Selective formation of *cis*-diacyl, *cis*-PPh_2R rhodium(III) complexes by the reaction of rhodium(III) *cis*-diacyl, *trans*-PPh_2R complexes with aliphatic diamines†

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The *cis*-diacyl, *trans*-PPh_2R complex [RhCl(PPh_2(*o*-C_6H_4CO))$_2$(pyridine)] (**1**) reacts with substituted aliphatic diamines to afford selectively cationic *cis*-diacyl, *cis*-PPh_2R, diamine derivatives [Rh(PPh_2(*o*-C_6H_4CO))$_2$(NN′)]$^+$ (NN′ = 1,2-diphenylethylenediamine, **2**; 1,2-propanediamine, **3**; N-methylethylenediamine, **4**; N,N-dimethylethylenediamine, **5**; N,N′-dimethylethylenediamine, **6**; N,N,N′-trimethylethylenediamine, **7**) with high stereoselectivity depending on the N-donor ligand employed. Complexes **2** and **3** contain a single isomer, while **4** is a mixture of two isomers, **4a** and **4b**. Formation of **4a** occurs first and is followed by isomerisation to **4b** until the equilibrium **4a**:**4b** = 1:4 ratio is attained. In contrast, **5** and **6** contain a single isomer. More basic amino groups prefer positions *trans* to an acyl group while less basic amino groups are *trans* to a phosphine group. The preferred intramolecular N—H ··· O hydrogen bond formation between an amino and an acyl coordinated ligands, *trans* to the phosphorus atoms, appears to be relevant to the selectivity observed. **7** is a mixture of two isomers **7a** and **7b** in a **7a**:**7b** = 5.7:1 ratio. N,N,N′,N′-tetramethylethylenediamine or N,N′-diphenylethylenediamine led to the elimination of the N-donor ligands and the formation of a mixture of isomers of [Rh_2(μ-Cl)(μ-PPh_2(*o*-C_6H_4CO))$_2$(PPh_2(*o*-C_6H_4CO))$_2$]$^+$ (**8**), where the Rh atoms are triply bridged by two acyl groups in a head-to-tail arrangement and by a chloride. The reaction of [Rh(PPh_2(*o*-C_6H_4CO))$_2$(ndmeen)]ClO_4 (**5**) with acids led to the displacement of the diamine and the formation of a [**8a**]$^+$:[**8b**]$^+$:[**8c**]$^+$ = 1:1:3 mixture. **8c**, containing the weakest σ-donor oxygen atoms *trans* to the strongest σ-donor acyl groups, represents the most electronically favourable geometry for **8**. All the complexes were fully characterized spectroscopically. Single crystal X-ray diffraction analysis was performed on **5**, **6**, **8a** and **8b**.

Introduction

Organometallic rhodium complexes containing phosphorus ligands play an important role in the transformation of many organic compounds.[1,2] More recently, nitrogen ligands are being more widely used in the design of regio- and/or enantioselective catalytic systems.[3] Rhodium(I) complexes such as [Rh($CO)_2$(diamine)][Rh($CO)_2Cl_2$], in the absence of a phosphorus ligand, are able to catalyze the hydroformylation of olefins under mild conditions and afford also a novel route to 1,2,3,4-tetrahydroquinolines in a highly chemo- and regioselective manner and in good isolated yields.[4] Other rhodium systems with chiral amino-containing bidentate ligands allow the reduction of α-acylaminocinnamate derivatives or of prochiral carbonyl compounds with excellent enantioselectivities.[5]

Noyori's pioneering reports on ruthenium complexes [$RuCl_2$(diamine)(phosphine)$_2$], containing both diamine and phosphine or diphosphine ligands, as catalysts in the reduction of C=O and C=N double bonds have been of paramount importance in research involving diamines as ligands. High efficiency, chemoselectivity, and, in the case of prochiral ketones, enantioselectivity were attained.[6] Ruthenium dihydrides [RuH_2(diamine)(PR_3)$_2$], which can potentially exist as several geometric isomers, have been proposed to be among the active catalysts for these reactions.[7] Taking into account electronic considerations, the most stable isomer would be the *cis*-dihydride, *trans*-PR_3 isomer, with the hydrides *trans* to the amino groups, since the hydride, having the largest *trans* influence and being the best σ-donor, would prefer to be *trans* to the amino group with the lowest *trans* influence, being the weakest σ-donor.[8,9] Though less favourable from this point of view, some octahedral complexes of the platinum metals containing *trans*-hydride ligands have also been reported.[10] Studies on the formation of [RuH_2(diamine)(PR_3)$_2$] have shown a succession of isomerisation reactions so that the least stable *trans*-dihydride, *cis*-PR_3 isomer is formed first and isomerises to the most stable *cis*-dihydride, *trans*-PR_3 isomer, *via* the *cis*-dihydride, *cis*-PR_3 intermediate, to reach equilibrium mixtures of the two latter isomers containing a higher proportion of the most stable isomer.[7c] Cationic [MH_2(amine)$_2$(PR_3)$_2$]$^+$ (M = Rh, Ir) have been reported to be of the *cis*-dihydride, *trans*-PR_3 type.[11] Calculations on [IrHCl(PMe_3)$_4$]$^+$ complexes have shown that the *trans*- and *cis*-H, Cl structures are nearly isoenergetic.[9]

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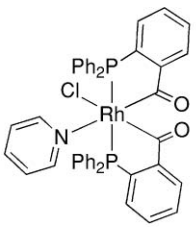
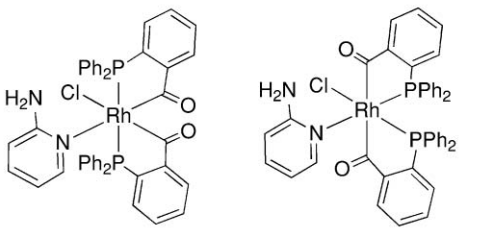
Recently we have reported on the formation of rhodium(III) bis(acylphosphine) complexes containing acyl groups, whose *trans* effect is almost as high as that of hydride.[12] [RhCl(PPh_2(*o*-C_6H_4CO))$_2$(pyridine)] (**1**) is the expected *cis*-diacyl, *trans*-PPh_2R complex, while [RhCl(PPh_2(*o*-C_6H_4CO))$_2$(2-aminopyridine)] (**1′**) contains a mixture of *cis*-diacyl, *trans*-PPh_2R and *trans*-diacyl, *cis*-PPh_2R isomers (Scheme 1), the most and least electronically favoured respectively. Also, the reaction of **1′** with bidentate N-donors was extraordinarily selective to afford [Rh(PPh_2(*o*-C_6H_4CO))$_2$(NN′)]$^+$ complexes that were only *cis*-diacyl, *trans*-PPh_2R isomers when NN′ = diimines. When NN′ contained amino groups, isomerisation reactions were observed, assisted by ion pairing formation *via* hydrogen bonding, to afford *cis*-diacyl, *cis*-PPh_2R derivatives.[13] We report now on the reactions of **1**, a *cis*-diacyl, *trans*-PPh_2R complex, with differently substituted chelating diamines to give different isomer ratios of *cis*-diacyl, *cis*-PPh_2R, complexes, depending on the diamine. Crystallographic studies on the obtained complexes are also reported.



