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Novel monopentamethylcyclopentadienyl alkoxides of La and Ce; X-ray crystal structure of $(C_5Me_5Ce(OCMe_3)_2)_2$

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Abstract

Treatment of monomeric $(C_5Me_5)_2LnCH(SiMe_3)_2$ (Ln = La and Ce) compounds with $HOCMe_3$ gives the novel compounds $(C_5Me_5Ln(OCMe_3)_2)_2$. An X-ray diffraction study of the cerium analogue reveals a dimeric structure with two symmetrically bridging and two terminal alkoxide ligands in a *cis* configuration. Crystal data: monoclinic space group $P2_1/c$, a 13.163(5), b 17.429(4), c 18.988(4) Å, β 100.75(2)°, V 4279.7 Å^3 and $Z = 4$. Least-squares refinement leads to a final R (based on F) value of 0.044 for 4860 observed reflections. Treatment of $(C_5Me_5)_2CeCH(SiMe_3)_2$ with an excess of 2,6-di-t-butylphenol at room temperature gives $(C_5Me_5)_2$(2,6-di-t-butylphenoxo)cerium. Tris(2,6-di-t-butylphenoxo)cerium and C_5Me_5H are formed when the mixture is heated to 80 °C. The intermediate (C_5Me_5)bis(2,6-di-t-butylphenoxo)cerium is not observed under these conditions.

Introduction

The organometallic chemistry of the early lanthanides (La–Nd) is developing rapidly. Most investigations have involved complexes containing bridged dicyclopentadienyl [1] or substituted cyclopentadienyl ligands [2]. The pentamethylcyclopentadienyl group in particular seems to be a very suitable co-ligand, and a number of bis(pentamethylcyclopentadienyl) early lanthanide halide, carbyl, and amido complexes have been reported [3]. However, only a few stable mono-cyclopentadienyl or substituted cyclopentadienyl complexes are known viz: $C_5Me_5LnI_2 \cdot 3THF$ (Ln = La and Ce) [4], $(C_5Me_5NdCl_3)(Na(OEt_2)_2)$ [3b], $C_5Me_5Nd(N(SiMe_3)_2)_2$ [3b], $(Li(THF)_2)_2(\mu\text{-}Cl)_4(C_5H_5)Ln \cdot THF$ (Ln = La and Nd) [5] and $HmiLnCl_2$ (Ln = La and Nd, Hmi = heptamethylindenyl) [6]. As a part of a

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program aimed at developing general methods for the synthesis of mono-C_5Me_5 early-lanthanide complexes we have begun to examine the removal of C_5Me_5 ligands from well-defined bis-C_5Me_5 complexes by use of protic acids. This approach has been used succesfully to synthesize mixed-ligand ytterbium organometallics involving cyclopentadienyl and chelating ligands (e.g. β-diketonates) starting from $(C_5H_5)_3Yb$ [7]. We describe here the reactions of $(C_5Me_5)_2LnCH(SiMe_3)_2$ (Ln = La and Ce) with $HOCMe_3$ and 2,6-di-t-butylphenol. These alcohols were chosen because bulky alkoxide ligands are attractive in respect of their high solubility and large size, which offer the possibility of obtaining stable sterically-saturated complexes. The CMe_3 groups also simplify NMR spectroscopy, which is especially useful for the identification of paramagnetic cerium(III) complexes.

