_2Ti(O_2SR)Cl$ (R = Me and Et) *via* the SO_2 insertion is given in the patent literature (*99a*).

Insertion of SO_2 into the Ti—Me bonds of $MeTiCl_3$ and $MeTiBr_3$ has recently been reported (*28a*).

2. *Zirconium*

Reaction of Cp_2ZrMe_2 with neat SO_2 affords $CpZr(O_2SC_5H_5)(O_2SMe)_2$ at −78°C, and what is thought to be $(C_5H_5SO_2)_2ZrSO_3$ at room temperature (*132*). Treatment of $Cp_3ZrC_5H_5$ with SO_2 at room temperature yields $CpZr(O_2SC_5H_5)_3$. Insertion also occurs into the Zr—Cp bond of $Cp_2Zr(Me)Cl$ to give what is tentatively formulated as $CpZr(O_2SC_5H_5)(O_2SMe)Cl$ (*131*). Reaction between $(Cp_2ZrCl)_2O$ and SO_2 furnishes $[CpZr(O_2SC_5H_5)O]_n$ and Cp_2ZrCl_2; the former gives $[CpZr(O_2SC_5H_5)SO_3]_n$ on further treatment with SO_2.

B. Vanadium Triad

Neither SO_2 insertion nor desulfination studies have been reported for these elements.

C. Chromium Triad

1. *Chromium*

Sulfur dioxide insertion has been effected with $CpCr(NO)_2R$ [R = Me (*61*), CH_2Ph (*61*, *71*, *76*), and Ph (*71*, *76*)] in neat SO_2; the first two compounds also undergo this reaction in hexane solution at room temperature (*61*). The isolated *S*-sulfinate with R = CH_2Ph does not eliminate SO_2 upon heating or photolysis (*61*).

The ion $PhCH_2Cr(H_2O)_5{}^{2+}$ decomposes rapidly when treated with SO_2 (*4*).

2. *Molybdenum*

The alkyls $CpMo(CO)_3R$ (R = Me, Et, and CH_2Ph) readily insert SO_2 (*57*); these reactions were the subject of a kinetic study (*71*, *76*). When R = CH_2Ph, the *O*-sulfinato intermediate was detected spectroscopically (*72*, *73*). Contrasting with the above behavior is the apparent lack of reactivity of $CpMo(CO)_3CF_3$ (*57*) and $CpMo(CO)_3CH_2CN$ (*124*) toward neat SO_2. However, the dicarbonyl $CpMo(CO)_2(PPh_3)Me$ does afford the corresponding *S*-sulfinate, the reaction proceeding much more rapidly than that of its parent tricarbonyl, $CpMo(CO)_3Me$ (*57*). The photochemically induced desulfination of $CpMo(CO)_3S(O)_2$-CH_2Ph furnishes $CpMo(CO)_3CH_2Ph$ (35% yield); in contrast, irradiation of $CpMo(CO)_3S(O)_2Me$ yields $[CpMo(CO)_3]_2$ (*57*).

The reactions of $CpMo(CO)_3CH_2C(R){=}CR'R''$ and $CpMo(CO)_2$-$[P(OPh)_3]CH_2C(R){=}CR'R''$ with SO_2 have been investigated for several different allyl groups and under various experimental conditions (*43*, *110*, *117*). The unsubstituted allyl $CpMo(CO)_3CH_2CH{=}CH_2$ reacts rapidly with neat SO_2 to yield a zwitterionic olefin complex (*117*) which on storage in sulfur dioxide affords $CpMo(CO)_3S(O)_2CH_2CH{=}CH_2$ (*43*). The substituted allyls $CpMo(CO)_3CH_2CH{=}CMe_2$ (*43*), $CpMo(CO)_3CH_2CH{=}CHPh$ (*43*, *98*), and $CpMo(CO)_3CH_2CH{=}CHCl$

(*43*) give the unrearranged *S*-sulfinates only, with the last-mentioned complex yielding also $CpMo(CO)_3Cl$, the main product. In contrast, $CpMo(CO)_3CH_2CH{=}CHMe$ furnishes almost exclusively the rearranged *S*-sulfinate (*43, 98*). Most of the above products were isolated in low yields.

Treatment of $CpMo(CO)_2[P(OPh)_3]CH_2CH{=}CMe_2$ and $CpMo(CO)_2[P(OPh)_3]CH_2CH{=}CHPh$ with neat SO_2 affords the unrearranged *S*-sulfinates (*110*). However, the behavior toward SO_2 of $CpMo(CO)_2[P(OPh)_3]CH_2CH{=}CHMe$ is more complex and contrasts with that of its parent tricarbonyl (see above). When the reaction is conducted in liquid SO_2 at reflux or at −50°C, the unrearranged product comprises 80 and 60%, respectively, of the *S*-sulfinate mixture; the same reaction in benzene or chloroform solution gives an unrearranged/rearranged *S*-sulfinate ratio of 80:20. The different product distributions for $CpMo(CO)_3CH_2CH{=}CHMe$ and $CpMo(CO)_2[P(OPh)_3]CH_2CH{=}CHMe$ may be rationalized by mechanistic considerations given in Section V, B on electronic and/or steric grounds.

The propargyl complexes $CpMo(CO)_3CH_2C{\equiv}CR$ [R = H, Me (*111, 124, 138*), Ph (*111, 124*), and $CH_2Mo(CO)_3Cp$ (*124*)] and $CpMo(CO)_2[P(OPh)_3]CH_2C{\equiv}CMe$ (*124*) on treatment with SO_2 yield metal-vinyl derivatives containing a sultine ring (see Section V, C).

Several h^3-allyl complexes of the type $[h^3\text{-}CH_2C(R)CH_2]Mo(CO)_2L_2X$ and $[h^3\text{-}CH_2C(R)CH_2]Mo(CO)_2L_3{}^+X^-$ were found to be inert to liquid SO_2 (*70*).

3. *Tungsten*

Although alkyl complexes of formula $CpW(CO)_3R$ are virtually inert to neat SO_2 at reflux (*57*), they can be sulfinated at higher temperatures. Accordingly, the *S*-sulfinates with R = Me, Et, and CH_2Ph were prepared from the corresponding metal alkyls and SO_2 at 50°–55°C (*87*).

The allyls $CpW(CO)_3CH_2CH{=}CHMe$ and $CpW(CO)_3CH_2CH{=}CMe_2$ yield the rearranged and the unrearranged *S*-sulfinate, respectively, when treated with SO_2 at reflux (*43*). Both products were obtained in small quantities.

The complexes $CpW(CO)_3\overline{C{=}C(R)S(O)OC}H_2$ (R = Me and Ph) result from the action of SO_2 on the appropriate propargyl derivative in pentane (*87*).

D. Manganese Triad

1. *Manganese*

Several *S*-bonded sulfinates of the general type $RS(O)_2Mn(CO)_5$ [R = Me (*65*, *66*), Et (*66*), CH_2Ph (*65*, *66*), and Ph (*66*)] have been isolated by treating the appropriate metal alkyl or aryl with liquid SO_2. Whereas the reaction of the metal alkyls proceeds readily at −10°C, that of $PhMn(CO)_5$ requires temperatures of 35–45°C and affords also $PhC(O)Mn(CO)_5$. In the insertion with the R = Me and CH_2Ph complexes, the intermediate *O*-sulfinate was detected by NMR spectroscopy (*72*, *73*). The last-mentioned reactions were studied kinetically (*71*, *76*). The acyls $MeC(O)Mn(CO)_5$ and $CF_3C(O)Mn(CO)_5$, as well as $CF_3Mn(CO)_5$, failed to react with neat SO_2 at reflux (*66*). The insertion with *cis*-$MeMn(CO)_4PPh_3$ at various temperatures yields *cis*-$MeS(O)_2Mn(CO)_4PPh_3$ (*68*). The stereochemistry of the sulfination of *cis*-$MeMn(CO)_4{}^{13}CO$ (*109*) was already mentioned in Section III, H.

Attempts at extrusion of SO_2 from $PhCH_2S(O)_2Mn(CO)_5$ by the application of heat or UV light have been unsuccessful (*66*).

Treatment of $CH_2{=}CHCH_2Mn(CO)_5$, $MeCH{=}CHCH_2Mn(CO)_5$, $Me_2C{=}CHCH_2Mn(CO)_5$, $CH_2{=}C(Cl)CH_2Mn(CO)_5$, and $PhCH{=}CHCH_2Mn(CO)_5$ with sulfur dioxide affords the corresponding *S*-sulfinates (*64*, *67*). The 2-butenyl and 3-methyl-2-butenyl complexes react with rearrangement, whereas the cinnamyl derivative affords the corresponding unrearranged allylsulfinate. Surprisingly, $ClCH{=}CHCH_2$-$Mn(CO)_5$ yields $Mn(CO)_5Cl$ and an unidentified oil when treated with either neat SO_2 or SO_2 in pentane (*67*).

The propargyl complexes $RC{\equiv}CCH_2Mn(CO)_5$ [R = H (*124*, *125*, *138*), Me (*124*, *138*), and Ph (*92*, *93*)] and $HC{\equiv}CCH_2Mn(CO)_4PPh_3$ (*8*) undergo cycloaddition reactions with SO_2 to give the corresponding sultine ring-containing derivatives. Unexpectedly, $HC{\equiv}CCH_2Mn$-$(CO)_3(PPh_3)_2$ does not take part in this reaction (*8*).

2. *Rhenium*

The *O*-bonded $MeS(O)ORe(CO)_5$, formed initially in SO_2 insertion with $MeRe(CO)_5$, displays moderate stability in solution and was studied spectroscopically (*73*). A kinetic study of its formation was also conducted

(*71*, *76*). The final, thermodynamic product of the insertion reaction of $\mathrm{MeRe(CO)_5}$ and of the analogous benzyl complex is the isolable *S*-sulfinate, $\mathrm{RS(O)_2Re(CO)_5}$ (R = Me and $\mathrm{CH_2Ph}$) (*66*).

The allyl $\mathrm{Me_2C{=}CHCH_2Re(CO)_5}$ reacts with neat $\mathrm{SO_2}$ at reflux to form the rearranged *S*-sulfinate, $\mathrm{CH_2{=}CHC(Me)_2S(O)_2Re(CO)_5}$ (*67*).

E. Iron Triad

1. *Iron*

By far the most extensively and intensively investigated sulfur dioxide insertion reactions have been those of complexes $\mathrm{CpFe(CO)_2R}$ and $\mathrm{(R'_xCp)Fe(CO)_2R}$. Iron alkyls of formula $\mathrm{CpFe(CO)_2R}$ exhibit a broad spectrum of reactivity toward neat $\mathrm{SO_2}$. Known to react virtually instantaneously are the complexes with R = Me, Et (*12*, *13*, *71*, *74*, *75*), *i*-Pr (*71*, *75*), and $\mathrm{CH_2SiMe_3}$ (*71*, *74*, *75*); reacting sufficiently rapidly to yield at least some isolable *S*-sulfinate are the derivatives with the groups $\mathrm{CH_2CMe_3}$, $\mathrm{CH_2CHMe_2}$, $\mathrm{CH_2CH_2CN}$, $\mathrm{CMe_3}$, $\mathrm{CH_2SMe}$, $\mathrm{CH_2C_6H_4OMe}$-*p* (*71*, *75*), $\mathrm{CH_2CH_2CMe_3}$ (*71*, *75*, *133*, *134*), $\mathrm{CH_2OMe}$ (*71*, *74*, *75*), $\mathrm{CH_2Ph}$ (*12*, *13*, *71*, *74*, *75*), CH(Me)Ph (*2*, *71*, *75*), $\mathrm{CH_2C_6H_4F}$-*p* (*43*), $\mathrm{CH_2CH_2C{\equiv}CMe}$ (*124*), and 1-Naph (*83*); and not giving any detectable products at temperatures up to −10° or 25°C are the compounds with R = $\mathrm{CH_2C_6F_5}$ (*17*), $\mathrm{CH_2CN}$ (*43*, *71*, *75*), $\mathrm{CH_2C(O)Me}$ (*71*, *75*), and $\overline{\mathrm{CHC(Me)_2C(O)N(SO_2NHPh)C}}\mathrm{H_2}$ (*141*). Interestingly, $\mathrm{CpFe(CO)_2S(O)_2Me}$ also arises, in low yield, from reaction of $\mathrm{[CpFe(CO)_2]_2SnMe_2}$ with $\mathrm{SO_2}$ in ether (*44*). The reactive iron aryls are listed in Table III; furthermore, $\mathrm{CpFe(CO)_2C_6F_5}$ is, as expected, inert to $\mathrm{SO_2}$ (*13*). Other unreactive $\mathrm{CpFe(CO)_2R}$ complexes include those with R = C(O)Me, C(O)Ph (*13*), $\mathrm{CH{=}CH_2}$, $\mathrm{C{\equiv}CMe}$, $\mathrm{CH{=}C{=}CH_2}$, and $\mathrm{CH{=}C{=}CHMe}$ (*124*). The dinuclear $\mathrm{CpFe(CO)_2CH_2CH_2CH_2Fe(CO)_2Cp}$ affords both the mono- and di-*S*-sulfinate when treated with liquid $\mathrm{SO_2}$ [Eq. (31)] (*13*).

$$\begin{aligned}&\mathrm{CpFe(CO)_2CH_2CH_2CH_2Fe(CO)_2Cp + SO_2 \longrightarrow}\\ &\qquad\mathrm{CpFe(CO)_2S(O)_2CH_2CH_2CH_2Fe(CO)_2Cp\ +}\\ &\qquad\qquad\mathrm{CpFe(CO)_2S(O)_2CH_2CH_2CH_2S(O)_2Fe(CO)_2Cp}\end{aligned} \tag{31}$$

Complexes of general formula $\mathrm{(R'_xCp)Fe(CO)_2R}$ which are known to insert SO_2 include $IndFe(CO)_2CH_2Ph$, $(MeCp)Fe(CO)_2R$ (R = CH_2Ph and p-C_6H_4Me), and $(Me_5Cp)Fe(CO)_2R$ (R = CH_2Ph and Ph); $(Me_5Cp)Fe(CO)_2R$ (R = CH_2CN and C_6F_5) do not react (*71*, *75*).

Sulfur dioxide insertion reactions of CpFe(CO)LR (L = P- or As-donor ligand) proceed much more readily than those of $CpFe(CO)_2R$. Accordingly, $CpFe(CO)(PPh_3)R$ (R = Me and CH_2Ph), $CpFe(CO)(AsPh_3)CH_2Ph$, and $CpFe(CO)[P(n\text{-}Bu)_3]Me$ form the corresponding *S*-sulfinates very rapidly either in neat SO_2 or in SO_2-saturated organic solutions (*59*). The *S*-sulfinate $CpFe(CO)(PPh_3)S(O)_2Me$ also results from reaction between solid $CpFe(CO)(PPh_3)Me$ and gaseous SO_2. Further examples of the insertion are provided by the phosphite complexes $CpFe(CO)[P(OR)_3]Me$ (R = Me, *n*-Bu, and Ph) (*119*).

The detection and identification of the *O*-sulfinato intermediates in some of these reactions (*72*, *73*) are discussed in Section III, B. Kinetic studies on the insertion with a number of $CpFe(CO)_2R$ and $(R'_xCp)Fe(CO)_2R$ alkyls and aryls (*71*, *74*, *75*, *77*) are treated in various parts of Section III; stereochemical investigations on $CpFe(CO)_2R$ and (R′R″Cp) Fe(CO)LR (*2*, *7*, *133*, *134*, *138*) are presented in Section III, H.

Sulfur dioxide extrusion has been reported only for $CpFe(CO)_2S(O)_2C_6F_5$ [Eq. (32)]. This desulfination can be effected either photochemically or thermally in toluene at reflux (*43*). Other $CpFe(CO)_2S(O)_2R$ complexes [R = CCl_3 (*43*), Me, CH_2Ph, and Ph (*13*)] resist loss

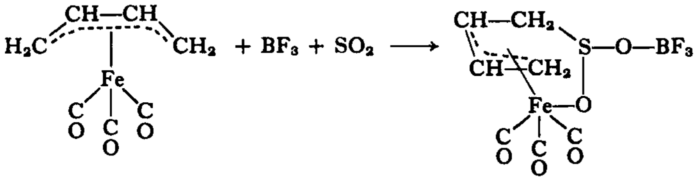
$$CpFe(CO)_2S(O)_2C_6F_5 \longrightarrow CpFe(CO)_2C_6F_5 + SO_2 \qquad (32)$$

of SO_2 under comparable conditions, as do also $CpFe(CO)(L)S(O)_2R$ (*59*).

The insertion reactions have also been investigated with a number of allyl complexes of the types $CpFe(CO)_2CH_2C(R){=}CR'R''$ (*43*, *98*, *117*), $(MeCp)Fe(CO)_2CH_2C(R){=}CR'R''$, $(Me_5Cp)Fe(CO)_2CH_2C(R){=}CR'R''$, and $(1,3\text{-}Ph_2Cp)Fe(CO)_2CH_2C(R){=}CR'R''$ (*110*). The crotyl complexes (R = R′ = H, R″ = Me) afford the rearranged *S*-sulfinates under all experimental conditions employed (*43*, *98*, *110*). The cinnamyl derivative (R = R′ = H, R″ = Ph) of $(Me_5Cp)Fe(CO)_2$ yields only the unrearranged *S*-sulfinate (*110*), but the analogous derivatives of $CpFe(CO)_2$ and $(MeCp)Fe(CO)_2$ furnish mixtures of the two isomeric products (*43*, *110*). The behavior of the 3-methyl-2-butenyl complexes (R = H, R′ = R″ = Me) has been studied in greatest detail and found to be sensitive to both substitution on the h^5-cyclopentadienyl ring and the experimental conditions for the insertion. Accordingly, in liquid SO_2 at reflux the ratio of the rearranged to the unrearranged *S*-sulfinate (which does not change with time) is 25:75 for $CpFe(CO)_2$, $(MeCp)Fe(CO)_2$, and $(1,3\text{-}Ph_2Cp)Fe(CO)_2$, but 0:100 for $(Me_5Cp)Fe(CO)_2$ (*43*, *110*). The relative amount of the rearranged *S*-sulfinate obtained in the synthesis can usually be increased by employing either lower temperatures or SO_2 solutions in organic solvents. Polarity and/or dielectric constant of the solvent appear to be important determinants, since the ratio of the rearranged to the unrearranged *S*-sulfinate from $CpFe(CO)_2CH_2CH{=}CMe_2$ increases as a function of the medium in the order $MeCN \sim MeNO_2 < C_6H_6 <$ pentane (*43*). The behavior of $CpFe(CO)_2CH_2CH{=}CH_2$ toward neat SO_2 (*117*) was already mentioned in Section V, B.

Iron–propargyl complexes of formula $CpFe(CO)_2CH_2C{\equiv}CR$ [R = Me (*25*, *111*, *124*), Ph (*111*, *124*), and $CH_2Fe(CO)_2Cp$ (*124*)] react with SO_2 to afford $CpFe(CO)_2\overline{C{=}C(R)S(O)OC}H_2$. The behavior toward sulfur dioxide of analogous cyclopropyl and cyclopropylmethyl complexes (*37*, *56*) was discussed in Section V, D.

An interesting insertion of SO_2BF_3 (and SO_2SbF_5) occurs into one of the h^4-butadiene carbon–iron bonds of $(h^4\text{-}C_4H_6)Fe(CO)_3$ [Eq. (33)] (*26*). The structure of (XVIII) was determined crystallographically (*22*). No reaction takes place in the absence of BF_3.



(33)

(XVIII)

2. *Ruthenium*

The alkyls $CpRu(CO)_2R$ having R = Me and CH_2Ph react with neat SO_2 to give the corresponding isolable *S*-sulfinates. The kinetics of these reactions were examined (*71*, *76*).

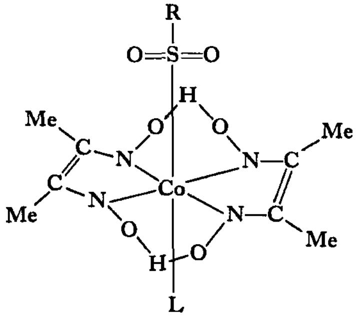
A study was reported on the desulfination of some arenesulfonyl halides, RSO_2X, using $Ru(PPh_3)_3Cl_2$ (*15*).

F. Cobalt Triad

1. *Cobalt*

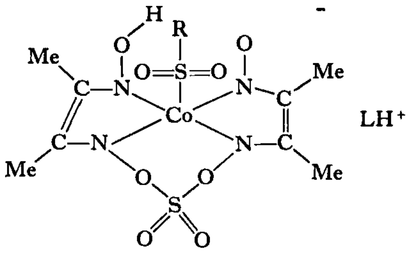
Sulfur dioxide was found to insert into the Co—C bonds of $K_3[PhCH_2Co(CN)_5]\cdot 2H_2O$ (*140*) and $K_3[MeCo(CN)_5]$ (*82*) to yield the corresponding *S*-sulfinates. Heating $K_3[MeS(O)_2Co(CN)_5]$ at 110°C does not result in extrusion of SO_2. Treatment of $K_3[PhCH_2S(O)_2Co(CN)_5]\cdot 2H_2O$ with MeI affords $MeS(O)_2CH_2Ph$.

Cobalt(III) complexes of the type $RCo(L_2)_2L$ and $RCo(L_4)L$ (L_2 = dmgH; L_4 = salen, salophen, or bae), which do not insert CO (*137*), generally react readily with liquid SO_2. The following $RS(O)_2Co(dmgH)_2L$ *S*-sulfinates (XIX) have been synthesized in this manner: R = Me, L = py (*36*, *82*, *144*), isoquin, PPh_3, $AsPh_3$, and SMe_2 (*82*); R = CH_2Ph, L = py (*82*, *144*) and isoquin (*82*); R = Et, L = $AsPh_3$; and R = *i*-Pr and *n*-C_8H_{17}, L = py (*82*). No reaction was observed between $PhCo(dmgH)_2py$ and SO_2, even at 50°C (*36*). Moist sulfur dioxide promotes the insertion with $MeCo(dmgH)_2py$ and gives rise to formation of another, main product when R = Me, L = py and isoquin or when R = CH_2Ph, L = isoquin. The latter contains two molecules of SO_2 for each $RCo(dmgH)_2py$ and has been assigned tentative structure (XX) (*82*).



(XIX)

Further studies on reactions of $RCo(dmgH)_2py$ with SO_2 have shown that the insertion occurs, albeit slowly and/or with low yield of the *S*-sulfinate, when R = $(CH_2)_2CH{=}CH_2$, $(CH_2)_4CH{=}CH_2$, $CH_2\overline{CH(CH_2)_3C}H_2$, and $\overline{CH(CH_2)_4C}H_2$ (*32*). With wet SO_2, an



(XX)

important competing process is formation of appropriate olefins. No stable products could be isolated when R = CH=C=CH$_2$ or CH$_2$C≡CH, and no reaction was observed when R = CH=CH$_2$, CH=CHPh, or C(Ph)=CH$_2$. The allyls RR'C=CHCH$_2$Co(dmgH)$_2$py (R = H, R' = Me; R = R' = Me; and R = H, R' = Ph) were also investigated; the first inserts SO$_2$ with rearrangement and the last two without.

Analogous complexes of cobalt(III) containing a tetradentate ligand (L$_4$) have furnished strictly parallel results. Accordingly, the insertion was observed to occur either in neat SO$_2$ or in DMF solution with RCo(salen)H$_2$O when R = Me (*36*, *82*, *100*) or Et (*36*, *100*), but not when R = Ph or C$_6$F$_5$ (*36*). The complexes MeCo(salophen)H$_2$O (*36*) and MeCo(bae)H$_2$O (*82*) also yield the corresponding *S*-sulfinates on treatment with sulfur dioxide.

2. *Rhodium*

Reaction of (h^3-C$_3$H$_5$)Rh(PPh$_3$)$_2$Cl$_2$ with sulfur dioxide at 20°C affords CH$_2$=CHCH$_2$Rh(SO$_2$)(PPh$_3$)$_2$Cl$_2$, which from its mass spectrum is thought to contain separately bonded σ-C$_3$H$_5$ and SO$_2$ (*129*). Treatment with SO$_2$ of CHF$_2$CF$_2$Rh(CO)(PPh$_3$)$_2$ (*139*) and RC≡CRh(CO)(PPh$_3$)$_2$ (R = Me and Et) (*16*) gives the corresponding five-coordinate, SO$_2$-containing complexes.

The elimination of SO$_2$ occurring in the reaction shown in Eq. (34)

$$\mathrm{CpRh(CO)(PPh_3)CH_2CN^+ + PhSO_2^- \longrightarrow CpRh(PPh_3)(Ph)CH_2CN + CO + SO_2} \qquad (34)$$

has been suggested to proceed via a rhodium sulfinate complex (*45*). Evolution of SO$_2$ has been observed also from RS(O)$_2$Rh(CO)L$_2$Cl$_2$ (R = Me and p-C$_6$H$_4$Me, L = PMe$_2$Ph or AsMe$_2$Ph) on melting (*41*).

The catalytic desulfination of several arenesulfonyl halides has been studied using $Rh(PPh_3)_3Cl$ and $Rh(CO)(PPh_3)_2Cl$ (*15*).

3. *Iridium*

No examples are known of sulfur dioxide insertion into Ir–C σ bonds. Reaction between $RC{\equiv}CIr(CO)(PPh_3)_2$ [R = Me, Et, *n*-Bu, or $C(OH)Me_2$] and SO_2 affords five-coordinate $RC{\equiv}CIr(CO)(SO_2)(PPh_3)_2$ (*16*).

The extrusion of SO_2 from $RS(O)_2Ir(CO)(PPh_3)_2Cl_2$ to give $RIr(CO)(PPh_3)_2Cl_2$ occurs on heating in toluene at 110°C when R = Ph and p-C_6H_4Me, but not when R = alkyl, p-C_6H_4Cl, p-$C_6H_4NO_2$, and p-C_6H_4OMe (*30*). In contrast, the desulfination of five-coordinate $RS(O)_2Ir(PPh_3)_2Cl_2$ proceeds much more readily; this reaction [Eq. (19)] was the subject of a kinetic study (*88*) and is discussed fully in Section IV.

Arenesulfonyl chlorides, RSO_2Cl, are catalytically desulfinated in the presence of $Ir(CO)(PPh_3)_2Cl$ (*15*). The isolation of complexes of formulas $RSO_2Ir(CO)(PPh_3)_2Cl_2$, $RSO_2Ir(CO)(PPh_3)Cl_2$, $RIr(CO)(SO_2)(PPh_3)Cl_2$, and $RIr(CO)(PPh_3)Cl_2$ suggests the following sequence of reactions for this process:

$$RSO_2Ir(CO)(PPh_3)_2Cl_2 \xrightarrow{-PPh_3} RSO_2Ir(CO)(PPh_3)Cl_2 \xrightarrow{\text{desulfination}}$$

$$RIr(CO)(SO_2)(PPh_3)Cl_2 \xrightarrow{-SO_2} RIr(CO)(PPh_3)Cl_2 \xrightarrow{PPh_3} RIr(CO)(PPh_3)_2Cl_2 \quad (35)$$

G. Nickel Triad

1. *Nickel*

The reaction of $CpNi(PR_3)Me$ (R = Ph or *n*-Bu) with neat SO_2 to give $CpNi(PR_3)S(O)_2Me$ (*107*) represents the only known sulfur dioxide insertions into a Ni–C bond.

2. *Palladium*

Reaction between $(h^3\text{-}C_3H_5)_2Pd$ and SO_2 at -40°C affords $(h^3\text{-}C_3H_5)PdS(O)_2CH_2CH{=}CH_2$; in solution an equilibrium appears to exist between structures in which the allyl double bond is coordinated and uncoordinated to the metal (*102*).

Palladium(II) chloride catalyzes reaction of SO_2 with ethylene [Eq. (36], the mechanism of which is postulated to involve sulfur dioxide insertion into a Pd—C bond (*85*), *viz.*, Eq. (37).

$$3CH_2{=}CH_2 + SO_2 \xrightarrow[70°C]{PdCl_2} MeCH_2S(O)_2CH_2CH{=}CHMe \qquad (36)$$

$$MeCH_2PdCl + SO_2 \longrightarrow MeCH_2SO_2PdCl \qquad (37)$$

The reaction of palladium(II) complexes with arenesulfinic acids or their salts to yield the organic biaryls appears to proceed by formation of palladium sulfinato compounds and their desulfination (*53a*).

3. *Platinum*

Square-planar platinum(II) complexes of formulas $RPtL_2Cl$ and R_2PtL_2 can be converted by SO_2 to the corresponding *S*-sulfinates of the same stereochemistry, but temperatures of 45°–50°C are needed for these reactions. Using neat SO_2 in a sealed tube the following have been sulfinated: *trans*-$PtL_2(Ph)Cl$ (L = PEt_3, $AsEt_3$, $SeEt_2$, and $TeEt_2$) (*46, 47*), *trans*-$Pt(PEt_3)_2(Me)Cl$, *trans*-$Pt(SeEt_2)_2(p\text{-}C_6H_4Cl)Cl$, and *trans*-$Pt(SeEt_2)_2Ph_2$ {to *trans*-$Pt(SeEt_2)_2[S(O)_2Ph]_2$} (*47*). The compounds *cis*-$Pt(PPh_3)_2Ph_2$ (*47*) and *trans*-$Pt(PMe_2Ph)_2Ph_2$ (*28*) also give *S*-sulfinates when treated with SO_2; however, these materials could not be satisfactorily characterized. The cyanomethyl derivative *trans*-$Pt(PPh_3)_2(CH_2CN)Cl$ does not insert SO_2, even at 60°C (*47*), whereas *trans*-$Pt(PPh_3)_2(Me)I$ yields *trans*-$Pt(PPh_3)_2(Me)(I\text{-}SO_2)$, characterized by X-ray crystallography (*114, 115*).

Dissolution of $(h^3\text{-}C_3H_5)_2Pt$ in liquid SO_2 at −40°C produces $(h^3\text{-}C_3H_5)PtS(O)_2CH_2CH{=}CH_2$ (*102*). Contrasting with the preceding reaction is the insertion with $(h^3\text{-}C_3H_5)Pt(PPh_3)_2{}^+Cl^-$ in neat SO_2 at room temperature which leads to rearrangement of the C_3H_5 substrate [Eq. (38)] (*130*).

$$(h^3\text{—}C_3H_5)Pt(PPh_3)_2{}^+Cl^- + SO_2 \longrightarrow$$
$$cis\text{-}Pt(PPh_3)_2[S(O)_2CH{=}CHMe]Cl + trans\text{-}Pt(PPh_3)_2[S(O)_2CH{=}CHMe]Cl \qquad (38)$$

Sulfur dioxide extrusion from *p*-$MeC_6H_4S(O)_2Pt(PPh_3)_2Cl$ (*31*) and *trans*-$Pt(PMe_2Ph)_2[S(O)_2C_6H_4Me$-*p*]Cl (*20*) has been effected, respectively, by heating at 200°–210°C and at reflux in toluene solution.

The use of $Pt(PPh_3)_4$ as a catalyst in the desulfination of RSO_2X has been described (*15*).

H. Copper Triad

Sulfur dioxide insertion into the Au–Me bonds of $MeAu(PMe_2Ph)$ and $Me_3Au(PMe_2Ph)$ has afforded $MeS(O)_2Au(PMe_2Ph)$ and $Me_2Au(PMe_2Ph)S(O)_2Me$, respectively (*80*). Similarly, the sulfinates *o*-$CH_2{=}CHC_6H_4S(O)_2AuPPh_3$ and *o*-$CH_2{=}CHCH_2C_6H_4S(O)_2AuPPh_3$ result upon treatment of the appropriate aryl complexes with SO_2 (*6*).

I. Lanthanides and Actinides

There have been no reports of SO_2 insertion into a metal–carbon bond of the lanthanide and actinide elements.

VII

INSERTION OF OTHER UNSATURATED MOLECULES

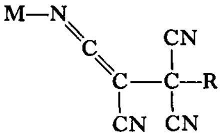
A. Introduction and Scope

This part of the review brings together insertion reactions of several diverse unsaturated molecules into transition metal–carbon σ bonds. Most of the reactions presented here have appeared in the literature since about 1969–1970; they thus attest to a marked recent growth of interest in this field.

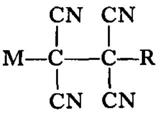
Treatment of the subject in this section is not intended to be comprehensive. Instead, emphasis has been placed on the types of molecules reacting, the mode of the insertion (and/or elimination) and the structure of the product derived. The presentation is further restricted by excluding the insertion of the olefins, acetylenes, and other unsaturated hydrocarbons, as well as their fluorinated analogs. The above reactions are numerous enough to comprise a separate topic for review. Those involving the olefins have been often discussed in the context of Ziegler-Natta polymerization by metal complexes (e.g., *10*, *11*, *63*, *69*, *108*). The reactions of unsaturated fluorocarbons have also received attention (*18*, *27*, *135*, *inter alia*). However, included herein by exception are the insertion reactions of tetracyanoethylene, since they differ considerably from those of the other olefins. As will be seen later in this section, the information presently available on most of the reactions covered is inadequate to warrant comparisons or detailed discussions.

B. Tetracyanoethylene

Tetracyanoethylene inserts into the M—R bonds of $CpFe(CO)_2R$ (R = Me, Et, *n*-Pr, and CH_2Ph) (*118*, *121a*), $CpCr(NO)_2R$ (R = Me and CH_2Ph) (*61*, *118*), and $CpMo(CO)_2(L)Me$ [L = PPh_3 and $P(OPh)_3$] (*118*, *121a*) to furnish metal keteniminato (XXI) and cyanoalkyl (XXII) complexes. For $CpFe(CO)_2R$, the reactivity decreases in the approximate order R = CH_2Ph > Me ~ Et ~ *n*-Pr ≫ Ph. Little is known about the mechanism of these reactions.



(XXI)



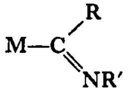
(XXII)

Metal-allyl complexes of formulas $CpFe(CO)_2CH_2C(R) = CR'R''$ and $CpMo(CO)_3CH_2C(R) = CR'R''$, as well as analogous propargyl and cyclopropylmethyl complexes, react with $(CN)_2C{=}C(CN)_2$ to give cycloaddition products (*21a*, *56*, *120*, *121*) of the type discussed in Section V.

C. Alkyl and Aryl Isocyanides

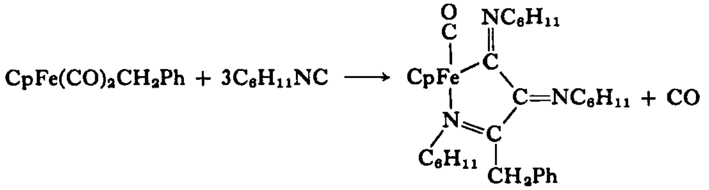
The insertion reactions of alkyl and aryl isocyanides were recently reviewed (*126*, *142*) and will not be treated exhaustively in the present article.

The isocyanides (R'NC) insert into Mo—R, Fe—R, Ni—R, Pd—R, and Pt—R bonds to afford metal imino complexes (XXIII). Some of



(XXIII)

these products undergo further reaction, the structural result of which is multiple interposition of R'NC into a metal–carbon bond, e.g. (*143*),



(39)

The mechanism of the isocyanide insertion has been examined for the coordinatively unsaturated platinum(II) alkyls and aryls (*127*); it involves an ionic intermediate in which both R'NC and R are coordinated to the metal [Eq. (40)]. Coordinatively saturated alkyl complexes are believed

$$\mathrm{RPt(PR''_3)_2X \xrightarrow{R'NC} RPt(R'NC)(PR''_3)_2{}^+X^- \longrightarrow Pt(PR''_3)_2[C(R){=}NR']X} \qquad (40)$$

to react via simultaneous interaction of R'NC with the metal and with the σ carbon of R (*142*). However, no definitive evidence exists for the proposed pathway.

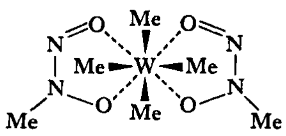
D. Sulfur Trioxide

Reaction between sulfur trioxide and $RRe(CO)_5$ (R = Me, Ph, and p-C_6H_4Me) in CCl_4 and at 0°C leads to the formation of the sulfonato complexes, $RS(O)_2ORe(CO)_5$ (*95*). In contrast, propargyl derivatives of $CpFe(CO)_2$, $CpMo(CO)_3$, and $Mn(CO)_5$ yield metal-vinyl compounds containing a sultone ring, $\mathrm{M\overline{C{=}C(R)S(O)_2OC}H_2}$ (*92*, *93*, *111a*).

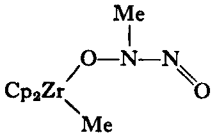
E. Nitric Oxide

Hexamethyltungsten is quantitatively converted to $Me_4W[ON(Me)NO]_2$ (XXIV) by the action of nitric oxide in petroleum ether (*48*, *113a*). The structure of the product was determined by X-ray crystallography.

Under similar experimental conditions, Cp_2ZrMe_2 and NO afford



(XXIV)



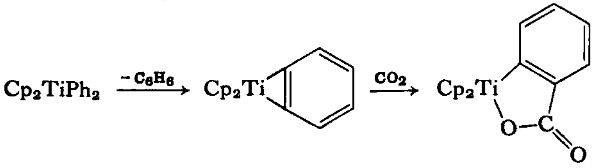
(XXV)

$Cp_2Zr(Me)[ON(Me)NO]$ of proposed structure (XXV) (*132*).[3] The complex $Cp_2Zr(Me)Cl$ also inserts two molecules of NO to give $Cp_2Zr[ON(Me)NO]Cl$, as does Cp_2TiMe_2 to yield $\{Cp_2Ti(Me)[ON(Me)NO]\}_n$.

F. Carbon Dioxide

Reactions of carbon dioxide with transition metal compounds, including the alkyls and aryls, have been recently reviewed (*130a*).

Treatment of Cp_2TiPh_2 with CO_2 in xylene at 80°–90°C results in the formation of $Cp_2\overline{TiOC(O)C}_6H_4$ (XXVI) whose structure was elucidated crystallographically (*86*). The product is believed to arise through CO_2 insertion into a Ti—C bond [Eq. (41)] (*86a*). Carbon dioxide also inserts into the Ti—C bonds of Cp_2TiMe_2 (*86a*) and $(PhCH_2)_4Ti$ (*145*), the Zr—C bonds of $(PhCH_2)_4Zr$ (*145*), and the Cu—C bond of $MeCu(PPh_3)_2$ etherate (*98a*).



(41)

(XXVI)

Nickel(II) carboxylato complexes of formula $(RCO_2)_2NiL_2 \cdot xH_2O$ ($R = C_6F_5$, p-C_6F_4OMe, or p-C_6F_4OEt; L_2 = bipy, $x = 2$ or L_2 = *o*-phen, $x = 1$) can be converted to the corresponding organonickel compounds, R_2NiL_2, upon treatment in boiling toluene (*34*). However, when L_2 = *o*-phen and $x = 1$, the decarboxylation requires use of benzoyl peroxide in boiling benzene. Apart from this one exception, the above CO_2 extrusion reactions are thought to involve heterolysis of the R—CO_2 bond and electrophilic attack of nickel on the R group.

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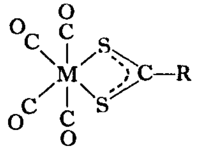
[3] Recently it was suggested (*113a*) that this complex most likely contains a chelate ON(Me)NO group.

G. Carbon Disulfide

The insertion of CS_2 into transition metal–carbon bonds was reported by Lindner *et al.* in 1970 (*94*, *96*). Reaction between $RM(CO)_5$ (M = Mn, R = Me, Ph, and *p*-C_6H_4Me; M = Re, R = Me, Ph, *p*-C_6H_4Me, and *p*-C_6H_4Cl) and CS_2 at 90°–150°C under pressure affords the corresponding dithiocarboxylato tetracarbonyl complexes, $RCS_2M(CO)_4$ (XXVII). When R = CH_2Ph, rearrangement to R = *p*-C_6H_4Me accompanies the insertion. The reactivity of $RRe(CO)_5$ follows the order R = Ph ≫ Me > CH_2Ph ≫ CF_3. The complexes of manganese are more reactive than those of rhenium.



(XXVII)

H. Dinitrogen

Insertion of N_2 into Ti—R bonds has been proposed, but no products containing Ti—N=N—R could be isolated (*130b*). In contrast, extrusion of dinitogren from an M—N=N—R fragment is a known reaction, e.g. (*104*),

$$p\text{—}O_2NC_6H_4N_2Pt(PPh_3)_2Cl \longrightarrow p\text{—}O_2NC_6H_4Pt(PPh_3)_2Cl + N_2 \qquad (42)$$

I. Dioxygen

Cobalt(III) alkyl complexes of formula $RCo(dmgH)_2py$ react with dioxygen to produce the corresponding peroxo derivatives, ROOCo-$(dmgH)_2Py$ (*53*). This insertion proceeds readily at ambient temperatures even in the absence of light when R = $CH(R')C_6H_4X$ (X = R' = H; X = H, R' = Me; X = *p*-OMe, R' = Me; X = H, R' = Et; etc.). However, when R = Et, *n*-Pr, *i*-Pr, CH_2CHMe_2, *n*-C_5H_{11}, $\overline{CH(CH_2)_4CH_2}$, $\overline{CH(CH_2)_4CH(OH)}$, $CH_2\overline{CH(CH_2)_3O}$, and CH(Me)-$CO_2Me$, the reaction requires irradiation with visible light at −30° to

0°C. The optically active alkyl complex with R = $CH(Ph)CH_2OH$ inserts O_2 to yield the corresponding optically active peroxo derivative.[4] By contrast, the optically active cobalt alkyl with R = $CH(Me)CH_2Me$ undergoes racemization in the course of the photochemical insertion (*78a*). These reactions likely proceed through homolysis of the Co—R bond.

Recently, additional studies have been communicated on the insertion of O_2 into the Co—R bond of $RCo(dmgH)_2L$ (*55a*, *55b*, *55c*, *97a*). Insertion of oxygen into Ti—C (*28a*, *145*) and Zr—C (*145*) bonds has also been observed.

J. Tetrasulfur

Photolysis with visible light of $RCo(dmgH)_2py$ in the presence of S_8 has afforded a series of $RS_4Co(dmgH)_2py$ complexes [R = Et, *n*-Pr, $(CH_2)_4Me$, $\overline{CH(CH_2)_4C}H_2$, $\overline{CH(CH_2)_4C}H(OH)$, CH_2Ph, CH(Me)Ph, and $CH_2CH{=}CHMe$] (*55*). These reactions also give $(py)(dmgH)_2Co{-}S_4{-}Co(dmgH)_2py$ and RS_4R.

K. Germanium(II) and Tin(II) Chlorides

Germanium(II) chloride inserts into the Fe—Me bond of $CpFe(CO)_2Me$ according to Eq. (43) (*101*). The same product may be obtained, but in lower yield, from $CpFe(CO)_2Me$ and $Cs^+GeCl_3^-$ in THF (*35*).

$$CpFe(CO)_2Me + GeCl_2\cdot C_4H_8O_2 \xrightarrow[60^\circ\text{–}105^\circ C]{\text{dioxane}} CpFe(CO)_2Ge(Me)Cl_2 + C_4H_8O_2 \qquad (43)$$

Tin(II) chloride also reacts with $CpFe(CO)_2Me$ to afford $CpFe(CO)_2Sn(Me)Cl_2$ (*35*). However, $SnBr_2$ behaves differently toward the above iron alkyl, yielding $CpFe(CO)_2SnBr_3$ and $CpFe(CO)_2Br$.

L. Chlorosulfonyl Isocyanate

Although $ClSO_2NCO$ does not react at ambient temperatures with the alkyls $CpFe(CO)_2R$ (R = Me and CH_2Ph), with $CpFe(CO)_2CH_2C(Me){=}CH_2$ it affords a 1:1 complex which has been formulated as (XXVIII)

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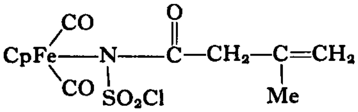
[4] More recent work (*78a*) showed racemization to occur both in the photochemical and in the thermal insertion of O_2 with this complex.



$\mathrm{CpFe(CO)_2{-}N(SO_2Cl){-}C({=}O){-}CH_2{-}C(Me){=}CH_2}$

(XXVIII)

(*141*). It is thought that (XXVIII) arises through the intermediacy of the corresponding zwitterionic olefin species of the type discussed in Section V, B. Several similar iron-allyl complexes of general formula $\mathrm{CpFe(CO)_2CH_2CH{=}CRR'}$ have yielded cycloaddition rather than insertion products with $\mathrm{ClSO_2NCO}$, perhaps because of the higher stability of their respective dipolar olefin intermediates. Chlorosulfonyl isocyanate undergoes 1,3-cycloaddition also with the propargyl moiety of a number of $\mathrm{MCH_2C{\equiv}CR}$ compounds where M = $\mathrm{CpFe(CO)_2}$, $\mathrm{CpMo(CO)_3}$, and $\mathrm{Mn(CO)_5}$ (*141*).

VIII

CONCLUSION

From the foregoing treatment of the subject it is clear that the name accorded the insertion reactions has no more than a structural implication. Mechanistically, these processes represent many diverse classes of reactions. Thus, CO insertion involves intramolecular transfer of a coordinated alkyl group, SO_2 insertion is best regarded as an electrophilic cleavage of the M—R linkage, O_2 and S_4 insertions in all probability proceed via a radical pathway as does the insertion of acetylenes into the Pt—Me bond of some platinum(II) methyl complexes (*5*), and the only known insertion of $\mathrm{ClSO_2NCO}$ likely involves a zwitterionic olefin intermediate. Clearly, further work is needed before mechanistic uncertainties with regard to the various types of insertion will have been satisfactorily resolved. In the meantime, related synthetic investigations will no doubt produce numerous new and interesting organometallic compounds.

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Organozinc Compounds in Synthesis

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I

INTRODUCTION

The first example of the preparation of organozinc compounds was reported by Frankland in 1849 (*138*). They were the first synthetically useful organometallic reagents, but were almost entirely superseded by the more conveniently prepared and more reactive Grignard reagents after 1900. However, recent developments in organozinc chemistry have demonstrated their new utility in organic synthesis. For example, the Simmons-Smith reaction, the reaction of zinc-copper couple and methylene iodide with olefins, proceeds via an intermediate organozinc species and is one of the most useful routes to cyclopropane derivatives. The Reformatsky reaction, the reaction of carbonyl compounds with α-halo-esters in the presence of zinc which also proceeds via an organozinc intermediate, has ensured its utility in the synthesis of β-hydroxy esters and has been developed extensively. The coupling reaction of organozinc compounds with reactive halides still finds some synthetic utility. Many of these synthetic reactions are not achieved by Grignard reagents or organolithium reagents. Recently a monograph was published on the synthesis and reactions of organozinc compounds which covers the literature up to and including 1962 (*447*). In the present review, we shall describe developments mainly after 1960 in synthetic reactions using organozinc compounds.

II

REACTIONS OF ZINC CARBENOIDS

In this chapter are described synthetic reactions which proceed via intermediate zinc carbenoids. A representative reaction of carbenes and carbenoids would be the methylene transfer reaction with olefins to give cyclopropane derivatives. The reaction is largely influenced by the nature of the carbene or carbenoid. Divalent carbon intermediates, carbenes, produced by photolysis or thermal decomposition of diazo compounds or ketene derivatives possess two nonbonding electrons which may have antiparallel spins (singlet state) or parallel spins (triplet state). The reaction of the singlet carbene with olefins gives cyclopropane derivatives stereospecifically, but is accompanied by an insertion reaction into the C—H bonds. The reaction of the triplet carbene with olefins gives cyclopropane derivatives in a nonstereospecific way and is accompanied by hydrogen abstraction, since the triplet carbene is a biradical. Carbenoids, however, give cyclopropane derivatives stereospecifically without hydrogen abstraction, and C—H insertion is not significant. Thus carbenoids are more important than free carbenes for synthetic purposes.

Carbenoids can be classified into two types: (a) complexes of carbene with metals or metallic compounds and (b) organometallic compounds where halogen or another substituent of higher electronegativity is attached to the α-carbon. Carbenes have been shown to act as ligands in transition metal complexes of Fe, Rh, Ru, Co, W, Mo, Cr, Mn, Re, Pd, and Pt (*68*). Carbenoids of type (a) also include the intermediates in the catalytic decomposition of diazo compounds by metals or metallic compounds. The intermediate formation of carbenoids is believed due to the considerable change of the nature of reaction caused by the presence of a metal or metallic compound. This type of catalytic action is given by compounds of Cu, Fe, Co, Ni, Ir, and other transition metals. Carbenoids of type (a) may also include the intermediate in the reaction of methylene iodide with Cu (*65*). Carbenoids of type (b) include α-halogenoorganometallic and related compounds of Li (*263*, *264*), Na (*113*, *140*, *272*, *464*, *532*), K (*118*), Mg (*413*, *414*), Zn (*42*, *155*, *159*, *456*, *457*, *459*), Cd (*164*), Hg (*433*, *435*, *438*), Al (*199*, *200*, *336*), Si (*38*, *129*, *444*), Sn (*436*, *437*), Pb (*520*), P (*33*, *74*, *304*, *305*), and other non-transition metals. In this type of organometallic compound, an electropositive metal and an electronegative substituent are attached to the same carbon atom, facilitating α-elimination. In some cases, the free-carbene stage is claimed to be attained in the α-elimination, e.g., in the reaction of Hg carbenoids (*438*). Carbenoids of Li, Zn, and Al are generally considered to react without first undergoing α-elimination, i.e., the free carbene is not thought to be involved in the reaction of these carbenoids.

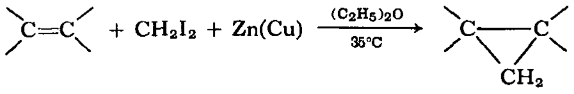
A. Synthesis of Cyclopropane Derivatives from Olefins

1. *Methylene Transfer Reaction with Olefins*

Emschwiller first presented evidence for the formation of iodomethylzinc iodide (I) by the reaction of methylene iodide with zinc-copper couple in ether (*124*). An ether solution of (I) gives methylene iodide and methyl iodide when treated with iodine and water, respectively, and evolves a considerable amount of ethylene when heated at prolonged

$$CH_2I_2 + Zn(Cu) \xrightarrow{(C_2H_5)_2O} \underset{\text{(I)}}{ICH_2ZnI} \qquad (1)$$

reflux. Simmons and Smith (*42*, *43*, *456*, *457*, *459*) as well as Doering and LaFlamme (*121*) carried out the reaction in the presence of olefins and found a new synthetic route to cyclopropane derivatives. This



(2)

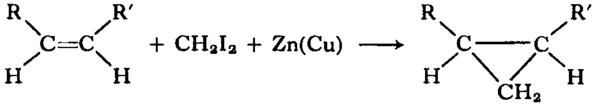
reaction is usually called the Simmons-Smith reaction. The active intermediate of the reaction must involve the Zn–CH_2I linkage, and could be either (I) or (II) or a mixture of both.[1] The equilibrium $2RZnX \rightleftharpoons R_2Zn\cdot ZnX_2$ normally lies far to the left (*116*, *125*, *126*), so it is quite possible that (I) is more important than (II). This intermediate reacts

$$\underset{\text{(I)}}{2ICH_2ZnI} \rightleftharpoons \underset{\text{(II)}}{(ICH_2)_2Zn\cdot ZnI_2}$$

in a kinetically bimolecular process with olefins to give cyclopropane derivatives and zinc iodide (*42*). The electrophilic nature of the reaction was shown by the effect of substituents (*457*), and the yield of cyclopropane derivatives decreases with increasing solvent basicity (*42*). A large steric effect was also noted (*42*, *409*).

The reaction is not accompanied by the insertion of methylene groups into the C—H bond attached to the olefinic linkage (*457*). The latter is a serious side reaction in the light-induced methylenation of olefins by diazomethane, giving inseparable isomeric hydrocarbons along with the desired cyclopropane derivatives (*23*, *119*, *387*, *465*, *554*). Isomerization of the olefin is not observed and no rearranged cyclopropane derivatives are produced (*457*).

The reaction gives cyclopropane derivatives in a stereospecific way (*112*, *121*, *456*, *457*, *459*). Reactions with *cis*- and *trans*-olefins give the corresponding *cis*- and *trans*-cyclopropane derivatives, respectively.[2] The light-induced methylenation of olefins by diazomethane is less stereospecific due to the presence of triplet carbene (*18*). Halocarbenes add to olefins to give halocyclopropanes stereospecifically (*87*, *120*, *389*, *462*,



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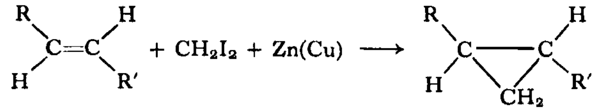

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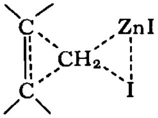
[1] Hydrolysis of the Simmons-Smith reagent gives a large amount of CH_3I together with a small amount of CH_4 (*127*), consistent with either (I) or (II).

[2] Some exceptions were reported with small olefins (*127*, *431*). Nonstereospecificity was also reported in the Simmons-Smith reaction of an α,β-unsaturated ketone, *cis*-chromindogenide (*121a*).

463), but these must be further treated to obtain halogen-free structures. Thus the Simmons-Smith reaction is one of the most useful routes for synthesis of cyclopropane derivatives.

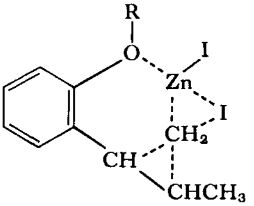
A cis addition mechanism is generally accepted for the reaction, because cis addition to an olefinic bond generally occurs with predominant attack at trans bonds, and the Simmons-Smith reagent attacks preferentially one of the trans olefinic bonds of *trans,trans,cis*-1,5,9-cyclododecatriene and then the cis double bond of the monoadduct (*378*). The close correspondence in relative rates of olefins for the cyclopropane formation by the Simmons-Smith reaction with those for diimide reduction and peroxide epoxidation supports the concept (*409*). The latter two reactions are generally considered to proceed via cis addition.

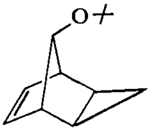
A transition state of type (III) was suggested for the Simmons-Smith reaction on the basis of experimental observations (*42*, *456*, *457*, *459*).



(III)

The presence of ether functions in olefins frequently facilitates the Simmons-Smith reaction (*457*). For example, 1-(*o*-methoxyphenyl)-propene gives a higher yield of a cyclopropane than the *meta* and *para* isomers, and coordination of (I) with ether oxygen was suggested (*42*, *457*).





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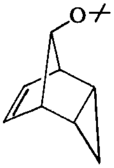
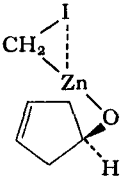


(V)

This type of coordination is useful for highly stereoselective syntheses of cyclopropane derivatives. Reaction of Δ^2-cyclohexenyl methyl ether with the Simmons-Smith reagent gives *cis*-2-bicyclo[4.1.0]heptyl methyl ether without the trans isomer (*103*). The Simmons-Smith reaction with 7-*tert*-butoxynorbornadiene gives *syn-exo*-(IV) and *syn-endo* isomer (V) without the anti isomers (*260*).

Ester groups also show a similar effect of coordination and have been employed in highly stereoselective methylenation. Methyl 1,4-dihydrobenzoate gives a bis adduct of methylene in which two cyclopropyl rings are predominantly in the cis configuration (*460*). Comparing this result with that obtained by carrying out the Simmons-Smith reaction on 1,4-dihydrobenzene, which results predominantly in a trans configuration of the cyclopropyl rings (*276*), it is seen that the carbomethoxyl group exerts a profound directing influence on the reaction (*460*). Methyl dihydrohydrindacenecarboxylate gives a bis adduct of methylene where the ester group and two cyclopropyl groups are in the cis configuration (*39*, *190*). The result was also ascribed to a directing effect of the carbomethoxyl group (*190*). The directing effect of the ester group was utilized in a partial asymmetric synthesis of cyclopropane derivatives of (−)-menthyl crotonate, *trans*-3-pentenoate, senecioate, fumarate, cinnamate, and *trans*-4-phenyl-3-butenoate (*222*, *422*, *424a*) and cinnamate (*75*). Cyclopropane derivatives with optical activity can be obtained by carrying out the Simmons-Smith reaction of various achiral olefins in the presence of (−)-menthol (*423*, *424a*).

The Simmons-Smith reaction with cyclopenten-4-ol gives exclusively the cis isomer of bicyclo[3.1.0]hexan-3-ol (*94*, *540*, *541*). Cleavage of the Simmons-Smith reagent by the hydroxyl group would give a salt (VI), and intramolecular methylene transfer would then yield *cis*-bicyclo-[3.1.0]hexan-3-ol after hydrolysis (*42*). An alternative mechanism was suggested which includes the formation of a complex like (VII) instead of (VI) (*103*). This high degree of stereoselectivity of the Simmons-Smith reaction with olefinic derivatives containing a hydroxyl group has been successfully employed in organic syntheses. Preparation of *endo*-bicyclo[5.1.0]octan-3-ol and *endo*-bicyclo[5.1.0]octan-4-ol (*92*); (+)-*cis*-bicyclo[4.1.0]heptan-2-ol (*198*); *cis*-tricyclo[4.3.1.0]decan-8-ol (*404*); tricyclo[7.1.0.0^{5,7}]decan-3-ol with two cyclopropane rings cis to each other and to the hydroxyl group (*403*); *cis*-bicyclo[4.1.0]heptan-2-ol, *cis*-bicyclo[5.1.0]octan-2-ol, *cis*-bicyclo[3.1.0]hexan-2-ol, *cis*-1-methyl-



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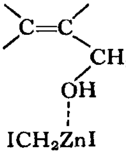

(VII)

bicyclo[4.1.0]heptan-2-ol, *cis*-6-methylbicyclo[4.1.0]heptan-2-ol, and *cis*-1,6-dimethylbicyclo[4.1.0]heptan-2-ol (*103*); *cis*-tricyclo[4.4.1.$0^{1,6}$]undec-8-en-3-ol (*461*), bicyclo[4.1.0]-heptan-2-ol (*410*), tricyclo[4.3.1.$0^{1,6}$]-decan-8-ol, and tricyclo[4.4.1.$0^{1,6}$]-undecan-3-ol (*474*); *cis*-1,1,5,5-tetramethylspiro[2.3]hexan-4-ol (*37*), and several steroids (*105*, *182*, *183*, *388*, *427*, *484*, *537*) were reported. In these cases, the syn addition is predominant over the anti addition.[3] However, preferential anti addition was recently found in some larger and relatively complicated cyclic molecules. *Anti*-bicyclo[7.1.0]deca-4,7-dien-2-ol and *anti*-bicyclo[8.1.0]-undeca-4,7-dien-2-ol were selectively prepared (*167*). Bis and tris adducts of methylene to 2,4,7-cyclononatrienol are mixtures of syn and anti isomers (*536*). The reactions with cyclohexen-3-ol, *cis*-5-methylcyclohexen-3-ol, *trans*-5-methylcyclohexen-3-ol, and cyclohexen-4-ol were shown to give cyclopropane derivatives where the hydroxyl group and the cyclopropyl ring are in the cis configuration with high stereoselectivity. In contrast, 3-cyclohexenylmethanol yields a 45:55 mixture of cis and trans products. From data on relative reactivity, the reaction with allylic cyclohexenols was concluded to occur through the quasiequatorial hydroxyl conformation, and a dimeric structure for the reactive organometallic species was proposed (*77*). Highly selective anti addition was observed with cycloocten-3-ol and cyclononen-3-ol, whereas syn addition is predominant for cyclohepten-3-ol, cyclohexen-3-ol, and cyclopenten-3-ol. The result was explained by assuming complexation between the hydroxyl group and the reagent, followed by the methylene transfer to the nearest face of the double bond (*398*). Competitive kinetics was reported to establish that, in contrast to the allylic cyclohexen-3-ols, the homoallylic cyclohexen-4-ols react through the axial hydroxyl conformer (*473*).

The Simmons-Smith reaction has been applied to other olefins containing a hydroxyl group (*15*, *21*, *95*, *103*, *240*, *307*, *391*, *458*, *461*, *473*), α,β-unsaturated ketones (*15*, *21*, *37*, *91*, *538*), α,β-unsaturated esters (*36*, *168*, *457*, *458*), α,β-unsaturated ethers (*457*), vinyl esters (*111*, *457*, *458*, *534*), cyclic enamines (*43*), steroids (*46*, *239*, *269*, *299*, *484*), monosaccharides (*13a*, *13b*, *203–205*), thujopsene (*104*), dihydrohydrindacene (*39*), *cis-cis-cis*-1,4,7-cyclononatriene (*44*, *402*), 1,4-cyclohexadiene (*276*, *461*), benzocyclobutadiene (*489*), metallic vinyl compounds (*432*), and

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[3] The terms, syn and anti selectivity and syn and anti configuration are used in the sense defined by Moss (*350*).

other various types of simple and complicated olefinic compounds (*21*, *35*, *36*, *42*, *60*, *80a*, *95*, *112*, *127*, *168*, *254*, *258*, *265*, *286*, *300*, *345*, *431*, *442*, *443*, *445*, *452*, *456–459*, *466*, *497*, *527*, *539*, *558*).

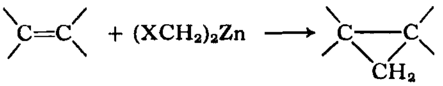
Chloroiodomethane has been used instead of methylene iodide to methylenate cyclic enamines (*43*). Methylene bromide was applicable to the Simmons-Smith reaction instead of methylene iodide when highly active zinc-copper couple was used (*298*, *558*). The resulting $BrCH_2ZnBr$ is an effective methylene transfer reagent.

The Simmons-Smith reaction often starts very slowly and proceeds quite slowly at room temperature. The method of the preparation of active zinc-copper couple has been improved (*93*, *196*, *298*, *376*, *443*, *466*). The use of zinc dust/cuprous chloride instead of zinc-copper couple gives higher yields in the Simmons-Smith reaction (*407*). The reaction with homoallylic alcohols of low reactivity was facilitated by use of excess Simmons-Smith reagent and distillation of ether to a half-volume followed by heating in a stainless steel tube (*182*). The Simmons-Smith reaction was successfully applied to vinyl trimethylsilyl ethers to prepare, after methanolysis, cyclopropyl alcohols unobtainable by other methods (*109*). Here, the zinc-silver couple was used instead of the zinc-copper couple, and the quenching of the reaction mixture of the Simmons-Smith reaction was improved by using pyridine under nonaqueous conditions.

The reaction of diazomethane with zinc halides has been studied previously by several workers (*70*, *326*, *475*), and the formation of a zinc halide—methylene complex was suggested. Wittig and Schwarzenbach (*542*) demonstrated the formation of iodomethylzinc iodide (I) and bis(iodomethyl)zinc (VIII) by the reaction of zinc iodide with diazomethane. The reaction of diazomethane with zinc chloride gives bis(chloromethyl)zinc (IX) (*544*).

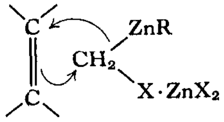
$(ICH_2)_2Zn$ (VIII) $(ClCH_2)_2Zn$ (IX)

Solutions of (I), (VIII), and (IX) in ether react with olefins to give the corresponding cyclopropane derivatives (*200*, *427a*, *542–546*). Burger and Huisgen (*64*) concluded that the Simmons-Smith reagent [CH_2I_2 +



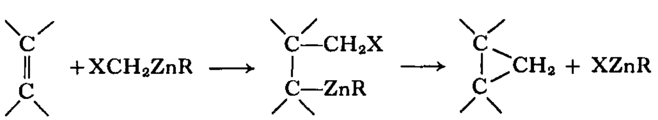
(5)

Zn(Cu)] and the Wittig-Schwarzenbach reagent [CH_2N_2 + ZnI_2] give rise to the formation of one and the same carbenoid. Zinc chloride catalyzes the reaction (5) and an explanation in terms of $ZnCl_2$-assisted elimination of chloride ion via a transition state (X) was suggested to be most probable (*546*). The possibility of a two-step (addition and elimination) mechanism [Eq. (6)], (*200*) which was proposed for the reaction of



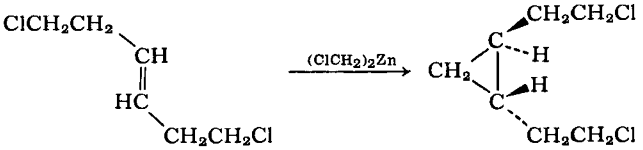
(X)

aluminum carbenoid with olefin (*199*), was renounced (*546*) because



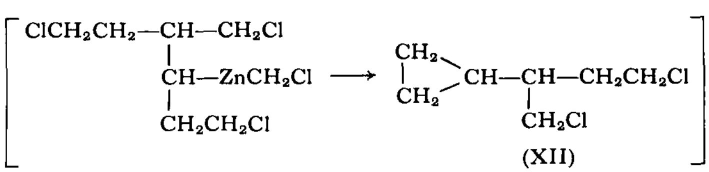
(6)

the reaction of $(ClCH_2)_2Zn$ with *trans*-1,6-dichloro-3-hexene gives (XI) without (XII) [Eq. (7)].



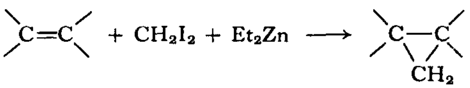
(7)

(XI)



(XII)

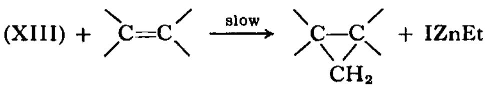
The authors discovered a remarkable improvement of the Simmons-Smith reaction by using diethylzinc instead of zinc-copper couple (*155*, *159*, *160*, *162*, *234a*, *373*, *518a*). Reaction (8) is electrophilic and proceeds



(8)

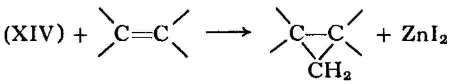
stereospecifically. The *cis*- and *trans*-olefins afford cyclopropanes whose configuration are cis and trans with respect to the substituents of the starting olefins. No insertion of methylene group into the C—H bond linked to the olefinic double bond is observed. Thus the mechanism of reaction (8) is closely related to that of the Simmons-Smith reaction. However, reaction (8) is much more rapid than the corresponding Simmons-Smith reaction, and methylene iodide must be added slowly to moderate the reaction. The first step of reaction (8) was shown to be the formation of ethyl iodide and iodomethylethylzinc (XIII), which undergoes methylene transfer reaction with olefins. Since two ethyl–zinc

$$CH_2I_2 + Et_2Zn \xrightarrow{\text{fast}} \underset{\text{(XIII)}}{ICH_2ZnEt} + EtI \qquad (9)$$


(10)

bonds of diethylzinc are utilizable, reactions (11) and (12) are also conceivable (*162*). The active species of reaction (8) may include ICH_2ZnEt,

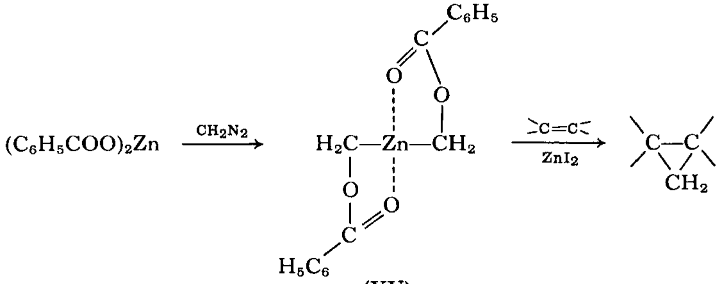
$$IZnEt + CH_2I_2 \longrightarrow \underset{\text{(XIV)}}{ICH_2ZnI} + EtI \qquad (11)$$


(12)

ICH_2ZnI, and/or $(ICH_2)_2Zn$, or associated complexes containing these molecules. Reaction (1) between zinc metal and methylene iodide is heterogeneous and rather slow, whereas reactions (9) and (11) are homogeneous and much faster than (1). As a result, reaction (8) proceeds much more rapidly than the Simmons-Smith reaction.

Reaction (8) is particularly suitable for the conversion of cationically polymerizable olefins such as vinyl ether to the corresponding cyclopropane derivatives. The Simmons-Smith reaction with this class of olefins often gives lower yields of cyclopropane derivatives due to polymerization, while reaction (8) results in high yields of cyclopropyl ethers (*159*, *162*). The reaction is also applicable to the conversion of olefins containing a hydroxyl group to cyclopropane derivatives with a high degree of stereoselectivity (*367*). Among organic halides only methylene iodide works well in the conventional Simmons-Smith reaction. Although methylene bromide will react if highly active zinc-copper couple is used (*298*), yields of cyclopropane derivatives were very low when chloroiodomethane (*43*, *457*) and ethylidene iodide (*459*) were employed. However, ethylidene iodide (*160*, *367*, *368*), benzal iodide (*160*, *370*), and various polyhalo methanes of the type of CHXYI (here, X and Y are F, Cl, Br, or I) (*343*, *344*, *371*) can all be used in reaction (8). Since diethylzinc takes fire in air, the reaction is usually carried out in a nitrogen atmosphere. However, the presence of a small amount of oxygen as well as the irradiation of UV light and the presence of azobis(isobutyronitrile) increases both the reaction rate and the yield of the product (*343*, *344*). A useful modification was proposed which involves a preceding reaction of ethyl iodide with zinc-copper couple to prepare diethylzinc and/or ethylzinc iodide in solution followed by the addition of methylene iodide and olefin (*424*, *424a*).

Wittig and Jauterat (*547*) prepared a complex (XV) from diazomethane and zinc benzoate, which undergoes the methylene transfer reaction with olefins. Reactions (2), (5), (8), and (13) can be understood as transfer reactions of various types of zinc-methylene complexes to olefinic double bonds.

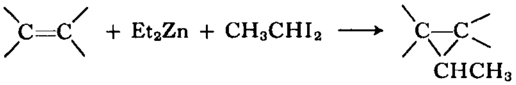


(XV)

(13)

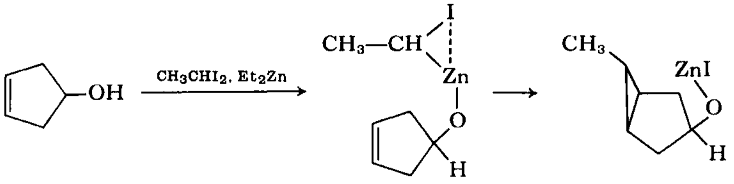
2. *Alkylidene Transfer Reaction with Olefins*

The light-induced reaction of diazoethane with propylene gives a 1.4:1 mixture of *cis*- and *trans*-dimethylcyclopropane in poor yield (*139*); intramolecular rearrangement in the intermediate ethylidene (*59*) predominates over the cycloaddition. Intramolecular rearrangement in the zinc carbenoid likewise predominates over the cycloaddition to olefinic linkage in the reaction of *gem*-diiodoalkane and zinc-copper couple with cyclohexene (*19*, *257*, *366*). The action of zinc-copper couple on higher alkyl *gem*-diiodides, $CH_3CH_2C(CH_3)_2CHI_2$, $(CH_3)_2CHC(CH_3)_2CHI_2$, and $CH_3CH_2C(C_2H_5)_2CHI_2$ gives mainly olefinic products (*257*). The reaction of cyclohexene with ethylidene iodide and zinc-copper couple gives *exo*-7-methylnorcarane in a poor yield (*459*). The reaction of 1-iodoethyl benzoate and zinc-copper couple with cyclohexene gives a 1:1.9 mixture of *endo*- and *exo*-7-methylnorcarane in 29% yield (*547*). On the other hand, the reaction of olefins with diethylzinc and ethylidene iodide gives the corresponding methylcyclopropanes in much better yields (*367*). At present, reaction (14) is the only synthetically useful



(14)

one-step route to methyl-substituted cyclopropane derivatives from olefins. The reaction was shown to be syn-selective,[3] i.e., the syn isomer generally predominated over the anti isomer in the product, although exceptions were observed in the case with olefins containing hydroxyl group (*367*). The anti isomer predominates over the syn isomer in reaction (14) with allyl alcohol, crotyl alcohol, and cyclopenten-4-ol, which can be explained by an intramolecular mechanism, e.g. (*367*),



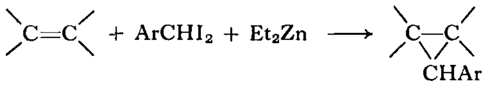
(XVI)

(15)

The predominant formation of the thermodynamically less stable syn isomer is synthetically valuable, since the anti isomers can always be obtained from the corresponding syn isomers by base-catalyzed isomerization (*89*, *350*). Electrostatic interaction between the methyl group of the methylcarbenoid and the substituents on the olefin was proposed to explain the syn selectivity of the reaction (*367*).

3. *Arylmethylene Transfer Reaction with Olefins*

The carbenoid decomposition of an aryldiazomethane catalyzed by zinc halides in the presence of olefins is a convenient method for the synthesis of arylcyclopropanes (*184*). The reaction is syn-selective and yields are generally as good as or better than those obtained by previously described methods (*89*, *270*, *271*). A transition state similar to that proposed for the Simmons-Smith reaction was suggested (*184*). The stability of the α-halobenzylzinc halide was shown by iodometric titrations to decrease in the order: X = I > Br > Cl (*185*). The reaction of aryldiiodomethane and diethylzinc with olefins gives the corresponding arylcyclopropane derivatives in good yields (*160*, *370*). The reaction is

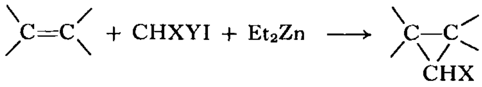


(16)

also useful as a synthetic route to arylcyclopropanes. The reaction shows larger syn selectivity than lithium phenylcarbenoids (*89*). An electron-donating substituent attached to the aryl group of the arylcarbenoid of zinc enhances the syn selectivity. The syn selectivity is larger in ether than in *n*-pentane, contrary to the case of the lithium phenylcarbenoid.

4. *Halomethylene Transfer Reaction with Olefins*

Considerable information has accumulated on the cycloaddition of halocarbene and carbenoid to olefins (*389*). Known procedures to prepare halocarbenes and carbenoids include photoinduced decomposition of halodiazomethane (*90*), reaction of haloform with base (*118*), polyhalomethane with alkyllithium (*86*, *87*, *338*), $(CH_3)_3SnCF_3$ with NaI (*436*), $CCl_3P(O)(OC_2H_5)_2$ with KF (*33*), and pyrolysis of CX_3COONa (*113*, *532*), $C_6H_5HgCX_3$ (*435*), $(C_6H_5)_3SnOCOCCl_3$ (*437*), $(CF_3)_nPF_{5-n}$ (*74*, *304*, *305*), $CF_3Fe(CO)_4I$ (*255*), CCl_3SiCl_3 (*38*, *129*, *444*), and $(C_6H_5)_3PbCCl_3$ (*520*). The halocarbenoid of zinc is also useful as a halomethylene transfer reagent to olefins. The $Zn(CHCl_2)_2$ prepared from $LiCHCl_2$ and $ZnCl_2$ reacted with cyclohexene in benzene to give 7-chloronorcarane (*262*). The reaction of diethylzinc and CCl_4 in the presence of cyclohexene gives dichloronorcarane in a low yield (*446*). The reaction of cyclohexene and diethylzinc with $CHFI_2$, $CHCl_2I$, $CHBr_2I$, or CHI_3 gives 7-fluoro-, 7-chloro-, 7-bromo-, or 7-iodonorcarane, respectively (*343*, *344*, *371*). Dihalomonoiodomethanes afford only a



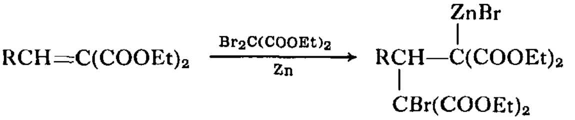
(17)

(X, Y = F, Cl, Br, or I)

small amount of iodonorcarane, and diethylzinc was suggested to react mainly with the iodine of polyhalo methane to give an α-dihalomethylzinc compound. The yield of 7-halonorcarane suggests that the halogen in the dihalomethylzinc compound undergoes α-elimination with the zinc moiety in the order: I, Br > Cl > F. Endo isomers of 7-fluoro-, 7-chloro-, and 7-bromonorcarane form predominantly over their exo isomers. However, the selectivity of formation of 7-iodonorcarane depends upon the source of the iodocarbenoid of zinc. The endo isomer forms predominantly in the reaction with $CHClI_2$ or $CHBrI_2$, while exo isomer is predominant in the reaction with CHClBrI or CHI_3.

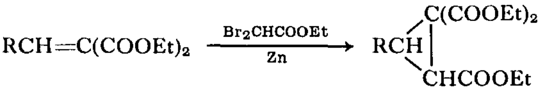
5. *Miscellaneous Reactions of Organozinc Compounds which Give Cyclopropane Derivatives from Olefins*

The reaction of an alkylidene malonate with dibromomalonate in the presence of zinc gives the 1,4-adduct of the Reformatsky reagent (*175*).

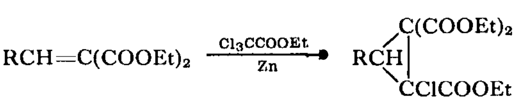


$$RCH{=}C(COOEt)_2 \xrightarrow[Zn]{Br_2C(COOEt)_2} RCH\!-\!\overset{\displaystyle ZnBr}{\underset{\displaystyle CBr(COOEt)_2}{C}}(COOEt)_2 \qquad (18)$$

The intermediate Reformatsky reagent $BrZnC(Br)(COOEt)_2$ is an α-halogenoorganozinc compound, which can be regarded as a bis(carbethoxy)carbenoid of zinc. The reaction of alkylidene malonate with polyhaloacetate in the presence of zinc gives cyclopropane derivatives (*176*). Addition of ethyl bromocyanoacetate to aromatic aldehydes in the presence of zinc gives, after treatment with ice-AcOH, mixtures of (XVII) and (XVIII) (*531*, *556*). A two-step (addition and elimination)



(19)



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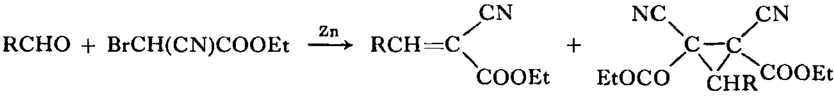


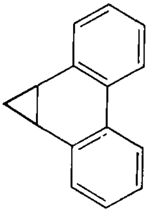
(XVII) (XVIII) (21)

mechanism would be suitable for these reactions as well as the formation of cyclopropane carboxylate from ethylzinc chloride and α-chloroacrylate (*247*).

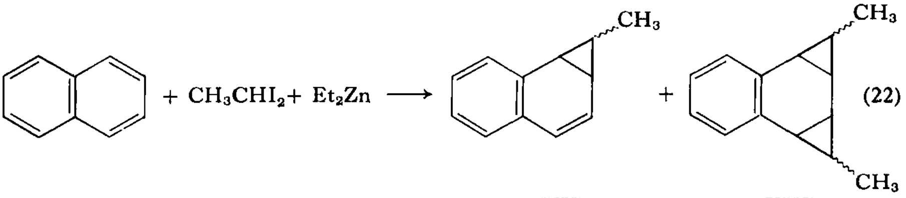
B. Reaction of Zinc Carbenoids with Aromatic Carbon–Carbon Double Bonds

1. *Cycloaddition*

The reaction of phenanthrene with zinc dust and methylene iodide in 1,2-dimethoxyethane gives 9,10-dihydro-9,10-methanophenanthrene (XIX) in 25% yield (*408*). The reaction of naphthalene with diethylzinc and ethylidene iodide gives norcaradiene derivatives, i.e., a 1:3.5 mixture of endo and exo isomers of (XX) and a 1:9.6:3.9 mixture of exo,exo,exo, endo and endo,endo isomers of (XXI) in 14% and 7% yields, respectively (*368*). The anti isomer predominates in the monoadduct (XX), and this fact was explained by the step-by-step addition mechanism. The ratio of *syn*- to *anti*-methyl groups in the diadduct (XXI) was calculated from the isomer ratio to be 1.9. The result indicates that the addition of the methylcarbenoid to the monoadduct (XX) is syn-selective.



(XIX)

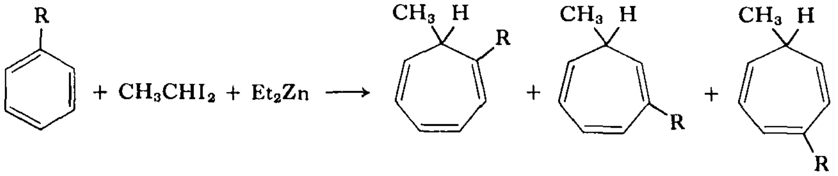


(22)

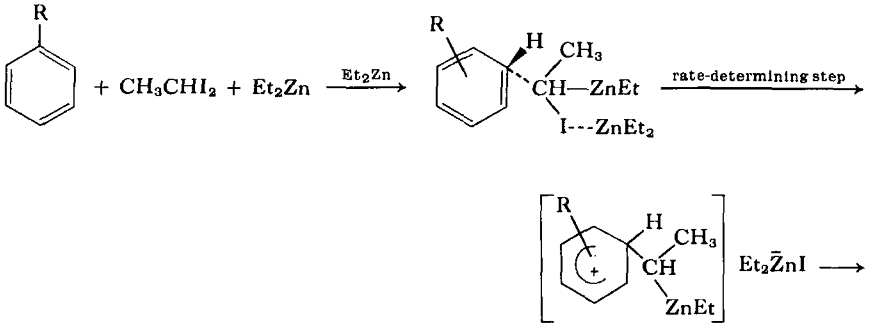
(XX) (XXI)

2. *Ring Expansion*

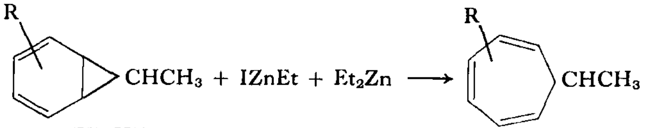
Ring expansion of aromatic compounds by carbene, carbethoxycarbene, chlorocarbene, and carbenoid is well known (*256*, *336*, *351–356*). Müller and co-workers reported the reaction of aromatic compounds with carbene generated from a catalytic decomposition of diazomethane with copper salts, and proposed a bimolecular two-step mechanism involving an inverse ylid for the reaction. Miller (*336*) proposed another bimolecular two-step mechanism for the reaction of benzene with alkylcarbenoids of aluminum. Baldwin and Smith (*25*) proposed a concerted mechanism for the reaction of aromatic compounds with carbethoxycarbene. Reaction of alkylbenzene with diethylzinc and ethylidene iodide gives 7-methylcyclohepta-1,3,5-triene derivatives in 31–44% yield (*369*). The relative reactivity of alkylbenzene in reaction (23) shows a good correlationship with that in the Friedel-Crafts alkylation. Partial rate factors evaluated for the ring expansion of toluene satisfied the selectivity relationship (*477*), $\log p_f^{Me} = 1.310 \log (p_f^{Me}/m_f^{Me})$ where p_f^{Me} and m_f^{Me} are para and meta partial rate factors for toluene, respectively. Based on these results, it was concluded that the rate of the ring-expansion reaction was determined by the σ-complex formation step. The stepwise mechanism of Eq. (24) was proposed for the ring-expansion reaction (*369*). Reaction (24) is assumed to proceed via a norcaradiene intermediate (XXIII).



(23)



(XXII)



(XXIII) (XXIV) (24)

The formation of norcaradiene derivatives with naphthalene [reaction (22)] lends some support to this scheme. This mechanism resembles a bimolecular two-step process suggested for the reaction of chloromethylaluminum compounds with olefins (*199–201*). On the other hand, a bimolecular one-step methylene transfer mechanism is generally accepted for the formation of cyclopropane derivatives by the reaction of halomethylzinc compounds with olefins. This difference between the mechanism proposed for the cyclopropane formation from olefin and that for the ring expansion of aromatic compound may be ascribable to the difference in the stability of intermediates; the benzenium ion (XXII) may be more stable than an alkylcarbonium ion (*369*).

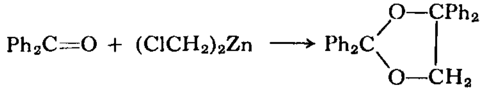
C. Reaction of Zinc Carbenoids with Carbonyl Groups

The reaction of aldehydes with the Simmons-Smith reagent in the presence of an excess amount of zinc dust gives the corresponding olefins in 29–63% yields (*192*, *193*, *341*). The reaction is nucleophilic, unlike

$$\mathrm{RCHO} + \mathrm{CH_2I_2} + \mathrm{Zn(Cu)} \xrightarrow{\text{excess Zn}} \mathrm{RCH{=}CH_2} \qquad (25)$$

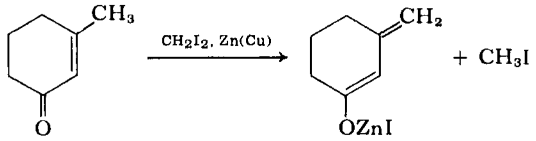
methylene transfer to olefins (*193*, *197*, *341*). The reaction is not restricted to CH_2I_2 and can be applied to CH_2Br_2, CH_2ClBr, and CH_2ClI (*342*). However, no reaction between the Simmons-Smith reagent and formylamino group was reported (*40*, *41*).

Usually reaction (25) is not applicable to ketones (*193*), although a ketone function in a steroid was replaced by methylene group with use of the Simmons-Smith reagent in the presence of excess zinc-copper couple (*517*). The reaction of bis(chloromethyl)zinc with benzophenone gives dioxoranes in a poor yield (*546*). The Simmons-Smith reagent undergoes the methylene transfer to the C=C bond of α,β-unsaturated



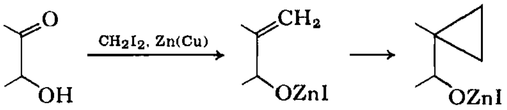
$$\mathrm{Ph_2C{=}O} + \mathrm{(ClCH_2)_2Zn} \longrightarrow \mathrm{Ph_2C}\begin{cases}\mathrm{O{-}CPh_2}\\ \mathrm{O{-}CH_2}\end{cases} \qquad (26)$$

ketones (*37*, *301*, *538*). However, enolizable ketones react as shown in Eq. (27) (*301*). The Simmons-Smith reagent replaces the carbonyl



(27)

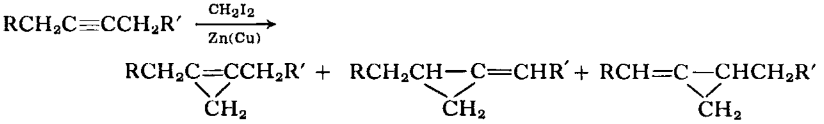
oxygen of ketones containing a neighboring hydroxyl group by the methylene and 1,1-ethano groups (*191*).



(28)

D. Reaction of Zinc Carbenoids with Other Unsaturated Bonds

The reaction of the Simmons-Smith reagent with a carbon–carbon triple bond gives cyclopropene and its isomers (*72*), along with small amounts of allene derivatives (*123*, *529*). Terminal acetylenic groups give

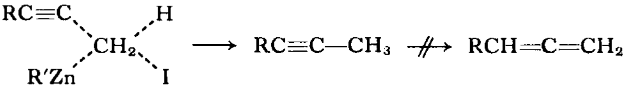


$$\text{RCH}_2\text{C}\equiv\text{CCH}_2\text{R}' \xrightarrow[\text{Zn(Cu)}]{\text{CH}_2\text{I}_2} \underset{\text{CH}_2}{\text{RCH}_2\text{C}{=}\text{CCH}_2\text{R}'} + \underset{\text{CH}_2}{\text{RCH}_2\text{CH}{-}\text{C}}{=}\text{CHR}' + \text{RCH}{=}\underset{\text{CH}_2}{\text{C}{-}\text{CH}}\text{CH}_2\text{R}' \quad (29)$$

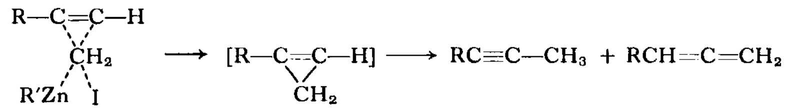
methylacetylene and allene derivatives (*528*). The reaction was explained

$$\text{C}_6\text{H}_5\text{C}\equiv\text{CH} \xrightarrow[\text{Zn(Cu)}]{\text{CH}_2\text{I}_2} \text{C}_6\text{H}_5\text{C}\equiv\text{CCH}_3(37\%) + \text{C}_6\text{H}_5\text{CH}{=}\text{C}{=}\text{CH}_2\,(3\%) \quad (30)$$

by the insertion of a methylene group into the acetylenic C—H bond. However, the isomerization of acetylene to allene is negligible under the reaction conditions, and isomerization of cyclopropene is not excluded.

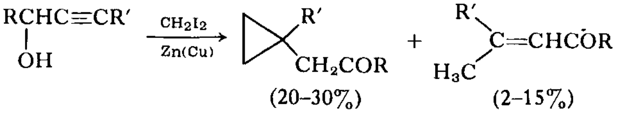


$$\left(\text{RC}\equiv\text{C}\cdots\text{H},\ \text{CH}_2,\ \text{R}'\text{Zn}\cdots\text{I}\right) \longrightarrow \text{RC}\equiv\text{C}{-}\text{CH}_3 \not\longrightarrow \text{RCH}{=}\text{C}{=}\text{CH}_2 \quad (31)$$



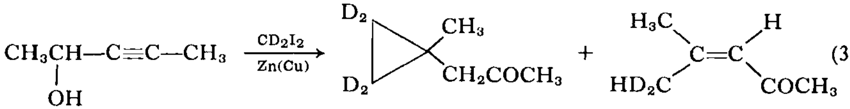
$$\left(\text{R}{-}\text{C}{=}\text{C}{-}\text{H},\ \text{CH}_2,\ \text{R}'\text{Zn}\ \ \text{I}\right) \longrightarrow [\text{R}{-}\underset{\text{CH}_2}{\text{C}{=}\text{C}}{-}\text{H}] \longrightarrow \text{RC}\equiv\text{C}{-}\text{CH}_3 + \text{RCH}{=}\text{C}{=}\text{CH}_2 \quad (32)$$

The Simmons-Smith reagent undergoes a transannular reaction with cyclooctyne to give bicyclo[3.3.0]octane derivatives (*547a*). The reaction of Simmons-Smith reagent with α-hydroxyacetylenic compounds has been studied (*524*). Although the mechanism of this reaction is not elucidated,



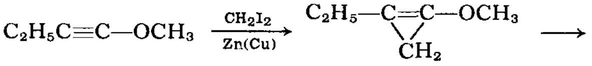
(33)

it is noteworthy that the use of CD_2I_2 with 3-pentyn-2-ol resulted in the formation of (XXV) and (XXVI).[4] The reaction products from the



(XXV) (XXVI) (34)

Simmons-Smith reagent with (XXVII) were explained to be derived from the initially formed (XXVIII) (*235*).

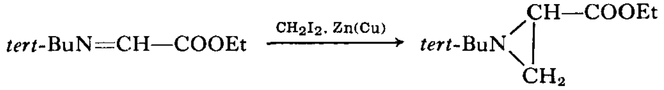


$$C_2H_5C{\equiv}C{-}OCH_3 \xrightarrow[Zn(Cu)]{CH_2I_2} C_2H_5{-}\underset{\diagdown\ \diagup \atop CH_2}{C{=}C}{-}OCH_3 \longrightarrow$$

(XXVII) (XXVIII) (35)

The reaction of allene derivatives with Simmons-Smith reagent gives mono- and dimethylenated products (*30*, *31*, *34*, *405*, *518*, *530*).

The reaction of Simmons-Smith reagent with an iminoester gives an aziridine derivative (*28*).



(40%) (36)

E. Miscellaneous Reactions of Zinc Carbenoids

Usually zinc carbenoids do not insert into olefinic C—H bonds, although the Simmons-Smith reagent was reported to attack ether to give products resulting from insertion of a methylene group into the α-C—H bond (*42*, *185*). As has been mentioned above, the formation of methylacetylene derivatives from terminal acetylene derivatives may proceed via insertion of methylene into the C—H bond (*528*).

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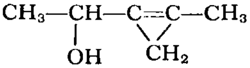
[4] A private communication suggested the formation of



$$CH_3{-}\underset{OH}{CH}{-}\underset{\diagdown\ \diagup \atop CH_2}{C{=}C}{-}CH_3$$

during the reaction (33) with 3-pentyn-2-ol (*110*).

Zinc carbenoids also insert into Si—H and Sn—H bonds (*372*, *434*).

$$R^1R^2R^3SiH \xrightarrow{CH_2I_2,\ Zn(Cu)} R^1R^2R^3SiCH_3 \qquad (37)$$

$$R^1R^2R^3SiH \xrightarrow{RCHI_2,\ Et_2Zn} R^1R^2R^3SiCH_2R \quad (R = H, CH_3) \qquad (38)$$

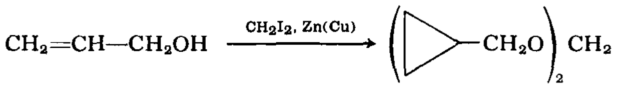
$$R^1R^2R^3SnH \xrightarrow{RCHI_2,\ Et_2Zn} R^1R^2R^3SnCH_2R \quad (R = H, CH_3) \qquad (39)$$

The formation of *n*-propyl and *n*-butyl iodides is a side reaction in the preparation of cyclopropane derivatives from olefins by the reaction with diethylzinc and *gem*-diiodoalkanes (*163*). This side reaction is enhanced by the presence of lithium or magnesium halides, and was explained in terms of insertion of the zinc carbenoid into the carbon–iodine bond (*245*).

The reaction of bis(dichloromethyl)zinc with mercuric chloride gives bis(dichloromethyl)mercury in 93% yield (*262*). The reaction of iodomethylzinc iodide or bromomethylzinc bromide in tetrahydrofuran with an appropriate metal or organometallic halide was used in the preparation of $(CH_3)_3SnCH_2I$, $(CH_3)_3SnCH_2Br$, $(CH_3)_2Sn(CH_2I)_2$, $(CH_3)_2Sn(CH_2Br)_2$, $(CH_3)_2(C_6H_5)SnCH_2I$, $(C_6H_5)_3SnCH_2I$, $Sn(CH_2I)_4$, $(C_6H_5)_3PbCH_2I$, $Hg(CH_2I)_2$, and $Hg(CH_2Br)_2$ (*439*). A homogeneous solution of iodomethylzinc iodide produced by the reaction of equimolar quantities of ethylzinc iodide and methylene iodide in tetrahydrofuran is much superior to the Simmons-Smith reagent (*440*, *441*). The reaction was extended to include use of CH_3CHI_2, $(CH_3)_3SiCHI_2$, and $(CH_3)_3SnCHI_2$ (*440*).

