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[Rh{NC$_5$H$_3$-2,6-(CH$_2$P^{t}Bu$_2$)$_2$}(PCy$_3$)][BAr$^F_4$]: A Latent Low-Coordinate Rhodium(I) PNP Pincer Compound

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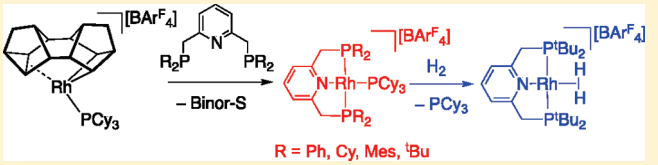
Supporting Information

ABSTRACT: An expedient new route to the cationic [(PNP^{tBu})Rh(L)]$^+$ metal fragments (PNP^{tBu} = κ^3-NC$_5$H$_3$-2,6-(CH$_2$P ^{t}Bu$_2$)$_2$; L = CO, acetone, ethene, MeCN, N$_2$) by the synthesis of, then substitution of PCy$_3$ in, [(PNP^{tBu})Rh(PCy$_3$)][BAr$^F_4$] is reported. This synthetic route also allows for the synthesis of the new dihydrogen complex [(PNP^{tBu})Rh(H$_2$)][BAr$^F_4$]. [(PNP^R)Rh(PCy$_3$)][BAr$^F_4$] (R= Ph, Cy, Mes) are also reported, in which the PCy$_3$ ligand is more tightly bound to the metal center.

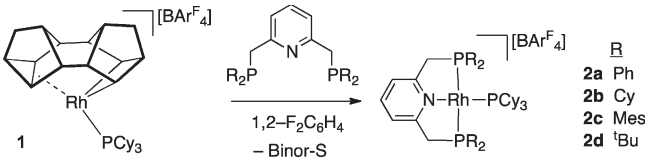


Multidentate "pincer" type−ligands exemplified by PNP^R, PCP^R, and PONOP^R play an ever-increasing role in organometallic and catalytic chemistry (PNP^R = κ^3-NC$_5$H$_3$-2,6-(CH$_2$PR$_2$)$_2$; PCP^R = κ^3-C$_6$H$_3$-1,3-(CH$_2$PR$_2$)$_2$; PONOP^R = κ^3-NC$_5$H$_3$-2,6-(OPR$_2$)$_2$; R = alkyl, aryl).[1−3] One of the attractive properties of these ligand sets is their apparent ability to support the generation of low-coordinate reactive metal species that are implicated in many catalytic cycles, as demonstrated by their role in alkane dehydrogenation[4,5] and the characterization of a σ-methane complex.[6] In some cases these ligands can also act in a noninnocent manner, undergoing reversible dearomatization and subsequent cooperative reactivity between the ligand and the metal.[7−10] With regard to group 9 complexes of PNP^R ligands, cationic complexes of the general formula [(PNP^{tBu})Rh(L)]$^+$ (L = weakly bound ligand[11−13]) are potentially useful precursors to such reactive 14-electron species. Here we report a new route to [(PNP^{tBu})Rh(L)]$^+$ cations by the expedient synthesis and onward reactivity of [(PNP^{tBu})Rh(PCy$_3$)][BAr$^F_4$], in which steric pressure between the ^{t}Bu and Cy groups invokes a reactive {(PNP^{tBu})Rh}$^+$ fragment which combines readily with a variety of ligands (CO,[11] acetone,[11] ethene,[12] MeCN,[12] N$_2$[13]) to give [(PNP^{tBu})Rh(L)][BAr$^F_4$]. We demonstrate that this synthetic route to a latent 14-electron complex allows for the synthesis of the new dihydrogen complex [(PNP^{tBu})Rh(H$_2$)][BAr$^F_4$] and also report the synthesis of [(PNP^R)Rh(PCy$_3$)][BAr$^F_4$] (R = Ph, Cy, Mes), in which the PCy$_3$ ligand is more tightly bound.

