ALUMINIUM

ANNUAL SURVEY FOR THE YEAR 1979*

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CONTENTS

1. INTRODUCTION REVIEWS

The pattern of the 1979 review is similar to that of earlier surveys in this series. There is, however, no separate section on molecular structure. Crystallographic studies are discussed in context but those concerned especially with structural aspects will find full details in references 10, 25, 45, 51, 113, 114, 115, 120, 122, 132, 133 and 134.

A Russian book [1] on the chemistry and technology of organoaluminium compounds has been published, and there is a new comprehensive account of Ziegler-Natta catalysts and polymerisation [2].

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*Aluminium Annual Survey covering the year 1978, see J. Organometal. Chem. 189(1980) 17-63. No reprints available.

Organoaluminium compounds are discussed in three reviews, on random and block copolymers by ring-opening reactions [3], on ring-opening polymerisation of bicyclic acetals, oxalactone and oxalactam [4], and on cationic olefin polymerisation using alkyl halide-alkylaluminium initiator systems [5], which are published together as 'Advances in Polymer Science' Vol. 28. Three further reviews, on cationic polymerisation of vinyl monomers [6], on polymerisation of conjugated dienes [7] and on Ziegler-Natta and related catalysts [8] are published in another series on polymer chemistry. Accounts of olefin metathesis [9], selectivity control in nickel-catalysed olefin oligomerisation [10], catalytic codimerisation of ethylene and butadiene [11] and sequential copolymerisation [12] have also appeared.

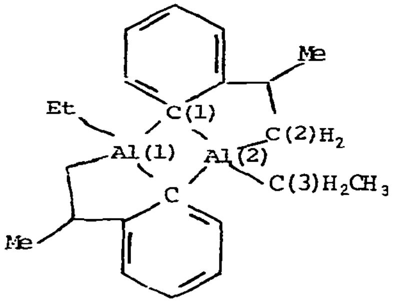
A summary [13] of the organometallic chemistry of the group 3 elements, with emphasis on properties, methods of preparation and reactions, has been given in 'Comprehensive Organic Chemistry' Vol. 3 and accounts [14-16] of the use of the organometallic compounds of group 3 in organic syntheses have appeared in two other books and a review. The applications of organozirconium compounds, many of which are made from organoaluminium compounds, have also been discussed [17]. There have been extensive reviews on complexes of organoaluminium compounds with carbonyl derivatives [18] and ethers [19].

As in previous years, there is a chapter [20] on the organometallic chemistry of the group 3 elements in the Chemical Society Specialist Periodical Report which describes work published in 1978.

2. TRIALKYL- AND TRIARYLALUMINIUMS

Several reports describe the use of catalysts for the synthesis of trialkylaluminiums. For example, the reaction between alkyl halides, activated aluminium and sodium may be catalysed by $[(RO)_nTiCl_{4-n}]$ (R = alkyl, n = 1-3) and AlR_mX_{3-m} (R = alkyl, X = halogen, m = 1-3) or polyaluminoxanes [21]. The synthesis of tripropylaluminium from aluminium, hydrogen and propene [22] may be catalysed by chlorides of titanium, vanadium or nickel [23]. The manufacture of phenetole etherates $R_3Al.OPhEt$ ($R = C_6H_{13}$, C_7H_{15} or C_9H_{19}), which are mild alkylating agents for tin(IV) chloride, has also been described [24].

There is continued interest in the structures of alkyl- and aryl-aluminium compounds. The 1-ethyl-3-methyl-1-alumina-indane dimer has the centrosymmetric structure (1), with Al(1)-C(1) 210.4, Al(2)-C(1) 216.8, Al(2)-C(2) 197.4 and Al(2)-C(3) 196.4 pm [25]. The Al(1)-Al(2) distance is the shortest reported so far for arylaluminium compounds, but it is longer than that in several alkylaluminiums. The structure of (1) suggests that electronic



(1)

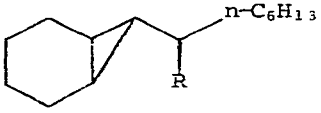
and steric factors may cause considerable distortion of electron-deficient bridge bonds. Attempts have also been made to examine molecular shapes by CNDO/2 calculations [26] which have indicated that the perpendicular conformation of $R_2AlCH_2EH_3$ (R = Me, H, or Cl; E = C or Si) is more stable than the coplanar conformation.

The enthalpies of mixing of alkylaluminium compounds with some metal chlorides were tablulated in last year's survey. More details have been given in a further paper [27]. Exothermic heats of mixing are associated with complex formation between alkylaluminium compound and halide and with alkylations in which chlorine becomes bound to aluminium . There is no evidence for complex formation between bis(η-cyclopentadienyl)lead(II) and trimethylaluminium [28].

As in previous years, the principal uses of alkylaluminium compounds have been as alkylating agents. Acetates and acetylacetonates (pentane-2,4-dionates) are convenient substrates. Thus dimethylzinc [29] may be made in 88% yield from anhydrous zinc acetate and trimethylaluminium, and tribenzylaluminium reacts with pentane-2,4-dionato derivatives of titanium(III), vanadium(III), chromium (III) [30] and manganese(II) [31] to give benzyl-metal compounds. In several cases these form crystalline complexes e.g., $[(PhCH_2)_2Mn.Al(C_5H_7O_2)_3]$ with tris(pentane-2,4-dionato)-aluminium. Triphenylaluminium etherate is a useful reagent for conversion of tris(pentane-2,4-dionato)manganese, in the presence of tricyclohexylphosphine, into $[Ph_2MnPR_3]$ (R = cyclo-C_6H_{11}-). Reactions of this compound with a range of carbonyl compounds have been described [32].

The alkylation of benzyl, cyclopropylmethyl and allyl acetates has been the subject of a detailed stereochemical study [33]. The compounds $PhCHR^1OCOMe$ (R^1 = Ph or Me) with R^2_3Al gave the alkylated compounds $PhCHR^1R^2$; the acetate (2) (R = OCOMe) gave with Et_3Al (2) (R= Et) and, with $Et_2AlC{\equiv}CBu^n$, (2) (R = $C{\equiv}CBu^n$). The stereochemistry of methylations of the acetates (3) and (4) (R^1 = OCOMe, R^2 = H or D;

R^2 = OCOMe, R^1 = H or D) may be explained in terms of carbocationic



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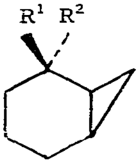

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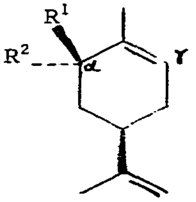
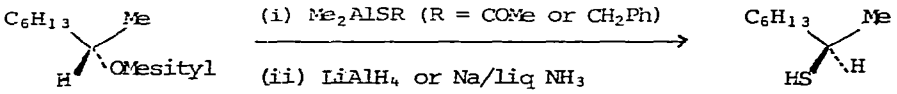


(4)

intermediates, which methyl groups attack from the less hindered side. In contrast, the reactions of the allyl phosphonates (4) [R^1 = H or D, R^2 = OPO(OEt)$_2$] with Me_2AlX (X = OPh, SPh or NHPh) in hexane proceeded largely with inversion of configuration to give (4) (R^1 = X, R^2 = H or D). In more polar solvents, e.g., ether or tetrahydrofuran (THF), the stereochemical purity of the product was less, and the proportion of γ, as opposed to α, attack was greater, as expected if a partly separated cationic intermediate was involved [34]. Inversion was also observed for the sequence in reaction 1.



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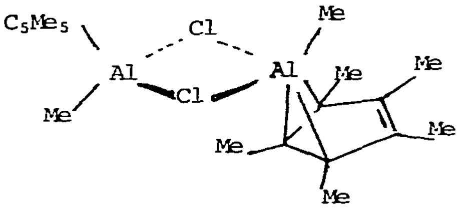
3. ALKYL AND ARYLALUMINIUM HALIDES

Patents [35] [36] describe the production of long-chain compounds R_2AlCl(R = C_4–$_{40}$-alkyl) from short-chain chlorides and ethylene in xylene with titanium chloride as catalyst, and the separation of dialkylaluminium chlorides from sesquichlorides by distillation from alkali metal halides [37]. Alkylaluminium halides have been applied as alkylating agents for halo- and alkoxy-silanes [38] or for lead derivatives, e.g., PbS, PbO or $PbCl_2$ [34], or used as catalysts for redistribution of silanes (e.g., $Me_4Si + Me_2SiCl_2 \rightarrow 2Me_3SiCl$) [40] or for production of organomagnesium compounds R_2Mg (R = Ph, n-C_6H_{13}, or n-C_8H_{17}) from magnesium and chlorides RCl [41]. Phenylaluminium dichloride has been postulated as a key intermediate in a homogeneously catalysed Fischer-Tropsch synthesis [42]. Dimethylaluminium chloride may be used to convert trialkylgalliums R_3Ga(R =

alkyl with 2 or more C atoms) to trimethylgallium for the semiconductor industry [43].

Apparatus for metal vapour synthesis is now becoming widely available. The cocondensation of aluminium vapour and toluene or xylene yields green pyrophoric slurries which react with aryl halides to give high yields of arylaluminium sesquichlorides, and with phenylmercury to give a 54% yield of triphenylaluminium after only 3 h [44]. Black slurries may also be obtained in hexane but these are less reactive than those made in aromatic solvents, which may contain Al-arene π-complexes (See ref. 195).

Molecules of the compound $[Me(C_5Me_5)AlCl]_2$ (5), obtained from the reaction between C_5Me_5MgCl and dimethylaluminium chloride, have the usual chlorine-bridged structure but the Al-Cl bridge bonds are unusually long [Mean Al-Cl 238.8(3) pm; Al-Cl-Al 96.44(9)°] indicating that the interaction between monomers is weak [45]. The Al-C distances [Al-C(Me) 191.6(7); Al-C(C_5Me_5) 209.5(7), 225.4(8), 227.9(8), 249.9(6) and 251.7(7) pm] suggest that the coordination may be regarded as trihapto;



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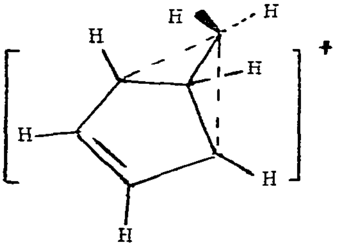
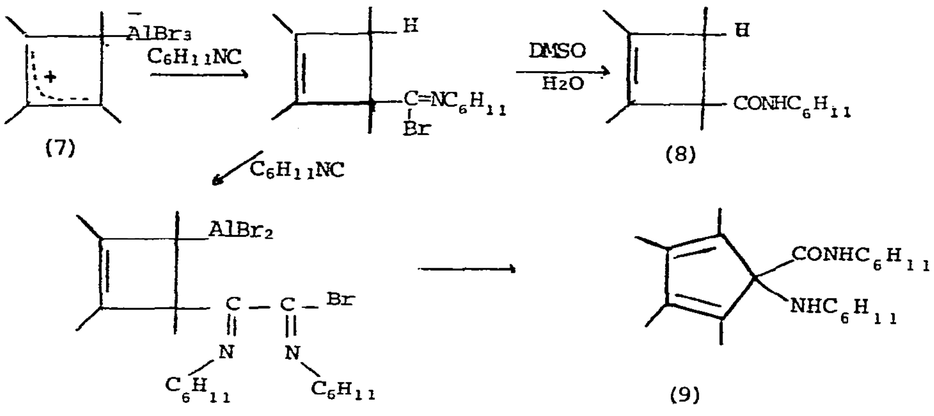


(6)

the aluminium compound is then isoelectronic with protonated benzvalene (6) which has been postulated as a transient carbocation.

There is a further paper in the series describing reactions of aluminium halide-cyclobutadiene complexes [46]. Although the reaction between the compound (7) and one equivalent of cyclohexylisocyanide yields, after hydrolysis, the cyclobutene derivative (8), the product from (7) and two equivalents of $C_6H_{11}NC$ is (9), formed by an unusual ring-expansion.

