Alkyl-bridged Complexes of the *d*- and *f*-Block Elements. Part 2.[1] Bis[bis(η-cyclopentadienyl)methylmetal(III)] Complexes, and the Crystal and Molecular Structure of the Yttrium and Ytterbium Species

By **John Holton** and **Michael F. Lappert,*** School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ
Denis G. H. Ballard and **Ronald Pearce,** Imperial Chemical Industries Limited, Corporate Laboratory, P.O. Box 11, The Heath, Runcorn, Cheshire WA7 4QE
Jerry L. Atwood and **William E. Hunter,** Department of Chemistry, The University of Alabama, Alabama 35486, U.S.A.

The reaction of $[(\eta\text{-}C_5H_5)_2MMe_2AlMe_2]$ (M = Y, Dy, Ho, Er, Tm, or Yb) and pyridine in equimolar amounts gives a series of complexes $[\{M(\eta\text{-}C_5H_5)_2Me\}_2]$ assigned a dimeric structure on the basis of ^1H and ^{13}C n.m.r. (M = Y) and i.r. data, and by crystal and molecular structural determinations of $[\{M(\eta\text{-}C_5H_5)_2Me\}_2]$ (M = Y or Yb). A similar reaction of $[(\eta\text{-}C_5H_5)_2ScMe_2AlMe_2]$ with a Lewis base L gives $[Sc(\eta\text{-}C_5H_5)_2Me(L)]$ (L = pyridine or tetrahydrofuran). Other reactions described are of $[\{Y(\eta\text{-}C_5H_5)_2Me\}_2]$ with Lewis bases (an amine, phosphine, or phosphine oxide) or with a Lewis acid $[Al_2Me_nCl_{6-n}]$ (n = 2, 4, or 6). A single-crystal *X*-ray analysis of the isostructural $[\{M(\eta\text{-}C_5H_5)_2Me\}_2]$ has been carried out to *R* 0.048 (Y) or 0.066 (Yb) and *R'* 0.055 (Y) or 0.061 (Yb); the complexes have an approximately tetrahedral metal environment (space group $P2_1/n$) with the YMe_2Y unit in the yttrium complex remarkably similar to $AlMe_2Al$ in $[Al_2Me_6]$. Important average bond lengths (Å) and angles for the yttrium complex (Yb in parentheses) are: Y–C (cyclopentadienyl) 2.655(18) [2.613(13)] and Y–Me 2.545(11) [2.511(35)]; Y–C–Y 87.7(3) [86.6(3)] and Me–Y–Me 92.3(3) [93.4(4)].

In our continuing search for that presently elusive species, the electron-deficient bridging alkyl of the *d*- or *f*-block elements, we now turn from the heterometallic complexes, exemplified in Part 1[1] by the bis(η-cyclopentadienyl)metal(III) tetra-alkylaluminates, to the homometallic complexes $[\{M(\eta\text{-}C_5H_5)_2Me\}_2]$. A preliminary communication has appeared.[2]

In considering strategy towards the planned synthesis of these novel complexes we noted several pertinent facts. First, using aluminium compounds as a model, it seemed striking that Al forms not only many di-μ-Me-bridged complexes but also numerous di-μ-Cl analogues. Secondly, dimethyl-bridged heterometallic complexes appeared to be more obviously realisable than corresponding homometallic transition-metal complexes; we noted that the known $Mg[AlMe_4]_2$ has di-μ-Me-heterometallic bridges. Thirdly, by choosing as reagents a di-μ-Cl-bridged binuclear transition-metal complex and $Li[AlMe_4]$, a clear synthetic route was at hand; this concept was exemplified in Part 1,[1] $[\{M(\eta\text{-}C_5H_5)_2Cl\}_2] \longrightarrow [(\eta\text{-}C_5H_5)_2M(\mu\text{-}Me)_2AlMe_2]$. Fourthly, just as di-$\mu$-Cl-bridged bimetallic complexes are cleaved by bases, so there was the expectation (with precedent in organoaluminium chemistry) that MMe_2Al complexes would behave similarly; this is an important theme of the present paper: $[(\eta\text{-}C_5H_5)_2M(\mu\text{-}Me)_2AlMe_2] \longrightarrow [\{M(\eta\text{-}C_5H_5)_2Me\}_2]$. The results are also of significance as a contribution to the organometallic chemistry of the Group 3A elements and the lanthanoids, which is as yet sparsely documented.[3] This is particularly true for metal–carbon σ-bonded complexes. Stable or well characterised materials are only obtained by a careful choice of ligand.

The simple methyl complexes, *e.g.* $[YMe_3]$, appear to be polymeric materials, soluble only in donor solvents, and have not been isolated in a pure state.[4] With the more bulky neopentyl or trimethylsilyl ligands discrete stable complexes have, however, been obtained. These include the homoleptic $[Y\{CH(SiMe_3)_2\}_3]$[5] and $[Sc\{CH_2SiMe_2(C_6H_4OMe\text{-}o)\}_3]$,[6] and the heteroleptic $[MR_3(thf)_2]$ [thf = tetrahydrofuran; M = Sc or Y; $R = CH_2SiMe_3$,[6] $CH(SiMe_3)_2$,[5] or CH_2Bu^t;[6] and M = Tb, Er, or Yb, $R = CH_2SiMe_3$[7]]. Additionally, the six-co-ordinate metal complexes $[MR_3]$ (with the chelating ligand $R = (CH_2)_2PMe_2$ and M = La, Pr, Nd, Sm, Gd, Ho, Er, or Lu) have been described.[8] Lanthanoid Grignard analogues were believed to be formed by treating the metal (Eu, Yb, or, less convincingly, La, Ce, or Sm) with an alkyl or aryl iodide.[9] The simple phenylmetal(III) complexes $[MPh_3]$ (M = Sc or Y),[4] like the methyls, are somewhat ill defined. However, the corresponding '-ate' complexes $[MR_4]^-$ (M = La or Pr, R = Ph;[4] M = Yb or Lu, $R = C_6H_3Me_2\text{-}2,6$[10]) have been prepared and are more fully characterised, including a single-crystal *X*-ray diffraction analysis of $[Li(thf)_4][Lu(C_6H_3Me_2\text{-}2,6)_4]$.[10] A metal(II) complex, $[Yb(C_6F_5)_2(thf)_4]$, has been prepared *via* the mild arylmercury(II) reagent.[11] Two alkynyl complexes, $[Sc(C{\equiv}CPh)_3]$[4] and $[Eu(C{\equiv}CMe)_2]$,[12] are known.

