The synthesis of a sterically hindered samarium(II) bis(amidinate) and conversion to its homoleptic trivalent congener†

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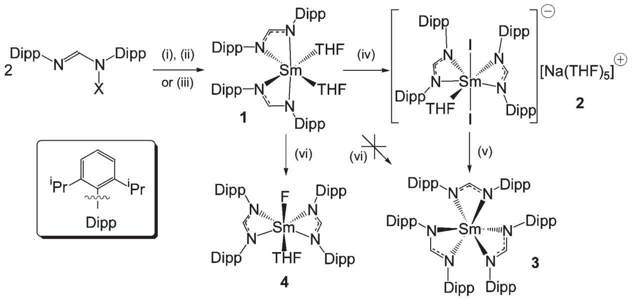
The first divalent samarium bis(amidinate) has been prepared and aspects of its novel chemistry, including the preparation of a sterically hindered homoleptic Sm(III) tris(amidinate), explored.

Samarium compounds have dominated research in the area of divalent lanthanoid organometallic species ever since Kagan's seminal report of SmI_2 as a coupling/reducing agent in organic synthesis.[1] To this end, the samarocene family of compounds ($SmCp'_2$, Cp′ = a cyclopentadienide), in particular the decaalkylsamarocenes, have attracted considerable attention as one-electron reductants in the organometallic arena.[2] By contrast, developments using other ligand supports have been sparse. Amidinates $[\{R^1NC(R^2)=NR^1\}^-]$ represent a sterically and electronically tuneable family of ligands that, owing to commensurate size–charge characteristics to the $(C_5R_5)^-$ donor set, can be considered Cp′ analogues.[3,4] Surprisingly, no divalent samarium bis(amidinate) complexes have been reported.[5] Given the ease by which amidinates can be modified (*e.g.* inclusion of chiral, electron withdrawing or sterically demanding moieties)[3] and the proposed participation of organosamarium species in several Sm(II) mediated C–C coupling reactions (*e.g.* Barbier and Reformatzky),[6] paths to this compound class are attractive to a broad synthetic audience. Herein we describe the three-way synthesis of a sterically hindered Sm(II) bis(amidinate) and some preliminary studies of its novel chemistry.

As illustrated in Scheme 1, $[Sm(DippForm)_2(THF)_2]$ (**1**) [DippForm = $\{(2,6\text{-}^iPr_2C_6H_3)NC(H)=N(2,6\text{-}^iPr_2C_6H_3)\}^-$] can be prepared in high yield by reaction of sodium metalated DippForm with $[Sm(I)_2(THF)_2]$,§ the one-pot reaction of excess samarium metal with bis(pentafluorophenyl)mercury[7] and DippFormH, or transamination of $[Sm\{N(SiMe_3)_2\}_2(THF)_2]$ and DippFormH in tetrahydrofuran.† Structural data indicate dark green **1** consists of *cisoid*-$[Sm(DippForm)_2(THF)_2]$ units (see Fig. 1)†¶ that are isomorphous to the related alkaline earth compounds $[M(DippForm)(THF)_2]$, where M = Sr or Ba.[8] The DippForm ligands coordinate in an η^2-fashion with samarium to nitrogen bond lengths [Sm(1)–N(1) 2.529(3) Å, Sm(1)–N(4) 2.617(3) Å] that are necessarily longer than those observed in related trivalent samarium guanidinate species (*e.g.* five-coordinate $[Sm(C\{N(SiMe_3)_2\}\{N(c\text{-}C_6H_{11})\}_2)_2\{CH(SiMe_3)_2\}]$; 2.395(4)–2.426(4) Å,[9] six-coordinate ionic radii; Sm^{2+} 1.18 Å, Sm^{3+} 0.96 Å).[10]



Scheme 1 *Reagents and conditions*: (i) X = Na, 1.0 eq. $[Sm(I)_2(THF)_2]$, −2.0 eq. NaI, THF, RT, 2 h; (ii) X = H, >1.0 eq. Sm^0, 1.0 eq. $[Hg(C_6F_5)_2]$, −1.0 eq. Hg^0, −2.0 eq. C_6F_5H, THF, RT, 12 h; (iii) X = H, 1.0 eq. $[Sm\{N(SiMe_3)_2\}_2(THF)_2]$, −2.0 eq. $HN(SiMe_3)_2$, THF, RT, 2 h; (iv) 0.5 eq. $[Sm(I)_2(THF)_2]$, 1.0 eq. NaI, −0.5 eq. "Sm^0", THF, RT, 1 day; (v) hexane, $-^1/_3$ eq. $[SmI_3(THF)_{3.5}]$, −1.0 eq. NaI, 35 °C–RT; (vi) 0.5 eq. $[Hg(C_6F_5)_2]$, 0.5 eq. DippFormH, −1.0 eq. "C_6F_4", THF, RT, 24 h.

