#### SUPPLEMENTARY INFORMATION

# Formation of a cyclooctatetraenylsamarium(III) inverse sandwich that ring-opens tetrahydrofuran

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#### 1. Syntheses

#### General

The lanthanoid compounds described here are highly air and moisture sensitive, and were prepared and handled with vacuum-nitrogen line techniques and in a dry box in an atmosphere of purified nitrogen. [Sm(DippForm)<sub>2</sub>(thf)<sub>2</sub>] was prepared by the literature method.<sup>1</sup> Samarium metal was from Eutectix. Large chunks were filed in the drybox before use. Solvents (toluene, thf,  $C_6D_6$  and hexane) were pre-dried by distillation over sodium or sodium benzophenone ketyl before being stored under an atmosphere of nitrogen. Cyclooctatetraene (C<sub>8</sub>H<sub>8</sub>) was purchased from Sigma Aldrich, degassed and stored over dried 4Å molecular sieves. IR spectra were recorded as Nujol mulls between NaCl plates using an Agilent Technologies Cary 630 FTIR instrument within the range 4000-700 cm<sup>-1</sup>. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded with a Bruker DPX 300MHz spectrometer or a Bruker 400MHz instrument. Chemical shifts were referenced to the residual <sup>1</sup>H and <sup>13</sup>C resonances of the deuterated solvents (<sup>1</sup>H, <sup>13</sup>C). Microanalyses were determined by the Chemical Analysis Facility, Macquarie University, and all the samples were sealed in tubes under nitrogen. Melting points were determined in sealed glass capillaries under nitrogen and are uncalibrated. Crystals were immersed in crystallography oil, and were measured on a Rigaku SynergyS diffractometer or the MX1 beamline at the Australian Synchrotron (see details below). Crystal data and refinement details are given in Table S1. CCDC 2219717-2219719 for compounds 1-3, contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

#### **General procedure for 1-3**

 $C_8H_8$  (0.09mmol) was added dropwise to a Schlenk flask charged with [Sm(DippForm)<sub>2</sub>(thf)<sub>2</sub>] (0.18mmol) in 5mL of toluene (for 1) or thf (for 2 and 3) under a nitrogen atmosphere. After standing undisturbed for one day (for 1) or two days (for 2 and 3) at room temperature, the resulting crystals were isolated. Samples were dried in vacuo before being sent for elemental analysis. Although satisfactory %C analyses were obtained in all cases and reasonable %N values in two cases, %H were consistently high.

#### [Sm<sub>2</sub>(DippForm)<sub>4</sub>(COT)] 1

Red crystals were obtained after concentrating the solution and leaving it overnight at room temperature. (0.12 g, 72%), (Found: C, 69.87; H, 8.61; N, 6.01; C<sub>108</sub>H<sub>148</sub>N<sub>8</sub>Sm<sub>2</sub> (1859.1, after

the loss of any toluene of solvation) requires C, 69.77; H, 8.02; N, 6.03%). IR (Nujol): 3060m, 2728w, 1665m, 1594m, 1517s, 1363m, 1337m, 1289s, 1255m, 1235m, 1190s, 1116m, 1081w, 1056m, 1030m, 1018m, 932m, 907w, 798m, 764m, 764s, 754s, 741s, 728s, 694m cm <sup>-1</sup>. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300 MHz): 10.71 (s, 4H, NC*H*N), 8.34 (s, 8H, C<sub>8</sub>*H*<sub>8</sub>), 7.2 - 6.9 (m, 24H, aromatic Hs), 2.35 (m,16H, Dipp-C*H*), 2.11 (Toluene-C*H*<sub>3</sub>), 1.5 - -2.0 (96H, Dipp-C*H*<sub>3</sub>). <sup>13</sup>C NMR (75.5 MHz, C<sub>6</sub>D<sub>6</sub>, 296K): 21.42 (Toluene: *C*H<sub>3</sub>), 22.73 (Dipp- *C*H<sub>3</sub>), 67.90 (*C*<sub>8</sub>H<sub>8</sub>), 125.70 (Toluene: *C*H(4)), 128.70 (Toluene: *C*H(3,5)), 129.34 (Toluene: *C*H(2,6)), 137.90 (Toluene: *C*H(1)), 124.38, 127.39, 132.90 (aromatic C resonances – not assigned). Crystals used for NMR measurements were taken directly from under toluene supernatant. Alternatively, dissolution of **1** in C<sub>6</sub>D<sub>6</sub> and leaving it undisturbed overnight yielded red crystals of complex **1**·4C<sub>6</sub>D<sub>6</sub> suitable for X-ray crystallography.

