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Coordination of 2,2′-Bipyridyl and 1,10-Phenanthroline to Yttrium and Lanthanum Complexes Based on a Scorpionate Ligand

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Reaction of yttrium and lanthanum trichloride with 1 equiv of sodium or potassium hydrotris(3,5-dimethylpyrazolyl)borate and 1 equiv of 2,2′-bipyridine gives good yields of the complexes $[MCl_2(Tp^{Me2})(C_{10}H_8N_2)]$ (M = Y (**1**), La (**2**)). The analogous compounds with 1,10-phenanthroline, $[MCl_2(Tp^{Me2})(C_{12}H_8N_2)]$ (M = Y (**3**), La (**4**)), have been obtained by a similar procedure. The solid-state structures of **2**–**4** were determined by single-crystal X-ray diffraction and revealed that the compounds are all seven-coordinate with capped octahedral geometry. In contrast, reaction of yttrium trichloride with 1 equiv of sodium hydrotris(3,5-dimethylpyrazolyl)borate in the presence of 1 equiv of neocuproine affords $[YCl_3(Tp^{Me2})][Na(neoc)_3)]$ (**5**). Compounds **1** and **2** provide an entry for the synthesis of complexes containing the bipyridyl ligand in a radical anionic form or in a dianionic form. Reaction of **1** and **2** with an excess of sodium amalgam gives $[Y(Tp^{Me2})(bipy)(THF)_2]$ (**6**) and $[La(Tp^{Me2})_2(bipy)]$ (**7**), respectively. The structures of both compounds have been determined by X-ray crystallography. Compound **7** can be oxidized with iodine to give $[La(Tp^{Me2})_2(bipy)]I$ (**8**).

Introduction

Neutral and monoanionic 1,10-phenanthroline and 2,2′-bipyridyl ligands have been used in coordination chemistry of the f elements from the 1960s, when the first homoleptic complexes $Ln(L)_4$[1−3] (Ln = Y, Ce, Nd, Eu, Yb and L = bipy; Ln = Yb and L = phen) were reported. More recently, the synthesis and characterization by spectroscopic methods and/or X-ray structural determination of an increasing number of lanthanide complexes containing these ligands have been reported.[4−10] Only one complex with the bipyridyl ligand in its dianionic form is known, the trinuclear $[Yb_3(bipy)_3(THF)_6]$.[11] The reported complexes have been obtained by metathesis of LnX_3 or LnX_2 compounds with the lithium salt of the bipyridyl in the mono- or dianionic form[1−3,7−11] or by interaction of bipyridine with lanthanides in a low oxidation state.[4−6,11] For several years, we have been studying the chemistry of lanthanides with hydrotris(pyrazolyl)borate ligands, a versatile class of ancillary ligands that have found application in coordination chemistry of almost all of the elements of the Periodic Table.[12] Among the hydrotris(pyrazolyl)borate ligands, one of the most popular is hydrotris(3,5-dimethylpyrazolyl)borate because of its easy preparation and the steric control afforded by the methyl groups in the 3 position of the pyrazolyl rings. Complexes

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of the type [$LnX(Tp^{Me2})_2$] and half-sandwich complexes [$LnX_2(Tp^{Me2})$] are known, but the preparation of mono-$Tp^{R,R'}$ complexes is problematic as a result of the potential for ligand redistribution reactions.[13] Although high-yield syntheses and characterization of the complexes [$LnX_2(Tp^{Me2})(THF)_n$] (Ln = Y, Nd, Yb) have been reported, including the X-ray structural determination of [$NdCl_2(Tp^{Me2})(THF)$][14] and [$YbCl_2(Tp^{Me2})(THF)$],[15] in many instances attempted crystallizations of these types of complexes over a prolonged period have resulted in the isolation of dimethylpyrazole adducts [$LnX_2(Tp^{Me2})(dmpzH)$]. The structures of [$LnCl_2(Tp^{Me2})(dmpzH)$] (Ln = Y, Pr, Yb, Lu)[14−16] have been determined. The hydrocarbyl derivatives [$LnR_2(Tp^{Me2})$] (Ln = Y, La, Nd; R = Ph, CH_2SiMe_3), which were found to be active ethylene polymerization catalysts, have been reported,[17] but other authors indicated that attempts to derivatize the half-sandwich halides resulted in the formation of the bis-Tp^{Me2} complexes.[18]

In contrast to the lack of stability found for the THF adducts of the mono-Tp^{Me2} complexes, Sun and Wong reported the structural characterization of [$NdCl_2(Tp^{Me2})(L)$] (L = 4,4′-di-*tert*-butyl-2,2′-bipyridyl), a compound obtained when $NdCl_3$ was reacted with 2 equiv of KTp^{Me2} in the presence of the substituted bipyridine.[19] Although the complex was isolated in low yield and no spectroscopic characterization has been reported, the isolation of a mono-Tp^{Me2} compound, even if the synthesis has been deliberately performed to achieve the bis-Tp^{Me2} complex, indicated that neutral chelating nitrogen donor ligands were able to stabilize the half-sandwich complexes.

With this in mind, we decided to use 2,2′-bipyridine, 1,10-phenanthroline, and neocuproine to stabilize mono-Tp^{Me2} complexes with yttrium and lanthanum and to reduce the bipyridyl ligand in the coordination sphere of the preformed complexes. The aim of this study was to open a new way for the preparation of complexes containing the bipyridyl ligand as a radical anion or as a dianion.

Here we report full details of the synthesis and characterization of [$LnCl_2(Tp^{Me2})(L)$] complexes (Ln = Y, La; L = bipy, phen) and the result of the reduction of the bipyridyl complexes with sodium amalgam.

Results and Discussion

Addition of 1 equiv of sodium or potassium hydrotris(3,5-dimethylpyrazolyl)borate to a slurry of $LnCl_3(THF)_n$ (Ln = Y, La) in THF followed by addition of 1 equiv of 2,2′-bipyridine or 1,10-phenanthroline results in the formation of the corresponding [$LnCl_2(Tp^{Me2})(L)$] complexes, which precipitate from THF as white solids. Either the potassium or the sodium salt can be used in these reactions with equally good yields. The compounds can be separated from the sodium or potassium chloride by extraction with chloroform or dichloromethane (eqs 1 and 2 using sodium salt).

