New Methoxo-, Hydroxo-, and Pyrazolate-bridged Complexes of Rhodium(III). Crystal Structures of $[\{Rh(C_5Me_5)\}_2(mpz)(OMe)_2][ClO_4]$ (mpz = 3-methylpyrazolate), $[\{Rh(C_5Me_5)\}_2(Hdmpz)_2(OH)_2][BF_4]_2$ (Hdmpz = 3,5-dimethylpyrazole), and $[\{Rh(C_5Me_5)\}_2(pz)_2(OH)]$-$[ClO_4]$(pz = pyrazolate) †

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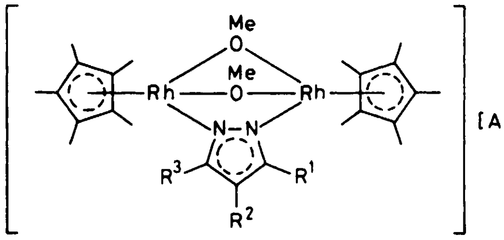
The tri-μ-hydroxo-dirhodium cation $[\{Rh(C_5Me_5)\}_2(OH)_3][ClO_4]$ (1) reacts with pyrazole type ligands (HL), in methanol, to give $[\{Rh(C_5Me_5)\}_2(L)(OMe)_2][ClO_4]$ complexes, containing one bridging pyrazolate ligand and two bridging methoxo-groups. Reactions of complex (1) with an equimolecular amount of pyrazole (Hpz), in the absence of methanol, gave mixtures of the μ-hydroxo-μ-pyrazolate complexes $[\{Rh(C_5Me_5)\}_2(pz)(OH)_2][ClO_4]$ and $[\{Rh(C_5Me_5)\}_2(pz)_2(OH)][ClO_4]$, but only the latter was isolated. Di-μ-hydroxo-complexes $[\{Rh(C_5Me_5)\}_2(HL)_2(OH)_2][A]_2$ [HL = 3,5-dimethylpyrazole (Hdmpz) or 3(5)-methyl,5(3)-phenylpyrazole (Hmppz); A = ClO_4 or BF_4] are obtained by addition of the appropriate pyrazole to $[\{Rh(C_5Me_5)\}_2(OH)_3][ClO_4]$ in acetone or methanol, or the pyrazole and base to the solvated complex $[Rh(C_5Me_5)(Me_2CO)_3][BF_4]_2$, in acetone. However, the μ-hydroxo-di-μ-pyrazolate complexes $[\{Rh(C_5Me_5)\}_2(L)_2(OH)][A]$ were obtained by addition of pyrazole itself and base to $[Rh(C_5Me_5)(Me_2CO)_3][A]_2$. Single-crystal *X*-ray structure determinations have been carried out on $[\{Rh(C_5Me_5)\}_2(mpz)(OMe)_2][ClO_4]$ (Hmpz = 3-methylpyrazole), $[\{Rh(C_5Me_5)\}_2(Hdmpz)_2(OH)_2][BF_4]_2$, and $[\{Rh(C_5Me_5)\}_2(pz)_2(OH)][ClO_4]$. They show two rhodium atoms per cation, each η^5-bonded to a C_5Me_5 group, bridged by the proposed methoxo, hydroxo, or pyrazolate ligands. The rhodium–rhodium distances are 3.200(1), 3.360(1), and 3.488(1) Å, respectively.

The synthesis and reactions of binuclear pentamethylcyclopentadienyl–rhodium(III) complexes have been extensively studied.[1] Although several hydroxo-bridged compounds have been reported,[2] all attempts to isolate related alkoxo-bridged derivatives have been unsuccessful.[3] The latter complexes have been invoked as probable intermediates in the preparation of various hydrido-bridged compounds.[4]

As a continuation of our studies on rhodium complexes containing azolate ligands,[5,6] we report new binuclear rhodium pyrazolate complexes containing the pentamethylcyclopentadienyl group and methoxo- or hydroxo-bridging ligands. These compounds are of interest because there are still relatively few stable and accessible alkoxo- or hydroxo-complexes of the platinum metals. Furthermore, there is an increasing interest in the inorganic chemistry of methanol.



	R¹	R²	R³	A
(2)	H	H	H	ClO_4
(3)	Me	H	H	ClO_4
(4)	Me	H	Me	ClO_4
(5)	Me	H	Br	ClO_4
(6)	H	Br	H	ClO_4
(8)	Me	H	H	BF_4

(7) HL = indazole, A = ClO_4

Results and Discussion

Methoxo-complexes.—The tri-μ-hydroxo-complex $[\{Rh(C_5Me_5)\}_2(OH)_3][ClO_4]$ (1) reacted with pyrazole type ligands (HL), in methanol, to give binuclear complexes of formula $[\{Rh(C_5Me_5)\}_2(L)(OMe)_2][ClO_4]$ [HL = pyrazole (Hpz), (2); 3-methylpyrazole (Hmpz), (3); 3,5-dimethylpyrazole (Hdmpz), (4); 3(5)-bromo-5(3)-methylpyrazole (Hbmpz), (5); 4-bromopyrazole (Hbpz), (6); or indazole (Hind), (7)]. Their i.r. spectra showed two strong bands at *ca.* 1 015 cm^{-1} [ν(CO)][7] and at *ca.* 490 cm^{-1} [ν(RhO)], indicative of the presence of methoxide groups. The ^1H n.m.r. spectrum of complex (4) consisted of four peaks at δ 1.63 (C_5Me_5), 2.93 (OMe), and 2.50 and 6.03 p.p.m. (dmpz) with intensities in the ratio 30 : 6 : 6 : 1. These data suggested that the cations contain one bridging pyrazolate and two bridging methoxide groups. The *X*-ray structure determination of complex (3) (see below) completely substantiates this conclusion. It is likely that the intermediate $[\{Rh(C_5Me_5)\}_2(OMe)_3]^+$, formed by the reaction of (1) with methanol,[3a] is protonated by a pyrazole ligand to form a 'methanol intermediate', which immediately reacts with the pyrazolate group to give complexes (2)—(7). The presence of

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† Di-μ-methoxo-μ-3-methylpyrazolato-N^1N^2-bis[(η-pentamethylcyclopentadienyl)rhodium(III)] perchlorate, di-μ-hydroxo-bis[(3,5-dimethylpyrazole-N^2)(η-pentamethylcyclopentadienyl)rhodium(III)] tetrafluoroborate, and μ-hydroxo-di-μ-pyrazolato-N^1N^2-bis-[(η-pentamethylcyclopentadienyl)rhodium(III)] perchorate.

