Reaction of $[RhH(NH_2C_6H_4PPh_2\text{-}o)_2Cl]Cl$ with Air; Characterisation of the Products by *X*-Ray Structure Analysis of *cis*-$[Rh(NH_2C_6H_4PPh_2\text{-}o)(NHC_6H_4PPh_2\text{-}o)Cl_2]$ and *trans*-$[Rh(NH_2C_6H_4PPh_2\text{-}o)_2Cl_2][p\text{-}MeC_6H_4SO_3]\cdot MeCN$ [‡]

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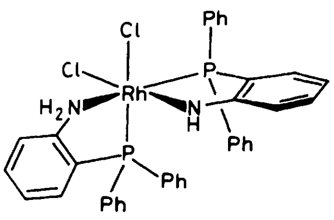
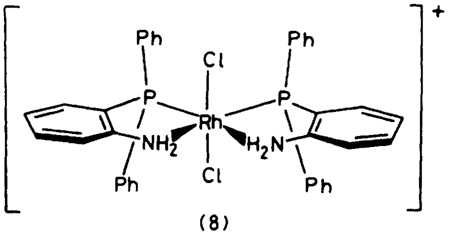
The chlorohydridorhodium(III) complex of (*o*-diphenylphosphinophenyl)amine, $[RhH(NH_2C_6H_4PPh_2\text{-}o)_2Cl]Cl$ (1a), formed by oxidative addition of HCl to $[Rh(NH_2C_6H_4PPh_2\text{-}o)_2]BF_4$ (2b), was found to react with air to give two products. These have been characterised by *X*-ray structure analysis as the *cis*-dichloro-complex $[Rh(NH_2C_6H_4PPh_2\text{-}o)(NHC_6H_4PPh_2\text{-}o)Cl_2]$ (6), containing an amino- and amido-donor group, and the *trans*-dichloro-complex $[Rh(NH_2C_6H_4PPh_2\text{-}o)_2Cl_2][p\text{-}MeC_6H_4SO_3]$ (8). Crystals of (6) are monoclinic, space group $P2_1/n$, with $a = 17.153(3)$, $b = 18.667(3)$, $c = 9.891(2)$ Å, $\beta = 91.77(3)°$, and $Z = 4$. Blocked full-matrix refinement using 3 501 unique data [$I \geqslant 3\sigma(I)$, $3 \leqslant \theta \leqslant 25°$] gave $R = 0.0487$, $R' = 0.0511$. Complex (8) crystallises, with a molecule of acetonitrile as solvate, in the monoclinic space group $I2/c$ with $a = 18.394(4)$, $b = 14.380(3)$, $c = 16.378(3)$Å, $\beta = 96.67(4)°$, and $Z = 4$. Blocked full-matrix refinement of 2 741 reflections with $I \geqslant 3\sigma(I)$ ($3 \leqslant \theta \leqslant 25°$) gave $R = 0.0638$ and $R' = 0.0698$. The cation of (8) has exact C_2 symmetry. A mechanism for the reaction is proposed which involves peroxo- and hydrogenperoxo-species.

We are interested in the rhodium complexes of (*o*-diphenylphosphinophenyl)amine (H_2L), in view of their possible catalytic activity. H_2L [1] is the first example of a hybrid ligand containing a 'soft' phosphorus and a 'hard' primary aromatic amine donor set, and has the additional feature in that upon co-ordination the amino-group can be readily deprotonated to form an amido-donor group.[1,2] In common with other late transition metals [3-5] few rhodium-amido-complexes [6-9] are known. We found that the chlorohydrido-complex $[RhH(H_2L)_2Cl]Cl$ (1a), prepared from $[Rh(H_2L)_2]BF_4$ (2b), on exposure to air gave a mixture of unknown composition from which we have isolated two products (6) and (8); these have been characterised by *X*-ray structure analysis. The structures of (6) and (8) together represent an example of two complexes in which the differences in the stereochemical requirements of amido- and amino-donor atoms may be examined.

A number of workers [10-15] have commented on the air sensitivity of some rhodium and iridium complexes, although few of the reaction products have been identified. The identification of (6) and (8) has allowed us to suggest a mechanism for the reaction involving peroxo- and hydrogenperoxo-intermediates.



(6)



(8)

Results and Discussion

The reaction of two equivalents of H_2L with $[\{Rh(cod)Cl\}_2]$ (cod = cyclo-octa-1,5-diene) under nitrogen gives *cis*-$[Rh(H_2L)_2]X$ [$X = Cl^-$ (2a), BF_4^- (2b), or $p\text{-}MeC_6H_4SO_3^-$ (2c)]. When hydrochloric acid is added to an acetone suspension of freshly prepared (2b), *cis*-P,H-*trans*-Cl-$[RhH(H_2L)_2Cl]Cl$ (1a) is formed (Scheme 1). Exposure of an acetone-water solution of (1a) to air results in the formation of a dark brown crystalline material, shown by *X*-ray diffraction to be *cis*-P,*cis*-Cl,Cl-*trans*-NH^--$[Rh(H_2L)(HL)Cl_2]$ (6), with the structure shown in Figure 1. The addition of toluene-*p*-sulphonic acid to the mother-liquor gave crystals of *cis*-P,-*trans*-Cl-$[Rh(H_2L)_2Cl_2][p\text{-}MeC_6H_4SO_3]$ (8), with the structure shown in Figure 2. We have shown that compound (6) (*cis*-Cl) can only be converted to (8) under forcing conditions (100 °C, *ca.* 24 h). From this we deduced that the neutral species (7) (*trans*-Cl) was one of the components of the complex reaction mixture, see Scheme 1. The chloride anion in (1a) is important since a solution of the BF_4^- salt (1b) yields neither (6) nor (8) on exposure to air.

