THE FORMATION AND REACTIONS OF SOME ORGANOMETALLIC COMPOUNDS

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Summary

The Formation and Reactions of Some Organometallic Compounds

The original work described in this thesis can be divided into three parts.

(a) In the first, a study of the reactions of halides of several metals or metalloids with alkali metal derivatives of aluminium alkyls was undertaken. In particular, the reactions of halides of tin, lead, phosphorus, arsenic, antimony, and bismuth with lithium tetraethylaluminate were studied. Alkylation of the group IV and VB elements was observed in every instance. Alkyls of the form MEt_n (M = Sn, Pb, P, As, Sb, and Bi; n = valency of metal or metalloid) were isolated from the reaction mixtures, indicating an overall stoichiometry corresponding to:

$$LiAlEt_4 + MX_n \rightleftharpoons MEt_n + LiAlEt_{4-n}X_n.$$

(b) The second part involves the reactions of several organometallic compounds with titanium halides.

The results of investigations of the reactions of tetraethyllead, and of triethyl-aluminium etherate, with bis(cyclopentadienyl)-titanium dichloride indicated that bis(cyclopentadienyl)-ethyltitanium compounds were being formed. However, pure compounds could not be isolated from the reaction mixtures.

It was shown that the reaction of lithium tetraethylaluminate with titanium tetrachloride followed the known course of the reactions of simple lithium alkyls and aluminium alkyls with titanium halides. Absorption complexes were apparently formed between reduced titanium halides and the metal alkyls.

The reactions of bis(cyclopentadienyl)titanium dichloride with triethylplumbyl sodium and with triethylstannyl lithium were also investigated. The results of these investigations indicated the formation of unstable, bimetallic products according to the general equation:

$$MM'R_3 + Cp_2TiCl_2 \longrightarrow Cp_2TiCl.M'R_3 + MCl$$

(where M = alkali metal, M' = Pb or Sn).

The reaction of liquid ammonia with bis(cyclopentadienyl)-titanium dichloride was also studied during these investigations. Ammonobasic titanium compounds were formed.

(c) In the final part, preliminary investigations of some new preparations of perfluoroalkyl derivatives of metals were begun. Four types of reaction were studied.

The reaction of heptafluoropropyl iodide with triethylstannane apparently formed triethyl-heptafluoropropyl-tin, but isolation of pure perfluoroalkyl-tin compounds was not achieved.

Alkyl-perfluoroalkyl exchange between aluminium alkyls and perfluoroalkyl iodides was studied. The results showed that some exchange could be effected when lithium tetraethylaluminate was used in the reaction, whereas no exchange was observed with pure triethylaluminium.

Reactions of halides of tin, lead, and titanium with lithium bis(heptafluoropropyl)diiodoaluminate were also investigated. Although evidence for the formation of perfluoroalkyl derivatives of tin and lead was obtained, pure metal perfluoroalkyl compounds were not isolated. The reaction with bis(cyclopentadienyl)titanium dichloride resulted in replacement of some chloride groups by iodide groups.

Finally, some attempts to decarboxylate trifluoroacetate salts of tin and lead by heating the compounds in vacuum were made. Triethyltin trifluoroacetate was not appreciably affected when heated at 200° *in vacuo*, and although triethyl-lead trifluoroacetate decomposed below this temperature, decarboxylation did not occur.

Statement

This thesis contains no material which has been accepted for the award of any other degree or diploma in any University. To the best of the author's knowledge and belief, the thesis contains no material previously published or written by another person, except when due reference is made in the text of the thesis.

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INTRODUCTION

Throughout this thesis the term "organometallic" is used to describe any compound in which one or more organic group is bound to a metal by direct carbon to metal bonds.[1] In appropriate instances, the definition has been extended to include analogous derivatives of elements of a metalloidal or non-metallic nature.[2] The broadened definition thus includes such compounds as triphenylphosphine, $(C_6H_5)_3P$, and dibutylfluoroborane, $(C_4H_9)_2BF$, as well as more conventional organometallics like methyl-lithium, CH_3Li, ethylmagnesium bromide, C_2H_5MgBr, and trimethylstannane, $(CH_3)_3SnH$. It excludes, among other borderline cases, chelate compounds and salts of organic acids.

In the discussion which follows the symbols "R" and "R_f" are used to designate alkyl and fluoroalkyl groups respectively. Specific organic groups are frequently abbreviated to the symbols approved by the Chemical Society of London.[3]

The present study was undertaken to gain a clearer understanding of the nature of a number of organometallic systems, known as Ziegler catalysts,[4] which have been used to catalyze the low pressure polymerization of α-olefins. These initial aims were subsequently modified to include a more general investigation of the formation and reactions of some organometallic compounds which are commonly used in Ziegler catalyst systems. In particular, the study involves an investigation of the syntheses and chemical reactions of simple alkyls of aluminium, tin, and lead, and of alkali metal salts of these alkyls. A number of systems containing these organometallic compounds mixed with inorganic halides have been examined. Some new modes of preparation of fluorocarbon derivatives of metals have also been investigated.

The material in this thesis is grouped into several sections in the following manner. Chapter 1 reviews the literature having a direct bearing on the compounds and reactions studied. To facilitate a discussion of the chemical reactivity of the organometallic compounds used in this study, the molecular structure of some of these compounds is first considered. This is followed by a brief survey of the types of reactions encountered in related investigations. Finally, a short report on the chemistry of the so-called Ziegler catalysts is presented. Chapter 2 deals with some practical observations and some theoretical considerations of the reactions used in the preparations of aluminium alkyls and of the alkali metal derivatives of alkyls of aluminium, tin, and lead. While the preparations of these compounds do not, in general, represent original work, they nevertheless presented some problems which seemed to warrant special discussion. In the subsequent chapters, the original work is described.

The results of the reactions of aluminium alkyls, and of lithium aluminium tetra-alkyls, with halides of a number of metals and non-metallic elements are discussed in chapter 3. Chapter 4 includes a discussion of the reactions of triethylaluminium etherate, tetraethyl-lead, triethylplumbyl sodium and triethylstannyl lithium with bis(cyclopentadienyl)titanium(IV) dichloride. Attempts to prepare fluoroalkyl derivatives of aluminium, tin, lead, and titanium by new methods are discussed in chapter 5. These investigations are of a preliminary nature and further work is intended.

A description of the experimental work carried out in this study is given in the final chapter. Some general remarks on the techniques used in the handling and manipulation of organometallic compounds are followed by a detailed description of the preparations of organometallic compounds, and subsequently by the reactions discussed in the preceding chapters.

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CHAPTER 1

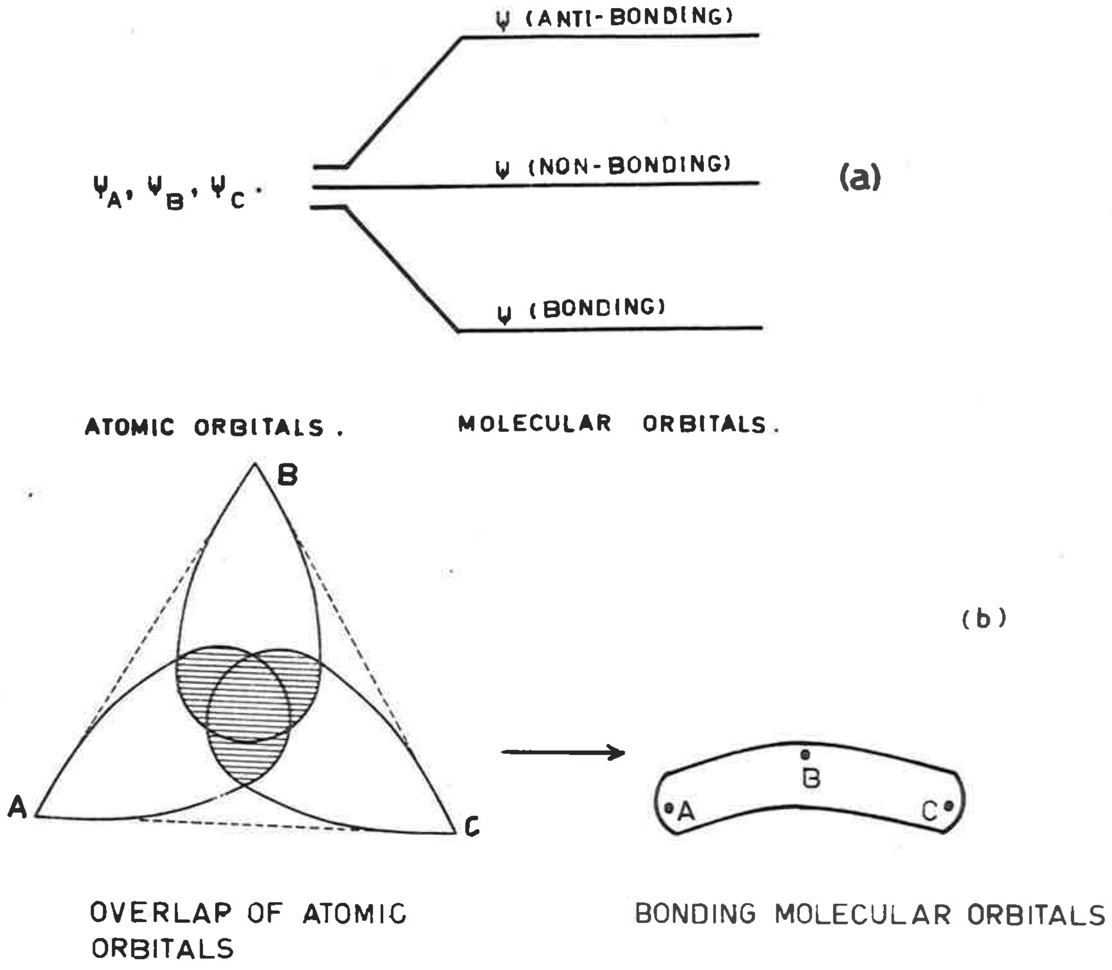
The Structures and Reactions of Some Organometallic Compounds

1. Some special types of organometallics.-

(a) Electron-deficient compounds.

The term "electron-deficient" is applied to compounds for which the number of two-centre bonds exceeds the number of valence electron pairs.[1] Although the hydrides of boron provide the best known examples of electron-deficient molecules, the property is general to many other chemical compounds. Discovery of the polymeric nature of trimethyl-aluminium,[2] and of tetramethyl-platinum,[3] together with the advent of new physical evidence, led to the realization that a number of organometallic compounds are also electron-deficient. It is with the lower alkyls of aluminium that the present discussion is principally concerned.

All electron-deficient compounds are composed, in part, of atoms (very often metals) which have fewer valence electrons than low energy bonding orbitals, and which are combined with other atoms or groups containing no unshared electron pairs. For some time this situation posed a serious problem for the classical theories of valency. The theory of electron-deficient bonding now proposes[1] that bonding is delocalized so as to make use of all the low energy orbitals of the 'metal'. For instance, three atoms may each supply a single atomic orbital, and interaction between the three atomic orbitals yields bonding, non-bonding, and anti-bonding three-centre molecular orbitals (Fig. 1.1). Bonding results from the accommodation of two



<u>Fig.1.1</u> The formation of three-centre molecular orbitals from three atomic orbitals.

electrons in the bonding orbital.

The above principles may be illustrated by considering the structures of aluminium trichloride and of trimethyl-aluminium.

In many compounds of aluminium, the metal expands its covalency to four (or more in some special instances), the aluminium forming four bonds that are directed approximately towards the corners of a tetrahedron. This can be achieved by the polymerization of 'AlX_3' units, or alternatively by the formation of coordination compounds with donor molecules, e.g.

$$(AlCl_3)_2 + 2\ Et_3P \longrightarrow 2\ Et_3P{\cdot}AlCl_3.$$

Aluminium trichloride, which is dimeric in the gas phase,[4] has been assigned a bridge structure (Fig. 1.2). The terminal Al-Cl linkages are formed by the overlap of an aluminium sp^3 hybrid orbital with a p orbital of a chlorine. The bridging chlorine atoms form normal electron pair bonds with one aluminium in the same manner, but also make use of a non-bonding electron pair to form a dative bond to a second aluminium atom. In this way, both the aluminium and chlorine atoms attain completed electron shells.

However, since methyl groups do not have any electron pairs available for donation, the structure of the trimethyl-aluminium dimer cannot be represented by such a system of conventional electron pair bonds. Nevertheless, a bridge structure is indicated by the infra-red spectrum,[5] and has been confirmed by X-ray crystallographic analysis.[6] The structure shown in figures 1.2 and 1.3 is thus favoured for trimethyl-aluminium. The molecular dimensions of this model are summarized in table 1.1.

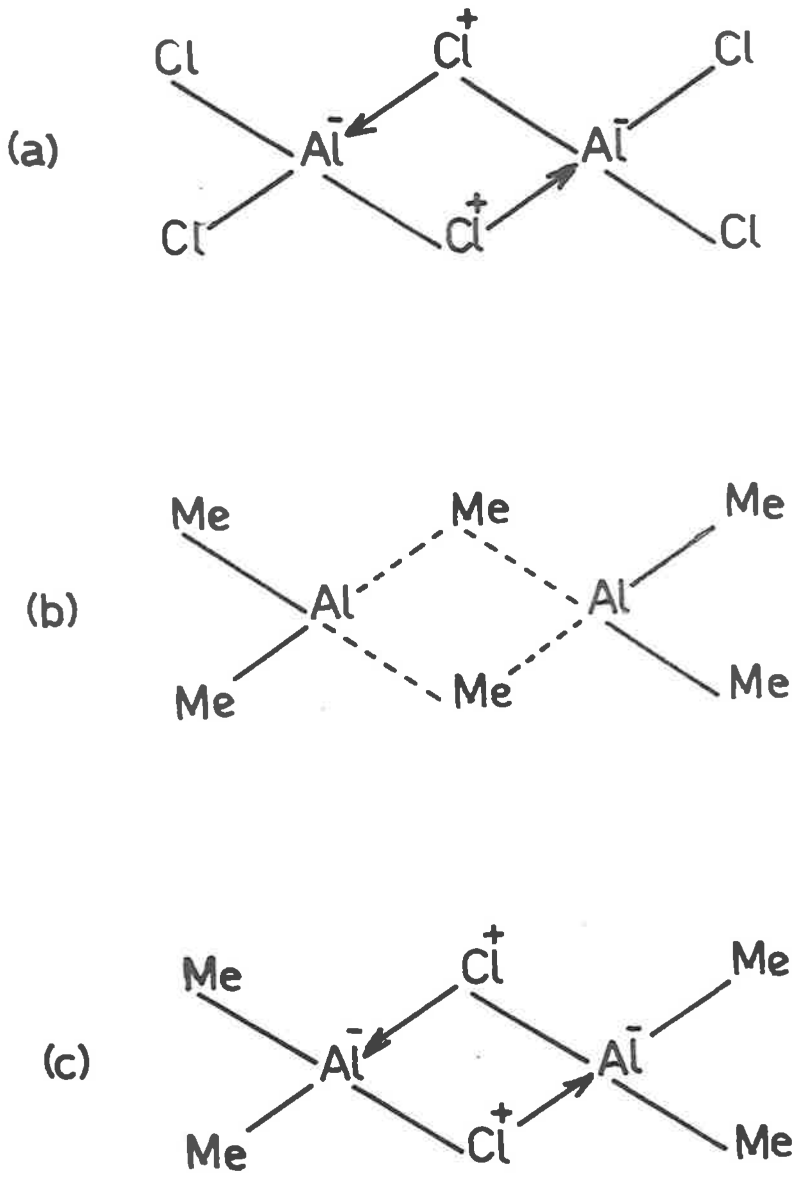


Fig. 1.2 Stuctural formulae of dimeric aluminium compounds: (a) aluminium trichloride, (b) trimethyl-aluminium, (c) dimethyl-aluminium chloride.

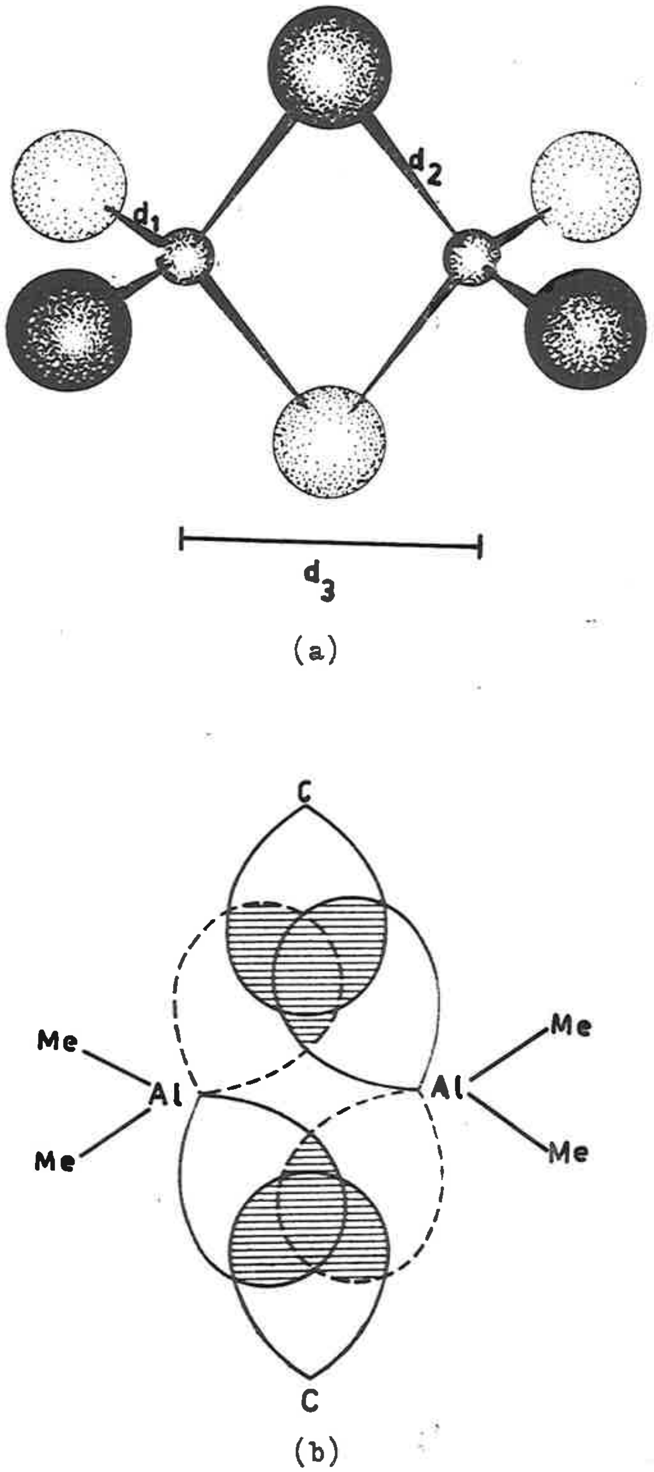


Fig. 1.3 Schematic representation of (a) the molecular stucture of trimethyl-aluminium, and (b) the bonding atomic orbitals in the bridge of trimethyl-aluminium.

Table 1.1

Comparison of the calculated and observed molecular dimensions for the trimethyl-aluminium dimer

a). Bond distances.	Calc.	Obs.
Terminal Al-C single bond length, (d_1)	2.03A°	1.99A°
Bridged Al-C half bond length, (d_2)	2.21A°	2.24A°
Al-Al single bond length, (d_3)	2.52A°	2.55A°

b). Bond angles.	
Normal tetrahedral angle	109°
Al-C-Al angle	70°
C-Al-C internal angle	110°
C-Al-C external angle	124°

The bond distance d_1 is found to correspond quite well with the calculated Al-C single bond length. Similarly, the distance d_2 agrees closely with the calculated[7] length of a half bond from aluminium to carbon. The acuteness of the Al-C-Al angle reduces the distance d_3 to approximately that required for an Al-Al single bond. This suggests there will be a substantial contribution of metal-metal bonding within the structure.

The most satisfactory explanation of the bridge bonding is that it is due to the formation of three-centre molecular orbitals compounded from (Al sp^3 + C sp^3 + Al sp^3). These orbitals are occupied by a pair of electrons so that the Al-C-Al could be regarded as a bent single bond. Alternatively, each Al-C bridge linkage could be viewed as a half bond.[8]

It follows that the sharp Al-C-Al bridge angle is a result of the metal sp^3 hybrid orbitals tending to attain better overlap with the one tetrahedral orbital of the bridge methyl (Fig. 1.3).

Higher alkyls of aluminium have less tendency to dimerize since the larger alkyl groups would hinder the necessary close approach for bonding with the C sp^3 hybrid orbitals.[9] In the same way, because of the greater size of the metal atoms, there is rather less tendency for alkyls of gallium, indium, and thallium to dimerize[6] (although trimethyl-indium does form a tetramer[10]). However, although boron atoms have a smaller atomic volume than aluminium, trimethylborane shows no tendency towards association. It is generally accepted that this lack of association is due to a hyperconjugation effect which plays a major role in determining the structure of boron alkyls.[11] The low electronegativity possessed by boron is also considered to be significant.

Mixed alkyl-aluminium halides are also dimeric, both in the vapour state and as solutions, and have been assigned[12] the structure shown in figure 1.2. Methyl bridged structures have also been proposed,[13] but seem less satisfactory. The bridge structure was previously indicated by electron diffraction studies.[14]

This constitution of aluminium alkyls leads to rapid reaction with Lewis bases, or other nucleophilic reagents. Thus the trimethylaluminium dimer is readily dissociated, for instance, by reaction with a tertiary amine, tertiary phosphine, alkyl ether, thioether, dialkyl selenide, or dialkyl telluride,[15] e.g.

$$Me_6Al_2 + 2\ PMe_3 \longrightarrow 2\ Me_3Al{\cdot}PMe_3.$$

Saturation of the electron-deficiency in this way appreciably diminishes the chemical reactivity of an aluminium alkyl. In contrast to simple aluminium alkyls, the products possess both a high dipole moment[16] and a high electrical conductivity.[17] These properties have been used to follow the course of such reactions.

The bridge in the dimethyl-aluminium chloride dimer, which is not electron-deficient, is also readily split by a strong donor such as trimethylamine, e.g.

$$Me_4Al_2Cl_2 + 2\ NMe_3 \longrightarrow 2\ Me_2AlCl{\cdot}NMe_3.$$

The cleavage in this case can be attributed to the relatively weak donating properties of chlorine.

Trialkyl aluminium compounds also form a number of complexes with other organometallics,[18] e.g. $LiAlEt_4$ and $MgAl_2Me_8$, and with alkali metal halides,[19] e.g. $K^+AlEt_2Cl_2^-$ and $Na^+Al_2Et_6F^-$. These compounds are also less reactive than the simple aluminium alkyls. They will be discussed more fully in the next section.

(b) Alkali metal derivatives of organometallic compounds.*

Aluminium forms a number of well characterized double salts

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* Nomenclature of bimetallic alkyls: Several systems for the naming of these compounds have been adopted in the recent literature. In accordance with the nomenclature used in recent Chemical Society publications, the compounds will be named as follows: $LiAlEt_4$ - lithium tetraethylaluminate, $NaPbEt_3$ - triethylplumbyl sodium, $LiSnEt_3$ - triethylstannyl lithium.

of the form $M^+(AlX_4)^-$, (M = alkali metal, X = halogen).[20] In the same way, aluminium alkyls tend to add alkyl ions to form compounds of the type $MAlR_4$.[21] The following table lists the known alkali metal complexes of this type.

Table 1.2

Known alkali metal derivatives of aluminium alkyls

Alkali metal	Alkyl group Me	 Et	 Higher R
Lithium	+	+	+
Sodium	+	+	+
Potassium	-	-	+
Rubidium	-	-	-
Cesium	-	-	-

Similar compounds with other organometallics are also known, e.g. $Mg(AlR_4)_2$, $Na(ZnR_3)$.

Fused lithium tetraethylaluminate has a specific conductivity of ca. 10^{-3} $ohms^{-1}$ cm^{-1}, whereas sodium tetraethylaluminate is a much better electrolyte (specific conductivity = $4 - 5 \times 10^{-2}$ $ohms^{-1}$ cm^{-1}).[22] These conductivity measurements indicate that lithium tetraethylaluminate has an essentially covalent and therefore electron-deficient structure, whereas the sodium analogue is appreciably ionic. The structures shown in figure 1.4 therefore seem feasible.

It seems reasonable to predict that the bonding in the lithium compound may be due to the overlap of a distorted sp hybrid orbital of the lithium with a sp^3 hybrid orbital of a bridge carbon,

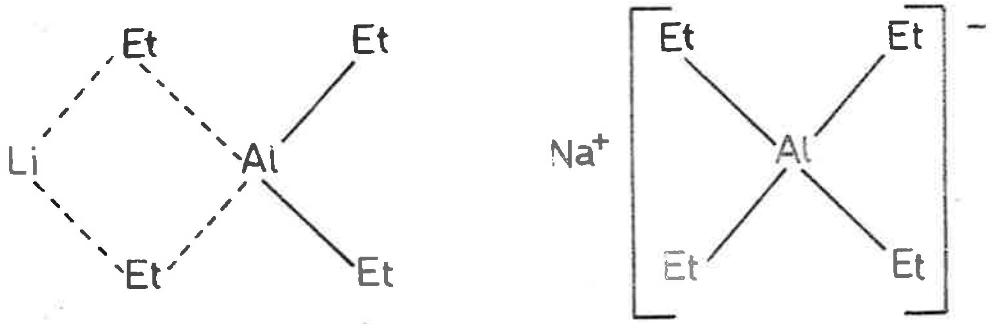


Fig. 1.4 Structural formulae of alkali metal derivatives of aluminium alkyls: (a) lithium tetraethylaluminate, (b) sodium tetraethylaluminate.

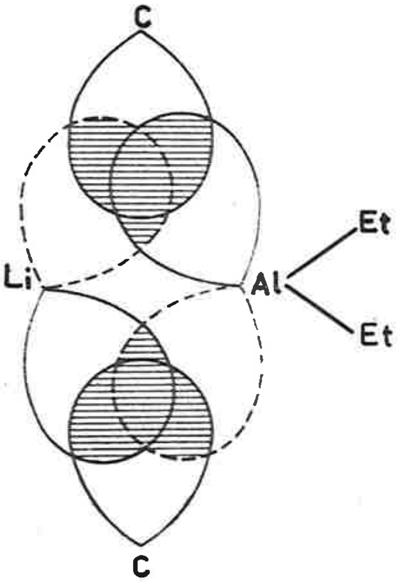


Fig. 1.5 Schematic representation of possible bonding atomic orbitals in the bridge of lithium tetraethylaluminate.

coupled with the previously described (C sp^3 + Al sp^3) interaction (Fig. 1.5); i.e. three-centre molecular orbitals are formed from (Li sp + C sp^3 + Al sp^3) and the bonding orbitals are each occupied by a pair of electrons.

A large number of compounds of the general formula $MAlR_nX_{4-n}$ have also been described in the literature.[19] It has been established[23] that the formation of such complex species is favoured as the ratio of halogen to alkyl increases. Thus, whereas $KAlEt_2Cl_2$ has been prepared, $KAlEt_3Cl$ is too unstable to be isolated. Furthermore, the stability of these compounds is favoured by large cations and small anions. Hence lithium forms no alkyl aluminium complexes except lithium tetra-alkylaluminates. Table 1.3 illustrates these principles.

Table 1.3[23]

Stable 1:1 complexes formed from triethyl-aluminium and halides of the cations shown[23]

	H^-	F^-	Cl^-	Br^-	I^-
Li^+	+	-	-	-	-
Na^+	+	+	-	-	-
K^+	+	+	+	-	-
Rb^+	+	+	+	+	-
Cs^+	+	+	+	+	-
R_4N^+	+	+	+	+	+

These compounds are essentially ionic in nature, e.g. $Na^+(AlEt_3F)^-$.

Although the group IVB metals generally show no tendency to expand their covalency above four, a few bimetallic alkyl complexes of these elements, in which a co-ordination number of four is maintained, are known,[24] e.g. $NaPbEt_3$, Na_2SnMe_2. These compounds are generally quite unstable and hence are not isolated, but are used immediately for further reactions. Even though relatively little physical information is available, they can almost certainly be formulated as ionic species, e.g. $M^+(R_3M')^-$. If this is so, the $(R_3M')^-$ anion is analogous to a carbanion and hence is a strong nucleophilic reagent. This is consistent with their chemical behaviour. The lead compounds can, for instance, form a new Pb-C bond by a nucleophilic displacement of a group attached to carbon,[25] e.g.

$$R_3PbM + R'X \longrightarrow R_3PbR' + MX.$$

It has been established[26] that an equilibrium of the form

$$LiSnEt_3 \rightleftharpoons LiEt + SnEt_2$$

exists when some of the tin compounds are dissolved in ether. This equilibrium is particularly interesting in that it represents a spontaneous and reversible change between tin(II) and an anionic species derived from tin(IV).

The preparations and chemical reactions of these compounds are discussed more fully in subsequent chapters.

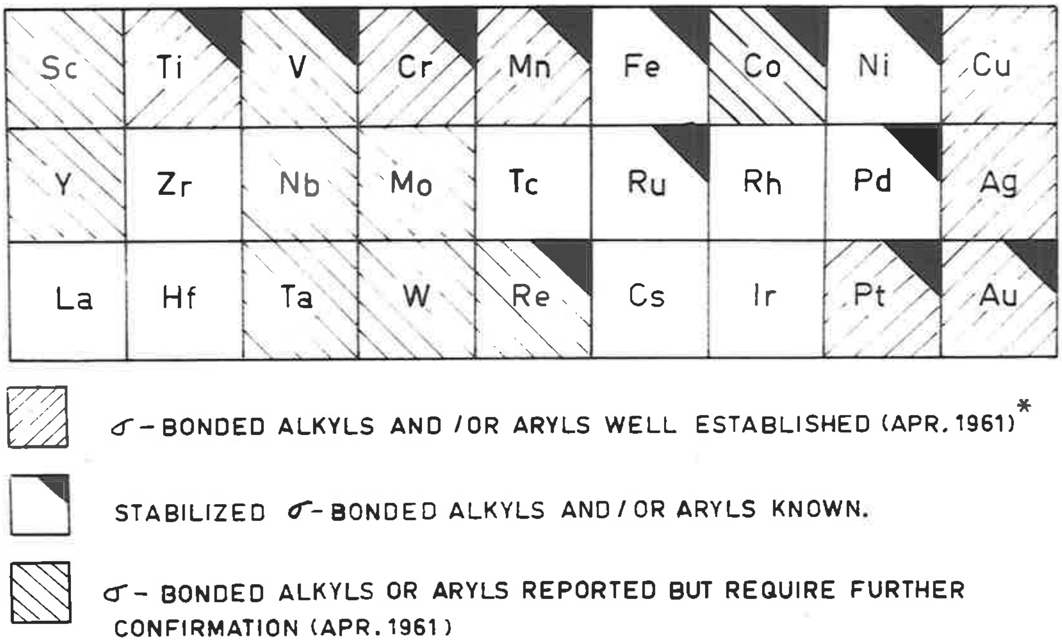
(c) Transition metal alkyls.[27]

At the present time there are relatively few transition metals which are known to form isolable organometallics of the type MR_n or $MR_{n-x}X_x$ (M = transition metal, R = alkyl group, X = anionic group such as halide, n = valence of transition metal). Many workers have endeavoured to prepare them in the classical manner, but with the exception of the stable methyl-platinum polymers,[3] and a few compounds of titanium,[28] manganese,[29] and gold,[30] none have been satisfactorily characterized (Fig. 1.6). However, recent investigations in the field of Ziegler polymerization catalysts, which are generally composed of mixtures of normal metal alkyls and transition metal compounds, have given great stimulus to the study of such transition metal alkyls. The results of these investigations will be discussed in a subsequent section of this chapter.

Very recently, a number of quite different σ-bonded alkyl and aryl complexes of transition metals have been described.[31] These compounds, which are remarkably stable, are of the general form $MR_{x+y}L_z$ or $MR_xX_yL_z$ (L = uncharged ligand). Typical examples are $(C_5H_5)_2TiMe_2$, $EtMn(CO)_5$, and $MePtCl(PEt_3)_2$. (See "stabilized σ-bonded alkyls" in Fig. 1.6.)

Two factors have contributed most to these recent successes in the preparations of organo-derivatives of transition metals. Firstly, it has been found that close attention must be paid to the experimental conditions (e.g. a low temperature must be maintained throughout the preparation and isolation of titanium alkyls). Secondly, it has become apparent that certain electronic conditions must be realized for maximum stability (e.g. it is significant that all the most stable transition metal organometallics contain transition metals which have attained the electronic configuration of the next inert gas, or only a few electrons short of this number).

As a result of these observations, a clearer understanding



Sc ▧	Ti ▨ ◥	V ▧ ◥	Cr ▨ ◥	Mn ▨ ◥	Fe ◥	Co ▧ ◥	Ni ◥	Cu ▨
Y ▧	Zr	Nb ▧	Mo ▧	Tc	Ru ◥	Rh	Pd ◥	Ag ▨
La	Hf	Ta ▧	W ▧	Re ▧ ◥	Cs	Ir	Pt ▨ ◥	Au ▨ ◥

▨ σ - BONDED ALKYLS AND / OR ARYLS WELL ESTABLISHED (APR. 1961)*

◥ STABILIZED σ- BONDED ALKYLS AND / OR ARYLS KNOWN.

▧ σ - BONDED ALKYLS OR ARYLS REPORTED BUT REQUIRE FURTHER CONFIRMATION (APR. 1961)

Fig. 1.6 Transition metal alkyls and aryls.

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* Only aryl compounds of Cr and Cu well authenticated. Results for Sc, Y, and V are very inconclusive.

of the theory of bonding in transition metal alkyls is beginning to emerge. Jaffé has pointed out[32] that transition metal-carbon σ-bonds are thermodynamically unstable, and that the electronegativity difference between a transition metal and carbon is insufficient to lead to stable ionic bonds. Recent developments of these principles are discussed below.

Since the discussion in subsequent chapters is principally concerned with titanium alkyls, a few specific remarks about the bonding in these compounds will be presented first. These will be followed by some more general remarks about the stability of transition metal alkyls.

The first compound containing an authentic titanium-carbon bond to be studied was phenyl-titanium tri-(isopropoxide), $PhTi(PrO^i)_3$. This aryl-titanium derivative was isolated in 1953 by Herman and Nelson.[33] These workers anticipated that titanium(IV) could form moderately stable σ-bonds to other hydrocarbon groups provided that there were at least two electronegative groups also attached to titanium. They proceeded to investigate the factors affecting the stability of compounds of the general form R_nTiX_{4-n}, and ascertained that:

(i) the stability of the Ti-C bond is greatest in those compounds where the R group is relatively negative, e.g. phenyl, naphthyl;

(ii) the most stable alkyl-titanium compounds are those in which only one, or at most two, R groups are attached to titanium;

(iii) the stability is enhanced if the X groups are of an optimum electronegativity - between that of fluorine and that of chlorine.

In addition they concluded that although more than one R group causes instability in titanium(IV) compounds, dialkyl-titanium(II) and trialkyl-titanium(III) compounds would probably be relatively stable. Since then, a number of compounds containing methyl-titanium(IV) and ethyl-titanium(IV) linkages have been prepared.

It seems pertinent at this stage to compare, on theoretical grounds, the type of bonding expected in titanium halides and in titanium alkyls. Coates[34] has pointed out that since there is a large electronegativity difference between titanium and halogens, it is feasible to consider that the titanium-halogen bond in titanium halides will be strongly polar. Calculations, based on the Slater radial functions,[35] show the maximum radial functions for neutral titanium in the $3d^3 4s$ configuration to be

$$r_m\ (3d) = 2.7\ A^\circ$$
$$r_m\ (4s) = 5.1\ A^\circ$$

whereas, for a valence electron in chlorine,

$$r_m\ (3p) = 1.5\ A^\circ.$$

Such diffuse titanium orbitals cannot overlap effectively with the rather compact chlorine orbitals, and so strong bonding cannot be realized between neutral titanium and chlorine. If, however, polarisation of the atoms is considered, the orbitals of titanium would contract as the metal became more positive, whereas the chlorine orbitals would expand thus allowing better orbital overlap between $Ti^{\delta+}$ and $Cl^{\delta-}$. In actual fact, the position is somewhat more complex than this since it is necessary to consider some p orbital contribution to achieve maximum bonding power. Ultimately, then, bonding in titanium tetrahalides is best considered in terms of overlap between contracted $Ti^{\delta+}$ orbitals, formed from an admixture of a small proportion of sp^3 hybrid orbitals with the d^3s orbitals, and expanded p orbitals of $Cl^{\delta-}$.

With the titanium-carbon bond in titanium alkyls, the tetrahedral orbitals of carbon are again much more compact than the 3d and 4s orbitals of titanium, but here the weaker electronegativity of carbon relative to chlorine eliminates the possibility of considerable orbital contraction due to polarization. For this reason, orbital overlap is small, resulting in weak bonding. Indeed, but for p orbital contribution of the type mentioned above in the titanium halide discussion, it is considered unlikely that titanium σ-alkyls would be formed at all.

In a much more general approach to the theory of bonding in these compounds, the instability has been considered in terms of the special electronic structures of the transition metals.[31] In effect, this theory is concerned with a consideration of the energy gap between the highest occupied d orbital of the metal, and the lowest antibonding molecular orbital. Promotion of electrons from such a filled d orbital into an antibonding σ-orbital of the metal-carbon bond should weaken the metal-carbon bond. Alternatively, if the d orbitals are empty (as with the titanium compounds) promotion of electrons from the carbon-metal bonding orbitals into a vacant metal d orbital will cause a weakening of the carbon-metal bond. As a consequence, stable organometallics can only be formed when the energy difference between the highest energy orbital which contains electrons and the lowest energy orbital which does not is greater than a certain minimum energy difference (Fig. 1.7). In general, most organo-transition metal derivatives do not meet this requirement since the transition metals possess close d energy levels. Furthermore, these d orbitals are on an energy level very close to the valency s and p orbitals.

It is considered that the metal-carbon bond, rather than other metal-ligand bonds, is affected since dissociation of the metal-carbon bond will very likely produce an unstable entity (e.g. a hydrocarbon radical or carbanion), whereas dissociation of the familiar ligands generally results in the formation of ions (e.g. NO_3^-), or of neutral molecules (e.g. NH_3), all of which are stable. This latter dissociation is likely to be reversible, but the metal-carbon bond dissociation will almost invariably be irreversible.

Stabilization of transition metal alkyls can often be achieved by complexing them with donors such as tertiary phosphines, carbon monoxide, and cyclopentadiene. In these compounds, the energy difference referred to above is increased by lowering the energy of the non-σ-bonding orbitals. This lowering of energy results from a combination of these non-σ-bonding orbitals with π-type orbitals of low energy on suitable ligands. In this way the stability of compounds like $EtMn(CO)_5$, $(PEt_3)_2PdMeBr$, and $C_5H_5Mo(CO)_3CH_3$, can be readily explained.

