Homo- and Hetero-binuclear Complexes containing the Anion $[Rh(C_5Me_5)\{PO(OMe)_2\}_2(pyrazolate)]^-$ as Ligand. Crystal Structure of $[(C_5Me_5)Rh\{\mu\text{-}PO(OMe)_2\}_2(\mu\text{-}C_3H_3N_2)\text{-}Ru(C_6H_6)]ClO_4\cdot CH_2Cl_2$†

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The neutral rhodium(III) complex $[Rh(C_5Me_5)I\{PO(OMe)_2\}\{P(OH)(OMe)_2\}]$ reacts with pyrazole-type ligands [HL = pyrazole (Hpz), 3-methylpyrazole, or 3,5-dimethylpyrazole] in the presence of $AgClO_4$ yielding cationic complexes of the general formula $[Rh(C_5Me_5)\{PO(OMe)_2\}\{P(OH)(OMe)_2\}(HL)]ClO_4$. They react with Na_2CO_3 in aqueous solutions with formation of the neutral complexes $[Rh(C_5Me_5)\{PO(OMe)_2\}_2(HL)]$. Addition of NaH in tetrahydrofuran to the cationic complexes or thallium acetylacetonate in MeOH to the neutral compounds affords the corresponding bimetallic derivatives $[(C_5Me_5)Rh\{PO(OMe)_2\}_2LM]$ (M = Na or Tl). These complexes react with halide compounds such as $[\{M(ring)Cl_2\}_2]$ [M(ring) = $Rh(C_5Me_5)$, $Ir(C_5Me_5)$, $Ru(C_6H_6)$, $Ru(C_6H_5Me)$, $Ru(MeC_6H_4Pr^i\text{-}p)$ or $Ru(C_6Me_6)$], $[MBr(CO)_5]$, $[(PtMe_3I)_4]$ or $[\{Rh(\mu\text{-}Cl)(cod)\}_2]$ (cod = cycloocta-1,5-diene) to give cationic or neutral complexes of the type $[(C_5Me_5)Rh\{\mu\text{-}PO(OMe)_2\}_2(\mu\text{-}L)\text{-}M(ring)]ClO_4$ or $[(C_5Me_5)Rh\{PO(OMe)_2\}_2(\mu\text{-}L)ML_n]$ [ML_n = $Re(CO)_3$, $Mn(CO)_3$, $PtMe_3$ or Rh(cod)]. The crystal structure of $[(C_5Me_5)Rh\{\mu\text{-}PO(OMe)_2\}_2(\mu\text{-}pz)Ru(C_6H_6)]ClO_4\cdot CH_2Cl_2$ has been determined by X-ray diffraction methods: monoclinic, space group $P2_1/c$, a = 11.179(1), b = 17.039(1), c = 18.186(2) Å, β = 94.85(1)° and Z = 4. The complex cation consists of one rhodium and one ruthenium atom bridged by two phosphonate and one pyrazolate anion. An η^5-C_5Me_5 and an η^6-C_6Me_6 group complete the co-ordination spheres of the metals, which show no direct intermetallic interaction.

Metal complexes containing simultaneously a secondary phosphonate and a secondary phosphite as ligands in a *cis* arrangement present a symmetrical hydrogen system $L_nMP(OR)_2O\cdots H\cdots OP(OR)_2$ (R = Me, Et or Ph) where the hydrogen-bonded proton can easily be removed to form an anionic bis(phosphonate) complex, which can act as a bidentate chelating ligand through the oxygens.[1] When these complexes contain additionally an halogen atom as ancillary ligand, as occurs in the anions $[Ru(C_6Me_6)Cl\{PO(OMe)_2\}_2]^-$ or $[Rh(C_5Me_5)I\{PO(OMe)_2\}_2]^-$, they can react as tridentate ligands with the halogen atom as one of the donor centres.[2] However, in some reactions these complexes only act as *O,O*-donor ligands probably due to the labile halogen-donor site.[2b]

In order to favour the behaviour of the complex as a tridentate ligand we have designed new anionic complexes with a pyrazolate group instead of the halogen atom. Pyrazolate has been actively investigated as a versatile exobidentate bridging ligand,[3] and, usually, the metal–nitrogen bonds formed are reasonably strong and retain the binuclear nature of the resulting complexes during stoichiometric or catalytic reactions.[4]

In this paper we describe the preparation of mononuclear cationic complexes of general formula $[Rh(C_5Me_5)\{PO(OMe)_2\}\{P(OH)(OMe)_2\}(HL)]ClO_4$ [HL = pyrazole (Hpz) **1**, 3-methylpyrazole (Hmpz) **2** or 3,5-dimethylpyrazole (Hdmpz) **3**] and their mono- or bi-deprotonated derivatives $[Rh(C_5Me_5)\{PO(OMe)_2\}_2(HL)]$ (HL = Hpz **4** or Hmpz **5**) and $[(C_5Me_5)Rh\{PO(OMe)_2\}_2LM]$ (M = Na, L = pz **6**; M = Tl, L = pz **7**, mpz **8** or dmpz **9**). We also report the synthesis and properties of a series of binuclear cationic or neutral complexes of general formulae $[(C_5Me_5)Rh\{\mu\text{-}PO(OMe)_2\}_2(\mu\text{-}L)ML_n]ClO_4$ [L = pz, ML_n = $Rh(C_5Me_5)$ **10**, $Ir(C_5Me_5)$ **11**, $Ru(C_6H_6)$ **12**, $Ru(C_6H_5Me)$ **13**, $Ru(MeC_6H_4Pr^i\text{-}p)$ **15**, $Ru(C_6Me_6)$ **16**; L = mpz, ML_n = $Ru(C_6H_5Me)$ **14**] and $[(C_5Me_5)Rh\{\mu\text{-}PO(OMe)_2\}_2(\mu\text{-}L)ML_n]$ [L = pz, ML_n = $Re(CO)_3$ **17**, $Mn(CO)_3$ **19**, $PtMe_3$ **20**, Rh(cod) **21** (cod = cycloocta-1,5-diene); L = mpz, ML_n = $Re(CO)_3$ **18**] which contain the anion of the complexes **6**–**8** acting as a chelating ligand. The crystal and molecular structure of complex **12**·CH_2Cl_2 is also reported.

Part of this work has been the subject of a preliminary communication.[5]

Results and Discussion

Pyrazole-type ligands react in refluxing acetone with the

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

neutral rhodium(III) compound $[Rh(C_5Me_5)I\{PO(OMe)_2\}\{P(OH)(OMe)_2\}]$[2b] in the presence of $AgClO_4$ to give cationic complexes of general formula $[Rh(C_5Me_5)\{PO(OMe)_2\}\{P(OH)(OMe)_2\}(HL)]ClO_4$, where HL = pyrazole (Hpz) **1**, 3-methylpyrazole (Hmpz) **2** or 3,5-dimethylpyrazole (Hdmpz) **3**. The hydrogen-bonded proton of the phosphonate group is neutralized by reaction with sodium carbonate, in aqueous solution, to give neutral complexes $[Rh(C_5Me_5)\{PO(OMe)_2\}_2(HL)]$ (HL = Hpz **4** or Hmpz **5**). When this reaction was carried out starting from complex **3** a yellow solid was obtained but, owing to its instability to moisture, the analyses did not agree well with the above formulation. However this compound prepared *in situ* could be used to obtain the thallium(I) derivative **9** (see above).

