Mixed-valence Pyrazolate Rhodium Complexes. Molecular Structure of [(C$_5$Me$_5$)ClRhCl(pz)Rh(tfb)]·CH$_2$Cl$_2$ (Hpz = Pyrazole; tbf = Tetrafluorobenzobarrelene) [†]

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Mixed-valence rhodium(III)–rhodium(I) complexes containing pyrazolate(1–) (pz) and/or chlorine groups as bridging ligands have been prepared. The structure of [(C$_5$Me$_5$)ClRhCl(pz)Rh(tfb)]·CH$_2$Cl$_2$ [tfb = tetrafluorobenzobarrelene (5,6,7,8-tetrafluoro-1,4-dihydro-1,4-ethenonaphthalene)], prepared by reacting [Rh(C$_5$Me$_5$)Cl$_2$(Hpz)] with [Rh(acac)(tfb)] [acac = acetylacetonate(1–)], has been determined by X-ray diffraction methods. This heterobridged complex is composed of two rhodium atoms (Rh^{III} and Rh^I) bridged by a chlorine atom and a pyrazolate group. The rhodium–rhodium distance is 3.715(2) Å. The preparation and properties of the homobridged neutral and cationic complexes [(C$_5$Me$_5$)XRh(pz)$_2$RhL'$_2$] [X = Cl, L'$_2$ = tfb, cyclo-octa-1,5-diene (cod), (CO)$_2$, or (CO)(NCBu^t); X = pz, L'$_2$ = tfb], [(C$_5$Me$_5$)L″Rh(pz)$_2$RhL'$_2$][ClO$_4$] [L″ = pyridine (py), MeCN, or Hpz, L'$_2$ = tfb; L″ = py, L' = CO], and [(C$_5$Me$_5$)(Hpz)RhCl$_2$Rh(tfb)][ClO$_4$] are reported.

Mixed-valence complexes containing an element in more than one oxidation state are of considerable interest owing, in part, to the potential interplay of additive and co-operative effects between metal centres across a bridging ligand.[1,2] We have recently reported several binuclear pyrazolate rhodium complexes with the metal centres in oxidation states I,[3–5] II,[5] or III.[6,7] We have now extended our work to mixed-valence pyrazolate rhodium complexes. The synthetic strategy that we report in this paper is related to previous studies from this laboratory,[8–10] in which rhodium complexes containing ligands with acidic N–H protons react with acetylacetonate complexes to form a variety of di- or tetra-nuclear complexes.

Figure 1. Binuclear dispositions proposed for complex (1) (C$_5$Me$_5$ and tfb omitted)

Results and Discussion

Heterobridged Complexes.—Treatment of [Rh(C$_5$Me$_5$)Cl$_2$(Hpz)] (Hpz = pyrazole)[11] with [Rh(acac)(tfb)] [acac = acetylacetonate(1–), tfb = tetrafluorobenzobarrelene (5,6,7,8-tetrafluoro-1,4-dihydro-1,4-ethenonaphthalene)][12] (1:1 molar ratio, acetone, room temperature, 24 h), leads to the formation of the dinuclear complex [(C$_5$Me$_5$)ClRhCl(pz)Rh(tfb)] (1) in ca. 60% yield. Unreacted starting materials are recovered from the reaction medium when equimolecular amounts of [Rh(C$_5$Me$_5$)Cl$_2$(Hdmpz)] (Hdmpz = 3,5-dimethylpyrazole)[11] and [Rh(acac)(tfb)] are treated in a similar way or refluxed in acetone for 4 h. The i.r. spectrum, in the solid state, of complex (1) shows bands characteristic of the tfb ligand,[13] and although two bands at 230 and 265 cm^{-1} could be tentatively attributed
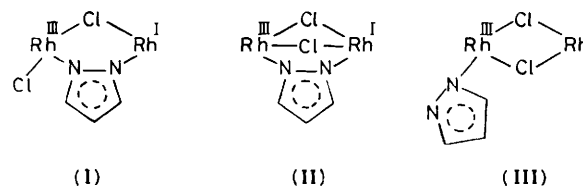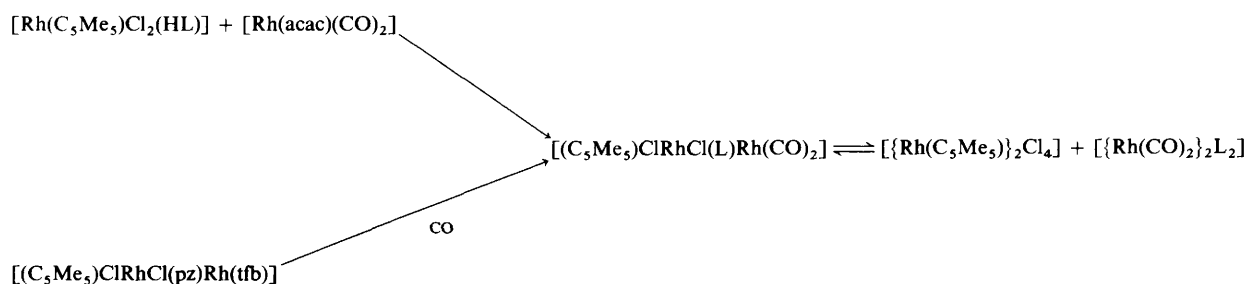
to metal–chlorine stretching vibrations, this i.r. region is obscured by the tfb absorptions making the assignment uncertain. Complex (1) presents a slight electrical conductivity in polar solvents such as acetone (10 Ω^{-1} cm^2 mol^{-1}), probably due to ionic dissociation of one of the chlorine ligands. Initially three binuclear dispositions (I)—(III) could be proposed (Figure 1) and the X-ray crystal-structure determination of [(C$_5$Me$_5$)ClRhCl(pz)Rh(tfb)]·CH$_2$Cl$_2$ (1) confirms the presence of the heterobridged disposition (I) (see below).

