

## Synthesis of Mixed Cp/Tp<sup>Me2</sup> Lanthanide Complexes from Lanthanocene Precursors and their Structures and Reactivities

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Reaction of Cp<sub>2</sub>LnCl with 1 equiv of KTp<sup>Me2</sup> in toluene gives the mixed Tp<sup>Me2</sup>/Cp lanthanide complexes Cp<sub>2</sub>Ln(Tp<sup>Me2</sup>) (Ln = Yb (**1a**), Er (**1b**), Dy (**1c**)), while unexpected complexes CpLn(Tp<sup>Me2</sup>)Cl(THF) (Ln = Yb (**2a**), Er (**2b** · THF), Dy (**2c**), Y (**2d**)) are obtained when the reactions are carried out in THF. Complex **2b** can also be formed by the reaction of CpErCl<sub>2</sub>(THF)<sub>3</sub> with 1 equiv of KTp<sup>Me2</sup> in THF. Moreover, complex **1a** can also be obtained from the reaction of Cp<sub>3</sub>Yb and KTp<sup>Me2</sup>. The results not only represent an efficient and versatile method for the synthesis of mixed Cp/Tp<sup>Me2</sup> lanthanide complexes but also provide new insight into the reactivity of Cp<sub>2</sub>LnCl. Furthermore, the reactivities of complexes **1a–c** toward proton-donating reagents are examined. It has been found that **1b** reacts with benzotriazole (C<sub>6</sub>H<sub>4</sub>NHN<sub>2</sub>) in THF to yield a lanthanide metallomacrocylic complex [(Tp<sup>Me2</sup>)CpEr(μ-N<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>] (**3**), while the reaction of **1a** with 1 equiv of 2-aminopyridine in THF gives an unexpected oxide complex [(Tp<sup>Me2</sup>)Yb(2-HNC<sub>5</sub>H<sub>4</sub>N)]<sub>2</sub>(μ-O) (**4**). Presumably, the oxide ligand of compound **4** results from adventitious water. In addition, treatment of **1c** with 2 equiv of 3,5-dimethylpyrazole yields a completely Cp-abstracted product (Tp<sup>Me2</sup>)Dy(Pz<sup>Me2</sup>)<sub>2</sub>(THF) (**5**), which can also be directly obtained from a three-component reaction of Cp<sub>2</sub>DyCl, KTp<sup>Me2</sup>, and 3,5-dimethylpyrazole in THF. These results further indicate that the new mixed Tp<sup>Me2</sup>/Cp lanthanide complexes are practical and versatile precursors for the synthesis of poly(pyrazolyl)borate lanthanide derivatives. All new compounds have been characterized by elemental analysis and spectroscopic methods. The structures of complexes **1a,b** and **2–5** have also been determined through single-crystal X-ray diffraction analysis.

### Introduction

Poly(pyrazolyl)borate anion (Tp) ligands are currently attracting considerable attention due to both their potential as an alternative to cyclopentadienyl ligands and their outstanding performance in conferring organometallic complexes higher reactivity and new reaction patterns.<sup>1–4</sup> In contrast to the ever-growing literature on poly(pyrazolyl)borate complexes of transition metals,<sup>1,2</sup> examples of lanthanide species incorporating these functionalities remain scarce.<sup>3–5</sup> This is surprising, given the expectation that the poly(pyrazolyl)borate ligands could introduce novel features into the catalytic behavior, structure, reactivity, and stability of lanthanide complexes.<sup>4,5</sup> There does not appear to be a large effort to expand upon this class of compounds, which is

probably due to the lack of viable synthetic methodologies to access these complexes. For example, replacement of a halide (X<sup>−</sup>) of Tp<sup>Me2</sup>LnX<sub>2</sub> or (Tp<sup>Me2</sup>)<sub>2</sub>LnX with other anionic ligands, such as alkyl, amido, and alkoxy, remains a significant challenge,<sup>3a,6</sup> despite this having been established in the past as a very powerful and efficient method for the

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synthesis of various lanthanocene derivatives.<sup>7</sup> Therefore, the development of a new strategy capable of constructing poly(pyrazolyl)borate lanthanide frameworks from a rather simple poly(pyrazolyl)borate alkali metal precursor is highly desirable.

Cyclopentadienyl complexes have occupied a dominant place in the organometallic chemistry of rare earth metals.<sup>7a,b,8</sup> However, only a few mixed Cp/Tp lanthanide complexes have been reported so far and are mainly synthesized from the corresponding divalent Ln(II) (only Sm and Yb) starting materials.<sup>9a-c</sup> Considering that dicyclopentadienyl chloride complexes of rare earths provide a reaction system in which the cyclopentadienyl and chloride ligands can be selectively replaced by the same or different groups, we were interested in the potential of preparing poly(pyrazolyl)borate lanthanide complexes from them. Herein, we report the first successful synthesis of a series of new tris(3,5-dimethylpyrazolyl)borate lanthanide complexes using Cp<sub>2</sub>LnCl and Cp<sub>3</sub>Ln precursors, featuring an unusual solvent-dependent reactivity of complexes Cp<sub>2</sub>LnCl.

## Experimental Section

**General Procedure.** All operations involving air- and moisture-sensitive compounds were carried out under an inert atmosphere of purified argon or nitrogen using standard Schlenk techniques.

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The solvents THF, toluene, and *n*-hexane were refluxed and distilled over sodium benzophenone ketyl under nitrogen immediately prior to use. (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>LnCl and KTp<sup>Me2</sup> were prepared by the literature methods.<sup>10,11</sup> KBH<sub>4</sub> and 3,5-dimethylpyrazole were purchased from Aldrich and were used without purification. Elemental analyses for C, H, and N were carried out on a Rapid CHN-O analyzer. Infrared spectra were obtained on a NICOLET FT-IR 360 spectrometer with samples prepared as Nujol mulls. <sup>1</sup>H NMR data were obtained on a Bruker DMX-500 NMR spectrometer.

**Synthesis of Cp<sub>2</sub>YbTp<sup>Me2</sup> (1a).** **Method A.** A 30 mL toluene solution of KTp<sup>Me2</sup> (0.534 g, 1.59 mmol) and Cp<sub>2</sub>YbCl (0.538 g, 1.59 mmol) was stirred at room temperature for 24 h. The precipitate was removed by centrifugation, and the solution was concentrated to ca. 15 mL under reduced pressure. Red crystals of **1a** were obtained by slow diffusion of *n*-hexane. Yield: 0.713 g (75%). C, H, N anal. (%) calcd for C<sub>25</sub>H<sub>32</sub>N<sub>6</sub>Yb: C, 50.01; H, 5.37; N, 14.00. Found: C, 49.79; H, 5.21; N, 14.26. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub> 7.16): δ 7.65 (s, 10H, C<sub>5</sub>H<sub>5</sub>), 5.62 (s, 2H H-4(Tp<sup>Me2</sup>)), 5.02 (s, 1H H-4(Tp<sup>Me2</sup>)), 2.49 (3H, CH<sub>3</sub>), 2.22 (6H, CH<sub>3</sub>), 2.02 (6H, CH<sub>3</sub>), 1.87 (3H, CH<sub>3</sub>). IR (Nujol): 3106 s, 2468 s, 1540 s, 1439 s, 1420 s, 1358 s, 1204 s, 1033 s, 1013 s, 986 m, 795 s, 784 s, 683 m, 636 m cm<sup>-1</sup>.

