Rhodium(I) Complexes with $OPPy_2Ph$ and $OPPy_3$ (Py = 2-Pyridyl), and Their Behavior in Hydrogenation Reactions

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Dedicated to Professor Angel Alberola on the occasion of his 70th birthday

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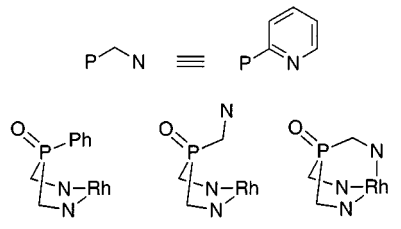
The reaction of $[Rh_2(\mu\text{-}Cl)_2(COD)_2]$ (COD = 1,5-cyclooctadiene) or $[Rh_2(\mu\text{-}Cl)_2(TFB)_2]$ (TFB = tetrafluorobenzobicyclo[2.2.2]octatriene) with the N-donor chelating ligand $OPPy_2Ph$ (Py = 2-pyridyl) in the presence of $TlBF_4$ affords cationic complexes $[Rh(diene)(OPPy_2Ph)](BF_4)$ (**1**, diene: COD; **2**, diene: TFB). Compounds **1** or **2** react with CO to give $[Rh(CO)_2(OPPy_2Ph)](BF_4)$ (**4**), which is also obtained by treatment of $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ with $OPPy_2Ph$ and $TlBF_4$. In a similar way, the complexes $[Rh(diene)(OPPy_3)](BF_4)$ (**5**, diene: COD; **6**, diene: TFB) are obtained when using $OPPy_3$; they react with CO to give $[Rh_2(\mu\text{-}CO)_3(OPPy_3)_2](BF_4)_2$ (**9**). The behavior of the complexes in solution is reported. The complexes with $OPPy_3$, **5** and **6**, show equivalence of the three Py groups in their NMR spectra. Complex **5** is square-planar in the solid state, and in solution, and the uncoordinated and coordinated Py groups undergo fast exchange in solution. Complex **6** is pentacoordinated in the solid state and in solution, and its Py groups exchange their coordination sites in a fast topomerization process. The single-crystal X-ray structures of **5** and **6** have been solved. The behavior of **1** and **5** as catalysts in hydrogenation reactions of cyclohexene, acetone, and cyclohexanone is also reported.

Introduction

Recent years have seen a renascence of interest in the study of multidentate nitrogen-donor ligands and their use in homogeneous catalysis.[1] N-donor ligands have some advantages over P-donors: mainly their higher stability towards oxidation, allowing a longer life for the catalysts. Because of this, cationic complexes of rhodium(I) with diolefins and N-donor ligands have been studied in catalyzed reduction processes of unsaturated organic compounds,[2] and the scope of these reactions has successfully been extended to the synthesis of chiral products, with fairly good enantiomeric excess.[1,3] Amongst the N-donor ligands, the most widely used are anionic substituted pyrazolylborates, because they can stabilize both rhodium(I) and rhodium(III) complexes, and it is possible to modulate the steric hindrance around the metal by properly choosing the substituents on the Pz rings.[4] The most important electronic variation that can be introduced onto ligands is a change in overall charge, and neutral tris-chelate ligands have indeed been tested in parallel with anionic pyrazolates $[HB(^RPz)_3]^-$. Good results have been obtained with substituted 1,4,7-triazacyclononane,[5] while other neutral *fac*-terdentate ligands, such as trispyrazolylmethane or trispyridylmethane have been less intensely studied in comparison.[6] Terdentate planar ligands such as *terpy* cannot be compared with the previous ones because of their very different geometrical restrictions and electronic properties.[7]

We have shown previously that, in Pd chemistry, $OPPy_2Ph$ (Py = 2-pyridyl) coordinates through the N atoms, in such a way that the two pyridyl rings are disposed obliquely respective to the coordination plane of the metal, giving rise to a six-membered ring in a "boat" conformation, with the Ph group lying above the metal.[8] $OPPy_3$ behaves similarly, but the third Py group can pentacoordinate the metal (as happens in some fluxional process intermediates), enabling $OPPy_3$ to act either as a bidentate or as a tridentate ligand. Pentacoordination might be more accessible for Rh than for in Pd. We report here the synthesis of complexes of rhodium(I) with these ligands and diolefins (COD = 1,5 cyclooctadiene and TFB = tetrafluorobenzobicyclo[2.2.2]octatriene) or carbon monoxide, as well as the behavior of the cationic diolefin complexes in catalytic hydrogenation of ketones and olefins.



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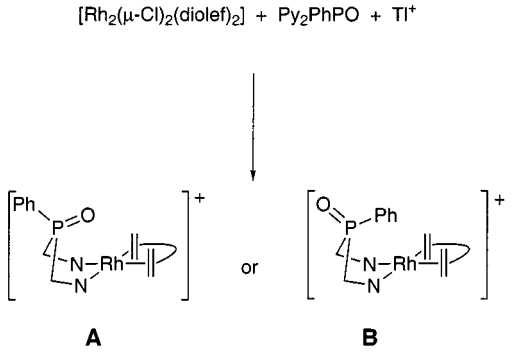
Results and Discussion

a) Complexes with $OPPy_2Ph$

The complexes $[Rh(COD)(OPPy_2Ph)](BF_4)$ (**1**) and $[Rh(TFB)(OPPy_2Ph)](BF_4)$ (**2**) were prepared as yellow, crystalline solids by treatment of $OPPy_2Ph$ with the corresponding $[Rh_2(\mu\text{-}Cl)_2(diene)_2]$ in the presence of $TlBF_4$. Their IR spectra in the solid state show the expected ν(P=O) band at wavelengths similar to those of the free ligands, which rules out coordination of the oxygen in the complexes .

