New *N*-pyrazole, *P*-phosphinite hybrid ligands and corresponding Rh(I) complexes: X-ray crystal structures of complexes with [Rh, N, P-phosphinite, Cl, (CO)] core

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ABSTRACT

Two new *N*-pyrazole, *P*-phosphinite hybrid ligands 3-(3,5-dimethyl-1*H*-pyrazol-1-yl)propyldiphenylphosphinite (**L**^{3}) and 2-(3,5-diphenyl-1*H*-pyrazol-1-yl)ethyldiphenylphosphinite (**L**^{4}) are presented. The reactivity of these ligands and two other ligands reported in the literature (3,5-dimethyl-1*H*-pyrazol-1-yl)methyldiphenylphosphinite (**L**^{1}) and 2-(3,5-dimethyl-1*H*-pyrazol-1-yl)ethyldiphenylphosphinite (**L**^{2}) towards [RhCl(CO)$_2$]$_2$ (**1**) have been studied and complexes [RhCl(CO)**L**] (**L** = L^2 (**2**), L^3 (**3**) and L^4 (**4**)) have been obtained. For **L**^{1} only decomposition products have been achieved. All complexes were fully characterised by analytical and spectroscopic methods and the resolution of the crystalline structure of complexes **2** and **3** by single-crystal X-ray diffraction are also presented. In these complexes, the ligands are coordinated via κ^2(N,P) to Rh(I), forming metallocycles of seven (**2** and **4**) or eight (**3**) members and finish its coordination with a carbonyl monoxide and a *trans*-chlorine to phosphorus atom. In both complexes, weak intermolecular interactions are present. NMR studies of complexes **2–4** show the chain N–(CH$_2$)$_x$–O becomes rigid and the protons diastereotopic.

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1. Introduction

During the last century the interest for the coordination and the organometallic chemistry has increased impressively. The potential applicability of complexes where the metal is coordinated to organic ligands by a heteroatom (N, O, S, P, etc.) has focused the interest of many laboratories [1]. In particular, hybrid ligands (molecules with two or more different hetereoatoms) have been studied for its potential hemilabile properties [2]. Our group has previously reported several functionalized thioether-, amino- and phosphino- containing pyrazole ligands: *NSN* [3], *NSSN* [3a,4], *NN′* [5], *NN′N* [5d,6] and *NP* [5c,7] and has studied their reactivity with Pd(II), Pt(II) and Rh(I). It is well known, ligands contain pyrazole group have been studied extensively in the last decades and it has been used in many fields [8]. Moreover, during the last years the phosphinite group [P(OR)R′$_2$] has experimented an important attention in the coordination chemistry for its capability to modulate electronic and steric properties against phosphines and many utilities has been investigated [9].

Alexandratos et al. have used phosphorylated calixarenes for the selective complexation of metal ions in solution and onto inorganic and organic polymers [9d]. Braunstein et al. focus their studies in the hybrid and sometimes hemilabile ligands and its applicability onto homogenous catalysis. Also, they take a look on new applications like nanomaterials of magnetic and catalytic interest by covalent anchoring of metal complexes and clusters into mesoporous materials also are described [2c]. Mukaiyama et al. have used phosphinites as intermediate species to prepare chiral hydrosulphides, amines, nitriles and isocyanides from easily available chiral alcohols using a condensation reaction with oxidation–reduction [9a]. Finally, it is explored the application of phosphinite complexes in the asymmetric homogeneous catalysis. Recently, Agbossou et al. [9c] and Castillon et al. [9b], and in the 1990s RajanBabu [9e] have presented studies of phosphinite complexes and studies in catalytic reactions.

Following the interest of hybrid ligands, our group has published a paper with the synthesis and characterisation of two new *N*-pyrazole, *P*-phosphinite ligands and its reactivity towards Ru(II) [10]. In this paper we present the synthesis and characterisation of two new *N*-pyrazole, *P*-phosphinite hybrid ligands and study of their coordination towards Rh(I). X-ray crystal structure of two Rh(I) complexes with core [N, P-phosphinite, Cl, (CO)] are presented.

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2. Results and discussion

2.1. Synthesis of the ligands

Ligands (3,5-dimethyl-1*H*-pyrazol-1-yl)methyldiphenylphosphinite (**L**[1]) and 2-(3,5-dimethyl-1*H*-pyrazol-1-yl)ethyldiphenylphosphinite (**L**[2]) were prepared as described in the literature [10]. It is the first time 3-(3,5-dimethyl-1*H*-pyrazol-1-yl)propyldiphenylphosphinite (**L**[3]) and 2-(3,5-diphenyl-1*H*-pyrazol-1-yl)ethyldiphenylphosphinite (**L**[4]) are described. The same route is used for four ligands (Scheme 1). A small excess of freshly distilled triethylamine is added to a dry THF solution of the appropriate pyrazol-alcohol precursor: **L**[1], (3,5-dimethyl-1*H*-pyrazol-1-yl)methanol [11]; **L**[2], 2-(3,5-dimethyl-1*H*-pyrazol-1-yl)ethanol [12]; **L**[3], 3-(3,5-dimethyl-1*H*-pyrazol-1-yl)propanol [13] and **L**[4], 2-(3,5-diphenyl-1*H*-pyrazol-1-yl)ethanol [14]. An equivalent amount of diphenylphosphine chloride is added and the solution is stirred for 12 h. Filtration and evaporation lead an oily product. The ligands **L**[3] and **L**[4] were characterised by elemental analysis, mass spectrometry and IR, ^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H}, COSY, HSQC and NOESY NMR experiments. All of them are in agreement with expected proposed ligands [10,15]. The ^{31}P{^{1}H} NMR shows peaks at δ = 114.3 ppm for **L**[3] and δ = 116.7 ppm for **L**[4] indicate the presence of the phosphinite group [10,16].