**Method B.** A mixture of KTp<sup>Me2</sup> (0.548 g, 1.63 mmol) and Cp<sub>3</sub>Yb (0.600 g, 1.63 mmol) in 50 mL of toluene was stirred at room temperature for three days. The solution color turned slowly from green to red. The reaction mixture was subsequently worked up by the method described above. Red crystals of **1a** were obtained in 68% yield, 0.664 g.

**Method C.** A mixture of KTp<sup>Me2</sup> (0.218 g, 0.65 mmol) and Cp<sub>3</sub>Yb (0.239 g, 0.65 mmol) in 20 mL of THF was stirred at room temperature for seven days. The solution color turned slowly from green to red. The precipitate was removed by centrifugation, and the solution was concentrated to ca. 5 mL under reduced pressure. Red crystals of **1a** were obtained by slow diffusion of *n*-hexane. Yield: 0.498 g (51%).

**Synthesis of Cp<sub>2</sub>ErTp<sup>Me2</sup> (1b).** Following the procedure described for **1a**, reaction of Cp<sub>2</sub>ErCl (0.355 g, 1.07 mmol) with KTp<sup>Me2</sup> (0.360 g, 1.07 mmol) in 30 mL of toluene yielded **1b** as pink crystals. Yield: 0.520 g (82%). C, H, N anal. (%) calcd for C<sub>25</sub>H<sub>32</sub>N<sub>6</sub>Er: C, 50.50; H, 5.42; N, 14.13. Found: C, 50.39; H, 5.33; N, 14.27. IR (Nujol): 3107 s, 2468 s, 1540 s, 1439 s, 1422 s, 1358 s, 1204 s, 1033 s, 1010 s, 983 m, 796 s, 783 s, 683 m, 634 m cm<sup>-1</sup>.

**Synthesis of Cp<sub>2</sub>DyTp<sup>Me2</sup> (1c).** Following the procedure described for **1a**, reaction of Cp<sub>2</sub>DyCl (0.436 g, 1.33 mmol) with KTp<sup>Me2</sup> (0.447 g, 1.33 mmol) in 40 mL of toluene yielded **1c** as pale yellow crystals. Yield: 0.540 g (69%). C, H, N anal. (%) calcd for C<sub>25</sub>H<sub>32</sub>N<sub>6</sub>Dy: C, 50.90; H, 5.47; N, 14.25. Found: C, 50.82; H, 5.36; N, 14.36. IR (Nujol): 3106 s, 2468 s, 1541 s, 1439 s, 1420 s, 1359 s, 1201 s, 1034 s, 1009 s, 986 m, 796 s, 784 s, 683 m, 635 m cm<sup>-1</sup>.

**Synthesis of CpYb(Tp<sup>Me2</sup>)Cl(THF) (2a).** A 15 mL THF solution of KTp<sup>Me2</sup> (0.420 g, 1.25 mmol) was added to the 10 mL THF solution of Cp<sub>2</sub>YbCl (0.423 g, 1.25 mmol) at room temperature. The mixture was stirred for 24 h, and a small amount of colorless precipitate was removed by centrifugation. Then, the solution was concentrated to about 10 mL. Diffusing *n*-hexane into the THF solution gave a mixture containing primarily orange crystals of **2a** and a colorless powder of CpK. The pure crystals of **2a** were collected manually and were washed with *n*-hexane for characterization purposes. Yield: 0.432 g

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**Table 1.** Crystal and Data Collection Parameters of Complexes **1a**, **1b** and **2b**·THF

	<b>1a</b>	<b>1b</b>	<b>2a</b>	<b>2b</b>	<b>2b</b> ·THF
formula	C <sub>25</sub> H <sub>32</sub> N <sub>6</sub> BYb	C <sub>25</sub> H <sub>32</sub> N <sub>6</sub> BEr	C <sub>24</sub> H <sub>35</sub> N <sub>6</sub> BOClYb	C <sub>24</sub> H <sub>35</sub> N <sub>6</sub> BOClEr	C <sub>28</sub> H <sub>43</sub> N <sub>6</sub> BO <sub>2</sub> ClEr
fw	600.42	594.64	642.88	637.10	709.20
cryst color	red	pink	orange	pink	pink
cryst dimens (mm)	0.22 × 0.10 × 0.06	0.22 × 0.10 × 0.06	0.25 × 0.15 × 0.14	0.12 × 0.08 × 0.05	0.25 × 0.15 × 0.12
crystal system	monoclinic	monoclinic	triclinic	triclinic	orthorhombic
space group	Cc	Cc	P1	P1	P2(1)2(1)2(1)
unit cell dimensions					
<i>a</i> (Å)	8.747(4)	8.627(7)	10.024(6)	9.988(4)	10.057(16)
<i>b</i> (Å)	21.798(9)	21.432(17)	10.865(7)	10.840(4)	16.81(3)
<i>c</i> (Å)	12.859(5)	12.849(10)	14.138(9)	14.144(5)	18.39(3)
$\alpha$			71.225(8)	71.260(5)	
$\beta$ (deg)	96.273(4)	96.412(10)	88.812(7)	89.031(4)	
$\gamma$ (deg)			68.413(7)	68.591(4)	
<i>V</i> (Å <sup>3</sup> )	2437.1(17)	2361(3)	1347.3(15)	1341.3(9)	3110(9)
<i>Z</i>	4	4	2	2	4
<i>D</i> <sub>calcd</sub> (g·cm <sup>-3</sup> )	1.636	1.673	1.585	1.577	1.515
$\mu$ (mm <sup>-1</sup> )	3.862	3.580	3.597	3.255	2.819
<i>F</i> (000)	1196	1188	642	638	1436
radiation ( $\lambda = 0.71073$ Å)	Mo K $\alpha$	Mo K $\alpha$	Mo K $\alpha$	Mo K $\alpha$	Mo K $\alpha$
temp (K)	293.2	293.2	293.2	293.2	293.2
scan type	$\omega$ -2 $\theta$	$\omega$ -2 $\theta$	$\omega$ -2 $\theta$	$\omega$ -2 $\theta$	$\omega$ -2 $\theta$
$\theta$ range (deg)	1.87–25.01	1.90–26.00	1.53–25.01	1.53–25.01	1.64–26.01
<i>h, k, l</i> range	−9 ≤ <i>h</i> ≤ 10 −21 ≤ <i>k</i> ≤ 25 −15 ≤ <i>l</i> ≤ 8	−10 ≤ <i>h</i> ≤ 8 −26 ≤ <i>k</i> ≤ 24 −15 ≤ <i>l</i> ≤ 15	−11 ≤ <i>h</i> ≤ 11 −12 ≤ <i>k</i> ≤ 12 −16 ≤ <i>l</i> ≤ 13	−11 ≤ <i>h</i> ≤ 11 −9 ≤ <i>k</i> ≤ 12 −16 ≤ <i>l</i> ≤ 16	−12 ≤ <i>h</i> ≤ 12 −20 ≤ <i>k</i> ≤ 20 −20 ≤ <i>l</i> ≤ 22
no. of reflns measured	3846	5244	5475	5520	14027
no. of unique reflns	2281 ( <i>R</i> <sub>int</sub> = 0.0402)	3391 ( <i>R</i> <sub>int</sub> = 0.0465)	4606 ( <i>R</i> <sub>int</sub> = 0.0282)	4612 ( <i>R</i> <sub>int</sub> = 0.0206)	6066 ( <i>R</i> <sub>int</sub> = 0.0421)
completeness to $\theta$	98.5% ( $\theta = 25.01$ )	99.6% ( $\theta = 26.00$ )	97.2% ( $\theta = 25.01$ )	97.6% ( $\theta = 25.01$ )	99.5% ( $\theta = 26.01$ )
refinement method	full-matrix least squares on <i>F</i> <sup>2</sup>	full-matrix least squares on <i>F</i> <sup>2</sup>	full-matrix least squares on <i>F</i> <sup>2</sup>	full-matrix least squares on <i>F</i> <sup>2</sup>	full-matrix least squares on <i>F</i> <sup>2</sup>
data/restraints/params	2281/3/265	3391/3/277	4606/1/304	4612/1/304	6066/8/331
goodness-of-fit on <i>F</i> <sup>2</sup>	1.132	1.028	1.039	1.052	1.093
final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0364 <i>wR</i> <sub>2</sub> = 0.0898	<i>R</i> <sub>1</sub> = 0.0545 <i>wR</i> <sub>2</sub> = 0.1411	<i>R</i> <sub>1</sub> = 0.0434 <i>wR</i> <sub>2</sub> = 0.1119	<i>R</i> <sub>1</sub> = 0.0292 <i>wR</i> <sub>2</sub> = 0.0699	<i>R</i> <sub>1</sub> = 0.0459 <i>wR</i> <sub>2</sub> = 0.0969
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0373 <i>wR</i> <sub>2</sub> = 0.0904	<i>R</i> <sub>1</sub> = 0.0592 <i>wR</i> <sub>2</sub> = 0.1442	<i>R</i> <sub>1</sub> = 0.0473 <i>wR</i> <sub>2</sub> = 0.1145	<i>R</i> <sub>1</sub> = 0.0356 <i>wR</i> <sub>2</sub> = 0.0720	<i>R</i> <sub>1</sub> = 0.0527 <i>wR</i> <sub>2</sub> = 0.0996
largest diff. peak and hole (e <sup>-</sup> ·Å <sup>-3</sup> )	1.350 and −2.497	3.711 and −1.547	2.010 and −2.334	1.443 and −0.508	1.314 and −0.668

