Alkyl-bridged Complexes of the *d*- and *f*-Block Elements. Part 1. Di-μ-alkyl-bis(η-cyclopentadienyl)metal(III)dialkylaluminium(III) Complexes and the Crystal and Molecular Structure of the Ytterbium Methyl Species

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Reaction of $[\{M(\eta\text{-}C_5H_5)_2Cl\}_2]$ with $Li[AlR_4]$, or in some cases $Mg[AlR_4]_2$, affords the novel crystalline complexes $[(\eta\text{-}C_5H_5)_2M(\mu\text{-}R)_2AlR_2]$ (M = Sc, Y, Gd, Dy, Ho, Er, Tm, or Yb, R = Me; or M = Sc, Y, or Ho, R = Et). The yttrium, unlike the scandium, complexes are fluxional at 40 °C, but at −40 °C bridging and terminal alkyl groups give distinct n.m.r. signals; $\Delta G^\ddagger$ for site exchange in $[(\eta\text{-}C_5H_5)_2Y(\mu\text{-}Me)_2AlMe_2]$ is 15.9 kcal mol^{-1} at 392 K. A di-μ-alkyl-bridged structure is confirmed by i.r. (bridging CH_3 band at 1 250 and 1 235 cm^{-1}), variable-temperature ^1H and ^{13}C n.m.r. (M = Sc or Y), and *X*-ray studies (M = Yb). Additional data are given on the less stable $[(\eta\text{-}C_5H_5)_2Ti(\mu\text{-}Me)_2AlMe_2]$, $[Ti(\eta\text{-}C_5H_5)_2(AlMe_3Cl)]$, and $[(\eta\text{-}C_5H_5)_2Ti(\mu\text{-}H)_2AlMe_2]$ (structure deduced in part from e.s.r. spectra). A single-crystal *X*-ray analysis of $[(\eta\text{-}C_5H_5)_2Yb(\mu\text{-}Me)_2AlMe_2]$ has been carried out to *R* 0.036 and *R'* 0.042; the complex has an approximately tetrahedral Yb and Al environment (space group $Pna2_1$) with the $YbMe_2Al$ unit strikingly similar to $AlMe_2Al$ in $[Al_2Me_6]$. Important bond lengths (t = terminal, b = bridge) and angles are: Yb–C (cyclopentadienyl, average) 2.61(3), Yb–C_b 2.59(3), Al–C_b 2.18(5), and Al–C_t 2.00(1) Å; Yb–C–Al 79.9(1.6) and C–Al–C 113.3(8)°.

STRUCTURAL inorganic chemistry at the molecular level is conventionally described in terms of the central metal ion(s) and the associated ligands. The latter are generally held to occupy either terminal or, in di- or poly-nuclear complexes, bridging positions. Hydride or hydrocarbyl (R^-) ligands, being free from electrons in non-bonding orbitals, may only enter into bridging situations by means of electron-deficient bonding, *i.e.* where the number of constituent atomic orbitals exceeds the number of available electrons. For this reason electron-deficient molecules are often encountered among hydrides or alkyls of the *s* block and main-group 3 elements, which have available energetically low-lying vacant *p* orbitals.

The formation of electron-deficient alkyl bridges in di- or poly-nuclear metal complexes is well established for the light *s*-block (Li, Be, or Mg), aluminium, and (in the solid state) the heavier Group 3B elements.[1] That this is not an exclusive property of these metals has been made clear in some recent reports of transition-metal complexes which contain alkyl bridges between adjacent metal atoms. Indeed, such a chemistry may become general within the transition-metal series. The relevant bonding problems in, for example, bridged metal complexes, $[M_2L_6]$, have been discussed.[2]

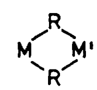
The present collaboration derives from the complementary interests of our three groups in polymerisation catalysts (Runcorn) and the chemistry (Sussex) and structural characterisation (Alabama) of transition-metal alkyls. The initial impetus was provided by the discovery of the novel methyl-bridged titanium– and yttrium–aluminium complexes $[(\eta\text{-}C_5H_5)_2M(\mu\text{-}Me)_2\text{-}AlMe_2]$.[3a] This new class of electron-deficient, early, transition-metal alkyl has been much extended to include scandium and the later lanthanoid metals and an *X*-ray analysis of two complexes (M = Y or Yb) has established the alkyl-bridged structure.[3b]

Stimulated by this discovery and of the first structurally authenticated electron-deficient transition-metal alkyl, $[\{Cu(CH_2SiMe_3)\}_4]$,[4] we considered that such complexes may well be a feature of a wider range of *d*- and *f*-block metals, because these metals also have energetically accessible vacant atomic orbitals. A principal objective of this series is to examine this hypothesis.

We recognise electron-deficient alkyl bridges to be of two types: either single (1) or double (2), where, respectively,

M—R—M′

(1)



(2)

tively, one or two alkyl groups join a pair of adjacent metal atoms. Such bonding may be homo- (M = M′) or hetero-metallic (M ≠ M′). Bridges of higher order, as in $[(LiMe)_4]$, where a methyl group spans three metal atoms,[5] have not been reported in the transition-metal series. Examples of singly bridged alkyls are authenticated (*X*-ray) for $[\{Cu(CH_2SiMe_3)\}_4]$,[4] but may be present in $[Re(CH_2SiMe_3)_4]$ if this [6a] proves to have a cluster structure. Double bridges occur more extensively. Examples of homometallic complexes are to be found in the well characterised $[\{M(\eta\text{-}C_5H_5)_2Me\}_2]$ (M = Y, Dy, Ho, Er, or Yb),[7] $[(MnR_2)_x]$ ($R = CH_2Bu^t$, $x = 4$; $R = CH_2CMe_2Ph$, $x = 2$; or $R = CH_2SiMe_3$, $x = n$),[6b] $[Cr_2(CH_2SiMe_3)_4(PMe_3)_2]$,[6b] and $[\{Ni(\eta\text{-allyl})Me\}_2]$ (allyl = C_3H_5, C_4H_7, or C_5H_9),[8] and may occur in the less well characterised $[\{Zr(\eta\text{-}C_5H_5)_2Me\}_2]$.[9] Examples of heterometallic bridges are in $[(\eta\text{-}C_5H_5)_2M(\mu\text{-}R)_2AlR_2]$ (M = Ti, Sc, Y, Gd, Dy, Er, Ho, Tm, or Yb; R = Me; M = Sc or Y, R = Et),[3] and $[(\eta\text{-allyl})Ni(\mu\text{-}Me)_2AlMe_2]$ (allyl = C_3H_5, C_4H_7, or C_5H_9).[8]

Doubly bridged species containing only one alkyl group (*e.g.* μ-halogeno-μ-alkyl) are exceedingly rare, but may occur in $[Ti(\eta\text{-}C_5H_5)_2(AlMe_3Cl)]$ (this work and ref. 10) and $[Ni(\eta\text{-allyl})\{MgMe_2Cl(OEt_2)\}]$,[8] and are commonly proposed as intermediates in halide–alkyl exchange reactions.[11] Other bridges, *e.g.* di-μ-halogeno or -alkoxo, are, of course, well known,[12] but may be described as electron-precise, in contrast to the electron-deficient (*cf.* also H^- as a bridging ligand) types under discussion.

