# **ORGANOMETALLICS**

ARTICLE

# A Dearomatized Anionic PNP Pincer Rhodium Complex: C—H and H—H Bond Activation by Metal—Ligand Cooperation and Inhibition by Dinitrogen

Leonid Schwartsburd,<sup>+</sup> Mark A. Iron,<sup>‡</sup> Leonid Konstantinovski,<sup>‡</sup> Eyal Ben-Ari,<sup>†</sup> and David Milstein<sup>\*,†</sup>

<sup>†</sup>Department of Organic Chemistry and <sup>‡</sup>Department of Chemical Research Support, The Weizmann Institute of Science, Rehovot 76100, Israel

Supporting Information



The anionic dearomatized complex  $[(PNP^*)Rh^{I}Cl]K$  (2; PNP = 2,6-bis((di-*tert*-butylphosphino)methyl)pyridine, PNP<sup>\*</sup> = deprotonated PNP) was prepared by reaction of the aromatic (PNP)Rh<sup>I</sup>Cl complex 1 with KN(SiMe<sub>3</sub>)<sub>2</sub> in dry benzene. Spectroscopic characterization and DFT calculations confirm a nonaromatic square-planar structure of complex 2. Under an atmosphere of dry argon, 2 undergoes facile C–H activation of benzene by cooperation between the metal center and the pincer ligand, with aromatization of the ligand, to form the complex (PNP)Rh<sup>I</sup>(C<sub>6</sub>H<sub>5</sub>) (3a). This reaction is inhibited by dinitrogen, which reacts with 2 to form the complex (PNP\*)Rh<sup>I</sup>(N<sub>2</sub>) (4), indicating higher stabilization of the 14-electron (PNP\*)Rh<sup>I</sup> species 5 by dinitrogen as compared with chloride. Similarly, treatment of 2 with CO results in KCl liberation to form the dearomatized (PNP\*)Rh<sup>I</sup>CO (8). In a protic environment, the dearomatized complex 2 is quickly reprotonated to regenerate the aromatic starting complex 1. Upon treatment with MeI, 2 undergoes oxidative addition to form the nonaromatic (PNP\*)Rh<sup>III</sup>(CH<sub>3</sub>)Cl (10), while the dearomatized ligand remains intact. Complex 2 undergoes facile activation of H<sub>2</sub> to form the monohydride (PNP)Rh<sup>II</sup>(H) (11a) and with D<sub>2</sub> to form (PNP)Rh<sup>I</sup>(D) (11b) with benzylic-D incorporation, via metal–ligand cooperation by aromatization of the ligand. The reactivity of 2 with H<sub>2</sub> is significantly higher than that of 4.

# ■ INTRODUCTION

Metal—ligand cooperation plays an important role in homogeneous catalysis by metal complexes,<sup>1–3</sup> such as in the hydrogenation of polar bonds by ruthenium amido complexes.<sup>1b,c</sup> Recently, we discovered a new mode of metal—ligand cooperation involving reversible dearomatization of pyridine- and acridine-based pincer complexes.<sup>3–9</sup>

Metal—ligand cooperation via reversible dearomatization can play a key role in the catalytic O—H bond activation of alcohols,<sup>3</sup> exemplified by the direct coupling of alcohols to form esters with the liberation of  $H_{22}^{4a,b}$  the hydrogenation of esters to alcohols under mild pressure,<sup>4c</sup> the dehydrogenative coupling of alcohols with amines to produce amides<sup>4d</sup> and polyamides,<sup>4c,f</sup> the dehydrogenative amidation of esters with amines,<sup>4g</sup> and the acylation of alcohols with esters.<sup>4h</sup> These reactions are catalyzed by the dearomatized (PNN\*)Ru<sup>II</sup>(H)(CO) complex (PNN = 2-((di*tert*-butylphosphino)methyl)-6-(diethylaminomethyl)pyridine; PNN\* = deprotonated PNN).<sup>4</sup> Furthermore, this powerful complex promotes splitting of water to H<sub>2</sub> and O<sub>2</sub> in consecutive heatand light-induced steps.<sup>5</sup> Very recently, a bipyridine-based PNN analogue of this complex was shown to be effective in the direct hydrogenation of amides to form amines and alcohols.<sup>4i</sup> The dearomatized (PNP\*)Ru<sup>II</sup>(H)(CO) analogue (PNP = 2,6-bis-((di-*tert*-butylphosphino)methyl)pyridine; PNP\* = deprotonated PNP) is effective in the N-H bond activation of amines and ammonia,<sup>6a</sup> the coupling of alcohols and amines to form imines and  $H_{2}$ , <sup>6b</sup> and the dehydrogenation of secondary alcohols to ketones. <sup>6c</sup> Further, the complex  $(iPrPNP)Fe^{II}(H)(CO)(Br) (iPrPNP = 2,6$ bis((diisopropylphosphino)methyl)pyridine), also believed to operate by metal-ligand cooperation, was very recently reported to be highly efficient in the hydrogenation of ketones at room temperature and mild pressure.<sup>6d</sup> Long-range metal-ligand cooperation involving dearomatization of the central acridine ring was recently reported for an acridine-based (PNP)Ru<sup>II</sup>(H)Cl(CO) complex,<sup>6e</sup> which catalyzes the dehydrogenative coupling of alcohols to form acetals<sup>6f</sup> and the selective coupling of primary alcohols with ammonia to give primary amines.<sup>6g</sup> Metal—ligand cooperation

Received:February 3, 2011Published:April 22, 2011

Scheme 1



by aromatization—dearomatization is involved in the very effective catalytic hydrogenation of  $CO_2$  by a PNP-iridium complex.<sup>7</sup>

Recent reports from our group describe C–H activation processes that involve metal–ligand cooperation by reversible dearomatization of the ligand with no change in the formal oxidation state of the metal.<sup>8</sup> The dearomatized (PNP\*)Ir<sup>I</sup>(COE) complex activates C–H bonds in benzene and acetone to yield the aromatic (PNP)Ir<sup>I</sup>(C<sub>6</sub>H<sub>5</sub>)<sup>8a</sup> and (PNP)Ir<sup>I</sup>(CH<sub>2</sub>COCH<sub>3</sub>)<sup>8b</sup> complexes, respectively (COE = cyclooctene). Our studies indicate that the dearomatized oxidative addition intermediates (PNP\*)Ir<sup>III</sup>(H)(R) (R = C<sub>6</sub>H<sub>5</sub>, CH<sub>2</sub>COCH<sub>3</sub>) are involved.<sup>8a,b</sup> Indeed, the nonaromatic (PNP\*)Ir<sup>III</sup>(H)(C<sub>6</sub>H<sub>5</sub>) was prepared independently by deprotonation of the cationic [(PNP)Ir<sup>III</sup>(H)(C<sub>6</sub>H<sub>5</sub>)]BF<sub>4</sub> complex<sup>8c</sup> at -78 °C. When the complex is warmed to room temperature, proton transfer to the side "arm" occurs, with aromatization and concomitant reduction of the metal center, to give the (PNP)Ir<sup>IC</sup>(C<sub>6</sub>H<sub>5</sub>) complex.<sup>8a</sup>

The (PNP)Ir<sup>1</sup>(R) complexes react with H<sub>2</sub> to exclusively form the *trans*-dihydride (PNP)Ir<sup>III</sup>(H)<sub>2</sub>(R) complexes, and with D<sub>2</sub> the *trans* hydrido-deuteride (PNP)Ir<sup>III</sup>(H)(D)(R) complexes are formed, with one deuterium atom incorporated into a benzylic position.<sup>8a,b</sup> Computational studies corroborate an unobserved equilibrium between the aromatic (PNP)Ir<sup>I</sup>(R) complex and the nonaromatic (PNP\*)Ir<sup>III</sup>(H)(R) complex, which is the species that activates H<sub>2</sub>.<sup>8b,9</sup>

The  $(PNP^*)Ir^{III}(H)(C_6H_5)$  complex can be trapped by treating the  $(PNP^*)Ir^{III}(C_6H_5)$  complex with CO, forming the nonaromatic  $(PNP^*)Ir^{III}(CO)(H)(C_6H_5)$  complex.<sup>8a</sup> Treatment of the complex  $(PNP)Ir^{I}(CH_2COCH_3)$  with CO results in elimination of acetone to form the dearomatized  $(PNP^*)Ir^{I}CO$  complex, involving proton migration from the ligand "arm" to the acetonyl moiety with concomitant dearomatization.<sup>8b</sup> The PNP ligand and the metal center also act jointly in benzene C–H activation by  $(PNP)Ir^{I}(CH_2COCH_3)$ , resulting in substitution of the acetonyl group by a phenyl group.<sup>8b</sup>

Following the metal-ligand cooperation studies with pyridinebased pincer iridium complexes, we decided to examine the potential of rhodium-based systems. Preparation of the nonaromatic (PNP<sup>\*</sup>)Rh<sup>I</sup>(N<sub>2</sub>) complex has been recently reported.<sup>10</sup> In this paper, we report the preparation and reactivity of an electron-rich, *anionic* dearomatized  $[(PNP^*)Rh^ICl]K$  complex. The PNP ligand and the metal of the dearomatized complex act jointly in the activation of a benzene C–H bond. This reaction is inhibited by dinitrogen coordination to form the  $(PNP^*)Rh^I(N_2)$  complex or by reprotonation of the benzylic position in the ligand by adventitious water to regenerate the  $(PNP)Rh^ICl$  starting complex. The dearomatized complex is also capable of H–H bond activation by metal–ligand cooperation via reversible dearomatization of the ligand.

