

## Bis(phosphinimino)methyl derivatives of Ca, Sr and Ba: facile access to heavier alkaline earth organometallic chemistry

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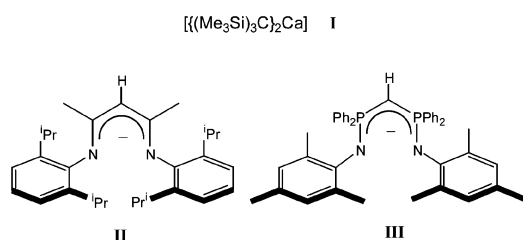
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A series of mononuclear and arene-soluble bis(phosphinimino)methyl derivatives of the heavier alkaline earth metals, calcium, strontium and barium, have been obtained by straightforward addition of two molar equivalents of  $[\text{KN}(\text{SiMe}_3)_2]$  to a mixture of  $[\text{CH}_2(\text{Ph}_2\text{P}=\text{NC}_6\text{H}_2\text{-Me}_3\text{-2,4,6})_2]$  and  $\text{Ml}_2$  ( $\text{M} = \text{Ca, Sr, Ba}$ ) in THF.

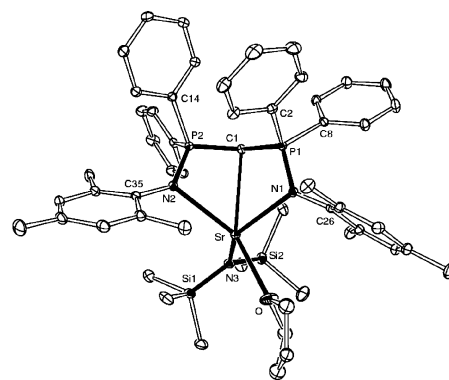
Despite the utility of their lighter congener magnesium in both organic and organometallic synthesis, the organometallic chemistry of the heavier alkaline earth (Ae) metals (Ca, Sr, Ba) developed only slowly during the 20th century. The electropositive nature of the metals and the large radii of the dipoisitive cations facilitate redistribution processes that commonly lead to ill-defined mixtures. Despite these difficulties there have been a number of recent reports concerning organometallic compounds and it is clear that these highly reactive species are potentially useful reagents.<sup>1</sup> These investigations have been prompted by both a fundamental interest in reactivity and structure and the application of mononuclear Ae derivatives as, for example, molecular precursors for the chemical vapour deposition (CVD) of superconducting oxides or as polar initiators for anionic polymerisation.<sup>2</sup> Particularly noteworthy, with reference to the current work, are the use of the bulky tris(trimethylsilyl)methyl ligand in the synthesis of the two-coordinate diorganocalcium compound, **I**,<sup>3</sup> and a recent application of the increasingly prominent aryl-substituted  $\beta$ -diketimino ligand **II** to the synthesis of both homo- and heteroleptic derivatives of Ca, Sr and Ba.<sup>4</sup>



Our own interest arises as part of our recently initiated programme of research that aims to apply bulky and kinetically-stabilising ligand systems to the study of low-coordinate metal centres. The *N*-mesityl-substituted bis(phosphinimino)methyl ligand, **III**, belongs to a broad class of heteroatom-substituted carbanionic ligands,  $\text{H}_n\text{E}_{3-n}\text{C}^-$  (*e.g.*  $\text{E} = \text{R}_3\text{Si, RS, R}_2\text{P, R}_2(\text{O})\text{P}$ ;  $n = 0, 1, 2$ ), stabilised by a combination of negative hyperconjugation and polarisation effects and that also provide considerable steric stabilisation when bonded to reactive metal centres.<sup>5</sup> We have previously studied three-coordinate alkoxo- and amido-zinc complexes supported by **III**, as potential catalysts for the living ring opening polymerisation (ROP) of cyclic polyethers and esters.<sup>6</sup> Although capable of producing high molecular weight material at elevated temperatures (*ca.* 60 °C), these reactions demonstrated no evidence for 'living' behaviour. We reasoned that this was due to sluggish initiation, a result of the sterically demanding nature of the alkoxo and amido initiating groups and resultant overcrowding of the metal centre. In the hope that such problems could be circumvented through the application of analogous compounds

