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Rhodium complexes containing the hybrid *P*,*O* ligand $PPh_2NHC(O)Me$ or its anion, $[PPh_2N{\cdots}C({\cdots}O)Me]^-$ †

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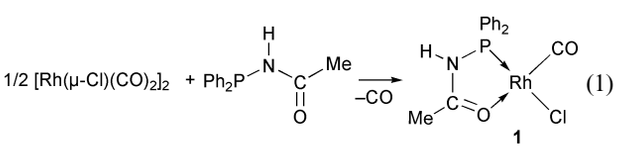
The coordination behaviour of the heterofunctional phosphine ligand $PPh_2NHC(O)Me$ towards Rh(I) is reported and examples of neutral and cationic complexes containing mono- or bi-dentate modes of coordination are found. The X-ray structure of $[Rh\{PPh_2NHC(O)Me\}(CO)Cl]\cdot CH_2Cl_2$ (**1**·CH_2Cl_2) shows that the *P*,*O*-chelate is almost planar and coplanar with the Rh(I) square-plane. An unusual example of coordination is found in the dimer $[Rh\{\mu\text{-}PPh_2N{\cdots}C({\cdots}O)Me\}(CO)]_2$ (**2**), which contains the bidentate, anionic ligand that bridges two rhodium atoms *via* the oxygen; it is probable that the neutral ligand can form similar complexes, such as **11** and **12**. Displacement of the *P*,*O* ligand by CO or RNC ligands occurs in **1** but not in **2**.

Introduction

The continuing interest in the coordination behaviour of new functional ligands applies in particular to phosphines, which are ubiquitous in coordination and organometallic chemistry, and various systems have been studied, in particular those which combine a soft phosphine moiety with a hard oxygen functionality.[1–3] Their asymmetry may be of interest for the occurrence of hemilability and for allowing a stereo-electronic control of the active metal centre. For example, the ketophosphine ligand $PPh_2CH_2C(O)Ph$ readily displays hemilabile behaviour in Ru(II) and Rh(III) complexes.[4,5] We recently began to study the coordination properties of ligands of the type $PPh_n\{NHC(O)CH_3\}_{3-n}$ (n = 1, 2),[6] *i.e.* acetamido anologues of the ketophosphines $PPh_n\{CH_2C(O)R'\}_{3-n}$.[7] Modifications of the chelating ability and of the hemilabile behaviour were anticipated, owing to the different electronic influences of the NH- and CH_2-groups and to changes in the P–N–C *versus* P–C–C bond angle in the α-position to the P atom.[8] Furthermore, deprotonation of the NH group should be easy and lead to anionic chelating ligands related to the phosphinoenolates obtained from the corresponding ketophosphines, whose square-planar Rh(I) complexes catalyse the activation of alkanes by transfer-hydrogenation.[9] We report here investigations on the coordination properties of the acetamide-derived ligand $PPh_2NHC(O)Me$ in Rh(I) complexes.

Results and discussion

Slow addition of a dichloromethane solution of $PPh_2NHC(O)Me$ (P,O)‡ to a solution of $[Rh(\mu\text{-}Cl)(CO)_2]_2$ in dichloromethane results in CO evolution and formation of **1**, [eqn. (1)].



(1)

1

The $^{31}P\{^1H\}$ NMR spectrum of **1** in dichloromethane is unchanged over the temperature range 293–193 K and consists of a doublet (δ_P 104.8, $^1J_{RhP}$ 174 Hz); the large downfield shift of the phosphorus resonance from that of the free phosphine ($\Delta\delta_P$ *ca.* +80 ppm) is consistent with the formation of a five-membered chelate ring. The IR spectrum supports the presence of a carbonyl group [ν(C≡O) 1997 cm^{-1} (CH_2Cl_2); 1990 cm^{-1} (KBr)]. Chelation of the amide group *via* the oxygen atom results in a shift of ν(C=O) from 1714 cm^{-1} (free ligand) to 1579 cm^{-1}.

In order to confirm the structure of **1** in solution, the reaction in eqn. (1) was carried out with $[Rh(\mu\text{-}Cl)(^{13}CO)_2]_2$ (100% ^{13}CO). In this case, the $^{31}P\{^1H\}$ NMR shows additional coupling ($^2J_{PC}$ 17.9 Hz) and the carbonyl resonance in the $^{13}C\{^1H\}$ NMR spectrum is a doublet of doublets (δ_C 187, $^1J_{RhC}$ 77.4, $^2J_{PC}$ 18 Hz); the low value of $^2J_{PC}$ is entirely consistent with CO being *cis* to the phosphorus. The broad (in $CDCl_3$) N–H resonance (δ_H 10.5) at room temperature is 4 ppm downfield from the free ligand and in the range observed for Pd(II) complexes containing this chelating ligand.[6] This is consistent with electron withdrawal from the ligand on coordination.

