Rhodium Chemistry

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Isolation of a PBP-Pincer Rhodium Complex Stabilized by an Intermolecular C–H σ Coordination as the Fourth Ligand**

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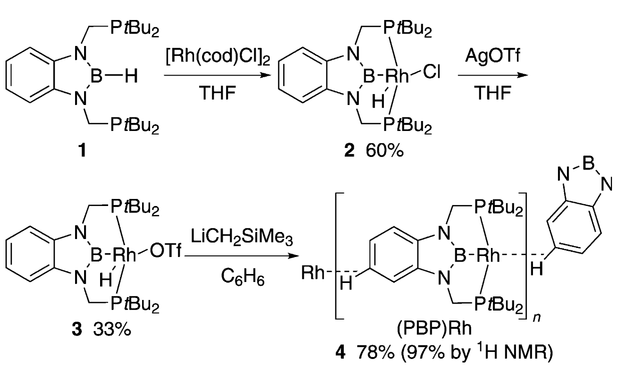
Coordinatively unsaturated transition metal complexes are one of the most important intermediates in organometallic chemistry because of their reactivity towards a variety of ligands. A vacant coordination site on the metal center can accept a substrate or can cleave a variety of chemical bonds to allow metal-catalyzed reactions. Among the bond cleavage reactions, oxidative addition[1] of non-polar (H–H, C–H) or polar (O–H, N–H) bonds to coordinatively unsaturated complexes is one of the most important elementary reactions. In contrast to the well-studied H–H bond cleavage employed for homogeneous hydrogenation in industry,[2] the other three reactions are still not ready to be used in bulk processes despite their potential for new industrial uses, such as the dehydrogenation of alkanes and the addition of heteroatoms to C–C multiple bonds.[3] Recently, rhodium and iridium complexes with a meridional and tridentate pincer ligand have gained attention because of their ability to undergo oxidative addition to these C–C multiple bonds.[3b,4] From a mechanistic point of view, a T-shaped, 14-electron pincer complex possessing an open coordination site is an assumed intermediate in the reaction of such complexes with X–H bonds (X = C or a heteroatom). Although some pincer-ligated fourth period transition metal complexes possessing a T shape have been synthesized and characterized as stable species, owing to the partial occupation of a d orbital with high-spin character,[5] similar fifth and sixth period transition metal complexes have been elusive because of their high reactivity at the vacant d orbital on the metal center. As the only exception and as a model of such a T-shaped rhodium complex, a methane-coordinated cationic $[(PNP)Rh(CH_4)]^+$ species with a weak C–H σ coordination and its dynamic properties were characterized by NMR spectroscopy.[6]

Recently, we have reported the synthesis of a boron-containing PBP pincer ligand and its complexation with iridium metal to show the strong σ-donation ability of the PBP ligand.[7] Considering the very strong *trans* influence of the boryl ligand, a low-coordinated species having a vacant site in the position *trans* to the boryl ligand may be stabilized. Herein, we report the synthesis, crystal structures, and reactivity of a PBP-rhodium complex stabilized by intermolecular C-H σ-coordination, which acts as a fourth ligand.

A PBP pincer ligand was introduced to a rhodium center by the reaction of precursor hydroborane **1** with $[Rh(cod)Cl]_2$ (cod = 1,5-cyclooctadiene) to give the corresponding [(PBP)Rh(H)]Cl complex **2** in 60 % yield (Scheme 1). Experimental and theoretical study of **2** showed that **2** was a boryl complex possessing a very weak B–H interaction, as can be seen in the following data. The rhodium complex **2** showed a characteristic hydride signal at δ_H −22.09 as a broad doublet of triplets resonance in the ^1H NMR, coupled with ^{31}P, ^{103}Rh, and ^{11}B. On the other hand, decoupling of the ^{11}B nucleus in the ^1H NMR spectra induced a sharpening of the hydride signal (Figure 1). A similar sharpening of signals in the hydride region of the $^1H\{^{11}B\}$ NMR spectra was reported with related σ-borane complexes.[8] This apparent spin communication between hydrogen and boron atoms is in contrast to the case of the corresponding [(PBP)Ir(H)]Cl complex.[7] Reflecting its symmetrical structure, the ^{31}P nuclei in **2** resonated as a doublet signal coupled with ^{103}Rh in their ^{31}P NMR spectra. The solid state structure of **2** was unambiguously determined by X-ray crystallography to show its mononuclear structure (Figure 2). The difference Fourier



Scheme 1. Syntheses of PBP-pincer Rh complexes. cod = 1,5-cyclooctadiene, Tf = trifluoromethanesulfonate.

