ALUMINIUM

ANNUAL SURVEY COVERING THE YEAR 1976*

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CONTENTS

1. INTRODUCTION. REVIEWS

Organoaluminium compounds are finding increasing use as synthetic reagents in both organic and inorganic chemistry, and references to them are scattered over a large number of journals. This survey covers papers on organoaluminium compounds published in 1976 and a few, from the previous years, which were omitted from earlier surveys.

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* Aluminium, Annual Survey covering the year 1975, see J. Organometal. Chem. 130 (1975) 303 - 344.

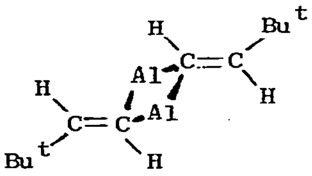
A volume [1] in the series of Chemical Society Specialist Periodical Reports covers the 1975 literature and contains chapters on the organometallic compounds of aluminium, gallium, indium and thallium [2] and on diffraction studies [3]. Spectroscopic properties are reported in another series [4]. Several reviews describe the use of organoaluminium compounds in chemical synthesis. Two form part of a general survey [5]; two others [6,7] describe contributions from particular research groups to understanding reactions of aluminium derivatives with substances having double bonds or carbonyl functions and compare reactions of boron and aluminium compounds. A major review [8] describes the use of diisobutylaluminium hydride and triisobutylaluminium as reducing agents in organic synthesis; this subject is set in the context of reductions by other complex hydrides in another concise but very clear account [9]. There have been reviews on olefin metathesis [10,11] and on the 'liquid clathrate' compounds $M[Al_2Me_6X]nArH$ (M = alkali metal or NMe_4; $X = N_3$, SCN, SeCN, Cl, Br or I; ArH = arene) [12]. Aluminium compounds are referred to in two almost identical reviews on organometallic peroxides [13,14] (ref. [14] is the more detailed), in an account of the reactions of carbon dioxide with organometallic derivatives [15], and in a review of reactions of metal atoms with organic compounds [16].

2. MOLECULAR STRUCTURE AND BONDING

The first structure determination of a vinyl-bridged organoaluminium dimer has been described [17]. The molecules of di-(μ-_trans_-,3,3-dimethyl-1-but-1-enyl)(tetraisobutyl)dialuminium (1), made from diisobutylaluminium hydride and 3,3 -dimethylbut-1-yne, $Bu^tC{\equiv}CH$, are centrosymmetric with equal Al-C(vinyl) distances of 210 pm. The plane of the vinyl groups is perpendicular to that of the planar Al_2C_2 ring which has dimensions similar to the Al_2C_2 rings in Al_2Me_6, $Al_2(C_3H_5)_6$ and Al_2Ph_6. (See (1a) in which $\underline{Al}$-Bu^i groups are omitted for clarity). The bonding appears to be similar to that in the phenyl and cyclopropyl compounds, with possible interaction between filled p-orbitals of the bridging

$(Bu^tCH{=}CHAlBu^i{}_2)_2$

(1)



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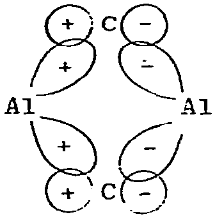
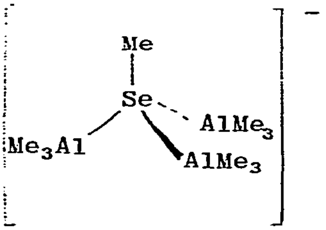


(2)

carbon and unfilled orbitals of the Al atoms (2), but the Al_2C_2 ring in $Al_2(C_3H_5)_6$ is not planar. The structure differs from that of $(Ph_2AlC{\equiv}CPh)_2$, in which the phenylethynyl bridge is unsymmetrical.

Compounds $K[Al_2Me_6X]$, where X = halogen or pseudohalogen, form complexes with arenes [12]. A pure sample of the compound $K[Al_2Me_6SeCN],nC_6H_6$, from KSeCN(1 mol) and Al_2Me_6(1 mol) in benzene, could not be isolated, but on heating at 80°C, two compounds were obtained. The major product was $K[Al_2Me_6CN]$ and an X-ray study of the minor product $K[MeSe(AlMe_3)_3],2C_6H_6$ showed that it contained the anion (3) with an Al-Se distance, the first to be recorded,



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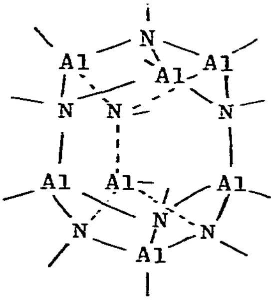


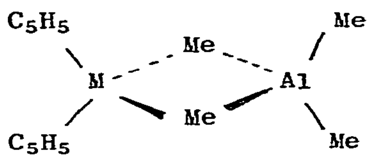
Me groups omitted

(4)

of 257.8(5) pm [18]. This is longer than predicted from tables of covalent radii, but may reflect the fact that the selenium atom is four-coordinate. The Al-C bond distances (199 pm) and CAlC bond angles (114-9°) are normal. Benzene molecules trapped in the lattice are disordered.

The compound $(MeAlNMe)_7$ (4) is obtained by heating equimolar amounts of trimethylaluminium and methylamine at 210°C [19]. The molecules have C_{3v} symmetry; each aluminium and each nitrogen is four-coordinate and bound to one methyl group and three other atoms within the cage. The molecular dimensions are Al-N, 191(4), Al-C 198(7), N-C 156(6) pm, Al-N-Al 89(1) or 120(1), N-Al-N 90(2) or 110(2)°.

Several X-ray structure determinations have been made on compounds containing aluminium and another metal. The compounds $(\eta\text{-}C_5H_5)_2MMe_2AlMe_2$, (M = Sc,Gd,Dy,Ho,Er,Tm,Yb) are made from the chlorides $[(\eta\text{-}C_5H_5)_2MCl]_2$ and $LiAlMe_4$ in toluene, and the yttrium and ytterbium compounds are isostructural (5). The average Al-C distance (210 pm) is normal and the M-Al distances, 305.6(Y) and 303(Yb) pm, are only a little larger than the Al-Al distance in hexamethyldialuminium. The MCAl angles (ca 80°) are also similar to the AlCAl angle in Al_2Me_6 [20]. The structure of another compound (7) in the remarkable series isolated from the reaction between triethylaluminium and bis(cyclopentadienyl) zirconium dichloride, has been elucidated [21]. As in the compound (6), described in



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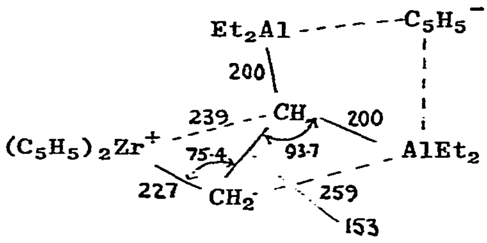
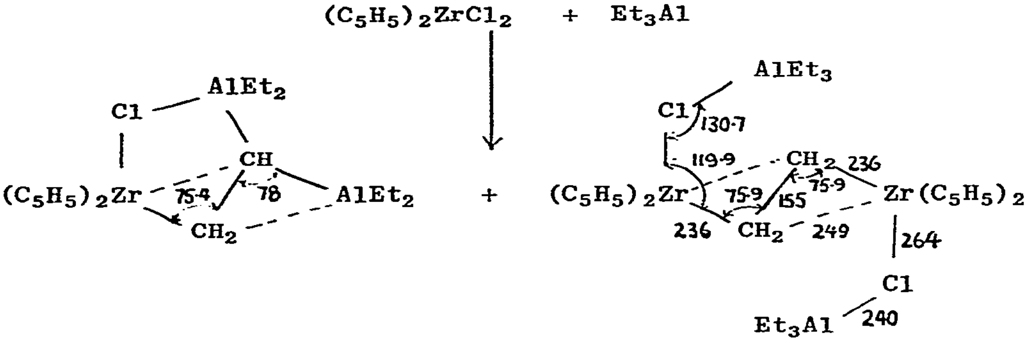


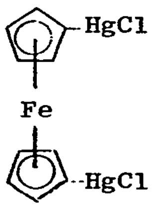
(8)

In this section, distances in pm, angles in °.



(6) (7)

last year's survey, the Zr-CH_2-C angle is only about 76°. A similar angle is found in compound (8) which may be considered as derived from (6) by replacement of the chloride by the cyclopentadienide anion. In the solid, the $C_5H_5^-$ anions are arranged symmetrically between two Zr^+ centres and, as shown by ^1H NMR, the three distinct C_5H_5-groups persist in hydrocarbon solutions. Compound (8), and also compounds (6) and (7) in the presence of an excess of triethylaluminium, react with alk-1-enes and 1,3-dienes. The products from (6) and (7), especially in the presence of water, are very active catalysts for polymerisation of alk-1-enes, particularly ethylene. A new type of bridging cyclopentadienyl group is found [22] in the compound $[(\eta\text{-}C_5H_5)Fe(\eta\text{-}C_5H_3)Al_2Me_3Cl]_2$ (9) made by the reaction between trimethylaluminium and the substituted ferrocene (10).



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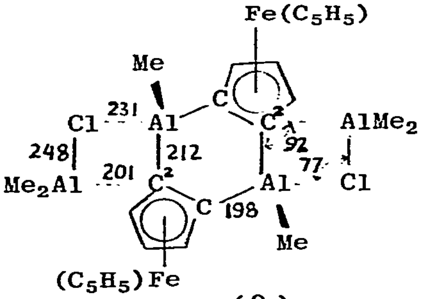


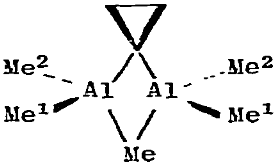
(9)

It is possible that compound (9) is formed by rearrangement of a ferrocene derivative related to (10) by replacement of one ClHg-substituent by Me_2Al- and the other by ClMeAl-. The carbon atom C^2, which forms part of a cyclopentadienyl ring and also bridges two aluminium atoms, has an environment similar to those found in the compounds $[MoH(\eta C_5H_5)(\eta C_5H_4)]_2Al_3Me_5$ (11) and $[Mo(\eta C_5H_4)_2Al_2Me_3]_2$ (12), described in earlier surveys, but there is no evidence for Al-Fe bonding in the ferrocenyl derivative (9).

3. SPECTROSCOPIC PROPERTIES

Electronic absorption and fluorescent spectra of triphenylaluminium, trimesitylaluminium and tri(1-naphthyl)-aluminium in methylcyclohexane or diethylether have been compared with spectra of the lithium, boron, and gallium derivatives [23]. The intense long-wavelength bands associated with transitions involving the aromatic systems are affected by interactions with empty metal p-orbitals but a quantitative discussion is made difficult by lack of complete structural data.

IR, mass and NMR spectra [24] have confirmed that the cyclopropyl group forms particularly strong bridges between aluminium atoms in dimeric alkyls. Thus strong peaks assigned to $[(C_3H_5)_5Al_2]^+$ appear in 70 eV mass spectra of hexa(cyclopropyl)dialuminium, even though the peak from $Me_5Al_2^+$ in the spectrum of trimethylaluminium is weak. The compounds (13,14) and possibly (15) were identified from NMR spectra of mixtures of trimethyl- and tri(cyclopropyl)aluminium in toluene at various mole ratios and various temperatures: again preferential location of cyclopropyl groups in bridging positions was demonstrated.



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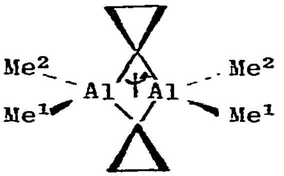

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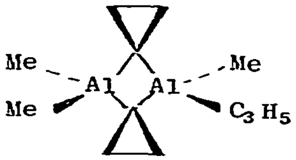
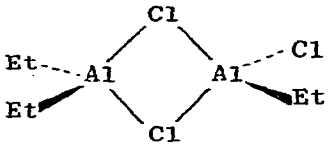


(15)

Methyl group exchange between hexamethyldialuminium and the species (13–15) was slow on the NMR timescale, but two intramolecular exchange processes were identified. First, bridge-terminal methyl-group exchange in the compound (13) was shown to have an activation energy of 66 kJ mol^{-1}. This is consistent with a mechanism involving a single-bridged intermediate, as has been postulated for several other mixed-bridge species in which one of the groups makes stronger bonds than methyl. Secondly, rotation of the cyclopropyl group about a perpendicular from the α-carbon to the Al–Al axis {see arrow in (14)} makes the terminal methyl groups {1 and 2 in (13) and (14)} equivalent. The activation energy, from NMR measurements at various temperatures, is about 46 kJ mol^{-1}.

An attempt has been made to derive structural information on dialkyl(cyclopentadienyl)aluminium compounds from analysis of IR bands associated with vibrations of the cyclopentadienyl rings [25]. h^5-Bonding was deduced for the C_5H_5 of the etherate $Et_2Al(C_5H_5),OEt_2$, and h^2- or h^3- bonding in the associated ether-free compounds $[R_2Al(C_5H_5)]_n$ [R=Me, Et; n=1.2–1.5]. ^{13}C NMR spectra of these compounds have also been described [26]. Measurements on a range of cyclopentadienyl-metal derivatives show that neither ^{13}C chemical shifts nor ^{13}C–^1H coupling constants provide criteria for assigning π- or σ- bonded structures. No signal has been detected from the carbon atoms of the methyl groups in $Me_2AlC_5H_5$ and it is assumed that this is due to broadening by quadrupolar relaxation from the ^{27}Al nucleus. For the same reason, ^{13}C signals from α-carbon atoms of Al-ethyl groups are much broader than those from β-carbon atoms.

