ORGANOMETALLIC COMPOUNDS

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I. Introduction

A. CONCEPT OF THE CARBON-METAL BOND

1. *Metallic Character*

Classically organometallic chemistry is considered to deal with substances containing a direct carbon-metal bond. The scope of this field, how-

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ever, expands as the definition of a metallic element is liberalized. If both physical properties such as high thermal and electrical conductivity, remarkable cohesiveness and luster, and chemical characteristics understood under the term "base-former," are considered to define metallic character, probably three-fourths of the elements have acceptable metallic credentials. The demarcation between organometallic compounds and certain excluded types, therefore, is bound to be hazy if based upon such a general notion of metallic character, and the distinction can only become sharp by arbitrary selection of "typical" metals. Certain organometalloid compounds, such as of boron, silicon, arsenic, selenium, tellurium, and even iodine, exhibit some behavior reminiscent of organometallic types, and their consideration in organometallic chemistry can be justified by the more general treatment of the elements thus achieved. However, divergence from typical organometallic character is to be expected of such metalloid types for two reasons. First, since the carbon-metal bond owes its reactivity in part to the difference in the electron-attracting tendencies of the atoms involved, the diminished polarity of the carbon-metalloid bond will be reflected in its lessened reactivity. Second, reactions typical of organometallic compounds such as rapid oxidation, facile cleavage by protic agents, and complex formation seem to require unfilled electronic orbitals in the metallic atom of the carbon-metal bond. That certain organic derivatives of the metalloids and nonmetals (Groups IVA–VIIA) have no low-lying unfilled orbitals rationalizes their inertness toward Lewis bases and oxidation of their carbon-element bond. For the purposes of organometallic chemistry it may be useful to define an organometallic compound in electronic terms; that is, as one containing carbon σ-bonded to a more electropositive element which has available low-lying p-orbitals in the combined state. By way of illustration this definition would include boron alkyls, but exclude silicon and arsenic alkyls, as the former has an electronic sextet about boron, whereas in the latter two the metalloid atoms possess octets.[1]

2. Evolving Concept of the Chemical Bond

A sustaining influence on the growth of organometallic chemistry has been the recognition of the variegated nature of the carbon-metal bond. Indeed, from its inception with the study of zinc alkyls by Frankland (*39*) in 1849 organometallic chemistry has contributed consistently and significantly to valence theory. Frankland's notion of valence as a fixed number,

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[1] Although silicon has available $3d$-orbitals, and arsenic available $4d$- and $4f$-orbitals, these are higher in energy. The electronic definition would limit the term organometallic compound to those alkyls of Groups I to III and to any transition metal alkyl containing a σ-carbon-metal bond. The common feature of these alkyls would be the availability of np-orbitals on the metal atom.

Gomberg's and Paneth's (*43*) studies of free organic radicals, the bridge structure of metal alkyls (*103*), the organic sandwich complexes of the transition metals (*71*, *86*), all have in their turn spurred the theory of the chemical bond on to fresh viewpoints.

Almost every recognized bond type finds its counterpart in organometallic chemistry. To the traditional ionic and covalent carbon-metal bonds involving outer *s*- and *p*-orbitals of the metal have been added the aromatic-transition metal π-complexes, where, for example, π-electrons of the cyclopentadienyl anion, the benzene system, or the cycloheptatrienyl cation help bind the organic moiety to the transition metal by utilization of the latter's *d*-orbitals. These new organometallic π-complexes in general do not exhibit the properties of ordinary organometallic compounds. In addition, the π-bonding involves at least several carbon atoms in relation to one metal atom, so that the concept of an isolated carbon-metal bond becomes less meaningful. Finally, the vigorous research devoted to such π-complexes in recent years combines with the above-mentioned factors to make their consideration in a separate chapter desirable (see Vol. 1, of this series, Chapter 2 by Prof. E. O. Fischer and Dr. H. P. Fritz).

B. General Characteristics of Organometallic Compounds

To place the recent advances in organometallic chemistry in proper perspective and to serve as an introduction to the chemist unfamiliar with this branch of chemistry, it is thought desirable to indicate here the salient features of traditional organometallic chemistry. The reader desiring further details may consult any of several excellent references (*24*, *72*, *76*, *101*).

1. *Organometallic Bonding*

a. Ionic Type. By an ionic organometallic compound is meant that in which the carbon atom in the organic moiety is anionic in character and is attracted to the metal cation in a nondirectional, electrostatic fashion. A close analogy to ionic metal alkyls is the alkali halide. The phenomena associated with electrostatic bonding in the latter case, such as formation of electrolyte solutions, high melting point, and insolubility in nonsolvating solvents are encountered with the alkyls of sodium, potassium, rubidium, and cesium. The sodium alkyls, $R^{\ominus}Na^{\oplus}$, thus are nonvolatile, generally colorless solids which are insoluble in hydrocarbons and which will decompose before melting. Their violent reaction with protic solvents prevents observation of electrical conductivity in these solutions, but solutions in diethylzinc are electrolytes.

Factors favoring the ionization of the carbon-metal bond are a high electropositivity of the metal as in alkali and alkaline earth alkyls and the formation of a carbanion of some stability, for example,

$$R{-}C{\equiv}C^{\ominus} \quad \text{and} \quad CH_2{=}CH{-}CH_2^{\ominus}.$$

The former, an acetylenic anion, is stabilized by the increased electronegativity of *sp*-hybridized carbon and the latter, the allyl anion, by the π-delocalization of the negative charge.

b. Covalent Type. The majority of organometallic compounds possesses a directed, though polar, covalent bond between the carbon and metal atoms. This implies that the electron cloud representing the position probability of the electron pair is denser about the carbon atom. The degree of unequal sharing of the electron pair in the σ-bond,

$$\overset{\delta-}{C}{-}\overset{\delta+}{M},$$

is assessed by reference to empirically established electronegativity scales whose values seek to assign relative electron-seeking tendencies to the elements. Although there is some disagreement among the various scales proposed, the values in general increase with electron-attracting or nonmetallic character. Typical values from the widely accepted Pauling scale range from 0 to 4: Cs, 0.7; Ba, 0.8; Mg, 1.2; Al, 1.5; B, 2.0; C, 2.5; and F, 4.0. Suggested relationships exist for converting electronegativity differences between the carbon and metal atom into "partial ionic character" percentages (*101*). Such measures of carbon-metal bond polarity present a useful semiquantitative tool for correlating chemical reactivity with structure. Other factors, however, such as available metal orbitals, steric demands, and electron cloud polarizability often must be given explicit consideration (Section IV.A).

With the directional covalent bonding occurring in this class of organometallic compounds the molecular unit and hence molecular structure become distinct and meaningful. Since such molecular units have polar bonds, however, intermolecular forces often cause extensive association. Trimethylaluminum, for example, exists as a stable dimer, $[Al(CH_3)_3]_2$ and others exist as polymers (Section III.A).

c. Transition Metal d-Orbital Complexes. The enhanced stability and unique properties of this class of compounds point to a distinct variety of covalent bonding. Transition metals, that is, elements with unfilled (n-1) d-orbitals, tend to form stable complexes with various unsaturated organic systems, although they yield only unstable organometallic compounds of the conventional type. These π-complexes seem to involve sharing between the unsaturated system's π-orbitals and the unfilled d-orbitals of the transition metal. Besides the aromatic types already mentioned in Section I.A.2, complexes with olefins, acetylenes, and dienes have been characterized.

d. Borderline and Excluded Classes. The admittance of the above transition metal complexes as a branch of organometallic chemistry reopens the question of whether certain metallic derivatives of organic systems are not also qualified to be included. If the delocalized cyclopentadienyl anion is a fitting moiety for an organometallic compound, then one would ask whether an enolate-anion, containing some of the negative charge on carbon, is not also acceptable. Perhaps the recognition of two main branches of organometallic compounds would resolve the difficulty: on the one hand, classical organometallic compounds, as delineated above; on the other hand, organometallic π-complexes involving organic π-electron donors (without regard for carbon-metal bonds) and metal atom acceptors (compare Section I.A.2). Enolate salts could be included in this latter group, as could any organic type possessing unshared electron pairs which could assume π-donor bond character:

$$R-\ddot{A}-M \leftrightarrow R-\overset{\oplus}{A}=\overset{\ominus}{M}.$$

This would embrace alkoxides (ROM), carboxylate salts (RCOOM), amides (R_2NM) and other similar metallic salts of acidic organic compounds. Classical organometallic chemistry would then limit itself to those compounds containing a direct σ-bond between carbon and a metal.

2. Chemical Properties

a. Reactivity of the Carbon-Metal Bond. The most characteristic feature of the carbon-metal bond is the ease with which it gives way to C-C, C-H, C-O, C-X bonds on the one hand, and M-X, M-O and M-N bonds on the other hand. Consequently, organometallic compounds generally are reactive toward various inorganic and organic reagents. This might be summarized by pointing out that many organometallic compounds are spontaneously flammable in air, decompose upon relatively mild heating, hydrolyze readily and tend to add to unsaturated organic compounds. Their great reactivity has long made them unexcelled synthetic tools in the laboratory. Although any one chemical reaction is probably not sufficiently unique to characterize a carbon-metal bond, the presence of a carbon-metal bond in a given substance can usually be ascertained if several of the following reactions are observed.

b. Behavior toward Inorganic Reagents. (1) Oxygen. The most arresting property of many organometallic compounds is their strongly exothermic oxidation in air. Alkyls of alkali, alkaline earth, and boron families usually generate sufficient heat in oxidizing to catch fire. As illustrated for the dimer of triethylaluminum controlled oxidation in the absence of moisture, however, leads to the formation of an alkoxide:

$$[Al(C_2H_5)_3]_2 + 3O_2 \rightarrow [Al(OC_2H_5)_3]_2 + \text{heat}. \tag{1}$$

(2) Hydrogen. Hydrogen, on the other hand, can cleave many carbon-metal bonds smoothly with the formation of the corresponding hydrocarbon and metal hydride. In a remarkable example of such hydrogenolysis phenylpotassium has been found to be cleaved by hydrogen at ordinary temperatures in the absence of pressure or catalysts (*43*):

$$C_6H_5K + H_2 \rightarrow C_6H_6 + KH. \qquad (2)$$

The synthetic utility of hydrogenolysis in organometallic synthesis recently has been re-emphasized in the work of Ziegler and Köster with aluminum and boron alkyls (Sections II.A and IV.C).

(3) Water. The sensitivity of organometallic compounds to hydrolytic cleavage varies from the spectacular to the mild: alkyls of Groups IA, IIA, IIIA react with water explosively to yield the corresponding hydrocarbon and metallic hydroxide:

$$C_2H_5Na + HOH \rightarrow C_2H_6 + NaOH, \qquad (3)$$

$$C_6H_5MgX + HOH \rightarrow C_6H_6 + Mg(OH)X, \qquad (4)$$

$$(C_2H_5)_3Al + 3HOH \rightarrow 3C_2H_6 + Al(OH)_3. \qquad (5)$$

Alkyls of mercury, silicon, tin, among others, show a slow cleavage in aqueous medium and usually require an acidic or basic medium to effect complete cleavage. In any event, such hydrolytic cleavages furnish a general method of analysis of organometallic compounds. If the group R in R_nM gives rise to a volatile hydrocarbon, RH, this may be quantitatively estimated as a check on either the purity of a known organometallic sample or the number of carbon-metal bonds per formula in a new substance. Moreover, the resulting aqueous solution can be analyzed to determine the amount of metal cation formed.

(4) Mineral Acids. Similar to water, almost any desired inorganic acid can effect full or partial cleavage of several carbon-metal bonds in an organometallic compound. The most useful synthetically are, however, the gaseous hydrogen halides dissolved in inert solvents such as benzene and chloroform. Again, with very reactive organometallic compounds the reaction is completed rapidly:

$$R_2Mg + 2HX \rightarrow 2RH + MgX_2. \qquad (6)$$

The reaction may be viewed as an analog of the reaction of a stronger acid with the salt of a weaker acid. Here the stronger acid, HX, liberates the weaker acid, RH. If the original organometallic system is moderately reactive and has several carbon-metal bonds, conditions can usually be found which lead predominantly to a stepwise cleavage of these bonds. An illustration is the preparation of either triphenyltin halide or diphenyltin dihalide by treating tetraphenyltin in chloroform solution with varying amounts of hydrogen halide gas:

$$(C_6H_5)_4Sn + HX \rightarrow (C_6H_5)_3SnX + C_6H_6, \qquad (7)$$

$$(C_6H_5)_4Sn + 2HX \rightarrow (C_6H_5)_2SnX_2 + 2C_6H_6 \qquad (8)$$

(5) Halogens. The foregoing comments concerning the selective cleavage of certain carbon-metal bonds in a molecule are also valid for the behavior toward molecular halogen. A favorite reagent for converting fully alkylated metal derivatives into alkylmetal halides is iodine. For a metal bearing different organic radicals there is often a preference as to which group is cleaved. For example, a dialkyldiaryllead compound will lose preferentially aromatic groups upon treatment with iodine:

$$R_2Ar_2Pb + 2I_2 \rightarrow R_2PbI_2 + 2ArI. \qquad (9)$$

(6) Metals. The behavior of metals towards organometallic compounds depends on whether the metal alkyl is simple or mixed. By a simple organometallic compound is meant one bearing only R groups on the metal (R_3Al); by a mixed type is understood one having both R and acid-radical or X groups on the metal (R_2AlCl). The effect of an active metal on mixed organometallic compounds is usually the extraction of the X group and the formation of the simple organometallic compound:

$$3R_2AlCl + 3Na \rightarrow 2R_3Al + 3NaCl + Al, \qquad (10)$$

$$xRGeCl + xK \rightarrow (RGe)_x + xKCl. \qquad (11)$$

The simple organometallic compounds usually react with metals by displacement, when the more reactive can displace the less reactive metal from the compound. The most important example of this is the utilization of organomercury compounds to obtain the more reactive metal alkyls of such metals as sodium, lithium, and aluminum:

$$R_2Hg + xNa \rightarrow 2RNa + \text{Na-amalgam}. \qquad (12)$$

Although the displacement power of a metal approximately parallels its oxidation potential in aqueous solution, there are indications that this is not always the case.