#### RESULTS AND DISCUSSION

Reaction of (PNP)Rh<sup>I</sup>Cl (1) with Benzene in the Presence of a Base To Form (PNP)Rh<sup>I</sup>(C<sub>6</sub>H<sub>5</sub>) (3a). Formation of the Dearomatized [(PNP\*)Rh<sup>I</sup>Cl]K (2). Treatment of our previously reported complex (PNP)Rh<sup>I</sup>Cl 1<sup>11</sup> with an equimolar amount of KN(SiMe<sub>3</sub>)<sub>2</sub> in dry benzene under an atmosphere of dry argon for 12 h at room temperature results in quantitative formation of the known (PNP)Rh<sup>I</sup>(C<sub>6</sub>H<sub>5</sub>) complex  $3a^{12}$  with concomitant formation of KCl and HN(SiMe<sub>3</sub>)<sub>2</sub> (Scheme 1). Interestingly, after addition of KN(SiMe<sub>3</sub>)<sub>2</sub> to the benzene solution of 1 an orange precipitate is formed. Subsequently, full consumption of the precipitate results in a homogeneous dark brown solution of 3a (by <sup>31</sup>P{<sup>1</sup>H} NMR analysis).

In one experiment, the orange precipitate was separated from the benzene solution at an early stage of the reaction (after 3 h). The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of the precipitate redissolved in dry THF revealed formation of the dearomatized anionic complex 2 (Scheme 1), while the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of the benzene solution revealed full consumption of complex 1 and formation of some 3a. Further reaction of the separated 2 with dry benzene under an atmosphere of dry argon gave a quantitative amount of 3a (Scheme 1). In fact, complex 2 is a separable reaction intermediate in the reaction of 1 with benzene in the presence of base. Note that, in the absence of KN(SiMe<sub>3</sub>)<sub>2</sub>, no transformation of 1 in benzene is observed, even upon prolonged heating at 80 °C.



Figure 1. DFT optimized structures of 1, anionic 2, and 4.

Dry samples of **2** are relatively stable at -35 °C under an atmosphere of dry argon (up to 2 weeks). Complex **2** was characterized by <sup>31</sup>P{<sup>1</sup>H}, <sup>1</sup>H, and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy and by elemental analysis. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **2** displays a characteristic AB pattern of doublets at 57.6 ppm ( $J_{P-P} = 345 \text{ Hz}$ ,  $J_{Rh-P} = 151 \text{ Hz}$ ) and 49.2 ppm ( $J_{P-P} = 345 \text{ Hz}$ ,  $J_{Rh-P} = 151 \text{ Hz}$ ) and 49.2 ppm ( $J_{P-P} = 345 \text{ Hz}$ ,  $J_{Rh-P} = 147 \text{ Hz}$ ), indicating nonequivalent phosphorus atoms. The high Rh–P coupling constants indicate that **2** is formally a Rh<sup>1</sup> complex (cf. **1**,  $J_{Rh-P} = 145 \text{ Hz}$ ). A one-proton doublet at 3.31 ppm ( $J_{P-H} = 3.2 \text{ Hz}$ ) in the <sup>1</sup>H NMR spectrum and a doublet at 63.84 ppm ( $J_{P-C} = 46.4 \text{ Hz}$ ) in the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum, assigned to the Py–*CH*–P group, indicate the formation of a dearomatized PNP\* system. Signals at 6.00, 5.67, and 5.11 ppm in the <sup>1</sup>H NMR spectrum are attributed to three different protons of the dearomatized pyridine backbone.

A number of anionic transition-metal complexes lacking strong  $\pi$ -acceptor ligands capable of lowering the electron density at the metal center (such as CO, olefins, and electron-withdrawing phosphines) have been reported to date.<sup>13</sup> Among them are the recently reported dearomatized anionic complexes  $[(PNN^*)Pt^{II}(Cl)(R)]Li(R = CH_3, C_6H_5)$ , with a decoordinated hemilabile amine arm,<sup>13a</sup> and the anionic doubly deprotonated complexes  $[(PNP^{**})M^{II}(X)]Y$  (PNP<sup>\*\*</sup> = doubly deprotonated PNP; M = Pd, Pt; X = Cl, Me; Y = Li, K).<sup>13b</sup>

The DFT-optimized structures (Figure 1) illustrate a symmetry distortion in the square-planar geometry on going from  $\mathbf{1}^{11b}$  to the anionic **2**. Selected bond lengths are given in Table 1. The lengths of the C(1)-C(2) and C(2)-P(1) bonds, which involve the unaffected benzylic position C(2), are almost the same for 1 and the anionic **2**. In the optimized structure of the anionic **2**, the bond length of C(3)-C(4) is shorter than C(1)-C(2) by 0.110 Å, while the bond length of C(4)-P(2) is shorter than C(2)-P(1) to a lesser extent (0.089 Å), indicating that the dearomatized form contributes dominantly to the structure of the anionic **2**, with a significant stabilizing participation of the aromatic phosphorylide

Table 1. Selected Bond Lengths (Å) for DFT Optimized Structures of 1, Anionic 2, and 4

bond	1	anionic 2	4
N(1)-Rh	2.028	2.061	2.091
Rh-Cl	2.466	2.527	
Rh-P(1)	2.286	2.256	2.318
Rh-P(2)		2.308	2.345
C(1) - C(2)	1.506	1.511	1.509
C(3) - C(4)		1.401	1.396
C(2) - P(1)	1.865	1.863	1.853
C(4) - P(2)		1.774	1.767

configuration. The corresponding bond lengths in the optimized structure of the neutral dearomatized (PNP\*) $Rh^{I}(N_{2})$  complex 4 (Figure 1) are very similar to those in the anionic 2 (Table 1).

Significantly, the reaction of the dearomatized complex 2 (formed in situ or purified) with dry  $C_6D_6$  under an atmosphere of dry argon yields the aromatic complex 3b, with incorporation of deuterium into the benzylic position (Scheme 1). The <sup>1</sup>H NMR spectrum indicates incorporation of one deuterium atom into the benzylic position (27% deuterium incorporation by integration). The  ${}^{2}H{}^{1}H{}$  NMR spectrum of the 3b has a benzylic-D signal at 2.80 ppm and three phenyl-D signals at 8.13, 7.24, and 6.98 ppm. This indicates involvement of the ligand arm in the C-H bond activation process. The reaction of 2 with benzene (Scheme 2) most likely involves formation of the dearomatized 14-electron Rh<sup>I</sup> species 5<sup>14</sup> with concomitant liberation of KCl, benzene precoordination to give 6, and intramolecular benzene C-H bond activation, resulting in the Rh<sup>III</sup> intermediate 7 followed by proton migration to the side arm and aromatization to yield the Rh<sup>1</sup> phenyl complex 3a. The overall process involves no overall change in the formal metal oxidation state (Scheme 2).

#### Scheme 2



#### Scheme 3



Dinitrogen was found to inhibit the C-H bond activation process by formation of the known dinitrogen complex 4<sup>10</sup> (Scheme 1). Treatment of 1 with an equimolar amount of  $KN(SiMe_3)_2$  in dry benzene under an atmosphere of dry nitrogen (rather than dry argon) for 12 h at room temperature results in formation of the dearomatized complex  $(PNP^*)Rh^{I}(N_2)$  (4; 91%) and only a small amount of the complex (PNP) $Rh^{1}(C_{6}H_{5})$  (3a; 9%) (Scheme 1). After addition of  $KN(SiMe_3)_2$  to the benzene solution of 1, complex 2 was formed as a precipitate (Scheme 1). Subsequently, 2 reacted with dinitrogen to give 4 and to a smaller extent with benzene to give 3a (Scheme 1). The reaction of 2 with dinitrogen probably involves the intermediacy of the dearomatized 14-electron Rh<sup>1</sup> species 5 with liberation of KCl (Scheme 2). Attempting to perform the reverse reaction by treatment of 4 with excess tetrabutylammonium chloride as a soluble chloride source in dry THF at room temperature under dry argon was unsuccessful. The observation that N<sub>2</sub> is more tightly bound to complex 4 than chloride to 2 might be a result of the anionic nature of 2 and the steric hindrance imposed by the *t*-Bu groups.<sup>15</sup>

