ALKYL DERIVATIVES OF THE GROUP II METALS

B. J. Wakefield

Department of Chemistry and Applied Chemistry, University of Salford, Lancashire, England

I. Introduction

All the elements of Group II (with the exception of radium) are known to form alkyl derivatives. The compounds from magnesium and mercury are of very great interest and importance, the former because of their usefulness in synthesis, and the latter because of their physiological activity; as a consequence, so many of the compounds have been prepared and the literature on their properties is so extensive that a detailed account of their chemistry, even if confined to recent advances, is beyond the scope of a review article. Nevertheless, recent studies of the alkyl derivatives of all the Group II metals have revealed a pattern of structure and behavior that may make possible some rationalization of the properties and reactions of metal alkyls in general, and promise to lead to a greater insight into the nature of carbon-metal bonds.

Good accounts of the older chemistry of the alkyl derivatives of the Group II metals have been given in monographs on organometallic chemistry [e.g., Coates (*95*)]; it is the purpose of this article to attempt to systematize some of the mass of experimental data recorded during the past few years. The emphasis will be on the structural chemistry of the compounds. A detailed account of their reactions is not attempted, although the more important work on the influence of structure and solvation on reactivity is reviewed.

The Group II metals can form two covalent bonds, making use of the two electrons in their outermost *s* orbital. If one of the bonds is to carbon, and the other to another atom or group, the resulting compound may be written as R–M–X. (Throughout this review, any alkyl or aryl group is designated R; where an aryl group is specifically indicated, the symbol Ar is used.) In such a compound, as all the Group II metals are more electropositive than carbon, the carbon-metal bond will have some polar character: $R^{\delta-}$–$M^{\delta+}$–X. The reactivity of the metal alkyls has often been considered (particularly by organic chemists) to lie in the partial carbanionic character of the alkyl group; the electron-deficient character of the metal has too often been overlooked. It is now becoming increasingly clear that the reactivity of the metal alkyls may be governed by the carbanionic character of the alkyl group, by the electron-deficient character of the metal, or by both (cf., e.g., *1, 138, 141–143, 215, 299*).

In the case of the alkyl derivatives of the Group II metals, the electron deficiency of the metal in the simple compound R–M–X (which may in some cases have no more than transient existence) may be reduced by either intramolecular or intermolecular interactions. In the first case, electrons may be available from the groups R or X within the same molecule; in the second case, electron-donating ligands may coordinate with the metal atom. The electron-donating ligands may be other R–M–X molecules, or other species such as solvent molecules. In the discussion below, the simple, unsolvated dialkyl derivatives of the metals are taken as a basis in examining the effect of other groups attached to the metal, and of the addition of other electron donors, on the structures and reactivities of the compounds.

II. Compounds Containing the System C–M–C; the Dialkyl Derivatives of the Metals

A. SIMPLE, UNSOLVATED DERIVATIVES

1. *Structure*

a. Dialkylberyllium, -magnesium, -calcium, -strontium, and -barium Compounds. Although diethylzinc was the first true organometallic compound to be characterized (*167*), simple unsolvated derivatives of the more electropositive Group II metals have until recently been much less accessible, and those of calcium, strontium, and barium have not been prepared. (Bis(cyclopentadienyl)calcium is noted in Section II,D below.) The preparation of dimethylcalcium, -strontium, and -barium has been reported (*340*). However, the method described, which involved the reaction of the metals with methyl iodide in pyridine followed by prolonged extraction of the resulting solids with boiling pyridine, seemed suspect in view of the high reactivity of organocalcium compounds toward pyridine (*80*), and all attempts to repeat the preparation of dimethylcalcium led to materials superficially similar to those described, but which gave hydrogen, not methane, on hydrolysis, and appeared to be complexes of pyridine and bipyridyls with calcium hydride (*78*, *298*).

It has recently been discovered that, in contrast to the Grignard reagents, dialkylmagnesium compounds prepared in diethyl ether may readily be desolvated (*247*) (and that dimethylmagnesium even crystallizes from diethyl ether without attached solvent) (*112*). A new general method for preparing unsolvated dialkylmagnesium compounds involves the reaction of an alkyllithium compound with the corresponding alkylmagnesium chloride in diethyl ether (Eq. 1), followed by desolvation (*247*):

$$RLi + RMgCl \rightarrow R_2Mg(s) + LiCl \qquad (1)$$

Unsolvated alkylmagnesium halides, which are now readily accessible (see Section II,A,1 below), have been used as sources of unsolvated dialkylmagnesium compounds (*191*), and may prove to be useful starting materials for the preparation of unsolvated dialkyl derivatives of other metals. For example, unsolvated di-*n*-butylberyllium has been prepared by the reaction of a solution of *n*-butylmagnesium iodide in benzene with beryllium chloride[1] (*192*).

Both dimethylberyllium (*403*) and dimethylmagnesium (*459*) have been shown by X-ray crystallography to exist in the solid state as long-chain polymers, with methyl groups forming bridges between the tetrahedrally coordinated metal atoms. The structure of diethylmagnesium is similar, with methylene bridges between the metal atoms (*460*). The magnesium compounds are involatile (*459*, *460*), but dimethylberyllium may be sublimed and the vapor is believed to contain monomeric, dimeric, and trimeric molecules, with possibly higher polymers also (*100*). Diisopropylberyllium is reported to be dimeric both in benzene solution and in the vapor state (*98*); di-*n*-butylberyllium is dimeric in benzene (*192*). Recent determinations of the structure of di-*tert*-butylberyllium by infrared and Raman spectroscopy (*114*) and electron diffraction (*201*) have revealed that it is unique among the dialkylberyllium compounds in being monomeric, even in the liquid state (*114*). Di-*n*-pentylmagnesium is reported (*191*) to be largely dimeric in benzene.

The nature of the bonding in these polymeric molecules (and in the analogous aluminum compounds) has been extensively discussed [see Coates (*95*), pp. 57, 58, and 130], and it is generally accepted that they contain electron-deficient bonds, with two electrons in orbitals linking one carbon and two metal atoms (or possibly with four electrons in orbitals linking two carbon and two metal atoms) (*451*). In such a situation, although the molecule as a whole is electron-deficient, the deficiency on the metal atom is somewhat reduced, and it has attained a coordination number of 4. The observation that the higher beryllium alkyls show less tendency to polymerize than dimethylberyllium has been explained in terms of steric interference between the alkyl groups (*460*). The observations that di-*n*-pentylmagnesium is dimeric in benzene (*191*), and that dimethylmagnesium crystallizes from diethyl ether free from solvent (*112*), seem to indicate that the tendency of dialkylmagnesium compounds to form alkyl-bridged polymers is at least as great as that of the beryllium compounds.

The reactions of the simple, unsolvated derivatives of the more electropositive metals have been little studied; where the dialkyl derivatives are mentioned, it is almost invariably solvated complexes of the

---

[1] The conditions employed for this reaction are evidently fairly critical, as a similar experiment in which magnesium and magnesium halides were not removed from the reaction mixture failed to yield any di-*n*-butylberyllium (*455*).

simple compounds that are referred to. The action of heat, oxygen, and compounds containing "active" hydrogen on the dialkyl derivatives of the metals leads in certain cases to compounds of the formula R–M–X (these reactions are reviewed in the appropriate sections below). It is reported that pyrolysis of dimethylmagnesium gives polymers with the composition $(MgCH_2)_n$ (*500*), and that dimethylberyllium similarly yields $(BeCH_2)_n$ (*195*).

b. Dialkylzinc, -cadmium, and -mercury Compounds. In contrast to the derivatives of the more electropositive Group II metals, the dialkylzinc, -cadmium, and -mercury compounds have little or no tendency to association, and are believed to have simple, linear structures [see Coates (*95*), pp. 63–82]; the mercury compounds show almost no indication of electron deficiency and, although the zinc and cadmium compounds readily function as electron acceptors (see Section II,B below), their electron deficiency is not reflected in their structures. [Crystallographic determinations have confirmed the linear configuration for diphenylmercury (*502*) and di-*p*-tolylmercury (*267*); the high dipole moment of diphenylmercury must be due to atom polarization (*267*).]

The simplicity of the structures of these compounds has prompted a number of studies of their physical properties (see, e.g., *66*, *67*, *207*, *253*, *428*). In particular, the van der Waals volumes and radii of zinc, cadmium, and mercury have been calculated (*67*); values were chosen that yielded the correct number of external degrees of freedom per molecule (assuming free rotation about metal-carbon bonds), when linked with density and heat of vaporization data for the dimethyl derivatives. Similarly, analysis of the vibrational spectra of dimethylzinc, cadmium,- and -mercury [and of bis(trifluoromethyl)mercury] (*253*) gave values for the carbon-metal stretching force constants and carbon-metal-carbon bending force

TABLE I

CONSTANTS DERIVED FROM MEASUREMENTS ON DIMETHYL DERIVATIVES OF GROUP II METALS

Compound	Van der Waals radius of metal (Å) (*67*)	Carbon-metal stretching force constant (md $Å^{-1}$) (*253*)	Carbon-metal-carbon bending force constant (md $Å^{-1}$) (*253*)
Me_2Zn	1.39	2.05	0.41
Me_2Cd	1.62	2.45	0.51
Me_2Hg	1.70	2.39	0.31

constants. The constants derived from measurements on the dimethyl derivatives are given in Table I.

With the classical methods of preparation (reaction of alkyl iodides with zinc, reaction of Grignard reagents with zinc chloride), it has been found difficult to obtain the less volatile dialkylzinc compounds free from halide and ether (*426*, *428*); the pure compounds were obtained, however, by an alkyl-exchange reaction between dimethyl (or diethyl)-zinc and a trialkylboron compound:

$$3Me_2Zn + 2R_3B \rightarrow 2Me_3B + 3R_2Zn \tag{2}$$

The method should also be suitable for the synthesis of dialkylcadmium compounds (*425*, *426*).

As in the case of the derivatives of beryllium and magnesium, the reactions of the dialkylzinc and -cadmium compounds have usually been studied in electron-donating solvents, and in addition the profound effect of other components of the systems has often not been realized. For example, standard textbooks on organic chemistry refer to the synthesis of ketones by the reaction of acyl chlorides with dialkylcadmium compounds. However, Kollonitsch (*257*) pointed out in 1960 that dialkylcadmium compounds, free from the magnesium salts and diethyl ether with which they are associated when prepared by the usual procedure, are unreactive toward acyl chlorides. Subsequent work by Kollonitsch (*255*, *256*) and by French workers (*122*, *132*, *152*, *211*, *226*, *276*, *293*, *416*) has emphasized the effect that metal salts can have on the reactivity of organocadmium and organozinc compounds (see Section IV,B,2 below).

In contrast to the derivatives of the more electropositive metals, dialkylmercury compounds do not normally interact with electron donors, and their chemistry has been intensively studied since they provide a particularly suitable subject for investigations on the mechanism of electrophilic substitution reactions. An excellent general account of such studies has been given (*124*), and some of the more important and interesting recent work is reviewed here (see particularly Sections II,B,2*b* and IV,A,4).

In addition to their electrophilic substitution reactions, the dialkyl derivatives of mercury (*39*) [and of zinc (*173*, *354*) and cadmium (*353*)] undergo homolytic reactions, and are indeed well-known sources of alkyl radicals. For example, thermolysis or photolysis of dialkylmercury compounds has in recent years been used in the study of benzyl (*38*, *40*), vinyl (*387*), and heptafluoroisopropyl (*160*) radicals. [Somewhat surprisingly, bis(nonafluoro-*tert*-butyl)mercury appears to decompose thermally by some route other than via perfluoro-*tert*-butyl radicals (*160*).]

B. COMPLEXES OF THE DIALKYL DERIVATIVES WITH ELECTRON DONORS

The interaction of the alkyl derivatives of the Group II metals with electron donors has in recent years aroused interest under three main headings: (a) correlation of the existence and stability of the complexes with properties of the metal and of the donor molecules, (b) the extent to which the polymeric structure of the beryllium and magnesium derivatives is broken down by electron donors, and (c) the effect of complex formation on the reactivity of the compounds. The chemistry of donor-acceptor complexes of beryllium, zinc, cadmium, and mercury derivatives has been reviewed (*432*).

1. *Formation and Stability*

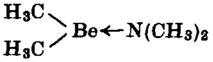
Dialkylberyllium compounds form complexes with diethyl ether, which are desolvated only with difficulty (*95*). On the other hand, simple dialkylmercury compounds do not normally form stable complexes even with strong electron donors, such as 1,4-dioxan (*411*, *432*) or 2,2′-bipyridyl (*102*). (Complexes of perfluoroalkyl derivatives are discussed in Section II,C.) Derivatives of the other metals reveal wide variations within these limits. It would be convenient in considering the formation and stability of the complexes to have a list of electron donors in order of electron-donating capacity (Lewis basicity, nucleophilicity). Unfortunately very little quantitative information is available, partly because of the difficulty of defining a general parameter applicable in other than limited circumstances (*359*). Little attempt has yet been made to apply the concept of hard and soft acids and bases to these complexes, but this concept seems likely to be useful in this field.

Among the measures of electron-donating capacity that may be applicable to studies on the stability of donor-acceptor complexes are the following. (*i*) The heats of formation of the complexes between boron trifluoride and some ethers have been measured (*70*). (*ii*) More recently, the effect of various solvents on $J(^{119}\mathrm{Sn}{-}^{1}\mathrm{H})$ for trimethyltin bromide was investigated (*182*). The coupling constants were taken as a measure of the "nucleophilicity" of the solvents. (*iii*) The shift of the magnetic resonance due to the chloroform proton in various solvents has similarly been taken as a measure of the "basicity" of the solvents (*283*). The results of these determinations give some measure of electron-donating capacities, but the importance of steric factors in complex formation must also be emphasized. In particular, many bifunctional ethers, amines, etc. (e.g., 1,4-dioxan, *N*,*N*,*N*′,*N*′-tetramethylethylenediamine, 2,2′-bipyridyl), function as exceptionally strong complexing agents.

Complex formation for each of the metals is considered below, and some aspects of the influence of solvation on reactivity are then discussed.

a. Complexes of Dialkylberyllium Compounds. Dialkylberyllium compounds, as was stated, are highly electron-deficient, and readily form complexes with ethers, amines, etc. In many cases the complexes are very stable, and the donor ligands are not easily removed. It is reported (*105*) that complexes are not formed between dimethylberyllium and donors such as trimethylarsine or dimethyl sulfide, although diphenylberyllium forms stable complexes with dimethyl sulfide (*115*). The comparatively "soft" sulfur and arsenic donors are apparently less able to break down the alkyl-bridging system to coordinate with the "hard" beryllium.

The structures of the dialkylberyllium complexes are of interest, because of their tendency to form polymers and because of the variable number of ligands attached. Dimethylberyllium forms 1 : 1 complexes with trimethylamine, trimethylphosphine, and dimethyl ether (*105*). The trimethylamine complex is volatile, and the vapor is largely monomeric, although there may be some association at lower temperatures and in the condensed phase. The structure I, in which beryllium is three-coordinate,



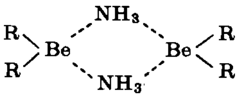
$(H_3C)_2Be \leftarrow N(CH_3)_2$

(I)

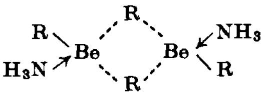
seems probable (*105*). The trimethylphosphine and dimethyl ether adducts are much less stable than the trimethylamine adduct. Stable 1 : 1 complexes are formed between diphenylberyllium and dimethyl ether, diethyl ether, dimethyl sulfide, trimethylamine, and trimethylphosphine (*115*).

Apart from the simple 1 : 1 complexes, a number of adducts with other stoichiometries has been reported. Vapor pressure measurements on the dimethylberyllium-trimethylphosphine and dimethylberyllium-dimethyl ether systems gave indications of the existence of complexes such as $(Me_2Be)_2 \cdot L_3$, $(Me_2Be)_2 \cdot L$, and $(Me_2Be)_3 \cdot L$ (*105*). Such complexes were not amenable to study and characterization, but it has proved possible to observe some dialkylberyllium-trimethylamine adducts in addition to the 1 : 1 compound. It was at first believed that, with an excess of trimethylamine and at temperatures below 10°, a complex with the composition $(Me_2Be)_2 \cdot (NMe_3)_3$ was formed, and no indication of a complex $Me_2Be \cdot (NMe_3)_2$ was observed. However, it was shown (*343*) that a diethylberyllium-bis(trimethylamine) complex was stable below –35°, and a subsequent reinvestigation (*50*) of the dimethylberyllium-trimethylamine system disclosed that a bis(trimethylamine) adduct was formed below 0°, rather than the 2:3 adduct previously reported. The earlier results were confused by the very slow uptake of trimethylamine by the 1:1 adduct. A stable dimethylberyllium-bis(pyridine) adduct, m.p. 91°–92°, has also been reported (*102*). Similarly, tensimetric studies (*115*) revealed the existence of a number of 1:2 complexes of diphenylberyllium with electron donors. Those with dimethyl ether, dimethyl sulfide, and trimethylphosphine were stable at 0° (although the last two were partly dissociated in benzene), but those with diethyl ether and trimethylamine had appreciable dissociation pressures under similar conditions; steric factors are thought to account for the differences in stability.

At low temperatures, dialkylberyllium compounds form 1:1 complexes with primary and secondary amines (*101*, *158*, *172*) and ammonia (*288*), but at higher temperatures alkyl groups are displaced from beryllium (see Section VI,A below). Dimeric ammonia-bridged (II) or alkyl-bridged (III) structures have been proposed (*288*) for the complexes between ammonia and dimethyl- or diethylberyllium.

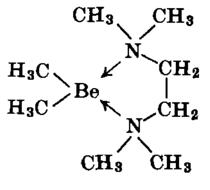


(II)

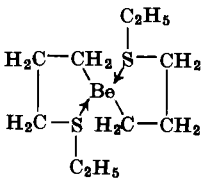


(III)

Dialkylberyllium compounds form stable and remarkably unreactive 1:1 complexes with a number of bidentate ligands, such as 1,2-dimethoxyethane, 2,5-dithiahexane, *N*,*N*,*N*′,*N*′-tetramethylethylenediamine, *N*,*N*,*N*′,*N*′-tetramethyl-*o*-phenylenediamine, and 2,2′-bipyridyl (*50*, *102*, *115*, *158*). These complexes are monomeric in benzene solution (*102*), and so presumably is the complex between diethylberyllium and 1,4-dioxan (*409*). It seems likely that these complexes have structures such as IV, involving four-coordinate beryllium (*102*). Bis(4-thiahexyl)-beryllium probably has the interesting chelated structure V, and the structure of bis(5-oxahexyl)beryllium is presumably similar (*29*).



(IV)



(V)

The complexes between dialkyl- and diarylberyllium compounds and 2,2′-bipyridyl are colored; for example, the diethylberyllium compound is red ($\lambda_{max} = 461$ mμ, $\epsilon = 3.7 \times 10^3$). It is argued (*102*) that the color of the complexes is due to transitions involving electron transfer from the beryllium-carbon bonds to the lowest unoccupied orbital of the bipyridyl.

Unstable complexes, of unknown structures, are reported (*406*, *408*; cf. *480*) to be formed between unsolvated diethylberyllium and various salts, including alkali-metal fluorides, potassium cyanide, and tetraalkylammonium chlorides; ionic rather than coordinated structures seem likely for these complexes (further details are given in Section II,E below).

b. *Complexes of Dialkylmagnesium Compounds.* In view of the tenacity with which Grignard reagents retain diethyl ether (*95*, p. 52; *412*, *413*), it is remarkable that dialkylmagnesium compounds are readily desolvated (*247*). The case of dimethylmagnesium, where alkyl bridging is apparently very strong, is particularly interesting. The compound is only sparingly soluble in diethyl ether, and is monomeric (and presumably solvated) in this solvent (*223a*, *435*). It is reported, however, that it crystallizes as an unsolvated polymer (*112*). On the other hand, diphenylmagnesium forms stable, monomeric complexes, which may be crystallized, with two moles of diethyl ether (*412*, *413*) or tetrahydrofuran (*104*), and di-*tert*-butylmagnesium forms a 1 : 2 complex with tetrahydrofuran (*104a*).

Stable 1 : 1 complexes between dialkylmagnesium compounds and bidentate ligands, such as 1,2-dimethoxyethane and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine, have been described (*104*, *104a*, *489*). These complexes resemble their beryllium analogs, being in many cases volatile, and monomeric in solution. No indication of the formation of compounds with six-coordinate magnesium has been observed (*104*).

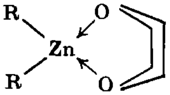
c. *Complexes of Dialkylcalcium, -strontium, and -barium Compounds.* Simple dialkylcalcium, -strontium, and -barium compounds have not been authenticated, either unsolvated or as complexes with donor solvents (but see Section II,E below), although the small amount of triphenylacetic acid formed, when the product from the reaction of barium with triphenylmethane in liquid ammonia was carboxylated, indicated that some bis(triphenylmethyl)barium had been formed (*185*). It is of interest that tetrahydrofuran complexes of bis(triphenylgermyl)-strontium and -barium have been isolated (*20*).

d. *Complexes of Dialkylzinc Compounds.* The formation of complexes by dialkylzinc compounds is uncomplicated by competing self-association of the organometallic compounds. Dimethylzinc and diphenylzinc form complexes in solution with simple cyclic ethers (*18*, *419*) (and it seems likely that similar complexes would be formed with acyclic ethers, although they have not been described). The complexes, as might be expected from the comparatively low electron-accepting capacity of zinc, are not highly stable. Thus, although the 1:1 dimethylzinc-ethylene oxide complex appeared to distill unchanged [*419*; but see Thiele and Zdunneck (*432*), p. 336], a study of the proton n.m.r. spectrum of the complex in cyclohexane solution showed that its heat of formation is only -9.1 kcal mole^{-1}, and that it is partly dissociated in solution except at low temperatures (*18*). With tetrahydrofuran and pentamethylene oxide, dimethylzinc forms crystalline complexes containing a 1:2 zinc-to-ether ratio (*419*); it seems likely that steric factors are important in determining whether formation of a 1:2 complex is possible. With diethylzinc and longer-chain dialkylzinc compounds, no stable adduct could be isolated even with tetrahydrofuran, although there was interaction in solution (*430*).

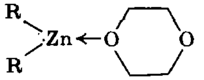
Dimethyl- and diarylzinc compounds yield stable complexes with tertiary amines, including trialkylamines and pyridines (*292*, *427*, *430*). Both a 1:1 and a less stable 1:2 complex are formed between dimethylzinc and trimethylamine; with triethylamine and pyridine only the 1:2 adducts were isolated (and these tended to dissociate in benzene solution) (*421*). A stable complex of diethylzinc with triethylamine has not been isolated, but the n.m.r. spectra of mixtures of the components reveal the presence of a 1:1 complex (*414*). The benzyl and higher-alkyl zinc compounds form stable complexes with pyridine, etc., but not with triethylamine (*430*). Complexes are also formed at low temperatures with secondary amines, but these tend to react further to give alkylzinc amides (see Section VI,C) (*432*, p. 339). [The complexes formed between dialkynylzinc compounds and ammonia (*303*) may also be mentioned here.]

Stable 1:1 complexes are formed between dialkylzinc compounds and a number of types of bifunctional electron donor, including diethers (*18*, *420*), diamines (*18*, *329*, *421*, *427*, *430*), diphosphines (*150*, *318*), and diarsines (*318*). Complex formation between diethylzinc or diphenylzinc and dioxan could be inferred from the high dipole moments of the zinc compounds in dioxan solution (*234*, *405*, *410*), and crystalline dioxanates of numerous dialkylzinc compounds have since been isolated (*332*, *392*, *420*). The dioxanates are 1:1 complexes, and are believed to have chelated structures (VI), rather than structures such as VII (*18*, *432*, p. 337), and the complexes of many other diethers are presumably similar. However, 1,2-dimethoxyethane and 1,3-dimethoxypropane give bis(etherates), which probably have structures such as VIII (*420*).

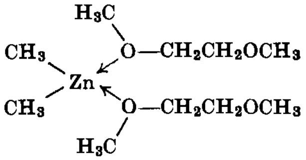
It seems likely that the 1:1 complexes of dialkylzinc compounds with diamines (*430*) and compounds such as tetramethyltetrazene, tetraphenylethylenediphosphine, and tetramethyl-*o*-phenylenediarsine (*318*) have chelated structures, such as IX. The constitution of the solid complex of diethylzinc with diazabicyclooctane (*379*) has not yet been established, but should be interesting. Tetraphenylethylenediphosphine gives a 2:1 adduct with diphenylzinc (*318*), and tetrakis(diphenylphosphinomethyl)methane gives monomeric 1:2 complexes with diethylzinc and diphenylzinc, but a polymeric 1:4 complex with dimethylzinc; a structure involving methyl bridges between zinc atoms has been suggested for the last complex (*150*). The interesting suggestion has been made (*318*) that the complexes of phosphorus- or arsenic-containing ligands may be stabilized by d_π-d_π back-bonding of electrons from the 3*d* orbitals of zinc to empty *d* orbitals of phosphorus or arsenic. However, such evidence as is available (e.g., the greater stability of diaryl than dialkyl complexes) indicates that any such back-donation is not of great importance in these complexes (but see below). Steric factors appear to be significant in the stabilization of complexes with bifunctional ligands, as no stoichiometric addition compounds of dimethylzinc and 1,3-dioxan could be isolated (*420*). It would be of interest to know whether the sulfur atom in the dimethylzinc–1,4-thioxan complex (*420*) is bonded to zinc, in view of the instability of complexes of dimethylberyllium with dialkyl sulfides.



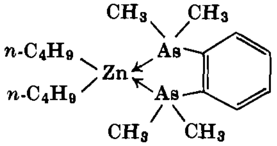
(VI)



(VII)



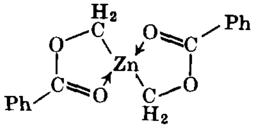
(VIII)



(IX)

Bis(benzoyloxymethyl)zinc probably has the structure X (*476*), and presents an interesting example of intramolecular coordination, somewhat analogous to the beryllium compounds noted under (*a*) above.

The complexes of dialkylzinc compounds with 2,2′-bipyridyl and 1,10-phenanthroline are of great interest because of their spectroscopic



(X)

properties. Coates and Green (*102*, *103*) noted that the complexes of dimethylzinc with these ligands were colored, and the ultraviolet and visible absorption spectra of a number of complexes of this type were measured by Noltes and van den Hurk (*319*) and Thiele (*429*). It was observed that the long-wavelength absorption band of the complexes was at shorter wavelength and had higher intensity for more electronegative alkyl groups. The data for the longest-wavelength absorption bands of some bipyridyl complexes are given in Table II. The data could be explained very satisfactorily in terms of electron transfer from the organozinc component to the coordinating ligand. Transfer from the metal-carbon bonds (see Section II,B,1*a* above) seems highly unlikely in this system, and it is most probable that the *d* orbitals of the zinc atom are concerned. Molecular orbital calculations do in fact indicate that the observed spectroscopic properties of the complexes can be explained in terms of interaction between the 3*d* orbitals of zinc and the highest filled and lowest unfilled orbitals of the ligands. [Similar considerations presumably also apply to the 1:2 complexes of dialkylzinc compounds with pyridine, quinoline, and isoquinoline (*430*).] The stabilities of some dialkylzinc–2,2′-bipyridyl complexes have recently been determined by a dielectric titration technique (*316*). The order of stability was *tert*-butyl > isopropyl > ethyl > methyl, the reverse of the order for the corresponding series of tetramethylethylenediamine complexes. It is thus apparent that d_π-bonding to zinc is important in the ground state of the bipyridyl complexes.

