Combined B–H and Si–H Bond Activations at Ruthenium

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Ramaraj Ayyappan,[a,‡] Koushik Saha,[b] Urminder Kaur,[b] Sourav Gayen,[b] Laure Vendier,[a] Sylviane Sabo-Etienne,[a] Sundargopal Ghosh,*[b] Sébastien Bontemps*[a]

[a] LCC-CNRS, Université de Toulouse, CNRS, 205 route de Narbonne, 31077 Toulouse Cedex 04, France.

[b] Department of Chemistry, Indian Institute of Technology Madras, Chennai 600036, India.

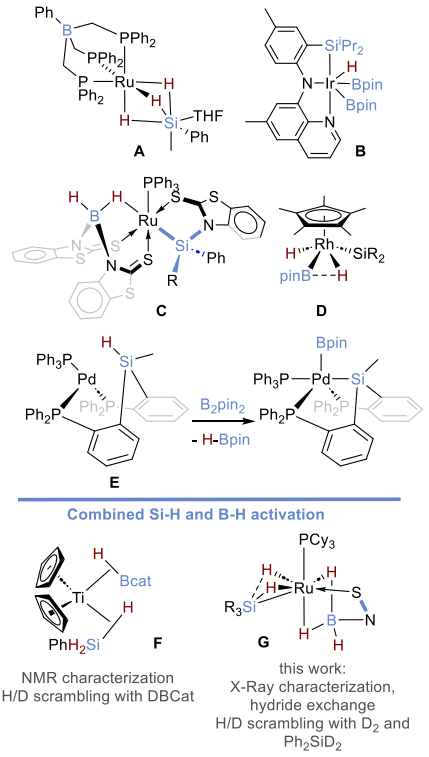
‡ *Present address*: Indian Institute of Science Education and Research Thiruvananthapuram (IISER-TVM), Maruthamala PO, Vithura, Thiruvananthapuram - 695551. Kerala, India

ABSTRACT: The coordination of 2-mercaptobenzothiazolyl (mbz) and 2-mercaptopyridyl (mp) to a [Ru]–H precursor led to the isolation of two hydrido(dihydroborate) complexes [RuH(PCy_3)$_2${κ^3-H,H,S-$(H)_2$BH(L)}] (L = mbz (**1a**), mp (**1b**)). Oxidative addition of secondary and tertiary silanes to **1a** and **1b** afforded the dihydrido ruthenium(IV) [$RuH_2(SiPh_2R)(PCy_3)$}{κ^3-H,H,S-$(H)_2$BH(L)}] (R = H, L = mbz (**2a**), mp (**2b**); R =Me, L = mbz (**2c**)) featuring a coordinated borohydride moiety and a silyl ligand in weak interaction with the two hydride ligands of the ruthenium center. 1D and 2D NMR investigations at different temperatures as well as D_2 reactivity enabled to characterize exchange between every Si–H, Ru–H and B–H hydride sites.

The coordination chemistry of Si–H or B–H bonds toward metal centers has been the subject of a multitude of investigations aiming at characterizing every step of E–H bond activation (E = B or Si) from the weakest interactions to the ultimate breaking of the bond at a metal center (M) with or without the assistance of a co-ligand.[1-10] These studies fueled the knowledge and comparisons on reduction and functionalization reactions by boranes or silanes both in stoichiometric and catalytic conditions.

However, the combination of both boron and silicon, and hydrides in the coordination sphere of a metal center is much rarer. We have selected representative examples in Scheme 1. Complexes **A**-**D** exhibit such specific features. The tris(diphenylphosphinomethyl)borato ligand in complex **A** is an example of ligand featuring an anionic charge in the backbone, with a borate moiety. Complex **A** shows that such ligand can support a Ru center able to activate silanes ($RR'SiH_2$).[11] Complex **B** was used in dehydrogenative borylation of alkynes[12] and complex **C** is the result of silane activation at Ru bearing a di(mercaptobenzothiazolyl)borate ligand.[13] Complex **D** features a boryl, silyl and two hydride ligands at a single Rh center. Remaining H···Bpin interaction was evidenced in solid-state by short contact in the X-ray diffraction analysis and in solution by B-H coupling observed in ^{1}H NMR analysis. This complex was shown to release hydroborane and not hydrosilane upon thermic activation.[14] Finally, complex **E** was reacted with B_2pin_2 to generate two isomeric boryl complexes differing by the relative positioning of the boryl and silyl moieties (cis-B,Si, shown in Scheme 1 and trans-B,Si, not drawn).[15] Theoretical investigation proposed that these boryl complexes were generated via Si–H and B–H activation.

