

## Synthesis and Solid-State Structures of Pyrazolymethane Complexes of the Rare Earths

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In this paper, we report the first examples of trispyrazolymethane complexes of rare earths. Reaction of  $\text{LnCl}_3$  with  $\text{Tpm}^*$  (tris(3,5-dimethylpyrazolyl)methane) in THF or acetonitrile gives good yields of the  $[\text{Ln}(\text{Tpm}^*)\text{Cl}_3]$  ( $\text{Ln} = \text{Y}, \text{Ce}, \text{Nd}, \text{Sm}, \text{Gd}, \text{Yb}$ ).  $\text{Tpm}^*$  adducts of the lanthanide triflates  $[\text{Ln}(\text{Tpm}^*)(\text{OTf})_3(\text{THF})]$  ( $\text{Ln} = \text{Y}, \text{Ho}, \text{Dy}$ ) may also be prepared. The X-ray crystal structures of  $[\text{Y}(\text{Tpm}^*)\text{Cl}_3]$ ,  $[\text{Sm}(\text{Tpm}^*)\text{Cl}_3(\text{THF})]$ , and  $[\text{Ln}(\text{Tpm}^*)(\text{OTf})_3(\text{THF})]$  ( $\text{Ln} = \text{Y}, \text{Ho}$ ) are reported. The halide/triflate complexes may be used to prepare the aryloxide complexes  $[\text{Ln}(\text{Tpm}^*)(\text{OAr}^{\text{Me}_2})_3]$  ( $\text{Ln} = \text{Y}, \text{Nd}, \text{Sm}, \text{Yb}$ ;  $\text{Ar}^{\text{Me}_2} = \text{C}_6\text{H}_3\text{-2,6-(CH}_3)_2$ ), which are fluxional in solution as a result of interactions between the  $\text{Tpm}^*$  and the aryloxide groups. The structures of the Nd and Sm complexes have been determined. Finally, the reaction of  $[\text{Nd}(\text{BH}_4)_3(\text{THF})_3]$  with  $\text{Tpm}^*$  in THF results in the displacement of two THF molecules to give  $[\text{Nd}(\text{Tpm}^*)(\text{BH}_4)_3(\text{THF})]$ . Infrared spectra are consistent with tridentate borohydride coordination. The X-ray structures of these compounds indicate that the  $\text{Tpm}^*$  ligand is less strongly bound than its anionic trispyrazolylborate analogues.

### Introduction

The molecular chemistry of the rare earths has seen major advances in the past 10–15 years.<sup>1–3</sup> The availability of ever-bulkier ancillary ligands has made possible the stabilization of unusual oxidation states, surprising coordination environments, and unexpected reactivity.<sup>4</sup> Although cyclopentadienyl-based (Cp) ligands have largely dominated this area, a number of alternative approaches have been used.<sup>5,6</sup> The anionic trispyrazolylborate (Tp) ligands have been successfully used as ancillaries for the 4f block.<sup>7</sup> By contrast, with the effectively planar Cp ligands, the tripodal pyrazolylborate ligands have the advantage of providing greater lateral

protection to the metal center. By adjusting the steric demand of the substituents in the 3-position of the pyrazolyl groups, it has proved possible to isolate well-behaved lanthanide complexes which have proved remarkably robust for ligand redistribution. Of particular interest are half-sandwich complexes in which a single ancillary group controls the coordination sphere of the metal center. A series of remarkable divalent complexes have been reported in recent years by Takats, most notably hydrides, several hydrocarbyls, and related derivatives.<sup>8–10</sup> Curiously, trivalent complexes have proved more difficult to prepare, and we are aware of only two examples of half-sandwich Tp/hydrocarbyl complexes.<sup>11–13</sup>

The neutral analogues of Tp ligands, the trispyrazolylmethane (Tpm), have not received the same attention as the borates, primarily because of the absence of efficient

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synthetic protocols. This changed a few years ago when Reger reported a high-yielding route for the synthesis of several Tpm compounds, and this has led to a steady increase in their use.<sup>14</sup> Tpm complexes have been applied both to transition metals and to the labile s-<sup>15–17</sup> and p-blocks<sup>18,19</sup> where direct comparisons with Tp chemistry have been made. The area has recently been reviewed.<sup>20,21</sup> While our work was in progress, we became aware of Mountford's synthesis of some halides, aryloxides, and hydrocarbyl complexes of scandium and yttrium.<sup>22</sup> In this paper, we report the syntheses and characterization of a number of simple derivatives of tris(3,5-dimethylpyrazolyl)methane (Tpm\*) of yttrium and the lanthanides which complement and extend Mountford's work.

## Experimental Section

**General Procedures and Instrumentation.** All reactions were carried out under nitrogen under anhydrous conditions using standard Schlenk and glove box techniques. Solvents were distilled at atmospheric pressure either from alkali metal/benzophenone ketyl (ethers and hydrocarbons) or calcium hydride (dichloromethane and acetonitrile) or by passage over activated alumina columns<sup>23</sup> and stored under nitrogen in Young's valve ampoules over sodium mirrors (except dichloromethane and acetonitrile, which were stored over activated molecular sieves). Lanthanide halides were prepared from the oxide or hydrated chloride by the NH<sub>4</sub>Cl method.<sup>24</sup> Lanthanide triflates were prepared by reaction of a slight excess of the appropriate oxide with hot 1 M triflic acid. After filtration, the water was removed under reduced pressure, and the salt was dehydrated under dynamic vacuum at 150 °C.<sup>25</sup> The (3,5-dimethylpyrazolyl)methane (Tpm\*) was prepared by the method of Reger;<sup>14</sup> sodium-2,6-dimethylphenoxide was prepared by reaction of 2,6-dimethylphenol with an excess of sodium hydride in THF.

<sup>1</sup>H and <sup>13</sup>C-{<sup>1</sup>H} NMR spectra were recorded on Bruker Avance 500, VXR-400, and AMX-300 spectrometers in Wilmad NMR tubes equipped with Young's valves. Spectra were referenced internally to residual protio solvent (<sup>1</sup>H) or solvent (<sup>13</sup>C) resonances and are reported relative to tetramethylsilane. <sup>11</sup>B spectra were referenced externally to BF<sub>3</sub>·Et<sub>2</sub>O. FT-IR spectra were recorded on a Nicolet 205 FT-IR spectrometer as KBr pellets. CHN elemental analyses were carried out by Ms. Gillian Maxwell of the UCL Chemistry Analytical Services section.

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[Y(Tpm\*)Cl<sub>3</sub>], **1a**. Tpm\* (500 mg, 1.6 mmol) was dissolved in MeCN (20 mL) in a Schlenk flask to produce a pale yellow solution. This was then added gradually, with stirring, to a separate flask containing a clear, colorless solution of YCl<sub>3</sub> (330 mg, 1.6 mmol) in MeCN (50 mL). A white precipitate formed immediately. Stirring was continued for 1 h, and the solid was isolated by filtration and dried under dynamic vacuum overnight to give [Y(Tpm\*)Cl<sub>3</sub>] as a white, sparingly soluble powder. Yield: 660 mg (52%). Anal. Calcd for C<sub>16</sub>H<sub>22</sub>N<sub>6</sub>Cl<sub>3</sub>Y: C, 38.9; H, 4.5; N, 17.0. Found: C, 38.6; H, 4.3; N, 17.5. IR (KBr pellet, cm<sup>-1</sup>): 3129 m, 3095 w, 2924 m, 1560 s, 1458 s, 1414 s, 1379 s, 1304 s, 1261 s, 1155 w, 1109 m, 1040 s, 981 m, 905 m, 861 s, 795 m, 705, 633 w, 482 m. <sup>1</sup>H NMR (CD<sub>3</sub>CN, 400 MHz, 293 K): δ 7.90 (s, 1H, C-H), 6.08 (s, 3H, Tpm 4-CH), 2.64 (s, 9H, 5-Me), 2.52 (3-Me). Large colorless crystals suitable for X-ray diffraction were obtained by slow diffusion of solutions of YCl<sub>3</sub> and Tpm\* in MeCN in a sealed tube.