(7) Metal Halides and Other Salts. The more reactive organometallic types will exchange their alkyl groups for the halogen or acid anion of the salt of some less reactive metal or metalloid. Thus the reactive lithium and magnesium (Grignard) alkyls can form metal alkyls from many other metal salts. For example,

$$SnCl_4 + 4RMgX \rightarrow R_4Sn(R_3SnCl, R_2SnCl_2, RSnCl_3) + 4MgXCl. \qquad (13)$$

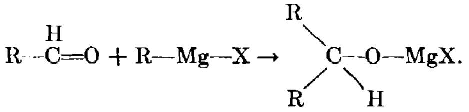
(8) Lewis Bases. The unfilled electronic orbitals in the metal atoms of many organometallic compounds favor complex formation by acceptance

of electronic pairs from suitable donors or Lewis bases. A wide variety of donors including ammonia, amines, ethers, hydride ions, halide ions, and carbanions form strong complexes with the alkyl derivatives of Groups I-III. The driving force toward complex formation is so pronounced in Group IIIA alkyls that they complex with themselves to form bridge dimers (except boron).

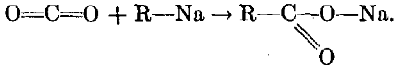
c. *Behavior toward Organic Reagents.* Although not of immediate concern to the inorganic chemist the reactivity of organometallic compounds toward organic systems further delineates the chemical character of this bond and may suggest analogous applications in inorganic chemistry.

(1) Addition to Multiple bonds. Organic compounds containing carbon bonded doubly or triply either to another carbon atom or a nonmetal such as O or N generally add organometallic reagents. It seems logical to include the inorganic reagent, carbon dioxide, under this heading.

$$(C_6H_5)_2C{=}CH_2 + R{-}Li \rightarrow (C_6H_5)_2CLi{-}CH_2R. \qquad (14)$$



$$R{-}\overset{H}{C}{=}O + R{-}Mg{-}X \rightarrow \overset{R}{\underset{R\quad H}{C}}{-}O{-}MgX. \qquad (15)$$



$$O{=}C{=}O + R{-}Na \rightarrow R{-}\underset{\overset{\Vert}{O}}{C}{-}O{-}Na. \qquad (16)$$

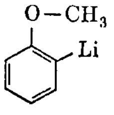
The facility with which organometallic reagents add to unsaturated systems varies so noticeably, that a useful classification of organometallic reactivity can be based on the ease of addition to certain unsaturated systems. Highly reactive types (R—Na) will react with both olefinic and carbonyl linkages, moderately reactive types (R—Mg—X) will react only with the carbonyl linkage, and unreactive types (R_2—Hg) will react with neither. It should be borne in mind, however, that solvent and other experimental conditions can influence the reactivity of a given organometallic type (compare Section IV.A.1).

A sensitive, qualitative color test (*50a*) for R-M types of at least moderate reactivity has been devised based upon the addition of R-M to the carbonyl group of Michler's ketone. This test is very useful in monitoring the formation or consumption of organometallic reagents.

(2) Metalation. The exchange occurring between R—M and organic compounds containing an acidic hydrogen bonded to carbon is termed metalation.

$$R'{-}H + R{-}M \rightarrow R{-}H + R'{-}M. \qquad (17)$$

Due to the electronegativity difference between hydrogen and carbon the hydrogen atoms in all organic compounds may be considered acidic to some extent. Metalation of an organic compound by RM, however, is more facile when the carbon atom to be metalated is adjoined by more electronegative groups, or when the carbon anion formed is stabilized by charge delocalization. The metalation of anisole in the ortho position by RLi (Formula I)



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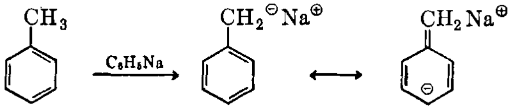
illustrates the former case, whereas the metalation of toluene (Formula II) by phenylsodium shows the favorable influence of charge delocalization (Formula III).



II III (18)

The synthetic utility of metalating organic systems with organolithium compounds has been reviewed recently (*49a*).

(3) Halogen-Metal Interconversion. Quite analogous to metalation is the observed exchange between R—M and organic halides:

$$R'\text{—}X + R\text{—}M \rightarrow R'\text{—}M + R\text{—}X. \qquad (19)$$

Just as aromatically bonded hydrogen is more acidic than aliphatically bonded hydrogen, it is observed that aromatically bonded halogen is more "cationic" than the halogen in alkyl halides. Thus aryl bromides react with alkyllithium compounds to form aryllithium derivatives and alkyl bromides:

$$\text{Ar—Br} + \text{R—Li} \rightarrow \text{Ar—Li} + \text{R—Br}. \qquad (20)$$

The interested reader is referred to a recent survey of this reaction for its scope and limitations (*69a*).

3. Physical Properties

As previously mentioned almost every recognized type of bonding is represented in the diversified types of organometallic compounds known. Consequently, no extensive generalization of the physical properties of all organometallic compounds obtains. There seem to be three broad classes of R_nM as to physical properties: ionic or saline, associated covalent, and unassociated covalent. The existence of ion pairs in ionic R_nM types and the strong bonding existing between molecular units in associated covalent types (as in dimerized aluminum alkyls and polymeric beryllium alkyls) render correlation of physical properties difficult. Only in the third class, unassociated covalent RM types, are there readily understandable trends in the physical properties within the family. This is true of the alkyls of the carbon family (C, Si, Ge, Sn, Pb). Mendeleeff's enviable success in predicting accurately the boiling point and density of tetraethylgermane some fifteen years before Winkler first prepared it was possible because such alkyls are unassociated.

4. General Preparative Methods

The classical methods which have proved most serviceable for the preparation of organometallic compounds already have received some indirect attention in Section I.B.2. However, for convenience the equations are given here.

(a) Interaction of metal and alkyl halide:

$$M^m + nR\text{—}X \rightarrow R_nMX_{m-n}. \qquad (21)$$

(b) Metal exchange:

$$M + R\text{—}M' \rightarrow M' + R\text{—}M. \qquad (22)$$

M more reactive than M′

(c) Alkyl-halogen exchange:

$$nR\text{—}M + M'X_n \rightarrow nMX + M'R_n(\text{or } M'R_nX_m). \qquad (23)$$

R—M more reactive than R_nM'

(d) Metal-hydrogen exchange (metalation):

$$R\text{—}M + R'\text{—}H \rightarrow R\text{—}H + R'\text{—}M. \qquad (24)$$

(e) Halogen-metal exchange:

$$R\text{—}M + R'\text{—}Br \rightarrow R\text{—}Br + R'\text{—}M. \qquad (25)$$

An extensive review of these and other specialized methods of preparing organometallic compounds has appeared (*70*).

C. DEVELOPMENT OF ORGANOMETALLIC CHEMISTRY

1. Significant Periods

In retrospect the history of organometallic chemistry appears to have been molded largely by key discoveries in synthesis. New preparative techniques have given prominence successively to different metal alkyls. Each class of metal alkyls in its turn has had its own impact upon various aspects of pure and applied chemistry. Some of the more fruitful discoveries which made new organometallic types readily accessible are: (a) Frankland's (*39*) discovery of zinc alkyls, 1849; (b) Dimroth's (*34*) studies on aromatic mercuration, 1898; (c) Grignard's (*55*) preparation of organomagnesium halides, 1900; (d) Schlenk's (*106*) researches on organoalkali compounds, 1914; (e) Ziegler's (*141*) preparation of lithium alkyls, 1930; (f) the preparation of ferrocene (*71*, *86*) as the first sandwich organometallic π-complex, 1951; and (g) Ziegler's (*140*) preparation of aluminum alkyls via olefin and hydride, 1955.

2. Contributions to the General Advance of Chemistry

Interestingly enough, organometallic chemistry was born of the researches of Bunsen (*18a*) and Frankland (1849) concerning the existence of uncombined radicals or element imitators. In isolating cacodyl which was thought to be $(CH_3)_2As$, Bunsen thought that he had obtained the first "free" radical. As mentioned in Section I.A.2, however, organometallic chemistry has amply repaid valence theory this debt of parentage by furnishing the structural chemist with new challenges and insights into the nature of the chemical bond.

Some other contributions of organometallic compounds to fundamental research are: (a) the detection of free alkyl radicals by the pyrolysis of lead alkyls; (b) the classification of hydrocarbon acidity via organoalkali compounds; (c) the study of Lewis acid-base interactions with Group III alkyls; (d) the development of the concept of electron-deficient compounds by the study of metal alkyls; (e) the discovery of stereospecific olefin polymerization; and (f) the investigation of nucleophilic additions to unsaturated organic compounds via reactive metal alkyls.

The importance of organometallic compounds in synthesis to both the organic and inorganic chemist should be apparent from the discussion in Section I.B.2. However, the sensitivity of many organometallic compounds to solvolysis and oxidation, their poisonous and flammable character, the necessity of utilizing large quantities of solvent and relatively expensive starting materials, all have tended to suppress until recently their widespread industrial use. The production of tetraethyllead as an antiknock additive, of methylchlorosilanes as silicone intermediates, and of organomercury antiseptics may be cited as exceptions.

3. Bridge between Inorganic and Organic Chemistry

The study of the carbon-metal bond offers excellent opportunity for a rapprochement of the inorganic and the organic chemist. The fertility of an interdisciplinary field lies in the meeting of different viewpoints. Here the extensive knowledge of the electronic and steric characteristics of organic groups can be pooled with the known chemistry of the metals, thus leading to a more intimate and broader understanding of the chemical bond.

D. RENAISSANCE IN ORGANOMETALLIC CHEMISTRY AND ITS SOURCES

In recent years organometallic compounds have ceased to be exclusively the object of academic research. Almost every major industrial chemical research laboratory in the world has initiated extensive research in organometallic chemistry. In addition to the general increase in chemical research following World War II the prominence of this field can be owed to certain pacesetting discoveries. A principal factor in awakening industrial interest has been the researches of Ziegler and co-workers with aluminum alkyls. The realization that these alkyls with various co-catalysts can convert olefins, dienes, and acetylenes into superior polymers and ring compounds has been of first-rate importance to organic synthesis. The utility of these same alkyls in the preparation of boron alkyls and hydrides, in the electroplating of aluminum, and the synthesis of tetraethyllead has stimulated the imagination of the inorganic chemist.

A similar role has been played by Wittig and co-workers in extending the horizons of aromatic organometallic chemistry. Investigation of the complexes formed between aryl alkali compounds as phenyllithium and Lewis bases of type R_nM has resulted in the synthesis of ylides of nitrogen and phosphorus, metalloids in rare valence states, and organometallic σ-complexes of unique structure.

A thoroughly unexpected postwar breakthrough was the synthesis of the first aromatic type of transition metal sandwich complex known as dicyclopentadienyliron (II) or ferrocene. Realization of this intriguing structure has stimulated the synthesis of many similar types.

Two major fields of inorganic chemistry which have had a considerable impact on recent organometallic chemistry are those of metal hydride and metal carbonyl research. The former owes much of its present vigor to the studies of Schlesinger's group (*69*), whereas metal carbonyls have received much attention from Hieber and co-workers (*65*). Schlesinger's aluminum hydride complexes proved very helpful in Ziegler's study of aluminum alkyls, and metal carbonyl chemistry has guided the development of the field of transition metal π-complexes.

The amount of recent research in organometallic chemistry has gone up exponentially and many researchers have contributed significantly. Space does not permit consideration of each metal alkyl type, however. The following discussion will aim rather at emphasizing new preparative methods of some generality, as well as recent viewpoints on the structure and reactivity of carbon-metal bonds.

II. New Preparative Techniques and Procedures

A. Metal Hydrides and Olefins

1. *Lithium and Aluminum Hydrides*

The addition of metal and metalloid hydrides to carbon-carbon double bonds is not a new reaction, having been observed from time to time with silanes of the type R_3SiH under free-radical conditions (*42*, *85*) and with boron hydrides (*68*). The versatility of such hydride-olefin interactions, nevertheless, first became evident with the recent researches of Ziegler with lithium and aluminum alkyls (*139*). The observation that attempted distillation of ethyllithium led to decomposition into lithium hydride, ethylene, and higher olefins prompted the following formulation of the reaction course (*see 18*):

$$\begin{gathered} CH_3{-}CH_2{-}Li \rightleftarrows CH_2{=}CH_2 + LiH, \\ CH_2{=}CH_2 + CH_3CH_2Li \rightleftarrows CH_3CH_2CH_2CH_2Li, \\ CH_3CH_2CH_2CH_2Li \rightleftarrows CH_3CH_2CH{=}CH_2 + LiH, \text{ etc.} \end{gathered} \tag{26}$$

As this implied that LiH can add reversibly to ethylene and thus effect its catalytic conversion to higher olefins, Ziegler was prompted to study the behavior of alkali hydrides towards ethylene in hopes of achieving polymerization. However, tarry reaction products hindered its realization with lithium hydride. Utilization of lithium aluminum hydride instead led to a rapid conversion of ethylene into higher α-olefins. This in turn suggested that perhaps aluminum alkyls and hydride were more active than lithium. Consequently, the fundamental chemistry of aluminum alkyls and hydrides was extensively studied. The fruits of this research to the field of organic synthesis have been very abundant: the synthesis of higher olefins, fatty alcohols, and desirable polymers such as high-density polyethylene and stereospecific polymers of dienes.

