Three- and Four-co-ordinate, Hydrocarbon-soluble-Aryloxides of Scandium, Yttrium, and the Lanthanoids; *X*-Ray Crystal Structure of Tris(2,6-di-t-butyl-4-methylphenoxo)scandium†

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Five new classes of crystalline, hydrocarbon-soluble group 3A metal (M) aryloxides are reported: $[M(OAr)_3]$, (**1**), $[M(L)(OAr)_3]$ [L = tetrahydrofuran (thf) or $P(O)Ph_3$], $[M(OAr)_2(\mu\text{-}OAr)_2Na(thf)_2]$, $Li[Yb(Cl)(OAr)_3]$, and $[\{Y(Cl)(OAr)(\mu\text{-}OAr)\}_2]$ ($Ar = C_6H_2Me\text{-}4\text{-}Bu^t_2\text{-}2,6$), ranging for (**1**) from M^{3+} being the $3d^0$, $4d^0$, to the $4f^n$ (n = 0, 1, 2, 3, 9, 10, 11, or 13) ion; the title compound (**1**) (M = Sc) has an approximately trigonal planar ScO_3 skeleton (Sc 0.13 Å out of the O_3 plane) with av. Sc–O 1.869(15) Å, av. O–Sc–O 119.5(2)°, and av. Sc–O–C 168.4(5)°.

The chemistry of Sc, Y, and the lanthanoid elements, collectively here designated as M, is dominated by complexes in which M is in a high co-ordination number (c.n.) environment. Indeed only seven compounds of c.n. = three or four are crystallographically authenticated and these represent just four types: $[M\{N(SiMe_3)_2\}_3]$ (M = Sc,[1] Nd,[2] Eu,[1] or Yb[1]),

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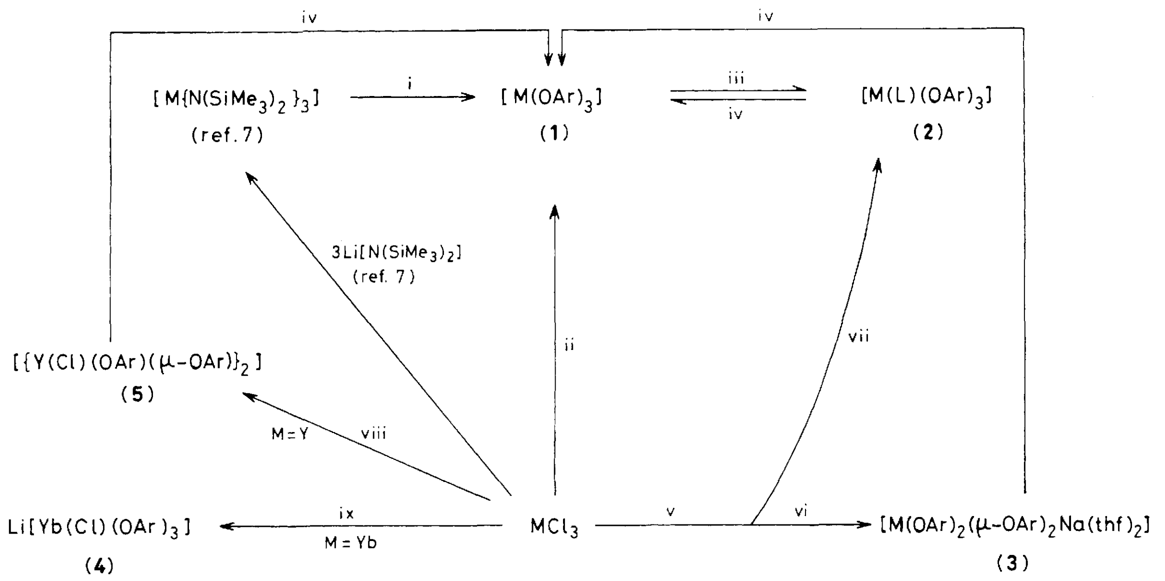
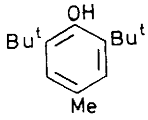
† No reprints available.