(54%). C, H, N anal. (%) calcd for C<sub>24</sub>H<sub>35</sub>N<sub>6</sub>BOClYb: C, 44.84; H, 5.49; N, 13.07. Found: C, 44.63; H, 5.41; N, 13.22. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub> 7.16):  $\delta$  6.30 (s, 5H C<sub>5</sub>H<sub>5</sub>),  $\delta$  5.60 (br, 3H H-4(Tp<sup>Me2</sup>)),  $\delta$  3.57 (m, 4H THF),  $\delta$  1.44 (m, 4H THF),  $\delta$  1.36 (9H, CH<sub>3</sub>),  $\delta$  0.91 (9H, CH<sub>3</sub>). IR (Nujol): 3107 s, 2557 s, 1647 w, 1608 m, 1544 s, 1493 w, 1437 s, 1415 s, 1361 s, 1203 s, 1070 s, 1034 s, 1009 s, 840 m, 806 s, 779 s, 694 m, 640 m cm<sup>-1</sup>.

**Synthesis of CpEr(Tp<sup>Me2</sup>)Cl(THF)·THF (2b·THF).** Following the procedure described for **2a**, reaction of Cp<sub>2</sub>ErCl (0.296 g, 0.89 mmol) with KTp<sup>Me2</sup> (0.299 g, 0.89 mmol) gave **2b**·THF as pink crystals. Yield: 0.360 g (57%). C, H, N anal. (%) calcd for C<sub>28</sub>H<sub>43</sub>N<sub>6</sub>BO<sub>2</sub>ClEr: C, 47.42; H, 6.11; N, 11.85. Found: C, 47.18; H, 6.00; N, 12.03. IR (Nujol): 3094 m, 2554 s, 1650 w, 1610 w, 1542 s, 1416s, 1365 s, 1200 s, 1071 s, 1010 s, 860 m, 840 m, 812 s, 777 s, 696 m, 647 s cm<sup>-1</sup>.

**Synthesis of CpDy(Tp<sup>Me2</sup>)Cl(THF) (2c).** Following the procedure described for **2a**, reaction of Cp<sub>2</sub>DyCl (0.308 g, 0.94 mmol) with KTp<sup>Me2</sup> (0.316 g, 0.94 mmol) gave **2c** as yellow crystals. Yield: 0.253 g (43%). C, H, N anal. (%) calcd for C<sub>24</sub>H<sub>35</sub>N<sub>6</sub>BOClDy: C, 45.59; H, 5.58; N, 13.29. Found: C, 45.42; H, 5.50; N, 13.43. IR (Nujol): 3107 s, 2556 s, 1648 w, 1608 w, 1544 s, 1440 s, 1417 s, 1363 s, 1201 s, 1070 s, 1016 s, 863 m, 837 m, 806 s, 780 s, 695 m, 665 m, 645 m cm<sup>-1</sup>.

**Synthesis of CpY(Tp<sup>Me2</sup>)Cl(THF) (2d).** Following the procedure described for **2a**, reaction of Cp<sub>2</sub>YCl (0.298 g, 1.17 mmol) with KTp<sup>Me2</sup> (0.394 g, 1.17 mmol) gave **2d** as colorless crystals. Yield: 0.304 g (47%). C, H, N anal. (%) calcd for C<sub>24</sub>H<sub>35</sub>N<sub>6</sub>BOClY: C, 51.59; H, 6.31; N, 15.04. Found: C, 51.49; H, 6.20; N 15.27. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub> 7.16):  $\delta$  6.54 (s, 5H C<sub>5</sub>H<sub>5</sub>),  $\delta$  5.81 (s, 3H H-4(Tp<sup>Me2</sup>)),  $\delta$  3.57 (t, 4H THF),  $\delta$  2.05 (9H, CH<sub>3</sub>),  $\delta$  1.71 (9H, CH<sub>3</sub>),  $\delta$  1.41 (m, 4H THF). IR (Nujol): 3107 s, 2557 s, 1647 w, 1608 w, 1544 s,

1439 s, 1416 s, 1362 s, 1202 s, 1069 s, 1034 s, 1009 s, 866 m, 840 m, 806 s, 779 s, 694 m, 646 s cm<sup>-1</sup>.

**Synthesis of CpEr(Tp<sup>Me2</sup>)Cl(THF) (2b).** A 10 mL THF solution of KTp<sup>Me2</sup> (0.255 g, 0.76 mmol) was added to the 20 mL THF solution of CpErCl<sub>2</sub>(THF)<sub>3</sub> (0.395 g, 0.76 mmol) at room temperature. The mixture was stirred for 24 h, and the precipitate was removed by centrifugation. Then, the solution was concentrated to ca. 10 mL. Pink crystals of **2b** were obtained by slow diffusion of *n*-hexane to THF. Yield: 0.295 g (61%). C, H, N anal. (%) calcd for C<sub>24</sub>H<sub>35</sub>N<sub>6</sub>BOClYb: C, 45.25; H, 5.54; N, 13.19. Found: C, 45.07; H, 5.51; N, 13.28. IR (Nujol): 3108 s, 2556 s, 1648 w, 1607 m, 1541 s, 1415 s, 1361 s, 1201 s, 1070 s, 1034 s, 1009 s, 838 m, 806 s, 780 s, 695 m, 646 s cm<sup>-1</sup>.