The intermediate formation of a zinc carbenoid *tert*-$BuCOCH(ZnCl)_2$ was postulated for the reaction of α,α′-dichloropinacoline with zinc-copper couple which produces *trans*-tripivalylcyclopropane (*78*).

The Simmons-Smith reaction with allyl alcohol was reported to give dicyclopropylcarbinoxymethane (XXIX) in addition to cyclopropylcarbinol (*307*). This reaction is a useful one-step route to dicyclopropylcarbinoxymethanes. Reaction of the Simmons-Smith reagent with



(40)

(XXIX)

benzoyl chloride in dioxane gives benzoic anhydride. The same reaction in ether gives ethyl benzoate, and in tetrahydrofuran gives 4-chloro- and 4-iodobutyl benzoates (*496*).

III

GRIGNARD-TYPE ADDITION REACTIONS OF ORGANOZINC COMPOUNDS

Organozinc reagents are generally much less reactive than Grignard reagents and organolithium reagents in addition reactions with carbonyl and other unsaturated compounds. This is the reason why organozinc reagents were almost entirely superseded by Grignard reagents in organic syntheses. On the other hand, their low reactivity is the basis of the synthetic utility of organozinc compounds for the preparation of ketones from acid halides. However, electron-attracting substituents such as carbalkoxyl, cyano, and amido groups enhance the reactivity of organozinc compounds, especially when they are attached to an α-carbon. This type of organozinc compound is the intermediate of the Reformatsky reaction. Allylic, benzylic, propargylic, and related organozinc reagents also show high reactivity toward carbonyl and other unsaturated compounds. These kinds of organozinc reagents are intermediates in the Zaitsev reaction. Grignard-type addition reactions have also been found for various other organozinc compounds.

A. Reformatsky and Related Reactions

The reaction of a carbonyl compound with an α-haloester in the presence of zinc is commonly known as the Reformatsky reaction. The reaction has been developed extensively. At present, the reaction is applied

$$XCR^1R^2COOR^3 + R^4COR^5 + Zn \longrightarrow R^4R^5C(OH)CR^1R^2COOR^3 \qquad (41)$$

not only to aldehydes and ketones, but also to esters, acid halides, nitriles, imines, nitrones, imides, ketenes, and epoxides. 1,2- and 1,4-additions to α,β-unsaturated carbonyl compounds have also been reported. Moreover, various halogen compounds can be used instead of α-halo esters, e.g., γ-halo-α,β-unsaturated esters, α-halo polyesters, α-polyhalo esters, α-polyhalo polyesters, α-halonitriles, α-haloamides, α-halothioesters, and acyl halides. Three reviews cover the literature up to and including 1971 (*173*, *268*, *453*), and the present work omits the details of the Reformatsky and related reactions.

B. *Zaitsev and Related Reactions*

Allylic, benzylic, propargylic, and related organic halides react with many aldehydes and ketones in the presence of zinc to form alcohols. This reaction (the Zaitsev reaction) has been used in the synthesis of alcohols containing unsaturated groups. For example,

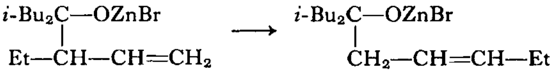
$$R^1CH{=}CH{-}CH_2X + R^2COR^3 + Zn \longrightarrow R^1CH{=}CH{-}CH_2CR^2R^3OH \quad (42)$$

The reaction has been studied by many workers. A review (*447*) covers the literature on this subject up to and including 1960, and the present work covers the years 1961–1972. This type of reaction with γ-halo-α,β-unsaturated esters is included in the reviews on the Reformatsky reaction.

1. *Reaction of Allylic Organozinc Compounds*

The substitution of Zn for Mg in the Grignard reaction with aldehydes, ketones, esters, acid anhydrides, and nitriles was reported to be successful in the cases of allyl, benzyl, crotyl, cinnamyl, propargyl, phenylpropargyl, and 1-methylallyl bromides (*169*). γ-Ethylallyl-, γ-vinylallyl- and γ-ethynylallylzinc bromides react with ketones, ethyl formate, and *N*,*N*-dimethylformamide with allylic rearrangement (*335*). Other examples of the reactions of allylic organozinc bromides with carbonyl compounds have been reported (*170*, *178*, *179*, *189*, *390*). Unlike normal dialkylzincs, diallylzinc reacts with ketones and aldehydes even in the absence of a metal halide in ether (see Section III,C) to give the expected alcohols containing the unsaturated group in excellent yields (*2*, *6*).

In the reaction of allylic organozinc reagents with carbonyl derivatives (e.g., diisobutyl ketone), isomerization of the branched product (XXX) occurs to the thermodynamically more stable linear product (XXXI) (*333*). The ratio of linear to branched alcohol increases with longer reaction time, and this was taken as evidence that the branched alcoholate isomerizes with rupture of the C-3—C-4 bond into the thermodynamically more stable linear alcoholate. The results were interpreted in terms of reversible condensation (*332*). Allylic rearrangements in the

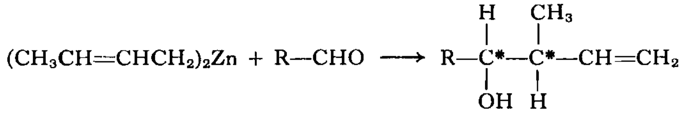


$$\begin{array}{l} i\text{-Bu}_2\text{C—OZnBr} \\ \quad\ \ | \\ \text{Et—CH—CH=CH}_2 \end{array} \longrightarrow \begin{array}{l} i\text{-Bu}_2\text{C—OZnBr} \\ \quad\ \ | \\ \text{CH}_2\text{—CH=CH—Et} \end{array}$$

(XXX) (XXXI)

reaction of γ-ethylallylmetal reagents with aldehydes and ketones were reported to occur in the sequence Al > Mg > Zn (*27*). In their action on carbonyl compounds, α-ethylenic and γ-unsaturated (ethylenic or acetylenic) organozinc halides show the same rearrangement as occurs with a simple allylzinc halide (*334*). The hydrolysis of crotylzinc bromide gives 1-butene, *cis*-2-butene, and *trans*-2-butene, and the product distribution depends on the nature of solvent (*11*).

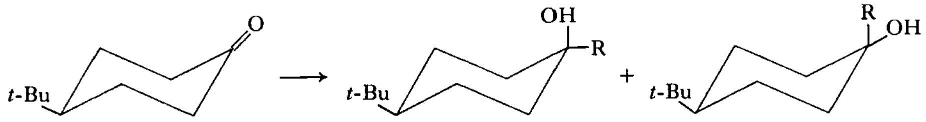
Several papers are concerned with the threo–erythro stereoselectivity of the reaction of allylic organozinc reagents with carbonyl compounds. The addition (involving allylic rearrangement) of crotylzinc derivatives to various aldehydes occurs stereoselectively, and the relative amount of *threo*-alcohol increases with increasing steric demand of the group R (*tert*-Bu, 84%; *i*-Pr, 70%; *n*-Pr, 46%) and in the sequence of metals Mg < Zn < Cd (*3*, *7*). The temperature or the polarity of the solvent



$$(\text{CH}_3\text{CH=CHCH}_2)_2\text{Zn} + \text{R—CHO} \longrightarrow \text{R—}\overset{\overset{\text{H}}{|}}{\underset{\underset{\text{OH}}{|}}{\text{C}^*}}\text{—}\overset{\overset{\text{CH}_3}{|}}{\underset{\underset{\text{H}}{|}}{\text{C}^*}}\text{—CH=CH}_2 \qquad (43)$$

has little influence on the threo/erythro ratio (*3*, *7*).

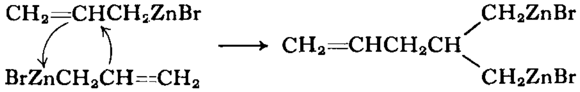
The stereochemistry of addition of an allylic organozinc reagent to a carbonyl group has received considerable attention. Both diallyl- and dicrotylzinc in their reactions with alkyl-substituted cyclohexanones display a strong preference for equatorial attack (formation of the *trans*-alcohol) on the carbonyl group (*5*, *6*), e.g.,



84% 10% (R = Allyl) (44)

In the reaction of crotylzinc reagents with substituted cyclohexanone, the stereoselectivity decreases with increasing distance of the substituent from the carbonyl group, e.g., the percentage of equatorial attack decreases from 88.5% in 2-methyl- to 75% in 3-methyl-, and to 65% in 4-methylcyclohexanone (*6*). In a comparative study of this type of reaction, the highest stereoselectivity was observed for diallylzinc and the following sequence has been observed: Mg < Cd < Zn (*6*, *7*).

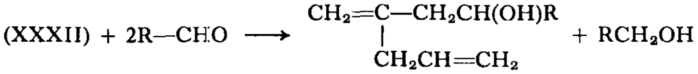
Reaction of allylzinc bromide with various reactants affords, in addition to the normal products, compounds containing the group $CH_2{=}C(CH_2CH{=}CH_2)CH_2{-}$ in yields of 10–15% (*96*). These products may be formed via a dimeric allylzinc reagent (XXXII). Reaction of (XXXII)



$$\begin{matrix} CH_2{=}CHCH_2ZnBr \\ BrZnCH_2CH{=}CH_2 \end{matrix} \longrightarrow CH_2{=}CHCH_2CH\begin{matrix} CH_2ZnBr \\ CH_2ZnBr \end{matrix} \qquad (45)$$

(XXXII)

with an aldehyde for example would then proceed as shown in Eq. (46).



$$(XXXII) + 2R{-}CHO \longrightarrow \begin{matrix} CH_2{=}C{-}CH_2CH(OH)R \\ | \\ CH_2CH{=}CH_2 \end{matrix} + RCH_2OH \qquad (46)$$

(XXXIII)

1,4-Addition of allylic organozinc reagents to alkylidene malonates (*106*, *107*) and alkylidene cyanoacetates (*107*) has also been reported.

Allylic organozinc reagents undergo addition reactions even across isolated (unconjugated) olefinic double bonds. Allylzinc bromide was reported to display both terminal and nonterminal addition reactions of this type (*321*, *323*, *329*). γ-Ethylallylzinc bromide reacts with allylic

$$CH_2{=}CHCH_2ZnBr + CH_2{=}CH(CH_2)_nNEt_2 \longrightarrow$$
$$CH_2{=}CHCH_2CH_2CH_2(CH_2)_nNEt_2 + CH_2{=}CHCH_2CH(CH_3)(CH_2)_nNEt_2 \qquad (47)$$

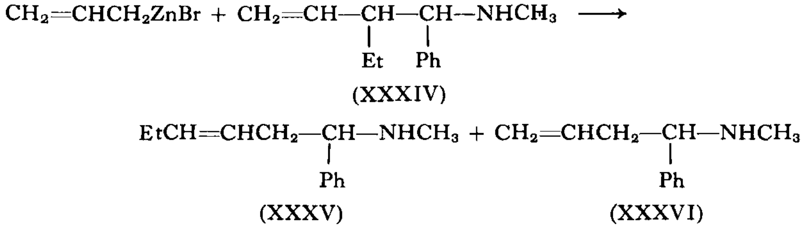
rearrangement (*321*). Both the yield and the mode of addition were

$$EtCH{=}CHCH_2ZnBr + CH_2{=}CH(CH_2)_nNEt_2 \longrightarrow$$
$$CH_2{=}CHCH(Et)CH_2CH_2(CH_2)_nNEt_2 + CH_2{=}CHCH(Et)CH(CH_3)(CH_2)_nNEt_2 \qquad (48)$$

reported to vary notably with the value of *n*. The reactivity of allylzinc bromide was further illustrated by the successful additions across the double bond of several olefinic alcohols and ethers (*321*).

In the presence of allylzinc bromide, a branched olefinic amine

(XXXIV) rearranges slowly to give a 7% yield of (XXXV) along with a 30% yield of dealkylated compound (XXXVI) (*331*). The formation of

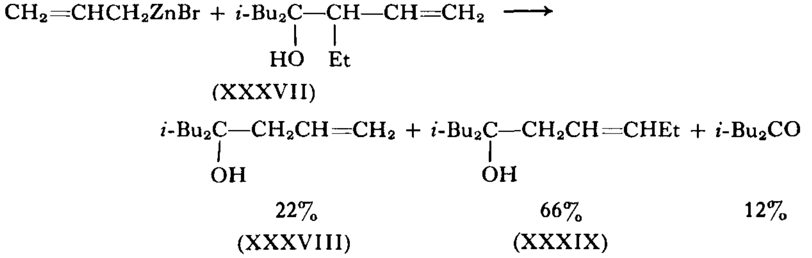


$$\mathrm{CH_2{=}CHCH_2ZnBr + CH_2{=}CH{-}\underset{\displaystyle Et}{CH}{-}\underset{\displaystyle Ph}{CH}{-}NHCH_3} \longrightarrow$$

(XXXIV)

$$\underset{\text{(XXXV)}}{\mathrm{EtCH{=}CHCH_2{-}\underset{\displaystyle Ph}{CH}{-}NHCH_3}} + \underset{\text{(XXXVI)}}{\mathrm{CH_2{=}CHCH_2{-}\underset{\displaystyle Ph}{CH}{-}NHCH_3}} \qquad (49)$$

(XXXV) and (XXXVI) indicates the occurrence of heterolytic cleavage of the C-3–C-4 bond of the amine (XXXIV). In the presence of an excess of allylzinc bromide, only the amines (XXXIV) and (XXXVI) are isolated. Similar types of reactions have been observed in the reactions of allylic organozinc reagents with unsaturated alcohols (*333*). The reaction of allylzinc bromide with the branched alcohol (XXXVII) forms both the allylcarbinol (XXXVIII) and the rearranged linear alcohol (XXXIX) (*333*).

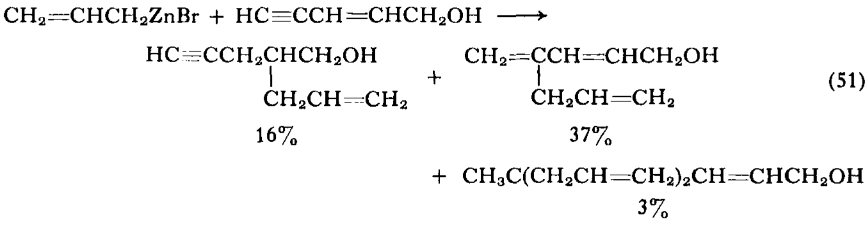


$$\mathrm{CH_2{=}CHCH_2ZnBr} + i\text{-}\mathrm{Bu_2\underset{\displaystyle HO}{C}{-}\underset{\displaystyle Et}{CH}{-}CH{=}CH_2} \longrightarrow$$

(XXXVII)

$$\underset{\substack{22\% \\ \text{(XXXVIII)}}}{i\text{-}\mathrm{Bu_2\underset{\displaystyle OH}{C}{-}CH_2CH{=}CH_2}} + \underset{\substack{66\% \\ \text{(XXXIX)}}}{i\text{-}\mathrm{Bu_2\underset{\displaystyle OH}{C}{-}CH_2CH{=}CHEt}} + \underset{12\%}{i\text{-}\mathrm{Bu_2CO}} \qquad (50)$$

The remarkable reactivity of allylic organozinc reagents is reflected in their addition to a variety of conjugated and unconjugated acetylenic triple bonds. Allyl- and crotylzinc bromides undergo the addition reactions to acetylenic triple bonds in phenylacetylene and phenylethynylmagnesium bromide (*172*). Allylzinc bromide reacts with pent-2-ene-4-yne-1-ol as shown in Eq. (51) (*322*). Allylzinc bromide reacts with



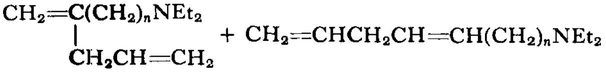
$$\mathrm{CH_2{=}CHCH_2ZnBr + HC{\equiv}CCH{=}CHCH_2OH} \longrightarrow$$

$$\underset{16\%}{\mathrm{HC{\equiv}CCH_2\underset{\displaystyle CH_2CH{=}CH_2}{CH}CH_2OH}} + \underset{37\%}{\mathrm{CH_2{=}\underset{\displaystyle CH_2CH{=}CH_2}{C}CH{=}CHCH_2OH}} \qquad (51)$$

$$+ \underset{3\%}{\mathrm{CH_3C(CH_2CH{=}CH_2)_2CH{=}CHCH_2OH}}$$

terminal acetylenic amines to give mainly the branched products (XL), contrary to the addition reaction with olefinic amines, which predominantly affords the linear products (*374*). In the reaction with non-terminal acetylenes the mode of addition depends on the nature of the zinc reagent (*374*).

$$CH_2{=}CHCH_2ZnBr + HC{\equiv}C(CH_2)_nNEt_2 \longrightarrow$$



$$\underset{\text{(XL)}}{\begin{array}{l}CH_2{=}C(CH_2)_nNEt_2\\ \;|\\ CH_2CH{=}CH_2\end{array}} + \underset{\text{(XLI)}}{CH_2{=}CHCH_2CH{=}CH(CH_2)_nNEt_2} \qquad (52)$$

$$CH_2{=}CHCH_2ZnBr + CH_3C{\equiv}C(CH_2)_2NEt_2 \longrightarrow CH_3C(CH_2CH{=}CH_2){=}CH(CH_2)_2NEt_2 \qquad (53)$$

$$CH_3CH{=}CHCH_2ZnBr + CH_3C{\equiv}C(CH_2)_2NEt_2 \longrightarrow CH_3CH{=}C(CH_2CMe{=}CH_2)(CH_2)_2NEt_2 \qquad (54)$$

The reaction of γ-ethylallylzinc bromide with aldimines ($RCH{=}NR'$) gives $R'NHCHRCH_2CH{=}CHEt$ (predominant) and $R'NHCHRCHEtCH{=}CH_2$ (*56*, *330*). The reaction of γ-ethylallylzinc bromide with nitriles (RCN) gives $RCOCHEtCH{=}CH_2$ and $RCOCEt{=}CHCH_3$ (*56*). Allyl- and γ-ethylallylzinc bromides were reported to react with an imino ether $PhN{=}CHOEt$ to give $PhNHCH(CH_2CH{=}CH_2)_2$ (*395*, *396*). The reaction of allylzinc bromide with an iminocarbonate $PhN{=}C(OEt)_2$ gives a secondary amine $PhNHC(CH_2CH{=}CH_2)_3$, and the reaction of crotyl- and γ-ethylallylzinc bromides gives imino ethers $PhN{=}C(OEt)CHRCH{=}CH_2$ (*397*).

Unlike their saturated analogs, allylic organozinc compounds are sufficiently nucleophilic to open the epoxide ring. Reaction of diallyl- and dicrotylzinc with propylene oxide gives $CH_3CH(OH)CH_2CHRCH{=}CH_2$. The reaction with styrene oxide involves attack on the benzylic carbon atom to afford $PhCH(CH_2OH)CHRCH{=}CH_2$. In the presence of $MgBr_2$ and $ZnBr_2$, the reaction gives the mixture of $PhCH_2CH(OH)CHRCH{=}CH_2$ (55–80%) and $PhCH(CH_2OH)CHRCH{=}CH_2$ (20–45%) (*4*). A detailed study of the reaction of diallylzinc with styrene oxides revealed negative Hammett ρ-values of -1.7 (*8*) and -0.5 (*10*). The stereochemistry of the reaction of diallylzinc with 1-phenyl-1,2-epoxypropane has been studied (*9*). The cis isomer gives $PhCH(CH_2CH{=}CH_2)CH(OH)CH_3$ (92%) and $PhCH(OH)CH(CH_2CH{=}CH_2)CH_3$ (8%), whereas the trans isomer affords $PhCH(CH_2CH{=}CH_2)$-

$CH(OH)CH_3$ (100%). Reaction of diallylzinc with 1-phenyl-2,3-epoxypropane was also studied (*45*).

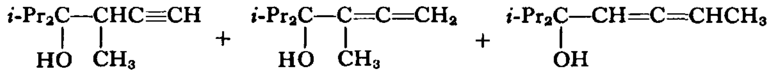
2. *Reaction of Propargylic and Allenic Organozinc Compounds*

As was mentioned before, propargylic organozinc reagents readily undergo Grignard-type addition reactions with carbonyl and other unsaturated compounds (*169*, *186*). Recently, rearrangements were demonstrated in these systems. The reaction of propargylzinc bromide with aldehydes and ketones gives rise to a mixture of β-acetylenic and α-allenic alcohols (*171*).

$$HC{\equiv}CCH_2ZnBr + RCOR' \longrightarrow HC{\equiv}CCH_2C(OH)RR' + H_2C{=}C{=}CHC(OH)RR' \quad (55)$$

The organozinc reagent derived from 3-bromo-1-butyne which has the allenic structure (XLII) affords a mixture of three isomeric alcohols upon reaction with diisopropyl ketone, indicating the strong tendency of rearrangement in the systems (*171*). The proportion of allenic alcohol formed relative to the acetylenic isomer increases with increasing solvating capacity of the solvent in the series dioxane < DME < THF < DMSO < DMF < HMPA, and with decreasing electrophilicity of the carbonyl carbon atom (*171*, *347*). The nature of the reaction of propargylic organozinc reagent with carbonyl compound was investigated in greater detail (*177*, *346*). The rearrangement and stereochemistry of the reaction of propargylic organozinc reagent with aldimines has also been investigated in detail (*348*, *349*, *375*).

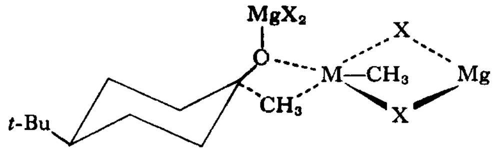
$$\underset{\text{(XLII)}}{CH_3CH{=}C{=}CHZnBr} + i\text{-}Pr_2CO \longrightarrow \quad (56)$$



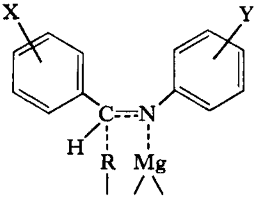
$$i\text{-}Pr_2\underset{HO}{\underset{|}{C}}{-}\underset{CH_3}{\underset{|}{C}}HC{\equiv}CH + i\text{-}Pr_2\underset{HO}{\underset{|}{C}}{-}\underset{CH_3}{\underset{|}{C}}{=}C{=}CH_2 + i\text{-}Pr_2\underset{OH}{\underset{|}{C}}{-}CH{=}C{=}CHCH_3$$

C. *Grignard-Type Addition Reactions of Miscellaneous Organozinc Compounds*

Unlike the Reformatsky and Zaitsev reagents, saturated organozinc reagents display little reactivity toward carbonyl and other unsaturated compounds. In the reaction with α,β-unsaturated ketones, dialkylzincs undergo 1,4-addition without carbonyl addition (*246*). However, small amount of added metal halides increase the reaction rate. The yields of carbinols formed in the reaction of a variety of aldehydes and ketones with (a) pure R_2Zn, (b) $R_2Zn + 2MgX_2$, (c) $2RMgX + ZnX_2$ clearly demonstrated the activating effect of metal halides on the reactivity of organozinc compounds (*311*). The kinetics remains unchanged (*312*). Dipropylzinc shows a stronger tendency towards equatorial attack on the carbonyl group of 4-*tert*-butylcyclohexanone than the corresponding Grignard reagent (*5*), but dimethylzinc shows a greater amount of axial attack (formation of the thermodynamically less stable *cis*-alcohol) than the methylmagnesium halide (*237*). A four-center transition state (XLIII) containing strongly associated magnesium halide was proposed for the reaction involving equatorial attack (*237*). The reaction of Pr_2Zn with $PhCHO$ gives $PhCH(OH)Pr$ and $PhCH_2OH$ by addition and reduction, respectively. The presence of Bu_4NX salts enhances the addition reaction (*79*). The stereochemistry of both addition and reduction of *in situ* *n*-propylzinc reagent with 4-*tert*-butylcyclohexanone has been studied (*238*).



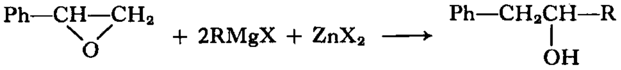
(XLIII)



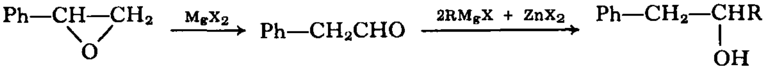
(XLIV)

Unlike allylic and propargylic organozinc reagents, normal dialkylzinc compounds are relatively unreactive toward Schiff bases. However, the reagent formed *in situ* from $2RMgX + ZnX_2$ readily adds across the C=N double bond to afford the expected amines (*492*, *494*). The negative Hammett ρ-value of the reaction as well as the strong influence of the presence of magnesium halides on the rate of the reaction were explained in terms of a transition state (XLIV) in which the electrophilicity of the unsaturated carbon atom is enhanced by complexation of the magnesium halide to the nitrogen atom (*493*, *494*). Bis(ethoxymethyl)zinc obtained by the reaction of zinc halides with the corresponding Grignard reagent reacts with various carbonyl compounds to give the expected β-hydroxy ethers unobtainable by other methods (*32*).

Unlike dialkylmagnesium compounds, normal dialkylzincs do not react with epoxides. However, the *in situ* reagents $2RMgX + ZnX_2$ readily give secondary alcohols without primary alcohols (*108*). Since dialkylmagnesium affords exclusively the primary alcohol $PhCH(R)-CH_2OH$, it was assumed that the reaction actually took place with phenylacetaldehyde formed by MgX_2-catalyzed isomerization of styrene oxide rather than with styrene oxide itself (*108*). Even without metal halides, dialkylzinc compounds will react with epoxide to give ring opening in dimethyl sulfoxide (*157*).

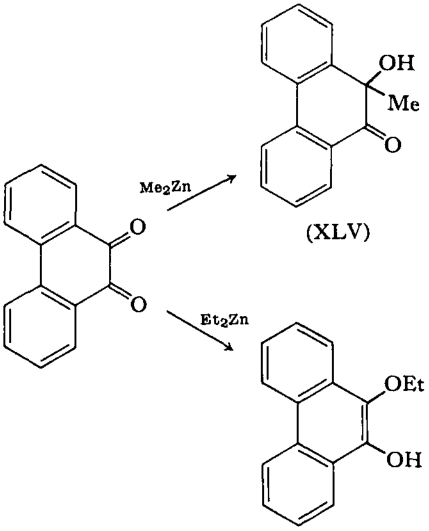


$$\text{Ph—CH—CH}_2\text{(O)} + 2\text{RMgX} + \text{ZnX}_2 \longrightarrow \text{Ph—CH}_2\text{CH(OH)—R} \qquad (57)$$



$$\text{Ph—CH—CH}_2\text{(O)} \xrightarrow{\text{MgX}_2} \text{Ph—CH}_2\text{CHO} \xrightarrow{2\text{RMgX} + \text{ZnX}_2} \text{Ph—CH}_2\text{—CHR(OH)} \qquad (58)$$

A different mode of the reaction of dimethylzinc and diethylzinc was observed in reactions with various *o*-quinones and benzils (*122*). The treatment of phenanthrene quinone with dimethylzinc gives (XLV), while diethylzinc affords (XLVI). 1,2-Naphthoquinone derivatives also give carbinol ketones with dimethylzinc, while they afford monoethyl



(XLV)

(XLVI)

(59)

ethers of the corresponding hydroquinones with diethylzinc. Benzil does not react with dimethylzinc, but reacts with diethylzinc to give benzoin ethyl ether. The action of dimethylzinc and diethylzinc was compared with that of diazomethane and diazoethane.

IV

COUPLING REACTIONS OF ORGANOZINC COMPOUNDS

1. *Reaction with Acid Halides*

Two reviews cover the literature before 1960 on ketone synthesis by the reaction of organozinc compounds with acid halides (*447*, *450*). Although this reaction was formerly believed to occur simply between organozinc compounds and acid halides, metallic halides play an important role in the reaction. The *in situ* reagents $2RMgX + ZnX_2$ readily react with acid halides to afford ketones, but the salt-free (isolated) diorganozinc is unreactive toward acid halides. The mechanisms of the reaction of dibutylzinc with various acid halides were studied with special attention to the role of Lewis acids (*327*, *328*). The introduction of $AlCl_3$, $MgBr_2$, and $ZnBr_2$ increases the yield of ketones.

The application of the ketone synthesis has continued. Phenylethynyl and vinylethynyl ketones have been synthesized by the reaction of appropriate acid halides with phenylethynylzinc chloride (*521*, *522*) and vinylethynylzinc chloride (*552*), respectively.

The Reformatsky reagent from diethyl bromomalonate reacts with a variety of aldehydes. The resulting alcoholates react with acetyl chloride to give the corresponding acetates (*174*).

2. *Reaction with α-Halo Ethers*

The reaction of the Reformatsky reagents with α-chloro ethers gives β-alkoxycarboxylic acid esters (*73*, *290*, *291*, *294*, *526*). For example,

$$R^1OCH_2Cl + R^2CHBrCOOR^3 + Zn \longrightarrow R^1OCH_2CHR^2COOR^3 \qquad (290)$$

$$O(CH_2Cl)_2 + RCHBrCOOR' + Zn \longrightarrow O(CH_2CHRCOOR')_2 \qquad (291)$$

$$R^1OCH_2Cl + R^2OOCCH_2CHBrCOOR^2 \longrightarrow R^2OOCCH_2CH(CH_2OR^1)COOR^2 \qquad (294)$$

$$CH_3OCH(CH_3)Cl + R^2OOCCH_2CHBrCOOR^2 \longrightarrow R^2OOCCH_2CH(CH(CH_3)OCH_3)COOR^2 \qquad (294)$$

A complete product study was reported on the reaction of bis(chloromethyl) ether with α-bromoisobutyrate in the presence of zinc (*557*). The reaction of chloromethyl benzoate with a Reformatsky reagent RCH-(ZnBr)COOR′ gives $PhC(OH)(OCH_2CHRCOOR')(CHRCOOR')$ (*296*).

α-Halo ketones undergo similar reactions with α-chloro ethers (*293*, *295*). For example,

$$O(CH_2Cl)_2 + RCHBrCOCH_2R' + Zn \longrightarrow RCH(CH_2OCH_2Cl)COCH_2R' \longrightarrow RCH(CH_2OH)COCH_2R' \quad (60)$$

$$CH_3OCHCl_2 + RCHBrCOCH_2R' + Zn \longrightarrow RCH(CHClOCH_3)COCH_2R' \longrightarrow RCH(CHO)COCH_2R' \quad (61)$$

Allylzinc bromide reacts with chloromethyl methyl ether in a similar manner (*96*).

$$ClCH_2OCH_3 + CH_2{=}CHCH_2ZnBr \longrightarrow CH_3OCH_2CH_2CH{=}CH_2 \quad (62)$$

3. *Miscellaneous Coupling Reactions*

Coupling reaction of Reformatsky reagent with allyl halide was reported (*73*, *526*).

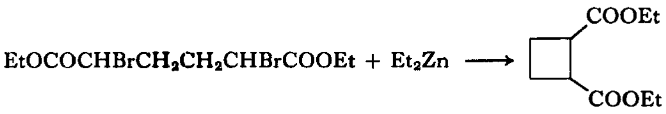
α-Bromo esters are alkylated by diethylzinc (*490*), but α,α′-dialkylated

$$EtOCOCHBr(CH_2)_nCOOEt + Et_2Zn \longrightarrow EtOCOCH(Et)(CH_2)_nCOOEt \quad (63)$$

esters could not be prepared in an analogous way (*490*). Similar coupling reactions of Reformatsky reagents with trityl chloride have been reported (*236*).

γ-Butylallylzinc bromide was treated with allyl bromide to give $CH_2{=}CHCH_2CH(Bu)CH{=}CH_2$ (95%) and $CH_2{=}CHCH_2CH_2CH{=}CHBu$ (5%). The allylic rearrangement decreased in the series Zn > Mg > Li (*56*).

The intramolecular Wurtz-type coupling of dihaloorganic compounds with use of metallic zinc is a classical synthetic route to cyclic compounds. For example, cyclopropane derivatives can be prepared from 1,3-dihalopropanes (*29*, *189a*, *248*, *451*), and cyclobutane derivatives from 1,4-dihalobutanes (*71*). These reactions presumably proceed via the intermediate formation of organozinc compounds. The reaction of diethylzinc with esters of α,α′-dibrominated aliphatic dicarboxylic acids leads to the formation of a cis–trans mixture of cyclic products via intramolecular Wurtz-type coupling (*490*). For example,



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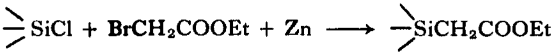
Carbethoxymethyl-substituted silanes have been prepared via the *in situ* prepared Reformatsky complex (*128*, *236*, *400*). Organogermyl



(65)

chlorides react similarly with Reformatsky reagents (*236*, *273*).

The interaction of α-haloorganozinc halides with Grignard reagents producing an organozinc intermediate involves a classical Wurtz-type coupling rather than the carbenoid insertion into the Mg—C bond (*80*).

$$\text{RMgX} + \text{X'CHR'ZnX'} \longrightarrow \text{RCHR'ZnX'} + \text{MgXX'} \qquad (66)$$

The reaction of diarylzinc with aryldiazonium salts directly forms the corresponding azo compounds in good yields (*99*).

V

MISCELLANEOUS SYNTHETIC REACTIONS WITH ORGANOZINC COMPOUNDS

Formerly, carbon dioxide was used as an inert gas in handling organozinc compounds. However, the Reformatsky reagent and allylic organozinc reagent show exceptional reactivity toward CO_2. Reaction of diallylzinc with carbon dioxide under very mild conditions gives vinylacetic acid in a quantitative yield (*169*, *491*). γ-Ethyl-, γ-vinyl-, and γ-ethynylallylzinc bromides react with carbon dioxide with allylic rearrangement (*335*). The Reformatsky reagents from ethyl bromoacetate and methyl α-bromoisobutyrate react with carbon dioxide to give the corresponding α-carboxyesters in 16.5% and 50% yields, respectively (*55*). Dibutyl- and diisopropylzinc react with carbon monoxide at atmospheric pressure in the presence of potassium *tert*-butoxide to give, after hydrolysis, the corresponding acyloins (*406*). The reaction of the Reformatsky reagent with carbon suboxide has also been reported (*102*).

Reformatsky reagents react with α-amino ethers to give β-amino esters (*67*). Acetals undergo alkoxymethylation of Reformatsky reagents (*98*).

$$\mathrm{XCR^1R^2COOR^3 + R^4R^5NCHR^6OR^7 + Zn \longrightarrow R^4R^5NCHR^6CR^1R^2COOR^3} \qquad (67)$$

$$\mathrm{XCR^1R^2COOR^3 + CR^4R^5(OR^6)_2 + Zn \xrightarrow{CH_3COCl} R^6OCR^4R^5CR^1R^2COOR^3} \qquad (68)$$

There is a competition between alkoxymethylation and acylation in this reaction. Alkoxymethylation by cleavage of acetals is also applicable to alcoholates obtained by condensing Reformatsky reagents with aldehydes and ketones (*98*, *174a*).

$$\mathrm{XZnOCR^4R^5CR^1R^2COOR^3 + R^6R^7C(OR^8)_2 \xrightarrow{CH_3COCl} R^8OCR^6R^7CR^4R^5CR^1R^2COOR^3} \qquad (69)$$

Allylic organozinc compounds react with amino ether and aminothio ether to give unsaturated amines in good yields (*96*, *329*). For example,

$$\mathrm{CH_2{=}CHCH_2ZnBr + BuOCH_2NEt_2 \longrightarrow \underset{59\%}{CH_2{=}CH(CH_2)_2NEt_2} + \underset{17\%}{CH_2{=}CH(CH_2)_5NEt_2}} \qquad (70)$$

$$\mathrm{EtCH{=}CHCH_2ZnBr + PhSCH_2NEt_2 \longrightarrow \underset{60\%}{CH_2{=}CHCHEtCH_2NEt_2} + \underset{11\%}{CH_2{=}CHCHEt(CH_2)_2CHEtCH_2NEt_2}} \qquad (71)$$

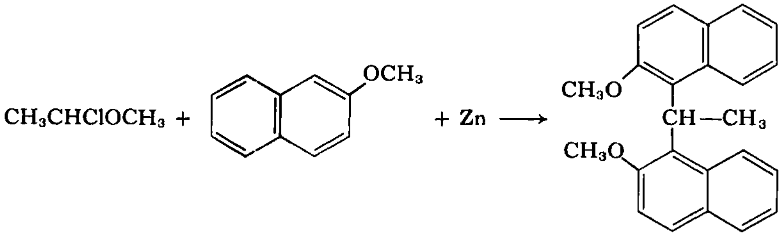
The reactions of α-chloro ethers with phenols and phenol ethers in the presence of zinc afford diarylmethanes. For example,

$$\mathrm{2PhOH + ClCH_2OR + Zn \longrightarrow HOC_6H_4CH_2C_6H_4OH} \qquad (\mathit{288, 289})$$

$$\mathrm{2PhOR' + ClCH_2OR + Zn \longrightarrow R'OC_6H_4CH_2C_6H_4OR'} \qquad (\mathit{288, 289})$$

$$\mathrm{2PhOH + EtOCHClCH_2Cl + Zn \longrightarrow ClCH_2CH(C_6H_4OH)_2 \longrightarrow HOC_6H_4CH{=}CHC_6H_4OH} \qquad (\mathit{289})$$

This reaction was extended to prepare α,α′-bis(substituted phenyl)- or α,α′-bis(substituted naphthyl)alkanes (*292*). The reaction is thought to involve two intermediate steps: (1) reaction of $\mathrm{CH_3CHClOCH_3}$ with Zn to give $\mathrm{CH_3CHO}$, $\mathrm{ZnCl_2}$, and $\mathrm{C_2H_6}$; (2) reaction of $\mathrm{CH_3CHO}$ with two equivalents of β-methoxynaphthalene yielding α,α′-bis(2-methoxy-1-naphthyl)ethane.



(72)

(R)(+)-Phenyl *p*-tolyl sulfoxide is obtained from (−)-menthyl (S) (−)-*p*-toluenesulfinate and diphenylzinc (*202*).

VI

POLYMERIZATIONS BY ORGANOZINC COMPOUNDS

Organozinc compounds have been widely used as components of initiators for polymerizations of various monomers. Although a tremendous number of the research works on the subject are available in the literature, this chapter describes only the main features of the use of organozinc compounds as initiators for polymerizations. All patents were omitted in this review.

Combinations of dialkylzincs or alkylzinc halides with titanium tetrachloride and other compounds of transition metals are used, together with various additives in some cases, for the Zieglar-Natta-type stereospecific homopolymerizations and copolymerizations of ethylene, propylene, styrene, and other α-olefins (*20*, *22*, *47–52*, *76*, *130–136*, *188*, *241*, *244*, *251*, *252*, *266*, *267*, *287*, *365*, *411*, *426*, *448*, *449*, *454*, *467*, *469*, *482*, *483*, *555*). These types of catalyst systems were used for the stereospecific polymerization of optically active olefins to afford optically active polymers (*69*, *82*). Polymerization was stereoselective when the asymmetric carbon was α to the double bond, less stereoselective when β to the double bond, and nonstereoselective when γ to the double bond (*85*). Combinations of optically active organozinc compounds with transition metal compounds are used to polymerize racemic olefins to give optically active polymers (*83*, *84*, *392*). Organozinc compounds were used as chain-transfer agents for the polymerizations of olefins by $\mathrm{AlEt_3}$–α–$\mathrm{TiCl_3}$ and other Ziegler-Natta catalysts in order to regulate molecular weight of the resulting polymers (*13*, *16*, *17*, *101*, *114*, *115*, *194*, *306*, *363*, *415*, *429*, *525*). The diethylzinc–α-titanium trichloride system gives low molecular weight polymers of diene hydrocarbons (*253*, *523*). Diethylzinc and titanium tetrachloride polymerizes alkynes (*535*).

Dialkylzinc initiates anionic polymerization of polar vinyl monomers such as acrylic nitriles (*206*, *364*, *428*), acrylic esters (*206*, *516*), vinyl and related ketones (*142*, *320*, *506*), and conjugated dienes substituted by a polar group (*143*). Organozinc compounds in the presence of cocatalysts initiate the cationic polymerization of vinyl ethers (*161*, *209*, *361*, *416*, *471*). The combinations of organozinc compounds with oxygen (*141*, *144*, *145*, *418*, *455*), nickel peroxide (*362*), active hydrogen compounds (*149*), metal halides (*210*), polyhalomethanes (*161*, *162*), and carbon disulfide (*308*) polymerize various vinyl monomers by radical mechanisms. Calcium zinc tetraethyl complex (*146*, *148*, *150*) and a combination of *n*-butyllithium and diethylzinc (*283*) are effective catalysts for the stereospecific polymerization of methyl methacrylate, styrene, and other conjugated vinyl monomers. Diethylzinc polymerizes vinyl sulfones to give low molecular weight polymers (*53*).

Dialkylzinc initiates homo- and copolymerization of aldehydes such as acetaldehyde (*151*, *234*, *310*, *487*, *533*), formaldehyde (*310*, *495*), butyraldehyde (*468*), glutardehyde (*386*), cyanopropionaldehyde (*479*), chloroacetaldehyde (*233*, *234*, *324*, *325*, *412*, *495*, *533*), and dichloroacetaldehyde (*325*). Aluminum triisopropoxide (*485*) and phosphorus compounds (*339*) were proposed as additives for the polymerizations. Polymerization of optically active aldehydes was also reported (*1*).

The most important application of organozinc compounds for polymerization is as initiators for ring-opening polymerization of ethylene oxide, propylene oxide, and other olefin oxides. Organozinc compounds such as dialkylzinc, diarylzinc, and alkylzinc halide polymerize olefin oxides. However, the catalytic activity is much enhanced by the addition of appropriate amount of cocatalysts. Both the rate of polymerization and the molecular weight of the resulting polymer are considerably raised. The cocatalysts are water and alcohols (*12*, *24*, *54*, *61–63*, *165*, *166*, *181*, *225*, *226*, *228*, *230*, *231*, *249*, *277*, *279*, *313*, *358*, *360*, *394*, *401*, *418*, *499*, *503*, *519*), enolizable ketones (*229*, *419*, *420*, *505*), primary and secondary amines (*12*, *66*, *486*, *488*), nitro, nitroso, and other compounds containing the N—O bond (*158*, *357*, *359*), organic halides (*314a*), oxygen (*285*, *418*), phosphorus compounds (*242*, *243*, *550*), dimethyl sulfoxide and other Lewis bases (*157*, *158*, *227*), ferric chloride and other metal halides and oxides (*12*, *384*, *385*, *399*), metal chelates (*137*), and silica, alumina, and other solid acids (*147*, *152*, *314*). Polymerizations by these catalyst systems are generally considered to proceed via a coordinated anionic mechanism with ethylene oxide, propylene oxide, styrene oxide, butadiene oxide, and glycidyl ethers. But the polymerization of epihalohydrins by these catalysts was claimed to be cationic (*498*). These catalyst systems are used as initiators for polymerization of epoxysilanes (*514*); cyclopolymerization of diepoxide (*476*); homo- and copolymerization of glycidamide (*195*); copolymerizations of ethylene oxide and/or propylene oxide with glycidyl ethers (*180*, *187*), epihalohydrins (*282*), tetrahydrofuran (*280*, *281*), sulfur dioxide (*425*), acid anhydride (*217*, *318*, *549*), and *N*-carboxyanhydrides of amino acids (*509*, *512*); copolymerization of styrene oxide with butadiene oxide (*513*), epichlorohydrin with 1,1′-(1,1′-expoxydiethyl)ferrocene (*26*), olefin oxides with carbon dioxide (*217a–221*, *261*) and olefin oxides with pyromellitic dianhydride (*481*); and terpolymerization of epichlorohydrin, propylene oxide, and glycidyl ethers (*278*). Graft copolymerization of ethylene oxide and propylene oxide on polyacrylamide was performed by the catalyst systems (*207*). An interesting copolymerization of vinyl and related ketones (vinyl monomers) with olefin oxides (cyclic ethers) was realized using diethylzinc as an initiator (*502*).

An interesting behavior of the polymerization would be the formation of optically active polymers from racemic olefin oxides (*81*, *153*, *154*, *162a*, *208*, *212–214*, *215a*, *250*, *274*, *275*, *316*, *393*, *500*, *504*, *507*, *508*, *510*, *511*). The catalyst systems consist of dialkylzinc and optically active alcohol or amino acid. In the polymerization, one enantiomer of the racemic monomer is selectively introduced in the polymer.

The catalyst systems are also effective as initiators for ring-opening polymerization of olefin sulfides (*57*, *58*, *224*, *232*, *284*, *285*, *297*, *303*, *548*). Asymmetric selection polymerization has also been performed with olefin sulfides (*14*, *156*, *430*, *470–472*).

Organozinc compounds initiate, with cocatalysts in some cases, polymerizations of *N*-carboxyanhydrides of amino acids (*211*, *215*, *309*, *315*, *317*, *319*, *501*, *509*, *512*, *515*, *553*), ketenes (*337*, *551*), the cyclic dimer of acrylonitrile (*478*), cyclobutene (*100*), lactones (*97*, *302*, *381–383*), lactams (*380*), lactam ethers (*379*), lactides (*117*), isocyanates (*259*), aldimines (*421*), and α-hydroxycarboxylic acid anhydrosulfites (*216*), and trimerization of isocyanate (*377*).

Diethylzinc was used as a catalyst for the preparation of polyesters from terephthalaldehyde via the Tischenko reaction (*480*), and for the polycondensation of ethylene glycol with dimethyl terephthalates to afford polyethylene terephthalate (*340*). Benzylzinc chloride has been used as a catalyst for polycondensation of benzyl chloride (*223*).

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^{13}C NMR Chemical Shifts and Coupling Constants of Organometallic Compounds

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I

INTRODUCTION

From the time of the first direct observation of a ^{13}C NMR signal in 1957 (*128*) until about 1968, the use of ^{13}C NMR spectroscopy was in the hands of the few specialists who were prepared to build their own spectrometers. During this period, attention was focused on the ^{13}C

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NMR spectra of organic compounds, and the measurement of the ^{13}C NMR spectra of organometallic compounds received little attention. The use of the ^{13}C nucleus in NMR spectroscopy of organometallic compounds was principally for the measurement of ^{13}C coupling constants to more sensitive nuclei, mainly ^{1}H, and the use of the resulting satellites to measure the ^{13}C NMR chemical shifts by INDOR (*122*). Since 1968, with advances in the sensitivity of commercial ^{13}C NMR spectrometers, the number of papers containing ^{13}C NMR data on organometallic compounds has rapidly increased. Thus, as with any review covering a rapidly developing subject, during the period between writing this review and publication, a number of significant developments will have appeared. The review covers the literature up to December, 1972, and papers published between then and June, 1973 have been included in a brief form in proof.

There are several recent texts dealing with ^{13}C NMR spectroscopy in general and the reader is referred to these texts for further information (*117*, *135*, *171*, *186*, *214*). The purpose of this review is to cover only the ^{13}C NMR spectroscopy of organometallic compounds, paying particular attention to the chemical shifts and coupling constants of carbon atoms directly attached to metals and metalloids.

For convenience, the review is divided into four sections dealing with (I) experimental techniques, (II) ^{13}C chemical shifts of σ-bonded carbon atoms, (III) ^{13}C chemical shifts of π ligands, and (IV) ^{13}C coupling constants.

II

RECENT EXPERIMENTAL TECHNIQUES OF RELEVANCE TO ORGANOMETALLIC CHEMISTRY

In this review, it is assumed that the reader is familiar with the general experimental techniques used in ^{13}C NMR spectroscopy which have been reviewed previously (*117*, *135*, *171*, *186*, *214*). However, some techniques have appeared since the publication of these reviews and are of use in organometallic chemistry.

The assignment of ^{13}C NMR resonances can be difficult. In order to maximize sensitivity, it is usual to measure ^{13}C NMR spectra with complete proton decoupling. The proton coupling may be retained with some increase in sensitivity by the use of "off-center" double resonance

(*216*). From the multiplicity of the pattern observed it is possible to determine the number of protons attached to each carbon atom. Thus a carbon atom with one proton attached appears as a doublet, but the separation is less than $^1J(^{13}C—^1H)$ on account of the perturbation caused by the ^{1}H irradiation. This technique is often of considerable assistance in assigning ^{13}C NMR signals. However, instances can arise where carbon atoms are attached to the same number of protons and their signals are unassignable. In many cases the ^{1}H NMR spectra of such compounds are completely analyzable, and then the ^{13}C NMR resonances may be assigned by identifying the hydrogen to which each carbon is attached in the ^{1}H NMR spectrum. This is done by use of "off-center" double resonance at several places in the ^{1}H NMR spectrum and plotting the "^{13}C chemical shift" of each line against the ^{1}H irradiating frequency. It is found that the points form lines intersecting at the ^{13}C chemical shift and ^{1}H chemical shift of the proton attached to that particular carbon (*19*, *75a*). This technique has been applied to [Mo(CO)$_3$(π-cycloheptatriene)] where there are three ^{13}C resonances assignable to the carbon atoms bearing one hydrogen atom each and the ^{1}H NMR spectrum is completely assignable (*15*, *161*).

The sign of coupling constants can in favorable cases be determined by "spin-tickling" experiments which have been described elsewhere (*111*, *122*). Such techniques are difficult to apply when part of the spectrum is extremely complex, as for the ^{1}H NMR spectrum of PPh$_3$. However, by the use of selective ^{1}H decoupling and observing the ^{13}C NMR spectrum of PPh$_3$, it was possible to show that $^1J(^{31}P—^{13}C) = -12.51$ Hz, $^2J(^{31}P—^{13}C) = +19.65$ Hz, and $^3J(^{31}P—^{13}C) = +6.80$ Hz (*31*, *32*, *208*). In principle, this technique can be extended to most organometallic derivatives to determine the relative signs of metal–carbon coupling constants.

There are two problems which are common in organometallic ^{13}C NMR spectroscopy.

(a) Long spin–lattice relaxation times, T_1, are usually found for carbon atoms with no protons attached, e.g., metal carbonyls or metal isocyanides (*212*). As a consequence, signals due to these ^{13}C nuclei are very easily saturated when observed in the continuous wave mode or take a long time to recover when observed by Fourier transform spectroscopy, and the signals are therefore difficult to detect. This difficulty can be removed by the addition of a paramagnetic compound to reduce the length of T_1 (*10*). For example, addition of $\sim 0.2\,M$ [Cr(acac)$_3$] to [Fe(CO)$_5$] causes a 40-fold increase in the strength of the ^{13}CO signal with no detectable contact shift (*91*). The addition of a paramagnetic compound will remove the nuclear Overhauser effect, reducing the intensity of the signals due to carbon atoms with hydrogen atoms attached, but will cause all signals to be true in intensity to the number of carbon atoms giving rise to each signal (*88*, *126*, *127*, *134a*).

(b) For a number of metals, nuclei with a nuclear spin quantum number, I, greater than $\frac{1}{2}$ are in 100% or nearly 100% abundance. This has already caused problems in the observation of ^{13}C NMR spectra of complexes of manganese and cobalt (*24*, *65*, *80*, *91*, *129*). Both these elements have 100% abundant nuclei with $I > \frac{1}{2}$ (^{55}Mn, $I = \frac{5}{2}$; ^{59}Co, $I = \frac{7}{2}$). The metal nuclei will couple to ^{13}C nuclei attached to them to produce six (for ^{55}Mn) or eight (for ^{59}Co) lines of equal intensity. This coupling may be partially or completely removed by relaxation of the metal nucleus resulting from interaction of the nuclear quadrupole with electric-field gradients. For manganese and cobalt, it would appear that such effects normally produce broad carbonyl resonances, but signals due to the cyclopentadienyl group attached to manganese are sharp (*91*). In theory, this broadening, and consequent difficulty to detect a signal, could also apply to organometallic derivatives of the following elements, although for all elements in parentheses satisfactory ^{13}C NMR spectra have been reported for their organometallic derivatives: (lithium), beryllium, (boron), (sodium), aluminum, potassium, scandium, vanadium, copper, gallium, (arsenic), rubidium, niobium, indium, (antimony), cesium, lanthanum, tantalum, rhenium, (iridium), gold, and (bismuth).

There are several ways in which these difficulties can, in principle, be reduced, eliminated, or taken advantage of, but as yet no reports have appeared of the application of any of these methods to ^{13}C NMR spectra of organometallic compounds.

(a) The signal-to-noise ratio of a digitized weak signal can often be improved by mathematical treatment with a consequential loss in resolution (77). This loss in resolution is a minor problem when the resonance is already broad.

(b) If there is a good signal-to-noise ratio, and the ^{13}C NMR signal shows badly resolved fine structure, then the resolution can be improved at the expense of the signal-to-noise ratio by the reverse of the method described in the preceding section (a) (77).

Programs to perform these mathematical treatments are normally included in the standard software package for a Fourier transform computer system.

(c) Decoupling the metal nucleus should provide sharp ^{13}C resonances.

(d) On cooling, relaxation of quadrupolar nuclei becomes faster (*8*). Thus, in principle, ^{13}C resonances broadened by coupling to a quadrupolar nucleus may be sharpened by cooling the sample or resolved into its individual components to give $^{1}J(M—^{13}C)$ by heating the sample. Alternatively, the viscosity of the solution may be raised to increase the relaxation rate of the quadrupolar nuclei.

(e) From a complete line shape analysis of the broad line it is possible to determine $^{1}J(M—^{13}C)$ (*184*, *215*). When the line width is insufficient to determine $^{1}J(M—^{13}C)$ by complete line shape analysis, the Carr-Purcell spin-echo pulse train may be used, with various pulse repetition times (*20*).

The marked dependence of $^{2}J(^{31}P—M—^{31}P)$ on stereochemistry for complexes of the platinum group metals has been used in ^{1}H NMR spectroscopy for several years (*109*, *115*). For methyl or *tert*-butyl tertiary phosphines, when the two phosphines are mutually trans then a triplet pattern results, but if the two phosphines are mutually cis, then a doublet pattern results as a consequence of the spectrum being of the $AA'X_nX'_n$ type and the dependence of $^{2}J(^{31}P—M—^{31}P)$ on stereochemistry. Exactly the same behavior is found in ^{13}C NMR spectroscopy with the advantage that the technique is far more versatile and is not normally troubled by resolution problems. Thus for *mer*-$[RhCl_3(CO)(PBu^n{}_2Ph)_2]$ triplet patterns have been observed for six of the eight different carbon atoms in the tertiary phosphine ligand (*164*). When $^{2}J(^{31}P—M—^{31}P)$ is small (<100 Hz) it is possible to determine this parameter from the ^{13}C NMR spectrum (*16*, *17*, *161*).

During recent years, with the introduction of complete ^{1}H decoupling, tetramethylsilane has been commonly accepted as the internal ^{13}C NMR reference, and the direction of increasing frequency (decreasing magnetic field) is taken as being positive (*5*, *134*, *230*). Literature results, quoted with respect to other reference compounds, have been re-referenced to T.M.S. using Eqs. (1–3)

$$\delta(\mathrm{TMS}) = \delta(\mathrm{CS_2\ internal}) + 192.8 \tag{1}$$

$$\delta(\mathrm{TMS}) = \delta(\mathrm{C_6H_6}) + 128.5 \tag{2}$$

$$\delta(\mathrm{TMS}) = \delta(\mathrm{CH_3{}^{13}CO_2H}) + 178.3 \tag{3}$$

bearing in mind that most early publications had the reverse sign convention, i.e., that increasing magnetic field was taken as being positive.

III

^{13}C CHEMICAL SHIFTS OF σ-BONDED CARBON ATOMS

There have been a number of theoretical treatments of ^{13}C chemical shifts (*43*, *64*, *72*, *167*). Normally three factors are thought to affect ^{13}C chemical shifts: a diamagnetic shielding term, a paramagnetic shielding term, and a term containing the contributions from anisotropy in the magnetic susceptibility of neighboring atoms or groups. Often, the paramagnetic shielding term is considered to be dominant for ^{13}C chemical shifts. However, for transition metal hydrides, it is known that anisotropy in the magnetic susceptibility of the transition metal is important producing shifts of up to 50 ppm (*30*, *137*, *168*, *213*). Thus anisotropic contributions from transition metals to ^{13}C chemical shifts cannot be neglected *a priori*. Indeed it has recently been suggested that this term may be important in most ^{13}C chemical shifts (*52b*, *167*).

The ^{13}C chemical shifts of each major group of compounds will be discussed in turn.

A. *Methyl Compounds*

Correlations in ^{13}C chemical shifts found for methyl derivatives of organic compounds may apply to organometallic compounds. There is a poor linear relationship between the electronegativity, E, of the substituent, X, and the ^{13}C chemical shift for Me_nX (*209*). A similar poor linear relationship is found for Et_nX. The deviations were attributed to near-neighbor magnetic anisotropy. This linear relationship can be considerably improved by including the number of lone pairs, m, on the substituent, X (*29*); see Eq. (4).

$$\delta(Me_nX) = -105.5 + 55E - 13m \qquad (4)$$

Use of Eq. (4) predicts an electronegativity of 1.76 for the $Ir(PEt_3)_3$ moiety in *fac*-$[IrMe_3(PEt_3)_3]$, which is not too unreasonable. A similar equation has been found for ethyl derivatives. It has recently been suggested that it is best to make a diamagnetic correction before making any such plot (*167*). The corrected shift increases across the period of the ligand X, but also increases down the group of the ligand. CNDO/2 calculations have been performed on a number of methyl derivatives of the type Me_nX including [Me_4Si]. The ^{13}C chemical shifts were found to agree quite well with the calculated paramagnetic shielding term (*189*).

There have been numerous reports of the ^{13}C chemical shifts of methyl groups attached to metals and metalloids (see Tables I to III; all tables are collected at the end of this chapter, see pp. 166–206), but very few discussions of the chemical shift data. The ^{13}C chemical shifts of some siloxanes have been discussed in terms of changes in the paramagnetic term (*76*). The ^{13}C chemical shifts of [$Me_nSn(SMe)_{4-n}$] have also been discussed (*218*). As *n* increases the methyl–tin, ^{13}C chemical shift moves to low field, but it was concluded from the behavior of the ^{119}Sn chemical shifts that the electron-withdrawing capacity of the SMe group(s) does not play the most important role in the variation of the chemical shifts of the ^{13}C nuclei.

The use of the *O*-trimethylsilyl group in conformational analysis and in ^{13}C NMR spectroscopy has also been described (*198*).

In addition to the data listed in Tables I to III, ^{13}C chemical shifts have been reported for methyl groups attached to phosphorus (*27*, *39*, *80a*, *98*, *99*, *100a*, *101*, *147*, *160*, *169*, *188a*, *197a*, *225a*).

B. Phenyl Compounds

A number of workers have reported the ^{13}C NMR spectra of monosubstituted phenyl groups and correlated the shifts with molecular parameters. It has been shown for organic compounds that the chemical shift of the *para*-carbon in monosubstituted benzenes is linearly related to the total π-electron density at the para position in these compounds. Also the shift separation of the *meta*- and *para*-carbons appears to be linearly related to the π-electron density on the *para*-carbon due to resonance interaction with the substituent (*49*, *156*). Spiesecke and Schneider have reported a good linear relationship between the *para*-carbon chemical shift of monosubstituted benzenes and the Hammett σ-para constant, but no such relationship appears to exist for the other carbon chemical shifts, except between the ^{13}C chemical shift for the substituted carbon atom (corrected for magnetic anisotropy effects of the substituent) and the electronegativity of the substituent (*210*).

Recently Nelson *et al.* have shown that the ^{13}C chemical shifts of the carbon atoms of monosubstituted phenyl rings are proportional to the CNDO/2 calculated total charge densities (*178*). It was concluded that it is possible to estimate the total charge density at the *meta*- or *para*-carbon atoms for a monosubstituted benzene to ±0.005 charge unit simply by measuring the ^{13}C NMR spectrum. A similar, but less accurate linear relationship exists for all the carbons in the phenyl ring. There is also a linear relationship between the ^{13}C chemical shift for the para position and the Hammett σ value for the substituent. This linear relationship has previously been reported for phenylphosphorus derivatives (*193*).

It is therefore possible to derive a considerable amount of information about the electron distribution in phenyl rings by ^{13}C NMR spectroscopy. As yet there is only a little information on the ^{13}C NMR shifts of phenyl groups attached to metals and metalloids and this is given in Table IV.

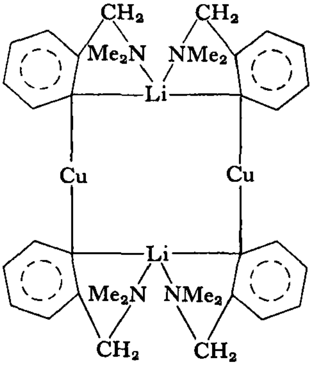
In addition to the data given in Table IV, ^{13}C chemical shifts have also been reported for a number of phenyl derivatives of phosphorus (*31*, *32*, *100a*, *101*, *113*, *160*, *188a*, *193*, *225a*).

C. Organolithium Compounds

The ^{13}C NMR spectra of organolithium derivatives have received considerable attention. At $-60°C$, the ^{7}Li NMR spectrum of 57% ^{13}C-enriched methyllithium shows a pattern due to lithium–carbon coupling which can only readily be explained in terms of a tetramer $[LiMe]_4$ with three methyl groups attached to each lithium. The ^{13}C chemical shift of the methyl group determined by INDOR is -16 ppm in tetrahydrofuran. It was concluded that the shift is due to 0.1 electrons on each methyl group and the bond is predominantly covalent (*151*, *152*). A similar result is found for $[(Me_3{}^{13}C)Li]_4$ and $^{1}J(^{13}C—^{7}Li)$ was observed even at $+80°C$. However, for $[(Pr^{13}CH_2)Li]_4$, $^{1}J(^{13}C—^{7}Li)$ was only observed at $-70°C$ in ether. As for methyllithium, it was concluded that for *n*- and *tert*-butyllithium, there is substantial covalent bonding (*150*).

It had been concluded from ^{13}C NMR measurements on $[Ph_nCH_{3-n}Li]$ ($n = 1, 2, 3$) that the carbon attached to lithium is essentially sp^2-hybridized in tetrahydrofuran solution (*222*). However, this conclusion in the case of benzyllithium was later revised and it was then concluded that the CH_2 carbon is essentially sp^3-hybridized (*223*).

^{13}C NMR spectroscopy has been used to give weight to the suggestion of five-coordinate carbon in (I). The metallated carbon is at 168.1 ppm and shows ^{7}Li coupling, while [o-$Me_2NCH_2C_6H_4Cu$] has the ^{13}C NMR signal at 157.1 ppm (*220*).



(I)

D. *Carbene Compounds*

The large low-field chemical shifts of 362.3 to 253.7 ppm found for metal–carbene complexes are in the region where signals due to carbonium ions are found (*80*, *123*) (see Table V). This has led to the suggestion that the carbene carbon is very electron deficient, and even best described as a carbonium ion (*45*, *80*). As a consequence the ^{13}C chemical shifts have been interpreted in terms of charge on the carbene carbon atom. Hence as [$(OC)_5WC(OMe)Me$] and [$(OC)_5WC(SMe)Me$] have approximately the same carbene chemical shifts it was concluded that there is an almost equivalent degree of charge transfer in the case of oxygen and sulfur (*123*). In a detailed discussion of the ^{13}C chemical shifts of carbene carbon atoms, it has been suggested that the large low field shift arises from a second-order paramagnetic term on the neighboring metal atom which induces paramagnetic currents on the carbene carbon atom. Consistent with this interpretation, it is interesting to note that the ^{13}C NMR signal of the σ-keto carbon in [$(C_5H_5)Fe(CO)_2$-$COMe$] also appears at very low field, 254.4 ppm (*52a*, *80*). Linear relationships were found between the carbene carbon chemical shift and the metal-to-ligand charge transfer band frequency (*52a*).

E. Carbonyl Chemical Shifts

There have been many reports of the ^{13}C chemical shifts of metal carbonyls (see Tables VI to X). In spite of the wealth of data available, the factors affecting ^{13}C chemical shifts have not as yet been fully identified.

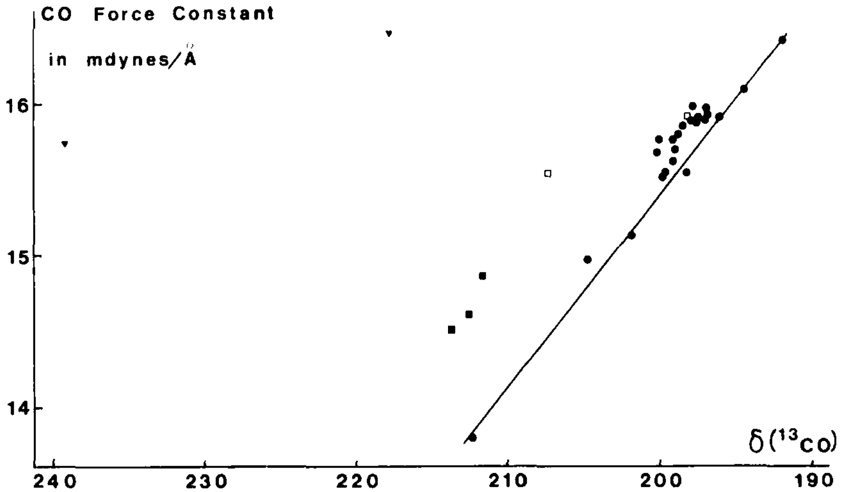


FIG. 1. A plot of the ^{13}C chemical shift, δ(^{13}CO), against the force constant for the carbonyl group in some tungsten carbonyl compounds. ●, $[W(CO)_{6-n}L_n]$; □, $[W(CO)_5CMe(SMe)]$; ■, $[(arene)WCO)_3]$ or $[(C_7H_8)W(CO)_3]$; and ▼, $[(C_5H_5)W(CO)_3Me]$. [Reproduced with permission from *J. Chem. Soc., Dalton Trans.* 2012 (1973).]

In one of the early reports of the ^{13}C chemical shifts of metal carbonyls it was suggested that there is a rough correlation between the estimated metal–carbon bond orders and carbonyl carbon shieldings (*129*). This suggestion has subsequently been partially justified by the observation of a linear correlation between the ^{13}C chemical shift and the Cotton-Kraihanzel force constant for the complexes $[W(CO)_5L]$ (L = Group Vb donor ligand) (*93*). This linear relationship appears to be more general, with other tungsten complexes falling on this line (see Fig. 1). The small deviations found for the $[(arene)W(CO)_3]$ complexes may be in part due to the approximations inherent in the Cotton-Kraihanzel force constant treatment. Similar linear relationships have subsequently been found for the series of complexes $[Cr(CO)_5L]$, $[Mo(CO)_5L]$, $[(C_5H_5)Fe(CO)_2X]$, and *cis*-$[RuCl_2(CO)_2L_2]$ (*89, 94, 95*). As a consequence of the existence of these linear relationships it has been suggested that for a given metal, changes in M—C—O π-bonding exert a dominant influence on ^{13}C carbonyl chemical shifts (*93*). Linear relationships have also been reported between the carbonyl chemical shifts and Taft inductive (σ_I) parameters and reductive half-wave potentials for $[(C_5H_5)Fe(CO)_2X]$ complexes (*94*).

^{13}C NMR spectroscopy has proved useful in an investigation of ^{13}CO binding to hemoglobin (*170*). Sperm whale myoglobin has only one ^{13}CO signal but all forms of hemoglobin examined (human, mouse, and rabbit) gave two signals of equal intensity due to the different magnetic environments experienced by carbon monoxide bound to α and β subunits.

There has been only two reports of the ^{13}C chemical shift of a bridging carbonyl group in $[(C_5H_5)Fe(CO)_2]_2$ at 275.1 ppm (*90*) and $[(C_5H_5)_2Rh_2(CO)_3]$ at 231.8 ppm (*77a*). These chemical shifts are very different from that normally found in organic chemistry for ketones, e.g., acetone + 204.1 ppm (*112*), and is much closer to the values reported for metal-carbenes (see Table V) and carbonium ions, e.g., $[Me_2C^+OH]$ at 250.3 ppm (*182*).

F. Miscellaneous Compounds

The ^{13}C chemical shifts of some ethyl, vinylic, and acetylide derivatives are given in Table XI. In the case of ethyl groups for Et_nX, an approximately linear relationship was found between the electronegativity of X and both the CH_2 and CH_3 ^{13}C chemical shifts (*209*). Similarly, a linear relationship has been found for $[(PhCH_2)_nX]$ between $\delta(^{13}CH_2)$ and the electronegativity of X, but points due to $[(PhCH_2)_4Ti]$ and $[(PhCH_2)_4Zr]$ fall well off the line (*229a*). These deviations from the linear relationship were ascribed to electronic interactions between the metal and the CH_2 carbon. For vinyl derivatives, rough linear relationships were demonstrated between the ^{13}C chemical shifts of carbon-1 in $M—C^1H{=}C^2H_2$ and the corresponding ^{13}C chemical shifts of the substituted carbon atom in phenyl compounds, and between the ^{13}C chemical shift of carbon-2 and the *ortho*-carbon chemical shifts in phenyl derivatives (*155*). It was therefore suggested that similar inductive, resonance, and neighbor effects occur in both sets of compounds. The ^{13}C chemical shifts of $[Bu^n{}_3GeC{\equiv}CH]$ and $[PhC{\equiv}CSiMe_3]$ were discussed in terms of charge on the carbon atoms (*136*, *194*, *195*). Data were also given for [$HC{\equiv}C{-}OSiMe_3$] (*194*, *195*). ^{13}C NMR spectroscopy has been used to determine the position of deuterium in [$Me_3SnCHMeCHMeCCl_2H$] and [$Me_3SnCHMeEt$] (*200a*).

^{13}C Chemical shifts have been reported for [Me_3CCH_2HgX] (*203*) (see Table XII), σ-allylic derivatives (see Table XIII), σ-cyclopentadienyl derivatives (see Table XIV), and miscellaneous compounds (see Table XV). In the case of fluxional σ-cyclopentadienyl derivatives, it has been shown that ^{13}C chemical shifts can be used to differentiate between fluxional σ-cyclopentadienyl derivatives and π-cyclopentadienyl derivatives (*103*). The ^{13}C NMR spectrum of [$Sb(cyclopropyl)_5$] has only two carbon resonances, showing that the molecule is fluxional (*56*) and the ^{13}C NMR spectrum of the naturally occurring organometallic compound, 5′-deoxyadenosylcobalamin, has been reported (*65*). For a number of norbornane and allylic derivatives of palladium and platinum, a number of linear relationships have been found between ^{13}C chemical shifts of various carbon atoms. It was suggested that a term due to paramagnetic shielding by the metal was dominant (*52b*).

^{13}C NMR chemical shifts have been reported for a number of carboranes (Table XVI). Using revised ^{13}C NMR chemical shift data, it was suggested that there is a relationship between the ^{13}C NMR chemical shift and the carbon coordination number (*217*). It is therefore feasible to use ^{13}C NMR chemical shifts to obtain structural information on carboranes.

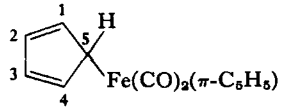
Also, of marginal relevance to this review, the ^{13}C NMR spectra of a number of phosphorus derivatives have been reported (*23*, *27*, *32*, *80a*, *98*, *99*, *100a*, *101*, *113*, *133*, *148*, *160*, *169*, *188a*, *194*, *195*, *197a*, *202b*, *208*, *225a*).

G. Fluxional Molecules

^{13}C NMR spectroscopy is a useful new tool to investigate kinetic problems. Attention has been focused on cyclopentadienyl and related complexes, and in a number of cases thermodynamic parameters have been derived in spite of experimental difficulties. First, in a typical experiment, on increasing the temperature, two or more sharp ^{13}C signals broaden, vanish into the noise, then a broad singlet appears and sharpens. Thus from line shape analysis it is possible to determine rates of exchange near the slow and fast exchange limits, but not in the temperature region of intermediate rate of exchange unless other signals are also affected. Second, a problem which is rarely mentioned, is the accurate measurement of temperature. Most variable temperature units pass a stream of hot or cold gas over a measuring thermocouple and then the sample. The use of a high-power ^1H decoupling field warms the sample and the thermocouple, with the possible introduction of an error.

It has been shown that either $[(C_5H_5)MgCl]$ or $[(MeC_5H_4)MgCl]$ gives rise to only one set of ^{13}C resonances at room temperature but two sets at −67°C which were attributed to $[(RC_5H_5)MgCl]$ and $[(RC_5H_4)Mg(OR')]$ (*84*).

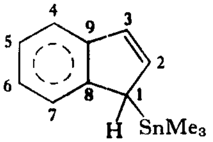
At +52°C, $[(\pi\text{-}C_5H_5)Fe(CO)_2(\sigma\text{-}C_5H_5)]$ has two sharp ^{13}C NMR signals of equal intensity, but on cooling to −78°C the signal due to the σ-cyclopentadienyl group broadens and splits into three resonances (*48*). Analysis of the line shapes showed that the rearrangement pathway for the σ-cyclopentadienyl ring is a series of 1,2-shifts with no contribution from 1,3-shifts. Arrhenius plots gave $E_a = 10.7 \pm 0.5$ kcal/mole and $\log A = 12.6 \pm 0.5$. The value of E_a is a little larger than that determined by ^1H NMR spectroscopy. On further cooling to −88°C the signals due to carbons 1 and 4 broaden, and this was ascribed to hindered rotation about the iron–carbon bond {numbering as in (II)}.



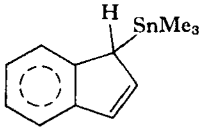
(II)

The variable-temperature ^{13}C NMR spectra of some 5-isomers of $[(C_5H_5)SiMe_nCl_{3-n}]$ ($n = 1, 2,$ or 3), $[(C_5H_5)GeMe_3]$, $[(1\text{-}CH_3C_5H_4)\cdot GeMe_3]$, $[(2\text{-}CH_3C_5H_4)GeMe_3]$, $[(C_5H_5)SnMe_3]$, $[(C_5H_5)HgMe]$, and $[(\pi\text{-}C_5H_5)Fe(CO)_2(\sigma\text{-}C_5H_5)]$ have been observed. Activation parameters were determined for $[(C_5H_5)GeMe_3]$ ($E_a = 10.7 \pm 0.9$ kcal/mole; $\Delta G = 13.4 \pm 0.9$ kcal/mole) and $[(C_5H_5)SnMe_3]$ ($E_a = 6.4 \pm 1.0$ kcal/mole; $\Delta G = 7.2 \pm 1.0$ kcal/mole). For the derivatives of silicon or germanium, the olefinic signals are unsymmetrically broadened by 1,2-shifts at lower migration rates (*102*, *104*). The ^{13}C chemical shift data for a number of σ-cyclopentadienyl groups are given in Table XIV.

Similar variable-temperature ^{13}C NMR spectroscopy has been used to determine $E_a = 13.8 \pm 0.8$ kcal/mole and $\ln A = 11.7 \pm 0.8$ for the 1 to 3 exchange in trimethylstannylindene; see structures (III) and (IV).



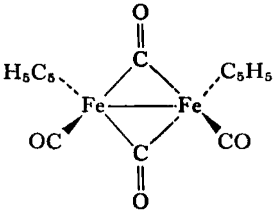
(III)



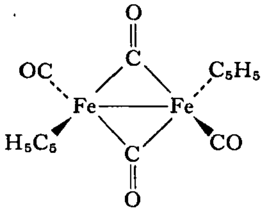
(IV)

These parameters could not readily be obtained by ^1H NMR spectroscopy on account of spin-coupling effects. It is likely that, as the free energy of activation is 8.2 kcal/mole larger than that found for $[(C_5H_5)SnMe_3]$, the tin migration occurs via a 1,2-shift (*200*).

The potentialities of ^{13}C NMR spectroscopy to examine fluxional processes in metal carbonyls has yet to be fully realized. It has been reported that for $[Fe(CO)_5]$, $[Fe(CO)_4(PEt_nPh_{3-n})]$, $[Fe_3(CO)_{12}]$, $[(\text{norbornadiene})Fe(CO)_3]$, $[Fe(CO)_3(Me_2PCH_2CHPMe)]$, and $[(C_5H_5)Mo(CO)_3]_2$ where more than one ^{13}C NMR carbonyl signal should be observed, only one is, in fact, observed (*1*, *24*, *25*, *54*, *90*, *129*). For $[Fe(CO)_5]$ and $[Fe(CO)_4(PEt_nPh_{3-n})]$ the observation of $^1J(^{57}Fe—^{13}C)$ or $^2J(^{31}P—Fe—^{13}C)$ shows that the mechanism of exchange is intramolecular (*159*). In the case of $[(C_5H_5)Fe(CO)_2]_2$ it has been possible to observe both high-temperature fluxional and low-temperature static behavior (*90*). The temperature behavior of the ^{13}C (carbonyl) resonance is shown in Fig. 2. At +55°C only one carbonyl resonance is observed at 243.0 ppm, but on cooling this signal broadens, vanishes (−12°C), and at −59°C three sharp resonances are observed at 275.1, 243.0, and 210.9 ppm. On further cooling, the signal at 243.0 vanishes. $[(C_5H_5)Fe(CO)_2]_2$ exists in solution as a mixture of cis and trans isomers, (V) and (VI). At 55°C there is rapid cis–trans isomerism and interconversion of bridging and terminal carbonyl groups. On cooling to −59°C the cis–trans isomerism and interconversion of bridging and terminal carbonyl groups in the cis isomer become slow. For the trans isomer interconversion of the bridging and terminal



(V)



(VI)

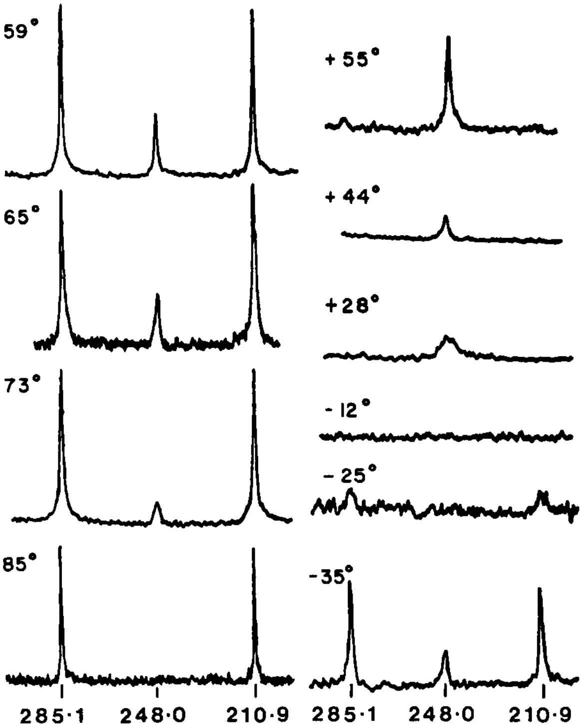


FIG. 2. The variable temperature ^{13}C NMR spectrum of the carbonyl groups of $[Fe(CO)_2(C_5H_5)]_2$. [Reprinted from *J. Amer. Chem. Soc.* **94**, 2551 (1972). Copyright 1972 by the American Chemical Society. Reprinted by permission of the copyright owners.]

carbonyl groups is still fast at −59°C but slows on further cooling. Variable temperature ^{13}C NMR spectroscopy has failed to stop fluxional processes in $[(Bu^tNC)_4Mo(CN)_4]$ (*179a*). Similarly, there is no evidence of ligand inequivalence in the ^{13}C NMR spectrum of $[Co(CNBu^t)_5]^+$ or $[Co(CNMe)_5]^+$, even at −160°C (*171a*).

At 63.2°C, the ^{13}C NMR spectrum of $[Rh_4(CO)_{12}]$ shows a 1:4:6:4:1 quintet (*55*). Thus the molecule must be fluxional. On cooling to 7.5°C the signal broadens and vanishes. At 20°C, the ^{13}C NMR spectrum of $[(C_5H_5)_2Rh_2(CO)_3]$ only shows a triplet for the carbonyl resonance, but on cooling to −80°C, this signal splits into a triplet due to the bridging carbonyl carbon atoms and a doublet due the terminal carbon atoms (*77a*).

At 20°C, the ^{13}C NMR spectrum of $[Os(CO)(NO)(C_2H_4)(PPh_3)_2]$-$[PF_6]$ shows only one ethylene resonance at 49.3 ppm but on cooling to −80°C, two resonances are observed at 54.4 ppm and 43.6 ppm. This behavior provides evidence that the ethylene molecule occupies an in-plane orientation in the *pseudo* octahedral ground state geometry (*116a*).

At room temperature the ^{13}C NMR spectrum of $[(C_8H_8)Fe(CO)_3]$ shows only two signals, one due to the carbonyl groups (*193a*). On cooling to −120°C, the signal due to the cyclooctatetraene ring splits into four, as would be expected from ^1H NMR investigations, but also two carbonyl signals are observed in the ratio 2:1, implying that the carbonyl groups are also static. Line-shape analysis gives different rate constants for the rotation of the cyclooctatetraene ring and the carbonyl groups. It was therefore concluded that the two processes are independent.

H. Relaxation Measurements

The use of relaxation measurements in ^{13}C NMR spectroscopy has been reviewed (*23*, *139a*), but as yet only applied to six examples in organometallic chemistry, namely some chromium carbenes, some substituted ferrocenes, $[Ph_2SiH_2]$, 5′-deoxyadenosylcobalamin, $[Ni(CO)_4]$, and $[Fe(CO)_5]$ (*48a*, *65*, *131*, *143*, *212*). Such measurements can give valuable information on molecular tumbling and rapid internal rotational motions and be useful in assigning resonances (*223a*).

A detailed investigation of the ^{13}C nuclear spin–lattice relation time, T_1, in liquid $[Ni(CO)_4]$ and $[Fe(CO)_5]$ as a function of temperature and resonance frequency has been carried out (*212*). It was concluded that relaxation occurs only by two mechanisms, i.e., spin–rotation interaction and anisotropic chemical shift. It was possible to obtain the anisotropic chemical shift difference of 440 ppm for $[Ni(CO)_4]$ and 408 ppm for $[Fe(CO)_5]$ and the spin–rotation constants. Apparent activation energies for diffusion of 1.0 kcal/mole for $[Ni(CO)_4]$ and 2.9 kcal/mole for $[Fe(CO)_5]$ were derived.

In the case of two monosubstituted ferrocenes, the measurement of carbon-13 spin–lattice relaxation times, T_1, has been used to investigate preferred rotational motion (*143*). The substituent in one ferrocene ring (ring A) "anchors" this ring, causing the correlation time to increase and shorten T_1. The unsubstituted ferrocene ring (ring B) is still free to rotate about its C_5 axis and consequently T_1 for ring B is longer than T_1 for ring A. From the ratio of the measured T_1's it is possible to calculate the ratio of the rotation rates of rings A and B. The results are given in Table XVII. As the ratio of rotation rates is relatively small it was suggested that the energy barrier to independent B ring rotation is very small. Also, from the absolute values of the measured T_1's it was possible to show that the overall tumbling rates for these compounds correspond to molecular correlation times of $\sim 1.5 \times 10^{-11}$ sec.

One experimental difficulty in carrying out such measurements is that paramagnetic species interfere. The absence of interference from paramagnetic species can be shown if the ^{13}C—^{1}H nuclear Overhauser enhancement is close to the theoretical maximum of 2.0.

^{13}C Spin–lattice relaxation times have also been reported for Ph_2SiH_2, namely *ortho*-carbon 5.5 sec, *meta*-carbon 5.5 sec, and *para*-carbon 3 sec. These data were interpreted as showing that there is preferential rotation about the silicon–phenyl bond (*131*).

Spin–lattice relaxation times have been used to assist in the assignment of the ^{13}C NMR spectrum of the naturally occurring organometallic compound, 5′-deoxyadenosylcobalamin (*65*). In the context of assignment of resonances and the determination of unknown structures, spin–lattice times offer information on the number of protons attached to carbons in fused-ring structures and can be used to detect groups that have internal motion.

I. Paramagnetic Compounds

If the complex is paramagnetic, then the ^{13}C chemical shift can occur over a much wider range (see Table XVIII). These large chemical shifts arise from either contact shifts due to delocalization of unpaired electron density from the metal to the ligand or from pseudo contact shifts due to the magnetic field produced by the unpaired electron density. The interpretation of such shifts is generally difficult, but a sensitive criterion for π-delocalization using methyl substituents has been proposed on the basis of theoretical considerations (*66*), namely Eq. (5)

$$\sigma_{\mathrm{con}}^{^{13}\mathrm{CH}} / \sigma_{\mathrm{con}}^{\mathrm{C}^1\mathrm{H}} = -\tfrac{1}{2}(\gamma_{\mathrm{H}}/\gamma_{\mathrm{C}}) \div -2 \tag{5}$$

where $\sigma_{\mathrm{con}}^{^{13}\mathrm{CH}}$ and $\sigma_{\mathrm{con}}^{\mathrm{C}^1\mathrm{H}}$ are the contributions to the ^{13}C and ^{1}H chemical shifts, respectively, of the methyl group due to indirect exchange polarization contact interactions, and γ_{H} and γ_{C} are the gyromagnetic ratios of ^{1}H and ^{13}C nuclei, respectively. For the complexes $[M(C_5H_4Me)_2]$ (M = V, Cr, Co, Ni), this ratio was only found (-2.5) for $[Ni(C_5H_4Me)_2]$, implying that π- delocalization is dominant in this case. However, this mechanism does not explain the upfield ^{13}C resonances found for $[V(C_5H_4R)_2]$ and $[Cr(C_5H_4R)_2]$ (R = H, Me) (*4*, *34*).

IV

^{13}C CHEMICAL SHIFTS OF π-BONDED CARBON ATOMS

^{13}C Chemical shifts have been reported for coordinated π ligands such as olefins, acetylenes, allylic groups, dienes, cyclopentadienyl groups, and arenes. There appear to be two major factors which can cause the chemical shift of the π ligand to move from the shift found for the free ligand.

First, it has been shown that for sp^2 carbon atoms, the ^{13}C chemical shift is proportional to charge on the carbon atom and moves to low frequency (high field) with increasing charge (*125*, *211*). The gradient is 167.8 ppm per electron. This approach has been used to totally account for the ^{13}C chemical shift in $[(MeC_5H_4)MgCl]$ where the reasonable charge distribution of $[MeC_5H_4]^{0.75-}[MgCl]^{0.75+}$ is calculated. Using this approach charge distributions of $[C_6H_6]^{0.92-}[Cr(CO)_3]^{0.92+}$, $[C_3H_5]^{1.0-}Pd^{2.1+}[C_5H_5]^{1.1-}$, $[C_5H_5]^{1.8-}{}_2Fe^{3.6+}$, and $[(PPh_3)_2Pt]^{1.1+}$-$[C_2H_4]^{1.1-}$ are predicted. It is clear that the charge separation is overestimated, but is in the expected sense. For example, experiments have shown that for $(C_6H_6)_2Cr$, the charge on each benzene ring is 0.55 electron, as opposed to the 0.92 electron calculated from the ^{13}C NMR chemical shifts (*12*).

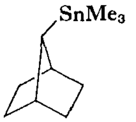
Second, it is known that a methyl group attached to a transition metal has a ^{13}C chemical shift of about 0 ppm (see Table I), while a free sp^2 carbon has a ^{13}C chemical shift of about 130 ppm. It is thus possible to consider that the bonding of a π ligand to a metal converts the hybridization from sp^2 to a position intermediate between sp^2 and sp^3. Consistent with this postulate, it is known that when a π ligand coordinates to a transition metal, the carbon–carbon bond lengthens. For example, in $(C_6H_6)_2Cr$ the carbon–carbon bond length is 1.423 Å as compared to the value of 1.394 Å in free benzene (*40a*, *106*). It is therefore probable that both these mechanisms are operative in producing the shift on coordination of a π ligand.

Each type of π ligand will now be discussed separately.

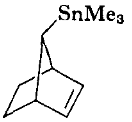
A. Olefin and Acetylene Complexes

A limited quantity of data on olefin and acetylene π complexes have been published (see Table XIX). It will be observed that coordination shifts of between $\sim$30 ppm downfield and 115.2 ppm upfield are found. The magnitude of the olefin coordination shift appears to approximately correspond to the strength of the olefin–metal interaction, with the smallest coordination shifts being found for the weak silver-olefin complexes and the largest coordination shift being found for the very strong rhodium-norbornadiene complex [(norbornadiene)Rh(C_5H_5)] (*21*, *183*). Similarly for the platinum-olefin complexes, the increased carbon shielding correlates with the change in IR stretching frequency of the carbon–carbon double bond (*6*). Factors affecting the ^{13}C chemical shift of a coordinated olefin or acetylene have been discussed, and two explanations were given, one based on a σ-bonding valence-bond style treatment and the other based on a π-bonding molecular orbital style treatment. Both explanations qualitatively explained the shifts.

The ^{13}C chemical shifts of (VII) to (IX) have been measured to investigate the possibility of π-bonding between tin and the olefin. In the norbornadiene derivative only 1.1 ppm separation is found between the two types of olefinic carbon, showing that there is very little or no tin–olefin π-bonding (*119*). ^{13}C NMR spectroscopy has also been used to investigate the interaction of a wide range of olefins with silver(I) (*17a*).



(VII)



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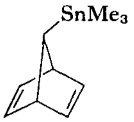
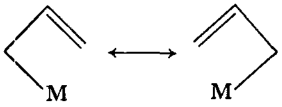


(IX)

B. π-Allylic Complexes

There have been a number of measurements of the ^{13}C NMR spectra of π-allylic ligands attached to transition metals, especially palladium (see Table XX). The ^{13}C chemical shifts of the π-allylic ligands appear to be quite characteristic. Terminal and central carbon atoms have shifts of 45 to 78 ppm, and 90 to 130 ppm, respectively. The ^{13}C chemical shifts of the π-allylpalladium system have been interpreted in terms of a valence-bond structure (*162*, *163*). It is known that the ^{13}C chemical shifts of the σ-2-methylallyl group in $[IrCl_2(CH_2CMe{=}CH_2)(CO)(AsMe_2Ph)_2]$ are 10.6 (Ir—CH_2), 145.2 (—CMe=), and 107.9 ppm (=CH_2). Thus it is possible to explain the shifts of the terminal π-allyl carbons as the average of the σ-bonded carbon and free olefin as predicted by the canonical forms (X) and (XI) but this treatment does not fully explain the ^{13}C chemical shifts, and other contributions, e.g., ionic, are necessary. When $[(C_3H_5)PdCl]_2$ is treated with PPh_3 to yield $[(C_3H_5)PdCl(PPh_3)]$, the ^{13}C chemical shift of the carbon trans to PPh_3 moves to low field, implying a greater olefinic character. This is consistent with the known X-ray structure (*162*, *163*).

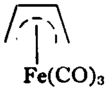


(X) (XI)

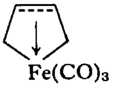
The ^{13}C chemical shifts of $[(1\text{-}MeC_3H_4)NiX]_2$ have also been reported and interpreted in terms of electron density on the π-allylic ligand (*47*). As part of an investigation of the structure of $Ru_3H(CO)_9C_6H_9$ which contains an allylic group, the ^{13}C NMR spectrum was measured (*78*).

C. Diene and Related Complexes

At present ^{13}C NMR chemical shift data are only available for three diene complexes, $[(C_4H_4)Fe(CO)_3]$, $[(C_4H_6)Fe(CO)_3]$, and $[(C_{13}H_{27}CH{=}CH{-}CH{=}CHCO_2Me)Fe(CO)_3]$ (see Table XXI). For the butadiene derivative (*188*, *192*), it was felt that the ^{13}C chemical shift and coupling constant data are more consistent with (XII) rather than (XIII).



(XII)



(XIII)

^{13}C NMR data have also been reported for $[(C_8H_8)Fe(CO)_3]$, $[\{C(\overset{\cdots}{-}CH_2)_3\}Fe(CO)_3]$, and $[\{C(\overset{\cdots}{-}CH_2)_2(\overset{\cdots}{-}CHCH{=}CH_2)\}Fe(CO)_3]$ (see Table XXI) (*18*, *75*, *193a*).

D. π-Cyclopentadienyl Complexes

Of all the π ligands, there is the most ^{13}C NMR shift information available for the π-cyclopentadienyl ligand (see Tables XXII and XXIII) with chemical shifts covering the range of 68.2 to 121.3 ppm. A linear relationship between the ^{1}H and ^{13}C chemical shifts of the π-cyclopentadienyl ligand has been reported (*129*). This linear relationship appears to be far more extensive, with many organic and organometallic compounds falling on or near the line. There is considerable information available on the chemical shifts of the π-cyclopentadienyl ligand in the complexes $(C_5H_5)Fe(CO)_2X$, but attempts to correlate the ^{13}C NMR chemical shifts with parameters such as the CO force constant or Taft parameters failed (*94*).

Data have also been reported for a number of substituted π-cyclopentadienyl ligands (see Table XXIV). In the case of the magnesium complexes, a linear correlation between ^{13}C chemical shift and charge density was used to calculate the charge density on the cyclopentadienyl ring (*84*, *125*, *211*). The results conflicted with the charge density calculated by Hückel molecular orbital theory, and it was felt that the charge density calculated from ^{13}C NMR data is more reliable. On this basis, ferrocene has approximately the charge distribution $[C_5H_5]^{1.8-}{}_2Fe^{3.6+}$!

E. π-Arene and π-Cycloheptatriene Complexes

At present, there are only ^{13}C NMR data available for π-arene and π-cycloheptatriene complexes of chromium, molybdenum, and tungsten (*80*, *158*, *161*) (see Table XXV). The ^{13}C chemical shifts of the complexed arene were interpreted in terms of the mobile bond order at each carbon atom (*2*). It was possible to account for the ^{13}C chemical shifts by postulating a reduction in the mobile bond order from 1.0 in the arene to ~0.65 in the complex, in agreement with known bond length.

V

^{13}C COUPLING CONSTANTS

In the preceding sections the ^{13}C chemical shifts of carbon atoms attached to metals have been reported, but in no case has anything more than a qualitative interpretation of the chemical shift been given. Coupling constants are generally more readily calculated (*174*). It has been shown that J_{XC} can be divided into three components (*190*), Eq. (6),

$$J_{XC} = J_{XC}^{(1)} + J_{XC}^{(2)} + J_{XC}^{(3)} \qquad (6)$$

where $J_{XC}^{(1)}$ is the orbital term which is zero unless there is multiple bonding between X and C, $J_{XC}^{(2)}$ is the spin-dipolar term which is generally less than 10% of J_{XC}, and $J_{XC}^{(3)}$ is the Fermi contact term which is normally considered to be dominant (*114*). There have been few molecular orbital calculations of the Fermi contact term for organometallic compounds. $^1J(^{13}C—^1H)$ and $^2J(^{119}Hg—C—^1H)$ have been calculated for a number of compounds of the type CH_3HgX and, after allowance for the effect of nuclear charge, the agreement between theory and experiment is quite good (*110*). It therefore may be valid to use the Fermi contact term in the interpretation of ^{13}C coupling constants of organometallic compounds.

