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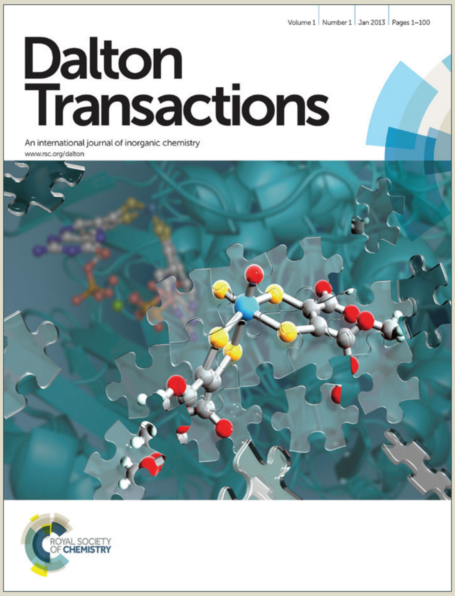

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C–H and H–H Bond Activation via Ligand Dearomatization/Rearomatization of aPN^{3}P–Rhodium(I) Complex

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A neutral complex PN^{3}P-Rh(I)Cl(**2**) was preparedfrom a reaction of the PN^{3}P pincer ligand (**1**) with $[Rh(COD)Cl]_2$ (COD =1,5-cyclooctadiene). Upon treatment with a suitable base,H–H and C_{sp^2}–H activation reactions can be achieved through the deprotonation/reprotonation of one of the N–H arms and dearomatization/rearomatization of the central pyridine ring with the oxidation state of Rh remaining I.

There have been increasing research interests in PNP-type pincer rhodium complexes because of thehighly electron-donating properties of the ligands that could enhance the reactivity of Rh metal toward C–C, C–halide, C–H, O–H, N–H, H–H, *etc.* bond activation reactions (Fig. 1).[1-37]The reactivities and catalytic activities of these complexes were found very sensitive to the ligand structures. Among them, the pyridine-based pincer complexes are of particular interest. Heinekey and Goldberg and co-workers demonstrated that one of the CH_2 arms of **I-Cl**can be deprotonated,leading to the dearomatization of the central pyridine ring.[16, 18]C-H bonds of benzene and O-H bonds can be readily cleaved without the change of the oxidation state of the Rh center. Similar reactions on Ru analogues by the Milstein group have found various applications especially for metal-ligand cooperative catalysis in dehydrogenative reactions.[38-40] Milstein and co-workers also reported that the potassium salt of the dearomatized intermediated **[II-Cl]**Kcould bind nitrogen or CO to give relatively inactive Rh^{I} complexes or react with benzene and hydrogen to give **I-Ph**and **I-H**, respectively, with the elimination of KCl (Scheme 1).[28] Upon treatment of **I-Cl** with a Ag^{I} salt, the Rh^{I} center was oxidized to Rh^{II} instead of abstraction of the chloride ligand.[15]Amazingly, when the CH_2 groups were replaced by O, Brookhart and co-workers showed that a Rh^{I}σ-methane complex could be observed in solution.[22]These observations clearly indicate that the properties of these complexes can be significantly influenced by the nature of the CH_2 or O “spacers”. It is thus interesting to see what would be achieved when they are replaced by the NH groups.

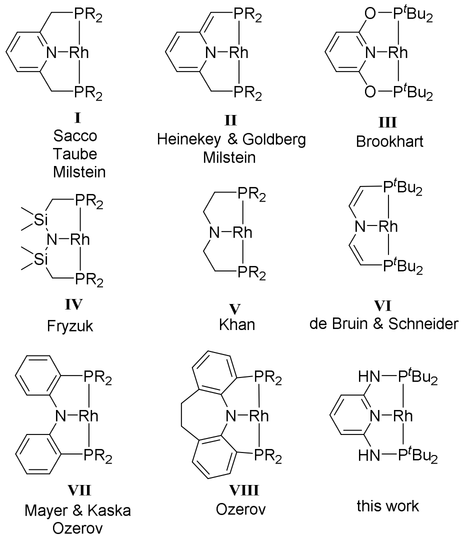
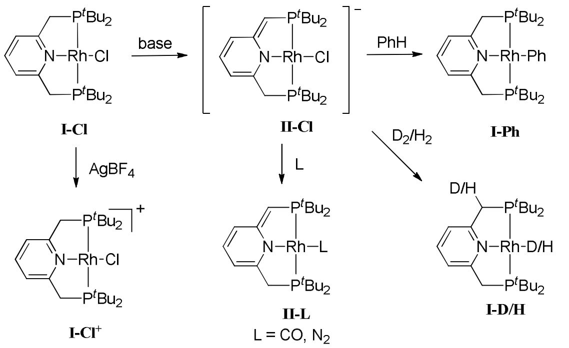


