

A Novel High-yield Route to Organic Derivatives of Group 2 Metals; X-Ray Structure of $[\{\text{Ba}(\text{OTf})_2\}_4(\text{py})_{14}]\cdot\text{py}$ (OTf = OSO_2CF_3) and NMR Spectral Characterisation of $[\text{Ba}(\text{NR}_2)(\mu\text{-NR}_2)_2\text{Na}(\text{thf})_2]$ (R = SiMe_3)†

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Treatment of $\text{M}(\text{OTf})_2$ [from $\text{MO} + 2 \text{HOTf}$; $\text{OTf} = \text{OSO}_2\text{CF}_3$ and $\text{M} = \text{Ca}$ **1**, Sr **2** or Ba **3**] with 2MOAr or 2MNR_2 ($\text{M} = \text{Na}$ or K , $\text{Ar} = \text{C}_6\text{H}_2\text{Bu}^t\text{-2,6-Me-4}$; $\text{R} = \text{SiMe}_3$) in thf at 0°C affords $[\text{Ca}(\text{OAr})_2(\text{thf})_3]$ **4**, $[\text{M}(\text{OAr})_2(\text{thf})_4]$ ($\text{M} = \text{Sr}$ **5** or Ba **6**), $[\text{M}(\text{NR}_2)_2(\text{thf})_2]$ ($\text{M} = \text{Ca}$ **7** or Sr **8**) or $[\text{Ba}(\text{NR}_2)(\mu\text{-NR}_2)_2\text{Na}(\text{thf})_2]$ **9**; the new compounds **1–3** have been characterised by their NMR spectra in pyridine, and the pyridine adduct of **3** also by X-ray diffraction: crystalline $[\text{Ba}_4(\eta^2\text{-OTf})_2(\mu\text{-OTf})_2(\mu_3\text{-OTf})_4(\text{py})_{14}]\cdot\text{py}$ **10** is unique among metal triflates in having three different bonding modes for the $-\text{OTf}$ ligand.

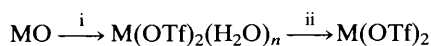
Mono- or bi-nuclear lipophilic, and often volatile, compounds of the alkaline earth metals having monohapto ligands X^- have only been known since 1990. They include aryloxides, amides and alkyls; the first in each class to have been X-ray characterised were $[\text{Ca}(\text{OAr})_2(\text{thf})_3]$,¹ $[\text{Ba}(\text{NR}_2)_2(\text{thf})_2]$ ² and $[\text{Ca}(\text{CHR}_2)_2(1,4\text{-dioxane})_2]$ ³ ($\text{thf} = \text{OC}_4\text{H}_8$, $\text{Ar} = \text{C}_6\text{H}_2\text{Bu}^t\text{-2,6-Me-4}$ and $\text{R} = \text{SiMe}_3$). The precursor to such a complex has usually been the metal (M) activated by various means, e.g., by metal vapour synthesis, amalgamation, reduction of MI_2 , or dissolution in liquid ammonia.⁴

We now report (i) a simple route to such MX_2L_n compounds, (ii) the anhydrous triflates $\text{M}(\text{OTf})_2$ ($\text{OTf}^- =$

$-\text{OSO}_2\text{CF}_3$ and $\text{M} = \text{Ca}$ **1**, Sr **2** or Ba **3**), (iii) the NMR spectral characterisation of **1–3**,[‡] (iv) the X-ray structure of crystalline $[\text{Ba}_4(\eta^2\text{-OTf})_2(\mu\text{-OTf})_2(\mu_3\text{-OTf})_4(\text{py})_{14}]\cdot\text{py}$ **10** (Fig. 1) and (v) a novel lipophilic mixed barium–sodium amide.