Single crystals of **1**·CH_2Cl_2, suitable for X-ray analysis, were grown by slow diffusion of THF/diethyl ether (1 : 3) into a solution of **1** in dichloromethane. A view of the structure is shown in Fig. 1 and is entirely consistent with the solution

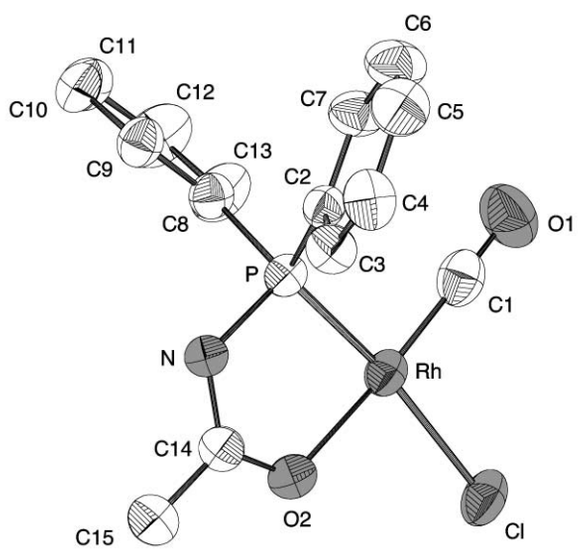


Fig. 1 Molecular geometry of [Rh(*P*,*O*)(CO)Cl] (**1**). The H atoms, including the NH atom, are not shown for clarity. Thermal ellipsoids correspond to 50% probability.

† Dedicated to Dr Jean-Marie Basset on the occasion of his 60th birthday, with our congratulations and best wishes.
‡ Abbreviations used: free ligand, P,O; monodentate coordination through P: *P*,O; bidentate coordination through P and O: *P*,*O*.

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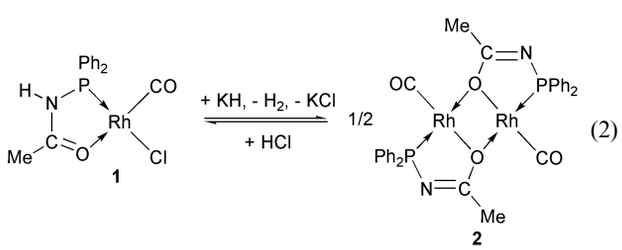
Table 1 Selected intramolecular bond distances (Å) and angles (°) for [Rh(*P*,*O*)(CO)Cl]·CH_2Cl_2 (**1**·CH_2Cl_2)

Rh–Cl	2.372(1)	Rh–C(1)	1.794(7)
Rh–P	2.180(1)	Rh–O(2)	2.094(4)
C(1)–O(1)	1.155(7)	C(14)–O(2)	1.265(6)
N–C(14)	1.337(6)		
Cl–Rh–C(1)	95.6(2)	Cl–Rh–P	170.88(6)
Cl–Rh–O(2)	88.2(1)	C(1)–Rh–P	93.1(2)
C(1)–Rh–O(2)	176.2(2)	P–Rh–O(2)	83.1(1)
N–C(14)–O(2)	120.9(5)	P–N–C(14)	118.0(4)

structure. The chelating ligand forms a five-membered ring with the metal in which the P–N–C–O moiety is almost planar and coplanar with rhodium, which adopts a slightly distorted square-planar geometry. The bite angle of 83.1° is comparable to those found for other Rh(I) complexes containing the chelating ketophosphine $PPh_2CH_2C(O)Ph$.[9] The O(2)–C(14) bond distance in the chelate ring [1.265(6) Å] is shorter than a single C–O bond distance. These values also compare with those found in the Pd(II) complexes 80.5(1) and 1.244(7) Å, respectively.[6] The values of the bond distances around the Rh centre are in agreement with those found for analogous neutral Rh(I) carbonyl complexes and selected bond distances and angles are given in Table 1.

The N–H proton in **1** can be removed by addition of a source of hydride. Thus, on addition of a suspension of **1** in THF to a suspension of KH or NaH in THF, the colour changes from orange to give a new brown/black complex, **2**. In the ^1H NMR spectrum of **2**, there is no evidence for the N–H proton and elemental analysis shows the absence of chloride. The formation of **2** is completely reversible and addition of HCl to a solution of **2** in CH_2Cl_2 results in reformation of **1**. The mass spectrum (FAB) of **2** suggests a dimeric formulation [eqn. (2)] but all attempts to obtain crystals of **2**, suitable for X-ray analysis, failed.



(2)

Spectroscopic data (Table 2) are entirely in agreement with the above formulation of **2**. The $^{31}P\{^1H\}$ NMR spectrum of **2** in CH_2Cl_2 consists of a doublet (δ_P 114.2, $^1J_{RhP}$ 153 Hz) and $^{103}Rh\{^{31}P\}$ HMQC measurements show only one ^{103}Rh resonance (δ_{Rh} −68). Consistent with the presence of the anionic ligand, the value of ν(C≡O), compared to **1**, shifts to lower frequency, 1965 cm^{-1}, and this increased electron density is also delocalised over the coordinated amidate group [ν(C···N) + ν(C···O) 1465 cm^{-1}].

