ALUMINIUM

ANNUAL SURVEY COVERING THE YEAR 1981*

J. DAVID SMITH

School of Chemistry and Molecular Sciences,
University of Sussex,
Brighton BN1 9QJ, England

CONTENTS

---

*Aluminium. Annual survey covering the year 1980, see J. Organometal. Chem. 227 (1981) 241-287.

1. INTRODUCTION REVIEWS

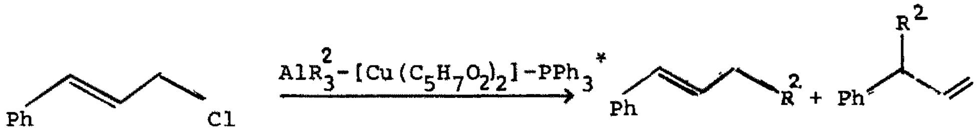
As in previous years, research on organoaluminium compounds is described in a wide range of journals. For many authors, the interest lies in the uses of organoaluminium compounds, for example, in organic syntheses or as components in catalytic systems: the reagents are generated in situ and little attempt is made to examine the structures of the molecular species involved. For other authors,the interest lies in the interactions between aluminium and neighbouring atoms. In 1981, as in other years, new types of coordination between organic groups and aluminium have been discovered. No attempt has been made in this survey to include a comprehensive account of organoaluminium compounds in polymer chemistry or to summarise the extensive patent literature.

A volume in the series of specialist periodical reports published by the Royal Society of Chemistry deals with the literature on organometallic compounds published in 1980: there is a detailed section on aluminium [1]. A similar but less full account appears in another established review series [2]. Industrially important compounds are described in an article [3] on σ-bonded organometallics, which gives process descriptions for trialkylaluminiums and ethylaluminium sesquichloride. World production of alkylaluminium compounds is given as 1-2 × 10^5 tonnes y^{-1}. The uses of organoaluminium compounds are covered in a book on organometallic synthesis [4], which describes experimental techniques, purification, characterisation and spectral data, and gives detailed recipes for the preparation of diisobutylaluminium hydride, diisobutyl(Z)-(1-trimethylsilyl-2-phenylethenyl)aluminium, diphenylaluminium chloride, phenylaluminium dichloride, triphenylaluminium, diphenyl(phenylethynyl)aluminium and tribenzylaluminium. An important summary paper [5] is intended to bring the potential and scope of alkylaluminium halides to the attention of synthetic organic chemists; the use of organoaluminium reagents is also described in a review [6] of selective synthetic reactions. Shorter sections on organoaluminium compounds are found in reviews on stereospecific syntheses of alkenyl derivatives [7], on spectroscopic properties of organometallic compounds [8], and on aromatic compounds of the main group elements [9]. In the literature on polymer chemistry, there have been reviews on initiation of carbocationic polymerisation [10] and on active centres in cycloalkene polymerisation and alkene metathesis [11]: both give information about organoaluminium compounds.

2. TRIALKYLALUMINIUMS

A patent [12] describes a process for the production of aluminium alkyls in which the crude reaction mixture from aluminium, hydrogen and alkene is continuously freed from solid impurities using a tubular filter. Another patent [13] claims that removal of finely divided solid impurities from organoaluminium compounds is facilitated by addition of perlite before filtration. The documentation of the mass spectra of organoaluminium derivatives, begun two years ago, continues with the publication [14] of the breakdown patterns for $Al(CH_2CH_2Ph)_3$, tris[2-(cyclohex-3-en-1-yl)ethyl]aluminium, $Al(CH_2CH_2SiMe_3)_3$, $Al(n\text{-}C_6H_{13})_3$, $Al(n\text{-}C_9H_{19})_3$. In all cases only peaks from monomers were observed. Alkyl radicals R were eliminated from AlR_3, followed by alkanes and alkenes, including ethylene.

As in previous years, trialkylaluminiums have been used mainly for alkylations of compounds with halogens or with oxygen functions. For example, publications from two research groups describe improvements in the procedure for conversion of acid chlorides R^1COCl or thiocarboxylates R^1COSPh (R^1 = Ph or $CH_2{=}CH(CH_2)_8$-) to ketones R^1COR^2 (R^2 = Me, Et, or Bu^i). Yields of 70-95% may be achieved using a mixture of AlR^2_3 (2 mol), $[Cu(C_5H_7O_2)_2]$ (1 mol)† and PPh_3 (2 mol) in tetrahydrofuran (THF), without reaction of the alkyl AlR^2_3 with the ketone product [15]. With cinnamyl chloride (1) the products (2) and (3) are obtained in 59:41 mole ratio (R^2 = Me) or 24:76 mole ratio (R^2 = Et). Alternatively [16], the acid chloride-aluminium



(1) (2) (3)

1

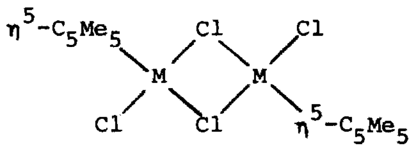
---

*Throughout this survey $C_5H_7O_2$ = pentane-2,4-dionato.

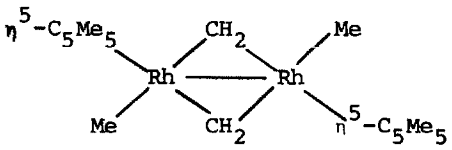
chloride adducts $[R^1CO][AlCl_4]$ may be treated with trialkylaluminiums. Good yields of ketones R^1COR^2 (R^1 = Me or Ph, R^2 = n-C_6H_{13}-) may be obtained. The method works well (yields 65-88%) for the preparation of unsaturated ketones (R^1 = CH_2=CMe-, MeCH=CH-, Me_2C=CH-, PhCH=CH-, Me(CH=CH)$_2$-, 2-furyl, CH_2=CH$(CH_2)_8$-; R^2 = Et, n-C_6H_{13} or n-C_8H_{17}) [16], provided that the temperature is kept low. In some cases and especially when R^2 is branched (e.g. R^2 = Bu^i or $Bu^tCH_2CHMeCH_2$-) mixtures of ketones, e.g., (4) and (5) (Equation 2), as well as some chloroketones, are formed.

$$[MeCO][AlCl_4] + AlBu^i_3 \rightarrow \underset{(4)}{MeCOBu^i} + \underset{(5)}{MeCOCH{=}CMe_2} \qquad \underline{2}$$

Alkylaluminium compounds have also been used to convert transition metal halides to transition metal alkyls. For example, $[TiCl_2(\eta^5\text{-}C_5H_5)_2]$ reacts with $Al(SiMe_3)_3.OEt_2$ in pentane, or with $Li[Al(SiMe_3)_4]$, to give the complex $[TiCl(SiMe_3)(\eta^5\text{-}C_5H_5)_2]$. There is no reaction with the second chlorine. The compound $[TiCl(GeMe_3)(\eta^5\text{-}C_5H_5)_2]$ may be obtained similarly. The reaction between $[TiCl_2(\eta^5\text{-}C_5H_5)_2]$ and $Na[Al(SiMe_3)_4]$ is more complex: the species in the initially produced blue solution are extremely reactive and decompose to $[TiCl(SiMe_3)(\eta^5\text{-}C_5H_5)_2]$ on work up [17]. Halides of the early transition metals are known to be reduced by alkylaluminium compounds: however, it now appears that, under certain circumstances, halides of the later transition elements may be oxidised. The iridium(III) complex (6) (M = Ir) is converted in low (11%)



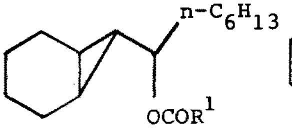
(6)



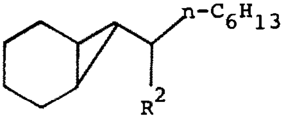
(7)

yield by reaction with trimethylaluminium into the Ir(V) compound $[Ir(\eta^5-C_5Me_5)Me_4]$, which has been shown by X-ray analysis to have a four-legged piano stool structure [18]. The rhodium analogue (6) (M = Rh) reacts with trimethylaluminium to give the complex (7) in 15% yield [19]. The other products formed in these complex redox reactions have not been characterised, but it has been suggested that the pyrolyses of compounds such as (7) and $[Ir(\eta^5-C_5Me_5)Me_4]$ may throw light on the mechanism of Fischer-Tropsch reaction.

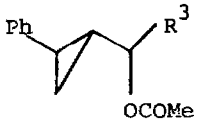
Alkylations may also involve replacement of oxygen-containing groups such as carboxylates or phosphonates. As reported in a preliminary communication in 1979, the aluminium compounds $AlMe_3$, $AlEt_3$ or $AlEt_2(C\equiv CBu)$ convert the cyclopropylmethyl esters (8) (R^1 = Me or Ph) into the derivatives (9) (R^2 = Me, Et, or $C\equiv CBu$). In contrast, alkylation of phenyl- or vinyl-substituted



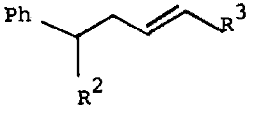
(8)



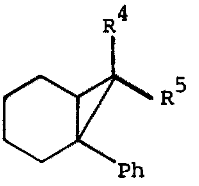
(9)



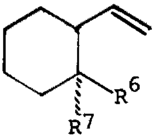
(10)



(11)

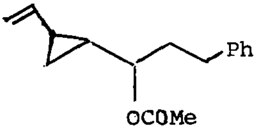


(12)

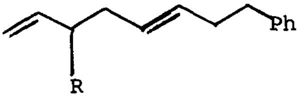


(13)

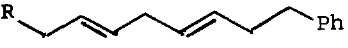
cyclopropylmethyl acetates leads to ring opening [20]. A detailed study shows that both diastereomers of (10) (R^3 = Me or H) with AlR^2_3 (R^2 = Me, Et or Bu^i) give almost exclusively the compounds (11) in which the configuration at the newly formed C=C bond is trans. Since the stereochemistry of the product is almost independent of that of the starting material, it is assumed that alkylation involves planar carbocationic intermediates. Similarly the esters (12) (R^4 = H, R^5 = CH_2OCOMe or R^4 = CH_2OCOMe, R^5 = H) on treatment with trimethylaluminium give the compounds (13) (R^6 = Me, R^7 = Ph or R^6 = Ph, R^7 = Me), and alkylation of the vinylcyclopropyl compound (14) gives (15) and (16) (R = Me, Et or Bu^i). Alkylation takes place predominantly at the cyclopropane carbon (for R = Me (15):(16) = 83:17), and the configuration at the new C=C bond



(14)

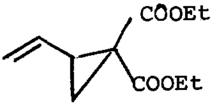


(15)

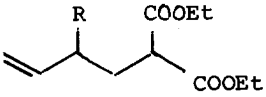


(16)

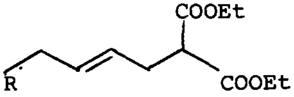
is again trans. Alkylation of the dicarboxylate (17) using trialkylaluminiums gives a 96:4 mixture of (18) and (19) (R = Me, Et or C≡CBu). The regioselectivity is reversed using $Li[AlMe_4]$: the ratio of (18):(19) is 8:92. Similarly the β-ketoester (20) gives the 1:5 homoconjugate addition products (21) with trimethylaluminium but the 1:7 products (22) with $Li[AlMe_4]$.



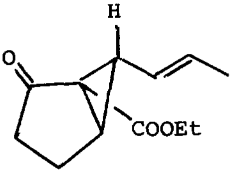
(17)



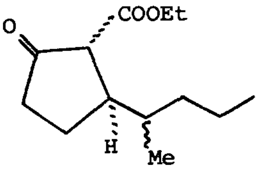
(18)



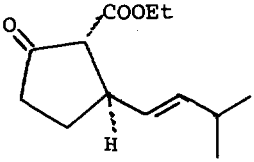
(19)



(20)



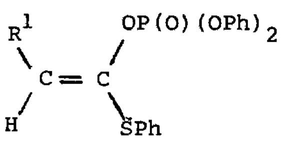
(21)

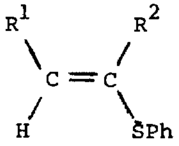


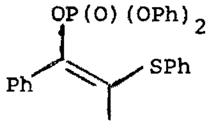
(22)

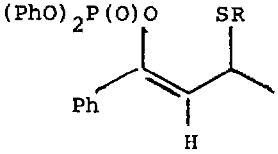
In most of these reactions, an excess of trialkylaluminium is used and it is suggested that complex formation at oxygen functions is partly responsible for the observed regioselectivity. A further example of alkylation of an acetate is found in work on propargyldicobalt hexacarbonyl compounds. Thus $[Co_2(CO)_6(HC{\equiv}CCHPhOCOMe)]$ is converted in 91% yield to $[Co_2(CO)_6(HC{\equiv}CCHMePh)]$ by reaction with trimethylaluminium under remarkably mild conditions (in CH_2Cl_2 at -78°C). The same compound may be obtained in much lower yield along with some $[\{Co_2(CO)_6\}_2(HC{\equiv}CCHPhCHPhC{\equiv}CH)]$ by the direct reaction between trimethylaluminium and the salt $[Co_2(CO)_6(HC{\equiv}CCHPh)]BF_4$ [21].

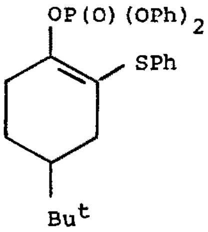
Two further papers on the alkylation of phosphates have appeared. The esters (23) are converted by trimethylaluminium in the presence of $[Pd(PPh_3)_4]$ as catalyst into the alkenyl sulphides (24) in good yield [22]. With triethyl- or triisobutyl-aluminium, hydrogenated as well as alkylated products are obtained, especially in non-polar solvents. Other enol phosphates (25)-(27) may be alkylated similarly. In all cases, ketones, e.g., $R^1CH_2COR^2$

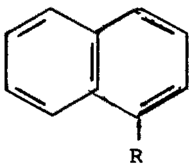

(23)


(24)


(25)


(26)

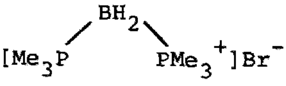

(27)


(28)

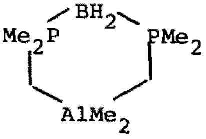
from (24), may be obtained from the alkenyl sulphides by treatment with $TiCl_4$-H_2O-MeCOOH. The phosphates (28) (R = $OP(O)(OEt)_2$) may be converted quantitatively into E-1-(1-naphthyl)-hex-1-ene (28) (R = CH=CHBu) by treatment with E-1-hexenyldiisobutylaluminium in the presence of bis(pentane-2,4-dionato)nickel as catalyst. This catalyst was not effective for the reaction between triethylaluminium and (28) (R = $OP(O)(OEt)_2$) but in the presence of $[NiCl_2(Ph_2PCH_2CH_2CH_2PPh_2)]$ a good yield of (28) (R = Et) could be obtained [23]. It has been reported [24] that the interaction of triethylaluminium and tris(pentane-2,4-dionato)iron yields

$[AlEt_2(C_5H_7O_2)]$ when the Al/Fe ratio is 3 and $[Al(C_5H_7O_2)_3$ when the Al/Fe ratio is <1 (see also Section 10).

