

σ -Borane and Dihydroborate Complexes of Ruthenium

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Much attention is being paid to σ -complexes, due to their fundamental importance and the role they might play during the oxidative addition and reductive elimination steps occurring in a wide variety of catalytic processes.¹ The chemistry of dihydrogen and silane complexes has blossomed in the last 15 years.^{1,2} A very good amount of knowledge of their properties has been obtained, thanks in particular to the improvement of NMR and X-ray analyses. In such a context, it is remarkable that only very few σ -borane compounds have been isolated. Activation of a boron hydride by a transition metal complex leads to a versatile chemistry due to the different bonding modes that can be adopted. The use of neutral borane reagents such as the base adduct $\text{BH}_3 \cdot \text{PR}_3$ or the three-coordinated borane HBR_2 proved to be the best candidates to isolate true σ -borane complexes of groups 4 to 7.^{1,3–6} The titanocene catecholborane complexes reported by Hartwig et al. are perhaps the most representative examples, and they are active catalysts for the hydroboration of vinylarenes.⁵

Our group has developed an excellent entry to a wide range of dihydrogen and silane complexes from the bis(dihydrogen) complex $\text{RuH}_2(\text{H}_2)_2(\text{PCy}_3)_2$ (**1**).⁷ We now report the synthesis, structure, and preliminary catalytic activity of ruthenium complexes coordinating either one or two pinacolborane ligands bonded in different modes, that, σ -coordination and dihydridoborate ligation.

Room-temperature reaction of (**1**)^{7c} with excess pinacolborane (HBpin) proceeds rapidly with gas evolution, and after workup, the new complex $\text{RuH}[(\mu\text{-H})_2\text{Bpin}](\sigma\text{-HBpin})(\text{PCy}_3)_2$ (**2**) was isolated in very high yield and characterized by NMR and X-ray diffraction (Scheme 1).^{8,9} The formulation as a σ -borane(dihydroborate) complex is supported by the following observations. The molecular structure is shown in Figure 1. The ruthenium atom is in a pseudo-octahedral environment with the phosphines in axial positions. The four coordination sites in the equatorial plane are occupied by one hydride H(1), one $\sigma\text{-B(2)-H(2)}$ bond of a pinacolborane ligand, and the two hydrogens H(3) and H(4) of a dihydridopinacolborate ligand. The Ru–B(2) distance of 2.157 (5) Å is significantly shorter than the Ru–B(1) distance (2.188(5) Å), but they are both longer than the sum of the covalent radii of Ru and B (2.13 Å). This tendency contrasts with what is generally observed for group 8 boryl complexes showing M–B distances shorter (Ru, Os, Co, Rh, Ir, Pt) or similar (Fe) to the sum of the covalent radii.¹⁰ Keeping in mind the uncertainties in hydride positions, the $\sigma\text{-B(2)-H(2)}$ distance, 1.35 (3) Å, appears shorter than the B(1)–H(3) and B(1)–H(4) distances which are 1.58 (3) and 1.47 (3) Å respectively, although the differences are not significant at the 3σ level.¹¹ Similar $\sigma\text{-B-H}$ distances were reported for σ -borane complexes of three-coordinated boron.^{5,6} Further evidence of a σ -borane coordination is given by the close resemblance between the X-ray structure of **2** and that of the previously reported tris(trimethylphosphine) complex $\text{RuH}[(\mu\text{-}$

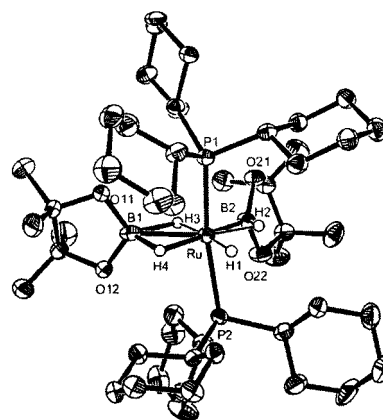
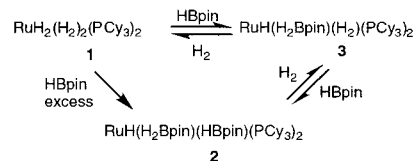


