Structure and Reactivity of Rhodium(I) Complexes Based on Electron-Withdrawing Pyrrolyl-PCP-Pincer Ligands

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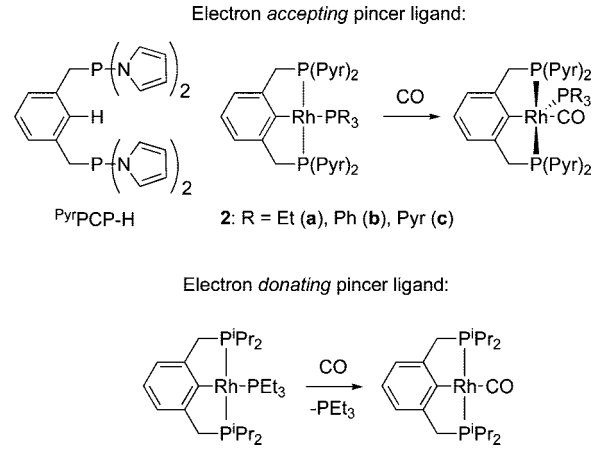
Rhodium complexes based on the electron-withdrawing PCP-type pincer ligand dipyrrolylphoshinoxylene (DPyPX, ^{Pyr}PCP) were synthesized and their reactivity was studied. Reaction of $Rh^{I}(^{Pyr}PCP)PR_3$ (**2**) (R = Et (**a**); Ph (**b**); Pyr (pyrrolyl, NC_4H_4) (**c**); Pyd (pyrrolydinyl, NC_4H_8) (**d**)) with MeI was strongly dependent on the sterics and nucleophilicity of PR_3. Complex **2a** (PEt_3 cone angle, Θ°, 132°) reacted with MeI to give isomers of $Rh^{III}(^{Pyr}PCP)Me(I)PEt_3$, **3**. Reaction of **2b** ($\Theta°_{PR3}$ = 145°, R = Pyd (**2d**), Ph (**2b**), Pyr (**2c**)) with MeI was accompanied by release of PPh_3 and is thought to proceed via the 14*e* intermediate $Rh^{I}(^{Pyr}PCP)$. While the $PPyd_3$ complex **2d** reacted with MeI to give $[Rh^{III}(^{Pyr}PCP)Me(I)_2][MePPyd_3]$, **4a**, the $PPyr_3$ complex **2c** did not react, owing to steric hindrance around Rh^{I} and the low nucleophilicity of $PPyr_3$. The aptitude of complexes **2** toward activation of H_2 was also examined. Our results support the involvement of 14*e* intermediates in the olefin hydrogenation process. The ancillary ligand substitution at the Rh^{I} center of **2** was found to proceed by an associative mechanism. ML_5 d^8 intermediates were clearly detected by $^{31}P\{^{1}H\}$ NMR at 213 K during equilibrium between **2a** and **2c**.

Introduction

Since the pioneering work of Moulton and Shaw[1] pincer-type ligands have attracted much scientific interest.[2] Late transition metal complexes based on pincer ligands of the PCP type were found to be active in a variety of important catalytic processes[2a] and in the activation of strong bonds.[2b,c] They were also invaluable for mechanistic studies and for the stabilization of unusual structures,[2d] and useful as functional materials.[2e] Although PCP ligands with a variety of electron-donating phosphine substituents have been widely explored, electron-accepting substituents were introduced only recently.[3−5]

^{Pyr}PCP-H (Scheme 1) was the first reported highly electron accepting PCP-type pincer ligand.[3,4] Its synthesis was inspired by the work of Molloy and Petersen,[6] who demonstrated that *N*-pyrrolyl phosphines possess exceptional electron-accepting properties. The π-accepting ability of trispyrrolylphosphine, $PPyr_3$, was found to be similar to that of $P(C_6F_5)_3$ and to exceed those of phosphites such as $P(OPh)_3$. Contrary to many perfluoroalkyl moieties, pyrrole-like precursors are readily available and easily amenable to structural variations.

Scheme 1. ^{Pyr}PCP-H and the Coordination Mode of ^{Pyr}PCP-Based Rhodium(I) Complexes



The high electron-accepting ability of the pyrrolyl moieties in ^{Pyr}PCP and the rigidity and synergetic effects typical of pincer-type ligands[2] are combined in order to create electron-deficient and structurally well-defined metal centers. We have reported that ^{Pyr}PCP-based rhodium(I) complexes possess significantly different coordination chemistry from those of Rh^{I} complexes based on electron-donating pincer-type ligands.[3] Namely, the π-accepting nature of the ^{Pyr}PCP ligand disfavors formation of

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the coordinately unsaturated ML_4 complexes, leading to formation of the first stable d^8 ML_5 PCP complexes (Scheme 1).

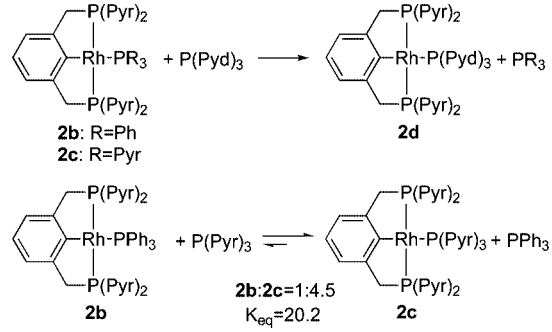
We present here a study of the reactivity of $Rh^I(^{Pyr}PCP)PR_3$ (R = Et, Ph, Pyr, Pyd) complexes. Understanding the effect of the electron-accepting ^{Pyr}PCP pincer ligand on the reactivity of the rhodium(I) center is essential for the development of catalytic applications of this type of complexes.

Results and Discussion

Preparation of $Rh^I(^{Pyr}PCP)PR_3$ (R = Et, Ph, Pyr) Complexes. PCP-based rhodium(III) compounds are easily prepared by oxidative addition of the Ar−H bond of α,α′-diphosphine-*m*-xylenes to rhodium(I) metal centers.[1,7] Similarly, the compounds $Rh^{III}(^{Pyr}PCP)H(PR_3)Cl$ (**1a**, R = Et; **1b**, R = Ph) were obtained by the reaction of equivalent amounts of ^{Pyr}PCP-H, $[Rh^I(COE)_2\mu Cl]_2$, and PR_3 (R = Et, Ph) in THF at 65 °C.[8] Subsequent reaction of **1a**,**b** with KO^{t}Bu resulted in deprotonation of the hydride ligand and formation of the rhodium(I) complexes $Rh^I(^{Pyr}PCP)PR_3$ (**2a**, R = Et; **2b**, R = Ph), respectively, as previously described.[3] However, $Rh^{III}(^{Pyr}PCP)H(PPyr_3)Cl$, bearing the electron-accepting ancillary ligand $PPyr_3$, could not be prepared either via oxidative addition of the Ar−H bond of ^{Pyr}PCP-H to rhodium(I) (cyclometalation) or by direct reaction of $Rh^I(^{Pyr}PCP)PPyr_3$,[3] **2c**, with HCl. The latter reaction resulted in decomposition of **2c**. It appears that in the ^{Pyr}PCP/$PPyr_3$/Rh system coordination of three highly electron accepting pyrrolylic moieties to the rhodium center retards oxidative addition of the Ar−H bond or protonation of the rhodium(I) metal center. Complex **2c** was prepared by adding 1 equiv of $PPyr_3$ to the PPh_3 complex **2b** followed by 1 equiv of MeOTf to precipitate the displaced PPh_3 as its phosphonium salt.[3] Indeed, the metal center of **2c** has a significantly lower electron density than in the case of **2a**,**b**, as reflected by its low back-donation ability to carbon monoxide. Thus, the CO stretch in the IR spectrum of $Rh^I(^{Pyr}PCP)PPyr_3(CO)$ appears at a significantly higher frequency (2007 cm^{-1}) than in the case of $Rh^I(^{Pyr}PCP)PPh_3(CO)$ (1987 cm^{-1}) or $Rh^I(^{Pyr}PCP)PEt_3(CO)$ (1975 cm^{-1}).[3] The synthetic route toward **2c** described above took advantage of its low oxidative addition reactivity, enabling removal of the displaced PPh_3 with MeOTf without affecting the metal center.

Ancillary Ligand Exchange in Complexes 2a−d. Ligand substitution reactions at rhodium(I) centers were reported to follow both associative[9] and dissociative[10] mechanisms. In our previous report[3] we considered d^8 ML_5 rhodium $Rh^I(^{Pyr}PCP)PR_3(CO)$ compounds (Scheme 1) as "arrested intermediates" in associative ancillary ligands exchange. In the current work we studied exchange between monodentate phosphines coordinated to the ^{Pyr}PCP-based rhodium(I) center.

Scheme 2. Ancillary Ligand Exchange of Complexes 2b−d (room temperature, toluene)



The phosphines $PPyr_3$, PPh_3, and $PPyd_3$ (trispyrollidinylphosphine) were reported as isosteric, possessing the same cone angle of 145°.[6] Reaction of 1 equiv of $PPyd_3$ with either $Rh^I(^{Pyr}PCP)PPh_3$, **2b**, or $Rh^I(^{Pyr}PCP)PPyr_3$, **2c**, at room temperature (r.t.) resulted in phosphine exchange to form the complex $Rh^I(^{Pyr}PCP)PPyd_3$, **2d**, accompanied by release of 1 equiv of either PPh_3 or $PPyr_3$, respectively (Scheme 2). However, addition of either 1 equiv of $PPyr_3$ to **2b** or 1 equiv of PPh_3 to **2c** resulted in equilibrium between **2b** and **2c**, strongly shifted toward formation of **2c** at 295 K (K_{eq} = 20.2) (Scheme 2).

Orange crystals of **2c** were obtained at room temperature by slow diffusion of hexane into a concentrated THF solution. Yellow crystals of **2d** were obtained from a saturated pentane solution. The single-crystal X-ray structures of **2b**,[3] **2c**, and **2d** reveal distorted square-planar geometries (Table 1; Figure 1). Counterintuitively, despite the electron-withdrawing pincer ligand, the $Rh-P_{ancillary}$ bond was found to be remarkably shorter for the electron-withdrawing $PPyr_3$, $Rh-PPyr_3$ being 2.244 Å, as compared with $Rh-PPh_3$ (2.315 Å) and $Rh-PPyd_3$ (2.320 Å) (Table 1). It should be mentioned that the single-crystal X-ray structures of **2b**[3] and **2c** (Figure 1, left) did not reveal any pronounced $\pi-\pi$ interactions between ^{Pyr}PCP and either $PPyr_3$ or PPh_3, which might have affected their coordination. Moreover, the smallest sum of $C_{ipso}-Rh$ and $Rh-P_{ancillary}$ bond lengths was found for **2c** (4.351(4) Å), while the largest was for **2d** (4.433(4) Å). Therefore, it is likely that the ancillary ligand coordination to the ^{Pyr}PCP-based Rh^I is governed by the *trans* influences between the ^{PCP}aryl and the ancillary ligands, despite the overall reduction in electron density caused by chelation of ^{Pyr}PCP.

However, our results indicate that coordination of $PPyd_3$ is thermodynamically more favorable than coordination of either PPh_3 or $PPyr_3$, leading to complete substitution of PPh_3/$PPyr_3$ with 1 equiv of $PPyd_3$. A possible reason for stabilization of the $PPyd_3$ adduct may be interaction of a C−H bond with the rhodium center. We found that the distance between H39B and rhodium in **2d** (Figure 1, right; Table 1) is relatively short, 2.82(3) Å, compared to the hydrogen atoms closest to rhodium in the compounds **2b** (Rh−H42C, 2.94(3) Å) and **2c** (Rh−H53A, 2.97(3) Å) (Table 1). Such M−H(C) bonds in square-planar d^8 complexes[11] are usually described as anagostic, largely elec-

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(8) Synthesis of **1a**,**b** by cyclometalation required heating of the reaction mixture to 65 °C. Therefore, preparation of $Rh^{III}(^{Pyr}PCP)H(PPyd_3)Cl$ was not possible using this procedure because of the thermal instability of $PPyd_3$. Compound **2d** was prepared by synthesis of $Rh^I(^{Pyr}PCP)$(norbornene) with subsequent norbornene substitution with $PPyd_3$.

