Reactivity of Binuclear Pyrazolate-bridged Rhodium Complexes with Isocyanides. Molecular Structure of $[Rh_2(\mu\text{-pz})I_2(CNBu^t)_2(\mu\text{-}Ph_2PCH_2PPh_2)_2]BF_4$ (pz = pyrazolate)†

Daniel Carmona, Luis A. Oro,* and Pedro L. Pérez
Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-Consejo Superior Investigaciones Científicas, 50009 Zaragoza, Spain
Antonio Tiripicchio and Marisa Tiripicchio-Camellini
Istituto di Chimica Generale ed Inorganica, Università di Parma, Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., Viale delle Scienze, 43100 Parma, Italy

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The CO groups of $[Rh_2(\mu\text{-pz})I_2(CO)_2(\mu\text{-dppm})_2]ClO_4$ (pz = pyrazolate, dppm = $Ph_2PCH_2PPh_2$) have been gradually substituted by reaction with isocyanides CNR (R = Bu^t or C_6H_4Me-*p*) to give $[(OC)IRh(\mu\text{-pz})(\mu\text{-dppm})_2RhI(CNR)]ClO_4$ [R = Bu^t (**3**) or C_6H_4Me-*p* (**4**)] *via* $[(OC)IRh(\mu\text{-pz})(\mu\text{-CO})(\mu\text{-dppm})_2RhI(CNR)]ClO_4$ [R = Bu^t (**1**) or C_6H_4Me-*p* (**2**)] and, finally, $[Rh_2(\mu\text{-pz})I_2(CNR)_2(\mu\text{-dppm})_2]ClO_4$ [R = Bu^t (**7**) or C_6H_4Me-*p* (**8**)] *via* $[Rh_2(\mu\text{-pz})I_2(\mu\text{-CO})(CNR)_2(\mu\text{-dppm})_2]ClO_4$ [R = Bu^t (**5**) or C_6H_4Me-*p* (**6**)]. The CO bridging groups of (**1**), (**2**), (**5**), and (**6**) are ketonic carbonyls according to their spectroscopic properties. The reactivity of $[Rh_2(\mu\text{-pz})I_2(CO)_2(\mu\text{-dpam})_2]ClO_4$ (dpam = $Ph_2AsCH_2AsPh_2$) with isocyanides was studied for comparison. The structure of the BF_4^- analogue of (**7**), $[Rh_2(\mu\text{-pz})I_2(CNBu^t)_2(\mu\text{-dppm})_2]BF_4$ (**7b**), has been determined by *X*-ray diffraction methods. Crystals are monoclinic, space group $P2_1/n$ with unit-cell parameters a = 20.347(8), b = 21.221(8), c = 14.514(6) Å, β = 94.11(2)°, and Z = 4. The structure has been solved from diffractometer data by Patterson and Fourier methods and refined by block-matrix least squares to R = 0.0630 for 4 969 observed reflections. In the cationic complex the two Rh atoms, at a distance of 2.829(3) Å, are connected by a triple bridge, involving two dppm ligands and the pyrazolate anion.

Considerable interest has been shown recently in the coordination chemistry of rhodium with pyrazole and pyrazolate-type ligands.[1–26] In this context, we have reported the preparation of bis(diphenylphosphino)methane (dppm)–rhodium A frame complexes of general formula $[Rh_2(\mu\text{-L})(CO)_2(\mu\text{-dppm})_2]ClO_4$ and $[Rh_2(\mu\text{-L})I_2(CO)_2(\mu\text{-dppm})_2]ClO_4$ (L = pyrazolate-type ligand), in which the pyrazolate anion acts as a capping ligand.[19]

On the other hand, complexes containing bridging carbonyl ligands are, generally, accompanied by metal–metal bonds.[27] Only recently have examples in which bridging carbonyls are not accompanied by metal–metal bonds (ketonic carbonyls[28]) been reported,[11,24,25,29–45] some of these examples being in rhodium chemistry.[11,24,25,29–34] In particular, we have described the preparation of binuclear rhodium complexes in which a ketonic carbonyl is supported by pyrazolate bridging groups in the absence of dppm ligands.[24,25]

In this paper we report the reactions of $[Rh_2(\mu\text{-L})I_2(CO)_2(\mu\text{-dppm})_2]ClO_4$, and related bis-diphenylarsino)methane (dpam) complexes, with isocyanide ligands (CNR), leading to the formation of ketonic carbonyls supported, simultaneously, by dppm or dpam, and pyrazolate bridging ligands. In addition this reactivity shows an interesting set of reactions in which, alternatively, the making or breaking of a metal–metal bond occurs.

Results and Discussion

The dirhodium(II) complex, $[Rh_2(\mu\text{-pz})I_2(CO)_2(\mu\text{-dppm})_2]ClO_4$, prepared by transannular oxidative addition of molecular iodine to $[Rh_2(\mu\text{-pz})(CO)_2(\mu\text{-dppm})_2]ClO_4$,[19] reacts with stoicheiometric amounts of t-butyl isocyanide ($CNBu^t$) or *p*-tolyl isocyanide (CNC_6H_4Me-*p*) to give the asymmetric compounds $[(OC)IRh(\mu\text{-pz})(\mu\text{-CO})(\mu\text{-dppm})_2RhI(CNR)]ClO_4$ [R = Bu^t (**1**) or C_6H_4Me-*p* (**2**)]. This reaction involves the transformation of a terminal carbonyl to a bridging carbonyl ligand, accompanied by rhodium–rhodium bond cleavage. Since both rhodium atoms in the dirhodium compound $[Rh_2(\mu\text{-pz})I_2(CO)_2(\mu\text{-dppm})_2]ClO_4$ are 18-electron centres, we suspect that one iodine ligand can dissociate before reaction with the CNR ligands, to give the intermediates $[(OC)IRh(\mu\text{-pz})(\mu\text{-dppm})_2Rh(CO)(CNR)]^{2+}$ which were not detected. Iodide dissociations have been postulated in reactions where iodine ligands are replaced by CNMe groups in saturated rhodium–dppm A frame compounds.[34] The second step would be movement of the terminal carbonyl group attached to the rhodium atom supporting the isocyanide ligand into the bridging position, accompanied by cleavage of the Rh–Rh bond. These CO groups exhibit low values for their stretching frequencies [1 695 (**1**), 1 690 cm^{-1} (**2**) (in CH_2Cl_2)], in line with those reported for carbonyl ligands bridging two metals not bonded to each other.[11,24,25,29–45] The substitution of terminal CO groups in A frame rhodium complexes by isocyanide ligands is well documented,[26,34,46–48] but no ketonic carbonyls have been found in this reaction. Recently, Cowie *et al.*[45] have described the related transformation of a terminal to a bridging ketonic carbonyl ligand accompanied by Ir–Ir bond cleavage, and have proposed that this transformation takes place in order to remove excess of electron density from the second metal atom. In our case a similar effect could be operating: the good π-acceptor group, CO, moves from the rhodium atom that

