Synthesis of a New Potentially Hemilabile Ligand: 1-[2-(Diphenylphosphanyl)ethyl]-3,5-dimethylpyrazole, and Comparison of Its Bonding Properties with the Related 1-[2-(Ethylamino)ethyl]-3,5-dimethylpyrazole Ligand toward Rh^{I}

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The new ligand 1-[2-(diphenylphosphanyl)ethyl]-3,5-dimethylpyrazole (**2**) has been prepared by the reaction of 1-(chloroethyl)-3,5-dimethylpyrazole and PPh_2Li. The bidentate N,N ligand 1-[2-(ethylamino)ethyl]-3,5-dimethylpyrazole (**1**) and **2** react with $[Rh(COD)(THF)_2][BF_4]$ to give $[Rh(COD)(\mathbf{1})][BF_4]$ (**3**) and $[Rh(COD)(\mathbf{2})][BF_4]$ (**4**), respectively. Substitution of 1,5-cyclooctadiene with carbon monoxide in the latter complexes generates $[Rh(CO)_2(\mathbf{1})][BF_4]$ (**5**) and $[Rh(CO)_2(\mathbf{2})][BF_4]$ (**6**), respectively. Treatment of $[Rh(COD)(THF)_2][BF_4]$ with two equivalent amounts of **2** results in the complex $[Rh(\mathbf{2})_2][BF_4]$ (**7**), which converts to $[Rh(CO)(\mathbf{2})_2][BF_4]$ (**8**) on reaction with carbon monoxide. Ligand **2** in complex **8** exhibits a hemilabile character. The single-crystal X-ray structures of **3**, **4**, and **7** are reported.

Introduction

In recent years the use of hemilabile ligands in coordination and organometallic chemistry has increased because of their potential applications in catalysis. Many bidentate ligands containing two donor centres of different strengths, such as mixed phosphorus-heteroatom ligands, have been reviewed in recent reports and articles.[1,2,3] Their interest in catalysis arises from the easy decoordination of the weak donor centre without the displacement of the ligand, which should confer a better stability to the reaction intermediates. Mixed ligands containing phosphorus along with oxygen, nitrogen or sulphur donor atoms have specifically been designed for use in catalytic reactions such as hydrogenation,[4,5,6] oligomerisation,[7] and hydroformylation of olefins.[8]

Pyrazole-derived molecules are good candidates for the preparation of interesting N,N′ or N,P mixed ligands, owing to their ease of synthesis and the possibility of electronic and steric modulation of their properties. Pyrazole-amines have been extensively studied as ligands for hard transition metal cations.[9] These studies have led to remarkable structures for the resulting complexes, some of which can be regarded as bioinorganic models.[10,11] Some reviews about pyrazole chelating ligands in biological model systems have recently appeared.[12,13]

In pursuing investigations on pyrazole-based polydentate ligands, we have directed our efforts toward the study of their reactivity with soft transition metal ions, in order to compare their behaviour with that of the well-known tris(pyrazolyl)borate anion.[14] Very recently, we have described the coordinating properties of bis[(3,5-dimethylpyrazolyl)methyl]ethylamine toward Rh^{I}. This ligand, which contains two different N donor centres, leads to a $\kappa^2 \rightleftarrows \kappa^3$ equilibrium in solution, revealing its hemilabile character through the reversible decoordination of the amino group. The κ^3 coordination mode has been found in the solid state structure determinations.[15]

In the present paper, we extend this work to a new family of N,P ligands of the phosphanylalkylpyrazole type. Prior to our investigations, only the diphenylphosphanylmethylpyrazole has been described in this class of ligands.[16] We report the synthesis of 1-[2-(diphenylphosphanyl)ethyl]-3,5-dimethylpyrazole and the study of its bonding properties toward Rh^{I}. For comparative purposes, the reactivity of the related N,N′ bidentate ligand 1-[2-(ethylamino)ethyl]-3,5-dimethylpyrazole toward Rh^{I} has also been investigated.

Results and Discussion

The ligand 1-[2-(ethylamino)ethyl]-3,5-dimethylpyrazole (**1**) was synthesised according to a procedure previously described by Driessen.[17]

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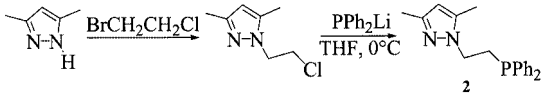
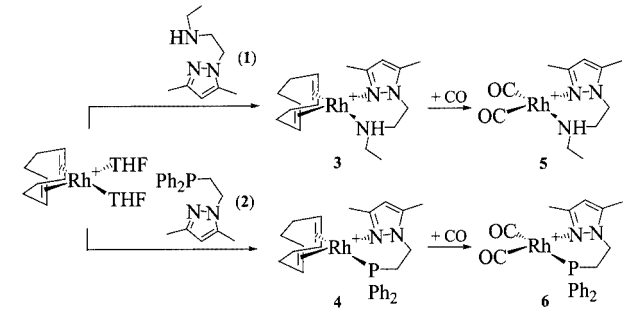
The new ligand 1-[2-(diphenylphosphanyl)ethyl]-3,5-dimethylpyrazole (**2**) was prepared by reaction of 1-(chloroethyl)-3,5-dimethylpyrazole[18] with PPh_2Li, which is generated in situ by deprotonation of PPh_2H by *n*BuLi in tetrahydrofuran, at 0 °C (Scheme 1). The new ligand, isolated in an 83% yield as a colourless oil, was characterised by C, H, and N elemental analyses, IR, ^1H-, ^{13}C, and ^{31}P NMR spectroscopy, and by electron impact mass spectrometry. In the ^{31}P NMR spectrum, the diphenylphosphanyl moiety gives a singlet at $\delta = -20.9$ ppm.



Scheme 1

1-[2-(ethylamino)ethyl]-3,5-dimethylpyrazole (**1**) or 1-[2-(diphenylphosphanyl)ethyl]-3,5-dimethylpyrazole (**2**) react with one equivalent of $[Rh(COD)(THF)_2][BF_4]$, which is generated in situ from the reaction of $[Rh(COD)Cl]_2$ and $AgBF_4$ in tetrahydrofuran, to give the complexes $[Rh(COD)(\mathbf{1})][BF_4]$ (**3**) (89% yield) and $[Rh(COD)(\mathbf{2})][BF_4]$ (**4**) (94% yield), respectively (Scheme 2). Elemental analyses of both complexes are consistent with their formulation.