1 cis-diacyl, trans-PPh_2R



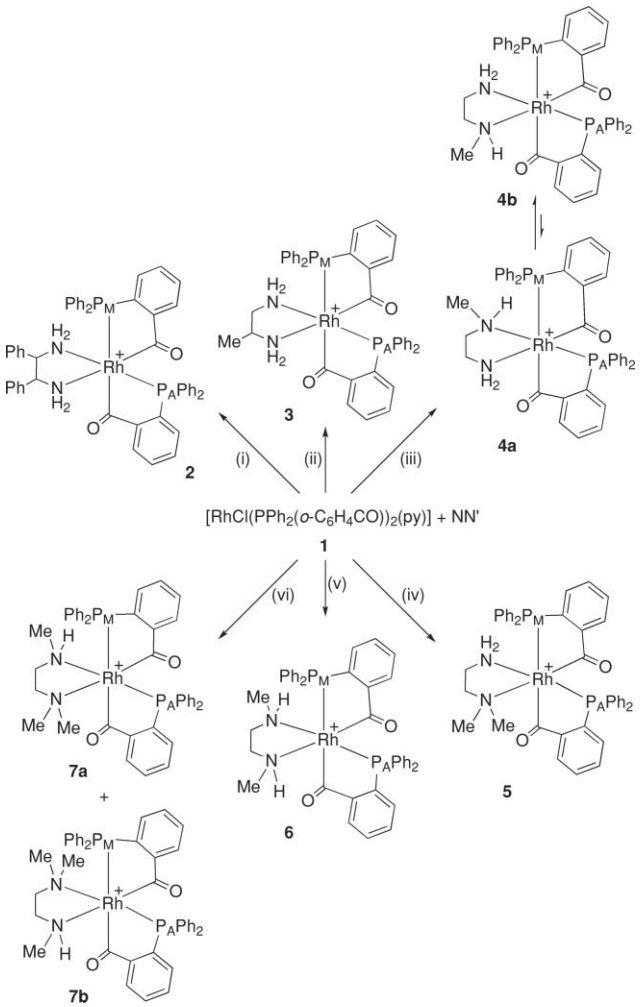
1′ cis-diacyl, trans-PPh_2R **1′** trans-diacyl, cis-PPh_2R

Scheme 1

Results and discussion

The reaction of **1** with different aliphatic chelating diamines proceeds with displacement of the pyridinic ligand and also of chloride to afford selectively cationic *cis*-diacyl, *cis*-PPh_2R, diamine complexes [Rh(PPh_2(*o*-C_6H_4CO))$_2$(NN′)]$^+$ (NN′ = 1,2-diphenylethylenediamine (stien), **2**; 1,2-propanediamine (pn), **3**; N-methylethylenediamine (meen), **4**; N,N-dimethylethylenediamine (ndmeen), **5**; N,N′-dimethylethylenediamine (dmeen), **6**; N,N,N′-trimethylethylenediamine (trimeen), **7**) (Scheme 2), which were isolated as the corresponding perchlorate salts by addition of sodium perchlorate (see Experimental section). The obtained complexes show the expected features in their IR spectra, their FAB spectra contain the parent peaks and they behave as 1:1 electrolytes in acetone solution.[14]

1,2-Diphenylethylenediamine, containing two primary amino groups, leads to complex [Rh(PPh_2(*o*-C_6H_4CO))$_2$(stien)]ClO_4 (**2**) (Scheme 2i) that was fully characterized by spectroscopic means.



Scheme 2

The $^{31}P\{^1H\}$ NMR spectrum contains two doublets of doublets consistent with an AMX pattern due to two mutually *cis* phosphorus atoms (J(P,P) of 15 Hz). The resonance at lower field (P_A, 57.8 ppm) agrees with a phosphorus atom being *trans* to nitrogen (J(Rh,P) = 156 Hz),[8] while the resonance at higher field (P_M, 15.9 ppm) is consistent with a phosphorus atom *trans* to an acyl group (J(Rh,P) = 74 Hz).[15] Accordingly, the $^{13}C\{^1H\}$ NMR spectrum shows two doublets of doublets at low field. The resonance at lower field (C_A, 237.7 ppm) is due to the acyl group *trans* to phosphorus (J(P,C) = 105 Hz), while the resonance at higher field (C_M, 231.4 ppm) corresponds to the acyl group *trans* to nitrogen. The ^1H NMR spectrum contains four resonances due to the amino groups in a broad range, 5.38–1.48 ppm. The corresponding chemical shift values could well result as a combination of a downfield shift due to coordination to the metal that can be enhanced by some extent of hydrogen bond formation,[13b,16] and an upfield shift due to the ring current effects originated by the aromatic rings of the phosphine.[17] The non-symmetric 1,2-diaminopropane gives selectively a single complex, **3**, although two isomers are possible. The relative stereochemistry of the amino groups remains uncertain and the structure shown in Scheme 2ii is tentative. The ^{31}P chemical resonances of the acylphosphine fragments in **3** (P_A, 63.5 ppm; P_M, 26.9 ppm) appear at

lower field than in **2**, and the resonances due to the amino groups appear in the 3.80–1.23 ppm range.

The reaction of **1** with N-methyl-substituted-ethylenediamines may afford different isomers and the selectivity of the reaction depends markedly on the diamine employed. N-Methylethylenediamine led to the formation of compound $[Rh(PPh_2(o\text{-}C_6H_4CO))_2(meen)]ClO_4$ (**4**). By following the course of this reaction by NMR we observed the initial formation of isomer **4a**, shown in Scheme 2iii, formulated as containing the primary amino group *trans* to an acyl group. **4a** then undergoes an isomerisation reaction to afford **4b**, until a mixture of both complexes in a *ca.* **4a**:**4b** = 1:4 ratio is attained. We find most likely that **4b** contains the more basic of the amino groups *trans* to an acyl group as observed in complex **5** (*vide infra*). The isomerisation reaction is rather slow at room temperature (3 days) and can be made faster by heating in $CHCl_3$ (3 h). By addition of $NaClO_4$, **[4b]**ClO_4 can be obtained pure, probably due to a lower solubility. Upon dissolution, the isomerisation of **[4b]**ClO_4 into **[4a]**ClO_4 occurs until the **4a**:**4b** = 1:4 ratio equilibrium mixture is reached. The spectroscopic features of compound **4** are similar to those of **3**. The resonances due to the amino groups for **4b** appear in the 5.09–0.95 ppm range.

In contrast to this behaviour, the reaction of **1** with N,N-dimethylethylenediamine is totally selective to the formation of only one isomer, compound $[Rh(PPh_2(o\text{-}C_6H_4CO))_2(ndmeen)]ClO_4$ (**5**) shown in Scheme 2iv, containing the more basic of the amino groups *trans* to an acyl group. As expected, N,N′-dimethylethylenediamine affords only one compound $[Rh(PPh_2(o\text{-}C_6H_4CO))_2(dmeen)]ClO_4$ (**6**) shown in Scheme 2v. Complexes **5** and **6** show similar spectroscopic features to those of **4**. The ^{31}P chemical shifts of the acyl-phosphine fragments in **5** or **6** (P_A, 60.8 or 62.8 ppm; P_M, 20.2 or 20.9 ppm) appear at higher field than in **3**, and the resonances due to the amino groups appear at 4.04 and 3.10 ppm for **5** or at 5.09 and 4.35 ppm for **6**.

Complexes **5** and **6** could also be characterised by single crystal X-ray diffraction. **5** crystallizes in the $P2_1/c$ monoclinic group and **6** crystallizes in the *Pbca* orthorhombic group. Fig. 1 and Fig. 2 show ORTEP views of complexes **5** and **6** respectively with the labelling schemes of the asymmetric unit. Selected bond distances and angles are listed in Table 1. In both complexes the formula unit consists of one complex cation $[Rh(PPh_2(o\text{-}C_6H_4CO))_2(ndmeen)]$ for **5** or $[Rh(PPh_2(o\text{-}C_6H_4CO))_2(dmeen)]$ for **6** and a perchlorate anion. The coordinative environment of the rhodium atom is distorted octahedral with four positions occupied by the two bidentate acyl-phosphine ligands and the other two positions occupied by the also bidentate diamino ligand. The P1–Rh–P2 angles (98.39 (5) and 97.70(3)°) confirm that in both **5** and **6** the phosphorus atoms are mutually *cis*, and *trans* to an acyl or to an amino group. In complex **5**, the P2–Rh–N2 angle (167.8(1)°) indicates that a phosphorus atom is *trans* to the primary amino group and consequently the more basic dimethylamino group is *trans* to acyl (C1–Rh–N1 = (165.0(2)°). Inspection of the bond lengths in these complexes shows that the Rh–N, Rh–P and Rh–C distances are in the expected ranges,[13,17b] and that the corresponding values for each type of bond differ significantly and agree with the *trans* influence order of the ligands: acyl ≫ phosphine > amine.[12,18] The difference between the Rh–N1 and Rh–N2 bond lengths of 0.108(2) Å in complex **6**, containing secondary amino groups, follows this order. The rather large difference between the Rh–N1 and Rh–N2 bond lengths of

Table 1 Selected bond lengths (Å) and angles (deg) for **5** and **6** including the hydrogen bonds