**Synthesis of [(Tp<sup>Me2</sup>)CpEr( $\mu$ -N<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)]<sub>3</sub> (3).** (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>ErTp<sup>Me2</sup> (0.683 g, 1.15 mmol) and benzotriazole (0.137 g, 1.15 mmol) were mixed in 30 mL of THF at room temperature. After stirring for 24 h, all of the volatile substances were removed under a vacuum to give a pink powder. Recrystallization of the pink solid in THF/hexane gave **3** as pink crystals. Yield: 0.448 g (56%). C, H, N anal. (%) calcd for C<sub>86</sub>H<sub>112</sub>N<sub>27</sub>B<sub>3</sub>O<sub>2</sub>Er<sub>3</sub>: C, 49.42; H, 5.40; N, 18.09. Found: C, 49.27; H, 5.35; N, 18.26. IR (Nujol): 3107 m, 1602 m, 1544 s, 1415 s, 1260 s, 1203 s, 1120 s, 1067 s, 1037 s, 864 m, 790 s, 755 s, 696 s, 644 m cm<sup>-1</sup>.

**Synthesis of [Tp<sup>Me2</sup>Yb(2-HNC<sub>5</sub>H<sub>4</sub>N)]<sub>2</sub>( $\mu$ -O) (4).** Cp<sub>2</sub>YbTp<sup>Me2</sup> (0.348 g, 0.58 mmol) and 2-aminopyridine (0.055 g, 0.58 mmol) were mixed in 20 mL of THF at room temperature. After stirring for 24 h, all of the volatile substances were removed under a vacuum to give a red powder. Recrystallization of the red solid in THF/hexane gave **4** as orange crystals. Yield: 0.146 g (44%). C, H, N anal. (%) calcd for C<sub>40</sub>H<sub>54</sub>N<sub>16</sub>B<sub>2</sub>OYb<sub>2</sub>: C, 42.04; H, 4.76; N, 19.61. Found: C, 41.98; H, 4.77; N, 19.83. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub> 7.16):  $\delta$

**Table 2.** Crystal and Data Collection Parameters of Complexes **2c**, **2d**, and **3-5**

	<b>2c</b>	<b>2d</b>	<b>3</b>	<b>4</b>	<b>5</b>
formula	C <sub>24</sub> H <sub>35</sub> N <sub>6</sub> BOCIDy	C <sub>24</sub> H <sub>35</sub> N <sub>6</sub> BOCIY	C <sub>86</sub> H <sub>112</sub> N <sub>27</sub> B <sub>3</sub> O <sub>2</sub> Er <sub>3</sub>	C <sub>40</sub> H <sub>54</sub> N <sub>16</sub> B <sub>2</sub> OYb <sub>2</sub>	C <sub>29</sub> H <sub>44</sub> N <sub>10</sub> BODY
fw	632.34	558.75	2090.24	1142.69	722.05
cryst color	yellow	colorless	pink	orange	yellow
cryst dimens (mm)	0.15 × 0.12 × 0.08	0.25 × 0.20 × 0.10	0.20 × 0.12 × 0.10	0.12 × 0.10 × 0.08	0.25 × 0.15 × 0.12
cryst syst	triclinic	triclinic	monoclinic	monoclinic	triclinic
space group	P $\bar{1}$	P $\bar{1}$	P2(1)/c	P2(1)/n	P $\bar{1}$
unit cell dimensions					
<i>a</i> (Å)	9.985(3)	9.982(5)	14.693(5)	14.988(6)	9.287(3)
<i>b</i> (Å)	10.867(4)	10.871(5)	22.729(7)	20.357(8)	10.275(3)
<i>c</i> (Å)	14.173(5)	14.169(7)	28.708(9)	17.065(7)	18.371(6)
$\alpha$	71.333(4)	71.189(6)			73.968(4)
$\beta$ (deg)	89.122(4)	89.006(6)	100.926(4)	115.328(5)	79.964(4)
$\gamma$ (deg)	68.664(4)	68.583(6)			86.524(4)
<i>V</i> (Å <sup>3</sup> )	1348.1(8)	1346.1(11)	9414(5)	4706(3)	1658.9(9)
<i>Z</i>	2	2	4	4	2
<i>D</i> <sub>calcd</sub> (g cm <sup>-3</sup> )	1.558	1.379	1.475	1.613	1.445
$\mu$ (mm <sup>-1</sup> )	2.898	2.293	2.710	3.999	2.290
<i>F</i> (000)	634	580	4208	2256	734
radiation	Mo K $\alpha$	Mo K $\alpha$	Mo K $\alpha$	Mo K $\alpha$	Mo K $\alpha$
temp (K)	293.2	293.2	293.2	293.2	293.2
scan type	$\omega$ -2 $\theta$	$\omega$ -2 $\theta$	$\omega$ -2 $\theta$	$\omega$ -2 $\theta$	$\omega$ -2 $\theta$
$\theta$ range (deg)	2.14–26.01	2.14–25.01	1.41–26.01	1.52–25.01	2.06–27.14
<i>h</i> , <i>k</i> , <i>l</i> range	–12 ≤ <i>h</i> ≤ 11 –13 ≤ <i>k</i> ≤ 11 –17 ≤ <i>l</i> ≤ 9	–11 ≤ <i>h</i> ≤ 11 –12 ≤ <i>k</i> ≤ 12 –10 ≤ <i>l</i> ≤ 16	–18 ≤ <i>h</i> ≤ 17 0 ≤ <i>k</i> ≤ 28 0 ≤ <i>l</i> ≤ 35	–17 ≤ <i>h</i> ≤ 17 –24 ≤ <i>k</i> ≤ 21 –20 ≤ <i>l</i> ≤ 19	–11 ≤ <i>h</i> ≤ 11 –13 ≤ <i>k</i> ≤ 8 –23 ≤ <i>l</i> ≤ 15
no. of reflns measured	6101	5555	18445	19198	8229
no. of unique reflns	5162 ( <i>R</i> <sub>int</sub> = 0.0293)	4631 ( <i>R</i> <sub>int</sub> = 0.0547)	18445 ( <i>R</i> <sub>int</sub> = 0.0000)	8278 ( <i>R</i> <sub>int</sub> = 0.0469)	6965 ( <i>R</i> <sub>int</sub> = 0.0186)
completeness to $\theta$	96.9% ( $\theta$ = 26.01)	97.7% ( $\theta$ = 25.01)	99.6% ( $\theta$ = 26.01)	99.6% ( $\theta$ = 25.01)	94.9% ( $\theta$ = 27.14)
refinement method	full-matrix least squares on <i>F</i> <sup>2</sup>	full-matrix least squares on <i>F</i> <sup>2</sup>	full-matrix least squares on <i>F</i> <sup>2</sup>	full-matrix least squares on <i>F</i> <sup>2</sup>	full-matrix least squares on <i>F</i> <sup>2</sup>
data/restraints/params	5162/1/304	4631/1/310	18445/17/1049	8278/2/562	6965/1/392
goodness-of-fit on <i>F</i> <sup>2</sup>	1.075	0.956	1.020	0.947	1.089
final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0344 <i>wR</i> <sub>2</sub> = 0.0871	<i>R</i> <sub>1</sub> = 0.0593 <i>wR</i> <sub>2</sub> = 0.1411	<i>R</i> <sub>1</sub> = 0.0444 <i>wR</i> <sub>2</sub> = 0.1060	<i>R</i> <sub>1</sub> = 0.0324 <i>wR</i> <sub>2</sub> = 0.0662	<i>R</i> <sub>1</sub> = 0.0330 <i>wR</i> <sub>2</sub> = 0.0897
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0394 <i>wR</i> <sub>2</sub> = 0.0971	<i>R</i> <sub>1</sub> = 0.0813 <i>wR</i> <sub>2</sub> = 0.1491	<i>R</i> <sub>1</sub> = 0.0759 <i>wR</i> <sub>2</sub> = 0.1118	<i>R</i> <sub>1</sub> = 0.0506 <i>wR</i> <sub>2</sub> = 0.0706	<i>R</i> <sub>1</sub> = 0.0385 <i>wR</i> <sub>2</sub> = 0.0926
largest diff. peak and hole (e <sup>-</sup> Å <sup>-3</sup> )	1.079 and –1.106	0.889 and –1.069	2.048 and –0.620	1.168 and –0.827	1.395 and –1.096

6.99–7.32 (m, 8H C<sub>5</sub>H<sub>4</sub>N),  $\delta$  5.61 (s, 6H H-4(Tp<sup>Me2</sup>)),  $\delta$  4.47 (s, 2H HNC<sub>5</sub>H<sub>4</sub>N),  $\delta$  2.20 (18H, CH<sub>3</sub>),  $\delta$  2.04 (18H, CH<sub>3</sub>). IR (Nujol): 3310 m, 3107 w, 2519 s, 1617 s, 1541 s, 1517 m, 1276 m, 1192 s, 1069 s, 1039 s, 993 s, 837 m, 807 s, 767 s, 696 m, 625 w cm<sup>-1</sup>.

