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MONO- AND BINUCLEAR QUINALDINATE COMPLEXES OF RHODIUM WITH (P—P) DONOR LIGANDS. CRYSTAL STRUCTURE OF [Rh₂(quin)₂(CO)₂(μ-dppm)]. OXIDATIVE ADDITION REACTIONS—V*

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Abstract—Reactions of $[Rh(quin)(CO)_2]$ (quin = 2-quinaldinate, C_9H_6N -COO⁻) with diphosphine ligands [dppm (bis(diphenylphosphino)methane) or dppe ([1,2-bis(diphenylphosphino)ethane)] gave two types of compound, $[Rh_2(quin)_2(CO)_2(\mu-P--P)]$ and [Rh(quin)(P--P)] (P--P = dppm, dppe) depending on the Rh : P--P molar ratio employed, 2 : 1 or 1 : 1, respectively. The binuclear $[Rh_2(quin)_2(CO)_2(\mu-P--P)]$ species present a squareplanar environment for each rhodium atom, which are bonded by a P--P bridging ligand. These results were also proved by the resolution of the crystal structure of $[Rh_2(quin)_2(CO)_2(\mu-dppm)]$. The molecular structure shows the two CO groups occupying *trans* positions. This could prevent the formation of possible binuclear CO-free species. The Rh--Rh intramolecular distance was consistent with no formal Rh--Rh bond. The addition of I₂ or CH₃I to the above $[Rh_2(quin)_2(CO)_2(\mu-P--P)]$ gave rise to the corresponding binuclear hexacoordinate rhodium(III) compounds $[Rh_2(I)_2(X)_2(quin)_2(CO)_2(\mu-P--P)]$ (X = I, CH₃). Two isomers were detected in solution by ¹H and ³¹P NMR spectroscopy for $[Rh_2(I)_2(CH_3)_2(quin)_2(CO)_2(\mu-P--P)]$.

The substitution reactions of CO groups in $[Rh(L-L')(CO)_2]$ complexes $(L-L' = O-O, N-O \text{ or } S-S \text{ donor anionic bidentate ligands) by P-donor monodentate ligands (PR₃) seem to be dependent on the donor properties of L-L' and PR₃ ligands. Thus, the monocarbonyl derivatives <math>[Rh(L-L')(CO)(PR_3)]$ (L-L' = O-O or N-O) were obtained with triarylphosphines as substituent ligands,¹ but weaker donor ligands like triphenylphosphite gave rise to the disubstituted

species $[Rh(L-L')|P(OPh)_{3|2}]$.² The latter behaviour was also observed with triarylphosphines when S-S ligands were present in the starting compounds.³

In addition, it has been proposed that the substitution of the second CO group occurs through a pentacoordinate intermediate of the type $[Rh(L-L')(CO)(Pr_3)_2]$,⁴ whose stability also depends on the nature of L-L' and PR_3 ligands. So, in previous papers we have reported that the reactions of $[Rh(N-O)(CO)_2]$ [N-O = pyC (2-pyridinecarboxylate, $C_5H_4N-COO^-$), quin (2-quinaldinate, $C_9H_6N-COO^-$)] with PR_3 (R = 4-CH₃O-C₆H₄-, 4-CH₃-C₆H₄-, 4-F-C₆H₄-, 4-F-C₆H₄-,

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Cl—C₆H₄—) yielded the monosubstituted [Rh(N— O)(CO)(PR₃)] compounds.^{5,6} However, the intermediate pentacoordinate species [Rh(N—O)(CO) (PR₃)₂](N—O = quin) have been isolated, but their low stability in solution prevented the formation of [Rh(quin)(PR₃)₂].⁶

In order to produce CO-free square-planar complexes with phosphine ligands from $[Rh(quin) (CO)_2]$ we consider that (P-P) donor ligands with a strong chelating effect should stabilize the intermediate pentacoordinate species of the type [Rh(quin)(CO)(P-P)].