Figure 1.Examplesof PNP-type pincer Rh models.



Scheme 1.Selected reactions of PNP-Rh complex **I-Cl**.

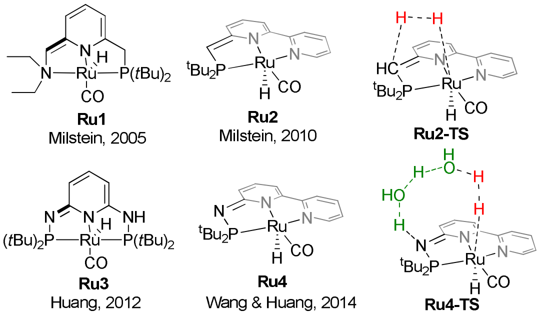
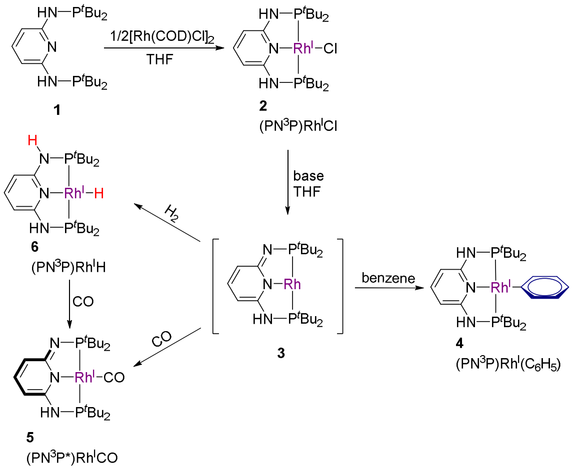


Figure 2.Selected examples of PNP-type Rucomplexes.

Utilizing the ligand (**1**) first synthesized by the Kirchner group[41] and some by us,[42-49] we have recently demonstrated that replacing the CH_2spacer in thepyridine-based pincer complex with an NH resulted in a new class of complexes with different thermodynamic and kinetic properties andin several cases, the catalytic activities of the corresponding new complexes were enhanced or completely altered.[42-49]For example, while **Ru1** efficiently catalyzes the dehydrogenative acylation of amines with alcohols,[50]**Ru3**favors the dehydrogenative coupling of amines to imines.[44]**Ru4** effectively catalyzes the ester hydrogenation even in the presence of water, and computational studies suggest that two protic molecules such as water are needed to facilitate the hydrogen activation (**Ru4-TS**),[47] where such a proton shuttle is not required for Milstein's **Ru3**(Fig. 2).[49, 51]In this article, we extend the coordination chemistry to Rh and report the synthesis and characterization of a series of $(PN^3P)Rh^I$ complexes(Scheme 2).



Scheme 2. Reactions of the new $(PN^3P)Rh^I$ complexes.