TABLE II

ABSORPTION BANDS OF COMPLEXES OF DIALKYLZINC COMPOUNDS WITH 2,2′-BIPYRIDYL, IN TOLUENE SOLUTION (*319*)

R (in R_2Zn)	λ_{max}(mμ)	log ϵ_{max}
iso-C_3H_7	480	2.63
C_2H_5	420	2.77
C_6H_5	350	2.91
C_6F_5	309	4.15

e. Complexes of Dialkylcadmium Compounds. As expected, dialkylcadmium compounds show less tendency than dialkylzinc compounds to form complexes with electron donors. Thus, although dimethylcadmium forms crystalline 1:1 complexes with bifunctional ligands (1,4-dioxan, 2,2′-bipyridyl, etc.) (*102*, *332*, *422*), complexes with even strong monofunctional ligands (tetrahydrofuran, pyridine) dissociated so readily that they could not be purified (*422*). However, stable complexes, $R_2Cd \cdot (HMPT)_2$, have recently been isolated from the products of the reaction of alkyl iodides with cadmium in hexamethylphosphorotriamide (*91*). It has been noted that the dipole moments of diethylcadmium (*411*) and diphenylcadmium (*405*) in dioxan solution are less than those of the corresponding zinc and magnesium compounds. The interpretation of these results is not straightforward; the dipole moment could vary because of variations of the carbon-metal-carbon angle, or because of variations in the polarity of the carbon-metal bonds at a constant carbon-metal-carbon angle. Crystalline dioxanates of some diarylcadmium compounds were isolated, but were readily desolvated (*331a*). The 2,2′-bipyridyl and 1,10-phenanthroline complexes, like the corresponding zinc compounds, are colored (*102*, *422*) and presumably have similar constitutions.

f. Complexes of Dialkylmercury Compounds. Simple dialkylmercury compounds normally show no signs of complex formation even with such powerful electron donors as 2,2′-bipyridyl (*102*), diazabicyclooctane (*379*), and hexamethylphosphorotriamide (*455*), although an oscillometric titration technique (*346*) and analysis of the ^1H n.m.r. spectra (*343a*) gave some indication of interaction between diphenylmercury and donor ligands. However, the perfluoroalkylmercury compounds (see Section II,C below), where the electron density on mercury is reduced by the inductive effect of the highly electronegative perfluoroalkyl group, form complexes with strong electron donors such as pyridine oxide, sulfolane, piperidine, ethylenediamine (*345*, *346*), 2,2′-bipyridyl (*33*), and 1,10-phenanthroline (*119*, *120*); some of these complexes are sufficiently stable to be isolated and purified, and bis(tetrafluoro-4-pyridyl)mercury, with its exceptionally electron-withdrawing organic groups, forms a stable complex (m.p. 181°) with 2,2′-bipyridyl (*89*).

2. *Influence of Coordination on Reactivity*

The influence of coordination in increasing the nucleophilic reactivity and in decreasing the electrophilic reactivity of metal alkyls has been discussed (*141*, *143*, *454*) (and see Section I), and a general review of the subject has been given (*322*). However, much more work has to be carried out on the nature of carbon-metal bonds and on the mechanisms of their reactions, and a full understanding of the role of coordination is still far from realization. Moreover, it has been pointed out (*380*) that, in many reactions of alkyllithium compounds, the solvent may play a kinetic role in addition to its thermodynamic role in solvating the metal.

Two aspects of the problem are reviewed briefly here: first, the phenomenon of the exchange of alkyl groups between metal alkyl molecules (and the associated problem of the configurational stability of the alkyl groups); second, the influence of coordination on the reactivity of the alkyl derivatives in some representative reactions.

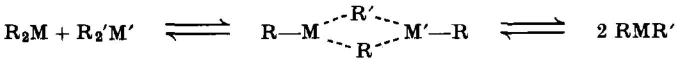
a. Alkyl-Group Exchange. When this subject was reviewed in 1965 (*278*), the information then available could be summarized as follows. The proton magnetic resonance spectra of simple dialkyl derivatives of magnesium, zinc, and cadmium indicated that alkyl groups were being exchanged at a rate faster than, or comparable with, the n.m.r. time scale (*137*, *292*). The rates of exchange could be estimated in some cases, and were in the order cadmium < zinc < magnesium derivatives. For the corresponding mercury derivatives, and for mixtures of these with the zinc and cadmium derivatives, exchange was slow if it occurred at all (*292*). These results are incidentally difficult to reconcile with the reported (*254*, *331a*) preparation of unsymmetrical dialkylzinc and dialkylcadmium compounds. However, it is true that exchange is slow for dialkylcadmium compounds in the absence of electron donors, and for dialkylzinc compounds in the absence of alkylzinc halides (*64*), and recent work (*2*, *391*) provides unequivocal support for the original findings. The n.m.r. spectra of bis(perfluoroalkyl)mercury compounds showed $^{19}F—^{199}Hg$ coupling, indicating that exchange was slow for these compounds (*123*).

At elevated temperatures, mixtures of dimethylmercury and bis(trideuteromethyl)mercury gave rise to some of the mixed compound, CH_3HgCD_3 (*137*), and mixtures of dimethylmercury with diphenyl- or dibenzylmercury were in equilibrium with the appropriate mixed compounds (*350*). It appeared at first that a random distribution of organic groups was involved in these equilibria, but subsequent work, using a variety of dialkylmercury compounds, has demonstrated that the position of equilibrium depends on the nature of the groups (*369*). Thus, for example, whereas the equilibrium at 90° formulated as

$$R_2Hg + R_2'Hg \rightleftharpoons 2RHgR' \qquad (3)$$

lay largely on the left-hand side ($K_{eq} = 1.8$) when $R = CH_3$ and $R' = C_2H_5$, it lay largely on the right-hand side ($K_{eq} = 130$) when $R = C_2H_5$ and $R' =$ *cis*-$CH_3CH{=}CH—$. As expected, the distribution of alkyl groups between dialkylmagnesium and dialkylmercury compounds could be correlated with the relative stabilities of the carbanions corresponding to the alkyl groups (*139*).

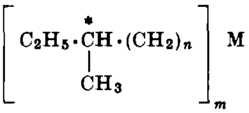
In the work reviewed earlier, little effect of the solvent polarity on the exchange rates was noted, and it was concluded that the exchange reaction proceeds by a nonionic mechanism, or one in which the transition state has little polar character. However, the donor strength of the solvent has some effect. For example, in solvent-free dimethylcadmium (*137*, *292*) and diethylcadmium (*69*) and in their solutions in hexane, exchange is sufficiently slow for $^{1}H—^{111}Cd$ and $^{1}H—^{113}Cd$ spin-spin coupling to be observed. In donor solvents such as tetrahydrofuran (*137*) and pyridine (*202*, *292*), however, exchange is rapid in the n.m.r. time scale. For mixtures of dimethylzinc and dimethylcadmium, in a series of solvents, the rate of exchange was significantly higher in donor solvents (*292*). On the other hand, it has recently been reported (*223a*) that the rates of exchange of alkyl groups between dialkylmagnesium compounds are retarded by solvents such as dimethoxyethane and tetramethylethylenediamine, but catalyzed by magnesium bromide. It has been suggested (*292*) that exchange of alkyl groups occurs by a mechanism involving an alkyl-bridged, four-center transition state (Eq. 4):



$$R_2M + R_2'M' \rightleftharpoons R{-}M\overset{R'}{\underset{R}{\cdots}}M'{-}R \rightleftharpoons 2\,RMR' \qquad (4)$$

Such evidence as is available is in general consistent with this idea: (a) in the mixtures of dialkylmercury compounds, the mixed species RHgR′ are produced, indicating that alkyl groups are transferred one at a time (*137*, cf. *350*, *369*), (b) the fact that rates of exchange are lower at higher dilution suggests a bimolecular rate-determining step (*292*), and it has been found that the exchange of methyl groups between dimethylmagnesium and methyl(cyclopentadienyl)magnesium is second order (first order in each reagent) (*223a*), and that the alkyl-exchange reaction between dialkylmagnesium and dialkylmercury compounds follows reversible second order kinetics (*139*), and (c) the effect of donor solvents could be to solvate the transition state (*292*). It has recently been observed (*202*) that methyl exchange in solutions of dimethylcadmium is strongly catalyzed by traces of alcohols or oxygen, and care must therefore be taken in interpreting many earlier results.

Besides being interesting and important in itself, the recent work on the configurational stability of the α-carbon atoms in alkyl derivatives of the Group II metals may furnish information on the mechanism of the alkyl-exchange reaction. Studies have also been made on the racemization of a series of optically active compounds of type XI, where $n = 1–4$ and M = Li, Mg, Be, Zn, Cd, B, Al (*273*, *274*). It was found that, except in the cases of beryllium, boron, and aluminum, racemization was not rapid even at 100° (*274*). The behavior of the derivatives of the three exceptional metals may be ascribed to reactions of the type shown in Eq. (5), which are known to occur with these compounds (*99*). The case of the beryllium compounds is interesting, as the racemization observed in hexane solution is suppressed in dioxan solution, possibly because coordination of the metal prevents protophilic attack on the β-hydrogen atom (*274*). These results seem to indicate that the reactions formulated in Eq. (5) are not in general important in alkyl-exchange reactions of the Group II metals.



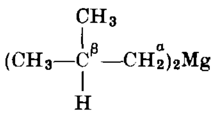
$$\left[C_2H_5\cdot\underset{CH_3}{\overset{*}{C}}H\cdot(CH_2)_n\right]_m M$$

(XI)

(5)

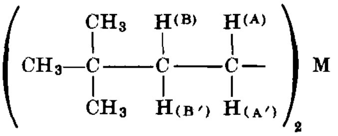
Although organomercury compounds with asymmetric α-carbon atoms are known (see, e.g., *220*, *362*), similar derivatives of the other Group II metals have not been authenticated,[2] save in the exceptional case of 2,2-diphenyl-1-methyl-1-cyclopropyl derivatives (*124*, p. 127; *456*) where inversion at the α-carbon atom would be extremely difficult. However, recent studies on the proton magnetic resonance spectra of dialkyl derivatives of magnesium and other metals have shown that, even in systems where alkyl exchange might be expected to be rapid, and with alkyl groups where inversion at the α-carbon atom is not prevented, the α-carbon atom may be configurationally stable.

Studies have been made (*164*) on bis(2-methylbutyl)magnesium (XII) and bis(3,3-dimethylbutyl) derivatives (XIII). In the former compound



$$(CH_3-\underset{H}{\overset{CH_3}{C^{\beta}}}-\overset{\alpha}{C}H_2)_2Mg$$

(XII)



$$\left(CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{H^{(B')}}{\overset{H^{(B)}}{C}}-\underset{H^{(A')}}{\overset{H^{(A)}}{C}}-\right)_2 M$$

(where M = Mg, Zn, or Hg)

(XIII)

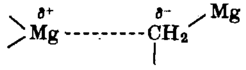
---

[2] When optically active bis(1,4-dimethylpentyl)mercury was allowed to react with the corresponding Grignard reagent, and the product carboxylated, the resulting acid was claimed to preserve a trace of optical activity (*362*).

(XII), the α-methylene protons are magnetically nonequivalent even when rotation about the C^{α}—C^{β} bond is fast, and at 0° in diethyl ether the proton magnetic resonance signal for the α-methylene protons corresponded to the AB portion of an ABX system. As the temperature was raised, the pattern changed to that for the A_2 portion of an A_2X system, and it was possible to calculate activation parameters for inversion at the α-carbon atom. Experiments on the dialkylmagnesium compounds in tetrahydrofuran or dioxan unfortunately gave inconsistent results, and reagents prepared from the Grignard reagent by precipitation with dioxan differed from those prepared from the dialkylmercury compound. However, all the data fitted the isokinetic relationship,

$$\Delta H^* = 370\Delta S^* + 19{,}400 \tag{6}$$

suggesting that there was a common inversion mechanism in all the solvents, and it was proposed that the kinetic data are best interpreted in terms of intermolecular electrophilic displacement on carbon (XIV). Unimolecular dissociation into free carbanions was ruled out for this system. Dineohexylmagnesium, -zinc, and -mercury (XIII) were studied



(XIV)

by Witanowski and Roberts (*472*). At 30° in diethyl ether, all three compounds had n.m.r. spectra of the AA′BB′ type. Dineohexylmercury preserved this pattern up to 150°, but at high temperatures the spectra for the other compounds coalesced to the A_2B_2 pattern. The activation energies for inversion at the α-carbon atom were calculated to be approximately 20 kcal mole^{-1} for the magnesium compound and 26 kcal mole^{-1} for the zinc compound. In contrast to Fraenkel's results, little difference was observed between the magnesium compound prepared from the Grignard reagent and that prepared from dineohexylmercury. Moreover, no change in inversion rate with concentration was observed, suggesting a unimolecular, S_E1 mechanism for inversion (or conceivably a reaction within a polymeric complex, whose degree of polymerization did not change over the concentration range studied).

Further information on the carbon-magnesium and carbon-zinc bonds comes from an analysis (*268*) of the proton magnetic resonance spectra of phenyllithium, diphenylmagnesium, and diphenylzinc in diethyl ether; the *ortho*-protons were, surprisingly, deshielded and this deshielding was accounted for in terms of the anisotropy of the carbon-metal bonds.

Clearly, more work remains to be carried out in this field. In particular, some attempt to correlate alkyl-exchange rates with rates of inversion would be valuable. [It has recently been reported (*223a*) that the rate of exchange of alkyl groups between 3,3-dimethylbutyl(cyclopentadienyl)magnesium and bis(3,3-dimethylbutyl)magnesium is substantially faster than the rate of inversion, and must therefore proceed with retention of configuration.] Some light may also be thrown on the n.m.r. studies by the results of more conventional investigations of the mechanisms of the reactions of metal alkyls [see (*b*) below].

b. Other Reactions. Three important types of reaction are briefly considered here: addition reactions (e.g., to carbonyl groups), electrophilic substitution reactions, and metallation reactions (which may be regarded as a special case of electrophilic substitution). All these reactions are affected by solvation, and the observed solvent effects have given valuable information on the reaction mechanisms. Unfortunately some results have to be treated with caution, as many trace impurities (especially metal halides and alkoxides) may have profound effects on reaction rates (e.g., see *202, 257, 454*).

Although the addition of Grignard reagents to carbonyl compounds, nitriles, etc., has been intensively studied (*24, 454*) (see Section IV,B,1*a* below), little quantitative work has been carried out on similar reactions of the dialkyl derivatives of the Group II metals. The reaction of di-*n*-butylmagnesium with acetone, methyl acetate, methyl trifluoroacetate, and *sec*-butyl crotonate was much slower in tetrahydrofuran than in diethyl ether (*221, 223*), which is consistent with the view (*21, 27*) that the rate-determining step in such reactions is displacement of a solvating molecule from the metal atom by the carbonyl oxygen. On the other hand, the reaction of di-*n*-butylmagnesium with azobenzene was somewhat faster in tetrahydrofuran than in diethyl ether.

No relevant studies of similar reactions of zinc and cadmium compounds have been made; in fact, pure dialkylzinc or -cadmium compounds do not normally react with carbonyl compounds, although they may do so in the presence of metal halides [*86, 212*; but see Chenault and Tatibouët (*91*)]. It may be relevant also that the complexes of dimethylzinc with 2,2′-bipyridyl, etc., are reported to be much less reactive toward oxygen than the uncomplexed reagents (*102, 421*).

In general, electrophilic substitution reactions involving dialkyl derivatives of the Group II metals proceed by bimolecular mechanisms. The classification of these mechanisms, as developed by a number of workers [leading references: (*183, 232, 295*)], has recently been refined and extended; Abraham and Hill (*1*) recently examined published data on a number of electrophilic aliphatic substitution reactions (including metallation reactions), and classified them according to three mechanisms, which are designated S_E2, S_Ei, and S_EC. The second of these (substitution, electrophilic, internal) could be further subdivided, as the reactions tended toward the other types of mechanism (substitution, electrophilic, bimolecular; substitution, electrophilic, via coordination). The crucial steps for the four types of mechanism are illustrated schematically in Fig. 1, where the reagent is represented as E–N. The application of this classification to the reactions of alkyl derivatives of the Group II metals is discussed below. However, a further mechanism, namely S_E1, must first be mentioned. As even a benzyl derivative of an electropositive metal, magnesium, apparently gives rise to comparatively free carbanions only in a highly nucleophilic solvent, hexamethylphosphorotriamide (*147*), it might be expected that electrophilic analogs of S_N1 reactions will be rarely encountered. However, a few reactions of organomercury compounds have been found to proceed according to kinetics that indicate an S_E1 mechanism. These include the alkyl-exchange reaction between *p*-nitrobenzylmercuric bromide and mercuric bromide in dimethylsulfoxide (*246*), the reaction of β-chlorovinylmercuric chloride with iodine in dimethylsulfoxide (*47, 48*), and possibly the protolysis of dibenzylmercury [(*46*), see also (*210a*)] or phenylmercuric bromide (*49*) by hydrochloric acid in certain solvent systems. In these cases, ionization was favored by the nature of the organic groups and by the media, and the results have been interpreted (*214*) in terms of dissociation to an ion pair in the rate-determining step. [Some of these reactions could involve catalysis by halide ion (*94*) (Section VII,A below), and the present author suggests that the possibility should be considered that the rate-determining step in some of the reactions may conceivably involve dissociation of complexes between the organomercury compounds and the solvents.] In the one case where an S_E1 mechanism was claimed for a reaction of a simple dialkylmercury compound (the reaction between di-*sec*-butylmercury and diethylthallium bromide in dimethylformamide) (*205, 232*), it has now been shown that the original results were misinterpreted (*238*).

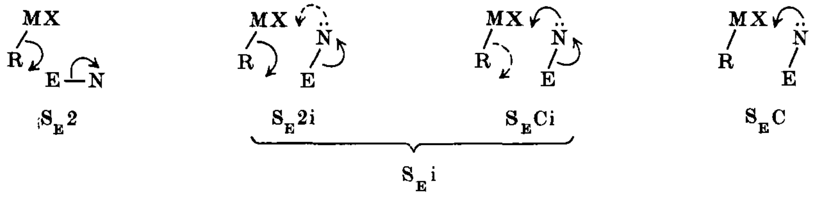


FIG. 1. Mechanisms of electrophilic aliphatic substitution reactions (cf. *1*).

Numerous reactions of alkyl derivatives of the Group II metals may be cited as examples of the classification outlined above, but only a few representative ones are surveyed here. Most of the substitution reactions of alkylmercuric compounds proceed according to second order kinetics, and with retention of configuration. Further information on the mechanisms is obtained by a study of steric, polar, and solvent effects on the rate of reaction (*1*). For example, in the one-alkyl exchange reaction between alkylmercuric salts and mercuric salts, which proceeds according to these kinetics, added salts increased the rate constant (confirming an S_E2 mechanism), and the reaction rates were greatly influenced by the steric effect of the alkyl groups (*227*, *228*). Polar solvents might lower activation energies for such reactions by solvating the transition states (*1*). On the other hand, in the reaction of dialkylzinc compounds with phenylmercuric chloride (leading to alkylphenylmercury compounds and alkylzinc chlorides), although the kinetics are as usual (first order in each reactant), it has proved difficult under some conditions to disentangle solvent, polar, and steric effects on the reaction rates (*5*). However, for the reaction in diethyl ether at 35°, the rate depended on the polar effect of the alkyl group, and the S_Ei (probably S_ECi) mechanism was proposed.

Very striking solvent effects have been observed in a number of metallation reactions. In general, these are accelerated by increasing solvation, suggesting that carbanionic attack is dominant, although, for some reactions of Grignard reagents with 1-alkynes, increasing solvation appears to decrease the rate of reaction[3] (*206*, *481*). Thus, Russian workers have found that methylmagnesium bromide is more reactive in metallating 1-alkynes in more strongly electron-donating solvents (*492*), that diethylzinc scarcely reacts with phenylacetylene in heptane but does react in strongly donating solvents (*323*), and that diethylcadmium reacts with phenylacetylene only slowly even in 1,2-dimethoxyethane but more rapidly in more strongly donating solvents (e.g., dimethylsulfoxide) and much more rapidly in the presence of complexing agents such as 2,2′-bipyridyl (*324*). Analogous phenomena have been noted (*197*) in the metallation of decaborane by dialkylzinc and -cadmium compounds: the rate of reaction depended on the solvating power of the solvent.

Investigations on metallation using one of the most strongly nucleophilic solvents known, hexamethylphosphorotriamide, have yielded very striking results. Hydrocarbons such as toluene are normally metallated

---

[3] In these cases, the kinetics of the reactions were not straightforward, and the situation was complicated by the possibility that the solutions contained several types of organomagnesium species (see Section IV,B,1*a* below).

only by organosodium and organopotassium compounds, but in "hexametapol" they undergo metallation even by Grignard reagents (*126*).

Metallation by Grignard reagents involving metal-halogen exchange (the above examples involving metal-hydrogen exchange) is also reported to be promoted by strongly electron-donating solvents (*492*).

C. BIS(PERHALOGENOALKYL) DERIVATIVES

The perfluoroalkyl and perfluoroaryl derivatives of the Group II metals have recently aroused particular interest, partly as a consequence of the general interest in fluoro-organic chemistry, and partly because of the influence of fluorine substitution in increasing the polarization of carbon-metal bonds. General reviews have been published on fluorocarbon derivatives of metals (*415*, *438*), on pentafluorophenyl derivatives of the the elements (*87*), and on Grignard and organolithium reagents derived from di- and polyhalogen compounds (*209*).

No perfluoroalkyl derivatives of beryllium, calcium, strontium, or barium have been recorded. A number of perfluoro-organomagnesium compounds (generally the perfluoroalkylmagnesium halides) has been prepared as solutions in ethers, where they are presumably solvated (*438*, pp. 150–153; *87*, pp. 281–282; *209*). Polyfluorophenyl derivatives of magnesium are particularly readily accessible, as the hydrogen atom in a compound such as pentafluorobenzene is sufficiently acidic to be replaced by magnesium when allowed to react with an alkylmagnesium halide (*204*). The rate of exchange of pentafluorophenyl groups attached to magnesium is slow on the n.m.r. time scale in diethyl ether at 22° (see Section IV,B,1*a* below), and thus it was possible to distinguish $C_6F_5Mg(hal)$ and $(C_6F_5)_2Mg$ species in solutions of pentafluorophenylmagnesium halides (*153*).

Very few perfluoroalkyl derivatives of zinc and cadmium have been reported (*438*, pp. 200 and 201; *87*, p. 297). Those reported are perfluoroalkylmetallic halides, with the exception of bis(pentafluorophenyl)zinc and -cadmium. Both these compounds form stable complexes with ligands such as 2,2′-bipyridyl (*319*, *375a*), and the zinc compound forms a moderately stable diethyl etherate (*318*). Bis(perfluoroalkyl)mercury compounds have been synthesized by a number of interesting routes, including the reaction of tris(perfluoroalkyl)phosphines with mercuric oxide (*198*), the addition of mercuric fluoride to perfluoroalkenes (*13*, *264*, *294*, *296*, *482*), pyrolytic decarboxylation of mercuric salts of perfluoroalkanecarboxylic acids (*118–120*), and reaction of perfluoroaryl iodides with mercury (*57*, *117*). In contrast to the unsubstituted dialkylmercury compounds, the perfluoro derivatives form complexes with strong electron donors (see Section II,B, 1*e* above). Bis(tetrafluoro-4-pyridyl)-

mercury, as expected for such exceptionally electronegative organic groups, forms a stable complex with 2,2′-bipyridyl (*89*). There is also evidence that bis(trifluoromethyl)mercury (which is soluble in water) forms labile 1 : 1 complexes with halide ions in aqueous solution (*144*, *145*, *151*) (see Section VII,A below).

The crystal structure of bis(pentafluorophenyl)mercury differs from that of the simple diarylmercury compounds in that the C–Hg–C angle is 176.2 ± 1.2° instead of 180°, and the rings are not coplanar (*266*). Bis(pentafluorophenyl)mercury (*88*) is highly stable to heat and undergoes displacement of the *para*-fluorine atoms by certain nucleophiles (such as hydroxide and methoxide ions) without the carbon-mercury bond being affected (*84*) although, with halogens, hydrazine, and lithium aluminum hydride (*84*), cleavage of carbon-mercury bonds occurs. [Cleavage also occurs very readily with iodide ion in aqueous ethanol (*129*).] It does not readily undergo transmetallation reactions, and failed to react with zinc or cadmium (*83*).

The novel chemistry of the pentafluorophenyl derivatives of the metals has tended to overshadow studies of the corresponding pentachlorophenyl derivatives. Pentachlorophenyl derivatives of magnesium (*341*, *348*) and mercury (*130*, *339*) have been reported, however, and some of their reactions investigated, and there are already indications that the chemistry of the pentachlorophenyl compounds may differ considerably from that of the pentafluorophenyl compounds. For example, complexes of bis(pentachlorophenyl)mercury with 2,2′-bipyridyl or 1,10-phenanthroline could not be obtained (although an unstable complex with 3,4,7,8-tetramethyl-1,10-phenanthroline was isolated) (*130*). The interesting suggestion has been made (*339*) that, in pentachlorophenylmercury derivatives, intramolecular donor-acceptor interaction is possible between the *o*-chlorine atoms and mercury, and the nuclear quadrupole resonance spectra of pentachlorophenylmercuric chloride and bis(pentachlorophenyl)mercury give some support to this idea (*68a*, *490*).

It is convenient to mention at this point the extensive studies on the use of metallic derivatives of polyhalogen compounds in synthesis, especially as sources of reactive intermediates—arynes and carbenes. *o*-Halogenophenylmagnesium halides are widely used precursors of arynes (*209*, *210*), and a number of α-halogenoalkyl derivatives of the Group II metals have been used as methylene-transfer agents. [The problem of establishing whether free carbenes are intermediates in some or all of these methylene transfer reactions (*209*, reference 44) will not be discussed here.] Leading references are as follows: (1) magnesium derivatives (*209*, *446*, *447*, *478*), (2) zinc derivatives (*61*, *236*, *275*, *384*, *395*, *450*, *479*), and (3) mercury derivatives (*60*, *269*, *270*, *334*, *368*, *385*, *386*).

D. DIALKENYL DERIVATIVES

1. 1-Alkenyl Derivatives

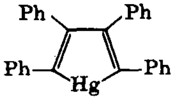
Compounds of the general formula $R \cdot CH{=}CH{-}M{-}X$ (where M represents a Group II metal) are of interest because of the possibility of interaction between the π-electrons of the $C{=}C$ bond and vacant orbitals of the metal atom. Such interaction would be most apparent in the absence of electron-donating solvents, but, although many vinyl and other 1-alkenyl derivatives have been prepared, they have almost all been solvated. There is thus little evidence so far for such interactions, and in a related series, the ultraviolet (*196*) and n.m.r. (*7a*) spectra of arylmercury compounds show little or no evidence for resonance interaction between mercury and the π-system.

When the chemistry of vinylmetallic compounds was reviewed in 1962 (*383*), the only divinyl derivatives of the Group II metals that had been isolated were divinylzinc (*36*) and divinylmercury (*34*, *37*, *308*, *370*). The synthesis of divinylcadmium from divinylmercury and cadmium has since been reported in a patent (*163*), although an earlier attempt, using vinylmagnesium bromide and cadmium chloride, was unsuccessful (*35*). Divinylmagnesium, -beryllium, -calcium, -strontium, and -barium have not been described. Dipropenyl- and diisopropenylmercury are known (*301*), and evidence has been obtained for a number of diallenic zinc compounds (*177*). A few more of the 1-alkenylmetallic halides have been reported (discussed in Section IV), but the structural chemistry of these compounds remains a potentially profitable field for investigation. The only detailed studies have been of the mercury derivatives, which proved particularly amenable to investigation by n.m.r. Exchange of alkyl groups in these compounds is slow on the n.m.r. time scale, and the spectra show splitting of the proton resonance signals by $^{1}H{-}^{199}Hg$ coupling. The spectra of divinylmercury (*297*) and of bis(*cis*-propenyl)-, bis(*trans*-propenyl)-, and bis(isopropenyl)mercury (*301*) have been analyzed. The spectra were consistent with simple, monomeric molecules, with chemical shifts of the orders predicted. In the cases of the propenyl derivatives, the $^{1}H{-}^{199}Hg$ coupling constants provided evidence for the absolute configurations of the molecules.

The claim (*68*) that the major product from the reaction of the dilithio compound XV with mercuric chloride has the structure XVI seems to need further justification, particularly in view of the inconsistent molecular weight data (cf. *95*, pp. 80 and 81); the first cyclic, *monomeric* organomercury compounds to be authenticated contain eleven-membered rings (*28a*).

$LiCPh{=}CPh{-}CPh{=}CPhLi$

(XV)



(XVI)

(Some aspects of reactions involving electrophilic substitution at unsaturated carbon are reviewed in Section IV.)

2. *Bis(allylic) and Bis(cyclopentadienyl) Derivatives*

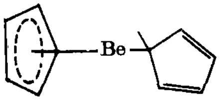
These compounds are of great interest because several different types of bonding may be envisaged for them. Thus, for example, an allyl derivative could exist in an ionic form, with the allyl anion stabilized by charge delocalization; as a σ-bonded covalent compound; or as a π-bonded complex. In fact there is some evidence for all three types of constitution.

a. Allylic Derivatives. The diallyl derivatives of beryllium, calcium strontium, and barium have not been reported, and diallylmagnesium has been obtained only in solution (*11*, *467*). The extensive work on allylmagnesium halides is reviewed (Section IV,B,1*b* below), but as an example of one of the extremes of the possible structural types we mention here the recent evidence that, in very strongly electron-donating solvents (e.g., hexamethylphosphorotriamide), 2-butenylmagnesium bromide exists almost entirely as a salt of the *cis*-2-butenyl carbanion (*8*, *9*). Several bis(allylic) derivatives of zinc (*423*, *426*, *431*) and cadmium (*425*) have been obtained as pure solids via the reaction of the dimethyl derivatives with tris(allylic)boron compounds. At room temperature, the proton magnetic resonance spectra of these compounds (and of diallylmagnesium) (*467*) indicated that the α- and γ-protons were magnetically equivalent (*425*, *431*), and protolysis of the dicrotyl derivatives gave a mixture of 1- and 2-butenes (*11*, *177*, *425*). It was thus not possible to distinguish between π-allylic structures or rapidly equilibrating σ-bonded structures. (Ionic structures seem highly unlikely in these instances.) However, it has been reported (*467*, *468*) that at −100°, the proton magnetic resonance spectrum of diallylyzinc is that of a σ-allyl derivative, with no isomerization to the propenyl derivative. Furthermore, a recent analysis of the n.m.r. spectra of dicrotylzinc and bis(2-methylallyl)zinc revealed that the former compound had a spectrum of the ABX_3Y_2 type, corresponding to a σ-bonded crotyl derivative (*423*).

