

**ESI for : The synthesis of a sterically hindered samarium(II)
bis(amidinate) and conversion to its homoleptic trivalent congener**

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Experimental

N,N'-Bis(2,6-diisopropylphenyl)formamidine, DippFormH, was synthesised according to a modified published procedure.¹ [Na(DippForm)(THF)₃],² [Sm(I)₂(THF)₂],³ [Hg(C₆F₅)₂]⁴ and [Sm{N(SiMe₃)₂}₂(THF)₂]⁵ were prepared by literature procedures. Samarium metal was purchased from Tianjiao International Trading Co. (USA), stored under purified nitrogen and freshly filed prior to use. Sodium bis(trimethylsilyl)amide (1.0 M in THF) was purchased from Aldrich. Tetrahydrofuran (THF) and hexane were dried over sodium, freshly distilled from sodium benzophenone ketyl and freeze-thaw degassed prior to use. Toluene was dried over sodium and freshly distilled from Na/K alloy prior to use. All manipulations were performed using conventional Schlenk or glovebox techniques under an atmosphere of high purity dinitrogen in flame-dried glassware. Infrared spectra were recorded as Nujol mulls sandwiched between sodium chloride plates on a Nicolet Nexus FTIR spectrophotometer. ¹H NMR spectra were recorded at 300.13 MHz and ¹⁹F NMR spectra were recorded at 282.40 MHz using a Bruker AC300 spectrometer, with chemical shifts referenced to the residual ¹H or ¹³C resonances of the *deutero*-benzene solvent used or an external CCl₃F standard in *deutero*-acetone (δ = 0). Melting points were determined in sealed glass capillaries under dinitrogen and are uncorrected. Samarium analyses were conducted on accurately weighed samples by complexometric titration with [Na₂(EDTA)] and xylenol orange indicator after digestion in concentrated HNO₃/H₂SO₄.

[Sm(DippForm)₂(THF)₂] (1)

Method (i): A tetrahydrofuran (40 cm³) 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 cm³). 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 cm³) 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.).

Method (ii): Tetrahydrofuran (20 cm³) was added to a Schlenk flask charged with samarium metal filings (0.15 g, 1.00 mmol), [Hg(C₆F₅)₂] (0.37 g, 0.69 mmol) and DippFormH (0.51 g, 1.40 mmol). The resulting slurry was stirred at ambient temperature for 12 hours before filtration (to remove elemental mercury and samarium metal) and removal of all volatiles *in vacuo*. The dark green microcrystalline material obtained was extracted into toluene (20 cm³) and concentrated to the point of crystallisation (ca. 15 cm³). Placement at -10 °C overnight gave **1** as deep green rhombohedral plates (0.58 g, 82 % by [Hg(C₆F₅)₂]), m.p. 202 °C (dec.).

Method (iii): A tetrahydrofuran (20 cm³) solution of DippFormH (0.51g, 1.40 mmol) was added to a cooled (0 °C) solution of [Sm{N(SiMe₃)₂}(THF)₂] (0.43 g, 0.70 mmol), also in tetrahydrofuran (20 cm³). After stirring for two hours, the deep green solution was dried *in vacuo* to remove all volatiles and extracted into fresh toluene (20 cm³). Concentration to the point of crystallisation (ca. 15 cm³) and placement at -10 °C overnight gave **1** as deep green rhombohedral plates (0.39 g, 55 %), m.p. 201 °C (dec.). Samarium analysis (%) calcd for C₅₈H₈₆N₄O₂Sm₁: 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 (C₆D₆, 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; OCH₂, THF), 3.22 (br s, 48H; CH₃, *i*Pr), 1.65 (br s, 8H; CH₂, THF).

[Na(THF)₅][Sm(I)₂(DippForm)₂(THF)] (2)

[Sm(I)₂(THF)₂] (0.17 g, 0.31 mmol) in tetrahydrofuran (20 cm³) was added dropwise to a deep green THF solution of **1** prepared *in situ* by method (i) (0.60 mmol scale) and stirred for 24 hours. This resulted in a gradual loss of dark green colouration to render a light yellow solution with visible metallic[‡] precipitate. Filtration and removal of all volatiles *in vacuo* provided a colourless powder. Extraction into toluene (5 cm³) followed by standing for three days yielded colourless rectangular blocks of **2** (0.56 g, 59 % by **1**), m.p. 178 °C. Samarium analysis (%) calcd for C₇₄H₁₁₈I₂N₄Na₁O₆Sm₁: Sm 9.48; found: Sm 9.56; IR (Nujol): 1931 w sh, 1866 w sh, 1800 w sh, 1666 s, 1587 m sh, 1488 m sh, 1456 s br, 1381 m sh, 1362 m sh, 1332 m sh, 1287 s sh, 1257 m, 1234 m sh, 1181 s sh, 1098 m sh, 1058 m, 1043 m, 1000 w sh, 953 w sh, 822 m sh, 799 s sh, 767 m sh, 754 s sh cm⁻¹; ¹H NMR (C₆D₆, 300 K): δ = 7.92-7.35 (br m, 14H; Ar-H and NC(H)N), 3.67 (br s, 8H; CH, *i*Pr), 3.51 (br m, 24H, OCH₂, THF), 1.63 (br m, 24 H; CH₂, THF), 1.21 (br s, 48H; CH₃, *i*Pr).