Formation of 3a from 4 at room temperature can be excluded (Scheme 1), since under these conditions 4 is stable in benzene. Only with prolonged heating can reactivity of 4 with benzene be observed. Heating a benzene solution of 4 at 80 °C under an atmosphere of dry nitrogen for 12 h results in the formation of 3a in 40% purity accompanied by decomposition byproducts (by <sup>31</sup>P{<sup>1</sup>H} NMR analysis). Apparently, N<sub>2</sub> coordination to the metal center in 4 inhibits formation of the reactive intermediate 5, which is essential for the C–H bond activation process (Scheme 2). Traces of N<sub>2</sub> have been shown to inhibit dehydrogenation reactions of hydrocarbons catalyzed by the (PCP)Ir(H)<sub>2</sub> complexe by formation of [(PCP)Ir]<sub>2</sub>(N<sub>2</sub>) and (PCP)Ir(N<sub>2</sub>) complexes (PCP = 2,6-bis((di-*tert*-butylphosphino)methyl)benzene).<sup>16</sup>

Reaction of [(PNP\*)Rh<sup>I</sup>CI]K (2) with CO. Formation of the Nonaromatic Complex (PNP\*)Rh<sup>I</sup>(CO) (8). In analogy to the reaction with dinitrogen, treatment of complex 2 with a slight excess of CO in dry THF at room temperature under dry argon Scheme 4



Scheme 5



results in formation of the nonaromatic (PNP\*)Rh<sup>I</sup>(CO) complex 8 with concomitant liberation of KCl (Scheme 3). A color change from orange to pink is observed during the reaction. Complex 8 can also be prepared by deprotonation of the cationic complex [(PNP)Rh<sup>I</sup>(CO)]BF<sub>4</sub> (9)<sup>17</sup> with an equimolar amount of KN(SiMe<sub>3</sub>)<sub>2</sub> in dry THF (Scheme 3).

Complex 8 was characterized by <sup>31</sup>P{<sup>1</sup>H}, <sup>1</sup>H, and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of 8 displays a characteristic AB pattern of doublets at 77.0 ppm ( $J_{P-P} = 244$  Hz,  $J_{Rh-P} = 125$  Hz) and 74.2 ppm ( $J_{P-P} = 244$  Hz,  $J_{Rh-P} = 125$  Hz), indicating nonequivalent phosphorus atoms. In the <sup>1</sup>H NMR spectrum a one-proton doublet at 3.65 ppm ( $J_{P-H} = 4.4$  Hz) corresponds to the Py–CH–P group and signals at 6.42, 6.36, and 5.37 ppm correspond to the three different protons of the dearomatized pyridine backbone. The carbonyl carbon gives rise to a doublet of apparent triplets centered at 199.21 ppm ( $J_{Rh-C} =$ 66.1 Hz,  $J_{P-C} = 12.6$  Hz) in the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum. The IR spectrum of 8 shows a sharp band at  $\nu_{CO}$  1946 cm<sup>-1</sup>, indicating a significantly higher degree of back-bonding to CO than in the aromatic cationic complex 9 ( $\nu_{CO}$  1982 cm<sup>-1</sup>), as expected.

Protonation of [(PNP\*)Rh<sup>I</sup>Cl]K (2) To Regenerate the Aromatic Complex (PNP)Rh<sup>I</sup>Cl (1). The dearomatized complex 2 is quickly protonated to regenerate the initial aromatic complex 1 (Scheme 4). Thus, treatment of 2 with an equivalent amount of



water (or excess) in THF results in formation of 1, along with an immediate color change from orange to red. Reaction of 2 with an equivalent amount of  $D_2O$  in THF yields complex 1a, with incorporation of deuterium into the benzylic position (by  ${}^{2}H{}^{1}H{}$  NMR analysis) (Scheme 4).

Reaction of [(PNP\*)Rh<sup>I</sup>Cl]K (2) with CH<sub>3</sub>I. Exclusive Formation of the Nonaromatic Complex (PNP\*)Rh<sup>III</sup>(CH<sub>3</sub>)Cl (10). The addition of methyl iodide (in excess) as an electrophilic reagent to a solution of 2 in THF under an atmosphere of dry argon leads to the immediate and exclusive formation of the nonaromatic (PNP\*)Rh<sup>III</sup>(CH<sub>3</sub>)Cl complex 10 (Scheme 5). This reaction is accompanied by a color change from orange to dark green. Thus, in complex 2 electrophilic addition is favored at the metal center over the benzylic position. Electrophilic addition of methyl triflate to the deprotonated benzylic position of a dearomatized (PNP\*)Cu<sup>I</sup> complex has been reported.<sup>18</sup>

Complex 10 was characterized by <sup>31</sup>P{<sup>1</sup>H}, <sup>1</sup>H, and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy, mass spectroscopy, and elemental analysis. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of 10 displays a characteristic AB pattern of doublets at 53.3 ppm ( $J_{P-P} = 390 \text{ Hz}$ ,  $J_{Rh-P} = 101 \text{ Hz}$ ) and 44.7 ppm ( $J_{P-P} = 390 \text{ Hz}$ ,  $J_{Rh-P} = 105 \text{ Hz}$ ), indicating nonequivalent phosphorus atoms. The low Rh–P coupling constants (compared to those of the Rh<sup>1</sup> complexes 1–4) indicate that 10 is a Rh<sup>III</sup> complex. A one-proton doublet at 3.55 ppm ( $J_{P-H} = 5.9 \text{ Hz}$ ) in the <sup>1</sup>H NMR spectrum and a doublet at 63.09 ppm ( $J_{P-C} = 52.7 \text{ Hz}$ ) in the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum, assigned to the Py–CH–P group, indicate conservation of the dearomatized PNP\* system. A doublet of apparent triplets centered at 3.77 ppm ( $J_{Rh-C} = 28.2 \text{ Hz}$ ,  $J_{P-C} = 4.5 \text{ Hz}$ ) in the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum and a doublet of apparent triplets centered at 2.19 ppm ( $J_{Rh-H} = 2.9 \text{ Hz}$ ,  $J_{P-H} = 4.8 \text{ Hz}$ ) in the <sup>1</sup>H NMR spectrum are assigned to the methyl ligand coordinated in the apical position, as found in related systems.<sup>19</sup>

Reaction of [(PNP\*)Rh<sup>1</sup>Cl]K (2) vs (PNP\*)Rh<sup>1</sup>(N<sub>2</sub>) (4) with H<sub>2</sub>. Formation of the Aromatic Complex (PNP)Rh<sup>1</sup>H (11a). The nonaromatic complex 2 is capable of H–H bond activation via metal–ligand cooperation by aromatization of the ligand. Treatment of 2 with excess H<sub>2</sub> in dry THF under an atmosphere of dry argon at room temperature for 16 h results in formation of the aromatic Rh<sup>1</sup>-H complex 11a with concomitant liberation of KCl (Scheme 6).<sup>20</sup> Significantly, in order to prepare the complex 11a from the nonaromatic dinitrogen complex 4 under an atmosphere of dry nitrogen at room temperature (Scheme 6), hydrogen pressure is required for 96 h. Thus, the reactivity of complex 2 is significantly higher than that of complex 4.

The reaction of **2** with excess  $D_2$  in dry THF under an atmosphere of dry argon yields the aromatic  $Rh^I$ -D complex **11b**, with incorporation of deuterium into the benzylic position (Scheme 6). The <sup>2</sup>H{<sup>1</sup>H} NMR spectrum of the **11b** in THF has a Rh-D signal at -13.51 ppm and a benzylic-D signal at 3.16 ppm. This indicates involvement of the ligand arm in the H–H bond activation process. The overall process involves

cooperation between the metal and the ligand and no overall

change in the formal metal oxidation state. Complex **11a** was characterized by  ${}^{31}P{}^{1}H$ ,  ${}^{1}H$ , and  ${}^{13}C{}^{1}H$ } NMR spectroscopy. The  ${}^{31}P{}^{1}H$  NMR spectrum of **11a** exhibits a doublet at 83.2 ppm ( $J_{Rh-P} = 165.9 \text{ Hz}$ ), arising from the two equivalent phosphorus atoms. The high Rh–P coupling constant indicates formation of a Rh<sup>1</sup> complex. The benzylic protons give rise to one virtual triplet at 2.92 ppm ( $J_{P-H} = 3.0 \text{ Hz}$ ) in the  ${}^{1}H$  NMR spectrum, implying rearomatization of the PNP ligand. The aromaticity of the ligand backbone is further indicated by the  ${}^{1}H$  and  ${}^{13}C{}^{1}H$  NMR spectra. The hydride gives rise to an apparent quartet centered at -12.82 ppm integrating to 1H.

