Communication

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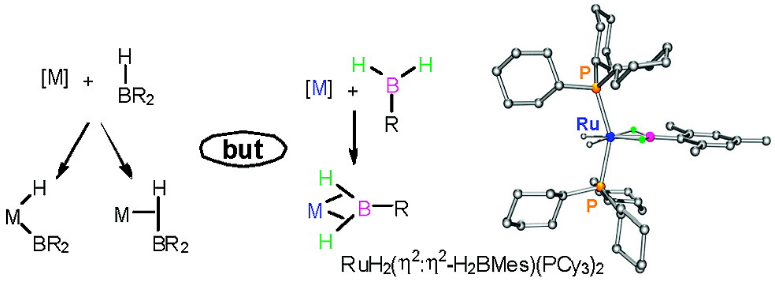
J. Am. Chem. Soc., **2007**, 129 (28), 8704-8705• DOI: 10.1021/ja0733538 • Publication Date (Web): 27 June 2007



Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

J|A|C|S COMMUNICATIONS

Published on Web 06/27/2007

Mesitylborane as a Bis(σ-B−H) Ligand: An Unprecedented Bonding Mode to a Metal Center

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Borane compounds are key reagents for a wide variety of metal-mediated organic transformations. One important class of such reactions is the catalyzed hydroboration of olefins, and more recently important findings have been disclosed concerning direct alkane or arene borylation.[1−3] These reactions are generally dominated by the use of disubstituted boranes of general formulation HBRR′ (R, R′ = alkyl, pinacol, catechol). Coordination of the borane compound to the metal center is an important step often preceding the activation process.[4−6] Although often invoked as intermediates, few examples of σ-borane complexes have been isolated.[4,7−15] The final activation stage leads to oxidative addition with formation of the corresponding hydrido boryl species.[16,17]

The situation can prove more complicated in the presence of polyhydride metal precursors. In that case, a dihydroborate coordination can be favored depending in particular on the Lewis acidity of the borane.[12] In this context, we became interested in exploratory chemistry of monosubstituted boranes H_2BR. To the best of our knowledge, even though mesitylborane (H_2BMes) has been available since the 1990s,[18] no investigation has been carried out on the coordination properties of this potential ligand. Herein we report its reaction with a polyhydride ruthenium center leading to the isolation of a complex which represents the first example of one borane bound to a metal center through two σ-B−H bonds.

Room-temperature reaction of $RuH_2(\eta^2\text{-}H_2)_2(PCy_3)_2$ (**1**) in toluene with a stoichiometric amount of H_2BMes proceeds with rapid gas evolution. After workup, a yellow powder analyzed as $RuH_2(\eta^2{:}\eta^2\text{-}H_2BMes)(PCy_3)_2$ (**2**) was isolated (74% yield) and fully characterized by NMR and X-ray diffraction crystallography (Scheme 1).[19] An alternative synthesis of complex **2** was also developed by reacting the chloro dihydrogen complex $RuHCl(\eta^2\text{-}H_2)(PCy_3)_2$ (**3**) with lithium mesitylborohydride. **2** was again isolated in very good yield (71%).

The ^1H NMR spectrum of **2** in C_7D_8 exhibits at 296 K in the hydride region a broad singlet and a triplet in a 1:1 integration ratio at δ −5.90 and δ −11.05, respectively. Upon phosphorus decoupling the triplet (J_{P-H} = 25.2 Hz) collapsed into a singlet, whereas the singlet sharpened upon boron decoupling. T_1 measurements on the hydride resonances rule out the presence of any (η^2-H_2) ligand in **2**. The integrations of the hydride and the mesityl resonances are in agreement with a species bearing one mesityl group and four hydrogens around the ruthenium. The $^{11}B\{^1H\}$ NMR spectrum shows a broad signal centered at δ 58 in a region characteristic of a three-coordinated boron atom and downfield of that of mesitylborane in C_7D_8 (δ 22).

The X-ray structure of **2** was determined at 110 K (Figure 1 and Table 1).[20] The Ru atom is in a pseudo-octahedral environment with the phosphines in axial positions. The coordination sites in the equatorial plane are occupied by four coplanar hydrogen atoms H1, H2, H3, and H4. The Ru−B distance of 1.938 (4) Å is the shortest Ru−B bond ever reported, much shorter than the sum of the covalent radii (2.09 Å), thus suggesting an interaction between the metal center and the boron atom.