based upon larger and potentially much more reactive Ae metals, we have turned our attention to the synthesis of a series of calcium, strontium and barium compounds. This reasoning was vindicated when Chisholm reported that several calcium-centred alkoxides and amides supported by both **II** and sterically demanding trispyrazolylborate ligands display remarkable activity for the living ROP of *rac*-lactide.<sup>4b</sup>

Room temperature addition of two molar equivalents of  $[\text{KN}(\text{SiMe}_3)_2]$  to a slurry of either  $\text{CaI}_2$  or  $\text{SrI}_2$  in a THF solution of an equimolar quantity of the ligand precursor  $[\text{CH}_2(\text{Ph}_2\text{P}=\text{NC}_6\text{H}_2\text{-Me}_3\text{-2,4,6})_2]$  resulted in the formation of the heteroleptic bis(phosphinimino)methyl complexes  $[\text{III-Ca}\{\text{N}(\text{SiMe}_3)_2\}\cdot\text{THF}]$  and  $[\text{III-Sr}\{\text{N}(\text{SiMe}_3)_2\}\cdot\text{THF}]$ , compounds **1** and **2** respectively.<sup>†</sup> Multinuclear NMR spectra of both **1** and **2** at 298 K were consistent with time averaged  $\text{C}_{2v}$ -symmetric structures in solution. This observation may be explained by rapid dissociation and recoordination of the THF molecule and a reorganisation of the bis(phosphinimino)methyl ligand by an as yet undefined mechanism. This latter contention is required in order to make the configurations on either side of the molecule equivalent. The nature of these dynamic processes could not be further elucidated because solid compounds precipitated upon lowering the temperature of NMR samples in *d*<sub>8</sub>-toluene. Crystals of both **1** and **2** suitable for single crystal X-ray diffraction analysis were grown by slow cooling of toluene solutions.<sup>‡</sup> Although **1** provided only very weak diffraction with limited higher angle data, it was clear that **1** and **2** were isostructural. The structure of **2** is illustrated in Fig. 1 and selected bond lengths and angles for both **1** and **2** are presented in the caption. Both structures contain five-coordinate alkaline earth metal centres which form part of a boat-shaped six-membered MNPCPN metallacycle. In this manner the bis(phosphinimino)methyl ligand acts as a tridentate donor through both the phosphinimino nitrogen centres and the C(1)

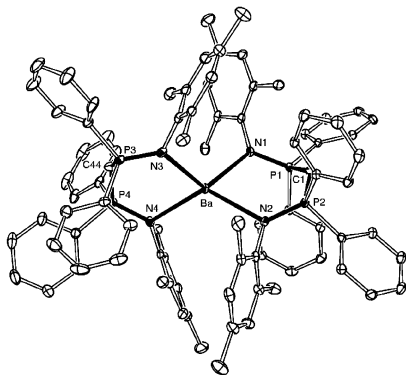


**Fig. 1** The molecular structure of **2** (20% probability ellipsoids). Selected bond distances (Å) and angles (°): **1**: Ca–N(1) 2.411(6), Ca–N(2) 2.467(6), Ca–N(3) 2.331(6), Ca–O 2.433(5); N(1)–Ca–N(2) 103.31(18), N(1)–Ca–O 84.86(18), N(2)–Ca–N(3) 109.68(19), N(2)–Ca–O 134.1(2), N(3)–Ca–O 94.80(19). **2**: Sr–N(1) 2.5557(17), Sr–N(2) 2.5951(17), Sr–N(3) 2.4740(18), Sr–O 2.5674(18); N(1)–Sr–N(2) 98.97(5), N(1)–Sr–O 85.99(6), N(2)–Sr–N(3) 109.74(6), N(2)–Sr–O 136.78(7), N(3)–Sr–O 96.72(6).

