

Bifunctional Rhodium Complex Featuring a Silyl-1,8-naphthyridine κ^2Si,N -Chelate Ligand: Cooperation of Metal and Pendant Base for Capture and Bond-weakening of BH_3

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A dirhodium complex bearing a newly-designed silyl-1,8-naphthyridine ligand (napySi), $[\text{Rh}(\kappa^2Si,N\text{-napySi})(\text{H})(\mu\text{-Cl})]_2$ (**1**), was synthesized. Reaction of complex **1** with excess $\text{BH}_3\bullet\text{SMe}_2$ afforded a mononuclear borane adduct $\text{Rh}[\kappa^4Si,N,H,\text{H-napySi}](\text{BH}_3)(\text{H})\text{Cl}$ (**2**), revealing that rhodium and the uncoordinated naphthyridine nitrogen cooperatively captured BH_3 and weakened its two B–H bonds. Complex **2** contains a $\text{Rh}(\mu\text{-H})_2\text{B}$ core composed of two Rh–H–B 3-center 2-electron (3c–2e) bonds where one Rh–H interaction is considerably weakened by strong *trans*-influence of the silyl ligand moiety.

Keywords: Bifunctional complex | Silyl ligand | 1,8-Naphthyridine backbone

Cooperative bond activation by a metal center and an adjacent basic site in bifunctional transition-metal complexes has recently attracted considerable attention as a useful concept for design and synthesis of catalysts.¹ For instance, cooperation of a coordinatively-unsaturated metal center (Lewis acid) and an uncoordinated ligand moiety (Lewis base) enables metal complexes to function as frustrated Lewis pairs (FLPs) for bond-activation reactions.^{1c,1d} Carmona, Poveda et al. reported that a coordinatively-unsaturated (2-pyridyl)iridium complex **A** (Chart 1a),² generated from a 2-pyridylidene(phenyl) complex by elimination of benzene, cleaved the H–H bond of dihydrogen by cooperation of the Ir center and the pyridine nitrogen to give a hydrido(carbene) complex.^{2b} Bera et al. also developed a rhodium complex ligated by a 1,8-naphthyridine (napy) substituted *N*-heterocyclic carbene (complex **B** in Chart 1a)³ as a catalyst for hydration of nitriles through cooperative O–H activation of H_2O by the Rh center and the nitrogen at the 1-position of the napy group.⁴ In these reactions, generation of a vacant coordination site on a metal center near a

basic nitrogen site is thought to be the key to success in cooperative bond activation.

In the present study, we designed a new FLP-type bifunctional metal complex by employing a methylene-linked silyl-1,8-naphthyridine chelate ligand “napySi” (complex **C** in Chart 1b).⁵ Since the napy backbone is rigid, napySi can coordinate to a single metal ion with a κ^2Si,N -coordination mode, and the nitrogen at the 8-position of napy remains uncoordinated.^{3,4} Furthermore, due to strong *trans*-influence of the silyl ligand moiety of napySi,⁶ a vacant coordination site trans to this moiety is expected to be generated easily and located near the uncoordinated basic nitrogen of napy (Chart 1b). Herein, we report the synthesis of a rhodium–napySi complex and its reaction with $\text{BH}_3\bullet\text{SMe}_2$ leading to capture and bond-weakening of BH_3 through formation of a B–N(napy) dative bond and two Rh–H–B 3-center 2-electron (3c–2e) bonds.

Treatment of a ligand precursor, 2-(di-*tert*-butylsilyl)methyl-7-methyl-1,8-naphthyridine (napySi(H)), with 0.5 molar equiv. of $[\text{RhCl}(\text{coe})_2]_2$ in toluene at room temperature for 24 h gave a dirhodium complex $[\text{Rh}(\kappa^2Si,N\text{-napySi})(\text{H})(\mu\text{-Cl})]_2$ (**1**) as yellow crystals in 71% yield via Si–H oxidative addition and dissociation of all COE molecules (Scheme 1). Both of the ^1H and $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra of **1** show ^{103}Rh -coupled doublet signals; i.e. the hydrido hydrogen signal at -20.15 ppm ($^1J_{\text{RhH}} = 30.4\text{ Hz}$) and the silyl silicon signal at 79.4 ppm ($^1J_{\text{RhSi}} = 37\text{ Hz}$).