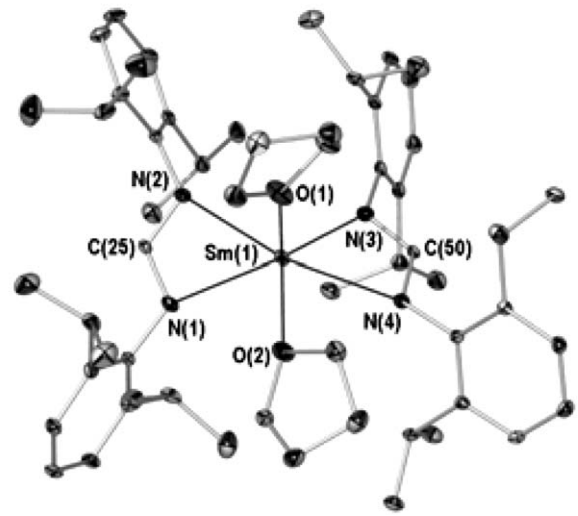


Fig. 1 Molecular structure of **1**, POV-RAY illustration, 40% thermal ellipsoids, all hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Sm(1)–N(1) 2.529(3), Sm(1)–N(4) 2.617(3), Sm(1)–O(1) 2.560(3), Sm(1)–O(2) 2.599(3), N(1)–C(25) 1.323(4), N(2)–C(25) 1.317(4), N(1)–Sm(1)–N(2) 52.9(1), N(1)–C(25)–N(2) 120.6(3), O(1)–Sm(1)–O(2) 79.1(1) O(1)–Sm(1)–C(25) 103.3(1), O(1)–Sm(1)–C(50) 111.1(1), C(25)–Sm(1)–C(50) 134.9(1).

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† Electronic supplementary information (ESI) available: full experimental and X-ray structure determination data for compounds **1**–**4**. See http://www.rsc.org/suppdata/cc/b5/b501447f/

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During syntheses of **1** by salt elimination [Scheme 1 (i)] small quantities (*ca.* 5%) of colourless crystalline co-product (**2**) were repeatedly isolated after further work-up of reaction media. Further to ^{1}H NMR spectra, which indicate an approximate THF:DippForm ratio of *ca.* 3:1,† and a coloration indicative of trivalent samarium (*i.e.* loss of dark divalent colour), **2** was identified by XRD methods as the *samarate* [Na(THF)$_5$][Sm(I)$_2$(DippForm)$_2$(THF)].†¶ Compound **2** presumably arises from coordination of sodium iodide to a trivalent [Sm(I)(DippForm)$_2$(THF)$_n$] intermediate. It is possible that this is generated by disproportionation of excess SmI$_2$ with **1** to yield elemental samarium as a co-product,[11] however at this early stage other redox paths cannot be discounted. To further investigate, 0.5 molar equivalents of [Sm(I)$_2$(THF)$_2$] were added to a pre-prepared solution of **1** [generated *in situ* by (i), Scheme 1 under meticulously anaerobic conditions] as an intentional synthesis of **2**.† This resulted in gradual loss of the dark green colour of **1** over a period of 24 hours to give **2** in moderate yield.[12]† Dissolution in hexane, to effect loss of NaI from **2**, resulted in redistribution§ to give homoleptic [Sm(DippForm)$_3$] (**3**) with concomitant precipitation of NaI and [Sm(I)$_3$(THF)$_{3.5}$].[13] Recrystallisation of the mother liquor from toluene yielded samples of **3** suitable for X-ray structure determination (see Fig. 2).†¶

The considerable buttressing about the samarium of **3** is evidenced by extended Sm–N bonds relative to other six-coordinate trivalent samarium compounds [Sm(1)–N(3) 2.462(6) Å, Sm(1)–N(6) 2.467(6) Å], and uncharacteristic twisting[14] of the 2,6-^{i}Pr$_2$C$_6$H$_3$ groups, such that they lie non-perpendicular to the SmNCN metalacyclic planes [**1**; C(1)–C(6) ring 59.5(2)°, C(13)–C(18) ring 56.8(2)°]. Indeed, the geometry about the samarium centre is near trigonal planar if one considers the DippForm ligands single point donors located at the carbon of the 1,3-diazaallyl unit [Σ C–Sm–C angles = 359.9(6)°].

