View Article Online / Journal Homepage / Table of Contents for this issue

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

Hero J. Heeres, Auke Meetsma, and Jan H. Teuben

Department of Chemistry, University of Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands

Published on 01 January 1988. Downloaded by University of Illinois at Chicago on 24/10/2014 14:23:51.

Tris(2,6-di-t-butylphenoxo)cerium reacts with $(C_5Me_5)Li$ in pentane to form (η^5-C_5Me_5)bis(2,6-di-t-butylphenoxo)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-stoicheiometric 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, 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-butylphenoxo)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-butylphenoxo)cerium (**1**).

Stirring (C_5Me_5)Li and tris(2,6-di-t-butylphenoxo)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].

$$(C_5Me_5)Li + Ce(OAr)_3 \xrightarrow[80\,^\circ C]{toluene} \underset{(1)}{(C_5Me_5)Ce(OAr)_2} + LiOAr$$

Scheme 1. OAr = 2,6-di-t-butylphenoxide.

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 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)° 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)°. 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]

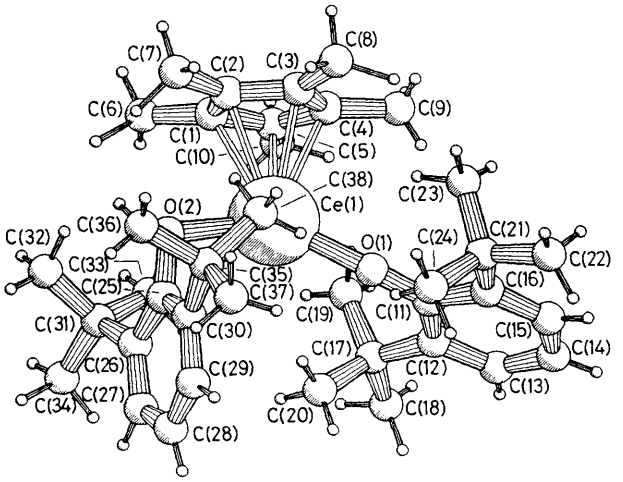

Figure 1. Molecular structure and labelling scheme for (**1**). Selected bond lengths (Å) and angles (°): Ce(1)–CG(1), 2.479(2); Ce(1)–O(1), 2.245(3); Ce(1)–O(2), 2.257(3); O(1)–C(11), 1.341(5); O(2)–C(25), 1.354(5); Ce(1)–O(2)–C(25), 105.0(2); Ce(1)–O(1)–C(11), 158.6(2); O(1)–Ce(1)–O(2), 135.2(1) [CG(1)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

† *Spectral data* for (**1**): ^{1}H 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, β = 112.02(1)° T = 130 K, V = 1742.6(3) Å^3, D_c = 1.307 g cm^{-3}, Z = 2, $F(000)$ = 718, μ(Mo-K_α) = 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.

View Article Online

Published on 01 January 1988. Downloaded by University of Illinois at Chicago on 24/10/2014 14:23:51.

Currently we are exploring the use of (**1**) for further substitution chemistry. As a specific example we mention the metathesis of (**1**) with $LiCH(SiMe_3)_2$ in pentane, giving substitution of the two aryloxide ligands with the formation of the first salt and solvent free mono(C_5Me_5)-lanthanide-bis-alkyl complex, $(C_5Me_5)Ce[CH(SiMe_3)_2]_2$ (**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 $CH_2(SiMe_3)_2$ and a yet unidentified organocerium complex.

$$\underset{(\mathbf{1})}{(C_5Me_5)Ce(OAr)_2} + 2LiR \xrightarrow[\text{room temp.}]{\text{pentane}} \underset{(\mathbf{2})}{(C_5Me_5)CeR_2} + 2LiOAr$$

Scheme 2. OAr = 2,6-di-t-butylphenoxide, R = $-CH(SiMe_3)_2$.

We thank Shell Research B.V. for financial support.

Received, 7th March 1988; Com. 8/00911B

§ *Spectral data* for (**2**): ^1H n.m.r. (300 MHz, C_6D_6, 21 °C): δ 2.84 (s, lw = 28 Hz, 15H), δ −7.61 (s, lw = 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 microanalytical results were obtained (lw = linewidth at half maximum).

References

1 P. N. Hazin, J. C. Huffman, and J. W. Bruno, *Organometallics,* 1987, **6**, 23.
2 M. Booij, N. H. Kiers, H. J. Heeres, A. Meetsma, and J. H. Teuben, *J. Organomet. Chem.*, submitted for publication.
3 M. F. Lappert and R. G. Smith, The Second International Conference on the Basic and Applied Chemistry of f-Transition and Related Elements, Lissabon, 1987, Abstract No. P(II)1.
4 P. B. Hitchcock, M. F. Lappert, and R. G. Smith, *Inorg. Chim. Acta,* 1987, **139**, 183; P. B. Hitchcock, M. F. Lappert, A. Singh, R. G. Taylor, and D. Brown, *J. Chem. Soc., Chem. Commun.,* 1983, 561; L. R. Chamberlain, L. D. Durfee, P. E. Fanwick, L. M. Kobriger, S. L. Latesky, A. K. McMullen, B. D. Steffey, I. P. Rothwell, K. Folting, and J. C. Huffman, *J. Am. Chem. Soc.,* 1987, **109**, 6068; S. M. Beshouri, P. E. Fanwick, I. P. Rothwell, and J. C. Huffman, *Organometallics,* 1987, **6**, 2498.
5 W. J. Evans, T. P. Hanusa, and K. R. Levan, *Inorg. Chim. Acta,* 1985, **110**, 191.
6 L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, NY, 1960, p. 260.
7 W. W. Porterfield, 'Inorganic Chemistry, A Unified Approach,' Addison-Wesley Publishing Company, 1984, p. 180.
8 T. D. Tilley, R. A. Andersen, and A. Zalkin, *J. Am. Chem. Soc.,* 1982, **104**, 3725.
9 K. H. den Haan, J. L. de Boer, J. H. Teuben, A. L. Spek, B. Kojić-Prodić, G. R. Hays, and R. Huis, *Organometallics,* 1986, **5**, 1726.
10 G. Jeske, L. E. Schock, P. N. Swepston, H. Schumann, and T. J. Marks, *J. Am. Chem. Soc.,* 1985, **107**, 8103.
11 H. J. Heeres, J. Renkema, M. Booij, A. Meetsma, and J. H. Teuben, *Organometallics*, in the press.