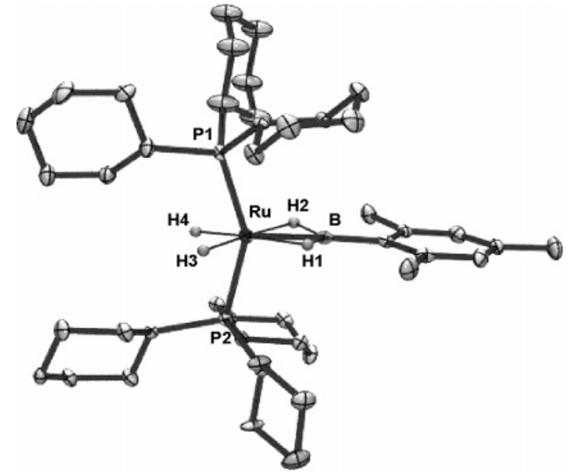
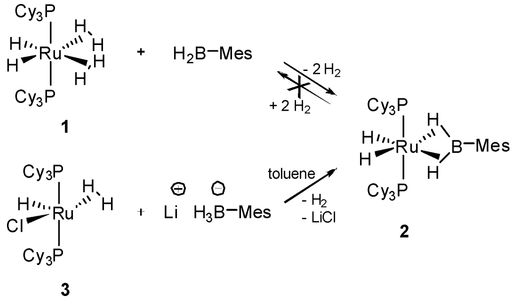


Figure 1. X-ray crystal structure of $RuH_2(\eta^2{:}\eta^2\text{-}H_2BMes)(PCy_3)_2$ **2**.

Scheme 1. Synthesis of **2** via Two Different Pathways



While X-ray data have become more and more reliable for hydrogen location, computational studies have proven a valuable complementary tool in securely locating the positions of the H atoms.[12,21] In addition, calculations offer the advantage to analyze in detail the mesitylborane coordination mode. **2** has been optimized at the B3PW91 level (see Supporting Information). The optimized geometry is in excellent agreement with the experimental structure (see Table 1). The Ru−P and B−C bonds are computed slightly too long but the other geometrical parameters are reproduced accurately. All the experimental and computational data are indicative of a borane adduct to a Ru^{II} dihydrido fragment.

The geometry of the free borane has also been optimized at the B3PW91 level and the B−H bonds are computed to be 1.197 Å, while the B−C bond is 1.535 Å. Upon coordination there is thus

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10.1021/ja0733538 CCC: $37.00 © 2007 American Chemical Society

Table 1. Comparison between Selected Geometrical Parameters (Distances in Å, Angles in Degrees) for the Experimental and Calculated Structures for **2**. Calculated Geometrical Parameters for H_2BMes Are Also Given.

	exptl	calcd	H_2BMes
Ru−B	1.938(4)	1.957	
Ru−P1	2.3186(9)	2.362	
Ru−P2	2.2952(9)	2.338	
B−C1	1.543(5)	1.554	1.535
Ru−H3	1.61(3)	1.614	
Ru−H4	1.59(3)	1.608	
Ru···H1	1.73(3)	1.778	
Ru···H2	1.77(3)	1.788	
B−H1	1.24(3)	1.324	1.197
B−H2	1.29(3)	1.315	1.197
H1−B−H2	123(2)	122.7	116.8
P1−Ru−P2	150.87(3)	152.1	
P1−Ru−B	108.89(11)	107.7	
P2−Ru−B	100.19(11)	100.1	
Ru−B−C1	177.1(3)	177.4	
P1−Ru−B−P2	178.3	178.4	

a significant increase of both bond distances (B−H = 1.315/1.324 Å, B−C = 1.554 Å, **2**) that could be interpreted as the result of a synergetic transfer of electron density: σ-donation from σ(BH) to Ru and π-back-donation from Ru into the vacant p orbital on B. These bonding interactions are reminiscent of the classical Dewar−Chatt−Duncanson model for bonding of alkene or H_2 to transition-metal complexes.[4] To evaluate the reaction energy of the transformation shown in Scheme 1, the bis(dihydrogen) complex **1** has also been optimized at the B3PW91 level. The computed reaction energies are clearly indicative of an irreversible exothermic reaction ($\Delta E = -18.5$ kJ mol^{-1}, $\Delta G = -43.2$ kJ mol^{-1}). This is in agreement with the experimental observations where, in contrast to the reversible process observed in the case of the σ-pinacolborane complex $RuH_2(\eta^2\text{-HBpin})(\eta^2\text{-}H_2)(PCy_3)_2$,[12] no reaction was observed for **2** after prolonged saturation of the solution with H_2, as monitored by ^1H and ^{31}P NMR.

The difference in bonding strength for the σ-H−H vs σ-B−H bonds has been rationalized with an NBO analysis of the electronic structure of **1** and **2**.[22] While the σ-donating NBOs have nearly the same population in **1** (1.70 e, $\sigma(H_2)$) and **2** (1.74 e, σ(BH)), the π back-bonding situation differs significantly between the two compounds. The "vacant" p atomic orbital at boron (LP*(B)) exhibits a significant increase of population upon coordination (0.51 e, **2**; 0.15, free H_2BMes), whereas the population of $\sigma^*(H_2)$ in **1** only increases by 0.14 e upon coordination. The NBO analysis thus shows that even though σ-donation for two B−H bonds is comparable to σ-donation for two H−H bonds, the Lewis acidity of boron renders the borane strongly accepting toward Ru, thus stabilizing **2** with respect to **1**.