The reaction of (1) with carbon monoxide has been studied. After 15 min of bubbling carbon monoxide through dichloromethane solutions of complex (1), the i.r. spectrum, in this solvent, presents bands at 2 080s, 2 010s, and 1 990m and a shoulder at 2 065 cm^{-1}, due to v(CO) absorptions. More lengthy treatment with CO, under the same conditions, does not alter either the number or the relative intensity of the bands. From the solution an orange solid can be isolated. The ^{1}H n.m.r. spectrum, in CDCl$_3$, of this material consists of broad and ill defined signals, but clearly shows the absence of tfb peaks[14] and the presence of two pentamethylcyclopentadienyl singlets (δ 1.67 and 1.61 p.p.m.). In order to obtain additional information about the nature of these products, reactions of [Rh(C$_5$Me$_5$)Cl$_2$(Hpz)] and [Rh(C$_5$Me$_5$)Cl$_2$(Hdmpz)] with [Rh(acac)(CO)$_2$][15] were carried out in both dichloromethane and acetone. When the reactions were carried out in dichloro-

$[Rh(C_5Me_5)Cl_2(HL)]$ + $[Rh(acac)(CO)_2]$

$[(C_5Me_5)ClRhCl(L)Rh(CO)_2]$ $\rightleftharpoons$ $[\{Rh(C_5Me_5)\}_2Cl_4]$ + $[\{Rh(CO)_2\}_2L_2]$

CO

$[(C_5Me_5)ClRhCl(pz)Rh(tfb)]$

Scheme. L = pz or dmpz

methane, i.r. solution measurements showed similar v(CO) band patterns to those found in the carbonylation reaction of complex (1). The ^1H n.m.r. spectrum, in $CDCl_3$, of the material isolated from the reaction of $[Rh(C_5Me_5)Cl_2(Hpz)]$ is analogous to that described above. However, when using acetone the addition of the pyrazole complexes to solutions of $[Rh(acac)(CO)_2]$ causes the precipitation of the well known complex $[\{Rh(C_5Me_5)\}_2Cl_4]$,[16] characterized by analytical and spectroscopic methods. In the remaining solution the complexes $[\{Rh(CO)_2\}_2L_2]$ (L = pz[17] or dmpz[3]) are present, according to solution i.r. data. All these observations permit us to propose the reactions shown by the Scheme: both preparative routes lead to the formation of the heterobridged rhodium(III)–rhodium(I) complexes, which easily undergo a redistribution reaction to give dimeric homovalent rhodium complexes probably due to the high stability of the final products.[4,18] The slight solubility of $[\{Rh(C_5Me_5)\}_2Cl_4]$, in acetone, shifts the equilibrium to the right in this solvent. We have previously observed redistribution reactions for related azolato-rhodium-(I)[19,20] and -rhodium(III)[8] complexes.

Homobridged Complexes.—The existence of the well known acetylacetonate complex $[Rh(C_5Me_5)(acac)Cl]$ (2),[21] potentially provides a preparative route to dinuclear rhodium(III)–rhodium(I) complexes with two pyrazolate groups acting as bridging ligands. Thus, the reaction in acetone of (2) with the cationic complexes $[RhL'(Hpz)_2][ClO_4]$ [L' = tfb or cyclo-octa-1,5-diene (cod)][22] in the presence of stoicheiometric amounts of KOH leads to the precipitation of the corresponding neutral complexes $[(C_5Me_5)ClRh(pz)_2RhL']$ [L' = tfb (3) or cod (4)]. Again, a different behaviour was observed for the Hdmpz ligand. Thus, complex (2) reacts with $[RhL'(Hdmpz)_2][ClO_4]$ (L' = tfb or cod) and KOH in acetone to form $[\{RhL'(dmpz)\}_2]$[17] and $[Rh(C_5Me_5)(acac)-(Hdmpz)][ClO_4]$ (5) according to analytical and spectroscopic data. Complex (5) was also prepared by treating an acetone solution of (2) with $AgClO_4$ and adding Hdmpz.

Alternatively, complexes (3) and (4) can be prepared by reacting the neutral complex $[Rh(C_5Me_5)(acac)(pz)]$ (6) with $[RhCl(L')(Hpz)]$ [L' = tfb (7) or cod (8)].* Complex (6) reacts with the cationic rhodium(I) complex $[Rh(tfb)(Hpz)_2][ClO_4]$ in the presence of KOH to give $[(C_5Me_5)(pz)Rh(pz)_2Rh(tfb)]$ (9). The ^1H n.m.r. spectrum of (9) in $CDCl_3$ shows the presence of two types of pyrazolate groups in relative intensity ratio 2:1 as a consequence of the existence of terminal and bridging pyrazolyl groups (see Experimental section).

Carbonylation of (3) or (4) causes the displacement of the co-ordinated diolefin and the formation of the dicarbonyl complex $[(C_5Me_5)ClRh(pz)_2Rh(CO)_2]$ (10). The v(CO) i.r. pattern

observed for this complex (see Table 1) is characteristic of a square-planar rhodium(I) complex with two carbonyls in a *cis* disposition. The ^1H n.m.r. spectra of complexes (3) and (10) show the existence of only three types of pyrazole CH protons (see Experimental section) and consequently we propose that the two pyrazolyl groups in both complexes are acting as bridging ligands. We suspect that the chlorine ligand is only co-ordinated to the rhodium(III) atom, although the presence of a Rh^{III}–Cl–Rh^I bridge cannot be completely excluded. In fact, this situation is probably present in the intermediate of the reactions of (6) with (7) or (8).