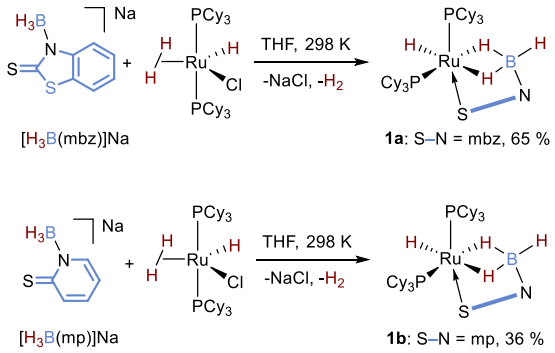
To our knowledge, the combined activation of Si–H and B–H bond has only been studied once at a Ti center (complex **F**, Scheme 1) with hydrosilane ($PhSiH_3$) and hydroborane (H-BCat) ligands.[16] The archetypal bisboranetitanocene complex [Cp_2Ti($HBCat)_2$][17] was reacted with phenylsilane resulting in the formation of the σ-silane-σ-borane titanocene complex **F**. The relative orientation of both sigma ligands was determined by NOESY NMR investigation. Hydride exchange was evidenced by the reaction of [Cp_2Ti($DBCat)_2$] with phenylsilane resulting in the partial deuteration of the phenylsilane ligand. A silyldihydroborate intermediate was proposed to explain this H/D scrambling.



Scheme 1. Relevant examples of complexes featuring both Si and B elements around a metal center.

The use of BH_3 adducts of 2-mercaptobenzothiazolyl (mbz) and 2-mercaptopyridyl (mp) in coordination chemistry led to the isolation of a variety of new structures featuring a hydroborate ligand with different transition metal centers.[18] Notable examples are [Cp*Ru(CO)(κ^2-H, S))BH_2(mbz)] and [Rh{κ^3-H,H,S-$(H)_2$BH(mp)}(NBD)] complexes involving Ru–H–B bond in hydroboration reaction.[19-20] Using these ligands, we wished to explore the combined presence of Si-H and B-H bonds at a metal center with a 4-coordinate boron moiety. In the present work, oxidative addition of hydrosilanes ($Ph_2(R)$Si-H) is described with [RuH$(PCy_3)_2${κ^3-H,H,S-$(H)_2BH_3$(L)}] (L = mbz or mp) complexes. In-depth multinuclear NMR and D_2 scrambling established the H/D exchange between B–H and Si–H and Ru–H moieties.

Treatment of [RuH(H_2)Cl$(PCy_3)_2$] with mono-substituted trihydroborate ligands Na[H_3B(L)] (L = mbz, mp) resulted in the formation of ruthenium dihydridoborate complexes **1a** and **1b**, isolated in good yields as a yellow and red powder, respectively (Scheme 2). The spectral features gathered from NMR for **1a** and **1b** (Table S1) and X-Ray diffraction analysis for **1b** indicate a facial arrangement of the H_3B(L) ligand {κ^3-H,H,S} where two of the σ(B–H) bonds of the BH_3 unit and the sulphur atom of the heterocycle coordinate with the ruthenium. One phosphine ligand is in axial position while the other is in the equatorial plane completed by a hydride ligand. Both complexes exhibit similar spectral characteristics. Key NMR parameters of **1a** are highlighted here. The Ru–H resonates at δ –11.98, as a doublet of doublet due to cis interaction with the two phosphines ($^2J_{H\text{-}P}$ of 35.4 and 26.8 Hz) in the ^{1}H NMR spectrum. The three B-H signals appear distinctively: the two Ru–H–B signals at δ –9.72 (d, $^2J_{H\text{-}P}$ = 36.3 Hz) and –4.57 (br s) while the terminal B–H resonates at δ 4.86 as detected by ^{1}H{^{11}B} NMR analysis. The relative arrangement of the hydride and B–H hydrogens around ruthenium was identified using selective decoupling ^{1}H{^{11}B] and ^{1}H-^{31}P{^{1}H} HMQC experiments. The ^{31}P{^{1}H} NMR spectrum reveals an AX pattern with the presence of two doublets at δ 69.4 and 57.8 with cis $^2J_{P\text{-}P}$ of 21.3 Hz, while the ^{11}B{^{1}H} NMR spectrum reveals a singlet at δ 11.7.



