Catecholborane Bound to Titanocene. Unusual Coordination of Ligand σ-Bonds

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Isolated examples of complexes formed by coordination of small molecules only through an X−H bond or "σ complexes" are rare and are limited to those involving dihydrogen or silanes.[1,2] Closely related "agostic" complexes, involving coordination of an X−H bond of a ligand with another point of attachment to the metal, are more generally known and include those for X−H bonds of first row elements. Isotope effect measurements and labeling studies along with gas phase transition metal chemistry and organometallic reactions in alkane matrices suggest that σ- and agostic complexes are important intermediates in C−H activations.[3,4]

We report the synthesis, structure, and preliminary reaction chemistry of set of complexes with unusual coordination of neutral boranes through σ-bonds. The compounds are distinct from those containing anionic borates stabilized by electrostatic effects[5] or metallocarboranes and polyboranes with agostic B−H bonds.[6−9] The borane complexes we report are likely to be important in oxidative additions of B−H bonds, and their geometry depicts partial X−H bond cleavage of sp^2-hybridized X−H bonds.

Reaction of 3−5 equiv of catecholborane (HBcat) or 4-(methylcatechol)borane (HBcat′) and titanocene dimethyl (**2**) at −35 °C for 1−2 d evolved methane, formed *B*-(methylcatechol)-borane, and precipitated the compounds $Cp_2Ti(HBcat)_2$ (**1a**, cat = $O_2C_6H_4$; **1b**, 4-MeC_6H_4) in 60−95% yields. **1a** is a yellow solid that is insoluble in aromatic solvents, extremely temperature sensitive in solution, and reactive toward both THF and methylene chloride at low temperatures. **1b** is equally sensitive thermally, but is slightly soluble in toluene at low temperatures.

These properties precluded NMR spectroscopic identification of isolated **1a**, but the greater solubility of **1b** made it amenable to spectroscopic characterization at −45 °C. NMR spectral data for **1a** were obtained during reaction of **2** with catecholborane by simple one- and two-dimensional NMR techniques. Both **1a** and **1b** showed ^{11}B NMR signals at 45 ppm, which are located downfield of free catecholborane but upfield of isolated metallocene boryl complexes and suggest partial metal−boron bond character.[10] Compound **1a** showed a single Cp resonance. Compound **1b** consisted of two isomers with different orientations of the aromatic methyl groups. Three cyclopentadienyl resonances were observed in an approximate ratio of 1:1:2 corresponding to equal ratios of the C_2 and C_s isomers of **1b**. Thus, interconversion between coordination to the two faces of the borane is slow on the NMR time scale at −45 °C. A single set of catecholate resonances were observed for **1a**, but again two sets of aromatic resonances and two methyl groups of almost equal intensity were observed for **1b**. The hydride signal for both complexes was broad due to remaining B−H interaction, and separate signals for **1b-C_2** and **1b-C_s** were not resolved. Infrared vibrations involving the hydrides of **1a** and **1b** were observed between 1611 and 1680 cm^{-1}. This assignment was confirmed by synthesis of **1b-d_2** from $DB(O_2C_6H_4\text{-}4\text{-}Me)$. Compound **1b-$d_2$** displayed no bands between 1611 and 1680 and showed bands in the region between 1160 and 1250 cm^{-1}. The low ν_{B-H} of **1a** and **1b** suggests a low B−H bond order relative to free catecholborane (ν_{B-H} of 2660 cm^{-1}).

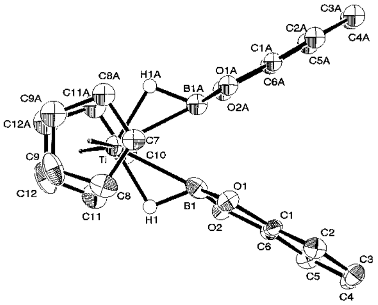

Figure 1. ORTEP drawing of **1a**. Hydrogen atoms (except B−H) were omitted for clarity. Selected distances (Å) and angles (deg): Ti−B 2.335(5), Ti−H 1.74(4), B−H 1.25(3), B−Ti−B 53.8(2), H−Ti−H 117(2), B−Ti−H1 32(1), B−Ti−H1A 86(1), Ti−B−H1 47(2), Ti−H−B 101(2), Ti−B−O 125.4(3), 126.0(3), O−B−O 108.5(4).