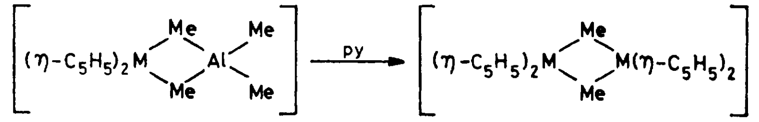
A more extensive range of alkyl or aryl complexes exists with the 'stabilising' cyclopentadienyl ligand. These include the metal(III) complexes described in our preliminary communication,[2] $[\{M(\eta\text{-}C_5H_5)_2R\}_n]$ [M = Y, Gd, Dy, Ho, Er, or Yb, R = Me, n = 2;[2] M = Gd, Er, or Yb, R = Ph;[13] M = Sc, Gd, Ho, Er, or Yb, $R = C{\equiv}CPh$;[13,14] M = Sc, $R = (CH_2)_2PPh_2$[15]], $[Ho(\eta\text{-}C_5H_5)(C{\equiv}CPh)_2]$,[13] $[(\eta\text{-}C_5H_5)_2M(\mu\text{-}R)_2AlR_2]$ (M = Sc, Y, Gd, Dy, Ho, Er, Tm, or Yb, R = Me; M = Sc, Y, or Ho, R = Et),[1] and the cerium(IV) complexes $[Ce(\eta\text{-}C_5H_5)_3R]$ and $[Ce(indenyl)_2R_2]$ (R = Me, Et, Ph, or CH_2Ph).[16]

In Part 1[1] results were described relating to the preparation of the dimethyl-bridged metal(III) tetra-alkylaluminates $[(\eta\text{-}C_5H_5)_2M(\mu\text{-}R)_2AlR_2]$. We now give details (*cf.* ref. 2) of the preparation and characterisation of the corresponding homometallic Group 3A metal complexes $[\{M(\eta\text{-}C_5H_5)_2Me\}_2]$ (M = Y, Dy, Ho, Er, Tm, or Yb); the crystal and molecular structures of the Y and Yb complexes definitively establish the double methyl bridge. During the course of this work three of the complexes [{M(η-C_5H_5)$_2$Me}$_n$] (M = Gd, Er, or Yb) were reported independently;[13] they were obtained by an alternative procedure [from the metal(III) chloride and LiMe], and their structures were discussed in terms of a monomeric pseudo-seven-co-ordinate metal environment.[17] Using the same procedure we have now prepared the ytterbium complex and find it to be esentially identical to that obtained from the tetramethylaluminate (see below).

It is interesting that while [(η-C_5H_5)$_2$TiMe$_2$AlMe$_2$] is significantly less stable than the Group 3A metal analogues, attempts to prepare [{Ti(η-C_5H_5)$_2$R}$_n$] (R = Me or Et) have failed;[18] in contrast, [Ti(η-C_5H_5)$_2$(CH$_2$Bu^t)] is stable and monomeric, perhaps because of the presence of the bulkier alkyl ligand.

RESULTS AND DISCUSSION

Preparation.—The complexes [{M(η-C_5H_5)$_2$Me}$_2$] (M = Y, Dy, Ho, Er, Tm, or Yb) were prepared according to equation (1), using an equimolar quantity of the base pyridine (py). In principle, the substrate [(η-C_5H_5)$_2$M(μ-Me)$_2$AlMe$_2$] has two potential acceptor sites, M or Al, with equation (1) showing the latter as the more electrophilic.



+ AlMe$_3$(py) (1)

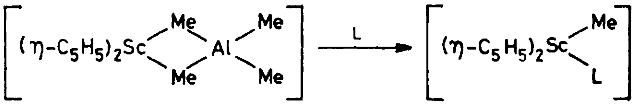
TABLE 1

Data on the methyl-lanthanoid complexes

Complex	Colour	Yield (%)	M.p. (θ_c/°C)	μ(calc.)/ B.M.	Analysis [a] (%)			
					C	H	M	Al
[{Y(η-C_5H_5)$_2$Me}$_2$]	Colourless	87	>158 (decomp.)		56.4 (56.4)	5.7 (5.7)	37.7 (38.0)	0.0
[{Dy(η-C_5H_5)$_2$Me}$_2$]	Pale yellow	78	>165 (decomp.)	9.9 (10.6)	43.1 (43.0)	4.25 (4.3)	54.5 (52.8)	
[{Ho(η-C_5H_5)$_2$Me}$_2$]	Straw	84	>160 (decomp.)	10.0 (10.6)	42.8 (42.6)	4.2 (4.2)		
[{Er(η-C_5H_5)$_2$Me}$_2$]	Pink	82	>159 (decomp.)	9.5 (9.6)	42.2 (42.3)	3.9 (4.2)	51.9 (53.5)	0.0
[{Tm(η-C_5H_5)$_2$Me}$_2$]	Pale green	82	>160 (decomp.)	7.5 (7.6)	42.4 (42.1)	4.2 (4.2)		
[{Yb(η-C_5H_5)$_2$Me}$_2$]	Orange-red	81	>165 (decomp.)	4.0 (4.5)	41.8 (41.5)	4.4 (4.1)	53.7 (54.4)	0.0
[Sc(η-C_5H_5)$_2$Me(py)] [b]	Cream	71			69.8 (71.4)	6.5 (6.7)		
[Sc(η-C_5H_5)$_2$Me(thf)]	Cream	85			68.9 (68.7)	8.1 (8.1)		

[a] Calculated values are given in parentheses. [b] N, 4.5 (5.2%).

The di(η-cyclopentadienyl)methylmetal(III) complexes were isolated in high yield (*ca*. 80%) as air-sensitive crystalline solids (Table 1). They are soluble in dichloromethane, hot toluene, or benzene, partially soluble in cold toluene or benzene, but insoluble in saturated hydrocarbon solvents. The complexes are thermally stable for short periods up to *ca*. 150 °C, whereafter they slowly decompose without melting. The mode of decomposition is under investigation.



+ ½[Al$_2$Me$_6$] (2)

Reaction of [(η-C_5H_5)$_2$Sc(μ-Me)$_2$AlMe$_2$] with the Lewis base (L) [py or tetrahydrofuran (thf)] took a different course [equation (2)], whence Sc rather than Al is the more electrophilic centre. The pale yellow adducts [Sc(η-C_5H_5)$_2$Me(L)] were obtained in high yield (*ca*. 70%) and were purified by crystallisation from toluene. For the pyridine product (L = py) the base L was readily removed *in vacuo*. After prolonged evacuation a material was obtained that did not correspond to the expected [{Sc(η-C_5H_5)$_2$Me}$_2$] and has not yet been identified. The thf adduct was more stable *in vacuo*, but attempted sublimation (160 °C, 10^{-4} mmHg) * resulted in decomposition.

From equations (1) and (2) it appears that in a related series of complexes Lewis acidity increases in the order: lanthanoid ≈ yttrium < aluminium < scandium.

