Unprecedented Transformation of a Hydrotris(pyrazolyl)borate Ligand at a Metal Center: Synthesis and Rearrangement of the First Mixed Tp/Cp Lanthanide Complex, Sm(TpMe2)2(Cp)

I. Lopes,[†] G. Y. Lin,[‡] A. Domingos,[†] R. McDonald,[‡] N. Marques,*,[†] and J. Takats*,[‡]

Departamento de Química, ITN, Estrada Nacional 10 P-2686, Sacavém Codex, Portugal Department of Chemistry, University of Alberta Edmonton, AB, Canada T6G 2G2

The organometallic chemistry of the lanthanide elements has witnessed an explosive growth and spectacular developments since the introduction of the pentamethylcyclopentadienyl ligand system to this area of chemistry, with the trivalent and divalent states benefiting equally.[1,2] The $(C_5Me_5)_2LnR$ (R = H, alkyl) compounds have been shown to be exceptional catalysts,[3] while in particular, the arene-soluble $(C_5Me_5)_2Sm(THF)_{1-2}$[4] and its solvent-free parent $(C_5Me_5)_2Sm$[5] can affect unique organic transformations,[6] which have been attributed to the strong reducing ability of Sm(II) and to the coordinative unsaturation of the metal center.[7]

Given the demonstrated importance of steric factors in lanthanide chemistry, the design and use of alternatives to the C_5Me_5 ligand have become an area of active investigation.[8,9] In this context, we[10] and Sella et al.[11] have initiated an extensive investigation into the synthesis and reactivity of hydrotris-(pyrazolyl)borate $(Tp^{R,R'})$ anchored lanthanide(II) complexes. It was shown that $Sm(Tp^{Me_2})_2$ (**1**), despite its insolubility, undergoes one-electron-transfer reactions with a variety of reagents yielding soluble compounds which have proven amenable to structural characterization.[10,11] The compound is particularly suitable to isolate a series of $Sm(Tp^{Me_2})_2L$ derivatives, where L is the radical anionic form of the ligand (L = azobenzene, quinones, benzophenone, dioxygen).

However, despite the plethora of cyclopentadienyl-based complexes and the emerging importance of the Tp-supported

lanthanides, mixed Tp/Cp derivatives are unknown. Here we wish to report the synthesis of the first mixed Tp/Cp lanthanide complex, $Sm(Tp^{Me_2})_2(Cp)$, and the subsequent, unprecedented transformation of the Tp ligand on the samarium center.

Addition of TlCp to a slurry of $Sm(Tp^{Me_2})_2$ in THF resulted in immediate formation of a black precipitate of thallium metal and a yellow solution. Concentration of the THF solution yielded yellow crystals of $Sm(Tp^{Me_2})_2(Cp)$ (**2**) in ca. 65% yield. Although the analytical data are consistent with the elemental composition, the spectroscopic data clearly indicate different coordination modes for the two Tp^{Me_2} ligands.[12] Thus the $^{11}B\{^1H\}$ NMR spectrum shows two signals at −5.23 and −6.98 ppm and there are two B−H resonances in the ^1H NMR spectrum at 5.05 and −4.10 ppm. Similarly, the infrared spectrum exhibits two $\nu(B-H)$ stretching vibrations at 2565 and 2448 cm^{-1}. The positions of these IR bands are indicative of an η^3- and an η^2-coordinated Tp^{Me_2} ligands,[13a] however, the difference in frequency is larger than the literature values and suggests additional Sm−HB agostic interaction in the latter ligand[13b,c] and this is further supported by the unusually high field position of one of the B−H resonances. Finally, the single ^1H NMR resonance at 9.94 ppm, accounting for 5H, is in accord with an η^5-Cp ligand. A single-crystal X-ray study confirmed the bonding postulate.[14] A view of the molecular structure is shown in Figure 1. It is interesting that, although both Tp and Cp ligands are known to exhibit variable coordination modes, the preference here is for the Cp ligand to maintain its symmetrical bonding to samarium. The spatial requirement for this bonding mode is clearly too large to be accommodated by the pocket made available in other $Sm(\eta^3-Tp^{Me_2})_2L$ complexes, and one of the Tp^{Me_2} ligands responds by pealing off one of its pyrazolyl moieties. Apparently, the electronic demand of the Sm-(III) center is such that it necessitates formation of a Sm−HB agostic interaction also. Although the Sm−N(pz) distances are similar to those found in other $Sm(Tp^{Me_2})_2L$ complexes, the Sm−C(Cp) lengths are some 0.05 Å longer than in $Sm(\eta^5-Cp)_3(THF)$,[15] reflecting the more congested nature of **2**.