Scheme 1. *Abbreviations:* Ar = $C_6H_2Me\text{-}4\text{-}Bu^t{}_2\text{-}2,6$, M = Sc, Y, or a $4f^n$ metal, thf = tetrahydrofuran. *Reagents and conditions:* i, 3 ArOH, n-C_6H_{14}, 20 °C, 12 h, then reflux, 12 h; ii, 3 $NaOAr(OEt_2)$, thf, reflux, $\geqslant$36 h; iii, L [= thf or $P(O)Ph_3$], PhH, 20 °C, 18 h; iv, sublime *in vacuo*; v, 3 $NaOAr(OEt_2)$, thf, 20 °C, 16 h, then successive reflux, 24 h, solvent removal *in vacuo*, n-C_5H_{12}, and filtration; vi, precipitate from v; vii, filtrate from v; viii, $[Li(\mu\text{-}OAr)(OEt_2)]_2$, PhMe, 20 °C, 72 h, then reflux, 5 h; ix, $[Li(\mu\text{-}OAr)(OEt_2)]_2$, PhMe, 20 °C, 48 h, then reflux, 36 h. *Isolation procedures*: (**1**) sublimation at 250—260 °C/10^{-3} Torr; (**2**), crystallisation at −30 °C [n-C_5H_{12} for (**2**) or (**3**); PhMe for (**4**) or (**5**)]. *Characterisation*: compounds (**1**) [M = Sc (150—152), Y (178—180), La (195—197), Pr (y, 200—204), Nd (bv, 220—221), Dy (214—216), Ho (y, 198—200), Er (p, 180—182), or Yb (m, 215—218): colours: y = yellow, bv = blue-violet, p = pink, and m = maroon and m.p.s/°C, in parentheses)], (**2**) [L = thf and M = Sc, Y, La, Pr, Nd, Dy, Ho, Er, or Yb; or L = $P(O)Ph_3$ and M = Yb], (**3**) (M = La or Yb), (**4**) (maroon), and (**5**) are crystalline, gave satisfactory microanalytical results, showed for (**1**) parent molecular ions $(\mathbf{1})^+$ in the mass spectra and monomeric cryoscopic behaviour in C_6H_{12}, and provided reasonable ^1H and ^{13}C n.m.r. spectra in C_6D_6 for the colourless Sc, Y, and La complexes; assignment of structures (**3**) (M = La) and (**5**) is based on the ^1H n.m.r. observation of distinct $\overline{\mathrm{O}}\mathrm{Ar}_{\mathrm{terminal}}$ and $\overline{\mathrm{O}}\mathrm{Ar}_{\mathrm{bridging}}$ signals.

$[La\{N(SiMe_3)_2\}_3\{P(O)Ph_3\}]$,[3] $[Lu(C_6H_2Me_3\text{-}2,4,6)_4]^-$,[4] and $[Yb\{CH(SiMe_3)_2\}_3Cl]^-$.[5]

We now report well-characterised, hydrocarbon-soluble, crystalline monomeric [(**1**)—(**4**) in Scheme 1] or dimeric [(**5**)] aryloxometal(III) complexes of five distinct classes, derived from the bulky phenol (**6**) (= ArOH) (we have also made some similar compounds using $2,6\text{-}Bu^t{}_2C_6H_3OH$ or $2,4,6\text{-}Bu^t{}_3C_6H_2OH$). The three-co-ordinate homoleptic complexes $[M(OAr)_3]$, (**1**), are especially noteworthy, (i) because this c.n. is unusual in transition metal chemistry,[6] (ii) because of their volatility, and (iii) because of the demonstration by *X*-ray crystallography of a *ca.* D_{3h} trigonal planar MO_3 skeleton for M = Sc (by contrast, the amides[7] have a C_{3v} MN_3 arrangement[1,2]).



(**6**)

Whereas *alkoxides* of Sc, Y, and the lanthanoids are often organic solvent-soluble and volatile, they are nevertheless oligomers, by solution molecular weight.[8] A rare single crystal *X*-ray analysis of a chloride-containing tris(isopropoxy)-neodymium(III), shows a structure based on a hexamer with one of the 18 $\overline{\mathrm{O}}\mathrm{Pr}^i$ groups replaced by $\overline{\mathrm{Cl}}$.[9] By contrast, previous examples of *aryloxides* have been insoluble, involatile, and presumably polymeric;[10] except for two examples of aryloxo(chloro)metal complexes, (**7**) and (**8**), which we have already briefly described.[11]

$[Y(OAr)_2(\mu\text{-}Cl)_2Li(thf)_2]$ (**7**)

$[M(Cl)(OAr)(\mu\text{-}Cl)_2Li(thf)_2]$ (**8**) (M = Y, La, or Er)