Supplementary data available (No. SUP 23985, 81 pp.): H-atom coordinates, structure factors, thermal parameters, full bond distances and angles, torsion angles. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Table 1. Analytical, i.r. data, and yields for the methoxo-complexes

	Analysis [a] (%)				
Complex	C	H	N	I.r.[b] (cm^{-1})	Yield (%)
(2)	42.6	5.3	4.1	1 010vs,[c] 485vs [d]	75 [e]
	(42.6)	(5.6)	(4.0)		
(3)	43.5	5.9	4.0	1 015vs,[c] 490vs [d]	83,[e] 50 [f]
	(43.4)	(5.7)	(3.9)		
(4)	43.8	6.1	4.0	1 015vs,[c] 485vs [d]	75,[e] 62 [g]
	(44.2)	(5.9)	(3.8)		
(5)	39.4	5.5	3.3	1 015vs,[c] 495vs [d]	80,[e] 51 [f]
	(39.1)	(5.0)	(3.5)		
(6)	37.8	4.8	3.9	1 010vs,[c] 485vs [d]	83 [e]
	(38.3)	(4.9)	(3.6)		
(7)	45.7	5.8	3.7	1 010vs,[c] 485vs [d]	68 [e]
	(46.1)	(5.5)	(3.7)		
(8)	44.6	6.3	4.2	1 010vs,[c] 495vs [d]	50 [h]
	(44.2)	(5.8)	(4.0)		

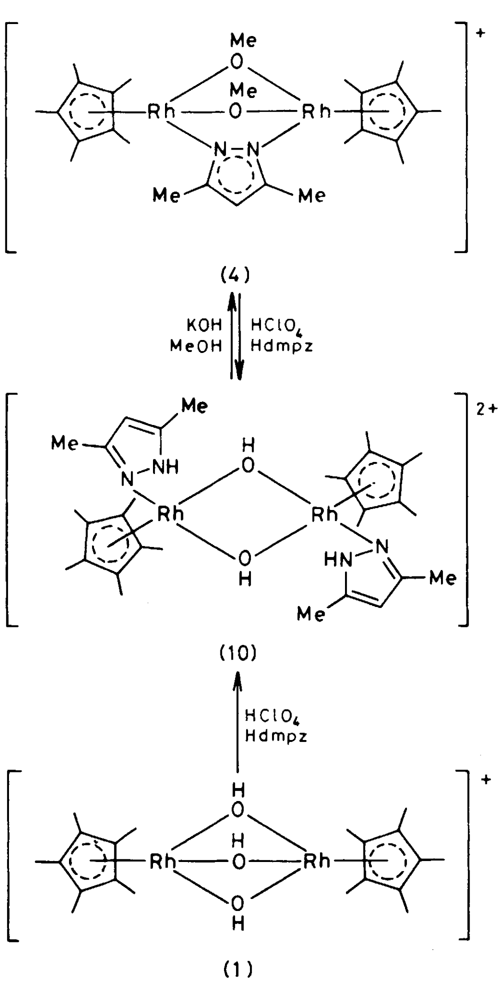
[a] Calculated values are given in parentheses. [b] Nujol mulls. [c] ν(CO) for the methoxo-groups. [d] ν(RhO). [e] Prepared from (1). [f] Prepared from (9a). [g] Prepared from (10). [h] Prepared from (9b).

the bridging pyrazolate group seems to be required in order to stabilize the methoxo-bridges.

An alternative route, which we have used for the synthesis of complexes (3), (5), and $[\{Rh(C_5Me_5)\}_2(mpz)(OMe)_2][BF_4]$ (8), involved the reaction of the solvated complexes $[Rh(C_5Me_5)(Me_2CO)_3][A]_2$ [A = ClO_4 (9a) or BF_4 (9b)] with Hmpz or Hbmpz and triethylamine in acetone, followed by addition of methanol.

Elemental analysis and representative properties of these perchlorate complexes are listed in Table 1.

Hydroxo-complexes.—Interestingly, the addition of perchloric acid to complexes (4) or (1), in the presence of Hdmpz, produced $[\{Rh(C_5Me_5)\}_2(Hdmpz)_2(OH)_2][ClO_4]_2$ (10).* The i.r. spectrum showed two bands at 3 590 and 3 300 cm^{-1}, assigned to ν(OH) and ν(NH) respectively. Furthermore the ^1H n.m.r. spectrum showed the presence of Hdmpz as a co-ordinated neutral ligand [δ 2.48 (12 H), 6.16 (2 H), and 11.69 p.p.m. (NH)]. The reaction (4) ⟶ (10) was reversed by adding KOH in MeOH to a methanolic solution of complex (10). No further changes were observed by adding $HClO_4$ or KOH to complex (10). These data and an *X*-ray structural analysis of the analogous complex $[\{Rh(C_5Me_5)\}_2(Hdmpz)_2(OH)_2][BF_4]_2$ (11) confirmed the double hydroxo-bridged formulation (Scheme 1).



Scheme 1.

Complex (10) was also formed by reacting the tri-μ-hydroxo-complex (1) with Hdmpz (1 : 2 molar ratio) in acetone in the absence of $HClO_4$. However, when the reaction was carried out with Hpz (1 : 2) or Hmpz (1 : 3), binuclear complexes of formula $[\{Rh(C_5Me_5)\}_2(L)_2(OH)][ClO_4]$ [HL = Hpz (12) or Hmpz (13)] were obtained. The i.r. spectra of these complexes showed one band at *ca.* 3 590 cm^{-1} due to ν(OH) and a ν(RhO) band at *ca.* 510 cm^{-1}. The ^1H n.m.r. spectrum of complex (12) showed the presence of one pyrazolate anion {δ 7.43 [4 H, d, *J*(HH) 2.0 Hz] and 6.19 (2 H, t)} per C_5Me_5 group [δ 1.75 (30 H, s)]. All these spectroscopic data, together with an *X*-ray structural determination of complex (12), supported the triple-bridged formulation involving two *exo*-bidentate pyrazolate ligands and one bridging hydroxo-group. Presumably these complexes are formed by protonation by the weak acids HL of the hydroxo-bridges of (1), to form 'aqua-intermediates', which react with L$^-$ to give the pyrazolate complexes. Attempts to obtain the triple pyrazolate-bridged complex, $[\{Rh(C_5Me_5)\}_2(pz)_3]^+$, have been unsuccessful, but the existence of the intermediate $[\{Rh(C_5Me_5)\}_2(pz)$-