These spectroscopic data are in agreement with the values found for related rhodium carbonyl dimers containing phosphinothiolate ligands *e.g.* $[Rh(SC_6H_4PPh_2\text{-}\kappa^2P,S)(CO)]_2$ (**3**) (δ_P 60.5, $^1J_{RhP}$ 158 Hz, ν(C≡O) 1946 cm^{-1}) and $[Rh(SCH_2CH_2PPh_2\text{-}\kappa^2P,S)(CO)]_2$ **4** (δ_P 63.7, $^1J_{RhP}$ 158 Hz, ν(C≡O) 1947 cm^{-1}). The methods of preparation of **2**, **3** and **4** are similar and involve the reaction of the appropriate ligand with $[Rh(\mu\text{-}Cl)(CO)_2]_2$ in the presence of a base. It should be noted that **3** and **4** have been shown to be four times more active in catalysing the carbonylation of MeOH than the well-known catalyst $[RhI_2(CO)_2]^-$.[10]

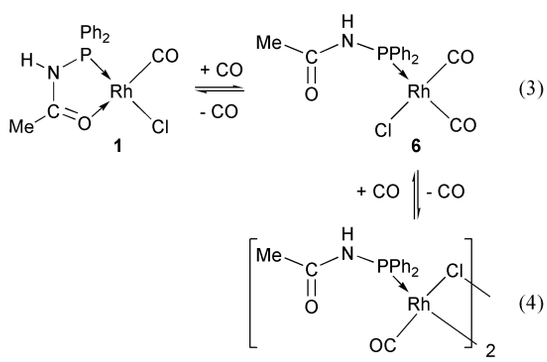
Although the exact catalytic mechanism for the carbonylation of MeOH by **3** and **4** is still unclear, the formation of a mononuclear species [Rh(*P*,*S*)(CO)I], (**5**) (*P*,*S* = $SC_6H_4PPh_2$ or $SCH_2CH_2PPh_2$), analogous to **1**, is likely to be involved but catalytic experiments using **1** have not yet been carried out.

Table 2 $^{31}P\{^1H\}$ NMR data (CD_2Cl_2 unless otherwise stated) for $PPh_2NHC(O)Me$ and related Rh(I) complexes

Compound	δ_P (ppm)	$^1J_{RhP}$/Hz	*Trans*-group
Free P,O	30.4 (minor) 22.3 (major)[a]		
Monodentate *P*,O			
6	49.5	127	CO
7	49.7	126	PPh_3
8	53.3	128	CNR
9	55.1	130	CNR
Bidentate *P*,*O*/neutral			
1	104.8	174	Cl
2	114.2	153	O-bridge
Chelating *P*,*O*/cationic			
11	109.2	181	O-bridge
12	109.0	184	O-bridge
13	94.6	156	PPh_3
14	93.3	129	PPh_3
15	81.9	122	P (*P*,*O*)

[a] At room temperature, there are two resonances due to the keto/iminol equilibrium.

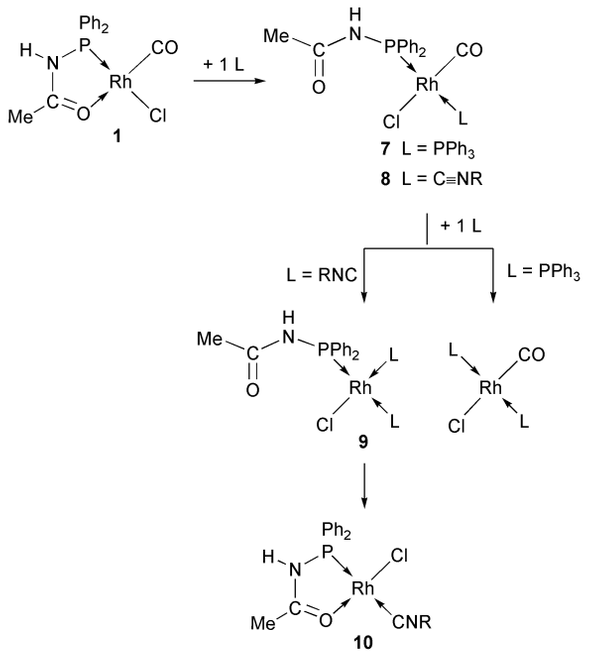
The reaction of **1** with CO to give **6** is completely reversible [eqn. (3)]. The IR spectrum of **6** in CH_2Cl_2 solution, under an atmosphere of CO, shows two strong ν(C≡O) bands (2020 and 1996 cm^{-1}), consistent with the proposed *cis*-geometry. The value of ν(C=O) for the amide group (1708 cm^{-1}) is close to that of the free ligand, in-keeping with monodentate coordination of the ligand. Consistent with the opening of the chelate ligand in **1**, there is a large high field shift ($\Delta\delta_P$ *ca.* −55 ppm) of the phosphorus resonance for **6** (δ_P 49.5, $^1J_{RhP}$ = 127 Hz).



(3)
(4)

The structure of **6** in solution has been unambiguously established by carrying out the reaction of **1** with ^{13}CO (100% ^{13}CO). The $^{31}P\{^1H\}$ NMR spectrum of **6** (100% ^{13}CO) at 193 K shows additional couplings, ($^2J_{PC\,trans}$ *ca.* 122, $^2J_{PC\,cis}$ *ca.* 7 Hz) and, on increasing the temperature, the resonance broadens (coalescence temperature 213 K, $\Delta G^{\#}$ = 41.6 KJ mol^{-1}) but there is little change in the chemical shift. It is thus unlikely that this broadening results from an equilibrium involving a mono-/bi-dentate interconversion of the P,O ligand and we presently favour an equilibrium involving a monomer/chloro-bridged dimer, through loss of CO, with retention of the monodentate P,O ligand [eqn. (4)].

