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# Oxidative Addition Reactions of Organorhodium(I) Complexes Containing the Tridentate Ligand 2,6-Bis(diphenylphosphanylmethyl)pyridine [Rh(PNP)R] ($R = CH_3$, $C_6H_5$) with Iodine and Methyl Iodide and Investigation of the Reductive Elimination

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*Dedicated to Professor Helmut Werner on the occasion of his 65th birthday*

**Keywords:** Rhodium(III) complexes / Tridentate ligand / Oxidative addition / Reductive elimination / C–C coupling

As part of studies aimed at delineating the mechanism of the rhodium complex-catalyzed hydroamination of olefins, the model complexes [Rh(PNP)R] (R = $CH_3$ **1a**, $C_6H_5$ **1b**) have been investigated with regard to oxidative addition reactions. The reaction of $I_2$ with **1a** leads to both *trans*- and *cis*-[Rh(PNP)($CH_3$)$I_2$] (*trans*: **2a**, *cis*: **2a′**), whereas with **1b** only *trans*-[Rh(PNP)($C_6H_5$)$I_2$] (**2b**) is obtained. The rhodium(III) complexes [Rh(PNP)($CH_3$)RI] (**3a**,**b**) are formed by the reaction of **1a**,**b** with $CH_3I$. The new organorhodium(III) complexes **2a**,**b** and **3a**,**b** have been characterized by $^{31}P$-, $^{1}H$-, and $^{13}C$-NMR spectrometry, as well as by EI mass spectrometry. The hydrocarbons $RCH_3$ are reductively eliminated in the reaction of [Rh(PNP)($CH_3$)RI] (**3a**,**b**) with $TlBF_4$ in acetone, while the reaction of **3b** and $TlBF_4$ in THF/$CH_3CN$ leads to the stable rhodium(III) complex [Rh(PNP)($CH_3$)($C_6H_5$)($CH_3CN$)]$BF_4$ (**5**). Complex **5** has been characterized by X-ray crystallography.

## Introduction

Detailed model studies have been initiated aimed at elucidating the reaction mechanism of the rhodium complex-catalyzed hydroamination of ethylene.[1] For the first time, the process was shown to be catalyzed by a cationic ethylene rhodium(I) complex under normal conditions.[2] For these studies, model complexes containing the 2,6-bis(diphenylphosphanylmethyl)pyridine-rhodium(I) fragment [Rh(PNP)]$^+$ as a stable structural unit were synthesized and characterized.[3]

Since the formation and cleavage of an Rh−C σ-bond is expected to play an essential role in this catalytic cycle, organorhodium(I) complexes [Rh(PNP)R] (R = $CH_3$, $C_6H_5$) were synthesized and investigated with regard to the coordination of ethylene and protolysis. It was found that with protic acids such as $HSO_3CF_3$ and [$HN(CH_3)_3$]Cl, these organorhodium(I) complexes react by immediate release of the hydrocarbon HR, presumably via reductive elimination from an initially formed hydrido organorhodium(III) complex.[4]

While a hydrido organorhodium(III) complex, which might have been expected to be formed by oxidative addition of the protic acid, could not be isolated or detected in these cases, a stable monohydrido chloro rhodium(III) complex [Rh(PNP)HCl($CH_3CN$)]$SO_3CF_3$ is accessible by oxidative addition of $HSO_3CF_3$[4] to the related chloro rhodium(I) complex [Rh(PNP)Cl].[3b,5] Since the oxidative addition and the reductive elimination involved in numerous other rhodium-complex catalyzed processes are of general importance[6] it seemed therefore interesting to study these reaction steps at the [Rh(PNP)]$^+$ fragment.

In this paper, we report on oxidative addition reactions of the organorhodium(I) complexes [Rh(PNP)R] (R = $CH_3$, $C_6H_5$) with $I_2$ and $CH_3I$, as well as on the conditions under which the obtained diorganorhodium(III) complexes [Rh(PNP)($CH_3$)RI] undergo reductive elimination.

## Results and Discussion

### Oxidative Addition Reactions of [Rh(PNP)R] ($R = CH_3$, $C_6H_5$) with $I_2$ and $CH_3I$

In order to show that stable PNP-organorhodium(III) complexes are accessible, the reactivity of organorhodium(I) complexes **1a**,**b** with iodine and methyl iodide, which are known as suitable reagents for oxidative addition to rhodium(I) complexes,[7] was investigated. Both organorhodium(I) complexes **1a**,**b** were found to react smoothly with iodine to give the corresponding rhodium(III) complexes [Rh(PNP)$I_2$R] **2** [Eqs. (1) and (2)], which were isolated as brown, air-stable solids.