^{13}C NMR spectra of the compounds Et_6Al_2, $Et_4Al_2Cl_2$, $Et_3Al_2Cl_3$ (16) and $Et_2Al_2Cl_4$ have been interpreted in terms of the already well-established structures of these compounds [27]. Spectra of $Et_3Al_2Cl_3$ and $Et_2Al_2Cl_4$ were much improved by use of ^{13}C-enriched samples (from ^{13}C-ethyl chloride and aluminium sand). The activation energy for exchange of ethyl groups between the two sites in

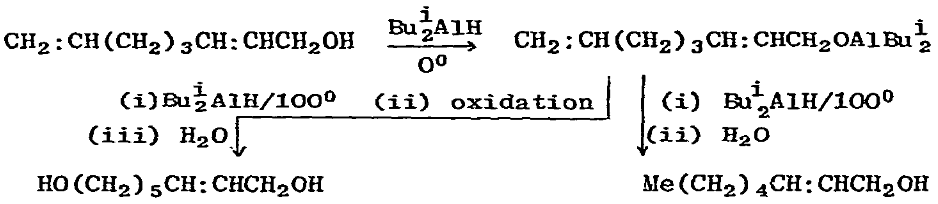


(16)

ethylaluminium sesquichloride (16) has been found by bandshape analysis to be 51.3 ± 6.3 kJ mol^{-1}.

4. PREPARATIONS

In the patent literature, it is claimed [28] that yields of aluminium alkyls from aluminium dispersion, hydrogen and alkenes are improved by addition of 0.1 to 1.6 wt. % of an alloy of tungsten or titanium. Preparations of alkyl- and alkenylaluminium chlorides [29,30] and procedures for recovery of dialkylaluminium halides from reaction mixtures obtained in production of zinc alkyls from trialkylaluminiums [31,32], have also been described. Reactions between aluminium halides, aluminium and ethylene give the dialuminium compounds $X_2AlCH_2CH_2AlX_2$ (X=Cl, Br, or I) [33]. Other reports describe the preparation of tris[ω-(3-methyl-1-cyclohex-4-enyl)propyl]aluminium, from triisobutylaluminium and dimers of penta-1,3-diene [34], sodium diethylalanate $NaAlEt_2H_2$ from sodium, aluminium, hydrogen and triethylaluminium [35], and the compounds $\{RCH_2CH{:}CH(CH_2)_5\}_3Al$ (R=MeO or PhO) from $RCH_2CH{:}CH(CH_2)_3CH{:}CH_2$ and diisobutylaluminium hydride [36]. The compound $\{PhOCH_2CH{:}CH(CH_2)_5\}_3Al$ gives the alkenyl ether $PhOCH_2CH{:}CH(CH_2)_4Me$ on acid hydrolysis and the alcohol $PhOCH_2CH{:}CH(CH_2)_5OH$ after oxidation. Similar reactions are observed with the compound $CH_2{:}CH(CH_2)_3CH{:}CHCH_2OH$.



$$CH_2{:}CH(CH_2)_3CH{:}CHCH_2OH \xrightarrow[0^{0}]{Bu^{i}_2AlH} CH_2{:}CH(CH_2)_3CH{:}CHCH_2OAlBu^{i}_2$$

$$CH_2{:}CH(CH_2)_3CH{:}CHCH_2OAlBu^{i}_2 \xrightarrow{\text{(i) }Bu^{i}_2AlH/100^{0}\text{ (ii) oxidation (iii) }H_2O} HO(CH_2)_5CH{:}CHCH_2OH$$

$$CH_2{:}CH(CH_2)_3CH{:}CHCH_2OAlBu^{i}_2 \xrightarrow{\text{(i) }Bu^{i}_2AlH/100^{0}\text{ (ii) }H_2O} Me(CH_2)_4CH{:}CHCH_2OH$$

Tris(3-trimethylsilylpropyl)aluminium may be obtained by hydroalumination of allyl(trimethyl)silane and subsequent distillation of the trialkylaluminium produced; the course of the reaction has now been confirmed by IR and NMR spectroscopy [37].

$$Me_3SiCH_2CH{=}CH_2 + Bu^i_2AlH \xrightarrow{90-95^oC} Me_3Si(CH_2)_3AlBu^i_2$$

$$\downarrow \text{distillation 1 Torr}$$

$$[Me_3Si(CH_2)_3]_3Al + 2Bu^i_3Al$$

The reactions of the Grignard reagents $RMe_2Si(CH_2)_nMgX$ (X=halogen; n=1: R=Me, Bu, C_8H_{17}, Me_3SiO; n=3: R=Me) with aluminium chloride in ether yield the trialkylaluminium etherates $[RMe_2Si(CH_2)_n]_3Al,OEt_2$ from which the halides $RMe_2Si(CH_2)_nAlCl_2$ may be obtained by treatment with aluminium chloride in hexane.[38]. Difficulties associated with the preparation of tricyclohexylaluminium have been reviewed [39]. The completely halogen-free compound has not been made but the purest product (obtained as an etherate) was produced by addition of aluminium chloride to a solution of the Grignard reagent in benzene. The compound $C_6H_{11}AlCl_2$ and etherates of $(C_6H_{11})_2AlX$ (X=Cl or Br) and $C_6H_{11}AlBr_2$ have also been obtained. The solvent recommended for the preparation of dialkylcyclopentadienylaluminiums is cyclohexane; benzene and toluene are exceedingly difficult to remove - presumably because of donor-acceptor compound formation [25].

Another approach to the preparation of organometallic compounds, at present used mainly for laboratory experiments, is by reaction between metal vapours and organic substrates. The progress made in aluminium chemistry has been discussed [16] in a general review devoted mainly to transition metal compounds. The reaction between propene and aluminium gives (after hydrolysis with D_2O) $CH_2DCHMeCHMeCH_2D$, CH_3CHDCH_2D and $MeCHDCH_2CHMeCH_2D$ but the mechanism of the dimerisation is not yet clear. The reactions between cis- or trans-but-2-enes and aluminium are not stereospecific except in the presence of a Lewis base such as dimethyl ether or trimethylamine. Two interesting suggestions are that metal atoms syntheses give organometallic compounds with Al-Al bonds (See also Section 12 below) or aluminacyclopropane intermediates.

Trace impurities in organoaluminium compounds required for the semiconductor industry may be removed, according to a patent [40], by passage through powdered silica. A procedure has been worked out [41] for the determination of impurities in organometallic compounds by hydrolysis, extraction with pentane, and analysis of the concentrated solution by gas chromatography.

5. ALKYLATIONS. REACTIONS WITH HALIDES

Patents have described examples of the production of alkyltin trichlorides by alkylation of tin(IV) chloride with trialkylaluminiums in the presence of a donor to remove the dialkylaluminium chloride product [42], and the reaction between dimethylaluminium chloride and lead(II) oxide [43,44]. Mixed methylethyllead alkyls may be made by reaction between lead oxide and dimethyl- and diethylaluminium chlorides in the presence of donors D such as KCl, NaCl, PhCN or PhOMe [45]

$$\begin{aligned} & PbO + Me_2AlCl + Et_2AlCl + D \rightarrow Me_{4-n}PbEt_n + Pb \\ & \quad + MeClAlOAlClMe.D. + EtClAlOAlClEt.D. \end{aligned}$$

Similar reactions are observed with lead(II) sulphide and lead(II) chloride but the yields of alkyllead compounds are lower. The proportion of ethyl groups in the products is higher than expected for a statistical distribution of methyl and ethyl groups.

Trimethylsilylmethyltitanium trichloride has been made by the reaction between titanium(IV) chloride and tris(trimethylsilylmethyl)aluminium etherate [46]. Trimethylaluminium alkylates tungsten(VI) chloride in isopentane. By addition of trimethylamine the compound Me_2AlCl,NMe_3 is precipitated. This may be filtered off at -78^0, leaving a solution of hexamethyltungsten(VI) [47]. Further details have been given [48] of the preparation of the rhenium alkyls $ReMe_6$ and $ReOMe_4$ from trimethylaluminium, but no pure products have been isolated from the reaction between trimethylaluminium and manganese(II) halides or tris(acetylacetonato)manganese(III).

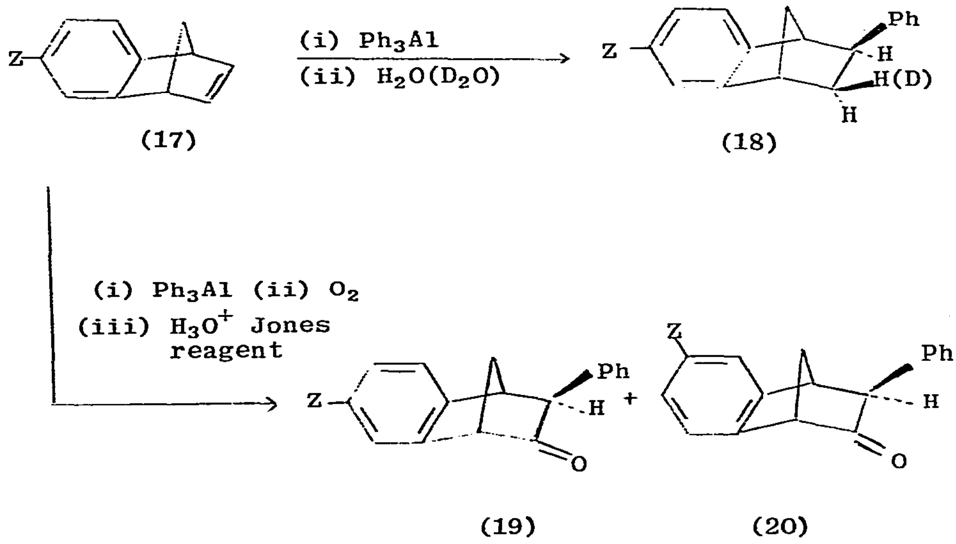
Only tertiary alkyl halides are easily alkylated with trialkylaluminiums. Thus chlorotriphenylmethane reacts vigorously at 20^0 with trimethylaluminium in benzene or toluene with quantitative formation of 1,1,1-triphenylethane Ph_3CMe. With triethyl- or triisobutyl-aluminium the principal reaction (90-97%) is reduction with formation of triphenylmethane Ph_3CH and ethylene or propene [50]. The reaction between primary alkyl halides and trialkylaluminiums is slow: thus no interaction is observed between triethylaluminium and ^{14}C-labelled EtBr at 150°. In the presence of transition metal halides, however, exchange of ethyl groups between bromoethane and triethylaluminium is observed.

$$(C_2H_5)_3Al + {}^{14}C_2H_5Br \rightleftarrows ({}^{14}C_2H_5)(C_2H_5)_2Al + C_2H_5Br$$

An attempt has been made to analyse the effects of solvation by Ph_2O, PhOEt, Et_2O and pyridine which slow the exchange reaction [51].

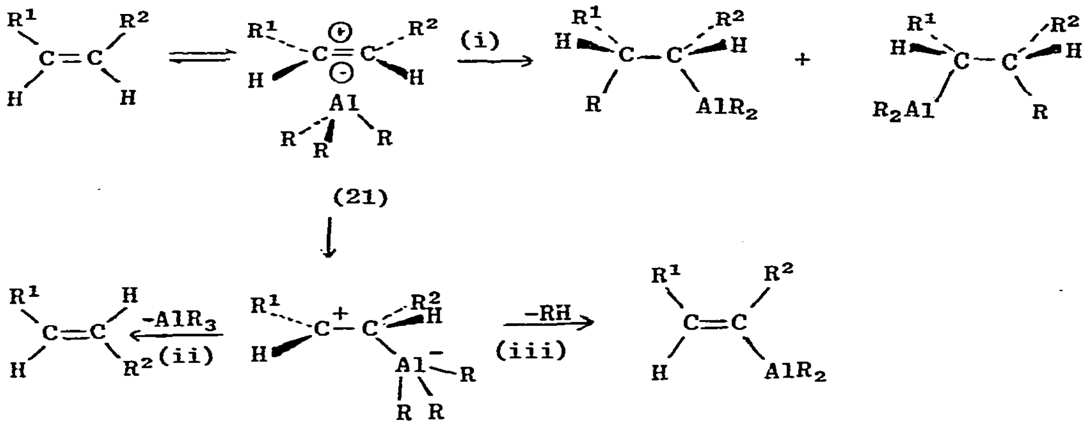
6. REACTIONS WITH CARBON-CARBON DOUBLE AND TRIPLE BONDS

Triphenylaluminium reacts faster with alkynes than with closely related alkenes. This order of reactivity is the reverse of that for most electrophilic additions to carbon-carbon unsaturated systems, and the electronic and steric factors involved have been examined in some detail [52,53].



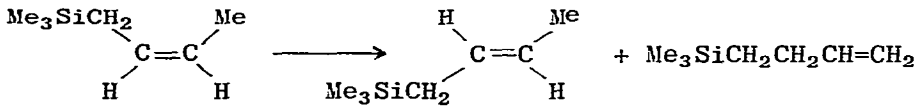
The benzonorbornadiene (17 Z=H) reacted smoothly with triphenylaluminium in refluxing benzene to give, after hydrolysis with H_2O or D_2O, phenylbenzonorbornenes (18 Z=H). This showed that the carbalumination had been exclusively exo,syn, without skeletal rearrangement. For the compounds (17 Z=Cl, Me, or F) a similar clean reaction was found, and the direction of addition was determined by oxidation of the organoaluminium intermediates to the ketones (19) and (20) which could be readily identified. The relative reactivities of the benzonorbornadienes with various Z were 0.66(Cl), 0.80(F), 1.00(H) and 1.30(Me), and detailed consideration of the relative rates and product ratios suggested that the transition state in the rate-determining step was the π-complex (21)

Scheme 1 Carbalumination of alkenes



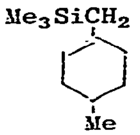
In another series of experiments, the rates of reaction of triphenylaluminium with the following compounds were found to decrease in the order: norbornadiene > *cis*-β-methylstyrene > *trans*-β-methylstyrene ~ 1,2-dihydronaphthalene ~ 1,1-dimethylindene > *cis*-1,2-diphenylethylene > 3,3,3-triphenylpropene > *trans*-1,2,-diarylethylenes ~ phenylcyclopropanes. The regiospecificity found for unsymmetrical alkenes could again be explained by steric effects in the collapse of the intermediate (21). Because the carbalumination reactions were slow, vigorous reaction conditions, e.g., 2-3 days in refluxing mesitylene, had to be used and several side reactions were observed. These could all be accommodated; thus reaction (i) leads to carbalumination, reaction (ii) gives isomerisation of the original alkene and reaction (iii) leads to metallation of vinylic carbon atoms. The greater reactivity of alkynes compared with alkenes, and of norbornadienes compared with *cis*- and *trans*- 1,2-diphenylethylene, is in part attributed to steric interactions between groups attached to the C_2 fragment and groups attached to the aluminium atom.