Scheme 2

We were able to prepare X-ray quality crystals of complexes **3** and **4**, and we performed a crystal structure determination for both complexes. The molecular structures of the complexes consist of discrete $[Rh(COD)(\mathbf{1})]^+$ and $[Rh(COD)(\mathbf{2})]^+$ cations, respectively, and BF_4^- anions. Perspective views of the cation complexes are given in Figures 1, and 2, respectively. Selected bond lengths and angles are provided in Table 1, and the details of the data collection and crystal data are summarised in Table 2. A slightly distorted square-planar geometry is observed around Rh in both structures. Thus, in **3**, the Rh atom deviates by 0.025 Å from the mean coordination plane formed by two N donor atoms of the ligand and the centroid of the olefinic C=C bonds of the COD ligand. In **4**, the Rh atom deviates by 0.139 Å from the mean plane formed by the donor N and P atoms of the ligand and the centroid of the olefinic C=C bonds of the COD ligand. The Rh−N distances of 2.116(3) and 2.148(3) Å for **3**, and of 2.141(2) Å for **4** fall between the experimental values reported for related complexes.[15,19,21] The Rh−P bond length of 2.274(1) Å for **4** is also similar to those found in the literature.[19,22] Due to

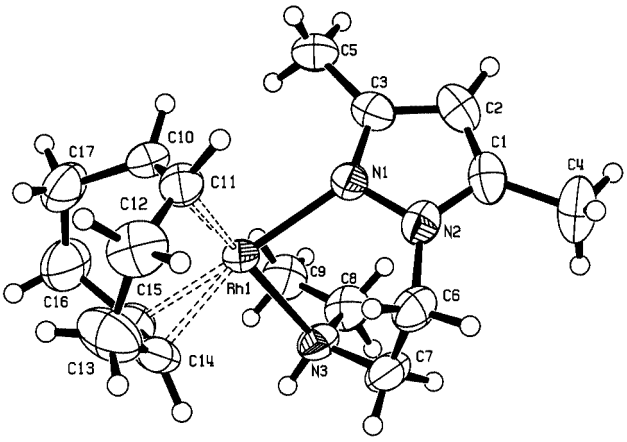


Figure 1. A perspective view of the cation $[Rh(COD)(\mathbf{1})]^+$ showing the numbering scheme

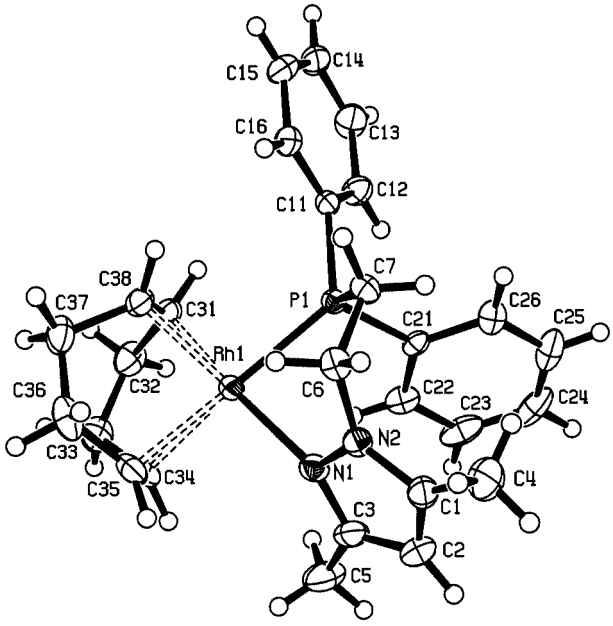


Figure 2. A perspective view of the cation $[Rh(COD)(\mathbf{2})]^+$ showing the numbering scheme

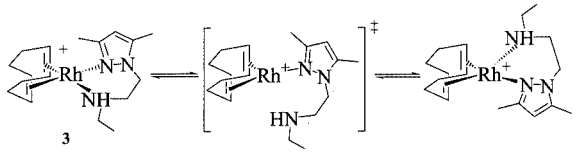
the different *trans* effect of the donor atoms in **4**, the Rh−C bonds *trans* to phosphorus [2.236(2) and 2.216(2) Å] are longer than the Rh−C bonds *trans* to nitrogen [2.132(2) and 2.129(2) Å].[19] The N1−Rh1−N3 angle [82.90(14)°] for **3** and the N1−Rh1−P1 angle [82.68(5)°] for **4** are smaller than 90°, but are consistent with the reported angles for similar complexes.[15,19] It is worth noting that in both structures the six-membered rings formed by the bidentate ligands coordinated to rhodium adopts a boat-type conformation, the Rh1 and C6 (both structures) atoms are at the apex of the boat.

The ^1H NMR spectrum for **3** recorded at 293 K (250 MHz) shows three signals with the relative intensity 2:1:1 at $\delta = 4.37$, 4.29, and 4.21 ppm for the non-equivalent olefinic protons of the 1,5-COD ligand *trans* to the pyrazole ring and *trans* to the amino group. This is fully consistent with the solid state structure, which shows that the nitrogen

Table 1. Selected bond lengths [Å] and angles [°] for compounds [Rh(COD)(**1**)][BF_4] (**3**), [Rh(COD)(**2**)][BF_4] (**4**), and [Rh(**2**)$_2$][BF_4] (**7**)

	3		**4**		**7**
C10−C11	1.385(7)	C34−C35	1.372(4)	N1−Rh1	2.119(2)
C10−Rh1	2.158(4)	C34−Rh1	2.236(2)	N3−Rh1	2.113(2)
C11−Rh1	2.133(4)	C35−Rh1	2.216(2)	P1−Rh1	2.207(1)
C14−C15	1.365(7)	C31−C38	1.392(3)	P2−Rh1	2.223(1)
C14−Rh1	2.135(4)	C31−Rh1	2.132(2)	C3−N1−N2	105.2(2)
C15−Rh1	2.125(5)	C38−Rh1	2.129(2)	C3−N1−Rh1	130.54(18)
N1−Rh1	2.116(3)	N1−Rh1	2.141(2)	N2−N1−Rh1	123.31(17)
N3−Rh1	2.148(3)	P1−Rh1	2.2743(6)	C8−N3−N4	106.1(2)
C8−N3−C7		C21−P1−C11	103.88(10)	C8−N3−Rh1	132.0(2)
C8−N3−Rh1	112.5(3)	C21−P1−C7	105.48(10)	N4−N3−Rh1	121.83(17)
C7−N3−Rh1	111.2(3)	C11−P1−C7	106.01(10)	N3−Rh1−N1	88.37(9)
N1−Rh1−C15	165.68(17)	C21−P1−Rh1	110.32(7)	N3−Rh1−P1	176.60(6)
N1−Rh1−C11	93.48(16)	C11−P1−Rh1	122.77(7)	N1−Rh1−P1	89.13(7)
C15−Rh1−C11	96.06(18)	C7−P1−Rh1	107.13(7)	N3−Rh1−P2	83.43(6)
N1−Rh1−C14	155.60(18)	C38−Rh1−C31	38.13(9)	N1−Rh1−P2	171.77(6)
C15−Rh1−C14	37.37(19)	C38−Rh1−N1	152.51(8)	P1−Rh1−P2	99.03(3)
C11−Rh1−C14	82.32(18)	C31−Rh1−N1	168.78(8)	C21−P1−C31	103.58(12)
N1−Rh1−N3	82.90(14)	C38−Rh1−C35	81.90(9)	C21−P1−C12	102.49(13)
C15−Rh1−N3	92.02(17)	C31−Rh1−C35	97.09(9)	C31−P1−C12	100.43(12)
C11−Rh1−N3	158.13(17)	N1−Rh1−C35	90.01(8)	C21−P1−Rh1	118.66(9)
C14−Rh1−N3	92.08(16)	C38−Rh1−C34	88.02(9)	C31−P1−Rh1	119.34(9)
N1−Rh1−C10	100.18(16)	C31−Rh1−C34	80.46(9)	C12−P1−Rh1	109.66(9)
C15−Rh1−C10	81.23(18)	N1−Rh1−C34	100.71(8)	C51−P2−C41	102.25(13)
C11−Rh1−C10	37.66(18)	C35−Rh1−C34	35.89(9)	C51−P2−C14	102.07(13)
C14−Rh1−C10	91.14(17)	C38−Rh1−P1	97.17(6)	C41−P2−C14	103.47(13)
N3−Rh1−C10	164.19(17)	C31−Rh1−P1	92.81(6)	C51−P2−Rh1	126.40(9)
		N1−Rh1−P1	82.68(5)	C41−P2−Rh1	111.87(10)
		C35−Rh1−P1	162.20(7)	C14−P2−Rh1	108.31(10)
		C34−Rh1−P1	161.72(7)		