The addition of $NCBu^t$ or PPh_3 to complex (10) in dichloromethane causes the partial displacement of the co-ordinated carbonyl groups. The isolated molecules present one single v(CO) band at 1 990 cm^{-1} (CH_2Cl_2 solution) suggesting the formation of $[(C_5Me_5)ClRh(pz)_2Rh(CO)(NCBu^t)]$ (11) [v(CN) at 2 170 cm^{-1}] and $[(C_5Me_5)ClRh(pz)_2Rh(CO)(PPh_3)]$ (12). Complex (12), however, has not been isolated pure.

Reaction of complex (3) with silver perchlorate followed by the addition of a stoicheiometric amount of a nitrogen donor ligand L" leads to the formation of the cationic complexes $[(C_5Me_5)L''Rh(pz)_2Rh(tfb)][ClO_4]$ [L" = pyridine (py) (13), MeCN (14),† or Hpz (15)]. Complex (15) can also be prepared by reaction of (6) with $[Rh(tfb)(Hpz)_2][ClO_4]$.

Bubbling carbon monoxide through dichloromethane solutions of (13) causes the displacement of the co-ordinated diolefin and the formation of $[(C_5Me_5)(py)Rh(pz)_2Rh(CO)_2][ClO_4]$ (16). As expected, this complex can be alternatively prepared by reacting (10) with silver perchlorate and pyridine.

Finally, the cationic complex $[(C_5Me_5)(Hpz)RhCl_2Rh(tfb)]$-$[ClO_4]$ (17), containing two bridging chlorine ligands, has been prepared by reacting $[Rh(C_5Me_5)Cl_2(Hpz)]$[11] with the solvated intermediate $[Rh(tfb)(Me_2CO)_x]^+$.[23]

In conclusion, mixed-valence rhodium(III)–rhodium(I) complexes containing '$Rh^{III}(C_5Me_5)$' and '$Rh^IL'_2$' [L'$_2$ = tfb, cod, (CO)$_2$, or (CO)(NCBu^t)] units with bridging chlorine and pyrazolate groups can be prepared. Interestingly, the presence of methyl groups in 3,5-positions on the pyrazolate ring produces a marked change in the reactivity. This different behaviour has been recently observed in related pentamethylcyclopentadienyl-rhodium(III) pyrazolate complexes.[6]

Analytical, molecular weight, conductance, and i.r. data and yields for the new dinuclear complexes are collected in Table 1.

Molecular Structure of $[(C_5Me_5)ClRhCl(pz)Rh(tfb)]\cdot CH_2$-$Cl_2$ (1).—The structure of complex (1) is illustrated in Figure 2 with the atom labelling used in the corresponding Tables.

The complex consists of two rhodium atoms, in two different formal oxidation states [Rh(2), oxidation state III; Rh(1), oxidation state I], with pseudo-octahedral and square-planar

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* Complex (6) was prepared by treating complex (2) with K(pz) and complexes (7) and (8) were obtained by cleaving the chlorine bridge in the appropriate $[\{RhCl(L')\}_2]$ dimers with Hpz.

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† In the preparation of complex (14) the reaction was carried out in acetonitrile as solvent.

Table 1. Analysis, molecular weight, conductance, and i.r. data and yields for the new dinuclear complexes

Complex	Analysis[a] (%) C	H	N	M^a	Λ^b	I.r.[c] (cm^{-1})	Yield (%)
(1)	42.7 (42.6)	3.9 (3.4)	4.2 (4.0)		10	1 490vs, 1 100s, 890s, 845s^d	60
(3)	45.3 (45.6)	3.9 (3.7)	7.6 (7.6)	680 (736)		1 490vs, 1 100s, 890s, 845s^d	66^e 75^f
(4)	46.0 (46.6)	5.4 (5.4)	9.0 (9.0)				50^e 68^f
(9)	48.0 (48.5)	4.5 (3.9)	10.7 (10.9)			1 490vs, 1 100s, 890s, 850s^d	55
(10)	38.3 (38.2)	3.5 (3.7)	9.5 (9.9)	635 (566)		2 010s,^{g} 2 080s^{g,h}	60
(11)	42.5 (42.5)	4.7 (4.9)	10.7 (11.3)			1 990s,^{g,h} 2 170s^{g,i}	52
(13)	44.8 (45.0)	3.7 (3.7)	8.1 (8.0)		125	1 600m;^{j} 1 100vs, 620s;^{k} 1 490vs, 890s, 845s^d	79
(14)	42.6 (42.8)	3.5 (3.6)	8.3 (8.3)		138	1 490vs, 845s;^{d} 2 290w, 2 320w;^{i} 1 100vs, 620s^k	80
(15)	42.2 (42.8)	3.8 (3.6)	9.4 (9.7)		138	1 490vs, 890s, 845s^d 1 100vs, 620s;^{k} 3 220s^m	47^l 45^n
(16)	38.4 (38.9)	4.0 (3.7)	9.6 (9.9)		132	2 010s, 2 080s;^{h} 1 600m;^{j} 1 100vs, 620s^k	30° 25^p
(17)	37.0 (37.2)	3.4 (3.1)	3.5 (3.5)		136	1 490vs, 890m, 845;^{d} 1 100vs, 620s;^{k} 3 220m^m	57

