Rhodium Complexes containing Substituted Hydrazines†

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The crystal structure of *trans*-[Rh(CO)$(PPh_3)_2(OClO_3)$] has been determined, and it has been established that the perchlorate group is easily displaced by substituted hydrazines to give *trans*-[Rh(CO)$(PPh_3)_2$L]-ClO_4 (L = $NH_2NH_{2-x}R_x$; x = 1 or 2; R = Me or Ph). X-Ray crystallography shows that for all these complexes the unsymmetrically substituted hydrazine co-ordinates to rhodium *via* the NH_2 group.

The study of transition-metal complexes containing hydrazine or substituted hydrazine ligands is of interest for two reasons. First, they are involved as intermediates in the conversion of dinitrogen into ammonia and amines and much work has already been done in this area.[1,2] Secondly, it has recently been discovered that rhodium hydrazine complexes have a high catalytic activity in homogeneous hydrogenation reactions;[3] this is an important new development but catalytic studies on the substituted hydrazine complexes described in this paper have not yet been carried out.

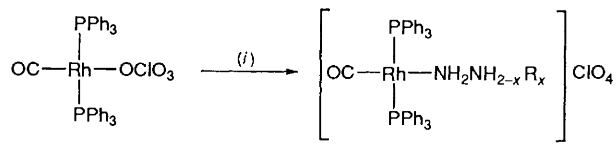
Hydrazine has long been used as a reducing agent in the preparation of hydride complexes of rhodium.[4,5] Examples of crystallographically and/or spectroscopically characterised rhodium complexes containing hydrazine as a ligand have appeared only recently.[3,6,7] For other metals, crystallographic studies have established that hydrazine can co-ordinate as a monodentate,[8–10] bridging[11–13] or bidentate[14] ligand. For substituted hydrazines, there is a large amount of work on complexes containing hydrazido-(1−) and -(2−) ligands, but few have been structurally characterised with monodentate substituted hydrazines.

For unsymmetrically substituted hydrazines there are two possible isomers for the monodentate mode of co-ordination. Studies on the free substituted hydrazines suggest that they are all less basic than hydrazine itself, but this has to be contrasted with methylamines which are all more basic than ammonia.[15] However, data have not yet been reported which distinguish the basicities of the inequivalent nitrogen atoms in unsymmetrically substituted hydrazines, although there is some evidence that protonation of the unsymmetrically alkyl-substituted hydrazines occurs at the substituted nitrogen atom.[16] There are presently insufficient structural data available to be sure whether substitution, particularly methyl substitution, should favour co-ordination *via* the most substituted nitrogen (electronic effects) or disfavour such co-ordination (steric effects). The only structurally characterised complexes containing methyl-substituted hydrazines are *trans*-[Rh(PPh_3)(NHMe-NHMe)Cl_4],[17] $[Ru(cod)(NH_2NMe_2)_3H]^+$ (cod = cycloocta-1,5-diene)[18] and [Ru(PPh_3)(NH_2NHMe)L′][19] [H_2L′ = 1,2-bis(*o*-mercaptophenylthio)ethane]. The first complex contains a symmetrically substituted hydrazine so it sheds no light on the preferred mode of ligand co-ordination to rhodium. For the ruthenium complexes, it is the NH_2 group which is co-ordinated suggesting a steric rather than an electronic preference. In the case of phenyl-substituted hydrazines, both electronic and steric effects favour co-ordination to the metal *via* the least-substituted nitrogen, and this is confirmed in those complexes which have been crystallographically characterised.[20,21]

This paper shows that the O-bonded perchlorate group in *trans*-[Rh(CO)$(PPh_3)_2(OClO_3)$] **1** is easily displaced by unsymmetrically substituted hydrazines to give *trans*-[Rh(CO)-$(PPh_3)_2$L]ClO_4 (L = $NH_2NH_{2-x}R_x$; x = 1 or 2; R = Me or Ph) which have been shown by X-ray crystallography always to involve co-ordination of the hydrazine *via* the unsubstituted nitrogen (see Scheme 1). Spectroscopic studies are also reported and show that there is no evidence for other isomers in solution.

Results and Discussion

The structure of *trans*-[Rh(CO)$(PPh_3)_2(OClO_3)$] **1** is shown in Fig. 1. It consists of a square-planar arrangement around rhodium with an O-bonded perchlorate group. This structure should be compared with that of the related compound $[Rh(PPh_3)_3]ClO_4$[22] which contains an ionic perchlorate. In



1

	x	R
2	1	Me
3	2	Me
4	1	Ph
5	2	Ph

Scheme 1 (*i*) $NH_2NH_{2-x}R_x$, x = 1 or 2, R = Me or Ph

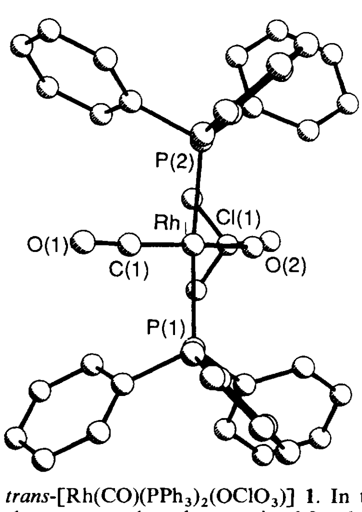


Fig. 1 View of *trans*-[Rh(CO)$(PPh_3)_2(OClO_3)$] **1**. In this structure and the others, hydrogen atoms have been omitted for clarity

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

the latter compound the triphenylphosphine ligands adopt an approximate T-shaped structure with a slight distortion of the *trans*-phosphines away from the unique phosphine. Presumably, replacement of this bulky triphenylphosphine ligand by carbon monoxide allows the perchlorate group to co-ordinate to rhodium.