Oxygen is essential to the reaction as solutions of (1) are

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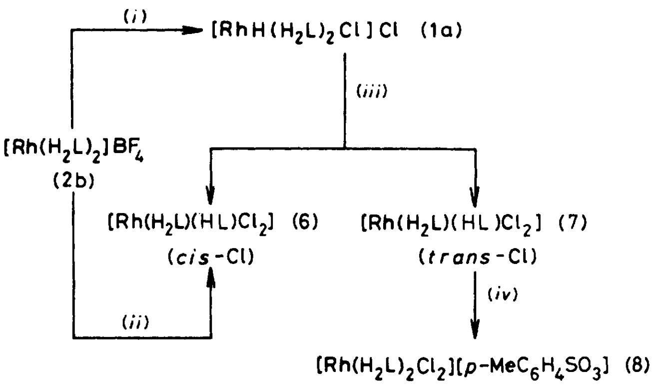
[‡] *cis*-Dichloro[(*o*-diphenylphosphinophenyl)amido-*N*,*P*][(*o*-diphenylphosphinophenyl)amine-*N*,*P*]rhodium(III) and *trans*-dichlorobis[(*o*-diphenylphosphinophenyl)amine-*N*,*P*]rhodium(III) toluene-*p*-sulphonate–acetonitrile (1/1) respectively.

Supplementary data available (No. SUP 56011, 22 pp.): thermal parameters, H-atom co-ordinates, full bond lengths and angles, least-squares plane data. See Instructions for Authors, *J. Chem. Soc., Dalton Transactions*, 1984, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.



Scheme 1. (*i*) HCl; (*ii*) LiCl, acetone, O_2; (*iii*) acetone, H_2O, O_2; (*iv*) p-$MeC_6H_4SO_3H$

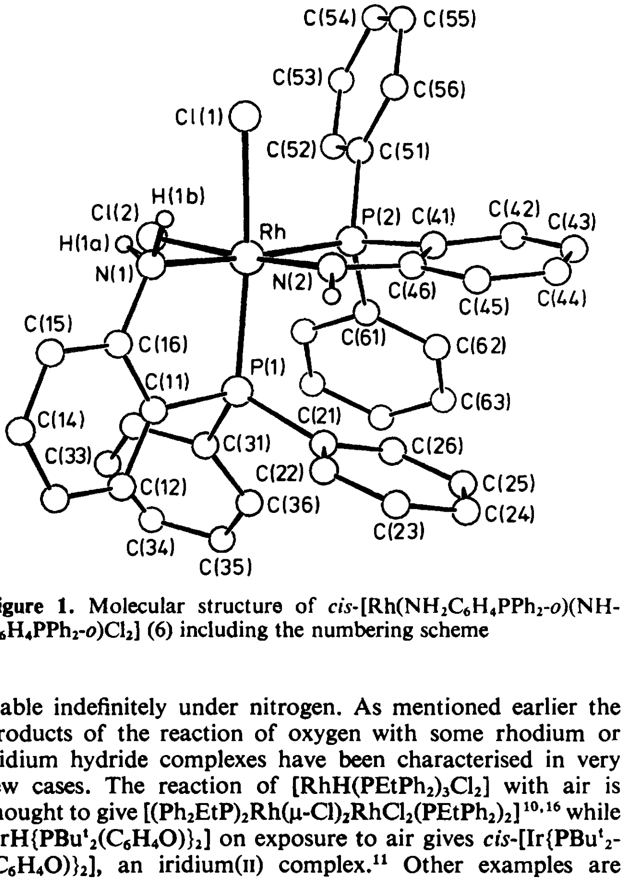


Figure 1. Molecular structure of *cis*-$[Rh(NH_2C_6H_4PPh_2\text{-}o)(NHC_6H_4PPh_2\text{-}o)Cl_2]$ (6) including the numbering scheme

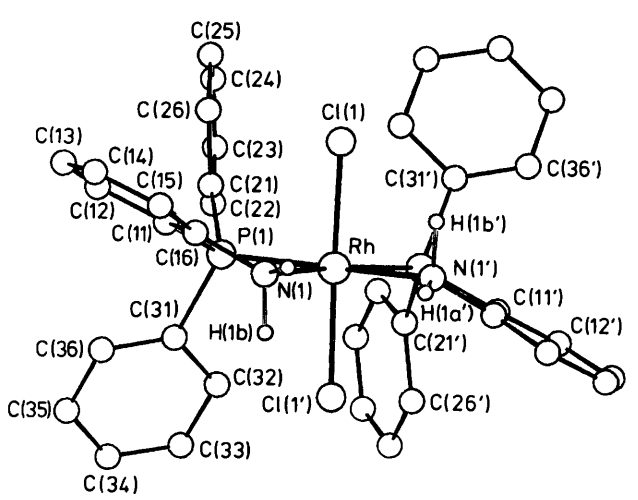


Figure 2. The structure of the cationic complex *trans*-$[Rh(NH_2C_6H_4PPh_2\text{-}o)_2Cl_2]^+$ (8) including the numbering scheme