[+] Part 54: See ref.[4]

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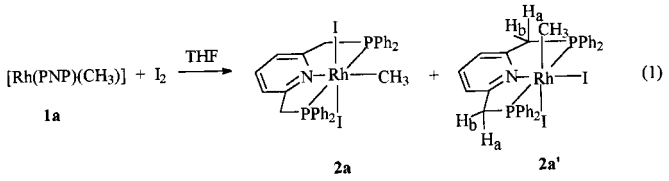
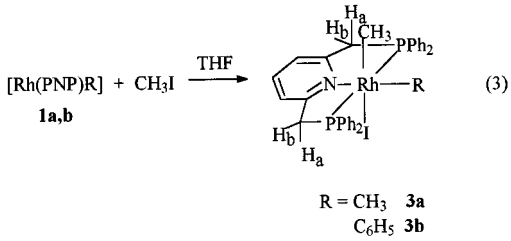
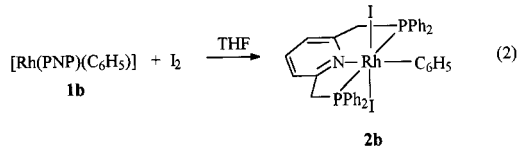



In the case of the methyl complex, the formation of the *trans* as well as of the *cis* addition product (**2a** and **2a′**, respectively) was established by NMR spectrometry. The two isomers constantly crystallize as a mixture, however, no further attempts were made to separate **2a** and **2a′** by other methods. In the $^{31}$P-NMR spectrum, two doublets are observed at δ = 14.3 ($J_{P-Rh}$ = 99 Hz) for **2a** and at δ = 23.3 ($J_{P-Rh}$ = 106 Hz) for **2a′**, in an intensity ratio of 3:2. The phosphorus-rhodium coupling constants are markedly lower in comparison to those in the organorhodium(I) complexes **1a**,**b**, indicating the $Rh^{III}$ oxidation state.[8] Accordingly, in the $^1$H-NMR spectrum, two discrete methyl group signals are observed at δ = 1.99 for **2a** and at δ = 0.43 for **2a′**, with the same relative intensities of 3:2. The corresponding characteristic signal patterns of the methylene protons of the PNP ligand, a pseudo triplet at δ = 4.84 for **2a** and two doublets of pseudo triplets at δ = 4.49 and 4.80 for **2a′**, are consistent with the symmetry of these *trans* and *cis* isomers. In the $^{13}$C-NMR spectrum, two discrete signals at δ = −18.4 and δ = 8.7 are observed for the methyl groups, while for the methylene groups of the PNP ligand, two signals appear at δ = 44.7 and δ = 46.7, showing slightly different intensities.

The phenyl complex **1b** forms exclusively the *trans* addition product **2b** on reaction with iodine [Eq. (2)]. The $^{31}$P-NMR spectrum exhibits only one doublet at δ = 18.8 ($J_{P-Rh}$ = 105 Hz). The pseudo triplet for the methylene group is seen at δ = 4.90 in the $^1$H-NMR spectrum, consistent with the $C_2$ symmetry of the *trans*-diiodo complex **2b**. The $^1$H-NMR signals of the phenyl moiety in **2b** are slightly downfield shifted compared to those found for **1b**, appearing at δ = 6.88 and 7.96.

In the mass spectra of **2a**,**a′** (analyzed as an isomeric mixture) and of **2b**, peaks are observed corresponding to the fragments $[M - I]^+$, $[M - R]^+$, $[M - I - R]^+$, $[M - I - I]^+$, and $[M - I - I - R]^+$. Additionally in the mass spectrum of **2a**,**a′**, a peak at *m*/*z* = 142 is found, which can be assigned to $[CH_3I]^+$ as the product of reductive elimination.

The reactions of **1a**,**b** with methyl iodide [Eq. (3)] led to the diorganorhodium(III) complexes [Rh(PNP)($CH_3$)RI] **3a**,**b**, which were isolated as pale-yellow air-stable solids and characterized by $^{31}$P-, $^1$H-, and $^{13}$C-NMR spectrometry, as well as by mass spectrometry.

The $^{31}$P-NMR signals observed at δ = 26.5 ($J_{P-Rh}$ = 120 Hz) for **3a** and at δ = 30.5 ($J_{P-Rh}$ = 119 Hz) for **3b** are downfield shifted in comparison to the signals of the corresponding diiodo complexes **2a** and **2b**. The increased phosphorus-rhodium coupling constants in **3a**,**b** in comparison to those in **2a**,**b** may be arised by coordination of the more basic methyl ligand instead of one iodo ligand, respectively. In the $^1$H-NMR spectrum of the dimethyl complex **3a**, two discrete methyl signals are observed at δ = −0.35 and δ = 1.02, suggesting the coordination of two distinct methyl groups in a mutual *cis*-arrangement. This is confirmed by the resonances of the methylene protons of the PNP ligand, which appear as two doublets of pseudo triplets at δ = 4.31 and 4.66, consistent with the inequivalence of the methylene protons arising from the *cis* orientation of the methyl groups. Accordingly, in the $^{13}$C-NMR spectrum, two discrete signals for the methyl groups are observed at δ = −14.5 and 6.9.

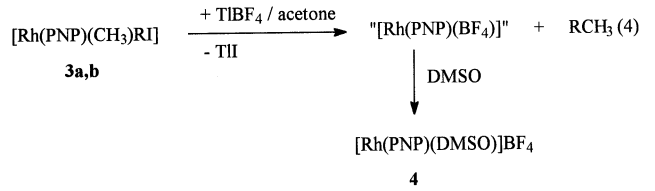
The $^1$H-NMR signal of the methyl group in the methyl phenyl complex **3b** appears at δ = 0.35, while the phenyl group gives rise to multiplets at δ = 6.90 and 7.68. The typical signal pattern for the non-equivalent methylene protons, as observed for **3a**, is seen in the spectrum of **3b** at δ = 4.34 and 4.80. The $^{13}$C-NMR signal for the methyl group in **3b** appears at δ = 8.8, while the phenyl group signals are seen at δ = 121.5, 125.9, and 142.3.