The perchlorate group in complex **1** is easily displaced by the substituted hydrazine $NH_2NH_{2-x}R_x$ (x = 1 or 2, R = Me or Ph) to give the monodentate hydrazine complexes **2–5** (see Scheme 1). X-Ray studies show that the substituted hydrazine is always co-ordinated *via* the NH_2 group (Figs. 2–4). While this is not surprising for the phenylhydrazines, it is somewhat unexpected for the methylhydrazines, thus indicating that the steric factor is more important than the electronic one. In agreement with these structures, the IR spectra of all the compounds show one band in the carbonyl-stretching region, whilst the ^{31}P NMR spectra each consist of just one doublet (see Table 1) with no evidence for the presence in solution of the other isomer in which the substituted nitrogen is co-ordinated to the metal.

Selected bond lengths and angles in compounds **1–4** are given in Table 2 and atom positions in Table 3. The co-ordination around Rh is close to square planar, as shown by the angles at Rh given in Table 2. The cation in **5** appears to be very similar, but crystal structure refinement was not possible beyond R = 0.09 and bond lengths and angles are therefore not given. The Rh–P bond lengths, in the range 2.315(6)–2.353(3) Å [mean 2.338(11) Å], are a little longer than the mean 2.30(5) Å given by Orpen *et al.*,[23] based on 44 structures involving four-co-ordinate Rh and PPh_3; all the compounds described in this paper are of Rh^I whereas those given by Orpen include different oxidation states. Other bond lengths are normal.

Fig. 5 shows a view of complex **2** along the P···P axis. In all the complexes studied, when viewed along this axis, each phenyl ring bonded to one P atom is approximately eclipsed with another phenyl ring bonded to the other P atom; this is shown by the torsion angles C–P–P–C given in Table 2, which are close to 0°, rather than to *ca.* 60° which would correspond to a staggered configuration. In compounds **2–4**, the nitrogen atom bonded to Rh is also approximately eclipsed with two of these carbon atoms, see the torsion angles C–P–Rh–N, while the carbonyl carbon is in a staggered configuration. Compound **1** is similar, with the perchlorate O atom taking the place of the hydrazine N atom. It is also surprising that the methyl group [C(2)] on the substituted hydrazine in **2** lies between two eclipsed phenyl rings (Fig. 5).

In each of the compounds **2–4** the perchlorate counter ion makes no specific interaction with the Rh atom. In compound **1** the perchlorate is directly co-ordinated to Rh, with d(Rh–O) = 2.140(7) Å, this being comparable to d(Rh–O) in six-co-ordinate rhodium(III) complexes,[24] 2.10 and 2.17 Å, and also to the Rh–N distances in compounds **2–4**. Therefore, for **1** it does not appear that the Rh–$OClO_3$ bond is particularly weak.