RESULTS AND DISCUSSION

We have previously reported that addition of Lewis Bases to the straightforwardly prepared C−C σ complexes [Rh(Binor-S)(PR$_3$)][BAr$^F_4$] (Binor-S = 1,2,4,5,6,8-dimetheno-*S*-indacene, R = ^{i}Pr, Cy (**1**); Ar^F = C$_6$H$_3$(CF$_3$)$_2$) leads to reductive elimination of free Binor-S, the generation of {Rh(PR$_3$)}$^+$ fragments, and the subsequent rapid coordination of the Lewis base.[14−16]

Scheme 1



In a similar manner, we now report that addition of the pincer ligands PNP^R (R = Ph, Cy, Mes, ^{t}Bu; Mes = 2,4,6-Me$_3$C$_6$H$_2$) to [Rh(Binor-S)(PCy$_3$)][BAr$^F_4$] (**1**) results in the formation of the new Rh(I) complexes [(PNP^R)Rh(PCy$_3$)][BAr$^F_4$] (**2a**, R = Ph; **2b**, R = Cy; **2c**, R = Mes; **2d**, R = ^{t}Bu), which are all isolated in reasonable yield by recrystallization (Scheme 1). The NMR spectroscopic data in CD$_2$Cl$_2$ for **2a**,**b** are unremarkable and are fully consistent with pseudo-square-planar structure with time-averaged C_{2v} symmetry. In particular, two mutually coupled signals are observed in the ^{31}P{^{1}H} NMR spectrum in a 2:1 ratio, and a single, integral 4H environment is observed for the PNP^R methylene protons in the ^{1}H NMR spectrum. For **2c** the bulky Mes group has restricted rotation of the aryl groups, and C_2 symmetry is observed: i.e., six equal-intensity (6H) methyl and two CH$_2$ environments in the ^{1}H NMR spectrum (CD$_2$Cl$_2$). The ^{31}P{^{1}H} NMR spectrum shows two mutually coupled signals in a 2:1 ratio that also couple to ^{103}Rh. The structure of **2c** was confirmed by single-crystal X-ray diffraction, and although the final structural refinement was poor, the connectivity was confirmed (Supporting Information). For PNP^{tBu} steric influences now become more important and the ^{31}P{^{1}H} NMR spectrum of the isolated material in 1,2-C$_6$H$_4$F$_2$ solution shows two species, one with bound PCy$_3$ (δ 63.3, 2P, dd; δ 47.4, 1P, dt) identified as **2d** and one with a broad signal at δ 67.3 that is accompanied by free PCy$_3$ (δ 11.2). In the ^{1}H NMR spectrum

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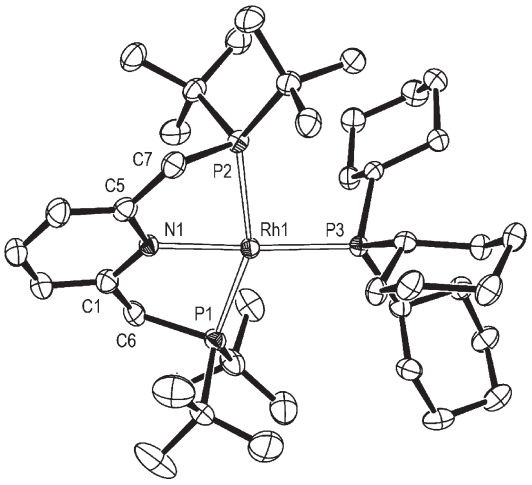


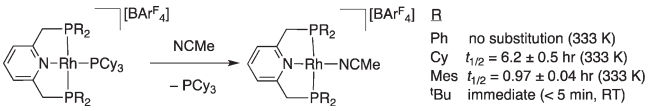
Figure 1. Solid-state structure of **2d**. Thermal ellipsoids are depicted at the 50% probability level. Hydrogen atoms and the anion are omitted for clarity. Key bond lengths (Å) and angles (deg): Rh1−N1, 2.159(2); Rh1−P1, 2.3470(9); Rh1−P2, 2.4240(9); Rh1−P3, 2.3293(8); N1−Rh1−P3, 174.51(7); P1−Rh1−P2, 155.45(3); ∠{lsq plane (Rh1, N1, P1, P2, P3); lsq plane (N1, C1, C2, C3, C4, C5, C6, C7)}, 25.31(7); N1−C1−C6−P1, 36.2(4); N1−C5−C7−P2, 28.5(4).