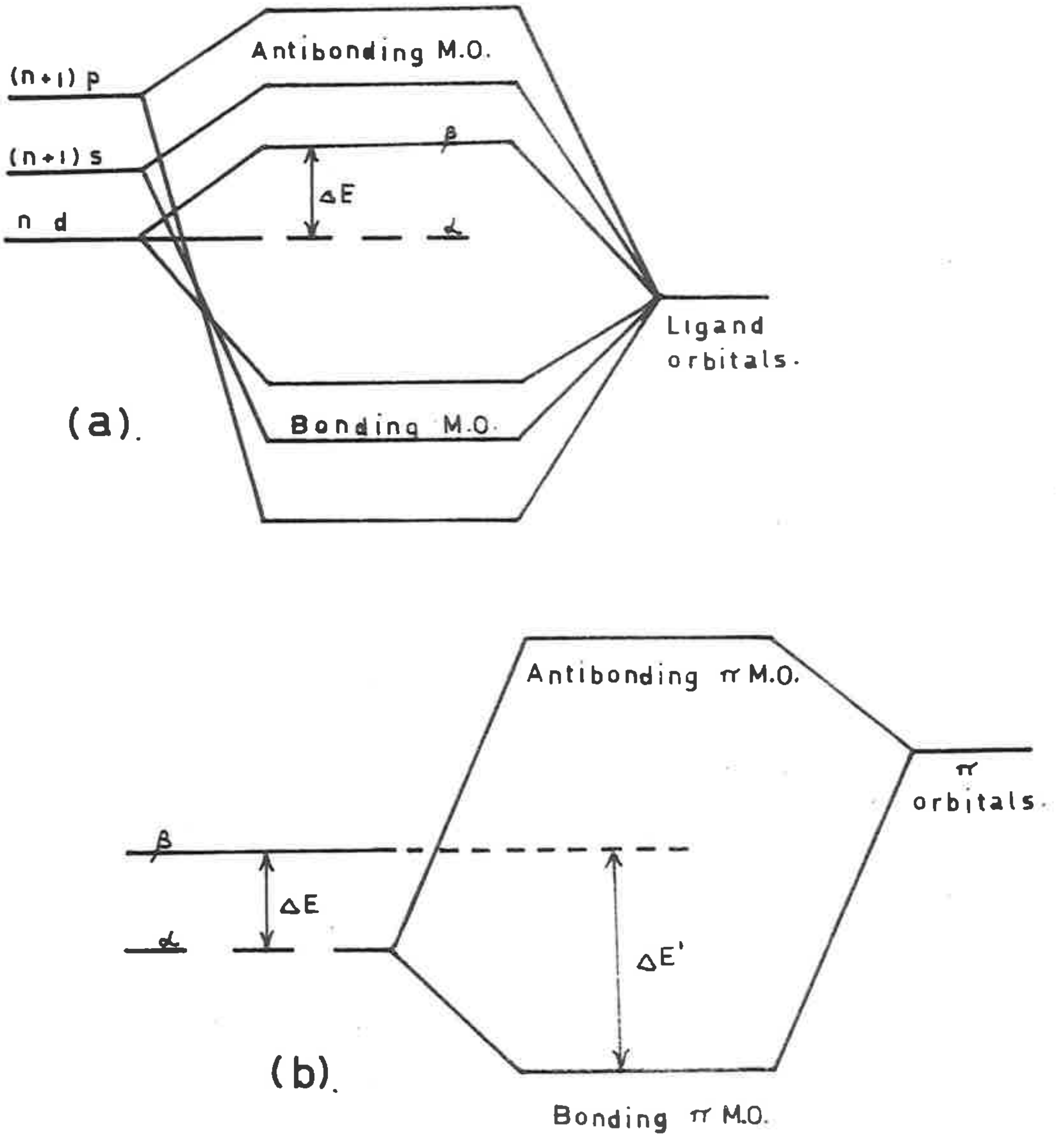


Fig. 1.7 Diagrammatic representation of the energy difference between the highest occupied electronic level (α) and the lowest vacant electronic level (β) of transition metal complexes.
(a) General case.
(b) The effect of π-bonding for acceptor ligand orbitals.

(d) Fluorocarbon derivatives of metals.

The terms "fluoroalkyl" and "perfluoroalkyl" are used to denote partially and fully fluorinated alkyl groups respectively.[37] Thus $C_2F_4H\cdot$ is an example of a fluoroalkyl group, and $C_3F_7\cdot$ is typical of perfluoroalkyl groups.

Although a large number of fluorocarbon derivatives of the non-metallic elements have been thoroughly investigated, especially by Emeléus[38] and Haszeldine[39] and their coworkers, relatively little is known of fluoroalkyl-metal compounds. Only a few such compounds have been satisfactorily characterized. These are briefly discussed below.

Perfluoroalkyl-lithium derivatives can be prepared in high yield by an exchange reaction involving a lithium alkyl and perfluoroalkyl iodides,[40] e.g.

$$RLi + C_3F_7I \longrightarrow C_3F_7Li + RI.$$

Perfluoroalkyl derivatives of magnesium,[41] zinc,[42] and mercury[43] can be prepared from the appropriate metal and a perfluoroalkyl iodide. The magnesium and zinc derivatives must be prepared in a basic solvent, such as tetrahydrofuran, but the mercury compounds are best obtained in the absence of a solvent.

$$Hg + R_fI \xrightarrow[\text{ultraviolet}]{\text{heat}} R_fHgI \xrightarrow{Cd/Hg} (R_f)_2Hg.$$

Perfluoroalkyl Grignard reagents have also been prepared by exchange reactions between perfluoroalkyl iodides and arylmagnesium halides,[44] e.g.

$$PhMgBr + R_fI \longrightarrow R_fMgI + PhBr.$$

With the exception of the mercury derivatives, these perfluoroalkyl compounds are much less thermally stable than their hydrocarbon analogues.

Normal alkyl derivatives of metals are most generally prepared by the treatment of the appropriate metal halides with an alkyl of lithium, magnesium, zinc, or mercury. However, attempts to extend this method of synthesis to the preparation of fluoroalkyl derivatives of metals has, in general, proved disappointing. This is no doubt largely due to the relative instabilities of the lithium, magnesium, and zinc compounds. However, even the more stable mercury derivatives have not yielded new perfluoroalkyl-metal compounds in those reactions with metals or metal halides which have been investigated.[43]

Some degree of success with this type of reaction has been achieved by adding the metal halide and perfluoroalkyl iodide simultaneously to magnesium in tetrahydrofuran,[37] e.g.

$$R_{4-n}SnCl_n + R_fI \xrightarrow{\text{Mg in THF}} R_{4-n}Sn(R_f)_n \qquad n = 1,2.$$

In addition, Griffiths and Burg[45] have prepared bis(trifluoromethyl)-mercury by treating mercuric oxide with tris(trifluoromethyl)phosphine.

Recently, a number of stable fluorocarbon derivatives of tin and lead have been prepared by exchange reactions between the metal alkyls and perfluoroalkyl iodides,[46] e.g.

$$R_4Pb + R_fI \xrightarrow[\text{ultraviolet}]{\text{heat or}} R_3PbR_f + RI$$

and by cleavage reactions involving bimetallic alkyls and perfluoroalkyl iodides,[47] e.g.

$$R_3Sn.SnR_3 \ + \ R_FI \xrightarrow[\text{ultraviolet}]{\text{heat or}} R_3SnR_F \ + \ R_3SnI.$$

Within the last few years, a large number of fluorocarbon derivatives of transition metals have been prepared.[37] In contrast to their hydrocarbon analogues, these compounds are generally quite stable.

The properties of many of the fluoroalkyl-metal compounds described above are markedly different from those of their normal alkyl-metal analogues. Some of the most distinctive differences are listed below.

(i) Many metals, which normally form stable alkyls, yield only unstable fluoroalkyl derivatives. On the other hand, there is a marked increase in the stability of fluoroalkyl derivatives of transition metals over their normal alkyl analogues.

(ii) Although dimethyl-mercury is a typical covalent liquid which is quite insoluble in water, bis(trifluoromethyl)mercury is a white crystalline solid which readily dissolves in water forming a 1.3 molar solution, the aqueous solution behaving as a weak electrolyte.

(iii) From mixed alkyl-perfluoroalkyl derivatives of tin and lead, alkyl groups are preferentially cleaved by acids and perfluoroalkyl groups by bases.

(iv) Whereas dissociation of the metal-carbon bond in a metal alkyl will generally yield a reactive hydrocarbon radical, thus making the dissociation irreversible, dissociation of a metal-perfluoroalkyl linkage often produces a metal fluoride and an unsaturated fluorocarbon.

It seems important to consider what impact such developments in fluorocarbon-metal chemistry have had on the theory of the metal-carbon bond.

An attempt to correlate the existing ideas on the theory of the fluorocarbon-metal bond is presented below.

Many of the above-mentioned properties are understandable in terms of the high electronegativity of fluoroalkyl groups. It has been established[36] that the effective electronegativity of a trifluoromethyl group lies between that of fluorine and that of chlorine (Table 1.4).

Table 1.4

Comparison of the electronegativities of perfluoroalkyl, alkyl, and halide groups

Group	Electronegativity (Pauling scale)
F	4.0
(CF_3)	3.3
Cl	3.0
C	2.7
(CH_3)	-
H	2.1

This property leads to an explanation of both the instability of fluoroalkyl derivatives of many metals, and the contrasting stability of many transition metal fluorocarbon derivatives. A consideration of the electronegativities of the various metals and metalloids which are known to form fluoroalkyl derivatives (Table 1.5) indicates that the electronegativity difference between the fluoroalkyl group and the metal or metalloid may be of primary importance in determining which elements will form stable $M-R_f$ linkages.

Table 1.5

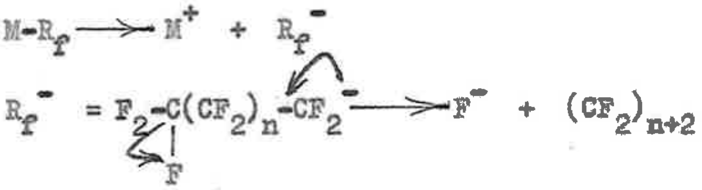
Electronegativities of metals and metalloids known to form fluoroalkyl derivatives

Metal	Electronegativity (Pauling scale)
Pb	2.4
As	2.0
B	2.0
Hg(II)	1.9
Si	1.8
Sb	1.8
Sn	1.7
Al	1.5
Zn	1.5
Mg	1.2
Li	1.0

It is at once obvious that elements with an electronegativity greater than that of tin (with the notable exception of boron) are known to form stable fluoroalkyl-metal derivatives, whereas aluminium, zinc, magnesium, and lithium form derivatives which are notably unstable. It seems reasonable to consider that the bonds between perfluoroalkyl groups and these latter metals are appreciably dissociated into metal ions and fluorinated carbanions. This dissociation will probably be irreversible because the fluorinated carbanions are chemically reactive. In solution they undergo reactions of the type[48].

$$R_F\cdot \; + \; RH \longrightarrow R_FH \; + \; R\cdot \qquad \text{(where RH = solvent)}$$

However, a number of fluoroalkyl-metal derivatives decompose without the formation of much 'R_fH', indicating that an alternative mode of fluorinated carbanion decomposition must exist. Furthermore, this alternative decomposition mechanism is necessary to account for the observed formation of metal fluorides and unsaturated fluorocarbons. Hasseldine[49] has suggested that the metal-fluoride bond could be formed by the breakdown of the fluorinated carbanion according to one of the following schemes:

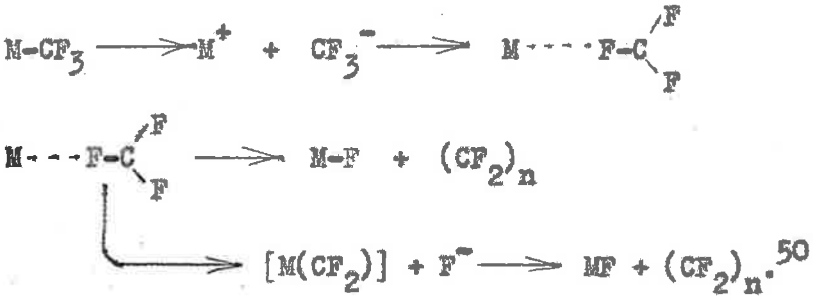


or

$$CF_3MgI + CF_3I \longrightarrow CF_3MgF + CF_2I_2$$

$$2\ CF_2I_2 \xrightarrow{Mg} C_2F_4.$$

Alternatively, the acceptor properties of the metals could influence the dissociated fluorinated carbanion so that a fluorine of the carbanion becomes co-ordinated with the metal. In this way, a metal-fluoride bond could be formed by breakdown of the fluorinated group according to:



or

It is difficult to explain the observation[42] that perfluoroalkylzinc compounds do not react with carbon dioxide in spite of the fact that rapid reaction between carbon dioxide and 'R_f^-' would be expected. Such a reaction is observed with perfluoroalkyl Grignard reagents.

With transition metal compounds, the high electronegativity of the fluoroalkyl groups could be expected to induce orbital contraction of the d and s orbitals of the transition metal. In this way, the possibility of good overlap, and hence strong bonding, is enhanced.

The high electronegativity of fluoroalkyl groups also leads to a simple explanation of the water solubility of perfluoroalkyl-mercury derivatives. However, it has been fairly well established[51] that the conductivity of aqueous solutions of perfluoroalkyl-mercury compounds is due to the formation of complex ionic species in which the nature of the $Hg-R_f$ linkages is unaffected.

It was recently pointed out that it may be more pertinent, in some instances, to consider the electron density on the α-carbon of a perfluoroalkyl group rather than the electronegativity of the group as a whole. This is particularly true in seeking to explain the cleavage of metal-carbon bonds, in mixed alkyl-perfluoroalkyl-metal derivatives, by acids and bases. Although Pitcher and Skinner[52] have established that the relative ease of cleavage of organic groups from metals may be correlated with the electronegativity of the organic groups, it was recently observed that perfluoroalkyl groups do not fit into the series in the expected manner. In spite of the high electronegativity of perfluoroalkyl groups, both phenyl and alkyl groups are preferentially cleaved from metals by acids.

In mixed alkyl-perfluoroalkyl-metal derivatives, the inductive factor renders an unfluorinated carbon atom more electron rich than a fluorinated carbon. Since cleavage by acids involves an electrophilic attack on the carbon, e.g.

$$\overset{\delta+}{M}-\overset{\delta-}{C}- + H^{+} \longrightarrow M^{+} + -C-H$$

the unfluorinated group will be preferentially cleaved. However, cleavage by bases probably involves a nucleophilic attack on the metal atom, e.g.

$$\overset{\delta+}{M}-\overset{\delta-}{C}- + OH^{-} \longrightarrow MOH + C.$$

so that the perfluoroalkyl group is displaced easily on account of the high polarity of the bond between the metal and the perfluoroalkyl group.

With alkyl perfluorovinyl-metal compounds, the perfluorovinyl groups are preferentially cleaved by acids. This can be explained in terms of the effect of hybridization differences on the electron density at a particular carbon. In the perfluorovinyl-tin compounds, the fluoro group is bound to tin through a carbon atom which is sp^2 hybridized, not sp^3 as in the perfluoroalkyl derivatives. The presence of a filled p π-orbital in the perfluorovinyl derivatives is sufficient to attract the attacking electrophilic reagent.

2. The alkylation of inorganic halides by metal alkyls.

Many organometallic compounds react with other metal halides (or metalloid halides) to produce compounds containing a new carbon-metal bond. Indeed, this is the most commonly used method for preparing alkyl derivatives of all but the most electropositive elements. In general, it is considered that the reactions proceed according to:

$$MX + M'R \longrightarrow MR + M'X.$$

The general reaction may be illustrated by referring specifically to the conversion of stannic chloride to tetraethyl-tin by a Grignard reagent, e.g.

$$SnCl_4 + 4\ EtMgCl \longrightarrow SnEt_4 + 4\ MgCl_2.$$

It is generally accepted[53] that the driving force of such reactions is the decrease in energy of the system by the formation of a strong M'-X bond at the expense of the weaker M-X bond. Thus, as a general rule, it may be said that a halide of a metal will react in this way with an alkyl of a more electropositive metal.

Some of the organometallic compounds most commonly used to alkylate other metal halides are listed below.

Strong alkylating agents: RLi, RMgX, R_2Zn, R_3Al.

Weak alkylating agents : R_2Hg, R_4Pb.

Among the first metal alkyls to be used for such synthetic purposes were the organo-zinc compounds. However, their use as alkylating agents has now been almost entirely superseded by the use of the more reactive Grignard reagents. Grignard reagents are certainly the best known, and probably the most important, of all the metal alkyls used in synthetic chemistry. They have been widely used to alkylate a variety of metal halides, as well as many compounds of the non-metallic elements. In recent years, alkyl-lithium compounds have become increasingly important as alkylating agents because they are somewhat more reactive than Grignard reagents. This greater reactivity of alkyl-lithium compounds has led to their use in the preparation of a few organometallics, such as trimethyl-gold[54] and trimethyl-thallium,[55] which cannot be obtained with Grignard reagents.

It has recently been realized that alkyl-aluminium compounds have some properties which are distinctly different from those of magnesium and lithium alkyls. Thus alkylation with alkyl-aluminium compounds can be carried out without the expensive solvents required for Grignard and alkyl-lithium reagents. In this way, ether-free metal alkyls can be conveniently prepared. Mercury and lead alkyls act as mild alkylating agents towards reactive metal halides; of the two, tetra-alkyl-lead compounds are usually preferred.

3. The chemistry of Ziegler catalysts.

(a) Introduction.

Ziegler catalysts, which are generally composed of mixtures of normal metal alkyls and transition metal halides, are effective for the low pressure polymerization of α-olefins to polymers having a sterically regular structure.[56] Since the discovery of these systems by Ziegler[57] and his co-workers, a great deal has been done in an attempt to elucidate the nature of the catalysts, and the peculiar mechanism which gives rise to polymers having a stereoregular structure. A comparison of the experimental results obtained by different workers often shows these to be more or less contradictory. However, this may indicate little more than that the reaction conditions employed are critical in determining the nature of the products obtained from a particular reaction. In this discussion, it is assumed that this is so, and it is the purpose of this section to correlate the vast amount of published work on this topic into a brief summary of the present position in the field of Ziegler catalysis.

Since most investigations have been carried out on systems containing aluminium alkyls and titanium halides, the discussion will be concerned mainly with such systems. The material will be divided into three sections dealing, in turn, with the reduction of the transition metal, the formation of complexes, and the mechanism of polymerization.

(b) Reduction of the transition metal.

It has long been known[27b] that treatment of a transition metal halide with a metal alkyl often results in reduction of the transition metal. The collective observations of many individual workers[58] have indicated that there are a large number of factors which may influence the extent of reduction of a transition metal halide in this way. As has already been pointed out, careful control of the reaction conditions may preclude reduction of the transition metal altogether, and σ-alkyls of a few transition metals have been isolated in this way, e.g. tetramethyl-titanium has been prepared from titanium tetrachloride and methyl-lithium at -80°C.[59]

These low temperature reactions almost certainly indicate the nature of the first step in the reduction of a transition metal by a metal alkyl. Thus, as a first step in the reduction of a titanium halide by an aluminium alkyl, alkylation of the titanium species can be postulated, e.g.

$$TiX_4 + AlR_3 \longrightarrow RTiX_3 + AlR_2X$$

$$TiX_4 + 2\ AlR_3 \longrightarrow R_2TiX_2 + 2\ AlR_2X.$$

It is well known that these titanium σ-alkyls are thermally unstable, and will decompose, often below room temperature, with gas evolution and the formation of reduced titanium species. The following equations have been suggested[58] as representing the possible modes of such decomposition reactions.

$$RTiCl_3 \longrightarrow TiCl_3 + R^{\bullet}$$

$$R_2TiCl_2 \longrightarrow RTiCl_2 + R^{\bullet}$$

$$RTiCl_2 \longrightarrow TiCl_2 + R^{\bullet}$$

There are conflicting reports about a further mode of decomposition. The reactions

$$RTiCl_3 \longrightarrow TiCl_2 + RCl$$

$$(TiCl_2 + TiCl_4 \longrightarrow TiCl_3)$$

and $$TiCl_4 + R^{\bullet} \longrightarrow TiCl_3 + RCl$$

have been suggested[60] to account for the formation of alkyl halides, but many other workers dispute the existence of alkyl halides in the gaseous reaction products from such decompositions.

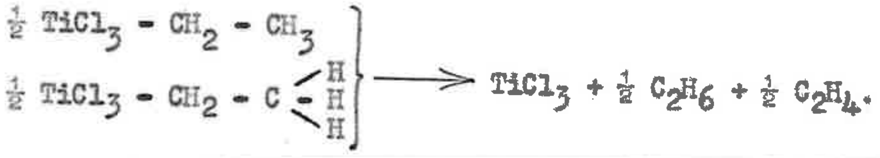
The fate of the 'R' radical has also been the cause of considerable speculation, but the following reactions probably contribute most to the decomposition of this species.[60b]

$$2\,R^{\bullet} = 2\,C_2H_5^{\bullet} \longrightarrow C_2H_4 + C_2H_6$$

$$2\,C_2H_5^{\bullet} \longrightarrow C_4H_{10}$$

$$C_2H_5^{\bullet} + R'H \longrightarrow C_2H_6 + R'^{\bullet} \qquad (R'H = \text{solvent}).$$

Recent evidence[61] indicates that such a homolytic fission to yield free alkyl radicals does not account for all the experimental observations (e.g. the absence of reaction with the solvent). de Vries favours a bimolecular disproportionation according to



$$\left.\begin{array}{l} \tfrac{1}{2}\,TiCl_3 - CH_2 - CH_3 \\ \tfrac{1}{2}\,TiCl_3 - CH_2 - C \begin{array}{l} \diagup H \\ - H \\ \diagdown H \end{array} \end{array}\right\} \longrightarrow TiCl_3 + \tfrac{1}{2}\,C_2H_6 + \tfrac{1}{2}\,C_2H_4.$$

A hydrogen on the β-carbon atom is essential for such disproportionation, and evidence is cited to illustrate that compounds containing no such hydrogen are relatively stable.

Among the more obvious of the factors which appear to affect the extent of reduction of titanium in such reactions are the ratio of reactants, the order of addition of the reactants, the temperature, and the nature of the 'R' group.

(c) The formation of complexes.

Rather earlier than the isolation of the simple alkyl-titanium compounds, some remarkable organometallic complexes were prepared from bis(cyclopentadienyl)titanium dichloride and aluminium alkyls.[27c] These compounds can act as homogeneous catalysts for the low pressure polymerization of ethylene, and represent the only stable catalysts of the Ziegler type which have been isolated. Notwithstanding this, a great deal of speculation has been entered into on the nature of other Ziegler catalysts. Several suggestions have been made concerning the nature of the initiating species, but in general, all of the suggestions can be classified into one of three types. This general classification is considered below.

(i) Bimetallic complexes.

As mentioned previously, complexes can be isolated from the interaction of bis(cyclopentadienyl)titanium dichloride and aluminium alkyls. One such complex has been characterized by x-ray crystallographic analysis[62] and is known to have the structure shown in figure 1.8.a. Breslow and Newburg[63] have shown that related organometallic complexes can act as soluble catalysts for the low pressure polymer-

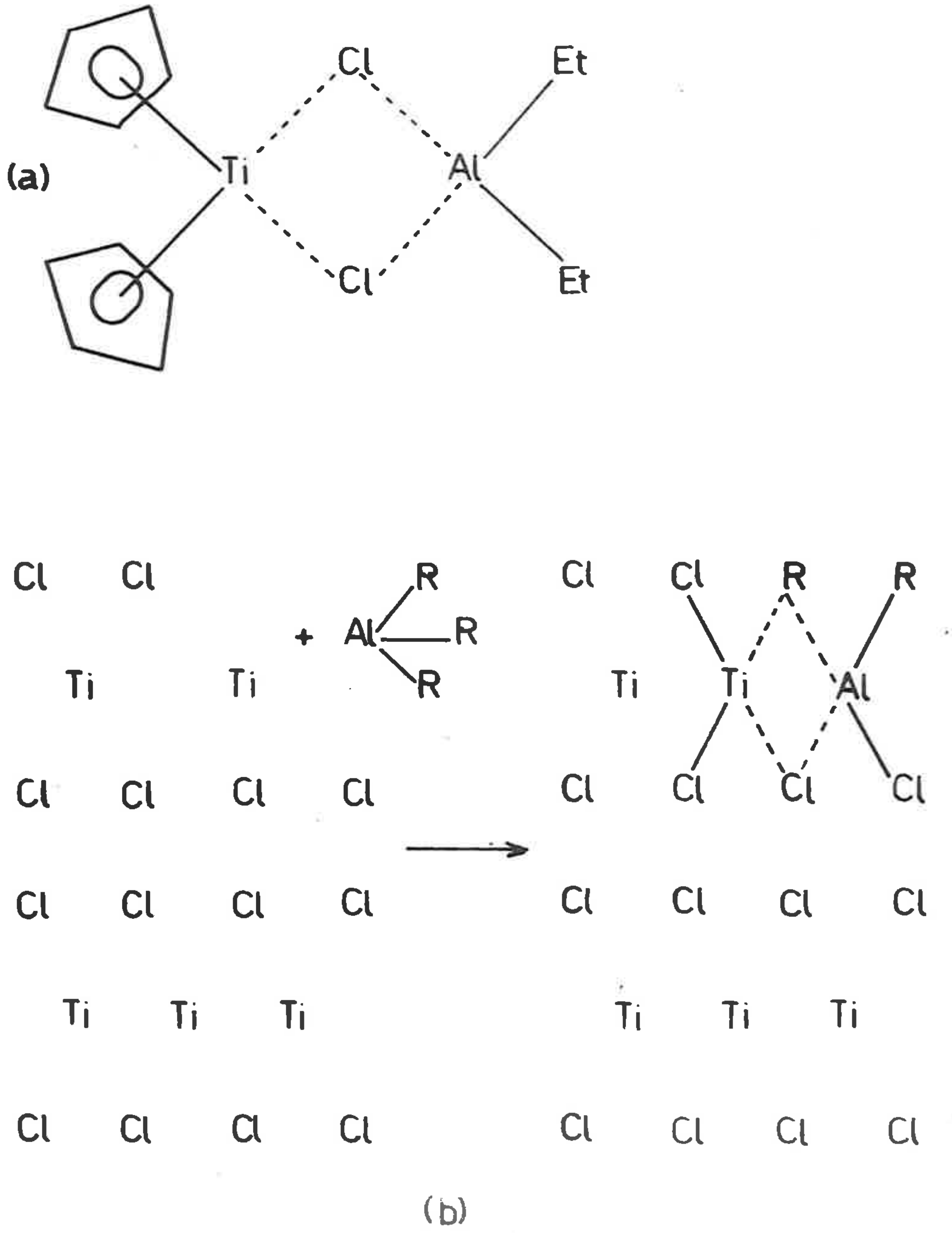


Fig. 1.8 Complexes formed by the interaction of aluminium alkyls and titanium halides.
(a) Soluble complex.
(b) Adsorption complex.

ization of ethylene.

(ii) Adsorption complexes.

When aluminium alkyls react with titanium tetrachloride at room temperature, dark coloured precipitates are invariably formed. These heterogeneous systems are perhaps the most efficient of the known Ziegler catalysts. The general opinion seems to be[58] that these precipitates are composed essentially of reduced titanium halides on the surface of which metal alkyl is chemisorbed. The extent of chemisorption, and thus the chemical composition of the precipitate, is determined by the experimental conditions. Natta[64] has suggested that such chemisorption leads to the formation of bridge-bond complexes (Fig. 1.8.b.)

(iii) Ionic complexes.

In view of the evidence which suggests that Ziegler type polymerizations probably proceed via an anionic mechanism, Uelzmann[65] has suggested that a cation is the most likely initiator for α-olefin polymerization. Consequently several ionic complexes have been predicte to result from the interaction of metal alkyls with transition metal compounds, e.g.

$$TiCl_4 + AlR_3 \longrightarrow (TiCl_3)^+(AlR_3Cl)^-.$$

(d) <u>The mechanism of Ziegler type polymerizations</u>.

There is ample evidence from kinetic studies of Ziegler type polymerization systems to conclude that an "anionic type" mechanism operates.[66] Additional experimental evidence favours a "hair-like" growth of the polymer from an active centre on the catalyst surface[66] (Fig. 1.9). In addition to these two features, any proposed mechanism

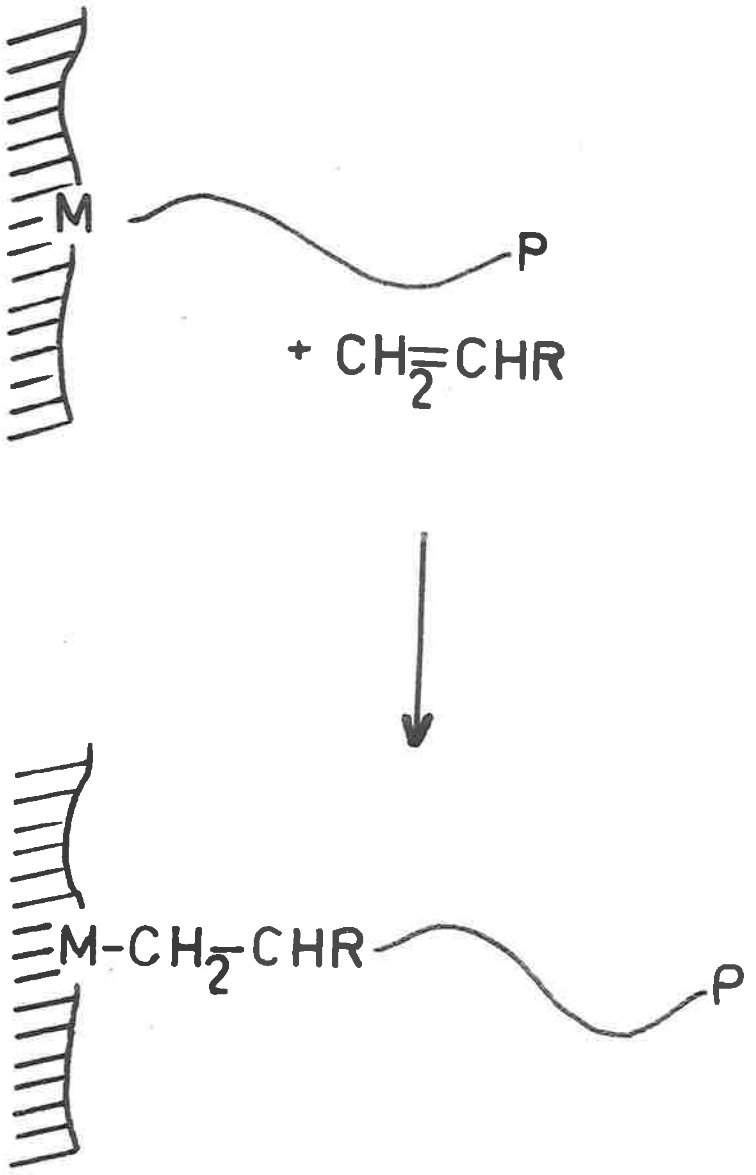


Fig. 1.9 Diagrammatic representation of "hair-like" growth in Ziegler-type polymerizations.

for Ziegler polymerizations must explain the stereoregular structure of the polymers produced.[67] It is generally considered that polymerization occurs on two metal atoms, thus preventing rotation of the polymer chain as well as controlling the orientation of the adding monomer. A crude representation of stereospecific polymerization of this type is given in figure 1.10. The orientation of the adding monomer is controlled by the fact that '$-CH_2$' is more able to give a carbanion than '$-CHR$' and thus the 'CH_2' end of the monomer is oriented towards the electropositive metal. (In ethylene polymerization, the monomer probably forms a π-type complex with the transition metal.) Steric factors control the disposition of 'R' groups.

Very many workers have suggested mechanisms which are based on this model.[58]

It has been observed[68] that termination of the polymerization produces vinylidine bonds, presumably through the transfer of a hydride ion from the '$-CHR$' of the last monomeric unit to a metal on the catalyst surface, e.g.

$$(\text{complex})\text{-M-CH}_2\text{-CHR}\sim\text{P} \longrightarrow (\text{complex})\text{-M-H} + \text{CH}_2 = \text{CR}\sim\text{P}.$$

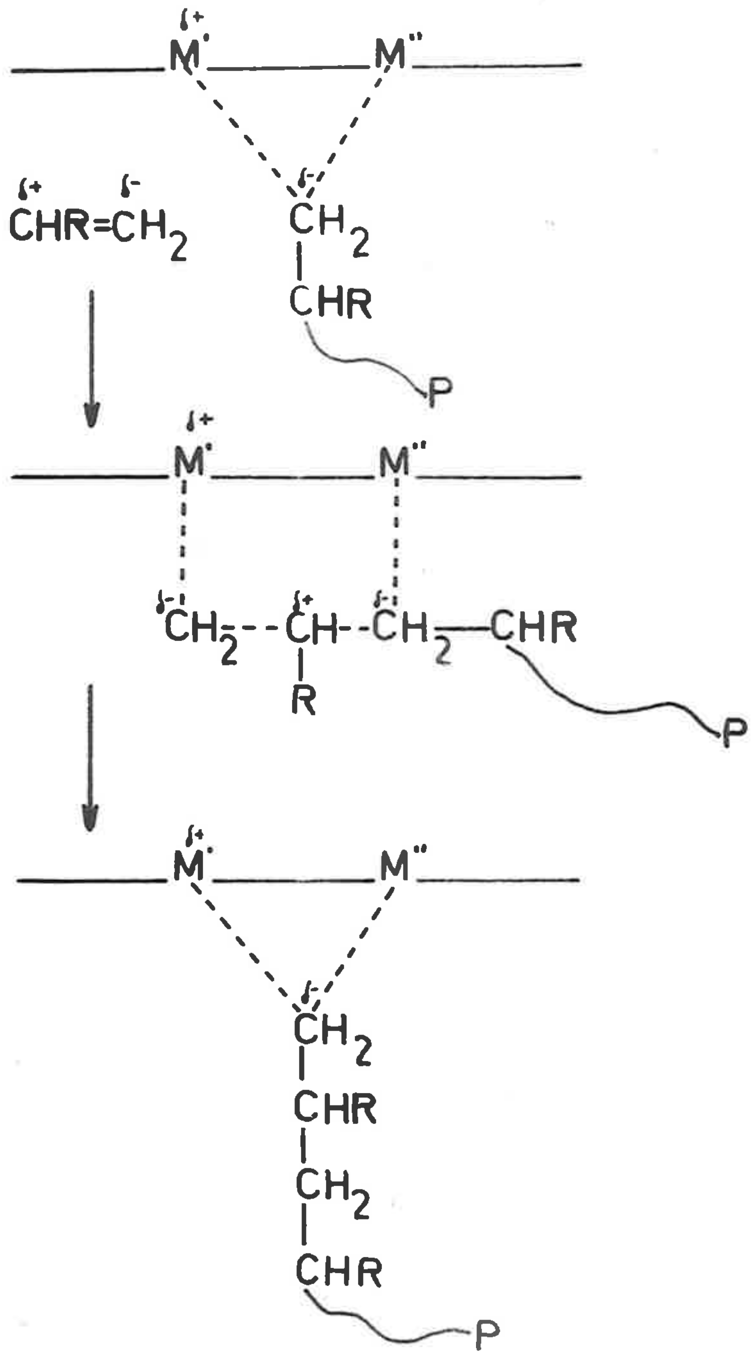


Fig. 1.10 Diagrammatic representation of the mechanism of Ziegler-type polymerizations of α-olefins.
M'=Ti; M"=Al.

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CHAPTER 2

Some Notes on the Synthesis of Certain Organometallics

1. Aluminium alkyls.-

Many of the reactions investigated in this study involved the use of simple aluminium alkyls, or of complex compounds derived from them. Before these organometallics became commercially available, it was necessary to undertake their preparation in the laboratory. As a consequence of the tremendous current interest in organo-aluminium chemistry, numerous preparative routes to alkyl-aluminium compounds have been described in the literature.[1] These are summarized in table 2.1.

Of the methods listed, it seemed that treatment of aluminium with an alkyl halide provided the most convenient entry into the general synthesis of organo-aluminium compounds. This has long been recognised as the most satisfactory method for the direct preparation of the lower alkyl-aluminium halides. It has been successfully applied to the preparation of alkyl-aluminium halides from methyl and ethyl chlorides, bromides, and iodides, and a few higher alkyl halides.[2]

The product from these interactions usually consists of an equimolar mixture of alkyl-aluminium dihalide and dialkyl-aluminium halide. As these two constituents are only difficultly separable, the mixture is frequently referred to as an "alkyl-aluminium sesquihalide". The formation of the sesquihalide is approximately quantitative.

An interesting feature of the reactions using alkyl iodides is the possibility of thermal disproportionation of the products, e.g.

Table 2.1

Methods available for the preparation of aluminium alkyls

a). Alkyl-aluminium halides.

(i) $\mathrm{2\,Al + 3\,RX \longrightarrow R_2AlX + RAlX_2.}$

(ii) $\mathrm{Al_2Mg + 4\,RX \longrightarrow 2\,R_2AlX + MgX_2.}$

b). Conversion of alkyl-aluminium halides to trialkyl-aluminium compounds.

(iii) $\mathrm{R_2AlX + NaF \longrightarrow R_2AlF + NaX}$

$\mathrm{R_2AlF + NaF \longrightarrow Na[R_2AlF_2]}$

$\mathrm{3\,Na[R_2AlF_2] \xrightarrow{heat} 2\,R_3Al + Na_3AlF_6.}$

(iv) $\mathrm{[R_2AlX + RAlX_2] + 3\,Na \longrightarrow R_3Al + Al + 3\,NaX.}$

(v) $\mathrm{[R_2AlI + RAlI_2] \xrightarrow{heat} R_3Al + AlI_3.}$

c). Direct preparation of aluminium-trialkyls.

(vi) $\mathrm{2\,Al + 3\,R_2Hg \longrightarrow 2\,R_3Al + 3\,Hg.}$

(vii) $\mathrm{Al_2Mg_3 + 6\,RX \longrightarrow 2\,R_3Al + 3\,MgX_2.}$

(viii) $\mathrm{AlX_3 + 3\,CH_2N_2 \longrightarrow (CH_2X)_3Al + 3\,N_2.}$

(ix) $\mathrm{Al + 3\,C_nH_{2n} + 3/2\,H_2 \longrightarrow (C_nH_{2n+1})_3Al.}$

(x) $\mathrm{AlH_3 + 3\,C_nH_{2n} \longrightarrow (C_nH_{2n+1})_3Al.}$

(xi) $\mathrm{2\,Al + 3\,C_nH_{2n+1}X + 3\,NaH + 3\,C_nH_{2n} \longrightarrow}$

$\mathrm{2\,(C_nH_{2n+1})_3Al + 3\,NaX.}$

d). Solvated alkyl-aluminium compounds.