methyl carbon atom. The respective M–C(1) distances of 2.713(7) and 2.861(2) Å for **1** and **2** are longer than those of other structurally authenticated compounds containing Ae–sp<sup>3</sup>C σ bonds, for example the Ca–C bond of the two-coordinate **I** [2.459(9) Å]<sup>3</sup> and the Sr–C bonds of the homoleptic strontium benzyl complex  $[\{2\text{-Me}_2\text{N}(\alpha\text{-Me}_3\text{SiCH})\text{C}_6\text{H}_4\}_2\text{Sr}(\text{THF})_2]$  [2.798(2), 2.770(2) Å].<sup>7</sup> They are however comparable to those observed in the ‘ate’ complexes  $[\text{Ca}\{\text{Al}(\text{CH}_2(\text{SiMe}_3)_4)\}_2\{\text{N}(\text{SiMe}_3)_2\}_2]$  [2.678(3), 2.638(3) Å]<sup>8</sup> and  $[\text{Sr}(\text{THF})_2\{\text{Zn}(\text{CH}_2\text{SiMe}_3)_3\}_2]$  [2.857(7), 2.806(8) Å] in which the methyl carbon atom bridges between the two dissimilar metal centres.<sup>9</sup> We have noted previously that the M–N bond lengths observed when **III** acts as a strictly bidentate chelate to either three- or four-coordinate metal centres are almost identical to those of analogous complexes supported by β-diketiminato ligands such as **II**. In **1** and **2** the corresponding bond lengths are significantly longer than those reported in both the directly analogous heteroleptic calcium derivative  $[\text{II-Ca}\{\text{N}(\text{SiMe}_3)_2\}\cdot\text{THF}]$  [2.352(1), 2.370(1) Å]<sup>4b</sup> and the homoleptic derivatives  $[\text{II}_2\text{M}]$  [M = Ca, 2.374(1), 2.384(1) Å; M = Sr, 2.506(2), 2.513(2) Å]<sup>4a</sup> signifying diminished charge donation as a result of the additional M–C(1) interactions.

A similar reaction of two molar equivalents of  $[\text{KN}(\text{SiMe}_3)_2]$  with a single equivalent of both  $[\text{CH}_2(\text{Ph}_2\text{P}=\text{NC}_6\text{H}_2\text{-Me}_3\text{-2,4,6})_2]$  and  $\text{BaI}_2$  also resulted in the isolation of a single product, **3**, after crystallisation from toluene solution. Analysis by multinuclear NMR spectroscopy indicated that **3** was free of THF and did not contain a coordinated –N(SiMe<sub>3</sub>)<sub>2</sub> ligand. A further X-ray structural analysis confirmed that **3** was the homoleptic barium derivative  $[(\text{III})_2\text{Ba}]$  illustrated in Fig. 2. Although **3** does not crystallise with crystallographic C<sub>2</sub> symmetry, the C(1)- and C(44)-containing ligands differ only slightly in conformation. In contrast to both **1** and **2** the Ba–C(1) [3.949 Å] and Ba–C(44) [3.580 Å] distances are too long to indicate the formation of a direct Ba–methyl carbon interaction. It is likely that formation of a homoleptic six-coordinate complex is prevented by crowding within the ligand. Although the bis(phosphinimino)methyl ligands are bidentate, the Ba–N distances of **3** are also longer than those observed in both the homoleptic β-diketiminato barium complex  $[(\text{II})_2\text{Ba}]$  [range: 2.695(2)–2.742(2) Å]<sup>4a</sup> and the terminal β-diketiminato ligand of a related heteroleptic cluster complex formed from reaction of  $[\text{Ba}\{\text{N}(\text{SiMe}_3)_2\}_2(\text{THF})_2]$  and the *N*-cyclohexyl-substituted analogue of the β-iminoamine precursor to **II** [2.689(4), 2.635(4) Å].<sup>10</sup>