Scheme 2. Synthesis of ruthenium (II) dihydridoborate complexes 1a and 1b complexes 1a and 1b.

In the solid-state IR spectrum, the B–H and Ru–H stretching frequencies were respectively identified at 2461 and 1990 cm^{-1} for **1a** and at 2436 and 1959 cm^{-1} for **1b**. Monocrystals of **1b** suitable for X-ray diffraction analysis were obtained from a saturated Et_2O solution at 213 K. In accordance with NMR study in solution, the X-ray diffraction analysis revealed a distorted octahedral geometry containing facial arrangement of the {H_3B(mp)} ligand around the ruthenium center (Figure 1). The two phosphines are cis to one another with ∠P–Ru–P = 105.89(4)°. The Ru–P2 distance of 2.3052(10) Å is shorter compared to the Ru–P1 distance 2.3254(11) Å due to the different trans donor ligands (BH vs S) and the difference between equatorial and axial site occupancy. The Ru–B separation of 2.225(5) Å in **1b** is comparable to those of dihydridoborate complexes such as [Cp*Ru{κ^3-H,H,S-$(H)_2$BH(mbz)}] (2.216(6) Å), and [RuH{(μ-$H)_2$BMeCH_2SMe}$(PCy_3)_2$] (2.266(8) Å) and smaller than the sum of their covalent radii (2.30 Å).[21] The alternating carbon-carbon bond distances in pyridine ring suggest the presence of dearomatized pyridine ring containing 2-thione donor (C1–S1 1.692(4) Å).[22] The bond distances discussed here compare well with the DFT optimized structure of **1b** (Table S7) enabling to ascertain the location of the hydride atoms.

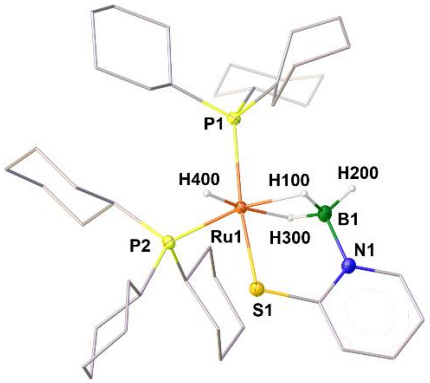
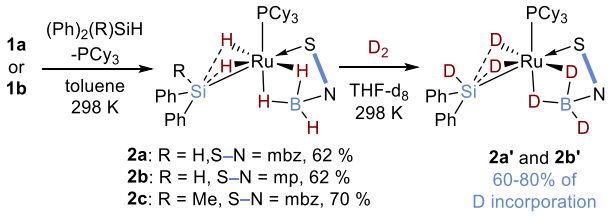


Figure 1. . Solid-state molecular structure of of **1b**. Partial thermal ellipsoids were drawn at 75% probability. Ru-H and B-H hydrogen atoms were located in the difference Fourier map and isotropically refined. Ellipsoids of all the carbon atoms and the hydrogen atoms associated with the carbon atoms were omitted for clarity. Selected bond lengths (Å): Ru1–B1 2.225(5), Ru1–P1 2.3254(11), Ru1–P2 2.3052(10), B1–N1 1.540(6), Ru1–S1 2.3516(11), Ru1–H300 1.82(4), Ru1–H100 1.78(3), Ru1–H400 1.51(4).

Hydrido complexes **1a** and **1b** were reacted with secondary and tertiary silanes. The reactions of **1a** and **1b** with Ph_2SiH_2 led to the formal oxidative addition of the Si–H bond and the displacement of one PCy_3 ligand. The resulting ruthenium (IV) silyl dihydride complexes [$RuH_2(SiPh_2H)(PCy_3)$-{κ^3-H,H,S-$(H)_2$BH(L)}] (L = mbz (**2a**), mp (**2b**)) are shown in Scheme 3. Similarly, complex **2c** [$RuH_2(SiPh_2Me)(PCy_3)$-{κ^3-H,H,S-$(H)_2$BH(mbz)}] was synthesized by the reaction of **1a** with Ph_2MeSiH (Scheme 3).



