# ALUMINIUM

# ANNUAL SURVEY COVERING THE YEAR 1977*

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## CONTENTS

## 1. INTRODUCTION REVIEWS

This survey follows the pattern of previous years. Many papers describe the use of organoaluminium compounds as reagents in organic synthesis and an increasing number refer to applications in which organoaluminium compounds are combined with derivatives of other metals.

The Chemical Society Specialist Periodical Report [1] covering the 1976 literature on organometallic chemistry has a chapter on the compounds of

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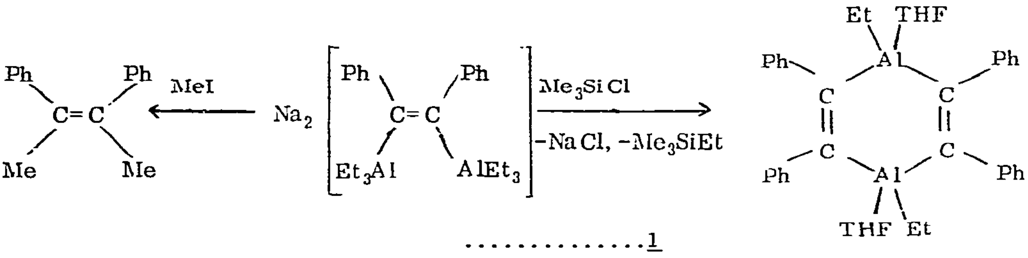
*Aluminium, Annual Survey covering the year 1976, see J. Organometal. Chem., 147 (1978) 127-181. No reprints available.

aluminium, gallium, indium, and thallium [2]. Structure determinations by diffraction [3] and spectroscopic [4] [5] methods, and applications in syntheses [6], have also been documented. There is a chapter (259 pp) on compounds of aluminium in a new book [7] on the chemical analysis of organometallic compounds, and a substantial authoritative account of aluminium compounds in a review of the structures of main group organometallic compounds with electron-deficient bridge bonds [8]. Other important reviews cover rearrangements of unsaturated organoboron and organoaluminium compounds [9] and exchange reactions of organoaluminiu compounds [10]. Many references to studies involving organoaluminium compounds are given in reviews on alkene metatheses [11], Ziegler catalysis [13], and the polymerisation and copolymerisation of butadiene [14]. Brief sections on aluminium are found in reviews on organic peroxides of the main group III elements [15], arynes and carbenes derived from organoelement compounds [16] (This has an account of compounds with the Al-CH$_2$-hal system), intramolecular coordination in organic derivatives of non-transition elements [17], and on polarography of organometallic compounds of non-transition elements [18]. A review on alkylaluminium compounds has appeared in a series on dangerous chemical reactions [19].

## 2. MOLECULAR STRUCTURES

The structure of the donor-acceptor complex Me$_3$Al,OMe$_2$ has been determined by gas-phase electron diffraction [20]. The main molecular parameters are Al-C 197.3(11), Al-O 201.4(4), O-C 143.6(3) pm, O-Al-C 98.7(15), Al-O-C 122.6(5), C-O-C 114.5(17)$^{\circ}$. The O-C distance and C-O-C angle are greater than in free dimethyl ether and the three valencies at oxygen are almost coplanar. It is suggested that the planarity at oxygen results from Al...C(O) repulsions. In the ion [Me$_3$AlOCOMe]$^-$, isolated as a tetramethylammonium salt, the Al-O distance, [183(1) pm], found by X-ray diffraction, is shorter than that in Me$_3$Al,OMe$_2$ [21]. The Al-C distance is 202(2) pm and the C-O-Al angle 137(1)$^0$. The compound [Me$_4$N][Me$_3$AlOCOMe] is one of a series derived from trialkylaluminiums and ionic compounds MX (M$^+$ = alkali or R$_4$N$^+$, X$^-$ = halide, pseudohalide or oxyanion). Many of these complexes react with aromatic hydrocarbons: for example, a dense liquid of composition {[Me$_4$N]-[Al$_2$Me$_6$OCOMe] 6.3 C$_6$H$_6$} separates from benzene solutions of [Me$_4$N][Me$_3$AlOCO-Me].

There have been X-ray structural determinations of two compounds (1, 2) with aluminium-containing heterocycles [22, 23]. The ate complex (3), made from triethylaluminium, sodium and diphenylethyne, reacts with iodomethane to give cis-2, 3-diphenylbut-2-ene(4), but with trimethylchlorosilane in tetrahydrofuran (THF) the product is the heterocycle (1) (Equation 1) [22].



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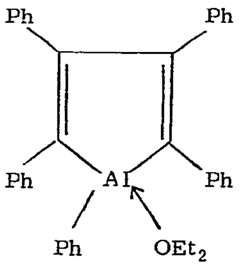
(4) (3) (1)

The molecule (1) is centrosymmetrical with the $Al_2C_4$ ring almost planar. Molecular parameters are Al-O 190.7(3), Al-C 198.4(4), C=C 136.2(5) pm, C-Al-O 103.7(4), C-Al-C 114.5(8)°. The five-membered ring in (pentaphenyl)aluminacyclopentadiene-diethyl ether (2) is also planar, with mean bond distances Al-C 196.6(6), C=C 136.0(8), C-C 151.6(9) pm [23]. The Al-C(Ph)distance [197.9(6) pm] is normal and the Al-O bond [190.7(5) pm] is again shorter than in $Me_3Al, OMe_2$ (see above).



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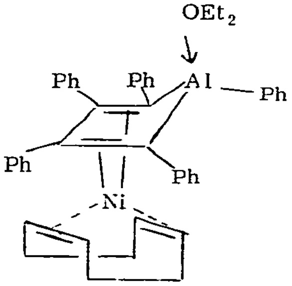


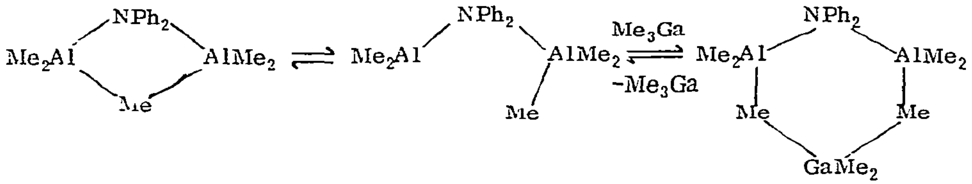
(5)

Compound (2), which is obtained from the reaction between 1, 2, 3, 4-tetraphenyl-1, 4-dilithiumbutadiene and phenylaluminium dichloride [24], reacts with bis-(cyclooctadiene)nickel in diethyl ether to give red crystals of the complex (5). The aluminium atom is now bent away from the nickel atom suggesting that the hybridisation at the adjacent carbon atoms corresponds to $sp^3$ rather than $sp^2$. Mean bond lengths are Al-C 195.7(3), C=C 140.7(4), C-C 149.8(4), Al-C(Ph) 197.5(3), Al-O 197.7(3) pm. The bond length changes in the aluminacyclopentadiene on complex formation may be explained in terms of back donation from filled d orbitals on Ni into the $\pi^*$ orbital of the $C_4(Al)$ system. The Ni-Al distance is slightly less than the sum of the covalent radii, possibly indicating some metal-

metal interaction. Other X-ray studies are described in Sections 8 (ref 106) and 10 (ref 117 and 118) below.

## 3. SPECTROSCOPIC AND THERMODYNAMIC PROPERTIES

$^{13}$C NMR spectra [25] of tri-t-butylaluminium and tris(trimethylsilyl)-aluminium [26] have been described, and spectra of tripent-4-enylaluminium and its trimethylamine adduct have been recorded as part of a study of metal-double bond interactions [27]. However, $^{13}$C parameters give much less useful information than $^1$H NMR and cryoscopic measurements. The intramolecular exchange of methyl groups between bridge and terminal sites in μ-methyl-μ-diphenylamido tetramethyldialuminium (6) is first order in the mixed bridged compound [28].



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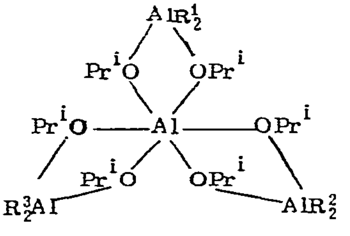
Exchange of methyl groups between compound (6) and trimethylgallium is also first order in (6) and independent of Me$_3$Ga concentration. Both processes are thought to involve breaking of methyl bridge bonds (Equation 2). Mixtures of hexamethyldialuminium and the tetramer [Al(OPr$^i$)$_3$]$_4$ (7a $R^1 = R^2 = R^3 = OPr^i$) have been studied by $^1$H, $^{13}$C and $^{27}$Al NMR [29]. $^1$H NMR spectra are complicated by overlapping signals from the complexes (7b $R^1$ = Me, $R^2 = R^3 = OPr^i$ or 7c $R^1 = R^2$ = Me, $R^3 = OPr^i$). $^{13}$C signals from methyl groups attached to aluminium are broadened by quadrupole effects but sharp peaks are obtained from isopropoxy groups. Pulsed techniques may be used to supplement continuous-wave measurements. The spin-lattice relaxation time $T_1$ is about twice as long for protons of terminal methyl groups as for those in bridging methyl groups. Aluminium atoms



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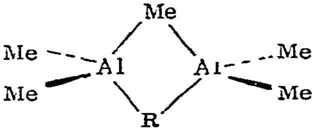

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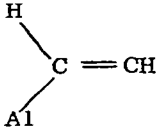


(9)

at the centre and in the wings of the structures (7) may also be distinguished by relaxation times. The results have been interpreted in terms of the complexes (7a-7c) and, at high $AlMe_3/Al(OPr^i)_3$ mole ratios, the compounds (8 R = Me or $OPr^i$). Some chemical ionisation mass spectra have also been reported.

Enthalpies of mixing of trimethylaluminium with the donors $Me_3As$, $Me_3Sb$, $Me_2S$, $Me_2Se$, and $Me_2Te$ have been determined [30].

## 4. PREPARATION OF ORGANOALUMINIUM COMPOUNDS

The very reactive species obtained by the interaction of aluminium atoms and acetylene has been trapped in neon matrixes and shown [31] by ESR to have the vinyl structure (9).

Several patents [32-36] describe the synthesis of alkylaluminium compounds from aluminium, hydrogen and alkenes, the manufacture of alkylaluminium sesquichlorides [37], and the safe disposal of industrial sludges during manufacture of organoaluminium compounds [38]. A mathematical model for continuous production of alkylaluminium sesquichlorides has been described and optimum parameters worked out for methyl- [39], and ethyl-aluminium [40], systems. Ethyl phenyl ether complexes of higher alkylaluminium compounds $R_3Al, OEtPh$ [$R = Bu^n$, $C_5H_{11}$, $C_8H_{17}$] have been synthesised from reactions between aluminium and magnesium metals, iodoalkanes and ethyl phenyl ether in octane at 90-105°C (Equation 3).

$$2Al + 3Mg + 6RI + 2PhOEt \longrightarrow 2R_3Al,OEtPh + 3MgI_2 \qquad \ldots\ldots\ldots 3$$

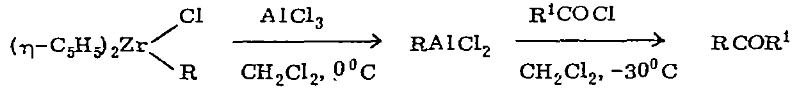
Under these conditions, cleavage of the ether and preferential formation of organomagnesium compounds are much reduced and 80-90% yields of alkylaluminium compounds are obtained. The ethyl phenyl ether may be quantitatively displaced by stronger donors such as 1,2-dimethoxyethane, dimethoxymethane, dioxan or dipentyl ether [41]. Optically active alkylaluminium compounds $(RCHMeCH_2)_3Al$ ($R = Pr^i$ or $Bu^t$) may be obtained in 73-82% yield from the reaction betweem triethylaluminium and the boron alkyls $(RCHMeCH_2)_3B$, which are themselves obtainable from the optically active Grignard reagents $RCHMeCH_2MgCl$ and $F_3B,OEt_2$ in diethyl ether [42]. The optical purity of the products may be estimated by bromination or carbonation.

The preparation of dialkylaluminium chlorides from aluminium(III) chloride and trialkylaluminiums is complicated by side reactions when the alkyl group is bulky or complex. As a more convenient low-temperature method, the reaction between trialkyl and the hydrogen chloride complex $CuSO_4.2HCl$ is suggested [43]. At 20$^0$ only one alkyl group is cleaved so that the compounds $R_2AlCl$ may be obtained in good yield. When the complex $[MePhH^+Al_2Cl_7^-, 2MePh]$ is used as a source of HCl (Equation 4) high yields of the halides $R_2AlCl$ ($R = Pr^i$ or $C_8H_{17}$) may be obtained at $0^0C$. If the reaction mixture is heated to $60^0C$, the dialkylaluminium

$$R_3Al + [MePhH^+Al_2Cl_7^-, 2MePh] \longrightarrow R_2AlCl + 3MePh + Al_2Cl_6 + RH \qquad \ldots\ldots\ldots 4$$

compounds $R_2AlCl$ and aluminium(III) chloride react to give the dialides $RAlCl_2$.

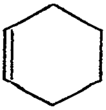
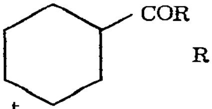
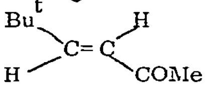
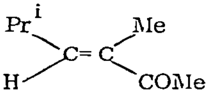
An interesting trend in current organometallic chemistry is the increasing use of one-pot reactions involving derivatives of two different metals. Thus reactions between the zirconium compounds $(\eta\text{-}C_5H_5)_2ZrClR$ and aluminium(III) chloride yield the compounds $RAlCl_2$ which may be used in situ as mild alkylating agents e.g. for acid chlorides (Equation 5 and Table 1) [44].



$$(\eta\text{-}C_5H_5)_2Zr\begin{matrix}Cl\\R\end{matrix} \xrightarrow[CH_2Cl_2,\ 0^0C]{AlCl_3} RAlCl_2 \xrightarrow[CH_2Cl_2,\ -30^0C]{R^1COCl} RCOR^1 \qquad \ldots\ldots\ldots\ldots 5$$

The starting alkylzirconium compounds are readily available from hydrozirconation, using $(\eta\text{-}C_5H_5)_2Zr(H)Cl$, of alkenes or alkynes and the reaction times for the transformations in Table 1 are much shorter than with reagents containing only zirconium. Transmetallation from zirconium to aluminium occurs predominantly with retention of configuration at carbon. The acylation works well for primary alkyl- and alkenyl-aluminium derivatives but extensive side reactions are found with secondary alkylaluminium compounds. Both terminal and internal alkenes are converted to the same ketone. Organozirconium species with a remote double bond may cyclise, e.g. $[(\eta\text{-}C_5H_5)_2ZrCl(CH_2)_4CH{=}CH_2]$ gives $(cyclo\ C_5H_9)CH_2AlCl_2$. The ready availability of acyl-transition metal derivatives raises the possibility that transacylation from zirconium to aluminium may be effected in the same way [45]. When $[(\eta\text{-}C_5H_5)_2Zr(Cl)COR]$ ($R = CH_2CH_2Bu^t$) is treated with aluminium(III) chloride in dichloromethane, the solution shows NMR signals which are characteristic of the compound $(Cl_2AlCOR)_x$. This is hydrolysed by $D_2O$ to the aldehyde RCDO, suggesting that the acylaluminium compound may indeed be formed in the absence of species such as aldehydes with which it may condense. The scope of the transacylation is, however, not yet clear.

