QUARTERLY REVIEWS

ORGANOMETALLIC COMPOUNDS OF THE FIRST THREE PERIODIC GROUPS

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The study of organometallic compounds, which dates from Frankland's preparation of diethylzinc in 1849—just a century ago—has resulted in the development of a number of valuable reagents for organic syntheses, the most notable being the Grignard reagents and the organo-lithium and -cadmium compounds. In addition, it has provided experimental material on which advances in valency theory have been based. This is a particular feature both of the earliest work by Frankland, which included the first clear exposition of a system of valency, and of the most recent discoveries about the properties and structures of metal alkyls, which, like the problems raised by the boron hydrides and related compounds, require significant extensions to current valency theory. The latter aspect is emphasised in this Review, which is restricted to the elements of the first three groups of the Periodic Table, since the organo-compounds of some of these elements provide structural and valency problems of a type not common among organo-derivatives of other groups.

The alkyls of these elements include compounds with the properties of salts, *e.g.*, methylpotassium, $K^+CH_3^-$, and covalent molecular compounds like dimethylmercury, $HgMe_2$, neither type presenting any serious problem. But there are also a number of compounds, like ethyl-lithium, dimethylberyllium, and trimethylaluminium, the properties of which exclude formulation as salts; these are now known to be associated. Trimethylaluminium, for example, is dimeric and should be represented as Al_2Me_6. In the metal alkyls that are associated, the number of available valency electrons is less than twice the minimum number of covalent bonds which must be present in the molecule; this requires that some of the bonds must have an order of less than one, since there are not enough electrons to form electron-pair single bonds. Such molecules have been termed " electron deficient ". Generally they occur among the compounds of elements (of the first three groups and to some extent the transition metals) having more stable available low-energy orbitals than valency electrons; *e.g.*, beryllium has available two, three, or four low-energy orbitals (the *sp*, sp^2, and sp^3 groups) but only two valency electrons, and aluminium, which can form a stable sp^3 low-energy set of tetrahedral orbitals, has only three valency electrons (see R. E. Rundle [34]).

In the molecule Al_2Me_6 it is probable that the aluminium atoms make use of their four stable orbitals, but with the inevitable result that some bonds in the molecule must have less than two electrons each. This type of compound cannot occur when there is a very large electronegativity difference between the bonded atoms, since the structure then becomes ionic. Thus all the alkali metals except lithium, the least electropositive, form ionic alkyls, and they all form ionic halides (but the ether-solubility of LiBr and LiI is noteworthy). Electron-deficient molecules are found predominantly among the compounds of lithium, beryllium, magnesium, boron, aluminium, and, to some extent, gallium.

Preparative Methods

Three general types of reaction are available for the preparation of organometallic compounds. The most direct method, reaction between a metal and an organic halide, frequently leads to metal organo-halides, *e.g.*,

$$\mathrm{Mg + EtBr \longrightarrow EtMgBr}\ \text{(a typical Grignard compound)}$$
$$\mathrm{Li + MeI \longrightarrow LiMe + LiI}$$
$$\mathrm{Al + MeI \longrightarrow Al_2Me_6 + Al_2Me_4I_2 + Al_2Me_2I_4 + Al_2I_6}$$
$$\mathrm{Si + MeCl \xrightarrow{(Cu)} SiMe_3Cl + SiMe_2Cl_2 + SiMeCl_3}$$

The last example finds industrial application in the manufacture of silicone polymers, but the silicon has to be activated by alloying with copper (see copper, below). Another industrial modification is the use of a lead–sodium alloy for the manufacture of tetraethyl-lead :

$$\mathrm{Pb + 4Na + 4EtCl \longrightarrow PbEt_4 + 4NaCl}$$

The other two general preparative methods are less direct since they both involve the conversion of one organometallic compound into another. The reaction between an organometallic compound and a metal, *e.g.*,

$$\mathrm{HgMe_2 + 2Na \longrightarrow Hg + 2NaMe}$$
$$\mathrm{3HgMe_2 + 2Ga \longrightarrow 3Hg + 2GaMe_3}$$

usually proceeds in such a direction as to *form a more reactive from a less reactive compound.* It is thus particularly useful for the preparation of highly reactive organo-compounds by the use of the relatively unreactive and easily manipulated mercury dialkyls and diaryls.

On the other hand, the reaction between an organometallic compound and a halide usually leads to the formation of a less reactive product from a more reactive starting material, *e.g.*,

$$\mathrm{4EtMgBr + SnCl_4 \longrightarrow SnEt_4 + 2MgBr_2 + 2MgCl_2}$$
$$\mathrm{2MeMgI + HgCl_2 \longrightarrow HgMe_2 + MgI_2 + MgCl_2}$$

This reaction is useful for the preparation of organometallic compounds from the rather highly reactive but easily accessible Grignard and organolithium reagents.

The Alkali Metals

The true organo-derivatives of the alkali metals, compounds in which the metal is bonded to carbon, provide some of the most reactive compounds known to Chemistry. The alkyls of sodium and potassium react with all organic compounds with which they have been tested, with the exception of the paraffin hydrocarbons. The lithium derivatives are less reactive and have found extensive synthetic use.

Physical Properties.—The organo-alkali compounds fall into two classes, those with salt-like and those with covalent properties.[1] The alkyls and aryls of sodium, potassium, rubidium, and cæsium are colourless solids, insoluble in paraffin hydrocarbons and benzene ; they cannot be vaporised without decomposition, and give conducting solutions in dimethylzinc. They are commonly described as salts, *e.g.*, K^+Et^-. Their conducting solutions in dimethylzinc, diethylzinc, and trimethylaluminium probably contain compounds of the type $M_2^+[ZnEt_2R_2]^=$, $M^+[AlMe_3R]^-$; the compound $RbZnEt_3$ [2] has been isolated (colourless crystals, m.p. 70—75°). The conductivity of these solutions is low, but of the order to be expected for salts dissolved in solvents of low dielectric constant, in which the salt would exist mainly in the ion-pair form. Some of the salt-like compounds containing benzyl, triphenylmethyl, and similar groups are highly coloured (usually orange or red) and are frequently quite soluble in organic solvents.

On the other hand, the lithium derivatives, with the exception of methyl-lithium, behave as covalent compounds. They are colourless and dissolve in non-polar solvents ; they may be distilled or sublimed in a high vacuum, but their vapour pressures are remarkably low. Ethyl-lithium, m.p. 95°, which may be crystallised from benzene, is non-conducting when fused and, although it would be expected from its molecular weight (36) to boil at a very low temperature, yet it can be distilled or sublimed only with some difficulty and would appear to be highly associated. Measurements of molecular weight by the freezing point of solutions in benzene indicate about a six-fold degree of association. *n*-Butyl-lithium has a vapour pressure of $\sim 4{\cdot}5 \times 10^{-4}$ mm. at 60° and $\sim 2 \times 10^{-3}$ mm. at 70° (corresponding to a latent heat of sublimation of 33 kcals./mole).[3] The dipole moment in benzene solution, 0·97 D,[4] would seem inadequate to allow this low volatility to be attributed to dipole association, although dipole clusters may have been present in the solutions used for these measurements, in which case the dipole moment of a single *n*-butyl-lithium molecule may be greater. The association may be of a predominantly chemical nature similar to that which causes the dimerisation of BH_3, $AlMe_3$, and other " electron-deficient " molecules.