Reaction of ligand **1**with $[Rh(COD)Cl]_2$ (COD = cyclooctadiene, 0.5 equiv) in dry THF under argon exclusively furnished the $(PN^3P)Rh^ICl$ complex (2). The $^{31}P\{^1H\}$ NMR spectrum displays one doublet at 107.9 ppm (JRhP = 153 Hz), suggesting that the two phosphorus atoms are magnetically equivalent and that the complex adopts a symmetric arrangement. This is in good agreement of the X-ray crystal structureof complex **2**which shows a rhodium in a square-planar geometry (Fig.3). The C1–N1 and C5–N2 bond lengths are roughly the same. The N3–Rh1–Cl1 angle of 177.12° is linear, as the P1–Rh1–P2 angle (165.33°) is deviated from linearity, comparable to the analogous $(PNP)Rh^I$ complexes.[15]

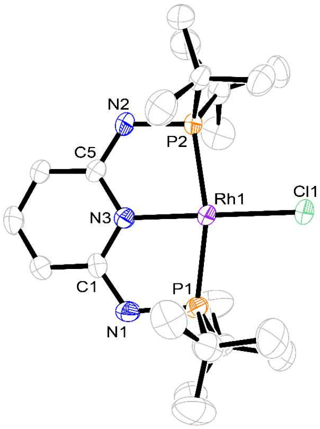


Figure 3. ORTEP drawing of complex $(PN^3P)Rh^ICl$ (**2**) at 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): C1–N1 1.375(6), C5–N2 1.367(6), Rh1–N3 2.030(6), Rh1–Cl1 2.379(1), Rh1–P1 2.261(1), Rh1–P2 2.264(1). Selected bond angles (deg): N3–Rh1–Cl1 177.12(11), P1–Rh1–P2 165.33(4), N3–Rh1–P1 82.18(10), P1–Rh1–Cl1 97.98(4), Cl1–Rh1–P2 96.69(4), P2–Rh1–N3 83.17(10).

With complex **2** in hand, we were able to examine its reactivity. A suspension of **2** with an equimolar amount of $KN(SiMe_3)_2$ in dry benzene under argon slowly reacted as the organic solid gradually disappeared within 10 days at room temperature to afford a homogeneous orange solution of $(PN^3P)Rh^I(C_6H_5)$ (**4**), presumably via the generation of intermediate **3** even though it was not observed spectroscopically.[28] The $^{31}P\{^1H\}$ NMR spectrum of **4** gave a doublet at 108.63 ppm (J_{RhP} = 180 Hz), again indicating equivalent phosphorus atoms, while the N-H protons display a singlet at 4.65 ppm in the ^1H NMR spectrum. The X-ray structure of **4** reveals a slightly distorted square-planar geometry around the rhodium atom, in which the phenyl ring islocated *trans* to the pyridine moiety and approximately perpendicular to the pyridine plane (Fig. 4).

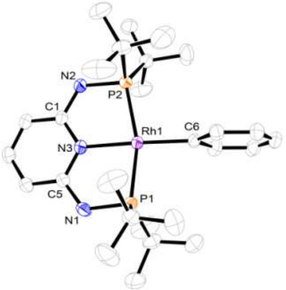


Figure 4. ORTEP drawing of complex $(PN^3P)Rh^I(C_6H_5)$ (**4**) at 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): C1–N2 1.368(3), C5–N1 1.371(3), Rh1–C6 2.034(2), Rh1–N3 2.085(2), Rh1–P1 2.245(1), Rh1–P2 2.268(1). Selected bond angles (deg): C6–Rh1–N3 173.43(8), P1–Rh1–P2 162.37(2), C6–Rh1–P1 97.14(6), N3–Rh1–P1 82.50(5), C6–Rh1–P2 99.30(6), N3–Rh1–P2 81.89(5).

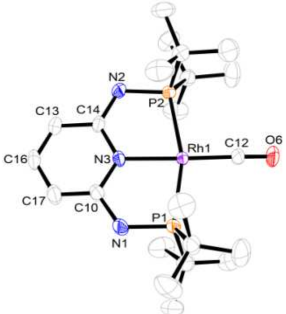


Figure 5. ORTEP drawing of $(PN^3P^*)Rh^ICO$ (**5**) at 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): C10–N1 1.391(5), C14–N2 1.331(5), C13–C14 1.428(5), C13–C16 1.348(6), C16–C17 1.391(6), C10–C17 1.375(6), Rh1–C12 1.812(4), Rh1–N3 2.063(3), Rh1–P1 2.288(1), Rh1–P2 2.296(1). Selected bond angles (deg): Rh1–C12–O6 178.6(5), C12–Rh1–N3 176.58(19), P1–Rh1–P2 161.65(4), C12–Rh1–P1 99.92(13), N3–Rh1–P1 82.37(9), C12–Rh1–P2 98.38(13), N3–Rh1–P2 79.39(9).

