Pentamethylcyclopentadienylrhodium Complexes with the Pyridazine Ligand. Molecular Structure of $[\{Rh(C_5Me_5)\}_2(\mu\text{-}Cl)_2(\mu\text{-pydz})][ClO_4]_2\cdot H_2O$ (pydz = pyridazine)†

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The preparation and characterization of the new mononuclear complexes $[Rh(C_5Me_5)Cl_2(pydz)]$, $[Rh(C_5Me_5)Cl(pydz)_2][X]$, and $[Rh(C_5Me_5)(acac)(pydz)][X]$ (pydz = pyridazine, X = BF_4 or ClO_4, acac = acetylacetonate) are reported. The mononuclear complex $[Rh(C_5Me_5)Cl_2(pydz)]$ reacts with the solvated species $[Rh(C_5Me_5)L_3][X]_2$ (L = acetone) to form $[\{Rh(C_5Me_5)\}_2(\mu\text{-}Cl)_2(\mu\text{-pydz})][X]_2$. The structure of the latter complex (X = ClO_4) has been determined by *X*-ray diffraction methods. Crystals are monoclinic, space group $P2_1/n$ with $Z = 4$ in a unit cell of dimensions $a = 22.276\,1(9)$, $b = 7.940\,7(1)$, $c = 19.359\,5(8)$ Å, and $\beta = 109.824(3)°$. The structure was solved by Patterson analysis and refined by full-matrix least-squares methods to $R = 0.047$ for 3 970 observed reflections. The cation consists of two $Rh(C_5Me_5)$ moieties triply bridged by two chlorine atoms and a pyridazine group. The latter co-ordinates in an *exo*-bidentate manner through the two nitrogen atoms. The two rhodium atoms are separated by 3.397(1) Å. Attempts to isolate homovalent double-bridged complexes of general formula $[Rh_2(C_5Me_5)_2Cl_2(pydz)_2]^{2+}$ or mixed-valence rhodium(III)–rhodium(I) complexes of formulae $[(C_5Me_5)ClRh(\mu\text{-}Cl)(\mu\text{-pydz})Rh(tfb)]^+$ or $[(C_5Me_5)ClRh(\mu\text{-pydz})_2Rh(tfb)]^{2+}$ (tfb = 5,6,7,8-tetrafluoro-1,4-dihydro-1,4-ethenonaphthalene) have been unsuccessful.

Considerable interest has recently been shown in rhodium complexes with pyrazole (Hpz) and pyrazolate-type ligands.[1–5] In these compounds the pyrazolate groups act either as *exo*-bidentate[1–5] or, less frequently, as unidentate ligands.[2,3] In particular, the use of pyrazolate-type ligands has proved to be important for the isolation of some unusual methoxo-, hydroxo-, and pyrazolato-bridged pentamethylcyclopentadienylrhodium complexes.[4,5] Furthermore, we have recently reported the synthesis of mixed-valence pyrazolate rhodium complexes,[6,7] as well as related heteronuclear complexes,[8] using specific reactions designed to link the two metal-containing fragments.

We have now explored the chemical and co-ordinative behaviour towards $Rh(C_5Me_5)$ moieties of pyridazine (pydz), a neutral ligand which, like the pyrazolate anion, has two adjacent nitrogen atoms available for co-ordination and, therefore, it can attach to the metals in an unidentate or bridging mode.[9,10]

Results and Discussion

Mononuclear Complexes.—The well known complex $[\{Rh(C_5Me_5)Cl\}_2(\mu\text{-}Cl)_2]$[11] (**1**) reacts with pyridazine (pydz) to give the neutral complex $[Rh(C_5Me_5)Cl_2(pydz)]$ (**2**). The ^1H n.m.r. spectrum of this compound, in $CDCl_3$, at 313 K shows a broad signal centred at 9.38 p.p.m. for the protons adjacent to the N atoms. At 273 K two signals are observed for these protons, the temperature of coalescence being *ca.* 293 K. On cooling down to 223 K, the limiting low-temperature spectrum was not reached. These observations suggest that a fluxional process involving metal transfer between the two nitrogen-donor sites on the pyridazine ring is occurring. Processes of this type have been observed previously, in palladium compounds, for related nitrogen-containing heterocycles.[12]