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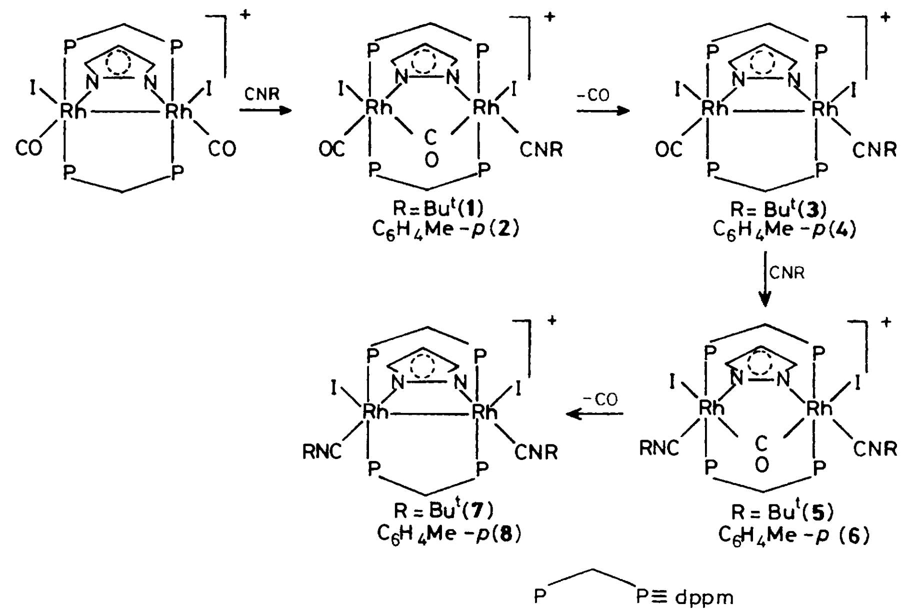
† Di-μ-[bis(diphenylphosphino)methane]-μ-pyrazolato-N^1N^2-bis-[iodo(t-butyl isocyanide)rhodium(II)] (*Rh–Rh*) tetrafluoroborate.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.



Scheme.

supports a greater positive charge to the rhodium atom which is richer in electron density and which retains its co-ordinated iodine atom.

Interestingly, the Rh–Rh bond can be restored by bubbling molecular nitrogen through refluxing chloroform solutions of complexes (**1**) and (**2**). Under these conditions the asymmetric dirhodium(II) compounds [(OC)IRh(μ-pz)(μ-dppm)$_2$RhI(CNR)]ClO$_4$ (R = Bu^t (**3**) or C$_6$H$_4$Me-p (**4**)] are obtained. Further addition of the corresponding CNR ligand to these complexes [(**3**) and (**4**)] gives rise to the symmetrical compounds [Rh$_2$(μ-pz)I$_2$(μ-CO)(CNR)$_2$(μ-dppm)$_2$]ClO$_4$ (R = Bu^t (**5**) or C$_6$H$_4$Me-p (**6**)]. After bubbling molecular nitrogen (in refluxing chloroform) through (**5**) and (**6**) complexes of formula [Rh$_2$(μ-pz)I$_2$(CNR)$_2$(μ-dppm)$_2$]ClO$_4$ [R = Bu^t (**7**) or C$_6$H$_4$Me-p (**8**)] are formed. These two reactions are similar to that described above for (**1**) and (**2**), the reaction occurring at the second rhodium centre (see Scheme).

The above-mentioned dirhodium(II) complexes, (**3**) and (**4**), and (**7**) and (**8**), can also be obtained by oxidation of the dirhodium(I) complexes [(OC)Rh(μ-pz)(μ-dppm)$_2$Rh(CNR)]ClO$_4$ [R = Bu^t (**9**) or C$_6$H$_4$Me-p (**10**)] and [Rh$_2$(μ-pz)(CNR)$_2$(μ-dppm)$_2$]ClO$_4$ [R = Bu^t (**11**) or C$_6$H$_4$Me-p (**12**)]. Complexes (**9**)—(**12**)* were obtained by reaction of [Rh$_2$(μ-pz)(CO)$_2$(μ-dppm)$_2$]ClO$_4$ with 1 or 2 equivalents of CNR. Interestingly, the reaction can be reversed by treatment with carbon monoxide. Thus, when carbon monoxide was bubbled through dichloromethane solutions of complex (**11**) or (**12**) at atmospheric pressure and room temperature the CNR ligands were displaced, with formation of the dicarbonyl complex [Rh$_2$(μ-pz)(CO)$_2$(μ-dppm)$_2$]ClO$_4$ *via* the asymmetric complexes (**9**) and (**10**), respectively, according to i.r. solution measurements.

Although no formation of ketonic carbonyl compounds of formulae [(OC)Rh(μ-pz)(μ-CO)(μ-dppm)$_2$Rh(CNR)]ClO$_4$ and [Rh$_2$(μ-pz)(μ-CO)(CNR)$_2$(μ-dppm)$_2$]ClO$_4$, related to the isolated di-iodide complexes (**1**) and (**2**), and (**5**) and (**6**), was detected, these intermediates could be involved in the reactions. However, the latter di-iodide compounds do not react with carbon monoxide (1 atm., 20 °C).