As for (i), the precursor was the readily available metal oxide, hydroxide or carbonate, *via* the anhydrous $\text{M}(\text{OTf})_2$ **1–3**, Scheme 1. In this way, the preparation in high yield under mild conditions of the known aryloxides $[\text{Ca}(\text{OAr})_2(\text{thf})_3]$ (76%) **4**, $[\text{M}(\text{OAr})_2(\text{thf})_4]$ **5** ($\text{M} = \text{Sr}$, 70%) or **6** ($\text{M} = \text{Ba}$, 73%) and bis(trimethylsilyl)amides $[\text{M}(\text{NR}_2)_2(\text{thf})_2]$ of Ca **7** (82%) and Sr **8** (79%) has been achieved;[§] however, surprisingly, from $\text{Ba}(\text{OTf})_2$ and 2NaNR_2 under similar conditions there was obtained [*cf.* (v)] the benzene-soluble compound $[\text{Ba}(\text{NR}_2)(\mu\text{-NR}_2)_2\text{Na}(\text{thf})_2]$ (47%) **9**, Scheme 2.

The evidence for the above formulation of **9** rests at this time on (a) ^1H , ^{13}C , ^{23}Na and variable-temperature ^{29}Si NMR spectra (two distinct ^{29}Si environments in a 2:1 ratio at low temperature, coalescing to a singlet at ambient temperature)[¶] (b) an alternative synthesis from $[\text{Ba}(\text{NR}_2)_2(\text{thf})_2]$ and NaNR_2 and (c) analogy with the X-ray authenticated isoleptic ytterbium(II) compound.⁵



Scheme 1 Abbreviations: $\text{M} = \text{Ca}$, Sr , Ba ; $-\text{OTf} = -\text{OSO}_2\text{CF}_3$. Reagents and conditions: i, 5% excess of metal oxide, 2 HOTf ; dist. H_2O ; reflux, 4 h, followed by removal of water *in vacuo*; ii, 200°C at 10^{-5} Torr, 6 h; 98%; *N.B.*, when $\text{M} = \text{Sr}$, the hydroxide was used rather than the oxide, but reaction conditions were similar.

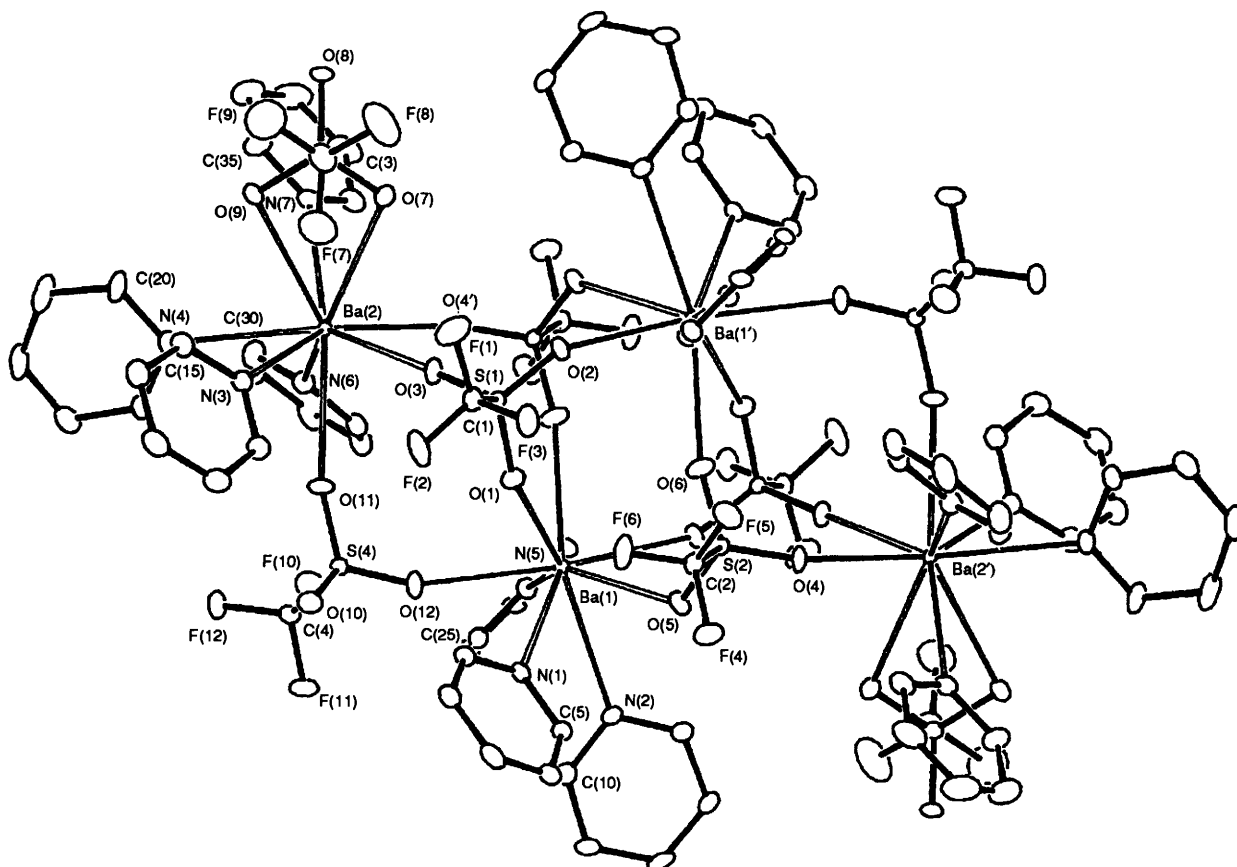
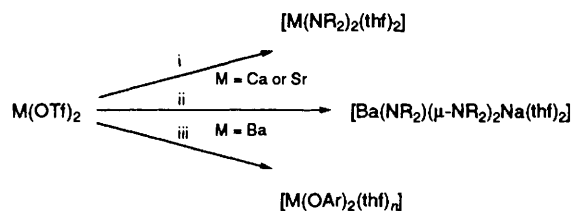


