

Pyrazolate A-Frame Rhodium Complexes. Crystal Structures of $[\text{Rh}_2(\mu\text{-dmpz})(\text{CO})_2(\mu\text{-dppm})_2][\text{ClO}_4]$ and $[\text{Rh}_2(\mu\text{-dmpz})\text{I}_2(\text{CO})_2(\mu\text{-dppm})_2][\text{ClO}_4]^\dagger$

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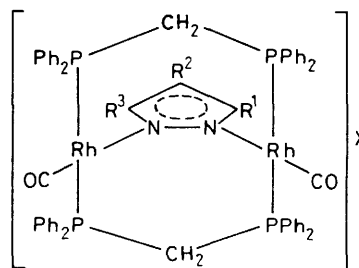
New complexes of formula $[\text{Rh}_2(\mu\text{-L})(\text{CO})_2(\mu\text{-dppm})_2]^+$, having the A-frame type structure with different pyrazolate-type groups L as bridgehead ligand, have been prepared from *trans*- $[\text{Rh}_2\text{Cl}_2(\text{CO})_2(\mu\text{-dppm})_2]$ (dppm = $\text{Ph}_2\text{PCH}_2\text{PPh}_2$). Iodine undergoes transannular oxidative addition to $[\text{Rh}_2(\mu\text{-L})(\text{CO})_2(\mu\text{-dppm})_2][\text{ClO}_4]$ to produce rhodium(II) complexes $[\text{Rh}_2(\mu\text{-L})\text{I}_2(\text{CO})_2(\mu\text{-dppm})_2][\text{ClO}_4]$ with direct rhodium–rhodium bonds. The crystal structures of the complexes $[\text{Rh}_2(\mu\text{-dmpz})(\text{CO})_2(\mu\text{-dppm})_2][\text{ClO}_4]$ and $[\text{Rh}_2(\mu\text{-dmpz})\text{I}_2(\text{CO})_2(\mu\text{-dppm})_2][\text{ClO}_4]$ (dmpz = 3,5-dimethylpyrazolate) have been determined by X-ray methods. The former crystallises in the monoclinic space group $P2_1/a$ with unit-cell dimensions $a = 22.560(9)$, $b = 26.649(9)$, $c = 10.221(7)$ Å, $\beta = 102.68(3)^\circ$, and $Z = 4$. The structure has been refined to $R = 0.072$ on the basis of 4 342 observed reflections. The latter crystallises in the monoclinic space group $P2_1/n$ with $a = 16.855(6)$, $b = 14.713(3)$, $c = 14.008(4)$ Å, $\beta = 90.66(2)^\circ$, and $Z = 2$. The structure has been refined to $R = 0.078$ (3 048 observed reflections). In both complexes two rhodium atoms are triply bridged by two molecules of dppm and by a dmpz ligand through its nitrogen atoms. In the first complex each Rh atom has a square-planar co-ordination, in the second the oxidative addition of iodine results in a change in co-ordination to octahedral and formation of a metal–metal bond [Rh–Rh 2.725(2) Å].

The first rhodium complex with an A-frame geometry, $[\text{Rh}_2(\mu\text{-S})(\text{CO})_2(\mu\text{-dppm})_2]$ (dppm = $\text{Ph}_2\text{PCH}_2\text{PPh}_2$), was reported in 1977.¹ Since then other examples of formula $[\text{Rh}_2(\mu\text{-Y})(\text{CO})_2(\mu\text{-dppm})_2]^{(2-n)+}$ have been described, where Y^n includes anionic or neutral single atoms or small molecules such as H^- ,² Cl^- ,^{3–5} Br^- ,⁶ RCOO^- ,^{2,7} SR ,⁸ Se ,⁸ $\text{PH}(\text{C}_6\text{H}_{11})$,⁸ and $\text{C}_2\text{R}^1\text{R}^2$ ($\text{R}^1 = \text{H}$, $\text{R}^2 = \text{H}$ or Ph).² The flexibility of the two *trans*- μ -dppm ligands is seen in the range of rhodium–rhodium distances (2.24–3.38 Å),⁹ that allows the two metal centres to engage in a variety of unusual reactions. Recent investigations on pyrazolate complexes of rhodium^{10–12} or iridium^{13–15} have shown that the pyrazolate group can act as a bridging ligand, leading to binuclear complexes with a wide range of intermetallic separations. These ligands might be expected to be useful in the construction of new A-frame complexes with a N-donor molecule acting as capping ligand.

We now report the preparation of complexes of the types $[\text{Rh}_2(\mu\text{-L})(\text{CO})_2(\mu\text{-dppm})_2]^+$ and $[\text{Rh}_2(\mu\text{-L})\text{I}_2(\text{CO})_2(\mu\text{-dppm})_2]^+$ [L = pyrazolate (pz), 3-methylpyrazolate (mpz), 3,5-dimethylpyrazolate (dmpz), 4-bromopyrazolate (bpz), or indazolate (idz)] as well as the X-ray structure determinations of $[\text{Rh}_2(\mu\text{-dmpz})(\text{CO})_2(\mu\text{-dppm})_2][\text{ClO}_4]$ and $[\text{Rh}_2(\mu\text{-dmpz})\text{I}_2(\text{CO})_2(\mu\text{-dppm})_2][\text{ClO}_4]$. These structural studies show that the ' $[\text{Rh}_2(\mu\text{-L})(\mu\text{-dppm})_2]$ ' unit can absorb a considerable contraction of the bridged framework, arising through rhodium–rhodium bond formation accompanying oxidation at each rhodium atom.