[Ce(Tpm\*)Cl<sub>3</sub>], **1b**. CeCl<sub>3</sub> (125 mg, 0.51 mmol) was stirred in THF (80 mL) to give a beige suspension. Upon addition of Tpm\* (150 mg, 0.51 mmol), the solid dissolved to give a slightly turbid, beige solution. After stirring for 2 h, the solution was filtered. The volume of the filtrate was reduced to 5 mL, and hexane was added. Upon cooling to -20 °C, an off-white, semicrystalline material precipitated. Drying under vacuum at 50 °C yielded [Ce(Tpm\*)Cl<sub>3</sub>]. Yield: 120 mg (34%). Anal. Calcd for C<sub>16</sub>H<sub>22</sub>N<sub>6</sub>Cl<sub>3</sub>Ce: C, 35.3; H, 4.1; N, 15.4. Found: C, 35.7; H, 4.3; N, 15.0. IR (KBr pellet, cm<sup>-1</sup>): 3141 w, 3086 w, 2970 m, 2890 m, 1564 s, 1456 s, 1415 m, 1379 m, 1306 s, 1268 s, 1037 s, 976 w, 904 m, 858 s, 823 m, 709 sh, 702 sh, 481 w. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz, 293 K): δ 1.93 (s, 9H, 5-Me), 2.3 (v br s, 9H, 3-Me, fwhh = 140 Hz), 4.21 (s, 3H, Tpm 4-CH), 6.40 (s, 1H, C-H).

[Nd(Tpm\*)Cl<sub>3</sub>], **1c**. NdCl<sub>3</sub> (400 mg, 1.6 mmol) was stirred in THF (10 mL) to give a pale-blue suspension. Upon addition of Tpm\* (480 mg, 1.6 mmol), the solid partially dissolved to give a pale-blue suspension. After stirring for 2 h, the solution was filtered. The volume of the filtrate was reduced to 5 mL, and hexane was added. Upon cooling to -20 °C, a light-blue, semicrystalline material precipitated. Decanting off the solid and drying under reduced pressure yielded [Nd(Tpm\*)Cl<sub>3</sub>(THF)], which desolvated upon heating to give [Nd(Tpm\*)Cl<sub>3</sub>]. Yield: 480 mg (54%). Anal. Calcd for C<sub>16</sub>H<sub>22</sub>N<sub>6</sub>Cl<sub>3</sub>Nd: C, 35.0; H, 4.0; N, 15.3. Found: C, 35.3; H, 4.3; N, 14.9. IR (KBr pellet, cm<sup>-1</sup>): 3140 w, 3086 w, 2970 m, 2890 m, 1564 sh, 1558 sh, 1458 s, 1415 m, 1380 m, 1307 s, 1262 s, 1031 s, 904 m, 858 s, 823 m, 710 sh, 701 sh, 481 w. <sup>1</sup>H NMR (CD<sub>3</sub>CN, 400 MHz, 293 K): δ 1.94 (s, 9H, 3-Me), 2.34 (s, 1H, Tpm C-H), 3.09 (s, 9H, 5-Me), 7.36 (s, 3H, Tpm 4-CH).

[Sm(Tpm\*)Cl<sub>3</sub>], **1d**. The reaction was carried out as for **1c** using SmCl<sub>3</sub> (860 mg, 3.3 mmol) in THF to afford a white powder which desolvated under vacuum. Yield: 960 mg (52%). Anal. Calcd for C<sub>16</sub>H<sub>22</sub>N<sub>6</sub>Cl<sub>3</sub>Sm: C, 34.6; H, 4.0; N, 15.1. Found: C, 34.4; H, 4.0; N, 14.9. IR (KBr pellet, cm<sup>-1</sup>): 3138 w, 3084 w, 2970 m, 2890 m, 1562 sh, 1558 sh, 1460 s, 1416 m, 1380 m, 1304 s, 1262 s, 1038 s, 980 w, 906 m, 860 s, 821 m, 721 m, 708 sh, 636 m, 482 w. <sup>1</sup>H NMR (CD<sub>3</sub>CN, 400 MHz, 293 K): δ 1.67 (s, 9H, 3-Me), 1.80 (m, 4H, THF), 3.62 (m, 4H, THF), 2.76 (s, 9H, 5-Me), 6.00 (s, 3H, Tpm 4-CH), 8.59 (s, 1H, Tpm C-H). Crystals of [Sm(Tpm\*)Cl<sub>3</sub>(THF)]·THF, **1d-a**, were obtained by layering SmCl<sub>3</sub> and Tpm\* solutions in THF in sealed glass tube.

[Gd(Tpm\*)Cl<sub>3</sub>], **1e**. The reaction was carried out in THF analogous to the procedure for **1a** using GdCl<sub>3</sub> (33 mg, 0.13 mmol) and Tpm\* (38 mg, 0.13 mmol) to afford [Gd(Tpm\*)Cl<sub>3</sub>(THF)] as a white, microcrystalline powder which desolvated upon removal of solvent under vacuum. Yield: 52 mg (74%). Anal. Calcd for C<sub>16</sub>H<sub>22</sub>N<sub>6</sub>Cl<sub>3</sub>Gd: C, 34.2; H, 3.9; N, 15.0. Found: C, 34.7; H, 4.3;

N, 14.6. IR (KBr pellet,  $\text{cm}^{-1}$ ): 3138 w, 3098 w, 2970 m, 2919 m, 2874 m, 1564 s, 1458 s, 1415 m, 1381 m, 1305 s, 1266 s, 1108 w, 1039 s, 980 w, 906 m, 861 s, 82 m, 806 m, 794 m, 707 sh, 482 w. The compound was NMR silent.

**[Yb(Tpm\*)(Cl)<sub>3</sub>], 1f.** The reaction was carried out in THF analogous to the procedure describe for **1a** using YbCl<sub>3</sub> (94 mg, 3.4 mmol) and Tpm\* (100 mg, 3.4 mmol) to afford Yb(Tpm\*)(Cl)<sub>3</sub> as a cream-colored, THF-insoluble powder. Yield: 124 mg (64%). Anal. Calcd for C<sub>16</sub>H<sub>22</sub>N<sub>6</sub>Cl<sub>3</sub>Yb: C, 33.3; H, 3.8; N, 14.5. Found: C, 33.6; H, 3.7; N, 14.2. IR (KBr pellet,  $\text{cm}^{-1}$ ): 3132 m, 3090 w, 2970 w, 2920 m, 1561 s, 1456 s, 1411 s, 1380 s, 1301 s, 1259 s, 1155 w, 1109 m, 1041 s, 980 m, 905 m, 859 s, 795 m, 704 m, 635 w, 483 m. Insolubility precluded the recording of <sup>1</sup>H NMR spectra.

**[Y(Tpm\*)(OTf)<sub>3</sub>·THF], 2a.** Tpm\* (300 mg, 1.0 mmol) in THF was added dropwise to a slightly turbid solution of Y(OTf)<sub>3</sub> (540 mg, 1.0 mmol) in THF. A clear, pale-yellow solution was produced, and stirring was continued overnight. The solution was filtered, and the volume of THF was decreased under reduced pressure until the product began to precipitate from solution. Precipitated product was redissolved by warming the flask. The flask was then placed inside a dewar and placed in a freezer at  $-20\text{ }^{\circ}\text{C}$  overnight for slow cooling. [Y(Tpm\*)(OTf)<sub>3</sub>(THF)] formed as clear, flat crystals. Yield: 370 mg (41%). Anal. Calcd for C<sub>23</sub>H<sub>30</sub>N<sub>6</sub>O<sub>10</sub>S<sub>3</sub>F<sub>9</sub>Y: C, 30.5; H, 3.3; N, 9.3. Found: C, 29.9; H, 3.2; N, 9.5. IR (KBr pellet,  $\text{cm}^{-1}$ ): 3150 w, 2998 m, 2938 m, 1570 m, 1460 m, 1424 m, 1328 s, 1208 s br, 1018 s, 911 w, 860 m, 804 w, 707 m, 633 s, 586 w, 512 m. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN, 293 K):  $\delta$  1.84 (m, 4H, THF), 2.43 (s, 9H, 3- or 5-Me), 2.59 (s, 9H, 3- or 5-Me), 3.67 (m, 4H, THF), 6.16 (s, 3H, Tpm 4-CH), 7.96 (s, 1H, Tpm C-H).