5		**6**	
Rh–P1	2.460(1)	Rh–P1	2.465(1)
Rh–P2	2.304(1)	Rh–P2	2.293(1)
Rh–C20	2.068(5)	Rh–C20	2.061(3)
Rh–Cl	2.009(5)	Rh–C1	2.003(3)
Rh–N2	2.155(4)	Rh–N2	2.174(2)
Rh–N1	2.374(4)	Rh–N1	2.282(2)
C20–O2	1.222(6)	C20–O2	1.221(3)
C1–O1	1.213(6)	C1–O1	1.220(3)
N2–H21	0.91	N1–H1	1.07
N2–H22	0.95	N2–H2	1.10
O2···H21	2.08	O2···H2	1.83
O2A···H22	2.37	O6···H1	2.11
N2···O2	2.793(6)	N2···O2	2.766(3)
N2···O2A	3.022(6)	N1···O6	3.074(4)
P1–Rh–P2	98.39(5)	P1–Rh–P2	97.70(3)
P1–Rh–C20	168.5(2)	P1–Rh–C20	171.8(1)
P1–Rh–N2	92.7(1)	P1–Rh–N2	94.7(1)
P1–Rh–C1	84.1(2)	P1–Rh–C1	83.8(1)
P1–Rh–N1	100.6(1)	P1–Rh–N1	99.4(1)
P2–Rh–C20	82.6(2)	P2–Rh–C20	82.1(1)
P2–Rh–N2	167.8(1)	P2–Rh–N2	166.8(1)
P2–Rh–C1	88.9(2)	P2–Rh–C1	88.4(1)
P2–Rh–N1	104.3(1)	P2–Rh–N1	102.9(1)
C20–Rh–N2	85.6(2)	C20–Rh–N2	85.0(1)
C20–Rh–C1	84.4(2)	C20–Rh–C1	88.0(1)
C20–Rh–N1	90.2(2)	C20–Rh–N1	88.6(1)
C1–Rh–N2	87.1(2)	N2–Rh–C1	88.3(1)
N1–Rh–N2	78.6(2)	N2–Rh–N1	79.6(1)
C1–Rh-N1	165.0(2)	C1–Rh–N1	167.7(1)
N2-H21···O2	133.4	N2-H2···O2	140.1
N2-H22···O2A	125.4	N1-H1···O6	148.7

(A) –x + 1, –y + 2, –z + 1.

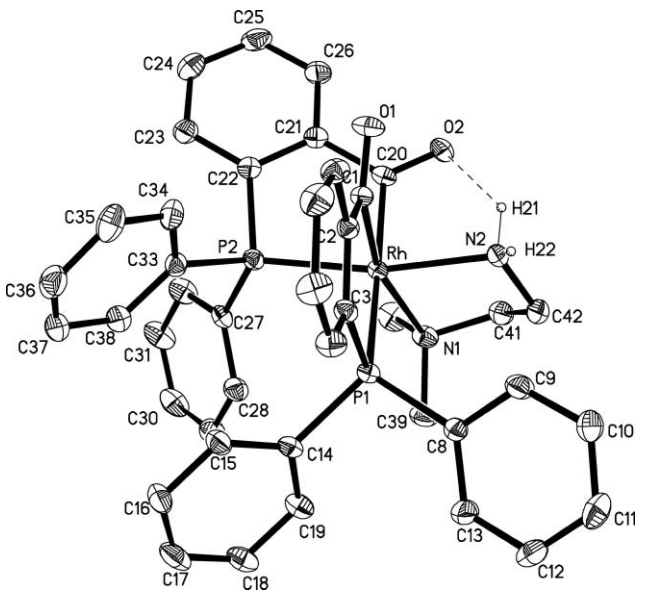


Fig. 1 ORTEP view of the cation in compound **5** showing the atomic numbering (20% probability ellipsoids) and the intramolecular hydrogen bond. The labelling of some carbon atoms and the hydrogen atoms except two have been omitted for clarity.

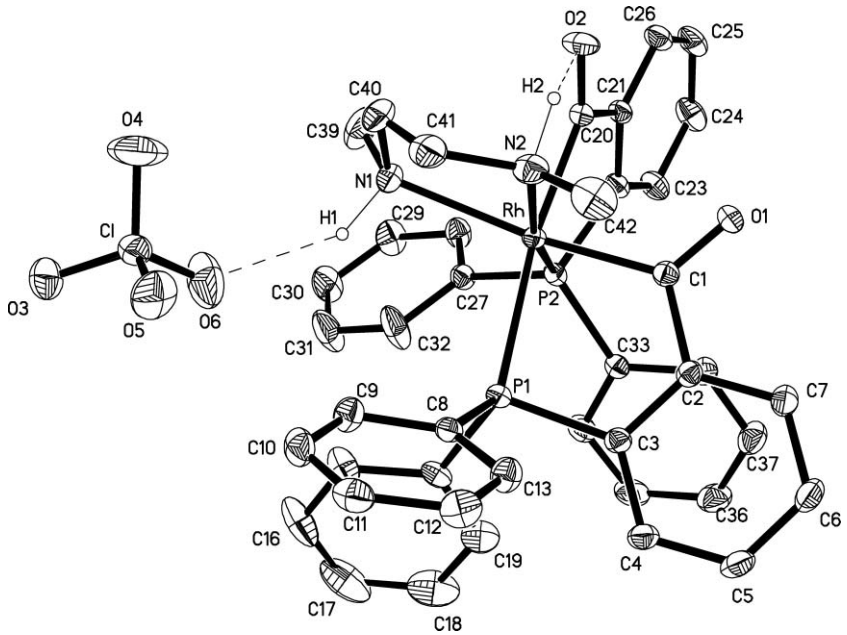


Fig. 2 ORTEP view of **6** showing the atomic numbering (40% probability ellipsoids) and the intramolecular and intermolecular hydrogen bonds. The labelling of some carbon atoms and the hydrogen atoms except two have been omitted for clarity.

0.219(4) Å in complex **5** can also be related to a higher difference of steric crowding between the dimethylamino group (N1) and the primary amino group (N2).

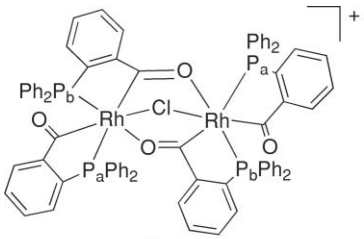
In both complexes **5** and **6**, the N2 atom of the amino group *trans* to phosphorus forms a strong intramolecular hydrogen bond with the oxygen atom of the acyl group *trans* to the other phosphorus atom N2–H21 $\cdots$ O2 for **5** (N2 $\cdots$ O2 = 2.793(6) Å) and N2–H2 $\cdots$ O2 for complex **6** (N2 $\cdots$ O2 = 2.766(3) Å). Hydrogen bonding plays a key role in chemical and catalytic processes among others and metals can play a considerable and varied role in hydrogen bonding.[19] We observe that the intramolecular hydrogen bond formation in **5** and **6** occurs between the amino group with the shortest Rh–N distance (*trans* to P_A) and the acyl group with the longest Rh–C distance (*trans* to P_M) suggesting that the relative situation of both groups appears most suitable for the formation of this strong hydrogen bond. We believe that the formation of these hydrogen bonds is relevant to the preference observed in **5** to locate the more basic amino group *trans* to the acyl group thus making the primary amino group *trans* to phosphorus and available for the observed intramolecular hydrogen bond formation. In related *cis*-diacyl, *cis*-PPh_2R [$Rh(PPh_2(o\text{-}C_6H_4CO))_2$(2-(aminomethyl)pyridine)]ClO_4, containing a primary amino group *trans* to acyl, no intramolecular hydrogen bond formation has been observed.[13b] Steric effects in these crowded molecules may also play a role in the observed selectivity.

The N2 atom of the primary amino group in complex **5** also forms a weaker intermolecular hydrogen bond, N2–H22 $\cdots$ O2A, with the O2 atom of a centrosymmetric cation (N2 $\cdots$ O2A = 3.022(6) Å). This intermolecular interaction leads to the formation of dimers. In complex **6** the N1 atom of the amino group not involved in the intramolecular hydrogen bond, forms a weaker intermolecular hydrogen bond, N1–H1 $\cdots$ O6, with the oxygen atom of the perchlorate anion (N1 $\cdots$ O6 = 3.074 (4) Å) (see Fig. 2).

