A Novel High-yield Route to Organic Derivatives of Group 2 Metals; X-Ray Structure of $[\{Ba(OTf)_2\}_4(py)_{14}]\cdot py$ (OTf = OSO_2CF_3) and NMR Spectral Characterisation of $[Ba(NR_2)(\mu\text{-}NR_2)_2Na(thf)_2]$ (R = $SiMe_3$)[†]

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Treatment of $M(OTf)_2$ [from MO + 2 HOTf; OTf = OSO_2CF_3 and M = Ca **1**, Sr **2** or Ba **3**] with 2MOAr or $2MNR_2$ (M = Na or K, Ar = $C_6H_2Bu^t_2$-2,6-Me-4; R = $SiMe_3$) in thf at 0 °C affords $[Ca(OAr)_2(thf)_3]$ **4**, $[M(OAr)_2(thf)_4]$ (M = Sr **5** or Ba **6**), $[M(NR_2)_2(thf)_2]$ (M = Ca **7** or Sr **8**) or $[Ba(NR_2)(\mu\text{-}NR_2)_2Na(thf)_2]$ **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 $[Ba_4(\eta^2\text{-}OTf)_2(\mu\text{-}OTf)_2(\mu_3\text{-}OTf)_4(py)_{14}]\cdot py$ **10** is unique among metal triflates in having three different bonding modes for the ^-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 $[Ca(OAr)_2(thf)_3]$,[1] $[Ba(NR_2)_2(thf)_2]$[2] and $[Ca(CHR_2)_2(1,4\text{-dioxane})_2]$[3] (thf = OC_4H_8, Ar = $C_6H_2Bu^t_2$-2,6-Me-4 and R = $SiMe_3$). 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 $M(OTf)_2$ (OTf^- = $^-OSO_2CF_3$ and M = Ca **1**, Sr **2** or Ba **3**), (*iii*) the NMR spectral characterisation of **1–3**,[‡] (*iv*) the X-ray structure of crystalline $[Ba_4(\eta^2\text{-}OTf)_2(\mu\text{-}OTf)_2(\mu_3\text{-}OTf)_4(py)_{14}]\cdot py$ **10** (Fig. 1) and (*v*) a novel lipophilic mixed barium–sodium amide.

$$MO \xrightarrow{\text{i}} M(OTf)_2(H_2O)_n \xrightarrow{\text{ii}} M(OTf)_2$$

Scheme 1 *Abbreviations*: M = Ca, Sr, Ba; ^-OTf = $^-OSO_2CF_3$. *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 M = Sr, the hydroxide was used rather than the oxide, but reaction conditions were similar.

As for (*i*), the precursor was the readily available metal oxide, hydroxide or carbonate, *via* the anhydrous $M(OTf)_2$ **1–3**, Scheme 1. In this way, the preparation in high yield under mild conditions of the known aryloxides $[Ca(OAr)_2(thf)_3]$ (76%) **4**, $[M(OAr)_2(thf)_4]$ **5** (M = Sr, 70%) or **6** (M = Ba, 73%) and bis(trimethylsilyl)amides $[M(NR_2)_2(thf)_2]$ of Ca **7** (82%) and Sr **8** (79%) has been achieved;[§] however, surprisingly, from $Ba(OTf)_2$ and $2NaNR_2$ under similar conditions there was obtained [*cf.* (*v*)] the benzene-soluble compound $[Ba(NR_2)(\mu\text{-}NR_2)_2Na(thf)_2]$ (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 $[Ba(NR_2)_2(thf)_2]$ and $NaNR_2$ and (*c*) analogy with the X-ray authenticated isoleptic ytterbium(II) compound.[5]