Because of the widespread utility of aluminum alkyls preparative methods have been developed which place these compounds among the potentially cheapest organometallic reagents. Since aluminum hydride adds to ethylene at moderate temperatures,

$$(AlH_3)_n + 3nCH_2{=}CH_2 \rightarrow nAl(CH_2CH_3)_3, \tag{27}$$

a simple, elegant synthesis of aluminum alkyls was envisioned: the formation of aluminum hydride *in situ* by the reaction of activated aluminum and hydrogen gas and then subsequent introduction of the olefin:

$$Al + \tfrac{3}{2}H_2 + 3CH_2{=}CHR \rightarrow Al(CH_2CH_2R)_3. \tag{28}$$

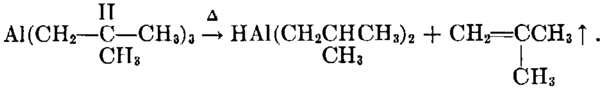
Two limitations on the synthesis are, first, that the olefins utilized must have a terminal double bond (α-olefins) and, second, that the use of the simplest olefin, ethylene, and other straight chain olefins in such a one-step synthesis is not feasible. The reason is that at the required temperature (120–150°) triethylaluminum reacts with ethylene to form higher aluminum alkyls (see Section IV.C.6). The latter so-called "growth" or *Aufbau* reaction [Eq. (84)] is useful for producing higher olefins, but it must be avoided in synthesizing triethylaluminum. Thus a useful two-step procedure is employed: first, triethylaluminum (prepared via conventional methods), aluminum, and hydrogen are interacted at higher temperatures to form diethylaluminum hydride:

$$2(CH_3CH_2)_3Al + Al + \tfrac{3}{2}H_2 \rightarrow 3(CH_3CH_2)_2AlH, \qquad (29)$$

then the ethylene is introduced at a lower temperature (60–70°), where the undesired "growth" reaction is slow, but where diethylaluminum hydride can still add smoothly to ethylene (*140*):

$$(CH_3CH_2)_2AlH + CH_2{=}CH_2 \rightarrow Al(CH_2CH_3)_3. \qquad (30)$$

Other interesting aspects of this new synthesis of aluminum alkyls stem from the fact that hydride additions to olefins are reversible. In the first place this means that favorably constituted aluminum alkyls should lose olefin readily upon being heated. Such branched-chain alkyls as triisobutylaluminum will evolve isobutylene upon heating at 150–180°:

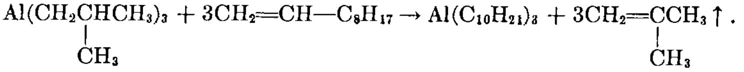

(31)

$$Al(CH_2{-}\overset{H}{\underset{CH_3}{C}}{-}CH_3)_3 \xrightarrow{\Delta} HAl(CH_2\underset{CH_3}{C}HCH_3)_2 + CH_2{=}\underset{CH_3}{C}CH_3\uparrow. \qquad (31)$$

The resulting diisobutylaluminum hydride is an excellent liquid reducing agent toward unsaturated systems. Likewise, branched beryllium alkyls such as diisopropyl and di-*t*-butyl derivatives decompose to give the corresponding olefins and polymeric beryllium hydride (*25*, *59*). Analogously, diethylmagnesium yields upon pyrolysis magnesium hydride (*40*). The existence of an equilibrium between hydride and olefin on the one hand, and aluminum alkyl on the other makes possible a transalkylation process known as the "displacement" or *Verdrängung* process. If one heats an aluminum alkyl with a different olefin, one can expect the following:

$$\begin{array}{l} Al(CH_2{-}CH_2R)_3 \rightleftarrows HAl(CH_2{-}CH_2R)_2 + CH_2{=}CHR\uparrow \qquad (32) \\ HAl(CH_2{-}CH_2R)_2 + CH_2{=}CHR' \rightleftarrows Al(CH_2CH_2R)_2(CH_2{-}CH_2R') \\ \qquad\qquad\qquad\qquad\qquad\qquad \downarrow\uparrow \\ \qquad\qquad\qquad\qquad HAl(CH_2CH_2R)(CH_2{-}CH_2R') + CH_2{=}CHR, \text{ etc.} \end{array}$$

The equilibrium point will depend on the temperature and the nature of the R and R′ groups. However, by using the added olefin ($CH_2{=}CHR'$) in generous excess and/or by allowing the generated olefin ($CH_2{=}CHR$) to escape, one can effectively prepare new aluminum alkyls. Thus the heating of triisobutylaluminum with decene-1 at 125° leads to a practically quantitative formation of tri-*n*-decylaluminum, since the volatile isobutylene escapes:

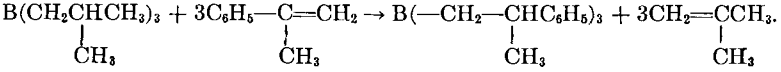


$$\mathrm{Al(CH_2\underset{\substack{|\\ CH_3}}{C}HCH_3)_3 + 3CH_2{=}CH{-}C_8H_{17} \rightarrow Al(C_{10}H_{21})_3 + 3CH_2{=}\underset{\substack{|\\ CH_3}}{C}CH_3\uparrow .} \qquad (33)$$

The generality of this transalkylation reaction is reflected in the successful synthesis of higher organoboron (*73*) and organogallium alkyls (*142*) from olefins with triisobutylborane and triisobutylgallium, respectively.

2. Boron Hydrides

The synthesis of trialkylboranes by addition of diborane (*68*) or aluminum borohydride (*9*) to olefins and other unsaturated systems has found only limited application because of the hazards of working with boron hydrides. The aforementioned discussion of aluminum alkyls, nevertheless, points up the potentialities of analogous reactions with boron. The current intense interest in "exotic" or high-energy fuels involving boron has caused many researchers to refocus their attention on the addition of boron hydrides to olefins. In place of utilizing free diborane, new procedures have either used "masked" boron hydride or generated it *in situ*. Working in Ziegler's laboratories Köster has found that the transalkylation reaction utilizing triisobutylborane will effect the addition of borane to both terminal and internal double bonds as in α-methylstyrene and cyclohexene (*73*):



$$\mathrm{B(CH_2\underset{\substack{|\\ CH_3}}{C}HCH_3)_3 + 3C_6H_5{-}\underset{\substack{|\\ CH_3}}{C}{=}CH_2 \rightarrow B({-}CH_2{-}\underset{\substack{|\\ CH_3}}{C}HC_6H_5)_3 + 3CH_2{=}\underset{\substack{|\\ CH_3}}{C}CH_3.} \qquad (34)$$

The tri-2-phenylpropylborane formed can be oxidized and hydrolyzed to 2-phenylpropanol-1, thus representing [as with aluminum alkyls (*140*)] an overall anti-Markownikoff hydration of α-olefins. Besides employing trialkylboranes as a source of boron hydrides, similar additions have been accomplished by heating olefins with boron hydride-amine complexes. As the latter are not as oxygen-sensitive, they are easier to handle (*73*):

$$\mathrm{3CH_2{=}CHR + BH_3{:}NR_3 \rightarrow B(CH_2{-}CH_2R)_3 + NR_3.} \qquad (35)$$

A procedure for bringing about the interaction of olefins with boron hydrides generated *in situ* recently has been reported by Brown and Subba Rao (*14, 15*). This reaction which has been termed hydroboration is effected by adding the olefin to a mixture of sodium borohydride and aluminum chloride in diethylene glycol dimethyl ether. Other ethers (tetrahydrofuran) and other halides (gallium and boron halides) are also effectual when used with sodium borohydride. Added to the great convenience and high yield (90%) accompanying this synthesis of trialkylboranes, the reaction seems able to isomerize olefins with internal double bonds into tri-*n*-alkylboranes.[2] Illustrations of this are the hydroborations of 3-hexene and a mixture of isomeric decenes. In each case the principal product obtained by oxidation and hydrolysis of the trialkylborane is the primary alcohol. This implies that an equilibrium between boron hydride and olefin versus the trialkylborane is set up. Stability considerations seem to lead to predominance of the tri-*n*-alkylborane:

$$CH_3CH_2CH{=}CHCH_2CH_3 + R_2BH \rightleftarrows R_3B \rightleftarrows R_2BH + \text{2-hexene, etc.} \qquad (36)$$

3. Hydrides of Group IV

As an extrapolation of the peroxide-catalyzed addition of trichlorosilane to olefins (*38*, *115*) new aryl silanes and germanes of the type $(C_6H_5)_3MR$ have been prepared by the addition of triphenylsilane and triphenylgermane to olefins in the presence of benzoyl peroxide (*42*, *85*).

$$(C_6H_5)_3SiH + CH_2{=}CH{-}R' \rightarrow (C_6H_5)_3SiCH_2CH_2{-}R'. \qquad (37)$$

There is indication that triphenylgermane is more reactive than triphenylsilane in this reaction. The germane hydride is able to add to the double bond in triphenylallylgermane in high yield, whereas triphenylsilane will not add under the same conditions (*47*).

Since triphenyltin hydride tends to interact with benzoyl peroxide to yield triphenyltin benzoate and other products (*44*), a peroxide-catalyzed addition of this hydride to olefins is overshadowed by decomposition products. However, polar unsaturated compounds such as acrylonitrile add triphenyltin hydride readily via a supposed ionic mechanism (*122*, *123*). The reaction offers a new pathway to functional organotin derivatives of high biocidal activity:

$$(C_6H_5)_3SnH + CH_2{=}CHCN \rightarrow (C_6H_5)_3SnCH_2CH_2CN. \qquad (38)$$

The possibility of synthesizing alkyl and alkenyl silanes from olefins and acetylenes with silane, SiH_4, has been investigated by White and Rochow (*128*). With ethylene various ethyl derivatives of silane and disilane were obtained under conditions suggestive of a free-radical mechanism:

$$SiH_4 + CH_2{=}CH_2 \xrightarrow{500°C} (C_2H_5)_nSiH_{4-n} + S_nH_{2n+2} + C_2H_5Si_2H_5. \qquad (39)$$

4. Stereospecificity of Hydride Addition

There is reason to believe that alkylaluminum and alkylboron hydrides approach and add to the unsaturated linkage in a strictly *cis*-fashion. Al-

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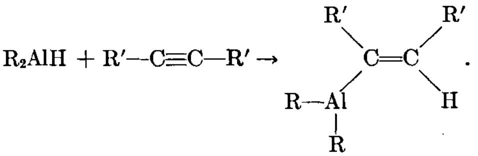
[2] Attempts to prepare tri-*t*-butylborane and tri-*sec*-butylborane from boron trichloride and the corresponding Grignard reagent demonstrate the ease with which these types rearrange: for example, tri-*iso*-butylborane is formed instead of tri-*t*-butylborane (*62*).

though this is difficult to demonstrate with ordinary olefinic systems, the *cis*-character of the addition has been proved with acetylenes. Thus diethylaluminum hydride adds smoothly to diphenylacetylene and diethylacetylene at room temperature to give pure *cis*-olefins upon hydrolysis (*133*). If one accepts the unlikelihood of rearrangement during hydrolysis, the addition must be formulated:



(40)

By the use of deuterated dialkylaluminum hydride for the addition and/or heavy water for hydrolysis, specifically deuterated olefins may be prepared. Likewise, hydroboration of certain olefins has now been shown to occur in a *cis*-fashion (*16*).

B. Aluminum Alkyls as Alkylating Agents

The availability of the aluminum alkyls in pure state makes their use as alkylating agents for the synthesis of other organometallic compounds quite feasible. One of the general approaches is the interaction of the metal or metalloid halide with the trialkylaluminum (*105*):

$$3MX_n + nR_3Al \rightarrow 3MR_n + nAlX_3. \qquad (41)$$

This method has the advantage over the use of ethereal solutions of magnesium and lithium alkyls in that the metal alkyls can be prepared ether-free. In certain cases, however, not all the alkyl groups of R_3Al are available. Thus in the preparation of gallium and indium alkyls the reaction proceeds according to the following equation (*142*):

$$GaX_3 + 3AlR_3 \rightarrow GaR_3 + 3AlR_2X. \qquad (42)$$

In the synthesis of boron alkyls, on the other hand, the employment of BF_3 allows the following stoichiometry (*73*):

$$BF_3 + AlR_3 \rightarrow BR_3 + AlF_3. \qquad (43)$$

Another important point in this procedure is that occasionally the R_2AlCl formed can interfere with high yields. Although gallium bromide gives 85% yields according to Eq. (42), gallium chloride yielded only 40–45% of triethylgallium. The decrease in yield is due to the binding of one-half of the gallium chloride by the diethylaluminum chloride:

$$\begin{aligned} &GaCl_3 + 3Al(C_2H_5)_3 \rightarrow Ga(C_2H_5)_3 + 3Al(C_2H_5)_2Cl \\ &GaCl_3 + 3Al(C_2H_5)_2Cl \rightarrow Ga[Al(C_2H_5)_2Cl_2]_3. \end{aligned} \qquad (44)$$

This hypothesis is made quite probable by the isolation of the complex between gallium chloride and diethylaluminum chloride. Moreover, inclusion of potassium chloride in the reaction mixture to complex with the dialkylaluminum halide and free the gallium chloride raises the yield to 90% of triethylgallium (*142*).

$$3KCl + Ga[Al(C_2H_5)_2Cl_2]_3 \rightarrow GaCl_3 + 3K[Al(C_2H_5)_2Cl_2]. \qquad (45)$$

C. METHYLENATION VIA DIAZOMETHANE

Recently, interest has been revived in the preparation of chloromethyl derivatives of the more electronegative metals by the interaction of the metal halide with diazomethane. Thus germanium tetrachloride upon treatment with an ethereal diazomethane solution and copper powder at −60° yields 94% of chloromethylgermanium trichloride (*110*):

$$GeCl_4 + CH_2N_2 \xrightarrow[-60^\circ]{Cu} ClCH_2GeCl_3 + N_2\uparrow . \qquad (46)$$

Vigorous investigation, especially by Yakubovich and co-workers, indicates that the scope of this reaction includes the metal halides of mercury, thallium, germanium, tin, arsenic, antimony, and bismuth. Metalloid halides of silicon and phosphorus also react (*107*). The promise of the reaction lies in the formation of organometallic compounds containing the potentially reactive $Cl{-}CH_2{-}$ grouping (*109*). Since the net effect is the insertion of the methylene group, $-CH_2-$, into MX_n, the reaction has been termed methylenation. Another related reaction which allows the transformation of certain hydrides into organometallic compounds has been discovered by Lesbre (*78*), namely the reaction of diazoalkanes with stannanes. Tri-*n*-butylstannane yields methyltri-*n*-butyltin with diazomethane whereas tri-*n*-butyltin chloride does not react (see *111*):

$$(C_4H_9)_3SnH + CH_2N_2 \rightarrow (C_4H_9)_3SnCH_3 + N_2\uparrow . \qquad (47)$$

Use of substituted diazoalkanes, such as ethyl diazoacetate, leads to functional tin alkyls. The potential applications in preparing interesting alkylboranes from boron hydrides should be apparent.