atom of the amino group coordinated to rhodium constitutes a stereogenic centre. Lowering the temperature to 243 K induces the splitting of the signals at δ = 4.37 ppm. On the other hand, increasing the temperature to 323 K results in the broadening of all the signals, and the coalescence of the signals for the olefinic protons of 1,5-COD to a single signal centred at δ = 4.35 ppm is observed at 310 K. This clearly demonstrates that complex **3** undergoes a dynamic process in solution. The coalescence temperature corresponds to a $\Delta G^{\ddagger}$ value of 15(±1) kcal·mol^{-1}.[20] The averaging of the resonances for the olefinic protons of 1,5-COD can reasonably be interpreted in terms of decoordination of one end of the ligand **1**, rotation, and recoordination, thus revealing the hemilabile character of ligand **1** in complex **3**. However, the experimental data do not allow for the unambiguous determination of the end of the ligand which eventually decoordinates. Indeed, except a general broadening of the signals, there are no significant changes in the chemical shifts for the protons of the methyl and ethyl groups of the ligand. Scheme 3 shows the proposed mechanism for this process.



Scheme 3

In the case of complex **4**, the ^{1}H NMR spectrum at room temperature shows three signals characteristic of the CH (δ = 5.59 ppm) and the methyl substituents (δ = 2.34, 2.22 ppm) of the pyrazolyl group. The other resonances are broad signals centred at δ = 5.29 (4 H), 3.71 ppm (2 H) and a large signal between δ = 3.2 and 1.8 ppm (10 H). The signals at δ = 5.29 and 3.71 ppm are in the area characteristic of the olefinic protons of 1,5-COD *trans* to a phosphorus atom and *trans* to a nitrogen atom.[19] Thus, we can deduce that the signal at δ = 5.29 ppm is due to the two olefinic protons of 1,5-COD and the two protons of the methylene group bonded to the nitrogen of the pyrazolyl ring. The large signal is due to both the protons of the methylene group bonded to phosphorus and the alkyl protons of 1,5-COD. These observations suggest that complex **4** undergoes a fluxional process, and variable-temperature experiments were performed at 500 MHz. By lowering the temperature to 230 K, each resonance splits into two more signals at δ = 5.43 and 5.25 ppm for the olefinic protons *trans* to the phosphorus atom, and δ = 3.85 and 3.46 ppm for the olefinic protons *trans* to the nitrogen atom, leading to four signals for the non equivalent olefinic protons of 1,5-COD. The coalescence temperature of the δ = 5.43 and 5.25 ppm resonances occurs at 280 K, while the resonances at δ = 3.85 and 3.46 ppm coalescent 290 K. This corre-

sponds to a $\Delta G^{\ddagger}$ value of 13(±1) kcal·mol^{-1} [20]. No significant differences other than the narrowing of the two signals at δ = 5.33 and 3.68 ppm are observed when the temperature was raised to 333 K. The ^{31}P NMR spectra, recorded in the same temperature range, show a doublet at δ = 28.4 ppm ($^{1}J_{Rh,P}$ = 146.3 Hz), with no other changes, other than a slight displacement with temperature. From these observations it is clear that the fluxional process implies an exchange between the two protons of 1,5-COD which are *trans* to the phosphorus atom, and between the two protons which are *trans* to the nitrogen only. No exchange between the two groups of protons could be evidenced. All this has been corroborated by ^{1}H NMR spin transfer experiments on the olefinic proton resonances. The dynamic behaviour of complex **4** can thus be rationalised in terms of boat-boat configuration inversion of the six-membered ring Rh1−P1−C7−C6−N2−N1 (see Figure 2) in solution. No evidence for a hemilabile behaviour of ligand **2** in complex **4** − that would have led to an averaging of *all* the olefinic proton resonances − could be obtained in the temperature range allowed by the thermal stability of the complex.

In complexes **3** and **4**, the ligand 1,5-COD was displaced by carbon monoxide when the gas was bubbled though the solutions of the complexes in dichloromethane at room temperature, giving [Rh(CO)$_2$(**1**)][BF$_4$] (**5**) and [Rh(CO)$_2$(**2**)][BF$_4$] (**6**), respectively (Scheme 2). Complex **6** reverted back to some extent to complex **4** on evaporation of the solvent. Thus, several cycles of bubbling with carbon monoxide and vacuum drying were necessary to eliminate free 1,5-COD in order to get complex **6** in a reasonable yield.

The IR spectrum of **5** shows two strong absorption bands at 2098 and 2033 cm^{-1} due to νCO vibrations. The ^{1}H NMR spectrum proves the absence of the ligand 1,5-COD, and the appearance of two doublets at δ = 182.5 ppm ($J_{Rh,C}$ = 69.8 Hz) and δ = 181.5 ppm ($J_{Rh,C}$ = 67.3 Hz) in the ^{13}C NMR spectrum confirms the presence of two CO ligands coordinated to the rhodium atom.