Experimental

General considerations

All the compounds are extremely air sensitive and manipulations were carried out by Schlenk or glovebox techniques under nitrogen or argon. Solvents were distilled from Na/K alloy prior to use. $HOCMe_3$ (Merck) and 2,6-di-t-butylphenol (Janssen) were stored under nitrogen over molecular sieves (4 Å) at 50 °C. C_5Me_5H was made by Burger's method [8] and converted into C_5Me_5Li as described in ref. 9. $LiCH(SiMe_3)_2$ was prepared by a published procedure [10] and sublimed (90 °C/0.01 mmHg) before use. $(C_5Me_5)_2CeCH(SiMe_3)_2$ was prepared as described in ref. 11 and the lanthanum analogue similarly. Tris(2,6-di-t-butylphenoxo)cerium * was prepared in 65% yield by a slightly modification of the procedure described for the corresponding yttrium complex [12], the reaction mixture being stirred under reflux for 4 d instead of 8 h. IR spectra were recorded on a Pye–Unicam SP3-300 spectrophotometer with Nujol mulls between KBr discs. NMR spectra were recorded on a Bruker WH-90 or Varian VXR-300 spectrometer. Chemical shifts are reported in parts per million and were referenced to residual protons in deuterated solvents (benzene-d_6: δ 7.15; toluene-d_8: δ 6.98). ^{13}C chemical shifts were referenced to benzene-d_6 (δ 127.96). Elemental analyses were performed at the Microanalytical Department of the University of Groningen under supervision of Mr A.F. Hamminga.

1. The synthesis of $(C_5Me_5Ce(OCMe_3)_2)_2$ (1)

$HOCMe_3$ (0.35 ml; 3.6 mmol) was added from a syringe to a stirred solution of 1.02 g (1.8 mmol) $(C_5Me_5)_2CeCH(SiMe_3)_2$ in pentane (20 ml) at room temperature. The color of the solution immediately changed from red to light-green. The solution was stirred for another 15 min and then concentrated to ca. 5 ml. Crystallization at −80 °C gave 0.42 g (0.50 mmol, 56%) of **1** as yellow crystals. IR (cm^{-1}): 2710(w), 2130(w), 1380(m), 1350(m), 1220(m), 1195(s), 1170(s), 1020(m), 990(vs), 920(vs), 800(m), 770(m), 750(m), 520(m), 500(s), 490(m). ^1H NMR (benzene-d_6, 25 °C): δ 11.80 (s, *lw* 15 Hz, 9H); δ 6.87 (s, *lw* 19 Hz, 15H); δ −35.45 (s, *lw* 33 Hz, 9H). ^{13}C NMR (benzene-d_6, 25 °C): δ 162.3 (s, C_5Me_5); δ 124.1 (s, $OCMe_3$); δ 54.6 (q,

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* The synthesis of this compound by treatment of $Ce[N(SiMe_3)_2]_3$ with 2,6-di-t-butylphenol in pentane was reported recently [13].

J(C–H) 123 Hz, OCMe_3); δ 11.2 (q, J(C–H) 125 Hz, C_5Me_5); δ −5.6 (s, OCMe$_3$); δ −18.6 (q, J(C–H) 120 Hz, OCMe_3). Anal. Found: C, 51.27; H, 7.79; Ce, 33.23; mol wt (C_6H_6), 760. $C_{18}H_{33}CeO_2$ calcd.: C, 51.28; H, 7.89; Ce, 33.24%; mol wt (C_6H_6), 843.

2. *The synthesis of* $(C_5Me_5La(OCMe_3)_2)_2$ *(2)*

Complex **2** was prepared from $(C_5Me_5)_2LaCH(SiMe_3)_2$ in 30% yield by a procedure similar to that described for **1**. IR (cm^{-1}): 2720(w), 1380(m), 1355(s), 1220(s), 1190(s), 1170(s), 1020(m), 985(vs), 920(s), 800(w), 770(s), 750(m), 510(s), 490(s), 460(m). ^{1}H NMR (benzene-d_6, 20 °C); δ 2.20 (s, 15H); δ 1.33 (s, 9H); δ 1.27 (s, 9H). ^{13}C NMR (benzene-d_6, 20 °); δ 119.1 (s, C_5Me$_5$); δ 73.6 (s, OCMe$_3$); δ 71.0 (s, OCMe$_3$); δ 34.4 (q, J(C–H) 124 Hz, OCMe_3); δ 33.5 (q, J(C–H) 125 Hz, OCMe_3); δ 11.6 (q, J(C–H) 125 Hz, C_5Me_5). Anal. Found: C, 51.49, H, 7.88; La, 32.79. $C_{18}H_{33}LaO_2$ calcd.: C, 51.43; H, 7.91; La, 33.04%.