Preparation and Chemical Properties.—The lithium alkyls and aryls are generally prepared by the reaction between lithium metal and the appropriate halide. Ether may be used as solvent in the preparation of methyl- and phenyl-lithium, but since it slowly reacts with other lithium alkyls light petroleum is preferred for such cases. With the exception of methyl iodide,

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[1] K. Ziegler, F. Crossman, H. Kleiner, and O. Schäfer, *Annalen*, 1929, **473**, 1.

[2] A. v. Grosse, *Ber.*, 1926, **59**, 2653.

[3] E. Warhurst, *Faraday Soc. Discussions*, 1947, **2**, 239.

[4] A. Young and M. T. Rogers, *J. Amer. Chem. Soc.*, 1946, **68**, 2748.

chlorides and bromides give better yields than iodides, since the iodides undergo the Würtz reaction more readily, resulting in loss of product, *e.g.*,

$$\begin{aligned} 2Li + C_4H_9I &\longrightarrow LiC_4H_9 + LiI \\ LiC_4H_9 + C_4H_9I &\longrightarrow C_8H_{18} + LiI \end{aligned}$$

For synthetic use, lithium derivatives are never isolated, but are allowed to react further in the solution in which they are prepared (as is usual with Grignard reagents). When it is necessary to prepare pure solvent-free organo-lithium compounds, the reaction between lithium and the appropriate organo-mercury compound is more suitable:

$$2Li + HgEt_2 \longrightarrow 2LiEt + Hg$$

Methyl-lithium is not satisfactorily obtained in this way, but may be prepared by taking advantage of its insolubility in benzene or light petroleum, in which it is precipitated in a double decomposition:

$$2LiEt(sol.) + HgMe_2(sol.) \longrightarrow 2LiMe \downarrow (insol.) + HgEt_2(sol.)$$

Organo-derivatives of the other alkali metals are prepared by the organo-mercury method with light petroleum as solvent for the mercury compound; a suspension of the organo-alkali compound appears on continued shaking of the reaction mixture.

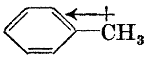
The salt-like nature of the very reactive alkali-metal alkyls implies that they may be regarded as derived from acids, namely, the corresponding hydrocarbons. Thus, ethylsodium may be regarded as the sodium salt of the very weak acid ethane. Consequently, one might expect ethane to be formed from ethylsodium by the action of any stronger acid; this occurs with benzene:

$$NaEt + Ph{\cdot}H \longrightarrow NaPh + C_2H_6$$

which should therefore be regarded as a stronger acid than ethane. Reactions of this type provide about the only way of comparing the relative acidities of such exceedingly weak acids.[5, 6] Toluene is a stronger acid than benzene, since it forms benzylsodium and benzene from phenylsodium:

$$NaPh + PhMe \longrightarrow Na{\cdot}CH_2Ph + C_6H_6$$

This is in accordance with the direction of the dipole moment of toluene (I). In this way an order of hydrocarbon acidities may be drawn up and linked with those of the more familiar weak acids:



(I.)

$$C_2H_6 < C_6H_6 < CH_3Ph < CH_2Ph_2 < CHPh_3 < \text{xanthen} < \text{aniline} < \text{fluorene} < \text{phenylacetylene} < \text{alcohols} < \text{phenol}$$

Hydrogen (H_2) would appear to behave as a stronger acid than benzene, since it displaces benzene from the alkali-metal phenyls:[7]

$$K{\cdot}C_6H_5 + H_2 \longrightarrow KH + C_6H_6$$

This is one of the very few non-catalysed reactions of molecular hydrogen at

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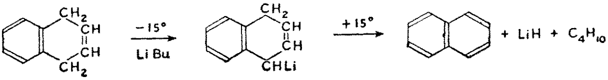
[5] J. B. Conant and G. W. Wheland, *J. Amer. Chem. Soc.*, 1932, **54,** 1212.
[6] W. K. McEwen, *ibid.*, 1936, **58,** 1124.
[7] H. Gilman, A. L. Jacoby, and (Miss) H. Ludeman, *ibid.*, 1938, **60,** 2336.

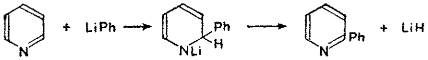
room temperature. The relative rates of this reaction illustrate the order of reactivities of the alkali-metal aryls, since the reaction rate decreases in the order Cs, Rb, K, Na, Li.

The replacement of hydrogen by an alkali-metal atom, by reaction of an aromatic compound with an alkali-metal alkyl, is called *metalation.* Thus, as mentioned above, toluene is metalated in the side chain by ethylsodium. The orientation of nuclear metalation is sometimes rather abnormal ; while aryl ethers, thioethers, and tertiary amines are metalated by *n*-butyl-lithium in the *ortho*-position, triphenylamine is metalated in the *meta*-position. The orientation of aromatic metalation is readily determined by subsequent reaction with carbon dioxide and identification of the resulting carboxylic acid.

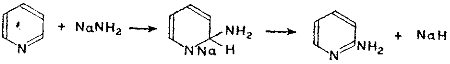
The metalation of a partly reduced aromatic system sometimes results in dehydrogenation with the formation of the fully aromatic ring. For example, 1 : 4-dihydronaphthalene is metalated by *n*-butyl-lithium at − 15° but splits off lithium hydride at about + 15° on continued stirring in ether :



A typical *addition* reaction is the synthesis of 2-aryl-pyridines by the reaction between pyridine and lithium aryls. Phenyl-lithium adds to pyridine, and on being heated in boiling toluene for several hours, splits off lithium hydride, giving 2-phenylpyridine : [8]



This is rather similar to the Tschitschibabin reaction between pyridine and sodamide, which requires similar experimental conditions :



The synthetic applications of organo-lithium compounds have recently been reviewed by G. Wittig.[9]

Copper, Silver, and Gold

Grignard reagents readily react with Group Ib halides, and by working at sufficiently low temperatures it is sometimes possible to isolate organometallic compounds. Usually, however, these decompose very readily to give the free metal and a hydrocarbon :

$$2Cu{\cdot}C_6H_5 = 2Cu + C_6H_5{\cdot}C_6H_5$$

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[8] *Org. Synth.*, Coll. Vol. II, p. 517, New York, 1943.

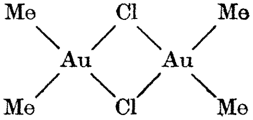
[9] " Newer Methods of Preparative Organic Chemistry ", Interscience, New York, 1948.