stable indefinitely under nitrogen. As mentioned earlier the products of the reaction of oxygen with some rhodium or iridium hydride complexes have been characterised in very few cases. The reaction of $[RhH(PEtPh_2)_3Cl_2]$ with air is thought to give $[(Ph_2EtP)_2Rh(\mu\text{-}Cl)_2RhCl_2(PEtPh_2)_2]$[10,16] while $[IrH\{PBu^t_2(C_6H_4O)\}_2]$ on exposure to air gives *cis*-$[Ir\{PBu^t_2(C_6H_4O)\}_2]$, an iridium(II) complex.[11] Other examples are $[Rh(NH_3)_5H]^{2+}$ which reacts with oxygen to give $[Rh(NH_3)_4(OH)(O_2H)]^+$; [12] in contrast $[Rh(NH_3)_4(H_2O)H]^{2+}$ reacts with air only upon ultraviolet irradiation.[17] The complex *trans*-$[Rh(en)_2(OH)H]^+$ (en = ethylenediamine) on reaction with oxygen gives a mixture of *trans*-$[Rh(en)_2(OH)(O_2H)]^+$ and *trans*-$[Rh(en)_2(OH)_2]^+$ the relative amounts of which depend upon the pH of the final solution.[13]

Although we cannot be certain of the mechanism of formation of (6) and (8) from (1a) we suggest the sequence of reactions shown in Scheme 2. The initial step involves the loss of hydrogen chloride from (1a) by reductive elimination. This reaction appears to be an equilibrium which is driven to the right by the subsequent irreversible reaction of (2a) with oxygen. Evidence for this equilibrium (step A) comes from the contrasting effects of added acid or base. The addition of an equimolar amount of triethylamine leads to a more rapid development of the colour of the reaction products, while the addition of an equimolar amount of hydrochloric or tetrafluoroboric acid to solutions of (1a) completely inhibits the reaction. Further evidence for step A is provided by the observation that (2a) can be detected when the reaction of (1a) with air is followed by ^{31}P n.m.r. spectroscopy. Indeed (6) can be readily prepared by stirring in air an acetone solution of (2b) with excess lithium chloride (Scheme 1).

Step B involves the reaction of oxygen with (2a) to give the rhodium(III) peroxo-complex (O_2^{2-}) (3). Similar reactions of other Rh^I species are well established.[14,15] For example, the analogous complex, $[Rh(NMe_2C_6H_4PPh_2\text{-}o)_2]^+$ reacts with oxygen to give $[Rh(NMe_2C_6H_4PPh_2\text{-}o)_2(O_2)]^+$, which has been isolated as its SbF_6^- salt.[18] Complex (3) however is able to react further by transfer of a proton from the co-ordinated amino-group to one of the oxygen atoms giving rise to the five-co-ordinate monodentate hydrogenperoxo (O_2H^-) species (4) (step C), a reaction that is not possible for $[Rh(NMe_2C_6H_4PPh_2\text{-}o)_2(O_2)]^+$. However, proton transfer also appears to occur in the reaction of $[Rh(PPh_3)_3Cl(O_2)]$ with acetylacetone (Hacac), to give $[Rh(PPh_3)_2(acac)Cl(O_2H)]$.[19]

In the next step (D) chloride ion enters the co-ordination sphere of (4) to give the co-ordinatively saturated chlorohydrogenperoxo-complex (5). In the final step the hydrogenperoxo-ligand is displaced by a second chloride ion. The increased yield of (6) when the reaction is carried out in the presence of added chloride ion suggests that this step may be reversible, while the failure of the BF_4^- salt (1b) to give (6) and (8) can be attributed to an insufficiency of chloride ions to form the dichloro-species.

The transient species (3)—(5) could not be detected when the reaction was followed by ^{31}P n.m.r. and so the stereochemistry of these intermediates is unknown. We are therefore unable to say in which step (C, D, or E) the products (6) and (7) originate. Indeed the *cis*-Cl product (6) may be the preferred geometry (see Experimental section) only because of its greater insolubility.

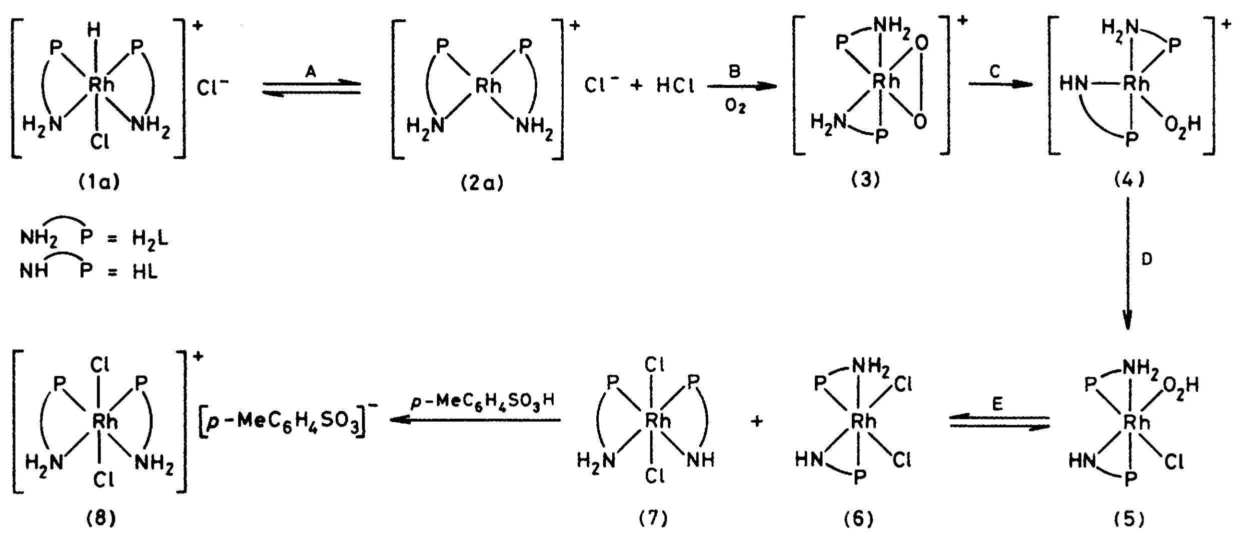
We assume that the hydrogenperoxide ion, dissociated in step E, reacts with the proton released in step A to give hydrogen peroxide. Although it is clear from the low yields of (6) and (8) that side-reactions occur, the overall reaction for Scheme 2 may be written as shown below.