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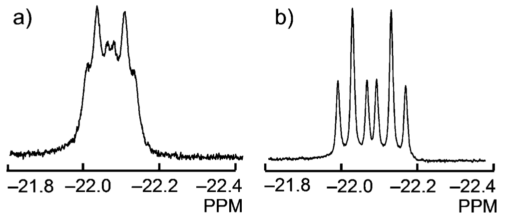


Figure 1. Hydride signals of **2** observed in a) ^{1}H and b) $^{1}H\{^{11}B\}$ NMR spectra.

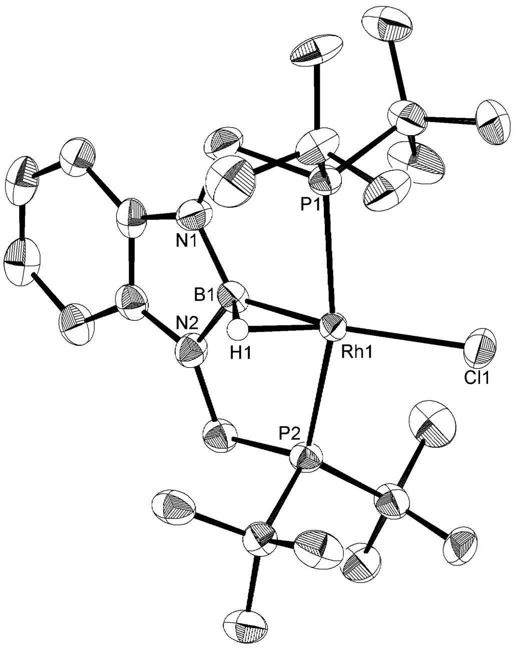


Figure 2. ORTEP drawing of **2**. Thermal ellipsoids set at 50% probability; hydrogen atoms, except H1, are omitted for clarity.

map of **2** showed that the Rh–H bond leans against the boron atom, indicating a contribution of a borane–Rh^{I} type structure.[9] In contrast to the typical σ-borane complexes, the B–Rh bond in **2** (1.980(7) Å) is considerably shorter, which shows a strong two-center–two-electron bond between the boron and rhodium atoms. A metal–hydride vibration band in the IR spectrum of **2** appeared at 2122 cm^{-1}, which is higher than those of typical bridging M-H-B bands observed around 1600 cm^{-1} in σ-borane complexes,[9a] probably owing to the more dominant Rh-H character of **2**. The proximity between the boron atom of the PBP ligand and the hydrogen atom attached to the rhodium center was confirmed by a DFT calculation. The optimized structure of **2** reproduced the experimental structure with apparently short B–H distances (1.5696 Å for optimized **2**), in contrast to the previously reported B–H distance (2.0191 Å) of [(PBP)Ir(H)]Cl.[7a] The calculated vibrational frequency at 2146 cm^{-1} corresponded to the M–H stretch and was consistent with the experimentally observed value. The addition of silver triflate to **2** induced an anion exchange from chloride to triflate to form [(PBP)Rh(H)]OTf complex **3** in 33% yield (Scheme 1; Tf = trifluoromethanesulfonate). All the features of **3** in the spectroscopic, crystallographic, and theoretical studies were similar to those of **2** (see the Supporting Information).

Treatment of **3** with 1 equiv of $LiCH_2SiMe_3$ in C_6H_6 induced reduction at the rhodium center to Rh^{I} by deprotonation and elimination of trifluoromethanesulfonate (Scheme 1). The resulting product was isolated as a crystalline compound in 78% yield and the crystal was structurally characterized to include a unit of (PBP)Rh **4** as an asymmetric unit (Figure 3). Selected bond distances and angles in **4** were summarized in Table 1 with **2** as a reference compound.