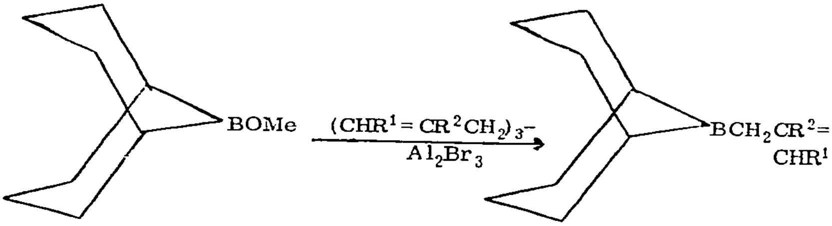
Table 1 Preparation of ketones from alkenes or alkynes by hydrozirconation, transmetallation and reaction with acid chlorides

| | | | yield | reaction time |
|---|---|---|---|---|
| $Bu^tCH=CH_2$ | $\longrightarrow$ | $Bu^tCH_2CH_2COMe$ | 98% | 30 mins |
| n-octenes | $\longrightarrow$ | $n\text{-}C_8H_{17}COMe$ | 98% | 60 mins |
|  | $\longrightarrow$ |  R = Me or Ph | 64% | 45 mins |
| $Bu^tC\equiv CH$ | $\longrightarrow$ |  | 97% | 45 mins |
| $Pr^iC\equiv CMe$ | $\longrightarrow$ |  | 98% | 45 mins |

## 5. ALKYLATIONS

This section describes reactions in which organoaluminium compounds are used to effect replacement of nucleophiles by alkyl groups and reactions in which organoaluminium compounds serve as Lewis acids in electrophilic alkylations.

The reaction between the alkoxides $[(\eta\text{-}C_5H_5)Ti(OR)_3]$ (R = Et or $Pr^i$) and trimethylaluminium gives a brown liquid, thought to be the complex $[(\eta\text{-}C_5H_5)TiMe(OR)_2.AlMe_2OR]$. Cleaner methylations to $[(\eta\text{-}C_5H_5)TiMe(OR)_2]$ may be obtained using MeLi or MeMgBr as alkylating agents [46]. The sesquibromides $(CHR^1=CR^2CH_2)_3Al_2Br_3$ ($R^1 = R^2 = H$; $R^1 = Me$, $R^2 = H$; $R^1 = H$, $R^2 = Me$), made in situ from the bromides and aluminium metal in ether, have proved useful for replacement of OMe to give B-allyl derivatives (Equation 6) [47].



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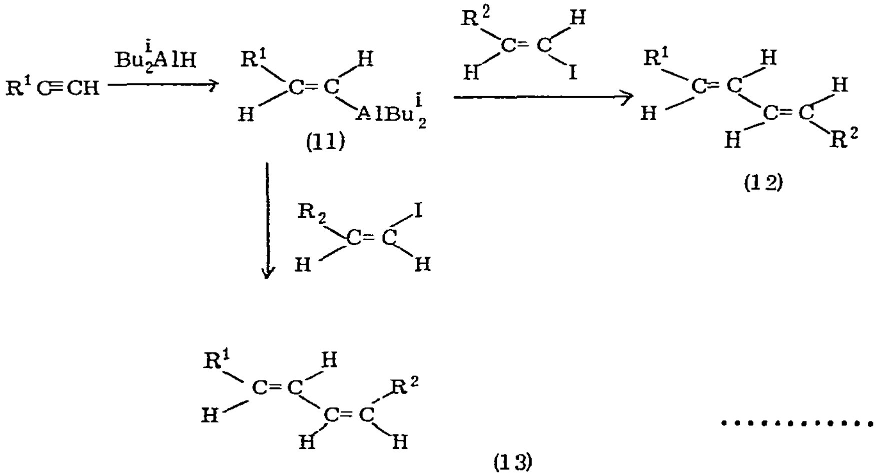
In other alkylations, chlorine atoms are replaced [44]. Besides the examples of Table 1, details have been given for the preparation of 3-trimethylsilylpropyl ketones $Me_3Si(CH_2)_3COR$ (R = Me, Pr, $C_5H_{11}$, $C_7H_{15}$, $C_9H_{19}$ or $C_{11}H_{23}$) [48]. Methylenebis(dichloroaluminium) (10), made from aluminium metal and dichloromethane, reacts with phosphorus(III) chloride to give the useful synthetic intermediate $Cl_2PCH_2PCl_2$ [49] (Equation 7).

$$\underset{(10)}{Cl_2AlCH_2AlCl_2} + 2PCl_3 \longrightarrow Cl_2PCH_2PCl_2, 2AlCl_3$$

$$\xrightarrow{POCl_3,\ KCl} Cl_2PCH_2PCl_2 \qquad \dots\dots\dots\dots\dots\dots 7$$

Tricyclopentadienyluranium chloride may also be alkylated by triethylaluminium, but, like the methyltitanium compounds mentioned above, the products are complexed either by excess triethylaluminium or diethylaluminium chloride [50]. Rapid alkyl group exchange between the compounds $(C_5H_5)_3UR^1$ and $AlR^2_3$ has been demonstrated by NMR.

Alkenylations may also be effected using organoaluminium reagents [51]. Alkenylaluminium compounds compounds (11, R = $C_5H_{11}$, $Bu^n$ or $Bu^t$), easily made by hydroalumination of alkynes, react in the presence of $[Ni(C_5H_7O_2)_2]/PPh_3$ or $[PdCl_2(PPh_3)_2]$ as catalysts, with alkenyl iodides ($C_5H_7O_2$ = acetylacetonato or pentane-2,4-dionato). Good yields of the cross-coupled products (12) or (13) ($R^2$=$Bu^n$ $R^1$=$Bu^n$, $Bu^t$ or $C_5H_{11}$) and only small amounts of homocoupled compounds, are obtained (Equation 8). The reactions are highly stereospecific so that the proportions of the predominant EE(12) or EZ(13) isomers in the diene products are > 90%.



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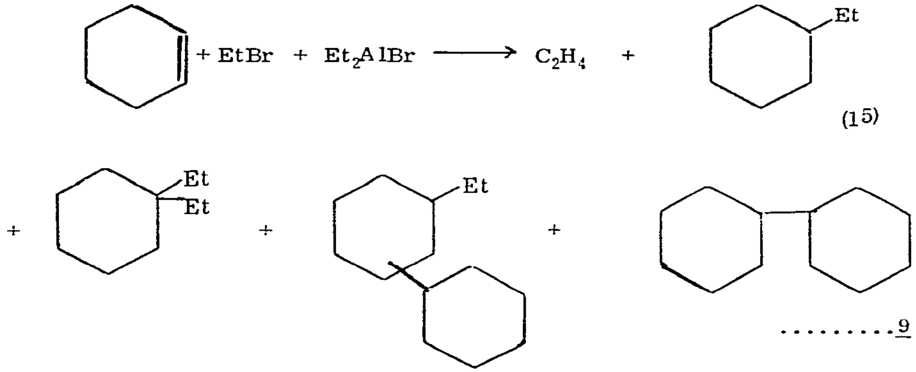
One of the more important applications of trimethylaluminium is in production of trimethylgallium for the electronics industry. Since separation of trace impurities in the trimethylgallium produced is crucial, an attempt has been made to calculate separation factors from thermodynamic information [52]. Data for $Me_3Al$, $Me_2AlCl$, and a wide range of other organometallic compounds, have been given.

The use of organoaluminium compounds as Lewis acids to assist in electrophilic alkylation is illustrated in studies on reactions with cyclohexene [53] (Equation 9)



(15)

(14)

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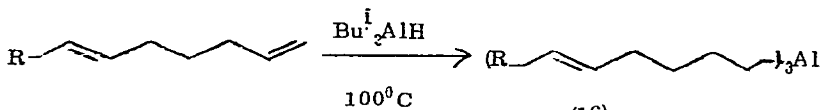
The yields of various products depend on the cyclohexene/bromoethane mole ratio and also on the temperature. At 0°C, the major product is the ethylbicyclohexyl (14) of unknown structure and ethylcyclohexane (15). At 60°, ethylcyclohexane (15) predominates and at 80°, with an excess of cyclohexene, a high proportion of polymeric material is formed. These products suggest that cations $[C_6H_{10}Et]^+$ and $[C_6H_{11}]^+$ formed from cyclohexene and the ethyl carbonium ion are important intermediates. In the presence of an excess of triethylaluminium the cyclohexyl cation is deprotonated and the principal products are ethane and ethylcyclohexene. Similar reactions with other cyclic alkenes have been studied.

## 6. REACTIONS WITH CARBON-CARBON DOUBLE AND TRIPLE BONDS

A patent [54] claims that alkenes $C_2H_4$ and $C_3H_6$ may be separated from alkanes by reaction with the complexes $[CuAlR^1Cl_2R^2, nL]$ ($R^1$ = Me,Et or $Bu^i$; $R^2$ = Cl or Br; n = 1 or 2; L = cyclohexene, pent-1-ene or benzene) made by mixing the components in L as solvent.

Trialkenylaluminiums may be obtained from hydralumination of dienes by diisobutylaluminium hydride. (Equation 10)



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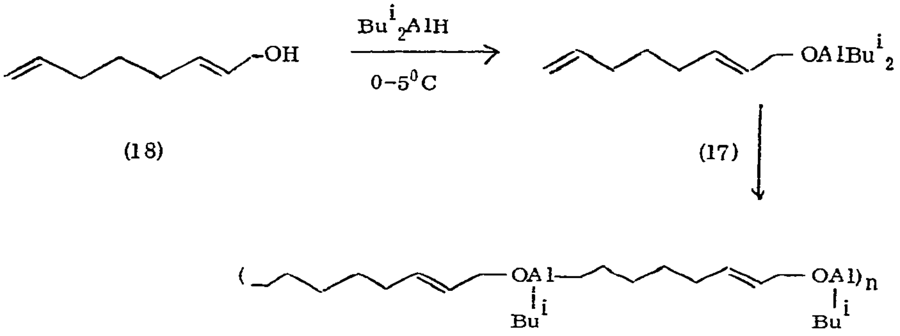
The derivatives (16, R = H, OMe or OPh) have been obtained by this method and identified by their reactions with water or oxygen [55]. The dienyl derivative (17), may be made from dienol (18) and diisobutylaluminium hydride, but on heating in the presence of catalytic amounts of $Bu^i_2AlH$ the product polymerises by intermolecular hydroalumination (Equation 11).



(18)

(17)

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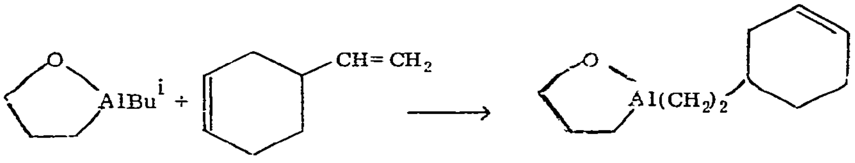
Although the aluminium compound (17) is stable up to 150°C, the corresponding derivative from allyl alcohol and diisobutylaluminium hydride undergoes intramolecular hydroalumination to form compound (19). This reacts with vinylcyclohexene at 150°C to give (20) which is oxidised and hydrolysed to 1, 3-propanediol and 4-(2-hydroxyethyl)cyclohexene. [58]

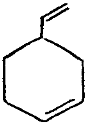
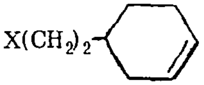
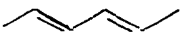
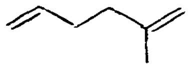
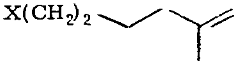
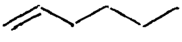
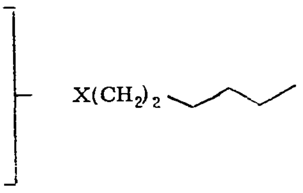


(19) (20) .........12

The reactions between triethylaluminium and chloroalkenes in which both chlorine and the double bond are adjacent to an aromatic ring may result in alkylation at chlorine as well as addition across the double bond. Thus $PhClC{:}CH_2$ and triethylaluminium in benzene give, as main product, PhCHMeEt, together with smaller amounts $Ph_2CH_2$, $Ph_2CHMe$, $PhCH_2CH_2Ph$. [57]

Several papers describe hydroaluminations catalysed by transition metal compounds. The reaction between bis(cyclopentadienyl)titanium dichloride and lithium aluminium hydride yields a complex $[(\eta\text{-}C_5H_5)_2Ti(AlH_3)_2]$ which catalyses the isomerisation of terminal to internal alkenes [58] [59] under mild conditions (35$^0$C for 5 h). In the presence of an excess of lithium aluminium hydride the main products from alkenes RCH=CH$_2$ (R = Bu$^n$, $C_6H_{13}$, Ph, cyclohex-3-enyl) are the salts $Li^+[R(CH_2)_2AlH_3]^-$ (21). Internal alkenes are rather unreactive towards hydrometallation under these conditions. The alkylaluminates (21) may be oxidised to alcohols $RCH_2CH_2OH$,e.g.,by $O_2/H_2O_2/NaOH$, by m-chloroperbenzoic acid or by $O_2$/aq. HCl and converted into 1-bromoalkanes by treatment with bromine [60]. Since terminal double bonds react much more rapidly than internal double bonds, alkenols may be obtained in good yield. The catalytic activities of $ZrCl_4$, $TiCl_4$, $VCl_4$, $[Ti(\eta\text{-}C_5H_5)_2Cl_2]$ and $[Zr(\eta\text{-}C_5H_5)_2Cl_2]$ for selective hydroaluminations of dienes , have been compared [61]. Titanium (IV) chloride is the most effective. The alkenylaluminium compounds may be converted to halides by treatment with N-bromo- or N-chlorosuccinamide or into alkenes by hydrolysis (Table 2). Tetrahydrofuran(THF), dimethoxyethane, diglyme or triglyme may be used as

Table 2 Hydroaluminations catalysed by titanium(IV) chloride [61, 62]

| Alkene | Product | Yield (%) |
|---|---|---|
|  |  | 97(X = H) 76(X = Cl) 79(X = Br) |
|  |  | 94(X = H) 70(X = Br) |
|  |  | 90(X = H) 71 (X = Br) |
|  | | 99(X = H) |
|  |  | 98(X = H) 79(X = Br) |
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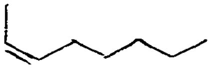
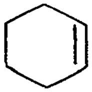
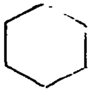
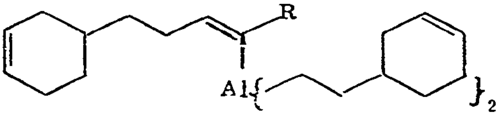
|  |  | 98(X = H) 84 (X = Br) |
|  |  | 46(X = H) |

as solvents, but not diethyl ether. Reactivities towards $LiAlH_4$ decrease in the series $RCH{=}CH_2 > R_2C{=}CH_2 > RCH{=}CHR$ but here, with a large AlH/Ti mole ratio, isomerisation of internal to terminal alkenes is observed. Towards a particular alkene (e.g. hex-1-ene) the reactivity decreases: $LiAlH_4 > AlH_3 > AlH_2Cl > AlHCl_2$ [62]. From $\alpha,\omega$-dienes, mono- or di-aluminium compounds may be obtained by control of the Al/alkene mole ratio, apparently without cyclisation reactions [62]. Organoaluminium intermediates are also implicated in the hydrometallation of a range of terminal and internal alkenes using bis(diisopropylamino)alane $AlH(NPr^i_2)_2$ catalysed by bis(cyclopentadienyl)titanium dichloride [63].