The chelating ability of 1,2-bis(diphenylphosphino)ethane (dppe) has been well established,^{7,8} therefore it should be an appropriate ligand for our proposal. However, this ability decreases in its counterpart bis(diphenylphosphino)methane (dppm), which tends to act as monodentate or bridge between two metals,⁹ and thus has been extensively used to produce compounds with Rh—Rh bonds.⁹⁻¹¹

In this work we have studied the reactivity of $[Rh(quin)(CO)_2]$ with dppe and dppm. The reactions with I_2 and CH_3I of the binuclear isolated products were also studied as an extension of the previous results obtained in the related reactions with $[Rh(N-O)(CO)(PR_3)]$ (N-O = 2-pyC,⁵ 2-quin¹²).

RESULTS AND DISCUSSION

The reactions carried out and the obtained products are represented in Scheme 1.

 $[Rh_2(quin)_2(CO)_2(\mu-P-P)] (P-P = dppe, dppm)$ complexes

The reactions of $[Rh(quin)(CO)_2]$ with (P-P) donor ligands (P-P = dppe, dppm) in a 2:1

Rh: P—P molar ratio yield $[Rh_2(quin)_2(CO)_2(\mu$ -P—P)], formulated on the basis to their analytical (Table 1) and spectroscopic data. The crystal structure of the complex $[Rh_2(quin)_2(CO)_2(\mu$ -dppm)] has been resolved.

The $[Rh_2(quin)_2(CO)_2(\mu-dppe)]$ derivative is a stable yellow solid, sparingly soluble in the common solvents. This fact prevents its ¹H and ¹³C NMR spectroscopic study. The related $[Rh_2(quin)_2(CO)_2(\mu-dppm)]$ is a bright green-black solid only stable under N₂ in the darkness. This compound is soluble as a non-electrolyte in CH₂Cl₂ or CHCl₃, but its solutions are unstable even in the above conditions and decomposition occurs after a few days.

The ¹H NMR spectrum (Table 2) of $[Rh_2 (quin)_2(CO)_2(\mu-dppm)]$ shows one triplet at δ 4.19 ppm (²J(H--P) = 12.7 Hz) assigned to the dppm -CH₂-group, indicating the chemical equivalence of the two phosphorus atoms. The above data suggest a bridging coordination of the dppm ligand.

In addition, the ¹³C NMR spectrum (Table 3) presents 10 singlets and four signals (a singlet, two doubles and a triplet) assigned to the resonances of the two equivalent quinaldinate ligands and the four equivalent phenyl groups of the dppm ligand, respectively. The triplet attributed to the resonance of the methylenic carbon (δ 28.8 ppm, ¹J(C—P) 23.5 Hz) proves that the two phosphorus atoms are equivalent. The low solubility of the compound precluded the detection of signals for the CO groups.

The ³¹P NMR spectra of the $[Rh_2(quin)_2(CO)_2 (\mu-P-P)]$ species (P-P = dppe, dppm) were recorded, although 30,000 accumulations were necessary for the dppe derivative. Both spectra are characteristic of an AA'XX' spin system with a J(X-X') value of 0.0 Hz¹³ (Fig. 1a). The δ and J



[Rh2(I)2(X)2(quin)2(CO)2(µ-P-P)] (2 isomers)

P-P = dppe. dppm $X = I, CH_3$

Scheme 1.