Results and Discussion

Binuclear complexes (1)–(3) and $[\text{Rh}_2(\mu\text{-idz})(\text{CO})_2(\mu\text{-dppm})\text{Cl}]$ (4) are readily obtained by the addition of pyrazolate-type ligands L to a suspension of *trans*- $[\text{Rh}_2\text{Cl}_2(\text{CO})_2(\mu\text{-dppm})_2]$ ¹⁶ in acetone (Rh:L = 2:1). Complexes (1)–(4) are also obtained when the preparative reaction was conducted in the presence of excess of pyrazolate (Rh:L = 1:5) at room temperature or even in refluxing toluene. The reaction of $[\text{Rh}_2(\mu\text{-L})_2(\text{CO})_4]$ complexes with bis(diphenylphosphino)methane (Rh:dppm = 1:1) in several solvents results in the displacement of one pyrazolate group L with formation of $[\text{Rh}_2(\mu\text{-L})(\text{CO})_2(\mu\text{-dppm})_2]^+$ cations.



	R ¹	R ²	R ³	X
(1)	H	H	H	Cl
(2)	Me	H	H	Cl
(3)	Me	H	Me	Cl
(6)	H	H	H	ClO ₄
(7)	Me	H	H	ClO ₄
(8)	Me	H	Me	ClO ₄
(9)	H	Br	H	ClO ₄
(13)	H	H	H	BPh ₄
(14)	Me	H	Me	BPh ₄
(15)	H	Br	H	BPh ₄

[†] Bis- μ -[bis(diphenylphosphino)methane-PP']- μ -(3,5-dimethylpyrazolato-NN')-bis[carbonylrhodium(I)] perchlorate and bis- μ -[bis(diphenylphosphino)methane-PP']- μ -(3,5-dimethylpyrazolato-NN')-bis[carbonyliodorhodium(II)] (Rh–Rh) perchlorate.

Supplementary data available (No. SUP 56171, 6 pp.): H-atom coordinates, thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii–xix. Structure factors are available from the editorial office.

Table 1. Analytical^a and physical data

Compound	Analysis (%)			$\nu(\text{CO})^b/\text{cm}^{-1}$	$\Lambda_M^c/\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$	Yield (%)
	C	H	N			
(1)	59.2 (58.3)	5.0 (4.2)	2.8 (2.5)	1 998vs, 1 986s (sh)	106	80
(2)	58.3 (58.6)	5.0 (4.3)	2.2 (2.4)	1 997vs, 1 983s (sh)	119	75
(3)	59.1 (59.0)	5.5 (4.4)	2.4 (2.4)	1 993vs, 1 980s (sh)	105	70
(4)	59.7 (59.9)	5.1 (4.2)	2.7 (2.4)	2 000vs, 1 984s (sh)	112	79
(5)	58.2 (59.0)	4.8 (4.4)	2.4 (2.4)	1 992vs, 1 979s (sh)	<i>d</i>	85
(6)	55.3 (55.2)	4.2 (4.0)	2.7 (2.3)	2 000vs, 1 986s (sh)	135	84
(7)	55.2 (55.5)	4.4 (4.1)	2.3 (2.3)	1 998vs, 1 983s (sh)	125	85
(8)	55.1 (55.9)	4.6 (4.2)	2.2 (2.3)	1 995vs, 1 980s (sh)	133	80
(9)	50.9 (51.8)	3.7 (3.6)	2.3 (2.2)	2 002vs, 1 988s (sh)	128	90
(10)	57.1 (56.8)	4.3 (4.0)	2.2 (2.2)	2 003vs, 1 987s (sh)	132	91
(11)	56.3 (55.9)	4.6 (4.1)	2.6 (2.3)	1 995vs, 1 981s (sh)	<i>d</i>	85
(12)	55.2 (55.2)	4.6 (3.9)	2.6 (2.3)	1 992vs, 1 975s (sh)	<i>d</i>	70
(13)	66.7 (67.0)	5.2 (4.8)	1.9 (2.0)	1 998vs, 1 976vs ^e	88	70
(14)	67.1 (67.3)	4.8 (4.9)	1.9 (1.9)	1 991vs, 1 972vs ^e	86	83
(15)	63.9 (63.4)	4.6 (4.4)	2.0 (1.9)	2 000vs, 1 976vs ^e	88	86
(16)	69.1 (68.0)	4.6 (4.7)	2.2 (1.9)	1 989vs, 1 962vs ^e	85	64
(17)	45.6 (45.5)	4.1 (3.3)	2.0 (1.9)	2 052s	138	80
(18)	45.1 (45.9)	4.0 (3.4)	2.0 (1.9)	2 056s	139	85
(19)	46.2 (46.3)	4.0 (3.5)	1.5 (1.9)	2 055s	149	78
(20)	42.2 (43.2)	3.6 (3.0)	1.7 (1.8)	2 056s	132	69
(21)	47.2 (47.2)	3.6 (3.3)	2.3 (1.9)	2 054s	130	87
(22)	46.2 (46.3)	3.6 (3.4)	2.2 (1.9)	2 056s	—	84

^a Required values are given in parentheses. ^b In dichloromethane unless otherwise stated. ^c Acetone solutions. ^d See text. ^e Nujol mull.

On the other hand, the reaction of *trans*-[Rh₂Cl₂(CO)₂(μ-dppm)₂] with stoichiometric amounts of 3,3',5,5'-tetramethyl-4,4'-bipyrazole (H₂tmbpz) and potassium hydroxide gives the tetranuclear complex [Rh₄(μ-tmbpz)(CO)₄(μ-dppm)₄]Cl₂ (**5**). Formally, this complex is derived from [Rh₂(μ-dmpz)(CO)₂(μ-dppm)₂]Cl by direct bonding through the C(4) atoms of two equivalent pyrazolate units. The tetranuclear formulation was established from measurements of the equivalent conductivity in acetone over the 10⁻⁴–10⁻³ mol dm⁻³ range. The value of *A* in Onsager's equation ($\Lambda_e = \Lambda_0 - A\sqrt{c}$) was 925, in accord with a 1:2 electrolyte.¹⁷