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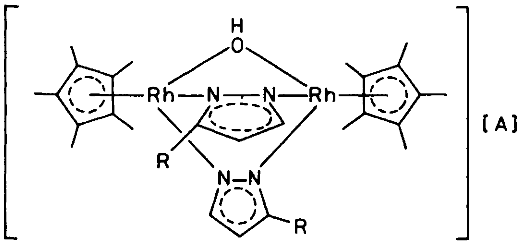
* The formation of (10) from (1) may be compared to the formation of double hydroxo-bridged rhodium(III) complexes by protonation with perchloric acid of $[\{Rh(tacn)\}_2(OH)_3]^{3+}$ (tacn = 1,4,7-triazacyclononane).[8]

Table 2. Crystal structure determinations for complexes (3), (11), and (12)

Complex	$[\{Rh(C_5Me_5)\}_2(mpz)(OMe)_2][ClO_4]$	$[\{Rh(C_5Me_5)\}_2(Hdmpz)_2(OH)_2][BF_4]_2$	$[\{Rh(C_5Me_5)\}_2(pz)_2(OH)][ClO_4]$
Formula	$C_{26}H_{41}ClN_2O_6Rh_2$	$C_{30}H_{48}B_2F_8N_4O_2Rh_2$	$C_{26}H_{37}ClN_4O_5Rh_2$
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/n$	$C2/c$
a/Å	22.366(3)	11.7094(7)	25.425 0(13)
b/Å	11.085(1)	15.612 8(12)	16.343 0(5)
c/Å	12.252(1)	10.172 0(7)	16.448 0(7)
β/°	107.59(1)	92.44(1)	120.53(1)
U/Å^3	2 895.6(6)	1 857.9(2)	5 887.0(4)
Z	4	2	8
D_c/g cm^{-3}	1.649	1.566	1.640
F(000)	1 464	888	2 944
μ/cm^{-1}	106.47	79.93	104.79
Crystal size (max.—min.)/mm	0.34—0.07	0.24—0.19	0.45—0.16
$\theta_{max.}$/°	65	65	65
Reflections measured	2 551	3 320	4 379
Unique data [$I > n\sigma(I)$]	2 297 (n = 3)	3 003 (n = 2)	3 600 (n = 2)
Refined parameters	212	337	502
R^a	0.072	0.048	0.061
R'^b	0.079	0.055	0.070

^{a} $R = \Sigma|\Delta|/\Sigma|F_o|$. ^{b} $R' = (\Sigma w\Delta^2/\Sigma wF^2)^{\frac{1}{2}}$; $\Delta = |F_o| - |F_c|$, observed reflections only.



	R	A
(12)	H	ClO_4
(13)	Me	ClO_4
(14)	H	BF_4

$$\begin{array}{c} [\{Rh(C_5Me_5)\}_2(OH)_3]^+ + 3Hpz \\ (1) \\ \Big\downarrow{k_1} \\ [\{Rh(C_5Me_5)\}_2(pz)(OH)_2]^+ + 2Hpz + H_2O \\ \Big\downarrow{k_2} \\ [\{Rh(C_5Me_5)\}_2(pz)_2(OH)]^+ + Hpz + 2H_2O \\ (12) \\ \Big\downarrow{k_3} \\ [\{Rh(C_5Me_5)\}_2(pz)_3]^+ \end{array}$$

Scheme 2.

$(OH)_2][ClO_4]$, related to the methoxo-bridged complex (2), was inferred from ^{1}H n.m.r. spectroscopy. Thus the ^{1}H n.m.r. spectrum of an equimolar mixture of complex (1) and Hpz in $CDCl_3$ showed the presence of only (12) and $[\{Rh(C_5Me_5)\}_2(pz)(OH)_2]^+$ {δ 7.86 [2 H, td, J(RhH) 8.5, J(HH) 2.1], 6.48 [1 H, t, J(HH) 2.1 Hz], 2.88 (2 H, br, s), 1.64 (30 H, s)}, together with unreacted starting complex (1), in the ratio 18 : 64 : 18, as well as the formation of water. The addition of more pyrazole caused the complete formation of (12). All these observations can be accounted for by assuming that the rate of formation of $[\{Rh(C_5Me_5)\}_2(pz)(OH)_2]^+$, k_1, is slower than the rate of formation of the bis(pyrazolate) complex (12) from $[\{Rh(C_5Me_5)\}_2(pz)(OH)_2]^+$, k_2, and that the rate constant k_3 for the subsequent reaction is very small (Scheme 2).

These double- or triple-bridged complexes can be also prepared by reacting $[Rh(C_5Me_5)(Me_2CO)_3][A]_2$ [A = ClO_4 (9a), BF_4 (9b)] with pyrazole ligands, in acetone, in the presence of base (potassium hydroxide or triethylamine). The triple-bridged complexes (12) and $[\{Rh(C_5Me_5)\}_2(pz)_2(OH)][BF_4]$ (14) were obtained with pyrazole,* but the double hydroxo-bridged complexes (11) and $[\{Rh(C_5Me_5)\}_2(Hmppz)_2(OH)_2][BF_4]_2$ (15) [Hmppz = 3(5)-methyl-5(3)-phenylpyrazole] were obtained with Hdmpz and Hmppz. The steric properties of the pyrazole ligands seem to play a decisive role in directing the reaction. Thus, methyl (or phenyl) groups on the 3,5-substituted pyrazole ligands favour the formation of double hydroxo-bridged complexes.

In summary, from the data so far available it seems that complexes with only one bridging pyrazolate and two OMe are formed for all systems, but complexes with two bridging pyrazolates and one OH are preferentially formed when the pyrazoles are unsubstituted or have only a single 3-methyl substituent. On the other hand, 3,5-dimethyl (and similar) pyrazoles go into terminal positions as in the di-μ-hydroxo-complexes (10) or (11). Further extensions of this work are under study.

Molecular Structures of $[\{Rh(C_5Me_5)\}_2(mpz)(OMe)_2][ClO_4]$ (3), $[\{Rh(C_5Me_5)\}_2(Hdmpz)_2(OH)_2][BF_4]_2$ (11), *and* $[\{Rh(C_5Me_5)\}_2(pz)_2(OH)][ClO_4]$ (12).—The structures of the three cations are illustrated in Figures 1—3, in each case with the atom labelling used in the corresponding Tables. Crystal data are given in Table 2. Selected bond lengths and angles (together with the estimated standard deviations) are listed in Tables 3—5.