The IR spectrum of **6** shows two strong absorption bands at 2103 and 2042 cm^{-1} in the νCO region. Its ^{1}H NMR spectrum confirms the decoordination of the 1,5-COD ligand. The ^{13}C NMR spectrum displays resonances assigned to the two CO ligands as doublet of doublets at δ = 184.8 ppm ($J_{Rh,C}$ = 67 Hz, $J_{P,C}$ = 16 Hz) for the CO *trans* to the nitrogen atom, and at δ = 179.9 ppm ($J_{Rh,C}$ = 60 Hz, $J_{P,C}$ = 104 Hz) for the CO *trans* to the phosphorus atom. The ^{31}P NMR spectrum of **6** displays a doublet at δ = 30.2 ppm with $J_{Rh,P}$ = 120.9 Hz.

The reaction of [Rh(COD)(THF)$_2$][BF$_4$], generated in situ from the reaction of [Rh(COD)Cl]$_2$ and AgBF$_4$ in tetrahydrofuran, and two equivalent amounts of the ligand **1** led to **3** only. This is not surprising since it is known that NN ligands cannot displace 1,5-COD in [Rh(COD)(NN)]BF$_4$ complexes.[23] The same reaction starting with **2** resulted in the formation of a yellow-orange complex **7** in a 92% yield. Elemental analyses and spectroscopic data supported the formation of the [Rh(**2**)$_2$][BF$_4$] complex. The ^{1}H and ^{13}C NMR spectra display the expected signals of the ligand, whereas the ^{31}P NMR spectrum shows a doublet at δ = 44.9 ppm with $^{1}J_{Rh,P}$ = 171 Hz. This complex was also characterised by X-ray crystallography. The molecular structure of **7** consists of discrete [Rh(**2**)$_2$]$^{+}$ cations and BF$_4^{-}$ anions. The cation complex is shown in Figure 3, selected bond lengths and angles are provided in Table 1, and the details of the data collection and crystal data are summarised in Table 2. The structure shows a planar geometry around the rhodium atom, the phosphorus atoms of the two **2** ligands are in a *cis* position. The metal slightly deviates from the mean coordination plane formed by the two N and the two P donor atoms by 0.031 Å. The Rh−N [2.119(2) and 2.113(2) Å] and the Rh−P bond lengths [2.207(1) and 2.223(1) Å] are consistent with those found in the literature.[19,21,22] Phenyl rings are oriented face to face at a distance of 3.287 Å, suggesting a π-π stacking interaction[24]. The P1−Rh1−P2 angle [99.03(3)°] is larger than 90°, and as a consequence the N3−Rh1−P2 angle [83.43(6)°] is more acute than the others [N3−Rh1−N1 = 88.37(9)°; N1−Rh1−P1 = 89.13(7)°].

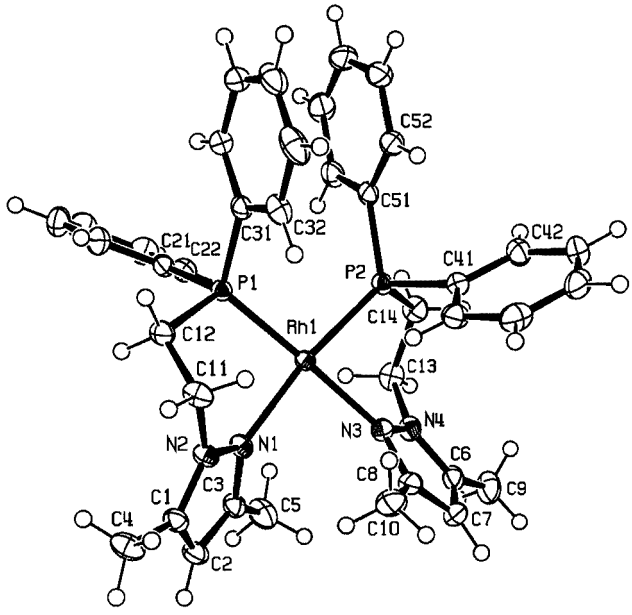
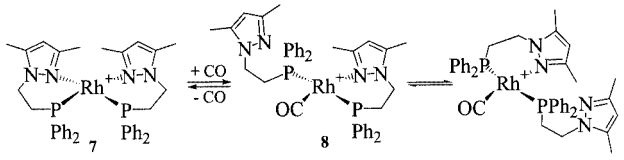


Figure 3. A perspective view of the cation [Rh(**2**)$_2$]$^{+}$ showing the numbering scheme

To prove the hemilabile behaviour of the ligand **2** in **7**, carbon monoxide was bubbled into a solution of the complex in dichloromethane. This led to the formation of a new compound that was characterised by IR and NMR spectroscopy as [Rh(CO)(**2**)$_2$][BF$_4$] (**8**). Evaporation of the solvent under vacuum or the bubbling of nitrogen into the solution of **8** slowly regenerated **7**. In solution, **8** shows a νCO absorption band at 2014 cm^{-1}. At room temperature the ^{1}H, ^{13}C, and ^{31}P NMR spectra indicate that the two **2** ligands are equivalent, thus suggesting a fluxional process in solution. Variable temperature ^{31}P{^{1}H} and ^{1}H NMR experiments were performed. The most informative results were obtained from the ^{31}P{^{1}H} experiments in CD_2Cl_2 solution. Indeed, the room temperature spectrum shows a doublet at

δ = 25.8 ppm ($J_{Rh,P}$ = 122 Hz). Lowering the temperature first induces a progressive broadening of the signal to give a broad resonance centred at δ = 23.9 ppm at 193 K. At 173 K, the lowest temperature we could attain, a slightly broad ABX spin system appears. The parameters of the system (δ_A = 28.1 ppm, δ_B = 19.5 ppm; $J_{A,B}$ = 291 Hz, $J_{A,X}$ = 120 Hz, $J_{B,X}$ = 125 Hz) are consistent with a square planar structure in which the two phosphorus atoms are in a *trans* position, and only one of the two **2** ligands is κ^2-coordinated, the second one is κ^1-coordinated by the phosphorus atom to rhodium. At the same temperature the ^{1}H NMR spectrum shows broad resonances only. The coalescence temperature, in the $^{31}P\{^1H\}$ NMR spectra lead to a $\Delta G^{\ddagger}$ value of 8($\pm$1) kcal·mol^{-1}.[20] The fluxionality observed for **8** most likely results from an exchange between the κ^2 and κ^1 modes of bonding for the two **2** ligands, by the opening of one of the rhodium-pyrazolyl bonds. The same type of dynamic process was previously observed for the [Ir(PN)$_2$(CO)][PF$_6$] complex [PN = 1-(2-pyridyl)-2-(diphenylphosphanyl)ethane],[23] and this is frequently observed in complexes containing two hemilabile bidentate ligands.[2,3] Scheme 4 summarises our observations.



Scheme 4

The catalytic activity of complexes **4** and **7** has been evaluated for the hydroformylation of styrene. Under our experimental conditions (dichloromethane as the solvent, 20 bar of a 1:1 mixture of CO and H_2, 50 °C) a low conversion was observed (1% for **4** and 10% for **7**), and only the branched aldehyde was detected.