Single crystal X-ray analysis of **1** revealed the chlorido-bridged dirhodium structure having a crystallographic C_2 axis (Figure 1): Two $\text{Rh}(\text{napySi})(\text{H})\text{Cl}$ fragments are connected through a butterfly-like $\text{Rh}_2(\mu\text{-Cl})_2$ core.⁷ Each of the Rh centers adopts a distorted square pyramidal geometry with a κ^2Si,N -type napySi ligand where the silyl coordinating moiety with strong

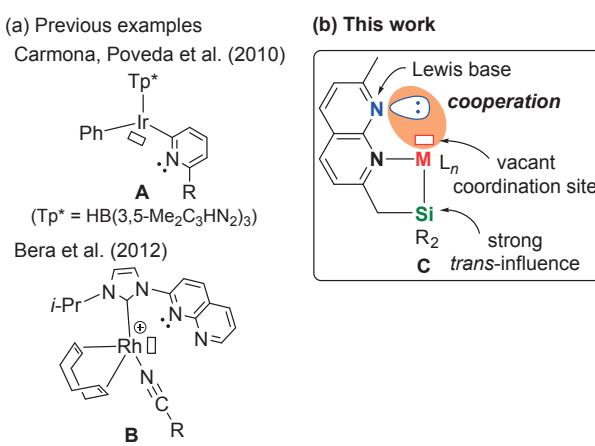
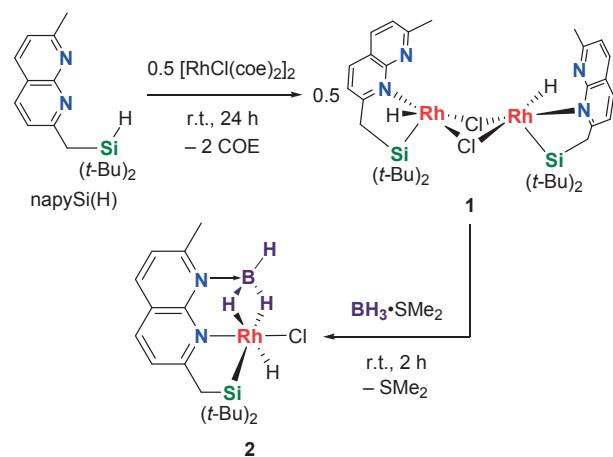


Chart 1.



Scheme 1. Synthesis of Rh-napySi complex **1** and its reaction with $\text{BH}_3\bullet\text{SMe}_2$ to give a borane adduct **2**.

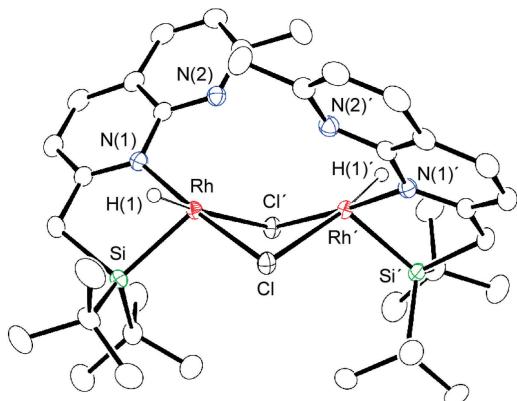


Figure 1. Molecular structure of **1**. Thermal ellipsoids are drawn at the 50% probability level, and all hydrogen atoms except the hydrido hydrogen are omitted for clarity. Selected bond distances (\AA) and angles ($^\circ$): Rh–Si 2.2648(4), Rh–N(1) 2.0138(12), Rh–Cl 2.3499(3), Rh–Cl' 2.5568(4), Rh–H(1) 1.47(2), Rh...Rh' 3.3486(2), Rh...N(2) 2.8785(13), Si–Rh–N(1) 83.99(4), Si–Rh–Cl 100.198(14), Si–Rh–Cl' 112.785(14), Si–Rh–H(1) 74.4(9), N(1)–Rh–Cl 175.74(4), Cl'–Rh–H(1) 172.0(8), Rh–Cl–Rh' 85.962(12).

trans-influence occupies the apical position. Thus, the vacant coordination site on Rh is located *trans* to the silyl silicon, forming a reaction pocket between this site and the uncoordinated basic nitrogen N(2) (Rh...N(2) 2.8785(13) \AA) as expected (Chart 1b). The Rh–Cl' distance (2.5568(4) \AA) is significantly longer than that of Rh–Cl (2.3499(3) \AA). This is obviously because the *trans*-influence of the hydrido hydrogen H(1) *trans* to Cl' is stronger than that of the naphthyridine nitrogen N(1) *trans* to Cl.