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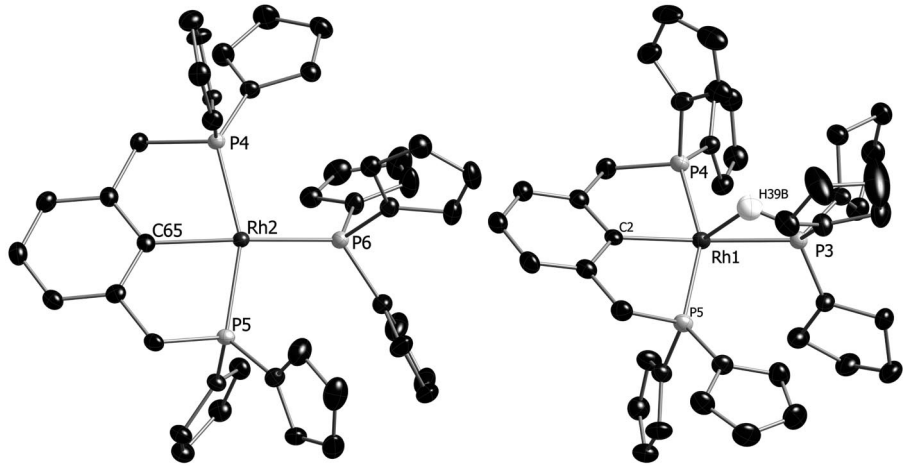

Figure 1. ORTEP diagrams of molecules of complexes **2c** (left) and **2d** (right) at the 50% probability level. Hydrogen atoms, except H39B, were omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) of 2b,[3] 2c, and 2d

Rh(^{Pyr}PCP)PPyd$_3$, **2d**		Rh(^{Pyr}PCP)PPh$_3$, **2b**		Rh(^{Pyr}PCP)PPyr$_3$, **2c**	
Rh1−C2$_{ipso}$	2.113(3)	Rh1−C1$_{ipso}$	2.079(3)	Rh2−C65$_{ipso}$	2.107(3)
Rh1−P4	2.212(1)	Rh1−P2	2.228(1)	Rh2−P4	2.266(1)
Rh1−P5	2.257(1)	Rh1−P3	2.229(1)	Rh2−P5	2.236(1)
Rh1−P3$_{ancillary}$	2.320(1)	Rh1−P4$_{ancillary}$	2.315(1)	Rh2−P6$_{ancillary}$	2.244(1)
C2−Rh1−P4	79.24(7)	C1−Rh1−P2	80.98(8)	C65−Rh2−P4	79.06(9)
C2−Rh1−P5	77.05(7)	C1−Rh1−P3	77.88(7)	C65−Rh2−P5	78.16(9)
C2−Rh1−P3	173.12(7)	C1−Rh1−P4	172.43(7)	C65−Rh2−P6	171.83(8)
P4−Rh1−P5	155.14(3)	P2−Rh1−P3	154.12(3)	P4−Rh2−P5	157.10(3)
Rh1−H39B	2.82(3)	Rh1−H42C	2.94(3)	Rh2−H53A	2.97(3)

trostatic interactions.[12] Structural characteristics of the Rh−H39B bond in **2d** meet those anagostic interactions observed for several square-planar d^8 complexes. Namely, the Rh−H distance of 2.82(3) Å and the Rh−H−C angle of 116° fall within the range of ca. 2.3−2.9 Å and ca. 110−170°, respectively.[12]

It is worthwhile to mention the stronger *trans* influence of PPyd$_3$ as compared to PPh$_3$. While the Rh−PPh$_3$ and Rh−PPyd$_3$ bond lengths are similar, 2.315 and 2.320 Å, respectively, the C$_{ipso}$−Rh bond of **2d** (2.113 Å) is longer than that of **2b** (2.079 Å), as a result of coordination of the stronger electron donor, PPyd$_3$, *trans* to the *ipso* carbon.

Next we studied exchange with PEt$_3$. Reaction of 1 equiv of PEt$_3$ (cone angle 132°[13]) with Rh^I(^{Pyr}PCP)PPh$_3$, **2b**, at room temperature resulted in formation of Rh^I(^{Pyr}PCP)PEt$_3$, **2a**, accompanied by release of 1 equiv of PPh$_3$ (Scheme 3). However, reaction of either 1 equiv of PEt$_3$ with Rh^I(^{Pyr}PCP)-PPyr$_3$, **2c**, or 1 equiv of PPyr$_3$ with **2a** resulted in equilibrium between **2a** and **2c**, which was strongly shifted toward formation of **2a** at 295 K (K_{eq} = 12.2) (Scheme 3). At 295 K, the ^{31}P{^{1}H} NMR spectrum showed broad signals at chemical shifts similar to those of **2a** and **2c**. Upon cooling to 213 K, the ^{31}P{^{1}H} NMR spectrum showed signals that could be attributed to pentacoordinate compounds of the type d^8 ML$_5$, Rh(^{Pyr}PCP)(PEt$_3$)PPyr$_3$, **2a′**,**c′**, with both monodentate phosphines coordinated to the rhodium center (Scheme 3, Table 2). Relying on the ^{31}P{^{1}H} NMR (213 K) spectrum of compounds **2a′** and **2c′** (Table 2) we can conclude that **2a′** and **2c′** are two stereoisomers that differ by the position of the monodentate phosphines: PEt$_3$ is bound in the *apical* position in **2a′** (double quartet at 8.1, $^1J_{RhP}$ = 93 Hz, $^2J_{PP}$ = 42 Hz) and in an equatorial position in **2c′** (triple doublet of doublets at 1.4, $^2J_{PP}$ = 202 Hz, $^1J_{RhP}$ = 142 Hz, $^2J_{PP}$ = 44 Hz). X-ray diffraction study of the compound Rh^I(^{Pyr}PCP)PEt$_3$CO[3] points out the possibility of *cisoid* coordination of ^{Pyr}PCP.

Scheme 3. Ancillary Ligand Exchange of Complexes 2a−c (room temperature, toluene)

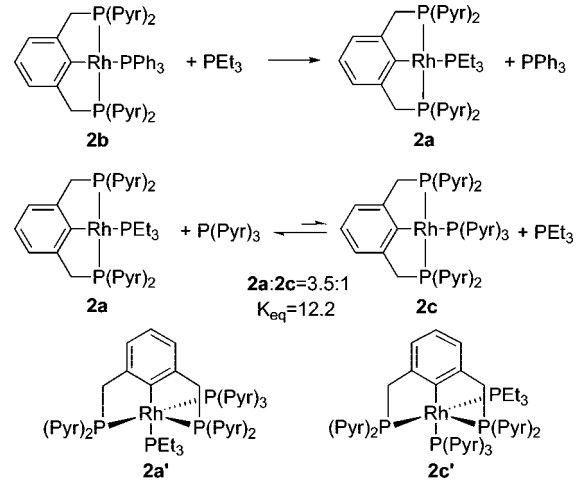

Table 2. Signals of 2a′ and 2c′ in ^{31}P{^{1}H} NMR (213 K, tol-d_8) Spectrum

P atom	chemical shift	multiplicity	coupling constants
2a′-^{Pyr}PCP	120.3	ddd	$^2J_{PP}$ = 312 Hz, $^1J_{RhP}$ = 192 Hz, $^2J_{PP}$ = 44 Hz
2a′-PPyr$_3$	98.9	m	
2a′-PEt$_3$	8.1	dq	$^1J_{RhP}$ = 93 Hz, $^2J_{PP}$ = 42 Hz
2c′-^{Pyr}PCP	112.46	ddd	$^2J_{PP}$ = 201 Hz, $^1J_{RhP}$ = 191 Hz, $^2J_{PP}$ = 42 Hz
2c′-PPyr$_3$	obscured by other peaks		
2c′-PEt$_3$	1.4	tdd	$^2J_{PP}$ = 202 Hz, $^1J_{RhP}$ = 142 Hz, $^2J_{PP}$ = 44 Hz

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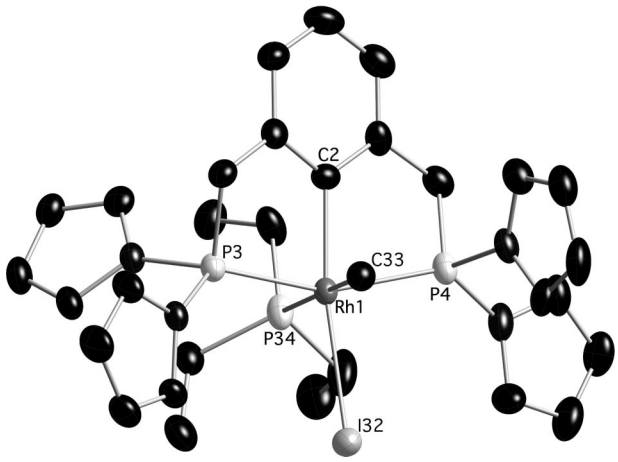


Figure 2. ORTEP diagram of a molecule of complex **3a** at the 50% probability level. Hydrogen atoms were omitted for clarity.

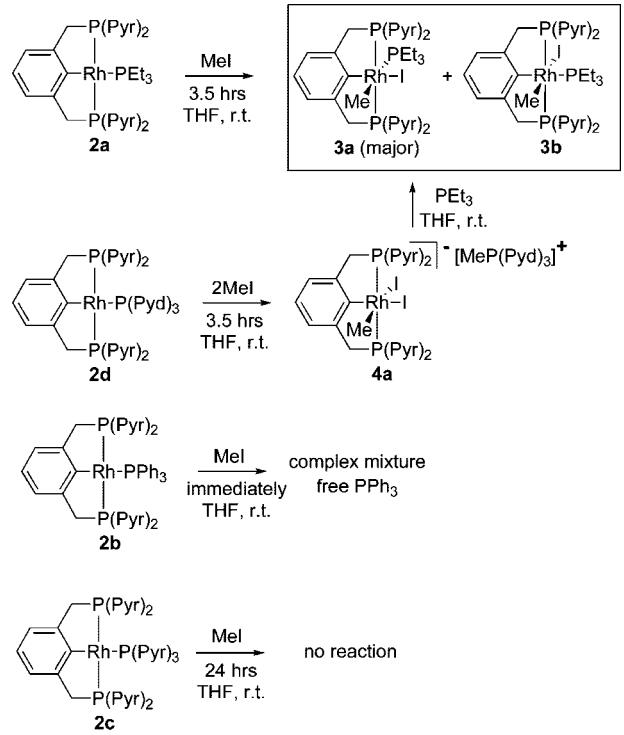
The equilibrium between **2a** and **2c** is a clear example of associative ancillary ligand exchange of a square-planar d^8 ML_4 metal center. Associative ligand exchange is likely to be more suitable for electron-deficient metal centers. This is due to two facts: first, the dissociative pathway demands formation of highly electron deficient 14*e* species; second, filled−filled orbital repulsions between HOMO orbitals of a d^8 ML_4 compound (d_{z^2}) and an incoming ligand are less pronounced for electron-deficient d^8 ML_4 complexes, because of overall reduction in the energy of the metal d-orbitals.[3]

H_2 Activation by 2a−d. Although no reaction was observed when 1 equiv of hydrogen gas was added to **2a**−**d**, activation of H_2 was evident from the ability of complexes **2a**−**d** to catalyze the hydrogenation of styrene to ethyl benzene. In a typical experiment, a 1 mL toluene-d_8 solution containing 0.029 mmol of the complex and 30 equiv of styrene was stirred at room temperature under H_2 (25 psi) and analyzed after 30 min, for the purpose of comparison between complexes **2a**−**d**. The conversion to ethyl benzene after that period was **2b** (22%), **2a** (9.4%), **2d** (1.7%), and **2c** (0.5%). However, some decomposition was observed in the cases of **2c**,**d**, rendering comparison impossible in these cases. No decomposition was observed with **2a**,**b** under the same reaction conditions. The higher catalytic activity of **2b** for styrene hydrogenation as compared with **2a** might be due to PPh_3 being more loosely bound than PEt_3, suggesting that 14*e* intermediates are the active species during olefin hydrogenation[14] with ^{Pyr}PCP-rhodium(I).

Reaction of 2a−d with MeI. The nucleophilicity of **2** was examined using MeI as an electrophile. Oxidative addition of alkyl halides to transition metals is a process of much interest since it is involved in important catalytic processes, such as carbonylation of alkyl[15] and aryl[16] halides and the iodide-promoted methanol carbonylation to acetic acid.[17]

Reaction of **2a** with 1 equiv of MeI in THF was complete after 3.5 h at room temperature (Scheme 4), leading to formation of three new compounds, **3a**−**c**. Multinuclear NMR analysis revealed the geometries of the main products **3a** (80% yield by $^{31}P\{^1H\}$ NMR) and **3b** (15% NMR yield). However, we could not establish the geometry of the very minor product (5%), **3c**.

