Lipophilic Strontium and Calcium Alkyls, Amides and Phenoxides; X-Ray Structures of the Crystalline Square-planar [{*trans*-$Sr(NR'_2)_2(\mu$-1,4-dioxane)}$_\infty$] and Tetrahedral [CaR_2(1,4-dioxane)$_2$]; R' = $SiMe_3$, R = $CH(SiMe_3)_2$†

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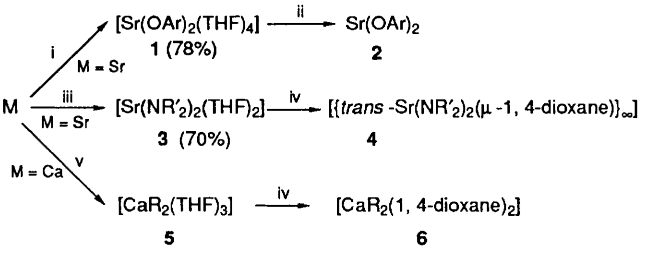
Treatment of pyrophoric strontium powder in tetrahydrofuran with ArOH (Ar = $C_6H_2Bu^t_3$-2,4,6) or HNR'_2 at ambient temperature affords crystalline [$Sr(OAr)_2(THF)_4$] or [$Sr(NR'_2)_2(THF)_2$] **3**, respectively, and **3** with 1,4-dioxane yields crystalline [{*trans*-$Sr(NR'_2)_2(\mu$-1,4-dioxane)}$_\infty$] **4**; co-condensation of calcium vapour and RBr in THF at 77 K affords [$CaR_2(THF)_3$] **5**, which with 1,4-dioxane gives [CaR_2(1,4-dioxane)$_2$] **6**; X-ray structures reveal the alkaline earth metal environment to be square-planar for **4** [Sr-N 2.449(7), Sr-O 2.533(9) Å] but tetrahedral for **6** [Ca-C 2.483(5), Ca-O 2.373(4) Å] with dioxane as a bridging bidentate **4** or monodentate **6** ligand.

We recently reported (*i*) the synthesis and characterisation of the lipophilic calcium and barium compounds [$M(OAr)_2(THF)_3$] [M = Ca, *n* = 3 **I** or M = Ba and *n* = 4 **II**], [{Ca(OAr)(μ-OAr)}$_2$] **III** and [{$Ca(NR'_2)(\mu$-$NR'_2)$ (THF)}$_2$] **IV**, (**I**–**IV** represent the corresponding compound numbers from the reference) and (*ii*) the X-ray structure of crystalline **I**, having a distorted trigonal bipyramidal structure (Ar = $C_6H_2Bu^t_2$-2,6-Me-4, R' = $SiMe_3$, THF = OC_4H_8).[1] These were the first well defined simple phenoxides and amides of the alkaline earth metals. Of organic derivatives of the alkaline earth metals only some cyclopentadienyls, including the X-ray authenticated [Sr{η-$C_5H_3(SiMe_3)_2$-1,3}$_2$(THF)],[2] had previously been decribed (*cf.* ref. 1). Further contributions to this area relate to (*a*) [$M(CPh_3)Cl(THF)_n$] (M = Ca or Ba and *n* = 2, or M = Sr and *n* = 4) and **III**,[3] and (*b*) the X-ray authenticated compounds [$HBa_5(O)(OPh)_3(THF)_8$], [$H_3Ba_6(O)(OBu^t)_{11}(OCEt_2CH_2O)(THF)_3$], and [$H_4Ba_6(O)(OCH_2CH_2OMe)_{14}$];[4] see also note added in proof, footnote ¶.

We now extend our studies to the hydrocarbon-soluble, crystalline, colourless (*i*) amides and phenoxides of strontium [$Sr(OAr)_2(THF)_4$] **1**, $Sr(OAr)_2$ **2**, [$Sr(NR'_2)_2(THF)_2$] **3**, [{*trans*-$Sr[NR'_2]_2(\mu$-1,4-dioxane)}$_\infty$] **4**; and (*ii*) alkyls of calcium [$CaR_2(THF)_3$] **5** and [CaR_2(1,4-dioxane)$_2$] **6** [R = $CH(SiMe_3)_2$]. Their synthesis is summarised in Scheme 1. The assigned structures for **1** and **3**–**6** are consistent with their NMR spectra‡ and for **4** and **6** single crystal X-ray diffraction



Scheme 1. *Abbreviations*: Ar = $C_6H_2Bu^t_2$-2,6-Me-4; R' = $SiMe_3$; R = $CH(SiMe_3)_2$; THF = OC_4H_8. *Reagents and conditions*: i, 2ArOH, THF, 25 °C, 3 h; ii, PhMe, 80 °C/10^{-2} Torr, 30 min; iii, $2NHR'_2$, THF, 25 °C, 24 h; iv, 1,4-dioxane; v, RBr, THF, MVS experiment, co-condensation at 77 K.