**Synthesis of Tp<sup>Me2</sup>Dy(Pz<sup>Me2</sup>)<sub>2</sub>(THF) (5).** Method A. Cp<sub>2</sub>-DyTp<sup>Me2</sup> (0.378 g, 0.64 mmol) and 3,5-dimethylpyrazole (0.124 g, 1.28 mmol) were mixed in 20 mL of THF at room temperature. After stirring for 24 h, all of the volatile substances were removed under a vacuum to give a yellow powder. Recrystallization of the yellow solid in THF/hexane gave **5** as pale yellow crystals. Yield: 0.332 g (72%). C, H, N anal. (%) calcd for C<sub>29</sub>H<sub>44</sub>N<sub>10</sub>BODY: C, 48.24; H, 6.14; N, 19.40. Found: C, 48.38; H, 6.17; N, 19.13. IR (Nujol): 3107 m, 2556 s, 1541 s, 1517 m, 1201 s, 1070 s, 1035 s, 863 m, 837 m, 806 s, 778 s, 697 m, 650 s cm<sup>-1</sup>.

**Method B.** (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>DyCl (0.444 g, 1.35 mmol) and KTp<sup>Me2</sup> (0.454 g, 1.35 mmol) were mixed in 30 mL of THF at room temperature. After stirring for 3 h, 3,5-dimethylpyrazole (0.260 g, 2.70 mmol) was added and continuously stirred for 24 h. The precipitate was removed by centrifugation, and the solution was concentrated to ca. 5 mL. Yellow crystals of **5** were obtained by slow diffusion of *n*-hexane to THF. Yield: 0.565 g (58%).

**X-Ray Data Collection, Structure Determination and Refinement.** Suitable single crystals of complexes **1a,b** and **2–5** were sealed under argon in Lindemann glass capillaries for X-ray structural analysis. Diffraction data were collected on a Bruker SMART Apex CCD diffractometer using graphite-monochromated Mo K $\alpha$  ( $\lambda$  = 0.71073 Å) radiation. During the intensity data collection, no significant decay was observed. The intensities were corrected for Lorentz-polarization effects and empirical absorption

with the SADABS program.<sup>12</sup> The structures were solved by the direct method using the SHELXL-97 program.<sup>13</sup> All non-hydrogen atoms were found from the difference Fourier syntheses. The H atoms were included in calculated positions with isotropic thermal parameters related to those of the supporting carbon atoms but were not included in the refinement. All calculations were performed using the SHELXL program. A summary of the crystallographic data and selected experimental information is given in Tables 1 and 2. Bond lengths and angles are given in Tables 3 and 4.

## Results and Discussion

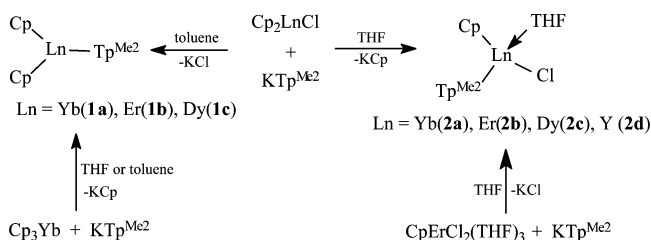
Treatment of Cp<sub>2</sub>YbCl (Cp = C<sub>5</sub>H<sub>5</sub>) with 1 equiv of KTp<sup>Me2</sup> (Tp<sup>Me2</sup> = tris(3,5-dimethylpyrazolyl)hydroborate) in toluene at room temperature afforded the chloride-exchange product Cp<sub>2</sub>YbTp<sup>Me2</sup> (Ln = Yb (**1a**), Er (**1b**), Dy (**1c**)) in high yield, while the unexpected cyclopentadienyl-exchange products CpLn(Tp<sup>Me2</sup>)Cl(THF) (Ln = Yb (**2a**), Er (**2b**), Dy (**2c**), Y (**2d**)) were obtained in moderate yields when the reactions were carried out in THF (Scheme 1). Although the metathesis reactions of Cp<sub>2</sub>LnCl toward ML (M = alkali metals) have been studied extensively, to our knowledge, in no case has elimination of CpM in preference to MCl been observed. Encouraged by the result, we further examined the scope of cyclopentadienyl lanthanide complexes as

(12) Sheldrick, G. M. *SADABS*; University of Göttingen: Göttingen, Germany, 1998.

(13) Sheldrick, G. M. *SHELXL-97*; University of Göttingen, Göttingen, Germany, 1997.

**Table 3.** Bond Lengths (Å) and Angles (deg) for **1a** and **1b**

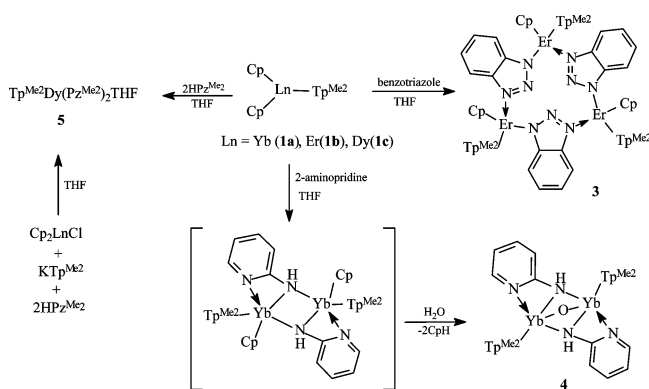
	Ln = Yb ( <b>1a</b> )	Ln = Er ( <b>1b</b> )
Ln(1)–N(4)	2.346(8)	2.288(11)
Ln(1)–N(2)	2.395(8)	2.359(11)
Ln(1)–C(7)	2.571(5)	2.523(7)
Ln(1)–C(8)	2.562(4)	2.545(7)
Ln(1)–C(5)	2.574(4)	2.554(7)
Ln(1)–C(1)	2.607(4)	2.552(8)
Ln(1)–C(6)	2.624(5)	2.589(8)
Ln(1)–C(9)	2.609(6)	2.624(8)
Ln(1)–C(4)	2.624(5)	2.621(8)
Ln(1)–C(10)	2.647(5)	2.650(7)
Ln(1)–C(2)	2.677(5)	2.616(9)
Yb(1)–C(3)	2.687(4)	2.658(6)
B(1)–N(5)	1.525(12)	1.488(17)
B(1)–N(1)	1.548(11)	1.497(16)
B(1)–N(3)	1.568(11)	1.548(16)
N(4)–Ln(1)–N(2)	88.7(3)	88.4(4)
N(5)–B(1)–N(1)	109.2(7)	109.8(10)
N(5)–B(1)–N(3)	110.3(7)	109.5(10)
N(1)–B(1)–N(3)	112.5(6)	112.2(10)