Several papers describe the formation of di- or tri-enylaluminium compounds by carbalumination or hydroalumination of alkynes. For example, the



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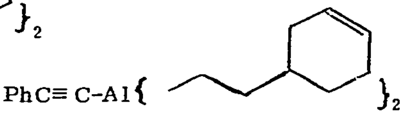
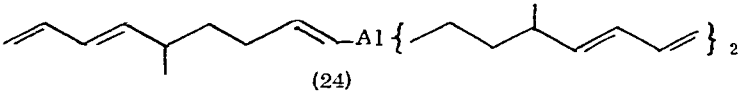


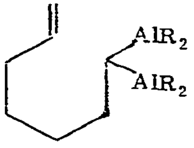
(23)

reaction between acetylene and tris[2-cyclohexenyl)ethyl]aluminium yields the dienyl derivative (22 R = H). [64]. The reaction with phenylacetylene is more complicated, since metallation giving (23), as well as carbalumination giving (22, R = Ph) is observed. The compound (24) may be made similarly from acetylene and $(CH_2{:}CHCH{:}CHCHMeCH_2CH_2)_3Al$.



(24)

The reactions between diethyl- or diisobutyl-aluminium hydride and hept-1-ene-6-yne in diethyl ether give the bis(dialkylaluminia)hept-1-enes (25 R = Et or Bu$^i$) [65]. The analogous compound (26) is obtained similarly. The



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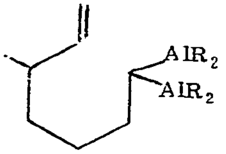

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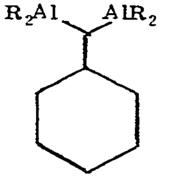

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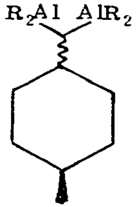
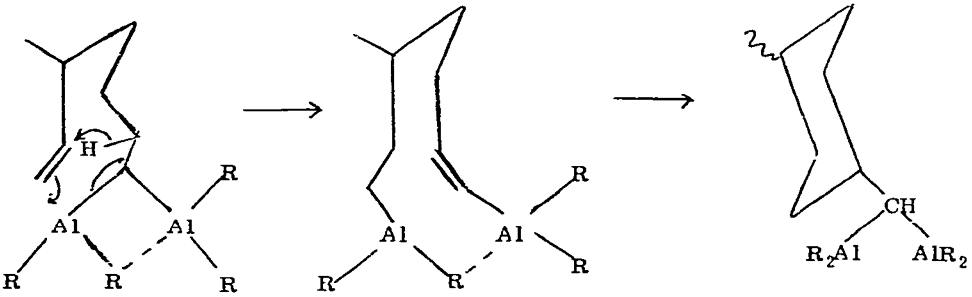


(28)

compounds (25) and (26) may be isolated as ether adducts: in the absence of ether, or with an excess of ether-free triethylaluminium, they rearrange to the cyclohexyl compounds (27) and (28). This rearrangement is thought to involve an intramolecular alkene exchange (Equation 13).



(26)

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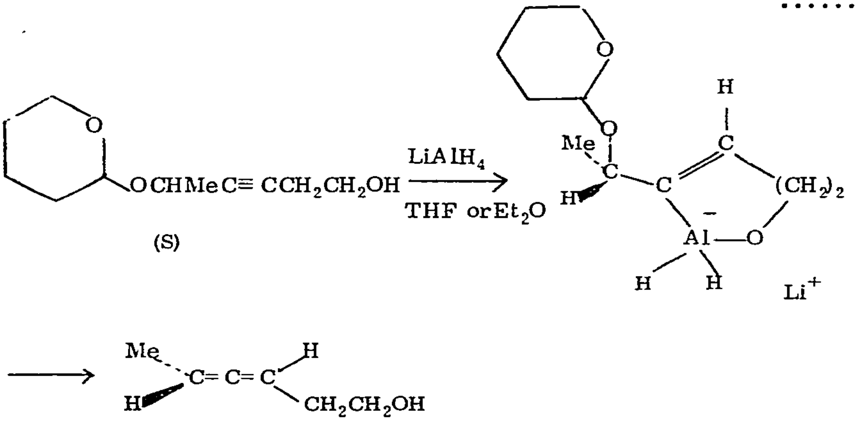

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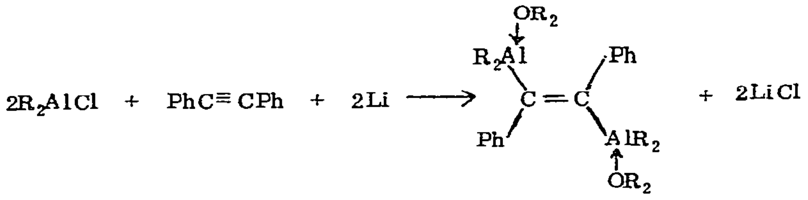
The formation of chiral allenic alcohols from alkynols is also thought to involve an intramolecular hydroalumination, this time on an alkynyl group (Equation 14) [66]. Enantiomeric purities of 75-90% may be achieved.

The reaction between halides $R_2AlCl$ (R = Et, $Pr^i$, $Bu^i$, or Ph) and the alkyne PhC≡CPh in the presence of lithium sand in ether or THF yields the <u>trans</u>-dialuminium stilbenes (29) which may be obtained as colourless crystals. (Equation 15).

It would be interesting to know more about the mechanism of this unusual reaction [67]. The reaction between 1, 2-diphenylethyne and ethylaluminium chlorides has also been studied in the absence of lithium metal [68]. The products are phenylalkenes or phenylalkanes, and may also involve incorporation of solvent. Some

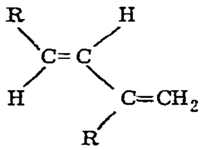


$$2R_2AlCl + PhC\equiv CPh + 2Li \longrightarrow (29) + 2LiCl \quad ........15$$

(29)

1, 2, 3-triphenylazulene is also observed.

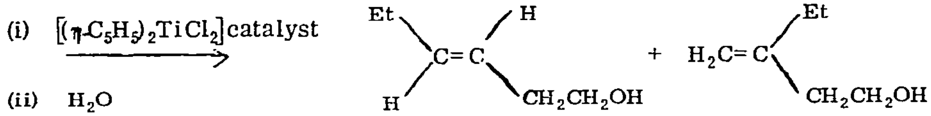
The reactions between organoaluminium compounds and alkynes may be catalysed by transition metal compounds. Thus the reaction between alk-1-ynes and trisobutylaluminium in the presence of catalytic amounts of bis(N-methylsalicylaldimine)nickel, yields the head-to-tail dimers (30 R = Bu$^n$, EtCHMe-, Pr$^i$CHMe-, Bu$^t$CHMe-, EtCHMeCH$_2$-, EtCHMe(CH$_2$)$_2$-) which are not otherwise readily available. Other products are 1, 3, 5- and 1, 2, 4-trialkylbenzenes. The optimum Bu$^i_3$Al/Ni mole ratio for formation of dimeric and trimeric products seems to be about 60. Formation of dienes relative to aromatic compounds is favoured by substitution at the 3-position of the alk-1-yne and by an excess of trisobutylaluminium over alkyne [69]. Experiments with chiral alkynes show that both dimerisation and cyclotrimerisation occur without racemisation [70]. For preparation of optically active trialkylbenzenes from chiral alkynes catalysis by trisobutylaluminium/titanium chloride appears to be better than catalysis by trisobutylaluminium /bis-(N-methylsalicylaldimine)nickel.



(30)

The alkylation of alkynols with organoaluminium reagents may be promoted by bis($\eta$-cyclopentadienyl)titanium dichloride (Equation 16). The isomeric alkenols (31) and (32) are formed in about equal amounts. The alkynols $CH_3C\equiv CCH_2CH_2OH$, $HC\equiv CCH_2CH_2CH_2OH$ and $HC\equiv CCH_2CH_2CHOHCH_3$ react similarly [71]. Alkynols may also be alkylated by conversion to complexes (33 $C_5H_7O_2$ = pentane-2, 4-dionato), followed by treatment with diethylaluminium chloride or triethylaluminium (Equation 17) [72].

$$2.5\ Et_2AlCl + HC\equiv CCH_2CH_2OH \xrightarrow[CH_2CH_2]{0^0C} Al_{2.5}(OCH_2CH_2C\equiv CH)Et_4Cl_{2.5}$$

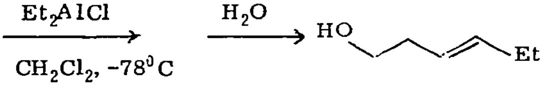


(31) (32)

........16

$$HC\equiv C(CH_2)_2OH \xrightarrow[C_5H_5N/C_6H_6]{TiCl_2(C_5H_7O_2)_2} [TiCl(OCH_2CH_2C\equiv CH)(C_5H_7O_2)_2]$$

(33)



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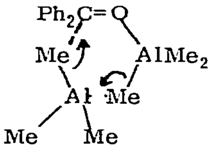
## 7. REACTIONS WITH CARBONYL COMPOUNDS

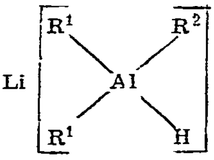
There is continued interest in the mechanism of the reactions between trimethylaluminium and ketones. Cryoscopic and NMR spectroscopic measurements on mixtures of $Al_2Me_6/Et_2O$ $Al_2Me_6/Ph_2CO$ and $Al_2Me_4Cl_2/Ph_2CO$ have been interpreted as providing more circumstantial evidence for the six-membered transition state (36) for the reaction between the complex $Ph_2CO{,}AlMe_3$ and trimethylaluminium [73].



(34)

The ketones $R^1COPh$ (35, $R^1$ = Et, $Pr^i$ or $Bu^t$) react with the chiral alkylaluminium compounds $[(\underline{S})\text{-}MeCHR^2CH_2]_3Al$ (36, $R^2$ = Et, $Pr^i$ or $Bu^t$) to give, after hydrolysis, the alcohols $R^1CH(OH)Ph$. The (S)-alcohol is formed in all cases except when $R^1 = R^2 = Bu^t$ in (35) and (36); then the (R)-enantiomer is formed selectively. For the ethyl ketones (35 $R^1$= Et), the optical yield of the (S)-alcohol increases as the size of $R^2$in (36) increases. This is not the case, however, for the isopropyl or t-butyl ketones (35, $R^1$= $Pr^i$ or $Bu^t$) [74]. In another study [75], the stereoselectivity of the reduction of 4-t-butylcyclohexanone with the reagents

($37$, $R^1 = Bu^i$) made from diisobutylaluminium hydride and the alkyl lithium $R^2Li$, has been examined. The highest ratio of axial (38a) to equatorial (38b) products is obtained with ($37$, $R^2 = Bu^t$). The reducing agents ($37$, $R^1 = R^2 = Pr^i$, $Bu^s$ or cyclo-$C_6H_{11}$) have also been made from dialkylmagnesium and $LiAlH_4$. They have been used to convert 2-methylcyclohexanone into 2-methylcyclohexanols with a cis/trans ratio of 68/32. The stereoselectivity of the aluminium compounds is, however, inferior to that of $Li[BBu^s{}_3H]$ [76].



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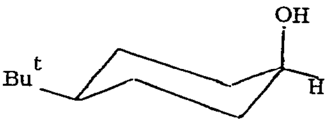
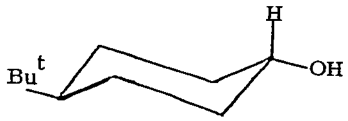


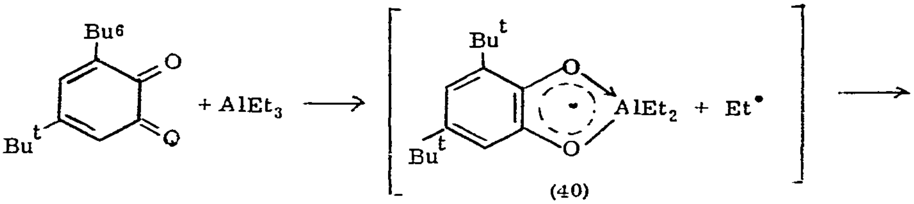
(38a)



(38b)

The reaction of tetraethylaluminates $M[AlEt_4]_2$ (M = Ca, Sr or Ba) with aldehydes was described last year. A further paper [77] gives details of reactions with benzophenone, benzoyl chloride, and acetic anhydride. The reaction between $CaAl_2Ph_8$ and benzophenone in hexane at $20^0C$ gives the crystalline donor-acceptor complex $CaAl_2Ph_8.Ph_2CO$ (39). Hydrolyses show that transfer of phenyl groups from metal to carbon is slow at $20^0$. At $100^0C$ four of the eight phenyl groups in the organometallic compound may be transferred. The corresponding reaction between benzophenone and $CaAl_2Me_8$ shows that six Al-methyl groups are transferred. It is not at present known whether calcium or aluminium is the acceptor atom in the complex (39). Benzoyl chloride reacts only slowly at $0^0C$ with $CaAl_2Ph_8$ but at $65^0C$ the complex $Ph_2CO,AlPh_3$ is obtained. The alkylaluminates $MAl_2R_8$ (R = Et or Pr) react with benzoyl chloride or acetic anhydride more readily than does $CaAl_2Ph_8$.

The o-quinones 3, 5- and 3, 6-di-t-butyl-1, 2-benzoquinone react with alkyls of group III elements $MEt_3$ (M = Al, Ga, In or Tl) at $-96^0C$ to give coloured solutions which slowly fade [78]. After warming and hydrolysis a mixture of isomeric phenols may be isolated. These observations have been interpreted in terms of reactions such as 18.



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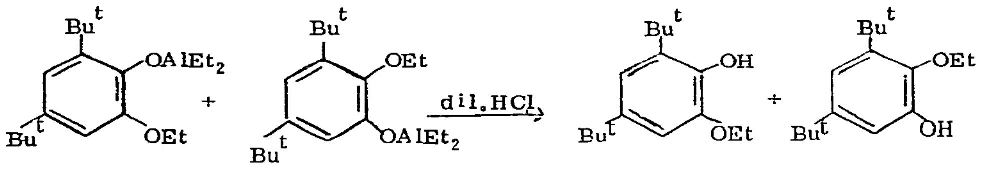

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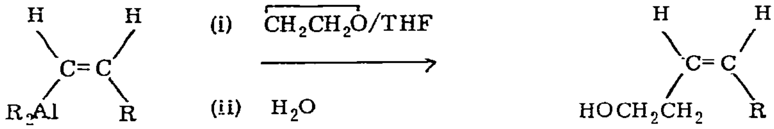
The radical (40) is detected by ESR, and formation of the ethyl radical is inferred from disproportionation products, or products from attack on solvent.

