The Synthesis and Structure of the Alkaline Earth Metal Organic Compounds $[M(OAr)_2(thf)_n]$ [M = Ca, n = 3 (1) or 0; M = Ba, n = 4] and $[\{Ca(NR_2)(\mu NR_2)(thf)\}_2]$, and the *X*-Ray Structure of (1) (Ar = $C_6H_2Bu^t{}_2$-2,6-Me-4; R = $SiMe_3$; thf = OC_4H_8)†

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Treatment of highly reactive, pyrophoric calcium or barium (obtained by co-condensation of the appropriate metal vapour and toluene) in tetrahydrofuran with (i) ArOH (Ca more reactive than Ba) affords the phenoxide $[M(OAr)_2(thf)_n]$ [M = Ca and n = 3 (**1**), or n = 0 after heating at 80 °C and 10^{-2} Torr; M = Ba, n = 4], or (ii) R_2NH (for M = Ca) yields $[\{Ca(NR_2)(\mu\text{-}NR_2)(thf)\}_2]$ [also obtained from (**1**) + $2LiNR_2$ in $n\text{-}C_6H_{14}$; Ar = $C_6H_2Bu^t{}_2$-2,6-Me-4; R = $SiMe_3$)]; the *X*-ray structure of crystalline (**1**) shows a distorted trigonal bipyramidal Ca environment with the thf ligands in apical sites.

The chemistry of the alkaline earth metals is dominated by the ionic character of the majority of their compounds. These generally have metal co-ordination numbers ⩾ 6. Very few organic derivatives, which are generally involatile and insoluble in organic solvents, have been structurally characterised. Exceptions are the lipophilic cyclopentadienyls: (i) $[M(\eta\text{-}C_5Me_5)_2]$ (M = Ca,[1] Sr,[2] and Ba[2]) for which diffraction data are available (gas: Ca,[1,3] Sr,[4] and Ba;[4] crystal: Ba[5]), and (ii) the *X*-ray - characterised $[Sr\{\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_2(thf)]$ (thf = tetrahydrofuran).[6] Their monomeric structures may be contrasted with those of the crystalline polymeric $[\{Ca(C_5H_5)_2\}_\infty]$.[7]

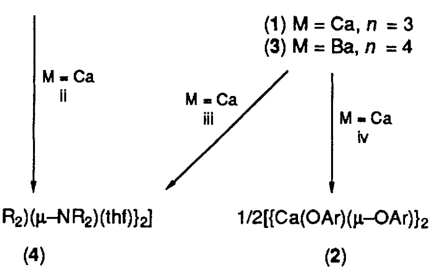
We now report on the synthesis (Scheme 1) of the novel, hydrocarbon-soluble, crystalline, colourless 2,6-di-t-butyl-4-methylphenoxides $[Ca(OAr)_2(thf)_3]$ (**1**), $[\{Ca(OAr)(\mu\text{-}OAr)\}_2]$ (**2**), $[Ba(OAr)_2(thf)_4]$ (**3**), and the bis[bis(trimethylsilylamide)] $[\{Ca(NR_2)(\mu\text{-}NR_2)(thf)\}_2]$ (**4**) (Ar = $C_6H_2Bu^t{}_2$-2,6-Me-4; R = $SiMe_3$). The assigned structures for (**1**)—(**4**) are consistent with their NMR spectra‡ and, for (**1**), single crystal *X*-ray diffraction data [structure determinations for (**3**)—(**4**) are in progress].§

A feature of the synthesis is the use of a highly reactive (pyrophoric) powder form of the alkaline earth metal, obtained by co-condensation of the metal vapour (from an ingot of the appropriate metal) and toluene,[8a] using the metal vapour synthesis (MVS) apparatus of ref. 8b. Calcium was significantly more reactive than barium in its reaction with the phenol ArOH; the former in thf afforded the phenoxide (**1**) at ambient temperature, whereas the latter required prolonged heating under reflux to yield (**3**). The Ca/2ArOH reaction did not proceed in refluxing hexane, even in the presence of $Me_2N(CH_2)_2NMe_2$.

A new strategy for synthesis of a metal amide, which may have some generality, is the $\bar{O}Ar/\bar{N}R_2$ exchange reaction, providing here a route to the calcium amide (**4**) from $[Ca(OAr)_2(thf)_3]$ (**1**) and $2/3[Li(\mu\text{-}NR_2)]_3$. The n-hexane-insoluble $[Li(\mu\text{-}OAr)(thf)]_2$[9] was readily removed. This procedure is an extension of that we reported earlier of an $\bar{O}Ar/(hydrocarbyl)^-$ exchange reaction,[10] which is already proving widely applicable;[11] we shall shortly describe its use for preparing alkaline earth metal bis(trimethylsilyl)methyls.