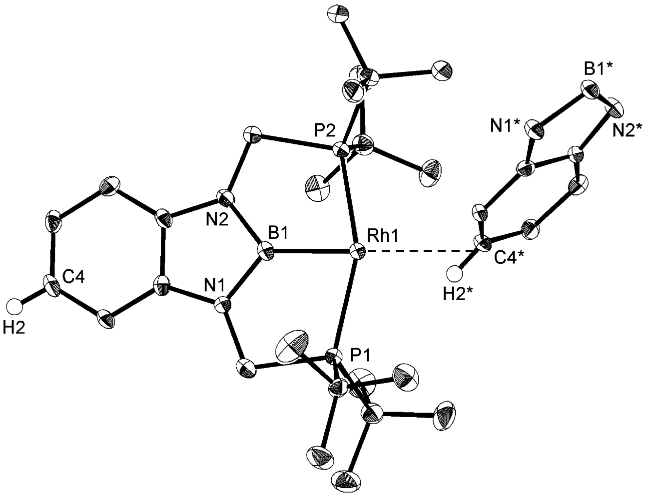


Figure 3. ORTEP drawing of **4**. Thermal ellipsoids set at 50% probability; hydrogen atoms, except H2, are omitted for clarity. A part of the adjacent molecule (numbered with asterisks) shows an intermolecular interaction with **4** (-----).

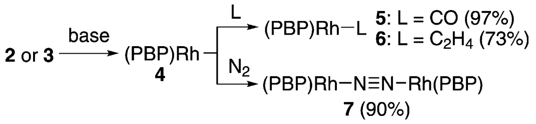
Table 1: Selected bond distances [Å] and angles [°] of **2** and **4**.[a]

Complex	B–Rh	P–Rh	B–N	P-Rh-P	N-B-N
2	1.980(7)	2.3417(16) 2.3431(16)	1.412(9) 1.434(8)	158.08(6)	107.1(6)
4	1.948(3)	2.2924(9) 2.2991(8)	1.448(3) 1.449(3)	155.11(2)	103.70(19)

[a] Sum of angles around boron is 359.9° for complex **2** and 360.0° for complex **4**.

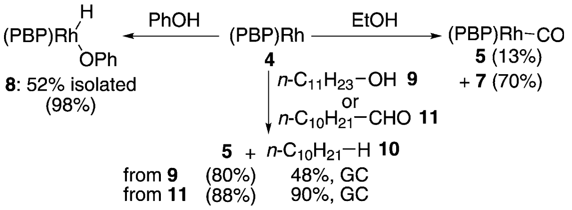
In the crystal lattice, **4** has an intermolecular C–H σ interaction[10] (Rh1–H2* = 2.18(2) Å, Rh1–C4* = 2.766(2) Å) between Rh and the C–H bond of the benzene ring to form an infinite network structure. Complex **4** is also a rare example of a crystallographically characterized intermolecular C–H σ complex of a benzene ring. The T-shaped structure of **4** can be considered as a model of a reactive intermediate, which activates the C–H bond of an alkane, in a catalytic transfer/dehydrogenation reaction using PCP-pincer Ir complexes.[3b] The coexistence of this complex with various aromatic compounds, such as benzene, toluene, and naphthalene, in the recrystallization procedure resulted in no incorporation of these aromatic molecules, although a similar intermolecular interaction would be anticipated. The Rh–B and Rh–P distances in **4** are shorter than those in **2**, indicating stronger back-donation from Rh^{I} to the B or P atoms in **4**. In accord with this shortening, the angles around the Rh and B centers are also perturbed. One might expect that four distinct aromatic signals would be observed in the ^{1}H NMR spectrum of **4** if the network structure remained intact in solution. In fact, however, C_6D_6, [D_{14}]methylcyclohexane, and [D_8]toluene solutions of **4** showed only two aromatic CH signals in the ^{1}H NMR spectrum. Cooling the [D_8]toluene solution down to −90 °C did not cause any change in peak shape. This suggests either 1) rapid exchange of intermolecular interaction with solvents, or 2) the intermolecular interaction does not exist in solution. The ^{31}P NMR spectrum, which shows a larger J_{RhP} (192 Hz) compared to that of **3** (124 Hz), was also informative and supports the existence of the Rh$^{\mathrm{I}}$ species in solution.[11] DFT calculations of monomeric **4** without the network structure and the **4**–C_6H_6 complex were performed for an estimation of the complexation energy between the three-coordinate structure of **4** and the C−H bond of benzene and was found to be 12.1 kcal mol^{-1} (see the Supporting Information). This value was slightly larger than the calculated methane-complexation energy of 7.3 kcal mol^{-1} with the B3LYP method for the [(PNP)Rh(CH$_4$)]$^+$ complex.[6] Isolation of **4** enabled us to confirm the ^{1}H NMR yield for the formation of **4** from **3** as 97 %. This near-quantitative formation of **4** from **3** allowed us to prepare **4** from **3** in situ to estimate the reactivity of **4**.