Complexes (**2**) and (**3**) react with silver perchlorate yielding the corresponding perchlorate salts (**7**) and (**8**). An alternative route for the preparation of these complexes involves the addition of the corresponding pyrazolate group to [Rh₂(CO)₂(Me₂CO)₂(μ-dppm)₂][ClO₄]₂²⁻ {prepared *in situ* by adding silver perchlorate to *trans*-[Rh₂Cl₂(CO)₂(μ-dppm)₂]}. Complexes (**6**), (**9**), and (**10**) (L = idz) were prepared by this route. Elemental analyses and representative properties of the isolated complexes

are listed in Table 1. In particular, conductivity measurements in acetone at different concentrations of complex (**7**) gave a slope for Onsager's equation of 290 indicating a 1:1 electrolyte.¹⁷

When the dianions tmbpz²⁻ (ref. 18) or 2,2'-bi-imidazole¹⁹ (bim²⁻) are added to [Rh₂(CO)₂(Me₂CO)₂(μ-dppm)₂]²⁺ tetranuclear complexes of formula [Rh₄(μ-tmbpz)(CO)₄(μ-dppm)₄][ClO₄]₂ (**11**) and [Rh₄(μ-bim)(CO)₄(μ-dppm)₄][ClO₄]₂ (**12**) are obtained. Analytical and other data are listed in Table 1. The values of the slope *A* in Onsager's equation (acetone solutions) for (**11**) and (**12**) are, respectively, 960 and 717 confirming that they are 1:2 electrolytes.¹⁷ The ³¹P n.m.r. spectrum of complex (**11**) shows a symmetric multiplet, similar to those observed for the related binuclear complexes (**3**), (**6**), and (**8**) (AA'A''A'''XX' spin system). The values of δ(P) (22.9–25.3 p.p.m.) and [¹J(RhP)] + [^{*}J(RhP)] (128.9–137.5 Hz) are in the usual ranges for related Rh–dppm complexes.^{2,4,6,7,20–24} Possible structures for the cations of these tetranuclear complexes are shown in Figure 1. The ability of the tetramethylbipyrazolate

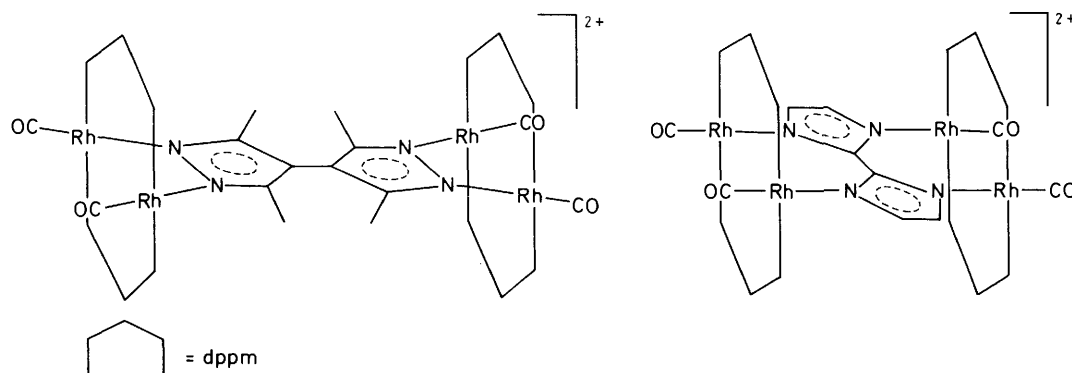


Figure 1. Possible structures for the cationic complexes $[\text{Rh}_4(\mu\text{-tmbpz})(\text{CO})_4(\mu\text{-dppm})_4]^{2+}$ and $[\text{Rh}_4(\mu\text{-bim})(\text{CO})_4(\mu\text{-dppm})_4]^{2+}$

and bi-imidazolate dianions to act as bridging ligands in rhodium complexes has been previously reported.²⁵⁻²⁷

The electronic spectra of the rhodium(I) perchlorate complexes show a band at *ca.* 495 nm, with molar absorption coefficients in the range 9 000–19 000 $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$. Such bands could be considered as proximity-shifted charge-transfer absorptions, due to the proximity of the two metal coordination spheres.^{28,29}

As expected the tetraphenylborate complexes (13)–(15) and $[\text{Rh}_2(\mu\text{-idz})(\text{CO})_2(\mu\text{-dppm})_2][\text{BPh}_4]$ (16) (Table 1) are obtained by the addition of excess of $\text{Na}[\text{BPh}_4]$ to methanolic solutions of the corresponding perchlorate salts.

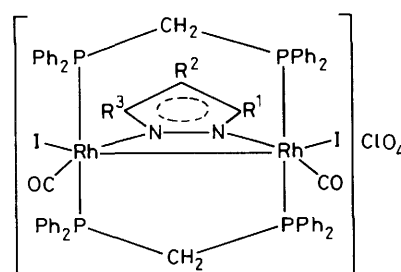
Oxidation of the perchlorate complexes (6)–(10) by molecular iodine (1:1 mol ratio) produces an intensification of the red colour due to formation of 1:1 adducts. Further addition of iodine produces no other changes.* These complexes exhibit carbonyl-stretching frequencies that are *ca.* 65 cm^{-1} higher than those of the starting materials, which by comparison with related systems^{28,29} is consistent with their formulation as the rhodium(II) binuclear complexes (17)–(20) and $[\text{Rh}_2(\mu\text{-idz})\text{I}_2(\text{CO})_2(\mu\text{-dppm})_2][\text{ClO}_4]$ (21). The electrical conductivities of complexes (17)–(21), in acetone, are very similar to those observed for (6)–(10); consequently the iodine is firmly bound to the rhodium atoms. Complex (21) shows a value of *A* in Onsager's equation of 240 (in acetone), characteristic of a 1:1 electrolyte.¹⁷

Addition of methyl iodide to the perchlorate salts (6) and (7) results in the growth of a new carbonyl-stretching band at 2 120 cm^{-1} , but the reaction is not complete, even in pure methyl iodide as solvent. The shift of $\nu(\text{CO})$ suggests that a rhodium(III) complex was formed in solution. However, the starting material was recovered after concentration and work-up of the solution.