There is continued interest in the addition of organoaluminium hydrides across carbon-carbon double and triple bonds [6,7,36,54]. Hydroalumination of 1-trimethylsilylocta-2,6-diene proceeds without a shift in the double bond to give $Al(CHMeCH_2CH_2CH_2CH=CHCH_2SiMe_3)_3$ but, in other cases, dialkylaluminium hydride is easily eliminated, so that the main organic product is the isomerised alkene. Thus, 1-trimethylsilyl-*cis*-but-2-ene (22) and diisobutylaluminium hydride at 80°C give the rearranged products (23) and (24),



(22) (23) (24)

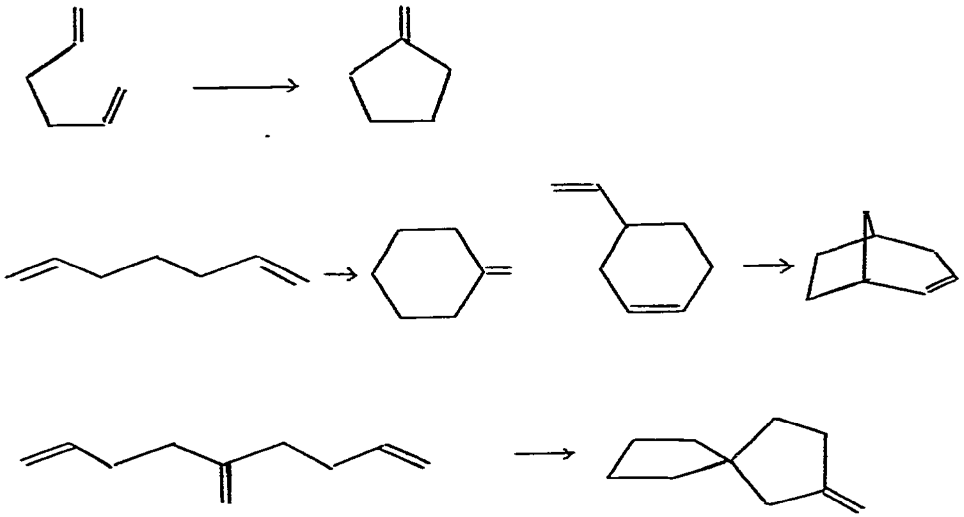
and 1-trimethylsilyl-5-methyl-2,6-heptadiene gives 1-trimethylsilylmethyl-4-methylcyclohexene (25) [54,55].



(25)

(In the very brief report [55] it is also alleged that Bu^i_2AlH reacts with allyltrimethylsilane to give $(PrMe_2Si)_3Al)$. Other examples of rearrangements using catalytic amounts of diisobutylaluminium hydride are given in Scheme 2 [56].

Scheme 2 Rearrangements using Bu^i_2AlH catalyst[a]



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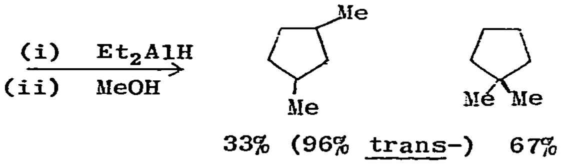
[a] In mineral oil, 115-210°, 40-50h

The reactions between various methyl-substituted hexa-1,5-dienes e.g. (26)(27) and diethylaluminium hydride give(after hydrolysis with methanol) dimethylcyclopentanes in which one of the possible diastereoisomers predominates. The stereoselectivity is attributed to differences in thermodynamic stability of conformers in the cyclisation step [57].

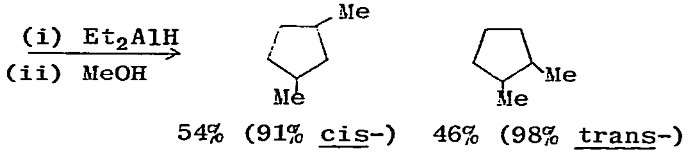
$CH_2=CMe-CH_2-CH_2-CH=CH_2$

(26)



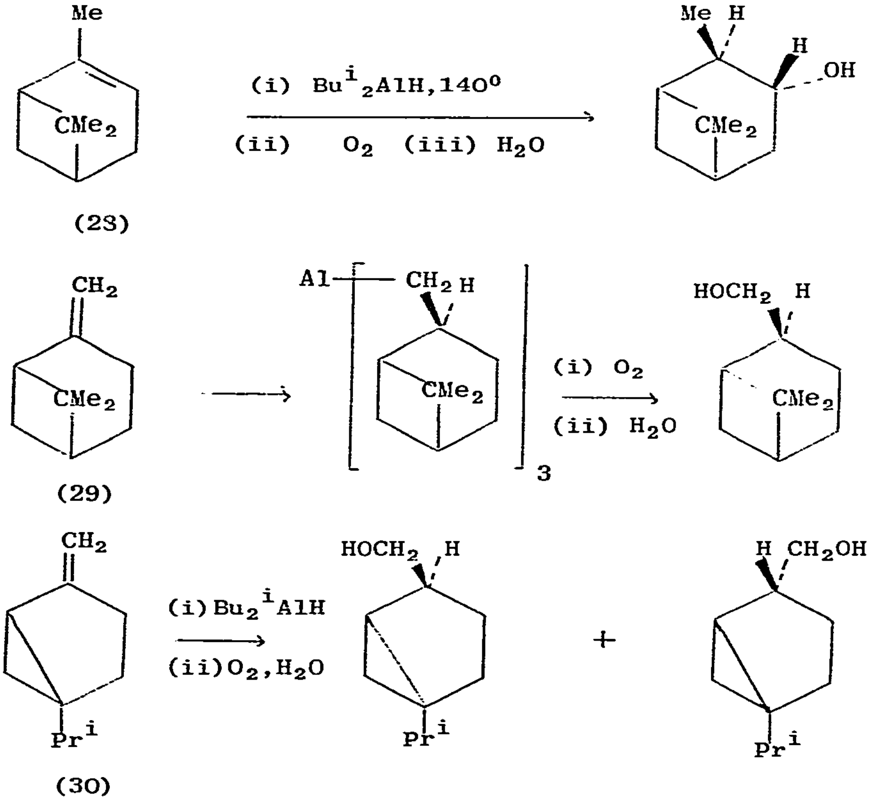
$CH_2=CH-CHMe-CH_2-CH=CH_2$

(27)



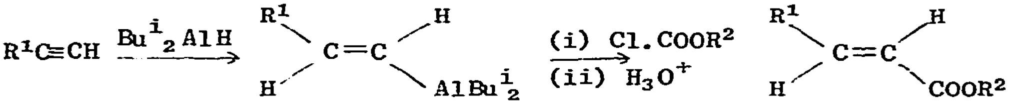
It has been suggested that the hydroalumination of α- and β-pinenes (28) (29) under vigorous conditions is determined mainly by steric factors (Scheme 3): the products are the same as are obtained from hydroboration and the addition is highly stereoselective. The terpene (30)

Scheme 3 Hydroalumination of cyclic alkenes



however, in which the double bond is unhindered, gives a mixture of isomers [58].

The addition of dialkylaluminium hydrides to substances with carbon-carbon triple bonds gives alkenylaluminium compounds which have been used in a variety of stereoselective syntheses. For example trans-α,β- unsaturated esters, (31) R^1=Bu^n, C_6H_{13}, Pr^i, cycloC_6H_{11} or Bu^t, may be made in yields of 64–74% and with isomeric purity > 98%. The unsaturated

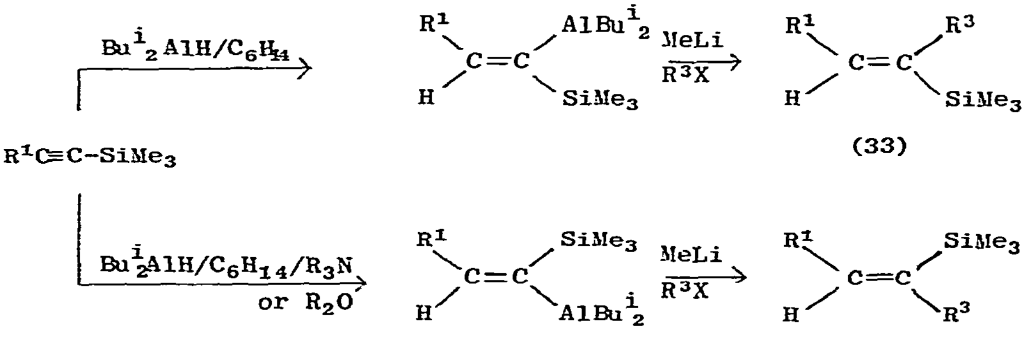


(32) (31)

esters are not reduced either by the vinylalanes (32) or by the diisobutylaluminium chloride formed during the reaction. When tetrahydrofuran is added before chloroformate to trans-hex-1-en-1-yldiisobutylalane (32, R^1=Bu^n) the product is hex-1-ene almost quantitatively [59].

Reactions of alkenyldialkylaluminiums, made by hydroalumination of alkynes, with alkyllithiums give alkenylate complexes e.g. $Li\{(AlBu^i_2Me(CR^2{=}CHR^1)\}$ which react with alkyl halides to provide a stereospecific synthesis of trisubstituted ethylenes e.g. (33) (34). For alkynyltrimethylsilanes, the stereochemistry of the hydroalumination step (Scheme 4) may be determined by choice of solvent. [60,61]. Similarly, the alkyne n-$C_6H_{13}C{\equiv}CSiEt_3$ may

Scheme 4 Hydroalumination of alkynyltrimethylsilanes

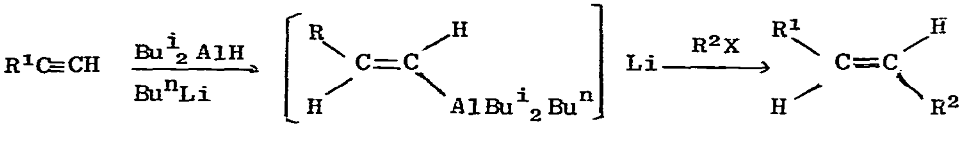


(33)

(34)

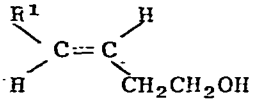
be converted in 68% yield to a mixture of alkenes (c.f. 33 and 34, $R^1 = C_6H_{13}$, $R^3 =$ Me) with 93% of the E-isomer (33). The alkenylsilanes may be stereospecifically bromodesilylated to give substituted vinyl bromides which may be used in further syntheses.

A similar reaction with terminal alkynes $R^1C{\equiv}CH$ gives *trans*- alkenes (60-80% yield, over 98% stereoisomeric purity) in a simple, one-pot synthesis.



(36) (35)

When R^2 is tertiary, e.g. 1-methylcyclohexyl, some coupling with the normal or isobutyl groups attached to aluminium is observed; usually the alkyl group R^2 couples preferentially with the *Al*-alkenyl group in the ate complex (36) [62]. The reaction of the complex (36) with ethylene oxide gives high yields of the *trans*-3-alkenols (37); polymerisation of the ethylene oxide may be prevented by the addition of a small amount of tributylamine [63].



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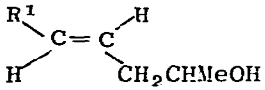

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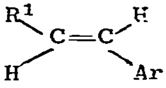


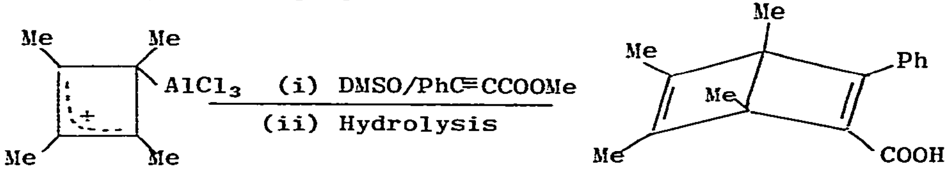
(39)

Propylene oxide reacts similarly to give exclusively secondary alcohols (38), but styrene oxide gives a 1:1 mixture of the two possible regio-isomers [64]. The coupling of alkenyldialkylalanes with aryl halides to give the *trans* alkenyl compounds (39) is catalysed by tetrakis(triphenylphosphine)nickel. Yields of 80-90% may be obtained and the proportion of *trans*-isomer in the product is > 99% [65]. It is possible that the alkenyl group is transferred from aluminium to nickel in a reaction intermediate.

A similar transfer of ethyl from aluminium to titanium is suggested to explain the ethylation of the alk-3-yn-1-oxy complex $TiCl(OCH_2CH_2C{\equiv}CH)(acac)_2$ [acac = acetylacetonato] by diethylaluminium chloride under mild conditions [66]. Catalysis by zirconium tetrachloride is noted in the reactions between lithium tetrahydroalanate and alkenes, which are thought to involve zirconium-hydride and zirconium-alkyl intermediates and subsequent transfer of alkyl groups from zirconium to aluminium [67].

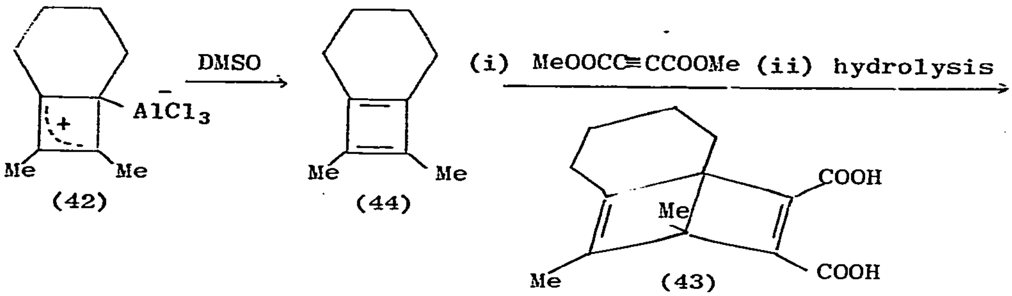
In reactions between alkylaluminium compounds and terminal alkynes there is always the chance that metallation - with formation of alkane and alkynylaluminium derivatives - may take precedence over addition. It has been shown that the alkaline earth tetraalkylalanates $M(AlEt_4)_2$ (M=Ca,Sr, or Ba) react with terminal alkynes to give the mixed alkylalkynylalanates $M[AlEt_{4-n}(C{\equiv}CR)_n]_2$ in stepwise fashion,with rapid replacement of four ethyl groups and much slower replacement of the others [68].