Complex **4** easily reacted with π-acceptor ligands, such as CO or ethylene, to give the corresponding 16-electron square-planar Rh complex [(PBP)Rh(L)], where L = CO (**5**) or ethylene (**6**). These species formed similar structures to PCP or PNP pincer Rh$^{\mathrm{I}}$ complexes.[12] Complexes **5** and **6** could be independently synthesized by a sequential reaction of **2** or **3** with base, followed by the addition of the desired L species (Scheme 2). Both complexes were structurally characterized by X-ray crystallographic analysis (see the Supporting Information). The characteristic bond length and carbonyl vibration of **5** (C≡O = 1.142(4) Å; ν_{CO} = 1933 cm^{-1}) obtained from X-ray and IR analysis showed that the diaminoboryl ligand has a weak π-acceptor character similar to that of the benzene-based PCP system (C≡O = 1.148(4) Å; ν_{CO} = 1931 cm^{-1}). The shorter C=C bond (1.366(9) Å) of the ethylene ligand in **6** was compared with that of the previously reported [(PBP)Ir(C$_2$H$_4$)] (1.393(5) Å)[7a] to show that the Rh atom may be less π basic than the Ir atom.[13] Exposure of **4** to N$_2$ afforded dinitrogen-bridged dinuclear complex **7**, as was confirmed by X-ray analysis (see the Supporting Information). In contrast to the case of the PCP-ligated Ir complex,[14] a solution of **7** did not give any mononuclear terminal dinitrogen complex upon exposure to N$_2$ atmosphere. The N≡N bond length (1.106(4) Å) in **7** is comparable to that in [(PCP)Rh-N≡N-Rh(PCP)] (1.108(3) Å),[12d] but is shorter than that in [(PCP)Ir-N≡N-Ir(PCP)] (1.134(3) Å),[14b] which shows both a similar ability between the diaminoboryl ligand and the phenyl ligand to act as a π acceptor, and the weaker π basicity of Rh vs. Ir. The Raman N≡N stretch (2063 cm^{-1}) of **7** was higher than that of the corresponding [(PCP)Ir-N≡N-Ir(PCP)] (1979 cm^{-1}) [14b] in the solid state, which again supports the weaker π basicity of Rh vs. Ir.



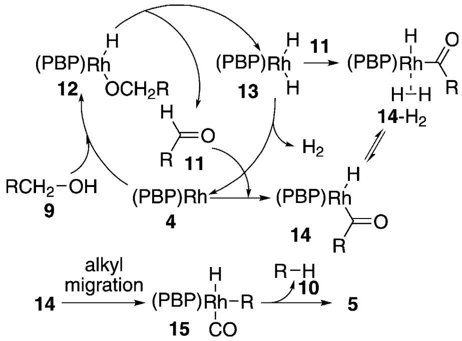
Scheme 2. Reaction of (PBP)Rh (**4**) generated in situ with π-acceptor ligands. Yields from **4** given in parentheses are estimated by ^{1}H NMR spectroscopy.