3. *The synthesis of* $(C_5Me_5)_2$ *(2,6-di-t-butylphenoxo)cerium (3)*

2,6-Di-t-butylphenol (0.327 g, 1.6 mmol) was added to a solution of 0.903 g (1.6 mmol) of $(C_5Me_5)_2CeCH(SiMe_3)_2$ in pentane (50 ml). The deep red solution was stirred for 30 min at room temperature and then concentrated to ca. 20 ml. Crystallization at −80 °C gave 0.647 g (1.1 mmol, 69%) of **3** as deep red crystals. IR (cm^{-1}): 3040(w), 2720(w), 2110(w), 1575(m), 1400(s), 1350(m), 1250(s), 1195(w), 1090(m), 1010(m), 850(s), 810(m), 790(m), 735(s), 630(m). ^{1}H NMR (benzene-d_6, 20 °C): δ 7.93 (d, $lw < 10$ Hz, 2H); δ 7.28 (t, $lw < 10$ Hz, 1H); δ 2.79 (s, lw 12 Hz, 30H); δ −7.5 (s, lw 24 Hz, 18H). ^{13}C NMR (benzene-d_6, 20 °C); δ 194.3 (s, OC_6H$_3$); δ 165.6 (s, C_5Me$_5$); δ 149.8 (s, OC_6H$_3$); δ 126.2 (d, J(C–H) 154 Hz, OC_6H$_3$); δ 120.0 (d, J(C–H) 158 Hz, OC_6H$_3$); δ 35.3 (s, CMe$_3$); δ 20.0 (q, J(C–H) 125 Hz, CMe_3); δ 5.6 (q, J(C–H) 125 Hz, C_5Me_5). Anal. Found: C, 66.42; H, 8.35; Ce, 22.87. $C_{34}H_{51}CeO$ calcd.: C, 66.30; H, 8.35; Ce, 22.75%.

X-ray data collection, structure determination and refinement for 1

A yellow crystal of the title compound, obtained by slowly cooling a saturated pentane solution to −30 °C, was mounted in a glass-capillary under argon. The space group was shown to be the centric $P2_1/c$ from the systematic absences. A summary of the data collection parameters is given in Table 1.

The cerium atom positions were determined by use of the direct program Multan [14]. Difference Fourier maps based on the cerium atoms showed the positions of the C_5Me_5 and oxygen ligands, and revealed the presence of rotational disorder in the CMe$_3$ groups. Three orientations of equal occupancy (1/3) were resolved for each CMe$_3$ group and refined in alternate cycles. High thermal motion (but no resolvable disorder) was observed for the C_5Me_5 ligands. The hydrogen atoms were not included in the final refinement. Refinement of the nonhydrogen atoms with anisotropic temperature factors and of the disordered carbon atoms with isotropic thermal parameters in alternate cycles led to final values of $R = 0.044$ and $R_w = 0.047$. The final positional parameters are given in Table 2.

Results and discussion

As a start to this investigation we devised a general route to $(C_5Me_5)_2LnX$ derivatives (X = carbyl, amido, hydride; Ln = La and Ce) starting from

Table 1

Crystal data, summary of intensity data collection and structure refinement for **1**

Color/Shape	Yellow/parallelepiped
Mol. wt	843.2
Space group	$P2_1/c$
Temp., °C	20
Cell Constants [a]	
a, Å	13.163(5)
b, Å	17.429(4)
c, Å	18.988(4)
β, deg	100.75(2)
Cell Vol., Å^3	4279.7
Formula units/unit cell	4
D_{calc}, gcm^{-3}	1.31
μ (calc), cm^{-1}	20.0
Diffractometer/Scan	Enraf-Nonius CAD4/θ-2θ
Range of rel. transm. factors, %	85/100
Radiation, graphite monochromator	Mo-K_α (λ 0.71073 Å)
Crystal dimensions, mm	$0.35 \times 0.45 \times 0.75$
Scan width	$0.80 + 0.35 \tan \theta$
Standard reflections	(10,0,0), (0, 12,0), (0,0,18)
Decay of standards	±2%
Reflections measured	8132
2θ range, deg	$2 \leq 2\theta \leq 50$
Range of h,k,l	+15, +20, ±22
Reflections observed ($F_o \geq 5\sigma(F_o)$) [b]	4860
Computer programs [c]	SHELX [16]
Structure solution	MULTAN [14]
No. of parameters varied	208
Weights	$(\sigma(F_0)^2)^{-1}$
GOF	1.97
$R = \Sigma \lVert F_o \rvert - \lvert F_c \rVert / \Sigma \lvert F_o \rvert$	0.044
R_w	0.047
Largest feature final diff. map	$0.6e^-/\text{Å}$