$$[RhH(H_2L)_2Cl]Cl + O_2 \longrightarrow [Rh(H_2L)(HL)Cl_2] + H_2O_2$$

Table 1. Selected bond lengths (Å) and angles (°) for (6) and (8) *

	(6)	(8)		(6)	(8)		(6)	(8)
Rh–Cl(1)	2.419(2)	2.342(2)	Cl(1)–Rh–Cl(2)	88.7(1)	169.9(1)	Rh–P(1)–C(31)	124.4(2)	118.8(3)
Rh–Cl(2)	2.384(2)		Cl(1)–Rh–P(1)	167.9(1)	91.1(1)	C–P(1)–C range	100.8—107.1(2)	104.8—106.7(4)
Rh–P(1)	2.271(2)	2.295(2)	Cl(1)–Rh–P(2)	90.1(1)	95.1(2)	Rh–P(2)–C(41)	101.2(2)	
Rh–P(2)	2.262(2)		Cl(1)–Rh–N(1)	85.0(1)	86.8(2)	Rh–P(2)–C(51)	118.1(2)	
Rh–N(1)	2.143(5)	2.145(8)	Cl(1)–Rh–N(2)	87.4(1)	86.1(2)	Rh–P(2)–C(61)	117.4(2)	
Rh–N(2)	2.018(5)		Cl(2)–Rh–P(1)	95.6(1)		C–P(2)–C range	103.6—108.8(2)	
N(1)–C(16)	1.449(8)	1.468(12)	Cl(2)–Rh–P(2)	95.9(1)		Rh–N(1)–C(16)	118.0(4)	113.3(6)
N(2)–C(46)	1.364(8)		Cl(2)–Rh–N(1)	89.1(2)		Rh–N(2)–C(46)	120.0(4)	
N(1)–H(1a)	0.76	0.92	Cl(2)–Rh–N(2)	176.1(1)		Rh–N(1)–H(1a)	88	116
N(1)–H(1b)	1.05	1.06	P(1)–Rh–P(2)	100.7(1)	105.2(1)	Rh–N(1)–H(1b)	105	99
N(2)–H(2a)	0.98		P(1)–Rh–N(1)	83.7(1)	81.9(2)	H(1a)–N(1)–H(1b)	105	91
Mean P–C	1.818	1.804	P(1)–Rh–N(2)	88.3(1)	172.6(4)	Rh–N(2)–H(2a)	131	
			P(2)–Rh–N(1)	173.0(1)		P(1)–C(11)–C(16)	117.7(5)	116.0(7)
			P(2)–Rh–N(2)	83.9(2)		P(2)–C(41)–C(46)	113.6(5)	
			N(1)–Rh–N(2)	90.8(2)	91.0(4)	N(1)–C(16)–C(11)	118.4(6)	118.8(8)
			Rh–P(1)–C(11)	102.1(2)	100.6(3)	N(2)–C(46)–C(41)	120.6(6)	
			Rh–P(1)–C(21)	114.3(2)	119.4(3)			

* For compound (8) atoms Cl(2), P(2), and N(2) represent the symmetry related atoms Cl(1′), P(1′), and N(1′) respectively.



Scheme 2. For (3), (4), and (5) only one of the possible isomers is drawn

The neutral molecule (6) has the structure shown in Figure 1, and that of the cationic complex (8) is shown in Figure 2. Selected bond lengths and angles for both structures are given in Table 1.

In complexes (6) and (8) the Rh^{III} atom exhibits approximately octahedral co-ordination geometry. The maximum deviations from regularity occur in the angles subtended by the nitrogen- and phosphorus-donor atoms and may be explained by the steric requirements of the chelate rings. In (6) the angles from the H_2L and HL^- ligands are equal with experimental error, being P(1)–Rh–N(1) 83.7(1) and P(2)–Rh–N(2) 83.9(2)° respectively. In the cationic complex (8) where both ligands are in the neutral form, H_2L, and are equivalent by space group symmetry, the corresponding angle P–Rh–N is 81.9(2)°.