As expected, when the cationic complexes **1**–**3** were treated with a slight excess of sodium hydride in tetrahydrofuran, an immediate evolution of hydrogen was observed. Attempts to obtain the sodium compounds as pure samples from these solutions were unsuccessful. The yellow solids isolated always contain variable quantities of sodium perchlorate, $[(C_5Me_5)Rh\{PO(OMe)_2\}_2LNa]\cdot xNaClO_4$, and it was not possible to remove completely the inorganic salt by recrystallization from organic solvents. In this context it is worth mentioning that the property of incorporating sodium salts was previously observed for similar organometallic anionic complexes.[2,6] Nevertheless, pure samples of the sodium derivative $[(C_5Me_5)Rh\{PO(OMe)_2\}_2(pz)Na]$ **6** can be prepared by reaction of the neutral complex **4** with sodium hydride in tetrahydrofuran solution. On the other hand, when the neutral complexes **4**, **5** or the homologous Hdmpz derivative prepared *in situ* were treated with thallium acetylacetonate in methanol, the corresponding thallium bimetallic derivatives $[(C_5Me_5)Rh\{PO(OMe)_2\}_2LTl]$ (L = pz **7**, mpz **8** or dmpz **9**) were obtained. Both sodium and thallium bimetallic complexes are easily hydrolysed in aqueous solution regenerating the corresponding neutral monoprotonated complexes.

All new complexes were characterized by elemental analyses, IR and NMR spectroscopies. In particular, the IR spectra show the presence of the ν(P=O) and δ(P=O) bands, and the ν(N–H) bands of the starting complexes **1**–**3** (Table 1). The ^1H NMR spectra are consistent with the proposed formulations, showing the inequivalence of the protons of the pyrazole groups, the presence of a triplet signal for the C_5Me_5 ligand, and the characteristic pattern of two virtual triplets, with a slight difference in the coupling constants due to the presence of two pairs of non-isochronous OMe groups.[2b] The ^{31}P NMR decoupled spectra show the expected doublets due to coupling to the rhodium nucleus (Table 2).

The sodium or thallium compounds can be used as starting materials for the formation of cationic or neutral binuclear complexes. Thus, the reaction, in acetone, of mixtures of the sodium derivatives $[(C_5Me_5)Rh\{PO(OMe)_2\}_2LNa]\cdot xNaClO_4$ (obtained *in situ* by reaction of the cationic complexes **1**–**3** with sodium hydride in tetrahydrofuran and subsequent change of the solvent to acetone) with the binuclear complexes $[\{M(C_5Me_5)Cl_2\}_2]$ (M = Rh or Ir) or $[\{Ru(arene)Cl_2\}_2]$ yields cationic complexes of the type $[(C_5Me_5)Rh\{\mu\text{-}PO(OMe)_2\}_2(\mu\text{-}L)M(ring)]ClO_4$ [L = pz; M(ring) = $Rh(C_5Me_5)$ **10**, $Ir(C_5Me_5)$ **11**, $Ru(C_6H_6)$ **12**, $Ru(C_6H_5Me)$ **13**, $Ru(MeC_6H_4Pr^i\text{-}p)$ **15**, $Ru(C_6Me_6)$ **16**; L = mpz, M(ring) = $Ru(C_6H_5Me)$ **14**]. These complexes were isolated as stable microcrystalline yellow-orange solids. Their IR spectra show the expected strong and broad band at 1100 cm^{-1} corresponding to overlapping bands of ν(P=O) and of the non-co-ordinating ClO_4^- anion. The ^1H NMR spectra show the resonances of the corresponding M(ring) moiety and the signals due to the anionic organometallic tripod ligand. Interestingly, the virtual triplets assigned to the phosphonate groups exhibit an increase in the separation of their signals (Δ = 65–70 Hz) showing that the co-ordination of the anionic ligand causes a decrease in symmetry.

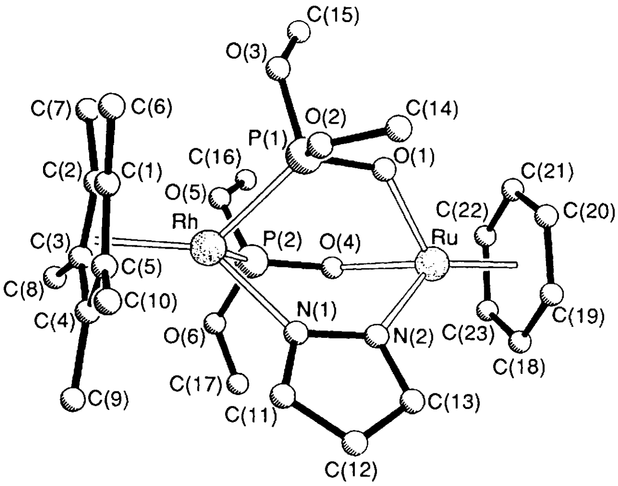

Fig. 1 Structure of the cation of compound **12** showing the labelling scheme

On the other hand, the utility of the thallium complexes **7** and **8** for further synthetic purposes was demonstrated by their clean reaction with bromide complexes in tetrahydrofuran solutions, forming quantitatively the insoluble TlBr salt and the corresponding heterobimetallic complexes in high yields. Thus, neutral binuclear tricarbonyl complexes of the type $[(C_5Me_5)Rh\{\mu\text{-}PO(OMe)_2\}_2(\mu\text{-}L)M(CO)_3]$ (M = Re, L = pz **17** or mpz **18**; M = Mn, L = pz **19**) were obtained by treating complexes **7** or **8** with the corresponding $[MBr(CO)_5]$ compound. Similar results, but with minor yields, can be obtained by treating in tetrahydrofuran the pentacarbonyl complexes with the sodium derivatives obtained *in situ*. The IR spectra of complexes **17**–**19** in the solid state show three carbonyl stretching frequencies in the range 2020–1850 cm^{-1} (Table 1). The spectra in chloroform or acetone solutions show an identical pattern at 2010, 1880, 1860 cm^{-1} ($CHCl_3$) for **17**, 2000, 1870, 1860 cm^{-1} ($CHCl_3$) for **18** and 2020, 1905, 1885 cm^{-1} (Me_2CO) for **19**. For complexes of the type $[ReL(CO)_3]$, where L is a symmetrical tripod ligand, two carbonyl ν(CO) bands are usually observed (A and E modes of an ideal C_{3v} local symmetry).[7] In our case the lack of symmetry of the tripod ligand causes the splitting of the E band. The NMR spectra show the characteristic signals of the co-ordinated anionic complexes (Table 2).

