Inorg. Chem. **2002**, *41*, 6761–6768

Inorganic Chemistry
Article

Facile Pyrazolylborate Ligand Degradation at Lanthanide Centers: X-ray Crystal Structures of Pyrazolylborinate-Bridged Bimetallics

Ângela Domingos,[†] Mark R. J. Elsegood,[‡] Anna C. Hillier,[§] Guanyang Lin,[||] Sung Ying Liu,[§] Irene Lopes,[†] Noémia Marques,[†] Graham H. Maunder,[§] Robert McDonald,[||] Andrea Sella,*[,§] Jonathan W. Steed,[⊥] and Josef Takats[||]

Departamento de Química, ITN, Estrada Nacional 10, 2686-953 Sacavém, Portugal,
Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2,
Christopher Ingold Laboratories, Department of Chemistry, UCL, 20 Gordon Street,
London WC1H 0AJ, United Kingdom, Chemistry Department, Loughborough University,
Loughborough, Leicestershire, LE11 3TU United Kingdom, and Department of Chemistry,
King's College London, Strand, London, WC2R 2LS United Kingdom

Received June 18, 2002

Adventitious hydrolysis of a number of different complexes with the molecular formula $Ln(Tp^{Me2})_2X$ [Tp^{Me2} = (HB-(dmpz)$_3$), where X is a basic anionic ligand] in various solvents, yielded crystals of highly insoluble dimers of the general formula $[Ln(Tp^{Me2})(\mu\text{-}BOp^{Me2})]_2$ (**1**) [Ln = La, Ce, Sm; BOp^{Me2} = $(HBO(dmpz)_2)^{2-}$; dmpzH = 3,5-dimethylpyrazole]. The results of several single-crystal X-ray determinations are reported. One metal nitrogen distance, that lying across from the two negatively charged bridging oxygen atoms, is 0.06 Å longer than the others, suggesting an unusual trans influence at a lanthanide center. The formation of **1** is proposed to involve the intermediacy of $Ln(Tp^{Me2})_2OH$ formed by protonolysis with adventitious water.

Introduction

The molecular chemistry of the lanthanides has advanced considerably over the past few years.[1,2] Ligand design has played a key role in these advances, as control of the coordination sphere of the large, labile and predominantly ionic metal centers requires the use of sterically demanding ancillaries capable of providing kinetic stabilization. Although substituted cyclopentadienyl ligands[2] have been widely used, there has been a considerable upsurge of interest in other alternatives, including polycyclic hydrocarbons such as CHT[3] and COT,[4] chelating alkoxides,[5−7] salen-type ligands,[8] multidentate amides,[9−12] porphyrinogens,[13−16] and other macrocycles.[17−20]

The tris-pyrazolylborate (Tp) ligands are an appealing alternative as they have found wide application in binding with most elements of the periodic table.[21−23] One of the most attractive features of the Tp ligands as a class is their steric tunability. Thus, in recent years, a rich chemistry of the f-elements has been uncovered involving both bis-Tp metallocene analogues and an exciting variety of half-sandwich complexes of both 2+ and 3+ oxidation states.[24,25]

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* To whom correspondence should be addressed. Address: Christopher Ingold Laboratories, Department of Chemistry, UCL, 20 Gordon Street, London, WC1H 0AJ United Kingdom. Tel.: +44 20 7679 4687. Fax: +44 20 7679 7463. E-mail: a.sella@ucl.ac.uk.

[†] ITN.

[‡] Loughborough University.

[§] UCL.

[||] University of Alberta.

[⊥] King's College London.

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10.1021/ic025801c CCC: $22.00

Although widely used and extensively promoted in the literature as ancillaries, the Tp ligands are subject to a range of reactions and rearrangements. Insertion of formaldehyde[26] and CO_2[27] into the B−H bond of Bp ligands and hydroboration of acyl and iminoacyl complexes of molybdenum[28] lead to the formation of heteroscorpionate ligands. Ligand rearrangements, believed to involve either 1,2-borotropic or 1,2-metallatropic shifts, have been observed for a number of ligands of intermediate steric demand.[29−34] More problematic has been the observation of partial and even complete degradation of such ligands within the coordination sphere of metals. Such reactions have been described both for main-group metal complexes[35−38] and for transition metals.[39−50] This propensity to decomposition has become particularly manifest for the Tp^{Me2} ligand bound to lanthanide centers. Attempts to prepare half-sandwich complexes of the type $[Ln(Tp^{Me2})X_2]$ have resulted in the isolation of dimethylpyrazole adducts $[Ln(Tp^{Me2})X_2(dmpzH)]$, dimethyl pyrazole being the logical product of Tp^{Me2} hydrolysis. Efforts to crystallize the more sterically crowded sandwich complexes of the type $[Ln(Tp^{Me2})_2X]$ have repeatedly resulted in the isolation of bimetallic decomposition products containing a heteroscorpionate ligand, which are the focus of this paper. These products, which are believed to result from hydrolysis by adventitious water, generally form during the extended periods required for growth of X-ray quality crystals. In this paper, we report the structures of these bimetallics and speculate on the mechanism of their formation.