Compounds **1** and **2** can adopt two conformations: with either the oxygen (**A**) or the aromatic free ring (**B**) towards the metal. In any case, the coordination plane of the metal is not a symmetry plane (Scheme 1). Their ^1H NMR spectra in $CDCl_3$ show signals for only one conformer in each case: six nonequivalent nuclei for the 1,5-COD ligand in **1**; and two aliphatic and two olefinic signals for **2**. In order to determine which conformer is present in solution, a NOESY spectrum of **1** was recorded. As shown in Figure 1, both olefinic protons give NOEs with the pyridine H-6, while one of them gives a clear NOE cross peak with the phenyl group. This supports conformer **B**, with the phenyl ring towards the metal; in line with the situation found for Pd[8] and analogous tris(pyrazolyl)borate complexes of rhodium(I).[4k−4m]



Scheme 1. Diolefin: COD (**1**); TFB (**2**)

In deuterated acetone, however, complexes **1** and **2** are fluxional and exhibit exchange between the upper and lower halves of the COD or TFB, respectively. Both feature olefinic protons in coalescence at room temperature, while at −60 °C these have split into two well defined signals. For **2**, this exchange is also observable in the ^{19}F NMR spectrum, which changes from an ABCD spin system pattern at −40 °C to an AA′BB′ one at room temperature (Figure 2). The ^{31}P NMR spectra are not affected by the exchange, showing only one doublet for each compound in all the temperature range studied. This suggests that the fluxionality observed in the ^1H and ^{19}F spectra is not associated with any conformational change in the coordinated ligand $OPPy_2Ph$. On the contrary, the solvent-dependence of the process strongly points to a pentacoordinated intermediate in which either the Py groups, the double bonds, or both, exchange their coordination sites. These fluxional processes are common in $[Rh(diene)(L-L)]^+$ complexes, and it has been shown that the exchange rate in noncoordinating solvents is increased by the presence of traces of Cl^- anions, or by adventitious acetone.[7,9,10]

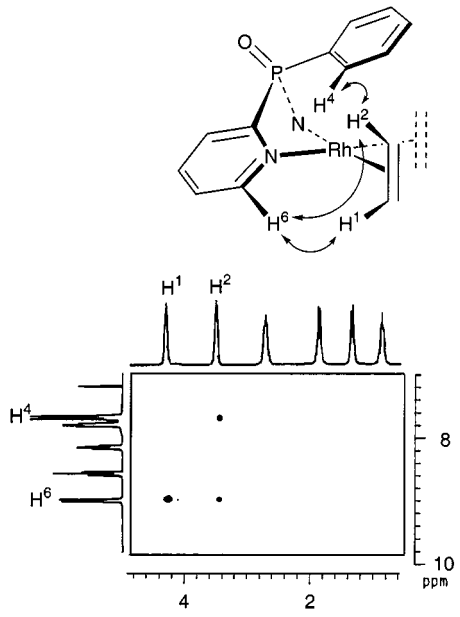


Figure 1. NOESY spectrum of **1** in $CDCl_3$ at 273 K

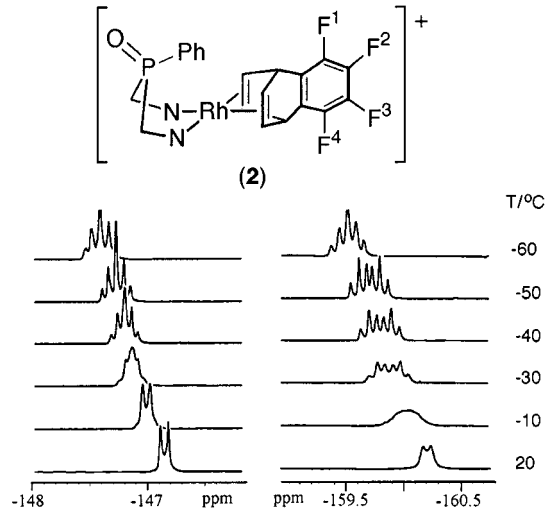
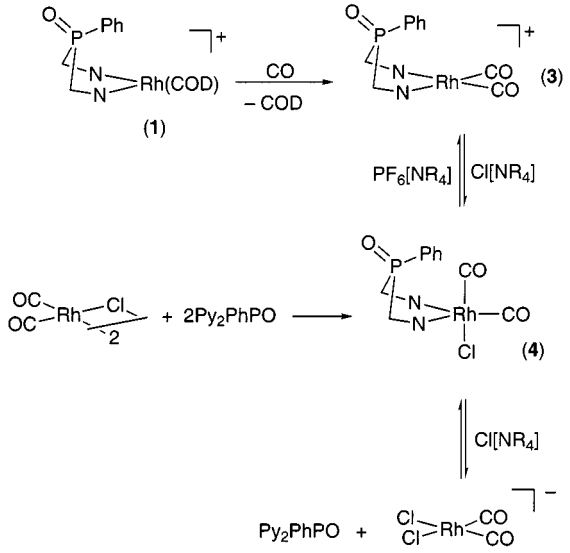


Figure 2. ^{19}F NMR spectra of **2** in $[D_6]$acetone at different temperatures. F^1 and F^4 (ca. −147) become equivalent at room temperature, due to diolefin rotation. The same is observed for F^2 and F^3 (ca. −160)

By bubbling CO through a dichloromethane solution of **1**, it is easy to obtain a dicarbonyl complex $[Rh(CO)_2(OPPy_2Ph)]BF_4$ (**3a**), which shows ν(CO) at 2104 and 2047 cm^{-1} [(Equation (1)].

$$[Rh(COD)(OPPy_2Ph)] + CO \rightarrow [Rh(CO)_2(OPPy_2Ph)]BF_4 + COD \quad (1)$$