In (6) the chloro-ligands occupy *cis* positions with a Cl(1)–Rh–Cl(2) angle of 88.7(1)°. The Rh–Cl(1) bond *trans* to P(1) is significantly longer (0.035 Å, 17σ) than that of Rh–Cl(2) which is *trans* to the amido-nitrogen donor N(2), and confirms a marked difference in the *trans* influence of these two types of donors. A lower *trans* influence of the amido-group relative to the phosphine group was earlier deduced indirectly from comparison of the structures of the *cis* and *trans* isomers of $[Pt(HL)_2]$.[4] The chlorine atoms in (8) are mutually *trans* with equivalent Rh–Cl bond lengths of 2.342(2) Å. This distance is significantly shorter than those in (6) (mean 2.402 Å) and the difference may be attributed to two factors, first a small contraction in the covalent radius of Rh in (8) due to its cationic nature, and secondly a markedly higher *trans* influence for the organophosphino- and amido-donor groups relative to the chloro-ligand. In (8) the Cl–Rh–Cl angle is 169.9(1)°; this marked deviation from the ideal value (180°) for regular octahedral co-ordination results in a bending over of the two chloro-ligands to form strong H-bonds with a proton of each of the amino-donor groups [Cl(1) · · · H(1b) 2.51 Å]. A similar bending of *trans*-chlorine donor atoms was observed in the structure of the complex dichlorobis[*o*-(diphenylphosphino)anisole]ruthenium(II) where a Cl–Ru–Cl angle of 165.7° was attributed to intramolecular steric crowding between the chlorine atoms and the phenyl groups.[20] In (8) there is no evidence of this, the shortest contact distance to the chloro-ligands (apart from the amino-groups) is to a phenyl hydrogen of an adjacent molecule.

In the neutral molecule (6) there is a small but significant difference between the bonds from the P donor atoms, Rh–P(1) [2.271(2) Å] and Rh–P(2) [2.262(2) Å]; this may be attributed to the greater electronegativity of a chloro compared to an amino-N donor, which would reduce the π-donation to P(1), *trans* to Cl(1), compared to that to P(2) which is *trans* to N(1). In (8) the Rh–P bond lengths are equal by space group symmetry, Rh–P(1) 2.295(2) Å; they are however, significantly longer than the mean value of 2.266(2) Å observed for the corresponding bonds in (6). This is consistent with enhanced π back donation of electron density from the metal atom to the two phosphorus ligands in the neutral compound (6) compared to the cationic compound (8).

The equivalent Rh–N bonds in (8) [Rh–N(1)] have a length of 2.145(8) Å which does not differ significantly from the Rh–N(1)(amino) distance in (6) of 2.143(5) Å. The amido-N to metal bond in (6), Rh–N(2) 2.018(5) Å, is markedly shorter than the corresponding bond from the amino-N atom, Rh–N(1) 2.143(5) Å. Similar differences in bond lengths between these donor groups have been found before in neutral and deprotonated complexes of this ligand[4] but this is the first time that the structure of a compound with both forms present in the same molecule has been reported. However in this case the two types of N-donor are *trans* to different groups; the longer Rh–N(1) bond may in part be due to the greater *trans* influence of an organophosphine compared to a chloro-ligand.

The chelate rings in (8) are folded in opposite directions about the donor atoms (Figure 2) so that the dihedral angle between the least-squares plane through the co-ordinated atoms Rh, N(1), N(1′), P(1), and P(1′) and the phenyl ring of each chelate ring is 26.9°. The bending of the ligand appears to be due to a 'twisting' at N(1) which allows H(1b) to approach the chloro-ligand sufficiently closely for H-bonding to occur, Cl ··· H(1b) 2.51 Å. In contrast the chelate ring of the equivalent amino-ligand in (6) [Rh, P(1), N(1), C(11), and C(16)] is almost planar [maximum deviation, N(1) 0.02 Å]. The second chelate ring containing the amido-nitrogen donor [Rh, P(2), N(2), C(41), and C(46)] is slightly less planar [maximum deviations, C(41) -0.05 and C(46) 0.05 Å].

The chelate rings in both (6) and (8) show marked angular distortions; the maximum total angle possible in a pentagon is 540° with a planar arrangement which is 8° less than the total of 548° required for ideal values for octahedral co-ordination at the Rh atom, sp^3 hybridisation at the P and N atoms, and sp^2 hybridisation at the phenyl carbon atoms. The greatest distortions occur in the folded chelate ring of the cationic *trans*-complex (8) where the total of the angles is only 530.6°. Surprisingly,[3] although the angles at Rh [81.9(2)°], P(1) [100.6(3)°], and the carbon atoms [116.0(7) and 118.8(8)°] are less than the ideal values, as might be expected, the angle at the amino-N atom is considerably greater [113.3(6)°] than the ideal tetrahedral values for sp^3 hybridisation at this atom. In the almost planar chelate rings of the neutral compound (6) the angles at Rh and P are slightly larger than in (8) although they are still considerably smaller than the ideal values, [83.7(1) at Rh and 102.1(2) at P(1) for the amino-ring and 83.9(2) at Rh and 101.2(2)° at P(2) for the amido-ring]. Surprisingly the intraring angles at the nitrogen atoms in both the amino- and amido-chelate rings of (6) are even larger than in (8) with respective values of 118.0(4)° at N(1) and 120.0(4)° at N(2). The angle at the amido-nitrogen atom may be explained by involvement of the lone-pair of electrons in π-bonding to the rhodium atom with consequent sp^2 hybridisation at this atom, but no such explanation is possible for the large angles at the amino-atoms in both complexes.