**Scheme 1**

precursors. It was found that complex **1a** could also be obtained from the reaction of Cp<sub>3</sub>Yb with KTp<sup>Me2</sup> in either toluene or THF. Noticeably, the reaction rate of Cp<sub>3</sub>Yb with KTp<sup>Me2</sup> significantly depends on the nature of the solvents. The change of the solution color from dark green to orange indicated that the reaction needed one week more in THF, but only 3~4 days in toluene. This difference may be attributed to the lower solubility of the byproduct KCp in toluene compared to that in THF, leading to the increase of the reaction rate; further, the steric hindrance from the coordinated THF might also be unfavorable to the approach of the ligand Tp<sup>Me2</sup> to the Cp<sub>3</sub>Yb(THF) moiety, though the solubility of KTp<sup>Me2</sup> is higher in THF than in toluene. It should be noted that only one cyclopentadienyl ligand could be replaced by Tp<sup>Me2</sup> with the formation of **2** in the reaction of Cp<sub>2</sub>LnCl with KTp<sup>Me2</sup>. In addition, attempts to synthesize (Tp<sup>Me2</sup>)<sub>2</sub>YbCp from Cp<sub>3</sub>Yb and KTp<sup>Me2</sup> were also unsuccessful, and only **1a** was obtained, even with excess KTp<sup>Me2</sup>. In contrast to the preferable elimination of KCp in the

**Table 4.** Bond Lengths (Å) and Angles (deg) for **2a–d**

	<b>2a</b> (Ln = Yb)	<b>2b</b> ·THF (Ln = Er)	<b>2b</b> (Ln = Er)	<b>2c</b> (Ln = Dy)	<b>2d</b> (Ln = Y)
Ln(1)–O(1)	2.372(5)	2.363(6)	2.382(3)	2.404(3)	2.386(4)
Ln(1)–N(5)	2.398(5)	2.441(7)	2.408(4)	2.454(4)	2.430(4)
Ln(1)–N(3)	2.501(5)	2.507(7)	2.508(3)	2.526(4)	2.520(4)
Ln(1)–N(1)	2.497(6)	2.486(7)	2.510(4)	2.530(4)	2.522(4)
Ln(1)–Cl(1)	2.573(2)	2.575(3)	2.5897(16)	2.6107(17)	2.5996(19)
Ln(1)–C(20)	2.663(7)	2.703(9)	2.668(5)	2.680(6)	2.695(6)
Ln(1)–C(16)	2.669(7)	2.682(9)	2.676(5)	2.688(5)	2.687(5)
Ln(1)–C(19)	2.690(8)	2.678(9)	2.693(5)	2.693(6)	2.717(6)
Ln(1)–C(17)	2.697(7)	2.670(9)	2.706(5)	2.721(5)	2.711(5)
Ln(1)–C(18)	2.698(7)	2.665(8)	2.713(5)	2.723(5)	2.733(6)
N(5)–Ln(1)–N(1)	85.65(18)	74.1(2)	85.07(12)	85.00(14)	84.74(14)
N(5)–Ln(1)–N(3)	75.43(18)	85.9(2)	75.48(12)	75.12(13)	74.90(13)
N(3)–C(17)–N(1)	74.28(17)	74.1(2)	74.10(12)	73.65(13)	73.66(13)

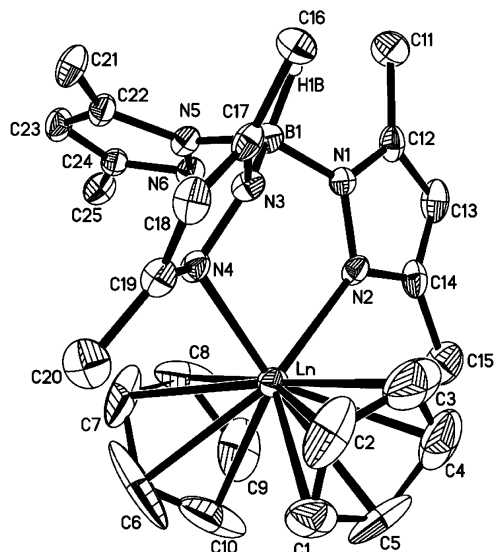
**Scheme 2**

reaction of Cp<sub>2</sub>ErCl with KTp<sup>Me2</sup> in THF, CpErCl<sub>2</sub>(THF)<sub>3</sub> reacted with 1 equiv of KTp<sup>Me2</sup> under the same conditions, to yield a KCl-elimination product CpEr(Tp<sup>Me2</sup>)Cl(THF) (**2b**), as shown in Scheme 1.

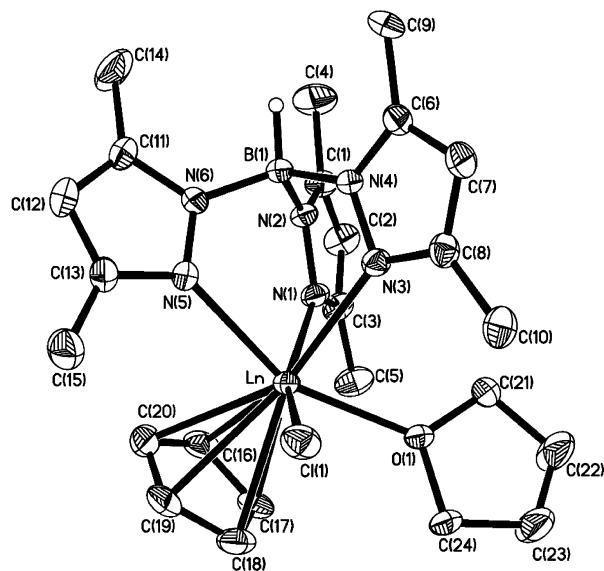
Mixed Cp/Tp lanthanide complexes are rare. To the best of our knowledge, no information on their reactivity has been reported. With mixed Cp/Tp lanthanide complexes **1** and **2** in hand, we next explored the use of them as intermediates in the synthesis of poly(pyrazolyl)borate lanthanide derivatives. As shown in Scheme 2, complexes **1a–c** exhibit high reactivity, and the number of cyclopentadienyl groups liberated from Cp<sub>2</sub>LnTp<sup>Me2</sup> complexes depended on the stoichiometric ratio of **1** to proton-donating reagents. Treatment of Cp<sub>2</sub>ErTp<sup>Me2</sup> (**1b**) with 1 equiv of benzotriazole led to the formation of mono cyclopentadienyl abstraction product [(Tp<sup>Me2</sup>)CpEr(μ-N<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>] (**3**). However, the reaction of Cp<sub>2</sub>YbTp<sup>Me2</sup> (**1a**) with 2-aminopyridine in THF at room temperature gave the unexpected [Tp<sup>Me2</sup>Yb(2-HNC<sub>5</sub>H<sub>4</sub>N)]<sub>2</sub>(μ-O) (**4**) in 44% yield. Presumably, **4** resulted from the partial hydrolysis of a Tp<sup>Me2</sup>Yb(2-HNC<sub>5</sub>H<sub>4</sub>N)Cp intermediate, as observed in the reactions of other organolanthanides with adventitious water.<sup>14</sup>

Cp<sub>2</sub>DyTp<sup>Me2</sup> (**1c**) reacted with 2 equiv of 3,5-dimethylpyrazole to give the complete Cp-abstracted product (Tp<sup>Me2</sup>)Dy(Pz<sup>Me2</sup>)<sub>2</sub>(THF) (**5**). Significantly, compound **5** could also be directly obtained by a three-component reaction of Cp<sub>2</sub>DyCl, KTp<sup>Me2</sup>, and 3,5-dimethylpyrazole.