Further papers have appeared describing reactions of aluminium chloride-cyclobutadiene complexes with substances having carbon-carbon triple bonds. The complex (40), in the presence of dimethylsulphoxide (DMSO) reacts with the ester $PhC{\equiv}CCOOMe$ to give, after hydrolysis, the chiral and resolvable Dewar benzene derivative (41), which may be isomerised thermally to a biphenyl derivative or photochemically to a substituted prismane [69].



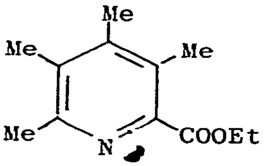
(40) (41)

The complex (42), made from 2,8-decadiyne and aluminium chloride gives a dark red solution in dichloromethane. It reacts with dimethyl acetylenedicarboxylate and DMSO to give the compound (43), probably by the intermediate cyclobutadiene in which double bonds are localised as in (44) [70].



(42) (44) (43)

An n.m.r. study shows that the methyl resonances in (42) become equivalent above 92° – a much higher temperature than is required for rapid interconversion of methyl groups in (40). The complex (40) reacts with ethyl cyanoformate to give the pyridine derivative (45) probably via an intermediate Dewar pyridine. [71]



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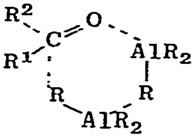
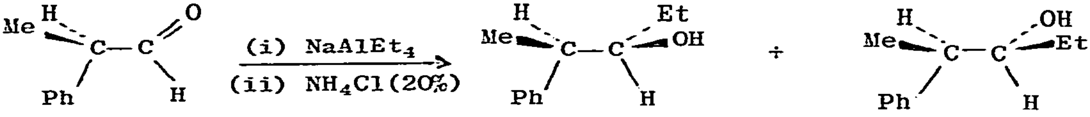


(46)

7. REACTIONS WITH CARBONYL COMPOUNDS

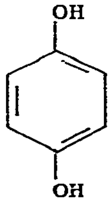
The first step in the reaction between carbonyl and organoaluminium compounds is almost certainly formation of donor-acceptor complex. Complexes of anisole, methyl benzoate and methyl propionate with the aluminium compounds Me_3Al, Me_2AlCl and $MeAlCl_2$ have been described [72]. Trimethylaluminium gives only 1:1 complexes but dimethylaluminium chloride gives 1:2 complexes which are detected by NMR and IR spectroscopy. The structure proposed for the 1:2 complexes (46) has sometimes been considered for the transition state in the subsequent addition reaction, but this view has recently been criticised [73]. Complexes with methylaluminium dichloride easily disproportionate. On heating, methyl benzoate and trimethylaluminium give dimethylphenylcarbinol, Me_2PhCOH, but the reaction between methyl benzoate and dimethylaluminium chloride is more complicated [74].

The sesquichloride $(CH_2{=}C{=}CH)_3Al_2Br_3$, made from 3-bromoprop-1-yne and aluminium in tetrahydrofuran adds to paraformaldehyde to give the alcohol $HC{\equiv}CCH_2CH_2OH$ in 63% yield. Similarly, 3-bromobut-1-yne gives $HC{\equiv}CHMeCH_2OH$ [75]. Tetraalkylalanates M^1AlR_4 or $M^2(AlR_4)_2$ are also good alkylating agents for aldehydes and ketones and reaction mixtures may be cleaner than with the free trialkylaluminiums. Thus four of the eight ethyl groups in the alkaline earth compounds $M^2(AlR_4)_2$ (M^2=Ca, Sr, or Ba) react with aldehydes RCHO (R=Me, Et or Pr) to give alcohols RCH(OH)Et with small amounts of RCH_2OH and RCOEt. Under the same conditions two of the four ethyl groups in $LiAlEt_4$ are reactive [76]. These addition reactions are catalysed by nickel(II) chloride, which also enhances addition relative to reduction. The reaction between 2-phenylpropanal and $NaAlEt_4$ in ether gives mainly the erythro product (47) but in pentane roughly equal amounts of ethythro and threo (48) compounds are obtained. The nickel chloride apparently does not affect the stereoselectivity [77].



(47) (48)

With α,β-unsaturated carbonyl compounds either 1,2- or 1,4- addition may be observed. In a survey of the reactions of benzoquinone with organoaluminium compounds it has been shown [78] that the main products with trialkylaluminiums AlR_3 are hydroquinone (49) and the alkylhydroquinones (50) from 1,4-addition and subsequent enolisation.



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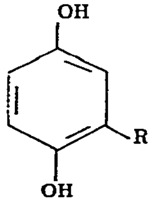

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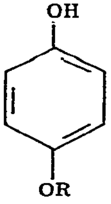
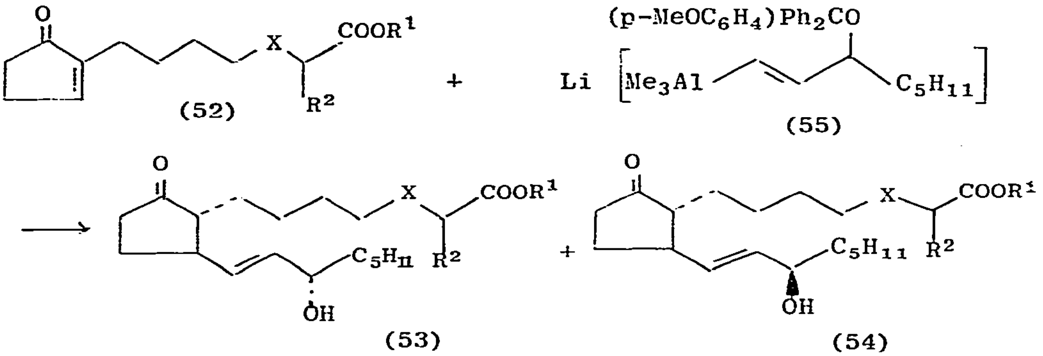


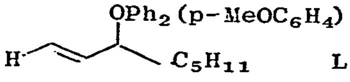
(51)

With dichlorides $RAlCl_2$, *p*-alkoxyphenols (51) are formed in addition to the other products and there is some ESR evidence that the mechanism may involve radical intermediates.

The 1,4-addition of organoaluminium compounds to cyclopentenones has been widely exploited for the introduction of the second chain in prostaglandin syntheses.



For example, the cyclopentenones (52, R^1=Me, X=CH_2: R^2=H, Me or Et; R^1=Et, R^2=Ph, X=CH_2; R^1=Et, R^2=H: X=O or S) are converted after hydrolysis and removal of the $(p\text{-}MeOC_6H_4)Ph_2C$- groups into ~ 1:1 mixtures of the esters (53) and (54). The ate complex (55) is made from the octen-3-ol, (56) protected as the p-anisyldiphenylmethyl ether, by treatment with (i) butyllithium and (ii) trimethylaluminium in heptane. This procedure avoids hydralumination of propargylic ethers which may result in cleavage of C-O bonds [79]. Experiments with the related alanate complex (57) show that in hydrocarbon there is non-selective transfer of octenyl, isobutyl or hydride to the cyclopentenone: in ether, however, octenyl transfer predominates. In THF formation of cyclopentenone polymer is appreciable.



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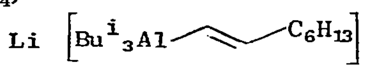

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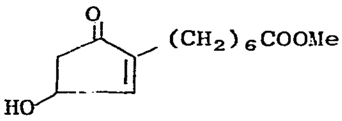
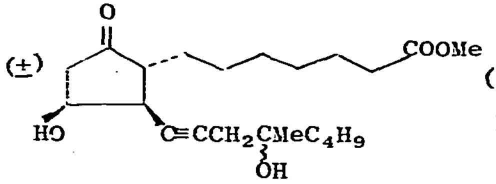


(58)

1,4-Additions of *Al*-alkynyl or -alkenyl groups to the cyclopentenone (58) have been observed [80]. Thus reaction with dimethyl(4-methyl-4-triethylsilyloxy-1-octynyl)aluminium gives the product (59), and the alkenylaluminium compound made from diisobutylaluminium hydride and 4-methyl-4-triethylsilyloxy-1-octyne gives the compound (60) at -60^{0}C



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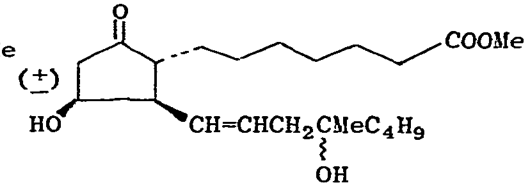
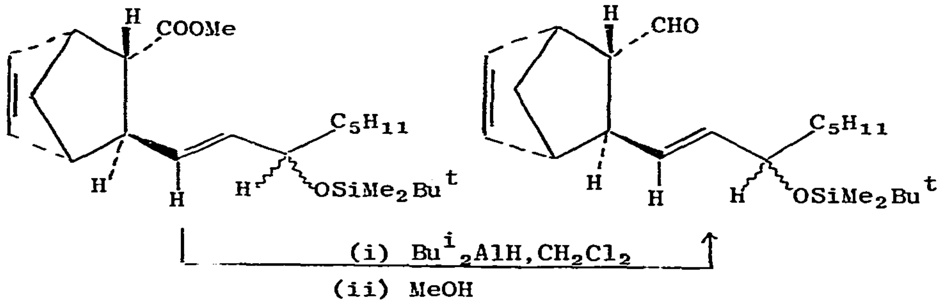


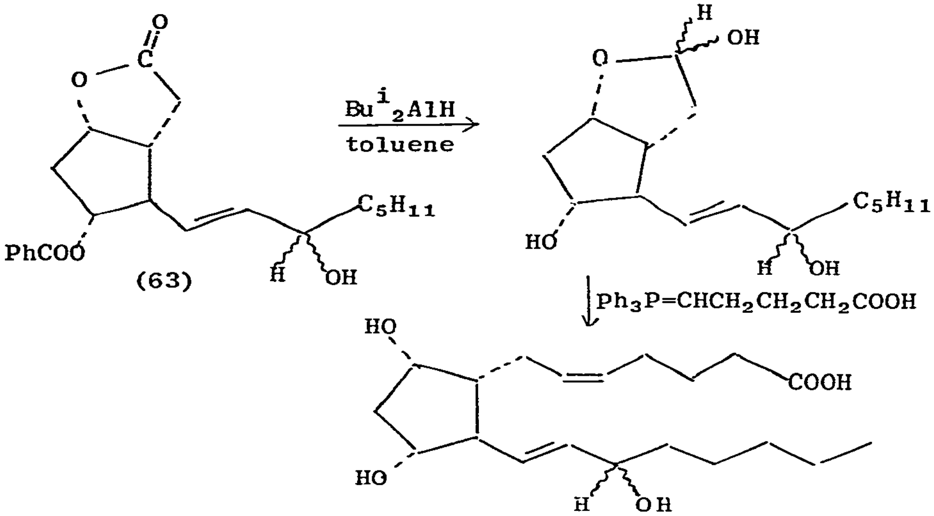
(60)

A second series of applications of organoaluminium compounds in prostaglandin synthesis involves the use of diisobutylaluminium hydride as reducing agent [8]. For example, the ester (61) has been reduced to the compound (62) from which the second side chain may be developed by the reaction of the aldehyde function with a Wittig reagent [81]



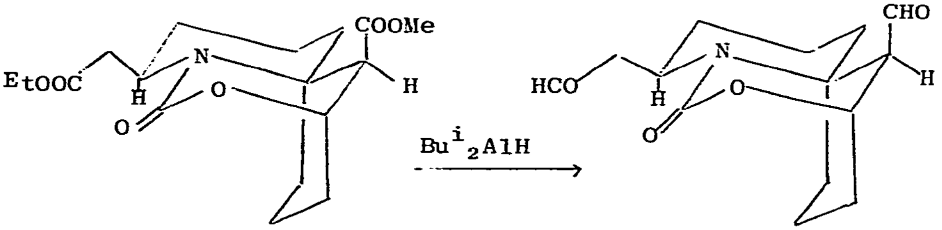
(61) (62)

In several similar syntheses [82-85] lactones such as (63) have been reduced by diisobutylaluminium hydride in toluene at -78^{0}C and the hemiacetals produced have been condensed with Wittig reagents. Acetyl, benzoyl or tetrahydropyranyl protecting groups have been used for hydroxyl functions.



(63)

The preferential reduction of terminal compared with cyclic esters is shown in the compound (64) in which the lactone is not attacked by 2.5 mol. Bu^i_2AlH at -78°C [86].



(64)

In some cases, reductions with diisobutylaluminium hydride lead to rearrangements (Scheme 5). For example, the compound dehydrocordrastine (65) is converted to the spirobenzylisoquinolines (66) [87], and the epoxyketone (67) rearranges, perhaps by an intermediate aluminate to the spiroalkene (68) [88].