Treatment of a Grignard reagent RMgX with anhydrous cupric chloride has been used as a method for preparing compounds R_2. Sometimes it is possible to add cupric chloride and the organic halide to magnesium and ether, without preparing the Grignard solution as a separate stage. Phenyl-copper and -silver have been isolated, but decompose rapidly on storage. The reaction between Grignard reagents and auric bromide (in ether) gives derivatives of the type R_2AuBr, which have been studied comprehensively by C. S. Gibson and his collaborators.[10] Trimethylgold has very recently been prepared in ethereal solution at − 65° from methyl-lithium and a suspension of auric bromide.[11] It probably exists as an etherate, $Me_3\overset{-}{Au}\text{–}\overset{+}{O}Et_2$, and decomposes above − 35° to − 40° to give gold, methane, and ethane. Stabler compounds capable of recrystallisation at room temperature were obtained by the addition of electron-donor molecules, *e.g.*, ethylenediamine, benzylamine, or α-aminopyridine :

$$2Me_3\overset{-}{Au}\text{–}\overset{+}{O}Et_2 + NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2 \longrightarrow Me_3\overset{-}{Au}{\cdot}\overset{+}{N}H_2{\cdot}CH_2{\cdot}CH_2{\cdot}\overset{+}{N}H_2{\cdot}\overset{-}{Au}Me_3$$

An ethereal solution of trimethylgold reacts rapidly with ethereal hydrogen chloride, giving the relatively stable dimethylauric chloride :

$$2Me_3\overset{-}{Au}\text{–}\overset{+}{O}Et_2 + 2HCl \longrightarrow$$



$$+ 2CH_4 + 2Et_2O$$

Cuprous and silver methyls and ethyls are formed in an interesting reaction which has been the subject of recent kinetic studies.[12] Addition of a solution of silver nitrate in methyl or ethyl alcohol to a solution of tetramethyl-lead at temperatures of −10° to − 60° gives a precipitate of methyl-silver :

$$AgNO_3 + PbMe_4 \longrightarrow AgMe + PbMe_3NO_3$$

or a solution which decomposes into silver and *ethane* according to the first-order law. It is remarkable that the methyl radicals, which are probably the primary decomposition product, do not form methane by reaction with solvent molecules.

Similarly the addition of alcoholic cupric nitrate to tetramethyl-lead precipitates primrose-coloured methylcopper, which does give methane on subsequent decomposition and reaction of $CH_3\cdot$ with solvent molecules. The ratio of ethane to methane over the complete course of formation and decomposition was 1 : 2, in accordance with the scheme :

$$\begin{array}{lrcl}
\text{Stage I.} & Cu^{++} + PbMe_4 & \longrightarrow & Cu^{+} + PbMe_3^{+} + CH_3\cdot \\
 & 2CH_3\cdot & \longrightarrow & C_2H_6 \\
\text{Stage II.} & Cu^{+} + PbMe_4 & \longrightarrow & CuMe + PbMe_3^{+} \\
 & CuMe + \text{solvent} & \longrightarrow & CH_4
\end{array}$$

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[10] Reviewed by Sir G. T. Morgan and F. H. Burstall, " Inorganic Chemistry, A Survey of Modern Developments ", Heffer, 1936, pp. 373—375.

[11] H. Gilman and L. A. Woods, *J. Amer. Chem. Soc.*, 1948, **70**, 550.

[12] C. E. H. Bawn and F. J. Whitby, *Faraday Soc. Discussions*, 1947, **2**, 228.

These solid copper and silver methyls are polymeric compounds of some kind, and may be salts; even if they are salts containing CH_3 anions it would still be possible for methyl radicals to be formed on their decomposition.

Evidence for the reverse type of reaction, *viz.*, the formation of an organo-compound from a metal and a radical, has been obtained by W. M. Whaley and E. B. Starkey,[13] who found that a benzene suspension of phenyldiazonium borofluoride decomposed on boiling with copper powder, giving a solution, the reactions of which were those to be expected of phenylcopper:

$$Ph{\cdot}N_2^+ \ BF_4^- \longrightarrow C_6H_5{\cdot} \xrightarrow{(Cu)} CuPh$$

This reaction is somewhat similar to the formation of organo-derivatives of mercury, arsenic, and antimony by the decomposition of aryldiazonium halides in acetone or ethyl acetate in the presence of these elements.[14]

There is convincing evidence for the transitory formation of methylcopper in the reaction between copper and methyl chloride at 350°: [15]

$$2Cu + MeCl \longrightarrow CuCl + CuMe$$

The methylcopper was detected by its decomposition into copper and a gas which removed a lead mirror; at 250° the half-life of the methylcopper was about 0·002 second. This discovery was a result of an investigation into the mechanism of the direct formation of methylsilicon chlorides (for the manufacture of silicone polymers) from methyl chloride and a copper–silicon alloy; the presence of copper is necessary for a satisfactory reaction.

All attempts to prepare organo-derivatives of copper, silver, and gold by reaction between the metal and mercury alkyls or aryls have resulted in the formation of hydrocarbons, but none of the desired product.

Beryllium and Magnesium

In contrast to the very extensive investigations which have been carried out on Grignard reagents, the simple organo-derivatives MgR_2 and the corresponding beryllium compounds BeR_2 have received little attention.

Dimethylberyllium may be prepared by refluxing a mixture of beryllium metal and dimethylmercury with a little mercuric chloride as catalyst in an inert atmosphere. Vacuum-sublimation gives dimethylberyllium as white needles. The same compound may also be prepared from methylmagnesium iodide and the etherate of beryllium chloride: [16]

$$BeCl_2,2Et_2O + 2MeMgI \longrightarrow BeMe_2 + MgI_2 + MgCl_2 + 2Et_2O$$

The product is separated from the reaction mixture by " ether-distillation "; ether is allowed to drip on the hot reaction mixture, whereupon it rapidly evaporates and carries some methylberyllium into the receiver. By keeping the receiver warm, the beryllium compound is condensed together with some ether, excess of which evaporates, is condensed, and allowed again to fall

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[13] F. A. Bolth, W. M. Whaley, and E. B. Starkey, *J. Amer. Chem. Soc.*, 1943, **65,** 1456; W. M. Whaley and E. B. Starkey, *ibid.*, 1946, **68,** 793.

[14] W. A. Waters, " The Chemistry of Free Radicals ", Oxford, 1946, Chap. 8.

[15] D. T. Hurd and E. G. Rochow, *J. Amer. Chem. Soc.*, 1945, **67,** 1057.

[16] H. Gilman and F. Schulze, *J.*, 1927, 2663.

on the reaction mixture. Dimethylberyllium is much more volatile in the presence of ether than when pure; its melting point has not been observed, since it sublimes without melting. The few other known beryllium dialkyls (ethyl, propyl, and *n*-butyl) are liquid at room temperature.

Grignard-like compounds have been prepared from the metal and methyl (or ethyl) iodide, the reaction requiring catalysis by a little mercuric chloride,[17] *e.g.*,

$$\text{Be} + \text{MeI} \longrightarrow \text{Me·BeI}$$

All these compounds are highly reactive to oxygen and moisture, and the dialkyls react rapidly with carbon dioxide (dimethylberyllium inflames in this gas).