The redistribution of bis(amide) supported lanthanoid halides when extracted into low polarity solvents, as per the formation of **3** from **2**, is not unusual;[15] however disproportionation of divalent to tri- and zero valent samarium, tentatively the source of **2**,[12] has limited precedent, there being one literature example using tetradentate Schiff bases as support ligands for Sm(II).[11] Interestingly, the authors of this report suggest that the significant spatial bulk of the Schiff bases contribute to the redox process observed. Further, the steric congestion of **3**, as illustrated in Fig. 2(b), and our failure to generate homoleptic lanthanoid complexes of DippForm by salt elimination[16] make the redistribution step noteworthy.

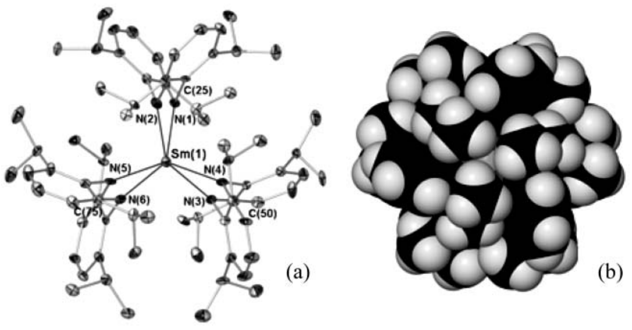

Fig. 2 **(a)** Molecular structure of **3**, POV-RAY illustration, 40% thermal ellipsoids, all hydrogen atoms and lattice solvent omitted for clarity. Selected bond lengths (Å) and angles (°): Sm(1)–N(1) 2.448(6), Sm(1)–N(3) 2.462(6), Sm(1)–N(5) 2.467(6), N(1)–C(25) 1.331(8), N(2)–C(25) 1.351(8), N(1)–Sm(1)–N(2) 56.5(2), N(1)–C(25)–N(2) 120.1(8), C(25)–Sm(1)–C(50) 120.0(2), C(25)–Sm(1)–C(75) 118.9(2), C(50)–Sm(1)–C(75) 121.0(2). **(b)** Space filling depiction of **3** [same perspective as **(a)**].

Due to the unexpected generation of **3** from **2**, direct synthesis of **3** using divalent **1** [see Scheme 1 (vi)]† in redox transmetallation/ligand exchange was attempted.[7] Previous studies of this type using HDippForm, the Ln (= lanthanoid) elements La, Nd or Tm and [Hg(C$_6$F$_5$)$_2$] in a 3:1:1.5 ratio provide the monomeric fluoride bis(amidinate) complexes [Ln(F)(DippForm)$_2$(THF)], by heterolytic cleavage of a 2-position C–F bond of a [Ln(C$_6$F$_5$)(DippForm)$_2$(THF)$_n$] intermediate,[17] however these metals do not possess a typically stable divalent oxidation state. Unfortunately, as per the aforementioned metals, a [Ln(F)(DippForm)$_2$(THF)] species, where Ln = Sm (**4**),† was isolated in high yield indicating an analogous C–F activation mechanism.[17] As depicted in Fig. 3, complex **4** is a discrete monomer of composition [Sm(F)(DippForm)$_2$(THF)] with similar geometry to **1**.†¶ Akin to **1** and **3**, the coordination environment about the metal centre can also be described using the 1,3-diazaallyl carbons as point donors. This provides a near tetrahedral geometry [**1** C(25)–Sm(1)–O(1) 103.3(1)°, C(50)–Sm(1)–O(1) 111.1(1)°; **4** C(25)–Sm(1)–F(1) 105.0(1)°, C(25)–Sm(1)–O(1) 111.9(1)°], in which the Sm–N bond lengths differ from those of **1** in a manner consistent with a transition from di- to trivalent samarium† [Sm(1)–N(1) 2.443(3) Å, Sm(1)–N(2) 2.454(3) Å].[9] The Sm–F bond compares well to the only literature example of a terminal samarium fluoride, a seven coordinate bis-Tp [Tp = hydrido tris(pyrazolyl)borate] supported complex from Takats and Sella [2.090(7) Å; six coordinate **4** 2.093(2) Å].[18] Location of a single broad ^{19}F{^{1}H} NMR resonance at −24.8 ppm