single environments due to the ^{t}Bu groups and PNP backbone are observed for both species, indicating time-averaged C_{2v} symmetry for both. Variable-temperature studies were frustrated by this mixture reacting with suitable low-temperature solvents, e.g. CD_2Cl_2, to give unidentified products. We speculate this occurs via the reaction of a putative $\{(PNP^{tBu})Rh\}^+$ fragment. In contrast, **2a**−**c** are stable in CD_2Cl_2. Addition of excess PCy_3 (10 equiv) pushes the equilibrium between the two species in complete favor of **2d** and enables clean $^{31}P\{^1H\}$ NMR spectra to be acquired for **2d**. We have not been able to identify the other species in equilibrium with **2d** at low [PCy_3] but suggest that it might be a $\{(PNP^{tBu})Rh\}^+$ fragment, [**2d**−PCy_3]$^+$, stabilized by solvent (difluorobenzene), agostic interactions, or rapid/reversible C−H activation from the ^{t}Bu ligands.[17,18] The solid-state structure of **2d** (Figure 1) shows the expected pseudo-square-planar environment around Rh. The Rh−P distances are all relatively long (2.3293(8) − 2.4240(9) Å), indicative of the steric pressure (cf. $[(PNP^{tBu})Rh(CO)][BF_4]$ 2.301(3) Å[11]). The PNP^{tBu} ligand is twisted, with the pyridine group lying 25.31(7)° relative to the N1, P1, Rh1, P2, P3 plane. The related complexes $[(PNP^{tBu})Rh(PR_3)][BF_4]$ (R = Et, Ph) have been previously synthesized from reduction of the Rh(II) complex $[(PNP^{tBu})Rh(acetone)][BF_4]_2$ with PR_3/H_2O.[11]

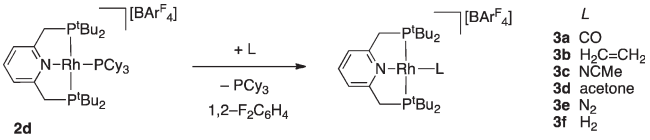
Increasing steric pressure between the pincer and PCy_3 ligands by changing the appended groups on the PNP^R ligand is demonstrated by the relative rates of substitution of the PCy_3 ligand in **2a**−**d** by excess MeCN to form $[(PNP^R)Rh(NCMe)][BAr^F{}_4]$ and free PCy_3 (Scheme 2). **2a** does not undergo exchange at 333 K and **2b**,**c** undergo substitution at 333 K that follows a first-order rate law with the latter being considerably faster, while for **2d** exchange is effectively instant at *room temperature*. The exchange of phosphine ligands in Rh(I) pincer systems has been previously reported.[19,20]

We have extended this substitution chemistry with **2d**, as it is a useful precursor to the reactive $\{(PNP^{tBu})Rh\}^+$ fragment through ultimate dissociation of PCy_3. Thus, addition of a variety of Lewis bases to **2d** gives the known cations $[(PNP^{tBu})Rh(L)]^+[BAr^F{}_4]^-$ salts and 1 equiv of PCy_3 (L = CO,[11] acetone,[11] ethene,[12] MeCN,[12] N_2[13]) in quantitative yield by NMR spectroscopy (**3a**−**3e**; Scheme 3). The liberated PCy_3 can be conveniently removed by washing with pentane. A further demonstration that **2d** acts as such a precursor comes from addition of H_2 (1 atm) to **2d**, which immediately forms the new complex $[(PNP^{tBu})Rh(H_2)][BAr^F{}_4]$ (**3f**).

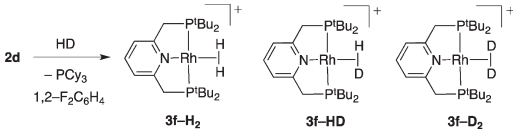
Scheme 2



Scheme 3



Scheme 4[a]



[a] $[BAr^F{}_4]^-$ anions not shown.