Alternatively, the crystalline calcium amide (**4**) was prepared by heating reactive calcium powder with hexamethyldisilazane under reflux in thf. There was no significant reaction at ambient temperature. The structure of (**4**) was established by molecular weight determination (cryoscopy in C_6H_6) and ambient-temperature ^1H and ^{13}C NMR spectroscopy.‡

The molecular structure of $[Ca(OAr)_2(thf)_3]$ (**1**) is illustrated in Figure 1. The calcium atom is co-ordinated by five oxygen atoms in a distorted trigonal bipyramidal (tbp) geometry, with two thf groups axial, O(3)–Ca–O(5) 177.8(3)°. The bonds from calcium to the $\bar{O}Ar$ ligands, average 2.206(6) Å, are shorter than those to the thf ligands: equatorial 2.378(7) Å, and axial (average) 2.418(7) Å. The atoms Ca, O(1), O(2), and O(4) are coplanar within 0.001 Å. The large O(1)–Ca–O(2) angle in the equatorial plane, 151.8(3)°, is attributable to the bulk of the aryl groups. This is



Scheme 1. *Abbreviations*: Ar = $C_6H_2Bu^t{}_2$-2,6-Me-4; R = $SiMe_3$, thf = OC_4H_8. *Reaction conditions*: i (M = Ca), 2ArOH, thf, 25 °C, 3 h; i (M = Ba), 2ArOH, thf, reflux, 3 h; ii, $2R_2NH$, thf, reflux, 3 h; iii, $2/3[Li(\mu\text{-}NR_2)]_3$, C_6H_{14}, 25 °C, 3 h; iv, 80 °C at 10^{-2} Torr, 3 h.

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† No reprints available.

‡ ^1H NMR chemical shifts (δ in ppm, C_6D_6, 305 K, for ^1H at 250 MHz and for ^{13}C at 125.8 MHz), ^1H: (**1**) 1.33 (m, 12H), 1.37 (s, 36H), 2.23 (s, 6H), 3.49 (m, 12H), and 7.04 (s, 4H); (**3**) 1.26 (m, 16H), 1.52 (s, 36H), 2.34 (s, 6H), 3.46 (m, 16H), and 7.15 (s, 4H); (**4**) 0.26 (s, 36H), 0.34 (s, 36H) 1.26 (m, 8H), and 3.55 (m, 8H); (**2**) 1.40 (s, 36H), 1.60 (s, 36H), 2.28 (s, 6H), 2.45 (s, 6H), 7.14 (s, 4H), and 7.24 (s, 4H). ^{13}C: (**1**) C(1) 163.6, C(2) 137.1, C(3) 125.6, C(4) 119.6, (2,6-$Bu^t{}_2$) 35.4, 31.5, (4-Me) 21.7, (thf) 69.0, 25.2; (**3**) C(1) 164.6, C(2) 136.3, C(3) 125.7, C(4) 119.4, (2,6-$Bu^t{}_2$) 34.9, 30.9, (4-Me) 21.6, (thf) 68.2, 25.4; (**4**) Me 5.2, 2.3, (thf) 68.7, 25.1; (**2**) 161.4, 155.8, C(2) 137.9, 136.4, C(3) 125.3, C(4) 121.7, (2,6-$Bu^t{}_2$) 35.0, 34.6, 33.3, 31.0, (4-Me) 21.6, 21.2.

§ *Crystal data for* (**1**): $C_{42}H_{70}CaO_5 \cdot C_4H_8O$, M = 767.2, monoclinic, space group $P2_1$ (No. 4), a = 9.891(8), b = 15.563(6), c = 15.449(9) Å, β = 95.52(5)°, U = 2367.1 $Å^3$, Z = 2, D_c = 1.08 g cm^{-3}, $F(000)$ = 844. $\mu(Mo\text{-}K_\alpha)$ = 1.7 cm^{-1}.

Data were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71069 Å). 4350 Unique reflections measured for $2 < \theta < 25°$ of which 2219 were considered observed [$I > 3\sigma(I)$]. The structure solution was by heavy-atom methods and refinement was by full-matrix least-squares. Hydrogen atoms were fixed at calculated positions except for those of the *para*-methyl groups and the solvate thf moieties. The final residuals were R = 0.076, R_w = 0.096. 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.

Table 1. Selected *X*-ray structural data on bivalent metal(II) bis(2,6-di-t-butylphenoxides).

Compound[a]	Av. M–O(Ar) /Å	(Ar)OMO(Ar) /°	Av. MOC-(sp^2)/°	Ref.
[Mg(OAr′)(μ-OAr′)(thf)]$_2$[b]	1.821(3)	—	173.6	14
[Ca(OAr)$_2$(thf)$_3$] (**1**)	2.206(6)	151.8(3)	175.9	This work
[Ge(OAr)$_2$]	1.818(8)	92.0(4)	128.6(7)	15
[Sn(OAr)$_2$]	2.008(4)	88.2(4)	128.6(4)	15
[Yb(OAr)$_2$(thf)$_2$]	2.137(9)	119.9(4)	175.3	12
[Yb(OAr)$_2$(thf)$_3$]	2.206(18)	154.8(10)	168.9	12
[Zn(OAr′)$_2$(thf)$_2$][b]	1.887(6)	121.7(3)	129.8	16

[a] Ar = $C_6H_2Bu^t{}_2$-2,6-Me-4; Ar′ = $C_6H_3Bu^t{}_2$-2,6; thf = OC_4H_8. [b] Data refer to the terminal $\bar{\mathrm{O}}$Ar′ ligand.