Attempts at isolating neutral carbonyl complexes with $OPPy_2Ph$ were unsuccessful. The reaction of $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ with $OPPy_2Ph$ (1:1) was monitored in deuterated chloroform by NMR techniques. The ^{31}P and ^1H



Scheme 2

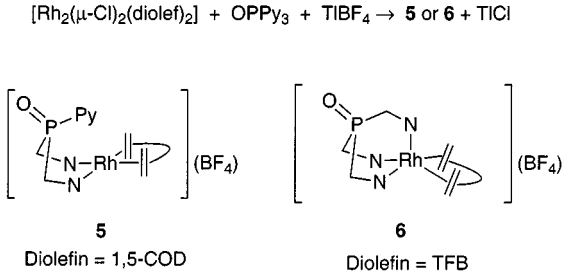
NMR spectra at room temperature show a mixture of the cation in complex **3** (9%, presumably with Cl^- as the counter-anion), the desired chlorocarbonyl compound $[RhCl(CO)_2(OPPy_2Ph)]$ **4** (70%) and free ligand $OPPy_2Ph$ (21%) (Scheme 2). In agreement with the NMR results, the Infrared spectrum of a comparable solution in CH_2Cl_2 at room temperature shows six carbonyl bands, corresponding to a mixture of the three *cis* dicarbonyl complexes in equilibrium: two from the cationic compound **3**, two from the neutral chlorodicarbonyl complex **4** (at 2035 and 2095 cm^{-1}), and two corresponding to the anion $[Rh(Cl)_2(CO)_2]^-$ (at 2071 and 1995 cm^{-1}).[11] At −60 °C, there is a small change in the ratio of products, but no new signals appear. The addition of an excess of $[Et_3BzN]Cl$ to the solution shifts the equilibrium completely, displacing the $OPPy_2Ph$ ligand, and only $[Rh(Cl)_2(CO)_2]^-$ is observed in the IR spectrum. In contrast, the addition of a large amount of $[Bu_4N][PF_6]$ shifts the equilibrium toward **3**, and the other two complexes disappear.

The donor ability of the $OPPy_2Ph$-N,N ligand can be evaluated from the stretching bands of the carbonyl groups in the IR spectra of the complexes. For all of these, the ν(CO) values are shifted to higher frequency, not only relative to the analogous complexes with bipyridine, but also relative to the complexes with monodentate pyridine or other nonplanar chelating ligands like bispyrazolylmethane or bidentate imidazolyl ligands like $(mim)_2CH_2$ (mim = *N*-methylimidazol-2-yl).[12] Since the geometry of the ligand does not permit a good π interaction with the metal, this has to be attributed more to a poorer donor ability in the $OPPy_2Ph$-N,N ligand than to a higher π acceptor character. This is reinforced by the electron-withdrawing ability of the P=O group, compared to geometrically similar ligands such $(Py)_2S$.[12c] The overall effect is that $OPPy_2Ph$-N,N behaves as a rather labile N-donor ligand, which can easily be removed from the rhodium (I) complexes.

b) Complexes with $OPPy_3$

Diolefin Complexes

The diolefin complexes $[Rh(COD)(OPPy_3)](BF_4)$ (**5**) and $[Rh(TFB)(OPPy_3)](BF_4)$ (**6**) were prepared as yellow, crystalline solids by treatment of $OPPy_3$ with the corresponding $[Rh_2(\mu\text{-}Cl)_2(diene)_2]$ in the presence of $TlBF_4$ (Scheme 3). In these compounds, the $OPPy_3$ ligand can act either in bidentate or in tridentate fashion, giving tetracoordinated or pentacoordinated complexes, respectively. For ligands containing pyridyl groups, the values of $\nu(CN)_{Py}$ indicate whether they are coordinated or not:[9,13] the uncoordinated Py groups exhibit this band at 1574 cm^{-1}, but it moves to higher frequency when coordinated. The IR spectrum of **5** in the solid state shows two bands at 1587 and 1572 cm^{-1}, one of coordinated and one of free Py; thus the compound seems to be square-planar with only two coordinated Py groups. In contrast, the IR spectra of **6** in the solid state shows just one $\nu(CN)_{Py}$ absorption at 1586 cm^{-1}; hence the three Py groups are coordinated and the compound is pentacoordinated in the solid state. In agreement with this interpretation, the ν(P=O) bands in **5** (1206 cm^{-1}) appear at almost the same value as in the free ligand, while the coordination of the third Py group shifts this stretching band to 1230 cm^{-1} in **6**. This shift has previously been observed in other complexes in which the $OPPy_3$ ligand coordinates in a tridentate mode,[14] and is related to the decrease in the CPC angle around the phosphorus, which is accompanied by an increase in the P=O strength, as also observed, for instance, in strained cyclic ketones.[15−17]



Scheme 3. Diolefin: COD (**5**); TFB (**6**)

In order to evaluate these structural hypotheses and other structural features, the structures of **5** and **6** were deter-

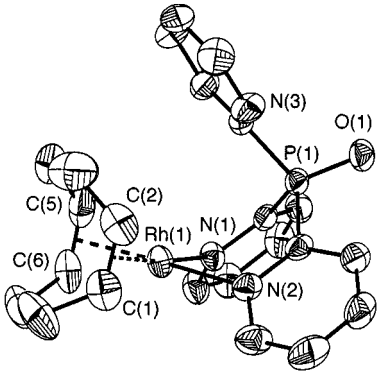


Figure 3. ORTEP plot of $[Rh(COD)(OPPy_3)](BF_4)$·acetone (**5**·Me_2CO)