Experimental

Microanalyses were performed at the Analytische Laboratorien, Germany, the Canadian Microanalytical Service Ltd., Canada, and the Australian Microanalytical Service, Australia. ^{31}P N.m.r. spectra were recorded on a Bruker HFX90 spectrometer operating at 36.43 MHz using 8- and 10-mm concentric tubes. A 0.2 mol dm^{-3} solution of trimethyl phosphate in D_2O was used as external reference and lock. Positive chemical shifts are downfield and are reported relative to phosphoric acid (85%). ^{1}H N.m.r. spectra were recorded on a Bruker HFX90 spectrometer using $CDCl_3$ as solvent and $SiMe_4$ as reference. I.r. spectra were obtained from Nujol or hexachlorobutadiene mulls on a Perkin-Elmer 457 spectrometer.

Rhodium trichloride trihydrate was obtained from Johnson Matthey Ltd. [{Rh(cod)Cl}$_2$] was prepared by a modification * of the published procedure.[21] The ligand H_2L was prepared by the published procedure.[1] Unless otherwise stated reactions were performed in a glove-box under a nitrogen atmosphere.

cis-[Rh(H_2L)$_2$]Cl (2a).—[{Rh(cod)Cl}$_2$] (400 mg, 0.82 mmol) and H_2L (960 mg, 3.46 mmol) were stirred in methanol (30 cm^3) for 30 min. Precipitation of the product was completed by the slow addition of water (6 cm^3). The yellow microcrystalline solid was collected by filtration, washed with water, and dried (80% yield).

cis-[Rh(H_2L)$_2$]BF_4 (2b) *and cis*-[Rh(H_2L)$_2$][*p*-MeC$_6$H$_4$SO$_3$] (2c).—Addition of [NH$_4$][BF$_4$] or [NH$_4$][*p*-MeC$_6$H$_4$SO$_3$] (5 mmol) to the initial reaction mixture (see above), gave the BF_4^- or *p*-MeC$_6$H$_4$SO$_3^-$ salt as yellow microcrystals in 90—95% yield [Found for (2c): C, 62.15; H, 4.85; N, 3.35. $C_{43}H_{39}N_2O_3P_2RhS$ requires C, 62.30; H, 4.75; N, 3.40%]. The compounds are air-sensitive in the solid state and particularly so in solution. ^{31}P N.m.r. [in *NN*-dimethylformamide (dmf)]: δ 56.8 p.p.m. [^1J(Rh–P) = 171 Hz].

cis-P,H-*trans*-Cl-[RhH(H_2L)$_2$Cl]Cl (1a).—Freshly prepared *cis*-[Rh(H_2L)$_2$]BF_4 (2b) (300 mg, 0.41 mmol) was suspended in acetone (10 cm^3) and concentrated aqueous hydrochloric acid (10 mol dm^{-3}, 6 drops) added. The solution was stirred for 30 min. Diethyl ether (15 cm^3) was slowly added to complete precipitation of the white solid which was collected by filtration and washed with a small amount of acetone–diethyl ether (1 : 1) then diethyl ether and finally dried to give (1a) in 70—85% yield (Found: C, 59.10; H, 4.70; Cl, 9.65; N, 3.70. $C_{36}H_{33}Cl_2N_2P_2Rh$ requires C, 59.30; H, 4.60; Cl, 9.70; N, 3.85%). I.r.: ν(Rh–H) at 2 080 cm^{-1}. ^{1}H N.m.r.: δ -15.53 p.p.m. [Rh–H, ^1J(Rh–H) = ^2J(P–H) = 21 Hz]. ^{31}P N.m.r. (dmf): δ 52.5 p.p.m. [^1J(Rh–P) = 120 Hz].

cis-P,H-*trans*-Cl-[RhH(H_2L)$_2$Cl]BF_4 (1b).—To a suspension of freshly prepared *cis*-[Rh(H_2L)$_2$]Cl (2a) (470 mg, 0.68 mmol) in acetone (15 cm^3) was added tetrafluoroboric acid (50% in water, 0.5 cm^3) and the solution stirred for 30 min. Slow addition of diethyl ether (45 cm^3) gave (1b) as a white precipitate which was collected by filtration, washed with a small amount of acetone–diethyl ether (1 : 1) then diethyl ether and finally dried (80% yield) (Found: C, 55.15; H, 4.40; Cl, 4.35; N, 3.45. $C_{37.5}H_{36}BClF_4N_2O_{0.5}P_2Rh$ requires C, 55.60; H, 4.50; Cl, 4.40; N, 3.50%). The solid compounds (1a) and (1b) are air- and light-sensitive.

cis-P,*cis*-Cl,Cl-*trans*-NH$^-$-[Rh(H_2L)(HL)Cl$_2$] (6).—*Method* A(i). Complex (1a) (500 mg, 0.7 mmol) was dissolved in acetone (100 cm^3) and water (10 cm^3), and after filtration left

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* We used an 18-h reflux.