Conclusions

In this work we have described the synthesis of the new potentially hemilabile N,P bidentate ligand, 1-[2-(diphenylphosphanyl)ethyl]-3,5-dimethylpyrazole (**2**). The reaction of **2** and the related N,N′ bidentate ligand 1-[2-(ethylamino)ethyl]-3,5-dimethylpyrazole (**1**) with the rhodium(I) complex [Rh(COD)(THF)$_2$]BF$_4$ has led to the complexes [Rh(COD)(**1**)]BF$_4$ (**3**) and [Rh(COD)(**2**)]BF$_4$ (**4**), which have been fully characterised. Both these compounds exhibit a fluxional process in solution that can be interpreted in terms of a hemilabile behaviour of the ligand **1** in complex **3**, and a boat-boat ring inversion of the six-membered ring formed on coordination of the ligand **2** in complex **4**. The 1,5-COD ligand in complexes **3** and **4** can easily be displaced by carbon monoxide, leading to the complexes [Rh(CO)$_2$(**1**)]BF$_4$ (**5**) and [Rh(CO)$_2$(**2**)]BF$_4$ (**6**), respectively. The reaction of two equivalents of **2** with [Rh(COD)(THF)$_2$]BF$_4$ leads to [Rh(**2**)$_2$][BF$_4$] (**7**), in which the phosphorus atoms are in a *cis* position. The latter complex reversibly absorbs one molecule of CO to afford complex [Rh(**2**)$_2$(CO)][BF$_4$] (**8**). NMR studies of complex **8** show a dynamic exchange between the κ^2 and κ^1 modes of bonding for the two **2** ligands, by the opening of one of the rhodium-pyrazolyl bonds. In spite of this hemilabile property of ligand **2**, complex **7** shows a low activity for the catalytic hydroformylation of styrene.

Experimental Section

General Procedures: All chemicals were used as received from commercial suppliers, unless otherwise indicated. Reactions were carried out under a dinitrogen atmosphere using vacuum line and Schlenk techniques. Solvents were dried and distilled according to standard procedures and stored under nitrogen. NMR spectra were acquired on a Bruker AC200, AC250, Avance DPX250, or Avance DRX500 spectrometer in $CDCl_3$ solutions, unless otherwise indicated. All the chemical shifts are given in ppm and are referenced with respect to residual protons in the solvent for ^{1}H spectra, to solvent signals for ^{13}C spectra and to external H_3PO_4 for ^{31}P spectra. IR spectra were recorded on a Perkin−Elmer 2000 spectrophotometer with KBr pellets or in dichloromethane solutions with CaF_2 cells. Elemental analyses were performed at the Laboratoire de Chimie de Coordination on a Perkin−Elmer 2400 CHN analyser or at the Universitat Autònoma de Barcelona on a Carlo Erba CHNS EA-1108 apparatus. Electronic impact mass spectra were measured by the staff of the Mass Spectrometry Service at the Université Paul Sabatier (Toulouse). [Rh(COD)Cl$_2$] was prepared according to a literature procedure.[25]

Synthesis of 1-(Chloroethyl)-3,5-dimethylpyrazole:[18] 3,5-Dimethylpyrazole (1.00 g, 10.4 mmol), 40% aq. NaOH (12 mL), tetrabutylammonium bromide (TBAB, 0.483 g, 1.5 mmol), toluene (20 mL), and 1-bromo-2-chloroethane (10 mL, 17.23 g, 120 mmol) were mixed and heated to reflux for 48 h. The mixture was allowed to cool to room temperature, the phases were separated and the aqueous phase was extracted with 3 × 20 mL of dichloromethane. The extracts were combined with the organic phase and the solvents were then removed under vacuum. Addition of diethyl ether (15 mL), filtration and evaporation of the solvent yielded 1-(chloroethyl)-3,5-dimethylpyrazole as a colourless oil. Yield: 88%. M.p. 20−22 °C. $C_7H_{11}ClN_2$ (158.6) (%): calcd. C 53.00, H 6.99, N 17.66; found C 52.69, H 6.63, N 17.83. IR (neat between KBr cells): $\tilde{\nu}$ [cm^{-1}] = 3046 (νC−H$_{ar}$), 2967−2871 (νC−H$_{al}$), 1555 (νC=C$_{ar}$, νC=N$_{ar}$), 1463 (δCH$_{3as}$), 1426 (δC=C$_{ar}$, δC=N$_{ar}$), 1388−1188 (νC−N), 860 (νC−Cl). ^{1}H NMR (250 MHz, $CDCl_3$, 20 °C): δ [ppm] = 5.74 (s, 1 H, CH pyrazole), 4.19 (t, $^3J_{H,H}$ = 6.3 Hz, 2 H, CH_2CH$_2$Cl), 3.79 (t, $^3J_{H,H}$ = 6.3 Hz, 2 H, CH$_2$CH_2Cl), 2.21 (s, 3 H, CCH$_3$), 2.15 (s, 3 H, CCH$_3$). $^{13}C\{^1H\}$ NMR (63 MHz, $CDCl_3$, 20 °C): δ [ppm] = 148.2 (*C*CH$_3$), 139.7 (*C*CH$_3$), 105.1 (CH pyrazole), 49.6 (*C*H$_2$CH$_2$Cl), 43.0 (CH$_2$*C*H$_2$Cl), 13.4 (C*C*H$_3$), 11.0 (C*C*H$_3$). Mass spectroscopic data (EI, *m*/*z*): 158[M$^{+\cdot}$], 122 [M$^+$ − Cl], 109 [M$^+$ − CH$_2$Cl], 96 [M$^{+\cdot}$− C$_2$H$_3$Cl].

Synthesis of 1-[2-(Diphenylphosphanyl)ethyl]-3,5-dimethylpyrazole (2): A solution of *n*BuLi (100 μL, 1.6 mmol, 1.6 M in hexane) was added dropwise to a stirred solution of PPh$_2$H (300 μL, 1.724 mmol) in tetrahydrofuran (10 mL) at 0 °C. After 30 min, the solution of PPh$_2$Li was added dropwise to a stirred solution of 1-(chloroethyl)-3,5-dimethylpyrazole (0.325 g, 2.0 mmol) in tetrahydrofuran (20 mL) at 0 °C. The mixture was maintained at 0 °C for 1 h. The temperature was then raised to room temperature and

