

Synthesis and Molecular Structures of Hydrotris(dimethylpyrazolyl)borate Complexes of the Lanthanides

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The reaction of lanthanide triflates with 2 equiv of potassium hydrotris(dimethylpyrazolyl)borate (Tp^{Me_2}) gives good yields of complexes of composition $\text{Ln}(\text{Tp}^{\text{Me}_2})_2\text{OTf}$. For La (**2**), Ce (**3**), Pr (**4**), and Nd (**5**) the complexes are seven-coordinate in the solid state with the triflate group coordinated to the metal in unidentate fashion. Complex **5** crystallizes in the monoclinic space group $P2_1/c$ with $a = 17.629(3) \text{ \AA}$, $b = 12.740(2) \text{ \AA}$, $c = 18.163(3) \text{ \AA}$, $\beta = 107.35(1)^\circ$, $V = 3893(1) \text{ \AA}^3$, $Z = 4$, and $R_w = 0.0458$. For the complexes of Y (**1**), Sm (**6**), Eu (**7**), Gd (**8**), Dy (**9**), Ho (**10**), and Yb (**11**), the smaller size of the metal ion leads to ejection of the triflate from the coordination sphere and the complexes are ionic in the solid state with a six-coordinate metal center. Complex **11** crystallizes in the monoclinic space group $C2/m$ with $a = 16.593(7) \text{ \AA}$, $b = 13.671(5) \text{ \AA}$, $c = 8.746(2) \text{ \AA}$, $\beta = 91.66(3)^\circ$, $V = 1983(1) \text{ \AA}^3$, $Z = 2$, and $R_w = 0.0416$. In solution, however, complex **6** adopts a seven-coordinate molecular structure with the triflate ion within the first coordination sphere.

Introduction

Major advances in the coordination and organometallic chemistry of the lanthanides have been made through the use of increasingly sterically demanding ancillary ligands, of which substituted cyclopentadienyls are the most widely used class.¹ Although not as electronically tunable as the cyclopentadienyls, the polypyrazolylborates have found wide application as ancillary ligands capable of stabilizing the smallest cations such as Be^{2+} as well as metal ions as large as Pb^{2+} and U^{3+} .² The hydrotrispyrazolylborate ligands ($\text{Tp}^{\text{R,R}}$) are significantly larger than the cyclopentadienyl since their nonplanarity permits substituents to extend beyond the face capped by the ligand itself. For early transition metals, the cone angles for Cp and Cp^* have been estimated as 100° and 142° ,³ whereas for Tp and Tp^{Me_2} they are 184° and 224° , respectively, although, because of the difference in metal to ligand distances these values should be treated, at best, as upper limits. Since steric saturation of the lanthanide coordination sphere is of critical importance in determining both structure and reactivity, $\text{Tp}^{\text{R,R}}$ ligands therefore appear well suited to satisfying the coordination requirements of the trivalent lanthanide metal center.

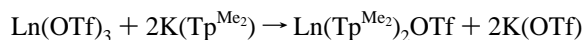
Some hydrotrispyrazolylborate complexes of the lanthanides in oxidation state +3 were reported previously. Stainer and Takats prepared complexes of the type $[\text{LnTp}_3]$ and were able to show both crystallographically⁴ and by NMR in solution⁵ for the ytterbium complex that two of the ligands were bound in η^3 fashion and one in η^2 coordination mode. Several preparations of heteroleptic complexes of the type $[\text{LnTp}_2\text{X}]$ have been reported, but these have tended to be plagued by ligand redistribution reactions unless the X ligand were carefully chosen. Thus, Takats and co-workers prepared $[\text{LnTp}_2(\text{acac})]$

($\text{acac} = 2,4\text{-pentanedionate}$).⁶ More recently Moss and Jones prepared a number of complexes where $\text{X} = \text{acac}$, oxalate, or tropolonate, and characterized them crystallographically.⁷ Reger and co-workers prepared the corresponding carboxylates, which proved to be dimeric.⁸

We have recently begun to explore the chemistry of the lanthanides with the more sterically encumbered trispyrazolylborates as ancillary ligands. We chose the dimethyl-substituted analogue Tp^{Me_2} because of its ease of synthesis and because it seemed appropriate to compare the behavior of the complexes of the larger ligand with the less bulky analogues that were the subject of earlier studies. We also hoped to suppress ligand redistribution reactions, observed for example by Takats in attempts to prepare LnTp_2Cl ,⁹ by increasing the steric saturation around the metal without the need for additional ancillary ligands which might diminish reactivity. Some of this work has been communicated previously.¹⁰

Results and Discussion

The complexes of formula $\text{LnTp}^{\text{Me}_2}_2\text{OTf}$ may be prepared by straightforward metathesis of a slight excess of the appropriate lanthanide triflate with $\text{K}(\text{Tp}^{\text{Me}_2})$ in THF at room temperature.