The ready reaction of alkylaluminium halides with water has been exploited in the production of two catalyst systems. Thus chiral alkoxyaluminium compounds, made from optically active alcohols and ethylaluminium dichloride have been used to catalyse asymmetric Diels-Alder reactions [47]. The complex $EtAlCl_2.H_2O$, described last year, is apparently easily converted to an aluminoxane which functions in hexane as a highly selective catalyst for polymerisation of isobutene in the presence of other alkenes [48].



(7)

(8)

(9)

DMSO = dimethylsulphoxide

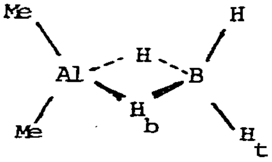
The salt $[Me_4N][Et_3AlClAlEt_3]$, first described 20 years ago by Ziegler, decomposes simultaneously by two distinct routes (Equation 2). The chloromethane is not detected in the products, since it reacts immediately with the excess of hexaethyldialuminium to give methane, ethylene and ethylaluminium chlorides. The adduct $[Et_3Al.NMe_3]$ has almost the same volatility as Et_6Al_2 and codistils with it [49].

$$\begin{tikzcd} {[}Me_4N{]}{[}Et_3AlClAlEt_3{]} \arrow[r] \arrow[d] & {[}Me_4N{]}{[}Et_3AlCl{]} + \tfrac{1}{2}{[}Et_6Al_2{]} \\ {[}Et_3Al.NMe_3{]} + MeCl + \tfrac{1}{2}{[}Et_6Al_2{]} & \end{tikzcd} \qquad \underline{2}$$

4. ALKYLALUMINIUM HYDRIDES

Procedures for the commercial preparation of hydrides R_2AlH ($R = Me, Et, Bu^tCH_2$) by reactions involving alkyl exchange and β-elimination have been described in a patent [50].

A study of the structures of dimethylaluminium tetrahydroborate Me_2AlBH_4 (10), and its gallium analogue by gas-phase electron diffraction has shown that both molecules are monomeric with symmetry C_{2v} [51].



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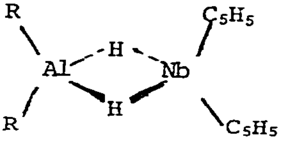


(11)

Mean bond length and angles are: Al–C 192.9(4), Al–B 212.8(8), Al–H_b 177.0(32), B–H_b 123.0(17), B–H_t 120.7(17) pm, C–Al–C 118.4(7), H_b–Al–H_b 70.6(48)°. It seems that replacement of CH_3 by BH_4 in methylaluminium compounds results in only small changes in molecular dimensions. Similar double hydride bridges have been postulated to explain the reactions between bis(cyclopentadienyl)niobium dichloride and reducing agents such as $LiAlH_4$ or $Na[AlH_2Et_2]$ [52]. The reduction of the niobium (IV) compound $[(C_5H_5)_2NbCl_2]$ gives a Nb(IV) hydride which disproportionates, so that the products detected are the Nb(V) hydride $[(C_5H_5)_2NbH_3]$ and the compound $[(C_5H_5)_2NbH_2AlR_2]$ (11) (R = H or Et). The compound (11) reacts with water to give $[(C_5H_5)_2NbH_3]$; with D_2O, only one D atom is incorporated into the niobium fragment, suggesting that the hydride bridge is cleaved asymmetrically, with both hydrogen atoms remaining on niobium.

The reaction between triethylaluminium and the hydride $[(COD)_{1\cdot5}NiLi_2H_2]$ (12) (COD = cycloocta-1,5-diene), however, leads to separation of the nickel and aluminium (Equation 3).

$$[(COD)_2Ni] \xrightarrow{Li/THF} [(COD)_2NiLi_2(THF)_4] \xrightarrow{H_2} \underset{(12)}{[(COD)_{1.5}NiLi_2H_2]} + \tfrac{1}{2}COD$$

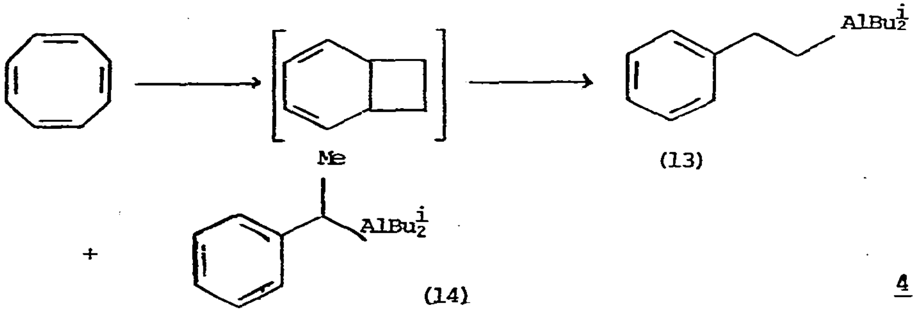
$$\xrightarrow{2Et_3Al} [(COD)_2Ni] + 2Li[AlEt_3H] \qquad \underline{3}$$

Complex (12) reacts with ethylene to give $[Li(THF)_4][EtNi(C_2H_4)_2]$ and ethyllithium [53].

5. ADDITION TO CARBON-CARBON DOUBLE BONDS

There is continued interest in the synthetic potential of hydroalumination.

Cyclooctatetraene reacts with diisobutylaluminium hydride to give products (13) and (14) in 4:1 mole ratio (Equation 4). It is possible that a cyclobutane is an intermediate in the rearrangement of the carbon skeleton [54].



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(14)

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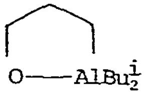
The reaction of the cyclic alkoxide (15) with a number of substrates was described last year; reactions with hex-1-ene, 4-vinylcyclohexene, sabinene (16), camphene (17) and β-pinene (18) have now been documented [55]. The stereoselectivity of (15) is better than that of diisobutylaluminium hydride, but not as good as that of 9-borabicyclo [3,3,1]nonane. Rather vigorous reaction conditions (120-140°C) have been employed.

Many of the other papers on hydroalumination describe catalysed reactions under much milder conditions. A very full study [56] of the reaction between $LiAlH_4$ and alkenes (Equation 5) in the presence of transition metal halides has covered reactions of oct-1-ene, hex-1-ene, styrene, 2-ethylhex-1-ene, cis-hex-2-ene, trans-hex-2-ene, cyclohexene, and 1-methylcyclohexene as well as the alkynes phenylacetylene, oct-1-yne, diphenylacetylene and hex-2-yne. The effectiveness of the transition metal compounds decreased in the order Co(II) > Ni(II) > Fe(II) > Fe(III) > Ti(III) > Cr(III) > V(III) > Mn(II) > Cu(I) > Zn(II). Only $CoCl_2$, $NiCl_2$ and $TiCl_3$ may be used catalytically. Catalysis is slower for di- and tri-substituted compounds (19) (R^1, R^2 = H or only R^1 = H) than for corresponding monosubstituted alkenes (19) (R^1, R^2, R^3 = H). In another paper [57] hydroalumination using bis(dialkylamino)alanes and $[(\eta\text{-}C_5H_5)_2TiCl_2]$ as catalyst is described. Thus oct-1-ene in benzene at 40°C is converted in 93% yield in 10 min. to $[n\text{-}C_8H_{17}Al(NPr^i_2)_2]$.



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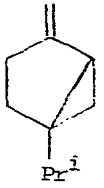

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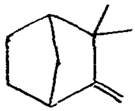

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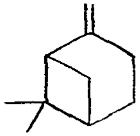


(18)

$$R^1R^2C = CR^3R^4 \quad + \quad LiAlH_4 \longrightarrow Li[H_3AlCR^1R^2CR^3R^4H] \qquad \underline{5}$$

(19)

With more highly substituted alkenes the rate falls e.g., styrene ∿ oct-1-ene > 3,3-dimethylbut-1-ene > methylene cyclohexane > 2-ethyl-hex-1-ene >> cis-hex-2-ene ∿ trans-hex-2-ene >> cyclohexene >>> 2-methylbut-3-ene ∿ 2,3-dimethylbut-2-ene ∿ 1-methylcyclohexene. The bis(dialkylamino)alanes may be made by direct synthesis from aluminium, hydrogen and secondary amine in an autoclave. Several other alanes have been tried as catalysts: $[\mathrm{HAl\{N(SiMe_3)_2\}_2}]$ gave much poorer regioselectivity than did $[\mathrm{HAl(NPr^i_2)_2}]$, and the Al-H bond in compounds such as $\mathrm{HAl(OR)_2}$ (R = Me, $\mathrm{Pr^i}$, $\mathrm{Bu^t}$) appeared to be insufficiently reactive to give good yields (C.f. also Section 6 below and ref.78).

Alkylaluminium compounds, prepared by titanium(IV) chloride-catalysed hydroalumination, may be converted to acetates by reaction with lead (IV)acetate [58] (Equation 6). This constitutes a

$$\mathrm{LiAlH_4 + 2RCH = CH_2 \xrightarrow{TiCl_4} \underset{(20)}{Li[Al(CH_2CH_2R)_2H_2]} \xrightarrow{2Pb(OCOMe)_4} 2RCH_2CH_2OCOMe} \qquad \underline{6}$$

one-pot synthesis of primary acetates from alkenes (anti- Markownikoff esterfication) which can also be used to make α,ω-diacetates or unsaturated acetates from non-conjugated dienes. Hydroalumination, catalysed by titanium(IV) chloride, may be also used for one-pot synthesis of ketones [59] (Equation 7). Details have been given for

$$\mathrm{LiAlH_4 + \underset{(21)}{4R^1CH = CH_2} \xrightarrow[THF]{TiCl_4} \underset{(23)}{LiAl(CH_2CH_2R^1)_4} \xrightarrow[CuCl]{R^2COX(22)} 4R^1CH_2CH_2COR^2} \qquad \underline{7}$$

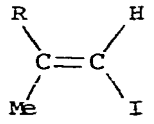
reactions between (21) ($\mathrm{R^1}$ = H, $\mathrm{Bu^n}$, MeCH = $\mathrm{CHCH_2}$–, $\mathrm{CH_2}$= $\mathrm{CMeCH_2CH_2}$– and cyclohex-3-enyl and acyl compounds (22) ($\mathrm{R^2}$ = Ph, Me, Et, $\mathrm{Pr^i}$, $\mathrm{Bu^n}$ $\mathrm{MeOCOCH_2CH_2}$–; X = Cl or $\mathrm{CO_2R^2}$). Thus one double bond in a diene may be selectively attacked, and remote ester functions do not interfere. The reaction in THF does not proceed without the Cu(I) catalyst, or in the presence of a free radical scavenger. As a variant, the compounds (23) may be treated with methyl vinyl ketone or acrolein in the presence of copper(II) acetate, to give 3-alkylpropanals (24) ($\mathrm{R^2}$ = H) or 4-alkyl-but-2-ones (24)($\mathrm{R^2}$ = Me) [60]. The $\mathrm{TiCl_4}$ or $[(\eta\text{-}\mathrm{C_5H_5})_2\mathrm{TiCl_2}]$ may be incorporated into cross-linked polystyrene

$$\mathrm{\underset{(20)}{Li[Al(CH_2CH_2R^1)_2H_2]} + 2CH_2{=}CHCOR^2 \xrightarrow{4Cu(OCOMe)_2} \underset{(24)}{R'(CH_2)_4COR^2}} \qquad \underline{8}$$

supports [61, 62]. Catalysts in which this incorporation is effected in three different ways have been described. Compared with homogeneous catalysts, the supported catalysts are more effective at achieving mono- rather than di-hydroalumination of α,ω-dienes [62].

When alkenes (21) are treated with a twofold molar excess of both $[(\eta\text{-}\mathrm{C_5H_5})_2\mathrm{TiCl_2}]$ and trialkylaluminium $\mathrm{R^2_3Al}$ ($\mathrm{R^2}$ = Me, Et. $\mathrm{Bu^n}$, $\mathrm{Bu^i}$) in dichloromethane at 23°C, alkenes $\mathrm{H_2C = CR^1R^2}$ are obtained in a single step [63]. Branched alk-1-enes give lower yields than unbranched; internal alkenes do not react. The group R^1 in the alkene may contain functional groups such as Br, OH or CO.OR not directly adjacent to the double bond. The mechanism of the reaction and the fate of the titanium have not been elucidated.