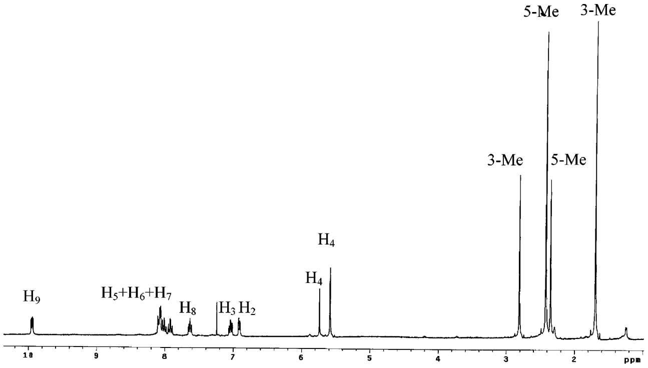

Figure 1. ^1H NMR spectrum of [$YCl_2(Tp^{Me2})(bipy)$] **(1)** in $CDCl_3$.

$$LnCl_3(THF)_n + NaTp^{Me2} + bipy \rightarrow [LnCl_2(Tp^{Me2})(bipy)] + NaCl \quad (1)$$
$$Ln = Y\ (\mathbf{1}),\ La\ (\mathbf{2})$$

$$LnCl_3(THF)_n + NaTp^{Me2} + phen \rightarrow [LnCl_2(Tp^{Me2})(phen)] + NaCl \quad (2)$$
$$Ln = Y\ (\mathbf{3}),\ La\ (\mathbf{4})$$

Some of the compounds reported here give low values for carbon and/or nitrogen in combustion analysis. This occurs even for crystallized material and is probably due to variable amounts of solvent retained in the lattice.

The infrared spectra of the complexes were found to exhibit ν(B−H) stretching vibrations in the range 2535−2545 cm^{-1}, consistent with tridentate Tp^{Me2} ligands.[20]

In solution, the ^1H NMR spectra of **1**−**4** at room temperature were similar and exhibited two sets of resonances assigned to the Tp^{Me2} ligand in the intensity ratio 2:1 and eight resonances assigned to the bipyridyl or the phenanthroline ligands. This pattern is consistent with a C_s molecular symmetry, with the neutral ligand lying in the mirror plane of the complex. As a representative, the ^1H NMR spectrum of **1** is shown in Figure 1.

One of the resonances due to the bipyridyl and phenanthroline ligands is shifted to very low field. Assignment of all of the resonances was done by COSY and NOE difference experiments, with the proton that experiences the largest shift to low field being the one on the carbon adjacent to the nitrogen atom between the two pyrazolyl rings that flank the mirror plane (we assigned this proton as H_9; Chart 1). The shift is probably due to ring current effects of the pyrazolyl groups.

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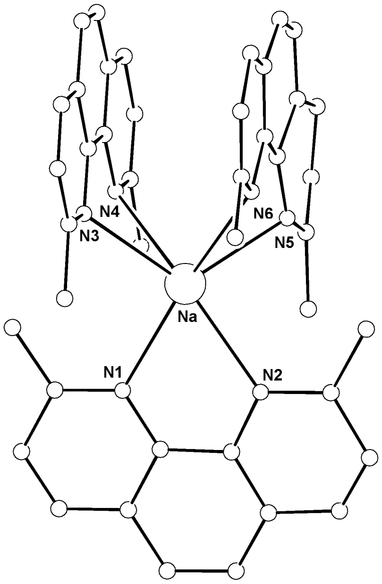
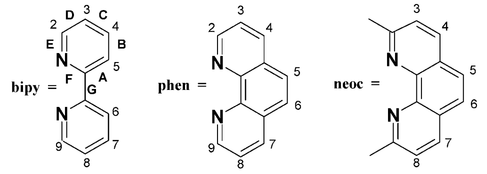


Figure 2. Molecular diagram of the cation in $[YCl_3(Tp^{Me2})][Na(neoc)_3]\cdot$THF (**5**).

Chart 1. Diagram Showing an Atom and Bond Labeling Scheme of the N−N Chelating Ligands



The ^{13}C NMR spectra at room temperature gave analogous information. Ten or twelve signals for the carbons of the bipyridyl or phenanthroline, respectively, and two resonances for the C-4 carbon atoms and four (or three due to accidental overlap) for the methyls of the Tp^{Me2} ligand are observed as required by the molecular symmetry.

Stirring a slurry of $YCl_3(THF)_n$ with 1 equiv of $NaTp^{Me2}$ and 1 equiv of neocuproine does not lead to the formation of insoluble compounds as in the case of bipyridyl and phenanthroline. Instead, a mixture of compounds soluble in THF is formed. One of them could be identified by X-ray diffraction analysis and shown to be $[YCl_3(Tp^{Me2})][Na(neoc)_3]\cdot$THF (**5**). Because of the low quality of the crystals and, consequently, the poor quality of data/refinement, the structure will not be discussed, but the connectivity of the atoms could be established without ambiguity. In the anion, the yttrium center is six-coordinated by the three nitrogen atoms of the Tp ligand and the three chlorine atoms arranged in an octahedral configuration. In the cation, the sodium ion is surrounded by the six nitrogen atoms of three neocuproine ligands displaying a trigonal-prismatic geometry, with the bases of the trigonal prism defined by N1, N3, N4 and N2, N5, N6 (Figure 2).

Compounds **2**−**4** were characterized by X-ray diffraction methods. The molecular structure of **2** is shown in Figure 3, and selected bond lengths and angles are given in Table 1.

The compound crystallizes with one molecule of dichloromethane in the lattice. No significant intermolecular contacts between the molecules were observed. The metal center is seven-coordinated by the tridentate Tp^{Me2} ligand, two bound chloride ions, and the two nitrogens of the bipyridyl ligand arranged in a capped octahedron. The tripodal ligand occupies one of the triangular faces, while the two chlorine atoms and N2 form the other staggered triangular face, and N1 is capping the latter face of the octahedron. Distortion from the octahedral geometry can be inferred from the angle of 5.7° between the two triangular faces and from the range of orthogonal bond angles (Table 1). The average La−N(Tp) distance (2.600 Å) and the average La−Cl bond length (2.748(2) Å) compare with those in $[NdCl_2(Tp^{Me2})(L)]$ (L = 4,4′-di-*tert*-butyl-2,2′-bipyridyl)[19] (ave Nd−N(Tp) = 2.55 Å and ave Nd−Cl = 2.677 Å), taking into account the difference between the ionic radii.[21] The average La−N bond length to the neutral bipyridyl ligand is 2.699(5) Å, a value that compares with those found in $[La(NO_3)_3(bipy)_2]$[22] (2.66(1) Å) and $[1,3\text{-}(Me_3C)_2C_5H_3]_2Yb(bipy)]$[5] (2.503(4) Å), after correction of the ionic radii.[21] The pyridyl rings are twisted with respect to each other, with a torsion angle of 16.7°, and the C(5)−C(6) bond length is 1.484(8) Å. These values are close to those found in free bipyridyl [C5−C6 = 1.490(3) Å][23] and $[1,3\text{-}(Me_3C)_2C_5H_3]_2Yb(bipy)$[5] = [15° and 1.48(1) Å]; (entries 1 and 2 in Table 2).