It should be noted that no reaction was observed for the aromatic complex 1 with excess  $H_2$  in dry THF at room temperature. Reversible  $H_2$  addition to the complex 1 is in accord with theoretical calculations, which predict that a rigid square-planar geometry should disfavor oxidative addition and favor reductive elimination of  $H_2$ .<sup>21</sup>

#### SUMMARY

Reaction of the aromatic pincer complex (PNP)Rh<sup>I</sup>Cl (1) with base in benzene under an atmosphere of dry argon results in the formation of the dearomatized anionic [(PNP\*)Rh<sup>1</sup>Cl]K complex 2, which undergoes facile C-H activation of benzene by cooperation between the metal center and the pincer ligand, with aromatization of the ligand, to form the complex  $(PNP)Rh^{1}(C_{6}H_{5})$  (3a). Nitrogen gas inhibits this process by reaction with 2 to form the dearomatized complex  $(PNP^*)Rh^1(N_2)$  (4) with concomitant liberation of KCl. This is probably a result of a more favorable coordination of dinitrogen to the 14-electron (PNP\*)Rh<sup>I</sup> species 5 as compared with chloride. Similarly, treatment of 2 with CO results in KCl liberation to form the dearomatized (PNP\*)Rh<sup>1</sup>CO (8). In a protic environment, the benzylic position of the dearomatized complex 2 is quickly reprotonated to regenerate the initial aromatic complex 1. Reaction of 2 with MeI as an electrophilic reagent occurs exclusively at the metal center (rather than at the arm), yielding the nonaromatic (PNP\*)Rh<sup>III</sup>(CH<sub>3</sub>)Cl (10). Complex 2 reacts with H<sub>2</sub> by cooperation between the metal center and the pincer ligand to form the complex (PNP)Rh<sup>1</sup>(H) (11a) and with  $D_2$  to form (PNP)Rh<sup>I</sup>(D) (11b) with benzylic-D incorporation, with aromatization of the ligand and no change in the formal oxidation state of the metal. The reactivity of the anionic chloride complex 2 with  $H_2$  is significantly higher than that of the dinitrogen complex 4. Further experimental and theoretical investigations on metal-ligand cooperation via aromatization-dearomatization, and its implications on catalytic design, are in progress.

## EXPERIMENTAL SECTION

**General Procedures.** All experiments (if not mentioned otherwise) with metal complexes and the phosphine ligand were carried out under an atmosphere of purified argon in an MBRAUN Unilab

glovebox or using standard Schlenk techniques. All glassware was rigorously dried. All solvents were reagent grade or better. All nondeuterated solvents and some deuterated solvents ( $C_6D_6$  for reactions and THF- $d_8$ ) were refluxed over sodium/benzophenone ketyl and distilled under an argon atmosphere. Additional deuterated solvents were used as received. All the solvents were degassed with argon and kept in the glovebox over 4 Å molecular sieves. Commercially available reagents were used as received. The complex (PNP)Rh<sup>I</sup>Cl (1) was prepared according to the literature procedure.<sup>11a</sup>

Analysis. The NMR spectra were recorded at 400 MHz (<sup>1</sup>H), 100 MHz (<sup>13</sup>C), and 162 MHz (<sup>31</sup>P) using a Bruker Avance-400 NMR spectrometer and at 500 MHz (<sup>1</sup>H), 126 MHz (<sup>13</sup>C), and 202 MHz (<sup>31</sup>P) using a Bruker Avance-500 NMR spectrometer. All spectra were recorded at 23 °C. <sup>1</sup>H NMR and <sup>13</sup>C{<sup>1</sup>H} NMR chemical shifts are reported in parts per million downfield from tetramethylsilane. <sup>1</sup>H NMR chemical shifts were referenced to the residual hydrogen signals of the deuterated solvents (3.58 ppm, THF-d<sub>8</sub>; 7.15 ppm, C<sub>6</sub>D<sub>6</sub>), and the <sup>13</sup>C NMR chemical shifts were referenced to the <sup>13</sup>C signals of the deuterated solvents (67.4 ppm, THF-d<sub>8</sub>; 128.0 ppm, C<sub>6</sub>D<sub>6</sub>). <sup>31</sup>P NMR chemical shifts are reported in ppm downfield from H<sub>3</sub>PO<sub>4</sub> and referenced to an external 85% solution of phosphoric acid in D<sub>2</sub>O. Abbreviations used in the description of NMR data are as follows: b, broad; s, singlet; d, doublet; t, triplet; m, multiplet; v, virtual; app, apparent; Py, pyridine; Ph, phenyl. IR spectra were measured with a Nicolet-6700 FT-IR spectrometer. Elemental analyses were performed by the Unit of Chemical Research Support, Weizmann Institute of Science.

Reaction of (PNP)Rh<sup>I</sup>Cl (1) with KN(SiMe<sub>3</sub>)<sub>2</sub>. Formation of [(PNP\*)Rh<sup>I</sup>Cl]K (2). A benzene solution (2 mL) of KN(SiMe<sub>3</sub>)<sub>2</sub> (10.2 mg, 0.051 mmol) was added to a stirred dark red benzene solution (1 mL) of 1 (24.7 mg, 0.046 mmol) under an argon atmosphere. After 3 h a noticeable amount of orange precipitate was present in the solution. The precipitate was separated from the solution by centrifugation, washed with pentane, and dried under vacuum, giving 22.0 mg (85% yield) of 2 as an orange solid. The <sup>31</sup>P{<sup>1</sup>H} and <sup>1</sup>H NMR spectra of the solid redissolved in dry THF-*d*<sub>8</sub> revealed formation of 2.

<sup>31</sup>P{<sup>1</sup>H} NMR (THF-*d*<sub>8</sub>): 57.6 (dd (AB), 1P,  $J_{P-P} = 345$  Hz,  $J_{Rh-P} = 151$  Hz), 49.2 (dd (AB), 1P,  $J_{P-P} = 345$  Hz,  $J_{Rh-P} = 147$  Hz). <sup>1</sup>H NMR (THF-*d*<sub>8</sub>): 6.00 (t,  $J_{H-H} = 7.4$  Hz, 1H, Py H4), 5.67 (d,  $J_{H-H} = 8.5$  Hz, 1H, Py H3), 5.11 (d,  $J_{H-H} = 6.3$  Hz, 1H, Py H5), 3.31 (d,  $J_{P-H} = 3.2$  Hz, 1H, Py -CHP), 2.63 (d,  $J_{P-H} = 7.8$  Hz, 2H, Py-CH<sub>2</sub>P), 1.38 (m, 36H, P-*t*-Bu). <sup>13</sup>C{<sup>1</sup>H} NMR (THF-*d*<sub>8</sub>): 174.02 (d,  $J_{P-C} = 24.4$  Hz, Py C2), 162.72 (d,  $J_{P-C} = 9.0$  Hz, Py C6), 127.93 (s, Py C4), 109.18 (d,  $J_{P-C} = 17.8$  Hz, Py C3), 95.98 (d,  $J_{P-C} = 11.2$  Hz, Py C5), 63.84 (d,  $J_{P-C} = 46.4$  Hz, Py-CHP), 37.44 (d,  $J_{P-C} = 13.3$  Hz, Py-CH<sub>2</sub>P), 36.21 (m, P-C(CH<sub>3</sub>)<sub>3</sub>), 30.14 (d,  $J_{P-C} = 6.6$  Hz, P-C(CH<sub>3</sub>)<sub>3</sub>). Assignment of <sup>13</sup>C{<sup>1</sup>H} NMR signals was confirmed by <sup>13</sup>C DEPT. Anal. Found (calcd for C<sub>23</sub>H<sub>42</sub>ClKNP<sub>2</sub>Rh): C, 48.32 (48.30); H, 7.44 (7.40).

Reaction of (PNP)Rh<sup>I</sup>Cl (1) with Benzene in the Presence of KN(SiMe<sub>3</sub>)<sub>2</sub>. Formation of (PNP)Rh<sup>I</sup>(C<sub>6</sub>H<sub>5</sub>) (3a). A benzene solution (2 mL) of KN(SiMe<sub>3</sub>)<sub>2</sub> (14.6 mg, 0.073 mmol) was added to a stirred dark red benzene solution (1 mL) of 1 (35.5 mg, 0.067 mmol) under an argon atmosphere. After the addition, 2 was formed as an orange precipitate and gradually consumed during 12 h, resulting in a homogeneous dark brown solution. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum revealed formation of the previously reported complex 3a,<sup>12</sup> which was present in >90% purity. The reaction solution was evaporated, leaving a dark brown residue. The residue was extracted with pentane, leaving an off-white KCl remainder. The pentane solution was filtered through a cotton pad and evaporated to dryness, giving 36.1 mg (94% yield) of 3a as a dark brown solid. Complex 3a was identified by its <sup>31</sup>P{<sup>1</sup>H} and <sup>1</sup>H NMR spectra, which were the same as those reported in the literature.<sup>12</sup> Reaction of [(PNP\*)Rh<sup>1</sup>Cl]K (2) with Benzene. Formation of (PNP)Rh<sup>1</sup>(C<sub>6</sub>H<sub>5</sub>) (3a). Solid 2 (22.0 mg, 0.039 mmol) was stirred in benzene (3 mL) under an argon atmosphere until a clear homogeneous dark brown solution was formed (for 9 h). The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of the solution revealed formation of 3a, which was present in >90% purity. The reaction solution was evaporated, leaving a dark brown residue. The residue was extracted with pentane, leaving an off-white KCl remainder. The pentane solution was filtered through a cotton pad and evaporated to dryness, giving 20.2 mg (90% yield) of 3a as a dark brown solid. The spectroscopic properties of 3a were as reported in the literature.<sup>12</sup>