Reaction of **1** with other ligands, such as PPh_3, RNC (R = 2,6-$Me_2C_6H_4$), is related but different to that observed with CO (see Scheme 1). The $^{31}P\{^1H\}$ NMR spectrum of **7** shows two sets of doublets of doublets due to the inequivalent P atoms, *P*,O ($\delta_{P(A)}$ 49.7, $^1J_{RhP(A)}$ 126, $^2J_{P(A)P(B)}$ 356 Hz) and PPh_3 ($\delta_{P(B)}$ 27.4, $^1J_{RhP(B)}$ 122, $^2J_{P(A)P(B)}$ 356 Hz); the large value of $^2J_{P(A)P(B)}$



Scheme 1

unambiguously confirms the *trans* arrangement of the two phosphine groups and the shift to high field (compared to **1**) is consistent with a monodentate *P*,O ligand.

Further addition of PPh_3 to **7** results in displacement of the P,O ligand and formation of *trans*-$[Rh(PPh_3)_2(CO)Cl]$; this reaction can be reversed, but in order to completely reverse the reaction, it is necessary to add excess P,O ligand.

Complex **8** is formed on addition of RNC to **1** (Scheme 1) and the $^{31}P\{^1H\}$ NMR data (δ_P 53.3, $^1J_{RhP}$ 128 Hz) are similar to those found for **6** and **7**. The low value of $^1J_{RhP}$ thus appears to be typical of phosphorus *trans* to π-acceptor ligands such as PPh_3, CO or RNC.

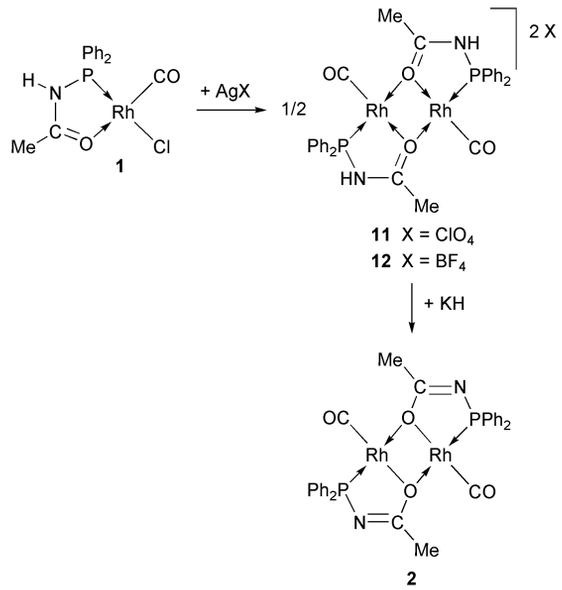
The IR spectrum of **8** (CH_2Cl_2) shows two absorptions at 2001 and 2158 cm^{-1} ascribed to ν(C≡O) and ν(C≡N), respectively. Further addition of one molar equivalent of RNC to **8** results in the formation of **9** with the disappearance of the ν(C≡O) band and the phosphorus resonance remains in the monodentate *P*-bonded region (δ_P 55.1, $^1J_{RhP}$ 130 Hz); the IR spectrum (KBr) has two strong ν(C≡N) bands at 2126 and 2098 cm^{-1}, consistent with the *cis*-arrangement of the RNC ligands. Complex **9** is not stable in $CHCl_3$ or CH_2Cl_2 solution and, after 1 day, a new complex is formed, [δ_P 88.7, $^1J_{RhP}$ 91.5 Hz; ν(C≡N) 2150 cm^{-1}], which is formulated as **10** (Scheme 1). However, we have not been able to isolate a pure complex from these solutions.

Halide abstraction and formation of the cationic dimeric complexes **11** and **12** occurs on addition of $AgClO_4$ and $AgBF_4$ to a solution of **1** in CH_2Cl_2 and THF, respectively (Scheme 2).

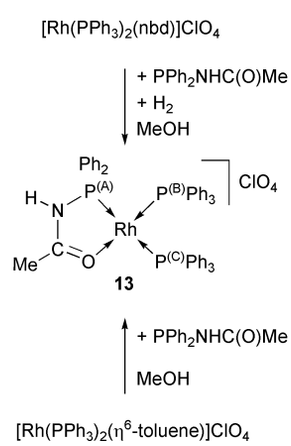
Elemental analysis and spectroscopic data are consistent with the formulations of **11** and **12**; both the $^{31}P\{^1H\}$ NMR spectrum (δ_P 109.2, $^1J_{RhP}$ 181 Hz) and the IR spectrum (KBr) [ν(C≡O) 2006; ν(C=O) 1653 cm^{-1}] of **11** are consistent with coordination of the *P*,*O* ligand shown in Scheme 2.