Complex (**2**) reacts with stoicheiometric amounts of silver salts and pyridazine to form the expected cationic derivatives $[Rh(C_5Me_5)Cl(pydz)_2][X]$ [X = BF_4 (**3a**) or ClO_4 (**3b**)]. An alternative route for the synthesis of complexes (**3**) is the reaction of $[Rh(C_5Me_5)Cl(acac)]$ (acac = acetylacetonate)[13] with equimolar amounts of tetrafluoroboric or perchloric acid and the required amount of pyridazine. The acetylacetonate compound $[Rh(C_5Me_5)Cl(acac)]$ also reacts with stoicheiometric amounts of silver salts and pyridazine to give the cationic complexes $[Rh(C_5Me_5)(acac)(pydz)][X]$ [X = BF_4 (**4a**) or ClO_4 (**4b**)]. The i.r. spectra of complexes (**2**)—(**4**) show all the expected ligand and anion absorptions [(**3**) and (**4**)] together with ν(Rh–Cl) absorptions in the range 255—285 cm^{-1} [(**2**) and (**3**)]. In particular, a strong ν(C=N) band is observed at *ca.* 1 570 cm^{-1}, obscured by the ν(CO) absorptions in complexes (**4**). Analytical and other physical data are reported in Table 1. Conductivity measurements on complexes (**3**) and (**4**) confirm the mononuclear nature of the cation. We propose that, in the solid state, the pyridazine ligand is acting as unidentate in complexes (**2**)—(**4**), retaining one nitrogen atom per ligand capable of further co-ordination.

Homovalent Binuclear Complexes.—Interestingly, complex (**2**), containing unidentate pyridazine and terminal chloride

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† Di-μ-chloro-μ-[pyridazine-*N*(Rh),*N*′(Rh′)]-bis[η-pentamethylcyclopentadienylrhodium(III)] bis(perchlorate) monohydrate.

Supplementary data available (No. SUP 56582, 4 pp.): H-atom co-ordinates, thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Table 1. Analytical and i.r. data, conductivity measurements, and yields for the new complexes

Complex	Analysis[a] (%) C	H	N	I.r.[b] (cm^{-1})	Λ_M/ Ω^{-1} cm^2 mol^{-1}	Yield (%)
(2)	43.2 (43.2)	4.9 (4.9)	7.4 (7.2)	1 565s;[c] 270s, 255s[d]		94
(3a)	41.5 (41.5)	4.5 (4.45)	11.3 (10.8)	1 565s;[c] 280s[d]	147	87[e]
(3b)	39.6 (40.55)	4.5 (4.35)	10.7 (10.5)	1 570s;[c] 285s[d]	149	94[f]
(4a)	44.3 (45.3)	4.9 (5.2)	5.4 (5.6)	1 570vs, 1 365vs[g]	152	84
(4b)	44.4 (44.2)	5.2 (5.1)	5.0 (5.4)	1 570vs, 1 370vs[g]	132	77
(5a)	35.4 (36.0)	4.2 (4.3)	3.7 (3.5)	1 575w;[c] 250w[d]		80
(5b)	34.5 (34.9)	4.2 (4.15)	3.8 (3.4)	1 580w;[c] 250w[d]		86

[a] Calculated values are given in parentheses. [b] Nujol mulls. [c] ν(C=N). [d] ν(Rh–Cl). [e] Prepared from **(2)**. [f] Prepared from [$Rh(C_5Me_5)Cl(acac)$]. [g] ν(CO).

