Borane Complexes

Rhodium Silyl Boryl Hydride Complexes: Comparison of Bonding and the Rates of Elimination of Borane, Silane, and Dihydrogen[**]

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Transition-metal "σ complexes"[1] of dihydrogen[2] and of silanes[3] are common, and transition-metal σ-borane complexes are now known.[4–11] Dihydrogen complexes are intermediates in the oxidative addition that occurs during hydrogenation, and they are intermediates of the reductive elimination that occurs during dehydrogenation. Similarly, silane complexes are probably intermediates in the oxidative additions of silanes that occur during hydrosilylation,[12] and borane complexes have been shown to be intermediates in catalytic hydroboration.[5] Borane complexes are also likely intermediates[13] in the borylation of alkanes[14,15] and arenes.[15–19]

A complex with hydride, silyl, and boryl groups bound to the metal center of the same complex could adopt a structure with a σ-dihydrogen, -silane, or -borane ligand. No complexes of this type have been isolated in pure form, but compounds with this collection of ligands would allow direct assessment of the similarities and differences between the three types of σ complexes. Herein, we report the synthesis, experimental and calculated structures, as well as the reaction chemistry of $[Cp^*RhH_2(Bpin)(SiR_3)]$ ($Cp^* = C_5Me_5$, Bpin = (pinacolato)-boryl) complexes, which contain two hydrides, one silyl and one boryl group. Our data suggests that this complex contains partial B–H bonding and that borane eliminates from this complex faster than dihydrogen or silane.

Reaction of the known bis(silyl) dihydride **1a**[20] with a large excess of HBpin in refluxing cyclohexane formed $[Cp^*RhH_2(SiEt_3)(Bpin)]$ (**2a**) in 90% yield, as determined by NMR spectroscopy with an internal standard [Eq. (1)]. In addition to a single pinacol methyl resonance at $\delta = 1.09$ ppm

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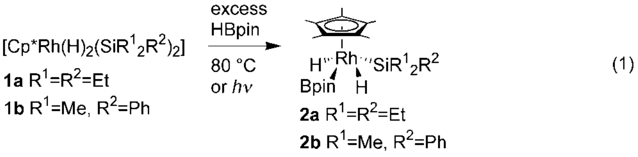
and ethyl resonances from the silyl group, the ^{1}H NMR spectrum of **2a** contained a doublet at $\delta = -12.7$ ppm ($^{1}J_{Rh\text{-}H} = 42.0$ Hz) for the hydride ligands. The ^{11}B NMR spectrum contained a resonance at $\delta = 40$ ppm, which confirmed the presence of a boryl ligand. Though **2a** formed in high yield by NMR spectroscopy, we were unable to isolate crystalline material from these reactions.

However, irradiation of the bis(silyl) complex **1a** and HBpin in cyclohexane for 18 h allowed the isolation of crystalline silyl boryl dihydride **2a** in 61% yield. Reaction of [Cp*$RhH_2(SiMe_2Ph)_2$] (**1b**)[21] with excess HBpin formed *trans*-[Cp*$RhH_2(SiMe_2Ph)$(Bpin)] (**2b**) under similar photochemical conditions in 78% yield [Eq. (1)]. Longer reaction times did not cause replacement of the second silane of **2a** or **2b** with borane to form [Cp*Rh(H)$_2$(Bpin)$_2$] (**3**).



Reaction of B_2pin_2 with **1** formed a single major product, but the conversion of **1** was incomplete before this major species underwent further reaction. We previously formulated the major species as the bisboryl **3**, based on the presence in the NMR spectra of a broad resonance signal for hydride groups and new resonances for pinacol methyl groups.[15] With **2a** now in hand, the spectral features of the major product generated from **1** and B_2pin_2 clearly result from **2a**.

The structure of **2a** was confirmed by X-ray crystallography.[22] All hydride units were located in the electron difference map and were freely refined isotropically. Figure 1 shows a view of **2a** along the Cp*–Rh axis. The boryl and silyl ligands are located in mutually *trans* positions of the four-legged piano stool structure of **2a**. The Rh–Si bond length of 2.3681(15) Å is similar to the 2.379(2) Å Rh–Si separation in the bis(silyl) complex **1a**.[20]

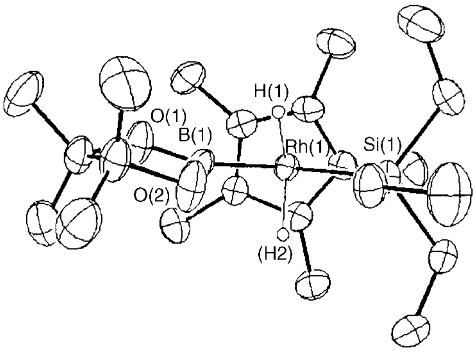


Figure 1. Molecular structure of **2a** (thermal ellipsoids set at 30% probability). Selected bond lengths [Å] and angles [°]: Rh(1)-H(1) 1.57(5), Rh(1)-H(2) 1.59(4), Rh(1)-Si(1) 2.3681(15), Rh(1)-B(1) 2.038(5), Rh(1)-Cp*$_{cent}$ 1.919(4); Si(1)-Rh(1)-H(1) 70.3(15), H(1)-Rh(1)-B(1) 55.7(16), B(1)-Rh(1)-H(2) 67.9(14), H(2)-Rh(1)-Si(1) 66.5(15).