In the mass spectra of **3a** and **3b**, peaks are observed corresponding to the fragments $[M - CH_3]^+$, $[M - CH_3 - R]^+$, and $[M - CH_3 - R - I]^+$. Additionally, in the mass spectrum of **3b**, a peak at *m*/*z* = 91 can be observed, attributable to $[C_7H_7]^+$. This suggests that toluene is reductively eliminated from the methyl phenyl complex **3b** following C−C bond formation.

## Investigation of the Reductive Elimination of Hydrocarbons by C−C Bond Formation from [Rh(PNP)($CH_3$)RI]$BF_4$ 3a,b

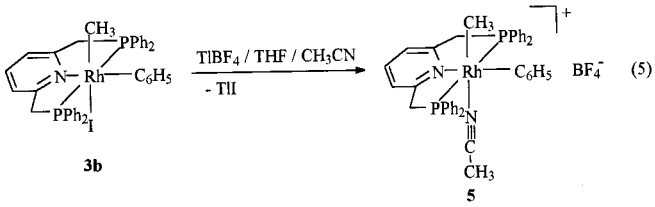
In a manner analogous to the reductive elimination of the hydrocarbon from the proposed hydrido organorhodium(III) intermediates by formation of a C−H bond,[4,9] the reactivity of the diorganorhodium(III) complexes **3a**, **b** was investigated. The aforementioned mass spectral observation of toluene generation from **3b** gave a prior indication of C−C bond formation between the two organo moieties. After addition of $TlBF_4$ to a solution of **3a** or **3b** in acetone, TlI precipitated while the solution changed colour from pale yellow to dark-red during 1−2 days indicating the

change of the oxidation state from $Rh^{III}$ to $Rh^{I}$. Indeed, the hydrocarbon which is formed by reductive elimination from **3a** and **3b**, respectively [Eq. (4)], has been proved. Carrying out the reaction of **3a** and $TlBF_4$ in [$D_6$]acetone in a sealed NMR tube the singlet of the liberated ethane could be observed in the $^1$H-NMR spectrum while the signals of complex **3a** disappeared. Whereas the toluene reductively eliminated from **3b** was detected in the filtrate of the reaction solution by gas chromatography. The dark colour of the solutions indicated a decomposition reaction, most likely as a consequence of the weak coordination of the acetone, which does not have sufficient donor strength to stabilize the remaining $[Rh^{I}(PNP)]^+$ fragment. In order to prove that the rhodium was present in the +I oxidation state, some DMSO was added to the solution. The corresponding stable rhodium(I) complex $[Rh(PNP)(DMSO)]BF_4$ **4** was obtained, which was identified by comparison of its $^{31}$P-NMR spectrum with that of an authentic sample (cf. ref.[3b]).




Clearly, the cleavage of the iodo ligand from the octahedral diorganorhodium(III) complex **3a**,**b** leads to a kinetically unstable five-coordinate complex, which cannot be stabilized by the weakly coordinating acetone used as solvent. This confirms the dissociative mechanism of the reductive elimination.[9]

However, when the reaction of **3b** with $TlBF_4$ was carried out in the presence of the more strongly coordinating acetonitrile, a stable six-coordinate methyl phenyl acetonitrile rhodium(III) complex $[Rh(PNP)(CH_3)(C_6H_5)(CH_3CN)]BF_4$ **5** was obtained [Eq. (5)], which was isolated as an air-stable, white, crystalline solid and characterized by $^{31}$P-, $^1$H-, and $^{13}$C-NMR spectrometry, as well as by X-ray crystal structure analysis.




In the $^{31}$P-NMR spectrum of **5**, the doublet at $\delta = 32.7$ ($J_{P-Rh} = 117$ Hz) is somewhat downfield shifted compared to the corresponding signal in the iodo complex **3b**. While the $^1$H- and $^{13}$C-NMR signals of the phenyl moiety appear at approximately the same chemical shifts as found for **3b**, the signals for the methyl moiety of **5** are somewhat upfield shifted in both the $^1$H- ($\delta = 0.09$) and the $^{13}$C-NMR spectra ($\delta = 2.0$), compared to those in **3b**. This may be interpreted in terms of the differential *trans* influence of the respective *trans*-coordinated ligands ($I^-$ **3b**; $CH_3CN$ **5**).

For the coordinated acetonitrile in **5**, a singlet is observed at $\delta = 1.45$ in the $^1$H-NMR spectrum, while in the $^{13}$C-NMR spectrum, two signals are observed at $\delta = 2.0$ and 128.5. In the IR spectrum, the two bands characteristic of end-on coordinated acetonitrile[9] are seen at $\tilde{\nu} = 2281$ and 2376 $cm^{-1}$. The coordination of the pyridine of the PNP ligand is indicated by two bands at $\tilde{\nu} = 1574$ and 1606 $cm^{-1}$,[11] while a strong band at $\tilde{\nu} = 1062$ $cm^{-1}$ is characteristic of the non-coordinated $BF_4^-$ anion.[12]

Single crystals of **5** of X-ray quality were obtained from a solution of the complex in acetone overlayered with diethyl ether. X-ray crystal structure analysis confirmed the *cis*-arrangement of the organo moieties in the octahedral complex cation of **5**, which is an essential structural prerequisite for the reductive elimination of toluene. The molecular structure of the complex cation $[Rh(PNP)(CH_3)(C_6H_5)(CH_3CN)]^+$ is shown in Figure 1.