Furthermore, similar results were obtained when the neutral complex **4**, in chloroform solution, was treated with the tetrameric platinum(IV) complex $[(PtMe_3I)_4]$ in the presence of thallium ethoxide, the neutral complex $[(C_5Me_5)Rh\{\mu\text{-}PO(OMe)_2\}_2(\mu\text{-}pz)PtMe_3]$ **20** being formed. Its ^1H NMR spectrum shows the characteristic peaks of the anionic ligand and only one resonance assigned to the methyl groups bonded to the platinum(IV) atom. This signal shows two ^{195}Pt–H couplings, corresponding to the hydrogen of the methyl group co-ordinated *trans* to the nitrogen atom (^2J = 66 Hz) and to the two methyl groups *trans* to the oxygen atoms (^2J = 78 Hz).[8] The ^{31}P NMR spectrum shows the characteristic doublet signal due to coupling to the rhodium, with the corresponding platinum satellites (^2J = 33.2 Hz).

For complexes **10**–**20** the metal centre of the organometallic fragments has a strong tendency to obey the 18-electron rule and, in all cases, the anionic complex is acting as an O,O,N tripod ligand. The crystal structure of complex **12**, obtained by diffractometric methods, confirms this. Fig. 1 shows the structure of the complex cation and the most relevant bond angles and distances are given in Table 3. The cation consists of one rhodium and one ruthenium atom bridged by two phosphonates and one pyrazolate group. The phosphonate anions are co-ordinated to the rhodium through the phosphorus and to the ruthenium through the oxygen atom. An

Table 1 Analytical, IR data and yields for the new complexes

Complex	Analysis[a] (%)			IR[b] (cm^{-1})	Yield (%)
	C	H	N		
1 $[Rh(C_5Me_5)\{PO(OMe)_2\}\{P(OH)(OMe)_2\}(Hpz)]ClO_4$	32.6 (32.7)	5.3 (5.1)	4.5 (4.5)	3320[c]	94
2 $[Rh(C_5Me_5)\{PO(OMe)_2\}\{P(OH)(OMe)_2\}(Hmpz)]ClO_4$	33.8 (33.9)	5.4 (5.3)	4.3 (4.4)	3320[c]	65
3 $[Rh(C_5Me_5)\{PO(OMe)_2\}\{P(OH)(OMe)_2\}(Hdmpz)]ClO_4$	35.2 (35.0)	5.7 (5.5)	4.3 (4.3)	3320[c]	60
4 $[Rh(C_5Me_5)\{PO(OMe)_2\}_2(Hpz)]$	38.2 (39.0)	6.1 (6.0)	5.3 (5.3)	1105,[d] 570[e]	76
5 $[Rh(C_5Me_5)\{PO(OMe)_2\}_2(Hmpz)]$	39.1 (40.1)	6.2 (6.2)	5.2 (5.2)	1100,[d] 570[e]	53
6 $[(C_5Me_5)Rh\{PO(OMe)_2\}_2(pz)Na]$	37.2 (37.4)	5.6 (5.5)	4.9 (5.1)	1160,[d] 590[e]	66
7 $[(C_5Me_5)Rh\{PO(OMe)_2\}_2(pz)Tl]$	27.6 (28.0)	4.3 (4.2)	3.8 (3.9)	1130,[d] 570[e]	80
8 $[(C_5Me_5)Rh\{PO(OMe)_2\}_2(mpz)Tl]$	29.5 (29.2)	4.5 (4.4)	3.7 (3.8)	1105,[d] 580[e]	91
9 $[(C_5Me_5)Rh\{PO(OMe)_2\}_2(dmpz)Tl]$	30.5 (30.2)	4.6 (4.5)	3.7 (3.7)	1100,[d] 570[e]	45
10 $[(C_5Me_5)Rh\{\mu\text{-}PO(OMe)_2\}_2(\mu\text{-}pz)Rh(C_5Me_5)]ClO_4$	37.6 (37.7)	5.4 (5.3)	3.3 (3.3)	600[e]	87
11 $[(C_5Me_5)Rh\{\mu\text{-}PO(OMe)_2\}_2(\mu\text{-}pz)Ir(C_5Me_5)]ClO_4$	34.1 (34.1)	4.9 (4.8)	2.9 (3.0)	600[e]	71
12 $[(C_5Me_5)Rh\{\mu\text{-}PO(OMe)_2\}_2(\mu\text{-}pz)Ru(C_6H_6)]ClO_4\cdot CH_2Cl_2$	33.9 (34.4)	4.7 (4.5)	3.3 (3.5)	600[e]	53
13 $[(C_5Me_5)Rh\{\mu\text{-}PO(OMe)_2\}_2(\mu\text{-}pz)Ru(C_6H_5Me)]ClO_4$	36.7 (35.3)	5.1 (4.7)	3.3 (3.4)	600[e]	78
14 $[(C_5Me_5)Rh\{\mu\text{-}PO(OMe)_2\}_2(\mu\text{-}mpz)Ru(C_6H_5Me)]ClO_4$	36.0 (36.2)	4.8 (5.0)	3.3 (3.4)	600[e]	55
15 $[(C_5Me_5)Rh\{\mu\text{-}PO(OMe)_2\}_2(\mu\text{-}pz)Ru(MeC_6H_4Pr^i\text{-}p)]ClO_4$	38.1 (37.8)	5.2 (5.1)	3.4 (3.3)	585[e]	81
16 $[(C_5Me_5)Rh\{\mu\text{-}PO(OMe)_2\}_2(\mu\text{-}pz)Ru(C_6Me_6)]ClO_4$	39.3 (39.1)	5.8 (5.4)	3.3 (3.2)	600[e]	75
17 $[(C_5Me_5)Rh\{\mu\text{-}PO(OMe)_2\}_2(\mu\text{-}pz)Re(CO)_3]$	30.2 (30.2)	3.8 (3.9)	3.3 (3.5)	2000,[f] 1875,[f] 1850[f] 1105,[d] 600[e]	90
18 $[(C_5Me_5)Rh\{\mu\text{-}PO(OMe)_2\}_2(\mu\text{-}mpz)Re(CO)_3]$	30.2 (31.2)	4.0 (4.0)	3.4 (3.5)	2000,[f] 1870,[f] 1850[f] 1110,[d] 595[e]	54
19 $[(C_5Me_5)Rh\{\mu\text{-}PO(OMe)_2\}_2(\mu\text{-}pz)Mn(CO)_3]$	36.4 (37.3)	4.7 (4.8)	4.5 (4.2)	2020,[f] 1900,[d] 1870[f] 1125,[d] 595[e]	90
20 $[(C_5Me_5)Rh\{\mu\text{-}PO(OMe)_2\}_2(\mu\text{-}pz)PtMe_3]$	31.4 (31.5)	5.2 (5.2)	3.7 (3.7)	1105,[d] 585[e]	66
21 $[(C_5Me_5)Rh\{\mu\text{-}PO(OMe)_2\}_2(\mu\text{-}pz)Rh(cod)]$	39.9 (40.8)	5.9 (5.8)	3.3 (3.8)	1070,[d] 570[e]	69

[a] Calculated values are given in parentheses. [b] In KBr. Typical absorption bands of the unco-ordinated perchlorate anion were observed at 1100 and 620 cm^{-1}. For the cationic complexes the ν(P=O) band is masked by the strong and broad band of the perchlorate anion at 1100 cm^{-1}. [c] ν(N–H). [d] ν(P=O). [e] δ(P=O). [f] ν(CO).