2.2. Synthesis and characterisation of the complexes

Treatment of [RhCl(CO)$_2$]$_2$ (**1**) with **L**[2]–**L**[4] ligands in 1 metal/1 ligand ratio in dry CH$_2$Cl$_2$ lead to [RhCl(CO)**L**] (L = L[2] (**2**), L[3] (**3**) and L[4] (**4**)) complexes as a yellow powder with a moderate yield for **2** (43%) and **3** (52%) and a yellowish-brown powder with a good yield for **4** (86%) (Scheme 2 and Section 4). Reaction of **L**[1] with **1** only products of decomposition are detected. The complexes **2**–**4** are air-stable. However, complex **4** is air-sensitive in solution and decomposes after 48 h.

The complexes **2**–**4** were characterised by elemental analysis, mass spectrometry, conductivity measurements, IR and NMR spectroscopies. All NMR experiments were recorded in CDCl$_3$ solution. Elemental analysis of products **2**–**4** are consistent with a formula [RhCl(CO)**L**]. MS–ESI(+) of all compounds gives peaks with *m/z* values of 455 (100%) (**2**), 469 (100%) (**3**) and 579 (100%) (**4**), attributable to [Rh(CO)**L**]$^+$ (**L** = **L**[2], **L**[3] and **L**[4]). Molar conductance of 10^{-3} M solutions of complexes **2**–**4** in acetone shows values between 2 and 17 Ω^{-1} cm^2 mol^{-1}, attributable to non-electrolyte compounds [17]. The IR spectra of **2**–**4** do not show significant differences respect to the free ligands. In complexes **2**–**4** the band v (CO) at 2003 cm^{-1} (**2**), 2003 cm^{-1} (**3**) and 1989 cm^{-1} (**4**) is observed. The ^{1}H, ^{1}H{^{31}P}, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectra and other NMR studies give information about the coordination and disposition of the ligands towards Rh(I). The values of ^{31}P{^{1}H} NMR show phosphorus atom is connected to Rh(I). The spectra show a doublet at δ = 125.9 ppm ($^1J_{RhP}$ = 181.4 Hz) (**2**), δ = 130.9 ppm ($^1J_{RhP}$ = 188.2 Hz) (**3**) and δ = 125.5 ppm ($^1J_{RhP}$ = 178.2 Hz) (**4**). Chemical shifts and coupling constants agree with the values of other Rh, P-phosphinite complexes described in the literature [16]. The ^{1}H and ^{13}C{^{1}H} NMR do not show important differences between the spectra of free ligands and the complexes in the aromatic and methyl regions. However, ^{1}H NMR was studied in detail (^{1}H{^{31}P}, COSY, HSQC and NOESY NMR experiments) to make the assignment of the signals of the chain N–(CH$_2$)$_x$–O. As it can be observed, when the ligands act as κ^2 to the metal the protons of the chain become diastereotopics. Spectrum ^{1}H NMR of **2** shows signals at δ = [6.19 (1H), 4.00 (3H) ppm], spectrum of **3** shows signals at δ = [5.52 (1H), 4.47 (1H), 4.18 (1H), 3.58 (1H), 2.01 (2H) ppm] and spectrum of **4** shows signals at δ = [6.60 (1H), 4.35 (1H), 3.88 (2H) ppm]. HSQC and ^{1}H{^{31}P} NMR experiments show the signals appear at δ = [6.19, 4.00 (**2**); 5.52, 4.18 (**3**); 6.60, 4.35 (**4**) ppm] corresponds to protons N–C*H*$_2$. NOE interaction between the signals at δ = [4.00 (**2**), 4.18 (**3**), 4.35 (**4**) ppm] and methyl linked to the pyrazole is observed. Also, X-ray diffraction of compounds **2** and **3**

L[1]: R=CH$_3$, x=1
L[2]: R=CH$_3$, x=2
L[3]: R=CH$_3$, x=3
L[4]: R= C$_6$H$_5$, x=2

Scheme 1.

[RhCl(CO)**L**] (L = **L**[2]-**L**[4]) (**2-4**)

Scheme 2.

Fig. 1. ORTEP drawing of [RhCl(CO)**L**²] (**2**) showing all non-hydrogen atoms and the atom-numbering scheme; 50% probability amplitude displacement ellipsoid shown.

Fig. 2. ORTEP drawing of [RhCl(CO)**L**³] (**3**) showing all non-hydrogen atoms and the atom-numbering scheme; 50% probability amplitude displacement ellipsoid shown.

2.3. Crystal and molecular structure of complexes 2 and 3

The structures of complexes **2** and **3** are confirmed by single-crystal X-ray diffraction.