D. ORGANOMETALLIC σ-COMPLEXES

As has been mentioned in Section I.A., most organometallic compounds have unfilled electronic orbitals and hence can display Lewis acid behavior. In recent years Wittig (*134*) has devoted intensive study to the preparative possibilities of complexes between different aryl organometallic compounds. In most cases the bond between the organic moiety and metal has σ-character, being symmetrical to the bond axis. This type is exemplified by complexes between phenyllithium and organometallic acceptors such as triphenylborane and diphenylberyllium:

$$C_6H_5Li + B(C_6H_5)_3 \rightarrow Li[B(C_6H_5)_4]. \tag{48}$$

Such complexes possess sharply reduced chemical reactivity and consequently they often tend to stabilize the valence state of the acceptor metallic atom. Lithium tetraphenylboronate requires heating in acid solution in order to effect cleavage of the boron-carbon bonds and is quite stable in air toward oxidation. The acceptance of the phenyl anion has satisfied the electronic demands of boron. A direct preparation of analogous alkyl complexes has been realized by heating lithium aluminum hydride with ethylene under pressure (*139*):

$$LiAlH_4 + 4CH_2{=}CH_2 \rightarrow Li[Al(C_2H_5)_4]. \tag{49}$$

The attainment of outermost filled *s*- and *p*-orbitals (complete octet) is the limit of first period elements. With metalloids of higher principal quantum number *d*-orbitals can also be filled. Pentaphenylantimony, tetraphenyltellurium, and triphenyliodine form complexes of decreasing stability with phenyllithium:

$$LiC_6H_5 + Sb(C_6H_5)_5 \rightarrow Li[Sb(C_6H_5)_6]. \tag{50}$$

Another system forming σ-complexes involving *d*-orbitals seems to be dicyclopentadienyldiphenyltitanium which forms complexes with one or more equivalents of phenyllithium (*118*, *119*):

$$(C_5H_5)_2Ti(C_6H_5)_2 + LiC_6H_5 \rightarrow Li[(C_5H_5)_2Ti(C_6H_5)_3]. \tag{51}$$

This also appears to be the case with the previously elusive triphenylchromium. Hein and Weiss (*61*) have isolated from the interaction of chromium (III) chloride and an excess of phenyllithium a solid red substance which is the etherate of such a complex:

$$CrCl_3 + 6LiC_6H_5 \rightarrow Li_3[Cr(C_6H_5)_6] + 3LiCl. \tag{52}$$

No sandwich or π-complex seems to be involved. One might observe in general that the isolation of organometallic compounds of low stability may often succeed if complex formation with solvent, metallic salt, or an RM type is provided for (See Section IV.A.3). For example, disubstituted platinum (II) and palladium (II) derivatives have been prepared successfully as the bis(triethylphosphine) complexes in the following reaction (*19*, *20*):

$$2RLi + M[(C_2H_5)_3P]_2X_2 \rightarrow M[(C_2H_5)_3P]_2R_2 + 2LiX. \tag{53}$$

An intriguing new organometalloid complex type has resulted from renewed attempts to prepare pentacovalent nitrogen derivatives. These are the phosphorus and nitrogen ylides (*134*). If one treats a tetramethylammonium salt with phenyllithium, one obtains a salt complex of lithium halide with trimethylammonium methylide:

$$[N(CH_3)_4]^{\oplus}I^{\ominus} + LiC_6H_5 \rightarrow (CH_3)_3\overset{\oplus}{N}\text{—}\overset{\ominus}{C}H_2 \,.\, LiI + C_6H_6. \qquad (54)$$

Although this nitrogen ylide allows of only a betaine structure, the phosphorus analog may involve some π-double bonding:

$$R_3\overset{\oplus}{P}\text{—}\overset{\ominus}{C}H_2 \leftrightarrow R_3P{=}CH_2. \qquad (55)$$

This has led to interesting phosphorus-boron complexes. Pentaphenyl phosphorus will donate a phenyl anion to triphenylborane:

$$P(C_6H_5)_5 + B(C_6H_5)_3 \rightarrow [P(C_6H_5)_4]^{\oplus}[B(C_6H_5)_4]^{\ominus}. \qquad (56)$$

Analogously, interaction with triphenylphosphorus methylide leads to a betaine complex:

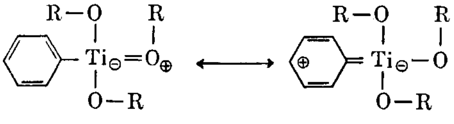
$$(C_6H_5)_3\overset{\oplus}{P}\text{—}\overset{\ominus}{C}H_2 + B(C_6H_5)_3 \rightarrow (C_6H_5)_3\overset{\oplus}{P}\text{—}CH_2\text{—}\overset{\ominus}{B}(C_6H_5)_3. \qquad (57)$$

E. ORGANOMETALLIC COMPOUNDS OF TRANSITION METALS AND METALLOIDS

As an extension of the previous discussion, it can be observed that difficultly preparable organometallic compounds can often be obtained by careful choice of structural features. Besides utilizing the stabilizing influence of complexing agents the location of electronegative substituents on the metal seems to stabilize the carbon-metal bond. The notion has been advanced that the strong negative field of an oxygen or halogen atom decreases the promotion energy necessary for a given hybridization of the metal's orbitals and consequently stabilizes that state. Herman and Nelson (*63*) found, for example, that in attempting to synthesize ordinary titanium-carbon bonds they could obtain an isolable phenyltitanium (IV) triisopropoxide by interaction of phenyllithium with the titanium orthoester:

$$Ti(i\text{-}OC_3H_7)_4 + LiC_6H_5 \rightarrow (C_6H_5)Ti(OC_3H_7) + LiOC_3H_7. \qquad (58)$$

Replacement of more than one isopropoxyl group led to very unstable products; hence, the presence of these groups promotes the stability of the phenyl-titanium bond. However, another factor not to be overlooked is that the corresponding alkyltitanium trialkoxides were too unstable to be isolated. This may indicate the stabilizing influence of *both* the alkoxide (Formula IV) and the phenyl group (Formula V) is not only due to the strong negative field of these groups, but also to π-electron donation into titanium atom's unfilled orbitals.



IV V

Whatever the explanation, the enhanced stability of organometallic compounds bearing phenyl, chloro, or similar groups is often observed. The long sought-after methyl derivatives of titanium have been prepared recently by the interaction of trimethylaluminum with titanium tetrachloride. The CH_3TiCl_3 and $(CH_3)_2TiCl_2$ types thus isolated (*37*) are much more stable than might be suspected. Again, dicyclopentadienyldiphenyltitanium results from treating dicyclopentadienyltitanium dihalide with phenyllithium (*118*). The phenyl groups seem to be bonded in a σ-fashion. Other organometallic compounds of transition metals containing an ordinary sigma carbon-metal bond seem to be alkylmanganese pentacarbonyls (*27*), phenylvanadium bromide (*8*), methylcobalttetracarbonyl (*66*), and benzylchromium salts (*2*).

The organic moiety most suitable to establish a stable sigma carbon-metal bond in difficult cases seems to be an electronegative radical such as the phenyl or acetylenic group. Examples of new and interesting phenyl organometallic compounds are triphenylchromium (*64*), pentaphenylantimony, tetraphenyltellurium, and triphenyliodine (*134*). Nickel and other metals can be transformed into acetylides (*89*).

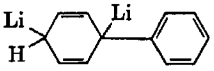
A class of organometalloid compounds awakening a considerable amount of current interest is the perfluoroalkyls. The high electronegativity of fluorine confers interesting properties on these derivatives. Trisperfluoromethylstibine, for example, has sharply reduced donor properties and can even behave as an acceptor towards pyridine. The general method of synthesis of antimony or arsenic derivatives entails the interaction of the metal with trifluoromethyl iodide to give $(CF_3)_3M$, $(CF_3)_2MI$, and CF_3MI_2. Reaction of $(CF_3)_2MI$ with metals leads to $(CF_3)_2M—M(CF_3)_2$ (*29, 35, 58*).

F. Preparation of Vinyl Organometallic Compounds in Tetrahydrofuran

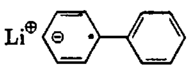
The excellent donor or complexing characteristics of tetrahydrofuran have popularized its use in organometallic chemistry. The finding of Normant (*91*) that difficultly accessible vinyl and aryl Grignard reagents can easily be prepared from the organic halide and magnesium in tetrahydrofuran, has made vinyl-type organometallic compounds just as available as other organometallic types. In typical recent utilizations, vinyl derivatives of mercury (*6*), germanium (*108*), tin (*112*), and Group VB elements (*84*) have been prepared by treating the respective metallic halide with vinylmagnesium halide in tetrahydrofuran. These vinyl derivatives promise to be valuable in both theoretical and industrial application. The situation of a π-bond in the vinyl group adjacent to the metal atom may allow p_π–d_π electronic interactions, whereas the industrial chemist envisions such vinyl derivatives as potentially polymerizable organic intermediates.

G. Alkali Metal Adducts with Unsaturated Hydrocarbons

Schlenk's (*106*) classical work on the addition of alkali metals to unsaturated carbon-carbon bonds has been the subject of recent re-evaluation. The highly colored solid obtained by Schlenk and co-workers by shaking biphenyl with lithium, for example, was formulated as (Formula VI). A 2:1 adduct of this kind is not compatible with the physicochemical studies of Weissman, Lipkin, and Paul. By working in tetrahydrofuran they obtained a green solution containing alkali metal and biphenyl in 1:1 proportions. Conductimetric and especially electron spin resonance results are compatible with the free radical-anion formulation (Formula VII) (*7, 80, 127*). Similar 1:1 or 2:1 adducts of alkali metal and many aromatic hydrocarbons are now readily obtainable by simply stirring the hydrocarbon and metal in tetrahydrofuran. The pronounced paramagnetic character of such solutions makes them electronically analogous to solutions of alkali metals in liquid ammonia (*67*). Whether these adducts should be considered as organometallic compounds is a moot question.



VI



VII

H. Electrolytic Preparation of Organometallic Compounds

A recent procedure for the preparation of lead and other alkyls of potential industrial application is an electrolytic process utilizing an aluminum cathode, a lead anode, and an electrolyte of $NaF \cdot 2Al(C_2H_5)_3$. Passage of current leads to a quantitative formation of tetraethyllead at the anode and the deposition of high-purity aluminum on the cathode. It has been suggested that the purified aluminum obtained as a by-product may help meet the cost of electrical current and raw materials (*145*):

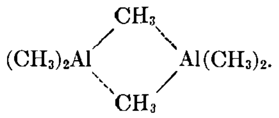
$$Al(99\%) + \tfrac{3}{2}H_2 + 3C_2H_4 \rightarrow Al(C_2H_5)_3. \qquad (59)$$

$$3Pb + 2[Al(C_2H_5)_3]_2NaF \xrightarrow{\text{electrolysis}} 4Al(99.95\%) + 3Pb(C_2H_5)_4 + 2NaF.$$

III. Structure and Bonding in Organometallic Compounds

A. AUTOCOMPLEXATION

Characteristic of most reactive RM compounds is their existence as two or more R_nM units closely associated with each other. The nature of these metal alkyl complexes has been extensively studied via X-ray crystal analysis by Rundle and co-workers, who showed that the α-carbon atom of the alkyl groups forms a bridge between metal atoms in different RM units. Thus, the dimer of trimethylaluminum may be viewed as



Steric interactions explain why the degree of association of R_3Al decreases in the order: methyl > ethyl > isopropyl (*103*). To bring such unique bonding in consonance with modern electronic theory the electron pair of the bridge bond is considered to be delocalized in a three-center (Al—C—Al) molecular orbital. Rundle notes that such "electron-deficient compounds" (that is, metal having more low-energy orbitals than valence electrons) will assume a configuration in which all low-energy orbitals may in some way be involved in the bonding (*103*). This principle rationalizes the behavior of polymeric dimethylberyllium (*114*), tetrameric tetramethylplatinum (*103*), and tetrameric trimethylindium (*1*).

Lithium alkyls in ether or benzene show a mean degree of association of from three to seven, whereas phenyl- and benzyllithium are dimeric in ether (*17, 135*). The lower degree of association in ether may stem from etherate formation. The structure of these auto-complexes may be analogous to that of beryllium and aluminum alkyls, or perhaps a lithium atom acts as a Lewis acid; that is, $Li^{\oplus}[Li(C_6H_5)_2]^{\ominus}$. Wittig (*135*) favors this formulation over a phenyl bridging scheme.

The structure of the most commonly encountered organometallic, namely the Grignard reagent, has been under dispute since its discovery. Recent investigations confirm that RMgX is dimerized and solvated in ether (*113*). Bridging by halogen atoms seems to be responsible for the observed association, although alkyl bridges cannot be excluded. Some attempt has been made to correlate the degree of association with the nature of different alkyl groups and halogen in RMgX, but no clear pattern emerges.

Recently, the equilibrium postulated by Schlenk to exist between various species in the Grignard reagent:

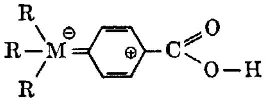
$$R_2Mg \,.\, MgBr_2 \overset{A}{\rightleftarrows} R_2Mg + MgBr_2 \overset{B}{\rightleftarrows} 2RMgBr, \qquad (60)$$

has been subjected to a radioactive exchange test. Since an equimolar mixture of diethylmagnesium and magnesium bromide dissolved in ether displays the same kinetics toward 1-hexyne as the ordinarily prepared Grignard solution (Section IV.A.3), it seems reasonable to consider that both involve the same or similar complexes. Now the mixing of radioactive $Mg^{28}Br_2$ with R_2Mg and subsequent precipitation of $MgBr_2$ with dioxane gives almost complete (95%) recovery of Mg^{28}. If equilibrium B were involved, one would expect 50% recovery. A better formulation of the Grignard reagent thus appears to be $R_2Mg \cdot MgBr_2$ and equilibrium A (*31*).