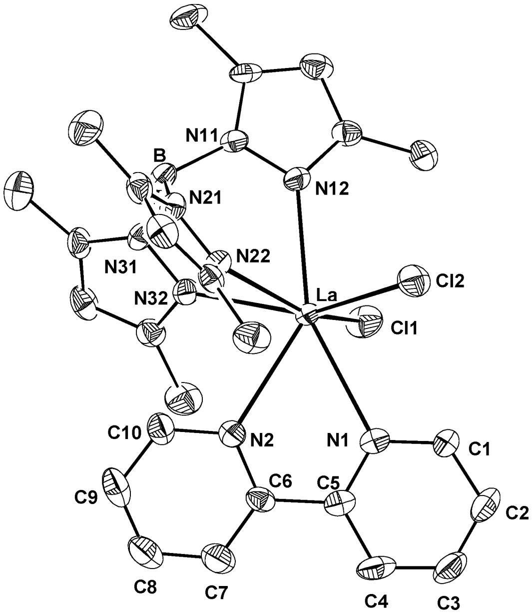


Figure 3. ORTEP diagram of $[LaCl_2(Tp^{Me2})(bipy)]$ (**2**), using 40% probability ellipsoids.

Although the ionic radii of the center atoms of **3** and **4** are different, both compounds are isomorphous and their structures are very similar to that of compound **2**. As a representative, the molecular structure of **3** is shown in Figure 4 (analogous atomic numbering scheme is used for **4**), and selected bond lengths and angles are listed in Table 1.

The average Y−N(Tp) and Y−Cl bond lengths of 2.448(6) and 2.600(2) Å, respectively, are slightly longer than the

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Table 1. Selected Bond Lengths (Å), Angles (deg), and Ranges for **2**·CH_2Cl_2, **3**·CH_2Cl_2, and **4**·CH_2Cl_2

	2·CH_2Cl_2	**3**·CH_2Cl_2	**4**·CH_2Cl_2
ave M−N(Tp)	2.600(4)	2.448(6)	2.604(6)
range M−N(Tp)	2.622(4)−2.574(4)	2.473(6)−2.433(6)	2.617(6)−2.591(6)
ave M−N	2.699(5)	2.544(6)	2.698(6)
ave M-Cl	2.748(2)	2.600(2)	2.737(2)
N(Tp)−M−N(Tp)	72.10(14)−73.81(14)	75.0(2)−78.1(2)	71.6−74.8
Cl(1)−M−Cl(2)	109.67(6)	106.27(7)	107.57(7)
N(2)−M−Cl(1)	111.34(11)	109.59(15)	108.47(14)
N(2)−M−Cl(2)	114.57(11)	117.63(14)	117.24(14)

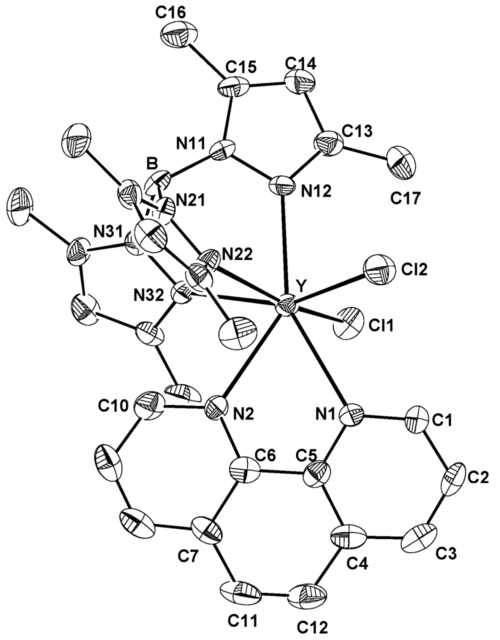

Figure 4. ORTEP diagram of [$YCl_2(Tp^{Me2})$(phen)] (**3**), using 40% probability ellipsoids.

Table 2. Selected Bond Distances (Å) of the Neutral (**1**−**3**), Monoanionic (**4**−**6**), and Dianionic (**7** and **8**) Bipyridyl Ligands

	A	B	C	D	E	F	G
1. free bipy	1.35	1.34	1.38	1.38	1.39	1.39	1.49
2. [1,3-$(Me_3C)_2C_5H_3]_2$Yb(bipy)	1.35	1.34	1.37	1.38	1.39	1.39	1.48
3. **2**·CH_2Cl_2	1.35	1.34	1.38	1.36	1.37	1.38	1.48
4. $Cp^*{}_2$Sm(bipy)	1.38	1.35	1.37	1.41	1.34	1.42	1.43
5. $Cp^*{}_2$Yb(bipy)	1.38	1.36	1.40	1.42	1.39	1.42	1.43
6. **7**·2THF	1.39	1.34	1.38	1.41	1.34	1.42	1.44
7. [$Yb_3(bipy)_3(THF)_6$]	1.44	1.39	1.36	1.43	1.36	1.46	1.41
8. **6**·0.5C_7D_8	1.43	1.37	1.34	1.42	1.33	1.43	1.35

corresponding distances in [$YCl_2(Tp^{Me2})$(dmpzH)][14] (2.402 and 2.555 Å, respectively), as expected for the higher coordination number of **3**. The average Y−N(phen) distance (2.544(6) Å) compares with the Yb−N(phen) bond length of 2.50 Å in [1,3-$(Me_3C)_2C_5H_3]_2$Yb(phen)].[5] The La−N(Tp) and La−Cl bond lengths (ave 2.604(6) and 2.737(2), respectively) are very similar to the corresponding distances in **2**, and the average La−N(phen) of 2.698(6) Å is similar to the corresponding distance in [La $(NO_3)_3(phen)_2$][24] (2.67(3) Å).

Formation of the ionic compound **5** is not surprising in view of the short distances observed in the solid-state structures of complexes **2**−**4** between the proton adjacent to one of the nitrogen atoms of the bipyridyl or phenanthroline (H_9) and the C-3 of one pyrazolyl ring. A short distance between the proton adjacent to the other nitrogen atom (H_2) and one of the chloride ligands has been noted too. Hence, replacement of these protons by methyl groups hampers coordination of the neocuproine to the metal center and results in the formation of the ionic complex.

Reduction of 1 and 2 with Sodium Amalgam: A New Route for Complexes Containing Mono- and Dianionic Bipyridyl Ligands

When a slurry of compounds **1** and **2** in THF is stirred with an excess of sodium amalgam, there is the formation of dark solutions. Filtration and removal of the solvent furnishes dark powders, which may be crystallized from THF to provide [$Y(Tp^{Me2})$(bipy)$(THF)_2$] (**6**; eq 3) and [$La(Tp^{Me2})_2$(bipy)] (**7**; eq 4), respectively. Compound **6** was obtained

$$[YCl_2(Tp^{Me2})(bipy)] + \text{excess } Na(Hg) \rightarrow \underset{\mathbf{6}}{[Y(Tp^{Me2})(bipy)(THF)_2]} + 2NaCl \quad (3)$$

$$[LaCl_2(Tp^{Me2})(bipy)] + \text{excess } Na(Hg) \rightarrow \underset{\mathbf{7}}{[La(Tp^{Me2})_2(bipy)]} + \text{other products} \quad (4)$$

as a dark green solid in 70% yield and **7** as a dark brown solid in low yield. We demonstrated that it was not necessary to isolate **1** and **2** in order to reduce them to **6** and **7**. Stirring YCl_3 with 1 equiv of $NaTp^{Me2}$, 1 equiv of bipyridine, and an excess of sodium amalgam led to **6** in a similar yield, while the reaction of $LaCl_3$ with 2 equiv of KTp^{Me2}, 1 equiv of bipyridine, and an excess of sodium amalgam afforded **7** in 75% yield (eq 5).