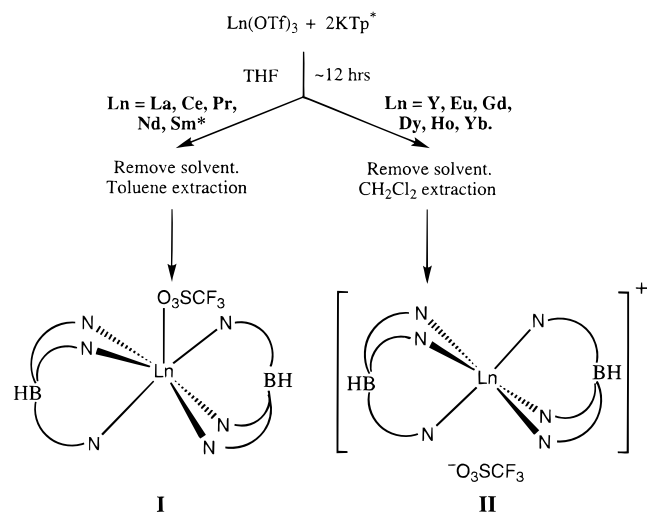
Triflates rather than chlorides were chosen as starting materials partly because of the ease of preparation of the anhydrous materials, but also because the poorly ligating triflate ion might be expected to be a better leaving group and simplify the

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Scheme 1



problems of purification of products.¹¹ The reactions proceed smoothly at room temperature, giving either slightly turbid solutions (due to the formation of sparingly soluble potassium triflate) or a dense precipitate, as shown in Scheme 1. After removal of solvent, it was possible to extract the complexes of the lighter lanthanides into warm toluene. Slow cooling overnight yielded analytically pure complexes. The resulting products for La (2), Ce (3), Pr (4), Nd (5), and Sm (6) were obtained as microcrystalline solids soluble in aromatic and chlorinated solvents. In contrast, the products of the reaction for Y (1)¹² and the heavier lanthanides Eu (7), Gd (8), Dy (9), Ho (10), and Yb (11) failed to dissolve significantly in toluene and it was found necessary to extract the reaction mixture with dichloromethane, from which the complexes $\text{LnTp}^{\text{Me}_2}\text{OTf}$ were obtained upon removal of solvent. Analytically pure samples were obtained by recrystallization from dichloromethane/petroleum ether mixtures. All of the complexes were of the expected colors for trivalent ions. The cerium complex, 3, was found to display a strong blue luminescence under UV light both in the solid and in solution, which we presume to result from excitation to the lowest excited electronic configuration ($4f^05d^1$) as has been reported for a wide range of Ce(III) complexes.¹³ The other complexes did not appear to be luminescent.

For the diamagnetic complexes of Y (1) and La (2), the ^1H NMR spectra were almost superimposable and structurally uninformative, simply showing three peaks for the methyl and methine groups of the ligands. Spectra were also recorded for the paramagnetic compounds of Ce (3), Pr (4), Nd (5), Sm (6), Eu (7), and Yb (11), showing three reproducible but shifted ^1H NMR peaks in the ratio of 3:3:1, again consistent with the Tp^{Me_2} ligands being equivalent in solution. The ^{13}C NMR spectra of these complexes gave analogous information. Spectra of the remaining lanthanides were too broad to be readable. Plots of ^1H chemical shifts versus $1/T$ for the ligand peaks in 4, 5, and 7 were linear, consistent with simple Curie–Weiss behavior, and therefore with monomeric complexes whose structure is invariant with temperature.¹⁴

The sharp difference in solubility in complexes of identical stoichiometry suggested to us that, as a result of the gradual

contraction in the ionic radius across the series, the early complexes might consist of neutral species with a coordinated triflate anion (I), whereas those of the heavier lanthanides might exist as an ion pair (II), the steric demand of the tris-(dimethylpyrazolyl)borate ligands forcing the triflate ion out of the metal coordination sphere. Indeed, comparison of the infrared spectra of the two types of complex revealed striking differences. All the compounds displayed a prominent peak in the region of 2560 cm^{-1} due to the B–H stretching vibration. For the complexes of the smaller ions, 1 and 6–11, the infrared spectra were essentially superimposable and in particular displayed a strong band at 1275 cm^{-1} , which has been assigned to a combined C–F/S–O vibration of the free triflate ion.¹⁰ A similar band is observed in tetraethylammonium triflate. In contrast, the band is shifted to about 1204 cm^{-1} for the complexes of the earlier elements 2–5, suggesting a significant structural change as a result of the larger ionic radii at the beginning of the series.

In the hopes of establishing the nature of these complexes in solution, infrared spectra were recorded in CDCl_3 solution, a solvent transparent in the range $1200\text{--}1300\text{ cm}^{-1}$. Complexes 1 and 7–11 showed a broad band at 1264 cm^{-1} , slightly shifted from the value observed in the solid state, consistent with an uncoordinated triflate group. In contrast, this band was entirely absent for complexes 2–6. Hence, we believe that in these complexes the triflate ion enters the coordination sphere of the metal when dissolved in a fairly nonpolar solvent. For the europium complex 7, this peak at 1264 cm^{-1} was much weaker than in 8, possibly implying an equilibrium between the two structures. In considering these results, we note that complexes 6 and 7 appear to exist in solution with a coordinated triflate ligand but as a separated ion pair in the solid state and may therefore be regarded as occupying the crossover point between the two structural types, with the Tp^{Me_2} ligands capable of accommodating the necessary structural change.

Attempts to substantiate this structural change by vapor pressure osmometry in benzene or dichloromethane solution using the Signer method were unsuccessful.²² Definitive confirmation of the solid state structures was obtained from single-crystal X-ray diffraction studies of the neodymium, 5, and ytterbium, 11, complexes.