We have undertaken preliminary studies of **1–3** as catalysts for the ROP of *rac*-lactide in THF solution. Both the heteroleptic derivatives **1** and **2** polymerise 100 or 200 equivalents of monomer in less than one minute whilst **3**



**Fig. 2** The molecular structure of **3** (20% probability ellipsoids). Selected bond distances (Å) and angles (°): Ba–N(1) 2.768(2), Ba–N(2) 2.736(2), Ba–N(3) 2.756(2), Ba–N(4) 2.754(2); N(1)–Ba–N(2) 89.30(7), N(1)–Ba–N(4) 114.74(7), N(2)–Ba–N(3) 110.86(7), N(2)–Ba–N(4) 126.95(7), N(3)–Ba–N(4) 96.10(7).

displays no similar reactivity. We are continuing to study this chemistry and the reactivity of **1–3** as readily synthesised precursors to further heavy Ae organometallic derivatives.

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## Notes and references

† Selected spectroscopic data for **1**: m.p. 189–191 °C (dec). Anal. Calc. for C<sub>53</sub>H<sub>69</sub>CaN<sub>3</sub>OP<sub>2</sub>Si: C 69.01, H 7.56, N 4.56; Found: C 68.86, H 7.68, N 4.59%. δ<sub>H</sub> (500 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C) 0.39 (s, 18H, SiMe<sub>3</sub>), 1.04 (m, 4H, THF), 2.11 (s, 1H, PCHP) 2.16 (s, 6H, 4-Me), 2.24 (s, 12H, 2,6-Me), 3.36 (m, 4H, THF), 6.78 (s, 4H, 3,5-H,mes), 6.84 (m, 8H, 3,5-H, PhP), 6.92 (m, 4H, 4-H,PhP), 7.61 (m, 8H, 2,6-H,PhP). δ<sub>C</sub> (125.8 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C) 6.1 (SiMe), 16.0 (t, PCHP, <sup>1</sup>J<sub>PC</sub> = 137 Hz), 20.7 (4-Me,mes), 22.6 (2,6-Me,mes), 24.8 (THF), 68.6 (THF), 127.7 (Ar), 129.3 (Ar), 129.9 (Ar, J<sub>PC</sub> = 20 Hz), 132.1 (Ar), 132.7 (Ar), 137.4 (Ar, J<sub>PC</sub> = 89 Hz), 146.0 (Ar). δ<sub>p</sub> (202.5 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C) 8.03. δ<sub>Si</sub> (99.4 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C) –16.3. **2**: m.p. 195–198 °C (dec). Anal. Calc. for C<sub>53</sub>H<sub>69</sub>CaN<sub>3</sub>OP<sub>2</sub>SiSr: C 65.63, H 7.19, N 4.33; Found: C 65.63, H 7.23, N 4.17%. δ<sub>H</sub> (500 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C) 0.44 (s, 18H, SiMe<sub>3</sub>), 1.05 (m, 4H, THF), 2.15 (s, 6H, 4-Me), 2.21 (s, 1H, PCHP), 2.27 (s, 12H, 2,6-Me), 3.48 (m, 4H, THF), 6.79 (s, 4H, 3,5-H,mes), 6.84 (m, 8H, 3,5-H, PhP), 6.92 (m, 4H, 4-H,PhP), 7.59 (m, 8H, 2,6-H,PhP). δ<sub>C</sub> (125.8 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C) 6.3 (SiMe, <sup>1</sup>J<sub>SiC</sub> = 52 Hz), 15.9 (t, PCHP, <sup>1</sup>J<sub>PC</sub> = 132 Hz), 20.6 (4-Me,mes), 23.0 (2,6-Me,mes), 24.7 (THF), 68.7 (THF), 127.7 (Ar), 129.9 (Ar), 130.2 (Ar), 132.4 (Ar), 133.3 (Ar), 137.0 (Ar, J<sub>PC</sub> = 89 Hz), 145.7 (Ar). δ<sub>p</sub> (202.5 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C) 10.79. δ<sub>Si</sub> (99.4 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C) –14.0. **3**: m.p. 210–212 °C. Anal. Calc. for C<sub>86</sub>H<sub>86</sub>BaN<sub>4</sub>P<sub>4</sub>0.5(C<sub>7</sub>H<sub>8</sub>): C 72.49, H 6.13, N 3.78; Found: C 72.61, H 6.18, N 3.61%. δ<sub>H</sub> (500 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C) 2.03 (s, 12H, 4-Me), 2.10 (s, 2H, PCHP), 2.30 (s, 24H, 2,6-Me), 6.82 (m, 16H, 3,5-H, PhP), 6.88 (s, 16H, 3,5-H,mes), 6.90 (m, 8H, 4-H,PhP), 7.50 (m, 16H, 2,6-H,PhP). δ<sub>C</sub> (125.8 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C) 16.2 (t, PCHP, <sup>1</sup>J<sub>PC</sub> = 146 Hz), 20.9 (4-Me,mes), 22.3 (2,6-Me,mes), 127.6 (Ar), 129.1 (Ar), 129.8 (Ar, J<sub>PC</sub> = 33 Hz), 132.3 (Ar), 134.1 (Ar), 138.8 (Ar, J<sub>PC</sub> = 94 Hz), 145.8 (Ar). δ<sub>p</sub> (202.5 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C) 8.44.