When compound **2** was sealed in a tube under vacuum and heated at 165 °C overnight, the initial yellow powder transformed into an intensely yellow colored crystalline solid. The ^1H NMR spectrum of the solid indicated complete consumption of **2** and, its complexity, the presence of two new compounds in approximately equal amounts. Recrystallization of this solid from a toluene/hexane mixture yielded yellow crystals (**3**). The structure of **3** was established by single-crystal X-ray diffraction,[16] while the nature of the other compound present in the residue was deduced as $Sm(\eta^3- Tp^{Me_2})_2(\eta^2-3,5-Me_2pz)$ (**4**) by comparison of its ^1H NMR spectrum with that of an authentic sample.[17]

<hr>

† ITN.

‡ University of Alberta.

(1) Ln(III): (a) Wayda, A. L.; Evans, W. J. *Inorg. Chem.* **1980**, *19*, 2190. (b) Tilley, T. D.; Andersen, R. A. *Inorg. Chem.* **1981**, *20*, 3267. (c) Watson, P. L.; Whitney, J. F.; Harlow, R. L. *Inorg. Chem.* **1981**, *20*, 3271. (d) Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8091. Ln(II): (e) Tilley, T. D.; Andersen, R. A.; Spencer, B.; Ruben, H.; Zalkin, A.; Templeton, D. H. *Inorg. Chem.* **1980**, *19*, 2999. (f) Watson, P. L. *J. Chem. Soc., Chem. Commun.* **1980**, 652. (g) Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 6507.

(2) For recent reviews, see: (a) Edelmann, F. T. *Comprehen.Organomet. Chem. II* **1996**, *4*, 11. (b) Schumann, H.; Meese-Marktscheffel, J. A.; Esser, L. *Chem. Rev.* **1995**, *95*, 865. (c) Schaverien, C. J. *Adv. Organomet. Chem.* **1994**, *36*, 283.

(3) (a) Yasuda, H.; Ihara, E. *Adv. Polym. Sci.* **1997**, *133*, 53. (b) Obora, Y.; Ohta, T.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1997**, *119*, 3745.

(4) Evans, W. J.; Grate, J. W.; Choi, H. W.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 941.

(5) (a) Evans, W. J.; Hughes, L. A.; Hanusa, T. P. *J. Am. Chem. Soc.* **1984**, *106*, 4270. (b) Evans, W. J.; Hughes, L. A.; Hanusa, T. P. *Organometallics* **1986**, *5*, 1285.

(6) Evans, W. J.; Rabe, G. W.; Ziller, J. W.; Doedens, R. J. *Inorg. Chem.* **1994**, *33*, 2719 and references therein.

(7) Evans, W. J.; Forrestal, K. J.; Leman, J. T.; Ziller, J. W. *Organometallics* **1996**, *15*, 527.

(8) Edelmann, F. T. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2466.

(9) Hou, Z.; Zhang, Y.; Yoshimura, T.; Wakatsuki, Y. *Organometallics* **1997**, *16*, 2963.

(10) (a) Takats, J. *J. Alloys Compd.* 1997, *249*, 52. (b) Lin, G. Y.; Lopes, I.; Zhang, X. W.; Domingos, A.; Marques, N.; Takats, J. Manuscript in preparation.