Table 2. Other redistribution reactions

Reaction number	Starting materials (molar ratio)	Conditions of reaction (solvent, time)	Rhodium-containing reaction products
(1)	[$Rh(C_5Me_5)(acac)Cl$], HBF_4, [$RhCl(pydz)(tfb)$]* (1:1:1)	Acetone, 1 h	[{$RhCl(tfb)$}$_2$], **(1)**, **(3a)**, **(5a)**, **(6)**
(2)	**(2)**, [{$RhCl(tfb)$}$_2$], $AgBF_4$ (2:1:2)	Acetone, 1 h	[{$RhCl(tfb)$}$_2$], **(1)**, **(3a)**, **(5a)**, **(6)**
(3)	**(2)**, [{$RhCl(tfb)$}$_2$], $AgClO_4$ (2:1:2)	Acetone, 4 h	[{$RhCl(tfb)$}$_2$], **(1)**, **(3b)**, **(5b)**, **(6)**
(4)	**(1)**, [$RhCl(pydz)(tfb)$],* $NaBF_4$ (1:2:2)	MeOH, 1 h	[{$RhCl(tfb)$}$_2$], **(1)**, **(3a)**, **(5a)**, **(6)**
(5)	**(4a)**, [$RhCl(pydz)(tfb)$],* HBF_4 (1:1:1)	Acetone, 4 h	[$Rh_2(pydz)_2(tfb)_2$]$^{2+}$, **(1)**, **(3a)**, **(5a)**, **(6)**
(6)	**(3b)**, [{$RhCl(tfb)$}$_2$], $AgClO_4$ (1:2:2)	Acetone, 1 h	[$Rh_2(pydz)_2(tfb)_2$]$^{2+}$ **(1)**, **(3b)**, **(5b)**, **(6)**

* See ref. 9.

ligands, reacts with solvated pentamethylcyclopentadienylrhodium species [$Rh(C_5Me_5)L_3$][X]$_2$ (L = Me_2CO, X = BF_4 or ClO_4)[14] yielding the triple-bridged cationic complex [{$Rh(C_5Me_5)$}$_2$(μ-Cl)$_2$(μ-pydz)][X]$_2$ [X = BF_4 **(5a)** or ClO_4 **(5b)**]. Analytical data support the proposed formulation and although electrical conductivity measurements at different concentrations, in acetone solution, are not conclusive the *X*-ray structure determination of complex **(5b)** (see below) completely substantiates this proposal.

Attempts to prepare homovalent double-bridged complexes of general formula [$Rh_2(C_5Me_5)_2Cl_2(pydz)_2$]$^{2+}$ by linking of two mononuclear pentamethylcyclopentadienylrhodium fragments have been unsuccessful. Thus, mixtures of complexes **(1)**, **(3a)**, **(5a)**, and most probably [{$Rh(C_5Me_5)$}$_2$(μ-Cl)(μ-pydz)$_2$]$^{3+}$ **(6)**, consistent with the ^1H n.m.r. data,* are formed from the reaction of complex **(3)** with stoicheiometric amounts of [$Rh(C_5Me_5)Cl(acac)$] and tetrafluoroboric acid, or by reacting **(2)** with equimolecular amounts of silver tetrafluoroborate, where [$Rh(C_5Me_5)Cl(pydz)(Me_2CO)$]$^+$ fragments are initially formed.

Other Redistribution Reactions.—We have recently reported some homo- and hetero-bridged mixed-valence pyrazolate complexes of formula [(C_5Me_5)ClRh(μ-pz)$_2$RhL$'_2$] (pz = pyrazolate; L$'_2$ = diolefin, L$'$ = CO) and [(C_5Me_5)ClRh(μ-Cl)(μ-pz)Rh(tfb)] (tfb = 5,6,7,8-tetrafluoro-1,4-dihydro-1,4-ethenonaphthalene).[6] The latter reacted with carbon monoxide to form [(C_5Me_5)ClRh(μ-Cl)(μ-pz)Rh(CO)$_2$] which easily underwent a redistribution reaction to give **(1)** and [{$Rh(CO)_2$}$_2$(μ-pz)$_2$]. In this context, we report our unsuccessful attempts to prepare mixed-valence rhodium(III)–rhodium(I) complexes stabilized by bridging pyridazine ligands. Thus, the mononuclear or the homovalent binuclear complexes of rhodium(III), **(1)**, **(3)**, **(5)**, and **(6)**, and the homovalent binuclear complexes of rhodium(I), [{$RhCl(tfb)$}$_2$][16] and [$Rh_2(pydz)_2(tfb)_2$]$^{2+}$,[9] were obtained as final products from reactions (1)—(6) (Table 2), suggesting the formation of the non-isolable intermediates [(C_5Me_5)ClRh(μ-Cl)(μ-pydz)Rh(tfb)]$^+$ [reactions (1)—(4)] and [(C_5Me_5)ClRh(μ-pydz)$_2$Rh(tfb)]$^{2+}$ [reactions (5) and (6)]. Support for these mixed-valence intermediates comes from the characterization of the above mentioned related mixed-valence pyrazolate-bridged complexes.[6]