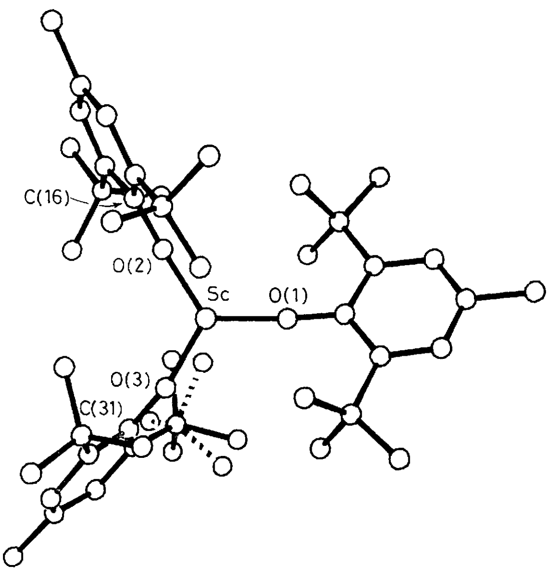


Figure 1. The molecular structure of $[Sc(OC_6H_2Me\text{-}4\text{-}Bu^t{}_2\text{-}2,6)_3]$ and the atom numbering scheme. Relevant dimensions are: Sc–O(1) 1.889(5), Sc–O(2) 1.854(5), Sc–O(3) 1.865(5) Å, O(1)–Sc–O(2) 123.3(2), O(1)–Sc–O(3) 120.1(2), O(2)–Sc–O(3) 115.1(2), Sc–O(1)–C(1) 173.1(5), Sc–O(2)–C(16) 163.8(5), Sc–O(3)–C(31) 168.3(5)°.

From Scheme 1 it will be seen that the aryloxide ligand is introduced either *via* the alkali metal reagent $[M'OAr(OEt_2)]_n$

(M′ = Li and $n = 2$, or M′ = Na and n is not determined)[12] and MCl_3 or, for $[M(OAr)_3]$, ArOH and $[M\{N(SiMe_3)_2\}_3]$; and may be not only terminally bound but also bridging, as in complexes (**3**) and (**5**). It is interesting that in complex (**5**) there is preference for $\bar{O}Ar$ rather than $\bar{C}l$ bridging; in (**8**) the assignment of structure (*i.e.*, the reverse preference) was based[11] solely on analogy with that for (**7**), in which only a single $\bar{O}Ar$ environment was observed on the n.m.r. time scale at ambient temperature. Other 2,6-di-t-butylphenoxo-metal complexes have recently attracted much attention, *inter alia* for derivatives of Ge^{II}, Sn^{II}, Pb^{II}, P^{II}, Ti^{III}, Hf^{IV}, Ta^{V}, Th^{IV}, and U^{IV}.[13]

Crystal data: $C_{45}H_{69}O_3Sc$, triclinic, $P\bar{1}$, $a = 9.851(2)$, $b = 15.138(6)$, $c = 15.706(8)$ Å, $\alpha = 70.38(4)$, $\beta = 82.59(3)$, $\gamma = 80.57(3)°$, $Z = 2$. The crystal used gave only limited diffraction data. Least-squares refinement, based on 2077 reflections measured on a CAD-4 diffractometer with Mo-K_α radiation, converged at R 0.12.‡

The Sc atom is trigonally planar co-ordinated by the three oxygen atoms. The deviation of the Sc atom from this plane is only 0.13 Å and the average of the three O–Sc–O angles is 119.5°. The very large Sc–O–C angles (av. 168.4°) are presumably a reflection of the steric crowding. The structure is illustrated in Figure 1.

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‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

References

1 J. S. Ghotra, M. B. Hursthouse, and A. J. Welch, *J. Chem. Soc., Chem. Commun.*, 1973, 669.
2 R. A. Andersen, D. H. Templeton, and A. Zalkin, *Inorg. Chem.*, 1978, **17**, 2317.
3 D. C. Bradley, J. S. Ghotra, F. A. Hart, M. B. Hursthouse, and P. R. Raithby, *J. Chem. Soc., Dalton Trans.*, 1977, 1166.
4 S. A. Cotton, F. A. Hart, M. B. Hursthouse, and A. J. Welch, *J. Chem. Soc., Chem. Commun.*, 1972, 1225.
5 J. L. Atwood, W. E. Hunter, R. D. Rogers, J. Holton, J. McMeeking, R. Pearce, and M. F. Lappert, *J. Chem. Soc., Chem. Commun.*, 1978, 140.
6 *Cf.* P. G. Eller, D. C. Bradley, M. B. Hursthouse, and D. W. Meek, *Coord. Chem. Rev.*, 1977, **24**, 1.
7 D. C. Bradley, J. S. Ghotra, and F. A. Hart, *J. Chem. Soc., Dalton Trans.*, 1973, 1021.
8 *Cf.* D. C. Bradley, R. C. Mehrotra, and D. P. Gaur, 'Metal Alkoxides,' Academic Press, 1978.
9 R. A. Andersen, D. H. Templeton, and A. Zalkin, *Inorg. Chem.*, 1978, **17**, 1962.
10 *Cf.* K. C. Malhrotra and R. L. Martin, *J. Organomet. Chem.*, 1982, **239**, 159.
11 M. F. Lappert, A. Singh, J. L. Atwood, and W. E. Hunter, *J. Chem. Soc., Chem. Commun.*, 1981, 1191.
12 B. Çetinkaya, I. Gümrükçü, M. F. Lappert, J. L. Atwood, and R. Shakir, *J. Am. Chem. Soc.*, 1980, **102**, 2086.
13 P. B. Hitchcock, M. F. Lappert, A. Singh, R. G. Taylor, and D. Brown, *J. Chem. Soc., Chem. Commun.*, 1983, 561; and references therein.