Highly dilute reaction solutions deposited single crystals of **1a** over the course of several days at 35 °C. An ORTEP drawing of **1a** is provided in Figure 1; the two halves of the molecule are related by crystallographic symmetry. In addition to the spectroscopic data and the the reaction chemistry described below, several structural features confirmed the presence of hydrides in **1a**, which were located in the difference map and were refined isotropically. The B−Ti−B angle of 55° was too small for the compound to be a Ti(IV) bis-boryl complex, considering the typical angles in metallocene systems.[11] Further, the Ti−B distance of 2.335(5) Å was significantly longer than that of metallocene boryl complexes.[12−14] Indeed, the hydrides were located and observed in the difference map and are displayed in the difference map position.

The B−B distance was 2.11 Å, 0.23−0.25 Å longer than those in polynuclear $B_2H_6^{2-}$ complexes[15−17] and more than 0.4 Å longer than those in catBBcat molecules or their Lewis base adducts.[18,19] The H−Ti−H angle was 117°, much greater than the typical 94−97° angles in d^0 Cp_2ML_2 compounds.[11] In contrast, the angle between the midpoint of the B−H bond, the titanium, and the midpoint of the other B−H bond is 81°, exactly in the range of L−M−L angles typically observed for d^2 Cp_2ML_2 compounds.[11] These data are consistent with a d^2

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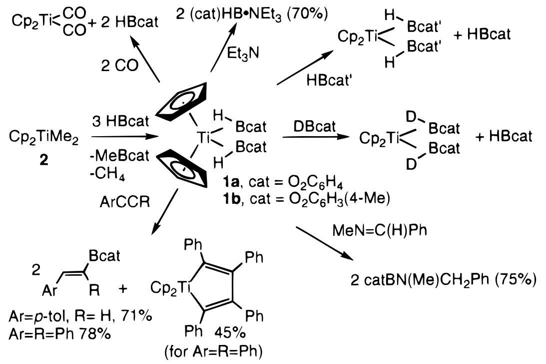
Scheme 1



titanocene complex with coordination of the B−H bond in neutral catecholborane. The B−H distance was 1.268 Å, while the Ti−H distance was 1.779 Å, typical for bridging hydrides.[20] The geometry at boron is distinct from a Lewis acid/base complex. Interestingly, the boron lay in a plane containing the Ti and the two oxygens, with the hydride lying above this plane.

The reaction chemistry (Scheme 1) of **1a** and **1b** was dominated by borane displacement and additions to C−C and C−N multiple bonds. For example, 2 atm of CO displaced HBcat after 1 d at −10 °C. $Cp_2Ti(CO)_2$[21] was formed in 88% yield and HBcat in 93% yield, as determined by ^1H NMR integration of the products against an internal standard. Reaction of triethylamine with a slurry of **1a** in C_6D_6 gave amine-ligated catecholborane ($Et_3NB(H)cat$) in 70% yield by ^1H NMR spectroscopy. The doublet in the ^{11}B NMR spectrum located upfield of catecholborane identified $Et_3NB(H)cat$, along with its indpendent synthesis by addition of Et_3N to catecholborane. The titanium products of this reaction were paramagnetic and have not yet been firmly identified.

1a and **1b** underwent interconversion upon addition of free borane. For example, reaction between 4-methylcatecholborane and a slurry of **1a** in toluene-d_8 at −35 °C generated **1b**, while addition of 20 equiv of catecholborane to a toluene solution of **1b** at −35 °C deposited **1a** and formed free 4-methylcatecohoborane in 98% yield by ^1H NMR spectroscopy. Reaction between 10 equiv of $DB(O_2C_6H_3\text{-}4\text{-}Me)$ and **1b** at −10 °C led to exchange of deuterium into the hydride position, as determined by ^2H NMR spectroscopy of the reaction mixture at −10 °C.