$$LaCl_3(THF)_n + 2KTp^{Me2} + bipy + Na(Hg) \rightarrow \underset{\mathbf{7}}{[Ln(Tp^{Me2})_2(bipy)]} + 2KCl + NaCl \quad (5)$$

Both compounds are soluble in ethereal and aromatic solvents. The IR spectra of **6** and **7** showed bands at 2540 and 2500 cm^{-1}, respectively, arising from the ν(B−H) stretch of a tridentate pyrazolylborate.[20]

The room temperature ^1H NMR spectrum of **6** in toluene-d_8 exhibited three peaks in the ratio 3:3:1 assigned to the trispyrazolylborate ligand, four resonances assigned to the bipyridyl ligand (significantly shifted to the high field in comparison with those in the spectrum of **1** or free bipyridyl), and two resonances due to the α and β protons of the THF molecules. The high symmetry found in solution is not in

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accord with the structure found in the solid, probably because of fast exchange of the THF molecules, as discussed by Bianchoni and co-workers for $[YCl_2(Tp^{Me2})(THF)]$.[14] In contrast, the room temperature ^1H NMR spectrum of **7** did not show any resonance due to the bipyridyl ligand giving the indication of the presence of an anionic radical species. Evidence for the presence of a radical anion could also be inferred from the magnetic measurements and from the solid-state structure of **7** (see below).

The magnetic susceptibility temperature dependence of compound **7** was obtained by the extraction method with magnetic fields up to 5 T. This compound is paramagnetic because no magnetic transitions were observed down to 1.6 K. The inverse of the magnetic susceptibility curve is almost linear in the entire temperature range, and a Curie−Weiss behavior can be detected with $\theta = -5.6$ K and an effective Bohr magneton number per formula unit, $\mu_{eff} = 1.5\mu_B$/fu. The negative Curie temperature and the lower effective moment than the expected value for a single electron, $\mu_{eff} = 1.73\mu_B$/fu calculated with $\langle g \rangle = 2.0$, suggest the presence of antiferromagnetic interactions. However, the presence of some impurities in the sample due to some oxidation is a more plausible explanation because an anomaly at about 43 K, typical of oxygen contamination, is observed in the temperature dependence of the ac susceptibility. The temperature dependence of χ_pT for several magnetic fields is almost field independent. Each curve is also nearly independent of the temperature, as expected for a paramagnetic compound.

One plausible explanation for the formation of **6** and **7** by reducing **1** and **2** in the same experimental conditions resides in the different ionic radii of yttrium and lanthanum. The reduction of the bipyridyl ligand is slow and proceeds in two steps. In the first step, it is likely that an intermediate complex of the type $[LnCl(Tp^{Me2})(bipy)]$ is formed. In the case of yttrium, this complex is stable enough to allow further reduction of the bipyridyl ligand with the formation of **6**. However, for the larger lanthanum ion, that intermediate is too unstable and rearrangement to $[La(Tp^{Me2})_2(bipy)]$ is faster than the second reduction step of the bipy ligand.

Compound **7** could be oxidized to $[La(Tp^{Me2})_2(bipy)]I$ (**8**) by reaction with iodine in toluene. The compound is obtained as a yellow precipitate in 78% yield. Because of the low solubility of the compound in common solvents, it was not possible to grow crystals adequate for X-ray diffraction analysis, but the NMR spectrum allowed the formulation of **8** as the ionic compound, $[La(Tp^{Me2})_2(bipy)]I$. In solution, the room temperature ^1H NMR spectrum exhibited four resonances associated with the bipyridyl ligand, together with six singlets assigned to the Tp^{Me2} methyl protons and three for the pyrazolyl ring protons (Figure 5).

Thus, the observed spectrum is consistent with a C_2-symmetric structure and similar to those observed for $[Sm(Tp^{Me2})_2(X-X)]$[25] complexes, where X−X is a symmetrical bidentate ligand.

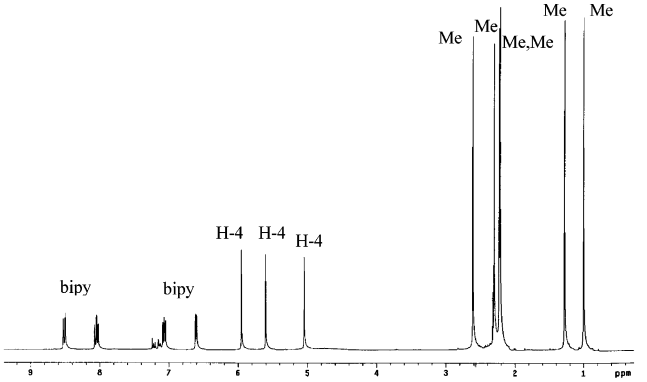

Figure 5. ^1H NMR spectrum of $[La(Tp^{Me2})_2(bipy)]I$ (**8**) in C_6D_6.

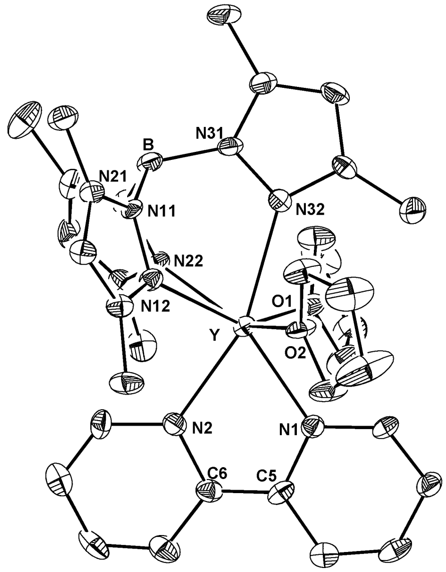

Figure 6. ORTEP diagram of $[Y(Tp^{Me2})(bipy)(THF)_2]$ (**6**), using 20% probability ellipsoids.

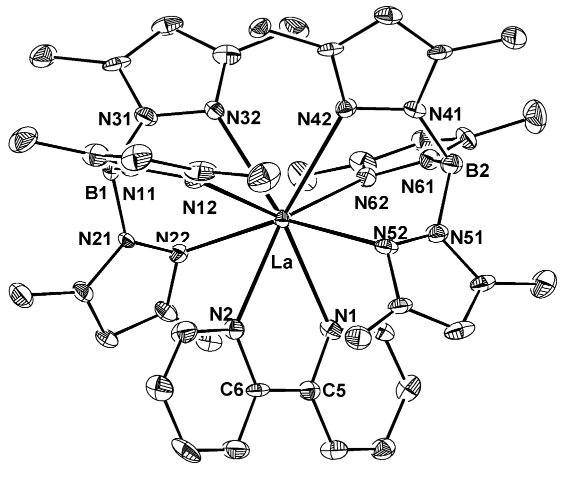

Figure 7. ORTEP diagram of $[La(Tp^{Me2})_2(bipy)]$ (**7**), using 20% probability ellipsoids.