η^5-pentamethylcyclopentadienyl and an η^6-benzene ring complete the co-ordination spheres of rhodium and ruthenium, respectively. The geometries around the metals are the usual pseudo-octahedral 'three-legged piano stool' commonly found for six-co-ordinated $(C_5Me_5)Rh^{III}$ or (arene)Ru^{II} derivatives.

Regarding the phosphonate bridging ligands, the rhodium–phosphorus bond lengths [Rh–P(1) 2.243(3) and Rh–P(2) 2.235(3) Å] are slightly shorter than those found in the dimethyl phosphonate pentamethylcyclopentadienyl compound $[\{(C_5Me_5)RhI[\mu\text{-}PO(OMe)_2]_2Tl\}_2]$ [2.265(2) and 2.262(2) Å].[2b] The ruthenium–oxygen distances are also slightly shorter than that found in $[Ru_2(CO)_6(\mu\text{-}\eta^2\text{-}C{\equiv}CBu^t)(\mu\text{-}Ph_2P{=}O)]$ [2.135(2) Å].[9] The phosphoryl P=O bond distances, 1.527(6) and 1.500(7) Å, compare well with the values reported for the related pentanuclear compound $[\{Ni(C_5H_5)[\mu\text{-}PO(OMe)_2]_2\}_4U]$ [average 1.51(1) Å] where the uranium atom is connected to each Ni by a double phosphonate bridge[10] or with those observed in the trinuclear $PdRh_2$ derivative $[Pd\{\mu\text{-}Cl)[\mu\text{-}PO(OMe_2)_2]Rh(cod)\}_2]$ [average 1.506(4) A] where the two phosphorus ligands bridge the palladium to the two rhodium atoms.[1c] These values are clearly indicative of a remaining partial double-bond character.[11] The P–OMe bond distances, average 1.574(6) Å, are in the normal range.[11]

The Rh–N(1) bond distance [2.105(8) Å] compares well with distances found in other binuclear pyrazolate-bridged pentamethylcyclopentadienylrhodium(III) complexes such as $[\{Rh(C_5Me_5)\}_2(\mu\text{-}OH)(\mu\text{-}pz)_2]ClO_4$ [average 2.092(7) Å],[12] $[\{Rh(C_5Me_5)\}_2(\mu\text{-}PPh_2)(\mu\text{-}pz)_2]BF_4$ [average 2.092(4) Å][13] and $[\{Rh(C_5Me_5)\}_2(\mu\text{-}Cl)(\mu\text{-}pz)_2]BF_4$ [average 2.091(9) Å].[14] Analogously, the Ru–N(2) distance [2.106(7) Å] is similar to those found in other binuclear pyrazolate-bridged arene-ruthenium(II) compounds such as $[\{Ru(MeC_6H_4Pr^i\text{-}p)\}_2(\mu\text{-}OH)(\mu\text{-}pz)_2]BPh_4$ [average 2.086(3) Å],[15] $[\{Ru(MeC_6H_4Pr^i\text{-}p)\}_2(\mu\text{-}OH)_2(\mu\text{-}pz)]BF_4$ [average 2.078(3) Å],[16] $[\{Ru(C_6H_6)\}_2(\mu\text{-}Cl)(\mu\text{-}pz)_2]Cl$ [average 2.087(5) Å][17] and $[\{Ru(C_6H_6)\}_2(\mu\text{-}Cl)_2(\mu\text{-}pz)]Cl$ [average 2.068(4) Å].[17]

The C_5Me_5 ligand presents different Rh–C(ring) distances as a consequence of the asymmetry of the co-ordination around the metal. In this respect the C–C distances suggest some degree of localization into an 'ene-enyl' form, as previously observed for some $(C_5Me_5)Rh^{III}$ complexes.[18] The Rh(1) atom lies 1.900(1) Å from the least-squares plane through the five-

Table 2 NMR[a] chemical shifts (δ) and coupling constants (Hz) for the isolated complexes

	^{1}H				^{31}P-$\{^1$H$\}$	
			HL			
Complex	C_5Me_5 [^4J(PH)]	OMe [^3J = ^5J(PH)]	H^3[Me]/H^5[Me]	H^4	δ	^1J(RhP)
1	1.72 (t) [4.5]	3.80 (vt) [11.5) 3.98 (vt) [11.0]	8.23 (d) 7.63 (d) ^3J(HH) = 2.5	6.47 (t)	104.32 (d)	180.2
2	1.75 (t) [4.5]	3.79 (vt) [11.5] 3.96 (vt) [11.0]	[2.53 (s)] 7.50 (d) ^3J(HH) = 2.0	6.20 (m)	104.62 (d)	181.7
3[b]	1.71 (t) [4.7]	3.84 (vt) [11.3] 3.93 (vt) [11.0]	[2.23 (s)] [2.42 (s)]	6.50 (m)	103.41 (d)	184.6
4[c]	1.74 (t) [4.0]	3.50 (vt) [11.0] 3.65 (vt) [11.5]	7.72 (d) 7.66 (d) ^3J(HH) = 2.25	6.40 (t)	89.58 (d)	180.2
5	1.72 (t) [4.0]	3.48 (vt) [11.0] 3.65 (vt) [11.5]	[2.35 (s)] 7.55 (s, br)	6.10 (m)		
6	1.60 (t) [4.0]	3.58 (vt) [11.5] 3.67 (vt) [11.0]	7.73 (d) 7.52 (d) ^3J(HH) = 1.75	6.29 (t)		
7	1.66 (t) [4.0]	3.62 (vt) [11.0] 3.68 (vt) [11.5]	7.64 (d) 7.62 (d) ^3J(HH) = 2.0	6.31 (t)	94.49 (d)	184.34
8	1.76 (t) [4.0]	3.66 (vt) [11.0]	[2.26 (d)] 7.42 (d) ^3J(HH) = 1.75	6.03 (d)		
9	1.59 (t) [4.0]	3.65 (vt) [11.0] 3.90 (vt) [10.5]	[2.15(s)] [2.24(s)]	5.96 (s,br)		
10	1.73 (t) [4.0] 1.63 (s)	2.98 (vt) [11.5] 3.74 (vt) [11.5]	8.02 (d) 7.33 (d) ^3J(HH) = 2.0	6.49 (t)	101.80 (d)	178.8
11	1.77 (t) [4.0] 1.57 (s)	3.02 (vt) [11.5] 3.75 (vt) [11.5)	7.97 (d) 7.39 (d) ^3J(HH) = 2.2	6.47 (t)	100.34 (d)	178.8
12[d,e]	1.67 (t) [4.0]	3.03 (vt) [11.5] 3.78 (vt) [11.5)	8.67 (d) 7.23 (d) ^3J(HH) = 2.0	6.59 (t)	101.45 (d)	177.3
13[f]	1.66 (t) [4.0]	2.99 (vt) [11.5] 3.79 (vt) [11.5]	8.68 (d) 7.18 (d) ^3J(HH) = 2.0	6.46 (t)	101.90 (d)	177.3
14[g]	1.66 (t) [4.0]	3.08 (vt) [11.5] 3.86 (vt) [11.5]	2.23 (s) 7.10 (m)	6.19 (m)	100.90 (d)	177.7
15[d,h]	1.67 (t) [4.0]	2.94 (vt) [11.7] 3.75 (vt) [11.3]	8.57 (d) 7.11 (d) ^3J(HH) = 2.1	6.39 (t)	107.60 (d)	177.6
16[i]	1.67 (t) [4.0]	2.85 (vt) [11.5] 3.71 (vt) [11.5]	8.10 (d) 7.15 (d) ^3J(HH) = 2.1	6.43 (m)	101.50 (d)	177.4
17[d]	1.78 (t) [4.0]	3.06 (vt) [11.5] 3.76 (vt) [11.7]	7.69 (d) 7.39 (d) ^3J(HH) = 2.25	6.32 (t)	96.30 (d)	177.2
18	1.77 (t) [4.0]	3.10 (vt) [11.5] 3.75 (vt) [11.5]	2.66 (s) 7.23 (m)	6.09 (m)	95.00 (d)	177.8
19	1.76 (t) [4.0]	3.01 (vt) [11.5] 3.76 (vt) [11.3]	8.05 (d) 7.39 (d) ^3J(HH) = 2.0	6.34 (t)	99.00 (d)	175.0
20[j]	1.80 (t) [4.0]	2.97 (vt) [11.7] 3.73 (vt) [11.3]	7.48 (d) 7.35 (d) ^3J(HH) = 2.0	6.25 (t)	100.40 (d)[k]	176.9
21[l]	1.82 (t) [4.0]	3.46 (vt) [11.0] 3.60 (vt) [11.5]	7.97 (d) 7.12 (d) ^3J(HH) = 2.0	6.14 (t)	94.50 (d)[m]	185.0