Analyses							
	[Fo	und (Ca	lc.)]		IR (cm ⁻¹	, KBr discs)	P—P
Compound	%C	%H	%N	v(C≡O)	$v_{as}(OCO)$	$v_{sym}(OCO)$	absorption
$[Rh_2(quin)_2(CO)_2(\mu-dppm)]$	56.4	3.3	2.7	1962 vs	1650 vs	1333 vs	1483, 1434
	(57.0)	(3.4)	(2.8)				1100, 695
$[Rh_2(quin)_2(CO)_2(\mu-dppe)]$	56.9	3.5	2.8	1952 vs	1660 vs	1325 vs	1480, 1430
	(57.4)	(3.6)	(2.8)				1099, 692
[Rh(quin)(dppm)]	62.7	4.5	2.1	_	1632 vs	1338 vs	1435, 1095
	(63.8)	(4.3)	(2.1)				696
[Rh(quin)(dppe)]	63.5	4.4	2.0		1650 vs	1330 vs	1432, 1098
	(64.2)	(4.5)	(2.1)				693
$[Rh_2(I)_4(quin)_2(CO)_2(\mu-dppm)]$	37.1	2.3	1.8	2070 vs	1670 vs	1330 vs	1490, 1432
	(37.7)	(2.5)	(1.9)				1102, 694
$[Rh_2(I)_4(quin)_2(CO)_2(\mu-dppe)]$	37.9	2.3	1.8	2070 vs	1660 vs	1332 vs	1480, 1430
	(38.1)	(2.4)	(1.8)				1100, 690
$[Rh_{2}(I)_{2}(CH_{3})_{2}(quin)_{2}(CO)_{2}(\mu-dppm)]$	45.8	3.2	2.1	2050 vs	1660 vs	1330 vs	1470, 1430
	(46.2)	(3.2)	(2.2)				1100, 693
$[Rh_{2}(I)_{2}(CH_{3})_{2}(quin)_{2}(CO)_{2}(\mu-dppe)]$	46.8	3.2	2.2	2050 vs	1660 vs	1330 vs	1485, 1435
	(46.6)	(3.3)	(2.2)				1100, 693

Table 1. Analytical and IR data of the compounds

values deduced from the spin system are specified in Table 2. The ${}^{1}J(P-Rh)$ and J(Rh-Rh) values are consistent with a +1 formal oxidation state in a square-planar environment for the rhodium atoms^{6,14} and the absence of intramolecular metalmetal bond. The size of the chain between the two phosphorus atoms for the dppe derivative can prevent the approach of the two metals, in accordance with the above results. However, this is not evident for the dppm derivative, which shows a metal-metal interaction in the solid state deduced from its crystal structure. It is then possible to suggest that for the above compound the proposed metal-metal interaction would disappear in solution.

On the other hand, from the NMR study and the larger σ -trans effect of the nitrogen relative to the oxygen of the 2-quinaldinate ligand,¹ two possibilities (A, B) could be suggested to describe the environment of the rhodium atoms in these complexes (Fig. 2). Their IR spectra (Table 1) show in the carbonyl stretching region only one band at 1960 cm⁻¹, indicating a relative *trans* position of the carbonyl ligands,¹⁵ and so structure A seems more probable. On the other hand, from the positions of the $v_{as}(OCO)$ and $v_{sym}(OCO)$ stretching bands a monodentate coordination of the carboxylate group of the 2-quinaldinate ligands is deduced.⁶

Complexes containing two *trans* μ -dppm ligands have been well established,⁹ but very few data from binuclear rhodium compounds containing only one single bridging dppm ligand have been reported, and usually they present some other bridging ligands and a Rh—Rh bond.¹¹

In order to confirm our above structural proposal we were interested in resolving the crystalline structure of one of the studied complexes.

Crystal structure of [Rh₂(quin)₂(CO)₂(µ-dppm)]

The unit cell of $[Rh_2(quin)_2(CO)_2(\mu-dppm)]$ contains four discrete well separated molecules. A view of neighbouring binuclear molecules showing the molecular packing is shown in Fig. 3. In Fig. 4¹⁶ two perspective views of the molecule and the coordination around each metal are shown. Selected bonds distances and angles are listed in Table 4.