Bridges involving hydrocarbyl groups other than alkyl are known also: these have included the singly bridging (*i*) aryl ligand, *e.g.* the homometallic $[\{Cu(C_6H_4CH_2NMe_2\text{-}o)\}_4]$ [13] and the heterometallic $[M_2Li_2(C_6H_4CH_2NMe_2\text{-}o)_4]$ (M = Cu,[13b] Ag,[13c] or Au [13d]) or $[Au_2Zn_2Ph_6]$;[13e] (*ii*) another arene-derived ligand, *e.g.* the bridging benzyne in $[Os_3(CO)_7(C_6H_4)(PPh_2)]$,[14] (*iii*) a cyclopentadienyl-derived ligand, *e.g.*[15] in $[Fe(\eta\text{-}C_5H_4)(\eta\text{-}C_5H_5)\{Au_2(PPh_3)_2\}]^+$; and doubly bridged complexes, *e.g.* di-μ-aryl as in $[\{Ti(\eta\text{-}C_5H_5)_2Ph\}_2]$ [16] or di-μ-alkynyl as in $[\{Sc(\eta\text{-}C_5H_5)_2(C{\equiv}CPh)\}_2]$.[17] There has been much speculative discussion about bridges of these types in compounds considered to be intermediates in Ziegler–Natta catalysis. They may serve a number of possible roles: alkylating, stabilising, or solvating the metal centre.[18]

In this paper we give full details (see ref. 3 for preliminary communications) of the preparation and properties of $[(\eta\text{-}C_5H_5)_2M(\mu\text{-}R)_2AlR_2]$ (M = Ti, Sc, Y, Gd, Dy, Ho, Er, Tm, or Yb) and some related complexes of Ti^{III} and *X*-ray structural data for the complexes where M = Yb (the Y structure is discussed elsewhere [19]). These transition-metal–aluminium species, especially where M = Ti, serve as useful models for hypothetical doubly alkyl-bridged intermediates in Ziegler–Natta catalyst systems. In Part 2 full details will be provided of the related, and chemically derived, doubly bridged homometallic complexes $[\{M(\eta\text{-}C_5H_5)_2Me\}_2]$.[7]

RESULTS AND DISCUSSION

Preparation and Properties.—The reaction of lithium tetra-alkylaluminates(III) with the appropriate chlorodi-(η-cyclopentadienyl)lanthanoid, in toluene, gave high yields of the title complexes [equation (1); M = Sc, Y, Gd, Dy, Ho, Er, Tm, or Yb, R = Me; or M = Sc, Y, or Ho, R = Et]. The air-sensitive complexes were, in

$$[\{M(\eta\text{-}C_5H_5)_2Cl\}_2] + 2Li[AlR_4] \longrightarrow 2[(\eta\text{-}C_5H_5)_2M(\mu\text{-}R)_2AlR_2] + 2LiCl \quad (1)$$

many cases, highly coloured (see Table 1) and were obtained as needles from toluene–hexane mixtures at −30 °C. They were soluble in toluene, benzene, or methylene chloride, but insoluble in saturated hydrocarbon solvents (the ethyl complexes being slightly soluble). The complexes of the early lanthanoids (Sm and Gd) were insoluble in toluene and, for this reason, are thought to be more ionic. An increase in ionicity from right to left across the lanthanoid series may be related to the effects of the lanthanoid contraction. With a decrease in size of the lanthanoid(III) ion from left to right there is an increase in the polarising power α (charge/radius; charge = 3+) and hence an increase in metal–ligand covalent character.

TABLE 1

Analytical data, yields, colours, and melting points for $[(\eta\text{-}C_5H_5)_2M(\mu\text{-}R)_2AlR_2]$ and $[Ti(\eta\text{-}C_5H_5)_2(AlMe_3Cl)]$

Complex		Yield		M.p.	Analysis (%) [a]			
M	R	(%)	Colour	(θ_c/°C)	C	H	M	Al
Sc	Me	67	Pale yellow	108—110 [b]	63.8 (64.1)	8.4 (8.5)	17.3 (17.4)	10.1 (10.3)
Y	Me	78	Colourless	143 [c]			28.6 [d] (29.0)	9.0 (8.8)
Gd	Me	45	White	>170 (decomp.)	44.4 (44.9)	6.2 (5.9)		
Dy	Me	65	Pale yellow	145—146	43.6 (44.3)	5.8 (5.8)	42.9 (42.8)	6.9 (7.1)
Ho	Me	78	Straw	142—143	44.0 (44.0)	5.9 (5.8)	43.7 (43.2)	6.8 (7.1)
Er	Me	76	Pink	133—135	43.2 (43.7)	5.8 (5.8)	43.6 (43.5)	7.0 (7.0)
Tm	Me	60	Pale green	>130 (decomp.)	43.6 (43.5)	5.9 (5.7)		
Yb	Me	72	Orange-red	133—135	42.8 (43.1)	5.6 (5.7)	45.1 (44.3)	6.8 (6.9)
Sc	Et	62	Pale yellow		69.8 (67.9)	9.5 (9.5)		
Y	Et	70	Colourless		59.9 (59.7)	8.4 (8.35)	24.2 (24.5)	6.8 (7.45)
Ho	Et	73	Straw		49.2 (49.3)	7.0 (6.9)		
Ti	Me	58	Deep green				17.8 [d] (18.1)	9.9 (10.15)
$[Ti(\eta\text{-}C_5H_5)_2(AlMe_3Cl)]$		46	Deep green				16.5 [e] (16.8)	9.6 (9.4)

[a] Calculated values are given in parentheses. [b] Sublimation 100 °C (0.1 mmHg). [c] Sublimation 120 °C (0.05 mmHg). [d] Li and Cl were absent. [e] Cl, 12.4 (12.4%).

The complex $[(\eta\text{-}C_5H_5)_2Gd(\mu\text{-}Me)_2AlMe_2]$ was recrystallised from methylene chloride, although only as a microcrystalline material. The yellow samarium complex was insoluble in methylene chloride and was not isolated free from LiCl; hence it has not been fully characterised.

The complexes were thermally very stable, melting, in most cases, without decomposition (Table 1). The exceptions are $[(\eta\text{-}C_5H_5)_2Tm(\mu\text{-}Me)_2AlMe_2]$, which decomposed at >130 °C, and $[(\eta\text{-}C_5H_5)_2Gd(\mu\text{-}Me)_2AlMe_2]$ which did not melt but slowly decomposed at >170 °C. The high value for the latter may again be a consequence of an increase in ionicity. The tetraethyl complexes were much less stable, slowly decomposing at room temperature, in solution or in the solid state. The scandium or yttrium complexes $[(\eta\text{-}C_5H_5)_2M(\mu\text{-}Me)_2AlMe_2]$ can be purified by sublimation at 100 °C (0.1 mmHg) * and 120 °C (0.05 mmHg), respectively. In contrast, attempts to purify $[(\eta\text{-}C_5H_5)_2Gd(\mu\text{-}Me)_2AlMe_2]$ in a similar manner resulted in isolation of $[Gd(\eta\text{-}C_5H_5)_3]$.