Experimental Section

All preparations and manipulations were carried out using standard Schlenk line and drybox techniques in an atmosphere of dinitrogen or helium.[51,52] Oxygen-free nitrogen or helium was purified by passage over columns containing 3-Å molecular sieves and MnO or BASF catalyst.[53] THF was predried over 5-Å molecular sieves or sodium wire and distilled under nitrogen from sodium or potassium/benzophenone before use. $[Sm(Tp^{Me2})_2OH]$[54] was prepared by reaction of $[Sm(Tp^{Me2})_2C{\equiv}CPh]$[55] with traces of moisture. Infrared spectra were recorded as KBr pellets on a Nicolet 205 FTIR spectrometer. Elemental analyses were performed by Mr. Alan Stones of the UCL Analytical Services and Ms. Darlene Mahlow of the University of Alberta Analytical Section.

Deliberate Preparation of $[Sm(Tp^{Me2})(\mu\text{-}BOp^{Me2})]_2$, 1-Sm. In a drybox, solid $[Sm(Tp^{Me2})_2OH]$ (0.150 g, 0.205 mmol) was dissolved in THF (5 cm^3). A clear colorless solution was formed. From this solution, colorless single crystals appeared spontaneously at room temperature. After 5 h, 0.027 g material was collected. An additional 0.022 g of material was collected after the solution was allowed to stand for a further 4 days. Yield: 0.049 g (32%). Better yields of the same material can be obtained from smaller-scale preparations. Elemental analysis. Calcd. for $C_{58}H_{90}B_4N_{20}O_4Sm_2$ $[C_{50}H_{74}B_4N_{20}O_2Sm_2{\cdot}(THF)_2]$ (%): C 47.20, H 6.15, N 18.98. Found: C 47.03, H 6.13, N 18.62. FT-IR (microscope, cm^{-1}) 3653 (w, ν_{OH}), 2541 (m), 2522 (m), 2391 (s, ν_{BH}); (Nujol mull, cm^{-1}) 3650 (w, ν_{OH}), 2541 (w), 2522 (w), 2392 (s), 2361 (s), 2338 (s, ν_{BH}).

Crystallography. (Fractional empirical formulas reflect the disorder modeled as resulting from partial occupancy of OH in place of BH on the borinate ligand as discussed in the Results section.)

Crystal Data for 1-La·toluene: $C_{64}H_{89.89}B_4La_2N_{20}O_{2.11}$, colorless crystal of dimensions 0.30 × 0.26 × 0.24 mm, $M = 1494.27$, triclinic space group $P\bar{1}$, $a = 11.4544(8)$, $b = 11.6978(8)$, $c = 14.0848(9)$ Å, $\alpha = 75.076(2)$, $\beta = 84.196(2)$, $\gamma = 76.606(2)°$, U

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= 1772.3(2) Å^3, $Z = 1$, $F(000) = 765$, $D_c = 1.400$ g cm^{-1}, μ(Mo Kα) = 1.246 mm^{-1}, $T = 160(1)$ K; 11 123 reflections (7377 unique with $R_{int} = 0.0186$) were collected on a Bruker AXS SMART 1K CCD area detector diffractometer with narrow frames (0.3° in ω) and three-dimensional profile fitting using graphite-monochromated Mo Kα radiation ($\lambda = 0.710$ 73 Å).

Crystal Data for 1-Ce: $C_{50}H_{74}B_4Ce_2N_{20}O_2$, dark red crystal of dimensions 0.08 × 0.08 × 0.06 mm, $M = 1310.77$, triclinic space group $P\bar{1}$, $a = 11.5241(4)$, $b = 11.7349(4)$, $c = 13.4637(5)$ Å, $\alpha = 113.438(2)$, $\beta = 103.181(2)$, $\gamma = 103.734(13)$°, $U = 1520.73(9)$ Å^3, $Z = 1$, $F(000) = 666$, $D_c = 1.532$ g cm^{-1}, μ(Mo Kα) = 1.246 mm^{-1}, $T = 120(2)$ K; 22 513 reflections (5834 unique with $R_{int} = 0.0186$) were collected on a Nonius KappaCCD area detector diffractometer equipped with a rotating-anode FR591 generator using graphite-monochromated Mo Kα radiation ($\lambda = 0.710$ 73 Å).

Crystal Data for 1-Sm·toluene: $C_{64}H_{89.18}B_4N_{20}O_{2.82}Sm_2$, colorless crystal of dimensions 0.37 × 0.17 × 0.13 mm, $M = 1527.79$, triclinic space group $P\bar{1}$, $a = 10.3414(6)$, $b = 12.2610(7)$, $c = 14.6537(8)$ Å, $\alpha = 101.062(2)$, $\beta = 90.090(2)$, $\gamma = 106.609(2)$°, $U = 1744.28(17)$ Å^3, $Z = 1$, $F(000) = 780$, $D_c = 1.454$ g cm^{-1}, μ(Mo Kα) = 1.726 mm^{-1}, $T = 160(1)$ K; 12 045 reflections (7667 unique with $R_{int} = 0.0183$) were collected on a Bruker AXS SMART 1K CCD area detector diffractometer with narrow frames (0.3° in ω) and three-dimensional profile fitting using graphite-monochromated Mo Kα radiation ($\lambda = 0.710$ 73 Å).