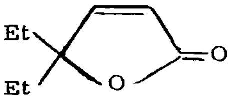
A detailed study [79] has been made of the reaction between alkenylaluminium compounds (41, R = Et, $Bu^n$, $Bu^i$, $C_6H_{13}$ or $C_8H_{17}$) and epoxides. In the presence of strongly basic ethers the main product from compounds (41) and ethylene oxide is the cis-alkenol (42) (Equation 19). In weakly basic solvents,



(41) (42) ……….19

30-40% of the reactant (41, R=Et) is converted to the (2-ethylcyclopropyl)methanol an isomer of (42). With propylene oxide the main product is that from alkylation at the less-substituted carbon. An excess of ether also stabilises the alkenylaluminium compounds (41) themselves, apparently by slowing down formation of dialuminium species,e.g.. $(Et_2Al)_2CHCHEtCH{=}CHEt$. A large excess of the cyclic ether leads to high-boiling products by multiple insertion reactions.

The reactions of alkyl derivatives of zinc, magnesium, lithium and aluminium with methyl formate have been compared [80]. Although RZnBr, RMgBr, and RLi (R = $CH_2{=}CHCH_2$) give both $(CH_2{=}CHCH_2)_2CHOH$ (43) and $CH_2{=}CHCH_2$-$CHMeCH_2OH$, $R_3Al_2Br_3$ gives only (43). The lactone (44) reacts with triethylaluminium to give after hydrolysis the ether (45) but (46) gives a more complicated mixture



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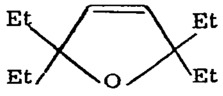

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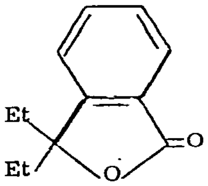
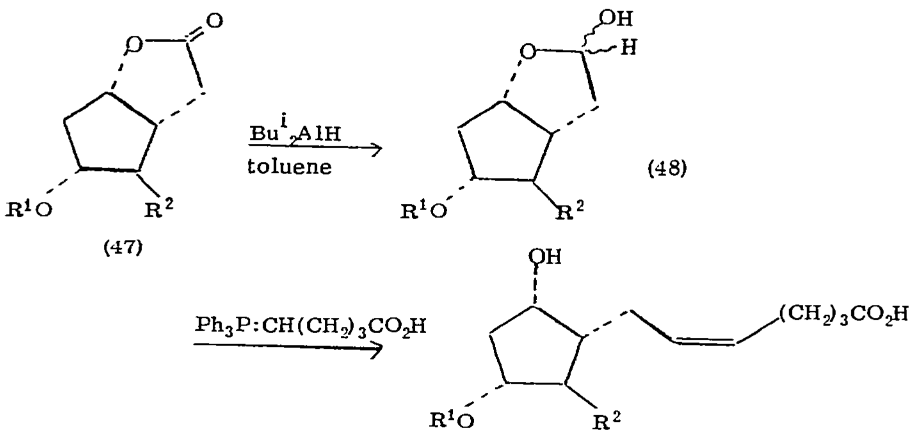


(46)

of products [81]. Diisobutylaluminium hydride in toluene at $-70$ to $-40^0$C has become a standard reagent, in synthesis of prostaglandins and related compounds, for reduction of the lactone (47) to the hemiacetal (48) before introduction of the second chain by a Wittig reaction (Equation 20). Many examples of this [82-86] and similar [87-90] procedures have been described.



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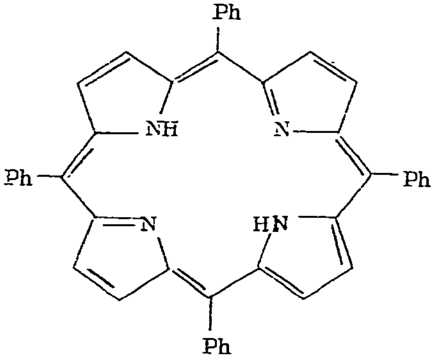
As part of an investigation of the background to photosynthesis, the reaction between tetraphenylporphin (TPP $H_2$) (49) and triethylaluminium has been examined [91]. The products are ethane and a compound TPPAlEt (50) which



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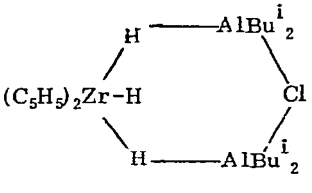


(51)

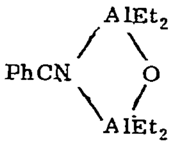
absorbs carbon dioxide in the presence of 1-methylimidazole and visible light. Propioni acid, the product from insertion of $CO_2$ into the Al-Et bond, is detected in the solution obtained on acidification of the reaction mixture. It is likely that a donor-acceptor complex is formed between compound (50) and 1-methylimidazole. Since neither triethylaluminium nor 1-methylimidazole absorbs in the visible, the Al-Et bond seems to be activated by absorption of the porphin ring.

A quite different system which is able to also activate small molecules towards reaction with organoaluminium compounds is obtained from bis(cyclopentadienyl)zirconium dichloride and diisobutylaluminium hydride. These compounds react to give a complex formulated as (51), which absorbs carbon monoxide (2 mol.) at 1-4 atm. and 20°C. More carbon monoxide may be absorbed after treatment of complex (51) with more diisobutylaluminium hydride. After hydrolysis a mixture of linear alcohols $CH_3OH$ - $C_4H_9OH$ is obtained. Experiments with $^{13}CO$ show that $^{13}C$ is incorporated into each unit of the alcohol chain. 2-Methylprop-1-ene and cis- and trans-$Me_2CHCH_2CH=CHCHMe_2$ (from alkylation of CO,followed by reduction and elimination) are also produced [92].

## 8. ORGANOALUMINIUM ALKOXIDES AND RELATED COMPOUNDS

The oxidation of but-2-enylaluminium sesquibromide by air at -80 to -100°C has been studied [93]. The reduction by triphenylphosphine of the peroxides produced gives $MeCHOHCH=CH_2$ (70%), from $MeCH(OOAlR_2)CH=CH_2$ (R = Br or $CH_2$-CH=CH-Me), E-$MeCH=CHCH_2OH$ (22%) and Z-$MeCH=CHCH_2OH$ (8%),from $MeCH=CHCH_2OOAlR_2$.

Patents describe the preparation of aluminoxanes by hydrolysis of alkylaluminium chlorides [94] and by treatment of alkylaluminium chlorides with lead(II) oxide [95]. IR and NMR spectra of mixtures of trimethylaluminium and water in dimethoxymethane are said [96] to show the presence of complexes of dimethylaluminium hydroxide, $[Me_2AlOH(MeOCH_2OMe)_n]$ n = 1 or 2. Above -15°C, these complexes react with any excess of trimethylaluminium to form complexes of tetramethylaluminoxane $(Me_2Al)_2O$. The ethyl compound $(Et_2Al)_2O$ was described in the 1976 Survey. A further paper [97] describing cryoscopic, IR and NMR studies suggests that with benzonitrile this forms a complex (52). The phenoxides $2\text{-}XC_6H_4OAlMe_2$ (X = Me, MeO or Cl) are associated in benzene,



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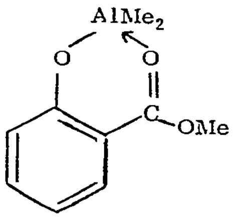

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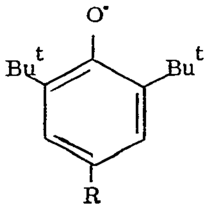
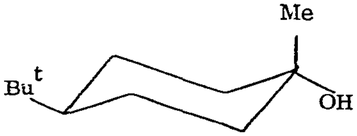


(54)

perhaps because the aluminium octet is completed by inter- rather than intramolecular coordination [98]. $2\text{-MeOCOC}_6H_4OAlMe_2$ is, however, monomeric. Support for the chelate structure (53) is claimed from IR and NMR spectra and from a study of complex formation with the strong donor hexamethylphosphoramide. Compound (53) forms the weakest complexes of the series of Lewis acids studied ($Me_3Al$, $AlCl_3$ and phenoxides $2\text{-XC}_6H_4OAlMe_2$ and $3,4\text{-Cl}_2C_6H_3OAlMe_2$). The phenoxides react with traces of air to give yellow solutions. ESR spectra show that these contain 2,6-di-t-butyl-4-alkylphenoxy radicals (54, R = Me or $Bu^t$) together with unidentified radicals containing aluminium and 2,6-di-t-butyl-4-alkylphenoxy groups [99].

The reactions between methylaluminoxanes and 4-t-butylcyclohexanone gives hydrolysis products which contain 60-65% of the axial alcohol (55) and 35-40% of the equatorial (56), suggesting that methylation is predominantly from the equatorial side [100]. By comparison, methylation of 4-t-butylcyclohexanone using trimethylaluminium-etherate gives a mixture containing 75% of the axial alcohol. No addition of the Al-O bond across the carbonyl function is observed.

(55)

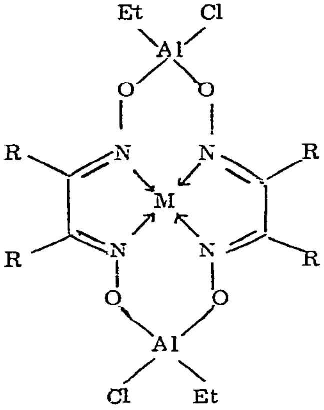


(56)

The high thermal stability of diethyl(neopentyloxy)aluminium, which is unchanged after 40 h at 230°C, is attributed to the lack of β-hydrogen atoms [101]. It was shown some years ago that when the compound $Ph_3SiOAlMe_2$ was heated at 250°C there was extensive scrambling of phenyl and methyl groups but the SiOAl sequence was preserved. In contrast, $Ph_3COAlMe_2$ gave mainly $Ph_3CMe$. Corresponding reactions with germanium and tin derivatives are now reported [101]. When the compound $Ph_3GeOAlMe_2$ is heated at 220°C for 40 h an 86% yield of methyltriphenylgermane is obtained. The tin compound $Ph_3SnOAlMe_2$ appears to be unstable even at 20°C. Thus when $Ph_3SnOH$ is treated with trimethylaluminium the stannane $Ph_3SnMe$ is formed in 96% yield.

The main stimulus for research into organoaluminium alkoxides arises from their use as components of Ziegler-Natta catalysts (see also Section 12). Patents describe preparation of hydrocarbon-soluble material [102,103].

The dimethylglyoxime complexes (57, M = Ni, R = Me or Ph; M = Pd, R = Me) form adducts in which pyridine is coordinated to aluminium [104]. The diethylaluminium salicylaldoxime complexes (58) appear to be similar to the diisobutyl- and diphenylaluminium complexes described in earlier years [105]; the pyridine adducts are said to have the pyridine coordinated to the transition metal.



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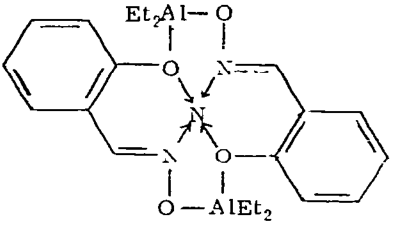
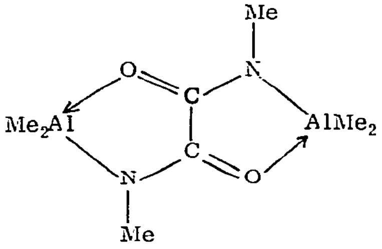


(58)

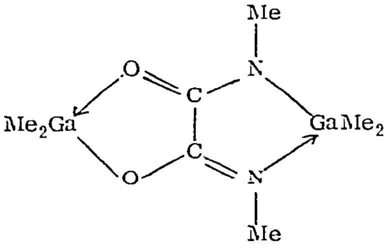
The derivatives (59, R = Me, M = Al or Ga) may be obtained by reaction 21 [106]. The aluminium compound has been shown by X-ray methods to have the

$$2Me_3M + (CONHR)_2 \longrightarrow 2CH_4 + \underset{(59)}{Me_2M(CONR)_2MMe_2} \qquad \ldots\ldots.\underline{21}$$

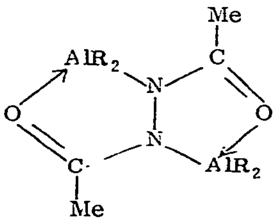
centrosymmetrical *trans*-structure (59a); in contrast, molecules in crystals of



(59a)



(59b)

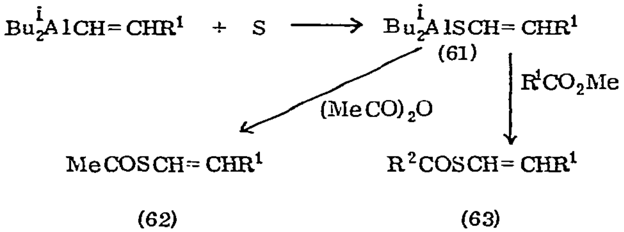


(60)

the gallium analogue have the cis-structure (59b), though NMR spectra suggest the presence of both cis- and trans-isomers in solution [106]. The reactions between trialkyls $R_3Al$ (R = Me, Et) and N,N'-diacetylhydrazine give compounds (60) which appear from spectroscopic evidence to have a centrosymmetrical $Al_2O_2N_2C_2$ skeleton [107]. The preparation of alkanesulphonates by reaction of trialkyls $(RMe_2SiCH_2)_3Al$ with sulphur trioxide has also been described [108].

## 9. ORGANOALUMINIUM SULPHIDES

Procedures have been given for the preparation of bis(dimethylaluminium) sulphide, $(Me_2Al)_2S$, from trimethylaluminium and hydrogen sulphide [109] and methylchloroaluminium sulphides $(Me_{2-n}AlCl_n)_2S$ (n = 0, 1 or 2) from $Me_{3-n}AlCl_n$ and lead(II) sulphide [110]. Alkenylaluminium compounds react with sulphur to give the sulphides (61) which may be converted with high selectivity into trans-thioenolesters (62, $R^1$ = Et, Pr, Bu or n-$C_6H_{13}$) or (63, R=Bu; $R^2$ = Me, n-$C_5H_{11}$, Ph) Equation 22 [111].



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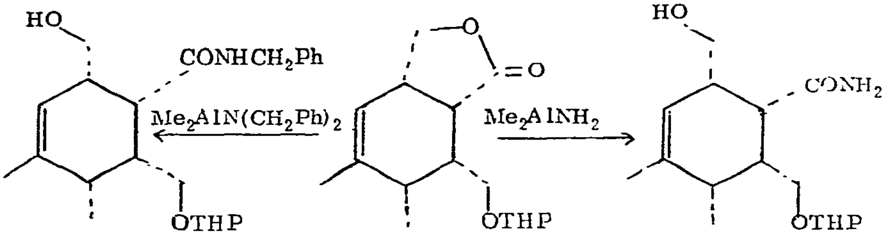
## 10. REACTIONS OF ORGANOALUMINIUM COMPOUNDS WITH ORGANIC NITROGEN AND PHOSPHORUS DERIVATIVES

Trialkylaluminium compounds react with secondary amines to form amides $(R^1_2AlNR^2_2)_n$. These compounds, which may be generated in situ or prepared as stock solutions, have been suggested as reagents for the conversion of esters to amides in high yield and under mild conditions (25-41°C in dichloromethane) [112]. For example, the lactone (64) gives an 80% yield of the amide (65) and an 83% yield of the hydroxyamide (66). (Equation 23).