Scheme 4. Reaction of 2a−d with MeI



All three products are Rh^{III} complexes based on $^1J_{RhP}$ coupling constants. Namely, the $^{31}P\{^1H\}$ NMR spectrum of **3a** revealed a doublet of doublets at δ 113.8 ppm with $^1J_{RhP} = 144.5$ Hz and $^2J_{PP} = 24.1$ Hz and a doublet of triplets at δ −14.4 ppm with $^1J_{RhP} = 74.8$ Hz (**3b**,**c** showed similar signals to those of **3a** in the $^{31}P\{^1H\}$ NMR). PEt_3 is coordinated *trans* to the CH_3 group in **3a**, as deduced from the $^{13}C\{^1H\}$ NMR spectrum, which revealed a doublet of doublets of triplets at δ –3.32 with $^2J_{PC,\ trans} = 72.7$ Hz, $^1J_{RhC} = 15.5$ Hz, and $^2J_{PC,\ cis} = 6.6$ Hz for Rh-*C*H_3. In complex **3b** PEt_3 is bound *cis* to CH_3, which appeared in the $^{13}C\{^1H\}$ NMR spectrum as a doublet of quartets at δ −4.8 with $^1J_{RhC} = 15.8$ Hz and $^2J_{PC,\ cis} = 5.3$ Hz. The geometry of **3a** was also revealed by a single-crystal X-ray study (Figure 2, Table 3). Yellow prismatic crystals of **3a** were obtained at room temperature from a concentrated MeOH solution of a mixture of complexes **3**. Complex **3a** exhibits a distorted octahedral coordination geometry, with a ligand arrangement consistent with the multinuclear NMR data.

Reaction of **2d** with 2 equiv of MeI was complete after 3.5 h at room temperature, resulting in quantitative formation of $[Rh(^{Pyr}PCP)Me(I)_2][MePPyd_3]$, **4a** (Scheme 4). When 1 equiv of MeI was used, only half the amount of **2d** was consumed to give **4a**, the other half of **2d** remaining unreacted. The $^{31}P\{^1H\}$ NMR spectrum of **4a** showed a doublet at δ 113.5 ppm with $^2J_{RhP} = 151.3$ Hz for ^{Pyr}PCP and a singlet at δ 43.86 for $[MePPyd_3]^+$. The aryl *ipso* carbon, C_{ipso}-Rh, appeared as a doublet of triplets at δ 169.1 with $^1J_{RhC} = 34.0$ Hz (unresolved triplet) in the $^{13}C\{^1H\}$ NMR. The methyl group, Rh-CH_3, appeared in the ^1H NMR spectrum as a triplet of doublets at δ 0.116 with $^3J_{PH} = 6.3$ Hz and $^2J_{RhH} = 1.92$ Hz, and in the $^{13}C\{^1H\}$ NMR spectrum it gave rise to a doublet of triplets at δ −0.233 with $^1J_{RhC} = 22.3$ Hz and $^2J_{PC} = 4.7$ Hz. Reaction of **4a** with 1 equiv of PEt_3 resulted in formation of **3a** and **3b** (90% and 10% yield by $^{31}P\{^1H\}$ NMR, respectively) accompanied by precipitation of $[MePPyd_3]I$ (Scheme 4). The prevaling formation of **3a** indicates a stronger *trans* influence of the methyl ligand compared to the aryl ligand. The *trans* influence is reflected by the weaker binding of the iodide *trans*

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Table 3. Selected Bond Lengths (Å) and Angles (deg) of 3a, 4b, and 2e

Rh(^{Pyr}PCP)Me(I)PEt$_3$, **3a**		[Rh(^{Pyr}PCP)Me(I)$_2$]NBu$_4$, **4b**		Rh(^{Pyr}PCP)CO, **2e**	
Rh1−C2$_{ipso}$	2.068(5)	Rh1−C2$_{ipso}$	2.048(6)	Rh1−C1$_{ipso}$	2.094(2)
Rh1−P3	2.274(2)	Rh1−P3	2.268(2)	Rh1−P1	2.249 (1)
Rh1−P4	2.280(2)	Rh1−P4	2.287(2)	Rh1−P2	2.270(1)
Rh1−C33	2.156(5)	Rh1−C34	2.115(5)	Rh1−C25	1.884(3)
Rh1−I32	2.791(1)	Rh1−I32	2.784(1)	C25−O1	1.147(3)
Rh1−P34$_{ancil.}$	2.434(2)	Rh1−I33	2.815(1)	C1−Rh1−P1	78.10(8)
C2−Rh1−C33	86.4(2)	C2−Rh1−C34	91.4(3)	C1−Rh1−P2	78.70(7)
C2−Rh1−P34	95.3(2)	C2−Rh1−I33	88.7(2)	P1−Rh1−P2	156.75(3)
C2−Rh1−I32	169.7(2)	C2−Rh1−I32	179.8(2)	C1−Rh1−C25	174.3(1)
P34−Rh1−I32	93.7(1)			Rh1−C25−O1	175.8(2)

to the methyl group in **4b** (Figure 3 and Table 3 describe the single-crystal X-ray study of **4b** (*vide infra*)). Addition of an excess of PEt_3 did not result in further reaction.

Addition of 1 equiv of MeI to Rh^I(^{Pyr}PCP)PPh$_3$, **2b**, resulted in immediate formation of an inseparable complex product mixture. However, based on the $^{31}P\{^1H\}$ NMR spectrum (doublets at 114−116 ppm, $^1J_{RhP}$ = 148−150 Hz) one can conclude that oxidative addition of MeI to rhodium(I) took place, accompanied by dissociation of PPh_3.

Remarkably, *no reaction was observed during more than 24 h after addition of MeI to Rh^I(^{Pyr}PCP)PPyr$_3$*, **2c**.

It seems that the reaction of **2** with MeI strongly depends on the sterics and nucleophilicity of the ancillary ligand bound to ^{Pyr}PCP-Rh^I. The remarkable stability of **2c** toward oxidative addition of MeI can arise from low nucleophilicity of the metal center as well as from the steric hindrance caused by the relatively bulky $PPyr_3$. Unlike $PPyd_3$, dissociation of $PPyr_3$ from the rhodium center cannot be promoted by formation of its phosphonium iodide salt, since $PPyr_3$ is not nucleophilic enough to react with MeI. This quaternization reaction drives the dissociation equilibrium of $PPyd_3$ to the right and also generates the iodide anion, which might also affect the oxidative addition reaction.

In order to explore the iodide effect on the oxidative addition of MeI, complex **2c** was reacted with 1 equiv of MeI in the presence of 1 equiv of the iodide salt [NBu$_4$]I. Interestingly, as opposed to the lack of reaction in the absence of iodide, the reaction was complete after 2.5 h, leading to formation of **4b**

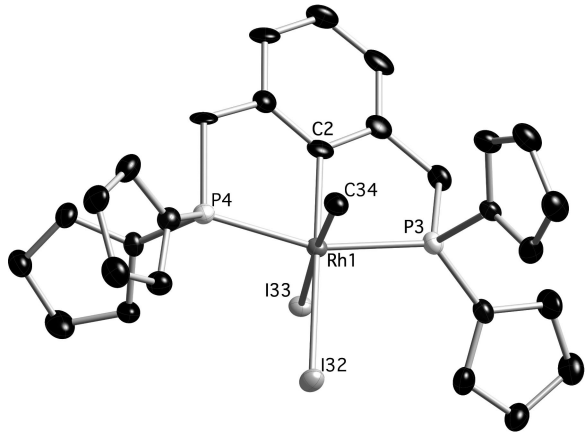
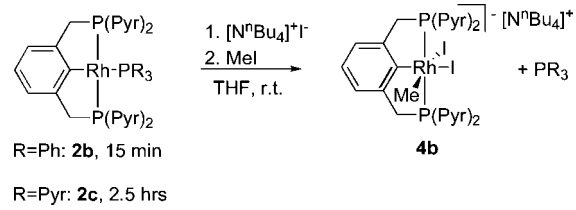


Figure 3. ORTEP diagram of a molecule of complex **4b** at the 50% probability level. Hydrogen atoms and counteranion [NBu$_4$]$^-$ were omitted for clarity.

Scheme 5. Effect of Iodide on the Reaction of 2b,c with MeI



R=Ph: **2b**, 15 min

R=Pyr: **2c**, 2.5 hrs

4b

accompanied by release of $PPyr_3$ (Scheme 5).[18] Colorless prismatic crystals of **4b** were obtained from a 1:1 THF/pentane solution. The single-crystal X-ray structure of **4b** revealed a distorted octahedral geometry with *cis* arrangement of the iodide ligands (Figure 3). As mentioned above, the stronger *trans* influence of the methyl ligand as compared with the aryl ligand results in weaker binding of the iodide *trans* to the methyl group, than to the aryl, as reflected in the bond lengths: 2.815 and 2.784 Å, respectively.

In order to examine the impact of steric hindrance on the lack of reactivity of **2c** with MeI, we explored the reaction of Rh^I(^{Pyr}PCP)CO, **2e**, with MeI. Unlike **2c**, complex **2e** has a strongly π-accepting, but sterically undemanding ancillary ligand (CO).

The synthesis of **2e** is summarized in the Scheme 6. The cationic rhodium(I) precursor [Rh(COE)$_2$(THF)$_n$](OTf)[19] was prepared *in situ* by adding 2 equiv of AgOTf to [Rh^I(COE)$_2\mu$Cl]$_2$ in THF at room temperature. Then 2 equiv of ^{Pyr}PCP-H and an excess of norbornene were added, and the reaction mixture was heated in THF at 70 °C for 40 min. Subsequent addition of KO^{t}Bu resulted in formation of the rhodium(I) complex Rh^I-(^{Pyr}PCP)(nor) (nor = norbornene), which was stable only in the presence of excess norbornene, making impossible its purification and full characterization. The $^{31}P\{^1H\}$ NMR spectrum of Rh^I(^{Pyr}PCP)(nor) revealed a doublet at 132 ppm with $^1J_{RhP}$ = 201 Hz, which is characteristic of ^{Pyr}PCP-Rh^I complexes. The methylene protons of the ^{Pyr}PCP appeared in the ^{1}H NMR spectrum at 4.29 ppm as a virtual triplet with $^2J_{PH}$ = 3.6 Hz, indicating the C_{2v} symmetry of the complex. Bubbling of CO through the crude solution of Rh^I(^{Pyr}PCP)(nor) resulted in formation of **2e**. The $^{31}P\{^1H\}$ NMR spectrum of **2e** exhibited a doublet at 119.8 ppm ($^1J_{RhP}$ = 194.4 Hz). The methylene protons of the ^{Pyr}PCP gave rise to a virtual triplet at 4.49 ppm with $^2J_{PH}$ = 4.7 Hz in ^{1}H NMR, thus indicating the C_{2v} symmetry of the complex. The *ipso* carbon, C_{ipso}-Rh, appeared as a doublet of

(18) $^{31}P\{^1H\}$ NMR (THF) showed a significant broadening of the spectrum of **2c** in the presence of [NBu$_4$]I: full width at half-height (fwhh) was equal to 25 Hz in the presence of 1 equiv of [NBu$_4$]I and 7 Hz for pure **2c**. No compound, other than **2c**, was observed at low temperature (down to 213 K). The same shapes of signals were observed at a certain temperature, whether reached by cooling or heating.

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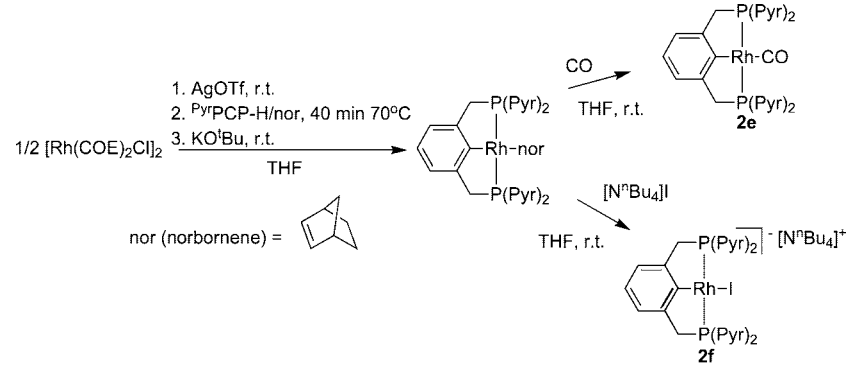
Scheme 6. Synthesis of Complexes 2e,f



triplets at 172.16 ppm ($^1J_{RhC}$ = 28.2 Hz, $^2J_{PC}$ = 9.25 Hz) in the $^{13}C\{^1H\}$ NMR spectrum. The carbonyl group gave rise to a doublet of triplets at 196.62 ppm ($^1J_{RhC}$ = 55.3 Hz, $^2J_{PC}$ = 14.2 Hz) in the $^{13}C\{^1H\}$ NMR spectrum and exhibited a strong IR absorption band at 1969 cm^{-1}. Yellow crystals of **2e** were obtained by slow diffusion of pentane into a concentrated THF solution of **2e**. The single-crystal X-ray structure of **2e** exhibits a distorted square-planar geometry (Figure 4, Table 3), in agreement with the multinuclear NMR spectra.