Results

In the course of attempting to crystallize a variety of complexes with the general formula Ln(Tp^{Me2})$_2$X (Ln = La, Ce, Sm; X = OPh, Mn(CO)$_5$, SePh, C_5H_5, NPh_2, Ph_2CO, $CH_3C(O)Ph$, TCNE, S-2-pyr) from a range of solvents (ether, toluene, THF), colorless, blocklike crystals were isolated on a number of separate occasions. Curiously, the crystals of the cerium complex were blood red. A more direct and rational route to the Sm complex was simply to dissolve small quantities of [Sm(Tp^{Me2})$_2$OH][54] in benzene or THF. Crystals of **1-Sm** could then be isolated in moderate yields. Because the reaction was not particularly clean, no detailed kinetic studies were carried out. However, qualitative observations clearly showed that the formation of **1-Sm** proceeded significantly more quickly in THF than in toluene and in more concentrated solutions.

Because isolation of **1** was, in general, serendipitous, elemental analyses and infrared spectra were obtained in only a few cases. The infrared spectra of crystals isolated from the degradation of [Sm(Tp^{Me2})$_2$OH] in benzene, from the slow crystallization of [Sm(Tp^{Me2})$_2$](TCNE)[56a] from THF, and from the crystallization of [Sm(Tp^{Me2})$_2$]Mn(CO)$_5$[56b] were found to be superimposable. Two distinct types of B−H stretching absorptions were visible: one split pair at 2541 and 2522 cm^{-1}, in the region characteristic of tridentate Tp^{Me2}, and an intense sharp band at 2392 cm^{-1}, the low-energy shift of which suggested the presence of an electronegative element attached to the boron. In addition, a high-frequency band around 3500 cm^{-1} was sometimes observed and was assigned to an OH vibration. Unfortunately, the ^{1}H NMR spectra of the crystals could not be recorded owing to the low solubility of the compound in a variety of NMR solvents, including hydrocarbons, THF-d_8, and acetone-d_6.

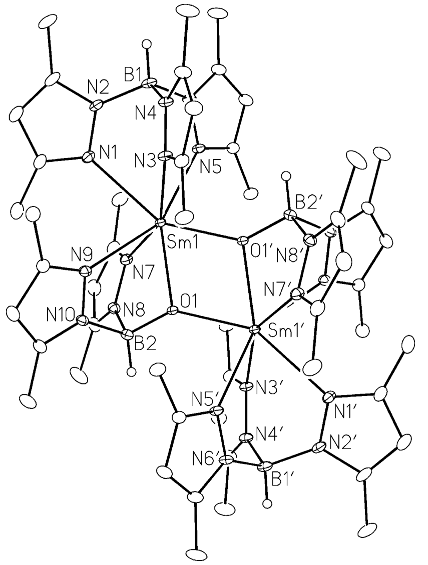

Figure 1. View of **1-Sm** showing the atomic numbering scheme.

Table 1. Selected Bond Lengths and Angles for **1-La·Toluene**, **1-Ce**, and **1-Sm·Toluene**

1-La·toluene		1-Ce		1-Sm·toluene	
La−O1	2.294(1)	Ce−O1	2.383(3)	Sm1−O1	2.239(1)
La−O1′	2.406(1)	Ce−O1′	2.281(3)	Sm1−O1′	2.317(1)
La−N1	2.618(1)	Ce−N12	2.684(4)	Sm1−N1	2.590(2)
La−N3	2.717(1)	Ce−N22	2.594(4)	Sm1−N3	2.522(2)
La−N5	2.607(1)	Ce−N32	2.591(3)	Sm1−N5	2.527(2)
La−N7	2.618(1)	Ce−N42	2.596(4)	Sm1−N7	2.523(2)
La−N9	2.623(1)	Ce−N52	2.602(3)	Sm1−N9	2.519(2)
La−La′	3.8505(3)	Ce−Ce′	3.8210(5) Å	Sm1−Sm1′	3.7142(3)
La−B1	3.733(2)	Ce−B1	3.705(5) Å	Sm1−B1	3.629(3)
La−B2	3.230(2)	Ce−B2	3.195(5) Å	Sm1−B2	3.120(3)
O1−B2	1.432(2)	O1−B2	1.428(5)	O1−B2	1.427(3)
O1−La1−O1′	70.01(4)	O1−Ce−O1′	69.99(11)	O1−Sm1−O1′	70.76(6)

X-ray Crystallography. In total, 11 datasets were collected for the Sm complex, **1-Sm**, and one each for the complexes **1-La** and **1-Ce**. Toluene and ether solvates were structurally determined in a number of different space groups. The crystallographic details are available as Supporting Information, and the key bond distances for each of the molecules are shown in Table 1. As all of the structures are very similar, data for only one of the structures, **1-Sm·toluene**, for which some of the best data were obtained, are used in the discussion.