Scheme 5 Rearrangements during reductions with diisobutylaluminium hydride

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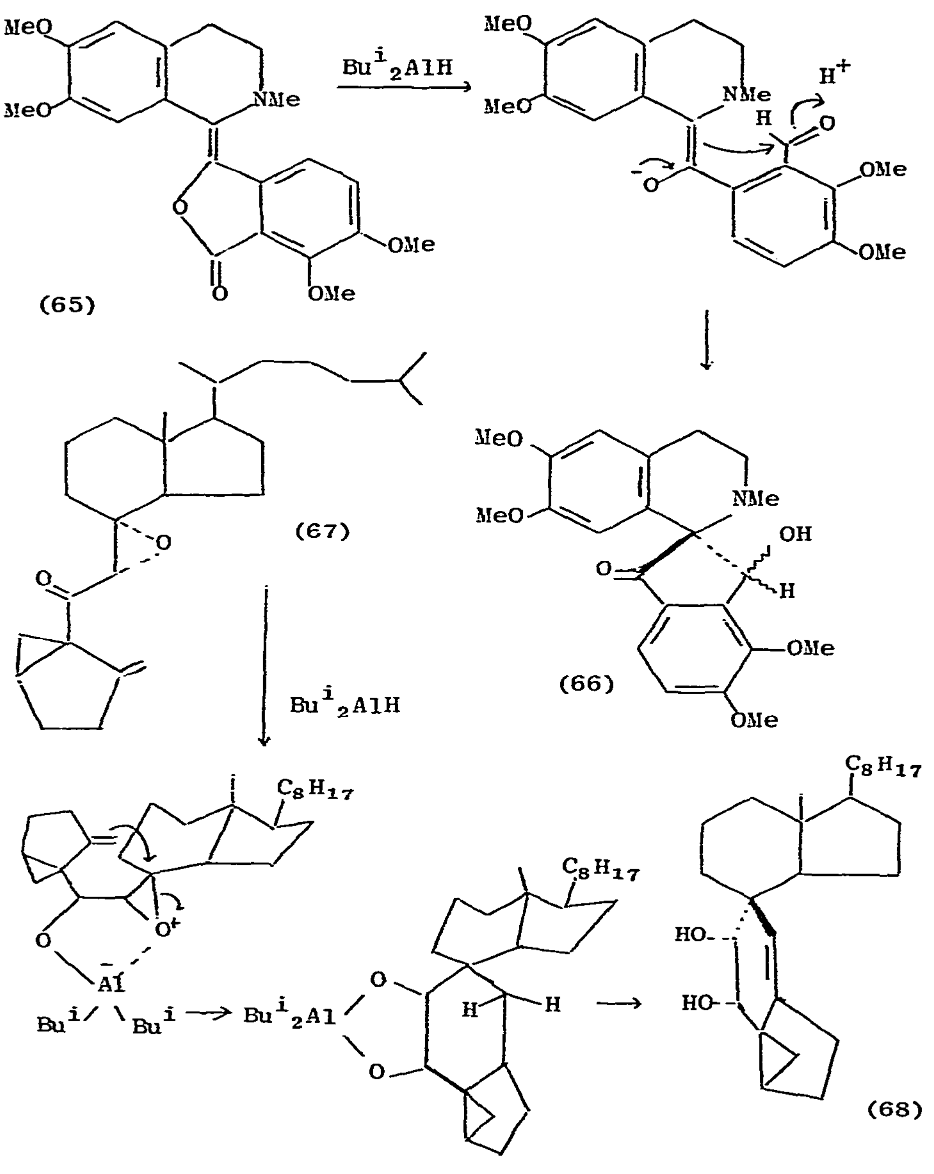
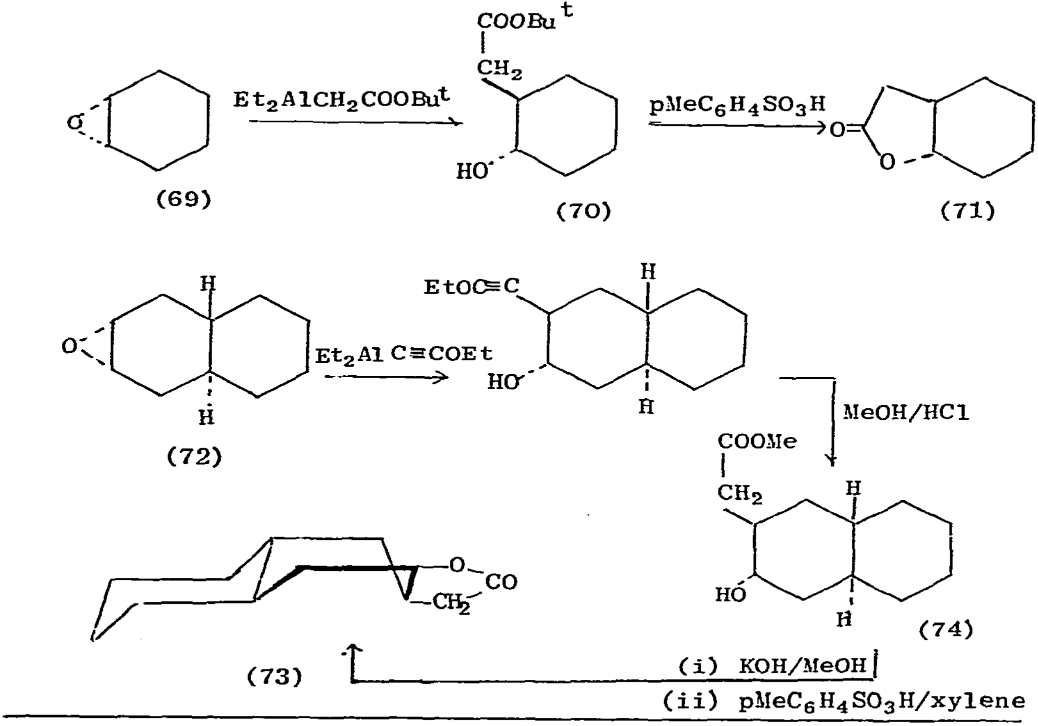
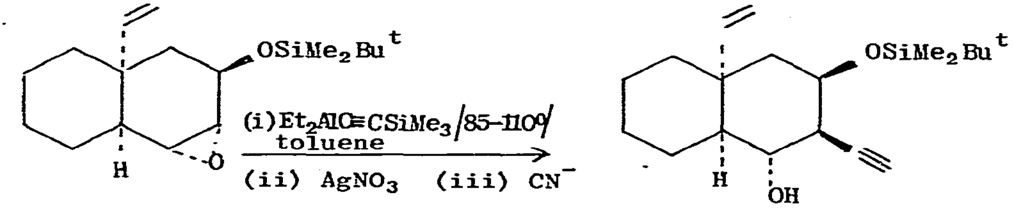


Synthetic applications of reactions between alkylaluminium compounds and epoxides have also been explored. In one study [89], a method for conversion of epoxides to trans-fused γ-lactones is described (Scheme 6). The compound (69) reacts with $Et_2AlCH_2COOBu^t$, made from $LiCH_2COOBu^t$ and diethylaluminium chloride, to give the ester (70) which may be transformed to the lactone (71). Similarly, the epoxide (72) may be converted into the known boat lactone (73), with no evidence for formation of stereoisomers of the ester (74)

Scheme 6 Reactions of epoxides

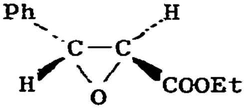


As another example of a highly regioselective epoxide ring opening by organoaluminium compounds, the ethynyl alcohol (75) may be obtained in 80% yield from the epoxide (76) [90].



(76) (75)

Reactions of tetraalkylaluminates with epoxides, like reactions with aldehydes and ketones, are catalysed by nickel halides and are highly stereospecific [91]. The less substituted carbon atom of the epoxide ring is alkylated with inversion of configuration. For example, alkylation of the epoxide (77) gives the product (78) quantitatively. In contrast, tributylaluminium gives mainly the isomer (79)



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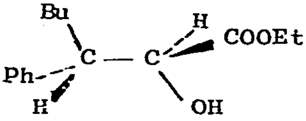

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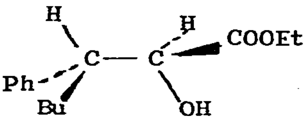
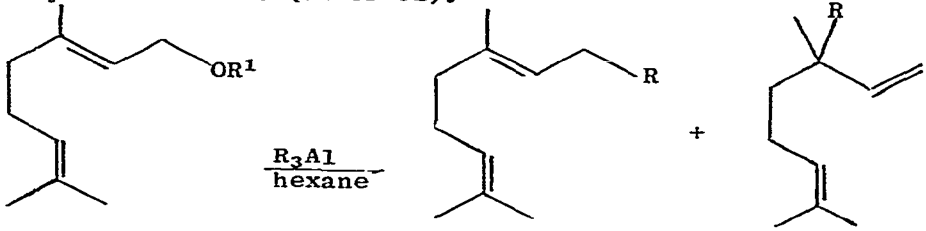


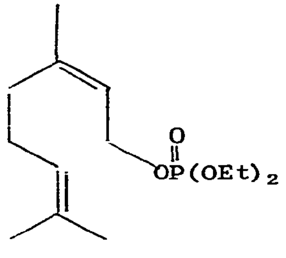
(79)

Finally, reductions with alkylaluminium compounds may lead to complete removal of oxygen functions from organic compounds. Geranyl esters (80) may be reduced to the alkyl derivatives (81 or 82).



(80) (81) (82)

Yields of 60-90% with mainly isomer (81) were obtained for R^1=$COCH_3$, CHO, or COOEt and R=Me, Et or Bu^i. For R^1=tetrahydropyranyl, trimethylaluminium was the only effective alkylating agent [92]. For R^1=$P(O)(OEt)_2$, reaction with trimethylaluminium in dichloromethane gave a 9:1 mixture of (81) and (82) in 90% yield. Neryl diethylphosphate, (83) however, reacted with trimethylaluminium to give small amounts of limonene (84) and terpinolene (85) but the main product was 4-t-butyl-1-methylcyclohexene (86, R=Me).



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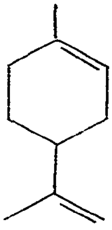

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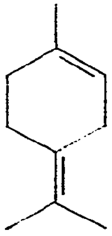

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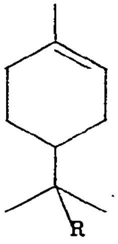
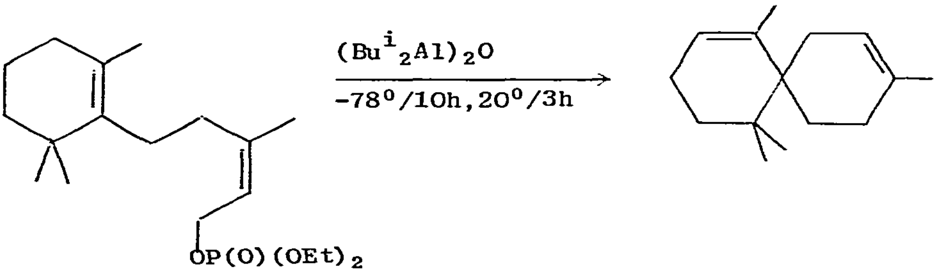


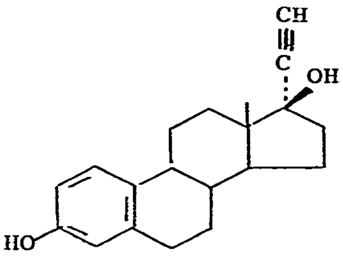
(86)

Similar products were obtained from reactions with triethyl- or triisobutylaluminium. With reagents Me_2AlR (R=SBu^t, SPh, NHPh or OPh) in hexane, substitution products, e.g., (81) predominated, but cyclisations were promoted by dichloromethane. Tetraisobutyldialuminoxane, from water and diisobutylaluminium hydride in THF, was an even more effective reagent for promoting cyclisation reactions, possibly because of ready formation of a chelate complex with the phosphate residue. Thus the cyclisation of the phosphate (87) to the spiro compound (88) was effected in hexane with a yield of 72% [93].



(87) (88)

Reduction of the ethynyl alcohol (89) by triisobutylaluminium in boiling toluene gave the ethyl derivative (90) [94]; in contrast, reduction with aluminium hydride gave the allene (91).



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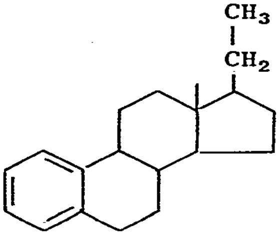

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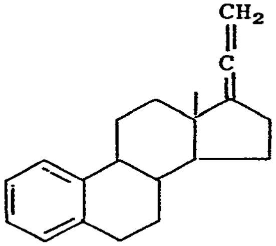


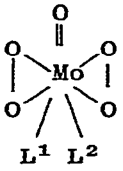
(91)

Another example of cleavage of an ethoxy-group from carbon is found in the reaction of the carbene complex $(CO)_5WC(OEt)CH=CPhNMe_2$ with triethylaluminium in THF to give the cumulene $(CO)_5M=C=C=CPhNMe_2$ [95].

8. ORGANOALUMINIUM ALKOXIDES AND RELATED COMPOUNDS

A method for estimation of the flammability of metal alkyl solutions has been described [96]. Many aluminium compounds have been tested.

Reactions of trimethyl- and triisobutyl-aluminium with t-butyl and benzoyl peroxides have been shown to be similar to those of triethyl- and triphenylaluminium. [13,14,97]. Thus trimethylaluminium and di-t-butyl peroxide give ethane, methane, t-butyl methyl ether and butoxypentamethyl dialuminium, and the mixture appears to indicate concurrent homolytic and heterolytic reaction mechanisms. Diisobutylaluminium hydride reacts with peroxides similarly but the proportion of the products attributed to homolytic reactions is higher than for trialkyl derivatives. There also appears to be some reduction of the peroxide by the aluminium hydride and hydrolysis by the resulting t-butyl alcohol. Triisobutylaluminium and diisobutylaluminium hydride have been oxidised by peroxomolybdenum complexes (92 L=bipyridyl,pyridine or hexamethylphosphoramide, HMPT). The best yields (69-75%) of isobutanol, after hydrolysis, are with L^1 absent and L^2 =HMPT. With normal alkyls AlR_3 ($R=C_4H_9$, C_6H_{13} or C_8H_{17}) the products are very similar to those from oxidations with molecular oxygen and it is concluded that the reaction mechanism involves radical intermediates [98].



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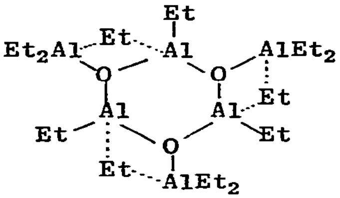
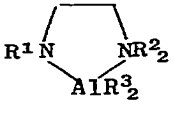


(93)

Proton magnetic resonance spectra of tetraethylalumoxane $(Et_2Al)_2O$ at various temperatures are said to show ethyl groups in bridging positions between aluminium atoms (93). Spectra from mixtures of $(Et_2Al)_2O$ and tetramethyllead have been interpreted as indicating the presence of tetraethyllead and the compound $Me_2Et_2Al_2O$ with a structure like (93) but with methyl groups in bridging positions [99].