[Sm(DippForm)₃].⁵/₂C₇H₈ (3.⁵/₂C₇H₈)

Dissolution of **2** (0.43 g, 0.27 mmol) into warm (35 °C) hexane (40 cm³) resulted in immediate precipitation of NaI and [SmI₃(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 cm³) followed by placement at -10 °C overnight gave the title compound as small light yellow irregular prisms (0.19 g, 72 %), m.p. 221 °C. Samarium analysis (%)

[‡] This material is lustrous in appearance and reacts violently with water. In addition, we found it to be insoluble in all common laboratory solvents.

Supplementary Material (ESI) for Chemical Communications

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calcd for $C_{75}H_{105}N_6Sm_1$ (**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).

[Sm(F)(DippForm)₂(THF)] (4)

Tetrahydrofuran (20 cm^3) was added to a Schlenk flask charged with samarium filings (0.07 g, 0.47 mmol), $[Hg(C_6F_5)_2]$ (0.37 g, 0.69 mmol) and DippFormH (0.51 g, 1.40 mmol) and left to stir for 24 hours under a purified nitrogen atmosphere. Filtration followed by drying under vacuum yielded a light yellow powdered material that was extracted into toluene (10 cm^3) and cooled to -30° to give **4** as light yellow rhombohedral prisms (0.36 g, 81 % by $[Hg(C_6F_5)_2]$), m.p. 276 $^\circ C$ (dec.). Samarium analysis (%) calcd for $C_{54}H_{78}F_1N_4O_1Sm_1$: Sm 15.52; found: Sm 15.67; IR (Nujol): 1937 w sh, 1862 w sh, 1797 w sh, 1651 m sh, 1594 m, 1537 s, 1472 s, 1389 m sh, 1375 m sh, 1291 m, 1230 m, 1108 s, 1093 m sh, 1069 m, 1021 w, 982 w, 934 m sh, 865 w, 822 w, 762 s sh, 699 w cm^{-1} ; 1H NMR (C_6D_6 , 300 K): δ = 7.32-6.90 (br m, 14H; Ar-H and NC(H)N), 3.51 (br s, 8H; CH, *i*Pr), 3.42 (br m, 4H; OCH_2 , THF), 1.56 (br m, 4H; CH_2 , THF), 0.89 (br s, 48H; CH_3 , *i*Pr); ^{19}F NMR (C_6D_6 , 300 K): δ = -24.8 (br s, Sm-F).

X-Ray structure determination

Crystalline samples of compounds **1-4** were mounted on glass fibres in silicone oil at -150(2) °C (123(2) K). Data were collected on an Enraf-Nonius Kappa CCD diffractometer using graphite monochromated Mo_{Kα} X-ray radiation ($\lambda = 0.71073 \text{ \AA}$). Data were corrected for absorption by the DENZO-SMN package.⁶ Lorentz polarisation and absorption corrections were applied. Structural solution and refinement was carried out using the SHELX suite of programs^{7,8} with the graphical interface X-Seed.⁹

Abbreviated data

Crystal data for **1**: C₅₈H₈₆N₄O₂Sm₁, $M = 1021.66$, triclinic, $P-1$ (No. 2), $a = 12.1023(2)$, $b = 12.7993(3)$, $c = 19.6691(5) \text{ \AA}$, $\alpha = 84.4520(10)$, $\beta = 86.800(2)$, $\gamma = 63.9530(10)^\circ$, $V = 2724.19(10) \text{ \AA}^3$, $Z = 2$, $D_c = 1.246 \text{ g/cm}^3$, $F_{000} = 1080$, $\mu = 1.121 \text{ mm}^{-1}$, $2\theta_{\text{max}} = 56.56^\circ$, 24871 reflections collected, 13029 unique ($R_{\text{int}} = 0.0571$). Final $\text{GooF} = 1.044$, $R1 = 0.0542$, $wR2 = 0.904$, R indices based on 10328 reflections with $I > 2\text{sigma}(I)$ (refinement on F^2), 602 parameters, 0 restraints.