A. *Direct Metal–Carbon Coupling Constants*

Direct coupling constants have been measured between carbon and the following metals or metalloids: ^7Li, ^{11}B, ^{29}Si, ^{31}P, ^{51}V, ^{57}Fe, ^{59}Co, ^{73}Ge, ^{77}Se, ^{95}Mo, ^{103}Rh, ^{111}Cd, ^{113}Cd, ^{117}Sn, ^{119}Sn, ^{125}Te, ^{183}W, ^{195}Pt, ^{199}Hg, and ^{207}Pb, and values of $^1J(M—^{13}C)$ are given in Tables XXVI to XXIX. In addition there are a number of metal nuclei with $I = \frac{1}{2}$ for which $^1J(M—^{13}C)$ has not yet been reported, presumably due to problems of sensitivity and/or exchange: ^{89}Y (100% abundant), ^{107}Ag (51.82%), ^{109}Ag (48.18%), ^{115}Sn (0.35%), ^{123}Te (0.87%), ^{187}Os (1.64%), ^{203}Tl (29.50%), and ^{205}Tl (70.50%). It can also be anticipated that in the near future $^1J(M—^{13}C)$ will be measured either directly or indirectly for a number of quadrupolar metal nuclei, e.g., ^9Be, ^{27}Al, ^{55}Mn, ^{69}Ga, ^{71}Ga, ^{75}As, and ^{93}Nb.

A molecular orbital expression for the contact contribution to the spin–spin coupling between directly bonded nuclei is given by Eq. (7)

$$\begin{aligned} ^1J(M—^{13}C) &= -\tfrac{64}{9}\beta^2\gamma_M\gamma_C h \sum_i^{\text{occ}} \sum_j^{\text{unocc}} (^3\Delta E_{i\to j})^{-1} \\ &\quad \times (\psi_i|\delta(r_M)|\psi_j)(\psi_j|\delta(r_C)|\psi_i) \end{aligned} \qquad (7)$$

where β is the Bohr magneton, γ is the magnetogyric ratio, and $^3\Delta E_{i\to j}$ is the triplet excitation energy between the occupied molecular orbital ψ_i and the unoccupied molecular orbital ψ_j (*185*). This expression has so far proved too complex to apply to organometallic systems. However, using LCAO approximations and only the one-center integrals involving s orbitals on the two atoms, a value of ${}^1J({}^{29}\mathrm{Si}—{}^{13}\mathrm{C}) = -7.77$ Hz has been calculated for [MeSiHCl$_2$] as compared to the observed value of -66 Hz (*57*, *143*). Most of the other calculated coupling constants involving mainly coupling to hydrogen or fluorine were in good agreement with experiment.

The additional approximation of introducing a mean triplet excitation energy, ΔE, leads to the well-known simplified Fermi contact equation, Eq. (8),

$$\begin{aligned} {}^1J(\mathrm{M}—{}^{13}\mathrm{C}) &= -\gamma_\mathrm{M}\gamma_\mathrm{C}\frac{\hbar}{2\pi}\frac{256\pi^2}{9}\beta^2\langle \mathrm{S_M}(0)\rangle^2 \\ &\quad \times \langle \mathrm{S_C}(0)\rangle^2\alpha_\mathrm{M}{}^2\alpha_\mathrm{C}{}^2/\Delta E \end{aligned} \tag{8}$$

where $\alpha_\mathrm{C}{}^2$ and $\alpha_\mathrm{M}{}^2$ are the s-electron densities in the bonding orbital of carbon and the metal, respectively, and $\langle \mathrm{S_C}(0)\rangle^2$ and $\langle \mathrm{S_M}(0)\rangle^2$ are the valence s-electron densities.

In view of the approximations made in deriving Eq. (8), this equation can only be considered at best as semiquantitative. Using a more sophisticated version of this equation, ${}^1J(\mathrm{M}—{}^{13}\mathrm{C})$ has been calculated for [MMe$_4$] (M = ^{13}C, ^{29}Si, ^{73}Ge, ^{119}Sn, ^{207}Pb) (*60*).

With the additional assumption (*121*, *206*) in Eq. (9)

$$\langle S_\mathrm{M}(0)\rangle^2 \propto \left(\frac{Z_\mathrm{M}^*}{n_\mathrm{M}}\right)^3 \tag{9}$$

where Z_M^* is the effective nuclear charge of the s orbital used by the metal atom in forming the carbon–metal bond and n_M is the principal quantum number of that orbital, ${}^1J(\mathrm{M}—{}^{13}\mathrm{C})$ for the complexes [M(CH$_3$)$_4$] can be related to ${}^1J({}^{13}\mathrm{C}—{}^{13}\mathrm{C})$ by Eq. (10).

$${}^1J(\mathrm{M}—{}^{13}\mathrm{C}) = \left(\frac{\alpha_\mathrm{MC}{}^2}{\alpha_\mathrm{CC}{}^2}\right)\left(\frac{\Delta E_\mathrm{C}}{\Delta E_\mathrm{M}}\right)\left(\frac{Z_\mathrm{M}^*}{Z_\mathrm{C}^*}\right)^3\left(\frac{n_\mathrm{C}}{n_\mathrm{M}}\right)^3\left(\frac{\gamma_\mathrm{M}}{\gamma_\mathrm{C}}\right){}^1J({}^{13}\mathrm{C}—{}^{13}\mathrm{C}) \tag{10}$$

[Erroneously, $(n_\mathrm{C}/n_\mathrm{M})$ was inverted in the text, but in the calculations the correct equation was used (*226*).] The fractional s character of the carbon orbital forming the carbon–metal bond is given by α_{MC}^2 and γ is the magnetogyric ratio of the central atom; α_{MC}^2 was calculated using the empirical relationships given in Eqs. (11) and (12).

$$^1J(^{13}C—^1H) = 500\,\alpha_{CH}^2 \tag{11}$$

$$\alpha_{MC}^2 = 1 - 3\,\alpha_{CH}^2 \tag{12}$$

Z_M^* can be estimated from ^2J(M—C—H), atomic beam experiments, optical hyperfine splittings, a formula due to Goldsmit, or Hartree-Fock calculations, with the value obtained from ^2J(M—C—H) being preferred (*96*, *207*). ΔE is assumed to be invariant. Using these figures it is possible to calculate $^1J(M—^{13}C)$ for [MMe_4] (M = Si, Ge, Sn, and Pb) to within 10% of the observed value. The calculated value for $^1J(^{73}Ge—^{13}C)$ is different from that previously reported, presumably due to the erroneous use of the magnetic moment instead of the magnetogyric ratio in Eq. (10).

Instead of using Eq. (10), it has been modified in two ways. First, in order to use published values of Z_M^* a relativistic correction, K_M, has to be introduced. Second, to allow for coordination at the central metal atom being different from tetrahedral a term α_M^2/α_C^2 is introduced where α_M^2 is the fractional *s* character of the metal orbital forming the carbon–metal bond, i.e., Eq. (13).

$$^1J(M—^{13}C) = \left(\frac{\alpha_M^2}{\alpha_C^2}\right)\left(\frac{\alpha_{MC}^2}{\alpha_{CC}^2}\right)\left(\frac{\Delta E_C}{\Delta E_M}\right)\left(\frac{Z_M^*}{Z_C^*}\right)^3\left(\frac{n_C}{n_M}\right)^3 \times \left(\frac{\gamma_M}{\gamma_C}\right)\left(\frac{K_M}{K_C}\right){}^1J(^{13}C—^{13}C) \tag{13}$$

The results are given in Table XXX. In all cases reasonable agreement is found with experimental results, and predicted values are given for [$AlMe_4$]$^-$, [$Mn(CO)_6$]$^+$, [$Fe(CO)_4$]$^{2-}$, [$Os(CO)_5$], and [$TlMe_3$]. It is amazing in view of the number of approximations made that the agreement is so good.

For a number of methyl-tin complexes, it has been shown that a linear relationship exists between $^1J(^{119}Sn—^{13}C)$ and $^2J(^{119}Sn—C—^1H)$ (see Fig. 3) (*141*, *146*). It is important to note the nonzero intercept. By making approximations similar to those involved in deriving Eq. (8) to derive an analogous equation for $^2J(M—C—^1H)$ it can be shown that a plot of $^1J(^{119}Sn—^{13}C)$ against $^2J(^{119}Sn—C—^1H)$ should pass through the

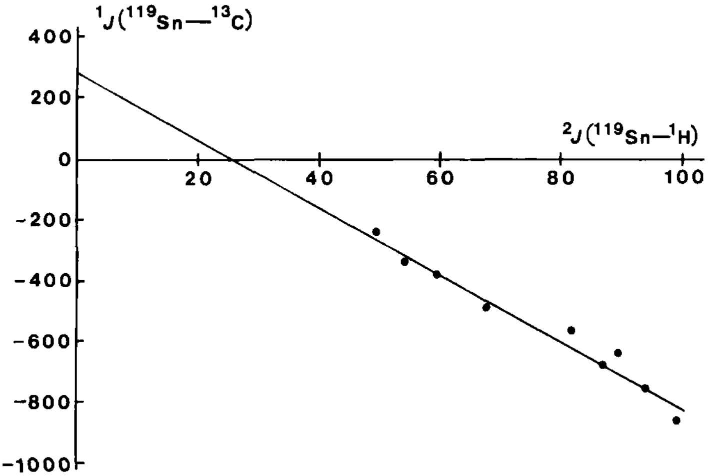


FIG. 3. A plot of $^1J(^{119}Sn-^{13}C)$ against $^2J(^{119}Sn-^1H)$ for some methyl tin complexes. [Reproduced with permission from *J. Chem. Soc.*, *A* 528 (1967).]

origin. Thus for the methyl-tin system these approximations are not valid. However, for methyl-platinum complexes, two linear relationships of this type appear to exist, with complexes of the types *trans*-[PtMeCl-$(AsMe_3)_2$] and *trans*-$[PtMeL(AsMe_3)_2]^+[PF_6]^-$ [L = CO, CNMe, C(OMe)Me, NCC_6F_5] falling on one line and complexes of the types *cis*-$[PtMe_2Q_2]$ and *fac*-$[PtMe_3XQ_2]$ (Q = $AsMe_3$, $AsMe_2Ph$, PMe_2Ph; X = Me, Cl, Br, I) falling on the other line (*41*, *42*, *45*, *46*). The second line can be drawn so as to pass through the origin (see Fig. 4). Examination of the more limited data for methyl- and neopentyl-mercury compounds indicates that a similar relationship exists (*154*, *203*, *226*). By the use of such relationships it is possible to estimate $^1J(M—^{13}CH_3)$ from the more readily measured $^2J(M—C—^1H)$.

There have been a number of attempts to correlate the magnitude of $^1J(M—^{13}CH_3)$ with bond strength and trans effect. For the pair of complexes *cis*-$[PtMe_2(EMe_2Ph)_2]$ (E = P, As) it is found that both ν(Pt—C) and $^1J(^{195}Pt—^{13}C)$ increase on going from E = P to E = As, and it was suggested that this was due to greater platinum–carbon bond strength when E = As (*41*). Subsequently, the magnitude of $^1J(^{195}Pt—^{13}C)$ and $^2J(^{195}Pt—C—^1H)$ was taken to reflect the hybridization of platinum and the nature of the trans ligand (*45*). A similar behavior is found for $^1J(^{183}W—^{13}C)$ (*93*, *158*, *161*). Values are given in Tables

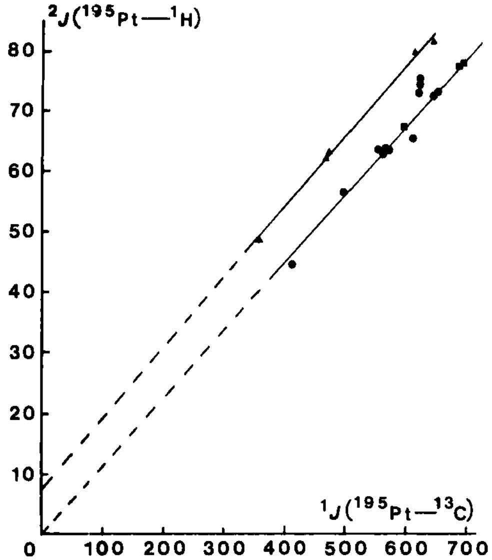
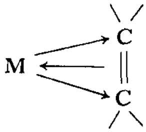


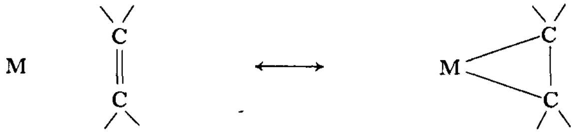
FIG. 4. A plot of $^1J(^{195}Pt-^{13}C)$ against $^2J(^{195}Pt-^1H)$ for some methyl-platinum complexes: ▲, *trans*-[PtMeX(AsMe$_3$)$_2$] and *trans*-[PtMeL(AsMe$_3$)$_2$]$^+$[PF$_6$]$^-$; ■. *cis*-[PtMe$_2$L$_2$]; and ●, [*fac*-PtMe$_3$XL$_2$].

XXVIII and XXIX. It will also be noticed that for the complexes *fac*-[PtMe$_3$X(AsMe$_2$Ph)$_2$] there is also a small cis influence on $^1J(^{195}Pt—^{13}C)$.

$^1J(M—^{13}C)$ has also been reported for olefins and acetylenes π-bonded to rhodium and to platinum (*6*, *21*, *46*, *87*). In the case of rhodium, $^1J(^{103}Rh—^{13}C)$ is between 10 and 16 Hz for a π-bonded olefin (see Table XXVII), while for the σ-bonded carbon in [(C$_5$H$_5$)Rh(σ-C$_3$H$_5$)(π-C$_3$H$_5$)], $^1J(^{103}Rh—^{13}C)$ is 26 Hz. It was suggested the bonding of the olefin results from a 60% contribution from a *dsp*^{2}-metal orbital and sp^3-carbon orbital (*21*). For the olefins and acetylenes π-bonded to platinum $^1J(^{195}Pt—^{13}C)$ is between 18 and 195 Hz (see Table XXIX) compared to the range of 360 to 1000 Hz reported for carbon σ-bonded to platinum. It was found that $^1J(^{195}Pt—^{13}C)$ is less for a π-bonded acetylene than for a π-bonded ethylene. This was considered as evidence for the Chatt-Dewar-Duncanson molecular orbital model (*39*, *63*) of π-bonding (XIV), rather than the formally equivalent valence-bond treatment, (XV) and (XVI) (*46*). However, no allowance appears to have been made for the effect on the hybridization at the carbon of the pseudo-cyclopropane structure proposed in the valence-bond treatment. It is



(XIV)



(XV) (XVI)

known that for neopentane $^1J(^{13}C—^{13}C)$ is 36.2 Hz (*226*) while for cyclopropyl bromide $^1J(^{13}C—^{13}C)$ is 13.3 Hz (*224*). In the case of the cyclopropyl bromide a consistent explanation was given in terms of the percent *s*-characters of the carbon hybrid orbitals. Recently, variations in $^1J(^{119}Sn—^{13}C)$ and $^1J(^{183}W—^{13}C)$ have been discussed in terms of the Fermi contact mechanism (*26*, *65a*).

The absence of $^1J(^{13}C—^{29}Si)$ and $^3J(^1H—^{13}C)$ in $[Me_3Si^{13}CN]$ has been taken as evidence of cyanide exchange (*22*). Direct metal–carbon coupling constants have also been reported for $[W(CO)_5L]$ (*93*), $[Me_3Sn(\sigma\text{-}C_5H_5)]$ (*104*) (to the fluxional C_5H_5 of 19 Hz), and a number of phosphorus compounds (*1a*, *16*, *17*, *27*, *31*, *32*, *41*, *70*, *80a*, *81*, *92*, *98*, *99*, *100a*, *101*, *113*, *140*, *147*, *148*, *160*, *169*, *188a*, *197a*, *202b*, *208*).

B. *Indirect Coupling Constants*

There have been a number of reports of indirect coupling constants to carbon in organometallic compounds (see Tables XXXI and XXXII). Several trends are discernible. For transition metal complexes, the trends in $^2J(^{13}C—M—^{31}P)$ and $^2J(^{13}C—M—^1H)$ appear to follow those observed for $^2J(^{31}P—M—^1H)$ and $^2J(^{31}P—M—^{31}P)$. For complexes of ruthenium, osmium, rhodium, iridium, palladium, and platinum, it is generally found that $^2J(A—M—B)$ (A, B = ^{13}C, ^{31}P, ^{1}H) is large when A and B are mutually trans and is small when A and B are mutually cis; and for derivatives of $[M(CO)_6]$ (M = Cr, Mo, W) and $[Fe(CO)_5]$, ^2J (A—M—B) is generally small for both cis and trans coupling (*17*, *82*, *116*, *179*, *180*). In the case of $^2J(^{31}P—M—^{31}P)$ this behavior of the coupling constants has been qualitatively interpreted using the molecular orbital treatment due to Pople and Santry (*17*, *179*, *185*). It should be equally valid to apply this treatment to coupling constants involving carbon. Equation (10) has been extended with reasonable success to some indirect mercury—carbon coupling constants (*225a*).

The use of ^{13}C coupling to protons is well illustrated in the demonstration of the fluxional behavior of $[(C_5H_5)W(CO)_3H]$ (*79*). Below −70°C, the ^1H NMR hydride signal shows ^{183}W satellites and ^{13}C satellites $^2J(^{13}C—H) = 18.5$ Hz due to the "cis" carbonyl groups and $^2J(^{13}C—H) = 5.5$ Hz due to the "trans" carbonyl groups. As the temperature is raised, the "cis" and "trans" (^{13}CO) satellites begin to broaden and then coalesce to an averaged ^{13}CO coupling constant of 14.1 Hz.

A number of other long-range coupling constants have been reported (see Tables XXXI and XXXII). Indirect coupling constants have also been reported for phosphorus compounds (*17*, *23*, *27*, *80a*, *92*, *98*, *100*, *100a*, *101*, *113*, *133*, *140*, *147*, *148*, *160*, *188a*, *202a*, *202b*, *208*, *226a*).

C. Direct Carbon–Hydrogen and Carbon–Fluorine Coupling Constants

There have been a large number of papers published containing measurements of $^1J(^{13}C—^1H)$ for organometallic compounds (see Tables XXXIII to XXXVI). One reason for interest in $^1J(^{13}C—^1H)$ is Eq. (11), which is based on the Fermi contact term, Eq. (7) and has been used to calculate the s characters of carbon orbitals in the C—H and C—X bonds (*120*, *206*), as described earlier (Section V, A). This approach has been severely criticized (*11*, *97*). The equation was modified to allow for the effective nuclear charge Z_{eff} [Eq. (14)].

$$^1J(^{13}C—^1H) = A(Z_{\text{eff}})^3\alpha_C^2 \tag{14}$$

where A is a constant (*105*). For some methyl-tin compounds Z_{eff} for the carbon has been calculated by the Del Re method. It was concluded that the variation in Z_{eff} can account for only a very small fraction of the total change and may even be neglected in most cases. $^1J(^{13}C—^1H)$ has also been related to the C—H bond length and the C—H stretching force constant (*28*, *172*, *173*). It has been reported that $^1J(^{13}C—^1H)$ for the methyl group is found to correlate linearly with the product $E_X \times \gamma_{X-C}$, where E_X is the electronegativity of the substituent X and γ_{X-C} is the X—C bond distance (*229*). This relationship was used to predict values of $^1J(^{13}C—^1H)$. CNDO/2 calculations have been carried out to calculate $^1J(^{13}C—^1H)$ including the compounds $[SiMe_4]$ and $[SiMe_3F]$ (*189*).

For compounds of the types $[XC_6H_4SiMe_3]$, $[XC_6H_4\mathbf{CH_2}SiMe_2H]$,

$[XC_6H_4SiMe_2SiMe_2H]$, $[XC_6H_4SiMe_2H]$, and $[XC_6H_4SiMeH_2]$, linear relationships have been reported between the Hammett σ constant for X and $^1J(^{13}C—^1H)$ (*38*, *87*, *176*). In the case of $[XC_6H_4SiMe_3]$, the results were interpreted in terms of (*p–d*) π back-bonding, but the values found for $^1J(^{29}Si—^1H)$ for $[XC_6H_4SiMe_2H]$ and $[XC_6H_4SiMeH_2]$ are inconsistent with this view. However, the magnitude $^1J(^{13}C—^1H)$ for compounds belonging to the series $[Me_{4-n}X(OMe)_n]$ and $[Me_{4-n}X'(SMe)_n]$, where $n = 1$ to 4, X = C, Si, or Ge and X′ = C or Si has been measured, and it was concluded that the results indicate the presence of (p–d) π-bonding between silicon and oxygen atoms (*59*). Similarly it has been concluded from $^1J(^{13}C—^1H)$ for $[Me_3MNMe_3]$, M = C, Si, Ge, and Sn, that there is a decrease in (p–d) π-bonding between the metal and nitrogen atoms on going from M = Si to M = Sn (*157*).

For complexes of the type $[Me_nSiX_{4-n}]$ it has been reported that $^1J(^{13}C—^1H)$ is an additive property of the α substituent, provided that the α substituent is not very electronegative (*71*). Data have also been reported for $[SiH_{4-n}(NMe_2)_n]$ (*36*). An empirical linear relationship has been shown to exist between $^1J(^{13}C—^1H)$ and the proton chemical shift. This has been used to determine nonlocal contributions to the proton chemical shift for $[Me_4Ge]$, $[Me_4Sn]$, and $[Me_4Pb]$ (*67*).

A direct correlation of the activation energy and velocity constant with $^1J(^{13}C—^1H)$ for the reaction of methyl radicals with $[Me_4M]$ (M = Si, Ge, Sn, Pb) has been found (*40*). A similar correlation exists for methylchlorosilanes (*44*). The solvent dependence of $^1J(^{13}C—^1H)$ for $[Me_2Pb(acac)_2]$ has been interpreted in terms of the amount of positive charge on the central metal atom (*7*).

$^1J(^{13}C—^1H)$ has also been reported for a series *trans*-$[Pt(PPh_3)_2MeX]$, but was found to be only slightly dependent on the nature of X (*53*). For $[Me_3CCH_2HgX]$ a linear relationship exists between $^1J(^{13}C—^1H)(CH_2)$ and $^2J(^{199}Hg—^1H)$ (*203*).

The observation of $^1J(^{13}C—^1H)$ can give information on $J(H—H)$ not readily obtained by other methods. For example, the ^1H NMR spectrum of ferrocene shows a singlet due to the ten equivalent protons and no information on the magnitude of $J(H—H)$ is obtained. At higher sensitivity, a second-order spectrum due to $[(^{13}C^{12}C_4H_5)Fe(C_5H_5)]$ is observed (*58*). Analysis of this spectrum yields not only $^1J(^{13}C—^1H)$ but $^2J(^{13}C—^1H)$, $^3J(^{13}C—^1H)$, $^2J(^1H—^1H)$, and $^3J(^1H—^1H)$ for $[Fe(C_5H_5)_2]$. $J(^1H—^1H)$ has also been measured from ^{13}C NMR satellites for

$[Ru(C_5H_5)_2]$, $[Co(C_5H_5)_2]Cl$, $[(C_6H_6)Cr(CO)_3]$, $[(p\text{-xylene})Cr(CO)_3]$, $[(\text{mesitylene})Cr(CO)_3]$, $[(2\text{-}MeC_3H_4)Pd(C_5H_5)]$, $[(C_5H_5)SnMe_3]$, and selenophane (*58*, *74*, *103*, *163*, *191*). This technique has also been used to demonstrate that a compound, which could be $[(Me_3Si)_2C{=}C{=}CH_2]$ or $[Me_3SiCH{=}C{=}CHSiMe_3]$, is the latter compound (*204*).

^{13}C NMR satellites can be used to differentiate between fluxional σ- and π-bonded cyclopentadienyl groups. It is found that for a π-bonded cyclopentadienyl group $^1J(^{13}C{-}^1H)$ is between 174 and 181 Hz, but for a fluxional σ-bonded cyclopentadienyl group $^1J(^{13}C{-}^1H)$ is between 159 and 161 Hz (*103*, *104*). It was concluded that $[C_5H_5SnMe_3]$ and $[(C_5H_5)_2Hg]$ probably have fluxional σ-bonded cyclopentadienyl groups (*103*, *178a*). It was also possible to estimate the values of $J(H{-}H)$ from the ^{13}C NMR satellites.

^{13}C NMR satellites have also been used to demonstrate that $[(RC_5H_4)Fe(CO)_2CH{=}CH{-}CH{=}CHFe(CO)_2(C_5H_4R')]$ (R,R′ = H or Me) is fluxional with 1,3-shifts of the metal–carbon bonds (*35*). Unfortunately later work showed the molecule to be static (*5*).

For a number of carboranes, $^1J(^{13}C{-}^1H)$ has been found to be very dependent on the nature of the carborane, covering the range of 204 Hz for $[1,2\text{-}B_{10}H_{10}C_2H_2]$ to 140 Hz for $[Me_3NH][7,9\text{-}B_9C_2H_{12}]$ (*52*) (see Table XXXIII). It was concluded that since the *s* character of the C—H bond in the icosahedral molecules should not change significantly, the effective nuclear charge dependence of $^1J(^{13}C{-}^1H)$ coupling constant may be important.

The measurement of $^1J(^{13}C{-}^1H)$ for π complexes has aroused some interest and values are given in Table XXXIV. When acetylene coordinates to platinum in $[(Ph_3P)_2Pt(C_2H_2)]$, $^1J(^{13}C{-}^1H)$ decreases from 250 to 210 Hz (*53*). The fractional *s* character of the carbon in the C—H bond was used to calculate the C—C—H bond angle of the coordinated acetylene to be 139°, as compared to 140° found in $[(Ph_3P)_2Pt(PhC{\equiv}CPh)]$ (*95a*). When ethylene coordinates to platinum in $[(Ph_2P)_2Pt(C_2H_4)]$, $^1J(^{13}C{-}^1H)$ decreases from 156 to 146.5 Hz. The calculated dihedral angle of 128° is in poor agreement with the angle of 110° found for $[(PPh_3)_2Ir(CO)Br\{C_2(CN)_4\}]$ (*149*).

Values between 157 and 165 Hz have been reported for $^1J(^{13}C{-}^1H)$ for the π-allyl group in $[(1\text{-}MeC_3H_4)NiX]_2$ (X = Cl, Br, I) and $[(2\text{-}MeC_3H_4)Pd(C_5H_5)]$ (*47*, *163*). These values seem to be typical for any π-bonded noncyclic ligand (see Table XXXIV).

For cyclic ligands, the decrease in ring angle would be expected to increase the carbon *s* character in the C—H bond, and on this basis a value of 264 Hz for $^1J(^{13}C—^1H)$ for ferrocene is predicted (*175*). This value is far larger than is observed but $^1J(^{13}C—^1H)$ does increase along the series $[(C_6H_6)Cr(CO)_3]$, 173 Hz; $[(C_5H_5)_2Fe]$, 175.1 Hz; and $[(C_4H_4)Fe(CO)_3]$, 191 Hz (*58*, *74*, *188*). In the case of the [(arene)-$Cr(CO)_3$] complexes the value of $^1J(^{13}C—^1H)$ was discussed in terms of change of charge on the aromatic ring (*74*).

In addition to the data discussed above, $^1J(^{13}C—^1H)$ has been reported for $[Bu^n{}_3GeC{\equiv}CH]$ (*194*, *195*), $[Me_3SnC{\equiv}CMe]$, $[Et_3GeC{\equiv}CMe]$, $[Et_2AsC{\equiv}CMe]$, $[PhSeC{\equiv}CMe]$, $[Ph_3MC{\equiv}CH]$ (M = Si, Ge, Sn), $[Me_3SiC{\equiv}CH]$ (*202*), $[Me_nGeCl_{4-n}]$, $[Me_nGeH_{4-n}]$ (n = 1 to 4) (*219*), $[(Me_3Si)_3SiH]$ (*33*), $[(PhCH_2)_4Sn]$, $[(PhCH_2)_3SnH]$, $[(PhCH_2)_3SnCl]$, $[(PhCH_2)_2SnCl_2]$, $[(Me_3SiNMe)_nSnMe_{4-n}]$ (n = 1 to 4) (*197*), $[Me_4N]^+$ $[(\pi\text{-}7,8\text{-}B_9C_2H_{10})_2C_6H_4Co]^-$ (*86*), $[Me_3SnCF_2CFHCF_3]$, [Me_3SnCF_2-CF_2H], $[Me_3Sn(CF_2)_4H]$ (*50*), and a number of phosphorus compounds (*1a*, *16*, *17*, *41*, *70*, *81*, *140*, *142*, *147*, *148*, *169*, *194*, *195*).

There have been relatively few measurements of $^1J(^{13}C—^{19}F)$ for organometallic compounds. A linear relationship, Eq. (15),

$$^1J(^{13}C—^{19}F) = -(1060r_{CX} + 115) \qquad (15)$$

has been reported, where r_{CX} is the carbon–substituent bond length in nanometers (*138*). Using this relationship, $^1J(^{13}C–^{19}F)$ was predicted for $(CF_3)_3B$, $(CF_3)_3As$, and $(CF_3)_4Pb$. $^1J(^{13}C–^{19}F)$ of 302 Hz has been reported for $Me_3SnCF_2CFHCF_3$ (*50*). The empirical procedure of additive parameters developed for HCXYZ compounds by Malinowski has been extended to FCXYZ compounds (*107*, *108*). Values of $^1J(^{13}C—^{19}F)$ for some organometallic compounds are given in Table XXXVII. $^2J(^{13}C—^{19}F)$ has also been reported for Me_3PF_2 (*30*).

TABLE I[a]

THE ^{13}C CHEMICAL SHIFTS OF METHYL DERIVATIVES OF TRANSITION METALS

Compound	$\delta(^{13}C)$	References
$[MeMn(CO)_5]$	-9.4	*91*
$[MeW(CO)_3(C_5H_5)]$	-28.9	*80*
$[MeFe(CO)_2(C_5H_5)]$	-23.5	*80*
$[Me_3Ir(PEt_3)_3]$	-8.9	*161a*
$[MeIrClI(CO)(AsEt_2Ph)_2]$	-13.8	*164*
$[MeIrClI(CO)(AsMe_2Ph)_2]$	-12.3	*164*
cis-$[PtMe_2(PMe_2Ph)_2]$	3.3	*41*
cis-$[PtMe_2(AsMe_2Ph)_2]$	-3.0	*41*
cis-$[PtMe_2(AsMe_3)]$	-4.1	*45*
cis-$[PtMe_2(COD)]^b$	4.7	*46*
trans-$[PtMeCl(AsMe_3)_2]$	-28.4	*45*
trans-$[PtMe(CO)(AsMe_3)_2][PF_6]$	-6.9	*45*
trans-$[PtMe(CNMe)(AsMe_3)_2][PF_6]$	-13.9	*45*
trans-$[PtMe\{C(OMe)Me\}(AsMe_3)_2][PF_6]$	-15.9	*45*
trans-$[PtMe(NCC_6F_5)(AsMe_3)_2][PF_6]$	-25.5	*45*
trans-$[PtMe(C_2H_4)(PMe_2Ph)_2][PF_6]$	5.6	*46*
trans-$[PtMe(MeC{\equiv}CMe)(PMe_2Ph)_2][PF_6]$	-4.2	*46*
fac-$[PtMe_3I(PMe_2Ph)_2]$	2.9^c 5.8^d	*42*
fac-$[PtMe_3Cl(AsMe_2Ph)_2]$	8.1^c -9.4^d	*42*
fac-$[PtMe_3Br(AsMe_2Ph)_2]$	6.9^c -4.8^d	*42*
fac-$[PtMe_3I(AsMe_2Ph)_2]$	4.5^c 2.2^d	*42*
fac-$[PtMe_3I(AsMe_3)_2]$	2.0^c -0.8^d	*45*
cis-$[PtMe_4(AsMe_2Ph)_2]$	4.4^c -13.4^d	*42*

[a] In all the Tables the ^{13}C shifts are relative to Me_4Si (0.0 ppm). See Section II.

[b] COD = 1,5-cyclooctadiene.

[c] Methyl trans to phosphorus or arsenic.

[d] Methyl trans to halogen or methyl.

TABLE II

THE ^{13}C CHEMICAL SHIFTS OF METHYL DERIVATIVES OF SILICON, GERMANIUM, TIN, AND LEAD

Compound	δ(^{13}C)	References
[Me_4Si]	0	*5, 134, 209* *226, 230*
[$(Me_3Si)_2O$]	−1.2	*76*
[$(Me^1{}_3SiO)_2SiMe^2{}_2$]	C-1 −1.2 C-2 −0.7	*76*
[$(Me^1{}_3SiO)_3SiMe^2$]	C-1 −1.6 C-2 −2.1	*76*
[$(Me_3SiO)_4Si$]	−1.3	*76*
[$\overline{(Me^1{}_2SiO)_3(CH_2Cl)Me^2SiO}$]	C-1 −0.3 C-2 3.1	*76*
[$Me^1{}_3SiO(SiMe^2{}_2O)_2SiMe^1{}_3$]	C-1 −1.4 C-2 −0.7	*76*
[$Me^1{}_3SiO(SiMe^2{}_2O)_3SiMe^1{}_3$]	C-1 −1.3 C-2 −0.6	*76*
[$Me^1{}_3SiO(SiMe^2{}_2O)_4SiMe^1{}_3$]	C-1 −1.4 C-2 −0.7	*76*
[$Me^1{}_3SiO(SiMe^2{}_2O)_4SiMe^1{}_3$]	C-1 −1.3 C-2 −0.6	*76*
[Me_3SiOMe]	1.9	*76*
[Me_3SiCl]	14	*111a*
[$Me_2Si(OMe)_2$]	5.1	*76*
[Me_2SiCl_2]	0	*111a*
[$MeSi(OMe)_3$]	10.3	*76*
[$MeSiCl_3$]	−20	*111a*
[$Me_2SiC(CMe_2CH_2)C(CMe_2CH_2)$]	−6.4	*127a*
[$Me_3Si(C_5H_5)$]	−1.2 −2.0	*102, 104*
[$Me_2ClSi(C_5H_5)$]	1.0	*104*
[$MeCl_2Si(C_5H_5)$]	1.3 2.4	*102, 104*
[$Me_3Si(C_3H_5)$]	−1.5	*104*
[$Me_2ClSi(C_3H_5)$]	2.4	*104*
[$MeCl_2Si(C_3H_5)$]	5.2	*104*
[$MeSi(C_3H_5)_3$]	−5.7	*104*
[$SiMe_2O$]$_3$	1.1	*76*
[$SiMe_2O$]$_4$	0.3	*76*
[$SiMe_2O$]$_5$	0.7	*76*
[Me_4Ge]	−0.8 −1.4	*209, 226*
[$Me_3Ge(C_5H_5)$]	−0.9 −2.4	*102, 104*
[$Me_3Ge(1-MeC_5H_4)$]	−0.7	*104*
[$Me_3Ge(2-MeC_5H_4)$]	−0.7	*104*
[Me_4Sn]	−8.6 −9.1 −9.3	*119, 209* *218, 226*

Continued

TABLE II—*Continued*

Compound	$\delta(^{13}C)$	References
$[Me_3Sn(C_5H_5)]$	-6.6 -7.2	*102, 104*
$[(Me_3Sn)_2C_5H_4]$	-1.5	*102*
$[Me_3Sn(indenyl)]$	-9.1	*200*
$[Me_3Sn(norbornane)]$	-10.9	*119*
$[Me_3Sn(norbornene)]$	-7.2	*119*
$[Me_3Sn(norbornadiene)]$	-10.2	*119*
$[Me_3Sn(C_4H_7)]$	-11.1	*119*
$[Me_3SnCH_2CH_2COOMe]$	-11.2	*119*
$[Me_3Sn(CH_2)_4Ph]$	-11.3	*119*
$[Me_3SnW(CO)_2(PR_3)(C_5H_5)]$	-6	*94a*
$[Me_3SnCHMeCHMeCHCl_2]$[a]	-9.52 -10.12	*200a*
$[Me_3SnCHMeEt]$	-11.74	*200a*
$[Me_3SnC_6H_4X]$	-9.9 to -11.6	*65a*
$[Me_3SnCH_2C_6H_4X]$	-10.1 to -10.5	*65a*
$[Me_3SnCH_2CH{=}CH_2]$	-10.5	*65a*
$[Me_3SnCH{=}C{=}CH_2]$	-10.4	*65a*
$[Me_3SnSMe]$	-5.4[b]	*218*
$[Me_2Sn(SMe)_2]$	-2.6[b]	*218*
$[MeSn(SMe)_3]$	1.0[b]	*218*
$[Me_4Pb]$	-2.6 -3.4	*209, 226*
$[Me_6Pb_2]$	6.0	*51*

[a] Two enantiomers.

[b] Dubious value as sign convention was not defined.

TABLE III

THE ^{13}C CHEMICAL SHIFTS OF METHYL DERIVATIVES OF METALS AND METALLOIDS NOT INCLUDED IN TABLES I AND II

Compound	δ(^{13}C)	References
$[MeLi]_4$	−9.2 to −16.2[a]	*151, 152*
$[MeMgI]$	−14.5	*130*
$[Me_2Zn]$	−4.2	*226*
$[Me_2Cd]$	1.0	*226*
$[Me_2Hg]$	23.5	*62, 226*
$[MeHg(C_5H_5)]$	15.6	*104*
$[1-MeB_5H_9]$	−12.2	*72*
cis-$[PtMe_2(As\mathbf{Me}_3)_2]$	11.6	*45*
cis-$[PtMe_2(As\mathbf{Me}_2Ph)_2]$	10.6	*41*
trans-$[PtMeCl(As\mathbf{Me}_3)_2]$	7.9	*45*
trans $[PtMe(CO)(As\mathbf{Me}_3)_2][PF_6]$	10.0	*45*
trans-$[PtMe(CNMe)(As\mathbf{Me}_3)_2][PF_6]$	9.6	*45*
trans-$[PtMe\{C(OMe)Me\}(As\mathbf{Me}_3)_2][PF_6]$	9.5	*45*
trans-$[PtMe(NCC_6F_5)(As\mathbf{Me}_3)_2][PF_6]$	8.3	*45*
fac-$[PtMe_3Cl(AsMe_2Ph)_2]$	5.9 7.2	*42*
fac-$[PtMe_3Br(AsMe_2Ph)_2]$	6.5 8.2	*42*
fac-$[PtMe_3I(As\mathbf{Me}_2Ph)_2]$	7.5 10.1	*42*
fac-$[PtMe_3I(As\mathbf{Me}_3)_2]$	8.6	*45*
cis-$[PtMe_4(As\mathbf{Me}_2Ph)_2]$	5.8	*42*
$[IrCl_2(CO_2Me)(CO)(As\mathbf{Me}_2Ph)_2]$	7.6 7.8	*164*
$[IrCl_2(CH_2CMe{=}CH_2)(CO)(As\mathbf{Me}_2Ph)_2]$	5.7 8.6	*164*
$[IrClIMe(CO)(As\mathbf{Me}_2Ph)_2]$	6.5 16.0	*164*

[a] Solvent-dependent.

TABLE IV

THE ^{13}C CHEMICAL SHIFTS OF SOME PHENYL DERIVATIVES[a]

Compound	δ(M—C)	δ(*ortho*)	δ(*meta*)	δ(*para*)	References
[PhLi]	171.7	141.4	126.1	125.4	*118*
[PhMgBr]	164.4	139.9	125.8	124.6	*118*
$[(C_5H_5)_2TiPh_2]$	192.9	136.0	127.3	124.3	*80*
cis-$[PtPh_2(PEt_3)_2]$	165.0	136.9	127.1	121.0	*166*
trans-$[PtPh_2(PEt_3)_2]$	164.0	140.7	127.4	121.4	*166*
$[PtPh_2Cl_2(PEt_3)_2]$	130.5	138.9	127.8	125.6	*166*
$Na[BPh_4]$	165.5	137.3	126.6	122.8	*161a*
$[PhSnMe_3]$	141.6	135.6	128.0	128.0	*65a*
$[Ph_3PMo(CO)_5]$	136.4	133.7	129.3	130.7	*92*
$[Ph_3P]$	138.3	134.4	129.2	129.3	*92*
$[Ph_3As]$	140.5	134.3	129.3	129.0	*92*
$[AsPh_4]Cl$	122.4	134.5	132.5	135.9	*161a*
$[Ph_3Sb]$	139.3	136.8	129.4	129.2	*92*
$[Ph_5Sb]$	—	134.6	127.5	127.9	*13*
$[Ph_3Bi]$	131.1	138.1	131.0	128.3	*92*
cis-$[PtMe_2(AsMe_2Ph)_2]$	139.5	131.8	128.9	129.5	*42*
fac-$[PtMe_3Cl(AsMe_2Ph)_2]$	136.8	131.9	129.5	—	*42*
fac-$[PtMe_3Br(AsMe_2Ph)_2]$	136.5	131.9	129.4	130.0	*42*
fac-$[PtMe_3I(AsMe_2Ph)_2]$	135.9	131.8	129.3	129.8	*42*
cis-$[PtMe_4(AsMe_2Ph)_2]$	137.5	132.6	129.7	130.5	*42*

[a] Data have also been reported for $[XC_6H_4SnMe_3]$ (*65a*).

TABLE V
THE ^{13}C CHEMICAL SHIFTS OF CARBENE DERIVATIVES OF TRANSITION METALS

Compound	$\delta(^{13}C)$	References
$[(OC)_5CrC(OMe)Me]$	362.3 360.2	*80, 123*
$[OC)_5CrC(OEt)Me]$	357	*48a*
$[(OC)_5CrC(OMe)Ph]$	354.5 351.4	*52a, 123*
$[(OC)_5CrC(OEt)Ph]$	351	*48a*
$[(OC)_5CrC(OMe)(4-MeOC_6H_4)]$	342.8	*52a*
$[(OC)_5CrC(OMe)(4-ClC_6H_4)]$	350.1	*52a*
$[(OC)_5CrC(OEt)$(ferrocenyl)$]$	332.0	*52a*
$[(OC)_5CrC(OEt)(2-$furanyl$)]$	313.6	*52a*
$[(OC)_5CrC(OEt)($2-thienyl$)]$	319.8	*52a*
$[(OC)_5CrCO($2-thienyl$)][NMe_4]$	276.2	*52a*
$[(OC)_5CrC(NHMe)Me]$	276 284.8	*48a, 52a*
$[(OC)_5CrC(NHMe)Ph]$	289	*48a*
$[(OC)_5CrC(NHPr^i)Me]$	274	*48a*
$[(OC)_5CrC(NHC_6H_{11})Et]$	284.3	*48a, 52a*
$[(OC)_5CrC(NMe_2)Me]$	271	*48a*
$[(OC)_5CrC(NMe_2)Ph]$	277.5	*52a*
$[(OC)_5CrC(NH_2)(2-$furanyl$)]$	255.6	*52a*
$[(OC)_5CrC(NH_2)($2-thienyl$)]$	271.8	*52a*
$[(OC)_5CrC(NC_4H_8)($2-furanyl$)]$	253.7	*52a*
$[(OC)_5CrC(NC_4H_8)Ph]$	271.3	*52a*
$[(OC)_5CrC(NC_4H_8)($2-thienyl$)]$	266.9	*52a*
$[(OC)_5CrC(NC_5H_{10})Ph]$	270.5	*52a*
$[(OC)_5WC(OMe)Me]$	332.9	*123*
$[(OC)_5WC(OMe)Ph]$	321.9	*52a*
$[(OC)_5WC(SMe)Me]$	332.5	*123*
$[(OC)_5WC(NHMe)Me]$	255.7[a] 258.7[a]	*123*
trans-$[PtMe\{C(OMe)Me\}(AsMe_3)_2][PF_6]$	321.0	*45*

[a] Two isomers.

TABLE VI

THE ^{13}C CHEMICAL SHIFTS OF THE CARBONYL LIGAND IN SOME DERIVATIVES OF MANGANESE, RUTHENIUM, OSMIUM, COBALT, RHODIUM, NICKEL, AND PLATINUM

Compound	δ(^{13}C)	References
$[MeMn(CO)_5]$	214	*91*
$[(MeC_5H_4)Mn(CO)_3]$	226	*91*
$[Ru_3(CO)_9(C_6H_9)H]$	192.1 196.6 198.5 199.3 199.7	*78*
$[Ru_3(CO)_9(CMe)H_3]$	189.3 190.1	*36a*
cis-$[RuCl_2(CO)_2(PEt_3)_2]$	195.4	*95*
cis-$[RuCl_2(CO)_2(PEt_2Ph)_2]$	193.9	*95*
cis-$[RuCl_2(CO)_2(PEtPh_2)_2]$	193.7	*95*
cis-$[RuCl_2(CO)_2(PBu^n{}_2Bu^t)_2]$	197.3	*95*
cis-$[RuCl_2(CO)_2(PEt_2Bu^t)_2]$	197.4	*95*
cis-$[RuCl_2(CO)_2(PMeBu^t{}_2)_2]$	198.3	*95*
cis-$[OsCl_2(CO)_2(PPr^n{}_2Bu^t)_2]$	177.6	*95*
$[Os(CO)(NO)(C_2H_4)(PPh_3)_2][PF_6]$	182.9	*116a*
$[Co_3(CO)_9CBr]$	186.2	*80*
$[Rh_4(CO)_{12}]$	189.5	*55*
$[(C_5H_5)_2Rh_2(CO)_3]$	191.8 231.8[a]	*77a*
$[Ni(CO)_4]$	191.6 193	*24, 25, 129*
trans-$[PtMe(CO)(AsMe_3)_2][PF_6]$	178.7	*45*

[a] At −80°C. Fluxional at room temperature.

TABLE VII
THE ^{13}C CHEMICAL SHIFTS OF THE CARBONYL LIGAND IN SOME DERIVATIVES OF CHROMIUM

Compound	δ(^{13}C)			References
$[Cr(CO)_6]$	212.1	212.5	214.6	*26, 52a, 93*
	cis		*trans*	
$[Cr(CO)_5C(OMe)Me]$	216.9 217.6		223.8 223.6	*80, 123*
$[Cr(CO)_5C(OEt)Me]$	217		226	*48a*
$[Cr(CO)_5C(OMe)Ph]$	216.7 218.4		224.6 226.0	*52a, 123*
$[Cr(CO)_5C(OEt)Ph]$	218		226	*48a*
$[Cr(CO)_5C(OMe)(4\text{-}MeOC_6H_4)]$	218.4		225.5	*52a*
$[Cr(CO)_5C(OMe)(4\text{-}ClC_6H_4)]$	217.3		224.9	*52a*
$[Cr(CO)_5C(OEt)(ferrocenyl)]$	218.7		224.1	*52a*
$[Cr(CO)_5C(OEt)(2\text{-}furanyl)]$	218.4		225.5	*52a*
$[Cr(CO)_5(OEt)(2\text{-}thienyl)]$	218.7		224.9	*52a*
$[Cr(CO)_5CO(2\text{-}thienyl)][NMe_4]$	223.6		227.6	*52a*
$[Cr(CO)_5CMe(NHMe)]$	218 219.2		223 224.4	*48a, 52a*
$[Cr(CO)_5C(NHMe)Ph]$	218		224	*48a*
$[Cr(CO)_5C(NHPr^i)Me]$	218		224	*48a*
$[Cr(CO)_5C(NHC_6H_{11})Et]$	219.8		224.4	*52a*
$[Cr(CO)_5C(NMe_2)Ph]$	219.0		225.2	*52a*
$[Cr(CO)_5C(NMe_2)Me]$	218		224	*48a*
$[Cr(CO)_5C(NH_2)(2\text{-}furanyl)]$	219.5		224.7	*52a*
$[Cr(CO)_5C(NH_2)(2\text{-}thienyl)]$	220.8		226.2	*52a*
$[Cr(CO)_5C(NC_4H_8)(2\text{-}furanyl)]$	219.2		225.5	*52a*
$[Cr(CO)_5C(NC_4H_8)Ph]$	219.2		225.5	*52a*
$[Cr(CO)_5C(NC_4H_8)(2\text{-}thienyl)]$	218.7		224.9	*52a*
$[Cr(CO)_5C(NC_5H_{10})Ph]$	218.4		225.5	*52a*
$[Me_4N][Fe\{1,7\text{-}B_9H_9CHPCr(CO)_5\}_2]$	217.9		224.3	*14*
$[Cr(CO)_5(CNC_6H_4Me\text{-}4)]$	216.5		218.7	*52a*
$[Cr(CO)_5(CNPr^i)]$	216.3		218.2	*52a*
$[(Norbornadiene)Cr(CO)_4]$	226.8[a]		234.5[a]	*158, 161*
$[(C_6H_6)Cr(CO)_3]$		233.8		*80*
$[(Mesitylene)Cr(CO)_3]$		235.1		*158, 161*
$[(Durene)Cr(CO)_3]$		235.5		*158, 161*
$[(C_6Me_6)Cr(CO)_3]$		236.3		*161*
$[(C_7H_8)Cr(CO)_3]$		232.7		*158, 161*

[a] Relative assignment unknown.

TABLE VIII
THE ^{13}C CHEMICAL SHIFTS OF THE CARBONYL LIGAND IN SOME DERIVATIVES OF MOLYBDENUM

Compound	$\delta(^{13}C)$			References
$[Mo(CO)_6]$	202.0	204.1		*26, 93*
	cis		*trans*	
$[Mo(CO)_5PPh_3]$	206.5		211.0	*26, 92*
$[Mo(CO)_5P(OMe)_3]$	206.4		209.2	*26*
$[Mo(CO)_5P(OEt)_3]$	206.8		208.7	*26*
$[Mo(CO)_5P(OPr^i)_3]$	206.3		209.7	*80*
$[Me_4N][7,9\text{-}B_9H_{10}CHPMo(CO)_5]$	197.6		200.2	*14, 217*
trans-$[Mo(CO)_4\{P(OMe)_3\}_2]$	210.3		—	*26*
cis-$[Mo(CO)_4(Ph_2PCH_2CH_2PPh_2)]$	210.6		218.5	*26*
[(Norbornadiene)Mo$(CO)_4$]	215.4	215.2	214.8[a]	*129, 158, 161*
	218.8	219.0	218.2[a]	
$[Mo(CO)_3(C_5H_5)]_2$		218.6		*129*
$[Mo(CO)_3(C_5H_5)Cl]$		225.6		*129*
[(*m*-Xylene)Mo$(CO)_3$]		223.1		*80*
[(Mesitylene)Mo$(CO)_3$]		223.7		*158, 161*
[(Durene)Mo$(CO)_3$]		224.4		*158, 161*
$[(C_6Me_6)Mo(CO)_3]$		225.9		*161*
$[(C_7H_8)Mo(CO)_3]$		220.6		*158, 161*
$[(C_5H_5)Mo(CO)_2(NO)]$		227.3		*129*

[a] Relative assignment unknown.

TABLE IX
THE ^{13}C CHEMICAL SHIFTS OF THE CARBONYL LIGAND IN SOME DERIVATIVES OF TUNGSTEN

Compound	δ(^{13}C)			References
$[W(CO)_6]$	192.4	192.1	193.7	*26, 52a, 80, 93*
	cis		*trans*	
$[W(CO)_5C(OMe)Me]$	197.6		203.6	*123*
$[W(CO)_5C(OMe)Ph]$	198.6		204.6	*52a*
$[W(CO)_5C(SMe)Me]$	198.1		207.4	*123*
$[W(CO)_5C(NHMe)Me]$	198.9[a]		203.4[a]	*123*
	199.4[a]		203.4[a]	
$[W(CO)_5P(OMe)_3]$	196.5 196.2		199.5 198.8	*26, 161*
$[W(CO)_5P(OEt)_3]$	197.2		199.6	*26*
$[W(CO)_5PEt_3]$	198.5		200.2	*161*
$[W(CO)_5PBu^n{}_3]$	198.6		200.4	*26, 52a, 93*
$[W(CO)_5P(OPh)_3]$	194.5		197.0	*93*
$[W(CO)_5P(OBu^n)_3]$	196.1		198.8	*93*
$[W(CO)_5PPh(OBu^n)_2]$	196.9		200.0	*93*
$[W(CO)_5PPh_2(OBu^n)]$	197.5		199.0	*93*
$[W(CO)_5PPh_3]$	198.0		199.8	*93*
$[W(CO)_5AsPh_3]$	197.5		199.7	*93*
$[W(CO)_5SbPh_3]$	197.0		199.1	*93*
$[W(CO)_5BiPh_3]$	197.8		198.3	*93*
$[W(CO)_5NH_2C_6H_{11}]$	199.1		201.9	*93*
cis-$[W(CO)_4(PEt_3)_2]$	204.7		204.4	*161*
trans-$[W(CO)_4(PEt_3)_2]$	204.7		—	*161*
$[W(CO)_4(Ph_2PCH_2CH_2PPh_2)]$	204.6		204.6	*26*
$[W(CO)_3Me(C_5H_5)]$	239.2		217.8	*80*
fac-$[W(CO)_3(PEt_3)_3]$		212.4		*161*
$[W(CO)_3(mesitylene)]$		212.6		*158, 161*
$[W(CO)_3(durene)]$		213.7		*158, 161*
$[W(CO)_3(C_6Me_6)]$		215.7		*161*
$[W(CO)_3(C_7H_8)]$		211.6		*158, 161*
$[W(CO)_2(PMe_3)(SnMe_3)(C_5H_5)]$		192		*94a*
$[W(CO)_2(PMe_2Ph)(SnMe_3)C_5H_5)]$		192		*94a*
$[W(CO)_2(PMePh_2)(SnMe_3)(C_5H_5)]$		193		*94a*
$[W(CO)_2\{P(OMe)_3\}(SnMe_3)(C_5H_5)]$		209		*94a*
$[W(CO)_2\{P(OPh)_3\}(SnMe_3)(C_5H_5)]$		220		*94a*

[a] Two isomers.

TABLE X
THE ^{13}C CHEMICAL SHIFTS OF THE CARBONYL LIGAND IN SOME DERIVATIVES OF IRON

Compound	$\delta(^{13}C)$	References
$[Fe(CO)_5]$	209.6 211.9 213.1 213.5	*24, 25, 54, 129*
$[Fe(CO)_4(C_3F_7)I]$	198.8	*129*
$[Fe(CO)_4(PEt_3)]$	215.3	*161a*
$[Fe(CO)_4(PEt_2Ph)]$	215.0	*161a*
$[Fe(CO)_4(PEtPh_2)]$	214.8	*161a*
$[Fe(CO)_3(PPh_3)_2]$	215.5	*161a*
$[Fe(CO)_3(PEt_3)_2]$	216.7	*161a*
$[Fe(CO)_3(Me_2PCH_2CH_2PMe_2)]$	221.5	*1*
$[\{C(\overset{\cdots}{-}CH_2)_3\}Fe(CO)_3]$	211.6	*75*
$[\{C(\overset{\cdots}{-}CH_2)_2(\overset{\cdots}{-}CHCH{=}CH_2)\}Fe(CO)_3]$	214.8	*18*
$[(C_4H_4)Fe(CO)_3]$	209.0	*188*
$[(C_4H_6)Fe(CO)_3]$	209 211.7	*188, 192*
$[(C_8H_8)Fe(CO)_3]$	210.7 212.8[a]	*193a*
$[Fe(CO)_2(C_5H_5)Cl]$	212.9 213.3	*80, 94*
$[Fe(CO)_2(C_5H_5)Br]$	213.2 213.5	*80, 94*
$[Fe(CO)_2(C_5H_5)I]$	213.8 213.6 213.7	*80, 94, 129*
$[Fe(CO)_2(C_5H_5)CN]$	211.1 211.4	*80, 94*
$[Fe(CO)_2(C_5H_5)COMe]$	215.7 215.4	*80, 94*
$[Fe(CO)_2(C_5H_5)Me]$	218.4 218.3	*80, 94*
$[Fe(CO)(C_5H_5)(CN)_2]K$	219.2	*80*
$[Fe(CO)(C_5H_5)(CNBz)_2]Br$	212.1	*80*
$[Fe(CO)_2(C_5H_5)C_6F_5]$	214.6	*94*
$[Fe(CO)_2(C_5H_5)COPh]$	215.1	*94*
$[Fe(CO)_2(C_5H_5)(4\text{-}ClC_6H_4)]$	216.8	*94*
$[Fe(CO)_2(C_5H_5)Ph]$	217.1	*94*
$[Fe(CO)_2(C_5H_5)Bz]$	217.9	*94*
$[Fe(CO)_2(C_5H_5)Et]$	218.6	*94*
$[Fe(CO)_2(C_5H_5)SnMe_3]$	215.7	*94*
$[Fe(CO)_2(C_5H_5)SnPh_3]$	215.7	*94*
$[Fe(CO)_2(C_5H_5)GeMe_3]$	213.2	*94*
$[Fe(CO)_2(C_5H_5)GePh_3]$	216.3	*94*
$[Fe(CO)_2(C_5H_5)SiMe_3]$	216.5	*94*
$[Fe(CO)_2(C_5H_5)SiPh_3]$	216.5	*94*
$[Fe(CO)_2(C_5H_5)]_2$	210.9 285.1	*90*
$[Fe(CO)_2(NO)_2]$	207	*24, 25, 129*
$[Fe(CO)_3SMe]_2$	209.4	*129*
Sperm whale Myoglobin-CO	207.7 207.4[b]	*170*
Human hemoglobin-CO-A	206.5 206.1	*170*
Human hemoglobin-CO-F	206.5 206.1	*170*
Mouse hemoglobin-CO	206.4 205.9	*170*
Rabbit hemoglobin-CO	208.0 206.0	*170*

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[a] At −120°C, there are two types of CO.

[b] pH-dependent.

TABLE XI

THE ^{13}C CHEMICAL SHIFTS OF SOME ETHYL, VINYLIC, ACETYLIDE, AND ETHYLIDENE DERIVATIVES OF SOME METALS AND METALLOIDS

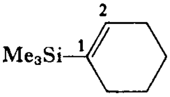
Compound	δ(^{13}C) Carbon-1	δ(^{13}C) Carbon-2	References
[MgBr(C^{1}H$_2$C^{2}H$_3$)]	−2.9	12.2	*130*
[H$_3$Ru$_3$(CO)$_9$CMe]		47.2	*36a*
[Si(C^{1}H$_2$C^{2}H$_3$)$_4$]	1.8	6.0	*209*
[Sn(C^{1}H$_2$C^{2}H$_3$)$_4$]	−0.3	10.8	*209*
[Pb(C^{1}H$_2$C^{2}H$_3$)$_4$]	10.6	15.7	*209*
[IrClIMe(CO){As(C^{1}H$_2$C^{2}H$_3$)$_2$Ph}$_2$]	14.1 17.1	9.3 9.8	*164*
[Me$_3$CCH$_2$HgC^{1}H=C^{2}H$_2$]	178.8	133.4	*203*
[Cl$_3$SiC^{1}H=C^{2}H$_2$]	131.6	138.5	*155*
[Si(C^{1}H=C^{2}H$_2$)$_4$]	134.3	135.3	*155*
[Me$_3$SiC^{1}Et=C^{2}H$_2$]	153.5	123.5	*104*
[Me$_3$SiC^{1}H=C^{2}Me$_2$]	124.9	151.4	*104*
[MeCl$_2$SiC^{1}H=C^{2}Me$_2$]	120.5	153.3	*104*
	139.9	136.2	*104*
[Cl$_2$Sn(C^{1}H=C^{2}H$_2$)$_2$]	135.0	140.4	*155*
[Sn(C^{1}H=C^{2}H$_2$)$_4$]	136.0	136.4	*155*
[Pb(C^{1}H=C^{2}H$_2$)$_4$]	145.2	134.9	*155*
PhC^2≡C^{1}SiMe$_3$	92.5	85.7	*136*
[Bu$^n{}_3$GeC^1≡C^{2}H]	91.5	84.8	*194,195*

TABLE XII

THE ^{13}C CHEMICAL SHIFTS OF SOME NEOPENTYLMERCURY DERIVATIVES[a]

[(C^{3}H$_3$)$_3$C^{2}C^{1}H$_2$HgX]

X	δ(^{13}C) Carbon-1	δ(^{13}C) Carbon-2	δ(^{13}C) Carbon-3
Me	62.6	33.4	35.3
CH$_2$CMe$_3$	63.2	33.9	35.8
CH=CH$_2$	55.8	33.8	35.7
CN	47.8	33.3	34.8
Cl	52.8	33.5	34.3
Br	56.6	33.9	34.4
O$_2$CMe	45.3	33.1	34.0
ONO$_2$	47.0	32.8	33.3

[a] From ref. (*203*).

TABLE XIII

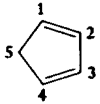
THE ^{13}C CHEMICAL SHIFTS OF SOME σ-ALLYLIC DERIVATIVES OF SOME METALS AND METALLOIDS

$MC^1H_2C^2H{=}C^3H_2$

Compound	δ(^{13}C) Carbon-1	Carbon-2	Carbon-3	References
$[(C_5H_5)Fe(CO)_2(C_3H_5)]$	32.7	172.2	134.9	*48*
$[IrCl_2(CHCMe{=}CH_2)(CO)(AsMe_2Ph)_2]$	10.6	145.2	107.9	*162*
$[SiMe_3(C_3H_5)]$	25.4	135.3	113.5	*104*
$[SiMe_2Cl(C_3H_5)]$	28.3	133.0	116.3	*104*
$[SiMeCl_2(C_3H_5)]$	29.6	130.6	118.9	*104*
$[SiCl_3(C_3H_5)]$	31.6	128.1	120.6	*104*
$[SiMe(C_3H_5)_3]$	21.5	134.8	114.4	*104*
$[SiCl(C_3H_5)_3]$	23.2	132.4	116.9	*104*
$[SnMe_3(CH_2CH{=}CH_2)]$	18	137.1	110.0	*65a*

TABLE XIV

THE ^{13}C CHEMICAL SHIFTS OF SOME σ-CYCLOPENTADIENYL DERIVATIVES OF SOME METALS AND METALLOIDS



Compound	$\delta(^{13}C)$					References
	Carbon-1	Carbon-2	Carbon-3	Carbon-4	Carbon-5	
$[5\text{-}(\sigma\text{-}C_5H_5)Fe(CO)_2(\pi\text{-}C_5H_5)]$	145.3	121.6	121.6	145.3	28.2	*48, 102*
$[5\text{-}(C_5H_5)SiMe_3]$	134.0	131.3	131.3	134.0	52.5	*102, 104*
	133.1[a]	130.5[a]	130.5[a]	133.1[a]	52.1	
$[5\text{-}(C_5H_5)SiMe_2Cl]$	133.0	133.7	133.7	133.0	54.0	*104*
$[5\text{-}(C_5H_5)SiMeCl_2]$	131.9	135.6	135.6	131.9	53.3	*102, 104*
	131.5[a]	134.1[a]	134.1[a]	131.5[a]	54.3	
$[5\text{-}(C_5H_5)GeMe_3]$	133.9	129.8	129.8	133.9	52.1	*102–104*
	133.8[a]	129.8[a]	129.8[a]	133.8[a]	51.3	
$[5\text{-}(1\text{-}MeC_5H_4)GeMe_3]$	144.9	126.7	130.2	131.5	55.6	*104*
$[5\text{-}(2\text{-}MeC_5H_4)GeMe_3]$	128.8	139.9	133.1	134.6	52.8	*104*
$[5\text{-}(C_5H_5)SnMe_3]$	114.3[b]	114.3[b]	114.3[b]	114.3[b]	114.3[b]	*104*
$[5\text{-}(C_5H_5)HgMe]$	117.7[b]	117.7[b]	117.7[b]	117.7[b]	117.7[b]	*104*
$[1\text{-}(C_5H_5)SiMe_3]$	147.9	142.7	138.4	140	45.7	*104*
$[1\text{-}(C_5H_5)SiMe_2Cl]$	144.3	145.7	140.5	133.9	45.7	*104*
$[1\text{-}(C_5H_5)SiMeCl_2]$	141.0	148.3	142.0	133.8	45.6	*104*
$[C_5H_4\{SnMe_3\}_2]$	134.5[b]	127.3[b]	—	—	51.5	*102*

[a] No assignments made.

[b] Fluxional.

TABLE XV

THE ^{13}C CHEMICAL SHIFTS OF SOME MISCELLANEOUS COMPOUNDS[a]

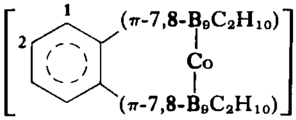
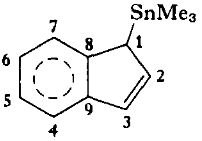
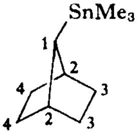
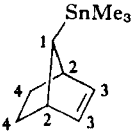
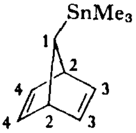
Compound		δ(^{13}C)		References
$\mathrm{PhCH_2Li}$		18.3 to 29.8		*222, 223*
$\mathrm{Ph_2CHLi}$		79		*222*
$\mathrm{Ph_3CLi}$		91		*222*
$\mathrm{Me_3CLi}$		11		*150*
$\mathrm{Pr^nCH_2Li}$		11		*150*
$[\mathrm{MgCl(CH_2Ph)}]$		22.2		*130*
$[\mathrm{Mg(CH_2Ph)_2}]$		21.9		*130*
$[\mathrm{MgBr}(\mathbf{CH_2}\mathrm{CH_2Ph})]$		10.8		*130*
$[\mathrm{MgBr}\{\mathbf{CH_2}\mathrm{(CH_2)_2Ph}\}]$		7.9		*130*
$[\mathrm{MgBr}(\mathbf{CH_2}\mathrm{Et})]$		11.3		*130*
$[\mathrm{MgBr}(\mathbf{CH_2}\mathrm{Pr^n})]$		5.9		*130*
$[\mathrm{MgBr}(\mathbf{CH_2}\mathrm{Bu^n})]$		7.4		*130*
$[\mathrm{MgBr(CHMe_2)}]$		8.9		*130*
$[\mathrm{MgBr}\{\overline{\mathbf{CH}\mathrm{(CH_2)_4CH_2}}\}]$		23.4		*130*
$[\mathrm{MgBr}\{\mathbf{CH}\mathrm{[(CH_2)_2]_2CHBu^t}\}]$		22.9		*130*
$[\mathrm{Ti(CH_2Ph)_4}]$		98.8		*229a*
$[\mathrm{Zr(CH_2Ph)_4}]$		74.5		*229a*
$[\mathrm{(C_5H_5)Fe(CO)_2(CN)}]$		154.7		*80*
$[\mathrm{(C_5H_5)Fe(CO)(CN)_2}]\mathrm{K}$		159.0		*80*
$[\mathrm{(C_5H_5)Fe(CO)(CNBz)_2}]\mathrm{Br}$		147.4		*80*
$[\mathrm{(C_5H_5)Fe(CO)_2COMe}]$		254.4		*80*
$[\mathrm{Hg(CH_2Ph)_2}]$		47.0		*229a*
$[\mathrm{Me_4N}]$ 	C-1,2	120.5	124.1	*86*
$[\mathrm{B(CH_2Ph)_3}]$		37.5		*229a*
$[\mathrm{B(C^3H_2C^2H_2C^1H_3)_3}]$	C-1	18.4		*225a*
	C-2	17.8		
	C-3	31.7		
$[\mathrm{B\{C^1H(C^2H_3)_2\}_3}]$	C-1	20.5		*225a*
	C-2	17.8		
$[\mathrm{Al(CH_2Ph)_3}]$		21.0		*229a*
$[\mathrm{Si(CH_2Ph)_4}]$		29.0		*229a*
$[\mathrm{Sn(CH_2Ph)_4}]$		20.5		*229a*

TABLE XV—*Continued*

Compound	δ(^{13}C)			References
	C-1, 44.9 C-2, 134.4 C-3, 125.8 C-4, 124.8	C-5,6, C-7, C-8, C-9,	122.1 124.3 146.6 142.9	*200*
	C-1, 37.9 C-2, 38.5	C-3, C-4,	30.7 28.4	*119*
	C-1, 52.1 C-2, 46.6	C-3, C-4,	25.3 137.9	*119*
	C-3, 144.3	C-4,	145.5	*119*
[Sn(CH_2Ph)Me_3]^b	20.5			*65a*
[Sn$Me_3C^1H{=}C^2{=}C^3H_2$]	C-1	75.2		*65a*

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[a] Data are also available for [$Me_3SnCHMeCHMeCHCl_2$] and [$Me_3SnCHMeEt$] but no assignments were made (*200a*).

[b] Data were also given for [$Me_3Sn(CH_2C_6H_4X)$] (*65a*).

TABLE XVI
THE ^{13}C CHEMICAL SHIFTS OF SOME CARBORANES

Compound	$\delta(^{13}C)$	Carbon coordination number	References
$[HCB_{10}H_8Br_2CH]$	53.1	—	*217*
$[Me_3SiCB_{10}H_{10}CSiMe_3]$	66.8	—	*217*
$[MeSCB_{10}H_{10}CSMe]$	72.7	—	*217*
$[1,2\text{-}B_{10}C_2H_{12}]$	49.1 55.5	6	*52, 217*
$[1,7\text{-}B_{10}C_2H_{12}]$	49.0 55.4	6	*52, 217*
$[1,12\text{-}B_{10}C_2H_{10}]$	62.5	6	*217*
$[1,6\text{-}B_8C_2H_{10}]$	32.4 (57.1)	6 (5)	*217*
$[4,5\text{-}B_7C_2H_9]$	69.3	5	*217*
$[1,6\text{-}B_4C_2H_6]$	77.2	5	*217*
$[3,6\text{-}B_5C_2H_7]$	80.0	5	*217*
$[2,3\text{-}B_9C_2H_{11}]$	86.5	5	*217*
$[1,5\text{-}B_3C_2H_5]$	102.4	4	*217*
$Cs[B_{11}H_{11}CH]$	45.3	—	*52*
$[Me_3NH][7,8\text{-}B_9C_2H_{12}]$	38.0	—	*52*
$[Me_3NH][7,9\text{-}B_9C_2H_{12}]$	38.0	—	*52*
$[MeB_5H_8]$	−12.2	—	*225*
$[Me_4N][(\pi\text{-}7,8\text{-}B_9C_2H_{10})_2C_6H_4Co]$	38.6	—	*86*

TABLE XVII
THE ^{13}C SPIN-LATTICE RELAXATION TIMES FOR SOME MONOSUBSTITUTED FERROCENES, $[(C_5H_5)Fe(C_5H_4X)]$, (X = H, COMe, *n*-Bu)[a,b]

Substituent, X	Assignment	T_1 (sec) ($\pm 15\%$)	Spinning ratio $\frac{\text{Ring B}}{\text{Ring A}}$
H		14.3	
Acetyl	Ring A	3.2 3.2	
	Ring B	6.2	~4
	$COCH_3$	7.9	
n-Butyl	Ring A	2.5 2.6	
	Ring B	6.0	~7
	$\alpha\text{-}CH_2$	2.0	
	$\beta\text{-}CH_2$	2.0	
	$\gamma\text{-}CH_2$	2.8	
	$\delta\text{-}CH_3$	3.6	

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[a] From ref. (*143*).

[b] Ring A is the substituted ring, and ring B is the unsubstituted ring.

TABLE XVIII
THE ^{13}C CHEMICAL SHIFTS OF SOME PARAMAGNETIC TRANSITION METAL COMPLEXES[a]

Compound	Assignment	$\delta(^{13}C)$	References
$[Eu(C_5H_5)_3(CNC_6H_{11})]$	C_5H_5	−74.1	*3*
$[V(C_5H_5)_2]$	—	−790	*34*
$[V(C_5H_4Me)_2]$	Ring carbons	−494 (2)	*4*
		−725 (3)	
	Methyl	942 (1)	
$[Cr(C_5H_5)_2]$	—	−570	*34*
$[Cr(C_5H_4Me)_2]$	Ring carbons	−494 (1)	*4*
		−368 (2)	
		−106 (2)	
	Methyl	411 (1)	
$[Co(C_5H_5)_2]$	—	549	*34*
$[Co(C_5H_4Me)_2]$	Ring carbons	413	*4*
		707	
	Methyl	9 (1)	
$[Ni(C_5H_5)_2]$	—	1430	*34*
$[Ni(C_5H_4Me)_2]$	Ring carbons	1207 (5)	*4*
	Methyl	−434 (1)	

[a] The relative intensities of the signals are given in parentheses.

TABLE XIX
THE ^{13}C CHEMICAL SHIFTS OF SOME π-OLEFINIC AND π-ACETYLENIC COMPLEXES OF METALS[i]

Compound	$\delta(^{13}C)$	Coordination Shift	References
$[Os(CO)(NO)(C_2H_4)(PPh_3)_2][PF_6]$	54.4	67.2	*116a*
$[(C_2H_4)_2Rh(C_5H_5)]$	60.0	61.6	*21*
$[(C_2H_4)_2Rh(acac)]$[a]	36.3	85.3	*21*
$K[(C_2H_4)PtCl_3]$	67.1 to 75.1	56.2 to 48.2	*46, 80, 187*
trans-$[PtMe(C_2H_4)(PMe_2Ph)_2][PF_6]$	84.4	37.2	*46*
$[(Ph_3P)_2Pt(C_2H_4)]$	39.6	82.0	*46*
$[(MeCHCH_2)Fe(CO)_2(C_5H_5)][CF_3CO_2]$	58.0[b]	60.6	*6*
	88.8[c]	48.0	
$[(MeCHCH_2)_2Rh(acac)]$[a]	63.8 65.0[b,d]	54.8 53.6	*6*
	75.8[c]	61.0	
$[(MeCHCH_2)_2Ag][BF_4]$	109.4[a]	9.2	*6*
	138.5[c]	−1.7	
K[(*cis*-2-Butene)$PtCl_3$]	89.3	34.4	*187*
K[(*trans*-2-Butene)$PtCl_3$]	87.8	37.3	*187*
[(Cyclopentene)Ag][NO_3]	126.2	4.4	*183*
[(Cyclohexene)Ag][NO_3]	122.8	4.4	*183*
$[(Cyclohexene)Hg]^{2+}$	157.7	−30.5	*181*
$[(C_{10}H_{12})PdCl_2]$[e]	133.1	2.8	*187*
$[(C_{10}H_{12})PtCl_2]$[e]	116.6	19.3	*187*
$[(COD)RhCl]_2$[f]	78.5	49.3	*187*
$[(COD)Rh(C_5H_5)]$[f]	62.4	65.4	*21*
[(COD)Rh(acac)][a,f]	76.0	51.8	*21*
[(COD)Rh(tfac)][f,g]	76.3	51.5	*21*
[(COD)Rh(hfac)][f,h]	78.2	49.6	*21*
$[(COD)IrCl]_2$[f]	62.1	65.7	*187*
$[(COD)PdCl_2]$[f]	117.2	10.6	*187*
$[(COD)PtCl_2]$[f]	100.6	27.2	*187*
$[(COD)PtI_2]$[f]	103.2	24.6	*46*
$[(COD)PtMe_2]$[f]	98.8	29.0	*46*
$[(COD)Pt(CF_3)_2]$[f]	111.0	16.8	*46*
[(Norbornadiene)Cr$(CO)_4$]	76.0	68.1	*158, 161*
[(Norbornadiene)Mo$(CO)_4$]	79.6	64.5	*158, 161*
[(Norbornadiene)Rh(C_5H_5)]	28.7	115.2	*21*
trans-$[PtMe(MeC{\equiv}CMe)(PMe_2Ph)_2]$	69.5	—	*46*
$[(Ph_3P)_2Pt(MeC{\equiv}CMe)]$	112.8	—	*46*

[a] acac = acetylacetonate. [b] Terminal carbon atom. [c] Central carbon atom. [d] Two isomers. [e] $C_{10}H_{12}$ = cyclopentadiene dimer. [f] COD = 1,5-cyclooctadiene. [g] tfac = trifluoracetylacetonate. [h] hfac = hexafluoroacetylacetonate. [i] See also an extensive collection of ^{13}C NMR data for alkenes complexed to silver(I) (*17a*).

TABLE XX

THE ^{13}C CHEMICAL SHIFTS OF SOME COMPLEXES CONTAINING A π-ALLYLIC LIGAND

Compound	$\delta(^{13}C)$			References
	Carbon-1	Carbon-2	Carbon-3	
$[Ru_3(CO)_9H(C_6H_9)]$	[a]	119.8	[a]	*78*
$[(1\text{-}MeC_3H_4)NiCl]_2$	70.0	106.9	48.0	*47*
$[(1\text{-}MeC_3H_4)NiBr]_2$	71.2	105.6	49.6	*47*
$[(1\text{-}MeC_3H_4)NiI]_2$	76.3	105.5	52.4	*47*
$[(C_3H_5)PdCl]_2$	63.2	111.9	63.2	*80, 162*
	62.8	111.3	62.8	
$[(C_3H_5)PdBr]_2$	65.2	111.3	65.2	*162*
$[(C_3H_5)PdI]_2$	68.0	110.2	68.0	*162*
$[(C_3H_5)Pd(acac)]$[b]	55.8	113.5	55.8	*162*
$[(C_3H_5)Pd(C_5H_5)]$	45.8	95.0	45.8	*162*
$[(C_3H_5)PdCl(PPh_3)]$	62.0	118.7	79.4	*162*
$[(2\text{-}MeC_3H_4)PdCl]_2$	61.7	127.9	61.7	*162*
$[(2\text{-}MeC_3H_4)PdBr]_2$	64.4	127.2	64.4	*162*
$[(2\text{-}MeC_3H_4)PdI]_2$	67.6	125.6	67.6	*162*
$[(2\text{-}MeC_3H_4)Pd(acac)]$[b]	54.8	129.2	54.8	*162*
$[(2\text{-}MeC_3H_4)Pd(C_5H_5)]$	47.0	112.2	47.0	*162*
$[(1\text{-}MeC_3H_4)Pd(acac)]$[b]	73.6	113.3	51.6	*163*
$[(1\text{-}PhC_3H_4)Pd(acac)]$[b]	75.0	108.8	[c]	*163*
$[(1\text{-}BzC_3H_4)Pd(acac)]$[b]	77.6	112.0	52.6	*163*
$[(1\text{-}Me\text{-}3\text{-}PhC_3H_3)Pd(acac)]$[b]	70.6[d]	109.5	71.4[d]	*163*
[(Cyclooctadienyl)Pd(acac)][b]	68.0[d]	103.6	73.6[d]	*163*
[(Cyclooctadienyl)Pd(C_5H_5)]	62.2[d]	91.1	67.1[d]	*163*

[a] Not observed.

[b] acac = acetylacetonate.

[c] Not observed. Probably obscured by CH_2Cl_2 solvent.

[d] Relative assignment uncertain.

TABLE XXI

THE ^{13}C CHEMICAL SHIFTS OF SOME COMPLEXED π-DIENES OR SIMILAR LIGANDS

Compound	$\delta(^{13}C)$	References
[(Cyclobutadiene)Fe(CO)$_3$]	61.0	*188*
[(Butadiene)Fe(CO)$_3$]	C-1,4, 36 41.1	*188, 192*
	C-2,3, 81 85.8	
$[(C_{13}H_{27}CH{=}CHCH{=}CHCOOMe)Fe(CO)_3]$	64 85	
$[(C_8H_8)Fe(CO)_3]$	62.8 89.2 120.5	*193a*
	129.1	
$[\{C^1\underset{\cdots}{-}C^2H_2)_3\}Fe(CO)_3]$	C-1, 105.0	*75*
	C-2, 53.0	
$[\{C^1\underset{\cdots}{-}C^2H_2)_2(\underset{\cdots}{-}C^3HC^4H{=}C^5H_2)\}Fe(CO)_3]$	C-1, 105.2	*18*
	C-2, 51.9 52.5	
	C-3, 80.2	
	C-4, 137.6	
	C-5, 118.7	

TABLE XXII

THE ^{13}C CHEMICAL SHIFTS OF THE π-CYCLOPENTADIENYL LIGAND COMPLEXED TO SODIUM, MAGNESIUM, TITANIUM MANGANESE, MOLYBDENUM, TUNGSTEN, RHODIUM, AND PALLADIUM

Compound	$\delta(^{13}C)$	References
$[(C_5H_5)Na]$	102.1	*129*
$[(C_5H_5)_2Mg]$	108.6	*129*
$[(C_5H_5)MgCl]$	103.8	*84*
$[(C_5H_5)_3YCNC_6H_{11}]$	111.6	*3*
$[(C_5H_5)_2TiCl_2]$	121.3	*80*
$[(C_5H_5)_2TiPh_2]$	116.8	*80*
$[(C_5H_5)Mn(CO)_3]$	75	*129*
$[(C_5H_5)Mo(CO)_3Cl]$	94.9	*129*
$[(C_5H_5)Mo(CO)_3COC_3F_7]$	94.9	*129*
$[(C_5H_5)Mo(CO)_3CH_2SMe]$	93.2	*129*
$[(C_5H_5)Mo(CO)_3CF_3]$	91.9	*129*
$[(C_5H_5)Mo(CO)_3Et]$	91.7	*129*
$[(C_5H_5)Mo(CO)_2(NO)]$	93.6	*129*
$[(C_5H_5)W(CO)_3COCF_3]$	94.1	*129*
$[(C_5H_5)W(CO)_3Me]$	92.4	*80*
$[(C_5H_5)W(CO)_2(PR_3)SnMe_3]$	86 to 87	*94a*
$[(C_5H_5)Rh(C_2H_4)_2]$	87.8	*21*
$[(C_5H_5)Rh(CO)_2]$	87.6	*21*
$[(C_5H_5)Rh(cyclooctadiene)]$	86.5	*21*
$[(C_5H_5)Rh(norbornadiene)]$	84.8	*21*
$[(C_5H_5)Pd(C_3H_5)]$	94.7	*162, 163*
$[(C_5H_5)Pd(2\text{-}MeC_3H_4)]$	94.7	*162, 163*
$[(C_5H_5)Pd(cyclooctadienyl)]$	95.2	*163*

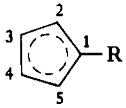
TABLE XXIII

THE ^{13}C CHEMICAL SHIFTS OF THE UNSUBSTITUTED π-CYCLOPENTADIENYL LIGAND COMPLEXED TO IRON

Compound	δ(^{13}C)	References
$[(C_5H_5)Fe(CO)_2(C_3H_5)]$	111.0	*48*
$[(C_5H_5)Fe(CO)_2]_2$	106.7	*90*
$[(C_5H_5)Fe(CO)_2(MeCH{=}CH_2)][CF_3CO_2]$	91.3	*6*
$[(C_5H_5)Fe(CO)_2GeMe_3]$	87.7	*94*
$[(C_5H_5)Fe(CO)_2COMe]$	87.1 86.5 86.9	*80, 94, 129*
$[(C_5H_5)Fe(CO)_2COPh]$	87.1	*94*
$[(C_5H_5)Fe(CO)_2CH_2Ph]$	86.7	*94*
$[(C_5H_5)Fe(CO)_2(4\text{-}ClC_6H_4)]$	86.7	*94*
$[(C_5H_5)Fe(CO)_2Ph]$	86.3	*94*
$[(C_5H_5)Fe(CO)_2Et]$	86.3	*94*
$[(C_5H_5)Fe(CO)_2C_6F_5]$	86.0	*94*
$[(C_5H_5)Fe(CO)_2(\sigma\text{-}C_5H_5)]$	85.9 87.1	*48, 102, 104*
$[(C_5H_5)Fe(CO)_2Cl]$	85.9 85.6	*80, 94*
$[(C_5H_5)Fe(CO)_2Br]$	85.9 85.4	*80, 94*
$[(C_5H_5)Fe(CO)_2Me]$	85.7 85.3	*80, 94*
$[(C_5H_5)Fe(CO)_2SiPh_3]$	84.5	*94*
$[(C_5H_5)Fe(CO)(CNCH_2Ph)_2]Br$	85.3	*94*
$[(C_5H_5)Fe(CO)_2I]$	84.7 84.8	*80, 94*
$[(C_5H_5)Fe(CO)_2GePh_3]$	84.7	*94*
$[(C_5H_5)Fe(CO)_2SiMe_3]$	84.2	*94*
$[(C_5H_5)Fe(CO)_2SnPh_3]$	83.3	*94*
$K[(C_5H_5)Fe(CO)(CN)_2]$	82.6	*80*
$[(C_5H_5)Fe(CO)_2CN]$	82.3 85.9	*80, 94*
$[(C_5H_5)Fe(CO)_2SnMe_3]$	81.4	*94*
$[(C_5H_5)Fe(C_5H_4COMe)]$	69.9	*132*
$[(C_5H_5)Fe(C_5H_4Me)]$	69.3	*165*
$[(C_5H_5)Fe(C_5H_4CH_2NMe_2)]$	69.1	*165*
$[(C_5H_5)Fe(C_5H_4CH_2OMe)]$	68.9	*165*
$[(C_5H_5)Fe(C_5H_4Bu^n)]$	68.7	*132*
$[(C_5H_5)Fe(C_5H_4)(EtO)CCr(CO)_5]$	71.3	*52a*
$[(C_5H_5)_2Fe]$	68.2 69.2	*129, 132*

TABLE XXIV

THE ^{13}C CHEMICAL SHIFTS FOR SOME MONOSUBSTITUTED π-CYCLOPENTADIENYL COMPLEXES, AND $(1,3\text{-}Me_2C_5H_3)MgCl$



Compound	$\delta(^{13}C)$			References
	Carbon-1	Carbon-2,5[a]	Carbon-3,4[a]	
$[(MeC_5H_4)MgCl]$	116.1	104.1	101.6	*84*
$[(Me_3SiC_5H_4)MgCl]$	112.6	112.5	105.7	*84*
$[(1,3\text{-}Me_2C_5H_3)MgCl]$	114.4[b]	105.2[c]	101.4[d]	*84*
$[(MeC_5H_4)Mn(CO)_3]$	100.9	80.1	79.4	*91*
$[(Bu^nC_5H_4)Fe(C_5H_5)]$	89.3	67.3	68.3	*132*
$[(MeC_5H_4)Fe(C_5H_5)]$	84.8	67.9	69.9	*165*
$[(MeOCH_2C_5H_4)Fe(C_5H_5)]$	84.4	68.7	69.8	*165*
$[(Me_2NCH_2C_5H_4)Fe(C_5H_5)]$	84.4	68.4	70.8	*165*
$[(MeCOC_5H_4)Fe(C_5H_5)]$	80.3	69.8	72.0	*132*
$[(OC)_5CrC(OEt)C_5H_4FeC_5H_5]$	94.9	73.2	75.3	*52a*

[a] Relative assignment uncertain. [b] Carbon-1,3. [c] Carbon-2. [d] Carbon-4,5.

TABLE XXV

^{13}C NMR CHEMICAL SHIFTS OF SOME ARENE AND CYCLOHEPTATRIENE LIGANDS AND THEIR COMPLEXES WITH $M(CO)_3$, M = Cr, Mo, W[a]

	Free ligand	$[LM(CO)_3]$		
	L	Cr	Mo	W
L = C_6H_6	128.5	93.7	—	—
L = *m* – xylene				
^{13}C (C-1,3)	—	—	115.6	—
^{13}C (C-2)	—	—	96.4	—
^{13}C (C-5)	—	—	98.2	—
^{13}C (C-4,6)	—	—	92.7	—
$^{13}CH_3$	—	—	21.5	—
L = mesitylene				
$^{13}CH_3$	21.4	21.0	21.2	20.9
^{13}CH	127.6	92.4	94.7	90.9
^{13}CMe	138.6	111.5	111.7	111.1
L = durene				
$^{13}CH_3$	19.2	18.6	19.1	18.9
^{13}CH	131.6	99.0	101.4	97.3
^{13}CMe	134.4	107.6	118.8	107.9
L = hexamethylbenzene				
$^{13}CH_3$	16.9	17.4	18.0	17.9
^{13}CMe	132.5	107.5	111.7	107.9
L = cycloheptatriene				
$^{13}CH_2$ (C-7)	28.7	24.8	28.0	28.7
^{13}CH (C-1,6)	121.3	57.6	61.3	52.3
^{13}CH (C-2,5)	127.3	99.0	98.1	94.2
^{13}CH (C-3,4)	131.3	101.9	103.7	101.7

[a] From refs. (*80*) and (*161*).

TABLE XXVI

VALUES OF $^{1}J(\text{M}—^{13}\text{C})$ FOUND FOR COMPLEXES OF LITHIUM, BORON, SILICON, GERMANIUM, TIN, LEAD, SELENIUM, AND TELLURIUM

Compound	M	$^{1}J(\text{M}—^{13}\text{C})$	References
$[\text{LiMe}]_4$	^{7}Li	14.5 15	*151*
$[\text{LiBu}^t]$	^{7}Li	11	*150*
$[\text{LiBu}^n]$	^{7}Li	14	*150*
$\text{Na}[\text{BPh}_4]$	^{11}B	49.5	*225*
$[\text{MeB}_6\text{H}_9]$	^{11}B	72.6	*72*
$[\text{SiMe}_4]$	^{29}Si	40.5 51 −52, 50.3	*61, 153, 226*
$[\text{PhSiMe}_3]$	^{29}Si	66.5 (Ph)	*136*
$[(\text{CH}_2{=}\text{CH})_4\text{Si}]$	^{29}Si	70	*136*
$[(\text{CH}_2{=}\mathbf{CH})_2\text{SiMe}_2]$	^{29}Si	66	*136*
$[(\text{CH}_2{=}\mathbf{CH})\text{SiMe}_3]$	^{29}Si	64	*136*
$[\text{PhC}^2{\equiv}\text{C}^1\text{SiMe}_3]$	^{29}Si	C-1, 83.6 C-2, 16.1	*136*
$[\text{Me}_2\text{SiC}(\text{CMe}_2\text{CH}_2)\text{-}\text{C}(\text{CMe}_2\text{CH}_2)]$	^{29}Si	58	*127a*
$[\text{SiHCl}_2\text{Me}]$	^{29}Si	−66	*143*
$[\text{GeMe}_4]$	^{73}Ge	18.7	*60*
$[\text{SnMe}_4]$	^{119}Sn	330 340	*141, 226*
$[\text{SnEt}_4]$	^{117}Sn	307.4	*225*
	^{119}Sn	321.5	*225*
$[\text{Sn}_2\text{Me}_6]$	^{119}Sn	−240	*146*
$[\text{SnMe}_3\text{Br}]$	^{119}Sn	−380 −494[a]	*141*
$[\text{SnMe}_2\text{Cl}_2]$	^{119}Sn	−566 to −864[a]	*141*
$[\text{SnMeBr}_3]$	^{119}Sn	−640	*141*
$[\text{SnMe}_3(\text{C}_5\text{H}_5)]$	$^{117,119}\text{Sn}$	19[b]	*104*
$[\text{SnMe}_3\text{C}_6\text{H}_4\text{X}]$	^{119}Sn	343.6 to 356.8[c]	*65a, 196a*
	^{119}Sn	439.0 to 520.2[d]	
$[\text{SnMe}_3\text{CH}_2\text{Ph}]$	^{119}Sn	322, 327[c]	*65a*
$[\text{SnMe}_3\text{CH}_2\text{CH}{=}\text{CH}_2]$	^{119}Sn	325[c] 298[d]	*65a*
$[\text{SnMe}_3\text{CH}{=}\text{C}{=}\text{CH}_2]$	^{119}Sn	356[c] 382[d]	*65a*
$[\text{Sn}(\mathbf{CH_2}\text{CH}{=}\text{CH}_2)_4]$	^{119}Sn	250	*104*
$[\text{PbMe}_4]$	^{207}Pb	+250	*145, 226*
$[\text{Pb}_2\text{Me}_6]$	^{207}Pb	+28	*51*
$[\text{SeMe}_2]$	^{77}Se	−62.0	*69, 114*
$[\text{SeMeH}]$	^{77}Se	−48	*69*
$[\text{SeMe}_3]\text{I}$	^{77}Se	−50	*144*
$[\text{Se}_2\text{Me}_2]$	^{77}Se	−75	*144*
$[\text{TeMe}_2]$	^{125}Te	+158.5 162	*69*, 144

[a] Solvent-dependent.

[b] Fluxional molecule.

[c] Coupling to methyl group.

[d] Coupling to the other directly bonded carbon atom.

TABLE XXVII

VALUES OF ^{1}J(M—^{13}C) FOR COMPLEXES OF VANADIUM, MOLYBDENUM, IRON, COBALT, RHODIUM, CADMIUM, AND MERCURY

Compound	M	^{1}J(M—^{13}C)	References
$[V(CO)_6]^-$	^{51}V	146	*129*
$[Mo(CO)_6]$	^{95}Mo	68	*161*
$[Fe(CO)_5]$	^{57}Fe	23.4	*159*
$[Co(CO)_4]^-$	^{59}Co	287	*139*
$K_3[Co(CN)_6]$	^{59}Co	127	*139*
$[Rh(CO)_2Cl]_2$	^{103}Rh	68.8	*55*
$[Rh_4(CO)_{12}]$	^{103}Rh	17	*55*
$[(C_5H_5)_2Rh_2(CO)_3]$	^{103}Rh	45[f,g] 83[f,h]	*77a*
$[(H_2C{=}CHCH_2)Rh(C_5H_5)(C_3H_5)]$	^{103}Rh	26	*21*
$[(C_2H_4)_2Rh(C_5H_5)]$	^{103}Rh	14	*21*
$[(MeC^1H{=}C^2H_2)_2Rh(acac)]$	^{103}Rh	Carbon-1 15.5 Carbon-2 13.7	*6*
$[(COD)RhCl]_2$[a]	^{103}Rh	14.6	*187*
$[(COD)Rh(C_5H_5)]$[a]	^{103}Rh	14[b]	*21*
$[(COD)Rh(acac)]$[a,c]	^{103}Rh	14[b]	*21*
$[(COD)Rh(tfac)]$[a,d]	^{103}Rh	14[b]	*21*
$[(COD)Rh(hfac)]$[a,e]	^{103}Rh	16[b]	*21*
$[(Norbornadiene)Rh(C_5H_5)]$	^{103}Rh	10	*21*
$[CdMe_2]$	^{111}Cd	512	*226*
	^{113}Cd	537.5	*226*
$[HgMe_2]$	^{199}Hg	687.4 689 690 692	*62, 154, 225a, 226*
$[HgBu^n{}_2]$	^{199}Hg	+656	*225, 225a*
$[Hg(CH_2CMe_3)_2]$	^{199}Hg	684	*203*
$[Hg(CH_2CMe_3)Me]$	^{199}Hg	690	*203*
$[Hg(CH_2CMe_3)CH{=}CH_2]$	^{199}Hg	820	*203*
$[Hg(CH_2CMe_3)CH{=}CH_2]$	^{199}Hg	934	*203*
$[Hg(CH_2CMe_3)CN]$	^{199}Hg	1404	*203*
$[Hg(CH_2CMe_3)Cl]$	^{199}Hg	1514	*203*
$[HgPh_2]$	^{199}Hg	1186	*225, 225a*
$[HgEt_2]$	^{199}Hg	648	*225a*
$[HgPr^n{}_2]$	^{199}Hg	659	*225a*
$[HgPr^i{}_2]$	^{199}Hg	633.6	*225a*
$[Hg(CH{=}CH_2)_2]$	^{199}Hg	1159	*225a*

[a] COD = 1,5-cyclooctadiene. [b] Olefinic carbon. [c] acac = acetylacetonate.
[d] tfac = trifluoroacetylacetonate. [e] hfac = hexafluoroacetylacetonate. [f] At −80°C.
[g] Bridging carbonyl group. [h] Terminal carbonyl group.

