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

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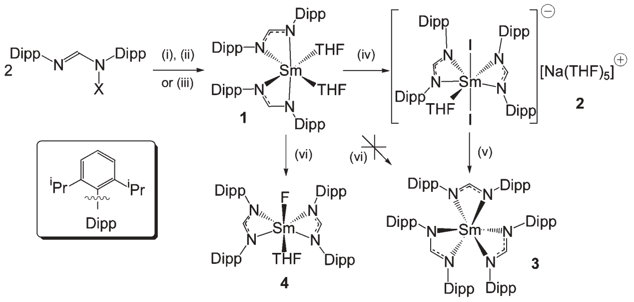
Received (in Cambridge, UK) 28th January 2005, Accepted 17th March 2005
First published as an Advance Article on the web 7th April 2005
DOI: 10.1039/b501447f

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.

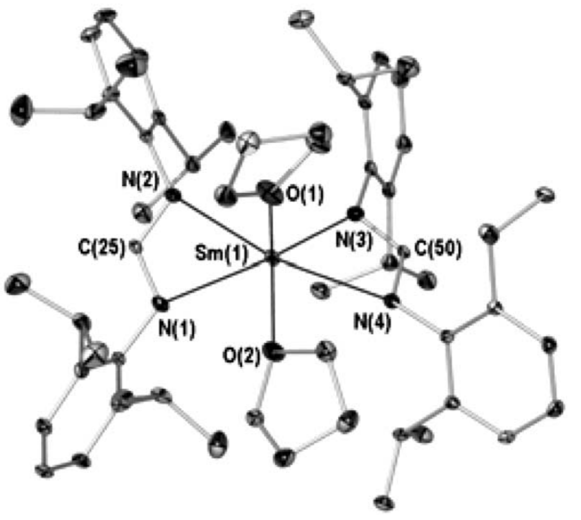


Fig. 1 Molecular structure of **1**, POV-RAY illustration, 40% thermal ellipsoids, all hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Sm(1)–N(1) 2.529(3), Sm(1)–N(4) 2.617(3), Sm(1)–O(1) 2.560(3), Sm(1)–O(2) 2.599(3), N(1)–C(25) 1.323(4), N(2)–C(25) 1.317(4), N(1)–Sm(1)–N(2)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

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

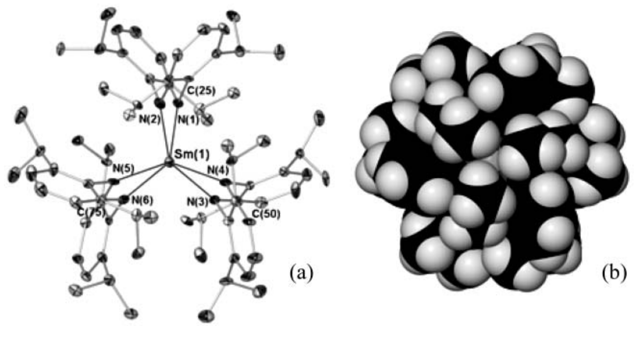

Fig. 2 **(a)** Molecular structure of **3**, POV-RAY illustration, 40% thermal ellipsoids, all hydrogen atoms and lattice solvent omitted for clarity. Selected bond lengths (Å) and angles (°): Sm(1)–N(1) 2.448(6), Sm(1)–N(3) 2.462(6), Sm(1)–N(5) 2.467(6), N(1)–C(25) 1.331(8), N(2)–C(25) 1.351(8), N(1)–Sm(1)–N(2) 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)**].

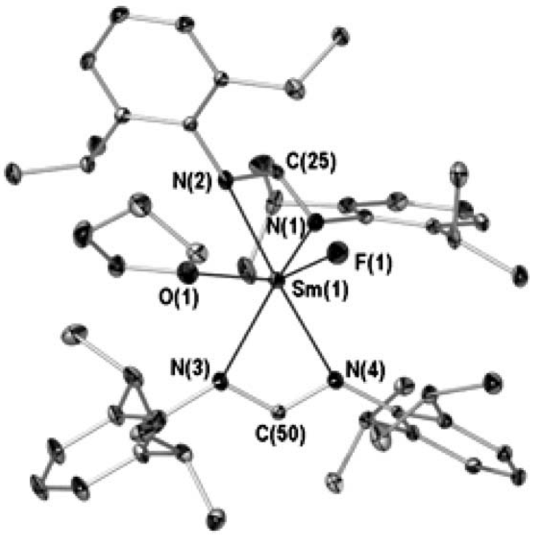

Fig. 3 Molecular structure of **4**, POV-RAY illustration, 40% thermal ellipsoids, all hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Sm(1)–F(1) 2.093(2), Sm(1)–O(1) 2.457(2), Sm(1)–N(1) 2.443(3), Sm(1)–N(2) 2.454(3), N(1)–C(25) 1.320(4), N(2)–C(25) 1.340(4), O(1)–Sm(1)–F(1)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

We would like to thank the Australian Research Council for continued financial support and Prof. Glen B. Deacon for invaluable discussions.

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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}; ^1H 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}; ^1H 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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