Scheme 3. Synthesis of the silyl ruthenium (IV) dihydridoborate complexes 2a-c and reactivity toward D_2.

We decided to probe the unique presence of several types of hydrides in these complexes by means of NMR studies and deuteration experiments. NMR spectral characteristics of **2a**, **2b** and **2c** are similar. Key NMR parameters of **2a** are highlighted here. The P and B nuclei were characterized at δ 74.0 and 12.5, respectively, close to the corresponding signals of **1a**. In the ^{29}Si{^{1}H} NMR spectrum, a singlet is noted at δ 5.7 indicating

the formation of a silyl ligand. Figure 2 shows ^{1}H NMR (Figure 2a), 1D HSQC ^{1}H (Figure 2b) and 1D HSQC ^{1}H analyses, with several selective decoupling (Figure 2c-e). While only $J_{P\text{-}H}$ coupling is apparent on the ^{1}H NMR spectrum (Figure 2a), the selective 1D HSQC ^{1}H{^{31}P} experiments (Figure 2c) provided $J_{Si\text{-}H}$ of 12 Hz, supporting weak secondary interactions between silicon and ruthenium hydrides. The Ru–H···Si hypervalent interactions were also characterized by 2D ^{1}H-^{29}Si HMQC experiments.

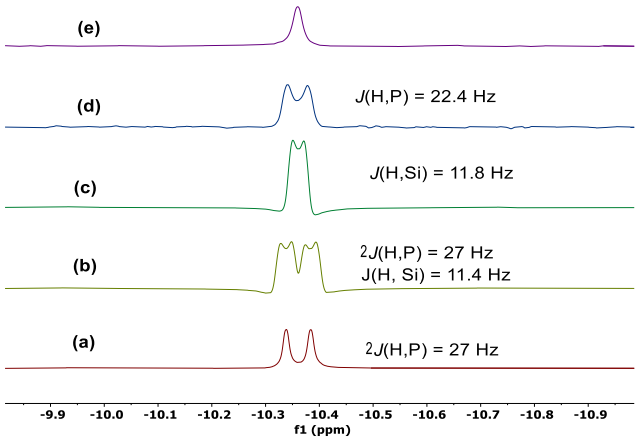


Figure 2. Selective 1D ^{1}H HSQC NMR spectral stack plot of **2a** in tol-d_8 at 298 K. (a) ^{1}H, (b) 1D HSQC selective ^{1}H, (c) ^{1}H{^{31}P}, (d) ^{1}H{^{29}Si} and (e) ^{1}H{^{31}P}{^{29}Si}.