Reaction of (PNP)Rh<sup>I</sup>Cl (1) with  $C_6D_6$  in the Presence of KN(SiMe<sub>3</sub>)<sub>2</sub>. Formation of (PNP)Rh<sup>I</sup>( $C_6D_5$ ) (3b). A  $C_6D_6$  solution (1 mL) of KN(SiMe<sub>3</sub>)<sub>2</sub> (5.8 mg, 0.029 mmol) was added to a stirred dark red  $C_6D_6$  solution (0.5 mL) of 1 (14.0 mg, 0.026 mmol) under an argon atmosphere. After the addition, 2 was formed and gradually consumed during 12 h, resulting in a homogeneous dark brown solution. The <sup>31</sup>P{<sup>1</sup>H} and <sup>1</sup>H NMR spectra of the solution revealed formation of complex 3b. The reaction solution was evaporated, leaving a dark brown solid. The <sup>2</sup>H{<sup>1</sup>H} NMR spectrum of the solid redissolved in dry  $C_6H_6$  showed a signal at 2.80 ppm, indicating deuterium incorporation into the benzylic position. The solvent was removed under reduced pressure, and the residue was dissolved in pentane, followed by filtration through a cotton pad. Evaporation of pentane gave 13.4 mg (89% yield) of 3b as a dark brown solid.

<sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>): 59.4 (m,  $J_{Rh-P}$  = 172 Hz). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): 6.97 (t,  $J_{H-H}$  = 7.5 Hz, 1H, Py H4), 6.45 (d,  $J_{H-H}$  = 7.5 Hz, 2H, Py H3,5), 2.85 (distorted vt,  $J_{P-H}$  = 3.1 Hz, 3H, Py–CH<sub>2</sub>P), 1.25 (vt,  $J_{P-H}$  = 6.0 Hz, 36H, P–*t*-*Bu*). <sup>2</sup>H{<sup>1</sup>H} NMR (C<sub>6</sub>H<sub>6</sub>; measured without <sup>2</sup>H lock): 8.13 (bs, Ph D), 7.24 (bs, Ph D), 6.98 (bs, Ph D), 2.80 (bs, Py–CDHP).

Reaction of [(PNP\*)Rh<sup>1</sup>Cl]K (2) with  $C_6D_6$ . Formation of (PNP)Rh<sup>1</sup>( $C_6D_5$ ) (3b). Solid 2 (10.0 mg, 0.018 mmol) was stirred in  $C_6D_6$  (1.5 mL) under an argon atmosphere until a clear homogeneous dark brown solution was formed (for 9 h). The <sup>31</sup>P{<sup>1</sup>H} and <sup>1</sup>H NMR spectra of the solution revealed formation of complex 3b. The reaction solution was evaporated, leaving a dark brown solid. The <sup>2</sup>H{<sup>1</sup>H} NMR spectrum of the solid redissolved in dry  $C_6H_6$  showed a signal at 2.80 ppm, indicating deuterium incorporation into the benzylic position. The solvent was removed under reduced pressure, and the residue was dissolved in pentane, followed by filtration through a cotton pad. Evaporation of pentane gave 9.1 mg (87% yield) of 3b as a dark brown solid.

Reaction of (PNP)Rh<sup>I</sup>Cl (1) with KN(SiMe<sub>3</sub>)<sub>2</sub> under Nitrogen. Formation of (PNP\*)Rh<sup>I</sup>(N<sub>2</sub>) (4). Under nitrogen, a benzene solution (1 mL) of KN(SiMe<sub>3</sub>)<sub>2</sub> (4.1 mg, 0.021 mmol) was added to a stirred dark red benzene solution (0.5 mL) of 1 (10.0 mg, 0.019 mmol). After the addition, 2 was formed and gradually consumed during 12 h, resulting in a clear homogeneous bright red solution. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of the solution revealed formation of the previously reported complex 4<sup>10</sup> (91% NMR yield) together with complex 3a (9% NMR yield). The reaction solution was evaporated, leaving a bright red residue. The residue was extracted with pentane, leaving an off-white KCl remainder. The pentane solution was filtered through a cotton pad and evaporated to dryness, yielding 9.3 mg of a bright red solid, which contains 4 (91%) and 3a (9%). The <sup>31</sup>P{<sup>1</sup>H} and <sup>1</sup>H NMR analysis, IR spectroscopy, and mass spectroscopy confirmed the formation of the previously reported 4.<sup>10</sup>

Reaction of [(PNP\*)Rh<sup>I</sup>CI]K (2) with N<sub>2</sub>. Formation of (PNP\*)Rh<sup>I</sup>(N<sub>2</sub>) (4). Under nitrogen, solid 2 (10.0 mg, 0.018 mmol) was stirred in benzene (1.5 mL) for 9 h, resulting in a clear homogeneous bright red solution. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of the solution revealed formation of the previously reported complex 4<sup>10</sup> (93% NMR yield) together with complex 3a (7% NMR yield). The reaction

solution was evaporated, leaving a bright red residue. The residue was extracted with pentane, leaving an off-white KCl remainder. The pentane solution was filtered through a cotton pad and evaporated to dryness, giving 8.9 mg of a bright red solid, which contains 4 (93%) and 3a (7%).

Reaction of [(PNP\*)Rh<sup>1</sup>Cl]K (2) with CO. Formation of (PNP\*)Rh<sup>1</sup>(CO) (8). In a THF solution (0.5 mL) of 2 (15.0 mg, 0.026 mmol) under an argon atmosphere, in a screw-capped NMR tube equipped with a septum, was injected CO (1.0 mL, 0.045 mmol). The solution changed from orange to pink. The <sup>31</sup>P{<sup>1</sup>H} spectrum of the solution revealed formation of 8. The solution was evaporated, leaving a pink residue. The residue was extracted with pentane, leaving an off-white KCl remainder. The pentane solution was filtered through a cotton pad and evaporated to dryness, giving 12.0 mg (88% yield) of 8 as a pink solid.

Reaction of [(PNP)Rh<sup>1</sup>(CO)]BF<sub>4</sub> (9) with KN(SiMe<sub>3</sub>)<sub>2</sub>. Formation of (PNP\*)Rh<sup>1</sup>(CO) (8). A THF solution (2 mL) of KN-(SiMe<sub>3</sub>)<sub>2</sub> (7.2 mg, 0.036 mmol) was added to a THF solution (2 mL) of 9<sup>16</sup> (20.0 mg, 0.033 mmol). The solution was stirred for 6 h, accompanied by a color change from yellow to pink. The <sup>31</sup>P{<sup>1</sup>H} spectrum of the solution revealed formation of 8. The solution was evaporated, leaving a pink residue. The residue was extracted with pentane, leaving a KBF<sub>4</sub> remainder. The pentane solution was filtered through a cotton pad and evaporated to dryness, giving 15.9 mg (92% yield) of 8 as a pink solid.

<sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>): 77.0 (dd (AB), 1P,  $J_{P-P} = 244$  Hz,  $J_{Rh-P} = 125$  Hz), 74.2 (dd (AB), 1P,  $J_{P-P} = 244$  Hz,  $J_{Rh-P} = 125$  Hz). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): 6.42 (m, 1H, Py H4), 6.36 (d,  $J_{H-H} = 8.7$  Hz, 1H, Py H3), 5.37 (d,  $J_{H-H} = 6.3$  Hz, 1H, Py H5), 3.65 (d,  $J_{P-H} = 4.4$  Hz, 1H, Py -CHP), 2.73 (d,  $J_{P-H} = 8.9$  Hz, 2H, Py-CH<sub>2</sub>P), 1.46 (d,  $J_{P-H} = 12.8$  Hz, 18H, P-t-Bu), 1.08 (d,  $J_{P-H} = 12.9$  Hz, 18H, P-t-Bu). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>): 199.21 (d app t,  $J_{Rh-C} = 66.1$  Hz,  $J_{P-C} = 12.6$  Hz, CO), 172.93 (m, Py C2), 160.39 (m, Py C6), 132.33 (s, Py C4), 114.20 (d,  $J_{P-C} = 18.6$  Hz, Py C3), 97.44 (d,  $J_{P-C} = 11.6$  Hz, Py C5), 64.28 (dd,  $J_{P-C} = 49.5$  Hz,  $J_{P-C} = 1.8$  Hz, Py-CHP), 36.55 (m, P-C(CH<sub>3</sub>)<sub>3</sub>), 35.31 (d,  $J_{P-C} = 16.3$  Hz, Py-CH<sub>2</sub>P), 34.74 (m, P-C(CH<sub>3</sub>)<sub>3</sub>), 29.86 (d,  $J_{P-C} = 6.0$  Hz, P-C(CH<sub>3</sub>)<sub>3</sub>), 29.13 (d,  $J_{P-C} = 5.8$  Hz, P-C(CH<sub>3</sub>)<sub>3</sub>). Assignment of <sup>13</sup>C{<sup>1</sup>H} NMR signals was confirmed by <sup>13</sup>C DEPT. IR (thin film):  $\nu_{CO}$  1946 cm<sup>-1</sup>. Anal. Found (calcd for C<sub>24</sub>H<sub>42</sub>NOP<sub>2</sub>Rh): C, 54.85 (54.86); H, 8.03 (8.06).