The tetrafluoborate complex **12** is almost insoluble in CH_2Cl_2, $CHCl_3$, THF and MeOH. However, in acetone it is possible to obtain the $^{31}P\{^1H\}$ NMR spectrum (δ_P 109, $^1J_{RhP}$ 184 Hz), which is similar to that of **11**. For both **11** and **12** ($CDCl_3$) the N–H resonances (δ 10.5) are coincident and broad. Addition of KH to a solution/suspension of **11** or **12** in THF results in deprotonation of the *P*,*O* ligand and formation of **2**, *vide supra*.

The cationic Rh(I) chelate complex $[Rh(P,O)(PPh_3)_2]ClO_4$ (**13**) can be synthesised by addition of P,O (1 equiv.) to a MeOH solution of $[Rh(PPh_3)_2(\eta^6\text{-toluene})]ClO_4$ followed by stirring



Scheme 2



Scheme 3

(4 h) at room temperature (see Scheme 3). However, the best synthetic route to **13** is *via* the addition of P,O (1 equiv.) to a solution of $[Rh(PPh_3)_2(nbd)]ClO_4$ in CH_2Cl_2 under an atmosphere of H_2.

The $^{31}P\{^1H\}$ NMR spectrum of **13** (see Fig. 2) consists of three sets of resonances which unambiguously establishes the structure; the *P*,*O* resonance is a doublet of doublets of doublets [$\delta_{P(A)}$ 94.6, $^1J_{RhP(A)}$ 156, $^2J_{P(A)P(B)}$ 38, $^2J_{P(A)P(C)}$ 310 Hz],

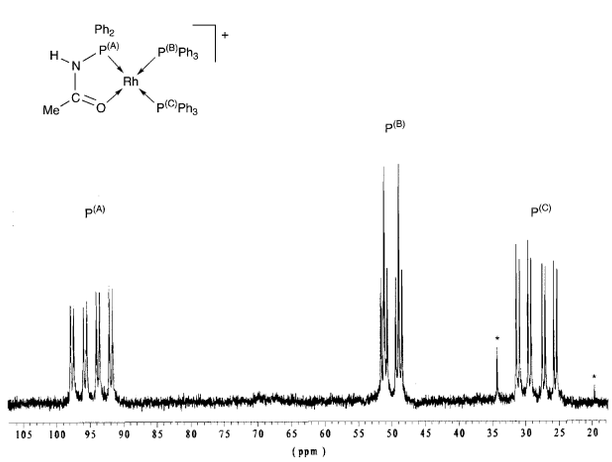
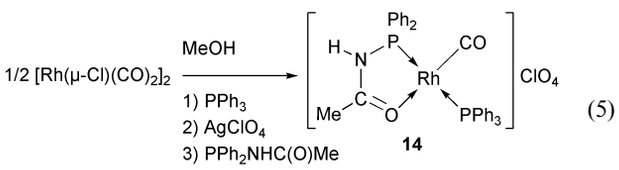


Fig. 2 $^{31}P\{^1H\}$ NMR spectrum of $[Rh(P,O)(PPh_3)_2]ClO_4$ (**13**) in CH_2Cl_2 at room temperature. The starred peaks correspond to impurities.

the PPh_3 resonance *trans* to the oxygen is a doublet of triplets [$\delta_{P(B)}$ 50, $^1J_{RhP(B)}$ 177, $^2J_{P(B)P(A)}$ 38, $^2J_{P(B)P(C)}$ 38 Hz] and the resonance due to PPh_3 *trans* to phosphorus is also a doublet of doublets of doublets [$\delta_{P(C)}$ 28.8, $^1J_{RhP(C)}$ 140, $^2J_{P(C)P(B)}$ 38, $^2J_{P(C)P(A)}$ 310 Hz] (see Fig. 2 for labelling scheme).

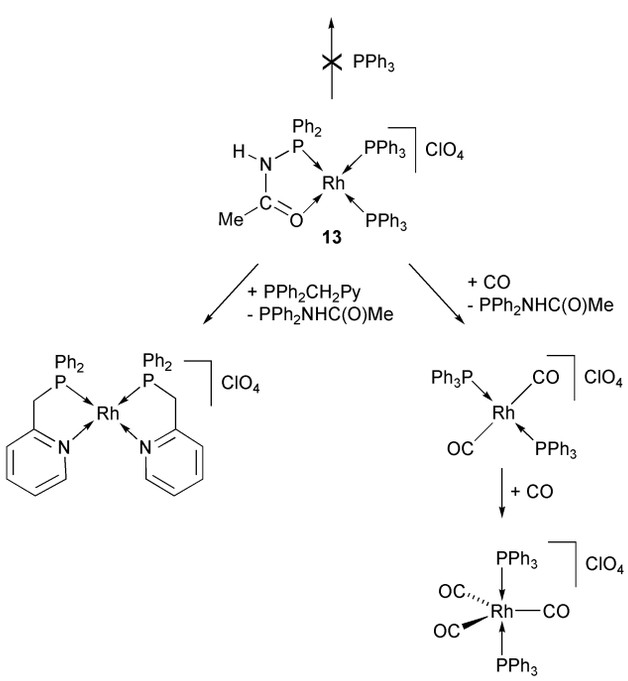
The synthesis of the related cationic, Rh(I) carbonyl complex [Rh(*P*,*O*)(CO)(PPh_3)]ClO_4 (**14**) has been achieved by the slow addition of PPh_3 and $AgClO_4$ to a MeOH solution of [Rh(μ-Cl)$(CO)_2]_2$ followed by addition of the P,O ligand (Rh : P,O = 1 : 1) [eqn. (5)].