The heterocycle (67) has been obtained by the reaction 24, and characterised by comparison of the IR spectrum with that of the gallium analogue [113].

Reactions between trialkylaluminium compounds and primary amines yield the oligomeric compounds $(R^1AlNR^2)_n$ which are used as initiators in the polymerisation of acrylic compounds, as cocatalysts in the polymerisation of alkenes and dienes and as stereoselective reducing agents for organic compounds e.g. steroidal diketones [114,115]. Syntheses of oligomeric

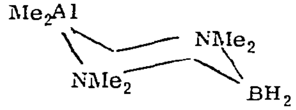


(65) (64) (66) .......23

THP = tetrahydropyranyl

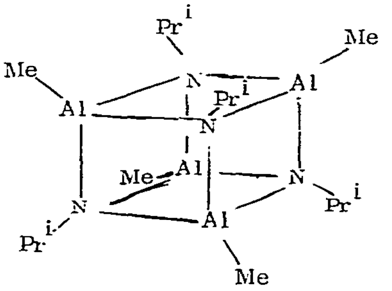
$$[(Me_3N)_2BH_2]Cl + 2BuLi \longrightarrow Me_2NCH_2BH_2NMe_2CH_2Li$$

$\xrightarrow{Me_2AlI}$



(67) ..........24

iminoalanes $(MeAlNPr^i)_6$, $[(EtAlNPr^i)_4(HAlNPr^i)_2]$, and $(EtAlNPr^i)_4$ have been described [116]. N-Isopropyliminoalane may be obtained as tetramer (68), from the reaction between trimethylaluminium and isopropylamine or as hexamer (69) from the alkylation of the compound $(HAlNPr^i)_6$ with trimethylaluminium. Both forms have been characterised by X-ray methods.



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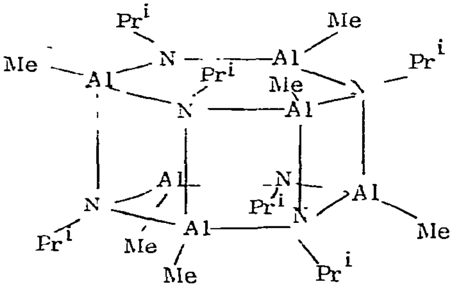


(69)

In $(MeAlNPr^i)_4$ (68) mean bond lengths are Al–N, 192.3(1), N–C 148.5(9), and Al–C 194.6(11) pm [117]. The hexamer (69) which has $\bar{3}$ symmetry is obtained as mixed crystals with $HMe_5Al_6N_6Pr^i_6$ [118]. This has random occupancy by hydrogen of one of the six sites adjacent to aluminium. The Al–N bond lengths alternate in the six membered rings [190.8(2) and 192.6(2) pm]; in the four membered rings two Al–N bond distances are 196.4(2) pm. Other bond lengths are Al–C 197.7(3) and N–C 151.4(3) pm. NMR spectra of materials of composition $[(HAlNR^2)_m(R^1AlNR^2)_n]$ are complicated because the symmetry of the $(HAlNR^2)_n$ cage is lowered by partial alkylation and because samples almost always contain mixtures of partially substituted species. Assignments have been given for $[(HAlNBu^t)_3(MeAlNBu^t)]$, $[(HAlNBu^t)_2(MeAlNBu^t)_2]$, $[(MeAlNPr^i)_4]$ and $[(EtAlNPr^i)_4]$. Signals from N-alkyl groups adjacent to Al-alkyl groups are found at higher field than those from N-alkyl groups adjacent to Al–H [119].

Trialkylaluminiums react with compounds containing unsaturated nitrogen functions to give complexes which subsequently rearrange to insertion products. The complex (70) formed between methacrylonitrile and trimethylaluminium has been detected by $^{13}C$ NMR; at 80–110°C it rearranges to the azomethine derivative (71), isolated as a pale yellow solid [120].

$$\underset{(70)}{H_2C{=}CMeCN\rightarrow AlMe_3} \longrightarrow \underset{(71)}{H_2C{=}CMe{-}CMe{=}N{-}AlMe_2}$$

The molecular complexity of (71) has not been established but kinetic measurements relating to its formation have been reported. An alternative route to azomethine derivatives of aluminium is from N-chloro-2-propanimine (72) (Equation 25).

$$\underset{(72)}{2Me_2C{=}NCl} + 2EMe_3 \longrightarrow \underset{(73)}{[Me_2C{=}NEMe_2]_2} + 2MeCl$$

$$E = B,\ Al\ \text{or}\ Ga. \qquad \ldots\ldots\ldots\ldots\ 25$$

The vibrational spectra of compounds (73) suggest that they have $D_{2h}$ symmetry with four-membered $E_2N_2$ rings [121].

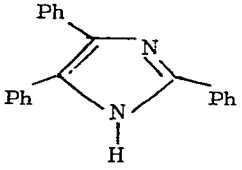
Pherylazomethines $PhCH{=}NR$ (R = Pr, Bu, cyclo-$C_6H_{11}$, $PhCH_2CH_2$, $PhCH_2$ or Ph) are reduced by trimethyl- or triisobutyl-aluminium to the secondary amines $PhCH_2NHR$ [122]. Reductions using diethylaluminium chloride are not achieved in benzene but are successful in boiling mesitylene or tetralin. The reactions between cyclic enamines e.g. N(1-cyclohexenyl)piperidine and trimethylaluminium have also been described [123]. Alkylidenephenylhydrazines e.g. PhCH=NNHPh react with triethylaluminium to give, after hydrolysis, products resulting from cleavage of the N-N bond [124].

Further details have been published of the reactions, described briefly in last year's Survey, of organoaluminium azomethine derivatives with alkali metal [125]. The compound (74) obtained from phenyl cyanide and diethylaluminium hydride, reacts with sodium or potassium to give complexes (75, M = Na or K) which may be hydrolysed to benzaldehyde and compound (76) (Equation 26).

$$\underset{(74)}{Et_2AlN{=}CPhH} \xrightarrow[C_6H_6 \text{ or } C_6H_{14}]{M} \underset{(75)}{[Et_2AlNMCHPhCHPhNMAlEt_2.2Et_2AlN{:}CPhH]}$$

$$\xrightarrow{H_2O} \underset{(76)}{H_2NCHPhCHPhNH_2} + 2PhCHO \qquad \ldots\ldots\ldots\ldots \underline{26}$$

In polar solvents such as THF or tetramethylethylenediamine, three or four molecules of (74) may condense so that, besides (76), the imidazole (77) or pyrazine (78) are obtained.



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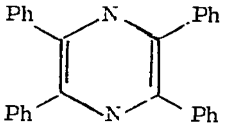
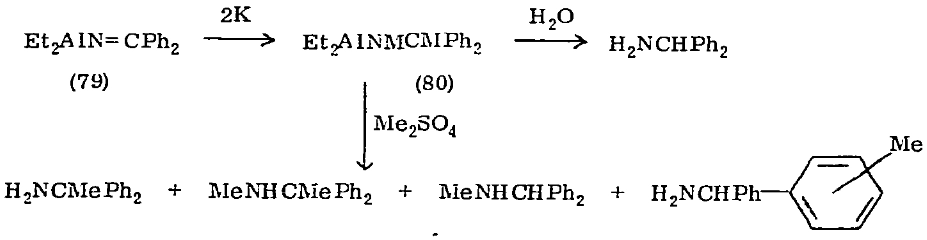


(78)

The azomethine derivative (79) reacts with potassium according to equation 27. There seems to be some charge delocalisation in the intermediate (80) since it gives both N- and C-methylated products, including those from electrophilic substitution in the aromatic ring, on treatment with dimethyl sulphate.



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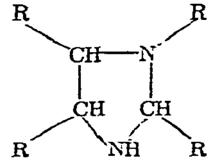
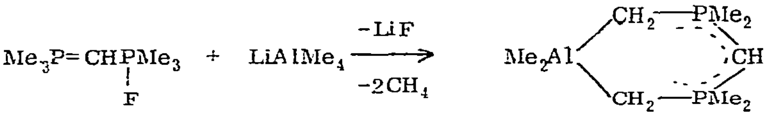
The compound $Bu^i_2AlN{=}CH$(cyclo $C_6H_{11}$) does not react with alkali metals in THF. Surprisingly, however a complex like (75) is formed in hexane and this may be hydrolysed to cyclic products such as (81, R = cyclo $C_6H_{11}$).



(81)

The diphosphido derivatives $R_2AlPPh_2$ (R = Ph, $4MeC_6H_4$, or $Bu^i$) react with cyanides $R^1CN$($R^1$ = Ph or Me) at 150-200°C to give substituted azomethine compounds $R_2AlN{=}CR^1PR_2$ [126]. Another interesting phosphorus-containing organoaluminium compound (82), obtained by the reaction 28 [127], may be



(82) .........28

considered as a derivative of the double ylide $Me_3P{=}C{=}PMe_3$ (83). The gallium analogue of (82) has also been made and its structure has been confirmed by X-ray diffraction. The ylidic character of the methine proton in (82) is shown by its high-field NMR signal. In its reaction with trimethylaluminium, the ylide (83) reacts in the tautomeric form $H_2C{=}PMe_2{-}CH{=}PMe_2{-}CH_2{-}H$ in the same way that pentane-2,4-dione reacts with trimethylaluminium as the enol O=CMe-CH=CMe-O-H

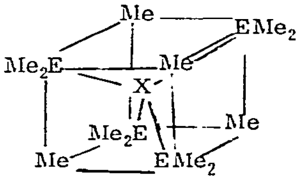
## 11. DIALKYLALUMINIUM HYDRIDES

Hydroaluminations and reductions of carbonyl functions have been discussed in Sections 6 and 7. Patents describe the formation of dialkylaluminium hydrides [33, 34, 128] and their use as reducing agents for conversion of tetra-alkoxysilanes to silane [129] and triphenylphosphine oxide to triphenylphosphine [130]. Diisobutylaluminium hydride reduces chiral silicon compounds with retention of configuration [131]; it is suggested that reagents which favour 1,2-addition to enones react with silicon compounds with retention and those that favour 1,4-addition react with inversion.

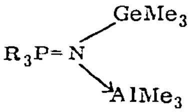
Organoaluminium ate-complexes $LiAlH_nR_{4-n}$ (R = Me, Et or Ph) have been detected in ether solutions of lithium aluminium hydride and methyl- or phenyl-lithium [75, 132]-magnesium [76, 133] or -zinc [134-136] derivatives. Details have been given of complex equilibria involved.

## 12. DONOR-ACCEPTOR COMPLEXES

Syntheses of dioxan complexes of diethylaluminium halides have been described [137]. Molecular orbital calculations have been made on the complexes of trimethylaluminium with ammonia, methyl-, ethyl-, dimethyl-, trimethyl- [138] and triethyl-amine and with trimethylphosphine [139]. There are still considerable difficulties in calculating dissociation energies of such complexes from first principles. The compounds $M_2X$ (M = K or Cs; X = O, S or Se) form a series of complexes with trimethyl-aluminium, -gallium, or -indium. Vibrational spectra suggest that these contain the ions (84, E = Al, Ga or In) in which the Group VI anions are surrounded tetrahedrally by metal atoms linked also by bridging methyl groups [140]. Other donor-acceptor complexes of trimethylaluminium are with N-trimethylgermylphosphinimines (85, $R_3$ = $\mathrm{Pr}^n_3$, $\mathrm{Pr}^i_3$, $\mathrm{PhMe_2}$, $\mathrm{Bu^iMe_2}$, $\mathrm{Bu}^n_3$, $\mathrm{Bu}^i_3$, $\mathrm{Ph_3}$ or $\mathrm{Bu^t_2Me}$ but not $\mathrm{Bu}^t_3$) [141] and with uranium(VI)hexaisopropoxide, [142]. The complex $(\mathrm{Me_3Al})_6\mathrm{U(OPr^i)_6}$ is an involatile green oil, for which structure (86) is proposed. Uranium(VI) chloride is reduced to uranium metal by trimethylaluminium. The compound $[\mathrm{Bu_4N}][\mathrm{AlMe_3I}]$ has been



(84)



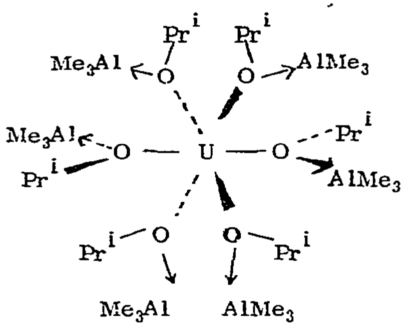
(85)

made for comparison with the complex borohydride $[\mathrm{Bu_4N}][\mathrm{Al(BH_4)_3I}]$ [143], and the complexes $[\mathrm{M(Al_2R_6)NO_3}]$ (M = K, Rb, Cs or $\mathrm{Et_4N}$; R = Me or Et), which form liquid clathrates with aromatic hydrocarbons, have now been described in a patent [144] (c.f. previous Annual Surveys). Ethylaluminium dichloride, but not diethylaluminium chloride or tri ethylaluminium, is effective in promoting conversion of carbene complexes of tungsten to carbyne complexes, but none of the alkylaluminium compounds is as efficient as aluminium(III) chloride [145].

## 13. REACTIONS OF ORGANOALUMINIUM COMPOUNDS WITH TRANSITION METAL DERIVATIVES

The increasing emphasis on transition metal catalysed reactions of organoaluminium compounds has led to continued attempts to characterise species containing both aluminium and another metal.

The reaction between the alkoxide $Ce(OPr^i)_4,L$ ($L = Pr^iOH$ or pyridine) and triethylaluminium at about 100°C in the presence of cyclooctatetraene gives a yellow crystalline complex formulated as (87), on the basis of evidence from IR, NMR and mass spectra and decomposition with alcohol or $D_2O$. Compound (87) forms a crystalline adduct with methyl cyanide but the base may be easily removed in vacuum [146].



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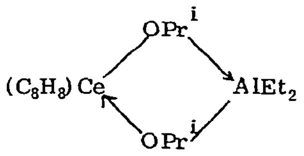
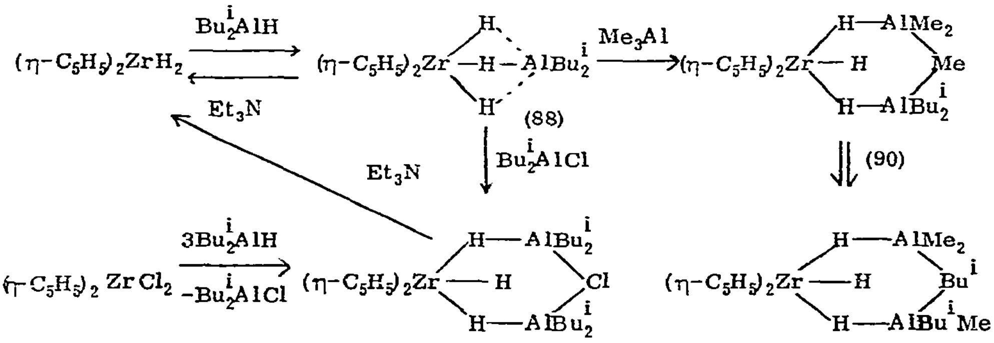


(87)

A study by NMR and cryoscopic techniques [147] of the reactions between diisobutylaluminium hydride and bis(cyclopentadienyl)zirconium derivatives $(\eta\text{-}C_5H_5)_2ZrX_2$ (X = Cl, H or alkyl) has revealed the formation of mixed metal hydride complexes such as (88-93). These species must be considered in discussion of zirconium-promoted reactions of aluminium hydrides.