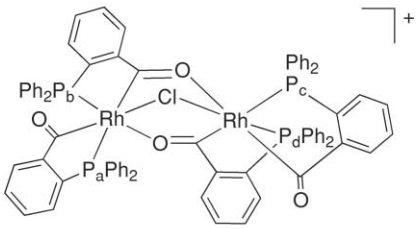
According to the previous results, the reaction of **1** with N,N,N′-trimethylethylenediamine, containing a secondary and a tertiary amino group, affords a mixture of two isomers **7a**:**7b** = 5.7:1, shown in Scheme 2vi. Complex **7** was characterized spectroscopically. Its spectral features are similar to those of complexes **2–6** and the resonance due to the amino group appears at 5.10 ppm. Following our previous results we propose that the most abundant isomer **7a** contains the more basic amino group *trans* to an acyl group.

Attempts to isolate diacyl complexes similar to **2–7** using more sterically demanding aliphatic diamines such as N,N,N′,N′-tetramethylethylenediamine or N,N′-diphenylethylenediamine proved unsuccessful. Instead, the formation of a mixture of isomers **8a** and **8b** (Scheme 3) of the dimer cationic species [Rh_2(μ-Cl)(μ-$PPh_2(o\text{-}C_6H_4CO)$)$_2$($PPh_2(o\text{-}C_6H_4CO)$)$_2$]$^+$ (**8**) occurred. Most likely these ligands also promote the displacement of pyridine and chloride from **1**, but their higher steric hindrance leads to the elimination of these N-donor ligands and to the formation of **8**. The protonation of **1** also affords the formation of **8** along with pyridinium salts, therefore the reaction of **1** with aqueous $HClO_4$ or with $HBF_4{\cdot}OEt_2$ allowed the isolation of a [**8a**]A:[**8b**]A = 1:1.5 mixture (A = ClO_4 or BF_4).

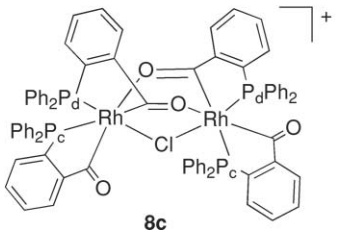
Compound [**8**]ClO_4 behaves as 1:1 electrolyte in acetone solution and the FAB spectrum shows the $[M]^+$ peak at 1397 as expected for such a dinuclear species. It shows an IR stretch at 1653 cm^{-1} due to the terminal acyl groups and a strong stretch at 1548 cm^{-1} that can be assigned to bridging acyl groups. Consequently the $^{13}C\{^1H\}$ NMR spectrum contains multiplets at *ca.* 220 ppm due to terminal acyl groups and also resonances at *ca.* 260 ppm, with high J(P,C) coupling constants of *ca.* 100 Hz, that we assign to bridging acyl groups with carbon atoms *trans* to phosphorus atoms. Bridging acyls can be described by acyl ↔ oxycarbene resonance structures and the energy of the *ν*(C=O) band and the shift of the carbon atom in the ^{13}C NMR spectrum



8a



8b



8c

Scheme 3

toward lower field have been reported to be strongly dependent on the amount of oxycarbene character present in the bridging acyl ligands.[20] Carbene-like character has been proposed for several 1,1-bis(diphenylphosphino)methane rhodium(I) complexes such as $[Rh_2(\mu\text{-}CH_3CO)(CO)_2(\mu\text{-dppm})_2]$ (ν(C=O), 1485 cm^{-1}; δ^{13}C=O, 322.0 ppm),[21] or $[RhM(CF_3SO_3)(CO)_2(\mu\text{-CO})(\mu\text{-}CH_3CO)(\mu\text{-dppm})_2]CF_3SO_3$ (δ^{13}C=O, 304.8 (M = Ru) or 313.3 (M = Os) ppm),[22] while for $[RhRu(CO)_2(\mu\text{-}(CH_3)_2C{=}CCH_2CH_2CO)(\mu\text{-dppm})_2]CF_3SO_3$ (δ^{13}C=O, 250.7 ppm) a lower carbene-character has been suggested.[23] Comparison of these data with those of **8** suggests a low oxycarbene character for the acyl bridges in **8**.

The $^{31}P\{^1H\}$ NMR spectrum of the mixture of **8a** and **8b** consists of two sets of resonances. Two doublets of doublets consistent with an AMX pattern form one set due to **8a** containing two equivalent rhodium fragments. The other set is formed by four doublets of doublets due to the presence of four non-equivalent acylphosphine fragments, two per rhodium atom of **8b**. The J(P,P) coupling constants agree with both phosphorus atoms bonded to the same rhodium atom being mutually *cis* and the J(Rh,P) coupling constants agree with phosphorus atoms being *trans* to oxygen or to acyl in **8a** or to oxygen, chlorine or acyl in **8b**.

We succeeded in isolating compounds [**8a**]BF_4 and [**8b**]ClO_4 as single crystals suitable for X-ray diffraction by fractional crystallization. These compounds crystallize in the *C*2*c* and *P*2(1)/*n* monoclinic groups respectively. For **8a** the Cl atom and the B atom lie on a twofold axis, therefore the asymmetric unit consists of a half dimeric cation and a half BF_4^- anion. For **8b** the asymmetric unit consists of a dinuclear cation and a ClO_4^- anion. Figs. 3 and 4 show ORTEP views of the cations with the labelling scheme of the asymmetric unit. Selected bond distances and angles are listed in Table 2. In both isomers two acyl groups in a head-to-tail arrangement and a chloride bridge the Rh atoms.

In **8a** the geometry around each Rh atom is pseudo-octahedral with the chloro ligand *trans* to the carbon atoms of terminal acyl groups. The bridging Rh–Cl distance (2.510(3) Å) is similar to

Table 2 Selected bond lengths (Å) and angles (deg) for **8a** and **8b**

8a		**8b**			
Rh1–P1	2.372(3)	Rh1–P1	2.387(2)	Rh2–P3	2.388(2)
Rh1–P2	2.249(3)	Rh1–P2	2.266(2)	Rh2–P4	2.254(2)
Rh1–C20	2.01(1)	Rh1–C20	2.030(6)	Rh2–C58	2.040(6)
Rh1–C1	1.96(1)	Rh1–C1	1.992(6)	Rh2–C39	2.011(6)
Rh1—CL	2.510(3)	Rh1–CL1	2.454(2)	Rh2–CL1	2.514(2)
Rh1–O2	2.18(1)	Rh1–O4	2.292(4)	Rh2–O2	2.144(4)
C20–O2A	1.22(1)	C20–O2	1.246(6)	C39–O3	1.201(7)
C1–O1	1.26(3)	C1–O1	1.220(7)	C58–O4	1.240(7)
Rh1-Rh1A	3.522(2)	Rh1-Rh2	3.582(1)		
P1–Rh1–P2	101.8(1)	P1–Rh1–P2	99.8(1)	P3–Rh2–P4	101.5(1)
P1–Rh1–C20	175.2(3)	P1–Rh1–C20	177.6(2)	P3–Rh2–C58	175.7(2)
P1–Rh1–O2	85.7(2)	P1–Rh1–CL1	88.7(1)	P3–Rh2–O2	86.4(1)
P1–Rh1–C1	83.5(3)	P1–Rh1–C1	84.3(2)	P3–Rh2–CL1	98.7(1)
P1–Rh1—CL	96.5(1)	P1–Rh1–O4	95.6(1)	P3–Rh2–C39	84.2(2)
P2–Rh1–C20	81.9(3)	P2–Rh1–C20	81.4(2)	P4–Rh2–C58	80.2(2)
P2–Rh1–O2	167.6(2)	P2–Rh1–CL1	168.1(1)	P4–Rh2–O2	168.8(1)
P2–Rh1–C1	87.8(4)	P2–Rh1–C1	84.8(2)	P4–Rh2–CL1	101.9(1)
P2–Rh1–CL	102.9(1)	P2–Rh1–O4	104.4(1)	P4–Rh2–C39	89.0(2)
C20–Rh1–O2	90.1(3)	C20–Rh1–CL1	89.9(2)	C58–Rh2–O2	90.8(2)
C20–Rh1–C1	93.7(4)	C20–Rh1–C1	93.8(3)	C58–Rh2–CL1	84.3(2)
C20–Rh1–CL	85.5(3)	C20–Rh1–O4	86.1(2)	C58–Rh2–C39	92.3(3)
O2–Rh1–C1	83.3(4)	C1–Rh1–CL1	87.7(2)	O2–Rh2–CL1	84.5(1)
O2–Rh1–CL	85.8(2)	C1–Rh1–O4	170.6(2)	O2–Rh2–C39	83.9(2)
CL–Rh1-C1	169.1(4)	CL1–Rh1–O4	82.9(1)	CL1–Rh2–C39	167.9(2)

(A) –x, y, –z + 3/2.