ORTEP pictures and selected bonds distances and and angles are shown in Fig. 1 (**2**), Fig. 2 (**3**) and Table 1. The structures of complexes **2** and **3** consist of discrete Rh(I) molecules. The metal is connected to the pyrazole–phosphinite ligands via κ^2(N,P) building a metallocycle ring of seven (**2**) and eight (**3**) members, and finishes its coordination with a carbonyl monoxide and a *trans*-chlorine respect phosphorus atom.

Rh(I) has a slightly distorted square-planar geometry. The distortion of the geometry is observed by the values of distances

Table 1
Selected bond lengths (Å) and angles (°) for **2** and **3**

2		3	
Rh–C(8)	1.805(3)	Rh–C(21)	1.819(3)
Rh–N(1)	2.109(2)	Rh–N(1)	2.125(3)
Rh–P	2.2065(10)	Rh–P	2.2065(11)
Rh–Cl	2.3858(11)	Rh–Cl	2.3811(11)
P–O(2)	1.6260(18)	P–O(1)	1.617(2)
C(8)–Rh–N(1)	176.84(9)	C(21)–Rh–N(1)	174.45(11)
C(8)–Rh–P	92.18(9)	C(21)–Rh–P	93.66(10)
N(1)–Rh–P	90.36(7)	N(1)–Rh–P	86.56(8)
C(8)–Rh–Cl	89.32(9)	C(21)–Rh–Cl	90.87(10)
N(1)–Rh–Cl	88.25(7)	N(1)–Rh–Cl	89.10(8)
O–P–Rh	113.48(7)	O–P–Rh	114.05(9)
C(9)–P–Rh	116.78(9)	C(9)–P–Rh	120.57(10)
C(15)–P–Rh	117.84(9)	C(15)–P–Rh	114.23(10)

between Rh and the main plane N1–P–CO–Cl [0.02 Å (**2**), 0.03 Å (**3**)], the values of Cl–Rh–CO angles [89.32°(9) (**2**), 90.87°(10) (**3**)] and the values of N1–Rh–P bite angles [90.36°(7) (**2**), 86.56°(8) (**3**)]. All of them are in agreement with the ones found in the bibliography [18–20]. The phosphorus atom also differs from the ideal tetrahedral geometry as it can be observed in the values of the O–P–Rh angles [113.48°(7) (**2**), 114.05°(9) (**3**)], C(9)–P–Rh angles [116.78°(9) (**2**), 120.57°(10) (**3**)] and C(15)–P–Rh angles [117.84°(9) (**2**), 114.23°(10) (**3**)].

The bond distances Rh–N [2.109(2) Å (**2**), 2.125(3) Å (**3**)], Rh–Cl [2.3858(11) Å (**2**), 2.3811(11) Å (**3**)] and Rh–CO [1.805(3) Å (**2**), 1.819(3) Å (**3**)] are in agreement with the values described in the literature: Rh–N [2.110–2.200 Å], Rh–Cl [2.372–2.409 Å] and Rh–CO [1.805–1.837 Å] [18–20]. The bond distances Rh–P [2.2065(10) Å (**2**), 2.2065(11) Å (**3**)] are longer than the distances described in the literature: Rh–P [2.154–2.186 Å] [18–20].

As our knowledge it is the first time Rh(I) structures with core: *N,P*-phosphinite [P(OR¹)(R²)₂ where R¹ is an alkylic chain and R² is –C₆H₅], Cl, CO have been described. Similar structures with other phosphinite or phosphorus functional groups have been published previously: phosphite [P(OR)₃] [18], phosphonite [P(OR)₂R] [19] and phosphinite [P(OR¹)(R²)₂ where R¹ is an alkylic or allylic chain and R² is N] [20].

Complex **2** shows weak intermolecular interactions M···H and M=C=O···H typical from organometallic compounds [21]. The distance of Rh···H(19) is 3.133 Å and Rh=C=O···H(11) is 2.582 Å, in agreement with the values observed in the literature: [2.6–3.2 Å] and [2.5–2.6 Å], respectively. Also a non-covalent interaction π–π stacking is presented (Fig. 3). The angle between the centroids formed by the two rings C15–C16–C17–C18–C19–C20 is 0° confirming a perfect face to face interaction. The distance between their centroids is 3.917 Å. Similar values are found in the literature [3.0–4.6 Å] [22]. However, only C16 and C17 build a parallel displaced π–π stacking interaction. The distance between the pair of carbons is 3.362 Å, in agreement with the interval found in the bibliography [3.3–3.8 Å] [22].

In complex **3**, a non-covalent CH···O interaction is observed (Fig. 4). The distance detected between H(5)···O is 2.720 Å [23].

3. Conclusion

The present paper reports the synthesis and characterisation of two new *N*-pyrazole, *P*-phosphinite hybrid ligands (**L**³ and **L**⁴). The reaction of these ligands and two other ligands reported in the literature (**L**¹ and **L**²) towards [RhCl(CO)₂]₂ (**1**) has been studied. Complexes [RhCl(CO)**L**] (**L** = **L**² (**2**), **L**³ (**3**) and **L**⁴ (**4**)) are obtained.

The coordination modes of the ligands (**L**²–**L**⁴) in complexes **2**–**4** do not depend neither on the groups of the pyrazole in 3,5-positions (methyl, phenyl) nor the length of the chain N–(CH₂)ₓ–O

show a short distance between one proton of N–CH_2 and the CH_3(5) moiety [2.578 Å (**2**), 2.193 Å (**3**)] (Figs. 1 and 2). This distance is shorter than the other proton of N–CH_2 against CH_3(5) moiety [3.892 Å (**2**), 3.538 Å (**3**)].