Crystals of **6** and **7** appropriate for X-ray diffraction studies were obtained by crystallization from THF solutions. However, the best crystals of **6** were obtained in a NMR tube from a toluene-d_8 solution. The ORTEP diagrams of **6** and **7** are represented in Figures 6 and 7, respectively, and relevant metrical parameters are collected in Tables 2 and 3.

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Table 3. Selected Bond Lengths (Å), Angles (deg), and Ranges for $\mathbf{6}\cdot 0.5C_7D_8$ and $\mathbf{7}\cdot 2THF$

	$\mathbf{6}\cdot 0.5C_7D_8$	$\mathbf{7}\cdot 2THF$
ave M−N(Tp)	2.473(8)	2.68(6)
range M−N(Tp)	2.488(8)−2.460(8)	2.612(10)−2.751(10)
ave M−N	2.282(8)	2.620(10)
ave Y−O	2.434(6)	
N(Tp)−M−N(Tp)	74.5(2)−78.1(3)	66.4(3)−87.9(3)
N1−C5−C6−N2 torsional angle	1.6	0.4

Compound **6** is seven-coordinated by the three nitrogen atoms of the Tp ligand, the two nitrogen atoms of the bipyridyl ligand, and the two oxygen atoms of the THF molecules. The coordination geometry can be described as capped octahedral with the two staggered triangular faces defined by the tripodal ligand and by the two oxygen atoms and N2 of the bypiridyl ligand, with the latter face being capped by N1. The average Y−N(Tp) of 2.473(8) Å is in line with the corresponding distance in **3** (2.448(6) Å). The average Y−O bond length of 2.434(6) Å compares with the average Yb−O bond length of 2.46 Å in $[\{Yb(\mu^2\text{-bipy})(thf)_2\}_3]$, the only known lanthanide complex with a dianionic bipyridyl ligand reported by Schumann et al.[11] This latter compound does not provide a good comparison for the Y−N(bipy) distance of 2.282(8) Å in **6** because in $[\{Yb(\mu^2\text{-bipy})(thf)_2\}_3]$ each bipyridyl is bridging two ytterbium atoms through two bonds of 2.47 Å and two bonds of 2.57 Å length. The same holds for the value of 2.329(6) Å observed for the corresponding distance in the complex $[(Cp^*{}_2Yb)_2(2,2'\text{-bipyrimidine})]$ reported by Andersen et al.,[6] in which a dianionic bipyrimidine ligand is bridging two $Cp_2{}^*Yb$ units. As observed by other authors,[5,6,11,26] the acceptance of electrons into the lowest unoccupied molecular orbital of neutral bipy results in shortening of the C5−C6 bond and in flattening of the bipyridyl ligand. In compound **6**, the C5−C6 distance is 1.35 Å, a shortening of 0.13 Å relative to the value found in the neutral chelating bipy ligand in **2**. Such pronounced shortening has been observed also in $[(Cp^*{}_2Yb)_2(2,2'\text{-bipyrimidine})]$ (1.359(1) Å),[6] but in $[\{Yb(\mu^2\text{-}C_{10}H_8N_2)(thf)_2\}_3]$[11] and $[Na_2(bipy)(dme)_2]_\infty$,[27] the shortening is smaller (0.08 and 0.11 Å, respectively).

In compound **7**, the metal center is eight-coordinated, with the lanthanum atom bound in tridentate fashion by two pyrazolylborate ligands and in bidentate fashion by the bipyridyl ligand through both nitrogen atoms. Polytopal analysis suggests that the metal coordination geometry is best described as being dodecahedral.[28] This coordination geometry has been found already in other $[Sm(Tp^{Me2})_2(X{-}X)]$ compounds.[25,29] The intersecting trapezoids (defined by the atoms N12, N2, N1, N62 and N22, N32, N42, N52) make a dihedral angle of 82° rather than the ideal 90°. The trapezoids are almost planar, with normalized ϕ angles of 0.6° and 2.2°. The average La−N(Tp) distance is 2.68(6) Å (range 2.612(10)−2.751(10) Å), a value in line with those of 2.645(7) and 2.647(3) Å in $[La(Tp^{Me2})_2(MeCN)(O_3SCF_3)]$ and $[La(Tp^{Me2})_2(NO_3)]$,[29] respectively, but 0.08 Å larger than the corresponding values in the mono-Tp^{Me2} compounds (2.600(4) Å in **2** and 2.604 Å in **4**). The increased coordination number for **7** is also reflected in the long average La−N distance to the bipyridyl of 2.620(10) Å, 0.1 Å larger than the values of 2.432(2) and 2.32 Å found in $Cp^*{}_2Sm(bipy)$[4] and $Cp^*{}_2Yb(bipy)$,[5] respectively, after correction of the ionic radii. The two Tp ligands are mutually staggered and bent back from each other at an angle of 145.9(4)°. The two pyrazolyl rings nearest the bipyridyl ligand are very twisted about their B−N bonds, with B−N−N−La torsion angles of 59.3 and 63.9°.

Conclusions

A series of $[LnCl_2(Tp^{Me2})(N{-}N)]$ complexes, where N−N is phenanthroline or bipyridyl, have been prepared. Reflecting the steric saturation around the metal center in these complexes, neocuproine does not fit into the coordination sphere of the metal leading to the ionic compound $[YCl_3(Tp^{Me2})][Na(N{-}N)_3]$. The bipyridyl ligand can be reduced in the coordination sphere of the preformed complexes leading to $[Y\ (Tp^{Me2})(N{-}N)(THF)_2]$ or $[La(Tp^{Me2})_2(N{-}N)]$, with the result of the reaction being dependent on the ionic radius of the metal involved.

Experimental Section

General Procedures. All preparations and subsequent manipulations were carried out using standard Schlenk line and drybox techniques in an atmosphere of dinitrogen. THF, toluene, chloroform, dichloromethane, and *n*-hexane were dried by standard methods and degassed prior to use. THF or toluene used in the crystallization of **6** and **7** were dried over K and vacuum distilled. The deuterated solvents for NMR (benzene-d_6 and toluene-d_8) were vacuum distilled from K and dichloromethane-d_2 and chloroform-d_1 from P_2O_5. Bipyridyl was purified by sublimation. Anhydrous phenanthroline and neocuproine were obtained by refluxing the hydrates in toluene using a Dean−Stark receiver followed by sublimation. $LnCl_3(THF)_x$ (Y, $x = 2.3$; La, $x = 1.5$) were synthesized by published methods.[30] The THF content for the yttrium and lanthanum trichlorides was established by elemental analysis. The ligands, potassium and sodium hydrotris(3,5-dimethylpyrazolyl)borate (Na/KTp^{Me2}), were prepared as described by Trofimenko.[31] ^1H and ^{13}C NMR spectra were recorded on a Varian INOVA-300 spectrometer at 300 and 75 MHz, respectively. Spectra were referenced internally using the residual proton resonances relative to tetramethylsilane (toluene-d_8, 2.09 ppm; chloroform-d_1, 7.24 ppm; dichloromethane-d_2, 5.32 ppm). Proton and carbon assignments were made using COSY, HETCOR, and NOE difference experiments. IR spectra were recorded on a Perkin-Elmer 577 spectrophotometer. Carbon, hydrogen, and nitrogen analyses were performed in-house using a EA110 CE Instruments automatic analyzer.

dc magnetizaton and ac susceptibility measurements were performed on a polycrystalline sample (in the temperature range

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1.6−300 K) and magnetic fields up to 5 T using a MAGLAB System 2000 (Oxford Instruments). ac susceptibility (ac field = 1.0 Oe, f = 1000 Hz) was made under zero external field. Magnetization data were corrected for contributions due to the sample holder and core diamagnetism, estimated from Pascal constants.