Complex **1** readily reacted with excess $\text{BH}_3\bullet\text{SMe}_2$ at room temperature within 2 h to give a mononuclear BH_3 adduct $\text{Rh}[\kappa^4\text{Si},\text{N},\text{H},\text{H}-\text{naphSi}(\text{BH}_3)](\text{H})\text{Cl}$ (**2**) as a red powder in 70% isolated yield (Scheme 1). In this reaction, capture and bond-weakening of BH_3 occurred through rhodium–nitrogen cooperation, accompanied by cleavage of the chloride bridge bonds of complex **1**.

The molecular structure of **2** determined by X-ray crystallography (Figures 2 and S13) clearly shows that complex **2** contains a $\text{Rh}(\mu-\text{H})_2\text{B}$ core supported by a $\mu\text{-}\kappa^2\text{Si},\text{N}:\kappa^1\text{N}$ -type naphSi ligand.^{7,8} The positions of all hydrogen atoms of BH_3 and Rh–H were located from a differential Fourier map and refined. The rhodium center adopts a distorted octahedral geometry in which the Si–Rh–H(1) and H(2)–Rh–H(3) angles (ca. 60°) are much narrower than the Si–Rh–H(2) and H(1)–Rh–H(3) angles (ca. 120°). The boron center of BH_3 is coordinated to the naphthyridine nitrogen N(2) (B–N(2) 1.581(4) \AA) and is consequently pyramidalized. The following three structural features indicate that the $\text{Rh}(\mu-\text{H})_2\text{B}$ core consists of two Rh–H–B 3c–2e bonds: (1) The Rh–H(2) and Rh–H(3) distances (1.88(3) and 1.97(4) \AA , respectively) are longer than the terminal Rh–H(1) bond distance (1.54(4) \AA) and are similar to those (ca. 1.8–2.2 \AA) of bridging-ligand-supported $\text{Rh}(\mu-\text{H})_2\text{B}$ cores of previously-reported complexes.⁸ (2) The B–H(2) and B–H(3) distances (1.18(3) and 1.20(4) \AA , respectively) are also slightly longer than the terminal B–H(4) bond (1.09(4) \AA). (3) The Rh–H(2)–B and Rh–H(3)–B bonds are seriously bent (94(2) and 89(2) $^\circ$, respectively) and the bond angles are close to each

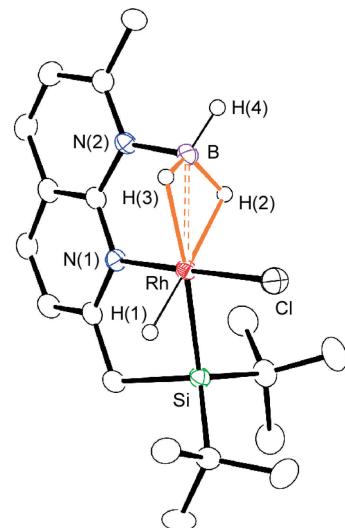
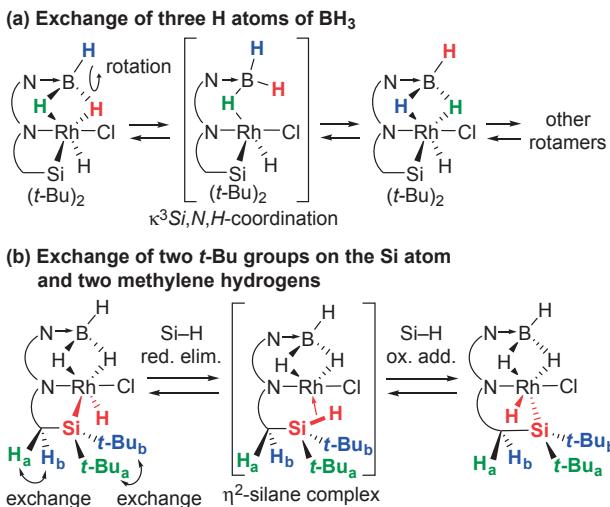