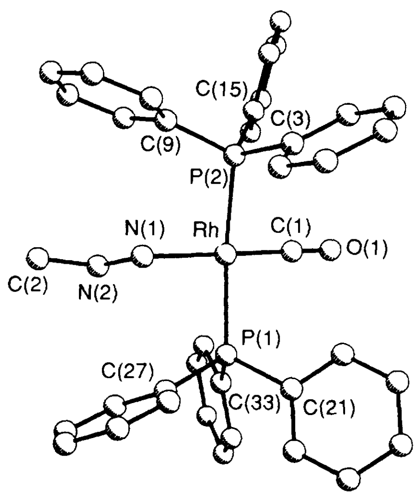


Fig. 2 View of the cation *trans*-$[Rh(CO)(PPh_3)_2(NH_2NHMe)]^+$ **2**

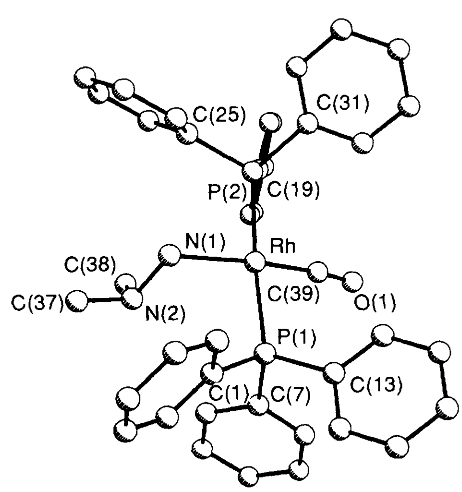


Fig. 3 View of the cation *trans*-$[Rh(CO)(PPh_3)_2(NH_2NMe_2)]^+$ **3**

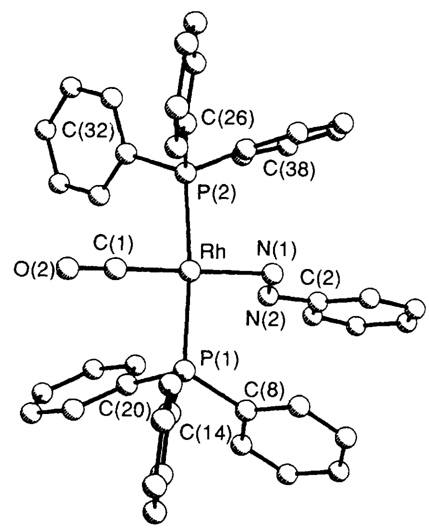


Fig. 4 View of the cation *trans*-$[Rh(CO)(PPh_3)_2(NH_2NHPh)]^+$ **4**

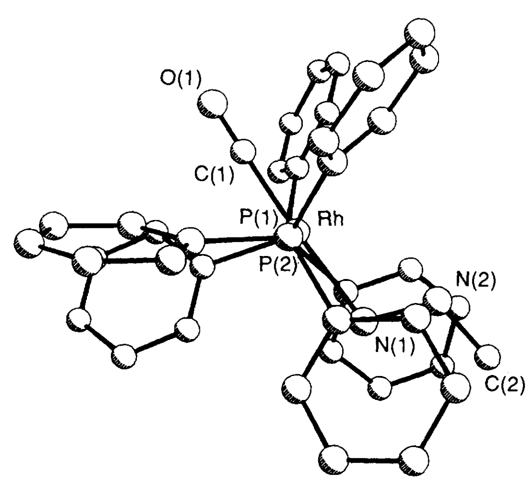


Fig. 5 View of the cation in complex **2** along the P···P direction, showing the eclipsed configurations of the phenyl rings bonded to different P atoms, and the preferred orientations of the carbonyl and hydrazine groups

Table 1 The $^{31}P-\{^1H\}$ NMR [a] and IR [b] data for rhodium complexes containing substituted hydrazines

Complex	δ(P)	$^1J(Rh-P)/Hz$	$\tilde{\nu}(CO)/cm^{-1}$
2 $[Rh(CO)(PPh_3)_2(NH_2NHMe)]ClO_4$	32.3	128.6	2005.6
3 $[Rh(CO)(PPh_3)_2(NH_2NMe_2)]ClO_4$	32.0	129.0	2007.6
4 $[Rh(CO)(PPh_3)_2(NH_2NHPh)]ClO_4$	31.8	126.5	2005.0
5 $[Rh(CO)(PPh_3)_2(NH_2NPh_2)]ClO_4$	30.9	128.7	2000.0

[a] Recorded in a solution of CH_2Cl_2 at 243 K. [b] Recorded as solutions in CH_2Cl_2.

Table 2 Selected bond lengths (Å) and angles (°) for complexes **1**–**4** (see Scheme 1)

	1	**2**	**3**	**4**
Rh–P	2.340(4)	2.345(6)	2.332(3)	2.338(5)
	2.347(4)	2.315(6)	2.353(3)	2.332(5)
Rh–N	—	2.12(2)	2.16(1)	2.14(1)
Rh–O	2.140(7)	—	—	—
Rh–C	1.80(1)	1.85(3)	1.82(1)	1.84(2)
Rh–N–N	—	109(1)	110.1(7)	111.8(8)
P–Rh–N	—	89.6(4)	89.0(2)	90.9(4)
		91.0(4)	93.1(2)	91.0(4)
P–Rh–O	92.1(3)			
	92.8(3)			
P–Rh–P	168.0(1)	170.3(2)	175.3(1)	170.5(1)
N–Rh–C	—	177(1)	172.6(6)	178.9(6)
O–Rh–C	170.7(5)	—	—	—
Torsion angles				
Rh–N–N–C	—	−170	170.5(7)	−176.8(8)
C–P–Rh–N [a]	—	−6.0(8)	−16.1(4)	3.4(4)
		−13.2(9)	0.7(5)	6.1(4)
C–P–Rh–O	−1.2(4)	—	—	—
	3.5(4)			
C–P–Rh–C [b]	52.5(5)	58(1)	54.6(6)	64.1(5)
	68.6(5)	44(1)	51.7(6)	66.9(6)
C–P–P–C [c]	0.7(4)–	−18.0(7) to	−12.4(4) to	5.6(5)
	2.0(5)	−20.2(10)	−15.5(4)	11.2(6)

[a] The angles C(9)–P(2)–Rh–N(1) and C(27)–P(1)–Rh–N(1) are given for complex **2**, and equivalent angles for the others (see Fig. 5). [b] The angles C(1)–P(1)–Rh–C(21) and C(1)–P(2)–Rh–C(15) for complex **2** and equivalent angles for the others (see Fig. 5). [c] The range is given for the torsion angles C(3)–P(2)–P(1)–C(21), C(9)–P(2)–P(1)–C(27) and C(15)–P(2)–P(1)–C(3) in complex **2**, and for equivalent groups of angles in the others (see Fig. 5).