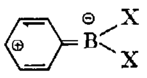
B. Carbon-Metal Bonding

Current work promises to lead to a better understanding of the carbon-metal bond. The determination of the dissociation energies of the carbon-metal bonds of mercury (*22*, *36*, *99*), cadmium (*77*, *99*), zinc (*98*), and the alkyls of Group III (*83*, *120*) and Group V elements (*81*, *82*) promises to offer an approach to estimating intrinsic bond energies of the σ-covalent bonds. To do this, however, one will have to have some way of calculating the valence state energies of the combined metal atoms. Thus, though the boron-carbon bond has a greater mean dissociation energy than that of the gallium-carbon bond, the valence state energy of sp^2-hybridized gallium would appear to be greater than that of boron. Consequently, the difference in intrinsic bond energies may be still smaller or reversed in sign (*83*).

Another aspect of the carbon-metal bond which is receiving increased attention is π-donor interactions between adjacent unsaturated systems and unfilled metal orbitals. Chatt and Williams (*21*) have sought to assess the importance of d_π–p_π bonding in Group IVA elements by comparing the dissociation constants of benzoic acid substituted in the para position by R_3M, where $M = C$, Si, Ge, Sn. Enhanced acidity of the carboxylic acid is interpreted as resulting from the withdrawal of π-electrons from the the phenylene ring, thus facilitating proton loss (Formula VIII). Arylboranes also evidence such π-interactions. Electric moment measurements of aryldichloroboranes in solution (*28*) give values compatible with resonance structures such as Formula IX.

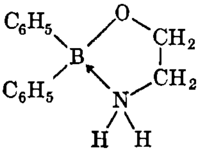


VIII

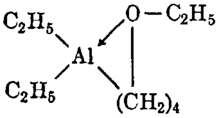


IX

Another manner in which intramolecular electron donation can help to fill the available orbitals of the metal atom is via a cyclic σ-bond between the metal atom and some function having an unshared pair. Such derivatives have an enhanced chemical stability. β-Aminoethyl diphenylborinate (Formula X) (*79*) and 1-(4-ethoxybutyl)diethylaluminum (Formula XI) (*3*) exemplify this interesting type of bond.



X



XI

C. METAL-METAL BONDING

A word should be inserted about those organometallic compounds thought to contain metal-metal bonding. This field may well receive considerable attention in future research. Various compounds of the type R_3—M—M—R_3 have been prepared involving elements of Group IV (*10, 12, 13, 46, 95*). Although susceptible to cleavage by sodium-potassium alloy, they do not seem to dissociate into free radicals except when M is carbon and *R* is an aryl radical. In Group III alkyls there is some evidence that the colorless dianion exists,

$$[(CH_3)_3Ga{-}Ga(CH_3)_3]^{\ominus\ominus},$$

as does the sodium triphenylborane adduct,

$$[(C_6H_5)_3{-}B{-}B{-}(C_6H_5)_3]^{\ominus\ominus} \qquad (23).$$

The existence of hexamethyldiplatinum, $(CH_3)_3Pt$—$Pt(CH_3)_3$ (*49*) and the possible existence of R—Hg—Hg—R (*54*) are further instances. (Compare ref. *103* for possible metal-metal bonding in associated alkyls.)

IV. Reactivity and Reaction Pathways of Organometallic Compounds

A. STRUCTURE AND REACTIVITY

1. *Nature of the Metal*

It seems fair to state that the nature of the metal is more important than the R group in determining the gross behavior of R_nM types. Relative reactivities of organometallic compounds within a given family or horizontal period of the periodic chart have been estimated by their rate of addition to unsaturated compounds (for example, benzonitrile). The resulting empirical correlations show that R_nM types of the A family metals in Groups

IA and IIA increase in reactivity with increasing atomic weight. Conversely, R_nM compounds of the B family metals of the same group decrease in reactivity. Thus in Groups IA and IIA, RCs and R_2Ba compounds are the most reactive whereas in Groups IB and IIB, RCu and R_2Zn have the greatest reactivity. In a given period, however, the reactivity seems to decrease with atomic number increase; hence, the order, RNa $>$ R_2Mg $>$ R_3Al. These rules covering the most typical organometallic types can be supplemented by generalizations for Groups III–VII (*43*). Since the reactivity of R_nM types increases with increasing metallic character of M, broadly speaking, the reactivity of R_nM varies somewhat inversely to the electronegativity index of M (*101*). Indeed, there is a tendency to readjust electronegativity values of metals by reason of the chemical behavior of their organometallic compounds.[3] It should be remembered, however, that these reactivity correlations are drawn largely from the behavior of R_nM in *ether solution* containing *metal halides.* Since Group III alkyls form very stable complexes with both ether and metal halides, possibly their observed lower order of reactivity compared to alkyls of Group I and II cannot be related to the intrinsic reactivity of their carbon-metal bond. It may simply express the relative stability and inertness of *R_3M complexes.* The great reactivity of ether-free R_3Al discussed in Sections II.A.1 and IV.C.6 points out the need for further reactivity evaluations.

An additional hindrance to relating the reactivity of R_nM types to the electronic configuration of the metal involved is the tendency for extensive intermolecular associations of organometallic compounds. The extent to which alkyls of the boron family dimerize is a function of both the size and electric field of the metal atom. The reactivity of monomeric triethylborane versus that of dimeric triethylaluminum is therefore less readily analyzed into electronic effects.

2. Nature of the Organic Moiety

With a given metal atom the reactivity of R_nM is profoundly influenced by the nature of the R group. A recent example is the addition of Grignard reagents to the $\rangle C{=}N{-}$ linkage in benzophenone anil. The allyl Grignard reagent adds almost quantitatively, whereas the *n*-propyl analog gives no discernible reaction in the same period of time (*45*). Empirical reactivity series of various organomagnesium and other organometallic compounds have been established (*43*). Such experimentally determined "electronegativities" of organic radicals do not distinguish the various structural factors

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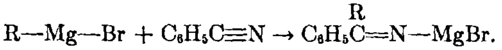
[3] The interaction of RLi with $(C_6H_5)_3MH$ (M = Si, Ge, Sn) is illustrative. While the silicon and tin hydrides undergo some hydrogen-alkyl exchange to give $(C_6H_5)_3M{-}R$, the germanium analog undergoes metalation to yield $(C_6H_5)_3Ge{-}Li$ (*46a*). This supports a higher electronegativity for Ge versus Si and Sn.

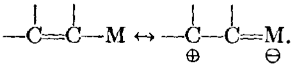
involved. Rationalization of reactivity based upon the electronic and steric factors involved in the R group would be preferable. This cannot be done at present without some ambiguity for the reasons discussed in the previous section. However, some beginning can be made. In the first place, one can envisage that steric factors could increase or decrease the reactivity of the carbon-metal bond. Thus if R is bulky, the compound R—M may be less associated as $(R{-}M)_x$ and hence the monomeric R—M may react more readily. Moreover, the repulsive forces existing between the metal atom and a bulky organic group may weaken the carbon-metal bond and thereby aid reaction. The greater reactivity of the 2,4,6-trimethylphenyl Grignard reagent compared to that of the phenyl reagent versus benzonitrile is a case in point:



$$R{-}Mg{-}Br + C_6H_5C{\equiv}N \rightarrow C_6H_5\overset{R}{C}{=}N{-}MgBr. \qquad (61)$$

Conversely, a decreased reactivity of R—M types involving bulky R groups can be related to steric interference either with solvation by ether or with the substrate molecule. Such complexation seems to be important in aiding heterolysis of the carbon-metal bond. Witness the failure of *t*-butylmagnesium halide to add to di-*t*-butyl ketone, although methylmagnesium halide adds with no special difficulty.

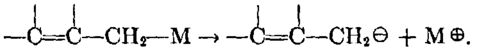
In the second place, the electronic nature of the R group can modify the polarity of the carbon-metal bond. The importance of π-bonding in the structure of metal alkyls is discussed in Section III.B. As far as chemical reactivity is concerned, however, a greater electron-attracting power of R should enhance the polarity of the carbon-metal bond and thus increase its chemical reactivity. In addition, if the R group is unsaturated, the reactivity of the organometallic compound changes markedly. Situation of the unsaturation on the carbon atom of C—M bond as in phenyl, vinyl, or acetylenic R—M types usually results in some stabilization of the bond if π-metal orbital overlap can occur:



$$-\overset{|}{C}{=}\overset{|}{C}{-}M \leftrightarrow -\underset{\oplus}{\overset{|}{C}}{-}\underset{\ominus}{\overset{|}{C}}{=}M.$$

That such bonding is operative in many carbon-metal bonds is indicated by the superior stability of phenyl and acetylenic derivatives of the transition metals (Section II.E) and the reduced reactivity of vinylboranes (*92, 93*). Trivinylborane, for example, has a reduced acceptor tendency towards ammonia and does not react with oxygen. Investigations have aimed at looking for similar effects with vinylstannanes (*112*) and vinylgermanes (*108*). Yet in alkynylgermanes and alkynylstannanes it appears that the adjacent triple bond labilizes the carbon-metal bond. Both types undergo facile hydrolysis, and bis(triethylgermyl)acetylene is rather sensitive to oxygen (*56*, *57*).

If instead the R group contains unsaturation α, β to the carbon-metal bond, the lability of the bond is increased. With the possible exception of ionic alkyls (already ionized) the allyl and benzyl derivatives of a given metal show the greater reactivity. The sensitivity of tetrabenzyllead and of tribenzylbismuth (*4*) to oxidation exemplifies this increased reactivity. One can rationalize this enhanced reactivity by the ease of cleaving the bond:



$$-\overset{|}{C}=\overset{|}{C}-CH_2-M \rightarrow -\overset{|}{C}=\overset{|}{C}-CH_2^{\ominus} + M^{\oplus}. \qquad (62)$$

Whether the cleavage is heterolytic, as above, or homolytic, the allylic-type anion or radical would be stabilized by π-electron delocalization.

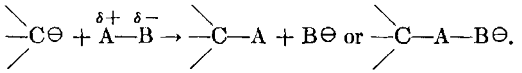
3. Role of the Reaction Medium

The importance of solvent in the reactions of the polar carbon-metal bond has already been adverted to. Evidence indicates that reactions of lithium and magnesium alkyls go more rapidly in ether than in benzene. The acceleration seems to be due to more extensive complexation of ether molecules with the metal moiety which thereby facilitates heterolysis of the carbon-metal bond. On the other hand, solvation seems to aid the formation of many difficult-to-obtain organometallic compounds. It would appear that such solvent complexation stabilizes certain valence states of metals and hinders homolytic decomposition. The recent widespread introduction of solvents more basic than diethyl ether, namely, tetrahydrofuran (THF) and glycol ethers (*10*, *91*, *100*, *102*), has played a significant part in new synthetic schemes. Herwig and Zeiss (*64*) have obtained the long-sought triphenylchromium (III) from chromium (III) salts and phenyl Grignard in THF, whereas the same reaction in diethyl ether leads to aromatic π-complexes of chromium, Hein's "polyphenylchromiums" (*60*, *138*).

Besides facilitating such displacement reactions THF and other solvents aid the reaction of metals with organic compounds. The preparation of unsaturated hydrocarbon-metal adducts is immeasurably more rapid in such ethers. Thus, although lithium and biphenyl react very slowly in diethyl ether to form a 1:1 adduct (several days), the same reaction in THF proceeds momentarily (compare Section II.G).

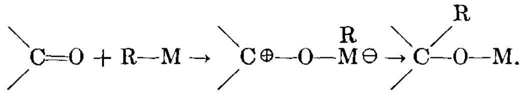
B. CLEAVAGE OF THE CARBON-METAL BOND

Highly ionic carbon-metal bonds such as presumably exist in organosodium compounds consist of carbanion-sodium cation pairs and the reaction with the substrate molecule may be viewed as a nucleophilic attack:



$$\rangle C^{\ominus} + \overset{\delta+}{A}-\overset{\delta-}{B} \rightarrow \rangle C-A + B^{\ominus} \text{ or } \rangle C-A-B^{\ominus}. \tag{63}$$

A similar behavior is to be expected of the highly polar, covalent carbon-metal bond as occurs in lithium, magnesium, and aluminum alkyls. Here, however, initial complexation with the substrate seems to precede the heterolysis of the carbon-metal bond:



$$\rangle C=O + R-M \rightarrow \rangle C^{\oplus}-O-\overset{R}{M}^{\ominus} \rightarrow \rangle \overset{R}{C}-O-M. \tag{64}$$

Where the nature of the metal or experimental conditions render such auxiliary complexation with either the substrate or the solvent less favorable, there is an increased tendency towards homolysis of the carbon-metal bond. Treatment of organolithium and organomagnesium alkyls with transition metal halides leads to metal halide reduction and hydrocarbon, suggestive of the transitory formation of metal alkyls (*48*), decomposing thereupon into a lower salt and free alkyl radicals:

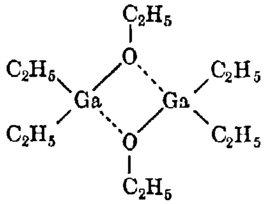
$$MX_n + RLi \rightarrow LiX + RMX_{n-1} \rightarrow MX_{n-1} + R^{\cdot}. \tag{65}$$

The detection of free radicals from such Grignard reactions using anthracene as a scavenger has been studied recently (*90*). The extremely unstable silver alkyls resulting from the treatment of lead alkyls with silver nitrate decompose rather easily to yield alkyl radicals (compare behavior of isobut-1-enylsilver) (*51*, *52*).