**[Ho(Tpm\*)(OTf)<sub>3</sub>(THF)], 2b.** The preparation of **2b** was carried out analogous to that of **2a** using Tpm\* (200 mg, 0.67 mmol) and Ho(OTf)<sub>3</sub> (410 mg, 0.67 mmol) in THF. [Ho(Tpm\*)(OTf)<sub>3</sub>(THF)] formed as clear crystals which desolvated upon removal of solvent. Yield: 290 mg (45%). Anal. Calcd for C<sub>23</sub>H<sub>30</sub>N<sub>6</sub>O<sub>10</sub>S<sub>3</sub>F<sub>9</sub>Ho: C, 28.2; H, 3.1; N, 8.6. Found: C, 27.6; H, 3.1; N, 8.4. IR (KBr pellet,  $\text{cm}^{-1}$ ): 3152 w, 2994 m, 2932 m, 1570 m, 1462 m, 1422 m, 1390 w, 1337 s, 1208 s br, 1021 s, 909 w, 861 m, 802 w, 707 m, 636 s, 586 w, 512 m. The compound was NMR silent.

**[Dy(Tpm\*)(OTf)<sub>3</sub>(THF)], 2c.** The preparation of **2c** was carried out analogous to that of **2a** using Tpm\* (130 mg, 0.44 mmol) and Dy(OTf)<sub>3</sub> (270 mg, 0.44 mmol). [Dy(Tpm\*)(OTf)<sub>3</sub>(THF)] was formed as flat, colorless crystals. Yield: 180 mg (42%). Anal. Calcd for C<sub>23</sub>H<sub>30</sub>N<sub>6</sub>O<sub>10</sub>S<sub>3</sub>F<sub>9</sub>Dy: C, 28.2; H, 3.1; N, 8.6. Found: C, 27.8; H, 3.0; N, 8.5. IR (KBr pellet,  $\text{cm}^{-1}$ ): 3145 w, 2996 m, 2930 m, 1569 m, 1465 m, 1419 m, 1391 w, 1337 s, 1206 s br, 1187 s, 1019 s, 909 w, 861 m, 802 w, 767 w, 705 m, 636 s, 586 w, 511 m. The compound was NMR silent.

**[Y(Tpm\*)(OAr<sup>Me2</sup>)<sub>3</sub>], 3a.** A turbid, white solution of YCl<sub>3</sub> (150 mg, 0.77 mmol) in THF was stirred in a Schlenk flask. To this was added dropwise a pale-yellow solution of Tpm\* (230 mg, 0.77 mmol) to afford a yellow solution and a white precipitate. After stirring for 2 h, NaOAr<sup>Me2</sup> (330 mg, 2.3 mmol) in THF (10 mL) was added dropwise to the suspension with stirring. The white solid dissolved during the addition of the aryloxide, and upon stirring for 2–3 h further, a white precipitate of NaCl formed. The suspension was allowed to settle overnight, and the salt was removed by filtration. The volume of the filtrate was reduced to 10 mL, and the solution was placed in a freezer at  $-25\text{ }^{\circ}\text{C}$ . After ca. 48 h, [Y(Tpm\*)(OAr<sup>Me2</sup>)<sub>3</sub>] had formed as large, colorless crystals. Yield: 470 mg (82%). Anal. Calcd for C<sub>40</sub>H<sub>49</sub>N<sub>6</sub>O<sub>3</sub>Y: C, 64.0; H, 6.6; N, 11.2. Found: C, 63.8; H, 6.7; N, 11.0. IR (KBr pellet,  $\text{cm}^{-1}$ ): 3137 w, 3100 w, 3008 m, 2915 s, 2849 m, 1590 s, 1566 m, 1463 s, 1427 s, 1379 m, 1306 s, 1285 s, 1241 m, 1090 m,

1038 m, 979 w, 906 w, 859 m, 800 w, 759 m, 746 m, 705 s, 531. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300 MHz, 293 K):  $\delta$  1.95 (s, 18H, Me-OAr), 2.06 (s, 9H, 3- or 5-Me), 2.58 (s, 9H, 3- or 5-Me), 5.94 (s, 3H, Tpm 4-CH), 6.31 (t,  $J = 7.2\text{ Hz}$ , 3H, OAr *p*-H), 6.78 (d,  $J = 7.2\text{ Hz}$ , 6H, OAr *m*-H), 8.05 (s, 1H, Tpm C-H). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>-Cl<sub>2</sub>, 75.44 MHz, 293 K):  $\delta$  11.48 (OArMe), 13.28 (3- or 5-Me), 17.59 (3- or 5-Me), 68.75 (Tpm CH), 107.94 (Tpm 4-CH), 114.54 (*p*-OAr), 126.60 (2-C-OAr), 127.76 (*m*-OAr), 140.00 (5-C Tpm\*), 155.12 (3-C Tpm\*), 162.89 (d,  $J_{\text{YC}} = 5.4\text{ Hz}$ , ipso-OAr).

**[Nd(Tpm\*)(OAr<sup>Me2</sup>)<sub>3</sub>], 3b.** The reaction was carried out analogous to the procedure for **3a** using NdCl<sub>3</sub> (250 mg, 0.100 mmol), Tpm\* (290 mg, 0.100 mmol), and HOAr<sup>Me2</sup> (360 mg, 0.300 mmol). After filtration, a light-greenish solution resulted from which light-blue, block-like crystals of Nd(Tpm\*)(OAr<sup>Me2</sup>)<sub>3</sub> were obtained which desolvated upon removal of solvent. Yield: 520 mg (69%). Anal. Calcd for C<sub>40</sub>H<sub>49</sub>N<sub>6</sub>O<sub>3</sub>Nd: C, 59.6; H, 6.1; N, 10.4. Found: C, 59.6; H, 6.2; N, 10.3. IR (KBr pellet,  $\text{cm}^{-1}$ ): 3135 w, 3108 w, 2920 s, 2855 s, 1600 w, 1563 m, 1475 s br, 1429 s, 1380 m, 1300 s, 1275 s, 1236 m, 1159 m, 1088 w, 1033 m, 978 w, 857 m, 820 s, 794 m sh, 721 m, 512 s. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz, 204 K):  $\delta$  0.34 (br s, 18H, Me-OAr), 0.49 (s, 9H, 5-Me), 2.62 (s, 1H, Tpm C-H), 4.65 (br s, 9H, 3-Me), 6.72 (s, 3H, Tpm 4-CH), 6.91 (br t,  $J = 5.1\text{ Hz}$ , 3H, *p*-H), 8.50 (br, 6H, *m*-H). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 100.58 MHz, 293 K):  $\delta$  8.03 (3- or 5-Me), 11.76 (3- or 5-Me), 15.55 (OArMe), 64.55 (Tpm CH), 119.27 (Tpm 4-CH), 122.05 (*p*-OAr), 128.17 (*m*-OAr), 141.38 (br, 2-OAr), 146.08 (Tpm\* qt), 151.65 (Tpm\* qt), 210.95 (br, ipso-OAr).

**[Sm(Tpm\*)(OAr<sup>Me2</sup>)<sub>3</sub>], 3c.** The preparation of **3c** was carried out analogous to that of **3a** using SmCl<sub>3</sub> (150 mg, 0.57 mol), Tpm\* (170 mg, 0.57 mmol), and NaOAr<sup>Me2</sup> (250 mg, 1.88 mol). The dark-orange solution of Sm(Tpm\*)(OAr<sup>Me2</sup>)<sub>3</sub> in THF was filtered to remove the NaCl, and the volume of THF was reduced under vacuum. The flask was placed in a Dewar flask and put in the freezer for crystallization. After 2 days, large pale-orange crystals of Sm(Tpm\*)(OAr<sup>Me2</sup>)<sub>3</sub> had formed. Yield: 310 g (65%). Anal. Calcd for C<sub>40</sub>H<sub>49</sub>N<sub>6</sub>O<sub>3</sub>Sm: C, 59.0; H, 6.1; N, 10.3. Found: C, 59.5; H, 6.5; N, 10.0. IR (KBr pellet,  $\text{cm}^{-1}$ ): 3140 w, 3105 w, 2923 s, 2852 s, 1606 w, 1568 m, 1475 s br, 1423 s, 1380 m, 1309 s, 1260 s, 1159 m, 1109 w, 1036 m, 956 w, 860 m, 818 s, 796 m sh, 707 m, 509 s. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300 MHz, 293 K):  $\delta$  1.22 (s, 18H, Me-OAr), 1.62 (s, 9H, 3-Me), 2.18 (s, 9H, 5-Me), 4.91 (s, 1H, Tpm C-H), 5.23 (s, 3H, *p*-H), 5.80 (s, 3H, Tpm 4-CH), 6.81 (s, 6H, *m*-H).