Experimental

General Procedures and Materials.—The NMR spectra were recorded on either a Bruker WM 200 or AMX 400 spectrometer and ^{31}P chemical shifts are referenced to external H_3PO_4 (85% in D_2O), IR spectra on a Perkin-Elmer 1720-X Fourier-transform spectrometer in CH_2Cl_2 solution using cells with CaF_2 windows.

Solvents were dried using standard procedures and stored under a nitrogen atmosphere. All manipulations were carried out using Schlenk techniques under a nitrogen atmosphere.

Substituted hydrazines were supplied by Aldrich and NH_2NHMe, NH_2NMe_2, and NH_2NHPh were used as received; NH_2NPh_2 was received as the hydrochloride which was converted into the free hydrazine using the following procedure. The hydrochloride $NH_2NPh_2{\cdot}HCl$ (5 g) was dissolved in methanol (10 cm^3) and transferred to a separating funnel. An aqueous solution (40 cm^3) containing K_2CO_3 (20 g) was added and the mixture shaken well. The greasy white precipitate of NH_2NPh_2 was extracted with diethyl ether (5 × 20 cm^3) and, after drying the ether extract and removal of ether *in vacuo*, a pale brown liquid was obtained. This was used directly for the preparation of the complex containing NH_2NPh_2.

Preparations.—$[Rh(CO)(PPh_3)_2(OClO_3)]$ **1**. This complex was prepared using the previously reported procedure.[25] X-Ray-quality crystals were obtained by addition of hexane (10 cm^3) to a solution containing the compound (0.1 g) in dichloromethane (5 cm^3) and cooling this solution to −30 °C for 7 d.

$[Rh(CO)(PPh_3)_2(NH_2NHMe)]ClO_4$ **2**. The compound NH_2NHMe (0.01 cm^3) was added to a solution of $[Rh(CO)(PPh_3)_2(OClO_3)]$ (0.1 g) in ethyl acetate (10 cm^3) followed by addition of heptane (10 cm^3). Storing this solution for 1 week at −30 °C gave yellow crystals of the product. Yield 0.075 g, 71% (Found: C, 56.5; H, 4.5; N, 3.5. Calc. for $C_{38}H_{36}ClN_2O_5P_2Rh$: C, 57.0; H, 4.5; N, 3.5%).

$[Rh(CO)(PPh_3)_2(NH_2NMe_2)]ClO_4$ **3**. A solution containing $[Rh(CO)(PPh_3)_2(OClO_3)]$ (0.5 g) and NH_2NMe_2 (0.1 cm^3) in methanol (30 cm^3) was stored at −30 °C and after 2 weeks yellow crystals of the product were obtained. Yield 0.43 g, 80% (Found: C, 57.6; H, 4.7; N, 3.4. Calc. for $C_{39}H_{38}ClN_2O_5P_2Rh$: C, 57.5; H, 4.7; N, 3.4%).

$[Rh(CO)(PPh_3)_2(NH_2NHPh)]ClO_4$ **4**. To a solution containing $[Rh(CO)(PPh_3)_2(OClO_3)]$ (0.1 g) in dichloromethane (5 cm^3) was added NH_2NHPh (0.015 cm^3). After stirring for a few minutes followed by addition of hexane (10 cm^3), yellow crystals of the product started to form after 1 h. The crystals were removed after 3d, washed with hexane (3 × 10 cm^3) and dried *in vacuo*. Yield 0.09 g, 79% (Found: C, 59.7; H, 4.5; N, 3.2. Calc. for $C_{43}H_{38}ClN_2O_5P_2Rh$: C, 59.8; H, 4.4; N, 3.3%).

$[Rh(CO)(PPh_3)_2(NH_2NPh_2)]ClO_4$ **5**. To a solution of $[Rh(CO)(PPh_3)_2(OClO_3)]$ (0.5 g) in methanol (30 cm^3) was added NH_2NPh_2 (0.15 cm^3). Storing this solution at −30 °C for 2 weeks produced pale yellow-green crystals of the product. Yield 0.56 g, 90% (Found: C, 62.6; H, 4.5; N, 3.0. Calc. for $C_{49}H_{42}ClN_2O_5P_2Rh$: C, 62.7; H, 4.5; N, 3.0%).

Crystal Structure Determinations.—*Crystal data, data collection and processing.* Details are given in Table 4. All data were recorded on a Rigaku AFC6S diffractometer at 25 °C, using graphite-monochromatised Cu-Kα radiation, λ = 0.71069 Å, scan width between 0.094 + 0.30 tan θ for complex **4** and 1.37 + 0.30 tan θ for **3**, scan speed 8° min^{-1} for **1** and **2**, 4° min^{-1} for **3** and **4**, $2\theta_{max} = 50°$. Three standard reflections were measured every 150; no significant decay was observed except in **1**, for which a linear decay of 4% was corrected for during data processing. Empirical absorption corrections were applied by the TEXSAN system;[26] the maximum and minimum transmission factors are given in Table 4. The unit cells **1**, **3** and **5** were determined from diffractometer angles for 25 automatically centred reflections with $25 < 2\theta < 31°$; for **2** and **4**, 20 reflections with $7 < 2\theta > 11.5°$ were used.