C. REACTION PATHWAYS

1. *Oxidation*

Depending upon the metal concerned, controlled oxidation of metal alkyls may cease before all carbon-metal bonds are converted to C—O—M groupings. It is interesting to compare the behavior of triethyl derivatives of Group III elements toward air oxidation: the aluminum analog oxidizes completely to $(C_2H_5O)_3Al$, the boron derivative may form either $(C_2H_5)B(OC_2H_5)_2$ or $(C_2H_5)_2B(OC_2H_5)$, and triethylgallium and triethylindium stop after having formed $(C_2H_5)_2MOC_2H_5$. Presumably the presence of the ethoxy group leads to stabilization towards further oxidation by intermolecular complexation as dimer in the diethylgallium ethoxide (XII) (*24*, *142*):



XII

and as polymer in the diethylindium ethoxide (infusible solid) (*104*, *142*); or by intramolecular complexation in

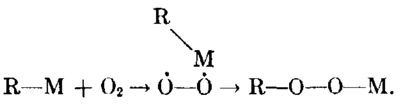
$$R_2B{-}OR \leftrightarrow R_2\overset{\ominus}{B}{=}\overset{\oplus}{O}{-}R.$$

Although air oxidation may not oxidize all carbon-metal bonds in an organometallic compound, reagents such as alkaline hydrogen peroxide cleave such compounds completely to the alcohol and metal base:

$$R_n{-}M \xrightarrow[NaOH]{H_2O_2} nR{-}OH + M^{n+} + nOH^-. \qquad (66)$$

Such reactions have great preparative significance for alcohol production from olefins (Section II.A.2).

The mechanism of the air oxidation is not completely clear. It is significant that excepting organometalloids only those $R_n{-}M$ compounds react whose metal has unfilled *p*-orbitals of the highest principal quantum number. Since the oxygen molecule is a diradical in the ground state, interaction between $R_n{-}M$ and oxygen may involve initially a one-electron bond between the metal's *p*-orbital and the oxygen with a subsequent 1,3-shift (via a three-electron bridge bond?) of the R group to yield the hydroperoxide salt: (compare Section IV.C.4).



$$R{-}M + O_2 \rightarrow \overset{R\diagdown\;\;\;\;\;\;\;\;}{\dot{O}{-}\overset{M}{\dot{O}}} \rightarrow R{-}O{-}O{-}M. \qquad (67)$$

Such a formulation seems more appealing than initial complexation, as alkyls of boron and zinc oxidize readily despite their seeming reluctance to form complexes with oxygen-type donors. That hydroperoxides are formed and that these give eventually the alkoxides has been demonstrated for several metal alkyls. Recently the corresponding alkyl hydroperoxides have been prepared in good yield by treating the Grignard reagents with oxygen-saturated solvents at −70° (*124*, *125*). Similarly peroxides of boron

(*96*) and cadmium alkyls (*30*) have been isolated by controlled oxidation. The rapidity of such oxidations makes a radical chain process attractive, but neither aldehydes nor aromatic amines appear to interfere with the reaction (*125*). Thus the formulation given in Eq. 67 or an analogous electron-transfer process would seem more acceptable.

2. Hydride Formation

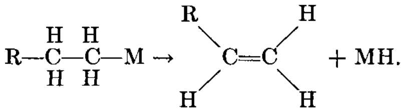
The formation of metal hydrides from organometallic compounds is an interesting transformation attracting more and more attention. There are several ways in which this conversion can be brought about. The first method, that of hydrogenolysis via molecular hydrogen, has been mentioned in Section I.B.2. Within the last few years this method has gained new prominence as a feasible preparation of boron hydrides. It has been found that trialkylboranes, prepared readily from boron trifluoride and aluminum alkyls, can be cleaved by hydrogen under pressure at 200° in the presence of amines, to give BH_3-amine complexes. Such complexes can be converted into alkali borohydrides by the addition of the desired alkali hydride (*74*):

$$H_3B{:}NR_3 + NaH \xrightarrow[\text{ether}]{100^\circ} NaBH_4 + NR_3. \qquad (68)$$

Similarly, the useful liquid reducing agent, diethylaluminum hydride, can be readily made by heating triethylaluminum with hydrogen under pressure:

$$Al(C_2H_5)_3 + H_2 \rightarrow HAl(C_2H_5)_2 + C_2H_6. \qquad (69)$$

Almost nothing is known about the effect of catalysts on these hydrogenolyses, but the known behavior of such metal alkyls suggests that at higher temperatures an equilibrium obtains between the olefin and metal hydride (Section II.A.1):



$$R{-}\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}M \rightarrow \begin{matrix} R & & H \\ & C{=}C & \\ H & & H \end{matrix} + MH. \qquad (70)$$

The olefin may be reduced subsequently to the alkane, leaving the metal hydride.[4] That such an equilibrium is likely is strongly supported by the products of the thermal decomposition of triisobutylgallium. At 160° this compound decomposes to give gallium metal, hydrogen, and isobutylene in nearly a 1:1.5:3.0 ratio. Very little isobutane is found. This suggests

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[4] Alternatively, one can envisage a direct hydrogenolysis of the carbon-metal bond to form the alkane and the metal hydride. The driving force would be the liberation of the weaker acid (RH) by the stronger acid (H_2).

an equilibrium involving unstable gallium hydride, which at this temperature reverts to the elements (*142*).

Another method of preparing metal hydrides from organometallic compounds is by means of the following exchange reaction:

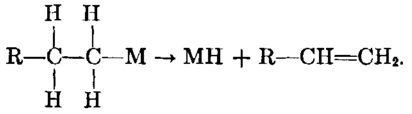
$$\text{R—M} + \text{M}'\text{—H} \rightarrow \text{R—M}' + \text{M—H}. \qquad (71)$$

A recent example is the preparation of a magnesium hydride, HMgX, by treating the Grignard reagent with diborane (*129*):

$$6\text{R—Mg—X} + B_2H_6 \rightarrow 6\text{HMgX} + 2\text{BR}_3. \qquad (72)$$

The method seems to offer promise of alkylating certain boron hydrides (compare *126*). In addition, hydrides of tin and silicon seem to undergo an analogous reaction. Thus it has been observed that triphenyltin hydride reacts with methyllithium to yield mainly lithium hydride and triphenylmethyltin (*50*).

A third procedure follows from the above and subsequent discussions and that is the controlled thermal elimination of olefin from R—M to yield metal hydrides where the latter are sufficiently stable:



$$\text{R}-\underset{\text{H}}{\overset{\text{H}}{\text{C}}}-\underset{\text{H}}{\overset{\text{H}}{\text{C}}}-\text{M} \rightarrow \text{MH} + \text{R—CH=CH}_2. \qquad (73)$$

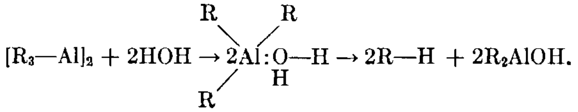
Diisobutylaluminum hydride can be prepared conveniently by heating the triisobutylaluminum between 150° and 180° to remove one equivalent of isobutylene (compare Section II.A.1).

3. *Cleavage by Active Hydrogen Compounds*

The negatively polarized carbon atom in organometallic compounds formally can be considered as a carbanion, $R^{\ominus}$, either actually (RNa) or potentially (R_3Al). Since the corresponding hydrocarbon, RH, is usually a very weak acid, the carbanion, $R^{\ominus}$, is a very strong base. Consequently, most H-A compounds, where A is an electronegative element or moiety, will give up a proton to $R^{\ominus}$ and thus cleave the carbon-metal bond:

$$\text{R—M} + \text{H—A} \rightarrow \text{R—H} + \text{M—A}. \qquad (74)$$

Cleavage reactions of R—M by means of water and acids cited in Section I.B.2 are of this general type. Other suitable H—A species are NH_3, RNH_2, R_2NH, ROH and acidic hydrocarbons such as terminal alkynes (R—C≡C—H) and cyclopentadiene types. Although such reactions have as their driving force the generation of the weaker acid, the mechanism of cleavage of R—M by active hydrogen compounds is not fully elucidated at the present. There are certain recognizable similarities between this cleavage reaction and organometallic oxidation. Again it is seen that R—M compounds susceptible to facile cleavage possess unfilled low-lying *p*-orbitals on the metal atom. It would seem that initial attack on R—M is complexation by H—A if the A moiety possesses an unshared electron pair. Separation of R—H may then occur by a 1,3 shift. The hydrolysis of R_3Al can be represented schematically:



$$[R_3\text{—}Al]_2 + 2HOH \rightarrow 2R_3Al{:}\underset{H}{O}\text{—}H \rightarrow 2R\text{—}H + 2R_2AlOH. \qquad (75)$$

The plausibility of this formulation is enhanced by the known resistance of trialkylboranes to hydrolysis (*121*). This stability would seem understandable in terms of steric shielding of the relatively small boron atom by the alkyl groups to approach of water molecules. Alcoholysis of Group III alkyls is of varying facility. Contrasted with inertness of R_3B, the aluminum alkyls undergo rupture of all three bonds in alcohol:

$$R_3Al + 3R'\text{—}OH \rightarrow 3RH + 3(R'O)_3Al, \qquad (76)$$

but gallium (*142*) and indium alkyls (*104*) allow cleavage of only one carbon-metal bond, leading to R_2MOR'. As both hydrolysis and alcoholysis involve the rupture of oxygen-hydrogen bonds, some researchers have sought to learn whether this bond is broken in the rate-determining step by employing deuterated water and alcohol. The deuterated compound should react more slowly if the hydrogen-oxygen bond is ruptured in the rate-determining step. One study of the hydrolysis of methylmagnesium iodide showed no apparent preference for breaking O-H over O-D bonds in the reaction; the methane obtained contained deuterium in the same proportion as deuterium was present in the water (*91a*). Alcoholysis of certain organolithium and Grignard reagents in deuterated methanol showed a slight acceleration over ordinary methanol. This unusual isotope effect might suggest a stronger oxygen-hydrogen bond in the transition state over that in the reactants, but the cause is not yet certain (*130*). Since both the RLi and RMgX compounds prepared in ether from the metal and RX contain metal salts, and are themselves extensively solvated and associated, the system is perhaps too complex to permit unambiguous conclusions to be drawn.

The interaction of 1-alkynes and alkyl Grignard reagents has been the subject of much recent attention (*32*, *33*, *136*). By measurement of the rate of evolution of RH the reactivity of RMgX towards 1-hexyne was evaluated:

$$R\text{—}Mg\text{—}X + C_4H_9C{\equiv}C\text{—}H \rightarrow C_4H_9C{\equiv}C\text{—}Mg\text{—}X + RH. \qquad (77)$$

The Grignard reagents showed the following order of increasing reactivity: methyl < *n*-propyl < ethyl < *iso*-propyl < allyl. Although the electrolysis decomposition potentials of these Grignard reagents increase in the inverse order, the complex character of the organomagnesium halides in ether prevents any simple mechanistic interpretation of this correlation (*32*). It has been proposed that the reactivity of RMgX is proportional to the number of β-hydrogens in R. However, the reactivity differences might be due to varying degrees of autocomplexation of the Grignard reagents (compare Section IV.A.1). Experiments with 1-hexyne-d_1 showed that the rate of cleavage was decreased by a factor of 4.3 compared to ordinary 1-hexyne. In the light of previous discussion this would suggest that the C-H bond is ruptured in the rate-determining step (*33*).

4. *Lewis Acid Character*

Much recent investigation has been devoted to evaluating the tendency of organometallic compounds to act as electron pair acceptors (*116*). The possibilities of carbanions acting as donors is considered in Section II.D dealing with organometallic σ-complexes. Three main types of donors have been considered in these studies: first, amines and their Group V analogs; second, ethers and their Group VI analogs; and third, halide ions. Although Groups IA, IIA, and IIIA metal alkyls form Lewis salts with the aforementioned bases, the stability of such salts with metal alkyls of the same period increases with the group number: thus, the stability of $R_nM \leftarrow OR_2$ seems to increase in the order, RNa < R_2Mg < R_3Al. Such a gradation is reasonable in terms of an increasing nuclear charge in M (for elements of the same principal quantum number) causing an enhanced electronegativity, and consequently greater acceptor tendencies in R—M. The variation of acceptor properties for metal alkyls of a given periodic family has been examined most thoroughly for Group IIIA elements, both by comparing the heats of dissociation of $R_3M \leftarrow NR_3$ complexes, as Coates has done (*26*), and by correlating dipole moments of solutions of R_3M in donor solvents, as carried out by Strohmeier (*117*). Both methods give the following sequence of decreasing acceptor character: B < Al > Ga > In > Tl. The exceptional behavior of boron alkyls versus trialkylamine, that is, the formation of no measurably stable complex, is attributed to steric hindrance by the neighboring alkyl groups in establishing a stable boron-nitrogen bond (F-strain). The observed variation from aluminum alkyls through thallium alkyls can be owed to the increasing atomic radius of M in R_3M causing a decrease in the bond strength of M—N via the shielding effect of underlying filled electron levels. As the effective nuclear charge of M is weakened, the bond strength of the Lewis salt decreases. A similar variation in acceptor strength has been noted with the metal alkyls of Group II: Be < Mg > Zn > Cd > Hg.

To a first approximation these trends seem to carry over to ether and halide complexes also. For example, the lower aluminum alkyls form very stable monoetherates, $R_3Al \leftarrow OR_2$ (*5*), whereas gallium and especially indium alkyls can be prepared in ether solution and isolated free of ether (*104*). A striking illustration of this difference in complexation tendencies among family members is the behavior of Group III alkyls towards alkali fluorides: triethylaluminum complexes with either sodium or potassium fluoride, the corresponding gallium alkyl complexes only with potassium fluoride, and the indium alkyl complexes with neither fluoride. This sharp distinction has interesting applications in separating these metal alkyls from each other (*142*).