[a] Measured in $CDCl_3$ at room temperature unless otherwise stated. Chemical shifts relative to $SiMe_4$ and 85% H_3PO_4 in D_2O as standards. s = Singlet, d = doublet, t = triplet, vt = virtual triplet and m = multiplet. [b] δ 9.4 (s, br, NH), 10.93 (s, br, POH). [c] δ 13.62 (s, br, NH). [d] In CD_2Cl_2. [e] δ 5.72 (s, 6 H, ring). [f] δ 2.23 (s, Me), 5.47 (m, 3 H, ring), 5.85 (m, 2 H, ring). [g] δ 2.76 (s, Me), 5.60 (m, 3 H, ring), 5.97 (m, 2 H, ring). [h] δ 1.25 (d, 2Me, J = 6.92), 2.13 (s, Me), 2.8 (m, CH), 5.47 (d, 2H, ring, J = 6.32), 5.57 (d, 2 H, ring, J = 6.23 Hz). [i] δ 2.07 (s, 6Me). [j] δ 0.95 [s, 2Me *trans* O, $^2J(^{195}PtH)$ = 78; Me *trans* N, $^2J(^{195}PtH)$ = 66 Hz]. [k] $^2J(^{195}PtP)$ = 33.2 Hz. [l] δ 4.08 (s, br, 4 H, CH=CH), 2.52 (m, 4 H, CH_2), 1.82 (m, 4 H, CH_2 masked by C_5Me_5 resonance). [m] In [$^2H_8$]toluene (100 °C).

membered carbocyclic ring. This distance is longer than those usually found in pentamethylcyclopentadienylrhodium(III) compounds.[19] The methyl groups of the C_5Me_5 ligand point away from the rhodium atom [range of deviation: 0.088–0.229(11) Å].

Finally, the homobimetallic neutral rhodium complex [$(C_5Me_5)Rh\{\mu\text{-}PO(OMe)_2\}_2(\mu\text{-}pz)Rh(cod)$] **21** can be obtained by reaction, in methanol, of the binuclear complex [$\{Rh(\mu\text{-}Cl)(cod)\}_2$] with **1** in the presence of potassium hydroxide or with the thallium derivative **7** in dichloromethane solution. The rhodium(I) atom of complex **21** can be a 16- or a 18-electron metal centre, with the anionic complex ligand acting in a bi- or tri-dentate fashion, respectively. We have studied this system by NMR spectroscopy in solution. At room temperature the ^{31}P-$\{^1H\}$ NMR spectrum in chloroform consists of a very broad signal centred at δ 97. On cooling this resonance splits into two broad signals which appear as two sharp doublets of doublets at −60 °C. At this temperature the chemical shifts and the coupling constants can be accurately measured. There are two types of phosphorus coupled to rhodium: δ(P_A) 90.6, $^1J(RhP_A)$ = 176.5, $^2J(P_AP_B)$ = 89.5 Hz; δ(P_B) 107.8, $^1J(RhP_B)$ = 197.0 Hz. At 100 °C, in toluene, the spectrum consists of only one doublet centred at δ 94.5 with a coupling constant of 185.0 Hz. All these experimental data can be accounted for by assuming that complex **21** has a ground state having a terminal and a bridging phosphonate ligand as is shown in Fig. 2(*a*). As the temperature increases the two phosphorus nuclei become equivalent. We propose that this implies the co-ordination of the terminal phosphonate group through its free oxygen atom to the unsaturated rhodium–cyclooctadiene moiety, rendering the rhodium(I) a 18-electron five-co-ordinated centre [Fig. 2(*b*)]. Consistently, the ^1H NMR spectra show no appreciable variations in the proton pyrazolate signals with temperature, as expected for a pyrazolate group that retains its bridging co-ordination mode. However, the

Table 3 Selected bond lengths (Å) and angles (°) for the complex $[(C_5Me_5)Rh\{\mu\text{-}PO(OMe)_2\}_2(\mu\text{-}pz)Ru(C_6H_6)]ClO_4\cdot CH_2Cl_2$

