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Synthesis of a homoleptic Sm(II) bis(phosphinimino)methanide

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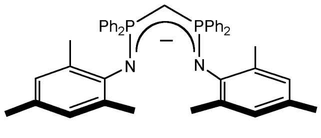
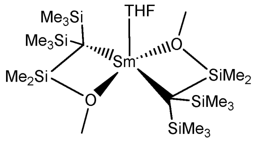
Reaction of two molar equivalents of [$KN(SiMe_3)_2$] and a mixture of [$CH_2(Ph_2P{=}NC_6H_2\text{-}Me_3\text{-}2,4,6)_2$] and SmI_2 in THF resulted in the formation of a stable homoleptic samarium dialkyl without additional solvent coordination.

The past two decades have witnessed the widespread emergence of Sm(II) complexes as potent single electron reductants for organic synthesis.[1] Much of this attention has focussed upon the readily available reagent samarium(II) iodide, which is capable of promoting a number of bond-forming processes either through radical or anionic intermediates.[2] Solubility considerations dictate that much of this chemistry is performed in THF and, while this solvent is appropriate for many applications, radical processes can be suppressed by the susceptibility of this solvent toward facile H-atom abstraction.[2] We have become interested in the synthesis of lipophilic and ether-free organometallic Sm(II) complexes with a view to circumventing this limitation. Flowers *et al.* have recently demonstrated, through a combination of cyclic voltammetry and stopped flow kinetic studies, that reactions of [$Sm\{N(SiMe_3)_2\}_2(THF)_2$] with alkyl iodides occur by modified electron transfer mechanisms in comparison to SmI_2-mediated processes.[3] This effect is attributed to the structure of the homoleptic samarium amide. We are also mindful therefore of the possibility that appropriate steric tuning of the supporting ligand environment may provide a means to modulate the selectivity of reactions with reducible substrates. In this latter respect, it is notable that the reactivity of π-bonded organosamarium species such as Cp^*_2Sm has been intensively studied and has given rise to a rich and, in some cases, surprising reductive chemistry.[4]



I



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The *N*-mesityl-substituted bis(phosphinimino)methyl ligand, **I**,[5] belongs to a broad class of heteroatom-substituted carbanionic ligands, $H_nE_{3-n}C^-$ (*e.g.* E = R_3Si, RS, R_2P, $R_2(O)P$; n = 0, 1, 2), stabilised by a combination of negative hyperconjugation and polarisation effects. We have recently demonstrated that **I** provides an appropriate environment for the isolation of stable organometallic molecules of the heavier alkaline earth elements, Ca, Sr and Ba.[6] In particular, our synthesis of a four-coordinate diorganobarium derivative, I_2Ba, **1**, indicated that **I** may be equally suitable for the preparation of complexes of the similarly large and electropositive divalent lanthanide elements that are unsolvated by additional external bases. Definitive reports of divalent lanthanide complexes containing Ln–C σ-bonds are a rarity,[7] while structurally characterised charge neutral Sm(II) dialkyls are restricted to the five-coordinate THF adduct [$Sm\{C(SiMe_3)_2(SiMe_2OMe)\}_2\text{-}(THF)$], **2**.[7e] We now report a simple synthesis and the structural characterisation of a homoleptic Sm(II) bis(phosphinimino)methanide complex which is isolated without coordination from additional donor solvent.

Addition of two molar equivalents of [$KN(SiMe_3)_2$] to a mixture of SmI_2 and two equivalents of the ligand precursor [$CH_2(Ph_2P{=}NC_6H_2\text{-}Me_3\text{-}2,4,6)_2$] in THF at room temperature generated an intense purple solution.† Crystallisation at room temperature from toluene resulted in the isolation of a single deep purple compound, **3**. The acquisition of sharp ^1H NMR resonances around the normal chemical shift range of 1–10 ppm is a common feature of Sm(II) ($4f^6$) organometallic chemistry.[8] The ^1H NMR spectrum of **3** in toluene-d_8, with signals lying between 2.03–8.47 ppm, was therefore reminiscent of that observed for the analogous homoleptic organobarium complex, **1**,[6] and revealed that **3** was free of THF and did not contain a coordinated $-N(SiMe_3)_2$ ligand. Furthermore, the observation of a single resonance in the room temperature $^{31}P\{^1H\}$ NMR spectrum at 273.9 ppm indicated symmetrical chelation and the presence of a single ligand environment on the NMR timescale.