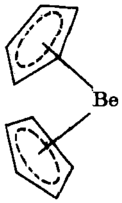
The protolysis of dicrotylmagnesium resembles that of the corresponding Grignard reagent (see Section IV,B,1*b*), and gives a mixture of butenes in proportions depending on the nucleophilicity of the solvent (*11*). On the other hand, the proportions from the zinc and cadmium derivatives were relatively unaffected by the solvating power of the solvent (*177*), and the unlikelihood of ionic structures for these reagents was thus confirmed. Although these protolysis studies gave little information regarding the possible solvation of the zinc and cadmium reagents, bis(allylic) derivatives of zinc (*423*, *424*) and cadmium (*425*) do form stable complexes with 2,2′-bipyridyl.

Diallylmercury at ambient temperatures gives an n.m.r. spectrum corresponding to a "frozen" σ-allyl structure, but, on the addition of salts such as mercuric halides, rapid interconversion of allyl and propenyl groups occurs, leading to a spectrum of the AX_4 type (*349*).

b. Cyclopentadienyl Derivatives. Bis(cyclopentadienyl)derivatives of beryllium, magnesium, calcium, and mercury have been prepared. There is also a patent reference (*71*) to compounds of the formula C_5H_5ZnR (where R = Et, Ph, *tert*-Bu), but no information has been given on the structure or reactions of these compounds.



(XVII)



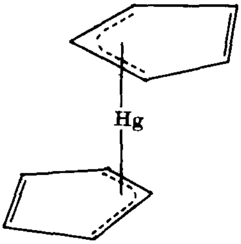
(XVIII)

Bis(cyclopentadienyl)beryllium attracted interest from its first preparation (from cyclopentadienylsodium and beryllium chloride), because of its high dipole moment ($\mu_{25^\circ} = 2.46 \pm 0.06$ D in benzene, 2.24 ± 0.09 D in cyclohexane) (*159*). The infrared (*169*) and far-infrared (*170*) spectra of the compound were analyzed, in an attempt to reconcile them with structures such as XVII and XVIII that would account for the high dipole moment. However, it was subsequently found that in the crystal, bis(cyclopentadienyl)beryllium had a centrosymmetric molecular structure, with a lattice in the same space group as ferrocene (*377*); electron diffraction measurements on gaseous bis(cyclopentadienyl)beryllium confirmed that the molecule had a "sandwich" structure with planar, symmetrical, staggered C_5H_5 rings (*19*). The molecule was considered to be largely ionic, accounting for the high dipole moment. The electron diffraction study (*19*) further revealed the most interesting feature of the structure of the molecule: the beryllium atom occupies two alternative positions on the common axis of the rings, 1.485 ± 0.005 Å from one ring and 1.980 ± 0.010 Å from the other. The infrared spectra of the solid and of solutions have now been reconciled with the structure found by electron diffraction (*171*).

Bis(cyclopentadienyl)magnesium is a well-known compound, being readily prepared from cyclopentadienylmagnesium halides (*469*) or by the direct reaction of magnesium with cyclopentadiene (*30*). However, although it appears to be similar to bis(cyclopentadienyl)beryllium in physical and spectroscopic properties (*169*, *170*, *229*), its molecular structure has not been determined. Bis(cyclopentadienyl)magnesium is a very valuable intermediate in the preparation of cyclopentadienyl derivatives of other metals (*58*, *360*, *361*), and bis(cyclopentadienyl)beryllium was used to prepare the first organometallic derivative of plutonium, tris(cyclopentadienyl)plutonium (*42*).

Bis(cyclopentadienyl)calcium has been prepared by the reaction of cyclopentadiene with calcium carbide (*497*, *498*). A few reactions of this compound were reported, but its structure has not been investigated.

The constitution of bis(cyclopentadienyl)mercury, a somewhat unstable solid prepared from cyclopentadienylsodium and mercuric chloride (*470*), is a subject of controversy. It has been argued (*470*, *471*) from the fact that the compound forms an adduct with maleic anhydride and from its spectroscopic properties (infrared, ultraviolet. n.m.r.) that it possesses a σ-bonded structure. However, the interpretation of both the chemical and the spectroscopic evidence has been questioned (*309*). A comparison of the proton magnetic resonance data recorded by the two groups of workers is instructive. Nesmeyanov and his co-workers record a singlet, with no signs of fine structure even at 200°K (*146*, *309*), while Wilkinson and Piper (*471*) recorded a singlet at approximately −5.6 ppm relative to tetramethylsilane, with a broad shoulder at approximately −5.3 ppm.[4] It is possible that the explanation for the observed discrepancies may lie in the effect of traces of mercury salts on the rate



(XIX)

---

[4] The reference (*471*) gives chemical shifts of 1.5 and 1.8 ppm relative to the aromatic protons of toluene, which have here been taken as having a chemical shift of −7.17 ppm relative to tetramethylsilane.

of interconversion of different forms of the molecules (cf. *349*). Besides a tautomeric σ-bonded system and a π-cyclopentadienyl structure, a third possibility involving π-allylic bonding (XIX) has been suggested (*121*). The problem remains unresolved, although a very recent communication (*284a*) reports that in sulfur dioxide at −70°, the n.m.r. spectrum of bis(cyclopentadienyl)mercury does show splitting consistent with a σ-bonded structure.

3. *1-Alkynyl Derivatives*

Besides the acetylides and carbides (not discussed here), a number of noteworthy bis(1-alkynyl) derivatives of the Group II metals have been described.

It has recently been reported (*342*) that concentration of solutions of "phenylethynylmagnesium bromide" in tetrahydrofuran yields a mixture of two stereoisomers of a complex of bis(phenylethynyl)magnesium with four moles of solvent. A series of 1-alkynyl derivatives of zinc and cadmium has been described by Nast and his co-workers (*303*, *305*). These include crystalline compounds of the formula $(\mathrm{Ph{\cdot}C{\equiv}C})_2\mathrm{M}$, prepared by the reaction of the diphenyl derivatives of the metals with phenylacetylene in liquid ammonia. Both the zinc and the cadmium compounds are soluble in liquid ammonia, and the zinc compound forms a crystalline complex, $(\mathrm{Ph{\cdot}C{\equiv}C})_2\mathrm{Zn{\cdot}2NH_3}$ at −78°. Alkylethynylmercury compounds, $\mathrm{R{\cdot}Hg{\cdot}C{\equiv}CH}$, have also been reported (*259*).

E. COMPLEX ORGANOMETALLIC ANIONS

It has long been recognized (*95*) that dialkylzinc compounds form complexes with alkyl derivatives of the more electropositive metals, and from the compositions of the complexes and their electrochemical properties they have been formulated as salts of alkylzinc anions. A largely ionic structure, $\mathrm{Li^+[AlEt_4]^-}$, has been confirmed for the analogous lithium tetraethylaluminate (*181*), and the stability of the tetraethylaluminate anion has recently been manifested in the observation that the n.m.r. spectrum of the lithium salt in dimethoxyethane shows $^1\mathrm{H}$—$^{27}\mathrm{Al}$ spin-spin coupling (*327*).

Complexes similar to the zinc derivatives are formed by some of the other Group II metals, and are described below. The more electropositive metals of the group (magnesium, calcium, strontium, barium) can also function as the positive counterions. Complexes of the type described here have been classified as "ate" complexes (*473*), and the importance of such complexes in the reactions of organometallic compounds is beginning to be realized (*435*, *474*).

1. *Alkylberyllium and Alkylmagnesium Anions*

Both diphenylberyllium and diphenylmagnesium react with phenyllithium to form complexes, $LiMPh_3$. The beryllium complex may be isolated as a crystalline etherate, but the magnesium complex dissociates in diethyl ether (*477*). In contrast, a study of the ^1H and ^7Li n.m.r. spectra of mixtures of methyllithium and dimethylmagnesium in diethyl ether suggests that species such as $Li_2Mg(CH_3)_4$ and $Li_3Mg(CH_3)_5$ are present, rather than the simple 1:1 complexes (*381*). In the analogous phenyl system, some of the complex Li_2MgPh_4 is present, but not the 3:1 complex (382). In the mixed systems, methyllithium plus diphenylmagnesium or phenyllithium plus dimethylmagnesium, mixed 2:1 complexes, $Li_2MgMe_{4-n}Ph_n$, were observed, and there was a tendency for the phenyl groups to be involved in these complexes, rather than in those of the type Li_4Me_3Ph found in mixtures of methyllithium with phenyllithium (*382a*). Very recently, a crystalline 2:1 complex of methyllithium with dimethylberyllium (*460b*) and a liquid 1:1:1 complex of *n*-butyllithium, dimethylmagnesium and diethyl ether (*104a*) have been isolated; the crystal structure of the beryllium complex contains $BeMe_4$ groups, with the methyl groups at the corners of distorted tetrahedra (*460b*).

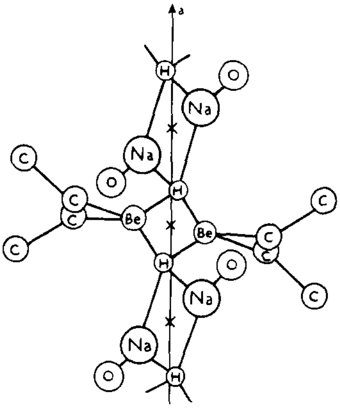


Fig. 2. Crystal structure of the etherate of sodium hydridodiethylberyllate. [Reproduced from Adamson and Shearer (*7*) by permission of the Chemical Society and the authors.]

Dialkylberyllium compounds also react with alkali-metal hydrides (*96*, *475*) to form complex hydrides, which have been formulated as salts of $[HBeR_2]^-$ anions. However, in the solid state the etherate from the interaction of sodium hydride and diethylberyllium in diethyl ether has the dimeric structure shown in Fig. 2 (see Section III below) (*7*).

Complexes of diethylberyllium with various salts such as alkali-metal fluorides or cyanides and tetraalkylammonium salts have been described (*406*, *408*). These are of variable composition (ratio of diethylberyllium to salt from 1 : 1 to 4 : 1 or higher) and unknown structure. Their solutions in ethers and in hydrocarbons conduct electricity[5] (*408*), suggesting ionic structures. Electrolysis of the complexes results in deposition of beryllium carbide and beryllium at the cathode (*407*).

2. *Alkylzinc Anions*

Dialkylzinc compounds are particularly characterized by their tendency to form complex alkylzinc anions. In fact liquid diethylzinc itself has a slight electrical conductivity, consistent with ionization as represented in Eq. (7) (*235*), and a complex of ethylsodium and diethylzinc was among the earliest organometallic compounds known (*457*). The

$$2Et_2Zn \rightleftharpoons EtZn^+ + ZnEt_3^- \qquad (7)$$

ability of dialkylzinc compounds to form complexes of this type even in nonpolar solvents has recently been illustrated by an n.m.r. study of mixtures of ethyllithium and diethylzinc in benzene, which revealed the presence of the 1 : 1 complex, $LiZnEt_3$ (*436*).

From the large number of examples reported, it seems that complex formation is the general rule for combinations of the alkyl derivatives of the alkali metals, calcium, strontium, and barium, with dialkyl- and diarylzinc compounds. [Leading references to these complexes: (*187*, *190*, *200*, *230*, *344*, *457*, *477*).] The complexes of dialkylcalcium, -strontium, and -barium compounds are of interest (*187*, *190*), as the uncomplexed derivatives of the alkaline earth metals are unknown (see Section II,A,1*a* above). With phenyllithium, diphenylzinc is reported (*477*) to form a second complex, $Li_3Zn_2Ph_7$, and n.m.r. studies (*381*) indicate that, in diethyl ether, complexes such as $Li_2Zn(CH_3)_4$ and $Li_3Zn(CH_3)_5$ may be formed. The complex, $Li_2Zn(CH_3)_4$, has very recently been isolated, and its crystal structure determined; the structure contains tetrahedral $Zn(CH_3)_4$ groups (*460a*). Lithium hydride reacts with diphenylzinc in diethyl ether to form a crystalline monoetherate of $Li[HZnPh_2]$, analogous to the beryllium complex [*475*].

3. *Alkylcadmium and Alkylmercury Anions*

Cadmium and mercury show much less tendency than zinc to participate in alkylmetallic anions. The only mercury compounds of this type

---

[5] These results are in conflict with an earlier report (*480*) that the conductivity of solutions of dimethylberyllium in diethyl ether was not markedly increased by the addition of salts.

that have been characterized are 1-alkynyl derivatives, such as $Ba[Hg(C{\equiv}C{-}R)_4]$ (*304*); similar derivatives of cadmium have been prepared (*305*). There is apparently little interaction between phenyllithium and diphenylcadmium in diethyl ether, although a crystalline complex was obtained on the addition of dioxan to the solution (*477*); ethyllithium and diethylcadmium form a solvated 1:1 complex in tetrahydrofuran, but not in benzene (*436*). It seems likely that there is complex formation between diphenylbarium and diphenylcadmium (*186*). No evidence has been obtained for the existence of complexes between phenyllithium and diphenylmercury (*477*).

It would be of interest to know whether complex formation takes place between organolithium compounds and bis(perfluoroalkyl)-mercury compounds.

4. *Salts of Group II Metal Cations*

Some calcium, strontium, and barium salts of tetraalkylzincate ions were mentioned above. Besides the Group II metals, several others are capable of participating in complex organometallic anions, and the alkaline earth metals and magnesium are sufficiently electropositive to function as the cations in "ate" complexes. Thus, for example, complexes such as $Mg[AlMe_4]_2$ (*499*) and $Ca[AlEt_4]_2$ (and the corresponding strontium and barium compounds) have been reported (*277*, *277a*).

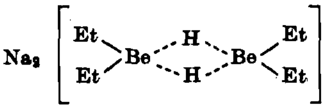
III. Compounds Containing the System C–M–H; the Alkylmetallic Hydrides

A number of alkylberyllium hydrides have been reported during the last few years, and these give indications of providing a promising field for study. Alkylmagnesium hydrides may also exist, although they have not yet been characterized, and one phenylzinc hydride has been reported.

A. ALKYLBERYLLIUM HYDRIDES

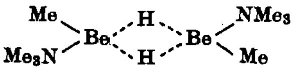
In 1952 Wittig and Hornberger reported briefly that lithium hydride reacted with ethereal diphenylberyllium to give a crystalline complex, which they formulated as $Li[BePh_2H]\cdot Et_2O$ (*475*). Ten years later, Coates and Cox reported similar complexes, such as $Na[BeEt_2H]$, from diethylberyllium and sodium hydride (*96*). Complexes were also formed between dimethylberyllium and sodium hydride and between diethylberyllium and lithium hydride. Diethylberyllium did not react with magnesium hydride.

The sodium hydride-diethylberyllium complex was believed to be unsolvated, and a dimeric structure (XX) with hydrogen bridges was suggested. A subsequent X-ray crystallographic study has confirmed this hypothesis, except that the crystals did in fact contain two moles of ether in each dimeric unit, as illustrated in Fig. 2 (*7*).



(XX)

Coates and his co-workers have now reported a range of alkylberyllium hydride derivatives. Treatment of the dialkylberyllium-sodium hydride complexes with ethereal beryllium chloride gave solutes with compositions corresponding to the formula $Be_3R_4H_2$ (*53*, *96*). On evaporation of ether from a solution of "$Be_3Me_4H_2$," dimethylberyllium was lost, leaving hydride-rich residues (*51*, *53*). When donor molecules were added to the solutions, mixtures of solvated dialkylberyllium compound and solvated alkylberyllium hydride were obtained (*51*, *53*). The latter were dimers, with compositions such as $(BeEtH \cdot Me_3N)_2$ (from ethylberyllium hydride and trimethylamine). Ethereal solutions of "RBeH" were also formed from dialkylberyllium compounds and trialkyltin hydrides (*51*) and from ethylberyllium bromide and lithium hydride (*52*). Hydrogen-bridged structures, such as XXI, were proposed for the dimers, and a comparison of the infrared (*51*) and n.m.r. (*55*) spectra of the complexes and of their deuterium analogs has confirmed

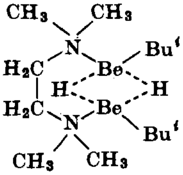


(XXI)

the hypothesis. The n.m.r. signals due to the methyl protons of $(BeMeH \cdot Me_3N)_2$ showed splitting, which varied with temperature; this splitting was ascribed to *cis-trans* isomerism about the hydride bridge, and values of ΔH and ΔS were calculated for interconversion of the isomers (*55*). Some alkylberyllium hydride complexes may be prepared directly (*116*). Thus, the trimethylamine complex of phenylberyllium hydride is prepared in one stage from diphenylberyllium, beryllium chloride, sodium triethylborohydride, and trimethylamine, and is a dimer, $(BePhH \cdot Me_3N)_2$, in benzene (*116*); the analogous complex with trimethylphosphine in place of trimethylamine dissociates in benzene solution. Similarly, the trimethylamine complex of methylberyllium hydride is obtained by the reaction of dimethylberyllium, triethylstannane, and trimethylamine in the presence of diethyl ether.

Some reactions of the alkylberyllium hydride derivatives have been reported (*52, 116*). The simple etherates reduce carbonyl compounds (see also Section V,A below), and several of the hydrides (e.g., sodium diethylberyllium hydride, ethylberyllium hydride etherate) add to alkenes.

It seems likely (see Section II,B,2*a*) that, on heating, dialkylberyllium compounds may decompose to beryllium hydride and alkenes via alkylberyllium hydrides, and pyrolysis of diisopropylberyllium does indeed give isopropylberyllium hydride (*98*). It has recently been reported (*372*) that thermal decomposition of di-*tert*-butylberyllium leads to isobutylberyllium hydride, which forms a 2:1 complex (XXII) with tetramethylethylenediamine. It has been suggested (*194*) that a polymeric substance with the composition $(HBeCH_2CH_2BeH)_n$ is formed when diethylberyllium is pyrolyzed.



(XXII)

B. ALKYL DERIVATIVES OF OTHER GROUP II METAL HYDRIDES

It has been suggested (*41*) that the ethoxymagnesium hydride formed when diethylmagnesium in diethyl ether is treated with silane arises from fission of the solvent by ethylmagnesium hydride. It seems possible that alkylmagnesium hydrides may also be intermediates in the pyrolysis of dialkylmagnesium compounds (the end products including magnesium hydride and alkenes) (*247, 466*). Such compounds have not yet been isolated, and hence nothing is known about their structures.

The only other recorded member of this class of compounds is a crystalline product, formulated as $Li[ZnPh_2H] \cdot Et_2O$, from the interaction of lithium hydride with diphenylzinc in diethyl ether (*475*). It seems likely that this complex has a structure similar to that of the analogous beryllium complexes.

IV. Compounds Containing the System C–M–Halogen; the Alkylmetallic Halides

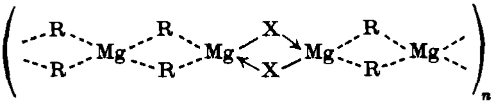
Representatives of this class of compound, the Grignard reagents, are of course the most familiar of all organometallic compounds. However, significant advances have been made in recent years in the study both of the Grignard reagents and of other compounds of the class.

A. UNSOLVATED ALKYLMETALLIC HALIDES

The Grignard reagents are *solvated* alkylmagnesium halides, from which it is almost impossible to remove solvent molecules (*95*, p. 52; *412*, *413*). Furthermore, alkylmetallic halide derivatives of the Group II metals often tend to disproportionate to the metal halide and the dialkyl derivative of the metal; thus, for example, the reaction of beryllium chloride with unsolvated *n*-butylmagnesium iodide led to di-*n*-butylberyllium (*192*). However, the alkylmercuric halides are well known, and unsolvated alkylmagnesium, alkylcadmium, and alkylzinc halides have been prepared and studied.

1. *Alkylmagnesium Halides*

The pioneering work of Bryce-Smith and his co-workers, followed by Zakharkin and his colleagues, on unsolvated alkylmagnesium halides has been reviewed (*454*). Their results may be briefly summarized as follows. Under carefully controlled conditions, *n*-alkyl- and arylmagnesium chlorides, bromides, and iodides may be readily prepared in nondonor solvents, by the direct reaction of magnesium with the alkyl or aryl halide (*74–76*, *79*, *493*, *494*, *496*). In general, the unsolvated reagents resemble the conventional Grignard reagents in their reactions, although some significant differences have been noted [see Wakefield (*454*)]. The compositions and structures of the unsolvated alkylmagnesium halides are so far ill-defined; they generally contain an excess of C—Mg over C–halogen bonds, and may have polymeric structures of type XXIII (*74*).



(XXIII)

Since the review (*454*) referred to, little further has been published on the subject. *n*-Pentylmagnesium compounds have been prepared in benzene solution (*191*). Di-*n*-pentylmagnesium was soluble in this solvent, and the *n*-pentylmagnesium halides tended to disproportionate, depositing magnesium halide. In the case of the iodide, disproportionation did not proceed to completion, and the material remaining in solution was a polymer with the empirical formula R_5Mg_3I. Unsolvated alkylmagnesium halides (of unknown constitution) have also been prepared via adsorption of gaseous alkyl halides on magnesium films (*180*).

The crystal structure of material prepared by desolvation of some ethereal alkylmagnesium halides was found to be that of a mixture of dialkylmagnesium compound and magnesium halide (*458*); this finding does not necessarily apply to alkylmagnesium halides prepared in the absence of donor solvents.

In an investigation of the Wurtz-type side reaction occurring during the preparation of unsolvated alkylmagnesium halides, Bryce-Smith and Cox showed, by using cumene as a radical trap, that free radicals were formed in the reaction mixture (*75*). In a recent study (*495*), Russian workers found that thermal decomposition of unsolvated alkylmagnesium halides led to alkenes, but not to free radicals. In the presence of an alkyl halide, however, radicals derived both from the alkylmagnesium halide and from the alkyl halide were formed; homolytic reactions of this type were suppressed in donor solvents. Some alkyl-exchange reactions were also noted, *n*-butylmagnesium iodide and methyl iodide in heptane at 80° giving some methylmagnesium iodide.

2. *Alkylzinc Halides*

The classical synthesis of diethylzinc (*167*) involved the disproportionation of ethylzinc iodide. However, the disproportionation is apparently reversible (Eq. 8), as the reaction of zinc iodide with an excess of diethylzinc leads to a crystalline solid with the composition EtZnI (*235*):

$$Et_2Zn + ZnI_2 \rightleftharpoons 2EtZnI \qquad (8)$$

Ethylzinc bromide and ethylzinc chloride have recently been prepared via the reaction of diethylzinc with the zinc halides (*65*). The ethylzinc halides were crystalline, sharp-melting solids. The bromide and chloride gave clear solutions in hydrocarbon solvents, although ethylzinc iodide was soluble in nonpolar solvents only in the presence of diethylzinc; in its absence, the solutions deposited zinc iodide (*64*). [Ethylzinc iodide dissolves in diethylzinc to give a slightly conducting solution (*235*).] The preparation of unsolvated alkylzinc halides by removal of solvent from the solvated reagents has been described (*174*, *331*), but no information (apart from C and H analyses) was given on the constitution of the products.

Ethylzinc chloride and bromide are tetrameric in benzene solution, and a cubic arrangement of zinc and halogen atoms (Fig. 3) has been suggested for the tetramers (*65*).

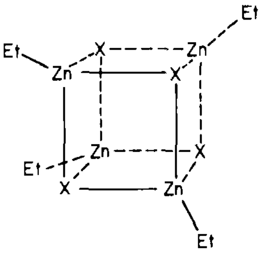


FIG. 3. Ethylzinc halide tetramers (X = Cl, Br) (*65*).

A recent determination (*300*) of the crystal structure of unsolvated ethylzinc iodide disclosed the presence of polymeric chains, with iodine bridges between the zinc atoms (Fig. 4).

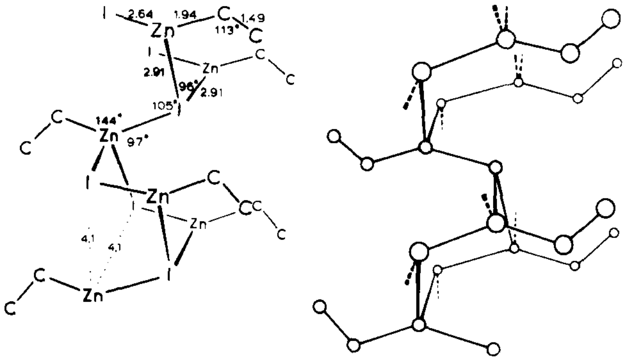


FIG. 4. Crystal structure of ethylzinc iodide. [Reproduced from Moseley and Shearer (*300*) by permission of The Chemical Society and the authors.]

Proton magnetic resonance studies on hydrocarbon solutions of the ethylzinc halides (*64*) showed that there was exchange of ethyl groups, and confirmed that in the cases of the chloride and bromide the equilibrium (Eq. 8) lay almost entirely to the right. For ethylzinc iodide, the situation was complicated by the precipitation of zinc iodide referred to above.

3. *Alkylcadmium Halides*

Few investigations comparable to those on the unsolvated alkylzinc halides have been carried out on the corresponding cadmium compounds. However, compounds with the composition of alkylcadmium halides (RCdX) have been isolated (*390*), although their structure has not been established.

Alkylcadmium halides are only sparingly soluble in diethyl ether and dioxan (*254*), and are thus presumably only weakly, if at all, solvated by these solvents. (However, the chemistry of solutions of "alkylcadmium halides" in donor solvents is reviewed in Section IV,B,2*d* below.)

4. *Alkylmercuric Halides*

The simple alkylmercuric halides are well-known compounds, with properties consistent with largely covalent, monomeric structures (*95*). There is little in their structural chemistry that can be included under the heading "recent advances." However, certain aspects of their reactions continue to attract attention. These include the mechanisms of their substitution reactions, and the possible formation of complex salts of the alkylmercuric ion (see Section VII,A below for a discussion of the latter). A detailed survey of the extensive work on the mechanisms of the substitution reactions is beyond the scope of this article, and in any case this topic has been the subject of recent reviews (*44*, *124*, *232*, *364*, *365*) (see also Section II,B,2 above). However, in view of the current interest in the interactions between the alkylmetallic halide, metal halide, and dialkyl derivatives of the other Group II metals, some of the recent conclusions concerning the interactions of such mercury compounds are summarized here. These studies have been noteworthy for the difficulties involved in obtaining results from which unambiguous conclusions could be drawn, and indeed in obtaining reproducible experimental data. Reactions of the types shown in Eqs. (9–12) have been studied,

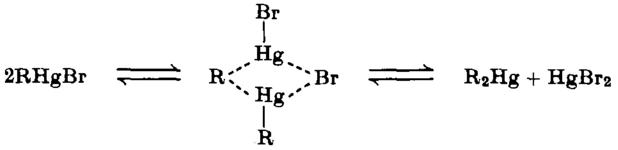
$$\mathrm{R_2Hg + HgX_2 \rightleftharpoons 2RHgX} \tag{9}$$

$$\mathrm{RHgX + Hg^*X_2 \rightleftharpoons RHg^*X + HgX_2} \tag{10}$$

$$\mathrm{RHg^*X + R'HgX \rightleftharpoons RHgX + R'Hg^*X} \tag{11}$$

$$\mathrm{R_2Hg + RHg^*X \rightleftharpoons R_2Hg^* + RHgX} \tag{12}$$

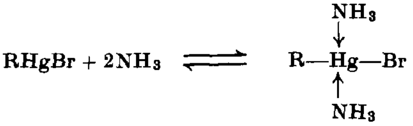
where X = halogen, and Hg* represents labeled mercury. It seems to be generally agreed from studies using optically active alkyl groups [e.g., $\mathrm{R = Ph{\cdot}CH(CO_2Et)}$] that all these reactions proceed with retention of configuration (*362*, *363*) and that they are in fact equilibria, although the position of equilibrium may lie or be displaced far to one side (*350*, *363*, *365*). Controversy has arisen, however, concerning the mechanisms of the reactions, and in particular concerning reactions of the type in Eq. (9), which are displaced to the left under the influence of ammonia on diphenylmercury. For the "symmetrization" of esters of α-bromomercuriphenylacetic acid by ammonia in chloroform, Reutov *et al.* (*363*, and references therein) have proposed the mechanism represented by Eqs. (13 and 14), where $R = Ph \cdot CH(CO_2Et)$:



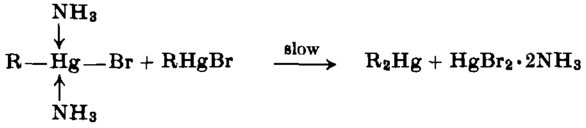
$$2\mathrm{RHgBr} \rightleftharpoons \mathrm{R}\begin{array}{c}\mathrm{Br}\\ | \\ \mathrm{Hg}\\ \vdots \\ \mathrm{Hg}\\ | \\ \mathrm{R}\end{array}\mathrm{Br} \rightleftharpoons \mathrm{R_2Hg} + \mathrm{HgBr_2} \qquad (13)$$

$$\mathrm{HgBr_2} + 2\mathrm{NH_3} \rightleftharpoons \mathrm{HgBr_2 \cdot 2NH_3} \qquad (14)$$

However, Jensen and Rickborn (*241*) have pointed out inconsistencies in the Russian workers' kinetic data, and have suggested alternative mechanisms involving complex formation between the alkylmercuric halide and ammonia, as represented by Eqs. (15 and 16):



$$\mathrm{RHgBr} + 2\mathrm{NH_3} \rightleftharpoons \mathrm{R{-}}\underset{\underset{\mathrm{NH_3}}{\uparrow}}{\overset{\overset{\mathrm{NH_3}}{\downarrow}}{\mathrm{Hg}}}\mathrm{{-}Br} \qquad (15)$$



$$\mathrm{R{-}}\underset{\underset{\mathrm{NH_3}}{\uparrow}}{\overset{\overset{\mathrm{NH_3}}{\downarrow}}{\mathrm{Hg}}}\mathrm{{-}Br} + \mathrm{RHgBr} \xrightarrow{\text{slow}} \mathrm{R_2Hg} + \mathrm{HgBr_2 \cdot 2NH_3} \qquad (16)$$

Both American and Russian workers have in fact obtained evidence for the formation of unstable donor-acceptor complexes between alkylmercuric halides and ammonia (*241*, *366*), and the Russians now apparently accept a mechanism of the general type proposed by Jensen and Rickborn (*365*).