Compound (3) presents an internal disorder, giving rise to a crystallographic two-fold axis relating the two halves of the cation and passing through the mpz ligand, which produces an averaged geometry. Compound (11) has an internal

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* Complexes (12) or (14) are prepared in good yield from the solvated complexes (9a) or (9b) by using different Rh : Hpz or Hpz : base (NEt_3 or KOH) ratios.

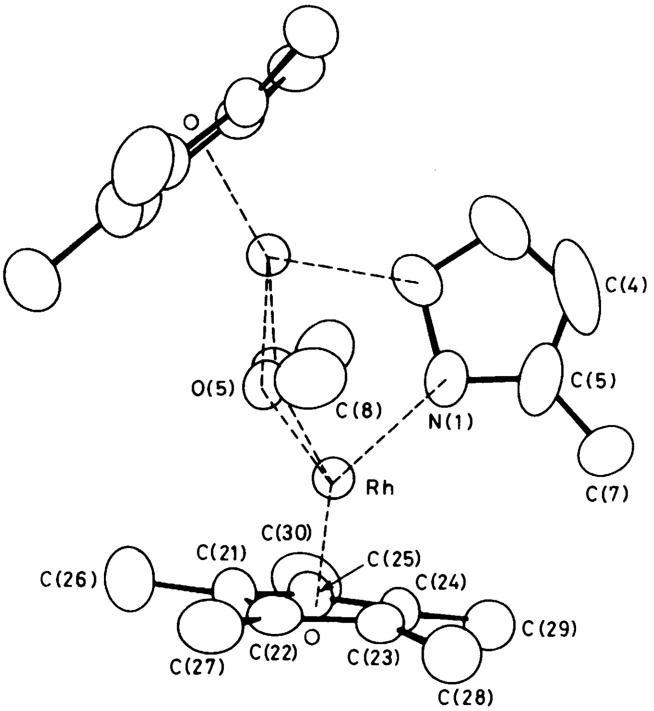

Figure 1. View of the cation $[\{Rh(C_5Me_5)\}_2(mpz)(OMe)_2]^+$ with the atomic numbering scheme. The C atom symmetry-related to C(7) has been omitted to match the chemical formula (see text)

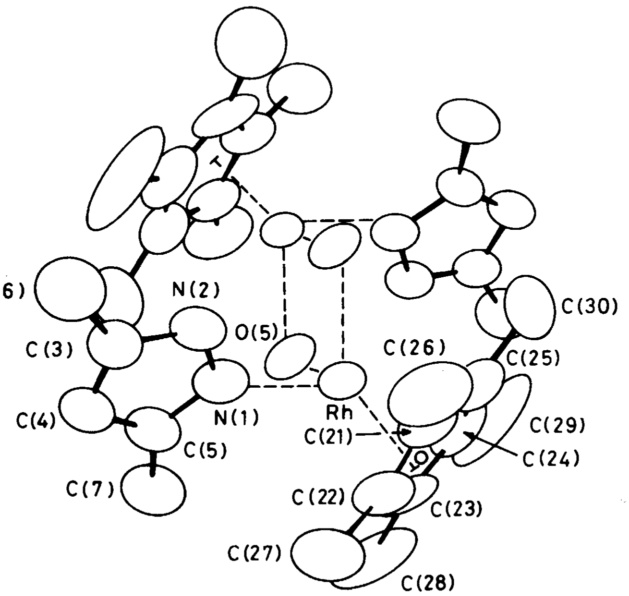

Figure 2. View of the cation $[\{Rh(C_5Me_5)\}_2(Hdmpz)_2(OH)_2]^{2+}$ with the atomic numbering scheme

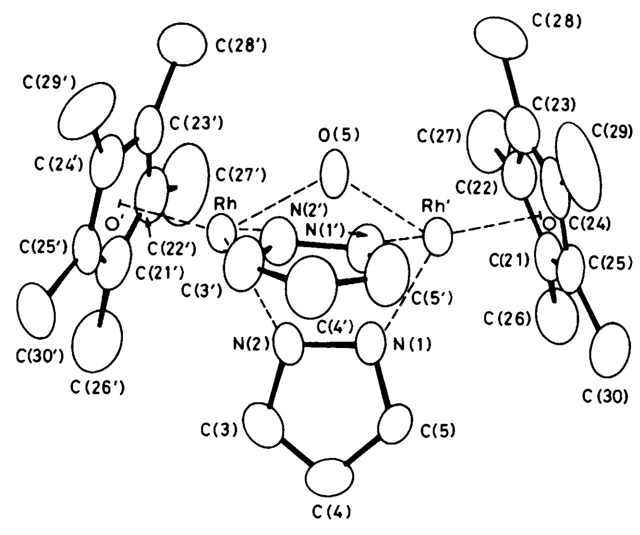

Figure 3. View of the cation $[\{Rh(C_5Me_5)\}_2(pz)_2(OH)]^+$ with the atomic numbering scheme

Table 3. Selected bond distances (Å) and bond angles (°) for $[\{Rh(C_5Me_5)\}_2(mpz)(OMe)_2][ClO_4]$ (3) *

Rh–N(1)	2.082(7)	○–Rh–O(5)	129.3(2)
Rh–O(5)	2.098(5)	○–Rh–O(5′)	128.9(2)
Rh–O(5′)	2.100(6)	○–Rh–N(2)	137.7(2)
Rh–○	1.773(4)	O(5)–Rh–O(5′)	76.0(2)
Rh–C(21)	2.121(9)	O(5)–Rh–N(1)	81.6(3)
Rh–C(22)	2.154(9)	O(5′)–Rh–N(1)	81.5(2)
Rh–C(23)	2.158(8)	Rh–N(1)–N(2)	115.6(5)
Rh–C(24)	2.162(8)	Rh–N(1)–C(5)	138.3(6)
Rh–C(25)	2.160(9)	Rh–O(5)–Rh′	99.3(3)
O(5)–C(8)	1.398(14)	Rh–O(5)–C(8)	116.4(6)

* N(1) and N(2), C(3) and C(5), and C(6) and C(7) are related by the two-fold axis; ○ represents the centroid of the C_5 independent ring.