Synthesis. [YCl$_2$(Tp^{Me2})(bipy)] (1). A solution of NaTp^{Me2} (0.532 g, 1.66 mmol) in 10 mL of anhydrous THF was slowly added to a stirred suspension of YCl$_3$(THF)$_{2.3}$ (0.600 g, 1.66 mmol) in 5 mL of THF. The reaction mixture was stirred for 1 h at room temperature, and then a solution of 2,2′-bipyridyl (0.259 g, 1.66 mmol) in 10 mL of THF was added. The mixture was stirred overnight, and the resulting precipitate was separated by centrifugation, washed with THF, and dried in a vacuum. The white solid was extracted with anhydrous chloroform. Removal of the solvent affords the compound that was further washed with hexane and dried in a vacuum. Yield: 59% (0.60 g). Crystallization from a dichloromethane solution gives crystals of [YCl$_2$(Tp^{Me2})(bipy)]·CH$_2$Cl$_2$. Elem. anal. Calcd for YC$_{25}$N$_8$H$_{30}$BCl$_2$·CH$_2$Cl$_2$: C, 44.73; H, 4.62; N, 16.05. Found: C, 45.33; H, 3.04; N, 14.62. IR (Nujol mulls) (B−H): 2535 cm^{-1}. ^{1}H NMR (CDCl$_3$, 20 °C): δ 9.95 (1H, d, H$_9$), 8.10−7.98 (3H, complex multiplet, H$_5$ + H$_6$ + H$_7$), 7.92 (1H, m, H$_4$), 7.63 (1H, m, H$_8$), 7.04 (1H, m, H$_3$), 6.90 (1H, m, H$_2$), 5.74 [1H, H-4(1Tp^{Me2})], 5.58 [2H, H-4(2Tp^{Me2})], 2.81 [3H, 3-Me(1Tp^{Me2})], 2.42 [6H, 5-Me(2Tp^{Me2})], 2.35 [3H, 5-Me(1Tp^{Me2})], 1.70 [6H, 3-Me (2Tp^{Me2})]. ^{13}C NMR (CDCl$_3$, 20 °C): δ 154.9 (C$_{quat}$ bipy), 154.7 (C-9 bipy), 151.7 [C-3(1Tp^{Me2})], 151.3 (C-2 bipy), 149.9 [C-3(2Tp^{Me2})], 144.7 [C-5(2Tp^{Me2})], 143.9 [C-5(1Tp^{Me2})], 140.3 (C-4 bipy), 139.7 and 120.6 (C-5,6,7 bipy), 125.6 (C-8 bipy), 125.1 (C-3 bipy), 120.4 (C$_{quat}$ bipy), 106.38 [C-4(1Tp^{Me2})], 105.99 [C-4(2Tp^{Me2})], 15.6 [3-Me(1Tp^{Me2})], 13.9 [3-Me(2Tp^{Me2})], 13.2 [5-Me(2Tp^{Me2})], 13.1 [5-Me(1Tp^{Me2})].

[LaCl$_2$(Tp^{Me2})(bipy)] (2). Compound **2** was prepared as described for **1** using 0.905 g (2.83 mmol) of NaTp^{Me2}, 1.000 g (2.83 mmol) of LaCl$_3$(THF)$_{1.5}$, and 0.442 g (2.83 mmol) of 2,2′-bipyridyl. The final product was isolated as a microcrystalline white powder, yield 75% (1.41 g). Analytically pure samples were obtained by crystallization from dichloromethane. Anal. Calcd for LaC$_{25}$N$_8$H$_{30}$BCl$_2$·CH$_2$Cl$_2$: C, 41.74; H, 4.31; N, 14.98. Found: C, 41.79; H, 4.10; N, 14.44. IR (Nujol mulls) (B−H): 2540 cm^{-1}.^{1}H NMR (CDCl$_3$, 20 °C): δ 9.76 (1H, d, H$_9$), 8.11−8.01 (3H, complex multiplet, H$_5$ + H$_6$ + H$_7$), 7.93 (1H, m, H$_4$), 7.64 (1H, m, H$_8$), 7.29 (1H, d, H$_2$), 7.09 (1H, m, H$_3$), 5.72 [1H, H-4(1Tp^{Me2})], 5.60 [2H, H-4(2Tp^{Me2})], 2.77 [3H, 3-Me(1Tp^{Me2})], 2.41 [6H, 5-Me(2Tp^{Me2})], 2.36 [3H, 5-Me(1Tp^{Me2})], 1.79 [6H, 3-Me(2Tp^{Me2})]. ^{13}C NMR (CDCl$_3$, 20 °C): δ 153.0 (C$_{quat}$ bipy), 152.84 (C-9 bipy), 150.9 (C-2 bipy), 150.6 [C-3(1Tp^{Me2})], 149.1 [C-3(2Tp^{Me2})], 145.0 [C-5(1Tp^{Me2})], 144.4 [C-5(1Tp^{Me2})], 140.2 (C-4 bipy), 140.2 and 121.4 (C-5,6,7 bipy), 125.7 (C-8 bipy), 125.2 (C-3 bipy), 121.2 (C$_{quat}$ bipy), 105.8 [C-4(1Tp^{Me2})], 105.6 [C-4(2Tp^{Me2})], 14.6 [3-Me(1Tp^{Me2})], 13.4 [3-Me(2Tp^{Me2})], 13.2 [5-Me(3Tp^{Me2})].