Crystal data for **2**: C₁₄₈H₂₃₆I₄N₈O₁₂Sm₂, $M = 3173.73$, monoclinic, $P2_1/c$ (No. 15), $a = 26.7632(3)$, $b = 14.3697(2)$, $c = 41.5794(5) \text{ \AA}$, $\beta = 91.7860(10)$, $V = 15982.8(3) \text{ \AA}^3$, $Z = 4$, $D_c = 1.319 \text{ g/cm}^3$, $F_{000} = 6536$, $\mu = 1.560 \text{ mm}^{-1}$, $2\theta_{\text{max}} = 56.60^\circ$, 61917 reflections collected, 30037 unique ($R_{\text{int}} = 0.0572$). Final $\text{GooF} = 1.031$, $R1 = 0.0603$, $wR2 = 0.1742$, R indices based on 16943 reflections with $I > 2\text{sigma}(I)$ (refinement on F^2), 1618 parameters, 0 restraints.

Crystal data for **3**: C_{92.5}H₁₂₅N₆Sm₁, $M = 1471.34$, monoclinic, $P2_1/n$ (No. 14), $a = 13.1662(2)$, $b = 37.9133(8)$, $c = 16.4994(3)$ Å, $\beta = 96.1070(10)$, $V = 8189.3(3)$ Å³, $Z = 4$, $D_c = 1.193$ g/cm³, $F_{000} = 3136$, $\mu = 0.765$ mm⁻¹, $2\theta_{\max} = 56.74^\circ$, 44716 reflections collected, 18160 unique ($R_{\text{int}} = 0.1993$). Final $\text{Goof} = 0.956$, $R1 = 0.0938$, $wR2 = 0.1435$, R indices based on 6734 reflections with $I > 2\sigma(I)$ (refinement on F^2), 939 parameters, 0 restraints.

Crystal data for **4**: C₅₄H₇₈F₁N₄O₁Sm₁, $M = 968.55$, monoclinic, $P2_1/n$ (No. 14), $a = 20.4714(2)$, $b = 12.1996(2)$, $c = 21.6593(3)$ Å, $\beta = 110.0650(10)$, $V = 5080.93(12)$ Å³, $Z = 4$, $D_c = 1.266$ g/cm³, $F_{000} = 2036$, $\mu = 1.199$ mm⁻¹, $2\theta_{\max} = 56.48^\circ$, 32459 reflections collected, 12173 unique ($R_{\text{int}} = 0.0518$). Final $\text{Goof} = 1.044$, $R1 = 0.0605$, $wR2 = 0.1572$, R indices based on 10645 reflections with $I > 2\sigma(I)$ (refinement on F^2), 566 parameters, 0 restraints.

Variata

For compound **1**, the maximum peak of residual electron density (1.843 e Å⁻³) is located 0.892 Å from Sm(1).

For compound **2**, data were very poor due to consistent twinning of samples. The 'DAMP 0 0' command was used to attain satisfactory thermal parameters and completion to $2\theta = 52.00^\circ$ is 79.8 %. This structure is included for connectivity only. Five peaks of residual electron density (the maximum five remaining; 2.369-1.990 e Å⁻³) form a lattice THF with low partial occupancy. Attempts to model this occupancy were thwarted by the poor quality of data.

For compound **3**, the 'DAMP 0 0' command was used to attain satisfactory thermal parameters. In addition, the methyl of one toluene of solvation (C83) was disordered over two sites of partial occupancy. These were modelled successfully with occupancies of 58:42, C(83A) and C(83B) respectively. The maximum peak of residual electron density ($1.200 \text{ e } \text{Å}^{-3}$) is located 1.281 Å from Sm(1).

For compound **4**, the maximum peak of residual electron density ($3.806 \text{ e } \text{Å}^{-3}$) is located 0.819 Å from Sm(1).

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary numbers 262796-262799. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 (0)1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

References

1. R.M. Roberts, *J. Org. Chem.*, 1949, **14**, 277.
2. M. L. Cole, A. J. Davies, C. Jones, P. C. Junk, *J. Organomet. Chem.*, 2004, **689**, 3093.
3. J. -L. Namy, P. Girard, H. B. Kagan, *Nouv. J. Chim.* 1981, **5**, 479.
4. G. B. Deacon, J. E. Cosgriff, E. T. Lawrence, C. M. Forsyth, D. L. Wilkinson in *Herrman-Brauer, Synthetic Methods of Organometallic and Inorganic Chemistry*, 3rd Ed. 1997, Ed. W. A. Herrmann, Thieme, Stuttgart, Germany.
5. W. J. Evans, D. K. Drummond, H. Zhang, J. L. Atwood, *Inorg. Chem.*, 1988, **27**, 575.

6. Z. Otwinowski, W. Minor, *"Processing of X-ray Diffraction Data Collected in Oscillation Mode"*, *Methods in Enzymology*, 276: *Macromolecular Crystallography, Part A*, 1997, **307**, Eds. C.W. Carter, R.M. Sweet, Academic Press, USA.
7. G.M. Sheldrick, SHELXL-97, University of Göttingen, Germany, 1997.
8. G.M. Sheldrick, SHELXS-97, University of Göttingen, Germany, 1997.
9. L. J. Barbour, *J. Supramol. Chem.*, 2001, **1**, 189.