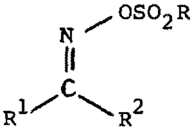
For alkylation of boric oxide, the reactivity of organoaluminium compounds is said to decrease in the order $AlCl_2R > Al_2Cl_3R_3 > AlClR_2 > AlR_3$ (R = Me or Et). The simultaneous preparation of triethylboron and ethylaluminium dichloride from aluminium, chloroethane and boric oxide has been described [25]. The alkylation of hexaborane(10) with trimethyl- and triethyl-aluminium has been reported [26], but so far the only products which have been isolated have been the trialkylborons. Hexaborane(10) and triisobutylaluminium form a complex which is stable enough in an excess of $AlBu^i_3$ to be characterised by NMR. The phosphonium salts (29) react with lithium tetramethylmetalates $Li[MMe_4]$ (M = Al or Ga) to give methane and sublimable compounds which appear from spectroscopic studies to have cyclic structures (30) [27].



(29)

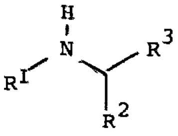


(30)

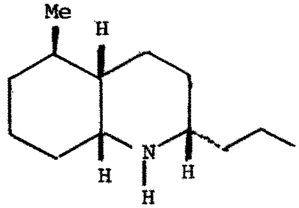


(31)

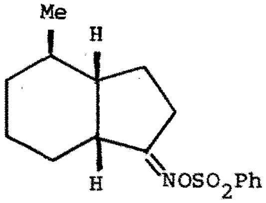
Finally, trialkylaluminiums AlR^3_3 have been used for alkylations of the iminocarbonium ions produced by Beckmann rearrangements. This makes possible the conversion of a wide range of oxime sulphonates (31) into imines and, after reduction with diisobutylaluminium hydride, into amines (32) [28]. For example, the naturally occurring alkaloid (33) may be obtained stereospecifically (>99% pure) from the oxime sulphonate (34) in 60% yield by treatment with tri-n-propylaluminium.



(32)



(33)

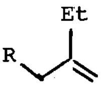


(34)

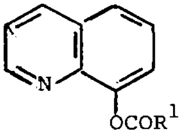
3. ALKYLALUMINIUM HALIDES

Apart from the report [25] already mentioned, and a brief paper [154] describing the formation of $AlCl(CH_2CH_2R)_2$ (R = Bu, C_6H_{13}- or C_8H_{17}-) and di(cyclohexyl)aluminium chloride from alkenes and $AlClBu^i_2$, there is little on the preparation of alkylaluminium halides. A correction has been made concerning the space group of $Cs[AlI_2Me_2]$; this should be Ccmm rather than $C222_1$ [29].

There are several reports of alkylaluminium halides as alkylating agents. The compounds $AlCl_2R^1$ (R^1 = Et, n-$C_{10}H_{21}$ n-$C_{12}H_{25}$-, n-$C_{14}H_{29}$-. n-$C_{16}H_{33}$-, $Me_3Si(CH_2)_3$-) react with phosphorus(V) oxide chloride to give complexes $R^1POCl_2.AlCl_3$. These may be converted by treatment with an excess of amine R^2_2NH (R^2 = Me or Et) into good yields of the phosphonic acid diamides $R^1PO(NR^2_2)_2$ [30]. More examples of the alkylation of alk-1-enes by diethylaluminium chloride in the presence of catalytic amounts of $[Zr(OBu)_4]$ have been documented [31]. Good yields of the alkenes (35) (R = n-C_4H_9-, n-C_6H_{13}-, n-C_8H_{17}-, n-$C_{10}H_{21}$-, <u>cis</u>-MeCH=CH.CH_2–) have been obtained. β-Substituted alkenes, e.g.,



(35)



(36)

$(HC{\equiv}CCH_2)_2CHOEt$

(37)

3-methyleneheptane and 5-methyleneundecane are not alkylated. Diisobutylaluminium chloride is ineffective as an alkylating agent. The quinoline derivatives (36) react with dialkylaluminium chlorides AlR^2_2Cl, alkylaluminium sesquichlorides, or alkylaluminium dichlorides to give the ketones R^1COR^2 [32] (C.f. ref. [15] and [16]). In previous surveys there have been accounts of the use of unsaturated organoaluminium sesquichlorides for the preparation of an enormous range of unsaturated alcohols and amines. Papers published in 1981 give conditions for the preparation of the ethers (37) from propynylaluminium sesquibromides or the ethers (38) from allylaluminium compounds (Equation <u>3</u> R^1 = H, Me, Et, or Bu;

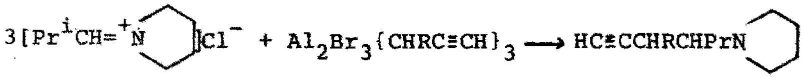
$$Al_2Br_3\{CH_2C(R^2)=CHR^1\}_3 + 3(PhO)_2CHOEt \xrightarrow{-55^oC} \underset{(38)}{3\{CH_2=C(R^2)CHR^1\}_2CHOEt} \qquad \underline{3}$$

R^2 = H or Me). By using the less reactive organo-magnesium or -zinc reagents the mixed acetals (39) (R^3 = $CH_2{=}CHCHMe-$, $CH_2{=}CHCH_2-$ or $PhC{\equiv}C-$) may be obtained. With allylaluminium compounds these give the ethers (40) (R^1, R^2 = H or Me) which are not easily made by other routes (Equation 4)

$$Al_2Br_3\{CH_2C(R^2){=}CHR^1\}_3 + \underset{(39)}{R^3CH(OEt)OPh}$$

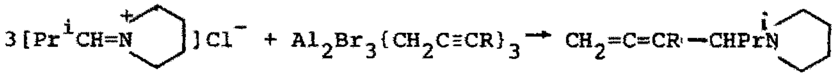
$$\xrightarrow{-55^\circ C} \underset{(40)}{CH_2{=}CR^2CHR^1CHR^3OEt} \qquad 4$$

Allylic rearrangements are common in this area of chemistry [33]. α-Allenic and α- and β-acetylenic amines may be made similarly from immonium salts (Equations 5 (R = H or Me) and



5

and 6 (R = Me, Et or Bu). An extended series of similar



6

reactions has been documented [34]. A further paper [35] describes the best routes to the tertiary amines $R^1R^2CH{-}NR^3_2$ (R^1 = unsaturated group, R^2, R^3 = alkyl) using analogous reactions from immonium salts as starting materials.

Two papers describe the reaction of alkylaluminium chlorides with acidic compounds. It is claimed from NMR measurements that the hydroperoxide $PhMe_2COOH$ reacts with methylaluminium dichloride at 0-5°C in 1,2-dimethoxyethane to give methane and the peroxyaluminium compound $AlCl_2OOCPhMe_2$ which rearranges at >10°C to the acetone complex $AlCl_2OPh.OCMe_2$.

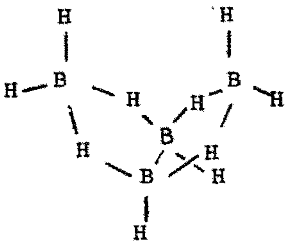
t-Butyl hydroperoxide gives $AlCl_2OOBu^t$ which decomposes slowly in dimethoxyethane and more quickly in non-polar solvents to give the t-butoxide $AlCl_2(OBu^t)$ [36]. The reaction between diethylaluminium chloride and aluminosilicates such as kaolin or montmorillonite has been examined in connection with the use of mineral fillers in polyalkenes. Only about 10% of the total water, as shown by dehydration at 800°C, is accessible to the alkylaluminium compound [37]. It is suggested that some of the silicon atoms in the clays may be alkylated.

The reaction between benzene and diethylaluminium chloride at high temperatures yields small quantities of alkyl-benzenes and other decomposition products, but $AlClEt_2$ is a less effective catalyst than is $AlCl_3$ for this degradation [38].

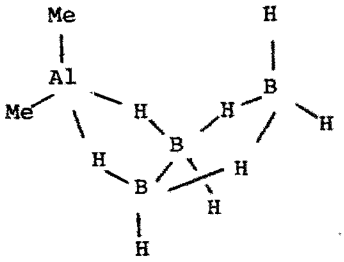
3. ALKYLALUMINIUM HYDRIDES

The reaction between sodium hydride (1 mol) and trimethylaluminium (2 mol) in toluene is catalysed by the macrocyclic ether 15-crown-5. The product which crystallises is $Na[Me_3Al\text{-}H\text{-}AlMe_3]$ [39]. A single crystal X-ray determination shows that the Al-H-Al system is linear, with the Al-H bond length (165 pm) very similar to that in $[Me_2AlH]_2$ (168 pm).

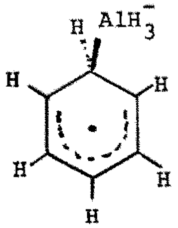
Two other structural determinations emphasize the close relationship between boron and aluminium. The molecules $Me_2AlB_3H_8$ (41) and $Me_2GaB_3H_8$, made from $MClMe_2$ (M = Al or Ga) and the salt $[Me_4N][B_3H_8]$, have been shown [40] by electron diffraction to have a skeleton like that of B_4H_{10} (42). For (41)



(42)



(41)



(42)

the important molecular parameters are Al-C 193.2(8) Al-B 230.7(8) Al-H 190.6(41) pm, C-Al-C 126.8(15)° and the dihedral angle defining the folding of the AlB_3 skeleton is 117.6(7)°. The reaction between trimethylaluminium and diborane in benzene at 100°C for 40 h yields trimethylborane, hydrogen, and a non-volatile amorphous pyrophoric solid AlB_4H_{11}. From the reactions of this substance with HCl, water and sodium borohydride, it is suggested that the structural unit in the polymer may be similar to that in B_5H_{11} [41].

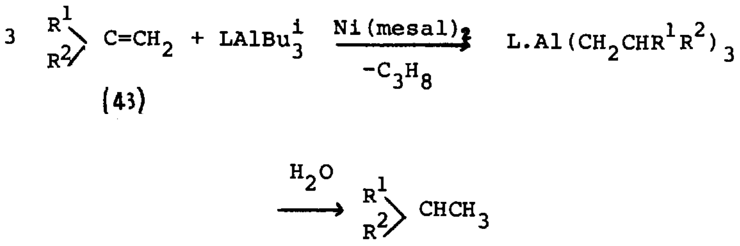
ESR measurements [42] have shown that the radical anion $AlH_3^{\bullet -}$ adds to ethylene to give the β-substituted ethyl radical $[{}^{\bullet}CH_2CH_2AlH_3]^-$ and to benzene to give the cyclohexadienyl radical anion (42).

There are two references to formation of alkylaluminium hydrides in work where the main interest is in the isolation of other products. Lithium aluminium hydride reacts with trialkylboranes to give first $Li[R_3BH]$ and AlH_3 and then $Li[R_2BH_2]$ and AlH_2R. For good yields of $Li[R_3BH]$ the second step must be suppressed and this is effectively achieved by addition of tetramethylethylenediamine [43]. The reaction between diphenylzinc and lithium aluminium hydride in mole ratios 2:1 to 1:2 gives a precipitate of ZnH_2 and the compounds $Li[AlPh_nH_{4-n}]$ in solution [44]. It was reported earlier that the corresponding reaction between dimethylzinc and lithium aluminium hydride yields complexes with three different metals e.g. $LiZnAlMe_2H_4$.

5. ADDITION TO CARBON-CARBON DOUBLE BONDS

Further patents describe the addition of trialkylaluminiums or alkylaluminium hydrides to alkenes. One [45] deals with production of C_4-C_{10} alk-1-enes from ethylene and triethylaluminium, another [46] is concerned with manufacture of branched chain alcohols from 2-ethyl-hex-1-ene and diisobutyl-aluminium hydride, and a third [47] describes production of high yields of decan-1-ol from dec-5-ene and diisobutylaluminium hydride in the presence of $Al(Bu^s)_3$ and various titanium compounds as catalysts. The catalytic nature of the ionic hydrogenation of isoalkenes has also been discussed [48].

The study of reactions of optically active organoaluminium compounds has continued with an investigation of the reaction between alkenes $R^1R^2C{=}CH_2$(43) (R^1 = Ph, R^2 = Me, Et, Pr^i or Bu^t; R^1 = Me, R^2 = Bu^t) and triisobutylaluminium in the presence of a series of optically active bases L [49] (Equation 3). For example, from (43) (R^1 = Pr^i, R^2 = Ph and L = (–)-N,N-dimethylmenthylamine) a 67% yield of R-Pr^iCHPhMe was obtained after hydrolysis and a 68% yield of R-Pr^iCHPhCH_2OH after oxidation and hydrolysis. The S-isomer was isolated in 38% yield after hydrolysis of the aluminium alkyl made from (43) and $AlBu^i_3$ in the presence of (+)-(S,S)-2,3-dimethoxy-1,4-bis(N,N-dimethylamino)butane.



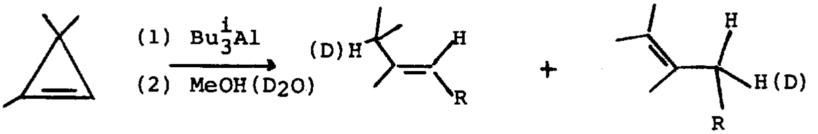
$$3\ {R^1 \atop R^2}\!\!>C{=}CH_2 + LAlBu^i_3 \xrightarrow[-C_3H_8]{Ni(mesal)_2} L.Al(CH_2CHR^1R^2)_3$$

(43)

$$\xrightarrow{H_2O} {R^1 \atop R^2}\!\!>CHCH_3 \qquad 7$$

mesal = N-methylsalicylideneaminato

The chiral bases may be recovered without racemisation, and reused. The formation of the alkanes (44) and (45) from the reaction between 1,3,3-trimethylcyclopropene (46) and triisobutylaluminium (Equation 8) suggests [50] that the carboalumination involves carbonium ion intermediates as suggested by Eisch in 1976.



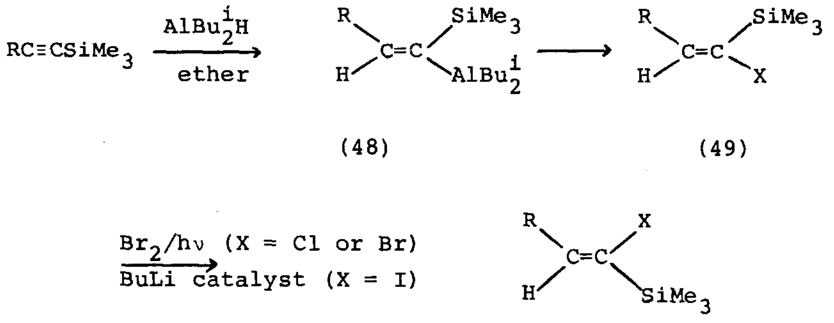
8

(46) (44) (45)

The hydroalumination of trimethylvinylsilane under vigorous conditions (140-150°C 10 h) has been reexamined [51]. The principal products are the dimer $Me_3SiCH{=}CHCH_2CH_2SiMe_3$ and the alkyl $Me_3SiCH_2CH_2Al(C_6H_{13})(CHMeSiMe_3)_2$ (47) which has been characterised by mass spectroscopy and by deuterolysis giving $Me_3SiCHDMe$ and $Me_3SiCH_2CH_2D$. Although these compounds are obtained in about the correct proportions for the formula (47), the total yield is only about 65%. The isolation of E - $Me_3SiCH{=}CHCH_2CH_2SiMe_3$ and $Me_3Si(CH_2)_4SiMe_3$, is said to indicate that the hydrolysis proceeds via radical intermediates. The reactions of (47) with sulphur dioxide and with hex-1-ene (giving $Me_3SiCH{=}CH_2$ and $Al(C_6H_{13})(C_2H_4SiMe_3)_2$ and with phenylacetylene (giving Me_3SiEt and $Al(C{\equiv}CPh)(C_2H_4SiMe_3)_2$) have also been reported [51].