Rh–P(1)	2.243(3)	Ru–O(1)	2.063(7)
Rh–P(2)	2.235(3)	Ru–O(4)	2.082(7)
Rh–N(1)	2.105(8)	Ru–N(2)	2.106(7)
Rh–C(1)	2.265(10)	Ru–C(18)	2.153(12)
Rh–C(2)	2.175(12)	Ru–C(19)	2.172(12)
Rh–C(3)	2.250(10)	Ru–C(20)	2.166(12)
Rh–C(4)	2.263(9)	Ru–C(21)	2.162(11)
Rh–C(5)	2.284(9)	Ru–C(22)	2.159(11)
		Ru–C(23)	2.153(13)
C(1)–C(2)	1.434(18)	C(18)–C(19)	1.437(22)
C(1)–C(5)	1.377(18)	C(18)–C(23)	1.419(22)
C(2)–C(3)	1.395(21)	C(19)–C(20)	1.375(22)
C(3)–C(4)	1.400(19)	C(20)–C(21)	1.425(21)
C(4)–C(5)	1.451(17)	C(21)–C(22)	1.367(21)
		C(22)–C(23)	1.415(24)
N(1)–N(2)	1.388(10)	P(1)–O(1)	1.527(6)
N(1)–C(11)	1.329(13)	P(1)–O(2)	1.605(9)
N(2)–C(13)	1.334(14)	P(1)–O(3)	1.554(10)
C(11)–C(12)	1.353(16)	P(1)–O(4)	1.500(7)
C(12)–C(13)	1.376(15)	P(2)–O(5)	1.595(12)
		P(2)–O(6)	1.540(14)
P(1)–Rh–P(2)	90.8(1)	O(1)–Ru–O(4)	85.9(3)
P(1)–Rh–N(1)	85.8(2)	O(1)–Ru–N(2)	87.3(3)
P(1)–Rh–G(1)*	125.7(2)	O(1)–Ru–G(2)*	124.3(3)
P(2)–Rh–N(1)	87.0(2)	O(4)–Ru–N(2)	86.3(3)
P(2)–Rh–G(1)*	125.7(2)	O(4)–Ru–G(2)*	126.6(3)
N(1)–Rh–G(1)*	129.0(3)	N(2)–Ru–G(2)*	131.9(3)
C(5)–C(1)–C(2)	107.7(11)	C(23)–C(18)–C(19)	120.0(14)
C(1)–C(2)–C(3)	109.0(12)	C(18)–C(19)–C(20)	119.8(13)
C(2)–C(3)–C(4)	107.3(11)	C(19)–C(20)–C(21)	119.5(13)
C(3)–C(4)–C(5)	108.2(11)	C(20)–C(21)–C(22)	121.6(14)
C(4)–C(5)–C(1)	107.6(11)	C(21)–C(22)–C(23)	120.4(12)
		C(22)–C(23)–C(18)	118.8(12)
C(11)–N(1)–N(2)	107.8(7)	O(1)–P(1)–O(2)	108.7(4)
N(1)–N(2)–C(13)	106.6(7)	O(1)–P(1)–O(3)	107.1(4)
N(2)–C(13)–C(12)	109.8(9)	O(2)–P(1)–O(3)	99.2(6)
C(13)–C(12)–C(11)	105.8(10)	O(4)–P(2)–O(5)	108.8(5)
C(12)–C(11)–N(1)	110.0(9)	O(4)–P(2)–O(6)	106.7(5)
		O(5)–P(2)–O(6)	97.8(6)

* G(1) and G(2) represent the centroids of the pentamethylcyclopentadienyl and benzene ligands.

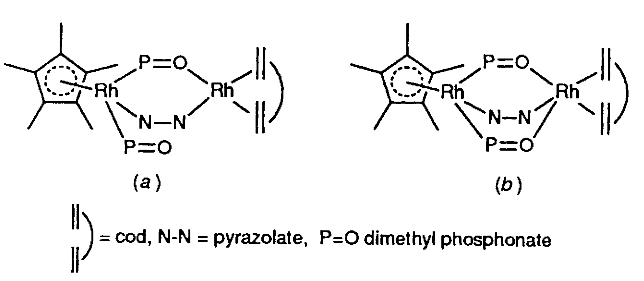

Fig. 2 Proposed structures for complex **21** in solution (see text)

olefinic cod resonances appear as two broad multiplets at −60 °C in $[^2H_8]$toluene and as only one broad singlet above −20 °C, and the phosphonate methyl resonances change from four not well resolved doublets at −60 °C to two virtual triplets above +20 °C. In summary, the rhodium(I) in complex **21** is four-co-ordinated at −60 °C, one of the phosphonate groups remaining terminal, while at higher than room temperature it is essentially five-co-ordinated with the two phosphonate and the pyrazolate groups acting as bridging ligands.

Catalytic Studies.—We have studied the behaviour of complexes **1**, **4**, **7** and **10**–**21** as catalyst precursors in the hydrogen-transfer reaction from propan-2-ol to acetophenone in the presence of potassium hydroxide [equation (1)]. In general, the

$$Me_2CHOH + Me(Ph)C{=}O \longrightarrow Me_2C{=}O + Me(Ph)CHOH \quad (1)$$

results show a very low activity for the complexes. Only the binuclear Rh–Ru cationic complexes **12**, **13**, **15** and **16** show a moderate activity, giving conversions of 60, 35, 40 and 80% after 10 h and 90, 62, 70 and 100% after 24 h of reaction, respectively.

Experimental

All reactions were carried out under purified nitrogen by using Schlenk-tube techniques. Reagent-grade solvents were dried, distilled and stored under a nitrogen atmosphere. The starting materials $[Rh(C_5Me_5)I\{PO(OMe)_2\}\{P(OH)(OMe)_2\}]$,[2b] $[\{Rh(C_5Me_5)Cl_2\}_2]$,[20] $[\{Ir(C_5Me_5)Cl_2\}_2]$,[20] $[\{Ru(arene)Cl_2\}_2]$ (arene = C_6H_6,[21] C_6H_5Me,[22] $MeC_6H_4Pr^i\text{-}p$[22] or C_6Me_6[23]), $[(PtMe_3I)_4]$[24] and $[\{Rh(\mu\text{-}Cl)(cod)\}_2]$,[25] were prepared according to reported methods.

Infrared spectra were recorded on a Perkin Elmer 567 spectrophotometer (range 4000–200 cm^{-1}). The C, H and N analyses were carried out with a Perkin Elmer 240B microanalyser. The NMR spectra were recorded on Varian XL-100 and XL-200 spectrometers. Chemical shifts are reported relative to $SiMe_4$ and 85% H_3PO_4 in D_2O as internal and external standards, respectively.

Preparations.—$[Rh(C_5Me_5)\{PO(OMe)_2\}\{P(OH)(OMe)_2\}(HL)]ClO_4$ (HL = Hpz **1**, Hmpz **2** *or* Hdmpz **3**). A solution of the complex $[Rh(C_5Me_5)I\{PO(OMe)_2\}\{P(OH)(OMe)_2\}]$ (584.2 mg, 1.00 mmol) in acetone (15 cm^3) was treated with silver perchlorate (207.3 mg, 1.00 mmol) and the corresponding pyrazole HL (1.00 mmol). The resulting mixture was boiled under reflux for 2 h in the absence of light. The silver iodide formed was filtered off through Kieselguhr, the solution obtained was concentrated under reduced pressure to a small volume and slow addition of diethyl ether gave microcrystalline solids, which were filtered off, washed with diethyl ether and air-dried. Recrystallization from acetone–diethyl ether led to yellow crystals.

$[Rh(C_5Me_5)\{PO(OMe)_2\}_2(HL)]$ (HL = Hpz **4** *or* Hmpz **5**). To an aqueous solution of the complex **1** or **2** (0.60 mmol) was added sodium carbonate (127.2 mg, 1.20 mmol). The solution was extracted with chloroform (2 × 15 cm^3), the organic layer dried with anhydrous magnesium sulfate, and then filtered off. The yellow oils obtained by evaporation to dryness were dissolved in pentane, and the solution cooled to −30 °C overnight to give the complexes as yellow crystals. When the reaction was carried out with complex **3** as starting compound a very hygroscopic yellow solid was obtained in 78% yield.

$[(C_5Me_5)Rh\{PO(OMe)_2\}_2(pz)Na]$ **6**. Addition of a slight excess of sodium hydride (6.5 mg of 80% dispersion in mineral oil, 0.22 mmol) to a solution of complex **4** (104.8 mg, 0.20 mmol) in anhydrous tetrahydrofuran (10 cm^3) produced immediate evolution of hydrogen. The suspension formed was stirred until the evolution of hydrogen ceased and the excess of sodium hydride was filtered off. The resulting solution was evaporated to dryness, and the residue extracted with dichloromethane. Slow addition of pentane led to the formation of yellow crystals, which were filtered off, washed with pentane and vacuum dried. Alternatively, this complex can be prepared starting from complex **1**, using a large excess of sodium hydride and work-up as above. In this case the isolated complex always contains variable quantities of sodium perchlorate.