All of these complexes are moderately air- and moisture-sensitive and soluble in THF and toluene. They were fully characterized by elemental analysis and spectroscopic features, which are in good agreement with the proposed structures. For example, in the IR spectra, two distinct types of B–H stretching



**Figure 1.** Molecular structures (30% thermal ellipsoids) of Cp<sub>2</sub>Ln(Tp<sup>Me2</sup>) (Ln = Yb (**1a**), Er (**1b**)). Hydrogen atoms have been removed for the sake of clarity.

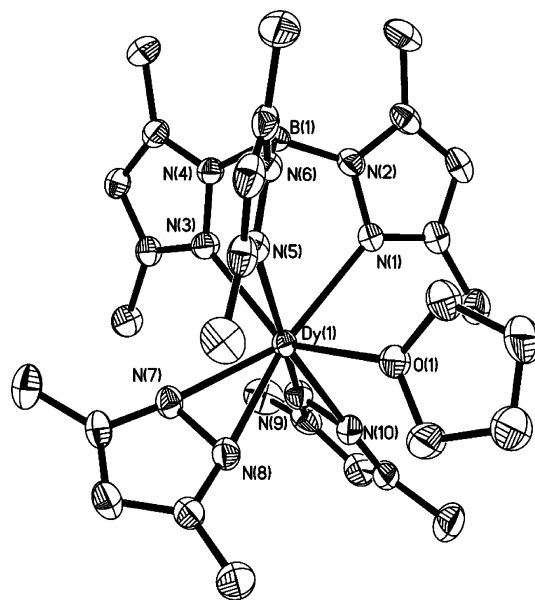


**Figure 2.** Molecular structures (30% thermal ellipsoids) of CpLn(Tp<sup>Me2</sup>)Cl(THF) (Ln = Yb (**2a**), Y (**2b**), Dy (**2c**), Er (**2d**·THF)). Hydrogen atoms have been removed for the sake of clarity.

absorptions were visible: for **1a–c** one characteristic peak at 2470 cm<sup>-1</sup> attributable to the B–H stretching absorption of κ<sup>2</sup>-Tp<sup>Me2</sup> was observed, while that of κ<sup>3</sup>-Tp<sup>Me</sup> for **2–5** appeared at ca. 2560 cm<sup>-1</sup>.<sup>4</sup> In the <sup>1</sup>H NMR spectrum of **2d**, in addition to a singlet for 4H-Tp<sup>Me2</sup> at 5.8 ppm are seen two singlets for the Me-Tp<sup>Me2</sup> proton at about 2.0 and 1.7 ppm, two multiplets for THF protons at about 3.6 and 1.4 ppm, and a singlet for Cp ring protons at about 6.5 ppm. Compound **1a** shows two septets for the nonequivalent pyrazolyl groups, indicating that the solid-state κ<sup>2</sup>-bonding of the Tp<sup>Me2</sup> ligand is maintained in solution (vide infra). The solid-state structures of all of these compounds have been determined by X-ray single-crystal diffraction analysis.

Complexes **1a** and **1b** are the first dicyclopentadienyl lanthanide complexes containing the poly(pyrazolyl)borate ligand. Figure 1 shows the molecular structures of **1a** and **1b**; both of them are isostructural and isomorphous. In **1a**, the ytterbium atom carries two η<sup>5</sup>-Cp groups and one κ<sup>2</sup>-tris(3,5-dimethylpyrazolyl)borate ligand, of which one pyrazolyl moiety is not coordinated to the center metal. The κ<sup>2</sup>-bonding mode of the Tp<sup>Me2</sup> ligand has previously been observed in (Tp<sup>Me2</sup>)<sub>2</sub>SmCp.<sup>9a</sup> No Yb–HB agostic interaction is observed in **1a** with the orientation of the B–H bond away from the metal center.

Complexes **2a–d** crystallize from the solvent mixture of THF and hexane at room temperature in the triclinic system, space group *P* $\bar{1}$ . Structural data (Figure 2) show that complexes **2a–d** are isostructural. Each of them is a solvated monomer with the lanthanide ion bonded to one η<sup>5</sup>-Cp ring, one κ<sup>3</sup>-Tp<sup>Me2</sup> ligand, one chloride ion, and a coordinated THF molecule in a distorted tetrahedral geometry. The four apexes of the tetrahedron are occupied by a centroid of the Cp ring and that of the N1N3N5 triangle of the Tp<sup>Me2</sup> ligand, the Cl atom, and the THF oxygen atom. Both of the Ln–C(Cp ring) and Ln–N(Tp<sup>Me2</sup>) distances are in the normal range.<sup>9c</sup> The overall coordination geometry of **2a–d** is similar to that

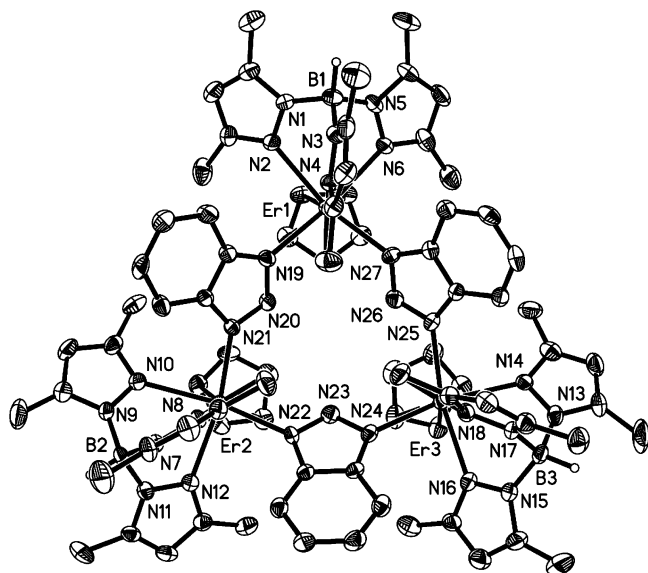


**Figure 3.** Molecular structure (30% thermal ellipsoids) of **3**. Hydrogen atoms have been removed for the sake of clarity.

**Table 5.** Bond Lengths (Å) and Angles (deg) for **3**

Er(1)–N(19)	2.431(5)	Er(2)–N(12)	2.449(5)
Er(1)–N(27)	2.431(5)	Er(2)–N(10)	2.465(6)
Er(1)–N(6)	2.457(5)	Er(2)–N(8)	2.481(6)
Er(1)–N(2)	2.489(5)	Er(3)–N(24)	2.436(5)
Er(1)–N(4)	2.502(6)	Er(3)–N(25)	2.441(5)
Er(1)–C(18)	2.633(6)	Er(3)–N(16)	2.456(6)
Er(1)–C(17)	2.650(7)	Er(3)–N(14)	2.467(5)
Er(1)–C(19)	2.651(7)	Er(3)–N(18)	2.488(6)
Er(1)–C(16)	2.659(7)	N(19)–N(20)	1.331(7)
Er(1)–C(20)	2.662(7)	N(19)–C(26)	1.344(8)
Er(2)–N(22)	2.411(6)	N(20)–N(21)	1.328(7)
Er(2)–N(21)	2.427(5)		
N(19)–Er(1)–N(27)	94.32(18)	N(24)–Er(3)–N(25)	97.42(17)
N(22)–Er(2)–N(21)	93.85(17)		

of Sm(CpPPPh<sub>2</sub>)(Tp<sup>Me2</sup>)(I)(THF).<sup>9c</sup> The molecular structure of complex **2b**·THF is identical with that of complex **2b**; only the additional lattices of the THF molecule render



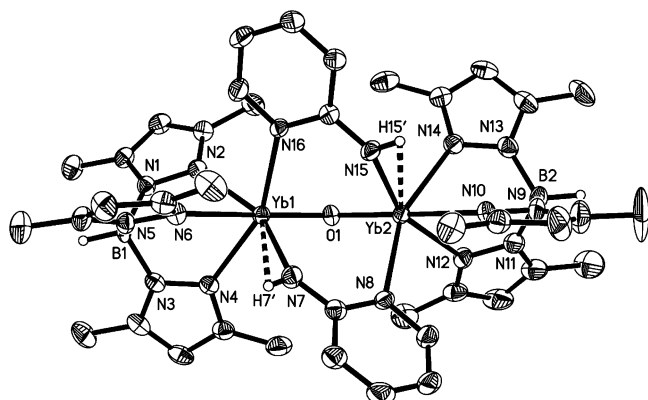
**Figure 4.** Molecular structure (30% thermal ellipsoids) of **4**. Hydrogen atoms have been removed for the sake of clarity.