The same groups of workers have proposed alternative mechanisms for symmetrization by diphenylmercury. The Russian workers had proposed that the first stage of the reaction was represented by Eq. (13) (*367*). However, Jensen and Miller (*239*) demonstrated that in chloroform an initial, rapid reaction involving a 1 : 1 ratio of reactants occurred, followed by a slow reaction leading to the symmetrical product, and proposed the scheme shown in Eqs. (17 and 18):

$$\mathrm{RHgBr + Ph_2Hg \xrightarrow{fast} RHgPh + PhHgBr} \tag{17}$$

$$\mathrm{RHgPh + RHgBr \longrightarrow R_2Hg + PhHgBr} \tag{18}$$

An alternative for the second stage was Eq. (19),

$$\mathrm{2\ RHgPh \longrightarrow R_2Hg + Ph_2Hg} \tag{19}$$

followed by another reaction as in Eq. (17). The Russian workers have since (*45*) obtained kinetic results consistent with these suggestions, and favoring the reaction corresponding to Eq. (19) as the second stage.

Yet another example of the difficulty in obtaining consistent experimental data for these reactions is provided by a reaction of the type shown in Eq. (9), but proceeding to the right. In the reaction between alkylarylmercury compounds (RHgAr) and ^{203}Hg-mercuric halides, leading to mixtures of alkylmercuric halide and arylmercuric halide, alternative claims were that (*i*) both products contained ^{203}Hg (*140*), and (*ii*) only the arylmercuric halide contained ^{203}Hg (*310*). The latter view has now been accepted by the American school (*139*).

It is evident that, in studies on the mechanisms of reactions of organomercury compounds, great attention has to be paid to the experimental conditions used. In particular, it has been pointed out that peroxides or combinations of mercury and mercury(I) salts (both of which could arise inadvertently) have a catalytic effect on a number of reactions (*168, 231*).

As in the case of the dialkylmercury compounds (see Section II,B,2*a* above), the rate of exchange of alkyl groups between alkylmercuric halide molecules is low, and ^{1}H—^{199}Hg spin-spin coupling is readily observable. The proton magnetic spectra of compounds of the general formula RHgX have consequently aroused considerable interest. For a series of compounds, CH_3HgX and CH_3CH_2X, it has been found that $J(^{1}H—^{199}Hg)$ increases with increasing electronegativity of the group X (*208*). As alkenylmercuric halides are configurationally stable, the influence of the hybridization of the carbon atom attached to mercury and of the geometry of the systems on $J(^{1}H—^{199}Hg)$ has been investigated (*461, 462*). Compounds studied include the vinylmercuric halides, *cis*- and *trans*-2-chlorovinylmercuric halides, and methylethynylmercury. The spectra for a number of compounds of known stereochemistry were consistent with $J(^{1}H—^{199}Hg)$ of approximately 600 cycles sec^{-1} when H and Hg are *trans*, and approximately 100 cycles sec^{-1} when H and Hg are *gauche* (*262*).

Besides vicinal ^1H—^{199}Hg coupling, long-range ^1H—^{199}Hg coupling through four bonds has been reported for neopentylmercuric halides (*397*).

The proton magnetic resonance spectrum of methylmercuric iodide is of particular interest (*162*, *203*, *208*, *350*). At higher temperatures in pyridine, the spectrum showed a single sharp band with no satellites; as the temperature was lowered, satellites appeared and became progressively sharper until at –35° their width was comparable with that of the main peak. However, the obvious explanation—exchange of methyl groups at the higher temperatures (cf. *208*, *350*)—is apparently untenable, as the line width of the main peak did not change with temperature (*203*). The spectra have now been interpreted (*162*, *203*, *396a*) in terms of a chain of relaxation effects involving transitions in the ^{199}Hg nucleus and rapid relaxation in the ^{127}I nucleus It has also been observed (*162*) that the spectra of pure samples of methylmercuric thiocyanate in pyridine solution show no evidence for rapid methyl exchange (contrast Hatton *et al.* (*208*)].

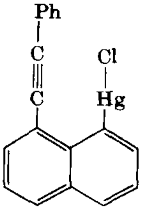
The mercury-chlorine and mercury-bromine stretching frequencies (near 320 cm^{-1} and near 230 cm^{-1}, respectively) for aryl-, alkyl-, and perfluoroalkylmercuric halides have been determined (*109*), and more recently the vibrational spectra of methylmercuric chloride, bromide, iodide, and cyanide have been analyzed, and force constants calculated (*193*); the carbon-mercury stretching force constant varied from 2.50×10^5 dynes cm^{-1} for the iodide to 2.78×10^5 dynes cm^{-1} for the cyanide (see Table I).

As was mentioned above, alkyl- and 1-alkenylmercuric halides are configurationally stable. The preparation and structural assignment of the *cis* and *trans* isomers of 4-methylcyclohexylmercuric bromide (*237*), 4-*tert*-butylcyclohexylmercuric bromide (*16*), and propenylmercuric chloride (*93*) have recently been reported. The crystal structure of *trans*-2-chlorovinylmercuric chloride has been determined, and its configuration confirmed (*330*).

Protolysis of allylmercuric halides leads to rearranged products (cf. the corresponding derivatives of the other Group II metals); crotylmercuric bromide, for example, leads almost exclusively to 1-butene on reaction with hydrochloric or acetic and perchloric acids (*398*). Protolysis of 1-alkenylmercuric halides generally proceeds without rearrangement, and with retention of configuration; the kinetics of acidolyses of a number of alkenylmercuric halides have been reported (*307*).

The problem of the structure of allylmercuric derivatives has been referred to above (Section II,D,2*a*). Further information on this subject has been provided by the ultraviolet spectrum of allylmercuric iodide

(*263*), which revealed interaction between the C=C and Hg—I chromophores; it was suggested that the mercury atom must be situated close to the double bond, so that, even if the compound does not have a π-allylic structure, the carbon-mercury σ-bond must be very long and easily deformed. On the other hand, and in contrast also to analogous alkylmagnesium derivatives (see Section IV,B,1*b* below), there is no sign of an interaction between the mercury atom and the multiple bond in 1-phenylethynyl-8-naphthylmercuric chloride (XXIV) (*136*) or in 3-butenylmercuric chloride (*326*).



(XXIV)

B. Solvated Alkylmetallic Halides

1. *The Grignard Reagent*

a. The Constitution of the Grignard Reagent. The state of knowledge on this subject was reviewed in 1966 (*454*) and in 1967 (*24*), and subsequent work has not materially affected the conclusion reached in the former review, namely, that the Grignard reagent is best represented by an extended equilibrium of the type formulated in Fig. 5. The later work has

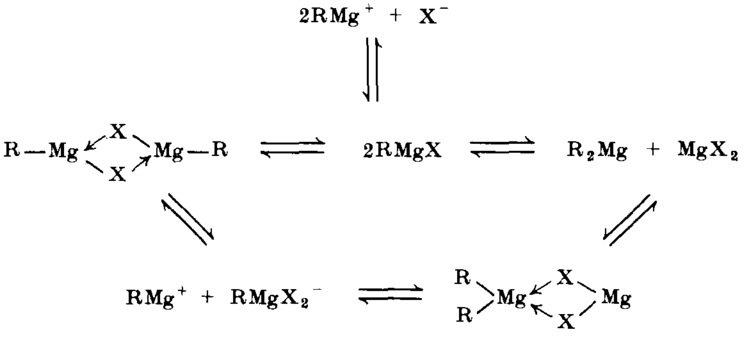
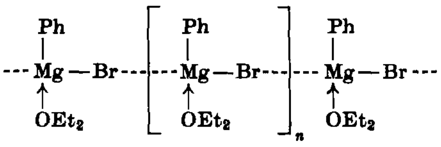


Fig. 5. Equilibria in Grignard reagents (X = halogen; solvent molecules omitted).

served to provide more conclusive evidence toward resolving some points of controversy, and to clarify the factors affecting the relative proportions of the various possible species in solution.

In the scheme shown in Fig. 5, association involving halogen bridging rather than alkyl bridging has been indicated. Arguments in favor of this formulation have been advanced (*454*), but powerful experimental evidence has now been provided by measurements of the variation in degree of association of various alkylmagnesium halides with concentration in diethyl ether (*28*). Association was least for alkyl groups favoring alkyl bridging (i.e., methyl, ethyl), and greatest for the compounds that might be expected to have the greatest positive charge on magnesium. For phenylmagnesium bromide, the graph of i against concentration was almost linear, with no marked change in slope near $i = 2$, and linear association of type XXV was proposed.



$$\cdots\underset{\underset{\displaystyle OEt_2}{\uparrow}}{\overset{\overset{\displaystyle Ph}{|}}{Mg}}-Br\cdots\left[\cdots\underset{\underset{\displaystyle OEt_2}{\uparrow}}{\overset{\overset{\displaystyle Ph}{|}}{Mg}}-Br\cdots\right]_n\cdots\underset{\underset{\displaystyle OEt_2}{\uparrow}}{\overset{\overset{\displaystyle Ph}{|}}{Mg}}-Br\cdots$$

(XXV)

Further investigations on exchange reactions have been carried out by the Dutch school (*56*, *62*). A study (*62*) of possible equilibria involving diethylmagnesium and ^{14}C-labeled ethylmagnesium bromide in diethyl ether was inconclusive, because of rapid statistical exchange of ethyl groups; but the observation that ^{28}Mg became statistically distributed, when labeled magnesium bromide was mixed with diethylmagnesium or ethylmagnesium bromide, indicated that all three species were involved in the equilibria (unless the exchange was catalyzed by impurities).

Smith and Becker have shown (*399*, *400*), by measuring the heats of mixing of solutions of dialkylmagnesium compounds and magnesium halides in diethyl ether, that an almost instantaneous reaction takes place, involving a 1 : 1 ratio of the reactants and leading to a largely monomeric product. The conclusion was that for the systems studied (R = Et, Ph; X = Br, I; concentrations of the order of 0.1 *M* in diethyl ether), the equilibrium (Eq. 20) is rapidly established, and lies far to the right. On the other hand, the effect of the solvent on the constitution of the Grignard reagent was illustrated by the observation (*399a*) that in tetrahydrofuran, although reaction was almost instantaneous, and the products largely monomeric, conversion to RMgX was incomplete. Similarly, while the polarographic behavior of some organomagnesium com-

$$R_2Mg + MgX_2 \rightleftharpoons 2RMgX \qquad (20)$$

pounds in 1,2-dimethoxyethane was consistent with the equilibrium (Eq. 20), it indicated that the equilibrium constant was of the order of 4 when R = $PhCH_2$, Ph, Me_2CH, or Et; and X = Br (*347*). [In view of the hypotheses that transient "magnesious" species may be involved in some reactions of "nascent" organomagnesium compounds (*63*, *78*, *298*), the proposal that RMgX undergoes one-electron reduction at the mercury cathode to give RMg•, which subsequently decomposes to R• and Mg, is of interest.] Similarly, the effect of the nature of the alkyl group on the constitution of the Grignard reagent has been illustrated by some n.m.r. studies. For ethereal solutions of pentafluorophenylmagnesium bromide and iodide, in which aryl-group exchange was slow on the n.m.r. time scale at room temperature, it was possible to distinguish two sets of signals in the ^{19}F n.m.r. spectrum (*153*). One set corresponded to bis(pentafluorophenyl)magnesium and the other to other pentafluorophenylmagnesium species (possibly C_6F_5MgX, although dimeric species were not ruled out, as the degree of association of the solutes was not determined); the chemical shifts of the two sets of signals varied with concentration, although the shifts for bis(pentafluorophenyl)magnesium alone were independent of concentration. Similar observations enabled the ratio 2["RMgX"]/["R_2Mg"] to be determined from the ^{19}F n.m.r. spectra of several fluoroaryl Grignard reagents (*153a*). Another system in which alkyl exchange was sufficiently slow for different alkylmagnesium species to be distinguished by n.m.r. involved mixtures of ethyl- and phenylethynylmagnesium compounds. For mixtures of ethyl- and phenylethynylmagnesium bromides, it was deduced (*351*) that the solutions contained mainly "RMgX" rather than "R_2Mg" species.

Further complexes of alkylmagnesium halides have been characterized. The 1:1 complex of *p*-fluorophenylmagnesium bromide with tetramethylethylenediamine is monomeric in benzene (*153b*), but the 1:1 complex of *tert*-butylmagnesium chloride with diethyl ether is monomeric (*104a*). The latter complex probably has a halogen-bridged structure, similar to that recently established for $[EtMgBr,Et_3N]_2$ by X-ray crystallography (*435a*).

The infrared spectra of solid methylmagnesium chloride and methylmagnesium bromide diethyl etherates showed bands corresponding to ether coordinated to dimethylmagnesium, to methylmagnesium halide, and to magnesium halide (*220*). The ether was so tightly bound as to exclude the possibility that the reagents were mixtures containing free magnesium halide. However, only very limited deductions about the structure of the reagents in solution may be made from such observations on the solids. A further attempt to differentiate between alkylmagnesium species in solution involved measuring the C—D stretching frequencies for α-deutero-organomagnesium reagents (*244*). However, in every case, any difference in frequency between the dialkylmagnesium compounds and the corresponding Grignard reagents was insignificant. (On the other hand, the C—D stretching frequency for $(CH_2D)_2Hg$ in chloroform was clearly distinguishable from that for $CH_2D \cdot HgBr$.)

Recent work on the configurational stability of Grignard reagents may lead to further insights into the nature of the carbon-metal bond in these compounds and into the mechanism of the alkyl-exchange reaction. The results of Roberts *et al.* (*472*) and of Fraenkel *et al.* (*164*) on the configurational stability of primary dialkylmagnesium compounds have been summarized (Section II,B,2*a*). The results on the corresponding alkylmagnesium halides (*164*, *165*, *464*, *465*) are qualitatively similar to those for the dialkylmagnesium compounds, the rates of inversion being slow on the n.m.r. time scale at low temperatures, and depending on the nature of the solvent and on the concentration of the reagent as well as on the temperature. In addition, the rate of inversion of the halides depends on the nature of the halogen; thus, 3-methylbutylmagnesium chloride undergoes inversion at the α-carbon atom much more rapidly than the bromide, and addition of magnesium bromide to a solution of the chloride slows its rate of inversion (*464*). Both groups of workers find that the inversion reaction exhibits a kinetic order greater than 1, and a bimolecular mechanism seems most likely. The observation (*464*) that the rate of inversion is lower in more strongly electron-donating solvents supports the view that electrophilic attack on the Grignard reagent (by species containing the grouping —MgX) is involved. A study of the relative rates of alkyl exchange and of inversion would be valuable.

Although many of the examples studied are atypical, in that they involve rigid ring systems, secondary alkylmagnesium halides in general appear to undergo inversion at the α-carbon atom comparatively slowly. Whitesides and Roberts (*464*) demonstrated this fact by observing the proton n.m.r. spectra of 3,3-dimethylcyclobutylmagnesium bromide and 2,3-dimethylbutylmagnesium bromide. Three groups of workers have studied the n.m.r. spectra of the norbornylmagnesium (*216*, *240*, *265*) and bornylmagnesium (*216*) halides. Preparation of these reagents from either the *exo-* or *endo*-halide affords a mixture of *exo-* and *endo*-Grignard reagents of similar composition. However, in contrast to the earlier studies involving carboxylation of the mixtures (*373*), the spectra indicate that the isomeric reagents are not rapidly interconverted.

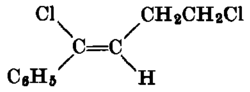
Further studies have been reported on the mechanism of the reactions of Grignard reagents with ketones [addition (*25*, *220*, *221*, *223*, *300a*, *325*, *400a*, *401*, *402*), reduction (*396b*, *441*, *449*), condensation (*439*), other reactions (*123*, *483*, *484*), and general (*23*, *249*, *251*, *252b*, *440*, *442*)], with esters (*222*, *223*), and with nitriles (*148*, *374*), but these have not furnished major advances in our knowledge of the constitution of the reagents. It has been confirmed (*401*, *402*) that ketone-Grignard complexes are intermediates in the reaction of methylmagnesium bromide with 2,4-dimethyl-4′-methylmercaptobenzophenone, and Holm (*220–223*) and Tuulmets (*251*) have interpreted the results of their investigations of the reactions of Grignard reagents with carbonyl compounds in terms of similar complexes. On the other hand, studies on reactions with methyl trifluoroacetate (*222a*) and with sterically hindered cyclobutanones (*252a*) indicate that addition to a carbonyl group can take place without the intermediacy of a ketone–Grignard complex. It has recently been suggested (*24*) that the reaction of methylmagnesium bromide with benzophenone may proceed by a termolecular mechanism. The difficulties in interpreting the many complexities of the kinetic data obtained for these reactions have been emphasized (*24*).

In the earlier review (*454*) it was emphasized that, in electron-donating solvents, solvent molecules form an integral part of the reagents, and later work has confirmed this generalization. Thus, the solvent effects in the reaction of ethylmagnesium bromide with benzonitrile are interpreted (*374*) in terms of specific solvent-Grignard complexes. Striking effects have been obtained by the use of extremely strong donors such as tetramethylurea (*279*) and hexamethylphosphorotriamide (HMPT) (*126*, *156*, *166*) as solvents for Grignard reagents; alkylmagnesium halides in HMPT enolize ketones (*156*) and even metallate hydrocarbons such as toluene (*126*). Grignard reagents form solid complexes with HMPT, but the complexes decompose on standing (*166*). An interesting example of the effect of coordination on reactivity involved the reaction of some substituted phenylmagnesium bromides with di-*tert*-butyl ketone (*325*): phenylmagnesium bromide itself did not react, *o*-methoxyphenylmagnesium bromide reacted smoothly (according to second order kinetics, first order in each reagent), and 2,6-dimethoxyphenylmagnesium bromide again failed to react. A recent interesting observation, and one that may have useful applications, is that optically active ethers show enhanced rotation when coordinated with Grignard reagents (*448*).

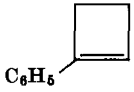
Further evidence has been obtained that radicals are involved in the formation of organomagnesium compounds from alkyl halides and magnesium. The reaction of several alkyl and aryl halides with magnesium in deuterated solvents led to deuterated products that indicated deuterium abstraction by radicals derived from the halides (*15*). However, in interpreting such results, the homolytic reaction between unsolvated alkylmagnesium halides and alkyl halides must be borne in mind (see Section IV,A,1 above) [cf. (*488*)]. A mechanism for the formation of Grignard reagents involving the reaction of anion radicals and radicals on the surface of the metal has been proposed (*22*).

b. Alkenylmagnesium Halides and Related Compounds. The stereochemistry of vinylic Grignard reagents has been studied. Under suitable conditions, it is possible to prepare geometrically isomeric reagents from the corresponding 1-bromo-1-alkenes, such as the 1-bromo-1-propenes (*306*) and the β-bromostyrenes (*486*, *487*). The reagents are apparently formed with retention of configuration (*320*), are configurationally stable, and react with mercuric chloride and carbon dioxide with retention of configuration. However, an n.m.r. study (*282*) on solutions of the Grignard reagents revealed that the apparent retention of configuration may not in fact be complete.

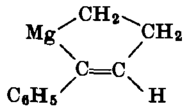
The reaction of *trans*-1,4-dichloro-1-phenyl-1-butene (XXVI) with magnesium in ether yields a variety of products, including 1-phenylcyclobutene (XXVII), whose formation is best rationalized in terms of the initial formation of the vinylic rather than the primary Grignard reagent (*311*), and *trans*-1-phenyl-1-butene (XXIX). The interesting suggestion has been made (*242*) that the intermediate leading to the formation of compound XXIX on hydrolysis is the cyclic magnesium compound (XXVIII).



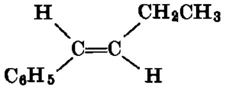
(XXVI)



(XXVII)



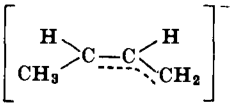
(XXVIII)



(XXIX)

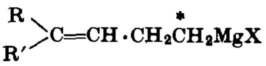
It has long been known that allylic Grignard reagents react to give products derived from the allylic isomer as well as those corresponding to the original halide, and more recent proton magnetic resonance studies (*463*) have shown that ethereal allylmagnesium bromide is either a rapidly equilibrating mixture of σ-bonded isomers, or has a structure with magnetically equivalent allylic protons. Any equilibrium between crotyl- and butenylmagnesium bromide lay almost entirely on the crotyl side. A similar type of isomerization has recently been reported (*312*) in the indene series, the coupling reaction of the Grignard reagent from metallation of 3-methylindene with allyl bromide giving a 3:1 mixture of 1-allyl-3-methylindene and 1-allyl-1-methylindene.

The constitution of allylic Grignard reagents has been further studied by French workers. Protolysis of crotylmagnesium halides (*8*, *9*) or dicrotylmagnesium (*11*, *12*) gave a mixture of 1-butene and *cis*- and *trans*-2-butene. The proportions of the products depended to some extent on the protolytic reagent, but varied relatively little with the halogen in the Grignard reagent. However, the nature of the solvent had a profound effect on the proportions of the products; in general, more strongly electron-donating solvents decreased the proportion of 1-butene, and increased the proportion of *cis*- to *trans*-2-butene. It has been suggested (*8*) that, in the more electron-donating solvents, the allylic group becomes more carbanionic in character, and in the strongest donors the reagent may be regarded as a salt of a *cis*-allylic carbanion (XXX). More recently it has been reported (*157*) that the reaction of 1-methyl-2-butenylmagnesium derivatives with a number of electrophilic reagents gave mainly *cis*-alkenyl products. It was suggested that these reactions proceed by an S_E2' mechanism; in the transition state, the allylic group possesses considerable carbanionic character, and a preferred *cis* configuration.



(XXX)

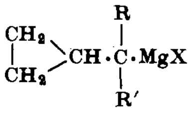
Organomagnesium compounds do not generally react with isolated double bonds, although the addition of allyl- and benzylmagnesium bromide to the double bond of allylic alcohols has been reported (*92*, *149*). However, numerous cases are now known of interactions between magnesium and double or triple bonds within the same molecule, but separated by two or more carbon atoms. In particular, it has been found by labeling experiments that allylcarbinyl reagents (XXXI) undergo a remarkable rearrangement, in which the α- and β-carbon atoms exchange positions (*394*). It was suggested that the rearrangement might take



$$\mathrm{RR'C{=}CH\cdot CH_2\overset{*}{C}H_2MgX}$$

(a) R = R′ = H
(b) R = R′ = Ph

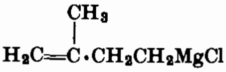
(XXXI)



(a) R = R′ = H
(b) R = R′ = Ph

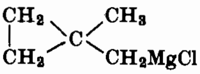
(XXXII)

place via the cyclopropylcarbinyl intermediate (XXXII), which could be prepared at low temperatures, although it was present only in low concentrations in the equilibrium mixtures at room temperature (*338*). Subsequent studies (*225*, *280*) have given further support to this hypothesis. Thus, although solutions of γ,γ-diphenylallylcarbinylmagnesium bromide (XXXIb) contained less than 0.3 % of the isomeric cyclopropyl derivative, conditions giving more carbanionic character to the organic group (e.g., more strongly electron-donating solvents, substitution of potassium for magnesium) increased the proportion of the cyclopropyl derivative (XXXIIb). A similar cyclopropylcarbinyl-to-allylcarbinyl rearrangement is involved in the formation of the Grignard reagents (XXXIII and XXXIV) as a result of the reaction of magnesium with 1,3-dichloro-2-(chloromethyl)-2-methylpropane (XXXV) (*290*, *291*).

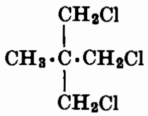


$H_2C{=}\overset{CH_3}{C}\cdot CH_2CH_2MgCl$

(XXXIII)



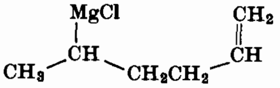
(XXXIV)



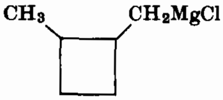
$CH_3\cdot\overset{CH_2Cl}{\underset{CH_2Cl}{C}}\cdot CH_2Cl$

(XXXV)

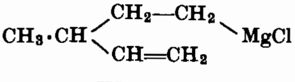
Some examples of the intramolecular reaction of magnesium with double bonds at the δ- and ϵ-positions have been reported. Thus, the isomerization of the Grignard reagent (XXXVI) from 5-chloro-1-hexene to the isomer (XXXVIII) probably proceeded via the cyclobutane derivative (XXXVII) (*217*, *218*), and the Grignard reagent (XXXIX) from 6-chloro-1-heptene in tetrahydrofuran rearranged to give the cyclopentane derivative (XL) (*371*). These rearrangements are reported



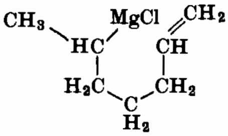
(XXXVI)



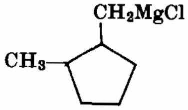
(XXXVII)



(XXXVIII)



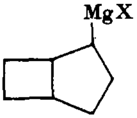
(XXXIX)



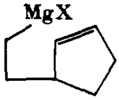
(XL)

(*358*) to proceed more rapidly in highly electron-donating solvents such as 1,2-dimethoxyethane and hexamethylphosphorotriamide.

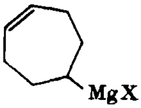
Some related ring-opening reactions have recently been reported, including the transformation of the reagent XLI to its isomers (XLII and XLIII) (*418*).



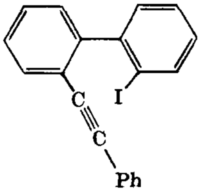
(XLI)



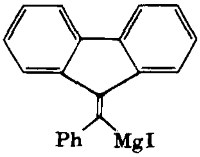
(XLII)



(XLIII)



(XLIV)



(XLV)

An intramolecular reaction between magnesium and a triple bond has been demonstrated by Dessy and Kandil (*136*, *248*); the reaction of 2-iodo-2′-(phenylethynyl)biphenyl (XLIV) with magnesium in tetrahydrofuran led to the rearranged derivative (XLV).