‡ *Crystal data*: 173 K, Nonius Kappa CCD diffractometer, λ(Mo Kα) = 0.71073 Å. **1**: C<sub>53</sub>H<sub>69</sub>CaN<sub>3</sub>OP<sub>2</sub>Si<sub>2</sub>, *M* = 922.31, monoclinic, *P*2<sub>1</sub>/*c* (No. 14), *a* = 12.6861(6), *b* = 22.9406(11), *c* = 18.2982(10) Å, β = 104.334(2)°, *V* = 5159.5(4) Å<sup>3</sup>, *Z* = 4, μ = 0.27 mm<sup>−1</sup>, 28754 collected reflections, 7073 independent reflections [*R*(int) = 0.226], *R* indices [*I* > 2σ(*I*)] *R*1 = 0.089, *wR*2 = 0.142, [all data] *R*1 = 0.174, *wR*2 = 0.172. **2**: C<sub>53</sub>H<sub>69</sub>N<sub>3</sub>OP<sub>2</sub>Si<sub>2</sub>Sr, *M* = 969.85, monoclinic, *P*2<sub>1</sub>/*c* (No. 14), *a* = 12.7105(1), *b* = 23.1523(2), *c* = 18.4217(1) Å, β = 104.566(3)°, *V* = 5246.85(7) Å<sup>3</sup>, *Z* = 4, μ = 1.17 mm<sup>−1</sup>, 66071 collected reflections, 11945 independent reflections [*R*(int) = 0.057], *R* indices [*I* > 2σ(*I*)] *R*1 = 0.039, *wR*2 = 0.082, [all data] *R*1 = 0.056, *wR*2 = 0.089. **3**: C<sub>86</sub>H<sub>86</sub>BaN<sub>4</sub>P<sub>4</sub>0.5(C<sub>7</sub>H<sub>8</sub>), *M* = 1482.88, triclinic, *P*1̄ (No. 2), *a* = 13.0294(2), *b* = 13.3312(2), *c* = 25.5773(4) Å, α = 100.566(1), β = 92.303(1), γ = 118.149(1)°, *V* = 3809.47(10) Å<sup>3</sup>, *Z* = 2, μ = 0.65 mm<sup>−1</sup>, 45010 collected reflections, 17111 independent reflections [*R*(int) = 0.063], *R* indices [*I* > 2σ(*I*)] *R*1 = 0.047, *wR*2 = 0.088, [all data] *R*1 = 0.080, *wR*2 = 0.098. CCDC 211013–211015. See <http://www.rsc.org/suppdata/cc/b3/b305430f/> for crystallographic data in CIF or other electronic format

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