The ν(CO) and ν(CN) i.r. bands for the new complexes are presented in Table 1. As expected, the increase in the oxidation state of the rhodium centres, from I to II, is accompanied by a shift of the isocyanide and terminal carbonyl stretching frequencies to higher energies (*ca.* 50 cm^{-1}).[19]

The terminal ν(CO) and ν(CN) frequencies of the complexes that contain μ-CO ketonic ligands, (**1**), (**2**), (**5**), and (**6**), are shifted to higher energies than those of the related complexes without the CO bridging group. These shifts could be explained in terms of the π-acceptor capacity of the additional μ-CO ligand, which, in an extreme formulation, can be considered as a CO^{2-} group. According to Hoffmann's theoretical calculations,[28] the rhodium atoms would then be in a formal oxidation state of III.

The ^{31}P-{^{1}H} n.m.r. spectra of the symmetrical compounds, (**7**), (**8**), (**11**), and (**12**), show the second-order AA′A″A‴XX′ pattern characteristic of this type of complex. The separation between the two major peaks, analysed as ^1J(Rh–P) + ^xJ(Rh–P),[31,47,49–51] also reflects the change in the oxidation state of the metal centres. Thus, for complexes (**7**) and (**8**) the two principal lines are separated by 93.4 and 90.7 Hz, respectively, while for (**11**) and (**12**) the separations are 140.9 and 138.2 Hz respectively. All the values are in good agreement with those reported in the literature for related A frame rhodium complexes.[19,26]

The ^{31}P-{^{1}H} n.m.r. spectra of complexes (**4**), (**5**), (**9**), and (**10**) show complicated asymmetric multiplets, while the asymmetric complexes (**1**)—(**3**) present two sets of resonances attributable to AA′BB′XY spin systems, consistent with two different rhodium environments.[52]

The ^{1}H n.m.r. spectra show signals due to the isocyanide and dppm groups in the appropriate intensity ratios in each case. The protons of the pyrazolate anion are obscured by the protons of the phenyl groups of the dppm ligands (Table 2).

We have also prepared the bis(diphenylarsino)methane (perchlorate) complex [Rh$_2$(μ-pz)(CO)$_2$(μ-dpam)$_2$]ClO$_4$† (**13**)

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* These complexes were communicated by us at the '5$^{\text{eme}}$ Conference Fechem de Chimie Organometallique,' Cap D'Agde, 1984, and have recently been reported, in full, as PF$_6$ derivatives by Woods and co-workers.[26]

† The hexafluorophosphate salt has been reported by Woods and co-workers.[26]

Table 1. Carbonyl and isocyanide stretching bands * for the new complexes

Complex	ν(CO)/cm^{-1}	ν(CN)/cm^{-1}
(1) [(OC)IRh(μ-pz)(μ-CO)(μ-dppm)$_2$RhI(CNBu^t)]ClO$_4$	2 085 1 695	2 205
(2) [(OC)IRh(μ-pz)(μ-CO)(μ-dppm)$_2$RhI(CNC$_6$H$_4$Me-*p*)]ClO$_4$	2 089, 1 690	2 190
(3) [(OC)IRh(μ-pz)(μ-dppm)$_2$RhI(CNBu^t)]ClO$_4$	2 030	2 170
(4) [(OC)IRh(μ-pz)(μ-dppm)$_2$RhI(CNC$_6$H$_4$Me-*p*)]ClO$_4$	2 027	2 157
(5) [Rh$_2$(μ-pz)I$_2$(μ-CO)(CNBu^t)$_2$(μ-dppm)$_2$]ClO$_4$	1 690	2 200
(6) [Rh$_2$(μ-pz)I$_2$(μ-CO)(CNC$_6$H$_4$Me-*p*)$_2$(μ-dppm)$_2$]ClO$_4$	1 690	2 180
(7) [Rh$_2$(μ-pz)I$_2$(CNBu^t)$_2$(μ-dppm)$_2$]ClO$_4$		2 165
(8) [Rh$_2$(μ-pz)I$_2$(CNC$_6$H$_4$Me-*p*)$_2$(μ-dppm)$_2$]ClO$_4$		2 152
(9) [(OC)Rh(μ-pz)(μ-dppm)$_2$Rh(CNBu^t)]ClO$_4$	1 982	2 120
(10) [(OC)Rh(μ-pz)(μ-dppm)$_2$Rh(CNC$_6$H$_4$Me-*p*)]ClO$_4$	1 984	2 103
(11) [Rh$_2$(μ-pz)(CNBu^t)$_2$(μ-dppm)$_2$]ClO$_4$		2 117
(12) [Rh$_2$(μ-pz)(CNC$_6$H$_4$Me-*p*)$_2$(μ-dppm)$_2$]ClO$_4$		2 105
(13) [Rh$_2$(μ-pz)(CO)$_2$(μ-dpam)$_2$]ClO$_4$	1 998	
(14) [Rh$_2$(μ-pz)I$_2$(CO)$_2$(μ-dpam)$_2$]ClO$_4$	2 053	
(15) [(OC)IRh(μ-pz)(μ-CO)(μ-dpam)$_2$RhI(CNBu^t)]ClO$_4$	2 083, 1 697	2 200
(16) [(OC)IRh(μ-pz)(μ-dpam)$_2$RhI(CNBu^t)]ClO$_4$	2 027	2 170
(17) [Rh$_2$(μ-pz)I$_2$(μ-CO)(CNBu^t)$_2$(μ-dpam)$_2$]ClO$_4$	1 683	2 205
(18) [Rh$_2$(μ-pz)I$_2$(CNBu^t)$_2$(μ-dpam)$_2$]ClO$_4$		2 168
(19) [(OC)Rh(μ-pz)(μ-dpam)$_2$Rh(CNBu^t)]ClO$_4$	1 983	2 120
(20) [Rh$_2$(μ-pz)(CNBu^t)$_2$(μ-dpam)$_2$]ClO$_4$		2 117

* In CH$_2$Cl$_2$ solution. All absorptions collected are very strong.