The formation of such Lewis complexes may find increasing application in stereochemical studies. Two cases in point might be cited. First, etherate formation allows the isolation of the optically active tri-2-methylbutylaluminum etherate (*97*). This compound is stable to racemization up to 100°. Second, diphenylpalladium (II) has recently been prepared as its bis-triethylphosphine complex in both a *cis-* and a *trans-*planar complex form (*20*). The latter seems to represent the first example of geometrical isomerism among organometallic compounds (Section II.D).

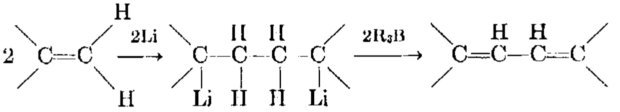
A final point concerning Lewis complex possibilities should be mentioned. The adducts formed between Group III organometallics and alkali metals are somewhat remindful of Lewis salt formation except only one electron is involved (compare oxidation of R—M, Section IV.C.1):

$$R_3B + Na^{\cdot} \rightarrow [R_3\overset{-}{B} \cdot \overset{+}{Na}]. \qquad (78)$$

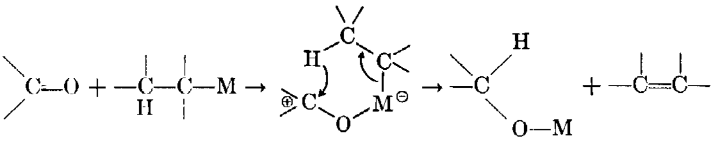
However, recent re-examination of $(C_6H_5)_3BNa$ has shown it to be diamagnetic, suggesting a better formulation to involve a dimer $[R_3B{-}BR_3]^{\ominus\ominus}$ (*23*).

5. *Thermal Dissociation*

Rupture of the carbon-metal bond in R_nM upon heating seems to involve either homolytic cleavage leading to free-radical fragments, $R^{\cdot}$ and $R_{n-1}{-}M$, or heterolysis giving rise to metal hydride and olefin. The latter reaction, representing the reversal of metal alkyl formation from olefins and metal hydrides, takes place with the more reactive alkyls (compare Sections II.A.1 and IV.C.2). Since it seems that metal hydrides add to unsaturates in a *cis* fashion, one might expect elimination in the same sense, rather than *trans* elimination [Eq. (73)], the less substituted olefin being formed preferentially (compare behavior of sodium alkyls) (*87, 88*). This suggests that methyl derivatives should be more stable, since the analogous alkene would be the reactive methylene; methyllithium gives CH_2Li_2 at 200–240° and $LiC{\equiv}CLi$ at 420°, whereas ethyllithium decomposes over 100° (*139*). This mode of decomposition is apparent in certain of the reactions of organometallic compounds: first, one can sometimes eliminate M—H from R—M by addition of a suitable complexing agent [that is, $(C_6H_5)_3B$]. Wittig has developed the following olefin synthesis (*134*):

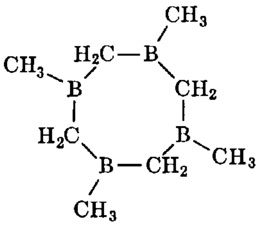

(79)

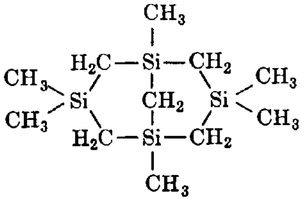
Second, certain R—M compounds interact with carbonyl compounds to give reduction products explained, formally at least, by the carbonyl compound removing M—H from R—M (via XIII):


XIII
(80)

The homolytic thermal dissociation of R—M, previously used by Paneth in generating and studying free alkyl radicals, occurs with the more electronegative alkyls, such as those of mercury, lead, and the metalloids. Currently there is much interest in evaluating carbon-metal bond dissociation energies from such pyrolyses (Section III.B).

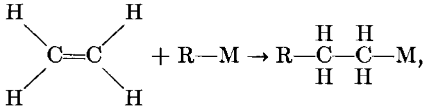
In cases involving the pyrolyses of organometalloid compounds where the carbon-metalloid bond has a high thermal stability, it has been found that heterocyclic organic compounds of novel structure are formed. Presumably the pyrolysis of trimethylborane leads to, among other products, an eight-membered ring (Formula XIV) (*53*), and the heating of tetramethylsilane yields besides a six-membered ring the interesting bicyclic type (Formula XV) (*41*):

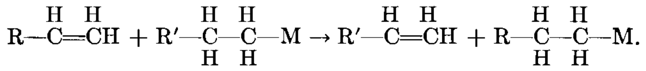

XIV


XV

6. Addition to Unsaturated Organic Compounds

The truly significant advance in the interaction of R—M with unsaturated organic compounds in the last several years is admission of the —C=C— and —C≡C— linkages as ordinary functional groups in organometallic synthesis. The instances of the addition of organomagnesium compounds to carbonyl, nitrile, or other heteroatom unsaturates of the type M≡N are countless, but similar reactions with the olefinic and acetylenic groupings have been of an *ad hoc* nature (see *72*). What seems to have delayed recognition of the additive possibilities of R—M on olefins is the traditional utilization of R—M in ether solution where etherate formation depresses the reactivity of the carbon-metal bond. Postwar research by Ziegler and co-workers (*140*) with lithium and subsequently aluminum alkyls has brought to light two main types of interactions, the addition reaction [Eq. (81)] and the displacement reaction [Eq. (82)]:


(81)

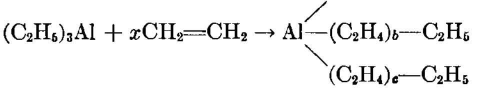


$$R{-}\overset{H}{C}{=}\overset{H}{C}H + R'{-}\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}M \rightarrow R'{-}\overset{H}{C}{=}\overset{H}{C}H + R{-}\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}M. \qquad (82)$$

The utility of the displacement or "Verdrängung" reaction in the synthesis of other organometallic compounds is considered in Section II.A.1. However, in organic synthesis two courses of the addition reaction are possible: either the olefin or acetylene reacts with a given carbon-metal linkage in a ratio of 1:1, this adduct being worked up to give product; or the unsaturated compound reacts with the carbon-metal bond successively to give long carbon chains. Illustrative is the behavior of $(C_2H_5)_3Al$ with an α-olefin, ethylene. One reaction observed is simple addition in ratio of C-Al:olefin of 1:1:

$$(C_2H_5)_3Al + 3CH_2{=}CH_2 \rightarrow (n\text{-}C_4H_9)_3Al. \qquad (83)$$

However, the tri-*n*-butylaluminum can react further with ethylene to give higher aluminum alkyls to yield the net equation:


$x = a + b + c$ (84)

This "growth" reaction is hindered by concurrently occurring olefin displacement reactions [Eq. (32)]. In essence, however, it presents a method of building long carbon chains from ethylene by using the initial aluminum alkyl as a framework. The exciting aspect is that introduction of certain transition metal halides in such a mixture accelerates growth of the carbon chain to an astounding rate, so that polyethylene polymers having average molecular weights up to three million are obtained (*140*).

Extension of these observations to acetylenes and conjugated dienes has led to interesting carbon ring compounds such as hexasubstituted benzenes from $RC{\equiv}CR$ and cyclododecatriene-1,5,9 from butadiene (*132*).

V. Applications of Organometallic Reagents in Research and Technology

A. Synthesis

In the discussions of the latest advances in the preparation and reactions of organometallic compounds the import to industrial synthesis has been alluded to. Development of feasible methods for the large-scale preparation of aluminum alkyls has placed in the hands of the industrial chemist a tool for converting lower olefins into higher aluminum alkyls (Section IV.C.6), or to higher fatty alcohols, RCH_2CH_2OH (Section II.A.2). Besides thus obtaining useful detergent and fatty acid intermediates from olefins, catalytic quantities of aluminum or other metal alkyls with a transition metal salt co-catalyst convert olefins to polyalkylenes of superior properties. High-density polyethylene, isotactic polypropylene, 1,2- and 1,4-polyalkadienes, and synthetic "natural" rubber have resulted from such metal alkyl-catalyzed polymerizations (compare *131*).

The practicality of preparing metal and metalloid hydrides in certain cases from the readily accessible metal alkyls has been receiving ever-increasing attention. Either by eliminating one or more moles of olefin from $(RCH_2CH_2)_nM$ thermally, or by cleaving the organometallic compound with hydrogen, one can obtain pure hydrides or partially alkylated hydrides. Diborane, obtained in the latter manner, is the keystone of syntheses leading to high-energy rocket fuels, whereas dialkylaluminum hydrides have been suggested as liquid reducing agents for functions susceptible to $LiAlH_4$.

B. Technology

The applications of organometallic agents in technology show every promise of increasing. The traditional use of tetraethyllead in motor fuels may eventually be replaced by some other type. Tin alkyls have gained some recent prominence both for the biocidal properties of certain trialkyltin derivatives and for the ultraviolet-discoloration protection offered vinyl plastics by dibutyltin dilaurate. Also attention should be drawn to the possibilities of metal plating and lead alkyl production by means of electrolytic reactions employing alkali fluoride-aluminum alkyl complexes. Finally, there has been some investigation (*143*) of the possibility of metal purification by means of preparing the R—M compound with the crude metal and then pyrolyzing the purified R—M compound to free the metal.

VI. Present Trends in Organometallic Research

Recent organometallic investigation has witnessed a resurgence of one of the most primary aspects of chemical research, namely the preparation and isolation in pure state of many new and intriguing types of compounds. This synthetic aspect seems destined to continue flourishing in the years ahead. Albeit preparative techniques have been refined to permit the formation of some type of carbon-metal bond with almost any known metallic element, our understanding of the factors governing the structure and reactivity of organometallic compounds is largely of a qualitative, empirical nature. It would seem therefore that future research in this field will aim at elucidating the structure of associated metal alkyls not only in the pure state but also in solution. Once a clearer picture is obtained of which species predominate, say in a solution of R_nM in ether, then the next step of interpreting the kinetic data of organometallic reactions in terms of known R—M species becomes more feasible. Correlations of reactivity with variations of the alkyl and metal moieties in R—M then can be more directly related to electronic and steric factors. In the case of unassociated metal alkyls, it would seem that there will be increasing effort expended in evaluating the electron-transmitting properties of carbon-metal bonds in terms of inductive and mesomeric effects.

Organometallic chemistry, therefore, will be a topic of mutual interest to the theoretical and to the synthetic chemist for many years to come.

LIST OF SYMBOLS

d_π-p_π	a pi interaction between a *d*- and a *p*- orbital.
$\delta-$, $\delta+$	a partial separation of charges.
⊖, ⊕	a full separation of charges.
←	a donor bond.

REFERENCES

1. Amma, E. L., and Rundle, R. E., *J. Am. Chem. Soc.* **80**, 4141 (1958).
2. Anet, F. A. L., and Leblanc, E., *J. Am. Chem. Soc.* **79**, 2650 (1957).
3. Bähr, G., and Müller, G. E., *Chem. Ber.* **88**, 251 (1955).
4. Bähr, G., and Zoche, G., *Chem. Ber.* **88**, 542 (1955); **90**, 1176 (1957).
5. Baker, E. B., and Sisler, H. H., *J. Am. Chem. Soc.* **75**, 4828, 5193 (1953).
6. Bartocha, B., and Stone, F. G. A., *Z. Naturforsch.* **13b**, 347 (1958).
7. de Boer, E., and Weissman, S. I., *J. Am. Chem. Soc.* **80**, 4549 (1958).

8. Bonner, E. F., Carrick, W. L., Kluiber, R. W., Reichle, W. T., Rugg, F. M., Smith, J. J. and Wartman, L. H., *Proc. 133rd Meeting Am. Chem. Soc.* p. 19R (1958).

9. Brokaw, R. S., and Pease, R. N., *J. Am. Chem. Soc.* **72,** 3237 (1950).

10. Brook, A. G., *J. Am. Chem. Soc.* **76,** 77 (1954).

11. Brook, A. G., Cohen, H. L., and Wright, G. F., *J. Org. Chem.* **18,** 447 (1953).

12. Brook, A. G., and Gilman, H., *J. Am. Chem. Soc.* **76,** 278 (1954).

13. Brook, A. G., Gilman, H., and Miller, L. S., *J. Am. Chem. Soc.* **75,** 4759 (1953).

14. Brown, H. C., and Subba Rao, B. C., *J. Am. Chem. Soc.* **78,** 5694 (1956).

15. Brown, H. C., and Subba Rao, B. C., *J. Org. Chem.* **22,** 1135 (1956).

16. Brown, H. C., and Zweifel, G., *J. Am. Chem. Soc.* **81,** 247 (1959).

17. Brown, T. L., and Rogers, M. T., *J. Am. Chem. Soc.* **79,** 1859 (1957).

18. Bryce-Smith, D., *J. Chem. Soc.* p. 1712 (1955).

18a. Bunsen, R., *Ann.* **42,** 14 (1842).