TABLE XXVIII
VALUES OF $^1J(^{183}W—^{13}C)$ FOR THE CARBONYL GROUP IN SOME COMPLEXES OF TUNGSTEN

Compound	$^1J(^{183}W—^{13}C)$				References
$[W(CO)_6]$		125.0	126		*26, 52a 80, 93, 161*
		cis[a]		*trans*[b]	
$[W(CO)_5PEt_3]$		129		142	*161*
$[W(CO)_5PBu^n{}_3]$	122	124.4		142.1	*26, 52a, 80*
$[W(CO)_5PPh_3]$		129		—	*93*
$[W(CO)_5AsPh_3]$		124		—	*93*
$[W(CO)_5SbPh_3]$		127		—	*93*
$[W(CO)_5BiPh_3]$		126		—	*93*
$[W(CO)_5P(OMe)_3]$	123	125.1	135	139.1	*26, 80, 93, 161*
$[W(CO)_5P(OEt)_3]$		125.1		138.5	*26, 80*
$[W(CO)_5NH_2C_6H_{11}]$		132		—	*161*
$[W(CO)_5C(OMe)Ph]$		125		—	*52a*
fac-$[W(CO)_3(PEt_3)_3]$		135			*161*
$[(Durene)W(CO)_3]$		186			*158*

[a] Carbonyl group cis to substituent.

[b] Carbonyl group trans to substituent.

TABLE XXIX
VALUES OF $^1J(^{195}Pt—^{13}C)$ FOR COMPLEXES OF PLATINUM

Compound	$^1J(^{195}Pt—^{13}C)$		References
	Methyl carbon(s)	Olefinic or acetylenic carbon(s)	
cis-$[PtMe_2(PMe_2Ph)_2]$	594	—	*41*
cis-$[PtMe_2(AsMe_3)_2]$	689	—	*45*
cis-$[PtMe_2(AsMe_2Ph)_2]$	685	—	*41*
trans-$[PtMe\{C(OMe)Me\}(AsMe_3)_2][PF_6]$	360 759[a]	—	*45*
trans-$[PtMe(CO)(AsMe_3)_2][PF_6]$	470 1000[b]	—	*45*
trans-$[PtMe(CNMe)(AsMe_3)_2][PF_6]$	476	—	*45*
trans-$[PtMe(C_2H_4)(AsMe_3)_2][PF_6]$	615	50	*46*
trans-$[PtMe(NCC_6F_5)(AsMe_3)_2][PF_6]$	616	—	*45*
trans-$[PtMe(MeC{\equiv}CMe)(AsMe_3)_2][PF_6]$	632	18	*46*
trans-$[PtMeCl(AsMe_3)_2]$	643	—	*45*
$K[(C_2H_4)PtCl_3]$	—	188 195	*46, 187*
$[(Ph_3P)_2Pt(C_2H_4)]$	—	194	*46*
$[(Ph_3P)_2Pt(MeC{\equiv}CMe)]$	—	52	*46*
K[(*cis*-2-Butene)$PtCl_3$]	—	174.5	*187*
K[(*trans*-2-Butene)$PtCl_3$]	—	178.1	*187*
$[(COD)PtCl_2]$[c]	—	153	*187*
$[(COD)PtI_2]$[c]	—	124	*46*
$[(COD)Pt(CF_3)_2]$[c]	—	56	*46*
$[(COD)PtMe_2]$[c]	773	55	*46*
$[(C_{10}H_{12})PtCl_2]$[d]	—	144	*187*
fac-$[PtMe_3Cl(AsMe_2Ph)_2]$	573[e] 652[f]	—	*42*
fac-$[PtMe_3Br(AsMe_2Ph)_2]$	567[e] 646[f]	—	*42*
fac-$[PtMe_3I(AsMe_3)_2]$	556[e] 623[f]	—	*45*
fac-$[PtMe_3I(AsMe_2Ph)_2]$	562[e] 625[f]	—	*42*
fac-$[PtMe_3I(PMe_2Ph)_2]$	501[e] 625[f]	—	*42*
cis-$[PtMe_4(AsMe_2Ph)_2]$	613[e] 413[f]	—	*42*
cis-$[PtPh_2(PEt_3)_2]$	817[g]	—	*166*
trans-$[PtPh_2(PEt_3)_2]$	594[g]	—	*166*
$[PtCl_2Ph_2(PEt_3)_2]$	815[g]	—	*166*
$[Pt(CN)_4]^{2-}$	1035[h]	—	*196*

[a] Carbene carbon. [b] Carbonyl carbon. [c] COD = 1.5-cyclooctadiene.
[d] $C_{10}H_{12}$ = cyclopentadiene dimer. [e] Carbon *trans* to phosphorus or arsenic.
[f] Carbon *trans* to halogen or methyl. [g] Phenyl carbon. [h] Cyanide carbon.

TABLE XXX

A COMPARISON OF COUPLING CONSTANTS CALCULATED USING EQ. (13) AND EXPERIMENTAL VALUES

Compound	n	γ (rad sec^{-1} $T^{-1} \times 10^{-8}$)	α_M	α_{MC}	Z^*	K	^1J(M—^{13}C) Observed	^1J(M—^{13}C) Calculated
[^{13}CH$_4$]	1	2.67519	1	0.25	1.00	1.00	125	111
[^{11}BPh$_4$]$^-$	2	0.85830	0.25	0.33	3.4	1.00	49.5	57.5
[^{13}CMe$_4$]	2	0.67266	0.25	0.256	3.44	1.00	36.2	(36.2)
[^{27}AlMe$_4$]$^-$	3	0.69707	0.25	0.25	6.0	1.02	—	58.7
[^{29}SiMe$_4$]	3	0.53143	0.25	0.291	6.63	1.02	50.2	70.3
[^{31}PMe$_4$]$^+$	3	1.0829	0.25	0.205	6.72	1.03	55.5	99.1
[^{51}V(CO)$_6$]$^-$	4	0.7031	0.167	0.50	8.2	1.06	116	88.6
[^{55}Mn(CO)$_6$]$^+$	4	0.6598	0.167	0.50	9.0	1.07	—	110
[^{57}Fe(CO)$_5$]	4	0.08645	0.20	0.50	9.3	1.07	23.2	19.2
[^{57}Fe(CO)$_4$]$^{2-}$	4	0.08645	0.25	0.50	9.3	1.07	—	24.0
[^{59}Co(CO)$_4$]$^-$	4	0.63173	0.25	0.50	9.6	1.075	287	194
[^{73}GeMe$_4$]	4	0.093320	0.25	0.256	11.6	1.11	18.7	26.8
[^{95}Mo(CO)$_6$]	5	0.1743	0.167	0.50	12.0	1.20	68	40
[^{111}CdMe$_2$]	5	0.5673	0.50	0.240	15.4	1.28	512	420
[^{119}SnMe$_4$]	5	0.9971	0.25	0.137	16.5	1.30	330	262
[^{183}W(CO)$_6$]	6	0.11132	0.167	0.50	15.6^a	1.98	126	137
[^{187}Os(CO)$_5$]	6	0.06161	0.20	0.50	19.0	2.06	—	91.6
[^{199}HgMe$_2$]	6	0.47691	0.50	0.222	20.7	2.25	689	808
[^{203}TlMe$_3$]	6	1.5289	0.333	0.25	21.4	2.32	—	2410
[^{207}PbMe$_4$]	6	0.55970	0.25	0.196	20.5	2.39	251	432

[a] Calculated using Eq. (9) in ref. (*207*) and data for [WMe$_6$] (*201*).

TABLE XXXI

VALUES OF INDIRECT COUPLING CONSTANTS INVOLVING CARBON, ACROSS METALS

Compound	Nature of coupling constant	Magnitude of coupling constant	References
$[\mathrm{HMn(CO)_5}]$	$^{2}J(^{1}\text{H—Mn—}^{13}\text{C})$	7.0[a] 14.0[b]	*227*
cis-$[\mathrm{HMn(CO)_4PPh_3}]$	$^{2}J(^{1}\text{H—Mn—}^{13}\text{C})$	5.2[a] 15.7[c] 12.1[d]	*227*
$\mathrm{Na[HMo_2(CO)_{10}]}$	$^{2}J(^{1}\text{H—Mo—}^{13}\text{C})$	4.3[b,e]	*227*
$\mathrm{Na[HW_2(CO)_{10}]}$	$^{2}J(^{1}\text{H—W—}^{13}\text{C})$	4.3[a] 3.5[b]	*227*
$[(\mathrm{C_5H_5})\mathrm{W(CO)_3H}]$	$^{2}J(^{1}\text{H—W—}^{13}\text{C})$	~ 5.5[a] 18.5[b]	*79*
$\mathrm{K_3[RhH(CN)_5]}$	$^{2}J(^{1}\text{H—Rh—}^{13}\text{C})$	56.2[a] 5.7[b]	*227*
$\mathrm{K_3[IrH(CN)_5]}$	$^{2}J(^{1}\text{H—Ir—}^{13}\text{C})$	37.2[a] 5.7[b]	*227*
trans-$[\mathrm{PtH(CN)(PEt_3)_2}]$	$^{2}J(^{1}\text{H—Pt—}^{13}\text{C})$	41.9	*227*
$\mathrm{HgMe_2}$	$^{3}J(^{1}\text{H—}^{13}\text{C})$	−1.8	*69*
		0.0	*154*
$[\mathrm{SiH_2Me_2}]$	$^{2}J(^{1}\text{H—Si—}^{13}\text{C})$	+6.0	*199*
$[\mathrm{SiHMe_3}]$	$^{2}J(^{1}\text{H—Si—}^{13}\text{C})$	+7.2	*199*
$[\mathrm{GeH_2Me_2}]$	$^{2}J(^{1}\text{H—Ge—}^{13}\text{C})$	+7.6	*199*
$[\mathrm{SnH_2Me_2}]$	$^{2}J(^{1}\text{H—Sn—}^{13}\text{C})$	+9.2	*199*
$[\mathrm{SnH_2Ph_2}]$	$^{2}J(^{1}\text{H—Sn—}^{13}\text{C})$	+10.4	*199*
$[\mathrm{SnHMe_3}]$	$^{2}J(^{1}\text{H—Sn—}^{13}\text{C})$	+10.8	*199*
$[\mathrm{PbHMe_3}]$	$^{2}J(^{1}\text{H—Pb—}^{13}\text{C})$	+15.5	*199*
$\mathrm{SeMe_2}$	$^{3}J(^{1}\text{H—}^{13}\text{C})$	+4.0	*69*
SeMeH	$^{2}J(^{1}\text{H—}^{13}\text{C})$	−2.4	*69*
$\mathrm{TeMe_2}$	$^{3}J(^{1}\text{H—}^{13}\text{C})$	+3.1	*69*
$[\mathrm{HgMe_2}]$	$^{2}J(^{13}\text{C—Hg—}^{13}\text{C})$	+22.4	*68*
$[\mathrm{SnMe_4}]$	$^{2}J(^{13}\text{C—Sn—}^{13}\text{C})$	+4.0	*199*
$[\mathrm{PbMe_4}]$	$^{2}J(^{13}\text{C—Pb—}^{13}\text{C})$	+5.0	*199*
$[\mathrm{SeMe_2}]$	$^{2}J(^{13}\text{C—Se—}^{13}\text{C})$	0.8	*69*
$[\mathrm{TeMe_2}]$	$^{2}J(^{13}\text{C—Te—}^{13}\text{C})$	0.2	*69*
$\mathrm{[Me_4N]_2Fe[1,7\text{-}B_9H_9CHPCr(CO)_5]_2}$	$^{2}J(^{13}\text{C—Cr—}^{31}\text{P})$	12[b]	*14*
$[\mathrm{Mo(CO)_5P(OMe)_3}]$	$^{2}J(^{13}\text{C—Mo—}^{31}\text{P})$	18.3[a] 7.3[b]	*26*

Continued

TABLE XXXI—*Continued*

Compound	Nature of coupling constant	Magnitude of coupling constant	References
[Mo(CO)$_5$P(OEt)$_3$]	$^2J(^{13}C—Mo—^{31}P)$	18.9^a 6.7^b	*26*
[Mo(CO)$_5$P(OPr^i)$_3$]	$^2J(^{13}C—Mo—^{31}P)$	12.2^a 14.6^b	*26, 80*
[Me$_4$N][7,9-B$_9$H$_{10}$CHPMo(CO)$_5$]	$^2J(^{13}C—Mo—^{31}P)$	26^a 8	*14, 217*
trans-[Mo(CO)$_4${P(OMe)$_3$}$_2$]	$^2J(^{13}C—Mo—^{31}P)$	13.4	*26*
cis-[Mo(CO)$_4$(Ph$_2$PCH$_2$CH$_2$PPh$_2$)]	$^2J(^{13}C—Mo—^{31}P)$	24.0^a 8.4^b	*26*
[W(CO)$_5$PEt$_3$]	$^2J(^{13}C—W—^{31}P)$	19^a 6^b	*161*
[W(CO)$_5$PBu^n$_3$]	$^2J(^{13}C—W—^{31}P)$	18.9^a 7.3^b	*26*
[W(CO)$_5$PPh$_3$]	$^2J(^{13}C—W—^{31}P)$	22^a 7^b	*93*
[W(CO)$_5$PPh$_2$OBu^n]	$^2J(^{13}C—W—^{31}P)$	27^a 9^b	*93*
[W(CO)$_5$PPh(OBu^n)$_2$]	$^2J(^{13}C—W—^{31}P)$	29^a 9^b	*93*
[W(CO)$_5$P(OBu^n)$_3$]	$^2J(^{13}C—W—^{31}P)$	36^a 9^b	*93*
[W(CO)$_5$P(OEt)$_3$]	$^2J(^{13}C—W—^{31}P)$	36.6^a 10.9^b	*26*
[W(CO)$_5$P(OMe)$_3$]	$^2J(^{13}C—W—^{31}P)$	37.2^a 11.6^b 36^a 10^b	*26, 161*
[W(CO)$_5$P(OPh)$_3$]	$^2J(^{13}C—W—^{31}P)$	45.4^a 10.5^b	*93*
cis-[W(CO)$_4$(PEt$_3$)$_2$]	$^2J(^{13}C—W—^{31}P)$	$15.2^{a,g}$ 6.3^b	*161*
trans-[W(CO)$_4$(PEt$_3$)$_2$]	$^2J(^{13}C—W—^{31}P)$	5	*161*
cis-[W(CO)$_4$(Ph$_2$PCH$_2$CH$_2$PPh$_2$)]	$^2J(^{13}C—W—^{31}P)$	9^b	*26*
fac-[W(CO)$_3$(PEt$_3$)$_3$]	$^2J(^{13}C—W—^{31}P)$	14^a 5.5^b	*161*
[(C$_5$H$_5$)W(CO)$_2$(PR$_3$)(SnMe$_3$)]	$^2J(^{13}C—W—^{31}P)$	17.5	*94a*
[(C$_5$H$_5$)W(CO)$_2${P(OR)$_3$}(SnMe$_3$)]	$^2J(^{13}C—W—^{31}P)$	25.0	*94a*
[Fe(CO)$_4$PEt$_3$]	$^2J(^{13}C—Fe—^{31}P)$	19	*161a*
[Fe(CO)$_4$PEt$_2$Ph]	$^2J(^{13}C—Fe—^{31}P)$	19	*161a*
[Fe(CO)$_4$PEtPh$_2$]	$^2J(^{13}C—Fe—^{31}P)$	19	*161a*
[Fe(CO)$_3$(PEt$_3$)$_2$]	$^2J(^{13}C—Fe—^{31}P)$	28	*161a*
[Fe(CO)$_3$(PPh$_3$)$_2$]	$^2J(^{13}C—Fe—^{31}P)$	28	*161a*
[Fe(CO)$_3$(Me$_2$PCH$_2$CH$_2$PMe$_2$)]	$^2J(^{13}C—Fe—^{31}P)$	6.9	*1*
cis-[RuCl$_2$(CO)$_2$(PEt$_3$]$_2$	$^2J(^{13}C—Ru—^{31}P)$	10.6	*95*

cis-$[RuCl_2(CO)_2(PEt_2Ph)_2]$	$^2J(^{13}C—Ru—^{31}P)$	11.0	*95*
cis-$[RuCl_2(CO)_2(PEtPh_2)_2]$	$^2J(^{13}C—Ru—^{31}P)$	10.6	*95*
cis-$[RuCl_2(CO)_2(PBu^n{}_2Bu^t)_2]$	$^2J(^{13}C—Ru—^{31}P)$	11.0	*95*
cis-$[RuCl_2(CO)_2((PEt_2Bu^t)_2]$	$^2J(^{13}C—Ru—^{31}P)$	10.9	*95*
cis-$[RuCl_2(CO)_2(PMeBu^t{}_2)_2]$	$^2J(^{13}C—Ru—^{31}P)$	10.7	*95*
cis-$[OsCl_2(CO)_2(PPr^nBu^t)_2]$	$^2J(^{13}C—Ru—^{31}P)$	7.3	*95*
$[Os(CO)(NO)(PPh_3)_2(C_2H_4)][PF_6]$	$^2J(^{13}C—Os—^{31}P)$	9	*116a*
cis-$[PtMe_2(PMe_2Ph)_2]$	$^2J(^{13}C—Pt—^{31}P)$	104[a] 9[b]	*41*
$[(Ph_3P)_2Pt(C_2H_4)]$	$^2J(^{13}C—Pt—^{31}P)$	24[g]	*46*
$[(Ph_3P)_2Pt(MeC\equiv CMe)]$	$^2J(^{13}C—Pt—^{31}P)$	27[g]	*46*
trans-$[PtMe(C_2H_4)(PMe_2Ph)_2][PF_6]$	$^2J(^{13}C—Pt—^{31}P)$	6	*46*
trans-$[PtMe(MeC\equiv CMe)(PMe_2Ph)_2][PF_6]$	$^2J(^{13}C—Pt—^{31}P)$	6	*46*
Sn_2Me_6	$^2J(^{119}Sn—Sn—^{13}C)$	−56	*146*
Pb_2Me_6	$^2J(^{207}Pb—Pb—^{13}C)$	+92	*51*

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[a] Coupling between mutually trans nuclei.

[b] Coupling between mutually cis nuclei.

[c] Carbonyl cis to PPh_3.

[d] Carbonyl trans to PPh_3.

[e] $^2J(^1H—Mo—^{13}C)$ (trans) is either 4.3 Hz or less than 3.0 Hz.

[f] Fluxional.

[g] $^2J(^{13}C—M—^{31}P)$(trans) + $^2J(^{13}C—M—^{31}P)$(cis).

TABLE XXXII
VALUE OF INDIRECT COUPLING CONSTANTS INVOLVING CARBON, NOT ACROSS METALS

Compound	Nature of coupling constant	Magnitude of coupling constant	References
$Na[BPh_4]$	$^2J(^{11}B—^{13}C)$	1.3	*161a*
	$^3J(^{11}B—^{13}C)$	2.6	*225*
$[PhC{\equiv}CSiMe_3]$	$^2J(^{13}C—^{29}Si)$	16.1	*136*
$[SnEt_4]$	$^2J(^{13}C—^{117,119}Sn)$	−23.5	*225*
$[(Ph_3P)_2Pt(MeC{\equiv}CMe)]$	$^2J(^{13}C—C—^{195}Pt)$	9	*46*
cis-$[PtMe_2(PMe_2Ph)_2]$	$^2J(^{13}CH_3—^{195}Pt)$	28	*41*
cis-$[PtMe_2(AsMe_2Ph)_2]$	$^2J(^{13}CH_3—^{195}Pt)$	20	*41*
cis-$[PtMe_2(AsMe_3)_2]$	$^2J(^{13}C—^{195}Pt)$	19	*45*
trans-$[PtMeCl(AsMe_3)_2]$	$^2J(^{13}C—^{195}Pt)$	53	*45*
trans-$[PtMe(CO)(AsMe_3)_2][PF_6]$	$^2J(^{13}C—^{195}Pt)$	42	*45*
trans-$[PtMe\{C(OMe)Me\}(AsMe_3)_2][PF_6]$	$^2J(^{13}C—As—^{195}Pt)$	50	*45*
	$^2J(^{13}C—C—^{195}Pt)$	86	*45*
	$^3J(^{13}C—^{195}Pt)$	67	*45*
trans-$[PtMe(NCC_6F_5)(AsMe_3)_2][PF_6]$	$^2J(^{13}C—^{195}Pt)$	49	*45*
cis-$[PtPh_2(PEt_3)_2]$	$^2J(^{13}C—C—^{195}Pt)$	36	*166*
	$^3J(^{13}C—C—C—^{195}Pt)$	64	*166*
	$^2J(^{13}C—P—^{195}Pt)$	16	*166*
trans-$[PtPh_2(PEt_3)_2]$	$^3J(^{13}C—C—C—^{195}Pt)$	42	*166*
	$^2J(^{13}C—P—^{195}Pt)$	23	*166*
$[PtCl_2Ph_2(PEt_3)_2]$	$^3J(^{13}C—C—C—^{195}Pt)$	51	*166*
	$^2J(^{13}C—P—^{195}Pt)$	20	*166*
fac-$[PtClMe_3(AsMe_2Ph)_2]$	$^2J(^{13}CH_3—^{195}Pt)$	∼ 10 ∼ 5	*42*
fac-$[PtBrMe_3(AsMe_2Ph)_2]$	$^2J(^{13}CH_3—^{195}Pt)$	11 4	*42*
fac-$[PtIMe_3(AsMe_2Ph)_2]$	$^2J(^{13}CH_3—^{195}Pt)$	∼ 10 ∼ 0	*42*
fac-$[PtIMe_3(AsMe_3)_2]$	$^2J(^{13}C—^{195}Pt)$	7	*45*
cis-$[PtMe_4(AsMe_2Ph)_2]$	$^2J(^{13}CH_3—^{195}Pt)$	7	*42*

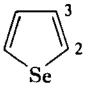
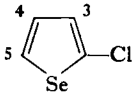
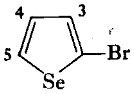
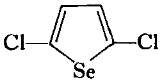
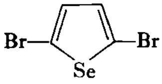
$[\mathrm{HgPh_2}]$	$^{2}J(^{13}\mathrm{C}{-}^{199}\mathrm{Hg})$	88	*225, 225a*
	$^{3}J(^{13}\mathrm{C}{-}^{199}\mathrm{Hg})$	101.6	*225, 225a*
	$^{4}J(^{13}\mathrm{C}{-}^{199}\mathrm{Hg})$	17.8	*225, 225a*
$[\mathrm{HgEt_2}]$	$^{2}J(^{13}\mathrm{C}{-}^{199}\mathrm{Hg})$	24	*225a*
$[\mathrm{HgPr^{n}_2}]$	$^{2}\mathrm{J}(^{13}\mathrm{C}{-}^{199}\mathrm{Hg})$	−25.2	*225a*
	$^{3}J(^{13}\mathrm{C}{-}^{199}\mathrm{Hg})$	102.6	
$[\mathrm{HgPr^{i}_2}]$	$^{2}J(^{13}\mathrm{C}{-}^{199}\mathrm{Hg})$	32.2	*225a*
$[\mathrm{HgBu^{n}_2}]$	$^{2}J(^{13}\mathrm{C}{-}^{199}\mathrm{Hg})$	−26.3	*225, 225a*
	$^{3}J(^{13}\mathrm{C}{-}^{199}\mathrm{Hg})$	100	*225, 225a*
$[\mathrm{MeHgCH_2CMe_3}]$	$^{3}J(^{13}\mathrm{C}{-}^{199}\mathrm{Hg})$	29.5	*203*
	$^{3}J(^{13}\mathrm{C}{-}^{199}\mathrm{Hg})$	71.5	*203*
$[\mathrm{Hg(CH_2CMe_3)_2}]$	$^{2}J(^{13}\mathrm{C}{-}^{199}\mathrm{Hg})$	29.0	*203*
	$^{3}J(^{13}\mathrm{C}{-}^{199}\mathrm{Hg})$	71.0	*203*
$[\mathrm{Hg(CH{=}CH_2)(CH_2CMe_3)}]$	$^{2}J(^{13}\mathrm{CMe_3}{-}^{199}\mathrm{Hg})$	31.0	*203*
	$^{2}J(^{13}\mathrm{CH_2}{-}^{199}\mathrm{Hg})$	38	*203*
	$^{3}J(^{13}\mathrm{C}{-}^{199}\mathrm{Hg})$	75.0	*203*
$[\mathrm{Hg(CN)(CH_2CMe_3)}]$	$^{2}J(^{13}\mathrm{C}{-}^{199}\mathrm{Hg})$	51.0	*203*
	$^{3}J(^{13}\mathrm{C}{-}^{199}\mathrm{Hg})$	120.0	*203*
$[\mathrm{HgCl(CH_2CMe_3)}]$	$^{2}J(^{13}\mathrm{C}{-}^{199}\mathrm{Hg})$	70.0	*203*
	$^{3}J(^{13}\mathrm{C}{-}^{199}\mathrm{Hg})$	149.0	*203*
$[\mathrm{HgBr(CH_2CMe_3)}]$	$^{2}J(^{13}\mathrm{C}{-}^{199}\mathrm{Hg})$	69.5	*203*
	$^{3}J(^{13}\mathrm{C}{-}^{199}\mathrm{Hg})$	148.0	*203*
$[\mathrm{Hg(O_2CCH_3)(CH_2CMe_3)}]$	$^{2}J(^{13}\mathrm{CMe_3}{-}^{199}\mathrm{Hg})$	71.0	*203*
	$^{3}J(^{13}\mathrm{C}{-}\mathrm{C}{-}\mathrm{C}{-}^{199}\mathrm{Hg})$	150.0	*203*
$[\mathrm{Hg(NO_3)(CH_2CMe_3)}]$	$^{2}J(^{13}\mathrm{C}{-}^{199}\mathrm{Hg})$	85.0	*203*
	$^{3}J(^{13}\mathrm{C}{-}^{199}\mathrm{Hg})$	170.0	*203*

TABLE XXXIII

VALUES OF $J(^{13}C^{1}H)$ FOR SOME MISCELLANEOUS COMPOUNDS

Compound	$^{1}J(^{13}C—^{1}H)$	References
$[MeLi)_4$	96 to 116[a]	*124, 151, 152*
$[PhCH_2Li]$	116 to 135[a]	*222, 223*
$[Ph_2CHLi]$	142	*222*
$[Pr^nCH_2Li]$	98 to 100[a]	*150*
$[Me_2Be]$	105.5	*124*
$[MeMgCl]$	107.7	*85*
$[Ti(CH_2Ph)_4]$	132.0	*229a*
$[Zr(CH_2Ph)_4]$	136.0	*229a*
$[\{(MeC_5H_4)Fe(CO)_2\}_2\mathbf{C_4H_4}]$	158	*35*
$[(\sigma\text{-}\mathbf{C_5H_5})Fe(CO)_2(\pi\text{-}C_5H_5)]$	161.2	*103*
trans-$[PtIMe(PPh_3)_2]$	133.0	*53*
trans-$[PtBrMe(PPh_3)_2]$	133.0	*53*
trans-$[PtClMe(PPh_3)_2]$	131.0	*53*
trans-$[PtMe(NO_3)(PPh_3)_2]$	132.5	*53*
trans-$[PtMe(NO_2)(PPh_3)_2]$	130.0	*53*
trans-$[PtMe(NCS)(PPh_3)_2]$	129.5	*53*
trans-$[PtMe(N_3)(PPh_3)_2]$	131.0	*53*
cis-$[PtMe_2(PMe_2Ph)_2]$	132.0	*41*
cis-$[PtMe_2(AsMe_2Ph)_2]$	125.9	*41*
$[Me_2Cd]$	126.6	*226*
$[Me_2Hg]$	129.6 130	*62, 68, 154 172, 226*
$[Hg(\mathbf{CH_2}Ph)_2]$	135.0	*229a*
$[MeHg\mathbf{CH_2}CMe_3]$	126.5	*203*
$[Hg(\mathbf{CH_2}CMe_3)_2]$	126.0	*203*
$[Hg(CH{=}CH_2)(\mathbf{CH_2}CMe_3)]$	127.5	*203*
$[Hg(CN)(\mathbf{CH_2}CMe_3)]$	133.8 to 135.0[b]	*203*
$[HgCl(\mathbf{CH_2}CMe_3)]$	135.0 to 138.0[b]	*203*
$[HgBr(\mathbf{CH_2}CMe_3)]$	135.5 to 139.0[b]	*203*
$[Hg(O_2CMe)(\mathbf{CH_2}CMe_3)]$	137.0 to 139.0[b]	*203*
$[Hg(NO_2)(\mathbf{CH_2}CMe_3)]$	138.0	*203*
$[Hg(C_6H_5)_2]$	160	*178a*
$[1,2\text{-}B_{10}H_{10}C_2H_2]$	204	*52*
$[1,7\text{-}B_{10}H_{10}C_2H_2]$	184	*52*
$Cs[B_{11}H_{11}CH]$	163	*52*
$[Me_3NH][7,8\text{-}B_9C_2H_{12}]$	142	*52*
$[Me_3NH][7,9\text{-}B_9C_2H_{12}]$	140	*52*
$[Me_4N][(\pi\text{-}7,8\text{-}B_9C_2H_{10})_2Co]$	140	*86*
$[B(CH_2Ph)_3]$	116.0	*229a*
$[Al_2Me_6]$	113	*172*
$[GaMe_3]$	122	*172*
$[InMe_3]$	126	*172*
cis-$[PtMe_2(As\mathbf{Me_2}Ph)_2]$	133.9	*41*

TABLE XXXIII—*Continued*

Compound	$^1J(^{13}C—^1H)$	References
[$Et_2AsC{\equiv}CH$]	132.8	*202*
[Me_2Se]	139.0 140.3	*69, 144*
[Me_3Se]I	145.8	*144*
[Me_2Se_2]	141.7	*144*
[MeSeH]	142.7	*69*
	C-2, 187.23 C-3, 164.62	*191*
	C-3, 169.15 C-4, 167.17 C-5, 189.96	*191*
	C-3, 169.69 C-4, 167.32 C-5, 189.58	*191*
	171.61	*191*
	171.42	*191*
[$PhSeC{\equiv}CMe$]	132.3	*202*
[Me_2Te]	139.7 140.7	*69, 144*
[Me_3Te]I	146.0	*144*

[a] Solvent-dependent.

[b] Concentration-dependent.

TABLE XXXIV

VALUES OF $J(^{13}C—^{1}H)$ FOR SOME π COMPLEXES OF TRANSITION METALS

Compound	$^{1}J(^{13}C—^{1}H)$	References
$[(C_2H_4)_2Rh(C_5H_5)]$	160	*21*
$[(C_2H_4)_2Rh(acac)]$[a]	158	*21*
$[(C_2H_4)Pt(PPh_3)_2]$	146.5	*53*
$[(C_2H_2)Pt(PPh_3)_2]$	210.0	*53*
$[(COD)Rh(C_5H_5)]$[b]	152[c]	*21*
$[(COD)Rh(acac)]$[a,b]	156	*21*
$[(COD)Rh(tfac)]$[b,d]	154	*21*
$[(COD)Rh(hfac)]$[b,e]	152	*21*
$[(nbd)Rh(C_5H_5)]$[f]	176[c]	*21*
$[(1\text{-}MeC_3H_4)NiCl]_2$	C-1, 159	
	C-2, 163	*147*
	C-3, 161	
	Me 124	
$[(1\text{-}MeC_3H_4)NiBr]_2$	C-1, 161	
	C-2, 165	*147*
	C-3, 161	
	Me 124	
$[(1\text{-}MeC_3H_4)NiI]_2$	C-1, 162	
	C-2, 161	*147*
	C-3, 161	
$[(2\text{-}MeC_3H_4)Pd(C_5H_5)]$	157.3 159.3	*163*
$[(C_4H_4)Fe(CO)_3]$	191	*188*
$[(C_4H_3X)Fe(CO)_3]$	187.4 to 196.8	*28a*
$[(C_4H_2R_2)Fe(CO)_3]$	189.2 189.5	*28b*
$[(C_4H_6)Fe(CO)_3]$	C-1,4, 161 160	*188, 192*
	C-2,3, 171 170	
$[(C_5H_5)Mn(CO)_3]$	175	*129*
$[(C_5H_5)Mo(CO)_3Et]$	175	*129*
$[(C_5H_5)_2Fe]$	174.81 6.30[g]	*58, 129,*
	7.22[h] 175	*172*
$[(\pi\text{-}C_5H_5)Fe(CO)_2(\sigma\text{-}C_5H_5)]$	180.8	*103*
$[\{(\pi\text{-}C_5H_5)Fe(CO)_2\}_2Sn(C_5H_5)_2]$	178.5	*103*
$[(C_5H_5)_2Ru]$	176.3 6.3[g] 7.3[h]	*58*
$[(C_5H_5)_2Co]Cl$	185.54 6.26[g] 7.17[h]	*58*
$[(C_5H_5)Rh(COD)]$[b]	167	*21*
$[(C_5H_5)Rh(C_2H_4)_2]$	174	*21*
$[(C_5H_5)Rh(nbd)]$[f]	172	*21*
$[(C_5H_5)Rh(CO)_2]$	176	*21*
$[(C_5H_5)Pd(2\text{-}MeC_3H_4)]$	171.1	*163*
$[(C_6H_6)Cr(CO)_3]$	173	*74*
$[(p\text{-}Xylene)Cr(CO)_3]$	C—H, 172	*74*
	Me 127.5	*74*
$[(Mesitylene)Cr(CO)_3]$	C—H, 172	
	Me 129.0	*74*

[a] acac = acetylacetonate. [b] COD = 1,5-cyclooctadiene. [c] Olefinic C—H. [d] tfac = trifluoroacetylacetonate. [e] hfac = hexafluoroacetylacetonate. [f] nbd = norbornadiene. [g] $^{2}J(^{13}C—^{1}H)$. [h] $^{3}J(^{13}C—^{1}H)$.

TABLE XXXV

VALUES OF $^1J(^{13}C—^1H)$ FOR SOME DERIVATIVES OF SILICON

Compound	$^1J(^{13}C—^1H)$	References
$[\mathrm{Me_4Si}]$	118.1 118.2 119 121 118, 120	*61, 67, 71,* *111a, 128, 172,* *206, 209, 226*
$[\mathrm{Me_3SiH}]$	119.2 119.35	*71, 111a*
$[\mathbf{Me}_3\mathrm{SiPh}]$	119.0	*111a*
$[\mathrm{Me_3SiF}]$	118.9 120.0	*71, 111a*
$[\mathrm{Me_3SiCl}]$	120.5 120.77	*71, 111a*
$[\mathrm{MeSiBr}]$	121.2	*71*
$[\mathrm{Me_3SiI}]$	121.8	*71*
$[\mathrm{Me_3SiCN}]$	122	*173*
$[\mathbf{Me}_3\mathrm{SiOMe}]$	118.0	*111a*
$[\mathbf{Me}_3\mathrm{SiOEt}]$	118.0	*111a*
$[\mathbf{Me}_3\mathrm{SiOAc}]$	119.5	*111a*
$[\mathrm{(Me_3Si)_2O}]$	117.9	*71*
$[\mathrm{(Me_3Si)_2S}]$	120.2	*71*
$[\mathrm{(Me_3Si)_2NH}]$	118.0	*71*
$[\mathrm{(Me_3Si)_3SiH}]$	120.5	*33*
$[\mathrm{Me_3SiNMeSnMe_3}]$	118.0	*197*
$[\mathrm{(Me_3SiNMe)_2SnMe_2}]$	117.5	*197*
$[\mathrm{(Me_3SiNMe)_3SnMe}]$	117.5	*197*
$[\mathrm{(Me_3SiNMe)_4Sn}]$	118.0	*197*
$[\mathrm{Me_3Si}\mathbf{C}_6\mathbf{H}_5]$	167 161.3	*102, 103*
$[\mathrm{Me_2SiH_2}]$	120.7 120.8	*71, 111a*
$[\mathrm{Me_2SiHF}]$	120.0	*71*
$[\mathrm{Me_2SiHCl}]$	121.8	*71*
$[\mathrm{Me_2SiHBr}]$	122.4	*71*
$[\mathrm{Me_2SiHI}]$	123.1	*71*
$[\mathrm{(Me_2SiH)_2O}]$	118.8	*71*
$[\mathrm{(Me_2SiH)_2S}]$	121.4	*71*
$[\mathrm{(Me_2SiH)_2NH}]$	119.5	*71*
$[\mathrm{(Me_2SiH)_3N}]$	119.3	*71*
$[p\text{-}\mathrm{Me_2NC_6H_4SiMe_2H}]$	120.1	*176*
$[p\text{-}\mathrm{MeOC_6H_4SiMe_2H}]$	120.4	*176*
$[p\text{-}\mathrm{MeC_6H_4SiMe_2H}]$	120.3	*176*
$[m\text{-}\mathrm{MeC_6H_4SiMe_2H}]$	120.5	*176*
$[\mathrm{C_6H_5SiMe_2H}]$	120.8	*176*
$[p\text{-}\mathrm{ClC_6H_4SiMe_2H}]$	121.0	*176*
$[m\text{-}\mathrm{ClC_6H_4SiMe_2H}]$	121.0	*176*
$[p\text{-}\mathrm{MeOC_6H_4SiMe_2H}]$	120.5	*38*
$[\mathrm{C_6H_5CH_2SiMe_2H}]$	120.9	*38*
$[p\text{-}\mathrm{ClC_6H_4CH_2SiMe_2H}]$	121.2	*38*
$[m\text{-}\mathrm{ClC_6H_4CH_2SiMe_2H}]$	121.6	*38*
$[m\text{-}\mathrm{FC_6H_4CH_2SiMe_2H}]$	121.3	*38*
$[p\text{-}\mathrm{MeC_6H_4CH_2SiMe_2H}]$	120.5	*38*

Continued

TABLE XXXV—*Continued*

Compound	$^1J(^{13}\text{C—}^1\text{H})$	References
$[m\text{-MeC}_6\text{H}_4\text{CH}_2\text{SiMe}_2\text{H}]$	120.6	*38*
$[m\text{-MeOC}_6\text{H}_4\text{CH}_2\text{SiMe}_2\mathbf{H}]$	121.0	*38*
$[p\text{-MeOC}_6\text{H}_4\text{Si}\mathbf{Me}_2\text{SiMe}_2\mathbf{H}]$	120.3	*38*
$[\text{C}_6\text{H}_5\text{Si}\mathbf{Me}_2\text{H}]$	120.5	*38*
$[p\text{-ClC}_6\text{H}_4\text{Si}\mathbf{Me}_2\text{SiMe}_2\text{H}]$	120.4	*38*
$[m\text{-ClC}_6\text{H}_4\text{Si}\mathbf{Me}_2\text{SiMe}_2\mathbf{H}]$	120.7	*38*
$[m\text{-FC}_6\text{H}_4\text{Si}\mathbf{Me}_2\text{SiMe}_2\text{H}]$	120.9	*38*
$[p\text{-MeC}_6\text{H}_4\text{Si}\mathbf{Me}_2\text{SiMe}_2\text{H}]$	120.5	*38*
$[m\text{-MeC}_6\text{H}_4\text{Si}\mathbf{Me}_2\text{SiMe}_2\mathbf{H}]$	120.5	*38*
$[m\text{-MeOC}_6\text{H}_4\text{Si}\mathbf{Me}\ \text{SiMe}_2\mathbf{H}]$	120.8	*38*
$[\mathbf{Me}_2\text{SiPh}_2]$	120.5	*111a*
$[\text{Me}_2\text{Si}(\mathbf{CH}_2\text{Ph})_2]$	122.5	*229a*
$[\mathbf{Me}_2\text{Si(OMe)}_2]$	118.5	*111a*
$[\mathbf{Me}_2\text{Si(OEt)}_2]$	118.2	*111a*
$[\mathbf{Me}_2\text{Si(OAc)}_2]$	121.3	*111a*
$[\mathbf{Me}_2\text{SiCl}_2]$	123.6	*111a*
$[p\text{-Me}_2\text{NC}_6\text{H}_4\text{SiMeH}_2]$	121.1	*176*
$[p\text{-MeOC}_5\text{H}_4\text{SiMeH}_2]$	121.4	*176*
$[p\text{-MeC}_6\text{H}_4\text{SiMeH}_2]$	121.5	*176*
$[m\text{-MeC}_6\text{H}_4\text{SiMeH}_2]$	121.5	*176*
$[\text{C}_6\text{H}_5\text{SiMeH}_2]$	121.6	*176*
$[p\text{-ClC}_6\text{H}_4\text{SiMeH}_2]$	121.6	*176*
$[m\text{-ClC}_6\text{H}_4\text{SiMeH}_2]$	122.1	*176*
$[\text{MeSiHF}_2]$	121.3	*71*
$[\text{MeSiHCl}_2]$	124.2 124.3	*71*
$[\text{MeSiHBr}_2]$	125.1	*71*
$[\text{MeSiHI}_2]$	126.4	*71*
$[(\text{MeSiHF})_2\text{O}]$	120.2	*71*
$[\mathbf{Me}\text{Si(OMe)}_3]$	119.1	*111a*
$[\mathbf{Me}\text{Si(OEt)}_3]$	119.2	*111a*
$[\mathbf{Me}\text{Si(OAc)}_3]$	123.4	*111a*
$[\text{MeSiH}_3]$	123.6	*111a*
$[\text{MeSiCl}_3]$	126 125.5	*28, 111a*
$[\text{Me}_3\text{Si}\mathbf{CH}{=}\text{C}{=}\mathbf{CH}\text{SiMe}_3]$	147	*204*
$[\text{Me}_3\text{SiC}{\equiv}\mathbf{CH}]$	236.2	*202*
$[\text{Ph}_3\text{SiC}{\equiv}\mathbf{CH}]$	239	*202*

TABLE XXXVI

VALUES OF $^1J(^{13}\mathrm{C}—^1\mathrm{H})$ FOR SOME DERIVATIVES OF GERMANIUM, TIN, AND LEAD

Compound	$^1J(^{13}\mathrm{C}—^1\mathrm{H})$	References
$[\mathrm{Me_4Ge}]$	124.5 124.4 124	*67, 206, 209, 219, 226*
$[\mathrm{Me_3GeH}]$	126.2	*219*
$[\mathrm{Me_3GeCl}]$	128.5	*219*
$[\mathrm{Me_{10}Ge_5}]$	126	*37*
$[\mathrm{Me_{12}Ge_6}]$	126	*37*
$[\mathrm{Me_{14}Ge_7}]$	126	*37*
$[\mathrm{Me_2GeH_2}]$	126.8	*219*
$[\mathrm{Bu^n_3GeC{\equiv}CH}]$	236	*128, 183, 195, 209*
$[\mathrm{Me_3Ge}\mathbf{C_5H_5}]$	161 167	*102*
$[\mathrm{Et_3GeC{\equiv}C}\mathbf{Me}]$	131	*202*
$[\mathrm{Et_3GeC{\equiv}CH}]$	236.2	*202*
$[\mathrm{Me_4Sn}]$	126 127.2 128 128.2 128.0	*67, 141, 206, 226*
$[\mathrm{Me_3SnH}]$	128.5	*83*
$[\mathrm{Me_3SnCl}]$	133.0	*28*
$[\mathrm{Me_3SnBr}]$	130.8 131.4^a	*141*
$[\mathbf{Me}_3\mathrm{SnNMeSiMe_3}]$	129.5	*197*
$[\mathbf{Me}_3\mathrm{SnCF_2CFHCF_3}]$	131.0	*50*
$[\mathbf{Me}_3\mathrm{SnCF_2CF_2H}]$	130.0	*50*
$[\mathbf{Me}_3\mathrm{Sn(CF_2)_3CF_2H}]$	130.4	*50*
$[\mathrm{Me_6Sn_2}]$	128.0	*146*
$[\mathrm{Me_2SnH_2}]$	126.5	*83*
$[\mathrm{Me_2SnCl_2}]$	136.0 to 136.4^a 137.8 138	*28, 141*
$[\mathbf{Me}_2\mathrm{Sn(NMeSiMe_2)_2}]$	129.5	*197*
$[\mathrm{MeSnH_3}]$	130	*83*
$[\mathrm{MeSnCl_3}]$	143.0	*28*
$[\mathrm{MeSnBr_3}]$	141.2	*141*
$[\mathrm{MeSnI_3}]$	140	*28*
$[\mathbf{Me}\mathrm{Sn(NMeSiMe_3)_3}]$	131.0	*197*
$[\mathrm{(PhCH_2)_4Sn}]$	133 132.0	*221, 229a*
$[\mathrm{(PhCH_2)_3SnCl}]$	133	*221*
$[\mathrm{(PhCH_2)_3SnH}]$	131	*221*
$[\mathrm{(PhCH_2)_2SnCl_2}]$	136	*221*
$[\mathrm{Me_3SnC_5H_5}]$	161.3 163	*102*
$[(\sigma\text{-}\mathrm{C_5H_5})_2\mathrm{Sn\{Fe(CO)_2(C_5H_5)\}_2}]$	161	*103*
$[\mathrm{Me_3SnC{\equiv}C}\mathbf{Me}]$	130	*202*
$[\mathrm{Et_3SnC{\equiv}}\mathbf{CH}]$	238	*202*
$[\mathrm{Me_4Pb}]$	133 134.2 134 132.5	*67, 83, 145, 206, 209, 226*
$[\mathrm{Me_3PbH}]$	136	*83*
$[\mathrm{Me_6Pb_2}]$	+134.4	*51*
$[\mathrm{Me_2Pb(acetylacetonate)_2}]$	144.6 – 153.6^a	*7*

^{a} Solvent-dependent.

TABLE XXXVII

VALUES OF $^1J(^{13}C—^{19}F)$ FOR SOME ORGANOMETALLIC COMPOUNDS

Compound	$^1J(^{13}C—^{19}F)$	References
$[Hg(CF_3)_2]$	356.3	*108*
$[Me_3SnCF_2CFHCF_3]$	302.0	*50*
$[As(CF_3)_2Cl]$	344.3	*108*
$[Se(CF_3)_2]$	331.3	*107*
$[Se(CF_3)_2]$	337.1	*107*
$[Hg(SeCF_3)_2]$	332.5	*107*

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The Organic Chemistry of Copper

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I

INTRODUCTION

Little is known of the nature of organocopper compounds despite their considerable use in organic syntheses over the last 20 years. Only recently has much attention been devoted to understanding their nature and reaction mechanisms. In most instances the copper reagents were treated with substrates without isolation. The first attempted preparation of an organocopper compound, ethylcopper from diethylzinc and copper(I) chloride, was reported by Buckton (*28*) in 1859. However, not until 1923 was the first such compound actually isolated, when Reich reported the preparation of impure phenylcopper from the reaction of phenylmagnesium bromide with copper(I) iodide in ether (*238*). Organocopper compounds and complexes have since proved to be versatile reagents and to possess many advantages over the usual reagents in organic syntheses. A variety of reactions use copper or copper salts as catalysts or reaction components. Accumulating evidence indicates that organocopper compounds may be transient intermediates in the Ullmann biaryl synthesis, in copper-catalyzed additions to olefins and α,β-unsaturated carbonyl compounds, and in copper-catalyzed decarboxylations.

This chapter is confined to the preparations, structures, and uses of organic compounds of copper and organocuprates, together with the reactions in which they may be intermediates. Bruce has reviewed in detail the well-defined complexes of copper(I) containing carbon monoxide (*25a*). Olefin and acetylene π-complexes of copper and other transition metals have also been reviewed elsewhere (*233a*); some later interesting studies discuss the formation of cycloolefin-copper(I) complexes (*130a*), and some unusually stable vinylmetallic-copper(I) complexes (*115a*), and bonding in various types of olefin-copper(I) complexes (*252d*).

II

PREPARATION OF ORGANOCOPPER REAGENTS

Organocopper compounds have been obtained by many methods; the one commonly employed is the metathetical reaction between an organometallic reagent wherein the metal is higher than copper in the electromotive series, and a copper salt. The nature of the reagent often depends on the method of preparation and the reaction conditions (*73*, *81*). The presence of an organocopper reagent in many reactions in which isolation is unnecessary can be demonstrated by the different reactivities of the new compound and its organometallic precursor; in preparations via

Grignard and lithium reagents the copper intermediates do not react with Michler's ketone (*40*, *60*, *69*, *119*) [Gilman Color Test I (*123*)].

The usual precautions taken when working with air- and water-sensitive reagents must be employed for working with organocopper compounds.

A. Reactions of Organometallic Compounds with Copper Salts

1. *Via Lithium and Grignard Reagents*

A general method for the preparation of organocopper compounds of the type RCu is the reaction of a Grignard or lithium reagent with an excess of a copper(I) salt. Copper(I) halides are usually employed, although the cyanide (*121*, *124*) and thiocyanate (*119*, *121*) are also found to be effective. For ease of preparation the copper(I) salt is often employed in the form of a solvent-soluble complex in which the ligand coordinated with copper is a phosphine, phosphite, disulfide, or tertiary amine. The most used complex is apparently the tetramer, $(\mathrm{CuI}\cdot n\mathrm{Bu_3P})_4$ (*152a*, *195a*). The organic moiety can be alkyl, allyl, vinyl, or aryl.

An attempt has been made to list in Table I all preparations of copper reagents of the type RCu from the reaction of a Grignard or lithium reagent with a copper salt, irrespective of whether or not a copper compound was actually isolated.

In 1952 Gilman and co-workers reported that the yellow, ether-insoluble methylcopper dissolved to give a clear colorless solution on addition of a further equivalent of methyllithium (*119*). The new copper compound, of composition $\mathrm{LiCu(CH_3)_2}$, is an "ate" complex now usually known as lithium dimethylcuprate. Mixed cuprates can be prepared from a preformed organocopper compound, RCu, and a lithium reagent (*147*, *259*, *298*, *301*).

$$\mathrm{RCu + R'Li \longrightarrow Li(RR'Cu)} \qquad (1)$$

Organocuprates are usually prepared by the careful addition of two equivalents of an organolithium reagent to one equivalent of a copper(I) halide or one of its complexes. Although Grignard reagents are claimed to give magnesium cuprates (*193*, *311*), Whitesides *et al.* (*297*, *300*) do not consider them to be convenient precursors. Methylmagnesium halides do not dissolve methylcopper (*119*) as does methyllithium, and other

TABLE I

ORGANOCOPPER COMPOUNDS FROM GRIGNARD AND LITHIUM REAGENTS

Copper compound, RCu[a]	Precursor RM	Conditions (°C)	References
Alkyl			
CH_3	Li, MgX	Et_2O, <0°	*82, 119, 125, 136, 139*
C_2H_5[b]	MgX	Et_2O, −40°[c]; THF, −78°	*104, 124, 283*
n-, *t*-C_4H_9	Li	Et_2O, −78°	*299, 302*
Neophyl	Li	Et_2O, −78°	*299*
$NCCH_2$	Li	THF, −25°	*66*
$C_2H_5O_2CCH_2$	Li	THF, −110°	*181*
$C_6H_5SCH_2$	Li	THF, −50°	*60*
$C_6H_5SO_2CH_2$	MgBr	Et_2O—THF—C_6H_6, −68°	*154*
$C_6H_5COCH_2$	Na	Et_2O, −60°	*154*
$C_6H_5C(=NR)CH_2$	Li, Na	THF, −60°	*154*
$(C_6H_5)_2P(O)CH_2$	Li	THF, −40°	*154*
$(CH_3)_3SiCH_2$	Li	Et_2O, −10°	*182*
Alicyclic			
Endo-2-Norbornyl	MgBr	Et_2O, −78°	*298*
Aralkyl			
$C_6H_5CH=NC(C_6H_5)H$	Na	DME	*155*
ArCHR Ar = Pyridyl or quinolyl; R = H, alkyl, aralkyl, or C_6H_5	Li	THF—Et_2O or DME—Et_2O, −60°	*155, 156, 160*
Tripticyl	Li	Et_2O	*307*
Allylic			
$CH_2=CHCH_2$	Li	Et_2O, −70°	*137*
$RCH=CHCH_2$ R = H; CH_3	MgCl	Et_2O, −40°	*64*
$(CH_3)_2C=CHCH_2CH_2$	MgBr	Et_2O, −80°	*260*
Vinylic			
$CH_2=CH$	Li, MgCl	THF, −60°	*64, 162*
$CH_3CH=CH$	Li, MgBr	Et_2O, THF, < −30°	*162, 294*
$(CH_3)_2C=CH$	Li	Et_2O, < −40°	*217*
$CH_3CH=CCH_3$	Li	Et_2O, < −30°	*294*
Acetylenic			
$CH_3C\equiv C$	Na	NH_3, −75°	*207*
Heterocyclic			
2-(C_4SH_3)	Li, MgI	Et_2O, 0–20°	*212, 214*
2-(C_4OH_3)	Li	Et_2O, 0°	*214*
2-(C_4SCl_3)	Li, MgCl	Et_2O, −30°; THF, −70°	*215, 264*
2,5-(C_4SCl_2)Cu_2	Li	THF, < −20°	*263*

TABLE I—*Continued*

Copper compound, RCu[a]	Precursor RM	Conditions (°C)	References
Aryl			
C_6H_5	Li, MgX	Et_2O, 0°	*73, 124, 238, 306*
2-/3-/4-$CH_3C_6H_4$	Li	Et_2O, 0°	*40*
2,2′-$(C_6H_4)_2Cu_2$	Li	Et_2O, −70°	*305*
2-[5-(2-C_4SH_3)C_5NH_3]	MgCl	THF	*164*
2-/4-$CH_3OC_6H_4$	Li, MgBr	Et_2O	*40*
2,6-$(CH_3O)_2C_6H_3$	Li	Et_2O	*21, 281c*
2,4,6-$(CH_3O)_3C_6H_2$	Li	Et_2O	*281c*
2-(6-$CH_3OC_{10}H_6$)	Li	THF	*281a*
4-[$(C_6H_5)_2P$]C_6H_4	Li	Et_2O	*281c*
2-[$(CH_3)_2NSO_2$]C_6H_4	Li	Et_2O	*281c*
2-/3-/4-$(CH_3)_2NC_6H_4$	Li	Et_2O	*281c*
R-2-[$(CH_3)_2NCH_2$]C_6H_3 R = H; 3-Cl; 5-Cl; 5-CH_3; 4-CH_3O; 5-CH_3O; 6-$(CH_3)_2NCH_2$	Li	Et_2O	*281b, 209b*
2-$(CH_3OCH_2)C_6H_4$	MgBr	Et_2O	*281b*
2,6-$(CH_3OCH_2)_2C_6H_3$	Li	Et_2O	*281b*
[2-$CuC_6H_4CH_2N(CH_3)CH_2$]$_2$	MgBr	THF, −20°	*289*
5-CH_3O-8-[$(CH_3)_2NCH_2$]$C_{10}H_5$	Li	Et_2O	*281b*
3-/4-FC_6H_4	MgBr	THF, 0°	*259*
2-/3-$CF_3C_6H_4$	MgX	Et_2O	*32, 34, 36*
4-HC_6F_4	MgBr	THF, 0°	*266*
4-BrC_6F_4	MgBr	THF, 0°	*266*
4-(C_5NF_4)	MgBr	THF, 0°	*266*
C_6F_5	Li	Et_2O, THF, −70°	*146, 287,*
	MgX	Et_2O, THF, 0°	*34, 97, 146*
4-$(C_6F_5O)C_6F_4$	MgBr	THF, 0°	*96*
C_6Br_5	MgBr	THF, 0°	*262*
4-$(Me_3Si)C_6Cl_4$	Li	THF, −78°	*288*
4-(C_5NCl_4)	Li	THF, −70°	*146*
	MgCl	THF, 0°	*100, 146*
C_6Cl_5	Li	THF, −70°	*146*
	MgCl	THF, 0°	*146*

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[a] No structural connotation: diverse compounds have been isolated from reactions of stoichiometry RM + CuX.

[b] Similar methods applicable to propylcopper.

[c] Temperature dependent on nature of halide ions present.

stoichiometric magnesium cuprates are also noted to be heterogeneous (*193*). Cuprate formation is applicable to all organolithium reagents, and many have been prepared and utilized in organic syntheses since their potential was first demonstrated by House *et al.* in 1966 (*139*). Surprisingly little is known about the structure of organocuprates. Only a a few have been isolated (*73*, *147*, *281f*), and only one of these was studied to determine its structure (*281f*).

In Table II are listed many of the cuprates whose preparations have been reported.

TABLE II
PREPARATION OF LITHIUM DIORGANOCUPRATES, LiR_2Cu

Cuprate,[a] R =	Conditions (°C)[b]	References
CH_3	Et_2O, $<0°$	*119*, *139*
iso-C_3H_7	Et_2O, $-15°$	*309*
n-C_4H_9[c]	Et_2O, $-20°$	*69*, *297*
n-C_4H_9[d]	THF, $-78°$	*297*
$CH_2{=}CHCH_2$	Et_2O, $-78°$	*297*
$CH_2{=}CH$	THF, $<-15°$	*58*
$CH_2{=}C(CH_3)$	THF, 0°	*282*
$RCH{=}CH$ R = alkyl	Et_2O, $<-30°$	*205*, *206*
$(CH_3)_2C{=}CH$	Et_2O, $<-40°$	*217*
3-$CH_3C_6H_4$	Et_2O, 0°	*40*
C_6H_5	Et_2O, 0°	*73*, *297*
2-$[(CH_3)_2NCH_2]C_6H_4$	Et_2O, $-30°$	*281f*
C_6F_5[e]	Et_2O or Et_2O—THF, $<0°$	*146*

[a] No structure implied.
[b] Phosphine, phosphite, or sulfide ligands may also be present.
[c] Also for C_2H_5 and *n*-C_7H_{15}.
[d] Also for CH_3, *sec*-C_4H_9, *t*-C_4H_9, $CH_2{=}CH$.
[e] Also for C_6Cl_5, 4-(C_5NCl_4), C_6HF_4.

Copper(II) chloride has often been employed in reactions with lithium and Grignard reagents to obtain organocopper(I) compounds. Two equivalents of the organometallic reagent are required, one of which is used to reduce Cu(II) to Cu(I). Unstable alkylcopper(II) compounds may be intermediates. The reaction is usually represented by the equation

$$2RLi + CuCl_2 \longrightarrow RCu^{I} + 2LiCl + \tfrac{1}{2}R_2$$

Copper(I) chloride is not recommended for the preparation of some copper compounds in ether. Examples are the preparation of the supposed magnesium diphenylcuprate from phenylmagnesium bromide (*193*), and in reactions with pentafluorophenyllithium (*146*) and trichloro-2-thienyllithium (*264*). Instead, the copper compounds can be obtained by using copper(I) iodide, or by employing a more basic solvent such as dimethoxyethane or THF (*146*, *264*).

Phenylcopper is best prepared by reaction of freshly prepared phenyllithium with copper(I) bromide (*73*), or by phenylmagnesium iodide with copper(I) iodide (*124*), both in ether. Various methods are claimed to give a purer sample of methylcopper than methods employing lithium and magnesium reagents (see Section II,A,2).

2. *Via Other Organometallic Reagents*

Methylcopper and ethylcopper have been prepared by the reaction of copper(II) nitrate with tetramethyllead or tetraethyllead, respectively, in alcohol at low temperatures (*13–15*, *76*, *80*, *125*). Copper sulfate can also be used, but not the chloride. Phenylcopper cannot be obtained by a similar reaction with tetraphenyllead (*73*, *125*). From a study of the reaction, Bawn and Whitby (*14*, *15*) proposed the sequence of reactions (2)–(4):

$$Cu^{2+} + Pb(CH_3)_4 \longrightarrow Cu^+ + Pb(CH_3)_3^+ + CH_3\cdot \tag{2}$$

$$2CH_3\cdot \longrightarrow C_2H_6 \tag{3}$$

$$Cu^+ + Pb(CH_3)_4 \longrightarrow CH_3Cu + Pb(CH_3)_3^+ \tag{4}$$

The radical mechanism was justified by the polymerization of various olefins by the [$Pb(CH_3)_4 + Cu(NO_3)_2$] system, but not by methylcopper. Recently, Clinton and Kochi (*49*, *50*) have reexamined each stage of the reaction for tetraethyllead in acetic acid solution. The decomposition was strongly catalyzed by copper(I), and acetolysis was found to occur by a metastable intermediate, ethylcopper:

$$Pb(C_2H_5)_4 + Cu^IO_2CCH_3 \longrightarrow Pb(C_2H_5)_3O_2CCH_3 + C_2H_5Cu \tag{5}$$

$$C_2H_5Cu + HO_2CCH_3 \longrightarrow C_2H_6 + CuO_2CCH_3 \tag{6}$$

The products, ethane and triethyllead acetate, were formed in equimolar amounts. More doubts existed about the first stage of the reaction in which an alkyl radical was formed by a redox reaction [Eq. (2)]. Only ethylene was obtained from the stoichiometric reaction of copper(II) acetate with tetraethyllead in acetic acid solution. Evolution of gas ceased on disappearance of the blue color of the copper(II) salt, indicating complete reduction to copper(I). The reduction of the copper salt of a weakly coordinating anion, such as the trifluoromethanesulfonate, was extremely rapid. Reduction of copper(II) was suggested to occur by transfer of an alkyl group from $Pb(C_2H_5)_4$ to form a metastable ethylcopper(II) intermediate which underwent rapid homolysis. Alkyl radicals liberated are efficiently scavenged by copper(II) salts present and so further oxidized.

$$Pb(C_2H_5)_4 + Cu^{II}X_2 \longrightarrow Pb(C_2H_5)_3X + C_2H_5Cu^{II}X \tag{7}$$

$$C_2H_5Cu^{II}X \longrightarrow C_2H_5\cdot + Cu^{I}X \tag{8}$$

$$C_2H_5\cdot + Cu^{II}X_2 \longrightarrow Et_{ox} + Cu^{I}X \tag{9}$$

A limiting factor in the preparation of methylcopper from tetramethyllead in alcoholic solution was the methanolysis reported by Costa *et al.* (*78*, *81*) to occur above −50°C by a homolytic mechanism,

$$CH_3Cu + ROH \longrightarrow CH_4 + CuOR \tag{10}$$

The view of Clinton and Kochi (*49*) is that this unfounded homolytic decomposition of an alkylcopper and the thermodynamically unfavored abstraction of the methanolic proton are simply explained by protonolysis, as occurs in acetic acid (Eq. (6)].

Several methods have been recommended for the preparation of pure methylcopper, each having advantages over previously reported methods. Costa *et al.* consider the $[Pb(CH_3)_4 + Cu(NO_3)_2]$ method superior to the Grignard route, as reproducible analyses are obtained (*82*). However, Thiele and Kohler recommend the reaction of zinc dialkyls with copper(II) chloride in ether at −78°C for the preparation of pure yellow methylcopper, red-brown ethylcopper, and orange propylcopper, uncontaminated by copper alkoxides (*277*). The mechanism was considered to be a reduction of copper(II) to copper(I) chloride, followed by the reaction of the latter with the zinc dialkyl. The results from the recent

$$Zn(CH_3)_2 + 2CuCl_2 \longrightarrow ZnCl_2 + 2CuCl + 2CH_3\cdot \tag{11}$$

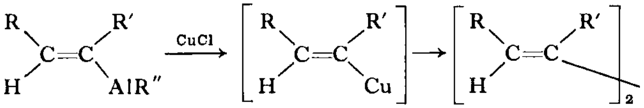
$$Zn(CH_3)_2 + 2CuCl \longrightarrow 2CH_3Cu + ZnCl_2 \tag{12}$$

reinvestigation (*49*, *50*) of the $[PbR_4 + Cu(NO_3)_2]$ system give some support to an alternative mechanism proposed, which involved formation of a very unstable dialkylcopper(II).

$$(CH_3)_2Zn + CuCl_2 \longrightarrow ZnCl_2 + (CH_3)_2Cu^{II} \qquad (13)$$

$$(CH_3)_2Cu^{II} \longrightarrow CH_3\cdot + CH_3Cu^{I} \qquad (14)$$

Recently, Yamamoto *et al.* (*310*) have reported that pure methyl(tris(triphenylphosphine))copper containing only complexed solvent molecules can be obtained by a method which was previously applied to the preparation of alkyl transition metal compounds. Copper(II) acetonylacetonate, dimethylaluminum ethoxide, and triphenylphosphine were reacted in the ratio 1:3:4 in either or toluene at −10°C. The triphenylphosphine complex was far more stable than previously described (*82*) and more stable than uncomplexed methylcopper. An aluminum–copper exchange was also postulated (*312*) to explain the high yield of stereospecifically pure diene from the addition of copper(I) chloride to a vinylalane in THF at 25°–35°C.



(15)

Two other exchange reactions have been reported: cyclopentadienylthallium and pentafluorophenylsilver react with a copper(I) halide to give cyclopentadienylcopper complexes (*86*) and pentafluorophenylcopper (*203*), respectively.

B. Copper–Halogen Exchange Reactions

$$RCu + R'X \longrightarrow RX + R'Cu \qquad (16)$$

Only perfluoro-*tert*-butyl copper has been prepared by this method. The compound was isolated in 72% yield from the reaction of *m*-(trifluoromethyl)phenylcopper with perfluoro-*tert*-butyl bromide in ether–dioxane at 0°C(*34*). Exchange and cross-coupling reactions occur simultaneously in many reactions between organocopper reagents and various organic halides (*69*, *97*, *174*, *217*, *220*, *266*, *297*). However, the method is only of limited use as the new reagent [R'Cu in Eq. (16)] and its precursor are capable of reacting with both species of halide, RX and R'X, present in the mixture.

The reaction of lithium dimethylcuprate with perhalobenzenes (*146*) may be classified as a copper–halogen exchange reaction, but the metal actually involved appears to be lithium. The overall reaction for pentafluoroiodobenzene is

$$\mathrm{Li[(CH_3)_2Cu] + 2C_6F_5I \longrightarrow Li[(C_6F_5)_2Cu] + 2CH_3I} \tag{17}$$

A small excess of methyllithium was required. For hexachlorobenzene, pentachloropyridine, 4-iodotetrachloropyridine, and pentafluoroiodobenzene a yellow methylcopper-like precipitate was observed during the addition of the arene to the cuprate. The sequence of reactions (18)–(20) was suggested, although this may be an oversimplification. According to

$$\mathrm{C_6Cl_5X + Li[(CH_3)_2Cu] \longrightarrow C_6Cl_5Li + CH_3Cu + CH_3X} \tag{18}$$
$$\mathrm{C_6Cl_5Li + CH_3Cu \longrightarrow Li(C_6Cl_5CuCH_3)} \tag{19}$$
$$\mathrm{C_6Cl_5X + Li(C_6Cl_5CuCH_3) \longrightarrow Li[(C_6Cl_5)_2Cu] + CH_3X} \tag{20}$$

the results of House *et al.* (*139*) lithium dimethylcuprate is not in equilibrium with its constituents, methyllithium and methylcopper. Of the two reagents with compositions ($2CH_3Li$ + CuI) and ($3CH_3Li$ + CuI), only the latter reacted with 4-methyl-2-pentanone (*139*), as does methyllithium. Cuprates with a stoichiometric composition greater than LiR_2Cu also give a positive color test with Michler's ketone (*40*), as do the more reactive lithium and magnesium reagents (*123*). Thus the reaction between perhaloarenes and lithium dimethylcuprate may proceed via lithium–halogen exchange, followed by an exchange of ligands with the cuprate. Tetrachlorothiophene in a similar reaction with the cuprate gave only a low yield of a trichloro-2-thienylcopper reagent, possibly because excess methyllithium was apparently not employed (*264*).

A more complexing solvent such as *N*,*N*-dimethylacetamide (DMAC) gave higher yields of products from the exchange reaction of a pentafluorophenylcopper reagent with various organic halides, compared to reactions in THF and Bu_2O (*97*).

C. *Metalation*

Pentafluorobenzene was not metalated by methylcopper or phenylcopper in ether at 0°C (*146*).

A new and interesting reagent for the metalation of compounds with acidic hydrogen atoms is copper(I) *tert*-butoxide (*280*). Unlike the very unstable copper(I) methoxide (*74*), the butoxide can be sublimed at

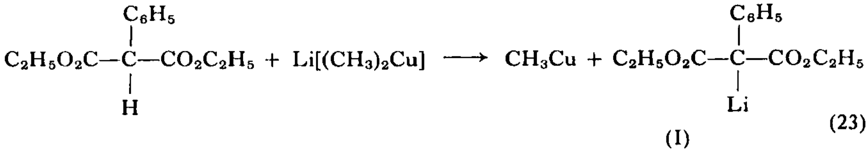
170°C/0.1 mm and is very soluble in organic solvents. The butoxide metalates phenylacetylene [Eq. (21)] and cyclopentadiene (see Section II,F). Metalation is the usual method of preparation of copper acetylides (see Section II,G).

$$C_6H_5C{\equiv}CH + CuOC(CH_3)_3 \longrightarrow C_6H_5C{\equiv}CCu + (CH_3)_3COH \qquad (21)$$

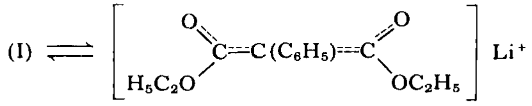
A reaction similar to the overall copper–halogen exchange observed on addition of perhaloarenes to lithium dimethylcuprate is also given by pentafluorobenzene, pentachlorobenzene, 2,3,5,6-tetrachloropyridine (*146*), and tetrafluorobenzenes (*144*). A small excess of methyllithium was again required, otherwise the reactions were very slow. Formation of methylcopper during the addition was not observed with the polyfluoroarenes, but a mechanism was proposed similar to that for the perhaloarenes (*146*). Equation (22) represents the overall reaction for pentafluorobenzene. In most cases, methane was evolved nearly quantitatively.

$$2C_6F_5H + Li[(CH_3)_2Cu] \longrightarrow Li[(C_6F_5)_2Cu] + 2CH_4 \qquad (22)$$

Compounds with acidic hydrogen atoms react rapidly with cuprates. Phenylacetylene has been mentioned as one example (*223*). Another is diethyl phenylmalonate (*144*), which on addition to lithium dimethylcuprate gave a rapid evolution of methane and the formation of a methylcopper-like precipitate which did not redissolve. Subsequent to the addition of benzoyl chloride and the customary work-up, only acetophenone and the phenylmalonate were isolated. The reaction may be summarized by Eq. (23). The failure to isolate the acylated product may be ascribed to the formation of the enolate, (II).



$$C_2H_5O_2C{-}\underset{\displaystyle H}{\overset{\displaystyle C_6H_5}{C}}{-}CO_2C_2H_5 + Li[(CH_3)_2Cu] \longrightarrow CH_3Cu + \underset{(I)}{C_2H_5O_2C{-}\underset{\displaystyle Li}{\overset{\displaystyle C_6H_5}{C}}{-}CO_2C_2H_5} \qquad (23)$$



(II)

D. Decarboxylation of Copper(I) Carboxylates

The formation of transient organocopper compounds has been inferred in many decarboxylations of copper(I) carboxylates or copper–carboxylic acid systems (*20*, *33*, *47*, *56*, *211*, *213*, *215*, *279*). Only one copper compound has been isolated, so far. The decarboxylation of copper(I) pentafluorobenzoate in quinoline proceeds smoothly at 60°C to give a pentafluorophenylcopper-quinoline complex (*33*, cf. *254*).

$$C_6F_5CO_2Cu \longrightarrow C_6F_5Cu + CO_2 \qquad (24)$$

The high-temperature pyrolysis of dry copper(II) heptafluoropropionate afforded only traces of C_3F_6, C_3F_7COF, and unidentified products (*183*). Such decarboxylations are worthy of reinvestigation in strong complexing solvents as a possible route to the stable perfluoroalkylcopper compounds (see Section II,E).

E. Perfluoroalkylcopper Compounds

Perfluoroalkylcopper compounds can be prepared directly from perfluoroalkyl halides and copper in dipolar aprotic solvents such as dimethyl sulfoxide or *N*,*N*-dimethylacetamide at elevated temperatures (*200*, *201*). Perfluoroheptylcopper and 3-(phenyl)hexafluoropropylcopper were isolated by precipitation from solution by addition of water, after it was discovered that their rates of hydrolysis were very slow (*200*). Solutions of the copper compounds in dimethyl sulfoxide (DMSO) are colorless when oxygen is rigorously excluded. The ease of formation and thermal stability of perfluoroalkylcopper compounds are exploited in performing *in situ* couplings of perfluoroalkyl iodides with aryl and vinyl halides (*29*, *30*, *199*, *200*, *201*, *278*). Cross-coupling of a perfluoroalkyl iodide with a suitable organic halide is effected by heating the two halides with excess copper in DMAC or DMSO at 100°–120°C for up to 3 hours. The method is suitable for fluoroalkyl iodides of the type $Y(CF_2)_nI$, where $n \geq 3$ and $Y = H$, C_6H_5, CO_2H, F, or I, and for CF_3I. 1,3-Diiodohexafluoropropane gave an α,ω-dicopper compound, as demonstrated by reaction with iodobenzene subsequent to filtering off the excess copper powder in a two-stage reaction. The perfluoroalkyl bromides and chlorides can be utilized in similar reactions if a bidentate

$$I(CF_2)_3I \xrightarrow{Cu} Cu(CF_2)_3Cu \xrightarrow{C_6H_5I} C_6H_5(CF_2)_3C_6H_5 \qquad (25)$$

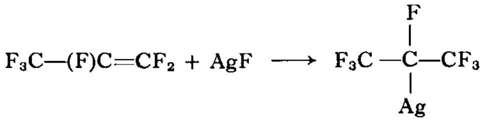
ligand such as 2,2′-bipyridyl is present (*199*, *278*); a dramatic effect on the rate of reaction of the bromides is observed and temperatures of ~60°C can be employed (100°–140°C for the chlorides). Coupling of 1,4-diiodooctafluorobutane with aryl iodides by copper also benefits from the addition of bidentate ligands. The intermediates of the type $Ar(CF_2)_4Cu$ appear to be stabilized against internal cyclization and decomposition, and react faster with aryl iodides at a lower temperature (~60°C) (*199*).

The importance of the α-fluorine atoms is clearly demonstrated by the low yield of product from the coupling of 1,1,1-trifluoroiodoethane with iodobenzene and the failure of *n*-butyl iodide to couple under similar conditions (*200*). *n*-Butyl iodide gave 1-butene only, and no evidence was reported to suggest the formation of a thermally unstable butylcopper compound. A previous attempt to react methyl iodide with copper also failed (*119*).

Tetrafluoroethylene was the only fluorine-containing product obtained from attempted coupling reactions with 1,2-dibromo- and 1,2-diiodotetrafluoroethane, and dibromodifluoromethane, perhaps via unstable copper compounds (*200*).

Perfluoro-*tert*-butylcopper was obtained by a copper–halogen exchange reaction (*34*) (see Section II,B).

A possible route to secondary perfluoroalkylcopper reagents may be a reaction between a copper(I) halide and a secondary perfluoroalkylsilver compound. The latter are easily prepared by the addition of silver fluoride to a perfluoroolefin in acetonitrile at 25°C (*202*): [Eq. (26)].



$$F_3C{-}(F)C{=}CF_2 + AgF \longrightarrow F_3C{-}\overset{\overset{\textstyle F}{|}}{\underset{\underset{\textstyle Ag}{|}}{C}}{-}CF_3 \qquad (26)$$

Probably, the method is not directly applicable to the preparation of copper compounds because of the thermal instability of copper(I) fluoride. No report of an exchange reaction between a perfluoroalkylmetallic reagent and a copper(I) halide was found, despite the large number of lithium, magnesium, and zinc compounds which have been prepared in the last 25 years (*259a*, *278b*). However, as many of these reagents are thermally unstable, and as they are prepared from the perfluoroalkyl iodides, such routes may be of little interest. Fluorinated 1-iodocyclobutenes have been coupled by reaction with an alkyllithium and copper(II) bromide, or by activated copper (*226a*); a three-center copper-containing intermediate may be involved.

There appears to be no report of an attempted preparation of a perchloroalkylcopper compound, despite the interest in polychloroalkyllithium reagents as carbene sources (*176*). Addition of chloroform to lithium dimethylcuprate which contained a stoichiometric excess of methyllithium in THF–ether at −80°C gave a methylcopper-like precipitate and then an intense red color but no isolable ketones subsequent to the addition of acetyl chloride (*144*).

F. Cyclopentadienylcopper and Indenylcopper

Wilkinson and Piper (*303*) obtained cyclopentadienyl(triethylphosphine)copper by following a method previously described in the patent literature which utilized the tri-*n*-propylphosphine ligand. The method consists of heating a mixture of cyclopentadiene, copper(I) oxide, and a phosphine ligand in a solvent such as petroleum ether or pentane. By

$$2C_5H_6 + Cu_2O + 2PR_3 \longrightarrow 2C_5H_5Cu\cdot PR_3 + H_2O \qquad (27)$$

replacing the phosphine ligand with *tert*-butyl isocyanide, Saegusa *et al.* have recently isolated cyclopentadienyl(*tert*-butyl isocyanide)copper and indenyl(tris-*tert*-butyl isocyanide)copper (*246*). A number of cyclopentadienylcopper complexes with various phosphine, phosphite, or isocyanide ligands were also obtained by reaction of the thallium derivative with the respective copper(I) halide–ligand complex in pentane or THF at 25°C (*86*). Cyclopentadiene was also metalated by copper(I) *tert*-butoxide, but a cyclopentadienylcopper compound was only isolated in the presence of a phosphine ligand (*280*). The apparent instability of the uncomplexed copper compound may explain the failure (*303*) of the reactions of the cyclopentadienylsodium and Grignard reagents with a copper(I) halide to yield cyclopentadienylcopper.

An interesting compound, cyclopentadienyl(manganese tricarbonyl) copper, was obtained from the boronic acid derivative on treatment with copper(II) acetate in aqueous 2% sodium hydroxide (*209*).

G. Acetylides

It is not intended to discuss in detail the preparation and reactions of copper acetylides as this has been the subject of three recent reviews (*11*, *221*, *261*). Contrary to the behavior of other copper compounds, the acetylides, $RC\equiv CCu$, are not hydrolyzed by water, and thus can be prepared by reaction of a terminal alkyne with an ammoniacal solution of copper(I) chloride [Eq. (28)]. Metalation can also be brought about by copper(I) chloride in a dipolar aprotic solvent (*126*) [Eq. (29)] or in the presence of triethyl phosphite [Eq. (30)], by copper(I) or copper(II) *tert*-butoxide (*280*) [Eq. (21)] and by lithium dimethylcuprate (*223*).

$$RC\equiv CH + Cu(NH_3)_2^+ \longrightarrow RC\equiv CCu + NH_3 + NH_4^+ \tag{28}$$

$$(C_4H_9)_2PC\equiv CH + CuCl \longrightarrow (C_4H_9)_2PC\equiv CCu + HCl \tag{29}$$

$$RC\equiv CH + CuCl + (C_2H_5O)_3P \longrightarrow RC\equiv CCu + C_2H_5Cl + HP(O)(OC_2H_5)_2 \tag{30}$$

Metalations of terminal alkynes by copper acetylides (*221*) and by alkylcopper (*223*) reagents were reported, although experimental details are lacking.

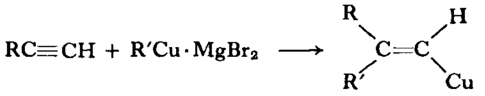
Alkali metal acetylides react with copper(I) halides to give either copper acetylides or ethynylcuprates (*261*), according to the ratio of the reactants. Ethynylcuprates have also been prepared by addition of an organolithium reagent to an organocopper compound of stoichiometric composition RCu, in which one of the organic groups is ethynyl (*300*, *311*).

$$CuI + nM(C\equiv CR) \longrightarrow M_{n-1}(RC\equiv C)_nCu + MI \tag{31}$$

$$(n = 1\text{–}3;\ M = Li, Na, K)$$

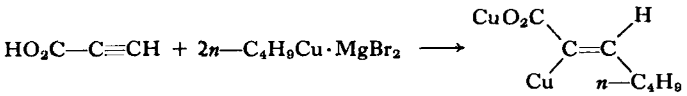
H. Miscellaneous Methods

Formation of metal–carbon bonds by addition of an organometallic reagent to an unsaturated compound or a diazonium compound is a little-used method in organocopper chemistry. Various alkylcopper reagents, ($RCu + MgX_2$ or LiX), add to acetylene or the alkynes, $RC\equiv CH$, in a cis manner in ether or ether–pentane at low temperatures (*223*). A π-complex is a probable intermediate. The vinylcopper addition product obtained is dependent on the nature of the alkyne, being sensitive to electronic effects in the latter:



(32)

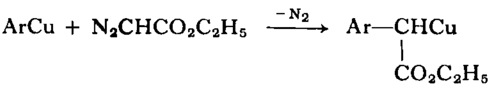
$$(R \text{ or } R' = C_2H_5;\ n-C_4H_9; C_6H_5)$$



(33)

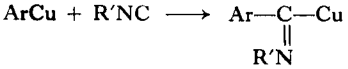
Similar additions have been reported for propynoates (*61*, *64*, *260*) and for a *trans*-2,4-pentadienoate ester (*64*) with dialkylcuprates and vinylcopper reagents.

Substituted diazomethanes, such as diazoacetic ester, react with some arylcopper compounds (*34*, *255*) by carbene insertion into the C—Cu bond [Eq. (34)]. Isonitriles are also reported (*281d*) to insert into an aryl—Cu bond [Eq. (35)] in benzene solution at 25°C.



$$\mathrm{ArCu} + \mathrm{N_2CHCO_2C_2H_5} \xrightarrow{-\mathrm{N_2}} \mathrm{Ar{-}\underset{\displaystyle CO_2C_2H_5}{\underset{|}{C}}HCu} \qquad (34)$$

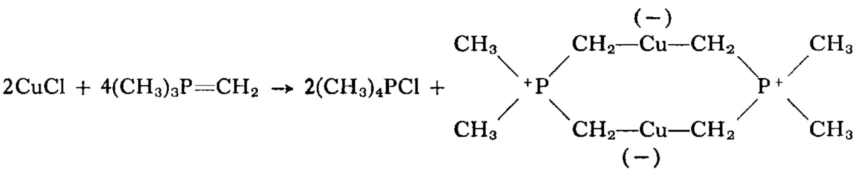
$(\mathrm{Ar} = \mathrm{C_6H_5};\ p\text{-}\mathrm{H_3CC_6H_4};\ \mathrm{C_6F_5})$



$$\mathrm{ArCu} + \mathrm{R'NC} \longrightarrow \mathrm{Ar{-}\underset{\displaystyle R'N}{\underset{\|}{C}}{-}Cu} \qquad (35)$$

$(\mathrm{Ar} = \mathrm{C_6H_5};\ o\text{-}[(\mathrm{CH_3})_2\mathrm{NCH_2}]\mathrm{C_6H_4})$

A very stable type of organocopper compound, a metalated ylide, is obtained from the reaction between copper(I) chloride and trimethylmethylenephosphorane in an aromatic solvent. The compound is soluble in aromatic and chlorocarbon solvents and can be sublimed (*256a*).



I. Isolation

Organocopper compounds such as methyl-, phenyl-, tolyl-, and ethynylcopper are easily isolated by virtue of their insolubility in the media employed in their preparations. Purification is often difficult as lithium and magnesium halides are not readily washed out of the copper compounds by cold ether (*82*, *214*) and because some compounds cling to small quantities of solvent on drying (*73*, *76*, *81*). If crystallization does not occur on standing, some copper compounds, such as pentafluorophenylcopper, may be precipitated as dioxinates after prior removal of lithium and magnesium halides as their dioxinates (*34*).

Some perfluoroalkylcopper compounds were precipitated from

N,*N*-dimethylacetamide (DMAC) or dimethyl sulfoxide (DMSO) solutions by addition of water, because of their insensitivity to hydrolysis (*200*).

III
NATURE OF ORGANOCOPPER REAGENTS

The nature of organocopper reagents appears to be dependent on the method of preparation and the stoichiometry. Specific examples are methylcopper (*76*, *310*), phenylcopper (*73*), and pentafluorophenylcopper (*34*, *37*, *147*). The best method of preparing pentafluorophenylcopper of composition C_6F_5Cu appears to be via the addition of copper(I) bromide to pentafluorophenylmagnesium bromide (*34*, *37*), since the lithium reagent and copper iodide gives an "ate" complex (*147*). An "ate" complex was also obtained from pentafluorophenyllithium and silver chloride in equimolar proportions (*265*). As shown in Table III, many of the isolated copper compounds gave somewhat incorrect or irreproducible analyses, and others contain metal halide and solvent molecules.

A. Structure

Little attention has been paid to the elucidation of the structures of organocopper compounds until recently. The structures of some copper compounds have been determined either by X-ray crystallography or by a combination of NMR and mass spectroscopic data, and the degree of association. Aggregation states have been determined mostly by cryoscopy, but occasionally by vapor pressure osmometry and ebulliometry where permitted by the stability of the organocopper compound (*36*, *37*, *281f*).

Although methylcopper and phenylcopper are generally considered to be polymeric because of their insolubility in organic solvents, no evidence exists to support this belief. The tolylcopper and *o*-anisylcopper compounds are reported to have low aggregation states which increase in size with time for various solutions (*40*); they are also ether-insoluble.

Ethynylcopper compounds are known to be polymeric. X-ray diffraction analysis indicated that they are composed of infinite zigzag chains of copper atoms, each bound to three ethynyl group by σ- and π-bonds

TABLE III
ISOLATED COPPER COMPOUNDS

Compound isolated[a]	Method of preparation	References
CH_3Cu[b]	$2CH_3MgBr + Cu(NO_3)_2$	*82*
CH_3Cu[c]	$2(CH_3)_4Pb + Cu(NO_3)_2$	*81*
CH_3Cu[d]	$0.6(CH_3)_2Mg + CuI$	*119*
CH_3Cu[e]	$(CH_3)_2Zn + CuCl_2$	*277*
$CH_3Cu \cdot P(C_6H_5)_3 \cdot \frac{1}{2}Et_2O$	$3(CH_3)_2AlOC_2H_5$ $+$ Cu(acetonylacetonate)$_2$ $+ 4P(C_6H_5)_3$	*310*
$CH_3Cu \cdot P(C_6H_5)_3 \cdot$Toluene		
C_2H_5Cu	$(C_2H_5)_2Zn + CuCl_2$	*277*
n-C_3H_7Cu	$(n\text{-}C_3H_7)_2Zn + CuCl_2$	*277*
$C_7F_{15}Cu$[d]	$C_7F_{15}I + Cu$	*200*
t-C_4F_9Cu[d,f]	$t\text{-}C_4F_9Br + m\text{-}CF_3C_6H_4Cu$	*34*
$C_6H_5(CF_2)_3Cu$[d]	$C_6H_5(CF_2)_3I + Cu$	*200*
$RM_{0.9}[(n\text{-}C_4H_9)_3P]_{1.1}$[g] R = *cis*/*trans*-$CH_3CH{=}CH$ or $(CH_3)_2C{=}CH$	$RLi + CuI(n\text{-}C_4H_9)_3P$	*294*
$C_5H_5Cu{—}L$[h]	$C_5H_5Tl + CuI{—}L$	*86*
	$C_5H_6 + Cu_2O + L$	*247, 303*
Indenyl-Cu(t-$C_4H_9NC)_3$[d]	$C_9H_8 + Cu_2O + 3t\text{-}C_4H_9NC$	*247*
$(C_4SH_3)Cu\text{-}2$[b]	$(C_4SH_3)Li\text{-}2 + CuBr$	*214*
C_6H_5Cu[c,i]	$C_6H_5MgBr + CuBr$	*238*
$(C_6H_5)_2Mg \cdot CuBr_{2.5} \cdot 3.5THF$	$C_6H_5MgBr + CuBr$	*73*
$(C_6H_5)_2Mg \cdot (C_6H_5Cu)_2 \cdot 6THF$	$2C_6H_5MgBr + CuBr$	*73*
$(C_6H_5)_6Cu_4Mg \cdot Et_2O$	$(C_6H_5)_2Mg + CuBr$	*258*
C_6H_5Cu[i]	$0.9C_6H_5Li + CuBr$	*73*
$(C_6H_5Cu)_4C_6H_5Li \cdot 3.5Et_2O$	$1.5C_6H_5Li + CuBr$	*73*
$C_6H_5Cu \cdot C_6H_5Li \cdot 0.4Et_2O$	$1.9C_6H_5Li + CuBr$	*73*
$C_6H_5Cu \cdot C_6H_5Li \cdot 3.25LiBr \cdot 4.2$Dioxane		
$4\text{-}CH_3C_6H_4Cu$	$0.95\ 4\text{-}CH_3C_6H_4Li + CuBr$	*40*
$(4\text{-}CH_3C_6H_4)_6Cu_4Mg \cdot Et_2O$	$(4\text{-}CH_3C_6H_4)_2Mg + CuBr$	*258*
$(4\text{-}CH_3C_6H_4)_6Cu_4Mg \cdot 5THF$		
$2\text{-}CH_3C_6H_4Cu$	$0.95\ 2\text{-}CH_3C_6H_4Li + CuBr$	*40*
$3\text{-}CH_3C_6H_4Cu$	$3\text{-}CH_3C_6H_4Li + CuBr$	*40*
$(3\text{-}CH_3C_6H_4)_2CuLi$	$2\ 3\text{-}CH_3C_6H_4Li + CuBr$	*40*
$2\text{-}CH_3OC_6H_4Cu$	$0.95\ 2\text{-}CH_3OC_6H_4Li + CuBr$	*40*
$2,6\text{-}(CH_3O)_2C_6H_3Cu$[b]	$2,6\text{-}(CH_3O)_2C_6H_3Li + CuBr$	*21*
$(2\text{-}CF_3C_6H_4Cu)_4$[d]	$2\text{-}CF_3C_6H_4MgBr + CuBr$	*32, 34*
$(3\text{-}CF_3C_6H_4Cu)_8$[d]	$3\text{-}CF_3C_6H_4MgBr + CuBr$	*34, 36*
$(3\text{-}CF_3C_6H_4)_6Cu_8$	$(3\text{-}CF_3C_6H_4Cu)_8$ decomp.	*36*
$(C_6F_5Cu)_4$[d]	$C_6F_5MgBr + CuBr$	*32, 34*
	$C_6F_5CO_2Cu$ decomp.	*33*[j]
$C_6F_5Li \cdot C_6F_5Cu \cdot MI \cdot 3.5$Dioxane	$C_6F_5Li + CuI$	*147*
$(C_6F_5)_2LiCu \cdot LiI \cdot 8.5$Dioxane	$2C_6F_5H + Li(CH_3)_2Cu$	*147*
$[(CH_3)_3SiCH_2Cu]_4$[d]	$(CH_3)_3SiCH_2Li + CuI$	*182*

TABLE III—*Continued*

Compound isolated[a]	Method of Preparation	References
2-/3-/4-[$(CH_3)_2N$]C_6H_4Cu[d,k]	RLi + CuBr	*281c*
2-[$(CH_3)_2NCH_2$]-X-C_6H_3Cu[d,l] X=H, 3-Cl, 5-Cl, 4-CH_3O, 5-CH_3O, 5-CH_3, 6-$(CH_3)_2NCH_2$	RLi + CuBr	*281b*
2,6-$(CH_3O)_2C_6H_3Cu$[d]	RLi + CuBr	*281c*
2,4,6-$(CH_3O)_3C_6H_2Cu$[d]	RLi + CuBr	*281c*
2-$(CH_3OCH_2)C_6H_4Cu \cdot MgBr_2$[d]	RMgBr + CuBr	*281b*
2-[$(CH_3)_2NSO_2$]C_6H_4Cu[d]	RLi + CuBr	*281c*
4-[$(C_6H_5)_2P$]C_6H_4Cu[d]	RLi + CuBr	*281c*
5-CH_3O-8-[$(CH_3)_2NCH_2$]$C_{10}H_5Cu$[d]	RLi + CuBr	*281b*
(2-[$(CH_3)_2NCH_2$]-X-C_6H_3)C(=NR)Cu[d] X = H, CH_3; R = *t*-C_4H_9 *c*-C_6H_{11}	ArCu + RNC	*281d*

[a] No structure is implied in the notation.
[b] Impure, containing variable quantities of metal halides.
[c] Somewhat impure according to analytical data for copper only.
[d] Isolated and purified; analytical data not reported.
[e] 1:1 Complexes with 2,2′-bipyridine and DMF also isolated.
[f] As dioxinate.
[g] Analysis of halide-free solution.
[h] Ligands, L, are phosphines, phosphites, isocyanides, and CO.
[i] Prepared in ether.
[j] Quinoline complex also obtained.
[k] Complexes with CuBr and AgBr also prepared.
[l] Complexes RCu·CuBr, RCu·$SnBr_2$, and RCu·$2MgBr_2$ (for X = H) also prepared.

(*71*, *127a*). These chains are broken down by phosphine ligands into smaller aggregates. Phenylethynyl(trimethylphosphine)copper was shown to be a tetramer with the four copper atoms in a "Z" shape (*72*). It is centrosymmetric and nearly flat apart from the phosphine groups. The proposed bonding in the complex is shown in Fig. 1. The terminal copper atoms are each bound to two phosphorus groups, and by weak unsymmetrical π-bonds to two ethynyl groups in a distorted tetrahedral arrangement. To the inner two copper atoms are attached three ethynyl groups by σ- and π-bonds in approximately trigonal arrangement. Since the degree of association in benzene solution was less than 4 and was lower still in nitrobenzene (*23*, *52*), there must be an equilibrium between tetramer and lower aggregation states in solution. The infrared

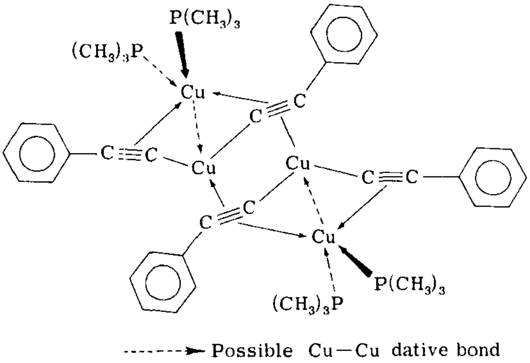
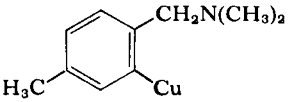


FIG. 1. Proposed bonding in $[C_6H_5C{\equiv}CCu \cdot P(CH_3)_3]_4$.

spectra of phenylethynylcopper and its complexes reveal strong interactions between copper and the C≡C orbitals, which are strongest for the polymeric compounds, $(RC{\equiv}C{-}Cu)_n$ (*41*, *52*). Observation of more than one distinct C≡C absorption for many complexes indicates the existence of different ethynyl group environments and of different aggregates (*52*). However, Garbusova *et al.* (*115b*) claim that infrared and laser Raman spectral data obtained by them for the polymeric phenylethynylcopper do not support the presence of both π and σ bonds as suggested by X-ray analysis.