The complexes consist of discrete dimers lying on a crystallographic inversion center (some of the other structures lie on two-fold axes), making only half of the molecule unique. No significant intermolecular contacts were noted in any of the structures. Each metal center is bound by two distinct types of borate ligand, one being a normal κ^3-Tp^{Me2}, and the other a hydrolysis product of Tp^{Me2}, BOp^{Me2}, in which one pyrazolyl group has been replaced by an oxygen atom that bridges between the two metal centers and the boron. Thus, the dimers have the molecular formula [Ln(Tp^{Me2})(μ-BOp^{Me2})]$_2$. The molecular structure and atom labelling scheme of **1-Sm·toluene** is shown in Figure 1.

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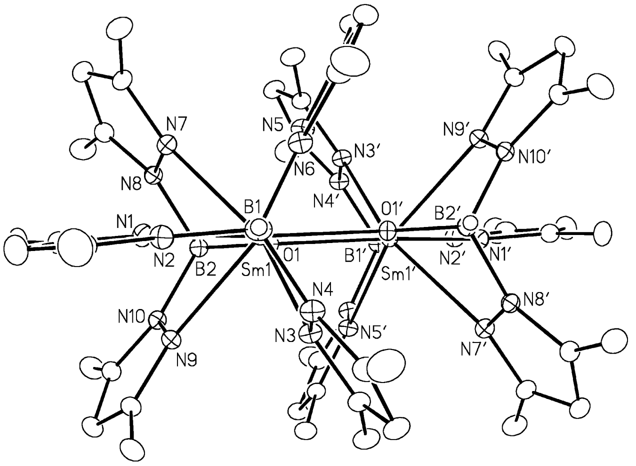

Figure 2. View of **1-Sm** down an axis between the two B···Sm···O vectors showing the coplanarity of the samarium, oxygen, and boron atoms.

The Sm, O, and B atoms are almost perfectly coplanar, as shown in Figure 2. The coordination geometry about the seven-coordinate metal centers can be described as forming a rather distorted capped trigonal antiprism, the cap being formed by the O1 atom of the BOp$^{\mathrm{Me2}}$ ligand and the two triangular faces of the prism being defined by N1, N3, N5 and N7, N9, O1′. An alternative way to visualize the structures is to consider the geometry around the metal as a tricapped trigonal pyramid. The three nitrogen atoms of the Tp$^{\mathrm{Me2}}$ ligand define the base, while the bridging oxygen, O1, from the pyrazolylborinate ligand defines the apex. The two nitrogen atoms of the borinate ligand and the oxygen atom from the other metal cap the three faces of the pyramid making X−Sm−O1 angles of 70 ± 2° to the apical oxygen. The metal coordination sphere is shown in Figure 3, which illustrates the two alternative polyhedra.

The average Sm(1)−N distance in **1-Sm·toluene** is 2.536(4) Å, similar to that observed in the seven-coordinate Sm^{3+} complexes [Sm(Tp$^{\mathrm{Me2}}$)$_2$Cl], 2.564(16) Å,[57] and [Sm(Tp$^{\mathrm{Me2}}$)$_2$OPh-4-Bu$^{\mathrm{t}}$], 2.572(5) Å.[58] It is striking, however, that N1, which lies at 173.6° relative to the Sm−Sm′ vector, is almost 0.06 Å further from the metal than the other nitrogen atoms in the coordination sphere. A very similar situation is observed in the related uranium complex [UBp$^{\mathrm{Me2}}$Cl(μ-BOp$^{\mathrm{Me2}}$)]$_2$,[59] a molecule containing an agostic B−H interaction, where a similarly arranged Bp$^{\mathrm{Me2}}$ nitrogen lies 0.04 Å further away. Because the Sm−Sm′ distance, 3.7142(3) Å, is obviously too long for there to be any significant interatomic interaction, we attribute this lengthening to the presence of the two negatively charged oxygens lying on either side of the Sm−Sm′ vector, subtending an angle of 70.76(6)°. We believe that this represents a rare example of a trans influence at a lanthanide center. Asymmetric bond lengths in Ln complexes have been observed before, for the most part in chalcogenolate chemistry.[60,61] Brennan and coworkers have drawn attention to these effects and noted consistent trends in bond lengths as a function of trans ligand in lanthanide chalcogenolate/chalcogenide clusters.[62−64] Differences in bond length in pyrazolylborate chemistry have also sometimes been observed in six-coordinate half-sandwich complexes, such as [Y(Tp$^{\mathrm{Me2}}$)Cl$_2$(dmpzH)],[65] and can now be seen to be consistent with Brennan et al.'s conclusions. Because covalent interactions are unlikely to be significant for the lanthanides, we believe that these observations can be attributed to a polarization of the samarium center by the electronegative anionic oxygen groups.[66−68]