Structure analysis and refinement. Direct methods[27–30] by full-matrix structure refinement on *F*, with all phenyl rings restrained to have C–C 1.40(2) Å and all C–C–C angles 120.0(9)°, with one overall U_{iso} refined for each ring. All other non-hydrogen atoms were treated as anisotropic and hydrogen atoms were placed in calculated positions with U_{iso} refined. The weighting scheme was based on counting statistics and included a factor ($p = 0.03$) to downweight the intense reflections. With **2** and **4** difficulty was experienced in location of the disordered ClO_4^- counter ion, and two orientations were used to model the disorder in this region. Other details are

Table 3 Fractional atomic coordinates

Atom	x	y	z	Atom	x	y	z
Complex **1**							
Rh	0.302 6(1)	0.157 28(6)	0.714 40(7)	C(14)	0.419 0(7)	0.014 5(4)	0.767 0(5)
Cl(1)	0.598 2(3)	0.154 4(2)	0.706 8(2)	C(15)	0.467 0(8)	−0.034 0(4)	0.725 1(4)
Cl(2)	0.185(1)	0.139 8(4)	0.966 2(5)	C(16)	0.569 4(9)	−0.065 6(3)	0.764 8(6)
Cl(3)	0.338 4(8)	0.216 3(5)	1.071 9(7)	C(17)	0.623 8(8)	−0.048 6(4)	0.846 4(6)
P(1)	0.280 5(4)	0.055 0(2)	0.718 0(3)	C(18)	0.575 9(9)	−0.000 2(4)	0.888 3(4)
P(2)	0.293 5(4)	0.259 7(2)	0.732 2(2)	C(19)	0.473 4(8)	0.031 4(3)	0.848 6(5)
O(1)	0.060(1)	0.162 7(5)	0.605 5(7)	C(20)	0.435 2(7)	0.294 9(4)	0.781 9(5)
O(2)	0.496 1(8)	0.152 7(5)	0.767 9(5)	C(21)	0.492(1)	0.270 7(4)	0.858 5(6)
O(3)	0.578(1)	0.203 6(7)	0.653(1)	C(22)	0.594(1)	0.299 4(5)	0.903 9(5)
O(4)	0.712(1)	0.157(1)	0.755 0(8)	C(23)	0.638 8(8)	0.352 4(5)	0.872 7(6)
O(5)	0.590(2)	0.106 2(7)	0.655(1)	C(24)	0.582(1)	0.376 7(4)	0.796 2(6)
C(1)	0.149(1)	0.159 2(7)	0.651 5(9)	C(25)	0.480 0(8)	0.347 9(4)	0.750 7(5)
C(38)	0.193(2)	0.196 6(9)	1.038(2)	C(26)	0.256 5(8)	0.299 7(4)	0.631 0(4)
C(2)	0.153 9(7)	0.032 0(4)	0.783 4(5)	C(27)	0.334 3(7)	0.290 4(4)	0.563 7(6)
C(3)	0.035 7(9)	0.059 6(4)	0.770 4(5)	C(28)	0.308 4(8)	0.319 3(4)	0.484 5(5)
C(4)	−0.063 3(7)	0.042 9(4)	0.819 5(7)	C(29)	0.205(1)	0.357 4(4)	0.472 7(5)
C(5)	−0.044 0(8)	−0.001 4(4)	0.881 7(6)	C(30)	0.127 0(7)	0.366 7(4)	0.540 0(6)
C(6)	0.074 1(9)	−0.029 0(4)	0.894 7(5)	C(31)	0.152 8(7)	0.337 8(4)	0.619 2(5)
C(7)	0.173 1(7)	−0.012 3(4)	0.845 5(6)	C(32)	0.169 2(7)	0.282 5(4)	0.803 0(5)
C(8)	0.244 3(9)	0.020 4(4)	0.613 7(5)	C(33)	0.197 8(6)	0.321 8(4)	0.871 2(6)
C(9)	0.150 0(8)	−0.022 4(4)	0.599 9(5)	C(34)	0.103 3(9)	0.338 7(4)	0.924 1(5)
C(10)	0.130(1)	−0.049 8(4)	0.519 2(7)	C(35)	−0.019 7(8)	0.316 4(5)	0.908 7(6)
C(11)	0.204(1)	−0.034 4(5)	0.452 2(5)	C(36)	−0.048 3(6)	0.277 1(4)	0.840 5(7)
C(12)	0.298(1)	0.008 5(5)	0.465 9(5)	C(37)	0.046 2(9)	0.260 2(4)	0.787 6(5)
C(13)	0.318 5(8)	0.035 9(4)	0.546 7(6)				
Complex **2**							
Rh	0.735 1(1)	0.177 7(2)	0.837 1(1)	C(28)	0.919(1)	−0.074(1)	0.888 6(7)
P(1)	0.761 3(3)	−0.020 5(5)	0.839 6(4)	C(29)	0.991 0(8)	−0.094(1)	0.877 1(8)