2. *Solvated Alkylberyllium Halides*

Compared with the Grignard reagents, the alkylberyllium halides have been very little studied. Dessy (*134*) observed no exchange of beryllium between mixtures of diphenylberyllium and ^{7}Be-beryllium bromide in diethyl ether or dioxan. However, there is apparently some interaction between dialkylberyllium compounds and beryllium halides in solution (*134*, *189*), and mixtures of the two have been preferred to dialkylberyllium compounds alone in synthesis (*52*). A true alkylberyllium halide, *tert*-butylberyllium chloride, has recently been isolated as a 1 : 1 complex with diethyl ether; it is believed to have a dimeric structure containing Me_3CBeCl units linked by chlorine bridges (*372*). Evidence has also been obtained (*25a*) that when equimolar amounts of dimethylberyllium and beryllium bromide are dissolved in diethyl ether, the predominant species in solution is CH_3BeBr.

The preparation and some reactions of acylberyllium halides, R•CO•BeX, have been described (*271*). They are reported to give aldehydes on hydrolysis, and to couple to give α-diketones.

3. *Solvated Alkylcalcium, -strontium, and -barium Halides*

Somewhat surprisingly, in view of the abundance and reactivity of calcium, organocalcium compounds have been very little studied. This is largely because meticulous attention to the experimental conditions is required for even moderate yields of the alkylcalcium halides to be obtained from the reaction of calcium with alkyl halides (*80*, and references therein). The constitution of the alkylcalcium halides is largely unknown, although in simple cases (e.g., methylcalcium iodide) there is apparently an excess of carbon-calcium bonds over carbon-halogen bonds in solution. However, triphenylmethylcalcium chloride has recently been prepared in good yield in tetrahydrofuran (THF) solution, from which a crystalline product with the composition $Ph_3CCaCl \cdot 2THF$ was obtained (*287*); one mole of tetrahydrofuran was removed on heating *in vacuo*. The alkylcalcium halides are reported (*80*) to resemble alkyllithium compounds rather than Grignard reagents in their reactivity; their high reactivity toward pyridine is particularly noteworthy (*80*), and they are able to catalyze the polymerization of isoprene and butadiene (*433*).

Although the preparation of phenylbarium iodide was described in 1927 (*188*), very little has subsequently been published on the alkylstrontium and -barium halides. However, triphenylmethylstrontium chloride and triphenylmethylbarium chloride resemble their calcium analog in forming complexes with two moles of tetrahydrofuran (*285*).

4. *Solvated Alkylzinc Halides*

The classical method for preparing alkylzinc iodides is the direct synthesis from alkyl iodides and zinc. It has generally been thought that alkylzinc bromides and chlorides could not be prepared similarly except from particularly reactive halides. However, methods have now been worked out (*174*, *176*, *243*, *491*) for this direct synthesis of alkylzinc bromides and benzyl- and allylzinc chlorides (*393*) by the use of zinc or zinc-copper couples and strongly solvating solvents. The interaction of zinc with α-bromo esters in the Reformatsky reaction is well known. Solutions of the organozinc intermediates have recently been obtained (*199*, *393*, *445*, *501*), and Reformatsky complexes from chloroacetic acid and ethyl chloroacetate (*252*) and from *N*,*N*-diethyl-α-bromoacetamide (*125*) have also been described. The constitutions of these solutions are complicated since, besides the possible types of species involved in simple alkylzinc halides, the Reformatsky complexes could involve species with zinc-oxygen instead of zinc-carbon bonds (*125, 178, 179, 317, 445, 501*).

Solutions of the simple alkylzinc halides in electron-donating solvents resemble in many respects the corresponding Grignard reagents. However, the zinc compounds are much less strongly solvated than the magnesium compounds, and there is not the striking difference between the solvated and unsolvated reagents noted above for the alkylmagnesium halides. Isolatable complexes of alkylzinc halides are in general formed only with strong electron donors such as dioxan (*254*, *332*, *388*, *389*) or tetramethylethylenediamine (*3*, *4*), although the isolation of arylzinc halide diethyl etherates has been reported (*388*, *389*). The most thoroughly studied alkylzinc halide reagent is the solution of ethylzinc iodide in diethyl ether or tetrahydrofuran, and there is now overwhelming evidence that the predominant species in such solutions is monomeric EtZnI (presumably solvated). The evidence may be briefly summarized as follows.

(*i*) Mixtures of equimolar amounts of diethylzinc and zinc iodide in ether or tetrahydrofuran give, on standing, solutions indistinguishable from reagents prepared by the action of a zinc-copper couple on ethyl iodide in the same solvents (*3*, *4*, *388*).

(*ii*) The species in such solutions are largely monomeric (i.e., EtZnI or mixtures of Et_2Zn and ZnI_2) (*3*, *4*).

(*iii*) Addition of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMED) to such solutions precipitates complexes with the composition EtZnI·(TMED) (*3*, *4*).

(*iv*) Addition of TMED to a freshly prepared mixture of diethylzinc and zinc iodide gives a complex with the composition ZnI_2·(TMED) (*3*, *4*).

(*v*) The Raman and infrared spectra of solutions of ethylzinc iodide in diethyl ether show a strong band near 510 cm^{-1}, which is polarized in the Raman spectrum, and is assigned as the C—Zn stretching vibration. The C—Zn stretching frequency for diethylzinc is at 470 cm^{-1}, and this band is absent for the solutions of ethylzinc iodide (*154a*, *155*).

It is thus concluded that the predominant species in solution is EtZnI, and that the position of any equilibrium (Eq. 21; X = I) lies far to the right. [It is apparently not possible to distinguish between Et_2Zn and EtZnI by proton magnetic resonance spectroscopy, probably because of rapid alkyl-group exchange in these systems (*154*).]

$$Et_2Zn + ZnX_2 \rightleftharpoons 2EtZnX \qquad (21)$$

For ethylzinc bromide and ethylzinc chloride the situation is less well established since, although the solutions contain monomeric species, addition of TMED or 2,2′-bipyridyl gave precipitates of the zinc halide complexes (*4*, *135*). In the case of the chloride, mixtures of ^{65}Zn-zinc chloride and unlabeled diethylzinc in diethyl ether or tetrahydrofuran showed statistical exchange of ^{65}Zn (*135*). These results are probably best interpreted in terms of a rapid equilibrium (Eq. 21); X = Br, Cl). Unpublished work [D. F. Evans and I. Wharf, quoted in Abraham and Rolfe (*4*)] on the infrared spectra of mixtures of diethylzinc with zinc bromide or zinc chloride in tetrahydrofuran is also reported to support this interpretation [see also (*154a*)].

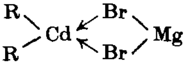
It has recently been reported (*284*; cf. *257*) that certain reactions of dialkylzinc compounds are "activated" by metal halides in a similar manner to those of alkylcadmium compounds (see Section IV,B,2*d* below).

The alkenylzinc halides have been little studied, although allylic derivatives have been used in reactions with carbonyl compounds in preference to the corresponding Grignard reagents (*295*). The products of protolysis of crotylzinc halides have been compared with those from the corresponding magnesium and cadmium derivatives (q.v.) (*9*, *10*). The proportions of the butene isomers were, in contrast to those from the Grignard reagents, relatively unaffected by the nucleophilicity of the solvent. It was concluded that solvation of the zinc reagents was comparatively weak, and that the allylic groups had little carbanionic character. The observation that the zinc derivatives gave a higher proportion of *cis*-2-butene than those of cadmium, and higher than those of magnesium in all but the most nucleophilic solvents, remains unexplained.

5. *Solvated Alkylcadmium Halides*

Although alkylcadmium halides are only weakly solvated, and stable complexes with donor molecules have not been isolated (*91*, *254*, *331*), the compounds have generally been prepared and studied in electron-donating solvents and are therefore considered here (rather than in Section IV,A,3 above).

Solutions of "alkylcadmium halides" have been prepared from the reaction of Grignard reagents with cadmium chloride, from the interaction of dialkylcadmium compounds with cadmium halides, and recently (*90*, *91*) directly from metallic cadmium and alkyl halides in strongly donor solvents. It has been generally considered until recently that such reagents could be considered as solutions of dialkylcadmium compounds, with perhaps some loose complex formation between the dialkylcadmium compounds and cadmium halides. Thus, for example, mixtures of ^{115}Cd-diethylcadmium with inactive cadmium bromide or of inactive diethylcadmium with ^{115}Cd-cadmium bromide in tetrahydrofuran showed no exchange of activity after 21 days (*175*). However, the enhanced solubility of diethylcadmium in the presence of cadmium bromide indicated that there was some interaction between the components, and precipitates with the composition RCdX have been prepared by the interacton of dialkylcadmium compounds with cadmium halides in diethyl ether (*333*, *390*). Later studies have revealed a very striking effect of metal halides on the reactivity of dialkylcadmium compounds. Thus, Kollonitsch first pointed out (*257*) that pure dialkylcadmium compounds were unreactive toward acyl chlorides, in contrast to the reagents employed in the classical ketone synthesis, which contained magnesium halides. [A similar effect was noted for the corresponding zinc compounds, but this has received only little further attention (*284*).] Subsequent studies by Kollonitsch (*255*, *256*, *258*) and French workers (*122*, *132*, *152*, *211–213*, *226*, *276*, *293*, *416*) have revealed many examples of the "activation" of organocadmium compounds by the addition of metal halides, and shown the usefulness of the activated reagents in synthesis. However, the mechanism of activation and the constitution of the solutions are still far from clear. Kollonitsch has emphasized that it is the *reactions* that are activated, and not necessarily only the organocadmium reagents. The activation has been rationalized in terms of complex formation between the metal halides (functioning as Lewis acids) and the acyl chlorides (*293*); zinc chloride and aluminum chloride are activating salts (*293*). However, activation by lithium bromide has been observed (*226*, *255*), and magnesium iodide has been reported (*255*) to be more effective than magnesium chloride (although this order of effectiveness of the magnesium halides has been questioned) (*226*, *293*). It has recently been proposed (*133*) that a complex, formulated as $[CH_3CO]^+[CdCl_3]^-$, is involved in the exchange of chlorine between acetyl chloride and cadmium chloride; this exchange was promoted by the addition of a quaternary ammonium salt. Activation of the alkylcadmium reagent may be involved, either instead of, or as well as, activation of the acyl chloride. There is in fact evidence that species containing both cadmium and the other metal involved are present in the solutions. Thus, whereas mixtures of dialkylcadmium compounds and cadmium halides in diethyl ether gave precipitates with the composition RCdX (*333*, *390*), complexes with the composition $RCdMgX_3 \cdot 2Et_2O$ have been isolated from the solutions resulting from the reaction of Grignard reagents with cadmium chloride in diethyl ether (*276*), and complexes with the composition $R_2Cd \cdot (MgX_2)_2 \cdot (HMPT)_n$ have been prepared via the interaction of Grignard reagents with cadmium chloride in hexamethylphosphorotriamide (*91*). Similarly, the infrared spectra of solutions of dialkylcadmium-magnesium bromide reagents show additional bands near 552 cm^{-1}, not present for either component alone, and attributed to non-colinear cadmium-bromine bonds such as those in the hypothetical complex, XLVI (*122*).



(XLVI)

Kinetic studies on the reactions of alkylcadmium reagents would be of interest; in the only one so far reported (*152*), it was found that the protolysis of diethylcadmium by isoamyl alcohol showed second order kinetics, and that the order was essentially the same when zinc chloride, aluminum chloride, or magnesium bromide was present, although the rates were increased by these halides.

Alkenylcadmium halides have been little studied. Protolysis of the reagent from crotylmagnesium chloride and cadmium chloride gave products little different from those from the corresponding zinc reagent (see Section IV,B,2*c* above) (*9*). The exchange reaction between "crotylzinc bromide" (from crotyl bromide and zinc) and cadmium chloride in strongly donor solvents has been briefly reported (*10*); the equilibrium is stated to lie 64% on the side of the crotylcadmium reagent.

6. *Solvated Alkylmercuric Halides*

There is some evidence that, in contrast to the dialkylmercury compounds, alkylmercuric halides may form complexes with strong electron donors. Thus, although the addition of ammonia to solutions of alkylmercuric halides has little effect on the positions of the ultraviolet absorption maxima, it lowers their intensities (*196*, *366*), and complexes of alkylmercuric halides with ammonia have been proposed as intermediates in symmetrization reactions (see Section IV,A,4 above). Unstable complexes of alkylmercuric halides with trialkylphosphines have also been reported (*106*). Stable complexes are formed between perhalogenoarylmercuric halides and ligands such as 1,10-phenanthroline and 2,2'-bipyridyl (*85a*, *120a*, *339*) (see Section II,C above).

V. Compounds Containing the System C–M–O; the Alkylmetallic Alkoxides and Alkylperoxides

Alkylmetallic alkylperoxides and alkoxides have been suggested to be intermediates in the oxidation of the dialkyl derivatives of the Group II metals, and during the last few years many alkylmetallic alkoxide derivatives of the Group II metals (except the alkaline earth metals) have been synthesized by various other routes. The chemistry of the compounds is of great interest, because of the possibility of back-donation of electrons from oxygen to the metals, or of intermolecular coordination of oxygen to the metals.

The chemistry of the alkylperoxides has recently been reviewed (*404*).

A. ALKYLBERYLLIUM ALKOXIDES AND ALKYLPEROXIDES

Although alkylberyllium alkylperoxides have not been characterized, evidence has been obtained (*286*) that methylberyllium methylperoxide, $CH_3BeOOCH_3$, is an intermediate in the oxidation of dimethylberyllium to beryllium methoxide by oxygen. Methylberyllium methoxide, which may also be a product of the oxidation of dimethylberyllium, has been prepared by the reaction of methanol with dimethylberyllium (*101*). It is soluble in benzene, in which it is dimeric,[6] and disproportionates to dimethylberyllium and beryllium methoxide on heating. Other alkylberyllium alkoxides have been prepared by analogous reactions (*115*) and by the reaction of alkylberyllium hydrides with carbonyl compounds (*52*). Phenylberyllium methoxide and methylberyllium benzyloxide are tetrameric in benzene solution (*52*, *115*), and may have cubane-type structures analogous to those of some of the alkylzinc alkoxides (see Section V,C below). However, the reaction of methylberyllium hydride with benzophenone in ether yields a crystalline complex, monomeric in benzene, which presumably contains three-coordinate beryllium and is formulated as $Me(Et_2O)BeOCHPh_2$ (*52*). When phenylberyllium methoxide is prepared in the presence of diethyl ether the initial product contains some ether, and it thus seems that there is competition between internal and external coordination of oxygen to beryllium in the presence of donor solvents. The reaction of dimethylberyllium with compounds such as 2-methoxyethanol and 2-dimethylaminoethanol leads to products with various degrees of polymerization, and whose structures promise to be of considerable interest (*97b*).

B. ALKYLMAGNESIUM ALKOXIDES AND ALKYLPEROXIDES

Although alkylperoxides may be involved in the autoxidation of organomagnesium compounds (*286*), and the product of the reaction of diethylmagnesium with a deficiency of oxygen in diethyl ether, at first presumed to be ethylmagnesium ethoxide (*452*), could possibly have been an alkylperoxide (*453*), no alkylmagnesium alkylperoxides have been isolated.

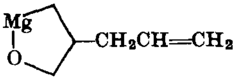
---

[6] Professor Coates has reported in a lecture that a reinvestigation showed methylberyllium methoxide to be *tetrameric* in benzene solution.

Alkylmagnesium alkoxides have been prepared by a variety of methods, and are indeed readily available. They may be synthesized via the interaction of an alkyl chloride, an alcohol, and magnesium in a solvent in which magnesium chloride is insoluble (*77*, *82*, *454*) (Eq. 22 gives the overall equation for this group of related procedures); by the partial

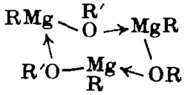
$$2RCl + R'OH + 2Mg \rightarrow RMgOR' + RH + MgCl_2 \qquad (22)$$

alcoholysis of dialkylmagnesium compounds (*108*; cf. *224*); and via the addition of dialkylmagnesium compounds to carbonyl groups (*108*). Alkylmagnesium alkoxides may be involved as intermediates in the reaction of Grignard reagents with carbonyl compounds (*396b*, *454*), and ethylmagnesium ethoxide is formed as a by-product of the pyrolysis of diethylmagnesium diethyl etherate (*59*). It has been suggested (*92*) that a cyclic alkylmagnesium alkoxide (XLVII) is a product of the reaction of an excess of allylmagnesium bromide with allyl alcohol.



(XLVII)

Like the beryllium compounds, the alkylmagnesium alkoxides are in general associated in solution (*77*, *108*) and in some cases form stable diethyl etherates (*108*), although these are readily desolvated. Degrees of association from 3 upward have been reported for the unsolvated compounds: *n*-butylmagnesium isopropoxide is trimeric in benzene (*77*); ethylmagnesium isopropoxide, ethylmagnesium *tert*-butoxide, and isopropylmagnesium isopropoxide are tetrameric in benzene (*108*); and ethylmagnesium *n*-propoxide, isopropylmagnesium methoxide, and isopropylmagnesium ethoxide have degrees of association in the range 7–8.4 in benzene (*108*). Ethylmagnesium ethoxide may be trimeric in diethyl ether [(*452*); but see also Vreugdenhil (*453*)]. Structures of type XLVIII have been proposed for the trimers; these formally involve



(XLVIII)

three-coordinate magnesium, but the possibility of additional Mg—O π-bonding (i.e., back-donation from an occupied n orbital on oxygen to a vacant orbital on adjacent magnesium) must be taken into account (*77*). By analogy with the corresponding zinc compounds (see below), the tetramers may have cubane-type structures (*108*). The ^1H n.m.r. spectra of some methylmagnesium alkoxides have been recorded, but yielded little information on the constitution of the reagents (*223a*).

C. ALKYLZINC ALKOXIDES AND ALKYLPEROXIDES

Methylzinc methoxide was recognized as an oxidation product of dimethylzinc over 100 years ago (*85*), and the process by which dialkylzinc compounds are oxidized to zinc alkoxides, via alkylzinc alkylperoxide and alkylzinc alkoxide intermediates, has been extensively studied (*404*, and references therein). The products of partial alcoholysis of dialkylzinc compounds are catalysts for the polymerization of alkene oxides, and have thus similarly aroused interest (*73*). Alkylzinc alkoxides also catalyze the trimerization of isocyanates, possibly by a mechanism involving a "template" coordination process (*315*).

Treatment of solutions of dialkylzinc compounds with the theoretical amount of an alcohol (or phenol) in general leads to solutions containing reagents with the composition RZnOR′ (*17, 110, 214*). Cryoscopic measurements have indicated that many of the reagents (including the interesting compound with the grouping C–Zn–O–Si–C, from dimethylzinc and trimethylsilanol) (*375*) are tetrameric in benzene solution (*110, 111*), and methylzinc methoxide (*6, 111*) and ethylzinc *tert*-butoxide (*289*) crystallize in the form of tetramers, in which the zinc and oxygen atoms are arranged in the near-cubic form shown diagrammatically in Fig. 6.

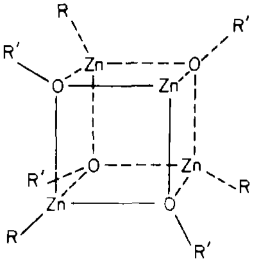
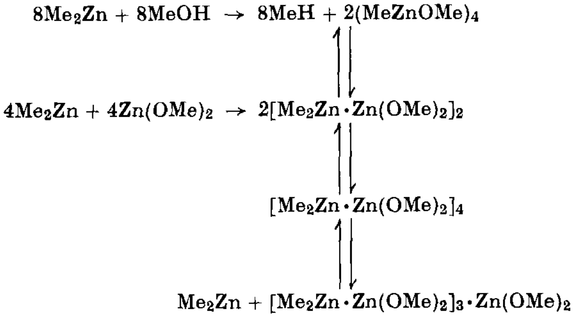


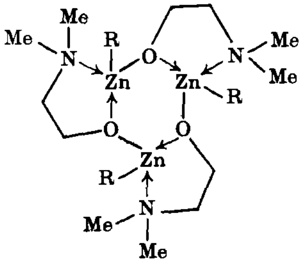
FIG. 6. Alkylzinc alkoxide tetramers: (*i*) R = R′ = Me (*6, 111*); (*ii*) R = Et, R′ = Me_3C (*289*).

Under certain conditions the cubic structure may persist in solution (*111*) even in the presence of pyridine, although the addition of 4-dimethylaminopyridine to a solution of methylzinc methoxide gives a crystalline adduct, $4\text{-}(Me_2N)C_5H_4N\cdot Zn(Me)OMe$, and methylzinc phenoxide tetramer gives a dimeric complex, $[Me(py)ZnOPh]_2$, with pyridine (*110*). However, in some cases the constitution of the reagents in solution is not straightforward. Bruce and his co-workers (*17*, *72*) have demonstrated, mainly by proton magnetic resonance studies, that methylzinc methoxide and ethoxide and phenylzinc methoxide and ethoxide may contain complex equilibrium mixtures. Thus, the reaction of dimethylzinc with methanol or with zinc methoxide, to give solutions of "methylzinc methoxide," may be represented by the scheme:



$$\begin{tikzcd}[column sep=small]
8Me_2Zn + 8MeOH \arrow[r] & 8MeH + 2(MeZnOMe)_4 \arrow[d, shift left] \\
4Me_2Zn + 4Zn(OMe)_2 \arrow[r] & 2[Me_2Zn \cdot Zn(OMe)_2]_2 \arrow[u, shift left] \arrow[d, shift left] \\
& [Me_2Zn \cdot Zn(OMe)_2]_4 \arrow[u, shift left] \arrow[d, shift left] \\
& Me_2Zn + [Me_2Zn \cdot Zn(OMe)_2]_3 \cdot Zn(OMe)_2 \arrow[u, shift left]
\end{tikzcd} \qquad (23)$$

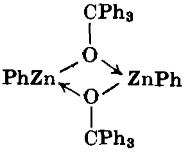
Monoalcoholyses of dimethylzinc and diphenylzinc with isopropanol, *tert*-butanol, and 2-methoxyethanol gave simpler reagents, containing species of the type $(RZnOR')_n$ (*72*; cf. *110*). Reagents prepared by mixing dimethylzinc with zinc *tert*-butoxide (or zinc *n*-dodecoxide) were more complex than the corresponding reagents prepared by alcoholysis.



(XLIX)

Although there is no evidence for chelation of the ether oxygen to zinc in methylzinc 2-methoxyethoxide (*72*, *111*), chelation has been postulated (*111*) to account for the properties of the products from the reaction of dialkylzinc compounds with 2-dimethylaminoethanol and with acetoxime. The former gives trimers, $(RZnOCH_2CH_2NMe_2)_3$, for which the structure XLIX was suggested. Acetoxime gives a tetramer, $(MeZnON{=}CMe_2)_4$ (*111*), whose crystal structure has recently been determined (*6*). The four zinc atoms are at the corners of a tetrahedron, and above each face of the tetrahedron is an acetoximate group with the oxygen attached to two zinc atoms, and the nitrogen to the third. The strength of the bonding maintaining the polymeric structure is sufficient to prevent its destruction by pyridine or 4-dimethylaminopyridine (*111*).

Although dimethylzinc does not react with benzophenone (except possibly to form a donor-acceptor complex), diethylzinc reacts with benzophenone to give ethylene and a trimer, $(EtZnOCPh_2)_3$, and diphenylzinc adds to the carbonyl group to give a *dimeric* product, $(PhZnOCPh_3)_2$ (*113*). *tert*-Butylzinc *tert*-butoxide, from di-*tert*-butylzinc and *tert*-butanol, has also been found to be dimeric in benzene (*113*). These dimeric and trimeric substances presumably have structures such as L, formally containing three-coordinate zinc (*111*). In the case of *tert*-butylzinc *tert*-butoxide, the dimeric structure is broken down by pyridine, and a monomeric complex, $Me_3CZn(py)OCMe_3$, is formed (*113*).



(L)

An intermediate in the reaction of diethylzinc with water is thought to be ethylzinc hydroxide (*214*).

D. ALKYLCADMIUM ALKOXIDES AND ALKYLPEROXIDES

These cadmium derivatives in many respects resemble their zinc analogs. For example, the autoxidation of dialkylcadmium compounds proceeds by a mechanism similar to that of dialkylzinc compounds (*404*). However, alkylcadmium alkylperoxides, unlike alkylzinc alkylperoxides, may be prepared by the reaction of the dialkyl derivative of the metal with an alkyl hydroperoxide (*127*):

$$R_2Cd + R'OOH \rightarrow RH + RCdOOR' \tag{24}$$

The reaction of two moles of dimethylcadmium with one mole of hydrogen peroxide probably gave the peroxide formulated as MeCdOOCdMe (*127*).

Alkylcadmium alkoxides are formed by monoalcoholysis of dialkylcadmium compounds, and are in several cases tetrameric in benzene (*107*, *375*), like the corresponding alkylzinc alkoxides; methylcadmium methoxide is isomorphous with methylzinc methoxide (*107*). Methylcadmium *tert*-butoxide is exceptional, being dimeric in benzene solution

(*107*); its structure is presumably similar to that of phenylzinc triphenylmethoxide (L) (*111*). Methylcadmium *tert*-butoxide is remarkably unreactive, being only slowly hydrolyzed by water or even by 6 *N* sulfuric acid (*107*).

A recent paper (*202*) on the catalysis of methyl exchange in dimethylcadmium by traces of oxygen or methanol suggests that there may be complications in the methanolysis of dimethylcadmium, as the tetrameric methylcadmium methoxide was apparently not involved.

The alkylcadmium alkoxides show only weak acceptor properties, and only one crystalline donor-acceptor complex has been reported (*107*). This complex, Me(py)CdOPh, from methylcadmium phenoxide and pyridine, was partly dissociated in benzene solution.

E. ALKYLMERCURIC ALKOXIDES AND ALKYLPEROXIDES

Russian workers have studied the autoxidation of dialkylmercury compounds, and have rationalized the process in terms of alkylmercuric alkylperoxide and alkoxide intermediates (*355*, *356*). Later the same school reported (*352*) the synthesis of phenylmercuric cumylperoxide, $PhHg{\cdot}OO{\cdot}CMe_2{\cdot}Ph$, by the reaction of phenylmercuric chloride with the sodium derivative of cumene hydroperoxide. The synthesis of isopropylmercuric isopropoxide has been claimed (*14*) and described (*357*); the substance was formed as a low-melting solid, soluble in hydrocarbons, by the reaction of isopropylmercuric chloride with sodium isopropoxide, and was reactive and somewhat unstable. The synthesis of several phenylmercuric alkoxides has been accomplished by a similar route, and by the reaction of phenylmercuric hydroxide with alcohols; some of their reactions were investigated, including that with haloforms to give phenyltrihalogenomethylmercury compounds (*219*).

Because of their instability, structural studies on the alkylmercuric alkoxides will be difficult. Phenylmercuric alkoxides have been reported (*219*) to be trimers in ethers or benzene, but solvated dimers in alcohols. In view of the very weak acceptor properties of alkylmercury compounds, the nature of the association in such systems merits investigation. Methylmercuric trimethylsiloxide is reported to be *monomeric* in benzene (*376*).

The alkylmercuric alkoxides and some related compounds (including sulfur analogs) appear to resemble the alkylzinc amides (see Section VI,C below) in undergoing insertion reactions with carbon dioxide, carbon disulfide, isocyanates, etc. However, no systematic investigation of these reactions has been reported, although the relevant references have been collated (*272*).

Most of the great number of organomercury compounds formulated with the system C–Hg–O are in fact largely covalent, although they are often regarded as salts of alkylmercuric cations (e.g., "alkylmercuric acetates"). Certain aspects of the chemistry of some of these compounds are reviewed (Section VII,A below), but a comprehensive account is beyond the scope of this article.

VI. Compounds Containing the System C–M–N; the Alkylmetallic Amides

The compounds formed by the reaction of primary and secondary amines with the dialkyl derivatives of several of the Group II metals have been studied; the beryllium derivatives have attracted particular attention. No alkylcalcium, -strontium, -barium, or -cadmium amides have been described.

The alkylmetallic amides present certain features in common with the corresponding alkylmetallic alkoxides, and a comparison of the two series is of interest.

A second class of compounds containing the grouping C–M–N comprises the alkylmetallic azides, $R{-}M{-}N_3$. Methylmercuric azide was the only known Group II metal derivative of this type until recently, but some further alkylmercuric azides have now been reported (*417*), and some alkylzinc azides have been prepared by the reaction of dialkylzinc compounds with chlorine azide (*302*).

A. ALKYLBERYLLIUM AMIDES

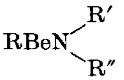
Following the pioneering work of Coates and his co-workers (*101*) the reactions of dialkylberyllium compounds with primary or secondary amines have been extensively studied, and the constitution of the products examined. The reactions generally proceed in stages, as formulated in Eq. (25) for a primary amine. In several cases the intermediate products have been obtained; the coordination complexes (LII) are discussed (Section II,B,1*a*) above, and the beryllium amides (LIV) fall outside the scope of this article. The substances reviewed here are the alkylberyllium amides (LIII); some examples of these compounds are listed in Table III.