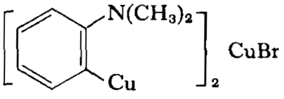
Several copper(I) cluster compounds have been described in recent years which contain either four (*84*, *134*), six (*134*), or eight (*198*) atoms. More recently, a number of organocopper reagents have also been shown to be cluster compounds of the above types. Pentafluorophenylcopper and *o*-(trifluoromethyl)phenylcopper were found to be tetramers (*32*) by cryoscopy or vapor pressure osmometry in benzene solution, or by mass spectrometry. The most abundant species in the mass spectra were the parent ions with the correct isotopic abundance patterns, a consequence of the remarkable stability of the copper tetramers at high temperatures (*32*). 2-Dimethylaminomethyl-5-methylphenylcopper (III) also exists in benzene solution as discrete tetramers (*281b*, *281c*). X-Ray diffraction



(III)

analysis of (III) confirmed the presence of a tetranuclear copper cluster with aryl bridging ligands. Direct Cu—Cu bonding was ruled out despite the short interatomic distances (*129*).

Arylcopper compounds containing the dimethylamino group as a substituent have proved to be an interesting class of compounds in view of their great stability. The dimethylaminophenylcopper reagents react with metal salts such as copper(I) and silver bromides to give well-defined stable complexes (*281c*), such as (IV), found to be dimeric in benzene solution. X-Ray diffraction analysis of (IV) shows the presence of a hexanuclear cluster of copper atoms which, with the two bridging bromine atoms, form a distorted octahedron (*130*) (Fig. 2). The Cu—Cu



(IV)

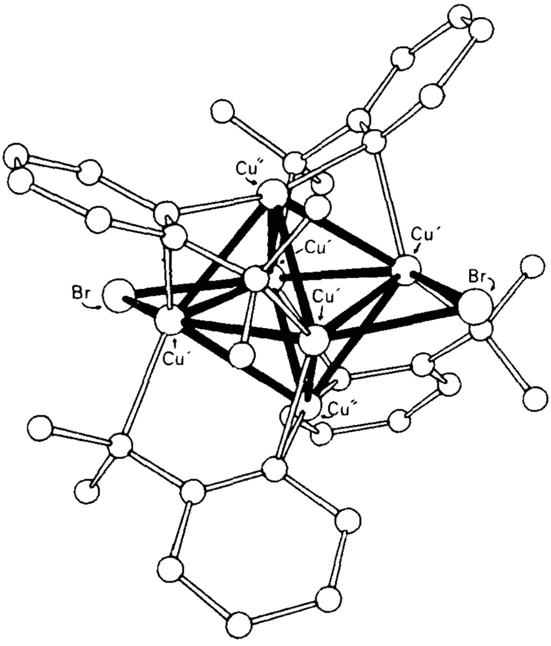
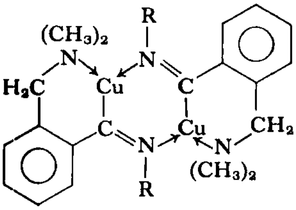


Fig. 2. The molecular stereochemistry of $[Cu(2\text{-}(CH_3)_2NC_6H_4)]_4(CuBr)_2 \cdot 1.5C_6H_6$, (IV).

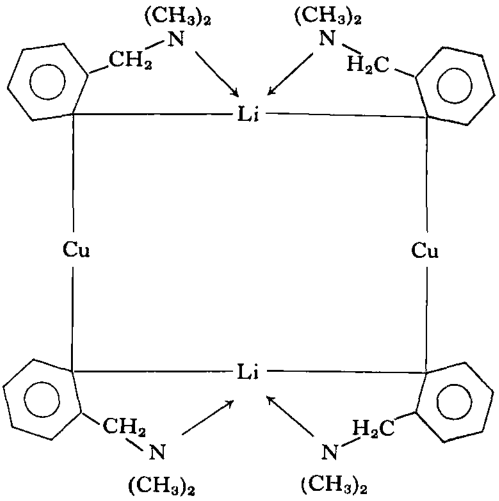
distance depends on whether the atoms are bridged by bromine or aryl ligands, and is shorter for the latter. Asymmetric bonding of the aryl groups to copper is implied by the presence of two bromine atoms bridging a total of four copper atoms.

The tetrameric *o*-(dimethylaminomethyl)phenylcopper, which is similar to (III) and probably possesses the same structural features, forms monomeric complexes with 1,2-bis(diphenylphosphino)ethane and -ethylene but not with triphenylphosphine (*281e*). Insertion of an isonitrile into the aryl—Cu bond occurs rather than formation of a complex (*281d*). The new copper compound is dimeric in benzene, and a six-membered ring structure involving heteroatom coordination bonding as in (V) is proposed. Triphenylphosphine breaks down the dimer (V) into a monomer in which the copper atom is probably tetrahedrally coordinated with the two nitrogen atoms and the phosphine ligand (*281d*).



(V)

Although much used in organic syntheses, little is known of the structure of cuprates of the type $LiCuR_2$. A number of arylcopper compounds have been isolated which, by analysis, are diarylcuprates (*40*, *73*, *147*, *281f*). Most also contained metal halide and solvent molecules. One of these cuprates, $LiCuAr_2$, in which the aryl moiety was 2-(dimethylaminomethyl)phenyl, was assigned structure (VI) on the basis of ^1H and ^{13}C NMR spectral data, and its existence as a dimer in benzene solution. All four aryl groups are bound in the same manner to a (Li_2Cu_2) metal cluster in which each group bridges a lithium and a copper atom. The dimethylamino groups are all considered to be coordinated to lithium, although there is an equilibrium between coordinated and free $(CH_3)_2NCH_2$ groups. From the results of low-temperature NMR studies, Whitesides and co-workers have suggested (*297*) that lithium dimethylcuprate is probably a tetrahedral metal cluster with face-centered bridging alkyl groups. A similar structure was also proposed by Corey (*69*).



(VI)

NMR spectral data for the dimethylcuprate anion have been reported by House *et al.* (*139*). The NMR signal for the methyl group remained sharp even at low temperatures. As methyllithium was added in excess of the stoichiometric ratio $Li(CH_3)_2Cu$, the coupling constant $J^{13}CH$ and the signal shifted. On the basis of these facts and the chemical behavior of the cuprates it was concluded that lithium dimethylcuprate was not in equilibrium with its constituents, CH_3Li and CH_3Cu. The formation of higher cuprates such as $Li_2(CH_3)_3Cu$ was indicated by the NMR data (*139*, *297*), but was not supported by chemical evidence (*139*). Methyl signals were found at higher field for methylcuprates than methylcopper complexes with phosphorus ligands (*136*). Addition of lithium iodide to pure methyl(tri-*n*-butylphosphine)copper, $Cu[P(C_4H_9)_3]CH_3$, effected a shift of the methyl signal to higher field, consistent with the suggestion that iodide ion complexes with copper and enhances the electron density of methylcopper. A complex of methyl copper with trimethyl phosphite, $Cu[P(OCH_3)_3]_3CH_3$, did not behave in a like manner, but here copper is already tetracoordinated (*136*). Methylcopper itself is too insoluble in organic solvents to record its NMR spectrum (*139*).

The complexes $Cu_4Mg(C_6H_5)_6 \cdot Et_2O$ and $Cu_4Mg(p\text{—}CH_3C_6H_4)_6 \cdot x$ THF (where x is probably 5) are considered to possess a discrete metal cluster with pendant aryl groups (*258*). Their ^1H NMR spectra suggested the presence of at least two aryl group environments on the metal cluster.

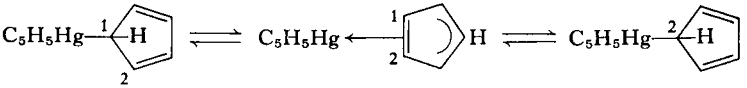
For the tolyl complex, the rate of exchange between tolyl groups in different environments increased with temperature. Two THF environments were also observed at 58°C. The spectra of a mixture of diphenylmagnesium and copper(I) bromide in ether indicated the presence of phenylmagnesium bromide and a slow exchange between phenylmagnesium species and the above phenylcopper complex (*258*). ^{1}H NMR spectra of pure arylcopper(I) compounds in which the aryl group is *o*-,*m*-,*p*-tolyl, *o*-anisyl, and 2,4-dimethylphenyl, have been described (*12*). The resonance peaks of the aromatic protons and the *ortho*-methyl groups were shifted downfield with respect to the parent arene, while those of *meta*- and *para*-methyl groups were shifted slightly upfield. Anomalous, much larger effects were observed for *o*-anisylcopper. An important feature of the ^{1}H NMR spectra of these arylcopper compounds was the magnetic anisotropy localized in the carbon–copper region. UV spectra and chemical shifts were similar to those of the aryllithium compounds, indicating that the aryl—Cu bond possesses some ionic character. Steric hindrance between *o*-methyl groups and copper was inferred from the temperature dependence of the spectra.

From the ^{19}F chemical shifts in the NMR spectra of *m*- and *p*-fluorophenylcopper were calculated the substituent parameters for copper. The zero value obtained for σ_I suggests that copper is electronically neutral, but a large σ_R value indicates that copper is capable of a d_π interaction with the aromatic nucleus (*37*). The high stability of pentafluorophenylcopper tetramer relative to many other arylcopper compounds may thus be the result of p_π interactions between the five fluorine atoms and the benzene ring increasing the charge density of the π-electron system (*37*).

m-(Trifluoromethyl)phenylcopper was found to be an octamer by consideration of the kinetics of its decomposition, and by cryoscopy and vapor pressure osmometry in benzene solution (*36*). Its ^{19}F NMR spectrum in ether at room temperature is a sharp singlet. Consequently, the suggested structure is a central copper cube with equivalent bridging benzotrifluoride groups. The initial decomposition product, $Cu_8(m\text{-}CF_3C_6H_4)_6$, is considered to be a Cu(0)—Cu(I) octanuclear cluster compound (*36*). For the octameric *m*-(trifluoromethyl)phenylcopper, the tetrameric ortho isomer, and pentafluorophenylcopper tetramer, the ^{19}F NMR spectra were found to vary with temperature. The changes are not considered to involve important structural alterations, but only variations in solvent complexes and rotamer populations (*32*, *37*). The spectra also resemble those of normal covalently bound compounds containing the above aryl groups.

The infrared spectra of many organocopper compounds have been reported (*40*, *41*, *73*, *75*, *77*) and compared favorably with the respective covalently bound organic halides. Bidentate phosphorus ligands coordinate more strongly with arylcopper compounds than monodentate ligands (*41*, *75*, *281e*). Substantial modification of the ligand spectrum is also seen in the infrared spectra of arylcopper complexes with bipyridyl or 1,10-phenanthroline (*41*).

The structure of cyclopentadienylcopper complexes has been a controversial subject for some years. When first prepared by Wilkinson and Piper in 1956, the triethylphosphine complex was considered to be σ-bonded on the basis of ambiguous spectral and chemical evidence (*303*). However, the stability, volatility, and solubility of the copper complex is atypical of known σ-bonded organocopper compounds. Thus, the ^1H NMR spectra of $Cu[P(C_2H_5)_3]C_5H_5$ was reexamined by Whitesides and Fleming (*296*). In liquid SO_2 solution at 0°C the complex exhibits only one sharp peak for the C_5H_5 protons. The signal broadens and splits on cooling as expected for a σ-bonded C_5H_5M compound. Averaging of the chemical shifts was considered to occur by a sequence of 1,3-copper shifts around the ring, provided that the observed shifts were correctly assigned. Later workers are of the opinion (*39*) that the assignment was incorrect and that 1,2-shifts occur. Rapid 1,2-shifts of mercury are suggested for bis(σ-cyclopentadienyl)mercury via an intermediate in which one of the double bonds is held to the metal atom by a π-bond (*51*) [Eq. (36)].



(36)

In actuality, X-ray crystallography shows that the complexes $Cu[P(C_2H_5)_3]C_5H_5$ and $Cu[P(C_6H_5)_3]C_5H_5$ are π-bonded (*87*, *95*). In both compounds, the copper atom is equidistant from all five ring carbons, and the C_5H_5 ring is virtually a perfect planar regular pentagon. Two enantiomers, as shown in Fig. 3, are present in an apparently equal and random distribution throughout the crystal.

The infrared spectra of many cyclopentadienylcopper complexes were examined and a π-bonded structure was proposed to account for the simplicity (*85*, *86*). Considerably decreased back-bonding from filled 3*d* copper orbitals to ligand orbitals relative to other transition metal

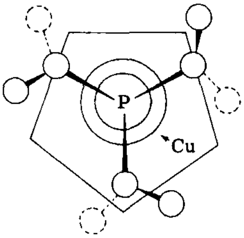


FIG. 3. Enantiomers of π-$C_5H_5Cu \cdot P(C_2H_5)_3$.

compounds was deduced from the high carbonyl and isonitrile stretching frequencies. Such behavior is typical for coordination of ligands to metals which are poor π-donors.

In a recent study of the IR and NMR spectra of the cyclopentadienylcopper and indenylcopper complexes with *tert*-butyl isocyanide, Saegusa and co-workers favored a π-bonded structure for the former, but were uncertain of the latter (*246*). As the indenylcopper complex was deuterated at only positions 1 and 3 a preference was expressed for a σ-bonded structure with 1,3-copper shifts. The structure of indenylcopper will doubtless be the subject of further research.

Ultraviolet spectral data have been reported for a few organocopper compounds (*36*, *77*, *253*, *303*). Methyl(triphenylphosphine)copper complexes were decomposed by UV light (*310*). The reaction of Grignard reagents with acid chlorides in the presence of copper(I) chloride, in which free radicals are supposedly formed via organocopper compounds, was also promoted by UV light (*103*).

Many organocopper compounds are reported to be diamagnetic, as are copper metal and the copper(I) ion (*36*, *40*, *75*, *277*). Methylcopper was reported as being paramagnetic (*77*, *253*), perhaps erroneously in view of a later report to the contrary (*277*).

Luong-Thi and Rivière consider it significant that diamagnetic copper compounds fail to react with α,β-unsaturated ketones (*190*) (see Section VII,A).

B. Stability

1. *Effect of Ligand*

In order to dissolve the copper(I) salts used to prepare the organocopper reagents and to stabilize these reagents once formed, a variety of ligands have been employed: for example, phosphines and phosphites (*23*, *52*, *75*, *86*, *135*, *136*), amines (*32*, *33*, *207*, *217*), and sulfides (*137*). Generally, organocopper compounds of stoichiometric composition RCu can be stabilized by coordination with a suitable phosphine ligand or by formation of an "ate" complex (*295*). Some discrepancies have been reported. Thus, a methylcopper-triphenylphosphine compound prepared in the presence of the ligand was apparently far more thermally stable than a similar compound prepared from a mixture of pure methylcopper and triphenylphosphine in ether at −80°C (*82*, *310*). Copper compounds also form stable complexes with ethers (*32*, *34*, *258*, *310*), metal salts (*270*, *281b*, *281c*), and triphenylboron (*75*, *306*), but not with aluminum, antimony, and arsenic compounds (*41*, *75*).

Cis–trans isomerization of α-(carboxymethyl)vinylcopper compounds via enolization is retarded by the presence of the complexing agents TMEDA or pyrrolidine (*61*, *260*). Other nitrogen-containing ligands, such as DMF, bipyridyls, and 1,10-phenanthroline did not stabilize pure methylcopper (*277*), or phenyl-, tolyl-, and *o*-anisylcopper compounds (*40*, *41*). The dimethylamino group as a substituent dramatically enhances the thermal and oxidative stabilities of arylcopper compounds, presumably by heteroatom coordination with copper (*281b*). Other stabilizing substituents are CH_3O–, CH_3OCH_2–, $(CH_3)_2NSO_2$–, and $(CH_3)_2NCH_2$– (*281b*, *281c*). The $(CH_3)_2N$– and $(CH_3)_2NCH_2$– groups are most effective in the ortho position. Tetrameric 2-(dimethylaminomethyl)phenylcopper (IV) is broken down by a bidentate diphosphine ligand to a monomeric complex in which copper is presumably tetrahedrally coordinated with the nitrogen and the two phosphorus atoms. Triphenylphosphine and (IV) do not form smaller aggregates (*281e*). Phenyl- and tolylcopper also form more stable complexes with the bidentate diphosphine ligand, 1,2-bis(diphenylphosphino)ethane. These arylcopper compounds and bis(diphenylphosphino)methane (DPPM) gave complexes which no longer contained an aryl–copper bond, which indicates an unspecified reaction of the copper compounds with the ligand (*41*). A phenylethynylcopper-DPPM complex was isolated.

For copper the 3*d* orbitals can be expected to make less than their full contribution to metal–ligand bonding as in other main group transition metal compounds (*51*). This is suggested by the infrared spectra of cyclopentadienylcopper complexes with methyl isocyanide or carbon monoxide, in which there is only a weak interaction between copper 3*d* orbitals and the $p\pi$-antibonding orbitals of the ligands. Moreover, this may explain why organocopper-carbonyl complexes are unstable and are seldom isolated. Unstable carbonyl complexes are formed by phenylethynylcopper (*208*), cyclopentadienylcopper (*86*), and perhaps by pure *n*-butyl(tributylphosphine)copper (*257*). Lithium di-*n*-butylcuprate, *n*-butylcopper (containing lithium iodide), and methyl[tris(triphenylphosphine)]copper can be carbonylated (*257*, *310*), perhaps via a complex in which CO inserts into the C—Cu bond. However, pure *n*-butylcopper and phenylcopper do not react or form complexes with carbon monoxide (*244*, *257*). For cyclopentadienylcopper compounds the order of decreasing ligand stability was $R_3P > (RO)_3P > RNC > CO$. The monodentate phosphorus ligand complexes could be more stable because of an optimum combination of the σ-donor and π-acceptor functions of the ligand (*86*).

Isocyanide complexes of phenylethynyl-, indenyl-, and cyclopentadienyl copper have been isolated (*86*, *172*, *246*). Organocopper-isocyanide complexes are assumed to be intermediates in certain organic syntheses (*245–252*). Isocyanides also insert into the aryl–copper bond (*281d*) [Eq. (35)].

Pyridine and quinoline greatly enhance the reactivity of lithium dipropenylcuprate, phenylcopper, and 2-thienylcopper towards aryl iodides (*212*, *217*, *220*). After due consideration of earlier mechanistic ideas (*7*, *269*), Burdon *et al.* (*31*) have proposed that the reaction of an organocopper compound, RCu, with an aryl halide in the presence of a ligand, L, such as pyridine, is a copper-assisted nucleophilic displacement of halide ion via aryl halide–ligand exchange with a complex of the type $RCuL_3$. Strong ligands, such as thiourea and *N*-methyl-2-pyrrolidone, are considered to be capable of forming a dissociated ion pair, $(CuL_4)^+R^-$, in which R^- may displace the halide.

Pentafluorophenylcopper tetramer is reported to form complexes with the π-bases 2-butyne and 1,5-cyclooctadiene (*32*).

Thermal stabilization of methylcopper by small quantities of magnesium halides has been reported by Costa *et al.* (*82*). The stability of ethylcopper is also very dependent on the nature of the magnesium halide present, the iodide having the greatest effect (*104*). Recent studies indicate that organocopper compounds, RCu, containing metal halides may be cuprates of the type M(RCuX) (*190*, *191*, *257*). The presence of phosphine ligands in solutions of dialkyl- or divinylcuprates is obviously beneficial as the reagents are formed and subsequently react more rapidly than the corresponding phosphine-free reagents (*135*, *297*). Dialkylcuprates are also reported to be more reactive than the pure alkylcopper reagent, RCu (*69*).

2. *Variation of* R

As long ago as 1923 it was realized that arylcopper compounds were more stable than their alkyl analogs, and that for a specific R group the order of decreasing stability for some related organometal compounds was RCu > RAg > RAu (*118*, *124*). Electronic effects and heteroatom coordination bonding to copper are important in stabilizing organocopper compounds. For (dimethylamino)phenylcopper the order of decreasing thermal stability of the isomers is ortho > para > meta (*281b*, *281c*). The $-N(CH_3)_2$ and $-CH_2N(CH_3)_2$ groups ortho to copper in arylcopper compounds enhance not only their thermal stability but also their resistance to oxidation and hydrolysis. Table IV lists the decomposition temperatures of a number of arylcopper compounds.

Few comparisons have been made among the relative stabilities of other classes of organocopper compounds. Generally, for simple derivatives, the order of decreasing stability is $RC{\equiv}CCu$ > Aryl–Cu > Alkyl–Cu. For vinylcopper compounds, 2-butenylcopper is more stable than propenylcopper (*294*). The higher homologs of methylcopper and lithium dimethylcuprate are less stable (*69*, *276*, *297*).

Perfluoroalkylcopper and perfluoroarylcopper compounds are noticeably more thermally stable than the corresponding alkyl and aryl compounds. Solutions of perfluoroalkylcopper compounds in DMSO or DMF are stable up to at least 120°C (*200*), whereas ether suspensions of alkylcopper compounds decompose at 0°C or below. Similarly, pure pentafluorophenylcopper tetramer decomposes at 210°C–220°C, and a sample has been kept in a Dry Ice chest for 5 years (*32*). However pure phenylcopper can be kept for no more than a few days, even under nitrogen (*73*). Solutions of pentafluorophenylcopper reagents containing metal halides in THF have been refluxed for 5 days or more without decomposition (*97*, *144*). Other stable perhaloarylcopper reagents are those in which the aryl moiety is perfluoro(*p*-phenoxyphenyl) (*96*), pentachlorophenyl, and 2,3,5,6-tetrachloropyridyl (*144*), none of which

TABLE IV

DECOMPOSITION TEMPERATURES OF SOME ARYLCOPPER COMPOUNDS[a]

Compound	Dec. (°C)	References
$3-[(CH_3)_2N]C_6H_4Cu$	<0	*281c*
$4-[(CH_3)_2N]C_6H_4Cu$	>100	*281c*
$2-[(CH_3)_2N]C_6H_4Cu$	140	*281c*
$(4-[(CH_3)_2N]C_6H_4Cu)_2CuBr$	175	*281c*
$(2-[(CH_3)_2N]C_6H_4Cu)_2CuBr$	200	*281c*
$(2-[(CH_3)_2N]C_6H_4Cu)_2AgBr$	185	*281c*
$2-[(CH_3)_2NCH_2]C_6H_4Cu\cdot L$	170	*281e*
$L = (C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$		
or *cis*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$		
$2-[(CH_3)_2NCH_2]—X—C_6H_3Cu$		
$X = H;\ 5-CH_3;\ 5-CH_3O$	170–205	*281b*
$X = 3-Cl;\ 5-Cl;\ 4-CH_3O$	120–145	*281b*
$X = 6-(CH_3)_2NCH_2$	>130	*281b*
$2-(+CH_2(CH_3)NCH_2]C_6H_4Cu)_2$	140	*289*
$(2-[(CH_3)_2NCH_2]—X—C_6H_3)_2CuLi$	178–192	*281f*
$X = H;\ 5-CH_3$		
$2-(CH_3OCH_2)C_6H_4Cu\cdot MgBr_2$	>110	*281b*
$2,6-(CH_3OCH_2)_2C_6H_3Cu$	170–174	*281b*
$2-(CH_3O)C_6H_4Cu$	150[b]	*40*
$2,6-(CH_3O)_2C_6H_3Cu$	185–186	*281c*
$2,4,6-(CH_3O)_3C_6H_2Cu$	198–202	*281c*
$4-[(C_6H_5)_2P]C_6H_4Cu$	>110	*281c*
$2-[(CH_3)_2NSO_2]C_6H_4Cu$	>150	*281c*
$8-[(CH_3)_2NCH_2]-5-(CH_3O)C_{10}H_5Cu$	162–165	*281b*
$(C_6F_5Cu)_4$	210–220	*32*
$[2-(CF_3)C_6H_4Cu]_4$	200–205	*32*
$[3-(CF_3)C_6H_4Cu]_8$	158	*36*
$3-(CH_3)C_6H_4Cu$	100[b,c]	*40*
2- or $4-(CH_3)C_6H_4Cu$	110–120[b]	*40*

[a] Determined by heating the solids in a nitrogen atmosphere, in a capillary tube.

[b] Described as explosion point: heating rate 5–10°/minute.

[c] Stability about the same as C_6H_5Cu.

have been isolated. The trichlorothienylcopper reagent must also be mentioned in this context (*264*).

3. *Thermal Decomposition*

Basically, three decomposition mechanisms have been described for organocopper compounds. One involves the formation of free radicals by homolysis of the carbon–copper bond. The other two are not heterolytic mechanisms, but neither do they involve the formation of free radicals: one is a dimerization and the other a disproportionation reaction of the group attached to copper. The possible existence of a fourth, heterolytic decomposition mechanism for certain types of organocopper compounds under suitable conditions should not be overlooked.

a. *Free-Radical Decomposition.* A mechanism involving homolysis of the carbon–copper bond is proposed for organocopper compounds which do not possess a β-hydrogen atom. Examples of this type investigated so far are neophylcopper (*299*), perfluoroalkylcopper compounds (*200*), methylcopper (*76*), and trimethylsilylmethylcopper (*182*).

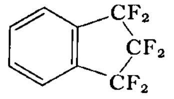
Neophyl(tri-*n*-butylphosphine)copper decomposes at temperatures between 30° and 120°C mainly, if not totally, by a free-radical mechanism. The usual products resulting from rearrangement of the neophyl radical were isolated [Eq. (37)], and no evidence was obtained to indicate the formation of an intermediate phenyl-substituted *tert*-butylcopper compound, $C_6H_5CH_2(CH_3)_2CCu$.

$$C_6H_5(CH_3)_2CCH_2Cu\cdot(n\text{-}C_4H_9)_3P \longrightarrow Cu^0 + (n\text{-}C_4H_9)_3P + C_6H_5(CH_3)_2CCH_2\cdot$$

$$\begin{tikzcd}
 & \text{H abstraction, dimerization} \\
C_6H_5(CH_3)_2CCH_2\cdot \arrow[ur] \arrow[dr] & \\
 & C_6H_5CH_2(CH_3)_2C\cdot \arrow[d] \\
 & \text{Disproportion, dimerization}
\end{tikzcd} \tag{37}$$

Perfluoroalkylcopper compounds when thermally decomposed in aprotic solvents gave mainly the products due to hydrogen abstraction (*200*). The decomposition of 3-phenylhexafluoropropylcopper in DMSO was examined more thoroughly. The major product arose from hydrogen abstraction by the 3-phenylhexafluoropropyl radical. Accompanying products were the dimer and those resulting from a cyclization and a reaction of the radical with the solvent. No olefins from the elimination

$$C_6H_5(CF_2)_3Cu \xrightarrow[\text{DMSO}]{\text{Heat}} C_6H_5(CF_2)_3H + C_6H_5(CF_2)_6C_6H_5 + C_6H_5(CF_2)_3CH_2SCH_3$$

+ 

(38)

of fluorine by an ionic mechanism were isolated, since it was suggested that perfluoro-*tert*-butylcopper decomposes by a heterolytic mechanism (*37*).

The decomposition of methylcopper also proceeds via a radical mechanism and gives either methane or varying quantities of methane and ethane, according to the conditions of the decomposition. Costa *et al.* have found that the decomposition of pure dry methylcopper or of a suspension in heptane gave methane, via methyl radicals, and copper metal only (*76*, *78*, *81*). Methylcopper reagents containing magnesium

$$CH_3Cu \longrightarrow CH_3\cdot + Cu^0 \xrightarrow{\text{Solvent}} CH_4 \qquad (39)$$

or lithium salts when decomposed in dry ether (*82*, *119*, *125*) gave a mixture of methane and ethane, the latter always being the major component. A similar result was obtained by thermal decomposition of methyl[tris(triphenylphosphine)]copper in the presence of solvent (*82*, *310*). The sterically hindered neopentylcopper is more thermally stable than methylcopper (*274*, *276*), and both are much more stable than some higher homologs of methylcopper (*276*).

Ethylcopper mainly decomposes by disproportionation, but a slow homolysis has been reported (*276*) and is suggested by the isolation of butane in certain decompositions (*13*, *80*).

b. *Disproportionation.* Whitesides *et al.* have demonstrated the involvement of copper(I) hydride in the disproportionation of alkylcopper compounds to alkane and alkene (*302*). *n*-Butyl(tri-*n*-butylphosphine)-copper decomposed in ether at 0°C within 4 hours to give equimolar proportions of *n*-butane and 1-butene, and 10% hydrogen. A further quantity of hydrogen was obtained by hydrolysis of the mixture on completion of the decomposition. The dominant pathway for the thermal decomposition of this copper compound was found to be a two-step process which did not involve free radicals. 1-Butene was formed by the β-elimination of copper(I) hydride [Eq. (40)], followed by reduction of a second molecule of the copper compound by this hydride [Eq. (41)] (see Section V). Isotopic dilution techniques were used to confirm the formation of copper(I) hydride. Formation of less than 0.1% octane is

$$C_2H_5CH_2CH_2Cu\cdot L \longrightarrow C_2H_5CH{=}CH_2 + HCu\cdot L \qquad (40)$$

$$C_2H_5CH_2CH_2Cu\cdot L + HCu\cdot L \longrightarrow C_4H_{10} + 2Cu^0 + 2L \qquad (41)$$

$$(L = (n\text{-}C_4H_9)_3P)$$

sufficient to establish that *n*-butyl radicals were not the precursors of *n*-butane and 1-butene. Furthermore, the thermal decomposition of hex-5-enyl(tri-*n*-butylphosphine)copper in ether yielded, besides 44% 1-hexene and 52% 1,5-hexadiene, only 3.5% of cyclized hydrocarbons arising presumably via the known rapid cyclization of 5-hexenyl radicals.

Wada *et al.* found that the decomposition of *n*-propylcopper in THF solution produced approximately equal amounts of propylene and propane (*283*), consistent with the results for *n*-butyl(tri-*n*-butylphosphine)-copper in ether, but not an appreciable quantity of hydrogen (*276*). Examination of the rate of decomposition of ethylcopper in THF at 0°C revealed an induction period which was removed by addition of partially decomposed ethylcopper. Its visible absorption and EPR spectra showed marked changes during the decomposition. The solution of ethylcopper in THF gradually turned purple, apparently without decomposition, but no EPR spectrum was obtained during this period; a paramagnetic species was detected only during the evolution of ethane and ethylene. This species, not a minor component, was probably a binuclear copper compound of the type RCu(I)Cu(0) in which the alkyl group is within the coordination sphere of both copper atoms. Another possibility is that the EPR spectrum was due to an alkyl radical complex with a binuclear Cu(I)Cu(I) species (*283*). The decomposition of *n*-propylcopper was also dramatically affected by catalytic amounts of soluble silver(0), palladium(0), and copper(0) species. Considering the results of Whitesides *et al.* (*302*), the autocatalytic decomposition of alkylcopper compounds in THF was expressed by Eq. (42)–(44).

$$\mathrm{RCu^{I} + Cu^{0} \longrightarrow RCu^{I}Cu^{0}} \tag{42}$$

$$\mathrm{RCu^{I}Cu^{0} \xrightarrow{Fast} R(-H) + Cu^{0} + Cu^{I}H} \tag{43}$$

$$\mathrm{RCu^{I} + Cu^{I}H \longrightarrow RH + 2Cu^{0}} \tag{44}$$

Alkylcopper compounds are more stable in THF than in ether solutions, even with the help of phosphine ligands, because of the ability of THF to form more stable complexes (*283*). A paramagnetic species was not detected in ether solution.

tert-Butyl(tri-*n*-butylphosphine)copper also disproportionates on decomposition in ether (*299*).

A mixture of two different alkylcopper compounds can, when thermally decomposed, give rise to cross-coupled dimers (*37*, *299*) and cross-disproportionation products (*275*), as in Eq. (45) and (46). The copper(I) hydride mechanism does not appear to be sufficient to explain the cross-disproportionation [Eq. (46)] observed by Tamura and Kochi (*275*, *276*).

$$R'Cu + R''Cu \longrightarrow R'R'' + 2Cu^0 \tag{45}$$

$$R'Cu + R''Cu \longrightarrow R'(-H) + R''H + 2Cu^0 \tag{46}$$

Decomposition of a mixture of ethylcopper and *n*-propylcopper gave more ethane and propene than the alternative cross-disproportionation products, whereas a mixture of ethylcopper and isopropylcopper gave more ethylene and propane. In the α,β-elimination of metal hydrides from primary, secondary, and tertiary alkylmetal compounds the ease of elimination generally decreases in the order *tert* > *sec* > *p*. Thus, isopropylcopper would be expected to undergo elimination of a β-hydride more readily than *n*-propylcopper. The order of thermal stability of some alkylcopper reagents, prepared by the reaction of two equivalents of alkylmagnesium halide with one equivalent of copper(II) chloride in THF but not isolated, was neopentyl > methyl ≫ *n*-propyl > ethyl > isopropyl (*276*). No clear choice between the hydride mechanism and direct dismutation for the decomposition of alkylcopper compounds with β-H atoms can be made on the basis of evidence available. Uneven disproportionation of a mixture of alkylcopper species may be a consequence of redox reactions between alkyl radicals and a copper species, analogous to the so-called electron-transfer oxidation of alkyl free radicals by copper(II) compounds (see Section VIII, D). The tendency of an alkylcopper to give less alkene than alkane is in accordance with the decreasing importance of elimination in electron-transfer oxidations according to the structure of the alkyl radical, namely *p* > *sec* > *tert*, and the corresponding increasing importance of substitution reactions. Copper(II) compounds might be formed by disproportionation of an alkylcopper(I) into an alkylcopper(II) species and copper metal, from which may also be obtained the paramagnetic species observed in the autocatalytic decomposition of ethylcopper (*276*). Tamura and Kochi

$$2RCu^{I} \longrightarrow R_2Cu^{II}(Cu^0) \longrightarrow [R\cdot RCu^{I}(Cu^0)] \tag{46a}$$

opine that further discussion of the disproportionation mechanism is best deferred in view of the autocatalysis.

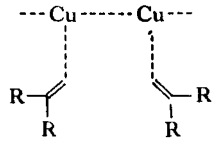
Obviously, great care should be taken to eliminate trace metals when studying the reactions of organocopper compounds. Semiquantitative flame spectrophotometric analysis of the residues from dissolution of commercial copper(I) iodide in di-*n*-butyl sulfide revealed the presence of iron, nickel, and chromium. Both iron and nickel salts were found to significantly effect some reactions of organocuprates (*297*).

c. *Dimerization.* Copper compounds in which the organic moiety is aryl or vinyl decompose into dimer, without the intervention of free radicals. Dimer was the major or only product isolated from the thermal decomposition of phenylcopper or *p*-tolylcopper in an aprotic solvent (*121*, *131*, *219*, *238*, *258*). Hashimoto and Nakano favored a free-radical mechanism for these decompositions (*131*), primarily on the grounds that the presence of the radical acceptor *p*-benzoquinone decreased the yields of dimers. However, aryl radicals were not detected, and the decomposition was alternatively explained as a bimolecular, non-free-radical decomposition, and an unknown reaction of the copper compound with the quinone. More recent studies of pentafluorophenylcopper and *o*-(trifluoromethyl)phenylcopper tetramers showed that their decomposition to dimers is non-free-radical and is catalyzed by copper metal (*32*, *37*). The decomposition must occur on the metal cluster. The octameric *m*-(trifluoromethyl)phenylcopper also decomposes to the dimer and copper metal, but no copper metal separates initially and the decomposition is not catalyzed by copper metal (*35–37*). A stable Cu(I)–Cu(0) cluster compound, $Cu_8[m\text{-}(CF_3)C_6H_4]_6$, was isolated. Kinetic data, obtained by following the decomposition in benzene solution by cryoscopy or ^{19}F NMR, only fitted the scheme shown, viz.,

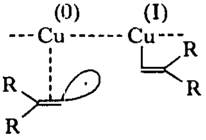
$$R_8Cu_8 \xrightarrow{k_1} R_2 + R_6Cu_8 \xrightarrow{k_2} R_2 + R_4Cu_8 \qquad (47)$$
$$[R = m\text{-}(CF_3)C_6H_4]$$

The *m*-(trifluoromethyl)phenyl groups are lost in pairs, stepwise, in a unimolecular reaction for which the ratio of the rate constants, k_1/k_2, is 28 at 73.7°C. Cairncross and Sheppard believe that this behavior may be typical of other arylcopper compounds which are not highly substituted by fluorine (*37*).

Thermal decomposition of *cis*- and *trans*-1-propenylcopper and their mono(tri-*n*-butylphosphine) complexes yields the hexadienes, with retention of configuration at the double bonds, and copper metal (*293*, *294*). The cis isomer is configurationally unstable under the conditions of room-temperature thermal decomposition. However, the isomerization could be almost completely suppressed by performing the thermal decomposition in a sealed tube at 90°C. Propenyl radical intermediates were eliminated on the grounds that their rate of dimerization with retention of configuration would have to be at least 100 times faster than their rate of isomerization and the usual rate of a diffusion-controlled reaction. Non-free-radical mechanisms could involve a four-center transition state, (VII), or a σ–π interconversion to an intermediate containing vinyl radicals π-bonded to a copper cluster, (VIII), or even by disproportionation to copper metal and an unstable copper(II) compound



(VII)



(VIII)

(*294*). Similar results were obtained for 2-butenylcopper (*294*).

d. *Heterolysis.* Pentafluorophenyllithium and Grignard reagents are thermally unstable and decompose to tetrafluorobenzyne by loss of metal fluoride (*149*, *259a*). The final product from the decomposition is an intractable "perfluoropolyphenylene." Pentafluorophenylcopper reagents are very stable in THF and can be refluxed for 5 days or more without decomposition (*97*, *144*). However, when the solvent is DMAC and the solution is heated for 8 hours at 100°C approximately 50% of the reagent decomposes to an intractable polymeric material. The decomposition is accelerated by the addition of decafluorobiphenyl, which suggests a heterolytic mechanism (*97*); pentafluorophenylcopper is more nucleophilic in DMAC than in THF. A suitable explanation of this behavior is provided by the views of Burdon *et al.* (*31*). It is suggested that a solution of a copper compound, RCu, in a solvent which is a ligand, L, for copper forms a species $RCuL_3$ which is in equilibrium with another copper species $(CuL_4)^+R^-$ [Eq. (49)]. The position of the equilibrium will depend on the strength of the ligand. The latter species is designated as a dissociated ion pair in which R^- may act partly or totally independently of the copper complex.

$$C_6F_5M \xrightarrow{-MF} [C_6F_4] \xrightarrow{C_6F_5M} o\text{-}C_6F_5\text{—}C_6F_4M \xrightarrow{-MF} [C_6F_5C_6F_3] \longrightarrow \text{polyphenyls} \tag{48}$$

$$RCu + nL \longrightarrow RCuL_3 \rightleftharpoons (CuL_4)^+R^- \tag{49}$$

The pentabromophenylcopper reagent (plus $MgBr_2$) in THF is very unstable compared to its fluorine analog and decomposes within 1 hour at reflux temperature to an intractable mixture of polyphenyls (*262*).

The mass spectrum of perfluoro-*tert*-butylcopper revealed only perfluoroisobutene. Based on this evidence and on its function as a fluorinating agent, Cairncross and Sheppard (*37*) have suggested a heterolytic decomposition mechanism involving elimination of unstable copper(I) fluoride.

$$(CF_3)_3CCu \longrightarrow (CF_3)_2C{=}CF_2 + CuF \tag{50}$$

4. *Effect of Aggregation*

Organocopper compounds can form mixed aggregates. For example, a mixture of pentafluorophenylcopper and *o*-(trifluoromethyl)phenylcopper tetramers forms mixed cluster compounds in which ligands have been exchanged. The products may be explained by either a cluster dissociation or a ligand exchange (*37*). Pentafluorophenylcopper tetramer and the octameric *m*-(trifluoromethyl)phenylcopper do not readily exchange when heated together in benzene at 80°C for 15 minutes. A small quantity of the compound $Cu_4(m\text{-}CF_3C_6H_4)(C_6F_5)_3$ was detected by mass spectroscopy. However, exchange must eventually occur as the thermal decomposition of a mixture of these two copper compounds affords the cross-dimerization product, $C_6F_5\text{-}C_6H_4CF_3\text{-}m$, as well as the symmetrical biphenyls. Ligand substitution in pentafluorophenylcopper can also be effected by other reagents, such as hydrogen chloride (*37*).

$$A_4Cu_4 + B_4Cu_4 \longrightarrow A_3BCu_4 + A_2B_2Cu_4 + AB_3Cu_4 \tag{51}$$
$$(A = C_6F_5;\ B = o\text{-}(CF_3)C_6H_4)$$

$$(C_6F_5Cu)_4 + HCl \longrightarrow (C_6F_5)_{4-n}Cl_nCu_4 + C_6F_5H \tag{52}$$
$$(n = 0\text{–}4)$$

Another effect of aggregation is to allow the formation of core-substituted clusters. *o*-(Trifluoromethyl)phenylcopper exchanges with its silver analog to give copper–silver tetranuclear compounds of the type $Ag_nCu_{4-n}(o\text{-}CF_3C_6H_4)_4$, the parent ions of which have been detected by mass spectroscopy. The C—Ag bonds break preferentially on thermal decomposition, leaving the copper compound (*37*). A mixed cluster compound was also isolated by Seitz and Madl (*258*). Core substitution obviously occurs in the preparation of the "ate" complex $Li_2Cu_2R_4$ from $(RCu)_4$ and $(RLi)_4$, where R is the *o*-(dimethylaminomethyl)phenyl group (*281f*).

$$(RCu)_4 + (RLi)_4 \longrightarrow Li_2Cu_2R_4 \tag{53}$$

C. Order of Reactivity

There is a paucity of information on the relative reactivities of various organocopper compounds. The relative reactivities of some alkylcopper reagents towards deuterido(tri-*n*-butylphosphine)copper vary only slightly with structure. An order of decreasing reactivity towards $Cu[P(n\text{-}C_4H_9)_3]D$ of *tert*-butyl > neophyl > isobutyl > *n*-butyl with relative reactivities of 3.3:3:1.3:1.0, respectively, was obtained in ether at 0°C (*299*). Some lithium dialkylcuprates are reported to be more reactive than the dimethylcuprate, which in turn is more reactive than methylcopper (*69*). The order of reactivity of some methylcopper complexes, according to the yield of acetophenone from their reactions with benzoyl chloride, is $LiCu(CH_3)_2 > Cu[P(n\text{-}C_4H_9)_3]CH_3 > CuCH_3$ (*295*).

Little differentiation between various polyhaloarylcopper compounds was achieved by reaction of pairs of reagents with a deficiency of acetyl chloride in THF–hexane at 0°C, although pentachlorophenylcopper and 2,3,5,6-tetrachloro-4-pyridylcopper reagents (containing metal halides) appear to be more reactive than a pentafluorophenylcopper reagent (*148*). The reaction of various RM compounds with benzalacetophenone has been used to differentiate between the more reactive kinds (1,2-addition) and the less reactive types (1,4-addition), of which phenylcopper (plus MX) is an example (*119*, *144*). However, none of the above polyhaloarylcopper (plus MX) reagents added to benzalacetophenone; only halogen-free intractable polymeric products were obtained (*144*). The obvious conclusion, that polyhaloarylcopper reagents are less reactive than phenylcopper, agrees with the idea expressed by van Koten and Noltes concerning the bridging abilities of various ligands when attached to a polynuclear metal cluster (*281f*): The order of increasing reactivity of organocuprates for the ligands $NC^- < RC{\equiv}C^- < Ar^- < Alk^-$ parallels the order of decreasing bridging ability of these ligands, $NC^- > RC{\equiv}C^- > Ar^- > Alk^-$.

IV

REDUCTION

Whitesides and co-workers have examined the reactivity of copper(I) hydride towards organocopper compounds as a model for the study of other transition metal hydride–metal alkyl systems (*301*). Copper(I) hydride, which is unstable above −20°C, was prepared from copper(I) bromide and diisobutylaluminum hydride in pyridine at −50°C and precipitated by dilution with ether. The solid, which contained about 25% pyridine but was otherwise very pure, formed a highly soluble complex with tri-*n*-butylphosphine. The complex reduces alkyl-, vinyl,- and arylcopper compounds to the corresponding hydrocarbons in high yields under mild conditions. Free radicals are not involved. Reduction of *endo*-2-norbornyl(tri-*n*-butylphosphine)copper with copper(I) hydride compounds was accomplished with complete retention of configuration, under conditions in which norbornene is not reduced. Similarly, *cis*- and *trans*-2-butenyl(tri-*n*-butylphosphine)copper were reduced to 2-butene with retention of configuration, and neophyl(tri-*n*-butylphosphine)copper was reduced to *tert*-butylbenzene. A mixed aggregate could be involved in these reductions (*301*). Salt-free *cis*-2-butenyl(tri-*n*-butylphosphine)copper was also reduced by tri-*n*-butyltin hydride on warming an ether solution from −78°C to room temperature. The products were 2-butene (40% yield, 78% cis) and *cis,cis*-2,4-hexadiene (11%) (*294*).

The coupling of β-bromostyrene with lithium diorganocuprates at a low temperature was also accompanied by reduction and elimination as important side reactions (*309*). The reaction is summarized by Eq. (54).

$$C_6H_5CH{=}CHBr \xrightarrow{Li(R_2Cu)} C_6H_5CH{=}CHR + C_6H_5CH{=}CH_2 + C_6H_5CH_2CH_2R + R(-H) \quad (54)$$

(R = *n*-propyl; *tert*-butyl)

A suitable explanation of the products may be that coupling and exchange occur initially, and then some of the large excess of cuprate decomposes by disproportionation to the alkene and copper(I) hydride (see Section III,B,3,b). Reduction and coupling to yield $C_6H_5CH_2CH_2R$ probably takes place on an aggregate containing styryl, alkyl, and hydride ligands, as styrenes, $C_6H_5CH{=}CHR$, are not reduced by dialkylcuprates.

Furthermore, no reduction products were isolated from a similar reaction between *trans*-β-bromostyrene and lithium diphenylcuprate, although considerable copper–halogen exchange probably occurred.

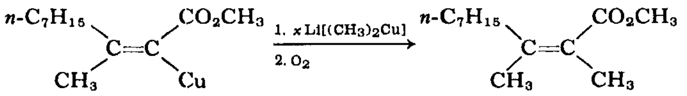
V

OXIDATION AND DIMERIZATION

The oxidation of organocopper compounds is a useful way of forming carbon–carbon bonds. Oxidative coupling of copper acetylides is well known (*44*, *112*, *237*, *261*). The reaction has been investigated by Whitesides *et al.* for alkyl-, vinyl-, and arylcuprates (*300*). High yields of dimers were obtained from many types of copper compounds: ethynyl, vinyl, aryl, primary alkyl, and secondary alkyl. Poor yields of dimers were obtained from tertiary alkylcopper compounds, and of cyclized product from the stoichiometric "ate" complexes prepared from equimolar proportions of alkyl-α,ω-di(magnesium bromide) and iodo(tri-*n*-butylphosphine)copper(I) (*300*). Higher yields of dimers were obtained by oxidation in THF or DME solution rather than in ether or hydrocarbons. The evidence against long-lived free radicals is as follows: First, high yields of R_2 were obtained from the decomposition of $LiCuR_2$ types in which R is the neophyl or *trans*-1-propenyl group. Second, partial oxidation of the di-*n*-butylcuprate (containing lithium salts and a phosphine) gave some uncomplexed *n*-butylcopper. As a variety of oxidants can be used to oxidize a cuprate to give the dimer in similar yields, Whitesides *et al.* consider their function to be one of an electron acceptor. A suggested oxidation mechanism involves formation of a di-*n*-butylcopper(II) compound which disproportionates to octane and *n*-butylcopper [Eq. (55)]. The latter can be further oxidized to octane; 1-butene and *n*-butanol are by-products (*300*).

$$[(n\text{-}C_4H_9)_2Cu^{I}]^{(-)} \xrightarrow{-4e} 2(n\text{-}C_4H_9)_2Cu^{II} \longrightarrow n\text{-}C_8H_{18} + 2n\text{-}C_4H_9Cu^{I} \qquad (55)$$

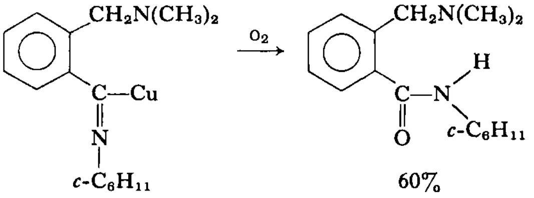
Mixed cuprates of the type LiCuR′R″ are oxidized to homo-coupled (R'_2 and R''_2) and/or cross-coupled (R′R″) dimers (*259*, *300*). Oxidation of a mixture of two cuprates containing a considerable excess of one affords the cross-coupled dimer in high yield (*61*, *292*, *297*). Oxidation



(56)

can be employed in the less effective coupling reactions of cuprates with organic halides where copper–halogen exchange is important: higher yields of cross-coupled products can be obtained by terminal oxidation of the mixture prior to hydrolysis (*297*).

Oxygen-containing products are obtained from O_2 oxidations of many arylcopper reagents. Whereas pentafluorophenylcopper gives decafluorobiphenyl (*34*, *97*), pentachlorophenylcopper and pentabromophenylcopper afford their respective phenols only (*262*, *272*). Phenyl-, tolyl-, and *o*-anisylcopper compounds autoxidize to a mixture of dimer and copper(II) phenates (*41a*). Another oxygen-containing product was obtained by the reaction illustrated in Eq. (57) (*281d*). Oxidative hydrolysis of perfluoroheptylcopper in ether gave perfluoroheptanoic acid (*200*), presumably via an unisolable perfluoroalkyl alcohol (*259a*).



(57)

$$C_7F_{15}Cu \cdot \xrightarrow[H_2O]{O_2} [C_7F_{15}OH] \longrightarrow C_6F_{13}CO_2H \qquad (58)$$

The thermal decomposition of aryl- and vinylcopper compounds is an alternative method of obtaining dimeric products from organocopper compounds. Both methods have been used extensively by Kauffmann and co-workers (*153–164*). Thermal decomposition of organocopper compounds of the type ZN=C(R)—CHRCu affords suitable precursors for a variety of 1,4-diketones. Thermal decomposition is not applicable to all organocopper compounds (see Section III,B,3). Various oxidations and dimerizations are listed in Table V.

Another method of obtaining dimeric products from organolithium and Grignard reagents is by reverse addition to an excess of a copper(II) salt (*159*, *161*). A number of polyphenylenes have been prepared by the reaction of aryl dilithium or di-Grignard reagents with an excess of copper(II) chloride, mostly in THF (*25*, *267*, *268*). The preparation of *m*-hexaphenylene (*267*) is illustrated by Eq. (59). Very low yields of *m*-pentaphenylene and *m*-decaphenylene were obtained from a similar reaction involving *m*-quinquiphenyl-3,3-''''di(magnesium bromide) (*268*).

TABLE V
Thermal and Oxidative Dimerization via Organocopper Compounds

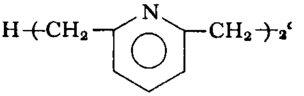
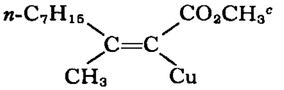
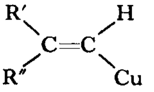
Copper compound[a]			Conditions		Dimer yield (%)	References
			Oxidant	Temp. (°C)		
Of type RCu[b]						
C_2H_5[c]			NO_2	2	80	*276*
n-C_3H_7[c]			O_2	−50	95	*276*
$H_5C_2O_2CCH_2$[c]			O_2	−50	73	*181*
$C_6H_5COCH_2$			—	35	11	*154*
$C_6H_5SO_2CH_2$[d]			—	20	20–25	*154*
$(C_6H_5)_2P(O)CH_2$[c]			O_2	20	43	*154*
X—N=C(Y)C(Z)H						
X	Y	Z				
C_6H_5	C_6H_5	H	—	35	42	*154*
$(CH_3)(C_6H_5)C{=}N$	C_2H_5	H	—	20[e]	54	*163*
$(CH_3)(C_6H_5)C{=}N$	C_6H_5	H	O_2	66[c]	52	*154*
$(C_6H_5)_2C{=}N$	C_6H_5	H	—	20[e]	96	*163*
			O_2	66[c]	84	*154*
$(C_6H_5)_2C{=}N$	C_6H_5	CH_3	—	20[e]	57	*163*
$(C_6H_5)_2C{=}N$	C_6H_5	C_2H_5	—	20[e]	76	*163*
$(C_6H_5)_2C{=}N$	1-$C_{10}H_7$	H	—	20[e]	80	*163*
$(C_6H_5)CH{=}N{-}C(C_6H_5)H$[f]			—	85	58	*155*
Aryl-C(R)H						
Aryl		R				
2-Pyridyl		H	—	60[e]	78	*155*
2-Pyridyl		CH_3	—	60[e]	63	*160*
2-Pyridyl		C_6H_5	—	60[e]	65	*160*
6-Methyl-2-pyridyl		H	—	60[e]	71	*160*
4-Pyridyl		H	—	60[e]	54	*160*
4-Pyridyl		CH_3	—	60[e]	40	*160*
4-Pyridyl		C_2H_5	—	60[e]	34	*160*
4-Pyridyl		C_6H_5	—	60[e]	65	*160*
2-Quinolyl		H	—	80[g]	69	*160*
4-Quinolyl		H	—	80[g]	58	*160*
2-Phenyl-4-quinolyl		H	—	80[g]	74	*160*
3-Methyl-2-quinoxalinyl		H	—	80[g]	61	*160*
			—	60	48	*156*
$CH_2{=}CH$[c]			—	20	60.5	*162*
$CH_3CH{=}CH$			—	0–25	84–100[h]	*294* (*162*)
$(CH_3)_2C{=}CH$[c]			—	20	97	*162*
$CH_3CH{=}CCH_3$			—	18	72–99[h]	*294*

TABLE V—*Continued*

	Conditions			
Copper compound[a]	Oxidant	Temp. (°C)	Dimer yield (%)	References
	O_2	−78	NG^i	*61*
				
R′ R″				
C_4H_9 C_2H_5	O_2	10	74.5^h	*223*
C_2H_5 C_4H_9	O_2	10	67.5^h	*223*
C_6H_5 C_2H_5	O_2	10	55^h	*223*
H C_4H_9	O_2	20	68.5^h	*223*
$2\text{-}(C_4SCl_3)^j$	$C_6H_3(NO_3)_3$	−20	75	*215*
$2\text{-}[5\text{-}(2\text{-}C_4NH_3)C_4SH_2]$	O_2	60	63	*164*
$2\text{-}[5\text{-}(2\text{-}C_4SH_2)C_5NH_3]^c$	O_2	60	5	*164*
C_6H_5	O_2	0^l	26.5	*41a*
	—	80^k	65–73	*131*
$2\text{-}/3\text{-}/4\text{-}CH_3C_6H_4$	O_2	0^l	16–32.5	*41a*
$4\text{-}CH_3C_6H_4$	—	80^k	62	*131*
$2\text{-}CH_3OC_6H_4$	O_2	0^l	19	*41a*
$3\text{-}CF_3C_6H_4$	O_2	NG^i	37	*37*
$4\text{-}CF_3C_6H_4$	O_2	NG^i	47	*37*
$4\text{-}FC_6H_4$	O_2	NG^i	25	*37*
$C_6F_5{}^c$	O_2	20	70–80	*97*
$4\text{-}(C_6F_5O)C_6F_4{}^c$	O_2	25	71	*96*
Of type $LiR_2Cu^{b,c}$				
$n\text{-}C_4H_9$	O_2	−78	84	*300*
$sec\text{-}C_4H_9$	O_2	−78	82	*300*
$t\text{-}C_4H_9$	O_2	−78	14	*300*
C_6H_5	O_2	−78	75	*300*
$trans\text{-}CH_3CH{=}CH$	O_2	−78	78	*300*
$C_6H_5C{\equiv}C$	O_2	15	67	*300*
Neophyl	O_2	−78	88	*300*

[a] The copper compounds were prepared and oxidized in ether solution without halide removal or isolation, unless otherwise indicated.

[b] No structural connotation.

[c] In THF.

[d] In Et_2O–THF–C_6H_6.

[e] In Et_2O–THF.

[f] In DME.

[g] In Et_2O–DME.

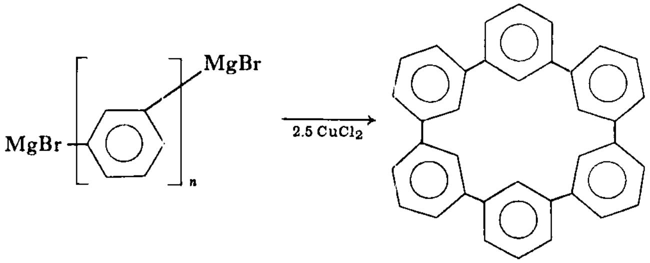
[h] Stereospecific

[i] NG = Not given.

[j] In pyridine

[k] In ether–xylene.

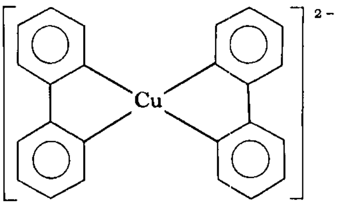
[l] Copper(II) phenates are important by-products.



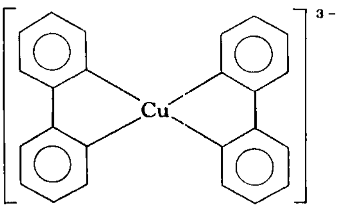
(59)

n	1	2	3	6
% Yield	1·1	11	22	45

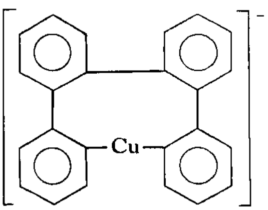
The reaction of 2,2′-dilithiobiphenyl, or the analogous Grignard reagent, with excess copper(II) chloride gave a mixture of products from which biphenylene and *o*-tetraphenylene were isolated (*235*, *304*). Other products were tetra- and octaphenyls. The reaction was explained in terms of the formation of a copper(II) "ate" complex (IX) which, under the influence of further Cu^{2+} ions, oxidatively couples to give a 60% yield of *o*-tetraphenylene. Two copper(I) "ate" complexes, (Xa) and (Xb), are probably formed from the reaction of 2,2′-dilithiobiphenyl with copper(I) chloride produced by the initial reduction, and give rise to the quaterphenyl, octaphenyl, and *o*-tetraphenylene (*304*). The complex (Xb) must be very stable since a good reaction with iodine was reported after 14 days.



(IX)



(Xa)



(Xb)

The dimerization reaction is also applicable to compounds containing N—Cu bonds (*153*, *155*, *157*, *163*) and S—Cu bonds (*122*).

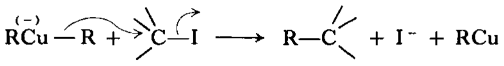
VI
SUBSTITUTION REACTIONS

A. Organic Halides

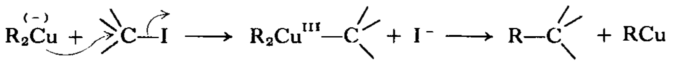
Organocopper compounds are useful reagents for coupling reactions with organic halides (*68*, *69*). Cross-coupling with organic halides is not unique to copper, but organocuprates of the type $Li(R_2Cu)$ are superior in every way to other main group transition metal "ate" complexes (*70*). The cuprates are generally more effective for such couplings than the lithium reagents, RLi, which can undergo competing coupling, exchange, and elimination reactions. The copper compounds are also more effective than other organometallic reagents, such as those of magnesium, zinc, and aluminum (*297*).

Since Corey and co-workers first described the coupling of dialkylcuprates with organic halides (*68*, *69*), Whitesides *et al.* have reported details of their examination of this reaction (*297*). The results of the reaction of typical diorganocuprates with alkyl halides indicate that the products of metal–halogen exchange are not, if they occur at all, important transitory intermediates. Reaction of lithium diphenylcuprate with 2-bromobutane proceeds with predominant (84–92%) inversion of configuration. The yield of coupled product can be improved by using a more basic solvent such as THF. Other organocopper compounds were also found to be more nucleophilic in solvents such as DMAC or hexamethylphosphorus triamide (HMPT) (*97*, *225a*).

A mechanism for carbon–carbon bond formation involving S_N2 displacement at carbon is consistent with the above observations. Two possible pathways for coupling were mentioned (*297*): (1) a simple displacement of halide by an alkyl group [Eq. (60)], and (2) displacement of the halide by the copper atom's *d* electrons, with inversion of configuration, to form a copper(III) species which decomposes with retention of



(60)



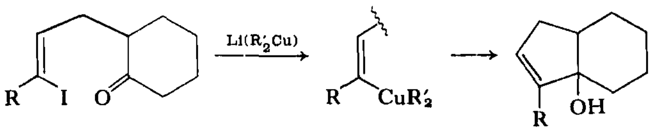
(61)

configuration. From a study of the reaction of sodium cyanocuprates with aryl and vinyl halides House and Fischer (*138*) have concluded that the coupling of organocopper compounds with organic halides does not involve preliminary ionization of the carbon–copper bond, since the groups most capable of providing carbanions are those which are the least reactive.

The consensus favors a transitory copper(III) intermediate in the reaction of a copper compound with an alkyl or vinyl halide (*37*, *57*, *65*, *185*, *297*), although Tamura and Kochi consider such an intermediate unlikely for alkyl halides (*276*). Collman (*57*) has suggested that organocopper compounds are representative of a number of d^8–d^{10} transition metal complexes which undergo oxidative addition to organic halides. Evidence has been obtained from the reaction of copper(I) carboxylates with organic halides (*185*) to support a mechanism involving nucleophilic attack by copper *d* electrons on the halide, giving a transient copper(III) intermediate with inverted configuration at carbon [Eq. (62)]. Nucleophilic displacement by the RCO_2^- anion does not occur and free-radical or carbonium ion intermediates do not participate in this direct preparation of esters from organic halides. A δ-halo ketone of the vinylic halide type and lithium di-*n*-butylcuprate, under suitable conditions of solvent and temperature, led to the formation of the cyclization product [Eq. (63)] in >90% yield, presumably via a copper(III) intermediate (*65*).

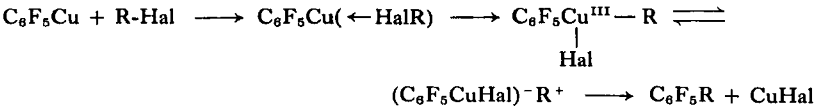
$$RCO_2Cu^I + R'\text{—}X \longrightarrow [RCO_2Cu^{III}(X)R'] \longrightarrow Cu^IX + RCO_2R' \qquad (62)$$

(R = Benzoate, pivalate; R′ = Neophyl, neopentyl)



(63)

A slightly different mechanism has been proposed by Cairncross and Sheppard (*37*) for the reaction of fluoroarylcopper compounds with substituted alkyl halides. Pentafluorophenylcopper can form a complex with bicyclooctyl bromide by coordination with the halogen atom. Such a complex may go directly to coupled product in a four-center process, or, depending on the nature of the group attached and the nature of the alkyl moiety, may form an ion pair which collapses to the coupled

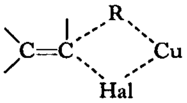


$$C_6F_5Cu + R\text{-}Hal \longrightarrow C_6F_5Cu(\leftarrow HalR) \longrightarrow \underset{\displaystyle Hal}{C_6F_5Cu^{III}}\!-R \rightleftharpoons$$
$$(C_6F_5CuHal)^-R^+ \longrightarrow C_6F_5R + CuHal \quad (64)$$

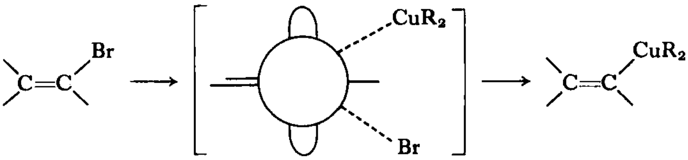
product. In the presence of a good carbonium ion trap none of the expected coupled product is obtained. Equation (65) represents the overall reaction of benzyl bromide with pentafluorophenylcopper in the presence of cumene.

$$C_6F_5Cu + C_6H_5CH_2Br \xrightarrow{\text{cumene}} C_6F_5H + CuBr + C_6H_5CH_2C_6H_4CH(CH_3)_2 \quad (65)$$

Burdon *et al.* (*31*) have proposed that aryl and vinyl halides, but not alkyl halides, couple with copper compounds via a four-center transition state (XI). Nucleophilic substitution of vinylic bromides by organocopper compounds, with retention of configuration, is in agreement with a concerted reaction involving six electrons, including those of the double bond (*174*). Klein and Levene propose that the copper species coordinates with the π-bond and rotates together with the bromine atom in such a way that there is a continuous partial overlap of the orbitals of both the forming and breaking bonds with the p orbital of the β-carbon atom until bromine leaves perpendicularly to the plane of the molecule, thus forming a copper(III) species.

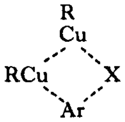


(XI)



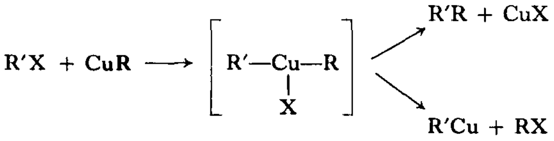
(66)

There is presumably more than a subtle difference between the reactions of alkyl and aryl halides with organocopper compounds, as a straightforward nucleophilic displacement of aryl halide by the *d* electrons of a copper species is hardly likely. Simple aryl halides are nearly all inert to the usual nucleophiles, such as alkoxides, unless strongly activated by electron-attracting groups in the ortho and para positions. However, coordination of the halogen to copper may be sufficient to weaken the aryl–halogen bond and allow nucleophilic attack by copper and the formation of a copper(III) state via intermediate (XII). Any



(XII)

mechanism proposed for the coupling of organocopper compounds with aryl halides must allow for copper–halogen exchange as an important side reaction (*297*). The collapse of the copper(III) species, (XIII), can account for both exchange and coupling products; viz.,



(XIII)

(67)

Direct nucleophilic displacement of halide ion by a group R, not necessarily organic, attached to copper is considered (*31*) to be important only in the presence of ligands, L, which strongly coordinate with copper and aid the formation of the species $(CuL_4)^+R^-$.

Castro *et al.* (*44*) found that the order of reactivity of various halides in coupling reactions with ethynylcopper compounds in DMF is ArSX, ArX > RCOX ≫ $ArCH_2X$, $RCH{=}CHCH_2X$, $ArCOCH_2X$ > RCH=CHX, Alkyl-X. A somewhat different order is observed for the reactivity of some organic halides towards perhaloarylcopper reagents in THF (*97*, *147*): Allyl ≫ Aryl > Alkyl; and perfluoroaryl, perfluorovinyl > aryl > perfluoroalkyl. Acid halides were also far more reactive than aryl iodides in ethereal solvents (*146*). The ease of halide displacement is I > Br > Cl.

1. *Alkyl Halides*

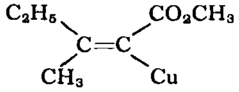
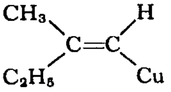
A noticeable feature of the majority of reactions of diorganocuprates with alkyl halides (Table VI) is that molar ratios of up to 5:1, respectively, are employed for most effective coupling. However, good yields of coupled products can be obtained when molar equivalents of the reactants are used, a useful procedure for the more "exotic" copper

TABLE VI
COUPLING WITH ALKYL HALIDES[a]

Copper compound	Alkyl halide	% Yield coupled product	References
Alkyl			
$CH_3Cu \cdot P(C_6H_5)_3$	C_2H_5I	NG	*310*
$Li(CH_3)_2Cu^b$	n-$C_5H_{11}I^d$	98^g	*297*
$Li(CH_3)_2Cu$	c-$C_6H_{11}I^d$	75	*68*
	n-$C_8H_{17}I^e$	97^g	*297*
	n-$C_{10}H_{21}I^d$	90	*68*
	c-4-(t-C_4H_9)$C_6H_{10}Br^d$	55	*68*
	$C_6H_5CH_2Br^d$	89	*68*
	$C_6H_5CH_2Cl^d$	80^g	*231*
	$C_6H_5CH(CH_3)Cl^d$	$40^{g,q}$	*231*
	$C_6H_5CHCl_2{}^d$	$40^{g,q}$	*231*
	1,2-$(ClCH_2)_2C_6H_4$	77^g	*231*
$C_2H_5O_2CCH_2Cu$	$C_6H_5CH_2Br^c$	62	*181*
$Li(n\text{-}C_4H_9)_2Cu^b$	n-$C_5H_{11}I^j$	$69^{g,h,i}$	*297*
	n-$C_5H_{11}Br^{c,j}$	98^g	*297*
	n-$C_5H_{11}Cl^{c,j}$	$80^{g,h}$	*297*
	n-$C_3H_7CHBrCH_3{}^{c,j}$	12^g	*297*
	$C_2H_5CBr(CH_3)_2{}^{c,j}$	$< 10^g$	*297*
$Li(n\text{-}C_4H_9)_2Cu$	n-$C_7H_{15}Cl^d$	75	*69*
	n-$C_{10}H_{21}I^d$	80	*69*
	$HO_2C(CH_2)_{10}I^d$	76^r	*69*
	$CH_3(C_6H_5)NCO(CH_2)_{10}I^d$	82	*69*
	$C_6H_5CH_2Br^d$	30^q	*69*
$Li(n\text{-}C_4H_9)_2Cu \cdot P(C_4H_9)_3$	c-$C_6H_{11}Br^{c,d}$	25^g	*297*
$Li(sec\text{-}C_4H_9)_2Cu \cdot P(C_4H_9)_3$	n-$C_5H_{11}Br^{c,d}$	94^g	*297*
$Li(sec\text{-}C_4H_9)_2Cu$	n-$C_5H_{11}I^{c,d}$	7^g	*297*
	n-$C_5H_{11}Cl^{c,d}$	64^g	*297*
$Li(t\text{-}C_4H_9)_2Cu \cdot P(C_4H_9)_3$	n-$C_5H_{11}Br^{c,d}$	92^g	*297*
$Li(t\text{-}C_4H_9)_2Cu$	n-$C_5H_{11}I/Cl$	$< 1^g$	*297*
Alicyclic			
endo-Norbornyl[p]	CH_3I	$79^{g,l}$	*292*
exo-Norbornyl[p]	CH_3I	$70^{g,l}$	*292*
Allylic and vinylic			
$Li(CH_2{=}CHCH_2)_2Cu \cdot S(C_4H_9)_2$	n-$C_5H_{11}I^{e,m}$	98^g	*297*
$Li(CH_2{=}CH)_2Cu \cdot P(C_4H_9)_3$	n-$C_8H_{17}I^{d,m}$	95^g	*297*
Li(*cis*/*trans*-$CH_3CH{=}CH)_2Cu \cdot P(OCH_3)_3$	n-$C_8H_{17}I$	66/73	*205*
$Li(CH_2{=}CCH_3)_2Cu$	c-4-$CH_3C_6H_{10}Br^{c,d}$	80	*282*
	c-4-$BrC_6H_9O^{c,d}$	65	*282*
	c-4-Br-1-$CH_3C_6H_8{}^{c,d}$	80	*282*
	c-2-Br/Cl-5-$CH_3C_6H_8O^{c,d}$	58/60	*282*
	$C_2H_5O_2CCH_2Br^{c,d}$	65	*282*

Continued

TABLE VI—*Continued*

Copper compound	Alkyl halide	% Yield coupled product	References
	CH_3I	25	*260*
cis-$C_2H_5CH{=}CHCu \cdot P(OC_2H_5)_3$	$C_6H_5CH_2Br^{l,n}$	45	*225b*
 + $P(OC_2H_5)_3$	*n*-$C_4H_9I/Br^{l,n}$	58/39	*225b*
	i-$C_3H_7I^{l,n}$	15	*225b*
	$C_2H_5OCH_2Cl^{l,n}$	55	*225b*
	$C_6H_5CH_2Br^{l,n}$	85	*225b*
Ethynyl			
$C_6H_5C{\equiv}CCu$	$C_6H_5CH_2Br^{o}$	90	*128*
$Li_2(C_6H_5C{\equiv}C)_3Cu$	*n*-$C_5H_{11}I^{k}$	$<1^{g}$	*297*
Aryl			
$Li(C_6H_5)_2Cu$	*c*-$C_6H_{11}Br^{e,m}$	10^{g}	*297*
	n-$C_8H_{17}I^{k}$	99^{g}	*297*
	$C_2H_5CHBrCH_3{}^{e,m}$	87^{g}	*297*
	$(CH_3)_3CBr^{m,p}$	$<1^{g}$	*297*
	Adamantyl $Br^{e,m}$	$<1^{g}$	*297*
$Li(C_6H_5)_2Cu^{c}$	$C_2H_5O_2CCH_2Br$	60	*282a*
$Li(4\text{-}CH_3C_6H_4)_2Cu^{c}$	$(CH_3)_2C{=}$ $CH(CH_2)_2CBrCH_3$	65	*282a*
$Li(4\text{-}CH_3OC_6H_4)_2Cu^{c}$	$C_6H_5CH_2Cl$	50	*282a*
C_6F_5Cu	$CH_2I_2{}^{c,u}$	70	*147*
	n-$C_4H_9I^{c}$	23	*147*
	$(C_6H_5)_2CHCl$	53	*37*
$C_6F_5Cu^{s}$	CH_3I^{t}	39	*37*
	Adamantyl Br	83	*37*
	1-Br-bicyclo[2.2.2]octane^{t}	83	*37*
	$C_6H_5CH_2Br^{v}$	40	*37*
	7-Cl Norbornadiene^{v}	63	*37*
	$(C_6H_5)_2CHCl^{v}$	85	*37*
	$(C_6H_5)_3CCl^{v}$	37–59	*37*
$3\text{-}CF_3C_6H_4Cu^{s}$	$C_6H_5CH_2Br^{v}$	51	*37*
	$(C_6H_5)_2CHCl^{v}$	45	*37*
	Adamantyl Br^{v}	48	*37*

N.G. = not given

[a] Unless otherwise specified, the copper compounds were prepared in ether with the indicated stoichiometry (no structural connotation), were not isolated, and contained lithium or magnesium halides. For the cuprates, the reaction ratio per C—Hal bond is 1 : 2, and the product yields are of isolated pure materials, unless otherwise stated.

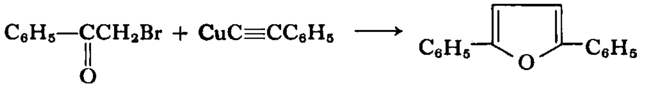
compounds. Dialkylcuprates react just as readily with alkyl bromides and chlorides as with alkyl iodides provided the solvent is THF and not ether (*297*), otherwise very long reaction times are necessary (*69*). Lithium halides formed during the preparation of "ate" complexes appear to have little effect on the reaction with organic halides. The initial rate of reaction appears to be slower for initially salt-free cuprates (*297*). Certain recommendations have been made for effecting coupling reactions between a diorganocuprate and an organic halide when one of the organic species is a secondary or tertiary alkyl group (*297*). Mixed cuprates of the type Li(RCuZ) in which Z is *t*-butoxy and can stabilize secondary and tertiary alkyl groups allow more economical use of the reagent (only 20–30% excess) in coupling with *n*-alkyl halides and acid chlorides (*231b*). Unsymmetrical cyanocuprates (Z = CN) can be used for similar reactions and in 1,4-additions (*126a*, *225*).

Organocopper compounds of stoichiometric ratio RCu do not always react with alkyl bromides (*29*, *44*, *66*, *147*, *181*). Where possible, a reaction may be effected at higher temperatures (*128*), in a more strongly coordinating solvent (*31*, *297*), or by means of the cuprate species (*297*). An unsubstantiated coupling reaction between phenylcopper and butyl bromide in an aromatic solvent was mentioned (*24*), although it is doubtful that an organocopper species was employed (*285*).

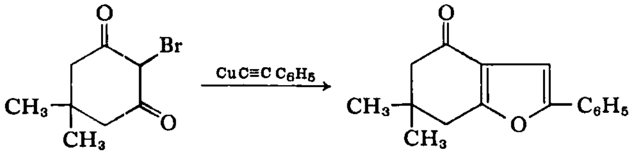
Footnotes to Table VI—*continued*

[b] Metal halide-free.
[c] Solvent is THF.
[d] Ratio is 5:1.
[e] Ratio is 3:1.
[f] Similar reactions with CH_3Cu inordinately slow.
[g] GLC determination.
[h] Yield slightly increased by oxidation with O_2.
[i] Solvent effect observed. 98% yield in THF.
[j] Ratio is 4:1.
[k] Ratio is 2:1.
[l] Stereospecific coupling.
[m] Solvent is THF–Et_2O.
[n] HMPT also present.
[o] Solvent is *N*-methyl-2-pyrrolidone.
[p] From norbornyl–HgBr + $2CuBr \cdot P(C_4H_9)_3$ + $5t\text{-}C_4H_9Li$.
[q] Dimer of alkyl halide an important by-product.
[r] Addition of $n\text{-}C_4H_9I$ to reaction mixture.
[s] Isolated copper compound.
[t] In hexane.
[u] Cairncross and Sheppard report a mixture of products from this halide (*37*).
[v] Solvent not given.

Phenylethynylcopper and phenacyl bromide afford intractable tars upon long reflux in DMF. However, at higher temperatures (~240°C) α-haloketones can be converted in one step to furan derivatives [Eqs. (68a), (68b)]; uncyclized acetylenic ketones are not isolated. The cyclization is catalyzed by copper(I) through the copper-coordinated enol (*128*). Reaction of α,α′-dibromoketones with an excess of a diorganocuprate is a new method for the α-alkylation of a ketone (*231a*). Only the monoalkyl derivative is isolated. The evidence points to the formation of a cyclopropanone intermediate which reacts with more of the cuprate to give an α-alkylated metal enolate.



(68a)



(68b)

Coupling between a pentafluorophenylcopper reagent and an alkyl halide is not a recommended route to the alkylpentafluorobenzenes if the alkyllithium reagent is available (*147*).

2. *Allyl Halides*

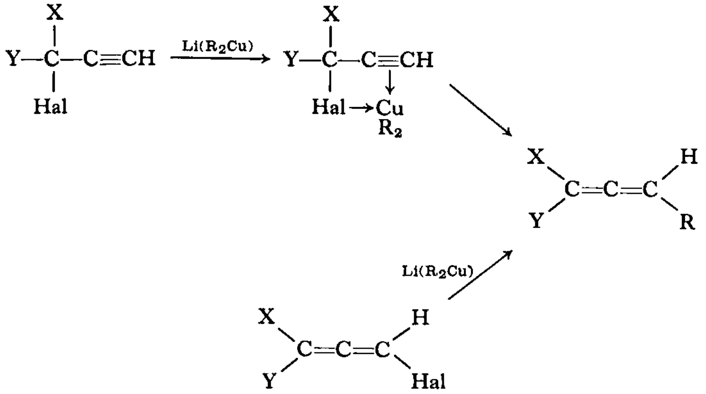
Organocopper compounds couple readily with allyl halides under mild conditions. In some instances the reactions are reported to be vigorous. Coupling of ethynylcopper compounds with allyl halides can be effected at the ambient temperature in the presence of halide or cyanide ligands (*221*). Isolation of some rearranged coupling products in certain reactions (*44*, *66*) may indicate the intermediacy of allylcopper(III) species. The reactions are summarized in Table VII.

3. *Allenyl and Propargyl Halides*

Ethynylcopper compounds and supposed magnesium diethynylcuprates react readily with propargyl halides to give 1,4-diynes as the major product [Eq. (69)]. Some of the ethynylallene rearrangement product is also formed (*221*). This is the only product obtained in protic media. Reaction of lithium dialkylcuprates with propargyl halides also

$$\mathrm{RC{\equiv}CCu + XCH_2C{\equiv}CR' \longrightarrow RC{\equiv}C{-}CH_2C{\equiv}CR' + RC{\equiv}C{-}CH{=}C{=}CHR'} \qquad (69)$$

affords allenes, perhaps via a π-complex (*151*). Identical products are obtained by the coupling of dialkylcuprates [Eq. (70): R=CH_3, C_2H_5, C_4H_9] with haloallenes (X or Y=H, CH_3, C_2H_5, C_3H_7, and Hal=Br or I) in the ratio 2.5:1. The yields of 1,3-disubstituted or 1,3,3-trisubstituted allenes are 64–87%.



(70)

4. *Vinyl Halides*

Coupling of ethynylcopper compounds with vinylic halides can be accomplished at high temperatures in pyridine or DMF solution. Ethynylcoppers were reported as not reacting with vinyl halides, especially under conditions which are suitable for coupling with aryl halides (*44*). However, successful coupling reactions with β-bromostyrene or the iodine-bearing carbon of 1-chloro-2-iodoethylene in refluxing pyridine or DMF have been reported (*29*, *30*). The role of the solvent in the coupling of ethynylcopper compounds with organic halides is not fully understood; reactions which fail in pyridine can be effected at higher temperatures either neat, or in nitrobenzene or some other high-boiling-point solvent. Reaction of ethynylcopper compounds with organic halides has been the subject of several reviews (*11*, *221*, *243*, *261*).

Di- and tetrasubstitution occur on refluxing a pyridine solution of an ethynylcopper compound with tetraiodoethylene (*29*, *30*), whereas

TABLE VII
REACTIONS WITH ALLYLIC HALIDES[a]

Copper compound	Allylic halide	% Yield coupled product	References
$Li(CH_3)_2Cu$	*cyclo*-3-Br-C_6H_9[b]	75	*68*
$Li(C_4H_9)_2Cu$	*cyclo*-3-Br-C_6H_9[b]	60	*69*
$C_2H_5O_2CCH_2Cu$[c]	*cyclo*-3-Br-C_6H_9	69	*181*
	$CH_3O_2CCH{=}CHCH_2Br$	89	*181*
	$CH_2{=}CBrCH_2Br$[d]	83	*181*
	trans-Geranyl Br	94	*181*
$NCCH_2Cu$[c]	*trans*-Geranyl Br	92	*66*
	trans-$C_7H_{15}C(I){=}CHCH_2Br$[d]	89	*66*
	$CH_2{=}CBrCH_2Br$[d]	92	*66*
	$CH_2{=}C(CO_2C_2H_5)CH_2Br$	89	*66*
	trans-$CH_3O_2CCH{=}$ $C(CH_3)CH_2Br$	67[e,f]	*66*
$C_6H_5SCH_2Cu$[c]	$CH_2{=}CHCH_2Br$	52[g]	*60*
	trans-Geranyl Br	76	*60*
$C_7F_{15}Cu$[h]	$CH_2{=}CHCH_2Br$	16	*53*
$Li(CH_2{=}CCH_3)_2Cu$	*cyclo*-3-Br-1-$CH_3C_6H_8$[b,c]	75	*282*
cis-*n*-$C_4H_9CH{=}CHCu$[i]	$CH_2{=}CHCH_2Br$	50	*223*
cis-*n*-$C_4H_9C(C_2H_5){=}CHCu$[i]	$CH_2{=}CHCH_2Br$	55	*223, 225a*
n-$C_4H_9C{\equiv}CMgBr + 1\% CuCl$	$CH_2{=}CHCH_2Br$[j]	88	*92*
$C_6H_5C{\equiv}CCu$[k]	$CH_2{=}CHCH_2Br$	83	*128*
$C_6H_5C{\equiv}CCu$[l]	$CH_3CH{=}CHCH_2Cl$	85[e,m]	*44*
Li(*n*-$C_4H_9CuC{\equiv}CC_5H_{11}$-*n*)[i]	$CH_2{=}CHCH_2Br$	89[n]	*221*
2-$(C_4SCl_3)Cu$[c]	$CH_2{=}CHCH_2Br$	62	*264*
2,5-$(C_4SCl_2)Cu_2$[c]	$CH_2{=}CHCH_2Br$	66	*263*
C_6H_5Cu	$CH_2{=}CHCH_2Br$	99	*224* (*124*)
2-$[(CH_3)_2NCH_2]C_6H_4Cu$[o]	$CH_2{=}CHCH_2Br$	95	*281b*
2,4,6-$(CH_3O)_3C_6H_2Cu$[o]	$CH_2{=}CHCH_2Br$	75	*281c*
C_6F_5Cu[c]	$CH_2{=}CHCH_2Br/Cl$	68/60	*147* (*34*)
C_6Cl_5Cu[c]	$CH_2{=}CHCH_2Br/Cl$	76/72	*147*
4-$(C_5NCl_4)Cu$[c]	$CH_2{=}CHCH_2Br$	58.5–76.4	*100, 147*
3-FC_6H_4Cu	$CH_2{=}CHCH_2Br$	67	*37*
4-FC_6H_4Cu	$CH_2{=}CHCH_2Br$	69	*37*
2-$CF_3C_6H_4Cu$	$CH_2{=}CHCH_2Br$	71	*37*
3-$CF_3C_6H_4Cu$	$CH_2{=}CHCH_2Br$	51	*37*
4-$CF_3C_6H_4Cu$	$CH_2{=}CHCH_2Br$	69	*37*

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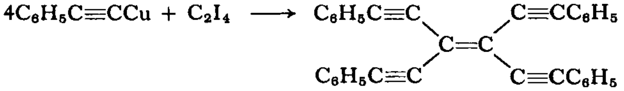
[a] Unless otherwise specified, the following reaction conditions apply: (1) the copper compounds were prepared in ether, and reacted without isolation in the presence of lithium or magnesium halides; (2) the product yields are of pure isolated materials; and (3) the reaction ratios RCu/C-Hal and LiR_2Cu/C-Hal are 1:1 and 1:2, respectively. No structural connotations in the representation of the copper compound.

polyhaloarylcopper reagents and other polyhaloethylenes in THF give bis(polyhaloaryl)acetylenes (*145*).



(71)

$$3C_6F_5Cu + C_2Br_4 \longrightarrow C_6F_5C{\equiv}CC_6F_5 \tag{72}$$

The reaction of perfluoroalkylcopper compounds, prepared *in situ* from the perfluoroalkyl iodide and copper, with sp^2-hybridized organic halides [Eq. (73)] in refluxing pyridine utilizes the thermal stability of the intermediate copper compounds and their failure to react with sp^3-hybridized halides (*29*, *30*).

$$I(CF_2)_3I + 2ICH{=}CHCl \xrightarrow{Cu} ClHC{=}CH{-}(CF_2)_3{-}CH{=}CHCl \tag{73}$$

Diorganocuprates couple readily with vinylic halides and have been employed in the synthesis of some natural products, e.g., fulvoplumieren and Cecropia juvenile hormone (*26*, *27*, *62*, *63*). Copper–halogen exchange can occur simultaneously (*174*, *309*). Successful coupling reactions of organocopper compounds with vinylic halides are listed in Table VIII.

Cyanomethylcopper in THF solution selectively reacts with allylic bromide in the presence of vinylic bromine atoms at a low temperature (*66*).

5. *Polyhaloalkanes and Polyhaloethylenes*

Posner and Brunelle have discovered a fast and complex reaction between benzotrichloride and an excess of lithium dimethylcuprate in

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Footnotes to Table VII—*continued*

[b] Ratio is 5:1.

[c] In THF.

[d] Vinylic halide unreactive.

[e] Total yield of isomers, perhaps indicating the formation of allylcopper(III) compounds.

[f] Isomers: 46% *cis*; 21% *trans*.

[g] As homologation product, 4-iodo-1-butene.

[h] In DMSO.

[i] HMPT added.

[j] Extremely slow reaction.

[k] In nitrobenzene at 240°C.

[l] Neat, or in DMF at elevated temperature.

[m] Same isomer ratio from *cis*- or *trans*-halide.

[n] Ethynyl group coupling product.

[o] No details given.

TABLE VIII
REACTIONS WITH VINYLIC HALIDES[a]

Copper compound	Vinylic halide	% Yield coupled product	References
$Li(CH_3)_2Cu$	*trans*-$C_6H_5CH{=}CHBr^{b,c}$	81	*68*
	$C_6H_5CH{=}C(Br)CO_2R^{b}$	$NG^{c,d}$	*174*
	trans-$RC(I){=}CHCH_2OH^{b}$	53^{c}	*62, 63*
	trans-$RCH{=}C(I)CH_2OH^{b}$	30^{c}	*63, 152*
$Li(C_2H_5)_2Cu$	*trans*-$C_6H_5CH{=}CHBr^{b}$	65^{c}	*69*
	trans-$C_7H_{13}C(I){=}CHCH_2OH^{b}$	78^{c}	*62*
$Li(iso\text{-}C_3H_7)_2Cu$	$C_6H_5CH{=}CHBr^{b}$	$\sim 67^{e}$	*309*
$Li(t\text{-}C_4H_9)_2Cu$	$C_6H_5CH{=}CHBr^{b}$	$\sim 70^{f}$	*309*
$Li(n\text{-}C_4H_9)_2Cu$	*cyclo*-1-$BrC_6H_9{}^{b}$	80	*69*
	cyclo-1-$ClC_6H_9{}^{b}$	60	*69*
	trans-*n*-$C_7H_{15}CH{=}CHI^{b}$	71^{c}	*69*
$n\text{-}C_3F_7Cu^{g,h}$	$C_6H_5CH{=}CHBr$	82	*30*
$C_7F_{15}Cu^{g,h,i}$	*trans*-$ClCH{=}CHI^{j}$	65	*30*
	trans-$ICH{=}CHI$	50	*30*
	$C_6H_5CH{=}CHBr$	95	*30*
$Cu(CF_2)_3Cu^{g,h}$	*trans*-$ClCH{=}CHI^{j}$		*30*
	$C_6H_5CH{=}CHBr$	95	*30*
$Li(trans\text{-}CH_3CH{=}CH)_2Cu$	$Fulvene{=}CHCl^{b}$	27^{c}	*26, 27*
$C_6H_5C{\equiv}CCu^{k}$	*trans*-$ClCH{=}CHI^{j}$	90	*29, 30*
	trans-$ICH{=}CHI$	90	*29, 30*
	C_2I_4	40	*29, 30*
	$C_6H_5CH{=}CHBr$	75	*29, 30*
$C_6H_5OCH_2C{\equiv}CCu^{k}$	*trans*-$ClCH{=}CHI^{j}$	70	*29, 30*
	trans-$ICH{=}CHI$	40	*29, 30*
$Li(C_6H_5)_2Cu$	*trans*-$C_6H_5CH{=}CHBr^{b}$	$90^{c,o}$	*297* (*309*)
	cis-$C_6H_5CH{=}CHBr^{b}$	$73^{c,o}$	*297*
$Li(p\text{-}CH_3C_6H_4)_2Cu^{m}$	$CH_2{=}CBrCH_3$	55	*282a*
$C_6Br_5Cu^{m}$	$CF_2{=}CFI^{l}$	50	*262*
$C_6F_5Cu^{m,n}$	$CF_2{=}CFI^{l}$	88	*266* (*273*)
$4\text{-}HC_6F_4Cu^{m}$	$CF_2{=}CFI^{l}$	45	*266*
$4\text{-}BrC_6F_4Cu^{m}$	$CF_2{=}CFI^{l}$	60	*266*
$4\text{-}(C_5NF_4)Cu^{m}$	$CF_2{=}CFI^{l}$	56	*266*
$4\text{-}(C_5NCl_4)Cu^{m}$	$CF_2{=}CFI^{l}$	84	*266*
$C_6Cl_5Cu^{m}$	$CF_2{=}CFI^{l}$	32	*266*

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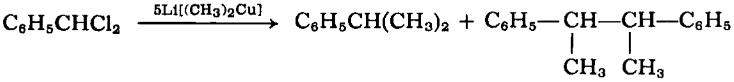
[a] Unless otherwise specified, the following reaction conditions apply: (1) the copper compounds were prepared in ether, and reacted without isolation in the presence of lithium or magnesium halides; (2) the product yields are of pure isolated material; and (3) the reaction ratios for RCu/C-Hal and LiR_2Cu/C-Hal are 1:1 and 1:2, respectively. No structural connotations in the representation of the copper compounds.

[b] Ratio is 5:1.

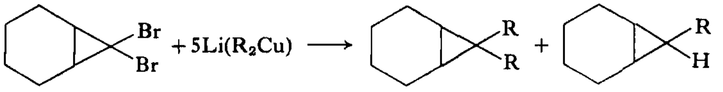
[c] Stereospecific.

ether at −78°C (*231*). At 0°C, benzal chloride also reacts with the dimethylcuprate to give a mixture of isopropylbenzene (40%) and 2,3-diphenylbutane (40%; 1:1 *dl-meso*). α-Chloroethylbenzene was not an intermediate. Neither was a carbene formed in this reaction, as the addition of cyclohexene did not give a norcarane derivative. Diphenyldichloromethane reacts with excess lithium dimethylcuprate under similar conditions to give tetraphenylethylene in good yield. Posner and Brunelle concluded that, for benzal chloride, the second chlorine atom is lost concurrently with the introduction of the first methyl group (*231*). It is conceivable that both halogen atoms become bound to copper and that the products are formed by decomposition of a copper(III) intermediate. The order of reactivity of the halides is $C_6H_5CCl_3 > C_6H_5CHCl_2 > C_6H_5CH_2Cl$, the relative reactivity of the latter two being 5:1, respectively.



$$C_6H_5CHCl_2 \xrightarrow{5Li[(CH_3)_2Cu]} C_6H_5CH(CH_3)_2 + C_6H_5-\underset{CH_3}{\underset{|}{C}H}-\underset{CH_3}{\underset{|}{C}H}-C_6H_5 \qquad (74)$$

7,7-Dibromonorcarane also reacts with dialkylcuprates (*68*, *69*). Products from both coupling and a possible copper–halogen exchange were isolated, but apparently no norcarane or 7-bromo-7-alkylnorcarane.



(75)

(R = CH_3; C_2H_5; C_4H_9)

The yield of the 7,7-dialkylnorcarane could be as low as 10% unless the respective alkyl bromide was added to the reaction mixture in great excess to circumvent the exchange (*69*).