NMR data for **3f** in 1,2-$C_6H_4F_2$ solution show a C_{2v}-symmetric structure and a low-frequency relative 2H signal at δ −10.79 (T_1 71 ± 2 ms, 500 MHz, 298 K) as a broad doublet of triplets showing coupling to ^{31}P and ^{103}Rh (5 and 27 Hz, respectively), confirmed by $^1H\{^{31}P\}$ NMR experiments. In contrast to the case for **2d**, **3f** is sufficiently stable in CD_2Cl_2 to allow for the collection of variable-temperature ^{1}H NMR spectra and the measurement of T_1 relaxation time as a function of temperature. At the lowest temperature accessed (200 K, 500 MHz) T_1 = 21.5 ms, clearly placing the ligand as dihydrogen.[21] Further support for this assignment comes from addition of HD(g) to a 1,2-$C_6H_4F_2$ solution of **2d**, which resulted in the rapid formation of a mixture of isotopomers, $[(PNP^{tBu})Rh(H_2)][BAr^F{}_4]$ (**3f-H$_2$**), $[(PNP^{tBu})Rh(HD)][BAr^F{}_4]$ (**3f-HD**), and $[(PNP^{tBu})Rh(D_2)][BAr^F{}_4]$ (**3f-D$_2$**), for which the ^{1}H NMR spectrum showed an overlapping set of signals for bound HD and H_2 in the high-field region (Scheme 4; Supporting Information). For the complex **3f-HD** a signal is observed at δ −10.73 as an apparent quartet of triplets that collapses to an apparent quartet on decoupling ^{31}P, which shows the H−D coupling to be 27 Hz, the same as the ^{103}Rh coupling, and J(PH) = 6 Hz. **3f-H$_2$** is observed in a relative molar ratio of 0.5 relative to **3f-HD**, consistent with a statistical distribution of H and D. The observation of HD coupling in **3f-HD** supports the assignment of a bound H_2 ligand and is very similar to that observed in the Co−dihydrogen complex (POCOP)Co(HD) (28 Hz, δ −11.2) as well as $(PCP^{tBu})Rh(HD)$ (33 Hz).[22] Remarkably, these dihydrogen isotopomers are stable under ESI-MS conditions, which shows

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all three in an approximate 1:2:1 ratio, respectively (Supporting Information). The observation of all three possible H/D exchange products suggests that an accessible dihydrogen/dihydride tautomerism operates for **3f** that invokes a dihydrogen/dihydride intermediate.[23] Complex **3f** adds to this small number of group 9 pincer complexes with dihydrogen ligands[6,23−26] and is also related to the σ-methane complex $[(PONOP)Rh(H_4C)][BAr^F{}_4]$ that is observed at low temperature in solution.[6]

In conclusion, we report a new route to a series of cationic $[(PNP^R)Rh(PCy_3)]^+$ salts. For PNP^{tBu} we also demonstrate ready displacement of the phosphine by a range of ligands, one of which is H_2, which forms the new dihydrogen complex $[(PNP^{tBu})Rh(H_2)][BAr^F{}_4]$. This expedient synthetic route to these materials potentially allows for a wide range of Rh(I) pincer complexes to be prepared from the same starting material (**1**) as well as for the relatively robust, noncoordinating $[BAr^F{}_4]^-$ anion to be incorporated straightforwardly into these salts.

EXPERIMENTAL SECTION

General Experimental Methods. All manipulations were performed under an atmosphere of argon, using Schlenk and glovebox techniques. Glassware was oven-dried at 130 °C overnight and flamed under vacuum prior to use. CH_2Cl_2, MeCN, and pentane were dried using a Grubbs type solvent purification system (MBraun SPS-800) and degassed by successive freeze−pump−thaw cycles. CD_2Cl_2 and 1,2-$C_6H_4F_2$ were dried over CaH_2, vacuum-distilled, and stored over 3 Å molecular sieves. Acetone (less than 0.0075% H_2O) was purchased from VWR and degassed by successive freeze−pump−thaw cycles. **1**,[27] PNP^{tBu},[12] PNP^{Mes},[28] PNP^{Cy},[29] and PNP^{Ph} [30] were prepared using literature methods. NMR spectra were recorded on a Bruker DRX 500 MHz spectrometer at 298 K, unless otherwise stated. Chemical shirts are quoted in ppm and coupling constants in Hz. Microanalyses were performed at Elemental Microanalysis Ltd. ESI-MS were recorded on a Bruker MicroOTOF instrument.[31]