The protons CH_2–O appear at δ = [4.00 (**2**), 4.47 and 3.58 (**3**), 3.88 (**4**)] ppm]. Finally, the protons N–CH₂–CH₂–CH₂–O of **3** appear at δ = 2.01 ppm.
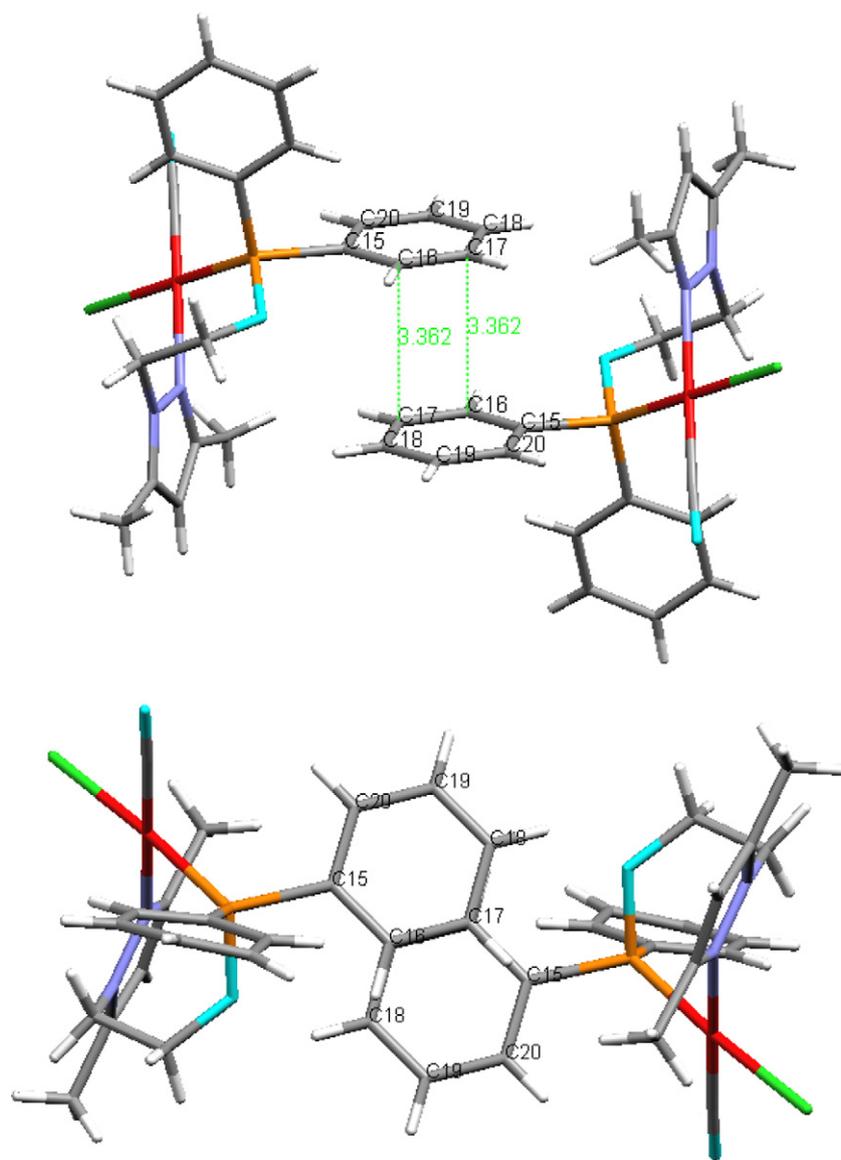
Fig. 3. Two different views from the parallel displaced π–π stacking interactions of [RhCl(CO)**L**^{2}] (**2**).
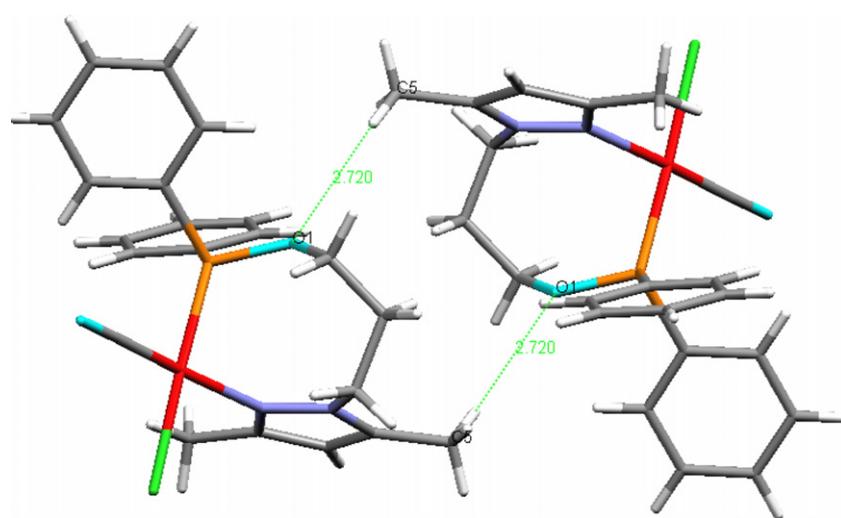
Fig. 4. View of CH···O interactions of complex [RhCl(CO)**L**^{3}] (**3**).

when x = 2, 3. However, when x = 1 (L^1) the formation of the corresponding complex is not observed. Probably, the effect of the ring size does not permit the formation of [RhCl(CO)L^1]. This behaviour has been observed previously in others ligands that contain only one CH$_2$ group between two heteroatoms [4b,4d,24].