(xii) $\mathrm{AlCl_3 + 3\,RMgX \xrightarrow{Et_2O} AlR_3.Et_2O + 3\,MgX_2.}$

(xiii) $\mathrm{LiAlH_4 + 4\,C_nH_{2n} \longrightarrow LiAl(C_nH_{2n+1})_4}$

$\mathrm{3\,LiAl(C_nH_{2n+1})_4 + AlCl_3 \xrightarrow{Et_2O} 4\,Al(C_nH_{2n+1})_3 + 3\,LiCl.}$

$$2\,RAlI_2 \longrightarrow R_2AlI + AlI_3$$
$$3\,R_2AlI \xrightarrow{slow} 2\,R_3Al + AlI_3.$$

Trimethyl-aluminium has, in fact, been obtained by the slow fractionation of the products from the interaction of aluminium and methyl iodide.[3]

In the present study, the reactions of aluminium, or an aluminium-magnesium mixture, with methyl bromide and methyl and ethyl iodides were investigated. In all reactions, the yield of crude alkyl-aluminium sesquihalide was essentially quantitative. Attempts, utilizing methods (iii), (iv), and (v) of table 2.1, to convert these alkyl-aluminium sesquihalides to trialkyl-aluminium compounds were made.

The thermal disproportionation of the iodides proceeded very slowly indeed, and considerable difficulty was experienced in obtaining an iodide-free product.

Conversion of the sesquihalide to a fluoride complex, and thermal decomposition of the latter, also yielded trialkyl-aluminium compounds, but again the yields were low.

The result of the interaction of the sesquihalide mixture with sodium probably calls for more detailed comment. The conversion of alkyl-aluminium halides to trialkyl-aluminium by treatment with sodium or sodium-potassium alloy has been reported by Grosse and Mavity.[2] They found that the reaction proceeds according to

$$R_3Al_2X_3 + 3\,Na \longrightarrow R_3Al + Al + 3\,NaX.$$

Subsequently, further investigations of the reaction have been reported in the patent literature.[4]

Grosse and Mavity stressed that an excess of sodium was to be avoided in the reaction since the trialkyl-aluminium formed would react further with excess sodium to give a non-volatile complex,[5] e.g.

$$4\ R_3Al\ +\ 3\ Na \longrightarrow 3\ NaAlR_4\ +\ Al.$$

Consequently, it seems that the best technique for the reaction would involve the slow addition of finely dispersed sodium (or sodium-potassium alloy) to the alkyl-aluminium sesquihalide. In this way, 80-90% conversion of the sesquihalide to trialkyl-aluminium can be obtained,[4a] whereas less than 50% conversion to trialkyl-aluminium is usually obtained when the sesquihalide is added to sodium.[2] Nonetheless, the greater technical difficulties associated with the former method of interaction prompted a re-investigation, in this study, of the effect of adding the sesquihalide to sodium. Obviously, this mode of addition will lead to the initial formation of sodium tetra-alkylaluminate. However, it is known[6] that subsequent reaction of this species with more alkyl-aluminium sesquihalide leads to the formation of aluminium trialkyl according to

$$6\ NaAlR_4\ +\ 2\ R_3Al_2X_3 \longrightarrow 5\ Al_2R_6\ +\ 6\ NaX,$$

thus overcoming the effects of the initial excess of sodium. In the present study, alkyl-aluminium sesquihalides were treated in this way, but the yields of trialkyl-aluminium obtained under the experimental conditions investigated were substantially lower than those reported by other workers. Two principal factors probably prevented better than moderate success from the method of interaction used. Firstly, the activity of the sodium was greatly inhibited by the formation, on its surface, of a hard crust of aluminium; and secondly, the extreme vigour of the reaction apparently led to thermal decomposition of the aluminium alkyls, liberating hydrocarbon gases and yielding involatile derivatives of sodium and aluminium. The former difficulty could probably be overcome, to some extent, by use of molten sodium,[4] or a mobile sodium-potassium alloy,[2] but it seems to be difficult to approach the theoretical yield of triethyl-aluminium under either condition. This observation can probably best be explained in the following terms. In the first instance, the use of molten sodium prevents the possibility of good control of the vigour of the reaction and, as a consequence, appreciable thermal decomposition of the aluminium alkyls can take place; on the other hand, the use of potassium to produce a mobile alkali metal alloy increases the possibility of forming thermally stable complexes of the form $K(AlR_2X_2)$, $K(AlRX_3)$, etc., thus binding up an appreciable proportion of the alkyl-aluminium halide in an inactive form. Notwithstanding these difficulties, small yields of triethylaluminium were obtained from the treatment of ethyl-aluminium sesquihalides with sodium.

These investigations were discontinued when commercial supplies of the required materials became available.

Subsequently, however, Dahlig[7] has reported a more complete investigation of this system. He discusses the conditions necessary for optimum yields of triethyl-aluminium, and has observed that by using a 5% excess of finely divided sodium and a high boiling solvent such as xylene (and thereby maintaining the reaction temperature at 140°C or less), and by heating the reaction mixture for at least 6 hours after all the alkyl-aluminium halide has been added, good yields of triethyl-aluminium are obtained.

Of related interest is a recent report in the patent literature[8] of conversion of ethyl-aluminium sesquihalide to triethyl-aluminium in 94% yield by treatment of the sesquihalide with calcium, magnesium, or zinc.

2. Bimetallic alkyls containing complex anions.-

The nature of bimetallic organometallic complexes of the form $M(M'R_n)$ was briefly surveyed in the last chapter. These organometallic complexes are frequently formed when an alkyl of an electropositive metal is mixed with another metal alkyl. Several examples of mixtures containing alkali metal alkyls and alkyls of metals of groups II and III were reported[11] in the early literature, but the investigators did not recognize the formation of complex anions. Compounds of similar type, in particular MBR_4, were first predicted[10] in 1937, and within a few years $LiBMe_3Et$ had been prepared[11] by the interaction of ethyl-lithium and trimethyl-boron. Subsequently, a large number of similar complex compounds containing such metals as beryllium, zinc, aluminium, tin and lead in place of boron have been reported in the literature. Three such compounds, namely lithium tetraethylaluminate, triethyl-plumbyl sodium, and triethylstannyl lithium, have been used in this study, and their preparations will be discussed in the following sections.

(a) Lithium tetraethylaluminate.

Lithium tetra-alkylaluminates have been prepared by several methods. The first detailed report[12] of the synthesis of a lithium tetra-alkylaluminate described the interaction of methyl-lithium and trimethyl-aluminium in ether. Lithium tetramethylaluminate is formed according to

$$\mathrm{LiMe} + \mathrm{AlMe_3} \longrightarrow \mathrm{LiAlMe_4}.$$

Baker and Sisler[13] have subsequently described the preparation, by an analogous technique, and isolation of lithium tetraethylaluminate; the yield of lithium tetraethylaluminate is 35%. Recently, these compounds, and higher alkyl analogues, have been synthesized by the interaction of olefins,[14] or of diazoalkanes,[15] with lithium tetrahydroaluminate, e.g.

$$\mathrm{LiAlH_4} \div \mathrm{C_nH_{2n}} \longrightarrow \mathrm{LiAl(C_nH_{2n+1})_4}.$$

The yields from such reactions are quite high, generally being greater than 90%.

The formation of alkali metal tetra-alkylaluminates by the direct reaction between an alkali metal and a trialkyl-aluminium compound, e.g.

$$4\ \mathrm{AlR_3} + 3\ \mathrm{Na} \longrightarrow 3\ \mathrm{NaAlR_4} + \mathrm{Al}$$

was mentioned in an earlier section of this chapter. Although this method of synthesis has been frequently used for the preparation of sodium tetra-alkylaluminates,[5] there are no detailed accounts of its application to the preparation of similar compounds of the other alkali metals. In this study it was found that lithium tetraethylaluminate can be formed in near quantitative yield by the treatment of lithium metal with either triethyl-aluminium or triethyl-aluminium etherate. The stoichiometry of the reaction corresponds to

$$4\ \mathrm{AlR_3} + 3\ \mathrm{Li} \longrightarrow 3\ \mathrm{LiAlR_4} + \mathrm{Al}.$$

The highest yields of lithium tetraethylaluminate were obtained when triethyl-aluminium etherate was added to a slight excess of finely divided lithium suspended in a small amount of gently refluxing ether;

under these conditions, lithium tetraethylaluminate was isolated in 95% yield.[16]

Kinetic measurements on such a system would be difficult, but it seems pertinent to speculate about possible reaction mechanisms for the formation of lithium tetraethylaluminate. It is generally accepted[17] that the general reaction

$$\mathrm{M} + \mathrm{M'R} \rightleftharpoons \mathrm{MR} + \mathrm{M'}$$

proceeds to the right when M is more electropositive than M'. It thus seems feasible that the initial alkylation of the lithium takes place according to

$$\mathrm{AlEt_3} + 3\,\mathrm{Li} \rightleftharpoons 3\,\mathrm{EtLi} + \mathrm{Al}.$$

Since there is no evidence that aluminium forms low valence compounds, it is somewhat difficult to visualize the individual steps in the reaction mechanism which give rise to ethyl-lithium in this manner. However, the following scheme, involving transient aluminium alkyl intermediates, is tentatively suggested.

$$\mathrm{Li} + \mathrm{Et_3Al} \rightleftharpoons \mathrm{LiEt} + (\mathrm{Et_2Al}\cdot)$$
$$2\,(\mathrm{Et_2Al}\cdot) \longrightarrow \mathrm{Et_3Al} + (\mathrm{EtAl}:)$$
$$2\,(\mathrm{EtAl}:) \longrightarrow (\mathrm{Et_2Al}\cdot) + \mathrm{Al} \qquad \text{etc.}$$

The formation of ethyl-lithium would be followed by the known reaction

$$\mathrm{EtLi} + \mathrm{Et_3Al} \qquad \mathrm{LiAlEt_4}.$$

Alternatively, the formation of lithium tetraethylaluminate may be connected in some way with the autodissociation of triethylaluminium[18] according to

$$2\,\mathrm{Et_3Al} \rightleftharpoons \mathrm{Et_4Al^-} + \mathrm{Et_2Al^+},$$

coupled with induced ionization of the lithium. Ion pairing would then yield lithium tetraethylaluminate and (Et_2Al) as before.

(b) Triethylplumbyl sodium.

Relatively few methods are available for the preparation of compounds of the type $MPbR_3$. The best general method involves addition of a solution of sodium in liquid ammonia to a tetra-alkyl-lead, tri-alkyl-lead halide, or hexa-alkyldilead compound,[19] e.g.

$$R_4Pb + 2\ Na \xrightarrow{1\ NH_3} NaPbR_3 + NaNH_2 + RH.$$
$$R_3PbX + 2\ Na \xrightarrow{1\ NH_3} NaPbR_3 + NaX.$$
$$R_3Pb.PbR_3 + 2\ Na \xrightarrow{1\ NH_3} 2\ NaPbR_3.$$

Since hexa-alkyldilead compounds are rather unstable, the last mentioned reaction is not generally applicable to the preparation of alkyl derivatives.

Triphenylplumbyl lithium has been prepared[20] by the interaction of phenyl-lithium with lead dichloride in ether, e.g.

$$3\ PhLi + PbCl_2 \longrightarrow LiPbPh_3 + 2\ LiCl.$$

but this method cannot be extended readily to the preparation of the alkyl analogues.

In the present study, triethylplumbyl sodium was prepared from tetraethyl-lead and sodium in a liquid ammonia/diethyl ether solvent system. The mixed solvent system was employed since this affords higher yields of triethylplumbyl sodium than are obtained in pure liquid ammonia. Gilman[19] reports the following yields

Solvent system	Yield obtained
NH_3	80%
NH_3/toluene	88%
NH_3/diethyl ether	95%.

The overall reaction involves reduction of the lead, and this could conceivably take place in either of the following ways

(i) $MR_4 + e^- \longrightarrow MR_3 + R^-$

followed by: $MR_3 + e^- \longrightarrow MR_3^-$

or (ii) $MR_4 + e^- \longrightarrow MR_3^- + R$

followed by: $R + e^- \longrightarrow R^-$

In each instance, the further reaction

$$R^- + NH_3 \longrightarrow RH + NH_2^-$$

would account for the formation of sodamide. It has been established[21] that reaction (ii) is favoured, at least in the reduction of tetramethyllead by an alkali metal in liquid ammonia.

The instability of triethylplumbyl sodium prevented its isolation, and it was necessary to use the solution 'in situ' (after removal of the insoluble sodamide by filtration) for an investigation of its reaction with bis(cyclopentadienyl)titanium dichloride.[22] Since the presence of liquid ammonia in this system effected the ammonolysis of the titanium derivative, thus complicating the reaction to be studied, some attempts to obtain triethylplumbyl sodium in an ammonia-free system were made. Initially, the triethylplumbyl sodium was prepared in a toluene/ammonia solvent mixture, and after the solution had been cooled to -80°C, the ammonia was slowly removed by vacuum distillation. The temperature was finally raised to 0°C to remove the last traces of ammonia. However, removal of the ammonia was followed by decomposition of the lead derivative, yielding hydrocarbon gases and unidentified lead derivatives.

Holliday and Pass[19] have considered the decomposition of the ion '$PbMe_3^-$' in liquid ammonia and postulate initial solvolysis of the ion according to

$$PbMe_3^- + NH_3 \longrightarrow PbMe_2NH_2^- + CH_4$$

followed by the decomposition reactions

$$PbMe_2NH_2^- + Na^+ \longrightarrow PbMe_2 + NaNH_2$$

$$2\ PbMe_2 \longrightarrow PbMe_4 + Pb.$$

Krause and Sessions[23] have observed that the tin analogue $NaSnMe_3$ decomposes above room temperature into hydrocarbons and tin-sodium alloy. It seems reasonable to suggest that a variety of such reactions contribute to the decomposition of the triethylplumbyl sodium.

A further attempt to prepare ammonia-free triethylplumbyl sodium was made by treating triethyl-lead chloride with sodium, and with sodium-potassium alloy, in ether or toluene. In no instance was any sign of a reaction observed below the reflux temperature of toluene.

(c) Triethylstannyl lithium.

As with their lead analogues, the trialkylstannyl alkali metal series can be prepared by the addition of an alkali metal to tetra-alkyltin or trialkyltin chloride in liquid ammonia,[24] e.g.

$$R_3SnBr + 2\ Na \xrightarrow{l\ NH_3} NaSnR_3 + NaBr.$$

The mechanism of this reaction is probably complicated by the initial interaction between product and starting material according to

$$R_3SnBr + NaSnR_3 \longrightarrow R_3Sn.SnR_3 + NaBr$$

which is followed by further reaction with sodium

$$R_6Sn_2 + 2\ Na \longrightarrow 2\ NaSnR_3.$$

The trialkylstannyl alkali metal compounds can also be obtained by reaction between tetra-alkyltin, trialkyltin halide, or hexa-alkylditin compounds and an alkali metal in an organic solvent[24] (preferably tetrahydrofuran or ethylene glycol dimethyl ether). A further synthetic route, the reaction between an alkyl derivative of an alkali metal and a tin(II) compound, also yields trialkylstannyl derivatives. This latter technique was employed in the present study. Triethylstannyl lithium was prepared by adding ethyl-lithium to a suspension of stannous chloride in diethyl ether at -10°C.[25] The reaction probably takes place in two distinct stages, e.g.

$$2\ EtLi + SnCl_2 \longrightarrow Et_2Sn + 2\ LiCl$$

$$EtLi + Et_2Sn \rightleftharpoons LiSnEt_3.$$

As indicated, experimental evidence suggests that the formation of triethylstannyl lithium from ethyl-lithium and diethyltin is probably a reversible reaction. The extent to which reaction with the 'Et_3Sn^-' species in this solution can be effected has been demonstrated by the addition of ethyl bromide to the solution. A 70% conversion of the ion to tetraethyl-tin is observed.

Triethylstannyl lithium is very unstable and was used in further reactions without isolation.

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CHAPTER 3

Reactions of Organo-aluminium Compounds with Various Metal and Metalloid Halides

1. General discussion of alkylation reactions with aluminium alkyls.-

(a) The scope of alkylation reactions with aluminium alkyls.

The general approach to the preparation of metal alkyls from the appropriate metal halide and an aluminium alkyl compound involves

$$3\ MX_n + n\ AlR_3 \rightleftharpoons 3\ MR_n + n\ AlX_3.$$

In many instances, not all the 'R' groups of the trialkyl-aluminium are easily transferable. Accordingly, for the present considerations, the simplified equation

$$mX + alR \rightleftharpoons mR + alX \quad (\text{where } m = 1/n\ M,\ al = 1/3\ Al)$$

will be discussed. As mentioned previously, the driving force of such a reaction is largely attributable to the decrease in energy of the system by the formation of a strong 'Al-X' bond at the expense of a weaker 'M-X' linkage. It thus seems pertinent to consider the 'M-X' bond strengths of several inorganic halides. This is done in table 3.1 for 'metal' halides used in the present study.

The tabulated values indicate that the formation of alkyls of group IVB and VB elements from halides of these elements and lithium or aluminium alkyls (or even from lithium tetra-alkylaluminates) is energetically favourable. It has been confirmed experimentally that these, and halides of several other metals, do in fact yield the appropriate metal alkyl when treated with an aluminium alkyl.

Table 3.1

Table of bond dissociation energies for several inorganic halides.[1]

	D kcal.
Li-Cl	115
Al-Cl	118
Sn-Cl	74?
Sn-Cl in $SnCl_4$	(76)
Pb-Cl	71
P-Cl in PCl_3	(78)
As-Cl in $AsCl_3$	(70)
Sb-F	92?
Sb-Cl	85?
Sb-Cl in $SbCl_3$	(74)
Bi-Cl	67

The figures in brackets represent values of bond energies; the bond dissociation energies were not readily obtainable.

Table 3.2 summarizes a number of the known reactions involving 'metal' halides and aluminium alkyls. Such reactions are not confined to metal halides; for instance, good yields of lead tetraalkyls have been obtained from the interaction of lead acetate,[25] lead oxide,[19] and lead sulphide[19] with aluminium alkyls.

(b) A possible mechanism for the reaction of aluminium alkyls with metal halides.

Before considering the mechanism of the reaction between aluminium alkyls and metal halides, it seems desirable to discuss the overall equilibrium reaction

Table 3.2

A summary of the alkylation of 'metal' halides with aluminium alkyls

Metal halide	Aluminium Alkyl	Remarks	Ref.
Zinc			
ZnX_2	AlR_3	80% Et_2Zn from $ZnCl_2$ and $AlEt_3$ in mineral oil[2]; 94% yield, no solvent[4]	2,3,4
ZnX_2	$R_3Al_2X_3$	-	5
Cadmium			
CdX_2	AlR_3	-	2,3,6
CdX_2	$R_3Al_2X_3$	-	5
Mercury			
HgX_2	AlR_3	59% Et_2Hg from $HgCl_2$ and Et_3Al in hexane[8]	7,8
HgX_2	$R_3Al_2X_3$	66% EtHgCl from $HgCl_2$ and $Et_3Al_2Cl_3$ [9]	5,9
HgX_2 + NaCl	AlR_3	90% Et_2Hg from $HgCl_2$, NaCl, and $AlEt_3$	10
Boron			
BX_3	AlR_3	90% Et_3B from BF_3 and Et_3Al in Et_2O [11]	3,5,7,11
BX_3 + NaCl	AlR_3	89% Et_3B from BCl_3, NaCl, and Et_3Al	10
Gallium			
GaX_3	AlR_3	40-45% Et_3Ga from $GaCl_3$ and Et_3Al; 85% Et_3Ga from $GaBr_3$ and Et_3Al	12
GaX_3 + MCl	AlR_3	90% Et_3Ga from $GaCl_3$, KCl, and Et_3Al[12]	10,12
Thallium			
TlX_3	AlR_3	62% Et_2TlCl from $TlCl_3$ and Et_3Al in Et_2O	8
Tin			
SnX_4	AlR_3	71% Et_4Sn from $SnCl_4$ and Et_3Al in hexane[8]	3,7,8,14, 15,16

SnX_4	$R_3Al_2X_3$	-	14,17
SnX_4 + NaCl	AlR_3	90% Et_4Sn from $SnCl_4$, NaCl, and Et_3Al	13
Lead			
PbX_2	AlR_3	46% Et_4Pb from $PbCl_2$ and Et_3Al in Et_2O;[19] or 100% in py	3,14,16,18,19
PbX_2	$R_3Al_2X_3$	-	14,17
PbX_2 + NaCl	AlR_3	-	6
Phosphorus			
PX_3	AlR_3	30% Et_3P from PCl_3 and Et_3Al[20]	7,9,14,20,21
Arsenic			
AsX_3	AlR_3	-	3,7,14,16
AsX_3	$R_3Al_2X_3$	-	14,17
AsX_3 + NaCl	AlR_3	80% Et_3As from $AsCl_3$, NaCl, and Et_3Al[10]	10,22
Antimony			
SbX_3	AlR_3	70% Et_3Sb from SbF_3 and Et_3Al in Et_2O[8]	3,6,7,8,14,16,22,23
SbX_3	$R_3Al_2X_3$	-	14,17
SbX_3 + NaCl	AlR_3	-	10,22
Bismuth			
BiX_3	AlR_3	86% Et_3Bi from $BiCl_3$ and $AlEt_3$ in Et_2O[8]	8,14,16
BiX_3	$R_3Al_2X_3$	-	14,17
BiX_3 + NaCl	AlR_3	85% Et_3Bi from $BiCl_3$, NaCl and Et_3Al[10]	10,22
Titanium			
TiX_4	AlR_3	100% reduction to $TiCl_3$ if $TiCl_4$: $AlEt_3 \leq 1:1$	24

$$mX + alR \rightleftharpoons mR + alX.$$

The reversibility of the reaction is presumably a result of the dealkylating effect which aluminium halides have on many metal alkyls. This property of aluminium halides is clearly illustrated by the observation[26] that lead tetra-alkyls are dealkylated even by dialkylaluminium halides. As a consequence, lead tetra-alkyls cannot be satisfactorily prepared from lead dichloride and aluminium alkyls under the usual conditions.[8]

The presence of aluminium halides can affect 'metal halide-aluminium alkyl' systems in other ways. For instance, aluminium halides, which are strong Lewis acids, can often form complexes in the reaction mixture with reactants, products, or even the solvent. Examples of such complexes are $Et_3P.AlCl_3$, $Ga(AlEt_2Cl_2)_3$, and $AlEtCl_2.Et_2O$. The formation of such complexes will obviously have some effect on the general equilibrium reaction. It is generally considered[27] that the equilibrium is displaced so as to form the most stable complex of aluminium possible. In many instances, this is simply the solvated aluminium halide. However, when complexes are formed between aluminium halides and either starting material or reaction product, the yield of product is often appreciably reduced.

An interesting aspect of this feature of the reactions is the effect of adding alkali metal halides to the systems. It is known[28] that alkali metal halides form stable complexes with aluminium halides, e.g. $NaAlCl_4$. The formation of such complexes makes it possible to bind up aluminium halides in an inactive form. This effect ought to permit the formation of high yields of metal alkyls which are otherwise not obtainable in satisfactory yield from the interaction of metal halides and aluminium alkyls. This has been demonstrated experimentally. Thus, although gallium tribromide gives 85% triethyl-gallium, gallium trichloride yields only 40-45% triethylgallium when the trihalide is treated with triethyl-aluminium. The marked difference in yield is attributed to binding of half the gallium trichloride according to:

$$GaCl_3 + 3\,AlEt_3 \longrightarrow GaEt_3 + 3\,AlEt_2Cl$$

$$GaCl_3 + 3\,AlEt_2Cl \longrightarrow Ga(AlEt_2Cl_2)_3.$$

The inclusion of potassium chloride in the reaction mixture increases the yield of triethyl-gallium to 90%. The increased yield is a result of the reaction[12]

$$3\,KCl + Ga(AlEt_2Cl_2)_3 \longrightarrow GaCl_3 + 3\,K(AlEt_2Cl_2).$$

Finally, before discussing the actual mechanism of the reactions, it seems necessary to consider the nature of the reacting aluminium alkyl species. It has already been pointed out that, as a result of their electron-deficient nature, aluminium alkyls are considerably associated. Although the degree of dissociation of the lower aluminium alkyls in solution is extremely low,[29] it is usually accepted that an equilibrium involving monomeric and dimeric forms of the aluminium alkyl exists in such solutions, e.g.

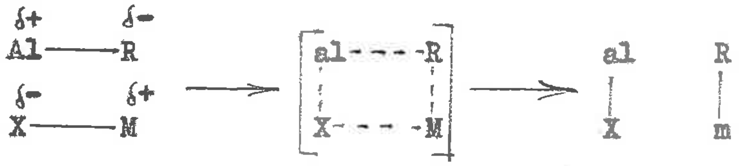
$$2\,AlR_3 \rightleftharpoons Al_2R_6.$$

Ziegler and Hobert[30] have shown that when such an equilibrium exists, the monomeric species is the reacting species if the dissociation is at all appreciable (e.g. the rate of absorption of unsaturated hydrocarbons by triethylaluminium in solution decreases markedly at dilutions where dimerization is significant[30]).

It has also been suggested that some autodissociation according to

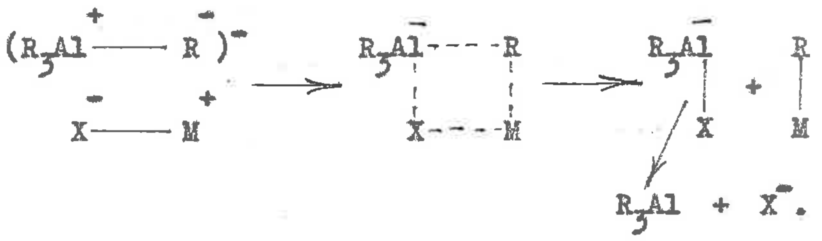
$$R_6Al_2 \rightleftharpoons R_2Al^+ + R_4Al^-$$

gives rise to a small but definite concentration of ionic species in solutions of aluminium alkyls. However, the small electrolytic conductivity of pure liquid triethyl-aluminium (K is probably less than $1 \times 10^{-10}\,\Omega^{-1}\,cm.^{-1}$) indicates that the concentration of these ions will be so small that there is no likelihood of them taking part in the alkylation reactions. It is thus apparent that the reactions involve interaction of 'AlR_3' units (either monomer or dimer) with the metal halide. It seems probable that the products are formed as a result of dipole-dipole interactions between polar Al-R and M-X linkages, e.g.



Notwithstanding the greater reactivity of the monomer, the extreme prevalence of the dimeric species in solutions of triethyl-aluminium suggests that the 'Al_2Et_6' species would play a major role in the reaction.

It has been pointed out that saturation of the electron deficiency of aluminium alkyls (e.g. by the formation of donor complexes) considerably diminishes the chemical reactivity of aluminium alkyls. Thus, triethyl-aluminium etherate and sodium tetraethylaluminate are much less reactive than triethyl aluminium. Nonetheless, both trialkyl-aluminium etherates and alkali metal tetra-alkylaluminates readily exchange their alkyl groups with halogens from other metals. It is interesting that the formation of these donor complexes is often accompanied by a marked increase in electrolytic conductivity (e.g. NaAlEt_4, $K \sim 4\text{–}5.10^{-2}\ \Omega^{-1}\ \text{cm.}^{-1}$.[32]) It thus seems apparent that alkylation reactions with these compounds may involve reaction of polar Al–R linkages of the complex anion rather than of the undissociated molecules, e.g.



2. The alkylation of inorganic halides with lithium tetraethylaluminate.[33]

(a) General considerations.

In the present section, the preparations of alkyls of the form MEt_n (M = Sn, Pb, P, As, Sb, Bi; n = valence of metal or metalloid) by the treatment of the analogous halides with solutions of lithium tetraethylaluminate are described.

The chemical reactivity of bimetallic alkyls of the form 'MAlR_4' (M = alkali metal, R = alkyl group) has not been extensively investigated. However, it was recently shown that such complexes may behave as mixtures of alkali metal alkyls and trialkyl-aluminium compounds. For instance, Frey and co-workers[34] have reported that sodium tetraethylaluminate behaves essentially as a mixture of ethyl-sodium and triethyl-aluminium in its reaction with metallic lead. Thus, when lead is alkylated with a 'sodium tetraethylaluminate-ethyl halide' mixture, triethyl-aluminium can be recovered from the reaction mixture. This indicates a stoichiometry corresponding to

$$2\ NaAlR_4 + Pb + 2\ RX \longrightarrow PbR_4 + 2\ NaX + 2\ AlR_3.$$

It seems reasonable to predict that the lithium analogue, '$LiAlR_4$' would behave similarly. Thus, it could be anticipated that lithium tetraethylaluminate would possess the alkylating properties expected of an equimolar mixture of ethyl-lithium and triethyl-aluminium.

It seems feasible therefore to postulate a stepwise alkylation scheme for the reactions studied. The first step in the alkylation scheme would involve the transfer of only one alkyl group to the metal, e.g.

$$MX_n + LiAlR_4 \longrightarrow MX_{n-1}R + LiAlR_3X.$$

Since lithium forms no stable alkyl-aluminium complexes except lithium tetra-alkylaluminates and mixed hydro-alkyl-aluminates, it can be anticipated that the '$LiAlR_3X$' species would dissociate into simple lithium and aluminium species. The relative electronegativities of lithium and aluminium would favour the formation of lithium halide rather than an alkyl-aluminium halide, e.g.

$$LiAlR_3X \longrightarrow LiX + AlR_3.$$

The trialkyl-aluminium so formed could then react with the metal halide in the established manner.

$$MX_{n-1}R + AlR_3 \rightleftharpoons MX_{n-2}R_2 + AlR_2X \quad \text{etc.}$$

In view of this suggested reaction scheme, it seems desirable to correlate the yields of MR_n obtained in this study with those obtained from the corresponding reactions using aluminium alkyls, and, for comparison, the appropriate Grignard reagent as alkylating agent. This is done in table 3.3.

Table 3.3

A comparison of the yields of MR_n obtained from the interaction of MX_n with lithium tetraethylaluminate, aluminium alkyls, and Grignard reagents (R = ethyl)

Metal halide	Yield of MR_n		
	AlR_3	RMgX	$LiAlR_4$[33]
$SnCl_4$	71%[8]	90%[35]	85%
$PbCl_2$	46%[19]	48%[36]	100%
PCl_3	30%[20]	70%[37]	10%
$AsCl_3$	-	40%[38]	31%
SbF_3	70%[8]	(60%[37])*	65%
$BiCl_3$	86%[8]	88%[40]	85%

* Yield refers to reaction with $SbCl_3$.

The results indicate that for the reactions studied lithium tetraethylaluminates are generally not superior to other common alkylating agents. Notwithstanding this, it seems probable that improved yields of 'MR_n' might be obtained if sodium tetra-alkylaluminates are used as alkylating agent. In this latter case, the transfer of alkyl groups to the element M would be favoured by the formation of a stable sodium-aluminium adduct such as $NaAlRX_3$.[41] Such compounds of lithium are relatively unstable, and hence aluminium will form stable co-ordination compounds in other ways, often to the detriment of good yields of product.

These sodium-aluminium systems would resemble, in essence, the 'sodium chloride-metal halide-aluminium alkyl' systems investigated by Jenkner.[6] He studied the alkylation of silicon, cadmium, antimony, and lead by treating a mixture containing sodium chloride and fluorides of these elements with aluminium alkyls. Here, as the '$AlRX_2$' or 'AlX_3' species are formed, they are immediately bound up as complex anions by the sodium chloride present. The use of sodium tetra-alkylaluminate, which would be expected to initially transfer only one alkyl group with the formation of sodium chloride and triethyl-aluminium, would thus be analogous to Jenkner's system.

(b) The treatment of some group IVB metal halides with lithium tetraethylaluminate.

(i) Reaction between tin(IV) tetrachloride and lithium tetraethylaluminate leads to the formation of tetraethyl-tin in 85% yield. The reaction can be represented as follows,

$$SnCl_4 + LiAlEt_4 \longrightarrow SnEt_4 + [LiCl + AlCl_3].$$

Equilibrium reactions, representing the formation of all the possible partially alkylated tin species, have been suggested[27] to account for the observed products from previously investigated interactions of tin(IV) halides and alkyl-aluminium compounds. The formation of alkyltin halides, and the observation[15] that not all the alkyl groups attached to aluminium are utilized when tin(IV) halides are alkylated with aluminium alkyls, suggest that the equilibria are of the form

$$SnX_4 + AlR_3 \rightleftharpoons RSnX_3 + AlR_2X$$

$$SnX_4 + 2\ AlR_3 \rightleftharpoons R_2SnX_2 + 2\ AlR_2X$$

etc.

However, since Johnson has found it necessary to isolate and further alkylate the trialkyltin halide with more trialkyl-aluminium to obtain tetra-alkyltin from such systems, it seems that further equilibria such as

$$SnR_4 + AlRCl_2 \rightleftharpoons SnR_3Cl + AlClR_2$$

must also operate. The relative proportions of partially alkylated tin species in the products from 'aluminium alkyl-tin tetrahalide' interactions would presumably depend upon the ratio of reactants used.

Koster[27] has observed that the R_nSnX_{4-n} compounds formed in this way can co-ordinate with aluminium halides to form such compounds as $Et_2SnCl_2.AlCl_3$, $Et_3SnCl.AlCl_3$. Although little is known about the stability of these adducts, it is apparent that they could further inhibit the formation of tetraethyl-tin.

Jenkner[13] has pointed out that such difficulties as those mentioned above can be overcome if NaCl is added to the reaction mixture. Under such conditions, good yields of tetraethyltin can be readily isolated, presumably because the sodium chloride co-ordinates with the aluminium halides which are formed, e.g.

$$3\ SnCl_4 + 4\ AlR_3 + 4\ NaCl \longrightarrow 3\ SnR_4 + 4\ NaAlCl_4.$$

Since the treatment of tin tetrachloride with lithium tetraethylaluminate produced virtually no alkyltin halides, it is probable that this reaction is also accompanied by the formation of complex halides, e.g. lithium tetrachloro-aluminate, or the moderately stable '$LiAlEtCl_3$'.[47]

(ii) Lead(IV) halides are markedly unstable, and consequently it was necessary to employ a lead(II) halide for the preparation of tetraethyl-lead. The interaction of lead dichloride and lithium tetraethylaluminate produced a mixture of organo-lead derivatives from which tetraethyl-lead was ultimately isolated in greater than 100% yield (calculation of the yield was based on conversion of the lead dichloride to tetra-ethyl-lead and lead in equimolar proportions). Throughout the reaction a quantity of black metallic lead was deposited and it seems probable that there was some interaction between this highly reactive metal and excess lithium aluminium alkyl, thus explaining the excessively high yield. Related investigations of similar organo-lead systems suggest that the following reaction scheme would be followed:[43]

$$3\ PbCl_2 + 2\ LiAlEt_4 \longrightarrow 3\ PbEt_2 + 2\ LiCl + 2\ AlCl_2Et$$

$$3\ PbEt_2 \longrightarrow Pb_2Et_6 + Pb$$

$$2\ Pb_2Et_6 \longrightarrow 3\ PbEt_4 + Pb.$$

The overall reaction is thus

$$6\ PbCl_2 + 4\ LiAlEt_4 \longrightarrow 3\ PbEt_4 + 3\ Pb + 4\ [LiCl + AlEtCl_2].$$

It seems pertinent to report that Gilman and Jones[44] have developed a method for utilizing all the lead in such systems. They have observed that the inclusion of an alkyl halide in the reaction mixture effects the conversion of all the lead salt to tetraalkyl lead, e.g.

$$PbI_2 + MeI + 3\ MeLi \longrightarrow PbMe_4 + 3\ LiI.$$

Furthermore, as an extension of this technique, Frey and co-workers have converted metallic lead to tetraethyl-lead by the action of lithium tetraethylaluminate and ethyl iodide on the metal. It is thus evident that utilization of all the lead in this system could be effected by inclusion of ethyl iodide in the reaction mixture.

In discussing the overall reaction for the formation of lead alkyls by the action of lithium tetraethylaluminate on lead halides, it seems important to consider the further observation[26] that lead alkyls are de-alkylated by aluminium halides and alkyl-aluminium halides, e.g.

$$PbEt_4 + AlCl_2Et \rightleftharpoons PbEt_3Cl + AlEt_2Cl.$$

This reaction has led some workers to believe that tetra-alkyl-lead compounds cannot be satisfactorily prepared from lead halides and aluminium alkyls (e.g. Zakharkin and Okhlobystin[8] claim that tetraethyl-lead cannot be obtained in satisfactory yield from lead dichloride and triethyl-aluminium). This observation appears to conflict somewhat with the result obtained in this study. However, since it was recently confirmed that quantitative conversion of lead dichloride to tetraethyl-lead can be attained with lithium tetraethylaluminate, it is obvious that, in some way, the system is simplified when lithium tetraethylaluminate, rather than triethylaluminium, is used as alkylating agent. Examination of the equations suggested for the formation of tetraethyl-lead, and its ultimate reaction with aluminium halides, indicate that the experimental conditions will be critical in determining whether or not good yields of tetraethyl-lead can be obtained. Evidently, tetraethyl-lead can only be obtained in high yield if the organo-lead species is first isolated as hexaethyldilead, or if the formation of reactive aluminium-chlorine linkages is prevented. Although the former condition is difficult to attain, the latter effect can be achieved in several ways, e.g. by using a large excess of lithium tetraethylaluminate and thus maintaining the aluminium in the system as triethylaluminium; possibly, by using a slight deficiency of lithium tetraethylaluminate to ensure the formation of chloro-aluminate ions; by adding sodium chloride to the system as in the tin reaction; or by using pyridine as the solvent. For instance, although the action of triethyl-aluminium on lead dichloride in hexane as solvent gives virtually no tetraethyl-lead, the interaction of lead difluoride and triethyl-aluminium in pyridine gives 100% yield of tetraethyl-lead.[18] The high yield from the second treatment is presumably due to the formation of inactive aluminium halide-pyridine adducts. The conditions employed in the present study suggest that the formation of complex chloro-aluminate ions assisted the production of tetraethyl-lead in high yield.

It is of interest to consider briefly the related investigation of the action of metal alkyls on lead(IV) salts. Frey and Cook[45] have shown that the reactions of lead(IV) salts with triethyl-aluminium, or other metal alkyls, give metallic lead as a major by-product. In addition, reactions with hexachloroplumbates give ethyl iodide as a further by-product, e.g.

$$2\ (PbCl_6)^{--} + 2\ EtM \longrightarrow 2\ EtPbCl_3 + 2\ M^+ + 6\ Cl^-.$$

$$2\ EtPbCl_3 \longrightarrow 2\ EtCl + 2PbCl_2$$

$$2\ PbCl_2 + 4\ EtM \longrightarrow Et_4Pb + Pb + 4\ MCl.$$

Thus these reactions are not significantly different from the lead(II) systems.