Reaction of **2e** with MeI resulted in C−C bond formation with the *ipso* carbon to give η^2-(^{Pyr}PCP-Me)Rh^{I}CO(I), **5** (Scheme 7). The reaction was complete after 2 weeks at ambient temperature (38% and 78% spectral conversions were observed after 3 and 7 days, respectively). The $^{31}P\{^1H\}$ NMR spectrum of **5** exhibited a doublet at 102.4 ppm ($^1J_{RhP}$ = 154.6 Hz). The methylene groups of the ^{Pyr}PCP ligand appeared at 4.84 ppm as a broad singlet in the ^1H NMR spectrum and as a virtual triplet at 38.89 ppm ($^1J_{PC}$ = 16.7 Hz) in the $^{13}C\{^1H\}$ NMR spectrum. The carbonyl group gave rise to a doublet of triplets at 181.5 ppm ($^1J_{RhC}$ = 76 Hz, $^2J_{PC}$ = 14 Hz) in the $^{13}C\{^1H\}$ NMR spectrum, and in the IR spectrum it gave rise to a strong absorption band at 2008 cm^{-1}. The $^{31}P\{^1H\}$ NMR spectrum of the phosphines and the $^{13}C\{^1H\}$ NMR spectrum of the methylene and the carbonyl groups revealed the *trans* coordination of the phosphines. No signal was detected for the aryl carbon bound to the rhodium center. The methyl group gave rise to a singlet at 1.42 ppm in the ^1H NMR spectrum and a singlet at 14.61 ppm in the $^{13}C\{^1H\}$ NMR spectrum, as confirmed by C−H correlation. The methylated ^{Pyr}PCP pincer ligand (^{Pyr}PCP-Me) was released from the metal center by its substitution with P^iPr_3 and was purified and characterized separately (Scheme 7).

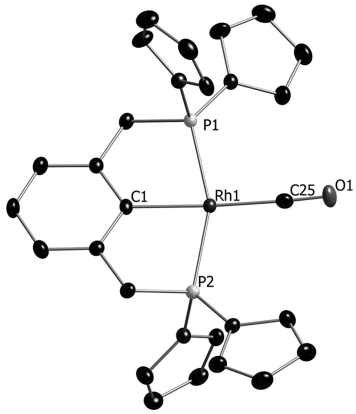


Figure 4. ORTEP diagram of a molecule of complex **2e** at the 50% probability level. Hydrogen atoms were omitted for clarity.

The reaction of **2e** with MeI, in contrast to the remarkable stability of **2c** toward MeI, highlights the impact of steric hindrance on reactivity of the metal center. It is important to mention that MeI attack is likely to proceed on the rhodium center of **2e**, rather than directly on the *ipso* carbon of the aryl ring; otherwise **2c** would be expected to react in a similar way to **2e**, since the *ipso* carbon is not strongly affected by sterics of an ancillary ligand, as can be seen from the single-crystal X-ray studies of the compounds **2b**−**e**. Consequently, addition of MeI to **2e** probably proceeds by an S_N2 mechanism.[20] Thus, nucleophilic attack of rhodium on the methyl group results in formation of an electron-deficient cationic rhodium(III) species, [Rh^{III}(^{Pyr}PCP)CO(Me)]$^+$, which undergoes C−C reductive elimination to give **5**. Square-planar d^8 rhodium complexes usually react easily with methyl iodide to afford octahedral d^6 compounds.[21] However, the electron density around the metal center plays a key role in the addition of MeI. For example, as published by our group, Rh^I(P^iPr_3)$_2$-η^2-OTf showed remarkable stability toward MeI addition, unlike Rh^I(PEt_3)$_3$Cl.[22] Although coordination of the electron-accepting ^{Pyr}PCP and $PPyr_3$ to rhodium(I) resulted in reduction of the electron density on the metal center, it is more likely that the stability of **2c** toward oxidative addition of MeI in the absence of added iodide, I^-, is due to steric hindrance at the metal center and low nucleophilicity of $PPyr_3$ (*vide infra*).

Although reaction of **2e** with MeI resulted in the demetalated rhodium(I) product **5**, and no Rh^{III}(^{Pyr}PCP)Me(I)CO was detected, this fact does not exclude the possibility of existence of Rh^{III}(^{Pyr}PCP)Me(I)CO. Indeed, reaction of **4** with CO in THF resulted in formation of Rh^{III}(^{Pyr}PCP)Me(I)CO, **6a** and **6b** (1:1), accompanied by dissociation of the corresponding iodide salt, as either [NBu_4]I or [$MePPyd_3$]I (Scheme 7). In the presence of an equivalent amount of [NBu_4]I or [$MePPyd_3$]I, CO binds reversibly to the rhodium center of **6a**,**b** and can be easily removed by bubbling N_2 through the reaction mixture. The $^{31}P\{^1H\}$ NMR spectrum of **6a**,**b** showed doublets at δ 120.5 ($^1J_{RhP}$ = 133.6 Hz) and 111.8 ($^1J_{RhP}$ = 135.4 Hz). The methyl groups, Rh-CH_3, appeared in the ^1H NMR spectrum as triplets of doublets at δ 0.303 ($^3J_{PH}$ = 8.16 Hz, $^2J_{RhH}$ = 1.81 Hz) and 0.014 ($^3J_{PH}$ = 6.04 Hz, $^2J_{RhH}$ = 2.1 Hz) and in the $^{13}C\{^1H\}$ NMR spectrum as doublets of triplets at δ −2.78 ($^1J_{RhC}$ = 15.5 Hz, $^2J_{PC}$ = 5.9 Hz) and −6.9 ($^1J_{RhC}$ = 20.47 Hz, unresolved

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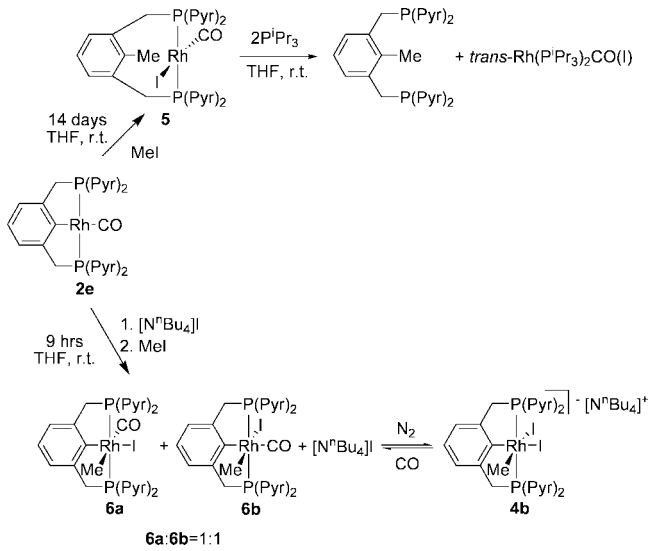
Scheme 7. Reaction of 2e with MeI



triplet). The carbonyl groups appeared at δ 189.5 and 180.9 ppm, and the aryl *ipso* carbons, C_{ipso}-Rh, appeared at 166.1 and 161.0 ppm in the $^{13}C\{^1H\}$ NMR spectrum.

Interestingly, formation of **6a**,**b** was also observed during reaction of **2e** with MeI in the presence of 1 equiv of $[NBu_4]I$. It was complete after 9 h, leading to the formation of **4b**, **6a**, and **6b** (9:1:1, respectively). The reaction was also examined at earlier stages, e.g., 4 h after adding MeI, and $^{31}P\{^1H\}$ NMR showed that ca. 70% of **2e** had reacted to give **4b**:**6a**:**6b** $\approx$ 4:1:1. Obviously, **4b** was formed after CO dissociation from **6a**,**b** in the presence of $[NBu_4]I$. No interaction was observed between **2e** and $[NBu_4]I$ at room temperature by $^{31}P\{^1H\}$ NMR, and $[Rh^I(^{Pyr}PCP)I][NBu_4]$, **2f**, was not observed after 3 days of stirring at room temperature. To confirm this, complex **2f** was prepared separately by reaction of $Rh^I(^{Pyr}PCP)$(nor) with $[NBu_4]I$ (Scheme 6). $^{31}P\{^1H\}$ NMR of **2f** exhibited a doublet at 108.2 ppm ($^1J_{RhP} = 221.27$ Hz). The methylene protons of the ^{Pyr}PCP appeared at 3.96 ppm as a virtual triplet with $^2J_{PH} = 4.2$ Hz in the ^{1}H NMR spectrum, thus indicating the C_{2v} symmetry of the complex. The *ipso* carbon, C_{ipso}-Rh, appeared as a doublet of triplets at 173.49 ppm ($^1J_{RhC} = 41.1$ Hz, $^2J_{PC} = 8.6$ Hz) in the $^{13}C\{^1H\}$ NMR spectrum.

In the presence of $[NBu_4]I$ C−C reductive elimination is prevented during the reaction of **2e** with MeI. This indicates that C−C reductive elimination probably proceeds by a dissociative mechanism, involving prior iodide dissociation to form the coordinatively unsaturated 16*e* cationic $[Rh^{III}(^{Pyr}PCP)Me(CO)]^+$ species. The requirement for ligand dissociation prior to C−H and C−C reductive elimination of octahedral rhodium(III) complexes was reported.[23]

Since $PPyd_3$ and $PPyr_3$ are isosteric, the rhodium center of **2d**, similarly to that of **2c**, seems to be too stericly hindered for a direct attack on MeI. The reaction proceeds via formation of $[MePPyd_3]I$ (Scheme 4). Once formed, $[MePPyd_3]I$ may be involved in the addition of MeI to the rhodium center. Indeed, in the presence of 1 equiv of $[NBu_4]I$ the reaction proceeded faster and was completed after 2 h. Nevertheless, almost 2 equiv of MeI were required to complete the reaction.

As concluded from the results described in the previous sections, the Rh−PPh_3 bond is the weakest among the examined Rh−PR_3 (R = Et, Pyd, Ph, Pyr). The reaction of Rh^I(PCP)PPh_3, **2b**, with MeI is fast. Although we did not succeed in separating the products, it is important to note that only 1 equiv of MeI was required to complete the reaction, which was accompanied by dissociation of PPh_3. These observations suggest involvement of 14*e* $Rh^I(^{Pyr}PCP)$ species in the reaction of **2b** with MeI. MeI addition to the highly electron deficient 14*e* species may proceed either by a three-centered mechanism[24] or by addition of iodide prior to methyl addition.[25] Dissociation of PPh_3 results in liberation of $Rh^I(^{Pyr}PCP)$ 14*e* species, which is likely to be more reactive toward MeI than PPh_3. Therefore, the amount of the phosphonium salt $[MePPh_3]I$, which can play the role of the iodide donor, like $[MePPyd_3]I$, is insufficient. Indeed, upon addition of 1 equiv of $[NBu_4]I$ the reaction of **2b** with 1 equiv of MeI was complete after 15 min, leading to quantitative formation of **4b** (Figure 3, Table 3) accompanied by release of PPh_3 (Scheme 5).[26] Addition of 1 equiv of $TlPF_6$ to **4b** in the presence of 1 equiv of PPh_3 resulted in formation of the same complex mixture as during reaction of **2b** with 1 equiv of MeI.

Acceleration of oxidative addition reactions by halide ions has been reported.[27] For example, the catalytic action of Pd^0L_2 complexes in cross-coupling of aryl halides with nucleophiles and in the Heck reaction was found to depend on the concentration of an additive anion, e.g., Cl^-, thus indicating involvement of a trivalent anionic complex, $[Pd^0L_2Cl]^-$, in the catalytic cycle, which makes the latter more efficient.[28] $[NBu_4]I$ can affect either the transition or ground state of the reaction of **2b**,**c** with MeI. Concerning its effect on the ground state, the much faster reaction of **2b**, compared to **2c**, points at $[Rh^I(^{Pyr}PCP)I]NBu_4$ as a reactive specie, since the Rh−PPh_3 bond is weaker than Rh−$PPyr_3$. Indeed, $[Rh^I(^{Pyr}PCP)I]NBu_4$ immediately reacted with MeI to give **4b**.

Conclusions

The reactivity of rhodium(I) complexes based on the recently reported strongly electron accepting PCP-pincer ligand dipyrrolylphoshinoxylene (^{Pyr}PCP) was investigated. Complexes of the type $Rh^I(^{Pyr}PCP)PR_3$ (R = Et, Ph, Pyr, PPyd) (**2**) were synthesized.

The ancillary ligand coordination is governed by *trans* effect, rather than by the overall reduction in electron density at the rhodium center caused by ^{Pyr}PCP chelation.