Comparing the rhodium-carbon distances of the σ-bonded methyl and phenyl groups [Rh−C(3) 2.085(3), Rh−C(11) 2.049(3)], only a very slight difference is apparent. The small difference in bond lengths of the two types of Rh−C bond may be viewed as reflecting the differential *trans* influence of the N($sp^2$) and N(sp) atoms of the coordinated pyridine moiety and acetonitrile ligand, respectively, which gives rise to an extension of the Rh−C($sp^2$) bond and a shortening of the Rh−C($sp^3$) bond. However, it may also be viewed as merely following the expected trend that the $sp^2$ carbon atom has a shorter distance to the rhodium atom than the $sp^3$ carbon atom.

Furthermore, it is interesting to compare the molecular structure of **5** with that of the related cationic $Rh^{III}$ complex $[Rh(PNP)ClH(CH_3CN)]SO_3CF_3$,[4] which contains the same structural unit $[Rh^{III}(PNP)(CH_3CN)]^+$, but with the hydrido ligand coordinated *trans* to the acetonitrile ligand. In both complexes, the N atom of the coordinated acetonitrile shows an identical distance to the rhodium atom of 2.14 Å, as a result of the comparable *trans* influence of the methyl and hydrido ligands. However, the distance of the pyridine N atom to the rhodium atom in **5** is significantly longer [Rh−N(2) 2.152(2) Å] than the corresponding Rh−N(py) distance in the hydrido chloro $Rh^{III}$ complex [Rh−N(2) 2.0656(17) Å].[4] This is consistent with the expected stronger *trans* influence of the phenyl group, which has a lower electronegativity than the chloro ligand coordinated *trans* to the pyridine. The end-on coordinated acetonitrile shows an almost linear arrangement of Rh−N(1)−C(1)−C(2) [C(1)−N(1)−Rh 172.0(2)°, N(1)−C(1)−C(2) 178.4(4)°], as was also found in the cationic $Rh^{III}$ complex $[Rh(PNP)ClH(CH_3CN)]SO_3CF_3$,[4] as well as in the cationic rhodium(I) complex $[Rh(PNP)(CH_3CN)]BF_4$.[3b]

## Conclusions

The organorhodium(I) complexes [Rh(PNP)R] smoothly undergo oxidative addition reactions with $I_2$ and $CH_3I$ to give the stable organorhodium(III) complexes $[Rh(PNP)RI_2]$ and $[Rh(PNP)(CH_3)RI]$, respectively.

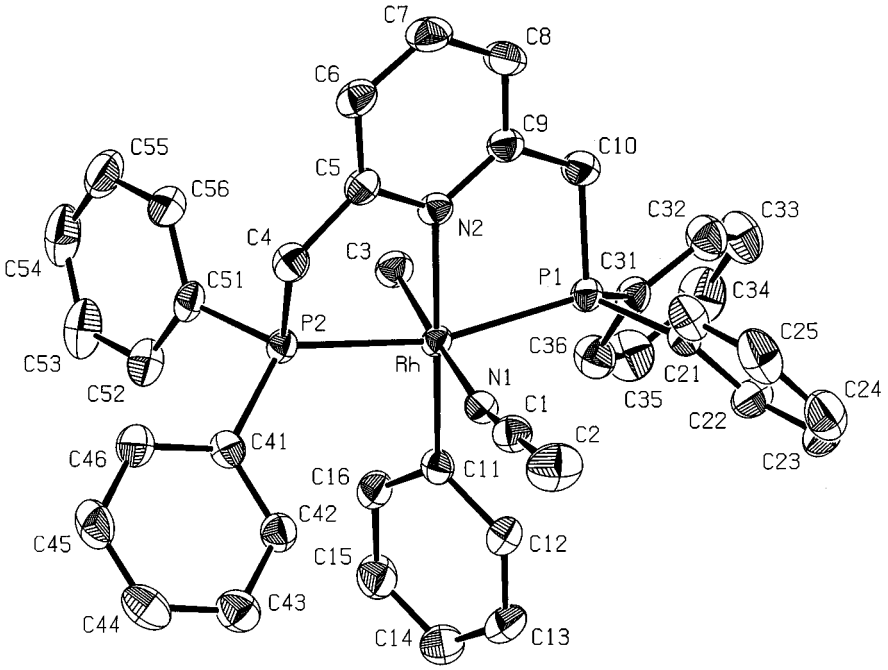



Figure 1. PLATON[13] drawing of the structure of the complex cation of $[Rh(PNP)(C_6H_5)(CH_3)(CH_3CN)]BF_4$ **5**. Selected bond lengths [Å] and angles [°]: Rh−N(1) 2.142(3), Rh−N(2) 2.152(2), Rh−C(3) 2.082(3), Rh−C(11) 2.049(3), Rh−P(1) 2.2913(9), Rh−P(2) 2.3098(8), P(1)−C(10) 1.848(5), P(2)−C(4) 1.835(3); P(1)−Rh−P(2) 164.58(3), N(1)−Rh−P(1) 93.92(7), N(1)−Rh−P(2) 89.55(7), N(1)−Rh−N(2) 88.56(9), C(3)−Rh−C(11) 91.77(12), N(1)−Rh−C(3) 176.65(11), N(2)−Rh−C(11) 179.9(2), C(1)−N(1)−Rh 172.0(2), N(1)−C(1)−C(2) 178.4(4).