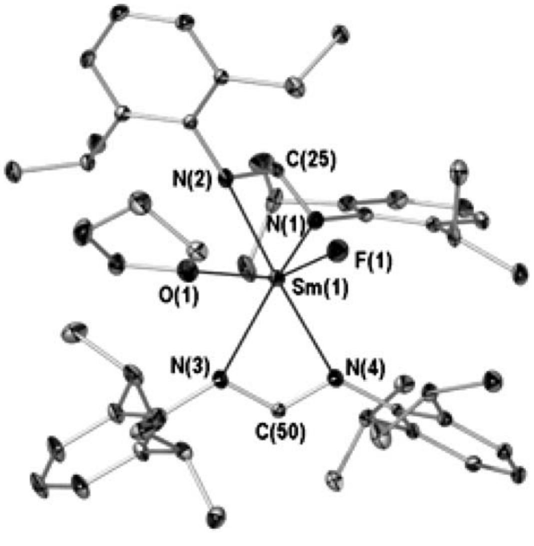

Fig. 3 Molecular structure of **4**, POV-RAY illustration, 40% thermal ellipsoids, all hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Sm(1)–F(1) 2.093(2), Sm(1)–O(1) 2.457(2), Sm(1)–N(1) 2.443(3), Sm(1)–N(2) 2.454(3), N(1)–C(25) 1.320(4), N(2)–C(25) 1.340(4), O(1)–Sm(1)–F(1) 82.2(1), N(1)–Sm(1)–N(2) 55.6(1), N(1)–C(25)–N(2) 118.1(3), O(1)–Sm(1)–C(25) 111.9(1), O(1)–Sm(1)–C(50) 105.1(1), F(1)–Sm(1)–C(25) 105.0(1), F(1)–Sm(1)–C(50) 117.9(1), C(25)–Sm(1)–C(50) 126.2(1).

confirms the inclusion of a fluoride ligand.† This differs considerably to the reported ^{19}F NMR resonance of the aforementioned Tp compound by some margin (−172.26 ppm).[18] However, this is not unexpected due to the direct metal contact of the fluoride to paramagnetic samarium(III) in both instances.

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Notes and references

§ *Method (i) for preparation of* **1**: a tetrahydrofuran (40 cm^3) solution of [Na(DippForm)(THF)$_3$] (0.72 g, 1.19 mmol) was added dropwise to a cooled (*ca.* 0 °C) deep blue solution of [Sm(I)$_2$(THF)$_2$] (0.33 g, 0.60 mmol), also in tetrahydrofuran (50 cm^3). The resulting deep green solution was gradually warmed to ambient temperature and stirred for two hours. Filtration, followed by removal of all volatiles *in vacuo*, gave a green powder that was extracted into toluene (10 cm^3) and placed at −10 °C overnight to yield deep green rhombohedral plates of **1** [0.43 g, 70% by {Na(DippForm)(THF)$_3$}], m.p. 201 °C (dec.). Samarium analysis (%) calcd for $C_{58}H_{86}N_4O_2Sm$: Sm 14.72; found: Sm 14.58; IR (Nujol): 1932 w sh, 1866 w sh, 1798 w sh, 1667 m sh, 1602 m, 1468 s br, 1389 s, 1365 s, 1272 m, 1231 s, 1108 m, 1009 m, 946 m, 917 m, 873 w, 829 w, 798 m sh, 756 s sh, 728 s sh, 687 s sh cm^{-1}; ^{1}H NMR (C_6D_6, 300 K): δ = 8.90 (br s, 8H; CH, *i*Pr), 7.45–6.9 (br m, 12 H; Ar–H), 6.3 [br s, 2H; NC(H)N], 3.45 (s br, 8H; OCH$_2$, THF), 3.22 (br s, 48H; CH$_3$, *i*Pr), 1.65 (br s, 8H; CH$_2$, THF).