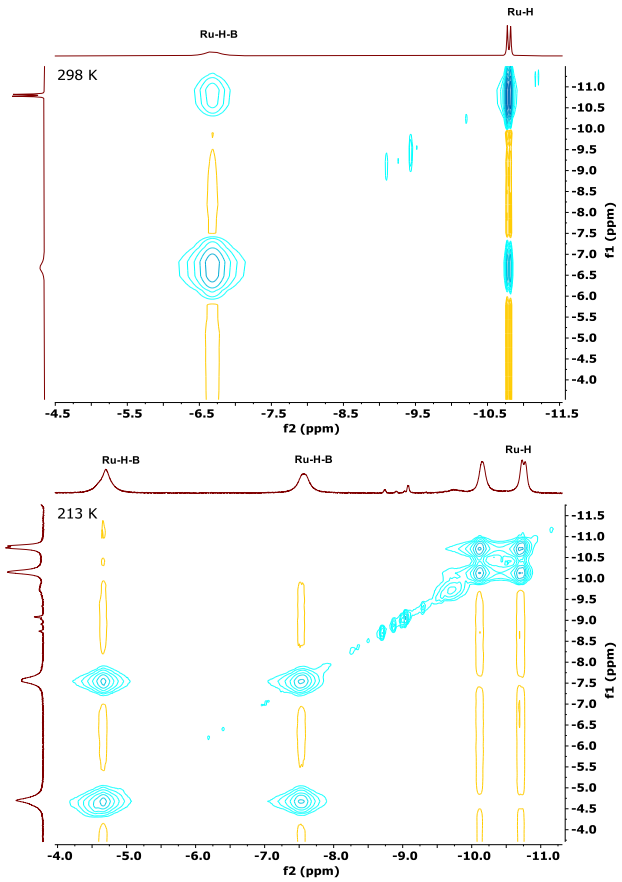


Figure 3. EXSY NMR analyses of Ru–H and Ru–H–B of **2a** at 298 K (top) and 213 K (bottom). (600.47 MHz, d_1 = 1.5 s, mixing time 0.05 s)

At 273 K, the terminal Si–H and B–H appear at δ 6.10 and 5.29, respectively. At this temperature, the two hydrides bonded to Ru (Ru–H) and the two hydrides bridging Ru and B (Ru–H–B) appear equivalent at δ –10.40 and –6.27, respectively (traces in Figure 3 top taken at 298 K). When lowering the temperature to 213 K, the two signals of Ru–H and Ru–H–B resolved to four signals at δ –10.75 (d, $^{2}J_{H\text{-}P}$ 32.6 Hz), –10.15 (s) for the two Ru-H, and at δ –7.57 (s) and –4.70 (s) for the two Ru–H–B. (traces Figure 3, bottom). The integral ratio of these four signals is identical (1:1:1:1). EXSY NMR experiments were then conducted to assess the exchange between the different hydrides (Figure 3). The Ru–H and Ru–H–B hydrides are in exchange at 298 K, (Figure 3, top) but frozen at 213 K. At this lower temperature, the hydrides of same type are still exchanging since cross-linked correlations are observed between the two Ru-H on one hand and the two Ru-H-B on the other hand (Figure 3, bottom).

In the solid-state IR spectrum of **2a**, Ru–*H*–B and Ru–*H* stretching frequencies are measured at 2502, and 2077, 1971 cm^{-1} respectively. Monocrystals suitable for X-ray diffraction analysis were obtained by layering toluene solution of **2a** or **2c** with n-pentane at –35°C. The solid-state molecular structures are shown in Figure 4. The B–H and Ru–H hydrogens of **2a** and **2c** were located in the Fourier map and refined isotropically. The Ru–Si bond distances are of 2.3538(6) and 2.3575(6) Å respectively for **2a** and **2c** and within the range of Ru–SiR$_3$ complexes (Table S3). Si···H–Ru distances of 2.183 and 1.941 Å were measured for **2a** and of 2.001 and 2.063 Å for **2c**. These distances are shorter than the sum of Van der Waals radii of silicon and hydrogen (3.4 Å) and correspond to secondary interactions between silicon and hydrogen atoms (SISHA) (1.9-2.4 Å), in line with small $J_{Si\text{-}H}$ observed in solution.[23] These interactions arise from the electrophilicity and hypervalency of the silicon atom and have been shown to be crucial catalytic intermediates.[24] The silicon atoms are out of the equatorial planes with Si–Ru–H acute angles (74.4(10)°, 63.8(10)° for **2a**; 59.8(8)°, 57.3(9)° for **2c**) in a distorted capped octahedral geometry[25-26] differing from other possible geometries encountered in Ru(silylhydride) complexes.[27-28] The bridging Ru–H–B distances are significantly longer 1.771, 1.823 Å as compared to the terminal Ru–H distances 1.640 and 1.593 Å. Similarly, the terminal B–H distance (1.018 Å) is shorter as compared to bridging Ru–H–B distances (1.224 and 1.286 Å). The geometrical parameters in the optimized structures of **2a** and **2c** are in good agreement with X-ray data (Table S7), and highlight the presence of secondary Si···H–Ru interactions in the range of 1.941-2.183 Å. According to our calculations, NPA charges of Ru-H200 and Ru-H400 in **2a** are notably more positive than the related Ru-H in **1a**.