It was shown that the diorganorhodium(III) complexes $[Rh(PNP)(CH_3)RI]$, in which the organo moieties are coordinated in a *cis* arrangement, C−C bond formation leading to the reductive elimination of the hydrocarbons $RCH_3$ is possible. This was realized by cleavage of the iodo ligand with $TlBF_4$ in the presence of acetone. Acetone is too weakly coordinating as a ligand to stabilize the resulting five-coordinate diorganyl rhodium(III) complex. However, when the reaction is carried out in the presence of the more strongly coordinating $CH_3CN$, the stable six-coordinate acetonitrile complex $[Rh(PNP)(CH_3)(C_6H_5)(CH_3CN)]BF_4$ is formed, confirming the dissociative mechanism of the reductive elimination.

The smooth oxidative addition reactions of the model compounds [Rh(PNP)R], and the stability as well as the reactivity of the Rh-C σ-bond in the rhodium-PNP complexes suggests that rhodium(I) has the potential to catalyze the hydroamination of olefins according to the proposed catalytic reaction mechanism.[4]

## Experimental Section

All reactions were carried out under dry argon. Acetone, [D$_6$]acetone, $CD_2Cl_2$, and $CDCl_3$ were refluxed over 4-Å molecular sieves and purged of oxygen by bubbling argon. THF and diethyl ether were refluxed over Na/benzophenone. Acetonitrile, DMSO, and methyl iodide were dried over 4-Å molecular sieves and distilled prior to use.

Infrared spectra were recorded from KBr pellets on a Perkin-Elmer FT-IR 16 spectrometer. − The $^1$H-, $^{13}$C{$^1$H}-, and $^{31}$P{$^1$H}-NMR spectra were recorded at 300, 75, and 121 MHz, respectively, on a Varian Gemini 300 NMR spectrometer. The $^1$H- and $^{13}$C-NMR shifts were referenced to the solvent signals, while the $^{31}$P-NMR shifts were referenced to external 85% $H_3PO_4$. − A Chrompack CP 9000 gas chromatograph was used for the identification of liquid organic compounds. − EI mass spectra were recorded on an AMD 402 spectrometer (AMD Intectra) at 70 eV. − C,H,N elemental analyses were carried out on a LECO CHN 932 analyzer, while Rh was determined using a photometric method.[14]

**Synthesis of $[Rh(PNP)RI_2]$ (R = $CH_3$ *trans:* 2a, *cis*: 2a′; $C_6H_5$ 2b):** 237 mg of $I_2$ (0.93 mmol) in 2 mL of THF was added to a solution of 552 mg (0.93 mmol) of **1a** in 4 mL of THF. After a few seconds, a brown, microcrystalline solid precipitated, and the reaction mixture was stirred for 10 min. After a further 30 min (without stirring), the solid was filtered off and washed with THF and diethyl ether. The crude product was recrystallized from refluxing THF. The recrystallized product was washed twice with THF and twice with diethyl ether and dried in vacuo.

**2a (*trans*)/2a′ (*cis*):** Yield: 498 mg (0.59 mmol, 63%); m.p. 295−298°C (dec.). − $C_{32}H_{30}I_2NP_2Rh$ (846.90): calcd. C 45.34, H 4.52, N 1.90, Rh 12.15; found C 45.43, H 4.33, N 1.73, Rh 12.03. − $^{31}$P NMR ($CD_2Cl_2$): δ = 14.3 (d, $J_{P-Rh}$ = 99 Hz, *trans*), 23.3 (d, $J_{P-Rh}$ = 106 Hz, *cis*). − $^1$H NMR ($CD_2Cl_2$): δ = 0.43 (td, $J_{H-P}$ = 6.2 Hz, $J_{H-Rh}$ = 2.2 Hz, 3 H, C$H_3$, *cis*), 1.99 (td, $J_{H-P}$ = 4.8 Hz, $J_{H-Rh}$ = 2.2 Hz, 3 H, C$H_3$, *trans*), 4.49 (d ps. t, $J_{Ha-Hb}$ = 17.3 Hz, $N_{H-P}$ = 4.4 Hz, 2 H, C$H_a$, *cis*), 4.80 (d ps. t, $J_{Ha-Hb}$ = 17.3 Hz, $N_{H-P}$ = 5.6 Hz, 2 H, C$H_b$, *cis*), 4.84 (vt, $N_{H-P}$ = 4.6 Hz, 4 H, C$H_a$, *trans*), 7.36−8.20 (m, PPh, py, *trans*/*cis*). − $^{13}$C NMR ($CD_2Cl_2$): δ = −18.4 (dt, $J_{C-P}$ = 8.9 Hz, $J_{C-Rh}$ = 16.1 Hz, *C*$H_3$, *trans*), 8.7 (dt, $J_{C-P}$ = 4.0 Hz, $J_{C-Rh}$ = 20.2 Hz, *C*$H_3$, *cis*), 44.7 (ps. t, *N* = 13.0 Hz, *C*$H_2$, *trans*), 46.7 (ps. t, *N* = 15.5 Hz, *C*$H_2$, *cis*), 121.3 (ps. t, *N* = 5.0 Hz, $C_{3,5\text{-py}}$), 121.5 (ps. t, *N* = 5.0 Hz, $C_{3,5\text{-py}}$), 127.9 (ps. t, *N* = 5.6 Hz, $PC_{meta}$, *trans*) 127.9 (ps. t, *N* = 5.0 Hz, $PC_{meta}$, *cis*), 128.3 (ps. t, *N* = 4.6 Hz, $PC_{meta}$, cis), 130.0 (s,