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† No reprints available.

‡ NMR chemical shifts [δ in ppm, $CD_3C_6D_5$ for **1**–**3** and C_6D_6 for **4**–**6**, 305 K for ^1H at 250 MHz and for ^{13}C at 125.8 MHz], ^1H: **1** 1.29 (m, 16H), 1.56 (s, 36H), 2.37 (s, 6H), 3.56 (m, 16H); 7.14 (m, 4H); **2** 1.37 (s, 36H), 2.02 (s, 6H), 7.01 (m, 4H); **3** 0.12 (s, 36H), 1.92 (m, 8H), 3.37 (m, 8H); **4** 0.28 (s, 36H), 3.38 (s, 8H); **5** −1.66 (s, 2H), 0.32 (s, 36H), 1.18 (m, 12H), 3.45 (m, 12H); **6** −1.81 (s, 2H), 0.31 (s, 36H), 3.30 (s, 16H); ^{13}C: **1** 27.1, 32.4, 38.4, 42.4, 76.2, 132.3, 136.4, 143.6, 163.4; **2** 21.6, 30.8 (br), 31.8 (br), 35.1, 136.3 (br); **3** 4.36, 23.9, 67.9; **4** 1.36, 67.3; **5** 4.2, 17.0, 25.2, 69.1; **6** 5.93, 17.2, 66.8.

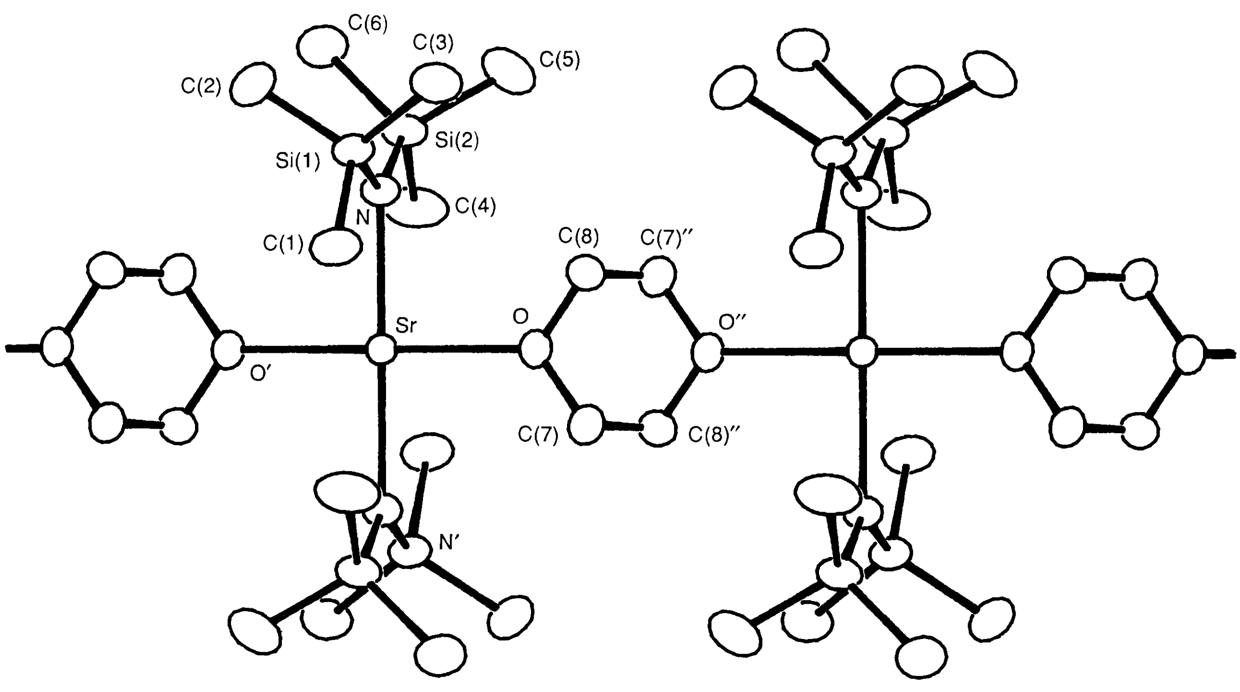

Fig. 1 X-Ray structures of [{*trans*-Sr(NR′$_2$)$_2$(μ-1,4-dioxane)}$_\infty$] (R′ = SiMe$_3$) **4**, with atom numbering scheme. Selected intramolecular bond lengths (Å) and angles (°): Sr–O 2.533(9), Sr–N 2.449(7), ⟨Si–N⟩ 1.688(8), Sr···C(1) 3.16(1) Å; O–Sr–N 89.6(3), O–Sr–N′ 90.4(3)°.

data;§ NMR data‡ are available also for the Sr phenoxide **2**, which probably has the structure [Sr(OAr)(μ-OAr)]$_2$.