Finally, a tetranuclear rhodium(II) complex of formula $[\text{Rh}_4(\mu\text{-tmbpz})\text{I}_4(\text{CO})_4(\mu\text{-dppm})_4][\text{ClO}_4]_2$ (22) was prepared by addition of 2 mol of molecular iodine to (11).

Description of the Crystal Structures of $[\text{Rh}_2(\mu\text{-dmpz})(\text{CO})_2(\mu\text{-dppm})_2][\text{ClO}_4]$ (8) and $[\text{Rh}_2(\mu\text{-dmpz})\text{I}_2(\text{CO})_2(\mu\text{-dppm})_2][\text{ClO}_4]$ (19).—The crystal structures consist of cationic binuclear rhodium complexes and perchlorate anions. Views of the cations, including the numbering schemes, are shown in Figures 2 and 3 respectively. Selected bond distances and angles are given in Tables 2 and 3 respectively.

In the cation of (8) two rhodium atoms are triply bridged by two dppm molecules and by a 3,5-dimethylpyrazolate ligand, through its nitrogen atoms. The square-planar co-ordination of



	R ¹	R ²	R ³
(17)	H	H	H
(18)	Me	H	H
(19)	Me	H	Me
(20)	H	Br	H

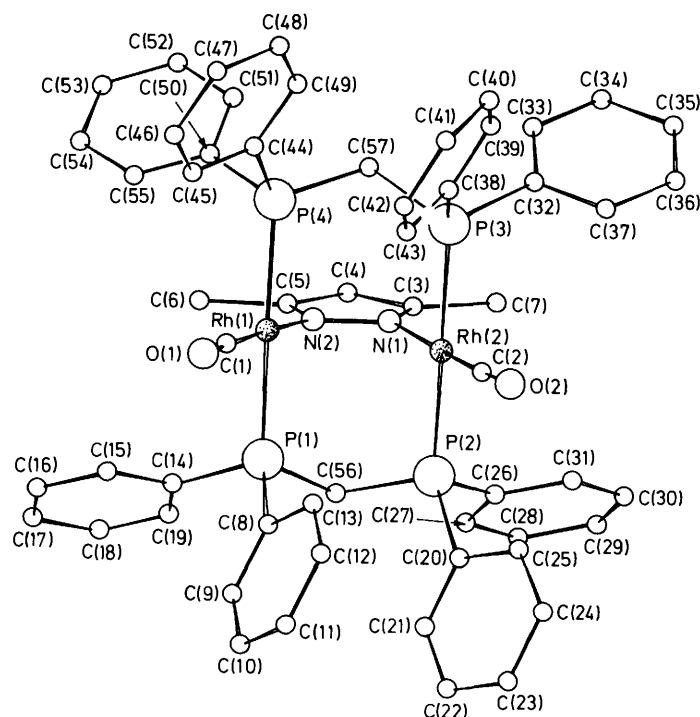


Figure 2. View of the complex $[\text{Rh}_2(\mu\text{-dmpz})(\text{CO})_2(\mu\text{-dppm})_2]^+$ with the atomic numbering scheme

* The electronic spectra of these rhodium(II) complexes show two or three intense absorptions in the 400–510 nm range.

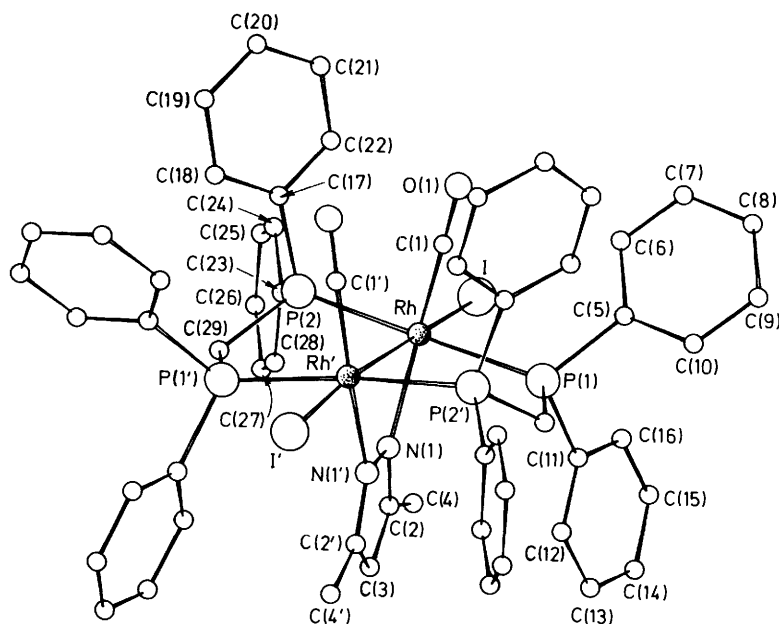


Figure 3. View of the complex $[\text{Rh}_2(\mu\text{-dmpz})\text{I}_2(\text{CO})_2(\mu\text{-dppm})_2]^+$ with the atomic numbering scheme

Table 2. Selected bond distances (Å) and angles (°) in complex (8)

(a) In the rhodium co-ordination sphere

Rh(1)–P(1)	2.303(6)	Rh(2)–P(2)	2.343(6)	C(1)–Rh(1)–P(4)	96.9(8)	C(2)–Rh(2)–P(3)	91.0(8)
Rh(1)–P(4)	2.328(6)	Rh(2)–P(3)	2.301(6)	P(4)–Rh(1)–N(2)	85.4(4)	P(3)–Rh(2)–N(1)	86.8(4)
Rh(1)–C(1)	1.80(3)	Rh(2)–C(2)	1.72(2)	N(2)–Rh(1)–P(1)	87.0(4)	N(1)–Rh(2)–P(2)	85.5(4)
Rh(1)–N(2)	2.08(1)	Rh(2)–N(1)	2.07(1)	P(1)–Rh(1)–C(1)	90.6(8)	P(2)–Rh(2)–C(2)	96.8(8)