(5)

The $^{31}P\{^1H\}$ NMR spectrum of **14** is temperature-independent over the range 193–293 K and consists of two resonances due to the *P*,O ligand [$\delta_{P(A)}$ 93.3, $^1J_{RhP(A)}$ 129, $^2J_{P(A)P(B)}$ 315 Hz] and PPh_3 [$\delta_{P(B)}$ 27.7, $^1J_{RhP(B)}$ 132, $^2J_{P(A)P(B)}$ 315 Hz]. In the IR spectrum (KBr) the ν(C≡O) and ν(C=O) vibrations occur at 1989 and 1576 cm^{-1}, respectively. Both sets of data are entirely consistent with the structure shown in eqn. (5).

It is of interest to compare the different reactivities of **13** and **14**. Complex **13** is stable for several weeks in CH_2Cl_2 solution and, as found for the related complex [Rh{$PPh_2CH_2C(O)$-Ph-κ^2*P*,*O*}$(PPh_3)_2]^+$, there is no reaction with H_2 or with an excess of PPh_3 and no dissociation of PPh_3 occurs. However, the chelate *P*,*O* ligand is replaced by the more strongly coordinating bidentate ligand 2-(diphenylphosphino)methylpyridine, to give [Rh(PPh_2CH_2py-κ^2*P*,*N*)$_2$]ClO_4 (δ_P 60.4, $^1J_{RhP}$ 168.5 Hz) (Scheme 4).



Scheme 4

When CO was bubbled through a solution of **13** in CH_2Cl_2, displacement of the P,O ligand occurred to give [Rh$(CO)_2$-$(PPh_3)_2]ClO_4$ (δ_P 22.3, $^1J_{RhP}$ 114 Hz),[11] which readily reacts further with CO to give the more stable five-coordinate complex [Rh$(CO)_3(PPh_3)_2]ClO_4$ (δ_P 32.2, $^1J_{RhP}$ 72 Hz).[12]

Unlike **13**, **14** does not react with CO at atmospheric pressure nor with other potentially bidentate P,N ligands. There is also no reaction of **14** with even a large excess of HBF_4 or HSO_3Me in acetone or CH_2Cl_2 solution; however, addition of HCl (3 equiv.) to an acetone solution of **14** gives the bis-chelate cationic complex [Rh(*P*,*O*)$_2$]ClO_4 (**15**) as a yellow precipitate and the neutral complex *trans*-[Rh$(PPh_3)_2$(CO)Cl], remains in solution.

Complex **15** is soluble in polar solvents such as MeOH and EtOH and the $^{31}P\{^1H\}$ NMR spectrum consists of one doublet (δ_P 81.9, $^1J_{RhP}$ 122 Hz); in the IR spectrum (KBr), the ν(CO) band due to the amide group occurs at 1593 cm^{-1}. Although bis-chelate Rh(I) complexes, such as [Rh(PPh_2CH_2py-κ^2*P*,*N*)$_2$]-ClO_4,[13] [Rh{$PPh_2(CH_2)_2$py-κ^2*P*,*N*}$_2$]PF_6[14] or [Rh{PPh_2CH_2C-(O)Ph-κ^2*P*,*O*}$_2$]PF_6,[9] prefer to adopt a *cis* geometry, the small value of $^1J_{RhP}$ for **15** (122 Hz compared to *ca.* 170 Hz) suggests that in this case the *trans*-configuration is adopted. This is consistent with the change in $^1J_{RhP}$ observed on going from *cis*-[Rh{$PPh_2(CH_2)_2$py-κ^2*P*,*N*}$_2$]PF_6 (171 Hz) to *trans*-[Rh-{$PPh_2(CH_2)_2$py-κ^2*P*,*N*}$_2$(CO)] (125 Hz).[14]

In their recent studies of the coordination properties of the related ligand $PPh_2NHC(O)Ph$,[15a] Woollins *et al.* have observed P-monodentate behaviour with Pt(II), Rh(III) and Ru(II) and P,O-chelation with Ni(II).[15b]

Experimental

All operations were carried out under a nitrogen atmosphere. Solvents were distilled and dried using published methods. The $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker AMX-200 or AMX-400 spectrometer. The $^{31}P\{^{103}Rh\}$ HMQC measurements were carried out on a Bruker AMX-200 spectrometer using a 10 mm probe, as described previously.[16] Chemical shifts are referenced to $SiMe_4$ (δ_C = 0) external 85% H_3PO_4 in D_2O (δ_P = 0) and 3.14 MHz at such a magnetic field that the protons in $SiMe_4$ resonate at exactly 100 MHz (δ_{Rh} = 0). IR spectra were recorded in solution, using CaF_2 cells previously purged with nitrogen, or as a KBr disc on a Perkin-Elmer 257 FTIR spectrometer. Elemental analyses were carried out by the microanalytical staff at the Universities of Liverpool and Strasbourg.

