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μ-Dialkyl Inner Transition Metal(III) Tetra-alkylaluminates; the Crystal and Molecular Structure of Di-μ-methyl-(dimethylaluminium)biscyclopentadienyl-yttrium and -ytterbium

By JOHN HOLTON, MICHAEL F. LAPPERT,* and GEOFFREY R. SCOLLARY
(*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)

and JERRY L. ATWOOD and WILLIAM E. HUNTER
(*Department of Chemistry, The University of Alabama, Alabama* 35486)

Summary The crystalline title compounds, $[M(C_5H_5\text{-}\eta)_2R_2AlR_2]$ (R = Me and M = Sc, Gd, Dy, Ho, Er, Tm, or Yb; R = Et and M = Sc or Y), were obtained by reaction of $[M(C_5H_5\text{-}\eta)_2Cl]_2$ and $Li[AlR_4]$ in toluene; the presence of the double alkyl bridge between M and Al was established by ^1H and ^{13}C n.m.r. spectra of the Sc and Y compounds $\{[Y(C_5H_5\text{-}\eta)_2Et_2AlEt_2]$, unlike the Sc analogue, is fluxional at room temperature showing rapid bridge and terminal Et exchange$\}$, and single-crystal *X*-ray analysis for the Y and Yb tetramethylaluminates.

UNTIL recently the formation of alkyl bridges in stable bi- or poly-nuclear metal complexes was thought to be an exclusive property of the *s*-block or Al and the heavier main group 3 elements.[1] However, a widely held model for Ziegler catalysis (*e.g.*, with $[TiCl_3]$–$AlEt_3$) involved the proposal of a transient alkyl-bridged intermediate, which received strong support from the recent isolation and spectroscopic characterisation of the unstable di-η-cyclopentadienyltitanium(III) tetramethylaluminate and its yttrium congener.[2] We now report on (i) the crystal and molecular structure of the latter and the ytterbium analogue (the first rare earth alkyls to be so characterised) (see Figure), (ii) synthetic and spectroscopic data on Sc and several of the lanthanide element (f^7 and f^9—f^{13}) complexes as well as the Sc and Y ethyl homologues (see Table), and (iii) variable temperature ^1H and ^{13}C n.m.r. data on the diamagnetic Sc and Y compounds, which have a bearing on bridge and terminal alkyl ligand site-exchange processes in solution.

TABLE

$[M(C_5H_5\text{-}\eta)_2R_2AlR_2]$[a]		Colour	M.p.[b]	Yield[c]
M	R		(°C)	(%)
Sc	Me	Pale yellow	108—110	67
Sc	Et	Pale yellow	d	62
Y	Et	Colourless	d	70
Gd	Me	Colourless	>200 (decomp.)	45
Dy	Me	Pale yellow	145—146	65
Ho	Me	Straw	142—143	78
Er	Me	Pink	133—135	71
Tm	Me	Pale green	130 (decomp.)	68
Yb	Me	Orange red	133—135	72

[a] All compounds are analytically pure, soluble in CH_2Cl_2 but insoluble in saturated hydrocarbons; i.r. spectra for R = Me complexes are similar with methyl vibrations at 1250, 1240, and 1190 cm^{-1}, and $(C_5H_5\text{-}\eta)^-$ vibrations at 3100, 1020, and 800 cm^{-1}; intense parent molecular ions found only for $[Sc(C_5H_5\text{-}\eta)_2Me_2AlMe_2]$ [b] In sealed capillary. [c] Based on: $\frac{1}{2}[M(C_5H_5\text{-}\eta)_2Cl]_2 + Li[AlR_4] \longrightarrow [M(C_5H_5\text{-}\eta)_2R_2AlR_2] + LiCl$ (in PhMe). [d] Thermally unstable; *e.g.*, Sc complex decomposes in CH_2Cl_2 solution at or near room temperature, in contrast to $[Sc(C_5H_5\text{-}\eta)_2Me_2AlMe_2]$ which sublimes without decomposition at 100 °C at 0·1 mmHg.

N.m.r. data for the Sc and Y compounds are consistent with a μ-dialkyl bridge in solution between the group 3A metal and Al. Complex $[Y(C_5H_5\text{-}\eta)_2Et_2AlEt_2]$ is fluxional at +40 °C, the ^1H n.m.r. spectrum showing two broad peaks at τ 8·78 and 10·20; but at −40 °C a limiting well resolved spectrum is obtained [η-C_5H_5: τ 3·80 (10H, s); YEt_2Al: 8·70 (6H, t) and 10·36 {4H, 8 line multiplet, J (^{89}Y–CH_2) 4·0 Hz}; $AlEt_2$: 8·99 (6H, t) and 10·19 (4H, q)]. The two Sc complexes are non-fluxional at room temperature [η-C_5H_5: τ 3·88 (R = Me) or 3·81 (R = Et) (10H, s); $ScMe_2Al$: 10·29 (6H, s.br); $ScEt_2Al$: 8·52 (6H, t) and 10·58 (4H, q); $AlMe_2$: 10·84 (6H, s); $AlEt_2$: 8·85 (6H, t) and 10·02 (4H, q)]. Variable temperature ^{13}C n.m.r. spectra give similar results. For example, limiting ^{13}C n.m.r. spectra for the two tetramethylaluminates show (chemical shifts are quoted as downfield from $SiMe_4$) η-C_5H_5 singlets at δ 113·2 (Sc) or 112·2 (Y) p.p.m., for $ScMe_2Al$ a broad singlet at 20·7 p.p.m. and for YMe_2Al a doublet at 7·86 p.p.m. {J (^{89}Y–C) 12·2 Hz; the first record of ^{89}Y–^{13}C coupling}, while the $AlMe_2$ signal is observed as a singlet at −6·3 (Sc, broad) or −7·9 (Y) p.p.m.