6. ADDITION TO CARBON-CARBON TRIPLE BONDS

The reaction, described some years ago, between diisobutylaluminium hydride and alkynylsilanes has been further developed for the stereoselective synthesis of 1-halo-alk-1-enes [52]. (Equation 9). Thus the silylalkenylaluminium compounds (48) (R = Bu, $n\text{-}C_6H_{13}-$, $cyclo\text{-}C_6H_{11}-$, Bu^t, $MeCH_2CH(OTHP)CH_2-$, MeCH(OTHP)- or Ph) react with N-chlorosuccinamide, Br_2 or I_2 to give the E -alkenes (49) (X = Cl, Br or I) which may be isomerised to the Z-isomers (50). All the



(48)

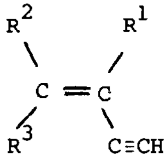
(49)

(50)

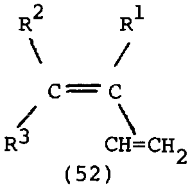
9

compounds (49) and (50) may be stereospecifically desilylated using sodium methoxide in methanol to give good yields of 1-haloalk-1-enes.

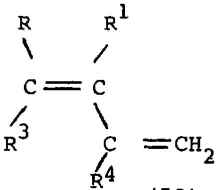
Trialkylaluminiums R^4_3Al react with 3-en-1-ynes (51) (R^1,R^2 and R^3 = H or Me), to give products which result from metalation, reduction (52) or carbalumination (53) or (54). The properties of these depend



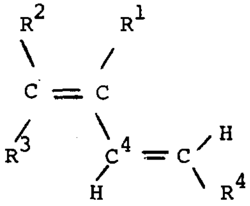
(51)



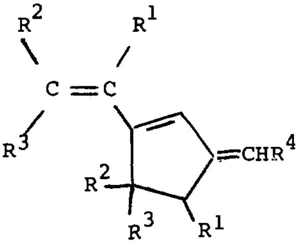
(52)



(53)

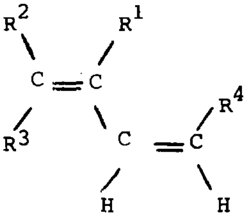


(54)

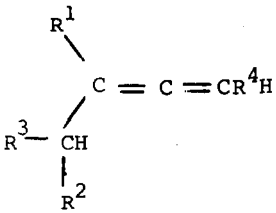


(55)

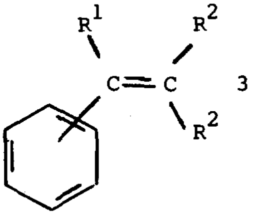
on both the enyne and the trialkylaluminium [53]. Metalation predominates with 4-alkyl- and 3,4-dialkyl-but-3-en-1-ynes but 3-alkyl-but-3-en-1-ynes give mainly 1-alkenyl-3-alkylidene-4-alkylcyclopentenes (55) together with (54), (56) and (57).



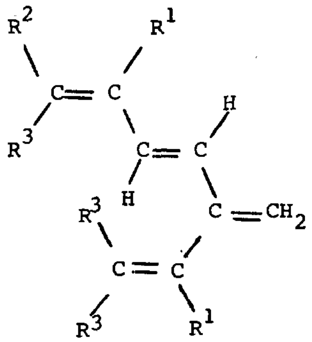
(56)



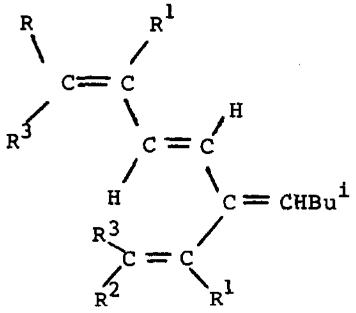
(57)



(60)



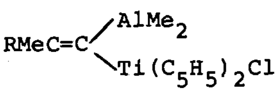
(58)



(59)

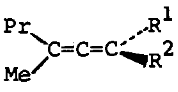
A detailed study of the reaction between $CH_2{=}CHMeC{\equiv}CH(D)$ and $AlBu^i_3$ suggests that the products arise from equilibria between alkenylaluminium compounds. In the presence of $[Ni(mesal)_2]$ or $[Mn(C_5H_7O_2)_3]$ the products are quite different: e.g. (58) and (59) or trimers (60) are formed in appreciable amounts. A detailed account [53] gives optimum conditions for isolation of (58) and (59) in sufficient yield (>60%) for the reactions to be used preparatively.

The formation of the 1,2-dimetalalkene (61) ($R = n\text{-}C_5H_{11}\text{-}$) from hept-1-ynyldimethylaluminium, trimethylaluminium and $[TiCl_2(\eta^5\text{-}C_5H_5)_2]$ was described in 1978. A cleaner material, free from dimethylaluminium chloride, is obtained from the heptynylalane and preformed $[TiClMe(\eta^5\text{-}C_5H_5)_2]$, and the compound (61) (R = Pr) is made similarly. The initial product, probably the E -isomer, rearranges slowly to a 60:40 mixture of E - and Z -isomers. The mechanism of the isomerisation is not yet established, but a process involving transmetalation has been ruled

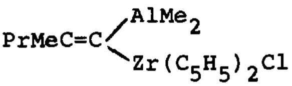


$$RMeC{=}C\genfrac{}{}{0pt}{}{\diagup AlMe_2}{\diagdown Ti(C_5H_5)_2Cl}$$

(61)



(62)



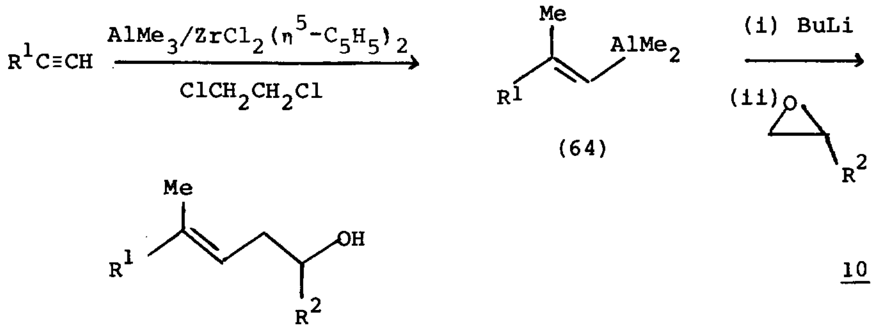
$$PrMeC{=}C\genfrac{}{}{0pt}{}{\diagup AlMe_2}{\diagdown Zr(C_5H_5)_2Cl}$$

(63)

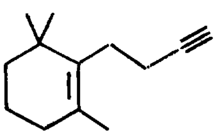
out. The compound (61) (R = Pr) reacts with cyclohexanone or benzaldehyde to give the allenes (62), showing that the carbene-like fragment may be preserved in a reaction sequence. The reaction between pent-1-ynyl-dimethylaluminium and a mixture of

$AlMe_3$ and $[ZrCl_2(\eta^5\text{-}C_5H_5)_2]$ or $[ZrClMe(\eta^5\text{-}C_5H_5)_2]$ gives (63) which unlike (61) appears to be stereochemically rigid [54].

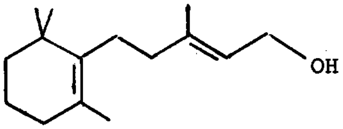
The alkenylaluminium compounds (64) obtained by the zirconium-catalysed carbalumination of alkynes react with epoxides to give the alcohols (65) (R^1 = n-C_5H_{11} or $Me_2C{=}CH(CH_2)_2$-; R^2 = H or Me) (Equation 10), which are useful intermediates for synthesis of terpenoids [55]. Another example of the same reaction is the conversion of the alkyne (66) into monocyclofarnesol (67) [56]. The carbometallation step has been



10



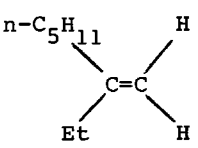
(66)



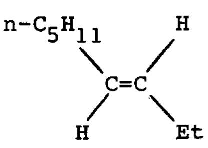
(67)

described in another paper [57] concerned with conversion of the alkynes $Z(CH_2)_nC{\equiv}CH$ (Z = OH, $OSiMe_2Bu^t$, SPh or I; n = 1 or 2) into (64) (R^1 = $Z(CH_2)_n$-). The Me_2Al-group is readily replaced by I to give intermediates useful in further syntheses.

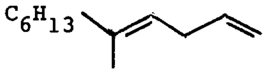
There has been discussion in the literature about whether the addition across the C≡C bond is a zirconium-assisted carboalumination or an aluminium-assisted carbozirconation. An NMR study [58] of the interaction between the compounds $[AlCl_{3-m}Me_m]$ and $[ZrCl_{2-n}Me_n(\eta^5\text{-}C_5H_5)_2]$ has shown that only in the case of $Me_3Al\text{-}[ZrCl_2(\eta5\text{-}C_5H_5)_2]$ is there significant exchange between Me and Cl groups. Further, rapid Me-Cl exchange is not required for carbometalation of hept-1-yne. The reaction between hept-1-yne and a 1:1 mixture of $AlEt_3$ and $[ZrClMe(\eta^5\text{-}C_5H_5)_2]$ gives the alkenes (68) and (69) with only traces of the corresponding methylated alkenes, and the reaction between hept-1-yne and $Me_3Al\text{-}[ZrCl(CD_3)(\eta^5\text{-}C_5H_5)_2]$ gives <4% deuterium incorporation. At least in these



(68)



(69)

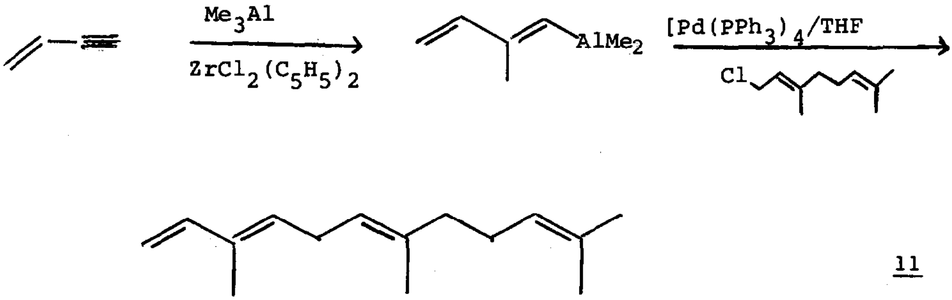


(70)

cases, therefore, the addition reaction proceeds by zirconium-assisted carboalumination.

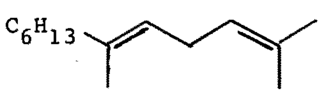
Another example of the use of $AlMe_3\text{-}TiCl_4$ for carbometalation tion is in the conversion of hex-3-yn-1-ol into Z -4-methylhex-3-en-1-ol, a key intermediate in the stereospecific synthesis of a juvenile hormone [59].

The alkenylaluminium compounds made by carbalumination of alkynes may be coupled easily and regio- and stereospecifically with allylic halides or acetates in the presence of catalytic amounts of palladium compounds. Several more examples of this reaction have been given [60]. Thus (64) ($R^1 = C_6H_{13}$-) reacts with allyl bromide in the presence of 5 mol % $[Pd(PPh_3)_4]$ to give (70) in 90% yield, with isoprenyl chloride to give (71) in 98% yield, and with geranyl chloride to give (72) in 92% yield. The stereo- and regio-chemistry of both carbon chains is preserved. A one-step synthesis of α-farnesene (73) (Equation 11)

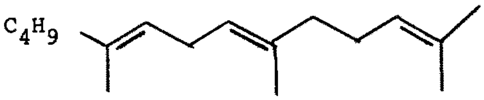


11

(73)

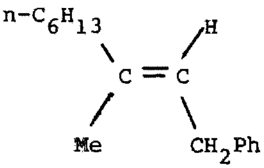


(71)

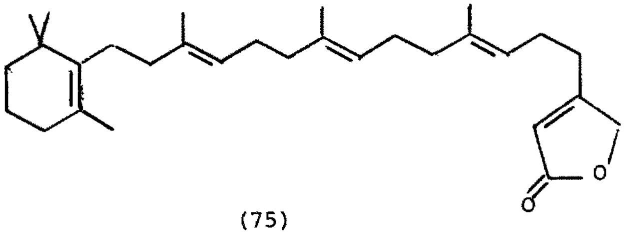


(72)

from geranyl chloride and butenyne is thus possible. Alkenylaluminium compounds may also be coupled to benzyl halides [61]. Thus the readily available (64) ($R^1 = n\text{-}C_6H_{13}$) reacts with benzyl chloride or bromide to give the allylated arene (74)

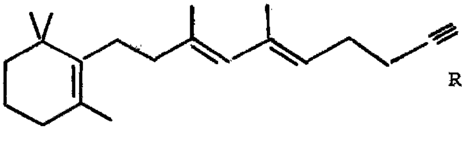


(74)

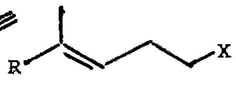


(75)

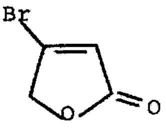
without formation of isomeric products. The addition of zinc chloride to the catalyst leads to lower yields. Compounds such as (74) may also be obtained from the cross coupling of $PhCH_2ZnBr$ and haloalkenes: in this case $[PdCl_2(PPh_3)_2]$-$AlBu^i_2H$ is an effective catalyst. The haloalkene may carry β-carbonyl substituents and the stereochemical integrity of the alkyl group attached to zinc may, with careful control of reaction conditions, be preserved in the cross-coupled product [62]. The zirconium-catalysed carbalumination of an alkyne and the $[PdCl_2(PPh_3)_2]$- $AlBu^i_2H$-catalysed cross-coupling of the alkenylaluminium product with a haloalkene are combined in a synthesis of mokupalide (75). The trienyne (76) (RC≡CH) is treated with (i) Me_3Al-$[ZrCl_2(\eta^5\text{-}C_5H_5)_2]$ (ii) BuLi (iii) C_2H_4O (see above) to give (77) (X = OH). This is converted to the alkenyl-zinc bromide (77) (X = ZnBr) which is coupled in the presence of $[PdCl_2(PPh_3)_2]$- $AlBu^i_2H$ with 4-bromo-2(5H)-furanone (78).



(76)



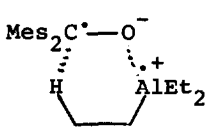
(77)



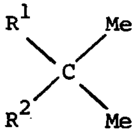
(78)

7. REACTIONS WITH CARBONYL COMPOUNDS

It has commonly been assumed that reactions between alkylaluminium compounds and carbonyl compounds involve polar intermediates. As part of a widespread search for radical intermediates in organo-metallic chemistry, the interaction of trialkylaluminiums with the hindered ketones Mes_2CO and MesPhCO (Mes = 2,4,6-$Me_3C_6H_2$-) has been examined [63]. Solutions in THF are coloured and show well defined ESR spectra associated with radical anion -radical cation pairs (79)



(79)

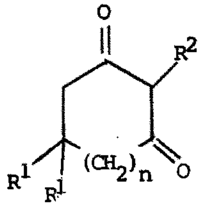


(80)

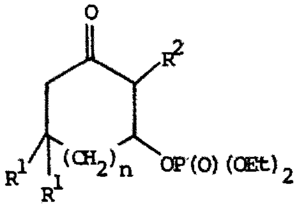
The rates of formation of the paramagnetic intermediates decrease in the series Et_3Al > Bu_3Al >> Me_3Al. As the colours and ESR signals fade, the product from dimesityl ketone is Mes_2CH_2; from mesityl phenyl ketone the products are MesPhCHOH and $MesPhCH_2$ in the ratio 7:3. It has been shown that $Mes_2CHOAlEt_2$ which could easily be formed by elimination of ethylene from (79) itself decomposes in THF to Mes_2CH_2. This work raises the possibility that reductions of less hindered ketones may likewise involve single electron transfer, though here of course the radical intermediates would be less easily detected.