Crystallographic Studies. Single-crystal X-ray diffraction confirmed the formulation of 5 as being $[\text{Nd}(\text{Tp}^{\text{Me}_2})_2\text{OTf}]$, the triflate ion lying within the inner coordination sphere of the metal. The molecular structure of 5 is shown in Figure 1. In contrast to those complexes prepared previously with the simple Tp ligand which are all eight coordinate (two Tp^{Me_2} ligands plus a bidentate or two unidentate ligands), the neodymium is seven coordinate, reflecting the increase in steric demand of the Tp^{Me_2} ligand and poor ligating power of the triflate anion. The two tridentate Tp^{Me_2} ligands are bent back in a manner reminiscent

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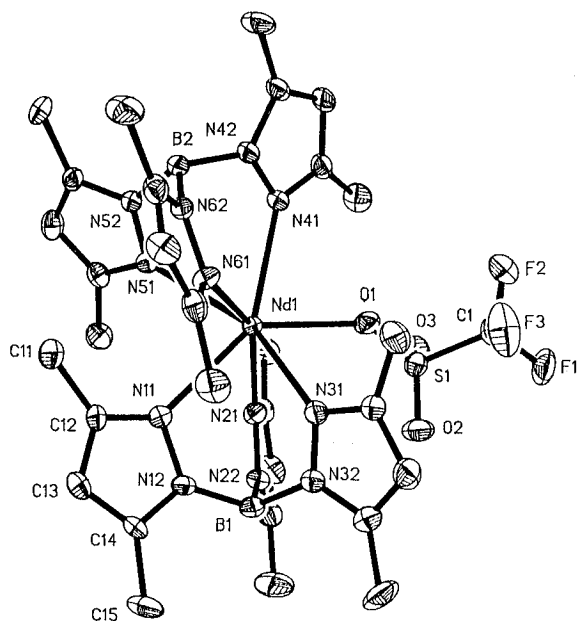


Figure 1. ORTEP view of $[\text{Nd}(\text{Tp}^{\text{Me}_2})_2\text{OTf}]$ (**5**) with 30% probability thermal ellipsoids and partial labeling scheme for the molecule. Hydrogen atoms have been omitted for clarity.

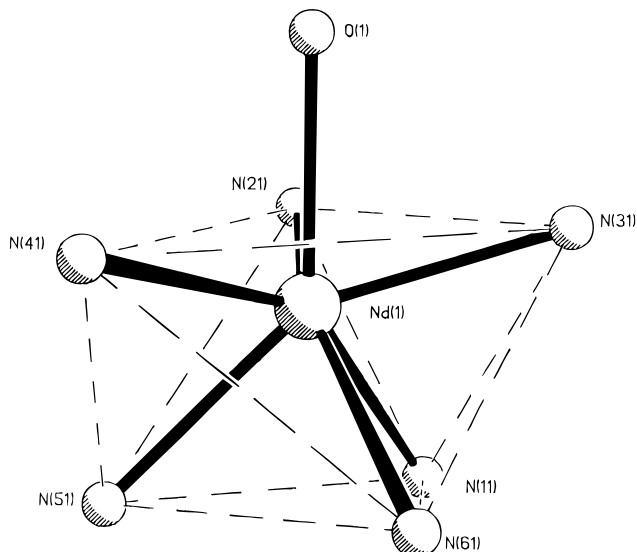


Figure 2. Inner coordination sphere of $[\text{Nd}(\text{Tp}^{\text{Me}_2})_2\text{OTf}]$ (**5**) showing the distorted capped octahedral arrangement of ligands.

of a bent metallocene with a B–Nd–B angle of 148° . The unidentate triflate group occupies the remaining coordination site, which, however, does not lie symmetrically between the two tripods but rather lies with O–Nd–B angles of 92.3 and 116.8° , respectively. This distortion presumably arises in order to accommodate the substituents of the triflate group within the wedge formed by the methyl groups of one of the tripods.

The metal center in **5** lies in an irregular geometry best described as being based on a distorted octahedron defined by the nitrogens of the pyrazolylborate ligands. The triflate group caps an expanded face defined by N21, N31, and N41, the opposing face being formed by N11, N51, and N61. The angle between these two planes is 5.4° . The inner coordination sphere is shown in Figure 2. The neodymium to nitrogen distances are unexceptional, ranging from $2.485(5)$ to $2.598(5)$ Å. The distances reported in the eight-coordinate complex $[\text{CeTp}_2(\text{MeC}(\text{O})\text{CHC}(\text{O})\text{Me})]$ are somewhat longer $2.583(3)$ to $2.664(3)$ Å, as expected for the slightly larger ion and expanded coordination sphere.¹⁵ The metal–oxygen distance is $2.421(5)$ Å. Similar

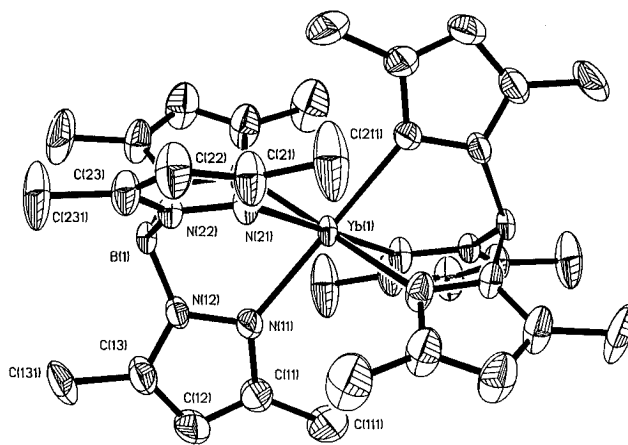


Figure 3. Molecular structure of the cation in $[\text{Yb}(\text{Tp}^{\text{Me}_2})_2]\text{OTf}$ (**11**) with 30% thermal ellipsoids and partial labeling scheme. Hydrogen atoms have been omitted for clarity.