The square-planar coordination about each rhodium atom is built up by the CO group, the bidentate (N—O) ligand and one of the phosphorus atoms of the bridging diphosphine ligand. Some deviations of ligand–Rh–ligand angles from 90° (Table 4) are observed. This fact is also observed in the related complex [Rh(quin)(CO)(PPh₃)] and attributed to the small bite angle of the 2-quinaldinate five membered chelate ring. The coordination planes are in an almost parallel disposition deduced from the dihedral angle of 11.0(7)° between the best least-squares planes O(11), N(11), C(1), P(1) and O(21), N(21), C(2), P(2) (Fig. 4b).¹⁷ The torsion angle N(11)—Rh(1)—Rh(2)—N(21) of 36(1)° indicates a rotation of both coordination

			1H NMR				1 P NMR		
Compound		δ(aromatic)	δ(-CH ₂ -) _{PP}	δ(CH ₃)	Ś	' <i>J</i> (P—Rh)	"J(P-Rh)	"J(PP)	¹ J(Rh—Rh)
$[Rh_2(quin)_2(CO)_2(\mu-dppm)]$		8.1-7.2 4.	19t [² J(HP) 12.7]		38.7m	169.8	1.4	36.5	0.0
$[Rh_2(quin)_2(CO)_2(\mu-dppe)]$					43.1m	167.7	-0.4	46.8	0.0
[Rh(quin)(dppm)]		8.0-6.3	3.72m, 2.83m	I	13.9bd ^a	ł			
[Rh(quin)(dppe)]		8.2-7.1	2.51m, 2.13m		57.7d	132.9		I	
	(major isomer)			$1.38s (6H)^{b}$	35.0m^{b}	116.3	29.3	48.5	0.0
[Rh ₂ (I) ₂ (CH ₃) ₂ (quin) ₂ (CO) ₂ (µ-dppm)]		8.5-7.1	5.50m						
	(minor isomer)			$1.24s~(6H)^{b}$	37.0bd ^b	~121			
	(major isomer)	3.57	7m (2H), 3.05m (2H) ^c	1.60s (3H), 1.10s (3H) ^c	41.2m ^e	112.5	-3.3	36.4	0.0
$[Rh_2(I)_2(CH_3)_2(quin)_2(CO)_2(\mu-dppe)]$		8.5-7.2							
	(minor isomer)		$3.3 \text{m} (4 \text{H})^{e}$	0.93s (6H) ^c	43.3m	112.5	-3.3	36.4	0.0

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^b2:1 relative intensity. relative intensity.

3:1

planes from the staggered dispositions to release the steric congestion of both guinaldinate rings (Fig. 4b).

The two carbonyl groups of each plane are in relatively trans positions. This fact agrees with the observed inability of this complex to produce COfree binuclear species, as will be explained below.

The phosphorus atoms are tetrahedrally surrounded with a mean P-C bond distance within the experimental error of 1.83(4) Å, similar to those of [Rh(L-L)(CO)(PPh₃)] complexes.¹

However, the mean Rh--P bond distance [2.224(9) Å] is lower than that found in the above mentioned mononuclear compounds.¹ In these complexes the Rh-P distance has been used to estimate the trans influence of the different donor atoms. These average distances are, respectively, 2.232(2), 2.260(2) or 2.300(2) Å when an O, N or S atom is trans to the P atom, in accordance with the known variation of the trans influence in the order S > N > O. In our complex $[Rh_2(quin)_2(CO)_2(\mu$ dppm)] the Rh—P bond distance [2.224(9) Å] is still shorter than that obtained when an oxygen atom is trans to P atom. It means that this cannot be used as the only guide to compare the *trans* influence in rhodium(I) complexes of the type [Rh(L-L')(CO)](P)] when the P-donor is not a monodentate ligand as in this case.

The average bite angle of the bidentate 2quinaldinate ligands is 78(1)°, suggesting a less effective metal-ligand bond relative to those with a bite angle of 90° (maximum overlap with dsp^2 orbitals), and consequently a weaker trans influence and a stronger Rh-P bond.