Compound **1a** also transferred boranes to alkynes and imines. Addition of a benzene-d_6 solution of *p*-tolylacetylene to solid **1a** led to the formation of *trans*-(*p*-tolyl)CH═CHBcat[22] in 71% yield. Addition of PhCCPh at −35 °C gave the hydroboration product in 78% yield and $Cp_2\overline{Ti(C(Ph){=}C(Ph)C(Ph){=}C}(Ph))$ in 45% yield. Reaction of *N*-methylbenzylidene imine with a slurry of **1a** in C_6D_6 at room temperature gave the hydroborated imine in 74% yield, which was identified by comparison of ^1H and ^{11}B NMR spectra of reaction solutions to ^1H and ^{11}B NMR spectra of the product amidoborane generated by direct hydroboration of *N*-methylbenzylidene imine and by addition of HNMeBz to catecholborane at 80 °C. These alkyne and imine hydroborations could occur by either direct reaction with **1a** or by borane dissociation and titanocene-catalyzed addition.

Compounds **1a** and **1b** can be described as Ti(IV) complexes of $B_2H_2cat_2^{2-}$, which is analogous to $B_2H_6^{2-}$, and **1a** and **1b** would be the first monomeric examples of a $B_2H_6^{2-}$-type compound.[23,24] However, the ^{11}B NMR signal of such a complex should be upfield of catecholborane, the hydride would be in a region characteristic of Ti(IV) complexes, and the infrared vibration would be near those of d^0 borohydrides.[25] In contrast, **1a** and **1b** can be described as as Ti(II) complexes containing two neutral coordinated boranes.[20] This description would predict some M−B bond character, a decrease in the B−H bond order, and facile dissociation of borane. Although **1a** and **1b** surely contain characteristics of both structural extremes, the spectroscopic and reactivity data for **1a** and **1b** suggest that Ti(II) is a more appropriate description.

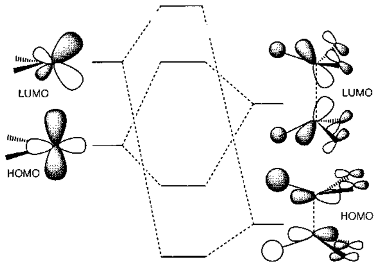


Figure 2. Two dominant orbital interactions in **1a** and **1b** and a localized bond rationalization for the planar geometry at boron.

Core potential ab initio MP2 calculations[26] on the model system $Cp_2Ti(HB(OH)_2)_2$ produced an optimized geometry that was very close to the experimental results. Important for structural confirmation, the computed positions of the bridging hydrogens were close to those determined by X-ray diffraction. Further, the calculations confirmed that the boron atom is not tetrahedral. It lies in the plane defined by the titanium and two oxygens. This planarity was also observed after optimization of $Cp_2Ti(HBH_2)_2$ without the catecholate oxygens.[27] An extended Hückel calculation of $Cp_2Ti(HB(OH)_2)_2$ yields the MO diagram in Figure 2.[11,28,29] There is good overlap between the HOMO and LUMO of both fragments, with one interaction involving donation of a B−H σ-bond and the other back-donation into the boron p-orbital. The planarity at boron is difficult to explain qualitatively. However, the MO analysis shows that such a geometry does maximize back-donation from Ti to B. This structure can also be generated formally by protonation of $Cp_2Ti(Bcat)_2^{2-}$ (with planar boron and π-bonding), while keeping in mind that the proton and π-bond draws analogies to a nonclassical ethyl cation that has relatively planar carbons.[30]

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Supporting Information Available: Spectroscopic data for **1a**,**b** and X-ray data for **1a** (19 pages). See any current masthead page for ordering and Internet access instructions.

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