(11) (a) Maunder, G. H.; Sella, A.; Tocher, D. A. *J. Chem. Soc., Chem. Commun.* **1994**, 885. (b) Hillier, A. C.; Liu, S. Y.; Sella, A.; Zekria, O.; Elsegood, M. R. J. *J. Organomet. Chem.* **1997**, *528*, 209.
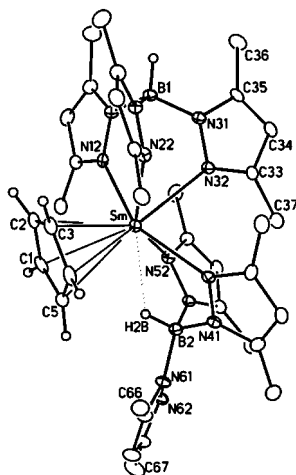
<hr>

(12) Analytical and spectroscopic data on the complexes are given in Supporting Information.

(13) (a) Akita, M.; Ohta, K.; Takahashi, Y.; Hikichi, S.; Moro-oka, Y. *Organometallics* **1997**, *16*, 4121. (b) Carvalho, A.; Domingos, A.; Gaspar, P.; Marques, N.; Pires de Matos, A.; Santos, I. *Polyhedron* **1992**, *12*, 1481. (c) Sun, Y.; Takats, J.; Eberspacher, T.; Day, V. *Inorg. Chim. Acta* **1995**, *229*, 315.

(14) X-ray data for **2**: Triclinic, yellow crystals; space group $P\bar{1}$, $a = 9.834$-(1) Å, $b = 15.822(2)$ Å, $c = 18.058(2)$ Å, $\alpha = 103.464(2)°$, $\beta = 106.315$-(2)°, $\gamma = 90.169(2)°$, $V = 2615.5(5)$ Å^3, and $Z = 2$ ($d_{calcd} = 1.326$ g·cm^{-3}). Refinement of the structure by full-matrix least-squares methods on F^2 was based on 9880 unique reflections ($2\theta_{max} = 51.7°$). Refinement of 625 parameters and 6447 observed reflections with $F_o > 4\sigma(F_o)$ converged to $R_1 = 0.0675$ and $\omega R_2 = 0.1636$.

(15) Wu, Z.; Xu, Z.; You, X.; Zhou, X.; Huang, X.; Chen, J. *Polyhedron* **1994**, *13*, 379.

(16) X-ray data for **3**: Monoclinic, yellow crystals; space group $P2_1/c$, $a = 8.3256(9)$ Å, $b = 20.008(2)$ Å, $c = 21.468(2)$ Å, $\beta = 93.725(10)°$, $V = 3568.6(6)$ Å^3, and $Z = 4$ ($d_{calcd} = 1.414$ g·cm^{-3}). Refinement of the structure by full-matrix least-squares methods on F^2 was based on 6124 unique reflections ($2\theta_{max} = 50.1°$). Refinement of 405 parameters and 5356 observed reflections with $F_o > 4\sigma(F_o)$ converged to $R_1 = 0.0653$ and $\omega R_2 = 0.1360$.

(17) A sample of **4** was obtained by reacting $Sm(Tp^{Me_2})_2Cl$ with K(Me$_2$-pz) in stoichiometric amounts.