[a] Least-squares refinement of $((\sin \theta)/\lambda)^2$ values for 25 refl. $\theta > 19°$. [b] Corrections: Lorentz-polarization and absorption (empirical, psi scan). [c] Neutral atom scattering factors and anomalous dispersion corrections from ref. 17.

$((C_5Me_5)_2LnCL)_n$ [11]. Monomeric salt-free complexes were obtained when bulky X groups, e.g. $CH(SiMe_3)_2$ and $N(SiMe_3)_2$ were used. The reaction of $(C_5Me_5)_2CeCH(SiMe_3)_2$ with 2 equivalents of $HOCMe_3$ in pentane gave C_5Me_5H and $CH_2(SiMe_3)_2$ (^{1}H NMR) and a single organocerium complex, which analyzed as $C_5Me_5Ce(OCMe_3)_2$ (**1**) (eq. 1).

$$(C_5Me_5)_2CeCH(SiMe_3)_2 + 2HOCMe_3 \rightarrow \underset{(\mathbf{1})}{C_5Me_5Ce(OCMe_3)_2} + C_5Me_5H + CH_2(SiMe_3)_2 \qquad (1)$$

Complex **1** was isolated in 55% yield as intense yellow, very air-sensitive crystals, which are readily soluble in aromatic and aliphatic hydrocarbons. Molecular weight determinations (cryoscopy in benzene) indicate that **1** is dimeric in solution. ^{1}H NMR and ^{13}C NMR spectra (benzene-d_6) both show a single C_5Me_5 ligand and the

Table 2

Final fractional coordinates for $[(\eta^5\text{-}C_5Me_5)Ce(O\text{-}t\text{-}Bu)_2]_2$