In summary, we report here an unprecedented coordination mode of a borane to a metal center. Mesitylborane is able to substitute the two σ-dihydrogen ligands in **1**. The experimental and theoretical data on $RuH_2(\eta^2{:}\eta^2\text{-}H_2BMes)(PCy_3)_2$ (**2**) are in favor of a $\{RuH_2(PCy_3)_2\}$ fragment coordinated by one H_2BMes molecule through two geminal σ-B−H bonds.[23] This coordination involves σ-donation to the ruthenium and π back-bonding from the ruthenium to the vacant p orbital of the boron. These two geminal σ-B−H bonds are responsible for the short Ru−B distance.[24] The chemistry of σ-complexes (dihydrogen and silanes) has been extensively developed over 25 years now, but the knowledge on the properties of the σ-borane class still remains at an early stage.[25] Definitively, the presence of an accepting p orbital on boron plays a crucial role in this area. Our results highlight the unique properties of a dihydroborane substrate and we are currently exploring both the coordination and the catalytic activity of this class of compounds.

Acknowledgment. We thank the CNRS and the ANR (Programme blanc ANR-06-BLAN-0060-01) for support (G.A., L.V., S.S.E.) and the German Academic Exchange Service (DAAD) for a postdoctoral fellowship (U.H.).

Supporting Information Available: X-ray crystallographic files for **2** (CIF); computational details and Cartesian coordinates for the structures calculated. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) A toluene solution (2 mL) of $MesBH_2$ (32.8 mg, 0.248 mmol) was added to a toluene suspension (4 mL) of **1** (170 mg, 0.242 mmol) and stirred at room temperature for 17 h. After removal of the solvent and addition of pentane, the precipitate was separated from the supernatant and dried under vacuum leading to **2** (148.5 mg, 74 %). Selected NMR (C_7D_8) data for **2**: ^1H NMR (293K, 500.33 MHz) δ: −11.26 (t, 2H, $^2J_{PH}$ = 25.3 Hz, RuH), −6.10 (br, 2H, Ru(σ-BH)), 1.20−2.20 (m, 66H, Cy), 2.04 (s, 3H, *p*-CH_3, Mes), 2.90 (s, 6H, *o*-CH_3, Mes), 6.74 (s, 2H, CH Mes). $T_{1\text{min}}$ (263 K, 500.33 MHz) δ: −11.13 (326 ms) −6.05 (138 ms). $^{31}P\{^1H\}$ NMR (293 K, 202.54 MHz) δ: 83.78 (s). $^{11}B\{^1H\}$ NMR (293 K, 160.52 MHz) δ: 58 (br). Anal. Calcd for $C_{45}H_{81}BP_2Ru$: C, 67.90; H, 10.26. Found: C, 68.26; H, 10.16.

(20) Crystals are triclinic, space group $P\bar{1}$, $a = 10.2779(6)$ Å, $b = 12.5838(7)$ Å, $c = 18.0772(10)$ Å, $\alpha = 84.103(4)°$, $\beta = 84.059(5)°$, $\gamma = 68.424(5)°$, $V = 2157.2(2)$ Å^3, $Z = 2.16678$ data were collected (8787 unique), $R = 0.0408$, GOF = 0.959.

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(22) In **2** the NPA charge on Ru is −0.731, while in **1** it is −0.953 pointing out to a more electron-rich metal center in the bis-dihydrogen complex.

(23) As noted by a reviewer, our findings weigh in to the argument that alkanes such as methane might be favored to bind to metal complexes via multiple C-H interactions.

(24) A similar case was found in a ruthenium complex where SiH_4 was trapped by two $RuH_2(PR_3)_2$ units. The multiple σ-interactions were responsible of the very short Ru-Si distances. See: Atheaux, I.; Donnadieu, B.; Rodriguez, V.; Sabo-Etienne, S.; Chaudret, B.; Hussein, K.; Barthelat, J.-C. *J. Am. Chem. Soc.* **2000**, *122*, 5664−5665. See also: Delpech, F.; Sabo-Etienne, S.; Daran, J. C.; Chaudret, B.; Hussein, K.; Marsden, C. J.; Barthelat, J. C. *J. Am. Chem. Soc.* **1999**, *121*, 6668−6682. Nikonov, G. I. *Angew. Chem., Int. Ed.* **2001**, *40*, 3353−3355.

(25) The first σ-borane complex $Cp_2Ti(\eta^2\text{-HBcat})_2$ to be characterized in 1996 remains the only one with two σ-B-H bonds (see ref 7).

JA0733538