Germinal dimethylation of ketones by trimethylaluminium under vigorous conditions (120-180° in xylene) was described in 1974. It has now been shown [64] that this reaction, which gives the products (80)(R^1R^2 = Pr_2; (cyclo-$C_3H_5)_2$, Ph_2 or $(CH_2)_n$; n = 5 or 11), may be effected in a few minutes at -30 to +20°C by dimethyl-titanium dichloride in dichloromethane. Good yields are also obtained with ketones having sulphide, chloride, thiophen, or aromatic functional groups. The reagent is best prepared *in situ* from dimethylzinc and titanium(IV) chloride, but geminal dimethylation of cyclohexanone with a 1:1 mixture of trimethylaluminium and titanium(IV) chloride is also successful.

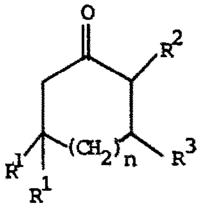
The $[Ni(C_5H_7O_2)_2]$-catalysed reaction between triethylaluminium and the enol phosphates (81) (R^1, R^2 = H or Me; n = 0 or 1) of the dicarbonyl compounds (82) has been shown to give β-alkylated α,β-unsaturated ketones (83). Best yields are obtained with about 2 equivalents of trialkylaluminium R^3_3Al [65].



(82)

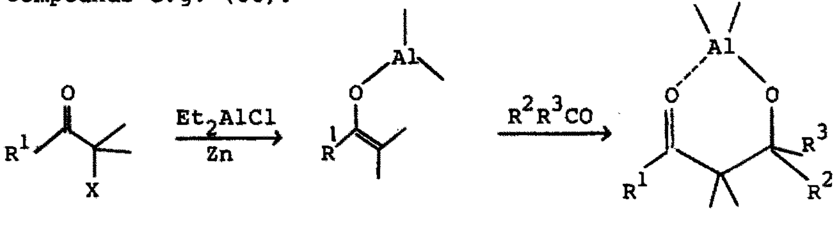


(81)

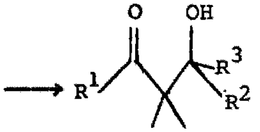


(83)

A new development of the aldol synthesis has been described [66]. By slow addition of α-haloketones (84) (R^1 = Ph or OEt, X = Cl or Br) or 2-bromocyclohexanone and carbonyl compounds R^2R^3CO (PhCHO, PhCH=CHCHO or cyclohexanone) to a suspension of zinc in diethylaluminium chloride, the enolates (85) may be converted to the chelates (86) which may be hydrolysed to give good yields of the hydroxyketones (87) (Equation 12). The condensation may be applied to the synthesis of a variety of cyclic compounds e.g. (88).

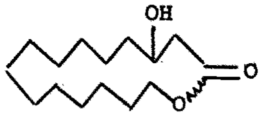


(84) (85) (86)



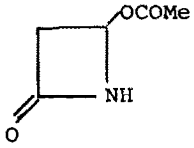
(87)

12

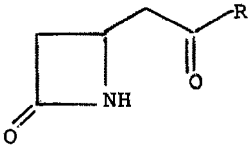


(88)

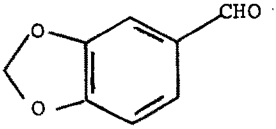
Enolates may also be made using diethylaluminium 2,2,6,6-tetramethyl-piperidide, which has been referred to in several previous surveys. Derivatives of α,β-unsaturated methyl ketones MeCOR (R = Ph,-CH=CHPh or-CH=CMe_2) may be added to 4-acetoxy-2-azetidienone (89) to give the products (90) which are useful intermediates in the synthesis of compounds having antibacterial activity [67].



(89)



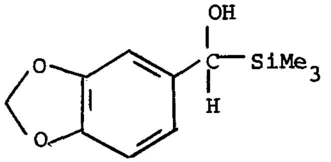
(90)



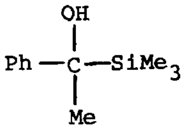
(91)

Reductions of a series of α,β-unsaturated ketones $R^1_2C{=}CR^2COR^3$ using triisobuylaluminium have been documented[68].The principal products are the carbinols $R^1_2C{=}CR^2\overset{R^3H}{C}OH$ but appreciable amounts of alkylated compounds $R^1_2C{=}CR^2C\,{}^{i}BuR^3OH$ are also detected. Some asymmetric induction is observed when optically active aluminium compounds, e.g. $Al(MeCHEtCH_2)_3$, are used. The reactions of lithium allylaluminate complex $Li[AlEt_3CH_2CH{=}CH_2]$ with α,β-unsaturated carbonyl compounds have been described briefly in a paper dealing mainly with boron compounds [69]. With PhCH=CHCOMe, the main product results from 1:2 rather than 1:4 addition.

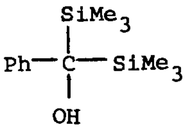
The aldehyde (91) is cleanly converted by $Al(SiMe_3)_3OEt_2$ to the alcohol (92) with utilisation of all three trimethylsilyl groups. The corresponding reaction with $Li[Al(SiMe_3)_4]$ is more complicated and several side reactions are detected [70]. Acetophenone does not react with $LiAl(SiMe_3)_4$ except in the presence of aluminium(III) chloride. Then the silylethanol (93) is formed but this rapidly decomposes to the vinylsilane $PhC(SiMe_3){=}CH_2$. Similarly the aluminium(III) chloride-ethyl benzoate complex reacts with $Al(SiMe_3)_2Et_2O$ to give (94) as the only silylated product.



(92)

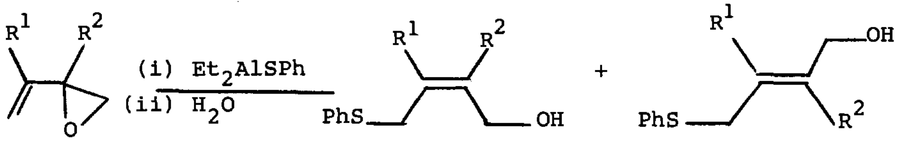


(93)

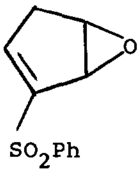


(94)

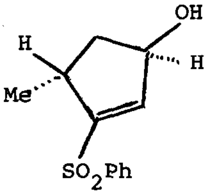
Reactions of $AlEt_2SPh$ with vinyl epoxides (95) (R^1 = H or Me; R^2 = Me or C_5H_{11} have also been documented [71]. The products, obtained in 78-94% yield are (96) and (97) with the Z-isomers (96) predominating (86-98%). The chiral epoxy-sulphone (98) reacts with a 1:1 CuMe-$AlMe_3$ mixture in THF at -78°C to give an 80% yield of the anti-allyl alcohol (99) almost uncontaminated with the syn isomer (100). It is interesting that (98) may be converted into (100) by treatment with LiMe-$LiClO_4$ in CH_2Cl_2-Et_2O. The compound dl- (101) reacts with CuMe-$AlMe_3$ in THF to give (102) cleanly without products from deprotonation [72].



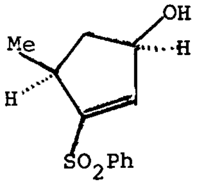
(95) (96) (97)



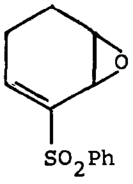
(98)



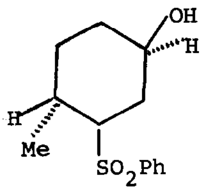
(99)



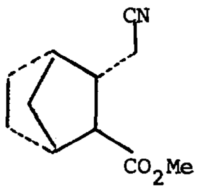
(100)



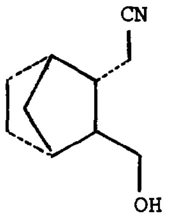
(101)



(102)



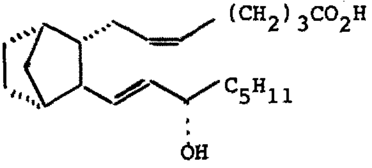
(103)



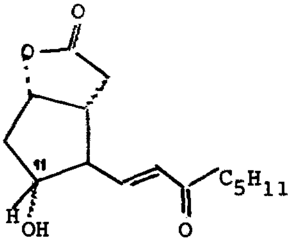
(104)

No attempt has been made in this survey to give a comprehensive account of the use of diisobutylaluminium hydride as a reducing agent for carbonyl functions. There have been examples of reductions of ketones [73-74], esters [75-78], lactones [79-80], and lactams [81-82]. Trimethylsilyl esters of simple carboxylic acids $RCOOSiMe_3$ (R = Ph, $PhCH_2$- $pMeOC_6H_4$-, n-C_7H_{15}-) and $Me_3SiO_2C(CH_2)_4CO_2SiMe_3$ give complex mixtures of products RCH_2OH, RCHO and RCO_2H [83]. A similar product mix was obtained by reduction of the ester (103) but the alcohol (104) could be isolated in 97% yield by using an $AlBu^i_2H$/ ester mole ratio of 4 [84]. This compound (104) is a useful starting material for the synthesis of the prostaglandin H_2 analogue (105): the B side chain may be introduced at the alcohol function, and subsequently the A side chain may be added by reaction of a Wittig reagent with the aldehyde formed by reduction of the nitrile function with diisobutylaluminium hydride.

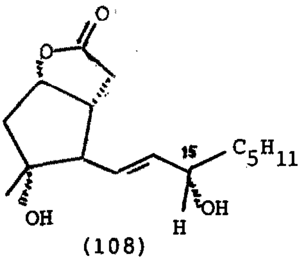
A detailed account [85] has been published of the use of diisobutylaluminium-2,6-di-t-butyl-4-methyl phenoxide (106) as a selective reducing agent in prostaglandin synthesis. A ten-fold excess converts the enone (107) into the 15S-allylic alcohol (108) in 95% yield without formation of the 15R-isomer. The high stereoselectivity is attributed to coordination of the aluminium compound at the C11 hydroxyl substituent since it is much reduced when the hydroxyl function is protected by THP or otherwise esterified. The selectivity is also diminished if the Bu^t-substituents in (106) are replaced by Me or H. The analogous reagent $Et_2AlOC_6H_2(2,6\text{-}Bu^t)(4\text{-}Me)$ gives reduction and ethylation products and $Me_2AlOC_6H_2(2,6\text{-}Bu^t)(4\text{-}Me)$ gives only methylation, showing that β-hydrogen atoms are essential for reduction. Several other examples of the use of (106) in prostaglandin synthesis have been described.



(105)

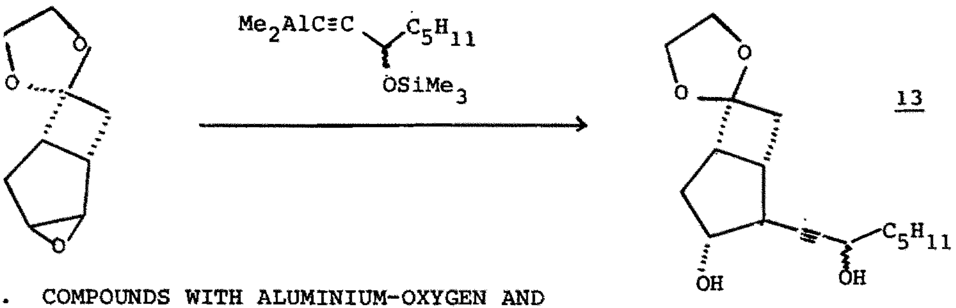


(107)



(108)

A different application of organoaluminium compounds is for the introduction of the B side chain (Equation 13)[86] [87].



13

8. COMPOUNDS WITH ALUMINIUM-OXYGEN AND ALUMINIUM-SULPHUR BONDS

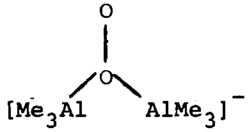
Organometallic compounds having aluminium-oxygen bonds are the subject of two patents. One [88] describes alkylaluminoxanes from the hydrolysis of trialkylaluminiums with stoichiometric amounts of water in hydrocarbon solvents. The other [89] is concerned with reactions of organoaluminium compounds with dialkyl phosphites and dialkyl phosphates. There is another report [90] on chemiluminescence observed in the interaction of peroxides and organoaluminium compounds. Radicals formed in the reaction between trialkylaluminiums R^1_3Al (R^1 = Et, Bu^i, or Ph) or Et_2AlOEt and peroxides $R^2_2O_2$ (R^2 = $PhCH_2$, Bu^t or $SiMe_3$) have been trapped by Bu^tNO [91]. Diethyl(tribenzylsiloxy)aluminium $(PhCH_2)_3SiOAlEt_2$, made from tribenzylsilanol and triethylaluminium is shown by cryoscopic measurements to be trimeric [92]. It decomposes during 50 h at 250°C with formation of ethane, ethylene, tribenzylsilane and triethylaluminium, with little exchange of radicals between aluminium and silicon.

The molecular structures of the complexes $Me_3AlO(CH_2)_3$ and Me_3AlSMe_2 have been found by gas-phase electron diffraction [93] The most important bond lengths and angles are for $Me_3AlO(CH_2)_3$: Al-C 196.5(7), Al-O 203(4), O-C 146.5(2) pm; OAlC 98.8(8), AlOC 123(4), COC 94.7(12)° and for Me_3AlSMe_2: Al-C 198.5(5), Al-S 255(2), S-C 181.7(5) pm; SAlC 96.0(10), AlSC 124(2), and CSC 99(3).° The angle between the Al-O bond and the OC_2 plane in $Me_3AlO(CH_2)_3$ is 37(7)° (in contrast to Me_3AlOMe_2 where the configuration at oxygen is almost planar). The angle between the AlS bond and the SC_2 plane in Me_3AlSMe_2 is 31(5)°. The reaction between the potassium oxide KO_2 and trimethylaluminium in aromatic solvents in the presence of a crown ether (c.f. Ref [39]) gives the compound [K dibenzo-18-crown-6][$Al_2Me_6O_2$] which is apparently stable for 24 h in boiling toluene. A single crystal X-ray study shows that the anion has the structure (109) in which the two aluminium atoms are joined by one oxygen of a bridging superoxo ligand. As expected, the O-O bond (147 pm) is long and its weakness is reflected in the low ν(O-O) at 851 cm^{-1} in the IR spectrum [94].

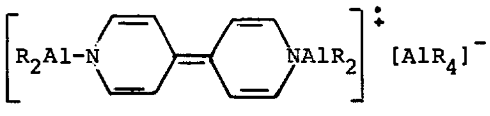
The mass spectra of the dialkyl(alkylthio)aluminiums R_2AlSR (R = Me, Et, Pr or Bu^i) or Bu^i_2AlSEt show peaks derived from dimeric species [95]. After initial loss of alkyl radicals, the fragmentation in the mass spectrometer involves mainly elimination of saturated hydrocarbons with possible formation of methylene bridges between aluminium atoms. Accurate mass measurements have shown that some of the peaks reported earlier (1969) in the mass spectrum of trimethylaluminium arise from oxidation products.