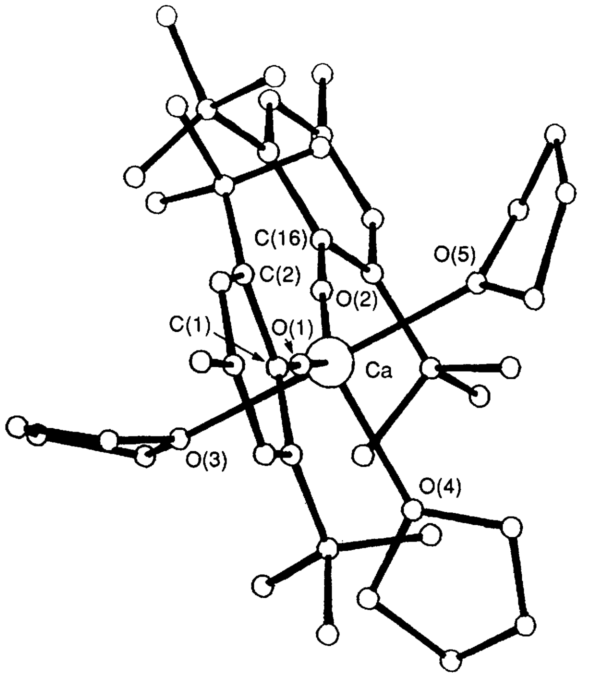

Figure 1. *X*-Ray structure of [Ca(OAr)$_2$(thf)$_3$] (**1**) [Ar = $C_6H_2Bu^t$-2,6-Me; thf = OC_4H_8] and atom numbering scheme. Selected bond lengths and angles: Ca–O(1) 2.201(6), Ca–O(2) 2.210(6), Ca–O(3) 2.418(7), Ca–O(4) 2.378(7), Ca–O(5) 2.419(7), O(1)–C(1) 1.305(10), O(2)–C(16) 1.346(11) Å; O(1)–Ca–O(2) 151.8(3), O(1)–Ca–O(3) 90.8(2), O(1)–Ca–O(4) 103.5(3), O(1)–Ca–O(5) 89.7(2), O(2)–Ca–O(3) 88.1(2), O(2)–Ca–O(4) 104.7(3), O(2)–Ca–O(5) 90.4(2), O(3)–Ca–O(4) 92.9(3), O(3)–Ca–O(5) 177.8(3), O(4)–Ca–O(5) 89.6(3)°.

also a major cause for the Ca–O–C (sp^2) angles to be essentially linear, 177.3(6) and 174.8(6)°, although $\overset{\curvearrowright}{\ddot{\mathrm{O}}\text{—}\mathrm{Ca}}$ π-bonding may be a contributory factor. The nature of phenoxide–metal binding for bivalent metal 2,6-di-t-butylphenoxides may be assessed from the data in Table 1.

The tbp configuration found for (**1**) contrasts with that for the isoleptic Yb^{II} complex [Yb(OAr)$_2$(thf)$_3$], which adopts a square-pyramidal co-ordination geometry with one thf ligand axial and a short Yb ··· Me contact of 3.4 Å to the methyl C atom of one of the OAr ligands filling the vacant sixth octahedral site.[12] There are no such contacts in the Ca complex (**1**), the shortest being Ca ··· C(8) 3.9 Å.

The only other calcium phenoxide for which structural data are available is [Ca{OC_6H_3-2,4-$(NO_2)_2$}$_2$]$(H_2O)_7$.[13] Each 2,4-dinitrophenoxide ligand co-ordinates *via* the phenoxide oxygen [Ca–O 2.361(5) Å] and one oxygen of an *ortho*-nitro group [Ca–O 2.507(5) Å].

Added in proof: Since submission of this paper a further paper has appeared concerning the preparation of activated Ca, Sr, and Ba products (M. J. McCormick, K. B. Moon, S. R. Jones, and T. P. Hanusa, *J. Chem. Soc., Chem. Commun.*, 1990, 778.) Compounds derived thus from included [Ca(OAr)$_2$ (thf)$_2$].

We thank Dr. F. G. N. Cloke for supervising the preparation of the reactive Ba and Ca samples on his MVS apparatus, and Lithco (and Dr. F. Reed), SERC, EEC (Stimulation Contract: ST 2000335), and Ministerio de Educacion y Ciencia, Spain, for support.

Received, 5th April 1990; Com. 0/01555E

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