Footnotes to Table VIII—*continued*

[d] Copper–halogen exchange is major reaction for R = H or CH_3. α-Bromocrotonic acid and esters undergo Cu–Hal exchange only.

[e] 40:60 coupled product reduced.

[f] 50:50 coupled product reduced.

[g] DMF or DMSO.

[h] *In situ* reactions: R_fI + Cu + vinyl Hal.

[i] Also reported to couple with $CF_2{=}CFI$ (*271*).

[j] Vinylic chloride unreactive.

[k] In pyridine.

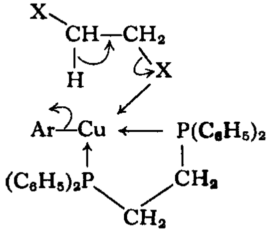
[l] Vinylic fluoride unreactive.

[m] In THF.

[n] Metal halide-free.

[o] GLC determination.

Arylcopper compounds react with carbon tetrachloride, although no reaction products have been reported (*40*), and complexes with 1,2-bis-(diphenylphosphino)ethane, $(ArCu)_2$ $DPPE_3$, react with 1,2-dichloroethane to give vinyl chloride (*41*). Van Koten and Noltes (*281e*) have observed a cleavage of the $H_2C—P$ bond in a 1 : 2 reaction of *o*-(dimethylaminomethyl)phenylcopper with DPPE ([Eq. (76)]; the cleavage can be explained by a concerted mechanism which takes place within a complex. A similar mechanism was proposed (*281e*) to explain the above reaction with 1,2-dichloroethane.



$$\longrightarrow ArH + CH_2{=}CHX + CuX \cdot DPPE \qquad (76)$$
$$[X = P(C_6H_5)_2 \text{ or } Cl]$$

Polyhaloarylcopper and trichloro-2-thienylcopper reagents react with a number of polybromo and polychloro ethanes and ethylenes to give disubstituted acetylenes in yields which can be as high as 87% (see Table IX) (*144*, *145*, *264*). The halogen compounds were C_2HX_5,

TABLE IX
SYNTHESIS OF DIARYLACETYLENES

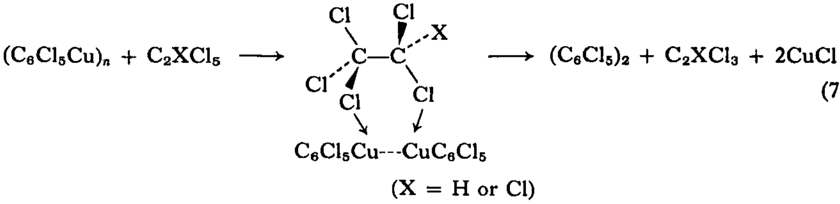
Copper compound RCu[a]	Organic halide	Ratio RCu/Halide	% Yield RC≡CR[b]
C_6F_5	*sym*-$C_2H_2Br_4$	4	47
	C_2Br_4	3	77[c]
	C_2HBr_3	3	71
C_6Cl_5	C_2HBr_5	4	49
	sym-$C_2H_2Br_4$	4	43
	C_2Br_4	3	87[c]
	sym-$C_2H_2Cl_4$	4	65.5
	C_2HCl_3	3	63
4-(C_5NCl_4)	C_2Br_4	4	13
	C_2HBr_3	3	39
2-(C_4SCl_3)	C_2HBr_3	3	36

[a] Stoichiometric ratio only—no structural connotation. Solution in THF refluxed with organic halide for up to 48 hours.

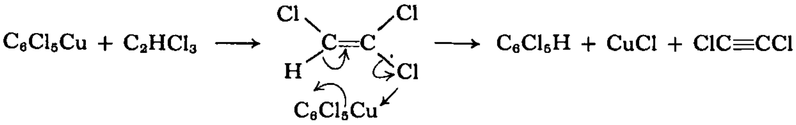
[b] Conditions not optimized.

[c] R_2 and RBr also isolated.

sym-$C_2H_2X_4$, C_2HX_3 (X=Br or Cl), and C_2Br_4. Tetrachloroethylene did not take part in these reactions, even on prolonged reflux in THF solution. Reaction of hexachloroethane with 2.5 equivalents of a pentachlorophenylcopper reagent gave decachlorobiphenyl (50%) and tetrachloroethylene. Decachlorobiphenyl (42%) and trichloroethylene were the products from a similar 1:1 reaction with pentachloroethane. A simple arylcopper–chlorine exchange cannot explain the products as pentachlorophenylcopper does not couple with hexachlorobenzene under the reaction conditions. The reactions probably occur on a copper aggregate with which is coordinated at least two chlorine atoms. Pentafluorophenylcopper is unreactive towards the chlorine-containing ethanes and ethylenes. However, pentafluorophenylcopper reagents and tetrabromoethylene gave bis(pentafluorophenyl)acetylene, decafluorobiphenyl, and bromopentafluorobenzene. Possible intermediates of the type $C_6F_5CX{=}CX_2$ and $C_6F_5C{\equiv}CX$ (X = H, Br, Cl) were not detected in the reaction mixture. The mechanism of the acetylene synthesis may be represented by Eq. (77) to (79).



(77)



(78)

$$2C_6Cl_5Cu + ClC{\equiv}CCl \longrightarrow C_6Cl_5C{\equiv}CC_6Cl_5 + 2CuCl \qquad (79)$$

Synthesis of diarylacetylenes via organocopper compounds is a propitious route to interesting acetylene ligands in transition metal chemistry. Acetylenes are not obtained from the reaction of perhaloaryllithium reagents with the aforementioned polyhalogenated ethanes and ethylenes. Not all copper compounds afford disubstituted acetylenes: (1) phenylcopper failed to react with tribromoethylene (*145*); (2) ethynylcopper compounds and tetraiodoethylene give tetraethynylethylenes (*29*, *30*); and (3) perfluoroalkylcopper reagents do not react with ethylenes which contain more than two reactive halogen atoms (*30*). The synthesis of acetylenes in yields as high as 87% (based on the alkene or alkane) has only been successful, so far, with perhalogenated phenyl-, pyridyl-, and thienylcopper reagents. An unsymmetrical diarylacetylene, $C_6F_5C{\equiv}CC_6Cl_5$, was obtained in poor yield, together with the two symmetrical disubstituted acetylenes from which it was easily separated, from the reaction of tribromoethylene with a mixture of pentafluoro- and pentachlorophenylcopper reagents (*288*).

Acetylenic products were not isolated from the reaction of a pentachlorophenylcopper reagent with four other polychloroalkanes and alkenes (*144*), namely, *cis*-1,2-dichloroethylene, 1,1,1-trichloroethylene, hexachloropropene, and 1-H-heptachloropropane. The latter two reacted vigorously at room temperature and gave ~30% decachlorobiphenyl and tar, whereas the other two gave a complex product mixture which appeared to contain polyphenyls.

Iodotrifluoroethylene reacts with various polyhaloarylcopper reagents (*97*, *262*, *266*, *273*), affording a convenient route to polyhalogenated styrenes, and with perfluoroheptylcopper (*271*). The method offers advantages over other published procedures for the synthesis of perfluorostyrene. Although many reactions of perhaloarylcopper complexes are similar to those of the lithium or magnesium analogs (*97*), the reactions with iodotrifluoroethylene are specific to the organocopper compounds. A minor by-product in the reactions involving 2,3,5,6-tetrafluorophenylcopper and magnesium bis(pentafluorophenyl)cuprate reagents was the respective diarylacetylene (*266*). Although the mode of its formation was not discovered, the acetylene could arise by an exchange–elimination sequence of reactions via trifluorovinylcopper. The vinylic fluorine atoms of the styrene product do not appear to participate in such reactions.

6. *Aryl Halides*

Aryl halides react with organocopper compounds by both exchange and coupling reactions. The coupling reactions are summarized in Table X. Many of the coupling products are not easily prepared in such high yields by alternative procedures. An explanation of the observed copper–halogen exchange reactions (*69*, *97*, *217*, *219*, *297*) is ligand transfer to give more stable bridging groups on copper clusters (*281f*). Yields of

TABLE X
REACTIONS WITH ARYL HALIDES[a]

Copper compound	Aryl halide	% Yield coupled product	References
CH_3Cu[b,c]	$1\text{-}IC_{10}H_7$[e]	33[g,h]	*297*
$Li(CH_3)_2Cu$[b]	$1\text{-}IC_{10}H_7$[e]	33[g,h]	*297*
$Li(CH_3)_2Cu$[b]	C_6H_5I[d]	46[g,h,i]	*297*
$Li(CH_3)_2Cu$[b,f]	C_6H_5I[d]	99[g]	*297*
$Li(CH_3)_2Cu$	C_6H_5I[d]	90[g]	*68*
$Li(C_4H_9)_2Cu$[c]	C_6H_5I[d]	< 1[g,h]	*297*
$Li(n\text{-}C_4H_9)_2Cu$	C_6H_5I[d,j]	75	*69*
$Li(CH_2{=}CCH_3)_2Cu$[k]	C_6H_5Br[d]	85	*282*
$(CH_3)_2C{=}CHCu$	$4\text{-}CH_3OC_6H_4I$	6	*217*
$Li[(CH_3)_2C{=}CH]_2Cu$[l]	$4\text{-}CH_3OC_6H_4I$[e]	65[m]	*217*
	$2\text{-}CH_3O_2CC_6H_4I$	0[n]	*217*
$RC\equiv CCu$[o]	ArI[p]	75–99	*43*, *44*, *195*, *204*, *226*, *269*
	$2\text{-}I\text{-}5\text{-}X\text{-}C_4SH_2$[p]	—	*4–6*, *90*
$C_6H_5C\equiv CCu$[o]	Ferrocenyl I	84	*236*
	1,1′-I_2Ferrocene	60	*236*
	$2\text{-}IC_4SH_3$	74	*236*
	C_6Cl_5I	49	*237*
	C_6F_5I	55	*237* (*31*, *114*)
	C_6F_5Br	33	*237*
	$1,2\text{-}I_2C_6F_4$	~43	*31*
$C_6F_5C\equiv CCu$[o]	C_6H_5I	74	*237*
Ferrocenyl—$C\equiv CCu$[o]	Ferrocenyl I	85	*236*
$\pi\text{-}C_5H_5Cu\cdot P(C_4H_9)_3$	$4\text{-}CH_3C_6H_4I$	50	*218*
	$2\text{-}CH_3O_2CC_6H_4I$	34	*218*
$2\text{-}(C_4OH_3)Cu$[o]	$4\text{-}CH_3OC_6H_4I$	7	*214*
$2\text{-}(C_4SH_3)Cu$[o]	$2\text{-}IC_4SH_3$	42	*214*
	$3\text{-}BrC_4SH_3$	14	*214*
	C_6H_5I	31 (50)	*214* (*212*)
	$2\text{-}CH_3O_2CC_6H_4I/Br$	50/13	*214*
	$2\text{-}/4\text{-}NO_2C_6H_4I$	56/70	*214*
	$4\text{-}CH_3OC_6H_4I$	55	*214*
	$2,6\text{-}(CH_3O)_2C_6H_3I$	56	*214*
$2\text{-}(C_4SCl_3)Cu$[k]	C_6H_5I	53	*264*
$2\text{-}(C_4SCl_3)Cu$[o]	$4\text{-}CH_3OC_6H_4I$	65	*215*
C_6H_5Cu[o]	$4\text{-}DC_6H_4I$	30[m]	*219*, *220*
	$2\text{-}CH_3OC_6H_4I$	33[g,n]	*220*
	$4\text{-}CH_3OC_6H_4I$	36[m]	*220*
	$2,6\text{-}(CH_3O)_2C_6H_3I$	60[g,m]	*220*
	$2\text{-}FC_6H_4I$	26[n]	*220*
	$2\text{-}ClC_6H_4I$	44[g,n]	*220*
	$2\text{-}NO_2C_6H_4I$	18[n]	*220*

Continued

TABLE X—*Continued*

Copper compound	Aryl halide	% Yield coupled product	References
	2-/4-$CH_3O_2CC_6H_4I$	28/29[m]	*220*
	C_6F_5I	86	*31*
2,6-$(CH_3O)_2C_6H_3Cu$[q]	2,4,6-$(NO_2)_3C_6H_2Cl$	36	*21*
$Li(C_6H_5)_2Cu$	1-$IC_{10}H_7$[d]	28–45[h,r]	*297*
C_6H_5MgBr + 9% CuCl	C_6H_5Br	0	*166*
C_6F_5Cu[k]	C_6H_5I/Br	57–71/0	*97, 147*
	2-$CH_3OC_6H_4I$	60	*147*
	C_6Cl_5I	44	*144*
	4-$(C_5NCl_4)I$	55	*144*
	C_6F_5I	74	*97*
	4-$C_6F_5OC_6F_4Br$	5[m]	*97*
	4-$CH_3OC_6F_4I$	70[m]	*97*
C_6Cl_5Cu[k]	C_6H_5I	55	*147*
	C_6F_5I	58	*144*
	4-$(C_5NCl_4)I$	58	*144*
4-$(C_5NCl_4)Cu$[k]	C_6H_5I	55.5	*147*
	C_6F_5I	47	*144*
	C_6Cl_5I	51	*144*
	4-$(C_5NCl_4)I$	72	*144*
C_6F_5Cu[b,s]	C_6H_5I	87	*34*
	3-/4-$CH_3O_2CC_6H_4I$	96/97	*259*
	3-/4-$NO_2C_6H_4Br$	85/85	*259*
	3-/4-$(CH_3)_2NC_6H_4I$	33/26	*259*
	3-/4-FC_6H_4I	73/78	*259*
C_6F_5Cu	2-$NO_2C_6H_4I$	27[t](94)	*33* (*37*)
$Li(CH_3)_2Cu$	Br[18]Annulene	52	*308*
3-$CF_3C_6H_4Cu$	2-$NO_2C_6H_4I$	59	*37*

---

[a] Unless otherwise specified the following reaction conditions apply: (1) the copper compounds were prepared in ether, and reacted without isolation in the presence of lithium or magnesium halides; (2) the product yields are of pure isolated materials; and (3) the reaction ratios for RCu/C-Hal and LiR_2Cu/C-Hal are 1:1 and 1:2, respectively (aryl chlorine and fluorine substituents are unreactive). No structural connotations in the representation of the copper compounds.

[b] Metal halide-free.

[c] $P(n\text{-}C_4H_9)_3$ present.

[d] Ratio is 5:1.

[e] Ratio is 3:1.

[f] Coupling promoted by addition of impurities present in commercial CuI.

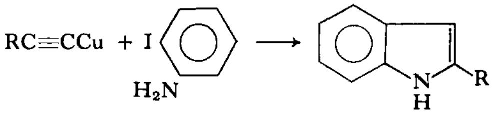
[g] GLC determination.

[h] Considerably increased by oxidation prior to termination. Cu-Hal exchange important.

[i] Coupling and exchange reactions proceed at about the same rate and are hardly affected by addition of $LiCH_3$ or LiHal.

the coupling product can be improved by oxidative termination of the reaction (*297*), or, in reactions involving dialkylcuprates, by addition of an excess of the alkyl halide (*69*). Polyhaloarylcopper compounds couple readily with simple aryl iodides and perhaloaryl iodides, apparently without competing copper–halogen exchange reactions, whereas lithium dimethylcuprate containing a stoichiometric excess of methyllithium undergoes ligand exchange exclusively with a number of perhalogenated arenes (*146*). Biphenyls of the type $C_6F_5C_6Cl_5$ can be prepared via copper compounds, but not from the reaction of pentachlorophenyllithium with a large excess of hexafluorobenzene at $-70°C$ (*144*); the desired biphenyls are apparently far more reactive than hexafluorobenzene towards nucleophilic substitutions.

Ethynylcopper compounds react readily with aryl halides. Those halides containing ortho $-OH$, $-CO_2H$, $-SH$, and $-NHR$ groups do not give the disubstituted acetylene product from the coupling reaction as expected, but either a benzofuran (or pyridofuran), a phthalide, a benzothiophene, or an indole, respectively (*43*, *44*, *195*, *226*, *269*). The heterocyclic synthesis is apparently a two-stage reaction, consisting of a homogeneous substitution followed by a heterogeneous copper-promoted cyclization. The order of effectiveness of the substituents in the cyclization reaction is $CO_2H > OH > NH$ (*43*). An ortho effect is observed



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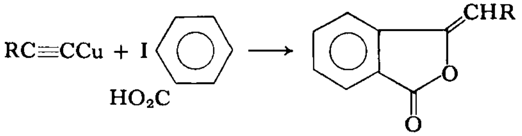


(81)

Footnotes to Table X—*continued*

[j] Cu-Hal exchange circumvented by addition of n-C_4H_9I.

[k] In THF.

[l] Pyridine added.

[m] Exchange also occurs.

[n] Exchange said to be important.

[o] In pyridine.

[p] See reviews (*243*, *261*) for synthesis of tolans, heterocyclic compounds, and thienylacetylenes.

[q] In DMF.

[r] Solvent effect observed.

[s] As dioxinate in benzene.

[t] In $N(C_4H_9)_3$.

with substituents such as NO_2 and CO_2H, but otherwise the heterocyclic synthesis is hardly affected by the substituent or its position. Unreactive halophenols, such as 4,6-dibromoresorcinol, promote dimerization of the ethynylcopper (*43*). The reaction of copper acetylides with iodothiophenes in refluxing pyridine (*4–6*, *90*, *204*) has often been used to prepare naturally occurring ethynylthiophenes. 2-Bromothiophene is unreactive, even during extended reflux periods (*6*).

Numerous perfluoroalkyl-substituted arenes have been prepared by the coupling of aryl iodides or bromides with perfluoroalkyl iodides in the presence of copper bronze in a dipolar aprotic solvent at elevated temperatures. Perfluoroalkyl bromides and chlorides can be utilized in similar reactions provided a bidentate ligand such as 2,2′-bipyridyl or 1,10-phenanthroline is added (*199*, *278*). Perfluoroalkylcopper reagents are believed to be intermediates in the couplings (*200*, *201*).

7. *1-Haloacetylenes*

The reaction of pentafluorophenylcopper with bromo(triethylsilyl)-acetylene in THF affords $C_6F_5C{\equiv}CSi(C_2H_5)_3$ in 85% yield (*286*). The triethylsilyl group can be effectively removed under mild conditions to give pentafluorophenylacetylene, hitherto available only with difficulty by alternative procedures. Other arylcopper compounds undergo similar reactions (*225c*). Copper-catalyzed reactions of ethynyl-Grignard reagents or the reactions of ethynylcopper compounds with 1-haloalkynes are well documented (*22*, *89*, *91*, *112*, *261*) and may be a special case of the well-known Cadiot-Chodkiewicz coupling (*112*). The triethylsilyl group is a good protecting group for a terminal alkyne in the Glaser or Cadiot-Chodkiewicz coupling reactions (*109–111*).

Little or no reaction occurs between an ethynylcopper compound and a 1-haloalkyne in toluene at 100°C, even after 8 hours (*117*).

8. *Acid Halides*

All types of organocopper reagents couple readily with acid halides (Table XI), affording an alternative synthesis of ketones. Posner and

$$2C_6F_5Cu + ClCO(CH_2)_2COCl \longrightarrow C_6F_5CO(CH_2)_2COC_6F_5 \qquad (82)$$

$$Li[(CH_3)_2Cu] + ClCO(CH_2)_4CO_2C_4H_9 \longrightarrow CH_3CO(CH_2)_4CO_2C_4H_9 \qquad (83)$$

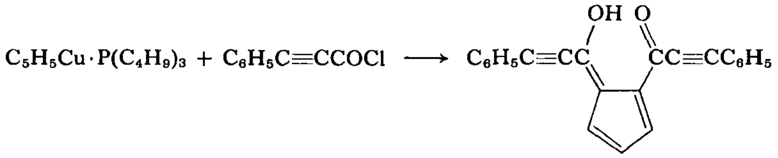
co-workers recommend that, in the reaction of cuprates with acid chlorides, a molar ratio of 3:1 be employed for most efficient coupling (*233*).

However, good yields of ketones can be obtained for an equivalent quantity of acid halide per group attached to copper. Suitable conditions exist for the coupling of dialkylcuprates with acid chlorides which contain other functional groups (*233*), such as carbonyl, carboxy, and cyano. The order of reactivity of these groups towards organocopper compounds is CHO > CO > CO_2R > CN. Benzoyl fluoride reacts very slowly with lithium dimethylcuprate.

Methylcopper is less reactive than lithium dimethylcopper towards acid halides (*295*), but the yield of methyl ketones can be increased by performing the reaction in hexamethylphosphorus triamide (HMPT) or CH_3CN (*224*).

Poor yields of ketones were obtained from the reaction of dialkylcuprates with levulinoyl chloride (*233*), and from pentafluorophenylcopper and malonyl chloride (*115*, *180*). The yields of the ketones from the reaction of polyhaloarylcopper reagents with succinoyl chloride were also lower than those from a number of other diacid chlorides (*101*). Acidic hydrogen atoms are the most likely source of trouble in these reactions.

Simple ketone products are not obtained from the reaction of a cyclopentadienylcopper compound with various acid chlorides (*188*); instead, diacylated or O-acylated products are isolated.



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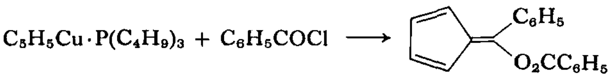

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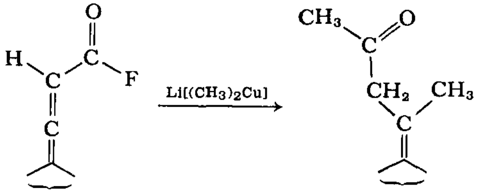
Lithium dimethylcuprate is less selective than dimethylcadmium in its reaction with a steroidal allenic acid fluoride (*88*). Whereas the cadmium compound in refluxing benzene solution reacts mainly with the



(86)

TABLE XI
REACTIONS WITH ACID HALIDES[a]

Copper compound	Acid halide RCOCl R =	% Yield ketone	References
Alkyl			
CH_3Cu	C_6H_5	56.5[k]	*125* (*224*)[h]
CH_3Cu[b,j]	C_6H_5	3	*125*
$Li(CH_3)_2Cu$	C_6H_5[f]	58	*143*
	$4\text{-}NO_2C_6H_4$[e]	50	*232*
	$3,5\text{-}(CF_3)_2C_6H_3$[e]	92	*232*
	$(C_6H_5)_2CH$[e]	93 (65[f])	*232* (*143*)
	$(C_6H_5)CH{=}CH$[f]	0[l]	*143*
	CH_3CHCl[f]	trace	*143*
	$(CH_3)_2CH$[f]	45	*143*
	$t\text{-}C_4H_9$[e]	84[g]	*232*
	$n\text{-}C_5H_{11}$[e]	81[g]	*232*
	cyclo-C_6H_{11}[e]	86[g]	*232*
	$\text{—}(CH_2)_4\text{—}$	92	*233*
	$CH_3O_2C(CH_2)_2$	< 20	*233*
	$n\text{-}C_4H_9O_2C(CH_2)_4$	83[g]	*233*
	$n\text{-}C_4H_9CO(CH_2)_4$	95	*233*
	$NC(CH_2)_{10}$	80	*233*
	$I(CH_2)_{10}$[t]	91	*233*
	$4\text{-}IC_6H_4$[t]	98	*233*
C_2H_5Cu	$[(CH_3)_2CH]_2CH$	80	*104*
$Li(C_2H_5)_2Cu$	$(C_6H_5)_2CH$[e]	80	*232*
	cyclo-C_6H_{11}[e]	71[g]	*232*
$Li(n\text{-}C_4H_9)_2Cu$	$4\text{-}NO_2C_6H_4$[e]	0	*232*
	$3,5\text{-}(CF_3)_2C_6H_3$[e]	75–80	*232*
	$(C_6H_5)_2CH$[e]	90	*232*
	$t\text{-}C_4H_9$[e]	90[g]	*232*
	$\text{—}(CH_2)_4\text{—}$	90	*233*
	$CH_3O_2C(CH_2)_2$	85	*233*
	$n\text{-}C_4H_9O_2C(CH_2)_4$	93[g]	*233*
	$n\text{-}C_4H_9CO(CH_2)_4$	83	*233*
	$NC(CH_2)_{10}$	> 95	*233*
	$I(CH_2)_{10}$[t]	93	*233*
	$4\text{-}IC_6H_4$[t]	85	*233*
	$n\text{-}C_5H_{11}$[e]	79[g]	*232*
	cyclo-C_6H_{11}[e]	80[g]	*232*
$Mg[(t\text{-}C_4H_9)_2Cu]_2$	$c\text{-}4\text{-}(t\text{-}C_4H_9)C_6H_{11}$[f]	60[n]	*193*
Vinyl			
$Li(CH_2{=}CCH_3)_2Cu$[c]	$(CH_3)_2CHCH_2$[d]	70	*282*
Ethynyl			
$n\text{-}C_4H_9C{\equiv}CCu$[o]	CH_3	70	*222*

TABLE XI—*Continued*

Copper compound	Acid halide RCOCl R =	% Yield ketone	References
n-$C_4H_9C{\equiv}CCu^{b,o}$	CH_3	10	*222*
n-$C_4H_9C{\equiv}CCu^{o}$	n-C_4H_9	95.5	*222*
	$CH_2{=}CH$	80	*222*
n-$C_5H_{11}C{\equiv}CCu^{o}$	CH_3	81.5	*222*
$C_6H_5C{\equiv}CCu^{o}$	CH_3	82	*222*
	C_6H_5	90	*222*
$Li(n\text{-}C_5H_{11}C{\equiv}CCuCH_3)^{o}$	CH_3	58^{p}	*222*
	$CH_3CH{=}CH$	78^{p}	*222*
	C_6H_5	71^{p}	*222*
Heterocyclic			
2-$(C_4SCl_3)Cu^{c}$	CH_3	76	*264*
	C_6H_5	58	*264*
	trans-$CH{=}CH$	55	*264*
	—$(CF_2)_3$—	22	*264*
2,5-$(C_4SCl_2)Cu_2{}^{c}$	CH_3	60–64	*263*
Aryl			
C_6H_5Cu	CH_3	54	*124*
	C_6H_5	55	*124* (*192*)
$Li(C_6H_5)_2Cu$	$C_6H_5{}^{f}$	59 (55^{c})	*143* (*282a*)
	$(C_6H_5)_2CH^{f}$	88	*143*
	c-4-(t-C_4H_9)C_6H_{11}	62^{m}, 85^{n}	*193*
	$(CH_3)_2CH^{f}$	67	*143*
	CH_3CHCl^{f}	15	*143*
	$CH_3{}^{f}$	55	*143*
$Li[(CH_3)_2NC_6H_4]_2Cu$	c-4-(t-C_4H_9)C_6H_{11}	50^{m}, 85^{n}	*193*
2-$[(CH_3)_2NCH_2]C_6H_4Cu^{q}$	4-$NO_2C_6H_4$	75	*281b*
4-$CH_3OC_6H_4Cu$	CH_3	52	*124*
$Li(CH_3OC_6H_4)_2Cu$	c-4-(t-C_4H_9)C_6H_{11}	50^{m}, 65^{n}	*193*
2,4,6-$(CH_3O)_3C_6H_2Cu^{q}$	4-$NO_2C_6H_4$	75	*281c*
$C_6Br_5Cu^{c}$	C_6H_5	90	*262*
4-$(Me_3Si)C_6Cl_4Cu^{c}$	CH_3	39	*288*
$C_6Cl_5Cu^{c}$	C_6H_5	71–85	*146*
	4-$NO_2C_6H_4$	74	*144*
	4-$CH_3OC_6H_4$	75.6	*144*
	1,4-C_6H_4—	61	*101*
	trans-$CH{=}CH$—	78.6	*101*
	—$(CH_2)_4$—	77.8	*101* (*99*)
	—$(CH_2)_2$—	45–59	*101*
	$(COCl)_2$	70.5	*101*
	—$(CH_3)_2C$—	52.5	*180*
	$ClCH_2{}^{t}$	78	*234*
	CH_3	65	*146*

Continued

TABLE XI—*Continued*

Copper compound	Acid halide RCOCl R =	% Yield ketone	References
$Li(C_6Cl_5)_2Cu$	CH_3	72	*146*
$Li(C_6Cl_5)_2Cu^{r}$	C_6H_5	65	*146*
$C_6F_5Cu^{c}$	C_6H_5	70	*146*
	$4\text{-}NO_2C_6H_4$	72 (67)	*34* (*144*)
	$4\text{-}CH_3OC_6H_4$	90	*144*
	$1,4\text{-}C_6H_4$	65	*101*
	trans-CH=CH—	68.8–75	*101*
	$—(CH_2)_4—$	76	*101*
	$—(CH_2)_2—$	25–63	*101*
	$—CH_2—$	$< 30^{t}$	*115*
	$—(CH_3)_2C—$	54.5	*180*
	$(COCl)_2$	71	*101*
	$ClCH_2^{t}$	48	*234*
	CH_3	64–76	*146*, *149*
C_6F_5Cu	CH_3	82.5–84	*146*
$Li(C_6F_5)_2Cu$	CH_3	64–79	*146*
$Li(C_6F_5)_2Cu^{r}$	$—(CH_2)_2—$	43	*101*
	$(COCl)_2$	52	*101*
$4\text{-}(C_5NCl_4)Cu^{c}$	C_6H_5	47–63	*100*, *146*
	$4\text{-}NO_2C_6H_4$	53.5	*144*
	$4\text{-}CH_3OC_6H_4$	54	*144*
	$1,4\text{-}C_6H_4—$	62	*101*
	trans-CH=CH—	30	*101*
	$—(CH_2)_4—$	66	*101*
	$—(CH_2)_2—$	59	*101*
	$(COCl)_2$	57	*101*
	CH_3	64	*146*
$Li(4\text{-}HC_6F_4)_2Cu^{r}$	C_3H_5	77	*144*
$Li(2\text{-}HC_6F_4)_2Cu^{r}$	CH_3	68	*144*
$C_6Cl_5C_6Cl_4Cu^{c,s}$	CH_3	82	*45*
$(C_{12}Cl_8)Cu_2^{c,s}$	CH_3	68	*45*
$4\text{-}HC_6Cl_4Cu^{c}$	C_3H_5	63	*148*
	CH_3	55	*148*
$2\text{-}CF_3C_6H_4Cu$	CH_3	60	*37*
$3\text{-}CF_3C_6H_4Cu$	$4\text{-}NO_2C_6H_4$	83	*37*

---

[a] Unless otherwise specified the following reaction conditions apply: (1) the copper compounds were prepared in ether, and reacted without isolation in the presence of lithium or magnesium halides; (2) the product yields are of pure isolated materials; and (3) the reaction ratios for RCu/C(O)-Cl and LiR_2Cu/C(O)-Cl are 1:1 and 1:2, respectively. No structural connotations in the representation of the copper compounds.

[b] Metal halide-free.

acid fluoride group, the cuprate in ether at 0°C also reacts with the allene moiety [Eq. (86)], presumably by a 1,4-conjugate addition reaction.

9. *Copper-Catalyzed Reactions*

Tamura and Kochi have recently investigated the well-known catalyzed reaction of Grignard reagents with alkyl halides, in THF solution (*274–276*). The active species was found to be an organocopper(I) complex, although none was isolated. Good yields of the coupling products were obtained from the copper-catalyzed reaction of various Grignard reagents with primary alkyl bromides, but reactions with secondary and tertiary alkyl halides gave only disproportionation products. Dialkylcuprates react with primary, secondary, and tertiary halides in the same manner (*297*).

Catalyzed reactions of Grignard reagents with organic halides and ketones in ether solution were studied extensively in the past, notably by Kharasch and co-workers (*166–171*). Copper salts were not effective catalysts for the coupling of Grignard reagents with aryl or vinyl halides, cobalt chloride being preferred (*166*, *167*). Noller and co-workers, in a reexamination of some reactions first reported (*187*) nearly 30 years ago, found that the deep red ether solution resulting from the addition of a catalytic quantity of a copper salt to a Grignard reagent was not a metallic sol but an organocopper-Grignard reagent complex (*227*). The mechanism

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Footnotes to Table XI—*continued*

[c] Solvent is THF.

[d] Ratio is 5:1.

[e] Ratio is 3:1.

[f] Ratio is 1:1.

[g] GLC determination.

[h] Solvent effect observed.

[i] The α-H atoms are acidic. Yield may be 0% (*180*).

[j] In alcohol.

[k] As oxime.

[l] Polymerized.

[m] Trans isomer.

[n] Cis isomer.

[o] HMPT added.

[p] Exclusive of methyl ketone.

[q] Details not given.

[r] THF–Et_2O 4:1.

[s] Substituent position(s) unknown. Many other acid halides reacted.

[t] Halide substituent unreactive under reaction conditions.

of the copper-catalyzed reaction of Grignard reagents with alkyl halides in ether was obscured by competing heterolytic and homolytic processes from decomposition of the intermediate copper compound (*228*, *276*). Free radicals and alkylcopper(II) species were eliminated as intermediates because no homo-coupled dimers were isolated from reactions performed in THF solution (*276*). A rate-determining step involving S_N2-type displacement of halide is suggested by the kinetics of the reaction.

Some ethynylcuprates also catalyze the reaction of Grignard reagents with alkyl halides (*311*).

The reaction of alkyl species with copper metal (*276*) and the subsequent reactions of organocopper intermediates may explain the slightly lower yields of Grignard reagents which were prepared from magnesium-copper alloys. Partial suppression of the ketonic products which are produced by free-radical reactions is observed when, in the reaction of methylmagnesium iodide with mesitoyl chloride, the Grignard reagent is prepared from magnesium-copper alloy (*169*).

Ionic and free-radical reactions leading to the formation of ketonic products can occur simultaneously in the copper-catalyzed reaction of a Grignard reagent with a sterically hindered acid halide. These reactions have been studied by Dubois and co-workers (*102–108*, *194*). Contrary to the report of Percival *et al.* (*229*), ferric chloride inhibits the catalytic role of copper and does not favor the formation of ketones (*106*, *108*). The scheme depicted in Fig. 4 is proposed (*103*) to account for the products of the reaction. Similar radical reactions were suggested by Kharasch *et al.* (*169*) to explain the role of cobalt chloride in like reactions.

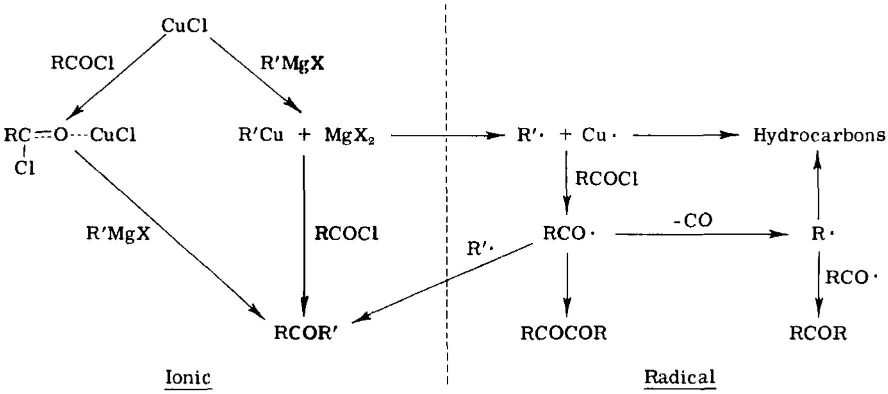


FIG. 4. Ionic and radical mechanisms in the syntheses of hindered ketones from the copper-catalyzed reaction of Grignard reagents with acid chlorides.

The decomposition of the intermediate organocopper reagent initiates the radical reactions. For example, the stability of ethylcopper varies considerably with the nature of the Grignard reagent from which it was prepared (*104*). The slower-reacting sterically hindered acid halides give higher yields of ketones derived from free-radical reactions (*103*). In the copper-catalyzed competition reaction between two acid halides, RCOCl, for a deficiency of a Grignard reagent, the observed (*194*) order of decreasing reactivity for the R group is $C_2H_5 > (CH_3)(C_2H_5)CH > (CH_3)_3CCH_2 > (C_2H_5)_2CH > (CH_3)_3C > (C_2H_5)_3C > [(CH_3)_2CH]_2CH > (CH_3)_3C(CH_3)_2C$. For the preparation of sterically hindered ketones in high yields, the recommended procedure is to add the Grignard reagent to a mixture of the acid chloride and a copper–copper chloride or copper–iodide catalyst at a low temperature (*102*, *105*).

B. *Halides of Elements Other Than Carbon*

Ethynylcopper compounds couple more readily with arylsulfenyl halides than with organic halides (*44*). No coupling product was obtained from the reaction of cyclopentadienyl(tri-*n*-butylphosphine)copper with *p*-toluenesulfonyl chloride (*188*). Polyhaloarylcopper reagents also failed to react with this acid chloride, and with thionyl chloride, sulfuryl chloride, and phosphorus trichloride (*146*, *288*). Trimethylsilylmethylcopper and a pentafluorophenylcopper reagent, which, according to its method of preparation, may be an "ate" complex (*147*), reacted with some silicon halides (*146*, *182*). (Pentafluorophenyl)trimethylsilane was obtained in 25% yield, together with some decafluorobiphenyl, from the reaction with chlorotrimethylsilane at the ambient temperature. From chlorodimethylphenylsilane and this pentafluorophenylcopper reagent in dioxane at 95°C was obtained (pentafluorophenyl)dimethylphenylsilane in 59% yield. Tetrachloro-4-pyridyl- and pentachlorophenylcopper reagents did not react with chlorosilanes under similar conditions. These reactions are purely academic because the preferred route to such compounds is via similar reactions of polyhaloaryllithium and Grignard reagents. Lithium dimethylcuprate reacts with silanes containing Si—H, Si—OCH_3, and Si—Hal bonds (*45a*). Coupling with optically active silanes occurs with retention of configuration for all but chlorosilanes.

Reactions between ethynylcopper compounds and some transition metal complexes afford unusual types of polynuclear heteroatom complexes. The reaction of phenylethynylcopper with $IrCl(CO)[P(C_6H_5)_3]_2$

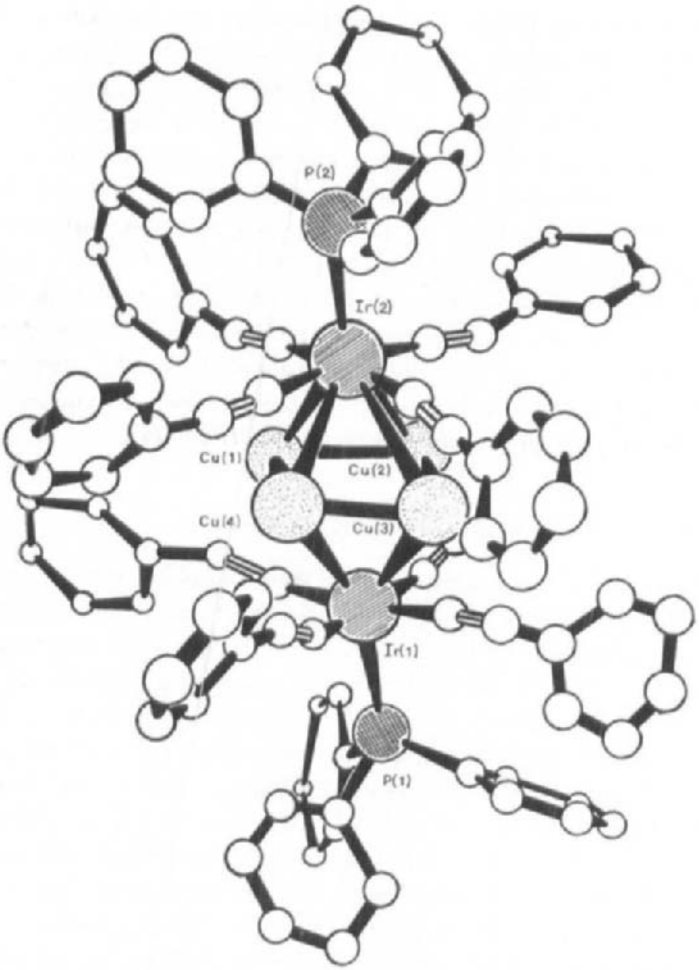


FIG. 5. The molecular stereochemistry of $Cu_4Ir_2[P(C_6H_5)_3]_2(C{\equiv}CC_6H_5)_8$. The phenyl group of the $C_6H_5C{\equiv}C$ group σ-bonded to Ir(1) and π-bonded to Cu(2) has been omitted for the sake of clarity.

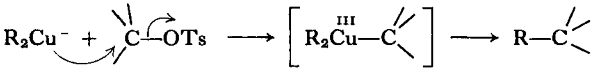
affords a purple, air-stable copper cluster complex, $Cu_4Ir_2[P(C_6H_5)_3]_2(C{\equiv}CC_6H_5)_8$. The molecule contains a slightly irregular Cu_4Ir_2 octahedron (see Fig. 5); the iridium atoms are at the apices and each is σ-bonded to four phenylethynyl ligands and a triphenylphosphine unit. Two phenylethynyl groups are asymmetrically π-bonded to each copper atom. The formal oxidation states of the metal atoms are Cu^0 and Ir^{IV}(*1*). Phenylethynylcopper and $(\pi\text{-}C_5H_5)Fe(CO)_2Cl$ afford the yellow-orange, air-stable complex $[(\pi\text{-}C_5H_5)Fe(CO)_2(C{\equiv}CC_6H_5)CuCl]_2$. The complex has a planar Cu_2Cl_2 ring; the phenylethynyl group is σ-bonded to the $(\pi\text{-}C_5H_5)Fe(CO)_2$ unit and π-bonded to copper. Bond lengths suggest back-bonding from filled copper orbitals into $C{\equiv}C$ π^*-orbitals, but no interaction between iron and copper atoms (*25b*). Ferrocene is obtained from the reaction between ferrous chloride and cyclopentadienylcopper complexes (*247*, *303*).

Other exchange reactions have been reported between organocopper compounds and mercuric halides (*40*, *73*, *209*).

C. Miscellaneous Substitution Reactions

1. *Esters*

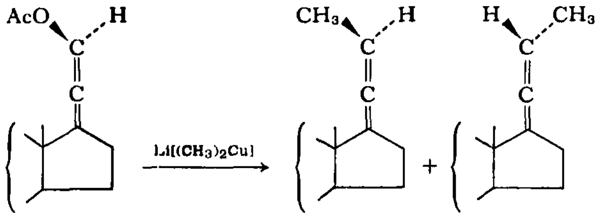
The tosylate group can be displaced from alkyl tosylates by dialkylcuprates (*256*, *297*, *301*), presumably by attack at carbon by the *d* electrons of copper. A transient copper(III) intermediate may be formed [Eq. (87)], as suggested for similar reactions with alkyl halides. An analogous reaction was reported between a copper(I) carboxylate and an alkyl tosylate (*185*). (Carboxyethyl)methylcopper, $C_2H_5O_2CCH_2Cu$, failed to react with butyl tosylate in THF (*181*). However, copper compounds of the type RCu are generally less reactive than the cuprates.



(87)

Ester groups are compatible with organocopper compounds and may be substituents in the organocopper compound or the substrate. A pentachlorophenylcopper reagent did not react with ethyl oxalate on heating for 48 hours in THF solution (*101*). Other esters can be recovered (*233*) from the more reactive lithium dialkylcuprates at temperatures below 18°C unless one or more of the hydrogen atoms are acidic. However, some allylic acetates on reaction with dialkylcuprates (*2*, *3*) appear to give a little of the product arising from a direct S_N2 displacement of acetate, together with the major product arising from an S_N2' displacement (see Section VII,B).

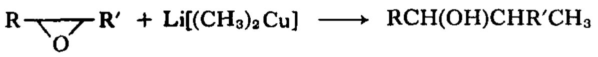
Stereochemically pure steroidal allenic acetates on reaction with lithium dimethylcuprate (*241*) in ether at 0°C yielded a mixture of the isomeric methylallenes [Eq. (88)], perhaps by electron donation by the copper species to the α-carbon atom.



(88)

2. *Oxiranes*

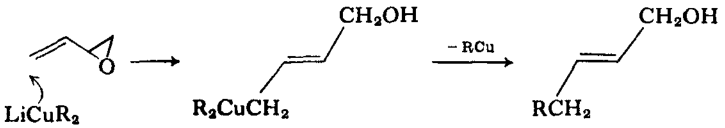
Lithium dimethylcuprate and diphenylcuprate are superior to organolithium reagents for the nucleophilic ring opening of oxiranes [Eq. (89)] under mild conditions (*133*). Methylcopper and its complexes with phosphorus ligands did not react, while a methylcopper reagent containing lithium cyanide and triethyl phosphite ligands, $Li(CH_3CuCN)\cdot P(C_2H_5O)_2$, reacted very slowly with cyclohexene oxide. In the reaction



(89)

$R' = H, R = (CH_2)_8CO_2CH_3$ (*133*)
$R' = H, R = (CH_2)_8COCH_3$ (*133*)
$R' = H, R = C_2H_5$ (*132, 133*)
$R' = CH_3, R = CO_2C_2H_5$ (*133*)

of diorganocuprates with vinyloxirane, the 1,4-addition product predominates [Eq. (90)]. The reaction is stereoselective for the *trans*-alcohol (*1a, 133*). The reaction is useful as a route to acyclic terpenes with an allylic alcohol terminus.



(90)

R	*n*-C_4H_9	C_6H_5	CH_3
Yield(%)	93	85	94
trans/cis	86/14	90/10	3.8/1 (92/8)

3. *Halogenation*

The facile iodination of organocopper compounds (*79*) is a useful reaction for the characterization of intermediate copper compounds which are formed by addition or insertion reactions (*61*, *223*, *294*, *304*). Bromine has also been used (*223*, *294*), but the yields may be low (~15%) compared with iodolysis, because of bromine's ability to function as an oxidant (*223*).

Arylcopper reagents, RCu, where R = C_6H_5, C_6F_5, C_6Cl_5, (4–C_5Cl_4N), and (2–C_4Cl_3S), readily react with iodine to give high yields of the corresponding aryl iodides. In addition to RI a little (2–8%) diarene, R_2, is also formed. When R is CH_3 or *n*-C_4H_9 the yield of the iodide is 64–70% and that of the dimer, R_2 is up to 24%. The more reactive symmetrical lithium diorganocuprates give lower yields of RI (59–86% when R is an aryl group and 46–60% when R is an alkyl group) and higher yields of R_2 (12–28% when R = aryl and 46% when R = *n*-C_4H_9) (*233b*).

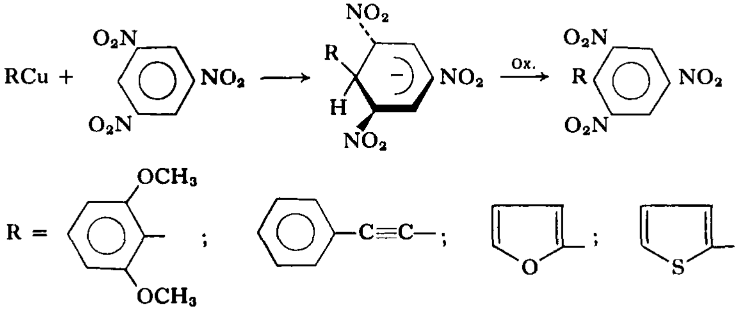
4. *Cyanoethylenes*

Tetracyanoethylene reacts with four equivalents of phenylethynylcopper in THF at 55°C to give (phenylethynyl)tricyanoethylene and tar (*281*). Other ethynylcopper compounds in similar reactions gave either the dimer of the copper compound or a compound of empirical formula $CuC_2(CN)_2$ which may be a chelate polymer joined by copper atoms.

5. *Meisenheimer Complexes*

Several organocopper compounds with 1,3,5-trinitrobenzene in pyridine, mostly at temperatures below 0°C, give intensely colored solutions due to the formation of Meisenheimer complexes (*21*, *216*, *290*). The proposed mechanism is a concerted reaction involving coordination of the nitro groups to copper and a heterolysis of the C—Cu bond. Although the strong red color is due to the accumulation of the complex, oxidation of the mixture sometimes gives only a low yield of the substitution product [Eq. (91)], or none at all, e.g., trichlorothienylcopper (*215*), phenylcopper (*21*), and hexynylcopper (*290*). The complexes have been isolated as pyridinium salts.

Picryl chloride in DMF reacts with 2,6-dimethoxyphenylcopper to give the substitution product without accumulation of a strongly colored



(91)

intermediate (*21*), although the reaction is more complex in pyridine. In some instances the organocopper compound is oxidized to its dimer by the nitrobenzene derivatives (*21*, *215*).

Similar reactions have been reported for a mixture of 2,6-dimethoxyiodobenzene, copper(I) oxide, and 1,3,5-trinitrobenzene in pyridine (*21*). Di- and triarylation can be effected under suitable conditions of catalyst, solvent, and temperature. No simple hypothesis can explain the experimental facts for the copper(I) oxide reactions.

6. *Diazo Compounds*

Arylcopper compounds decompose alkyldiazo compounds [Eq. (34)] (*34*, *37*, *255*). for which pentafluorophenylcopper is a very active catalyst. Bis(trifluoromethyl)diazomethane and pentafluorophenylcopper give perfluoro-2-phenylpropene under mild conditions, perhaps via elimination of copper(I) fluoride from an intermediate copper compound (*37*). Benzenediazonium compounds react in one of two ways (*37*): (1) diazo coupling with *m*-trifluoromethylphenylcopper to give *m*-trifluoromethylazobenzene in 93% yield; or (2) direct displacement with pentafluorophenylcopper to give a 16% yield of 2,3,4,5,6-pentafluorobiphenyl, as well as 75% decafluorobiphenyl and 65% azobenzene.

VII

ADDITION REACTIONS

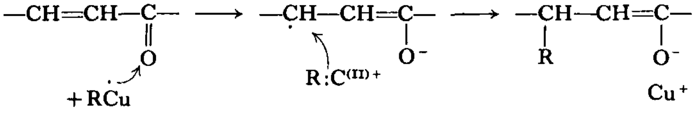
A. *α,β-Unsaturated Carbonyl Compounds*

The reaction of an organometallic reagent with an α,β-unsaturated ketone can occur by 1,2-addition to the carbonyl group and by 1,4-

addition to the conjugated system. Species such as alkyllithium and Grignard reagents react with the carbonyl group, whereas those compounds containing enolate and stabilized anions, such as organocopper reagents, give the 1,4-adduct. Attempts have been made to classify organometallic reagents according to their mode of reaction with benzalacetophenone. Phenylcopper was probably the first organocopper reagent to be reacted with this enone, from which was isolated the 1,4-adduct of the enolate anion resulting from the initial 1,4-addition reaction (*119*). Polyhaloarylcopper reagents containing lithium or magnesium halides, in which the aryl group was C_6F_5, C_6Cl_5, or 4-(C_5NCl_4), did not add to benzalacetophenone (*144*); only a polymeric material was isolated.

Since the scope and effectiveness of organocopper reagents in conjugate additions to α,β-unsaturated carbonyl compounds was first realized by House *et al.* in 1966 (*139*), the reaction has been used to stereospecifically place alkyl, vinyl, and aryl groups in the position β to a carbonyl function. Prior to 1966, additions to enones were generally effected by Grignard reagents in the presence of catalytic quantities of a copper salt. The catalysis was first reported by Kharasch and Tawney (*171*) in 1941. Posner has surveyed the conjugate addition of organocopper compounds and of Grignard reagents catalyzed by copper salts to α,β-unsaturated carbonyl compounds in a recent comprehensive review (*230*).

At present, the accepted mechanism of 1,4-addition involves the formation of either a charge-transfer complex or an anion-radical species by partial or complete electron transfer, respectively [Eq. (92)]. Collapse of the charge-transfer complex or transfer of an organic group from the copper(II) species which results from the second process, completes the addition sequence (*139*). Supporting evidence for this view of the

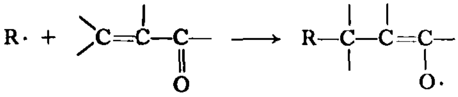


$$-CH{=}CH-\underset{\underset{O}{\|}}{C}- \;\; +RCu \longrightarrow -\underset{R:C^{(II)+}}{\dot{C}H}-CH{=}\underset{\underset{O^-}{|}}{C}- \longrightarrow -\underset{\underset{R}{|}}{CH}-CH{=}\underset{\underset{O^-\;Cu^+}{|}}{C}- \qquad (92)$$

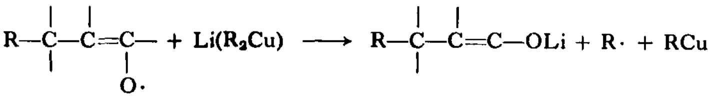
reaction is (1) the detection of an anion-radical by ESR spectroscopy in the reaction of lithium dimethylcuprate with fluorenone (*139*); and (2) the dimerization of isophorone (*135*). House and Umen have recently correlated the conjugate addition of lithium dimethylcuprate to enones with the polarographic reduction potentials of the ketones in an aprotic medium (*140*); α,β-unsaturated ketones undergo 1,4-addition if their reduction potential is greater than -2.4 V vs. sce. The tendency of a cuprate to give a 1,4-adduct is retarded by the presence of ligands which could, in theory, form reasonably stable anions (*137*). Failure of some allyl, cyano, and ethynyl cuprates to react with enones is ascribed to the delocalization of the electrons of the metal cluster into the ligands. Decreased reactivity is also reported for a solution of a mixed cuprate of 2-norbornylcopper containing mercuric compounds (*292*). Pure methylcopper and phenylcopper, or their phosphine complexes, are considered to have insufficient charge density on the copper atom to transfer an electron unless a negatively charged ligand, such as iodide or methyl, is bound to the metal cluster. Lithium halides are particularly effective (*189*). Copper compounds containing lithium or magnesium halides resulting from the preparation of a copper compound of the type RCu are effective in promoting conjugate additions (*136*, *189–192*); a cuprate of the type M(RCuX) is probably the reactive species. The addition reactions of copper compounds containing magnesium salts are less stereoselective than those containing lithium salts or lithium diorganocuprates.

An alternative mechanism for conjugate addition to α,β-unsaturated ketones is a free-radical chain process in which copper(I) would serve as the metallic center in a radical displacement reaction. However, the intermediacy of free radicals was excluded by studies of the reaction of *endo*-2-norbornylcopper with mesityl oxide (*298*), and of lithium dipropenylcuprate with cyclohexenone (*42*).

$$\mathrm{Li(R_2Cu)} \longrightarrow \mathrm{R}\cdot \qquad (93)$$



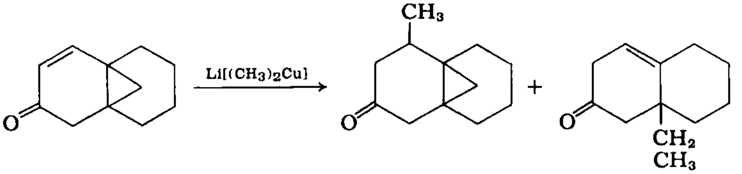
$$\mathrm{R}\cdot + \;{>}\mathrm{C{=}C{-}C({=}O){-}} \longrightarrow \mathrm{R{-}C{-}C{=}C(O\cdot){-}} \qquad (94)$$



$$\mathrm{R{-}C{-}C{=}C(O\cdot){-}} + \mathrm{Li(R_2Cu)} \longrightarrow \mathrm{R{-}C{-}C{=}C{-}OLi} + \mathrm{R}\cdot + \mathrm{RCu} \qquad (95)$$

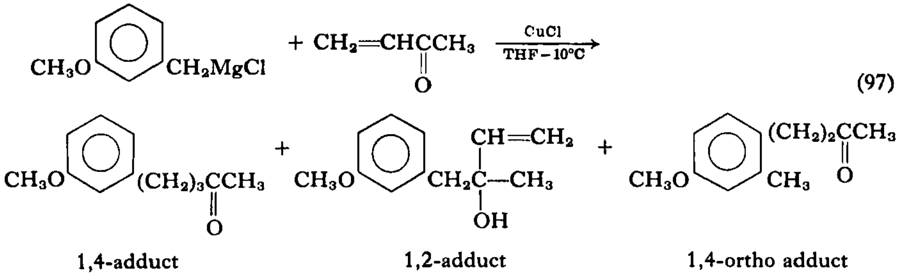
Another attractive, although unsupported, mechanism for the conjugate addition of organocopper compounds to α,β-unsaturated ketones has been proposed by Whitesides and Kendall (*298*). A feature of the generally accepted mechanism (*139*) is the formation of a copper(II) species which does not give any homo-coupled dimer, despite the known facile oxidation of lithium dialkylcuprates (see Section V). The most probable function of copper in conjugate addition to enones may be in assisting or participating in a nucleophilic attack on the C=C bond. Possible mechanisms involving oxidative addition of organic species to organocopper compounds have been discussed for reactions involving organic halides, alkyl esters, and vinyloxiranes (see Section VI,C,2). Copper compounds also add to unactivated olefins and acetylenes (see Section VII,B). Thus electron transfer to a conjugated carbonyl group is not a requirement for the addition of organocopper compounds to unsaturated carbon–carbon bonds.

Marshall and Ruden (*196*) have reported a conjugate addition of lithium dimethylcuprate to a cyclopropyl enone. The major products are the 1,4-adduct and one from a previously unreported 1,6-addition to the cyclopropyl ring [Eq. (96)]. 1,6-Conjugate additions are known for dienoates (*206*) and 2,2-di(carboxyethyl)vinylcyclopropane (*94*, cf. *59*).



(96)

Benzylmagnesium chloride reacts with methyl vinyl ketone to give a mixture of the 1,4-and 1,2-adducts in the ratio 4:1. Catalysis by copper(I) chloride does not dramatically increase this ratio. For 3-methoxybenzylmagnesium chloride and the same ketone [Eq. (97)] the ratio of 1,4-adduct:1,2-adduct:1,4-ortho adduct is 2:1:8. Copper catalysis alters this ratio to 15:1:3. Thus copper compounds may be very effective (*93*) in circumventing the benzylic rearrangement.

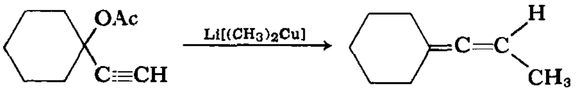


(97)

B. Other Unsaturated Compounds

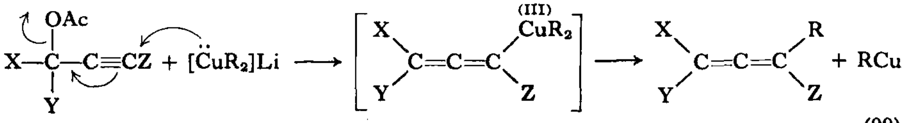
1. *Allylic and Propargylic Acetates*

The reaction of propargylic acetates with excess lithium dialkylcuprates [Eq. (98)] in ether between −10° and −5°C affords a novel allene synthesis (*240*, *241*) which cannot be effected with alkyllithium reagents. In similar reactions *n*-butylcopper was also ineffective. The



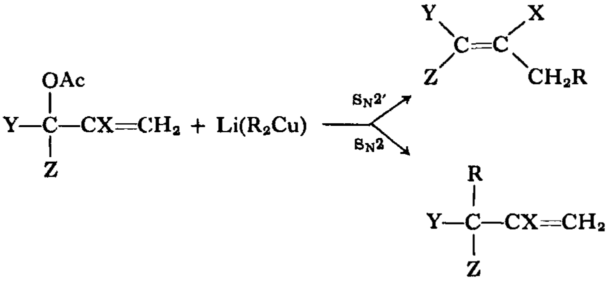
(98)

proposed S_N2' mechanism involves attack by the *d* electrons of copper on the acetylene followed by displacement of the acetate and transfer of an alkyl group by collapse of the copper intermediate [Eq. (99)]. A mixture of stereoisomers obtained as the intermediate is not configurationally stable.



(99)

Similar displacement reactions are reported for allylic acetates. The major product results from an S_N2' attack on the C=C bond and is also accompanied by some of the product apparently arising from a direct S_N2 displacement of acetate (*2*, *3*). THF as the medium, rather than ether, favored the latter product in a much slower alkylation. The overall reactions are given by Eq. (100). Methylcopper was ineffective. As the



(100)

reaction of two isomeric allylic acetates, (XIV) and (XV), with lithium di-*n*-butylcuprate gave virtually identical yields of the same two products [Eq. (101)], although (XV) reacted faster than (XIV), identical intermediates containing an allyl radical bound to copper can be postulated as shown in Fig. 6. The stereochemistry of the trisubstituted olefin formed is dependent on the nature of the substituents Y and Z in Eq. (100). When Z = H and X is small the reaction is stereospecific for the *trans*-olefin (*2*, *3*, *242*), and when X is large compared to the group attached

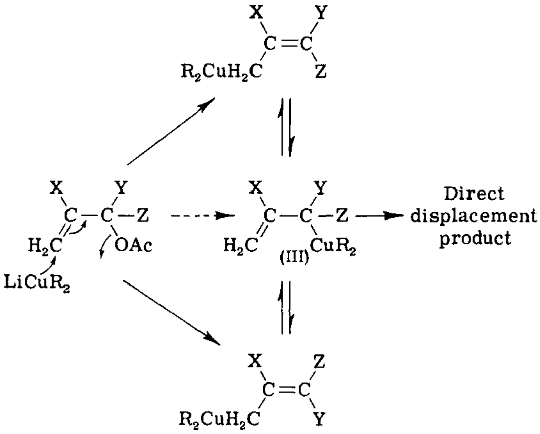
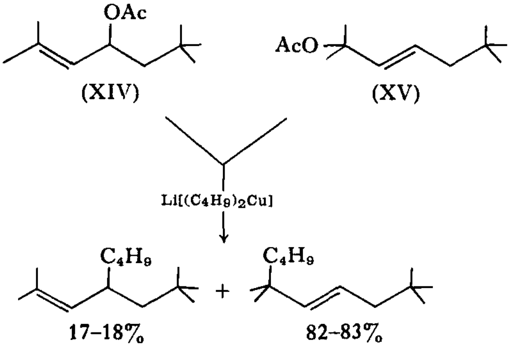


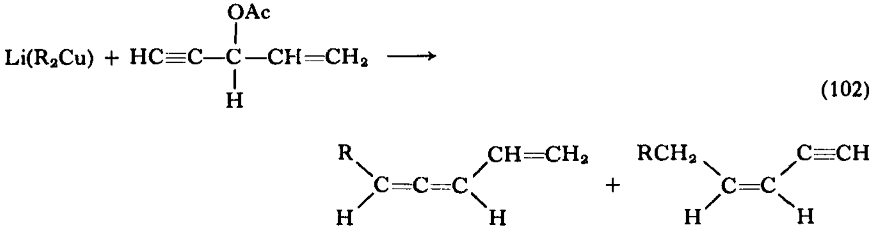
FIG. 6. Reaction of allylic acetates with dialkylcuprates.

to copper the *cis*-olefin is formed preferentially (*2*, *3*). For X = CH_3 and Z = H the proportion of *cis*-olefin in the product greatly increases for acid leaving groups such as dinitrobenzoate or trifluoroacetate which contain electron-attracting groups (*3*). The rate of the reactions is also affected by the medium. Thus the use of THF rather than ether decreases the rate of conjugate displacement of acetate and results in the formation of larger quantities of the nonstereoselective product and of the direct displacement product (*2*).



(101)

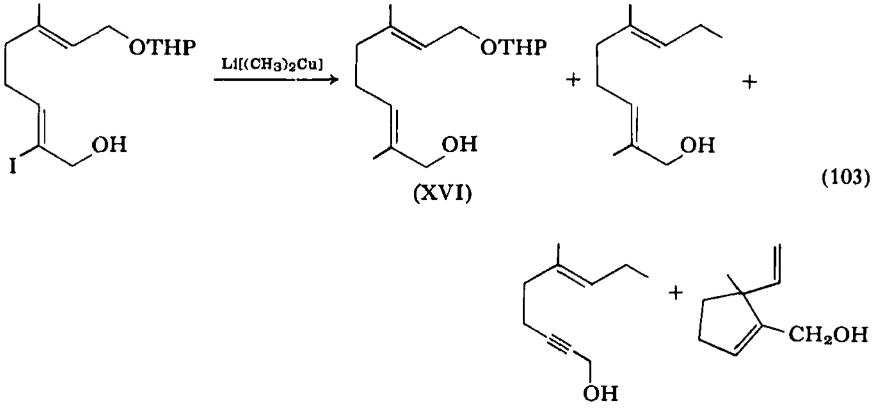
Descoins *et al.* have found that the reaction of some dialkylcuprates with 3-acetoxypent-1-en-4-yne gives an allene as the major product (*98*). Propargylic acetates are more reactive than the allylic acetates towards dialkylcuprates. With a carboxymethyl substituent on the terminal vinylic carbon [Eq. (102)] the dialkylcuprate added to the double bond and did not give an allene.



$$\mathrm{Li(R_2Cu) + HC{\equiv}C{-}\underset{\displaystyle H}{\overset{\displaystyle OAc}{C}}{-}CH{=}CH_2} \longrightarrow \tag{102}$$

(R = CH_3; n-C_4H_9; n-C_8H_{17})

On reaction of lithium dimethylcuprate with a vinylic halide which also contained a tetrahydropyranyl ether-protected allylic alcohol function (*152*), the product of coupling, (XVI), was obtained in poor yield (30%) and was accompanied by a 60% total yield of three other compounds [Eq. (103)]. The most significant of these represent products arising from the splitting off of the THP group, perhaps because of its allylic nature, by attack of the dimethylcuprate species and by an intermediate copper(III) compound on (XVI) or its precursor.



(XVI)

(103)

2. *Olefins and Acrylates*

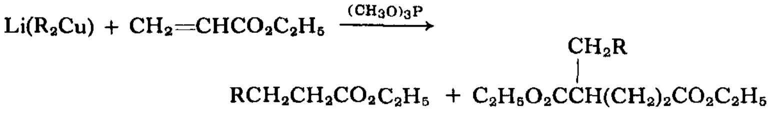
Perfluoroheptylcopper will add to olefins such as 1-heptene, 1-dodecene, cyclopentene, cyclohexene, and cycloheptene (*53*). The reactions are performed in DMSO at 110°C. Coe and Milner favor a mechanism involving the addition of perfluoroheptyl radicals to the C=C bond [Eq. (104)], rather than any nucleophilic addition process. Some olefins, such as norbornadiene and ethyl acrylate, are polymerized by this copper compound, which is known to decompose to perfluoroalkyl radicals.

$$C_7F_{15}Cu + CH_2{=}CH{-}CH_2R \longrightarrow C_7F_{15}CH_2{-}\dot{C}H{-}CH_2R \longrightarrow$$

$$C_7F_{15}CH_2{-}CH{=}CHR + C_7F_{15}CH_2CH_2CH_2R \quad (104)$$

The nature of the product varies with the olefin: (1) cyclopentene gave the olefinic product only; (2) cyclohexene and cycloheptene gave the saturated products only; and (3) 1-heptene and 1-dodecene gave a mixture of the disproportionation products.

Ethyl acrylate will react with vinylic cuprates, but at a much slower rate than α,β-unsaturated ketones and ethyl propynoates (*205*). Complexation with trimethyl phosphite is advantageous because the reactivities of the cuprate and resulting carbanion are increased. Glutarate esters are important by-products from the reaction of the intermediate carbanion with another molecule of the acrylate; the primary addition product was obtained in yields from 3.4% to 38% and the glutarate ester in 7.1–31% yield.



$$Li(R_2Cu) + CH_2{=}CHCO_2C_2H_5 \xrightarrow{(CH_3O)_3P}$$

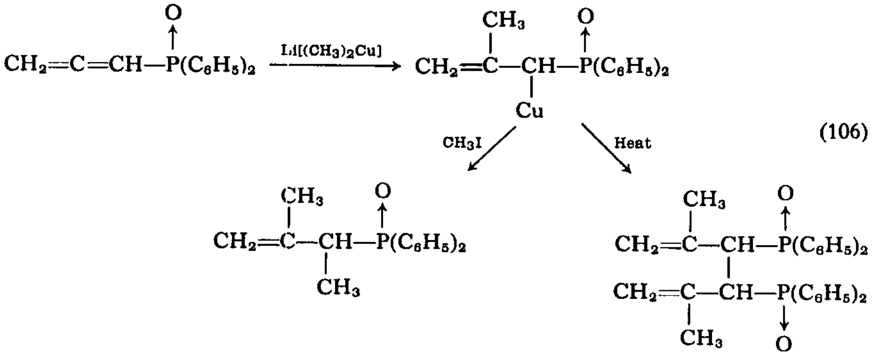
$$RCH_2CH_2CO_2C_2H_5 + C_2H_5O_2C\overset{\overset{\displaystyle CH_2R}{|}}{C}H(CH_2)_2CO_2C_2H_5 \quad (105)$$

(R = *cis*-$CH_3CH{=}CH{-}$; *cis*-*n*-$C_3H_7CH{=}CH{-}$;
cis-*n*-$C_5H_{11}CH{=}CH{-}$; *trans*-$CH_3CH{=}CH{-}$)

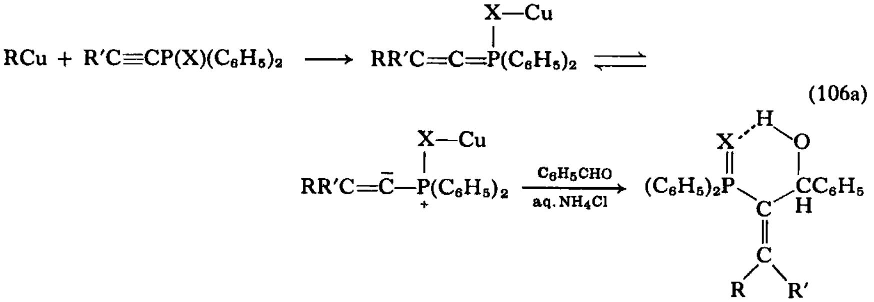
3. *Allenic and Acetylenic Phosphine Oxides*

Allenes are activated by a diphenylphosphine oxide substituent towards nucleophilic substitution at the β-carbon atom. Lithium dimethylcuprate adds quickly to the 1,2-bond to give, on hydrolysis, the olefin in 16–84% yield, according to the nature of the substituents (*16*). Optimum conditions were not reported. The intermediate α-copper compound resulting from the addition can be dimerized or reacted with methyl iodide [Eq. (106)]. Similar reactions involving methyllithium are complicated.

Ether solutions of magnesium cuprates undergo 1,4-additions to acetylenic phosphine oxides or sulfides, unlike organolithium reagents which eliminate the phosphorous group. The intermediate ylide carbanion can be treated with substrates such as benzaldehyde (*260a*).



(106)

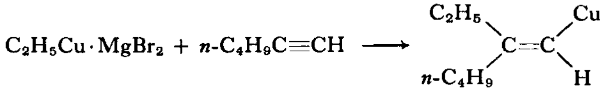


(106a)

(R or R′ = CH_3 or C_6H_5; X = O or S)

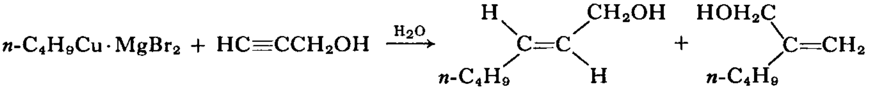
4. *Alkynes and Propynoates*

Organocopper compounds containing magnesium halides will add to acetylene and terminal alkynes (*223*). Preparation of the copper compound via a Grignard reagent is preferred to preparation via the lithium derivative, although magnesium chloride is the least effective halide. Ether is a good solvent for the addition, as the more coordinating solvents such as THF and HMPT favor metalation of the alkyne. Metalation of the more acidic acetylene and phenylacetylene is avoided by performing the addition in an ether–pentane mixture. The intermediate copper compound resulting from cis addition to the C≡C bond [Eq. (107)] can be dimerized, iodinated, hydrolyzed with D_2O, and coupled with allyl bromide stereospecifically. The addition is sensitive to electronic effects; nucleophilic addition takes place at C-2 for propynes, but at C-1 for propynoic acid. A substituent of intermediate electron-attracting power, such as CH_2OH or $CH(OC_2H_5)_2$, affords a mixture of both adducts. The vinylcopper reagents can be carbonated to give di- and



$$C_2H_5Cu\cdot MgBr_2 + n\text{-}C_4H_9C{\equiv}CH \longrightarrow (C_2H_5)(n\text{-}C_4H_9)C{=}C(Cu)(H) \qquad (107)$$

tri-substituted acrylic acids almost quantitatively if the solvent is HMPT and a catalytic quantity of $P(OC_2H_5)_3$ is added (*225a*).



$$n\text{-}C_4H_9Cu\cdot MgBr_2 + HC{\equiv}CCH_2OH \xrightarrow{H_2O} (H)(n\text{-}C_4H_9)C{=}C(CH_2OH)(H) + (HOH_2C)(n\text{-}C_4H_9)C{=}CH_2 \qquad (108)$$

Cis dimethylation of diphenylacetylene is reported for a stoichiometric magnesium dimethylcuprate reagent in THF (*186*). Lithium dimethylcuprate reacted with 1-hexyne in ether, but the products were not identified (*241*).

Stereospecific cis addition of dialkylcuprates (in excess) to propynoic acids or propynoates can be effected in ether at a very low temperature (*61*, *175*, *260*). The intermediate is configurationally unstable above −78°C and isomerizes, presumably via the enolate. Isomerization is retarded by THF as the medium (*61*) or by the presence of pyrrolidine (*260*) or TMEDA (*61*) as ligands. As a copper enolate is thermally stable at room temperature for long periods but addition of methyl-

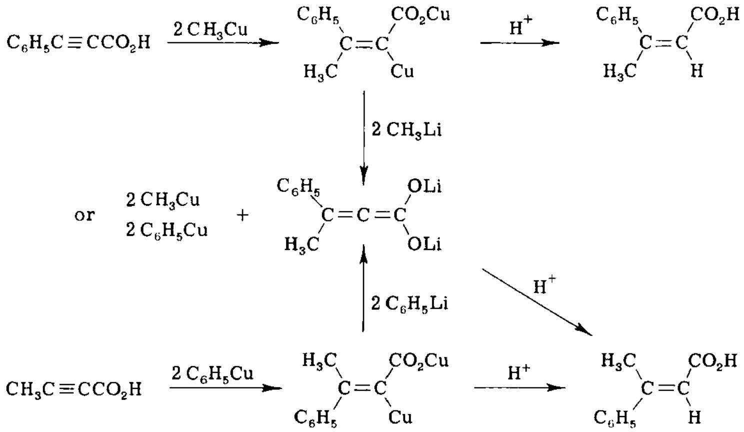


FIG. 7. Enolate stabilities.

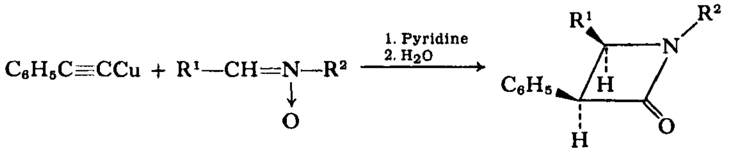
lithium causes isomerization, it is evidently a lithium enolate which is configurationally unstable (*175*). The reaction scheme in Fig. 7 illustrates the stability of the enolates obtained from phenylpropynoic and butynoic acids.

Cuprates of the type Li_nCuR_{n+1}, where $n > 1$, react with the carbonyl group of propynoate esters rather than give the conjugate addition product (*61*). Extension of the reaction of propynoate esters to vinylcopper compounds and allylcopper compounds affords a stereospecific synthesis of 1,3- and 1,4- dienes, respectively (*64*, *205*).

5. *Nitriles, Isocyanates, and Nitrones*

Organocopper compounds react slowly with nitriles or not at all (*124*, *233*). Only a low yield of benzanilide was obtained from the reaction between phenylcopper and phenyl isocyanate (*124*). Isocyanate insertion reactions with vinylcopper compounds in HMPT in the presence of $P(OC_2H_5)_3$ afford acrylamides (*225a*).

A useful stereoselective synthesis of *cis*-β-lactams (*173*) is the reaction of phenylethynylcopper with nitrones in pyridine at the ambient temperature.



(109)

C. Carbonyl Compounds

Ketones are much less reactive than aldehydes towards nucleophilic attack by dialkylcuprates in ethereal solvents (*233*); aldehydes can only be recovered at reaction temperatures below −90°C, whereas ketones can be recovered at temperatures up to −10°C. Catalytic quantities of copper salts also decrease the reactivity of Grignard reagents towards the carbonyl group (*168*). 1,2-Addition to the carbonyl group of α,β-unsaturated ketones is very slow compared to 1,4-addition, but occurs to a greater extent in THF compared to ether (*137*, *139*). The increased nucleophilicity of organocopper reagents in more coordinating solvents is demonstrated by the carbonation of a pentafluorophenylcopper reagent in DMAC but not in THF (*97*). Cuprates of the type Li_2CuR_3 also give the 1,2-adduct with enones (*137*) and give a positive reaction with Michler's ketone (*40*) in the Gilman color test for a reactive organometallic reagent (*123*). Pericyclocamphor reacts with lithium dimethylcuprate to give the *tert*-alcohol 1,2-addition product. In a similar reaction with lithium di-*n*-butylcuprate the ketone was reduced to the *sec*-alcohol, perhaps by a β-hydrogen transfer mechanism or copper(I) hydride (*257a*) (see Sections III, B, 3, b and IV).

Cyclization of δ- and ϵ-haloketones of the vinylic halide type by reaction with lithium dialkylcuprates (*65*, *67*) has been successfully applied to the synthesis of gibberellic acids. A vinylcopper(III) species is the probable intermediate (*65*) [Eq. (63)].

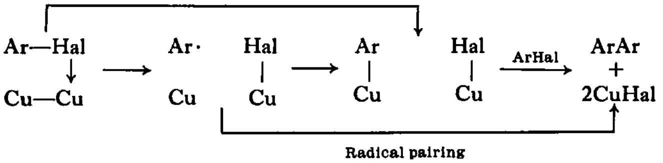
Of the less reactive copper compounds of type RCu, (carboxyethyl)-methylcopper did not react with butyraldehyde (*181*), and phenylcopper on addition to benzaldehyde gave only a 24% yield if benzhydrol (*124*).

VIII

ORGANOCOPPER COMPOUNDS AS INTERMEDIATES IN ORGANIC SYNTHESES

A. The Ullmann Reaction and Related Reactions

Two reviews have detailed the reactions of aryl halides with copper and copper compounds; these are (1) the Ullmann biaryl synthesis, by Fanta (*113*); and (2) copper-promoted reactions, by Bacon and Hill (*9*). The mechanism of the Ullmann biaryl synthesis was discussed; the possible routes are shown in Eq. (110). No evidence had been obtained



$$\begin{matrix} \text{Ar—Hal} \\ \downarrow \\ \text{Cu—Cu} \end{matrix} \longrightarrow \begin{matrix} \text{Ar}\cdot \\ \\ \text{Cu} \end{matrix} \quad \begin{matrix} \text{Hal} \\ | \\ \text{Cu} \end{matrix} \longrightarrow \begin{matrix} \text{Ar} \\ | \\ \text{Cu} \end{matrix} \quad \begin{matrix} \text{Hal} \\ | \\ \text{Cu} \end{matrix} \xrightarrow{\text{ArHal}} \begin{matrix} \text{ArAr} \\ + \\ \text{2CuHal} \end{matrix} \qquad (110)$$

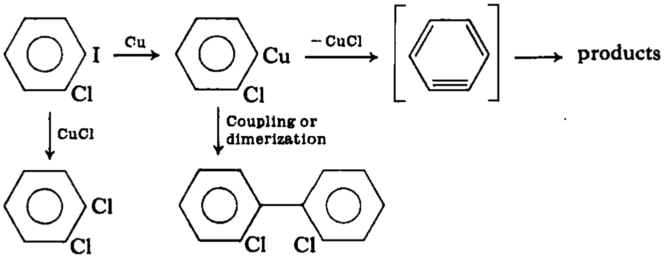
to indicate the intermediacy of free radicals or of organocopper compounds. At this time the few known arylcopper compounds were highly thermally unstable species and could be regarded as a source of either aryl radicals or ions at the temperatures normally employed; it is sometimes hard to distinguish between the two types of intermediates in the presence of copper because of a ready interconversion [Eq. (111)].

$$R\cdot + Cu^{2+} \longrightarrow R^+ + Cu^+ \qquad (111)$$

However, the Ullmann coupling reaction was remarkably specific for benzenoid or heteroaryl halides, although certain diarylalkyl halides were coupled by copper. Many features of the side reactions encountered in Ullmann coupling reactions could be explained by assuming the intermediacy of an arylcopper compound: in particular, the abnormal arylation, for a free-radical reaction, of *m*-dinitrobenzene by iodobenzene in the presence of copper; and the reductive dehalogenation of aryl halides by copper in the presence of proton donors such as carboxylic acids. Thus it was suggested that a study of the chemistry of organocopper compounds would aid the elucidation of the coupling mechanism.

Since then, experiments have been reported which indicate that (1) organocopper compounds will couple with aryl halides; (2) arylcopper compounds can be oxidatively and thermally dimerized; (3) arylcopper compounds are intermediates in the Ullmann reaction; (4) organocopper compounds are intermediates in copper-catalyzed decarboxylations; and (5) copper-promoted coupling reactions are not restricted to aromatic halides. The copper(I) oxide-promoted coupling reactions, however, have still to yield firm evidence of a copper intermediate.

An organocopper intermediate was detected by Lewin and Cohen in the reaction of *p*-iodotoluene with copper in a good complexing solvent (*184*). Analysis of protonated aliquots from a reaction performed in quinoline indicated an accumulation of *p*-tolylcopper to a maximum of 43% after 95 hours, at which point the iodide was consumed, and then a slow decrease to 0% by dimerization. Other experiments also indicate the formation of an arylcopper compound in Ullmann reactions (*127*, *141*, *210*). The isolation of deuterated products, presumably from the decomposition of an intermediate organocopper species in deuterated benzene and cyclohexane, suggested decomposition to free radicals (*127*). Decompositions of certain *o*-haloarylcopper intermediates by a benzyne mechanism cannot be totally excluded. The formation of a dichlorobenzene and by-products such as dibenzofuran and triphenylene from only the ortho isomer of the chloroiodobenzenes in Ullmann coupling reactions (*210*) suggests the sequence of reactions in Eq. (112). Evidence favoring an arylcopper intermediate was also obtained by varying the stoichiometric ratio of the reactants (*141*). A high 2,3-diiodonitrobenzene/copper ratio favored the formation of 2,2′-diiodo-6,6′-dinitrobiphenyl, whereas a low ratio favored the formation of 1,5-dinitrobiphenylene. The intermediate



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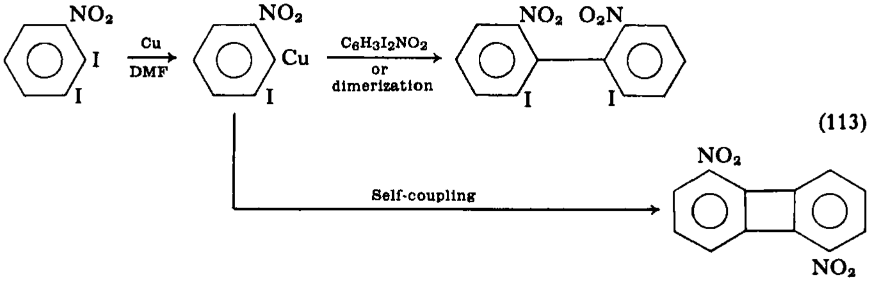
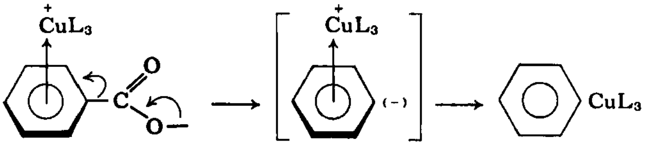


(113)

must be sufficiently long-lived in the absence of excess aryl iodide to accumulate and then either self-couple to give the biphenylene or react via a benzyne mechanism.

Copper-promoted coupling reactions are not restricted to aromatic or heteroaromatic halides; perfluorovinylic halides (*38*, *266*), and iodinated maleate and fumarate esters (*55*) are also dimerized by copper bronze. The high stereospecificity of the latter coupling argues against the participation of free radicals and supports an organocopper intermediate which undergoes self-coupling (and hydrolysis in the presence of a carboxylic acid). Perfluoroalkyl halides also react with copper bronze (*199–201*, *278*). The alkylcopper species is isolated, rather than the dimer, as no reaction takes place between the copper compound and an sp^3-hybridized halide.

The mass spectrum of copper(II) benzoate (*239*) at an electron energy of 50 V and 220°C indicates that a binuclear copper(I) benzoate is formed initially and then decomposes; the parent ion $(C_6H_5CO_2)_2Cu_2^+$, the metastable ions $(C_6H_5CO_2)(C_6H_5)Cu_2^+$ and $(C_6H_5)_2Cu_2^+$, and the ions $C_6H_5Cu_2^+$ and $C_6H_5Cu^+$ are observed. Copper(I) pentafluorobenzoate on decarboxylation in quinoline gave pentafluorophenylcopper (*33*), the only reported instance of the preparation of an organocopper compound via this method. Many attempts have been made to isolate intermediates from the decarboxylation of benzoic acids which contain one or more nitro groups as substituents in the presence of copper(I) oxide (*20*, *47*, *211*), or of the copper(I) nitrobenzoates (*33*, *46*), without success. The decarboxylation of the nitrobenzoates follows first-order kinetics up to 85% decomposition (*47*); a large negative entropy of activation indicates the loss of several degrees of freedom in the formation of an activated complex for decarboxylation, for which two possibilities have been suggested (*47*, *56*). Copper(I) nitrobenzoates were also believed to be intermediates in the copper(I) oxide-promoted decarboxylation of the free acids. Cohen and Schambach have obtained identical results, and also report that copper(II) salts are decarboxylated at approximately the same rate as the copper(I) salts because of a rapid reduction prior to decarboxylation. Homolytic cleavage of the C—C bond was ruled out by decarboxylation of propenoates with retention of configuration (*56*). Acceleration of the rate of decarboxylation by chelating agents may be a consequence of stabilization of the π-complex initially formed and/or increased electron-withdrawing power of the copper(I) ions.



(114)

An inert atmosphere is necessary for decarboxylation via organocopper intermediates to suppress oxidative decarboxylation to esters and salicylates (*150*), a well-known industrial route to phenols.

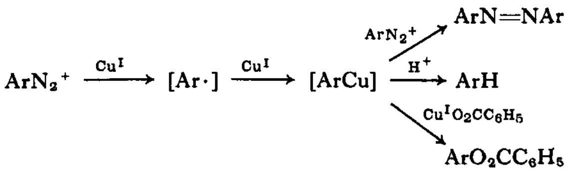
Decarboxylation of benzoates in the presence of an aryl halide (*20*, *33*, *211*) affords the biphenyl substitution products in yields of up to 50% if the medium is an *N*-heteroaromatic solvent. The solvent must be dry to avoid reductive dehalogenation (*54*). If the solvent is dry diglyme or xylene, an ester can be isolated in high yield (*54*).

$$C_6H_5CO_2Cu + IC_6H_4CH_3\text{-}p \longrightarrow C_6H_5CO_2C_6H_4CH_3\text{-}p \qquad (115)$$

The rapid decarboxylation of copper(I) trichloro-2-thienoate was, as expected, faster than that of 2-thienoic acid. Analysis of hydrolyzed aliquots indicated the accumulation of substantial quantities of trichloro-2-thienylcopper (*215*). The decarboxylations of furoic acid (*213*) and copper(I) phthalate, diphenate, and 2-phenylbenzoate (*48*) are also assumed to proceed via organocopper intermediates.

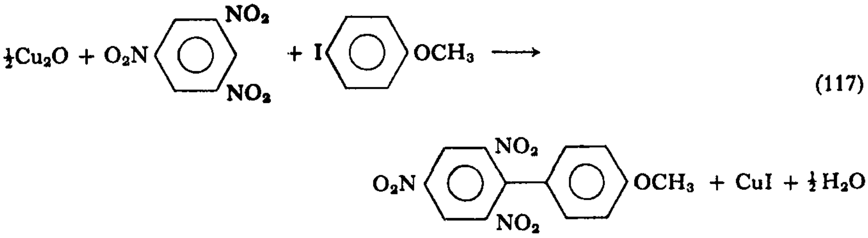
Alkanoic acids or their copper salts cannot be decarboxylated under the same conditions as those acids which contain a π-system (*56*), although fluorene-9-carboxylic acid appears to be an exception (*279*). 9-Fluorenylcopper is the supposed intermediate. Under certain conditions the decarboxylation of alkanoic acids by lead(IV) is catalyzed by copper(II) complexes; alkylcopper species have been proposed as intermediates (*179*).

Both the Sandmeyer and Meerwein reactions have been interpreted by heterolytic and homolytic mechanisms. Both reactions resemble halide replacements by involving solutions of complexes of Cu(I) with the reacting species, a diazonium compound. Cohen and Lewin have reported that a mixture of *p*-tolyldiazonium tetrafluoroborate and copper benzoate in aprotic solvents rapidly evolves nitrogen and forms toluene, bi(*p*-tolyl), *p*-tolyl benzoate, and *p,p*-dimethylazobenzene (*54*). As was earlier suggested by Kochi (*177*), the azobenzene derivative is believed to arise from a reaction between an arylcopper species and the diazonium compound. A similar mechanism was suggested for the analogous reaction with organic halides, although later evidence has suggested oxidative addition of the halide to the copper compound to form a copper(III) intermediate (*185*). The reaction of aryldiazonium tetrafluoroborates with copper in aromatic solvents was claimed to yield arylcopper compounds (*24*, *291*), but this has been denied by Warf (*285*).



(116)

The reactions between *m*-dinitrobenzene or 1,3,5-trinitrobenzene, aryl halides, and copper(I) oxide in quinoline (*17–19*, *21*) provide a simple synthesis of nitrobiphenyls uncontaminated by symmetrical biphenyls. These couplings may be related to the Ullmann reaction, the decarboxylative coupling of benzoic acids with aryl halides, and the preparation of ethers from phenols (*165*). Although no intermediates have been detected, Björklund and Nilsson have interpreted their results in terms of a metalation of the nitroarene by copper(I) oxide followed by coupling with the aryl halide in a rate-determining step. Any arylcopper species could be stabilized by coordination with the *o*-nitro groups. Equation (117) summarizes the coupling of 1,3,5-trinitrobenzene with *p*-iodoanisole. By-products arise from reductions of the nitro groups and the halide. Similar coupling reactions were reported for 2-phenylthiophene (*212*) and for mercaptans (*8*) which visibly formed copper salts. Another metalation may be involved in the formation of a Meisenheimer complex using silver oxide, but not from a mixture of cyclopentadiene, 1,3,5-trinitrobenzene, and copper(I) oxide in pyridine (*284*). However, this unexpected failure may be connected with the instability of cyclopentadienylcopper, unless complexed with isocyanide or phosphine ligands.



(117)

Bacon and Pande have presented their views of the possible reactions between aryl halides and copper(I) oxide in pyridine in a scheme (Fig. 8)

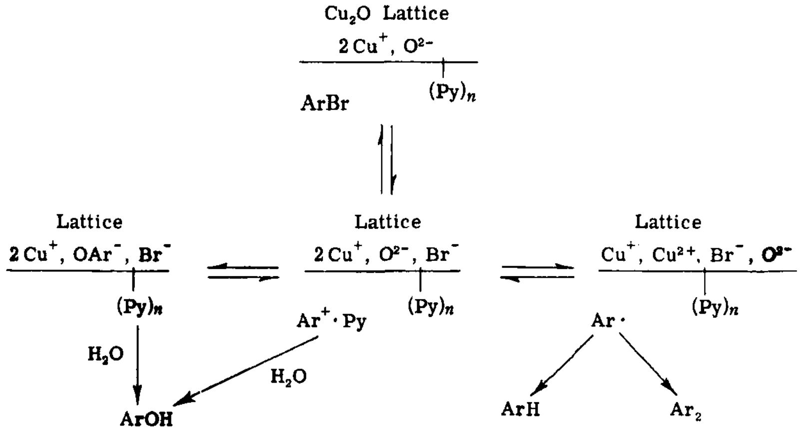
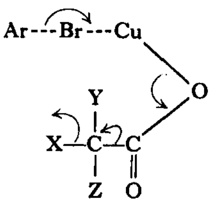


FIG. 8. Proposed scheme for the reaction of copper(I) oxide with aryl halides in pyridine.

which does not include the aryl anion (*10*); carbonium ions or aryl radicals were proposed to account for the various products. The reaction between 1-bromonaphthalene and copper(I) oxide in refluxing pyridine in the presence of various carboxylic acids or acid anhydrides has been interpreted in terms of a concerted mechanism in a coordination complex (XVII) (*8*). Bromine was replaced by Cl, H, or D when the acids were



(XVII)

chloroacetic acid, fluoroacetic acid and acetic anhydride, or deuteroacetic anhydride, respectively. As *o*-chlorobenzoic anhydride also gave 1-chloronaphthalene, benzyne may be an intermediate in the concerted or alternative stepwise reaction scheme. No evidence was obtained to prove the formation of transient carbenes or benzyne. The reactions promoted by copper(I) oxide are worthy of further detailed investigations.

B. Additions to Olefins

A complex catalyst comprised of a mixture of copper(I) oxide and an isocyanide, such as *tert*-butyl isocyanide (BNC) or cyclohexyl isocyanide (CNC) usually in excess, has considerable synthetic utility (*245–252*). Saegusa and co-workers have used copper(I)-isocyanide complexes to synthesize cyclopropanes, pyrrolines, and oxazolines, to dimerize α,β-unsaturated nitriles and carbonyl compounds, and as catalysts in the Michael addition reaction. A complex, Cu_2O—BNC, has been reacted with cyclopentadiene and with indene to give isolable copper compounds (*247*). The function of the complex is to metalate compounds containing acidic hydrogen atoms; in each instance an organocopper compound is assumed to be formed. Two good reviews are available on metal-isocyanide complexes (*278a*, *280a*).