Attempts to prepare $[(\eta\text{-}C_5H_5)_2Y(\mu\text{-}Me)_2InMe_2]$ by a

* Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa; 1 cal = 4.184 J.

similar procedure to that shown in equation (1) were unsuccessful, [{Y(η-C_5H_5)$_2$Me}$_2$] being isolated. This is presumably formed by loss of $InMe_3$ from the tetramethylindate. Unlike aluminium, the other Group 3 elements are not prone to forming strong electron-deficient bridges in their alkyls, *e.g.* BMe_3 and $GaMe_3$ are both monomeric, and $InMe_3$, although a weakly bound tetramer in the solid state, is monomeric in solution.[1] Although boron alkyls do not contain electron-deficient bridges they differ in this respect from many boron hydrides; it is interesting, therefore, that recently several lanthanoid tetrahydroborates [M(BH_4)(thf)(η-C_5H_5)$_2$] (M = Sm, Er, or Yb) and [M(BH_4)(η-C_5H_5)$_2$] (M = Er or Yb) have been prepared.[20]

The titanium(III) complex [(η-C_5H_5)$_2$Ti(μ-Me)$_2$AlMe$_2$] was prepared in a similar manner using either Li[$AlMe_4$] or Mg[$AlMe_4$]$_2$ as alkylating agent. It was markedly less stable than the lanthanoid complexes, decomposing slowly in the solid state to an unidentified purple oil or rapidly in toluene to a purple solution at ambient temperature. Somewhat surprisingly, the stability in solution was enhanced by addition of [Al_2Me_6]; at *ca.* 0 °C there was little apparent decomposition over 1 h in the presence of 0.5—5 mol of [Al_2Me_6] per mol of the titanium complex. This is in contrast with other observations on transition-metal alkyls where the thermal stability decreased in the presence of organoaluminium compounds.[21] The origin of this stabilisation may lie in affecting the equilibrium between the tetramethylaluminate and its presumed dissociation products [{Ti(η-C_5H_5)$_2$Me}$_2$] and [Al_2Me_6]. The homonuclear complex [{Ti(η-C_5H_5)$_2$Me}$_2$] is probably much less stable than [(η-C_5H_5)$_2$Ti(μ-Me)$_2$AlMe$_2$] and decomposes irreversibly at the temperatures studied. There is evidence that this methyltitanium(III) complex exists at low temperature: thus a soluble green species is formed at −70 °C in the reaction of [{Ti(η-C_5H_5)$_2$Cl}$_2$] with methyl-lithium in diethyl ether, but attempts to isolate it have been singularly unsuccessful.[22]

Interaction of [{Ti(η-C_5H_5)$_2$Cl}$_2$] and [Al_2Me_6] (slight excess) in toluene gave the adduct [Ti(η-C_5H_5)$_2$($AlMe_3$Cl)] which may be identical to a complex of the same formula reported earlier by Natta *et al.*[10] Its stability was similar to that of the titanium(III) tetramethylaluminate.

Attempts to prepare the related [Y(η-C_5H_5)$_2$($AlMe_3$Cl)], for which ^{1}H and ^{13}C n.m.r. data would be obtainable and from which an assignment of the μ-chloro-μ-methyl or di-μ-methyl structure would be possible, were unsuccessful; [{Y(η-C_5H_5)$_2$Cl}$_2$] was recovered unchanged after heating to *ca.* 100 °C with [Al_2Me_6] (excess) in toluene, and interaction of [{Y(η-C_5H_5)$_2$Me}$_2$] and [$Al_2Me_4Cl_2$] in benzene produced the insoluble [{Y(η-C_5H_5)$_2$Cl}$_2$].[23] Lack of success in the preparation of the yttrium complex may merely reflect the relative insolubility of the yttrium(III) chloro-complex. Experiments are in hand to examine the preparation of species containing mixed bridges, *e.g.* μ-alkyl-μ-halogeno, using cyclopentadienyl complexes with solubilising substituents on the cyclopentadienyl ring.

Reaction of [{Ti(η-C_5H_5)$_2$Cl}$_2$] with Na[$AlMe_2H_2$] in toluene proceeded less readily than with Li[$AlMe_4$]. After stirring overnight at ambient temperature a purple solution was obtained, which contained a mixture of products, the major component of which was identified by e.s.r. (see below) as [(η-C_5H_5)$_2$Ti(μ-H)$_2$AlMe$_2$]. Pure material was not obtained.

A comparative reaction between the titanium(IV) complex [Ti(η-C_5H_5)$_2$Cl$_2$] and Li[$AlMe_4$] (excess) was examined. Free [Al_2Me_6] and the known[24] [Ti(η-C_5H_5)$_2$Me$_2$] were obtained. Thus Li[$AlMe_4$] acts as a simple alkylating agent and shows no tendency to act as a reducing agent to give a titanium(III) product. Transient methyl-bridged titanium(IV)–aluminium complexes may be present in solution, but it is to be expected that the co-ordinatively saturated [Ti(η-C_5H_5)$_2$Me$_2$] will show a lesser tendency to form methyl bridges to aluminium than the unsaturated titanium(III) complex [{Ti(η-C_5H_5)$_2$Me}$_n$].

A number of reactions of Li[$AlMe_4$] or Mg[$AlMe_4$]$_2$ with the cyclopentadienyl-free [Ti(CH_2Ph)$_3$Cl] and [HfBr(η-C_3H_5)$_3$] were studied. These reactions appeared to give a mixture of products; however, from [HfBr(η-C_3H_5)$_3$] and Mg[$AlMe_4$]$_2$ the major product was tentatively identified as [Hf(η-C_3H_5)$_3$Me].

Spectroscopic Characterisation.—Lanthanoid(III) complexes, except those of lanthanum (f^0) and lutetium (f^{14}), are paramagnetic, often giving large contact shifts in the n.m.r. spectra.[25] Hydrogen-1 and ^{13}C n.m.r. investigations were therefore concentrated on the diamagnetic scandium and yttrium complexes.

N.m.r. data for solutions of the scandium or yttrium complexes are consistent with the presence of a μ-dialkyl bridge between aluminium and the Group 3A metal (Table 2). The complex [(η-C_5H_5)$_2$Y(μ-Me)$_2$AlMe$_2$] and the ethyl congener are fluxional at 40 °C, the ^{1}H n.m.r. spectra showing for the methyl complex a broad singlet and for the ethyl analogue two broad peaks in the high-field region. On cooling to −40 °C a well resolved spectrum is obtained, showing two different alkyl environments, bridging and terminal. The bridging alkyl groups are observed coupled to yttrium (^{89}Y, mono-

TABLE 2

Hydrogen-1 n.m.r. data[a] on [(η-C_5H_5)$_2$M(μ-R)$_2$AlR$_2$]

Complex		Assignment (τ)				
M	R	η-C_5H_5	MR_2Al		AlR_2	
Sc	Me	3.88 (s, 10 H)	10.29 (br, s, 6 H)		10.84 (s, 6 H)	
Y	Me[b]	3.82 (4.05)[d] (s, 10 H)	10.32 (10.20)[d] (d, 6 H)[c]		10.98 (10.09)[d] (s, 6 H)	
Sc	Et	3.81 (s, 10 H)	8.52 (t, 6 H)	10.58 (q, 4 H)	8.85 (t, 6 H)	10.01 (q, 4 H)
Y	Et[b]	3.80 (s, 10 H)	8.70 (t, 6 H)	10.36 (eight-line m, 4 H)[e]	8.99 (6 t, H)	10.19 (q, 4 H)

[a] In CD_2Cl_2 at room temperature, unless otherwise stated. [b] At −45 °C. [c] ^2J(^{89}Y–C^{1}H$_3$) 5.0 Hz. [d] In [$^2H_8$]toluene. [e] ^2J(^{89}Y–C^{1}H$_2$) 4.0 Hz.