Large block-like crystals of **3** that were suitable for single crystal X-ray diffraction analysis were grown by slow cooling of a warm and concentrated toluene solution.‡ The structure of **3** is illustrated in Fig. 1, while selected bond lengths and angles are provided by the figure caption. Compound **3** crystallises as a discrete, homoleptic monomer in which the two boat-shaped ligand moieties are mutually disposed in an approximately orthogonal fashion (the core structure of **3** is illustrated in Fig. 2). The two bis(phosphinimino)methanide ligands act as tridentate donors and, as a consequence, the samarium center is six-coordinate. The organobarium complex,

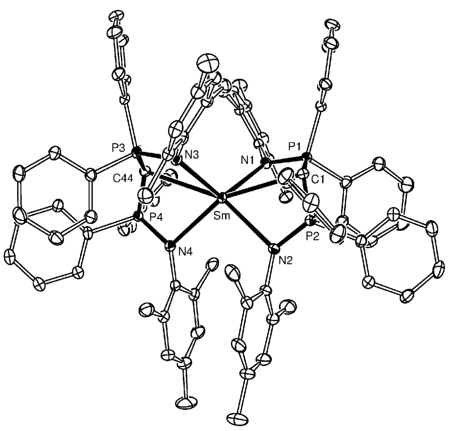

Fig. 1 The molecular structure of **3** (20% probability ellipsoids). Selected bond distances (Å) and angles (°): Sm–C(1) 2.900(5), Sm–C(44) 2.877(5), Sm–N(1) 2.606(4), Sm–N(2) 2.592(4), Sm–N(3) 2.608(4), Sm–N(4) 2.605(4) P(1)–N(1) 1.617(4), P(2)–N(2) 1.600(4), P(3)–N(3) 1.618(4), P(4)–N(4) 1.607(4), P(1)–C(1) 1.714(5), P(2)–C(1) 1.724(5), P(3)–C(44) 1.731(5), P(4)–C(44) 1.722(5), N(1)–Sm–N(2) 98.87(13), N(1)–Sm–N(4) 116.88(13), N(2)–Sm–N(3) 117.37(14), N(2)–Sm–N(4) 99.58(12), N(3)–Sm–N(4) 98.91(12).

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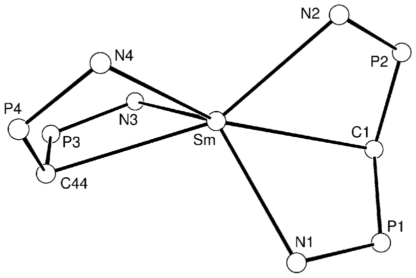

Fig. 2 Ligand coordination around **3**.

1, was an unambiguously four-coordinate molecule in which coordination of the two anions was provided by exclusive bidentate N∩N chelation.[6] In contrast, both ligands of compound **3** provide additional coordination through the methanide carbon centers C(1) and C(44). The respective distances to samarium [2.900(5), 2.877(5) Å], are only slightly longer than the Sm–C bonds of the dialkyl samarium compound **2** [2.85, 2.79 Å].[7e] As this latter complex is five-coordinate, the longer Sm–C bonds observed in compound **3** are not unexpected. The Sm–C distances of compound **3** are also significantly longer than in the only other crystallographically characterised Sm(II) complex containing a Sm–C σ-bond, the anionic species $[Sm(C_5Me_5)\{CH(SiMe_3)_2\}(C_5Me_5)K(THF)_2]_n$ [2.652(9) Å].[7a,b] The Sm–C bond distances in the Sm(III) bis(phosphinimino)methanide $[Sm\{CH(PPh_2NSiMe_3)_2\}Cl_2]_2$ [2.720 Å],[9] and the Sm(III) 'carbene' complex, $[Sm\{C(PPh_2NSiMe_3)_2\text{-}\kappa^3 C,N,N'\}(NCy_2)(THF)]$,[10] which contains a doubly deprotonated ligand [2.467(4) Å], are also shorter as expected for the trivalent lanthanide. The absence of THF as an anicillary base in **3** is, most likely, a consequence of the steric demands of the ligand, **I**.[11]