The oxygen atoms bridge the two metals unsymmetrically as a result of the tethering effect of the pyrazolyl groups. As expected from bridging groups, the Sm−O distances, 2.239(1) and 2.317(1) Å, are significantly longer than the Sm−O distances of 2.159(2) Å observed in the seven-coordinate complex [Sm(Tp$^{\mathrm{Me2}}$)$_2$OPh-4-Bu$^{\mathrm{t}}$],[58] 2.213(5) Å in [Sm(Tp$^{\mathrm{Me2}}$)$_2$OC$_6$H$_2$-(3,5-di-Bu$^{\mathrm{t}}$)(4-O)],[69] and 2.188(5) Å in the very crowded complex [Sm(Tp$^{\mathrm{Me2}}$)$_2$OC$_6$H$_3$-(2,6-di-Bu$^{\mathrm{t}}$)].[70] The BOp$^{\mathrm{Me2}}$ ligand is bent inward toward the metal, as shown by the very different Sm−B distances [Sm−B1, 3.629(1) and Sm−B2, 3.120(1) Å] and in the Sm−N−N angles, ∼100° vs ∼120°, for the two ligands. Similar structural features are observed in the coordination mode of the BOp$^{\mathrm{Me2}}$ ligand to U in [U(Bp$^{\mathrm{Me2}}$)Cl(μ-BOp$^{\mathrm{Me2}}$)]$_2$.[59] Furthermore, the U−O bond lengths, 2.312(5) and 2.204(5) Å, and the average U−N distance, 2.523(7) Å, are comparable to those noted above. This is consistent with the similar ionic radii reported for seven-coordinate Sm^{3+} and eight-coordinate U^{4+}.[71] The O(1)−Sm(1)−O(1′) angle in **1-Sm**, 70.76(6)°, is somewhat larger than the corresponding angle in the U complex, 66.5(2)°, a fact that is probably related to the smaller coordination number in **1-Sm·toluene**.

The Tp$^{\mathrm{Me2}}$ ligand is somewhat distorted from ideal C_3 symmetry, with some twisting (16.4°) of one pyrazolyl group around the B1−N4 bond. The angles at boron are essentially tetrahedral. By contrast, the BOp$^{\mathrm{Me2}}$ ligand shows virtually no twisting (dihedral/twist angles < 4°).

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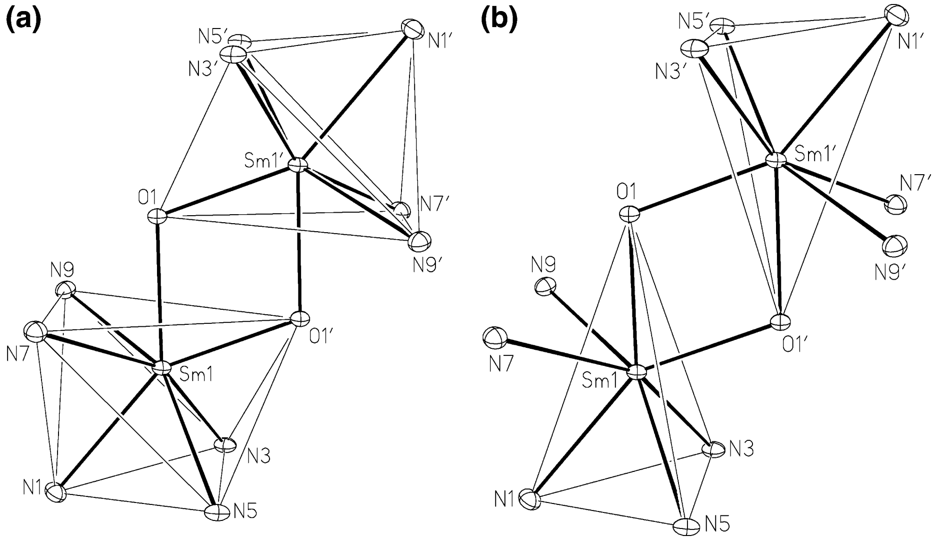

Figure 3. Two views of the metal coordination sphere in **1-Sm** showing (a) the capped trigonal antriprism or (b) the tricapped trigonal pyramidal arrangement of the ligands.

Finally, it is noteworthy that, in the refinement of several structures, moderately strong peaks appeared in the difference Fourier map close to the boron atom of the BOp^{Me2} ligand (B2). A possible explanation for these observations is that some compounds undergo double hydrolysis, giving a $[(dmpz)_2B(O)(OH)]^{2-}$ ligand, consistent with the OH stretching band observed in the IR spectra. The complexes containing this ligand cocrystallize with **1,** giving rise to the observed disorder. In the case of one structure, the disorder was modeled in terms of 59% H and 41% O, suggesting that the extent of this second hydrolysis might be quite significant. The structure of the pure double hydrolysis product has been published previously.[72]