isotopic, spin = ½), characterised as a doublet for the methyl complex [$^2J(^{89}Y-C^1H_3)$ 5.0 Hz] (Figure 1) and an

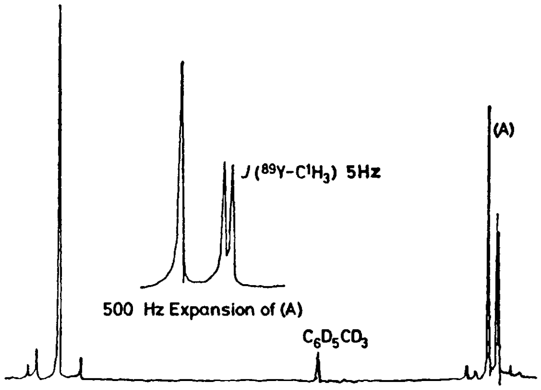


FIGURE 1 The ^{1}H n.m.r. spectrum of [$(\eta$-$C_5H_5)_2Y(\mu$-$Me)_2$-$AlMe_2$] in $C_6D_5CD_3$ at −40 °C

eight-line multiplet for the ethyl analogue due to coupling to the methyl protons as well as yttrium [$^2J(^{89}Y-C^1H_2)$ 4.0 Hz] (Figure 2). The scandium complexes [$(\eta$-$C_5H_5)_2Sc(\mu$-$R)_2AlR_2$] (R = Me or Et) are non-fluxional at room temperature and two distinct alkyl environments are observed. The resonances of the bridge-methyl and -methylene protons were, in each case, broad due to unresolved coupling to the quadrupolar scandium ($I = \frac{7}{2}$).

From line-shape ^{1}H n.m.r. studies at different temperatures for [$(\eta$-$C_5H_5)_2Y(\mu$-$Me)_2AlMe_2$] a value for the free energy of activation for the bridge–terminal site-exchange process was obtained, $\Delta G^\ddagger$ = 15.9 kcal mol^{-1} at 392 K. This may be compared with $\Delta G^\ddagger$ = 11.0 kcal mol^{-1} for [Al_2Me_6] in cyclopentane;[26] thus the bridge in the yttrium complex is considerably less labile than that in trimethylaluminium. Further data are required before any interpretation as to the mechanism of site exchange in the yttrium–aluminium complexes can be made. There has been much discussion in the literature as to the mechanism of bridge–terminal site exchange in aluminium alkyls, but to date distinctions between alternative processes have not been fully resolved.[27] At >100 °C the two methyl resonances in [$(\eta$-$C_5H_5)_2Sc$-$(\mu$-$Me)_2AlMe_2$] collapse to a singlet, again demonstrating rapid site exchange. It is interesting that the activation energy for site exchange should be appreciably higher for scandium than yttrium.

Variable-temperature ^{13}C n.m.r. spectra give similar structural results (Table 3). The limiting ^{13}C n.m.r. spectra of the yttrium complexes allowed the first measurement of the yttrium–carbon coupling constant [$^1J(^{89}Y-^{13}C)$ 12.2 Hz].

The i.r. spectra of the various methyl-bridged complexes, as paraffin or hexachlorobutadiene mulls, were essentially identical, as were those of the ethyl complexes. This provided a very useful diagnostic technique in the identification of new alkyl-bridged lanthanoid complexes. The cyclopentadienyl frequencies were observed (at 3 100m, 1 446m, 1 020s, and 800s,br cm^{-1}) in all the complexes and are consistent with other cyclopentadienyl complexes.[28] For [$(\eta$-$C_5H_5)_2M$-$(\mu$-$Me)_2AlMe_2$], bands at 1 440, 1 360 (asym CH_3 bend),

TABLE 3

Carbon-13 n.m.r. data [a] on [$(\eta$-$C_5H_5)_2M(\mu$-$R_2)AlR_2$]

Complex M	Complex R	η-C_5H_5	MR_2Al			AlR_2
Sc	Me	113.2 (s)		20.7 (s)		−6.3 (s)
Y	Me [c]	112.2 (s)		7.86 (d) [d]		−7.9 (s)
Sc	Et	112.1 (s)	34.9 (br, CH_2)	15.5 (s, CH_3)	1.5 (br, CH_2)	10.4 (s, CH_3)
Y	Et [c]	111.7 (s)	20.75 (d, CH_2) [d]	13.0 (s, CH_3)	−0.34 (s, CH_2)	10.4 (s, CH_3)

Assignment [b] (p.p.m.)

[a] In CD_2Cl_2 at 35 °C unless otherwise stated. [b] Chemical shifts are quoted as downfield from $SiMe_4$. [c] At −45 °C. [d] $^1J(^{89}Y-^{13}C)$ 12.2 Hz.

1 250, 1 235 (sym CH_3-bridge bend), and 1 190 cm^{-1} (sym CH_3-terminal bend) were assigned by comparison with [Al_2Me_6].[29] In a similar manner, for [$(\eta$-$C_5H_5)_2M(\mu$-$Et)_2AlEt_2$], bands at 2 790s, 2 730s (C–H stretch), 1 470s (asym CH_3 bend), 1 412s, 1 395m, 1 380m (CH_2–Al bend), 1 365 (sym CH_3 bend), 1 235 (CH_2 bend), 1 210m, 1 190m (CH_2–Al bend), 990s, 960s, 930m, and 905m cm^{-1} (C–C stretch) were assigned by comparison with [Al_2Et_6].[30] The skeletal modes and rocking frequencies in the 300—770 cm^{-1} region were not assigned.

With the exception of the scandium complex only a weak parent ion was observed in the mass spectrum of [$(\eta$-$C_5H_5)_2M(\mu$-$Me)_2AlMe_2$], the ion at highest m/e being

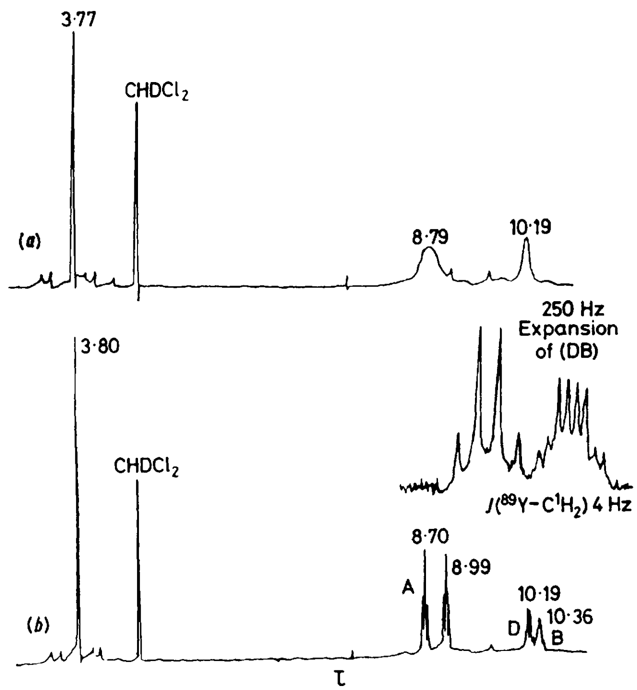


FIGURE 2 The ^{1}H n.m.r. spectra of [$(\eta$-$C_5H_5)_2Y(\mu$-$Et)_2$-$AlEt_2$] in CD_2Cl_2: (a) at 40 °C (b) at −40 °C

[$M(\eta$-$C_5H_5)_2(AlMe_3)]^+$. Generally, the fragmentation followed a similar course for all the methyl complexes:

loss of one methyl group and then rapid loss of $AlMe_3$ leading to the dominant metal-containing peak $[M(\eta\text{-}C_5H_5)_2]^+$. In most cases, no ions of the type $[M(\eta\text{-}C_5H_5)_2(AlMe_2)]^+$ or $[M(\eta\text{-}C_5H_5)_2(AlMe)]^+$ were noted.