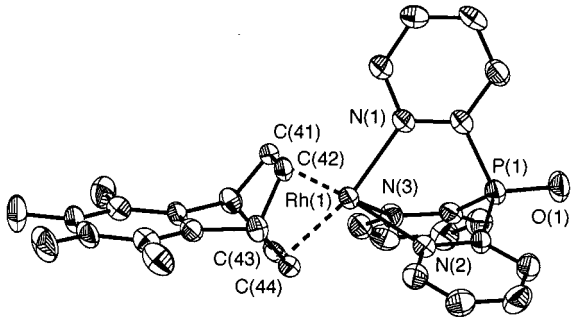


Figure 4. ORTEP plot of $[Rh(TFB)(OPPy_3)](BF_4)\cdot C_{2.5}O$ (**6**·$C_{2.5}O$)

Table 1. Selected bond lengths [pm] and angles [°] in $[Rh(COD)(OPPy_3)](BF4)\cdot Me_2CO$ (**5**·Me_2CO) and $[Rh(TFB)(OPPy_3)](BF_4)\cdot C_{2.5}O$ (**6**·$C_{2.5}O$)

5·Me_2CO		**6**·$C_{2.5}O$	
Bond lengths [Å]			
Rh(1)−N(1)	2.125(4)	Rh(1)−N(1)	2.126(6)
Rh(1)−N(2)	2.112(5)	Rh(1)−N(2)	2.279(5)
Rh(1)−C(1)	2.158(6)	Rh(1)−N(3)	2.269(5)
Rh(1)−C(2)	2.143(6)	Rh(1)−C(41)	2.061(6)
Rh(1)−C(5)	2.157(7)	Rh(1)−C(42)	2.068(6)
Rh(1)−C(6)	2.138(7)	Rh(1)−C(43)	2.169(7)
C(1)−C(2)	1.391(10)	Rh(1)−C(44)	2.155(7)
C(5)−C(6)	1.359(10)	C(41)−C(42)	1.436(9)
		C(43)−C(44)	1.366(10)
Bond angles [deg]			
N(2)−Rh(1)−N(1)	87.51(18)	C(41)−Rh(1)−N(1)	97.0(2)
N(2)−Rh(1)−C(6)	160.2(3)	C(42)−Rh(1)−N(1)	97.8(2)
N(1)−Rh(1)−C(6)	95.2(2)	N(1)−Rh(1)−C(44)	159.0(2)
N(2)−Rh(1)−C(2)	93.0(3)	N(1)−Rh(1)−C(43)	156.8(2)
N(1)−Rh(1)−C(2)	155.6(3)	C(41)−Rh(1)−N(3)	115.4(2)
N(2)−Rh(1)−C(5)	162.9(3)	C(42)−Rh(1)−N(3)	156.0(2)
N(1)−Rh(1)−C(5)	91.5(2)	N(1)−Rh(1)−N(3)	86.1(2)
N(2)−Rh(1)−C(1)	92.4(2)	C(44)−Rh(1)−N(3)	114.4(2)
N(1)−Rh(1)−C(1)	166.7(3)	C(43)−Rh(1)−N(3)	88.8(2)
		C(41)−Rh(1)−N(2)	154.4(2)
		C(42)−Rh(1)−N(2)	113.7(2)
		N(1)−Rh(1)−N(2)	86.4(2)
		C(44)−Rh(1)−N(2)	89.1(2)
		C(43)−Rh(1)−N(2)	116.3(2)
		N(3)−Rh(1)−N(2)	90.2(2)

mined by X-ray diffraction methods, and their corresponding ORTEP diagrams are shown in Figure 3 and Figure 4, respectively. Selected bond lengths and angles for both structures are listed in Table 1.

Molecular Structure of [Rh(COD)(OPPy$_3$)](BF$_4$)·Acetone (5·Acetone)

The rhodium atom has an essentially square-planar geometry. Its deviation from the plane defined by N1, N2, and the midpoints of the olefinic bonds is 0.038 Å. The neutral ligand is acting as an *N,N*-chelate, as expected, and the six-membered chelate ring shows a boat conformation. The Rh−N bond lengths (2.125 and 2.112 Å) are within the normal range for pyridine ligands bonded to Rh^I. The distance from the third nitrogen atom to the rhodium (3.975 Å) is clearly out of the bonding interaction range (sum of the van der Waals radii: 3.15 Å). The coordinated pyridyl rings are inclined relative to the coordination plane, making angles of 126.3° and 122.8°. The conformer found is the one that places the uncoordinated pyridyl ring above the coordination plane: similar to conformer **B** in Scheme 1. This structure should render the olefinic moieties above and below the coordination plane nonequivalent in the NMR.

Molecular Structure of [Rh(TFB)(OPPy$_3$)](BF$_4$)·xAcetone (6·xAcetone)

Its geometry can be described as distorted trigonal bipyramidal, with one of the nitrogen atoms (N1) and the midpoints of one olefinic bond (M2) in axial positions (angle N1−Rh1−M2 = 167.51°). The equatorial plane is defined by the other two nitrogen atoms (N2 and N3) and M1 (the midpoint between carbon atoms C41 and C42), with the rhodium atom lying 0.039 Å above this plane. From the rhodium, the distance to the axial nitrogen is shorter than those to the equatorial nitrogen atoms (2.126 vs. 2.279 and 2.269 Å), as found in other *tbp* structures.[18] The olefinic bond in the equatorial plane is longer than the one in the axial position, as a consequence of stronger π backbonding in the equatorial position. This effect also explains the shorter distances from rhodium to the carbon atoms in the equatorial double bond than to those in the axial double bond. Other interatomic distances in the TFB ligand are similar to the values obtained in other rhodium-TFB complexes. [19]