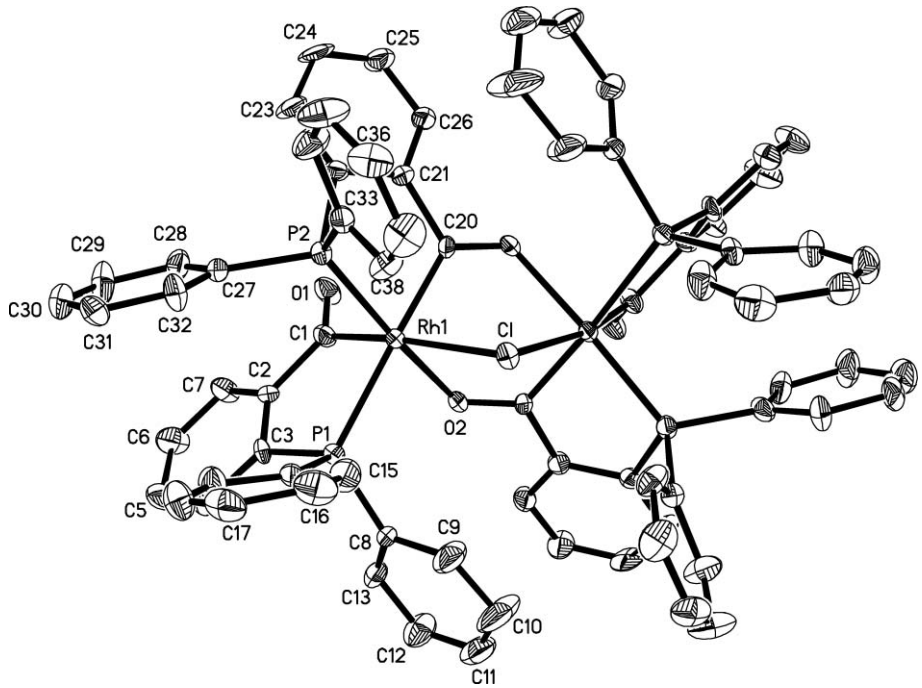


Fig. 3 ORTEP view of the cation in compound [**8a**]BF_4 showing the atomic numbering (20% probability ellipsoids). The hydrogen atoms and the labels of some carbon atoms have been omitted for clarity (symmetry operation –x, y, –z + 3/2).

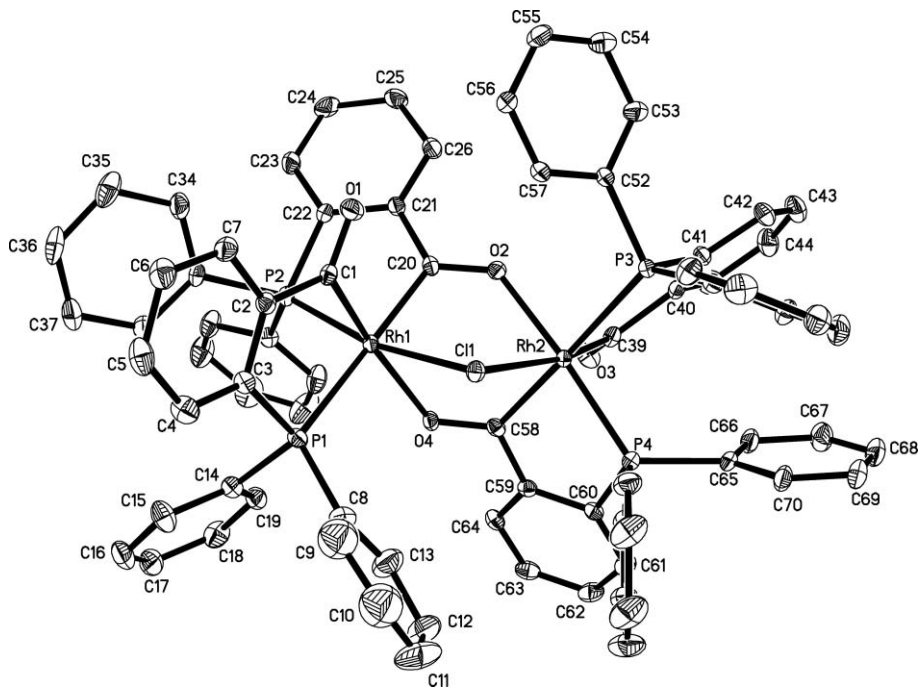


Fig. 4 ORTEP view of the cation in compound [**8b**]ClO_4 showing the atomic numbering (20% probability ellipsoids). The hydrogen atoms and the labels of some carbon atoms have been omitted for clarity.

the Rh–Cl distances reported for complexes containing a terminal or a bridging chlorine ligand *trans* to acyl (2.521(1) Å) or benzyl (2.507(2) and 2.522(2) Å) groups respectively.[13a,24] Carbene-like character in bridging acyls is reflected by shorter M–C and longer C–O bond distances than in terminal acyl ligands. The Rh–C and the C–O distances of the bridging and terminal acyl groups in **8a** are equal. Compared to other rhodium complexes with carbene-like character,[21–23] the Rh–C distances (2.01(1) Å) are in the upper end of the range reported (1.907(7)–2.05(2) Å) and the (C–O) distances (1.22(1) Å) are somewhat shorter than the range observed (1.24–1.29 Å). These observations confirm the low carbenoid character of the bridging acyl groups in **8**, suggested by the spectroscopic data. In **8b** the rhodium atoms Rh1 and Rh2 show a different disposition of the ligands. Consequently the

chlorine ligand is *trans* through Rh2 to the carbon atom of a terminal acyl group, as in **8a**, and to a phosphorus atom through the Rh1 atom. In accordance with the different *trans* influence, the Rh2–Cl distance (2.514(2) Å) is longer than the Rh1–Cl distance 2.454(2) Å. Other structural features are similar to those in **8a**. The Rh–P distances reflect the decreasing *trans* influence in the series: acyl (Rh1–P1 = Rh2–P3 = 2.387(2) Å) ≫ chlorine (Rh1–P2 = 2.266(2) Å) > oxygen (Rh2–P4 = 2.254(2) Å). The dihedral angles between the best least-square planes of the metallocycle and the condensed ring depend on the chelating or bridging-chelating nature of the ligand and also on the coordinative environment of the rhodium atom.[25] In all cases the highest deviation from planarity corresponds to the bridging-chelating ligands. Surroundings such as those in **8a** also lead to a larger deviation from planarity.

A third isomer, **8c** shown in Scheme 3, is also possible. In the reaction of **1** with acids the starting material contains mutually *trans* phosphorus atoms and the formation of **8** requires a displacement reaction and also an isomerisation reaction. We reasoned that by using a starting material containing *cis* phosphorus atoms, complex **8c** could be more easily obtained. **8c**, containing the weakest σ-donor oxygen atoms *trans* to the strongest σ-donor acyl groups, represents the most electronically favourable geometry for **8**. Indeed, the reaction of $[Rh(PPh_2(o\text{-}C_6H_4CO))_2(ndmeen)]ClO_4$ (**5**) with HCl led to the displacement of the diamine and the formation of a [**8a**]A:[**8b**]A:[**8c**]A = 1:1:3 mixture (A = ClO_4) where the most abundant isomer is **8c**. In **8c** a cisoid disposition of the phosphine groups of the bridging-chelating ligands binding to the same face of the complex, and also a cisoid disposition of the acyl-phosphine terminal groups is observed. Repeated attempts to obtain single crystals of **8c** to perform an X-ray diffraction study proved unsuccessful.