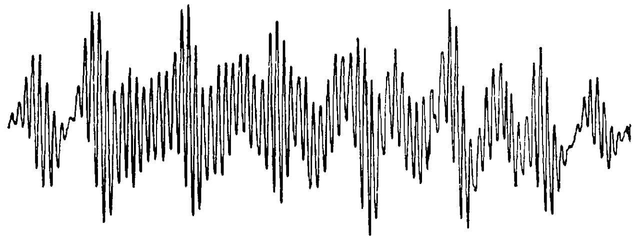


FIGURE 3 E.s.r. spectrum of $[(\eta\text{-}C_5H_5)_2Ti(\mu\text{-}H)_2AlMe_2]$ in toluene at *ca.* 20 °C: *g* 1.992; *a*(H) 4.65 G; *a*(Al) 6.9 G

An ion due to $[M(\eta\text{-}C_5H_5)_3]^+$ was also observed in some cases, probably from rearrangement. Similar rearrangement processes have been observed in a large number of cyclopentadienyl complexes.[31]

1 : 1 : 1 : 1 : 1 : 1 sextet.[32] A di-μ-methyl structure for $[Ti(\eta\text{-}C_5H_5)_2(AlMe_4)]$ appears reasonable, but is not firmly established. For $[Ti(\eta\text{-}C_5H_5)_2(AlMe_3Cl)]$ either a di-μ-methyl or a μ-chloro-μ-methyl structure is possible; the data do not allow a more precise assignment.

The e.s.r. spectrum of the solution obtained by reaction of $[\{Ti(\eta\text{-}C_5H_5)_2Cl\}_2]$ with $Na[AlMe_2H_2]$ showed the presence of two dominant species, the lesser of which was destroyed by heating to *ca.* 60 °C for a few minutes. The remaining signal (Figure 3) is assigned to the complex $[(\eta\text{-}C_5H_5)_2Ti(\mu\text{-}H)_2AlMe_2]$ by analogy with data on other di-μ-hydrido-titanium(III)–aluminium complexes.[33]

The Molecular Structure of $[(\eta\text{-}C_5H_5)_2Yb(\mu\text{-}Me)_2AlMe_2]$.—The molecular structure and atom-numbering scheme are shown in Figure 4, while Figure 5 presents a stereoscopic view of the unit-cell packing. Structural parameters are in Table 4. The range of compounds which exhibit three-centre two-electron bridge bonding of type (2) is not extensive. Structural data (Table 5) show that

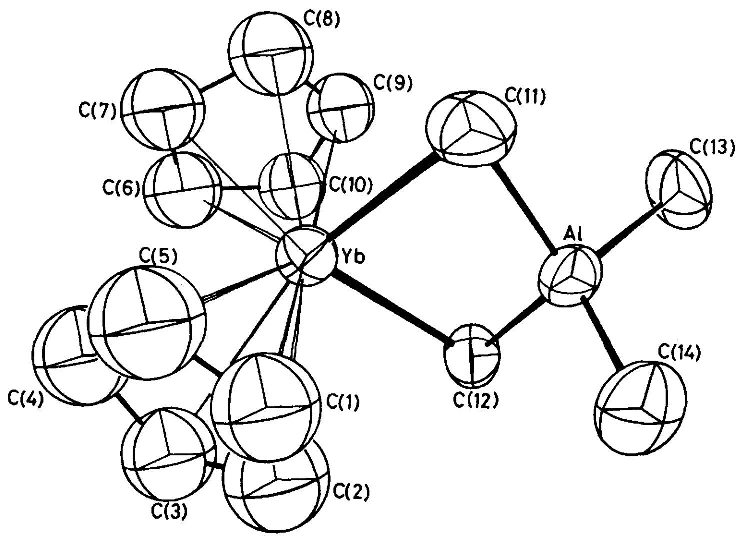


FIGURE 4 Diagram of $[(\eta\text{-}C_5H_5)_2Yb(\mu\text{-}Me)_2AlMe_2]$ showing the numbering system used, and anisotropic thermal motion (ellipsoids are sealed to enclose 50% probability) for Yb, Al, and methyl C atoms

The e.s.r. spectra of $[(\eta\text{-}C_5H_5)_2Ti(\mu\text{-}Me)_2AlMe_2]$ and $[Ti(\eta\text{-}C_5H_5)_2(AlMe_3Cl)]$ in toluene at *ca.* −40 °C showed a strong broadened signal at $g = 1.977$, without resolved

this type of bonding produces two geometrical manifestations: (*i*) the metal–carbon bridge bond length is significantly longer than a normal metal–carbon σ-bond

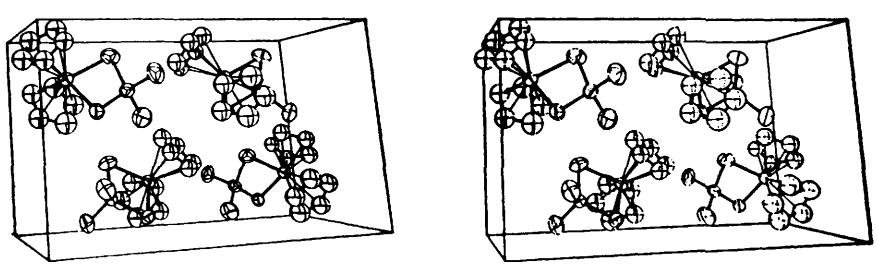


FIGURE 5 Stereoscopic view of the unit-cell packing in $[(\eta\text{-}C_5H_5)_2Yb(\mu\text{-}Me)_2AlMe_2]$

fine structure. These spectra were similar to those of the complexes $[(\eta\text{-}C_5H_5)_2Ti(\mu\text{-}Cl)_2AlR_2]$ notably in peak shape; for the latter the spectra were interpreted in terms of broadening *via* coupling to ^{27}Al ($I = \frac{5}{2}$) giving a

distance, and (*ii*) the metal–carbon–metal bond angle is small. For example, for trimethylaluminium,[34] the bridge bond length is 2.124(2) Å compared to the Al–C bond terminal distance of 1.952(4) Å, while the Al–C–Al bond angle is 75.7(1)°. For the complex [(η-C_5H_5)$_2$Yb(μ-Me)$_2$AlMe_2] quite similar values are found: 2.14(2) Å for the Al–C_b bond length, and 78.8° for the Yb–C–Al bond angle. The Yb–C_b length [2.58(3) Å] is much longer than the only known Yb–C σ-bond length; 2.38(1) Å in [Li(thf)$_4$][Yb{CH(SiMe_3)$_2$}$_3$Cl].[35]