Spectroscopic Characterisation.—The ^1H n.m.r. spectrum of the diamagnetic yttrium complex [{Y(η-C_5H_5)$_2$Me}$_2$] was characteristic of a doubly bridged methyl structure (Table 2). The spectrum showed a triplet (τ 10.81) for the bridge-methyl protons and was invariant between −40 and 40 °C. The methyl protons are found as a triplet due to coupling to two equivalent

---

* Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa; 1 B.M. ≈ 9.27×10^{-24} A m^2.

yttrium atoms, $^{1}J(^{89}\text{Y}-\text{C}^{1}\text{H}_3)$ 3.6 Hz (^{89}Y, spin = $\frac{1}{2}$, 100%). It is interesting to compare the ^{1}H n.m.r. spectrum of $[\{\text{Y}(\eta\text{-C}_5\text{H}_5)_2\text{Me}\}_2]$ with those of $[\text{Al}_2\text{Me}_6]$ [19] and $[\{\text{Ni}(\eta\text{-allyl})\text{Me}\}_2]$,[20] where the bridge-methyl protons are found at τ 10.67 and 12.1, respectively. The unusually strong shielding in the nickel case was ascribed to interaction with the non-bonding *d* electrons. This now seems likely, because in $[\{\text{Y}(\eta\text{-C}_5\text{H}_5)_2\text{Me}\}_2]$ and $[\text{Al}_2\text{Me}_6]$, where no *d* electrons are available for this type of interaction, the bridging alkyl protons occur at similar lower-field values.

TABLE 2

N.m.r. data [a]

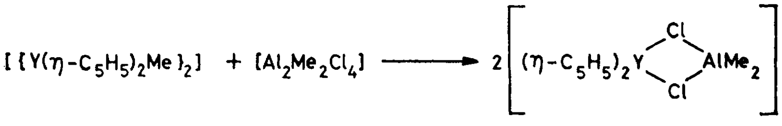
Complex	Technique	η-C$_5$H$_5$	Me	L
$[\{\text{Y}(\eta\text{-C}_5\text{H}_5)_2\text{Me}\}_2]$	^{1}H (τ)	3.79 (s)	10.81 (t) [b]	
	^{13}C (p.p.m.)	111.3	23.0 [c]	
$[\text{Sc}(\eta\text{-C}_5\text{H}_5)_2\text{Me(py)}]$	^{1}H (τ)	4.15 (s)	10.6 (s)	1.8, 2.65, 2.75, 2.95
$[\text{Sc}(\eta\text{-C}_5\text{H}_5)_2\text{Me(thf)}]$	^{1}H (τ)	3.86 (s)	9.97 (s)	6.75 (m), 8.8 (m)

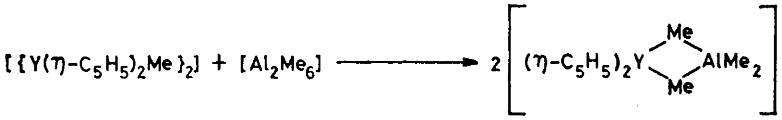
[a] At room temperature in dichloromethane. [b] $^{2}J(^{89}\text{Y}-\text{C}^{1}\text{H}_3)$ 3.6 Hz. [c] $^{1}J(^{89}\text{Y}-^{13}\text{C})$ 25.0 Hz.

The scandium complexes $[\text{Sc}(\eta\text{-C}_5\text{H}_5)_2(\text{Me})(\text{L})]$ (L = py or thf) showed broad singlets at τ 10.6 and 9.97, respectively, attributed to the methyl protons, and peaks corresponding to the ligands in the expected lower-field region (Table 2).

The $^{13}\text{C}-\{^{1}\text{H}\}$ n.m.r. spectrum of $[\{\text{Y}(\eta\text{-C}_5\text{H}_5)_2\text{Me}\}_2]$ is consistent with a dimeric structure. The bridging methyl-carbon atoms occur at 23.0 p.p.m. as a triplet due to coupling to two equivalent yttrium atoms with $^{1}J(^{89}\text{Y}-^{13}\text{C})$ 25.0 Hz (Table 2).

The i.r. spectra of the methyl-bridged complexes were essentially identical. The cyclopentadienyl frequencies were assigned as for $[(\eta\text{-C}_5\text{H}_5)_2\text{MR}_2\text{AlR}_2]$ [1] at 3 100m, 1 447m, 1 020s, and 790 s cm^{-1}. The methyl deformations were found at 1 368m and 1 195s cm^{-1}, assigned to the asymmetric CH$_3$ bend and the symmetric CH$_3$ bend, respectively. The strong band at *ca.* 1 195 cm^{-1} is characteristic of these complexes and of a methyl attached to a metal.[21] For instance, in the polymeric complexes $[(\text{MgMe}_2)_n]$ or $[(\text{BeMe}_2)_n]$ similar symmetric deformations occur at 1 193 and 1 209 cm^{-1}, or 1 250 and 1 260 cm^{-1}, respectively;[22] this may be compared with mononuclear complexes, *e.g.* SnMe$_4$ has absorptions at 1 198 and 1 205 cm^{-1},[23] and *trans*-$[\text{PtMe(I)(PR}_3)_2]$ has a band at 1 217 cm^{-1}.[24]


(3)


(4)

The i.r. spectra of $[\text{Sc}(\eta\text{-C}_5\text{H}_5)_2\text{Me(L)}]$ (L = py or thf) showed significant differences from the methyl-bridged species. The characteristic strong band at *ca.* 1 195 cm^{-1} was missing, the methyl deformations occurring as weak bands at 1 365, 1 350 (asymmetric CH$_3$ bend), 1 190, and 1 182 cm^{-1} (symmetric CH$_3$ bend). Bands were also observed due to the ligand: for L = py at 1 609, 1 590, 1 492, 1 449, 1 224, 1 160, 1 076, 1 048, 767, 710, and 640 cm^{-1}; and for L = thf at 925m, 869s, and 850s cm^{-1}. These compare reasonably with other py [25] or thf [26] metal complexes.

The mass spectra of the ytterbium and erbium complexes did not show a parent molecular ion, the ion at highest *m/e* being $[P - \text{Me}]^+$. Peaks were observed due to cyclopentadienyl rearrangement, *e.g.* $[\text{M}(\eta\text{-C}_5\text{H}_5)_3]^+$, with the most intense metal-containing peak being $[\text{M}(\eta\text{-C}_5\text{H}_5)_2]^+$.