Figure 2. Molecular structure of **2**. Thermal ellipsoids are drawn at the 50% probability level, and all hydrogen atoms except the hydrido and BH_3 hydrogens are omitted for clarity. Selected bond distances (\AA) and angles ($^\circ$): Rh–Si 2.2990(8), Rh–N(1) 2.031(2), Rh–Cl 2.3389(8), Rh–B 2.283(3), Rh–H(1) 1.54(4), Rh–H(2) 1.88(3), Rh–H(3) 1.97(4), B–N(2) 1.581(4), B–H(2) 1.18(3), B–H(3) 1.20(4), B–H(4) 1.09(4), Si–H(1) 2.02(4); Si–Rh–N(1) 84.77(7), Si–Rh–Cl 95.01(3), N(1)–Rh–Cl 177.66(8), Si–Rh–B 149.93(10), N(1)–Rh–B 79.47(11), Rh–B–N(2) 103.51(18), Si–Rh–H(1) 59.8(15), Si–Rh–H(2) 121.9(10), Si–Rh–H(3) 175.4(11), H(1)–Rh–H(2) 177.2(17), H(1)–Rh–H(3) 117.2(19), H(2)–Rh–H(3) 61.0(15), Rh–H(2)–B 94(2), Rh–H(3)–B 89(2).

other. In other words, the two B–H bonds of BH_3 are weakened by coordination.

To gain further insight into the bonding aspect of the $\text{Rh}(\mu-\text{H})_2\text{B}$ core, DFT calculations were performed on **2** (see the Supporting Information). The geometry of the optimized structure of **2**, abbreviated as **2-opt**, is nearly identical with that of the X-ray crystal structure (Table S3). It should be noted that the optimized Rh–H(3) (trans to Si) bond distance (2.050 \AA) is significantly longer than the Rh–H(2) (trans to H) bond distance (1.910 \AA) by 0.14 \AA . Moreover, the Wiberg bond index (WBI) of the former (0.12) is smaller than that of the latter (0.16) (Figure S15). These calculation results show that the Rh–H(3) bond is weaker than the Rh–H(2) bond. This is attributable to the difference of *trans*-influence: The *trans*-influence of the silyl ligand is generally stronger than that of the hydrido ligand.⁶

The three hydrogens of the BH_3 moiety of **2** were also characterized by solution NMR spectroscopy. Whereas the ^1H NMR spectrum of **2** in CD_2Cl_2 at room temperature showed no signals assignable to the BH_3 hydrogens, at low temperature (210 K), three inequivalent broad signals of BH_3 were observed at –1.47, 3.23, and 4.18 ppm with a 1:1:1 intensity ratio (Figure S11). This indicates that complex **2** exhibits a dynamic behavior in solution via exchange of the BH_3 hydrogens.^{8a,8b,8c–8g} This exchange is possibly caused by rotation of the BH_3 moiety around the B–N dative bond via interchange between $\kappa^4\text{Si},\text{N},\text{H},\text{H}$ and $\kappa^3\text{Si},\text{N},\text{H}$ coordination modes of naphSi(BH_3) (Scheme 2a).^{8a,8b,8c–8g} To obtain more simplified BH_3 signals, a ^{11}B decoupled ^1H ($^1\text{H}\{^{11}\text{B}\}$) NMR spectrum was measured at



Scheme 2. Possible mechanisms for the dynamic behaviors of **2** via (a) exchange of three H atoms of BH_3 and (b) exchange of two *t*-Bu groups and two methylene hydrogens.

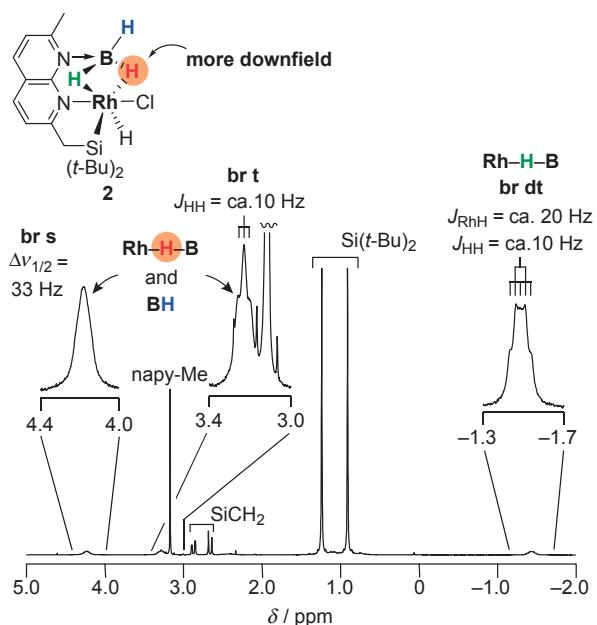


Figure 3. $^1\text{H}\{^{11}\text{B}\}$ NMR spectrum of **2** in the range of 5 to -2 ppm involving Rh–H–B and B–H signals (400 MHz, 210 K, CD_2Cl_2).