Table 4. Selected bond distances (Å) and bond angles (°) for $[\{Rh(C_5Me_5)\}_2(Hdmpz)_2(OH)_2][BF_4]_2$ (11) *

Rh–N(1)	2.120(5)	○–Rh–O(5)	130.9(3)
Rh–O(5)	2.186(4)	○–Rh–O(5′)	128.6(3)
Rh–O(5′)	2.172(6)	○–Rh–N(1)	128.1(3)
Rh–○	1.770(3)	O(5)–Rh–N(1)	87.5(2)
Rh–C(21)	2.122(6)	O(5)–Rh–O(5′)	79.0(2)
Rh–C(22)	2.157(6)	N(1)–Rh–O(5′)	86.2(2)
Rh–C(23)	2.134(7)	Rh–N(1)–N(2)	119.3(4)
Rh–C(24)	2.137(9)	Rh–N(1)–C(5)	134.6(4)
Rh–C(25)	2.151(8)		

* ○ Represents the centroid of the C_5 independent ring.

crystallographic centre of symmetry, again relating the two halves of the cation, but this does not seem to be a result of any kind of disorder. In compound (12) the whole cation is crystallographically independent.

The three complex cations are composed of two rhodiums, each η^5-bonded to a C_5Me_5 ligand, and separated by 3.200(1), 3.360(1) and 3.488(1) Å, in compounds (3), (11), and (12) respectively. These values exclude any significant metal–metal interactions.[2c] The mean Rh–C(ring) distances are very similar for the three cations (3), (11), and (12) at 2.151(4), 2.140(3), and 2.153(3) and 2.152(3) Å respectively. These values are in the range of those found in $Rh^{III}(C_5Me_5)$ complexes.[1] The distances of the metal atom to the least-squares plane through the C_5 rings are 1.773(4) Å for (3), 1.770(3) Å for (11), and 1.775(3) and 1.781(3) Å for (12).

The two rhodiums in complex (3) are bridged by two methoxo-groups, Rh–O 2.100(6) Å, and one pyrazolate group, Rh–N 2.082(7) Å. The angle Rh–O–Rh′, 99.3(3)°, falls between that of the methoxo-bridged palladium(II) complex $[Pd_2(hfacac)_2(OMe)_2]$ (hfacac = hexafluoroacetylacetonate),[9] 97.1°, and the related platinum(II) complex $[Pt_2(C_8H_{12}OMe)_2(OMe)_2]$ ($C_8H_{12}OMe$ = 8-methoxycyclo-

Table 5. Selected bond distances (Å) and bond angles (°) for $[\{Rh(C_5Me_5)\}_2(pz)_2(OH)][ClO_4]$ (12) *

Rh–O(5)	2.110(4)	Rh′–O(5)	2.104(4)
Rh–N(1)	2.095(6)	Rh′–N(2)	2.088(7)
Rh–N(1′)	2.089(7)	Rh′–N(2′)	2.098(6)
Rh–O	1.775(3)	Rh′–O′	1.781(3)
Rh–C(21)	2.163(8)	Rh′–C(21′)	2.160(7)
Rh–C(22)	2.139(8)	Rh′–C(22′)	2.145(9)
Rh–C(23)	2.138(9)	Rh′–C(23′)	2.141(8)
Rh–C(24)	2.167(7)	Rh′–C(24′)	2.167(8)
Rh–C(25)	2.149(6)	Rh′–C(25′)	2.150(6)
C(21)–C(22)	1.412(12)	C(21′)–C(22′)	1.385(13)
C(22)–C(23)	1.457(16)	C(22′)–C(23′)	1.465(16)
C(23)–C(24)	1.397(14)	C(23′)–C(24′)	1.408(13)
C(24)–C(25)	1.443(14)	C(24′)–C(25′)	1.433(12)
C(25)–C(21)	1.434(12)	C(25′)–C(21′)	1.415(14)
O–Rh–O(5)	124.7(2)	O′–Rh′–O(5)	125.0(2)
O–Rh–N(1)	132.6(2)	O′–Rh′–N(2)	132.5(2)
O–Rh–N(1′)	132.9(2)	O′–Rh′–N(2′)	132.5(2)
O(5)–Rh–N(1)	83.1(2)	O(5)–Rh′–N(2)	84.0(2)
O(5)–Rh–N(1′)	84.3(2)	O(5)–Rh′–N(2′)	83.8(2)
N(1)–Rh–N(1′)	81.5(2)	N(2)–Rh′–N(2′)	81.6(2)
Rh–N(1)–N(2)	119.8(4)	Rh′–N(2′)–N(1′)	119.5(5)
Rh–N(1)–C(5)	107.8(6)	Rh′–N(2′)–C(3′)	130.5(6)
Rh′–N(2)–N(1)	121.3(4)	Rh′–N(1′)–N(2′)	121.4(5)
Rh′–N(2)–C(3)	107.1(6)	Rh′–N(1′)–C(5′)	131.1(5)

* O, O′ Represent the centroids of the C_5 rings.

oct-4-en-1-yl),[10] 103.7°, the two previously reported structures of binuclear bridged methoxide complexes of the platinum group metals. The methyls of the bridging methoxo-groups adopt a relative *syn endo* configuration, probably to minimize the repulsions with the C_5Me_5 methyls.

The cation of complex (11) has the two $(\eta^5-C_5Me_5)Rh(Hdmpz)$ fragments mutually coupled *via* the hydroxo-groups [Rh–O 2.186(4) and 2.172(6) Å, Rh–O–Rh′ 101.0(2)°]. The mean value of the Rh–O distances is longer than that found (2.041 Å) for the related di-μ-hydroxo-complex $[Rh_2(tacn)_2(OH)_2(H_2O)_2][ClO_4]_4\cdot4H_2O$.[8] In complex (11), this difference may be due to the interligand repulsions between the methyl groups of each co-ordinated 3,5-dimethylpyrazole and the methyl groups of the C_5Me_5 ring co-ordinated to the other rhodium atom. The Rh–O–Rh′ angle is very similar to that found in the related complex $[Rh_2(tacn)_2(OH)_2(H_2O)_2][ClO_4]_4\cdot4H_2O$.[8]

The rhodiums in complex (12) are bridged by one hydroxo-group [Rh–O 2.110(4) and 2.104(4) Å, Rh–O(5)–Rh′ 111.7(2)°] and by two pyrazolate groups [Rh–N 2.089(7), 2.095(6), 2.098(6), and 2.088(7) Å]. The Rh–O bond distances are very similar to those found in the tri-μ-hydroxo-complex $[\{Rh(C_5Me_5)\}_2(OH)_3]OH\cdot11H_2O$,[2c] and the Rh–N bond distances are slightly shorter than those reported for the 4,5-bis(trifluoromethyl)-1,2,3-triazol-3-ato complex $[Rh_2(C_5Me_5)_2\{N_3C(CF_3)C(CF_3)\}_3(N_3)]$.[11] The value of the Rh–O–Rh′ angle is indicative of a low basicity for the hydroxo-bridge.[2c] As a consequence of the asymmetry of co-ordination about the metal, both C_5Me_5 rings show C–C distances (Table 5) suggesting some degree of localization into an 'ene-enyl' form, previously observed in $Rh^{III}(C_5Me_5)$ complexes.[12]

The different sizes of the bridging groups in complexes (3) and (12) hold the two C_5Me_5 rings in each complex so that they are not parallel but inclined to one another at angles of 47.0(8) and 43.3(3)° respectively. Obviously, the two rings in complex (11) are parallel. In complexes (11) and (12) the C_5Me_5 rings are staggered by 36 and 17.6(3)° respectively, while in complex (3) they are just eclipsed.

