

Application of the Sterically Demanding Hydrotris(3-*tert*-butyl-5-methylpyrazolyl)borate Ligand to Ln(II) Chemistry: Synthesis of a New Class of Mixed-Ligand Yb(II) Complexes[†]

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The last decade has witnessed an explosive growth in the organometallic chemistry of the Ln(II) elements.¹ This flurry of activity and interest can be traced directly to the easy availability of LnI₂ (Ln = Sm, Yb)² and the preparation therefrom of soluble and reactive bis-ligated complexes Ln(C₅Me₅)₂,³ Ln{N(SiMe₃)₂}(THF)₂ (Ln = Sm, Yb), and Yb{(NSiMe₃)₂CC₆H₄R}₂(THF)₂.⁵ However, despite the remarkable and often unique reactivity exhibited by these complexes, as shown in particular by Andersen,⁶ Evans,⁷ and their co-workers, the number of mono-ligated Ln(II) complexes “LLnX” (X = halide) remains surprisingly small. Since the reactive Ln–X site is the key for the synthesis of mixed-ligand “LLnER” (ER = amide, alkoxide, hydrocarbyl, hydride, etc.) type complexes, this lack of suitable starting material is a serious impediment for the development of this area of organo-lanthanide chemistry.

Evans *et al.* have reported the preparation and structure of [(C₅Me₅)Sm(μ-I)(THF)₂]₂⁸ and [(Me₃Si)₂NSm(μ-I)(DME)(THF)₂]₂,^{4a} but the complexes tend toward ligand redistribution to SmI₂(THF)₂ and SmL₂. Schumann *et al.*⁹ have synthesized Cp'YbCl(B)₂ (Cp' = C₅H₅, C₅Me₅; B = THF, 1/2 DME), but, to our knowledge, there are no reports on attempted derivatization of the complexes. The mixed-ligand complex (C₅-Me₅)Yb{Sn(CH₂tBu)₃}(THF)₂ has been reported by Cloke *et al.*¹⁰

Here we report that the sterically demanding hydrotris(3-*tert*-butyl-5-methylpyrazolyl)borate ligand (Tp^{Bu,Me})¹¹ provides a

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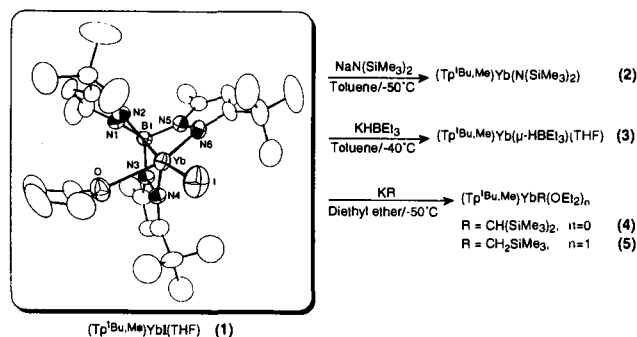
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Scheme 1



unique coordination environment which allows the isolation of soluble, monomeric (Tp^{Bu,Me})YbI(THF) (1) and (Tp^{Bu,Me})YbER type complexes.

Treatment of a THF solution of YbI₂ with 1 equiv of KTp^{Bu,Me} affords (Tp^{Bu,Me})YbI(THF) (1), after simple workup, as a yellow powder in quantitative yield.¹² Complex 1 is soluble in aromatic and ether-type solvents, but only sparingly soluble in hydrocarbons. The compound is stable in solution and has no tendency to disproportionate to Yb(Tp^{Bu,Me})₂ and YbI₂. The monomeric nature of 1 has been confirmed by single-crystal X-ray structure analysis.¹³ As shown in Scheme 1 the Yb center is five coordinate.¹⁴ The coordination geometry can be described as distorted trigonal bipyramidal with N6 and O(THF) occupying the axial sites, the N6–Yb–O angle being 145.8(2)°. The Yb–I bond length, 3.0536(8) Å, is comparable to the average Sm–I distance of 3.049(5) Å in (C₅Me₅)₂SmI(THF).¹⁵ Since the ionic radii of Yb²⁺ and Sm³⁺ are similar,¹⁶ the presence of fewer ligands in 1 gives a good indication of the large steric size of the Tp^{Bu,Me} moiety. The Yb–O(THF) bond at 2.447(6) Å is only slightly longer than 2.412(5) Å found in (C₅Me₅)₂Yb(THF)(C₇H₈)_{0.5}.^{3b} The average Yb–N(Pz) bond length is 2.45(3) Å, which is 0.1 Å shorter than the similar distances in Yb(Tp^{Ph})₂,¹⁷ but very close to those found in Yb(Tp^{Me})₂ (2.482(5) Å;¹⁷ 2.480(4) Å¹⁸).