3-Butenenitrile (allyl cyanide) is isomerized by the Cu_2O—CNC complex to 2-butenenitrile and its dimer (*248*). The key intermediate is

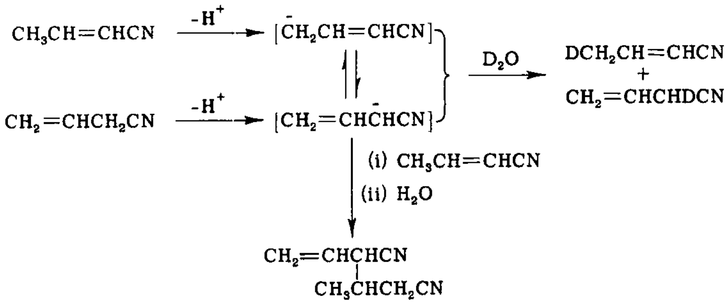
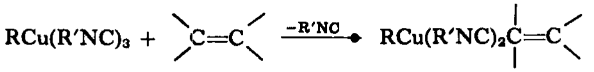


FIG. 9. Dimerization of butenenitriles by a Cu_2O—"CNC" catalyst.

considered to be an allyl carbanion bound to copper (also with isocyanide ligands) to account for the isomerization and the acidity of the α and γ hydrogen atoms. Figure 9 depicts the proposed reaction scheme. A similar reaction is reported for acrylonitrile (*245*); only a polymer is produced unless a mixture of *tert*-butanol and acetonitrile is employed as the solvent. The vinyl carbanion, $CH_2{=}\bar{C}HCN$, can be deuterated, and reacts with a further molecule of acrylonitrile to give the dimer by a Michael-type addition.

A cyclopentadienylcopper–*tert*-butyl isocyanide complex catalyzes the Michael addition of dimethyl methylmalonate to acrylonitrile at room temperature to give an 86% yield of the adduct (*249*). As the Cu_2O—BNC complex can also catalyze the addition of indene to methyl acrylate, the intermediate is most likely an organocopper complex. The reactions and kinetic data support the mechanism given by Eq. (118) to (120), involving metalation and nucleophilic attack by the carbanion on the olefin within the complex. Displacement of a solvent ligand by the olefin and coordination of the latter to the copper species are essential features of the mechanism. The rate of reaction is decreased if the compound with the

$$Cu(R'NC)_4 + RH \xrightarrow{-H} RCu(R'NC)_3 \tag{118}$$



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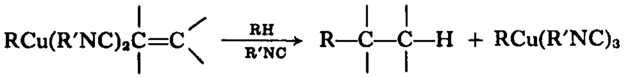
$$RCu(R'NC)_3 + {>}C{=}C{<} \xrightarrow{-R'NC} RCu(R'NC)_2C{=}C{<} \tag{119}$$

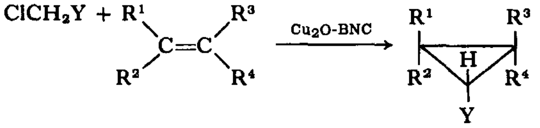


(120)

$$RCu(R'NC)_2C{=}C{<} \xrightarrow[R'NC]{RH} R{-}C{-}C{-}H + RCu(R'NC)_3 \tag{120}$$

active methylene group, RH, is added too rapidly so that it competes with the olefin for the copper species.

Cyclopropanes can be prepared in yields as high as 53% by the reaction of α-chloromethyl carbonyl compounds or nitriles with Cu_2O–BNC and a suitable olefin in refluxing benzene solution [Eq. (121)] (*250*). Chloro copper compounds, the supposed transient intermediates, are representative of a class of copper carbenoids. Other cyclopropanes can be prepared from α-ketoesters or α-diketones, an allyl or vinyl isocyanide, and copper(I) oxide [Eq. (122)] (*252*). Side reactions leading to formimidation proceed to an extent determined by the acidity of the active methylene compound. Cyclopropanes were also obtained from the addition of carenoid intermediates derived from trichloromethyl compounds and a Cu-RNC complex to olefins such as methyl acrylate (*252c*). Another route is the addition of diazoacetates to olefins in the presence of copper(I) trifluoromethanesulfonate (*252e*). Two indistinguishable mechanisms were postulated: (1) formation of a transient diazomethylcopper-olefin complex, and (2) a carbene-copper complex. Although the intermediate is indicated by the chemical studies, it could not be detected by low temperature NMR spectroscopy.



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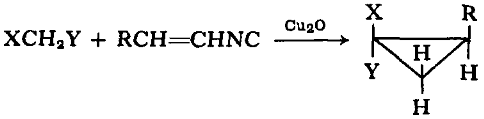
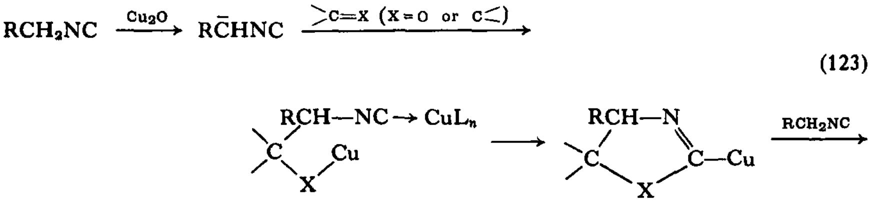


(122)

The reaction of an isocyanide containing an acidic hydrogen with copper(I) oxide and an activated olefin or a ketone [Eq. (123)] provides a synthesis of either pyrrolines or oxazolines, respectively (*251*, *252*). Addition of allyl bromide gave the coupling product with the allyl carbanion derived from allyl isocyanide. Oxazolines are obtained in yields as high as 95%, but not pyrrolines because of competing dimerization



(123)

and polymerization of the olefin. Arylcopper compounds do not form complexes with isocyanide ligands, but undergo one insertion reaction (*281d*) (Eq. 35).

C. *Miscellaneous Reactions*

Copper compounds are catalysts for the Michael addition reaction (*249*), olefin dimerizations (*245*, *248*), the polymerization of propylene sulfide (*142*), and the preparation of straight-chain poly phenol ethers by oxidation of 2,6-dimethylphenol in the presence of ethyl- or phenylcopper (*209a*). Pentafluorophenylcopper tetramer is an intriguing catalyst for the rearrangement of highly strained polycyclic molecules (*116*). The copper compound promotes the cleavage of different bonds in 1,2,2-trimethylbicyclo[1.1.0]butane compared to ruthenium or rhodium complexes. Methylcopper also catalyzes the decomposition of tetramethyllead in alcohol solution (*78*, *81*).

A Cu_2O—BNC complex will also oligomerize propiolactone (*252b*). α-Metalation of the latter may form an intermediate copper(I) acrylate complex which reacts with the lactone to give $CH_2{=}CHCO_2$-$(CH_2CH_2CO_2)_nCu$, where $n = 1$–3. The copper carboxylates present can be reacted with alkyl halides (*252a*). The Cu_2O—BNC complex will also induce ester interchange between phenyl acetate and benzyl chloride (*252a*). The products, benzyl acetate and benzyl phenyl ether, may be formed by a $C_6H_5CH_2OCu$—BNC complex and the phenoxide resulting from its reaction with the ester.

D. *Oxidation of Alkyl Radicals by Copper(II) Compounds*

The reactions of peroxides and hydroperoxides catalyzed by copper salts can be expressed by the generalized mechanism of Eqs. (124)–(126).

$$\mathrm{XOOY} + \mathrm{Cu^I} \longrightarrow \mathrm{XOCu^{II}} + \mathrm{YO}\cdot \qquad (124)$$

$$\mathrm{RH} + \mathrm{YO}\cdot \longrightarrow \mathrm{R}\cdot + \mathrm{YOH} \qquad (125)$$

$$\mathrm{R}\cdot + \mathrm{XOCu^{II}} \longrightarrow \mathrm{ROX} + \mathrm{Cu^I} \text{ etc.} \qquad (126)$$

Peroxides are reduced by a copper(I) salt to a copper(II) compound and an oxy free radical which can abstract hydrogen from a variety of compounds. The carbon free radical produced by the latter reaction is oxidized by copper(II) compounds. Alternatively, the alkyl radical can be generated directly from a diacylperoxide (*178*).

$$(RCO_2)_2 + Cu^{I} \longrightarrow R\cdot + CO_2 + RCO_2Cu^{II} \qquad (127)$$

The redox reactions of carbon free radicals and copper(II) compounds have been portrayed as ligand-transfer and electron-transfer processes (*178*). The electron-transfer oxidation of alkyl radicals by copper(II) complexes, which are efficient radical interceptors, is considered to proceed via a metastable alkylcopper species which is consumed primarily by oxidative elimination [Eq. (129)] and oxidative solvolysis [Eq. (130)] (*143b*). The anionic counterion exerts a dominant effect in the selection of pathways: acetate ions promote oxidative elimination, whereas trifluoromethanesulfonate ions promote oxidative solvolysis. The driving force for the latter pathway is provided by ligand dissociation from the alkylcopper species. The ready oxidation of methyl radicals by copper(II) acetate to methyl acetate takes place via a methylcopper species in which the acetate moiety may be transferred internally. Such a pathway, referred to as oxidative displacement, is usually unimportant for most alkyl radicals as a faster oxidative elimination is available; cationic methylation of arenes in acetonitrile is claimed (*143b*).

$$R\cdot + Cu^{II}X_2 \longrightarrow [RCu^{III}X_2] \qquad (128)$$

$$[RCuX_2] \longrightarrow R(-H) + HX + CuX \qquad (129)$$

$$[RCuX_2] \xrightarrow{HS} RS + HX + CuX \qquad (130)$$

$$[RCu^{III}X_2] \longrightarrow [RCu^{III}X^+X^-] \longrightarrow [R^+Cu^{I}XX^-] \text{ or } [R^+CuX_2^-] \qquad (131)$$

$$CH_3Cu(O_2CCH_3)_2 \longrightarrow CH_3O_2CCH_3 + CuO_2CCH_3 \qquad (132)$$

Copper(II) compounds also enhance the rate of decarboxylation of alkanoic acids with lead(IV) acetate by more efficient electron-transfer oxidation of the alkyl radicals produced; alkylcopper species may be intermediates (*179*).

Facile ligand-transfer oxidation of alkyl radicals is accomplished by copper(II) halides or pseudohalides (*143a*). Two processes occur simultaneously: (1) oxidative substitution via cationic intermediates and an alkylcopper species, as in electron-transfer oxidation processes; and (2) homolytic atom transfer. The former is akin to the oxidative displacement

$$R\cdot + CuCl_2 \longrightarrow [R\text{---}Cl\text{---}CuCl] \longrightarrow RCl + CuCl \qquad (133)$$

reported for methyl radicals and copper(II) acetate, but the latter is energetically the more favorable process and is usually the major course of the reaction. Alkyl moieties susceptible to cationic rearrangements, such as neopentyl, homoallylic, and β-arylethyl, have been used in all of these studies; the cationic pathway is important for radicals which can give stabilized carbonium ions. Free carbonium ions as such are not intermediates since the transfer of a ligand from a copper(II) compound can be effected in protic media without the intervention of the external nucleophile. Oxidative ligand transfer results are in sharp contrast to electron-transfer oxidations under comparable conditions: oxidative solvolysis invariably leads to complete cationic rearrangement of the alkyl moieties. Jenkins and Kochi (*143a*) propose that the ability of a radical to discriminate among several sites on a metal complex is a consequence of its degree of hardness with respect to the hard and soft acid–base classification.

One cannot distinguish between the analogous copper intermediates involved in oxidative electron-transfer and ligand-transfer reactions. In each the ionization of the ligand to copper(II) has an important role in the formation of carbonium ion intermediates. A reaction analogous to the copper-catalyzed decomposition of peroxides is the copper-promoted decomposition of diazonium salts (*178*). The diazonium ion and copper(I) afford aryl radicals which can undergo ligand-transfer oxidation with copper(II) halides (Sandmeyer reaction) or add to olefins (Meerwein reaction).

IX

ORGANOCOPPER(II) COMPOUNDS

The reduction of a copper(II) salt to a copper(I) compound by an organometallic reagent in which the metal is higher than copper in the electromotive series has been taken somewhat for granted, but probably involves a highly metastable organocopper(II) compound. Free radicals cannot be intermediates because the reaction between *trans*-propenyllithium and copper(II) chloride gave only 2,4-hexadiene with complete retention of configuration (*294*), despite the known rapid inversion of propenyl radicals. Clinton and Kochi have suggested that the reactions are worthy of investigation (*276*). In the reaction of tetraethyllead with copper(II) salts in acetic acid solution [Eqs. (7)–(9)] a proposed transient intermediate ethylcopper(II) compound decomposes to an ethyl radical and a copper(I) compound. The ethyl radicals are quickly scavenged by excess of the copper(II) salt and oxidized to ethylene. Alternatively, if the solvent is THF the gaseous product is butane. Butane is also produced by addition of ethylmagnesium halides to copper(II) salts in THF at −78°C (*275*, *283*). If the solvent is ether, the reaction of ethylmagnesium bromide with both copper(I) and copper(II) chlorides gives essentially equal quantities of ethane and ethylene (*120*). The reason for this solvent effect is not understood. A transitory orange coloration was reported on addition of ethyl-Grignard reagents to copper(II) chloride in THF at −78°C, which may be an indication of a transient ethylcopper(II) intermediate (*283*). Ethylcopper(I) can also be oxidized to butane (*276*); copper(II) compounds are assumed to be the intermediates (see Section V).

Although there are numerous examples of dimerizations of organometallic reagents by copper(II) salts, one particularly interesting example concerns 2,2′-dilithiobiphenyl (*304*). Wittig and Klar have proposed several transient copper(II) "ate" complexes and a stable copper(I) complex to account for the high yields of biphenylene and *o*-tetraphenylene. Diarylcopper(II) compounds were supposedly isolated, and characterized by elemental analysis, from diarylmercury compounds and copper at 120°C (*11*, *197*); an unlikely reaction.

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Compounds Derived from Alkynes and Carbonyl Complexes of Cobalt

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I

INTRODUCTION

The development of metal carbonyl chemistry has been discussed extensively in recent reviews (*1–3*), and it is clear that metal carbonyl

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compounds have considerable value as stoichiometric (*4*, *5*) and catalytic reagents (6) in chemical synthesis. Reactions involving alkynes and metal carbonyl compounds have been surveyed in a general way (*7*, *8*). This review is concerned specifically with the formation of organic and organometallic compounds from the reactions of alkynes with carbonylcobalt complexes.

II

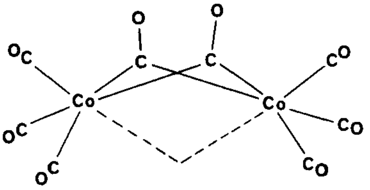
REACTIONS INVOLVING $Co_2(CO)_8$ AND RELATED COMPOUNDS

A. Preparation of Octacarbonyldicobalt

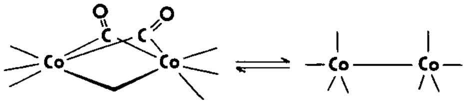
Solutions of octacarbonyldicobalt in hydrocarbon solvents can be prepared by a high-pressure reaction between a cobalt(II) compound such as cobalt carbonate and a mixture of carbon monoxide and hydrogen (*9*). Isolation of crystalline octacarbonyldicobalt from the solutions can be difficult, and consequently the preparation of solid $Co_2(CO)_8$ is better achieved from the reaction of CO and H_2 with cobalt(II) acetate in acetic acid as solvent (*10*, *11*). Octacarbonyldicobalt is insoluble in the latter solvent and may be isolated by simple filtration of the reaction mixture. Numerous other preparations of $Co_2(CO)_8$, including a low-pressure method (*12*), have been reported (*1*, *3*). The compound is available commercially.

Octacarbonyldicobalt is an orange, crystalline solid which decomposes to the purple cobalt(II) oxide or carbonate upon exposure to the air. It can be purified by sublimation at 25°C/0.1 mm, and it is soluble in hydrocarbon solvents. Thermal decomposition of octacarbonyldicobalt yields dodecacarbonyltetracobalt; this decomposition is slow at 25°C but is quite rapid at 50°–60°C. Continued heating of the compound ultimately yields cobalt metal.

The solid-state structure of octacarbonyldicobalt (*13*) is represented in (I). It has been established (*14*, *15*) that $Co_2(CO)_8$ exists in solution in two isomeric forms. One form (II) corresponds to the structure of the crystalline substance while the second isomer (III) has no bridging carbonyl groups. From a study of the temperature dependence of the infrared spectrum of $Co_2(CO)_8$ in pentane, Noack (*14*) has determined that the unbridged isomer (III) is the major component in the equilibrium



(I)



(II) (III)

mixture at room temperature; the ratio of (II):(III) is given as 43:57. At lower temperatures, the bridging isomer predominates. For instance, the ratio of (II):(III) is 84:16 at −104°C.

B. *Complexes of Cobalt Derived from $Co_2(CO)_8$ and $RC{\equiv}CR'$*

Solutions of octacarbonyldicobalt in petroleum solvents react readily at room temperature with a large variety of alkynes to give complexes of general formula $Co_2(CO)_6(RC_2R')$. The complexes are generally purified by chromatography on alumina, silica gel, or florisil and are obtained as red to dark violet liquids or solids. Most $Co_2(CO)_6(RC_2R')$ complexes are volatile and are readily soluble in organic solvents.

The formation of alkyne-hexacarbonyldicobalt complexes from the direct reaction of alkynes with octacarbonyldicobalt is represented by Eq. (1). Alkynes that undergo reaction according to the equation include

$$Co_2(CO)_8 + RC{\equiv}CR' \longrightarrow Co_2(CO)_6(RC_2R') + 2CO \qquad (1)$$

terminal alkynes (R′ = H), symmetrical disubstituted alkynes (R = R′), unsymmetrical disubstituted alkynes (R ≠ R′), diynes, triynes, and cyclic alkynes. The known complexes of formula $Co_2(CO)_6(RC_2R')$ are listed in Tables I–V. It has been reported that the two alkynes $(CO)_9Co_3CC{\equiv}CCCo_3(CO)_9$ (*53*) and $(CO)_9Co_3CC{\equiv}CC_2[Co_2(CO)_6]$-$CCo_3(CO)_9$ (*27*, *75*) do not react with $Co_2(CO)_8$ according to Eq. (1); this is presumably due to effective steric protection of the carbon–carbon triple bonds in these complex alkynes.

Although Eq. (1) represents the most general synthesis of the complexes $Co_2(CO)_6(RC_2R')$, several other reactions involving alkynes and/or carbonyl-cobalt compounds are known to give alkyne-hexacarbonyldicobalt complexes. These include the reactions of alkynes with $Hg[Co(CO)_4]_2$ (*21*, *48*, *54*, *57*, *73*), $ClHgCo(CO)_4$ (*84*), $Co_4(CO)_{12}$ (*31*,

TABLE I

KNOWN COMPLEXES OF FORMULA $Co_2(CO)_6(RC_2H)$

R	Color m.p., °C (b.p., °C)	References concerning Preparation	IR	NMR
H	Red oil, 13–13.6, (64–66/4 mm)	*16–24*[a]	*16, 17, 20–22, 25–27*[a]	*28, 29*[b]
D	—	*22*	*22, 26*	—
Me	Red-brown solid	*29–31*	*29, 30*	*29*
$ClCH_2$	—	*32*	—	—
$BrCH_2$	—	*32*	—	—
CF_3	Red oil	*33–36*	*35, 36*	*35, 36*[c]
$(HO)CH_2$	Orange-red solid, 52.2–52.6	*16, 17, 20, 32, 39*	*16, 17, 25, 40*	—
$(MeO)CH_2$	—	*32, 39, 41*	—	—
$(Ph_3CO)CH_2$	—	*32*	—	—
Me(OH)CH	Red, 36–38	*39, 41a*	—	—
Me(O)C	—	*42*	—	—
(MeO)(O)C	Brown-red solid	*43*	—	—
$MeCH_2$	—	Not reported	—	—
(Me)(Ph)(OH)C	—	*41a*	—	—
$(HO)CH_2CH_2$	—	*41*	—	—
$(MeO)(O)CCH_2$	—	*44*	—	—
$(CF_3O)(O)CCH_2$	—	*44*	—	—
$(CCl_3O)(O)CCH_2$	—	*44*	—	—
$(CCl_2CClO)(O)CCH_2$	Red solid, 64–65	*44*	—	—
$(PhO)(O)CCH_2$	89–90	*44*	—	—
$(p\text{-}NO_2C_6H_4O)(O)CCH_2$	133–134	*44*	—	—
$(3,5\text{-}(NO_2)_2C_6H_3O)(O)CCH_2$	102	*44*	—	—
n-Pr	—	*18, 25, 41*	*25*	—
i-Pr	—	*39*	—	*39*
$(HOCH_2)(Me)CH$	—	*45*	—	—
Me_2ClC	—	*32*	—	—
$Me_2(OH)C$	Red solid, 42–43.5	*32, 39, 41a*	—	—
$Me_2(MeO)C$	Red oil	*39*	—	*39*
$Me_2(CF_3CH_2O)C$	—	*41a*	—	—
$Ph_2(OH)C$	Red solid, 125 (dec.)	*39*	—	—
n-Bu	—	*32, 46*	—	—
$ICH_2(CH_2)_3$	—	*32*	—	—
Et(Me)(OH)C	—	*45*	—	—
tert-Bu	Red-brown, 13.0–14.5	*32, 47, 48*	—	—
$Me(CH_2)_4$	—	*16*	—	—

TABLE I—*Continued*

R	Color m.p., °C (b.p., °C)	References concerning		
		Preparation	IR	NMR
$BrCH_2(CH_2)_4$	—	*32*	—	—
$\underline{CH_2(CH_2)_3C}(OH)$	—	*41a*	—	—
$(MeO)(O)C(CH_2)_5$	—	*32*	—	—
$\underline{O(CH_2)_4C}(OH)CH_2$	—	*32*	—	—
$C_{19}H_{26}(OH)_2$	—	*49*	—	—
$CH_2{=}CH$	—	*41a, 45*	—	—
$CH_2{=}C(Me)$	Red-brown solid, 31.8–32.8	*17, 20, 32, 41a*	*17, 20*	—
$CH_2{=}C(Ph)$	—	*41a*	—	—
$\underline{CH_2(CH_2)_2CH{=}C}$	—	*41a*	—	—
$\underline{CH_2(CH_2)_3CH{=}C}$	—	*41a*	—	—
$\underline{CH_2(CH_2)_4C}(OH)$	—	*41a, 45*	—	—
Ph	Dark red oil	*16, 17, 20, 31, 32, 51*	*17, 20, 25*	—
p-FC_6H_4	—	*32*	—	—
o-ClC_6H_4	—	*32*	—	—
m-ClC_6H_4	—	*32*	—	—
p-ClC_6H_4	—	*32*	—	—
p-BrC_6H_4	—	*32*	—	—
o-MeC_6H_4	—	*32*	—	—
m-MeC_6H_4	—	*32*	—	—
p-MeC_6H_4	—	*32*	—	—
2,4-$Me_2C_6H_3$	—	*32*	—	—
3,4-$Me_2C_6H_3$	—	*32*	—	—
2,4,6-$Me_3C_6H_2$	—	*32*	—	—
2,6-Me_2-4-*tert*-Bu-C_6H_2	—	*32*	—	—
C_6F_5	Red solid	*31, 34, 52*	*34, 52*	*34, 52*[d]
Me_3Si	29.5	*41, 48*	*48*	—
Me_3Sn	—	*42*	—	—
n-BuO	—	*32*	—	—
$Co_3(CO)_9C$	Black solid, 100 dec.	*28, 53*	*27, 28*	*28*[e]

---

[a] The formation (*22*) and IR spectrum (*22, 26*) of the complex $Co_2(CO)_6(HC^{13}CH)$ have been reported also.

[b] UV spectrum (*21*).

[c] UV spectrum (*37*), mass spectrum (*38*).

[d] UV spectrum (*52*).

[e] UV spectrum (*27*), mass spectrum (*28*).

TABLE II
KNOWN COMPLEXES OF FORMULA $Co_2(CO)_6(RC_2R)$

R	Color m.p., °C (b.p., °C)	References concerning Preparation	IR	NMR	UV
D	—	*22*	*22, 26*	—	—
Me	Dark red oil	*17, 20, 31, 32, 68*	*17, 20, 29, 68*	*29, 68*[a]	—
$ClCH_2$	Red solid, 90 (dec.)	*30*	*30*[a]	—	—
$(HO)CH_2$	Orange-red needles, 135 (dec.)	*16*	*16*	—	—
$(Et_2N)CH_2$	Brown oil	*30, 54*	*30*	—	—
CF_3	Red solid, 114	*31, 37, 55, 56*	*55, 56*	*55, 56*	*37*[a,b]
CN	Red solid	*37*	*37*	—	*37*
HOOC[c]	Orange solid	*30*	*30*	—	*16*
(MeO)(O)C	Red solid, 47–50	*48*	*48*[a]	—	—
(EtO)(O)C	—	*57*	—	—	—
(*n*-PrO)(O)C	—	*57*	—	—	—
(*n*-BuO)(O)C	—	*57*	—	—	—
Et	—	*16, 32, 48, 58*	—	—	—
Me(OH)CH	Red solid, 100 (dec.)	*39*	—	—	—
n-Pr	—	*49*	—	—	—
i-Pr	Brown solid, 95	*39, 59*	*59*	—	—
$Me_2(OH)C$	Red-brown solid, 110 (dec.)	*39, 41a, 45, 54*	—	—	—
n-Bu	—	*60*	*60*	—	
Et(Me)(OH)C	—	*45, 54*	—	—	—
tert-Bu	Red-brown solid, 115–120 (dec.)	*61–63*	*61*	—	—
$CH_2{=}C(Me)$	—	*41a*	—	—	—
$MeCH{=}C(Me)$	—	*54*	—	—	—
$CH_2(CH_2)_4C(OH)$	—	*45, 54*	—	—	—
Ph	Deep purple crystals, 109.5–110.0	*16, 17, 20, 32*	*16, 17, 20, 25, 64, 65*	—	*17, 21*[a]
p-$NO_2C_6H_4$	Dark red solid, 125 (dec.)	*48*	*48*	—	—
p-$Me(O)CC_6H_4$	93–94	*66*	*66*	*66*	—
p-$Ph(O)CC_6H_4$	65 (dec.)	*66*	*66*	—	—
C_6F_5	Red crystals, 99–101 (dec.)	*31, 64*	*64*	*64*	*64*
p-$MeOC_6F_4$	Purple solid, 191 (dec.)	*64*	*64*	*64*	—

TABLE II—*Continued*

R	Color m.p., °C (b.p., °C)	References concerning			
		Preparation	IR	NMR	UV
C(OH)Ph(Me)	—	*54*	—	—	—
C(OH)Ph_2	Red-brown solid, 115 (dec.)	*39*	—	—	—
$SiMe_3$	Dark red solid, 110 (dec.)	*48*	*48*	—	—
$GeMe_3$	—	*42*	—	—	—
$SnMe_3$	—	*42*	—	—	—
$C_5H_5FeC_5H_4$	Green solid, 151–153	*67*	*67*	*67*	—

[a] Mass spectrum (*53a*).
[b] Mass spectrum (*38*).
[c] Isolated as dibasic salt.

TABLE III
KNOWN COMPLEXES OF FORMULA $Co_2(CO)_6(RC_2R')$

R	R′	Color, mp. (°C)	References concerning	
			Preparation	IR
Me	D	—	*29*	*29*
Me	CF_3	Red solid	*68*	*68*[a]
Me	*n*-Pr	—	*32*	—
Me	$(CH_2)_4C(O)OMe$	—	*32*	—
Me	Ph	Red-brown oil	*30, 48*	*30*
Me	$SiMe_3$	Red-black, 60–61	*69*	*69*[b]
Me	$CpFe(CO)_2$	60–61	*69a*	*69a*[c]
Et	$(CH_2)_3C(O)OH$	—	*32*	—
Et	$(CH_2)_2C(O)OMe$	—	*32*	—
n-Pr	C(O)OH	Red-brown solid, 83–85 (dec.)	*17, 20*	*17, 20*
n-Pr	$(CH_2)_3OH$	—	*32, 49*	—
n-Pr	$CH_2CH(OH)Me$	—	*49*	—
n-Pr	$CH_2CH{=}CH_2$	—	*49*	—
$MeCH(OH)CH_2$	$CH(Me)CH_2OH$	—	*49*	—
$MeCH(OH)CH_2$	$C(OH)Me_2$	—	*49, 41a*	—
$MeCH(OH)CH_2$	$C(Me){=}CH_2$	—	*49, 41a*	—
n-Bu	CH_2OH	—	*32*	—
n-Bu	CH_2Cl	—	*32*	—
n-Bu	CH_2Br	—	*32*	—
n-Bu	CH_2I	—	*32*	—

Continued

TABLE III—*Continued*

R	R′	Color, m.p. (°C)	References concerning Preparation	 IR
n-Bu	C(O)OH	—	*32*	—
n-Bu	C(O)OMe	—	*32*	—
n-Bu	CH(OH)Me	—	*32*	—
tert-Bu	CH_2OH	—	*32*	—
tert-Bu	C(O)Me	—	*42*	—
tert-Bu	Ph	Brown solid, 94–96	*43*, *59*	—
tert-Bu	$SnMe_3$	—	*42*	—
Me_3Si	CF_3	Red	*69*	*69*^{b}
Me_3Si	$GeMe_3$	—	*42*	—
Me_3Si	$SnMe_3$	—	*42*	—
$Me(CH_2)_4$	C(O)OH	Dark red oil	17, 20	*17*, *20*
$Me(CH_2)_4$	C(O)(OMe)	—	*32*	—
$\underline{CH_2(CH_2)_4CH}$	$\underline{CH_2(CH_2)_4C}(OH)$	—	*41a*	—
$\underline{CH_2(CH_2)_4CH}$	$\underline{CH_2(CH_2)_3CH}{=}C$	—	*41a*	—
$(HO)(Me)_2C$	$CH_2{=}C(Me)$	—	*41a*	—
Ph	C(O)OH	Purple-brown solid, 120 (dec.)	*16*, *17*, *20*, *32*, *41*	*17*, *20*
Ph	C(O)(OMe)	Dark red solid, 65	*48*	*48*
Ph	C(O)(OPh)	—	*48*	—
Ph	$C(OH)Ph_2$	Red-brown solid, 95 (dec.)	*39*	—
Ph	$C_6H_4C(O)Me$	63–63.5	*66*	*66*
Ph	$C_6H_4C(O)Ph$	133–4	*66*	—
Ph	*o*-HC_6F_4	Dark red solid, 84	*70*	*70*^{d}
Ph	C_6F_5	—	*31*, *70*	*70*^{d}
Ph	$SiMe_3$	Red-brown solid, 64	*48*, *69*	*48*, *69*
Ph	$N_3P_3F_5$	Red solid, 62–63	*71*	*71*^{e}
Ph	$CpFe(CO)_2$	—	*69a*	—
Ph	$CpFe(CO)(PMe_2Ph)$	—	*69a*	—
F	$CCo_3(CO)_9$	—	*53*	—

[a] NMR spectrum (*68*).

[b] NMR spectrum (*69*).

[c] Mass spectrum (*69a*).

[d] NMR spectrum (*70*).

[e] NMR, mass spectra (*71*).

TABLE IV

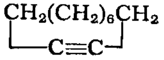
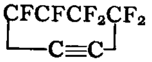
KNOWN COMPLEXES OF FORMULA $Co_2(CO)_6$(DIYNE)*, $(Co_2(CO)_6)_2$(DIYNE), AND $(Co_2(CO)_6)_3$(TRIYNE)

Diyne or triyne	Color, m.p. (°C)	References concerning: Preparation	IR	NMR
$HC\equiv CC\equiv CH$	—	*21*	*21*[a]	—
$MeC\equiv CC\equiv CMe$	Dark green solid, 134.5–135	*72*	*72*	*72*
$PhC\equiv CC\equiv CPh$	Dark green solid, 117–120 (dec.)	*72, 73*	*72, 73*	*72, 73*
$PhC\equiv CC\equiv CPh$*	Dark red solid, 57–59	*73*	*73*	—
$PhC\equiv CC_2Ph((C_5H_5)_2Ni_2)$*	Black solid, 156–158 (dec.)	*40*	—	—
$Me_2C(OH)C\equiv CC\equiv CC(OH)Me_2$	Dark green-black crystals	*17, 20*	*17, 20*	—
$Co_3(CO)_9CC\equiv CC\equiv CCCo_3(CO)_9$	Dark brown	*27, 74, 75*	*74, 75*[b]	—
$HC\equiv C(CH_2)_4C\equiv CH$	Red crystals, 85–85.4	*17, 20, 32*	*17, 32*	—
$ClC\equiv C(CH_2)_6C\equiv CCl$	Red solid, 68–69	*48*	*48*	—
p-$(PhC\equiv C)_2C_6H_4$	Black solid, 250	*72*	*72*	—
o-$(PhC\equiv C)_2C_6F_4$*	Dark red solid, 120	*76*	*76*	*76*
p-$(PhC\equiv C)_2C_6F_4$*	Dark red solid	*77*	—	—
p-$(PhC\equiv C)_2C_6F_4$	156 (dec.)	*77*	—	—
$HC\equiv C(CH_2)_8C(O)OCH_2C\equiv CH$	—	*78*	*78*	—
$PhC\equiv CGeEt_2C\equiv CPh$	Brown-black solid, 87–89	*79, 80*	*79, 80*	*79, 80*
$PhC\equiv CSiPh_2C\equiv CPh$	Brown-black, 144	*79, 80*	*79, 80*	*79, 80*
$HC\equiv CC\equiv CC\equiv CH$	—	*21*	*21*[a]	—
$As(C\equiv CH)_3$	Deep purple	*81*	—	—
1,2,4-$C_6H_3(C\equiv CH)_3$	Dark red solid, 120–130 (dec.)	*73*	*73*	—
1,3,5-$C_6H_3(C\equiv CH)_3$	Dark red solid, 127–128 (dec.)	*73*	*73*	—

[a] UV spectrum (*21*).
[b] UV spectrum (*74, 75*).

TABLE V

KNOWN COMPLEXES OF FORMULA $Co_2(CO)_6$(CYCLIC ALKYNE)

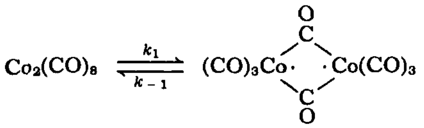
Cyclic alkyne	Color, m.p. (°C)	References concerning: Preparation	IR	NMR
 $\overline{CH_2(CH_2)_6CH_2C\equiv C}$	Dark red oil	*17, 20*	*17, 20*	—
 $\overline{CFCFCF_2CF_2C\equiv C}$	Red solid, 47–48	*82, 83*	*82, 83*	*82, 83*

48, 72), $Co_4(CO)_{11}PPh_3$ (*84*), $RCOCo(CO)_4$ (*58*), and $HCo(CO)_4$ (*23, 85*), and reactions between $Co_2(CO)_8$ and octafluorocyclohexa-1,3-diene (*86*), hexachlorocyclopropane (*75*) and disubstituted cyclopropenones (*60*). It has been reported (*27, 87*) also that $Co_2(CO)_6(RC_2R')$ complexes are formed when $Co_3(CO)_9CY$ complexes are heated in aromatic solvents.

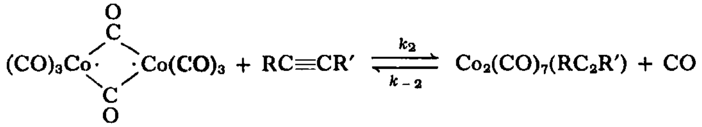
C. *Mechanism of Formation of Alkyne-hexacarbonyldicobalt Complexes*

The complexes $Co_2(CO)_6(RC_2R')$ are derived formally from $Co_2(CO)_8$ (I) through replacement of two bridging carbonyl groups by one alkyne unit. It has been suggested that formation of the complexes could proceed either by direct nucleophilic displacement (S_N2 mechanism) or by a mechanism involving prior dissociation of the $Co_2(CO)_8$ (S_N1 mechanism).

Tirpak and co-workers (*32, 46*) have interpreted their kinetic data in terms of the S_N2 mechanism represented in Eq. (2)–(4). The rate of the



$$Co_2(CO)_8 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (CO)_3Co\cdot(\mu\text{-}CO)_2\cdot Co(CO)_3 \qquad (2)$$



$$(CO)_3Co\cdot(\mu\text{-}CO)_2\cdot Co(CO)_3 + RC{\equiv}CR' \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Co_2(CO)_7(RC_2R') + CO \qquad (3)$$

$$Co_2(CO)_7(RC_2R') \xrightarrow{k_3} Co_2(CO)_6(RC_2R') + CO \qquad (4)$$

reaction in toluene solution and at atmospheric pressure was determined by monitoring the volume of carbon monoxide evolved as a function of time. Almasi and co-workers (*45*) have suggested that the first step in the reaction mechanism could be addition of the alkyne unit perpendicular to the Co—Co bond rather than homolytic splitting of the latter. Independent observations are purported to show that the reactions of $Co_2(CO)_8$ with carbon monoxide at high pressure and temperature (*88*) and with triphenylphosphine (*89*) follow a similar mechanism involving direct nucleophilic attack on $Co_2(CO)_8$.

The possibility of a dissociative mechanism is indicated by the observation (*90, 91*) that all eight carbonyl groups in $Co_2(CO)_8$ exchange with carbon monoxide at the same rate. The rate law for this exchange reaction is zero order in CO concentration, and the successive equilibria shown in Eqs. (5) and (6) are indicated. This type of dissociative

$$Co_2(CO)_8 \rightleftharpoons Co_2(CO)_7 + CO \tag{5}$$

$$Co_2(CO)_7 \rightleftharpoons Co_2(CO)_6 + CO \tag{6}$$

mechanism is supported by kinetic studies (*92*) of the thermal decomposition of $Co_2(CO)_8$ to $Co_4(CO)_{12}$ and CO. The rate equation for the reaction is given as

$$-d[Co_4(CO)_{12}]/dt = k[Co_2(CO)_8]^2(p_{CO})^{-4}$$

and supports a mechanism in which the rate-determining step is the dimerization of two $Co_2(CO)_6$ fragments formed from $Co_2(CO)_8$ by loss of CO. Recently, Ellgen (*93*) has reinvestigated the reaction between $Co_2(CO)_8$ and alkynes, and his kinetic data are interpreted in terms of the dissociative mechanism represented by Eqs. (7)–(9). It is assumed

$$Co_2(CO)_8 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Co_2(CO)_7 + CO \tag{7}$$

$$Co_2(CO)_7 + RC{\equiv}CR' \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Co_2(CO)_7(RC_2R') \tag{8}$$

$$Co_2(CO)_7(RC_2R') \xrightarrow{k_3} Co_2(CO)_6(RC_2R') + CO \tag{9}$$

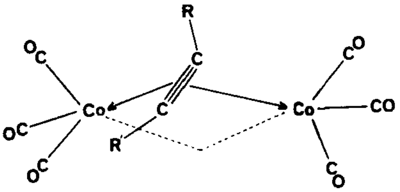
that the equilibrium between the two forms of $Co_2(CO)_8$ in solution, (II) $\rightleftharpoons$ (III), is established very rapidly and hence has no effect on the form of the rate equation. Ellgen has compared his mechanism with that advanced by Tirpak, and he points out that the two mechanisms are kinetically equivalent at constant pressure of CO and under the steady-state assumption for $[(CO)_3Co(CO)_2Co(CO)_3]$ in Eq. (2) and $[Co_2(CO)_7]$ in Eq. (7). He presents convincing evidence that his mechanism is to be preferred over the one due to Tirpak.

The inclusion in the reaction mechanism of a species $Co_2(CO)_7(RC_2R')$ is supported further by Ungvāry and Markó. These authors (*93a*) have discussed kinetic proof of the existence of $Co_2(CO)_7$(heptyne) in the reaction of $Co_2(CO)_8$ and 1-heptyne.

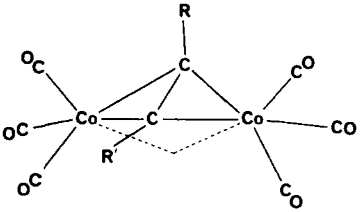
A study (*32*) of the reactions of various alkynes with $Co_2(CO)_8$ indicated there was no correlation between the rates of reaction and any electronic effect attributable to the substituents on the alkyne. This claim was disputed in a subsequent investigation (*45*). It is clear that electronic factors do have a significant effect (*30*) on the relative stabilities of the complexes $Co_2(CO)_6(RC_2R')$ and there are indications (*32*) that the size of substituents affects the rate of reaction of substituted alkynes with $Co_2(CO)_8$.

D. Structural Chemistry of $Co_2(CO)_6(RC_2R')$ Complexes

The molecular structure of each of the complexes $Co_2(CO)_6(PhC_2Ph)$ (*94*), $Co_2(CO)_6(C_6F_6)$ (*86*), $Co_2(CO)_6[(CO)_9Co_3CC_2H]$ (*28*), $Co_2(CO)_6$-$[(CO)_9CoCC{\equiv}CC_2CCo_3(CO)_9]$ (74, 75), $[Co_2(CO)_6]_3[As(C_2H)_3]$ (*81*), and $[Co_2(CO)_5(Ph_2PC_2CF_3)]_2$ (95) has been elucidated by X-ray analysis. The basic structure of each complex is derived from that of the parent carbonyl, $Co_2(CO)_8$, by replacement of the two bridging carbonyl groups with one alkyne unit (IV). The coordinated alkyne is normal to and above the Co—Co axis. If the alkyne is regarded as a bidentate ligand, there is sixfold coordination with distorted octahedral symmetry about each cobalt atom. The geometry about each ethynyl carbon atom is approximately tetrahedral and the overall geometry of the coordinated alkyne is similar to that of the cis-bent excited state of acetylene. Specific bond parameters for the above structures are summarized in Table VI.



(IVa)



(IVb)

The structural data for $Co_2(CO)_6(PhC_2Ph)$ have been used as the basis for two descriptions of the bonding in the compound (*96*). The alternative bonding schemes are represented schematically by (IVa) and (IVb). Some support for (IVa) emerged from a simple molecular orbital treatment of the bonding in the two models (*96*). In (IVa) the geometry about each cobalt atom is essentially trigonal bipyramidal so that the hybridization state of the metal is considered to be dsp^3. One of the hybrid orbitals (sp^2) is directed within the trigonal plane toward the midpoint of the coordinated $C{\equiv}C$ bond and this results in two orthogonal, localized, μ bonds from the alkyne, one to each cobalt atom. According to this description, the coordinated alkyne linkage will have approximate

TABLE VI

Structural Data on $Co_2(CO)_6$ (alkyne) Complexes

Complex	Distance (Å)				Angle(°)	References
	Co—Co	Co—CO_{av}	Co—C(alkyne)$_{av}$	C≡C	C≡C—R	
$Co_2(CO)_8$	2.52	1.80	—	—	—	*13*
$Co_2(CO)_6(PhC_2Ph)$	2.47	1.75	1.96	1.37[a]	138	*94*
$Co_2(CO)_6(C_6F_6)$	2.488(4)	1.81(2)	1.92(2)	1.36(3)	118.6(1.6) 122.6(2.0)	*86*
$Co_2(CO)_6[(CO)_9Co_3CC_2H]$	2.447(4)	1.78(2)	1.97(2)	1.34(2)	145.6(1.4)	*28*
$Co_2(CO)_6[(CO)_9Co_3CC{\equiv}CC_2CCo_3(CO)_9]$	2.461(8)	1.76(3)	1.96(3)	1.37(3)	138(2), 142(2)	*74*
$Co_2(CO)_6[(CO)_9Co_3CC{\equiv}CC_2CCo_3(CO)_9]$, $\frac{1}{2}C_6H_6$	2.469(6)	1.84(5)	2.00(4)	1.37(4)	140.2(2.8) 148.0(3.1)	*75*
$[Co_2(CO)_6]_3[As(C_2H)_3]$	2.471	—	1.96	1.32	141(1)	*81*
$[Co_2(CO)_5(Ph_2PC_2CF_3)]_2$	2.48, 2.46	—	—	1.38, 1.32	—	*95*
RC≡CR	—	—	—	1.203(2)	—	*97*

[a] Originally given as 1.46 (*94*) but later refined to 1.37 (*96*).

double-bond character as is required by the observed (*94*, *96*) carbon–carbon distance of 1.37 Å. With bonding scheme (IVb), each cobalt atom is in a d^2sp^3 hybridization state and the carbon atoms of the alkyne unit, which were initially in the hybridization state *sp*, have been rehybridized to sp^3. Clearly, this description requires the coordinated alkyne linkage to be a carbon–carbon single bond.

Recent discussions (*98–100*) of alkyne–metal bonding interactions indicate that bonding scheme (IVa) for $Co_2(CO)_6(RC_2R')$ complexes should be supplemented with a back-bonding component. The latter would result from the flow of electron density from filled *d* orbitals of cobalt into antibonding π^* orbitals of the $C{\equiv}C$ bond. It has been suggested (*100*) that this back-bonding contributes more to the stabilization of the alkyne–metal linkage than does the forward donation process. The synergic forward–back bond description requires a significant reduction in the coordinated $C{\equiv}C$ bond order.

A complete assignment of the infrared spectrum of $Co_2(CO)_6(HC_2H)$ has been made (*22*), and a peak at 1402.5 cm^{-1} was attributed to the $C{\equiv}C$ stretching frequency modified by coordination to the cobalt atoms. This peak is about 570 cm^{-1} below the $C{\equiv}C$ stretching frequency in free acetylene. A similar effect is observed with substituted acetylenes. Thus, with $MeC{\equiv}CH$, the $C{\equiv}C$ stretching frequency is lowered from 2142 to 1552 cm^{-1}, and with $MeC{\equiv}CMe$ from 2313 to 1633 cm^{-1}, upon coordination of the alkyne to the $Co_2(CO)_6$ moiety (*29*). The interpretation of these results is complicated by the fact that the coordinated $C{\equiv}C$ vibrations are coupled with other vibrations in the molecule (*101*). However, the results do indicate a considerable reduction in bond order for the coordinated alkyne and this is consistent with the bonding model discussed previously (*22*). Further spectroscopic evidence for an olefinic nature of the coordinated alkyne in $Co_2(CO)_6(RC_2R')$ complexes comes from NMR studies (*29*) which establish that the hybridization state of the ethynyl carbon atoms changes from *sp* to sp^2 upon coordination.

The proposed (*22*, *86*) similarity in the geometries of electronically excited alkynes and of coordinated alkynes in $Co_2(CO)_6(RC_2R')$ complexes has been verified (*26*) by a comparison of normal coordinate analyses of the $Co_2(HC_2H)$ part of $Co_2(CO)_6(HC_2H)$ and of the acetylene molecule in the ^1A_u excited state. This investigation (*26*) of the complex $Co_2(CO)_6(HC_2H)$ indicates that one electron is subtracted from the bonding π orbitals of $HC{\equiv}CH$ and one *d* electron is added to the antibonding π^* orbital of $HC{\equiv}CH$.

TABLE VII
$\nu_{C\equiv O}$ FOR SOME $Co_2(CO)_6(RC_2R')$ COMPLEXES

$Co_2(CO)_6(RC_2R')$, RC_2R' =	$\nu_{C\equiv O}$ (cm^{-1}), cyclohexane solution	References
HC_2H	2095m, 2053s, 2026vs, 1980vw	*25*, *37*
MeC_2H	2094m, 2054s, 2030s, 2021s, 2012m	*30*
$C_6F_5C_2H$	2098s, 2061vs, 2040vs, 2031vs, 2025sh, 1989w	*52*
CF_3C_2H	2112s, 2078vs, 2056vs, 2005w	*36*, *37*
MeC_2Me	2086s, 2045vs, 2023vs, 2011vs, 2006sh, 1978w	*68*
$Et_2NCH_2C_2CH_2NEt_2$	2088.5m, 2049.5s, 2027s, 2017s	*30*
$CH_2ClC_2CH_2Cl$	2102.5m, 2066.5s, 2045s, 2029.5m, 2021m	*30*
MeC_2CF_3	2104s, 2069vs, 2045vs, 2038vs, 2000w	*68*
$CF_3C_2CF_3$	2118s, 2084vs, 2058vs, 2020w, 2009w	*56*

Analysis of the infrared spectra of $Co_2(CO)_6(RC_2R')$ complexes in the carbonyl region shows five fundamental $C\equiv O$ stretching frequencies under high resolution (*25*); originally, only three terminal carbonyl stretching frequencies were observed (*16*, *17*, *65*). The nature of the alkyne substituents has an effect on the infrared spectra of $Co_2(CO)_6$-(RC_2R') complexes (*37*, *102*), and there is a correlation between the electronegativity of R/R′ and the carbonyl stretching frequencies. As shown in Table VII, $\nu_{C\equiv O}$ is highest for complexes in which the electronegativity of R and R′ is highest. This observation is consistent with the view that electronegative groups would increase the acceptor properties of the bridging alkyne and consequently reduce the flow-back of metal electrons into the π^* orbitals of the carbonyl groups.

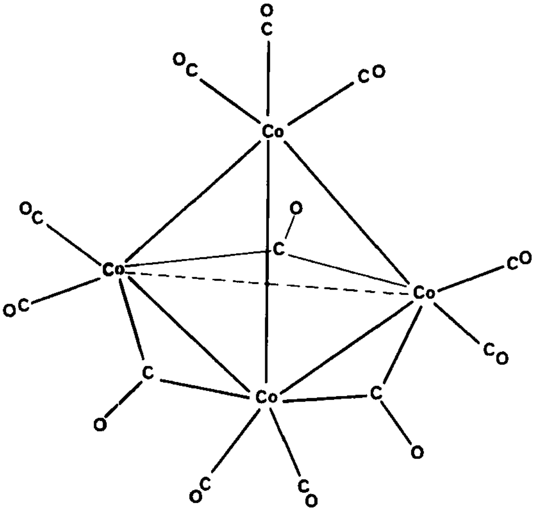
E. *Reactions Involving $Co_4(CO)_{12}$ and $RC\equiv CR'$*

Octacarbonyldicobalt decomposes readily at about 50°–60°C to give dodecacarbonyltetracobalt, and this thermal degradation reaction provides a convenient synthesis of $Co_4(CO)_{12}$ on a small scale (*103*). Larger quantities of $Co_4(CO)_{12}$ are better prepared by the reduction with hydrogen of an appropriate CoX_2 compound (e.g., X = 2-ethylhexanoate or acetylacetonate) in the presence of $Co_2(CO)_8$ [Eq. (10)] (*104*, *105*).

$$3Co_2(CO)_8 + 2CoX_2 + 2H_2 \longrightarrow 2Co_4(CO)_{12} + 4HX \tag{10}$$

Dodecacarbonyltetracobalt is a black, crystalline solid which sublimes at 90°C/1 mm with some decomposition to cobalt and carbon monoxide. It is sparingly soluble in organic solvents. $Co_4(CO)_{12}$ decomposes in air to the purple cobalt(II) oxide or carbonate but the rate of decomposition is much slower than that of $Co_2(CO)_8$.

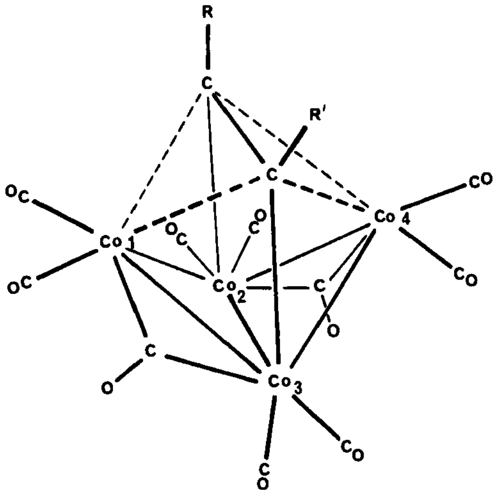
A representation of the solid-state structure of dodecacarbonyltetracobalt (*106*, *107*) is given in (V). In solution, the ratio of the intensities of the two ^{59}Co resonances in the NMR spectrum (*108*, *109*) of $Co_4(CO)_{12}$ is about 3:1. This implies that the crystal structure is retained in solution at room temperature. The infrared spectrum of $Co_4(CO)_{12}$ has generated considerable discussion (*110–115*); recently, Cotton *et al.* (*115a*) have provided spectroscopic evidence of the scrambling of CO groups in $Co_4(CO)_{12}$.



(V)

Dodecacarbonyltetracobalt reacts with alkynes at 20°–100°C to give complexes of stoichiometry $Co_4(CO)_{10}(RC_2R')$, [Eq. (11)] (*31*, *48*, *116*). μ-Alkyne-dicobalt complexes of formula $Co_2(CO)_6(RCR')$ can also be formed in this reaction and it has been established (*31*) that the mole ratio of reactants, the reaction time, and the temperature are all capable of drastically affecting the product distribution. The additional reactions summarized in Eqs. (12)–(18) have given $Co_4(CO)_{10}(RC_2R')$ complexes, but the yields are generally low. The known complexes of formula $Co_4(CO)_{10}(RC_2R')$ are listed in Table VIII.

$$Co_4(CO)_{12} + RC{\equiv}CR' \longrightarrow Co_4(CO)_{10}(RC_2R') + 2CO \qquad (11)$$



(VI)

An X-ray crystallographic investigation (*116*) of $Co_4(CO)_{10}(EtC_2Et)$ has revealed the structure shown in (VI). The structure is derived from that of the parent carbonyl, $Co_4(CO)_{12}$, by substitution of two bridging carbonyl groups with an alkyne unit coupled with a substantial modification of the Co_4 skeleton. The structure is different from that first postulated for $Co_4(CO)_{10}(RC_2R')$ complexes, where it was assumed that the basic tetrahedron of cobalt atoms remained intact (*48*, *117*).

$Co_2(CO)_6(RC_2R') + RC{\equiv}CR' \longrightarrow Co_4(CO)_{10}(RC_2R')$ (*48*) (12)

$Co_2(CO)_6(PhC_2Ph) + Fe(CO)_5 \longrightarrow Co_4(CO)_{10}(PhC_2Ph)$ (*117*) (13)

$Co_2(CO)_6(PhC_2H) + HCo(CO)_4 \longrightarrow Co_4(CO)_{10}(PhC_2H)$ (*31*) (14)

$Hg[Co(CO)_4]_2 + RC{\equiv}CR' \longrightarrow Co_4(CO)_{10}(RC_2R')$ (*21, 48, 84*) (15)

$2Co_3(CO)_6(\pi\text{-arene})CR \longrightarrow$
$Co_4(CO)_{10}(RC_2R) + 2\ \text{arene} + 2Co + 2CO$ (*118*) (16)

$Co_3(CO)_9CY + CF_3C{\equiv}CH \longrightarrow Co_4(CO)_{10}(CF_3C_2H)$ (*31*) (17)

$Co_2(CO)_8 + C_6F_5MgBr \longrightarrow Co_4(CO)_{10}(C_6F_4)$ (*119*) (18)

The alkyne fragment in $Co_4(CO)_{10}(RC_2R')$ complexes forms σ bonds with two cobalt atoms, and the resulting "olefinic" group forms a bent four-centered, μ-type bond with the remaining two cobalt atoms. The carbon–carbon distance for the coordinated $C{\equiv}C$ bond is 1.44 Å and this

TABLE VIII
KNOWN COMPLEXES OF FORMULA $Co_4(CO)_{10}(RC_2R')$

R	R′	Color, m.p. (°C)	References concerning		
			Preparation	IR	NMR
H	H	—	*21, 48*	*21, 48*	—
Me	H	Blue-black, 169 (dec.)	*31*	*31*	—
CF_3	H	Blue-black, ~200 (dec.)	*31*	*31*	*31*
Ph	H	Blue-black	*31, 48, 120*	*31*	*31*
C_6F_5	H	Blue-black	*31*	*31*	—
tert-Bu	H	—	*48*	—	—
Me_3Si	H	—	*48*	*48*	—
Me	Me	Black, 185 (dec.)	*31*	*31*	*31*
CD_3	CD_3	Blue	*118*	—	—
CF_3	CF_3	Black, 250	*31*	*31*	*31*
Me	CF_3	Blue	*68*	*68*	*68*
Et	Et	Violet, ~160	*48*	*48*	—
Ph	Ph	Blue-black, ~167	*48, 117, 118*	*48, 117*	—
Ph	C_6F_5	Blue-black, 125 (dec.)	*31*	*31*	*31*
Ph	CO_2Me	Blue	*48*	*48*	—
Ph	$SiMe_3$	—	*48*	—	—
C_6F_4 = tetrafluorobenzyne		Dark green	*119*	*119*	—

is typical of coordinated olefins. The bond length is longer than the mean value of 1.35 Å for the coordinated C≡C bond in $Co_2(CO)_6(RC_2R')$ complexes where the alkyne interacts with two metal atoms only.

The infrared spectra of $Co_4(CO)_{10}(RC_2R')$ complexes show absorptions due to bridging and terminal carbonyl groups. The number of carbonyl bands observed seems to be dependent on the symmetry of the alkyne (*31*). The fluorine NMR spectrum of $Co_4(CO)_{10}(CF_3C_2CF_3)$ indicates that the two trifluoromethyl groups are not equivalent. This possibly indicates that the structure is distorted, or that the coordinated alkyne is displaying a trans-bent or gauche configuration (*31*).

F. Chemical Behavior of $Co_2(CO)_6(RC_2R')$ and $Co_4(CO)_{10}(RC_2R')$ Compounds

1. Reactions with Carbon Monoxide

Studies of the kinetics of the exchange of carbon monoxide with the terminal carbonyl groups of $Co_2(CO)_6(PhC_2Ph)$ have been reported (*90, 121*). All six carbonyl groups of $Co_2(CO)_6(PhC_2Ph)$ exchange at the same rate, which is slow compared to that for complexes which contain bridging carbonyl groups such as $Co_2(CO)_8$ and the lactone complex $Co_2(CO)_9(n\text{-}PrC_2H)$. Consequently, it is reasonable to conclude that at least one bridging carbonyl group is required for rapid carbon monoxide exchange.

The rate of exchange of carbon monoxide with several other $Co_2(CO)_6(RC_2R')$ complexes in hexane has been investigated (*102*). The results indicate again that all six terminal carbonyl groups are kinetically equivalent and that carbon monoxide–carbonyl exchange is first-order-dependent on the metal carbonyl concentration but independent of carbon monoxide concentration. It was observed also that there is a regular variation of the rate constant with changes in the electronegativity of the alkyne substituents R and R′. The rate of exchange of carbon monoxide decreases as the electronegativity of R and R′ is increased. Thus, the rate-determining step is not dissociation of a carbonyl group from the metal; instead, it is probably a loosening of the alkyne–cobalt bond to give an activated complex. Consequently, the overall rate of carbon monoxide–carbonyl exchange in $Co_2(CO)_6(RC_2R')$ complexes is thought to be dependent on the strength of the alkyne–cobalt bond.

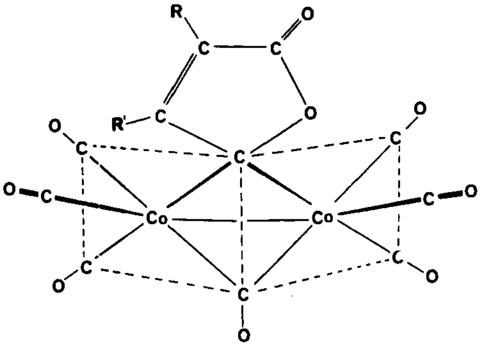
Under more severe conditions of temperature and pressure, the complexes $Co_2(CO)_6(RC_2R')$ react with carbon monoxide according to Eq. (19) to give lactone derivatives (*19*, *24*). Lactone complexes have been

$$Co_2(CO)_6(RC_2R') + 3CO \longrightarrow Co_2(CO)_9(RC_2R') \qquad (19)$$

formed at 70°C and ~200 atmospheres CO pressure from $Co_2(CO)_6(HC_2H)$ (*19*, *24*, *25*), $Co_2(CO)_6(n\text{-}PrC_2H)$ (*19*, *25*), and $Co_2(CO)_6(MeC_2Me)$ (*19*, *25*). Under similar conditions, $Co_2(CO)_6(CF_3C_2CF_3)$ (*56*), $Co_2(CO)_6(MeC_2CF_3)$ (*121a*), and $Co_2(CO)_6(C_6F_5C_2C_6F_5)$ (*64*) failed to give lactone complexes. Presumably, the reaction is influenced by the nature of the alkyne substituents R and R′.

Two crystalline forms of $Co_2(CO)_9(HC_2H)$ have been identified. One form is triclinic with a Co—Co separation of 2.46 Å and the other is orthorhombic with a Co—Co separation of 2.43 Å (*122*, *123*). The crystal structure of the triclinic form only has been published (*124*, *124a*). A representation of the molecular structure of this complex is given in (VII); it shows how the acetylene moiety is incorporated into a lactone ring.

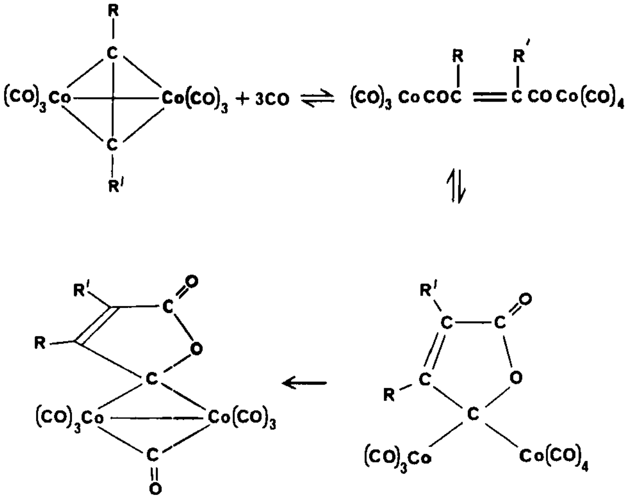
A mechanism for the formation of lactone complexes from $Co_2(CO)_6(RC_2R')$ has been proposed (Scheme 1) (*58*); it is based on studies of the



(VII)

reactions of alkynes with acyl-carbonylcobalt complexes. The mechanism involves carbon monoxide insertion between the acetylenic carbons and the cobalt atoms of $Co_2(CO)_6(RC_2R')$.

Few chemical reactions of lactone-carbonylcobalt complexes have been reported. Hydrogenation (*24*) of butenolactone-heptacarbonyldicobalt, $Co_2(CO)_9(HC_2H)$, gives γ-butyrolactone, butyric acid, and dodecacarbonyltetracobalt. Treatment of the same lactone complex with sulfuric acid in warm acetone (*50*, *125*) gives a cobalt cluster compound of formula $Co_3(CO)_9CCH{=}CHCOOH$. The use of methyl alcohol in place of acetone in the latter reaction yields $Co_3(CO)_9CCH{=}CHCOOMe$.



Scheme 1

It has been suggested (*126*) that cluster complexes such as these could be intermediates in the formation of dimethyl succinate from HC$\equiv$CH, CO, and $Co_2(CO)_8$ in methyl alcohol.

Some complexes of formula $Co_4(CO)_{10}(RC_2R')$ have been converted to the related complexes $Co_2(CO)_6(RC_2R')$ by reaction with carbon monoxide (*43*).

2. *Reactions with Organophosphines and Related Compounds*

As indicated in Eq. (20) (*22*, *31*, *36*, *48*, *89*), one or two carbonyl groups in $Co_2(CO)_6(RC_2R')$ complexes can be replaced by triphenylphosphine to give derivatives of formula $Co_2(CO)_{6-n}(PPh_3)_n(RC_2R')$, $n = 1$ or 2. Other methods used to obtain phosphine derivatives of this type are summarized in Eq. (21) (*31*, *48*) and (22) (*23*), and the known complexes are listed in Table IX.

$$Co_2(CO)_6(RC_2R') + nPPh_3 \longrightarrow Co_2(CO)_{6-n}(PPh_3)_n(RC_2R') \tag{20}$$

$$Co_4(CO)_{10}(RC_2R') + 2PPh_3 \longrightarrow Co_2(CO)_4(PPh_3)_2(RC_2R') \tag{21}$$

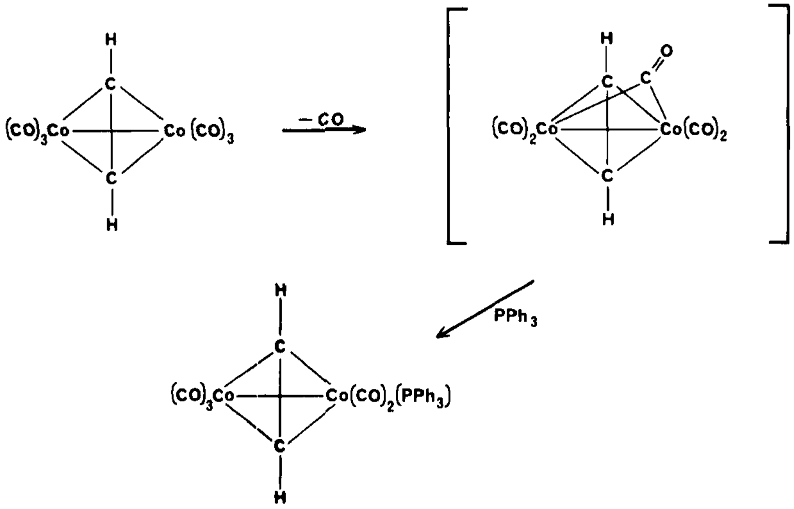
$$HCo(CO)_4 + HC{\equiv}CH + nPPh_3 \longrightarrow Co_2(CO)_{6-n}(PPh_3)_n(HC_2H) \tag{22}$$

The kinetics of the reaction of triphenylphosphine with the μ-alkyne complexes $Co_2(CO)_6(HC_2H)$ and $Co_2(CO)_6(EtC_2Et)$ have been investigated (*89*, *90*). Only monophosphine derivatives were formed below 60°C. In toluene, the reaction is first order and appears to involve a dissociation to a bridging carbonyl species as the first and rate-deter-

TABLE IX

KNOWN COMPLEXES OF FORMULA $Co_2(CO)_{6-n}(PPh_3)_n(RC_2R')$

RC$\equiv$CR'	n	Color, m.p. (°C)	References concerning Preparation	IR	NMR
HC$\equiv$CH	1	Violet, 130	*22*, *23*, *89*	*22*, *23*	*22*, *23*
HC$\equiv$CH	2	Red-brown, 207–208 (dec.)	*23*, *89*	*89*	—
CF$_3$C$\equiv$CH	2	Dark red, 211–213	*36*	*36*	*36*
MeC$\equiv$CCF$_3$	2	Purple-red, 185 (dec.)	*68*	*68*	*68*
CF$_3$$\equiv$CCF$_3$	2	Dark red, 180–183	*121a*	*121a*	*121a*
C$_6$F$_5$C$\equiv$CH	2	Purple, 197–198 (dec.)	*31*	*31*	*31*
PhC$\equiv$CPh	1	Red-violet, 150–155	*48*	*48*	—
PhC$\equiv$CPh	2	Red-violet, 143–145	*48*	*48*	—
C$_6$F$_5$C$\equiv$CC$_6$F$_5$	2	Purple, 164–165 (dec.)	*31*	*31*	*31*

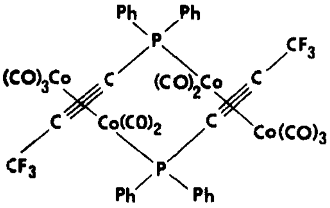


Scheme 2

mining step. The subsequent attack of triphenylphosphine on the bridging carbonyl species is presumably (*89*, *121*) a fast reaction. The proposed mechanism is summarized in Scheme 2.

Unusual phosphinoalkyne-pentacarbonyldicobalt complexes of formula $[Co_2(CO)_5(Ph_2PC_2R)]_2$, R = H, Me, CF_3, or *tert*-Bu, have been prepared recently (*95*). Related arsino complexes are known also. The structure of $[Co_2(CO)_5(Ph_2PC_2CF_3)]_2$ has been determined by X-ray crystallography (*95*), and the molecular structure (VIII) shows that the phosphinoalkyne is combining the coordinating powers of an alkyne and a phosphine. Phosphite ligands displace two carbonyl groups from $[Co_2(CO)_5(Ph_2PC_2R)]_2$ complexes to give the derivatives $[Co_2(CO)_4L(Ph_2PC_2R)]_2$, L = $(MeO)_3P$ or $(PhO)_3P$; phosphite substitution is believed to occur at the two $-Co(CO)_3$ groups (*95*).

Complexes of formula $Co_2(CO)_4L(PhC_2H)$ have been isolated (*51*)



(VIII)

from reactions of $Co_2(CO)_6(PhC_2H)$ with the bidentate ligands 1,2-bis(diphenylphosphino)tetrafluorocyclobutene and 1,2-bis(dimethylarsino)tetrafluorocyclobutene. The arsino ligand can exhibit monodentate behavior also and it then gives a complex of formula $Co_2(CO)_5L(PhC_2H)$.

At ~70°C, $Co_4(CO)_{10}(RC_2R')$ complexes react with triphenylphosphine to give the phosphine-dicobalt derivatives $Co_2(CO)_4(PPh_3)_2(RC_2R')$ and $Co_2(CO)_6(PPh_3)_2$ plus other amorphous products (*31*, *48*). $Co_4(CO)_{10}(PhC_2H)$ gives a paramagnetic cluster compound of formula $Co_3(CO)_7(PPh_3)_2 \cdot 2C_6H_6$ when it is treated with triphenylphosphine in benzene (*31*). $Co_4(CO)_8(PPh_3)_2(HC_2H)$ has been prepared from the reaction of $Co_4(CO)_{12}$ with $HC{\equiv}CH$ in the presence of triphenylphosphine (*23*).

3. *Exchange Reactions with Alkynes*

μ-Alkyne-hexacarbonyldicobalt complexes undergo facile exchange reactions with alkynes at ambient temperature (*30*, *48*, *73*). The exchange reaction Eq. (23) favors the formation of $Co_2(CO)_6(R''C_2R''')$ if the

$$Co_2(CO)_6(RC_2R') + R''C{\equiv}CR''' \rightleftharpoons Co_2(CO)_6(R''C_2R''') + RC{\equiv}CR' \qquad (23)$$

substituents R″ and R‴ are more electronegative than R and R′. Thus, the following order of ligand displacement has been established (*30*):

$$(CF_3)_2 > (COOMe)_2 > Ph_2 > Me, Ph > Me_2 > H, Ph = H, Me > H_2 > (CH_2NEt_2)_2$$

The increased stabilization of $Co_2(CO)_6(R''C_2R''')$ complexes with more electronegative alkyne substituents is associated with the strengthening of the alkyne–cobalt bond due to increased back-donation of the electrons from cobalt d orbitals to the π^* orbitals of the alkyne derivative.

4. *Formation and Reactions of $Co_3(CO)_9CCH_2R$ Complexes*

μ-Alkyne-hexacarbonyldicobalt complexes incorporating terminal alkynes are known to react with mineral acids in refluxing methanol to give complexes (*18*, *118*, *127*) of formula $Co_3(CO)_9CCH_2R$. The same complexes are formed from the direct reaction of $Co_2(CO)_8$ (*33–36*) or $Co_4(CO)_{12}$ (*31*) with terminal alkynes. In these latter reactions, it is probable that $Co_2(CO)_6(RC_2H)$ complexes are formed initially [Eq. (24a)] and that there is subsequent reaction with excess alkyne acting as an acid

[Eq. (24b)] (*128*). The formation of $Co_3(CO)_9CCH_2Ph$ from $Co_2(CO)_8$ and $PhC{\equiv}CCOOH$ (*129*) presumably follows a similar reaction pathway.

$$Co_2(CO)_8 + RC{\equiv}CH \longrightarrow Co_2(CO)_6(RC_2H) \qquad (24a)$$

$$Co_2(CO)_6(RC_2H) + H^+ \longrightarrow Co_3(CO)_9CCH_2R \qquad (24b)$$

An early proposal that the mechanism of these reactions involves the species $HCo(CO)_4$ seems to be discounted by the observation (*31*) that $Co_3(CO)_9CCH_2Ph$ is not a product of the direct reaction of $Co_2(CO)_6(PhC_2H)$ and $HCo(CO)_4$. The reaction between $Co_2(CO)_8$ and $CF_3C{\equiv}CH$ gives the expected product $Co_3(CO)_9CCH_2CF_3$ but a small amount of $Co_3(CO)_9CCH{=}CF_2$ is formed also (*121a*). The latter complex is presumably formed from $Co_3(CO)_9CCH_2CF_3$ by the elimination of HF.

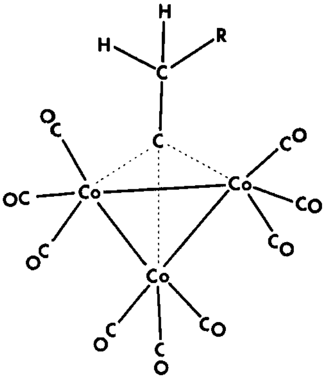
Complexes of formula $Co_3(CO)_9Y$ have also been isolated from several reactions that do not involve alkynes. A recent review (*125*) discusses in some detail these alternative preparations of the complexes and consequently they will not be reconsidered here.

The known complexes of formula $Co_3(CO)_9CCH_2R$ that have been prepared from reactions involving alkynes are listed in Table X. The

TABLE X
COMPLEXES OF FORMULA $Co_3(CO)_9CCH_2R$

R	Color, m.p. (°C)	References concerning			
		Preparation	IR	NMR	UV
H	Dark purple, 185 (dec)	*18, 127, 128*	*18, 128, 132*	*18, 128, 132, 133*	*128*
Me	—	*39, 129, 132*	*39, 132*	*39, 132*	—
CF_3	Red-black	*33, 36*	*34, 36, 128*	*34, 128*[a]	—
(MeO)OC	Dark violet, 55–56	*43*	—	—	—
Et	—	*39*	*39*	*39*	—
$HO(CH_2)_2$	Dark violet, 90 (dec.)	*43*	—	—	—
n-Pr	—	*18*	—	—	—
i-Pr	—	*39*	*39*	*39*	—
Ph_2CH	—	*39*	*39*	*39*	—
tert-Bu	Dark violet, 122–123	*43*	—	—	—
Ph	Dark violet, 68	*31, 128, 129*	*128*	*128*	*128*
p-BrC_6H_4	Dark violet, 110–114 (dec.)	*43*	—	—	—
C_6F_5	Dark red, 88–89.5	*52*	*52*	*52*	*52*
$Co_3(CO)_9CCD_3$	—	*118*	—	—	—

[a] Mass spectrum (*37*).



(IX)

complex $Co_3(CO)_9CCH_3$ is diamagnetic and possesses a dipole moment of ~1.6 D (*18*). On the basis of these physical data and the chemical decomposition reactions (*43*, *129*) of several $Co_3(CO)_9CCH_2R$ complexes, a structure was proposed in which one carbon atom is σ-bonded to three cobalt atoms (IX). The structure was confirmed by X-ray analysis (*130*) for the complex with R = H.

The decomposition with halogens of $Co_3(CO)_9CCH_2R$ complexes provides a useful synthesis of substituted 1,1,1-trihalogenoalkanes (*43*, *129*) [Eq. (25)]. Dimethyl malonate has been formed (*127*) in high yield

$$2Co_3(CO)_9CCH_2R + 9X_2 \longrightarrow 2RCH_2CX_3 + 6CoX_2 + 18CO \qquad (25)$$

from $Co_3(CO)_9CMe$ by a novel carbonylation reaction using methanol at 70°C [Eq. (26)]. This latter reaction may help in the development of a

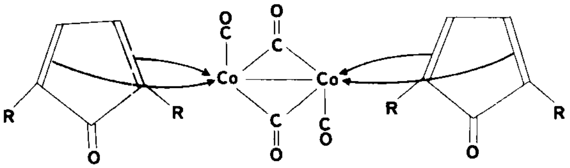
$$Co_3(CO)_9CMe + MeOH \longrightarrow MeCH(COOMe)_2 + Co_2O_3 \qquad (26)$$

better understanding of the mechanism of the catalytic carbonylation (*126*, *131*) of acetylene using $Co_2(CO)_8$ and alcohols; apparently, the complex $Co_3(CO)_9CMe$ was isolated from one of these carbonylation systems (*131*).

The reaction of both fluorocarbon and hydrocarbon alkynes with the complexes $Co_3(CO)_9CCH_3$, $Co_3(CO)_9CC_6H_5$, and $Co_3(CO)_9CCO_2Me$ has been investigated (*31*). The products obtained include substituted benzenes and organocobalt complexes of formula $Co_2(CO)_6$(alkyne) and $Co_2(CO)_4$(alkyne)$_3$. Treatment of some complexes $Co_3(CO)_9CR$ with OH^- in R'OH followed by the addition of HX produces $Co_4(CO)_{10}$-(RC_2R) in 15% yield (*131a*).

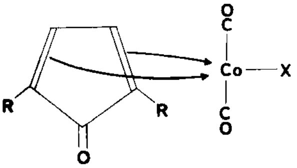
5. *Formation and Behavior of the Complexes $Co_2(CO)_6(RC_2R')_4$ and $Co_2(CO)_4(RC_2R')_3$*

a. *Formation.* μ-Alkyne-hexacarbonyldicobalt complexes can react with excess alkyne to give organometallic complexes of formula $Co_2(CO)_6(RC_2R')_4$ or $Co_2(CO)_4(RC_2R')_3$ as well as organic products such as cyclopentadienones, benzenes, and polymers. It seems that the nature of the products formed is determined by the alkyne substituents. Thus, complexes of formula $Co_2(CO)_4(RC_2R')_3$ are generally formed in reactions that involve electronegative substituents such as $—CO_2R$ or $—CF_3$, but complexes of formula $Co_2(CO)_6(RC_2R')_4$ are formed in addition to $Co_2(CO)_4(RC_2R')_3$ when the substituent R = H and R' is one of the bulky groups *tert*-Bu (*47*, *48*), Ph (*48*), or Me_3Si (*48*).



(X)

The infrared spectra and the products of chemical degradation (*48*) indicate that the complexes $Co_2(CO)_6(RC_2R')_4$ incorporate cyclopentadienone ligands. The suggested structure is shown in (X). The cyclopentadienone group has been cleaved from $Co_2(CO)_6(\textit{tert}\text{-}BuC_2H)_4$ by treatment with $FeCl_3$ in refluxing acetone. Treatment of $Co_2(CO)_6(\textit{tert}\text{-}BuC_2H)_4$ with halogens gives new cyclopentadienone complexes of formula $Co(CO)_2X[(\textit{tert}\text{-}BuC_2H)_2CO]$ (XI); the free cyclopentadienone is not released. It is interesting to note that $Co_2(CO)_6(\textit{tert}\text{-}BuC_2H)_4$ reacts with further amounts of *tert*-BuC≡CH to form 1,2,4-tris(*tert*-butyl)benzene (*43*).

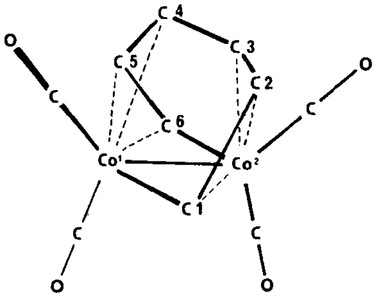


(XI)

Formation of the complexes $Co_2(CO)_4(RC_2R')_3$ from $Co_2(CO)_6(RC_2R')$ and excess alkyne (*47*, *48*, *63*, *68*, *128*, *134*, *135*) generally occurs in the temperature range 100°–160°C. The trisalkyne complex can be formed under comparable conditions from the direct reaction of alkynes with $Co_2(CO)_8$ (*33–36, 128*) or $Hg[Co(CO)_4]_2$ (*41, 48*) and also from reactions between alkynes and $Co_4(CO)_{12}$ (*48*) or $Co_4(CO)_{10}(RC_2R')$ (*48*). In general, the formation of $Co_2(CO)_4(RC_2R')_3$ complexes occurs at a somewhat lower temperature in the reactions involving tetracobalt species. It is possible also to form trisalkyne complexes that incorporate two different alkyne units. This can be achieved (*43, 68, 128, 134, 135*), for instance, by treating $Co_2(CO)_6(RC_2R')$ with a different alkyne $R''C{\equiv}CR'''$. The known complexes of formula $Co_2(CO)_4(RC_2R')_3$ and $Co_2(CO)_4(RC_2R')(R''C_2R''')_2$ are listed in Table XI. These complexes are generally dark violet to purple in color. They are volatile and are very soluble in organic solvents. The complexes are stable to chemical degradation, even by sulfuric acid in refluxing methanol.

b. *Structure of* $Co_2(CO)_4(RC_2R')_3$ *Complexes.* Treatment of $Co_2(CO)_6(HC_2H)$ with *tert*-$BuC{\equiv}CH$ gives the complex $Co_2(CO)_4(HC_2H)($*tert*-$BuC_2H)_2$ (*43, 137*). Initially, the complex was thought to contain a metalocycloheptatriene ring system, but X-ray analysis (*136*) of the solid reveals a molecular structure in which a six carbon atom unit bridges the two cobalt atoms (XII). This unusual six carbon atom bridging group is formed by the oligomerization of the three alkyne molecules and it has been described (*136*) by the colloquial term "fly-over bridge." A brief report (*138*) of the structure of $Co_2(CO)_4(PhC_2CO_2Me)_3$ and a detailed description (*139*) of the crystal and molecular structure of $Co_2(CO)_4(CF_3C_2H)_3$ indicate that each of these complexes incorporates a similar bridging arrangement.

The bridging group in $Co_2(CO)_4(RC_2R')_3$ complexes is composed of



(XII)

TABLE XI

KNOWN TRIS(ALKYNE)-TETRACARBONYLDICOBALT COMPLEXES

(*a*) $Co_2(CO)_4(RC_2R')_3$

			References concerning		
R	R′	Color, m.p. (°C)	Preparation	IR	NMR
H	CF_3	Purple, 121–122	*31, 33, 35, 36*	*35, 36*	*35, 36*[a]
H	*n*-Pr	—	*17*	—	—
H	*tert*-Bu[b]	Deep violet, 81	*47, 48*	*47, 48*	*136*[c]
H	$SiMe_3$	Red-violet	*48*	—	—
CF_3	CF_3	Purple, $\sim$150	*31, 34, 128*	*34, 128*	*34, 128*[d]
CO_2Me	CO_2Me	Blue-violet, $\sim$160 (dec.)	*48*	*48*	—
Ph	Ph	Red-violet, $\sim$185(dec.)	*48*	*48*	—
Ph	Me	Red-violet	*48*	—	—
Ph	CO_2Me	Red-violet, $\sim$200 (dec.)	*48*	*48*	—
Ph	CO_2Et	Dark violet $\sim$125 (dec.)	*48*	*48*	—

(*b*) $Co_2(CO)_4(RC_2R')(R''C_2R''')_2$

R	R′	R″	R‴	Color, m.p. (°C)	Preparation	IR	NMR
H	H	*tert*-Bu	H	Dark violet, 93–97 (dec.)	*43, 137*	—	*136*
CF_3	H	CF_3	CF_3	Purple	*134*	*134*	*134*
CF_3	CF_3	CF_3	H	Purple[e]	*128, 134*	*128, 134*	*128, 134*
CF_3	Me	CF_3	H	Purple	*68*	*68*	*68*
CF_3	Me	CF_3	CF_3	Purple	*68*	*68*	*68*
Me	Me	CF_3	H	Purple	*135*	*135*	*135*

[a] UV spectrum (*128*); mass spectrum (*37*).

[b] Monophosphine derivative prepared also.

[c] Dipole moment (*43*).

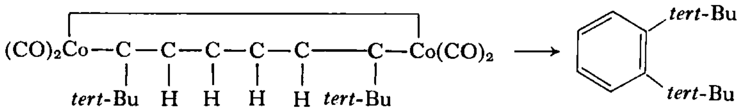
[d] UV spectrum (*128*).

[e] Two isomers isolated; isomer 1, m.p. 122°C (*128, 134*); isomer 2, m.p. 120°–121°C (*134*).

two allyl groups C-1–C-2–C-3 and C-4–C-5–C-6 which are joined by a single bond between C-3 and C-4. The allyl groups are each bonded to both cobalt atoms. The metal–ligand geometry indicates there are σ bonds between Co-1 and C-1 and between Co-2 and C-6 and π bonds between Co-1 and the allyl group C-4, C-5, C-6 and between Co-2 and the other allyl group C-1, C-2, C-3. A very symmetrical arrangement of atoms within the Co-1, C-1, C-6, Co-2 plane has been noted (*139*) for the complex $Co_2(CO)_4(CF_3C_2H)_3$. The two cobalt atoms in all three complexes are separated by a normal metal–metal bond distance. The nonbonded carbon atoms C-1 and C-6 are separated by 3.2 Å in $Co_2(CO)_4(HC_2H)$(*tert*-$BuC_2H)_2$ and by 3.05 Å in $Co_2(CO)_4(CF_3C_2H)_3$. The structure of $Co_2(CO)_4(HC_2H)$(*tert*-$BuC_2H)_2$ indicates the *tert*-butyl substituents are attached to carbon atoms C-1 and C-6. The trifluoromethyl groups in $Co_2(CO)_4(CF_3C_2H)_3$ are linked to C-1, C-3, and C-6.

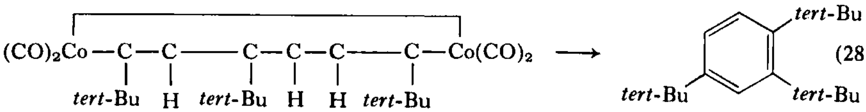
The nature of the bridging group in these complexes permits the existence of chiral forms, and these have been recognized (*139*) in the crystal structure of $Co_2(CO)_4(CF_3C_2H)_3$. Attempts to separate the chiral forms have failed (*121a*).

c. *Reactions of* $Co_2(CO)_4(RC_2R')_3$ *Complexes*. There are several reports describing the formation of substituted benzenes by the chemical or thermal degradation of $Co_2(CO)_4(RC_2R')_3$ complexes. The expected relationship between the arrangement of the substituents in the complexes and the benzenes has been confirmed in several instances. Thus, the bulky *tert*-butyl groups in $Co_2(CO)_4(HC_2H)$(*tert*-$BuC_2H)_2$ are known to be attached to C-1 and C-6 in the bridging group (XII), and *ortho*-bis(*tert*-butyl)benzene is formed (*43*) when the complex is degraded with bromine in carbon tetrachloride [Eq. (27)]. A similar observation



(27)

relates to the complex $Co_2(CO)_4$(*tert*-$BuC_2H)_3$ which can be chemically and thermally degraded to 1,2,4-tris(*tert*-butyl)benzene [Eq. (28)].



(28)

Comparison of the NMR spectra (*136*) of $Co_2(CO)_4$(*tert*-$BuC_2H)_3$ and $Co_2(CO)_4(HC_2H)$(*tert*-$BuC_2H)_2$ indicates that the former complex probably has *tert*-butyl groups on C-1, C-3, and C-6 of the bridging group (XII). Thermal degradation of the complex $Co_2(CO)_4(CF_3C_2H)_3$ gives 1,2,4-tris(trifluoromethyl)benzene (*121a*) and again the substituent arrangement in the benzene is closely related to that in the complex. These results are all consistent with the proposition that the benzene compounds are formed from the trisalkyne-dicobalt complexes by rupture of the two Co—C σ bonds and subsequent formation of a bond between C-1 and C-6.

Decomposition with bromine of the complexes $Co_2(CO)_4(PhC_2R)_3$ (R = Me, CO_2Me, or CO_2Et) gives 1,3,5-trisubstituted 2,4,6-triphenylbenzenes. The crystal structure of $Co_2(CO)_4(PhC_2CO_2Me)_3$ has been determined (*138*) but the substituent arrangement was not mentioned in the brief report of this structure. To be consistent with the above proposal, the complex presumably contains a 1,3,5-substituent arrangement in the bridging group.

There are a number of reports of the formation of substituted benzenes as well as trisalkyne-dicobalt complexes in the direct reaction of alkynes with $Co_2(CO)_8$ or $Co_2(CO)_6(RC_2R')$. This occurs, for example, in the reaction between $Co_2(CO)_8$ and $CF_3C{\equiv}CCF_3$ (*128*) at 155°C and in the reaction of $Co_2(CO)_6(CF_3C_2CF_3)$ with $CF_3C{\equiv}CH$ (*134*) at ~100°C. It seems reasonable to conclude that the benzene is formed in these reactions by thermal degradation of the complexes $Co_2(CO)_4(CF_3C_2CF_3)_3$ and $Co_2(CO)_4(CF_3C_2CF_3)(CF_3C_2H)_2$.

Extensive studies (*135*) of the formation of $Co_2(CO)_4(RC_2R')_3$ and $Co_2(CO)_4(RC_2R')(R''C_2R''')_2$ complexes from fluorocarbon alkynes have revealed two principal factors that affect the stability of these complexes towards decomposition to substituted benzenes. Thus, stable complexes are isolated only when (1) at least two CF_3 groups are incorporated as substituents in the bridging group, and (2) CF_3 substituents are attached to C-1 and C-6 of the bridging group.

There are few reports of other types of reactions involving $Co_2(CO)_4(RC_2R')_3$ complexes. Treatment of the complex $Co_2(CO)_4$(*tert*-$BuC_2H)_3$ with triphenylphosphine gives the monosubstituted derivative $Co_2(CO)_3(PPh_3)$(*tert*-$BuC_2H)_3$ (*48*), and reduction of $Co_2(CO)_4(RC_2R')_3$ complexes with $LiAlH_4$ gives aliphatic hydrocarbons (*47*).

6. *Chemical Modification of the Coordinated Alkyne in $Co_2(CO)_6(RC_2R')$ Complexes*

The substituents R and R' of the coordinated alkyne in $Co_2(CO)_6(RC_2R')$ complexes can undergo chemical reaction with retention of the alkyne–cobalt bond. For example, when the butynediol complexes

$Co_2(CO)_6[R'RC(OH)C_2C(OH)RR']$ are heated with acidic methanol, complexes of formula $Co_2(CO)_6(R'RCHC_2CHRR')$ are obtained. In a similar reaction using $Co_2(CO)_6(PhC_2Ph)$ in place of the butynediol complex, the alkyne–cobalt bond is destroyed and 1,1,4,4-tetraphenyl-1,3-butadiene is isolated (*39*). Nicholas and Pettit (*140*) have converted $Co_2(CO)_6[CH_2{=}C(Me)C_2CH_2CH(OH)Me]$ to $Co_2(CO)_6[(HO)(Me)_2CC_2CH_2CH(OH)Me]$ by reaction with HBF_4 in acetone followed by treatment with water. The same authors have reported (*41a*) several acid-catalyzed dehydration reactions involving *tert*-propargyl alcohol–cobalt carbonyl complexes.

Electrophilic substitution reactions of π-bonded organic ligands in transition metal complexes are well known. $Co_2(CO)_6(PhC_2Ph)$ undergoes a facile Friedel-Crafts acylation (*66*) to yield $Co_2(CO)_6(p\text{-}RC_6H_4C_2C_6H_5)$ and $Co_2(CO)_6(p\text{-}RC_6H_4C_2C_6H_4R\text{-}p)$. Release of the modified alkyne ligand from these complexes is accomplished easily with ceric ammonium nitrate in acetone. This is an important reaction sequence because acylation of free diphenylacetylene cannot be accomplished directly.

Complexes of stoichiometry $Co_2(CO)_6(RC_2SiMe_3)$ can be treated with base to form the terminal alkyne complexes $Co_2(CO)_6(RC_2H)$ (*69*) and treatment of the complexes $Co_2(CO)_6(RC_2SnMe_3)$ (R = H or *tert*-Bu), with MeCOCl and $AlCl_3$ gives $Co_2(CO)_6(RC_2COMe)$ (*42*).

A novel substituent modification reaction involves the use of the $Co_2(CO)_6$ moiety as an alkyne-protecting group. To induce carbon–carbon double bonds to undergo addition reactions selectively in the presence of carbon–carbon triple bonds, the triple bond can be rendered inert by reaction with $Co_2(CO)_8$. Addition reactions can then be carried out on the free olefinic group in the $Co_2(CO)_6(RC_2R')$ complex. Finally, the carbonylcobalt group can be removed with ceric ammonium nitrate or ferric nitrate. An example (*49*) of the overall reaction sequence is given in Eq. (29).

$$\begin{tikzcd}
CH_2{=}CHCH_2C{\equiv}CPr\text{-}n + Co_2(CO)_8 \arrow[r] & Co_2(CO)_6(CH_2{=}CHCH_2C_2Pr\text{-}n) \arrow[d, "BH_3.O_2"] \\
& Co_2(CO)_6(HO(CH_2)_3C_2Pr\text{-}n) \arrow[d, "Ce^{4+}"] \\
& HO(CH_2)_3C{\equiv}CPr\text{-}n \qquad (29)
\end{tikzcd}$$

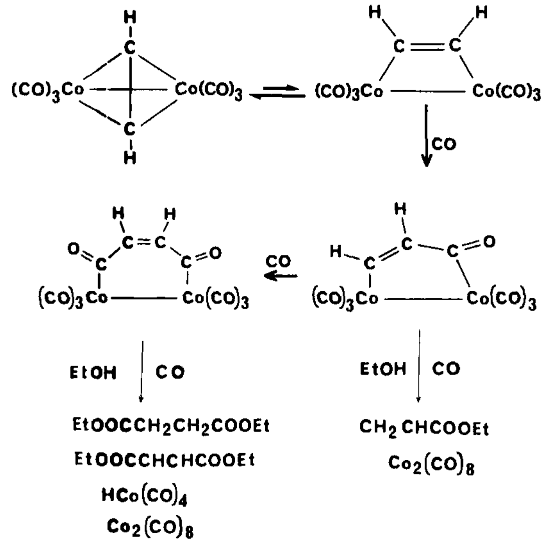
7. *The Chemical Degradation of* $Co_2(CO)_6(RC_2R')$ *Complexes*

Solutions of the complexes $Co_2(CO)_6(PhC_2Ph)$ and $Co_2(CO)_6$-(FcC_2Fc) (Fc = ferrocenyl) are oxidized by air at room temperature to give benzil (*17*), PhCOCOPh, and ferrocil (*67*), FcCOCOFc, respectively.

Decomposition of $Co_2(CO)_6(RC_2R')$ (*48*, *64*) and $Co_4(CO)_{10}(RC_2R')$ (*48*) complexes with bromine gives *trans*-α,β-dibromoolefins. With iodine, free alkynes have been liberated from $Co_2(CO)_6(RC_2R')$ complexes (*19*, *64*). The anion $Co(CO)_4^-$ has been detected in the iodine decomposition of $Co_2(CO)_6(n\text{-}PrC_2H)$. Several other reagents have been used to obtain the free alkyne from $Co_2(CO)_6(RC_2R')$ complexes. These include ceric ammonium nitrate in acetone (*49*, *66*), ferric nitrate in ethanol (*49*), sodium hydroxide in methanol (*64*), and triphenylphosphine in petroleum ether (*80*).

Treatment of $Co_2(CO)_6(RC_2R')$ complexes with aqueous acids in methanol reduces the coordinated alkyne to an olefin (*48*). Octafluoro-4,4′-dimethoxytolan is formed from $Co_2(CO)_6(C_6F_5C_2C_6F_5)$ by treatment with sodium hydroxide in methanol.