Atom	x/a	y/b	z/c
Ce(1)	0.14231(4)	0.62648(3)	0.83094(3)
Ce(2)	0.34239(4)	0.56063(3)	0.72157(3)
O(1)	0.2267(5)	0.6625(3)	0.7341(3)
O(2)	0.2541(5)	0.5212(3)	0.8173(3)
O(3)	−0.0137(5)	0.6022(4)	0.7856(3)
O(4)	0.2794(5)	0.4945(4)	0.6298(3)
C(1)	0.1884(9)	0.7165(6)	0.6758(6)
C(2)a [a]	0.081(2)	0.693(2)	0.638(1)
C(3)a	0.262(2)	0.698(1)	0.618(1)
C(4)a	0.203(2)	0.799(1)	0.709(1)
C(2)b	0.104(3)	0.663(2)	0.619(2)
C(3)b	0.272(2)	0.732(2)	0.636(1)
C(4)b	0.128(2)	0.775(2)	0.699(2)
C(2)c	0.072(3)	0.727(2)	0.669(2)
C(3)c	0.205(3)	0.680(2)	0.605(2)
C(4)c	0.259(2)	0.788(2)	0.692(2)
C(5)	0.2384(9)	0.4431(6)	0.8376(5)
C(6)a	0.332(2)	0.434(1)	0.916(1)
C(7)a	0.130(2)	0.436(1)	0.853(1)
C(8)a	0.261(2)	0.390(1)	0.775(1)
C(6)b	0.156(2)	0.448(2)	0.889(2)
C(7)b	0.188(3)	0.398(2)	0.773(2)
C(8)b	0.333(3)	0.415(2)	0.885(2)
C(6)c	0.116(3)	0.423(2)	0.812(2)
C(7)c	0.301(2)	0.391(2)	0.800(1)
C(8)c	0.267(3)	0.432(2)	0.913(2)
C(9)	−0.1233(9)	0.5885(8)	0.7569(6)
C(10)a	−0.167(2)	0.542(2)	0.813(2)
C(11)a	−0.173(2)	0.673(2)	0.741(2)
C(12)a	−0.112(2)	0.535(2)	0.683(1)
C(10)b	−0.167(3)	0.652(2)	0.704(2)
C(11)b	−0.123(3)	0.514(2)	0.709(2)
C(12)b	−0.178(3)	0.572(2)	0.815(2)
C(10)c	−0.186(3)	0.662(2)	0.768(2)
C(11)c	−0.138(3)	0.574(2)	0.682(2)
C(12)c	−0.149(3)	0.515(2)	0.800(2)
C(13)	0.237(1)	0.4533(9)	0.5644(6)
C(14)a	0.114(2)	0.458(2)	0.571(1)
C(15)a	0.290(2)	0.506(2)	0.506(1)
C(16)a	0.296(3)	0.389(2)	0.554(2)
C(14)b	0.235(2)	0.520(2)	0.501(2)
C(15)b	0.304(3)	0.362(2)	0.582(2)
C(16)b	0.132(3)	0.432(2)	0.555(2)
C(14)c	0.290(3)	0.463(2)	0.509(2)
C(15)c	0.121(3)	0.480(2)	0.539(2)
C(16)c	0.244(3)	0.364(2)	0.580(2)
C(17)	0.131(1)	0.7574(7)	0.9174(6)
C(18)	0.076(1)	0.698(1)	0.9487(7)
C(19)	0.148(1)	0.6455(8)	0.9791(6)
C(20)	0.249(1)	0.6680(7)	0.9684(5)
C(21)	0.237(1)	0.7374(6)	0.9296(5)
C(22)	0.086(1)	0.8291(7)	0.8841(7)
C(23)	−0.037(1)	0.696(1)	0.9559(8)
C(24)	0.126(1)	0.5755(8)	1.0231(6)

Table 2 (continued)

Atom	*x/a*	*y/b*	*z/c*
C(25)	0.354(1)	0.6323(8)	0.9983(6)
C(26)	0.327(1)	0.7850(7)	0.9119(7)
C(27)	0.5475(9)	0.5159(7)	0.7645(8)
C(28)	0.5415(8)	0.5839(9)	0.8005(7)
C(29)	0.5283(9)	0.6452(7)	0.7529(8)
C(30)	0.5282(9)	0.615(1)	0.6838(8)
C(31)	0.5407(9)	0.534(1)	0.6927(8)
C(32)	0.571(1)	0.4351(8)	0.798(1)
C(33)	0.558(1)	0.590(1)	0.8837(7)
C(34)	0.529(1)	0.7285(7)	0.770(1)
C(35)	0.524(1)	0.658(1)	0.6143(9)
C(36)	0.553(1)	0.476(1)	0.635(1)

[a] Designations a, b, c, refer to the threefold disorder observed for the ${}^tBu$ groups. Occupancy factors were fixed at 0.3333.

presence of two different $OCMe_3$ groups. The solid state structure, as determined by X-ray diffraction, confirms the dimeric nature of **1** (vide infra). The temperature dependence of the ^1H NMR resonances of **1** (20 to 105 °C, Fig. 1) are as expected for a paramagnetic compound, showing the linear Curie–Weiss relation between chemical shift and the reciprocal of the temperature. These data also indicate that exchange between bridging and terminal $OCMe_3$ groups is slow on ^1H NMR time scale even at 105 °C.