In addition it was also postulated that the trend of square-planar rhodium(I) to form complexes with higher coordination numbers increases when the bite angle decreases.¹ From these considerations it could be possible to suggest here the presence of an additional metal-metal bond. However, the Rh-Rh distance of 3.203(4) Å falls within the range previously reported for complexes containing no formal metal-metal bond. So, Rh ··· Rh intermolecular distances of 3.31,¹⁸ $3.27(1)^{19}$ and 3.34(1)¹⁹ Å have been obtained for complexes containing a weak intermolecular interaction. On the other hand, the "A-frame type" molecules $[Rh_2(CO)_2(\mu-Cl)(dppm)_2]BF_4^{20}$ and $[Rh_2(CO)_2(\mu-Cl)(dppm)_2]BF_4^{20}$ S)(dppm)₂],²¹ for which a metal-metal interaction was proposed, showed an intramolecular Rh-Rh distance of 3.1520(8) and 3.155(4) Å, respectively, the related "face to face" complex and $[Rh_2(Cl)_2(CO)_2(\mu$ -dppm)₂] with no formal metalmetal bond showed a Rh-Rh distance of 3.2386(5) Å,²² close to that reported here. In addition, the $[Rh(CO)_2(\mu-Cl)]_2$, where a metal-metal bond has

	Ph ₂ P	-CH,PPh,	$[Rh_{2}(quin)_{2}(CO)_{2}(\mu-c)]$	lppm)]
	δ (ppm)	J (Hz)	δ (ppm)	J (Hz)
C _{ipso}	138.6 (t)	¹ J(C—P) 4.0	130.6 (d)	¹ J(C—P) 28.1
C _o	132.6 (t)	$^{2}J(C-P)$ 10.8	133.0 (t)	$^{2}J(C-P)$ 5.4
\mathbf{C}_{m}	128.2 (t)	$^{3}J(C-P)$ 3.4	128.2 (d)	$^{3}J(C-P)$ 5.4
C _p	128.5 (s)	_	128.3 (s)	
-ĊH ₂ -	27.9 (t)	¹ J(CP) 23.1	28.8 (t)	$^{1}J(C-P) 23.5$
2-quin		_	172.4 (s, COO ⁻)	_
-			154.1 (s), 144.7 (s), 138.9 (s),	
			132.3 (s), 131.7 (s), 129.6 (s),	
			127.8 (s), 127.6 (s), 122.8 (s)	

Table 3. ¹³C NMR spectral data (CDCl₃ solution) of dppm and $[Rh_2(quin)_2(CO)_2 (\mu$ -dppm)]

s: singlet; d: doublet; t: triplet.



Fig. 1. ³¹P NMR spectra of (a) $[Rh_2(quin)_2(CO)_2(\mu-dppm)]$ and (b) $[Rh_2(I)_2(CH_3)_2(quin)_2(CO)_2(\mu-dppe)]$



Fig. 2. Proposed coordination environments in $[Rh_2(quin)_2(CO)_2(\mu-P-P)]$ (P-P = dppe, dppm).

been postulated, showed Rh—Rh distance of 3.12 Å. 18

From the above data it is possible that an intramolecular metal-metal interaction occurs in this case. Thus, each rhodium atom could be better seen as five-coordinate. However, this interaction must disappear in solution, according to the NMR study.

[Rh(quin)(P-P)](P-P = dppe, dppm) complexes

 $[Rh(quin)(CO)_2]$ reacts with dppe in CH_2Cl_2 or dppm in acetone in a 1:1 molar ratio to yield

[Rh(quin)(P—P)[(P—P = dppe, dppm). The same results were obtained when [Rh₂(quin)₂(CO)₂(μ -P—P)] were used as starting compounds.

The [Rh(quin)(dppe)] derivative is a stable yellow solid soluble in polar organic solvents, but the related [Rh(quin)(dppc)] orange compound is insoluble in acetone and ethanol and relatively soluble in CH_2Cl_2 and $CHCl_3$. Both compounds are unstable in solution and neutral in freshly prepared $CHCl_3$ solutions.