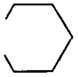
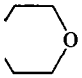
$$\underset{\text{(LI)}}{R_2Be} \xrightarrow{R'NH_2} \underset{\text{(LII)}}{R_2Be{\leftarrow}NH_2R'} \xrightarrow{-RH} \underset{\text{(LIII)}}{RBeNHR'} \xrightarrow[-RH]{R'NH_2} \underset{\text{(LIV)}}{Be(NHR')_2} \quad (25)$$

As indicated in Table III, the alkylberyllium amides that have been described have various degrees of association, but the majority of the compounds are dimeric or trimeric in solution in benzene. Structure LV has been proposed for the trimers, and structure LVI for the dimers (*115*). In general, it appears that trimers are formed when the substituents on beryllium and especially nitrogen are small, and that dimers are formed when the substituents are large (*97*, *115*). Both types of structure involve

TABLE III

ALKYLBERYLLIUM AMIDES


$RBeN(R')(R'')$

R	R′	R″	Degree of association[a]	Ref.
Me	H	H	polymer[b]	(*288*)
Me	H	Me	polymer[b]	(*101*)
Me	H	$CH_2CH_2NMe_2$	2	(*102*)
Me	Me	Me	3[c]	(*101*)
Me	Me	CH_2CH_2NHMe	2	(*102*)
Me	Me	$CH_2CH_2NMe_2$	2	
Me	Et	Et	3	(*97*)
Me	$CH_2CH_2CH_3$	$CH_2CH_2CH_3$	2	
Me	Ph	Ph	2	
Me	Ph	CH_2Ph[d]	2	
Me			*e*	(*172*)
Me			*e*	
Et	H	H	polymer[b]	(*288*)
Et	Me	Me	3	(*97*)
Et	Me	NH_2	polymer[b]	(*158*)
Et	Me	NHMe	polymer	
Et	Me	NMe_2	4	
Et	Et	Et	2	(*97*)
Et	Ph	Ph	2	
Me_2CH	Me	Me	3	
Me_3C	Me	$CH_2CH_2NMe_2$	1	
Ph	Me	Me	3	(*115*)
Ph	Me	$CH_2CH_2NMe_2$	2	
Ph	Ph	Ph	2	

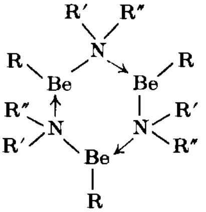
[a] In benzene solution, unless otherwise indicated.

[b] Insoluble: believed to be polymeric.

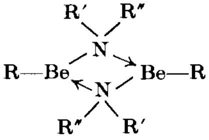
[c] Trimeric in benzene and in vapor; probably polymeric glass at room temperature (*54*).

[d] From methylberyllium hydride and benzylidene aniline (*52*).

[e] Not recorded.

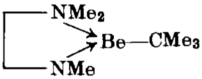


(LV)



(LVI)

three-coordinate beryllium, except where chelation makes four-coordination possible (e.g., when $R' = CH_2CH_2NMe_2$) (*115*). The proton magnetic resonance spectrum of the methylberyllium dimethylamide trimer is consistent with structure LV ($R = R' = R'' = Me$), with rapid interconversion of conformations throughout the temperature range studied (–90° to +25°) (*54*). The unique monomeric compound $Me_3CBeN(Me)CH_2CH_2NMe_2$ presumably has the chelated structure (LVII) (*97*).



(LVII)

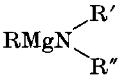
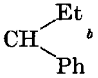
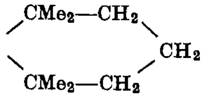
The alkylberyllium amide polymers involving three-coordinate beryllium are able to form complexes with pyridine or 2,2′-bipyridyl (*97*), although in some cases the situation is complicated by disproportionation processes. For example, the trimeric methylberyllium trimethylamide formed a dimeric 1:1 adduct, $[Me(Me_2N)pyBe]_2$, or a monomeric 1:2 adduct, $Me(Me_2N)py_2Be$, with the appropriate proportions of pyridine. The 2,2′-bipyridyl complex of methylberyllium dimethylamide rapidly underwent disproportionation, but both methylberyllium diphenylamide and ethylberyllium diphenylamide formed stable complexes; the ethylberyllium derivative, $Et(Ph_2N)bipyBe$, was shown to be monomeric in benzene.

B. ALKYLMAGNESIUM AMIDES

Although the reaction of dimethylmagnesium with an equimolar amount of dimethylamine led to bis(dimethylamino)magnesium, several alkylmagnesium dialkylamides have been prepared by the reaction of other dialkylmagnesium compounds with secondary amines (*104, 108, 112*). The products are recorded in Table IV.

TABLE IV

ALKYLMAGNESIUM DIALKYLAMIDES

			Degree of association[a]	Ref.
	 $RMgN(R')(R'')$			
R	R′	R″		
Et	Me	$CH_2CH_2NMe_2$	2	(*104*)
Et	Me	 $CH(Et)(Ph)$[b]	2	(*108*, *112*)
Et	Et	Et	*c*	(*112*)
Et	$CHMe_2$	$CHMe_2$	*c*	
Et	Ph	Ph	(polymer)[d,e]	
Et			2	
$CHMe_2$	$CHMe_2$	$CHMe_2$	2	(*108*, *112*)
$CHMe_2$	Ph	Ph	(polymer)[d,f]	(*112*)
$CHMe_2$	Me	$CH_2CH_2NMe_2$	2	(*104a*)
CMe_3	Me	$CH_2CH_2NMe_2$	2	

[a] In benzene solution, unless otherwise indicated.

[b] From diethylmagnesium and benzylidene aniline.

[c] The product obtained from diethyl ether solution contained ether molecules, which could not be removed except by displacement by tetrahydrofuran.

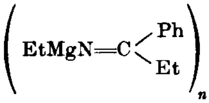
[d] Insoluble: presumed to be polymeric.

[e] Only weakly solvated by diethyl ether; addition of tetrahydrofuran gave monomeric $EtMgNPh_2 \cdot (THF)_2$.

[f] Bis(ether) complex, $Me_2CHMgNPh_2 \cdot (OEt_2)_2$, dissociated in toluene to give unsolvated polymer.

It has been suggested (*112*) that the tendency of these magnesium derivatives to polymerize is due to the high stability of alkyl bridges between magnesium atoms. The polymeric structure may be broken down by solvation (footnote *e* in Table IV), by chelation (as in the case where $R'' = CH_2CH_2NMe_2$), or, most interestingly, where bulky groups are attached to nitrogen. In cases of the last type, the dimeric products could be formulated with alkyl or nitrogen bridges between the magnesium atoms; in either case, the otherwise unrecorded three-coordinate magnesium must be involved (*108*, *112*).

The reaction of diethylmagnesium with benzonitrile in diethyl ether is reported (*112*), to give a polymeric product, formulated as structure LVIII.



$$\left(\mathrm{EtMgN{=}C}\begin{matrix}\nearrow \mathrm{Ph}\\ \searrow \mathrm{Et}\end{matrix}\right)_n$$

(LVIII)

C. Alkylzinc Amides

No methylzinc dimethylamide could be isolated from the product of the reaction of dimethylzinc with dimethylamine (*110*). However, a number of alkylzinc dialkylamides has been prepared by the reaction of dialkylzinc compounds (diethyl-, diisopropyl-, di-*n*-butyl-, and diphenylzinc) with secondary amines (diethylamine, diphenylamine, and *N*,*N*,*N'*-trimethylethylenediamine) (*110*, *313*). The compounds from dimethylzinc and trimethylethylenediamine and from dimethyl- and diethylzinc and diphenylamine are all dimeric in benzene (*110*); the first of these presumably has a chelated structure with four-coordinate zinc, but the other two must be formulated with three-coordinate zinc (*6*, *110*) (cf. the corresponding beryllium and magnesium compounds). Some *N*-alkylzinc diphenylketimines, from dialkylzinc compounds and diphenylketimine, are also reported to be dimeric in benzene (*338a*); in the case of *N*-methylzinc diphenylketimine, the dimeric structure was broken down by pyridine, to give a monomeric adduct, $Ph_2C{=}N \cdot ZnMe,2py$. The compounds formed by the reaction of dimethylzinc (and dimethylcadmium) with trimethylphosphinimide, $Me_3P{=}NH$, are tetrameric, and are formulated with cubane-type structures (*375b*).

The reactivity of the alkylzinc amides toward a second molecule of the amine is comparatively low (*2*, *159a*), and in a number of cases they are stable in the presence of an excess of the amine (*313*). They undergo, however, interesting insertion reactions with, for example, isocyanates, isothiocyanates, carbon dioxide, and carbon disulfide, leading to further compounds containing the groupings C–Zn–N, C–Zn–O, and C–Zn–S (*313*). Some representative reactions are:

$$\mathrm{EtZnNPh_2 + PhNCO \rightarrow EtZn \cdot NPh \cdot CO \cdot NPh_2} \tag{26}$$

$$\mathrm{EtZnNEt_2 + CS_2 \rightarrow EtZnS \cdot CS \cdot NEt_2} \tag{27}$$

The reaction of alkylzinc dialkylphosphides with isocyanates and isothiocyanates also gives compounds formulated with the grouping C–Zn–N (e.g., $EtZn \cdot NPh \cdot CO \cdot PPh_2$) (*314*).

The insertion reactions with isocyanates described above have been formulated as involving addition across the C=N bonds, leading to compounds with the C–Zn–N grouping. However, Coates and Ridley found (*111*) that the reaction of diethyl- or diphenylzinc with phenyl isocyanate gave tetrameric products, and pointed out that, if, as seems very likely, the NCO group acts as a three-atom bridging group between zinc atoms in the polymers, speculation as to whether addition takes place across C=N or C=O bonds, or whether the products contain C–Zn–N or C–Zn–O groupings, becomes unprofitable. The reaction of pyridine with the adduct of diethylzinc and phenyl isocyanate yielded a crystalline complex, EtpyZn•NPh•COEt, which was evidently largely dissociated in benzene solution.

It has been suggested (*315*) that the trimerization of isocyanates by organozinc amides proceeds via coordination of three molecules of isocyanate to a molecule of a trimeric alkylzinc urea, which acts as a "template."

D. ALKYLMERCURIC AMIDES

Until recently, a lone example of this class of compounds was methyl *N*-phenyl-*N*-(phenylmercuri)carbamate, $PhHg \cdot NPh \cdot CO_2Me$, obtained by the reaction of phenyl isocyanate with phenylmercuric methoxide (*128*). However, a series of compounds of this class has now been made by the reaction of phenylmercuric hydroxide with secondary amines (*260*).

VII. Compounds Containing Other C–M–X Groupings

A. SALTS OF ALKYLMERCURIC CATIONS

It is possible to consider the alkyl derivatives of the Group II metals, RMX, as salts of alkylmetallic cations, RM^+, and in some respects it is convenient to formulate them in this way. Thus, for example, alkylzinc cations may be involved in the self-ionization of dialkylzinc compounds (*235*), and it is possible that alkylmagnesium cations are the reactive species in the reaction of Grignard reagents with ketones (*26*). The reagents formed by the reaction of magnesium with dimethyl sulfate (*321*) and with trimethyl phosphate (*184*) may be thought of in this way, although their constitutions are in fact unknown.

Although the above examples are somewhat exceptional, alkylmercury compounds are often conveniently regarded as salts of alkylmercuric cations, in spite of the fact that they are generally largely covalent, and that truly ionic constitutions are rarely encountered [the alkylmercuric perchlorates are one example (*154*)]. This is largely because, owing to the stability of the carbon-mercury bond toward hydrolysis, many alkylmercury derivatives may be studied by the normal methods of aqueous solution chemistry. The chemistry of alkylmetallic cations has recently been well reviewed (*434*), but some of the more important recent advances in the chemistry of alkylmercuric cations are surveyed here (some of the results discussed in Section IV,A,4 above are also apposite to this section).

Alkylmercuric cations have been studied from two main points of view: the stability of their complexes with various ligands has been compared with that of complexes of the proton, on the one hand, and of the mercuric ion, on the other; and their capacity to increase their coordination number to above 1 has been investigated.

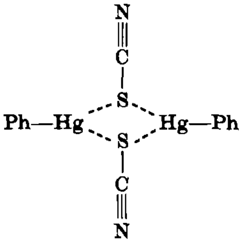
The equilibrium

$$RHgX + H_2O \rightleftharpoons RHgOH_2^+ + X^- \qquad (28)$$

has been studied by a variety of methods, including polarography (*396*, *437*), potentiometry (*378*), calorimetry (*378*), and absorption spectroscopy (*93a*, *378*, *396*). The simple equilibrium (Eq. 28) is complicated by a number of factors, including hydrolysis to alkylmercuric hydroxide, RHgOH, and formation of binuclear ions such as $(RHg)_2OH^+$ (see below) (*378*). However, some clear generalizations may be made, particularly from the comprehensive work of Schwarzenbach and Schellenberg (*378*) on complexes of the methylmercuric cation. In many respects, the methylmercuric cation resembles the proton, generally having a coordination number of 1, and forming stable complexes with many donor ligands. For example, the degree of dissociation of methylmercuric nitrate in water is remarkably similar to that of nitric acid under comparable conditions (*93a*). However, the methylmercuric cation is a soft acid whereas the proton is hard (*93a*, *378*), and this difference is reflected particularly in the high stability of complexes of the methylmercuric cation with sulfur donors, compared with the analogous proton complexes (*378*, *396*). An approximately linear relationship has been observed between the logarithm of the stability constants of complexes of methylmercury with a number of ligands, and the nuclear spin-spin coupling constants, $J(^{199}Hg\text{-}^1H)$, for the complexes (*374a*).

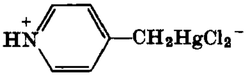
The formation of binuclear ions was mentioned above, and there is also evidence for the formation of trinuclear ions, such as $(RHg)_3S^+$ (*378*) and $(RHg)_3O^+$ (*93a*).

There is a growing body of information concerning the ability of alkylmercuric cations to achieve a coordination number of 2 or even 3. It was noted above (Section IV,B,6) that there is evidence for interaction between ammonia and alkylmercuric halides. With a strong, soft base, such as a trialkylphosphine, some alkylmercuric salts in fact form isolatable complexes, which are liable, however, to disproportionation (*106*). Similarly, methylmercuric perchlorate forms with pyridine a complex formulated as $[MeHgpy]ClO_4$; the corresponding trimethylamine complex dissociates too rapidly to be isolated (*106*). There is evidence, from electrophoresis (*31*) and anion-exchange chromatography (*32*), for the presence of the ion $[EtHg(SCN)_2]^-$ in solutions of ethylmercuric thiocyanate in aqueous potassium thiocyanate; a soft ligand is again involved. An analysis of the vibrational spectrum of phenylmercuric thiocyanate indicates that it is a dimer (LIX) (*131*), and thus provides another example of sulfur functioning as a donor to an organomercury group.

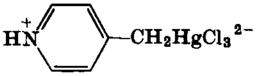


(LIX)

Several studies have been reported on complex formation between alkylmercuric halides and halide ions, particularly the iodide ion (another soft ligand). Complexes are evidently formed between allylmercuric iodide and iodide ion (*261*), and conductometric studies (*151*) suggest that, in the presence of potassium halides, trifluoromethylmercuric halides form complex ions such as $[CF_3HgBrI]^-$ and $[CF_3HgI_3]^{2-}$; the latter ion was reported to form salts with, for example, the zinc(II)-ethylenediamine complex. In related studies it was shown (*144*, *145*) that, although there is some weak interaction between bis(trifluoromethyl)mercury and halide ions in aqueous solution, the evidence (from cryoscopic measurements) is not in favor of the formation of ions of the type $[Hg(CF_3)_2X]^-$. Strong arguments have been advanced (*94*) that decomposition of the ions LX and LXI is involved in the chloride ion-catalyzed acidolysis of the 4-pyridiomethylmercuric chloride ion.



(LX)



(LXI)

Two recently reported reactions of alkylmercuric salts probably involve one-electron reduction of the alkylmercuric cation to the alkylmercury radical; these are the reduction of alkylmercuric perchlorates with chromous ion (*328*), and the electrolytic reduction of alkylmercuric acetates in carbon tetrachloride (*485*).

B. OTHER COMPOUNDS

1. Sulfur Compounds

Several sulfur analogs of the alkylberyllium (*97a*, *101*), alkylmagnesium (*104b*), alkylzinc (*110*), and alkylcadmium (*107*) alkoxides have been prepared by the reaction of the dialkyl compounds with thiols. These compounds in general have a higher degree of polymerization than the corresponding oxygen compounds. Thus, methylzinc methyl, *n*-propyl, and phenyl sulfides (*110*) and methylcadmium methyl and phenyl sulfides (*107*) are insoluble, and presumably polymeric. [Methylberyllium methyl sulfide was not characterized (*101*).] The degree of polymerization was not so great with bulky groups attached to sulfur. Thus, methylzinc isopropyl sulfide (*110*) and its cadmium analog (*107*) are hexamers in benzene, methylzinc and ethylzinc *tert*-butyl sulfides are pentamers (*110*), and methylcadmium *tert*-butyl sulfide is a tetramer (*107*). The pentameric structure of methylzinc *tert*-butyl sulfide persists in the solid state, and the crystal structure has been determined (*6*): the zinc atoms are all four-coordinate, but three, four-, and five-coordinate sulfur is involved. It has been suggested (*107*) that the hexamers may have structures based on two parallel six-membered rings of alternate metal and sulfur atoms. Several alkylberyllium alkyl sulfides (mostly with bulky groups attached to sulfur) are tetrameric in benzene (*97a*), as is ethylmagnesium *tert*-butyl sulfide (*104b*).

Some of the alkylzinc alkyl sulfides react with pyridine to give dimeric complexes, such as $(MepyZnSCMe_3)_2$ (see Section V,C above), and methylberyllium phenyl sulfide (*97a*) and some alkylmagnesium *tert*-butyl sulfides (*104b*) gave analogous complexes with ethers. In contrast, methylcadmium *tert*-butyl sulfide did not yield a pyridine adduct; the difference in behavior may be a consequence of the "softer" character of cadmium, resulting in preferential coordination to sulfur rather than to nitrogen.

The compounds formed by the reaction of carbon disulfide with alkylzinc amides (*313*) and phosphides (*314*) are formulated with the C–Zn–S system: $RZn{\cdot}S{\cdot}CS{\cdot}NR_2'$ and $RZn{\cdot}S{\cdot}CS{\cdot}PR_2'$.

The interaction of alkylmercuric cations with some sulfur ligands was mentioned above. A consequence of the tendency for the formation of binuclear complexes is the ready formation of bis(methylmercuric) sulfide from methylmercuric thiol; the dipole moment of this sulfide has been measured and compared with its oxygen and selenium analogs (*250*).

2. *Phosphorus Compounds*

Some alkylzinc dialkylphosphides have been prepared from the dialkylzinc compounds and dialkylphosphines (*110*, *314*). The compounds are polymeric (*110*, *314*) and reported (*314*) to be very reactive. They undergo insertion reactions analogous to those of the corresponding amides (*314*) (see Section VI,C above), and ethylzinc diphenylphosphide forms a quaternary salt, $[EtZn(PPh_2)Me]I$, with methyl iodide (*314*).

The reaction of dimethylberyllium with dimethylphosphine leads to an uncharacterized polymeric product (*101*).

3. *Miscellaneous Compounds*

A solution presumably containing ethylmagnesium borohydride, $EtMgBH_4$, resulted from the reaction of ethyllithium with chloromagnesium borohydride (*43*). It would be of interest to know whether other compounds containing the C–M–B system are formed as intermediates in the metallation of decaborane (*197*).

It seems likely (*443*) that compounds containing the system C–M–As are intermediates in the reaction of diethylmagnesium or diethylzinc with phenyl- or diphenylarsine.

Bis(methylmercuric) selenide has been prepared, and its dipole moment measured (*250*), and ethylberyllium ethylselenide has been obtained as a 1:2 complex with pyridine (*97a*).

The reaction of methylmercuric chloride with a solution containing the ion $[Fe(CO)_4]^{2-}$ is reported (*245*) to give a complex with the composition $(MeHg)_2Fe(CO)_4$, which may well contain the trimetallic system C–Hg–Fe–Hg–C.

VIII. Salts of Aromatic Radical Anions

The more electropositive Group II metals are able, like the alkali metals, to transfer electrons to suitable aromatic systems to form compounds that may be regarded as charge-transfer complexes or as salts of aromatic radical anions.

Following the preparation of naphthalenemagnesium in liquid ammonia (*233*), similar magnesium derivatives of biphenyl, phenanthrene, and anthracene (in liquid ammonia) (*281*) and of anthracene, pyrene, and 1,1-diphenylethylene (in hexamethylphosphorotriamide)

(*161*) have been reported. The calcium derivative of acenaphthylene has been prepared in tetrahydrofuran (*81*), and the uncharacterized materials formed by the action of calcium on a variety of aromatic systems in liquid ammonia (*444*) are probably similar in nature.

Naphthalenemagnesium has been isolated from its solution in liquid ammonia and redissolved in dipolar aprotic solvents, notably hexamethylphosphorotriamide (*336*). Spectroscopic studies of magnesium-aromatic hydrocarbon systems have suggested that, in hexamethylphosphorotriamide, solvent-separated ion pairs may be present in some cases (*335*, *337*).

REFERENCES

1. Abraham, M. H., and Hill, J. A., *J. Organometal. Chem.* (*Amsterdam*) **7**, 11 (1967).

2. Abraham, M. H., and Hill, J. A., *J. Organometal. Chem.* (*Amsterdam*) **7**, 23 (1967).

3. Abraham, M. H., and Rolfe, P. H., *Chem. Commun.* p. 325 (1965).

4. Abraham, M. H., and Rolfe, P. H., *J. Organometal. Chem.* (*Amsterdam*) **7**, 35 (1967).

5. Abraham, M. H., and Rolfe, P. H., *J. Organometal. Chem.* (*Amsterdam*) **8**, 395 (1967).

6. Adamson, G. W., Moseley, P. T., Shearer, H. M. M., and Spencer, C. B., *Chem. Soc. Autumn Meeting, Durham, 1967* Abstract D4.

7. Adamson, G. W., and Shearer, H. M. M., *Chem. Commun.* p. 240 (1965).

7a. Adcock, W., Hegarty, B. F., Kitching, W., and Smith, A. J., *J. Organometal. Chem.* (*Amsterdam*) **12**, P21 (1968).

8. Agami, C., Andrac-Taussig, M., and Prévost, C., *Bull. Soc. Chim. France* p. 1915 (1966).

9. Agami, C., Andrac-Taussig, M., and Prévost, C., *Bull. Soc. Chim. France* p. 2596 (1966).

10. Agami, C., and Prévost, C., *Compt. Rend.* **C262**, 304 (1966).

11. Agami, C., Prévost, C., and Brun, M., *Bull. Soc. Chim. France* p. 706 (1967).

12. Agami, C., Prévost, C., and Brun, M., *Compt. Rend.* **C263**, 1554 (1966).

13. Aldrich, P. E., Howard, E. G., Lim, W. J., Middleton, W. J., and Sharkey, W. H., *J. Org. Chem.* **28**, 184 (1963).

14. Aleksandrov, Yu. A., Druzhkov, O. N., Zhil'tsov, S. F., and Razuvaev, G. A., *Dokl. Akad. Nauk SSSR* **157**, 1395 (1964).

15. Aleksankin, M. M., Chizhov, B. V., Gol'denfel'd, I. V., and Gragerov, I. P., *Zh. Organ. Khim.* **1**, 1909 (1965).

16. Alexandrou, N. E., *J. Organometal. Chem.* (*Amsterdam*) **5**, 301 (1966).

17. Allen, G., Bruce, J. M., Farren, D. W., and Hutchinson, F. G., *J. Chem. Soc., B, Phys. Org.* p. 799 (1966).

18. Allen, G., Bruce, J. M., and Hutchinson, F. G., *J. Chem. Soc.* p. 5476 (1965).

19. Almenningen, A., Bastiansen, O., and Haaland, A., *J. Chem. Phys.* **40**, 3434 (1964).

20. Amberger, E., Streger, W., and Honigschmid-Grossich, R., *Angew. Chem.* **78**, 549 (1966).

21. Anteunis, M., *Bull. Soc. Chim. Belges* **73**, 655 (1964).

22. Aronoff, M. S., *Dissertation Abstr.* **26**, 7029 (1966).

23. Asenbush, J., and Tuulmets, A., *Org. Reactivity* (*Tartu*) **4**, Part 1, 174 (1967).

24. Ashby, E. C., *Quart. Rev.* (*London*) **21**, 259 (1967).

25. Ashby, E. C., Duke, R. B., and Neumann, H. M., *J. Am. Chem. Soc.* **89**, 1964 (1967).

25a. Ashby, E. C., Saunders, R., and Carter, J., *Chem. Commun.* p. 997 (1967).

26. Ashby, E. C., and Smith, M. B., *J. Am. Chem. Soc.* **86**, 4363 (1964).

27. Ashby, E. C., and Smith, M. B., *J. Am. Chem. Soc.* **86**, 4364 (1964).

28. Ashby, E. C., and Walker, F., *J. Organometal. Chem.* (*Amsterdam*) **7**, P17 (1967).

28a. Bähr, G., and Küpper, F.-W., *Chem. Ber.* **100**, 3992 (1967).

29. Bähr, G., and Thiele, K.-H., *Chem. Ber.* **90**, 1578 (1957).

30. Barber, W. A., *J. Inorg. & Nucl. Chem.* **4**, 373 (1957).

31. Barbieri, R., Faraglia, G., Giustiani, M., and Roncucci, L., *J. Inorg. & Nucl. Chem.* **27**, 1325 (1965).

32. Barbieri, R., Giustiani, M., and Cervo, E., *J. Inorg. & Nucl. Chem.* **26**, 203 (1964).

33. Barlow, L. R., and Davidson, J. M., *Chem. & Ind.* (*London*) p. 1656 (1965).

34. Bartocha, B., Brinkman, F. E., Kaesz, H. D., and Stone, F. G. A., *Proc. Chem. Soc.* p. 116 (1958).

35. Bartocha, B., Douglas, C. M., and Gray, M. Y., *Z. Naturforsch.* **14b**, 809 (1959).

36. Bartocha, B., Kaesz, H. D., and Stone, F. G. A., *Z. Naturforsch.* **14b**, 352 (1959).

37. Bartocha, B., and Stone, F. G. A., *Z. Naturforsch.* **13b**, 347 (1958).

38. Bass, K. C., *J. Organometal. Chem.* (*Amsterdam*) **4**, 1 (1965).

39. Bass, K. C., *Organometal. Chem. Rev.* **1**, 391 (1966).

40. Bass, K. C., and Nababsing, P., *J. Chem. Soc., C, Org.* p. 1184 (1966).

41. Bauer, R., *Z. Naturforsch.* **17b**, 201 (1962).

42. Baumgärtner, F., Fischer, E. O., Kanellakopulos, B., and Laubereau, P., *Angew. Chem.* **77**, 866 (1965).

43. Becker, W. E., and Ashby, E. C., *Inorg. Chem.* **4**, 1816 (1965).

44. Beletskaya, I. P., *Zh. Vses. Khim. Obshchestva im. D.I. Mendeleeva* **12**, 3 (1967).

45. Beletskaya, I. P., Artamkina, G. A., and Reutov, O. A., *Dokl. Akad. Nauk SSSR* **166**, 1347 (1966).

46. Beletskaya, I. P., Fedorov, L. A., Moskalenko, V. A., and Reutov, O. A., *Izv. Akad. Nauk SSSR, Ser. Khim.* p. 933 (1965).

47. Beletskaya, I. P., Karpov, V. I., and Reutov, O. A., *Dokl. Akad. Nauk SSSR* **161**, 586 (1965).

48. Beletskaya, I. P., Karpov, V. I., and Reutov, O. A., *Izv. Akad. Nauk SSSR, Ser. Khim.* p. 1135 (1966).

49. Beletskaya, I. P., Myshkin, A. E., and Reutov, O. A., *Zh. Organ. Khim.* **2**, 2086 (1966).

50. Bell, N. A., and Coates, G. E., *Can. J. Chem.* **44**, 744 (1966).

51. Bell, N. A., and Coates, G. E., *J. Chem. Soc.* p. 692 (1965).

52. Bell, N. A., and Coates, G. E., *J. Chem. Soc., A, Inorg., Phys., Theoret.* p. 1069 (1966).

53. Bell, N. A., and Coates, G. E., *Proc. Chem. Soc.* p. 59 (1964).

54. Bell, N. A., Coates, G. E., and Emsley, J. W., *J. Chem. Soc., A, Inorg., Phys., Theoret.* p. 49 (1966).

55. Bell, N. A., Coates, G. E., and Emsley, J. W., *J. Chem. Soc., A, Inorg., Phys., Theoret.* p. 1360 (1966).

56. Bickelhaupt, F., Blomberg, C., Vreugdenhil, A. D., Vink, P., and van Zanten, B., *2nd Intern. Symp. Organometal. Chem., Madison, Wisconsin, 1965* Abstracts p. 82.