9. REACTIONS WITH ORGANIC NITROGEN DERIVATIVES

Molecular complexities of a wide range of neutral chelated organoaluminium-nitrogen compounds have been studied. For the compounds $Me_2AlNEtC_2H_4NEt_2$, $Et_2AlNMeC_2H_4NMe_2$, $Ph_2AlNEtC_2H_4NMe_2$, $Cl_2AlNEtC_2H_4NMe_2$ and $Me_2AlSC_2H_4NMe_2$ the monomer (94) is the predominant species, but, in some cases, dimeric species may be detected in appropriate solvents at low temperatures. Compounds such as $Me_2AlNMeC_2H_4NMe_2$, $Me_2AlNMeC_3H_6NMe_2$, $Et_2AlNMeC_2H_4NMe_2$ and $Et_2AlNMeC_3H_6NMe_2$ appear to be mixtures of monomeric and dimeric species and the compounds $H_2AlNMeC_2H_4NMe_2$, $H_2AlNEtC_2H_4NMe_2$ and $Me_2AlOC_2H_4NMe_2$ are almost completely associated to dimers [100].



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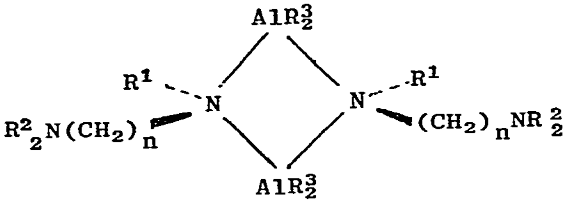


(95)

For the dimeric species, both cis- and trans-conformations are possible and the cis- (95) appears to be preferred in all cases. Various factors determine the stability of monomer relative to dimer but steric considerations are the most important, e.g., dimethylaluminium derivatives with an ethyl or larger group on nitrogen are monomeric, but corresponding dihydroaluminium compounds may be dimeric under comparable conditions.

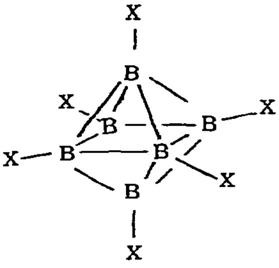
It is now clear that a whole series of organoaluminium-nitrogen cage compounds of general formula $(R^1AlNR^2)_n$ may be made. The heptamer $(MeAlNMe)_7$ (4) has been characterised by X-ray crystallography [19] and the compounds $(MeAlNPr^i)_6$ $(MeAlNPr^i)_4$ and $(EtAlNPr^i)_4$ by NMR and mass spectroscopy. The compounds $(MeAlNPr^i)_4$ and $(EtAlNPr^i)_4$ have been made by the direct interaction of trialkylaluminium and isopropylamine, and $(MeAlNPr^i)_6$ has been made from the hydride $(HAlNPr^i)_6$ and an excess of trimethylaluminium [101]. Several partially substituted compounds $(HAlNPr^i)_n$ $(MeAlNPr^i)_{6-n}$ have been isolated; a similar series of compounds has been described by another research group [102]. The compound $Me_2NAlNMe$ from the hydride H_2AlNMe_2 and methylamine, has been formulated as a heptamer.

The reaction between trimethylaluminium and the compound $B_2(NMe_2)_4$ at 0°C, in the dark and with continuous removal of volatile compounds, yields a pale yellow powder which has been formulated as $B_6(NMe_2)_{12}Al_6Me_{12}$ (96) [103].

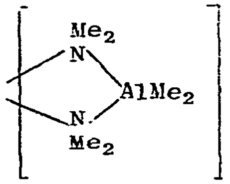
$$6B_2(NMe_2)_4 + 6Al_2Me_6 \longrightarrow 6Me_2NBMe_2 + 3(Me_2NAlMe_2)_2 + \underset{(96)}{B_6(NMe_2)_{12}Al_6Me_{12}}$$

$$B_6(NMe_2)_{12}Al_6Me_{12} + \xrightarrow{Hacac} 6Al(acac)_3 + 12CH_4 + \text{red residue.}$$

This reacts with acetylacetone (Hacac) to give methane and $Al(acac)_3$ quantitatively, but, surprisingly, hydrolysis at $pH>7$ yields dihydrogen as well as methane. There is no evidence from IR spectroscopy for B-H bonds in the compound (96) and so it is presumed that the reducing properties are associated with oxidation of B-B bonds. It is possible that the structure of (96) is as shown.



where X=



(96)

In another series of organoaluminium derivatives, nitrogen forms multiple bonds with a first or second row element. Reactions between sodium trialkylaluminatesand cyanides give the imidoaluminate complexes (97 R^1=Ph,MeC_6H_4 or Et) which are soluble in both polar solvents, e.g. ether or tetrahydrofuran, and in toluene or benzene [104]. Molecular weight measurements suggest that Na(Et_3AlN=CHPh) is dimeric in benzene and structural work would clearly be interesting.

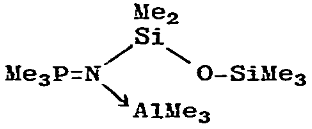
$$\mathrm{Na(R^2_3AlH) + R^1CN \rightarrow Na(R^2_3Al\text{-}N{=}CHR^1)} \qquad (97)$$

The compound (97 R^1=Ph) reacts with chlorotrimethylsilane to give ethyltrimethylsilane and $(Et_2AlN{=}CHPh)_2$ but the corresponding boron compound reacts differently [105].

$$\mathrm{Na(Et_3AlN{=}CHPh) \xrightarrow{Me_3SiCl} NaCl + Me_3SiEt + Et_2AlN{=}CHPh}$$

$$\mathrm{Na(Et_3BN{=}CHPh) \xrightarrow{Me_3SiCl} NaCl + Et_3B + Me_3SiN{=}CHPh}$$

Trimethylaluminium forms a non-fluxional 1:1 complex (98) with trimethylphosphinimidopentamethyldisiloxane [106]. However, NMR spectra of the complex with $(Me_3P{=}N)_2SiMe_2$ (99) show that exchange of trimethylaluminium between the two nitrogen atoms is rapid at 30^0 and slow at -60^0. At 100^0 the complex (99) dissociates into $(Me_3P{=}N)_2SiMe_2\,2AlMe_3$ and free bis(trimethylphosphinimido)dimethylsilane.



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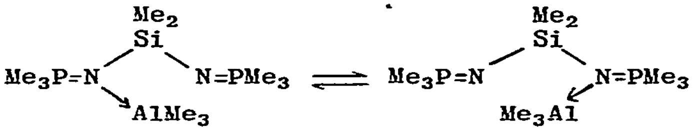
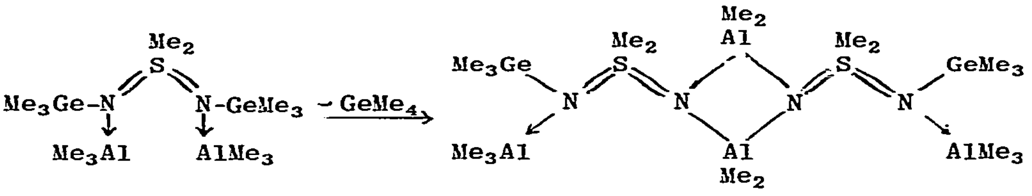


(99)

Trimethylaluminium also forms 1:1 complexes with sulphur diimides $R_2S(NSiMe_3)_2$ (R=Me or Et) and NMR spectra show that there is both intra- and inter-molecular exchange of trimethylaluminium between the two nitrogen sites. [107]. The germanium analogue $Me_2S(NGeMe_3)_2,AlMe_3$ reacts with an excess of trimethylaluminium to give the 1:2 adduct (100) which loses tetramethylgermanium to give the characterisable dimer (101) and finally the polymer (102).



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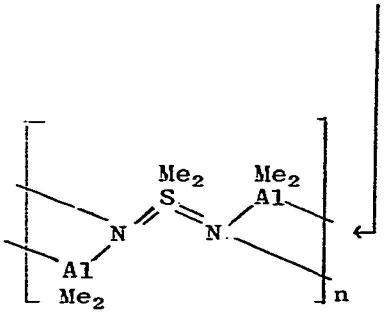

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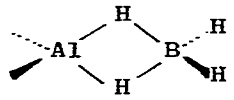


(103)

(102)

10. ORGANOALUMINIUM BOROHYDRIDES

Methylaluminium tetrahydroborates, $Al(BH_4)_2Me$ and $Al(BH_4)Me_2$, made from trimethylaluminium and the stoichiometric amount of aluminium borohydride, or less satisfactorily, from the methylaluminium chlorides and lithium borohydride [108], are volatile and monomeric in the vapour. It seems likely that the borohydride groups are bound to aluminium by double hydrogen bridges (103). Analogous compounds $Al(BH_4)Et_2$, $Al(BH_4)_2Et$, $Al(BH_4)_2Pr$ and $Al(BH_4)_2Bu^i$ have also been made by the proportionation route. In general, the compounds $Al(BH_4)_2R$ disproportionate less readily than $Al(BH_4)R_2$ [109]. A number of adducts e.g. $Al(BH_4)_2Me,L$ ($L=NMe_3$, NMe_2H, PMe_3, $AsMe_3$, OMe_2, OEt_2 or SMe_2) and $Al(BH_4)Me_2,L$ ($L=NMe_3$, PMe_3, OEt_2) have been characterised.

11. DONOR-ACCEPTOR COMPLEXES

Enthalpy changes (Table 1) associated with formation of donor-acceptor complexes with trimethyl-, triethyl- and triphenylaluminium have been compared[110]; more heat is released from complexes with triphenylaluminium than from corresponding trialkylaluminium complexes. No complexes with diphenyl ether or diphenyl sulphide were detected though they are mentioned in an Abstract title [111]. The heat of dimerisation of triphenylaluminium has been estimated as 75 kJ mol^{-1} of dimer.

Table 1 Enthalpy changes (kJ mol^{-1}) associated with the reaction $\frac{1}{2}Al_2R_6(soln.) + D(soln) \rightarrow D,AlR_3(soln)$ in benzene (values in cyclohexane in parentheses)

D	Me_3Al	Et_3Al	Ph_3Al
Et_2O			-54.7
Bu_2O	-48.1	-51.8(-47.2)	-52.3
MePhO		-30.1	
Pr_2S	-27.7	-31.0(-27.7)	-42.1
Et_3N	-71.5	-75.6	-87.5
$Me_2(cycloC_6H_{11})N$		-81.1(-77.4)	
Me_2PhN		-51.8	
C_5H_5N		-73.6	-95.4

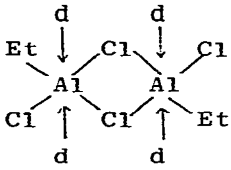
Table 2 Enthalpy changes (kJ mol^{-1}, error in least significant figures in parentheses) associated with the reaction
MX + nAlEt$_3$ → MX,nAlEt$_3$ [a]

MX	n		MX	n		
NaF	2	-27.6(8)	KF	2	-113.8(21)	80°
CsF	2	-192.5(33)	Me$_4$NCl	1	-46.0(17)	50°
KCl	2	-0.8(2)	Et$_4$NCl	2	-251.0(42)	50°
RbCl	2	-5.8(4)	Me$_4$NBr	2	-18.4(8)	50°
			Et$_4$NBr	1	-37.7(12)	50°
CsCl	2	-13.8(8)	Et$_4$NBr	2	-81.3(12)	50°
Me$_4$NCl	2	-74.5(17)	Et$_4$NI	2	-6.7(4)	50°

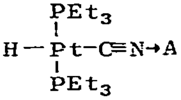
[a] All complexes liquid, except KF,2AlEt$_3$

Enthalpies of formation of complexes MX,2AlEt$_3$, where MX is an alkali or tetramethylammonium halide, predicted by Ziegler et al. in 1960, have now been determined experimentally (Table 2) [112], and the trends previously suggested have been confirmed.

Complexes EtAlI$_2$,L, Et$_2$AlI,L, (EtAlI$_2$)$_2$L. (L=2,2'- or 4,4'-bipyridine) have been described [113] and IR, Raman, ^{1}H and ^{31}P NMR spectroscopic data have been given for complexes of triethylaluminium with Bu$_3^t$P, (Me$_3$Si)$_3$P, Bu$_2^t$(Me$_3$Si)P, (Me$_3$Ge)$_3$P, (Me$_3$Sn)$_3$P [114]. Spectroscopic and cryoscopic data show that alkenylaluminium compounds Et$_2$AlCH=CHEt and Bu$_2^i$AlCH=CHBu^i form complexes only with strong donors such as phenyl cyanide or pyridine [115]. Complexes with PhCN rearrange slowly on standing to give insertion products. Much stronger complexes are formed between phenyl cyanide and the alumoxanes Me$_n$Cl$_{4-n}$Al$_2$O; these are made by careful addition of water to the alkylaluminium halide complexes Me$_n$AlCl$_{3-n}$.PhCN, but the proportion of phenyl cyanide to aluminium is rather ill-defined [116]. Because of the importance of donor-acceptor complexes in polymerisations and copolymerisations, a detailed NMR study has been made of the interaction of methacrylonitrile or methyl methacrylate ethylaluminium dichloride. In dichlormethane, 1:1, 1:2 and 2:1 complexes are detected and these have been assigned the structures (104), with donor molecules in some of the positions indicated by d. NMR spectra of solutions in toluene seem to indicate formation of a ternary complex involving methacrylic monomer, ethylaluminium dichloride and solvent [117]. In another study, IR, NMR and UV spectra of complexes between acrylonitrile and methyl methacrylate with Lewis acids Et_3Al, Et_2AlCl, $Et(EtO)AlCl$, $EtAlCl_2$, $MeAlCl_2$, $EtOAlCl_2$ and $AlCl_3$ have been described [118].