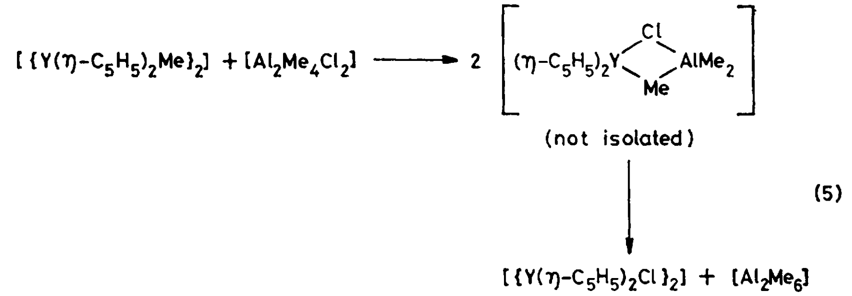
The electronic spectra in the range 350—900 nm and the magnetic moments of the highly coloured complexes $[\{\text{M}(\eta\text{-C}_5\text{H}_5)_2\text{Me}\}_2]$ (M = Dy, Ho, Er, or Tm) were recorded as dichloromethane solutions and were diagnostic of the respective lanthanoid(III) ion.[27,28]

Reactions of $[\{\text{Y}(\eta\text{-C}_5\text{H}_5)_2\text{Me}\}_2]$.—(*a*) *With Lewis bases.* Although the scandium adducts with L = thf or py, $[\text{Sc}(\eta\text{-C}_5\text{H}_5)_2\text{Me(L)}]$, are stable and isolable, the corresponding yttrium complexes appear to be less robust and have not been fully characterised. By observing the bridge protons in the ^{1}H n.m.r. spectrum, the reaction with base (and, indeed, other reactions) can be monitored; the triplet (τ 10.81) collapsed to a doublet (usually broad and unresolved) at lower field upon bridge-breaking. The complex $[\{\text{Y}(\eta\text{-C}_5\text{H}_5)_2\text{Me}\}_2]$ appears to react readily with hard donors such as amines, thf, or phosphine oxides (*e.g.* PPh$_3$O), but less readily with soft donors such as phosphines, *e.g.* PPh$_3$ or PEt$_3$. Neither the pyridine nor triphenylphosphine oxide adducts were isolated. Hydrogen-1 n.m.r. experiments showed loss of the triplet due to the bridging methyl protons and the pyridine complex showed a broad lower-field resonance (τ 9.67) attributed to the non-bridging methyl group.

The low thermal stability of the yttrium pyridine adduct, compared with the scandium analogue, again points to Y$^{\text{III}}$ being a weaker Lewis acid than Sc$^{\text{III}}$ [*cf.* equations (1) and (2)].

(*b*) *With alkyl- or alkylchloro-aluminium compounds.* The complex $[\{\text{Y}(\eta\text{-C}_5\text{H}_5)_2\text{Me}\}_2]$ reacted readily with an alkyl- or alkyl-chloroaluminium compound to give di-μ-alkyl- or di-μ-chloro-bridged species [equations (3) and (4)]; the mixed-bridge complex was considerably less stable. There are numerous well established examples of complexes with di-μ-chloro-bridges, and di-μ-alkyl analogues, while less common, are well documented.[1,29] Evidence for the existence of μ-alkyl-μ-chloro-bridges is sparse, but they are often postulated as a structural feature of reactive intermediates, *e.g.* in exchange reactions.[29] Only [Ti(η-C_5H_5)$_2$($AlMe_3Cl$)] has been isolated and characterised by analysis and e.s.r. spectroscopy, although the nature of the bridge was not determined.[15] Tetranuclear [Ru_2M_2] complexes (M = Zn or Mg) were believed to contain (μ-Cl,Me) bridges.[30]

In the light of the prior art, the instability of [Y(η-C_5H_5)$_2$($AlMe_3Cl$)], equation (5), is not unexpected. Failure to isolate [Y(η-C_5H_5)$_2$($AlMe_3Cl$)] may be a consequence of the insolubility of [{Y(η-C_5H_5)$_2$Cl}$_2$] in toluene as solvent. This would favour its disproportionation to the symmetrical dimers. Separate experiments demonstrated that no complex could be isolated from the reverse reaction, between [{Y(η-C_5H_5)$_2$Cl}$_2$] and excess of [Al_2Me_6]. Experiments are in hand to increase the solubility of a related yttrium(III) chloride dimer by using various substituted cyclopentadienyl ligands; this may lead to more stable mixed-bridge systems.



(5)

The crystal structure of [{Yb(η-C_5H_5)$_2$Me}$_2$] unambiguously demonstrates that the complex is dimeric in the solid state, rather than seven-co-ordinate and hence monomeric, as suggested by Tsutsui and Ely.[17] Since

$$[\{Yb(\eta\text{-}C_5H_5)_2Cl\}_2] + 2LiMe \longrightarrow \tfrac{1}{n}[\{Yb(\eta\text{-}C_5H_5)_2Me\}_n] + 2LiCl \quad (6)$$

the two samples were prepared by different methods, equation (1) or (6),[13] it was important to show that the samples were identical. Accordingly, we repeated the earlier synthesis, based on equation (6), and obtained orange-red crystals from benzene and showed that they were identical (i.r. and analysis) with those obtained from reaction according to equation (1).

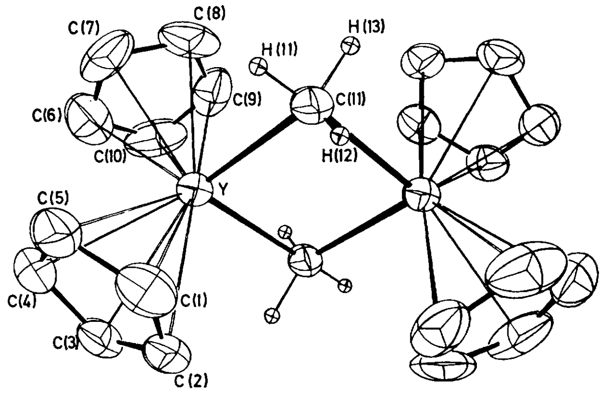


FIGURE 1 Diagram of [{Y(η-C_5H_5)$_2$Me}$_2$] showing the numbering system used, with the non-hydrogen atoms represented by their 50% probability ellipsoids for thermal motion

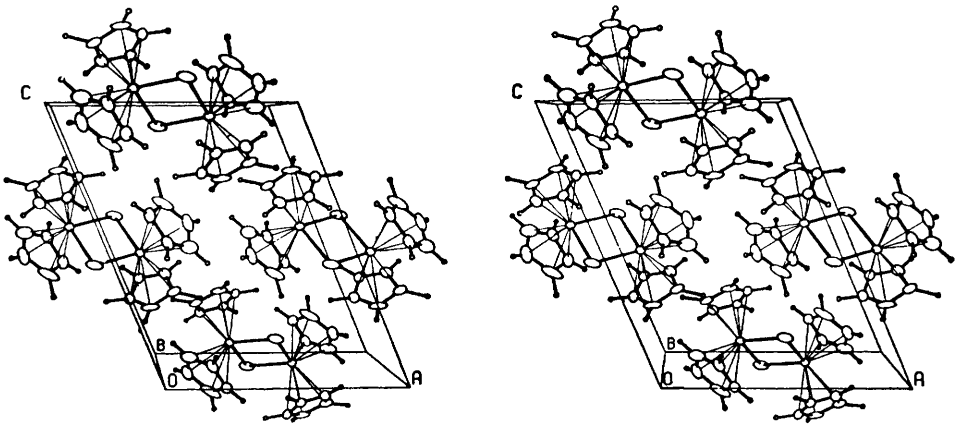
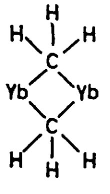
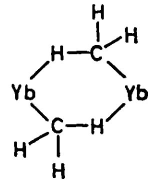