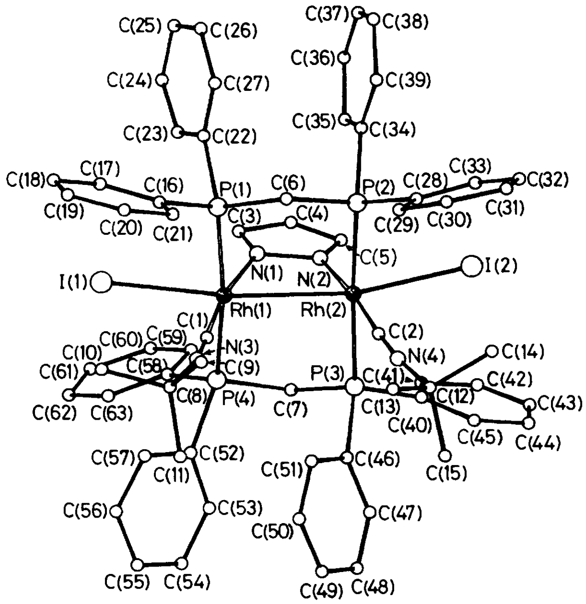

Figure. View of the structure of the cationic complex [Rh$_2$(μ-pz)I$_2$(CNBu^t)$_2$(μ-dppm)$_2$]$^+$ showing the atomic numbering. The hydrogen atoms have been omitted for clarity

following a similar procedure to that reported by us for the synthesis of the dppm complex.[19] This complex reacts with molecular iodine to give the dirhodium(II) compound [Rh$_2$(μ-pz)I$_2$(CO)$_2$(μ-dpam)$_2$]ClO$_4$ **(14)**. We assume, from the preparative method and spectroscopic and analytical data (Table 2), that complex **(14)** has a similar structure to that of the corresponding dppm complex, [Rh$_2$(μ-pz)I$_2$(CO)$_2$(μ-dppm)$_2$]ClO$_4$. In fact, complex **(14)** undergoes a similar set of reactions with CNBu^t to those described in the Scheme for the corresponding dppm complex. Thus, we have characterized the complex [(OC)IRh(μ-pz)(μ-CO)(μ-dpam)$_2$RhI(CNBu^t)]ClO$_4$ **(15)** by i.r. spectroscopy in solution, although we have not been able to isolate pure complex **(15)** in the solid state, because it easily loses the CO bridge yielding [(OC)IRh(μ-pz)(μ-dpam)$_2$RhI(CNBu^t)]ClO$_4$ **(16)**. This latter complex was prepared by bubbling molecular dinitrogen through solutions containing **(15)**, at room temperature and atmospheric pressure.

Similarly, we have detected, spectroscopically, in solution the complex [Rh$_2$(μ-pz)I$_2$(μ-CO)(CNBu^t)$_2$(μ-dpam)$_2$]ClO$_4$, **(17)**, and characterized, in the solid state, the compound [Rh$_2$(μ-pz)I$_2$(CNBu^t)$_2$(μ-dpam)$_2$]ClO$_4$ **(18)** by bubbling molecular nitrogen through a dichloromethane solution of **(17)**. Complexes **(16)** and **(18)** can be readily prepared by addition of molecular iodine to [(OC)Rh(μ-pz)(μ-dpam)$_2$Rh(CNBu^t)]ClO$_4$ **(19)** and [Rh$_2$(μ-pz)(CNBu^t)$_2$(μ-dpam)$_2$]ClO$_4$ **(20)** which, in turn, can be prepared from **(13)** by replacing one or two of the CO terminal groups by the CNBu^t ligand.

The ν(CO) and ν(CN) stretching frequencies of these dpam derivatives show similar trends to the corresponding dppm complexes (see Table 1).

However, the stability of the ketonic carbonyls supported by dpam ligands, in our compounds, seems to be less than that of the corresponding dppm derivatives. This is probably due to the larger 'bite' of the dpam ligand compared to dppm. Thus, for instance, the rhodium–rhodium distance in the complex [Rh$_2$(μ-dmpz)(CO)$_2$(μ-dppm)$_2$]ClO$_4$ is[19] 3.060 Å while in the homologous dpam complex [Rh$_2$(μ-dmpz)(CO)$_2$(μ-dpam)$_2$]PF$_6$·0.75CH$_2$Cl$_2$ (dmpz = 3,5-dimethylpyrazolate) it is 3.220 Å.[26] In this context it has been noted that dpam complexes exchange CO bridging groups more easily than do the corresponding dppm compounds.[50]

Crystal Structure of [Rh$_2$(μ-pz)I$_2$(CNBu^t)$_2$(μ-dppm)$_2$]BF$_4$ **(7b)**.—A view of the cationic complex **(7b)**, including the numbering scheme, is shown in the Figure. Selected bond distances and angles are given in Table 3. The two Rh atoms, at a distance of 2.829(3) Å, are connected by a triple bridge involving the dppm ligands through the P atoms and the pyrazolate anion through the N atoms. The dppm bridges are almost in the same plane [dihedral angle between the mean planes passing through Rh(1),P(1),C(6),P(2),Rh(2) and Rh(1),P(4),C(7),P(3),Rh(2) 2.2(1)°]. The pyrazolate bridge is almost perpendicular to the dppm ones, the dihedral angles between the mean planes passing through Rh(1),N(1),N(2),Rh(2) and Rh(1),P(1),C(6),P(2),Rh(2) and Rh(1),P(4),C(7),P(3),Rh(2) being 83.3(2) and 83.1(2)° respectively. The distorted octahedral

Table 2. Analytical,[a] ^{31}P-{^{1}H}[b] and ^{1}H n.m.r. data,[c] and conductivity measurements[d] for the new complexes