Conclusions

Cationic diacyl, bis(phosphine), aliphatic diamine rhodium(III) complexes adopt selectively the *cis*-diacyl, *cis*-PPh_2R geometry. In complexes containing N-methyl substituted diamines, more basic amino groups prefer positions *trans* to an acyl group while less basic amino groups are *trans* to a phosphine group. The preferred intramolecular N—H···O hydrogen bond formation between an amino and an acyl coordinated ligand, *trans* to phosphorus atoms, appears to be relevant to the selectivity observed. Elimination of the N-donor ligands allow the preparation of dimer complexes containing two acyl groups in a head-to-tail arrangement and a chloride bridging the Rh atoms. A mixture of three possible isomers can be obtained with a higher amount of the isomer showing the most electronically favourable geometry.

Experimental

General procedures

The preparation of the metal complexes was carried out at room temperature under nitrogen by standard Schlenk techniques. $[RhCl(PPh_2(o\text{-}C_6H_4CO))_2(py)]$ (**1**)[13a] was prepared as previously reported. Microanalyses were carried out with a Leco CHNS–932 microanalyser. Conductivities were measured in acetone solution with a Metrohm 712 conductimeter. IR spectra were recorded with a Nicolet FTIR 510 spectrophotometer in the range 4000–400 cm^{-1} using KBr pellets. NMR spectra were recorded with Bruker Avance DPX 300 or Bruker Avance 500 spectrometers, ^1H and $^{13}C\{^1H\}$ (TMS internal standard), $^{31}P\{^1H\}$ (H_3PO_4 external standard) and 2D spectra were measured from $CDCl_3$ solutions. Mass spectra were recorded on a VG Autospec, by liquid secondary ion (LSI) MS using nitrobenzyl alcohol as matrix and a caesium gun (Universidad de Zaragoza).

$[Rh(PPh_2(o\text{-}C_6H_4CO))_2(stien)]ClO_4$ (2). To a dichloromethane suspension of $[RhCl(PPh_2(o\text{-}C_6H_4CO))_2(py)]$ (60 mg, 0.075 mmol) was added stilbenodiamine (16.0 mg, 0.074 mmol) whereupon a yellow solution was formed. After stirring for 1 h, a methanol solution of $NaClO_4{\cdot}H_2O$ (10.5 mg, 0.075 mmol) was added. Evaporation to dryness and dissolution of the solid residue in dichloromethane was followed by filtration through Celite®. Addition of diethyl ether gave a yellow solid that was filtered off, washed with diethyl ether and vacuum dried. Yield: 75%. IR (KBr, cm^{-1}): 3344(s), 3293(s), ν(NH); 1648(s), ν(C=O). Λ_M (Ω^{-1} cm^2 mol^{-1}): 152 (acetone). ^1H NMR ($CDCl_3$): δ 5.38 (m, 1H, NH); 4.80 (m, 1H, CH); 4.31 (m, 1H, NH); 3.60 (m, 1H, CH); 3.33 (m, 1H, NH), 1.48 (m, 1H, NH). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 57.8 (dd, J(Rh,P) = 156 Hz, J(P,P) = 15 Hz, P_A); 15.9 (dd, J(Rh,P) = 74 Hz, P_M). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 237.3 (dd, J(P,C) = 105 Hz, J(Rh,C) = 30 Hz, RhC_AO); 231.4 (dd, J(P,C) = 10, J(Rh,C) = 29 Hz, RhC_MO); 64.7 (s, CH); 57.2 (s, CH). FAB-MS: calcd for $C_{52}H_{44}N_2O_2P_2Rh$, 893; obsd, 893 [M^+]. Anal. calc. for $C_{52}H_{44}ClN_2O_6P_2Rh$: C, 62.88; H, 4.47; N, 2.82; found: C, 62.56; H, 4.74; N, 2.88%.

$[Rh(PPh_2(o\text{-}C_6H_4CO))_2(pn)]ClO_4$ (3). To a chloroform suspension of $[RhCl(PPh_2(o\text{-}C_6H_4CO))_2(py)]$ (50 mg, 0.063 mmol) was added 1,2-propanediamine (4.7 mg, 0.063 mmol) whereupon a yellow solution was formed. After refluxing over 4 h, a methanol solution of $NaClO_4{\cdot}H_2O$ (8.9 mg, 0.063 mmol) was added. Evaporation to dryness and dissolution of the solid residue in dichloromethane was followed by filtration through Celite®. Addition of diethyl ether gave a yellow solid that was filtered off, washed with diethyl ether and vacuum dried. Yield: 59%. IR (KBr, cm^{-1}): 3323(m), 3283 (m), ν(NH); 1637(s), ν(C=O). Λ_M (Ω^{-1} cm^2 mol^{-1}): 121 (acetone). ^1H NMR ($CDCl_3$): δ 3.80 (s, 2H, NH); 2.93 (m, 1H, CH_2); 2.66 (s, 1H, NH); 2.34 (m, 1H, CH_2), 1.92 (s, 1H, CH); 1.23 (s, 1H, NH); 0.95 (m, 3H, CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 63.5 (dd, J(Rh,P) = 151 Hz, J(P,P) = 18 Hz, P_A); 26.9 (dd, J(Rh,P) = 79 Hz, P_M). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 239.6 (dd, J(P,C) = 109 Hz, J(Rh,C) = 30 Hz, RhC_AO); 234.2 (dd, J(P,C) = 9 Hz, J(Rh,C) = 29 Hz, RhC_MO); 53.2 (s, CH); 46.8 (s, CH_2); 20.0 (s, CH_3). Anal. calc. for $C_{41}H_{38}ClN_2O_6P_2Rh{\cdot}0.5CH_2Cl_2$: C, 55.54; H, 4.38; N, 3.12; found: C, 55.68; H, 4.96; N, 3.43%.

$[Rh(PPh_2(o\text{-}C_6H_4CO))_2(meen)]ClO_4$ (4). To a dichloromethane suspension of $[RhCl(PPh_2(o\text{-}C_6H_4CO))_2(py)]$ (40 mg, 0.05 mmol) was added N-methylethylenediamine (3.7 mg, 0.05 mmol) whereupon a yellow solution was formed. After stirring for 3 days, a methanol solution of $NaClO_4{\cdot}H_2O$ (7.0 mg, 0.05 mmol) was added. Evaporation of dichloromethane gave a yellow solid that was filtered off, washed with methanol and vacuum dried. Yield: 42%. IR (KBr, cm^{-1}): 3327(m), 3287(m), ν(NH); 1631(s), ν(C=O). Λ_M (Ω^{-1} cm^2 mol^{-1}): 127 (acetone). Data for **4a**. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 64.5 (dd, J(Rh,P) = 157 Hz,

J(P,P) = 18 Hz, P_A); 23.2 (dd, J(Rh,P) = 74 Hz, P_M). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 52.5 (s, CH_2); 43.3 (s, CH_2); 40.8 (s, CH_3). Data for **4b**. ^1H NMR ($CDCl_3$): δ 5.09 (s, 1H, NH); 3.98 (s, 1H, NH); 3.18 (m, 1H, CH_2); 2.60 (m, 2H, CH_2); 2.31 (m, 1H, CH_2); 1.82 (m, 3H, CH_3); 0.95 (m, 1H, NH). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 62.3 (dd, J(Rh,P) = 150 Hz, J(P,P) = 18 Hz, P_A); 23.8 (dd, J(Rh,P) = 80 Hz, P_M). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 240.1 (dd, J(Rh,C) = 30 Hz, J(P,CO) = 108 Hz, RhC_AO); 237.4 (dd, J(Rh,C) = 29 Hz, J(P,CO) = 8 Hz, RhC_MO); 56.5 (s, CH_2); 40.8 (s, CH_2); 38.9 (s, CH_3). FAB-MS: calcd for $C_{41}H_{38}N_2O_2P_2Rh$, 755; obsd, 755 [M^+]. Anal. calc. for $C_{41}H_{38}ClN_2O_6P_2Rh$: C, 57.59; H, 4.48; N, 3.28; found: C, 57.08; H, 4.07; N, 3.60%.

