A Novel High-yield Route to Organic Derivatives of Group 2 Metals; X-Ray Structure of [{Ba(OTf)₂}₄(py)₁₄]·py (OTf = OSO₂CF₃) and NMR Spectral Characterisation of [Ba(NR₂)(μ-NR₂)₂Na(thf)₂] (R = SiMe₃)†

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Treatment of M(OTf)₂ [from MO + 2 HOTf; OTf = OSO₂CF₃ and M = Ca **1**, Sr **2** or Ba **3**] with 2MOAr or 2MNR₂ (M = Na or K, Ar = C₆H₂Buᵗ₂-2,6-Me-4; R = SiMe₃) in thf at 0 °C affords [Ca(OAr)₂(thf)₃] **4**, [M(OAr)₂(thf)₄] (M = Sr **5** or Ba **6**), [M(NR₂)₂(thf)₂] (M = Ca **7** or Sr **8**) or [Ba(NR₂)(μ-NR₂)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 [Ba₄(η²-OTf)₂(μ-OTf)₂(μ₃-OTf)₄(py)₁₄]·py **10** is unique among metal triflates in having three different bonding modes for the ⁻OTf ligand.
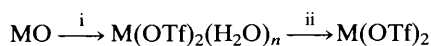
Mono- or bi-nuclear lipophilic, and often volatile, compounds of the alkaline earth metals having monohapto ligands X⁻ have only been known since 1990. They include aryloxides, amides and alkyls; the first in each class to have been X-ray characterised were [Ca(OAr)₂(thf)₃],[1] [Ba(NR₂)₂(thf)₂][2] and [Ca(CHR₂)₂(1,4-dioxane)₂][3] (thf = OC₄H₈, Ar = C₆H₂Buᵗ₂-2,6-Me-4 and R = SiMe₃). 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 MI₂, or dissolution in liquid ammonia.[4]

We now report (i) a simple route to such MX₂Lₙ compounds, (ii) the anhydrous triflates M(OTf)₂ (OTf⁻ =

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

Scheme 1 *Abbreviations*: M = Ca, Sr, Ba; ⁻OTf = ⁻OSO₂CF₃. *Reagents and conditions*: i, 5% excess of metal oxide, 2 HOTf; dist. H₂O; 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.

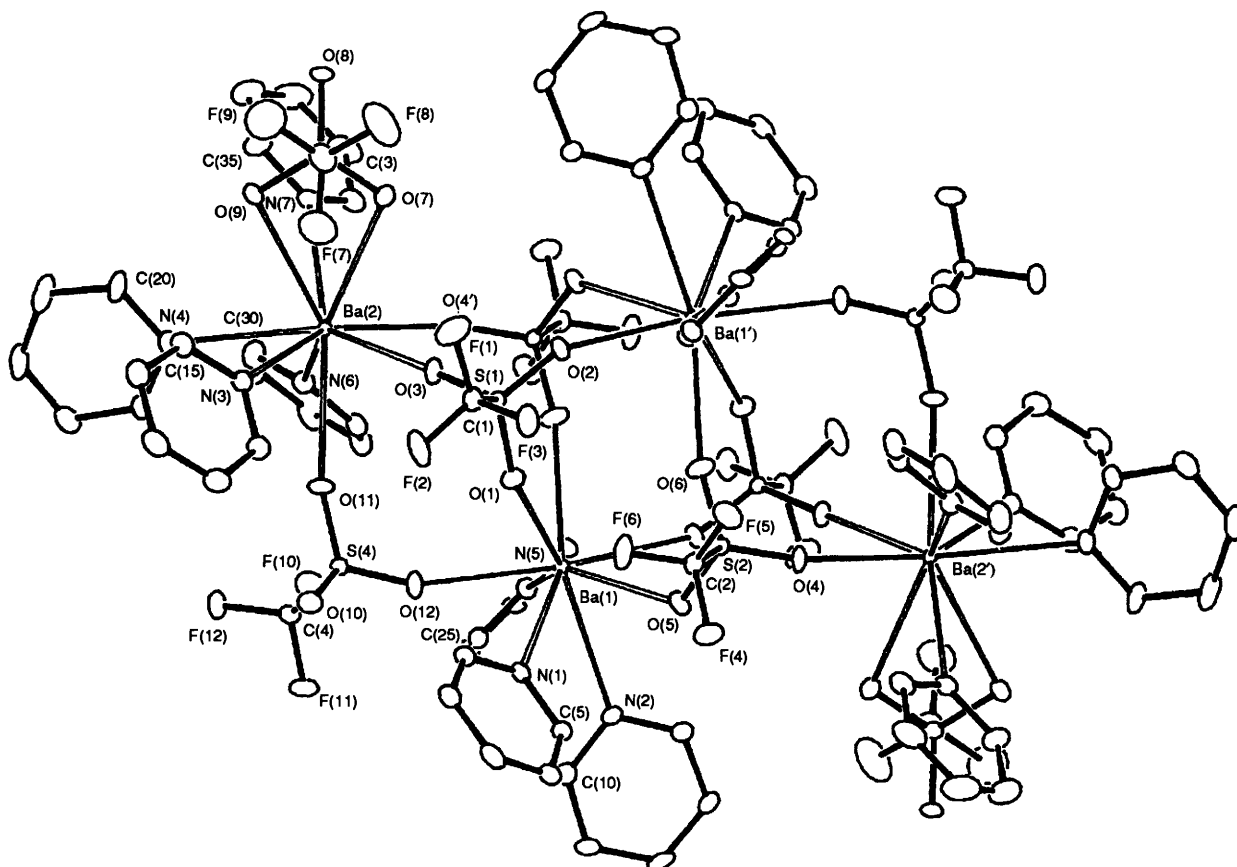⁻OSO₂CF₃ and M = Ca **1**, Sr **2** or Ba **3**), (iii) the NMR spectral characterisation of **1–3**,‡ (iv) the X-ray structure of crystalline [Ba₄(η²-OTf)₂(μ-OTf)₂(μ₃-OTf)₄(py)₁₄]·py **10** (Fig. 1) and (v) a novel lipophilic mixed barium–sodium amide.