Complex	Analysis/% C	Analysis/% H	Analysis/% N	^{31}P N.m.r. δ[e]/p.p.m.	^{31}P N.m.r. J(Rh–P)/Hz[f]	^{1}H N.m.r.[g] δ[h]	Λ_m/Ω^{-1} cm^2 mol^{-1}	Yield/%
(1)	46.6	4.3	2.7	13.1	105[i]	0.93(s), 2.60(m), 7—7.8(m)	122	85
	(47.0)	(3.7)	(2.7)	9.0	98			
(2)	47.4	3.1	2.7	21.4	113[i]			84
	(48.2)	(3.5)	(2.7)	9.6	100			
(3)	46.4	4.9	3.0	8.4	58.4[j]	1.04(s), 4.11(m), 6.30(br s), 7—8(m)	113	90
	(47.0)	(3.7)	(2.8)	2.2				
(4)	48.3	4.0	2.6	*k*			115	80
	(48.3)	(3.5)	(2.7)					
(5)	47.4	4.0	3.2	*l*		0.93(s), 2.5(m), 7—7.8(m)	133	88
	(48.4)	(4.1)	(3.5)					
(6)	51.4	4.0	3.7	6.4	110	2.33(s), 2.40(m), 6.5—8(m)		74
	(50.7)	(3.7)	(3.4)					
(7)	48.2	4.2	3.9	4.7	93.4	1.11(s), 3.84(m), 6.43(br s), 7—8(m)	428[m]	93
	(48.5)	(4.2)	(3.6)					
(8)	51.4	3.9	3.4	4.2	90.7	2.38(s), 4.24(m), 6.25(s), 6.5—8(m)	126	85
	(50.9)	(3.8)	(3.4)					
(9)	56.8	5.0	3.5	*n*			114	88
	(56.6)	(4.5)	(3.3)					
(10)	57.8	4.6	3.5	*o*			116	87
	(57.9)	(4.2)	(3.3)					
(11)	57.6	5.1	4.4	23.6	140.9	0.99(s), 3.34(m), 6.24(br s), 6.8—8(m)	113	89
	(57.9)	(5.0)	(4.3)					
(12)	59.9	4.6	4.1	24.1	138.2		127	80
	(60.2)	(4.6)	(4.1)					
(13)	47.9	3.4	1.7				112	93
	(48.1)	(3.4)	(2.0)					
(14)	41.0	3.1	1.9					83
	(40.6)	(2.9)	(1.7)					
(16)	41.9	4.1	2.8					85
	(42.1)	(3.4)	(2.5)					
(18)	42.7	3.9	2.6			1.00(s), 3.8[p] 6.14(br s), 7—8.2(m)		88
	(43.6)	(3.7)	(3.2)					
(19)	49.0	3.9	3.0					88
	(49.6)	(3.9)	(2.9)					
(20)	50.1	4.9	4.0			0.78(s), 3.7[p] 6.07(t) (J = 2 Hz), 6.9—8.2(m)		79
	(51.0)	(4.4)	(3.8)					

[a] Caclulated values in parentheses. [b] In $CHCl_3$–$CDCl_3$ (1:1) solution. [c] In $CDCl_3$. [d] At room temperature in *ca.* 5 × 10^{-4} mol dm^{-3} acetone solutions. [e] These chemical shifts are relative to 85% H_3PO_4. [f] These coupling constants are $|^1J(\text{Rh–P}) + {}^xJ(\text{Rh–P})|$, the separations between the major peaks in the AA′A″A‴XX′ multiplet, unless otherwise stated. [g] Key: s = singlet; t = triplet; m = multiplet; br = broad. [h] These chemical shifts are relative to $SiMe_4$. [i] Separation between the two major peaks of the two complex multiplets. [j] $|^2J(P_A\text{–C–}P_B) + {}^4J(P_A\text{–}P_{B'})|$ in the AA′BB′XY spin system.[52] [k] Multiplet centred at 5.4 p.p.m. [l] Multiplet centred at 8.5 p.p.m. [m] Value of A in Onsager's equation $\Lambda_e = \Lambda_o - A\sqrt{c}$. [n] Multiplet centred at 25 p.p.m. [o] Multiplet centred at 26 p.p.m. [p] Centre of the AB system.

co-ordination around each Rh atom is completed by an iodide ligand and by a carbon atom from the isocyanide ligand.

The structure of the cation of (**7b**) is comparable with that of $[Rh_2(\mu\text{-dmpz})I_2(CO)_2(\mu\text{-dppm})_2]^+$,[19] where the carbonyl groups are substituted for the isocyanide ligands and the 3,5-dimethylpyrazolate anion (dmpz) replaces the unsubstituted pyrazolate anion. This complex can be obtained by addition of iodine to $[Rh_2(\mu\text{-dmpz})(CO)_2(\mu\text{-dppm})_2]^+$. The most significant differences concern the Rh–Rh separation, which is shorter in the dmpz complex [2.725(2) Å]; the Rh–N bond distances, longer in the dmpz complex [2.09(1) Å]; and the Rh–P bond distances, almost equal in the dmpz complex [2.389(5) and 2.397(5) Å] unlike in (**7b**), where the dppm ligands bridge the metal atoms in an asymmetric way [2.355(5) and 2.391(5) Å for the Rh–P bonds involving the P(1) and P(2) atoms and 2.350(5) and 2.395(5) Å for the Rh–P bonds involving the P(3) and P(4) atoms].

Experimental

Infrared spectra were recorded on a Perkin-Elmer 577 spectrophotometer (range 4 000—200 cm^{-1}) using Nujol mulls between polyethylene sheets, or dichloromethane solutions between NaCl plates. Conductivities were measured at room temperature, in *ca.* 5 × 10^{-4} mol dm^{-3} acetone solutions, with a Philips PW 9501/01 conductimeter. The C, H, and N analyses were carried out with a Perkin-Elmer 240B microanalyzer. All reported complexes gave correct elemental analysis. Phosphorus-31 and ^{1}H n.m.r. spectra were recorded for $CDCl_3$–$CHCl_3$ (1:1) and $CDCl_3$ solutions, at room temperature on a Varian XL 200 spectrometer [32.2 (^{31}P) and 200 MHz (^{1}H)] using 85% H_3PO_4 and $SiMe_4$ as external standards, respectively. Solvents were dried and distilled before use.