after 15 h of stirring the solvent was evaporated under vacuum. 40 mL of dichloromethane were added to the residue and the salts were extracted with 2 × 10 mL of distilled water. Evaporation of the solvent from the organic phase gives 1-[2-(diphenylphosphanyl)-ethyl]-3,5-dimethylpyrazole (**2**) as a colourless oil. Yield: 83%. M.p. 20−22 °C. $C_{19}H_{21}N_2P$ (308.4) (%): calcd. C 74.01, H 6.86, N 9.08; found C 73.72, H 6.68, N 9.28. IR (neat between KBr cells): ṽ [cm^{-1}]: 3074−3046 (νC−H_{ar}), 2923 (νC−H_{al}), 1553 (νC=C_{ar}, νC=N_{ar}), 1482 (δCH_{3as}), 1435 (δC=C_{ar}, δC=N_{ar}), 1387−1184 (νC−N), 764−704 (νP−C, δC−H_{oop}). ^{1}H NMR (200 MHz, $CDCl_3$, 20 °C): δ [ppm] = 7.48−7.29 (m, 10 H, PPh_2), 5.71 (s, 1 H, CH pyrazole), 4.10−3.99 (m, 2 H, CH_2CH$_2$PPh$_2$), 2.61−2.53 (m, 2 H, CH$_2$CH_2PPh$_2$), 2.19 (s, 3 H, CCH_3), 2.06 (s, 3 H, CCH_3). ^{13}C{^{1}H} NMR (63 MHz, $CDCl_3$, 20 °C): δ [ppm] = 147.3 (*C*CH_3), 138.2 (*C*CH_3), 132.7−128.3 (PPh_2), 104.8 (CH pyrazole), 45.4 (d, $^2J_{P,C}$ = 25.0 Hz, *C*H$_2$CH$_2$PPh$_2$), 29.4 (d, $^1J_{P,C}$ = 14.4 Hz, CH$_2$*C*H$_2$PPh$_2$), 13.4 (C*C*H$_3$), 10.8 (C*C*H$_3$). ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$, 20 °C): δ [ppm] = −20.9 (PPh_2). Mass spectroscopic data (EI, *m*/*z*): 308 [M$^{+\cdot}$], 231 [M$^+$ − Ph], 123 [M$^+$ − PPh_2], 109 [M$^+$ − CH$_2$$PPh_2$], 96 [M$^{+\cdot}$ − $C_2H_3PPh_2$].

Synthesis of [Rh(COD)(1)][BF$_4$] (3): $AgBF_4$ (0.062 g, 0.320 mmol) was added to a solution of [Rh(COD)Cl$_2$] (0.079 g, 0.160 mmol) in tetrahydrofuran (20 mL). A white solid precipitated (AgCl). After 30 min of stirring the solid was filtered off and 1-[2-(ethylamino)-ethyl]-3,5-dimethylpyrazole ligand (**1**) (0.054 g, 0.320 mmol) was added to the filtrate, leading to the precipitation of complex **3** as a yellow solid. The complex was crystallised in a dichloromethane/ether mixture. Yield: 89%. M.p. 135−137 °C (dec.). $C_{17}H_{29}BF_4N_3Rh$ (465.1) (%): calcd. C 43.90, H 6.28, N 9.03; found C 43.82, H 6.16, N 8.90. IR (KBr): ṽ [cm^{-1}]: 3275 (νN−H), 2960−2835 (νC−H_{al} ligand+COD), 1553 (νC=C_{ar}, νC=N_{ar}), 1469 (δCH_{3as} ligand/δCH_2 COD), 1432 (δC=C_{ar} ligand+COD, δC=N_{ar}), 1386−1188 (νC−N), 1069−964 (νB−F), 801 (δ =CH_{oop} COD), 771 (δC−H_{oop} ligand+COD). ^{1}H NMR (500 MHz, $CDCl_3$, 20 °C): δ [ppm] = 5.87 (s, 1 H, CH pyrazole), 5.51, 4.56 (AB, 2 H, CH_2CH$_2$NHEt), 4.49, 4.40, 4.30, 4.21 (m, 4 H, =CH COD), 4.15 (b, 1 H, NH), 3.54, 2.41 (AB, 2 H, CH$_2$CH_2NHEt), 2.64 (m, 2 H, CH_2 COD), 2.41 (m, 1 H, CH_2CH$_3$), 2.31 (s, 3 H, CCH_3), 2.28 (s, 3 H, CCH_3), 2.19−2.11, 1.67 (m, 6 H, CH_2 COD), 1.71−1.65 (m, 4 H, CHH_{endo} COD), 1.44 (t, $^3J_{H,H}$ = 7.0 Hz, 3 H, CH$_2$CH_3), 1.30 (m, 1 H, CH_2CH$_3$). ^{13}C{^{1}H} NMR (63 MHz, $CDCl_3$, 20 °C): δ [ppm] = 149.4 (*C*CH_3), 142.4 (*C*CH_3), 108.0 (CH pyrazole), 83.6−81.4 (m, =CH COD), 49.8, 49.3 (*C*H$_2$*C*H$_2$NHCH$_2$CH$_3$), 32.2 (*C*H$_2$CH$_3$), 29.0,28.6 (CH_2 COD), 15.6 (CH$_2$*C*H$_3$), 14.0 (C*C*H$_3$), 11.3 (C*C*H$_3$).

Synthesis of [Rh(COD)(2)][BF$_4$] (4): $AgBF_4$ (0.062 g, 0.320 mmol) was added to a solution of [Rh(COD)Cl$_2$] (0.079 g, 0.160 mmol) in tetrahydrofuran (20mL). A white solid precipitated (AgCl). The solid was then filtered of and 1-[2-(diphenylphosphanyl)ethyl]-3,5-dimethylpyrazole (**2**) (0.099 g, 0.320 mmol) was added to the filtrate solution. After 1 h of stirring, the solvent was evaporated under vacuum and the residue was crystallised in a dichloromethane/ether mixture to give yellow crystals of complex **4**. Yield: 94%. M.p. 208−210 °C (dec.). $C_{27}H_{33}BF_4N_2PRh$ (606.3) (%): calcd. C 53.48, H 5.50, N 4.62; found C 53.06, H 5.17, N 4.41. IR (KBr): ṽ [cm^{-1}]: 3074 (νC−H_{ar}), 2994−2828 (νC−H_{al} ligand+COD), 1555 (νC=C_{ar}, νC=N_{ar}), 1483−1467 (δCH_{3as} ligand/δCH_2 COD), 1436−1428 (δC=C_{ar} ligand+COD, δC=N_{ar}), 1389−1162 (νC−N), 1102−948 (νB−F), 862 (δ =CH_{oop} COD), 777−700 (νP−C, δC−H_{oop} ligand+COD). ^{1}H NMR (250 MHz, $CDCl_3$, 20 °C): δ [ppm] = 7.37 (b, 10 H, PPh_2), 5.59 (s, 1 H, CH pyrazole), 5.29 (b, 2 H, = CH COD *trans* P), 5.33, 5.15 (AB, 2 H, CH_2CH$_2$PPh$_2$), 3.71 (b, 2 H, =CH COD *trans* N), 2.67 (b, 2 H, CH$_2$CH_2PPh$_2$), 2.48 (b, 4 H, CHH_{exo} COD), 2.34 (s, 3 H, CCH_3), 2.22 (s, 3 H, CCH_3), 2.16 (b, 4 H, CHH_{endo} COD). ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$, 20 °C): δ [ppm] = 149.4 (*C*CH_3), 143.1 (*C*CH_3), 132.7−128.6 (PPh_2), 108.0 (CH pyrazole), 104.8−103.4 (m, =CH COD *trans* P), 78.6−77.5 (m, =CH COD *trans* N), 48.5 (d, $^2J_{P,C}$ = 5.8 Hz, *C*H$_2$CH$_2$PPh$_2$), 27.9−27.4 (*C*H_2 COD), 27.6 (d, $^1J_{P,C}$ = 27.7 Hz, CH$_2$*C*H$_2$PPh$_2$), 15.2 (C*C*H$_3$), 11.3 (C*C*H$_3$). ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$, 20 °C): δ [ppm] = 28.4 (d, $^1J_{Rh,P}$ = 146.3 Hz, PPh_2).