[Rh(PPh$_2$(*o*-C$_6$H$_4$CO))$_2$(ndmeen)]ClO$_4$ (5). To a dichloromethane suspension of [RhCl(PPh$_2$(*o*-C$_6$H$_4$CO))$_2$(py)] (50 mg, 0.063 mmol) was added N,N-dimethylethylenediamine, (5.6 mg, 0.063 mmol) whereupon a yellow solution was formed. After stirring for 1 h, a methanol solution of $NaClO_4 \cdot H_2O$ (8.9 mg, 0.063 mmol) was added. Evaporation of dichloromethane gave a yellow solid that was filtered off, washed with methanol and vacuum dried. Yield: 69%. IR (KBr, cm^{-1}): 3330(m), 3237(w), ν(NH); 1634(s), ν(C=O). Λ_M (Ω^{-1} cm^2 mol^{-1}): 140 (acetone). ^1H NMR ($CDCl_3$): δ 4.04 (s, 1H, NH); 3.10 (s, 1H, NH); 2.85 (m, 2H, CH_2); 2.60 (m, 3H, CH_3); 1.95 (m, 2H, CH_2); 1.20 (m, 3H, CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 60.8 (dd, J(Rh,P) = 158 Hz, J(P,P) = 18 Hz, P_A); 20.2 (dd, J(Rh,P) = 76 Hz, P_M). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 236.0 (dd, J(Rh,C) = 31 Hz, J(P,CO) = 106 Hz, RhC_AO); 228.8 (dd, J(Rh,C) = 29 Hz, J(P,CO) = 7 Hz, RhC_MO); 61.4 (s, CH_2); 53.9 (s, CH_3); 51.3 (s, CH_3); 41.6 (s, CH_2). FAB-MS: calcd for $C_{42}H_{40}N_2O_2P_2Rh$, 769; obsd, 769 [M^+]. Anal. calc. for $C_{42}H_{40}ClN_2O_6P_2Rh \cdot 0.25CH_2Cl_2$: C, 57.00; H, 4.58; N, 3.15; found: C, 56.94; H, 3.98; N, 3.22%.

[Rh(PPh$_2$(*o*-C$_6$H$_4$CO))$_2$(dmeen)]ClO$_4$ (6). To a dichloromethane suspension of [RhCl(PPh$_2$(*o*-C$_6$H$_4$CO))$_2$(py)] (60 mg, 0.075 mmol) was added N,N′-dimethylethylenediamine, (6.6 mg, 0.075 mmol) whereupon a yellow solution was formed. After stirring for 1 h, a methanol solution of $NaClO_4 \cdot H_2O$ (10.5 mg, 0.075 mmol) was added. Evaporation of dichloromethane gave a yellow solid that was filtered off, washed with methanol and vacuum dried. Yield: 50%. IR (KBr, cm^{-1}): 3270(m), 3160(m), ν(NH); 1629(s), ν(C=O). Λ_M (Ω^{-1} cm^2 mol^{-1}): 130 (acetone). Data for **5a**. ^1H NMR ($CDCl_3$): δ 5.09 (s, 1H, NH); 4.35 (s, 1H, NH); 3.19 (m, 1H, CH_2); 2.42 (m, 3H, CH_2); 1.83 (m, 3H, CH_3); 1.29 (m, 3H, CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 62.8 (dd, J(Rh,P) = 156 Hz, J(P,P) = 18 Hz, P_A); 20.9 (dd, J(Rh,P) = 77 Hz, P_M). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 238.7 (dd, J(Rh,C) = 31 Hz, J(P,CO) = 106 Hz, RhC_AO); 235.2 (dd, J(Rh,C) = 29 Hz, J(P,CO) = 10 Hz, RhC_MO); 54.3 (s, CH_2); 52.1 (s, CH_2); 41.3 (s, CH_3); 39.1 (s, CH_3). FAB-MS: calcd for $C_{42}H_{40}N_2O_2P_2Rh$, 769; obsd, 769 [M^+]. Anal. calc. for $C_{42}H_{40}ClN_2O_6P_2Rh$: C, 58.04; H, 4.64; N, 3.22; found: C, 58.42; H, 5.02; N, 3.36%.

[Rh(PPh$_2$(*o*-C$_6$H$_4$CO))$_2$(trimeen)]ClO$_4$ (7). To a dichloromethane suspension of [RhCl(PPh$_2$(*o*-C$_6$H$_4$CO))$_2$(py)] (50 mg, 0.063 mmol) was added N,N,N′-trimethylethylenediamine (6.5 mg, 0.062 mmol). After stirring for 1 h, a methanol solution of $NaClO_4 \cdot H_2O$ (8.9 mg, 0.062 mmol) was added, whereupon a yellow solution was formed. Evaporation to dryness and dissolution of the solid residue in dichloromethane was followed by filtration through Celite®. Addition of diethyl ether gave a yellow solid that was filtered off, washed with diethyl ether and vacuum dried. Yield: 48%. IR (KBr, cm^{-1}): 3263(m), ν(NH); 1636(s), ν(C=O). Λ_M (Ω^{-1} cm^2 mol^{-1}): 107 (acetone). FAB-MS: calcd for $C_{43}H_{42}N_2O_2P_2Rh$, 783; obsd, 783 [M^+]. Anal. calc. for $C_{43}H_{42}ClN_2O_6P_2Rh \cdot 0.5CH_2Cl_2$: C, 56.45; H, 4.68; N, 3.03; found: C, 56.06; H, 4.24; N, 3.23%. Data for **7a**. ^1H NMR ($CDCl_3$): δ 5.10 (s, 1H, NH); 2.90 (m, 1H, CH_2); 2.85 (m, 3H, CH_3); 2.74 (m, 2H, CH_2); 2.35 (m, 1H, CH_2); 1.85 (m, 3H, CH_3); 1.12 (m, 3H, CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 57.8 (dd, J(Rh,P) = 156 Hz, J(P,P) = 15 Hz, P_A); 15.9 (dd, J(Rh,P) = 76 Hz, P_M). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 235.9 (dd, J(Rh,C) = 32 Hz, J(P,CO) = 104 Hz, RhC_AO); 231.6 (m, br, RhC_MO); 61.2 (s, CH_2); 54.5 (s, CH_3); 53.5 (s, CH_2); 51.5 (s, CH_3); 39.2 (s, CH_3). Data for **7b**. ^1H NMR ($CDCl_3$): δ 2.85 (m, 1H, CH_2); 2.40 (m, 3H, CH_3); 2.29 (m, 3H, CH_3); 2.20 (m, 1H, CH_2); 2.04 (m, 1H, CH_2); 1.73 (m, 3H, CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 61.4 (dd, J(Rh,P) = 162 Hz, J(P,P) = 18 Hz, P_A); 21.2 (dd, J(Rh,P) = 70 Hz, P_M). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 235.7 (dd, J(Rh,C) = 32 Hz, J(P,CO) = 104 Hz, RhC_AO); 231.6 (m, br, RhC_MO); 63.4 (s, CH_2); 55.7 (s, CH_2); 50.1 (s, CH_3); 45.0 (s, CH_3); 37.7 (s, CH_3).

[Rh$_2$(μ-Cl)(μ-PPh$_2$(*o*-C$_6$H$_4$CO))$_2$(PPh$_2$(*o*-C$_6$H$_4$CO))$_2$]BF$_4$ [8]BF$_4$. To a dichloromethane solution of [RhCl(PPh$_2$(*o*-C$_6$H$_4$CO))$_2$(py)] (50 mg, 0.063 mmol) was added $HBF_4 \cdot OEt_2$ (20.4 mg, 0.126 mmol). Stirring for 30 min gave a suspension. Filtration of the white [pyH]BF_4 through Celite®, followed by addition of diethyl ether to the solution gave a yellow solid containing a mixture of **8a** and **8b** (**8a**:**8b** = 1:1.5) that was filtered off, washed with diethyl ether and vacuum dried. Yield: 35%. Anal. calc. for $C_{76}H_{56}BF_4ClO_4P_4Rh_2 \cdot 0.5CH_2Cl_2$: C, 60.14; H, 3.76; found: C, 60.12; H, 3.99%.

[Rh$_2$(μ-Cl)(μ-PPh$_2$(*o*-C$_6$H$_4$CO))$_2$(PPh$_2$(*o*-C$_6$H$_4$CO))$_2$]ClO$_4$ [8]ClO$_4$.