Syntheses

Literature methods were used to prepare $PPh_2NHC(O)Me$[6] (abbreviated as P,O), [Rh(μ-Cl)$(CO)_2]_2$ [17] and [Rh(nbd)$(PPh_3)_2$]-ClO_4.[18]

2-(Diphenylphosphinomethyl)pyridine (PPh_2CH_2py)

A solution of *n*-butyllithium (15.6 mL of a 1.6 M solution in hexane, 25 mmol) was added to 2-picoline (2.33 g, 25 mmol) in dry THF (20 mL) at 253 K over 20 min. After stirring (1 h), the mixture was added to a solution of chlorodiphenylphosphine (5.5 g, 25 mmol) in dry THF (25 mL) at 213 K over 30 min followed by warming to 253 K over 45 min. The mixture was then cooled to 248 K and water (50 mL) added over 10 min, followed by stirring for 30 min. The product was obtained by extraction with an HCl solution (2 × 250 mL, 0.3 M), followed by neutralisation with a $NaHCO_3$ solution, and extraction with dichloromethane (3 × 100 mL). The solvent and any unreacted 2-picoline were removed *in vacuo*. The yield of crude product was 4.7 g (75%). The latter was dissolved in warm EtOH (50 mL) followed by addition of water (50 mL). Storing overnight at 243 K gave a cream coloured precipitate of the product. This was filtered off and dried in *vacuo*, yield 3.8 g, 60%. (Found: C, 77.80; H, 5.75; N, 5.00%. $C_{18}H_{16}NP$ requires C, 77.94; H, 5.82; N, 5.05%.) δ_P (CH_2Cl_2): −11.6. Other spectroscopic data are consistent with literature values.[19]

[Rh(*P*,*O*)(CO)Cl] (1)

A solution of P,O (0.27 g, 1.11 mmol) in CH_2Cl_2 (5 mL) was added dropwise to a solution of [Rh(μ-Cl)$(CO)_2]_2$ (0.22 g, 0.56 mmol) in CH_2Cl_2 (5 mL) at room temperature. The resulting

orange solution was stirred (2 h), evaporated to dryness and the residue washed with pentane to give the crude product as an orange powder, (yield 0.37 g, 80%). Yellow crystals of **1**·CH_2Cl_2, suitable for X-ray analysis, were obtained by slow diffusion of THF/Et_2O (1 : 3) into a dichloromethane solution of the crude product. (Found: C, 44.00; H, 3.45; N, 3.43%. Calc. for $C_{15}H_{14}ClNO_2PRh$: C, 43.95; H, 3.48; N, 3.42%.) δ_P (CD_2Cl_2): 104.8 (d, $^1J_{RhP}$ 174 Hz); δ_C (CD_2Cl_2): 187 (dd, CO, $^1J_{RhC}$ 77.4, $^2J_{PC}$ 18 Hz); δ_H ($CDCl_3$): 10.5 (br, NH); IR (KBr) ν(CO): 1997, 1579 cm^{-1}, ν(Rh–Cl) 283 cm^{-1}.

[Rh{μ-PPh_2N···C(···O)Me}(CO)]$_2$ (2)

A suspension of **1** in THF was added dropwise to a suspension of KH (KH : **1** = *ca.* 10 : 1) in THF at room temperature. After stirring (1 h), the colour changed from yellow/orange to brown/green. The suspension was filtered and the filtrate dried *in vacuo*; the residue was washed with pentane to give **2** as a brown/black powder, typical yield 65%. (Found: C, 48.30; H, 3.52; N, 3.76%. Calc. for $C_{30}H_{26}N_2O_4P_2Rh_2$: C, 48.28; H, 3.51; N, 3.75%.) δ_P (CD_2Cl_2): 114.2 ($^1J_{RhP}$ 153 Hz); δ_{Rh} −68; IR (KBr) ν(CO): 1965, 1465 cm^{-1}.

[Rh(μ-*P*,*O*)(CO)]$_2$[ClO_4]$_2$ (11)

To a solution of **1** (0.06 g, 0.15 mmol) in THF (10 mL) was added $AgClO_4$ (0.03 g, 0.15 mmol). After stirring at room temperature (2 h), the colour of the reaction mixture became green/brown. The resulting suspension was filtered; the product **11** was obtained by concentrating the filtrate *in vacuo* followed by washing with pentane, yield 0.05 g, 70%. (Found: C, 38.06; H, 3.00; N, 2.97%. Calc. for $C_{30}H_{28}Cl_2N_2O_{12}P_2Rh_2$: C, 38.04; H, 2.98; N, 2.96%.) δ_P (CD_2Cl_2): 109.2 ($^1J_{RhP}$ 181 Hz); δ_H (CD_2Cl_2): 10.5; IR (KBr) ν(CO): 2006, 1653 cm^{-1}.

A similar procedure was followed for the synthesis of the $[BF_4]^-$ salt, **12**, using $AgBF_4$ instead of $AgClO_4$. However, in this case, the yield was usually lower (*ca.* 60%).