19. Calvin, G., and Coates, G. E., *Chem. & Ind.* p. 160 (1958).

20. Chatt, J., and Shaw, B. L., communication to Calvin and Coates (*19*).

21. Chatt, J., and Williams, A. A., *J. Chem. Soc.* p. 4403 (1954).

22. Chernick, C. L., Skinner, H. A., and Wadso, I., *Trans. Faraday Soc.* **52,** 1088 (1956).

23. Chu, T. L., *J. Am. Chem. Soc.* **75,** 1730 (1953).

24. Coates, G. E., "Organo-metallic Compounds," Methuen, London, 1956.

25. Coates, G. E., and Glockling, F., *J. Chem. Soc.* p. 2526 (1954).

26. Coates, G. E., and Whitcombe, R. A., *J. Chem. Soc.* p. 3351 (1956).

27. Cotton, F. A., *Chem. Revs.* **55,** 551 (1955).

28. Curran, C., McCusker, P. A., and Makowski, H. S., *J. Am. Chem. Soc.* **79,** 5188 (1957).

29. Dale, J. W., Emeleus, H. J., Haszeldine, R. N., and Moss, J. H., *J. Chem. Soc.* p. 3708 (1957).

30. Davies, A. G., and Packer, J. E., *Chem. & Ind.* p. 1177 (1958).

31. Dessy, R. E., Handler, G. S., Wotiz, J. H., and Hollingsworth, C. A., *J. Am. Chem. Soc.* **79,** 3476 (1957).

32. Dessy, R. E., Hollingsworth, C. A., and Wotiz, J. H., *J. Am. Chem. Soc.* **77,** 4410 (1955).

33. Dessy, R. E., Wotiz, J. H., and Hollingsworth, C. A., *J. Am. Chem. Soc.* **79,** 358 (1957).

34. Dimroth, O., *Ber.* **31,** 2154 (1898).

35. Emeleus, H. J., and Haszeldine, R. N., *Science* **117,** 311 (1953).

36. Fairbrother, D. M., and Skinner, H. A., *Trans. Faraday Soc.* **52,** 956 (1956).

37. Farbwerke Höchst, Belgian Patent 553,477 (1956).

38. Fischer, A. K., West, R. C., and Rochow, E. G., *J. Am. Chem. Soc.* **76,** 5878 (1954).

39. Frankland, E., *Ann.* **71,** 171 (1849); **85,** 347 (1853).

40. Freundlich, W., and Claudel, B., *Bull. soc. chim. France* p. 967 (1956).

41. Fritz, G., and Raabe, B., *Z. anorg. u. allgem. Chem.* **286,** 149 (1956).

42. Gadsby, G. N., *Research* **3,** 338 (1950).

43. Gilman, H., *in* "Organic Chemistry" (H. Gilman, ed.), 2nd ed., Vol. 1, pp. 489–580. Wiley, New York, 1943.

44. Gilman, H., and Eisch, J., *J. Org. Chem.* **20,** 763 (1955).

45. Gilman, H., and Eisch, J., *J. Am. Chem. Soc.* **79,** 2150 (1957).

46. Gilman, H., and Gerow, C. W., *J. Am. Chem. Soc.* **77,** 5509 (1955).

46a. Gilman, H., and Gerow, C. W., *J. Am. Chem. Soc.* **78,** 5435 (1956).

47. Gilman, H., and Gerow, C. W., *J. Am. Chem. Soc.* **79,** 342 (1957).

48. Gilman, H., Jones, R. G., and Woods, L. A., *J. Am. Chem. Soc.* **76,** 3615 (1954).

49. Gilman, H., Lichtenwalter, M., and Benkeser, R. A., *J. Am. Chem. Soc.* **75,** 2063 (1953).

49a. Gilman, H., and Morton, J. W., *in* "Organic Reactions" (R. Adams, ed.), Vol. 8, Chapter 6. Wiley, New York, 1954.

50. Gilman, H., and Rosenberg, S. D., *J. Am. Chem. Soc.* **75,** 3592 (1953).

50a. Gilman, H., and Schulze, F., *J. Am. Chem. Soc.* **47,** 2002 (1925).

51. Glockling, F., *J. Chem. Soc.* p. 716 (1955).

52. Glockling, F., *J. Chem. Soc.* p. 3640 (1956).

53. Goubeau, J., and Epple, R., *Chem. Ber.* **90,** 171 (1957).

54. Gowenlock, B. G., and Trotman, J., *J. Chem. Soc.* p. 2114 (1957).

55. Grignard, V., *Compt. rend. acad. sci.* **130,** 1322 (1900).

56. Hartmann, H., and Ahrens, J. U., *Angew. Chem.* **70,** 75 (1958).

57. Hartmann, H., and Honig, H., *Angew. Chem.* **70,** 75 (1958).

58. Haszeldine, R. N., and West, B. O., *J. Chem. Soc.* p. 3880 (1957).

59. Head, E. L., Holley, C. E., Jr., and Rabideau, S. W., *J. Am. Chem. Soc.* **79,** 3687 (1957).

60. Hein, F., and Eisfeld, K., *Z. anorg. u. allgem. Chem.* **292,** 162 (1957).

61. Hein, F., and Weiss, R., *Z. anorg. u. allgem. Chem.* **295,** 145 (1958).

62. Hennion, G. F., McCusker, P. A., Ashby, E. C., and Rutkowski, A. J., *J. Am. Chem. Soc.* **79,** 5190 (1957).

63. Herman, D. F., and Nelson, W. K., *J. Am. Chem. Soc.* **75,** 3877 (1953).

64. Herwig, W., and Zeiss, H. H., *J. Am. Chem. Soc.* **79,** 6561 (1957).

65. Hieber, W., "FIAT Reviews of German Science 1939–1946: Inorganic Chemistry," Pt. II, pp. 108–145. Dieterich, Wiesbaden, 1948.

66. Hieber, W., Vohler, O., and Braun, G., *Z. Naturforsch.* **13b,** 192 (1958).

67. Holmes-Walker, W. A., and Ubbelohde, A. R., *J. Chem. Soc.* p. 720 (1954).

68. Hurd, D. T., *J. Am. Chem. Soc.* **70,** 2053 (1948).

69. Hurd, D. T., "Introduction to the Chemistry of the Hydrides." Wiley, New York, 1952.

69a. Jones, R. G., and Gilman, H., *in* "Organic Reactions" (R. Adams, ed.), Vol. 6, Chapter 7. Wiley, New York, 1951.

70. Jones, R. G., and Gilman, H., *Chem. Revs.* **54,** 835 (1954).

71. Kealy, T. J., and Pauson, P. L., *Nature* **168,** 1039 (1951).

72. Kharasch, M. S., and Reinmuth, O., "Grignard Reactions of Nonmetallic Substances," pp. 1384. Prentice-Hall, New York, 1954.

73. Köster, R., *Angew. Chem.* **68,** 383 (1956).

74. Köster, R., *Angew. Chem.* **69,** 94 (1957).

75. Köster, R., and Ziegler, K., *Angew. Chem.* **69,** 94 (1957).

76. Krause, E., and von Grosse, A., "Die Chemie der metallorganischen Verbindungen." Borntraeger, Berlin, 1937.

77. Laurie, C. M., and Long, L. H., *Trans. Faraday Soc.* **53,** 1431 (1957).

78. Lesbre, M., *Bull. soc. chim. France* p. 1204 (1957).

79. Letsinger, R. L., and Skoog, I., *J. Am. Chem. Soc.* **77,** 2491 (1955).

80. Lipkin, D., Paul, D. E., Townsend, J., and Weissman, S. I., *Science* **117,** 534 (1953).

81. Long, L. H., *J. Chem. Soc.* p. 3410 (1956).

82. Long, L. H., *Trans. Faraday Soc.* **53,** 1606 (1957).

83. Long, L. H., and Sackman, J. F., *Trans. Faraday Soc.* **54,** 1797 (1958).

84. Maier, L., Seyferth, D., Stone, F. G. A., and Rochow, E. G., *J. Am. Chem. Soc.* **79,** 5885 (1957).

85. Merten, H., and Gilman, H., *J. Am. Chem. Soc.* **76,** 5798 (1954).

86. Miller, S. A., Tebboth, J. A., and Tremaine, J. F., *J. Chem. Soc.* p. 632 (1952).

87. Morton, A. A., Lanpher, E. O., *J. Org. Chem.* **20,** 839 (1955).

88. Morton, A. A., Lanpher, E. O., *J. Org. Chem.* **21,** 93 (1956).

89. Nast, R., Vester, K., and Griesshammer, H., *Chem. Ber.* **90,** 2678 (1957).

90. Norman, R. O. C., and Waters, W. A., *J. Chem. Soc.* p. 950 (1957).

91. Normant, H., *Bull. soc. chim. France* p. 728 (1957).

91a. Orchin, M., Wender, I., and Friedel, R. A., *Anal. Chem.* **21,** 1072 (1949).

92. Parsons, T. D., and Ritter, D. M., *J. Am. Chem. Soc.* **76,** 1710 (1954).

93. Parsons, T. D., Silverman, M. B., and Ritter, D. M., *J. Am. Chem. Soc.* **79,** 5091 (1957).

94. Paul, D. E., Lipkin, D., and Weissman, S. I., *J. Am. Chem. Soc.* **78,** 116 (1956).

95. Pedley, J. B., Skinner, H. A., and Chernick, C. L., *Trans. Faraday Soc.* **53,** 1612 (1953).

96. Petry, R. C., and Verhoek, F. H., *J. Am. Chem. Soc.* **78,** 6416 (1956).

97. Pino, P., Lardicci, L., and Lorenzi, G. P., *Angew. Chem.* **70,** 599 (1958).

98. Price, S. J. W., and Trotman-Dickenson, A. F., *Trans. Faraday Soc.* **53,** 1208 (1953).

99. Price, S. J. W., and Trotman-Dickenson, A. F., *Trans. Faraday Soc.* **53,** 939 (1957).

100. Ramsden, H. E., Balint, A. E., Whitford, W. R., Walburn, J. J., and Cserr, R., *J. Org. Chem.* **22,** 1202 (1957).

101. Rochow, E. G., Hurd, D. T., and Lewis, R. N., "The Chemistry of Organometallic Compounds." Wiley, New York, 1957.

102. Rosenberg, S. D., Gibbons, A. J., and Ramsden, H. E., *J. Am. Chem. Soc.* **79,** 2137 (1957).

103. Rundle, R. E., *J. Phys. Chem.* **61,** 45 (1957).

104. Runge, F., Zimmermann, W., Pfeiffer, H., and Pfeiffer, I., *Z. anorg. u. allgem. Chem.* **267,** 39 (1951).

105. Sacharkin, L. I., and Ochlobysstin, O. J., *Repts. Acad. Sci. Ukr. S.S.R.* **116,** 236 (1957); *Chem. Zentr.* **129,** 11463 (1958).

106. Schlenk, W., Appenrodt, J., Michael, A., and Thal, A., *Ber.* **47,** 473 (1914).

107. Seyferth, D., *Chem. Revs.* **55,** 1155 (1955).

108. Seyferth, D., *J. Am. Chem. Soc.* **79,** 2738 (1957).

109. Seyferth, D., *J. Am. Chem. Soc.* **79,** 5881 (1957).

110. Seyferth, D., and Rochow, E. G., *J. Am. Chem. Soc.* **77,** 907 (1955).

111. Seyferth, D., and Rochow, E. G., *J. Am. Chem. Soc.* **77,** 1302 (1955).

112. Seyferth, D., and Stone, F. G. A., *J. Am. Chem. Soc.* **79,** 515 (1957).

113. Slough, W., and Ubbelohde, A. R., *J. Chem. Soc.* p. 108 (1955).

114. Snow, A. I., and Rundle, R. E., *Acta Cryst.* **4,** 348 (1951).

115. Speier, J. L., Jr., Zimmerman, R. E., and Webster, J., *J. Am. Chem. Soc.* **78,** 2278 (1956).

116. Stone, F. G. A., *Chem. Revs.* **58,** 101 (1958).

117. Strohmeier, W., and Hümpfner, K., *Z. Elektrochem.* **61,** 1010 (1957).

118. Summers, L., and Uloth, R. H., *J. Am. Chem. Soc.* **76,** 2278 (1954).

119. Summers, L., Uloth, R. H., and Holmes, A., *J. Am. Chem. Soc.* **77,** 3604 (1955).

120. Tannenbaum, S., and Schaeffer, P. F., *J. Am. Chem. Soc.* **77,** 1385 (1955).

121. Ulmschneider, D., and Goubeau, J., *Chem. Ber.* **90,** 2733 (1957).

122. van der Kerk, G. J. M., *Chem. & Ind.* p. 609 (1958).

123. van der Kerk, G. J. M., Luijten, J. G. A., and Noltes, J. G., *Chem. & Ind.* p. 352 (1956).

124. Walling, C., and Buckler, S. A., *J. Am. Chem. Soc.* **75,** 4372 (1953).

125. Walling, C., and Buckler, S. A., *J. Am. Chem. Soc.* **77,** 6032 (1955).

126. Wartik, T., and Schlesinger, H. I., *J. Am. Chem. Soc.* **75,** 835 (1953).

127. Weissman, S. I., Tuttle, T. R., Jr., and de Boer, E., *J. Phys. Chem.* **61,** 28 (1957).

128. White, D. G., and Rochow, E. G., *J. Am. Chem. Soc.* **76,** 3897 (1954).

129. Wiberg, E., and Strebel, P., *Ann.* **607,** 9 (1957).

130. Wiberg, K. B., *J. Am. Chem. Soc.* **77,** 5987 (1955).

131. Wilke, G., *Angew. Chem.* **68,** 306 (1956).

132. Wilke, G., *Angew. Chem.* **69,** 397 (1957).

133. Wilke, G., and Müller, H., *Chem. Ber.* **89,** 444 (1956).

134. Wittig, G., *Angew. Chem.* **70,** 65 (1958).

135. Wittig, G., Meyer, F. J., and Lange, G., *Ann.* **571,** 184 (1951).

136. Wotiz, J. H., Hollingsworth, C. A., and Dessy, R. E., *J. Am. Chem. Soc.* **77,** 103 (1955).

137. Zeiss, H. H., and Herwig, W., *J. Am. Chem. Soc.* **78,** 5959 (1956).

138. Zeiss, H. H., and Tsutsui, M., *J. Am. Chem. Soc.* **79,** 3062 (1957).

139. Ziegler, K., *Brennstoff-Chem.* **35,** 321 (1954).

140. Ziegler, K., *Angew. Chem.* **68,** 721 (1956).

141. Ziegler, K., and Colonius, H., *Ann.* **479,** 135 (1930).

142. Ziegler, K., and Eisch, J., unpublished studies presented in part before the Organometallic Symposium, sponsored by the Cincinnati Section, A.C.S., October 29, 1958.

143. Ziegler, K., and Gellert, H-G., *Angew. Chem.* **67,** 218 (1955).

144. Ziegler, K., Gellert, H-G., Martin, H., Nagel, K., and Schneider, J., *Ann.* **589,** 91 (1954).

145. Ziegler, K., and Lehmkuhl, H., *Z. anorg. u. allgem. Chem.* **283,** 414 (1956).