P(2)	0.700 6(3)	0.369 2(5)	0.812 6(3)	C(30)	0.997 1(7)	−0.096(1)	0.803(1)
O(1)	0.581(1)	0.134(2)	0.855(1)	C(31)	0.932(1)	−0.077(1)	0.740 9(7)
N(1)	0.848(1)	0.212(1)	0.832(1)	C(32)	0.860 1(7)	−0.057(1)	0.752 5(8)
N(2)	0.903(1)	0.204(1)	0.908(1)	C(21)	0.691 5(8)	−0.100(1)	0.765 1(7)
C(1)	0.638(1)	0.151(2)	0.848(2)	C(22)	0.707 2(7)	−0.214(1)	0.750 7(9)
C(2)	0.980(2)	0.245(2)	0.911(2)	C(23)	0.654(1)	−0.277(1)	0.694(1)
C(3)	0.637(1)	0.375(1)	0.713 6(7)	C(24)	0.584(1)	−0.226(2)	0.652 3(8)
C(4)	0.670 5(7)	0.340(1)	0.658(1)	C(25)	0.568 4(7)	−0.112(2)	0.667(1)
C(5)	0.627(1)	0.340(1)	0.581 5(9)	C(26)	0.622(1)	−0.049(1)	0.723(1)
C(6)	0.550(1)	0.374(1)	0.560 0(7)	Cl(1)[a]	0.833 4(5)	0.180 5(8)	0.595 9(5)
C(7)	0.515 6(7)	0.408(1)	0.615(1)	O(2)[a]	0.785 7(9)	0.080(1)	0.591(1)
C(8)	0.559(1)	0.409(1)	0.692 1(9)	O(5)[a]	0.790(1)	0.269(1)	0.546 6(9)
C(9)	0.783 4(7)	0.464(1)	0.822(1)	O(3)[a]	0.900 4(7)	0.152(2)	0.573 0(9)
C(10)	0.804 3(8)	0.510(1)	0.761 0(7)	O(4)[a]	0.858(1)	0.222(1)	0.673 4(6)
C(11)	0.872(1)	0.576(1)	0.774 6(8)	Cl(2)[b]	0.845 5(8)	0.152(1)	0.607(1)
C(12)	0.918 0(7)	0.595(1)	0.849(1)	O(6)[b]	0.868(2)	0.047(2)	0.578(2)
C(13)	0.897 2(8)	0.549(1)	0.910 3(7)	O(7)[b]	0.771(1)	0.137(2)	0.618(2)
C(14)	0.830(1)	0.484(1)	0.896 7(8)	O(8)[b]	0.841(2)	0.243(2)	0.552(1)
C(15)	0.650 5(8)	0.447(1)	0.868 7(8)	O(9)[b]	0.902(1)	0.182(3)	0.678(1)
C(16)	0.617 4(8)	0.555(1)	0.844 4(6)	C(33)	0.764 4(8)	−0.095(2)	0.926(1)
C(17)	0.582 6(7)	0.617(1)	0.889 9(9)	C(34)	0.771(1)	−0.025(1)	0.989(2)
C(18)	0.580 8(7)	0.573(1)	0.959 8(8)	C(35)	0.777(1)	−0.074(2)	1.060(1)
C(19)	0.613 8(8)	0.465(1)	0.984 2(6)	C(36)	0.777(1)	−0.194(3)	1.067(1)
C(20)	0.648 7(7)	0.403(1)	0.938 6(9)	C(37)	0.771(1)	−0.264(1)	1.004(2)
C(27)	0.854 0(7)	−0.055(1)	0.826(1)	C(38)	0.765(1)	−0.214(2)	0.933(1)
Complex **3**							
Rh	0.294 2	−0.000 4	0.370 7	C(5)	0.136 9(6)	0.389 4(7)	0.129 9(8)
P(1)	0.108 4(3)	0.200 8(3)	0.431 7(4)	C(6)	0.165 6(6)	0.322 8(7)	0.241 7(8)
P(2)	0.495 0(3)	−0.195 4(3)	0.320 6(3)	C(7)	−0.056 7(6)	0.188 7(7)	0.490 4(7)
O(1)	0.300(1)	−0.021 8(9)	0.680 5(9)	C(8)	−0.098 7(7)	0.237 1(7)	0.639 1(6)
N(1)	0.258(1)	0.003 5(8)	0.139(1)	C(9)	−0.224 1(7)	0.226 0(7)	0.682 7(5)
N(2)	0.110 1(8)	0.006 7(8)	0.091 3(9)	C(10)	−0.307 4(6)	0.166 5(7)	0.577 6(7)
C(37)	0.079(1)	0.031(1)	−0.055(1)	C(11)	−0.265 4(7)	0.118 1(7)	0.428 9(6)
C(38)	0.103(1)	−0.115(1)	0.094(1)	C(12)	−0.140 0(7)	0.129 2(7)	0.385 3(5)
C(39)	0.306(1)	−0.012(1)	0.563(1)	C(19)	0.474 3(7)	−0.325 8(5)	0.380 8(8)
C(31)	0.670 8(5)	−0.190 2(7)	0.408 8(6)	C(20)	0.335 9(6)	−0.317 7(5)	0.415 7(8)
C(32)	0.673 3(5)	−0.126 7(6)	0.559 1(6)	C(21)	0.319 6(5)	−0.418 9(6)	0.459 4(8)
C(33)	0.806 0(7)	−0.123 1(6)	0.630 4(5)	C(22)	0.441 7(7)	−0.528 1(5)	0.468 4(8)
C(34)	0.936 1(5)	−0.1831(7)	0.551 3(7)	C(23)	0.580 2(5)	−0.536 1(5)	0.433 5(8)

