

Cerium Aryloxides as Precursors for Monopentamethylcyclopentadienyl Organocerium(III) Compounds; X-Ray Crystal Structure of (η^5 -Pentamethylcyclopentadienyl)bis(2,6-di-*t*-butylphenoxy)cerium

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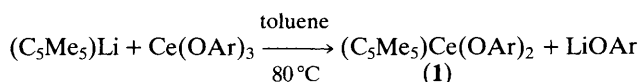
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Tris(2,6-di-*t*-butylphenoxy)cerium reacts with $(C_5Me_5)Li$ in pentane to form (η^5 - C_5Me_5)bis(2,6-di-*t*-butylphenoxy)cerium, whose structure was established by X-ray crystallography and which, on subsequent reaction with $LiCH(SiMe_3)_2$, gives a novel mono(C_5Me_5)cerium-bisalkyl complex, $(C_5Me_5)Ce[CH(SiMe_3)_2]_2$.

Well defined mono(C_5Me_5) complexes of the early lanthanides (La, Ce, Pr, and Nd) are scarce owing to easy loss of co-ordinated solvent,¹ non-stoichiometric salt complexation, and a strong preference for the formation of bis(C_5Me_5) complexes.² Only with very specific starting materials, *e.g.* metal iodides instead of metal chlorides, could stable complexes be obtained.¹

Recently Lappert *et al.*, have reported the use of lanthanide aryloxides ($M = La, Sm, \text{ and } Lu$) to synthesize salts and co-ordinated-solvent-free homoleptic lanthanide-alkyls.³ Here we describe the use of a cerium aryloxide, tris(2,6-di-*t*-butylphenoxy)cerium, as a convenient starting material for the selective introduction of one (C_5Me_5) group, giving (C_5Me_5)bis(2,6-di-*t*-butylphenoxy)cerium (**1**).

Stirring $(C_5Me_5)Li$ and tris(2,6-di-*t*-butylphenoxy)cerium in toluene at 80 °C over 20 h resulted in the formation of an intense yellow-orange suspension. After removal of the solvent, extraction of the residue with pentane, and crystallization at -80 °C, compound (**1**) was isolated as intense yellow crystals in 76% yield (Scheme 1). † (**1**) is very air-sensitive both in solution and the solid state and soluble in common solvents [Et_2O , tetrahydrofuran (THF), pentane, benzene, and toluene].



Scheme 1. OAr = 2,6-di-*t*-butylphenoxyde.

Crystals of (**1**), suitable for X-ray crystallographic analysis, were obtained by slowly cooling a saturated pentane solution to -30 °C. ‡ Figure 1 shows a PLUTO drawing of (**1**) with the adopted numbering scheme. The molecule crystallizes in monomeric units which consist of a cerium atom bonded to

† Spectral data for (**1**): 1H n.m.r. (300 MHz, 22 °C, C_6D_6) δ 9.91 (s, $lw = 23$ Hz, 4H), δ 9.02 (s, $lw = 18$ Hz, 2H) δ 2.71 (s, $lw = 80$ Hz, 15H), δ -4.6 (s, $lw = 200$ Hz, 36H). I.r. (KBr/Nujol, cm^{-1}): 3040, 2720, 2120, 1580, 1400, 1355, 1240, 1200, 1115, 1090, 1015, 880, 860, 820, 745, 640, 625, 540, 450. Satisfactory microanalytical results were obtained ($lw =$ linewidth at half maximum).

‡ Crystal data for (**1**): $C_{38}H_{57}CeO_2$ monoclinic, space group $P2_1$, cell dimensions: $a = 9.575(1)$, $b = 17.026(2)$, $c = 11.530(1)$ Å, $\beta = 112.02(1)^\circ$, $T = 130$ K, $V = 1742.6(3)$ Å³, $D_c = 1.307$ g cm^{-3} , $Z = 2$, $F(000) = 718$, $\mu(Mo-K\alpha) = 13.5$ cm^{-1} . The structure was solved by standard Patterson methods (Ce) and extension of the model was accomplished by DIRDIF. Anisotropic block-diagonal least-squares refinement for the non-hydrogen atoms and one common thermal parameter for the hydrogen atoms with 3703 observed reflections [$I > 2.5 \sigma(I)$] and 542 parameters converged at $R_F = 0.023$, $R_w = 0.028$, g.o.f. = 1.578. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