unidentate coordination by triflate ions to lanthanides has been observed by Schumann in the half-sandwich complex $[\text{Lu}(\eta^5\text{-Cp})(\text{THF})_3(\text{O}_3\text{SCF}_3)_2]$.¹⁶ The shorter average M–O distance of 2.23 Å in this complex is related to the smaller metal ion. The Tp^{Me_2} ligand itself is unremarkable, the angles at boron being tetrahedral, and the average B–N–N angle is 120° within experimental error. Thus, no distortion of the ligand seems to occur in order to accommodate the large metal ion.

In contrast to that of **5**, the molecular structure of complex **11** consists of discrete $[\text{Yb}(\text{Tp}^{\text{Me}_2})_2]^+$ cations and $[\text{CF}_3\text{SO}_3]^-$ anions. The metal center is therefore six coordinate. The molecular structure of the cation of **11** is shown in Figure 3. The metal center lies on a crystallographic C_2 axis and a mirror plane which includes one of the pyrazolyl rings. The two independent Yb–N distances, $2.304(5)$ and $2.347(6)$ Å, are at first sight remarkably short compared with those in **5** and with those in other trivalent ytterbium pyrazolylborate complexes $[\text{Yb}(\eta^3\text{-Tp})_2(\eta^2\text{-Tp})]$ ($2.401(8)$ – $2.601(6)$ Å)⁴ and $[\text{Yb}(\eta^3\text{-Tp})_2(\text{C}_7\text{H}_5\text{O}_2)]$ ($2.425(12)$ – 2.548 Å).¹⁷ However, the ejection of the triflate ion from the first coordination sphere and consequent reduction in the coordination number allows for the closer approach of the nitrogen atoms and therefore leads to an extremely compact structure in **11**. The Yb–N distances in the closely related six-coordinate divalent complex $[\text{Yb}(\eta^3\text{-Tp}^{\text{Me}_2})_2]$ (Yb–N = $2.480(4)$ Å) are significantly longer. The increase is entirely in line with the expected change in ionic radius which occurs upon reduction from Yb(III) to Yb(II)¹⁸ and is not accompanied by any significant distortion in the Tp^{Me_2} itself.

Conclusions

We have prepared a series of complexes of molecular formula $\text{Ln}(\text{Tp}^{\text{Me}_2})_2\text{OTf}$. Both the solubilities of these complexes and their infrared spectra suggest a structural change which results from the contraction in ionic radius across the lanthanide series. This is confirmed by X-ray structures of complexes from the two extremes of the series. It is intriguing that the samarium complex, **6**, gives an infrared spectrum consistent with the uncoordinated anion in the solid, yet the complex exists in chloroform (and presumably toluene) with the triflate within the coordination sphere. For the europium complex, **7**, there is evidence that both structural types coexist in chloroform solution and the complex shows a marked reduction in solubility in toluene in comparison with **6**. Finally, the absence of redistribution reactions with the Tp^{Me_2} ligand suggests that for the larger lanthanides it should be possible to replace the triflate

Table 1. Summary of Crystallographic Data for Complexes 5 and 11

	C ₃₁ H ₄₄ N ₁₂ B ₂ F ₃ O ₃ S ₁ Nd ₁ (5)	C ₃₁ H ₄₄ N ₁₂ B ₂ F ₃ O ₃ S ₁ Yb ₁ (11)
mol formula	C ₃₁ H ₄₄ N ₁₂ B ₂ F ₃ O ₃ S ₁ Nd ₁ (5)	C ₃₁ H ₄₄ N ₁₂ B ₂ F ₃ O ₃ S ₁ Yb ₁ (11)
mol wt	887.79	916.59
space group	<i>P</i> 2 ₁ / <i>c</i> (No. 14)	<i>C</i> 2/ <i>m</i> (No. 11)
<i>a</i> (Å)	17.629(3)	16.593(7)
<i>b</i> (Å)	12.740(2)	13.671(5)
<i>c</i> (Å)	18.163(3)	8.746(2)
β (deg)	107.35(1)	91.66(3)
<i>U</i> (Å ³)	3893(1)	1983(1)
ρ (calc) Mg m ⁻³	1.51	1.53
<i>Z</i>	4	2
cryst dimensions (mm)	0.50 × 0.40 × 0.06	0.32 × 0.34 × 0.75
<i>F</i> (000)	1804	922
abs coeff μ (Mo K α) (mm ⁻¹)	1.46	2.46
temp (K)	291	291
radiation (Å)	0.71073	0.71073
2 θ range (deg)	5 – 50	5 – 50
scan type	$\omega - 2\theta$	$\omega - 2\theta$
no of reflns	7441	3725
no. of unique reflns	6862	1888
reflns in final refinement (<i>I</i> ≥ 3 σ (<i>I</i>))	4756	1807
variables	478	137
<i>w</i> ⁻¹	$\sigma F^2 + 0.000473(F)^2$	$\sigma F^2 + 0.002663(F)^2$
<i>R</i> ^a	0.0456	0.0405
<i>R</i> _w ^b	0.0458	0.0416
GOF ^c	1.43	0.97
largest residual peak (e/Å ³)	0.65	2.20
($\Delta\sigma$) _{max}	0.001	0.011

$$^a R = \sum(|F_o| - |F_c|)/\sum|F_o|. \quad ^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}. \quad ^c \text{GOF} = [\sum(|F_o| - |F_c|)^2/\sum(N_{\text{reflns}} - N_{\text{params}})]^{1/2}.$$

ion within the first coordination sphere by other more reactive anionic groups. Such studies are in progress.¹⁹