[a] Calculated values are given in parentheses. [b] Ω^{-1} cm^2 mol^{-1}, $\simeq 5 \times 10^{-4}$ mol dm^{-3} acetone solutions. [c] Nujol mulls, unless otherwise stated. [d] tfb ligand. [e] Prepared starting from complex (2). [f] Prepared starting from complexes (6) and (7). [g] Dichloromethane solution. [h] v(CO). [i] v(CN). [j] py. [k] ClO$_4^-$. [l] Prepared starting from complex (3). [m] v(NH). [n] Prepared starting from complex (6). [o] Prepared starting from complex (13). [p] Prepared starting from complex (10).
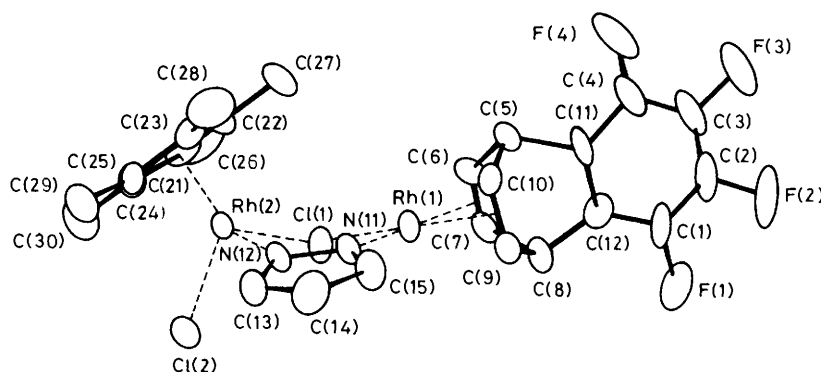
Figure 2. Molecular structure of [(C$_5$Me$_5$)ClRhCl(pz)Rh(tfb)]·CH$_2$Cl$_2$ (1), showing the crystallographic numbering scheme

co-ordinations respectively, and bridged by a chlorine atom and a pyrazolate ring. The separation between the two rhodium atoms is 3.715(2) Å, similar to those reported for the complexes [Rh$_3$(μ_3-tz)(μ-Cl)Cl(η^3-C$_3$H$_5$)$_2$(CO)$_4$]·0.5C$_2$H$_4$Cl$_2$ (Htz = 1,2,4-triazole) [3.712(1) Å]^{24} and [(C$_2$H$_4$)ClPtCl(pz)PtCl-(C$_2$H$_4$)] [3.717(1) Å]^{25} in which a chlorine and an azolate ligand also act as bridging groups between the metal atoms. The rhodium(III) atom is η^5 bonded to a C$_5$Me$_5$ ligand and, as a consequence of the asymmetry of co-ordination about the metal, presents different Rh–C(ring) distances. In this respect the C$_5$Me$_5$ ring shows C–C distances (Table 2) suggesting some degree of localization into an 'ene–enyl' form as has been previously observed in some Rh^{III}(C$_5$Me$_5$) complexes.^{6,21} The rhodium(III) atom is also co-ordinated to a terminal [Cl(2)] and a bridging [Cl(1)] chlorine ligand and to a nitrogen atom of the pyrazolate group [N(12)]. The terminal chlorine ligand is

significantly closer to the rhodium atom than the bridging chlorine ligand, as has been previously found in related rhodium complexes.^{24,26,27} The Rh(2)–N(12) bond distance is comparable to that found in other pyrazolate rhodium(III) complexes.^{6,7} If the centroid of the C$_5$Me$_5$ ring (G) is considered either as a tetrahedral site or the centre of a three *fac* octahedral site^{28} (Table 2), the environment of the Rh^{III} atom can be better ascribed to the octahedral option. The Rh^I atom displays a distorted square-planar co-ordination [the Cl(1)–Rh(1)–N(11) and C(67)–Rh(1)–C(109) planes make an angle of 6(1)° (Table 2)]. The Rh^I–Cl and Rh^I–N bonds are slightly shorter than the corresponding ones for the Rh^{III} atom, contradictory to the respective ionic radii. The Rh(1)–N(11) bond is relatively short in comparison with those found for related Rh^I–N bonds in pyrazolate complexes.$^{3-5}$ The Rh(2),Cl(1),Rh(1),N(11),N(12) ring has a twist conformation, with C_2 symmetry through

Table 2. Selected bond distances (Å), bond angles (°), torsion angles (°), and angles (°) between main planes*

Rh(1)-Cl(1)	2.375(6)	Rh(1)-C(10)	2.093(22)	Rh(2)-Cl(1)	2.434(6)	Rh(2)-C(23)	2.143(20)
Rh(1)-C(6)	2.095(20)	Rh(1)-N(11)	2.033(18)	Rh(2)-Cl(2)	2.385(7)	Rh(2)-C(24)	2.133(28)
Rh(1)-C(7)	2.125(27)			Rh(2)-N(12)	2.091(18)	Rh(2)-C(25)	2.165(27)
Rh(1)-C(9)	2.125(24)	Rh(1)-Rh(2)	3.715(2)	Rh(2)-C(21)	2.179(25)	Rh(2)-G	1.787(21)
				Rh(2)-C(22)	2.142(28)		

C(67)-Rh(1)-C(109)	71.8(9)	N(11)-Rh(1)-C(109)	98.2(8)	Cl(1)-Rh(2)-G	125.1(8)	N(12)-Rh(2)-Cl(1)	87.9(5)
Cl(1)-Rh(1)-N(11)	91.0(5)	Cl(1)-Rh(1)-C(109)	169.6(7)	Cl(2)-Rh(2)-G	125.2(8)	N(12)-Rh(2)-Cl(2)	88.6(6)
N(11)-Rh(1)-C(67)	169.7(8)	Cl(1)-Rh(1)-C(67)	99.2(6)	N(12)-Rh(2)-G	127.2(9)	Cl(1)-Rh(2)-Cl(2)	91.0(2)

C(21)-G-Rh(2)-Cl(1)	34(2)	C(21)-G-Rh(2)-Rh(1)	81(2)	N(12)-N(11)-Rh(1)-Cl(1)	-12.0(16)
C(21)-G-Rh(2)-Cl(2)	-88(2)	G-Rh(2)-Rh(1)-C(67)	-65(1)	N(11)-Rh(1)-Cl(1)-Rh(2)	26.2(5)
C(21)-G-Rh(2)-N(12)	152(2)	G-Rh(2)-Rh(1)-C(109)	76(2)	Rh(1)-Cl(1)-Rh(2)-N(12)	-30.8(5)
				Cl(1)-Rh(2)-N(12)-N(11)	31.5(15)
				Rh(1)-N(11)-N(12)-Rh(2)	-16.0(22)