**[Sm(Tpm\*)(OAr<sup>Me3</sup>)<sub>3</sub>], 3d.** The preparation of **3d** was carried out analogous to that of **3c** from SmCl<sub>3</sub> (317 mg, 1.23 mmol). Yield: 508 mg (48%). Anal. Calcd for C<sub>43</sub>H<sub>55</sub>N<sub>6</sub>O<sub>3</sub>Sm: C, 60.4; H, 6.5; N, 9.8. Found: C, 60.0; H, 6.8; N, 9.6. IR (KBr pellet,  $\text{cm}^{-1}$ ): 3135 w, 3112 m, 2925 s, 2892 s, 2848 s, 1610 w, 1562 m, 1475 s br, 1428 s, 1375 m, 1340 m, 1310 s, 1258 m, 1158 s, 1112 w, 1040 m, 960 w, 860 m, 835 w, 816 s, 795 m, 705 m, 500 s. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300 MHz, 293 K):  $\delta$  1.11 (s, 18H, *o*-Me), 1.65 (s, 9H, 3-Me), 2.23 (s, 9H, *p*-CH<sub>3</sub>), 4.93 (s, 9H, 5-Me), 4.97 (s, 1H, Tpm C-H), 5.77 (s, 3H, Tpm 4-CH), 6.78 (s, 6H, *m*-H). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 75.44 MHz, 293 K):  $\delta$  10.18 (3-Me), 17.62 (OAr-*o*-Me), 17.72 (5-Me), 20.98 (OAr-*p*-Me), 62.10 (Tpm CH), 106.13 (Tpm 4-CH), 122.83 (*p*-OAr), 125.35 (*o*-OAr), 128.97 (*m*-OAr), 137.96 (Tpm\* qt), 156.23 (Tpm\* qt), 161.26 (br, ipso-OAr).

**[Yb(Tpm\*)(OAr<sup>Me2</sup>)<sub>3</sub>], 3e.** The preparation of **3e** was carried out analogous to that of **3a** using YbCl<sub>3</sub> (187 mg, 0.67 mmol), Tpm\* (200 mg, 0.67 mmol), and NaOAr<sup>Me2</sup> (245 mg, 2.0 mmol). The pale-yellow solution yielded a mass of small, shiny crystals upon cooling to  $-20\text{ }^{\circ}\text{C}$ . These desolvated upon removal of solvent and pumping to dryness to give a cream-colored powder. Yield:

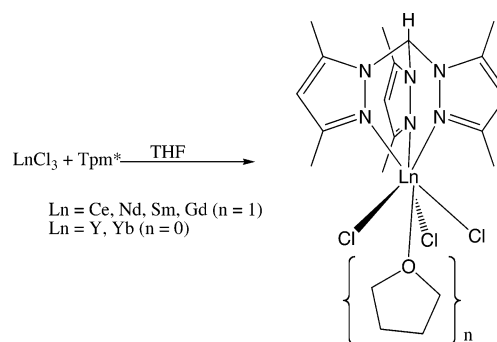
170 mg (30%). Anal. Calcd for  $C_{40}H_{49}N_6O_3Yb$ : C, 57.5; H, 5.9; N, 10.1. Found: C, 57.7; H, 5.9; N, 10.1. IR (KBr pellet,  $cm^{-1}$ ): 3140 w, 3106 w, 2907 s, 2851 m, 1606 m, 1570 m, 1470 s, 1423 s, 1375 m, 1306 s, 1253 s, 1160 sh, 1035 m, 1010 m, 1007 w, 955 w, 855 s, 820 s, 745 m, 707 m, 508 s.  $^1H$  NMR ( $CD_2Cl_2$ , 100.58 MHz, 204 K):  $\delta$  -52.1 (s, 9H, 3-Me), -32.1 (br s, 9H, Me-OAr), -6.3 (br s, 3H, *m*-H), 1.5 (t,  $J = 5.1$  Hz, 3H, *p*-H), 10.4 (br s, 3H, *m*-H), 22.1 (s, 9H, 5-Me), 78.9 (br s, 9H, Me-OAr), 74.1 (s, 1H, Tpm C-H).

[Nd(Tpm\*)( $BH_4$ )<sub>3</sub>(THF)], **4**. To a solution of Nd( $BH_4$ )<sub>3</sub>(THF)<sub>3</sub> (400 mg, 1.0 mmol) in THF (10 mL) was added slowly a solution of Tpm\* (298 mg, 1.0 mmol) in the same solvent (10 mL). The yellowish-green solution was allowed to stir overnight. The volume was reduced to 10 mL under reduced pressure, at which point some solid was beginning to precipitate. The solution was placed in a freezer at -20 °C overnight. The supernatant was decanted off, and the pale-blue powder dried in vacuo. Yield: 210 mg (38%). Anal. Calcd for  $C_{20}H_{42}N_6B_3ONd$ : C, 43.0; H, 7.6; N, 15.0. Found: C, 42.5; H, 7.3; N, 14.6. IR (KBr pellet,  $cm^{-1}$ ): 2962 m, 2895 m, 2461 s, 2452 s br, 2227 s br, 2160 (sh), 1566 m, 1457 s, 1414 m, 1371 m, 1306 m, 1262 s, 1171 s, 1096 s, 1036 m, 1007 m, 897, 860 s, 804 m, 721, 702 s, 482 w. IR (KBr pellet mull,  $cm^{-1}$ ): 2435 (sh), 2425, 2215, 2150 (sh).  $^{11}B$  NMR (THF, 160.46 MHz, 293 K):  $\delta$  168.

**X-ray Crystallographic Analysis.** Single crystals of **1a**·**2CH<sub>3</sub>CN**, **1d**·**a**·**THF**, **3b**·**3THF**, and **3c**·**3THF** were mounted on a glass fiber, and all geometric and intensity data were taken from this sample on a Bruker SMART APEX CCD diffractometer using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at  $150 \pm 2$  K. Data reduction and integration were carried out with SAINT+<sup>26</sup> and absorption corrections applied using the program SADABS.<sup>27</sup> Structures were solved by direct methods and developed using alternating cycles of least-squares refinement and difference Fourier synthesis. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically reasonable positions and allowed to ride on the atoms to which they were attached. Structure solution and refinement used the SHELXTL PLUS V6.12 program package.<sup>28</sup>

Single crystals of **2a** and **2b**·**2THF** were mounted on a thin glass fiber using silicon grease and were cooled on the diffractometer to 120 K using an Oxford Cryostream low-temperature attachment. Approximate unit cell dimensions were determined by the Nonius Collect program<sup>29</sup> from five index frames of width 2° in  $\phi$  using a Nonius Kappa CCD diffractometer with a detector-to-crystal distance of 30 mm. The Collect program was then used to calculate a data collection strategy to 99.5% completeness for  $\theta = 27.5^\circ$  using a combination of 2°  $\phi$  and  $\omega$  scans of 10–120 s  $deg^{-1}$  exposure times (depending on crystal quality). Crystals were indexed using the DENZO-SMN package,<sup>30</sup> and positional data were refined along with diffractometer constants to give the final unit cell parameters. Integration and scaling (DENZO-SMN, Scalepack<sup>2</sup>) resulted in unique data sets corrected for Lorentz and polarization effects and for the effects of crystal decay and absorption by a combination of averaging of equivalent reflections and an overall volume and scaling correction. Structures were solved using SHELXS-97 and developed via alternating least-squares

Scheme 1



cycles and difference Fourier synthesis (SHELXL-97) with the aid of the program XSeed.<sup>31</sup> All non-hydrogen atoms were modeled anisotropically, except one disordered THF molecule in the case of **2b**·**2THF**, while hydrogen atoms were assigned an isotropic thermal parameter 1.2 times that of the parent atom (1.5 for terminal atoms) and allowed to ride.