[YCl$_2$(Tp^{Me2})(phen)] (3). Compound **3** was obtained by the procedure described above for **1** by using 1.200 g (3.32 mmol) of YCl$_3$(THF)$_{2.3}$, 1.063 g (3.32 mmol) of NaTp^{Me2}, and 0.598 g (3.32 mmol) of phenanthroline. The compound was obtained as a microcrystalline white powder in 92% yield (1.958 g). Crystallization from dichloromethane gave analytically pure [YCl$_2$(Tp^{Me2})(phen)]·CH$_2$Cl$_2$. Anal. Calcd for YC$_{27}$N$_8$H$_{30}$BCl$_2$·CH$_2$Cl$_2$: C, 46.57; H, 4.47; N, 15.52. Found: C, 47.91; H, 4.43; N, 15.71. IR (Nujol mulls) (B−H): 2540 cm^{-1}.^{1}H NMR (CD$_2$Cl$_2$, 20 °C): δ 10.24 (1H, d, H$_9$), 8.50 (1H, m, H$_7$), 8.39 (1H, d, H$_2$), 8.00−7.87 (3H, complex multiplet, H$_5$, H$_6$, and H$_8$), 7.38 (1H, m, H$_4$), 7.04 (1H, m, H$_3$), 5.77 [1H, H-4(1Tp^{Me2})], 5.58 [2H, H-4(2Tp^{Me2})], 2.86 [3H, 3-Me(1Tp^{Me2})], 2.45 [6H, 5-Me(2Tp^{Me2})], 2.38 [3H, 5-Me(1Tp^{Me2})], 1.53 [6H, 3-Me(2Tp^{Me2})]. ^{13}C NMR (CD$_2$Cl$_2$, 20 °C): δ 155.0 (C-9 phen), 152.0 [C-3,5(Tp^{Me2})], 151.6 (C-4 phen), 150.4 [C-3,5(Tp^{Me2})], 145.9 (C$_{quat}$ phen), 145.4 [C-3,5(Tp^{Me2})], 144.8 [C-3,5(Tp^{Me2})], 139.8 (C-2 phen), 139.1 (C-7 phen), 129.5 (C$_{quat}$ phen), 129.0 (C$_{quat}$ phen), 127.7, 126.6, 125.1 (C 5,6,8 phen), 124.5 (C-3 phen), 106.4 [C-4(1Tp^{Me2})], 106.2 [C-4(2Tp^{Me2})], 15.5 [3-Me(1Tp^{Me2})], 13.8 [3-Me(2Tp^{Me2})], 13.2 [5-Me(3Tp^{Me2})].

[LaCl$_2$(Tp^{Me2})(phen)] (4). The compound was obtained as described for **1** by reacting LaCl$_3$(THF)$_{1.5}$ (0.364 g, 1.03 mmol) with 0.330 g (1.03 mmol) of NaTp^{Me2} and 0.184 g (1.03 mmol) of phenanthroline. The white compound was obtained with 93% yield (0.66 g). Anal. Calcd for LaC$_{27}$N$_8$H$_{30}$BCl$_2$·CH$_2$Cl$_2$: C, 43.56; H, 4.18; N, 14.51. Found: C, 43.05; H, 4.41; N, 14.27. IR (Nujol mulls) (B−H): 2545 cm^{-1}.^{1}H NMR (CDCl$_3$, 20 °C): δ 10.06 (1H, d, H$_9$), 8.50 (1H, m, H$_7$), 8.40 (1H, d, H$_2$), 7.99−7.88 (3H, complex multiplet, H$_5$, H$_6$, and H$_8$), 7.57 (1H, m, H$_4$), 7.40 (1H, m, H$_3$), 5.72 [1H, H-4(1Tp^{Me2})], 5.59 [2H, H-4(2Tp^{Me2})], 2.82 [3H, 3-Me(1Tp^{Me2})], 2.44 [6H, 5-Me(2Tp^{Me2})], 2.38 [3H, 5-Me(1Tp^{Me2})], 1.66 [6H, 3-Me(2Tp^{Me2})]. ^{13}C NMR (CDCl$_3$, 20 °C): δ 153.5 (C-9 phen), 151.1 (C-4 phen), 150.7 [C-3,5(Tp^{Me2})], 149.0 [C-3,5(Tp^{Me2})], 145.7 (C$_{quat}$ phen), 145.0 [C-3,5(Tp^{Me2})], 144.5 [C-3,5(Tp^{Me2})], 139.3 (C-2 phen), 138.8 (C-7 phen), 129.6 (C$_{quat}$ phen), 129.0 (C$_{quat}$ phen), 127.6, 126.5, 124.9 (C-5,6,8 phen), 124.0 (s, C-3 phen), 105.8 [C-4(1Tp^{Me2})], 105.6 [C-4(2Tp^{Me2})], 14.6 [3-Me(1Tp^{Me2})], 13.4 [3-Me(2Tp^{Me2})], 13.2 [5-Me(3Tp^{Me2})].

[Y(Tp^{Me2})(bipy)(THF)$_2$] (6). A solution of KTp^{Me2} (0.592 g, 1.76 mmol) in THF was added dropwise to a stirred suspension of YCl$_3$(THF)$_{2.3}$ (0.636 g, 1.76 mmol) in THF. The reaction mixture was stirred for 1 h at room temperature, and a solution of 2,2′-bipyridyl (0.275 g, 1.76 mmol) in 10 mL of THF was added, followed by addition of an excess of sodium amalgam (20.2 g, 4.40 mmol of Na). The mixture was stirred for 70 h. The precipitate was separated by centrifugation and the solvent removed under vacuum. The resultant solid was washed twice with hexane and dried. Compound **6** was obtained as dark green microcrystals in 71% yield (0.863 g). Anal. Calcd for YC$_{33}$N$_8$H$_{46}$BO$_2$: C, 57.74; H, 6.75; N, 16.32. Found: C, 52.24; H, 6.07; N, 16.72. IR (Nujol): 2540 (B−H), 975, 910 (bipyridyl dianion). ^{1}H NMR (C$_7$D$_8$): δ 6.84 (2H, d, J = 6.2 Hz, bipy), 6.69 (2H, d, J = 9.6 Hz, bipy), 5.64 (2H, m, bipy), 5.56 [3H, H-4(Tp^{Me2})], 4.92 (2H, m, bipy), 3.50 (8H, br, THF), 2.31 [9H, Me(Tp^{Me2})], 2.13 [9H, Me(Tp^{Me2})], 1.28 (8H, br, THF). ^{13}C{^{1}H} NMR (C$_7$D$_8$): δ 149.8 [C-3(Tp^{Me2})], 144.6 [C-5(Tp^{Me2})], 143.0 (C bipy), 124.3 (C bipy), 122.4 (C bipy), 113.3 (C bipy), 106.0 [C-4(Tp^{Me2})], 97.6 (C bipy), 70.1 (THF), 25.5 (THF), 13.4 [Me(Tp^{Me2})], 13.0 [Me(Tp^{Me2})].

The sample for X-ray diffraction analysis was obtained in a NMR tube from a toluene-d_8 solution.

[La(Tp^{Me2})$_2$(bipy)] (7). A solution of KTp^{Me2} (0.760 g, 2.26 mmol) in 10 mL of THF was slowly added to a stirred suspension of LaCl$_3$(THF)$_{1.5}$ (0.400 g, 1.13 mmol) in 5 mL of THF, followed by addition of a solution of 2,2′-bipyridyl in 10 mL of THF (0.176 g, 1.13 mmol). When the addition was complete, the sodium amalgam (10.400 g, 2.26 mmol of Na) was added. The resulting mixture was stirred for 30 h. After centrifugation, the supernatant was decanted off and the solvent removed under vacuum to give **7** as a dark brown solid in 90% yield (0.890 g). The product can be further purified by crystallization from THF. Anal. Calcd for LaC$_{40}$N$_{14}$H$_{52}$B$_2$: C, 54.01; H, 5.89; N, 22.05. Found: C, 50.54; H, 5.79; N, 18.58. IR (Nujol): 2500 (B−H), 940 (bipyridyl, radical ion).