Table 3 (*continued*)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Complex **3**							
C(35)	0.933 6(5)	−0.246 7(6)	0.401 0(6)	C(24)	0.596 5(5)	−0.435 0(6)	0.389 7(8)
C(36)	0.800 9(7)	−0.250 2(6)	0.329 7(5)	C(25)	0.537 6(9)	−0.259 0(7)	0.122 7(5)
C(13)	0.145 4(7)	0.325 1(5)	0.583 9(6)	C(26)	0.585 0(9)	−0.185 2(6)	0.056 5(7)
C(14)	0.043 6(6)	0.450 4(6)	0.611 4(7)	C(27)	0.613 5(9)	−0.224 6(6)	−0.095 8(7)
C(15)	0.067 6(7)	0.545 9(5)	0.729 5(8)	C(28)	0.594 7(9)	−0.337 8(7)	−0.181 9(5)
C(16)	0.193 5(7)	0.516 1(6)	0.820 1(6)	C(29)	0.547 4(9)	−0.411 5(6)	−0.115 7(7)
C(17)	0.295 4(6)	0.390 8(6)	0.792 7(7)	C(30)	0.518 8(8)	−0.372 1(6)	0.036 6(7)
C(18)	0.271 4(7)	0.295 3(5)	0.674 6(8)	Cl	0.579 7(3)	0.145 4(2)	1.012 8(3)
C(1)	0.056 2(7)	0.287 9(7)	0.283 0(7)	O(2)	0.529 4(7)	0.113 2(7)	0.860 4(4)
C(2)	−0.081 8(6)	0.319 6(7)	0.212 4(8)	O(3)	0.723 9(4)	0.054 5(5)	1.031 7(8)
C(3)	−0.110 5(6)	0.386 2(7)	0.100 5(8)	O(4)	0.479 8(6)	0.140 6(7)	1.111 1(6)
C(4)	−0.001 1(7)	0.421 0(7)	0.059 3(7)	O(5)	0.586 0(8)	0.273 4(4)	1.048 3(8)
Complex **4**							
Rh	0.976 44(9)	0.157 83(7)	0.833 96(7)	C(25)	1.044 5(6)	0.234 1(5)	1.047 4(6)
P(1)	0.885 2(3)	0.2245 (2)	0.899 7(2)	C(26)	1.036 0(7)	0.020 9(5)	0.705 2(5)
P(2)	1.087 6(3)	0.090 0(2)	0.790 8(2)	C(27)	0.936 5(6)	0.002 0(6)	0.680 1(6)
O(2)	0.921(1)	0.012 3(7)	0.897 3(8)	C(28)	0.894 2(5)	−0.049 5(6)	0.613 5(6)
N(1)	1.015 6(8)	0.264 1(6)	0.790 0(6)	C(29)	0.951 5(7)	−0.082 0(5)	0.572 2(5)
N(2)	1.076 6(8)	0.311 5(7)	0.858 8(7)	C(30)	1.051 0(7)	−0.063 0(6)	0.597 4(6)
C(1)	0.943(1)	0.068(1)	0.874(1)	C(31)	1.093 3(5)	−0.011 6(6)	0.663 9(6)
C(2)	1.101 7(7)	0.385 0(4)	0.835 6(6)	C(32)	1.180 1(6)	0.039 3(6)	0.877 4(5)
C(3)	1.169 8(7)	0.427 8(6)	0.900 2(4)	C(33)	1.245 9(8)	−0.012 8(6)	0.864 3(5)
C(4)	1.192 8(7)	0.503 1(6)	0.884 9(6)	C(34)	1.321 8(7)	−0.044 3(6)	0.933 1(7)
C(5)	1.147 7(8)	0.535 6(4)	0.805 0(7)	C(35)	1.332 1(7)	−0.023 6(7)	1.015 0(6)
C(6)	1.079 6(7)	0.492 8(6)	0.740 4(5)	C(36)	1.266 3(9)	0.028 5(7)	1.028 2(5)
C(7)	1.056 6(6)	0.417 5(5)	0.755 7(5)	C(37)	1.190 3(7)	0.059 9(6)	0.959 4(7)
C(8)	0.873 0(7)	0.329 4(4)	0.887 7(6)	C(38)	1.161 5(6)	0.154 4(5)	0.753 3(5)
C(9)	0.902 3(7)	0.380 0(5)	0.956 3(4)	C(39)	1.245 5(7)	0.188 5(6)	0.811 7(4)
C(10)	0.886 7(7)	0.459 1(5)	0.943 0(5)	C(40)	1.295 3(6)	0.245 8(6)	0.785 9(6)
C(11)	0.841 8(8)	0.487 7(4)	0.861 2(7)	C(41)	1.261 1(8)	0.269 1(6)	0.701 7(7)
C(12)	0.812 5(7)	0.437 2(6)	0.792 7(5)	C(42)	1.177 2(8)	0.235 0(6)	0.643 2(5)
C(13)	0.828 1(7)	0.358 0(5)	0.806 0(5)	C(43)	1.127 3(6)	0.177 7(6)	0.669 1(5)
C(14)	0.756 3(5)	0.198 9(6)	0.873 1(6)	Cl(1)[c]	0.350 7(5)	0.256 5(4)	0.060 3(5)
C(15)	0.701 8(7)	0.234 0(5)	0.915 3(5)	O(1)[c]	0.362(1)	0.324 9(6)	0.111 1(8)
C(16)	0.601 2(6)	0.219 2(6)	0.890 4(6)	O(3)[c]	0.385(1)	0.190 4(6)	0.114 4(8)
C(17)	0.555 1(5)	0.169 3(6)	0.823 2(6)	O(4)[c]	0.407(1)	0.264 2(9)	0.007 0(8)
C(18)	0.609 7(7)	0.134 1(6)	0.780 9(5)	O(5)[c]	0.248 3(6)	0.246(1)	0.008 7(9)
C(19)	0.710 3(7)	0.148 9(6)	0.805 9(6)	Cl(2)[d]	0.322 9(5)	0.278 2(4)	0.073 2(5)
C(20)	0.948 0(6)	0.207 0(5)	1.011 6(4)	O(8)[d]	0.274(1)	0.334 3(7)	0.107(1)
C(21)	0.908 2(5)	0.162 7(6)	1.059 6(5)	O(5)[d]	0.253(1)	0.246(1)	−0.003 5(7)
C(22)	0.964 9(7)	0.145 6(6)	1.143 5(5)	O(6)[d]	0.362(1)	0.217 6(8)	0.134 1(9)
C(23)	1.061 3(7)	0.172 7(6)	1.179 3(4)	O(7)[d]	0.401 8(9)	0.314 9(8)	0.056(1)
C(24)	1.101 1(5)	0.217 0(6)	1.131 3(6)				