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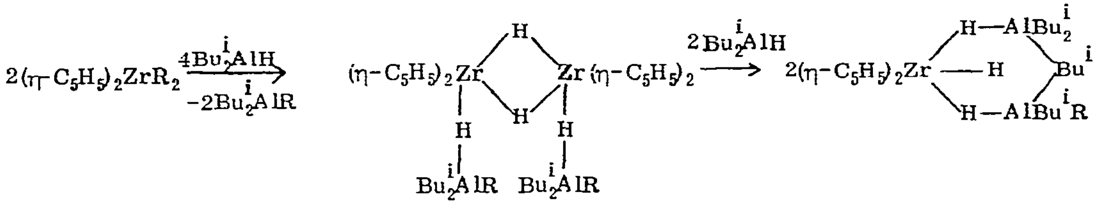
(91)



(92) (93)

R = $Bu^tCH_2CH_2$-

Sometimes, however, mixed metal species are not obtained, and the organoaluminium compounds serve as reducing agents. For example, the compound $[Nb(\eta-C_5H_5)Cl_4]$ reacts with ethylaluminium dichloride in the presence of 1, 2-bisdiphenylphosphinoethane (dppe) to give the Nb(III) derivative $[Nb(\eta-C_5H_5)Cl_3$-(dppe)] [148]. The tantalum compound $[Ta(\eta-C_5H_5)Cl_4]$ may be reduced by ethylaluminium dichloride to the compound $[Ta(\eta-C_5H_5)_2Cl_2]$ and tris(pentane-2, 4-dionato)molybdenum(III) may be reduced by triethylaluminium in the presence of dppe to give the seven-coordinate molybdenum(II) compound $[MoH(C_5H_7O_2)(dppe)_2]$ [149]. The reduction of tris(pentane-2, 4-dionato)iron with triethylaluminium in the presence of dppe at $-78^0C$ yields $[FeH_2(dppe)_2]$, assumed to be formed by decomposition of the alkyl $[FeEt_2(dppe)_2]$ formed initially. At $0^0C$ however, with less aluminium alkyl, it is possible to isolate the golden yellow crystalline complex $[Fe(dppe)(C_5H_7O_2)_2]$ [150].

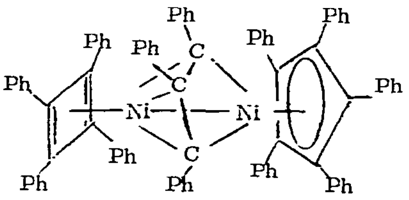
There have been two more reports on the reactions between tris(pentane-2, 4-dionato)cobalt and trimethyl- or triethyl-aluminium in the presence of 2, 2'-bipyridyl. High yields of the complexes $[CoR_2(bipy)_2][AlR_4]$ (R = Me or Et) are obtained from mixtures $[Co(C_5H_7O_2)_3]$ + 4 bipy + $8AlR_3$. Surprisingly the complexes are said to be "fairly stable" in air or in acetone. The tetralkylaluminate ion may be replaced $BPh_4^-$ or $Cl^-$ (with $CH_2Cl_2$ of crystallisation) [151]. With smaller $Me_3Al/[Co(C_5H_7O_2)_3]$ mole ratios, pure products, except for the pentane-2, 4-dionato derivatives $[Al(C_5H_7O_2)_3]$ or $[Me_2Al(C_5H_7O_2)]$ have not been isolated, but there is evidence for transfer of alkyl groups from aluminium to cobalt [152]. The reaction between bis(pentane-2, 4-dionato)nickel and tribenzylaluminium in the presence of triphenylphosphine and diethyl ether gives the benzylnickel compound $[Ni(C_5H_7O_2)(PhCH_2)(PPh_3), OEt_2]$. Benzyl-cobalt and -iron compounds also may be made [153]. The ethylnickel compound $[Ni(C_5H_7O_2)Et(PPh_3]$ made similarly from bis(pentane-2, 4-dionato)nickel and triethylaluminium, reacts with an excess of triethylaluminium at $-40^0C$ in the presence of triphenylphosphine to give $[Ni(\eta-C_2H_4)(PPh_3)_2]$ as the main product, probably by intermediate formation of an ethylnickel compound. Under similar conditions, diethyaluminium chloride gives the unstable orange substance [$NiClEt(PPh_3)_2$] and diethylaluminium bromide the nickel hydride [$NiBrH(PPh_3)_3$]. This may be obtained together with [$NiBr_2(PPh_3)_2$] from bis(pentane-2, 4-dionato)nickel and diethylaluminium bromide (Equations 29 and 30).

$$[Ni(C_5H_7O_2)_2] \quad + \quad 3Ph_3P \quad + \quad Et_2AlBr \longrightarrow \underset{(94)}{[NiBrH(PPh_3)_3]} \quad \ldots\ldots\ldots \quad \underline{29}$$

$$[Ni(C_5H_7O_2)_2] \quad + \quad 2Ph_3P \quad + \quad 2Et_2AlBr \longrightarrow \underset{(95)}{(Ph_3P)_2NiBr_2} \quad \ldots\ldots\ldots \quad \underline{30}$$

Highest yields of the product (94) are obtained with Ni:P:Al ratios of 1:1:0.16; Product (95) may be obtained quantitatively with reactant ratios 1:3:2. The compound [$NiBr_2(PPh_3)_2$] is not an intermediate in reaction 29 [154]. Nickel(II) stearate is reduced by triethylaluminium or ethylaluminium chlorides in benzene to give a number of soluble nickel complexes and precipitation of nickel(II)chloride and metallic nickel. The relative amounts of these products depend on the starting aluminium compounds and the Al/Ni mole ratio. Six alkylaluminium fragments are required for complete reduction of one nickel stearate molecule. The alkylaluminium chlorides are found to have greater reducing power than triethylaluminium but the reasons for this are not yet clear [155].

The structure of the organometallic compound (5), containing both aluminium and nickel has been described in Section 2 above. An attempt to make the compound [$(Ph_5C_4Al)_2Ni$], related to (5), by treatment of the dialkyl compound (2) with lithium powder and nickel(II)bromide, was unsuccessful [156]. The products were the nickel compounds (96) and [$C_4Ph_4NiC_4Ph_4$] (97). The structure of (96) has been confirmed by an X-ray study, but the formulation of (97) as a biscyclobutane complex is not established. It would be interesting to know how the $C_5Ph_5$ and $C_3Ph_3$ units of (96) are formed from the $C_4Ph_4$ units of (2).



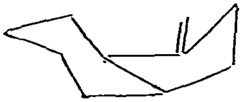
(96)

## 12. CATALYSIS

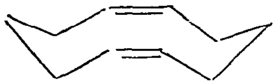
The isomerisation of heptenes has been studied using as catalyst triisobutylaluminium/bis(N-methylsalicylideneamine)nickel at $25^0$ without solvent. Linear heptenes are converted mainly to E-hept-2-ene, but branched-chain internal alkenes are largely unchanged. (S)4-methylhex-1-ene is converted to (S)-4-methylhex-2-ene without racemisation, and this suggests that the reaction may be useful for preparation of chiral alkenes. The mechanism is not clear but it may involve hydridonickel species [157].

Isomerisations of dienes or trienes using trisobutylaluminium have also been described [158, 159]. Cis-trans-cyclodeca-1, 5-diene(97) is isomerised, slowly at $40^0$C and more rapidly on heating, to the alkene (98). Cis, cis-cyclodeca-1, 6-diene (99) is recovered unchanged even after 20 h at $200^0$C[158]. Trans-d 1,4,9-triene (100) is isomerised at 160-$230^0$C to (98) (10-35%) and the hydrocarbon $C_{10}H_{18}$ (101) (12-40%). Considerable amounts of unidentified higher oligomers

(97)

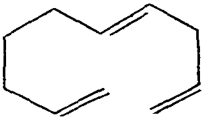


(98)

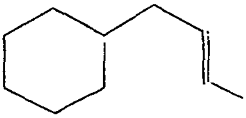


(99)

are also formed [159]. It is suggested that the starting compounds (97) and (100) give the same organoaluminium precursors of (98), but that the reaction of (100) with triisobutylaluminium gives in addition an alternative organoaluminium intermediate which leads to (101).



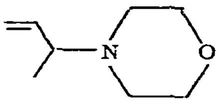
(100)

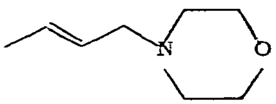


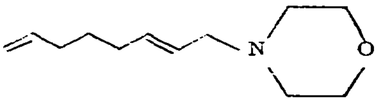
(101)

As in previous years, there is an extensive series of papers on alkene metathesis [11]. The compounds $[MoCl(NO)(CO)_2L_2]$ (L = $PPh_3$ or $AsPh_3$) have been isolated from solutions of $MoCl_3(NO)$ or $MoCl_3(NO)L_2$ with ethylaluminium dichloride in dichloromethane under carbon monoxide [160]. The metathesis of alkenes using $[Mo(CO)_5py]/RAlCl_2/Bu_4NCl$ (R = Me or Et) [161] and of deca-2, 8-diene with $Me_3Al_2Cl_3/[MoCl_2(NO)_2(PPh_3)]$ [162]. has been interpreted in terms of the well established mechanism involving metal-carbene intermediates. Evidence has been obtained from IR studies for interaction between the carbonyl oxygen and ethylaluminium dichloride as a Lewis acid, probably assisting in formation of unsaturated low-valent tungsten species [163]. The influence of solvent and Lewis acids, e.g., ethanol, ethylamine, triphenylphosphine, pyridine or dipyridyl on the $WCl_6/EtAlCl_2$ system has also been discussed [164]. Although metatheses of alkenes with primary or tertiary amino groups are not achieved with many catalysts, alkenes with quaternary amino groups e.g. $CH_2{=}CHCH_2NMe_3$-Br or trans $MeCH{=}CH(CH_2)_3NMe_3I$ (102). may be converted by [W(mesitylene)(CO)$_3$] / $EtAlCl_2/O_2$ or $[MoCl_2(NO)_2(PPh_3)_2]$ /$EtAlCl_2$ into α-ω derivatives, e.g., $[Me_3N(CH_2)_3CH{=}CH(CH_2)_3NMe_3]^{2+}2I^-$ from (102) [165]. Details of the activation procedures of catalysts $[W(C_5H_5)(CO)_3MR_3]$ (M = Ge or Sn, R = Me or Ph) by $Bu^iAlCl_2/O_2$ have also been described [166]. A metathesis catalyst may be obtained by attachment of $[Mo(Ph_3P)_2(NO)_2Cl_2]$ to polystyrene followed by activation using methylaluminium sesquichloride [167].

Organoaluminium compounds have been used as catalysts for reactions of butadiene with a series of substrates. For example, butadiene reacts with morpholine in the presence of triethylaluminium and bis(pentane-2,4-dionato) nickel to give the products (103)-(105).

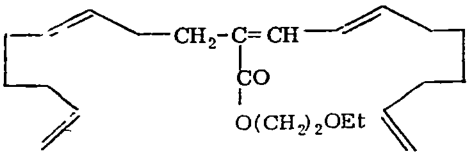

(103)


(104)

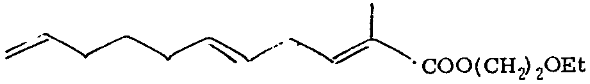

(105)

Good yields of each of the compounds (103)-(105) may be obtained by addition of appropriate phosphorus-containing donors e.g. $Bu_3P$ for (104), $PCl_3$ for (103), and $(p\text{-}PhC_6H_4O)_3P$ for (105) [168]. Similar control of reaction products by addition of donors is observed in the reactions between butadiene and esters of acrylic or methacrylic acids. For example, the main products from butadiene and 2-ethoxyethyl methacrylate at 80°C with $[Ni(C_5H_7O_2)_2]/AlEt_3$ are (106) and (107), and formation of (106) is favoured by addition of strong donors. The main product from butadiene and phenyl methacrylate is the compound (108) [169].

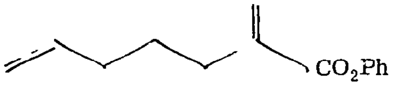
The catalytic system $Ni(C_5H_7O_2)_2$ / $Ph_3P$ /$Et_3Al$, may also be used for the reactions between butadiene and various silanes. Thus butadiene and trimethoxyvinylsilane give 1-trimethoxysilyldeca-2,5(or 6),9-triene (109) [170], and acrylonitrile and dimethylsilane react to give $Me_2SiHCHMeCN$ [171]. Hydrosilylations



(106)



(107)



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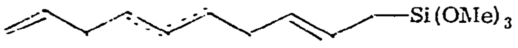

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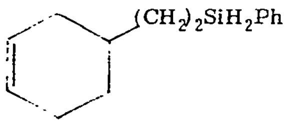

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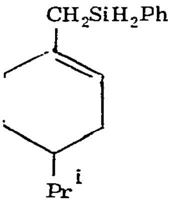
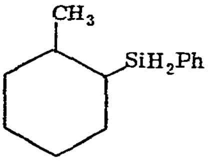
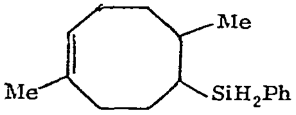


(111)

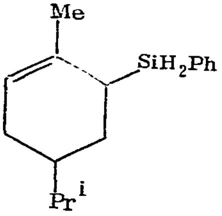
of $CH_2{=}CMeCO_2Me$, $(CH_2{=}CHCH_2)_2O$, and a number of deuteriosilylations [172] have also been described. Hydrosilylation of vinylcyclohexene with phenylsilane gives the product (110) but better yields are obtained with bis(formylcamphorato)nickel in place of bis(pentane-2, 4-dionato)nickel(II) [173]. All the nickel catalysts, however, give some disproportionation of phenylsilane into diphenylsilane and silane: the molybdenum complex $MoO_2(C_5H_7O_2)_2$ is even more active in this respect but the vanadium compound $VO(C_5H_7O_2)_2$ catalyses the hydrosilylation cleanly without disproportionation. Cycloocta-1, 5-diene, but not the 1, 3-isomer may be hydrosilylated but β-pinene reacts with opening of the cyclobutane ring and formation of the compound (111). Hydrosilylation of trisubstituted double bonds requires severe conditions. Oxobis(pentane-2,4-dionato)vanadium is used in preference to Ni or Mo compounds to avoid silane disproportionation and tris-(3-methylhepta-4,6-dienyl)aluminium or tris(pent-2-enyl)aluminium, made from triisobutylaluminium and penta-1,3-diene, are used in place of triisobutyl- or triethyl-aluminium. Under these conditions methylcyclohex-1-ene gives (2 methylcyclohexyl)phenylsilane (112) and 1,5-dimethylcycloocta-1,5-diene gives the silane (113). α-Pinene reacts with cleavage of the cyclobutane ring to give (114) [174]. The hydrosilylation of cyclohexadienes by triethoxysilane and using $Ni(C_5H_7O_2)_2$



(112)

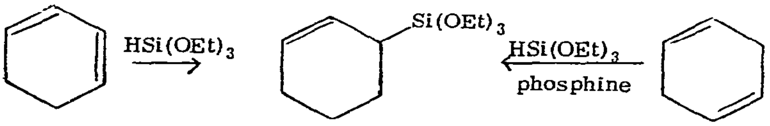


(113)



(114)

$AlEt_3$ as catalyst has also been described [175]. The main product from both 1,3 and 1,4-isomers is the cyclohexenylsilane (115). Equation 22.