Rhodium complex **4** reacted with phenol to give hydrido(phenoxo)rhodium complex **8** by an oxidative addition to an O−H bond (Scheme 3). Rhodium complex **8** was characterized by NMR and IR spectroscopy, as well as X-ray crystallography (See the Supporting Information). The behavior of the hydride ligand in **8** was similar to that of **2** and **3**: a B–H interaction was observed in the ^{1}H NMR spectrum, X-ray crystallographic analysis, and DFT calculations. The oxidative addition of an O−H bond to **4** is remarkably fast and finished in 5 min at −78 °C to give **8**. This is in contrast to the reported oxidative addition of a phenolic O−H bond to [Ir(cod)(PMe$_3$)$_3$]Cl, which required 3 h at 60 °C to afford [(PMe$_3$)$_3$Ir(OPh)(H)]Cl.[15] The higher reactivity of **8** may be attributed to the existence of a vacant coordination site at the Rh center in **4**. On the other hand, the reaction of **4** with EtOH in C_6D_6 at room temperature gave Rh$^{\mathrm{I}}$ carbonyl complex **5** in 13 % yield along with formation of dinitrogen complex **7**, which may be generated by contamination by dinitrogen during the injection of EtOH to an argon-filled NMR tube under air (Scheme 3). The use of longer-chain 1-undecanol **9** in place of EtOH enabled us to confirm the formation of decane **10** (48 %) with carbonyl complex **5** (80 %). Furthermore, addition of 1-undecanal **11** (which is a possible intermediate; see below) to **4** also produced decane **10** (90 %) with carbonyl complex **5** (88 %).



Scheme 3. Reaction of **4** with OH and aldehyde functionality. Yields given in parentheses are estimated by ^{1}H NMR spectroscopy.

Scheme 4 explains our proposed mechanism for the formation of **5** according to the literature describing similar reactions.[16] Considering the reaction of **4** with phenol (Scheme 3), the reaction of **4** with an alcohol should generate hydrido(alkoxo) Rh$^{\mathrm{III}}$ complex **12** through an oxidative addition to an O−H bond. The subsequent β-hydride elimination of **12** leads to the formation of aldehyde **11** and dihydrido complex **13**. Loss of dihydrogen from **13** regenerates Rh complex **4**. Then oxidative addition of the C−H bond of aldehyde **11** to **4** gives hydridoacyl complex **14**. Migration of the alkyl group in **14** affords the alkylhydrido Rh$^{\mathrm{III}}$ carbonyl complex **15**. Subsequent reductive elimination of alkane **10** from **15** generates the carbonyl complex **5**. The



Scheme 4. Proposed reaction mechanism for the formation of **5** from 1-undecanol (R = $C_{10}H_{21}$) and **4**.

rapid elimination of alkane from **15** is in contrast to a similar reductive elimination of CH_4 from [(PNP)Ir(H)(CH_3)CO] that required irradiation by light.[17] To support this mechanism, a tentative confirmation of the intermediacy of **13** and **14**-H_2 was achieved. Formation of **13** was confirmed by monitoring a reaction of **4** with dihydrogen and the subsequent evaluation with ^{1}H and ^{31}P NMR spectroscopy. The addition of 1-undecanal to **13** immediately induced the generation of **14**-H_2. This species was characterized both by ^{1}H NMR spectroscopy, which confirmed that the α-methylene proton in the spectrum appeared as a sharp triplet without coupling to Rh and P nuclei,[18] and by observing the characteristic vibrations of the acyl carbonyl group, metal–hydride, and σ-coordinating dihydrogen ligand in the IR spectrum (see the Supporting Information). Leaving a solution of **14**-H_2 at room temperature for 5 h afforded the rhodium carbonyl complex **5**.

In summary, rhodium metal was introduced to the boron-containing PBP pincer ligand system. The complexes [(PBP)Rh(H)]Cl and [(PBP)Rh(H)]OTf showed weak interaction between the boron atom and hydride ligand. Treatment of [(PBP)Rh(H)]OTf with a base afforded a T-shaped, 14-electron rhodium complex stabilized by an intermolecular interaction between the rhodium metal and the C–H bond of another molecule in the crystal lattice. The T-shaped molecule easily reacted with π-acceptor ligands to form the corresponding square planar complexes. In the reaction of the T-shaped complex with phenol or a primary alkyl alcohol, the complex underwent oxidative addition to the O–H bond of the alcohol to give the corresponding hydrido-phenoxido Rh^{III} complex or carbonyl Rh^{I} complex, respectively.

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