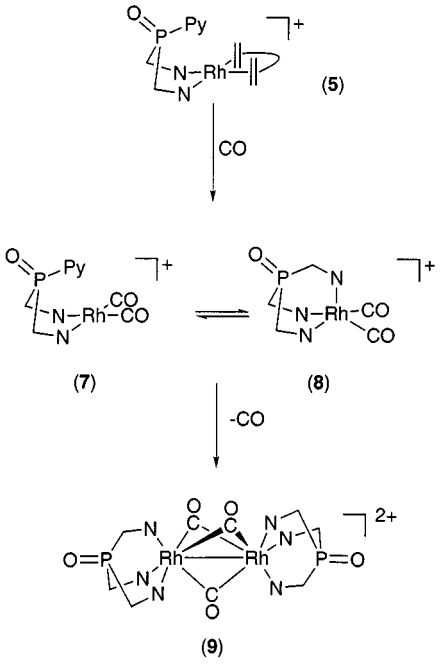
The hapticity of the $OPPy_3$ ligand (κ^2 or κ^3) depends on the diene coordinated to the rhodium. This dependence has been reported and studied for poly(pyrazolyl)borato complexes.[4i−4n] It has been proposed that dienes with a larger bite angle, such as COD, favor a κ^2 structure, while dienes with a smaller bite angle favor the κ^3 coordination mode. In complex **6**, the bite angle of the TFB ligand is 69.71°, resulting in a pentacoordinated structure with the three pyridyl rings bonded to the rhodium.

Behavior in Solution of Diolefin Complexes with OPPy$_3$

In spite of this solid state structural difference for **5** and **6**, in solution they behave more similarly. Their ^1H NMR spectra both show only one signal for all the olefinic protons, and the three Py rings are equivalent, while $J^{103}_{Rh-}{}^{31}_{P}$ is maintained even at high temperature (50 °C). The ^{19}F NMR spectrum of **6** corresponds to an AA′BB′ spin system, even at −60 °C. These data reveal the existence of fast intramolecular fluxional processes for both complexes; however, these are not the same in each case. In fact, their IR spectra in Cl_2CH_2 solution and in the solid state are almost identical. Hence, **5** remains square-planar [$\nu(CN)_{Py}$ at 1574 and 1589 cm^{-1}], with the free and the coordinated Py groups exchanging rapidly in solution. On the other hand, **6** remains pentacoordinated in solution [$\nu(CN)_{Py}$ at 1590 and 1586 cm^{-1}], and the observed equivalence of the Py groups and the fluorine nuclei is due to the fast exchange of coordination sites in the pentacoordinated complex.

Carbonyl Complexes

The carbonylation of **5** in dichloromethane gives a mixture of *cis*-dicarbonyls [ν(CO) at 2105 and 2049 cm^{-1}, and



Scheme 4

at 2085 and 2021 cm^{-1}], corresponding to the formation of square-planar (**7**) and pentacoordinated (**8**) complexes (Scheme 4). This process is followed by the precipitation of an insoluble product with only one ν(CO) absorption at 1836 cm^{-1}, elemental analysis of which agrees with the formulation $[Rh_2(\mu\text{-}CO)_3(OPPy_3)_2](BF_4)_2$ (**9**). Analogous products are obtained when using triazacyclononane,[5a] $HCPz_3$,[6b] $MeGaPz_3$,[6c] or $[HBPz_3]^-$ [4k] as ligands. By removing the solvent and washing the resulting oil with n-hexane, it is possible to obtain a mixture of **7**, **8**, and **9a**, but if the oil is then redissolved in tetrahydrofuran and refluxed for 30 min, all the monomeric dicarbonyls are transformed into **9a**.

The carbonylation process was monitored by ^1H and ^{31}P NMR spectroscopy. A solution of **5** was prepared under nitrogen and cooled in an ice bath at 0 °C. After bubbling CO through for 10 min, the solution was placed in the NMR probe, previously thermostated at 0 °C. The spectrum showed that all the starting compound **5** had reacted, giving free cyclooctadiene, only one group of pyridyl signals in the ^1H NMR, and one doublet at 13.2 ($^3J_{Rh\text{-}P}$ = 7.12 Hz) in the ^{31}P NMR. The spectrum did not change on cooling to −60 °C, showing that the exchange between the square-planar and pentacoordinated isomers is very fast. After warming the sample to 0 °C, nitrogen was bubbled through the solution until **9** started to precipitate; the spectra recorded at this point showed a decrease in intensity of the aromatic signals assigned to (**7** + **8**) relative to the signals of the residual 1,5-COD, reflecting the insolubility of **9a**. After the NMR experiment, the solution was left at room temp. for one hour, and a yellow-green solid was formed. The solution was filtered and the solid was characterized as **9a** by its IR spectrum. A GC of the solution showed that 1,5-cyclooctadiene was the only organic product of the reaction.

The reaction of $OPPy_3$ with $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ in dichloromethane proceeds with CO evolution, to give $[Rh_2(\mu\text{-}CO)_3(OPPy_3)_2][RhCl_2(CO)_2]_2$ (**9b**) as a dark red, insoluble compound [ν(CO) = 2066, 1989, and 1834 cm^{-1}]. Attempts at obtaining a neutral chlorocarbonyl complex were unsuccessful.

c) Catalytic Experiments

The hydrogenation of cyclohexene, acetone, and cyclohexanone, using the cationic complexes **1** and **5** as catalysts, was examined. Significant hydrogenation rates were only observed above 50 °C. An almost linear increase of the rate of hydrogenation with pressure was found. Hydrogenation of a 1:1 mixture of cyclohexene and cyclohexanone showed a clear preference for the hydrogenation of cyclohexene. Representative catalytic experiments are summarized in Table 2.