Furthermore, few structures have been described in the literature with [Rh, N, P(phosphinite), Cl, (CO)] core. We have contributed with the resolution of the single-crystal X-ray diffraction of two new Rh(I) complexes with this core.

4. Experimental

4.1. General details

All reactions were performed with the use of vacuum line and Schlenk techniques. All reagents were commercial grade and were used without further purification except triethylamine that was purified by distillation in KOH. All solvents were dried and distilled by standard methods. The elementals analysis (C, H, N) were carried out by the staff of the Chemical Analyses Service of the Universitat Autònoma de Barcelona on a Carlo Erba CHNS EA-1108 instrument separated by chromatographic column and termoconductivity detector. Conductivity measurements were performed at room temperature in 10^{-3} M acetone solutions employing a CyberScan CON 500 (Eutech instrument) conductimeter. Infrared spectra were run on a Perkin–Elmer FT-2000 spectrophotometer as KBr pellets in solid samples and with NaCl mulls in oily samples. The ^{1}H, ^{1}H{^{31}P}, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectra and COSY, HSQC and NOESY NMR spectra were run on a NMR-FT Bruker AC-250 spectrometer and on an Advance DRX500. All NMR experiments were recorded on CDCl$_3$ solvent under nitrogen. ^{1}H, ^{1}H{^{31}P} and ^{13}C{^{1}H} NMR chemical shifts (δ) were determined relative to internal TMS and are given in ppm. ^{31}P{^{1}H} NMR chemical shifts (δ) were determined relative to external 85% H$_3$PO$_4$ and are given in ppm. Electrospray Mass spectra (ESI+) were carried out by the staff of the Chemical Analysis Service of the Universitat Autònoma de Barcelona on an Esquire 3000 ion trap mass spectrometer from Bruker Daltonics. Mass experiments of the ligands were done on CH$_3$CN, CH$_3$OH or CH$_3$CN/CH$_3$OH solvents. Mass spectra of the complexes were done on CH$_3$CN/CHCl$_3$ solvents. The precursor complex [RhCl(CO)$_2$]$_2$ (1) is commercially available. The (3,5-dimethyl-1H-pyrazol-1-yl)-methanol, 2-(3,5-dimethyl-1H-pyrazol-1-yl)ethanol, 3-(3,5-dimethyl-1H-pyrazol-1-yl)propanol and 2-(3,5-diphenyl-1H-pyrazol-1-yl)ethanol were prepared as described in the literature [11–14]. The (3,5-dimethyl-1H-pyrazol-1-yl)methyldiphenylphosphinite (L^1) and 2-(3,5-dimethyl-1H-pyrazol-1-yl)ethyldiphenylphosphinite (L^2) ligands were prepared as described in the literature [10].

4.2. Synthesis of the ligands

4.2.1. Synthesis of 3-(3,5-dimethyl-1H-pyrazol-1-yl)propyldiphenylphosphinite (L^3)

A solution of 3-(3,5-dimethyl-1H-pyrazol-1-yl)propanol (6.48 mmol, 1.00 g) and triethylamine (6.78 mmol, 0.95 mL) in 20 mL of dry THF was prepared. PPh$_2$Cl (6.51 mmol, 1.23 mL) dissolved in 10 mL of dry THF was slowly added at room temperature and the mixture was stirred for 12 h. The triethylammonium chloride was formed and filtered off. Evaporation of the solvent in vacuum gave L^3 as yellowish-brown oil (yield: 97%, 2.12 g). Anal. Calc. for C$_{20}$H$_{23}$N$_2$OP: C, 70.99; H, 6.85; N, 8.28. Found: C, 70.55; H, 6.44; N, 8.31%. MS (ESI$^+$): m/z (%) 345 (100%) [L^3Li]$^+$, 137 (83%) [pz-CH$_2$CH$_2$CH$_2$]$^+$. IR: (NaCl, cm^{-1}) 3054 ν(C–H)$_{ar}$, 2949, 2928 ν(C–H)$_{al}$, 1552 ν(C=C/C=N)$_{ar}$, 1480, 1435 δ(C=C/C=N)$_{ar}$, 1048 ν(P–O–C), 740, 697 δ(C–H)$_{oop}$. ^{1}H NMR (CDCl$_3$ at 298 K, 250 MHz)