Fig. 1 The molecular structure of compound **10**



Scheme 2 Abbreviations: Ar = C₆H₂Bu^t-2,6-Me-4; R = SiMe₃; thf = tetrahydrofuran; M = Ca, Sr or Ba. Reagents and conditions: i, 2 NaNR₂, thf, 0 °C, 4 h then 25 °C, 12 h (then removal of thf *in vacuo* followed by extraction of product into *n*-hexane); ii, 2 NaNR₂, thf, 0 °C, 4 h then 25 °C, 12 h (followed by removal of thf *in vacuo* and extraction into toluene); iii, 2 KOAr, thf, 0 °C, 4 h then 25 °C, 12 h (followed by removal of thf *in vacuo* and extraction into toluene).

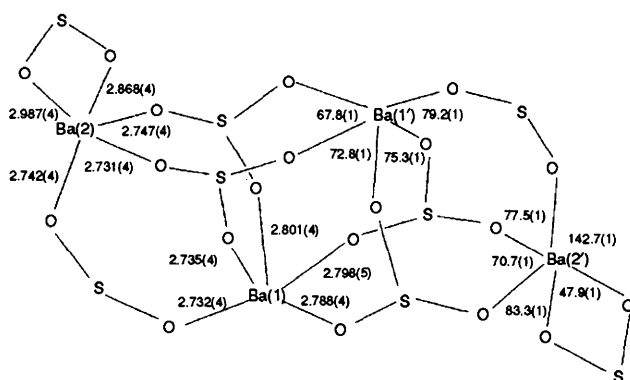


Fig. 2 The molecular structure of the skeletal arrangement for $[\{\text{Ba}(\text{OTf})_2\}_4(\text{py})_{14}] \cdot \text{py}$ ($-\text{OTf} = -\text{OSO}_2\text{CF}_3$) **10**, with selected bond lengths (Å) and angles (°)

Single crystals of the tetranuclear barium triflate **10** were obtained from Ba(OTf)₂ **3** by crystallisation from pyridine at 0 °C. The molecular structure of **10**, which has an inversion centre, is shown schematically in Fig. 2;|| for clarity the CF₃ groups and the pyridine ligands [two each for Ba(1) and Ba(1'); three each for Ba(2) and Ba(2')], as well as the O atoms not bonded to Ba, are omitted.