Experimental Section

All preparations and manipulations were carried out using standard Schlenk line and drybox techniques in an atmosphere of dinitrogen.²⁰ Oxygen-free nitrogen was purified by passage over columns containing 3 Å molecular sieves and MnO.²¹ All solvents were predried over 5 Å molecular sieves or sodium wire and distilled under nitrogen from appropriate drying agents (Na (toluene), K (benzene, tetrahydrofuran), Na/K alloy (petroleum ether bp 40–60 °C, pentane, diethyl ether), CaH₂ (CH₂Cl₂)) before use.

Lanthanide triflates were prepared from lanthanide oxides or carbonates (99.9%, Berkshire Ores) and aqueous trifluoromethanesulfonic acid (Aldrich).²² K(Tp^{Me2}) was prepared by published procedures.²³

Infrared spectra were recorded as KBr pellets or in CDCl₃ solution on a Nicolet 205 FTIR spectrometer. ¹H and ¹³C spectra in solution were recorded on Varian XL-200 and VXR-400 spectrometers at 200 and 400 and 100.6 MHz, respectively. Spectra were calibrated using residual proton (¹H) and solvent resonances (¹³C), respectively, and chemical shifts are reported relative to tetramethylsilane. Elemental microanalyses were determined by the Mr. Alan Stones of the UCL Analytical Services.

Preparation of [Ln(Tp^{Me2})₂OTf], Ln = La, Ce, Pr, Nd, Sm. In a typical preparation, K(Tp^{Me2}) (3.90 g, 11.6 mmol) and lanthanum triflate (3.40 g, 5.80 mmol) were stirred in THF (100 mL) at room temperature for 12 h. The solvent was removed from the resulting solution under reduced pressure. The solid was extracted with toluene (2 × 100 mL), leaving a residue that was shown by IR spectroscopy to consist mainly of potassium triflate. The combined toluene extracts were concentrated under reduced pressure. Colorless crystals were obtained by cooling the solution overnight to –25 °C. Analytically pure [La(Tp^{Me2})₂OTf] was obtained by decanting off the mother liquor and drying under dynamic vacuum.

2. White, yield: 70%. Anal. Calcd for LaC₃₁H₄₄N₁₂B₂F₃O₃S₁: C, 42.20; H, 5.03; N, 19.06. Found: C, 42.22; H, 4.99; N, 18.91. ¹H NMR (CDCl₃, 298 K): δ 1.85 (s, 18H, Me); 2.41 (s, 18H, Me); 5.73 (s, 6H, CH). ¹³C NMR (CDCl₃, 298 K): δ 12.9 (q, 3 or 5 Me); 13.5 (q, 5 or 3 Me); 106.3 (d, CH); 145.7 (s, 3 or 5 C); 150.2 (s, 5 or 3 C). IR (KBr pellet, cm⁻¹): 2963 (sh), 2929 (sh), $\nu_{\text{B-H}}$ = 2558 (sh), 1545

(s, sh), 1441 (s), 1420 (s), 1358 (m), 1331 (m), 1262 (m), 1234 (m), 1203 (vs), 1069 (m), 1033 (s), 1016 (s), 983 (w), 807 (s), 696 (w), 650 (m), 638 (m).

3. Pale yellow, yield: 68%. Anal. Calcd for CeC₃₁H₄₄N₁₂B₂F₃O₃S₁: C, 42.14; H, 5.02; N, 19.02. Found: C, 41.52; H, 4.84; N, 17.71. ¹H NMR (CDCl₃, 298 K): δ –14.3 (s, *w*_{1/2} = 58.2 Hz, 18H, Me); 6.0 (s, *w*_{1/2} = 11.7 Hz, 6H, CH); 7.3 (s, *w*_{1/2} = 10.9 Hz, 18H, Me). ¹³C NMR (CDCl₃, 298 K): δ 20.6 (q, 3 or 5 Me); 114.1 (d, CH); 145.1 (s, 3 or 5 C); 159.8 (s, 5 or 3 C).

4. Pale green, yield: 59%. Anal. Calcd for PrC₃₁H₄₄N₁₂B₂F₃O₃S₁: C, 42.10; H, 5.01; N, 19.01. Found: C, 42.39; H, 4.85; N, 18.86. ¹H NMR (CDCl₃, 298 K): δ 7.25 (s, 6H, CH); 5.4 (s, 18H, Me); –12.1 (s, *w*_{1/2} = 9.3 Hz, 18H, Me). ¹³C NMR (CDCl₃, 298 K): δ 19.4 (q, 3 or 5 Me); 125.6 (d, CH); 152.6 (s, 3 or 5 C); 164.1 (s, 5 or 3 C).