δ: 7.78–7.10 (m, 10H, C$_6$H$_5$), 5.66 (s, 1H, pz-CH), 3.97 (t, 2H, $^3J_{HH}$ = 7.1 Hz, pz-CH$_2$–CH$_2$–CH$_2$–O), 3.77 (dt, 2H, $^3J_{PH}$ = 8.6 Hz, $^3J_{HH}$ = 5.9 Hz, pz-CH$_2$–CH$_2$–CH$_2$–O), 2.12 (s, 3H, pz-CH$_3$), 2.10 (m, 2H, pz-CH$_2$–CH$_2$–CH$_2$–O), 2.04 (s, 3H, pz-CH$_3$) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$ at 298 K, 63 MHz) δ: 147.8 (pz-CCH$_3$), 142.2 (d, $^1J_{PC}$ = 18.2 Hz, O–P–C$_6$H$_5$), 139.3 (pz-CCH$_3$), 134.3 (d, $^1J_{PC}$ = 16.8 Hz, O–P–C$_6$H$_5$), 132.9–128.1 (C$_6$H$_5$), 105.1 (pz-CH), 67.4 (d, $^2J_{PC}$ = 19.7 Hz, pz-CH$_2$CH$_2$CH$_2$–O), 45.5 (pz-CH$_2$CH$_2$CH$_2$–O), 32.4 (d, $^3J_{PC}$ = 7.7 Hz, pz-CH$_2$CH$_2$CH$_2$–O), 13.9 (pz-CH$_3$), 11.3 (pz-CH$_3$) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$ at 298 K, 81 MHz) δ: 114.3 (s, O–P–(C$_6$H$_5$)$_2$) ppm.

4.2.2. Synthesis of 2-(3,5-diphenyl-1H-pyrazol-1-yl)ethyldiphenylphosphinite (L^4)

Ligand L^4 is prepared analogously L^3 using 2-(3,5-diphenyl-1H-pyrazol-1-yl)ethanol (3.78 mmol, 1.00 g), triethylamine (4.00 mmol, 0.56 mL) and PPh$_2$Cl (3.81 mmol, 0.72 mL). L^4 was obtained as brownish-green oil (yield: 65%, 1.10 g). Anal. Calc. for C$_{29}$H$_{25}$N$_2$OP: C, 77.66; H, 5.62; N, 6.25. Found: C, 77.53; H, 5.89; N, 6.24%. MS (ESI$^+$): m/z (%) 449 (100%) [L^4H]$^+$, 247 (48%) [pz-CH$_2$CH$_2$ + H$^+$]. IR: (NaCl, cm^{-1}) 3055 ν(C–H)$_{ar}$, 2939 ν(C–H)$_{al}$, 1550 ν(C=C/C=N)$_{ar}$, 1482, 1435 δ(C=C/C=N)$_{ar}$, 1041 ν(P–O–C), 739, 695 δ(C–H)$_{oop}$. ^{1}H NMR (CDCl$_3$ at 298 K, 250 MHz) δ: 7.81–7.62 (d, $^3J_{HH}$ = 7.7 Hz, 2H, ortho-C$_6$H$_5$), 7.55–7.10 (m, 8H, C$_6$H$_5$), 6.50 (s, 1H, pz-CH), 4.33 (m, 2H, pz-CH$_2$–CH$_2$–O), 4.20 (m, 2H, pz-CH$_2$–CH$_2$–O) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$ at 298 K, 63 MHz) δ: 151.4 (pz-CCH$_3$), 146.1 (pz-CCH$_3$), 135.9 (d, $^1J_{PC}$ = 7.2 Hz, C$_6$H$_5$), 135.6 (d, $^1J_{PC}$ = 7.2 Hz, C$_6$H$_5$), 132.2–125.9 (C$_6$H$_5$), 103.9 (pz-CH), 67.0 (d, $^2J_{PC}$ = 18.7 Hz, pz-CH$_2$CH$_2$–O), 50.7 (d, $^3J_{PC}$ = 8.6 Hz, pz-CH$_2$CH$_2$–O) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$ at 298 K, 81 MHz) δ: 116.7 (s, O–P–(C$_6$H$_5$)$_2$) ppm.

4.3. Synthesis of the complexes

4.3.1. Complexes [RhCl(CO)L] (L = L^2 (2), L^3 (3) and L^4(4))

The appropriate ligand (0.180 mmol: L^1, 0.056 g; L^2, 0.058 g; L^3, 0.061 g; L^4, 0.081 g), dissolved in dry CH$_2$Cl$_2$ (6 mL) was added to a solution of the rhodium complex [RhCl(CO)$_2$]$_2$ (1) (0.090 mmol, 0.035 g) in dry CH$_2$Cl$_2$ (6 mL). The solutions changed to a slightly yellowish-green colour immediately after the addition. After 12 h the solutions were yellowish-brown in the reactions of L^1, L^2 and L^3 and brown in L^4. The resulting solutions were concentrated till 5 mL. Cold diethyl ether was added dropwise to the solution of L^1, L^2 and L^3 to obtain a yellow pure solid. Hexane was added to the solution of L^4 to obtain a yellowish-brown pure solid.

The NMR spectra indicates [RhCl(CO)L] for L^2 (2), L^3 (3) and L^4 (4) were obtained. In the reaction of L^1 with [RhCl(CO)$_2$]$_2$ (1) only products of decomposition of the ligand were observed (yields: 43%, 0.038 g (2), 52%, 0.047 g (3), 86%, 0.095 g (4)).