FIGURE 2 Stereoscopic view of the unit-cell packing in [{Yb(η-C_5H_5)$_2$Me}$_2$]

The Molecular Structure of [{Y(η-C_5H_5)$_2$Me}$_2$] *and* [{Yb(η-C_5H_5)$_2$Me}$_2$].—The molecular structure and atom-numbering scheme for the yttrium complex is shown in Figure 1, and a stereoscopic view of the unit-cell packing of the ytterbium analogue is presented in Figure 2. From the crystal data it is evident that the two complexes are isostructural. In the preliminary communication only the structure of the ytterbium analogue was reported.[2] Although it was inferred that the two ytterbium atoms were linked together *via* an electron-deficient methyl bridge (1), situation (2) could not be



(1)



(2)

definitely ruled out. Because of high thermal motion, the presence of the 70-electron ytterbium atom, or an absorption problem, it was not possible to locate the hydrogen atoms of the methyl group. However, this ambiguity has now been resolved with the structure of the yttrium complex. (The metal has only 39 electrons, and the linear absorption coefficient is only 60% of that of [{Yb(η-C_5H_5)$_2$Me}$_2$].) Structure (1) is the correct choice.

The methyl hydrogen atoms were clearly visible on the difference-Fourier map and, although their positional parameters were not refined, substantiation for the placement is given in Table 3. The low-temperature *X*-ray structure of [$(AlMe_3)_2$][31] was carried out to resolve just such a bonding dilemma, and there also (1) was shown to be correct. The hydrogen atoms were not only located, but also refined to give the values listed in Table 3. Of particular importance is the fact that the shortest Al · · · H approach is 2.17(3) Å, and the Al–C$_b$ bond distances are 2.125(2) and 2.123(2) Å. For [{Y(η-C_5H_5)$_2$Me}$_2$] the shortest Y · · · H separation is 2.54 Å, while the Y–C$_b$ bond lengths are 2.553(10) and 2.537(9) Å. The C–H bond lengths and H–C–H angles are also reasonable for a methyl group.

TABLE 3

Comparison of the bonding parameters of the bridging methyl groups in [{Y(η-C_5H_5)$_2$Me}$_2$] and [$(AlMe_3)_2$][31]

Bond lengths (Å)	M = Al	M = Y
C(11)–H(11)	0.88(3)	0.93
C(11)–H(12)	0.94(4)	0.86
C(11)–H(13)	0.96(4)	1.15
M–C(11)	2.125(2)	2.553(10)
M–C(11)	2.123(2)	2.537(9)
M · · · H(11)	2.17(3)	2.63
M · · · H(12)		3.04
M · · · H(13)		3.29
M · · · H(11′)		3.45
M · · · H(12′)		2.54
M · · · H(13′)		2.63
C(11) · · · C(11′)	3.355(4)	3.67(2)
Angles (°)		
H(11)–C(11)–H(12)	102(3)	111
H(11)–C(11)–H(13)	100(3)	95
H(12)–C(11)–H(13)	100(3)	118

The average Y–C$_b$ bond length [2.54(1) Å, Table 4] is shorter than the 2.58(3) Å found in [(η-C_5H_5)$_2$YMe$_2$AlMe$_2$],[32] and the same holds for the Yb–C$_b$ distance [2.51(4) Å] compared to 2.58(1) Å in [(η-C_5H_5)$_2$YbMe$_2$AlMe$_2$].[1] However, the differences are of only marginal mathematical significance because of the large associated standard deviations. Comparing the two complexes [{M(η-C_5H_5)$_2$Me}$_2$], the Y–C lengths are longer than the Yb–C distance by 0.03 Å for the bridge situation, and 0.04 Å for the cyclopentadienyl groups. This is in reasonable agreement with the commonly reported difference in the M^{3+} radii, 0.02[33] to 0.06 Å.[34]

TABLE 4

Comparison of structural parameters for the yttrium and ytterbium complexes [{M(η-C_5H_5)$_2$Me}$_2$]

Bond lengths (Å)	M = Yb	M = Y
M–C(11)	2.536(17)	2.553(10)
M–C(11′)	2.486(17)	2.537(9)
M–C (electron deficient) av.	2.511(35)	2.545(11)
M–C(1)	2.628(16)	2.661(8)
M–C(2)	2.622(16)	2.683(9)
M–C(3)	2.622(18)	2.677(10)
M–C(4)	2.584(17)	2.640(10)
M–C(5)	2.604(18)	2.642(9)
M–C(6)	2.621(19)	2.660(12)
M–C(7)	2.622(18)	2.669(10)
M–C(8)	2.621(19)	2.653(9)
M–C(9)	2.622(20)	2.621(10)
M–C(10)	2.621(22)	2.641(11)
M–C (cyclopentadienyl), av.	2.613(13)	2.655(18)
C(1)–C(2)	1.34(3)	1.40(1)
C(2)–C(3)	1.38(3)	1.40(1)
C(3)–C(4)	1.36(3)	1.43(1)
C(4)–C(5)	1.39(3)	1.38(1)
C(5)–C(1)	1.40(3)	1.40(1)
C(6)–C(7)	1.36(3)	1.37(2)
C(7)–C(8)	1.36(3)	1.36(2)
C(8)–C(9)	1.40(3)	1.36(2)
C(9)–C(10)	1.35(3)	1.38(2)
C(10)–C(6)	1.39(3)	1.40(2)
Angles (°)		
M–C(11)–M′	86.6(5)	87.7(3)
C(11)–M–C(11′)	93.4(5)	92.3(3)
Cent 1–M–Cent 2	128.2	128.9
Cent 1–M–C(11)	105.9	106.1
Cent 1–M–C(11′)	110.0	110.2
Cent 2–M–C(11)	106.2	105.3
Cent 2–M–C(11′)	107.4	107.8
C(5)–C(1)–C(2)	108(1)	108(1)
C(1)–C(2)–C(3)	110(1)	109(1)
C(2)–C(3)–C(4)	106(1)	107(1)
C(3)–C(4)–C(5)	110(1)	107(1)
C(4)–C(5)–C(1)	106(1)	109(1)
C(10)–C(6)–C(7)	109(1)	106(1)
C(6)–C(7)–C(8)	108(1)	109(1)
C(7)–C(8)–C(9)	108(1)	109(1)
C(8)–C(9)–C(10)	109(1)	108(1)
C(9)–C(10)–C(6)	106(1)	108(1)

EXPERIMENTAL

General procedures and instruments were as described in Part 1.[1] The magnetic moments were measured using Evans' method with dichloromethane as a solvent and internal standard (contained in a sealed capillary).[35] The preparation of the tetramethylaluminates [(η-C_5H_5)$_2$M-Me$_2$AlMe$_2$] (M = Sc, Y, Dy, Ho, Er, Tm, or Yb) was described in Part 1.[1] The procedure for the preparation of each of the complexes [{M(η-C_5H_5)$_2$Me}$_2$] (M = Y, Dy, Ho, Er, Tm, or Yb) was essentially the same and is illustrated below for the case of the yttrium complex.