Synthesis of 2. In a Schlenk flask charged with **1** (0.050 g, 0.035 mmol) and PNP^{tBu} (0.014 g, 0.035 mmol) was added 1,2-$C_6H_4F_2$ (1 mL), and resulting solution was stirred at room temperature for 30 min. Recrystallization from 1,2-$C_6H_4F_2$−pentane gave the product as orange-red crystals. Yield: 0.031 g (**2d**, 54%). **2a**−**c** were prepared analogously in 46, 41, and 53% isolated yields, respectively. **2a**, **b** clathrate solvent, which could not be removed completely, even under prolonged high vacuum.

Complex ***2a***. ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 7.82−7.89 (m, 8H, *o*-C_6H_5), 7.70−7.74 (m, 8H, Ar^F), 7.56 (br, 4H, Ar^F), 7.42−7.53 (m, 13H, C_5H_3N {1H} + C_6H_5 {12H}), 7.05 (d, $^3J_{HH}$ = 7.7, 2H, C_5H_3N), 4.06 (app t, J_{PH} = 3.4, 4H, PCH_2), 1.36−1.72 (m, 24H, Cy), 0.98−1.09 (m, 3H, Cy), 0.58−0.70 (m, 6H, Cy). $^1H\{^{31}P\}$ NMR (CD_2Cl_2, 500 MHz, selected data): δ 7.86 (br d, $^3J_{HH}$ = 7.3, 8H, *o*-C_6H_5). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 202 MHz): δ 51.4 (dt, $^1J_{RhP}$ = 154, $^2J_{PP}$ = 35, 1P, PCy_3), 49.6 (dd, $^1J_{RhP}$ = 152, $^2J_{PP}$ = 35, 2P, PPh_2). $^{31}P\{^1H\}$ NMR (MeCN-d3, 202 MHz) δ 52.8 (dt, $^1J_{RhP}$ = 154, $^2J_{PP}$ = 34, 1P, PCy_3), 47.4 (dd, $^1J_{RhP}$ = 151, $^2J_{PP}$ = 34, 2P, PPh_2). ESI-MS (CH_2Cl_2, 60 °C, 4.5 kV, positive ion): *m*/*z* 858.296 $[M]^+$ (calcd 858.299).

Complex ***2b***. ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 7.70−7.75 (m, 9H, C_5H_3N {1H} + Ar^F {8H}), 7.56 (br, 4H, Ar^F), 7.33 (d, $^3J_{HH}$ = 7.7, 2H, C_5H_3N), 3.42 (app t, J_{PH} = 3.4, 4H, PCH_2), 0.87−2.28 (m, 77H, Cy). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 202 MHz): δ 54.4 (dt, $^1J_{RhP}$ = 161, $^2J_{PP}$ = 35, 1P, PCy_3), 49.6 (dd, $^1J_{RhP}$ = 139, $^2J_{PP}$ = 35, 2P, $PMes_2$). $^{31}P\{^1H\}$ NMR (MeCN-d3, 202 MHz): δ 55.6 (dt, $^1J_{RhP}$ = 162, $^2J_{PP}$ = 35, 1P, PCy_3), 50.3 (dd, $^1J_{RhP}$ = 140, $^2J_{PP}$ = 35, 2P, PCy_2). ESI-MS (CH_2Cl_2, 60 °C, 4.5 kV, positive ion): *m*/*z* 882.482 $[M]^+$ (calcd 882.487).