The beryllium dialkyls present a structural problem similar to that of the lithium alkyls (excepting lithium-methyl), since their evidently covalent character—their solubility in non-polar solvents such as benzene, and their volatility—excludes a polar formulation, *e.g.*, $Be^{++}(Me^{-})_2$. Their vapour pressures are, however, much lower than might be expected from a consideration of their molecular weights. Dimethylberyllium (M, 39) has a vapour pressure [18] of 1 mm. at 108° and 30·5 mm. at 158·6°; its latent heat of sublimation is 22 kcals./mole. The monomeric form of a dialkylberyllium should have a linear (*sp*) configuration and zero dipole moment, so the relative lack of volatility cannot very well be due to dipole association. Since the general chemistry of beryllium indicates a strong tendency for the element to form four-covalent bonds, it would appear probable that the alkyls are associated in such a way as to render this possible. As the element has only two valency electrons, the alkyls must, if they associate, behave as "electron-deficient molecules", in the same sense as diborane, B_2H_6, and trimethylaluminium, Al_2Me_6, are classed as electron-deficient.

The increase in the volatility of dimethylberyllium brought about by ether (an electron-donor molecule) is then due to the formation of a compound of the type $Me_2Be\{OEt_2\}_2$, analogous to the known dietherate of beryllium chloride $Cl_2Be\{OEt_2\}_2$. Vapour-density measurements [18] on dimethylberyllium indicate a considerable degree of association in the gas phase:

Temp., ° K.	450	456	462	468
Mol. wt.	70·7	67·8	64·1	62·6
Degree of association . . .	1·81	1·74	1·64	1·60

The intensely reactive dialkyls and diaryls of magnesium, which may be prepared from the metal and the appropriate mercury derivative, are much more salt-like in their physical properties, being non-fusible and non-volatile solids. They may, however, be very slowly ether-distilled and are soluble in the non-polar solvents benzene and dioxan. When heated,

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[17] H. Gilman and F. Schulze, *J. Amer. Chem. Soc.*, 1927, **49**, 2904.
[18] G. E. Coates and N. D. Huck, unpublished.

they decompose without melting or vaporisation, giving an olefin and magnesium hydride :[19]

$$MgEt_2 \longrightarrow MgH_2 + 2C_2H_4$$

Some of the Grignard compounds decompose in a similar way :

$$2EtMgI \xrightarrow[\text{vacuum}]{170-200°} MgI_2 + MgH_2 + 2C_2H_4$$

The magnesium hydride produced in these pyrolyses is insoluble in those organic solvents with which it does not react ; it was found to reduce benzophenone to diphenylcarbinol.

The organo-derivatives of calcium, strontium, and barium have received little attention ; phenylcalcium iodide, from calcium and iodobenzene in ether, is somewhat more reactive than the corresponding Grignard reagent, giving, for example, triphenylhydrazine with azobenzene in contrast to reduction to hydrazobenzene by phenylmagnesium iodide.

Zinc, Cadmium, and Mercury

The simple organo-derivatives of this group are normal covalent compounds, the volatility of which corresponds to their molecular weight. The molecules are linear, the metal forming two collinear *sp* bonds. The compounds show a striking change of reactivity, which diminishes from zinc to mercury ; dimethylzinc is spontaneously inflammable and reacts violently with water, whereas dimethylcadmium is slowly oxidised by air and hydrolysed by water, and dimethylmercury is inactive.

Zinc alkyls are readily prepared from dry zinc–copper couple and the alkyl iodide ; the alkylzinc iodide disproportionates on heating :

$$RI + Zn \longrightarrow RZnI$$
$$2RZnI \longrightarrow ZnR_2 + ZnI_2$$

Most of the organo-derivatives of the group may be conveniently obtained from the anhydrous metal halide and a Grignard reagent.

Once used extensively for synthetic purposes, the inconveniently inflammable organo-zinc compounds have been almost entirely superseded by the Grignard reagents ; zinc alkyls still find application, however, in the preparation of quaternary carbon compounds,[20] *e.g.*,

$$2Me_3CCl + ZnMe_2 \longrightarrow 2Me_4C + ZnCl_2$$

The relatively low reactivity of organo-cadmium compounds has been turned to advantage in a recently developed method for the preparation of ketones from acid chlorides :[21]

$$2R{\cdot}COCl + CdR'_2 \longrightarrow 2R{\cdot}CO{\cdot}R' + CdCl_2$$

The resulting ketone, which would react further with Grignard reagents, does not react with the organo-cadmium compound. The latter is not, for

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[19] D. B. Clapp and R. B. Woodward, *J. Amer. Chem. Soc.*, 1938, **60**, 1019; P. Jolibois, *Compt. rend.*, 1912, **155**, 353.

[20] C. R. Noller, *J. Amer. Chem. Soc.*, 1929, **51**, 594.

[21] J. Cason, *Chem. Reviews*, 1947, **40**, 15.

this purpose, isolated, but is prepared in ethereal solution by the addition of dry powdered cadmium chloride to the appropriate Grignard solution.

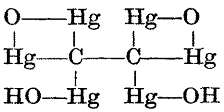
In addition to the simple derivatives such as the dimethyl, which are so useful in the preparation of organo-derivatives of other metals, mercury forms a very large number of organic compounds. The *mercuration* of aromatic compounds by reaction with mercuric acetate is a well-known reaction. Organo-mercuric compounds of the type RHgX undergo two noteworthy reactions; on treatment with nitrosyl chloride nitroso-compounds are formed:[22]

$$\mathrm{RHgX} + \mathrm{NOCl} \longrightarrow \mathrm{RNO} + \mathrm{HgXCl}$$

Electrolysis of RHgX in liquid ammonia solution results in the deposition, on the cathode, of a conducting solid of metallic appearance,[23] which decomposes at room temperature into equimolar proportions of Hg and HgR_2. This substance is easiest to obtain when R = Me, and the products become increasingly unstable as R becomes more complex. The cathode deposit is probably a metal consisting, in the product from methylmercuric compounds, of Hg^+–Me ions in a metallic lattice, together with the equivalent number of " free " electrons, *i.e.*, an organic metal. Electrolysis of *aqueous* solutions (preferably containing pyridine to increase solubility) of methylmercuric acetate gives a good yield of dimethylmercury by the disproportionation reaction:

$$\mathrm{Hg^+{-}Me} + \varepsilon \longrightarrow \mathrm{Hg^{\bullet}{-}Me} \longrightarrow \tfrac{1}{2}\mathrm{Hg} + \tfrac{1}{2}\mathrm{HgMe_2}$$

Numerous mercury derivatives of aldehydes, ketones, and carboxylic acids have been prepared, but the structure of few of the compounds has been determined. The remarkable compound known as ethane hexamercarbide[24] is obtained as a yellowish insoluble powder, unattacked by permanganate, chromic acid, hypochlorites, hydroxylamine, or hydrazine, by the prolonged action of yellow mercuric oxide and boiling aqueous alkali on ethyl, propyl, allyl, or amyl alcohol, acetaldehyde, cellulose, starch, or sucrose. The compound has the empirical formula $C_2O_4Hg_6H_2$, and since it forms salts $C_2O_2Hg_6X_2$ with acids (also insoluble), it has been given the structure (II). This structure is not compatible with the normally collinear bonds formed by bicovalent mercury and, considering the extreme insolubility of the substance, it would appear more likely to have a polymeric structure (III). The compound behaves as a base-exchange resin;[2]



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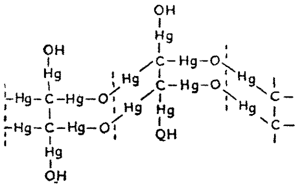

(III.)