$[(OC)IRh(\mu\text{-pz})(\mu\text{-CO})(\mu\text{-dppm})_2RhI(CNR)]ClO_4$ [R = Bu^t (**1**) *or* C_6H_4Me-*p* (**2**)].—To solutions of $[Rh_2(\mu\text{-pz})I_2(CO)_2(\mu\text{-dppm})_2]ClO_4$ (145.1 mg, 0.10 mmol) in dichloromethane (20 cm^3) the corresponding isocyanide (0.10 mmol) was added. The colour gradually changed from red-brown to orange. After 30 min the solutions were partially concentrated under reduced pressure. Slow addition of diethyl ether gave

Table 3. Selected bond distances (Å) and angles (°) for complex (**7b**)

Rh(1)–Rh(2)	2.829(3)		
Rh(1)–I(1)	2.738(3)	Rh(2)–I(2)	2.766(6)
Rh(1)–P(1)	2.355(5)	Rh(2)–P(2)	2.391(5)
Rh(1)–P(4)	2.395(5)	Rh(2)–P(3)	2.350(5)
Rh(1)–N(1)	2.056(12)	Rh(2)–N(2)	2.054(11)
Rh(1)–C(1)	1.92(2)	Rh(2)–C(2)	1.90(2)
N(1)–C(3)	1.40(2)	N(2)–C(5)	1.36(2)
C(3)–C(4)	1.40(2)	C(4)–C(5)	1.42(2)
N(1)–N(2)	1.36(2)	C(2)–N(4)	1.17(2)
C(1)–N(3)	1.14(2)	N(4)–C(12)	1.47(2)
N(3)–C(8)	1.53(2)	P(3)–C(7)	1.85(2)
P(1)–C(6)	1.84(2)	P(4)–C(7)	1.83(2)
P(2)–C(6)	1.84(2)		
Rh(2)–Rh(1)–I(1)	168.5(1)	Rh(1)–Rh(2)–I(2)	159.4(1)
Rh(2)–Rh(1)–N(1)	69.2(4)	Rh(1)–Rh(2)–N(2)	68.9(3)
Rh(2)–Rh(1)–P(1)	92.3(1)	Rh(1)–Rh(2)–P(2)	93.0(1)
Rh(2)–Rh(1)–P(4)	94.3(1)	Rh(1)–Rh(2)–P(3)	90.0(1)
Rh(2)–Rh(1)–C(1)	100.4(6)	Rh(1)–Rh(2)–C(2)	107.7(6)
I(1)–Rh(1)–N(1)	99.5(4)	I(2)–Rh(2)–N(2)	91.0(4)
I(1)–Rh(1)–P(1)	87.1(1)	I(2)–Rh(2)–P(2)	85.5(1)
I(1)–Rh(1)–P(4)	85.6(1)	I(2)–Rh(2)–P(3)	93.2(1)
I(1)–Rh(1)–C(1)	91.0(6)	I(2)–Rh(2)–C(2)	92.8(6)
N(1)–Rh(1)–P(1)	95.3(4)	N(2)–Rh(2)–P(2)	97.7(4)
N(1)–Rh(1)–P(4)	83.2(4)	N(2)–Rh(2)–P(3)	87.5(4)
N(1)–Rh(1)–C(1)	169.5(7)	N(2)–Rh(2)–C(2)	174.4(7)
P(1)–Rh(1)–P(4)	172.2(2)	P(2)–Rh(2)–P(3)	174.7(2)
P(1)–Rh(1)–C(1)	85.9(6)	P(2)–Rh(2)–C(2)	86.9(6)
P(4)–Rh(1)–C(1)	97.1(6)	P(3)–Rh(2)–C(2)	88.1(6)
Rh(1)–N(1)–N(2)	110.4(9)	Rh(2)–N(2)–N(1)	111.1(9)
P(1)–C(6)–P(2)	112.0(9)	P(3)–C(7)–P(4)	111.2(8)
Rh(1)–C(1)–N(3)	176.3(16)	Rh(2)–C(2)–N(4)	175.6(16)
C(1)–N(3)–C(8)	168.2(17)	C(2)–N(4)–C(12)	172.9(17)

complexes (**1**) and (**2**) as orange microcrystalline solids, which were filtered off, washed with diethyl ether, and air-dried.

$[(OC)IRh(\mu\text{-pz})(\mu\text{-dppm})_2RhI(CNR)]ClO_4$ [R = Bu^t (**3**) *or* C_6H_4Me-*p* (**4**)].—Dinitrogen at atmospheric pressure was bubbled, for 6 h, through refluxing chloroform solutions (*ca.* 10^{-2} mol dm^{-3}) of complexes (**1**) and (**2**). During this time the colour changed from orange to red-brown. Complexes (**3**) and (**4**) were isolated after partial concentration under reduced pressure and slow addition of diethyl ether.

Alternatively, these complexes can be prepared starting from $[(OC)Rh(\mu\text{-pz})(\mu\text{-dppm})_2Rh(CNBu^t)]ClO_4$ (**9**) and $[(OC)Rh(\mu\text{-pz})(\mu\text{-dppm})_2Rh(CNC_6H_4Me\text{-}p)]ClO_4$ (**10**) as follows. To solutions of (**9**) and (**10**) (0.10 mmol) in dichloromethane (20 cm^3) iodine (25.4 mg, 0.10 mmol) in the same solvent (5 cm^3) was added. The colour changed from violet-purple to red-brown. After stirring for 15 min the solutions were partially concentrated under reduced pressure, and slow addition of diethyl ether gave brown microcrystalline solids, which were filtered off, washed with diethyl ether, and air-dried.

$[Rh_2(\mu\text{-pz})I_2(\mu\text{-CO})(CNR)_2(\mu\text{-dppm})_2]ClO_4$ [R = Bu^t (**5**) *or* C_6H_4Me-*p* (**6**)].—The orange complexes (**5**) and (**6**) were prepared as described for (**1**) and (**2**), but starting from (**3**) and (**4**).

$[Rh_2(\mu\text{-pz})I_2(CNR)_2(\mu\text{-dppm})_2]ClO_4$ [R = Bu^t (**7**) *or* C_6H_4-Me-*p* (**8**)].—Bubbling of dinitrogen through refluxing chloroform solutions of complexes (**5**) and (**6**) [under similar conditions to those described for the preparation of (**3**) and (**4**) from (**1**) and (**2**)] gives (**7**) and (**8**), respectively.