It is interesting that in **10** the OTf⁻ ligand is found to be operating in three different bonding modes: (1) terminal η², (2) μ-bridging and (3) μ₃-bridging; in mode (1) the two Ba–O bond lengths differ slightly. Each of the modes (1)–(3) has previously been encountered in other metal triflates, but never simultaneously in a single compound.⁶ Furthermore, in related metal complexes containing neutral co-ligands, the triflate has usually been found as a non-coordinating anion as in [Hg(py)₂][OTf]₂⁷ or [Ln(OH₂)₉][OTf]₃ (Ln = a 4f metal).⁸ The Ba–N (*cf.* ref. 9) and Ba–O (*cf.* ref. 10) bond lengths are unexceptional.

We believe that the synthesis here described for alkaline earth metal aryloxides and bis(trimethylsilyl)amides **4–9**, based on the oxide MO (or its obvious chemical equivalent) *via* M(OTf)₂, is capable of extension to other ligands and a wider range of metals (*e.g.* Ln^{III}).¹¹ Likewise structural analogues of **10** are likely to be found for a wider range of metals than the Ba/Na or Yb/Na⁵ couples.

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Footnotes

† No reprints available

‡ NMR chemical shifts (δ) {at 300 K in NC₅D₅ for ¹⁹F (referenced to external CFCl₃) and NC₅D₅ + NC₅H₅ for ¹³C. ¹³C at 125.8 MHz and ¹⁹F at 75.39 MHz}. ¹³C: **1** 121.39 (q), ¹J (C–F) = 318.8 Hz; **2** 121.27 (q), ¹J (C–F) = 319.0 Hz; **3** 121.04 (q). ¹J (C–F) = 319.3; ¹⁹F: **1** –77.96; **2** –77.89; **3** –77.93.

§ Typically Ca(OTf)₂ (0.34 g, 1 mmol) was added to NaN(SiMe₃)₂ (0.37 g, 2 mmol) in thf solution at 0 °C; the mixture was stirred for 24 h. Removal of solvent *in vacuo*, followed by extraction with *n*-hexane and filtration, yielded [Ca{N(SiMe₃)₂}(thf)₂] (0.42 g, 82%).

¶ NMR chemical shifts (δ) {at 298 K in C₆D₆ for ¹H and C₆D₆ + C₆H₆ for ¹³C, ²³Na and ²⁹Si. ¹H at 360.14 MHz, ¹³C at 125.8 MHz, ²³Na at 63.63 MHz and ²⁹Si at 49.67 MHz}. ¹H: 0.21 (s, 54H), 1.33 (t, 8H), 3.51 (t, 8H); ¹³C: 4.44 (q), 24.21 (t), 67.56 (t); ²³Na: 13.53 (br s); ²⁹Si: 333 K, –16.2; 238 K, –13.86 and –17.80 (2:1); 208 K, –13.87 and –17.87 (2:1).

|| Crystal data for **3** [*T* = 173 K, Enraf-Nonius CAD-4 diffractometer, Mo–Kα radiation (λ = 0.71069 Å)], no crystal decay, full-matrix least-squares refinement with non-hydrogen atoms anisotropic. Hydrogen atoms freely refined isotropic. C₈₃H₇₅Ba₄F₂₄N₁₅O₂₄S₈, *M* = 2928.4, triclinic, space group P1̄ (no. 2), *a* = 12.392(4), *b* = 13.374(9), *c* = 18.941(6) Å, α = 82.77(4), β = 75.23(3), γ = 67.87(4)°, *U* = 2810 Å³, *Z* = 1, *D*_c = 1.73 g cm⁻³, *F*(000) = 1438, μ(Mo–Kα) = 16.3 cm⁻¹, specimen 0.2 × 0.2 × 0.2 mm. 7809 Unique reflections for 2 < θ < 23°, of which 1365 with |*F*²| > 2σ(*F*²) were used in the refinement; *R* = 0.038, *R*_w = 0.045, *S* = 1.5. The pyridine solvate molecule lies on an inversion centre with the N atom position disordered equally around the ring. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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