5. Pale blue, yield: 56%. Anal. Calcd for NdC₃₁H₄₄N₁₂B₂F₃O₃S₁: C, 41.95; H, 5.03; N, 18.93. Found: C, 42.04; H, 4.95; N, 18.94. ¹H NMR (CDCl₃, 298 K): δ 8.02 (s, *w*_{1/2} = 9.7 Hz, 6H, CH); 5.16 (s, *w*_{1/2} = 8.6 Hz, 18H, Me); –9.73 (s, *w*_{1/2} = 27.2 Hz, 18H, Me). ¹³C NMR (CDCl₃): δ –1.3 (q, 3 or 5 Me); 18.8 (q, 3 or 5 Me); 133.3 (d, CH); 159.7 (s, 3 or 5 C); 169.1 (s, 5 or 3 C).

6. White, yield: 55%. Anal. Calcd for SmC₃₁H₄₄N₁₂B₂F₃O₃S₁: C, 41.66; H, 4.96; N, 18.81. Found: C, 41.19; H, 4.76; N, 18.62. ¹H NMR (CDCl₃, 298 K): δ –1.4 (s, 18H, Me); 3.3 (s, 18H, Me); 5.4 (s, 6H, CH). ¹³C NMR (CDCl₃): δ 9.8 (q, 3 or 5 Me); 14.5 (q, 3 or 5 Me); 104.4 (d, CH); 146.7 (s, 3 or 5 C); 147.4 (s, 5 or 3 C).

Preparation of [Ln(Tp^{Me2})₂OTf], Ln = Y, Eu, Gd, Dy, Ho, Yb. In a typical preparation, a mixture of yttrium triflate (3.0 g, 5.6 mmol) and K(Tp^{Me2}) (3.75 g, 11 mmol) was stirred in THF (100 mL) for 12 h, during which time a heavy white precipitate formed. The solvent was removed under reduced pressure, and the solid residue was washed with toluene (2 × 20 mL). The solid was then extracted with dichloromethane (2 × 50 mL). Removal of solvent from the filtered extracts under reduced pressure yielded 3.6 g (77%) of [Y(Tp^{Me2})₂]-OTf as a white solid. Crystals of the compound could be grown by layering the dichloromethane solution with pentane, which were found to desolvate under dynamic vacuum.

1. White, yield: 77%. Anal. Calcd for YC₃₁H₄₄N₁₂B₂F₃O₃S₁: C, 44.73; H, 5.33; N, 20.19. Found: C, 44.63; H, 5.17; N, 19.93. ¹H NMR (CDCl₃, 298 K): δ 1.81 (s, 18H, Me); 2.47 (s, 18H, Me); 5.87 (s, 6H, CH). ¹³C NMR (CDCl₃): δ 12.6 (q, 3 or 5 CH₃); 13.3 (q, 5 or 3 CH₃); 106.7 (d, CH); 148.4 (s, 3 or 5 C); 150.4 (s, 3 or 5 C). IR (KBr pellet, cm⁻¹): 2962 (sh), 2931 (sh), $\nu_{\text{B-H}}$ = 2566 (sh), 1537 (s, sh), 1497 (w), 1442 (s), 1419 (s), 1357 (m), 1276 (s), 1225 (m), 1187

Table 2. Final Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) $U(\text{eq})$ for **5** (esd's in Parentheses)

	<i>x</i>	<i>y</i>	<i>z</i>	$U(\text{eq})^a$
Nd(1)	2330(1)	127(1)	2141(1)	29(1)
B(1)	4430(5)	189(7)	2952(5)	38(3)
B(2)	482(5)	-922(6)	2182(5)	40(3)
N(11)	3369(4)	-1164(4)	2986(3)	41(2)
N(12)	4140(3)	-786(5)	3266(3)	37(2)
N(21)	3462(3)	26(4)	1588(3)	40(2)
N(22)	4233(3)	133(4)	2065(3)	38(2)
N(31)	3263(4)	1234(4)	3134(3)	37(2)
N(32)	4061(4)	1175(4)	3209(3)	38(2)
N(41)	865(3)	438(4)	1321(3)	38(2)
N(42)	315(3)	55(4)	1673(3)	38(2)
N(51)	1620(3)	-1591(5)	1685(3)	40(2)
N(52)	901(3)	-1762(4)	1815(3)	36(2)
N(61)	1742(3)	-333(5)	3226(3)	38(2)
N(62)	972(3)	-693(4)	3017(3)	36(2)
C(11)	2620(5)	-2678(7)	3320(5)	64(4)
C(12)	3349(5)	-2021(5)	3414(4)	44(3)
C(13)	4071(5)	-2184(6)	3949(5)	54(3)
C(14)	4551(5)	-1390(6)	3864(5)	47(3)
C(15)	5402(5)	-1174(8)	4323(5)	62(4)
C(21)	2779(5)	-47(7)	193(4)	63(3)
C(22)	3499(5)	43(5)	860(4)	43(3)
C(23)	4282(5)	158(6)	870(4)	53(3)
C(24)	4731(5)	221(6)	1632(5)	49(3)
C(25)	5606(5)	329(9)	1950(6)	80(4)
C(31)	2344(5)	2442(7)	3500(5)	60(4)
C(32)	3154(5)	2123(6)	3469(4)	43(3)
C(33)	3868(5)	2632(7)	3763(5)	57(4)
C(34)	4422(5)	2034(6)	3588(5)	52(3)
C(35)	5303(6)	2237(8)	3734(6)	88(5)
C(41)	813(5)	1568(7)	181(4)	60(4)
C(42)	445(5)	1059(6)	749(4)	45(3)
C(43)	-336(5)	1110(6)	744(5)	50(3)
C(44)	-417(4)	480(6)	1322(4)	43(3)
C(45)	-1119(5)	244(7)	1573(5)	67(4)
C(51)	2557(5)	-2580(7)	1174(6)	66(4)
C(52)	1792(5)	-2482(6)	1366(4)	43(3)
C(53)	1194(5)	-3208(6)	1286(5)	52(3)
C(54)	638(4)	-2739(5)	1571(4)	38(3)
C(55)	-145(5)	-3171(6)	1626(5)	62(4)
C(61)	2839(5)	-22(7)	4465(4)	62(3)
C(62)	2009(5)	-341(6)	3997(4)	46(3)
C(63)	1401(5)	-681(7)	4280(4)	51(3)
C(64)	774(5)	-901(6)	3664(5)	49(3)
C(65)	-45(5)	-1292(8)	3634(6)	74(4)
C(1)	2382(6)	3849(7)	1432(5)	61(4)
F(1)	2823(4)	4638(4)	1300(3)	79(3)
F(2)	1664(3)	3972(4)	941(4)	97(3)
F(3)	2326(5)	4000(4)	2127(4)	111(4)
S(1)	2823(1)	2602(2)	1322(1)	45(1)
O(1)	2306(3)	1851(4)	1573(3)	48(2)
O(2)	3608(3)	2669(5)	1829(3)	64(2)
O(3)	2726(4)	2554(4)	518(3)	60(2)