57. Birchall, J. M., Hazard, R., Haszeldine, R. N., and Wakalski, A. W., *J. Chem. Soc., C, Org.* p. 47 (1967).

58. Birmingham, J. W., *Advan. Organometal. Chem.* **2**, 365 (1964).

59. Birnkraut, W. H., *Inorg. Chem.* **2**, 1074 (1963).

60. Blanchard, E. P., Blomstrom, D. C., and Simmons, H. E., *J. Organometal. Chem. (Amsterdam)* **3**, 97 (1965).

61. Blanchard, E. P., and Simmons, H. E., *J. Am. Chem. Soc.* **86**, 1337 (1964).

62. Blomberg, C., Vreugdenhil, A. D., van Zanten, B., and Vink, P., *Rec. Trav. Chim.* **84**, 828 (1965).

63. Blues, E. T., Ph.D. Thesis, University of Reading (1965).

64. Boersma, J., and Noltes, J. G., *J. Organometal. Chem. (Amsterdam)* **8**, 553 (1967).

65. Boersma, J., and Noltes, J. G., *Tetrahedron Letters* p. 1521 (1966).

66. Bondi, A., *J. Phys. Chem.* **68**, 441 (1964).

67. Bondi, A., *J. Phys. Chem.* **70**, 3006 (1966).

68. Braye, E. H., Hübel, W., and Caplier, I., *J. Am. Chem. Soc.* **83**, 4406 (1961).

68a. Bregadze, V. I., Babushkina, T. A., Okhlobystin, O. Yu., and Semin, G. K., *Teor. i Eksp. Khim.* **3**, 547 (1967).

69. Breuninger, V., Dreskamp, H., and Pfisterer, G., *Ber. Bunsenges. Physik. Chem.* **70**, 613 (1966).

70. Brown, H. C., and Adams, R. M., *J. Am. Chem. Soc.* **64**, 2559 (1942).

71. Brown, J. E., Shapiro, H., and De Witt, E. G., U.S. Patent 2,818,416 (1957).

72. Bruce, J. M., Cutsforth, B. C., Farren, D. W., Hutchinson, F. G., Rabagliati, F. M., and Reed, D. R., *J. Chem. Soc., B, Phys. Org.* p. 1020 (1966).

73. Bruce, J. M., and Farren, D. W., *Polymer* **6**, 509 (1965).

74. Bryce-Smith, D., *Bull. Soc. Chim. France* p. 1418 (1963).

75. Bryce-Smith, D., and Cox, G. F., *J. Chem. Soc.* p. 1050 (1958).

76. Bryce-Smith, D., and Cox, G. F., *J. Chem. Soc.* p. 1175 (1961).

77. Bryce-Smith, D., and Graham, I. F., *Chem. Commun.* p. 559 (1966).

78. Bryce-Smith, D., Morris, P. J., and Wakefield, B. J., unpublished work (1964).

79. Bryce-Smith, D., and Owen, W. J., *J. Chem. Soc.* p. 3319 (1960).

80. Bryce-Smith, D., and Skinner, A. C., *J. Chem. Soc.* p. 577 (1963).

81. Bryce-Smith, D., and Skinner, A. C., *J. Chem. Soc., C, Org.* p. 154 (1966).

82. Bryce-Smith, D., and Wakefield, B. J., *Proc. Chem. Soc.* p. 376 (1963).

83. Burdon, J., Coe, P. L., and Fulton, M. L., *J. Chem. Soc.* p. 2094 (1965).

84. Burdon, J., Coe, P. L., Fulton, M., and Tatlow, J. C., *J. Chem. Soc.* p. 2673 (1964).

85. Butlerow, A., *Z. Pharm. Chem.* **7**, 402 (1864).

85a. Canty, A. J., Deacon, G. B., and Felder, P. W., *Inorg. Nuclear Chem. Letters* **3**, 263 (1967).

86. Cermeno, F. A., *Anales Real Soc. Espan. Fis. Quim. (Madrid)* **B60**, 753 (1964).

87. Chambers, R. D., and Chivers, T., *Organometal. Chem. Rev.* **1**, 279 (1966).

88. Chambers, R. D., Coates, G. E., Livingstone, J. G., and Musgrave, W. K. R., *J. Chem. Soc.* p. 4367 (1962).

89. Chambers, R. D., Drakesmith, F. G., Hutchinson, J., and Musgrave, W. K. R., *Tetrahedron Letters* p. 1705 (1967).

90. Chenault, J., and Tatibouët, F., *Compt. Rend.* **C262**, 499 (1966).

91. Chenault, J., and Tatibouët, F., *Compt. Rend.* **C264**, 213 (1967).

92. Chérest, M., Felkin, H., Frajerman, C., Lion, C., Roussi, G., and Swierczewski, G., *Tetrahedron Letters* p. 875 (1966).

93. Chumaevski, N. A., and Borisov, A. E., *Dokl. Akad. Nauk SSSR* **161**, 366 (1965).

93a. Clarke, J. H. R., and Woodward, L. A., *Trans. Faraday Soc.* **66**, 3022 (1966).

94. Coad, J. R., and Johnson, M. D., *J. Chem. Soc., B, Phys. Org.* p. 633 (1967).

95. Coates, G. E., "Organo-Metallic Compounds," 2nd ed. Methuen, London, 1960.

96. Coates, G. E., and Cox, G. F., *Chem. & Ind. (London)* p. 269 (1962).

97. Coates, G. E., and Fishwick, A. H., *J. Chem. Soc., A, Inorg., Phys. Theoret.* p. 1199 (1967).

97a. Coates, G. E., and Fishwick, A. H., *J. Chem. Soc., A, Inorg., Phys., Theoret.* p. 635 (1968).

97b. Coates, G. E., and Fishwick, A. H., *J. Chem. Soc., A, Inorg., Phys., Theoret.* p. 640 (1968).

98. Coates, G. E., and Glockling, F., *J. Chem. Soc.* p. 22 (1953).

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

100. Coates, G. E., Glockling, F., and Huck, N. D., *J. Chem. Soc.* p. 4496 (1952).

101. Coates, G. E., Glockling, F., and Huck, N. D., *J. Chem. Soc.* p. 4512 (1952).

102. Coates, G. E., and Green, S. I. E., *J. Chem. Soc.* p. 3340 (1962).

103. Coates, G. E., and Green, S. I. E., *Proc. Chem. Soc.* p. 376 (1961).

104. Coates, G. E., and Heslop, J. A., *J. Chem. Soc., A, Inorg., Phys., Theoret.* p. 26 (1966).

104a. Coates, G. E., and Heslop, J. A., *J. Chem. Soc., A, Inorg., Phys., Theoret.* p. 514 (1968).

104b. Coates, G. E., and Heslop, J. A., *J. Chem. Soc., A, Inorg., Phys., Theoret.* p. 631 (1968).

105. Coates, G. E., and Huck, N. D., *J. Chem. Soc.* p. 4501 (1952).

106. Coates, G. E., and Lauder, A., *J. Chem. Soc.* p. 1857 (1965).

107. Coates, G. E., and Lauder, A., *J. Chem. Soc., A, Inorg., Phys., Theoret.* p. 264 (1966).

108. Coates, G. E., and Ridley, D., *Chem. Commun.* p. 560 (1966).

109. Coates, G. E., and Ridley, D., *J. Chem. Soc.* p. 166 (1964).

110. Coates, G. E., and Ridley, D., *J. Chem. Soc.* p. 1870 (1965).

111. Coates, G. E., and Ridley, D., *J. Chem. Soc., A, Inorg., Phys., Theoret.* p. 1064 (1966).

112. Coates, G. E., and Ridley, D., *J. Chem. Soc., A, Inorg., Phys., Theoret.* p. 56 (1967).

113. Coates, G. E., and Roberts, P. D., *J. Chem. Soc., A, Inorg., Phys., Theoret.* p. 1233 (1967).

114. Coates, G. E., Roberts, P. D., and Downs, A. J., *J. Chem. Soc., A, Inorg., Phys., Theoret.* p. 1085 (1967).

115. Coates, G. E., and Tranah, M., *J. Chem. Soc., A, Inorg., Phys., Theoret.* p. 236 (1967).

116. Coates, G. E., and Tranah, M., *J. Chem. Soc., A, Inorg., Phys., Theoret.* p. 615 (1967).

117. Cohen, S. C., Reddy, M. L. N., and Massey, A. G., *Chem. Commun.* p. 451 (1967).

118. Connett, J. E., Davies, A. G., Deacon, G. B., and Green, J. H. S., *Chem. & Ind. (London)* p. 512 (1965).

119. Connett, J. E., Davies, A. G., Deacon, G. B., and Green, J. H. S., *J. Chem. Soc., C, Org.* p. 106 (1966).

120. Connett, J. E., and Deacon, G. B., *J. Chem. Soc., C, Org.* p. 1058 (1966).

120a. Cook, J. D., and Wakefield, B. J., *J. Organometal. Chem. (Amsterdam)* **13**, 15 (1968).

121. Cotton, F. A., *Robert A. Welch Found. Conf. Chem. Res., Houston, Texas, 1965* p. 213; personal communication (1967).

122. Coudane, H., Henry-Basch, E., Michel, J., Marx, B., Huet, F., and Fréon, P., *Compt. Rend.* **C262**, 861 (1966).

123. Cowan, D. O., and Dolah, L. A., *J. Org. Chem.* **31**, 4296 (1966).

124. Cram, D. J., "Fundamentals of Carbanion Chemistry." Academic Press, New York, 1965.

125. Curé, J., and Gaudemar, M., *Compt. Rend.* **C264**, 97 (1967).

126. Cuvigny, T., and Normant, H., *Bull. Soc. Chim. France* p. 2000 (1964).

127. Davies, A. G., and Packer, J. E., *J. Chem. Soc.* p. 3164 (1959).

128. Davies, A. G., and Peddle, G. J. D., *Chem. Commun.* p. 96 (1965).

129. Deacon, G. B., *J. Organometal. Chem. (Amsterdam)* **9**, P1 (1967).

130. Deacon, G. B., and Felder, P. W., *Australian J. Chem.* **19**, 2381 (1966).

131. Dehnicke, K., *J. Organometal. Chem. (Amsterdam)* **9**, 11 (1967).

132. Deniau, J.-P., Henry-Basch, E., and Fréon, P., *Compt. Rend.* **C264**, 1560 (1967).

133. Desai, K. K., and Halder, B. C., *J. Indian Chem. Soc.* **43**, 734 (1966).

134. Dessy, R. E., *J. Am. Chem. Soc.* **82**, 1580 (1960).

135. Dessy, R. E., and Coe, G. R., *J. Org. Chem.* **28**, 3592 (1963).

136. Dessy, R. E., and Kandil, S. A., *J. Org. Chem.* **30**, 3857 (1965).

137. Dessy, R. E., Kaplan, F., Coe, G. R., and Salinger, R. M., *J. Am. Chem. Soc.* **85**, 1191 (1963).

138. Dessy, R. E., and Kitching, W., *Advan. Organometal. Chem.* **4**, 268 (1966).

139. Dessy, R. E., Kitching, W., Psarras, T., Salinger, R., Chen, A., and Chivers, T., *J. Am. Chem. Soc.* **88**, 460 (1966).

140. Dessy, R. E., Lee, Y. K., and Kim, J.-Y., *J. Am. Chem. Soc.* **83**, 1163 (1961).

141. Dessy, R. E., and Paulik, F. E., *Bull. Soc. Chim. France* p. 1373 (1963).

142. Dessy, R. E., and Paulik, F. E., *J. Am. Chem. Soc.* **85**, 1812 (1963).

143. Dessy, R. E., and Paulik, F. E., *J. Chem. Educ.* **46**, 185 (1963).

144. Downs, A. J., *J. Chem. Soc.* p. 5273 (1963).

145. Downs, A. J., *J. Inorg. & Nucl. Chem.* **26**, 41 (1964).

146. Dvoryatseva, G. G., Turchin, K. F., Materikova, R. B., Sheinker, Yu. N., and Nesmeyanov, A. N., *Dokl. Akad. Nauk SSSR* **166**, 868 (1966).

147. Ebel, H. F., and Schneider, R., *Angew. Chem. Intern. Ed. Engl.* **4**, 878 (1965).

148. Edelstein, H., and Becker, E. I., *J. Org. Chem.* **31**, 3375 (1966).

149. Eisch, J. J., and Husk, G. R., *J. Am. Chem. Soc.* **87**, 4194 (1965).

150. Ellerman, J., personal communication (1967); Ellerman, J., and Gruber, W. H., *Z. Naturforsch.* **22b**, 1248 (1967).

151. Emeléus, H. J., and Lagowski, J. J., *J. Chem. Soc.* p. 1497 (1959).

152. Emptoz, G., Henry-Basch, E., Coudane, H., and Fréon, P., *Compt. Rend.* **C262**, 655 (1966).

153. Evans, D. F., and Khan, M. S., *Chem. Commun.* p. 67 (1966).

153a. Evans, D. F., and Khan, M. S., *J. Chem. Soc., A, Inorg., Phys., Theoret.* p. 1643 (1967).

153b. Evans, D. F., and Khan, M. S., *J. Chem. Soc., A, Inorg., Phys., Theoret.* p. 1648 (1967).

154. Evans, D. F., and Maher, J. P., *J. Chem. Soc.* p. 5125 (1962).

154a. Evans, D. F., and Wharf, I., *J. Chem. Soc., A, Inorg., Phys., Theoret.* p. 783 (1968).

155. Evans, D. F., and Wharf, I., *J. Organometal. Chem. (Amsterdam)* **5**, 108 (1966).

156. Fauvarque, J., and Fauvarque, J.-F., *Compt. Rend.* **C262**, 488 (1966).

157. Felkin, H., Frajerman, C., and Gault, Y., *Chem. Commun.* p. 75 (1966).

158. Fetter, N. R., *Can. J. Chem.* **42**, 861 (1964).

159. Fischer, E. O., and Hofmann, H. P., *Chem. Ber.* **92**, 482 (1959).

159a. Fisel, S., Roman, L., Popescu, I., and Poni, M., *Rev. Roumaine Chim.* **12**, 511 (1967)

160. Fisher, I. P., Homer, J. B., and Lossing, F. P., *J. Am. Chem. Soc.* **87**, 957 (1965).

161. Fontanille, M., and Sigwalt, P., *Compt. Rend.* **C262**, 1208 (1966).

162. Ford, D. N., Wells, P. R., and Lauterbur, P. C., *Chem. Commun.* p. 616 (1967).

163. Foster, D. J., Charleston, S., and Tobler, E., U.S. Patent 3,087,947 (1963).

164. Fraenkel, G., and Dix, D. T., *J. Am. Chem. Soc.* **88**, 979 (1966).

165. Fraenkel, G., Dix, D. T., and Adams, D. G., *Tetrahedron Letters* p. 3155 (1964).

166. Fraenkel, G., Ellis, S. H., and Dix, D. T., *J. Am. Chem. Soc.* **87**, 1406 (1965).

167. Frankland, E., *J. Chem. Soc.* **2**, 263 (1849).

168. French, W. E., Inamoto, N., and Wright, G. F., *Can. J. Chem.* **42**, 2228 (1964).

169. Fritz, H. P., *Chem. Ber.* **92**, 780 (1959).

170. Fritz, H. P., and Schneider, R., *Chem. Ber.* **93**, 1171 (1960).

171. Fritz, H. P., and Sellmann, D., *J. Organometal. Chem. (Amsterdam)* **5**, 501 (1966).

172. Funk, H., and Masthoff, R., *J. Prakt. Chem.* [4] **22**, 255 (1963).

173. Galiulina, R. F., Druzhkov, O. N., Petukhov, G. G., and Razuvaev, G. A., *Zh. Obshch. Khim.* **35**, 1164 (1965).

174. Galiulina, R. F., Shabanova, N. N., and Petukhov, G. G., *Zh. Obshch. Khim.* **36**, 1290 (1966).

175. Garrett, A. B., Sweet, A., Marshall, W. L., Riley, D., and Touma, A., *Record Chem. Progr. (Kresge-Hooker Sci. Lib.)* **13**, 155 (1952).

176. Gaudemar, M., *Bull. Soc. Chim. France* p. 974 (1962).

177. Gaudemar, M., *Bull. Soc. Chim. France* p. 1475 (1963).

178. Gaudemar, M., *Bull. Soc. Chim. France* p. 3113 (1966).

179. Gaudemar, M., and Curé, J., *Compt. Rend.* **C262**, 213 (1966).

180. Gault, Y., *Tetrahedron Letters* p. 69 (1966).

181. Gerteis, R. L., Dickerson, R. E., and Brown, T. L., *Inorg. Chem.* **3**, 872 (1964).

182. Gielen, M., and Nasielski, J., *J. Organometal. Chem. (Amsterdam)* **1**, 173 (1964).

183. Gielen, M., Nasielski, J., Dubois, J. E., and Fresnet, P., *Bull. Soc. Chim. Belges* **73**, 293 (1964).

184. Gilman, H., and Atwell, W. H., *J. Organometal. Chem. (Amsterdam)* **7**, 521 (1967).

185. Gilman, H., and Bailie, J. C., *J. Am. Chem. Soc.* **65**, 267 (1943).

186. Gilman, H., Haubein, A. H., O'Donnell, G., and Woods, L. A., *J. Am. Chem. Soc.* **67**, 922 (1945).
187. Gilman, H., Meals, R. N., O'Donnell, G., and Woods, L., *J. Am. Chem. Soc.* **65**, 268 (1943).
188. Gilman, H., and Schulze, F., *Bull. Soc. Chim. France* **41**, 1333 (1927).
189. Gilman, H., and Schulze, F., *J. Chem. Soc.* p. 2663 (1927).
190. Gilman, H., and Woods, L. A., *J. Am. Chem. Soc.* **67**, 520 (1945).
191. Glaze, W. H., and Selman, C. M., *J. Organometal. Chem.* (*Amsterdam*) **5**, 477 (1966).
192. Glaze, W. H., Selman, C. M., and Freeman, C. H., *Chem. Commun.* p. 474 (1966).
193. Goggin, P. L., and Woodward, L. A., *Trans. Faraday Soc.* **62**, 1423 (1966).
194. Goubeau, J., and Rodewald, B., *Z. Anorg. Allgem. Chem.* **258**, 162 (1949).
195. Goubeau, J., and Walter, K., *Z. Anorg. Allgem. Chem.* **322**, 58 (1963).
196. Gowenlock, B. G., and Trotman, J., *J. Chem. Soc.* p. 1454 (1955).
197. Greenwood, N. N., and Travers, N. F., *Inorg. Nucl. Chem. Letters* **2**, 169 (1966).
198. Griffiths, J. E., *J. Am. Chem. Soc.* **82**, 5759 (1960).
199. Grob, C. A., and Brenneisen, P., *Helv. Chim. Acta* **41**, 1184 (1958).
200. Grosse, A. V., *Chem. Ber.* **59**, 2646 (1926).
201. Haaland, A., personal communication (1967).
202. Ham, N. S., Jeffery, E. A., Mole, T., Saunders, J. K., and Stuart, S. N., *J. Organometal. Chem.* (*Amsterdam*) **8**, P7 (1967).
203. Ham, N. S., Jeffery, E. A., Mole, T., and Stuart, S. N., *Chem. Commun.* p. 254 (1967).
204. Harper, R. J., Soloski, E. J., and Tamborski, C., *J. Org. Chem.* **29**, 2385 (1964).
205. Hart, C. R., and Ingold, C. K., *J. Chem. Soc.* p. 4372 (1964).
206. Hashimoto, H., Nakano, T., and Okada, H., *J. Org. Chem.* **30**, 1234 (1965).
207. Hatch, L. F., Sutherland, G., and Ross, K. J., *J. Org. Chem.* **14**, 1130 (1949).
208. Hatton, J. W., Schneider, W. G., and Siebrand, W., *J. Chem. Phys.* **39**, 1330 (1963).
209. Heaney, H., *Organometal. Chem. Rev.* **1**, 27 (1966).
210. Heaney, H., and Jablonski, J. M., *Tetrahedron Letters* p. 4529 (1966).
210a. Hegarty, B. F., Kitching, W., and Wells, P. R., *J. Am. Chem. Soc.* **89**, 4816 (1967).
211. Henry-Basch, E., Deniau, J.-P., Emptoz, G., Huet, F., Marx, B., and Michel, J., *Compt. Rend.* **C262**, 598 (1966).
212. Henry-Basch, E., Michel, J., and Fréon, P., *Compt. Rend.* **260**, 5809 (1965).
213. Henry-Basch, E., Michel, J., Huet, F., Marx, B., and Fréon, P., *Bull. Soc. Chim. France* p. 927 (1965).
214. Herold, R. J., Aggarwal, S. L., and Neff, V., *Can. J. Chem.* **41**, 1368 (1963).
215. Higgins, G. M. C., Saville, B., and Evans, M. B., *J. Chem. Soc.* p. 702 (1965).
216. Hill, E. A., *J. Org. Chem.* **31**, 20 (1966).
217. Hill, E. A., and Davidson, J. A., *J. Am. Chem. Soc.* **86**, 4663 (1964).
218. Hill, E. A., Richey, H. G., and Rees, T. C., *J. Org. Chem.* **28**, 2161 (1963).
219. Holan, G., *Tetrahedron Letters* p. 1985 (1966).
220. Holm, T., *Acta Chem. Scand.* **19**, 1819 (1965).
221. Holm, T., *Acta Chem. Scand.* **20**, 1139 (1966).
222. Holm, T., *Acta Chem. Scand.* **20**, 2821 (1966).
222a. Holm, T., *Acta Chem. Scand.* **21**, 2753 (1967).
223. Holm, T., *Tetrahedron Letters* p. 3329 (1966).

223a. House, H. O., Latham, R. A., and Whitesides, G. M., *J. Org. Chem.* **32**, 2481 (1967).

224. House, H. O., and Respess, W. L., *J. Org. Chem.* **30**, 301 (1965).

225. Howden, M. E., Maercker, A., Burdon, J., and Roberts, J. D., *J. Am. Chem. Soc.* **88**, 1732 (1966).

226. Huet, F., Michel, J., Bernardou, C., and Henry-Basch, E., *Compt. Rend.* **C262**, 1328 (1966).

227. Hughes, E. D., Ingold, C. K., Thorpe, F. G., and Volger, H. C., *J. Chem. Soc.* p. 1133 (1961).

228. Hughes, E. D., and Volger, H. C., *J. Chem. Soc.* p. 2359 (1961).

229. Hull, H. S., Reid, A. F., and Turnbull, A. G., *Australian J. Chem.* **18**, 249 (1965).

230. Hurd, D. T. J., *J. Org. Chem.* **13**, 711 (1948).

231. Inamoto, N., *J. Chem. Soc. Japan, Pure Chem. Sect.* **86**, 1223 (1965).

232. Ingold, C. K., *Helv. Chim. Acta* **47**, 1191 (1964).

233. Ivanoff, C., and Markov, P., *Naturwissenschaften* **50**, 688 (1963).

234. Jander, G., and Fischer, L., *Z. Elektrochem.* **62**, 965 (1958).

235. Jander, G., and Fischer, L., *Z. Elektrochem.* **62**, 971 (1958).

236. Jautelat, M., and Schwarz, V., *Tetrahedron Letters* p. 5101 (1966).

237. Jensen, F. R., and Gale, L. H., *J. Am. Chem. Soc.* **82**, 145 (1960).

238. Jensen, F. R., and Heyman, D., *J. Am. Chem. Soc.* **88**, 3438 (1966).

239. Jensen, F. R., and Miller, J., *J. Am. Chem. Soc.* **86**, 4734 (1964).

240. Jensen, F. R., and Nakamaye, K. L., *J. Am. Chem. Soc.* **88**, 3437 (1966).

241. Jensen, F. R., and Rickborn, B., *J. Am. Chem. Soc.* **86**, 3784 (1964).

242. Johnson, F., personal communication, cited in Newman and Kaugars (1965) (*311*).

243. Joly, R., and Bucourt, R., U.S. Patent 3,040,078 (1962).

244. Jullien, J., and Paillous, A., *Bull. Soc. Chim. France* p. 2236 (1965).

245. Kahn, O., and Bigorgne, M., *Compt. Rend.* **261**, 2483 (1965).

246. Kalyavin, V. A., Smolina, T. A., and Reutov, O. A., *Dokl. Akad. Nauk SSSR* **157**, 919 (1964).

247. Kamienski, C. W., and Eastham, J. F., *J. Organometal. Chem.* (*Amsterdam*) **8**, 542 (1967).

248. Kandil, S. A., and Dessy, R. E., *J. Am. Chem. Soc.* **88**, 3027 (1966).

249. Kask, S., and Tuulmets, A., *Org. Reactivity* (*Tartu*) 4, Part 1, 163 (1967).

250. Kesler, M., *Croat. Chem. Acta* **36**, 165 (1964).

251. Khimov, K., and Tuulmets, A., *Org. Reactivity* (*Tartu*) 4, Part 1, 195 (1967).

252. Kim, Y. S., *J. Korean Chem. Soc.* **9**, 1 (1965).

252a. Kimbrough, R. D., and Askins, R. W., *J. Org. Chem.* **32**, 3683 (1967).

252b. Kirrmann, A., and Rabesiaka, J., *Bull. Soc. Chim. France* p. 2370 (1967).

253. Kittila, A. B., *Dissertation Abstr. B* **27**, 780 (1966).

254. Kocheshkov, K. A., Sheverdina, N. I., and Paleeva, J. E., *Bull. Soc. Chim. France* p. 1472 (1963).

255. Kollonitsch, J., *J. Chem. Soc., A, Inorg., Phys., Theoret.* p. 453 (1966).

256. Kollonitsch, J., *J. Chem. Soc., A, Inorg., Phys., Theoret.* p. 456 (1966).

257. Kollonitsch, J., *Nature*, **188**, 140 (1960).

258. Kollonitsch, J., U.S. Patent 3,065,259 (1962).

259. Kraut, M., and Leitch, L. C., *Can. J. Chem.* **45**, 549 (1963).

260. Kravtsov, D. N., and Nesmeyanov, A. N., *Izv. Akad. Nauk SSSR, Ser. Khim.* p. 1741 (1967).

261. Kreevoy, M. M., Goon, D. J. W., and Kayser, R. A., *J. Am. Chem. Soc.* **88**, 5529 (1966).

262. Kreevoy, M. M., and Schaefer, J. F., *J. Organometal. Chem.* (*Amsterdam*) **6**, 589 (1966).

263. Kreevoy, M. M., Steinwand, P. J., and Straub, T. S., *J. Org. Chem.* **31**, 4291 (1966).

264. Krespan, C. G., *J. Org. Chem.* **25**, 105 (1960).

265. Krieghoff, N. G., and Cowan, D. O., *J. Am. Chem. Soc.* **88**, 1322 (1966)

266. Kunchur, N. R., and Mathew, M., *Chem. Commun.* p. 71 (1966).

267. Kunchur, N. R., and Mathew, M., *Proc. Chem. Soc.* p. 414 (1964).

268. Ladd, J. A., *Spectrochim. Acta* **22**, 1157 (1966).

269. Landgrebe, J. A., and Mathis, R. D., *J. Am. Chem. Soc.* **88**, 3545 (1966).

270. Landgrebe, J. A., and Mathis, R. D., *J. Am. Chem. Soc.* **88**, 3552 (1966).

271. Lapkin, I. I., Anvarova, G. Ya., and Povaritsnaya, T. N., *Zh. Obshch. Khim.* **36**, 1952 (1966).

272. Lappert, M. F., and Prokai, B., *Advan. Organometal. Chem.* **5**, 225 (1967).

273. Lardicci, L., and Lucarini, L., *Ann. Chim.* (*Rome*) **54**, 1233 (1964).

274. Lardicci, L., Lucarini, L., Palagi, P., and Pino, P., *J. Organometal. Chem.* (*Amsterdam*) **4**, 341 (1965).

275. Le Goff, E., *J. Org. Chem.* **29**, 2048 (1964).

276. Le Guilly, L., and Tatibouët, F., *Compt. Rend.* **C262**, 217 (1966).

277. Lehmkuhl, H., *Angew. Chem. Intern. Ed. Engl.* **3**, 107 (1964).

277a. Lehmkuhl, H., and Eisenbach, W., *Ann. Chem.* **705**, 42 (1967).