**Reaction of [(PNP\*)Rh<sup>1</sup>Cl]K (2) with H<sub>2</sub>O. Regeneration of 1.** To a stirred THF solution (1.5 mL) of **2** (10.0 mg, 0.018 mmol) under an argon atmosphere was added an aliquot of THF containing an equivalent amount of H<sub>2</sub>O (or excess). The immediate reaction was accompanied by a color change from orange to red. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of the solution revealed formation of complex **1**, which was present in >90% purity. The solvent was removed under reduced pressure, and the residue was dissolved in pentane, followed by filtration through a (0.2  $\mu$ m) Teflon filter. Evaporation of pentane gave 8.3 mg (89% yield) of **1** as a red solid. <sup>31</sup>P{<sup>1</sup>H} and <sup>1</sup>H NMR spectra of the solid confirmed the formation of **1**.

Reaction of [(PNP\*)Rh<sup>1</sup>Cl]K (2) with D<sub>2</sub>O. Deuterium Incorporation into the Benzylic Position of 1a. To a stirred THF solution (1.5 mL) of 2 (10.0 mg, 0.018 mmol) under an argon atmosphere was added an aliquot of THF containing an equivalent amount of D<sub>2</sub>O. The immediate reaction was accompanied by a color change from orange to red. Examination of the reaction solution by <sup>2</sup>H{<sup>1</sup>H} NMR showed a signal at 3.00 ppm, indicating deuterium incorporation into the benzylic position. The solvent was removed under reduced pressure. Examination of the <sup>1</sup>H NMR spectrum (in C<sub>6</sub>D<sub>6</sub>) indicated that the benzylic protons integrated at 70% of the normal intensity.

Reaction of [(PNP\*)Rh<sup>I</sup>Cl]K (2) with CH<sub>3</sub>I. Formation of (PNP\*)Rh<sup>III</sup>(CH<sub>3</sub>)Cl (10). To a stirred THF solution (2.0 mL) of 2 (12.2 mg, 0.021 mmol) under an argon atmosphere was added CH<sub>3</sub>I in

excess ( $5.0 \,\mu$ L, 0.080 mmol). The immediate reaction was accompanied by a color change from orange to dark green. The  ${}^{31}P{}^{1}H{}$  NMR spectrum revealed formation of complex **10**, which was present in >90% purity. The reaction solution was evaporated, leaving a dark green residue. The residue was extracted with pentane, leaving a white KI remainder. The pentane solution was filtered through a (0.2  $\mu$ m) Teflon filter and evaporated to dryness, giving 9.5 mg (81% yield) of **10** as a dark green solid.

<sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>): 53.3 (dd (AB), 1P,  $J_{P-P} = 390 \text{ Hz}$ ,  $J_{Rh-P} =$ 101 Hz), 44.7 (dd (AB), 1P,  $J_{P-P}$  = 390 Hz,  $J_{Rh-P}$  = 105 Hz). <sup>1</sup>H NMR  $(C_6D_6)$ : 6.43 (m, 1H, Py H4), 6.36 (d,  $J_{H-H}$  = 8.2 Hz, 1H, Py H3), 5.48 (d,  $J_{H-H}$  = 6.2 Hz, 1H, Py H5), 3.55 (d,  $J_{P-H}$  = 5.9 Hz, 1H, Py-CHP), 2.68 (dbd (AB),  $J_{H-H}$  = 16.9 Hz,  $J_{P-H}$  = 6.7 Hz,  $1H_A$ ,  $Py-CH_2P$ ), 2.53 (ddd (AB),  $J_{H-H} = 16.9$  Hz,  $J_{P-H} = 10.8$  Hz,  $J_{P-H} = 2.2$  Hz,  $1H_B$ , Py-CH<sub>2</sub>P), 2.19 (d app t,  $J_{Rh-H}$  = 2.9 Hz,  $J_{P-H}$  = 4.8 Hz, 3H, Rh $-CH_3$ ), 1.43 (d,  $J_{P-H}$  = 12.2 Hz, 9H, P-t-Bu), 1.40 (dd,  $J_{P-H}$  = 12.3 Hz,  $J_{P-H} = 0.7$  Hz, 9H, P-t-Bu), 1.18 (d,  $J_{P-H} = 12.3$  Hz, 9H, P-t-Bu), 1.09 (d,  $J_{P-H} = 11.7$  Hz, 9H, P-t-Bu). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>): 172.86 (bd, *J*<sub>P-C</sub> = 19.7 Hz, Py C2), 159.55 (m, Py C6), 131.30 (s, Py C4), 114.14 (d,  $J_{P-C}$  = 17.6 Hz, Py C3), 100.60 (d,  $J_{P-C}$  = 11.0 Hz, Py C5), 63.09 (d,  $J_{P-C}$  = 52.7 Hz, Py–CHP), 41.69 (dd,  $J_{P-C}$  = 20.8 Hz,  $J_{\rm P-C}$  = 3.5 Hz, P- $C(\rm CH_3)_3$ ), 37.55 (dd,  $J_{\rm P-C}$  = 18.7 Hz,  $J_{\rm P-C}$  = 6.6 Hz,  $P-C(CH_3)_3$ ), 35.86 (vt,  $J_{P-C} = 6.0$  Hz,  $P-C(CH_3)_3$ ), 35.28 (dd,  $J_{P-C} = 9.2 \text{ Hz}, J_{P-C} = 3.7 \text{ Hz}, P-C(CH_3)_3), 33.41 \text{ (d, } J_{P-C} = 16.7 \text{ Hz},$ Py-CH<sub>2</sub>P), 30.43 (bs, P-C(CH<sub>3</sub>)<sub>3</sub>), 29.81 and 29.78 overlapping (bs,  $P-C(CH_3)_3$ , 29.19 (bs,  $P-C(CH_3)_3$ ), 3.77 (d app t,  $J_{Rh-C}$  = 28.2 Hz,  $J_{P-C} = 4.5$  Hz, CH<sub>3</sub>). Assignment of <sup>13</sup>C{<sup>1</sup>H} NMR signals was confirmed by  ${}^{13}$ C DEPT. ES-MS: m/z 548.27 (calcd 547.93). Anal. Found (calcd for C<sub>24</sub>H<sub>45</sub>ClNP<sub>2</sub>Rh): C, 52.57 (52.61); H, 8.13 (8.28).

Reaction of [(PNP\*)Rh<sup>I</sup>Cl]K (2) with H<sub>2</sub>. Formation of (PNP)Rh<sup>I</sup>H (11a). In a THF solution (0.5 mL) of 2 (9.5 mg, 0.017 mmol) under an argon atmosphere, in a screw-capped NMR tube equipped with a septum, was injected an excess of dry H<sub>2</sub> (6.0 mL, 0.270 mmol). After 16 h at room temperature, the <sup>31</sup>P{<sup>1</sup>H} NMR analysis of the reaction solution revealed full consumption of 2 and formation of compound 11a, which was present in 70% purity, together with 30% of complex 1. The ratio was determined by integration. The reaction was accompanied by a color change from orange to brown. The solvent was evaporated, and the residue was extracted with cold (-35 °C) pentane (2 mL), followed by filtration through a (0.2  $\mu$ m) Teflon filter. Evaporation of pentane gave 4.1 mg (48% yield) of 11a as a brown solid.

Reaction of [(PNP\*)Rh<sup>1</sup>CI]K (2) with D<sub>2</sub>. Formation of (PNP)Rh<sup>1</sup>D (11b). In a THF solution (0.5 mL) of 2 (15.0 mg, 0.026 mmol) under an argon atmosphere, in a screw-capped NMR tube equipped with a septum, was injected an excess of dry D<sub>2</sub> (5.0 mL, 0.230 mmol). The <sup>31</sup>P{<sup>1</sup>H} NMR analysis indicated that after 16 h at room temperature 2 was fully consumed. The <sup>31</sup>P{<sup>1</sup>H} and <sup>2</sup>H{<sup>1</sup>H} NMR spectra of the reaction solution revealed formation of compound 11b, which was present in 70% purity, together with 30% of complex 1. The solvent was evaporated, and the residue was extracted with cold (-35 °C) pentane (2 mL), followed by filtration through a (0.2 µm) Teflon filter. Evaporation of pentane gave 5.3 mg (41% yield) of 11b as a brown solid.