Complex ***2c***. ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 7.70−7.74 (m, 8H, Ar^F), 7.56 (br, 4H, Ar^F), 7.14 (t, $^3J_{HH}$ = 7.7, 1H, C_5H_3N), 7.04 (s, 2H, $C_6H_2Me_3$), 6.81 (s, 2H, $C_6H_2Me_3$), 6.66 (d, $^3J_{HH}$ = 7.7, 2H, C_5H_3N), 6.62 (s, 2H, $C_6H_2Me_3$), 6.56 (s, 2H, $C_6H_2Me_3$), 4.68 (d, $^2J_{HH}$ = 13.6, 2H, PCH_2), 4.07 (dt, $^2J_{HH}$ = 13.6, J_{PH} = 4.6, 2H, PCH_2), 3.75 (s, 6H, $C_6H_2Me_3$), 2.92 (s, 6H, $C_6H_2Me_3$), 2.28 (s, 6H, $C_6H_2Me_3$), 2.05 (s, 6H, $C_6H_2Me_3$), 1.92−2.08 (m, 6H, Cy), 1.95 (s, 6H, $C_6H_2Me_3$), 1.72 (s, 6H, $C_6H_2Me_3$), 1.42−1.68 (m, 18H, Cy), 1.03−1.15 (m, 3H, Cy), 0.75−0.87 (m, 3H, Cy), 0.49−0.61 (m, 3H, Cy). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 202 MHz): δ 42.5 (dt, $^1J_{RhP}$ = 163, $^2J_{PP}$ = 32, 1P, PCy_3), 25.3 (dd, $^1J_{RhP}$ = 150, $^2J_{PP}$ = 32, 2P, $PMes_2$). $^{31}P\{^1H\}$ NMR (MeCN, 202 MHz): δ 43.2 (dt, $^1J_{RhP}$ = 162, $^2J_{PP}$ = 32, 1P, PCy_3), 25.8 (dd, $^1J_{RhP}$ = 151, $^2J_{PP}$ = 32, 2P, PPh_2). ESI-MS (CH_2Cl_2, 60 °C, 4.5 kV, positive ion): *m*/*z* 1026.482 $[M]^+$ (calcd 1026.487). Anal. Calcd for $C_{93}H_{96}BF_{24}NP_3Rh$ (1890.391 g mol^{-1}): C, 59.09; H, 5.12; N, 0.74. Found: C, 58.92; H, 5.04; N, 0.98.

Complex ***2d***. This compound is best characterized in 1,2-$C_6H_4F_2$ solution in the presence of excess PCy_3 to suppress ligand dissociation (0.008 g of **2d**, 0.014 g of PCy_3, 0.5 mL of 1,2-$C_6H_4F_2$). In the absence of excess PCy_3 a poorly characterized species, {[**2d**-PCy_3]}, is observed with δ 67.3 (br d, $^1J_{RhP} \sim 100$) alongside **2d** and uncoordinated PCy_3 in an approximate ratio of 1:0.85:0.5 in 1,2-$C_6H_4F_2$ by ^{31}P NMR spectroscopy.

^{1}H NMR (1,2-$C_6H_4F_2$, 500 MHz, selected data, intramolecular integrations): δ 7.82 (t, $^3J_{HH}$ = 7.9, 1H, C_5H_3N {[**2d**-PCy_3]}), 7.63 (t, $^3J_{HH}$ = 7.7, 1H, C_5H_3N {**2d**}), 7.54 (d, $^3J_{HH}$ = 7.9, 2H, C_5H_3N {[**2d**-PCy_3]}), 3.84 (app t, J_{PH} = 3, 4H, PCH_2 {[**2d**-PCy_3]}), 3.51 (app t, J_{PH} = 3, 4H, PCH_2 {**2d**}), 1.36 (br app t, J_{PH} = 6, 36H, ^{t}Bu {**2d**}), 1.21 (app t, J_{PH} = 7.2, 36H, ^{t}Bu {[**2d**-PCy_3]}). ^{1}H NMR (1,2-$C_6H_4F_2$ + 10 PCy_3/Rh, 500 MHz): δ 8.30−8.35 (m, 8H, Ar^F), 7.68 (br, 4H, Ar^F), 7.63 (t, $^3J_{HH}$ = 7.7, 1H, C_5H_3N), 3.51 (app t, J_{PH} = 3, 4H, PCH_2), 1.36 (obscured, 36H, ^{t}Bu). The 2H C_5H_3N resonance was not located, presumably as it is obscured by solvent resonances. $^{31}P\{^1H\}$ NMR (1,2-$C_6H_4F_2$ + 10 PCy_3/Rh, 202 MHz): δ 63.3 (br dd, $^1J_{RhP}$ = 140, $^2J_{PP}$ = 32, 2P, P^tBu_2), 47.4 (dt, $^1J_{RhP}$ = 159, $^2J_{PP}$ = 32, 1P, PCy_3). ESI-MS (1,2-$C_6H_4F_2$, 60 °C, 4.5 kV, positive ion): *m*/*z*, 778.423 $[M]^+$ (calcd 778.425). Anal. Calcd for $C_{73}H_{88}BF_{24}NP_3Rh$ (1642.108 g mol^{-1}): C, 53.40; H, 5.40; N, 0.85. Found: C, 53.57; H, 5.35; N, 0.92.