Catalysis of carboalumination by zirconium compounds is now well established. It has been found [64] that carboalumination provides a generally applicable highly stereo- and regio- (> 97%) selective route to (E)2-methyl-1-alkenyl iodides (25) (R = Ph, Bu^n, n-C_5H_{11}, H_2C = CMe-, Me_2C = $CH(CH_2)_2$-, or $PhSCH_2$-). The transfer of alkyl or alkenyl groups from zirconium to aluminium, postulated as a step in the catalytic process, has been developed in a preparative route to a new range of organoaluminium compounds. Two preliminary publications appeared in 1977; there is now a full paper [65]. The zirconium compounds $[(\eta\text{-}C_5H_5)_2ZrClR]$ (26) (R = alkyl or alkenyl), easily made from alkenes or alkynes and hydrides $[(\eta\text{-}C_5H_5)_2ZrHCl]$, react with aluminium(III) chloride in dichloromethane at 0°C to yield alkyl- or alkenyl-aluminium dichlorides $RAlCl_2$ (R = Bu^tCH_2CH_2-, n-C_8H_{17}-, cyclohexyl, trans- Bu^{t}HC = CH-) or (27)-(29). When R is primary unsaturated alkyl or alkenyl the dichlorides may be converted to ketones by treatment with acyl chlorides (For details, see Annual Survey for the year 1977). When R is secondary, side reactions involving hydrogen abstraction intrude. Vinyl groups are transferred from Zr to Al more easily than alkyl groups and transfer is effected with retention of configuration at carbon, suggesting that the transition state involves an alkyl or alkenyl bridge between the two metal atoms.



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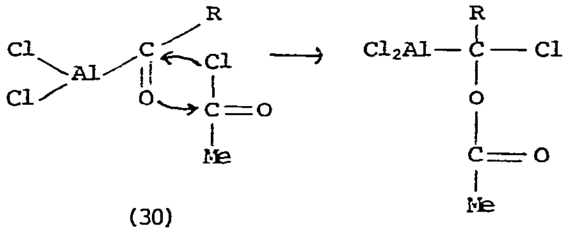

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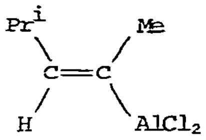

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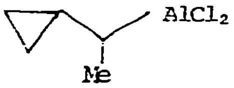

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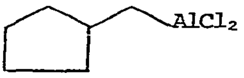
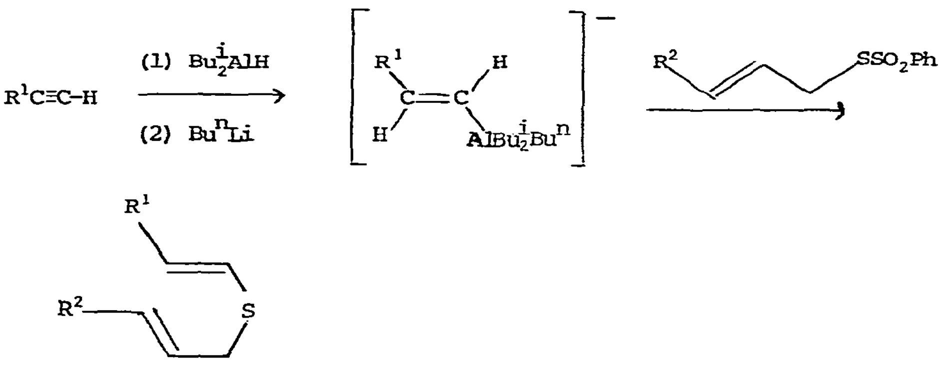


(29)

Acylzirconium compounds [$(\eta\text{-}C_5H_5)_2ZrClCOR$] are readily available from the reaction between carbon monoxide and alkyls (26); with aluminium chloride these yield acylaluminium compounds $RCOAlCl_2$ (R = $Bu^tCH_2CH_2$- or Bu^n), which react with acetyl chloride, perhaps via (30) to give, after hydrolysis, the chloroalkyl acetate RCHClOCOMe.

6. ADDITION TO CARBON-CARBON TRIPLE BONDS

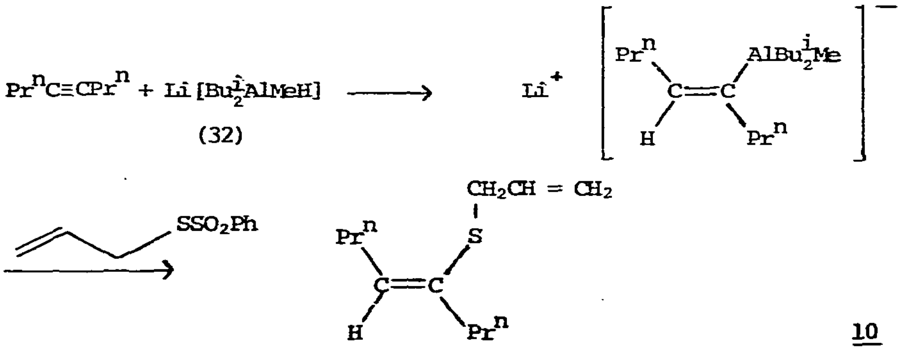
The highly stereoselective cis-addition of an Al-H bond to an alkyne has been exploited in the synthesis of allyl vinyl thioethers in which the stereochemistry of both allyl and vinyl fragments is controlled [66] (Equation 9). Yields of 55-65% have been obtained for (31) (R^1 = C_6H_{13}-, R^2 = $CH_2{=}CH.CH_2$, $CH_2{=}CMeCH_2$, trans-MeCH = $CHCH_2$,



(31)

9

$CH_2{=}CClCH_2$ or $PhCH_2$-). By using $Li[Bu^i_2AlMeH]$ (32), trans- addition to internal alkynes may be be effected: this provides a route to thioethers with vinyl groups having (Z)-stereochemistry (Equation 10). The reagent (32) reacts with symmetrically-substituted conjugated diynes to give good yields of the trans-enynes (33) (R = Bu^n, Pr^i, Bu^t or cyclo-C_6H_{11}) in a reaction which is both highly stereo- and



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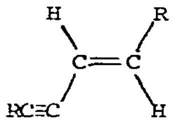
regio- selective. The dialkyne $Bu^tC\equiv C-C\equiv CBu^n$, however, gives a mixture of products (34) and (35), showing that the ate complex (32) does not discriminate between the triple bonds of unsymmetrical diynes [67].



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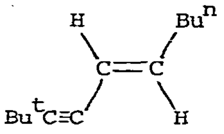

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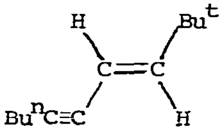
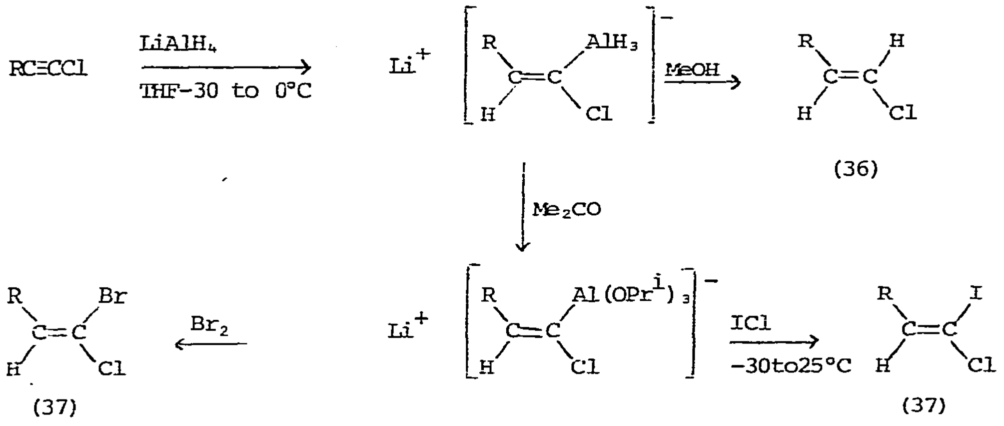


(35)

Another example of the use of hydroalumination is the conversion of chloroalkynes $RC\equiv CCl$ ($R = Bu^n$, $n-C_6H_{13}$, $cyclo-C_6H_{11}$ or



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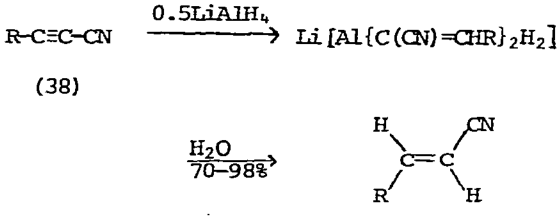
Bu^t) by $LiAlH_4$ in THF to (E)-1-chloro-alk-1-enes (36) or mixed 1,1-dihaloalk-1-enes (37), in which the carbon-halogen bonds may be used selectively in further syntheses [68] (Equation 11). Similarly, alk-2-yne nitriles (38) may be transformed stereospecifically in good yield to trans-alk-2-ene nitriles (39) ($R = Ph$, Et, Bu^n, $H_2C{=}CMe-$, or cyclohex-1-enyl) [69] (Equation 12). With dialkylamino-substituted alkynes (40) (R^1, R^2 = Et, Me or $PhCH_2$; R^3 = cyclohex-1-yl or Ph) the products are the (E)-allylamines (41), which are presumably formed via intermediates (42) (Equation 13) [70].

There have been several examples of the application of hydroalumination in the synthesis of natural products. Thus non-1-ene-8-yne (43), on treatment with diisobutylaluminium hydride and butyllithium,

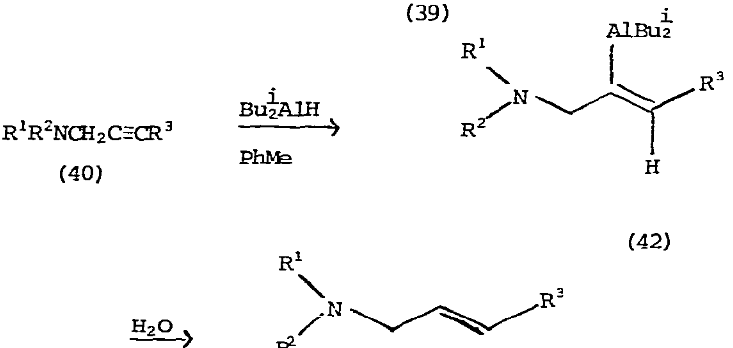


$R{-}C{\equiv}C{-}CN \xrightarrow{0.5LiAlH_4} Li[Al\{C(CN){=}CHR\}_2H_2]$

(38)

(39)

12



$R^1R^2NCH_2C{\equiv}CR^3$

(40)

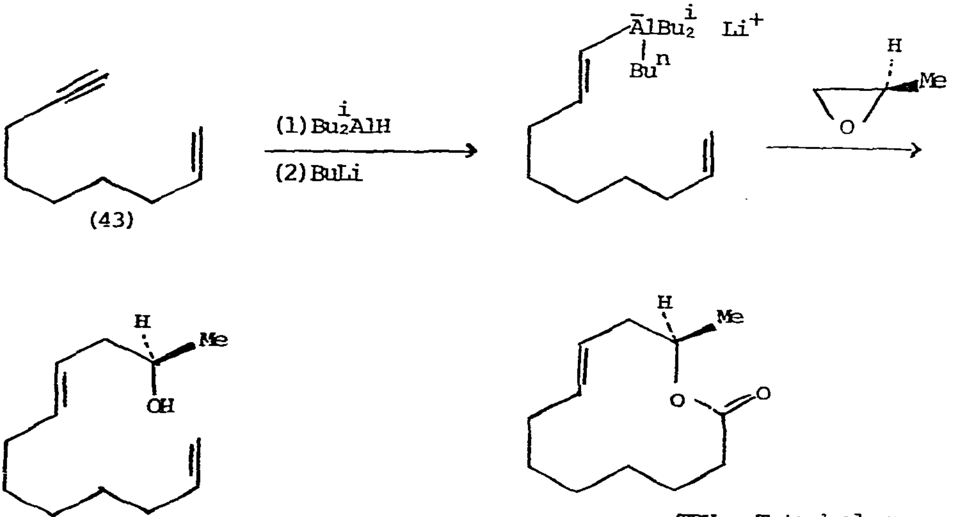
(42)

(41)

13

followed by (R)-methyloxiran gives the alcohol (44) with over 99% selectivity. This may be used as a starting material for the synthesis of the lactone (45) isolated from the fungus Cephalosporium recifei [71].