Table 2. Results of the catalysis experiments

Complex	Time[a] [min]	Cyclohexanone	Acetone	Cyclohexene[b]
1[c]	30	4.6	2.1	27 (30)
1[c]	60	18	7.5	55 (57)
1[c]	120	43	18	78 (80)
5[c]	30	12	6.0	47 (40)
5[c]	60	20	10	67 (61)
5[c]	120	48	20	78 (64)
1[d]	30	3.1		30
1[d]	60	13		54
1[d]	120	29		72
5[d]	30	8.5		11
5[d]	60	19		47
5[d]	120	36		56

[a] Reaction conditions: Catalyst 0.014 mmol; Substrate 28 mmol; solvent: 18 mL of a solution of NaOH 0.04 mol dm^{-3} in methanol; $P(H_2)$ 10 bar; T: 80 °C. – [b] The data in parentheses have been obtained using pure methanol as solvent, without base. – [c] The substrate was only cyclohexanone, only acetone or only cyclohexene in each case. – [d] The substrate was a mixture of cyclohexanone (1.4 mmol) and cyclohexene (1.4 mmol).

The behavior of the two catalysts is very similar. The conversion rates obtained with **5** are slightly higher than with **1**, while the selectivity follows the opposite trend. In the light of the very different chemical behavior found for the complexes with $OPPy_3$ and $OPPy_2Ph$, a greater difference had been expected for the catalytic experiments. The similarity in catalytic behavior suggests that probably, thanks to the poor donor ability of the ligands under catalytic conditions (low concentration of complex, large excess of substrates, and high pressure of hydrogen), there is decoordination of the nitrogen ligand to give the active compound, the complexes with $OPPy_3$ and $OPPy_2Ph$ being the resting state for the catalyst. This hypothesis is further supported by the observation that addition of an excess of ligand to the solution (complex: ligand ratio = 1:1) leads to a nearly 50% decrease in catalytic activity.

Conclusion

The $OPPy_3$ and $OPPy_2Ph$ ligands are nitrogen-based ligands containing sp^2-hybridized nitrogen donors. Com-

pared with geometrically analogous anionic pyrazolylborates, both similarities and differences are found. They are very similar in coordination and dynamic behavior. However, 2-pyridylphosphane oxides are weaker ligands than pyrazolylborates. Because of this they are unable to withstand working conditions currently used in catalytic reactions.

Experimental Section

General Remarks: All manipulations were conducted with rigorous exclusion of air. Solvents were dried by known procedures and distilled under nitrogen prior to use. − ^{1}H NMR (300.16 MHz), ^{19}F NMR (282.4 MHz), and ^{31}P NMR (121.4 MHz) spectra were recorded on a Bruker ARX 300 instrument equipped with a VT-100 variable-temperature probe. Chemical shifts are reported from tetramethylsilane (^{1} H), CCl_3F (^{19}F), or H_3PO_4 (85%) (^{31}P), with positive shifts downfield, and at ambient probe temperature unless otherwise stated. NOESY experiments were carried out with a standard program, operating in phase-sensitive mode, with a 5% random variation in the evolution time, to avoid COSY cross-peaks, and with a mixing time equal to T_1 of the olefinic signals as measured by inversion recovery. − Combustion CHN analyses were made on a Perkin−Elmer 2400 CHN microanalyzer. − Infrared spectra were recorded on a Perkin−Elmer 843 (range 4000−200 cm^{-1}) with Nujol mulls between polyethylene sheets, or in dichloromethane solution between NaCl plates. − The catalytic reactions were monitored by GLC on a Hewlett−Packard II 5890, using an HP-FFAP column and with mesitylene as internal standard. The precursors $[Rh_2(\mu\text{-}Cl)_2(1,5\text{-}COD)_2]$,[20] $[Rh_2(\mu\text{-}Cl)_2(TFB)_2]$,[21] $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ and the ligands $OPPy_2Ph$ and $OPPy_3$ were prepared by published methods.[22]

$[Rh(OPPy_2Ph)(COD)]BF_4$ (1): A suspension of $[Rh_2(\mu\text{-}Cl)_2(COD)_2]$ (200 mg, 0.41 mmol) in acetone (20 mL) was treated with $TlBF_4$ (236 mg, 0.81 mmol) and $OPPy_2Ph$ (238 mg, 0.85 mmol). After 30 min stirring at room temperature, the TlCl was filtered off and the yellow solution was concentrated to dryness in vacuum. The yellow residue was recrystallized from dichloromethane-diethyl ether, washed with diethyl ether and vacuum dried. Yield 409 mg (87%). − $C_{24}H_{25}BF_4N_2OPRh$ (578.16): calcd. C 49.86, H 4.36, N 4.82; found C 49.68, H 4.16, N 4.57. − ^{1}H NMR ($CDCl_3$): δ = 8.93 (m, 2 H), 8.56 (m, 2 H), 8.11 (m, 2 H), 7.82 (m, 3 H), 7.63 (m, 4 H), 4.14 (m, 2 H), 3.44 (m, 2 H), 2.64 (m, 2 H), 1.82 (m, 2 H), 1.22 (m, 2 H), 0.85 (m, 2 H). − ^{31}P NMR: δ = 18.7 (d, $^3J_{Rh\text{-}P}$ = 7.56 Hz). − IR (Nujol mull): $\nu(CN)_{Py}$ 1587 cm^{-1}; ν(P=O) 1203 cm^{-1}.

$[Rh(TFB)(OPPy_2Ph)]BF_4$ (2): A suspension of $[Rh_2(\mu\text{-}Cl)_2(TFB)_2]$ (100 mg, 0.14 mmol) in acetone (15 mL) was treated with $TlBF_4$ (80 mg, 0.28 mmol) and $OPPy_2Ph$ (77 mg, 0.28 mmol). After 30 min stirring at room temperature, the TlCl was filtered off and the yellow solution was concentrated to dryness in vacuum. The yellow residue was recrystallized from dichloromethane-diethyl ether, washed with diethyl ether and vacuum dried. Yield 139 mg (73%). − $C_{28}H_{19}BF_8N_2OPRh$ (696.2): calcd. C 48.31, H 2.75, N 4.02; found C 48.71, H 2.90, N 4.03. . − ^{1}H NMR ([D$_6$]acetone): δ = 9.04 (m, 2 H), 8.36 (m, 2 H), 8.14 (m, 2 H), 3.94 (m, 4 H), 1.65 (m, 4 H), 1.83 (m, 4 H). − ^{31}P NMR: δ = 18.6 (d, $^3J_{Rh\text{-}P}$ = 6.8 Hz). − ^{19}F NMR: δ = −147.15 (m, 2 F), −150.1 (4 F, BF_4^-), −160.20 (m, 2 F). − IR (Nujol mull): $\nu(CN)_{Py}$ 1589 cm^{-1}; ν(P=O) 1214 cm^{-1}.