Synthesis of [Rh(CO)$_2$(1)][BF$_4$] (5): Carbon monoxide was bubbled for 1 h into a solution of [Rh(COD)(**1**)][BF_4] (0.098 g, 0.211 mmol) in dichloromethane (20 mL). **5** was obtained in a 98% yield after evaporation of the solvent, and 1,5-COD was liberated under vacuum. $C_{11}H_{17}BF_4N_3O_2Rh$ (413.0) (%): calcd. C 31.99, H 4.15, N 10.17; found C 32.34, H 4.12, N 9.87. IR (CH_2Cl_2 solution, CaF_2 cells): ṽ [cm^{-1}]: 2099 and 2033 (νCO). ^{1}H NMR (250 MHz, $CDCl_3$, 20 °C): δ [ppm] = 6.08 (s, 1 H,CH pyrazole), 5.60, 4.45 (AB, 2 H, CH_2CH$_2$NHEt), 4.48 (b, 1 H, NH), 3.61, 2.65 (AB, 2 H, CH$_2$CH_2NHEt), 2.88 (m, 2 H, CH_2CH$_3$), 2.43 (s, 3 H, CCH_3), 2.38 (s, 3 H, CCH_3), 1.34 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, CH$_2$CH_3). ^{13}C{^{1}H} NMR (63 MHz, $CDCl_3$, 20 °C): δ [ppm] = 182.5 (d, $J_{Rh,C}$ = 69.8 Hz, CO), 181.1 (d, $J_{Rh,C}$ = 67.3 Hz, CO), 151.3 (*C*CH_3), 144.1 (*C*CH_3), 107.6 (CH pyrazole), 50.4, 49.6, 47.8 (*C*H$_2$*C*H$_2$NHCH$_2$CH$_3$, *C*H$_2$CH$_3$), 14.5 (C*C*H$_3$), 14.6 (CH$_2$*C*H$_3$), 11.1 (C*C*H$_3$).

Synthesis of [Rh(CO)$_2$(2)][BF$_4$] (6): Carbon monoxide was bubbled for 1 h into a solution of [Rh(COD)(**2**)][BF_4] (0.170 g, 0.280 mmol) in dichloromethane (20 mL), and **6** was obtained. The complex partially reverted back to the reactants when the solvent was evaporated under vacuum, therefore, six cycles of bubbling carbon monoxide and evaporation under vacuum were carried out in order to isolate **6** in a pure form. $C_{21}H_{21}BF_4N_2O_2PRh$ (554.1) (%): calcd. C 45.52, H 3.82, N 5.06; found C 45.02, H 3.49, N 5.21. IR (CH_2Cl_2 solution, CaF_2 cells): ṽ [cm^{-1}]: 2103 and 2042 (νCO). ^{1}H NMR (200 MHz, CD_3COCD_3, 20 °C): δ [ppm] = 7.82−7.56 (m, 10 H, PPh_2), 6.01 (s, 1 H, CH pyrazole), 5.08−4.91 (m, 2 H, CH_2CH$_2$PPh$_2$), 3.30−3.19 (m, 2 H, CH$_2$CH_2PPh$_2$), 2.38 (s, 3 H, CCH_3), 2.32 (s, 3 H, CCH_3). ^{13}C{^{1}H} NMR (63 MHz, CD_2Cl_2, 20 °C): δ [ppm] = 184.8 (dd, $J_{Rh,C}$ = 67 Hz, $J_{P,C}$ = 15.8 Hz CO), 179.9 (dd, $J_{Rh,C}$ = 60 Hz, $J_{P,C}$ = 103.5 Hz CO), 151.3 (*C*CH_3), 145.0 (*C*CH_3), 133.7−128.6 (PPh_2), 108.3 (CH pyrazole), 47.2 (*C*H$_2$CH$_2$PPh$_2$), 27.2 (d, $^1J_{P,C}$ = 30.3 Hz, CH$_2$*C*H$_2$PPh$_2$), 15.3 (C*C*H$_3$), 11.5 (C*C*H$_3$). ^{31}P{^{1}H} NMR (81 MHz, CD_3COCD_3, 20 °C): δ [ppm] = 30.2 (d, $^1J_{Rh,P}$ = 120.9 Hz, PPh_2).

Synthesis of [Rh(2)$_2$][BF$_4$] (7): $AgBF_4$ (0.062 g, 0.32 mmol) was added to a solution of [Rh(COD)Cl$_2$] (0.079 g, 0.160 mmol) in tetrahydrofuran (20 mL). After filtration of AgCl, 1-[2-(diphenylphosphanyl)ethyl]-3,5-dimethylpyrazole (**2**) (0.221 g, 0.717 mmol) was added to the filtrate solution. The solvent was then removed under vacuum and the yellow-orange residue of complex **7** was washed with pentane and crystallised in a dichloromethane/ether mixture. Yield: 92%. M.p. 147−150 °C (dec.). $C_{39}H_{44}BCl_2F_4N_4P_2Rh$ (891.4) (%): calcd. C 52.55, H 4.98, N 6.29; found C 52.57, H 4.93, N 6.19. IR (KBr): ṽ [cm^{-1}]: 3054 (νC−H_{ar}), 2960−2919 (νC-H_{al}), 1551 (νC=C_{ar}, νC=N_{ar}), 1480−1466 (δCH_{3as}), 1435−1429 (δC=C_{ar}, δC=N_{ar}), 1392−1177 (νC−N), 1098−999 (νB−F), 744−696 (νP−C, δC−H_{oop}). ^{1}H NMR (250 MHz, $CDCl_3$, 20 °C): δ [ppm] = 7.65 (b, 20 H, PPh_2), 5.57 (s, 2 H, CH pyrazole), 4.75 (m, 4 H, CH_2CH$_2$PPh$_2$), 2.70 (m, 4 H, CH$_2$CH_2PPh$_2$), 2.29 (s, 6 H, CCH_3), 1.79 (s, 6 H, CCH_3). ^{13}C{^{1}H} NMR (63 MHz, $CDCl_3$, 20 °C): δ [ppm] = 150.6 (*C*CH_3), 140.6 (*C*CH_3), 135.2−127.8 (PPh_2), 106.7 (CH pyrazole), 47.2 (*C*H$_2$CH$_2$PPh$_2$), 33.5 (d, $^1J_{P,C}$ = 28.0 Hz,