The structure of **2b**·**2THF** proved to contain two nondisordered THF molecules, each of 50% occupancy possibly because of partial desolvation. The remaining THF molecules were both disordered. The disorder was modeled successfully by adopting two sets of positions for the backbone CH<sub>2</sub> groups. As a result, H atoms were not included for these fragments.

## Results and Discussion

Tpm\* adducts of the lanthanide halides [Ln(Tpm\*)Cl<sub>3</sub>] (Ln = Y, **1a**; Ce, **1b**; Nd, **1c**; Sm, **1d**; Gd, **1e**; Yb, **1f**) may be prepared in good yield and purity from the anhydrous metal chloride and the ligand in polar solvents such as dry THF or acetonitrile. Complex **1a** has previously been reported by Mountford and co-workers.<sup>22</sup> In THF, the complexes differ considerably in their solubility. Complexes **1b** and **1c** are moderately soluble in THF. Complexes **1d** and **1e** show good solubility, and the metal halide dissolves instantly upon addition of solvent. On the other hand, with the smaller metal ions, very sparingly soluble precipitates of **1a** and **1f** are formed, which can be isolated as analytically pure. The difference in solubility appears to be related to their structures since only for **1a** and **1f** are the complexes obtained free of solvent. For the larger lanthanides, coordination of THF occurs. The THF molecule is quite weakly bound, as evidenced by elemental analyses which are high in carbon and hydrogen unless the samples are heated to about 50 °C under dynamic vacuum. The coordination of the THF presumably sufficiently disrupts crystal packing to make the complex soluble. On the other hand, Y and Yb are presumably too small to accommodate the additional ligand. The low solubility of these complexes in such polar solvents is slightly surprising in view of the absence of intermolecular contacts in the crystal structure (vide infra), though the similarity of the infrared spectra suggests largely similar solid-state structures. We note that similar insolubility has been noted for [M(Tpm\*)Cl<sub>3</sub>] (M = Sc, Y) by Mountford et al.<sup>22</sup> as well as by Bercaw for the 1,4,7-triazacyclononane

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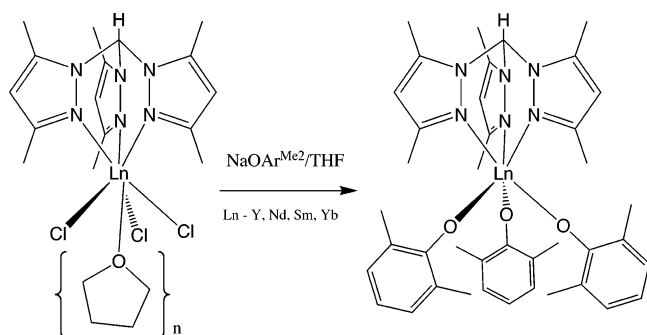
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(28) SHELXTL PLUS; Bruker AXS Inc.: Madison, WI, 2001.

(29) Collect; Nonius B.V.: Delft, The Netherlands, 1998.

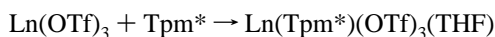
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Scheme 2



yttrium complex.<sup>32</sup> It may, therefore, simply result from the efficient packing of the relatively symmetrical molecules. As with the pyrazolylborates  $[\text{Ln}(\text{Tpm}^{\text{Me}_2})_2]$  ( $\text{Ln} = \text{Sm}, \text{Eu}, \text{Yb}$ ), which were also found to be very insoluble,<sup>33–36</sup> it may be possible to make these complexes more soluble by introducing substituents in the 4-position of the pyrazolyl groups.<sup>36</sup>

The corresponding triflates can be prepared analogous to the procedure in THF, but they are rather more soluble and are isolated as the THF adducts,  $[\text{Ln}(\text{Tpm}^*)(\text{OTf})_3(\text{THF})]$  ( $\text{Ln} = \text{Y}, \mathbf{2a}; \text{Ho}, \mathbf{2b}; \text{Dy}, \mathbf{2c}$ ). All show strong bands around  $1210 \text{ cm}^{-1}$  in the infrared spectrum, indicative of  $\kappa^1$ -coordinated triflate groups.<sup>25</sup>



These complexes are useful starting materials for simple aryloxides. Reaction of  $[\text{Ln}(\text{Tpm}^*)\text{Cl}_3]$  (isolated or simply prepared in situ) in THF with  $\text{NaOAr}^{\text{Me}_2}$  ( $\text{Ar}^{\text{Me}_2} = 2,6$ -dimethylphenoxide) yields the expected  $[\text{Ln}(\text{Tpm}^*)(\text{OAr}^{\text{Me}_2})_3]$  ( $\text{Ln} = \text{Y}, \mathbf{3a}; \text{Nd}, \mathbf{3b}; \text{Sm}, \mathbf{3c}; \text{Yb}, \mathbf{3e}$ ) in fairly good yield. The moderately sensitive compounds are very soluble in THF, less so in  $\text{CH}_2\text{Cl}_2$ , and virtually insoluble in hydrocarbon solvents. The compounds could be crystallized in the analytically pure form from the reaction mixture after filtration of salt. However, for the larger lanthanides (Nd and Sm), recrystallization must be carried out with care since the use of hot THF can result in the loss of the  $\text{Tpm}^*$  ligand. Thus, after two recrystallizations of  $\mathbf{3b}$  from hot THF, large pale-blue, block-like crystals of the trisaryloxide  $[\text{Nd}(\text{OAr}^{\text{Me}_2})_3(\text{THF})_3]$  were obtained. A closely related species, reported to have the stoichiometry  $\text{Nd}(\text{OAr}^{\text{Me}_2})_3$  and not fully characterized, has been used previously for polar monomer polymerization by Zhang and co-workers.<sup>37,38</sup> We presume this complex to be structurally analogous to the yttrium

complex  $[\text{Y}(\text{OAr}^{\text{Me}_2})_3(\text{THF})_3]$  reported by Evans.<sup>39</sup> Clark has reported the synthesis and structures of closely related species with the 2,6-diisopropylphenoxide,<sup>40</sup> including the structure of the samarium complex,  $[\text{Sm}(\text{OAr}^{\text{iPr}_2})_3(\text{THF})_2]$ .<sup>41</sup>

The  $^1\text{H}$  NMR spectra of the diamagnetic Y complex  $\mathbf{3a}$ , the mildly paramagnetic Nd complex  $\mathbf{3b}$ , and samarium complexes  $\mathbf{3c}$  and  $\mathbf{3d}$  are very simple, displaying the expected seven peaks indicative of a symmetrical and, therefore, fluxional coordination sphere. This is in contrast to Mountford's observations for the scandium complex where the more crowded coordination sphere around the smaller metal center results in slow rotation around the aryloxide metal axis and the observation of the distinct "up" and "down" methyl environments for the aryloxides. However, in the case of the yttrium complex  $\mathbf{3e}$ , the  $^1\text{H}$  NMR spectrum showed huge paramagnetic shifts (the spectrum is spread over 100 ppm), and at room temperature, only the *para*-hydrogen of the aryloxide and the  $\text{Tpm}^*$  peaks were visible. However, upon cooling to 204 K, two sets of broad singlets in a 9:3 ratio rose from the baseline. Since this is a molecule with a well-defined principal axis, it is reasonable to assume that protons aligned with that axis will be strongly deshielded (the central C–H of the  $\text{Tpm}^*$  ligand appears at +74 ppm), while hydrogens located  $90^\circ$  to that axis will undergo a strong upfield shift (the three methyl hydrogens of the  $\text{Tpm}^*$  appear at –52 ppm).<sup>42,43</sup> On this basis, integrating for nine protons, we have assigned the peak at +71 ppm to the down methyl groups of the aryloxide, and an analogous argument was used to assign the meta-protons of these ligands. The carbon-13 spectrum of  $\mathbf{3e}$  was largely uninterpretable due to the broadness of many of the peaks, the multiplicity of which could not be assigned.