Preparation of Bis[bis(η-cyclopentadienyl)methylyttrium-

(III)].—To a solution of $[(\eta\text{-}C_5H_5)_2YMe_2AlMe_2]$ (0.45 g, 1.47 mmol) in toluene (30 cm^3) was added dropwise an equimolar amount of pyridine (1.47 mmol) in toluene (3 cm^3) at room temperature. The mixture was stirred overnight whereupon a precipitate formed. Work-up was by one of two equally effective methods (*a*) or (*b*).

(*a*) Volatiles were removed *in vacuo*, and the residue was washed several times with n-pentane (5×5 cm^3). The remaining solid was then dissolved in hot toluene and allowed to cool slowly to -30 °C. (*b*) The mixture was heated to *ca.* 80 °C, with rapid stirring, and the precipitate dissolved. The solution was slowly cooled to room temperature and left overnight. If crystallisation did not occur then the solution was further cooled to -30 °C.

Either (*a*) or (*b*) gave colourless crystals, which, after washing with n-pentane and vacuum drying, were identified as the desired *product* (0.3 g) (see Table 1).

Preparation of Bis[bis(η-cyclopentadienyl)methylytterbium-(III)] (*see ref.* 13).—To a slurry of $[\{Yb(\eta\text{-}C_5H_5)_2Cl\}_2]$ (0.57 g, 1.7 mmol) in thf (20 cm^3) was added methyl-lithium (1.7 mmol) in diethyl ether (1 cm^3) at -78 °C. The mixture was stirred at low temperature for 2 h and then was slowly (12 h) allowed to warm, with stirring. The volume was reduced (to *ca.* 5 cm^3) *in vacuo* and toluene (15 cm^3) was added. The solution was filtered, and the volume was again reduced (to *ca.* 5 cm^3) *in vacuo*. n-Hexane was added to yield an orange precipitate and white solid. The mixed residue was filtered off and extracted with hot benzene using a Soxhlet apparatus. The benzene solution was concentrated and, after initiation of crystallisation by rapid freezing at -196 °C, orange-red crystals were deposited and identified as the desired *product* (0.19 g, 35%).

Preparation of $[Sc(\eta\text{-}C_5H_5)_2Me(L)]$ (L = py *or* thf).—(*a*) L = *Pyridine*. To a solution of $[(\eta\text{-}C_5H_5)_2ScMe_2AlMe_2]$ (0.64 g, 2.4 mmol) in toluene (20 cm^3) was added dropwise pyridine (2.4 mmol) in toluene (5 cm^3) at -20 °C. The mixture was allowed to warm slowly (12 h) to room temperature with stirring. Volatiles were removed. The residue was washed several times with n-pentane (3×5 cm^3). The remaining residue was extracted with toluene (20 cm^3), concentrated (to *ca.* half volume), and cooled to -30 °C. A white solid was deposited and, after washing with n-pentane and vacuum drying, was identified as *bis(η-cyclopentadienyl)methyl(pyridine)scandium* (0.46 g, 71%).

(*b*) L = *Tetrahydrofuran*. To a solution of $[(\eta\text{-}C_5H_5)_2ScMe_2AlMe_2]$ (0.49 g, 1.87 mmol) was slowly added thf (1.9 mmol) in toluene (1.5 cm^3) at -20 °C. The mixture was allowed to warm slowly (12 h) to room temperature with stirring. Volatiles were removed, and the residue washed several times with n-pentane (5×5 cm^3). The cream solid was identified as *bis(η-cyclopentadienyl)methyl(tetrahydrofuran)scandium* (0.42 g, 85%).

Reactions of $[\{Y(\eta\text{-}C_5H_5)_2Me\}_2]$ *with Lewis Bases.*—(*a*) *Triphenylphosphine*. To a solution of $[\{Y(\eta\text{-}C_5H_5)_2Me\}_2]$ (0.17 g, 0.73 mmol) in toluene (20 cm^3) was added triphenylphosphine (0.19 g, 0.73 mmol). The solution was stirred for 3 h, concentrated, and cooled to -30 °C. A ^{1}H n.m.r. spectrum (triplet at τ 10.8) of the white crystalline solid (in CH_2Cl_2) formed showed it to be the starting complex.

(*b*) *Triethylphosphine*. To a warm solution of $[\{Y(\eta\text{-}C_5H_5)_2Me\}_2]$ (0.27 g, 1.1 mmol) in toluene (30 cm^3) was added triethylphosphine (0.2 cm^3, 1.4 mmol). The solution was stirred for 3 d, volatiles were removed *in vacuo*, and the residue was washed with n-hexane (3×20 cm^3). A ^{1}H n.m.r. spectrum (triplet τ 10.8) was identical with that of the yttrium dimer.

(*c*) *Pyridine*. To a solution of $[\{Y(\eta\text{-}C_5H_5)_2Me\}_2]$ (0.38 g, 1.6 mmol) at 0 °C was added pyridine (1.7 mmol). The mixture was stirred for 1 h at 0 °C and for another hour at room temperature. Volatiles were removed *in vacuo*, and the residue washed with n-pentane (2×20 cm^3). A ^{1}H n.m.r. spectrum of the solid (in CH_2Cl_2) showed resonances at τ 2.65, 3.72, 3.94, and 9.67, and a series of multiplets (τ 1—3).

(*d*) *Triphenylphosphine oxide*. To a solution of $[\{Y(\eta\text{-}C_5H_5)_2Me\}_2]$ (1 mmol) in toluene (20 cm^3) was added the ligand (1 mmol). The mixture was stirred overnight, giving a yellow solution and white precipitate. The latter was filtered off and washed several times with n-hexane. A ^{1}H n.m.r. spectrum was complicated and no identification of the product was made, although no triplet at τ 10.8 was observed.