Experimental

Infrared spectra were recorded on a Perkin-Elmer 577 spectrophotometer (range 4 000—200 cm^{-1}) using Nujol mulls between polyethylene sheets. The C, H, and N analyses were carried out with a Perkin-Elmer 240B microanalyzer. ^1H N.m.r. spectra were recorded in $CDCl_3$ solutions at room temperature on a Varian XL 200 spectrometer, using $SiMe_4$ as internal standard. Solvents were dried and distilled before use.

The perchlorate complexes (1) and (9a), and the tetrafluoroborate analogue (9b), were prepared by modifying reported procedures.[2a,13]

Preparation of the Methoxo-complexes (2)—(7) *from* (1).—A mixture of (1) (0.10 mmol), and the corresponding pyrazole derivatives HL (0.10 mmol) in methanol (30 cm^3) was stirred for 30 min. The orange complexes (2), (6), and (7) precipitated spontaneously, whilst the complexes (3)—(5), also orange, were isolated after partial evaporation of the solvent, and subsequent addition of diethyl ether. Recrystallization from dichloromethane–diethyl ether led to red crystals in all cases.

Preparation of the Methoxo-complexes (3) *and* (5) *from* (9a).—To a solution of $[Rh(C_5Me_5)(Me_2CO)_3][ClO_4]_2$ (9a) [prepared *in situ* by treating $[\{Rh(C_5Me_5)\}_2Cl_4]$ [14] (0.10 mmol) with $Ag[ClO_4]$ (0.40 mmol) in acetone (20 cm^3)], the appropriate ligand HL (0.20 mmol) and NEt_3 (0.20 mmol) were added. The resulting solution was stirred for 1 h and vacuum-evaporated to dryness. The residue was extracted with dichloromethane (15 cm^3). The solution was concentrated under reduced pressure until dryness. The red oily residue was dissolved in methanol (20 cm^3) and stirred for 5 min. Addition of diethyl ether gave orange solids, which were filtered off, washed with diethyl ether and air-dried.

The complexes were characterized by comparison of their spectroscopic properties with those of authentic samples prepared from (1).

Complex (8) was also prepared according to this procedure from (9b).

Preparation of the Hydroxo-complex (10) *from* (4).—A mixture of (4) (36.7 mg, 0.05 mmol), Hdmpz (4.8 mg, 0.05 mmol) and an aqueous solution of $HClO_4$ (5.4 μl, 60% w/w, 0.05 mmol) in acetone (20 cm^3) was stirred for 20 min. The orange-yellow complex was isolated by partial vacuum-evaporation and subsequent addition of diethyl ether. Yield 72% (Found: C, 40.2; H, 5.6; N, 6.4. $C_{30}H_{48}Cl_2N_4O_{10}Rh_2$ requires C, 40.0; H, 5.4; N, 6.2%); ν(OH) 3 590vs, ν(NH) 3 300vs, ν(RhO) 480vs cm^{-1} (Nujol); δ_H (200 MHz; solvent $CDCl_3$, standard $SiMe_4$) 1.24 (30 H, s, 2 C_5Me_5), 2.48 (12 H, s, 4 CH_3), 6.16 (2 H, s, 2 CH), 11.69 p.p.m. (br, s, NH).

Preparation of the Hydroxo-complex (10) *from* (1).—A mixture of (1) (150.2 mg, 0.24 mmol), Hdmpz (46.0 mg, 0.48 mmol) and $HClO_4$ (26.1 μl, 60% w/w, 0.24 mmol) in acetone (20 cm^3) was stirred for 1 h. The orange-yellow complex (10) precipitated spontaneously and was isolated after partial evaporation and addition of diethyl ether. Yield 79%.

The complex was characterized by comparison of its spectroscopic data with those reported in the preceding preparation.

Preparation of the Methoxo-complex (4) *from* (10).—To a solution of (10) (54.5 mg, 0.06 mmol) in methanol (20 cm^3), KOH (0.6 cm^3, 0.098 mol dm^{-3}, 0.06 mmol) in the same solvent was added. The resulting solution was stirred for 1 h and vacuum-evaporated until dryness. The residue was extracted with dichloromethane (15 cm^3). The solution was

Table 6. Non-hydrogen atomic co-ordinates for compound (3)

Atom *	*X*/*a*	*Y*/*b*	*Z*/*c*
Rh	−0.069 41(2)	0.222 04(5)	0.162 08(5)
N(1)	−0.030 5(4)	0.052 6(6)	0.211 7(6)
C(4)	0	−0.136 0(12)	0.25
O(5)	0.023 1(3)	−0.260 1(5)	0.165 2(5)
C(5)	−0.047 5(6)	0.062 9(9)	0.194 8(9)
C(7)	−0.102 1(9)	−0.116 7(19)	0.137 4(16)
C(8)	0.044 9(6)	0.200 1(11)	0.084 4(9)
C(21)	−0.116 0(4)	0.380 8(8)	0.084 0(9)
C(22)	−0.150 7(4)	0.330 3(9)	0.153 4(8)
C(23)	−0.170 4(4)	0.211 4(8)	0.114 3(8)
C(24)	−0.150 2(4)	0.191 7(7)	0.014 4(7)
C(25)	−0.116 7(4)	0.297 2(7)	−0.004 3(8)
C(26)	−0.086 1(7)	0.504 5(10)	0.097 9(14)
C(27)	−0.162 1(5)	0.393 5(12)	0.252 4(11)
C(28)	−0.210 0(5)	0.132 2(11)	0.159 3(12)
C(29)	−0.167 5(8)	0.087 7(12)	−0.065 7(12)
C(30)	−0.0909(6)	0.313 4(12)	−0.102 5(9)
Cl	0.25	0.25	0
O(1)	0.262 0(18)	0.162 7(39)	0.091 0(36)
O(2)	0.305 8(27)	0.277 9(47)	−0.010 2(49)
O(3)	0.228 5(26)	0.201 4(53)	−0.124 3(46)
O(4)	0.234 6(15)	0.363 1(30)	0.017 4(31)

* C(7), O(1), O(2), O(3), and O(4) have population 0.5.