(104)



$H-\underset{PEt_3}{\overset{PEt_3}{Pt}}-C\equiv N\rightarrow A$

(105)

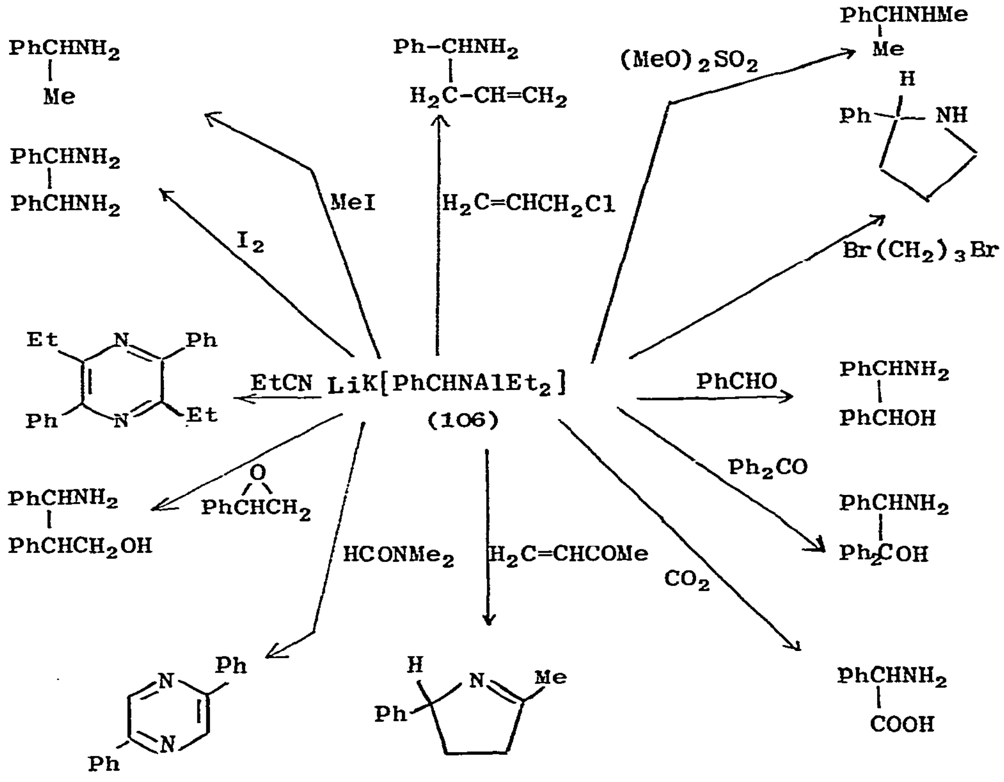
From time to time, methods are suggested for the determination of the relative strengths of Lewis acids (A). The latest [119] involves measurement of $^1J(Pt-H)$ in the adducts (105). The order deduced is $AlCl_3 > BAr_3 > BR_3 \sim CoCl_2 > AlAr_3 > ZnCl_2 > B(OAr)_3 > AlR_3 > AlR_2OR$ (Ar=aryl, R=alkyl). This differs from that from measurement of carbonyl stretching frequencies in $(C_5H_5)Fe(CO)_2CN,A$, which suggests that trimethylaluminium is a better Lewis acid than trimethylborane, but it is not clear how generally applicable such orders of acid strengths are.

12. ORGANOALUMINIUM COMPOUNDS INVOLVING OTHER METALS

This section describes organometallic compounds involving both aluminium and another metal, and also reactions of incompletely characterised mixtures from organoaluminium compounds and compounds of another metal. Some of the mixtures are catalysts for transformations of organic substrates; these are discussed further in Section 13.

The compound $(PhCH{=}NAlEt_2)_2$, made from diethylaluminium hydride and phenyl cyanide, reacts with potassium metal in the presence of naphthalene in tetrahydrofuran, to give what appears to be $PhCHKNKAlEt_2$. With lithium bromide, this gives an ether-soluble product (106), which reacts with a wide range of electrophiles (Scheme 7) [120]. Carbonyl compounds give 1,2-aminoalcohols and phenyloxiran gives the primary alcohol. In contrast, phenyloxiran and phenyllithium yield a secondary alcohol. The product from ethyl cyanide is remarkable.

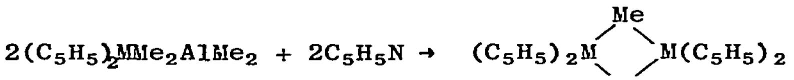
Scheme 7 Reactions of the lithium-potassium derivative of benzylidenamido(diethyl)aluminium [120]



Potassium metal reacts with compounds R^1R^2AlCl (R^1=Bu^i; R^2=Bu^i,OBu^i NMe_2) in hexane to give potassium chloride and a viscous residue which with MeOD yields R^1D, R^2D and D_2 [121]. It is suggested that the deuterium gas arises from hydrolysis of material with Al-Al bonds. If this is the case, the reaction may indicate an example of the stabilisation of a low oxidation state by large ligands.

Compounds with direct aluminium-silicon bonds have proved difficult to isolate. It is now reported that the reaction between aluminium sand, lithium, and catalytic amounts of mercury in dimethoxyethane gives a sublimable material which has the composition $LiAl(SiMe_3)_4.2MeOCH_2CH_2OMe$ [122]. Structural data would be interesting. In THF polymeric material is obtained [123].

The compounds (5) (See Section 2), which have electron diffiecient methyl bridges between aluminium and scandium, yttrium or a lanthanide element, react with pyridine to give aluminium-free alkyls (107), M=Y,Dy,Ho,Er,Yb)



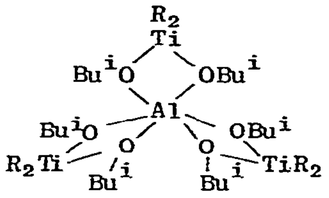
$$2(C_5H_5)_2MMe_2AlMe_2 + 2C_5H_5N \rightarrow (C_5H_5)_2M(\mu\text{-}Me)_2M(C_5H_5)_2$$

(5)

(107) $+ 2Me_3Al,C_5H_5N$

The scandium derivative (5, M=Sc), which, unlike the other compounds (5) shows no bridge-terminal methyl exchange by n.m.r. [20] reacts differently; the products are $(C_5H_5)_2ScMe,C_5H_5N$ and Al_2Me_6 [124]. The reaction between cerium tetraisopropoxide and triethylaluminium in the presence of cyclooctatetraene gives the crystalline compound $(C_8H_8)_2Ce$. At lower temperatures in cycloheptatriene, the main product is $(C_8H_8)_3Ce_2$, which is much more sensitive towards oxygen and less well characterised [125].

The reactions between alkylaluminium compounds $R^1{}_3Al$ (R^1=Me,Et or Bu^i) and alkoxides $M(OR^2)_4$ (M=Ti or V, R^2=Me, Et, Pr^n, Pr^i, Bu^n, Bu^i, Bu^t) have been studied by NMR and ESR [126]. Most detailed results have been obtained with the $Ti(OBu^t)_4$-Me_3Al system. Various complexes of M(III) appear to be involved in isoprene polymerisation,and molecular weight measurements by chemical ionisation mass spectrometry suggest that the catalyst giving 1,4-polymerisation is tris [di-μ-t-butoxodialkyltitanium(iii)]aluminium (108) or the corresponding vanadium complex. The catalytically inactive product obtained from $V(OBu^t)_4$ with a large Al/V mole ratio is probably $V(Me_2AlMe_2)_2$.



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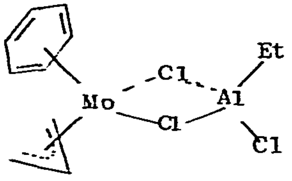

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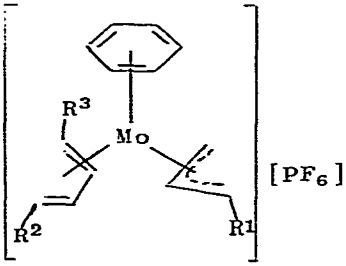


(111)

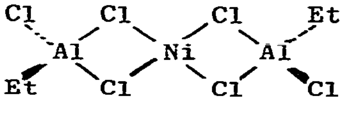
The $Ti(OBu^t)_4$-Et_3Al system also catalyses the dimerisation of ethylene, but, again, active sites disappear at high Al/Ti mole ratios [127]. It is suggested that the deactivation may be reduced by the addition of ethers or amines.

The dimer $[\{Mo(\eta\text{-}C_3H_5)(\eta\text{-arene})Cl\}_2]$ (109) reacts with ethylaluminium dichloride in benzene to give a violet solution: the soluble species has not been fully characterised but it may be (110), on the basis of NMR and chemical evidence. The initial complex (109) may be recovered on addition of diethyl ether [128]. The violet solution reacts with a wide range of dienes and, after hydrolysis and extraction with aqueous ammonium hexafluorophosphate , the complexes $[Mo(\eta\text{-}C_3H_5)(\eta\text{-}C_6H_6)(\eta\text{-diene})][PF_6]$ (111 R^1=H) may be isolated. Similar complexes together with alkanes are formed from the violet solution and monoalkenes. The mechanism of the alkene disproportionation has been examined in some detail; it seems that the role of the aluminium compound is as halide ion abstractor. The violet solution reacts with cyclic olefins such as norbornadiene, cycloocta-1,3,5,7-tetraene or cyclohepta-1,3,5-triene to give cations $[Mo(\eta\text{-}C_3H_5)(\eta\text{-arene})(\eta\text{-olefin})]^+$ analogous to that in (111). With cyclopentene, the products are $[Mo(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_6)Cl]$ (after hydrolysis with lithium chloride solution) or $Mo(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_6)$ (after hydrolysis with sodium dithionite solution). The violet solution reacts with cyclohexene to give the 17-electron cation $[Mo(\eta\text{-}C_6H_6)_2]^+$ isolated as fluorophosphate in 50% yield [129]. The reaction between trimethylaluminium and the dihydride $Mo(\eta\text{-}C_5H_5)_2H_2$ gives the compounds $\{MoH(C_5H_5)(C_5H_4)\}_2Al_3Me_5$ (11) and $[Mo(C_5H_4)_2Al_2Me_3]_2$ (12) which have Al-Mo bonds. Compound (11) reacts with allyl chloride to give, after extraction with ammonium hexafluorophosphate, the η-allyl derivative $[Mo(\eta\text{-}C_3H_5)(\eta\text{-}C_5H_5)_2][PF_6]$, and both (11) and (12) react with carbon dioxide to give, after hydrolysis with hydrobromic and, the carbonyl complex $[MoBr(\eta\text{-}C_5H_5)_2(CO)][PF_6]$. The tungsten hydride $[W(\eta\text{-}C_5H_5)_2H_2]$ also reacts with trimethylaluminium to give a yellow crystalline compound which is not isomorphous with either (11) or (12). The structure is not known, but the reactions with allyl bromide and carbon dioxide appear to be very similar to those of the molybdenum compounds [130].

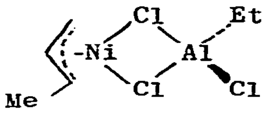
Organoaluminium compounds react with acetylacetonato-complexes of iron and cobalt with displacement of the acetylacetonato (acac) ligand and alkylation of the transition metal. In the presence of phosphines, metal-alkyl complexes may be isolated. For example [131], tris(acetylacetonato)-iron(III), triethylaluminium and triphenylphosphine give the complex $EtFe(acac)(PPh_3)_3$ which initiates polymerisation of styrene, acrylonitrile and methacrylonitrile. No alkyliron compound is obtained when dimethyl- or diethyl-aluminium ethoxide is used in place of triethylaluminium. Complete displacement of the acetylacetonato group may be achieved by trimethylaluminium but the resulting compound $Me_2Fe(PPh_3)_3$ is extremely reactive and must be manipulated below -10°. In the reaction between tris(acetylacetonato)cobalt(III), triethylaluminium (or diethylaluminium ethoxide) and triphenylphosphine under argon the products are ethylene complexes $Co(C_2H_4)(acac)(PPh_3)_2$ and $Co(C_2H_4)(PPh_3)_3$; under dinitrogen the complex $CoH(N_2)(PPh_3)_3$ is obtained.

With methylaluminium compounds, Me_3Al or Me_2AlOEt, the methylcobalt compound $MeCo(PPh_3)_3$, and the more reactive $MeCo(PPh_3)_2$, may be isolated. The reaction between tris(acetylacetonato)cobalt(III) and dialkylaluminium ethoxides R_2AlOEt (R=Me, Et, Pr^n, Bu^i) in the presence of phosphines other than triphenylphosphine gives complexes $CoR_2(acac)(PR^1_3)_2$ (PR^1_3=PEt_3, PBu_3, $PPhMe_2$ PPh_2Me) which appear from ^1H,^{31}P and ^{13}C NMR spectra to have an octahedral configuration with phosphine ligands trans. The complexes react with carbon monoxide to give ketones R_2CO and carbonyl complexes Co(acac)-$(CO)_2(PR^1_3)$ [132,133]. With the bidentate phosphine $Ph_2PCH_2CHPPh_2$, $Co(acac)_3$ and dimethylaluminium ethoxide give the red methylcobalt compound $MeCo(Ph_2PCH_2CH_2PPh_2)_2$ which reacts with carbon monoxide to give an acetyl complex $Co(COMe)(CO)_2(Ph_2PCH_2CH_2PPh_2)$ [134]. In the absence of phosphines, solids of ill-defined composition slowly precipitate from tris(acetylacetonato)cobalt(III) - trialkylaluminium mixtures in aromatic hydrocarbons. These mixtures, which are catalysts for hydrogenation of alkenes, are believed - on the basis of reactions with benzylbromide, diphenylmercury and styrene at various Al/Co mole ratios - to contain material with Co-H bonds [135].

The reaction between tris(acetylacetonato)nickel and triethylaluminium in the presence of triarylstibines yields triarylstibine-Ni(O) complexes $Ni(SbR_3)_4$. A similar reaction with $Pd(acac)_2$ gives palladium analogues $Pd(SbR_3)_4$ but the product from $Pt(acac)_2$ is a very reactive red oil from which no complex could be isolated. No characterisable products were obtained using zinc duct or hydrazine hydrate as reducing agents in place of triethylaluminium [136]. The reaction between nickel stearate or chloride and ethylaluminium dichloride or ethylaluminium sesquichloride gives an orange-brown complex which appears from its electronic spectrum to contain square planar nickel [137]. It has not been isolated analytically pure since it is slowly reduced to metallic nickel, but the active species in solution may be (112).