9. COMPOUNDS WITH ALUMINIUM-NITROGEN BONDS

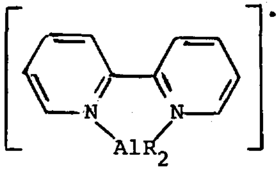
Paramagnetic species obtained from alkylaluminium compounds and nitrogen-containing heterocycles were referred to last year. Full accounts of these have now been published. Both pyridine and 4,4'-bipyridyl react with trialkylaluminiums AlR_3 (R = Me, Et or Cl) and alkali metals in THF to give ion pairs (110) which are stabilised by coordination in the donor solvent. 2,2'-Bipyridyl gives neutral radicals (111) which are persistent in



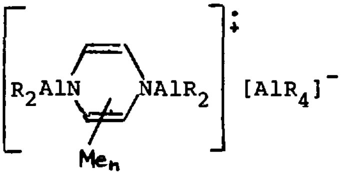
(109)



(110)



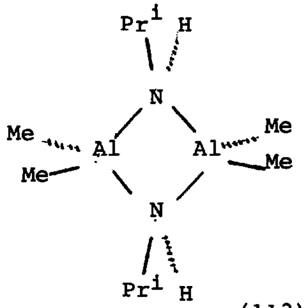
(111)



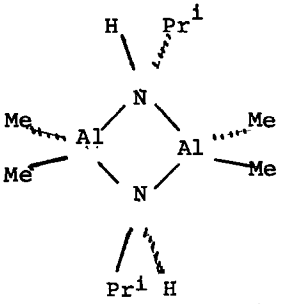
(112)

non-polar solvents [96]. Radical ion pairs (112) (n = 2 or 4) have been obtained with a range of methyl-substituted pyrazines [97]. The spin distributions have been studied by ESR spectroscopy and the effects of steric hindrance have been demonstrated. Similar radicals with K^+, Na^+, Li^+, $PhMg^+$, Me_2Ga^+, $PhBe^+$, Ph_2B^+ in place of R_2Al^+ have been discussed in two further papers [98] [99]. ESR measurements and calculations indicate that there is a gradation in the above series from ion pairs e.g., $K^+X^{\cdot-}$, to covalently bonded radical complexes, e.g., $[R_2AlX\bullet]^+$ (X =, e.g., bipyridyl) (111). Radical species in the system $NCCHMeCH_2N{:}NCH_2CHMeCN$ (AIBN)-AlR_3 (R = Me, Et or Bu^i) have also been described [100].

Bis(μ-isopropylamidodimethylaluminium) consists of a 2:1 mixture of cis-(113) and trans-(114) isomers both in the



(113)



(114)

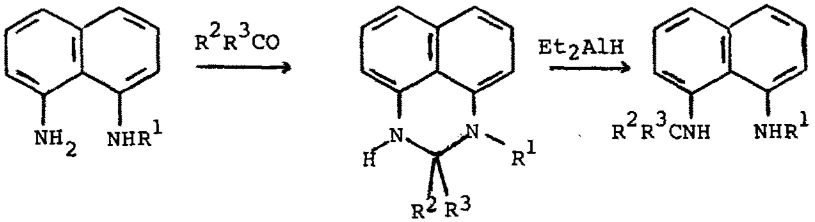
solid and in toluene over a wide temperature range [101]. The most important mean molecular parameters are Al-N 195.2(9) Al-C 196.1(6) and N-C 149.7(8) pm. It is not clear whether the persistent 2:1 (113):(114) mole ratio in solution results from a low free energy of interconversion or a high activation energy for the process. Similar cis-trans isomerism is found in the compounds $[MMe_2NMePh]_2$ (M = Al, Ga, or In) [102]. An X-ray study of the indium derivative shows only the trans-isomer in the solid but a mixture of cis- and trans-compounds in toluene, benzene or dichloromethane is detected by NMR. In solution the cis-isomer is the more abundant for the aluminium and gallium compounds but the trans is the more abundant for the indium derivative. For $[AlMe_2NMePh]_2$, the concentration of the cis-isomer increases with falling temperature: for the gallium compound the situation is reversed and the trans-isomer becomes the more stable at low temperatures. It is evident that the effects which determine the cis-/trans- ratio are subtle and complex.

Very little is at present known about the way in which dimeric or trimeric organoaluminium amides are formed. A study of the kinetics and mechanism for the elimination of hydrogen between dimethylaluminium hydride and benzylamine (Equation 14) shows that the rate is determined by a series of equilibria

$$[AlHMe_2]_3 + 3PhCH_2NH_2 \rightarrow 3/2[AlMe_2N(CH_2Ph)H]_2 + 3H_2 \qquad \underline{14}$$

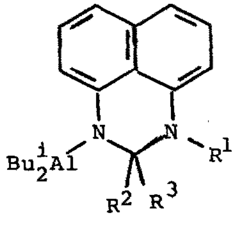
involving 1:1 and 1:2 complexes between $AlMe_2H$ and $PhCH_2NH_2$. As in the study of the reaction leading to formation of $[AlMe_2NMePh]_2$, described in the 1979 Survey, the elimination of hydrogen is thought to come from interaction of dissociated fragments of the $PhCH_2NH_2.AlHMe_2$ complex [103].

There have been several accounts of the use of alkylaluminium amides in organic syntheses. For example, selective N-alkylation of polyamines (115) (R^1 = n-C_7H_{15}, cyclo-$C_{12}H_{23}$) may be achieved under mild conditions by the transformations in Equation 15 (R^2R^3CO = n-$C_6H_{13}CHO$, PhCHO or $(CH_2)_{11}CO$), probably *via* the

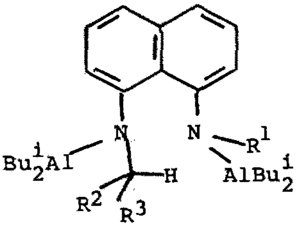


15

(115)

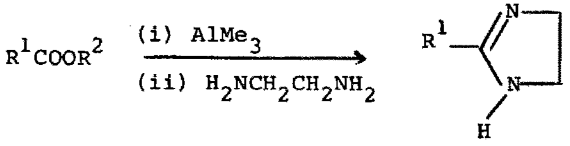


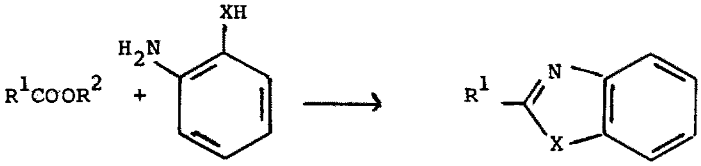
(116)



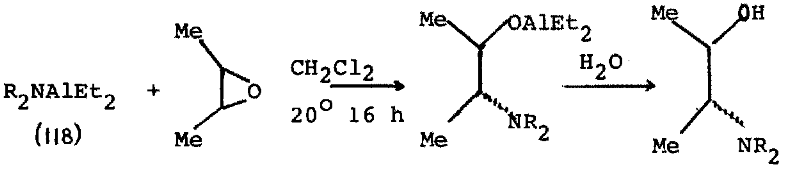
(117)

organoaluminium intermediates (116) and (117). Reactions of this type have been used for the synthesis of a wide range of macrocyclic polyamines [104]. A widely applicable one-step conversion of esters into 2-imidazolines, benzimidazoles, or benzthiazoles is shown in equations 16 and 17 (R = 2-thienyl, Ph, $PhCH_2$-, cyclo-C_6H_{11}, or radicals from various N-containing heterocycles. X = NH or S). The presumed intermediates, e.g. $Me_2AlNHCH_2CH_2NH_2$, in these reactions have not been isolated


16


17

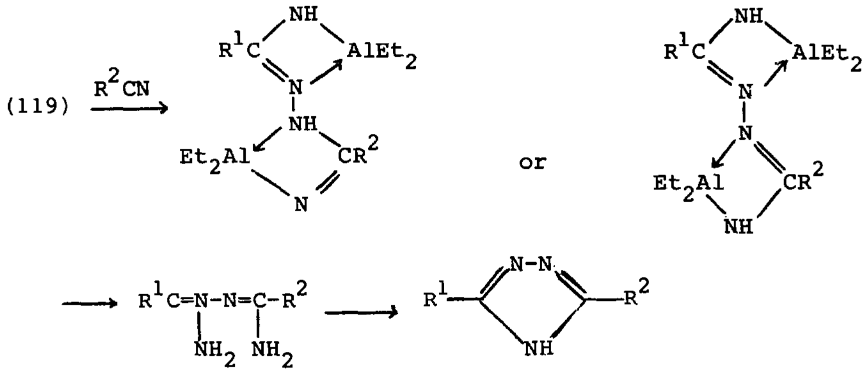
and their structures are at present unknown [105]. A further application is shown in Equation 18.


18

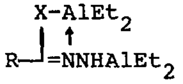
(R_2 = Et_2, HPh, HPr^n, $(CH_2)_4$ $(CH_2{=}CHCH_2)_2$ $(CH_2Ph)_2$)

Epoxides are converted into trans-β-amino alcohols in 44-86% yield. Again the organoaluminium reagents (118) are made in situ from triethylaluminium and amine and used without isolation or characterisation [106].

Bis(diethylalumino)-substituted amidrazones (119), made from $R^1C(:NNH_2)NH_2$ and triethylaluminium appear from cryoscopic measurements to be tetrameric (R^1 = Ph) or octameric (R^1 = n-C_5H_{11}) in benzene. These compounds react with nitriles to give, after hydrolysis, unsymmetrical N(aminomethylene)amidrazones which cyclise on heating to 200-250°C (Equation 19)

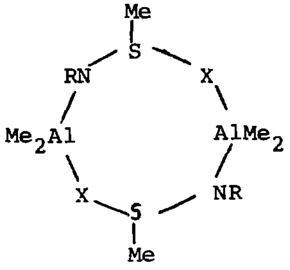


19

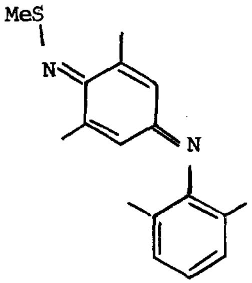


X = NR or O

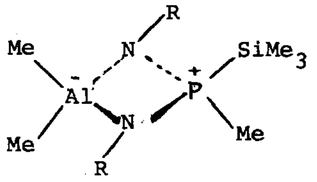
(119)



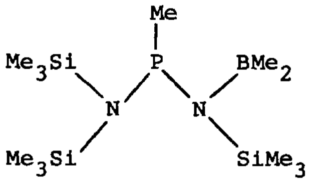
(120)



(121)



(122)



(123)

The corresponding carbohydrazides (119 X = O) may be made similarly from $RCONHNH_2$ and two equivalents of triethylaluminium.

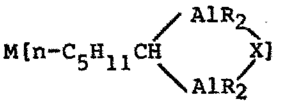
Several compounds with aluminium-nitrogen bonds in ring systems have been described. For example, the sulphur diimines RN=S=NR and the sulphinylanilines RN=S=O react with trimethylaluminium to give compounds (120) $[AlMe_2\{RNS(Me)NR\}]_2$ (R = $4-MeC_6H_4-$, $4-ClC_6H_4-$, $2,6-Me_2C_6H_3-$) and $[AlMe_2\{RNS(Me)O\}]_2$ (R = Me , Ph, $4-MeC_6H_4-$, $4-ClC_6H_4-$, $2,6-Me_3C_2H_3-$ and $2,4,6-Me_3C_6H_2-$) in which the S atom has been methylated [108]. NMR studies indicate the presence of several conformers in solution and also some dissociation to monomer. The sulphur diimine derivatives decompose slowly in $CDCl_3$ and rapidly in pyridine to give complex products. The compound (120) $R = 2,6\text{-}Me_2C_6H_3\text{-}$, $X = NR$ reacts with mercury(II) or tin(II) chlorides to give $[Cl_2Al\{RNS(Me)NR\}]_2$ and with t-butanol to give (121) for which X-ray and NMR studies indicate conformational isomers both in the solid and in solution [109].

Other interesting heterocycles have been obtained from the reaction between trimethylaluminium and the two-coordinate phosphorus compounds $Me_3SiNRP{=}NR$ ($R = SiMe_3$ or Bu^t). From NMR measurements [110], it appears that these have the structure (122). The product from the reaction between $(Me_3Si_2)NP{=}N(SiMe_3)$ and trimethylboron is different (123), suggesting that the initial step in the reaction between $Me_3SiNRP{=}NR$ and $AlMe_3$ may involve addition across the P=N bond to give a compound analogous to (123) and that this subsequently rearranges with migration of $SiMe_3$ from nitrogen to phosphorus and formation of (122).

10. ORGANOALUMINIUM COMPOUNDS INVOLVING OTHER METALS

This section is concerned with papers where the emphasis is on the composition or structure of the bimetallic organometallic compounds. Papers dealing mainly with the use of bimetallic systems as catalysts are referred to in the next section. The preparation of magnesium-aluminium compounds from Grignard reagents and aluminium alkoxides has been described [111]. Another patent [112] deals with preparation of magnesium-aluminium compounds which are soluble in hydrocarbons.

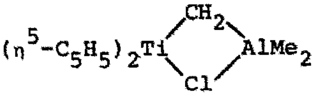
Binuclear organoaluminium complexes, which are assumed to have the structure (124) have been made from $n\text{-}C_5H_{11}CH(AlR_2)_2$ ($R = Et$ or Bu^i) and the alkali metal hydrides or fluorides in THF. There is some evidence for formation of less stable 2:1 complexes



(124) (X = H or F)

$Me_2Al(\mu C{\equiv}CMe)_2M(\mu C{\equiv}CMe)_2AlMe_2$

(125)

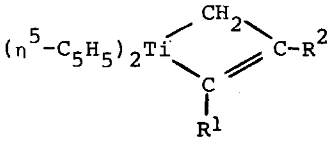


(126)

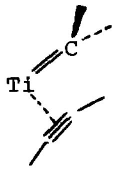
e.g. $Li_2[C_5H_{11}CH(AlBu^i_2)_2H_2]$. Some ^{27}Al NMR data has been given [113]. In another study [114], the complexes $MAl_2(C{\equiv}CMe)_4Me_4$

(M = Be or Mg) have been made from $[AlMe_2(C{\equiv}CMe)]_2$ and $(MeC{\equiv}C)_2M$ in 1,4-dioxan. From cryoscopic, spectroscopic and conductivity measurements it is suggested that the complexes consist of clusters in which the central Group 2 metal is linked to each of two $AlMe_2$ groups by two bridging propynyl groups (125).