The reaction of **1** with another equivalent of $HOCMe_3$ was monitored by ^1H NMR spectroscopy (toluene-d_8, 20 °C). Instead of C_5Me_5H formation, exchange between free $HOCMe_3$ and one of the alkoxide ligands took place. The $OCMe_3$ resonance at 11.61 ppm disappeared, and a new broad resonance at ca. 6 ppm was observed, and sharpened considerably upon heating to 80 °C (*lw*(80 °C) 650 Hz). Attempts to obtain the activation parameters for this fluctional process were

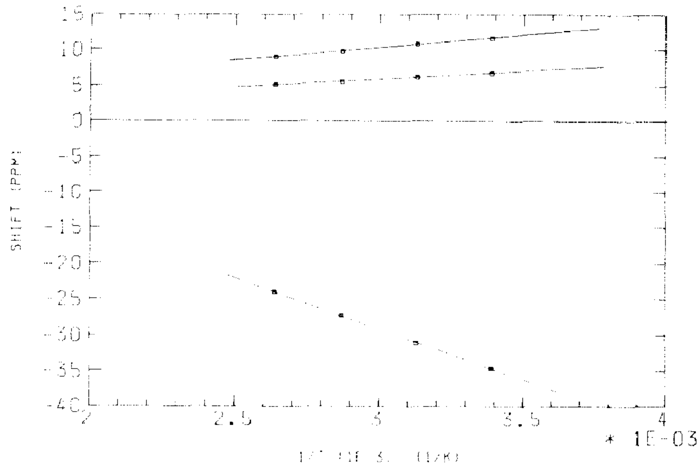

Fig. 1. Plot of paramagnetic shifts against the reciprocal of the temperature for the ^1H NMR resonances of $(C_5Me_5Ce(OCMe_3)_2)_2$ (**1**).

hampered owing to slow decomposition of **1** under the conditions used, to give free C_5Me_5H and unidentified cerium complexes. From these observations we tentatively assign the resonance at 11.61 ppm to the more accessible terminal $OCMe_3$ ligands.

White crystalline $(C_5Me_5La(OCMe_3)_2)_2$ (**2**) was obtained by a procedure similar to that used for **1**. The isolated yield (30%) is rather low owing to the extremely high solubility of the complex in hydrocarbons, which makes crystallization rather cumbersome. The IR and NMR spectral characteristics of **2** also suggest a dimeric structure. The ^1H NMR spectrum contains two distinct $OCMe_3$ groups, at 1.33 and 1.27 ppm. The ^{13}C NMR spectra in benzene-d_6 also show signals from two chemically inequivalent $OCMe_3$ groups, with quarternary carbon signals at 73.6 and 71.0 ppm and the methyl carbon resonances at 34.4 and 33.5 ppm.

In an attempt to obtain monomeric complexes of the $C_5Me_5Ce(OR)_2$ type, we examined the reaction of $(C_5Me_5)_2CeCH(SiMe_3)_2$ with 2,6-di-t-butylphenol. Treatment of $(C_5Me_5)_2CeCH(SiMe_3)_2$ with 2,6-di-t-butylphenol at room temperature gave $CH_2(SiMe_3)_2$ (^1H NMR) and intensely-red crystalline $(C_5Me_5)_2$(2,6-di-t-butylphenoxo)cerium (**3**, eq. 2).

$$(C_5Me_5)_2CeCH(SiMe_3)_2 + \text{2,6-di-t-butylphenol} \rightarrow \underset{(\mathbf{3})}{(C_5Me_5)_2\text{(2,6-di-t-butylphenoxo)cerium}} + CH_2(SiMe_3)_2 \quad (2)$$

The reaction of $(C_5Me_5)_2CeCH(SiMe_3)_2$ with 2 equivalents of 2,6-di-t-butylphenol was monitored by ^1H NMR spectroscopy (benzene-d_6). Fast reaction took place at room temperature, with quantitative formation of **3** and $CH_2(SiMe_3)_2$. C_5Me_5H was liberated when the mixture was heated to 80 °C, giving a mixture of tris(2,6-di-t-butylphenoxo)cerium (**4**) and **3** (eq. 3).

$$(C_5Me_5)_2CeCH(SiMe_3)_2 + 2\ \text{2,6-di-t-butylphenol} \xrightarrow{80\,^\circ C} C_5Me_5H + CH_2(SiMe_3)_2 + \tfrac{1}{2}\mathbf{3} + \tfrac{1}{2}\mathbf{4} \quad (3)$$

The outcome of the reaction can in principle be accounted for by assuming disproportionation of initially formed (C_5Me_5)bis(2,6-di-t-butylphenoxo)cerium (**5**) to **3** and tris(2,6-di-t-butylphenoxo)cerium. However monomeric **5** has been prepared independently, and is stable towards disproportionation under these conditions [15], so it is more likely that the rate of C_5Me_5H abstraction from **5** exceeds that of the first C_5Me_5H abstraction from **3**.