The synthetic usefulness of 1 is clearly documented by the examples shown in Scheme 1. Reaction with 1 equiv of NaN(SiMe₃)₂ affords orange (Tp^{Bu,Me})Yb{N(SiMe₃)₂} (2), in 61% isolated yield. In the solid state (Figure 1) the molecule has approximate C_s symmetry, with one of the pyrazolyl rings and the planar amido ligand defining the mirror plane.¹⁹ The Yb center has a distorted tetrahedral arrangement. The distortion is manifested by the amido nitrogen being 18.6° off the B1---Yb axis. Although steric repulsions may be largely responsible for this, electronic factors must also make a contribution. Indeed the two Yb–N1–Si angles are vastly different; in particular the angle to Si1 has contracted to 107.6(2)°. The resultant short Yb–C1 distance of 3.064(5) Å provides another example of agostic

(12) Spectroscopic and analytical data on the reported complexes are provided as supplementary material.

(13) X-ray data for 1: *a* = 11.334(3) Å, *b* = 16.276(5) Å, *c* = 18.695(9) Å, β = 99.87(3)°, *V* = 3398 Å³ with *Z* = 4 in space group P2₁/n. *T* = 20 °C, *R* = 0.041, *R*_w = 0.056, number of reflections (*F*_o ≥ 5σ(*F*_o)) = 3963, GOF = 2.44, number of reflections = 6535.

(14) Clearly, the tough “tetrahedral enforcer” image of these ligands, so apt with first-row transition metal ions, is somewhat tarnished by the large Yb(II) center. We have other examples of five-coordinate structures with Ln(II) ions; X. W. Zhang, unpublished results.

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(19) X-ray data for 2: *a* = 15.071(3) Å, *b* = 12.304(3) Å, *c* = 20.746(6) Å, β = 96.84(2)°, *V* = 3819.6 Å³ with *Z* = 4 in space group P2₁/c. *T* = 20 °C, *R* = 0.036, *R*_w = 0.036, number of reflections (*F*_o ≥ 5σ(*F*_o)) = 4885, GOF = 1.07, number of reflections = 7336.

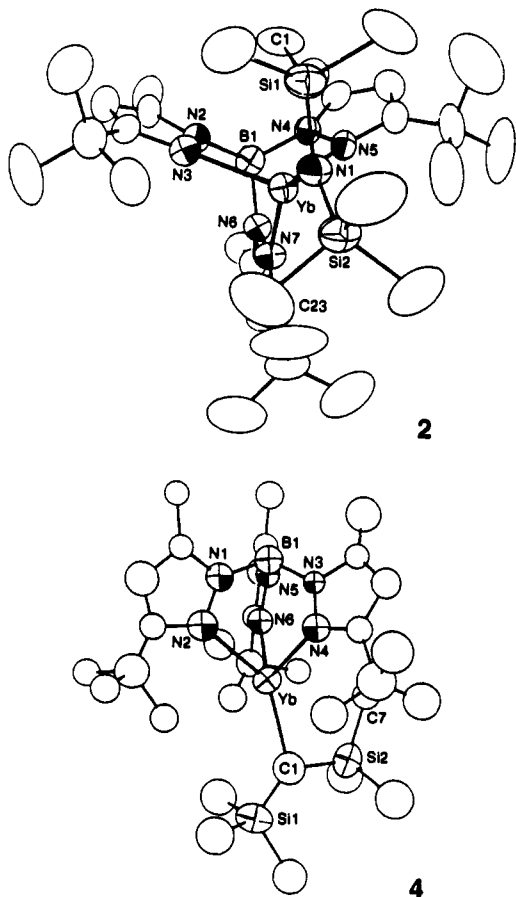


Figure 1. ORTEP views of complexes **2** and **4**; for clarity, only labels of relevant atoms are shown.

interaction in a Ln(II)-N(SiMe₃)₂ complex.²⁰ The agostic interactions are not strong enough to maintain a rigid structure in solution; all the pyrazolyl rings and SiMe₃ groups are NMR equivalent. The average Yb-N(pz) distance of 2.46(2) Å is identical to that observed in **1**, and the Yb-N1 length is 2.382(5) Å.