$PC_{para}$, *trans*), 130.2 (s, $PC_{para}$, cis), 130.5 (s, $PC_{para}$, cis), 132.3 (ps. t, $N$ = 4.7 Hz, $PC_{ortho}$, cis), 132.9 (ps. t, $N$ = 5.0 Hz, $PC_{ortho}$, *trans*), 133.9 (ps. t, $N$ = 5.0 Hz, $PC_{ortho}$, cis), 138.2 (s, $C_{4\text{-py}}$, *cis*), 138.5 (s, $C_{4\text{-py}}$, *trans*), 159.3 (ps. t, $N$ < 3 Hz, $C_{2,6\text{-py}}$, *cis*), 162.1 (ps. t, $N$ < 3 Hz, $C_{2,6\text{-py}}$, *trans*). − EI-MS: *m/z* (%): 832 (0.1) $[M - CH_3]^+$, 719 (1.2) $[M - I]^+$, 705 (100) $[M - CH_3 - I]^+$, 578 (21) $[M - CH_3 - I - I]^+$, 142 (16) $[CH_3I]^+$.

The synthesis of **2b** was carried out in the same manner as described for **2a/a′**, starting from 572 mg (0.87 mmol) of **1b** in 4 mL of THF and 222 mg of $I_2$ dissolved in 2 mL of THF. Yield: 565 mg (0.62 mmol, 71%); m.p. 293°C (dec.). − $C_{37}H_{32}I_2NP_2Rh$ (909.33): calcd. C 48.87, H 3.55, N 1.54, Rh 11.32; found C 49.05, H 3.95, N 1.31, Rh 11.42. − $^{31}$P NMR ($CD_2Cl_2$): δ = 18.8 (d, $J_{P-Rh}$ = 105 Hz). − $^1$H NMR ($CD_2Cl_2$): δ = 4.90 (ps. t, $N_{H-P}$ = 4.7 Hz, 4 H, C$H_2$), 6.88 (m, 3 H, Ph), 7.26−7.38 (m, 20 H, PPh), 7.60 (d, $J_{H-H}$ = 7.7 Hz, 2 H, 3,5-py), 7.82 (t, $J_{H-H}$ = 7.7 Hz, 1 H, 4-py), 7.96 (m, 2 H, Ph). − $^{13}$C NMR ($CD_2Cl_2$): δ = 48.1 (ps. t, $N$ = 15.7 Hz, *C*$H_2$), 121.5 (ps. t, $N$ = 5.3 Hz, $C_{3,5\text{-py}}$), 122.7 (s, Ph), 125.9 (s, Ph), 127.7 (ps. t, $N$ = 5.0 Hz, $PC_{meta}$), 130.3 (s, $PC_{para}$), 134.3 (ps. t, $N$ = 4.7 Hz, $PC_{ortho}$), 135.9 (ps. t, $N$ = 24.5 Hz, $PC_{ipso}$), 138.8 (s, $C_{4\text{-py}}$), 147.2 (ps. t, $N$ = 4.3 Hz, Ph), 160.4 (ps. t, $N$ < 3 Hz, $C_{2,6\text{-py}}$). − EI-MS: *m/z* (%): 832 (0.4) $[M - C_6H_5]^+$, 781 (12.5) $[M - I]^+$, 705 (100) $[M - I - C_6H_5]^+$, 655 (1.4) $[M - I - I]^+$, 578 (27) $[M - I - I - C_6H_5]^+$.

**Synthesis of [Rh(PNP)(CH$_3$)RI]** (R = $CH_3$ **3a**, $C_6H_5$ **3b**): To a solution of 571 mg (0.96 mmol) of **1a** in 6 mL of THF was added 60 µl of $CH_3I$ (Rh/$CH_3I$ = 1:1). After a few seconds, a pale-yellow microcrystalline solid precipitated and the reaction mixture was stirred for 10 min. After a further 30 min (without stirring), the solid was filtered off and washed with THF and diethyl ether. The crude product was recrystallized by extraction with refluxing THF. The recrystallized product was washed twice with THF, twice with diethyl ether, and dried in vacuo.