Table 7. Non-hydrogen atomic co-ordinates for compound (11)

Atom *	*X*/*a*	*Y*/*b*	*Z*/*c*
Rh	0.081 46(3)	0.081 82(2)	0.056 20(4)
N(1)	0.151 4(4)	0.082 2(3)	−0.132 7(5)
N(2)	0.243 7(4)	0.032 7(3)	−0.154 7(6)
C(3)	0.286 5(5)	0.048 5(4)	−0.272 4(6)
C(4)	0.221 8(5)	0.112 0(4)	−0.327 4(7)
O(5)	−0.084 8(3)	0.056 8(3)	−0.042 2(4)
C(5)	0.138 5(5)	0.131 8(4)	−0.239 3(6)
C(6)	0.387 5(8)	−0.000 5(6)	−0.318 7(10)
C(7)	0.044 5(7)	0.196 5(6)	−0.251 8(11)
C(21)	0.215 4(5)	0.121 7(4)	0.189 0(7)
C(22)	0.172 1(5)	0.194 9(4)	0.124 3(7)
C(23)	0.053 9(6)	0.201 9(4)	0.150 3(8)
C(24)	0.028 7(7)	0.133 0(6)	0.239 1(8)
C(25)	0.128 5(8)	0.085 4(5)	0.262 5(8)
C(26)	0.338 4(8)	0.092 5(7)	0.192 7(13)
C(27)	0.242 2(10)	0.253 1(6)	0.040 6(12)
C(28)	−0.024 6(10)	0.271 1(7)	0.100 1(16)
C(29)	−0.085 8(15)	0.124 8(15)	0.292 6(21)
C(30)	0.138 3(20)	0.007 2(9)	0.345 8(12)
B	−0.358 3(9)	0.166 1(6)	−0.067 8(11)
F(1)	−0.327 9(10)	0.122 8(6)	0.039 4(10)
F(1′)	−0.256 1(31)	0.178 0(60)	−0.123 2(72)
F(2)	−0.343 7(24)	0.130 4(10)	−0.187 3(16)
F(2′)	−0.415 1(53)	0.234 0(26)	−0.051 1(21)
F(3)	−0.472 1(14)	0.188 1(18)	−0.071 8(26)
F(3′)	−0.348 7(43)	0.104 1(26)	−0.029 8(43)
F(4)	−0.303 9(25)	0.239 1(9)	−0.061 0(16)
F(4′)	−0.409 0(101)	0.121 2(26)	−0.144 0(79)

* F atoms have population 0.57(4) and F′ have population 1 − 0.57(4).

Table 8. Non-hydrogen atomic co-ordinates for compound (12)

Atom *	*X*/*a*	*Y*/*b*	*Z*/*c*
Rh	0.167 19(1)	0.210 60(2)	0.156 98(2)
N(1)	0.192 1(2)	0.136 1(3)	0.274 8(4)
N(2)	0.251 4(2)	0.131 9(4)	0.344 7(4)
C(3)	0.257 1(3)	0.065 7(5)	0.396 6(5)
C(4)	0.202 1(4)	0.026 7(5)	0.362 0(5)
C(5)	0.162 7(3)	0.073 5(5)	0.285 7(5)
C(21)	0.073 6(3)	0.236 0(5)	0.116 8(5)
C(22)	0.103 7(3)	0.309 3(5)	0.119 2(5)
C(23)	0.123 2(4)	0.302 0(6)	0.050 2(6)
C(24)	0.104 1(4)	0.225 6(7)	0.007 0(5)
C(25)	0.075 2(3)	0.181 6(5)	0.049 8(4)
C(26)	0.043 8(5)	0.222 5(8)	0.172 9(7)
C(27)	0.114 0(6)	0.382 9(6)	0.182 3(8)
C(28)	0.154 2(7)	0.369 4(12)	0.027 6(16)
C(29)	0.111 0(7)	0.193 1(13)	−0.073 8(6)
C(30)	0.045 5(5)	0.099 3(6)	0.023 5(7)
O(5)	0.241 8(2)	0.281 8(3)	0.255 2(3)
Rh′	0.317 38(1)	0.208 53(2)	0.345 46(2)
N(1′)	0.233 9(2)	0.140 6(4)	0.151 2(4)
N(2′)	0.293 4(3)	0.143 4(4)	0.221 4(4)
C(3′)	0.323 9(4)	0.085 4(5)	0.204 1(5)
C(4′)	0.284 0(4)	0.043 7(6)	0.122 7(6)
C(5′)	0.229 2(4)	0.080 4(5)	0.092 3(5)
C(21′)	0.381 3(3)	0.212 3(6)	0.495 6(5)
C(22′)	0.360 8(4)	0.290 8(5)	0.463 1(6)
C(23′)	0.379 9(3)	0.309 3(5)	0.394 8(6)
C(24′)	0.410 7(3)	0.240 3(6)	0.388 1(5)
C(25′)	0.410 1(3)	0.178 2(5)	0.449 1(5)
C(26′)	0.375 3(7)	0.170 4(13)	0.573 7(7)
C(27′)	0.329 0(6)	0.349 5(10)	0.494 8(10)
C(28′)	0.366 8(5)	0.389 5(6)	0.341 9(10)
C(29′)	0.439 3(5)	0.235 1(10)	0.328 7(8)
C(30′)	0.441 3(5)	0.097 2(6)	0.468 6(9)
Cl(1)	0	0.510 4(3)	0.25
O(1)	0	0.420 6(12)	0.25
O(2A)	0.042 6(12)	0.553 0(13)	0.315 9(16)
O(2B)	0.007 7(10)	0.529 9(12)	0.175 3(13)
O(2C)	−0.059 4(11)	0.512 0(10)	0.216 4(36)
Cl(2)	0	−0.008 7(2)	0.25
O(3)	−0.036 2(6)	−0.054 1(11)	0.269 7(12)
O(4)	0.035 5(11)	0.041 4(11)	0.326 4(12)

* O(2A), O(2B), and O(2C) have population 0.5.

concentrated under reduced pressure and addition of diethyl ether led to the precipitation of an orange solid which was filtered off, washed with diethyl ether and air-dried. Yield 62%.