When the complex $Co_2(CO)_6(HC_2H)$ is heated in ethanol under pressure of carbon monoxide, the organic products ethyl acrylate, ethyl propionate, and diethyl succinate are formed (*23*). A mechanism (Scheme 3) has been proposed for this reaction, and it is interesting to note that



Scheme 3

the proposed structure for the reactive intermediate is the structure originally postulated for Co_2 $(CO)_6(RC_2R')$ complexes (16,17).

In saturated solvents, $Co_2(CO)_6(RC_2H)$ complexes react with norbornadiene to give $(\pi\text{-}C_5H_5)Co(CO)_2$ (*141*). The cyclopentadienyl ligand arises from a reverse Diels-Alder scission of norbornadiene. In aromatic solvents, $Co_4(CO)_9$(arene) complexes are formed; the fate of the alkyne was not determined. $Co_2(CO)_6(PhC_2Ph)$ reacts with norbornadiene to give $Co_2(CO)_4$(norbornadiene)$_2$ (*142*).

8. *The Thermal Decomposition of* $Co_2(CO)_6(RC_2R')$ *and* $Co_4(CO)_{10}(RC_2R')$ *Complexes*

$Co_2(CO)_6(C_6F_5C_2C_6F_5)$ has been decomposed thermally at 180°C in benzene to give perfluorotetracyclone, $C_4(C_6F_5)_4CO$ (*64*). Similarly, when $Co_2(CO)_6(FcC_2Fc)$ (Fc = ferrocenyl) is heated with excess diferrocenylacetylene, the blue compound tetraferrocenylcyclopentadienone (*67*) is formed in high yield.

$Co_2(CO)_6(PhC_2Ph)$ decomposes in refluxing methylcyclohexane and it has been reported (*17*) that free $PhC{\equiv}CPh$ cannot be isolated from the reaction mixture; the fate of the coordinated alkyne was not determined. The thermal decomposition in benzene and cyclohexane of $Co_2(CO)_6(PhC_2Ph)$ and the related complexes $Co_2(CO)_6(PhC_2C_6F_5)$, $Co_2(CO)_6(PhC_2C_6F_4H\text{-}o)$, and $Co_2(CO)_6(C_6F_5C_2C_6F_5)$ has been investigated in some detail. Substituted benzenes and cyclopentadienones are the major products of these reactions and the yield of cyclopentadienones relative to benzenes increases as the electronegativity of the alkyne substituent increases (*70*). The degradation of $Co_2(CO)_6(PhC_2H)$ in cyclohexane at ~ 180°C gives a variety of $Co_3(CO)_9CY$ complexes (*70*).

There are indications from preparative studies (*31*) that $Co_4(CO)_{10}(RC_2R')$ complexes decompose on heating to the analogous $Co_2(CO)_6(RC_2R')$ complexes. Qualitative observations indicate that fluorocarbon-substituted complexes exhibit greater thermal stability than their hydrocarbon analogs. The tetrafluorobenzyne complex $Co_4(CO)_{10}(C_6F_4)$ has been heated *in vacuo* to give octafluorofluorenone (*119*).

G. *Reactions of Mercury Carbonylcobalt Complexes and Alkynes*

The mercury carbonylcobalt compound $Hg[Co(CO)_4]_2$ has been obtained by treatment of the anion $[Co(CO)_4]^-$ with mercury salts

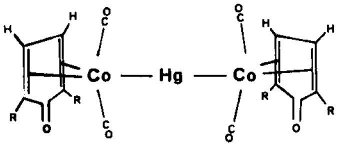
TABLE XII
KNOWN COMPLEXES OF FORMULA
$HgCo_2(CO)_6(RC_2H)_4$ AND $Hg_2Co_4(CO)_{12}(RC_2H)_2$

R	Color, m.p. (°C)	References concerning	
		Preparation	IR
	(*a*) $HgCo_2(CO)_6(RC_2H)_4$		
tert-Bu	Orange, ~170 (dec.)	*48*	*48*
$SiMe_3$	Orange, 150 (dec.)	*48*	*48*
	(*b*) $Hg_2Co_4(CO)_{12}(RC_2H)_2$		
tert-Bu	Violet-red, ~125 (dec.)	*48*	*48*
Ph	Dark red, ~120 (dec.)	*48*	*48*
H	—	*21*	*21*
$Me_2C(OH)$	—	*54*	—

(*143*, *144*) such as $Hg(CN)_2$, and by treatment of $Co_2(CO)_8$ with Na/Hg (*145*). $Hg[Co(CO)_4]_2$ is obtained as orange air-stable crystals of m.p. 81°–82°C. Determination of the molecular structure (*146*) of $Hg[Co(CO)_4]_2$ by X-ray diffraction has shown that the molecule has approximately D_{3d} symmetry. Interpretation of the Raman spectrum (*147*) of the complex in solution is in agreement with this symmetry arrangement.

$Hg[Co(CO)_4]_2$ reacts with disubstituted alkynes $RC{\equiv}CR'$ to give μ-alkyne complexes $Co_2(CO)_6(RC_2R')$ (*21*, *48*, *54*, *57*, *73*). It has been suggested that these reactions involve the initial formation of $\cdot Co(CO)_4$ radicals. Subsequent reaction of the $Co_2(CO)_6(RC_2R')$ complexes with excess alkyne may lead to the formation of $Co_2(CO)_4(RC_2R')_3$ complexes and/or substituted benzenes.

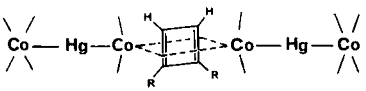
The reaction of $Hg[Co(CO)_4]_2$ with some terminal alkynes, $RC{\equiv}CH$, has given mercury carbonylcobalt-alkyne complexes. Thus, the reaction of $RC{\equiv}CH$ and $Hg[Co(CO)_4]_2$ at 100°C gives complexes of stoichiometry $HgCo_2(CO)_6(RC_2H)_4$. The complex with R = Ph has been isolated also from the reaction of tetracyclone with $Hg[Co(CO)_4]_2$ (*133*). The known complexes of this type are listed in Table XII.



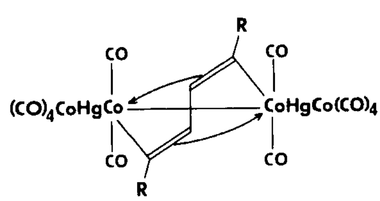
(XIII)

The structure represented in (XIII) has been postulated for $HgCo_2(CO)_6(RC_2H)_4$ complexes on the basis of chemical degradation reactions and spectroscopic studies. The complexes react with halogens to give cyclopentadienonedicarbonylcobalt halide complexes (*48*), and they can be degraded thermally to release the free cyclopentadienone (*43*, *133*).

The reaction of $RC{\equiv}CH$ and $Hg[Co(CO)_4]_2$ at ~80°C gives complexes of stoichiometry $Hg_2Co_4(CO)_{12}(RC_2H)_2$ (*21*, *48*, *54*). The known complexes of this formula are listed also in Table XII. The structure shown in (XIVa) has been suggested (*48*) for these complexes on the basis of spectroscopic investigations and chemical degradation reactions. This proposed structure has been questioned by Maitlis, who suggests (*148*) that the chemical reactivity of $Hg_2Co_4(CO)_{12}(RC_2H)_2$ complexes is more consistent with the structure shown in (XIVb).

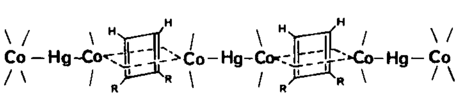


(XIVa)

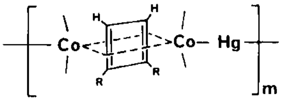


(XIVb)

The complex $Hg_2Co_4(CO)_{12}(PhC_2H)_2$ decomposes on standing in solution at 20°C, and a new complex of stoichiometry $Hg_3Co_6(CO)_{16}(PhC_2H)_4$ (XV) is precipitated. The latter complex decomposes in refluxing tetrahydrofuran to form a violet polymer (*48*) $[HgCo_2(CO)_4(RC_2H)_2]_m$ (XVI). Treatment of $Hg_2Co_4(CO)_{12}(RC_2H)_2$ complexes with carbon monoxide (*48*) gives low yields of mercury-free complexes of formula $Co_2(CO)_6(RC_2H)_4$. Alkanes and alkenes are formed when $Hg_2Co_4(CO)_{12}(RC_2H)_2$ complexes are treated with $LiAlH_4$.



(XV)



(XVI)

It has been observed (*84*) that reaction of $PhC{\equiv}CPh$ with $ClHgCo(CO)_4$ gives the complex $Co_2(CO)_6(PhC_2Ph)$.

H. Reactions of Alkynes with $RCo(CO)_4$ and Related Complexes

Heck (*149*) has discussed several alkyne insertion reactions involving alkyl- and acyl-tetracarbonylcobalt complexes. Most reactions seem to give tricarbonyl-π-(penteno-4-lactonyl)cobalt complexes and numerous other products. The reaction of $CF_3C{\equiv}CCF_3$ with $HCo(CO)_4$ results in reduction of the alkyne (*85*), but $Co_2(CO)_6(HC_2H)$ is formed (*150*) in the related reaction of $HC{\equiv}CH$ with $HCo(CO)_4$ in methanol.

III

REACTIONS INVOLVING (π-C_5H_5)$Co(CO)_2$ AND RELATED COMPOUNDS

A. The Formation and Properties of (π-C_5H_5)$Co(CO)_2$

Dicarbonyl-π-cyclopentadienylcobalt has been prepared from cobaltocene and carbon monoxide [Eq. (30)] (*151–153*). The product can be

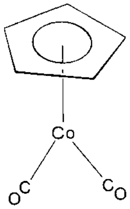
$$(\pi\text{-}C_5H_5)_2Co + 2CO \longrightarrow (\pi\text{-}C_5H_5)Co(CO)_2 + C_5H_5\cdot \qquad (30)$$

isolated in ~25% yield if the reaction is carried out under a carbon monoxide pressure of at least 60 atmospheres (*153*), but the yield falls to ~12% if the carbonylation reaction is performed at atmospheric pressure (*154*). A better preparative route involves the reaction between octacarbonyldicobalt and cyclopentadiene [Eq. (31)] (*153, 155, 156*). This reaction can be initiated photochemically in a variety of hydrocarbon

$$Co_2(CO)_8 + 2C_5H_6 \longrightarrow 2(\pi\text{-}C_5H_5)Co(CO)_2 + 4CO + H_2 \qquad (31)$$

solvents. The yield of crude product is ~48% and pure (π-C_5H_5)$Co(CO)_2$ is obtained from this by chromatography on alumina. It has been reported recently (*157*) that the yield of (π-C_5H_5)$Co(CO)_2$ can be increased to ~95% by treating $Co_2(CO)_8$ with freshly distilled cyclopentadiene in refluxing dichloromethane in the absence of light. Substituted compounds such as dicarbonyl-π-(trimethylsilycyclopentadienyl)cobalt are also prepared in this way. Altman and Wilkinson (*158*) have also isolated substituted dicarbonyl-π-cyclopentadienylcobalt complexes from the reaction of $Co_2(CO)_8$ with 6,6-dialkylfulvenes.

(π-C_5H_5)$Co(CO)_2$ is a dark red malodorous liquid with m.p. −22°C, and b.p. 139°–140°C/710 mm. It decomposes upon exposure to air and it is heat-sensitive. The infrared spectrum of solutions of the compound in CS_2 show ν_{CO} at 2028 and 1967 cm^{-1}, and the NMR spectrum of the CS_2 solution shows the cyclopentadienyl proton resonance as a sharp singlet at δ 5.00. The structure of the compound is represented in (XVII).

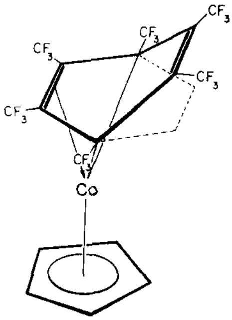


(XVII)

B. *The Formation of Organometallic Complexes from (π-C_5H_5)$Co(CO)_2$ and Alkynes*

Reactions between (π-C_5H_5)$Co(CO)_2$ and alkynes have been initiated photochemically and thermally. π-Tetramethylcyclopentadienone-π-cyclopentadienylcobalt is formed in high yield when a mixture of (π-C_5H_5)$Co(CO)_2$ and but-2-yne is exposed to sunlight for ~2 weeks, and a similar reaction involving diphenylacetylene in place of but-2-yne gives π-tetraphenylcyclopentadienone-π-cyclopentadienylcobalt in ~80% yield (*159*). In refluxing xylene, (π-C_5H_5)$Co(CO)_2$ and diphenylacetylene give π-tetraphenylcyclobutadiene-π-cyclopentadienylcobalt (60% yield) (*157*) in addition to the π-cyclopentadienone complex. Some hexaphenylbenzene and a trace of tetraphenylcyclopentadienone are formed also in this reaction. Apparently, the reaction between (π-C_5H_5)$Co(CO)_2$ and but-2-yne in refluxing xylene (*157*) does not give π-tetramethylcyclobutadiene-π-cyclopentadienylcobalt, and it has been suggested that a phenyl substituent may be important for the formation of cyclobutadiene complexes of this type (*160*). However, π-cyclobutadienecobalt complexes are not formed in the thermally induced reactions of (π-C_5H_5)$Co(CO)_2$ with the alkynes $C_6H_5C{\equiv}CC_6F_5$ and $C_6F_5C{\equiv}CC_6F_5$. Each of these alkynes reacts with (π-C_5H_5)$Co(CO)_2$ in hexane above 110°C to give π-cyclopentadienone-π-cyclopentadienylcobalt complexes (*161*). Perhaps the use of xylene as solvent in a system which permits the escape of carbon monoxide has as much influence as the substituent effect on the formation of cyclobutadiene complexes. Indirect support for this idea comes from the observation that π-cyclobutadiene-π-cyclopentadienylcobalt complexes are formed in reactions of alkynes with several (π-C_5H_5)Co(diolefin) compounds (*56*, *160*, *162*).

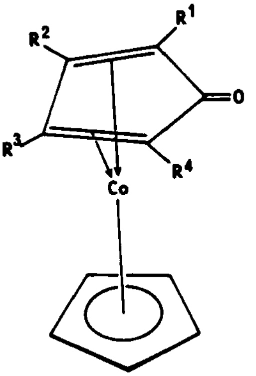
The reaction of (π-C_5H_5)Co$(CO)_2$ and hexafluorobut-2-yne in a hydrocarbon solvent at 110°C gives π-tetrakis(trifluoromethyl)cyclopentadienone-π-cyclopentadienylcobalt in high yield (*56*, *163*). In a recent reinvestigation (*164*) of this reaction, tetrahaptohexakis(trifluoromethyl)benzene-π-cyclopentadienylcobalt was isolated as a minor product (~5% yield at 100°–120°) together with the π-cyclopentadienonecobalt complex (~55% yield). The structure of the tetrahaptobenzene complex is presumably related to the known structure (*165*) of the analogous rhodium compound (XVIII).



(XVIII)

The unsymmetrical isomer 2,4-bis(pentafluorophenyl)-3,5-diphenylcyclopentadienone-π-cyclopentadienylcobalt is the only product isolated from the reaction of (π-C_5H_5)Co$(CO)_2$ and $C_6H_5C{\equiv}CC_6F_5$ (*161*). However, all possible isomers of the π-cyclopentadienone complex (XIX; R, R′ = Me, CF_3) are formed in the related reaction of (π-C_5H_5)Co$(CO)_2$ and $MeC{\equiv}CCF_3$ (*68*). Again, the unsymmetrical isomer is the major product, and it has been suggested that a strong preference for the formation of this isomer is due to attractive forces between hydrocarbon and fluorocarbon substituents in the transition state (*68*).

Two or sometimes three isomers of the π-cyclopentadienone-π-cyclopentadienylcobalt complexes have been isolated from reactions in xylene at 160°C of (π-C_5H_5)Co$(CO)_2$ and the terminal alkynes, $MeC{\equiv}CH$, $CF_3C{\equiv}CH$, *tert*-$BuC{\equiv}CH$, and $PhC{\equiv}CH$ (*166*). In these

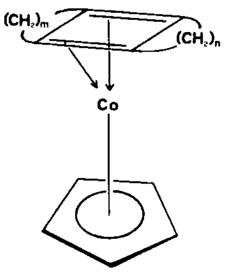


	R1	R2	R3	R4
(a)	R	H	R	H
(b)	R	H	H	R
(c)	H	R	R	H

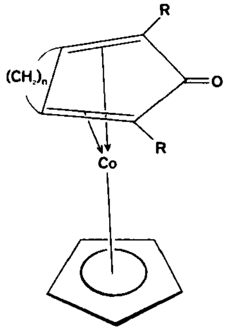
(XIX)

reactions, steric interactions between substituents seem to work against the formation of the 3,4-disubstituted isomers (XIXc), but the major substituent effect is an electronic one that favors the formation of the 2,5-disubstituted isomer (XIXb).

The reactions of (π-C_5H_5)Co(CO)$_2$ with several diynes have been studied. The macrocyclic alkadiynes 1,7-cyclododecadiyne, 1,7-cyclotridecadiyne, 1,7- and 1,8-cyclotetradecadiyne, and 1,8-cyclopentadecadiyne react with (π-C_5H_5)Co(CO)$_2$ to give π-cyclobutadienecobalt complexes (*167*) in which the cyclobutadiene ligand has been formed by the intramolecular transannular cyclization of the cyclic alkadiyne (XXa). The reaction with 1,8-cyclotetradecadiyne also gives the trimetallic complex (π-C_5H_5)$_3$Co$_3$(CO)($C_{14}H_{20}$) (*167*). The reaction of (π-C_5H_5)Co(CO)$_2$ with 2,8-decadiyne gives a cyclopentadienonecobalt



(XXa)



(XXb)

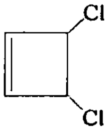
complex, (π-C_5H_5)Co($C_{10}H_{14}CO$) (*168*), in which the cyclopentadienone ligand has been formed by intramolecular cyclization of the alkadiyne with inclusion of carbon monoxide (XXb). Similar reactions with the conjugated diynes $RC{\equiv}C{-}C{\equiv}CR$ (R = Me, Ph) give cyclopentadienonecobalt complexes which are formed from two diyne units (*168*).

The known complexes of formula (π-C_5H_5)Co(cyclopentadienone) and (π-C_5H_5)Co(cyclobutadiene), are listed in Table XIII. π-Cyclopentadienone- and π-cyclobutadiene-π-cyclopentadienylcobalt complexes have been formed in a variety of other reactions that do not involve alkynes. These reactions are summarized in Eqs. (32)–(37).

$$(\pi\text{-}C_5H_5)Co(CO)_2 + \text{cyclopentadienone} \longrightarrow (\pi\text{-}C_5H_5)Co(C_4R_4CO) \quad (\mathit{157, 173}) \qquad (32)$$

$$(\pi\text{-}C_5H_5)Co(CO)_2 + \text{photo-}\alpha\text{-pyrone} \xrightarrow{\text{uv}} (\pi\text{-}C_5H_5)Co(C_4H_4) \quad (\mathit{177, 177a, 183}) \qquad (33)$$

$$NaCo(CO)_4 +$$



$$\xrightarrow{I_2} \xrightarrow{C_5H_6,\ \text{base}} (\pi\text{-}C_5H_5)Co(C_4H_4) \quad (\mathit{176}) \qquad (34)$$

$$(C_4Ph_4)Co(CO)_2Br + [(\pi\text{-}C_5H_5)Fe(CO)_2]_2 \longrightarrow (\pi\text{-}C_5H_5)Co(C_4Ph_4) \quad (\mathit{178\text{–}180}) \qquad (35)$$

$$Co_2(CO)_8 + [(\pi\text{-}C_5H_5)Pd(C_4Ph_4)]^+ \longrightarrow (\pi\text{-}C_5H_5)Co(C_4Ph_4) \quad (\mathit{179}) \qquad (36)$$

$$(\pi\text{-}C_5H_5)_2Co + (C_4Ph_4)PdBr_2 \longrightarrow (\pi\text{-}C_5H_5)Co(C_4Ph_4) \quad (\mathit{180}) \qquad (37)$$

In general, (π-C_5H_5)Co(C_4R_4) complexes are very stable thermally and chemically. For instance, (π-C_5H_5)Co(C_4Ph_4) is thermally stable to 360°C under nitrogen. Moreover, it is not affected by HCl, alcoholic KOH, $LiAlH_4$, CO under pressure, PPh_3, I_2, and dimethyl acetylenedicarboxylate (*156*). The chemical behavior of (π-C_5H_5)Co(C_4R_4) complexes is similar to that of ferrocene in that the complexes undergo electrophilic ring substitution reactions at the cyclopentadienyl ring (*157*).

(π-C_5H_5)Co(C_4R_4CO) complexes are stable thermally and few chemical reactions of these complexes have been reported. The complex (π-C_5H_5)Co[$C_4(CF_3)_4CO$] is soluble in concentrated H_2SO_4 and can be recovered unchanged by dilution of the solution with water. The ketonic carbonyl group in this and related complexes displays none of the characteristic chemical properties of an organic ketone (*163*). It has been shown that $(\pi\text{-}C_5H_5)Co(C_4R_4CO)$ complexes can exist in proteolytic equilibrium with hydroxycobalticinium salts (*173*).

C. Possible Intermediates in the Formation of π-Cyclopentadienone- and π-Cyclobutadiene-cobalt Complexes

The reactions of $(\pi\text{-}C_5H_5)Co(CO)_2$ with $RC{\equiv}CR'$ probably proceed by the replacement of carbonyl groups by alkyne units. Although complexes of formula $(\pi\text{-}C_5H_5)Co(CO)(RC_2R')$ have not been isolated, a closely related complex is known to exist. Thus, $(\pi\text{-}C_5H_5)Co(PPh_3)(PhC_2Ph)$ is formed (*174*) by treating the product of the reaction of $(\pi\text{-}C_5H_5)Co(PPh_3)I_2$ and *i*-PrMgBr with diphenylacetylene. This monoalkyne complex reacts further with diphenylacetylene to form a cobaltocyclopentadiene complex, $(\pi\text{-}C_5H_5)Co(PPh_3)(PhC_2Ph)_2$. The latter complex is converted to π-tetraphenylcyclobutadiene-π-cyclopentadienylcobalt by heating, and to π-tetraphenylcyclopentadienone-π-cyclopentadienylcobalt by heating with CO.

A recent study (*182*) of the reaction of $(\pi\text{-}C_5H_5)Co(CO)_2$ and $Me_3SiC{\equiv}CSiMe_3$ has revealed the existence of a μ-alkyne complex of formula $(\pi\text{-}C_5H_5)_2Co_2(CO)(Me_3SiC_2SiMe_3)$. The possibility that this complex is an intermediate in the formation of $(\pi\text{-}C_5H_5)Co(C_4R_4)$ complex from $(\pi\text{-}C_5H_5)Co(CO)_2$ and $RC{\equiv}CR$ has been considered. The μ-alkyne complex reacts with $PhC{\equiv}CPh$ in xylene at ~160°C to give the cyclobutadiene complexes $(\pi\text{-}C_5H_5)Co[C_4Ph_2(SiMe_3)_2]$ and $(\pi\text{-}C_5H_5)Co(C_4Ph_4)$.

D. Structure and Bonding in $(\pi\text{-}C_5H_5)Co(C_4R_4CO)$ Complexes

The crystal structures of two $(\pi\text{-}C_5H_5)Co(C_4R_4CO)$ complexes [R = Me (*184*), R = CF_3 (*185*)] have been determined by X-ray investigation. The structure of the complex with R = Me (XXIa) has been described as a sandwich in which the cobalt atom lies between two eclipsed rings. The carbon–carbon bond lengths of the (C_4Me_4CO) ring are essentially equal, indicating considerable delocalization of the π electrons over the five ring carbon atoms. The stabilization of the complex arises from strong π-bonding between both rings and the cobalt atom,

TABLE XIII

KNOWN COMPLEXES OF FORMULA (a) (π-C_5H_5)Co($C_4R^1R^2R^3R^4CO$) AND (b) (π-C_5H_5)Co($C_4R^1R^2R^3R^4$)

R^1	R^2	R^3	R^4	Color, m.p. (°C)	References concerning			
					Preparation	IR	NMR	UV
(a) (π-C_5H_5)Co($C_4R^1R^2R^3R^4CO$)								
Me	Me	Me	Me	Orange, 178–180	*159*	*159*	*161*	*170, 171*
CF_3	CF_3	CF_3	CF_3	Red, 264	*56*	*56, 163*	*56*	*171, 163*
Me	CF_3	CF_3	Me	Orange	*68*	*68*	*68*	—
Me	CF_3	Me	CF_3	Orange, 144.5	*68*	*68*	*68*	—
CF_3	Me	CF_3	Me	Orange	*68*	*68*	*68*	—
H	Me	H	Me	—	*166*	*166*	*166*	*166*
Me	H	H	Me	—	*166*	*166*	*166*	*166*
H	CF_3	H	CF_3	—	*166*	*166*	*166*	*166*
CF_3	H	H	CF_3	—	*166*	*166*	*166*	*166*
H	*tert*-Bu	H	*tert*-Bu	—	*166*	*166*	*166*	*166*
tert-Bu	H	H	*tert*-Bu	—	*166*	*166*	*166*	*166*
H	*tert*-Bu	*tert*-Bu	H	—	*166*	*166*	*166*	*166*
Me	—(CH_2)$_4$—		Me	—	*168*	—	—	—
Ph	Ph	Ph	Ph	Red, 327–329	*157, 159, 172–175*	*157, 159, 173*	*173*	*170*
H	Ph	Ph	Ph	Dark red, 218–219	*175*	*175*	*175*	—
Ph	H	H	Ph	—	*166*	*166*	*166*	*166*
H	Ph	H	Ph	—	*166*	*166*	*166*	*166*
Ph	*o*-HC_6F_4	Ph	*o*-HC_6F_4	Red, 228	*70*	*70*	*70*	*70*
Ph	C_6F_5	Ph	C_6F_5	Orange-red, 216-217	*161*	*161*	*161*	*161*
C_6F_5	C_6F_5	C_6F_5	C_6F_5	Orange, 311–312	*161, 169*	*161*	*161, 169*	*161*
Ph	Naphthyl	Naphthyl	Ph	Dark red	*169*	—	—	—
Ph	Naphthyl	Ph	Naphthyl	Dark Red	*169*	—	—	—
Naphthyl	Ph	Ph	Naphthyl	Dark red	*169*	—	—	—
Ph	Mesityl	Ph	Mesityl	Maroon, 339–340	*169*	—	—	—

(*b*) (π-C_5H_5)Co($C_4R^1R^2R^3R^4$)

H	H	H	H	Yellow, 88.5–89.0	*176–177a, 183*	*177, 177a*	*176–177a*	*177, 177a*
Me	Me	Me	Me	Yellow, 57	*177b, 180a*	*177b*	*177b*	—
Ph	Ph	Ph	Ph	Yellow-orange, 264	*56, 157, 162, 172, 174, 178–180a*	*56, 157, 162*	*56*	*162*
Ph	Me	Ph	Me	—	*160*	—	—	—
Ph	$SiMe_3$	Ph	$SiMe_3$[a,b]	Red-orange, 161–163	*160, 169, 182*	*182*	*182*	—
Ph	Ph	$SiMe_3$	$SiMe_3$[a]	Red-orange, 133–134	*160, 169, 182*	*182*	*182*	—
Ph	Si_2Me_5	Ph	Si_2Me_5	112–113	*182*	—	—	—
Ph	Ph	Si_2Me_5	Si_2Me_5	85–86	*182*	—	—	—
Ph	COMe	Ph	COMe	—	*160*	—	—	—
Ph	Ph	COMe	COMe	—	*160*	—	—	—
Ph	CHO	Ph	CHO	—	*160*	—	—	—
Ph	Ph	CHO	CHO	—	*160*	—	—	—
Ph	CF_3	Ph	CF_3	—	*160*	—	*160*	—
Ph	Naphthyl	Ph	Naphthyl	Yellow, 241–242	*169*	—	*169*	—
Ph	Ph	Naphthyl	Naphthyl	Dark red, 278–280	*169*	—	*169*	—
Ph	Mesityl	Ph	Mesityl	Golden, 260–262	*169*	—	—	—
Ph	H	Ph	H	—	*160*	*160*	—	—
Ph	Ph	H	H	—	*160*	*160*	—	—
H	H	H	COOH	Orange, 162–163	*177b*	*177b*	*177b*	—
H	H	H	C(O)Me	Yellow, 89	*176, 177b*	*177b*	*176, 177b*	—
H	H	H	COOMe	Yellow, 55–57	*177b*	—	—	—
—$(CH_2)_4$—		—$(CH_2)_4$—		Yellow, 85.5	*167*	*167*	*167*	—
—$(CH_2)_4$—		—$(CH_2)_5$—		Yellow, 75	*167*	*167*	*167*	—
—$(CH_2)_4$—		—$(CH_2)_6$—		Liquid	*167*	*167*	*167*	—
—$(CH_2)_5$—		—$(CH_2)_5$—		Yellow, 103–105	*167*	*167*	*167*	—
—$(CH_2)_5$—		—$(CH_2)_6$—		Yellow, 47–48	*167*	*167*	*167*	—
Fc[c]	Fc	Fc	Fc	279–281	*169*	—	—	—

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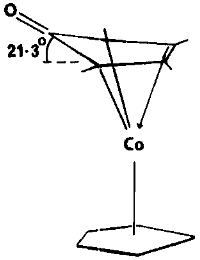
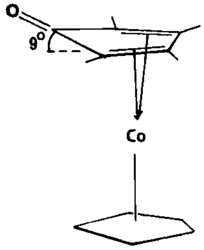
[a] Crystal structure (*180b*).

[b] Crystal structure (*180c*).

[c] Fc = (C_5H_5)Fe(C_5H_4).



(XXIa)



(XXIb)

which has a formal oxidation number of +1. However, the cyclopentadienone ring is not strictly planar; the ketonic carbonyl group is bent by 9° out of the plane of the other carbon atoms of the ring.

The structure of the complex with R = CF_3 (XXIb) is similar except that the cyclopentadienyl ring is staggered with respect to the cyclopentadienone ring; this has been explained in terms of minimizing C—F and H—F nonbonded interactions between the two rings. The distortion of the cyclopentadienone ring is greater in $(\pi\text{-}C_5H_5)Co[C_4(CF_3)_4CO]$ than in $(\pi\text{-}C_5H_5)Co(C_4Me_4CO)$; the dihedral angle between the carbonyl group and the C_4 plane is 21° for the fluorocarbon complex.

The bonding in these and related complexes has been the subject of considerable discussion (*170*, *171*, *184–188*) and a recent review (*189*) provides a detailed description of the bonding in $(\pi\text{-}C_5H_5)Co(C_4R_4CO)$ complexes.

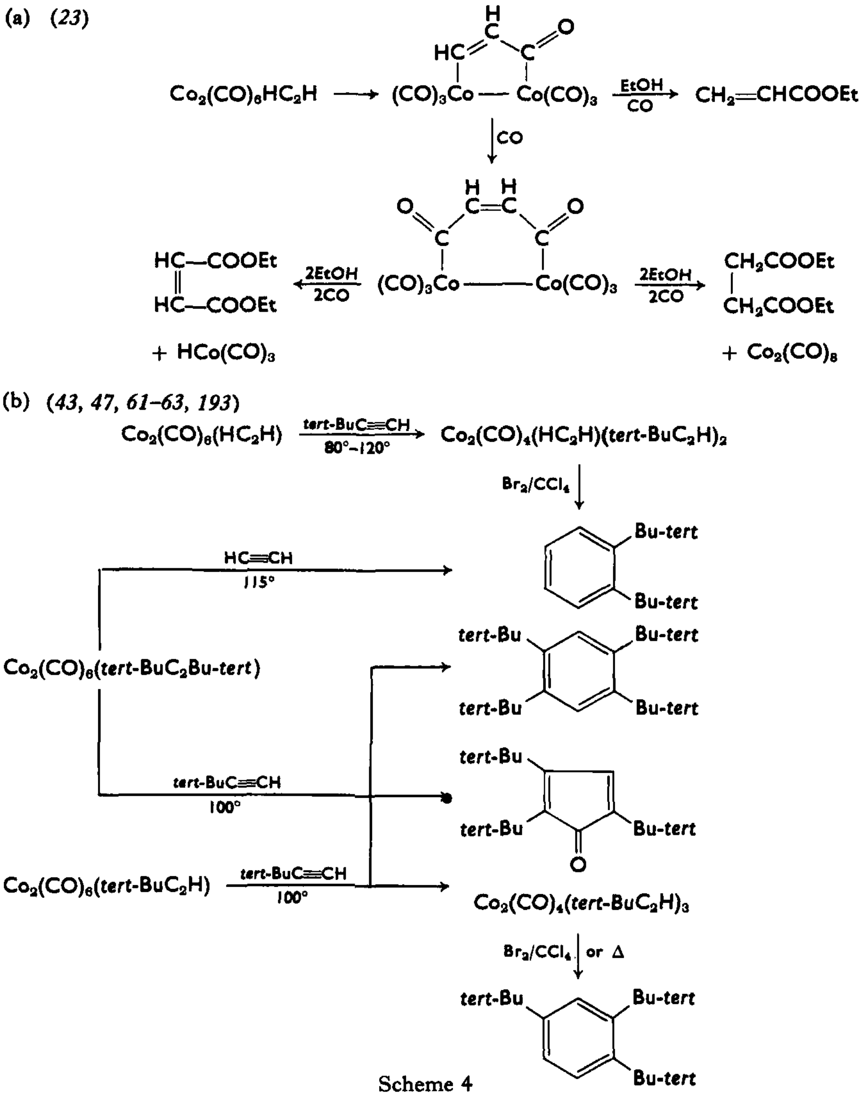
IV

THE FORMATION OF ORGANIC COMPOUNDS FROM ALKYNES AND CARBONYLCOBALT COMPLEXES

A. Stoichiometric and Catalytic Syntheses

The formation of organic compounds from reactions of alkynes and carbonylcobalt compounds has been mentioned briefly in preceding sections. Several reaction sequences that lead to the formation of organic products are summarized in Scheme 4. The most extensively studied reaction of this type is undoubtedly the cyclotrimerization of alkynes.

A recent review (*190*) lists some twenty alkynes that have been cyclotrimerized to substituted benzenes in the presence of carbonylcobalt catalysts. The catalysts that have been used in these reactions include



Scheme 4

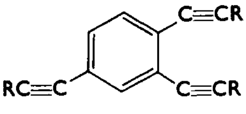
$Co_2(CO)_8$ and $Hg[Co(CO)_4]_2$ (*41*), (π-C_5H_5)$Co(CO)_2$ (*191*), $Co(CO)_3NO$ (*192*), $Co_2(CO)_6(RC_2R')$ (*193*), and $Co_4(CO)_{10}(RC_2R')$ (*48*). The trimerization reactions with symmetrically disubstituted alkynes, $RC{\equiv}CR$, lead inevitably to hexasubstituted benzenes. Unsymmetrical alkynes $RC{\equiv}CR'$ are trimerized generally to 1,2,4- rather than 1,3,5-trisubstituted benzenes. These cyclotrimerization reactions can be achieved readily by heating the appropriate alkyne with a few mole percent of the carbonylcobalt catalyst in a solvent such as dioxane, tetrahydrofuran, or *n*-heptane. Apparently, there is no pronounced solvent effect.

Carbonylcobalt complexes do not appear to be effective catalysts for the cyclotrimerization of certain alkynes. Thus, the alkynes $PhC{\equiv}CSiMe_3$, $Me_3SiC{\equiv}CSiMe_3$, *o*-$BrC_6H_4C{\equiv}CC_6H_4Br$-*o*, *tert*-$BuC{\equiv}CH$, *tert*-$BuC{\equiv}CBu$-*tert* (*41*, *190*), $PhC{\equiv}CBu$-*tert* (*59*), *i*-$PrC{\equiv}CPr$-*i* (*194*, *195*), and $CH_2{=}C(Me)C{\equiv}CC(Me){=}CH_2$ (*196*) do not participate readily in catalytic cyclotrimerization reactions. These alkynes all have bulky substituents and it seems logical to conclude that the cyclotrimerization reactions are sterically inhibited.

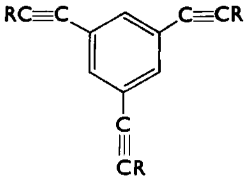
It is interesting to compare the successful catalytic cyclotrimerization of $Me_3SiC{\equiv}CH$ (*41*) with the observation that *tert*-$BuC{\equiv}CH$ does not undergo cyclotrimerization using carbonylcobalt catalysts. Bollinger (*59*) has suggested that this is related to the fact that the C—Si bond is longer than the C—C bond so that $Me_3SiC{\equiv}CH$ has slightly more room than does *tert*-$BuC{\equiv}CH$ for the cyclization reaction. This idea is supported by the observation that 1,2,4-tris(*tert*-butyl)benzene is distorted whereas 1,2,4-tris(trimethylsilyl)benzene is not (*197*).

Although 1,2,4-tris(*tert*-butyl)benzene is not formed by the catalytic trimerization of *tert*-$BuC{\equiv}CH$ using $Co_2(CO)_8$, it can be obtained by thermal decomposition of the trisalkyne complex $Co_2(CO)_4$(*tert*-$BuC_2H)_3$ (*47*). Under the conditions that lead to the formation of $Co_2(CO)_4$(*tert*-$BuC_2H)_3$, $Me_3SiC{\equiv}CH$ gives only a trace of the analogous complex $Co_2(CO)_4(Me_3SiC_2H)_3$ and a large yield of 1,2,4-tris(trimethylsilyl)benzene (*48*). It seems reasonable, therefore, to suggest that unstable $Co_2(CO)_4(RC_2R')_3$ complexes may be involved in the mechanism for the formation of substituted benzenes in the reactions of alkynes and $Co_2(CO)_8$ (*59*, *198*, *199*). It is possible, however, that the formation of benzenes and trisalkynecobalt complexes are competing reactions.

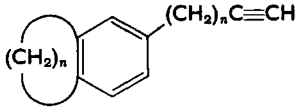
The trimerization of conjugated diynes, $RC{\equiv}CC{\equiv}CR$, with $Hg[Co(CO)_4]_2$ is not specific and leads to the formation of 1,2,4- and 1,3,5-substituted benzenes (XXIIa) and (XXIIb) respectively and polymers (*73*). With $(\pi\text{-}C_5H_5)Co(CO)_2$ in place of $Hg[Co(CO)_4]_2$ as catalyst, the yield of the 1,2,4-isomer (R = Ph) is significantly greater than that of the 1,3,5-isomer (*191*). Nonconjugated alkadiynes form dimers (XXIIc) and polymers in the presence of $Hg[Co(CO)_4]_2$ (*200*).



(XXIIa)



(XXIIb)

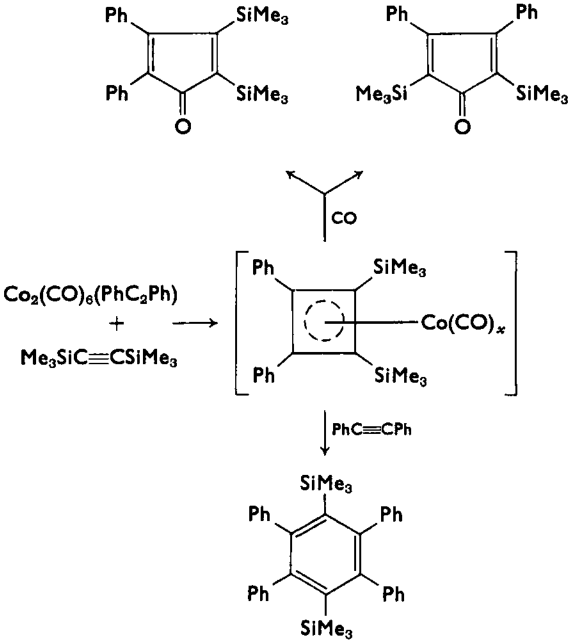


(XXIIc)

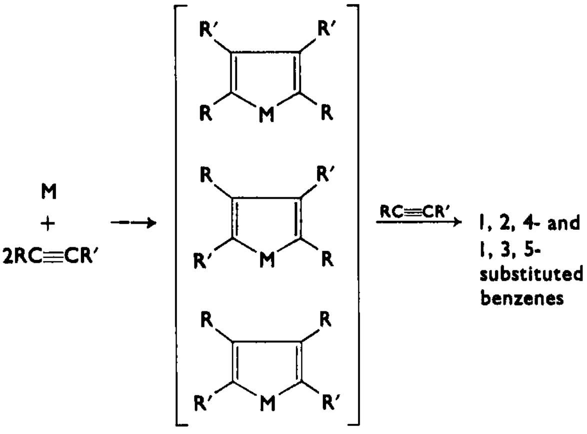
B. *Mechanism of the Cyclotrimerization Reactions*

Many individual experiments have given some information about the mechanism of cyclotrimerization reactions involving alkynes and carbonylcobalt complexes, but details of the overall mechanism remain obscure.

The reaction of $Co_2(CO)_6(PhC_2Ph)$ with $PhC\equiv CSiMe_3$ or $Me_3SiC\equiv CSiMe_3$ gives substituted cyclopentadienone and benzene products. The proposed arrangements of the substituents in these organic products can be explained only if the original acetylenic bond is ruptured. On the basis of this result, a mechanism has been proposed (Scheme 5) involving a



Scheme 5



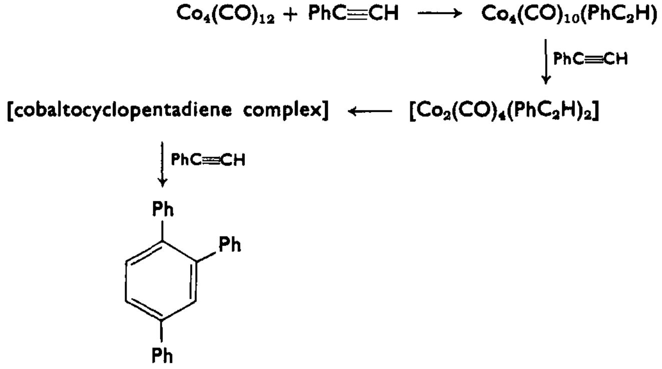
Scheme 6

cyclobutadiene intermediate which can undergo ring enlargement by CO or alkyne insertion into any of the four C—C ring linkages.

However, convincing evidence has emerged recently which works against participation of cyclobutadiene intermediates in these reactions. Whitesides and Ehmann (*198*) have shown that 1,2,3-trimethyl-4,5,6-tri(methyl-d_3)benzene is not a product in the $Co_2(CO)_8$ assisted cyclotrimerization of $MeC{\equiv}CCD_3$. This evidence establishes that the activity of the catalyst in this system does not depend on the generation of free or metal complexed cyclobutadiene intermediates.

The involvement of metalocyclopentadiene intermediates in the cyclotrimerization of alkynes (Scheme 6) has been established for some metal systems (*162*, *198*, *201–204*). However, there is no evidence to indicate participation of cobaltocyclopentadiene species in cyclotrimerization reactions involving carbonylcobalt complexes. It is worth noting, however, that 1,4-addition of an alkyne to such an intermediate would lead to the formation of 1,2,4- and 1,3,5-substituted benzenes. Moreover, the 1,2,4-derivative would be favored statistically. This line of reasoning has led to the incorporation of a cobaltocyclopentadiene intermediate in the mechanism proposed (*120*) (Scheme 7) for the $Co_4(CO)_{12}$-catalyzed cyclotrimerization of $PhC{\equiv}CH$.

The possibility that $Co_2(CO)_4(RC_2R')_3$ complexes are intermediates in the catalytic cyclotrimerization reactions has been alluded to in a previous section. Certainly, these complexes have been used as stoichio-



Scheme 7

metric reagents for the formation of ortho-disubstituted benzenes, but their possible role in catalytic reactions has not been verified.

Hübel (*41*, *190*) has listed a number of experimental observations that may have mechanistic implications, but clearly it is not yet possible to formulate a reaction scheme that is consistent with all the experimental data.

C. Further Applications of Alkyne-Cobalt Carbonyl Chemistry

The μ-alkyne complex $Co_2(CO)_6(PhC_2Ph)$ has been used as a catalyst for the polymerization of vinyl chloride (*205*) and the system [$RC{\equiv}CR$ + $Co_2(CO)_8$; R = alcohol or ester group] has been considered as an antiknock additive for motor fuels (*44*).

Alkynes are potentially useful as building blocks in the synthesis of numerous organic compounds, and the use of disubstituted alkynes permits the formation of ortho-disubstituted derivatives. However, the commercial development of alkyne chemistry has been hampered by the high cost of most acetylenes. Indeed, only acetylene and propyne can be regarded as low-cost chemicals. Perhaps recent progress in the synthesis of alkynes (*206–209*) will lead to further large-scale developments.

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The Literature of Organo-Transition Metal Chemistry 1972

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This article supplements previous accounts (*1*, *2*) of the secondary literature describing transition metal organometallics, and summarizes, as far as is practicable, trends and advances in this area of chemical literature. Coverage includes journals received in the author's library up to the end of December 1972.

There seems to be no stemming the flow of the primary literature, and the appearance of Volume 1 of the Chemical Society's Specialist Periodical Report on Organometallic Chemistry will be welcomed by all. Further details of this book, which covers both Main Group and Transition Metal derivatives, can be found in Section B. The *Journal of Organometallic Chemistry* continues to expand, with 1972 seeing the publication of thirteen volumes (34–46), which include subject reviews, annual reports, and preliminary communications, as well as the usual selection of papers. Fortunately it is now possible to purchase the individual volumes given over to the annual reviews.

Publication of all the lectures, both plenary and section, presented at the Fifth International Conference on Organometallic Chemistry at Moscow, also occurred during the year, in volume 30 of *Pure and Applied*

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Chemistry. The contents provide an interesting contrast to the corresponding lectures given at the Sixth Conference, held in Amherst, Massachusetts during August 1973.

Trends in organometallic chemistry were examined by considering the numbers of papers on various topics cited in *Annual Surveys of Organometallic Chemistry* (*3*). Growth factors calculated for the literature on organo-transition metal complexes suggest that some slowing down of the high rate of increase in citations over the period 1967–1969 (also coinciding with the introduction of multi-author surveys, however) will be apparent during the early seventies.

A. Textbooks

Although no new textbooks dealing specifically with organometallic chemistry have been published, several new volumes on inorganic chemistry deserve mention. These include the third edition of the well-known text by Cotton and Wilkinson. Salient advances reported in the literature up to mid-1971 are included. **Numbers follow those in the lists given in references (*1*) and (*2*).**

A1. F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 3rd ed. Wiley, New York, 1972. Preserves topicality by eliminating the more elementary topics now adequately covered by other texts, and by making extensive reference to material published in the last five years or so. See
Chapter 22, pp. 682–727: Complexes of π-acceptor (π-acid) ligands.
Chapter 23, pp. 728–769: Organometallic compounds of transition metals.
Chapter 24, pp. 770–800: Organometallic compounds in homogeneous catalytic reactions.

A87. J. E. Huheey, "Inorganic Chemistry—Principles of Structure and Reactivity." Harper, New York, 1972. Another good introductory text with a brief but up-to-date coverage of organometallic chemistry. See
Chapter 11, pp. 452–504: Organometallic chemistry.

Books on Organometallic Chemistry

A88. M. Herberhold, "Metal π Complexes," volume 2: Complexes with monoolefinic ligands. Part 1: General survey. Elsevier, Amsterdam, 1972. This is an English translation and revision of a stillborn German edition, and follows A23a. An excellent and detailed survey of transition metal complexes containing monoolefins, concentrating on historical and preparative aspects of metal π-complexes of olefinic hydrocarbons, and of monoolefins containing functional groups.

A89. A. N. Kost, ed., "Problems in Organic Chemistry." Izd. Mosk. Univ., Moscow, 1970, contains:
  89.1 A. N. Nesmeyanov and E. G. Perevalova: Ferrocene chemistry, pp. 5–28 (122).* A review of the authors' work.
A90. A. N. Nesmeyanov, "Elementorganicheskaya Khimiya" (Organoelement Chemistry—Selected works 1959–1969). Nauka, Moscow, 1970. Reprints of most of the author's more important papers.
A91. Y. A. Ol'dekop and N. A Maier, "Elementoorganicheskaya Khimiya" (Elementoorganic chemistry). Znanie, Moscow, 1971.

Compilations of Articles on Organometallic Themes

A92. E. L. Muetterties, ed., "Transition Metal Hydrides." Dekker, New York, 1971. Contains several articles of interest to organometallic chemists:
  92.1 E. L. Muetterties: Physical properties of hydrogen, deuterium and tritium, 1–9 (35).
  92.2 E. L. Muetterties: The transition metal-hydrogen interaction, pp. 11–31 (84).
  92.3 B. A. Frenz and J. A. Ibers: Molecular structures of transition metal hydride complexes, pp. 33–74 (111).
  92.4 J. P. Jesson: Stereochemistry and stereochemical nonrigidity in transition metal hydrides, pp. 75–201 (317).
  92.5 R. A. Schunn: Systematics of transition metal hydride chemistry, pp. 203–269 (394).
  92.6 C. A. Tolman: Role of transition metal hydrides in homogeneous catalysis, pp. 271–312 (137).
A93. G. N. Schrauzer, ed., "Transition Metals in Homogeneous Catalysis." Dekker, New York, 1971. Contains detailed surveys of the use of organo-transition metal complexes as catalysts for a variety of reactions:
  93.1 G. N. Schrauzer: Catalysis: Fundamental aspects and scope, pp. 1–11 (13).
  93.2 J. Kwiatek: Hydrogenation and dehydrogenation, pp. 13–57 (209).
  93.3 W. Keim: π-Allyl systems in catalysis, pp. 59–91 (211).
  93.4 E. W. Stern: Homogeneous metal-catalyzed oxidation of organic compounds, pp. 93–146 (194).
  93.5 D. T. Thompson and R. Whyman: Carbonylation, pp. 147–222 (207).
  93.6 F. D. Mango and J. H. Schachtschneider: Catalysis of symmetry forbidden reactions, pp. 223–295 (74).
  93.7 R. G. Linck, Electron-transfer catalysis, pp. 297–380 (341).

Other Books Containing Articles of Relevance to Organometallic Chemistry

Included below is a summary of the relevant articles which have appeared in the MTP International Review of Chemistry, briefly referred to last year (see article 76.1).

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* Figures in parentheses indicate the number of references quoted in each article.

A76. MTP International Review of Science, Chemistry (Series One), Butterworth, London, 1972. Published in 33 volumes and three index volumes, covering Inorganic, Physical, and Organic Chemistry. Series one covers the period 1967–1971, and most articles relevant to this survey appear in the Inorganic Chemistry series.

Physical Chemistry (series one).

Volume 10, ed. J. M. Robertson, contains:

76.2 B. A. Frenz and J. A. Ibers: Structural chemistry of transition metal complexes: (1) Five-coordination; (2) Nitrosyl complexes.

Inorganic Chemistry (Series One).

Volume 1, ed. M. F. Lappert, contains:

76.3 R. Snaith and K. Wade: Carboranes and metallocarboranes.

Volume 2, eds. C. C. Addison and D. B. Sowerby, contains:

76.4 J. A. McCleverty: Metal complexes containing Group VIB donor atoms.

Volume 4, ed. B. J. Aylett, is entirely devoted to organometallic derivatives of the Main group elements.

Volume 6, ed. M. J. Mays, is the corresponding volume concerned with organo-transition metal chemistry, consisting of:

76.5 R. D. Johnston: Carbonyl and other carbon donor complexes.

76.6 A. T. T. Hsieh and M. J. Mays: Complexes containing transition metal-Group IIB metal bonds.

76.7 F. Glocking and S. R. Stobart: Organometallic complexes containing Group III (B to Tl) and Group IV (Si to Pb) ligands.

76.8 S. D. Robinson: Transition metal complexes containing phosphorus, arsenic, antimony and bismuth donor ligands.

76.9 M. Green: σ-Carbon to transition metal complexes.

76.10 R. D. W. Kemmitt: Olefin and acetylene complexes.

76.11 J. Powell: Organometallic complexes containing three-electron ligands.

76.12 J. M. Davidson: Complexes of transition metal ions in the homogeneous catalysis of organic reactions.

76.13 T. A. Stephenson: Metal compounds containing six-electron and seven-electron organic ligands.

Volume 9, ed. M. L. Tobe, contains:

76.14 E. L. Muetterties: Stereochemical nonrigidity.

76.15 A. J. Deeming: Oxidative addition.

Organic chemistry (series one).

Volume 5, ed. W. Parker, contains:

76.16 L. A. Paquette: Metal-catalyzed reactions in strained ring systems.

A94. D. L. Kepert, "The Early Transition Metals." Academic Press, New York, 1972. A critical review of the chemistry of the elements of Groups IV, V, and VI, which includes a short description of the organometallic chemistry of these elements.

A95. V. Balzani and V. Carassiti, "Photochemistry of Coordination Compounds." Academic Press, New York, 1970. Chapter 17, pp. 323–356: Carbonyl complexes, complexes containing π-bonding organic ligands, and dithizonate complexes (256).

A96. R. I. Reed, ed., "Recent Topics in Mass Spectrometry." Gordon & Breach, New York, 1971. Contains lectures given to a NATO Study Institute, 1969, including:

96.1 G. A. Junk and H. J. Svec: Mass spectrometry of ferrocenes and related complexes, pp. 85–126.

A97. G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists." Wiley (Interscience), New York, 1972. Chapter 6, pp. 136–148:

Ions, radicals and complexes (45), contains a 3-page summary of work on organometallic complexes.

A98. N. N. Greenwood and T. C. Gibb, "Mossbauer Spectroscopy." Chapman & Hall, London, 1971. Chapter 9, pp. 221–238: Covalent iron compounds (41), treats binary carbonyls, carbonyl anions, hydride anions, substituted iron carbonyls, ferrocene and other π-cyclopentadienyl iron derivatives.

A99. D. A. Long, A. J. Downs, and L. A. K. Staveley, eds., "Essays in Structural Chemistry" (presented to L. A. Woodward). Macmillan, New York, 1971, containing articles by:

99.1 M. J. Ware: Vibrational studies of metal–metal bonding, pp. 404–432 (49). Of its nature this chapter refers to many transition metal organometallics.

99.2 J. R. Hall: Infrared and Raman spectra of organometallic and related compounds, pp. 433–456 (59). Deals mainly with Main Group methyl derivatives, but one section concerns di- and trimethylplatinum(IV) compounds (see pp. 438–446).

A100. F. Basolo, J. F. Bennett, and J. Halpern, eds., "Collected Accounts of Transition Metal Chemistry." Updated collection of 29 articles (nine on organometallics) originally published in volumes 1–4 of *Accounts of Chemical Research.*

Aspects of Catalysis

The importance of organometallic catalysts is such that an increasing number of books have been written describing the various processes which use these materials. Some of the more recent include:

A101. M. L. Bender, "Mechanisms of Homogeneous Catalysis from Protons to Proteins." Wiley, New York, 1971. This general discussion includes reference to organometallics.

A102. F. Dawans, J. P. Duran, and P. Teyssié, "Stereospecific Polymerization by Derivatives of Transition Metals." CNRS, Paris, 1969.

A103. P. Sigivalt, "Study of the Reaction Mechanism of Homogeneous Phase Stereospecific Polymerisations." CNRS, Paris, 1971.

A104. D. V. Sokolskii, "Katalitícheskoe Gidrirovaniya Rastorakh" (Hydrogenation catalysts in solutions). Nauka Kaz. SSR, Alma-Ata, 1971. Mainly concerns metal carbonyl complex formation and activation of homogeneous catalysts.

A105. N. S. Imyanitov, ed., "Gidroformilirovanie" (Hydroformylation). Khimiya, Leningrad, 1972. Collection of review articles on the title subject, including:

105.1 D. M. Rudkovskii and N. S. Imyanitov: Trends in the search for modifiers affecting the ratios of isomeric aldehydes, pp. 5–13 (>49).

105.2 N. S. Imyanitov: Electronic concepts in catalysis with metal carbonyls, pp. 13–26 (>39).

105.3 N. S. Imyanitov: Ideas on the hydride nature of hydrogen in metal hydrocarbonyls, pp. 27–31 (16).

105.4 N. S. Imyanitov: Role of polynuclear hydrocarbonyls in catalysis, pp. 34–37 (13).

105.4 N. M. Bogoradovskaya and N. S. Imyanitov: Iron carbonyls as catalysts of reactions of organic compounds, pp. 138–146 (75).

A106. D. V. Sokol'skii, ed., "Homogeneous Catalysis by Coordination Compounds." Izd. 'Ilim,' Frunze, 1970. Proceedings of a Conference held in 1969. Volume 3 contains:
  106.1 N. P. Keier, A. I. Men'kov, and N. N. Kundo: Chelated complexes in homogeneous catalysis, pp. 113–130 (35).
  106.2 N. M. Emanuel, Z. K. Maizus, I. P. Skibida, and V. G. Vinogradova: Homogeneous catalysis by compounds of variable valence metals in liquid-phase oxidation, pp. 131–159 (49).
  106 3 A. Pomogailo: Modification of complex catalysts [Ziegler catalysts], pp. 240–258 (30).
  [Titles of other articles in these two books had not been located in *Chemical Abstracts* at the end of 1972.]

Bio-organometallic Chemistry

The previous summaries [see Appendices in references (*1*) and (*2*)] have listed review articles concerned with complexes of biological interest (Section 34) and molecular nitrogen complexes (including nitrogen fixation) (Section 42). As interest grows in these topics, several books have appeared, and some of the more recent include:

A107. J. M. Pratt, "Inorganic Chemistry of Vitamin B_{12}." Academic, New York, 1972. See Chapter 13, pp. 222–225: Formation and cleavage of Co—C and Co—S bonds.

A108. H. R. V. Arnstein, ed., "Cobalamins," The Glaxo Symposium 1970. Churchill, London, 1971.

A109. G. Eichhorn, ed., "Inorganic Biochemistry." Elsevier, Amsterdam, 1972. Topics covered include bio-inorganic chemistry of nitrogen fixation.

A110. J. R. Postgate, ed., "Chemistry and Biochemistry of Nitrogen Fixation." Plenum, New York, 1971.

A111. ACS Advances in Chemistry Series, No. 100 (1971), Bioinorganic Chemistry. Proceedings of a symposium at Blacksburg, Virginia, June 1970, edited by R. E. Dessy, J. Dillard, and L. Taylor.

B. Reviews

A list of important review articles which came to our attention up to the end of 1972 is included in the Appendix. The following volumes of hardcover collections of reviews appeared:

B1. *Advances in Inorganic Chemistry and Radiochemistry*, volumes 14 and 15 (1972).

B2. *Progress in Inorganic Chemistry*, ed. S. J. Lippard, volumes 15 and 16 (1972); ed. J. O. Edwards, volume 17 (1972), Inorganic Reaction Mechanisms, Part II (Part I is volume 13).

B3. *Advances in Organometallic Chemistry*, volume 11 (1973).

A43. *Organometallic Reactions*, volumes 3 and 4 (1972).

As mentioned above, the *Journal of Organometallic Chemistry* now includes the subject and annual review sections. Articles of the former type are listed in the Appendix; the annual surveys appeared in Volumes 41, 45, and 48 as follows:

Volume 41: M. I. Bruce: Organic reactions of selected π complexes (1971), pp. 277–304 (123).
Volume 45: D. J. Darensbourg: Chromium, molybdenum and tungsten (1971), pp. 257–334 (230).
A. Wojcicki: Manganese, technetium and rhenium (1971), pp. 335–387 (203).
B. W. Rockett and G. Marr: Ferrocene (1971), pp. 389–423 (198).
Volume 48: M. I. Bruce: Organometallic structures-transition metals (1971), pp. 303–350 (289).
J. A. McCleverty: Iron, ruthenium and osmium (1971), pp. 351–433 (312).

Further volumes of the Chemical Society's Specialist Periodical Reports have appeared, and their usefulness is now beyond question. The first volume of a new series, *Organometallic Chemistry*, surveys the literature of 1971. Main Group elements are covered Group by Group (with the exception of Group V), whereas organotransition metal chemistry is covered by treating the different types of complex formed. In this respect, the treatment contrasts with that given in *Annual Reviews of Organometallic Chemistry*. For 1971, over 2500 references are covered in a volume of some 500 pages. The contents are listed below (B6.3).

B6. Specialist Periodical Reports. The Chemical Society, London.
6.1 "Spectroscopic Properties of Inorganic and Organometallic Compounds," ed. N. N. Greenwood, vols. 4 (1971), 5 (1972). In contrast to the first three volumes, coverage is restricted to NMR, NQR, microwave, vibrational, and Mössbauer spectroscopy.
6.2 "Mass Spectrometry of Organic and Organometallic Compounds," ed. D. H. Williams, vol. 2 (1973) contains:
M. I. Bruce: Organometallic and coordination compounds, pp. 193–263 (524), from mid-1970 to March 1972.
6.3 "Organometallic Chemistry," eds. E. W. Abel and F. G. A. Stone, vol. 1 (1972), surveys the literature of 1971 in seventeen chapters:
B. C. Crosse: Group I: The alkali and coinage metals, pp. 1–16 (110).
B. C. Crosse: Group II: The alkaline earths and zinc and its congeners, pp. 17–39 (155).
J. P. Maher: Group III: Boron, aluminium, gallium, indium, and thallium, pp. 40–103 (269).
T. Onak: Group III: The carboranes, pp. 104–116 (129).
D. A. Armitage: Group IV: The silicon group, pp. 117–183 (357).
E. W. Abel and F. G. A. Stone: Metal carbonyls, pp. 184–193 (86).
J. D. Cotton: Organometallic compounds containing metal-metal bonds, pp. 194–227 (179).

R. J. Mawby: Substitution reactions of metal and organometal carbonyls with Group V and VI donor ligands, pp. 228–253 (165).
J. A. Connor: Carbene, nitrene, and related complexes, pp. 254–260 (43).
M. I. Bruce: Complexes containing metal–carbon σ bonds, pp. 261–297 (188).
M. A. Bennett: Hydrocarbon–metal π complexes, pp. 298–343 (204).
M. Green: π-Allylic complexes, pp. 344–365 (77).
R. J. Mawby: π-Cyclopentadienyl, arene and related compounds, pp. 366–387 (126).
M. I. Bruce: Substitution reactions of hydrocarbon–metal π complexes, pp. 388–430 (193).
M. Green: Oxidative-addition and related reactions, pp. 431–454 (94).
F. J. McQuillin: Homogeneous catalysis, pp. 455–467 (135).
R. F. Bryan: X-ray and electron diffraction studies of organometallic compounds, pp. 468–500 (255).

6.4 "Electronic Structure and Magnetism of Inorganic Compounds," ed. P. Day, vol. 1 (1972) covers ESR, electronic spectra and magnetic properties of ionic solids and coordination compounds, some parts of which were covered by early volumes of B6.1.

C. Primary Journals

The *Journal of the Chemical Society* now appears in six parts, as a result of the amalgamation of The Chemical Society and the Faraday Society (together with the Royal Institute of Chemistry). These are:

Chemical Communications (*J. Chem. Soc. Chem. Commun.*), the section for urgent publication.

Dalton Transactions (*J. Chem. Soc., Dalton Trans.*), structure and reactions of inorganic and most organometallic compounds, partially succeeding *J. Chem. Soc.* (*A*).

Perkin Transactions, I and II (*J. Chem. Soc., Perkin Trans. I and II*), are now the organic and physical organic chemistry sections, respectively, replacing *J. Chem. Soc.* (*C*) and (*B*), respectively.

Faraday Transactions, I and II (*J. Chem. Soc., Faraday I and II*), are the physical chemistry and chemical physics parts. The former replaces *Trans. Faraday Soc.*, whereas Part II is essentially a new journal.

Reviews relevant to organo-transition metal chemistry, which have appeared in the new-style *Journal of Organometallic Chemistry*, are listed in the Appendix.

D. Abstract Journals

The continual increase in size of *Chemical Abstracts* is matched by the impressive Collective Indexes, the eighth of which has been computer-produced for the first time. Running to 80,000 pages in 46 volumes, and covering the period 1967–1971, it is expected to be completed in 1973.

During the year, an interesting proposal was made for the publication of a new type of abstract journal, in which each paper accepted would be published in a fixed format on a single sheet (*4*). The full version of the paper would be stored on microfilm, which would be available as necessary.

E. Conference Reports

Published proceedings of international conferences which have recently appeared include:

E2.5 5ICOMC, Moscow, August 1971. The plenary and section lectures, edited by Z. N. Parnes, are collected in *Pure Appl. Chem.* **30**, 335–635 (1972).

E17. International Meeting on Boron Compounds, Castle Liblice, June 1971. The main lectures appear in *Pure Appl. Chem.* **29**, 492–595 (1972).

E18. Colloques Internationaux du Centre National de la Recherche Scientifique, No. 191, "La Nature et les Propriétées des Liaisons de Coordination." CNRS, Paris, 1970. Proceedings of a meeting held in October 1969, containing several articles of interest to organometallic chemists.

F. Synthesis and Techniques

Included for the first time in this section are books and surveys on spectroscopic techniques which are of great use to the organometallic chemist. In addition to the *Chemical Society Specialist Periodical Reports* on Spectroscopic Properties of Inorganic and Organometallic Compounds (B6.1) and Mass Spectrometry (B6.2), a series of Annual Reviews (volumes 1 or 2) or Reports (volume 3 onwards) on Nuclear Magnetic Resonance Spectroscopy contains surveys of ^{19}F or ^{31}P NMR results appertaining to organo-transition metal complexes.

F14. Annual Review (Reports) on NMR Spectroscopy, ed. E. F. Mooney, Academic Press, New York.
Volume 1 (1968) contains:
14.1 E. F. Mooney and P. H. Winson: Fluorine-19 Nuclear Magnetic Resonance Spectroscopy, pp. 243–311 (182), esp. pp. 280–293, Organometallics.
Volume 2 (1969) contains:
14.2 J. F. Nixon and A. Pidcock: Phosphorus-31 Nuclear Magnetic Resonance Spectroscopy of Coordination Compounds, pp. 345–422 (111).

Volume 3 (1970) contains:
- 14.3 K. Jones and E. F. Mooney: Fluorine-19 Nuclear Magnetic Resonance Spectroscopy, pp. 261–421 (410), esp. pp. 340–369, Organometallic and metalloid compounds.

Volume 4 (1971) contains:
- 14.4 K. Jones and E. F. Mooney: Fluorine-19 Nuclear Magnetic Resonance Spectroscopy, pp. 391–495 (237), esp. pp. 450–468, Organometallic compounds.

Volume 5A (1972) contains:
- 14.5 R. Fields: Fluorine-19 Nuclear Magnetic Resonance Spectroscopy, pp. 99–304 (513), esp. pp. 255–286, Transition metal complexes of fluorinated molecules.

F15. N. N. Greenwood, E. J. F. Ross, and B. P. Straughan, "Index of Vibrational Spectra of Inorganic and Organometallic Compounds," Volume 1, 1935–1960. Butterworth, London, 1972. This publication arose as a result of literature surveys carried out for B6.1. Compounds are arranged by molecular formula, and for each, the physical state, type of spectrum (IR, Raman, etc.), and range are listed.

G. Data Compilations

A further volume of Gmelin dealing with the transuranium elements has a chapter describing known organometallic derivatives.

G6. "Gmelin's Handbuch der anorganischen Chemie," 8th ed., Gmelin-Institut, Verlag Verlag Chemie, Weinheim/Bergstrasse.
- 6.3. Transurane Part C (New Supplement Series, volume 4) (1972), Chapter 19, F. Baumgärtner and B. Kanellakopulos: Metallorganische Verbindungen, pp. 271–279.

References

1. M. I. Bruce, *Advan. Organometal. Chem.* **10**, 273 (1972).
2. M. I. Bruce, *Advan. Organometal. Chem.* **11**, 447 (1973).
3. I. Haiduc, *J. Chem. Soc.* **12**, 175 (1972).
4. See B. F. Somerville, *Chem. Eng. News*, **50** (24), p. 16 (1972).

Appendix*

As in the previous articles, this Appendix collects together and classifies some 150 review articles which have appeared during 1972, together with some earlier ones recently brought to our notice. The same classification scheme has been used, with reference numbers following on, although new entries have not been made in all categories. Two new categories result from the large number of articles appearing in Sections 28 and 29.

46. Olefin isomerization and dismutation reactions
47. Hydroformylation and related reactions

Numbers follow those in the Appendices in references (1) and (2).

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* A separate author index to the Appendix can be found on p. 405.

Ref. No.	Authors	Reference	Title	No. of pages (No. of ref.)	Comments
1. *Historical and biographical*					
1.20	A. N. Nesmeyanov	*Advan. Organometal. Chem.* **10**, 1 (1972)	My way in organometallic chemistry	78 (455)	
1.21	A. N. Nesmeyanov	*Vestn. Akad. Nauk SSSR* **41**, 25 (1971)	Points in the growth of organic chemistry	17 (0)	Russ. Structures, polymerization, stereochemistry of organometallics, over last 20 years
1.22	T. Tsuruta	*Kagaku No Ryoiki* **26**, 283 (1972)	Organometallic chemistry	4	Japan. Development of organometallic chemistry
4. *Organo-element chemistry*					
4.49	G. T. Seaborg	*Pure Appl. Chem.* **30**, 539 (1972)	Recent advances in the chemistry of organometallic compounds of the actinide elements	11 (21)	Section lecture, 5ICOMC
4.50	M. L. H. Green	*Pure Appl. Chem.* **30**, 373 (1972)	Some organic chemistry of molybdenum and related topics	16 (77)	Section lecture, 5ICOMC
4.51	H. C. Lewis and B. N. Storhoff	*J. Organometal. Chem.* **43**, 1 (1972)	Organometallic chemistry of rhenium	49 (226)	
4.52	L. Smik and J. Jaluvka	*Chem. Listy* **66**, 727 (1972)	Organic π complexes of the iron triad carbonyls	18 (161)	Czech.
4.53	P. M. Maitlis	*Ann. N.Y. Acad. Sci.* **172**, 523 (1971)	Chemistry of some novel rhodium and iridium complexes	10 (19)	Author's work. Esp. C_5Me_5Rh, Ir compounds
4.54	H. Buchholz, P. Heimbach, H. J. Hey, H. Selbeck, and W. Wiese	*Coord. Chem. Rev.* **8**, 129 (1972)	Carbon–carbon bond formation with the aid of nickel catalysts	10 (33)	Ni-catalyzed cycloaddition reactions of 1,3-dienes
4.55	M. F. Semmelhack	*Org. React.* **19**, 115 (1972)	Formation of carbon–carbon bonds via π-allyl nickel compounds	84 (110)	

Continued

Ref. No.	Authors	Reference	Title	No. of pages (No. of ref.)	Comments
4.56	J. F. Normant	*Synthesis* 63 (1972)	Organocopper(I) compounds and organocuprates in synthesis	18 (142)	
4.57	G. H. Posner	*Org. React.* **19**, 1 (1972)	Conjugate addition reactions of organocopper reagents	113 (204)	
5. *Metal carbonyls*					
5.17	C. W. Bradford	*Platinum Metals Rev.* **16**, 50 (1972)	Carbonyls of the platinum group metals	6 (20)	
5.18	M. I. Bruce	*J. Organometal. Chem.* **44**, 209 (1972)	Carbonyl chemistry of the Group IB metals	18 (121)	
5.19	I. S. Molnar	*Prot. Vitae* **16**, 205 (1971)	Significance of the constitutional nature of nickel carbonyls and their π-complex derivatives in poisonings and cancerogenesis	5 (32)	Acute and chronic toxic and cancerogenic effects of $Ni(CO)_4$ on humans
5.20	M. Nakayama	*Yuki Gosei Kagaku Kyokai Shi* **30**, 649 (1972)	New reagent—nickel tetracarbonyl	5 (30)	Japan. Reactions with organic compounds
5.21	R. Rosenfeld	*Plyn* **52**, 11 (1972)	Undesirable iron pentacarbonyl formation	4 (11)	Czech. Removal of carbonyls from town gas after storage
5.22	D. F. Shriver	*Chem. Brit.* **8**, 419 (1972)	New bonding patterns for the carbonyl ligand	3	
5.23	D. F. Shriver and A. Alich	*Coord. Chem. Rev.* **8**, 15 (1972)	The reaction of metal carbonyls with Lewis acids—carbon- and oxygen-bonded CO	6 (14)	
9. *Metal carbonyl hydrides*					
9.13	J. P. Jesson	*Du Pont Innovation* **4**, 8 (1972)	Stereochemistry of transition metal hydrides	5 (0)	PMR of H_2RhClP_3, etc.

9.14	H. D. Kaesz and R. B. Saillant	*Chem. Rev.* **72**, 321 (1972)	Hydride complexes of the transition metals	51 (395)	
9.15	L. Vaska and M. F. Werneke	*Ann. N.Y. Acad. Sci.* **172**, 546 (1971)	Activation of molecular hydrogen by metal complexes. Mechanism and some controlling factors	17 (52)	

11. *Compounds containing bonds between Transition Metals (including cluster compounds)*

11.19	P. Chini, A. Cavalieri, and S. Martinengo	*Coord. Chem. Rev.* **8**, 3 (1972)	Mixed cluster carbonyl anions containing nickel and cobalt	11 (41)	
11.20	R. B. King	*Progr. Inorg. Chem.* **15**, 287 (1972)	Transition metal cluster compounds	187 (382)	
11.21	D. V. Korol'kov	*Zh. Vses. Khim. Obshchest.* **17**, 316 (1972)	Nature of metal–metal bonds in transition element clusters	6 (60)	Russ.
11.22	C. I. Lepadatu	*Stud. Cercet. Chim.* **20**, 517 (1972)	Theory of cluster molecule stabilisation	5 (15)	Rom.
11.23	Y. Sasaki	*Kobutsugaku Zasshi* **10**, 141 (1971)	Coordination compounds with metal–metal bonds	11 (13)	Japan.
11.24	T. W. Thomas and A. E. Underhill	*Chem. Soc. Rev.* **1**, 99 (1972)	Metal–metal interactions in transition metal complexes containing infinite chains of metal atoms	22 (70)	Few organometallic examples
11.25	K. Yasufuku and H. Yamazaki	*Kagaku No Ryoiki* **25**, 1022 (1971)	Synthesis of mixed transition metal clusters	13 (129)	Japan.

13. *Lewis Base complexes—Group V donor atoms*

13.11	A. J. Carty	*Organometal. Chem. Rev., Sect. A* **7**, 191 (1972)	Organometallic complexes from organonitrogen derivatives containing N—N bonds	53 (152)	
13.12	M. Kilner	*Advan. Organometal. Chem.* **10**, 115 (1972)	Nitrogen groups in metal carbonyl and related complexes	84 (471)	
13.13	R. B. King	*Accounts Chem. Res.* **5**, 177 (1972)	Some recent studies on poly(tertiary phosphines) and their metal complexes	9 (32)	

Continued

Ref. No.	Authors	Reference	Title	No. of pages (No. of ref.)	Comments
13.14	W. Levason and C. A. McAuliffe	*Advan. Inorg. Chem. Radiochem.* **14**, 173 (1972)	Transition metal complexes containing bidentate phosphine ligands	81 (315)	
13.15	L. Malatesta and S. Cenini	*Chim. Ind.* (*Milan*) **53**, 1047 (1971)	Chemistry of coordination compounds. Coordination bonding	13 (11)	Ital. Low valent metal phosphine complexes
13.16	P. Rigo and A. Turco	*Coord. Chem. Rev.* **8**, 175 (1972)	Chemistry of phosphine-cyanide complexes of transition metals	10 (35)	
13.17	S. Trofimenko	*Chem. Rev.* **72**, 497 (1972)	Coordination chemistry of pyrazole-derived ligands	13 (179)	
14. *Lewis Base complexes—Group VI donor atoms*					
14.12	G. N. Schrauzer	*ACS, Advan. Chem. Ser.* **110**, 73 (1972)	Recent advances in the chemistry of transition metal complexes of unsaturated bidentate sulphur donor ligands (metal dithienes)	19	
15. *Metal–carbon σ-bonds*					
15.24	R. J. Angelici	*Accounts Chem. Res.* **5**, 335 (1972)	Carbamoyl and alkoxycarbonyl complexes of transition metals	7 (68)	
15.25	G. Costa	*Pure Appl. Chem.* **30**, 335 (1972)	The effect of the nature of ligands on the reactivity of the metal–carbon bond in cobalt chelates	18 (61)	Section lecture, 5ICOMC
15.26	G. Costa	*Coord. Chem. Rev.* **8**, 63 (1972)	Recent developments in the field of organometallic derivatives of cobalt chelates	13 (47)	
15.27	D. R. Fahey	*Organometal. Chem. Rev., Sect. A* **7**, 245 (1972)	σ-Bonded hydride and carbon derivatives of nickel	50 (140)	

15.28	K.-H. Thiele	*Pure Appl. Chem.* **30**, 575 (1972); *Usp. Khim.* **41**, 1180 (1972)	A contribution to the chemistry of organotransition metal halides	11 (14)	Section lecture, 5ICOMC
15.29	M. Hancock, M. N. Levy, and M. Tsutsui	*Organometal. React.* **4**, 1 (1972)	σ-π Rearrangements of organo-transition metals	72 (137)	
15.30	G. Wilkinson	*Pure Appl. Chem.* **30**, 627 (1972)	The transition metal-to-carbon σ bond	9 (39)	Section lecture, 5ICOMC
15.31	Y. Yamamoto and H. Yamazaki	*Coord. Chem. Rev.* **8**, 225 (1972)	Isocyanide insertion and related reactions	15 (47)	
16. *Fluorocarbon complexes*					
16.14	F. G. A. Stone	*Pure Appl. Chem.* **30**, 551 (1972)	The role of fluorocarbons in oxidative-addition and elimination reactions	23 (73)	Plenary lecture, 5ICOMC
18. *Hydrocarbon π-complexes—general reviews*					
18.8	A. Z. Rubezhov and S. P. Gubin	*Advan. Organometal. Chem.* **10**, 347 (1972)	Ligand substitution in transition metal π-complexes	71 (290)	
19. *Hydrocarbon π-complexes—olefins and acetylenes*					
19.22	P. M. Maitlis	*Pure Appl. Chem.* **30**, 427 (1972)	The oligomerisation of acetylenes induced by metals of the nickel triad	22 (67)	Section lecture, 5ICOMC
19.23	R. S. Nyholm	*Pure Appl. Chem.* **27**, 127 (1971)	Synthesis, structure and reactions of chelate metal–olefin complexes	18 (17)	Plenary lecture, 13ICCC
19.24	L. D. Pettit and D. S. Barnes	*Fortschr. Chem. Forsch.* **28**, 85 (1972)	Stability and structures of olefin and acetylene complexes of transition metals	55 (153)	
22. *Hydrocarbon π-complexes—cyclopentadienyl and arene*					
22.17	K. W. Barnett and D. W. Slocum	*J. Organometal. Chem.* **44**, 1 (1972)	Cyclopentadienyl complexes of chromium, molybdenum, and tungsten	37 (230)	

Continued

Ref. No.	Authors	Reference	Title	No. of pages (No. of ref.)	Comments
22.18	G. Marr and B. W. Rockett	*Educ. Chem.* **9**, 134 (1972)	Aromatic complexes of transition elements	4 (13)	
22.19	E. G. Perevalova and T. V. Nikitina	*Organometal. React.* **4**, 163 (1972)	Reactions of bis(π-cyclopentadienyl) transition metal compounds	257 (49)	
22.20	M. D. Rausch	*Pure Appl. Chem.* **30**, 523 (1972)	Recent studies in metal-cyclopentadienyl and metal-arene chemistry	16 (21)	Plenary lecture, 5ICOMC
22.21	H. Werner	*Fortschr. Chem. Forsch.* **28**, 141 (1972)	Ring ligand displacement reactions of arene metal complexes	41 (166)	
25. *Organic chemistry of metallocenes*					
25.49	B. Floris, G. Illuminati, P. E. Jones, and G. Ortaggi	*Coord. Chem. Rev.* **8**, 39 (1972)	Electron-donor properties of ferrocene	5 (35)	Basicity, α-protonation, electrophilic reactivity
26. *Metallocarborane complexes*					
26.7	M. F. Hawthorne	*Pure Appl. Chem.* **29**, 547 (1972)	Recent developments in the chemistry of polyhedral complexes derived from metals and carboranes	21 (32)	Main lecture, Int. Meeting Boron Compounds, Castle Liblice
26.8	M. F. Hawthorne and G. B. Dunks	*Science* **178**, 462 (1972)	Metallocarboranes that exhibit novel chemical features	10 (65)	Molecular rearrangements, polyhedral expansion and contraction
26.9	E. L. Muetterties	*Pure Appl. Chem.* **29**, 585 (1972)	*nido*-Metalloboranes	11 (26)	Main lecture, Int. Meeting Boron Compounds, Castle Liblice
26.10	L. J. Todd	*Pure Appl. Chem.* **30**, 587 (1972)	Recent developments in the study of carboranes	12 (27)	Section lecture, 5ICOMC

28. *Organic synthesis via organometallics*

28.43	H. W. Quinn	*Progr. Separ. Purif.* **4**, 133 (1971)	Hydrocarbon separations with silver(I) systems	37 (74)	
28.44	J. Tsuji	*Yukagaku* **15**, 297 (1966)	Organic synthesis by means of metal carbonyls		Japan.
28.45	J. Tsuji	*Yuki Gosei Kagaku Kyokai Shi* **25**, 984 (1967)	Synthetic reactions using palladium compounds	15 (138)	Japan.
28.46	J. Tsuji	*Yuki Gosei Kagaku Kyokai Shi* **22**, 884 (1964)	Organic synthesis by means of noble metal compounds	15 (95)	Japan.
28.47	J. Tsuji	*Kagaku (Kyoto)* **22**, 930 (1967)	Organic synthetic reactions using transition metal complexes	14 (89)	Japan.
28.48	J. Tsuji	*Fortschr. Chem. Forsch.* **28**, 41 (1972)	Organic synthesis by means of transition metal complexes—general patterns	44 (173)	
28.49	J. Tsuji and M. Hara	*Kagaku Kogyo* **21**, 496 (1970)	Organic synthesis using metal complexes	7 (28)	Japan.
28.50	J. Tsuji and K. Ohno	*Kagaku No Ryoiki, Zokan* **89**, 120 (1970)	Decarbonylation reactions		Japan.
28.51	S. Tsutsumi and M. Ryang	*Kagaku Kogyo* **23**, 481 (1972)	Organic synthesis by anionic carbonyl metal complexes	9 (27)	Japan Using $Ni(CO)_4$

29. *Catalysis by organometallics*

29.45	C. W. Bird	*Top. Lipid Chem.* **2**, 247 (1971)	Olefin reactions catalysed by transition metal compounds	35 (135)	
29.46	C. W. Bird	*Chem. Ind. (London)* 520 (1972)	Palladium-catalysed reactions in synthetic organic chemistry	3 (17)	
29.47	A. J. Chalk	*Ann. N.Y. Acad. Sci.* **172**, 533 (1971)	Olefin hydrosilation catalysed by Group VIII metal complexes	8 (35)	

Continued

Ref. No.	Authors	Reference	Title	No. of pages (No. of ref.)	Comments
29.48	G. Deak	*Magy. Kem. Lapja* **27**, 237 (1972)	Application of coordination compounds in organic syntheses	9 (34)	Hung.
29.49	P. M. Henry	*Ann. N.Y. Acad. Sci.* **172**, 483 (1971)	Mechanisms of palladium(II)-catalysed reactions	24 (67)	
29.50	R. Jira and W. Freiesleben	*Organometal. React.* **3**, 1 (1972)	Olefin oxidation and related reactions with Group VIII noble metal compounds	190 (>570)	
29.51	W. Kitching	*Organometal. React.* **3**, 319 (1972)	Oxymetallation	80 (188)	
29.52	J. Krepelka and J. Zachoval	*Chem. Listy* **66**, 673 (1972)	Catalytic properties of metals of Group VIII	20 (82)	Czech.
29.53	V. Macho	*Petrochemia* **10**, 3 (1970)	Application of laboratory results to homogeneous catalysis in practice	20 (30)	Slovak. Catalyst regeneration, effects of impurities
29.54	L. R. Linarte	*Rev. Inst. Mex. Petrol.* **4**, 63 (1972)	Homogeneous and heterogeneous catalysis with transition metal complexes	4 (33)	Span.
29.55	R. J. Kokes	*Catal. Rev.* **6**, 1 (1972)	Aspects of catalysis	20 (30)	P. H. Emmett Award Address. Olefin hydrogenation, isomerization, oxidation
29.56	J. Manassen	*Platinum Metals Rev.* **15**, 142 (1971)	Homogeneous catalysis with macromolecular ligands	2	Resin-bonded catalysts
29.57	J. Manassen	*Fortschr. Chem. Forsch.* **25**, 1 (1972)	The catalytic activity of organic and metallo-organic compounds in heterogeneous systems	38 (134)	pp. 28–31: Reaction types catalyzed by metals
29.58	J. Masek	*Chem. Listy* **66**, 128 (1972)	Reactivity of coordinated ligands and homogeneous catalysis	21 (42)	Czech.

29.59	P. Radu and F. Glatz	*Rev. Fiz. Chim., Ser. A* **8**, 441 (1971)	Complex compounds as hydrogenation catalysts	8	Rom.
29.60	Y. Saito	*Denki Kagaku* **40**, 175 (1972)	Homogeneous catalysis. Oxidation and reduction	7 (76)	Japan.
29.61	E. W. Stern	*Ann. N.Y. Acad. Sci.* **172**, 516 (1971)	Homogeneous catalysis. Applications and implications	7 (38)	Pd-catalyzed reactions
29.62	W. Strohmeier	*Fortschr. Chem. Forsch.* **25**, 71 (1972)	Homogeneous catalytic hydrogenation with Group VIII metal complexes	34 (63)	Carbonyl phosphine complexes
29.63	P. Teyssié	*Mem. Soc. Roy. Sci. Liege, Collect. 8th* **1**, 89 (1971)	Mechanisms and applications of catalysis by coordination complexes in polymerisation and organic synthesis	15 (15)	
29.64	J. Tsuji	*Kagaku* (*Kyoto*) **27**, 292, 382 (1972)	Wilkinson complexes		Japan.
29.65	G. J. M. van der Kerk	*DECHEMA* (*Deut. Ges. Chem. Apparatewesen*), *Monogr.* **68**, 75 (1971)	Organometallic compounds as homogeneous catalysts	31 (20)	
29.65	A. Vizi Orosz and L. Marko	*Magy. Kem. Lapja* **27**, 253 (1972)	Homogeneous catalytic hydrogenation in organic chemistry	7 (93)	Hung.
29.66	M. E. Vol'pin	*Z. Chem.* **12**, 361 (1972)	Some problems of homogeneous catalysis with transition metal compounds	9 (21)	

30. *Organometallic polymerization catalysts*

30.30	H. Hashimoto	*Senryo To Yakuhin* **17**, 198 (1972)	Transition metal-catalysed reactions with special reference to effects of ligands on butadiene oligomerisation	11 (29)	Japan.

Continued

Ref. No.	Authors	Reference	Title	No. of pages (No. of ref.)	Comments
30.31	S. L. Kapoor	*Petrol. Hydrocarbons* **6**, 161 (1971) [publ. in *Chem. Age India* **22** (11) (1971)]	Polymerisation with Ziegler-Natta catalysts	2 (0)	
30.32	G. Henrici-Olivé and S. Olivé	*Chem. Ing. Tech.* **43**, 906 (1971)	Olefin polymerisation with transition metal catalysts	9 (14)	
30.33	A. I. Makhin'ko and V. P. Konovalov	*Tr. Inst. Khim. Nefti Privr. Solei, Akad. Nauk Kaz. SSR* **2**, 130 (1970)	Mechanism of Ziegler polymerization	12 (50)	Russ.
30.34	Y. Mizuno	*Sekiyu To Sekiyo Kagaku* **16**, 113 (1972)	Patents on polymerisation catalysts for synthetic rubber. I. Polymerisation catalysts for butadiene. (i) Titanium polymerisation catalysts	3 (21)	Japan.
30.35	J. Ulbricht	*Plaste Kaut.* **19**, 162 (1972)	Mechanism of Ziegler-Natta polymerisation	7 (13)	
32. *Ligand reactivity in complexes*					
32.7	P. Souchay	*Bull. Soc. Chim. Fr.* 4121 (1972)	Influence of coordination on reactivity of organic compounds	22 (169)	
34. *Organometallic complexes of biological interest*					
34.7	V. Fica and G. Panaitescu	*Fiziol. Norm. Patol.* **17**, 301 (1972)	Present aspects of normal and pathologic physiology of cyanocobalamin metabolism	12 (73)	Rom. 1965–1970
34.8	A. Gajdos	*Presse Med.* **79**, 1849 (1971)	Biochemistry of vitamin B_{12}	4	

34.9	G. C. Perri	*Acta Vitaminol. Enzymol.* **25**, 101 (1971)	Physiological actions of vitamin B_{12}	21 (91)	Ital.
34.10	J. M. Wood and D. G. Brown	*Struct. Bonding (Berlin)* **11**, 47 (1972)	The chemistry of vitamin B_{12}-coenzymes	59 (146)	
35. *Electronic structures of organometallic complexes*					
35.13	P. S. Braterman	*Struct. Bonding (Berlin)* **10**, 57 (1972)	Spectra and bonding in metal carbonyls. A. Bonding	30 (110)	Nature of M—C, M—M bonds
35.14	G. Häfelinger	*Fortschr. Chem. Forsch.* **28**, 1 (1972)	Theoretical considerations for cyclic (pd) π systems	39 (129)	
35.15	F. R. Hartley	*Angew. Chem.* **84**, 657 (1972); *Angew. Chem., Int. Ed. Engl.* **11**, 596 (1972)	Metal-olefin and -acetylene bonding in complexes	11 (88)	
35.16	R. Mason	*Chem. Soc. Rev.* **1**, 431 (1972)	Valence in transition metal complexes	14 (52)	Chem. Soc. Tilden Lecture
35.17	T. Tanaka	*Kagaku (Kyoto)* **26**, 354 (1971)	Bonds of organometallic compounds	5 (31)	M—C bonds, stereochem. non-rigidity
35.18	C. A. Tolman	*Chem. Soc. Rev.* **1**, 337 (1972)	The 16- and 18-electron rule in organometallic chemistry and homogeneous catalysis	17 (90)	Reassessment of EAN rule
36. *Physical methods—infrared spectroscopy*					
36.10	S. F. A. Kettle and I. Paul	*Advan. Organometal. Chem.* **10**, 199 (1972)	Infrared intensities of metal carbonyl stretching vibrations	38 (138)	

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Ref. No.	Authors	Reference	Title	No. of pages (No. of ref.)	Comments
38. *Physical methods—mass spectrometry*					
38.6	M. J. Lacey and J. S. Shannon	*Org. Mass Spectrom.* **6**, 931 (1972)	Valence-change in the mass spectra of metal complexes	7 (26)	
38.7	J. Müller	*Angew. Chem.* **84**, 725 (1972); *Angew. Chem., Int. Ed. Engl.* **11**, 653 (1972)	Decomposition of organometallic complexes in the mass spectrometer	13 (112)	
38.8	T. Sata, Y. Ito, and T. Sasamoto	*Seramikkusu* **6**, 692 (1972)	Applications of mass spectrometry for inorganic materials	7 (31)	Japan.
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40.13	B. P. Biryukov and Y. T. Struchkov	*Itogi Nauki, Kristallokhim.* **7**, 142 (1971)	Structural chemistry of π complexes of transition metals with carbonyl ligands II. Carbonyl π complexes with metal–metal bonds	98 (247)	Russ.

40.14	C. Krüger	*Angew. Chem.* **84**, 412 (1972); *Angew. Chem., Int. Ed. Engl.* **11**, 387 (1972)	Automated X-ray structure determination as an analytical method	6 (23)	Several organometallics discussed
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42.30	Y. G. Borod'ko, A. E. Shilov, K. Isaka, Y. Takano, and A. Yamamoto	*Kagaku (Tokyo)* **26**, 234, 369, 535 (1971)	Complexes of molecular nitrogen	7+9 +8 (156)	Japan.
42.31	J. Chatt	*Bull. Soc. Chim. Fr.* 431 (1972)	Some aspects of the biology and chemistry of nitrogen fixation	5 (3)	
42.32	J. Chatt and G. J. Leigh	*Chem. Soc. Rev.* **1**, 121 (1972)	Nitrogen fixation	14 (37)	Chem. Soc. Liversidge Lecture
42.33	J. Fergusson and J. L. Love	*Rev. Pure Appl. Chem.* **20**, 33 (1970)	A survey of dinitrogen complexes of the transition metals	18 (93)	

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42.35	B. Jezowska-Trzebiatowska and P. Sobota	*Wiad. Chem.* **26**, 229 (1972)	Catalytic fixation of molecular nitrogen by complexes of transition metals	14 (28)	Pol.
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42.40	M. E. Vol'pin	*Zh. Vses. Khim Obshchest.* **17**, 396 (1972)	Reactions of organometallic compounds of transition metals with nitrogen and carbon dioxide	7 (28)	Plenary Lecture, 5ICOMC
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44.3	F. A. Cotton and C. M. Lukehart	*Progr. Inorg. Chem.* **16**, 487 (1972)	Transition metal complexes containing carbenoid ligands	127 (139)	

44.4	E. O. Fischer	*Pure Appl. Chem.* **30**, 353 (1972); *Usp. Khim.* **41**, 1161 (1972)	Recent aspects of transition metal carbonyl carbene complexes	20 (28)	Plenary lecture, 5ICOMC

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46.7	J. Tsuji	*Kagaku No Ryoiki, Zokan* **89**, 169 (1970)	Reactions with C—C bond scission	16	Japan. Olefin disproportionation

47. *Hydroformylation and related reactions*

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47.3	M. Orchin and W. Rupilius	*Catal. Rev.* **6**, 85 (1972)	On the mechanism of the oxo reaction	47 (79)	Using $HCo(CO)_4$
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47.7	M. Pribanic	*Kem. Ind.* **20**, 151 (1971)	Homogeneous catalysis by coordination compounds. II. Industrial use	6 (4)	Croat. Oxo reaction, Wacker-Höchst process
47.8	A. Rosenthal	*Advan. Carbohyd. Chem.* **23**, 59 (1968)	Applications of the oxo reaction to some carbohydrate derivatives	56 (112)	
47.9	M. Yamaguchi and K. Tano	*Sekiyu Gakkai Shi* **15**, 206 (1972)	Synthesis of carboxylic acids by carbonylation of olefins	5 (19)	Japan.

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[1] Author Index for appendix (pp. 389-404) to the article "The Literature of Organo-Transition Metal Chemistry 1972" by M. I. Bruce.

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Numbers in parentheses are reference numbers and indicate that an author's work is referred to although his name is not cited in the text. Numbers in italics show the page on which the complete reference is listed.

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