The scope and mechanism of carbometalations catalysed by trialkylaluminium-[$Ni(C_5H_7O)_2$] mixtures have been examined further. For example, the reaction between methyl magnesium bromide and silanes



(43)

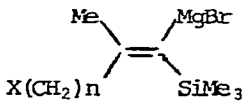
(44)

14

(45)

TPH = Tetrahydropyranyl

$X(CH_2)_nC{\equiv}CSiMe_3$ (46) (X = OTHP, OCHMeOEt or NEt_2; n = 2 or 3) in the presence of $Me_3Al/Ni(C_5H_7O)_2$ gives first the product (47) from cis- addition and then, with longer reaction times, the trans- product (48). After removal of the Me_3Si group with fluoride in DMSO, the products (49) (R = Me or $Me_2C{=}CHCMe_2$–) from (46) (n = 2; X = $Me_2C{=}CH$– or $Me_2C{=}CHCMe_2CMe{=}CH$–) are useful in terpene syntheses [72]. A detailed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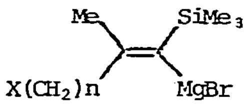
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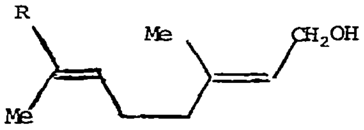
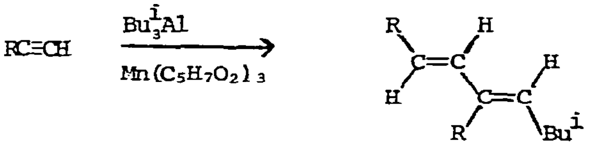

(49)

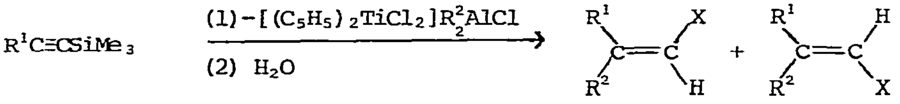
study has been made [74] of the products from the reaction between the alkynes $RC{\equiv}C{-}X$ (R = Bu^n, EtCHMe- or Bu^tCHMe-;X = H or D) and trisobutylaluminium both with and without a range of nickel compounds. Some of the complicated reactions pathways, involving alkyl- or hydrido-nickel complexes and transfer of organic groups between aluminium and nickel, have been mapped out. With Bu^i_3Al– $Mn(C_5H_7O_2)_3$ (40:1), the predominant reaction is dimerisation, and, although there are a number of side reactions, alkynes may be converted in satisfactory yields to (E,E)-1-isobutyl-2,4-dialkyl-buta-1,3-dienes (50) (Equation 15). Experiments with R = EtMeHC-, show that the


15

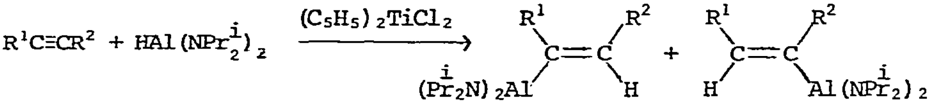
(50)

chirality of R is preserved. When the tris(pentane-2,4-dionato)-manganese in reaction 15 was replaced by iron(III) chloride a complex mixture of products was formed [75], with main components 2-alkyl-1-enes and trialkylbuta-1,3-dienes as well as linear oligomers and cyclic trimers. Again, the reaction between (S)-$EtMeHCC{\equiv}CH$ and triisobutylaluminium gave optically active products in high optical yield.

Carbaluminations may also be catalysed by bis(cyclopentadienyl)-titanium dichloride and related compounds. In reactions between alcohols $HO(CH_2)_nC{\equiv}CH$ and diethylaluminium chloride, good yields of carbometalated products are obtained when $[(C_5H_4Me)_2TiCl_2]$ is used as catalyst but only but-3-yn-1-ol gives good yields with $[(C_5H_5)_2TiCl_2]$, perhaps because this catalyst is easily reduced to Ti(III) species. Both catalysts are effective with alkynols $HOCHRCH_2C{\equiv}CH$ (R = Me or Et). However none of the reactions is highly regioselective. Alkynols $HOCH_2CH_2C{\equiv}CR$ (R = Me or Et) give only poor yields of ethylated products [76]. It has, however, been reported [77] that carbometalation of alkynylsilanes with $[(\eta\text{-}C_5H_5)_2TiCl_2]\text{-}\ R_2AlCl$ (R = Me or Et) is stereospecifically *cis*-,provided that Lewis bases are excluded. Thus the alkynylsilane (51) ($R^1 = n\text{-}C_6H_{13}$) (Equation 16) is converted into (52) and (53) ($X = SiMe_3$) in mole ratio 95:5. Phenylethynyltrimethylsilane (51) (R^1 = Ph), however, gives a 80:20 ratio of (52) and (53) ($X = SiMe_3$), suggesting that the phenyl group accelerates the Lewis base- induced decomposition which is thought to proceed via radical intermediates. In combination with carbometalation of $C_6H_{13}C{\equiv}CSiMe_3$ by MeMgBr, catalysed by $Ni(C_5H_7O_2)_2\text{-}Me_3Al$, as reported last year, either isomer (52) or (53) ($X = CH_2OH$) may be obtained in good yield. The hydrometalation of internal alkynes by bis(diisopropylamino)alane, catalysed by $(\eta\text{-}C_5H_5)_2TiCl_2$, also gives products with *cis*-stereochemistry [78] C.f. also ref. 57 (Equation 17). When R^1 = Me, R^2 = Pr the products (54) and (55) are formed in 53:47 mole ratio but in other cases, e.g., R^1 = Me, $R^2 = n\text{-}C_5H_{11}$; R^1 = Ph, R^2 = Me; $R^1 = C_6H_{13}$, $R^2 = SiMe_3$, the reaction is highly regiospecific and one product dominates. From a detailed examination of the products it appears that the regiochemistry is defined by the alkenyltitanium intermediate, but that the rate of the reaction is determined by the transmetalation step.

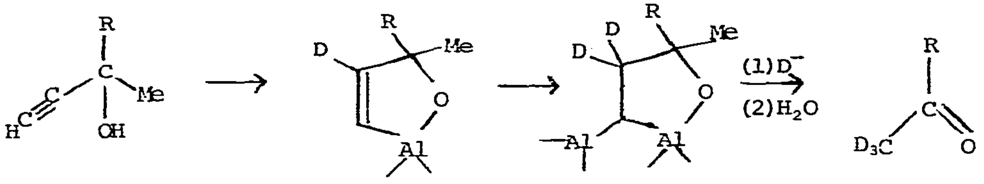


(51) (52) (53) 16



(55) (54) 17

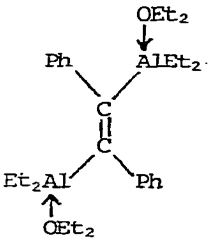
In the reduction of the alkyne (56) ($R = Me_2C{=}CHCH_2CH_2CMe{=}CHCH_2CH_2\text{-}$) by lithium aluminium deuteride in the presence of sodium methoxide [79], geranyl acetone, labelled with three deuterium atoms at C-1 (59) was obtained as an unexpected by-product. A bis(alanate) complex such as (58) has been suggested as a possible intermediate (Equation 18), but several aspects of this reaction remain obscure.



(56) (58) (59)

..........18

It was reported in 1977 that the reaction between diphenylacetylene and diethylaluminium chloride in the presence of lithium sand gives the substituted stilbene (59). The photochemical dimerisation of this to (60) has now been reported [80]. Compound (60) was characterised by an X-ray study in 1977.



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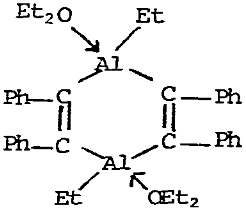


(60)

7. REACTIONS WITH CARBONYL COMPOUNDS

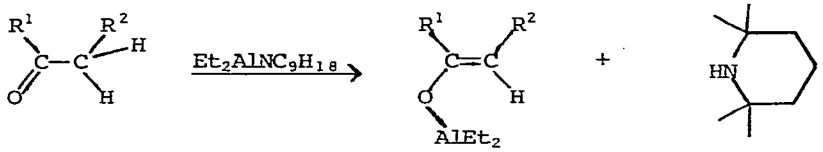
There have been three more papers describing the ongoing comprehensive study of organometallic compounds derived from unsaturated aliphatic bromides. The compounds $CH_2{=}C{=}CHCH_2Br$; $CH_2{=}C{=}CMeCH_2Br$ $MeCH{=}C{=}CHCH_2Br$ but not $CH_2{=}C{=}CHCHBrMe$ react with aluminium turnings in THF [81]. The resulting organoaluminium derivatives, with aldehydes R^1CHO ($R^1 = Pr^i$ or Ph), give $R^2CH{=}C{=}CR^3CH_2CHOHR^1$ (R^2, R^3 = H or Me) and with ketones Pr_2CO or PhCOMe give $R^2CH{=}C{=}CR^3CH_2C(OH)R^4R^5$ (R^4, R^5 = Me,Pr or Ph. There is no evidence for the rearranged products obtained in reactions using allenic magnesium derivatives. The aluminium compounds also react with the acetal $PhCH(OMe)_2$ to give $R^2CH{=}C{=}CR^3CH_2CH(OMe)Ph$ [82]. The greater reactivity of organometallic compounds of aluminium (compared with magnesium or zinc) towards acetals and ketals has been confirmed by experiments with a range of allyl bromides (Equations 19 and 20) (R^1 = H, Me, Et, Bu^n; R^2 = H or Me; $R^3 = Bu^nCHEt$-,

$$R^1CH{=}CR^2CH_2Al_{2/3}Br + PhCH(OMe)_2 \xrightarrow{Et_2O\ 35^\circ} PhCH(OMe)CHR^1CR^2{=}CH_2 \qquad \underline{19}$$

$$MeCH{=}CHCH_2Al_{2/3}Br + R^3R^4C(OR)_2 \xrightarrow[-40^\circ C]{Et_2O} R^3R^4C(OR)CHMeCH{=}CH_2 \qquad \underline{20}$$

n-C_6H_{13}, $BrCH_2$–, $EtOCH_2$–; R^4 = H or Et or $R^3R^4 = -(CH_2)_5-$). The allyl group is transposed in the products [83].

The effect of added salts on the rate of the reaction between trimethylaluminium and 4-t-butylcyclohexanone has been examined briefly. There is little effect on the stereochemistry: in all cases the reaction is slowed down, presumably by complex formation between the trimethylaluminium and the salt [84]. In other circumstances, however, the reaction between organoaluminium compounds and ketones may be considerably modified by interaction with bases. For example, diethyl (2,2,6,6-tetramethylpiperidido)aluminium has proved to be an excellent reagent for converting carbonyl compounds to aluminium enolates (Equation 21) [85]. These may be used in a wide range of crossed aldol condensations



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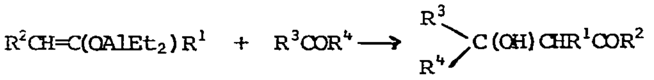
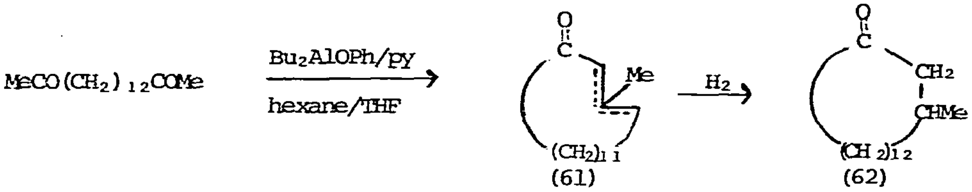


$$R^2CH{=}C(OAlEt_2)R^1 + R^3COR^4 \longrightarrow {}^{R^3}_{R^4}{>}C(OH)CHR^1COR^2 \qquad \underline{22}$$

(Equation 22). ($R^1 = OBu^t$ or Ph; R^1 = H or $CH_2{=}CH$– or $R^1R^2 = -(CH_2)_4-$ or $-(CH_2)_3CHMe-$; R^3 = Me, Pr^i or Ph; R^4 = H or Me, or $R^3R^4 = -(CH_2)_5-$). In a similar way, diisobutylaluminium phenoxide and pyridine (py) induce the rapid and regiospecific aldol condensation of octan-2-one (Equation 23). By careful control of the solvent and the concentration of Bu^i_2AlOPh, it has been possible to obtain good yields of the cyclic enone (61) by an intramolecular aldol condensation. The enones (61) may be hydrogenated to the naturally occurring fragrant compound muscone (62) [86].