(c) The treatment of halides of group VB elements with lithium tetraethylaluminate.

In all of the following reactions, the overall stoichiometry was based on the ultimate conversion of lithium tetraethylaluminate to lithium chloride and ethylaluminium dichloride. In this way, it was possible to take account of the relatively weak alkylating properties of alkyl-aluminium halides.

The treatment of phosphorus trichloride with excess lithium tetraethylaluminate produced a viscous product from which no free triethylphosphine could be isolated by distillation. Alkaline hydrolysis of this viscous reaction mixture liberated triethylphosphine in 10% yield. These results follow closely the general pattern observed by Zakharkin and Okhlobystin[20] in the alkylation of phosphorus trichloride by aluminium trialkyls. They observed that even with an excess of aluminium trialkyl, triethylphosphine is formed in less than 30% yield, and a considerable proportion of the Al-C bonds are preserved. These observations indicate that equilibria of the type

$$PEt_3 + AlClEt_2 \rightleftharpoons PClEt_2 + AlEt_3,$$

are probably established in these systems. With the experimental conditions employed in this study to isolate triethylphosphine, it was impossible to determine how much partially alkylated chlorophosphine was formed. Hydrolysis of the reaction mixture converted such probable products to the corresponding phosphonic acids. The observation that no free triethylphosphine was present in the initial reaction system can only be attributed to Lewis acid-base interaction between the trialkylphosphine and the aluminium halides, resulting in the formation of thermally stable adducts such as $Et_3P.AlEtCl_2$. Investigations of the stabilities of various Lewis base-aluminium halide adducts suggest[46] that such complexes would be more thermally stable than $Et_2O.AlEtCl_2$. The low yield of triethylphosphine obtained in these reactions may be attributed, in part, to interaction of some phosphorus trichloride with aluminium halide or with trialkylphosphine which would reduce the amount of effective phosphorus trichloride in the system. Weak complexes between phosphorus trichloride and aluminium trihalides have, in fact, been reported.[47] The 2:1 complex $2Me_3P.PCl_3$ is also known.[48] Yoke[49] has also reported the formation of a complex $LiAl(PHEt)_4$, but it is unlikely that similar complexes in which chloride or ethyl groups replace the hydrogen would be stable. All the adducts specifically mentioned above require that an appreciable proportion of the alkyl groups be transferred from aluminium to phosphorus. Since such an effect has not been observed in the reactions under consideration, it appears that the formation of complexes between halo-alkylphosphines and aluminium alkyls must occur. Although such complexes have not been extensively investigated, it seems feasible that they must exist. The formation of $PR_nX_{3-n}.AlR_3$, and similar adducts with AlR_2X would hinder the complete alkylation of phosphorus and this provides a more satisfactory explanation of the observed results.

Arsenic trichloride is alkylated by lithium tetraethylaluminate but the yield of triethylarsine is only 31%. Although trialkylarsines are weaker Lewis bases than their phosphorus analogues (e.g. Holmes has shown that $AsCl_3AlCl_3$ complexes do not exist), it seems reasonable that the low yield of triethylarsine is attributable to similar factors which operated in the triethylphosphine synthesis. Thus, the following reactions would contribute to the overall reaction.

$$AsCl_3 + LiAlEt_4 \longrightarrow Et_3As + AlEtCl_2 + LiCl$$

$$AsEt_3 + AlClEt_2 \rightleftharpoons AsEt_2Cl + AlEt_3$$

$$AsEt_3 + AlCl_2Et \longrightarrow Et_3As.AlCl_2Et.$$

The reactions between antimony trifluoride and lithium tetraethylaluminate proceeds smoothly and gives 65% yield of triethylstibine.

$$SbF_3 + LiAlEt_4 \longrightarrow SbEt_3 + LiF + AlEtF_2$$

In the course of the reaction a small amount of black antimony was precipitated. Since this is a common observation when antimony halides are alkylated with metal alkyls, it was not further investigated.

The reaction between bismuth trichloride and lithium tetraethylaluminate proceeds equally smoothly and gives an 85% yield of triethylbismuthine.

$$BiCl_3 + LiAlEt_4 \longrightarrow BiEt_3 + LiCl + AlEtCl_2.$$

The weaker electron donating properties of the antimony and bismuth compounds no doubt account for the higher yields of MR_n obtained in these two reactions. Complex formation with aluminium halo-alkyls and other halides would be significantly less.

3. The attempted formation of pentamethyl-antimony employing an aluminium alkyl.

Several classes of organo-derivatives of pentavalent antimony have been known for a long time, e.g. $RSbX_4$ and R_2SbX_3 (both unstable at room temperature), R_3SbX_2 and R_4SbX (both thermally stable).[50] However, the preparation of the penta-alkyl compound Me_5Sb,[51] has been a comparatively recent development in the organo-metallic chemistry of antimony(V). Pentamethylantimony was obtained from the interaction of trimethylstibine dichloride or tetramethylstibonium bromide and methyllithium, e.g.

$$Me_4SbBr + MeLi \longrightarrow Me_5Sb + LiBr.$$

It is a thermally stable liquid which is rapidly decomposed by air, water, halogens, etc. It forms both anions and cations of antimony, for example by the reactions

$$Me_5Sb + Ph_3B \longrightarrow Me_4Sb^+ + MePh_3B^-.$$
$$Me_5Sb + MeLi \longrightarrow Me_6Sb^- + Li^+.$$

No other 'R_5M' compounds have been well authenticated. It has been reported[51] that pentamethylarsenic is formed at low temperatures, but the compound could not be satisfactorily isolated. An earlier report[52] of the preparation of pentamethylarsenic certainly requires further confirmation, and a more recent description[53] of an attempt to prepare pentaethylarsenic from ethyl-lithium and tetraethylarsonium bromide reports that the products were triethylarsine and hydrocarbon gases. The interaction of tetramethylphosphonium iodide and methyl-lithium yields a methylene adduct[54] according to

$$Me_4PI + MeLi \longrightarrow Me_3P{=}CH_2 + LiI + CH_4.$$

An attempt was made in the present study to prepare pentamethylantimony by an alternative means - from antimony pentachloride and an aluminium alkyl. For comparison, the interaction of antimony trihalides with methylaluminium sesquihalide was also investigated.

Trialkylstibines are generally prepared by reaction between antimony trichloride and a Grignard or organo-lithium reagent.[55] As indicated in an earlier section of this chapter, aluminium alkyls have also been used to prepare alkylstibines. In this study, it was observed that when antimony trihalides and methylaluminium sesquibromide are mixed in a hydrocarbon solvent, a yellow oil separates. Trimethylstibine can be distilled from this oil only after it has been decomposed by hydrolysis. The insolubility of the oil in hydrocarbon solvents suggests that it may be an ionic species but no attempt was made to characterize it further.

The interaction of antimony pentachloride and methylaluminium sesquibromide in hydrocarbon solution resulted in the separation of a red oil and a white solid. Distillation of the mixture did not yield any pentamethylantimony. Some attempts to characterize the two reaction products were made, but it has not been possible to draw unequivocal conclusions from the results. Both the white solid and the red oil decomposed on exposure to oxygen or water. The red oil was involatile at moderate temperatures and hence could not be purified by distillation. The white solid could be recrystallized from boiling benzene, but upon successive recrystallizations, a considerable difference in the melting point of the initial and recovered solids was always observed. Both materials contained aluminium as well as antimony, and both were readily soluble in polar organic solvents. These observations and the knowledge that antimony(V) readily forms salt-like complexes (e.g. the reactions of Me_5Sb with Ph_3B and MeLi) indicates that these compounds may be ionic species of the form $(SbX_nR_{6-n})AlX_2$, $(SbX_nR_{4-n})AlX_4$, etc.

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CHAPTER 4

Reactions of Organometallic Compounds with Titanium Halides

1. Bimetallic organometallic compounds.-

Several organometallic compounds, containing aluminium and titanium, have recently been isolated and well characterized.[1] As mentioned in chapter 1, the complexes formed from aluminium alkyls and bis(cyclopentadienyl)titanium dichloride exhibit catalytic properties for the low pressure polymerization of α-olefins. As such, they represent the only isolable catalysts of the Ziegler type which have well defined structures.

In this chapter, a discussion is presented of investigations of several organometallic-titanium halide systems which are similar, in some ways, to those used to obtain the complexes mentioned above. The original work described in the following section of this chapter is concerned with the action of triethyl-aluminium etherate and of tetraethyl-lead on bis(cyclopentadienyl)titanium dichloride. These investigations were undertaken to gain a clearer understanding of some of the factors which affect the formation and stability of the bimetallic complexes. The next section includes a brief description of some essentially qualitative observations of the action of lithium tetraethylaluminate on titanium tetrachloride. The final section of the chapter describes the result of attempts to prepare new bimetallic compounds, similar to $Cp_2TiCl_2AlR_2$, but containing lead or tin in place of aluminium.

Before discussing the results of these investigations, it seems pertinent to consider just how general the formation of bimetallic complexes is to organometallic chemistry. Several examples of such compounds have already been mentioned in previous chapters. These complexes can be conveniently classified according to the type of metal-metal linkage in the compound. Complexes already considered include those with an ionic linkage such as sodium tetraethylaluminate, $Na^+(AlEt_4)^-$, the bridged compounds like $Cp_2Ti\langle\begin{smallmatrix}Cl\\Cl\end{smallmatrix}\rangle AlR_2$ and $R_2Al\langle\begin{smallmatrix}R\\R\end{smallmatrix}\rangle AlR_2$, co-ordination compounds of the type $R_3P.AlCl_3$, and organometallic compounds incorporating metal-metal σ-bonds, such as hexaethyldilead, $Et_3Pb-PbEt_3$. Indeed these compounds represent all the main classes of bimetallic complexes involving metal alkyls and other metal compounds which have been investigated. Other bimetallic organometallic compounds, involving transition metals linked through bridging carbonyl or nitrosyl groups, are also known[2] but will not be discussed here. The known bimetallic complexes of metal alkyls are summarized in table 4.1.

2. Metal alkyl-bis(cyclopentadienyl)titanium dichloride systems.-

(a) The action of aluminium alkyls on bis(cyclopentadienyl)-titanium dichloride in inert solvents.

Several investigations of aluminium alkyl-bis(cyclopentadienyl)titanium dichloride interactions have been reported in the literature, and, as indicated previously, a number of aluminium-titanium complexes have been isolated from these systems. A survey of these reactions therefore seems necessary before proceeding to a discussion of the reactions of metal alkyls with bis(cyclopentadienyl)-titanium dichloride investigated in this study.

Complexes of the general form $Cp_2TiCl_2AlR'R''$ (where R' and

Table 4.1

Bimetallic complexes of 'metal' alkyls

Classification: A - Metal-metal σ-bond.
B - Metal-metal co-ordinate bond.
C - Ionic metal-metal linkage.
D - Bridged metal-metal linkage.

Types of metals involved	Examples	Classification
Grp.I - Grp.II	$LiZnEt_3$ etc.	C
Grp.I - Grp.III	$NaBMe_4$, $LiAlEt_3Cl$ etc.	C
Grp.I - Grp. IV	$KGeEt_3$, $LiSnMe_3$, $NaPbEt_3$ etc.	C
Grp.I - Tr. met.	$LiMnMe_3$	?
Grp.II - Grp. II	$R-Be\left\langle{}^{R}_{R}\right\rangle Be\left\langle{}^{R}_{R}\right\rangle Be-R$ etc.	D
Grp.II - Grp. V	$R_2Be.(PMe_3)_2$ etc.	B
	$(PMe_4)^+(HgI_3)^-$ etc.[4]	C
Grp.III - Grp.III	$R_3Al.R'_3B$ etc.	D
Grp. III - Grp. V	$R_3\bar{B}.(NEt_3)^+$, $R_3Al.PMe_3$ etc.	B or C
Grp. III - Tr. met.	$Cp_2TiCl_2AlEt_2$ etc.	D
Grp. IV - Grp. IV	$R_3Sn.SnR_3$, $R_3Ge.SnR'_3$ etc.	A
Grp. V - Grp. V	$Me_2Sb.SbMe_2$ etc.	A
Grp. V - Tr. met.	$(Et_3P)_2PdMe_2$ etc.	B
Tr. met. - Tr. met.	$(MePtCl_3)_4$, $(MeAuBr)_4$	D

Except where other references are given, examples are taken from Coates' textbook on Organometallic Compounds.[3]

R" are alkyl or halide groups) have been thoroughly investigated by several workers. The first bimetallic complex of this type was isolated by Natta and co-workers[5] from the interaction of bis(cyclopentadienyl)titanium dichloride and triethyl-aluminium in heptane. The following stoichiometry accounts for the observed products from the reaction:

$$Cp_2TiCl_2 + AlEt_3 \longrightarrow Cp_2TiCl_2AlEt_2 + \tfrac{1}{2}C_2H_4 + \tfrac{1}{2}C_2H_6.$$

Subsequently, Natta[6] reported the preparations of the similar compounds $Cp_2TiCl_2AlEtCl$ and $Cp_2TiCl_2AlCl_2$ from the interaction of bis(cyclopentadienyl)titanium dichloride with diethyl-aluminium chloride and ethyl-aluminium chloride respectively. Breslow and co-workers[7] have also observed that interaction of bis(cyclopentadienyl)titanium dichloride with diethyl-aluminium chloride gives $Cp_2TiCl.AlEtCl_2$, as well as other complexes.

A stepwise mechanism has been suggested for the formation of these complexes. It has been postulated that the complexes isolated from these systems are formed after the titanium has been reduced by the aluminium alkyl, e.g.

$$\begin{array}{l} Cp_2TiCl_2 + AlR_2Cl \longrightarrow Cp_2TiClR + AlRCl_2 \\ \qquad\qquad\qquad\qquad\qquad\quad \llcorner\!\!\longrightarrow Cp_2TiCl + \tfrac{1}{2}C_2H_4 + \tfrac{1}{2}C_2H_6. \end{array}$$

The bis(cyclopentadienyl)titanium monochloride formed in this way can then form complexes with any alkyl-aluminium halides present, e.g.

$$Cp_2TiCl + AlRCl_2 \longrightarrow Cp_2TiCl_2AlClR.$$

The suggested mechanism is supported by the observation[1] that direct interaction between bis(cyclopentadienyl)titanium monochloride and aluminium alkyls or aluminium halides also yield these complexes.

An alternative mechanism has been proposed which involves reduction of the titanium within a cyclopentadienyl-titanium — alkyl-aluminium complex. It is suggested that initially a titanium(IV) complex is probably formed, e.g.

$$2\ Cp_2TiCl_2 + (Et_2AlCl)_2 \rightleftharpoons 2\ Cp_2TiCl_2.Et_2AlCl$$

and that alkyl exchange and subsequent homolytic fission of the titanium-alkyl bond takes place without breakdown of the complex, e.g.

$$Cp_2TiCl_2.Et_2AlCl \rightleftharpoons Cp_2EtTiCl.EtAlCl_2$$

$$Cp_2EtTiCl.EtAlCl_2 \longrightarrow Cp_2TiCl.EtAlCl_2 + Et^{\cdot}$$

However, since Breslow and co-workers[7b] have both refuted the possibility of alkyl exchange of the type shown and, in a separate publication,[7a] presented spectroscopic evidence for the formation of all the aluminium-titanium complexes shown in the above equations, the plausibility of this mechanism is still in doubt.

The formulation of these complexes as $Cp_2TiCl_2AlR'R''$ follows from analyses and other chemical investigations of the compounds. For instance, treatment of the complexes with anhydrous hydrogen chloride regenerates bis(cyclopentadienyl) titanium dichloride in good yield,[5] indicating that the cyclopentadienyl groups are still attached to the titanium after complex formation; and the action of diethyl ether[8] or tertiary amines[9] on the complexes causes their breakdown to form bis-(cyclopentadienyl)titanium monochloride and $AlR'R''Cl.NMe_3$.

The detailed molecular constitution of some $Cp_2TiCl_2AlR'R''$ complexes has been established by X-ray analysis. These investigations have revealed that the two metals are linked through bridging chlorine groups. The lattice structure of $Cp_2TiCl_2AlEt_2$ has been established[10]

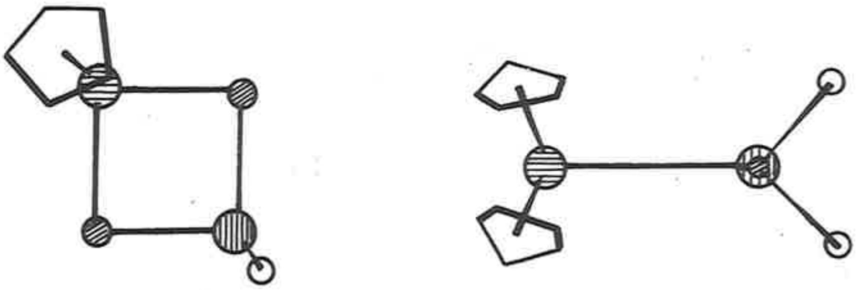


Fig. 4.1 Schematic representation of the molecular structure of bis(cyclopentadienyl)titanium dichloride.

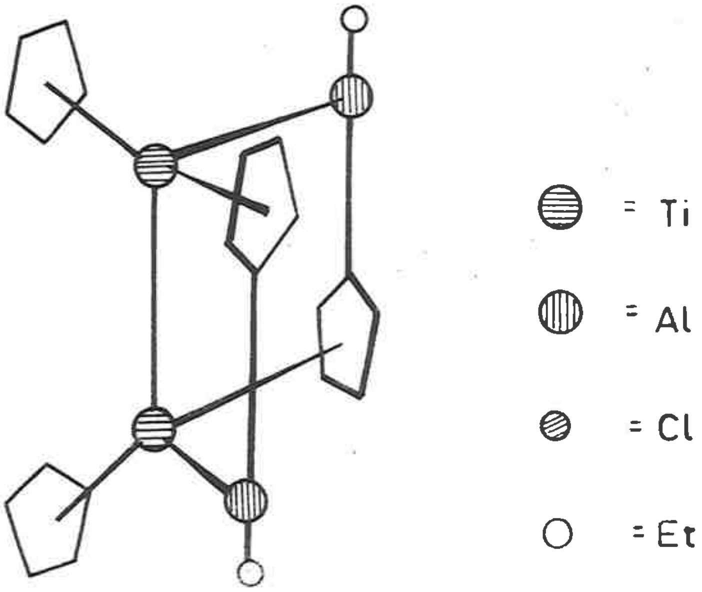


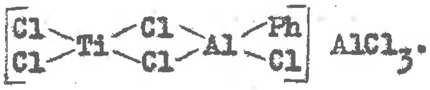
Fig. 4.2 Schematic representation of the molecular stucture of the compound $(C_5H_5)_2TiAl(C_2H_5)_2$.

in this way, and is shown in figure 4.1.

A few other compounds of different type but of related interest have been reported. For instance, Long[11] has investigated similar systems in which methyl-aluminium chloride and aluminium trichloride are used in place of the ethyl-aluminium compounds. On spectroscopic evidence, he has suggested the formation of two complexes in each instance, viz. $[Cp_2TiCl(RAlCl_3)]$ and $[Cp_2Ti(RAlCl_3)_2]$, (R = methyl or chloride group). The $[Cp_2Ti(RAlCl_3)_2]$ species are formed only when the ratio of Al:Ti is greater than 1:1. In contrast to most of the complexes described previously, these compounds are complexes of titanium(IV). Adema and co-workers[12] have also investigated bis(cyclopentadienyl)titanium dichloride-aluminium trichloride systems spectrophotometrically, but their results, which indicate the formation of the compounds $[Cp_2TiCl_2(AlCl_3)_2]$ and $[Cp_2TiCl_2(AlCl_3)_5]$, are not in agreement with those obtained by Long.

Natta and co-workers[13] have described the formation of two other titanium-aluminium complexes. One is formed from bis(cyclopentadienyl)titanium monochloride and triethyl-aluminium, and the analysis and chemical behaviour of this compound suggests the formulation $[Cp_2TiAlEt_2]_2$. X-ray analysis of the solid established the unusual spatial model shown in figure 4.2.

The other complex is formed by a Friedel-Crafts type reduction of titanium tetrachloride using aluminium and a little aluminium trichloride in benzene.[14] Natta and co-workers have reported that this complex is a bimetallic compound containing an aluminium-phenyl link, and suggest the structural formula



$$\left[\begin{matrix}Cl\\Cl\end{matrix}\!>\!Ti\!<\!\begin{matrix}Cl\\Cl\end{matrix}\!>\!Al\!<\!\begin{matrix}Ph\\Cl\end{matrix}\right] AlCl_3.$$

However, Martin and Vohwinkel[15] dispute this formulation and have presented additional evidence which indicates that the compound is actually an arene complex of titanium(II). They suggest the empirical formula $Al_2TiCl_8(C_6H_6)$ for the complex.

A similar complex, formulated by Natta and co-workers[16] as $(Al_2CoCl_5Ph)_2C_6H_6$ has also been described.

(b) The action of triethyl-aluminium etherate on bis(cyclopentadienyl)titanium dichloride.

As mentioned in the preceding section, complexes formed from aluminium alkyls and bis(cyclopentadienyl)titanium dichloride are ruptured when treated with diethyl ether,[8] e.g.

$$Cp_2TiCl.ClAlR'R'' + Et_2O \longrightarrow Cp_2TiCl + ClAlR'R''.Et_2O.$$

It seemed of interest therefore to investigate the action of triethyl-aluminium etherate on bis(cyclopentadienyl)titanium dichloride. In chapter 3, it was shown that the formation of etherates of aluminium alkyls does not prevent the exchange of alkyl groups from aluminium to other metals. Hence, in the system under study, alkylation (and consequently possible reduction) of the titanium seemed feasible. It seemed probable, however, that saturation of the electron-deficiency of the aluminium alkyl by the formation of the etherate prior to reaction with the titanium compound would inhibit subsequent complex formation.

The reaction between triethyl-aluminium etherate and bis-(cyclopentadienyl)titanium dichloride in tetrahydrofuran forms a soluble green compound. Evaporation of the solvents in vacuum yielded a heterogeneous mixture of brown and green solids. This solid mixture changed completely to a dark coloured solid within a few hours. Both the green and dark solids contained reduced titanium, but quantitative determinations of titanium(III) were not reproducible. Additional quantitative analyses of the solid residue were not attempted because of the apparent heterogeneity of the solid. Furthermore, quantitative handling of the solid was difficult because of its extreme sensitivity to traces of air.

It was subsequently realized that the chemical behaviour of this solid resembled that of the tetrahydrofuran complex of bis(cyclopentadienyl)titanium(II).[17] This latter compound exists in both green and brown forms. It has only been isolated from solution in the green form, but a rapid transformation to the brown species takes place within a few hours. The compound is very sensitive to oxygen. Although it reacts only very slowly with oxygen-free water, it is oxidized by dilute mineral acid solutions to the bis(cyclopentadienyl)titanium hydroxy cation, $\mathrm{Cp_2Ti(OH)^+}$. This latter property could explain the irreproducible nature of the attempted determinations of reduced titanium. Since facilities for semi-micro determinations of carbon and hydrogen in oxygen reactive materials were not available, no further attempts to confirm the constitution of the green and brown reaction products could be made. However, the following reaction scheme is intuitively suggested.

$$\mathrm{Cp_2TiCl_2 + Et_3Al.Et_2O \longrightarrow Cp_2TiEt_2 + Cl_2AlEt.Et_2O}$$

$$\mathrm{\hookrightarrow Cp_2Ti + 2Et^{\bullet}}$$

$$\mathrm{Cp_2Ti + THF \longrightarrow Cp_2Ti.THF.}$$

Since this mechanism requires the intermediate formation of bis(cyclopentadienyl)-alkyl-titanium compounds, some attempts were made to detect such compounds in this system. Bis(cyclopentadienyl)-diethyl-titanium,[18] bis(cyclopentadienyl)-methyl-titanium chloride,[19] and bis(cyclopentadienyl)-ethyl-titanium chloride[7b] have all been prepared by the action of a Grignard reagent on bis(cyclopentadienyl)titanium dichloride. Observations made during the development of these preparations indicate that the experimental conditions employed may considerably effect the possibility of isolating satisfactory yields of bis(cyclopentadienyl)-alkyl-titanium compounds from metal alkyl-bis(cyclopentadienyl)titanium dichloride systems. For instance, it has been suggested that excess metal alkyl and possibly titanium(III) compounds cause the autocatalytic decomposition of bis(cyclopentadienyl)-alkyl-titanium compounds. Furthermore, it has been reported that the solvent used in the preparation may have considerable effect on the amount of bis(cyclopentadienyl)-alkyl-titanium compound which can be isolated. Notwithstanding these difficulties, a small amount of a yellow-orange solid, which may be a bis(cyclopentadienyl)-alkyl-titanium compound, was isolated from the bis(cyclopentadienyl)titanium dichloride-triethyl-aluminium etherate systems. Less than 1% yield of assumed $Cp_2TiR'Et$ (R' = chloride or ethyl group) was obtained. The yellow-orange solid decomposed upon attempted sublimation. It did not seem to be affected upon exposure to dry air. Bis(cyclopentadienyl)titanium dichloride could be regenerated from the yellow-orange solid by treatment with hydrogen chloride, indicating that the cyclopentadienyl groups are still attached to titanium in the new compound.

Electron absorption spectra of solutions of bis(cyclopentadienyl)-titanium dichloride and the yellow-orange titanium derivative in toluene were compared and the results are shown in figure 4.3. Since the

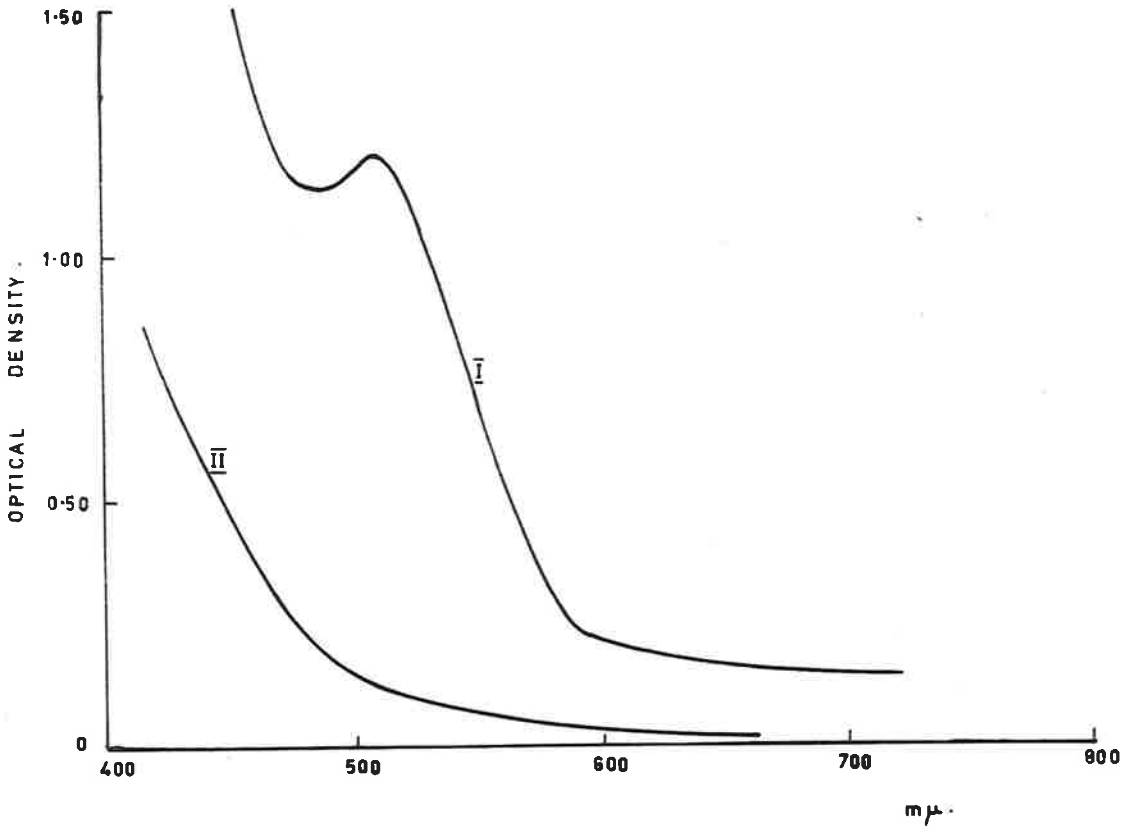


Fig. 4.3 Comparison of the spectra (visible region) of bis-(cyclopentadienyl)titanium dichloride (I) and the bis(cyclopentadienyl)-ethyl-titanium compound (II).

absorption maximum shown in the spectrum of bis(cyclopentadienyl)titanium dichloride is probably due to charge transfer between titanium and chlorine, the spectra indicate that groups other than chlorine are attached to titanium in the yellow-orange solid.

Inability to purify the product, and difficulties associated with analysing air reactive materials, rendered further confirmation of the nature of the product difficult. However, the results further support the suggestion that bis(cyclopentadienyl)-alkyl-titanium compounds are formed in the reaction.

(c) The action of tetraethyl-lead on bis(cyclopentadienyl)titanium dichloride.

Failure to obtain well authenticated bis(cyclopentadienyl)-alkyl-titanium derivatives from the interaction of triethyl-aluminium etherate and bis(cyclopentadienyl)titanium dichloride, and the report that titanium tetrachloride is rapidly converted to ethyl-titanium trichloride by treatment with tetraethyl-lead,[20] prompted an investigation of the action of tetraethyl-lead on bis(cyclopentadienyl)titanium dichloride.

When tetraethyl-lead and bis(cyclopentadienyl)titanium dichloride are mixed in the absence of a solvent, no reaction is observed. However, when bis(cyclopentadienyl)titanium dichloride is treated with tetraethyl-lead in an organic solvent, a white precipitate slowly forms. The white precipitate forms most quickly when the ratio of Pb:Ti is greater than 1:1. Isolation, and subsequent analysis of the white solid indicated it was predominantly triethyl-lead chloride.

Conversion of tetraethyl-lead to triethyl-lead chloride indicates that transfer of some alkyl groups from lead to titanium had occurred. However, no bis(cyclopentadienyl)-ethyl-titanium derivatives could be isolated from the reaction mixture. As mentioned previously, the observations of other workers indicate that unreacted lead alkyl could cause the autocatalytic decomposition of bis(cyclopentadienyl)-ethyl-titanium compounds so that inability to isolate undecomposed titanium alkyls from the system investigated is not altogether surprising. However, no other new titanium derivatives of well defined constitution could be isolated from the reaction mixture. This may indicate that a number of different titanium derivatives were formed by different modes of bis(cyclopentadienyl)-ethyl-titanium decomposition.

Some further observations, which support that bis(cyclopentadienyl)titanium dichloride was transformed to some new titanium species when treated with tetraethyl-lead, were made. Firstly, hydrolysis of the reaction mixture liberated a small amount of gaseous hydrocarbon. Since it is known that hydrolysis of titanium alkyls does, in some instances at least, liberate hydrocarbons (e.g. the aqueous hydrolysis of ethyl-titanium trichloride liberates ethane quantitatively[20]) whereas lead alkyls are extremely stable towards hydrolysis, this liberation of hydrocarbons can only be due to hydrolysis of titanium alkyls. Although the greater stability of cyclopentadienyl-alkyl-titanium compounds compared with simple titanium alkyls indicates that hydrolysis of the cyclopentadienyl derivative might be less than quantitative, the results obtained revealed that at least 20% conversion of bis(cyclopentadienyl)titanium dichloride to bis(cyclopentadienyl)-ethyl-titanium chloride had taken place when a mixture of chloroform solutions of bis(cyclopentadienyl)titanium dichloride and tetraethyl-lead was shaken for two hours.

Secondly, the absorption properties of bis(cyclopentadienyl)-titanium dichloride–tetraethyl-lead reaction solutions [viz. that bis-cyclopentadienyl)titanium dichloride solutions exhibit an absorption maximum at 518 mμ, whereas tetraethyl-lead does not absorb at this wavelength, and that bis(cyclopentadienyl)titanium dichloride solutions obey the Lambert-Beer law] made it possible to relate the concentration of bis(cyclopentadienyl)titanium dichloride in these solutions to the optical density of the reaction mixture. In this way it was observed that a gradual but continuous decrease of bis(cyclopentadienyl)titanium dichloride concentration occurred when solutions of the titanium compound were treated with tetraethyl-lead (see table 4.2).

Table 4.2

Variation of the molar concentration of bis(cyclopentadienyl)titanium dichloride in an equimolar mixture of bis(cyclopentadienyl)titanium dichloride and tetraethyl-lead

Time (hrs.)	Molar conc. of unchanged Cp_2TiCl_2
0	2.90 mM
3	2.50
7	2.47
20	2.22

Interference from the alkyl-lead halides formed during the reaction was eliminated by using ethyl acetate as solvent. Triethyl-lead chloride is soluble in this solvent.

It was further observed that the spectrum of bis(cyclopentadienyl) titanium dichloride changes considerably, but slowly, in the visible region when tetraethyl-lead is added to the titanium compound (see figure 4.4). This change in the spectrum demonstrates that a change in the nature of the titanium species is slowly taking place. The observed spectral changes are similar, in some respects, to those reported by Breslow and co-workers[8] for the interaction of bis(cyclopentadienyl)titanium dichloride and diethyl-aluminium chloride. However, the extreme slowness of the reaction when tetraethyl-lead is used, and the subsequent deterioration of the solutions, makes accurate interpretation and comparison of these spectra difficult.

The slowness of the reaction in chloroform may be due, in part, to a peculiar solvent effect. It is feasible that some decomposition of the alkylated titanium species according to

$$Cp_2TiClEt \longrightarrow Cp_2TiCl + Et^{\cdot}$$

would occur, and since it has been observed that bis(cyclopentadienyl)-titanium monochloride is oxidised by methylene chloride,[7] a similar reaction with chloroform can be expected. It is feasible therefore that decomposition of the alkylated titanium derivative may indirectly result in the reformation of bis(cyclopentadienyl)titanium dichloride. It is difficult, however, to explain similarly the slowness of the reaction in non-halogenated hydrocarbon solvents.

Although complete characterization of the products has not been achieved, the results indicate that the initial reaction can probably best be represented by an equilibrium of the type:

$$Cp_2TiCl_2 + PbEt_4 \rightleftharpoons Cp_2EtTiCl + PbEt_3Cl,$$

which favours dealkylation of the titanium derivative. It would seem that the bis(cyclopentadienyl)-ethyl-titanium compound is unstable in the presence of unreacted lead alkyl, and perhaps also in the solvents

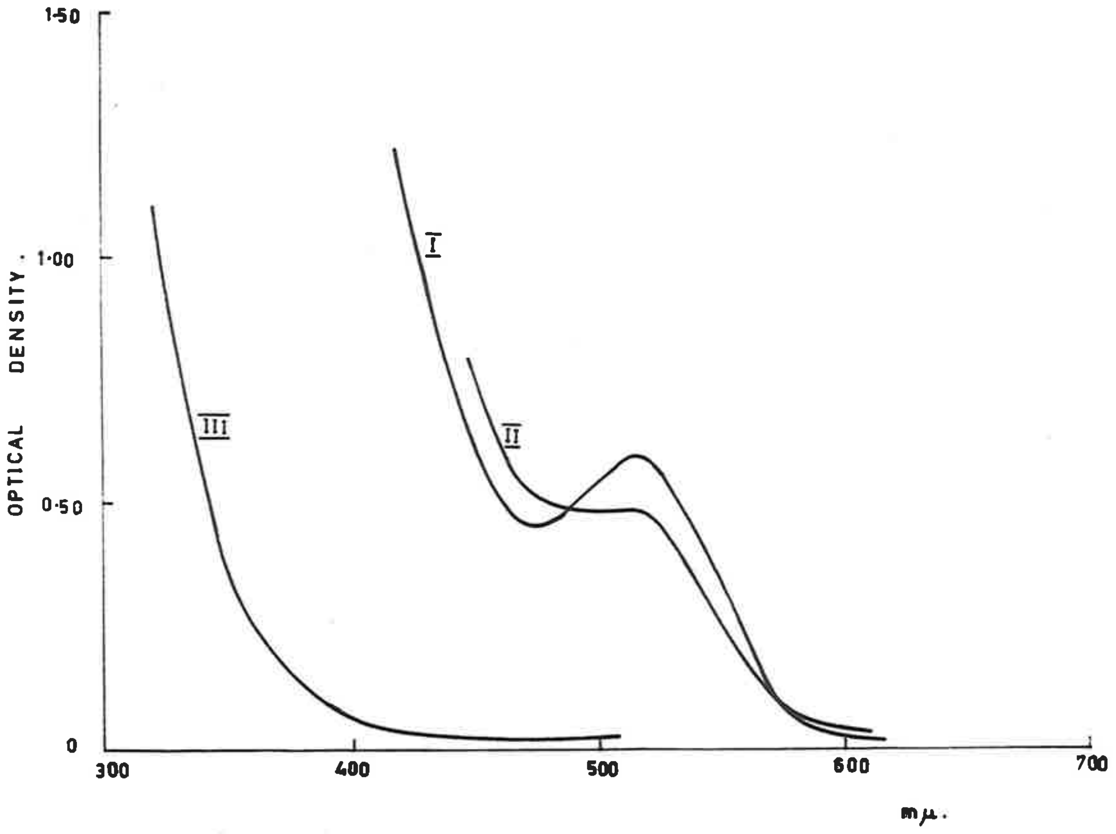


Fig. 4.4 Spectra (visible region):- the interaction of bis(cyclopentadienyl)titanium dichloride and tetraethyl-lead.
I- the spectrum of pure bis(cyclopentadienyl)titanium dichloride; II- the spectrum of the mixture after 2 hours; III- the spectrum of the mixture after 48 hours.

used, and decomposes to unidentified titanium derivatives. The removal of the titanium compound in this way would displace the equilibrium to the right, thus explaining the slow but continuous removal of colour from the solution.

3. Reactions of alkali metal derivatives of organometallics with titanium halides.-

(a) The action of lithium tetraethylaluminate on titanium tetrachloride.

Although bis(cyclopentadienyl)titanium dichloride - aluminium alkyl systems often yield well defined products, the products obtained from the interaction of titanium tetrahalides and aluminium alkyls are by no means so well authenticated. A considerable amount of work has been done on the latter systems, and this has been briefly surveyed in chapter 1. In general, the accumulated evidence indicates that the titanium is initially alkylated by the aluminium alkyl, and that the titanium alkyl so formed subsequently decomposes with the evolution of hydrocarbon gases and the formation of reduced titanium halides. It has been suggested that the alkyl-aluminium halides are then strongly adsorbed onto irregularities at the surface of the titanium halide, but the nature and extent of the adsorption have not been well established. In this study, the investigations of the alkylating properties of lithium tetraethylaluminate described in chapter 3 have been extended further to cover the reaction between titanium tetrachloride and lithium tetraethylaluminate.