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[22] L. I. Smith and F. L. Taylor, *J. Amer. Chem. Soc.*, 1935, **57**, 2460.

[23] C. A. Kraus, *ibid.*, 1913, **35**, 1732.

[24] K. A. Hofmann, *Ber.*, 1898, **31**, 1904; 1900, **33**, 1328.

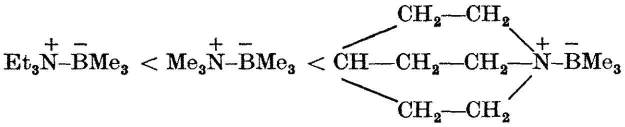
[25] Unpublished observations by the Reviewer.

on being shaken with aqueous potassium chloride the solid takes up Cl^- in exchange for OH^- ions, the effect being more marked with potassium bromide and still more with the iodide. Ions such as NO_3^- which do not so readily form covalent bonds are not exchanged in this way, but form salts [*e.g.*, $C_2O_2Hg_6(NO_3)_2$] only by the action of the free acid on the base.

Boron

The simple alkyls and aryls of boron, BR_3, are normal covalent compounds with none of the tendency to associate shown by its neighbours beryllium and aluminium. The lower members of the series, *e.g.*, BMe_3, are rather slowly hydrolysed by water, but are very sensitive to oxygen, spontaneously inflammable in air, and burn with a characteristic green flame. The chemistry of boron is dominated by the tendency for the element to become four-covalent, by acquiring the use of extra valency electrons. Thus, although the simple alkyls do not associate to achieve this end, as the hydride does ($BH_3 \longrightarrow B_2H_6$), they very readily show their electron deficiency by combining with a variety of electron-donor molecules, *e.g.*, ammonia, trimethylamine, and the phosphines.

The relative stabilities of compounds of the type $Me_3\overset{-}{B}-\overset{+}{N}R_3$ have been measured in order to compare the basic strengths of amines in a non-aqueous system,[26] and to examine the influence of steric effects on basic strength. Thus, although triethylamine forms a very much less stable compound with methylboron than does trimethylamine, yet quinuclidine forms a compound of exceptional stability :



In the last compound the carbon atoms of the quinuclidine molecule are held back from the nitrogen and exert no steric hindrance on reaction with another molecule.

Disproportionation reactions, which are quite common among the boron hydrides (*e.g.*, $6B_2H_5Cl \longrightarrow 5B_2H_6 + 2BCl_3$) also occur among the alkyl derivatives ; thus, treatment of chlorobisdimethylaminoborine with dimethylzinc does not give the expected methyl compound, but a mixture of the dimethyl derivative and trisdimethylaminoborine : [27]

$$\begin{tikzcd}
\{Me_2N\}_2BCl + ZnMe_2 & (\longrightarrow & \{Me_2N\}_2BMe) \arrow[dl] \arrow[d] \\
 & Me_2N{\cdot}BMe_2 + & \{Me_2N\}_3B
\end{tikzcd}$$

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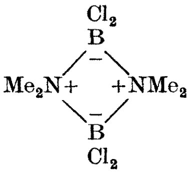
[26] H. C. Brown, M. D. Taylor, and M. Gerstein, *J. Amer. Chem. Soc.*, 1944, **66**, 431 ; H. C. Brown and M. D. Taylor, *ibid.*, 1947, **69**, 1332 ; H. C. Brown and Sei Sujishi, *ibid.*, 1948, **70**, 2878.

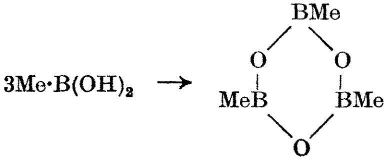
[27] Unpublished observations by the Reviewer.

The reactive and very easily hydrolysable liquid $Me_2N{\cdot}BCl_2$ is remarkable in that it slowly changes into a crystalline dimer of probable structure (IV), which is not attacked by prolonged boiling with water or dilute acids or alkalis.[28] The methyl derivative $Me_2N{\cdot}BMe_2$ does not dimerise, whereas the hydride $Me_2N{\cdot}BH_2$ dimerises but very readily dissociates to the monomeric form. A study of these compounds[29] shows that dimerisation is promoted when electron-attracting groups (*e.g.*, chlorine) are attached to the boron, and electron-repelling groups (*e.g.*, methyl) to the nitrogen; in this way the charges in the ring system become more evenly distributed over the molecule.



(IV.)

Although many arylboronic acids, $R{\cdot}B(OH)_2$, have been prepared and studied, particularly as regards their acid strengths and orientation on nitration, the simplest alkylboronic acids have only recently been isolated; they form anhydrides with surprising facility. Monomethylboronic acid [30] is dehydrated by passage over $CaSO_4,\frac{1}{2}H_2O$, giving a cyclic anhydride (V):



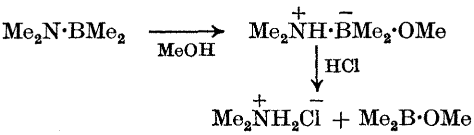
(M.p. – 38°; b.p. 79°.)

(V.)

Similarly the volatile dimethylborinic acid $Me_2B{\cdot}OH$ (v.p. 36 mm. at 0°) is readily dehydrated with phosphoric oxide to the anhydride $Me_2B{\cdot}O{\cdot}BMe_2$ (b.p. 43°). These anhydrides react with boron trifluoride, giving the previously unknown methylboron fluorides:

$$(BOMe)_3 + 2BF_3 \longrightarrow 3Me{\cdot}BF_2 + B_2O_3$$
$$3Me_2B{\cdot}O{\cdot}BMe_2 + 2BF_3 \longrightarrow 6Me_2{\cdot}BF + B_2O_3$$

The very volatile methyl ester of dimethylborinic acid (b.p. 25°) may be prepared by the following reactions:[31]



$$\begin{tikzcd}
Me_2N{\cdot}BMe_2 \arrow[r, "MeOH"'] & Me_2\overset{+}{N}H{\cdot}\overset{-}{B}Me_2{\cdot}OMe \arrow[d, "HCl"] \\
& Me_2\overset{+}{N}H_2\overset{-}{Cl} + Me_2B{\cdot}OMe
\end{tikzcd}$$

Aluminium

The aluminium alkyls and aryls are very reactive, and show many of the characteristics of electron-deficient molecules. Although they may be

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[28] E. Wiberg and K. Schuster, *Z. anorg. Chem.*, 1933, **213,** 89.