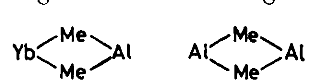
TABLE 4

Bond lengths (Å) and angles (°) with standard deviations in parentheses

Yb–C(1)	2.603(24)	Yb–C(6)	2.570(29)
Yb–C(2)	2.626(24)	Yb–C(7)	2.577(26)
Yb–C(3)	2.623(28)	Yb–C(8)	2.596(26)
Yb–C(4)	2.620(32)	Yb–C(9)	2.593(24)
Yb–C(5)	2.673(28)	Yb–C(10)	2.591(24)
Yb–C(11)	2.609(23)	Yb–C(12)	2.562(18)
Al–C(11)	2.165(22)	Al–C(12)	2.096(18)
Al–C(13)	2.014(25)	Al–C(14)	1.991(24)
C(1)–C(2)	1.41(3)	C(6)–C(7)	1.44(3)
C(2)–C(3)	1.47(3)	C(7)–C(8)	1.31(3)
C(3)–C(4)	1.44(4)	C(8)–C(9)	1.43(3)
C(4)–C(5)	1.33(4)	C(9)–C(10)	1.33(3)
C(5)–C(1)	1.36(4)	C(10)–C(6)	1.32(3)
Yb–Al	3.014(6)		
Yb–C(11)–Al	77.7(7)	Yb–C(12)–Al	80.0(6)
C(11)–Yb–C(12)	87.1(6)	C(11)–Al–C(12)	113.3(8)
Cent 1–Yb–Cent 2*	133.1	C(13)–Al–C(14)	118(1)
Cent 1–Yb–C(11)	107.8	C(13)–Al–C(11)	101(2)
Cent 1–Yb–C(12)	107.1	C(13)–Al–C(12)	107(1)
Cent 2–Yb–C(11)	104.5	C(14)–Al–C(11)	109(1)
Cent 2–Yb–C(12)	107.7	C(14)–Al–C(12)	107(1)
C(1)–C(2)–C(3)	104(3)	C(6)–C(7)–C(8)	106(2)
C(2)–C(3)–C(4)	105(2)	C(7)–C(8)–C(9)	107(2)
C(3)–C(4)–C(5)	110(3)	C(8)–C(9)–C(10)	108(2)
C(4)–C(5)–C(1)	109(3)	C(9)–C(10)–C(6)	109(2)
C(5)–C(1)–C(2)	111(3)	C(10)–C(6)–C(7)	108(2)

* Cent 1 denotes the centroid of ring 1, *etc.*

Even though the uncertainty in the metal–carbon bond length is large because of the high thermal motion



(3) (4)

of the carbon atoms, the structural parameters of the units (3) and (4) are strikingly similar. We infer, therefore, that the bonding in the two systems is similar. This point is discussed in some detail in Part 2 of this series.[7]

The average Yb–C(cyclopentadienyl) distance [2.61(3) Å] may be compared with 2.585(8) Å in [{Yb(η-C_5H_5)$_2$Cl}$_2$][36] and 2.611(13) Å in [{Yb(η-C_5H_5)$_2$Me}$_2$].[7] The average Al–C_t of 2.00(1) Å is normal, as is C_t–Al–C_t [118(1)°].

TABLE 5

Comparison of structural parameters for main-group organometallic compounds with electron-deficient bridging groups

Compound	Bridging group	Distance/Å M–C(bridge)	Distance/Å M–C(σ)	Angle/° M–C–M	Ref.
[(BeMe_2)$_2$]	Me	1.93		66.0	*a*
[{BeMe(C≡CMe)(NMe_3)}$_2$]	C≡CMe	1.87	1.75	77.2	*b*
[(MgMe_2)$_n$]	Me	2.24		75.0	*c*
[(MgEt_2)$_n$]	Et	2.26		72.0	*d*
Mg[AlMe_4]$_2$	Me	2.21 (Mg), 2.10 (Al)	1.96	77.7	*e*
Li[AlEt_4]	Et	2.30 (Li), 2.02 (Al)		77.2	*f*
[(AlMe_3)$_2$]	Me	2.123	1.952	75.7	34
[(AlPh_3)$_2$]	Ph	2.18	1.96	76.5	*g*
[Al_2Me_5(NPh_2)]	Me	2.142	1.945	78.9	*h*
[(η-C_5H_5)$_2$Yb(μ-Me)$_2$AlMe_2]	Me	2.18 (Al), 2.59 (Yb)	2.00 (Al)	78.8	This study
[(η-C_5H_5)$_2$Y(μ-Me)$_2$AlMe_2]	Me	2.10 (Al), 2.58 (Y)	1.98 (Al)	80.8	19

[a] A. I. Snow and R. E. Rundle, *Acta Cryst.*, 1951, **4**, 348. [b] B. Morosin and J. Howatson, *J. Organometallic Chem.*, 1971, **29**, 7. [c] E. Weiss, *J. Organometallic Chem.*, 1964, **2**, 314. [d] E. Weiss, *J. Organometallic Chem.*, 1965, **4**, 101. [e] J. L. Atwood and G. D. Stucky, *J. Amer. Chem. Soc.*, 1969, **91**, 2538. [f] R. L. Gerteis, R. E. Dickerson, and T. L. Brown, *Inorg. Chem.*, 1964, **3**, 872. [g] J. F. Malone and W. S. McDonald, *Chem. Comm.*, 1967, 444. [h] V. R. Magnuson and G. D. Stucky, *J. Amer. Chem. Soc.*, 1969, **91**, 254.

EXPERIMENTAL

All the experiments were performed under an atmosphere of pure dry argon in Schlenk glassware.[37] The solvents used were of reagent grade or better, and were freshly distilled from appropriate drying agents prior to use. Melting points were recorded in evacuated tubes and are uncorrected. Microanalyses for carbon and hydrogen were either carried out at the Microanalytical Laboratory of the University of Sussex, or at Butterworth's Microanalytical Consultancy. Metal analyses were by the Microanalytical Department of the Corporate Laboratory, I.C.I. Ltd. Infrared spectra were recorded as paraffin or hexachlorobutadiene mulls between CsI plates, using a Perkin-Elmer 457 (250—4 000 cm^{-1}) spectrometer. Hydrogen-1 n.m.r. spectra were obtained on Varian T60, A60, or 220 MHz instruments and ^{13}C n.m.r. spectra on a JEOL PFT100 spectrometer. Mass spectra were recorded on an A.E.I. MS9 or a Hitachi RMU-6 spectrometer. E.s.r. spectra were run on a Varian E9 instrument.

Preparations.—[{M(η-C_5H_5)$_2$Cl}$_2$]. These were obtained by well established procedures from Na[C_5H_5] and MCl_3 in tetrahydrofuran (thf):[38] [Tm(η-C_5H_5)$_2$Cl] is new, green-yellow (*ca.* 50% yield), sublimed at 200 °C (10^{-4} mmHg); [Y(η-C_5H_5)$_2$Cl] has been mentioned briefly,[39] but no details given: colourless crystals (70% yield), sublimed at 250 °C (10^{-3} mmHg) (Found: Cl, 13.8; Y, 35.0. $C_{10}H_{10}$ClY requires Cl, 13.9; Y, 34.9%).

Di-μ-methyl-bis(η-cyclopentadienyl)metal(III)*dimethylaluminium*(III), [(η-C_5H_5)$_2$M(μ-Me)$_2$AlMe_2] (M = Sc, Y, Gd, Dy, Ho, Er, Tm, *or* Yb). The method of preparation of each of these complexes was essentially the same, and is illustrated below for the case of scandium and gadolinium.