(115)

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Hydrosilylation of *cis*-penta-1,3-diene using the same catalyst gives $MeCH_2CH=CHCH_2Si(OEt)_3$ and $MeCH=CHCHMeSi(OEt)_3$ in the mole ratio 85:15. *Trans*-penta-1,3-diene appears to react faster than the *cis*-isomer.

Ziegler catalysts [13] for polymerisation and oligomerisation of alkenes have been obtained from $\eta^3$-allyl derivatives of transition metals and organoaluminium compounds [176]. A further note describes the effect of oxygen on the $Et_2AlCl$ $TiCl_3$ catalyst for propene or but-1-ene polymerisation. If small amounts of oxygen are admitted to the aluminium compound before addition of titanium trichloride, there is a marked increase in polymerisation activity without decrease in stereoregularity. Since similar effects are observed when ethanol is added in place of oxygen, it is thought that the enhanced catalytic activity may be associated with ethoxyaluminium compounds. Compare [102, 163, 164].

Chiral Ziegler-Natta catalysts, prepared, for example, from titanium(IV) chloride and a mixture of triisobutylaluminium and α-pinene, will selectively polymerise one enantiomer in a racemic mixture of alkenes. An account of experiments with a range of racemic alkenes has been published [178], but stereoselectivities achieved so far have been low. Cyclohexene may be polymerised under mild conditions (110°C for 24 h) using the $Re(CO)_5Cl/EtAlCl_2$ catalyst system. The polymer has a molecular weight 500-5000 (average 2500); spectroscopic evidence suggests that it is fully saturated and that the rings are retained [179].

Triethylaluminium has little effect on the polymerisation of methyl methacrylate in the presence of azobisisobutyronitrile (AIBN) as initiator, provided that the concentration of $Et_3Al$ is less than four times that of the AIBN. At $Et_3Al$/AIBN ratios of 4-5, however, there is a sudden decrease in yield and molecular weight. One mole of methyl methacrylate oligomer appears to be formed for every mole of $Et_3Al$ in excess of four times the AIBN concentration [180]. Triethylaluminium is also a concentration-dependent coinitiator and chain-transfer agent for radical polymerisation of methyl methacrylate in the presence of benzoquinone.

Organoaluminium compounds may act as Lewis acids, e.g., with benzyl chlorides, in systems for initiating cationic polymerisations. The reaction between $p\text{-}MeC_6H_4CH_2Cl$ and triethylaluminium in dichloromethane at -50 to -80°C has been shown to yield $p\text{-}MeC_6H_4CH_2Et$, $p\text{-}MeC_6H_4CH_3$ and oligomeric polybenzyls. The first two are thought to be formed from the $[p\text{-}MeC_6H_4CH_2]^+ [Et_3AlCl]^-$ ion pair and the polybenzyls from the $[p\text{-}MeC_6H_4CH_2]^+[Et_2AlCl_2]^-$ion pair [181]. Organoaluminium compounds are also used as Lewis acids in the tritiation of hydrocarbons with ethylaluminium dichloride and highly active tritiated water. The work described in previous Surveys on aromatic compounds and alkenes has been extended to alkanes [182]. Labelling of both cyclic and non-cyclic alkanes is observed for all molecules with at least one hydrogen attached to a tertiary carbon atom. Small amounts of impurities from skeletal isomerisation are observed, but these may normally be removed by gas chromatography. The complex $PbMe_3Cl$, $AlMeCl_2$ catalyses formation of the alkyls $PbMe_3Et$, $PhMe_2Et_2$ and $PbMeEt_3$ from mixtures of tetramethyl- and tetraethyl-lead [183].

## REFERENCES

1. E.W. Abel and F.G.A. Stone (Eds), 'Organometallic Chemistry', Vol 6, Chemical Society, London, (1978).
2. J.P. Maher, ref 1, p 80.

3. A.D. Redhouse in ref 1; M.B. Hursthouse in G.A. Sim and L.E. Sutton (Eds), 'Molecular Structure by Diffraction Methods Vol 4, Chemical Society, London (1976), p. 365.
4. T.R. Spalding in R.A.W. Johnstone (Ed), 'Mass Spectrometry,' Vol 4, Chemical Society, London (1977), p 268.
5. E.A.V. Ebsworth (Ed), 'Spectroscopic Properties of Inorganic and Organometallic Compounds', Vol 10, Chemical Society, London (1977), 1976 literature.
6. B.H. Freeland in H. Zimmer (Ed), 'Annual Reports in Inorganic and General Synthesis', Vol 5, Academic Press, New York (1977).
7. T.R. Crompton, 'Chemical Analysis of Organometallic Compounds', Vol 5, Academic Press, New York (1977), p 115.
8. J.P. Oliver, Adv. Organometal. Chem., 15 (1977) 235.
9. J.J. Eisch, Adv. Organometal. Chem., 16 (1977) 67.
10. J.P. Oliver, Adv. Organometal. Chem., 16 (1977) 111.
11. T.J. Katz, Adv. Organometal. Chem., 16 (1977) 283; J.J. Rooney and A. Stewart in ref 12, p 277.
12. C. Kemball (Ed), 'Catalysis', Vol 1, Chemical Society, London (1977).
13. A.D. Caunt in ref. 12, p 234.
14. D.H. Richards, Chem. Soc. Rev., 6 (1977) 235.
15. Yu. A. Aleksandrov and V.P. Maslennikov, J. Organometal. Library, 3 (1977) 103.
16. O.M. Nefedov, A.I. D'yachenko and A.K. Prokof'ev, Uspekhi Khim. 46 (1977) 1787; Russ. Chem. Rev. 46 (1977) 941.
17. A.K. Prokof'ev, Uspekhi Khim. 45 (1976) 1028; Russ. Chem. Rev. 45 (1976) 519.
18. S.G. Mairanovskii, Uspekhi Khim. 45 (1976) 604; Russ. Chem. Rev. 45 (1976) 298.
19. J. Leleu, Cah. Notes Doc. 87 (1977) 241; Chem. Abs., 88 (1977) 26 958.
20. A.Haaland, S. Samdal, O. Stokkeland, and J. Weidlein, J. Organometal. Chem., 134 (1977) 165.
21. J.L. Atwood, W.E. Hunter and K.D. Crissinger, J. Organometal. Chem., 127 (1977) 403.
22. H. Hoberg, V. Gotor, A. Milchereit, C. Krüger and J.C. Sekutowski, Angew. Chem., 89 (1977) 563; Angew. Chem. Internat. Edn. 16 (1977) 539.
23. C. Krüger, J.C. Sekutowski, H. Hoberg and R. Krause-Göing, J. Organometal. Chem., 141 (1977) 141.

24. H. Hoberg and R. Krause-Göing, J. Organometal. Chem., 127 (1977) C29.

25. H. Müller, L. Rösch, W. Erb and R. Zeisberg, J. Organometal. Chem., 140 (1977) C17.

26. L. Rösch, Angew. Chem. 89 (1977) 497; Angew Chem. Internat Edn. 16 (1977) 480.

27. M.J. Albright, J.N. St Denis and J.P. Oliver, J. Organometal. Chem.,125 (1977)1.

28. J.E. Rie and J.P. Oliver, J. Organometal. Chem. 133 (1977) 147.

29. M. Uetsuki and Y. Fujiwara, Bull. Chem. Soc. Japan 50 (1977) 673.

30. V.G. Tsvetkov, B.I. Kozyrkin, K.K. Fukin and R.F.Galiullina, Zhur. obshchei Khim.,47 (1977) 2155; J. Gen. Chem. U.S.S.R., 47 (1977) 1966.

31. P.H. Kasai, D. McLeod and T. Watanabe, J. Amer. Chem. Soc., 99 (1977) 3521.

32. R. Masotti, G. Biola, H. Guerpillon, Fr. Demande 2 315 506; Chem. Abs., 87 (1977) 184 667.

33. R. Masotti, G. Biola and H. Guerpillon, Ger. Offen. 2 628 746; Chem. Abs., 87 (1977) 135 882.

34. K.H. Mueller and H.J. Hubert,South African Pat. 75 01 499; Chem. Abs., 86 (1977) 90 010.

35. N.N. Korneev, A.F. Popov and N.K. Efimov, Khim. Prom. (1977) 90; Chem. Abs., 87 (1977) 6062.

36. G. Sonnek, H. Reinheckel and K-G. Baumgarten, DDR Pat. 122 253; Chem. Abs., 87 (1977) 135 888.

37. (Schering A-G), U.K. Pat. 1 456 224; Chem. Abs., 86 (1977) 190 195.

38. B. Thomalla, M. Zawadzki and S. Skrobocz, Pol. Pat. 84 750 ; Chem. Abs., 88 (1978) 37 958.

39. L. Synoradzki, S. Pasynkiewicz and M. Bolesławski, Przemysl Chem., 56 (1977) 525.

40. M. Bolesławski, S. Pasynkiewicz, A. Kunicki and L. Synoradzki, Przemysl. Chem., 56 (1977) 462.

41. L.V. Gaponik and V.P. Mardykin, Zhur. obshchei Khim.,47 (1977) 1579; J. Gen. Chem., U.S.S.R. 47 (1977) 1448.

42. G.P. Giacomelli, L. Lardicci and M. Bagnoli, Chimica e Industria, 58 (1976) 876.

43. Yu. A. Sangalov, Yu. B. Yasman, K.S. Minsker and Z.I. Khudaiberdina, Izvest. Akad. Nauk S.S.S.R. (Seriya Khim 26 (1977) 670; Bull. Acad. Sci. U.S.S.R. (Chem.) 26 (1977) 606.

44. D.B. Carr and J. Schwartz, J. Amer. Chem. Soc. 99 (1977) 638.

45. D.B. Carr and J. Schwartz, J. Organometal. Chem., 139 (1977) C21.

46. C. Blandy, R. Guerreiro and D. Gervais, J. Organometal. Chem. 128 (1977) 415.

47. G.W. Kramer and H.C. Brown, J. Organometal. Chem. 132 (1977) 9.

48. G. Sonnek, K-G. Baumgarten and H. Reinheckel, J. Organometal. Chem., 142 (1977) 23.

49. Z.S. Novikova, A.A. Prishchenko and I.F. Lutsenko, Zhur. obshchei Khim., 47 (1977) 775; J. Gen. Chem. U.S.S.R., 47 (1977) 707.

50. V.K. Vasil'ev, V.N. Sokolov and G.P. Kondratenkov, Doklady Akad. Nauk. S.S.S.R., 236 (1977) 360; J. Organometal. Chem., 142 (1977) C7.

51. S. Baba and E-I Negishi, J. Amer. Chem. Soc., 98 (1976) 6729.

52. A.M. Kut'in, I.A. Frolov and K.K. Fukin, Zhur. fiz. Khim., 51 (1977) 511; Russ. J. Phys. Chem., 51 (1977) 301.

53. W.K. Franke, H. Pohl and V. Böhnisch, Annalen (1977) 1862.

54. (Exxon Research) U.K. Pat. 1 484 775;Chem. Abs. 88 (1978) 105 552.

55. V.P. Yur'ev, A.V. Kuchin, T.O. Yakovleva, T. Yu. Ivanova and G.A. Tolstikov,Zhur.obshchei Khim., 46 (1976) 2559; J. Gen. Chem. U.S.S.R., 46 (1976) 2444.

56. A.V. Kuchin, V.P. Yur'ev, Izvest. Akad. Nauk. S.S.S.R. (Seriya Khim), 26 (1977) 252; Bull. Acad. Sci., U.S.S.R., (Chem), 26 (1977) 226.

57. A. Alberola, J.A. Delgado and M.N. Recio, Anales de Quími, 73 (1977) 877; Chem. Abs., 87 (1977) 184 588.

58. K. Isagawa, K. Tatsumi and Y. Otsuji, Chemistry Lett. (1976) 1145.

59. K. Isagawa, K. Tatsumi, H. Kosugi and Y. Otsuji, Chemistry Lett. (1977) 1017.

60. K. Isagawa, K. Tatsumi and Y. Otsuji, Chemistry Lett. (1977) 1117.

61. F. Sato, S. Sato, and M. Sato, J. Organometal. Chem., 131 (1977) C26.

62. F. Sato, S. Sato, H. Kodama and M. Sato, J. Organometal Chem., 142 (1977) 71.

63. E.C. Ashby and S.A. Noding, Tetrahedron Lett., (1977) 4579.

64. V.P. Yur'ev, F.G. Yusupova, G. Gailyunas and G.A. Tolstikov, Zhur. obshchei Khim.,47 (1977) 2242; J. Gen. Chem. U.S.S.R., 47 (1977) 2045.

65. R. Rienäcker and D. Schwengers, Annalen (1977) 1633.

66. L-I. Olsson and A. Claesson, Acta. Chem. Scand., B31 (1977) 614.

67. H. Hoberg and V. Gotor, J. Organometal. Chem., 127 (1977) C32.

68. A. Alberola and M.C. Borque, Anales de Quím. 73 (1977) 872; Chem. Abs. 87 (1977) 184 587.

69. A.M. Caporusso, G. Giacomelli and L. Lardicci, J. Org. Chem. 42 (1977) 914.

70. G. Giacomelli, A.M. Caporusso and L. Lardicci, J.C.S. Perkin I (1977) 1333.

71. L.C. Smedley, H.E. Tweedy, R.A. Coleman and D.W. Thompson, J. Org. Chem., 42 (1977) 4147.

72. H.E. Tweedy, R.A. Coleman and D.W. Thompson, J. Organometallic Chem., 129 (1977) 69.

73. E.C. Ashby and R.S. Smith, J. Org. Chem., 42 (1977) 425.

74. R. Menicagli, A.M. Caporusso. G.P. Giacomelli and L. Lardicci, Chimica e Industria, 58 (1976) 876.

75. G. Kovács, G. Galambos and Z. Juvancz, Synthesis (1977) 171.

76. L.I. Zakharkin and N.V. Grandberg, Izvest. Akad. Nauk S.S.S.R. (Seriya Khim.) 25 (1976) 2612; Bull. Acad. Sci., U.S.S.R., (Chem.)25 (1976) 2430.

77. L.I. Zakharkin. L.L. Ivanov, S. Ya.Zavizion, L.I. Fainshtein and T.G. Sorokina, Izvest. Akad. Nauk S.S.S.R. (Seriya Khim.) 25 (1976) 2557; Bull. Acad. Sci. U.S.S.R. (Chem.), 25 (1976) 2380.