The interaction of equimolar proportions of lithium tetraethylaluminate and titanium tetrachloride in an inert organic solvent produced a dark coloured deposit, or sometimes a dark brown oil. Hydrocarbon gases were simultaneously evolved. Molecular weight determinations indicated that these gases were essentially C_2-hydrocarbons and chemical tests revealed the presence of some unsaturated hydrocarbon. In view of the large number of reports on the nature of the gases evolved from such systems,[21] the gases were not further investigated.

When the reaction was carried out in tetrahydrofuran as solvent, a green solid formed as well as the dark deposit. Within a few hours, the dark deposit was completely transformed to the green solid.

Both the green solid and the dark deposit contained reduced titanium and consequently were rapidly decomposed upon exposure to the air. Thorough washing of the solids with a variety of organic solvents did not remove all the lithium and aluminium indicating the formation of adsorption complexes or of chemical compounds. Quantitative analyses of samples of the solids were not reproducible. It seems likely that the green solid is a solvated form of the brown deposit.

Since it was shown in the last chapter that lithium tetraalkylaluminates probably behave as mixtures of lithium alkyls and aluminium trialkyls, it can be anticipated that a complex variety of interactions can take place in this system. By analogy with related investigations of the interaction of titanium tetrahalide with ethyllithium[22] and with triethyl-aluminium[23] the following reactions are intuitively suggested. Doubtless, other reactions would also contribute to the overall stoichiometry.

$$\begin{tikzcd}[column sep=small] TiCl_4 + LiAlEt_4 \arrow[r] & TiCl_3R \arrow[d] & + \; LiCl \; + \; AlEt_3 \\ & TiCl_3 + \tfrac{1}{2}C_2H_4 + \tfrac{1}{2}C_2H_6. & \end{tikzcd}$$

$$\mathrm{TiCl_3 + AlR_3 \longrightarrow TiCl_2R + AlR_2Cl}$$
$$\mathrm{\hookrightarrow TiCl_2 + \tfrac{1}{2}C_2H_4 + \tfrac{1}{2}C_2H_6.}$$

etc.

$$\mathrm{TiCl_3 + nMR \longrightarrow TiCl_3.(MR)_n.}$$

etc.

$$\mathrm{TiCl_3 + LiCl \longrightarrow Li(TiCl_4).}$$

(b) <u>Reactions of alkali metal derivatives of group IV metal alkyls with bis(cyclopentadienyl)titanium dichloride.</u>[24]

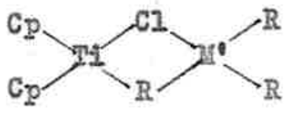
It is known[25] that some organometallic compounds of the form $M(M'R_n)$, (where M = alkali metal, M' = lead or tin, R = alkyl group) react with alkyl-metal halides in the following manner:

$$M(M'R_n) + R_3M'I \longrightarrow R_3M'.M'R_3 + MI.$$

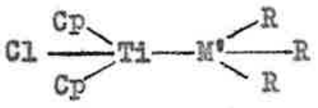
It thus seemed feasible that interaction of such $M(M'R_n)$ compounds with bis(cyclopentadienyl)titanium dichloride might lead to the preparation of new bimetallic organometallic compounds, e.g.

$$M(M'R_3) + Cp_2TiCl_2 \longrightarrow Cp_2TiCl.M'R_3 + MCl.$$

If titanium-group IV metal compounds of this type were formed, they could conceivably exist either as bridged complexes similar to the titanium-aluminium complexes discussed previously, e.g.



or as compounds with a direct metal-metal linkage, e.g.



In this section, investigations of the interaction of bis(cyclopentadienyl)titanium dichloride with triethylplumbyl sodium and with triethylstannyl lithium are discussed.

Triethylplumbyl sodium was prepared in liquid ammonia solvent systems from sodium and tetraethyl-lead,[26] e.g.

$$2(Na^{+}\ e) + PbEt_4 \longrightarrow NaEt + Na(PbEt_3)$$

$$NaEt + NH_3 \longrightarrow NaNH_2 + C_2H_6.$$

It was shown in chapter 2 that triethylplumbyl sodium cannot be easily isolated in a system free of liquid ammonia, and hence it was necessary to work in liquid ammonia as solvent for the reaction between triethylplumbyl sodium and bis(cyclopentadienyl)titanium dichloride. Consequently, it seemed necessary to investigate the effect of liquid ammonia on bis(cyclopentadienyl)titanium dichloride. Ammonolysis occurred when the solid titanium compound was placed in contact with liquid ammonia to yield a yellow slightly soluble product. The ammonia solution contained free chloride ions which could be precipitated as barium chloride on the addition of a solution of barium nitrate in liquid ammonia. Treatment of the solid with water liberated ammonia and dissolved out some ammonium chloride. These results indicate that the solid is a mixture of ammonium chloride and ammono-basic titanium compounds. A plausible reaction scheme is shown below:

$$Cp_2TiCl_2 + NH_3 \longrightarrow Cp_2TiNH_2X + NH_4Cl \qquad (X = NH_2 \text{ or } Cl).$$

The average ratio of Ti:N:Cl in the yellow solid product was 1:3·4:2, the variation in the nitrogen value being from 3.15 to 3.60. This ratio indicates that the idealized composition of the product mixture on a mole basis could be either

$$A : \left\{Cp_2TiClNH_2.NH_3 + NH_4Cl\right\},$$

or B: $\left\{Cp_2TiClNH_2 + Cp_2Ti(NH_2)_2 + 3\ NH_4Cl\right\}$,

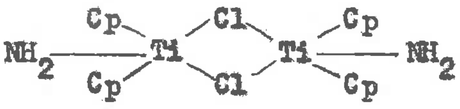
or C: $\left\{Cp_2Ti(NH_2)_2 + 2\ NH_4Cl\right\}$.

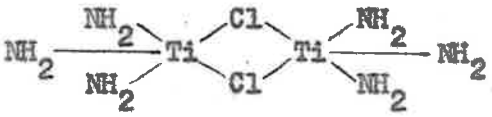
Repeated extraction of the solid with liquid ammonia failed to separate ammonium chloride from the ammono-basic titanium compound since the latter dissolved to a significant extent in liquid ammonia. It is possible that this solubility in liquid ammonia is a result of complex anion formation in the liquid ammonia solutions, e.g.

$$NH_4Cl + Cp_2TiClNH_2 \longrightarrow NH_4^+(Cp_2TiCl_2NH_2)^-.$$

Because the product constituents could not be separated, it has not been possible to establish which composition is correct. A similar problem of ammonium chloride contamination was met by Fowles and Nicholls[27] in the ammonolysis of titanium tetrahalides. They did not observe complete replacement of all four halogens in their reactions and since it seems unlikely that only half the cyclopentadienyl-titanium compound would be completely ammonolyzed rather than the total quantity, composition A is favoured.

It seems feasible to explain this inability to replace completely all the halogens in compounds of this type in terms of the formation of bridged compounds, the bridging halogens being those which cannot be substituted. Thus, compounds of the types shown below can be visualised





Since it has been claimed[26] that ammonium chloride will decompose triethylplumbyl sodium, the formation of ammonium chloride from the ammonolysis of bis(cyclopentadienyl)titanium dichloride further complicates the system under study. It was therefore considered advisable to further investigate the action of ammonium chloride on triethylplymbyl sodium in liquid ammonia. It was observed that the reaction leads to the evolution of gases and the formation of green solids in the reaction vessel. Removal of ammonia by vacuum distillation at -78° led to the simultaneous decomposition of the green solid to yield gaseous products and a grey coloured residue. From the latter, tetraethyl-lead and sodium chloride were extracted. Fractionation of the gaseous constituents separated, from the ammonia, a small amount of a compound which decomposed at room temperature into lead, tetraethyl-lead, gaseous hydrocarbons, and a non-condensible gas (presumably hydrogen).

It seems feasible that the following reaction would initially occur in this system:

$$Na(PbEt_3) + NH_4Cl \longrightarrow NH_4(PbEt_3) + NaCl.$$

Such an ammonium-lead salt is essentially a solvated alkyl-lead hydride, $HPbEt_3$. The reaction is similar to the known reaction between ammonium salts and trimethylstannyl sodium in liquid ammonia. In the latter reaction trimethylstannane separates as a heavy oil:

$$Me_3SnNa + NH_4^+ + X^- \longrightarrow Me_3SnH + NH_3 + NaX.$$

Thus it seems probable that the green solid contains the thermally unstable triethylplumbane, and the products collected indicate that the following modes of decomposition are possible:

$$2\,(Et_3PbH)NH_3 \begin{array}{l} \nearrow Et_3Pb.PbEt_3 + H_2 + 2NH_3 \\ \searrow 2Et_2Pb + 2C_2H_6 + 2NH_3. \end{array}$$

$$6\ Et_2Pb \longrightarrow [2\ Et_6Pb_2 + 2\ Pb] \longrightarrow 3\ Pb + 3\ PbEt_4.$$

Relatively few alkyl-lead hydrides have been isolated, but some investigations of trialkyl-lead hydrides have recently been reported. A comparison of the results obtained in these investigations with those reported above therefore seems pertinent.

Duffy and Holliday[29] have good evidence for the formation of trimethyl-lead hydride from trimethyl-lead chloride and potassium borohydride in liquid ammonia, and have observed that the product decomposes initially according to:

$$2\ Me_3PbH \longrightarrow Me_3Pb.PbMe_2H + CH_4.$$

This dilead compound decomposed further on warming to room temperature to yield lead, tetramethyl-lead, hydrogen and methane. The only other report of the preparation of trialkyl-lead hydrides involves the lithium tetrahydroaluminate reduction of trialkyl-lead halides. Becker and Cook[30] have prepared both trimethyl-lead hydride and triethyl-lead hydride in this way, and have observed that the hydrides decompose according to the equation

$$4\ R_3PbH \longrightarrow 2\ H_2 + 3\ PbR_4 + Pb.$$

It is thus apparent that various modes of trialkyl-lead hydride decomposition may be possible.

The reaction between bis(cyclopentadienyl)titanium dichloride and triethylplumbyl sodium in ammonia/diethyl ether solution forms a blue-green solid which contains neither free bis(cyclopentadienyl)-titanium dichloride nor the corresponding ammono-basic compound. The compound, when freed from ammonia, rapidly changed into a buff coloured solid; the change was irreversible and was accompanied by the liberation of gaseous hydrocarbons. The buff solid contained both lead and titanium. All the chlorine originally attached to titanium could be extracted from the solid product as sodium chloride by treatment with water. Treatment of the solid with nitric acid gave lead nitrate, ethane, and unidentified titanium derivatives. Some evidence was obtained that the product contained easily oxidizable groups. The product gave inconsistent analyses, but always had a low C:H ratio. The non-reproducible nature of these analyses can only be attributed to heterogeneity of the solid caused by different modes of the decomposition. The following equations are suggested as representing the formation of the initial blue-green bimetallic complex.

$$Cp_2TiCl_2 + 3\,NH_3 \longrightarrow Cp_2TiClNH_2.NH_3 + NH_4Cl$$

followed either by

$$Cp_2TiClNH_2.NH_3 + NaPbEt_3 \longrightarrow Cp_2TiNH_2PbEt_3 + NaCl$$

or

$$NaPbEt_3 + NH_4Cl \longrightarrow NH_4PbEt_3 + NaCl$$

$$Cp_2TiClNH_2.NH_3 + NH_4PbEt_3 \longrightarrow Cp_2TiNH_2.PbEt_3 + NH_4Cl.$$

The ammonium chloride would then react with sodamide formed in the preparation of triethylplumbyl sodium to yield sodium chloride.

The instability of the proposed bimetallic complex prevented its further characterization.

An investigation of the possibility of reducing bis(cyclopentadienyl)titanium dichloride in liquid ammonia was carried out by treating the titanium compound with a solution of sodium in liquid ammonia. A green coloured solid, believed to be a titanium(III) cyclopentadienyl derivative, was formed. This was, however, converted to a yellow ammono-basic titanium compound when the solvent was completely removed by evaporation. The ratio of Ti:N:Cl in this yellow solid was 1:2·3:2. The product has been reoxidized to a titanium(IV) compound, the idealized composition on a mole basis being

$$\left\{Cp_2TiClNH_2.NH_3 \;+\; NaCl\right\}.$$

The following reaction scheme is postulated to account for these observations.

$$\left.\begin{array}{ll} & Cp_2TiCl_2 \\ \text{or} & Cp_2TiClNH_2 \end{array}\right\} + (Na^+\ e) \longrightarrow Cp_2TiCl + \left\{\begin{array}{l} NaNH_2 \\ \text{or } NaCl \end{array}\right.$$

$$Cp_2TiCl + 2\,NH_3 \longrightarrow (Cp_2TiNH_2 + NH_4Cl) \rightleftharpoons NH_4^+(Cp_2TiClNH_2)^-.$$

$$NH_4^+(Cp_2TiClNH_2)xNH_3 \longrightarrow H^+(Cp_2TiClNH_2) + (x+1)NH_3 \quad .$$

$$\hookrightarrow Cp_2TiClNH_2 + H^\circ.$$

Triethylstannyl lithium was prepared in the absence of liquid ammonia by the reaction between ethyl-lithium and diethyl-tin in diethyl ether.[31] It was thus possible to carry out the reaction of this alkali metal derivative with bis(cyclopentadienyl)titanium dichloride in the absence of ammonia. The reaction yielded a yellow-brown solid and a green solution. Vacuum filtration of the reaction mixture and removal of the solvent from the filtrate yielded a yellow-brown solid. Both this solid and the original precipitate from the reaction were free of bis(cyclopentadienyl)titanium dichloride and contained both tin and titanium. The solids had nauseating odours characteristic of trialkyl-tin compounds. The precipitation of complex phenylborates and picrates from samples of the reaction solution indicated the probable existence of cyclopentadienyl-titanium cations in this solution. Part of the chlorine originally attached to the titanium could be extracted from the solid by water as lithium chloride. Carbon and hydrogen analyses of the solids were not informative, being found to be extremely low. Qualitative analyses of the freshly precipitated solids revealed the presence of some titanium(III) as well as titanium(IV). The solids were visibly heterogeneous. In accord with the equations for the reaction with triethylplumbyl sodium, the following reaction scheme is suggested.

$$Cp_2TiCl_2 + Li(SnEt_3) \longrightarrow Cp_2TiClSnEt_3 + LiCl.$$

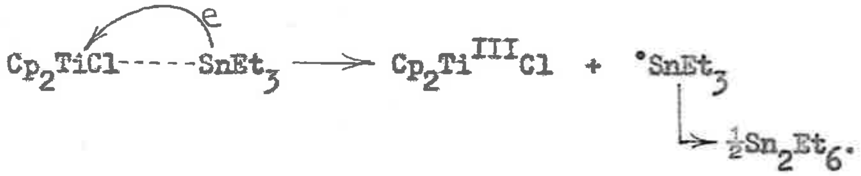
However, because of the probable partial dissociation of triethylstannyl lithium according to[31]

$$Li(SnEt_3) \rightleftharpoons LiEt + SnEt_2$$

the mechanism is almost certainly oversimplified.

The postulated bimetallic complex could not be isolated since it decomposed readily, even in solution, to the yellow brown solid.

The indication that some titanium(III) compounds are formed by decomposition of the initially formed complex could be explained as follows.



$$Cp_2TiCl\text{-----}SnEt_3 \longrightarrow Cp_2Ti^{III}Cl + {}^{\bullet}SnEt_3 \longrightarrow \tfrac{1}{2}Sn_2Et_6.$$

However, the green complex doubtless decomposed in several different ways.

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CHAPTER 5

An Exploratory Study of the Formation of Some Fluorocarbon Derivatives of Metals

1. General methods of synthesis of perfluoroalkyl-metal compounds.-

The preparations of perfluoroalkyl derivatives of some metals were briefly discussed in chapter 1, but the survey was by no means exhaustive. It would be of interest, therefore, to tabulate the feasible preparative routes to perfluoroalkyl-metal compounds, and to comment on the degree of success achieved with those syntheses which have been reported. This is done in table 5.1.

The table shows that only two methods have been successfully developed for the general preparation of perfluoroalkyl-metal compounds; the reactions of perfluoroalkyl iodides with metals, and exchange reactions involving metal alkyls (or aryls) and perfluoroalkyl iodides. Although metal alkyls have been used extensively to prepare new organometallic compounds, reactive perfluoroalkyl-metal compounds have not been so widely used for this purpose. This is doubtless because of the difficulties associated with the preparations of these compounds, and also because of their low thermal stability.

Since the synthesis of perfluoroalkyl derivatives of group III and IV metals, and of transition metals, has not been widely developed, possible new preparations of these compounds have been investigated in this study. The investigations reported here are preliminary in nature, and more work is intended.

Table 5.1

Preparative routes to perfluoroalkyl-metal compounds

Method of synthesis		Comments
(i)	Reactions involving free metals	
a)	$M + R_fI \rightarrow MR_fI$	Perfluoroalkyl derivatives of Mg,[1] Hg,[2] Zn,[3] (and the group V elements)[4] have been prepared in this way.
b)	$M + nR_f^* \rightarrow M(R_f)_n$	Recently investigated as a possible preparation of perfluoroalkyl-bismuth compounds.[5]
c)	$M + M'R_f \rightarrow MR_f + M'$	-
(ii)	Reactions involving metal halides	
a)	$MX + M'R_f \rightarrow MR_f + M'X$	Used relatively little. However, bis-trifluoromethyl-mercury has been synthesized from mercuric oxide and tris(trifluoromethyl)-phosphine.[6]
b)	$MF + C_2F_4 \rightarrow MC_2F_5$	Successfully employed for the preparation of perfluoroalkyl-mercury compounds.[7]
c)	$MX_2 + R_fI \rightarrow MR_fX_3$	Used to prepare germanium compounds.[8]
(iii)	Reactions involving organometallic compounds	
a)	$MR + R_fI \rightarrow MR_f + RI$	Has been used to prepare perfluoroalkyl derivatives of Li,[9] Mg,[10] Sn,[11] and Pb,[11] (as well as the group V elements).[12]

b)	$RM.MR + R_fI \rightarrow RMR_f + RMI$	Successful when M = Sn,[13] (As,[14] or P.[15])
c)	$MR + M'R_f \rightarrow MR_f + M'R$	Not extensively investigated for metals.
(iv)	Reactions of metal hydrides	
a)	$MH_2 + R_fI \rightarrow MR_fI + —$	Reported as preparation of perfluoroalkyl-aluminium complex.[16]
b)	$MH + R_fSCl \rightarrow MR_f + —$	Used to prepare trifluoromethyl-boron compounds.[17]
(v)	Miscellaneous reactions	
a)	$R_fCOOM \rightarrow R_fM + CO_2$	(Successful when M = As.)[18]
b)	$R_fCOM \rightarrow R_fM + CO$	Transition metal perfluoroalkyls have been prepared in this way.[19,20]
c)	$RM + (F) \rightarrow R_fM + (H)$	(F) = fluorinating agent - this method has not been extended to metal derivatives.

2. Reactions involving metal hydrides.

Hauptschein and co-workers[16] have reported the unusual behaviour of perfluoroalkyl iodides with lithium tetrahydroaluminate. They report that interaction of these compounds formed perfluoropropyl-aluminium complexes. A detailed study of the reaction between heptafluoropropyl iodide and lithium tetrahydroaluminate established the following step-wise reaction scheme.

$$\mathrm{LiAlH_4 + C_3F_7I \longrightarrow LiAlH_2(C_3F_7)I + H_2.}$$
$$\mathrm{LiAlH_2(C_3F_7)I + C_3F_7I \longrightarrow LiAlH(C_3F_7)I_2 + C_3F_7H.}$$
$$\mathrm{LiAlH(C_3F_7)I_2 + C_3F_7I \longrightarrow LiAl(C_3F_7)_2I_2 + HI.}$$

The overall stoichiometry for the reaction is thus:

$$\mathrm{LiAlH_4 + 3\,C_3F_7I \longrightarrow LiAl(C_3F_7)_2I_2 + C_3F_7H + HI + H_2.}$$

The nature of these aluminium complexes is not well established. Hauptschein and co-workers consider that the three complexes formed in the reaction may be average components of the symmetrical species shown below:

$$\mathrm{2\,LiAlH_2(C_3F_7)I \equiv \{LiAl(C_3F_7)_2H_2 + LiAlH_2I_2\}}$$
$$\mathrm{2\,LiAlH(C_3F_7)I_2 \equiv \{LiAlH_2(C_3F_7)_2 + LiAlI_4\}}$$
$$\mathrm{2\,LiAl(C_3F_7)_2I_2 \equiv \{LiAl(C_3F_7)_4 + LiAlI_4\}\,.}$$

However, because of the high lability of both alkyl and halide groups which are attached to aluminium, such a uniform rearrangement does not seem likely. It seems more feasible to propose that the lithium aluminium complex would break down to form lithium iodide and perfluoropropyl-aluminium compounds, e.g.

$$\mathrm{LiAl(C_3F_7)_2I_2 \longrightarrow LiI + Al(C_3F_7)_2I.}$$

The only other report of similar nature involves the formation of trifluoromethylboron difluoride from diborane and trifluoromethanesulphenyl chloride (CF_3SCl).[17] It is proposed that CF_3-S attack on the boron-hydride linkages forms H-S and trifluoromethylboron compounds.

In the present study, investigations of the interaction of metal hydrides with perfluoroalkyl iodides has been extended to the reaction between triethylstannane and heptafluoropropyl iodide.

Triethylstannane was prepared by the lithium tetrahydroaluminate reduction of triethyl-tin chloride in diethyl ether as solvent.[21] A liquid ammonia-diethyl ether mixture was used as solvent for the interaction of triethylstannane and heptafluoropropyl iodide. Liquid ammonia was incorporated in the system to bind up any hydrogen iodide formed during the anticipated reaction, e.g.

$$\begin{tikzcd}[row sep=small] Et_3SnH + C_3F_7I \arrow[r] & Et_3Sn(C_3F_7) + HI \arrow[d, "NH_3"] \\ & NH_4I. \end{tikzcd}$$

It seemed necessary to inhibit the formation of free hydrogen iodide since it is known that hydrogen halides cleave tin-alkyl linkages.[22]

The treatment of triethylstannane with heptafluoropropyl iodide caused the deposition of a white solid. The solid was isolated by filtration of the reaction mixture in vacuum. Chemical tests revealed that the solid contained ammonium iodide. Diethyl ether and ammonia were evaporated, in vacuum, from the filtrate, and the liquid residue was further fractionated to remove unchanged triethylstannane. Vapour pressure measurements on the liquid residue showed the presence of more than one organo-tin species (Fig. 5.1). The components

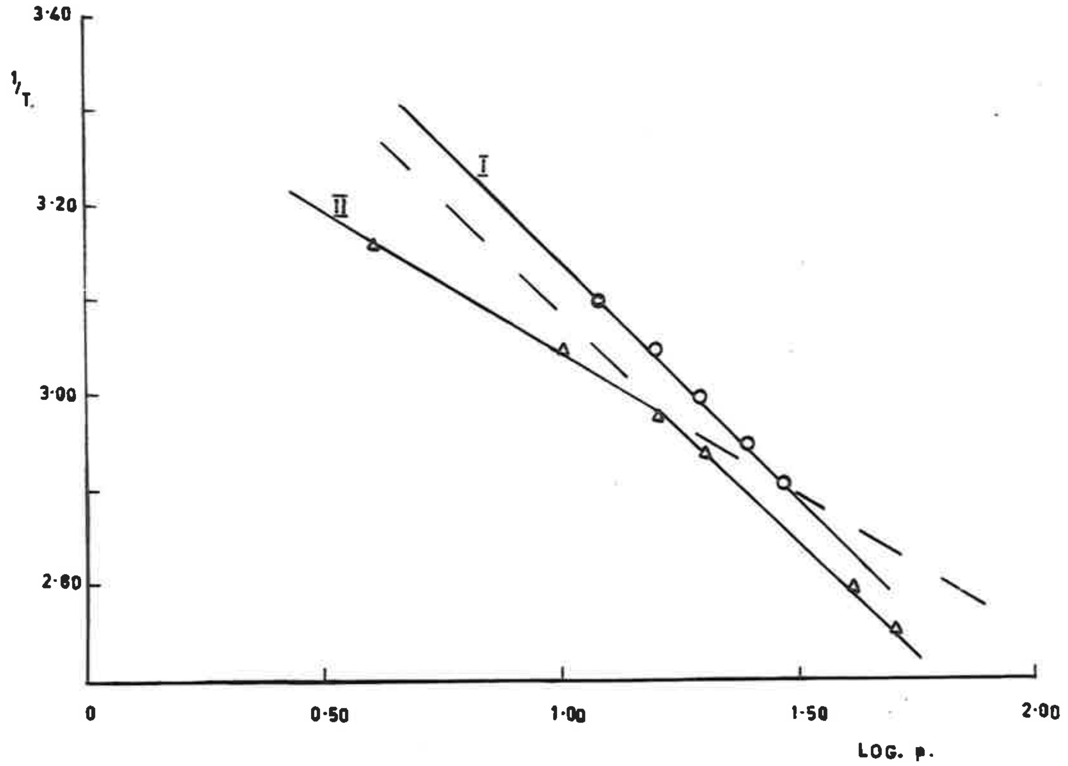


Fig. 5.1 Comparison of the vapour pressure-temperature relationship for triethylperfluoroethyltin (I) and the product from the interaction of triethylstannane and heptafluoropropyl iodide (II).

could not be separated by conventional vacuum fractionation techniques, and vapour phase chromatography was also ineffective because of inordinately long elution times. Consequently, separation of the product components could not be effected. However, the infra-red absorption spectrum of the liquid showed the presence of some fluoroalkyl groups (Fig. 5.2), and alkaline hydrolysis of the liquid liberated some heptafluoropropane. Further chemical analyses indicated that the product may be a mixture of triethyl-heptafluoropropyltin and other unfluorinated triethyltin species. Less than 20% yield of triethyl-heptafluoropropyltin was present in the product mixture.

The investigations have not been extended to the more volatile perfluoroalkyl-tin derivatives.

3. Alkyl-perfluoroalkyl exchange reactions.

Several exchange reactions which have been reported in the literature seem relevant to the exchange reactions involving aluminium alkyls to be considered in this section. These are surveyed below before the original work is discussed.

Firstly, it is often suggested that perfluoroalkyl iodides can be considered as pseudo-halogens, and consequently it seems pertinent to report the known reactions of dihalogens with trialkyl-aluminium compounds. It has been observed[23] that halogens cleave aluminium-alkyl bonds to form aluminium halides and alkyl halides, e.g.

$$R_3Al + X_2 \longrightarrow R_2AlX + RX.$$

Complete cleavage to aluminium trihalide can be achieved in a solvent which co-ordinates with the aluminium trihalide.

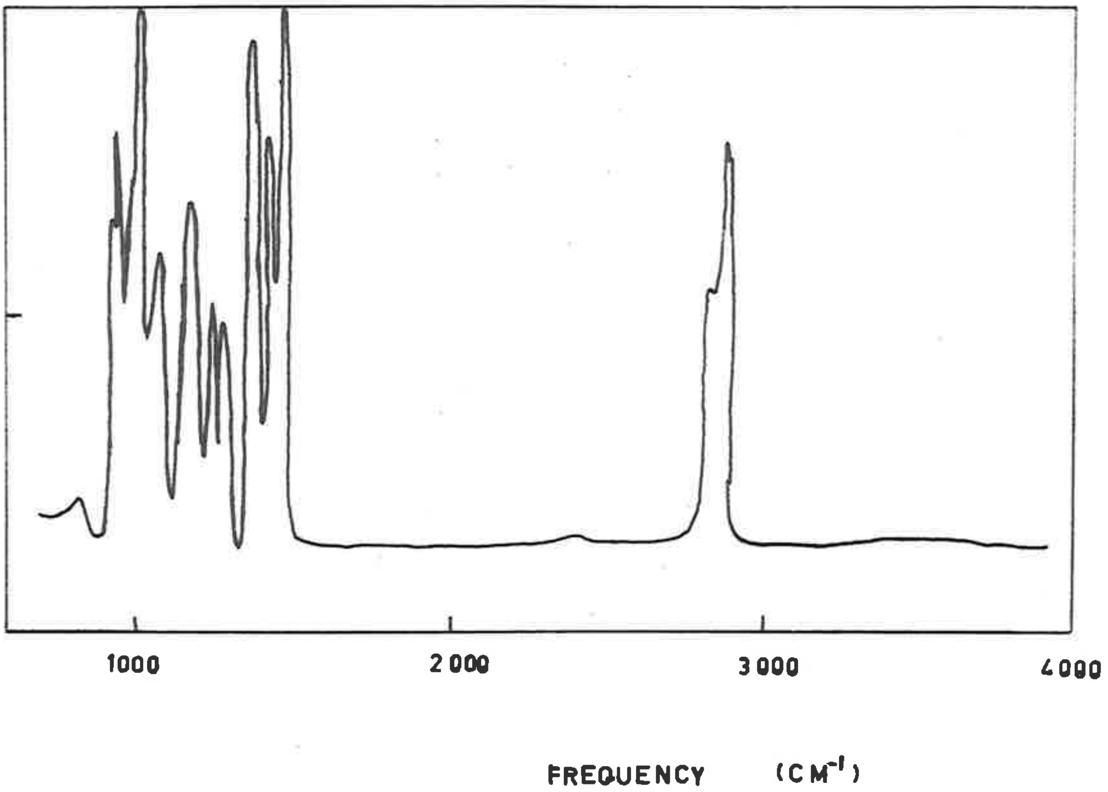


Fig. 5.2 Infra-red spectrum of the product from the interaction of triethylstannane and heptafluoropropyl iodide.

Secondly, a few investigations of exchange reactions involving metal alkyls and perfluoroalkyl iodides have recently been reported. For instance, an extensive investigation of the replacement of methyl groups by trifluoromethyl groups in systems containing trifluoromethyl iodide and trimethylphosphine, trimethyl-arsine or trimethyl stibine has been carried out by West and Haszeldine;[12a] an analogous investigation of the interaction of trifluoromethyl iodide with higher trialkylarsines has more recently been carried out by Cullen;[12b] McBee and co-workers have investigated similar systems involving alkyl-lithium,[9] or aryl-magnesium[10] reagents and perfluoroalkyl iodides; and Stone and co-workers[11] have observed that exchange of alkyl and perfluoroalkyl groups occurs in the system perfluoroalkyl iodide – tetraethyl-lead.

All the above mentioned observations indicate that exchange in aluminium alkyl – perfluoroalkyl iodide systems is feasible. However, Korshunov and Batalov[24] have recently shown that ethyl radical exchange in the system triethyl-aluminium – ethyl bromide requires the presence of a metal halide. They observed that no exchange takes place, even at 150°C, if a metal halide is not present. Furthermore, it is known that exchange in alkyl metal – perfluoroalkyl iodide systems is often sensitive to temperature (too low a temperature inhibits ready exchange whereas too high a temperature permits decomposition of the perfluoroalkyl-metal derivative).[9] These observations indicate that extensive investigations might be necessary to establish the conditions under which exchange in aluminium alkyl – perfluoroalkyl iodide systems will give satisfactory yields of perfluoroalkyl-aluminium compounds. The investigations reported below are therefore incomplete.

The treatment, in tetrahydrofuran at less than 0°C, of lithium tetraethylaluminate with heptafluoropropyl iodide in the molar ratio 1:3 liberated hydrocarbon and fluorocarbon gases. The gases were roughly separated by fractionation in vacuum. Fractions consisting of C_2-hydrocarbons (presumably a mixture of ethane and ethylene), C_3-fluorocarbons (possibly a mixture of heptafluoropropane and perfluoropropene), and other less volatile carbon compounds were isolated in this way, the fractions being identified by molecular weight measurements, vapour phase chromatography, and infra-red analysis. Samples of the reaction solution were also examined by vapour phase chromatography, and the formation of ethyl iodide was detected in this way. The reaction solution was evaporated to dryness in vacuum, and the white solid residue was shown to contain both iodide and fluoride ions.

These results indicate some exchange of alkyl and perfluoroalkyl groups (and also of iodide groups). By analogy with the reaction scheme suggested for the interaction of lithium tetrahydroaluminate and heptafluoropropyl iodide, the following scheme is tentatively proposed.

$$\begin{aligned}
&\mathrm{LiAlEt_4} + \mathrm{C_3F_7I} \longrightarrow \mathrm{LiAlEt_2(C_3F_7)I} + (\mathrm{Et^-} + \mathrm{Et^+}) \\
&\qquad\qquad\qquad\qquad\qquad \longrightarrow \mathrm{LiI} + \mathrm{AlEt_2(C_3F_7)}. \\
&\mathrm{AlEt_2(C_3F_7)} + \mathrm{C_3F_7I} \longrightarrow \mathrm{AlEt(C_3F_7)I} + (\mathrm{R_f^-}). \\
&\mathrm{AlEt(C_3F_7)I} + \mathrm{C_3F_7I} \longrightarrow \mathrm{Al(C_3F_7)_2I} + \mathrm{EtI}.
\end{aligned}$$

The ionic ethyl and perfluoropropyl groups presumably decomposed in diverse ways to form hydrocarbon and fluorocarbon compounds. Evaporation of the solvents from the perfluoropropyl-aluminium compounds presumably caused their decomposition to form aluminium fluoride compounds, e.g.

$$\text{al-}C_3F_7 \longrightarrow \text{alF} + C_3F_6.$$

It was further observed that the treatment of triethyl-aluminium with heptafluoropropyl iodide and pentafluoroethyl iodide did not cause exchange of ethyl and perfluoroalkyl groups under the conditions investigated. This may indicate that the formation of complex aluminium alkyl species, or at least the presence of other metallic salts, is necessary for exchange between triethyl-aluminium and perfluoroalkyl iodides.

4. Perfluoroalkylation of metal halides with lithium aluminium compounds.

It has already been pointed out that the instability of perfluoroalkyl-derivatives of lithium, magnesium, and zinc has imposed restrictions on the possible use of these reactive compounds to prepare new perfluoroalkyl-metal compounds. However, since solutions of lithium bis(heptafluoropropyl)diiodoaluminate, $LiAl(C_3F_7)_2I_2$, are relatively stable at moderate temperatures, and since it has been shown[25] that lithium aluminium alkyls are efficient alkylating agents, an investigation of the possibility of perfluoroalkylating such metals as tin, lead, and titanium by treating the appropriate metal halides with solutions of lithium bis(heptafluoropropyl)diiodoaluminate seemed worthwhile.

The interaction of diethyl ether solutions of lithium bis-(heptafluoropropyl)diiodoaluminate and triethyl-lead chloride formed lead diiodide and a pale brown liquid which was soluble in the solvent. The liquid was isolated by evaporation of the solvent in vacuum. It decomposed on attempted distillation, forming more lead diiodide and liberating hydrocarbon and fluorocarbon gases. This thermal decomposition, and the low volatility of the liquid, prevented its purification by vapour phase chromatography. Alkaline hydrolysis of the crude reaction product liberated heptafluoropropane; the quantity of heptafluoropropane liberated indicated that only about 10% conversion of triethyl-lead chloride to triethyl-heptafluoropropyl-lead had taken place. The infra-red absorption spectrum of the liquid confirmed the presence of perfluoroalkyl groups (Fig. 5.3).

The deposition of lead iodide during the reaction may be attributed to the formation and subsequent decomposition of alkyl-lead diiodide species. It is well established[26] that lead alkyls are readily de-alkylated by aluminium halides and it is known[27] that dialkyl-lead dihalides decompose to form lead diiodide and trialkyl-lead compounds. Thus, the following reaction scheme may account, in part, for the observed reaction products.

$$\mathrm{Et_3PbCl} + [\mathrm{LiAl(C_3F_7)_2I_2}] \longrightarrow \mathrm{Et_3PbC_3F_7} + [\mathrm{LiAl(C_3F_7)I_2Cl}].$$

$$\mathrm{Et_3PbC_3F_7} + 2\,\mathrm{alI} \rightleftharpoons \mathrm{EtPb(C_3F_7)I_2} \quad \text{etc.}$$

$$\mathrm{EtPb(C_3F_7)I_2} \longrightarrow \mathrm{PbI_2} + \mathrm{RR'_2PbI} + \mathrm{RI} \quad (\text{where R and R}' = \text{Et or } \mathrm{C_3F_7}).$$

It seems probable that the liquid product from the reaction contained a number of mixed alkyl-perfluoroalkyl-lead derivatives which could not be readily separated.