Alternatively, complexes (**7**) and (**8**) can be prepared starting from $[Rh_2(\mu\text{-pz})(CNBu^t)_2(\mu\text{-dppm})_2]ClO_4$ (**11**) and $[Rh_2(\mu\text{-pz})(CNC_6H_4Me\text{-}p)_2(\mu\text{-dppm})_2]ClO_4$ (**12**), respectively, with work up as described in the preparation of complexes (**3**) and (**4**) from (**9**) and (**10**).

$[(OC)Rh(\mu\text{-pz})(\mu\text{-dppm})_2Rh(CNR)]ClO_4$ [R = Bu^t (**9**) *or* C_6H_4Me-*p* (**10**)].—To solutions of $[Rh_2(\mu\text{-pz})(CO)_2(\mu\text{-dppm})_2]ClO_4$ (119.7 mg, 0.10 mmol) in dichloromethane (20 cm^3), the corresponding isocyanide (0.10 mmol) was added. The colour immediately changed from red to violet-purple. After 15 min, the solvent was partially removed *in vacuo* and diethyl ether was added to give complexes (**9**) and (**10**) as violet-purple microcrystalline solids, which were separated by filtration, washed with diethyl ether, and air-dried.

$[Rh_2(\mu\text{-pz})(CNR)_2(\mu\text{-dppm})_2]ClO_4$ [R = Bu^t (**11**) *or* C_6H_4Me-*p* (**12**)].—The violet-purple complexes (**11**) and (**12**) were prepared similarly to (**9**) and (**10**) by adding to solutions of $[Rh_2(\mu\text{-pz})(CO)_2(\mu\text{-dppm})_2]ClO_4$ the isocyanide ligands in a 1:2 molar ratio or by adding 1 mole equivalent of the corresponding isocyanide to complexes (**9**) and (**10**).

Reaction of Complexes (**11**) *and* (**12**) *with Carbon Monoxide*.—Carbon monoxide was bubbled through dichloromethane solutions (*ca.* 10^{-2} mol dm^{-3}) of complexes (**11**) and (**12**) at atmospheric pressure and room temperature. The reactions were monitored by i.r. spectroscopy. After 15 min of treatment, the carbonyl and isocyanide i.r. bands attributable to (**9**) and (**10**), respectively, were observed. After 1 h of reaction the only observable i.r. carbonyl pattern was that attributable to $[Rh_2(\mu\text{-pz})(CO)_2(\mu\text{-dppm})_2]ClO_4$,[19] along with bands assignable to the corresponding free isocyanides (R = Bu^t, 2 140; C_6H_4Me-*p*, 2 165 cm^{-1}).

$[Rh_2(\mu\text{-pz})(CO)_2(\mu\text{-dpam})_2]ClO_4$ (**13**).—Silver perchlorate (41.5 mg, 0.20 mmol) was added to a suspension of *trans*-$[Rh_2Cl_2(CO)_2(\mu\text{-dpam})_2]$ [53] (127.7 mg, 0.10 mmol) in acetone (20 cm^3). The resulting mixture was stirred in the absence of light, for 30 min and the AgCl formed removed by filtration. Addition to the filtrate of pyrazole (6.8 mg, 0.10 mmol) and a methanolic solution of KOH (0.1942 mol dm^{-3}, 0.51 cm^3, 0.1 mmol) gave an orange-red solution, which after filtration was evaporated to dryness under reduced pressure. The residue was extracted with dichloromethane (15 cm^3) and after filtration to remove any impurity was partially concentrated under reduced pressure. Slow addition of diethyl ether gave an orange-red solid, which was filtered off, washed with diethyl ether, and air-dried.

$[Rh_2(\mu\text{-pz})I_2(CO)_2(\mu\text{-dpam})_2]ClO_4$ (**14**).—To a solution of $[Rh_2(\mu\text{-pz})(CO)_2(\mu\text{-dpam})_2]ClO_4$ (137.3 mg, 0.10 mmol) in dichloromethane (20 cm^3) was added a stoicheiometric amount of iodine (25.4 mg, 0.10 mmol) in the same solvent (5 cm^3). The colour immediately changed from orange-red to red-brown. After stirring for 15 min the solution was partially concentrated under reduced pressure. Slow addition of diethyl ether gave a brown microcrystalline solid, which was filtered off, washed with carbon tetrachloride and diethyl ether, and air-dried.

All the remaining dpam complexes were prepared by using similar procedures to those described for their corresponding dppm compounds.

Crystal-structure Determination and Refinement of $[Rh_2(\mu\text{-pz})I_2(CNBu^t)_2(\mu\text{-dppm})_2]BF_4$ (**7b**).—Even if of small size, the crystals of the tetrafluoroborate complex (**7b**) were found suitable for *X*-ray analysis, unlike those of the perchlorate (**7**). A prismatic orange crystal of (**7b**) of approximate dimensions 0.05 × 0.15 × 0.23 mm was used.