Attempts to synthesise the heteroleptic amide $[\mathbf{I}Sm\{N(SiMe_3)_2\}]$ by a similar reaction protocol have, thus far, been unsuccessful. Addition of $[KN(SiMe_3)_2]$ (2 equiv.) to a THF solution of SmI_2 (1 equiv.) and **I**H (1 equiv.) resulted in the isolation of **3** as the only crystalline bis(phosphinimino)methanide-containing product. A similar observation was made during the synthesis of **1** and evidently the successful isolation of the less sterically congested heteroleptic amide is subtly dependent upon the radius of the divalent metal centre. This was surprising given our isolation of the strontium complex $[\mathbf{I}Sr\{N(SiMe_3)_2\}(THF)]$ and the similarity between the ionic radii (albeit determined for seven coordinate species) of Sr^{2+} [1.35 Å] and Sm^{2+} [1.36 Å].[12] A small quantity of colourless crystals were also isolated from this reaction. These were identified as the known homoleptic amide $[Sm\{N(SiMe_3)_2\}_3]$ by a further X-ray diffraction analysis.[13] The formation of a Sm(III)-containing species possibly indicates that reduction of the P(V) centres of **I** may be a competing reaction pathway in this chemistry, an assertion that was tentatively reinforced by the observation of additional signals at 6.05 and 31.2 ppm of the $^{31}P\{^1H\}$ NMR spectrum of the crude reaction mixture. Presumably this occurs by the intermediacy of the target amide which is insufficiently stabilised to prevent further reaction. We are continuing to study this chemistry and the reactivity of **3** with reducible small molecule substrates. Preliminary NMR analysis of reactions with carbonyl-containing compounds in toluene solution indicates that oxidation of the Sm(II) center occurs without degradation of the ligand architecture.

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Notes and references

† Preparation of $[Sm\{CH(PPh_2NC_6H_2\text{-}Me_3\text{-}2,4,6)_2\}_2]$ **3**. All experimental manipulations were performed under rigorously anaerobic conditions using Schlenk techniques. To a THF (30 mL) solution of SmI_2 (1.26 g, 3.1 mmol) and **I**H (4.06 g, 6.2 mmol) was added $[K\{N(SiMe_3)_2\}]$ (1.24 g, 6.2 mmol) in THF (20 mL) at room temperature. The resulting deep purple solution was stirred for 14 h at room temperature, before the solvent was removed and the reaction mixture extracted with toluene (40 mL). Filtration and concentration (*ca.* 20 mL), followed by slow cooling of the saturated solution produced **3**·2.5(toluene) as large deep purple/black crystals suitable for a single crystal X-ray analysis (3.78 g, 72%). The solvated toluene molecules could be removed by grinding of a sample and extended storage under dynamic vacuum. Selected spectroscopic data for **3**: mp 212–215 °C (dec). Anal. Calc. for $C_{86}H_{86}N_4P_4Sm$: C 71.23, H 5.99, N 3.86; Found: C 71.61, H 6.30, N 3.65. ^1H NMR (500 MHz, toluene-d_8, 25 °C): δ 2.02 (s, 2H, PCHP), 2.03 (s, 24H, 4-Me), 2.92 (s, 12H, 2,6-Me), 6.24, 6.25, 6.72, 7.01, 8.47 (Ar–H). $^{31}P\{^1H\}$ NMR (202.5 MHz, toluene-d_8, 25 °C): δ 273.9.

‡ Crystal data for **3**·2.5(toluene): 173 K, Nonius Kappa CCD diffractometer, λ(Mo Kα) = 0.71073 Å, $C_{86}H_{86}N_4P_4Sm.2.5(C_7H_8)$, M = 1680.15, triclinic, P (No. 2), a = 15.1670(1), b = 15.8289(2), c = 22.0330(3) Å, α = 68.814(1), β = 75.887(1), γ = 75.659(1)°, V = 4708.17(9) Å^3, Z = 2, μ = 0.74 mm^{-1}, 61602 collected reflections, 21366 independent reflections [R(int) = 0.074], R_{indices} [$I > 2\sigma(I)$] $R1$ = 0.064, $wR2$ = 0.161, [all data] $R1$ = 0.087, $wR2$ = 0.175. The disordered toluenes were refined with constraints and with H atoms omitted. The ordered toluene was included with the C6 ring as a rigid body. CCDC reference number 222067. See http://www.rsc.org/suppdata/dt/b3/b313034g/ for crystallographic data in CIF or other electronic format.

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