The interaction of diethyl ether solutions of lithium bis-(heptafluoropropyl)diiodoaluminate and triethyl-tin chloride formed a yellow solution from which a dark amber liquid was isolated by evaporation of the solvents. The liquid distilled slowly in vacuum, but its low volatility (v. pr. = 15 mm./70°) prevented good fractionation. Qualitative analyses of the liquid revealed the presence of tin and

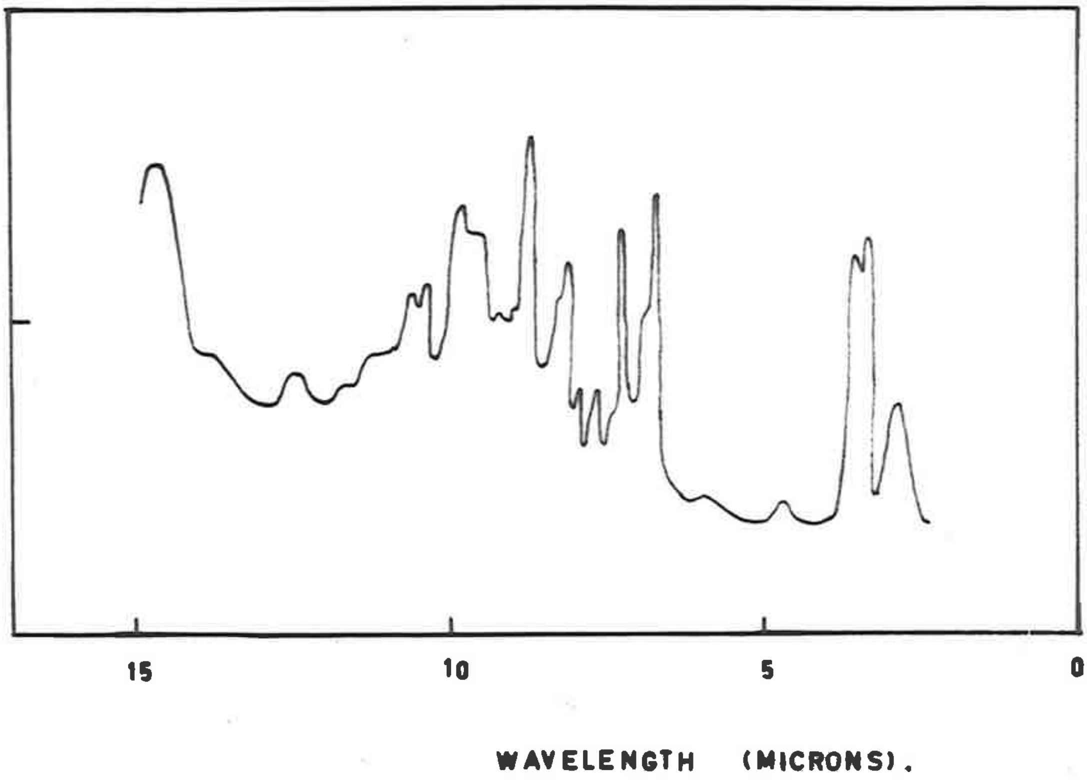


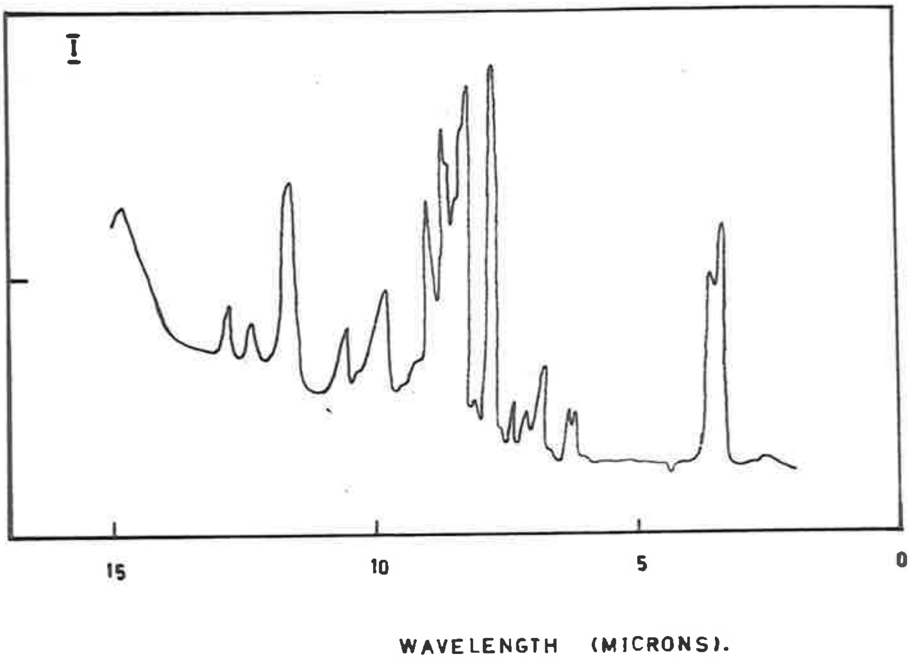
Fig. 5.3 Infra-red spectrum of the product from the interaction of triethyl-lead chloride and lithium bis(heptafluoropropyl)diiodoaluminate.

iodine, and alkaline hydrolysis liberated some heptafluoropropane. Quantitative determinations of carbon and hydrogen were in fair agreement with the average formula $Et_{2.4}(C_3F_7)_{0.4}SnI_{1.2}$, which indicates that the product is probably a mixture of several components. The infra-red absorption spectrum of the liquid confirmed the presence of perfluoroalkyl groups (see figure 5.4). The liquid was converted to white solids when treated with pyridine or ammonia, but attempted fractional crystallizations of the solids did not separate the constituents.

These results indicate that reactions, similar to those proposed for the lead reaction, had taken place.

In an attempt to determine whether perfluoroalkyl or iodide groups were preferentially transferred from the aluminium complex to other metals, tin tetraiodide was treated with lithium bis(heptafluoropropyl)diiodoaluminate. It was reasoned that any observable change in the nature of the tin species would indicate the transfer of perfluoroalkyl groups. However, no reaction was observed under the conditions investigated. This may indicate the total absence of group transfer, or the preferential transfer of iodide groups.

The interaction of methylene chloride solutions of bis(cyclopentadienyl)titanium dichloride and lithium bis(heptafluoropropyl)-diiodoaluminate formed a black solid. The solid slowly sublimed when heated in vacuum. Alkaline hydrolysis of the solid did not liberate heptafluoropropane, and the infra-red absorption spectrum did not reveal the presence of fluoroalkyl groups. Chemical analyses of the solid showed that about 3/4 of the chlorine originally attached to titanium in bis-



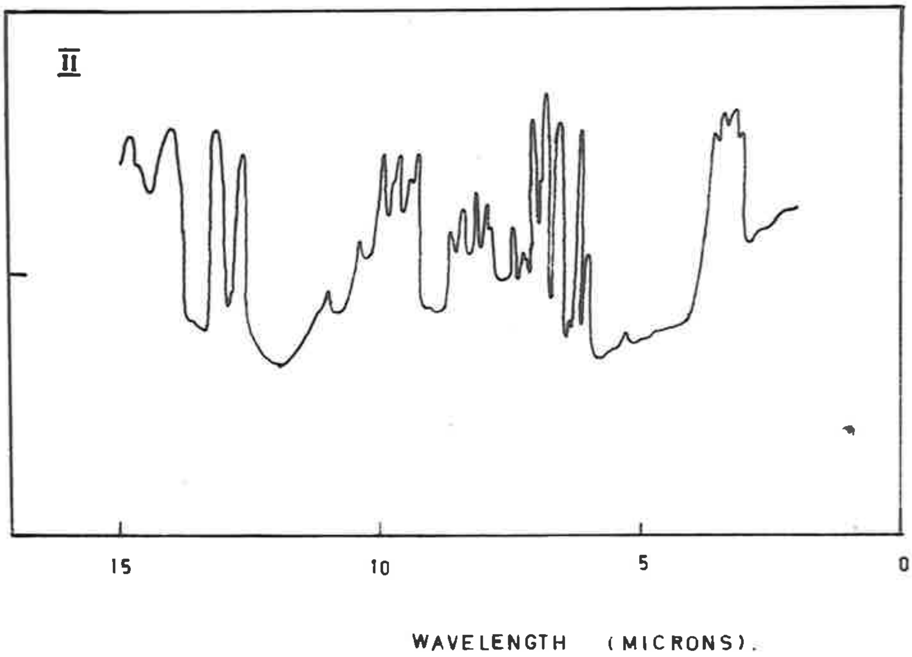


Fig. 5.4

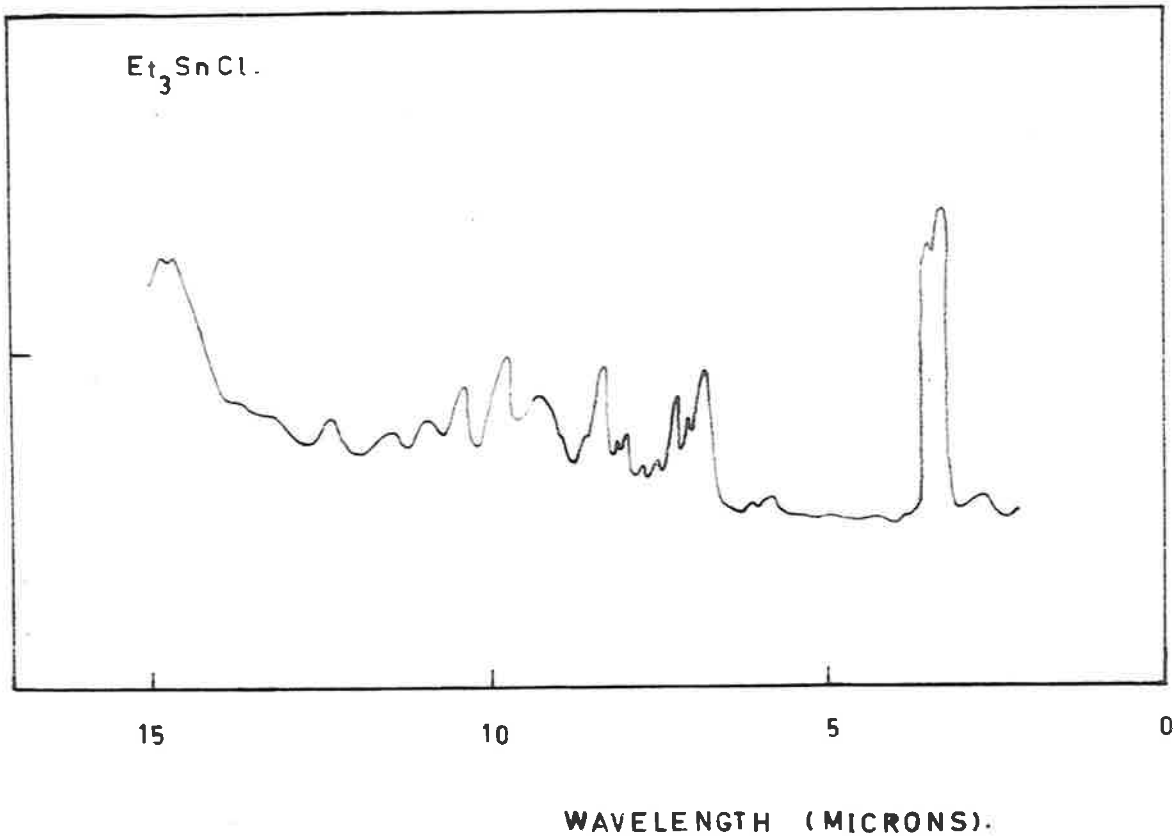


Fig. 5.4 Infra-red spectra of the product from the interaction of triethyltin chloride with lithium bis(heptafluoropropyl)diiodoaluminate (I), the pyridine adduct of this product (II), and pure triethyltin chloride.

(cyclopentadienyl)titanium dichloride had been replaced by iodine. The absorption spectrum, in the visible region, of the black solid in toluene resembled that of bis(cyclopentadienyl)titanium dichloride, but a considerable shift of the absorption spectrum maximum was noticed (Fig. 5.5). These results indicate that the reaction was essentially of the type:

$$Cp_2TiCl_2 + [LiAl(C_3F_7)_2I_2] \longrightarrow Cp_2TiClI + [LiAl(C_3F_7)_2ClI].$$

5. Some attempted decarboxylation reactions.

Trifluoroiodomethane has been prepared in high yield from the interaction of silver trifluoroacetate and iodine:[28]

$$\begin{tikzcd} AgOOCCF_3 + I_2 \arrow[r] & AgI + CF_3COOI \arrow[d, "heat"] \\ & CF_3I + CO_2. \end{tikzcd}$$

Haszeldine[29] has attempted to extend this type of reaction to the preparation of perfluoroalkyl derivatives of a few metals and metalloids. He anticipated interactions of the type

$$\begin{tikzcd} m\ AgOOCCF_3 + 2M \arrow[r] & (CF_3COO)_mAg + Ag_mM \arrow[d, "heat"] \\ & (CF_3)_mM + m\ CO_2, \quad (M = P,Hg,S), \end{tikzcd}$$

but obtained no evidence that the reaction had proceeded as shown. Haszeldine[29] has also studied the possible reaction:

$$3\ AgOOCCF_3 + MI_3 \xrightarrow{heat} M(CF_3)_3 + 3\ AgI + 3\ CO_2 \quad (M = P,As),$$

but again did not obtain trifluoromethyl derivatives of the metalloids used.

More recently, Cullen[30] has synthesized dimethyltrifluoromethylarsine by the thermal decomposition of dimethyltrifluoroacetoxyarsine.

$$Me_2AsOOCCF_3 \longrightarrow Me_2AsCF_3 + CO_2.$$

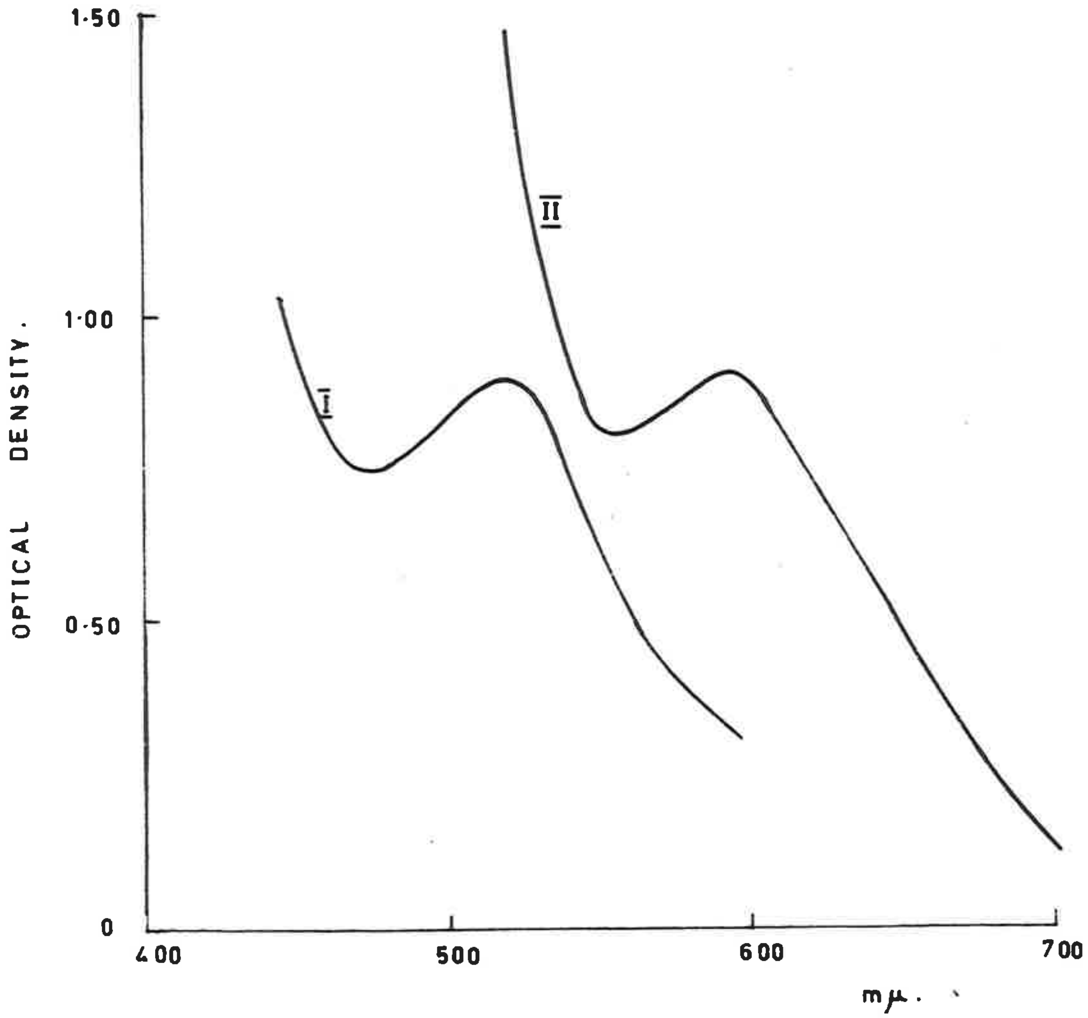


Fig. 5.5 Comparison of the spectra (visible region) of bis(cyclopentadienyl)titanium dichloride (I) and "$(C_5H_5)_2TiCl_{0.5}I_{1.5}$" (II).

In the present study, the possibility of extending this mode of synthesis to the preparation of perfluoroalkyl derivatives of tin and lead was investigated.

Triethyl-lead trifluoroacetate was prepared by cleavage of tetraethyl-lead with trifluoroacetic acid.

$$Et_4Pb + CF_3COOH \longrightarrow Et_3PbOOCCF_3 + EtH.$$

It is a white crystalline solid, stable in the air, which melts at 136-138°C. The infra-red absorption spectrum of the liquid is shown in figure 5.6. The solid decomposed when heated at 150-170° for 10-12 hours, but no carbon dioxide was evolved during the decomposition. Thus no decarboxylation of the lead compound had occurred. Hydrocarbon gases, ethyltrifluoroacetate, tetraethyl-lead, and a mixture of apparently unchanged triethyl-lead trifluoroacetate and lead bis(trifluoroacetate), were identified in the thermal decomposition products. The formation of the lead compounds can probably be explained in terms of the following rearrangements:

$$2\ Et_3PbOOCCF_3 \longrightarrow Et_4Pb + Et_2Pb(OOCCF_3)_2$$

$$2\ Et_2Pb(OOCCF_3)_2 \longrightarrow Pb(OOCCF_3)_2 + Et_3Pb(OOCCF_3) + EtOOCCF_3.$$

The decomposition of diethyl-lead bis(trifluoroacetate) follows the known mode of decomposition of dialkyl-lead salts.[27] An essentially similar reaction scheme was recently proposed for the thermal decomposition of triethyl-lead acetate.[31] Since the rearrangements probably involve the initial formation of free radicals, some radical combination according to

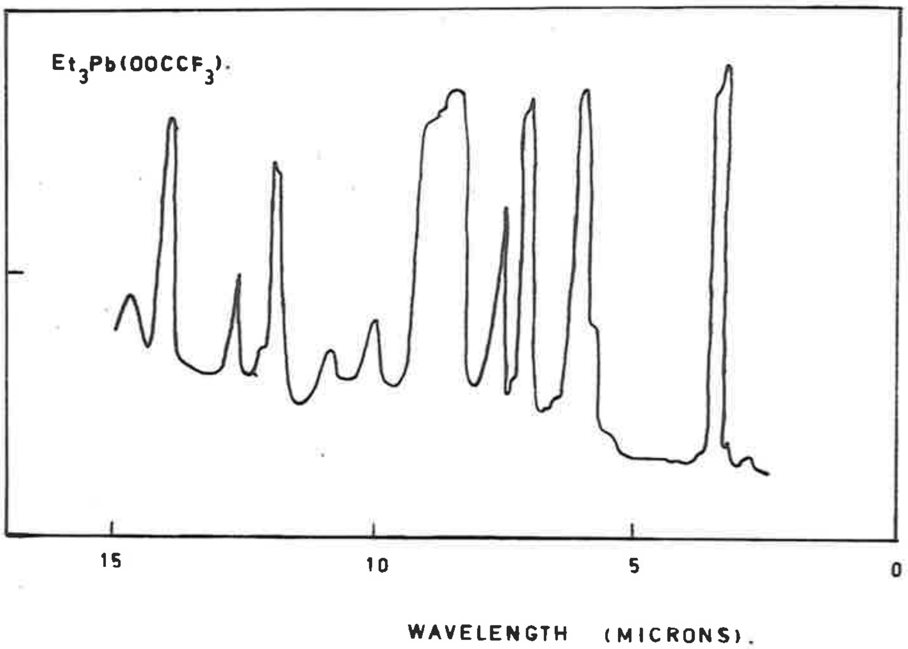


Fig. 5.6 Infra-red spectrum of triethyl-lead trifluoroacetate.

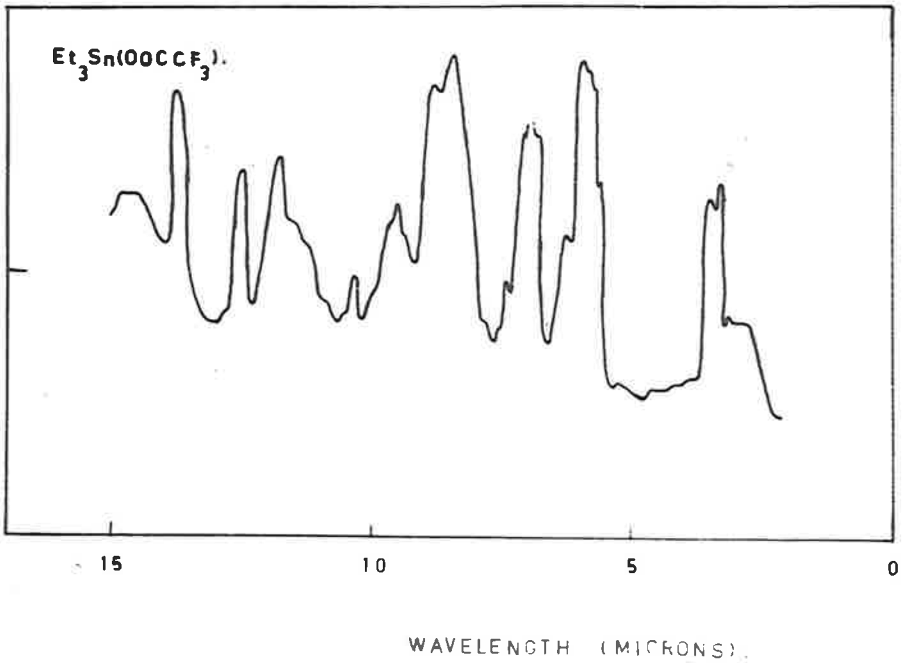


Fig. 5.7 Infra-red spectrum of triethyltin trifluoroacetate.

$$\begin{tikzcd}[row sep=small] & C_2H_6 + C_2H_4 \\ 2\,Et^{\bullet} \arrow[ur] \arrow[dr] & \\ & C_4H_{10} \end{tikzcd}$$

$$Et^{\bullet} + {}^{\bullet}CF_3COO \longrightarrow EtOOCCF_3$$

would presumably contribute to the overall reaction.

Triethyl-tin trifluoroacetate was prepared from triethyltinchloride and silver trifluoroacetate according to:

$$Et_3SnCl + AgOOCCF_3 \longrightarrow AgCl + Et_3SnOOCCF_3.$$

Other organometallic haloacetates have previously been prepared in this way.[32] Triethyltin trifluoroacetate is a pale yellow, air stable liquid. Its infra-red absorption spectrum is shown in figure 5.7. The liquid was heated at 150-200° for 10 hours, with the object of effecting its decarboxylation. However, only slight decomposition of the tin compound was observed under these conditions, and since carbon dioxide was not evolved, no decarboxylation had occurred. This greater thermal stability of the tin compound follows the known thermal properties of ethyl-tin and ethyl-lead compounds. The effect of higher temperatures was not investigated because of the thermal breakdown of tin-fluoroalkyl compounds at such temperatures.

In view of the low thermal stability of most other perfluoroalkyl-metal compounds, it does not seem likely that similar decarboxylation reactions will prove useful for the preparation of metal perfluoroalkyl compounds.

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CHAPTER 6

Experimental

This chapter is divided into five sections; section 1 includes a description of the general techniques used in these research studies, and sections 2-5 contain details of the experimental work relating to the discussion in chapters 2-5 respectively.

1. Techniques and instrumentation.-

(a) The handling of organometallic compounds.[1]

Almost all organometallic compounds are either extremely toxic or are readily decomposed upon exposure to air, to moisture, or both. Thus the experimental work connected with this study invariably required strict attention to personal safety or to the control of experimental reaction conditions. Many of the organometallics required special techniques for their preparation, purification, and manipulation. Some of these techniques are described below.

(i) Toxic materials.

Whenever toxic materials, such as diethylmercury or tetraethyllead, were handled, the apparatus to be used was assembled in a well ventilated fume-hood. Alternatively, it was often convenient to transfer these compounds, as solutions if necessary, from one closed system to another by means of an hypodermic syringe and needle. In all operations, good quality rubber gloves were worn. Disposal of volatile toxic materials was always preceded by decomposition with concentrated nitric acid.

(ii) Pyrophoric materials.[2]

A number of organometallics, such as the alkyls and aryls of the metals of the first three groups of the periodic table, are highly reactive, being spontaneously inflammable or readily decomposed upon exposure to traces of moisture and/or air. These compounds were always handled in apparatus from which air and moisture were rigorously excluded. In such cases the apparatus was dried for several hours at 120°, assembled while still hot, and successively evacuated and flushed with dry, oxygen-free nitrogen several times before use. A slow stream of nitrogen was maintained through the apparatus while it was in use.

Hypodermic syringes (B-D Yale glass syringes) fitted with either screw-on needles or Luer-Lok stopcocks (B-D Yale LL/S) and needles were frequently employed to handle these reactive compounds. The syringes and needles were dried at 120° and flushed with nitrogen before use. The syringes were usually lubricated with silicone grease to prevent "freezing" of the plunger.

The reactive alkyls were stored in glass sample containers, equipped with ground glass joints and fitted with Suba-seal rubber caps, and were blanketed with nitrogen at slightly greater than atmospheric pressure. The metal alkyls, or solutions of them, could be withdrawn from the sample containers and injected into reaction vessels through self-sealing rubber caps.

To handle a sample quantitatively, the following procedure was followed. A syringe, fitted with stopcock and needle, was flushed with dry nitrogen. A quantity of nitrogen, equal to the volume of alkyl to be withdrawn, was injected into the alkyl container. A sample of alkyl was then cautiously drawn into the syringe. Finally, nitrogen was drawn from the alkyl container into the remaining volume of the syringe. The stopcock was then closed and the needle was withdrawn and inserted into a small cork. In this condition the syringe could be conveniently weighed and subsequently transferred to the desired container. Immediately after transfer the syringe was rinsed in an inert solvent (e.g. kerosene) to prevent "freezing" of the plunger.

(iii) Volatile materials.

Any volatile materials could be handled in a conventional vacuum line which was built with provision for carrying out trap to trap distillation at low temperatures *in vacuo*.[3]

(iv) Inert atmosphere box.

Material transfers were often conveniently accomplished in an inert atmosphere box which was constructed of perspex. Even highly reactive materials such as aluminium trialkyls could be effectively handled in this way.

(v) The filtration of oxygen-reactive materials.

Two methods were frequently used for the filtration of solutions containing oxygen reactive compounds.

Method 1. Filtration was accomplished in a closed system of the type shown in figure 6.1. The solution to be filtered was contained in flask A. By inverting the filtration assembly, and partially evacuating flask B, rapid filtration through the sintered glass disk could be achieved.

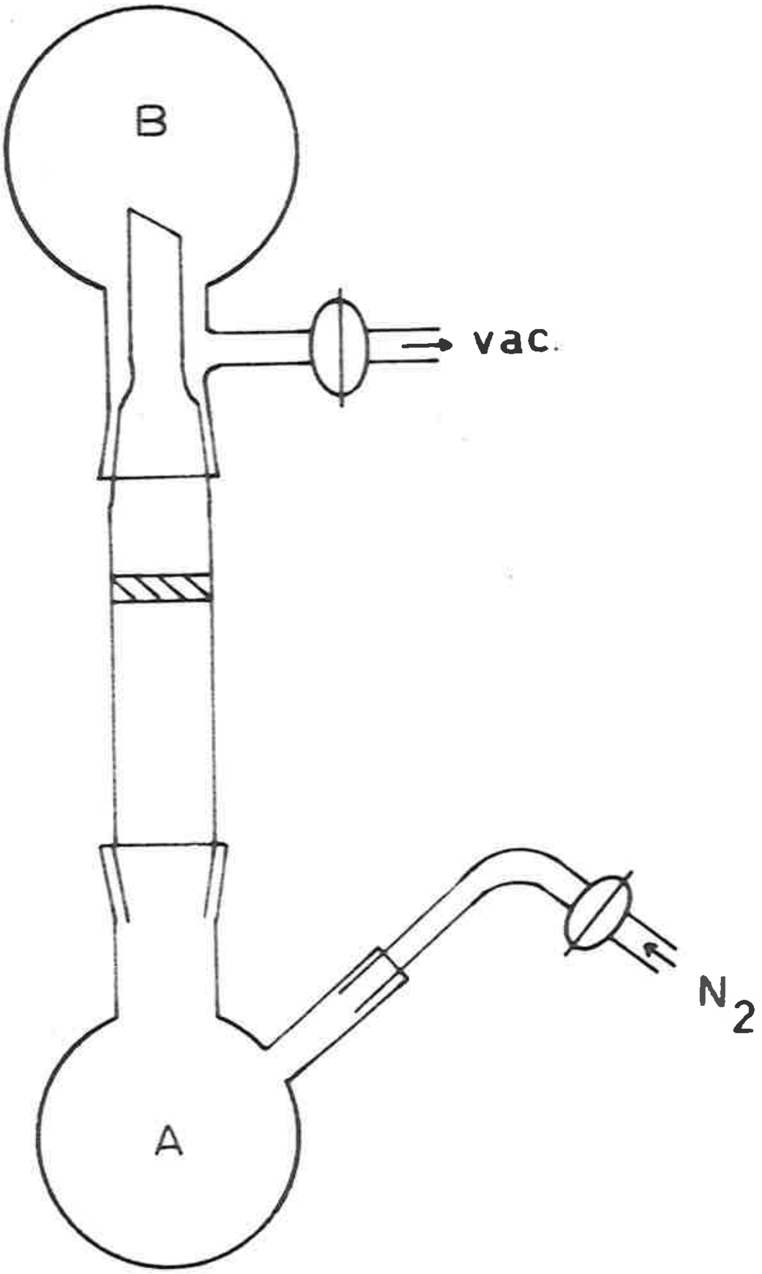

Fig. 6.1 Apparatus for the filtration of oxygen reactive materials.

Method 2. Small scale filtrations could also be carried out within the inert atmosphere box. These were done in the conventional manner using Quick-fit Buchner funnels and flasks. Suction was provided by connecting the Buchner flask to an evacuated bulb of suitable capacity.

(b) Inert gases.

High purity nitrogen was required as an inert "blanket" gas for many of the reactions investigated in these research studies. Nitrogen (C.I.G. Industrial grade - maximum impurities, O_2, 0.7%; rare gases, 0.1%; CO_2 and H_2, traces; H_2O, 270 v/m.) was freed of oxygen by passing the gas through a "scrubber-tower" containing a dilute acid solution of chromous chloride over zinc amalgam. The gas was subsequently dried by bubbling it through concentrated sulphuric acid and finally passing it through a column packed with Linde molecular sieves (type 4A).

Alternatively, a nitrogen-hydrogen mixture was employed and was purified by passing the gas mixture through a Model D 'Deoxo' gas purifier and subsequently through a column packed with Linde molecular sieves. This method had obvious advantages wherever flushing with nitrogen was preceded by evacuation of the apparatus. However, the relatively high hydrogen content of the resultant gas was a disadvantage if the gas was used as a blanket over aluminium alkyls. (Aluminium alkyls apparently react slowly with hydrogen).

Rapid purification of nitrogen was sometimes achieved by bubbling the gas through tri-isobutyl-aluminium.

(c) Purification of solvents.[4]

For most reactions it was important to remove traces of oxygen, peroxides, and moisture from the solvents to be used. The purification process generally employed for inert solvents included passage through a column of activated alumina to remove most of the peroxides followed by refluxing over sodium wire for 10-12 hr. The solvent was distilled first from the sodium wire and subsequently from lithium tetrahydroaluminate in an atmosphere of dry nitrogen. The solvents were used immediately.

Whenever solvents which reacted with sodium were required in a pure form, drying was achieved with a common desiccant such as anhydrous calcium chloride and finally with Linde molecular sieves. Removal of oxygen was accomplished by distillation *in vacuo*.

(d) Instrumentation.

Visible spectra.

Visible spectra were measured with a Unicam SP 500 spectrophotometer, using 1 cm. silica cells. Measurements were made at room temperature.

Solutions containing oxygen-reactive or moisture sensitive compounds were injected into the cells through self-sealing rubber caps.

Infra-red spectra.

Some of the infra-red spectra were measured with a Perkin-Elmer Model 137 Infracord. Other spectra were measured using a Perkin-Elmer Model 21 infra-red spectrophotometer. Both spectrophotometers were fitted with sodium chloride optics.

Liquid compounds were examined as liquid films between rock-salt plates, and solid compounds as Nujol or hexachlorobutadiene mulls. Gas fractions were examined in a 10 cm. glass cell (fitted with rock-salt plates) which could be connected to the vacuum line or to the vapour phase fractometer (see below). The identification of compounds by infra-red examination was based on comparison of the spectra with standard spectra shown in the "Catalog of Infra-red Spectral Data, American Petroleum Institute, Project 44", together with measured spectra of known samples.

Vapour phase chromatography.

Vapour phase chromatograms were measured with a Perkin-Elmer Model 154 vapour fractometer. A column packed with di-isodecylphthalate on firebrick was used throughout, and either nitrogen or hydrogen was used as the carrier gas.

A gas cell, suitable for use with the infra-red spectrophotometers, was constructed so that gas fractions emerging from the vapour phase fractometer could be collected directly (Fig. 6.2).

Molecular weights.

Molecular weights of volatile compounds were measured in the vacuum line by the Regnault method.[3]

Vapour pressures.[3]

Values of the vapour pressures of volatile liquids at various temperatures were measured with a conventional isoteniscope.

(e) Quantitative analyses of organometallic compounds.

(i) The analysis of alkyls of aluminium and lithium.[2a]

A bulb of ca. 20 ml. capacity, constructed with a side arm and vacuum stopcock and containing a few small steel "ball bearings", was fitted with a Suba-seal rubber cap. The vessel was thoroughly flushed with nitrogen, and was then weighed. A sample of the alkyl (or an aliquot of a solution of the alkyl) was injected into the vessel

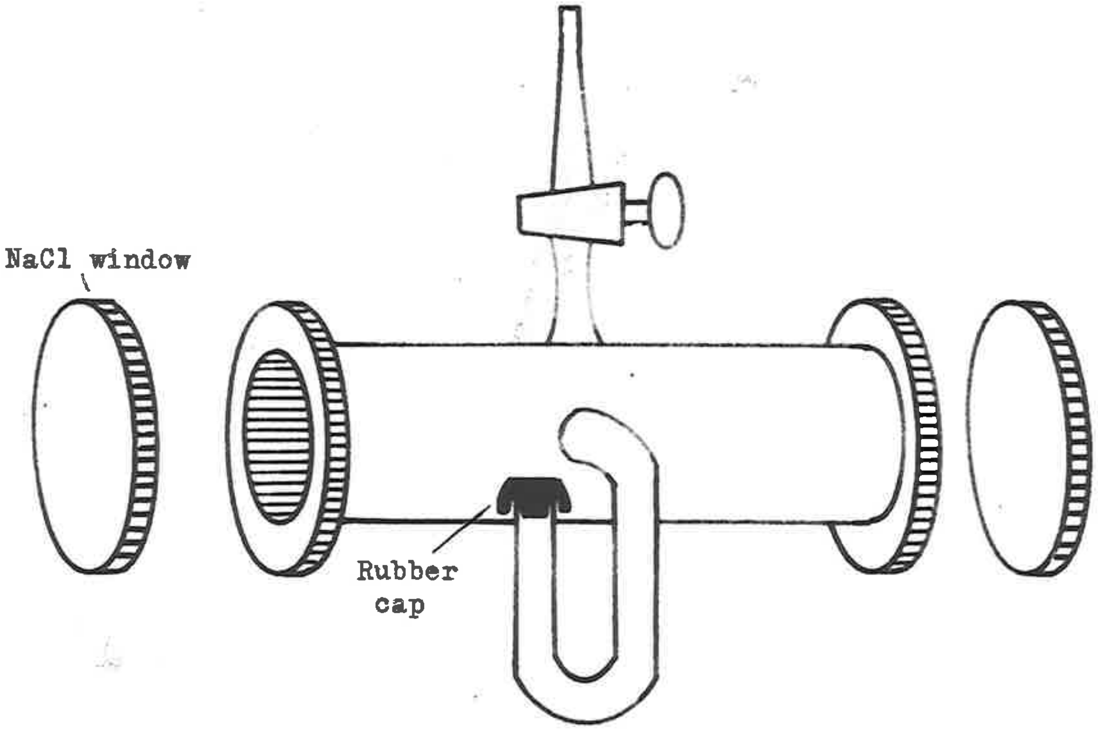

Fig. 6.2 Fraction collector / infra-red cell. (The cell is connected to the vapour phase fractometer through a hypodermic needle inserted through the rubber cap).

which was then reweighed. The alkyl was diluted with an inert solvent and the vessel was then connected to a gas burette. The alkyl sample was then cautiously decomposed with a few ml. of thoroughly de-oxygenated aqueous sulphuric acid solution (5%) added dropwise from a syringe. The vessel was shaken at intervals during the addition of the acid. The volume of liberated gas was measured and was corrected to normal temperature and pressure using the equation:

$$V_{N.T.P.} = (V' - v) \times 273/T \times (P - p)/760$$

(where V' = measured volume of gas; v = volume of sulphuric acid added; T = temperature of gas; P = atmospheric pressure; p = vapour pressure of water at T). The decomposition residue could be quantitatively examined for metal and halogen in the conventional manner.

(ii) The analysis for lead, tin, and titanium in organometallic compounds.

Many metals in organometallic compounds cannot be precipitated quantitatively unless the organic groups are first destroyed. This is usually done by treating the organometallic compound with a strong oxidizing acid.

Lead.

Two methods were used to determine lead in organometallic compounds.

Method 1.[5] A solution of the organo-lead compound was cooled to 0°, and the lead compound was decomposed by the addition of a solution of bromine in carbon tetrachloride (10%). The mixture was heated on a water bath until nearly dry. The residue of lead dibromide was boiled for a few minutes with absolute alcohol, and the mixture was cooled and filtered. The precipitate was weighed as $PbBr_2$.

Method 2. Lead was determined as the sulphate ash after destroying the organic groups with boiling concentrated nitric acid.

Tin and titanium.

Both tin and titanium were precipitated with cupferron and ignited to the metal oxides after destroying the organic groups with fuming perchloric acid. Whenever tin and titanium were both present, the tin was separated from the mixed oxides by heating to 450° with a large excess of ammonium iodide.

Titanium(III).

Solutions of titanium(III) compounds in dilute sulphuric acid (5%) were treated with excess ferric sulphate solution, and the ferrous iron so produced was determined by titration with permanganate solution.

(iii) Ammonobasic-titanium compounds.

These were decomposed with caustic soda solution (20%) and the ammonia was subsequently distilled into standard acid solutions and determined by titration with standard alkali.

(iv) Halides were estimated gravimetrically by silver halide precipitation from aqueous solutions. In some instances, it was necessary to first destroy the metal-halogen bond with boiling caustic soda solution.

(v) Micro-analyses for carbon and hydrogen were performed by the C.S.I.R.O. Microanalytical Laboratory, Melbourne.

2. The preparation of organometallics.-

Several organometallic compounds were required for the researches discussed in the preceding chapters, and the methods used for the preparations of these compounds will be described in this section.

Except where otherwise stated, all preparations were carried out in multi-neck flasks fitted with an inlet for nitrogen, a mechanical stirrer passing through a silicone oil seal, a reflux condenser, and either a dropping funnel with a pressure equalizer or a Suba-seal rubber cap through which solutions could be added by injection from a hypodermic syringe. A typical assembly is shown in figure 6.3.

All reactions were carried out with the careful exclusion of air and moisture.

(a) The preparation of ethyl-lithium.- This was prepared by the method of Gilman, Zoellner, and Selby[6] from lithium metal and ethyl bromide.

$$2\ Li + EtBr \longrightarrow LiEt + LiBr.$$

Gilman and co-workers have shown that the surface area of the lithium can have considerable influence on the yields of ethyl-lithium obtained by this method. In this preparation, the lithium was pre-treated in the following manner.