From this result it is clear that **5** is less stable towards the excess of alcohol than **1**. These differences can be rationalized on steric grounds. $C_5Me_5Ce(OCMe_3)_2$ is sterically unsaturated and dimerizes to **1**. In contrast, monomeric **5** is more open, and this results in enhanced reactivity towards alcohols.

The molecular structure of 1

To confirm the stoichiometry and assign the geometry of **1** and **2**, a crystallographic study was undertaken on the cerium analogue. The solid state structure of the molecule is depicted in Fig. 2. The molecule is dimeric with a cerium(III) ion coordinated to one η^5-C_5Me_5 ligand, one terminal $OCMe_3$, and two bridging $OCMe_3$ groups, giving the metal a formal coordination number of 6. The geometry

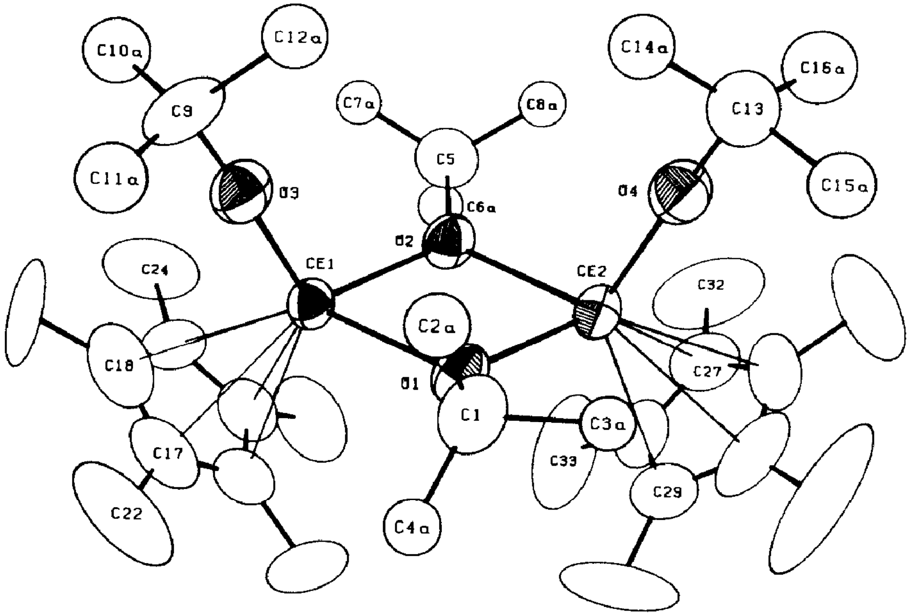

Fig. 2. X-Ray structure of $(C_5Me_5Ce(OCMe_3)_2)_2$, showing the numbering scheme. For clarity, only one orientation of each disordered $OCMe_3$ group is shown.

Table 3

Bond distances (Å) and angles (deg) for $[(\eta^5\text{-}C_5Me_5)Ce(O\text{-}t\text{-}Bu)_2]_2$

Atoms	Distance	Atoms	Distance
Ce(1)-O(1)	2.401(6)	Ce(1)-O(2)	2.396(6)
Ce(1)-O(3)	2.116(6)	Ce(1)-C(17)	2.83(1)
Ce(1)-C(18)	2.84(2)	Ce(1)-C(19)	2.82(1)
Ce(1)-C(20)	2.82(1)	Ce(1)-C(21)	2.82(1)
Ce(2)-O(1)	2.380(6)	Ce(2)-O(2)	2.431(6)
Ce(2)-O(4)	2.124(6)	Ce(2)-C(27)	2.78(1)
Ce(2)-C(28)	2.80(1)	Ce(2)-C(29)	2.82(1)
Ce(2)-C(30)	2.84(1)	Ce(2)-C(31)	2.80(1)
O(1)-C(1)	1.47(1)	O(2)-C(5)	1.44(1)
O(3)-C(9)	1.46(1)	O(4)-C(13)	1.45(1)
C-Cav.	1.6(1)		
C-C(Cp)	1.41(2)	C-Me(Cp)	1.52(3)
Cent1 [a]-Ce(1)	2.56	Cent2-Ce(2)	2.54