As for (i), the precursor was the readily available metal oxide, hydroxide or carbonate, *via* the anhydrous 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(NR₂)₂(thf)₂] of Ca **7** (82%) and Sr **8** (79%) has been achieved;§ however, surprisingly, from Ba(OTf)₂ and 2NaNR₂ under similar conditions there was obtained [cf. (v)] the benzene-soluble compound [Ba(NR₂)(μ-NR₂)₂Na(thf)₂] (47%) **9**, Scheme 2.

The evidence for the above formulation of **9** rests at this time on (a) ¹H, ¹³C, ²³Na and variable-temperature ²⁹Si NMR spectra (two distinct ²⁹Si environments in a 2:1 ratio at low temperature, coalescing to a singlet at ambient temperature)¶ (b) an alternative synthesis from [Ba(NR₂)₂(thf)₂] and NaNR₂ and (c) analogy with the X-ray authenticated isoleptic ytterbium(ɪɪ) compound.[5]

Fig. 1 The molecular structure of compound 10
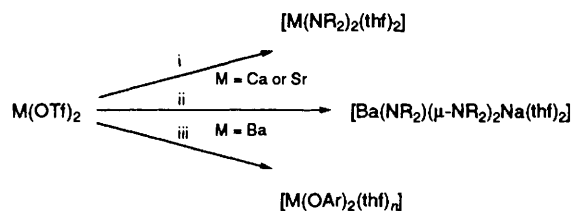
Scheme 2 *Abbreviations*: Ar = $C_6H_2Bu^t_2$-2,6-Me-4; R = $SiMe_3$; thf = tetrahydrofuran; M = Ca, Sr or Ba. *Reagents and conditions*: i, 2 $NaNR_2$, thf, 0 °C, 4 h then 25 °C, 12 h (then removal of thf *in vacuo* followed by extraction of product into *n*-hexane); ii, 2 $NaNR_2$, thf, 0 °C, 4 h then 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).
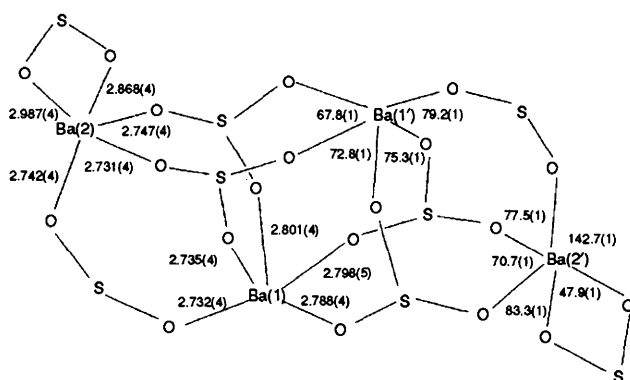

Fig. 2 The molecular structure of the skeletal arrangement for [{$Ba(OTf)_2$}$_4$(py)$_{14}$]·py (^-OTf = $^-OSO_2CF_3$) **10**, with selected bond lengths (Å) and angles (°)

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.

Footnotes

References

1 P. B. Hitchcock, M. F. Lappert, G. A. Lawless and B. Royo, *J. Chem. Soc., Chem. Commun.*, 1990, 1141.

2 B. A. Vaartstra, J. C. Huffman, W. E. Streib and K. G. Caulton, *Inorg. Chem.*, 1991, **30**, 121.

3 F. G. N. Cloke, P. B. Hitchcock, M. F. Lappert, G. A. Lawless and B. Royo, *J. Chem. Soc., Chem. Commun.*, 1991, 724.

4 *Cf.* T. P. Hanusa, *Chem. Rev.*, 1993, **93**, 1023; S. R. Drake, S. A. S. Miller, M. B. Hursthouse and K. M. A. Malik, *Polyhedron*, 1993, **12**, 1621.

5 T. D. Tilley, R. A. Andersen and A. Zalkin, *Inorg. Chem.*, 1984, **23**, 2271.

6 G. A. Lawrance, *Chem. Rev.*, 1986, **86**, 17.

7 R. Åkesson, M. Sandström, C. Stålhandske and I. Persson, *Acta Chem. Scand.*, 1991, **45**, 165.

8 A. Chatterjee, E. N. Maslen and K. J. Watson, *Acta. Crystallogr., Sect. B*, 1988, **44**, 381.

9 K. Brodersen, I. Beck, R. Beck, H. U. Hummel and G. Liehr, *Z. Anorg. Allg. Chem.*, 1984, **516**, 30.

10 F. C. J. M. van Veggel, M. Bos, S. Harkema, H. van de Bovenkamp, W. Verboom, J. Reedijk and D. N. Reinhoudt, *J. Org. Chem.*, 1991, **56**, 225; and refs. therein.

11 S. A. Holmes, D.Phil. Thesis, University of Sussex, 1991.