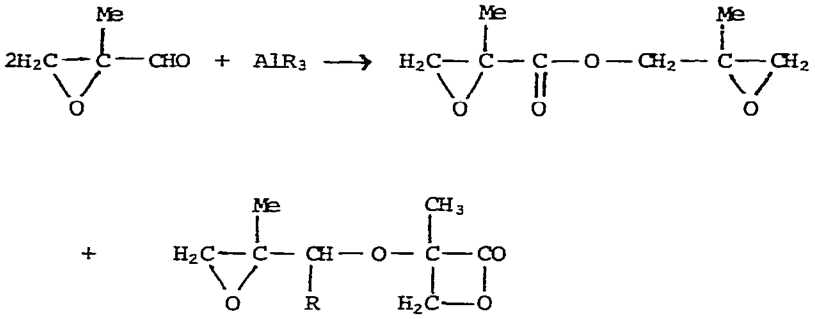
$$2CH_3COC_6H_{13} \xrightarrow[THF]{Bu^i_2AlOPh\ py} C_6H_{13}COCH{=}CMeC_6H_{13} + C_6H_{13}COCH_2CMe{=}CHC_5H_{11} \qquad \underline{23}$$



(61) (62)

24

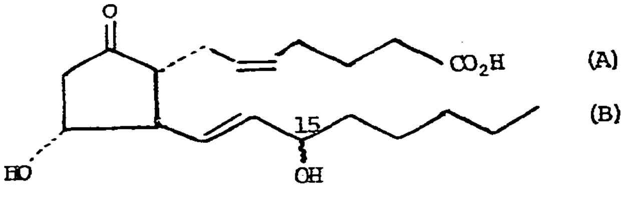
Another rearrangement which is found to be effected by trialkyaluminiums is shown in equation 25. Yields of the propiolactone derivative (63) (R = Et, Bu^n or Bu^i) were about 20%; higher yields were obtained with alkoxides in place of the alkyls [87].



(63)

25

Organoaluminium compounds have been widely used as reagents in the synthesis of prostaglandins such as (64). Work published in 1979 may be classified into three types: (i) syntheses involving the long established reduction of lactones such as (65) to the hemiacetal (66) or sometimes to an aldehyde, prior to the introduction of chain A by use of a Wittig reagent; (ii) syntheses involving the 1:4 addition of an organoaluminium compound to a cyclopentenone to introduce a previously assembled side chain B, and (iii) syntheses in which organoaluminium compounds are used to determine the stereochemistry of the hydroxyl substituent at C-15. No attempt has been made comprehensively to document syntheses of type (i) but examples are found in references [88]-[95].



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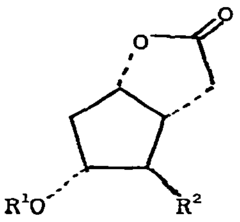

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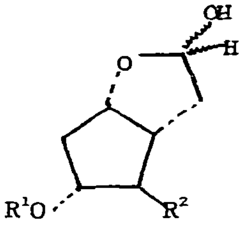
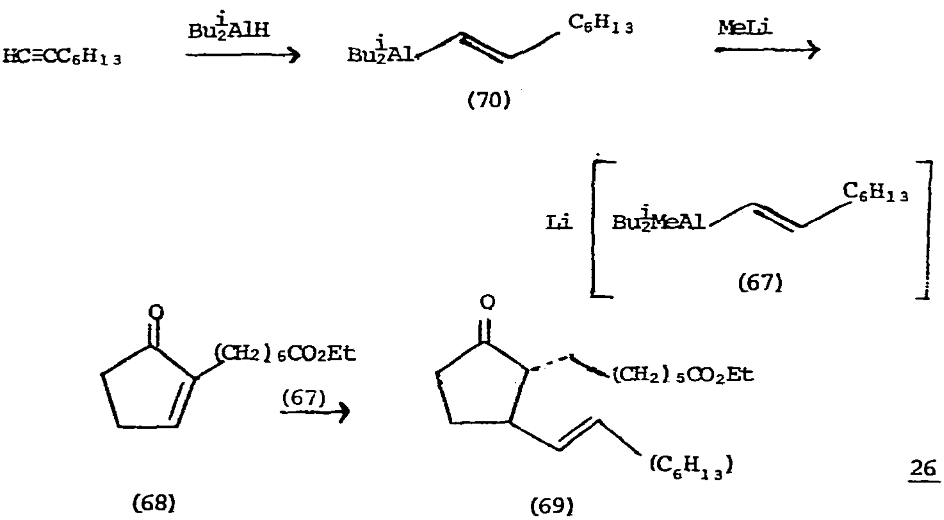


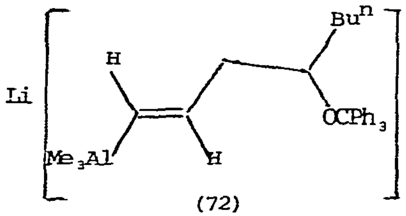
(66)

Two full accounts have been given of the use of organoaluminium reagents to introduce chain B of compounds such as (64). As a model reaction the ate complex (67) (Equation 26) reacted with the cyclopentenone (68) to give the 11,15 dideoxyprostaglandin E_1 (69) [96]. It is interesting that the alkenylaluminium compound (70) undergoes



26

only 1,2 addition to (68). In order to adapt equation 26 for the synthesis of (64) the tetrahydropyranyl (THP) group was used to protect the hydroxyl function of the ring and the acid function of chain (A). Finding a lithium alkenylalanate reagent which would accommodate the hydroxyl function of chain (B) was more difficult, but a suitable compound was prepared by the reaction between Me_3Al and *trans*- $LiCH{=}CHCHORC_5H_{11}$ ($R = CPh_2(C_6H_4OMe$-*p*$)$). Similarly (71), not readily made by other routes, was obtained from (72) and the cyclopentenone (73). Another method for introduction of the second side-



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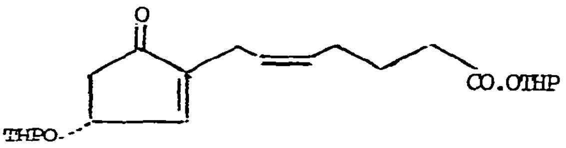

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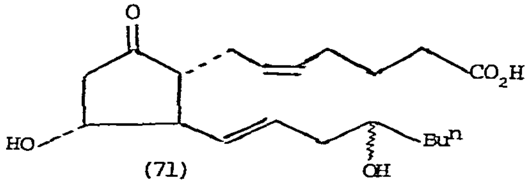
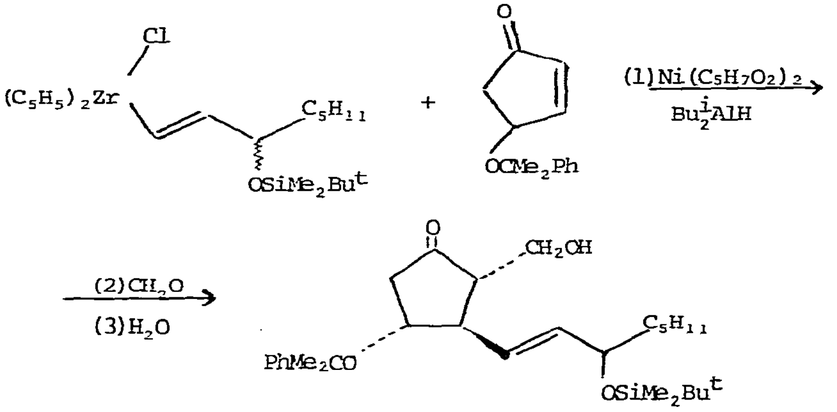


(71)

chain is illustrated in Equations 27 and 28 [97] in which diisobutylaluminium hydride and bis(pentane-2,4-dionato)nickel catalyse the conjugate addition of the alkenylzirconium compounds.



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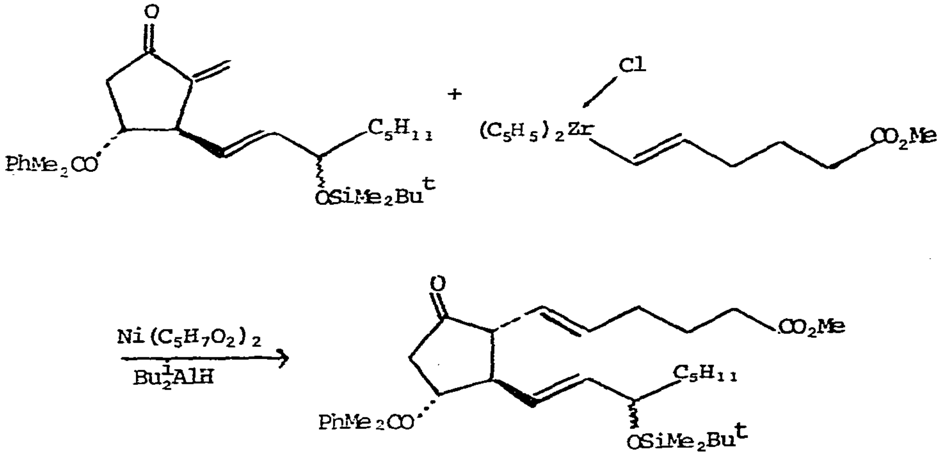

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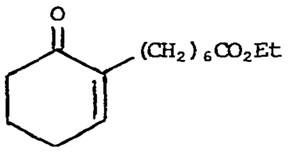
Prostaglandin analogues in which the cyclopentanone ring is replaced by a cyclohexanone ring have also been described [98]. Thus a second chain may be introduced into the cyclohexanone (73) by reaction with $\text{Li}[\underline{trans}\text{- Me}_2\text{Bu}^t\text{Al-CH}=\text{CHR}]$ ($\text{R} = \text{C}_6\text{H}_{13}$ or C_3H_7) to give (74) or with (75) to give (76).



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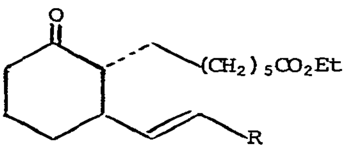

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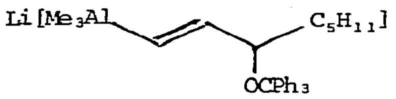

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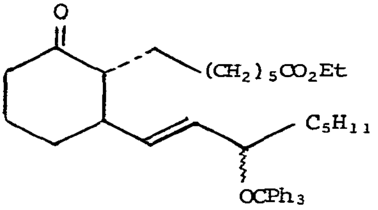
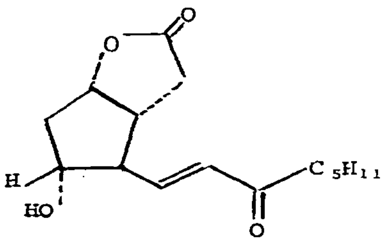


(76)

The third group of applications of organoaluminium compounds in prostaglandin synthesis involves the use of stereoselective reducing agents, such as diisobutylaluminium 2,6,di-t-butyl-4-methylphenoxide (77). This reacts with the enone (78) to give a 95% yield of (79). The ratio of 15S to 15R isomers is 92:8. Similarly the methyl ester (80) is reduced to (81) with 100% selectivity.