78. G.A. Razuvaev G.A. Abakumov, E.S. Klimov, E.N. Gladyshev, P. Ya Bayushkin, Izvest. Akad. Nauk S.S.S.R. (Seriya Khim.), 26 (1977) 1128; Bull. Acad. Sci., U.S.S.R., (Chem.) 26 (1977) 1034.

79. D.B. Malpass, S.C. Watson and G.S. Yeargin, J. Org. Chem., 42 (1977) 2712.

80. F. Barbot and P. Miginiac, J. Organometal. Chem., 132 (1977) 445.

81. G. Sonnek and H. Reinheckel, Z. Chem., 17 (1977) 335.

82. M.J. Dimsdale, R.F. Newton, D.K. Rainey, C.F. Webb, T.V. Lee and S.M. Roberts, J.C.S. Chem. Comm., (1977) 716.

83. J.J. Plattner and A.H. Gager, Tetrahedron Lett., (1977) 2479.

84. H. Niwa and M. Kurono Chemistry Lett., (1977) 1211.

85. P.A. Grieco, C.S. Pogonowski, S.D. Burke, M. Nishizawa, M. Miyashita, Y. Masaki, C-L. J. Wang and G. Majetich. J. Amer. Chem. Soc. 99 (1977) 4111.

86. A. Sugie, H. Shimomura, J. Katsube and H. Yamamoto, Tetrahedron Lett., (1977) 2759.

87. D. Reuschling, K. Kühlein and A. Linkies, Tetrahedron Lett., (1977) 17.

88. L. Novák, C. Szántay, Z. Visky and J. Marosfalvi, Synthesis (1977) 575.

89. G. Stork and T. Takahashi, J. Amer. Chem. Soc., 99 (1977) 1275.

90. P.A. Grieco, Y. Ohfune and G. Majetich, J. Amer. Chem. Soc. 99 (1977) 7393.

91. S. Inoue and N. Takeda, Bull. Chem. Soc. Japan, 50 (1977) 984.

92. L.I. Shoer and J. Schwartz, J. Amer. Chem. Soc., 99 (1977) 5831.

93. S. Czernecki, C. Georgulis and E. Michel J. Organometal. Chem., 140 (1977) 127.

94. S.R. Rafikov, K.S. Minsker, Yu. A. Sangalov, Yu. Ya. Nel'kenbaum, U.S.S.R., Pat. 566 844; Chem. Abs., 87 (1977) 152 373.

95. M. Bolesławski, S. Pasynkiewicz, K. Jaworski and A. Sadownik, Pol. Pat. 83 452; Chem. Abs., 87 (1977) 201 759.

96. S. Pasynkiewicz, A. Sadownik and A. Kunicki, J. Organometal. Chem., 124 (1977) 265.

97. A. Kunicki, J. Serwatowski, S. Pasynkiewicz and M. Bolesławski, J. Organometal. Chem., 128 (1977) 21.

98. S. Pasynkiewicz, K.B. Starowieyski, A.S. Peregudov and D.N. Kravtsov., J. Organometal. Chem., 132 (1977) 191.

99. M. Skowrońska-Ptasińska, K.B. Starowieyski and S. Pasynkiewicz, J. Organometal. Chem., 141 (1977) 149.

100. A. Sadownik, S. Pasynkiewicz and A. Kunicki, J. Organometal. Chem., 141 (1977) 275.

101. G.A. Razuvaev and L.P. Stepovik, Zhur. obshchei Khim., 46 (1976) 2550; J. Gen. Chem., U.S.S.R. 46 (1976) 2437.

102. M. Furusato, H. Sakurai, H. Morita, T. Ikegami and K. Maeda, Japan Kokai, 77 77016, 125 129; Chem. Abs., 87 (1977) 152 372; 88 (1977) 105 551.

103. T. Ikegami, H. Sakurai Y. Takashi, H. Morita and T. Sato, Japan Kokai 77, 71 421; Chem. Abs.,88 (1978) 23 133.

104. N. Voiculescu, Rev. Roumaine Chim., 22 (1977) 237; Chem. Abs., 87 (1977) 23 366.

105. N. Voiculescu, Rev. Roumaine Chim., 22 (1977) 451; Chem. Abs., 87 (1977) 39 570.

106. P. Fischer, R. Gräf, J.J. Stezowski and J. Weidlein, J. Amer. Chem. Soc., 99 (1977) 6131.

107. B. Eberwein, W. Lieb and J. Weidlein, Z. Naturforsch. 32b (1977) 32.

108. G. Sonnek, H. Reinheckel. G. Mueller and K.G. Baumgarten, DDR Pat. 122 095; Chem. Abs., 87 (1977) 53 435.

109. S. Pasynkiewicz, M. Bolesławski and A. Kunicki, Pol. Pat. 86 767; Chem. Abs., 87 (1977) 135 885.

110. S. Pasynkiewicz, M. Bolesławski and A. Kunicki, Pol. Pat. 86 768; Chem. Abs., 87 (1977) 135 884.

111. S. Warwel and B. Ahlfaenger, Chem-Ztg. 101 (1977) 103.

112. A. Basha, M. Lipton and S.M. Weinreb, Tetrahedron Lett. (1977) 4171.

113. N.E. Miller, J. Organometal. Chem., 137 (1977) 131.

114. M.P. Paradisi, G.P. Zecchini and A. Romeo, Tetrahedron Lett., (1977) 2369.

115. S. Cucinella, Chimica e Industria, 59 (1977) 696.

116. S. Cucinella, T. Salvatori and A. Mazzei, Ger. Offen. 2 700 454, Chem. Abs., 88 (1978) 7046.

117. G. Del Piero, M. Cesari, G. Dozzi and A. Mazzei, J. Organometal. Chem., 129 (1977) 281.

118. G. Del Piero, G. Perego, S. Cucinella, M. Cesari and A. Mazzei, J. Organometal. Chem., 136 (1977) 13.

119. C. Busetto, M. Cesari, S. Cucinella and T. Salvatori, J. Organometal. Chem., 132 (1977) 339.

120. Y. Koma, K. Iimura, S. Kondo, M. Takeda, J. Polymer Sci., Polymer Chem., Edn., 15 (1977) 1697.

121. F. Weller and K. Dehnicke, Chem. Ber., 110 (1977) 3935.

122. A. Alberola, F. Alonso Cermeno and A. Anton, Anales de Quím. 73 (1977) 886; Chem. Abs., 87 (1977) 184 589.

123. A. Alberola and F.J. Lopez Lopez, Anales de Quím, 73 (1977) 893; Chem. Abs., 87 (1977) 184 591.

124. A. Alberola, F. Alonso Cermeno and A. Anton, Anales de Quím, 73 (1977), 891; Chem. Abs., 87 (1977) 184 590.

125. H. Hoberg and U. Griebsch, Annalen (1977) 1516.

126. D. Giurgiu and I. Popescu, Rev. Roumaine Chim. 21 (1976) 1373; Chem. Abs., 86 (1977) 72 736.

127. H. Schmidbaur, O. Gasser, C. Krüger and J.C. Sekutowski, Chem. Ber. 110 (1977) 3517.

128. D.B. Malpass and S.C. Watson, Ger. Offen. 2 707 836; Chem. Abs., 88 (1978) 74 453.

129. V.L. Volkov, A.I. Kuznetzov, L.M. Antipin, U.S.S.R. Pat. 327 781; Chem. Abs., 86 (1977) 90 013.

130. D.B. Malpass and G.S. Yeargin, Ger. Offen. 2 714 721; Chem. Abs., 88 (1978) 89 842.

131. R.J.P. Corriu and C. Guerin, J.C.S. Chem. Commun., (1977) 74.

132. E.C. Ashby and A.B. Goel, J. Organometal. Chem., 135 (1977) 137.

133. E.C. Ashby and A.B. Goel, J. Amer. Chem. Soc., 99 (1977) 310; Inorg. Chem., 16 (1977) 1441, 2941.

134. E.C. Ashby and J.J. Watkins, Inorg. Chem., 16 (1977) 1445, 2070.

135. J.J. Watkins and E.C. Ashby, Inorg. Chem., 16 (1977) 2062, 2075.

136. E.C. Ashby and A.B. Goel, J. Organometal.Chem., 139 (1977) C89.

137. P.N. Gaponik, O.M. Baranov and V.P. Mardykin, Chem. Abs., 88 (1978) 23 015.

138. Z. Latajka, H. Ratajczak, K. Romanowska and Z. Tomczak, J. Organometal Chem., 131 (1977) 347.

139. M. Graffeuil and J.F. Labarre, J. Chim. phys. Phys-Chim Biol., 73, (1976) 1042.

140. K-H von. Dahlen and J. Dehnicke, Chem. Ber.,110 (1977) 383.

141. W. Wolfsberger, Z. Naturforsch. 32b (1977) 152.

142. E.R. Sigurdson and G. Wilkinson, J.C.S. Dalton (1977) 812.

143. A.C. Bond and F.L. Himpsl, J. Amer. Chem. Soc., 99 (1977) 6906.

144. J.L. Atwood, U.S. Pat. 4 024 170 Chem. Abs., 87 (1977) 135 883.

145. E.O. Fischer, S. Walz and W.R. Wagner, J. Organometal Chem., 134 (1977) C37.

146. A. Grèco, G. Bertolini and S. Cesca, Inorg. Chim. Acta 21 (1977) 245.

147. L.I. Shoer, K.I. Gell, J. Schwartz, J. Organometal. Chem. 136 (1977) C19.

148. J C. Daran, K. Prout, A. De Cian, M.L.H. Green and N. Siganporia, J. Organometal. Chem., 136 (1977) C4 .

149. T. Ito and A. Yamamoto, Inorg. Synth. 17 (1977) 61.

150. S.D. Ittel. Inorg. Chem., 16 (1977) 1245.

151. T. Yamamoto, M. Bundo and A. Yamamoto, Chemistry Lett. (1977) 833.

152. S. Pasynkiewicz and A. Pietrzykowski, J. Organometal. Chem. 142 (1977) 205.

153. K. Jacob, E. Pietzner, S. Vastag, K-H. Tiele, Z. anorg. allg. Chem., 432 (1977) 187.

154. A.N. Nesmeyanov, L.S. Isaeva and L.N. Lorens, J. Organometal Chem., 129 (1977) 421.

155. B.T. Pennington and J.E. Howell, J. Organometal. Chem., 136 (1977) 95.

156. H. Hoberg, R. Krause-Göing, C. Krüger, and J.C. Sekutowski, Angew. Chem., 89 (1977) 179; Angew. Chem., Internat. Edn. 16 (1977) 183.

157. G. Giacomelli, R. Menicagli and L. Lardicci, J.C.S. Perkin 1 (1976) 1904.

158. G.A. Tolstikov, U.M. Dzhemilev and S.S. Shavanov, Izvest. Akad. Nauk., S.S.S.R. (Seriya Khim) 24 (1975) 1872; Bull. Acad. Sci., (Chem) 24 (1975) 1754.

159. G.A. Tolstikov, U.M. Dzhemilev and S.S. Shavanov, Izvest. Akad. Nauk. S.S.S.R. (Seriya Khim) 25 (1976) 2595; Bull. Acad. Sci. U.S.S.R., (Chem) 25 (1976)2415

160. K. Seyferth, R. Taube, L. Bencze and L. Markó, J. Organometal. Chem., 137 (1977) 275.

161. V.W. Motz and M.F. Farona, Inorg. Chem., 16 (1977) 2545.

162. R.H. Grubbs and C.R. Hoppin, J.C.S. Chem. Comm., (1977) 634.

163. J.L. Bilhou and J.M. Basset, J. Organometal. Chem., 132 (1977) 395.

164. J. Beger, R. Sass and G. Zimmermann, J. prakt. Chem., 319 (1977) 790.

165. J-P. Laval, A. Lattes, R. Mutin and J.M. Basset, J.C.S. Chem. Comm., (1977) 502.

166. S. Warwel and W. Laarz, Z. Naturforsch. 32b (1977) 1145.

167. R.H. Grubbs, S. Swetnick and S.C.H. Su., J. Mol. Catal.3 (1977) 11; Chem. Abs., 88 (1978) 12 463.

168. U.M. Dzhemilev, A.Z. Yakupova and G.A. Tolstikov, Izvest. Akad. Nauk S.S.S.R. (Seriya Khim.), 24 (1975) 2379; 25 (1976) 1795; Bull. Acad. Sci., U.S.S.R. (Chem), 24 (1975) 2270; 25 (1976) 1691.

169. G.A. Tolstikov, U.M. Dzhemilev, O.S. Vostrikova and G.M. Latypov, Izvest. Akad. Nauk. S.S.S.R. (Seriya Khim.),26 (1977) 1542; Bull. Acad. Sci. U.S.S.R. (Chem.),26 (1977) 1415.

170. V.P. Yur'ev, F.G. Yusupova, G. Gailyunas and V.D. Sheludyakov, Izvest. Akad. Nauk S.S.S.R. (Seriya Khim.), 26 (1977) 1689; Bull Acad. Sci., U.S.S.R. (Chem.) 26 (1977) 1563.

171. I.M. Salimgareeva, V.V. Kaverin, A.A. Panasenko, S.R. Rafikov, N.S. Fedotov and V.P. Yur'ev, Doklady Akad. Nauk S.S.S.R., 236 (1977) 131.

172. V.P. Yur'ev, I.M. Salimgareeva, O. Zh. Zhebarov, I.I. Furlei and L.M. Khalilov Izvest. Akad. Nauk S.S.S.R. (Seriya Khim.) 26 (1977) 204.

173. V.P. Yur'ev, I.M. Salimgareeva, V.V. Kaverin and G.A. Tolstikov, Zhur. obshchei Khim., 47 (1977) 355; J. Gen. Chem. U.S.S.R., 47 (1977) 329.

174. V.P. Yur'ev, I.M. Salimgareeva and V.V. Kaverin, Zhur. obshchei Khim., 47 (1977) 592; J. Gen. Chem. U.S.S.R., 47 (1977) 541.

175. A.J. Cornish, M.F. Lappert and T.A. Nile, J. Organometal. Chem., 132 (1977) 133.

176. G. Wilke, Ger. Pat. 1 793 788, Chem. Abs ., 87 (1977) 135 956.

177. T. Masuda and Y. Takami, J. Polymer Sci. Polymer Chem. Edn. 15 (1977) 2033.

178. C. Carlini, R. Nocci and F. Ciardelli, J. Polymer Sci. Polymer Chem. Edn., 15 (1977) 767.

179. M.F. Farona and C. Tsonis, J.C.S. Chem. Comm., (1977) 363.

180. J. Grotewold and M.M. Hirschler, J. Polymer Sci. Polymer Chem. Edn., 15 (1977) 383, 393.

181. L.C. Reibel, J.P. Kennedy and Y-L. Chung, J. Org. Chem., 42(1977)690.

182. M.A. Long, J.L. Garnett and R.F.W. Vining, Tetrahedron Lett. (1976)4531

183. S. Pasynkiewicz, M. Bolesławski and K. Jaworski, Pol. Pat. 89 645; Chem. Abs., 87 (1977) 135 946.