X-Ray Structure of [{$Rh(C_5Me_5)$}$_2$(μ-Cl)$_2$(μ-pydz)][ClO_4]$_2$·H_2O **(5b)**.—The structure of the cation is illustrated in the Figure, with the atom labelling used in the crystallographic work. The complex cation consists of two Rh atoms, with angles around them (involving the Cl and N atoms and the centroids of the C_5Me_5 rings) consistent with pseudo-octahedral co-ordination (the 'three-legged piano stool'), enlarging the G–Rh–N angles (see Table 3). The intermetallic Rh–Rh distance [3.397(1) Å] exludes any metal–metal interaction. This value is slightly longer than that found for the related [{$Rh(C_5Me_5)$}$_2$(μ-OMe)$_2$(μ-mpz)]$^+$ (mpz = 3-methylpyrazolate) recently reported by us.[4] The two rhodium atoms are bridged by two chlorine atoms [mean Rh–Cl 2.435(1) Å], which form bridging angles of 88.3(1) and 88.6(1)°, and a pyridazine ligand *via* the two nitrogen atoms [Rh(1)–N(1) 2.16(1) and Rh(2)–N(2) 2.17(1) Å]. Thus, the pyridazine ligand co-ordinates in an *exo*-bidentate form. The N(1)–N(2) bond is almost coplanar with

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* The related pyrazolate cationic complex [{$Rh(C_5Me_5)$}$_2$(μ-Cl)(μ-pz)$_2$]$^+$ has been prepared previously.[15] ^1H N.m.r. data attributed to complex **(6)**: δ_H [200 MHz, $(CD_3)_2CO$, standard $SiMe_4$], 1.78 (30 H, s, C_5Me_5), 8.50 (4 H, m, pydz), 9.89 p.p.m. (4 H, m, pydz).

Table 3. Selected bond distances (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses*