(112)



(113)

The complex catalyses the polymerisation of butadiene to cis-1,4-polymer; the polymerisation rate is very similar to that found for η-allyl nickel compounds and perhaps an intermediate such as (113) is formed by reaction between the complex (112) and butadiene [137]. Alkene oligomerisation catalysts may be supported on silica gel and a comparative study has been made of the activities of catalysts from bis(cyclopentadienyl)nickel and various organoaluminium compounds [138,139]. The greatest conversion is observed with catalysts containing alkylaluminium dichlorides; catalysts from sesquichloride and dialkylaluminium chlorides are less effective. Trialkylaluminiums reduce the nickel centres on the adsorbent, giving decreased activity, and the very strong Lewis acids $AlCl_3$ and $TiCl_4$ give high molecular weight polymer which fills the catalyst pores [139]. The active site may be a η-C_3H_5Ni system on the surface [138] c.f. (113). It has been suggested [140] that the active species in the alkene dimerisation catalyst from the $Ni(PPh_3)_4$-$EtAlCl_2$ system is the compound $NiCl(PPh_3)_2$.

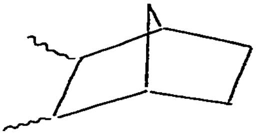
13. CATALYSIS

Organoaluminium compounds continue to find applications in catalytic systems. This account is not comprehensive but merely refers briefly to some of the areas which have been investigated. See also Section 12 above.

Butadiene may be copolymerised with acrylonitrile or methacrylonitrile in the presence of ethylaluminium dichloride to give 1:1 copolymers, but significant deviations from 1:1 composition are found when butadiene is copolymerised with methyl methacrylate(MMA) or methyl acrylate [141]. Copolymerisation of styrene and methyl α-chloroacrylate with diethylaluminium chloride yields a 1:1 copolymer, irrespective of the monomer feed composition [142]. Coisotacticities of several styrene-acrylic copolymers have been determined by NMR. For the styrene-MMA system with diethylaluminium chloride, the data fit the second-order rate expression Rate = k[MMA][styrene] and, since no increase in molecular weight is observed with increased reaction time, a mechanism involving living centres or diradicals is excluded [143].

There have been several kinetic studies using Ziegler - Natta catalysts. The polymerisation of methyl methacrylate with $VOCl_3/AlEt_2Br$ has been discussed in terms of the usual anionic mechanism [144]. In butadiene-methyl methacylate copolymerisation with $VOCl_3/EtAlCl_2$ a ternary complex between butadiene-methyl methacrylate and ethylaluminium dichloride has been proposed [145]. An attempt has been made to determine the number of active transition metal-alkyl sites for ethylene and propene polymerisations using titanium trichloride with Et_2AlCl, Et_3Al, $Bu^{i}{}_3Al$ cocatalysts by quenching with ^{14}CO [146]. The number of propagation centres increases with increasing temperature for Et_2AlCl and Et_3Al but not for $Bu^{i}{}_3Al$ cocatalysts; this is attributed to deactivation at lower temperatures by complex formation with the stronger Lewis acids. Ziegler-Natta catalysts are also modified by electron donors. The activity of $TiCl_3$-Et_2AlCl for propene polymerisation is diminished by ethers of low molecular weight, but enhanced by poly(propylene glycol)dimethylether $MeO(CHMeCH_2O)_nMe$ with $n > 7$. The greatest activity is observed when n=20 [147].

An examination by NMR of the polynorbornenes formed by Ziegler-Natta catalysts $TiCl_4$-$Bu^{i}{}_3Al$, $TiCl_4$-Et_3Al and $TiCl_4$-Et_2AlCl shows that the polymers have structure (114) whereas polymers from radical or cationic catalysts have structure (115)



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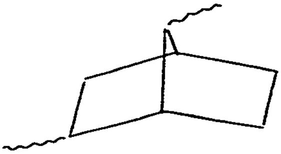

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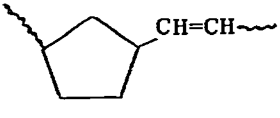


(116)

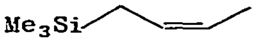
The Ziegler-Natta polymers also show some unsaturation attributed to the structure (116) either as a unit in a copolymer chain or in a separate polymer not separated in the extraction procedure [148]. Chlorine atoms in the titanium catalyst components may be replaced by alkoxy or acetoxy groups to form catalysts $TiCl_2(OR)_2-Bu^{i}_{3}Al$ or $TiCl_2(OCOR)-Bu^{i}_{3}Al$ (R=Me, CH_2Cl, $CHCl_2$, CCl_3 or CF_3) for butadiene polymerisation. A decreasing proportion of the *cis*-1,4-isomer is obtained as the electronegativity of the oxygen-bearing group is increased [149].

Halogen-free Ziegler catalysts for ethylene polymerisation may be derived from bis(cyclopentadienyl)dimethyltitanium and trimethylaluminium or from systems containing zirconium and aluminium related to (6) and (7). The activity of these compounds is enormously enhanced by addition of small amounts of water. Yields of 600 Kg polyethylene $(g.Ti)^{-1}$ and activities of 400 Kg polyethylene $(g.Ti)^{-1}$ h^{-1} have been quoted. The molecular weight of the polymers may be varied from 10^2-10^3 to 10^6-10^7 simply by changing the reaction temperature [150,21].

4-Methylpent-1-ene and 4-methylpent-2-ene may be polymerised using $TiCl_3-Et_3Al$ to give high molecular weight poly-4-methylpent-1-ene. 2-Methylpent-2-ene and 2-methylpent-1-ene give low yields of polyethylene or a mixture of polyethylene and 2-methylpent-1-ene oligomers. Some poly-4-methylpent-1-ene may be obtained from 2-methyl-pentenes by use of ternary catalyst systems, e.g., $TiCl_3-Et_2AlCl-(Ph_3P)_2PdCl_2$ or $TiCl_3-Et_2AlCl-Ni(SCN)_2$, but the details of the isomerisation mechanism are not yet clear [151].

Polymerisation of (-)propylene sulphide by triethylaluminium in the presence of various amounts of water gives material with irregularities such as head to head units or disulphide bonds. This has been explained by postulating simultaneous anionic and cationic initiation. In the presence of tetrahydrothiophene the cationic mechanism is inhibited and polymers without irregularities are formed [152].

More examples have been given of the use of organoaluminium compounds as components of hydrosilylation catalysts. The reaction between trimethylsilane and butadiene using $Ni(acac)_2-Et_3Al$ yields *cis*but-2-enyltrimethylsilane (117) and, with increasing amounts of butadiene, trimethyl-*cis*,*cis*-octa-2,6-dienylsilane (118) [153,154].



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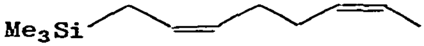
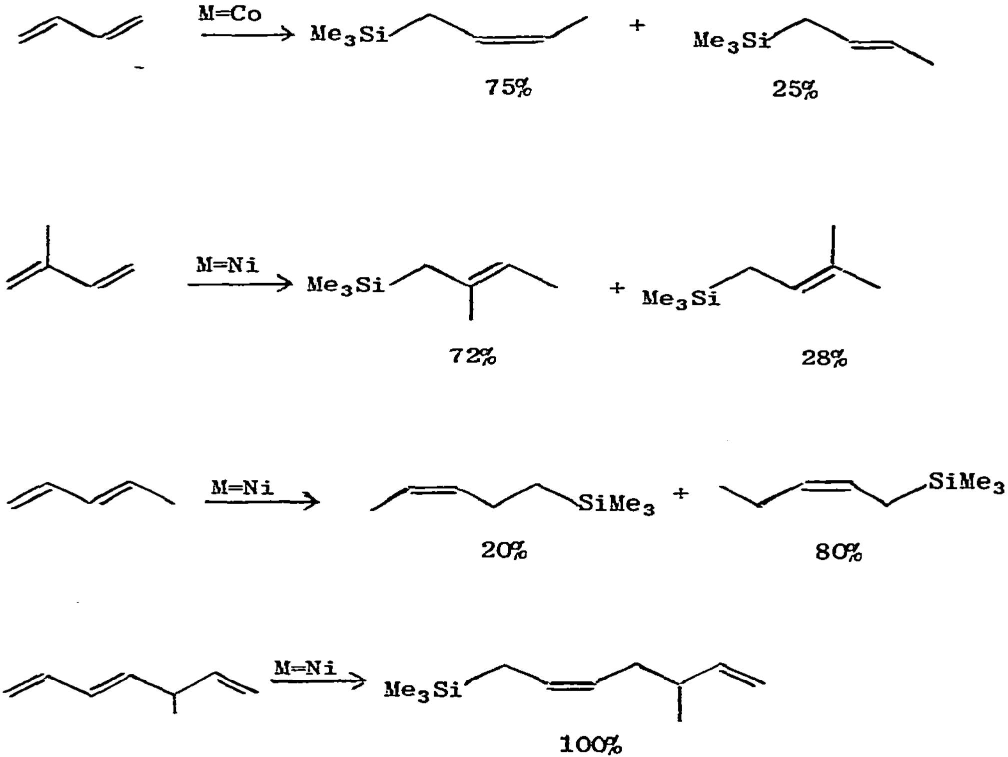


(118)

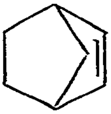
Reactions of trimethylsilane with dienes using Co- or Ni-(acac)$_2$/ Et$_3$Al catalysts are illustrated in Scheme 8. In 5-methylhepta-1,3,6-triene (119), the diene system is much more readily hydrosilylated than the vinyl group.

Scheme 8 Reactions of trimethylsilane with dienes with M(acac)$_2$-Et$_3$Al (M=Ni,Co) catalysts [153].



(119)

There have been many papers on alkene metathesis [10,11]; several discuss the role of organoaluminium compounds in formation of the key carbene-metal intermediates [155-166]. Metathesis catalysts such as $WCl_6/EtAlCl_2/EtOH$, $W(CO)_6/EtAlCl_2/EtOH$ and $Mo(CO)_6/EtAlCl_2/EtOH$ are also effective in inducing alkylation of arenes by cyclic alkenes such as norbornene (120). This reacts with benzene to give the compound (121) in 65% yield and with toluene to give a 1:3 mixture of (122) and (123). More complex skeletal arrangements occur with cyclooctatetraene and cyclododecatrienes; the products are (124) or (125) or the 3-phenyl isomers [167].



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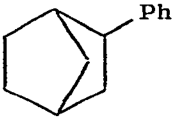

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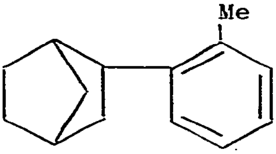

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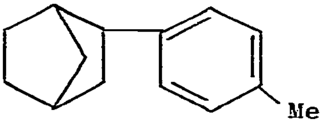

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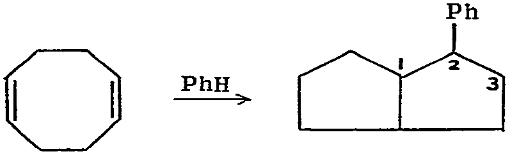

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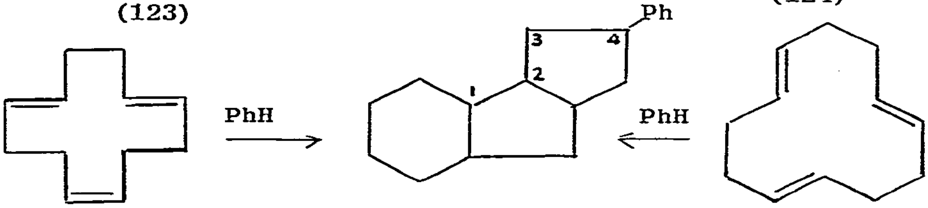
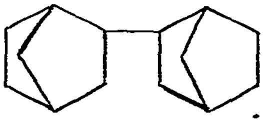


(125)

When norbornene (120) is stirred with the metathesis catalyst in hexane only polymeric material is isolated. In cyclohexane, however, a 25% yield of bisnorbornane (126) may be isolated; in methylene chloride, the products are 35% polymer, 35% bisnorbornane and 30% of 2,3-dinorbornylnorborane (127) [168].



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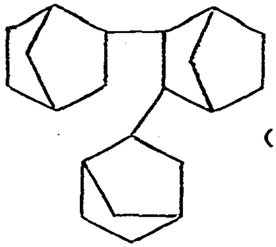

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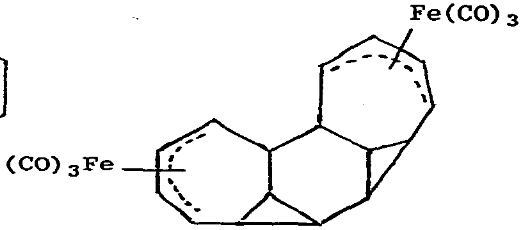

(128)

A skeletal rearrangement is observed when tricarbonylcyclooctatetraeneiron is treated with $WCl_6/EtAlCl_2/EtOH$ [169]. The product (128) is shown by an X-ray investigation to have a pentacyclic arrangement not so far found in a free hydrocarbon.

Organoaluminium compounds have been used as catalysts for deuteriation and tritiation of organic compounds. Thus complete and reproducible exchange of deuterium between C_6D_6 and anthracene, phenanthrene , chrysene and pyrene may be achieved using methylaluminium dichloride and hydrogen chloride as catalyst[170].Where reproducibility is less important, traces of water may be used as the source of HCl. Compounds which are most easily labelled are those which form π- complexes with the catalyst comparable to those formed by benzene; compounds which complex with the catalyst by the lone pair of a heteroatom are difficult to label. Aromatic compounds may be tritiated using $^1H^3HO$ and ethylaluminium dichloride catalyst. For toluene, 98.5% of the activity appears in the aromatic ring.

I thank Mr. J.C.T.R. Burkett St. Laurent for drawing my attention to some of the references.

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