**Table 6.** Bond Lengths (Å) and Angles (deg) for **4**

Yb(1)–O(1)	2.015(3)	Yb(2)–N(12)	2.424(4)
Yb(1)–N(7)	2.292(5)	Yb(2)–N(14)	2.435(5)
Yb(1)–N(16)	2.411(4)	Yb(2)–N(10)	2.487(4)
Yb(1)–N(2)	2.426(4)	Yb(2)–H(15')	2.53(6)
Yb(1)–N(4)	2.435(4)	B(1)–N(1)	1.506(8)
Yb(1)–N(6)	2.484(4)	B(1)–N(5)	1.541(7)
Yb(1)–Yb(2)	3.4788(12)	B(1)–N(3)	1.578(8)
Yb(1)–H(7')	2.59(6)	B(2)–N(9)	1.509(10)
Yb(2)–O(1)	2.021(3)	B(2)–N(11)	1.535(9)
Yb(2)–N(15)	2.276(5)	B(2)–N(13)	1.554(9)
Yb(2)–N(8)	2.409(5)		
O(1)–Yb(1)–N(7)	92.22(15)	N(15)–Yb(2)–N(8)	101.03(17)
O(1)–Yb(1)–N(16)	93.35(14)	Yb(1)–N(7)–H(7')	108(5)
N(7)–Yb(1)–N(16)	100.76(18)	Yb(2)–N(15)–H(15')	99(4)
O(1)–Yb(2)–N(15)	92.10(14)	Yb(1)–O(1)–Yb(2)	119.10(16)
O(1)–Yb(2)–N(8)	94.06(14)		

them different. As expected, the crystal parameters are also different from those of **2b** (Table 1).

In complex **3** (Figure 3, Table 5), each erbium atom is bonded to one  $\eta^5$ -Cp ring, one  $\kappa^3$ -Tp<sup>Me2</sup> ligand, and two nitrogen atoms from two benzotriazolates ligands, with distorted tetrahedral geometry. The three erbium centers are linked together through three deprotonated benzotriazole bridging ligands forming a 12-membered metallacycle with alternating benzotriazolates and



**Figure 5.** Molecular structure (30% thermal ellipsoids) of **5**. Hydrogen atoms except the hydrogen bond have been removed for the sake of clarity.

**Table 7.** Bond Lengths (Å) and Angles (deg) for **5**

Dy(1)–N(7)	2.318 (3)	Dy(1)–O(1)	2.446 (3)
Dy(1)–N(10)	2.359 (4)	Dy(1)–N(3)	2.483 (3)
Dy(1)–N(9)	2.361 (3)	Dy(1)–N(1)	2.505 (3)
Dy(1)–N(8)	2.383 (3)	Dy(1)–N(5)	2.518 (3)
N(10)–Dy(1)–N(9)	34.19 (12)	N(3)–Dy(1)–N(5)	74.45 (11)
N(7)–Dy(1)–N(8)	34.66 (11)	N(1)–Dy(1)–N(5)	79.00 (11)
N(3)–Dy(1)–N(1)	74.55 (11)		

erbiums. The two N–N bond lengths are approximately equal (N(19)–N(20), 1.331(7) Å; N(20)–N(21), 1.328(7) Å), indicating that the  $\pi$  electrons of the N=N double bond are delocalized owing to deprotonation of the bridging ligand. Consistent with this observation, the Er(1)–N(19) and Er(2)–N(21) distances, 2.432(5) Å and 2.427(5) Å, are also approximately equal and are intermediate between the values observed for the Ln–N single bond distance and the Ln–N donor bond distance. The structural skeleton of **3** is similar to that of lanthanocene imidazolates [Cp<sub>2</sub>Ln( $\mu$ -Im)]<sub>3</sub> (Ln = Yb, Er).<sup>15</sup>

The crystal structure of complex **4** reveals a solvent-free pseudosymmetric dimer (Figure 4). Selected bond distances and angles are compiled in Table 6. The X-ray analysis shows that two cyclopentadienyl groups are respectively replaced by 2-pyridylamido and bridging oxide ligands. Each ytterbium atom is coordinated to one  $\kappa^3$ -Tp<sup>Me2</sup> group, two bridging nitrogen atoms from the 2-pyridylamido ligand, and one bridging oxygen atom to form a distorted-octahedral geometry. The distances of Yb(1)–N(7) and Yb(2)–N(15) (2.292(5) Å and 2.276(5) Å) are in the expected range of Yb–N  $\sigma$  bonds, and the Yb(2)–N(8) and Yb(1)–N(16) (2.409(5) Å and 2.411(4) Å) distances are in the range of Yb–N donor bonds, which are slightly shorter than the observations in [Cp<sub>2</sub>Yb(HNC<sub>5</sub>H<sub>4</sub>N)]<sub>2</sub> (2.472(13) Å and 2.369(12) Å).<sup>16</sup> Interestingly, the residual hydrogen atom of the amino group contacts with the center metal through an agnostic hydrogen-bond interaction (Yb(1)–H(7), 2.59(6) Å; Yb(2)–H(15), 2.53(6) Å).<sup>17</sup>

As shown in Figure 5, compound **5** is a solvated monomer without cyclopentadienyl ligands. The Tp<sup>Me2</sup> ligand is coordinated to the central metal by a  $\kappa^3$ -bonding mode. Two nitrogen atoms of each pyrazolate ligand chelate with the Dy atom. The coordination number of the central metal Dy is 8. The Dy–N (Pz<sup>Me2</sup>) distances are comparable with the corresponding Dy–N distances in other organolanthanide pyrazolate complexes.<sup>18</sup>

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## Conclusions

We have developed an effective and versatile method to synthesize Cp<sub>2</sub>LnTp<sup>Me2</sup> and CpLnTp<sup>Me2</sup>(Cl) complexes directly from simple Cp<sub>2</sub>LnCl, CpLnCl<sub>2</sub>, and Cp<sub>3</sub>Ln starting materials. An unusual reactivity pattern of Cp<sub>2</sub>LnCl is observed in these processes. Furthermore, we find that the Cp ligands of Cp<sub>2</sub>LnTp<sup>Me2</sup> are readily replaced step-by-step with other organic and inorganic ligands, such as pyrazolate, triazolate, and 2-pyridylamino, via a protonation and thus demonstrate that these mixed Tp<sup>Me2</sup>/Cp lanthanide complexes would be of great synthetic potential.

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**Supporting Information Available:** Detailed experimental procedures, full characterization data, and X-ray data for **1–5** in cif format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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