Table 2. Fractional atomic co-ordinates for *cis*-[Rh($NH_2C_6H_4PPh_2$-*o*)($NHC_6H_4PPh_2$-*o*)Cl_2] (6)

Atom	*x*	*y*	*z*
Rh	0.125 22(3)	0.083 38(3)	0.467 53(5)
Cl(1)	−0.004 27(10)	0.117 08(9)	0.387 20(19)
Cl(2)	0.174 61(11)	0.125 53(11)	0.259 39(18)
P(1)	0.236 96(10)	0.027 77(9)	0.538 13(17)
P(2)	0.137 17(9)	0.188 93(9)	0.578 66(17)
N(1)	0.100 0(3)	−0.017 5(2)	0.372 5(5)
N(2)	0.076 2(2)	0.050 1(2)	0.639 4(5)
C(11)	0.226 8(3)	−0.059 6(3)	0.458 7(6)
C(12)	0.283 3(4)	−0.113 2(4)	0.468 2(7)
C(13)	0.271 5(4)	−0.179 1(4)	0.405 3(7)
C(14)	0.202 2(4)	−0.191 6(4)	0.332 9(7)
C(15)	0.145 8(4)	−0.139 6(3)	0.319 0(7)
C(16)	0.158 5(3)	−0.073 4(3)	0.383 3(6)
C(22)	0.220 1(2)	−0.055 8(2)	0.770 0(5)
C(23)	0.217 1(2)	−0.066 6(2)	0.909 2(5)
C(24)	0.237 6(2)	−0.011 3(2)	0.998 3(5)
C(25)	0.261 1(2)	0.054 8(2)	0.948 0(5)
C(26)	0.264 1(2)	0.065 6(2)	0.808 7(5)
C(21)	0.243 7(2)	0.010 3(2)	0.719 7(5)
C(32)	0.346 7(2)	0.054 3(2)	0.347 3(4)
C(33)	0.419 7(2)	0.073 1(2)	0.299 9(4)
C(34)	0.480 3(2)	0.090 7(2)	0.391 2(4)
C(35)	0.467 9(2)	0.089 5(2)	0.529 9(4)
C(36)	0.394 9(2)	0.070 7(2)	0.577 3(4)
C(31)	0.334 3(2)	0.053 1(2)	0.486 0(4)
C(41)	0.092 5(3)	0.168 1(3)	0.734 7(6)
C(42)	0.081 4(3)	0.215 8(3)	0.841 8(6)
C(43)	0.054 6(4)	0.191 9(4)	0.962 2(7)
C(44)	0.037 0(4)	0.119 9(4)	0.977 8(8)
C(45)	0.044 8(3)	0.071 9(3)	0.874 3(6)
C(46)	0.072 4(3)	0.095 2(3)	0.747 4(6)
C(52)	0.125 2(2)	0.316 2(3)	0.427 1(5)
C(53)	0.086 0(2)	0.376 4(3)	0.376 1(5)
C(54)	0.007 8(2)	0.387 4(3)	0.405 0(5)
C(55)	−0.031 2(2)	0.338 3(3)	0.484 9(5)
C(56)	0.008 0(2)	0.278 1(3)	0.536 0(5)
C(51)	0.086 2(2)	0.267 1(3)	0.507 1(5)
C(62)	0.260 4(2)	0.244 3(2)	0.744 2(3)
C(63)	0.336 7(2)	0.268 2(2)	0.767 1(3)
C(64)	0.388 5(2)	0.269 8(2)	0.661 1(3)
C(65)	0.363 8(2)	0.247 5(2)	0.532 0(3)
C(66)	0.287 5(2)	0.223 7(2)	0.509 1(3)
C(61)	0.235 8(2)	0.222 0(2)	0.615 2(3)

to stand exposed to air overnight, after which time dark brown crystals of (6) were collected by filtration, washed with acetone and water, and dried (35—40% yield). The addition of lithium chloride (150 mg, 5.33 mmol) to the initial reaction mixture increased the yield to 60%.

Method A(ii). To a solution of (1a) (500 mg, 0.7 mmol) dissolved in air-saturated acetone (100 cm^3) and water (10 cm^3), was immediately added triethylamine (5 drops). The solution was left exposed to air overnight. The product (6) (50% yield) was collected by filtration, washed with acetone, and dried.

Method B. A suspension of (2b) (150 mg, 0.20 mmol) and lithium chloride (90 mg, 2.12 mmol) in acetone (30 cm^3) was left to stir in air for 15 min giving (6) (30% yield) as a fine brown precipitate which was collected in the usual way. ^{31}P N.m.r. spectroscopy showed this product, on protonation, to be slightly impure. The product was purified by sequential protonation of a methanol suspension with tetrafluoroboric acid and deprotonation with triethylamine in acetone. I.r.: ν(Rh–Cl) at 310m, 290m, and 280(sh) cm^{-1}. ^{31}P N.m.r. (dmf): δ 41.2 p.p.m. [^1J(Rh–P) = 120 Hz]. A ^{31}P n.m.r. spectrum of (6) could be obtained by quickly recording the spectrum immediately after the addition of triethylamine to a dmf solution of the protonated analogue of (6) (Found: C, 59.55; H, 4.55; N, 3.70. $C_{36}H_{31}Cl_2N_2P_2Rh$ requires C, 59.95; H, 4.30; N, 3.85%).

cis-P,*trans*-Cl-[Rh(H_2L)$_2$$Cl_2$][*p*-$MeC_6H_4SO_3$] (8).—The filtrate from the preparation of (6) [Method A(i)] was evaporated under reduced pressure to remove the acetone, and the brown suspension redissolved by addition of acetonitrile (50 cm^3). Excess toluene-*p*-sulphonic acid was added to give a dark brown solution. Room-temperature crystallisation over 2 d gave yellow crystals of (8) which were collected by filtration, washed with acetonitrile, and dried, yield 15% (Found for the MeCN adduct: C, 57.55; H, 4.55; Cl, 6.7; N, 4.55. $C_{45}H_{42}Cl_2N_3O_3P_2RhS$ requires C, 57.45; H, 4.50; Cl, 7.55; N, 4.45%). I.r.: ν(Rh–Cl) at 350 cm^{-1}. ^{31}P N.m.r. (dmf): δ 35.5 p.p.m. [^1J(Rh–P) = 105 Hz].