4.3.1.1. [RhCl(CO)L^2] (2).
Anal. Calc. for C$_{20}$H$_{21}$N$_2$O$_2$PClRh: C, 48.95; H, 4.31; N 5.71. Found: C, 48.63; H, 4.08; N, 5.73%. Conductivity (1.04 × 10^{-3} M in acetone): 2 Ω^{-1} cm^2 mol^{-1}. MS (ESI$^+$): m/z (%) 455 (100%) [Rh(CO)L^2]$^+$. IR: (KBr, cm^{-1}) 3055 ν(C–H)$_{ar}$, 2915, 2878 ν(C–H)$_{al}$, 2003 ν(CO), 1550 ν(C=C/C=N)$_{ar}$, 1469, 1432 δ(C=C/C=N)$_{ar}$, 1052 ν(P–O–C), 724, 699 δ(C–H)$_{oop}$. ^{1}H NMR (CDCl$_3$ at 298 K, 250 MHz): δ = 7.86–7.27 (m, 10H, C$_6$H$_5$), 6.19 (m, 1H, pz-CH$_2$CH$_2$–O), 5.81 (s, 1H, pz-CH), 4.00 (m, 3H, pz-CH$_2$–CH$_2$–O), 2.23 (s, 3H, pz-CH$_3$), 2.15 (s, 3H, pz-CH$_3$) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$ at 298K, 63 MHz) δ: 151.6 (pz-CCH$_3$), 140.6 (pz-CCH$_3$), 133.5–128.7 (C$_6$H$_5$), 108.8 (pz-CH), 64.2 (d, $^2J_{PC}$ = 3.5 Hz, pz-CH$_2$CH$_2$–O), 48.0 (d, $^3J_{PC}$ = 5.2 Hz, pz-CH$_2$CH$_2$–O), 15.0 (pz-CH$_3$), 11.6 (pz-CH$_3$) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$ at 298 K, 81 MHz) δ: 125.9 (d, $^1J_{RhP}$ = 181.4 Hz, O–P–(C$_6$H$_5$)$_2$) ppm.

4.3.1.2. [RhCl(CO)L^3] (3).
Anal. Calc. for C$_{21}$H$_{23}$N$_2$O$_2$PClRh: C, 49.97; H, 4.59; N, 5.55. Found: C, 49.75; H, 4.52; N, 5.57%. Conductivity

(9.71 × 10^{-4} M in acetone): 2 Ω^{-1} cm^2 mol^{-1}. MS (ESI$^+$): m/z (%) 469 (100%) [Rh(CO)L^3]$^+$. IR: (KBr, cm^{-1}) 3050 ν(C–H)$_{ar}$, 2959, 2945, 2915 ν(C–H)$_{al}$, 2003 ν(CO), 1555 ν(C=C/C=N)$_{ar}$, 1437 δ(C=C/C=N)$_{ar}$, 1055 ν(P–O–C), 746, 701 δ(C–H)$_{oop}$. ^{1}H NMR (CDCl$_3$ at 298 K, 250 MHz) δ: 7.66–7.26 (m, 10H, C$_6$H$_5$), 5.66 (s, 1H, pz-CH), 5.52 (m, 1H, pz–CH_2–CH$_2$–CH$_2$–O), 4.47 (m, 1H, pz-CH$_2$–CH$_2$–CH_2–O), 4.18 (m, 1H, pz-CH_2–CH$_2$–CH$_2$–O), 3.58 (m, 1H, pz-CH$_2$–CH$_2$–CH_2–O), 2.15 (s, 3H, pz-CH_3), 2.08 (s, 3H, pz-CH_3), 2.01 (m, 2H, pz-CH$_2$–CH_2–CH$_2$–O) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$ at 298 K, 63 MHz) δ: 150.5 (pz-CCH$_3$), 141.4 (pz-CCH$_3$), 132.7–128.1 (C$_6$H$_5$), 108.4 (pz-CH), 66.0 (d, $^2J_{PC}$ = 1.2 Hz, pz-CH$_2$CH$_2$CH$_2$–O), 49.1 (pz-CH$_2$CH$_2$CH$_2$–O), 32.3 (d, $^3J_{PC}$ = 2.5 Hz, pz-CH$_2$CH$_2$CH$_2$–O), 14.7 (pz-CH$_3$), 12.0 (pz-CH$_3$) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$ at 298 K, 81 MHz) δ: 130.9 (d, $^1J_{RhP}$ = 188.2 Hz, O–P–(C$_6$H$_5$)$_2$) ppm.

4.3.1.3. [RhCl(CO)L^4] (4). Anal. Calc. for C$_{30}$H$_{25}$N$_2$O$_2$PClRh: C, 58.60; H, 4.10; N, 4.56. Found: C, 58.52; H, 4.48; N, 4.34%. Conductivity (1.02 × 10^{-3} M in acetone): 17 Ω^{-1} cm^2 mol^{-1}. MS (ESI$^+$): m/z (%) 579 (100%) [Rh(CO)L^4]$^+$. IR: (KBr, cm^{-1}) 3056 ν(C–H)$_{ar}$, 2955 ν(C–H)$_{al}$, 1989 ν(CO), 1552 ν(C=C/C=N)$_{ar}$, 1436 δ(C=C/C=N)$_{ar}$, 1029 ν(P–O–C), 764, 696 δ(C–H)$_{oop}$. ^{1}H NMR (CDCl$_3$ at 298 K, 250 MHz) δ: 7.92–7.85 (m, 2H, *ortho*-C$_6$H$_5$), 7.85–7.60 (m, 8H, C$_6$H$_5$), 6.60 (m, 1H, pz-CH_2CH$_2$–O), 6.50 (s, 1H, pz-CH), 4.35 (dd, 1H, $^2J_{HH}$ = 15.0 Hz, $^3J_{HH}$ = 3.5 Hz, pz-CH_2–CH$_2$–O), 3.88 (m, 2H, pz-CH$_2$–CH_2–O) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$ at 298 K, 63 MHz) δ: 154.6 (pz-CC$_6$H$_5$), 146.5 (pz-CC$_6$H$_5$), 136.3-128.0 (C$_6$H$_5$), 108.2 (pz-CH), 64.9 (pz-CH$_2$CH$_2$–O), 49.7 (d, $^3J_{PC}$ = 4.7 Hz, pz-CH$_2$CH$_2$–O) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$ at 298 K, 81 MHz) δ: 125.5 (d, $^1J_{RhP}$ = 178.2 Hz, O–P–(C$_6$H$_5$)$_2$) ppm.