Figure 1. ORTEP drawing of compound **2**. Selected bond lengths (Å): Ru–B(1), 2.188 (5); Ru–B(2), 2.157 (5); Ru–P(1), 2.3673 (13); Ru–P(2), 2.3571 (13); Ru–H(1), 1.48 (3); Ru–H(2), 1.58 (3); Ru–H(3), 1.49 (3); Ru–H(4), 1.55 (3); B(1)–H(3), 1.58 (3); B(1)–H(4), 1.47 (3); B(2)–H(2), 1.35 (3). Selected bond angles (deg): P(1)–Ru–P(2), 160.45 (3); B(1)–Ru–B(2), 113.68 (17); Ru–H(2)–B(2), 94.4 (20); H(4)–Ru–B(2), 153.6 (12); H(2)–Ru–B(2), 38.6 (11); B(2)–Ru–H(3), 67.5 (12); H(3)–Ru–H(1), 173.1 (19); H(4)–Ru–H(2), 166.3 (16); H(3)–Ru–H(4), 88.0 (17); H(1)–Ru–H(4), 85.3 (17); H(1)–Ru–H(2), 81.2 (17).

Scheme 1



$\text{H})_2\text{BH}_2](\text{PMe}_3)_3$.¹² In **2** the σ -borane ligand acts as a 2-electron donor, playing a similar role as PMe_3 in the latter complex.

The room-temperature ¹H NMR spectrum of **2** in the hydride region is featureless. However, at 233 K three well-resolved resonances are observed in a 2:1:1 ratio (Figure 2). The broad singlet at δ –11.4 is attributed to the two bridging hydrides of the dihydroborate ligand, the sharp triplet at δ –8.03, to the terminal hydride coupled to the two phosphorus ($^2J_{\text{P-H}} = 25$ Hz), and the broad singlet at δ –7.13, to the σ -bonded B–H proton. Upon ¹¹B decoupling, the two broad signals sharpened. A dihydrogen formulation can be ruled out on the basis of T_{min} values (around 100 ms at 300 MHz for the three signals). The ¹¹B NMR spectrum shows at 293 K, a very broad signal at δ 37.3 ($w_{1/2} = 640$ Hz), downfield of that of pinacolborane (δ 28.4). We were unable to measure any coupling constant between ¹H and ¹¹B.

When performing the reaction with only one equiv of pinacolborane, conversion of **1** to the new complex **3** is observed (Scheme 1, Figure 2). The integrations of the ¹H NMR signals at δ –8.83 and δ 1.25 are in agreement with a species bearing one pinacolboron ligand and five hydrogens around the metal.⁸ The high-field signal remains broad at all temperatures, indicative of a fast exchange.

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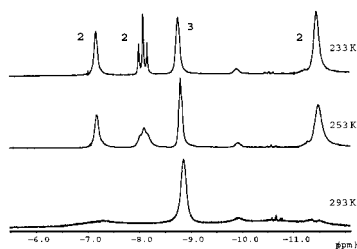
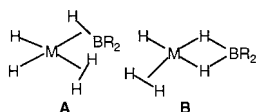


Figure 2. ^1H NMR spectra at variable temperature, in the hydride region (300 MHz, C_7D_8) showing a mixture of **2** and **3**.

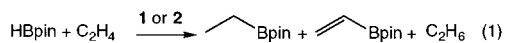
The $T_{1\text{min}}$ value of 40 ms at 253 K (300 MHz) is in agreement with the presence of a dihydrogen ligand. The ^{11}B NMR spectrum shows as for **2**, a very broad signal at δ 35.1 ($w_{1/2} = 509$ Hz). Conversion of **3** to **2** is obtained by increasing the pinacolborane concentration. Therefore **3** can be formulated as $\text{Ru}^{\text{H}_3\text{Bpin}}(\text{H}_2)(\text{PCy}_3)_2$. Two modes of coordination of the boron ligand can be proposed leading to a dihydride (σ -borane) (**A**) or hydrido(dihydroborate) (**B**) structure involving in each case a σ -dihydrogen ligand.^{13,14} All attempts to isolate **3** have failed.

Remarkably, **3** was also generated upon heating at 80 °C for 4 h, a mixture of **1** and B_2pin_2 (1.3 equiv), as a result of B–B bond breaking.

A C_7D_8 solution of **2** in a NMR tube was kept under dihydrogen atmosphere, and the reaction was monitored by ^1H , ^{31}P , ^{11}B NMR. Total conversion into **3** and HBpin was first observed. After several hours, conversion of **3** into **1** was finally achieved, and HBpin was gradually hydrolyzed into $\text{B}_2\text{pin}_2\text{O}$ due to traces of water.¹⁵ **3** is thus an intermediate in the formation of **2** and in the reverse reaction leading back to **1**. Although none of the two suggested structures **A** or **B** can be ruled out, all these observations and specifically the slow conversion of **3** into **1** are in favor of the dihydrogen-(dihydroborate) structure **B**, $\text{RuH}[(\mu\text{-H})_2\text{Bpin}](\text{H}_2)(\text{PCy}_3)_2$. This is another example of the ruthenium ability to accommodate hydrogens around its coordination sphere, either as terminal or bridging hydrides or as dihydrogen ligands.