**3a**: Yield: 390 mg (0.53 mmol, 55%); m.p. 214−220°C (dec.). − $C_{33}H_{33}INP_2Rh$ (735.39): calcd. C 53.90, H 4.52, N 1.90, Rh 13.99; found C 53.62, H 4.46, N 1.79, Rh 14.36. − $^{31}$P NMR ($CD_2Cl_2$): δ = 26.5 (d, $J_{P-Rh}$ = 120 Hz). − $^1$H NMR ($CD_2Cl_2$): δ = −0.35 (td, $J_{H-P}$ = 6.4 Hz, $J_{H-Rh}$ = 2.2 Hz, 3 H, C$H_3$), 1.02 (td, $J_{H-P}$ = 5.2 Hz, $J_{H-Rh}$ = 2.1 Hz, 3 H, C$H_3$), 4.31 (d ps. t, $J_{Ha-Hb}$ = 16.6 Hz, $N_{H-P}$ = 4.2 Hz, 2 H, C$H_a$), 4.66 (d ps. t, $J_{Ha-Hb}$ = 16.6 Hz, $N_{H-P}$ = 4.9 Hz, 2 H, C$H_b$), 7.32−7.41 (m, 12 H, PPh), 7.50 (d, $J_{H-H}$ = 7.6 Hz, 2 H, 3,5-py), 7.73 (t, $J_{H-H}$ = 7.6 Hz, 1 H, 4-py), 7.79 (m, 8 H, PPh). − $^{13}$C NMR ($CD_2Cl_2$): δ = −14.5 (dt, $J_{C-P}$ = 7.1 Hz, $J_{C-Rh}$ = 22.4 Hz, *C*$H_3$), 6.9 (dt, $J_{C-P}$ = 6.3 Hz, $J_{C-Rh}$ = 26.0 Hz, *C*$H_3$), 44.9 (ps. t, $N$ = 13.6 Hz, *C*$H_2$), 120.8 (ps. t, $N$ = 5.0 Hz, $C_{3,5\text{-py}}$), 127.9 (ps. t, $N$ = 5.0 Hz, $PC_{meta}$), 128.2 (ps. t, $N$ = 4.3 Hz, $PC_{meta}$), 129.4 (s, $PC_{para}$), 130.1 (s, $PC_{para}$), 131.8 (ps. t, $N$ = 4.8 Hz, $PC_{ortho}$), 134.3 (ps. t, $N$ = 5.8 Hz, $PC_{ortho}$), 137.4 (s, $C_{4\text{-py}}$), 159.3 (ps. t, $N$ < 3 Hz, $C_{2,6\text{-py}}$). − EI-MS: *m/z* (%): 719 (2) $[M - CH_3]^+$, 705 (100) $[M - CH_3 - CH_3]^+$, 578 (15) $[M - CH_3 - CH_3 - I]^+$.

**3b**: The complex was obtained in the same manner as described for **3a**, starting from 692 mg (1.05 mmol) of **1b** and 66 µl of $CH_3I$ in 7 mL of THF. − Yield: 528 mg (0.66 mmol, 63%); m.p. 186−195°C (dec.). − $C_{38}H_{35}INP_2Rh$ (797.46): calcd. C 57.23, H 4.42, N 1.76, Rh 12.90; found C 56.75, H 4.60, N 1.56, Rh 12.46. − $^{31}$P NMR ($CD_2Cl_2$): δ = 30.5 (d, $J_{P-Rh}$ = 119 Hz). − $^1$H NMR ($CD_2Cl_2$): δ = 0.35 (td, $J_{H-P}$ = 6.4 Hz, $J_{H-Rh}$ = 2.2 Hz, 3 H, C$H_3$), 4.34 (d ps. t, $J_{Ha-Hb}$ = 16.9 Hz, $N_{H-P}$ = 4.3 Hz, 2 H, C$H_a$), 4.80 (d ps. t, $J_{Ha-Hb}$ = 16.6 Hz, $N_{H-P}$ = 4.8 Hz, 2 H, C$H_b$), 6.90 (m, 3 H, Ph), 7.11−7.38 (m, 20 H, PPh), 7.56 (d, $J_{H-H}$ = 7.7 Hz, 2 H, 3,5-py), 7.68 (m, 2 H, Ph). 7.83 (t, $J_{H-H}$ = 7.7 Hz, 1 H, 4-py). − $^{13}$C NMR ($CD_2Cl_2$): δ = 8.8 (dt, $J_{C-P}$ = 5.5 Hz, $J_{C-Rh}$ = 26.7 Hz, *C*$H_3$), 46.3 (ps. t, $N$ = 14.1 Hz, *C*$H_2$), 121.1 (ps. t, $N$ = 5.1 Hz, $C_{3,5\text{-py}}$), 121.5 (s, Ph), 125.9 (s, Ph), 127.5 (ps. t, $N$ = 5.0 Hz, $PC_{meta}$), 128.2 (ps. t, $N$ = 4.7 Hz, $PC_{meta}$), 129.9 (s, $PC_{para}$), 130.0 (s, $PC_{para}$), 133.1 (ps. t, $N$ = 5.1 Hz, $PC_{ortho}$), 134.2 (ps. t, $N$ = 5.6 Hz, $PC_{ortho}$), 138.0 (s, $C_{4\text{-py}}$), 142.3 (ps. t, $N$ = 4.0 Hz, Ph), 159.7 (ps. t, $N$ < 3 Hz, $C_{2,6\text{-py}}$). − EI-MS: *m/z* (%): 781 (0.1) $[M - CH_3]^+$, 719 (0.8) $[M - C_6H_5]^+$, 705 (100) $[M - CH_3 - C_6H_5]^+$, 578 (17) $[M - CH_3 - C_6H_5 - I]^+$, 91 (57) $[C_7H_8 - H]^+$.

**Reactivity of 3a and 3b Toward TlBF$_4$: (a)** A mixture of 20 mg (0.027 mmol) of **3a** and 8 mg (0.027 mmol) of $TlBF_4$ in 0.7 mL of [$D_6$]acetone was shaken in a sealed NMR tube over 2 days. While TlI precipitated the solution changed colour to dark-red. In the $^1$H-NMR spectrum a singlet is found at δ = 0.82 for ethane, whereas the signals of **3a** completely disappeared.