(*a*) To a slurry of chlorodi(η-cyclopentadienyl)scandium

(0.954 g, 4.5 mmol) in toluene (40 cm^3) at 0 °C was added solid lithium tetramethylaluminate(III) (0.6 g, 6.38 mmol) in portions. The reaction mixture was allowed to warm up to room temperature and was then stirred for 24 h by which time the solution was colourless with a white precipitate. The solution was filtered and concentrated to a small volume. n-Hexane was floated on the surface and the mixture was cooled to −30 °C, depositing pale yellow needles which, after washing with pentane and vacuum drying, were identified as the required *product*. Details are in Table 1.

(*b*) To a slurry of chlorodi(η-cyclopentadienyl)gadolinium (0.98 g, 3 mmol) in toluene (40 cm^3) at 0 °C was added solid Li[$AlMe_4$] (0.47 g, 5 mmol) in portions. The mixture was allowed to warm up to room temperature and then stirred for 22 h by which time the solution was colourless with a white precipitate. Volatiles were removed and the residue was extracted with methylene chloride (3 × 10 cm^3). The methylene chloride solution was concentrated and cooled to −30 °C depositing a microcrystalline white solid of the required *product*. Details are in Table 1.

(*c*) *Attempted preparation of the samarium complex.* To a slurry of chlorodi(η-cyclopentadienyl)samarium (0.64 g, 2 mmol) in toluene (30 cm^3) was added Li[$AlMe_4$] (0.6 g, 6 mmol). The mixture was stirred for 2 d after which time the solution was colourless with a yellow precipitate. Volatiles were removed and the residue was extracted with boiling methylene chloride (100 cm^3). Very little complex dissolved and attempted crystallisation led to decomposition to an unidentified dark brown solid. The yellow precipitate could not be freed from LiCl and was not fully characterised.

Di-μ-ethyl-bis(η-cyclopentadienyl)metal(III)diethylaluminium(III), [(η-C_5H_5)$_2$M(μ-Et)$_2$AlEt_2] (M = Sc, Y, *or* Ho). The procedure for M = Sc is typical. To a slurry of [{Sc(η-C_5H_5)$_2$Cl}$_2$] (0.75 g, 3.6 mmol) in toluene (30 cm^3) at −20 °C was added lithium tetraethylaluminate(III) (0.61 g, 4.1 mmol) in portions. The mixture was stirred for 6 h at −20 °C and was then filtered. The solution was kept at *ca.* 0 °C and concentrated to *ca.* 5—10 cm^3. An equal volume of n-hexane was added and the mixture was cooled slowly to −90 °C, depositing pale yellow needles which, after washing with cold (−20 °C) n-pentane and vacuum drying, were identified as the required *product*. Details are in Table 1. The complex with M = Y was also prepared from Mg[$AlEt_4$]$_2$.

Attempted Preparation of [(η-C_5H_5)$_2$Y(μ-Me)$_2$InMe_2].—To a slurry of chlorodi(η-cyclopentadienyl)yttrium (0.29 g, 1.14 mmol) in toluene (20 cm^3) was added lithium tetramethylindate(III) (0.23 g, 1.3 mmol) at room temperature. A white precipitate immediately formed, but the reaction mixture was stirred overnight to ensure completion of the reaction. The solution was filtered, concentrated, and cooled to −30 °C. Colourless crystals were deposited and, after washing with n-pentane and vacuum drying, were identified as di(η-cyclopentadienyl)methylyttrium [^{1}H n.m.r., τ 3.79 (s, η-C_5H_5) and 10.81 (t, YMe_2Y); strong i.r. band at 1 195 cm^{-1}, ν(Y–Me)].

Di-μ-methyl-bis(η-cyclopentadienyl)titanium(III)dimethylaluminium(III).—A slurry of chlorodi(η-cyclopentadienyl)titanium(III) (5.53 g, 25.9 mmol) and Li[$AlMe_4$] (3.28 g, 33 mmol) in toluene (70 cm^3) was stirred at −20 °C for *ca.* 1 h, whereafter the temperature was slowly increased to 0 °C. The solution became green. Filtration at *ca.* 0 °C gave a fine white residue and a clear blue-green filtrate which was evaporated at *ca.* 0 °C to a blue-green solid. Crystallisation at low temperature from n-hexane–toluene gave the *product* as green crystals. Details are in Table 1. These crystals decomposed slowly over a period of 24 h to give an unidentified purple oil. This decomposition was more rapid in solution in toluene, a purple solution being produced within 1—10 h at ⩽0 °C. Addition of [Al_2Me_6] enhanced stability, there being little apparent change at 0 °C on addition of 0.5—5 mol per mol of titanium complex. The product was also prepared from Mg[$AlMe_4$]$_2$.

(Chlorotrimethylaluminato)di(η-cyclopentadienyl)titanium-(III).—A mixture of [{Ti(η-C_5H_5)$_2$Cl}$_2$] (3.58 g, 16.8 mmol) and [Al_2Me_6] (17 mmol) in toluene (28 cm^3) was stirred at *ca.* 0 °C for 2 h. The resulting green solution was evaporated at *ca.* 0 °C to *ca.* 4 cm^3, layered with hexane (15 cm^3), and cooled to −30 °C. The *product* was separated as deep green crystals. Its stability appeared to be similar to that of [(η-C_5H_5)$_2$Ti(μ-Me)$_2$AlMe_2].

Attempted Preparation of the Yttrium Analogue.—A mixture of [{Y(η-C_5H_5)$_2$Cl}$_2$] (3.64 g, 14.4 mmol) and [Al_2Me_6] (20 mmol) in toluene (35 cm^3) was heated at 90—100 °C for 2 h. Evaporation afforded a white solid that was shown (i.r. and n.m.r.) to be unchanged [{Y(η-C_5H_5)$_2$Cl}$_2$].

Reaction of [Ti(η-C_5H_5)$_2$$Cl_2$] *with an Excess of* Li[$AlMe_4$].—A mixture of [Ti(η-C_5H_5)$_2$$Cl_2$] (1.47 g, 5.9 mmol) and Li-[$AlMe_4$] (1.65 g, 17.6 mmol) in toluene (25 cm^3) was stirred at 0 °C for 2 h. The reaction mixture was warmed to ambient temperature and filtered to give a clear orange filtrate. Evaporation to dryness of the filtrate gave the known [Ti(η-C_5H_5)$_2$$Me_2$] as orange crystals (*via* crystallisation of the involatile residue from n-hexane solution at −70 °C) and a clear condensate that contained [Al_2Me_6].

Reaction of [HfBr(η-C_3H_5)$_3$] *with* Mg[$AlMe_4$]$_2$.—The complex [HfBr(η-C_3H_5)$_3$] and Mg[$AlMe_4$]$_2$ (0.5 mol per mol of Hf complex) in toluene solution were stirred for 6 h at −30 °C and then filtered to give a red-brown filtrate containing Hf, Al, Br, and Mg in g-atom ratio of 1.0 : 0.7 : 0.2 : 0.15. Evaporation gave a brown oil (Hf : Al ⩾ 2.2 : 1) for which ^{1}H n.m.r. spectroscopy in [$^2H_8$]toluene showed resonances at τ 4.45 (3 H, quintet, *J* 13 Hz), 6.96 (12 H, d, *J* 13 Hz), and 10.66 (3 H, s). Pure material was not isolated.