We have previously demonstrated that **1** serves as an efficient catalyst precursor for hydrosilylation or dehydrogenative silylation of ethylene leading to the formation of vinylsilanes.¹⁶ The activity of **1** as catalyst precursor for hydroboration was thus examined. Preliminary experiments show that in toluene, selective hydroboration of ethylene (3 bar) by HBpin (100 equiv) into $\text{C}_2\text{H}_5\text{Bpin}$ is achieved (100% yield by GC), whereas in THF a competitive reaction leads to the formation of the vinylborane $\text{C}_2\text{H}_3\text{Bpin}$ in 23% yield (eq 1).¹⁷ The boron products were characterized by NMR and GC–MS.



Remarkably, the same results were obtained when **2** was used as the catalyst precursor. Using 20 bar of ethylene favors the formation of vinylborane, a versatile reagent for organic synthesis. Indeed, 1000 equiv of HBpin were converted in 15 min at room temperature into 56% of $\text{C}_2\text{H}_3\text{Bpin}$ and 44% of $\text{C}_2\text{H}_5\text{Bpin}$. The role in the catalytic cycle of **2**, bearing a σ -borane, a dihydridoborate, and a hydride coordinated to the same metal, needs further investigations. Theoretical studies and the results with other olefins and boranes will be reported in due course.

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Supporting Information Available: Synthesis and characterization data for **2**, **3**, and $\text{B}_2\text{pin}_2\text{O}$ (PDF). X-ray structural data for **2** and $\text{B}_2\text{pin}_2\text{O}$ (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (8) **2**: ^1H NMR (C_7D_8 , 233 K, 300.13 MHz) -11.4 (br, 2H, $\text{Ru}[(\mu\text{-H})_2\text{Bpin}]$, -8.03 (t, 1H, RuH , $^3J_{\text{PH}} = 25$ Hz), -7.13 (br, 1H, RuHBpin), 1.24 (s, 24H, Bpin), $1.28–2.25$ (m, 66H, PCy_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_7D_8 , 293 K, 75.47 MHz) 24.9 (s, CH_3), 82.3 (s, C). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_7D_8 , 293 K, 121.49 MHz) 66.3 (s). $^{11}\text{B}\{^1\text{H}\}$ NMR (C_7D_8 , 293 K, 96.29 MHz) 37.3 (br, $w_{1/2}$ 640 Hz). Anal. Calcd for $\text{C}_{48}\text{H}_{94}\text{O}_4\text{B}_2\text{P}_2\text{Ru}$: C, 62.67; H, 10.30. Found: C, 62.45; H, 10.24. **3**: ^1H NMR (C_7D_8 , 293 K, 300.13 MHz) -8.83 (br, 5H), 1.25 (s, 12H, Bpin), $1.34–2.17$ (m, 66H, PCy_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_7D_8 , 293 K, 75.47 MHz) 25.1 (s, CH_3), 81.7 (s, C). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_7D_8 , 293 K, 121.49 MHz) 72.2 (s). $^{11}\text{B}\{^1\text{H}\}$ NMR (C_7D_8 , 293 K, 96.29 MHz) 35.1 (br, $w_{1/2}$ 509 Hz).
- (9) Crystal data for **2**: pale yellow crystal, $T = 160$ K, triclinic, $P\bar{1}$, $a = 12.118$ (5) Å, $b = 13.945$ (5) Å, $c = 15.406$ (5) Å, $\alpha = 93.277$ (5)°, $\beta = 102.539$ (5)°, $\gamma = 97.880$ (5)°, $Z = 2$, $R_1 = 0.0405$, $\text{GOF} = 0.929$.
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- (13) We have already reported the characterization of an analogous complex $\text{RuH}[(\mu\text{-H})_2\text{BBN}](\text{PCy}_3)_2$ resulting from the reaction of **1** with HBBN. See: Rodriguez, A.; Sabo-Etienne, S.; Chaudret, B. *Anal. Quim. Int. Ed.* **1996**, 131. We have also published an analogous dihydrogen(silane) complex. In that case, the X-ray structure showed the two phosphines in a cis position. See: Hussein, K.; Marsden, C. J.; Barthelat, J. C.; Rodriguez, V.; Conejero, S.; Sabo-Etienne, S.; Donnadiou, B.; Chaudret, B. *Chem. Commun.* **1999**, 543.
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