Mechanism of the Hydrolysis Reaction. In attempting to rationalize the fragility of the polypyrazolylborate ligands, it is worth mentioning that researchers have quite often alluded to such problems, both in the literature and anecdotally, quite often. In many cases, however, the products of Tp or Bp degradation have not been characterized or studied in detail. Often, the solution of X-ray crystal structures have been abandoned when fragmented ligands have become apparent. Because of the scanty nature of the information about this problem, it is therefore difficult to draw broad conclusions about the mechanisms by which such processes occur. In the case of the lanthanides, it is noteworthy that the more substituted Tp^{Me2} ligand appears to be more sensitive to degradation than Tp itself. For example, Jun et al. found that, at a Ru center in methanol, Tp^{Me2} and Bp^{Me2} ligands are completely degraded whereas isolable complexes are obtained using Bp and Bp^{4-Br}.[48] For the lanthanides, several Tp,[73−85] $HB(btz)_3$ (btz = benzotriazolyl),[86] and Tp^{py} [87] complexes have been prepared in aqueous or alcoholic solutions. Onishi and co-workers, however, have reported fragmented products from preparations of $TpLnX_2$-type complexes.[88,89]

By contrast, our attempts to prepare the corresponding Tp^{Me2} complexes in protic solvents either gave very poor yields or failed altogether, resulting in the isolation of considerable amounts of free pyrazole. In addition, several crystal structures have been determined in which dimethylpyrazole has been found to be bound to the lanthanide, as a result of fragmentation during crystallization: $[Ln(Tp^{Me2})Cl_2(dmpzH)]$ (Ln = Yb,[90] Y,[65] Lu[91]), $(dmpzH_2)[Yb(Tp^{Me2})Cl_3]$, and $[MCl(\mu\text{-}Cl)Tp^{Me2}(dmpzH)]_2$ (Ln = Pr, Nd).[90]

Although the more frequent observation of fragmentation of Tp^{Me2} complexes might simply reflect the fact that more

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work has been carried out with this ligand than with any others, it is probable that the methyl groups in the 5-position play a role in the instability of these complexes. Evidence has come to light suggesting that the bite angles of the pyrazolylborate ligands are somewhat mismatched with respect to the ionic radius of the lanthanide ions; thus, reaction of lanthanide Tp complexes with organolithium and Grignard reagents results in Tp ligand transfer from one metal to the other.[25] This mismatch might be relieved to some extent by distortion of the ligands away from idealized C_3 symmetry. As mentioned above, one pyrazolyl group in **1-Sm** shows a 16.4° twist around the B1−N4 bond. However, a number of reports from the lanthanide and heavy p-block element literature have appeared of Tp ligands in which very severe twisting of one or more pyrazolyl rings occurs.[26,58,92−95] Such rotations about the B−N bond are often accompanied by slight lengthening of the B−N distance; for example, in $[Yb(Tp^{Bu,Me})(\eta^5\text{-}C_5H_4SiMe_3)]$, the distances are 1.579(5) vs 1.550(5) and 1.534(5) Å. Hence, rotation about the B−N bond might serve to activate the bond toward electrophilic attack because the Lewis acidity of the metal might well increase the degree of polarization of the B−N bond. We note that, in the case of $[Sm(Tp^{Me2})_2SePh]$, the distortion of the ligand was such as to move the boron-bound 1-position nitrogen atom actually closer to the metal center than that in the 2-position.[58] Because it is now well-established that substituents in the 5-position tighten the bite angle of the Tp ligand, it is likely that this increases the propensity of the ligand to distort when bound to a large cation such as a lanthanide.[22] Thus, it would appear that the presence of methyl groups in the 5-position, ostensibly useful to protect the boron atom from attack, might, in fact, serve to destabilize the ligand by maximizing the steric crowding around it.[30,31]

Because hydrolysis of Tp ligands occurs readily at low pH in aqueous solution, direct protonation initially appears to offer a possible mechanism to account for the observed degradation. However, several lines of evidence militate against this hypothesis. Indeed, the use of weak acids, such as H_2S, or carefully controlled conditions allows for the isolation of the free acid form $HTp^{R,R}$.[36,93,96,97] Furthermore, protonation of a dangling pyrazolyl group has even been observed for a κ^2-Tp^{Me2} ligand coordinated to Rh[98] and Cu.[99] In addition, we have always observed hydrolysis in the presence of fairly basic ligands that could be expected to react preferentially with available solvent protons.