N(11)-N(12)-C(13)-C(14)-C(15)		C(21)-C(22)-C(23)-C(24)-C(25)	32(1)
N(11)-N(12)-C(13)-C(14)-C(15)		Cl(1)-Rh(1)-N(11)	17(1)
Cl(1)-Rh(1)-N(11)		C(67)-Rh(1)-C(109)	6(1)
N(12)-N(11)-Rh(1)		Rh(2)-N(11)-Cl(1)	23(1)

* C(67), C(109) and G indicate the midpoint of the C(6)-C(7), C(9)-C(10) bonds and the centroid of the C_5Me_5 ring respectively.

the N(11) atom, and with Rh(1) and N(12) 0.731(2) up and 0.451(19) Å down with respect to the plane defined by Rh(2), N(11), and Cl(1). [Cremer and Pope parameters[29] are q_2 = 0.534(9) Å, Φ = 23(2)° compared with a perfect twist at Φ = 18°.] A non-planar ring envelope conformation at Cl(1) has also been found in the complex [$Rh_3(\mu_3$-tz)(μ-Cl)Cl(η^3-$C_3H_5)_2(CO)_4$]·$0.5C_2H_4Cl_2$,[25] although in the complex [(C_2H_4)ClPtCl(pz)PtCl(C_2H_4)] the Pt_2ClN_2 ring is planar. The C_5Me_5 ring makes an angle of 71(1)° with the plane containing the four atoms of the co-ordinating olefinic bonds. The relative positions of these two groups, as viewed along the line joining their centroids, is such that the co-ordinating double bonds of tfb eclipse the C(21) atom and the C(23)-C(24) bond.

The pz ligand is planar as is normal for bridging pyrazolate groups and the geometry of the tfb moiety is within the values already reported.[14,30]

Experimental

Infrared spectra were recorded on a Perkin-Elmer 577 spectrophotometer (range 4 000—200 cm^{-1}) using Nujol mulls between polyethylene sheets or in dichloromethane between NaCl plates. Conductivities were measured in acetone with a Philips 9501/01 conductimeter in concentrations ranging from 10^{-3} to 10^{-4} mol dm^{-3}. Molecular weights were measured in $CHCl_3$ with a Knauer vapour pressure osmometer. The C, H, and N analyses were carried out with a Perkin-Elmer 240B microanalyzer. ^1H N.m.r. spectra were recorded in $CDCl_3$ at room temperature on a Varian XL 200 spectrometer, using $SiMe_4$ as standard. Solvents were dried and distilled before use and all reactions were carried out at room temperature, except where otherwise stated.

Preparation of [$Rh(C_5Me_5)$(acac)(Hdmpz)][ClO_4] (5).—To a solution of [$Rh(C_5Me_5)$(acac)Cl] (2) (112.0 mg, 0.30 mmol) in acetone (10 cm^3), $AgClO_4$(63.1 mg, 0.30 mmol) was added. The resulting suspension was stirred for 20 min and then filtered to remove the AgCl formed. To the yellow filtrate solid Hdmpz (29.1 mg, 0.31 mmol) was added. The resulting solution was stirred for 30 min and then partially concentrated under reduced pressure. Slow addition of diethyl ether gave a yellow microcrystalline solid which was filtered off, washed with diethyl ether, and air-dried. Yield 91% (Found: C, 44.3; H, 5.5; N, 5.0. $C_{20}H_{29}ClN_2O_6Rh$ requires C, 45.2; H, 5.5; N, 5.3%); v(NH) 3 240m, v(CO) 1 570s and 1 530s, v(ClO_4) 1 100vs and 625s cm^{-1} (Nujol); δ_H (200 MHz, $CDCl_3$, standard $SiMe_4$), 1.56 (15 H, s, C_5Me_5), 1.97 [6 H, s, 2 CH_3 (acac)], 2.20 [3 H, s, CH_3 (dmpz)], 2.36 [3 H, s, CH_3 (dmpz)], 4.97 [1 H, s, CH (acac)], 5.88 [1 H, s, CH (dmpz)], 10.84 p.p.m. (1 H, s, NH).

Preparation of [$Rh(C_5Me_5)$(acac)(pz)] (6).—Under nitrogen to a mixture of [$Rh(C_5Me_5)$(acac)Cl] (2) (315.2 mg, 0.85 mmol) and Hpz (57.6 mg, 0.85 mmol) in acetone (20 cm^3) was added KOH (8.3 cm^3, 0.1025 mol dm^{-3}, 0.85 mmol) in methanol. The resulting solution was stirred for 1 h and vacuum evaporated until dryness. The residue was extracted with dichloromethane (30 cm^3). The solution was concentrated under reduced pressure and addition of hexane (10 cm^3) led to the precipitation of an orange solid which was filtered off, washed with hexane, and vacuum dried. The product was recrystallized from dichloromethane-hexane. Yield 61% (Found: C, 52.8; H, 5.7; N, 7.1. $C_{18}H_{25}N_2O_2Rh$ requires C, 53.5; H, 6.2; N, 6.9%); v(CO) 1 570s and 1 530s cm^{-1} (Nujol).