(b) In the CO, dmpz, and dppm ligands

C(1)–O(1)	1.15(3)	C(2)–O(2)	1.20(3)	O(1)–C(1)–Rh(1)	176(2)	N(2)–C(5)–C(4)	111(2)
P(1)–C(8)	1.81(1)	P(2)–C(20)	1.84(1)	O(2)–C(2)–Rh(2)	177(2)	C(5)–C(4)–C(3)	103(2)
P(1)–C(14)	1.78(1)	P(2)–C(26)	1.80(1)	P(1)–C(56)–P(2)	111(1)	C(4)–C(3)–N(1)	110(2)
P(1)–C(56)	1.84(2)	P(2)–C(56)	1.86(2)	P(3)–C(57)–P(4)	113(1)	C(3)–N(1)–N(2)	108(1)
P(4)–C(44)	1.81(2)	P(3)–C(32)	1.83(2)	Rh(1)–N(2)–N(1)	115(1)	C(3)–N(1)–Rh(2)	139(1)
P(4)–C(50)	1.79(1)	P(3)–C(38)	1.84(2)	Rh(1)–N(2)–C(5)	138(1)	N(2)–N(1)–Rh(2)	113(1)
P(4)–C(57)	1.83(2)	P(3)–C(57)	1.85(2)	C(5)–N(2)–N(1)	107(1)	Rh(2)–P(3)–C(57)	113.6(6)
N(1)–N(2)	1.38(2)	N(1)–C(3)	1.36(3)	Rh(1)–P(1)–C(56)	113.6(6)	Rh(1)–P(4)–C(57)	109.7(6)
C(3)–C(4)	1.39(3)	C(4)–C(5)	1.40(3)	Rh(2)–P(2)–C(56)	108.8(6)		
N(2)–C(5)	1.34(2)	C(3)–C(7)	1.51(3)				
C(5)–C(6)	1.54(3)						

Table 3. Selected bond distances (Å) and angles (°) in (19)*

(a) In the rhodium co-ordination sphere

Rh–Rh'	2.725(2)	Rh'–Rh–P(1)	97.9(1)	P(1)–Rh–I	85.5(1)	P(1)–Rh–C(1)	91.0(6)
Rh–I	2.757(2)	Rh'–Rh–P(2)	98.8(1)	P(2)–Rh–I	87.5(1)	P(2)–Rh–N(1)	92.7(4)
Rh–P(1)	2.300(5)	Rh'–Rh–C(1)	91.8(5)	C(1)–Rh–I	92.3(5)	P(2)–Rh–C(1)	92.4(6)
Rh–P(2)	2.397(5)	Rh'–Rh–N(1)	71.1(4)	N(1)–Rh–I	105.1(4)	P(1)–Rh–P(2)	172.4(2)
Rh–C(1)	1.80(2)	Rh'–Rh–I	174.6(1)	P(1)–Rh–N(1)	86.1(4)	N(1)–Rh–C(1)	162.1(6)
Rh–N(1)	2.09(1)						

(b) In the CO, dmpz, and dppm ligands

P(1)–C(5)	1.85(1)	C(1)–O(1)	1.18(3)	P(1')–C(29)–P(2)	116(1)	N(1')–N(1)–C(2)	108(1)
P(1)–C(11)	1.81(1)	N(1)–N(1')	1.41(2)	Rh–C(1)–O(1)	176(1)	N(1)–C(2)–C(3)	109(1)
P(1)–C(29)	1.82(2)	N(1)–C(2)	1.33(2)	Rh–N(1)–N(1')	107(1)	C(2)–C(3)–C(2')	106(1)
P(2)–C(17)	1.81(1)	C(2)–C(3)	1.39(3)	Rh–N(1)–C(2)	143(1)	Rh–P(1)–C(29')	109.8(6)
P(2)–C(23)	1.83(1)	C(2)–C(4)	1.54(3)	Rh–P(2)–C(29)	112.0(6)		
P(2)–C(29)	1.84(2)						

* Primed atoms are related to unprimed ones by a two-fold axis.

each rhodium is completed by a carbon atom from a terminal carbonyl group. The C(1),N(2),P(1),P(4) and N(1),C(2),P(2),P(3) atoms deviate from the mean planes passing through them by $-0.033(25)$, $-0.011(14)$, $0.001(5)$, $0.001(5)$ and $-0.106(25)$, $-0.031(14)$, $0.004(5)$, $0.005(5)$ Å with Rh(1) and Rh(2) out of these planes by $-0.058(3)$ and $-0.055(3)$ Å respectively on the same side. The Rh(1)–Rh(2) separation, $3.060(3)$ Å, is indicative of a weak metal–metal interaction as confirmed by the deviation of each metal from square co-ordination towards the other metal. The cation as a whole possesses approximate C_{2v} symmetry with a pseudo-mirror passing through the Rh atoms and the dmpz ligand, and a pseudo-mirror through C(56) and C(57) bisecting the Rh–Rh vector.

Oxidation of complex (8) by molecular iodine yields (19). The cation of (19) can be derived from that of (8) by the coordination of an iodine atom to each rhodium and with compression of the Rh–Rh axis. Each Rh atom is thus octahedrally co-ordinated by two phosphorus atoms from dppm ligands, by a carbon of a terminal carbonyl, by the iodine [Rh–I $2.757(2)$ Å], by a nitrogen from the dmpz ligand, and by the other rhodium atom. The cation as a whole has approximate C_{2v} symmetry, but there is a crystallographic two-fold axis bisecting the Rh–Rh and N–N' vectors. The six-co-ordinated Rh in (19) can be obtained from the four-co-ordinated Rh in (8) by the approach of an iodine atom and of the other Rh atom at the apical positions.

The Rh–Rh distance [$2.725(2)$ Å] is typical for a single metal–metal bond, being the shortest of those reported²³ for similar binuclear 'A-frame' rhodium complexes [$2.7447(9)$ – $2.8415(7)$ Å]. In particular, this distance is well comparable to that found in $[\text{Rh}_2\text{Cl}_2(\mu\text{-dppm})_2(\mu\text{-CF}_3\text{C}_2\text{CF}_3)]$, $2.7447(9)$ Å,²³ where the hexafluorobut-2-yne ligand acts as a bridge through the acetylenic carbon atoms in a similar way to the dmpz ligand through the two nitrogen atoms.