Reduction of ethers and esters is less selective than that of hydroxy-ketones [99]. Similar high selectivities are obtained with (82) as reducing agent [100].



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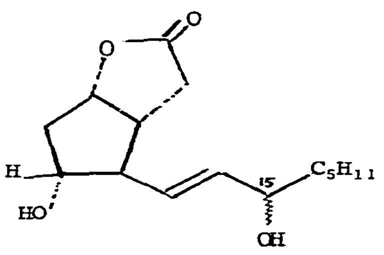

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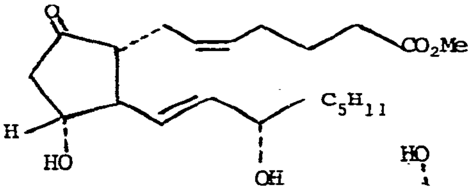

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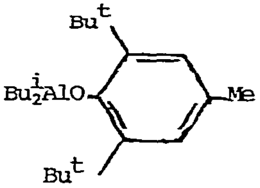

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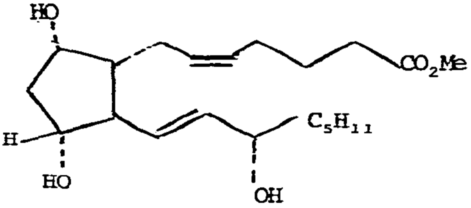
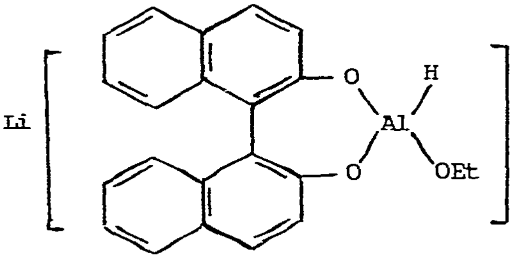


(81)

The reactions of organoaluminium compounds with amides [101] and p-quinones [102] have been described in a series of Spanish papers (See also ref. [125-6] below). In general reactions are complicated; those with quinones are thought to involve radicals as intermediates.



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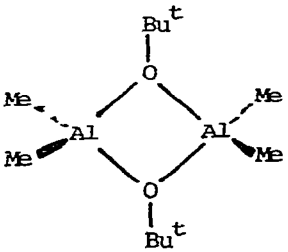

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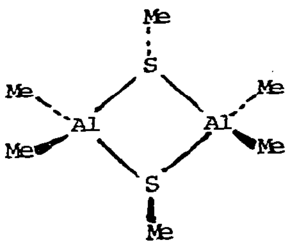


(84)

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

The removal of organoaluminium compounds from industrial residues by hydrolysis has been described in two patents [103] [104]. Another patent [105] covers manufacture of compounds $R^1(R^2O)AlX$ (R^1 = alkyl R^2 = alkyl, cycloalkyl, alkenyl, cycloalkenyl, acyl, alkanoyl, alkenoyl or aroyl) which are said to be antiperspirants. Aluminoxanes, used with tungsten(VI) chloride as catalyst for the ring-opening polymerisation of cyclooctatetraene [106], have been manufactured by a process [107] in which a trialkylaluminium in a hydrocarbon is treated with an aqueous emulsion in a hydrocarbon, and the product is removed continuously. Two further patents refer to salicylaldoxime [108] [109] and dimethylglyoxime [109] derivatives which have been described in previous surveys in this series. There is also a brief note [110] on the preparation of organoaluminium peroxides e.g., $(Ph_3SiO)_2AlOOBu^t$.

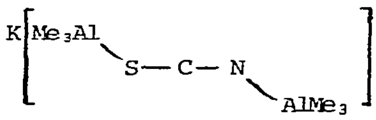
A very full account [111] of the thermal decomposition of the alkoxides of magnesium, zinc and aluminium includes details of several new organoaluminium derivatives $R^1_2AlOR^2$ (R^1 = Me or Ph, R^2 = Pr^i, cyclo-C_6H_{11}, Ph_2MeC-). All were isolated with solvent of crystallisation. The thermal decomposition was studied by thermogravimetry: most of the aluminium compounds only lost solvent or sublimed, but the cyclohexyl derivative gave benzene and cyclohexene between 195 and 375°C.

The use of ^{13}C NMR spectra in structural studies of alkoxides and amido derivatives has been examined [112]. In dimeric and trimeric alkoxides $(R^1R^2AlOC(1)H_2C(2)H_3)n$ (n = 2 or 3) only the shift of C(1) is sensitive towards electronic effects or molecular complexity. The variation in chemical shift over a range of compounds has been attributed to $p\pi$-$d\pi$ bonding between oxygen and aluminium. Mention of the structures of the dimers $[(Me_2AlOBu^t)_2]$ (83) [113] and $[(Me_2AlSMe)_2]$ (84) [114] determined by electron deffraction, was inadvertently omitted from previous annual surveys. The main molecular parameters are shown in Table 1. The alkoxide has molecular symmetry D_{2h}, with the three valencies at oxygen planar. In contrast, the sulphur derivative has symmetry C_{2h} with the SMe groups trans. During the last few years, structures of a number of compounds $M[R_3AlX]$ or $M[(R_3Al)_2X]$ (M = alkali metal and X = halogen or pseudohalogen) have been described. The latest in this series, that of $K[(Me_3Al)_2]SCN$ (85), is the first in which the thiocyanate group makes an (S,N) bridge between two main group atoms [115]. The Al-N bond [195.1(5) pm] is normal, but the Al-S distance [248.9(2) pm] implies that the second Me_3Al fragment is only weakly coordinated. The SCN group is linear and the S-C and C-N bond lengths are very similar to those in related compounds of transition metals.

Table 1 Molecular parameters for $[(Me_2AlOBu^t)_2]$ and $[(Me_2AlSMe)_2]$

		$[(Me_2AlOBu^t)_2]$ (83) [113]	$[(Me_2AlSMe)_2]$ (84) [114]
Al-O(S)	pm	186.4(6)	237.0(3)
Al-C	pm	196.2(15)	194.5(4)
O(S)-C	pm	141.9(12)	181.1(10)
Al-O(S)-Al	°	98.1(7)	94.5(6)
C-Al-C	°	121.7(17)	128.6(25)
Al-O(S)-C	°	130.9(4)	106.1(12)

Estimated standard deviations in least significant figures in parenthesis.



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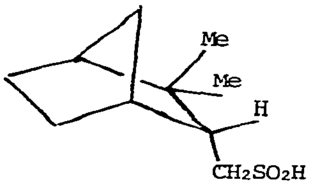
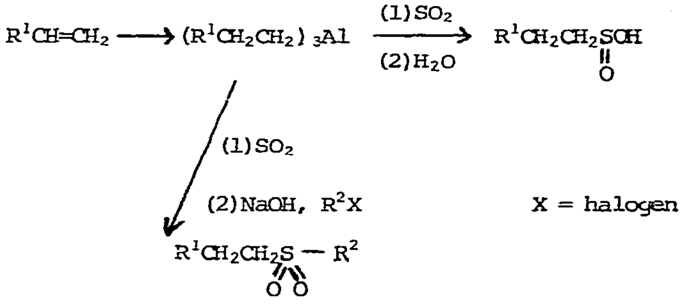


(86)

The reactions between trialkylaluminiums and sulphur dioxide yield products which may be hydrolysed to sulphinic acids or converted by treatment with alkyl halide and alkali to sulphones [116]. Since the alkylaluminium compounds are easily made from alkenes, a wide variety of sulphinic acids RSO_2H may be obtained (Equation 29). Details have been given for R = $C_{10}H_{21}$, $C_{11}H_{23}$, $C_{12}H_{25}$, $Ph(CH_2)_3$–, 1-naphthylpro-3-yl, and for sulphinic acids derived from 2-allylphenol and camphene (17). In the last case the reaction is highly stereospecific and only the endo-acid (86) is formed, without any of the exo-isomer.



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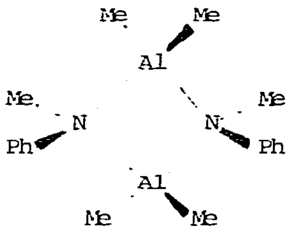
9. COMPOUNDS WITH ALUMINIUM-NITROGEN BONDS

Organoaluminium amido- and imido-compounds have been reviewed in a recent book [117]; ^{13}C spectra are discussed in ref. 112 .

Complexes of trialkylaluminium with primary or secondary amines decompose on heating with formation of alkanes and amido compounds (Equation 30). Two papers have appeared on the mechanism of this

$$\underset{(88)}{R^1_3AlNHR^2R^3} \rightleftharpoons R^1_3Al + NHR^2R^3 \longrightarrow R^1H + \underset{(87)}{R_2AlNR^2R^3} \qquad \underline{30}$$

reaction. The first [118] gives the temperature ranges (°C) over which amine complexes (88) decompose as follows: $Me_3AlNHMePh$ 20-25, $Me_3AlNHBu_2$ 120-8, $Me_3AlNH_2C_8H_{17}$ 65-73, $Bu^i_3AlNHMePh$ 186-198, $Bu^i_3AlNHBu_2$ 148-56, $Bu^i_3AlNH_2C_8H_{17}$ 107-115. The decomposition of complexes of Me_2Bu^iAl and $Me_2(MeC{\equiv}C)Al$ is complicated by reactions involving exchange of alkyl radicals between aluminium atoms. The second paper [119] describes a kinetic study of the decomposition of $Me_2HAlNHMePh$, and leads to the interesting conclusion that the elimination (Equation 30) is not a reaction of the complex (88), but a second-order reaction between monomeric Me_2AlH and amine. The product $Me_2AlNMePh$ is dimeric and is formed as a 4:1 mixture of cis- and trans- isomers (89) and (90). The decomposition of the trimers $(Me_2AlNHMe)_3$ (also present in solution as a mixture of cis- and trans- isomers) leads to the formation of both heptamer (90%) and octamer (10%) $(MeAlNMe)_n$ (n = 7 or 8), which have cage structures. A number of mixed amido-imido intermediates have been detected and one $[(Me_2AlNHMe)_2(MeAlNMe)_6]$, characterised by X-ray crystallography [120], has the structure (91). The main molecular parameters are: Al-N 191.0(6). Al-C 197(2), N-C 152(2) pm, N-Al-N 91.3(3) or 106.7(10), Al-N-Al, 88.4(3) or 115.6(10), N-Al-C 113.5(6), Al-N-C 111.4(11), C-Al-C 109(1)°. The corresponding gallium compound is similar. There is evidence from both X-ray data and NMR measurements on solutions that (91) is formed as an equimolar mixture of cis- and trans- isomers. The configurations at N^1 are related by a C_2 axis in



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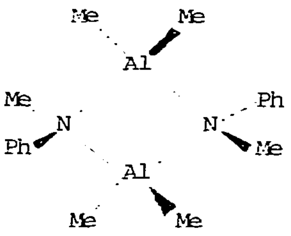

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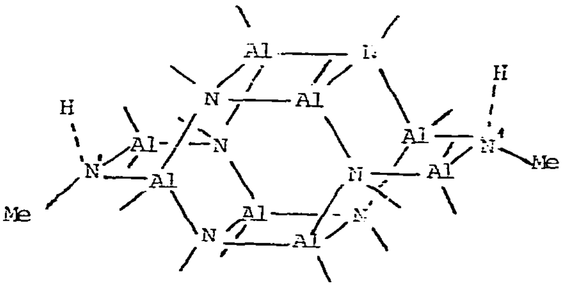
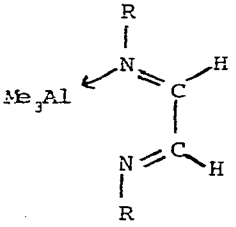


Methyl groups omitted, except those on N¹

(91)

the cis-isomer (shown) and by a centre of inversion in the trans-isomer [c.f. (89) and (90)].