[La(Tp^{Me2})$_2$(bipy)]I (8). A solution of iodine (1.24 mL, 0.0693 M) in toluene was added dropwise to a stirred solution of **7** (0.151

Table 4. Crystallographic Data for Complexes **2**·CH_2Cl_2, **3**·CH_2Cl_2, **4**·CH_2Cl_2, and **7**·$2OC_4H_8$

	2·CH_2Cl_2	**3**·CH_2Cl_2	**4**·CH_2Cl_2	**7**·$2OC_4H_8$
formula	$C_{26}H_{32}BN_8Cl_4La$	$C_{28}H_{32}BN_8Cl_4Y$	$C_{28}H_{32}BN_8Cl_4La$	$C_{48}H_{68}B_2N_{14}O_2La$
fw	748.12	722.14	772.14	1033.69
crystal system	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a, Å	10.2962(11)	10.3735(8)	10.3410(13)	14.555(4)
b, Å	18.8457(19)	18.5836(10)	18.787(2)	20.877(4)
c, Å	16.4794(18)	16.7130(9)	16.973(2)	17.339(4)
α, deg				
β, deg	94.762(7)	95.248(6)	93.259(11)	95.73(2)
γ, deg				
V, Å^3	3186.6(6)	3208.4(7)	3292.0(7)	5206(2)
Z	4	4	4	4
μ, mm^{-1}	1.706	2.184	1.655	0.872
ρ_{calc}, g cm^{-3}	1.559	1.495	1.558	1.319
independent reflns	6235	6956	7242	7866
observed [$I > 2\sigma(I)$]	4344	3440	4547	4005
no. of param	362	379	380	604
$R_1{}^a$	0.0480	0.0869	0.0656	0.0897
w$R_2{}^b$	0.0893	0.1094	0.1305	0.1814

[a] $R_1 = \Sigma|F_o| - |F_c||\Sigma||F_o|$. [b] $wR_2 = \{\Sigma[w(F_o{}^2 - F_c{}^2)^2]/\Sigma[w(F_o{}^2)^2]\}^{1/2}$. The values were calculated for data with $I > 2\sigma(I)$.

g, 0.17 mmol) in 10 mL of toluene. A yellow precipitate formed immediately. The mixture was stirred overnight, the supernatant was decanted off, and the precipitate was washed with toluene. The yellow solid was dried in a vacuum (0.135 g, 78%). Anal. Calcd for $LaC_{40}N_{14}H_{52}B_2I$: C, 47.27; H, 5.16; N, 19.29. Found: C, 49.86; H, 5.89; N, 17.02. ^1H NMR ($CDCl_3$): δ 8.51 (2H, dd, bipy), 8.05 (2H, m, bipy), 7.05 (2H, m, bipy), 6.61 (2H, dd, bipy), 5.95 [2H, H-4(Tp^{Me2})], 5.60 [2H, H-4(Tp^{Me2})], 5.05 [2H, H-4(Tp^{Me2})], 2.61 [6H, Me(Tp^{Me2})], 2.30 [6H, Me(Tp^{Me2})], 2.23 [6H, Me(Tp^{Me2})], 2.21 [6H, Me(Tp^{Me2})], 1.28 [6H, Me(Tp^{Me2})], 1.00 [6H, Me(Tp^{Me2})]. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 154.5, 150.9, 150.3, 149.5, 148.0, 147.8, 147.1, 145.1, 140.6, 129.0, 128.2, 125.0, 107.0, 106.9, 106.5 (Tp^{Me2} C-4), 13.9, 13.6, 13.5, 13.3, 11.5 (Me-Tp^{Me2}),

X-ray Crystallographic Analysis. Transparent crystals of [$LaCl_2$(Tp^{Me2})(bipy)]·CH_2Cl_2 (**2**·CH_2Cl_2), [YCl_2(Tp^{Me2})(phen)]·CH_2Cl_2 (**3**·CH_2Cl_2), and [$LaCl_2$(Tp^{Me2})(phen)]·CH_2Cl_2 (**4**·CH_2Cl_2) were obtained by crystallization from dichloromethane. Transparent crystals of [YCl_3(Tp^{Me2}][Na(neoc)$_3$]·OC_4H_8 were grown from a THF solution. Dark green crystals of [Y(Tp^{Me2})(bipy)(THF)$_2$]·$0.5C_7D_8$ (**6**·$0.5C_7D_8$) were grown from deutered toluene on a NMR tube and dark brown crystals of [La(Tp^{Me2})$_2$(bipy)]·$2OC_4H_8$ (**7**·$2OC_4H_8$) from a THF solution. Crystals were mounted in thin-walled glass capillaries in a nitrogen-filled glovebox. Data were collected at room temperature for **2**−**4** and **6** and at −10 °C for **7** on an Enraf-Nonius CAD4 diffractometer with graphite-monochromatized Mo Kα radiation. A summary of the crystallographic data is given in Table 4. Data were corrected[32] for Lorentz and polarization effects, for linear decay, and for absorption by empirical corrections based on Ψ scans. No correction was applied to **7** because of the collapse of the crystal. The structures were solved using Patterson methods[33] and successive difference Fourier techniques and refined by least-squares refinements on F^2 using SHELXL-97.[34] Compounds **2**−**4** are dichloromethane solvates. For **7** two disordered toluene solvent molecules of crystallization were located in the Fourier difference map. All of the non-hydrogen atoms were refined with anisotropic thermal motion parameters, and the contribution of the hydrogen atoms was included in calculated positions. Atomic scattering factors and anomalous dispersion terms were taken as in ref 34. The drawings were made with ORTEP-3.[35] Because of the lower quality of crystal **6**·$0.5C_7D_8$,[36] relevant geometrical parameters will not be given but details regarding structure solution and refinement will be deposited as Supporting Information.

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Supporting Information Available: Listings of crystallographic data, tables of positional and anisotropic parameters, positional parameters of hydrogen atoms, magnetic measurements, and NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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(36) Crystal data for **6**·$0.5C_7D_8$: $C_{33}H_{46}BN_8O_2Y·0.5C_7D_8$, fw = 732.57, triclinic, space group $P1$, a = 10.8213(16) Å, b = 12.422(3) Å, c = 15.495(2) Å, α = 69.366(15)°, β = 80.171(15)°, γ = 75.027(16)°, V = 1875.7(6) Å^3, Z = 2, and D_{calc} = 1297 mg/m^3. A total of 6542 unique reflections were used in the structure solution with refinement of 443 parameters. Final refinement converged at R_1 = 0.109 and ωR_2 = 0.152 for 2638 reflections with $I > 2\sigma(I)$.