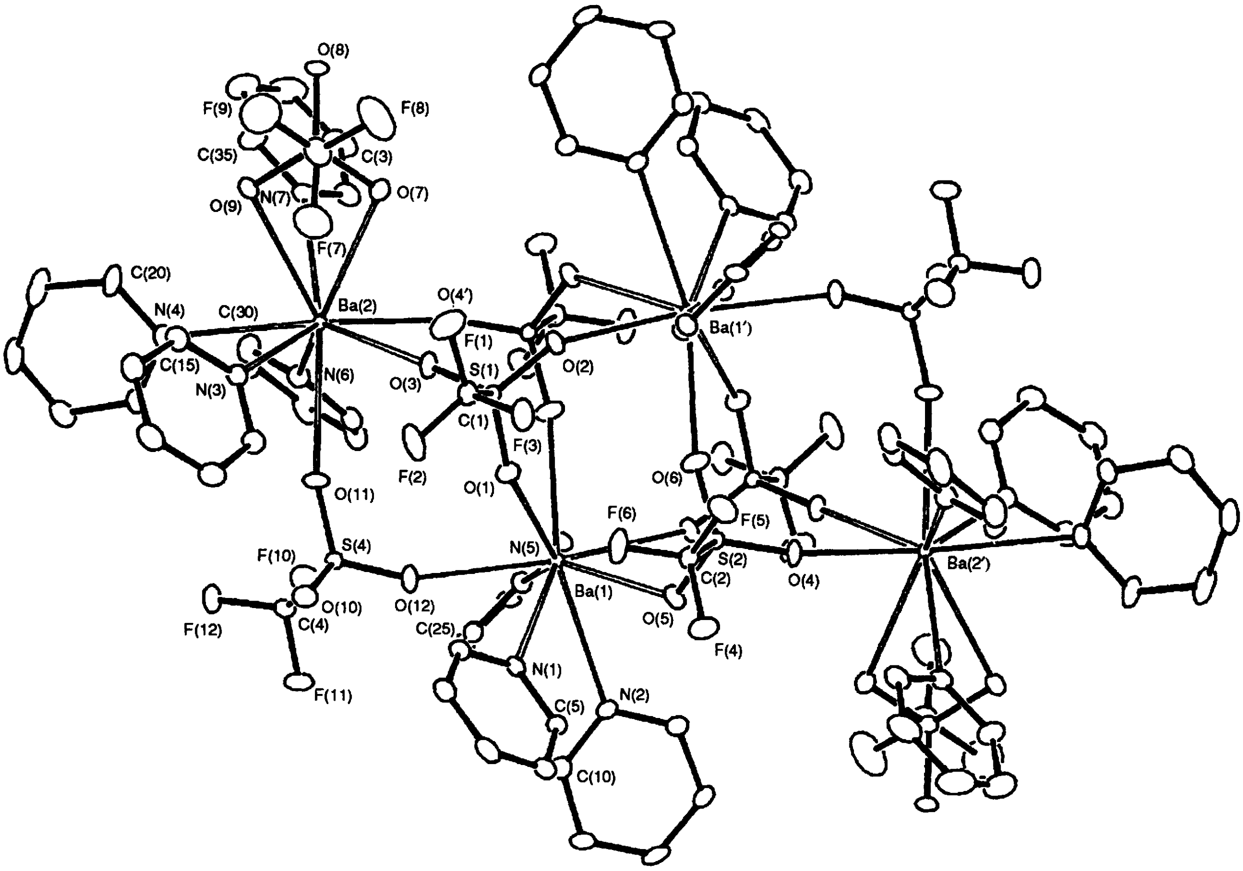
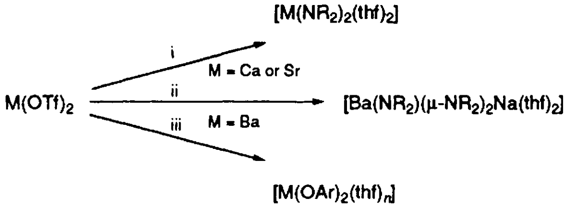


Fig. 1 The molecular structure of compound **10**



Scheme 2 *Abbreviations*: Ar = $C_6H_2Bu^t{}_2$-2,6-Me-4; R = $SiMe_3$; thf = tetrahydrofuran; M = Ca, Sr or Ba. *Reagents and conditions*: i, 2 $NaNR_2$, 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 $NaNR_2$, 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).

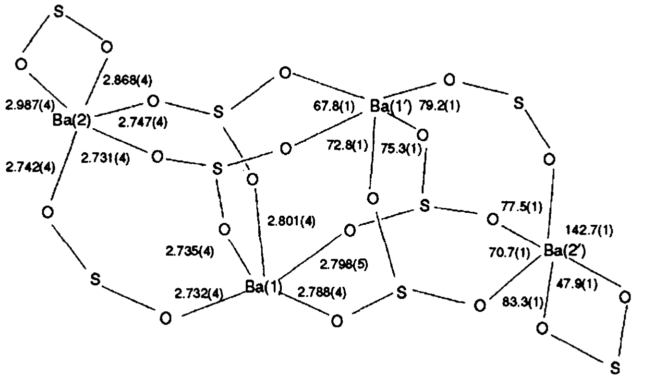


Fig. 2 The molecular structure of the skeletal arrangement for $[\{Ba(OTf)_2\}_4(py)_{14}]\cdot py$ (^-OTf = $^-OSO_2CF_3$) **10**, with selected bond lengths (Å) and angles (°)

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 CF_3 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 η^2, (2) μ-bridging and (3) μ_3-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 $[Hg(py)_2][OTf]_2$[7] or $[Ln(OH_2)_9][OTf]_3$ (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/Na[5] couples.

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Footnotes

[†] No reprints available

[‡] NMR chemical shifts (δ) {at 300 K in NC_5D_5 for ^{19}F (referenced to external $CFCl_3$) and NC_5D_5 + NC_5H_5 for ^{13}C. ^{13}C at 125.8 MHz and ^{19}F at 75.39 MHz}. ^{13}C: **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; ^{19}F: **1** −77.96; **2** −77.89; **3** −77.93.

[§] Typically $Ca(OTf)_2$ (0.34 g, 1 mmol) was added to $NaN(SiMe_3)_2$ (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 $[Ca\{N(SiMe_3)_2\}_2(thf)_2]$ (0.42 g, 82%).

[¶] NMR chemical shifts (δ) {at 298 K in C_6D_6 for ^1H and C_6D_6 + C_6H_6 for ^{13}C, ^{23}Na and ^{29}Si. ^1H at 360.14 MHz, ^{13}C at 125.8 MHz, ^{23}Na at 63.63 MHz and ^{29}Si at 49.67 MHz}. ^1H: 0.21 (s, 54H), 1.33 (t, 8H), 3.51 (t, 8H); ^{13}C: 4.44 (q), 24.21 (t), 67.56 (t); ^{23}Na: 13.53 (br s); ^{29}Si: 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. $C_{83}H_{75}Ba_4F_{24}N_{15}O_{24}S_8$, M = 2928.4, triclinic, space group $P\bar{1}$ (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 Å^3, 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 $2 < \theta < 23°$, of which 1365 with $|F^2| > 2\sigma(F^2)$ 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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