Communications to the Editor

J. Am. Chem. Soc., Vol. 121, No. 35, 1999 8111

Figure 1. ORTEP diagram of Sm(η^3-Tp^{Me_2})(η^2-Tp^{Me_2})(η^5-C$_5$H$_5$) (**2**), using 20% probability ellipsoids. Selected bond distances (Å) and angles (deg): Sm−N$_{ave}$ 2.58(2) (range 2.541(6)−2.612(6)), Sm−C$_{ave}$ 2.79(2) (range 2.763(8)−2.846(7)), N32−Sm−C$_5$H$_{5cent}$ 161.5.
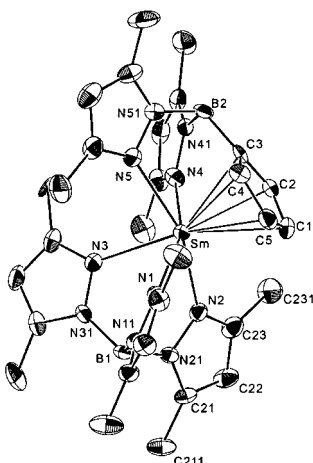
Figure 2. ORTEP diagram of Sm[HB(3,5-Me$_2$pz)$_2$(C$_5$H$_4$)](η^3-Tp^{Me_2}) (**3**), using 30% probability ellipsoids. Selected bond distances (Å) and angles (deg): Sm−N$_{ave}$ 2.53(1) (range 2.511(8)−2.542(8)), Sm−C1 2.776(10), Sm−C2 2.662(10), Sm−C3 2.584(9), Sm−C4 2.657(11), Sm−C5 2.766-(10), B2−C3 1.595(14), N3−Sm−C$_5$H$_{4cent}$ 172.3.

An ORTEP view of **3** is shown in Figure 2. The X-ray analysis revealed that the Sm atom is surrounded by one intact η^3-Tp^{Me_2} ligand and one uniquely modified ligand in which one of the pyrazolyl moieties has been replaced by a C$_5$H$_4$ ring, attached to boron via a B−C σ-bond (B(2)−C(3)), the result being formation of the novel, dianionic hydrobis(3,5-dimethylpyrazolyl)(cyclopentadienyl)borate ligand. The presence of the boratocyclopentadienyl ring, with its B−C bond and simultaneous coordination to samarium, results in a short Sm···B(2) distance (3.26 Å), compared to the Sm···B(1) distance of 3.51 Å, and an unusually short Sm−C(3) distance, 2.584(9) Å. The C$_5$H$_4$ group is unsymmetrically bonded to the Sm atom with Sm−C bond lengths ranging from 2.584(9) to 2.776(10) Å.[18] We believe that the asymmetry is not electronic in origin but that it is caused by the constrained nature of the [HB(3,5-Me$_2$pz)$_2$(C$_5$H$_4$)] ligand which leads to a slippage of the cyclopentadienyl ring of 0.235 Å, computed in terms of the Δ parameter defined by Mingos et al.[19] The molecule has approximately C_s symmetry with a noncrystallographic mirror plane passing through the B(1), Sm, B(2), and

C(3) atoms and the N(3)-containing pyrazolyl ring. This symmetry is retained in solution as can be inferred from the ^{1}H NMR spectrum, which shows three distinct sets of signals for the five pyrazolyl rings in the ratio 1:2:2. The protons of the C$_5$H$_4$ ring give rise to two resonances with an intensity ratio of 1:1.[12]

Although a balanced chemical equation for the reaction can be easily written

$$2\text{Sm}(\text{Tp}^{Me_2})_2(\text{Cp}) \xrightarrow{\Delta} \mathbf{3} + \mathbf{4} + \text{CpH}$$
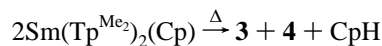
the mechanism of the transformation remains speculative. Activation of the C−H bond of η^5-cyclopentadienyl systems is well precedented in the literature and has been considered as a plausible pathway for the formation of dimeric, η^5:η^5-fulvalene- or η^1:η^5-cyclopentadienyl-bridged compounds.[20,21] However, in the present case, the absence of an oxidative addition pathway necessitates consideration of a different mechanism, namely deprotonation of the C$_5$H$_5$ moiety. Although direct deprotonation can be ruled out, the requisite increase in C−H acidity can be achieved by nucleophilic displacement of a pyrazolyl group from Tp^{Me_2} by the cyclopentadienyl ligand and formation of a transient HB(3,5-Me$_2$pz)$_2$(C$_5$H$_5$) ligand.[22a] Deprotonation of the latter by 3,5-dimethylpyrazolide[22b] is further facilitated by reaction of the liberated 3,5-dimethylpyrazole with **2** to give **4** and volatile CpH.[23] Formation of **3** and **4** in approximately equal amounts is consistent with this hypothesis. Indeed, in a control experiment we have established that **2** reacts with 3,5-dimethylpyrazole at room temperature in THF to yield **4** quantitatively.