### [Sm(DippForm)(COT)(thf)<sub>2</sub>] 2

Purple crystals were obtained after layering the reaction mixture using hexane antisolvent and concentrating afterwards. (0.0196 g, 29%), (Found: C, 64.57; H, 8.69; N, 5.60; C<sub>41</sub>H<sub>59</sub>N<sub>2</sub>O<sub>2</sub>Sm (762.25) requires C, 64.60; H, 7.80; N, 3.67 %). IR (Nujol): 2722m, 1667w, 1526s, 1324m, 1312m, 1285s, 1251m, 1188m, 1099w, 1054m, 1030m, 1008m, 927w, 889m, 873m, 770m, 758m, 722m, 705s cm<sup>-1</sup>. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300 MHz): 10.93 (s, 8H, C<sub>8</sub>*H*<sub>8</sub>), 8.31 (s, 1H, NC*H*N), 7.4 - 7.0 (m, 6H, aromatic Hs), 3.79 (8H, thf: α-C*H*<sub>2</sub>), 2.55 (m,4H, Dipp-C*H*), 1.56 (8H, thf: β-C*H*<sub>2</sub>), 1.16 – 1.18 (m, 24H, Dipp-C*H*), <sup>13</sup>C NMR (75.5 MHz, C<sub>6</sub>D<sub>6</sub>, 296K): 24.63 (Dipp-CH<sub>3</sub>), 25.95 (thf: β-*C*H<sub>2</sub>), 30.06 (Dipp-*C*H), 71.82 (thf: α-*C*H<sub>2</sub>), 82.58 (*C*<sub>8</sub>H<sub>8</sub>), 123.52, 124.48, 141.14, 143.97 (aromatic C resonances – not assigned).

## [Sm(DippForm)<sub>2</sub>(O-C<sub>4</sub>H<sub>8</sub>-DippForm)(thf)]·thf 3

Colourless crystals were obtained after concentrating the supernatant solution separated from the product **2** crystals and keeping it in the refrigerator overnight. (0.0254 g, 20%), M.p. 210°C, (Found: C, 71.91; H, 9.46; N, 5.83; C<sub>83</sub>H<sub>121</sub>N<sub>6</sub>O<sub>2</sub>Sm (1385.25, loss of one thf of crystallization) requires C, 72.60; H, 9.31; N, 5.71 %). IR (Nujol): 2723w, 1666m, 1637s, 1587m, 1525s, 1361m, 1319s, 1279s, 1235m, 1190m, 1112s, 1072m, 1056m, 1044m, 1030m, 933m, 873w, 800m, 767w, 755s cm <sup>-1</sup>. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300 MHz): 9.67 (s, 2H, Dipp-NCHN), 7.36 (s, 1H, Dipp-NCHN: RO-thf), 7.25 (m, 2H, N-CH<sub>2</sub>: RO-thf), 7.24 - 6.8 (m, 18H, aromatic Hs), 5.36 (m, 2H, CH<sub>2</sub>: RO-thf), 4.42 (m, 2H, CH<sub>2</sub>: RO-thf), 3.69 & 3.61 (2H+2H, Dipp-CH: RO-thf), 3.5 - 3.1 (8H, Dipp-CH), 2.89 (4H, thf:  $\alpha$ -CH<sub>2</sub>), 2.73 (2H, CH<sub>2</sub>: RO-thf), 1.5 - 0.8 (24H, Dipp-CH<sub>3</sub>: RO-thf; 48H, Dipp-CH<sub>3</sub>; 4H, thf:  $\beta$ -CH<sub>2</sub>). <sup>13</sup>C NMR (75.5 MHz, C<sub>6</sub>D<sub>6</sub>, 296K): 14.32, 23.04, 23.90, 24.51, 25.36, 28.59, 28.82, 31.96, 34.78, 51.58, 68.31, 72.59, 123.16, 123.25, 123.50, 123.55, 124.02, 124.71, 132.39, 139.97, 142.72, 145.49, 148.47, 151.56.

### Procedure for complex 1 giving 2 and 3 in thf

3 mL of thf was added to a Schlenk flask charged with complex 1 (0.05mmol). It was left undisturbed and the colour gradually changed from red to purple within 4 hours. Crystals of 2 were obtained after layering with hexane. The presence of 3 was found in the NMR spectrum of the remaining reaction mixture.

# 2. <sup>1</sup>H, <sup>13</sup>C NMR and IR Spectra of complexes



Fig. S1 <sup>1</sup>H NMR spectrum of  $[Sm_2(DippForm)_4(COT)] \cdot C_6D_6(1)$ 



Fig. S2 <sup>13</sup>C NMR spectrum of  $[Sm_2(DippForm)_4(COT)]$ ·C<sub>6</sub>D<sub>6</sub> (1)



Fig. S3 IR spectrum of  $[Sm_2(DippForm)_4(COT)] \cdot C_6 D_6(1)$ 



Fig. S4 <sup>1</sup>H NMR spectrum of [Sm(DippForm)(COT)(thf)<sub>2</sub>]·2thf (2)



Fig. S5 <sup>13</sup>C NMR spectrum of [Sm(DippForm)(COT)(thf)<sub>2</sub>]·2thf (2)



Fig. S6 IR spectrum of [Sm(DippForm)(COT)(thf)<sub>2</sub>]·2thf (2)



Fig. S7 <sup>1</sup>H NMR spectrum of [Sm(DippForm)<sub>2</sub>(O-C<sub>4</sub>H<sub>8</sub>-DippForm)(thf)] (3)



Fig. S8 <sup>13</sup>C NMR spectrum of [Sm(DippForm)<sub>2</sub>(O-C<sub>4</sub>H<sub>8</sub>-DippForm)(thf)] (3)