Finally, direct reaction of  $\text{Tpm}^*$  with  $[\text{Nd}(\text{BH}_4)_3(\text{THF})_3]$ <sup>44</sup> in THF results in the formation of  $\text{Nd}(\text{Tpm}^*)(\text{BH}_4)_3(\text{THF})$ , which may be isolated in the analytically pure form by cooling of concentrated solutions in THF. The highly moisture-sensitive solid is insoluble in hydrocarbon solvents but dissolves easily in the more polar THF. The infrared spectrum shows a strong terminal B–H stretching band at  $2425 \text{ cm}^{-1}$ , along with two overlapping broad bands at 2215 and  $2150 \text{ cm}^{-1}$ , consistent with tridentate  $\text{BH}_4$  ligands.<sup>45</sup>

**Crystallographic Studies.** Of the complexes described in the paper, six were crystallized and analyzed by X-ray diffraction. The complexes were either six or seven coordinate and, in all cases, had local  $C_3$  symmetry. They will, therefore, be discussed by coordination number rather than in the order in which they were presented in the preceding section.

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**Table 1.** Selected Average Bond Distances (Å) and Angles (°) for the Single-Crystal X-ray Diffraction Studies

| complex                                 | 1a·2CH <sub>3</sub> CN | 1d-a·THF  | 2a·2THF  | 2b·2THF   | 3b·3THF  | 3c·3THF  |
|---|------------------------|-----------|----------|-----------|----------|----------|
| Ln–N <sub>av</sub> /Å                   | 2.459(5)               | 2.572(5)  | 2.449(8) | 2.461(6)  | 2.599(5) | 2.565(5) |
| Ln–X <sub>av</sub> /Å                   | 2.555(2)               | 2.621(2)  | 2.243(7) | 2.258(12) | 2.207(5) | 2.180(3) |
| Ln–O <sub>ax</sub> /Å                   |                        | 2.486(3)  | 2.391(4) | 2.391(6)  |          |          |
| ∠(X–Ln–X) <sub>av</sub>                 | 100.35(5)              | 115.29(6) | 114.9(3) | 114.8(5)  | 107.3(2) | 107.3(2) |
| ∠(N–Ln–N) <sub>av</sub>                 | 73.8(2)                | 70.4(2)   | 73.4(3)  | 73.1(3)   | 68.2(2)  | 69.2(1)  |
| ∠(X–Ln–O <sub>ax</sub> ) <sub>av</sub>  |                        | 77.3(3)   | 77.0(3)  | 76.9(3)   |          |          |
| ∠(C <sub>Tpm</sub> –Ln–X) <sub>av</sub> | 117.5(2)               | 102.7(3)  | 103.4(3) | 103.52(4) | 111.6(2) | 111.8(2) |

**Table 2.** Summary of Crystal Data and Structure Refinement for Complexes 1a·2CH<sub>3</sub>CN, 1d-a·THF, 2a·2THF, 2b·2THF, 3b·3THF, and 3c·3THF

|                                       | 1a·2CH <sub>3</sub> CN   | 1d-a·THF   | 2a·2THF  | 2b·2THF  | 3b·3THF   | 3c·3THF  |
|---------------------------------------|--|--|--|--|---|--|
| formula                               | C <sub>20</sub> H <sub>28</sub> Cl <sub>3</sub> N <sub>8</sub> Y | C <sub>24</sub> H <sub>38</sub> Cl <sub>3</sub> N <sub>6</sub> O <sub>2</sub> Sm | C <sub>35</sub> H <sub>54</sub> F <sub>9</sub> N <sub>6</sub> O <sub>13</sub> S <sub>3</sub> Y | C <sub>31</sub> H <sub>46</sub> F <sub>9</sub> HoN <sub>6</sub> O <sub>12</sub> S <sub>3</sub> | C <sub>52</sub> H <sub>73</sub> N <sub>6</sub> NdO <sub>6</sub> | C <sub>52</sub> H <sub>73</sub> N <sub>6</sub> O <sub>6</sub> Sm |
| formula weight                        | 575.76   | 699.30   | 1122.93  | 1126.85  | 1022.40   | 1028.51  |
| g mol <sup>-1</sup>                   |  |  |  |  |   |  |
| a = Å                                 | 9.5040(6)  | 10.5541(16)  | 28.698(3)  | 29.2750(2)   | 12.5317(11)   | 12.4975(8)   |
| b = Å                                 | 16.3094(10)  | 13.335(2)  | 19.426(2)  | 19.6570(10)  | 16.2143(14)   | 16.2324(10)  |
| c = Å                                 | 17.1537(6)   | 21.004(3)  | 19.807(2)  | 19.8299(15)  | 16.3503(14)   | 16.3598(10)  |
| α,                                    | 90,  | 90,  | 90,  | 90,  | 60.7790(10),  | 60.6900(10),   |
| β,                                    | 94.378(3),   | 90,  | 97.185(2),   | 95.481(3),   | 77.2050(10),  | 77.2960(10),   |
| γ                                     | 90   | 90   | 90   | 90   | 82.5080(10)   | 82.4930(10)  |
| volume Å <sup>3</sup>                 | 2651.1(3)  | 2956.0(8)  | 10955(2)   | 11359.1(10)  | 2826.5(4)   | 2822.1(3)  |
| Z                                     | 4  | 4  | 8  | 8  | 2   | 2  |
| crystal system                        | monoclinic   | orthorhombic   | monoclinic   | monoclinic   | triclinic   | triclinic  |
| space group                           | <i>P</i> 2 <sub>1</sub> / <i>n</i>                               | <i>P</i> 2 <sub>1</sub> 2 <sub>1</sub>   | <i>C</i> 2/ <i>c</i>   | <i>C</i> 2/ <i>c</i>   | <i>P</i> $\bar{1}$  | <i>P</i> $\bar{1}$   |
| temperature K                         | 100(2)   | 150(2)   | 293(2)   | 120(2)   | 150(2) K  | 150(2) K   |
| wavelength Å                          | 0.71073  | 0.71073  | 0.71073  | 0.71073  | 0.71073   | 0.71073  |
| ρ <sub>calcd</sub> g cm <sup>-3</sup> | 1.443  | 1.571  | 1.362  | 1.318  | 1.201   | 1.210  |
| μ mm <sup>-1</sup>                    | 2.525  | 2.289  | 1.266  | 1.581  | 0.966   | 1.088  |
| independent reflns                    | 6006   | 7102   | 12804  | 7478   | 12977   | 12821  |
| no. of parameters                     | 298  | 325  | 605  | 616  | 587   | 587  |
| R1 <sup>a</sup>                       | 0.0614   | 0.0308   | 0.0881   | 0.0733   | 0.0502  | 0.0414   |
| wR2 <sup>b</sup>                      | 0.1442   | 0.0760   | 0.2502   | 0.1798   | 0.1447  | 0.1266   |

<sup>a</sup> R1 =  $\sum[F_o] - F_c / \sum F_o$ . <sup>b</sup> wR2 =  $\{\sum[w(F_o^2 - F_c^2)^2] / \{\sum[w(F_o^2)^2]\}^{1/2}$ . The values were calculated for  $I > 2\sigma(I)$ .

**Six-Coordinate Structures.** Slow diffusion of layered acetonitrile solutions of YCl<sub>3</sub> and Tpm\* yielded colorless crystals of [Y(Tpm\*)Cl<sub>3</sub>], **1a**. The complex crystallized as discrete six-coordinate molecules in the monoclinic space group *P*2<sub>1</sub>/*n* with two molecules of acetonitrile in the lattice. The molecular structure is shown in Figure 1 and is similar to that of the closely related trispyrazolylsilane [Y(MeSi(dmpz)<sub>3</sub>)Cl<sub>3</sub>] reported by Mountford<sup>22</sup> and the corresponding U(IV)–pyrazolylborate complex [U(TpMe<sub>2</sub>)Cl<sub>3</sub>].<sup>46</sup> The metal chloride distances, Y–Cl<sub>av</sub> 2.555(2) Å, are similar to those in Mountford's pyrazolylsilane (2.568(5) Å) and are similar to those reported for the related half-sandwich pyrazolylborate complex [(Tp<sup>Me,Me</sup>)YCl<sub>2</sub>(dmpzH)] (Y–Cl<sub>av</sub> 2.555(6) Å)<sup>47</sup> and [(Tp<sup>Me,Me</sup>)YCl<sub>2</sub>(phen)] (Y–Cl<sub>av</sub> 2.600(2) Å).<sup>48</sup> The Y–N distance, 2.459(2) Å, is also similar to that in the pyrazolylsilane.<sup>22</sup>

The isomorphous aryloxides **3b** and **3c** crystallized in the space group *P* $\bar{1}$  from a concentrated THF solution at –30 °C with three molecules of THF in the lattice. The molecular structure of the **3c** is shown in Figure 2.