The ancillary ligand substitution process at the ^{Pyr}PCP-based rhodium(I) center proceeds via an associative mechanism. An associative, contrary to dissociative, ligand exchange mechanism is likely to be more suitable for electron-deficient metal centers due to avoiding formation of electron-deficient 14*e* species and due to overall stabilization of the metal d-orbitals,[3] which leads

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(26) $^{31}P\{^1H\}$ NMR (THF) showed a slight broadening of the spectrum of **2b** in the presence of $[NBu_4]I$: fwhh was equal to 8 Hz in the presence of 1 equiv of $[NBu_4]I$ and 4.3 Hz for a pure **2b**. No compound, other than **2b**, was observed at low temperature (down to 213 K). The same shapes of signals were observed at a certain temperature, whether reached by cooling or heating.

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to reduced filled−filled orbital repulsions between HOMO orbitals of a d^8 ML_4 compound (d_{z^2}) and an incoming ligand.

Complexes **2** catalyze styrene hydrogenation to ethyl benzene. Comparison between the reactivities of **2a** and **2b** suggests, although does not prove, that a 14*e* intermediate is the active species in this process.

The ability of **2** to oxidatively add MeI depends on the sterics, nucleophilicity, and binding strength of the ancillary ligand to the rhodium center. The complexes $Rh^I(^{Pyr}PCP)L$ are thought to follow a two-step S_N2 mechanism when the metal center is not sterically hindered, e.g., L = PEt_3 (**2a**), CO (**2e**). Coordination of relatively bulky PR_3 (R = Pyd, Ph, Pyr; cone angle 145°) to the rhodium(I) sterically hinders nucleophilic attack by d^8 RhL_4 on MeI.

Reaction of $Rh^I(^{Pyr}PCP)PPh_3$, **2b**, with MeI is thought to proceed via the $Rh^I(^{Pyr}PCP)$ 14-electron species, owing to the relatively weak Rh−PPh_3 bond.

The inertness of $Rh^I(^{Pyr}PCP)PPyr_3$, **2c**, toward oxidative addition of MeI is due to a number of factors: steric hindrance at the metal center, Rh−$PPyr_3$ bond strength, and the low nucleophilicity of $PPyr_3$. Steric hindrance disfavors an S_N2 mechanism; strong binding of $PPyr_3$ to the rhodium center disfavors intermediacy of a 14-electron species; low nucleophilicity of $PPyr_3$ disfavors a reaction involving formation of $[MePPyr_3]I$, unlike the case of $Rh^I(^{Pyr}PCP)PPyd_3$, **2d**.

Experimental Section

General Procedures. All experiments with metal complexes and phosphine ligands were carried out under an atmosphere of purified nitrogen in a Vacuum Atmospheres glovebox equipped with a MO 40-2 inert gas purifier or using standard Schlenk techniques. All solvents were reagent grade or better. All nondeuterated solvents were refluxed over sodium/benzophenone ketyl and distilled under argon atmosphere. 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. $[Rh^I(COE)_2\mu Cl]_2$,[29] **1a**,**b**, and **2a**−**c**[3] were prepared according to a literature procedure.

^1H, ^{13}C, ^{31}P, and ^{19}F NMR spectra were recorded at 400, 100, 162, and 376 MHz, respectively, using a Bruker AMX-400 NMR spectrometer. All spectra were recorded at 295 K, unless otherwise noted. ^1H NMR and $^{13}C\{^1H\}$ NMR chemical shifts are reported in ppm downfield from tetramethylsilane and referenced to the residual signals of an appropriate deuterated solvent. ^{31}P NMR chemical shifts are reported in ppm downfield from H_3PO_4 and referenced to an external 85% solution of phosphoric acid in D_2O. ^{19}F NMR chemical shifts are reported in ppm downfield from $CFCl_3$ and referenced to an external solution of C_6F_6 (δ = −163 ppm) in $CDCl_3$.

Elemental analyses were performed by H. Kolbe, Mikroanalytisches Laboratorium, Muelheim, Germany.

Synthesis of $Rh(^{Pyr}PCP)PPyd_3$ (2d).

Synthesis of $Rh^I(^{Pyr}PCP)$norbornene. AgOTf (14.3 mg, 0.056 mmol) in THF (1 mL) was added dropwise to $[Rh^I(COE)_2\mu Cl]_2$ (20 mg, 0.028 mmol) in THF (1.5 mL). A gray precipitate appeared immediately. The resulting mixture was left at r.t. for 10 min while stirring, and then it was filtered through a Celite column (2 cm long, in a Pasteur pipette). To the resulting deep yellow solution was added dropwise the ligand ^{Pyr}PCP-H (24 mg, 0.056 mmol) in THF (0.5 mL) and norbornene (80 mg, 0.85 mmol). The mixture was heated at 70 °C for 40 min. To the resulting brown solution was added dropwise KO^{t}Bu (6.2 mg, 0.056 mmol) in THF (0.5 mL) while stirring. The reaction mixture became dark brown immediately. The yield of $Rh^I(^{Pyr}PCP)$norbornene was 60% by $^{31}P\{^1H\}$ NMR integration. The complex was not stable to vacuum and was stabilized only in the presence of excess norbornene, making impossible its purification and full characterization.

$^{31}P\{^1H\}$ NMR (THF-H_8): 132 (d, $^1J_{RhP}$ = 201 Hz). ^1H NMR (THF-H_8): 7.04 (br s, Py, 8 *H*C-N, 8H), 6.31 (br s, Py, 8 *H*C-HC-N, 8H), 4.29 (vt, $^2J_{PH}$ = 3.6 Hz, 2 Ar-H_2C-P, 4H).

Synthesis of 2d from $Rh^I(^{Pyr}PCP)$norbornene. To a crude solution of $Rh^I(^{Pyr}PCP)$norbornene (made from 50 mg of $[Rh^I(COE)_2\mu Cl]_2$) was added $PPyd_3$ (30.5 μL, 0.133 mmol), resulting in formation of **2d**. The product was dried by vacuum, extracted with pentane, dried, washed with a small amount of pentane (0.5 mL), and dried again to give 81.7 mg (76%) of **2d** as a yellow solid.

$^{31}P\{^1H\}$ NMR (C_6D_6): 122.4 (dd, $^1J_{RhP}$ = 214.4 Hz, $^2J_{PP}$ = 44.1 Hz, 2P), 110.6 (dt, $^1J_{RhP}$ = 147.4 Hz, 1P). ^1H NMR (C_6D_6): 7.13 (m, Pyr, *H*C-N, 8H), 6.95 (m, Ar), 6.26 (m, Pyr, *H*C-HC-N, 8H), 3.82 (vt, $^2J_{PH}$ = 3 Hz, Ar-CH_2-P, 4H), 2.92 (m, Pyd, H_2C-N, 12H), 1.37 (m, Pyd, H_3C-H_2C-P, 12H). $^{13}C\{^1H\}$ NMR (C_6D_6): 173.6 (ddt, $^2J_{PC,\ trans}$ = 87.4 Hz, $^1J_{RhC}$ = 27.9 Hz, $^2J_{PC,cis}$ = 10.2 Hz, C_{ipso}-Rh, 1C), 144.05 (vt, $^2J_{PC}$ = 12.3 Hz, Ar, *C*-C-Rh, 2C), 125.51 (s, Ar, *C*H-CH-C-C-Rh, 1C), 124.42 (vt, $^2J_{PC}$ = 3.4 Hz, Pyr, *C*H-N-P, 8C), 122.2 (vtd, $^3J_{PC}$ = 10.5 Hz, J = 3.8 Hz, Ar, *C*H-C-C-Rh, 2C), 111.73 (br s, Pyr, *C*H-CH-N-P, 8C), 53.61 (vtt, $^1J_{PC}$ = 16.5 Hz, J = 5.2 Hz, Ar-*C*H_2-P, 2C), 47.85 (d, $^2J_{PC}$ = 8.85 Hz, Pyd, *C*H_2-N-P, 6C), 25.95 (d, $^3J_{PC}$ = 6.18 Hz, Pyd, *C*H_2-CH_2-N-P, 6C). Anal. (%) Found (Calc): C 56.08 (55.89), H 6.07 (6.12).

Synthesis of $Rh^I(^{Pyr}PCP)CO$ (2e). CO was bubbled for 30 min through a brown crude solution of $Rh^I(^{Pyr}PCP)$norbornene (made from 100 mg of $[Rh^I(COE)_2\mu Cl]_2$; as described in the procedure for the synthesis of **2d**), resulting in formation of **2e**. The solvent was removed under vacuum, and the residue was washed with toluene (3 × 3 mL), dried under vacuum, redissolved in CH_2Cl_2, and filtered. The solvent was removed under vacuum to give 92 mg (59%) of **2e** as a yellow solid.

$^{31}P\{^1H\}$ NMR (THF-d_8): 119.76 (d, $^1J_{RhP}$ = 194.42 Hz). ^1H NMR (THF-d_8): 7.26 (m, Pyr, *H*C-N, 8H), 7.1 (d, $^3J_{HH}$ = 7.47 Hz, Ar, *meta* to Rh, 2H), 6.97 (t,$^3J_{HH}$ = 7.47 Hz, Ar, *para* to Rh, 1H), 6.28 (m, Pyr, *H*C-HC-N, 8H), 4.49 (vt, $^2J_{PH}$ = 4.7 Hz, Ar-CH_2-P, 4H). $^{13}C\{^1H\}$ NMR (THF-d_8): 196.62 (dt, $^1J_{RhC}$ = 55.3 Hz, $^2J_{PC}$ = 14.2 Hz, *C*═O, 1C), 172.16 (dt, $^1J_{RhC}$ = 28.2 Hz, $^2J_{PC}$ = 9.25 Hz, C_{ipso}-Rh, 1C), 147.61 (vtd, $^2J_{PC}$ = 14.9 Hz, $^2J_{RhC}$ = 2.1 Hz, Ar, *C*-C-Rh, 2C), 128.37 (s, Ar, *C*H-CH-C-C-Rh, 1C), 124.76 (vt, $^2J_{PC}$ = 4.46 Hz, Pyr, *C*H-N-P, 8C), 123.13 (vt, $^3J_{PC}$ = 12.7 Hz, Ar, *C*H-C-C-Rh, 2C), 113.40 (vt, $^3J_{PC}$ = 3.23 Pyr, *C*H-CH-N-P, 8C), 50.0 (vtd, $^1J_{PC}$ = 19.1 Hz, $^2J_{RhC}$ = 4.1 Hz, Ar-*C*H_2-P, 2C). IR (film): ν_{CO} = 1969 cm$^-$. Anal. (%) Found (Calc): C 53.43 (53.59), H 4.11 (4.14).

Reaction of $Rh^I(^{Pyr}PCP)PPh_3$ (2b) with $PPyd_3$. $PPyd_3$ (neat, 6.3 μL, 0.027 mmol) was added to a toluene (0.7 mL) solution of **2b** (21.9 mg, 0.027 mmol), resulting in formation of **2d** accompanied by release of 1 equiv of free PPh_3, as detected by $^{31}P\{^1H\}$ NMR.

Reaction of $Rh^I(^{Pyr}PCP)PPyr_3$ (2c) with $PPyd_3$. To a toluene (1 mL) solution of **2c** (23.5 mg, 0.031 mmol) was added $PPyd_3$ (neat, 7.1 μL, 0.031 mmol), resulting in formation of **2d** accompanied by release of 1 equiv of free $PPyr_3$, as detected by $^{31}P\{^1H\}$ NMR.

Reaction of $Rh^I(^{Pyr}PCP)PPh_3$ (2b) with PEt_3. PEt_3 (neat, 3.4 μL, 0.025 mmol) was added to a toluene (0.7 mL) solution of **2b** (19.7 mg, 0.025 mmol), resulting in formation of **2a** accompanied by release of 1 equiv of free PPh_3, as detected by $^{31}P\{^1H\}$ NMR.

Equilibrium between $Rh^I(^{Pyr}PCP)PEt_3$ (2a) and $Rh^I(^{Pyr}PCP)PPyr_3$ (2c). Addition of either 1 equiv of $PPyr_3$ (8.8 mg, 0.038 mmol) to **2a** (25.0 mg, 0.038 mmol) or 1 equiv of PEt_3 (neat, 4.5 μL, 0.033 mmol) to **2c** (25.5 mg, 0.033 mmol) in toluene (1 mL) resulted in equilibrium between **2a** and **2c** (**2a**:**2c** = 3.5:1).

(29) Hofmann, P.; Meier, C.; Englert, U.; Schmidt, M. U. *Chem. Ber.* **1992**, *125*, 353–365.