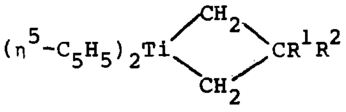
Considerable progress has been made during 1981 in elucidating the structures of the products obtained by the interaction of organoaluminium compounds and organometallic compounds of transition metals. Details of the structures of (127) ($R^1 = R^2 = Ph$; $R^1 = Ph$, $R^2 = SiMe_3$; $R^1 = R^2 = SiMe_3$), made by the reaction of alkyne $R^1C{\equiv}CR^2$ with the bimetallic compound (126), have been published [115]. Whereas the bis(trimethylsilyl) derivative (127) is reasonably well described as a cyclobutene complex (as shown), the detailed interatomic distances in the biphenyl compound indicate a tendency towards the alkyne-alkene structure (128). As reported in a preliminary communication last year, the compound (126) reacts with alkenes $H_2C{=}CR^1R^2$ give titanacyclobutanes (129). Structures of three of these ($R^1 = Bu^t$, $R^2 = H$; $R^1 = Ph$, $R^2 = H$;and $R^1 = R^2 = Me$) have been found by X-ray diffraction. In all cases the metallacyclic ring is planar [116]. The formation of a complexes (130), like (126) but with a long chain alkylidene bridge, has been achieved by the reaction between propenyltitanium compounds and diisobutylaluminium hydride (Equation 20) [117]. Unfortunately this



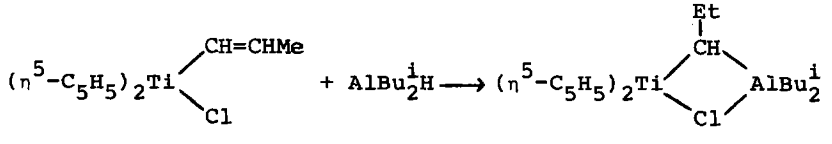
(127)



(128)



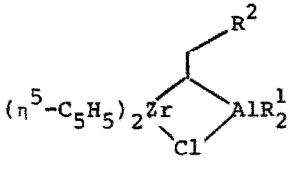
(129)



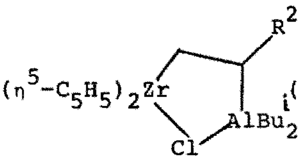
20

(130)

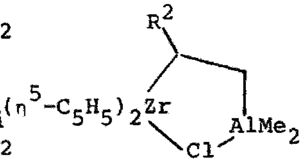
complex is rather unstable, but it has been characterised by NMR and by its reaction with cyclohexanone which gives propylidenecyclohexane. The zirconium compounds (131) (R^1 = Bu^i) and (132) (R^2 = Bu^t, Bu^n or Me) may be made similarly from [$ZrCl(\eta^5$-$C_5H_5)_2(CH{=}CHR^2)$] and $AlBu^i_2H$ and (131) (R = Me) from [$ZrHCl(\eta^5$-$C_5H_5)_2$] and $Al(CH{=}CHR^2)Me_2$. The regiospecificity of these reactions is greatest



(131)



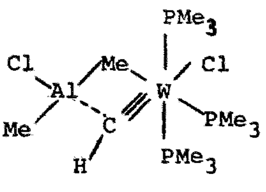
(132)



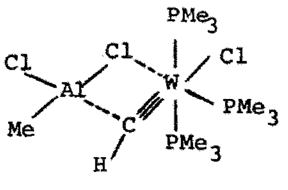
(133)

when R is large. For example when R^2 = Bu^t the ratios (131) (R = Bu^i):(132) or (131) (R = Me):(133) are >20. The zirconium like the titanium compounds give Wittig-type reactions with ketones.

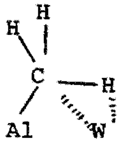
Bimetallic alkylidyne complexes of tungsten and aluminium have also been studied [118] [119]. The reaction between [$WCl_2(PMe_3)_4$] and two equivalents of $AlMe_3$ in toluene gives a red-brown solution. After addition of tetramethylethylenediamine, crystals of [$W(CH)Cl(PMe_3)_4$] may be obtained. On treatment with $AlMe_3$ or $AlMe_2Cl$ the formation of complexes (134) and (135) is detectable by NMR. Neither can be isolated pure, but an X-ray study has been completed of mixed crystals consisting of 82% (134) and (18%) (135). The W-C distance is 180.7(6) pm and the C-H distance 84(6) pm. The W-C-H angle is 163.8(44).°



(134)



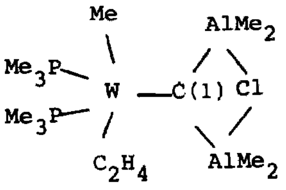
(135)



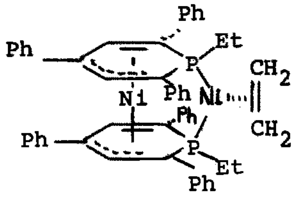
(136)

The non-linearity at C is attributed to interaction between aluminium and the methylidyne carbon(Al-C 211.3(6) pm). The distance between tungsten and the bridging atom (C or Cl) is

252.6 pm, close to the W-Cl distance, even though the bridging atom is 82% C. Hence the tungsten-methyl interaction is weak. It has been suggested that the bonding may be described by (136). The compounds (134) and (135) react with trimethylaluminium and ethylene to give the compound $[W(CAl_2Me_4Cl)Me(PMe_3)_2(\eta^2-C_2H_4)]$ which has been shown by X-ray diffraction to have the structure (137)[120].The W-C bond length (181.3 pm) is close to that expected for a triple bond: the compound may be regarded as a tungsten(IV) carbide complex $(W\equiv C)^-(Al_2Me_4Cl)^+$ in which there is



(137)



(138)

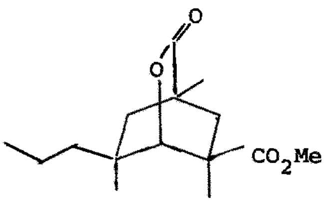
one "electron precise" and one "electron deficient" bridge between the two $AlMe_2$ groups. Other bond lengths and angles are: C(1)-Al 198.4(5), 204.3(5), Al-Me 194.8(3), Al-Cl 238.1(2) 237.1(3) pm; Al-C(1)-Al 97.06(23), Al-Cl-Al 78.85(9)°. The alkylidyne bridge in (137) is slightly asymmetric but much less so than in $[AlPh_2(C\equiv CPh)]_2$ described some years ago. This work indicates that the structures of the bimetallic intermediates involved in catalytic processes may be considerably more complex than envisaged so far.

The reduction of titanium(IV) chloride by a series of cyclohexylaluminium compounds R_3Al, R_2AlCl, $R_2AlClEt_2O$, $R_{1.5}AlCl_{1.5}Et_2O$ and $RAlCl_2Et_2O$ (R = cyclo-C_6H_{11}) has been studied [121]. 2,4,6-Triphenylphosphabenzene reacts with $[Ni[(C_5H_7O_2]_2]$ and $AlEt_2OEt$ to give a compound, which has been shown by a single crystal X-ray study [122] to have the structure (138).

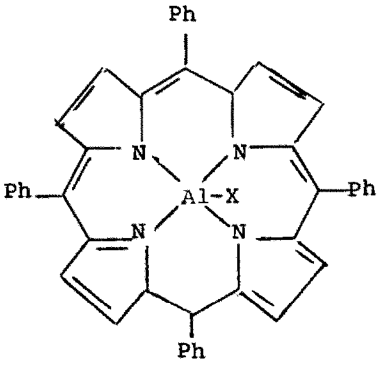
11. CATALYSIS

Organoaluminium compounds continue to be used in a wide variety of catalytic systems. Examples include the use of $[Mg_4Al_2Bu_{12}-(C_8H_{17})_2]$ as catalyst for the reaction between magnesium powder and chloro-alkanes BuCl and $C_8H_{17}Cl$ to give $[Mg(Bu)_n(C_8H_{17})_{2-n}]$ [123] and the use of $PdCl_2$-PPh_3-$AlBu^i_2H$ for the preparation of substituted allenes from reactions between Grignard reagents and allenic or propargylic halides [124]. A catalyst consisting of a chiral amine, bis(N-methylsalicylaldimine) nickel and triisobutylaluminium has been used in a study of asymmetric induction in the isomerization of racemic alk-1-enes to alk-2-enes [125]. The asymmetric induction may be enhanced by using the optically active tris[(R)-2,3-dimethylbutyl]aluminium in place of $AlBu^i_3$. The hydrogallation of alk-1-enes by $NaGaH_4$ is catalysed by $[TiCl_2(\eta^5-C_5H_5)_2]-NaAlEt_4$ [126] and the hydrogenation of a variety of alkenes and alkynes by $[RhCl_2(PR_3)_2]$ in the presence of triethyl-aluminium [127]. A detailed study [128] of the reactions of organozirconium compounds with unsaturated ketones catalysed by $Ni(C_5H_7O_2)_2-AlBu^i_2H$ has shown the presence of various Ni(I) active species.

As in previous years, the most extensive applications of organoaluminium compounds have been in the catalysis of reactions of alkenes. The gas phase oligomerisation of ethylene in the presence of π-allylnickel chloride-alumina-ethylaluminium sesquichloride is said to give more of the C_8-C_{14} fraction than liquid phase oligomerisation [129]. A detailed study has been made of the regioselective oligomerisation of isoprene, using a complex catalyst of $Ni(C_5H_7O_2)_2$-N-methylpyrrolidone-triethylaluminium-trialkylphosphine or trialkyl phosphite. Yields of up to 97% of cyclic dimers have been obtained [130]. The oligomerisation of styrene has been studied using a similar catalyst, $[Ni(S_2CNEt_2)_2]-AlClEt_2$ and phosphine or phosphite [131], and an extensive investigation has been made of the oligomerisation of cyclic C_5-C_8 and C_{12} alkenes using the $[Zr(C_5H_7O_2)_3Cl]-AlEtCl_2$ and related catalyst systems [132]. The reactions between C_{6-10} alk-1-enes and butadiene with $ZrCl_4-AlEt_2Cl$ as catalyst give products from 1,4-addition of alkenes to butadiene [133]. Homo- as well as co-dimers are formed: homodimers of hex-1-ene may be suppressed by addition of donors such as triphenylphosphine. The linear cooligomerisation of dichloro- and dimethoxy-vinylsilanes with butadiene in the presence of $Ti(OBu)_4-PPh_3-AlEt_3$ has also been described [134]. The reaction between methyl methacrylate and diethylaluminium chloride with azoisobutyronitrile as catalyst gives a crystalline trimer which has been shown [135] from ^{13}C NMR and mass spectroscopy to have the structure (139). Several related dimers and trimers have



(139)



(140)

been separated by chromatography and characterised spectroscopically [137].

There are many reports relating to both traditional [168] and so-called second generation Ziegler-Natta catalysts. The catalyst from solid $TiCl_3$ and $AlEt_2Cl$ which has been pretreated with propylene gives polypropylene with higher bulk density than catalyst which has not been pretreated [137]. The stereospecificity of the $TiCl_3$-$AtEt_3$ catalyst for polymerisation of propylene may be improved by replacing some of the triethylaluminium by $Et_2AlOP(O)(OEt)_2$ [138]. The factors affecting the alternating copolymers of butadiene and propylene using $TiCl_4$-ketone-$AlBu^i_3$ catalysts have been described [139, 140]. Phenylacetylene may be polymerised using heterogeneous $TiCl_3$-$AlEt_3$ or homogeneous WCl_6-$AlEt_3$ catalysts [141]. The catalysts $[TiCl_{4-n}(OPh)_n]$-$AlEt_2Cl$ for polymerisation of ethylene give the greatest yields when the Al-Ti ratios are 1.75, 2, 2.5 and 4 for n = 1, 2, 3 or 4 respectively [142]. A careful study of the polymerisation of propylene using $Ti(OBu)_4$-$Al_2Cl_3Et_3$ suggests that there are both soluble and insoluble catalysts. Below $21^{o}C$ homogeneous catalysts give isotactic polymer with a narrow molecular weight distribution. At higher temperatures solids precipitate, and the molecular weight distribution becomes bimodal and broad [143]. Several papers [144-146] are concerned with the polymerisation of <u>trans</u>-pentadiene by the soluble $Ti(OBu)_4$-AlR_3 system (R = Me, Et, Bu^i and n-C_8H_{17}). The catalytic mixture has been examined by ESR spectroscopy both in the absence and in the presence of diene, and the ESR signal has been associated with catalytic activity. Only a small fraction of the Ti-C bonds are considered to be active in polymerisation. The factors determining the molecular weight distribution, which is again broad and bimodal, and the stereoregularity of the polymer have been discussed. Catalysts based on $[TiClR^1(\eta^5\text{-}C_5H_5)_2]$ (R^1 = Me or Et) have also been examined in some detail. These compounds are activated for ethylene polymerisation by oxyaluminium compounds obtained by hydrolysis of $AlCl_nR^2_{3-n}$ (R^2 = Me or Et, n = 0, 1 or 2). Catalysts made by hydrolysis of ethylaluminium derivatives are more active and give narrower molecular weight distributions than those made by hydrolysis of methylaluminium compounds: the catalytic activity seems to be independent of the group R^1 attached to titanium, but to fall as the number of alkyl groups R^2 on aluminium is increased [147].

A detailed study has been made of the product distribution and rate of oligomerisation of ethylene using the soluble Ziegler catalyst $[TiClR(\eta^5\text{-}C_5H_5)_2]\text{-}AlEtCl_2$ (R = Et, Pr, C_5H_{11}, C_6H_{13}). Evidence has been found that formation of the primary complex is diffusion controlled and that there is transfer of ethyl groups from aluminium to titanium [148, 149]. A mathematical model has been developed for the complex kinetic system [150]. In chlorinated solvents such as dichloromethane or chloroethane the catalyst appears to be different: here also, however, the kinetics have been studied and a mathematical description of the process has been presented [151]. Work in another laboratory [152] has been on ESR experiments with $[TiCl_2(\eta^5\text{-}C_5H_5)_2]\text{-}Al_2Cl_3Et_3$ or $AlEt_2Cl$. Ethylene may be polymerised at -30°C using the catalytic system $TiCl_4\text{-}Al(SiMe_3)_3\text{-}Et_2O$ with Ti:Al 5:2; this appears to be the first example in which a polymerisation is initiated at a transition metal-silicon bond [154].

As in previous years, there have been a number of reports on polymerisations using soluble catalysts made from alkylaluminium and vanadium compounds. For example, accounts have appeared on the effect of anisole on the polymerisation of propylene with $(C_5H_7O_2)_2\text{-}AlEt_2Cl$ [155], on polymerisation of

[1-^{2}H]-1,3-pentadiene to trans-1,4-stereoregular polymer, using VCl_3-$AlEt_3$ [156], on ESR experiments during polymerisation of ethylene with [$VCl_2(\eta^5$-$C_5H_5)_2$]-$Al_2Cl_3Et_3$ or $AlEt_2Cl$ [157], and on 2,3,4,4-tetrachloro-2-butenoic acid esters as activators in copolymerisation of ethylene with other alkenes [158]. NMR and ESR measurements on the catalytic systems [$Ni(C_5H_7O_2)_2$]-propadiene-$AlBu^i_3$ for polymerisation of propadiene (allene) have also been described [159].

Supported Zeigler catalysts, usually based on magnesium halides (possibly with halides of other metals), electron donors (e.g. ethyl benzoate), titanium alkoxides and alkylaluminium compounds, have been described in a series of patents [160-164] and papers [165-168]. One report [169] concerning determination of active sites includes a review of the development of Ziegler-Natta systems. A patent [170] describes a magnesium-titanium-aluminium catalyst supported on a polyalkene having carboxylic acid groups. Other catalysts have been supported on active carbon [171-175].

These have been reports on the polymerisation of styrene [176] using diethylaluminium chloride in chloromethane and on the polymerisation and copolymerisation of styrene with other alk-1-enes or vinyl ethers using a catalyst from $LiAlR_4$ (R = Et, C_8H_{17}, $C_{10}H_{21}$ or $C_{16}H_{33}$)-$AlCl_3$-$TiCl_4$ [177]. Other reports have described the copolymerisation of styrene with methyl methacrylate or acrylonitrile using alkylaluminium dihalides [178] or diethylaluminium chloride in the presence of ultraviolet light [179], and the alternate copolymerisation of indene and methyl methacrylate in the presence of ethylaluminium sesquichloride [180].

Block copolymers have been obtained by a combination of anionic and Ziegler-Natta polymerisation [181]. If living polyisoprene or polystyrene, from polymerisations initiated by n-butyl-lithium is treated with aluminium(III) chloride, the resulting polymer has pendant aluminium groups. In the presence of titanium(IV) chloride, these provide points at which polyethylene may be grafted by Ziegler-Natta polymerisation. Triethyl- or triisobutyl-aluminium enhances the initiation of anionic polymerisation of butadiene by organosodium compounds: high yields of poly-1,2-butadiene are obtained [182].