Lithium metal was pounded flat, with a hammer, into a sheet of 1-2 mm. thickness. The sheet was cut, with scissors, into strips of about 1 cm. width. These strips were held in a shallow dish containing dry diethyl ether while the lithium surface was scraped free of surface oxide. The lithium was cut into small pieces directly into the reaction flask through a paper cone from which a rapid stream of nitrogen was emerging.

An ethereal solution of ethyl-lithium was prepared from the finely divided lithium (4.0 g., 0.58 mole) and ethyl bromide (27.5 g., 0.25 mole) in dry diethyl ether. The ethyl-lithium was not isolated, but was used *in situ*.

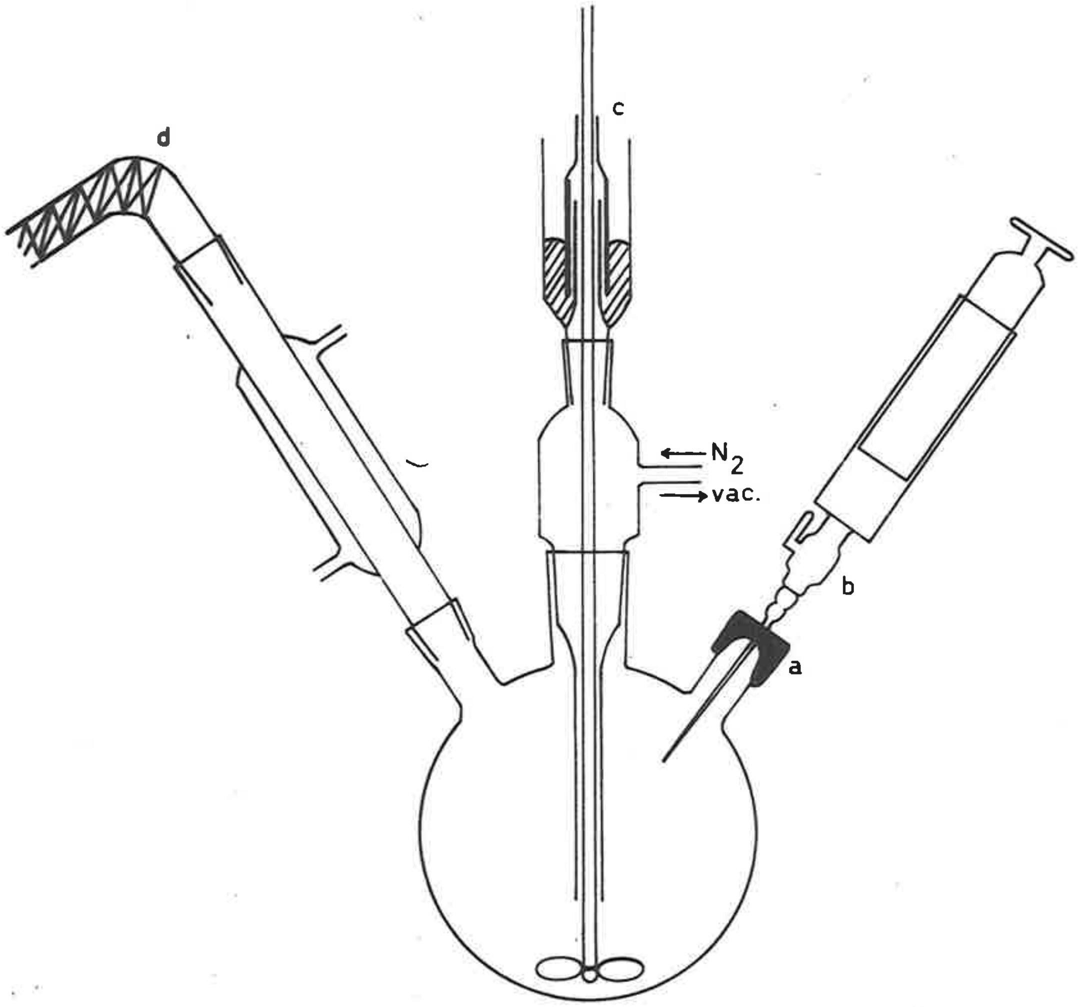

Fig. 6.3 General form of apparatus for reactions with air-sensitive organometallic compounds. a, Rubber syringe cap; b, hypodermic syringe with Luer-Lok stopcock; c, silicone oil-seal stirrer; d, drying tube.

The preparation was also accomplished in petroleum ether (boiling range 30-40°, pentane fraction) as solvent.

Yields varied between 50 and 90% (based on ethyl bromide).

(b) The preparation of diethyl-mercury.- This was prepared by the method of Gilman and Brown[7] from mercuric chloride and ethyl-magnesium bromide.

$$HgCl_2 + 2\ EtMgBr \longrightarrow Et_2Hg + 2\ MgX_2 \quad (X = Cl \text{ or } Br).$$

An ethereal solution of ethyl-magnesium bromide was prepared from "Grignard" magnesium (10.0 g., 0.42 mole) and ethyl bromide (42.0 g., 0.38 mole) in dry diethyl ether (200 ml.).

Diethyl-mercury was made from the Grignard solution and finely powdered mercuric chloride (45.0 g., 0.20 mole) in diethyl ether. The product contained ethyl-mercuric chloride as well as diethyl-mercury. The halide derivative was separated from the diethyl-mercury by heating the mixture and condensing the sublimate of ethyl-mercuric chloride on a "cold-finger" at 15°. The yield of diethyl-mercury was 16.0 g., (36% of the theoretical based on mercuric chloride), b.p. 158°/760 mm. (lit.[8] 159°/760 mm.); the yield of ethyl-mercuric chloride was 10.0 g., (22% of the theory) m.p. 190° (lit.[9] 192°).

(c) The preparations of aluminium alkyls.- During the early stages of these research studies, aluminium alkyls were not available from commercial sources.* Consequently, it was necessary to prepare samples of aluminium alkyls on a laboratory scale.

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* Later, triethyl-aluminium and trimethyl-aluminium were obtained in steel bottles from Ethyl Corporation, U.S.A. These compounds were used without purification.

The aluminium used in these reactions was granular aluminium which had been rinsed successively with moderately concentrated hydrochloric acid, air-free water, and acetone, and subsequently vacuum dried immediately before use.

(i) <u>The preparation of alkyl-aluminium halides.</u>

All the alkyl-aluminium halides were prepared from metallic aluminium and alkyl halides:

$$2\,Al + 3\,RX \longrightarrow R_3Al_2X_3.$$

In many instances, a halogen "scavenger" (e.g. magnesium or copper) was added to the system to promote the formation of dialkyl-aluminium halides.

Methyl-aluminium sesquibromide.- This was prepared by two techniques, both involving reaction between aluminium and methyl bromide.

Method 1. It was prepared by passing methyl bromide vapour at low pressures over an aluminium/copper couple. For the preparation, granular aluminium (ca. 200 g., 7.5 mole) was mixed with copper citrate powder (ca. 50 g.) in a round bottom flask through which a flow of nitrogen was maintained. The flask was gently heated, with occasional shaking, until the copper citrate was completely decomposed (i.e. the evolution of gases and moisture had ceased, and the copper species had changed in colour from green to red-brown). The resultant aluminium/copper couple was thoroughly dried by heating the metals *in vacuo* for several hours. The metal mixture was loosely packed into a glass tube (diam., 25 mm.; length, 75 cm.), and a few crystals of iodine (to act as a catalyst for the reaction) were mixed with the metals at the mouth of the tube. The tube was assembled as shown in figure 6.4, and methyl bromide (350 g., 3.65 mole) was condensed into flask A.

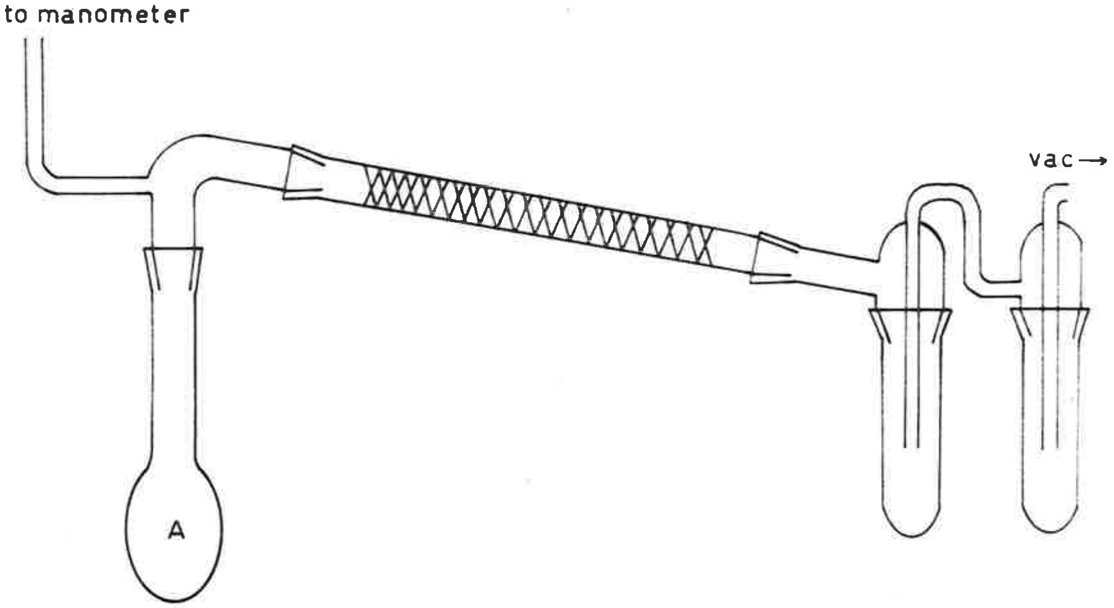

Fig. 6.4 Assembly used for the preparation of methylaluminium sesquibromide.

The whole apparatus was evacuated. By manipulation of cooling baths surrounding flask A, it was possible to slowly vaporize the methyl bromide. In this way, the methyl bromide vapours were brought into contact with the metal mixture in the tube. It was necessary to initiate the reaction by heating the aluminium in the vicinity of the added catalyst. Since the reaction was exothermic, heating was discontinued as soon as reaction commenced. Throughout the treatment, the methyl bromide pressure was maintained at ca. 1 atm. The product which formed solidified in the cooler parts of the tube, and blockages were avoided by the cautious application of a flame to those portions of the apparatus where the white solid accumulated. The product was freed of unchanged methyl bromide by fractional distillation _in vacuo_. The alkyl-aluminium product distilled in the range 195-225° at ca. 15 cm. Yields were nearly quantitative (i.e. ca. 1.2 mole of methyl aluminium sesquibromide). (Found: Al, 13.5; Br, 75.2: Calc. for $(CH_3)_2AlBr$: Al, 13.4; Br, 79.2%: Gas analysis: Sample, 0.102 g.: Gas at N.T.P., 34.6 ml.; Calc. for Me_2AlBr, 33.3 ml.). The analyses indicate that the product was rich in methyl-aluminium dibromide.

Method 2. Alternatively, methyl-aluminium sesquibromide was prepared by the method of Grosse and Mavity.[10] Methyl bromide (285 g., 3.0 mole) was condensed into a rotating autoclave of 500 ml. capacity containing aluminium (100 g., 3.7 mole) and a little iodine. The autoclave was thoroughly evacuated, and was finally heated, with rotation, for 24 hr. The product was syphoned (in a nitrogen atmosphere) into a flask and was subsequently distilled at reduced pressure. The temperature of the oil bath surrounding the distillation flask was raised to ca. 200°

near the end of the distillation. No attempt was made to separate the mono- and di-methyl-aluminium bromides. The yield of sesquihalide was nearly quantitative (i.e. ca. 1.0 mole of methyl-aluminium sesquibromide).

Dimethyl-aluminium iodide.- This was also prepared by the method of Grosse and Mavity[10] from an aluminium/magnesium mixture and methyl iodide.

$$2Al/1Mg + 4\,MeI \longrightarrow 2\,AlMe_2I + MgI_2.$$

A mixture of aluminium (21 g., 0.78 mole) and magnesium turnings (9 g., 0.38 mole), containing a crystal of iodine to act as a catalyst, was treated with methyl iodide (213 g., 1.5 mole). The mixture was heated at ca. 75° for 2-3 hr. The product was filtered *in vacuo*, and was subsequently distilled at reduced pressure. Slow fractionation of the liquid yielded a single fraction, b.p. 42-48°/ 1 mm. This was probably a mixture of dimethyl-aluminium iodide and a little trimethyl-aluminium. (Sample, 0.109 g.: Gas at N.T.P., 30.8 ml.; Calc. for Me_2AlI, 26.6 ml.).

Ethyl-aluminium sesqui-iodide.- This was prepared in similar manner from aluminium and ethyl iodide. The reaction proceeded smoothly at the reflux temperature of ethyl iodide. The products were not fractionated.

(ii) The preparation of trialkyl-aluminium compounds.

Several possible methods of trialkyl-aluminium synthesis were investigated, but in no instances were good yields of trialkyl-aluminium obtained. The methods used are described below.

The conversion of methyl-aluminium sesquibromide to trimethyl-aluminium with metallic sodium.- This reaction was discussed in detail in chapter 2. Sodium wire (21 g., 0.9 mole) was pressed directly into the reaction flask, and the flask was cooled to -78° with solid carbon dioxide. Methyl-aluminium sesquibromide (100 g., 0.295 mole) was cautiously added, in several portions, by rotation of a trap connected to the flask by means of an angled side-arm. The reaction was extremely vigorous. After the addition of all the sesquibromide, the mixture was heated in an oil bath at 100-150° for several hours. The products were fractionated under reduced pressure. The yield of trimethyl-aluminium was 2.1 g. (ca. 10% of the theoretical based on methyl-aluminium sesquibromide), b.p. 128°/760 mm. N_2 atm (lit.[11] 125.3°/760 mm.).

The vigour of the reaction was reduced when a diluent was used, but the yields were not greatly improved. Moreover, the yields were not improved when a sodium-potassium alloy was used in place of the sodium.

The conversion of methyl-aluminium sesquibromide to trimethyl-aluminium with sodium fluoride.- Methyl-aluminium sesquibromide (150 g., 0.44 mole) was treated with dry sodium fluoride (ca. 80 g.) added in small portions and with stirring. The reaction was exothermic. The mixture was heated at ca. 200° for several hours. Attempts to distil methyl-aluminium compounds from the reaction mixture resulted in the liberation of hydrocarbon gases and the formation of mixed aluminium halides.

The preparation of triethyl-aluminium from aluminium and diethylmercury.- A further attempt to prepare triethyl-aluminium was made using the method of Krause and Dittmar.[12] This preparation involved the treatment of metallic aluminium with diethyl-mercury.

$$2\ Al + 3\ Et_2Hg \longrightarrow 2\ Et_3Al + 3\ Hg.$$

An excess of granular aluminium (2 g., 0.075 mole) was mixed with diethyl-mercury (10 g., 0.04 mole) and the mixture was heated, with stirring, at ca. 100° for 1 hr. After this time the product was distilled from the reaction mixture at reduced pressure. The yield of triethyl-aluminium was 0.5 g. (18% of the theoretical based on diethyl mercury), b.p. 125-130°/50 mm. (calc.* for p = 50 mm., 127°).

The direct preparation of triethyl-aluminium from aluminium and ethyl iodide.[10]- This method was discussed in chapter 2.

An aluminium/copper couple was prepared from granular aluminium (13.5 g., 0.5 mole) and cupric citrate (ca. 6 g.) by the method described in the preparation of methyl-aluminium sesquibromide. Ethyl iodide (39.0 g., 0.26 mole) was added to the metal mixture at such a rate as to maintain gentle refluxing. After the complete addition of the ethyl iodide, the reaction mixture was stirred, with refluxing, for a further 2 hr. The liquid products were decanted and subsequently refluxed, under slightly reduced pressure, for 2 hr. The liquid was finally fractionated *in vacuo*. The yield of triethyl-aluminium was 5.0 g. (20% of the theoretical), b.p. 130°/50 mm.

(iii) The preparation of triethyl-aluminium etherate.-

Triethyl-aluminium etherate was prepared from ethyl-magnesium bromide and aluminium trichloride by the method of Krause and Wendt.[14]

$$AlCl_3 + 3\ EtMgBr \longrightarrow Et_3Al.Et_2O + 3\ MgX_2.$$

An ethereal solution of ethyl-magnesium bromide was prepared from

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* The vapour pressure-temperature relationship for triethyl-aluminium is expressed by: $\log_{10}p = (-A/T) + B$, $A = 2826$, $B = 8.778$.[13]

"Grignard" magnesium (38 g., 1.5 mole) and ethyl bromide (16 g., 1.5 mole) in dry diethyl ether (400 ml.). Triethyl-aluminium etherate was prepared by adding a solution of freshly sublimed aluminium trichloride (50 g., 0.37 mole) in dry diethyl ether to the Grignard solution. The yield of triethyl-aluminium etherate was 41 g. (56% of the theoretical based on aluminium trichloride), b.p. 112°/10 mm. (lit.[14] 112°/12 mm.).

(iv) The preparation of lithium tetraethylaluminate.

Two methods were used in this study to prepare lithium tetraethylaluminate.

Method 1. Lithium tetraethylaluminate was prepared from ethyl-lithium and triethyl-aluminium.[15]

$$\text{LiEt} + \text{AlEt}_3 \longrightarrow \text{LiAlEt}_4.$$

Ethyl-lithium was prepared from lithium (4.0 g., 0.6 mole) and ethyl bromide (27.5 g., 0.25 mole) in petroleum ether or diethyl ether. Triethyl-aluminium (32.0 g., 0.28 mole) was dissolved in diethyl ether and the solution was added dropwise, and with stirring, to the ethyl-lithium solution. The mixture was refluxed for a further 1 hr. The reaction mixture was filtered in a nitrogen atmosphere and the ethereal solution of lithium tetraethylaluminate was used in situ. Alternatively, the lithium tetraethylaluminate could be isolated in the following manner. The bulk of the ether was removed by evaporation in vacuo, and the remaining ether, which was tenaciously held, was removed under reduced pressure by heating the solvated product to ca. 80° in vacuo. The white solid so obtained was well washed with cold petroleum ether to remove excess triethyl-aluminium. The product could be recrystallized from boiling benzene. The yield of lithium tetraethylaluminate was 10.5 g. (28% of the theoretical based on triethyl-aluminium).

Method 2. Alternatively, lithium tetraethylaluminate was prepared directly from metallic lithium and triethyl-aluminium. This synthesis was discussed in detail in chapter 2.

Lithium metal (1.4 g., 0.20 mole), cut into small pieces as previously, was suspended in dry benzene (100 ml.). The mixture was stirred vigorously, and warmed, while triethyl-aluminium (42.0 g., 0.37 mole) in benzene (100 ml.) was slowly added. The mixture was finally refluxed for ca. 2 hr. The hot solution was filtered in a nitrogen atmosphere, to remove excess lithium and deposited aluminium. The lithium tetraethylaluminate crystallized from the benzene on cooling and was isolated by filtration. The yield was 21.2 g. (70% of the theoretical based on triethyl-aluminium).

The treatment of lithium metal (1.90 g., 0.27 mole) with triethyl-aluminium etherate (70.0 g., 0.36 mole) in diethyl ether (150 ml.) gave 49.3 g. (92%) lithium tetraethylaluminate. (Sample, 0.151 g.; Gas at N.T.P., 84.0 ml.; Calc. for $LiAl(C_2H_5)_4$, 89.6 ml.).

(d) The preparation of tin alkyls.

(i) Tetraethyl-tin.- This was prepared from ethyl-magnesium iodide and stannic chloride.[16]

$$4\ EtMgI + SnCl_4 \longrightarrow SnEt_4 + 4\ MgX_2.$$

An ethereal solution of ethyl-magnesium iodide was prepared from "Grignard" magnesium (10 g., 0.42 mole) and ethyl iodide (114 g., 0.75 mole) in dry diethyl ether (200 ml.).

Tetraethyl-tin was prepared by adding a slurry of stannic chloride (50 g., 0.19 mole) in dry diethyl ether to the Grignard solution.

The yield of tetraethyl-tin was 12.0 g. (26% of the theoretical based on stannic chloride), b.p. 62-5°/12mm.[16] (Found: C, 40.3; H, 8.4: Calc. for $Sn(C_2H_5)_4$, C, 40.8; H, 8.5%).

(ii) Triethyl-tin chloride.- This was prepared by a redistribution reaction involving tetraethyl-tin and stannic chloride according to the method of Korcheskov.[17]

$$3\ Et_4Sn + SnCl_4 \longrightarrow 4\ Et_3SnCl.$$

Tetraethyl-tin (14.1 g., 0.06 mole) and stannic chloride (5.2 g., 0.02 mole) were heated *in vacuo* at 200° for 2 hr. in a sealed tube. The yield of triethyl-tin chloride was quantitative. (Found: C, 29.6; H, 5.7; Cl, 14.9: Calc. for $(C_2H_5)_3SnCl$: C, 29.8; H, 6.2; Cl, 14.7%).

(iii) Triethyl-stannane.- This was prepared by the lithium tetrahydroaluminate reduction of triethyl-tin chloride.[18] For the preparation, a solution of triethyl-tin chloride (13.3 g., 0.055 mole) in dry diethyl ether (25 ml.) was added dropwise, at -20°, to a solution of lithium tetrahydroaluminate in diethyl ether (0.028 mole of $LiAlH_4$). The mixture was stirred for 1 hr. at 20°, and the bulk of the ether was then removed by distillation at atmospheric pressure. The product was distilled at reduced pressure, the fraction boiling at less than 60° being collected, b.p. 52°/20 mm. (calc., b.p. 48°/20 mm.)*

(e) The preparation of triethyl-lead chloride.-

This was prepared by the cleavage of tetraethyl-lead with dry hydrogen chloride.[19]

$$PbEt_4 + HCl \longrightarrow Et_3PbCl + EtH.$$

Tetraethyl-lead (Associated Ethyl Co. Ltd.) was dried over anhydrous

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* Vapour pressure constants for $(C_2H_5)_3SnH$, A = 2273, B = 8.36.[18]

magnesium sulphate, and was distilled *in vacuo* before use. The tetraethyl-lead (9.0 g., 0.028 mole) was treated with a solution of hydrogen chloride in diethyl ether (75 ml.) (solubility of hydrogen chloride in diethyl ether at 20° = 29 g./100 g. of solution). Alternatively, dry hydrogen chloride was bubbled through a solution of tetraethyl-lead in hexane.[20] The yields of triethyl-lead chloride were quantitative. m.p. 120° (decomp.) (lit.[21] 120° decomp.).

(f) The preparation of bis(cyclopentadienyl)titanium dichloride.- This was prepared by the method of Wilkinson and Birmingham[22] from sodium cyclopentadienide and titanium tetrachloride.

$$TiCl_4 + 2\ NaCp \longrightarrow Cp_2TiCl_2 + 2\ NaCl.$$

High yields of product were not obtained from the first attempts at the preparation. However, the following technique gave moderately good yields of bis(cyclopentadienyl)titanium dichloride.

Titanium tetrachloride (B.D.H. grade) was distilled at reduced pressure from bright copper turnings.

Dicyclopentadiene (b.p. 170°) is converted to cyclopentadiene (b.p., 43°) at ca. 160-165°. Dicyclopentadiene was cautiously heated at ca. 160°, and the cyclopentadiene was collected as it distilled from the molten dimer. The monomer was used soon after distillation to avoid the reformation of dimer. Alternatively, it was redistilled directly into the reaction flask.

Cyclopentadiene (13.0 g., 0.02 mole) was added dropwise, and with vigorous stirring, to finely divided sodium (4.5 g., 0.2 mole) in tetrahydrofuran (100 ml.). The mixture was stirred at room temperature until the evolution of hydrogen ceased. With complete exclusion of moisture and oxygen, a pale orange solution was obtained, but in the presence of traces of oxygen, a red-purple, turbid solution resulted. Good yields of bis(cyclopentadienyl)titanium dichloride were obtained only when pale orange solutions of sodium cyclopentadienide were used.

Titanium tetrachloride (18 g., 0.095 mole) was cautiously added to tetrahydrofuran (150 ml.) with stirring and ice cooling; the formation of the yellow-green solvate was vigorous. The solution of sodium cyclopentadienide was cooled in ice and was run slowly into the slurry of titanium tetrachloride with stirring and ice cooling. The reaction mixture was stirred at room temperature for a further 2-3 hr. The solvent was then removed by distillation at reduced pressure. The dark residue was transferred to a Soxhlet extraction apparatus, and repeatedly extracted with boiling chloroform through which a stream of dry hydrogen chloride was continuously passed. The extract was evaporated to dryness, and the residue was recrystallized from boiling toluene. Red crystals of bis(cyclopentadienyl)titanium dichloride were obtained in 60% yield, (13 g.), m.p. 285°. (Found: C, 48.5; H, 4.4; Ti, 19.3; Cl, 28.2. Calc. for $(C_5H_5)_2TiCl_2$: C, 48.2; H, 4.1; Ti, 19.2; Cl, 28.5%).

A quantity of black material which also formed in the reaction was not extracted by the chloroform. This compound was not characterized but obviously affected the yield of bis(cyclopentadienyl)titanium dichloride.

3. Reactions of aluminium alkyls with metal and metalloid halides.[23]

All reactions were performed with the careful exclusion of air and moisture. Multi-neck flasks, fitted with mechanical stirrer, reflux condenser, inlet for the passage of nitrogen, and "Suba-seal" rubber caps were used throughout.

(a) Tin tetrachloride and lithium tetraethylaluminate.- A solution of lithium tetraethylaluminate (20.0 g., 0.13 mole) in benzene (250 ml.) was stirred vigorously while tin tetrachloride (26.0 g., 0.10 mole) in benzene (60 ml.) was added at such a rate that gentle refluxing was maintained by the heat of the reaction. Refluxing was continued for 1 hr. after the complete addition of the tin tetrachloride. The reaction mixture was decomposed with aqueous ammonium chloride solution, and the aqueous layer was thoroughly extracted with benzene. The benzene fractions were combined, and the benzene removed by distillation. The residue of organo-tin compounds was dissolved in ether and was freed of small amounts of partially alkylated tin species by agitating the ethereal solution with aqueous/alcoholic potassium fluoride and filtering off the insoluble triethyl-tin fluoride. After removal of the ether, the tetraethyl-tin was fractionated under reduced pressure. The yield of tetraethyl-tin was 20.0 g. (85%), b.p. 59°/10 mm. (lit.[24] 51°/8 mm.). (Found: C, 40.2; H, 8.4. Calc. for $(C_2H_5)_4Sn$: C, 40.8; H, 8.5%).

(b) Lead dichloride and lithium tetraethylaluminate.- Similarly, a suspension of finely powdered lead dichloride (16.7 g., 0.06 mole) in diethyl ether (100 ml.) was treated with lithium tetraethylaluminate (6.5 g., 0.044 mole) in diethyl ether (50 ml.). A black suspension of lead immediately separated. After 2 hr. refluxing, subsequent hydrolysis, and extraction with ether, the ether was evaporated from the organo-lead product. The organo-lead mixture, presumably containing hexaethyldilead and tetraethyl-lead, was refluxed for 2 hr., and then fractionated under reduced pressure to give tetraethyl-lead (10.0 g., 106%), b.p. 92°/18 mm. (lit.[24] 90°/16 mm.), (Found: C, 29.0; H, 6.2; Calc. for $(C_2H_5)_4Pb$: C, 29.7; H, 6.2%).

(c) Phosphorus trichloride and lithium tetraethylaluminate.- Similarly, phosphorus trichloride (6.7 g., 0.05 mole) in diethyl ether (10 ml.) was slowly added, with vigorous stirring and ice cooling, to a solution of lithium tetraethylaluminate (10.0 g., 0.066 mole) in diethyl ether (100 ml.). A viscous product formed. Triethylphosphine could not be distilled from the reaction mixture. After 30 min. refluxing and subsequent hydrolysis with aqueous potassium hydroxide solution (20%), the triethylphosphine was extracted with ether. The triethylphosphine was isolated *via* the formation of the silver iodide adduct (by the method of Mann, Wells, and Purdie[25]) and was regenerated by heating *in vacuo*. The yield of triethylphosphine was 0.6 g. (10%). The carbon disulphide adduct formed red needles, m.p. 118-120° (decomp.), (lit.[26] 120° decomp.). (Found: C, 43.3; H, 7.8. Calc. for $(C_2H_5)_3P.CS_2$: C, 43.3; H, 7.7%).

(d) Arsenic trichloride and lithium tetraethylaluminate.- Similarly, arsenic trichloride (5.5 g., 0.03 mole) in diethyl ether (10 ml.) was added to lithium tetraethylaluminate (5.2 g., 0.035 mole) in diethyl ether (25 ml.), and triethylarsine was obtained by the same technique as was used to isolate triethylphosphine. The yield of triethylarsine was 2.5 g. (51%). The mercuric chloride adduct $[(C_2H_5)_3As.HgCl_2]_2$ formed white crystals, m.p. 162-3° (ethanol) (lit.[27] 162-3°) (Found: C, 16.9; H, 3.7. Calc. for $(C_2H_5)_3As.HgCl_2$: C, 16.6; H, 3.5%).

(e) Antimony trifluoride and lithium tetraethylaluminate.- Similarly, lithium tetraethylaluminate (10.0 g., 0.067 mole) in diethyl ether (50 ml.) was treated with a suspension of freshly sublimed antimony trifluoride (9.0 g., 0.05 mole) in diethyl ether (150 ml.). After refluxing the reaction mixture for 90 min., and subsequent hydrolysis with aqueous ammonium chloride solution, the triethylstibine was extracted with diethyl ether. The combined ether extracts were titrated with iodine in diethyl ether until the iodine colour just persisted. After evaporation of the ether, the residue of di-iodotriethylstibine was reconverted to triethylstibine by treatment with moist zinc powder (using the method of Morgan and Yarseley[28]). The yield of triethylstibine was 6.7 g. (65%). The triethylstibine was characterized by forming the mercuric iodide adduct of methyltriethylstibonium iodide, m.p. 54-6°, (Found: C, 10.4; H, 2.2; Hg, 24.9. Calc. for $C_7H_{18}SbI.HgI_2$: C, 10.5; H, 1.4; Hg, 24.3%).

(f) Bismuth trichloride and lithium tetraethylaluminate.- Similarly, lithium tetraethylaluminate (10.0 g., 0.067 mole) in diethyl ether (50 ml.) was treated with freshly sublimed bismuth trichloride (15.0 g., 0.046 mole) in diethyl ether (50 ml.). A large quantity of grey precipitate formed. After refluxing for 1 hr., and subsequent hydrolysis, the triethylbismuthine was extracted with diethyl ether. The bulk of the ether was removed by fractional distillation through an efficient column and the residue was further fractionated under reduced pressure. The yield of triethylbismuthine was 12.0 g., (85%), b.p. 90°/48 mm. (lit.[29] 96°/50 mm.). Qualitative tests indicated the absence of halogens in the product.

(g) Methyl-aluminium sesquibromide and antimony halides.- The treatment of methyl-aluminium sesquibromide (10.2 g., 0.03 mole) in heptane with solutions of antimony trichloride (3.4 g., 0.015 mole) or antimony tribromide (5.4 g., 0.015 mole) in heptane initially formed a white solid which immediately dissolved in the solvent. A yellow oil and some black solid subsequently separated from the heptane. Trimethylstibine could not be distilled from the reaction mixture. The reaction mixture was hydrolyzed with aqueous ammonium chloride solution (10%) and the methylstibines were extracted with heptane. The combined heptane extracts were fractionated under reduced pressure. Some trimethylstibine was isolated, but the product could not be completely freed of solvent. The yields of trimethylstibine were low (ca. 20%), b.p. 83°/760 mm. (lit.[11] 80.6°/760 mm.).

The addition of antimony pentachloride (8.3 g., 0.028 mole) in heptane to methyl-aluminium sesquibromide (9.4 g., 0.028 mole) in heptane formed an orange-red oil and a white solid. The reaction mixture was filtered <u>in vacuo</u> and the heptane was decanted from the red oil. The white solid was washed with heptane, and recrystallized several times from boiling benzene, (m.p. 147°, 89°, 81° ... on successive recrystallizations). The solid was very soluble in polar organic solvents. It decomposed vigorously in water, or dilute acids, and less vigorously upon exposure to the atmosphere. Qualitative tests revealed the presence of antimony(III), aluminium and chloride ions.

The red oil was freed of solvents by pumping <u>in vacuo</u> for several hours. It decomposed upon attempted distillation <u>in vacuo</u>, liberating hydrocarbon gases and other unidentified volatile materials. It also decomposed upon exposure to the atmosphere. Analyses revealed the presence of antimony (17.8%) and aluminium.

4. Reactions of titanium halides with organometallic compounds.-

Reactions 4(b) - 4(e) were performed with the careful exclusion of air and moisture.

(a) Bis(cyclopentadienyl)titanium dichloride and tetraethyl-lead.- Tetraethyl-lead (Associated Ethyl Co. Ltd.) was dried over anhydrous magnesium sulphate and was distilled under reduced pressure before use. The tetraethyl-lead (2.25 g., 0.07 mole) in chloroform (10 ml.) was added to a solution of bis(cyclopentadienyl)titanium dichloride (1.75 g., 0.07 mole) in chloroform (15 ml.), and the mixture was shaken for 2 hr. A white solid formed within a few hours. The reaction mixture was filtered in a nitrogen atmosphere and the collected solid was washed with cold pentane. The solid was recrystallized from boiling ethyl acetate. Lead (Found 62.9; Calc. for $(C_2H_5)_3PbCl$, 62.7%) and chlorine were found in the solid, m.p. 120° (decomp.) (lit.[21] 120° decomp. for triethyl-lead chloride). A small residue of white solid, not readily soluble in ethyl acetate, was also isolated (Found: C, 13.1; H, 2.7%). The filtrate from the reaction mixture was evaporated to dryness *in vacuo*. The pale orange residue contained titanium and lead, but no pure compounds could be isolated and characterized.

The triethyl-lead chloride formed more quickly when more than an equimolar proportion of tetraethyl-lead was used.

In a second run, a solution of bis(cyclopentadienyl)titanium dichloride (0.181 g., 7.2 mmole) in chloroform (10 ml.) was shaken with tetraethyl-lead (0.226 g., 7.0 mmole) for 2 hr., and the reaction mixture was hydrolyzed with a mixture of ethanol and water. (Gas at N.T.P.: 5.1 ml.; Calc. for $Cp_2TiCl(C_2H_5)$, 16.5 ml.).

In a third run, a solution of bis(cyclopentadienyl)titanium dichloride in ethyl acetate (2.9 mmolar) was treated with excess tetraethyl-lead, and the concentration of the titanium compound was measured colorimetrically at various intervals. The following values were recorded, the relationship between optical density and bis(cyclopentadienyl)titanium dichloride concentration being obtained from a Beer-Lambert law plot (Fig. 6.5).

Time (hr.)	Opt. dens.	Conc. (mmolar)
Start	0.720	2.90
3.0	0.621	2.50
7.0	0.614	2.47
20.0*	0.550	2.22

* After 7 hr., the solutions became turbid and centrifugation of the samples was necessary.

In a final run, the spectrum of bis(cyclopentadienyl)titanium dichloride was measured in the visible region at various times after tetraethyl-lead had been added to the titanium compound. The results were shown in figure 4.4.

(b) Bis(cyclopentadienyl)titanium dichloride and triethylaluminium etherate.

When triethyl-aluminium etherate (4.5 g., 0.024 mole) and bis(cyclopentadienyl)titanium dichloride (6.25 g., 0.025 mole) were heated in heptane at ca. 70°, a green solution formed. A dark brown solid was slowly deposited from the solution. The solid was isolated by filtration in a nitrogen atmosphere and was well washed with cold heptane. Reduced titanium, aluminium, chloride groups and ethyl groups were detected in the solid.

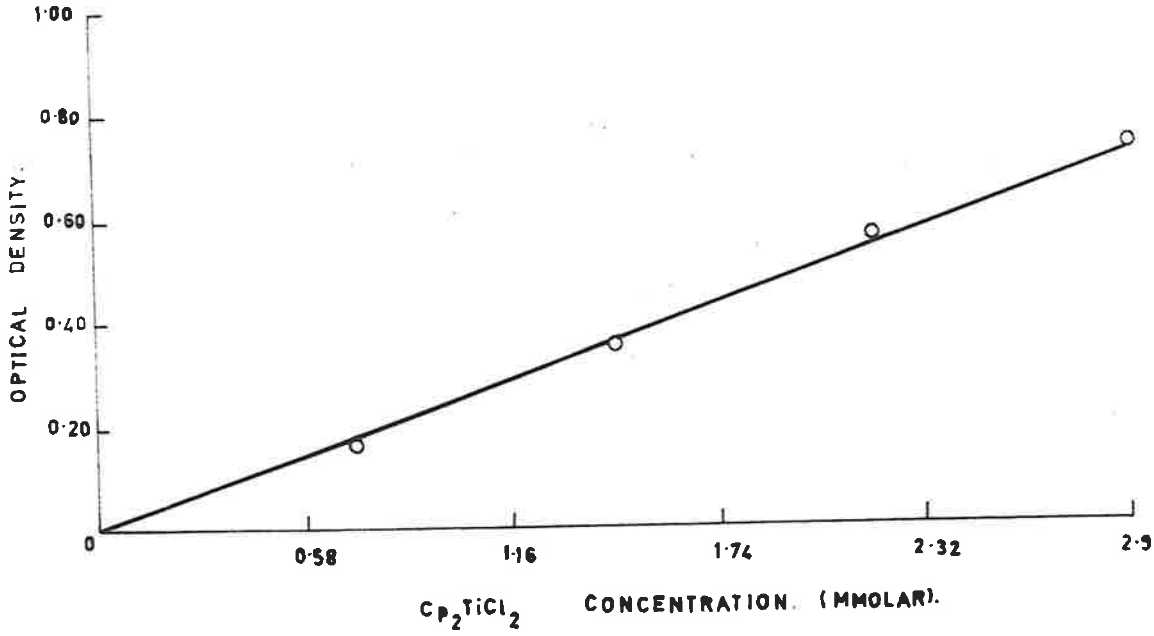

Fig. 6.5 Standard optical density versus concentration graph for solutions of bis(cyclopentadienyl)-titanium dichloride in toluene or ethyl acetate, (λ=520 m).

In a second run, a sample of the green solution was withdrawn from the reaction mixture and was evaporated to dryness in vacuo. A residue of green and brown solids remained. The green solid could not be readily separated from the other solids, and slowly decomposed to the dark solid.