Method a. To a methanol suspension of [RhCl(PPh$_2$(*o*-C$_6$H$_4$CO))$_2$(py)] (65 mg, 0.082 mmol) was added aqueous 11.7 M $HClO_4$ (24.7 mg, 0.246 mmol). Stirring for 3 h gave a yellow solid containing a mixture of **8a** and **8b** (**8a**:**8b** = 1:1.5) that was filtered off, washed with methanol and vacuum dried. Yield: 70%.

Method b. HCl gas was bubbled at room temperature through a methanol suspension of [Rh(PPh$_2$(*o*-C$_6$H$_4$CO))$_2$(ndmeen)]ClO$_4$ (**5**) (30 mg, 0.035 mmol) for 45 min whereupon dissolution of the solid occurred. Evaporation to dryness and dissolution of the solid residue in dichloromethane was followed by filtration through Celite®. Addition of diethyl ether gave a yellow solid containing a mixture of **8a**, **8b** and **8c** (**8a**:**8b**:**8c** = 1:1:3) that was filtered off, washed with diethyl ether and vacuum dried. Yield: 49%. IR (KBr, cm^{-1}): 1653(s), ν(C=O)$_t$; 1548(s), ν(C=O)$_b$. Λ_M (Ω^{-1} cm^2 mol^{-1}): 92 (acetone). FAB-MS: calcd for $C_{76}H_{56}ClO_4P_4Rh_2$, 1397; obsd, 1397 [M^+]. Anal. calc. for $C_{76}H_{56}Cl_2O_8P_4Rh_2$: C, 60.94; H, 3.77; found: C, 61.21; H, 4.08%.

Data for **8a**. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 61.9 (dd, J(Rh,P) = 181 Hz, J(P,P) = 15 Hz, P_b); 32.6 (dd, J(Rh,P) = 92 Hz, P_a). Data for **8b**. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 65.5 (dd, J(Rh,P) = 178 Hz, J(P,P) = 18 Hz, P_b); 64.3 (dd, J(Rh,P) = 172 Hz, J(P,P) = 18 Hz, P_d); 28.6 (dd, J(Rh,P) = 89 Hz, J(P,P) = 18 Hz) and 28.2 (dd, J(Rh,P) = 89 Hz, J(P,P) = 18 Hz) *for* P_a and P_c. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 269.1 (dd, J(Rh,C) = 31 Hz, J(P,C) = 114 Hz) and 264.6 (dd, J(Rh,C) = 31 Hz, J(P,C) = 113 Hz) for RhC_bO and

Table 3 Crystal data and structure refinement for compounds **5**, **6**, **8a** and **8b**

Crystal data	**5**	**6**	**8a**	**8b**
Empirical formula	$[C_{42}H_{40}N_2O_2P_2Rh]ClO_4$	$[C_{42}H_{40}N_2O_2P_2Rh]ClO_4$	$[C_{76}H_{56}Cl_1O_4P_4Rh_2]BF_4C_4H_{10}O$	$[C_{76}H_{56}Cl_1O_4P_4Rh_2]ClO_4$
Formula weight	869.06	869.06	1630.19	1497.81
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$Pbca$	$C2/c$	$P2_1/n$
a/Å	12.099(1)	15.477(1)	17.918(2)	20.297(1)
b/Å	15.619(1)	18.986(1)	18.406(2)	11.823(1)
c/Å	20.840(1)	26.371(1)	20.657(3)	28.380(2)
β/°	99.823(1)	—	92.365(3)	98.824(1)
Volume (Å^3)	3880.3(4)	7748.8(7)	6807(1)	6729.6(7)
Z	4	8	4	4
D(calcd), g cm^{-3}	1.488	1.490	1.591	1.478
Absorption coefficient (mm^{-1})	0.642	0.643	0.763	0.722
scan technique	ω and φ	ω and φ	ω and φ	ω and φ
F(000)	1784	3568	3312	3040
range (for data collection (°)	1.64 to 29.00	1.54 to 29.09	1.59 to 25.00	1.15 to 25.00
Index ranges	–16, –21, –28 to 16, 20, 28	–20, –25, –31 to 21, 25, 34	–21, –21, –24 to 21, 21, 22	–24, –13, –33 to 24, 14, 33
Reflections collected	36545	71166	25936	50730
Independent reflections	9649 [R(int) = 0.0790]	9838 [R(int) = 0.0726]	6001 [R(int) = 0.1735]	11825 [R(int) = 0.0864]
Completeness to theta	93.5%	94.7%	100%	100%
Data/restraints/parameters	9649/0/469	9838/0/489	6001/0/393	11825/6/799
R^a(refl. obser.) [$I>2\sigma(I)$]	0.0556(4706)	0.0361 (5640)	0.0845 (2267)	0.0497 (6562)
$Rw_F{}^b$ (all data)	0.1717	0.0918	0.2442	0.1514
Largest diff. peak and hole (e Å^{-3})	1.237 and –1.014	0.629 and –0.385	1.864 and –1.276	1.426 and –0.953

$^a \Sigma \| F_o \| - | F_c \| / \Sigma | F_o |$ $^b \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$.

RhC_aO; 222.2 (dd, J(Rh,C) = 30 Hz, J(P,C) = 8 Hz) and 218.0 (dd, J(Rh,C) = 29 Hz, J(P,C) = 7 Hz) for RhC_aO and RhC_cO. Data for **8c**. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 68.2 (dd, J(Rh,P) = 178 Hz, J(P,P) = 24 Hz, P_d); 26.4 (dd, J(Rh,P) = 89 Hz, P_c). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 265.8 (dd, J(Rh,C) = 33 Hz, J(P,C) = 117 Hz, RhC_aO); 219.0 (dd, J(Rh,C) = 29 Hz, J(P,C) = 7 Hz, RhC_cO).

X-ray structure determination of 5, 6, [8a]BF_4 and [8b]ClO_4

Good quality crystals of **5** and **6** suitable for X-ray experiments were obtained by slow diffusion of diethyl ether into dichloromethane solutions. Crystals of [**8a**]BF_4 and [**8b**]ClO_4 were obtained by fractional crystallisation. In both cases slow diffusion of diethyl ether into dichloromethane solutions afforded solids that were filtered. Yellow crystals of [**8a**]BF_4 were obtained by dissolution of the corresponding solid in chloroform and slow diffusion of diethyl ether into this solution. Yellow crystals of [**8b**]ClO_4 were obtained by slow diffusion of diethyl ether into the remaining original dichloromethane solution. A summary of the fundamental crystal and refinement data are given in Table 3. In all the cases a yellow crystal was resin epoxy coated and mounted on a Bruker Smart CCD diffractometer, with graphite-monochromated Mo-K_α ($\lambda = 0.71073$) radiation, operating at 50 kV and 20 mA. Data were collected over a hemisphere of the reciprocal space by combination of three exposure sets. All the structures were solved by direct methods and conventional Fourier techniques and refined by applying full-matrix least-squares on F^2 with anisotropic thermal parameters for the non-hydrogen atoms, with some exceptions. For **5**, the oxygen atoms of the ClO_4^- group were refined isotropically. For [**8b**]ClO_4, due to a non-resolvable positional disorder, the carbon atoms of one phenyl ring were refined with restrained C–C distances. Two carbon atoms in this phenyl ring and the oxygen atoms of the ClO_4^- group were refined isotropically. In compound [**8a**]BF_4, the BF_4^- anion was included with fixed isotropic contributions. In the last cycles of refinement some diffuse electronic residual density could not be properly modelled. Therefore, the SQUEEZE program, a part of the PLATON package of crystallographic software,[26] was used to calculate the solvent disorder area and remove its contribution to the overall intensity data. An improvement was observed in all refinement parameters and residuals when this procedure is applied. The number of electrons in the solvent region corresponds to one diethyl ether molecule per dimer molecule in the crystal. In all cases the hydrogen atoms were included with fixed isotropic contributions at their calculated positions determined by molecular geometry and refined riding on the corresponding bonded atom, except for the H1 and H2 bonded to N1 and N2 for **6** and **5**, which were located from the Fourier map included and were not refined. All the calculations were carried out with SHELX-97.[27]

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