Preparation of [RhCl(L')(Hpz)] [L' = tfb (7) *or* cod (8)].—To a suspension of [{RhCl(L')}$_2$] (0.52 mmol) in acetone was added Hpz (73.3 mg, 1.07 mmol). The resulting solution was stirred for 45 min and then partially concentrated under reduced pressure. Slow addition of diethyl ether gave a yellow microcrystalline solid which was filtered off, washed with diethyl ether, and air-dried. Yield for (7) 70% (Found: C, 40.9; H, 2.5; N, 6.2. $C_{15}H_{10}ClF_4N_2Rh$ requires C, 41.6; H, 2.3; N, 6.5%); v(NH) 3 220m, tfb bands at 1 490vs, 1 100s, 890s, and 845s cm^{-1} (Nujol). Yield for (8) 76% (Found: C, 41.7; H, 5.2; N, 8.8. $C_{11}H_{16}ClN_2Rh$ requires C, 42.0; H, 5.1; N, 8.9%); v(NH) 3 230m cm^{-1} (Nujol).

Preparation of [(C_5Me_5)ClRhCl(pz)Rh(tfb)]·CH_2Cl_2 (1).— A mixture of [$Rh(C_5Me_5)Cl_2$(Hpz)] (100.0 mg, 0.26 mmol) and [Rh(acac)(tfb)] (112.8 mg, 0.26 mmol) in acetone (25 cm^3) was stirred for 24 h. The resulting solution was partially concentrated under reduced pressure. Slow addition of diethyl ether gave an orange solid which was filtered off, washed with

diethyl ether, and air-dried. Recrystallization from dichloromethane–diethyl ether led to orange crystals.

Reaction of [Rh(C₅Me₅)Cl₂(Hdmpz)] *with* [Rh(acac)(CO)₂] *in Acetone.*—A mixture of [Rh(acac)(CO)₂] (91.9 mg, 0.36 mmol) and [Rh(C₅Me₅)Cl₂(Hdmpz)] (144.4 mg, 0.36 mmol) in acetone was stirred for 15 h. The deep red precipitate which formed was filtered off, washed with diethyl ether, and air-dried. This precipitate was characterized as [{Rh(C₅Me₅)}₂Cl₄] by comparison of its spectroscopic properties and analytical data with those an authentic sample.[16]

The resulting filtrate was vacuum-evaporated until dryness. The i.r. spectrum of the residue, dissolved in dichloromethane, showed ν(CO) bands at 2 080s, 2 070s, and 2 010s cm⁻¹, as expected for [{Rh(CO)₂}₂(dmpz)₂].

Similar behaviour was observed using Hpz as the ligand.

Preparation of [(C₅Me₅)ClRh(pz)₂RhL′][L′ = tfb (**3**) or cod (**4**)].—*Method A.* To a mixture of [Rh(C₅Me₅)(acac)Cl] (**2**) (0.27 mmol) and [RhL′(Hpz)₂][ClO₄] (0.27 mmol) in acetone (30 cm³) was added KOH (3.0 cm³, 0.0898 mol dm⁻³, 0.27 mmol) in methanol. The resulting suspensions were stirred for 48 h and vacuum-evaporated until dryness. The residues were extracted with dichloromethane (30 cm³). The solutions were concentrated under reduced pressure and the addition of hexane led to the precipitation of orange solids which were filtered off, washed with hexane, and vacuum-dried. The complexes were recrystallized from dichloromethane–acetone.

Method B. A mixture of [Rh(C₅Me₅)(acac)(pz)] (**6**) (0.25 mmol) and [RhCl(L′)(Hpz)] [L′ = tfb (**7**) or cod (**8**)] (0.25 mmol) in acetone (30 cm³) was stirred for 23 h. The resulting solutions were partially concentrated under reduced pressure. Slow addition of hexane gave orange solids which were filtered off, washed with hexane, and vacuum-dried. The complexes were recrystallized from dichloromethane–acetone.

¹H N.m.r. spectrum for (**3**): δ_H (200 MHz, CDCl₃, standard SiMe₄), 1.63 (15 H, s, C₅Me₅), 3.74 (4 H, m, olefinic protons of tfb), 5.60 (2 H, m, methinic-protons of tfb), 6.19 [2 H, t, *J*(HH) 2, CH-4], 6.94 [2 H, d, *J*(HH) 2, CH], 7.62 p.p.m. [2 H, d, *J*(HH) 2 Hz, CH].

Reaction of [Rh(C₅Me₅)(acac)Cl] (**2**) *with* [Rh(cod)(Hdmpz)₂][ClO₄].—To a mixture of [Rh(cod)(Hdmpz)₂][ClO₄] (219.5 mg, 0.44 mmol) and [Rh(C₅Me₅)(acac)Cl] (162.5 mg, 0.44 mmol) in acetone (25 cm³) was added KOH (4.95 cm³, 0.088 mol dm⁻³, 0.44 mmol) in methanol. The resulting suspension was stirred for 70 h and vacuum-evaporated until dryness. The residue was extracted with dichloromethane (25 cm³). The solution was concentrated under reduced pressure and the orange precipitate which formed was filtered off, washed with acetone, and air-dried. This complex was characterized as [{Rh(cod)(dmpz)}₂] by comparison of its spectroscopic properties and analytical data with those of an authentic sample. Yield 60% (Found: C, 51.0; H, 6.2; N, 9.2. C₂₆H₃₆N₄Rh₂ requires C, 50.7; H, 5.7; N, 9.3%); δ_H (200 MHz, CDCl₃, standard SiMe₄), 2.05 (8 H, m, CH₂), 2.39 (12 H, s, CH₃), 2.73 (8 H, m, CH₂), 4.45 [8 H, m, CH (cod)], 5.46 p.p.m. [2 H, s, CH (dmpz)].

The resulting filtrate was partially concentrated under reduced pressure. Slow addition of diethyl ether gave a yellow microcrystalline solid which was filtered off, washed with diethyl ether, and air-dried. This complex was characterized as [Rh(C₅Me₅)(acac)(Hdmpz)][ClO₄] (**5**) by comparison of its spectroscopic properties and analytical data with those of complex (**5**) prepared by another method (see above).