$[(C_5Me_5)Rh\{PO(OMe)_2\}_2LTl]$ (L = pz **7**, mpz **8** *or* dmpz **9**). A mixture of complex **4** (420.0 mg, 0.80 mmol), **5** (119.0 mg, 0.22 mmol) or the hygroscopic complex $[Rh(C_5Me_5)\{PO(OMe)_2\}_2(Hdmpz)]$ (338.0 mg, 0.61 mmol) and the stoichiometric amount of thallium acetylacetonate, in methanol (15 cm^3), was stirred at room temperature for 10 h. The mixture was evaporated to dryness and the residue extracted with diethyl ether. Partial evaporation of the solution and addition of pentane gave yellow crystals which were filtered off, washed with cold pentane, and vacuum dried.

$[(C_5Me_5)Rh\{\mu\text{-}PO(OMe)_2\}_2(\mu\text{-}pz)M(C_5Me_5)]ClO_4$ (M = Rh **10** *or* Ir **11**). To a solution of complex **1** (125.0 mg, 0.20 mmol) in anhydrous tetrahydrofuran (10 cm^3) was added an excess of sodium hydride (20 mg of 80% dispersion in mineral oil) and the mixture was stirred at room temperature until evolution of hydrogen ceased. The excess of sodium hydride was filtered off, the solution obtained was evaporated to dryness and the residue extracted with acetone. The binuclear complex $[\{M(C_5Me_5)Cl_2\}_2]$ (M = Rh or Ir) (0.10 mmol) was added and the suspension obtained stirred for 12 h. During this time the solution gradually changed from yellow to orange-yellow. The sodium chloride formed was filtered off through Kieselguhr, the solution concentrated to a small volume and the complexes precipitated by addition of diethyl ether. Red-orange (**10**) or yellow (**11**) crystals were obtaind from chloroform–diethyl ether.

$[(C_5Me_5)Rh\{\mu\text{-}PO(OMe)_2\}_2(\mu\text{-}L)Ru(arene)]ClO_4$ (L = pz, arene = C_6H_6 **12**, C_6H_5Me **13**, $MeC_6H_4Pr^i$-*p* **15** *or* C_6Me_6 **16**; L = mpz, arene = C_6H_5Me **14**). To a solution of complex **1** or **2** (0.24 mmol) in anhydrous tetrahydrofuran (10 cm^3) was added an excess of sodium hydride (15.0 mg of 80% dispersion in mineral oil). After stirring for 10 min the excess of sodium hydride was filtered off and the solution evaporated to dryness. The residue, dissolved in acetone (15 cm^3), was treated with the binuclear complex $[\{Ru(arene)Cl_2\}_2]$ (0.12 mmol) and the mixture stirred for 12 h at room temperature. The solid sodium chloride formed was filtered off through Kieselguhr, the solution concentrated to a small volume and the complexes precipitated by addition of diethyl ether. Yellow (**13**) or red-orange crystals (**14**–**16**) were obtained from acetone–diethyl ether.

In the case of complex **12**, owing to the low solubility of the ruthenium complex $[\{Ru(C_6H_6)Cl_2\}_2]$ in acetone, the reaction was carried out by irradiating the mixture in a water-bath of an ultrasonic laboratory cleaner (Branson 2200) with simultaneous strong agitation for 48 h. After evaporation to dryness, the residue was extracted with dichloromethane and chromatographed on neutral aluminium oxide, using dichloromethane as eluent. Orange-yellow crystals of complex **12** were obtained from dichloromethane–diethyl ether.

$[(C_5Me_5)Rh\{\mu\text{-}PO(OMe)_2\}_2(\mu\text{-}L)M(CO)_3]$ (M = Re, L = pz **17** *or* mpz **18**; M = Mn, L = pz **19**). The complexes can be prepared by the two methods described below.

(*i*) A mixture of complex **7** (145.5 mg, 0.20 mmol) and $[MBr(CO)_5]$ (M = Re or Mn) (0.20 mmol) in anhydrous tetrahydrofuran (20 cm^3) was boiled under reflux for 2 h. The thallium bromide formed was filtered off through Kieselguhr and the solution evaporated to dryness. The solid residue was dissolved in dichloromethane and chromatographed on Kieselgel (HF_{254}, type 60) using diethyl ether (**17**) or acetone (**19**) as eluent. Yellow crystals were obtained from dichloromethane–diethyl ether (**17**) or acetone–diethyl ether (**19**).

(*ii*) To a solution of complex **2** (127.8 mg, 0.20 mmol) in anhydrous tetrahydrofuran (10 cm^3) was added an excess of sodium hydride (20.0 mg of 80% dispersion in mineral oil). When the evolution of hydrogen had ceased the excess of sodium hydride was filtered off and a stoichiometric amount of $[ReBr(CO)_5]$ (81.2 mg, 0.20 mmol) was added to the filtrate. The solution was boiled under reflux for 5 h and then evaporated to dryness. The residue was extracted with the minimum amount of dichloromethane and a yellow solid was obtained by addition of pentane.

$[(C_5Me_5)Rh\{\mu\text{-}PO(OMe)_2\}_2(\mu\text{-}pz)PtMe_3]$ **20**. Complex **4** (98.0 mg, 0.17 mmol) was treated with $[(PtMe_3I)_4]$ (64.0 mg, 0.04 mmol) in chloroform (15 cm^3) in the presence of an excess of thallium ethoxide. The mixture was stirred at room temperature for 6 h and the thallium iodide formed filtered off through Kieselgel (HF_{254}, type 60). The solution was evaporated to dryness, and orange-yellow crystals were obtained from acetone–pentane.

$[(C_5Me_5)Rh\{\mu\text{-}PO(OMe)_2\}_2(\mu\text{-}pz)Rh(cod)]$ **21**. To a mixture of complex **1** (125.0 mg, 0.20 mmol) and $[\{Rh(\mu\text{-}Cl)(cod)\}_2]$ (49.3 mg, 0.10 mmol) in methanol (15 cm^3) was added KOH (11.2 mg, 0.20 mmol) in the same solvent. The resulting mixture was stirred for 1 h at room temperature and vacuum-evaporated to dryness. The residue was extracted with dichloromethane–diethyl ether (1:1), and yellow crystals were obtained by partial evaporation and addition of pentane.

Alternatively, this complex can be prepared by treating complex **7** (201.0 mg, 0.28 mmol) with $[\{Rh(\mu\text{-}Cl)(cod)\}_2]$ (68.0 mg, 0.14 mmol) in dichloromethane (15 cm^3). The mixture was stirred for 24 h at room temperature and then filtered (to eliminate the thallium chloride formed). The solution obtained was vacuum-evaporated, then pentane was added, and stirring was continued until a yellow solid formed. Yellow crystals were obtained from dichloromethane–pentane.