Reaction of $[\{Y(\eta\text{-}C_5H_5)_2Me\}_2]$ *with Alkyl- or Alkylchloroaluminium Compounds.*—(*a*) $[Al_2Me_2Cl_4]$. To $[\{Y(\eta\text{-}C_5H_5)_2Me\}_2]$ (0.05 g, 0.23 mmol) in toluene (15 cm^3) was added a solution of $[Al_2Me_2Cl_4]$ (0.23 mmol) in benzene (5 cm^3). The mixture was stirred for 2 h, and volatiles were removed *in vacuo*. The ^{1}H n.m.r. spectrum (τ 3.6 and 10.45) of the residue in CH_2Cl_2 served to identify $[(\eta\text{-}C_5H_5)_2YCl_2AlMe_2]$ (*cf.* ref. 1).

(*b*) $[Al_2Me_4Cl_2]$. To a solution of $[\{Y(\eta\text{-}C_5H_5)_2Me\}_2]$ (0.048 g, 0.2 mmol) in toluene (10 cm^3) was added $[Al_2Me_4Cl_2]$ (0.2 mmol) in benzene (7 cm^3). The mixture was stirred for 2 h and volatiles were removed *in vacuo*. The ^{1}H n.m.r. spectrum of the residue in CH_2Cl_2 showed resonances at τ 3.6, characteristic of $[\{Y(\eta\text{-}C_5H_5)_2Cl\}_2]$.

(*c*) $[Al_2Me_6]$. To a solution of $[\{Y(\eta\text{-}C_5H_5)_2Me\}_2]$ (0.03 g, 0.13 mmol) was added $[Al_2Me_6]$ (0.13 mmol) in benzene (6 cm^3). The mixture was stirred for 2 h and volatiles were removed *in vacuo*. The ^{1}H n.m.r. spectrum in CH_2Cl_2 showed peaks at τ 3.72, 10.33, and 10.96, which are characteristic of $[(\eta\text{-}C_5H_5)_2YMe_2AlMe_2]$.[1]

X-Ray Analysis.—Single crystals of the air-sensitive complexes were sealed in thin-walled capillaries under a dinitrogen atmosphere prior to *X*-ray examination. Final lattice parameters were determined for each complex from a least-squares refinement of the angular settings of 15 reflections ($2\theta > 40°$) accurately centred on an Enraf-Nonius CAD-4 diffractometer.

Crystal data. $C_{22}H_{26}Yb_2$, Monoclinic, $a = 10.656(5)$, $b = 7.535(4)$, $c = 13.216(5)$ Å, $\beta = 112.62(4)°$, $U = 979.2$ Å^3, $D_c = 2.16$ g cm^{-3}, $Z = 2$, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, $\mu(\text{Mo-}K_\alpha) = 99.7$ cm^{-1}; $2\theta_{\text{max.}} = 50°$, 1 435 reflections with $I > 3\sigma(I)$; details of data collection are as given in Part 1. Space group $P2_1/n$ from systematic absences $h0l$ for $h + l \neq 2n$ and $0k0$ for $k \neq 2n$.

$C_{22}H_{26}Y_2$, Monoclinic, $a = 10.715(4)$, $b = 7.607(4)$, $c = 13.388(5)$ Å, $\beta = 112.84(4)°$, $U = 1\,005.7$ Å^3, $D_c = 1.55$ g cm^{-3}, $Z = 2$, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, $\mu(\text{Mo-}K_\alpha) = 59.3$ cm^{-1}, $2\theta_{\text{max.}} = 50°$, 1 192 reflections with $I > 3\sigma(I)$; details of data collection as above. Space group $P2_1/n$.

Structure determination and refinement. For $[\{Yb(\eta\text{-}C_5H_5)_2Me\}_2]$. The existence of two dimers per unit cell in the space group $P2_1/n$ implied that the molecule must be situated about a crystallographic centre of inversion. The position of the ytterbium atom was revealed by the inspection of a Patterson map, and the calculation of a Fourier map phased on the metal atom allowed the location of all the

11 carbon atoms in the asymmetric unit. Isotropic least-squares refinement led to a discrepancy factor of $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o| = 0.092$. Anisotropic refinement produced R 0.068. The hydrogen atoms of the cyclopentadienyl rings were then placed at calculated positions 1.00 Å from the bonded carbon atoms, and anisotropic refinement of the non-hydrogen atoms was resumed. The final R values were R 0.066 and $R' = [w(|F_o| - |F_c|)^2/w(F_o)^2]^{\frac{1}{2}} = 0.061$. The largest parameter shifts in the final cycle of refinement were less than 0.01 of their estimated standard deviations. A final difference-Fourier showed no feature >0.6 e Å^{-3} except in the vicinity of the ytterbium atom: the hydrogen atoms of the bridging methyl group could not be located. The standard deviation of an observation of unit weight was 2.44. 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 given in Table 5(*a*).

TABLE 5

Final fractional co-ordinates

Atom	x/a	y/b	z/c
(*a*) $[\{Yb(\eta\text{-}C_5H_5)_2Me\}_2]$			
Yb	0.128 77(7)	0.474 26(8)	0.452 97(5)
C(1)	0.072 4(25)	0.509 9(27)	0.242 3(13)
C(2)	−0.006 3(20)	0.628 8(27)	0.264 6(14)
C(3)	0.072 2(20)	0.761 2(26)	0.331 7(14)
C(4)	0.203 5(20)	0.719 3(25)	0.351 3(15)
C(5)	0.208 2(23)	0.563 3(30)	0.296 8(14)
C(6)	0.259 1(22)	0.172 6(28)	0.511 5(18)
C(7)	0.239 1(21)	0.229 4(32)	0.601 6(19)
C(8)	0.317 2(26)	0.376 9(32)	0.640 0(17)
C(9)	0.385 8(22)	0.410 6(31)	0.570 8(21)
C(10)	0.349 3(26)	0.286 6(40)	0.490 5(20)
C(11)	0.084 8(19)	0.692 9(22)	0.581 4(13)
H(1)	0.028	0.392	0.201
H(2)	−0.110	0.639	0.252
H(3)	0.020	0.859	0.367
H(4)	0.286	0.773	0.394
H(5)	0.309	0.509	0.278
H(6)	0.230	0.071	0.462
H(7)	0.186	0.165	0.646
H(8)	0.330	0.445	0.722
H(9)	0.434	0.509	0.569
H(10)	0.394	0.265	0.429
(*b*) $[\{Y\{\eta\text{-}C_5H_5)_2Me\}_2]$			
Y	0.130 50(8)	0.473 03(11)	0.451 91(6)
C(1)	0.073 8(10)	0.509 5(16)	0.241 1(6)
C(2)	−0.009 7(10)	0.632 5(16)	0.262 6(7)
C(3)	0.072 0(11)	0.763 9(14)	0.329 7(8)
C(4)	0.209 7(10)	0.719 1(15)	0.350 3(8)
C(5)	0.207 9(10)	0.565 9(16)	0.294 6(7)
C(6)	0.262 0(13)	0.169 2(16)	0.509 2(11)
C(7)	0.243 4(11)	0.223 8(19)	0.599 9(11)
C(8)	0.318 0(13)	0.370 9(19)	0.639 6(8)
C(9)	0.385 1(10)	0.412 7(18)	0.574 6(12)
C(10)	0.353 4(13)	0.286 9(23)	0.494 7(10)
C(11)	0.088 6(9)	0.689 8(14)	0.581 2(7)
H(1)	0.043	0.400	0.195
H(2)	−0.112	0.627	0.235
H(3)	0.038	0.869	0.360
H(4)	0.241	0.841	0.396
H(5)	0.291	0.502	0.294
H(6)	0.216	0.062	0.462
H(7)	0.182	0.160	0.632
H(8)	0.321	0.435	0.707
H(9)	0.448	0.513	0.582
H(10)	0.385	0.275	0.431
H(11)	0.176	0.727	0.595
H(12)	0.032	0.773	0.553
H(13)	0.110	0.650	0.669