^a Equivalent isotropic U_{eq} defined as one-third of the trace of the orthogonalized U_{ij} tensor.

(m), 1146 (m), 1070 (s), 1048 (m), 1035 (s), 987 (w), 836 (m), 803 (m), 698 (w), 638 (s), 572 (w), 518 (w), 458 (w).

7. White, yield: 83%. Anal. Calcd for $\text{EuC}_{31}\text{H}_{44}\text{N}_{12}\text{B}_2\text{F}_3\text{SO}_3$: C, 41.58; H, 4.95; N, 18.77. Found: C, 41.25; H, 4.83; N, 18.47. ¹H NMR (CDCl_3 , 298 K): δ -0.14 (s, 18H, CH); 1.72 (s, 6H, Me); 10.93 (s, $w_{1/2} = 14.3$ Hz, 18H, Me). ¹³C NMR spectrum not observed.

8. White, yield: 69%. Anal. Calcd for $\text{GdC}_{31}\text{H}_{44}\text{N}_{12}\text{B}_2\text{F}_3\text{SO}_3$: C, 41.33; H, 4.88; N, 18.66. Found: C, 40.19; H, 4.78; N, 18.00. ¹H or ¹³C NMR spectrum not observed.

9. White, yield: 65%. Anal. Calcd for $\text{DyC}_{31}\text{H}_{44}\text{N}_{12}\text{B}_2\text{F}_3\text{SO}_3$: C, 41.10; H, 4.90; N, 18.55. Found: C, 40.44; H, 4.77; N, 17.89. ¹H or ¹³C NMR spectrum not observed.

10. Pale pink, yield: 65%. Anal. Calcd for $\text{HoC}_{31}\text{H}_{44}\text{N}_{12}\text{B}_2\text{F}_3\text{SO}_3$: C, 40.99; H, 4.88; N, 18.50. Found: C, 40.76; H, 4.78; N, 18.28. ¹H or ¹³C NMR spectrum not observed.

Table 3. Selected Bond Lengths (\AA) and Angles (deg) for **5** (esd's in Parentheses)

Nd(1)–N(11)	2.595(6)	B(1)–N(12)	1.518(11)
Nd(1)–N(21)	2.491(7)	B(1)–N(22)	1.545(10)
Nd(1)–N(31)	2.485(5)	B(1)–N(32)	1.551(11)
Nd(1)–N(41)	2.598(5)	B(2)–N(42)	1.525(10)
Nd(1)–N(51)	2.535(6)	B(2)–N(52)	1.558(11)
Nd(1)–N(61)	2.553(7)	B(2)–N(62)	1.534(10)
Nd(1)–O(1)	2.421(5)		
N(11)–Nd(1)–N(21)	72.3(2)	N(21)–Nd(1)–N(61)	149.1(2)
N(11)–Nd(1)–N(31)	74.5(2)	N(31)–Nd(1)–N(61)	84.5(2)
N(21)–Nd(1)–N(31)	83.4(2)	N(41)–Nd(1)–N(61)	85.1(2)
N(11)–Nd(1)–N(41)	147.3(2)	N(51)–Nd(1)–N(61)	77.3(2)
N(21)–Nd(1)–N(41)	123.7(2)	N(11)–Nd(1)–O(1)	138.3(2)
N(31)–Nd(1)–N(41)	131.2(2)	N(21)–Nd(1)–O(1)	77.8(2)
N(11)–Nd(1)–N(51)	80.7(2)	N(31)–Nd(1)–O(1)	73.7(2)
N(21)–Nd(1)–N(51)	101.6(2)	N(41)–Nd(1)–O(1)	74.3(2)
N(31)–Nd(1)–N(51)	151.9(2)	N(51)–Nd(1)–O(1)	134.4(2)
N(41)–Nd(1)–N(51)	68.6(2)	N(61)–Nd(1)–O(1)	125.3(2)
N(11)–Nd(1)–N(61)	77.1(2)		