It is more reasonable therefore to propose that $[Sm(Tp^{Me2})_2(OH)]$, generated in each case by protonolysis of a complex with adventitious water, is the common precursor to the formation of **1-Sm**. This is shown in eqs 1−3 below

$$[Sm(Tp^{Me2})_2X] + H_2O \rightarrow [(Tp^{Me2})_2SmOH] + HX \quad (1)$$

$$[(Tp^{Me2})_2SmOH] \rightarrow [Sm(Tp^{Me2})(BOp^{Me2})] + dmpzH \quad (2)$$

$$2[Sm(Tp^{Me2})(BOp^{Me2})] \rightarrow [Tp^{Me2}Sm(\mu\text{-}BOp^{Me2})]_2 \quad (3)$$

Consistent with the idea of protonolysis in step 1, we note that $[Sm(Tp^{Me2})_2Cl]$ is moderately stable to water, both in the solid and in solution. By contrast, the amido complex $[Sm(Tp^{Me2})_2NPh_2]$[70] reacts readily to give $[Sm(Tp^{Me2})_2OH]$ (observable by NMR spectroscopy) followed by the precipitation of **1**. These differences in reactivity also seem inconsistent with external nucleophilic attack at boron proposed, for example, by Bellachioma et al.[45] and Kläui et al.,[100] because the Cl and NPh_2 complexes are known to be structurally quite similar, but to differ in the basicity of the unidentate ligand.[57,70]

Step 2 is related to the intramolecular Tp^{Me2} attacks we have reported recently: $[Sm(Tp^{Me2})(\eta^5\text{-}C_5H_5)]$ can be transformed cleanly into $[Sm(Tp^{Me2})(HB(dmpz)_2C_5H_4)]$,[101] whereas $[Sm(Tp^{Me2})_2(C{\equiv}CPh)]$ yields $[Sm(Tp^{Me2})(HB(dmpz)_2\text{-}C{\equiv}CPh)(dmpz)]$[55] by processes that appear to involve displacement of pyrazolide from the boron. However, both of these transformations occur upon fairly strong heating. Because both $[Sm(Tp^{Me2})_2F]$ and $[Sm(Tp^{Me2})_2OPh]$ are known to be quite stable in solution up to 80 °C, the rapidity of the hydroxo fragmentation at room temperature suggests that the proton of the hydroxide might play an important role in this reaction.

It is interesting that several $Tp^{R,R}$-anchored metal hydroxo species have been isolated in the past few years, most notably the stable zinc complexes containing terminal hydroxide ligands studied by Parkin and Vahrenkamp and co-workers. Both terminal zinc[34,102] and hydroxo-bridged magnesium[36,37] complexes have been reported to be unstable in the presence of traces of water. Thus, external attack by water or by the coordinated hydroxo group of a second complex is an alternative possibility. However, the steric crowding around the hydroxo ligand makes it unlikely that it could act as a nucleophile attacking at the boron center of a second complex. In all cases, these complexes involve divalent metal centers, for which the hydroxy hydrogen can be expected to be significantly less acidic than for the hydroxide bound to a trivalent center as in $[Sm(Tp^{Me2})_2OH]$. Indeed the acidity of $[Sm(Tp^{Me2})_2OH]$ is evidenced by the observation that reaction with $[Yb(Tp^{t-Bu,Me})(\mu\text{-}H)]_2$ yields the oxo-bridged bimetallic $[(Tp^{Me2})_2Sm(\mu\text{-}O)YbTp^{t-Bu,Me}]$ and hydrogen.[54]

We therefore propose that twisting of a pyrazolyl group of one Tp^{Me2} ligand of $[Sm(Tp^{Me2})_2OH]$ lengthens and

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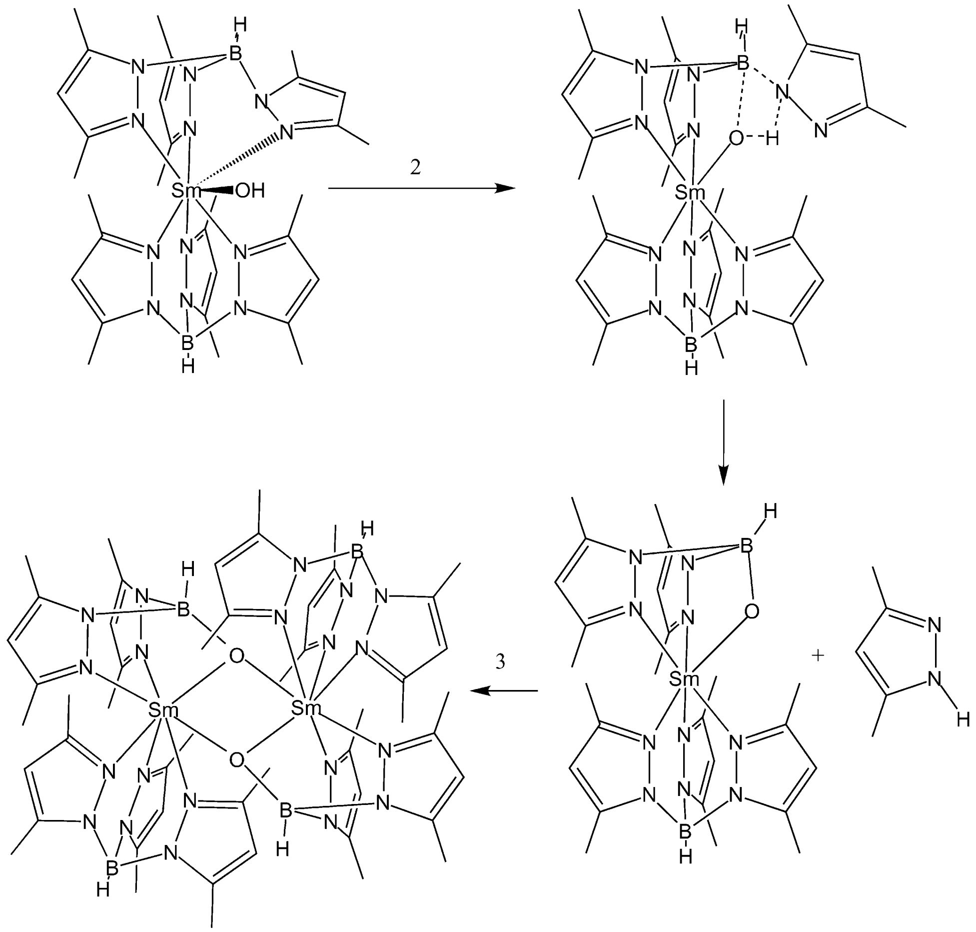