Several further papers have been published in the series describing the cationic polymerisation of isobutene using aromatic initiating systems. The reaction between triphenylaluminium and t-butyl chloride gives t-butylbenzene rapidly even at -60°C, but $ClMe_2C(CH_2)_5CMe_2Cl$ and triphenylaluminium do not give $PhMe_2C(CH_2)_5CMe_2Ph$ quantitatively under similar conditions: various alkenes are formed by proton eliminations [183]. The $Bu^tCl/AlPh_3$ and $ClMe_2C(CH_2)_5CMe_2Cl/AlPh_3$ systems initiate polymerisation of isobutene giving polymers with phenyl end groups [184]. These and unsaturated chain ends from proton eliminations have been oxidised to carboxyl end groups. After treatment with thionyl chloride, these may be coupled to living polystyryl anions to give isobutene-styrene block copolymers [185].

As in previous years organoaluminium compounds have been used in alkene metathesis catalysts [187-193].

Diethylaluminium chloride reacts with $\alpha,\beta,\gamma,\delta$-tetraphenylporphin to give the metalloporphin (140) which catalyses the polymerisation of ethylene oxide and propylene oxide to polymers with narrow molecular weight distributions [194, 195]. The polymerisation of 2-alkenylfurans has been investigated with a variety of catalysts containing AlR_3 (R = Et, Bu^i) or Et_2AlOEt and titanium or vanadium compounds. Control experiments with 5-methylfuran show that there is no polymerisation by ring opening. With 2-vinyl and 2-isopropenyl-furan crosslinking competes with linear vinyl polymerisation and the products are gels [196].

12. STRUCTURAL STUDIES

Data from diffraction studies on organoaluminium compounds are given in ref. [39], [40], [93], [94], [101], [119] and [120].

REFERENCES

1. P.G. Harrison in E.W. Abel and F.G. Stone (Eds.) 'Organometallic Chemistry' Vol.10, Royal Society of Chemistry, London (1982), p.64.
2. G. Davidson, Coord. Chem. Rev. 34 (1981) 74.
3. D.B. Malpass, L.W. Fannin, and J.J. Ligi in M. Grayson and D. Eckroth (Eds.) Kirk Othmer Encyl. Chem. Technol. Wiley, New York Vol.16 3rd. Edn. (1981) p.565.
4. J.J. Eisch 'Organometallic Synthesis Vol.2, Non Transition Metal Compounds,' Academic Press, New York, 1981.
5. B.B. Snider, D.J. Rodini, M. Karras, T.C. Kirk, E.A. Deutsch, R. Cordova, and R.T. Price, Tetrahedron, 37 (1981) 3927.
6. K. Oshima, H. Yamamoto, and H. Nozaki in: Z. Yoshida (Ed.) 'New Synthetic Methodology and Biologically Active Substances. Vol.6, Elsevier,Amsterdam (1981) p.19.
7. J.F. Normant and A.Alexakis, Synthesis, (1981) 841.
8. D.M. Adams and E.A.V. Ebsworth (Eds.), Spectroscopic properties of inorganic and organometallic compounds, Vol.14, Royal Society of Chemistry, London (1981).
9. P.G. Harrison in 'Rodd's Chemistry of Carbon Compounds' Supplement to 2nd Edn, Vol.3BC, Elsevier, Amsterdam (1981) p.189.
10. J.P. Kennedy and E. Maréchal, J. Polym. Sci. Macromol. Rev. 16 (1981) 123.
11. B.A. Dolgoplosk, J. Polym. Sci. Polym. Symp. 67 (1980) 99.
12. H.D. Garrison, U.S. Patent, 4 251 453; Chem. Abstr. 95 (1981) 62 395.
13. D.P. Skulkova, E.M. Danin, E.P. Makarova, L.F. Kornetova, G.I. Semenova, N.N. Korneev, and E.P. Bezukh, USSR Pat.81 819 108; Chem. Abstr., 95 (1981) 81 208.
14. V.N. Bocharev, A.I. Belokon', A.V. Kuchin, and S.I. Smogorzhevskii, Zh. Obshch. Khim., 51 (1981) 1240; J. Gen. Chem. USSR (Engl. Transl.) 51 (1981) 1050.
15. G.A. Tolstikov, F.Kh. Valitov and A.V. Kuchin, Zh. Obshch. Khim., 50 (1980) 2715; J. Gen. Chem. USSR (Engl. Transl.), 50 (1980) 2195. K. Takai, K.Oshima, and H. Nozaki, Bull. Chem. Soc, Jpn., 54 (1981) 1281.
16. G.A. Tolstikov, F.Kh. Valitov, and A.V. Kuchin, Zh. Obshch. Khim., 51 (1981) 1599; J. Gen. Chem. USSR (Engl. Transl.), 51 (1981) 1359.

17. L. Rösch, G.Altnau, W. Erb, J. Pickardt and N. Bruncks, J. Organomet. Chem., 197 (1980) 51.
18. K. Isobe, P.M. Bailey and P.M. Maitlis, J. Chem. Soc., Chem. Commun. (1981) 808.
19. K. Isobe, D.G. Andrews, B.E. Mann and P.M. Maitlis, J. Chem. Soc., Chem. Commun. (1981) 809.
20. T. Hiyama, Y. Morizawa, H. Yamamoto, and H. Nozaki, Bull. Chem. Soc. Jpn., 54 (1981) 2151.
21. S. Padmanabhan and K.M. Nicholas, J. Organomet. Chem., 212 (1981) 115.
22. M. Sato, K. Takai, K. Oshima, and H. Nozaki, Tetrahedron Lett., 22 (1981) 1609.
23. T. Hayashi, Y. Katsuro, Y. Okamoto, and M. Kumada, Tetrahedron Lett., 22 (1981) 4449.
24. T.V. Dmitrieva, G.V. Ratovskii, V.I. Donskikh, and F.K. Shmidt, Koord. Khim. 7 (1981) 1029; Chem. Abstr. 95 (1981) 115 642.
25. L. Synoradzki, M. Bolesławski, S. Pasynkiewicz, and T. Zawada, Przem. Chem. 60 (1981) 200; Chem. Abstr. 95 (1981) 62 290.
26. P.J. Dolan, D.C. Moody, and R. Schaeffer, Inorg. Chem. 20 (1981) 745.
27. H. Schmidbaur and G. Müller, Monatsh. Chem. 111 (1980) 1233.
28. K. Hattori, Y. Matsumura, T. Miyazaki, K. Maruoka, and H. Yamamoto, J. Am. Chem. Soc., 103 (1981) 7368.
29. R.E. Marsh, J. Cryst. Mol. Struct., 10 (1980) 163.
30. G. Sonnek, H. Reinheckel, and K-G. Baumgarten, Z. Chem. 21 (1981) 268.
31. U.M. Dzhemilev, A.G. Ibragimov, O.S. Vostrikova, G.A. Tolstikov, and L.M. Zelenova, Izv. Akad. Nauk SSSR, Ser. Khim., 30 (1981) 361; Bull. Acad. Sci. USSR Div. Chem. Sci. 30 (1981) 281.
32. G.A. Tolstikov, F.Kh. Valitov, and A.V. Kuchin, Zh. Obshch. Khim., 51 (1981) 1682; J. Gen. Chem. USSR (Engl. Transl.) 51 (1981) 1434.
33. F. Barbot and P. Miginiac, J. Organomet. Chem., 222 (1981) 1.
34. G. Courtois, M. Harama and P. Miginiac, J. Organomet. Chem. 218 (1981) 1.
35. G. Courtois, M. Harama, and P. Miginiac, J. Organomet. Chem., 218 (1981) 275.

36. M. Skowrońska-Ptasińska, S. Pasynkiewicz, and E. Sieczek J. Organomet. Chem. 206 (1981) 1.

37. N.S. Enikolopyan, F.S. D'yachkovskii, L.I. Chernaya, P.E. Matkovskii , Yu. N. Kolesnikov, G.P. Belov, and N.N. Bokii, Dokl. Akad. Nauk SSSR, 257 (1981) 633; Proc. Acad. Sci. USSR, 257 (1981) 106.

38. L.S. Benner, Y-H. Lai, and K.P.C. Vollhardt, J. Am. Chem. Soc., 103 (1981) 3609.

39. J.L. Atwood, D.C. Hrncir, R.D. Rogers, and J.A.K. Howard J. Am. Chem. Soc. 103 (1981) 6787.

40. C.J. Dain, A.J. Downs, and D.W.H. Rankin, J. Chem. Soc. Dalton Trans. (1981) 2465.

41. F.L. Himpsl and A.C. Bond, J. Am. Chem. Soc. 103 (1981) 1098.

42. J.R.M. Giles and B.P. Roberts, J. Chem. Soc., Chem. Commun. (1981) 1167.

43. H.C. Brown, J.L. Hubbard, and B. Singaram, Tetrahedron, 37 (1981) 2359.

44. E.C. Ashby and A.B. Goel, Inorg. Chem. 20 (1981) 1096.

45. W.E.Shewbart, S.A. Sims, B.D. Head, and G.E. White, US Patent 4 314 090 Chem. Abstr., 96 (1982) 103 613.

46. P. Haenssle, Ger. Offen. 2 925 627; Chem. Abstr., 95 (1981) 25 257.

47. P. Haenssle and R. Streck, Ger. Offen. 2 925 626; Chem. Abstr., 95 (1981) 62 394.

48. Yu.A. Sangalov, Yu. B. Yasman, I.F. Gladkikh, and K.S. Minsker, Dokl.Akad. Nauk SSSR, 261 (1981) 428; Chem. Abstr., 96 (1982) 84 994.

49. G. Giacomelli, L. Bertero, and L. Lardicci, Tetrahedron Lett. 22 (1981) 883.

50. H.G. Richey, B. Kubala, and M.A. Smith, Tetrahedron Lett., 22 (1981) 3471.

51. A.V. Kuchin, L.I. Akhmetov, V.P. Yur'ev, and G.A. Tolstikov, Zh. Obshch. Khim. 51 (1981) 1855; J. Gen. Chem. USSR (Engl. Transl.) 51 (1981) 1592.

52. H.P. On, W. Lewis and G. Zweifel, Synthesis (1981) 999.

53. A.M. Caporusso, G. Giacomelli, L. Lardicci, JCS Perkin I (1981) 1900.

54. T. Yoshida and E. Negishi, J. Am. Chem. Soc. 103 (1981) 1276.

55. M. Kobayashi, L. F. Valente, E. Negishi, W. Patterson, and A. Silveira, Synthesis (1980) 1034.
56. E. Negishi, A.O. King, W.L. Klima, W. Patterson and A. Silveira J. Org. Chem., 45 (1980) 2526.
57. C.L. Rand, D.E. Van Horn, M.W. Moore, and E. Negishi, J. Org. Chem., 46 (1981) 4093.
58. T. Yoshida and E. Negishi J. Am. Chem. Soc. 103 (1981) 4985.
59. M.D. Schiavelli, J.J. Plunkett, and D.W. Thompson, J. Org. Chem., 46 (1981) 807.
60. H. Matsushita and E. Negishi, J. Am. Chem. Soc. 103 (1981) 2882.
61. E. Negishi, H. Matsushita, and N. Okukado, Tetrahedron Lett., 22 (1981) 2715.
62. M. Kobayashi and E. Negishi, J. Org. Chem. 45 (1980) 5223.
63. E.C. Ashby and A.B. Goel, J. Organomet Chem. 221 (1981) C15.
64. M.T. Reetz, J. Westermann, and R. Steinbach, J. Chem. Soc., Chem. Commun., (1981) 237.
65. N. Fukamiya, M. Oki, and T. Aratani, Chem. Ind. (London), (1981) 606.
66. K. Maruoka, S. Hashimoto, Y. Kitagawa, H. Yamamoto, and H. Nozaki, Bull. Chem. Soc. Jpn. 53 (1980) 3301.
67. C.W. Greengrass and M.S. Nobbs, Tetrahedron Lett. 22 (1981) 5339.
68. G. Giacomelli, A.M. Caporusso, and L. Lardicci, Tetrahedron Lett., 22 (1981) 3663.
69. Y. Yamamoto, H. Yatagai, and K. Maruyama, J. Am. Chem. Soc., 103 (1981) 1969.
70. L. Rösch, G. Altnau, and W.H. Otto, Angew. Chem. 93 (1981) 607; Angew. Chem., Int, Ed. Engl. 20 (1981) 581.
71. A. Yasuda, M. Takahashi, and H. Takaya, Tetrahedron Lett., 22 (1981) 2413.
72. J.C. Saddler and P.L. Fuchs, J. Am. Chem. Soc., 103 (1981) 2112.
73. S. Danishefsky, R. Zamboni, M. Kahn, and S.J. Etheredge, J. Am. Chem. Soc., 103 (1981) 3460.
74. Y. Konishi, M. Kawamura, Y. Iguchi, Y. Arai, and M. Hayashi, Tetrahedron 37 (1981) 4391.

75. A.Barco, S. Benetti, G.P. Pollini, P.G. Baraldi, M. Guarneri, D. Simoni, and C. Gandolfi, J. Org. Chem. 46 (1981) 4518.

76. S. Ohuchida, N. Hamanaka, and M. Hayashi, J. Am. Chem. Soc. 103 (1981) 4597.

77. L.A. Paquette, H. Schostarez, and G.A. Annis, J. Am. Chem. Soc. 103 (1981) 6526.

78. J. Brugidou, J. Poncet, Chiche-Trinh Bich, and H. Christol, Tetrahedron Lett. 22 (1981) 4709.

79. J.K. Whitesell, R.S. Matthews, M.A. Minton, and A.M. Helbling, J. Am. Chem. Soc., 103 (1981) 3468.

80. J-P. Deprês, A.E. Greene, P. Crabbé, Tetrahedron 37 (1981) 621.

81. D.J. Hart, J. Org. Chem. 46 (1981) 367.

82. S. Takano, N. Tamura, and K. Ogasawara, J. Chem. Soc. Chem. Commun. (1981) 1155.

83. G.L. Larson, M. Ortiz, M. Rodriguez de Roca, Synth. Commun., 11 (1981) 583.

84. T. Kametani, T. Suzuki, S. Kamada, and K. Unno, J. Chem. Soc. Perkin Trans. 1, (1981) 3101.

85. S. Iguchi, H. Nakai, M. Hayashi, H. Yamamoto, and K. Maruoka, Bull. Chem. Soc. Jpn. 54 (1981) 3033.

86. R.F. Newton, and S.M. Roberts, Tetrahedron, 36 (1980) 2163.

87. R.J. Cave, C.C. Howard, G. Klinkert, R.F. Newton, D.P. Reynolds, A.H. Wadsworth and S.M. Roberts, J. Chem. Soc, Perkin Trans., 1 (1979) 2954.

88. N.N. Korneev, Yu. L. Lelyukhina, V.I. Ponomarenko, B.L. Irkhin, G.N. Kurilenko, Yu.P. Bazhenov, and O.G. Levina, U.S.S.R. Pat. SU 891 675; Chem. Abstr. 96 (1982) 181 425.

89. E.V. Chechegoeva, E.E. Nifant'ev, Yu.L. Lelyukhina, N.N. Korneev, I.V. Kalechits, I.M. Khrapova, E.I. Skvortsova, and A.V. Savitskii, U.S.S.R. Pat. 819 112; Chem. Abstr. 95 (1981) 98 017.