There are few significant differences between the most important structural parameters of the cations of (8) and (19) despite the change in formal oxidation state of the metals and the remarkable shortening of the metal–metal separation. The Rh–C [$1.80(3)$ and $1.72(2)$ Å in (8) and $1.80(2)$ Å in (19)] and Rh–N bonds [$2.07(1)$ and $2.08(1)$ Å in (8), $2.09(1)$ Å in (19)] are comparable. The Rh–P bonds [from $2.301(6)$ to $2.343(6)$ Å in (8), $2.388(5)$ and $2.397(5)$ Å in (19)] show the most notable differences, being clearly shorter in (8). The Rh–P distances found in similar systems range from $2.303(2)$ to $2.367(8)$ Å,²⁰ and from the present results it is clear that the longest Rh–P bonds are associated with the complexes having the metals in higher formal oxidation states. Also the P...P separations, in spite of the compression due to metal–metal bonding in complex (19), are practically the same [P(1)...P(2) $3.061(7)$ and P(3)...P(4) $3.064(6)$ Å in (8), P(1)...P(2') $3.107(8)$ Å in (19)], as are the angles at the phosphorus atoms [$108.8(6)$ – $113.6(6)^\circ$ in (8), $109.8(6)$ and $112.0(6)^\circ$ in (19)]. As expected, some differences in the conformations of the dppm ligands can be noted in the two complexes, as shown by the torsion angles Rh(1)P(4)–C(57)P(3) – 45.8 , P(4)C(57)P(3)Rh(2) 58.9 , Rh(1)P(1)C(56)P(2) 61.2 , and P(1)C(56)P(2)Rh(2) – 47.5° in (8), and RhP(2)C(29)–P(1') 44.0 and P(2)C(29)P(1')Rh – 24.6° in (19).

Experimental

Infrared spectra were recorded on a Perkin-Elmer 577 spectrophotometer (range 4000 – 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 conductivity meter. The C, H, and N analyses were carried out with a Perkin-Elmer 240B microanalyzer. Electronic spectra were recorded at 25°C in acetone solutions

on a Cary 17 spectrophotometer. Phosphorus-31 n.m.r. spectra were recorded for CDCl_3 solutions at room temperature on a Varian FT-80A spectrometer (32.2 MHz) using 85% H_3PO_4 as external standard. Solvents were dried and distilled before use.

Preparations.—**Chloride complexes (1)–(5).** A mixture of *trans*- $[\text{Rh}_2\text{Cl}_2(\text{CO})_2(\mu\text{-dppm})_2]$ (0.10 mmol), the corresponding pyrazole HL (0.10 mmol) or H_2tmbpz (0.05 mmol), and a methanolic solution of KOH (0.10 mmol) was stirred for 30 min in acetone (20 cm^3). The resulting red solutions were concentrated in vacuum until dryness and the residues were extracted with dichloromethane (15 cm^3) and filtered. Partial evaporation under reduced pressure and addition of diethyl ether led to the precipitation of red solids, which were recrystallised from acetone–diethyl ether.

Perchlorate complexes (6)–(12). Silver perchlorate (0.20 mmol) was added to a suspension of *trans*- $[\text{Rh}_2\text{Cl}_2(\text{CO})_2(\mu\text{-dppm})_2]$ (0.10 mmol) in acetone (20 cm^3). The resulting mixture was stirred, in absence of light, for 30 min and the AgCl formed removed by filtration. Addition to the filtrate of the corresponding HL (0.10 mmol), H_2tmbpz (0.05 mmol), or H_2bim (0.05 mmol) and a methanolic solution of KOH (0.10 mmol) gave red solutions, which after filtration were evaporated to dryness under reduced pressure. The residues were extracted with dichloromethane (15 cm^3) and after filtration to remove any impurity were partially concentrated under reduced pressure. Slow addition of diethyl ether gave red solids, which were filtered off, washed with diethyl ether, and air-dried.

Complexes (7) and (8) were also prepared as follows. To a solution of the chloride complex (2) or (3) (0.10 mmol) in acetone (20 cm^3) was added $\text{Ag}[\text{ClO}_4]$ (0.10 mmol) in 5 cm^3 of the same solvent. The resulting red suspensions were stirred, in absence of light, for 30 min and the AgCl formed filtered off. Partial evaporation of the filtrate under reduced pressure and addition of diethyl ether gave red solids, which were filtered off, washed with diethyl ether, and air-dried.

Complexes (13)–(16). An excess of $\text{Na}[\text{BPh}_4]$ (0.50 mmol) was added to solutions of the perchlorate salts (6) and (8)–(10) (0.10 mmol) in methanol (20 cm^3), and slow precipitation of red-violet solids was observed. After stirring for 15 min, these solids were filtered off, washed with methanol and diethyl ether, and air-dried.

Complexes (17)–(22). To solutions of the perchlorate salts (6)–(11) (0.10 mmol) in dichloromethane (20 cm^3), were added stoichiometric amounts of iodine in 5 cm^3 of the same solvent. The colour of the solutions immediately changed from red 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 carbon tetrachloride and diethyl ether, and air-dried.

Crystal Structure Determinations of $[\text{Rh}_2(\mu\text{-dmpz})(\text{CO})_2(\mu\text{-dppm})_2][\text{ClO}_4]$ (8) and $[\text{Rh}_2(\mu\text{-dmpz})_2(\text{CO})_2(\mu\text{-dppm})_2][\text{ClO}_4]$ (19).—**Crystal data.** $[\text{C}_{57}\text{H}_{51}\text{N}_2\text{O}_2\text{P}_4\text{Rh}_2][\text{ClO}_4]$, (8), $M = 1225.20$, monoclinic, $a = 22.560(9)$, $b = 26.649(9)$, $c = 10.221(7)$ Å, $\beta = 102.68(3)^\circ$, $U = 5995(5)$ Å³ (by least-squares refinement of the θ values, in the range 10 – 14° , of 23 reflections accurately measured), $\lambda = 0.71069$ Å, space group $P2_1/a$, $Z = 4$, $D_c = 1.357$ g cm^{-3} , $F(000) = 2488$. Red-brown prismatic crystals. Approximate dimensions of the crystal used in the analysis: $0.15 \times 0.32 \times 0.40$ mm, $\mu(\text{Mo-K}\alpha) = 7.37$ cm^{-1} .