For $[\{Y(\eta\text{-}C_5H_5)_2Me\}_2]$. Since the complex is isostructural with its Yb analogue the refined co-ordinates formed the starting point. Least-squares refinement with anisotropic temperature factors for the Y and C atoms, and cyclopentadienyl ring hydrogen atoms in calculated positions, led to R 0.055. The hydrogen atoms on the bridging carbon atom were then located on a difference-Fourier map, and further refinement of the non-hydrogen parameters gave final values of R 0.048 and R' 0.055. The largest parameter shifts in the final cycle of refinement were 0.01 of their estimated standard deviation. A final difference-Fourier showed no feature >0.5 e Å^{-3}. The standard deviation of an observation of unit weight was 2.01. 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 given in Table 5(*b*). Observed and calculated structure-factor amplitudes and thermal parameters for both structures are in Supplementary Publication No. SUP 22326 (13 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 of J. L. A.

[8/224 *Received*, 10*th February*, 1978]

REFERENCES

[1] Part 1, J. Holton, M. F. Lappert, D. G. H. Ballard, R. Pearce, J. L. Atwood, and W. E. Hunter, previous paper.

[2] J. Holton, M. F. Lappert, D. G. H. Ballard, R. Pearce, J. L. Atwood, and W. E. Hunter, *J.C.S. Chem. Comm.*, 1976, 480.

[3] *Cf.*, H. Gysling and M. Tsutsui, *Adv. Organometallic Chem.*, 1970, **9**, 361; R. G. Hayes and J. L. Thomas, *Organometallic Rev.*, 1971, **A7**, 1; M. Tsutsui, N. Ely, A. E. Gebala, and J. L. Atwood, *Ann. New York Acad. Sci.*, 1974, **239**, 160; M. Tsutsui, N. Ely, and R. Dubois, *Accounts Chem. Res.*, 1976, **9**, 217.

[4] F. A. Hart, A. G. Massey, and M. S. Saran, *J. Organometallic Chem.*, 1970, **21**, 147.

[5] G. K. Barker and M. F. Lappert, *J. Organometallic Chem.*, 1974, **76**, C45.

[6] M. F. Lappert and R. Pearce, *J.C.S. Chem. Comm.*, 1973, 126.

[7] J. L. Atwood, W. E. Hunter, R. D. Rogers, J. Holton, J. McMeeking, R. Pearce, and M. F. Lappert, *J.C.S. Chem. Comm.*, 1978, 140.

[8] H. Schumann and S. Hohmann, *Chem.-Ztg.*, 1976, **100**, 336.

[9] D. F. Evans, G. V. Fazakerly, and R. F. Phillips, *J. Chem. Soc.* (*A*), 1971, 1931.

[10] S. A. Cotton, F. A. Hart, M. B. Hursthouse, and A. J. Welch, *J.C.S. Chem. Comm.*, 1972, 1225.

[11] G. B. Deacon and D. G. Vince, *J. Organometallic Chem.*, 1976, **112**, C1.

[12] E. Murphy and G. E. Toogood, *J. Inorg. Nuclear Chem. Letters*, 1971, **7**, 755.

[13] M. Tsutsui and N. M. Ely, *Inorg. Chem.*, 1975, **14**, 2680.

[14] R. S. P. Coutts and P. C. Wailes, *J. Organometallic Chem.*, 1970, **25**, 117.

[15] L. E. Manzer, *Inorg. Chem.*, 1976, **15**, 2567.

[16] B. L. Kalsotra, R. K. Multani, and B. D. Jain, *J. Inorg. Nuclear Chem.*, 1973, **35**, 311.

[17] M. Tsutsui and N. Ely, *J. Amer. Chem. Soc.*, 1975, **97**, 3551.

[18] F. W. van der Weij, H. Scholtens, and J. H. Teuben, *J. Organometallic Chem.*, 1977, **127**, 299.

[19] E. G. Hoffmann, *Trans. Faraday Soc.*, 1962, **58**, 642.

[20] K. Fischer, K. Jonas, P. Misbach, R. Stabba, and G. Wilke, *Angew. Chem. Internat. Edn.*, 1973, **12**, 943.

[21] K. Nakamoto, 'Characterisation of Organometallic Compounds,' Interscience, New York, 1969, ch. 3.

[22] P. Krohmer and J. Goubeau, *Z. anorg. Chem.*, 1969, **369**, 238.

[23] N. Sheppard, *Trans. Faraday Soc.*, 1955, **51**, 1465.

[24] D. M. Adams, J. Chatt, and B. L. Shaw, *J. Chem. Soc.*, 1960, 2047.

[25] N. S. Gill, R. H. Nuttal, D. E. Scaife, and D. W. A. Sharp, *J. Inorg. Nuclear Chem.*, 1961, **18**, 79.

[26] J. Lewis, J. R. Miller, R. L. Richards, and A. Thompson, *J. Chem. Soc.*, 1965, 5850.

---

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

[27] L. Holleck and L. Hartinger, *Angew. Chem.*, 1955, **67**, 648.

[28] J. H. Van Vleck and A. Frank, *Phys. Rev.*, 1929, **34**, 1494, 1625.

[29] T. A. Mole and E. A. Jeffery, 'Organoaluminium Compounds,' Elsevier, Amsterdam, 1972.

[30] D. J. Cole-Hamilton and G. Wilkinson, *J.C.S. Dalton*, 1977, 797.

[31] J. C. Huffman and W. E. Streib, *Chem. Comm.*, 1971, 911.

[32] G. R. Scollary, *Austral. J. Chem.*, 1978, **31**, 411.

[33] F. A. Cotton and G. Wilkinson, 'Basic Inorganic Chemistry,' Wiley, New York, 1976, p. 448.

[34] M. C. Day and J. Selbin, 'Theoretical Inorganic Chemistry,' Reinhold, New York, 1969, p. 118.

[35] D. F. Evans, *J. Chem. Soc.*, 1959, 2003.