In all three complexes, each center is six coordinate with C<sub>3</sub> symmetry, and as a result, the geometry around the metal center is best regarded as trigonal antiprismatic, with one tighter triangle defined by the nitrogens and with a more open one defined by the X (X = Cl/OAr<sup>Me2</sup>) groups. This is seen clearly by comparing the ∠(N–Ln–N) and ∠(X–Ln–X) angles (~70 vs 100–108°). In comparing the chlorides with the aryloxides, it can be seen that the Ln–N distances are much longer in **3b** and **3c** (2.565(5) Å) than those in **1a** (2.459(5) Å), even when the differences in ionic radii are taken into account (Sm 1.098 and Y 1.040),<sup>49</sup> suggesting that the binding of the Tpm\* ligand is sensitive to changes in steric demand of the other ligands in the metal coordination sphere. The steric demand of the aryloxide ligands is also reflected in the angles subtended by the X ligands and the C<sub>3</sub> axis of the Tpm\* ligand (∠(C<sub>Tpm</sub>–Ln–X)<sub>av</sub>). Whereas

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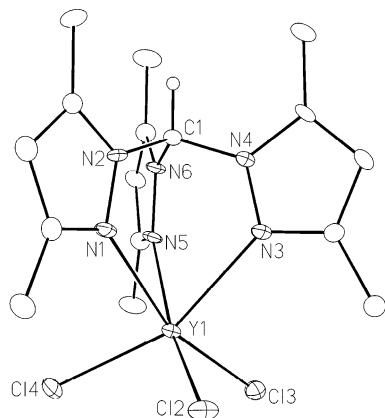


Figure 1. Molecular structure of **1a**; hydrogens omitted for clarity.

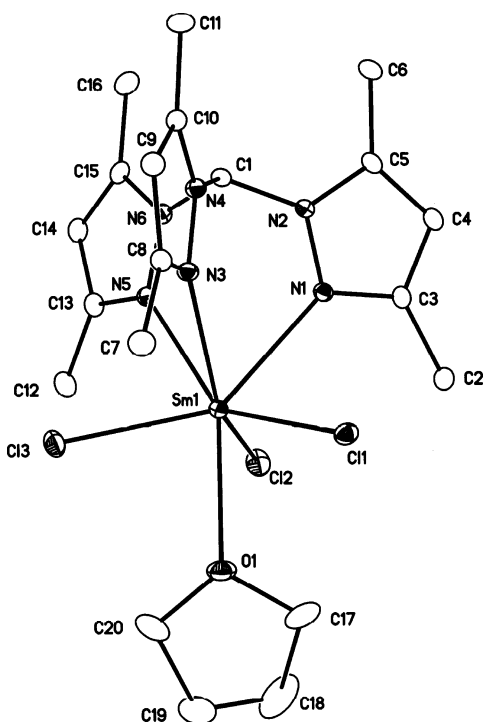


Figure 2. Molecular structure of **3b**; hydrogens omitted for clarity.

the chlorides bend back by  $117.5(2)^\circ$ , for the aryloxides, mutual interactions between the groups prevent further tightening and limit the angle to  $111.7(2)^\circ$ .

Compared with six-coordinate structures containing the isosteric but anionic  $\text{Tp}^{\text{Me}2}$  ligands, the average M–N distance is also considerably longer,  $2.44(1) \text{ \AA}$  for  $[\text{Sm}(\text{Tp}^{\text{Me}2})\text{I}]$  and  $2.443(7) \text{ \AA}$  for  $[\text{Sm}(\text{Tp}^{\text{Me}2})]\text{BPh}_4$ ,<sup>36</sup> consistent with the weaker interaction in the absence of a charge on the ligand.

For **3b** and **3c**, the aryloxide ligands lie almost aligned parallel to  $C_3$  axis of the  $\text{Tp}^{\text{Me}2}$  ligand (torsion angles are about  $14\text{--}17^\circ$ ). Hence, one methyl group of each aryloxide nestles in the groove between the pyrazolyl groups. This is consistent with the fluxional process observed in the  $^1\text{H}$  NMR spectra of **3e**, which may well involve concerted rotation of the aryloxides and the  $\text{Tp}^{\text{Me}2}$  ligands.

The Nd–O distances (av  $2.207(5) \text{ \AA}$ ) are similar to those observed by Clark and Watkin for  $\text{K}[\text{Nd}(\text{OAr}^{2,6\text{-iPr}})_4]$  ( $2.211(12) \text{ \AA}$ ),<sup>50</sup> despite the difference in coordination

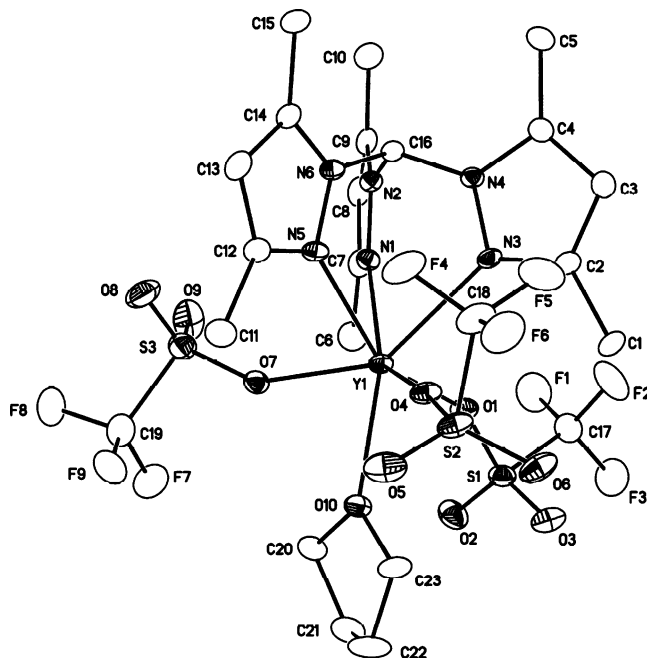


Figure 3. Molecular structure of **1d-a**; hydrogens omitted for clarity.

number and consistent with other related alkoxides.<sup>51–53</sup> Consistent with the bulk of the alkoxides, the angles between the alkoxides are larger than those in the other structures (O–Sm–O  $106.15(9)\text{--}107.59(9)^\circ$ ). The longer Sm–N also results in a slightly tighter bite angle for the  $\text{Tp}^{\text{Me}2}$  ligand. The corresponding distances and angles for **3b** are consistent with the difference in the six-coordinate ionic radii of Nd and Sm.<sup>49</sup>

The metal–nitrogen distances are similar in all three complexes (Y–N<sub>av</sub>  $2.459(5)$  **1a**,  $2.46(2)$  **2b**,  $2.449(8)$  **2a**), despite the differences in coordination number. The M–N distances for the neutral  $\text{Tp}^{\text{Me}2}$  ligand are somewhat longer than those in complexes of the corresponding anionic  $\text{Tp}^{\text{Me}2}$  ( $2.402 \text{ \AA}$  [ $(\text{Tp}^{\text{Me,Me}})\text{YCl}_2(\text{dmpzH})$ ]).<sup>47</sup> However, in the more sterically crowded complex isolated by Cheng and Takats,  $[(\text{Tp}^{\text{Me,Me}})\text{Y}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})]$ , the distances are similar ( $2.429\text{--}2.491 \text{ \AA}$ ).<sup>54</sup>

**Seven-Coordinate Structures.** When a slow diffusion experiment between  $\text{SmCl}_3$  and  $\text{Tp}^{\text{Me}2}$  was carried out in THF, crystals of  $[\text{Sm}(\text{Tp}^{\text{Me}2})\text{Cl}_3(\text{THF})]\cdot\text{THF}$ , **1d-a** were obtained. The molecular structure is shown in Figure 3. By contrast, with the unsolvated **1a**, **1d-a** is a seven-coordinate complex in which coordination of the additional THF ligand can presumably be accommodated by the larger coordination sphere of Sm than that of Y.