Crystal data. $C_{63}H_{65}BF_4I_2N_4P_4Rh_2$, *M* = 1 548.55, mono-

Table 4. Fractional atomic co-ordinates (× 10^4) with estimated standard deviations (e.s.d.s) in parentheses for non-hydrogen atoms of complex (**7b**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Rh(1)	1 702(1)	2 960(1)	1 773(1)	C(29)	1 638(8)	1 352(8)	−1 512(12)
Rh(2)	668(1)	2 223(1)	878(1)	C(30)	1 590(9)	851(9)	−2 186(13)
I(1)	2 518(1)	3 871(1)	2 550(1)	C(31)	991(10)	694(9)	−2 656(14)
I(2)	−500(1)	1 927(1)	−69(1)	C(32)	460(9)	1 047(9)	−2 533(13)
P(1)	2 183(2)	3 163(2)	375(3)	C(33)	460(9)	1 568(9)	−1 913(13)
P(2)	1 082(2)	2 393(2)	−615(3)	C(34)	799(8)	3 043(8)	−1 395(11)
P(3)	309(2)	1 956(2)	2 319(3)	C(35)	500(8)	3 548(8)	−1 052(12)
P(4)	1 265(2)	2 894(2)	3 259(3)	C(36)	324(9)	4 087(9)	−1 686(13)
N(1)	874(6)	3 495(6)	1 458(9)	C(37)	504(10)	4 033(10)	−2 581(15)
N(2)	370(6)	3 125(5)	1 103(9)	C(38)	804(10)	3 541(10)	−2 927(14)
N(3)	2 791(7)	1 973(7)	2 067(9)	C(39)	973(8)	2 995(9)	−2 336(13)
N(4)	1 164(7)	857(6)	744(10)	C(40)	−561(7)	1 800(7)	2 276(10)
C(1)	2 376(9)	2 334(9)	1 984(12)	C(41)	−1 016(8)	2 276(8)	2 450(11)
C(2)	1 008(9)	1 387(9)	796(12)	C(42)	−1 714(8)	2 157(8)	2 296(12)
C(3)	612(9)	4 089(9)	1 627(13)	C(43)	−1 933(9)	1 570(9)	2 051(13)
C(4)	−63(9)	4 068(9)	1 379(13)	C(44)	−1 484(9)	1 082(9)	1 927(13)
C(5)	−205(8)	3 452(8)	1 047(11)	C(45)	−776(9)	1 183(8)	2 044(12)
C(6)	1 975(8)	2 533(8)	−464(11)	C(46)	676(7)	1 310(7)	3 017(10)
C(7)	404(7)	2 643(7)	3 105(11)	C(47)	295(8)	1 025(8)	3 688(12)
C(8)	3 426(9)	1 601(10)	2 275(14)	C(48)	599(8)	595(8)	4 313(12)
C(9)	3 577(10)	1 237(10)	1 432(15)	C(49)	1 248(9)	445(9)	4 286(13)
C(10)	3 942(10)	2 123(10)	2 533(15)	C(50)	1 620(9)	730(10)	3 642(14)
C(11)	3 312(11)	1 144(11)	3 086(17)	C(51)	1 338(8)	1 163(8)	2 991(11)
C(12)	1 284(10)	184(9)	604(14)	C(52)	1 690(8)	2 414(8)	4 169(11)
C(13)	1 971(14)	51(13)	562(19)	C(53)	1 331(8)	2 158(8)	4 889(12)
C(14)	828(14)	13(14)	−314(20)	C(54)	1 681(10)	1 871(10)	5 659(14)
C(15)	993(9)	−170(9)	1 479(13)	C(55)	2 358(10)	1 836(9)	5 720(14)
C(16)	3 078(8)	3 157(8)	356(11)	C(56)	2 718(10)	2 114(10)	5 046(15)
C(17)	3 422(10)	3 711(9)	636(13)	C(57)	2 381(9)	2 382(9)	4 255(13)
C(18)	4 126(10)	3 721(9)	636(13)	C(58)	1 154(7)	3 638(7)	3 919(11)
C(19)	4 455(11)	3 182(11)	383(16)	C(59)	581(9)	3 979(9)	3 757(13)
C(20)	4 139(10)	2 647(10)	85(14)	C(60)	520(10)	4 544(10)	4 302(15)
C(21)	3 423(8)	2 628(8)	78(12)	C(61)	1 049(10)	4 720(10)	4 929(14)
C(22)	2 014(7)	3 918(7)	−208(10)	C(62)	1 588(9)	4 369(9)	5 107(14)
C(23)	1 803(8)	4 436(8)	244(12)	C(63)	1 665(8)	3 813(8)	4 558(12)
C(24)	1 724(9)	5 026(9)	−161(13)	F(1)	3 211(8)	1 340(8)	7 684(12)
C(25)	1 873(9)	5 083(9)	−1 110(14)	F(2)	4 046(9)	1 250(9)	8 688(14)
C(26)	2 080(10)	4 555(10)	−1 576(14)	F(3)	3 133(11)	1 184(10)	9 125(16)
C(27)	2 159(8)	3 982(8)	−1 132(12)	F(4)	3 378(11)	497(13)	8 341(16)
C(28)	1 048(8)	1 703(7)	−1 413(11)	B(1)	3 490(8)	1 093(8)	8 396(12)

clinic, space group $P2_1/n$, $a = 20.347(8)$, $b = 21.221(8)$, $c = 14.514(6)$ Å, $\beta = 94.11(2)°$, $U = 6\,251(4)$ Å^3 (by least-squares refinement of the θ values, in the range 18—35°, of 29 accurately measured reflections), $Z = 4$, $\lambda = 1.541\,78$ Å, $D_c = 1.646$ g cm^{-3}, $F(000) = 3\,072$, $\mu(\text{Cu-}K_\alpha) = 136.46$ cm^{-1}.

A Siemens AED diffractometer with θ—2θ scan mode and nickel-filtered Cu-K_α radiation was used; all the reflections with θ in the range 3—65° were measured. Of 10 552 independent reflections, 4 969, having $I > 2\sigma(I)$, were considered observed and used in the analysis. The individual reflection profiles were analysed,[54] the structure amplitudes were obtained after correcting for Lorentz and polarization effects. Data reduction, structure solution, and refinement were carried out on the GOULD-SEL 32/77 computer of the Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., Parma, using the SHELX 76[55] system of crystallographic computer programs. A correction for absorption was applied (maximum and minimum correction coefficients applied to F_o were 1.292 and 0.856),[56a] using ABSORB.[56b] The structure was solved by Patterson and Fourier methods and refined by block-matrix least squares (first with isotropic and then with anisotropic thermal parameters for the Rh, I, P, and N atoms). The hydrogen atoms were placed at their geometrically calculated positions and introduced in the final structure-factor calculation with fixed isotropic thermal parameters. In the last cycles of refinement a weighting scheme was used $w = k/[\sigma^2(F_o) + gF_o^2]$ with $k = 0.7493$ and $g = 0.0064$. Final R and R' values were 0.0630 and 0.0778. Atomic scattering factors corrected for anomalous dispersion of Rh, I, and P were taken from ref. 57, excepting those of the hydrogen atoms which were taken from ref. 58. Final atomic co-ordinates for the non-hydrogen atoms are given in Table 4.

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

Acknowledgements

We thank the Consejo Superior de Investigaciones Cientificas/Consiglio Nazionale delle Ricerche Joint Programme (8-1987/88) and Comisión Asesora de Investigación Científica y Técnica for financial support.

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Received 5th *July* 1988; *Paper* 8/02665C