As previously noted for the preparation of the Ca and Ba phenoxides **I–III** and the Ca amide **IV**,[1] an activated powdered form of the alkaline earth metal, obtained by co-condensation of the metal vapour and toluene [using a metal vapour synthesis (MVS) apparatus], was used for the preparation of complexes **1–4**. Hanusa and coworkers achieved metal (M) activation by a reductive procedure from MI$_2$,[3] while Caulton, *et al.*, prepared their barium complexes using as a starting material Ba granules in liquid THF.[4]

The calcium alkyl **5** was prepared in an MVS experiment by co-condensation of calcium metal and RBr in THF (v in Scheme 1) at 77 K. [Similar oxidative addition MVS preparations include that of Ni(C$_6$F$_5$)Br from Ni atoms and C$_6$F$_5$Br,[5a] and Ca(Br)C$_8$H$_{17}$ from Ca and 1-bromo-octane in THF.[5b]] We presume that a Grignard equivalent, Ca(Br)R(THF)$_n$, was an intermediate [*cf.* ref. 5(*b*)], which upon Schlenk metathesis gave [CaR$_2$(THF)$_3$] **5** and CaBr$_2$(THF)$_n$. It is noteworthy that the alkyl **5** and [CaR$_2$(1,4-dioxane)$_2$] **6** in C$_6$D$_6$ showed high field methyne signals at δ −1.74 ± 0.08. These values may be compared with that of δ −0.92 for LiC*H*$_2$Me in C$_6$D$_6$,[6] and indicate that the alkyls **5** and **6** have considerable carbanionic character.

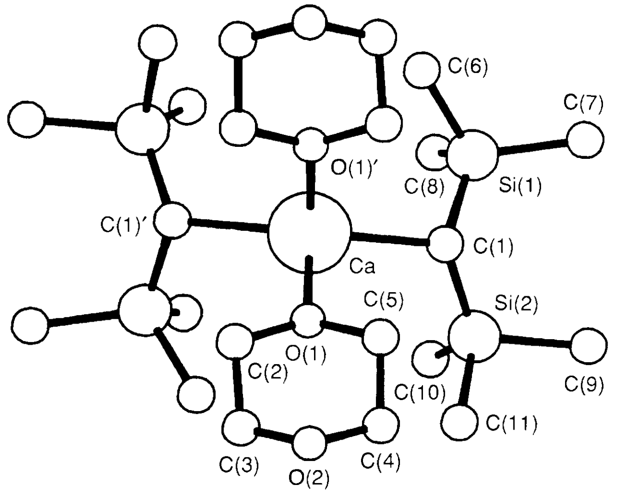

Fig. 2 X-Ray structure of [CaR$_2$(1,4-dioxane)$_2$] [R = CH(SiMe$_3$)$_2$] **6**, with atom numbering scheme. Selected intramolecular bond lengths (Å) and angles (°): Ca–O 2.373(4), Ca–C 2.483(5), ⟨Si–C(1)⟩ 1.810(6) Å; O(1)–Ca–O(1)′ 79.4(1), O(1)–Ca–C(1) 105.3(1), O(1)–Ca–C(1)′ 109.9(2), C(1)–Ca–C(1)′ 133.7(2)°.

The molecular structures of crystalline [{*trans*-Sr(NR′$_2$)$_2$-(μ-1,4-dioxane)}$_\infty$] **4** and [CaR$_2$(1,4-dioxane)$_2$] **6** are illustrated in Fig. 1 and 2, respectively.

Remarkably, the strontium atom in **4** is in a square-planar environment with the amide nitrogen atoms in *trans* positions. The Sr atoms lie on inversion centres and, therefore, have exactly planar coordination by O and N. They are linked in chains along the *a* axis of the crystal with the bridging dioxane

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§ *Crystal data* for **4**: C$_{16}$H$_{44}$N$_2$O$_2$Si$_4$Sr, *M* = 496.5, triclinic, space group $P\bar{1}$ (No. 2), a = 7.595(7), b = 8.575(6), c = 12.412(10) Å, α = 98.50(7), β = 99.59(7), γ = 114.20(6)°, *U* = 705.7 Å^3, *Z* = 1, D_c = 1.17 g cm^{-3}, *F*(000) = 264, μ(Mo-Kα) = 20.3 cm^{-1}.