$^{31}P\{^1H\}$ NMR (tol-d_8, 295 K): 126.9 (br s, PCP-**2a**, 2P), 121.4 (br dd, $^1J_{RhP}$ = 197.5 Hz, $^2J_{PP}$ = 45 Hz, PCP-**2c**, 2P), 111.3 (br d, $^1J_{RhP}$ = 165.6 Hz, $PPyr_3$-**2c**, 1P), 83.4 (br s, free $PPyr_3$), 18.7 (br s, PEt_3-**2a**, 1P), −7.8 (s, free PEt_3). ^1H NMR (tol-d_8, 295 K): 7.2−5.9 (Ar and Pyr of **2a**, **2c** and free $PPyr_3$), 3.75 (br s, **2c**, Ar-H_2C-P, 4H), 3.70 (br s, **2a**, Ar-H_2C-P, 4H), 1.47(m, free PEt_3, H_2C-P, 6H), 1.08 (m, PEt_3-**2a**, H_2C-P, 6H), 0.97 (m, free PEt_3, H_3C-H_2C-P, 9H), 0.83 (m, PEt_3-**2a**, H_3C-H_2C-P, 9H). $^{31}P\{^1H\}$ NMR (tol-d_8, 213 K): 120.3 (ddd, $^2J_{PP}$ = 312 Hz, $^1J_{RhP}$ = 192 Hz, $^2J_{PP}$ = 44 Hz, PCP-**2a′**, 2P), 112.46 (ddd, $^2J_{PP}$ = 201 Hz, $^1J_{RhP}$ = 191 Hz, $^2J_{PP}$ = 42 Hz, PCP-**2c′**, 2P), 98.9 (m, $PPyr_3$-**2a′**, 1P), 8.1 (dquartet, $^1J_{RhP}$ = 93 Hz, $^2J_{PP}$ = 42 Hz, PEt_3-**2a′**, 1P), 1.4 (tdd, $^2J_{PP}$ = 202 Hz, $^1J_{RhP}$ = 142 Hz, $^2J_{PP}$ = 44 Hz, PEt_3-**2c′**, 1P), the signal of the ancillary $PPyr_3$ of **2c′** is obscured by other peaks. ^1H NMR (tol-d_8, 213 K): 7.2−5.9 (Ar and Pyr of **2a′** and **2c′**), 4.05 (br d, AB pattern, $^2J_{HH}$ = 15 Hz, **2c′**, Ar-*H*(H)C-P, 2H), 3.82 (br d, AB pattern, $^2J_{HH}$ = 15 Hz, **2c′**, Ar-*H*(H)C-P, 2H), 3.44 (br d, AB pattern, $^2J_{HH}$ = 15.4 Hz, **2a′**, Ar-*H*(H)C-P, 2H), 3.34 (br d, AB pattern, $^2J_{HH}$ = 15.4 Hz, **2c′**, Ar-*H*(H)C-P, 2H), 1.43 (m, Et-**2c′**, H_2C-P, 6H), 1.36 (br s, Et-**2a′**, H_2C-P, 6H), 0.92 (m, Et-**2c′**, H_3C-H_2C-P, 9H), 0.61 (m, Et-**2a′**, H_3C-H_2C-P, 9H).

Equilibrium between $Rh^I(^{Pyr}PCP)PPh_3$ (2b) and $Rh^I(^{Pyr}PCP)$-$PPyr_3$ (2c). Addition of either 1 equiv of $PPyr_3$ (6.6 mg, 0.029 mmol) to **2b** (22.8 mg, 0.029 mmol) or 1 equiv of PPh_3 (7.7 mg, 0.029 mmol) to **2c** (22.5 mg, 0.029 mmol) in toluene (1 mL) resulted in equilibrium between **2b** and **2c** (**2b**:**2c** = 1:4.5).

Reaction of $Rh^I(^{Pyr}PCP)PR_3$ (R = Et (a); Ph (b); Pyr (c); Pyd (d)) with H_2. In a typical experiment a toluene-d_8 solution (1 mL, final volume) of catalyst (0.029 mmol) was incubated with styrene (0.87 mmol) under H_2 (25 psi) in an 80 mL glass pressure tube during 30 min at room temperature. No significant decrease in H_2 pressure was detected for **2a**,**c**,**d**, while the pressure decreased to 22.5 psi for **2b**. Percents of conversion were estimated by ^1H NMR spectroscopy, revealing reduction of styrene to ethyl benzene: **2a** 9.4%, **2b** 22%, **2c** 0.5%, **2d** 1.7%. Slight decay of **2c** (5−10%) and **2d** (up to 10%) was observed by $^{31}P\{^1H\}$ NMR.

Reaction of 2a with MeI. To a solution of **2a** (30.4 mg, 0.047 mmol) in toluene (1 mL) was added MeI (3 μL, 0.048 mmol), resulting in a deep red solution. $^{31}P\{^1H\}$ NMR showed no starting material left after incubation at RT for 1.5 h and formation of three products (**3**) in the ratio (estimated by $^{31}P\{^1H\}$ NMR) **3a**:**3b**:**3c** = 10:2:2.

$^{31}P\{^1H\}$ NMR (toluene-d_8) **3a**: 113.8 (dd, $^1J_{RhP}$ = 144.5 Hz, $^2J_{PP}$ = 24.1 Hz, 2P), −14.4 (dt, $^1J_{RhP}$ = 74.8 Hz, 1P); **3c**: 116.0 (dd, $^1J_{RhP}$ = 144.4 Hz, $^2J_{PP}$ = 25.9 Hz, 2P), −8.0 (dt, $^1J_{RhP}$ = 74.2 Hz, 1P); **3b**: 121.1 (dd, $^1J_{RhP}$ = 141.0 Hz, $^2J_{PP}$ = 31.3 Hz, 2P), −9.6 (dt, $^1J_{RhP}$ = 80.3 Hz, 1P). ^1H NMR (toluene-d_8) **3a**: 7.3−6.8 (Ar, *meta* and *para* to Rh, 3H; Pyr, *H*C-N, 8H), 6.15 (m, Pyr, *H*C-HC-N, 4H), 6.13 (m, Pyr, *H*C-HC-N, 4H), 3.90 (dvt, ABX_2, $^2J_{HH}$ = 16.7 Hz, $^2J_{PH}$ = 5.3 Hz, Ar-C*H*(H)-P, 2H), 3.69 (dvt, ABX_2, $^2J_{HH}$ = 16.7 Hz, $^2J_{PH}$ = 3.8 Hz, Ar-C*H*(H)-P, 2H), 1.12 (m, H_2C-P, 6H), 0.57 (m, H_3C-H_2C-P, 9H), 0.07 (br q, $^3J_{PH}$ = 6.4 Hz, H_3C-Rh, 3H). $^{13}C\{^1H\}$ NMR (C_6D_6) **3a**: 164.9 (ddt, $^1J_{RhC}$ = 32 Hz, $^2J_{C\text{-}PEt3}$ = 5 Hz, $^2J_{C\text{-}PPyr2}$ = 4 Hz, C_{ipso}-Rh, 1C), 141.95 (vtd, $^2J_{PC}$ = 11.2 Hz, J = 1.5 Hz, Ar, *C*-C-Rh, 2C), 124.45 (s, Pyr, *C*H-N-P, 8C), 123.7 (s, Ar, *C*H-CH-C-C-Rh, 1C), 123.32 (vt, $^3J_{PC}$ = 11.0 Hz, Ar, *C*H-C-C-Rh, 2C), 112.74 (vt, $^3J_{PC}$ = 2.46 Hz, Pyr, *C*H-CH-N-P, 4C), 112.37 (vt, $^3J_{PC}$ = 3.1 Hz, Pyr, *C*H-CH-N-P, 4C), 49.43 (vtd, $^1J_{PC}$ = 18.8 Hz, $^2J_{RhC}$ = 3.55 Hz, Ar-*C*H_2-P, 2C), 18.24 (d, $^1J_{PC}$ = 18.0 Hz, Et, P-*C*H_2, 3C), 9.65 (d, $^2J_{PC}$ = 5.6 Hz, Et, P-CH_2-*C*H_3, 3C), −3.32 (ddt, $^2J_{PC,\ trans}$ = 72.7 Hz, $^1J_{RhC}$ = 15.5 Hz, $^2J_{PC,\ cis}$ = 6.6 Hz, Rh-*C*H_3, 1C).

Reaction of 2d with MeI. A solution of **2d** (33 mg, 0.043 mmol) in THF (1 mL) was precooled to −25 °C. Then a MeI solution precooled to −25 °C (neat, 5.3 μL, 0.085 mmol) was added. The reaction mixture was left stirring at ambient temperature for 3.5 h, resulting in quantitative formation of **4a**. Since slight decomposition of **4a** occurred under reduced pressure, the product was precipitated at −25 °C with pentane, the upper solution was decanted, and the pale solid was dried to give 26 mg (58%) of the product.

$^{31}P\{^1H\}$ NMR (THF-d_8, 273 K): 113.5 (d, $^1J_{RhP}$ = 151.3 Hz, *P*Pyr_2, 2P), 43.86 (s, $[MePPyd_3]^+$, 1P). ^1H NMR (THF-d_8, 273 K): 7.58 (br s, Pyr, *H*C-N, 4H), 7.27 (br s, Pyr, *H*C-N, 4H), 7.10 (d, $^3J_{HH}$ = 7.4 Hz, Ar, *meta* to Rh, 2H), 6.83 (t, $^3J_{HH}$ = 7.4 Hz, Ar, *para* to Rh, 1H), 6.08 (m, Pyr, *H*C-HC-N, 8H), 4.59 (dvt, $^2J_{HH}$ = 16.9 Hz, $^2J_{PH}$ = 5.4 Hz, Ar-C*H*(H)-P, 2H), 4.40 (dvt, $^2J_{HH}$ = 16.9 Hz, $^2J_{PH}$ = 5.3 Hz, Ar-C*H*(H)-P, 2H), 3.22 (m, $[MePPyd_3]^+$, P-N-CH_2, 12H), 2.02 (d, $^2J_{PH}$ = 14.6 Hz, $[MePPyd_3]^+$, P-CH_3, 3H), 1.87 (m, $[MePPyd_3]^+$, P-N-CH_2-CH_2, 12H), 0.116 (td, $^3J_{PH}$ = 6.3 Hz, $^2J_{RhH}$ = 1.92 Hz, Rh-CH_3, 3H). $^{13}C\{^1H\}$ NMR (THF-d_8, 273 K): 169.1 (dt, $^1J_{RhC}$ = 34.0 Hz, unresolved t, C_{ipso}-Rh, 1C), 142.66 (vt, $^2J_{PC}$ = 11.9 Hz, Ar, *C*-C-Rh, 2C), 126.33 (s, Pyr, *C*H-N-P, 4C), 124.79 (s, Pyr, *C*H-N-P, 4C), 123.94 (s, Ar, *C*H-CH-C-C-Rh, 1C), 122.85 (vt, $^3J_{PC}$ = 11.7 Hz, Ar, *C*H-C-C-Rh, 2C), 111.24 (s, *C*H-CH-N-P, 4C), 110.76 (s, Pyr, *C*H-CH-N-P, 4C), 48.58 (vtd, $^1J_{PC}$ = 17.9 Hz, $^2J_{RhC}$ = 3.1 Hz, Ar-*C*H_2-P, 2C), 47.9 (d, $^3J_{PC}$ = 4.41 Hz, $[MePPyd_3]^+$, P-N-CH_2-*C*H_2, 6C), 27.19 (d, $^2J_{PC}$ = 7.88 Hz, $[MePPyd_3]^+$, P-N-*C*H_2, 6C), −0.233 (dt, $^1J_{RhC}$ = 22.3 Hz, $^2J_{PC}$ = 4.7 Hz, Rh-*C*H_3, 1C). Confirmed by DEPT. Anal. (%) Found (Calc): C 43.04 (43.16); H 4.96 (5.05).

Reaction of 4a with PEt_3. PEt_3 (neat, 4.6 μL, 0.034 mmol) was added to **4a** (35.5 mg, 0.034 mmol) in THF (1 mL), resulting in formation of **3a**:**3b** = 10:1. The solvent was removed under vacuum to give a brown, viscous solid. The products were recrystallized from MeOH (0.7 mL) during overnight at room temperature. The brown MeOH solution was decanted, and the resulting yellow crystals were rinsed with a small amount of MeOH (0.2 mL) and dried under vacuum, yielding the isomers (17.2 mg, 65%) as a yellow solid.

The *cis* to aryl coordination of the methyl group was confirmed by NOE. Anal. (%) Found (Calc): C 47.20 (46.99); H 5.18 (5.22).