78 mg (0.27 mmol) of $TlBF_4$ was added to a solution of 215 mg (0.27 mmol) of **3b** in 5 mL of acetone. After stirring overnight, a yellow precipitate of TlI was filtered off. Toluene was detected in the dark-red filtrate by means of gas chromatography. Upon addition of 0.5 mL of DMSO, the solution became orange-red in colour. The DMSO−rhodium(I) complex [Rh(PNP)(DMSO)]$BF_4$ (**4**) was detected by $^{31}$P-NMR spectroscopy (in acetone/external $C_6D_6$: δ = 40.2, $J_{P-Rh}$ = 148 Hz). This was consistent with an authentic sample, which was prepared from [Rh(PNP)($C_2H_4$)]$BF_4$ and DMSO.[3b]

**(b) In the Presence of CH$_3$CN:** 322 mg (0.4 mmol) of **3b** was suspended in a mixture of 7 mL of THF and 1 mL of acetonitrile. To this was added 120 mg of $TlBF_4$ and the mixture was stirred overnight. A yellow precipitate of TlI was deposited, which was filtered off. Diethyl ether was added dropwise to the pale-yellow filtrate, resulting in the precipitation of a white, crystalline solid. This was filtered off, washed with diethyl ether, and dried in vacuo. The solid was characterized as [Rh(PNP)($CH_3$)($C_6H_5$)($CH_3$CN)]$BF_4$ (**5**): Yield: 271 mg (0.34 mmol, 85%); m.p. 146°C (dec.). − $C_{40}H_{38}BF_4N_2P_2Rh$ (798.41): calcd. C 60.17, H 4.80, N 3.51, Rh 12.89; found C 60.30, H 5.28, N 3.75, Rh 12.57. − $^{31}$P NMR ($CDCl_3$): δ = 32.7 (d, $J_{P-Rh}$ = 117 Hz). − $^1$H NMR ($CDCl_3$): δ = 0.09 (td, $J_{H-P}$ = 6.6 Hz, $J_{H-Rh}$ = 1.5 Hz, 3 H, C$H_3$), 1.45 (s, 3 H, NC$H_3$), 4.30 (d ps. t, $J_{Ha-Hb}$ = 17.5 Hz, $N_{H-P}$ = 4.3 Hz, 2 H, C$H_a$), 4.47 (d ps. t, $J_{Ha-Hb}$ = 17.5 Hz, $N_{H-P}$ = 4.2 Hz, 2 H, C$H_b$), 6.95 (m, 3 H, Ph), 7.07−7.40 (m, 22 H, PPh, Ph), 7.75 (d, $J_{H-H}$ = 7.7 Hz, 2 H, 3,5-py), 7.99 (t, $J_{H-H}$ = 7.7 Hz, 1 H, 4-py). − $^{13}$C NMR ($CDCl_3$): δ = 2.03 (s, N*C*$H_3$), 2.03 (m, overlapped with the N*C*$H_3$ signal, *C*$H_3$), 44.7 (ps. t, $N$ = 13.7 Hz, *C*$H_2$), 120.4 (s, Ph), 122.5 (ps. t, $N$ = 5.6 Hz, $C_{3,5\text{-py}}$), 127.2 (s, Ph), 128.5 (br, *C*N), 128.7 (br, $PC_{meta}$), 130.7 (s, $PC_{para}$), 130.8 (s, $PC_{para}$), 131.7 (ps. t, $N$ = 18.3 Hz, $PC_{ipso}$), 132.7 (ps. t, $N$ = 5.7 Hz, $PC_{ortho}$), 132.9 (ps. t, $N$ = 5.6 Hz, $PC_{ortho}$), 138.1 (ps. t, $N$ < 4.0 Hz, Ph), 139.6 (s, $C_{4\text{-py}}$), 159.1 (ps. t, $N$ < 3 Hz, $C_{2,6\text{-py}}$). − IR (KBr): $\tilde{\nu}$ = 2281, 2376 $cm^{-1}$ ($CH_3CN$); 1574, 1606 (py); 1062 ($BF_4$).

**Crystal Structure Determination of Compound 5:** *Crystal Data:* $C_{40}H_{38}BF_4N_2P_2Rh \cdot (C_4H_{10}O)_{0.8}$, formula weight 857.79 g $mol^{-1}$, monoclinic, $P2_1/n$ (No. 14), $a$ = 12.6065(6), $b$ = 24.5689(10), $c$ = 13.5059(9) Å, β = 102.356(6)°, $V$ = 4086.3(4) Å$^3$, $Z$ = 4, $d_{calc}$ = 1.394 g $cm^{-3}$, $F$(000) = 1767. − *Data Collection:* STOE-IPDS,[14] Mo-$K_\alpha$ radiation (graphite monochromator, λ = 0.71073 Å), crystal size 0.34 × 0.30 × 0.26 $mm^3$, $T$ = 193(2) K, scan range 2.0 < θ < 25.7°; intensities were measured for 31092 reflections with 7411 unique reflections, of which 5469 were considered observed [$I \geq 2\sigma(I)$]. The reflections were corrected for Lorentz and polarization effects; μ = 0.55 $mm^{-1}$, no absorption correction. − *Structural Analysis and Refinement:* Preliminary positions of heavy atoms

were found by direct methods,[16] while positions of the other non-hydrogen atoms were determined from subsequent difference Fourier synthesis coupled with initial isotropic least-squares refinement.[17] An additional diethyl ether solvent molecule was located in the asymmetric unit and refined with 80% partial occupancy. With the exception of those of the solvent molecule, all hydrogen atoms were found in a difference Fourier map and refined with individual isotropic temperature parameters. Refinement: Full-matrix least-squares on $F^2$; 7070 reflections; 649 refined parameters; final $R_1 = 0.0333$, $wR_2 = 0.0806$, goodness-of-fit on $F^2 = 1.040$.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre (CCDC-100736). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) + 44-1223/336033; E-mail: deposit@ccdc.cam.ac.uk].

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