Atoms	Angle	Atoms	Angle
O(1)-Ce(1)-O(2)	74.7(2)	O(1)-Ce(1)-O(3)	107.0(2)
O(2)-Ce(1)-O(3)	111.8(2)	O(1)-Ce(2)-O(3)	74.4(2)
O(1)-Ce(2)-O(4)	109.1(2)	O(2)-Ce(2)-O(4)	107.0(2)
Ce(1)-O(1)-Ce(2)	106.1(2)	Ce(1)-O(1)-C(1)	127.0(6)
Ce(2)-O(1)-C(1)	122.6(6)	Ce(1)-O(2)-Ce(2)	104.7(2)
Ce(1)-O(2)-C(5)	124.9(6)	Ce(2)-O(2)-C(5)	125.4(6)
Ce(1)-O(3)-C(9)	176.9(7)	Ce(2)-O(4)-C(13)	176.6(7)
O-C-Cav.	107 (4)	C-C-Cav.	112 (8)
C-C-C(Cp)	108 (1)	C-C-Me(Cp)	126 (2)
Cent1-Ce(1)-O(1)	122.1	Cent2-Ce(2)-O(1)	122.9
Cent1-Ce(1)-O(2)	120.1	Cent2-Ce(2)-O(2)	123.3
Cent1-Ce(1)-O(3)	114.8	Cent(2)-Ce(2)-O(4)	113.8

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[a] Cent1 refers to the centroid of the Cp ring containing C(17)-C(21); Cent2, C(27)-C(31).

around the cerium (III) ion is best described as a distorted tetrahedron. Relevant bond lengths and angles, with estimated standard deviations, are given in Table 3.

The C_5Me_5 groups are η^5-coordinated, with endocyclic C–Ce bond distances between 2.78(1) and 2.84(2) Å. These values are in the range observed for $C_5Me_5CeI_2 \cdot 3THF$ [4] and $(C_5Me_5)_2CeCH(SiMe_3)_2$ [11]. The oxygens of the bridging $OCMe_3$ group and the two cerium atoms are coplanar within 0.017 Å, with a Ce–Ce distance of 3.822(1) Å. The sum of the internal angles is 359.9°.

The observed *cis*-configuration of the terminal $OCMe_3$ and C_5Me_5 ligands seems to be favoured because it minimizes the steric repulsions between the C_5Me_5 ring and the bridging $OCMe_3$ ligands. The angles O(1)–O(2)–C(5) and O(2)–O(1)–C(1) are 159.3(5) and 163.3(5)°, respectively, so the CMe_3 group of the bridging alkoxide ligands are pointed away from the bulky C_5Me_5 ring. The Ce–O terminal $OCMe_3$ distances (av. 2.120(4) Å) are at the short end of the range previously observed for a number of cerium complexes; viz. 2.14 Å (mean) for tris(2,6-di-t-butylphenoxo)cerium [13] and 2.23 Å (mean) for tris(2,6-di-t-butylphenoxo)bis($NCCMe_3$)cerium [13]. The Ce–O bridging $OCMe_3$ bond lengths (mean 2.40 Å) are rather long.

Supplementary material: Tables of atom coordinates, thermal parameters, complete tables of bond distances and angles and structure factors for **1** have been deposited at the National Auxiliary Publications Service no. 04644 P.O. Box 3513, Grand Central Station, New York, N.Y. 10017, U.S.A.

Conclusions

Alcoholysis of the Ce–C bonds of $(C_5Me_5)_2CeCH(SiMe_3)_2$ provides an attractive route to cerium alkoxides/aryloxides. The Ce–C σ-bond is easily cleaved, and the nature of the alcohol used and the reaction conditions determine whether the C_5Me_5 ligands will be liberated.

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