Crystal data for **6**: C$_{22}$H$_{54}$CaO$_4$Si$_4$, *M* = 535.1, monoclinic, space group *C*2/*c* (No. 15), a = 18.834(6), b = 9.922(2), c = 18.813(5) Å, β = 107.95(2)°, *U* = 3344.4 Å^3, *Z* = 4, D_c = 1.06 g cm^{-3}, *F*(000) = 1176, μ(Mo-Kα) = 3.4 cm^{-1}.

Data for both structures were collected on an Enraf-Nonius CAD4 diffractometer using monochromated Mo-Kα radiation (λ = 0.71069 nm) and with $2 < \theta < 25°$.

An absorption correction was applied for **4** but not for **6**. A correction for crystal decay was necessary for **4** but not for **6**. Structure solution was by heavy-atom methods for **4** and direct methods for **6** and non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated. For **4**, *R* = 0.093, *R*′ = 0.103 for 1434 reflections with $I > 3\sigma(I)$ out of 2477 unique reflections measured. For **6**, *R* = 0.066, *R*′ = 0.081 for 1539 reflections with $I > 3\sigma(I)$ out of 3125 unique reflections measured. The molecules of **6** lie on crystallographic twofold rotation axes. The 1,4-dioxane ligands in both **4** and **6** have the boat conformation. The rather high *R* factor for **4** is a reflection of the large crystal size (1.0 × 0.5 × 0.5 mm).

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited with the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

ligands also lying on inversion centres. There are intramolecular contacts of 3.16(1) Å between the Sr and C(1) atoms. The *nitrogen atoms* are in a trigonal planar environment.

The unexpected stereochemistry about Sr may, therefore, be due to agostic intramolecular $CH\cdots Sr$ interactions (for which there is no NMR spectral evidence in solutions of **4** in C_6D_6), making the Sr quasi-octahedral. Another recent example of an unexpected square-planar metal geometry was reported for $[Cd(OAr')_2(THF)_2]$ (Ar' = $C_6H_3Bu^t{}_2$-2,6);[7] while intermolecular interactions, involving a metal and a neighbouring $SiMe_3$, have been found in $[(MgR_2)_\infty)]$[8] and $[\{Li(CR'_2PMe_2)\}_2]_\infty$.[9]

The distorted tetrahedral metal environment for $[CaR_2(1,4\text{-dioxane})_2]$ **4** is not unexpected in covalent bonding terms. The same combination of ligands on Mg^{2+} yielded $[(MgR_2)_2(\mu\text{-}1,4\text{-dioxane}]$.[8]

We believe that the metal coordination number of four, is without precedent for crystalline Ca^{2+} or Sr^{2+} complexes having monodentate ligands.¶

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¶ *Note added in proof*: Since submission of this paper three relevant articles have appeared reporting (*i*) $[M(NR'_2)_2(THF)_2]$ (M = Mg, Ca, Sr or Ba) from $Hg(NR'_2)_2$, M and THF, and the X-ray structure of the Mg compound and its Mn analogue (D. C. Bradley, M. B. Hursthouse, A. A. Ibrahim, K. M. Malik, M. Motevalli, R. Möseler, H. Powell, J. D. Runnacles and A. C. Sullivan, *Polyhedron*, 1990, **9**, 2959.); (*ii*) $[Ca(NR'_2)_2(THF)_2]$, $[M(NR'_2)_2(DME)_2]$ (DME = 1,2-dimethoxyethane) and $[\{M(NR'_2)(\mu\text{-}NR'_2)\}_2]$, obtained from $M\text{-}Sn(NR'_2)_2$ (H. Westerhausen, *Inorg. Chem.*, 1991, **30**, 90.); and (*iii*) the preparation (from Ba and R'_2NH in THF) and X-ray structures of $[Ba(NR'_2)_2(THF)_2]$, $[\{Ba(NR'_2)(\mu\text{-}NR'_2)(THF)\}_2]$ and $[\{Ba(NR'_2)(\mu\text{-}NR'_2)\}_2]$ (B. A. Vaarstra, J. C. Huffman, W. E. Streib and K. G. Caulton, *Inorg. Chem.*, 1991, **30**, 121.).