Rh(1)–Cl(1)	2.448(2)	Rh(2)–Cl(1)	2.430(2)
Rh(1)–Cl(2)	2.431(2)	Rh(2)–Cl(2)	2.431(2)
Rh(1)–N(1)	2.163(6)	Rh(2)–N(2)	2.174(7)
Rh(1)–G(1)	1.775(7)	Rh(2)–G(2)	1.774(14)
Rh(1)–C(5)	2.120(8)	Rh(2)–C(15)	2.148(8)
Rh(1)–C(6)	2.154(8)	Rh(2)–C(16)	2.135(11)
Rh(1)–C(7)	2.184(7)	Rh(2)–C(17)	2.131(14)
Rh(1)–C(8)	2.138(6)	Rh(2)–C(18)	2.133(12)
Rh(1)–C(9)	2.163(7)	Rh(2)–C(19)	2.180(9)
N(1)–N(2)	1.350(7)	C(1)–C(2)	1.362(15)
N(1)–C(1)	1.339(11)	C(2)–C(3)	1.335(13)
N(2)–C(4)	1.334(13)	C(3)–C(4)	1.392(16)
C(5)–C(6)	1.456(12)	C(15)–C(16)	1.432(19)
C(6)–C(7)	1.412(11)	C(16)–C(17)	1.465(33)
C(7)–C(8)	1.426(11)	C(17)–C(18)	1.387(50)
C(8)–C(9)	1.436(12)	C(18)–C(19)	1.414(18)
C(9)–C(5)	1.423(11)	C(19)–C(15)	1.396(15)
G(1)–Rh(1)–Cl(1)	125.9(3)	G(2)–Rh(2)–Cl(1)	125.2(10)
G(1)–Rh(1)–Cl(2)	126.8(3)	G(2)–Rh(2)–Cl(2)	128.1(5)
G(1)–Rh(1)–N(1)	136.1(3)	G(2)–Rh(2)–N(2)	135.4(9)
Cl(1)–Rh(1)–Cl(2)	85.1(1)	Cl(1)–Rh(2)–Cl(2)	85.5(1)
Cl(1)–Rh(1)–N(1)	83.5(2)	Cl(1)–Rh(2)–N(2)	82.4(2)
Cl(2)–Rh(1)–N(1)	82.3(2)	Cl(2)–Rh(2)–N(2)	83.3(2)
Rh(1)–N(1)–C(1)	123.0(5)	Rh(2)–N(2)–C(4)	123.6(6)
Rh(1)–N(1)–N(2)	118.2(5)	Rh(2)–N(2)–N(1)	118.0(6)
Rh(1)–Cl(1)–Rh(2)	88.3(1)	Rh(1)–Cl(2)–Rh(2)	88.6(1)
N(1)–Rh(1)–G(1)–C(5)	164.3(5)		
N(1)–Rh(1)–G(1)–C(7)	20.1(8)		
N(2)–Rh(2)–G(2)–C(16)	163.1(9)		
N(2)–Rh(2)–G(2)–C(19)	19.7(22)		
C(7)–G(1) ··· G(2)–C(16)	−176.9(13)		
C(9)–G(1) ··· G(2)–C(18)	−177.2(13)		
C(5)–G(1) ··· G(2)–C(19)	−176.1(17)		
Rh(1)–N(1)–N(2)–Rh(2)	2.1(4)		

* G(1) and G(2) indicate the centroids of the two C_5Me_5 rings.

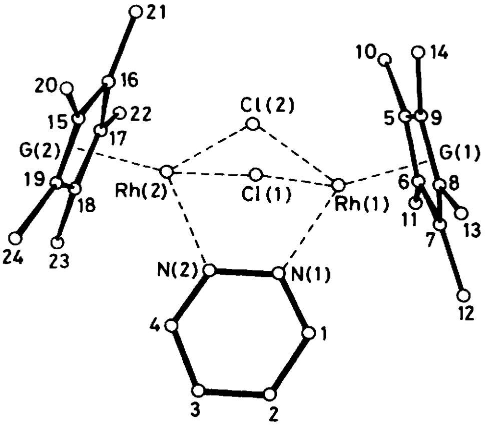

Figure. View of the cation with the atomic numbering scheme

the two Rh atoms [torsion angle Rh(1)–N(1)–N(2)–Rh(2) 2.1(4)°]. It is worth noting that the Rh–N distances are longer than those observed in related pyrazolate[4–7] and 2,2′-biimidazolate[17] pentamethylcyclopentadienylrhodium complexes. The lability found in the Rh–N(pyridazine) bonds could be a reflection of these large values and play an important role in the observed redistribution reactions.

Each Rh atom is η^5-bonded to a C_5Me_5 ligand, with Rh–C(ring) distances in the usual range found in $Rh^{III}(C_5Me_5)$ complexes.[4–7,17,18] The separation of the C_5Me_5 planes from the metals are also as usual [1.775(7), 1.774(14) Å]. The difference in size of the bridging groups does not allow the C_5Me_5 rings to be parallel but inclined to one another at an angle of 37.9(5)°. The C_5Me_5 rings are also staggered by 33(2)°.