A different form of amido-imido derivative of aluminium is obtained from hexamethyldialuminium and diazabutadienes R-N=CH-CH=N-R [121]. When R = 2,6-$Me_2C_6H_3$- or 2,4,6-$Me_3C_6H_2$-, it is possible to isolate



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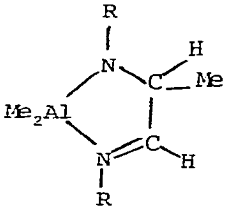

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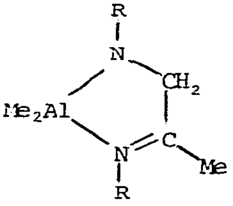
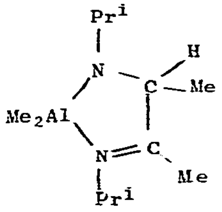


(94)

complexes, which have the structure (92), but when R = 4-ClC_6H_4-, 4-MeC_6H_4- or 4-$MeOC_6H_4$- the products are the compounds (93), in which one methyl group has been transferred from aluminium to carbon, and the amido-imido ligand with aluminium forms a 5-membered chelate ring. On heating both (92) and (93) rearrange to (94). The asymmetric diazabutadiene $Pr^iN=CH-CMe=NPr^i$ gives (95) which does not rearrange. A series of new amino-imino compounds may be synthesised by hydrolysis of complexes such as (94). NN'N''N'''-Tetramethyloxamide reacts with two equivalents of trimethylaluminium to give the compound $[(Me_2Al)_2C_2(NMe)_4]$ (96), in which the two fused five-membered rings are almost planar [122]. The X-ray structure determination gives Al-C 197.7(5), Al-N 190.6(3), N-C(2) 147.1(7), N-C(1) 132.2(3), C(1)-C(1)' 154.2(8) pm, C-Al-C 117.2(2), N-Al-N 85.7(1), Al-N-C(1) 113.6(3), N-C(1)-C(1)' 113.4(2)°. The structures of the gallium and indium analogues have also been determined.



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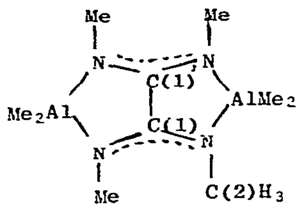


(96)

The compound $[(Me_2Al^{15}N_3)_3]$, made from trimethylaluminium and hydrazoic acid $[^{15}N_3]$ has been studied by NMR spectroscopy [123]. Spectra recorded over a range of temperatures show that there is exchange between α- and γ- nitrogen atoms of azido groups which is slow on the NMR time-scale at −100°C, but detectable at 35°C. A colourless crystalline complex $H_2C{=}CHCNAlMe_3$ has been isolated by slowly adding acrylonitrile to hexamethyldialuminium . A variety of spectroscopic evidence suggests that the aluminium is coordinated to the nitrogen atom of the nitrile [124].

Complicated mixtures are obtained in the reactions of organoaluminium compounds with azoxy- and azo-arenes [125]. The interaction of organoaluminium compounds and nitrosoarenes probably involves a hydroxylamine intermediate [126].

10. ORGANOALUMINIUM COMPOUNDS INVOLVING OTHER METALS

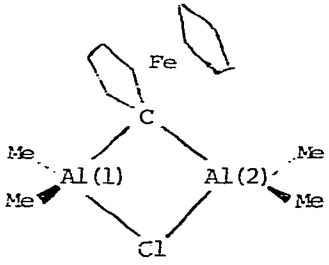
Lithium tetrakis(trimethylsilyl)aluminate was described in 1976. This compound has now been shown to react with zinc acetate in ether to give $(Me_3Si)_2Zn$ which slowly decomposes at 20°C (Equation 31) [127]. The corresponding cadmium compound, obtained from cadmium(II) chloride, is even less thermally stable. Bis(trimethylsilyl)mercury may, however, be made simply by the reaction between chlorotrimethylsilane, mercury and aluminium, in boiling THF [128]. Other donor solvents, e.g., THF or ether, may be substituted for 1,2-dimethoxyethane in (97), and the unsolvated compound may be obtained by repeated sublimination of the ether adduct. IR, Raman and NMR spectra have been documented [129]. There have been two more patents describing the preparation of organometallic compounds $mMgR_2.nAlR_3$ from alkyl halides, magnesium and either

$$Zn(OCOMe)_2 \ + \ Li[Al(SiMe_3)_4].\ 2DME \longrightarrow Zn(SiMe_3)_2 \qquad \underline{31}$$

DME = 1,2-dimethoxyethane

aluminium [130] or alkali metal tetraalkylaluminates [131].

During the last 10 years, the structures of several compounds containing both aluminium and a transition metal have been described. X-ray structures of three substances of this type have been published in 1979 and the structure of $[(cyclo\text{-}C_6H_{11})_3P(\eta^3\text{-}C_3H_5)NiClAlMe_2Cl]$ has been mentioned in a review [10]. The molecule of the ferrocenylalane (98), prepared by the reaction between $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4HgCl)]$ and hexamethyldialuminium has a mirror plane which contains Fe, Al and Cl atoms [132]. The dimethylaluminium fragments are normal [Al-C 1.941(8) pm C-Al-C 125.4(5)°], but the bridge bonds are unsymmetrical, probably because of the steric requirements of the ferrocenyl ligand [Al(1)-C 211.6(8), Al(2)-C 202.6(8), Al(1)-Cl 226.0(4), Al(2)-Cl 241.0(4) pm].



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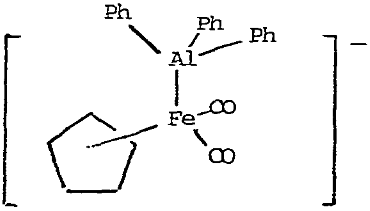


(99)

There is no direct Al-Fe bond. The structure of only one other ferrocenyl alane has been determined. This was shown in 1976 to have a bridging $C_5H_3\langle$ group between two aluminium atoms. The compound $[Et_4N][Ph_3AlFe(CO)_2(C_5H_5)]$, which has an anion (99), was made as part of a study of coordination of acceptors Ph_3E (E = Al, Ga, In) to metal carbonyl anions [133]. The Fe-Al distance (251.0 pm) is about that expected for a single bond. The Al-C [(202.3(3) pm] and mean C-C [138.5(2) pm] distances are similar to those in hexaphenyldialuminium. As in Ph_6Al_2, the C-C-C angles adjacent to Al [mean 114.3(3)°] are significantly less than 120°. The IR spectrum of the complex $[Bu_4N][Ph_3Al(\eta^5\text{-}C_5H_5)W(CO)_3]$ shows a strong absorption at 1600 cm^{-1} suggesting that in this case the Ph_3Al fragment is coordinated to the oxygen atom of a carbonyl group making a W-C-O-Al sequence. The Ph_3Al may be quantitatively removed by reaction with pyridine. It is interesting that the corresponding gallium compound appears to exist in solution as a mixture of isomers with either Ga-W or Ga-O bonds. The compounds $[(Ph_3P)_2N][Ph_3AlCo(CO)_4]$ and $[Pr_4N][Ph_3AlMn(CO)_5]$ appear to be thermally unstable at 20°C but it is tentatively suggested that Ph_3Al is coordinated to cobalt in the first and to oxygen in the second.

The third structure is of cis-bis(22'bipyridine)dimethyl cobalt(II) tetraethylaluminate (100) (R^1 = Me, R^1 = Et), which has transition metal and aluminium separated in cation and anion [134]. Compounds of this type obtained by the reaction of equation 32, are described as "inert" towards water, but they are converted slowly by dichloromethane, or more quickly by dry HCl in ether (Equation 33 R = Me) into $\mathrm{[CoMe_2(bpy)_2]Cl}$ (101) which is attacked only slowly even by dilute acids. With lower

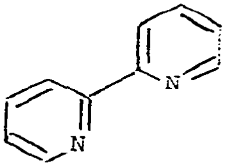
$$\begin{tikzcd} \mathrm{Co(C_5H_7O_2)_3 + bpy + AlR_3} \arrow[r, "\mathrm{Al/Co\ 1.5-2}"] \arrow[d, "\mathrm{Al/Co} > 7"] & \mathrm{[CoR_2(C_5H_7O_2)(bpy)]} \\ \mathrm{[CoR^1_2(bpy)_2][AlR^2_4]} & \end{tikzcd}$$

(102)

(100)

32

bpy =



$\mathrm{C_5H_7O_2}$ = pentane-2,4-dionato; R = Me or Et

$$\mathrm{[CoMe_2(bpy)_2][AlR_4]} \underset{\mathrm{HCl}}{\overset{\mathrm{LiAlR_4}}{\rightleftarrows}} \mathrm{[CoMe_2(bpy)_2]Cl} \qquad 33$$

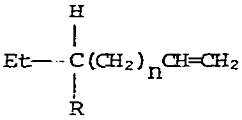
(101)

Al/Co mole ratios the neutral complexes (102) (R = Me, Et, Pr^n or Pr^i) are formed: it is suggested that with an excess of $\mathrm{AlR_3}$, the complexes (102) may be alkylated to $\mathrm{[CoR_3(bpy)_n]}$ which subsequently decompose to (100) ($R^1 = R^2$) [135]. A note [136] on UV spectroscopic studies of this reaction has appeared. Another note [137] describes the preparation of the known complexes $\mathrm{[(C_6H_{11})_3P)_2NiHX]}$ from $\mathrm{[EtNiP(C_6H_{11})_3(C_5H_7O_2)]}$ and $\mathrm{Et_2AlX}$ (X = Cl or Br). Several alkylcopper(I) complexes $\mathrm{RCuL_3}$ (L = tertiary phosphine, R = Me, Et, Pr^n or Pr^i) have been isolated from the reaction between $\mathrm{[Cu(C_5H_7O_2)_2]}$ and dialkylaluminium ethoxides [138], and the reaction between the alkoxide $\mathrm{[Ce(OPr^i)_4 \cdot B]}$ (B = $\mathrm{Pr^iOH}$ or pyridine) and triethylaluminium in the presence of cyclooctatetraene yields a bimetallic complex formulated as $\mathrm{[(C_8H_8)Ce(OPr^i)_2AlEt_2]}$ [139]. To explain the variable temperature NMR spectrum, a hemialkoxide bridged structure has been postulated.

11. CATALYSIS

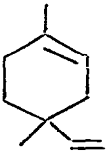
As in previous years, organoaluminium compounds have been used as components of an astonishing variety of catalytic systems. Work described in this section has been classified according to the type of reaction promoted, but coverage is far from comprehensive. No attempt has been made to summarise papers where the emphasis is on features of the reaction other than the catalyst system. Many of the reactions catalysed involve alkenes, e.g., isomerisation, oligomerisation [10], homo- and co-polymerisation [11], metathesis and hydrosilylation.