In an attempt to synthesize the hydride complex, reaction of **1** with a stoichiometric amount of KBHET₃ was carried out. However, instead of a hydride, crystallization from hexane gave (Tp^{tBu,Me})Yb(μ-HBET₃)(THF) (**3**), in 70% yield. The presence of the hydride bridge between Yb and BEt₃ was confirmed by ¹⁷¹Yb and ¹⁷¹Yb{¹H} NMR experiments; the 200 Hz ¹⁷¹Yb-¹H coupling constant is similar to the 170 Hz reported by Green²¹ for [{(C₅H₅)₂NbH₂]₂Yb-diglyme]. To our knowledge, this is the first example of a metal complex with a coordinated triethylborohydride ligand.

Alkylation of **1** provides a convenient route for the synthesis of the first well-characterized Ln(II) hydrocarbyl complexes.

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Reactions of **1** with 1 equiv of KR (R = CH(SiMe₃)₂, CH₂-SiMe₃) in diethyl ether at -50 °C give, after simple work-up, orange crystalline (Tp^{tBu,Me})Yb{CH(SiMe₃)₂} (**4**) and (Tp^{tBu,Me})Yb(CH₂SiMe₃)(OEt₂) (**5**), respectively. The compounds are freely soluble in aliphatic, aromatic, and ether type solvents and are thermally stable. The solid state structure of **4** was determined,²² and preliminary results reveal an arrangement similar to **2**. The CH(SiMe₃)₂ ligand is off the B1---Yb axis by 15.0°, and the ligand itself is distorted. The Yb-C-Si angles are very different (Yb-C1-Si1 = 132(3)° and Yb-C1-Si2 = 99(3)°), and the result is a short Yb---C7 distance (3.08 Å). There are few structural comparisons, but the Yb-C distance of 2.55(6) Å appears somewhat longer than the Yb-C(terminal Ph) bonds of 2.39(6)–2.46(4) Å in the mixed-valence Ph₂Yb(THF)-(μ-Ph)₃Yb(THF)₃ complex.²³

Preliminary reactivity studies have established that compound **2** readily undergoes metathetical reaction with HC≡CPh to afford dark red (Tp^{tBu,Me})Yb(C≡CPh) (**6**) in good yield. This contrasts the behavior of (C₅Me₅)₂Yb(OEt₂) toward HC≡CPh.²⁴ The latter complex undergoes electron transfer reaction and gives a mixed-valence complex. Compounds **4** and **5** also react with hydrogen at room temperature and 1 atm of H₂, **5** faster than **4**. Efforts are underway to characterize the products.

In summary, use of the sterically demanding ligand Tp^{tBu,Me} has resulted in the isolation of the soluble, mono-ligated (Tp^{tBu,Me})YbI(THF) (**1**). Compound **1** is a useful precursor to a new class of (Tp^{tBu,Me})YbER complexes (ER = HBET₃, N(SiMe₃)₂, C≡CPh, CH₂SiMe₃, CH(SiMe₃)₂). Complexes **4** and **5** are the first examples of well-characterized divalent lanthanide hydrocarbyl complexes. The reactivity of the complexes and that of the analogous Sm derivatives²⁵ are under active study.

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Supplementary Material Available: Spectroscopic and analytical data for complexes **1–6** and X-ray diffraction data including ORTEP diagrams, crystal and collection parameters, positional and anisotropic thermal parameters, and bond distances and angles for complexes **1**, **2**, and **4** (32 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(22) X-ray data for **4**: *a* = 16.731(10) Å, *b* = 18.459(11) Å, *c* = 27.260(19) Å, β = 92.10(5)°, *V* = 8413 Å³ with *Z* = 8 in space group *C2/c*. *T* = 20 °C, *R* = 0.147, *R_w* = 0.188, number of reflections (*F_o* ≥ 5σ(*F_o*)) = 2565, GOF = 3.81, number of reflections = 7936. This is preliminary data only, obtained on a poor quality crystal at room temperature. Attempts at obtaining better crystals and collecting high-quality data are underway.

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