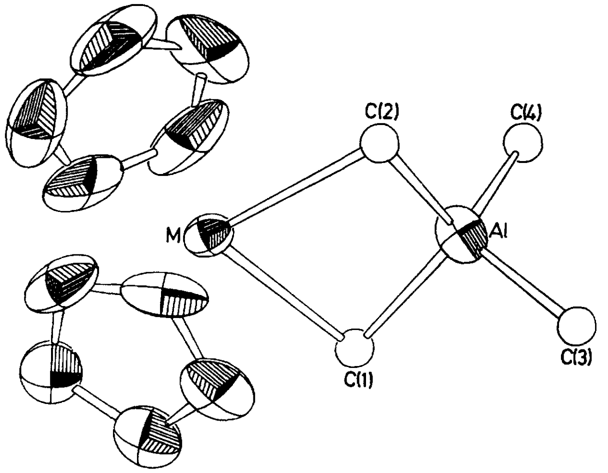

FIGURE. The molecular structure of $[M(C_5H_5\text{-}\eta)_2Me_2AlMe_2]$; interatomic distances (Å) and angles (degrees) for M = Y (or M = Yb in parentheses): M–Al, 3·056 (3·03); Al–C(1), 2·08 (2·02); M–C(1), 2·57 (2·53); Al–C(2), 2·11 (2·24); M–C(2), 2·60 (2·58); Al–C(3), 1·90 (2·14); M–C_5H_5-η, av. 2·62 (2·63); Al–C(4), 1·97 (1·94); ∠C(1)–M–C(2), 85 (87); C(1)–Al–C(3), 107 (112); C(1)–Al–C(2), 112 (111); C(2)–Al–C(4), 108 (107); M–C(1)–Al, 82 (83); C(4)–Al–C(3), 111; (118); M–C(2)-Al, 80 (78). E.s.d.s in the Y–C bond lengths are 0·02 Å, in the Yb–C bond lengths 0·04, and in the Al–C bond lengths <0·04, while e.s.d.s in bond angles are <1°.

Crystals, suitable for *X*-ray analysis, were grown from a toluene–hexane (1:1) mixture at −30 °C. *Crystal data:* $[Yb(C_5H_5\text{-}\eta)_2Me_2AlMe_2]$, orthorhombic, M 390·4, a = 17·866(5), b = 7·973(3), c = 10·871(3) Å, U = 1548·6 Å^3, D_m not measured, D_c 1·67 g cm^{-3}, Z = 4, μ(Mo-K_α) 63·8 cm^{-1}, space group $Pna2_1$. Intensity data were recorded on an Enraf-Nonius CAD-4 diffractometer using the ω–2θ scan technique. All reflections out to $2\theta = 50°$ in one independent octant were measured: 1124 reflections were considered having $I_{obs} \geqslant 2\sigma(I_{obs})$. The structure was solved by Patterson and difference Fourier techniques, and refined to R = 0·078.

Complex $[Y(C_5H_5\text{-}\eta)_2Me_2AlMe_2]$ belongs to the same space group, with a = 17·969(6), b = 7·988(4), c = 10·870(4) Å, Z = 4. Integrated diffraction intensities of 663 independent reflections [Mo-K_α Hilger and Watts Y290 automatic diffractometer, $I_{obs} \geqslant 3\sigma(I_{obs})$] provided for a straightforward structure determination. A full-matrix least-squares refinement of atomic co-ordinates (the cyclopentadienyl rings being treated as rigid groups) and anisotropic (Y, Al, and cyclopentadienyl carbons) and isotropic (methyl carbons) thermal parameters has converged to an unweighted discrepancy index, R = 0·052.

The molecular structure is represented in the Figure.

As illustrated by the crystal data, the Y and Yb tetramethylaluminates are isostructural. Although refinement difficulties were encountered with both structures, the essential features are in agreement. The aluminium is effectively tetrahedral with the average ∠C–Al–C being 109°. The *ca.* 80° average angle at the bridging carbon atom may be compared with the 75·7° value given for $(AlMe_3)_2$.[3] The Al–C average of *ca.* 2·10 Å compares favourably with 2·125 Å in trimethylaluminium.

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