Bis(cyclopentadienyl)titanium dichloride (1.9 g., 7.5 mmole) in methylene chloride* (20 ml.) was treated, at -20°, with triethylaluminium etherate (1.5 g., 7.5 mmole) in methylene chloride (5 ml.). The mixture was stirred for 3 hr. and the temperature was allowed to rise to room temperature. A 10 ml. sample of the dark reaction mixture was withdrawn and the solvents were evaporated in vacuo. The residue was only partly solid and contained a mixture of green and orange materials which transformed completely to an orange sludge within a few hours. When the orange residue was treated with anhydrous hydrogen chloride in diethyl ether, bis(cyclopentadienyl)titanium dichloride could be extracted from the mixture with methylene chloride.

In another run, a sample of the orange residue was heated in vacuo at 150° for ca. 15 mins. A small amount of bis(cyclopentadienyl)-titanium dichloride sublimed, but no volatile materials were formed by thermal decomposition of the orange compound. A further sample of the residue was hydrolyzed with dilute aqueous hydrochloric acid (5%) but again no volatile materials were evolved.

In a final run, bis(cyclopentadienyl)titanium dichloride (1.9 g., 7.5 mmole) in tetrahydrofuran (30 ml.) was treated at -20°

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* It has been shown[30] that methylene chloride is the most suitable solvent for use in the preparation of bis(cyclopentadienyl)titanium alkyl compounds.

with triethyl-aluminium etherate (1.4 g., 7.5 mmole). The reaction mixture was agitated for 2 hr. at -20°, and for a further 2 hr. at room temperature. The spectrum of an aliquot of the solution was scanned in the visible region. A second aliquot was hydrolyzed with propanol and was quickly evaporated to dryness. The orange residue was extracted with toluene, and the spectrum of the toluene extract was also scanned in the visible region. These spectra were shown in figure 4.3.

(c) Titanium tetrachloride and lithium tetraethylaluminate.- A slurry of titanium tetrachloride (9.5 g., 0.05 mole) in diethyl ether (10 ml.) was added at room temperature to a solution of lithium tetraethylaluminate (5.7 g., 0.05 mole) in diethyl ether. A dark brown oil immediately separated and the evolution of gases was observed. The gases were condensed at -183°, and were identified by molecular weight measurements as C_2- hydrocarbons. (Found: 30.2; Calc. for C_2H_4, 28.0; C_2H_6, 30.0). The gas mixture removed the colour from a solution of bromine in carbon tetrachloride.

Solvents were evaporated *in vacuo* from the reaction mixture and the residue of brown solids was washed with cold diethyl ether. The brown solid contained aluminium, titanium(III), lithium, chloride groups, and ethyl groups. A small amount of brown solid was extracted with boiling benzene, and a white solid was precipitated from the benzene solution by the addition of diethyl ether. The white solid had a low hydrocarbon content, (Found: C, 2.5; H, 4.8; Cl, 19.0; sulphate ash, 47.5%), and could not be identified.

In a second run, tetrahydrofuran was used as solvent. A green solid was deposited as well as the brown oil. Within a few hours, the brown oil was completely transformed to the green solid. The green solid decomposed upon exposure to the atmosphere. It was isolated by filtration in a nitrogen atmosphere. The solid contained aluminium, titanium(III), lithium, chloride groups, and ethyl groups. It was soluble in a number of organic solvents but could not be readily recrystallized.

(d) Triethylplumbyl sodium and bis(cyclopentadienyl)titanium dichloride.[31]

(i) The preparation of triethylplumbyl sodium.- This was prepared by the method of Gilman and Bindschadler.[32] For the preparation, a solution of sodium (0.5 g., 0.02 mole) in liquid ammonia (75 ml.) was added, at -46°, to a solution of tetraethyl-lead (3.2 g., 0.01 mole) in toluene (25 ml.). The reaction mixture was stirred (at -46°) for 6 min., and was filtered in vacuo before use. These authors report an 88% yield.

An attempt to isolate triethylplumbyl sodium.- With the reaction mixture at -78°, the ammonia was removed under reduced pressure. Extensive decomposition occurred, and a highly coloured solid remained. The solid was isolated by filtration in a nitrogen box. Qualitative analyses of different samples of the solid residue revealed the presence of lead and organic groups.

An additional attempted preparation of triethylplumbyl sodium.- An attempted preparation, in the absence of liquid ammonia, was carried out by adding a solution of triethyl-lead chloride (3.0 g., 0.01 mole) in toluene to a cooled suspension of sodium sand (0.5 g., 0.02 mole) in toluene. No reaction was observed between -78° and room temperature. Moreover, no reaction was observed when a liquid sodium/potassium alloy was used in place of the sodium.

(ii) The preparation of "ammoniated triethylplumbane".- Triethylplumbyl sodium was prepared in liquid ammonia from sodium (0.5 g., 0.02 mole) and tetraethyl-lead (3.2 g., 0.01 mole), and sufficient ammonium chloride (1.1 g., 0.02 mole) was added to decompose the sodamide present and to react with the triethylplumbyl sodium. Gaseous products were immediately evolved and orange and green solid products formed. Within a few minutes the solid material was completely green in colour. The ammonia was removed under reduced pressure from the cooled (-78°) reaction mixture. A moist grey solid residue remained. The residue was extracted, in turn, with diethyl ether and water. Evaporation of the ether extract yielded a liquid which was free of halogen and which contained lead and ethyl groups. This was identified as tetraethyl-lead by its infra-red spectrum. The spectrum showed strong bands at: liquid film: 2950 (s), 2850 (s), 1650 (m), 1450 (ms), 1410 (m), 1360 (ms), 1220 (m), 1150 (s), 1005 (s), 960 (ms), 940-930 (m). The aqueous extract yielded sodium chloride upon concentration.

Fractionation of the volatile constituents by trap to trap distillation in a vacuum system separated a preponderance of ammonia, a volatile hydrocarbon, and a small amount of a lead derivative. The latter decomposed in a short time to lead (identified by its chemical behaviour), tetraethyl-lead (identified by infra-red examination), gaseous hydrocarbons (M.W. Found 30.2. Calc. for C_2H_6, 30.0), and a non-condensible gas.

(iii) Ammonolysis of bis(cyclopentadienyl)titanium dichloride.- Finely powdered bis(cyclopentadienyl)titanium dichloride was treated (at -46°) with anhydrous liquid ammonia, the mixture being stirred continuously. Within 15 min., all the red titanium compound was converted to a yellow slightly soluble product. The ammonia was completely removed under reduced pressure, and the solid was pumped in vacuo for 12 hr. (Found: N, 16.9; 14.8. Calc. for $C_{10}H_{10}TiNH_2Cl.NH_3 + NH_4Cl$: N, 14.2%. Mol. ratio, Ti:N:Cl, 1:3·6:2, 1:3·2:2).

A sample of the solid was placed in vessel A of the apparatus shown in figure 6.6, and was repeatedly extracted with liquid ammonia. The filtrate was collected in B and the ammonia recycled to A. The extraction yielded a yellow-orange filtrate and virtually no residue. Addition of an ammonium chloride solution of barium nitrate to the yellowish filtrate caused the precipitation of barium chloride.

The dry yellow solid was easily hydrolyzed; treatment with water liberated ammonia and extracted ammonium chloride.

(iv) The reaction of bis(cyclopentadienyl)titanium dichloride with sodium in liquid ammonia.- Metallic sodium (0.02 g., 1 mmole) was dissolved in liquid ammonia. A suspension of bis(cyclopentadienyl)-titanium dichloride (0.25 g., 1 mmole) in toluene was added to the ammonia solution with continuous stirring. A green solid formed. As the solvents were removed under reduced pressure, the green material slowly changed to an orange-yellow residue. No green solid remained in the solvent-free residue. The residue was pumped in vacuo for 12 hr. (Found: N, 10.6. Calc. for $C_{10}H_{10}TiClNH_2.NH_3 + NaCl$, N, 9.2%. Mol. ratio, Ti:N:Cl, 1:2·3:2). Treatment with water released ammonia from the solid and extracted sodium chloride.

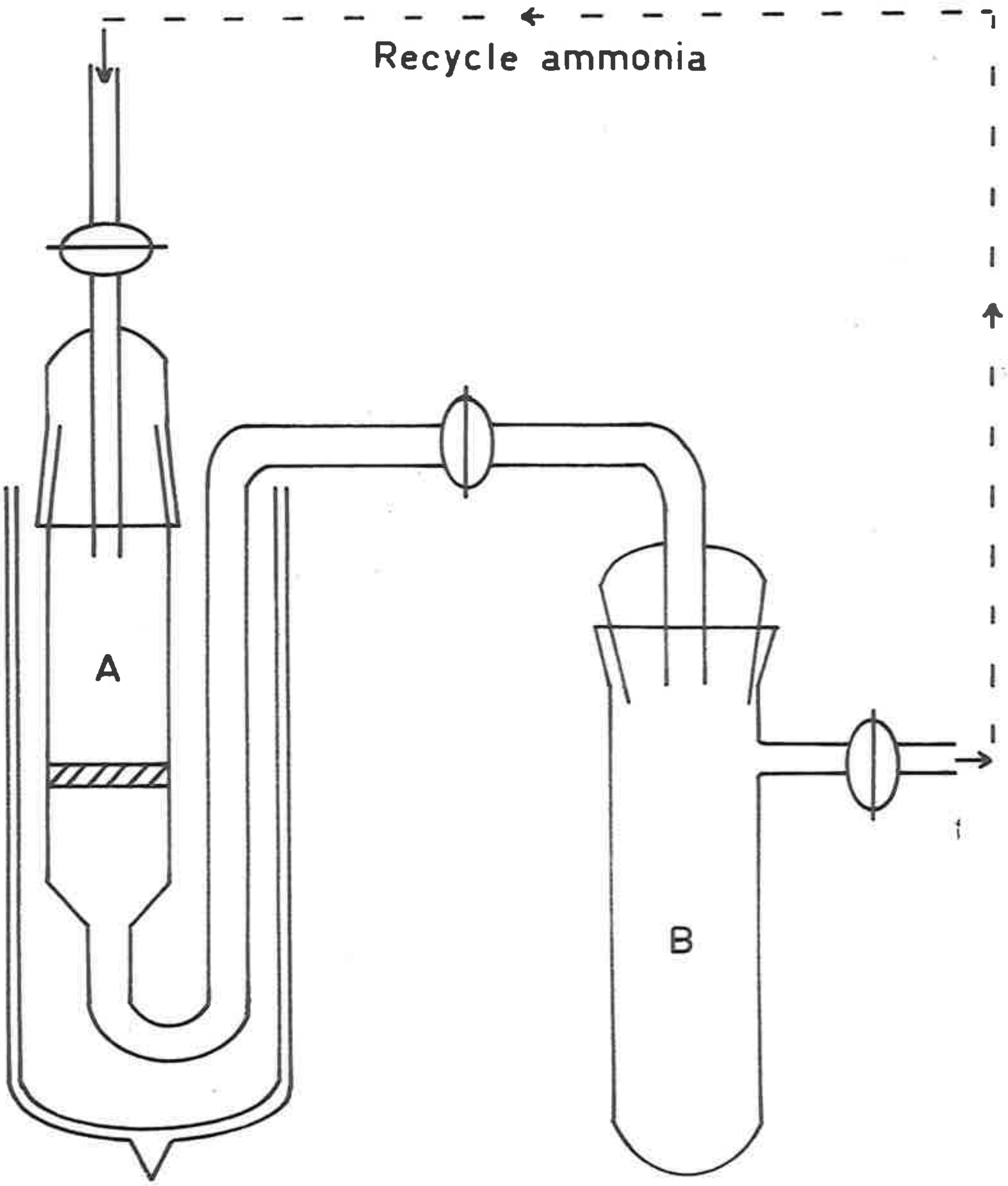


Fig. 6.6 Apparatus used for the preparation of ammonobasic-titanium compounds.

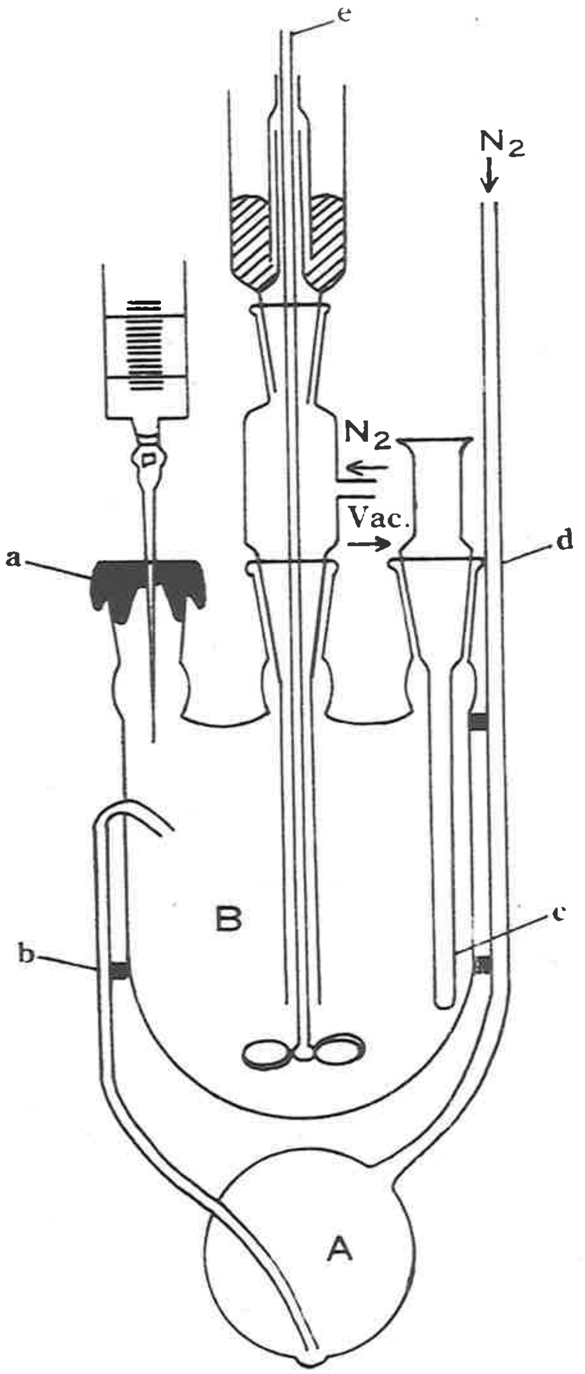
(v) The reaction of triethylplumbyl sodium with bis(cyclopentadienyl)titanium dichloride.- Using the apparatus illustrated in figure 6.7, triethylplumbyl sodium was prepared (on a 0.01 molar scale) in flask A in an ammonia/diethyl ether solvent mixture. Agitation was effected by bubbling nitrogen through the mixture. Simultaneously, liquid ammonia was condensed onto finely powdered bis(cyclopentadienyl)titanium dichloride (2.25 g., 90% of 0.01 mole) in flask B. After 10 min., the contents of A were forced by nitrogen pressure into flask B, and the resultant highly coloured mixture was stirred for 30 min.

The removal of ammonia under reduced pressure yielded a blue-green solid, insoluble in diethyl ether. The solid was isolated by filtration in a nitrogen atmosphere. It decomposed to a buff solid upon exposure to the atmosphere, vacuum drying, or aging in a dry, nitrogen atmosphere. The blue-green solid was not reformed by treatment of the buff solid with ammonia.

A sample of the buff solid was treated with hydrogen chloride in diethyl ether. Vacuum drying and toluene extraction of the residue yielded no bis(cyclopentadienyl)titanium dichloride.

A qualitative examination of the solid revealed the presence of both lead and titanium. Treatment of the solid with nitric acid yielded a hydrocarbon gas which was identified by molecular weight measurements as ethane, (M.W., Found: 30.1. Calc. for C_2H_6: 30.0). The residue from this treatment contained lead nitrate and a soluble, unidentified titanium species.

Examination of a slurry of the blue-green solid in diethyl ether revealed the presence of titanium(III) (or other easily



<u>Fig. 6.7</u> Reaction vessel for low temperature organometallic reactions (upper flask B, 250 ml capacity, lower flask A, 100 ml capacity). a, Rubber syringe cap; b, siphoning tube; c, thermometer well; d, nitrogen pressure inlet; e, mercury-seal stirrer. The vessel could be immersed in a suitable "cooling bath".

oxidizable groups).

Water extraction of the buff solid yielded sodium chloride, all the chlorine originally attached to the titanium being extracted. (Found: 0.019 mole of chloride as sodium chloride. Calc. for $(C_5H_5)_2TiCl_2$ added, 0.020 mole).

Samples of the buff solid were thoroughly washed with a variety of organic solvents and were finally pumped free of solvent for several hours. (Found: (i) C, 19.5; H, 3.7; sulphate ash, 48.1%; mol. ratio, C:H, 3:7; (ii) C, 4.8; H, 2.8%; mol. ratio, C:H, 1:7; Pb, 38.0; Ti, 23.8%; mol. ratio, Pb:Ti, 2:5; (iii) C, 4.2; H, 2.6%; mol. ratio, C:H, 1:7; (iv) C, 10.9; H, 2.3%; mol. ratio, C:H, 2:5). Analyses (ii) and (iii) were of samples which had been extracted with water, whereas analyses (i) and (iv) were of samples which had been washed only with organic solvents. The sample used for analysis (iv) has been kept in the atmosphere for several weeks before analysis.

The infra-red spectrum of the buff solid (nujol mull) revealed absorptions at: 3390 (ms), 2925 (vs), 2860 (sh), 2670 (w), 2083 (broad) (w), 1600 (ms), 1500 (s), 1435 (s), 1355 (s), 1325 (sh), 1242 (mw), 1110-broad (v). The bands at 1600 and 1500 indicate that aromatic cyclopentadienyl groups are probably still present in the buff solid.

(e) Bis(cyclopentadienyl)titanium dichloride and triethylstannyl lithium.

(i) The preparation of triethylstannyl lithium.[33] - Ethyl-lithium was prepared from lithium (0.9 g., 0.13 mole) and ethyl bromide (4.6 ml., 0.06 mole) in diethyl ether. A 50% yield (0.03 mole) of ethyl-lithium was obtained.

Stannous chloride was dehydrated by heating in vacuo for several hours. The ethyl-lithium solution was slowly added to a stirred suspension of finely ground stannous chloride (1.9 g., 0.13 mole) in diethyl ether, previously cooled to -10°. The reaction mixture was deep red in colour. Gilman and Rosenberg[33] report that the method gives a yield of ca. 70% triethylstannyl lithium.

(ii) The reaction of bis(cyclopentadienyl)titanium dichloride with triethylstannyl lithium.- A solution of triethylstannyl lithium (0.03 mole) was cooled to -10° and finely powdered bis(cyclopentadienyl)-titanium dichloride was added with continuous stirring. The reaction yielded a yellow-brown solid and a green supernatant liquid. The latter rapidly changed to a yellow colour upon exposure to air. The mixture was filtered in vacuo and the solid product was well washed with diethyl ether. Qualitative tests on the solid revealed the presence of tin, titanium (some reduced titanium), and lithium, as well as chloride groups and ethyl groups. Toluene extraction of the solid yielded no bis(cyclopentadienyl)titanium dichloride. The solid dissolved in acetone with decomposition and evolution of heat. Removal of the acetone under reduced pressure yielded an orange residue which could not be redissolved in acetone. The solid was partially soluble in water, again with decomposition, yielding a yellow solution and a white residue. It dissolved in nitric acid, but gradually deposited a white precipitate of hydrous stannic oxide. Complex tetraphenylborates and picrates could be precipitated from freshly prepared acid solutions.

Thermal decomposition of the solid, followed by aqueous extraction of the residue removed all the lithium as lithium chloride. Chlorine could still be detected in the solid residue.

The green supernatant liquid, which turned yellow on aging, yielded a yellow-brown solid upon removal of the solvent by evaporation. This solid apparently decomposed, even in a nitrogen atmosphere, to a greenish solid but finally reverted to a yellow-brown colour. This solid had all the properties of the above yellow-brown solid product. Both solids had unpleasant, nauseating odours.

A sample of the solid was thoroughly washed with diethyl ether and was freed of solvents by pumping *in vacuo*. (Found: C, 5.9; H, 3.8%; mol. ratio, C:H, 2:15).

5. Some attempted preparations of perfluoroalkyl derivatives of aluminium, tin, lead, and titanium.

(a) *The reaction of lithium tetrahydroaluminate with heptafluoropropyl iodide.*- Heptafluoropropyl iodide was prepared from the silver salt of perfluorobutyric acid and iodine by the method of Haszeldine.[34]

$$AgOOCC_3F_7 + I_2 \longrightarrow AgI + CO_2 + C_3F_7I$$

For the preparation, an intimate mixture of silver heptafluorobutyrate (160 g., 0.5 mole) and dry powdered iodine (180 g., ca. 0.75 mole) was cautiously heated, and the volatile materials were fractionated several times *in vacuo*. The yield of heptafluoropropyl iodide was almost quantitative. (M.W. Found: 303. Calc. for C_3F_7I, 296), b.p. 40°/760 mm.

A standard solution of lithium tetrahydroaluminate (36.8 ml.

0.05 mole $LiAlH_4$) in diethyl ether was treated at -78° with heptafluoropropyl iodide (45 g., 0.15 mole) in the manner described by Hauptschein and co-workers.[35]

$$LiAlH_4 + 3\,C_3F_7I \longrightarrow LiAl(C_3F_7)_2I_2 + H_2 + C_3F_7H + HI$$

The lithium bis(heptafluoropropyl)diiodoaluminate was not isolated but was used in situ for subsequent reactions. It was always used in a nitrogen atmosphere.

(b) The reaction of triethylstannane with heptafluoropropyl iodide.- Triethylstannane (8.4 g., 0.04 mole), dry diethyl ether (8 ml.), anhydrous ammonia (ca. 2.5 ml. at -78°), and heptafluoropropyl iodide (12.0 g., 0.04 mole) were condensed in vacuo into a pyrex Carius tube cooled to -183°. The evacuated tube was subsequently sealed, and the tube was transferred to a cooling bath at -78°. The tube was shaken at this temperature for 2 hr. A white solid formed. The volatile constituents in the tube were removed under vacuum, and were fractionated in the vacuum line. Ammonia contaminated with some diethyl ether (M.W., Found: 19.4; Calc. for NH_3, 17.0), and a mixture of diethyl ether and unchanged heptafluoropropyl iodide were separated in this way. The heptafluoropropyl iodide in this latter fraction was separated from the ether by vapour phase chromatography and was identified by infra-red absorption spectroscopy. The infra-red spectrum showed the following absorption bands: gas, 2 mm.: 2985 (w), 1575 broad (w), 1325 (s), 1265 (sh), 1240 (vs), 1230 (sh), 1150 (sh), 1130 (vs), 1070-1015 broad (m), 820 (s), 735 (s).

The white solid and the liquid residue in the tube were separated by filtration in vacuo. The solid contained ammonium and iodide ions. The liquid (ca. 2.8 g.) was distilled in vacuo (the vapour pressure-temperature relationship for this liquid was shown in figure 5.1) but it proved impossible to effectively fractionate the liquid. Furthermore, vapour phase chromatography could not be used for purification because of the long elution times. The infra-red absorption spectrum of the liquid showed the following bands: 2940 (s), 2910 (sh), 2860 (s), 1460 double band (m), 1420 (mw), 1380 (m), 1340 (ms), 1260 (m), 1220 (s), 1195 (vs), 1160 (s), 1095 (s), 1075 (m), 1115 broad (ms), 950 broad (m), 910 broad (w), 875 broad (w), 815 (m), 740 (mw), 725 (ms), (Fig. 5.2). The strong absorptions between 1400 and 1000 (in particular at 1340, 1220, 1195, 1160, 1095) can probably be attributed to C-F stretching frequencies.

A sample of the liquid was hydrolyzed in a sealed evacuated tube at 100-120° for 10 hr. with aqueous sodium hydroxide solution (20%) and the liberated gas was identified as heptafluoropropane by infra-red examination. (Sample, 0.212 g.: Gas at N.T.P., 2.5 ml.; Calc. for $(C_2H_5)_3SnC_3F_7$, 12.6 ml.). The infra-red spectrum showed the absorption bands: vapour phase, 2 mm.: 2980 (ms), 2860 (sh), 1410 (mw), 1375 broad (mw), 1345 (ms), 1270 (s), 1245-1220 (vs), 1185 (vs), 1140 (vs), 1105 (m), 1035 (vs), 830 (ms), 745 (sh), 740 (ms), 735 (sh), 710 (sh), 700 (mw).

(c) The reaction of lithium tetraethylaluminate with heptafluoropropyl iodide.

Heptafluoropropyl iodide (9.0 g., 0.03 mole) in tetrahydrofuran (30 ml.) was added dropwise and with stirring to lithium tetraethylaluminate (1.5 g., 0.01 mole) in tetrahydrofuran (20 ml.) at -78°. Gases evolved during the reaction were collected in a trap at -183°. The reaction mixture was stirred at -78° for 90 min., and finally at ca. 60° for 30 min. The evolved gases were distilled into the vacuum line and then fractionated; the main fraction collected at -183° (M.W.: Found 33.1).

Volatile material was distilled from the reaction mixture into the vacuum line, and rough fractionation was achieved by trap to trap distillation. The fraction condensing at -95° (M.W. 109.5) was further fractionated using a vapour phase fractometer containing a column packed with di-isodecylphthalate. Using a column temperature of 46°, and a nitrogen flow of 80 ml./min., three peaks were observed at elution times of 1.90, 4.10, and 9.76 mins. These peaks were identified as resulting from unchanged heptafluoropropyl iodide, ethyl iodide and tetrahydrofuran respectively. The second fraction, condensing at -140°, was shown by infra-red examination and molecular weight measurement, to be a mixture of fluorocarbon gases. (M.W. Found: 162.0; Calc. for C_3F_7H , 170. C_3F_6, 150); the infra-red spectrum showed the absorption bands: vapour phase 5 mm.: 3150 (w), 3100 (w), 2970 (s), 2850 (mw), 2770 (mw), 2700 (w), 2640 (mw), 2580 (mw), 2530 (m), 2460-2340 (m), 2260 (ms), 2200 (mw), 2150 (mw), 2100 (w), 2050 (w), 2005 (w), 1975 broad (m), 1855 broad (m), 1785 (vs), 1745 (m), 1680 (m), 1625 (m), 1480 (m), 1395 (s), 1365 (vs), 1265 (s), 1245-1200 (vs), 1175 (vs), 1135 (s), 1105 (mw), 1030 (vs), 825 (s), 760 (s), 740 (s).

Removal of the volatile constituents from the reaction mixture left a pale yellow-white residue. Hydrolysis of the residue with dilute sulphuric acid (5%) did not liberate hydrocarbon or fluorocarbon gases. The aqueous acid layer contained iodide and fluoride groups.

(d) The treatment of triethyl-aluminium with heptafluoropropyl iodide and with pentafluoroethyl iodide.- In similar manner, triethyl-aluminium (1.14 g., 0.01 mole) in diethyl ether (5 ml.) was treated with heptafluoropropyl iodide (9.0 g., 0.03 mole) in diethyl ether (5 ml.). No ethyl iodide was detected by vapour phase chromatography of the volatile constituents from the reaction mixture. Hydrolysis of the reaction mixture with propanol, and subsequent condensation of the volatile constituents, yielded only ethane. (M.W. Found: 30.5. Calc. for C_2H_6, 30.0). No heptafluoropropane was isolated. The residue contained iodide ions but no fluoride ions.

An identical result was observed when triethyl-aluminium was treated with pentafluoroethyl iodide.

(e) The reaction of lithium bis(heptafluoropropyl)diiodoaluminate with triethyl-lead chloride.- A solution of lithium bis(heptafluoropropyl)diiodoaluminate was prepared from lithium tetrahydroaluminate (0.05 mole) and heptafluoropropyl iodide (45 g., 0.15 mole) in dry diethyl ether by the method of Hauptschein and co-workers. To this solution, triethyl-lead chloride (16.5 g., 0.05 mole) in tetrahydrofuran (50 ml.) was added dropwise and with stirring. The mixture was gently refluxed for 2 hr. The reaction mixture was then hydrolyzed with aqueous ammonium chloride solution (10%) and the organo-lead compounds were extracted with diethyl ether. The ether extracts were combined and the organic solvents were evaporated under reduced pressure. A residue of yellow solids and a yellow-brown liquid remained. The solid was isolated by filtration and was recrystallized from boiling water. The solid was identified, by its characteristic chemical behaviour, as lead diiodide. A small amount of yellow powder, insoluble in hot water, was not identified.

The yellow-brown liquid (ca. 12 g.) decomposed when heated under reduced pressure to form more lead diiodide. The liquid also decomposed slowly at room temperature. Lead, iodide groups, and ethyl groups were detected in the solid. A sample of the liquid was hydrolyzed with aqueous potassium hydroxide solution (20%) in a sealed tube at 100° for 10 hr. (Sample, 1.519 g.; C_3F_7H at N.T.P., 8.0 ml. Calc. for $(C_2H_5)_3PbC_3F_7$, 75.0 ml.). The infra-red spectrum of the liquid showed absorption bands at: liquid film: 3390 (m), 2940 (s), 2860 (sh), 2700 (w), 2080 (w), 1440 (ms), 1420 (sh), 1360 (ms), 1330 (sh), 1290 (m), 1250 (m), 1220 (ms), 1210 (sh), 1150 (sh), 1140 (s), 1090 (mw), 1030 (sh), 1020 (ms), 960 (m), 940 (m), 800 broad (mw). The strong absorptions at 1360, 1290, 1220, and 1140, are probably C-F stretching bands.

(f) The reaction of lithium bis(heptafluoropropyl)diiodoaluminate with triethyltin chloride.-

Lithium bis(heptafluoropropyl)diiodoaluminate was prepared as previously on a 0.025 molar scale. Triethyltin chloride (6.0 g., 0.025 mole) in diethyl ether (20 ml.) was slowly added to the solution of the aluminium complex. The reaction mixture was refluxed for 90 min., and was subsequently hydrolyzed with aqueous ammonium chloride (10%). The organo-tin compounds were extracted into diethyl ether, and the combined ether extracts were dried. The bulk of the ether was removed by distillation at atmospheric pressure, and the last traces of ether by fractionation under reduced pressure. The residue consisted of a dark amber liquid which distilled slowly *in vacuo*, (b.p.

75°/15 mm.) with slight decomposition. 5.5 g. of amber coloured distillate were collected (Found: C, 18.8; H, 3.1%). A sample of the liquid was hydrolyzed with aqueous potassium hydroxide (20%) in a sealed tube at 100° for 10 hr. (Sample, 0.42 g.: C_3F_7H liberated at N.T.P., 5.0 ml. Calc. for $(C_2H_5)_3SnC_3F_7$, 25.0 ml.). The aqueous alkaline layer contained iodide ions. The infra-red spectrum of the liquid showed absorption bands at: liquid film: 2960 (ms), 2990 (m), 1630 (w), 1600 (w), 1450 (m), 1410 (mw), 1370 (mw), 1300 (vs), 1200 (vs), 1150 (s), 1110 (ms), 1020 broad (m), 960 broad (m), 850 (ms), 810 broad (w), 780 broad (w). The bands at 1300, 1200, 1150, 1110 are probably C-F stretching frequencies.

Treatment of the liquid with pyridine, or with anhydrous ammonia in ether, formed yellow and white solids. The solids did not possess sharp melting points and could not be fractionally crystallized. The infra-red spectrum of the pyridine adduct showed absorption bands at: nujol and hexachlorobutadiene mulls: (H.C.B. Mull), 3230 (ms), 3170 (s), 3080 (s), 2940 (s), 2900 (s), 2000 (w), 1850 (w); (nujol mull), 1630 (m), 1590 (s), 1520 (s); (H.C.B. mull), 1470 (s), 1430 (s), 1410 (sh), 1370 (w), 1350 (w), 1320 (m), 1250 (sh), 1230 (ms); (nujol mull), 1210 (ms), 1180 (ms), 1140 (m), 1060 (ms), 1050 (sh), 1035 (ms), 1030 (sh), 1005 (ms), 990 (sh), 960 broad (mw), 890 broad (w), 770 (ms), 745 (s), 710 (s).

(g) The reaction of lithium bis(heptafluoropropyl)diiodoaluminate with bis(cyclopentadienyl)titanium dichloride.-

A solution of lithium bis(heptafluoropropyl)diiodoaluminate, prepared on a 0.01 molar scale, was added, at -78°, to a stirred slurry of bis(cyclopentadienyl)titanium dichloride (1.25 g., 5 mmole) in methylene chloride (10 ml.). The reaction mixture was stirred at -78° for 2 hr., and for a further 30 min. at room temperature. The solvents were evaporated in vacuo. A black solid could be slowly sublimed from the solid residue at ca. 180-200° (Found: C, 32.6; H, 3.3; Ti, 12.3; Cl and I. $(C_5H_5)_2TiCl_{0.5}I_{1.5}$ requires C, 31.3; H, 2.6; Ti, 12.4%). Alkaline hydrolysis of the solid with aqueous potassium hydroxide did not liberate any heptafluoropropane. The infra-red spectrum of the solid resembled that of bis(cyclopentadienyl)-titanium dichloride; the spectrum showed bands at: (nujol mull and H.C.B. mull): (H.C.B. mull), 3040 (m), 1475 (m); (nujol mull), 1260 (ms), 1090 broad (m), 1010 broad (m), 860 broad (m), 795 broad (ms). The spectrum of the solid in toluene was also scanned in the visible region. This spectrum was shown in figure 5.5.

(h) The treatment of lithium bis(heptafluoropropyl)diiodoaluminate with stannic iodide.-

Tin tetraiodide was prepared from metallic tin and iodine in carbon tetrachloride, m.p. 144-5° (lit.[36] 143.5°). A solution of lithium bis(heptafluoropropyl)diiodoaluminate in diethyl ether was prepared on a 0.01 molar scale and was treated with a solution of tin tetraiodide (4.3 g., 5 mmole) in tetrahydrofuran (10 ml.). The reaction mixture was refluxed for 90 min. After evaporation of the solvents in vacuo, the tin tetraiodide was recovered unchanged.

(i) The thermal decomposition of triethyl-lead trifluoroacetate.- Tetraethyl-lead (3.2 g., 0.01 mole) was added dropwise with occasional stirring to a solution of trifluoroacetic acid (1.14 g., 0.01 mole) in diethyl ether (10 ml.). The reaction mixture was refluxed for 30 min.

A white solid formed and was isolated by filtration of the reaction mixture. The solid was washed with cold diethyl ether and was freed of solvents by pumping in vacuo. The yield of triethyl-lead trifluoroacetate was 3.2 g. (90% of the theoretical based on tetraethyl-lead), (Found: C, 24.3; H, 4.1. $(C_2H_5)_3PbOOCCF_3$ requires C, 23.6; H, 3.8%), m.p. 136-8°. The infra-red spectrum of the solid showed absorption bands at: nujol mull: 3010 (w), 3000 (s), 2900 (sh), 1700 (sh), 1640 (s), 1450 (s), 1400 (sh), 1370 (ms), 1200-1170 (s), 1160 (sh), 1145 (sh), 1020 (m), 965-940 (m), 840 (s), 790 (ms), 725 (s).

Triethyl-lead trifluoroacetate (2.5 g., 0.06 mole) was sealed in an evacuated Carius tube and was heated at 140-50° for 12 hr. The tube was opened in vacuo, and the volatile materials were condensed at -183°. The gases were identified as a mixture of ethane and ethylene by infra-red examination (the spectrum showed only the normal C-H and C-C frequencies for alkanes and alkenes) and molecular weight measurements (M.W. Found: 30.0. Calc. for C_2H_6, 30.0). Two liquid fractions were separated by fractional distillation in vacuo. The more volatile fraction was identified by infra-red examination as ethyl trifluoroacetate. The infra-red spectrum showed strong bands at: Gas, 5 mm.: 2985 (m), 1800 (s), 1470 (mw), 1390 (mw), 1340 (m), 1260 (sh), 1230 (vs), 1180 (vs), 1160 (sh), 1140 (vs), 1020 broad (m), 860 broad (m), 800 broad (ms), 735 broad (m). The less volatile fraction was identified as tetraethyl-lead by chemical analysis (Found: C, 29.8; H, 6.1. Calc. for $(C_2H_5)_4Pb$, C, 29.8; H, 6.2%) and its infra-red spectrum. The spectrum showed bands at: liquid film: 2950 (s), 2850 (s), 2700 (mw), 2650 (w), 2550 (w), 2400 (w), 2350 (w), 2100 (m), 1850 broad (w), 1650 (m), 1580 broad (w), 1450 (ms), 1410 (m), 1360 (ms), 1220 (m), 1150 (s), 1005 (s), 960 (ms), 940-930 (m). The waxy solid residue from the reaction was extracted with toluene, (Found: Pb, 48.5; C, 22.2; H, 3.3; F, 14.8. Calc. for $Pb(OOCCF_3)_2$, Pb, 48.9; C, 11.1. Calc. for $(C_2H_5)_3PbOOCCF_3$: Pb, 51.3; C, 23.6; H, 3.8%), m.p. 129-30°.

(j) The effect of heat on triethyltin trifluoroacetate.- Silver trifluoroacetate was prepared from silver carbonate (27.6 g., 0.1 mole) and trifluoroacetic acid (11.4 g., 0.1 mole) by the method of Haszeldine.[34]

Triethyltin chloride (6.0 g., 0.025 mole) was added slowly to a solution of silver trifluoroacetate (5.6 g., 0.025 mole) in tetrahydrofuran (30 ml.). A white solid formed immediately. The mixture was refluxed for 30 min. The solid was removed by filtration, and solvent was evaporated from the filtrate. The infra-red spectrum of the liquid showed bands at: liquid film: 3125 (w), 2940 (s), 2900 (s), 1770 (m), 1720 (sh), 1710 (sh), 1670 broad (vs), 1575 (m), 1440 (sh), 1420 (s), 1370 (ms), 1330 (w), 1280 (w), 1205-1175 (vs), 1140 (vs), 1050 multiple (ms), 965 (m), 920-870 broad (v), 850 (s), 795 (s), 730 (s).

The liquid (3.85 g., 0.012 mole) was heated at 180-200° for 10 hr. in a sealed evacuated Carius tube. Most of the liquid was recovered unchanged. A small amount of a gas, identified as ethane and ethylene by infra-red examination and molecular weight measurements, (M.W. Found: 30.3. Calc. for C_2H_6, 30.0), was isolated.

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Appendix

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"The Reaction of Alkali Metal Derivatives of Group IV Metal Alkyls with Bis(cyclopentadienyl)titanium(IV) dichloride".

By R.S. Dickson and B.O. West.

Aust. J. Chem., 1961, 14, 555.

"Transition Metal Alkyls".

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"The Reaction of Lithium Tetraethylaluminate with Some Halides of Group IV and VB Elements".

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Dickson, R., & West, B. (1961). The Reaction of Alkali Metal Derivatives of Group IV Metal Alkyls with Bis(cyclopentadienyl)titanium(IV) Dichloride. *Australian Journal of Chemistry*, *14*(4), 555-561.

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