$[Rh(CO)_2(OPPy_2Ph)]BF_4$ (3a): Carbon monoxide was bubbled through a solution of **1** (130 mg 0.225 mmol) in dichloromethane (20 mL) for 2 h. The resulting pale yellow solution was concentrated to 5 mL and diethyl ether was added. The yellow solid formed was filtered off, washed with diethyl ether and vacuum dried. Yield 80 mg (67%). − $C_{18}H_{13}BF_4N_2O_3PRh$ (525.9): calcd. C 41.09, H 2.47, N 5.34; found C 41.22, H 2.53, N 5.22. − ^{31}P NMR: δ = 19.6 (d, $^3J_{Rh\text{-}P}$ = 9.6 Hz). − ^{1}H NMR ($CDCl_3$): δ = 9.23 (m, Py), 8.58 (m), 8.22 (m), 7.82 (m), 7.64 (m, Ph). − IR (Nujol mull): ν(CO) 2092, 2035 cm^{-1}; $\nu(CN)_{Py}$ 1594 cm^{-1}; ν(P=O) 1212 cm^{-1}.

Reaction of $[Rh_2(\mu\text{-}Cl)_2(CO)_2]$ with $OPPy_2Ph$: $Rh_2(\mu\text{-}Cl)_2(CO)_4$ (220 mg, 0.55 mmol) and $OPPy_2Ph$ (320 mg, 1.1 mmol) were dissolved in 20 mL of dichloromethane. The solution was split into three aliquots; one was used as reference, another was used to study by IR the effect of adding $[Et_3BzN]Cl$, and the third was used to study by IR the reactivity with $[Bu_4N][PF_6]$.

$[Rh(CO)_2(OPPy_2Ph)][RhCl_2(CO)_2]$ (3b): $Rh_2(\mu\text{-}Cl)_2(CO)_4$ (110 mg, 0.27 mmol) and $OPPy_2Ph$ (80 mg, 0.27 mmol) were dissolved in 10 mL of dichloromethane. The solution was filtered and 5 mL of ethanol were added. After concentration to 5 mL, **3b** crystallized as yellow plates. Yield 135 mg (73%). − $C_{20}H_{13}Cl_2N_2O_5PRh_2$ (669.00): calcd. C 35.70, H 1.93, N 4.16; found C 35.91, H 2.00, N 4.11. − ^{31}P NMR ([D$_6$]acetone): δ = 19.97 (d, $^3J_{Rh\text{-}P}$ = 7.4 Hz). − ^{1}H NMR ([D$_6$]acetone): δ = 9.49 (m, Py), 8.68 (m), 8.56 (m), 8.01 (m), 7.86 (m, Ph), 7.78 (m), 7.51 (m). − IR: ν(CO) 2098, 2065, 2038, 1991 cm^{-1}; $\nu(CN)_{Py}$ 1590 cm^{-1}; ν(PO) 1213 cm^{-1}.

$[Rh(COD)(OPPy_3)]BF_4$ (5): The procedure was as described for **1**, but $OPPy_3$ (237 mg, 0.85 mmol) was added instead of $OPPy_2Ph$. Yield 790 mg (84%). − $C_{23}H_{24}BF_4N_3OPRh$ (579.2): calcd. C 47.70, H 4.18, N 7.26; found C 47.55, H 4.15, N 7.12. − ^{31}P NMR: δ = 14.7 (d, $^3J_{Rh\text{-}P}$ = 5.56 Hz). − ^{1}H NMR: δ = 9.00 (m, Py), 8.33 (m), 8.13 (m); 3.91, 1.65 and 1.86 (br. signals, COD). − IR (Nujol mull): $\nu(CN)_{Py}$ 1587 and 1572 cm^{-1}, ν(P=O) 1206 cm^{-1}. Single crystals of $5{\cdot}Me_2CO$ suitable for X-ray diffraction were formed by slow diffusion of a solution of the complex in acetone-ethanol (2:1) and *n*-hexane at room temperature.

$[Rh(TFB)(OPPy_3)]BF_4$ (6): The procedure was as described for **2**, but $OPPy_3$ (77 mg, 0.14 mmol) was used instead of $OPPy_2Ph$. Yield 135 mg (70%). − $C_{27}H_{18}BF_8N_3OPRh$ (697.1): calcd. C 46.52, H 2.60, N 6.03, found C 46.58, H 2.73, N 5.98. − ^{31}P NMR ([D$_6$]acetone): δ = 3.0 (d, $^3J_{Rh\text{-}P}$ = 6.8 Hz). − ^{19}F NMR: δ = −147.2 (m, 2 F), −150.3 (4 F, BF_4^-), −160.5 (m, 2 F). − ^{1}H NMR: δ = 9.64 (m, Py), 8.65 (m), 8.43 (m) and 7.96 (m), 6.13 (m, TFB) and 3.94 (m). − IR (Nujol mull): ν_{Py}(CN) 1586 cm^{-1}, νP=O 1230 cm^{-1}. Single crystals of $\mathbf{6}{\cdot}x Me_2CO$ suitable for X-ray diffraction were formed by slow diffusion of a solution of the complex in acetone-ethanol (2:1) into *n*-hexane at room temperature.