Treatment of complex **2** with one equivalent of ^{t}BuOK in dry THF under an atmosphere of CO resulted in the formation of the dearomatized (PN^{3}P*)Rh^{I}CO complex (**5**)(PN^{3}P* denotes the dearomatized ligand).An apparent color change from orange to dark green was observed during this reaction. Complex **5** was characterized by ^{31}P{^{1}H}, ^{1}H, and ^{13}C{^{1}H} NMR spectroscopy as well as Single crystal X-ray analysis. The ^{31}P{^{1}H} spectrum of **5** exhibits an AB system with two sets of doublet of doublet at 130.55 ppm (J_{PP} = 248 Hz, J_{RhP} = 124 Hz) and 121.58 ppm (J_{PP} = 248 Hz, J_{RhP} = 126 Hz), implying the two phosphorus atoms are now nonequivalent.[45] The ^{1}H NMR spectrum shows a doublet at 4.16 ppm for one proton corresponding to the N*H* group and three different signals at 6.85, 6.70 and 5.11 ppm in a 1:1:1 ratio for the dearomatized pyridine backbone. The carbonyl carbon was observed in the ^{13}C{^{1}H} NMR as a doublet of triplet at 200.05 ppm (J_{RhC} = 68.5 Hz, J_{PC} = 11.2 Hz). Crystals of **5**suitablefor the X-ray analysis were obtained by slow evaporation of a saturated toluene solution at room temperature. The solid state structure of **5**also adopts a slightly distorted square-planar geometry with the CO donor coordinated *trans* to the pyridine nitrogen atom (Fig. 5). In contrast to the aromatic structures **2** and **4**, one of the C-N bonds is found significantly longer than the other one: C10-N1 1.391Å vs. C14-N2 1.331Å. The bond distances of C13-C14 (1.428 Å) and C16-C17 (1.391 Å) are considerably longer than a typical C-C bond in pyridine. These observations are consistent with the assignment of a dearomatized pyridine ring.[28, 45]Complex **5** can be readily protonated to the cationic complex [(PN^{3}P)Rh^{I}CO]HCO$_2$ (**5a**) with the addition of excess amount of formic acid in benzene. The ^{31}P{^{1}H} spectrum exhibits a doublet at 131.95 ppm (J_{RhP} = 126 Hz) indicating that the rearomatization of the PN^{3}P ligand took place. The signals of two different protons of the pyridine ring at 7.54, and 6.48 ppm in the^{1}H NMR with a ratio to 1:2 further supported our assignment. Complex **5a** was also recrystallized to have its X-ray structure determined. The observed bonding parameters were in good agreement of the structure contained an aromatic pyridine moiety (Fig. 6).The CO stretching frequencies ν_{CO} for **5** and **5a** are 1952 cm^{-1} and 1969 cm^{-1}, respectively, indicative of a more electron-rich nature of Rh with the dearomatized ligand.

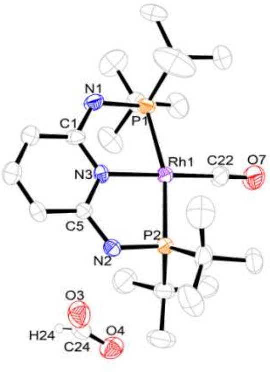


Figure 6. ORTEP drawing of complex [(PN^{3}P)Rh^{I}CO]HCO$_2$ (**5a**) at 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): C1–N1 1.370(8), C5–N2 1.375(7), Rh1–C22 1.827(6), Rh1–N3 2.060(4), Rh1–P1 2.297(2), Rh1–P2 2.294(2). Selected bond angles (deg): C22–Rh1–N3 179.2(3), Rh1–C22–O7 178.5(7), P1–Rh1–P2 164.26(5), N3–Rh1–P1 82.18(14), N3–Rh1–P2 82.08(14), C22–Rh1–P1 98.4(2), C22–Rh1–P2 97.3(2).