two terminal aryloxide ligands and a 'dished' η^5 -co-ordinated (C_5Me_5) ring, giving a formal co-ordination number of 5. Of great interest is the bonding of the aryloxide ligands. The Ce(1)-O(1)-C(11) angle of $158.6(2)^\circ$ is in the range as observed for O-bonded lanthanide, actinide and transition metal aryloxide complexes.⁴ The bonding of the other aryloxide ligand is unprecedented with an extremely small Ce(1)-O(2)-C(25) angle of $105.0(2)^\circ$. The Ce-O distances, 2.245(3) and 2.257(3) Å, do not differ significantly. These data do not fit into the pattern observed for a number of lanthanide, actinide and transition metal alkoxides and aryloxides: large M-O-C angles are coupled with short M-O distances, rationalized by assuming partial multiple bond character in the M-O-C linkage.⁵ The small angle could be the result of an interaction between the C(38)-methyl group and the cerium atom. The Ce(1)-C(38) distance is 3.097(5) Å, which is much shorter than the sum of the methyl van der Waals radius (2.0 Å)⁶ and the cerium metallic radius (1.82 Å).⁷ Also two of the hydrogen atoms bonded to C(38) are close to the cerium centre [Ce-H distances of 2.58 (3) and 2.88 (3) Å, which again are significantly shorter than the sum of the hydrogen van der Waals radius (1.2 Å)⁷ and the cerium metallic radius]. Similar interactions to reduce the electron-deficiency of Lewis acid metal centres are observed in a number of lanthanide and related complexes *e.g.* $Yb[N(SiMe_3)_2]_2(Me_2PCH_2CH_2PMe_2)$,⁸ $(C_5Me_5)_2YN(SiMe_3)_2$,⁹ $(C_5Me_5)_2YCH(SiMe_3)_2$,⁹ $Me_2Si(C_5Me_5)_2NdCH(SiMe_3)_2$,¹⁰ and $(C_5Me_5)_2CeCH(SiMe_3)_2$.¹¹

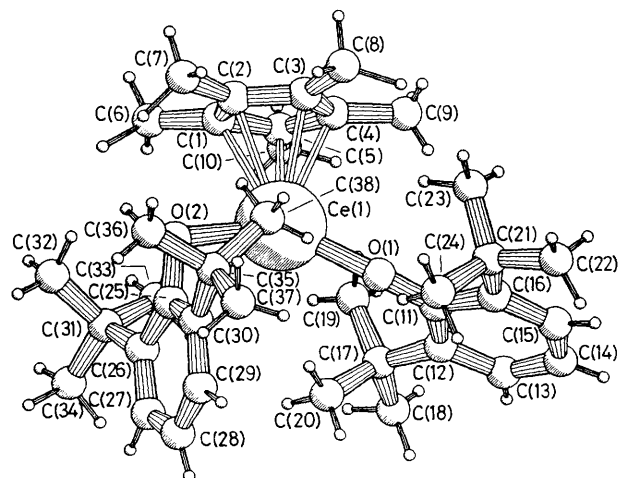
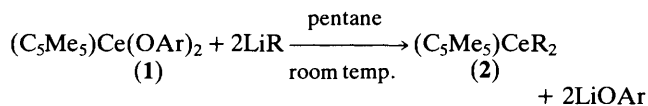


Figure 1. Molecular structure and labelling scheme for (**1**). Selected bond lengths (Å) and angles ($^\circ$): Ce(1)-CG(1), 2.479(2); Ce(1)-O(1), 2.245(3); Ce(1)-O(2), 2.257(3); O(1)-C(11), 1.341(5); O(2)-C(25), 1.354(5); Ce(1)-O(2)-C(25), $105.0(2)^\circ$; Ce(1)-O(1)-C(11), $158.6(2)^\circ$; O(1)-Ce(1)-O(2), $135.2(1)^\circ$ [CG(1) = ring centroid of C(1)C(2)C(3)C(4)C(5)].

Currently we are exploring the use of (1) for further substitution chemistry. As a specific example we mention the metathesis of (1) with $\text{LiCH}(\text{SiMe}_3)_2$ in pentane, giving substitution of the two aryloxy ligands with the formation of the first salt and solvent free mono(C_5Me_5)-lanthanide-bis-alkyl complex, $(\text{C}_5\text{Me}_5)\text{Ce}[\text{CH}(\text{SiMe}_3)_2]_2$ (2) (Scheme 2). Compound (2) is highly soluble in Et_2O , pentane and benzene. The compound is thermally rather labile. Slow decomposition takes place at room temperature (C_6D_6 , $t_{1/2}$ ca. 30 h) with the formation of $\text{CH}_2(\text{SiMe}_3)_2$ and a yet unidentified organocerium complex.



Scheme 2. OAr = 2,6-di-*t*-butylphenoxide, R = $-\text{CH}(\text{SiMe}_3)_2$.

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§ Spectral data for (2): ^1H n.m.r. (300 MHz, C_6D_6 , 21 °C): δ 2.84 (s, l_w = 28 Hz, 15H), δ -7.61 (s, l_w = 300 Hz, 36H), α -CH protons not observed. I.r. (KBr/Nujol, cm^{-1}): 2750, 2720, 1255, 1240, 1055, 1010, 855, 830, 780, 760, 710, 680, 660, 650, 580. Satisfactory micro-analytical results were obtained (l_w = linewidth at half maximum).

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