[29] E. Wiberg, FIAT Review of German Science (1939—46), Inorganic Chemistry, Vol. 1, 1948.

[30] A. B. Burg, *J. Amer. Chem. Soc.*, 1940, **62,** 2228.

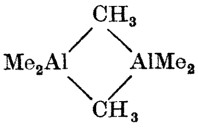
[31] Unpublished observations by the Reviewer.

prepared from aluminium by the dialkyl- (or diaryl-) mercury method, a new and more satisfactory method for larger-scale preparations has recently been described,[32] by which methyl iodide is heated under reflux with aluminium. After about twelve hours all the methyl iodide is consumed and the reaction vessel contains an equilibrium mixture of the methylaluminium iodides and trimethylaluminium :

$$Al + MeI \longrightarrow (AlMeI_2)_2 + (AlMe_2I)_2 + (AlMe_3)_2$$

The pressure is then reduced and trimethylaluminium is slowly taken off at high reflux ratio from a fractionating column ; the equilibrium is thus disturbed and about one-half of the theoretical methyl can be taken off as trimethylaluminium.

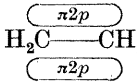
Trimethylaluminium, m.p. 15·1°, b.p. 130°, has the properties of a typical covalent compound, but is dimeric [32] both in benzene solution and as vapour. It is one of the very few associated electron-deficient alkyls of which the (geometrical) structure has been determined ; the infra-red absorption spectrum [33] indicates that the molecule has a bridge structure (VI). The positions of the hydrogen atoms are not revealed. Electron-diffraction data do not clearly distinguish between an ethane-like and a bridge model.[34] This result, together with others connected with different electron-deficient molecules (*e.g.*, diborane B_2H_6, and tetramethylplatinum $\{PtMe_4\}_4$), has presented quite a serious problem to valency theory. A bridge structure implies an unusual covalency for the bridge carbon atoms, which appear to form five covalent bonds. One interpretation of this and related problems is due to R. E. Rundle,[34] who suggests that a single carbon $2p$ atomic orbital may form one molecular orbital which binds two atoms by half-bonds. Thus, a non-hybridised p orbital may form covalent bonds in the following ways :



(VI.)

(1) a normal σ single bond, as in hydrogen chloride, H(1s)–Cl(3p) ;

(2) a normal π bond, forming the second component of a double bond, as in ethylene,



$$\overset{\pi 2p}{\underset{\pi 2p}{H_2C\text{——}CH_2}} ;$$

(3) each lobe of a p orbital may form a half-bond.

In each case the orbital holds two electrons of opposite spin, in accordance with Pauli's exclusion principle. Two reasonable sets of orbitals have been suggested for the trimethylaluminium molecule ; in each set a single C $2p$ orbital forms one molecular orbital which binds two aluminium atoms by half-bonds.

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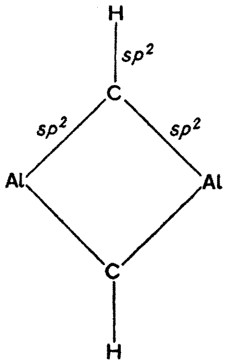
[32] K. S. Pitzer and H. S. Gutowsky, *J. Amer. Chem. Soc.*, 1946, **68**, 2204.

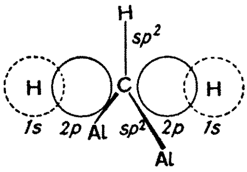
[33] K. S. Pitzer and R. K. Sheline, *J. Chem. Physics*, 1948, **16**, 552.

[34] N. R. Davidson, J. C. Hugill, H. A. Skinner, and L. E. Sutton, *Trans. Faraday Soc.*, 1940, **36**, 1212 ; L. Brockway and N. Davidson, *J. Amer. Chem. Soc.*, 1941, **63**, 3287 ; H. A. Skinner and L. E. Sutton, *Nature*, 1945, **156**, 601 ; R. E. Rundle, *J. Amer. Chem. Soc.*, 1947, **69**, 1327.

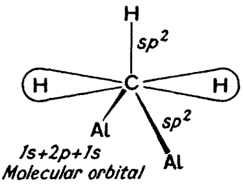
(*a*) The aluminium and the end carbon atoms are believed to be in the tetrahedral state, the bridge carbon atoms being in the trigonal state as in ethylene. Let all the bonds, except (for the moment) those involved in the carbon bridge, be supplied with two electrons each, as for normal single bonds. Of the 16 electrons left, let 12 be supplied to the six bonds formed by the trigonal bridge carbon atoms (two C–H and four C–Al bonds), allowing these each to form three single bonds (VII). Perpendicular to the plane of the sp^2 orbitals is a non-hybridised $2p$ orbital (VIII). There are now four electrons left over to supply both of the bridge carbon atoms, each of which can accommodate two electrons of opposed spin in its $2p$ orbital. This orbital combines with the two H(1*s*) orbitals to give *one* H(1*s*) + C($2p$) + H(1*s*) *molecular orbital* which holds two electrons and binds two hydrogen atoms (IX). In this way each of the four hydrogen atoms concerned is held to a carbon atom by a half-bond.



(VII.)



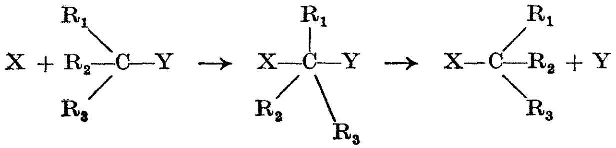
(VIII.)



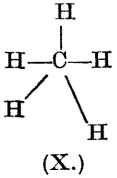
(IX.)

There is a fundamental difference between this type of bond and the " singlet link " which was at one time invoked to explain the boron hydrides. The latter involves the occupancy of a molecular orbital by one electron only, and would give a paramagnetic molecule contrary to experimental fact, while according to the above view one molecular orbital, which is doubly occupied, binds two atoms with half-bonds.

It is of some interest to note that this $sp^2 + 2p$ set of orbitals with the $2p$ orbital forming two half-bonds is identical with the calculated transition state in reactions of the type



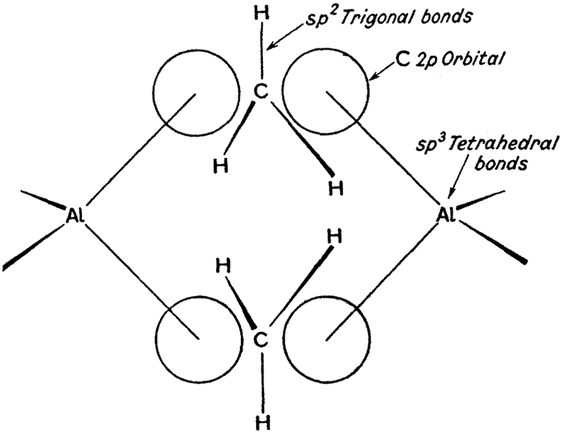
This type of reaction includes the Walden inversion. Quantum-mechanical calculations show that the transition state (X) in the reaction between hydrogen atoms and methane has a potential minimum of the order of 20 kcals./mole.[35] It may be significant that this is of the same magnitude as the heat of dissociation of Al_2Me_6.