278. Lockhart, J. C., *Chem. Rev.* **65**, 131 (1965).

279. Luttringhaus, H., and Dirksen, H.-W., *Angew. Chem. Intern. Ed. Engl.* **3**, 260 (1964).

280. Maercker, A., and Roberts, J. D., *J. Am. Chem. Soc.* **88**, 1742 (1966).

281. Markov, P., and Ivanov, C., *Compt. Rend.* **C264**, 1605 (1967).

282. Martin, G. J., and Martin, M. L., *Bull. Soc. Chim. France* p. 1636 (1966).

283. Martin, L., *Ann. Phys.* (*Paris*) [13] **7**, 35 (1962).

284. Marx, B., Henry-Basch, E., and Fréon, P., *Compt. Rend.*, **C264**, 527 (1967).

284a. Maslowsky, E., and Nakamoto, K., *Chem. Commun.* p. 257 (1968).

285. Masthoff, R., personal communication (1967).

286. Masthoff, R., *Z. Anorg. Allgem. Chem.* **336**, 252 (1965).

287. Masthoff, R., and Krieg, G., *Z. Chem.* **6**, 433 (1966).

288. Masthoff, R., and Vieroth, C., *Z. Chem.* **5**, 142 (1965).

289. Matsui, Y., Kamiya, K., and Nishikawa, M., *Bull. Chem. Soc. Japan* **39**, 1828 (1966).

290. McCaffery, E. L., and Shalaby, S. W., *J. Organometal. Chem.* (*Amsterdam*) **3**, 101 (1965).

291. McCaffery, E. L., and Shalaby, S. W., *J. Organometal. Chem.* (*Amsterdam*) **8**, 17 (1967).

292. McCoy, C. R., and Allred, A. L., *J. Am. Chem. Soc.* **84**, 912 (1962).

293. Michel, J., and Henry-Basch, E., *Compt. Rend.* **C262**, 1387 (1966).

294. Middleton, W. J., Howard, E. G., and Sharkey, W. H., *J. Am. Chem. Soc.* **83**, 2589 (1961).

295. Miginiac, P., and Miginiac, L., *Compt. Rend.* **258**, 236 (1964).

296. Miller, W. T., Freedman, M. B., Fried, J. H., and Koch, H. F., *J. Am. Chem. Soc.* **83**, 4105 (1961).

297. Moore, D. W., and Happe, J. A., *J. Phys. Chem.* **65**, 224 (1961).

298. Morris, P. J., Ph.D. Thesis, University of Reading (1965).

299. Morton, A. A., "Solid Organoalkali Metal Reagents." Gordon & Breach, New York, 1964.

300. Moseley, P. T., and Shearer, H. M. M., *Chem. Commun.* p. 876 (1966).

300a. Moseley, P. T., and Shearer, H. M. M., *Chem. Commun.* p. 279 (1968).

301. Moy, D., Emerson, M. T., and Oliver, J. P., *Inorg. Chem.* **2**, 1261 (1963).

302. Müller, H., and Dehnicke, K., *J. Organometal. Chem. (Amsterdam)* **10**, P1 (1967).

303. Nast, R., Künzel, O., and Müller, R., *Chem. Ber.* **95**, 2155 (1962).

304. Nast, R., and Richers, C., *Chem. Ber.* **97**, 3317 (1964).

305. Nast, R., and Richers, C., *Z. Anorg. Allgem. Chem.* **319**, 320 (1963).

306. Nesmeyanov, A. N., Borisov, A. E., and Osipova, M. A., *Dokl. Akad. Nauk SSSR* **169**, 602 (1966).

307. Nesmeyanov, A. N., Borisov, A. E., and Savel'eva, I. S., *Dokl. Akad. Nauk SSSR* **172**, 1093 (1967).

308. Nesmeyanov, A. N., Borisov, A. E., Savel'eva, I. S., and Golubeva, E. I., *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* p. 1490 (1958).

309. Nesmeyanov, A. N., Dvoryantseva, G. G., Kochetkova, N. S., Materikova, R. B., and Sheinker, Yu. N., *Dokl. Akad. Nauk SSSR* **159**, 847 (1964).

310. Nesmeyanov, N. A., and Reutov, O. A., *Tetrahedron* **20**, 2803 (1964).

311. Newman, M. S., and Kaugars, G., *J. Org. Chem.* **30**, 3294 (1965).

312. Nienhouse, E. J., *Chem. Commun.* p. 101 (1967).

313. Noltes, J. G., *Rec. Trav. Chim.* **84**, 126 (1965).

314. Noltes, J. G., *Rec. Trav. Chim.* **84**, 782 (1965).

315. Noltes, J. G., and Boersma, J., *J. Organometal. Chem. (Amsterdam)* **7**, P6 (1967).

316. Noltes, J. G., and Boersma, J., *J. Organometal. Chem. (Amsterdam)* **9**, 1 (1967).

317. Noltes, J. G., Creemers, H. M. J. C., and van der Kerk, G. J. M., *J. Organometal. Chem. (Amsterdam)* **11**, P21 (1968).

318. Noltes, J. G., and van den Hurk, J. W. G., *J. Organometal. Chem. (Amsterdam)* **1**, 377 (1964).

319. Noltes, J. G., and van den Hurk, J. W. G., *J. Organometal. Chem. (Amsterdam)* **3**, 222 (1965).

320. Normant, H., and Maitte, P., *Bull. Soc. Chim. France* p. 1439 (1959).

321. Normant, H., and Perrin, P., *Bull. Soc. Chim. France* p. 801 (1964).

322. Okhlobystin, O. Yu., *Usp. Khim.* **36**, 34 (1967).

323. Okhlobystin, O. Yu., and Zakharkin, L. I., *J. Organometal. Chem. (Amsterdam)* **3**, 257 (1965).

324. Okhlobystin, O. Yu., and Zakharkin, L. I., *Zh. Obshch. Khim.* **36**, 1734 (1966).

325. Oki, M., and Hirota, M., *Tetrahedron Letters* p. 1784 (1967).

326. Oliver, J. P., Smart, J. B., and Emerson, M. T., *J. Am. Chem. Soc.* **88**, 4101 (1966).

327. Oliver, J. P., and Wilkie, C. A., *J. Am. Chem. Soc.* **89**, 163 (1967).

328. Ouelette, R. J., and van Leuwen, B. G., *J. Org. Chem.* **30**, 3967 (1965).

329. Pajaro, G., Biagini, S., and Fiumani, D., *Angew. Chem.* **74**, 901 (1962).

330. Pakhomov, V. I., and Kitaigorodskii, A. I., *Zh. Strukt. Khim.* **7**, 860 (1966).

331. Paleeva, I. E., Sheverdina, N. I., Abramova, L. V., and Kocheshkov, K. A., *Dokl. Akad. Nauk SSSR* **159**, 609 (1964).

331a. Paleeva, I. E., Sheverdina, N. I., Delinskaya, E. D., and Kocheshkov, K. A., *Izv. Akad. Nauk SSSR, Ser. Khim.* p. 1083 (1967).

332. Paleeva, I. E., Sheverdina, N. I., and Kocheshkov, K. A., *Dokl. Akad. Nauk SSSR* **157**, 628 (1964).

333. Paleeva, I. E., Sheverdina, N. I., and Kocheshkov, K. A., *Izv. Akad. Nauk SSSR, Ser. Khim.* p. 1263 (1967).

334. Parkan, W. E., and Potoski, J. R., *Tetrahedron Letters* p. 2311 (1966).

335. Pascault, J.-P., Bartagnon-Weisrock, M., and Golé, J., *Compt. Rend.* **C264,** 220 (1967).

336. Pascault, J.-P., and Golé, J., *Compt. Rend.* **C264,** 115 (1967).

337. Pascault, J.-P., and Golé, J., *Compt. Rend.* **C264,** 326 (1967).

338. Patel, D. J., Hamilton, C. L., and Roberts, J. D., *J. Am. Chem. Soc.* **87**, 5144 (1965).

338a. Pattison, I., and Wade, K., *J. Chem. Soc., A, Inorg., Phys., Theoret.* p. 57 (1968).

339. Paulik, F. E., Green, S. I. E., and Dessy, R. E., *J. Organometal Chem. (Amsterdam)* **3**, 229 (1965).

340. Payne, D. A., and Sanderson, R. T., *J. Am. Chem. Soc.* **80**, 5324 (1958).

341. Pearson, D. E., Cowan, D., and Beckler, J. D., *J. Org. Chem.* **24**, 504 (1959).

342. Perucaud, M.-C., Ducom, J., and Vallino, M., *Compt. Rend.* **C264,** 571 (1967).

343. Peters, F. M., *J. Organometal. Chem. (Amsterdam)* **3**, 334 (1965).

343a. Petrosyan, V. S., and Reutov, O. A., *Zh. Org. Khim.* **3**, 2074 (1967).

344. Postis, J. de, *Compt. Rend.* **223**, 1006 (1946).

345. Powell, H. B., and Lagowski, J. J., *J. Chem. Soc., A, Inorg., Phys., Theoret.* p. 1282 (1966).

346. Powell, H. B., Maung, M. T., and Lagowski, J. J., *J. Chem. Soc.* p. 2484 (1963).

347. Psarras, T., and Dessy, R. E., *J. Am. Chem. Soc.* **88**, 5132 (1966).

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

349. Rappoport, Z., Sleezer, P. D., Winstein, S., and Young, W. G., *Tetrahedron Letters* p. 3719 (1965).

350. Rausch, M., and Van Wazer, J., *Inorg. Chem.* **3**, 761 (1964).

351. Raymond, R. P., *Dissertation Abstr. B* **27**, 1826 (1967).

352. Razuvaev, G. A., and Fedotova, E. I., *Dokl. Akad. Nauk SSSR* **169**, 355 (1966).

353. Razuvaev, G. A., and Pankratova, V. N., *Zh. Obshch. Khim.* **36**, 1702 (1966).

354. Razuvaev, G. A., Petukhov, G. G., Galiulina, R. F., and Shabanova, N. N., *Zh. Obshch. Khim.* **34**, 3812 (1964).

355. Razuvaev, G. A., Petukhov, G. G., Zhil'tsov, S. F., and Kudryavtsev, L. F., *Dokl. Akad. Nauk SSSR* **135**, 87 (1960).

356. Razuvaev, G. A., Petukhov, G. G., Zhil'tsov, S. F., and Kudryavtsev, L. F., *Dokl. Akad. Nauk SSSR* **141**, 107 (1961).

357. Razuvaev, G. A., Zhil'tsov, S. F., Aleksandrov, Yu. A., and Druzhkov, O. N., *Zh. Obshch. Khim.* **35**, 1152 (1965).

358. Rees, T. C., *Dissertation Abstr. B* **27**, 1426 (1966).

359. Reichardt, C., *Angew. Chem. Intern. Ed. Engl.* **4**, 29 (1965).

360. Reid, A. F., and Wailes, P. C., *Australian J. Chem.* **19**, 309 (1966).

361. Reid, A. F., and Wailes, P. C., *Inorg. Chem.* **5**, 1213 (1966).

362. Reutov, O. A., *Bull. Soc. Chim. France* p. 1383 (1963).

363. Reutov, O. A., *Record Chem. Progr. (Kresge-Hooker Sci. Lib.)* **22**, 1 (1961).

364. Reutov, O. A., *Usp. Khim.* **36**, 414 (1967).

365. Reutov, O. A., and Beletskaya, I. P., *Izv. Akad. Nauk SSSR, Ser. Khim.* p. 955 (1966).

366. Reutov, O. A., Beletskaya, I. P., and Artamkina, G. A., *Zh. Obshch. Khim.* **34**, 2817 (1964).
367. Reutov, O. A., Beletskaya, I. P., and Filippenko, L. R., *Nauchn. Dokl. Vysshei Shkoly, Khim. i Khim. Tekhnol.* **4**, 754 (1958).
368. Reutov, O. A., and Lovtsova, A. N., *Dokl. Akad. Nauk SSSR* **139**, 622 (1961).
369. Reynolds, G. F., and Daniel, S. R., *Inorg. Chem.* **6**, 480 (1967).
370. Reynolds, G. F., Dessy, R. E., and Jaffe, H. H., *J. Org. Chem.* **23**, 1217 (1958).
371. Richey, H. G., and Rees, T. C., *Tetrahedron Letters* p. 4296 (1966).
372. Roberts, P. D., and Coates, G. E., *Chem. Soc. Autumn Meeting, Durham, 1967* Abstract D3.
373. Sauers, R. R., and Kwiatkowski, G. T., *J. Org. Chem.* **27**, 4049 (1962).
374. Scala, A. A., and Becker, E. I., *J. Org. Chem.* **30**, 3491 (1965).
374a. Scheffold, R., *Helv. Chim. Acta* **50**, 1419 (1967).
375. Schindler, F., Schmidbaur, H., and Krüger, U., *Angew. Chem.* **77**, 865 (1965).
375a. Schmeisser, M., and Weidenbruch, M., *Chem. Ber.* **100**, 2306 (1967).
375b. Schmidbaur, H., and Jonas, G., *Angew. Chem.* **79**, 413 (1967).
376. Schmidbaur, H., and Schindler, F., *Angew. Chem.* **77**, 865 (1965).
377. Schneider, R., and Fischer, E. O., *Naturwissenschaften* **50**, 349 (1963).
378. Schwarzenbach, G., and Schellenberg, M., *Helv. Chim. Acta* **48**, 28 (1965).
379. Screttas, C. J., and Eastham, J. F., *J. Am. Chem. Soc.* **87**, 3276 (1965).
380. Screttas, C. J., and Eastham, J. F., *J. Am. Chem. Soc.* **88**, 5669 (1966).
381. Seitz, L. M., and Brown, T. L., *J. Am. Chem. Soc.* **88**, 4140 (1966).
382. Seitz, L. M., and Brown, T. L., *J. Am. Chem. Soc.* **89**, 1602 (1967).
382a. Seitz, L. M., and Brown, T. L., *J. Am. Chem. Soc.* **89**, 1607 (1967).
383. Seyferth, D., *Progr. Inorg. Chem.* **3**, 139 (1962).
384. Seyferth, D., Dertouzos, H., and Todd, L. J., *J. Organometal. Chem. (Amsterdam)* **4**, 18 (1965).
385. Seyferth, D., and King, R. B., *Ann. Surv. Organometal. Chem.* **1**, 44 (1964).
386. Seyferth, D., and King, R. B., *Ann. Surv. Organometal. Chem.* **2**, 54 (1965).
387. Sherwood, A. G., and Gunning, H. E., *J. Phys. Chem.* **69**, 2323 (1965).
388. Sheverdina, N. I., Abramova, L. V., and Kocheshkov, K. A., *Dokl. Akad. Nauk SSSR* **124**, 602 (1959).
389. Sheverdina, N. I., Paleeva, I. E., Abramova, L. V., Yakovleva, V. S., and Kocheshkov, K. A., *Izv. Akad. Nauk SSSR, Ser. Khim.* p. 1077 (1967).
390. Sheverdina, N. I., Paleeva, I. E., Delinskaya, E. D., and Kocheshkov, K. A., *Dokl. Akad. Nauk SSSR* **125**, 348 (1959).
391. Sheverdina, N. I., Paleeva, I. E., and Kocheshkov, K. A., *Izv. Akad. Nauk SSSR, Ser. Khim.* p. 587 (1967).
392. Sheverdina, N. I., Paleeva, I. E., Zaitseva, N. A., and Kocheshkov, K. A., *Dokl. Akad. Nauk SSSR* **155**, 623 (1964).
393. Siegel, A., and Keskeis, H., *Monatsh. Chem.* **84**, 910 (1953).
394. Silver, M. S., Shafer, P. A., Nordlander, J. E., Rüchardt, C., and Roberts, J. D., *J. Am. Chem. Soc.* **82**, 2646 (1960).
395. Simmons, H. E., Blanchard, E. P., and Smith, R. D., *J. Am. Chem. Soc.* **86**, 1347 (1964).
396. Simpson, R. B., *J. Am. Chem. Soc.* **83**, 4711 (1961).
396a. Simpson, R. B., *J. Chem. Phys.* **46**, 4775 (1967).
396b. Singer, M. S., Salinger, R. M., and Mosher, H. S., *J. Org. Chem.* **32**, 3821 (1967).
397. Singh, G., *J. Organometal. Chem. (Amsterdam)* **5**, 577 (1966).

398. Sleezer, P. D., Winstein, S., and Young, W. G., *J. Am. Chem. Soc.* **85**, 1890 (1963).
399. Smith, M. B., and Becker, W. E., *Tetrahedron* **22**, 3027 (1966).
399a. Smith, M. B., and Becker, W. E., *Tetrahedron* **23**, 4215 (1967).
400. Smith, M. B., and Becker, W. E., *Tetrahedron Letters* p. 3843 (1965).
400a. Smith, S. G., and Billet, J., *J. Am. Chem. Soc.* **89**, 6948 (1967).
401. Smith, S. G., and Su, G., *J. Am. Chem. Soc.* **88**, 3995 (1966).
402. Smith, S. G., and Su, G., *Tetrahedron Letters* p. 4417 (1966).
403. Snow, A. I., and Rundle, R. E., *Acta Cryst.* **4**, 348 (1951).
404. Sosnovsky, G., and Brown, J. H., *Chem. Rev.* **66**, 529 (1966).
405. Strohmeier, W., *Z. Elektrochem.* **60**, 58 (1956).
406. Strohmeier, W., and Gernert, F., *Chem. Ber.* **95**, 1420 (1962).
407. Strohmeier, W., and Gernert, F., *Z. Naturforsch.* **20b**, 829 (1965).
408. Strohmeier, W., Haecker, W., and Popp, G., *Chem. Ber.* **100**, 405 (1967).
409. Strohmeier, W., Humpfner, K., Miltenberger, K., and Seifert, F., *Z. Elektrochem.* **63**, 537 (1959).
410. Strohmeier, W., and Nützel, K., *Z. Elektrochem.* **59**, 538 (1955).
411. Strohmeier, W., and Seifert, F., *Z. Elektrochem.* **63**, 683 (1959).
412. Stucky, G. D., and Rundle, R. E., *J. Am. Chem. Soc.* **85**, 1002 (1963).
413. Stucky, G., and Rundle, R. E., *J. Am. Chem. Soc.* **86**, 4825 (1964).
414. Takashi, Y., *Bull. Chem. Soc. Japan* **40**, 1001 (1967).
415. Tamborski, C., *Trans. N. Y. Acad. Sci.* [2] **28**, 601 (1966).
416. Tatibouët, F., and Fréon, P., *Bull. Soc. Chim. France* p. 1496 (1963).
417. Thayer, J. S., *Organometal. Chem. Rev.* **1**, 158 (1966).
418. Theissen, R. J., *Dissertation Abstr. B* **27**, 1834 (1966).
419. Thiele, K.-H., *Z. Anorg. Allgem. Chem.* **319**, 183 (1962).
420. Thiele, K.-H., *Z. Anorg. Allgem. Chem.* **322**, 71 (1962).
421. Thiele, K.-H., *Z. Anorg. Allgem. Chem.* **325**, 156 (1963).
422. Thiele, K.-H., *Z. Anorg. Allgem. Chem.* **330**, 8 (1964).
423. Thiele, K.-H., Engelhardt, G., Köhler, J., and Arnstedt, M., *J. Organometal. Chem. (Amsterdam)* **9**, 385 (1967).
424. Thiele, K.-H., Hanke, W., and Zdunneck, P., *Z. Anorg. Allgem. Chem.* **337**, 63 (1965).
425. Thiele, K.-H., and Köhler, J., *J. Organometal. Chem. (Amsterdam)* **7**, 365 (1967).
426. Thiele, K.-H., and Köhler, J., *J. Prakt. Chem.* [4] **32**, 54 (1966).
427. Thiele, K.-H., and Köhler, J., *Z. Anorg. Allgem. Chem.* **337**, 260 (1965).
428. Thiele, K.-H., and Müller, J., *J. Prakt. Chem.* [4] **33**, 229 (1966).
429. Thiele, K.-H., and Rau, H., *Z. Chem.* **5**, 110 (1965).
430. Thiele, K.-H., and Schröder, S., *Z. Anorg. Allgem. Chem.* **337**, 14 (1965).
431. Thiele, K.-H., and Zdunneck, P., *J. Organometal. Chem. (Amsterdam)* **4**, 10 (1965).
432. Thiele, K.-H., and Zdunneck, P., *Organometal. Chem. Rev.* **1**, 331 (1966).
433. Tinyakova, E. I., and Eivasov, E. Z., *Izv. Akad. Nauk SSSR, Ser. Khim.* p. 1508 (1965).
434. Tobias, R. S., *Organometal. Chem. Rev.* **1**, 93 (1966).
435. Tochtermann, W., *Angew. Chem. Intern. Ed. Engl.* **5**, 351 (1966).
435a. Toney, J., and Stucky, G. D., *Chem. Commun.* 1168 (1967).
436. Toppet, S., Slinckx, G., and Smets, G., *J. Organometal. Chem. (Amsterdam)* **9**, 205 (1967).
437. Toropova, V. F., and Saikina, M. K., *Zh. Neorgan. Khim.* **10**, 1166 (1965).

438. Treichel, P. M., and Stone, F. G. A., *Advan. Organometal. Chem.* **1**, 143 (1964).
439. Tuulmets, A., *Org. Reactivity (Tartu)* **2**, Part 3, 391 (1965).
440. Tuulmets, A., *Org. Reactivity (Tartu)* **2**, Part 4, 76 (1965).
441. Tuulmets, A., *Org. Reactivity (Tartu)* 4, Part 1, 17 (1967).
442. Tuulmets, A., and Pilt, A., *Org. Reactivity (Tartu)* **2**, Part 4, 68 (1965).
443. Tzschach, A., and Häckert, H., *Z. Chem.* **6**, 265 (1966).
444. Utke, A. R., and Sanderson, R. T., *J. Org. Chem.* **29**, 1260 (1964).
445. Vaughan, W. R., Bernstein, S. C., and Lorber, M. E., *J. Org. Chem.* **30**, 1790 (1965).
446. Villieras, J., *Bull. Soc. Chim. France* p. 1511 (1967).
447. Villieras, J., *Bull. Soc. Chim. France* p. 1520 (1967).
448. Vink, P., Blomberg, C., Vreugdenhil, A. D., and Bickelhaupt, F., *Tetrahedron Letters* p. 6419 (1966).
449. Vitt, S. V., and Martinkova, N. S., *Izv. Akad. Nauk SSSR, Ser. Khim.* p. 1185 (1966).
450. Vo-Quang, Y., Vo-Quang, L., and Emptoz, G., *Compt. Rend.* **258**, 4586 (1964).
451. Vranka, R. G., and Amma, E. L., *J. Am. Chem. Soc.* **89**, 3121 (1967).
452. Vreugdenhil, A. D., and Blomberg, C., *Rec. Trav. Chim.* **84**, 39 (1965).
453. Vreugdenhil, A. D., Thesis, Free University, Amsterdam (1965).
454. Wakefield, B. J., *Organometal. Chem. Rev.* **1**, 131 (1966).
455. Wakefield, B. J., unpublished observation (1966).
456. Walborsky, K. M., and Young, A. E., *J. Am. Chem. Soc.* **83**, 2595 (1961).
457. Wanklyn, J., *Proc. Roy. Soc.* **9**, 341 (1858).
458. Weiss, E., *Chem. Ber.* **98**, 2805 (1965).
459. Weiss, E., *J. Organometal. Chem. (Amsterdam)* **2**, 314 (1964).
460. Weiss, E., *J. Organometal. Chem. (Amsterdam)* **4**, 101 (1965).
460a. Weiss, E., and Wolfrum, R., *Chem. Ber.* **101**, 35 (1968).
460b. Weiss, E., and Wolfrum, R., *J. Organometal. Chem. (Amsterdam)* **12**, 257 (1968).
461. Wells, P. R., and Kitching, W., *Australian J. Chem.* **17**, 1204 (1964).
462. Wells, P. R., Kitching, W., and Henzell, R. F., *Tetrahedron Letters* p. 1029 (1964).
463. Whitesides, G. M., Nordlander, J. E., and Roberts, J. D., *Discussions Faraday Soc.* **34**, 185 (1962).
464. Whitesides, G. M., and Roberts, J. D., *J. Am. Chem. Soc.* **87**, 4878 (1965).
465. Whitesides, G. M., Witanowski, M., and Roberts, J. D., *J. Am. Chem. Soc.* **87**, 2854 (1965).
466. Wiberg, E., and Bauer, R., *Chem. Ber.* **85**, 593 (1952).
467. Wilke, G., Bogdanovic, B., Hardt, P., Heinbach, P., Keim, W., Kröner, M., Oberkirch, W., Tanaka, K., Steinrücke, E., Walter, D., and Zimmermann, W., *Angew. Chem. Intern. Ed. Engl.* **5**, 151 (1966).
468. Wilke, G., *Robert A. Welch Found. Conf. Chem. Res., Houston, Texas, 1965* Lecture reported by D. Seyferth, *Ann. Surv. Organometal. Chem.* **2**, 46 (1965).
469. Wilkinson, G., and Cotton, F. A., *J. Am. Chem. Soc.* **76**, 1970 (1954).
470. Wilkinson, G., and Piper, T. S., *J. Inorg. & Nucl. Chem.* **2**, 32 (1956).
471. Wilkinson, G., and Piper, T. S., *J. Inorg. & Nucl. Chem.* **3**, 104 (1957).
472. Witanowski, M., and Roberts, J. D., *J. Am. Chem. Soc.* **88**, 737 (1966).
473. Wittig, G., *Angew. Chem.* **70**, 65 (1958).
474. Wittig, G., *Quart. Rev. (London)* **20**, 191 (1966).
475. Wittig, G., and Hornberger, P., *Ann. Chem.* **577**, 11 (1952).

476. Wittig, G., and Jautelat, M., *Ann. Chem.* **702**, 24 (1967).
477. Wittig, G., Meyer, F. J., and Lange, C., *Ann. Chem.* **571**, 167 (1951).
478. Wittig, G., and Wingler, F., *Chem. Ber.* **97**, 2139 (1964).
479. Wittig, G., and Wingler, F., *Chem. Ber.* **97**, 2146 (1964).
480. Wood, G. B., and Brenner, A., *J. Electrochem. Soc.* **104**, 29 (1957).
481. Wotiz, J. H., and Proffitt, G. L., *J. Org. Chem.* **30**, 1240 (1965).
482. Yakubovich, A. Ya., Rozenshtein, S. M., and Gitel', R. O., *Zh. Obshch. Khim.* **37**, 278 (1967).
483. Yasuda, Y., Kawabata, N., and Tsuruta, T., *J. Chem. Soc. Japan, Ind. Chem. Sect.* **69**, 936 (1966).
484. Yasuda, Y., Kawabata, N., and Tsuruta, T., *J. Org. Chem.* **32**, 1720 (1967).
485. Yosahida, K., and Tsutsumi, S., *J. Org. Chem.* **32**, 468 (1967).
486. Yoshino, T., and Manabe, Y., *J. Am. Chem. Soc.* **85**, 2860 (1963).
487. Yoshino, T., Manabe, Y., and Kikuchi, Y., *J. Am. Chem. Soc.* **86**, 4670 (1964).
488. Zakharkin, L. I., *Izv. Akad. Nauk SSSR, Ser. Khim.* p. 956 (1967).
489. Zakharkin, L. I., *Zh. Obshch. Khim.* **34**, 3125 (1964).
490. Zakharkin, L. I., Bregadze, V. I., and Okhlobystin, O. Yu., *J. Organometal. Chem.* (*Amsterdam*) **6**, 230 (1966), reference 13.
491. Zakharkin, L. I., and Okhlobystin, O. Yu., *Izv. Akad. Nauk SSSR, Ser. Khim.* p. 193 (1963).
492. Zakharkin, L. I., Okhlobystin, O. Yu., and Bilevich, K. A., *Tetrahedron* **21**, 881 (1965).
493. Zakharkin, L. I., Okhlobystin, O. Yu., and Strunin, B. N., *Dokl. Akad. Nauk SSSR* **144**, 1299 (1962).
494. Zakharkin, L. I., Okhlobystin, O. Yu., and Strunin, B. N., *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* p. 2254 (1961).
495. Zakharkin, L. I., Okhlobystin, O. Yu., and Strunin, B. N., *J. Organometal. Chem.* (*Amsterdam*) **4**, 349 (1965).
496. Zakharkin, L. I., Okhlobystin, O. Yu., and Strunin, B. N., *Tetrahedron Letters* p. 631 (1962).
497. Ziegler, K., *Angew. Chem.* **66**, 209 (1954).
498. Ziegler, K., Froitzheim-Kühlhorn, H., and Hafner, K., *Chem. Ber.* **89**, 434 (1956).
499. Ziegler, K., and Holzkamp, E., *Ann. Chem.* **605**, 93 (1957).
500. Ziegler, K., Nagel, K., and Patheiger, M., *Z. Anorg. Allgem. Chem.* **282**, 345 (1955).
501. Zimmerman, H. E., and Traxler, M. D., *J. Am. Chem. Soc.* **79**, 1920 (1957).
502. Ziolkowska, B., *Roczniki Chem.* **36**, 1341 (1962).