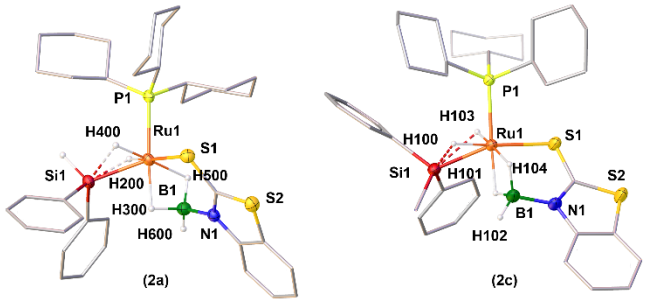


Figure 4. Solid-state molecular structures of **2a** and **2c**. Si-H, Ru-H and B-H hydrogen atoms were located in the difference Fourier map and isotropically refined. Partial thermal ellipsoids were

drawn at 75% probability. Ellipsoids of all the carbon atoms and the hydrogen atoms associated with the carbon atoms were omitted for clarity. The dotted lines represent secondary Si···H–Ru interactions. Selected bond lengths (Å): **2a**: B1–N1 1.520(3), Ru1–P1 2.3007(5), Ru1–B1 2.221(2), Ru1–Si1 2.3538(6), Ru1–S1 2.3837(6), Ru1-H300 1.77(3), Ru1-H500 1.83(2), Ru1-H200 1.64(3), Ru1-H400 1.59(3); **2c**: Ru1–B1 2.224(2), Ru1–P1 2.3173(5), B1–N1 1.533(3), Ru1–S1 2.3838(5), Ru1–Si1 2.3575(6), Ru1–H100 1.54(2), Ru1–H101 1.71(3), Ru1–H104 1.82(3), Ru1–H103 1.51(3).

To explore further the dynamics of the different hydrides, complexes **2a** and **2b** were exposed to 3 atm of D_2 in THF-d_8 at 298 K (Scheme 3). Deuterium incorporation was observed at the Ru–H–B and Ru–H sites, by the disappearance of the signals in ^{1}H NMR and the appearance of deuteride signals in ^{2}H NMR spectroscopy (ESI). The formations of free H–D (δ 4.51) and H_2 (δ 4.54) were noted in the ^{1}H NMR spectrum. For **2a**, after 3 weeks, a maximum deuteration level of 59% and 64% had been reached for Ru–H and Ru–H–B sites, respectively. Moreover, 78% and 69% deuteration of $SiHPh_2$ and terminal B–H hydrogens was also observed respectively. The formation of isotopomers was also reflected in the ^{31}P{^{1}H} NMR spectroscopy where the signals were slightly downfield shifted. H/D exchange for every hydride was also observed by reacting **1a** with D_2SiPh_2, which generated **2a'** within 3 days at room temperature. Similar observations were made for the reactivity of **2b** toward D_2 and for the reactivity of **1b** with D_2SiPh_2.

In conclusion, the synthesis of Ruthenium (II) dihydridoborate complexes 1a-1b, led to the generation of ruthenium (IV) silyl dihydride complexes 2a-2c. The silyl ligand features weak secondary silicon hydrogen interactions (Si···H–Ru, 1.941-2.183 Å) which were characterized by NMR spectroscopy, X-ray diffraction analysis and DFT calculations. These complexes are unique because they exhibit a rare combination of boron, silicon and hydride elements around a single metal center. The present study proved that all hydrides are in exchange in the NMR time scale and undergo scrambling with D_2(g). This was characterized by EXSY and ^{2}H NMR spectroscopy. This study showed that in these new complexes, Si–H bond activation can occur while preserving the dihydroborate ligand. It will be interesting to perform additional reactivity and catalytic studies to evaluate the competition between Si–H and B–H bond activation.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. It includes experimental details, compounds synthesis and characterization.

AUTHOR INFORMATION

Corresponding Author

Sundargopal Ghosh, sghosh@iitm.ac.in,
Sébastien Bontemps sebastien.bontemps@lcc-toulouse.fr

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NOTE

"The authors declare no competing financial interests."

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Oxidative addition of diphenyl- and methyldiphenyl-silanes onto ruthenium-borate complexes **1a**-**b** afforded **2a**-**c** featuring four different hydrogens bonded to the ruthenium. EXSY and H/D scrambling studies showed the rapid exchange between the Ru–H···Si and Ru–H–B hydrogens at 298 K.