4.4. X-ray crystal structures for complexes **2** and **3**

Suitable crystals for X-ray diffraction of compounds [RhCl(CO)**L**] (**L** = **L^2** (**2**) and **L^3** (**3**)) were obtained by slow diffusion of a CH$_2$Cl$_2$/diethylether solution in 1:2 ratio. Prismatic crystals were selected and mounted on a MAR 345 diffractometer with an image plate detector. Unit cell parameters were determined from 6566 reflections for **2** and 2078 reflections for **3** (3 < θ < 31°) and refined by least-squares method. Intensities were collected with graphite monochromatized Mo Kα radiation. 7173 reflections were measured in the range 3.21 ⩽ θ ⩽ 29.09 for **2** which 3790 were non-equivalent by symmetry (R_{int} (on I) = 0.026). Three thousand six hundred and ninety three reflections were assumed as observed applying the condition $I > 2\sigma(I)$. Ten thousand and five hundred and six reflections were measured in the range 3.02 ⩽ θ ⩽ 29.98 for **3** which 5427 were non-equivalent by symmetry (R_{int} (on I) = 0.043). Five thousand and four hundred and seventeen reflections were assumed as observed applying the condition $I > 2\sigma(I)$. Lorentz-polarization but no absorption corrections were made.

For **2** and **3**, the structure was solved by direct methods, using SHELXS-97 computer program [25] and refined by full-matrix least-squares method with SHELXL-97 computer program [26], using 7173 reflections for **2** and 10506 for **3**. The function minimised was $\sum w||F_o|^2 - |F_c|^2|^2$, where $w = [\sigma^2(I) + (0.0617P)^2 + 0.1036P]^{-1}$, and $P = (|F_o|^2 + 2|F_c|^2)/3$ for **2** and $w = [\sigma^2(I) + (0.0232P)^2 + 0.8872P]^{-1}$, and $P = (|F_o|^2 + 2|F_c|^2)/3$ for **3**. All H atoms were computed and refined, using a riding model, with an isotropic temperature factor equal to 1.2 times the equivalent temperature factor of the atom which is linked.

The parameters refined and other details concerning the refinement of the crystal structures are gathered in Table 2.

Table 2
Crystallographic data for [RhCl(CO)**L^2**] (**2**) and [RhCl(CO)**L^3**] (**3**)

	2	**3**
Formula	C$_{20}$H$_{21}$N$_2$O$_2$PClRh	C$_{21}$H$_{23}$N$_2$O$_2$PClRh
Formula weight	490.72	504.74
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
System, space group	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$
Unit cell dimensions		
a (Å)	8.321(4)	10.996(5)
b (Å)	11.549(4)	11.003(4)
c (Å)	11.655(9)	11.120(4)
α (°)	111.09(2)	67.47(3)
β (°)	97.21(2)	61.46(3)
γ (°)	93.66(2)	75.97(3)
U (Å^3)	1029.5(10)	1088.8(8)
Z	2	2
D_{calc} (g cm^{-3})	1.583	1.540
μ (mm^{-1})	1.054	0.999
$F(000)$	496	512
Crystal size (mm^3)	0.2 × 0.1 × 0.1	0.2 × 0.1 × 0.1
Crystal colour	Yellow	Yellow
hkl ranges	−10 ⩽ h ⩽ 10, −13 ⩽ k ⩽ 14, −14 ⩽ l ⩽ 14	−15 ⩽ h ⩽ 15, −14 ⩽ k ⩽ 13, −14 ⩽ l ⩽ 13
2θ Range (°)	3.21–29.09	3.02–29.98
Reflections collected/unique [R_{int}]	7173/3790 [0.0266]	10506/5427 [0.0434]
Completeness to θ (%)	68.7 (θ = 29.09°)	85.5 (θ = 29.98)
Absorption correction	None	None
Data/restrains/parameters	3790/3/247	5427/0/253
Goodness-of-fit on F^2	1.308	1.265
Final R indices [$I > 2 \sigma(I)$]	R_1 = 0.0394, wR_2 = 0.0978	R_1 = 0.0358, wR_2 = 0.0860
R indices (all data)	R_1 = 0.0400, wR_2 = 0.0981	R_1 = 0.0358, wR_2 = 0.0860
Largest difference in peak and hole (e Å^{-3})	0.933 and −0.816	0.471 and −0.442

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