The isomerisation of alk-1-enes to (E)alk-2-enes using as catalyst N-methylsalicylideneaminenickel(II)-triisobutylaluminium without solvent was described in 1976. The addition of an optically active amine (R)-NN-dimethyl-1-phenylethylamine reduces the rate of the reaction but makes possible chiral discrimination in isomerisation of racemic mixtures of alk-1-enes (103) (R = Me or Ph, n = 0, 1 or 2) [140]. Both (E)alk-2-ene and unchanged alk-1-ene are optically active and the R enantiomer is isomerised faster than the S. Another catalyst consisting of an iron salt or carbonyl and organoaluminium compound, has been used for alkene isomerisation, according to a patent [141].



$$\mathrm{Et{-}\overset{H}{\underset{R}{C}}(CH_2)_nCH{=}CH_2}$$

(103)



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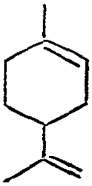
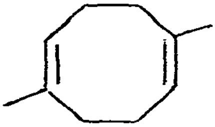


(105)

Olegomerisation of isoprene in the presence of Ni(C$_5$H$_7$O$_2$) -B(OC$_6$H$_{11}$)$_3$-AlEt$_3$ as catalyst gives dimers (104), (105) and (106), cyclic (107) and linear (108) trimers: under optinum conditions the yeild of (108) may be



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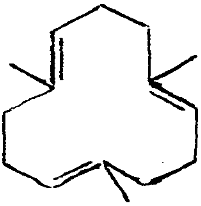
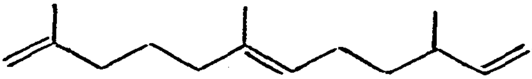
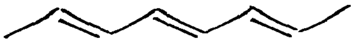


(107)

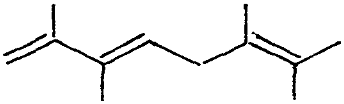


(108)

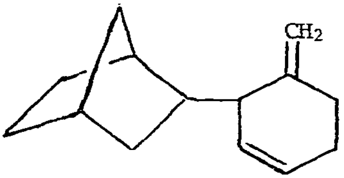
increased to ca 50% [142]. With $Ni(C_5H_7O_2)_2$- Ph_3P-Et_3Al the proportion of (108) was much smaller. The catalyst $Ni(C_5H_7O_2)_2$-Ph_3P-Bu^i_3Al may be used to convert butadiene into cycloocta-1,5-diene with 93-5% selectivity [143]. If ethyleneimine is added to the catalyst system, however, the main product (80% yield) is the linear dimer (E,E,E)-octa-2,4,6-triene (109). The mechanism of this reaction has been investigated by a series of deuteration experiments [144]. The catalyst $Zr(OBu)_4$-Ph_3P-Et_2AlCl with butadiene gives (109) together with some vinylcyclohexene [145]. 2,3-Dimethylbutadiene is converted with 80% yield to the dimer (110) and linear oligomers are formed with high selectivity from several other substituted 1,3-dienes. When bicyclo [2,2,1]hept-2-ene (norbornene) is heated with $Ni(C_5H_7O_2)_2$-$P(OEt_3)_3$-Et_3Al, the principal product is the diene (111) [146].



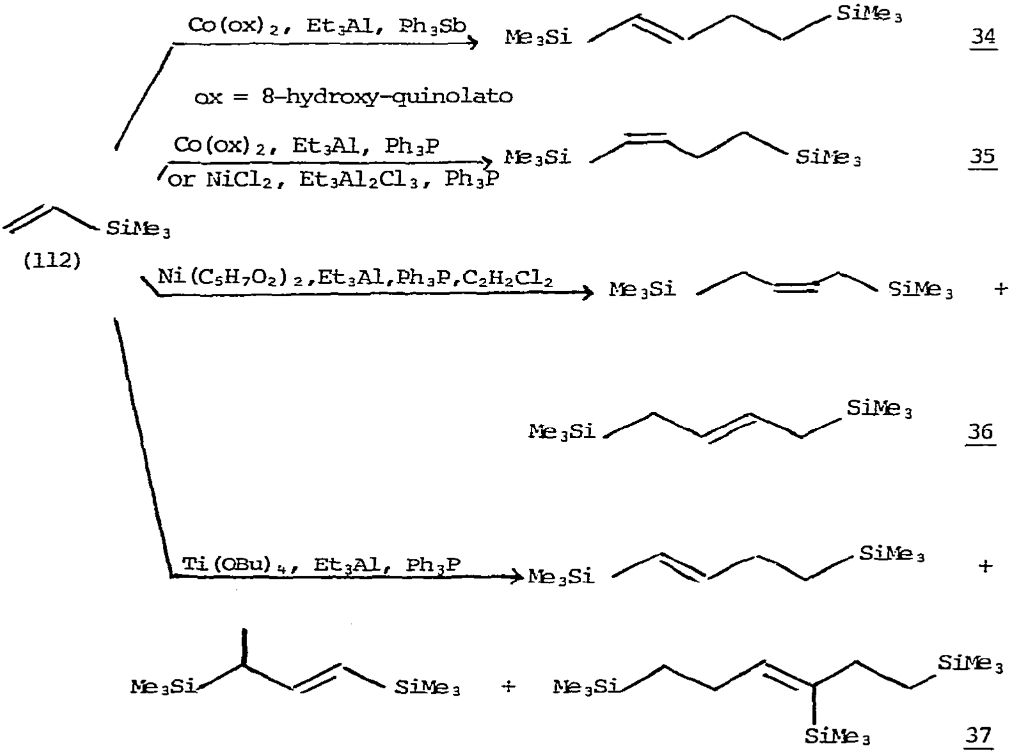
(109)



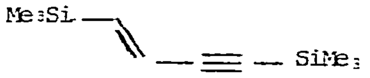
(110)

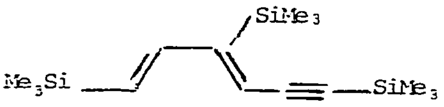


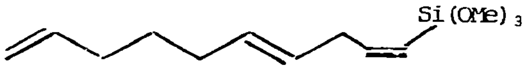
(111)



The range of catalysts described above for oligomerisation of alkenes has been applied to the oligomerisation of vinylsilanes [147] (Equations 34-37). Variations in the catalyst system lead to wide variations in the products. Ethynyltrimethylsilane reacts more readily than does the vinyl compound (112) in the presence of $Ni(C_5H_7O_2)_2$-Ph_3P-Et_3Al to give the di- and tri-silanes (113) and (114) [147]. Oligomerisations of vinylsilanes $H_2C{=}CHSiR_3$ (R_3 = $(MeO)_3$, $(MeO)_2Me$, Cl_3, or Cl_2Me) with $Ti(OBu)_4$-Ph_3P-Et_3Al as catalyst have also been examined [148].


(113)


(114)


(115)

Work on the linear cooligomerisation of vinylsilane with butadiene, referred to in last year's survey, has been republished [149]. Butadiene reacts with trimethoxy(vinyl)silane in the presence of $Ni(C_5H_2O_2)_2$-Ph_3P-Et_3Al to give the triene (115) without the range of biproducts found with trimethyl(vinyl)silane. There is a brief account [150] of the reactions between trimethoxy(vinyl)silane and either ethylene or propene in the presence of $Ti(OBu^n)_4$-Ph_3P-Et_3Al and between trimethyl(vinyl)silane and ethylene with $Co(ox)_2$-Ph_3P-Et_3Al as catalyst.

Ziegler-Natta catalysts again dominate those used for polymerisation of alkenes [2][8][151-3]. Chlorides containing titanium and some other metal e.g., V, Cr, Mn, Fe have been activated with triisobutylaluminium to give highly active catalysts for ethylene polymerisation [154][155]. Other catalysts have been made by incorporation of magnesium chloride or diphenylmagnesium and/ or ethyl benzoate [156-9] or various amines [160] or by replacing the titanium compound by the complex between 4-methylpent-1-ene and vanadium(III)chloride [161]. Several further papers have been published on monomer-isomerisation polymerisation or copolymerisation using $TiCl_3$-Et_3Al [162-5] [isomerisation may be assisted by bis(pentane-2,4-dionato)nickel], on the effect of changing the soluble cocatalyst in the heterogeneous reaction systems [166] and on the nascent structure and morphology of the polymer [167-8][158]. Another series deals with polymerisations of propene [169-172] or other alkenes [173-5] using soluble catalysts from VCl_4 or $V(C_5H_7O_2)_3$ and alkylaluminium compounds. ESR measurements on soluble catalysts derived from $[(\eta$-$C_5H_5)_2TiCl_2]$–

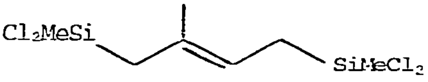
Et_3Al mixtures have also been described [176]. So called Ziegler-Natta catalyst systems from iron stearate and triethylaluminium [177-8] or from thallium(III)chloride and triethylaluminium [179] have been described, but there appears to be no account of the use of these systems for actual polymerisations.

Organoaluminium compounds continue to find uses as components, with transition metal compounds, of catalysts for alkene metathesis and ring opening polymerisations [3,9,106, 180-4], and for polymerisation of acrylates [185-6].

Another group of applications of organoaluminium compounds depends on their functioning as Lewis acids [5,6] [187]. A comprehensive study of the t-butylchloride-dimethyl(cyclopentadienyl)aluminium system as an initiator for polymerisation of isobutene has suggested that initiation is by $[Bu^t]^+$ cations and termination mainly by transfer of $[C_5H_5]^-$ from the $[Me_2Al(C_5H_5)Cl]^-$ ion [188-9]. The non-polymerisable alkene 2,4,4-trimethylpent-1-ene has served as a model for the study of initiating systems for cationic polymerisation. A detailed examination of the products from the interaction of this alkene with $p\text{-}MeC_6H_4CH_4Cl\text{-}Et_3Al$ in dichloromethane has given information about relative rates of various elementary reactions which has been important in making predictions about polymerisation of isobutene [190].

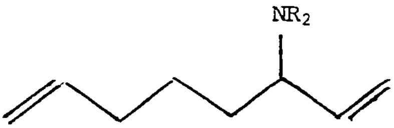
Reactions between methyldichlorosilane and various 1,3-dienes have been documented. Mixtures of $Ni(C_5H_5O_2)_2$ and R_3Al (R = Et or Bu^i) effectively catalyse 1,4-additions. With butadiene or isoprene, bis-silylated products (116) and (117) are also produced: yields of these may be increased to 65-70% by using an excess of silane [191]. In another study [192] of the catalysis of isoprene hydrosilylation using transition metal atoms, the addition of diethylaluminium chloride to ineffective catalysts from Cr, V or Ti vapours did not lead to any improvement.

(116)



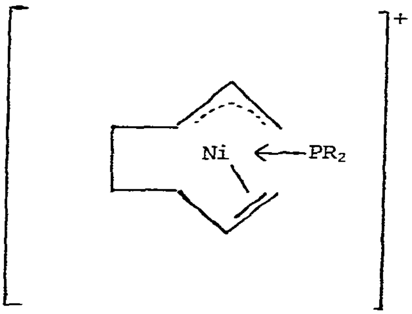
(117)

(118)



(119)

The catalyst system $Ni(C_5H_7O_2)_2$-Ph_3P-Et_3Al has also been used to effect the simultaneous dimerisation and amination of butadiene to give the dialkyl octadienylamines (118) and (119) [R = Me, Et, Bu^t or R_2 = $(CH_2)_5$]. Excellent yields (> 85%) of (118) may be obtained at low temperatures in toluene or at 20° in THF: the (118)/(119) ratio increases with increasing steric requirement of the amine. Bis (cycloocta-1,5-diene)nickel(0)-triphenylphosphine-triethylaluminium may also be used as catalyst [193]. Intermediates such as (120) may be involved.



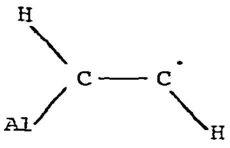
(120)

As a final example of the use of organoaluminium compounds in catalysis, the synthesis of arylalkynes (Equation 38) may be effected using $[Cl_2Pd(PPh_3)_2]$-Bu^i_2AlH (R = H, alkyl or aryl; X = I or Br) [194].

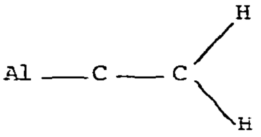
$$RC\equiv CZnCl + ArX \longrightarrow RC\equiv CAr \qquad \underline{38}$$

12. UNSTABLE INTERMEDIATES AND QUANTUM MECHANICAL CALCULATIONS

ESR signals from the purple matrices obtained by cocondensation of aluminium atoms with benzene or C_6D_6 have been attributed to an Al-η^2-C_6H_6 complex in which a half-filled p orbital on Al overlaps with an antibonding orbital associated with the C-C double bond [195]. The ESR spectrum of an Al-acetylene matrix was described in 1977 and the vinyl structure (121) was considered most likely for the species responsible. Self consistent field calculations, however, indicate that the vinylidene structure (122) may be more stable [196]. It is possible that at the low temperatures employed in the ESR study, the hydrogen transfer converting (121) into (122) may be slow so that the kinetically, rather than the thermodynamically, determined product may be observed. Calculations of this kind are becoming increasingly possible and may well throw light on a number of processes involving organometallic compounds as catalysts. C f. also ref. 26 .



(121)



(122)

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