The hydride positions suggested a structure with more residual B–H bonding than H–H or Si–H bonding, despite the caveats of defining hydride positions by X-ray diffraction. An ideal four-legged piano-stool structure would contain a mirror plane that is defined by the Cp* centroid, rhodium, silicon, and boron atoms. In such a piano-stool geometry, the two hydride units would lie in or near a vertical plane that would be orthogonal to this mirror plane. Although one of the hydrides in **2a** lies near this plane, the second hydride lies out of this plane on the side of boron atom. Thus, the H(1)-Rh(1)-B(1) angle of 55.7(16)° is measurably smaller than the H(2)-Rh(1)-B(1) angle of 67.9(14)° or the two H-Rh(1)-Si(1) angles (66.5° and 70.3°). The symmetrical starting complex **1a** contains H-Rh-Si angles of 65° and 69°.[20] The boron–hydride separation of the shorter B–H bond of 1.74(4) Å is 0.3 Å shorter than the longer boron–hydride bond. This distance is much longer than the B–H bonds of 1.30–1.36 Å in Mn, Re, and Ti σ-borane complexes.[7,10] However, it is shorter than the B–H bond in *trans*-[Rh(Cl)(H)(Bpin)(P*i*Pr$_3$)$_2$]. This complex has a long B–H separation of 2.013(5) Å, as determined by neutron diffraction, but an acute H-Rh-B angle that seems to result from B–H bonding.[19,23]

Considering the difficulty in defining the position of hydrides and the series of different binding modes available to **2a** and **2b**, we sought to provide further evidence for the B–H interaction by computing the ground-state structure of **2a** by DFT-B3LYP methods.[24,25] An overlay of the calculated and experimental structure of **2a** is provided in Figure 2. The separations and angles in the calculated structure are relatively close to those of the experimental structure. Although the unsymmetrical property of the computed structure is less pronounced than that of the experimental structure, both structures display geometries with separations appropriate for partial B–H bonding, one hydride that is closer to the boron atom than the other hydride, and one B-Rh-H angle that is smaller than the other B-Rh-H angle or the Si-Rh-H angles. As a result, even the computed structure in the gas phase lacks a mirror plane containing the Cp* centroid, rhodium, silicon, and boron.

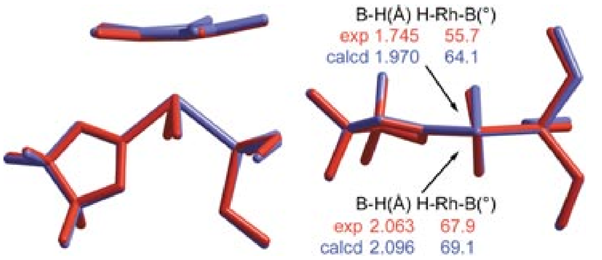
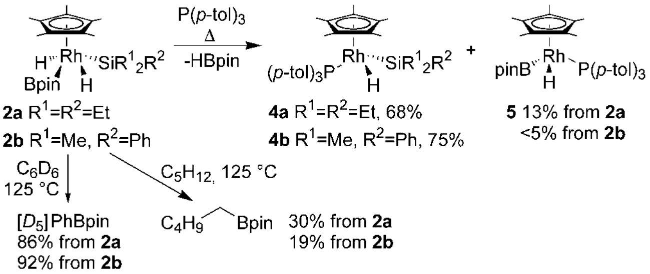


Figure 2. Overlay of the experimental and calculated (DFT-B3LYP) structure of [Cp*$RhH_2(SiEt_3)$(Bpin)]. The experimental structure is given in red and the computed structure is given in blue.

The solution ^{1}H NMR spectroscopic data of complexes **2a,b** show a small, direct scalar coupling between the hydride units and the boron center that further indicates the presence of B–H bonding. The single resonance signal for the two hydride units in **2a** and **2b** is slightly broadened (**2a**, $\omega_{1/2} = 11.7$ Hz; **2b**, $\omega_{1/2} = 12.1$ Hz) and sharpens upon ^{11}B decoupling (**2a**, $\omega_{1/2} = 8.2$ Hz; **2b**, $\omega_{1/2} = 8.2$ Hz). ^{1}H NMR spectra of compounds containing discrete, *cis*-disposed boryl and hydride ligands contain sharp hydride signals that remain unchanged upon ^{11}B decoupling.[17,26–28] Our NMR spectroscopic data imply that the B–H interactions in **2a**,**b** remain intact in solution, though the two hydride positions are averaged on the NMR time scale and the small magnitude of the scalar coupling suggests a weak interaction.