(X.)

The above formulation of Al_2Me_6 imparts a negative charge to each of the aluminium atoms and half a positive charge to each of the four hydrogen atoms held by half-bonds. It could very reasonably be objected that the relatively electropositive aluminium atoms could not hold a negative charge when bound to much more electronegative carbon atoms ; but it must be realised that this charge distribution corresponds to complete absence of polarity in all the covalent bonds. A small dipole moment in the expected direction $\overset{+\!\!\!\longrightarrow}{\mathrm{Al—C}}$, of about 2—2·5 D., in each Al–C bond would entirely remove the negative charges from the aluminium atoms, and in a similar way the fractional positive charges on the bridge hydrogen atoms would also be reduced.

(*b*) According to an alternative formulation, also due to R. E. Rundle,[34] the various atoms are in similar orbital states, but the half-bonds are confined to the ring (XI). The difference between the two models is very slight. The second model does not involve any charge inequalities in the fully covalent form, but it is likely to involve slightly greater steric strain. It is particularly interesting to note that triethyl- and tri-*n*-propyl-aluminium are dimeric, while the tri*iso*propyl compound is monomeric.[32] This is to be expected on either model, since more than one alkyl group attached to the bridge carbon atom would introduce serious steric strain.



(XI.)

In agreement with its electron-deficient character, trimethylaluminium reacts with a number of electron-donor molecules. These reactions, illus-

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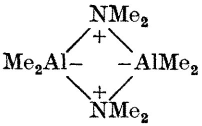
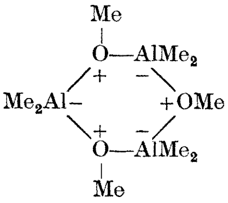
[35] E. Gorin, W. Kauzmann, J. Walter, and H. Eyring, *J. Chem. Physics*, 1939, **7**, 633.

trated below, result in the formation of normal molecules which can be formulated according to well-established valency theory:

$$Al_2Me_6 + 2NMe_3 \longrightarrow 2Me_3\overset{-}{Al}-\overset{+}{N}Me_3$$
$$Al_2Me_6 + 2OMe_2 \longrightarrow 2Me_3\overset{-}{Al}-\overset{+}{O}Me_2$$

The formation of etherates prevents the preparation of aluminium alkyls by the Grignard method. Some rather striking compounds [36] are formed by reaction with electron-donor molecules containing reactive hydrogen atoms; for example, with dimethylamine, the addition compound $Me_3\overset{-}{Al}-\overset{+}{N}HMe_2$ is first formed, but when heated above its melting point it loses methane and gives a substance $\{Me_2Al{\cdot}NMe_2\}_2$, which is dimeric, as shown by vapour-density measurements. A ring structure (XII) has been assigned to this compound. In this structure the aluminium atoms satisfy their tendency to form four-covalent bonds; thus, the substance is relatively unreactive and no longer combines with trimethylamine. The corresponding boron compound, $Me_2B{\cdot}NMe_2$ is monomeric; this provides a further illustration of the greater electron-deficient behaviour of aluminium; *e.g.*, trimethylboron and boron trichloride are monomeric while the aluminium compounds are dimeric; similarly, boron hydride (B_2H_6) is dimeric while aluminium hydride $(AlH_3)_n$ is polymeric.


(XII.)


(XIII.)

A similar reaction between trimethylaluminium and methyl alcohol gives a trimeric, six-membered cyclic compound (XIII). It is of some interest to note that the alkoxides of aluminium have been shown (by cryoscopic measurements in naphthalene) to be *tetra*meric,[37] like the alkoxides of thallium $(TlOR)_4$.[38]

Very little is known about organo-derivatives of the Group IIIA elements; the compound $ScEt_3{\cdot}OEt_2$ and the yttrium analogue have been described,[39] having been prepared by the Grignard method.

Gallium, Indium, and Thallium

The tendency of the third-group elements to form four-covalent bonds is well illustrated by the chemical behaviour of their organo-compounds.

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[36] H. C. Brown and N. R. Davidson, *J. Amer. Chem. Soc.*, 1942, **64,** 316.
[37] R. A. Robinson and D. A. Peak, *J. Physical Chem.*, 1935, **39,** 1125.
[38] N. V. Sidgwick and L. E. Sutton, *J.*, 1930, 1461.
[39] V. Plets, *Compt. rend. Acad. Sci. U.R.S.S.*, 1938, **20,** 27 (*Chem. Abs.* 1939, **33,** 2105).

Their electron-deficient character is much less marked than with the aluminium compounds and leads to association only in the case of gallium trichloride, the methylgallium hydrides, and digallane (Ga_2H_6).

Trimethylgallium (b.p. 55°), which is monomeric in the vapour state,[40] may be prepared from the chloride and dimethylzinc[41] or by heating metallic gallium with dimethylmercury.[42] The compound is very reactive, inflaming in the presence of air even at − 80°, and is rapidly hydrolysed. Stable compounds are formed with electron-donor molecules. The etherate (b.p. 98·3°) is obtained by direct combination or by the reaction between gallium trichloride and ethereal methylmagnesium iodide;[41] it is extensively dissociated as vapour but is much less reactive to air and moisture than the trimethyl. The ammine $Me_3\overset{-}{Ga}{-}\overset{+}{N}H_3$ and the similar compounds $Me_3\overset{-}{Ga}{-}\overset{+}{N}Me_3$ and $Me_3\overset{-}{Ga}{-}\overset{+}{N}Et_3$ are stable to dry air. Mixed alkyl halides are formed by the reaction between trimethylgallium or its ammine and ethereal hydrogen chloride;[41] the reaction with the ammine takes the following course:

$$(1)\ Me_3Ga,NH_3 + HCl + Et_2O \longrightarrow GaMe_3,OEt_2 + NH_4Cl$$
$$(2)\ Me_3Ga,OEt_2 + NH_4Cl \longrightarrow Me_2GaCl,NH_3 + OEt_2 + CH_4$$

The monoammine of dimethylgallium chloride is a solid, m.p. 54°, soluble in ether and appreciably volatile in a vacuum. The diammine, on the other hand, formed from the monoammine by absorption of ammonia at room temperature, is non-volatile, soluble in the polar solvents alcohol, acetone, and liquid ammonia, but insoluble in ether; it is probably a salt $NH_4^+[Me_2Ga(NH_2)Cl]^-$. The dichloride $MeGaCl_2$ results from the further action of hydrogen chloride, and also forms ammines.