$[\text{C}_{57}\text{H}_{51}\text{I}_2\text{N}_2\text{O}_2\text{P}_4\text{Rh}_2][\text{ClO}_4]$, (19), $M = 1479.01$, monoclinic, $a = 16.855(6)$, $b = 14.713(3)$, $c = 14.008(4)$ Å, $\beta = 90.66(2)^\circ$, $U = 3474(2)$ Å³ (by least-squares refinement of the θ values, in the range 10 – 16° , of 26 reflections accurately

Table 4. Fractional co-ordinates ($\times 10^4$) with estimated standard deviations (e.s.d.s) in parentheses for the non-hydrogen atoms in complex (8)

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Rh(1)	2 149(1)	1 797(1)	3 062(2)	C(20)	4 148(5)	779(5)	4 660(11)
Rh(2)	3 508(1)	1 989(1)	3 337(2)	C(21)	4 051(5)	264(5)	4 782(11)
Cl	1 943(4)	4 283(3)	9 422(10)	C(22)	4 392(5)	-3(5)	5 867(11)
P(1)	2 413(2)	962(2)	3 303(5)	C(23)	4 830(5)	244(5)	6 829(11)
P(2)	3 743(2)	1 137(2)	3 201(5)	C(24)	4 927(5)	758(5)	6 708(11)
P(3)	3 249(2)	2 825(2)	3 140(6)	C(25)	4 586(5)	1 026(5)	5 623(11)
P(4)	1 878(2)	2 625(2)	2 497(5)	C(26)	4 219(5)	1 013(5)	2 035(12)
O(1)	1 748(9)	1 771(7)	5 615(18)	C(27)	4 072(5)	676(5)	963(12)
O(2)	4 126(11)	2 152(8)	6 123(21)	C(28)	4 482(5)	588(5)	141(12)
N(1)	3 034(6)	1 912(5)	1 364(14)	C(29)	5 039(5)	837(5)	391(12)
N(2)	2 434(6)	1 778(6)	1 261(13)	C(30)	5 187(5)	1 175(5)	1 462(12)
C(1)	1 884(11)	1 780(9)	4 598(24)	C(31)	4 777(5)	1 263(5)	2 284(12)
C(2)	3 881(11)	2 075(9)	4 979(26)	C(32)	3 790(6)	3 177(5)	2 394(15)
C(3)	3 143(9)	1 929(7)	111(19)	C(33)	3 626(6)	3 416(5)	1 147(15)
C(4)	2 612(10)	1 819(9)	-833(20)	C(34)	4 063(6)	3 670(5)	620(15)
C(5)	2 190(9)	1 715(8)	-43(21)	C(35)	4 664(6)	3 685(5)	1 340(15)
C(6)	1 523(9)	1 548(9)	-507(24)	C(36)	4 829(6)	3 446(5)	2 587(15)
C(7)	3 757(9)	2 079(9)	-117(20)	C(37)	4 392(6)	3 192(5)	3 114(15)
O(3)	2 174(15)	3 817(12)	9 041(33)	C(38)	3 200(7)	3 183(6)	4 656(13)
O(4)	1 378(19)	4 306(15)	9 364(43)	C(39)	3 352(7)	3 692(6)	4 774(13)
O(5)	2 349(19)	4 587(16)	10 085(42)	C(40)	3 293(7)	3 959(6)	5 919(13)
O(6)	1 968(16)	4 550(14)	8 076(40)	C(41)	3 082(7)	3 717(6)	6 944(13)
O(7)	2 011(16)	4 783(14)	9 507(36)	C(42)	2 930(7)	3 208(6)	6 826(13)
O(8)	1 670(17)	4 180(14)	10 649(39)	C(43)	2 989(7)	2 941(6)	5 682(13)
O(9)	1 420(20)	4 058(17)	8 707(43)	C(44)	1 611(7)	3 037(5)	3 656(13)
O(10)	2 396(19)	3 997(16)	9 606(40)	C(45)	1 219(7)	2 835(5)	4 404(13)
C(8)	2 637(6)	699(5)	4 974(11)	C(46)	1 002(7)	3 136(5)	5 319(13)
C(9)	2 535(6)	194(5)	5 220(11)	C(47)	1 177(7)	3 639(5)	5 487(13)
C(10)	2 732(6)	-4(5)	6 511(11)	C(48)	1 570(7)	3 841(5)	4 739(13)
C(11)	3 031(6)	304(5)	7 557(11)	C(49)	1 787(7)	3 540(5)	3 823(13)
C(12)	3 133(6)	810(5)	7 312(11)	C(50)	1 267(5)	2 670(5)	1 047(12)
C(13)	2 936(6)	1 007(5)	6 020(11)	C(51)	1 288(5)	2 975(5)	-58(12)
C(14)	1 796(6)	572(5)	2 530(15)	C(52)	783(5)	3 009(5)	-1 125(12)
C(15)	1 267(6)	589(5)	3 029(15)	C(53)	257(5)	2 738(5)	-1 087(12)
C(16)	765(6)	300(5)	2 430(15)	C(54)	237(5)	2 433(5)	18(12)
C(17)	791(6)	-7(5)	1 331(15)	C(55)	742(5)	2 399(5)	1 085(12)
C(18)	1 320(6)	-24(5)	832(15)	C(56)	3 032(8)	787(6)	2 480(17)
C(19)	1 822(6)	265(5)	1 431(15)	C(57)	2 506(8)	2 946(7)	1 989(18)