NMR Experiments. *Reactions of* ***2a***−***c*** *with MeCN.* Solutions of **2a**−**c** (0.005 mmol) in MeCN (ca. 0.5 mL) were prepared in J. Young NMR tubes and monitored at 333 K in situ using $^{31}P\{^1H\}$ NMR spectroscopy. **2a**: no reaction observed after 70 h. **2b**: first-order substitution (R^2_{fit} = 0.993) of PCy_3 with a rate constant of (3.1 ± 0.2) × 10^{-5} s^{-1}. **2c**: first-order substitution (R^2_{fit} = 0.998) of PCy_3 with a rate constant of (1.99 ± 0.08) × 10^{-4} s^{-1}.

$[Rh(PNP^{Cy})(NCMe)]^+$: $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 202 MHz) δ 46.9 (d, $^1J_{RhP}$ = 135); ESI-MS (CH_2Cl_2, 60 °C, 4.5 kV, positive ion) *m*/*z* 643.282 $[M]^+$ (calcd 643.282). $[Rh(PNP^{Mes})(NCMe)]^+$: $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 202 MHz) δ 16.7 (d, $^1J_{RhP}$ = 135); ESI-MS (CH_2Cl_2, 60 °C, 4.5 kV, positive ion) *m*/*z* 787.280 $[M]^+$ (calcd 787.282).

Reaction of ***2d*** *with Lewis Bases: General Procedure.* Solutions of **2d** (8 mg, 0.005 mmol) in 1,2-$C_6H_4F_2$ (ca. 0.5 mL) were prepared in J. Young NMR tubes. Liquid reagents (0.01 mmol) were added under an atmosphere of argon. Gaseous reagents were added by placing the headspace of the J. Young NMR tube under the appropriate gas (1 atm). Reactions were monitored at 298 K immediately using $^{31}P\{^1H\}$ NMR spectroscopy and indicated rapid (<5 min) and quantitative formation of **3** and free PCy_3.

Reaction of ***2d*** *with Hydrogen.* Synthesis followed the general procedure. Removing the solvent in vacuo and redissolving in CD_2Cl_2 allowed characterization at low temperature. **3f** has limited stability in this solvent ($t_{1/2} \approx 16$ h).

Complex **3f**: ^{1}H NMR (1,2-$C_6H_4F_2$, 500 MHz, 298 K) δ 8.31−8.36 (m, 8H, Ar^F), 7.72 (t, $^3J_{HH}$ = 7.7, 1H, C_5H_3N), 7.69 (br, 4H, Ar^F), 7.43