Figure 4. Proposed mechanism for the fragmentation of the Tp^{Me2} ligand. Step 1 (not shown), which generates $[Sm(Tp^{Me2})_2OH]$, is followed by intramolecular displacement of dimethylpyrazole (step 2). Dimerization (step 3) then results in the formation of **1**.

polarizes the corresponding B−N bond. At the same time, this distortion brings the dmpz ligand into proximity of the OH group, and proton transfer occurs onto the boron-bound nitrogen, resulting in the formation of dimethylpyrazole. The proton transfer would then be accompanied by B−O bond formation via a four-centered transition state. Such an acid/base mechanism is supported by the observation that the decomposition of $[Sm(Tp^{Me2})_2OH]$ occurs somewhat more rapidly in the more polar THF solvent than in benzene or toluene. The fact that the reaction occurs faster at higher concentrations might indicate that the dimerization step 3 is rate-determining. It is worth noting that the product of step 2 is analogous to the borinate complex *trans*-$[Fe(COMe)\{\kappa^2\text{-}(mpz)OB(C_8H_{14})\}(CO)(PMe_3)]$ (mpz = 3-methylpyrazolyl) isolated by Bellachioma and co-workers.[45] Thus, the dimerization step 3 might simply reflect the steric unsaturation of the larger lanthanide coordination sphere.

As mentioned in the Crystallography section, there is also evidence that double hydrolysis of both a B−N bond and a B−H bond of the Tp^{Me2} ligand occurs, as evidenced by residual peaks observed in the Fourier difference maps, indicating that $[Sm(Tp^{Me2})(\mu\text{-}(dmpz)_2(HO)BO]_2$ cocrystallizes with the single hydrolysis product. Deng and co-workers have reported this dimer previously, which, as expected, has metrical parameters essentially identical to those seen for **1**.[72] Hydrolysis of the external B−H bond has been observed before, but only for metal-bound Bp-type ligands. In our case, the presence of the strongly Lewis acidic Ln(III) centers appears to be responsible for this further hydrolysis. Indeed, because binding water to the lanthanide center considerably enhances its pK_a, protons might well be available in close proximity to the boron for this transformation to occur. Alternatively, external nucleophilic attack at the now significantly less crowded boron, as proposed by Bellachioma et al.[45] and Kläui et al.[100] might be responsible for this further reaction.

Conclusions

We have shown that bimetallic heteroscorpionate complexes of the lanthanides are easily formed by hydrolysis of the Tp^{Me2} ligand. The formation of these complexes most likely occurs by intramolecular attack of a metal-bound hydroxo group on the boron of a distorted Tp^{Me2} ligand. It is possible, therefore, that ligand degradations reported by others and previously attributed to external attack by water on the B−N bond might instead involve water, activated toward heterolysis by binding to the metal center, attacking the B−N bond by a mechanism analogous to that proposed here. The observation that the hydrolysis reactions occur most often at Tp^{Me2} ligands might imply that the extra steric protection afforded by the 5-methyl substituents comes at the expense of greater susceptibility to hydrolysis. The heteroscorpionate structures also show evidence for an unusual trans influence at a lanthanide center.

Acknowledgment. We are grateful to the Royal Society and the University of London Central Research Fund for support (A.S.), to EPSRC for studentships to G.H.M. (GR/H31943) and A.C.H. (GR/K11338), to the NSERC of Canada and the University of Alberta (J.T.), to the PRAXIS XXI (2/2.1/QUI/386/74) (N.M.), and to NATO (N.M. and J.T.). We thank Prof. W. Clegg for use of the X-ray diffractometer and associated computer programs and facilities in Newcastle. We are also grateful to the EPSRC X-ray Crystallography Service for data collection on **1-Ce**. Prof. J. G. Brennan is thanked for helpful discussions. A.S. is grateful to the University of Alberta for a Visiting Professorship and to UCL for a leave of absence.

Supporting Information Available: Details of the preparation of $[Sm(Tp^{Me2})_2OH]$ and crystallographic information files (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

IC025801C