Table 2. Crystal data for compounds [Rh(COD)(**1**)][BF_4] (**3**), [Rh(COD)(**2**)][BF_4] (**4**), and [Rh(**2**)$_2$][BF_4] (**7**)

	3	**4**	**7**
Empirical formula	$C_{17}H_{29}BF_4N_3Rh$	$C_{27}H_{33}BF_4N_2PRh$	$C_{39}H_{44}BCl_2F_4N_4P_2Rh$
Molecular weight [g]	465.15	606.24	891.34
Temperature [K]	293(2)	160(2)	160(2)
Wavelength [Å]	0.71073	0.71073	0.71069
Crystal system	triclinic	monoclinic	monoclinic
Space group	*P*1 bar	$P2_1/n$	$P2_1/n$
a [Å]	7.2584(1)	14.168(1)	10.997(5)
b [Å]	10.872(2)	14.742(1)	18.247(5)
c [Å]	13.297(2)	12.550(11)	20.073(5)
α [deg]	95.55(2)	90	90
β [deg]	104.51(2)	90.55(1)	102.518(5)
γ [deg]	98.66(2)	90	90
Volume [Å^3]	994.3(2)	2621.1(4)	3932(2)
Z	2	4	4
$D_{calcd.}$ [g·cm^{-3}]	1.554	1.536	1.506
μ [mm^{-1}]	0.900	0.760	0.705
F(000)	476	1240	1824
θ range [deg]	3.95−25.97	2.13−26.03	2.20−26.05
Index ranges	$-8 \le h \le 8$	$-17 \le h \le 17$	$-13 \le h \le 13$
	$-13 \le k \le 13$	$-18 \le k \le 18$	$-22 \le k \le 22$
	$-16 \le l \le 16$	$-15 \le l \le 15$	$-24 \le l \le 24$
Reflections collected	9568	20361	30207
Independent reflections	3530 [R_{int} = 0.0528]	5134 [R_{int} = 0.0337]	7643 [R_{int} = 0.0380]
Completeness to θ_{max} (%)	90.5	99.1	98.1
Refinement method	full-matrix least-squares on F^2		
Data/Restraints/Parameters	3530/0/233	5134/0/327	7643/0/482
goodness of fit on F^2	1.084	1.028	1.021
Final *R* indices [$I > 2\sigma(I)$]	*R*1 = 0.0436	*R*1 = 0.0266	*R*1 = 0.0395
	*wR*2 = 0.1220	*wR*2 = 0.0623	*wR*2 = 0.1016
R indices (all data)	*R*1 = 0.0456	*R*1 = 0.0369	*R*1 = 0.0421
	*wR*2 = 0.1281	*wR*2 = 0.0655	*wR*2 = 0.1041
resid. elec. density e[·Å^{-3}]	0.970 and −0.725	0.556 and −0.320	1.536 and −1.151

$CH_2CH_2PPh_2$), 13.4 (CCH_3), 11.3 (CCH_3). $^{31}P\{^1H\}$ NMR (101 MHz, $CDCl_3$, 20 °C): δ [ppm] = 44.9 (d, $^1J_{Rh,P}$ = 171.1 Hz, PPh_2).

Synthesis of [Rh(CO)(2)$_2$][BF_4] (8): [Rh(**2**)$_2$][BF_4] (0.070 g, 0.087 mmol) in dichloromethane (20 mL) was bubbled with carbon monoxide for 1 h and [Rh(CO)(**2**)$_2$][BF_4] was obtained. The complex was characterised in solution after bubbling nitrogen to eliminate dissolved carbon monoxide, as it reverted back to **7** when the solvent was evaporated under vacuum. IR (CH_2Cl_2 solution, CaF_2 cells): ν̃ [cm^{-1}]: 2088 and 2014 (νCO). ^1H NMR (250 MHz, $CDCl_3$, 20 °C): δ [ppm] = 7.96−6.70 (m, 20 H, PPh_2), 5.50 (s, 2 H, CH pyrazole), 4.53 (m, 4 H, $CH_2CH_2PPh_2$), 2.94 (broad, 4 H, $CH_2CH_2PPh_2$), 2.09 (s, 6 H, CCH_3), 1.85 (s, 6 H, CCH_3). $^{13}C\{^1H\}$ NMR (63 MHz, $CDCl_3$, 20 °C): δ [ppm] = 190.1 (broad d, CO, $J_{Rh,C}$ = 72 Hz), 148.8 (CCH_3), 141.5 (CCH_3), 135.4−127.9 (PPh_2), 106.5 (CH pyrazole), 45.9 ($CH_2CH_2PPh_2$), 29.7 (t, $J_{P,C}$ = 12.5 Hz, $CH_2CH_2PPh_2$), 14.0 (CCH_3), 10.97 (CCH_3). $^{31}P\{^1H\}$ NMR (101 MHz, $CDCl_3$, 20 °C): δ [ppm] = 25.8 (d, $^1J_{Rh,P}$ = 122.5 Hz, PPh_2).

X-ray Crystallographic Study: Crystals of **3**, **4**, and **7** suitable for X-ray diffraction were obtained through recrystallisation from dichloromethane/diethylether mixtures. Data were collected at 293 K for **3** and 160 K for **4** and **7** on a STOE IPDS diffractometer. Full crystallographic data for the three complexes are gathered in Table 2. All calculations were performed on a PC-compatible computer using the WinGX system.[26] The structures were solved by using the SIR92 program,[27] which revealed in each instance the position of most of the non-hydrogen atoms. All remaining non-hydrogen atoms were located by the usual combination of full-matrix least-squares refinement and difference electron density syntheses by using the SHELXS-97 program.[28] Atomic scattering factors were taken from the usual tabulations.[29] Anomalous dispersion terms for Rh, and P (for complexes **4** and **7**) were included in F_c.[30] All non-hydrogen atoms were allowed to vibrate anisotropically. All the hydrogen atoms were set in idealised positions [R_3CH, C−H = 0.96 Å; R_2CH_2 = 0.97 Å; $C(sp^2)$−H = 0.93 Å; U_{iso} 1.2 time greater than the U_{eq} of the carbon atom to which the hydrogen atom is attached] and held fixed during refinements.

CCDC-184360 for **3**, 184358 for **4**, and CCDC-184359 for **7** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44−1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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