90. S.K. Minsker, R.G. Bulgakov, G.A. Tolstikov, V.A. Dodonov, L.P. Stepovik, U.M. Dzhemilev, and V.P. Kazakov, Izv. Akad. Nauk SSSR, Ser. Khim., (1981) 2413.

91. V.A. Dodonov, D.F. Grishin, L.I. Stepovik, and V.K. Cherkasov, Zh. Obshch. Khim., 51 (1981) 2245; J. Gen. Chem. USSR 51 (1981) 1930.

92. R.F. Galiullina, V.N. Pankratova, L.P. Stepovik, and V.A. Dodonov, Zh. Obshch. Khim. 51 (1981) 74; J. Gen. Chem. USSR (Engl. Transl.), 51 (1981) 65.
93. L. Fernholt, A. Haaland, M. Hargittai, R. Seip and J. Weidlein, Acta Chem. Scand. Ser. A, A35 (1981) 529.
94. D.C. Hrncir, R.D. Rogers, and J.L. Atwood, J. Am. Chem. Soc. 103 (1981) 4277.
95. V.N. Bochkarev, A.I. Belokon', A.V. Kuchin, and S.I. Smogorzhevskii, Zh. Obshch. Khim., 51 (1981) 1235; J. Gen. Chem. USSR (Engl. Transl.), 51 (1981) 1045.
96. W. Kaim, J. Organomet. Chem. 215 (1981) 325.
97. W. Kaim, J. Organomet. Chem. 215 (1981) 337.
98. W. Kaim, Chem. Ber. 114 (1981) 3789.
99. W. Kaim, Z.Naturforsch.Teil B. 36B (1981) 677.
100. N.S. Enikolopyan, F.S. D'yachkovskii, Z.M. Dzhabieva, P.E. Matkovskii, and A.F. Shestakov, Dokl. Akad.Nauk SSSR 261 (1981) 1145; Bull. Acad. Sci USSR 261 (1981) 535.
101. S. Amirkhalili, P.B. Hitchcock, A.D. Jenkins, J.Z. Nyathi and J.D. Smith; J. Chem. Soc. Dalton Trans., 1981, 377.
102. O.T. Beachley, C. Bueno, M.R. Churchill, R.B. Hallock, and R.G. Simmons, Inorg. Chem. 20 (1981) 2423.
103. O.T. Beachley, Inorg. Chem. 20 (1981) 2825.
104. H. Yamamoto and K. Maruoka, J. Am. Chem. Soc. 103 (1981) 4186.
105. G. Neef, U. Eder, and G. Sauer, J. Org. Chem., 46 (1981) 2824.
106. L.E. Overman and L.A. Flippin, Tetrahedron Lett. 22 (1981) 195.
107. T. Kauffmann, L. Bán, and D.Kuhlmann, Chem. Ber. 114 (1981) 3684.
108. J.M. Klerks, R. Van Vliet, G. Van Koten, and K. Vrieze, J. Organomet. Chem. 214 (1981) 1.
109. J.M. Klerks, G.Van Koten, K. Vrieze and P. Seignette, J. Organomet. Chem. 219 (1981) 9.
110. A.H. Cowley, J.E. Kilduff, and J.C. Wilburn, J. Am. Chem. Soc. 103 (1981) 1575.
111. (Asahi Chemical Industry Co.) Jpn. Kokai Tokkyo Koho JP 81 118 087; Chem. Abstr. 96 (1982) 69 199.
112. D.B. Malpass and L.W. Fannin, U.S.Patent 4 263 217; Chem. Abstr., 95 (1981) 62393.

113. V.V. Gavrilenko, L.A. Chekulaeva, V.A. Antonovich and L.I. Zakharkin, Izv. Akad. Nauk SSSR Ser. Khim. 30 (1981) 713; Bull. Acad. Sci. USSR, Div. Chem. Sci, 30 (1981) 505.

114. K.B. Starowieyski and A. Chwojnowski, J. Organomet. Chem. 215 (1981) 151.

115. R.J. McKinney, T.H. Tulip, D.L. Thorn, T.S. Coolbaugh, and F.N. Tebbe, J. Am. Chem. Soc. 103 (1981) 5584.

116. J.B. Lee, G.J. Gajda, W.P. Schaefer, T.R. Howard, T. Ikariya, D.A. Straus, and R.H. Grubbs, J. Am. Chem. Soc. 103 (1981) 7358.

117. F.W. Hartner and J. Schwartz, J. Am. Chem. Soc., 103 (1981) 4979.

118. P.R. Sharp, S.J. Holmes, R.R. Schrock, M.R. Churchill, and H.J. Wasserman, J. Am. Chem. Soc. 103 (1981) 965.

119. M.R. Churchill, A.L. Rheingold, and H.J. Wasserman, Inorg. Chem. 20 (1981) 3392.

120. M.R. Churchill and H.J. Wasserman, Inorg. Chem. 20 (1981) 4119.

121. T.S. Pritytskaya, A.M. Antipova, V.P. Mardykin, N.E. Strashevskaya, Zh. Prikl. Khim. 54 (1981) 2294; Chem. Abstr. 96 (1982) 85 690.

122. H. Lehmkuhl, R. Paul, C. Krüger, Y-H Tsay, R. Benn and R. Mynott, Justus Liebigs Ann. Chem. (1981) 1147.

123. (Schering, A.G) Belg. Pat. 881 874; Chem. Abstr. 95 (1981) 43 332.

124. T. Jeffery-Luong and G. Linstrumelle, Tetrahedron Lett. 21 (1980) 5019.

125. G. Giacomelli, L. Bertero, L. Lardicci, and R. Menicagli, J. Org. Chem. 46 (1981) 3707.

126. V.V. Gavrilenko, V.S. Kolesov, and L.I. Zakharkin, Izv. Akad. Nauk SSSR Ser. Khim., 29 (1980) 960.

127. J.P. Howe, K. Lung, and T.A. Nile, J. Organomet. Chem., 208 (1981) 401.

128. F.M. Dayrit and J. Schwartz, J. Am. Chem. Soc., 103 (1981) 4466.

129. D.B. Furman, L.A. Makhlis, N.V. Volchkov, A.M. Taber, I.V. Kalechits, V.E. Vasserberg, and O.V. Bragin, Izv. Akad. Nauk SSSR Ser. Khim. 1981 673.

130. P.W.N.M. Van Leeuwen and C.F. Roobeek, Tetrahedron 37 (1981) 1973.

131. A.G. Azizov, D.B. Akhmedov and S.M. Aliev, Neftekhimiya 21 (1981) 191; Chem. Abstr., 95 (1981) 25 720.

132. H-H. Bittrich, R. Bittrich, L. Sass, P. Zirz, P. Reich, and G. Zimmermann, J. Prakt. Chem., 323 (1981) 177.

133. O.S. Vostrikova, A.G. Ibragimov, G.A. Tolstikov, L.M. Zelenova, and U.M. Dzhemilev,Izv. Akad. Nauk SSSR Ser. Khim. 30 (1981) 1410; Bull. Acad. Sci. USSR, 30 (1981) 1132.

134. G.V. Nurtdinova, F.G. Yusopova, E.S. Monakhova, V.G. Lakhtin, G. Gailiunas, V.P. Yur'ev, Zh. Obshch. Khim. 50 (1980) 704.

135. K. Yamaguchi, K. Yokota, and Y. Takada, Makromol. Chem. 182 (1981) 669.

136. K. Yamaguchi, K. Yokota, and Y. Takada, Makromol. Chem. Chem. Rapid Commun. 2 (1981) 645.

137. (Mitsubishi Chemical Industries Co.Ltd.) Jpn. Kokai Tokkyo Koho 81 36 506; Chem. Abstr. 95 (1981) 62 994.

138. R.V. Cartwright, U.S. Pat. 4 260 711; Chem. Abstr., 95 (1981) 25902.

139. L.K. Kurnosova, E.N. Kropacheva, I.G. Zhuchikhina, N.A. Konovalenko, V.I. Anosov, and I.A. Ikonitskii; Vysokomol. Soedin. Ser. A. 23 (1981) 2225.

140. L.A. Kazaryan, E.N. Kropacheva and Yu.G. Kamenev; Vysokomol. Soedin. Ser.A 23 (1981) 2232.

141. L.S. Kol'tsova, A.I. Kuzaev, M.G. Chauser, and M.I. Cherkashin, Vysokomol. Soedin. Ser B, 23 (1981) 708.

142. K. Szczegot, M. Nowakowska, A. Krueger, Vysokomol. Soedin., Ser.A, 23 (1981) 2551.

143. Y. Doi, Y. Nishimura, and T. Keii, Polymer, 22 (1981) 469.

144. R.Clement, Eur. Polym. J. 17 (1981) 473.

145. R. Clement, Eur. Polym. J., 17 (1981) 895:

146. R. Clement,Eur. Polym. J. 17 (1981) 1293.

147. J. Cihlář, J. Mejzlík, O. Hamřík, R. Hudec, and J. Majer, Makromol. Chem. 182 (1981) 1127.

148. G. Fink, R. Rottler, and C.G. Kreiter, Angew. Makromol. Chem., 96 (1981) 1.

149. G. Fink and W. Zoller, Makromol. Chem., 182 (1981) 3265.

150. G. Fink, G. Doellinger, J. Appl. Polym. Sci. Appl. Polym. Symp. 36 (1981) 67.

151. A.V. Agasaryan, G.P. Belov, S.P. Davtyan, and M.L. Eritsyan, Eur. Polym. J. 17 (1981) 443.

152. A.E. Yildirim, Eur. Polym. J. 17 (1981) 551.

153. L. Rösch and G. Altnau, Angew. Chem. 93 (1981) 608; Angew Chem. Int. Ed. Engl 20 (1981) 582.

154. U.M. Dzmemilev, O.S. Vostrikova, A.G. Ibragimov, G.A. Tolstikov, and L.M. Zelenova, Izv. Akad. Nauk SSSR Ser. Khim. 30 (1981) 476.

155. S. Ueki, Y. Doi, and T. Keii, Makromol. Chem. Rapid Commun. 2 (1981) 403.

156. S. Destri, G. Gatti, and L. Porri, Makromol. Chem. Rapid Commun. 2 (1981) 605.

157. A.E. Yildirim, Eur. Polym. J., 17 (1981) 1029.

158. W. Zaar, M. Schroeder, G. Maahs, Eur. Pat. Appl. 24 485; Chem. Abstr. 95 (1981) 62 992.

159. J.G. Van Ommen, J.G.M. Van Rens, and P.J. Gellings, J. Mol. Catal. 13 (1981) 313.

160. (Denki Kagaku Kogyo K.K.) Jpn. Kokai Tokkyo Koho, 81 22 302; Chem. Abstr., 95 (1981) 62991.

161. (AsahI Chemical Industry Co.Ltd), Jpn. Kokai Tokkyo Koho, 81 26906; Chem Abstr. 95 (1981) 43 957.

162. (Mitsubishi Chemical Industries Co.Ltd) Jpn. Kokai Tokkyo Koho, 81 22304; Chem. Abstr., 95 (1981) 62 990.

163. H. Tanaka, Y. Moriya, K. Saito, S. Hori and Y. Mitsuda, Ger. Offen. 3 040 967; Chem. Abstr. 95 (1981) 62 997.

164. K. Lowery and F.L. Vance, U.S. Pat. 4 263 422; Chem. Abstr. 95 (1981) 43 960.

165. H. Franz, H. Meyer, and K-H. Reichert, Polymer 22 (1981) 226.

166. K. Soga and M. Terano, Makromol. Chem. 182 (1981) 2439.

167. Y. Doi, E. Suzuki, and T. Keii, Makromol. Chem. Rapid Commun. 2 (1981) 293.

168. A.D. Caunt, Br. Polym. J. 13 (1981) 22.

169. U. Giannini, Makromol. Chem. Suppl. 5 (1981) 216.

170. R.E. Hoff, U.S. Pat. 4 268 418; Chem. Abstr., 95 (1981) 25 907.

171. A.A. Baulin, Vysokomol. Soedin. Ser. A 23 (1981) 1315.

172. A. Munoz-Escalona, A. Martin, and J. Hidalgo, Eur. Polym. J., 17 (1981) 367.

173. A. Munoz-Escalona, C. Martinez, and J. Hidalgo, Polymer, 22 (1981) 1118.

174. R. John and M. Uhniat, Polimery (Warsaw) 26 (1981) 88; Chem. Abstr., 95 (1981) 25 717.

175. A.A. Baulin, A.G. Rodionov, S.S. Ivanchev, A.L. Gol'denberg, and I.S. Asinovskaya, Vysokomol Soedin. Ser B, 23 (1981) 262.

176. M. Di Maina, P. Narducci, and G. Pizzirani, Chim Ind. (Milan) 63 (1981) 253.

177. A. Mishra, Can. J. Chem., 59 (1981) 1425.

178. V.P. Mardykin, T.K. Morozova, T.S. Pritytskaya, A.M. Antipova, and L.V. Gaponik, Izv. Vyssh. Uchebn. Zaved. Khim. Tekhnol 24 (1981) 1018; Chem. Abstr. 96 (1982) 52 711.

179. E.V. Ignatova, G.S. Georgiev, M.B. Lachinov, V.P. Zubov, and V.A. Kabanov, Vysokomol. Soedin. Ser A 23 (1981) 1994.

180. S. Przybysz, M. Tardi, A. Polton, and P. Sigwalt, Eur. Polym. J., 17 (1981) 19.

181. P. Cohen, M.J.M. Abadie, F. Schué, and D.H. Richards, Polymer 22 (1981) 1316.

182. R.V. Basova, B.I. Nakhmanovich, E.V. Kristal'nyi, and A.A. Arest-Yakubovich, Dokl.Akad. Nauk SSSR, 258 (1981) 884, Proc. Acad. Sci. USSR, 258 (1981) 230.

183. J.P. Kennedy, D.Y.L. Chung, and L.C. Reibel, J. Polym. Chem. Ed. 19 (1981) 2721.

184. J.P. Kennedy and D.Y.L. Chung, J. Polym. Sci., Polym. Chem. Ed. 19 (1981) 2729.

185. J.P. Kennedy and D.Y. Chung and A. Guyot, J. Polym. Sci.Polym. Chem. Ed. 19 (1981) 2737.

186. A. Uchida, M. Hinenoya, and T. Yamamoto, J. Chem. Soc. Dalton Trans.,(1981) 1089.

187. A. Uchida and K. Hata, J. Chem. Soc. Dalton Trans., (1981) 1111.

188. A.J. Amass and J.A. Zurimendi, J.Mol. Catal. 8 (1980) 243.

189. A.J. Amass and J.A. Zurimendi, Eur. Polym. J. 17 (1981) 1.

190. K.J. Ivin, B.S.R. Reddy and J.J. Rooney, J. Chem. Soc. Chem. Commun. (1981) 1062.

191. B. Füllbier and G. Zimmermann, J. Prakt. Chem. 323 (1981) 319.

192. R. Nakamura, S. Matsumoto, and E. Echigoya, Chem. Lett., (1976) 1019.

193. (Japan Synthetic Rubber Co.Ltd.), Jpn. Kokai Tokkyo Koho, JP 81 123 923; Chem. Abstr., 96 (1982) 19 684.

194. T. Aida and S. Inoue, Macromolecules 14 (1981) 1166.

195. T. Aida, R. Mizuta, Y. Yoshida, and S. Inoue, Makromol. Chem. 182 (1981) 1073.

196. A. Grandini and C.D. Hernandez, Makromol. Chem. Rapid Commun. 2 (1981) 351.