Complex **2** was also evaluated for H–H bond activation involving metal-ligand cooperation. Treatment of **2** with equimolar of KH in dry THF under H$_2$ at the room temperature cleanly afforded the aromatic Rh–H complex (the formation of Rh-D was observed when H$_2$ was replaced by D$_2$ under the same condition).Complex **6** was characterized by ^{31}P{^{1}H}, ^{1}H, and ^{13}C{^{1}H} NMR spectroscopy. The ^{31}P{^{1}H} signal at δ135.0 ppm as a doublet with a coupling constant of 168 Hz suggests the two equivalent phosphorus atoms and a Rh(I) formal oxidation state. The hydride signal showed up as one apparent quartet at δ −11.60 ppm in ^{1}H NMR. Complex **6**could be quickly converted to the dearomatized complex **5** in the presence of CO, accompanied by a dramatic color change from brown to green and the formation of H$_2$. Since the crystal of **6** was not available, preliminary density functional theory calculations were conducted with Gaussian 09 package,[50]utilizing the M06[51] level of theory with Pople basis set 6-31G(d,p)[52] for non-metal atoms and SDD[53] for Rh (Fig. 7). The calculation results support the Rh-H structure (**6**) as the most stable isomer. Dearomatized (PN^{3}P*)Rh^I(H$_2$) and (PN^{3}P*)Rh^{III}H$_2$ complexes were found to be 2.5 and 21.9 kcal/mol less stable thanaromatized**6**, respectively.[28] Intriguingly, the transition state (**6TS**) located for the direct interconversion between these isomers was 51.4 kcal/mol, implying a more complicated mechanism for the hydrogen activation process. While we have demonstrated that in the analogous Ru system, two water molecules were required for the H$_2$ activation,[47] we do not consider it reasonable under this reaction condition.

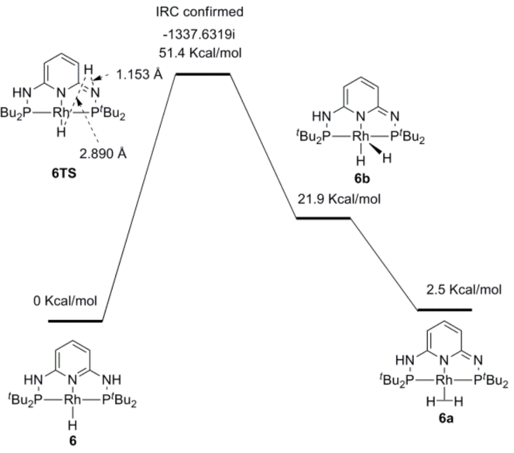


Figure 7. Relative energies of different isomers of complex **6**.

In summarize, we have demonstrated that complex (PN^{3}P)Rh^{I}Cl (**2**) is capable of activating benzene and H$_2$ effectively at room temperature upon treatment of a suitable base. In this regard, its apparent reactivities are similar to those of the mode **I** analogues. Facile C(sp^2)–H and H–H bond activation reactions via metal-ligand cooperation afforded complexes (PN^{3}P)Rh^I(C$_6$H$_5$) (**4**) and (PN^{3}P)Rh^{I}H (**6**). The dearomatized (PN^{3}P*)Rh^{I}CO (**5**) was obtained by reacting**2**with CO in the presence of a base. In a protic environment, the imine arm of **5** is quickly reprotonated to form an aromatic complex **5a**.Preliminary computational studies on the relative stabilities of difference isomers of complex **6** agree well with the experimental observation. However, the transition state calculations may suggest a difference kinetic behavior. Further development of applications and kinetic studies are ongoing and will be reported in due course.

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Notes and references

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†Electronic Supplementary Information (ESI) available: A summary of DFT results, experimental, characterization data of complexes**2**, **4**, **5**, **5a**, and **6**, and crystal structures of complexes **2**, **4**, **5**, and **5a**.

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