Table 4. Final Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **11** (esd's in Parentheses)

	<i>x</i>	<i>y</i>	<i>z</i>	$U(\text{eq})^a$
Yb(1)	0	0	0	43(1)
N(11)	653(3)	1082(4)	-1559(6)	69(2)
N(21)	1244(4)	0	1349(7)	58(2)
N(12)	1454(2)	923(3)	-1824(5)	54(1)
N(22)	1925(3)	0	521(6)	45(2)
B(1)	1888(4)	0	-1252(8)	45(2)
C(21)	1490(6)	0	2802(10)	86(4)
C(22)	2311(6)	0	2909(10)	90(4)
C(23)	2569(5)	0	1474(9)	68(3)
C(13)	1751(4)	1694(6)	-2529(8)	83(2)
C(11)	483(4)	1978(6)	-2145(12)	99(3)
C(12)	1150(5)	2361(6)	-2737(12)	108(3)
C(231)	3408(6)	0	932(13)	122(7)
C(211)	901(7)	0	4073(11)	150(10)
C(111)	-351(5)	2371(8)	-2040(15)	151(6)
C(131)	2612(5)	1769(8)	-2936(14)	139(5)
S(1)/C(1)	5451(2)	0	4458(4)	63(1)
F(1)/O(1)	5220(5)	0	2920(8)	104(3)
F(2)/O(2)	5861(4)	814(6)	4851(9)	153(3)

^a Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 5. Selected Bond Lengths (\AA) and Angles (deg) for **11**

Yb(1)–N(11)	2.304 (5)	N(12)–B(1)	1.529 (6)
Yb(1)–N(21)	2.347 (6)	N(22)–B(1)	1.550 (8)
N(11)–Yb(1)–N(21)	82.8(2)	N(11)–N(12)–B(1)	121.6(4)
N(21)–Yb(1)–N(11A)	97.2(2)	N(21)–N(22)–B(1)	121.5(5)
N(11)–Yb(1)–N(11B)	100.1(3)	N(12)–B(1)–N(22)	109.4(3)
N(11)–Yb(1)–N(11C)	79.9(3)	N(12)–B(1)–N(12A)	111.1(5)

11. White, yield: 82%. Anal. Calcd for $\text{YbC}_{31}\text{H}_{44}\text{N}_{12}\text{B}_2\text{F}_3\text{SO}_3$: C, 40.63; H, 4.84; N, 18.34. Found: C, 40.76; H, 4.78; N, 18.28. ¹H NMR (CDCl_3): δ 3.3 (s, 18H, Me); 5.19 (s, $w_{1/2} = 27.3$ Hz, 18H, Me); 6.19 (s, 6H, CH). ¹³C NMR (CDCl_3): δ 11.9 (q, 3 or 5 CH_3), 17.9 (q, 5 or 3 CH_3), 111.3 (d, CH), 158.8 (s, 3 or 5 C), 167.2 (s, 5 or 3 C).

Crystallography. All measurements were made on a Nicolet R3Mv four-circle diffractometer using $\text{Mo K}\alpha$ ($\lambda = 0.71073$ \AA) radiation. Crystallographic calculations were carried out with the SHELXTL PLUS suite of programs on a Microvax II computer.

A pale blue blocklike crystal of **5**, grown by slow cooling of an toluene solution, was mounted in a Lindemann capillary under nitrogen in a glovebox. The orientation matrix of the crystal and the unit cell were determined using 35 reflections chosen from a rotation photograph with 2θ in the range of 16 – 29° . Unit cell dimensions were confirmed by axial photographs. Data were collected by $\omega - 2\theta$ scans in a range $5^\circ \leq 2\theta \leq 50^\circ$. The intensities of three standard reflections monitored every 100 reflections showed no sign of crystal decay. Corrections for Lorentz and polarization and an empirical correction for absorption

were applied. The structure of **5** was solved by direct methods and developed by alternating cycles of difference Fourier syntheses and full-matrix least-squares procedures. Anisotropic thermal parameters were used in the final model for all non-hydrogen atoms. Hydrogen atoms were not located but placed in idealized positions $d(X-H) = 0.96 \text{ \AA}$ ($X = B, C$) and assigned a common isotropic thermal parameter ($U = 0.08 \text{ \AA}^2$).

A thin white plate of **11** grown by slow diffusion of pentane into a dichloromethane solution was mounted in a Lindemann capillary in the drybox. The orientation matrix and unit cell were determined using 29 reflections chosen from a rotation photograph with 2θ in the range $17-26^\circ$. Data were collected and the structure was solved as for **5**. The triflate ion lies across the mirror plane, and the ion was allowed to refine with a 50% occupancy of the CF_3 and SO_3 groups in the two sites.

Details of the experimental conditions appear in Table 1. Final atomic coordinates, selected bond lengths and bond angles are listed in Tables 3-5.

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Supporting Information Available: Tables of crystallographic data, atomic coordinates and isotropic displacement parameters, bond lengths and angles, anisotropic thermal parameters, and hydrogen positions for **5** and **11** (9 pages). Ordering information is given on any current masthead page.

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