X-*Ray Analysis of* [(η-C_5H_5)$_2$Yb(μ-Me)$_2$AlMe_2].—Single crystals of the air-sensitive complex were sealed in thin-walled capillaries under a nitrogen atmosphere prior to *X*-ray examination. Final lattice parameters were determined from a least-squares refinement of the angular settings of 15 reflections (2θ > 38°) accurately centred on an Enraf–Nonius CAD-4 diffractometer.

Crystal Data.—$C_{14}H_{22}AlYb$, M = 390.4, Orthorhombic, a = 17.866(5), b = 7.973(3), c = 10.871(3) Å, U = 1 548.6 Å^3, Z = 4, D_c = 1.67 g cm^{-3}, $F(000)$ = 756, Mo-K_α radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 63.8 cm^{-1}, space group $Pna2_1$ from systematic absences and refinement.

Data were taken on the diffractometer with graphite-crystal monochromated molybdenum radiation. The diffracted intensities were collected by the ω—2θ scan technique with a take-off angle of 3.0°. The scan rate was variable and was determined by a fast (20° min^{-1}) pre-scan. Calculated speeds based on the net intensity gathered in the pre-scan ranged from 7 to 0.2° min^{-1}. Moving-crystal moving-counter backgrounds were collected for 25% of the total scan width at each end of the scan range. In each intensity the scan width was determined by the equation: scan range = $A + B\tan\theta$, where A = 1.0° and B = 0.20°.

Aperture settings were determined in a like manner with $A = 4.0$ mm and $B = 0.87$ mm. Other diffractometer parameters and the method of estimation of the standard deviations have been described previously.[40] As a check on the stability of the instrument and crystal three reflections were measured after every 40 reflections; the standards fluctuated within a range of $\pm 3\%$.

One independent octant of data was measured out to $2\theta = 50°$. A slow scan was performed on a total of 1 288 unique reflections. Since these data were scanned at a speed which would yield a net count of 4 000, the calculated standard deviations were all very nearly equal. No reflection was subjected to a slow scan unless a net count of 25 was obtained in the pre-scan. Based on these considerations, the data set of 1 288 reflections (used in the subsequent structure determination and refinement) was considered observed, and consisted in the main of those reflections for which $I > 3\sigma(I)$. The intensities were corrected for Lorentz, polarisation, and absorption effects.

Full-matrix least-squares refinement was carried out using the Busing and Levy ORFLS program.[41] The function $w(|F_o| - |F_c|)^2$ was minimised. No corrections were made for extinction. Atomic scattering factors for Yb, Al, and C were taken from Cromer and Waber,[42] and the scattering for Yb was corrected for the real and imaginary components of anomalous dispersion using the values of Cromer and Liberman.[43] Scattering factors for hydrogen were from ref. 44.

Structure Determination and Refinement.—The existence of four molecules per unit cell implied no crystallographic symmetry restriction in the space group $Pna2_1$, but in $Pnma$ the molecule would have to contain either a centre of inversion or a mirror plane. Since the complex could reasonably possess the latter, $Pnma$ was first tried. Inspection of a Patterson map revealed the position of the ytterbium atom, but the calculation of a Fourier map phased on the metal atom did not lead to a meaningful interpretation. In the space group $Pna2_1$, however, the Fourier map interpretation led directly to the location of all the non-hydrogen atoms. Anisotropic least-squares refinement produced a final value of $R = (|F_o| - |F_c|)/|F_o| = 0.078$. This refinement was the basis of the previous report of the structure.[3b]

In order to obtain more reliable bonding parameters, a second crystal was used to collect the data set described in the previous section. With isotropic thermal parameters a value of $R = 0.13$ was obtained for the ytterbium and aluminium atoms alone. A Fourier map using these positions afforded the location of the non-hydrogen atoms (in positions near those found during the previous refinement). With anisotropic thermal factors for the ytterbium, aluminium, and four methyl carbon atoms, isotropic temperature factors for the ring carbon atoms, and ring hydrogen atoms included in calculated positions, we obtained R 0.036 and $R' = [w(|F_o| - |F_c|)^2/w(F_o)^2]^{\frac{1}{2}} = 0.042$. Anisotropic refinement of all the non-hydrogen atoms led to final values of R 0.026 and R' 0.033. Unfortunately, the anisotropic refinement led to much poorer values for the bond distances and angles associated with the C_5H_5 rings. It was therefore decided that the final cycle with isotropic ring carbon atoms probably contains more variable information and this is the basis for the subsequent bond distances and angles. Because of the extremely high thermal motion of the carbon atoms, the methyl hydrogen atoms could not be located. The largest parameter shifts in the final cycle of refinement were less than 0.10 of their estimated standard deviations. A final difference-Fourier showed no unaccounted electron density. The standard deviation of an observation of unit weight was 1.30. No systematic variation of $w(|F_o| - |F_c|)$ with $|F_o|$ or $(\sin\theta)/\lambda$ was noted. The final values of the positional parameters are in Table 6.

TABLE 6

Final fractional co-ordinates

Atom	x/a	y/b	z/c
Yb	0.594 66(3)	0.295 36(7)	−0.750 00
Al	0.744 9(3)	0.443 4(8)	−0.686 0(8)
C(1)	0.597 3(15)	−0.030 2(30)	−0.731 6(50)
C(2)	0.523 4(14)	0.015 2(31)	−0.701 0(25)
C(3)	0.530 9(15)	0.104 9(35)	−0.583 5(28)
C(4)	0.609 8(17)	0.103 6(39)	−0.556 0(32)
C(5)	0.646 3(16)	0.017 2(36)	−0.642 2(30)
C(6)	0.560 4(15)	0.401 5(36)	−0.996 1(27)
C(7)	0.497 2(14)	0.305 3(35)	−0.924 7(26)
C(8)	0.465 9(14)	0.391 1(34)	−0.835 6(26)
C(9)	0.508 9(14)	0.540 6(30)	−0.818 3(24)
C(10)	0.564 3(13)	0.539 2(31)	−0.899 6(24)
C(11)	0.727 0(14)	0.297 2(30)	−0.851 4(21)
C(12)	0.645 4(10)	0.512 0(25)	−0.597 3(19)
C(13)	0.790 7(10)	0.658 8(25)	−0.746 8(57)
C(14)	0.805 4(12)	0.310 4(35)	−0.567 1(25)
H(1)	0.605	−0.083	−0.812 *
H(2)	0.472	0.012	−0.733
H(3)	0.496	0.169	−0.531
H(4)	0.632	0.132	−0.485
H(5)	0.701	0.017	−0.644
H(6)	0.596	0.380	−1.033
H(7)	0.487	0.196	−0.963
H(8)	0.424	0.353	−0.789
H(9)	0.499	0.626	−0.758
H(10)	0.602	0.630	−0.904

* Hydrogen atoms in calculated positions. Isotropic thermal parameters of 6.0 Å^2 were assumed.

Observed and calculated structure-factor amplitudes and thermal parameters are in Supplementary Publication No. SUP 22336 (8 pp.).*

We thank the S.R.C. and I.C.I. Ltd. for the award of a C.A.S.E. studentship (to J. H.), and the National Science Foundation for partial support (to J. L. A.).

[8/165 *Received, 31st January, 1978*]

* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

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