Reaction of 2e with MeI. To a solution of **2e** (30 mg, 0.054 mmol) in THF (3 mL) was added MeI (neat, 3.5 μL, 0.056 mmol) while stirring. The resulting reaction mixture was left stirring at ambient temperature. The reaction was complete after 14 days, resulting in formation of **5** (38% and 78% conversions were observed by NMR after 3 and 7 days, respectively) together with some minor products, which gave $^{31}P\{^1H\}$ NMR spectra similar to **5**. No formation of **6a**,**b** was observed at any stage of the reaction. We were unable to isolate **5**, which was characterized in solution.

Upon addition of 2 equiv of P^iPr_3 to the reaction mixture, *trans*-$Rh(P^iPr_3)_2CO(I)$[30] was formed accompanied by release of ^{Pyr}PCP-Me. The solvent was evaporated, and the yellow residue was washed with a small amount of pentane to remove *trans*-$Rh(P^iPr_3)_2CO(I)$ (yellow solution). The remaining pale residue was treated with a small amount of Et_2O and recrystallized at −25 °C to give pure ^{Pyr}PCP-Me as a pale solid, 16 mg (67%).

Spectral Data for 5. $^{31}P\{^1H\}$ NMR (THF-d_8): 102.4 (d, $^1J_{RhP}$ = 154.6 Hz). ^1H NMR (THF-d_8): 8.46 (d, $^3J_{HH}$ = 7.6 Hz, Ar, *meta* to Rh, 2H), 7.60 (t, $^3J_{HH}$ = 7.6 Hz, Ar, *para* to Rh, 1H), 6.87 (br s, Pyr, *H*C-N, 8H), 6.22 (s, Pyr, *H*C-HC-N, 8H), 4.84 (br s, Ar-CH_2-P, 4H), 1.42 (s, Ar-CH_3, 3H), $^{13}C\{^1H\}$ NMR (THF-d_8): 181.5 (dt, $^1J_{RhC}$ = 76 Hz, $^2J_{PC}$ = 14 Hz, *C*O, 1C), 141.15 (s, Ar, *C*-CH_3, 1C), 132.18 (s, Ar, *C*-C-CH_3, 2C), 131.0 (s, Ar, *C*H-C-C-CH_3, 2C), 125.76 (s, Ar, *C*H-CH-C-C-CH_3, 1C), 125.08 (br s, Pyr, *C*H-N-P, 8C), 113.27 (s, Pyr, *C*H-CH-N-P, 8C), 38.89 (vt, $^1J_{PC}$ = 16.7 Hz, Ar-*C*H_2-P, 2C), 14.61 (s, Ar-*C*H_3, 1C). Confirmed by DEPT and HMQC. IR (film): ν_{CO} = 2008 cm$^-$.

Spectral Data for ^{Pyr}PCP-Me. $^{31}P\{^1H\}$ NMR ($CDCl_3$): 66.74 (s). ^1H NMR ($CDCl_3$): 6.97 (m, Pyr, *H*C-N, 8H), 6.73 (t, $^3J_{HH}$ = 7.7 Hz, Ar, *para* to Rh, 1H), 6.523 (d, $^3J_{HH}$ = 7.7 Hz, Ar, *meta* to

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Rh, 2H), 6.28 (m, Pyr, *H*C-HC-N, 8H), 3.72 (d, $^2J_{PH}$ = 2.47 Hz, Ar-CH_2-P, 4H), 2.25 (s, Ar-CH_3, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$): 135.14 (t, unresolved, Ar, *C*-CH_3, 1C), 132.2 (dd, $^2J_{PC}$ = 10.44 Hz, $^4J_{PC}$ = 2.36 Hz, Ar, *C*-C-CH_3, 2C), 129.0 (dd, Ar, $^3J_{PC}$ = 6.4 Hz, $^5J_{PC}$ = 3.5 Hz, *C*H-C-C-CH_3, 2C), 126.23 (t, $^4J_{PC}$ = 2.7 Hz, Ar, *C*H-CH-C-C-CH_3, 1C), 123.5 (d, $^2J_{PC}$ = 13.9 Hz, Pyr, *C*H-N-P, 8C), 112.14 (d, $^3J_{PC}$ = 4.1 Hz, Pyr, *C*H-CH-N-P, 8C), 37.2 (d, $^1J_{PC}$ = 14.5 Hz, Ar-*C*H_2-P, 2C), 15.99 (t, $^4J_{PC}$ = 5.4 Hz, Ar-*C*H_3, 1C). Confirmed by DEPT.

Synthesis of 6a,b. CO was bubbled through a THF-d_8 (1 mL) solution of **4a** (20 mg, 0.019 mmol) for a few minutes, resulting in formation of **6a**:**6b** = 1:1, accompanied by precipitation of [MePPyd$_3$]I. The complexes **6a**,**b** were not isolated because of slow decomposition to form **5**.

^{31}P{^{1}H} NMR (THF-d_8): 120.5 (d, $^1J_{RhP}$ = 133.6 Hz), 111.8 (d, $^1J_{RhP}$ = 135.4 Hz), 45.1 (s, I[MePPyd$_3$]). ^{1}H NMR (THF-d_8): 7.44 (m, Pyr, *H*C-N, 4H), 7.40 (m, Pyr, *H*C-N, 4H), 7.38−7.06(Ar, *meta* and *para* to Rh), 7.02 (m, Pyr, *H*C-N, 4H), 6.85 (m, Pyr, *H*C-N, 4H), 6.32 (br s, Pyr, *H*C-HC-N, 4H), 6.28 (br s, Pyr, *H*C-HC-N, 8H), 6.25 (br s, Pyr, *H*C-HC-N, 4H), 4.86 (dvt, ABX$_2$, $^2J_{HH}$ = 16.7 Hz, $^2J_{PH}$ = 5.8 Hz, Ar-C*H*(H)-P, 2H), 4.71 (dvt, ABX$_2$, $^2J_{HH}$ = 18.2 Hz, $^2J_{PH}$ = 5.8 Hz, Ar-C*H*(H)-P, 2H), 4.65 (dvt, ABX$_2$, $^2J_{HH}$ = 16.8 Hz, $^2J_{PH}$ = 5.7 Hz, Ar-C*H*(H)-P, 2H), 4.57 (dvt, ABX$_2$, $^2J_{HH}$ = 18.1 Hz, $^2J_{PH}$ = 5.3 Hz, Ar-C*H*(H)-P, 2H), 3.36 (m, P-N-CH_2, PPyd$_3$), 2.32 (d, $^2J_{RhH}$ = 14.9 Hz, P-CH_3, I[MePPyd$_3$]), 1.92 (m, P-N-CH$_2$-CH_2, I[MePPyd$_3$]), 1.59 (m, P-N-CH$_2$-CH_2, I[MePPyd$_3$]), 0.303 (td, $^3J_{PH}$ = 8.16 Hz, $^2J_{RhH}$ = 1.81 Hz, H_3C-Rh, 3H), 0.014 (td, $^3J_{PH}$ = 6.04 Hz, $^2J_{RhH}$ = 2.1 Hz, H_3C-Rh, 3H). ^{13}C{^{1}H} NMR (THF-d_8): 189.5 (m, unresolved, Rh-*C*O, 1C), 180.9 (m, unresolved, Rh-*C*O, 1C), 166.1 (dt, $^1J_{RhC}$ = 25.0 Hz, unresolved triplet, C_{ipso}-Rh, 1C), 161.0 (d, $^1J_{RhC}$ = 31.33 Hz, C_{ipso}-Rh, 1C), 142.78 (vt, $^2J_{PC}$ = 11.8 Hz, Ar, *C*-C-Rh, 2C), 142.28 (vt, $^2J_{PC}$ = 11.0 Hz, Ar, *C*-C-Rh, 2C), 125.15 (m, Pyr, *C*H-N-P, 4C), 125.06 (m, Pyr, *C*H-N-P, 4C), 124.80 (m, Pyr, *C*H-N-P, 4C), 124.20 (m, Pyr, *C*H-N-P, 4C), 114.06 (m, Pyr, *C*H-CH-N-P, 4C), 113.80 (m, Pyr, *C*H-CH-N-P, 4C), 113.40 (m, Pyr, *C*H-CH-N-P, 8C), 50.1 (vtd, $^1J_{PC}$ = 20.3 Hz, $^2J_{RhC}$ = 2.8 Hz, Ar-*C*H_2−P, 2C), 48.3 (vtd, $^1J_{PC}$ = 19.3 Hz, $^2J_{RhC}$ = 3.2 Hz, Ar-*C*H_2-P, 2C), 48.1 (d, $^3J_{PC}$ = 4.4 Hz, P-N-CH$_2$-*C*H_2, I[MePPyd$_3$], 6C), 27.2 (d, $^2J_{PC}$ = 7.8 Hz, P-N-*C*H_2, I[MePPyd$_3$], 6C), −2.78 (dt, $^1J_{RhC}$ = 15.5 Hz, $^2J_{PC}$ = 5.9 Hz, Rh-*C*H_3, 1C), −6.9 (dt, $^1J_{RhC}$ = 20.47 Hz, unresolved triplet, Rh-*C*H_3, 1C). Confirmed by DEPT.

Reaction of 2b with MeI at the Presence of [NBu$_4$]I. A THF (1 mL) solution of **2b** (20 mg, 0.025 mmol) was added to a THF (0.5 mL) suspension of [NBu$_4$]I (9.3 mg, 0.025 mmol), resulting in a yellow suspension. MeI (neat, 1.6 μL, 0.026 mmol) was added. The solution became clear yellow after 15 min stirring at r.t. ^{31}P{^{1}H} NMR showed quantitative formation of **4b** accompanied by PPh_3. The product was precipitated with pentane (6 volumes) at –25 °C. The soluble fraction was decanted, giving 19 mg (72%) of **4b** as pale brown crystals.

^{31}P{^{1}H} NMR (C_6D_6): 115.6 (d, $^1JP_{RhP}$ = 151.1 Hz). ^{1}H NMR (C_6D_6): 7.90 (br s, Pyr, *H*C-N, 4H), 7.51 (br s, Pyr, *H*C-N, 4H), 7.3 (br s, Ar, *para* to Rh, 1H), 7.1 (m, Ar, *meta* to Rh, 2H), 6.46 (m, Pyr, *H*C-HC-N, 4H), 6.35 (m, Pyr, *H*C-HC-N, 4H), 4.65 (dvt, $^2J_{HH}$ = 16.8 Hz, $^2J_{PH}$ = 5.4 Hz, Ar-C*H*(H)-P, 2H), 4.24 (dvt, $^2J_{HH}$ = 16.8 Hz, $^2J_{PH}$ = 5.2 Hz, Ar-C*H*(H)-P, 2H), 2.99 (m, NBu$_4$, N-CH_2, 8H), 1.37 (m, NBu$_4$, N-CH$_2$-(CH_2)$_2$, 16H), 1.03 (t, $^3J_{HH}$ = 6.9 Hz, NBu$_4$, N-(CH$_2$)$_3$-CH_3, 12H), 0.795 (td, $^3J_{PH}$ = 6.3 Hz, $^2J_{RhH}$ = 1.8 Hz, Rh-CH_3, 3H). ^{13}C{^{1}H} NMR (C_6D_6): 167.9 (dt, $^1J_{RhC}$ = 34.1 Hz, unresolved t, C_{ipso}-Rh, 1C), 142.06 (vt, $^2J_{PC}$ = 11.8 Hz, Ar, *C*-C-Rh, 2C), 126.21 (vt, $^2J_{PC}$ = 2.34 Hz, Pyr, *C*H-N-P, 4C), 124.56 (s, Pyr, *C*H-N-P, 4C), 124.01 (s, Ar, *C*H-CH-C-C-Rh, 1C), 122.73 (vt, $^3J_{PC}$ = 11.6 Hz, Ar, *C*H-C-C-Rh, 2C), 111.44 (vt, unresolved t, Pyr, *C*H-CH-N-P, 4C), 110.83 (vt, $^3J_{PC}$ = 2.69 Hz, Pyr, *C*H-CH-N-P, 4C), 58.68 (s, NBu$_4$, N-*C*H_2, 4C), 49.11 (vtd, $^1J_{PC}$ = 17.5 Hz, $^2J_{RhC}$ = 3.5 Hz, Ar-*C*H_2-P, 2C), 24.31 (s, NBu$_4$, N-CH$_2$-*C*H_2, 4C),. 19.95 (s, NBu$_4$, N-(CH$_2$)$_2$-*C*H_2, 4C), 14.06 (s, NBu$_4$, N-(CH$_2$)$_3$-*C*H_3, 4C), −0.07 (dt, $^1J_{RhC}$ = 22.1 Hz, $^2J_{PC}$ = 4.9 Hz, Rh-*C*H_3, 1C). Confirmed by DEPT and HSQC. Anal. (%) Found (Calc): C 47.29 (47.19); H 6.01 (5.99).