Hydrogen-transfer Reactions.—The reactions were carried out under nitrogen in a refluxing solution of propan-2-ol (dried and freshly distilled), with magnetic stirring in a round-bottomed flask (50 cm^3) fitted with a condenser and provided with a septum cap. In a typical procedure, a solution of the catalyst precursor (0.02 mmol) in propan-2-ol (8 cm^3) and KOH (0.01 mmol) in the same solvent (1 cm^3) was refluxed for 1 h and acetophenone (2.0 mmol, distilled previously) in propan-2-ol (1 cm^3) was injected. Samples of the refluxing system were taken at given times and analysed in a Hewlett-Packard capillary column (Carbowax 20 M, 25 m × 0.2 mm × 0.2 μm film). The peak areas were obtained with a Hewlett-Packard 3396 A integrator.

X-Ray Structure Determination of $[(C_5Me_5)Rh\{\mu\text{-}PO(OMe)_2\}_2(\mu\text{-}pz)Ru(C_6H_6)]ClO_4{\cdot}CH_2Cl_2$ **12**.—*Crystal data.* $C_{23}H_{36}ClN_2O_{10}P_2RhRu{\cdot}CH_2Cl_2$, $M = 886.85$, monoclinic, space group $P2_1/c$, $a = 11.179(1)$, $b = 17.039(1)$, $c = 18.186(2)$ Å, $\beta = 94.85(1)^\circ$, $U = 3451.7(5)$ Å^3 (refined from 60 carefully centred reflections, Mo-Kα radiation $\lambda = 0.710\,69$ Å), $Z = 4$, $D_c = 1.707 \text{ g cm}^{-3}$, crystal dimensions 0.493 × 0.232 × 0.228 mm, $F(000) = 1784$.

Data collection and processing. Four-circle Siemens AED-2 diffractometer (graphite-monochromated Mo-Kα radiation). Data collected at room temperature, ω–2θ scan technique ($3 \leqslant 2\theta \leqslant 50^\circ$). 9002 Reflections measured, 6091 unique (R_{int} 0.036), 3339 with $F \geqslant 5\sigma(F)$ used for calculations. An absorption correction based on the ψ-scan method ($\mu = 12.75 \text{ cm}^{-1}$) was applied (minimum and maximum transmission factors 0.784 and 0.626).[26]

Structure solution and refinement. The structure was solved by Patterson, extended by Fourier methods, and refined by full-matrix least squares for 394 parameters. All atoms were refined isotropically first, and in subsequent cycles with anisotropic thermal parameters for atoms forming the cationic complex. At this stage a model of disorder was established for the oxygen atoms of the perchlorate; two groups of oxygens with identical occupancy factors were included [O(71)–O(101) and O(72)–O(102)]. A dichloromethane solvent molecule was also included in the refinement (disordered in three positions) to account for the remaining peaks in the Fourier difference maps. The hydrogens were placed at their calculated positions and introduced in the final structure-factor calculations using a riding model and with a common fixed thermal parameter. The maximum peak in the final ΔF map had 0.68 e Å^{-3} close to the Rh atom. The final R and R' values were 0.0526 and 0.0564 respectively; weighting scheme $w = 1.00/[\sigma^2(F) + 0.000\,957F^2]$. The SHELXTL system of computer programs was used.[27] Atomic scattering factors, corrected for anomalous dispersion, were taken from ref. 28. Final atomic coordinates for the non-hydrogen atoms are given in Table 4.

Table 4 Atomic coordinates (× 10^4; × 10^5 for Rh and Ru atoms) for $[(C_5Me_5)Rh\{\mu\text{-}PO(OMe)_2\}_2(\mu\text{-}pz)Ru(C_6H_6)]ClO_4\cdot CH_2Cl_2$

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Ru	18 081(5)	22 167(5)	40 934(4)
Rh	54 217(5)	22 432(4)	40 532(4)
P(1)	4 126(2)	1 664(2)	3 213(2)
P(2)	4 242(2)	3 301(2)	4 064(2)
Cl	55(3)	882(2)	6 720(2)
O(1)	2 785(5)	1 798(5)	3 264(4)
O(2)	4 390(7)	739(5)	3 260(6)
O(3)	4 380(8)	1 811(9)	2 398(5)
O(4)	2 914(6)	3 200(4)	4 097(5)
O(5)	4 471(7)	3 845(6)	3 376(7)
O(6)	4 661(8)	3 885(6)	4 680(9)
O(71)[a]	606(21)	1 631(13)	6 723(11)
O(81)[a]	−314(28)	580(20)	6 021(18)
O(91)[a]	859(30)	352(20)	7 114(17)
O(101)[a]	−695(22)	762(15)	7 302(14)
O(72)[a]	−144(22)	1 698(15)	6 626(12)
O(82)[a]	275(19)	503(12)	6 046(11)
O(92)[a]	1 149(28)	830(21)	7 106(17)
O(102)[a]	−1 046(22)	655(15)	6 898(15)
N(1)	4 369(6)	1 757(5)	4 845(4)
N(2)	3 130(6)	1 723(5)	4 849(4)
C(1)	7 069(7)	1 746(7)	3 578(7)
C(2)	6 956(9)	2 576(8)	3 462(8)
C(3)	7 122(8)	2 956(6)	4 142(9)
C(4)	7 240(7)	2 376(7)	4 688(7)
C(5)	7 209(7)	1 616(6)	4 327(7)
C(6)	7 164(9)	1 129(8)	3 001(7)
C(7)	6 905(11)	2 958(9)	2 723(8)
C(8)	7 287(10)	3 815(7)	4 281(10)
C(9)	7 483(10)	2 515(8)	5 493(7)
C(10)	7 451(10)	833(7)	4 680(7)
C(11)	4 844(9)	1 356(7)	5 425(6)
C(12)	3 963(10)	1 081(8)	5 822(6)
C(13)	2 901(9)	1 311(7)	5 445(6)
C(14)	3 551(12)	196(8)	3 158(10)
C(15)	3 782(19)	2 244(10)	1 920(11)
C(16)	3 726(13)	4 411(9)	3 085(8)
C(17)	4 286(16)	3 980(14)	5 295(9)
C(18)	408(9)	2 169(10)	4 836(8)
C(19)	361(9)	1 466(8)	4 398(9)
C(20)	303(8)	1 517(9)	3 642(8)
C(21)	258(8)	2 270(9)	3 299(8)
C(22)	305(9)	2 945(8)	3 706(9)
C(23)	387(9)	2 913(8)	4 486(10)
Cl(2)[b]	−1 106(25)	450(17)	1 187(17)
Cl(3)[b]	1 034(17)	1 163(12)	1 469(10)
Cl(4)[b]	245(19)	1 435(10)	1 509(9)
Cl(5)[b]	−298(18)	98(10)	666(10)
Cl(6)[b]	1 372(18)	689(14)	1 195(12)
Cl(7)[b]	−1 028(15)	148(9)	835(9)
C(24)[b]	−523(25)	1 239(18)	1 568(16)
C(25)[b]	14(75)	521(30)	1 575(27)
C(26)[b]	246(41)	327(37)	1 522(25)

[a] Oxygen atoms of the disordered ClO_4^- anion. [b] Atom corresponds to model established for the disordered dichloromethane molecule.

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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