Crystals of  $[\text{Ln}(\text{Tp}^{\text{Me}2})(\text{OTf})_3(\text{THF})]$  (Ln = Y, **2a**; Ho, **2b**) were obtained by slow diffusion of layered THF solutions

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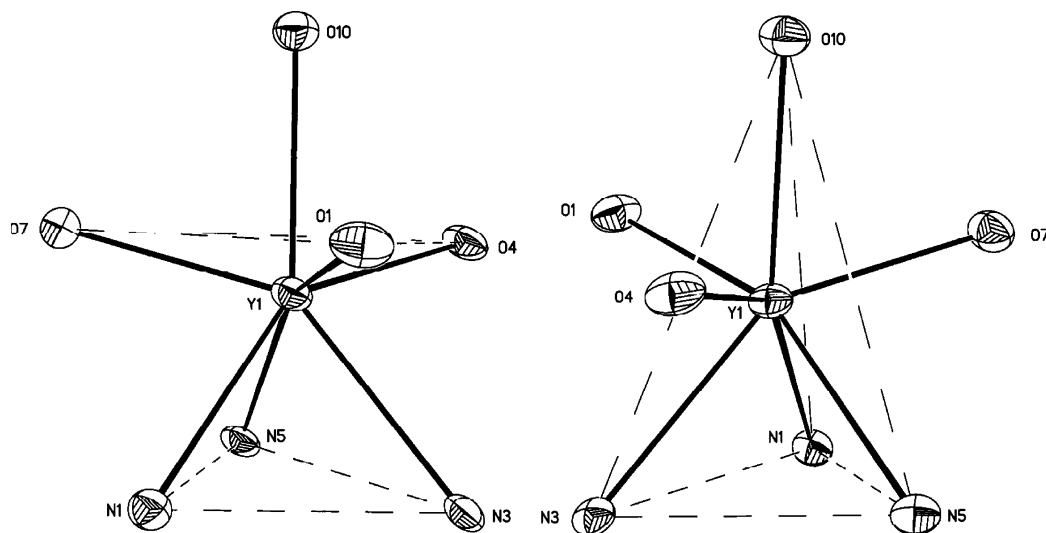


Figure 4. Molecular structure of **2a**; hydrogens omitted for clarity.

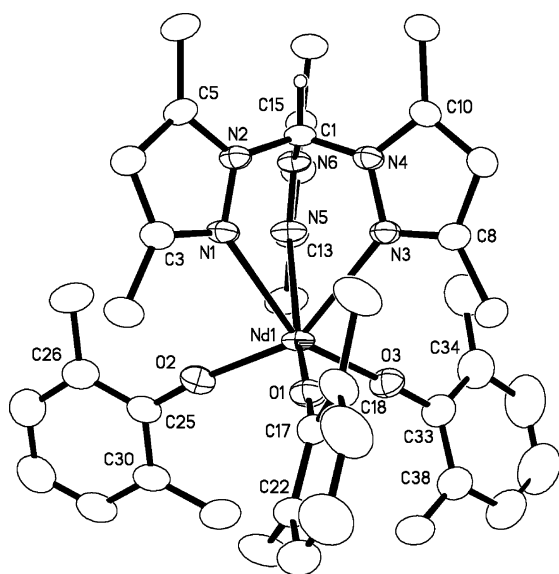


Figure 5. The inner coordination sphere of **2a** highlighting (a) the capped trigonal antiprismatic and (b) the tricapped trigonal pyramidal geometries.

of  $\text{Tpm}^*$  and  $\text{Ln}(\text{OTf})_3$  in a long tube. Consistent with the almost identical ionic radii of Y and Ho, the two crystals were isomorphous. As the molecular structures are extremely similar, the discussion will focus on **2a**, the molecular structure of which is shown in Figure 4.

The coordination spheres of all of these species may be described in two alternative ways: (a) as a trigonal antiprism defined by the  $\text{Tpm}^*$  and X (X = Cl, OTf) groups, with the THF lying on the  $C_3$  axis defined by the  $\text{Tpm}^*$  ligand, capping the triangular face defined by the X ligands; (b) as a tricapped trigonal pyramid, with the three nitrogen atoms of the  $\text{Tpm}^*$  ligand defining the base and with the THF oxygen defining the apex (see Figure 5). In the latter view, the chlorides cap the three faces of the pyramid, making Cl–Sm–O(1) angles of  $77 \pm 2^\circ$  to the apical/axial oxygen. The metal coordination sphere of **1d-a** is shown in Figure 5, which illustrates the two alternative polyhedra. Such geom-

etries have also been observed in lanthanide<sup>55,56</sup> and uranium pyrazolylborate complexes,  $[\text{U}(\text{Tp}^{\text{Me}_2})\text{Cl}_3\text{L}]$  (L = THF)<sup>57</sup> and  $\text{OP}(\text{OEt})_3$ ,<sup>58</sup> and are dictated by the tight bite angle of the tripodal ligand.

As with the six-coordinate species, the triangles defined by the nitrogens ( $\angle(\text{N}-\text{Ln}-\text{N})_{\text{av}} \sim 70-73^\circ$ ) are much tighter than those defined by the three X ligands ( $\angle(\text{X}-\text{Ln}-\text{X})_{\text{av}} \sim 115^\circ$ ). Surprisingly, perhaps the Ln–N distances are little changed between the six- and seven-coordinate species, suggesting a fairly flexible coordination sphere. However, the introduction of the THF ligand widens the angle between the anionic groups (e.g., **1a**  $100.35(5)^\circ$  vs **2a**  $114.9(3)^\circ$ ).

The average Sm–Cl distance, 2.621(2) Å, in **1d-a** is broadly similar to that observed in  $[\text{Tp}^*\text{SmCl}]$  2.637(3) Å,<sup>36</sup>  $[\text{SmCl}_3(\text{THF})_4]$  (2.683(5) Å),<sup>59</sup> and in the curious eight-coordinate hexakis(dimethyl)cyclotriphosphazene complex  $\text{LSmCl}_3$  (2.640(5) Å).<sup>60</sup> The Y–O distances in **2a** (2.243(7) Å) are a little shorter than those observed in the triazacyclononane derivative  $[\text{Y}(\text{TCMT})(\text{OTf})_2(\text{H}_2\text{O})]\text{OTf}$  (2.40(1) Å)<sup>61</sup> after correction for the difference in coordination number. The only other yttrium triflate in the Cambridge Crystallographic Database is too disordered to allow structural comparison.<sup>62</sup>

## Conclusions

We have shown that  $\text{Tpm}^*$  binds effectively to lanthanide centers and that a range of derivatives can be prepared. The

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crystal structures suggest that the ligand binds less tightly than in corresponding  $\text{Tp}^{\text{Me}2}$  structures. Although the ligands show no evidence for dissociation at room temperature, it appears that they can be displaced from the larger lanthanides upon reflux. On the other hand, the  $\text{Tpm}^*$  ligands appear to be significantly more robust than the  $\text{Tp}^*$  system, which has been shown previously to hydrolyze readily at lanthanide centers,<sup>63</sup> presumably as a result of the greater polarity of the B–N as opposed to the C–N bond. Pyrazolylmethanes may, therefore, be a useful addition to the class of neutral tridentate ancillaries for the f-block, especially in the context of electrophilic catalytic chemistry. However, their complexes have also been shown to be relatively insoluble, and it may be advantageous to use ligands, such as those with

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substituents in the 4-position of the pyrazolyl ring, designed to disrupt crystal packing in order to enhance their solubility in nonpolar solvents.

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**Supporting Information Available:** X-ray crystallographic files in CIF format for the structure determinations of  $[\text{Y}(\text{Tpm}^*)\text{Cl}_3]$  **1a**,  $[\text{Sm}(\text{Tpm}^*)\text{Cl}_3(\text{THF})]\cdot\text{THF}$  **1d-a**,  $[\text{Y}(\text{Tpm}^*)(\text{O}_3\text{SCF}_3)_3(\text{THF})]\cdot 3\text{THF}$  **2a**,  $[\text{Ho}(\text{Tpm}^*)(\text{O}_3\text{SCF}_3)_3(\text{THF})]\cdot 3\text{THF}$  **2b**,  $[\text{Y}(\text{Tpm}^*)(\text{O}-2,6-\text{C}_6\text{H}_3\text{Me}_2)_3]$  **3a**, and  $[\text{Nd}(\text{Tpm}^*)(\text{O}-2,6-\text{C}_6\text{H}_3\text{Me}_2)_3]$  **3b**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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