[a] Occupancy 0.67. [b] Occupancy 0.34. [c] Occupancy 0.535. [d] Occupancy 0.465.

given in Table 4. For compound **5** an approximate solution was found, but perhaps because of poor crystal quality it has not been possible to refine this structure satisfactorily. The TEXSAN-TEXRAY package,[26] with atom scattering factors, was used, and PLUTO[31] for illustrations.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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Table 4 Crystal structure analysis, crystal data and experimental details for complexes **1**–**5**

	1	**2**	**3**	**4**	**5**
Formula	$C_{37}H_{30}ClO_5P_2Rh\cdot CH_2Cl_2$	$C_{38}H_{36}ClN_2O_5P_2Rh$	$C_{39}H_{38}ClN_2O_5P_2Rh$	$C_{43}H_{38}ClN_2O_5P_2Rh$	$C_{49}H_{42}ClN_2O_5P_2Rh$
M	839.88	801.02	815.05	863.09	939.19
Appearance	Yellow air sensitive tablets	Yellow air sensitive tablets	Yellow air stable prisms	Yellow air stable plates	Yellow plates
System	Monoclinic	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2_1/c$	$P1$ (no. 1)	$P2_1/n$	$P\bar{1}$ (no. 2)
a/Å	10.550(3)	18.112(8)	9.786(3)	14.606(8)	20.92(1)
b/Å	22.734(5)	11.598(9)	11.487(4)	17.328(6)	21.11(1)
c/Å	15.456(4)	18.38(1)	9.300(3)	17.041(9)	11.226(5)
α/°	—	—	105.57(3)	—	97.74(4)
β/°	94.86(2)	107.51(4)	94.86(2)	115.57(4)	90.11(4)
γ/°	—	—	68.57(3)	—	63.58(4)
U/Å^3 Z	3694	3682	937	4011	4390
D_c/g cm^{-3}	4	4	1	4	4
$F(000)$	1.510	1.445	1.446	1.429	1.421
μ(Mo-Kα)/cm^{-1}	1704	1640	419	1768	1928
	7.99	6.57	6.47	6.09	5.62
Crystal dimensions/mm	0.25 × 0.40 × 0.50	0.40 × 0.30 × 0.40	0.30 × 0.10 × 0.45	0.40 × 0.50 × 0.40	
Reflections measured	7108	7072	3514	7646	
h, k, l ranges	0–13, 0–27, −18 to 18	0–22, 0–14, −22 to 22	0–12, −14 to 14, −11 to 11	0–17, 0–21, −20 to 20	
Unique reflections	6721	6846	3303	7344	
R_{merg}	0.074	0.067	0.024	0.047	
T_{max}, T_{min}	1.00, 0.84	1.28, 0.82	1.00, 0.93	1.09, 0.89	
Observed reflections	2264	1573	2713	2489	
Criterion	$I > 4\sigma(I)$	$I > 5\sigma(I)$	$I > 5\sigma(I)$	$I > 5\sigma(I)$	
Number parameters refined	190	137	117	162	
R	0.057	0.071	0.047	0.065	0.09
R'	0.062	0.076	0.054	0.073	
Final difference electron density (maximum, minimum)/e Å^{-3}	0.71, −0.50	0.65, −0.71	0.71, −0.62	1.01, −1.37	

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