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(d, $^3J_{HH}$ = 7.7, 2H, C_5H_3N), 3.61 (app t, J_{PH} = 3.4, 4H, PCH_2), 1.31 (app t, J_{PH} = 3.4, 36H, ^{t}Bu), −10.79 (br dt, $^1J_{RhH}$ = 26.8, $^2J_{PH}$ = 5, 2H, 71 ± 2 ms, RhH); $^{31}P\{^1H\}$ NMR (1,2-$C_6H_4F_2$, 202 MHz, 298 K) δ 83.0 (d, $^1J_{RhP}$ = 120); ^1H NMR (CD_2Cl_2, 500 MHz, 298 K, selected data) δ −11.0 (br d, $^1J_{RhH}$ = 25.9, 2H, RhH); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 202 MHz, 298 K) δ 83.2 (d, $^1J_{RhP}$ = 120); ^1H NMR (CD_2Cl_2, 500 MHz, 273 K, selected data) δ −10.9 (br d, $^1J_{RhH} \approx$ 20, 2H, RhH); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 202 MHz, 273 K) δ 83.0 (d, $^1J_{RhP}$ = 120); ^1H NMR (CD_2Cl_2, 500 MHz, 250 K, selected data) δ −10.9 (br d, $^1J_{RhH} \approx$ 20, 2H, RhH); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 202 MHz, 250 K) δ 82.7 (d, $^1J_{RhP}$ = 120); ^1H NMR (CD_2Cl_2, 500 MHz, 225 K, selected data) δ −10.8 (br d, $^1J_{RhH} \approx$ 20, 2H, RhH); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 202 MHz, 225 K) δ 82.5 (d, $^1J_{RhP}$ = 120); ^1H NMR (CD_2Cl_2, 500 MHz, 200 K, selected data) δ −10.8 (br d, $^1J_{RhH} \approx$ 20, 2H, RhH); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 202 MHz, 200 K) δ 82.3 (d, $^1J_{RhP}$ = 120); T_1 measurements (CD_2Cl_2, 500 MHz) 88 ± 2 ms (298 K), 63 ± 2 ms (273 K), 43.0 ± 0.7 ms (250 K), 28.1 ± 0.4 ms (225 K), 21.5 ± 0.6 ms (200 K), T_1(min, calc) = 20.3 ms (180 K) from a second order polynomial fit (R^2_{fit} = 0.999); ESI-MS (1,2-$C_6H_4F_2$, 60 °C, 4.5 kV, positive ion) m/z 500.206 $[M]^+$ (calcd 500.208).

Reaction of ***2d*** *with Deuterium Hydride.* Synthesis followed the general procedure. It resulted in quantitative formation of a 1:2:1 mixture of **3f-H$_2$**, **3f-HD**, and **3f-D$_2$** and free PCy_3. ^1H NMR (1,2-$C_6H_4F_2$, 500 MHz, selected data): δ 8.31−8.36 (m, 8H, Ar^F), −10.73 (app qt, J = 27, $^2J_{PH}$ = 6, 0.5H, Rh(HD)), −10.79 (obscured, 0.5H, Rh(H_2)); ESI-MS (1,2-$C_6H_4F_2$, 60 °C, 4.5 kV, positive ion) m/z 500.209 $[Rh](H_2)^+$ (calcd 500.208), 501.215 $[Rh](HD)^+$ (calcd 501.214), 502.221 $[Rh](D_2)^+$ (calcd 502.220), peak intensities approximately 1:2:1.

Crystallography. Details about the data collection and refinement for the X-ray structure of **2d** are documented in the Supporting Information (CIF).

Crystallographic Data for ***2d****:* $C_{73}H_{88}BF_{24}NP_3Rh$, M = 1642.07; monoclinic, $P2_1/n$ (Z = 4), a = 13.447 80(10) Å, b = 15.010 10(10) Å, c = 37.0273(4) Å, β = 94.5047(4)°, V = 7450.98(11) Å^3; T = 150(2) K, 5.10 ≤ θ ≤ 26.37° collected, 14 971 unique reflections (R_{int} = 0.0403), completeness to 26.37° 98.2%; final R_1 = 0.0469 ($I > 2\sigma(I)$), GoF = 1.035, maximum/minimum residual electron density 0.897/−0.514 e Å^{-3}.

■ ASSOCIATED CONTENT

Supporting Information. Figures giving a ball and stick X-ray structure of **2c** and NMR and ESI-MS spectra of the reaction between **2d** and hydrogen and deuterium hydride and a CIF file giving crystallographic data for **2d**. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data have also been deposited with the Cambridge Crystallographic Data Centre under CCDC 827146. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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