Table 3. Fractional atomic co-ordinates for the cation of *trans*-[Rh($NH_2C_6H_4PPh_2$-*o*)$_2$$Cl_2$][*p*-$MeC_6H_4SO_3$]·MeCN (8)

Atom	*x*	*y*	*z*
Rh	0	0.121 93(6)	0.25
Cl(1)	0.126 53(11)	0.107 59(16)	0.247 50(14)
P(1)	0.017 62(12)	0.218 88(16)	0.361 83(14)
N(1)	0.010 4(4)	0.017 4(5)	0.344 1(5)
C(11)	0.062 3(5)	0.141 2(6)	0.437 5(6)
C(12)	0.103 4(5)	0.165 3(7)	0.510 5(6)
C(13)	0.137 1(6)	0.097 3(8)	0.561 2(7)
C(14)	0.132 0(6)	0.007 0(9)	0.540 4(7)
C(15)	0.093 6(6)	−0.021 3(8)	0.470 7(6)
C(16)	0.056 3(5)	0.046 5(7)	0.419 1(6)
C(21)	0.078 3(5)	0.315 6(7)	0.360 1(6)
C(22)	0.052 0(6)	0.406 9(8)	0.345 4(7)
C(23)	0.102 4(7)	0.479 4(10)	0.331 4(8)
C(24)	0.174 6(8)	0.460 6(10)	0.336 8(8)
C(25)	0.203 5(7)	0.373 5(8)	0.356 3(7)
C(26)	0.155 4(6)	0.300 6(7)	0.367 7(6)
C(31)	−0.063 5(5)	0.265 9(6)	0.405 2(6)
C(32)	−0.118 0(5)	0.307 9(7)	0.350 9(6)
C(33)	−0.178 4(6)	0.348 7(8)	0.382 7(7)
C(34)	−0.182 1(6)	0.343 0(8)	0.465 8(7)
C(35)	−0.128 8(6)	0.304 4(8)	0.518 3(7)
C(36)	−0.068 2(5)	0.263 8(7)	0.487 5(6)

X-Ray Crystallography.—Crystal data for (6). $C_{36}H_{31}Cl_2N_2P_2Rh$, *M* = 727.4, monoclinic, *a* = 17.153(3), *b* = 18.667(3), *c* = 9.891(2) Å, β = 91.77(3)°, *U* = 3 165.54 $Å^3$ (by least-squares refinement on diffractometer angles for 25 automatically-centred reflections, λ = 0.710 69 Å), space group $P2_1/n$ ($P2_1/c$, no. 14), *Z* = 4, D_c = 1.526 g cm^{-3}, *F*(000) = 1 480. A dark brown crystal of size 0.17 × 0.21 × 0.23 mm, μ(Mo-K_α) = 7.51 cm^{-1}, was used in the data collection.

Crystal data for (8). $[C_{36}H_{32}Cl_2N_2P_2Rh]^+[C_7H_7O_3S]^- \cdot C_2H_3N$, *M* = 940.6, monoclinic, *a* = 18.394(4), *b* = 14.380(3), *c* = 16.378(3) Å, β = 96.67(4)°, *U* = 4 302.77 $Å^3$ (by least-squares refinement on diffractometer angles for 25 automatically-centred reflections, λ = 0.710 69 Å), space group $I2/c$, ($C2/c$, no. 16), *Z* = 4, D_c = 1.388 g cm^{-3}, *F*(000) = 1 928. A yellow crystal of size 0.20 × 0.22 × 0.35 mm, μ(Mo-K_α) = 6.08 cm^{-1}, was used in the data collection.

Data collection. Data were collected on a Philips PW1100 diffractometer in the θ range 3—25°, with a scan width of 0.70° for (6) and of 0.80° for (8), using the technique previously described.[22]

Structure solution and refinement.[23] The metal atoms in the two structures were located by Patterson synthesis and the remaining non-hydrogen atoms and the hydrogen atoms attached to the N atoms were found from subsequent difference-Fourier syntheses. The phenyl hydrogen atoms in both structures were placed in geometrically idealised positions (C–H 1.08 Å, C–C–H 120.0°) and were constrained to ride on the relevant C atom with a common isotropic thermal parameter which was refined. The nitrogen-bonded H atoms in (6) and (8) were included in the positions where they were found, with isotropic U values of 0.05 Å^2, but were not refined. Attempted refinement of (8) in the non-centrosymmetric space group Ic was unsatisfactory due to high parameter correlation between the atoms in the two halves of the cation which has virtual C_2 symmetry in this space group. Satisfactory refinement was obtained in the centrosymmetric space group $I2/c$ in which the cation has exact C_2 symmetry, with the anion and CH_3CN solvate molecule disordered about a crystallographic C_2 axis. In the final cycles of blocked full-matrix refinement the rhodium, phosphorus, and nitrogen atoms in both structures and the sulphur and oxygen atoms of the anion in (8) were assigned anisotropic thermal parameters. For both structures, final difference-Fourier maps showed no regions of significant electron density.

The final atomic co-ordinates are given in Tables 2 and 3 for (6) and (8) respectively. Final R and R' values were 0.0487 and 0.0511 for (6) and 0.0638 and 0.0698 for (8); the weighting scheme used was $w = 1/[\sigma^2(F_o)]$.

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