Similar behaviour was observed using [Rh(tfb)(Hdmpz)₂]-[ClO₄].

Preparation of [(C₅Me₅)(pz)Rh(pz)₂Rh(tfb)] (**9**).—To a mixture of [Rh(C₅Me₅)(acac)(pz)] (**6**) (52.6 mg, 0.13 mmol) and [Rh(tfb)(Hpz)₂][ClO₄] (73.7 mg, 0.13 mmol) in acetone (25 cm³) was added KOH (1.5 cm³, 0.088 mol dm⁻³, 0.13 mmol) in methanol. The resulting suspension was stirred for 30 h and vacuum-evaporated until dryness. The residue was extracted with dichloromethane (25 cm³). The solution was concentrated under reduced pressure and addition of hexane led to the precipitation of an orange solid which was filtered off, washed with hexane, and vacuum-dried. The complex was recrystallized from dichloromethane–hexane. ¹H N.m.r. spectrum: δ_H (200 MHz, CDCl₃, standard SiMe₄), 1.69 (15 H, s, C₅Me₅), 3.72 (4 H, m, olefinic protons of tfb), 5.62 (2 H, m, methinic protons of tfb), 5.97 [1 H, br s, CH (pz)], 6.11 [2 H, br s, CH (pz)], 6.32 [1 H, br s, CH (pz)], 6.91 [2 H, br s, CH (pz)], 6.97 [2 H, br s, CH (pz)], 7.72 p.p.m. [1 H, br s, CH (pz)].

Preparation of [(C₅Me₅)ClRh(pz)₂Rh(CO)₂] (**10**).—Bubbling of carbon monoxide (atmospheric pressure, room temperature) for 45 min through dichloromethane (15 cm³) solutions of (**3**) or (**4**) (0.18 mmol) led to yellow solutions which were partially concentrated under reduced pressure. The slow addition of hexane gave complex (**10**) as a yellow microcrystalline solid which was filtered off washed with hexane, and air-dried. ¹H N.m.r. spectrum: δ_H (200 MHz, CDCl₃, standard SiMe₄), 1.55 (15 H, s, C₅Me₅), 6.22 (2 H, br s, CH), 7.53 (2 H, br s, CH), 7.64 p.p.m. (2 H, br s, CH).

Preparation of [(C₅Me₅)ClRh(pz)₂Rh(CO)(NCBuᵗ)] (**11**).—A mixture of (**10**) (138.6 mg, 0.25 mmol) and NCBuᵗ (20.5 mg, 0.25 mmol) in dichloromethane was stirred for 45 min. The resulting solution was partially concentrated under reduced pressure. Slow addition of hexane led to the precipitation of a yellow solid which was filtered off, washed with hexane, and vacuum-dried. The complex was recrystallized from dichloromethane–hexane.

Preparation of [(C₅Me₅)L″Rh(pz)₂Rh(tfb)][ClO₄] [L″ = py (**13**) or Hpz (**15**)].—To a solution of [(C₅Me₅)(Me₂-CO)Rh(pz)₂Rh(tfb)][ClO₄] [prepared *in situ* by treating (**3**) (0.19 mmol) with AgClO₄ (0.19 mmol) in acetone (15 cm³)] the appropriate ligand L″ (0.19 mmol) was added. The resulting yellow solution was stirred for 20 min, and then partially concentrated under reduced pressure. The addition of hexane gave yellow solids which were filtered off, washed with hexane, and vacuum-dried. The complexes were recrystallized from dichloromethane–hexane.

The complex [(C₅Me₅)(MeCN)Rh(pz)₂Rh(tfb)][ClO₄] (**14**) was prepared in a similar way but using MeCN as solvent.

Complex (**15**) has been also prepared by the following route: a mixture of [Rh(tfb)(Hpz)₂][ClO₄] (56.2 mg, 0.10 mmol) and (**6**) (43.1 mg, 0.11 mmol) in acetone was stirred for 30 h. The resulting solution was partially concentrated under reduced pressure. Slow addition of hexane gave a yellow solid which was filtered off, washed with hexane, and air-dried. The complex was characterized by comparison of its spectroscopic data with those of samples prepared from (**3**).

Preparation of [(C₅Me₅)(py)Rh(pz)₂Rh(CO)₂][ClO₄] (**16**).—Bubbling of carbon monoxide (atmospheric pressure, room temperature) for 45 min through a dichloromethane solution (15 cm³) of (**13**) (158.4 mg, 0.18 mmol) gave a yellow solution which was partially concentrated under reduced pressure. The slow addition of hexane led to the precipitation of a yellow solid which was filtered off, washed with hexane, and air-dried. The complex was recrystallized from dichloromethane–hexane.

This complex has also been prepared by the following route:

Table 3. Final atomic co-ordinates

Atom	X/a	Y/b	Z/c
Rh(1)	0.248 5(1)	0.242 4(1)	0.212 1(1)
Rh(2)	0.020 6(1)	0.168 9(1)	0.194 9(1)
Cl(1)	0.111 5(3)	0.291 4(4)	0.268 5(5)
Cl(2)	−0.055 6(4)	0.287 6(5)	0.103 5(5)
C(1)	0.550 7(14)	0.375 4(29)	0.284 1(25)
C(2)	0.618 0(18)	0.337 4(36)	0.335 2(19)
C(3)	0.619 0(15)	0.257 4(38)	0.380 3(18)
C(4)	0.546 5(18)	0.191 5(37)	0.371 2(22)
C(5)	0.387 9(14)	0.183 1(16)	0.309 9(25)
C(6)	0.319 7(14)	0.252 7(23)	0.342 9(15)
C(7)	0.320 6(13)	0.337 7(21)	0.302 1(21)
C(8)	0.396 3(14)	0.348 1(19)	0.226 7(19)
C(9)	0.373 2(16)	0.267 1(17)	0.155 2(18)
C(10)	0.368 7(14)	0.177 3(19)	0.200 5(21)
C(11)	0.475 3(12)	0.235 8(22)	0.323 0(16)
C(12)	0.479 2(14)	0.322 6(16)	0.277 1(19)
F(1)	0.555 2(11)	0.464 1(14)	0.244 9(18)
F(2)	0.690 6(11)	0.397 6(27)	0.346 1(17)
F(3)	0.686 6(11)	0.220 8(31)	0.429 4(16)
F(4)	0.545 1(13)	0.112 0(24)	0.412 7(17)
N(11)	0.195 6(10)	0.177 2(13)	0.092 3(14)
N(12)	0.108 4(10)	0.160 6(15)	0.078 5(14)
C(13)	0.096 0(17)	0.134 2(24)	−0.014 3(17)
C(14)	0.174 7(22)	0.121 3(29)	−0.060 1(24)
C(15)	0.232 8(12)	0.156 6(17)	0.007 1(15)
C(21)	−0.035 3(19)	0.118 9(19)	0.333 2(17)
C(22)	0.036 7(15)	0.062 3(16)	0.307 5(24)
C(23)	0.020 9(15)	0.016 7(14)	0.217 7(18)
C(24)	−0.062 6(15)	0.048 0(21)	0.184 5(19)
C(25)	−0.094 9(18)	0.109 8(20)	0.258 8(20)
C(26)	−0.042 6(32)	0.179 6(25)	0.425 6(25)
C(27)	0.111 0(28)	0.053 7(32)	0.377 1(39)
C(28)	0.074 5(35)	−0.055 3(26)	0.161 4(73)
C(29)	−0.109 6(34)	0.015 5(38)	0.097 9(33)
C(30)	−0.179 6(18)	0.153 1(36)	0.258 3(33)
Cl(3)	0.200 4(7)	0.471 3(9)	0.046 4(10)
Cl(4)	0.080 9(9)	0.431 2(11)	−0.111 3(12)
C(16)	0.120 6(25)	0.397 2(29)	0.004 0(49)

to a solution of $[(C_5Me_5)(Me_2CO)Rh(pz)_2Rh(CO)_2][ClO_4]$ [prepared *in situ* by treating (**10**) (52.1 mg, 0.092 mmol) with $AgClO_4$ (19.6 mg, 0.094 mmol) in acetone (15 cm³)] was added py (7.5 mg, 0.093 mmol). The resulting yellow solution was stirred for 20 min, and then partially concentrated under reduced pressure. The addition of hexane gave a yellow solid which was filtered off, washed with hexane, and air-dried. The complex was recrystallized from acetone–hexane. The complex was characterized by comparison of its spectroscopic and analytical data with those of complex (**16**) prepared from (**13**) above.

Preparation of $[(C_5Me_5)(Hpz)RhCl_2Rh(tfb)][ClO_4]$ (**17**).— To a solution of $[Rh(tfb)(Me_2CO)_x][ClO_4]$ [prepared *in situ* by treating $[\{RhCl(tfb)\}_2]$ (149.5 mg, 0.21 mmol) with $AgClO_4$ (86.4 mg, 0.42 mmol)] in acetone (20 cm³) was added $[Rh(C_5Me_5)Cl_2(Hpz)]$ (154.7 mg, 0.41 mmol). The resulting yellow solution was stirred for 30 min and then partially concentrated under reduced pressure. The addition of hexane gave a yellow solid which was filtered off, washed with hexane, and air-dried. The complex was recrystallized from dichloromethane–hexane.

Crystal-structure Determination of $[(C_5Me_5)ClRhCl(pz)Rh-(tfb)]\cdot CH_2Cl_2$ (**1**).—*Crystal data.* $C_{25}H_{24}Cl_2F_4N_2Rh_2\cdot CH_2Cl_2$, orthorhombic, $M = 790.1$, $a = 15.6383(10)$, $b =$

13.9301(9), $c = 13.5233(7)$ Å, $U = 2\,946.0(3)$ Å³, $D_c = 1.782$ g cm⁻³, $Z = 4$, $F(000) = 1\,560$, $\mu = 131.17$ cm⁻¹ (max., min. transmission factors in the range 0.451—0.133). The title compound was crystallized by vapour diffusion from dichloromethane–diethyl ether. An orange crystal of dimensions $0.38 \times 0.13 \times 0.06$ mm was used to collect 2 833 independent reflections ($\theta_{max.} = 65°$) on a Philips PW1100 diffractometer using graphite-monochromatized Cu-K_α radiation ($\lambda = 1.54178$ Å) and bisecting geometry ($\omega/2\theta$ mode, 1.5° scan width). Two reflections were measured every 90 min in order to check the crystal stability. The intensities decayed 27% in 29 h. Unit-cell parameters were refined by least squares from 2θ values $(2 < \theta < 45°)$ of 90 reflections. The structure was solved by Patterson methods and the refinement carried out by full-matrix least squares based on F_o. Of the 2 833 independent data, 2 122 were considered observed $[I > 4\sigma(I)]$ and used in the refinement. Refinement converged at $R = 0.070$ and $R' = 0.072$. Weights were chosen as $w = K/[f(F_o)][g\,(\sin \theta/\lambda)]$, first fitting ΔF *versus* F_o to obtain $f(F_o)$ and then $\Delta^2 F/f^2(F_o)$ *versus* $\sin \theta/\lambda$ to obtain the g functions; K is a scale factor to ensure $\langle w\Delta^2 \rangle \sim 1$. The highest final residual electron density was 1.3 e Å⁻³ near the Rh atoms. Final atomic co-ordinates for the non-hydrogen atoms are given in Table 3. Most of the calculations were performed with the X-RAY 76 system[31] and the scattering factors were taken from ref. 32.

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