210 K (Figure 3) in which the BH_3 signals became significantly sharpened and were observed at -1.48 , 3.23 , and 4.18 ppm . The most upfield-shifted signal appeared as a broad double triplet coupled not only with rhodium (${}^1J_{\text{RhH}} = \text{ca. } 20\text{ Hz}$) but also with the terminal Rh–H hydrogen and one of the other BH_3 hydrogens ($J_{\text{HH}} = \text{ca. } 10\text{ Hz}$ each). The existence of the coupling with Rh–H was confirmed by observation of a ^1H – ^1H COSY cross peak (Figure S12) with the Rh–H signal that appears at -14.88 ppm as a broad doublet (${}^1J_{\text{RhH}} = 28.2\text{ Hz}$ and ${}^3J_{\text{HH}} = 9.4\text{ Hz}$) in the $^1\text{H}\{^{11}\text{B}\}$ NMR spectrum (Figure S11). We assigned the BH_3 signal at -1.49 ppm to Rh–H–B (trans to H(hydrido)) based on the observation of the significant coupling with Rh–H and on

comparison with the Rh–H–B ^1H NMR signal of a related complex $\text{Rh}[\kappa^3N,\text{H},\text{H}-2-(\text{methylamido})\text{pyridine}(\text{BH}_3)](\text{cod})$ (-1.63 ppm ; $J_{\text{RhH}} = 23.6\text{ Hz}$ and $J_{\text{HH}} = 12.5\text{ Hz}$).^{8a} The other two BH_3 signals at 3.23 and 4.18 ppm appeared as a broad triplet ($J = \text{ca. } 10\text{ Hz}$) and a broad singlet ($\Delta\nu_{1/2} = 33\text{ Hz}$), respectively. Although we have not determined which of them are assignable to the Rh–H–B (trans to Si) hydrogen, both the BH_3 signals are considerably shifted downfield in comparison with that of the Rh–H–B (trans to H) hydrogen.

Complex **2** was also found to exhibit other dynamic behavior involving exchange of two *t*-Bu groups and two methylene hydrogens of the napySi ligand.⁹ At room temperature, the ^1H NMR spectrum of **2** shows a broad singlet signal for each of the $\text{Si}(t\text{-Bu})_2$ and SiCH_2 protons of napySi at 1.12 and 2.75 ppm , respectively (Figure S11). Upon cooling the sample to 210 K, each of these signals splits into two signals (0.86 and 1.19 ppm) as singlets for $\text{Si}(t\text{-Bu})_2$ and into those (2.61 and 2.82 ppm) as a doublet and a doublet for SiCH_2 .¹⁰ This behavior possibly occurs through migration of the terminal hydrido ligand between the upper and lower sides of the naphthyridine plane via an η^2 -silane complex intermediate generated by partial Si–H reductive elimination (Scheme 2b). The facility of the dynamic behavior of **2** via Si–H reductive elimination is supported by the following structural feature: The Si–H(hydrido) interatomic distances of $2.02(4)\text{ \AA}$ (X-ray) and 2.136 \AA (DFT) imply the existence of secondary interactions between silicon and hydrogen (Si–H distance: 1.9 – 2.4 \AA).^{11,12}

In conclusion, we designed a new silyl-1,8-naphthyridine Si,N -chelate ligand “napySi” and synthesized bifunctional dirhodium complex **1** utilizing napySi. The reaction of **1** with $\text{BH}_3\cdot\text{SMe}_2$ led to capture and bond-weakening of BH_3 through cooperation of the Rh center with a vacant coordination site and the uncoordinated naphthyridine nitrogen site to give adduct **2**. The Rh–H bond trans to Si in the $\text{Rh}(\mu\text{-H})_2\text{B}$ core of **2** was weakened by strong *trans*-influence of the silyl coordinating moiety. This implies that complex **2** easily generates coordinatively unsaturated species by cleavage of the Rh–H bond trans to Si. Further studies on reactivity of complexes **1** and **2** toward organic compounds are in progress.

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Supporting Information is available on <https://doi.org/10.1246/cl.200489>.

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