Experimental

Infrared spectra were recorded on a Perkin-Elmer 577 spectrophotometer (range 4 000—200 cm^{-1}) using Nujol mulls between polyethylene sheets. Conductivities were measured in acetone with a Philips 9501/01 conductimeter at concentrations of 10^{-4}—10^{-3} mol dm^{-3}. The molecular weight of complex (**2**) was measured in $CDCl_3$ with a Knauer vapour-pressure osmometer. The C, H, and N analyses were carried out with a Perkin-Elmer 240B microanalyser. ^1H N.m.r. spectra were recorded in $CDCl_3$ or $(CD_3)_2CO$ solutions at room temperature on a Varian XL 200 spectrometer, using $SiMe_4$ as external standard. Solvents were dried and distilled before use and all reactions were carried out at room temperature.

Preparation of $[Rh(C_5Me_5)Cl_2(pydz)]$ (**2**).—To a suspension of $[\{Rh(C_5Me_5)Cl\}_2(\mu\text{-}Cl)_2]$ (**1**) (371.0 mg, 0.60 mmol) in acetone (10 cm^3), pydz (87.0 µl, 1.20 mmol) was added. Complex (**1**) dissolved and, immediately, the precipitation of a solid was observed. The resulting reddish suspension was stirred for 1 h and then filtered. The red-orange solid obtained was washed with diethyl ether and air-dried. ^1H N.m.r. spectrum: δ_H (200 MHz, $CDCl_3$, standard $SiMe_4$, room temperature), 1.62 (15 H, s, C_5Me_5), 7.56 (2 H, m, pydz), 9.30 p.p.m. (2 H, br m, pydz). *M* (osmometry), 301. $C_{14}H_{19}Cl_2N_2Rh$ requires 389.

Preparation of $[Rh(C_5Me_5)Cl(pydz)_2][X]$ [X = BF_4 (**3a**) *or* ClO_4 (**3b**)].—*Method A*. To a suspension of $[Rh(C_5Me_5)Cl_2(pydz)]$ (**2**) (0.29 mmol) in acetone (10 cm^3), pydz (0.30 mmol) and AgX (0.3 mmol) were added. The resulting suspension was stirred for 2 h and then filtered to remove the AgCl formed. The yellow filtrate was partially concentrated under reduced pressure and a yellow (X = BF_4) or orange (X = ClO_4) solid precipitated. The precipitation of this solid was completed by addition of diethyl ether. The product was filtered off, washed with diethyl ether, and air-dried.

Method B. A mixture of $[Rh(C_5Me_5)Cl(acac)]$ (0.42 mmol), pydz (0.84 mmol), and an aqueous solution of HBF_4 (52.2 µl, 54% w/w, 0.42 mmol) or $HClO_4$ (47.0 µl, 60% w/w, 0.42 mmol) in acetone (15 cm^3) was stirred for 30 min. The resulting yellow solution was partially concentrated under reduced pressure and a yellow (HBF_4) or orange ($HClO_4$) solid precipitated. The precipitation was completed by addition of diethyl ether. The solid was filtered off, washed with diethyl ether, and air-dried. ^1H N.m.r. spectrum of (**3a**): δ_H [200 MHz, $(CD_3)_2CO$, standard $SiMe_4$], 1.60 (15 H, s, C_5Me_5), 7.98 (4 H, m, pydz), 9.36 (2 H, m, pydz), 9.48 p.p.m. (2 H, m, pydz).

Preparation of $[Rh(C_5Me_5)(acac)(pydz)][X]$ [X = BF_4 (**4a**) *or* ClO_4 (**4b**)].—To a solution of $[Rh(C_5Me_5)Cl(acac)]$ (0.17 mmol) in acetone (15 cm^3), AgX (0.18 mmol) was added. The resulting solution was stirred, under nitrogen, for 30 min and then filtered to remove the AgCl formed. To the yellow filtrate was added pydz (0.20 mmol). The solution obtained was stirred for 30 min and then concentrated to *ca*. 3 cm^3. Addition of diethyl ether gave a yellow solid which was filtered off, washed with diethyl ether, and air-dried. ^1H N.m.r. spectrum of (**4a**): δ_H (200 MHz, $CDCl_3$, standard $SiMe_4$), 1.54 (15 H, s, C_5Me_5), 2.02