<sup>2</sup>H{<sup>1</sup>H} NMR (THF; measured without <sup>2</sup>H lock): 3.16 (bs, Py-CDHP), -13.51 (bm, Rh-D). <sup>31</sup>P{<sup>1</sup>H} NMR (THF): 82.2 (m,  $J_{Rh-P} = 166.4 \text{ Hz}$ ). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): 7.06 (t,  $J_{H-H} = 7.6 \text{ Hz}$ , 1H, Py H4), 6.56 (d,  $J_{H-H} = 7.6 \text{ Hz}$ , 2H, Py H3,5), 2.91 (bs, 3H, Py-CH<sub>2</sub>P), 1.39 (vt,  $J_{P-H} = 6.3 \text{ Hz}$ , 36H, P-*t*-Bu).

Reaction of (PNP\*)Rh<sup>1</sup>(N<sub>2</sub>) (4) with H<sub>2</sub>. Formation of (PNP)Rh<sup>1</sup>H (11a). Complex  $4^{10}$  was prepared in analogy to the literature procedure, using KOtBu (rather than MeLi) for deprotonation of the benzylic position.

*Method a.* In a THF solution (0.5 mL) of 4 (9.0 mg, 0.017 mmol), under an atmosphere of dry nitrogen in a screw-capped NMR tube equipped with a septum, was injected an excess of dry H<sub>2</sub> (6.0 mL, 0.270 mmol). The  ${}^{31}P{}^{1}H{}$  NMR analysis revealed that after 22 h at room temperature only 17% of 4 was converted to 11a.

Method b. A 90 mL Fischer–Porter tube equipped with a stirring bar was charged under nitrogen with a THF solution (4.0 mL) of 4 (19.6 mg, 0.037 mmol) and pressurized with hydrogen to 5.5 atm. The reaction solution was stirred at room temperature. The  ${}^{31}P{}^{1}H{}$  NMR analysis of the reaction solution revealed full consumption of 4 and formation of compound 11a after 96 h. The reaction was accompanied by a color change from bright red to dark brown. The solvent was evaporated, and the residue was extracted with pentane, followed by filtration through a (0.2  $\mu$ m) Teflon filter. Evaporation of pentane gave 16.7 mg (90% yield) of 11a (at 90% purity) as a brown solid.

<sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>): 83.2 (d,  $J_{Rh-P} = 165.9$  Hz). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): 7.06 (t,  $J_{H-H} = 7.6$  Hz, 1H, Py H4), 6.56 (d,  $J_{H-H} = 7.6$  Hz, 2H, Py H3,5), 2.92 (vt,  $J_{P-H} = 3.0$  Hz, 4H, Py-CH<sub>2</sub>P), 1.39 (vt,  $J_{P-H} = 6.3$  Hz, 36H, P-*t*-B*u*), -12.82 (vq, J = 20.5 Hz, 1H, Rh-*H*). <sup>1</sup>H{<sup>31</sup>P} NMR (C<sub>6</sub>D<sub>6</sub>): -12.82 (d,  $J_{Rh-H} = 19.2$  Hz, 1H, Rh-*H*). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>): 162.19 (dvt,  $J_{P-C} = 7.0$  Hz,  $J_{Rh-C} = 1.5$  Hz, Py C2,6), 129.50 (s, Py C4), 119.31 (vt,  $J_{P-C} = 4.8$  Hz, Py C3,5), 38.62 (dvt,  $J_{P-C} = 3.1$  Hz,  $J_{Rh-C} = 1.1$  Hz, Py-CH<sub>2</sub>P), 33.97 (dvt,  $J_{P-C} = 5.7$  Hz,  $J_{Rh-C} = 2.8$  Hz, P-C(CH<sub>3</sub>)<sub>3</sub>), 29.96 (vt,  $J_{P-C} = 4.7$  Hz, P-C(CH<sub>3</sub>)<sub>3</sub>). Assignment of <sup>13</sup>C{<sup>1</sup>H} NMR signals was confirmed by <sup>13</sup>C DEPT and by <sup>13</sup>C - <sup>1</sup>H HSQC correlation. Anal. Found (calcd for C<sub>23</sub>H<sub>44</sub>NP<sub>2</sub>Rh): C, 55.41 (55.31); H, 8.74 (8.88).

**Computational Methods.** All calculations were carried out using Gaussian09, revision A.02.<sup>22</sup> Two members of the M06 family of DFT functionals<sup>23</sup> were used: M06, a meta-hybrid functional containing 27% HF exchange,<sup>24</sup> and M06-L, its local (nonhybrid) variant.<sup>25</sup>

With these functionals, two basis set–RECP (relativistic effective core potential) combinations were used. The first, denoted SDD(d), is the combination of the Huzinaga–Dunning double- $\zeta$  (D95 V) basis set<sup>26</sup> on lighter elements with the Stuttgart–Dresden basis set–RECP combination<sup>27</sup> on transition metals; extra polarization functions (i.e. the D95(d) basis set) were added to phosphorus. The second, denoted SDB-cc-pVDZ, combines the Dunning cc-pVDZ basis set<sup>28</sup> on the maingroup elements and the Stuttgart-Dresden basis set–RECP<sup>27</sup> on the transition metals with an added f-type polarization exponent taken as the geometric average of the two f exponents given in the appendix of ref 29.

In order to improve the efficiency of the calculations, density-fitting basis sets (DFBS) were employed during the calculation of the Coulomb interaction. The automatic DFBS generation algorithm as implemented in Gaussian09 was employed.<sup>30</sup>

Geometries were optimized using the default pruned (75,302) grid, while the "ultrafine" (i.e., a pruned (99,590)) grid was used for evaluating the charges, especially essential for calculations with the M06 family of functionals.<sup>31</sup>

Geometry optimizations and frequency calculations were performed in the gas phase at the M06-L/SDD(d)/DFBS level of theory. The charges were reevaluated at the M06/SDB-cc-pVDZ level of theory. This combined level of theory is conventionally denoted as M06/SDBcc-pVDZ//M06-L/SDD(d)/DFBS.

# ASSOCIATED CONTENT

**Supporting Information.** Tables giving Cartesian coordinates (XYZ format) of the DFT optimized geometries and figures giving NMR spectra of the complexes **2**, **8**, **10**, and **11a**. This material is available free of charge via the Internet at http:// pubs.acs.org.

#### AUTHOR INFORMATION

#### Corresponding Author

\*E-mail: david.milstein@weizmann.ac.il. Fax: 972-8-9346569.

### ACKNOWLEDGMENT

This research was supported by the European Research Council under the FP7 framework (ERC No 246837), by the Israel Science Foundation, and by the Kimmel Center for Molecular design. D.M. holds the Israel Matz Professorial Chair of Organic Chemistry.

#### REFERENCES

 (a) Grutzmacher, H. Angew. Chem., Int. Ed. 2008, 47, 1814 and references therein. (b) Noyori, R.; Ohkuma, T. Angew. Chem., Int. Ed. 2001, 40, 40. (c) Clapham, S. E.; Hadzovic, A.; Morris, R. H. Coord. Chem. Rev. 2004, 248, 2201. (d) Ikariya, T.; Blacker, A. J. Acc. Chem. Res. 2007, 40, 1300. (e) Maire, P.; Buttner, T.; Breher, F.; Le Floch, P.; Grutzmacher, H. Angew. Chem., Int. Ed. 2005, 44, 6318. (f) Fryzuk, M. D.; MacNeil, P. A. Organometallics 1983, 2, 682. (g) Samec, J. S. M.; Backvall, J. E.; Andersson, P. G.; Brandt, P. Chem. Soc. Rev. 2006, 35, 237. (h) Casey, C. P.; Beetner, S. E.; Johnson, J. B. J. Am. Chem. Soc. 2008, 130, 2285. (i) Shvo, Y.; Czarkie, D.; Rachamim, Y. J. Am. Chem. Soc. 1986, 108, 7400. (j) Bullock, R. M. Chem. Eur. J. 2004, 10, 2366.

(2) For a review on PNP systems and their analogues see: (a) van der Vlugt, J. I.; Reek, J. N. H. *Angew. Chem., Int. Ed.* **2009**, *48*, 8832. Cooperativity in an aliphatic PNP-Ru complex: (b) Friedrich, A.; Drees, M.; Gunne, J. S.; Schneider, S. J. Am. Chem. Soc. **2009**, *131*, 17552.

(3) For a review on catalytic reactions of alcohols catalyzed by PNN- and PNP-Ru pincer complexes, based on metal-ligand cooperation, see: Milstein, D. *Top. Catal.* **2010**, *53*, 915.