[Rh(*P*,*O*)(PPh_3)$_2$]ClO_4 (13)

Hydrogen was bubbled through a solution containing [Rh(nbd)(PPh_3)$_2$]ClO_4 (0.10 g, 0.12 mmol) and P,O (0.03 g, 0.12 mmol) in dichloromethane (5 mL) for 5 min; the colour of the solution immediately changed from yellow/orange to deep red. Addition of petroleum ether (40–60) (10 mL) gave, after 3 days in the refrigerator, deep red needles of **13**, which were filtered off, washed with petroleum ether (40–60) (3 × 10 mL) and dried *in vacuo*, yield 0.09 g, 80%. (Found: C, 62.00; H, 4.58; N, 1.90%. Calc. for $C_{50}H_{44}ClNO_5P_3Rh$: C, 61.90; H, 4.57; N, 1.44%.) δ_P (CD_2Cl_2): 94.6 (ddd, P(A), $^1J_{RhP(A)}$ 156 Hz, $^2J_{P(A)P(C)}$ 310 Hz, $^2J_{P(A)P(B)}$ 38 Hz), 50 (dt, P(B), $^1J_{RhP(B)}$ 177 Hz, $^2J_{P(A)P(B)}$ = $^2J_{P(B)P(C)}$ 38 Hz), 28.8 (ddd, P(C), $^1J_{RhP(C)}$ 140 Hz, $^2J_{P(A)P(C)}$ 310 Hz, $^2J_{P(B)P(C)}$ 38 Hz) (see Fig. 2 for labelling scheme).

[Rh(*P*,*O*)(PPh_3)(CO)]ClO_4 (14)

To a solution of [Rh(μ-Cl)$(CO)_2]_2$ (0.163 g, 0.415 mmol) in MeOH (10 mL) was added slowly a suspension of PPh_3 (0.218 g, 0.83 mmol) in MeOH (20 mL); $AgClO_4$ (0.172 g, 0.83 mmol) was then added and the solution left to stir overnight. The suspension of AgCl was filtered off and a solution of P,O (0.204 g, 0.83 mmol) in MeOH (5 mL) was slowly added to the filtrate with stirring. Effervescence due to the evolution of CO was observed and concentration gave the product **14** as yellow crystals which were filtered off, washed with Et_2O (2 × 5 mL) and dried *in vacuo*, yield 0.49 g, 80%. (Found: C, 53.88; H, 3.81; N, 2.00%. Calc. for $C_{33}H_{29}ClNO_6P_2Rh$: C, 53.86; H, 3.97; N, 1.90%.) δ_P (CD_2Cl_2): 93.3 (dd, $^1J_{RhP}$ 129 Hz, $^2J_{PP}$ 315 Hz), 27.7 (dd, PPh_3, $^1J_{RhP}$ 132 Hz, $^2J_{PP}$ 315 Hz); δ_H ($CDCl_3$): 10.8 (b, NH); IR (KBr): ν(CO) 1989, 1576 cm^{-1}.

Table 3 X-Ray experimental data for complex **1**·CH_2Cl_2

Formula	$C_{16}H_{16}NO_2PCl_3Rh$
Molecular weight	494.55
Crystal system	monoclinic
a/Å	9.5442(2)
b/Å	16.4222(4)
c/Å	13.2981(2)
β/°	102.916(9)
V/Å^3	2031.6(2)
Temperature/K	173
Space group	$P2_1/n$
Z	4
μ/mm^{-1}	1.311
Number of data meas.	17433
Number of data	3550 with $I > 3\,\sigma(I)$
R, R_w [a]	0.053; 0.070

[a] $R = \Sigma_{hkl}(||F_{obs}| - |F_{calc}||)/\Sigma_{hkl}|F_{obs}|$; $R_w = [\Sigma_{hkl}w(|F_{obs}| - |F_{calc}|)^2/\Sigma_{hkl}wF_{obs}^2]^{1/2}$.

[Rh(*P*,*O*)$_2$]ClO_4 (15)

HCl in Et_2O (2 × 75 mL, 1 M) was added to a solution of [Rh(*P*,*O*)(PPh_3)(CO)]ClO_4 (0.5 g, 0.68 mmol) in acetone (10 mL) at room temperature. A yellow precipitate of the product was formed immediately; the complex **15** was filtered off, washed with hexane and dried *in vacuo*, yield 0.34 g, 75%. (Found: C, 48.85; H, 4.30; N, 4.10%. Calc. for $C_{28}H_{28}ClN_2O_6P_2Rh$: C, 48.82; H, 4.10; N, 4.09%.) δ_P (CD_2Cl_2): 81.9 (d, $^1J_{RhP}$ 122 Hz); IR (KBr) ν(CO): 1593 cm^{-1}.

X-Ray diffraction study

Yellow, single crystals of **1**·CH_2Cl_2 suitable for X-ray diffraction were grown by slow diffusion of THF/Et_2O (1 : 3) into a dichloromethane solution of the crude product. The X-ray experimental data are given in Table 3. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were calculated and fixed in idealized positions (d_{C-H} = 0.95 Å, $B_H = 1.3B_{equiv}$ for the carbon to which it was attached), except for the NH proton which was located in the difference Fourier map and refined with a fixed isotropic $B = 4$ Å^2.

CCDC reference number 192615.

See http://www.rsc.org/suppdata/dt/b2/b208735a/ for crystallographic data in CIF or other electronic format.

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