$[Rh_2(\mu\text{-}CO)_3(OPPy_3)_2](BF_4)_2$ (9a): Carbon monoxide was bubbled through a solution of **2** (150 mg 0.235 mmol) in dichloromethane (20 mL) for 2 h. The solvent was evaporated and the residue was dissolved in THF (10 mL) and refluxed for 30 min. The insoluble green solid formed was filtered off, washed with diethyl ether and vacuum dried. Yield 72 mg (60%). − $C_{33}H_{24}B_2F_8N_6O_5P_2Rh_2$ (1026.0): calcd. C 38.63, H 2.34, N 8.22; found C 38.70, H 2.41, N 8.17. − IR (Nujol mull): ν(CO) 1836 cm^{-1}; $\nu(CN)_{Py}$ 1593 cm^{-1}; ν(PO) 1236 cm^{-1}.

$[Rh_2(\mu\text{-}CO)_3(OPPy_3)_2][RhCl_2(CO)_2]_2$ (9b): $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ (100 mg, 0.25 mmol) and Py_3PO (155 mg, 0.55 mmol) were dissolved in 10 mL of dichloromethane; the solution was stirred until the CO evolution ceased (two hours). The insoluble dark red solid

Table 3. Crystal data and structure refinement for **5**·Me_2CO and **6**·$C_{2.5}O$

	5·Me_2CO	**6**·$C_{2.5}O$
	Crystal Data	
Empirical formula	$C_{26}H_{30}BF_4N_3O_2PRh$	$C_{29.5}H_{18}BF_8N_3O_2PRh$
Formula weight	637.22	743.16
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$C2/c$
a [Å]	8.572(2)	29.868(6)
b [Å]	16.374(5)	10.775(2)
c [Å]	19.790(5)	18.064(3)
β [deg]	99.192(5)	99.960(4)
V [Å^3]	2741.9(13)	5725.8(18)
Z	4	8
$D_{calcd.}$ [g cm^{-3}]	1.544	1.724
Absorption coefficient [mm^{-1}]	0.737	0.740
F(000)	1296	2952
Crystal size [mm]	0.04 × 0.10 × 0.11	0.03 × 0.11 × 0.11
	Data Collection	
Temperature [K]	303(2)	293(2)
Theta range for data collection	1.62 to 21.98°	2.01 to 23.31°
Wavelength [Å]	0.71073 (Mo-K_α)	0.71073 (Mo-K_α)
Index ranges	$-9 \le h \le 8$, $0 \le k \le 17$, $0 \le l \le 20$	$-33 \le h \le 32$, $0 \le k \le 11$, $0 \le l \le 20$
Reflections collected	10834	13388
Independent reflections	3336 (R_{int} = 0.0550)	4128 (R_{int} = 0.0487)
Observed reflections [$I > 2\sigma(I)$]	2196	2880
	Refinement	
Data/restraints/parameters	3336/0/345	4128/0/411
Goodness-of-fit on F^2	0.901	1.006
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0419, wR_2 = 0.0953	R_1 = 0.0506, wR_2 = 0.1388
R indices (all data)	R_1 = 0.0722, wR_2 = 0.1037	R_1 = 0.0773, wR_2 = 0.1583
Largest diff. peak and hole [e Å^{-3}]	0.571 and −0.364	2.483 and −0.505

formed, $[Rh_2(\mu\text{-}CO)_3(OPPy_3)_2][RhCl_2(CO)_2]_2$ was filtered, washed with dichloromethane and vacuum dried. Yield 145 mg (80%). − $C_{37}H_{24}Cl_4N_6O_9P_2Rh_4$ (1312.2): calcd. C 33.90, H 1.85, N 6.40; found C 33.91, H 1.80, N 6.42.

X-ray Crystallography: Suitable single crystals were mounted on glass fibers, and diffraction measurements were made using a Bruker SMART CCD area-detector diffractometer with Mo-K_α radiation (λ = 0.71073 Å).[23] Intensities were integrated from several series of exposures, each exposure covering 0.3° in ω, the total data set being a hemisphere.[24] Absorption corrections were applied, based on multiple and symmetry-equivalent measurements.[25] The structure was solved by Patterson synthesis or direct methods and refined by least-squares on weighted F^2 values for all reflections (see Table 3).[26] All nonhydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints. Hydrogen atoms were taken into account at calculated positions and their positional parameters were refined. Refinement proceeded smoothly to give R_1 = 0.0419 for **5**·acetone and R_1 = 0.0621 for **6**, based on the reflections with $I > 2\sigma(I)$. Further refinement for **6**, including a molecule of acetone with one carbon in a special position led to a final R_1 value of 0.0505 for **6**·$C_{2.5}O$. Hydrogen atoms of the acetone in **6**·$C_{2.5}O$ were not included in the calculations. Complex neutral-atom scattering factors were used.[27] Crystallographic data (excluding structure factors) for the structures **5**·acetone and **6**·$C_{2.5}O$ reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication numbers CCDC-144233 (**5**·Me_2CO) and CCDC-144234 (**6**·$C_{2.5}O$). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Catalytic Experiments. − Hydrogenation with Molecular Hydrogen: In each experiment, 0.014 mmol of the rhodium complex and 28 mmol of the substrate were dissolved in 18 mL of a 0.04 M solution of sodium hydroxide in methanol. After stirring for some minutes in order to dissolve the complex completely, the solution was transferred to a previously deaerated high pressure reactor containing a magnetic bar for stirring the solution; the reactor was then filled with the desired pressure of hydrogen and connected to a thermostated oil bath. The course of the reaction was followed by taking a sample of the solution at different times and refilling the reactor to the previous pressure. The solutions were analyzed by GC. The homogeneity of the catalysis was tested by adding a large excess of mercury to the reaction vessel (Hg:catalyst = 100:1).

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