(4) (a) Zhang, J.; Leitus, G.; Ben-David, Y.; Milstein, D. J. Am. Chem. Soc. 2005, 127, 10840. (b) Zhang, J.; Shimon, L. J. W.; Milstein, D. Dalton Trans. 2006, 107. (c) Zhang, J.; Leitus, G.; Ben-David, Y.; Milstein, D. Angew. Chem., Int. Ed. 2006, 45, 1113. (d) Gunanathan, C.; Ben-David, Y.; Milstein, D. Science 2007, 317, 790.(e) Milstein, D.; Gunanathan, C.; Gnanprakasam, B.; Balaraman, E.; Zhang, J. US Patent application pending. (f) Zeng, H.; Guan, Z. J. Am. Chem. Soc. 2011, 133, 1159. (g) Gnanaprakasam, B.; Milstein, D. J. Am. Chem. Soc. 2011, 133, 1682. (h) Gnanaprakasam, B.; Ben-David, Y.; Milstein, D. Adv. Synth. Catal. 2010, 352, 3169. (i) Balaraman, E.; Gnanaprakasam, B.; Shimon, L. J. W.; Milstein, D. J. Am. Chem. Soc. 2010, 132, 16756.

(5) Kohl, S. W.; Weiner, L.; Schwartsburd, L.; Konstantinovski, L.; Shimon, L. J. W.; Ben-David, Y.; Iron, M. A.; Milstein, D. *Science* **2009**, *324*, 74.

(6) (a) Khaskin, E.; Iron, M. A.; Shimon, L. J. W.; Zhang, J.; Milstein, D. J. Am. Chem. Soc. 2010, 132, 8542. (b) Gnanaprakasam, B.; Zhang, J.; Milstein, D. Angew. Chem., Int. Ed. 2010, 49, 1468. (c) Zhang, J.; Gandelman, M.; Shimon, L. J. W.; Rozenberg, H.; Milstein, D. Organometallics 2004, 23, 4026. (d) Langer, R.; Leitus, G.; Ben-David, Y.; Milstein, D. Angew. Chem., Int. Ed. 2011, 50, Early View, DOI: 10.1002/anie.201007406. (e) Gunanathan, C.; Gnanaprakasam, B.; Iron, M. A.; Shimon, L. J. W.; Milstein, D. J. Am. Chem. Soc. 2010, 132, 14763. (f) Gunanathan, C.; Shimon, L. J. W.; Milstein, D. J. Am. Chem. Soc. 2009, 131, 3146. (g) Gunanathan, C.; Milstein, D. Angew. Chem., Int. Ed. 2008, 47, 8661.

(7) Tanaka, R.; Yamashita, M.; Nozaki, K. J. Am. Chem. Soc. 2009, 131, 14168.

(8) (a) Ben Ari, E.; Leitus, G.; Shimon, L. J. W.; Milstein, D. J. Am. Chem. Soc. 2006, 128, 15390. (b) Schwartsburd, L.; Iron, M. A.; Konstantinovski, L.; Diskin-Posner, Y.; Leitus, G.; Shimon, L. J. W.; Milstein, D. Organometallics 2010, 29, 3817. For C-H oxidative addition to the aromatic [(PNP)Ir<sup>I</sup>(COE)]BF<sub>4</sub> complex see: (c) Ben-Ari, E.; Gandelman, M.; Rozenberg, H.; Shimon, L. J. W.; Milstein, D. J. Am. Chem. Soc. 2003, 125, 4714. (d) Ben-Ari, E.; Cohen, R.; Gandelman, M.; Shimon, L. J. W.; Martin, J. M. L.; Milstein, D. Organometallics 2006, 25, 3190.

(9) (a) Iron, M. A.; Ben-Ari, E.; Cohen, R.; Milstein, D. Dalton Trans. **2009**, 9433. (b) Zeng, G.; Guo, Y.; Li, S. Inorg. Chem. **2009**, 48, 10257. (10) (a) Kloek, S. M.; Heinekey, D. M.; Goldberg, K. I. Angew. Chem., Int. Ed. 2007, 46, 4736. (b) Kloek, S. M.; Heinekey, D. M.; Goldberg, K. I. Organometallics 2008, 27, 1454.

(11) (a) Hermann, D.; Gandelman, M.; Rozenberg, H.; Shimon, L. J. W.; Milstein, D. *Organometallics* **2002**, *21*, 812. The X-ray crystal structure of complex **1** was determined; see: (b) Feller, M.; Ben-Ari, E.; Tarkeshwar, G.; Shimon, L. J.W.; Leitus, G.; Diskin-Posner, Y.; Weiner, L.; Milstein, D. *Inorg. Chem.* **2007**, *46*, 10479.

(12) **3a** has been prepared previously by reaction of (PNP)Rh(OTf) with diphenylzinc, as described in ref 10.

(13) (a) Vuzman, D.; Poverenov, E.; Shimon, L. J. W.; Diskin-Posner, Y.; Milstein, D. *Organometallics* **2008**, *27*, 2627. (b) Feller, M.; Ben-Ari, E.; Iron, M. A.; Diskin-Posner, Y.; Leitus, G.; Shimon, L. J. W.; Konstantinovski, L.; Milstein, D. *Inorg. Chem.* **2010**, *49*, 1615 and references therein.

(14) An attempt to prepare **5** in situ in dry THF by the reaction of the cationic complex [(PNP)Rh<sup>I</sup>(THF)]BF<sub>4</sub> with an equimolar amount of KN(SiMe<sub>3</sub>)<sub>2</sub> at -35 °C under dry argon resulted in the formation of a mixture of products.

(15)  $N_2$  was reported to bind more strongly than ethylene to the T-shaped (<sup>tBu</sup>PCP)Rh<sup>I</sup> fragment, probably as a result of steric hindrance; see: Vigalok, A.; Ben-David, Y.; Milstein, D. *Organometallics* **1996**, *15*, 1839.

(16) (a) Lee, D. W.; Kaska, W. C.; Jensen, C. M. Organometallics **1998**, *17*, 1. and references therein.(b) Ghosh, R.; Kanzelberger, M.; Emge, T. J.; Hall, G. S.; Goldman, A. S. Organometallics **2006**, *25*, 5668.

(17) For preparation and characterization of complex 9 see ref 11b.
(18) van der Vlugt, J. I.; Pidko, E. A.; Vogt, D.; Lutz, M.; Spek, A. L. *Inorg. Chem.* 2009, 48, 7513.

(19) (a) Ozerov, O. V.; Guo, C.; Papkov, V. A.; Foxman, B. M. J. Am. Chem. Soc. 2004, 126, 4792. (b) Weng, W.; Guo, C.; Moura, C.; Yang, L.; Foxman, B. M.; Ozerov, O. V. Organometallics 2005, 24, 3487. (c) Feller, M.; Iron, M. A.; Shimon, L. J.; Diskin-Posner, Y.; Leitus, G.; Milstein, D. J. Am. Chem. Soc. 2008, 130, 14374.

(20) Complex 1 was also formed in the reaction as a byproduct, apparently as a result of reprotonation of 2 with adventitious water.

(21) (a) Dedieu, A.; Strich, A. Inorg. Chem. 1979, 18, 2940.
(b) Saillard, J. Y.; Hoffmann, R. J. Am. Chem. Soc. 1984, 106, 2006.
(c) Rybtchinski, B.; Ben-David, Y.; Milstein, D. Organometallics 1997, 16, 3786.

(22) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A.; , Jr., Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, Revision A.02; Gaussian, Inc., Wallingford, CT, 2009.

(23) Zhao, Y.; Truhlar, D. G. Acc. Chem. Res. 2008, 41, 157.

(24) Zhao, Y.; Truhlar, D. G. Theor. Chem. Acc. 2008, 120, 215.

(25) Zhao, Y.; Truhlar, D. G. J. Chem. Phys. 2006, 125, 194101.

(26) Dunning, T. H., Jr.; Hay, P. J. In *Modern Theoretical Chemistry 3. Methods of Electronic Structure Theory*: Schaefer, H. F., III, Ed.; Plenum Press: New York, 1977; Vol. 3, pp 1–28.

(27) Dolg, M. In *Modern Methods and Algorithms of Quantum Chemistry*; Grotendorst, J., Ed.; John von Neumann Institute for Computing: Jülich, Germany, 2000; Vol. 3, pp 507–540.

(28) Dunning, T. H., Jr. J. Chem. Phys. 1989, 90, 1007.

(29) Martin, J. M. L.; Sundermann, A. J. Chem. Phys. 2001, 114, 3408.

(30) (a) Dunlap, B. I. J. Chem. Phys. **1983**, 78, 3140. (b) Dunlap, B. I. J. Mol. Struct. (THEOCHEM) **2000**, 529, 37.

(31) Wheeler, S. E.; Houk, K. N. J. Chem. Theory Comput. 2010, 6, 395.