Reaction of 2c with MeI in the Presence of [NBu$_4$]I. A THF (2 mL) solution of **2c** (15.6 mg, 0.021 mmol) was added to a THF (2 mL) suspension, of [NBu$_4$]I (7.6 mg, 0.021 mmol), resulting in a yellow suspension. MeI (neat, 1.3 μL, 0.021 mmol) was added. The solution became clear yellow after 2.5 h stirring at r.t. ^{31}P{^{1}H} NMR showed quantitative formation of **4b** accompanied by $PPyr_3$. The product was precipitated with pentane (6 volumes) at –25 °C overnight. The soluble fraction was decanted, and the light brown solid was dried to give 19 mg (89%) of **4b**.

Reaction of 2e with MeI in the Presence of [NBu$_4$]I. To a suspension of [NBu$_4$]I (6.6 mg, 0.018 mmol) and **2e** (10 mg, 0.018 mmol) in THF (2 mL) was added MeI (neat, 1.1 μL, 0.018 mmol). The reaction was complete during 9 h stirring at ambient temperature. ^{31}P{^{1}H} NMR showed formation of **4b**:**6a**:**6b** = 9:1:1. The solution was left stirring at room temperature for 2 days, resulting in formation of **4b**.

Synthesis of [Rh^{I}(^{Pyr}PCP)I]NBu$_4$ (2f). To a brown crude solution of Rh^{I}(^{Pyr}PCP)norbornene (made from 50 mg of [Rh^{I}(COE)$_2$$\mu$Cl]$_2$ as described in the procedure for the synthesis of **2d**) was added [NBu$_4$]I (51.5 mg, 0.139 mmol). The resulting reaction mixture was stirred for 24 h at rt, resulting in formation of [Rh^{I}(^{Pyr}PCP)I]NBu$_4$. We were not able to purify the product either on a Florisil column or by extractions. The yield was estimated as at least 60% by ^{31}P{^{1}H} NMR spectrum integration.

^{31}P{^{1}H} NMR (THF-d_8): 108.2 (d, $^1J_{RhP}$ = 221.27 Hz). ^{1}H NMR (THF-d_8): 7.64 (m, Pyr, *H*C-N, 8H), 6.79 (d, $^3J_{HH}$ = 7.31 Hz, Ar, *meta* to Rh, 2H), 6.65 (t, $^3J_{HH}$ = 7.31 Hz, Ar, *para* to Rh 1H), 6.05 (m, Pyr, *H*C-HC-N 8H), 3.96 (vt, $^2J_{HP}$ = 4.2 Hz, Ar-H_2C-P, 4H), 3.24 (m, NBu$_4$, H_2C-N, 8H), 1.64 (m, NBu$_4$, H_2C-CH$_2$-N, 8H), 1.37 (m, NBu$_4$, CH_2-CH$_2$-CH$_2$-N, 8H), 0.96 (t, $^3J_{HH}$ = 7.4 Hz, NBu$_4$, CH_3-CH$_2$-CH$_2$-CH$_2$-N, 12H). ^{13}C NMR (THF-d_8): 173.49 (dt, $^1J_{RhC}$ = 41.1 Hz, $^2J_{PC}$ = 8.6 Hz, C_{ipso}-Rh, 1C), 146.11 (vtd, $^2J_{PC}$ = 15.2 Hz, $^2J_{RhC}$ = 2.2 Hz, Ar, *C*-C-Rh, 2C), 125.68 (vt, $^2J_{PC}$ = 3.8 Hz, Pyr, *C*H-N-P, 8C), 121.83 (vt, $^3J_{PC}$ = 12.3 Hz, Ar, *C*H-C-C-Rh, 2C), 121.42 (s, Ar, *C*H-CH-C-C-Rh, 1C), 110.53 (unresolved vt, Pyr, *C*H-CH-N-P, 8C), 59.19 (s, NBu$_4$, *C*H_2-N, 4C), 50.79 (vtd, $^1J_{PC}$ = 16.5 Hz, $^2J_{RhC}$ = 5.4 Hz, Ar-*C*H_2-P, 2C), 24.74 (s, NBu$_4$, *C*H_2-CH$_2$-N, 4C), 20.54 (s, NBu$_4$, *C*H_2-CH$_2$-CH$_2$-N, 4C), 14.05 (s, NBu$_4$, *C*H_3-CH$_2$-CH$_2$-CH$_2$-N, 4C).

Reaction of [Rh^{I}(^{Pyr}PCP)I]NBu$_4$ with MeI. To a crude solution of [Rh^{I}(^{Pyr}PCP)I]NBu$_4$ (prepared form 50 mg of [Rh^{I}(COE)$_2$$\mu$Cl]$_2$) was added MeI (neat, 8.7 μL, 0.139 mmol). ^{31}P{^{1}H} NMR (THF-H_8) showed formation of **4b** after 5 min at rt (about 70% spectral yield). The product was dried, extracted with toluene, dried, and quickly washed with Et_2O (2 × 5 mL). The remaining brown solid was dried, giving 101 mg (69%) of **4b**.

General Information for X-ray Analysis of the Structures 2c−e, 3a, and 4b. Data were collected with a Nonius KappaCCD diffractometer at 120(2) K, Mo Kα (λ = 0.71073 Å), graphite monochromator. The data were processed with Denzo-Scalepack. Structures were solved by direct methods with SHELXS-97 and refined with full matrix least-squares refinement based on F^2 by SHELXL-97.

X-ray Analysis of the Structure of Rh^{I}(^{Pyr}PCP)PPyr$_3$ (2c). Orange needles of **2c** were obtained by slow diffusion of hexane into a concentrated solution of **2c** in THF, in a 5 mm NMR tube, at room temperature.

Crystal data: $2C_{36}H_{35}N_7P_3Rh+1/2(C_6H_{14})$, 0.40 × 0.05 × 0.05 mm^3, triclinic, $P\bar{1}$, a = 9.180(0) Å, b = 17.938(4) Å, c = 22.503(5) Å, α = 79.923(3)° β = 78.612(1)° γ = 82.986(1)°, T = 120(2) K, V = 3562.4(12) Å^3, Z = 2, fw = 1566.15, D_c = 1.460 Mg m^{-3}, μ = 0.653 mm^{-1}.

Data collection and processing: $0 \le h \le 11$, $-22 \le k \le 23$, $-28 \le l \le 29$, frame scan width = 1.0°, scan speed 1.0° per 320 s, typical peak mosaicity 0.47°, 59 988 reflections collected, 16 144 independent reflections ($R_{int} = 0.049$).

Solution and refinement: 863 parameters with 0 restraints, final $R_1 = 0.0427$ (based on F^2) for data with $I > 2\sigma(I)$ and, $R_1 = 0.0630$ on 16 137 reflections, goodness-of-fit on $F^2 = 1.016$, largest electron density peak = 2.488 e Å^{-3}.

X-ray Analysis of the Structure of Rh^{I}(^{Pyr}PCP)PPyd$_3$ (2d). A saturated pentane solution of **2d** was put in a 20 mL vial, twice concentrated by evaporation under reduced pressure, and left overnight at room temperature in a closed evaporator without normalizing the pressure. Yellow chunks of **2d** were obtained.

Crystal data: $C_{36}H_{47}N_7P_3Rh$, 0.18 × 0.1 × 0.09 mm^3, monoclinic, $P2_1/n$, $a = 16.7698(2)$ Å, $b = 12.2296(3)$ Å, $c = 18.4779(3)$ Å, $\beta = 112.219(1)°$, $T = 120(2)$K, $V = 3508.1(1)$ Å^3, $Z = 4$, fw = 773.63, $D_c = 1.465$ Mg m^{-3}, $\mu = 0.661$ mm^{-1}.

Data collection and processing: $-22 \le h \le 20$, $0 \le k \le 16$, $0 \le l \le 24$, frame scan width = 1.0°, scan speed 1.0° per 70 s, typical peak mosaicity 0.411°, 45 263 reflections collected, 8732 independent reflections ($R_{int} = 0.104$).

Solution and refinement: 430 parameters with no restraints, final $R_1 = 0.0416$ (based on F^2) for data with $I > 2\sigma(I)$ and, $R_1 = 0.0742$ on 8331 reflections, goodness-of-fit on $F^2 = 0.980$, largest electron density peak = 0.932 e Å^{-3}.

X-ray Analysis of the Structure of Rh^{I}(^{Pyr}PCP)CO (2e). Yellow prism crystals of **2e** were obtained by slow diffusion of pentane into a concentrated solution of **2e** in THF, in a 5 mm NMR tube, at room temperature.

Crystal data: $C_{25}H_{23}N_4OP_2Rh$, 0.5 × 0.3 × 0.2 mm^3, triclinic, $P\bar{1}$, $a = 9.385(2)$ Å, $b = 10.736(2)$ Å, $c = 12.812(3)$ Å, $\alpha = 107.29(3)°$ $\beta = 106.06(3)°$ $\gamma = 99.08(3)°$, $T = 120(2)$K, $V = 1143.2(4)$ Å^3, $Z = 2$, fw = 560.32 g/mol, $D_c = 1.628$ Mg m^{-3}, $\mu = 0.914$ mm^{-1}.

Data collection and processing: 25 507 reflections collected, $0 \le h \le 12$, $-13 \le k \le 13$, $-16 \le l \le 15$, frame scan width = 1.0°, scan speed 1.0° per 20 s, typical peak mosaicity 0.381°, 5602 independent reflections ($R_{int} = 0.061$).

Solution and refinement: 298 parameters with 0 restraints, final $R_1 = 0.0325$ (based on F^2) for data with $I > 2\sigma(I)$ and $R_1 = 0.0396$ on 5194 reflections, goodness-of-fit on $F^2 = 1.095$, largest electron density peak = 1.926 e Å^{-3}.

X-ray Analysis of the Structure of Rh^{I}(^{Pyr}PCP)Me(I)PEt$_3$ (3a). Yellow prism crystals were obtained at room temperature from a concentrated MeOH solution of the mixture of **3**.

Crystal data: $C_{31}H_{41}IN_4P_3Rh$, 0.25 × 0.07 × 0.07 mm^3, orthorhombic, $Pca2_1$, $a = 16.2351(2)$ Å, $b = 10.6516(4)$ Å, $c = 19.0486(2)$ Å, $T = 120(2)$K, $V = 3294.2(1)$ Å^3, $Z = 4$, fw = 792.4 g/mol, $D_c = 1.598$ Mg m^{-3}, $\mu = 1.628$ mm^{-1}.

Data collection and processing: $0 \le h \le 21$, $0 \le k \le 13$, $0 \le l \le 24$, frame scan width = 1.0°, scan speed 1.0° per 60 s, typical peak mosaicity 0.551°, 31 184 reflections collected, 4251 independent reflections ($R_{int} = 0.093$).

Solution and refinement: 366 parameters with one restraint, final $R_1 = 0.0322$ (based on F^2) for data with $I > 2\sigma(I)$ and, $R_1 = 0.0460$ on 3899 reflections, goodness-of-fit on $F^2 = 1.078$, largest electron density peak = 0.855 e Å^{-3}.

X-ray Analysis of the Structure of [Rh^{I}(^{Pyr}PCP)Me(I)$_2$]-[NBu$_4$] (4b). Colorless prism crystals of **4b** were obtained from a THF/pentane (1:1) solution of **4b** in a 5 mm NMR tube. The crystals appeared after 3 days at room temperature.

Crystal data: $C_{25}H_{26}I_2N_4P_2Rh+C_{16}H_{36}N+C_4H_8O$, 0.25 × 0.25 × 0.15 mm^3, monoclinic, $P2_1$, $a = 13.2256(2)$ Å, $b = 15.7831(3)$ Å, $c = 13.3389(2)$ Å, $\beta = 119.5274(7)°$, $T = 120(2)$ K, $V = 2422.8(1)$ Å^3, $Z = 2$, fw = 1115.71 g/mol, $D_c = 1.529$ Mg m^{-3}, $\mu = 1.730$ mm^{-1}.

Data collection and processing: $-16 \le h \le 14$, $0 \le k \le 20$, $0 \le l \le 17$, frame scan width = 1.0°, scan speed 1.0° per 30 s, typical peak mosaicity 0.411°, 30 712 reflections collected, 6177 independent reflections ($R_{int} = 0.059$).

Solution and refinement: 511 parameters with one restraint, final $R_1 = 0.0317$ (based on F^2) for data with $I > 2\sigma(I)$ and $R_1 = 0.0424$ on 5522 reflections, goodness-of-fit on $F^2 = 1.142$, largest electron density peak = 2.943 e Å^{-3}.

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Supporting Information Available: CIF files containing X-ray crystallographic data for compounds **2c**, **2d**, **2e**, **3a**, and **4b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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