Method for preparation of **3**: dissolution of **2** (0.43 g, 0.27 mmol) into warm (35 °C) hexane (40 cm^3) resulted in immediate precipitation of NaI and [SmI$_3$(THF)$_{3.5}$] to leave **3** in solution. Filtration, followed by removal of volatiles *in vacuo*, yielded colourless **3** as a fine powder. Extraction into toluene (10 cm^3), followed by placement at −10 °C overnight, gave **3** as small, light yellow, irregular prisms (0.19 g, 72%), m.p. 221 °C. Samarium analysis (%) calcd for $C_{75}H_{105}N_6Sm$ (**3** without lattice toluene): Sm 12.12; found: Sm 11.89; IR (Nujol): 1932 w sh, 1865 w sh, 1798 w sh, 1665 m br, 1567 m, 1478 m, 1380 m sh, 1362 m, 1331 m sh, 1286 m, 1257 m, 1234 m sh, 1000 w sh, 956 w sh, 820 m, 797 s sh, 766 m sh, 753 s sh cm^{-1}; ^{1}H NMR (C_6D_6, 300 K): δ = 10.01 [br s, 3H; NC(H)N], 7.40–6.87 (br m, 18H; Ar–H), 4.01 (br s, 12H; CH, *i*Pr), 1.45 (br s, 72H; CH$_3$, *i*Pr).

¶ Crystal data for **1**: $C_{58}H_{86}N_4O_2Sm$, M = 1021.66, triclinic, $P\bar{1}$ (No. 2), a = 12.1023(2), b = 12.7993(3), c = 19.6691(5) Å, α = 84.4520(10), β = 86.800(2), γ = 63.9530(10)°, V = 2724.19(10) Å^3, Z = 2, D_c = 1.246 g cm^{-3}, F_{000} = 1080, μ = 1.121 mm^{-1}, $2\theta_{max}$ = 56.56°, 24871 reflections collected, 13029 unique (R_{int} = 0.0571). Final $GooF$ = 1.044, R_1 = 0.0542, wR_2 = 0.904, R indices based on 10328 reflections with $I > 2\sigma(I)$ (refinement on F^2), 602 parameters, 0 restraints.

Crystal data for **2**: $C_{148}H_{236}I_4N_8O_{12}Sm_2$, M = 3173.73, monoclinic, $P2_1/c$ (No. 15), a = 26.7632(3), b = 14.3697(2), c = 41.5794(5) Å, β = 91.7860(10)°, V = 15982.8(3) Å^3, Z = 4, D_c = 1.319 g cm^{-3}, F_{000} = 6536, μ = 1.560 mm^{-1}, $2\theta_{max}$ = 56.60°, 61917 reflections collected, 30037 unique (R_{int} = 0.0572). Final $GooF$ = 1.031, R_1 = 0.0603, wR_2 = 0.1742, R indices based on 16943 reflections with $I > 2\sigma(I)$ (refinement on F^2), 1618 parameters, 0 restraints.

Crystal data for **3**: $C_{92.5}H_{125}N_6Sm$, M = 1471.34, monoclinic, $P2_1/n$ (No. 14), a = 13.1662(2), b = 37.9133(8), c = 16.4994(3) Å, β = 96.1070(10)°, V = 8189.3(3) Å^3, Z = 4, D_c = 1.193 g cm^{-3}, F_{000} = 3136, μ = 0.765 mm^{-1}, $2\theta_{max}$ = 56.74°, 44716 reflections collected, 18160 unique (R_{int} = 0.1993). Final $GooF$ = 0.956, R_1 = 0.0938, wR_2 = 0.1435, R indices based on 6734 reflections with $I > 2\sigma(I)$ (refinement on F^2), 939 parameters, 0 restraints.

Crystal data for **4**: $C_{54}H_{78}FN_4OSm$, M = 968.55, monoclinic, $P2_1/n$ (No. 14), a = 20.4714(2), b = 12.1996(2), c = 21.6593(3) Å, β = 110.0650(10)°, V = 5080.93(12) Å^3, Z = 4, D_c = 1.266 g cm^{-3}, F_{000} = 2036, μ = 1.199 mm^{-1}, $2\theta_{max}$ = 56.48°, 32459 reflections collected, 12173 unique (R_{int} = 0.0518). Final $GooF$ = 1.044, R_1 = 0.0605, wR_2 = 0.1572, R indices based on 10645 reflections with $I > 2\sigma(I)$ (refinement on F^2), 566 parameters, 0 restraints.

CCDC 262796–262799. See http://www.rsc.org/suppdata/cc/b5/b501447f/ for crystallographic data in CIF or other electronic format.

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