Fig. S9 IR spectrum of [Sm(DippForm)<sub>2</sub>(O-C<sub>4</sub>H<sub>8</sub>-DippForm)(thf)] (3)

### 3. X-ray crystallography

Single crystals coated with viscous hydrocarbon oil were mounted on glass fibres or loops. Complex **2** was measured at the Australian Synchrotron on the MX1 macromolecular beamlines, data integration was completed using Blue-ice <sup>2</sup> and XDS <sup>3</sup> software programs. Complexes **1** and **3** were measured on a Rigaku SynergyS diffractometer. The SynergyS operated using microsource Cu-K $\alpha$  radiation ( $\lambda = 1.54184$  Å) for **3** and Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å) for **1** at 123 K. Data processing was conducted using CrysAlisPro.55 software suite.<sup>5</sup> Structural solutions were obtained by either direct methods <sup>4</sup> or charge flipping <sup>5</sup> methods and refined using full-matrix least-squares methods against F<sup>2</sup> using SHELX2015,<sup>6</sup> in conjunction with Olex2 <sup>5</sup> graphical user interface. All hydrogen atoms were placed in calculated positions using the riding model. Crystal data and refinement details are given in **Table S1**. CCDC 2219717-2219719 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

	1	2	3
Formula	$C_{132}H_{172}N_8Sm_2$	$C_{41}H_{59}N_2O_2Sm$	$C_{87}H_{129}N_6O_3Sm$
$M_r$	2171.47	762.25	1457.30
Crystal System	Triclinic	Orthorhombic	Triclinic
Space group	<i>P</i> -1	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	<i>P</i> -1
<i>a</i> (Å)	15.9605(2)	10.842(2)	12.6902(4)
b (Å)	17.7059(2)	18.607(4)	17.9896(7)
c (Å)	21.0634(3)	18.765(4)	20.6655(4)
α (°)	95.1820(10)	90	97.357(2)
β (°)	96.0570(10)	90	103.624(2)
γ (°)	98.3200(10)	90	108.342(3)
$V(Å^3)$	5823.06(13)	3785.6(13)	4246.3(2)
Ζ	2	4	2
$ ho_{\rm calc}, { m g \ cm^{-3}}$	1.238	1.337	1.140
$\mu$ , mm <sup>-1</sup>	1.050	1.586	5.551
$N_{ au}$	20432	47416	76924
$N(R_{int})$	20432 (-)	7196 (0.0654)	16575(0.1189)
$R_1(I > 2 \sigma(I))$	0.0448	0.0292	0.0763
$wR_2$ (all data)	0.1069	0.0767	0.1904
GOF	1.140	1.040	1.074

Table S1 Crystal data and structural refinement for lanthanoid complexes 1-3

### 4. Selected bond angles (°) and lengths (Å)

### 4.1 [Sm<sub>2</sub>(DippForm)<sub>4</sub>(COT)]·4C<sub>6</sub>D<sub>6</sub> 1

Sm1-COT(cen) 2.218, Sm2-COT(cen) 2.221, Sm1-N1 2.447(4), Sm1-N2 2.534(4), Sm1-N3 2.511(4), Sm1-N4 2.458(4), Sm2-N5 2.440(4), Sm2-N6 2.541(4), Sm2-N7 2.437(4), Sm2-N8 2.525(4), N1-Sm1-N2 54.98(12), N4-Sm1-N3 55.03(13), N7-Sm2-N8 55.25(12), N5-Sm2-N6 55.06(12).

### 4.2 [Sm(DippForm)(COT)(thf)<sub>2</sub>]·2thf 2

Sm1-COT(cen) 1.957, Sm-O1 2.553(4), Sm-O2 2.495(3), Sm-N1 2.542(4), Sm-N2 2.545(4), N1-C13 1.322(6), N2-C13 1.310(6), C13-N2-Sm 93.0(3), N2-C13-N1 120.6(4), N1-C13-Sm 60.3(2)

### 4.3 [Sm(DippForm)<sub>2</sub>(O-C<sub>4</sub>H<sub>8</sub>-DippForm)(thf)] 3

Sm1-O2 2.064(4), Sm1-N2 2.453(5), Sm1-O1 2.481(4), Sm1-N1 2.470(4), Sm1-N4 2.436(5), Sm1-N3 2.531(4), N2-C13 1.321(7), N1-C13 1.334(7), N6-C58 1.448(9), N4-C38 1.328(7), N3-C38 1.317(8), N6-C71 1.360(9), N5-C71 1.281(9),O2-Sm1-O1 85.73(16), N2-Sm1-N1 55.26(15), N4-Sm1-N3 54.52(15), C55-O2-Sm1 171.7(4), C13-N2-Sm1 92.0(3), C71-N6-C58 119.5(6), C71-N6-C67 119.8(5), C67-N6-C58 120.5(6), C38-N4-Sm1 95.2(3), C38-N3-Sm1 91.2(3), N2-C13-N1 118.6(5), N3-C38-N4 118.8(5), N5-C71-N6 123.9(6)

### 5. References

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