The calculated potential energy surface (PES) for shortening of the B–H bonding in **2a** is nearly flat (< 0.5 kcal mol^{-1} for the decrease in B–H separation from 1.970 Å to 1.670 Å), but the PES is steeper for shortening the H–Si separation. These results suggest that dissociation of borane should occur in preference to dissociation of silane. Further, the *trans* orientation of the hydride units should make dissociation of H_2 unfavorable.

Consistent with this prediction, heating of **2a** and **2b** at 100 °C with 1 equivalent of P(*p*-tol)$_3$ gave as the major products the silyl complexes [Cp*Rh(H)(SiR$^1_2$R^2){P(*p*-tol)$_3$}] (**4a**, $R^1 = R^2 = Et$; **4b**, $R^1 = Me$, $R^2 = Ph$; Scheme 1) in 68 % and 75 % yield. HBpin and pinBOBpin or B$_2$pin$_3$ were the major boron products. The rhodium products were identified by comparison of NMR spectral data to those of material prepared independently by reaction of the phosphine with bis(silyl) complexes **1a** at 100 °C for 16 h and **1b** at 150 °C for 3 h. Reaction of **2a** formed as minor products a small amount of free silane and [Cp*Rh(H)(Bpin){P(p-tol)$_3$}] (**5**) in 13 % yield. The half-life for elimination of borane from **2a** and **2b** was determined by monitoring the reactions of these complexes with excess PEt$_3$ by ^{1}H NMR spectroscopy. At 100 °C, the half-life for reaction of **2a** was 4.5 h, and the half-life for reaction of **2b** was 2 h.



Scheme 1. Reaction chemistry of silyl boryl hydride complexes **2a** and **2b**.

To determine if Cp*-rhodium silyl boryl complexes could be intermediates in the borylation and silylation of hydrocarbons,[15,29] we evaluated the reactivity of **2a** and **2b** with neat hydrocarbons (Scheme 1). Heating of **2a** and **2b** at 125 °C in C_6D_6 formed one equivalent of the phenylboronate ester [D$_5$]PhBpin in 86 % and 92 % yield, respectively (Scheme 1), as quantified by ^{1}H NMR spectroscopy and confirmed by GC/MS. Reactions of **2a** and **2b** with alkanes occurred in lower yields. Heating **2a** and **2b** in pentane at 125 °C in a sealed vessel formed the pentylboronate ester in 30 % and 19 % yield, as determined by GC (Scheme 1). Arylsilane or pentylsilane were not detected in these reaction mixtures. Several rhodium products are formed from these thermolysis reactions, and these materials have not yet been fully characterized. Because borane dissociates from **2a** and **2b** more readily than H_2 or silane, and the borylation of arenes and alkanes typically occurs through metal boryl complexes,[16,27,30,31] the mechanism of the reactions of **2a** and **2b** with hydrocarbons is likely to be complex.

In conclusion, two complexes that could possess a dihydrogen, silane, or borane ligand have been prepared. These complexes preferentially adopt geometries with σ-borane complexes and undergo dissociation of borane more rapidly than dissociation of silane or dihydrogen. This preference for dissociation of borane from **2a** and **2b** to generate a silyl hydride intermediate instead of dissociation of silane to generate a boryl hydride intermediate explains in part why the silyl complexes are less effective than [Cp*Rh(η^6-C$_6$Me$_6$)] as catalyst precursors for the borylation of hydrocarbons.

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[22] X-ray diffraction was performed on a Nonius KappaCCD diffractometer with graphite monochromated Mo-Ka radiation ($\lambda = 0.71073$ Å). Crystal data for **2a**: $C_{22}H_{44}BO_2RhSi$, $M_r = 482.38$, orthorhombic space group *P*212121 (No. 19), $a = 10.583(2)$, $b = 12.279(3)$, $c = 20.456(4)$ Å, $\alpha = 90$, $\beta = 90$, $\chi = 90°$, $V = 2658.2(9)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.205\ g\,cm^{-3}$, $\mu = 7.00\ cm^{-1}$, $T = 296(2)$ K, 6081 reflections (6081 unique), 252 refined parameters, $R = 0.0475$ (6081 data with $I > 2\sigma(I)$), $wR(F^2) = 0.0739$, residual electron density = 0.407 to −0.449 e^- Å^3. The hydride H atoms were revealed in the difference Fourier map and refined isotropically. CCCDC-247319 (**2a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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