Characterization of the complex was carried out by comparison of its spectroscopic properties with those of an authentic sample prepared from (1).

Preparation of the Hydroxo-complexes (12) *and* (13) *from* (1).—To solutions of (1) (0.08 mmol) in acetone (20 cm^3), Hpz (10.9 mg, 0.16 mmol) or, respectively, Hmpz (19.3 μl, 0.24 mmol) were added, in 5 cm^3 of the same solvent. After stirring for 30 min, the solutions were partially concentrated under reduced pressure. Slow addition of diethyl ether gave orange-yellow microcrystalline solids, which were filtered off, washed with diethyl ether, and air-dried.

Complex (12). Yield 76% (Found: C, 42.5; H, 4.8; N, 7.8. $C_{26}H_{37}ClN_4O_5Rh_2$ requires C, 43.0; H, 5.1; N, 7.7%); ν(OH) 3 585s, ν(RhO) 500vs cm^{-1} (Nujol); δ_H (200 MHz; solvent $CDCl_3$, standard $SiMe_4$) 1.75 (30 H, s, 2 C_5Me_5), 6.19 [2 H, t, *J*(HH) 2, 4-CH], 7.43 p.p.m. [4 H, d, *J*(HH) 2 Hz, 3,5-CH].

Complex (13). Yield 62% (Found: C, 44.7; H, 5.7; N, 7.2. $C_{28}H_{41}ClN_4O_5Rh_2$ requires C, 44.5; H, 5.5; N, 7.4%); ν(OH) 3 600s, ν(RhO) 520vs cm^{-1} (Nujol).

Preparation of the Hydroxo-complex (12) *from* (9a).—To a solution of $[Rh(C_5Me_5)(Me_2CO)_3][ClO_4]_2$ (9a) [prepared *in situ* by treating $[\{Rh(C_5Me_5)\}_2Cl_4]$ (151.4 mg, 0.24 mmol) with $Ag[ClO_4]$ (203.1 mg, 0.98 mmol) in acetone (20 cm^3)], Hpz (33.4 mg, 0.49 mmol) and NEt_3 (103.0 μl, 0.74 mmol) were added. The resulting solution was stirred for 30 min and vacuum-evaporated to dryness. The orange residue was extracted with dichloromethane (15 cm^3) and the solution partially concentrated under reduced pressure. Slow addition of diethyl ether gave an orange-yellow microcrystalline solid, which was filtered off, washed with diethyl ether, and air-dried. Yield 71%. Recrystallization from dichloromethane–diethyl ether solutions led to red crystals.

The complex was characterized by comparison of its spectroscopic properties with those of an authentic sample prepared from (1).

Complex (14) was also prepared according to this procedure from (9b). Yield 76%.

Preparation of the Hydroxo-complexes (11) *and* (15) *from* (9b).—To solutions of $[Rh(C_5Me_5)(Me_2CO)_3][BF_4]_2$ (9b) [prepared *in situ* by treating $[\{Rh(C_5Me_5)\}_2Cl_4]$ (0.07 mmol) with $Ag[BF_4]$ (0.30 mmol) in acetone (20 cm^3)], Hdmpz (0.15 mmol) and NEt_3 (20.8 µl, 0.15 mmol) [alternatively a methanolic solution of KOH (1.5 cm^3, 0.098 mol dm^{-3}, 0.15 mmol) was added] or Hmppz (0.15 mmol) and NEt_3 (20.8 µl, 0.15 mmol) were added. After stirring for 30 min, the solutions were vacuum-evaporated to dryness and the orange-yellow residues extracted with dichloromethane (15 cm^3). The resulting solutions were partially concentrated under reduced pressure. Slow addition of diethyl ether gave orange-yellow microcrystalline solids, which were filtered off, washed with diethyl ether, and air-dried. Recrystallization from dichloromethane–diethyl ether solutions led to red crystals.

Complex (11). Yield 55% (Found: C, 41.6; H, 5.7; N, 6.2. $C_{30}H_{48}B_2F_8N_4O_2Rh_2$ requires C, 41.1; H, 5.5; N, 6.4%); ν(OH) 3 595vs, ν(NH) 3 300vs, ν(RhO) 480vs cm^{-1} (Nujol).

Complex (15). Yield 60% (Found: C, 47.1; H, 5.5; N, 5.4. $C_{40}H_{52}B_2F_8N_4O_2Rh_2$ requires C, 48.0; H, 5.2; N, 5.6%); ν(OH) 3 580vs, ν(NH) 3 310vs, ν(RhO) 480vs cm^{-1} (Nujol).

Crystal Structure Determination.—The main characteristics of the structure determination are presented in Table 2. The samples were analyzed on a Philips PW 1100 diffractometer with graphite-monochromated Cu-K_α radiation (λ = 1.5418 Å). Unit-cell parameters were refined by least squares from the 2θ values ($2 < \theta \leqslant 45°$) of 68 [compound (3)], 62 [(11)], and 59 [(12)] reflections.

Data were measured at 1 min per reflection with ω/2θ scan amplitudes of 1.40, 1.40, and 1.50° respectively. No decay in the samples was detected. The irregular shape of the crystals prevented any correction for absorption.

The structures were solved by Patterson analysis and refined anisotropically by least-squares minimization of $\Sigma w\Delta^2$, with $w = 1$ initially and in the final stages values of w were chosen empirically to give no trends on $<w\Delta^2>$ *versus* $|F_o|$ or $\sin\theta/\lambda$. Compound (3) was refined initially in the non-centrosymmetric space group *Cc* but the analysis did not progress. A disordered model implying two symmetry-related Me groups, with population parameters 0.5, attached to C(3) and C(5) was set up and refined successfully in the *C*2/*c* space group, which we believe appropriately to describe the structure. H Atoms from a ΔF synthesis were included isotropically in the refinement. Final ΔF maps showed no electron density peaks greater than 1.0 [compound (3)], 0.6 [(11)], and 1.6 e $Å^{-3}$ [(12)] near the Rh atoms. The ClO_4^- group in compound (3), situated at a symmetry centre, presents disorder as is the case with the BF_4^- groups in compound (11) and a half of the ClO_4^- anions in compound (12), situated on a two-fold axis. The other ClO_4^- groups in the last compound, also as a two-fold axis, are ordered.

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Received 4*th November* 1983; *Paper* 3/1966