Table 4. Final fractional atomic co-ordinates with e.s.d.s in parentheses

Atom	*X/a*	*Y/b*	*Z/c*
Rh(1)	0.063 40(2)	0.194 45(6)	−0.167 60(3)
Rh(2)	−0.065 23(3)	0.016 85(7)	−0.295 88(3)
Cl(1)	−0.023 6(1)	0.302 2(2)	−0.273 4(1)
Cl(2)	−0.011 5(1)	−0.026 3(2)	−0.165 0(1)
N(1)	0.078 0(3)	0.030 1(8)	−0.248 4(3)
N(2)	0.028 9(3)	−0.034 2(8)	−0.301 6(3)
C(1)	0.138 5(4)	−0.013 4(11)	−0.247 0(5)
C(2)	0.149 0(4)	−0.116 5(13)	−0.298 0(6)
C(3)	0.099 2(5)	−0.176 0(13)	−0.352 9(5)
C(4)	0.038 8(5)	−0.129 5(13)	−0.353 4(5)
C(5)	0.063 2(3)	0.390 6(10)	−0.093 4(4)
C(6)	0.106 4(4)	0.436 6(10)	−0.132 2(4)
C(7)	0.155 7(3)	0.315 4(10)	−0.114 7(4)
C(8)	0.143 5(3)	0.191 0(10)	−0.068 0(4)
C(9)	0.088 3(4)	0.243 6(11)	−0.051 4(4)
C(10)	0.004 7(4)	0.489 0(13)	−0.095 1(6)
C(11)	0.101 7(5)	0.590 3(11)	−0.177 8(6)
C(12)	0.212 4(4)	0.329 4(14)	−0.139 6(5)
C(13)	0.183 0(5)	0.042 7(13)	−0.034 9(5)
C(14)	0.061 0(5)	0.154 2(15)	−0.000 7(5)
C(15)	−0.139 2(3)	−0.163 8(11)	−0.304 7(5)
C(16)	−0.160 5(4)	0.001 5(21)	−0.294 4(10)
C(17)	−0.159 3(6)	0.096 2(15)	−0.358 9(16)
C(18)	−0.136 0(7)	−0.006 2(19)	−0.402 1(7)
C(19)	−0.126 0(4)	−0.168 6(12)	−0.370 2(5)
C(20)	−0.136 1(5)	−0.314 4(19)	−0.257 1(7)
C(21)	−0.180 0(6)	0.055 2(44)	−0.232 5(17)
C(22)	−0.179 9(10)	0.276 0(18)	−0.377 5(29)
C(23)	−0.129 6(12)	0.038 2(41)	−0.474 1(10)
C(24)	−0.108 7(7)	−0.323 4(20)	−0.401 8(8)
Cl(3)	0.319 0(1)	0.113 6(3)	0.429 8(1)
Cl(4)	0.173 2(1)	0.382 7(4)	0.632 4(1)
O(1)	0.378 4(3)	0.184 1(13)	0.471 3(6)
O(2)	0.278 2(4)	0.236 9(15)	0.387 8(6)
O(3)	0.289 9(6)	0.052 0(23)	0.477 4(7)
O(4)	0.328 1(7)	−0.013 8(26)	0.389 1(12)
O(5)	0.155 2(6)	0.486 5(15)	0.570 4(5)
O(6)	0.203 4(6)	0.491 6(16)	0.691 4(6)
O(7)	0.123 4(7)	0.314 9(29)	0.645 0(12)
O(8)	0.218 5(10)	0.267 9(23)	0.630 5(14)
O(9w)	−0.001 6(9)	0.315 0(34)	0.521 8(12)

[6 H, s, CH_3 (acac)], 5.13 [1 H, s, CH (acac)], 7.90 (1 H, m, pydz), 8.05 (1 H, m, pydz), 8.75 (1 H, m, pydz), 9.25 p.p.m. (1 H, m, pydz).