Some interesting compounds result from the reduction of the ammines of trimethylgallium and dimethylgallium chloride by means of sodium in liquid ammonia.[41] In these reactions sodium acts as an electron donor and displaces ammonia, leaving the gallium with a negative charge and thereby still able to form four-covalent bonds. The reduction may be carried to two stages:

$$(1)\quad Na + 2Me_3\overset{-}{Ga}{-}\overset{+}{N}H_3 \longrightarrow Me_3\overset{-}{Ga}{-}\overset{+}{N}H_2{-}\overset{-}{Ga}Me_3 + Na^+ + \tfrac{1}{2}H_2 + NH_3$$
$$(2)\quad 2Na + 2Me_3\overset{-}{Ga}{-}\overset{+}{N}H_3 \longrightarrow Me_3\overset{-}{Ga}{-}\overset{-}{Ga}Me_3 + 2Na^+ + 2NH_3$$

Addition of ammonium bromide to the product of the second reaction re-forms trimethylgallium ammine. These compounds are analogous to some of the derivatives of diborane, $NH_4^+[\overset{-}{B}H_3{-}\overset{+}{N}H_2{-}\overset{-}{B}H_3]$ and $Na_2^{++}[B_2H_6]^{--}$.

The reduction of dimethylgallium chloride results in the appearance of a bright orange colour, which may be due to the $Me_2Ga^{\bullet}$ radical,

$$Me_2GaCl + Na \longrightarrow NaCl + Me_2Ga^{\bullet}$$

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[40] A. W. Laubengayer and W. F. Gilliam, *J. Amer. Chem. Soc.*, 1941, **63**, 477.

[41] C. A. Kraus and F. E. Toonder, *ibid.*, 1933, **55**, 3547; *Proc. Nat. Acad. Sci.*, 1933, **19**, 292.

[42] E. Wiberg, T. Johannsen, and O. Stecher, *Z. anorg. Chem.*, 1943, **251**, 114.

but the product obtained on evaporation of the ammonia (solvent) is the amide $Me_2Ga{\cdot}NH_2$, which may be sublimed in a vacuum:

$$Me_2\overset{-\bullet}{Ga}\text{–}\overset{+}{N}H_3 \longrightarrow Me_2Ga{\cdot}NH_2 + \tfrac{1}{2}H_2$$

The dimeric methyl hydrides of gallium which, like those of aluminium, are formed by the action of a glow discharge on a mixture of the trimethyl and hydrogen, are of particular interest in their disproportionation reaction with trimethyl- or (more conveniently) triethyl-amine to give the volatile (extrapolated b.p. 139°) dimeric hydride, digallane: [43]

$$3Ga_2H_2Me_4 + 4NEt_3 \longrightarrow Ga_2H_6 + 4Me_3\overset{-}{Ga}\text{–}\overset{+}{N}Et_3$$

The organo-derivatives of indium have received much less attention than those of gallium. The trimethyl, which may be prepared from the metal and dimethylmercury,[44] is a beautifully refracting crystalline solid, m.p. 88·4°, b.p. 135·8°; its vapour, like that of trimethylgallium, is monomeric.[45] Electron diffraction [46] shows that the molecule is planar, the indium atom making use of the trigonal set of sp^2 orbitals. The electron-deficient character of trimethylindium is very slight, since it is reported to form neither an ammine nor an etherate. Although the compound is spontaneously inflammable at room temperature in air at atmospheric pressure, very slow oxidation at − 78° appears to follow the rather remarkable course [44]

$$4InMe_3 + O_2 \longrightarrow 2(InMe_2)_2O + 2C_2H_6$$

Triphenylindium,[47] m.p. 291° (decomp.), is readily oxidised to amorphous phenylindium oxides of indefinite composition, but gives the mixed bromides $InPh_2Br$, $InPhBr_2$, and finally $InBr_3$ on treatment with bromine in benzene solution. The mixed bromides appear to have a salt-like character since they do not melt below 300°.

Although the chemistry of organo-thallium compounds has been intensively studied, it is only relatively recently that the simple TlR_3 derivatives have been prepared. Reaction between thallic chloride and Grignard reagents goes readily as far as the stage R_2TlX, which are true salts of the $[R_2Tl]^+$ cations. The latter are very stable and isoelectronic with the stable dialkyl- and diaryl-mercury compounds. The hydroxides, prepared by the action of silver oxide on the halides, are strong bases, their aqueous solutions absorbing carbon dioxide from the atmosphere. The general tendency of Group IIIB elements to form four-covalent bonds is still shown to some degree by thallium, since stable compounds, (XIV) and (XV), are formed from dimethylthallium hydroxide and acetylacetone or

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[43] E. Wiberg and T. Johannsen, *Angew. Chem.*, 1942, **55**, 38; *Naturwiss.*, 1941, **29**, 320.

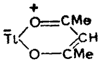
[44] L. M. Dennis, R. W. Work, E. G. Rochow, and E. M. Chamot, *J. Amer. Chem. Soc.*, 1934, **56**, 1047.

[45] A. W. Laubengayer and W. F. Gilliam, *ibid.*, 1941, **63**, 477.

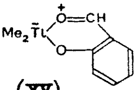
[46] L. Pauling and A. W. Laubengayer, *ibid.*, p. 480.

[47] W. C. Schumb and H. I. Crane, *ibid.*, 1938, **60**, 306.

salicylaldehyde. These *covalent* compounds are soluble in non-polar solvents and may readily be sublimed.[48]



(XIV)



(XV)

Triethylthallium may be prepared from diethylthallium chloride and ethyl-lithium.[49] It is a bright yellow liquid, b.p. (extrapolated) 192°, which readily decomposes above about 100°. Reactive in comparison with the chemically inert diethylthallium salts, the triethyl readily reverts to the latter by reaction with hydroxylic compounds, hydrogen halides, etc. :

$$TlEt_3 + H_2O \longrightarrow TlEt_2{\cdot}OH + C_2H_6$$

Although soluble in ether it does not form an etherate, and no compound with ammonia or trimethylamine has been described. Triphenylthallium undergoes a particularly interesting reaction when boiled in xylene solution [50] since the reactive monophenylthallium is formed :

$$TlPh_3 \longrightarrow TlPh + C_6H_5{\cdot}C_6H_5$$

and fairly rapidly disproportionates :

$$3TlPh \longrightarrow 2Tl + TlPh_3$$

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[48] R. C. Menzies, N. V. Sidgwick, E. F. Cutcliffe, and J. M. C. Fox, *J.*, 1928, 1288.

[49] H. P. A. Groll, *J. Amer. Chem. Soc.*, 1930, **52**, 2998 ; S. F. Birch, *J.*, 1934, 1132 ; E. G. Rochow and L. M. Dennis, *J. Amer. Chem. Soc.*, 1935, **57**, 486.

[50] H. Gilman and R. G. Jones, *ibid.*, 1940, **62**, 2357.