Table 5. Fractional co-ordinates ($\times 10^4$) with e.s.d.s in parentheses for the non-hydrogen atoms in complex (19)

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Rh	2 911(1)	2 992(1)	1 668(1)	C(16)	5 139(8)	1 589(8)	1 219(10)
I	3 637(1)	2 880(1)	-82(1)	C(17)	1 418(9)	4 395(8)	684(11)
P(1)	4 195(3)	2 676(4)	2 326(3)	C(18)	706(9)	4 743(8)	1 029(11)
P(2)	1 683(3)	3 211(3)	819(3)	C(19)	540(9)	5 668(8)	940(11)
O(1)	3 212(10)	4 984(11)	1 855(10)	C(20)	1 085(9)	6 245(8)	507(11)
N	2 629(9)	1 653(10)	2 023(10)	C(21)	1 796(9)	5 898(8)	162(11)
C(1)	3 090(11)	4 198(15)	1 750(10)	C(22)	1 963(9)	4 973(8)	251(11)
C(2)	2 719(11)	791(13)	1 753(13)	C(23)	1 592(8)	2 766(9)	-397(7)
C(3)	2 500	221(22)	2 500	C(24)	1 547(8)	3 317(9)	-1 206(7)
C(4)	3 025(14)	502(15)	769(14)	C(25)	1 489(8)	2 926(9)	-2 111(7)
C(29)	861(10)	2 600(14)	1 379(11)	C(26)	1 478(8)	1 982(9)	-2 207(7)
C(5)	5 030(7)	3 471(9)	2 127(10)	C(27)	1 523(8)	1 430(9)	-1 399(7)
C(6)	4 972(7)	4 213(9)	1 510(10)	C(28)	1 580(8)	1 822(9)	-493(7)
C(7)	5 614(7)	4 803(9)	1 412(10)	Cl*	4 044(6)	8 935(7)	4 909(7)
C(8)	6 313(7)	4 651(9)	1 931(10)	O(1)*	3 953(16)	9 826(15)	4 715(18)
C(9)	6 370(7)	3 909(9)	2 547(10)	O(21)*	3 643(35)	8 458(35)	4 186(35)
C(10)	5 729(7)	3 319(9)	2 645(10)	O(31)*	4 588(31)	8 413(33)	4 400(37)
C(11)	4 639(8)	1 598(8)	2 005(10)	O(41)*	3 866(32)	8 417(31)	5 694(29)
C(12)	4 492(8)	797(8)	2 505(10)	O(22)*	4 144(42)	8 426(35)	4 082(28)
C(13)	4 845(8)	-15(8)	2 217(10)	O(32)*	4 577(27)	8 334(30)	5 239(37)
C(14)	5 345(8)	-24(8)	1 431(10)	O(42)*	3 382(23)	8 424(31)	4 964(41)
C(15)	5 492(8)	778(8)	931(10)				

* The Cl and O(1) atoms have occupancy factors of 0.5, the other starred atoms of 0.25.

measured), $\bar{\lambda} = 0.71069 \text{ \AA}$, space group $P2_1/n$, $Z = 2$, $D_c = 1.414 \text{ g cm}^{-3}$, $F(000) = 1456$. Black prismatic crystals. Approximate dimensions of the crystal used in the analysis (sealed in a glass capillary): $0.22 \times 0.48 \times 0.70 \text{ mm}$, $\mu(\text{Mo-K}\alpha) = 15.17 \text{ cm}^{-1}$.

Data collection and processing. Complex (8): Siemens AED diffractometer, $\theta/2\theta$ mode, niobium-filtered Mo-K α radiation. 8960 Reflections measured ($3 \leq \theta \leq 23^\circ$, $\pm h, k, l$), of which 8389 were unique (merging $R = 0.032$) giving 4342 with $I \geq 2\sigma(I)$. Usual Lorentz and polarization reduction; absorption ignored because of the very low absorbance of the sample.

Complex (19): Philips PW 110 diffractometer, $\theta/2\theta$ mode, graphite-monochromated Mo-K α radiation. 6515 Reflections measured ($3 \leq \theta \leq 25^\circ$, $\pm h, k, l$), of which 6191 were unique (merging $R = 0.038$) giving 3048 with $I \geq 3\sigma(I)$. Usual Lorentz and polarization reduction; absorption correction by a semi-empirical method³⁰ (maximum and minimum transmission factors 1.185 and 1.00).

Structure analysis and refinement. Complex (8): Patterson and Fourier methods, oxygen atoms of the perchlorate anion statistically distributed in two positions of equivalent occupancy. Full-matrix least-squares refinement, Rh, Cl, P, O (of the carbonyls), N, and C(1)—C(7) atoms refined anisotropically, phenyl rings treated as rigid groups in the last cycles, hydrogen atoms placed in their geometrically calculated positions, but not refined. Unit weights gave satisfactory agreement analysis. Final R and R' 0.072 and 0.098. The program used is given in ref. 31. Final atomic co-ordinates for the non-hydrogen atoms are in Table 4.

Complex (19): Patterson and Fourier methods, perchlorate anion disordered [chlorine does not lie on the two-fold axis as expected, Cl and O(1) occupy general positions with occupancy factors of 0.5, O(21), O(31), O(41), O(22), O(32), and O(42) occupy general positions with occupancy factors of 0.25]. Full-matrix least-squares refinement, Rh, I, P, O (of the carbonyls), N, C(1)—C(4), and C(29) atoms refined anisotropically, phenyl rings treated as rigid groups in the last cycles, hydrogen atoms placed in their geometrically calculated positions, but not refined. Unit weights in all stages of the refinement. Final R and R' 0.078 and 0.091. The program used is given in ref. 31. Final atomic co-ordinates for the non-hydrogen atoms are in Table 5.

Atomic scattering factors, corrected for anomalous dispersion of Rh, I, P, and Cl, were taken from ref. 32. Calculations were performed on the CYBER 76 computer of the Centro di Calcolo Elettronico dell'Italia Nord-Orientale, Bologna, with financial support from the University of Parma.

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