Preparation of $[\{Rh(C_5Me_5)\}_2(\mu\text{-}Cl)_2(\mu\text{-pydz})][X]_2$ [X = BF_4 (**5a**) *or* ClO_4 (**5b**)].—To a suspension of complex (**1**) (0.12 mmol), in acetone (10 cm^3) was added AgX (0.48 mmol). The resulting solution was stirred, under nitrogen, for 30 min and then filtered to remove the AgCl formed. The orange filtrate was recovered over a suspension of complex (**2**) (0.24 mmol) in the same solvent (5 cm^3). Complex (**2**) dissolved and after a few minutes the precipitation of an orange (X = BF_4) or orange-red (X = ClO_4) solid was observed. The resulting suspension was stirred for 30 min and then concentrated to *ca.* 2 cm^3. The precipitation was completed by addition of diethyl ether. The solid was filtered off, washed with diethyl ether, and air-dried. Red crystals of complex (**5b**), suitable for *X*-ray analysis, were obtained by slow diffusion of a solution in acetone of the solvated complex $[Rh(C_5Me_5)L_3][ClO_4]$ (L = Me_2CO) into a dichloromethane solution of complex (**2**). ^1H N.m.r. spectrum of (**5a**): δ_H [200 MHz, $(CD_3)_2CO$, standard $SiMe_4$], 1.84 (30 H, s, C_5Me_5), 8.60 (2 H, m, pydz), 9.94 p.p.m. (2 H, m, pydz).

Redistribution Reactions.—Reaction conditions, starting materials, and rhodium-containing products from unsuccessful attempts at preparing mixed-valence pyridazine complexes are listed in Table 2. The reactions were carried out using *ca.* 10^{-2} mol dm^{-3} solutions.

Crystal Structure Determination.—*Crystal data.* $C_{24}H_{36}Cl_4N_2O_9Rh_2$, monoclinic, space group $P2_1/n$, $M = 844.18$, $a = 22.276\,1(9)$, $b = 7.940\,7(1)$, $c = 19.359\,5(8)$ Å, $\beta = 109.824(3)°$, $U = 3\,221.5(2)$ Å^3, $D_c = 1.741$ g cm^{-3}, $Z = 4$, $\mu = 120.53$ cm^{-1} (min., max. transmission factors were 0.106 and 0.272). A red prismatic sample of height 0.40 mm, with irregular octagonal basis and distances between the parallel lateral faces of 0.20, 0.16, 0.17, and 0.22 mm was used to collect 5 421 independent reflections up to $\theta = 65°$, on a Philips PW1100 diffractometer, with graphite-monochromated Cu-K_α radiation ($\lambda = 1.5418$ Å; $\omega/2\theta$ scans, scan width 1.5° and 1 min per reflection). No decay was observed. Unit-cell parameters were refined by least-squares from the 2θ values ($2 \leqslant \theta \leqslant 45°$) of 64 reflections. The structure was solved by Patterson analysis. 3 970 Observed reflections [$I > 3\sigma(I)$] were used in the least-squares refinement. Weights, $w = K/[f(F_o)^2][g(\sin\theta/\lambda)]$, were chosen empirically as to give no trends on $\langle w\Delta^2\rangle$ *vs.* $|F_o|$ or $\sin\theta/\lambda$. All hydrogen atoms were located on a difference synthesis, except those of the water molecule. They were included isotropically in the refinement, but in the last cycles those corresponding to the methyl groups of one C_5Me_5 ring C(20)—C(24) had to be kept fixed. This group presents quite high thermal factors on one side, namely around C(17), indicating a libration of the group around an axis parallel to the Rh(1)···G(2) direction, but away from G(2) and towards the C(15)–C(19) bond. No disorder model could be successfully fitted. Moreover, although the Rh–C(ring) distances are alike for both the C_5Me_5 groups the e.s.d.s involving the C(15) and C(19) atoms are greater. The final ΔF map showed no electron density > 1.1 e Å^{-3} near the Rh atoms. Final R and R' factors were 0.047 and 0.052 respectively. Most of the calculations were done with the X-RAY 76 System [19] and the atomic scattering factors were taken from ref. 20. The final atomic co-ordinates are given in Table 4.

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