In conclusion we have shown that the reactivity of Sm(Tp^{Me_2})$_2$ is not restricted to flat, rod-like substrates but it may also accommodate bulky multidentate ligands in its coordination sphere due to the haptotropism of the Tp^{Me_2} ligand. More importantly, the demonstration that thermally induced intramolecular C−H activation in compound **2** is a useful synthetic method for the preparation of the new HB(3,5-Me$_2$pz)$_2$(C$_5$H$_4$) ligand opens the way for the synthesis of an extended family of heteroscorpionates with organic functional groups by the rational preassembly of related ligand networks on samarium.[24]

Supporting Information Available: Analytical and spectroscopic data for all new complexes and summary of X-ray analyses, atomic coordinates, anisotropic thermal parameters, bond distances and angles, and equations of least-squares planes (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA984227U

(18) Sm^{III}−C(Cp) distances are between 2.62 and 2.82 Å, although the range in any single compound is usually much smaller; for specific examples see ref 2a,b.

(19) Mingos, D. M. P.; Forsyth, M. I.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1978**, 1363.

(20) (a) Brintzinger, H. H.; Bercaw, J. E. *J. Am. Chem. Soc.* **1970**, *92*, 6182. (b) Guggenberger, L. J.; Tebbe, F. *J. Am. Chem. Soc.* **1973**, *95*, 7870. (c) Pez, G. P.; Apgar, P.; Crissey, R. K. *J. Am. Chem. Soc.* **1982**, *104*, 482.

(21) (a) Hoxmeier, R. J.; Blickensderfer, J. R.; Kaesz, H. D. *Inorg. Chem.* **1979**, *18*, 3453 and references therein. (b) Nakajima, T.; Mise, T.; Shimuzu, I.; Wakatsuki, Y. *Organometallics* **1995**, *14*, 5598.

(22) (a) Attachment of the C$_5$H$_5$ moiety to boron is expected to substantially decrease the pK_a of the η^5-C$_5$H$_5$ ligand, between 29 and 39 (Crocco, G. L.; Gladysz, J. A. *J. Am. Chem Soc.* **1988**, *110*, 6110), toward that of CpH, 16 (Streitweiser, A., Jr.; Nebenzahl, L. L. *J. Am. Chem. Soc.* **1976**, *98*, 2188). (b) The pK_a of pyrazole, pzH, is 14.2 (Catalan, J. et al. *J. Am. Chem. Soc.* **1988**, *110*, 4105).

(23) The process is reminiscent of the formation of related boryl−^{a,b} and borato−cyclopentadienyl^{c-e} ligand systems. (a) Herberich, G. E.; Fischer, A. *Organometallics* **1996**, *15*, 58. (b) Larkin, S. A.; Golden, J. T.; Shapiro, P. J.; Yap, G. P. A.; Foo, D. M. J.; Rheingold, A. L. *Organometallics* **1996**, *15*, 2393. (c) Shafiq, F. A.; Abboud, K. A.; Richardson, D. E.; Boncella, J. M. *Organometallics* **1998**, *17*, 982. (d) Lancaster, S. J.; Thornton-Pett, M.; Dawson, D. M.; Bochmann, M. *Organometallics* **1998**, *17*, 3829.

(24) Support for this comes from our recent observation that the complex (Tp^{Me_2})$_2$SmCCPh undergoes smooth, clean conversion to Sm(η^3-Tp^{Me_2})[η^2-HB(3,5-Me$_2$pz)$_2$(CCPh)](η^2-3,5-Me$_2$pz) already at 100 °C; Lin, G. Y.; Takats, J. Manuscript in preparation.