The analytical data of the new compounds (Table 1) are consistent with a formulation of the type $[Rh(quin)(P-P)]_n$. The mass spectrum of the $[Rh(quin)(dppm)]_n$ complex presents the molecular peak at m/z 659 (relative intensity 0.5%) corresponding with the monomeric species. The mass spectrum of [Rh(quin)(dppe)] does not show the molecular peak for the monomeric species, but the highest peak appears at m/z 535. From the above results and considering the high chelating tendency of the dppe ligand,^{7,8} we assume the monomeric structure [Rh(quin)(P-P)] in solid state for both derivatives.



Fig. 3. Packing arrangement in $[Rh_2(quin)_2(CO)_2(\mu-dppm)]$ viewed down the a axis.



Fig. 4. (a) Perspective ORTEP view of [Rh₂(quin)₂(CO)₂(μ-dppm)] with atomic numbering scheme;
(b) A PLUTO plot of coordination around the rhodium atoms. (The phenyl rings of the dppm ligand have been omitted for clarity.)

Rh1—Rh2	3.203(4)	P2—C218	1.82(4)
Rh1—P1	2.24(1)	N11-C12	1.38(4)
Rh1—N11	2.17(3)	N11-C110	1.32(4)
Rh1—O11	2.10(2)	011-C111	1.31(4)
Rh1—C1	1.79(4)	O12-C111	1.18(5)
Rh2P2	2.21(1)	N21—C22	1.47(4)
Rh2N21	2.13(3)	N21—C210	1.35(4)
Rh2—O21	2.08(3)	O21-C211	1.31(5)
Rh2C2	1.86(4)	O22—C211	1.25(5)
P1—C3	1.87(5)	01C1	1.14(5)
P1C112	1.81(4)	O2—C2	1.17(5)
P1—C118	1.80(3)	C110-C111	1.46(5)
P2C3	1.84(5)	C210-C211	1.43(5)
P2	1.80(4)		
011—Rh1—C1	178(1)	Rh1—P1—C3	111(2)
N11—Rh1—C1	103(1)	C112-P1-C118	102(2)
N11 - Rh1 - O11	78(1)	C3-P1-C118	103(2)
P1—Rh1—C1	86(1)	C3—P1—C112	109(2)
P1Rh1	93(1)	Rh2—P2—C218	111(1)
P1—Rh1—N11	171(1)	Rh2-P2-C212	124(1)
O21—Rh2—C2	167(1)	Rh2—P2—C3	109(2)
N21—Rh2—C2	106(1)	C212-P2-C218	102(2)
N21—Rh2—O21	77(1)	C3P2C218	102(2)
P2Rh2C2	86(1)	C3—P2—C212	108(2)
P2Rh2O21	89(1)	Rh1-C1-O1	169(4)
P2—Rh2—N21	165(1)	Rh2—C2—O2	175(3)
Rh1—P1—C118	114(1)	P1-C3-P2	117(3)
Rh1-P1-C112	116(1)		

Table 4. Selected bond distances (Å) and angles (°) for $[Rh_2(quin)_2(CO)_2(\mu - dppm)]$

The IR spectra of both compounds (Table 1) present two absorption bands at ~1640 and ~1335 cm⁻¹, respectively assigned to the $v_{as}(OCO)$ and $v_{sym}(OCO)$, indicating a (N-O) bidentate coordination of the 2-quinaldinate ligand.⁶

The ³¹P NMR spectra should present two signals as doublet of doublets, consistent with the monomeric structure proposed above in which the two phosphorus atoms should be inequivalent. However, both spectra (Table 2) were deceptively simple, showing only one signal as doublet at δ 57.7 ppm [J(P-Rh) 132.9 Hz] and at δ 13.9 ppm (broad) for the dppe and dppm derivatives, respectively. This fact could be explained by the presence of an interchange in solution between the positions of the two phosphorus atoms. However, from the low resolution and δ value, an interchange process between monomeric [Rh(quin)(dppm)] and dimeric $[Rh_2(quin)_2(\mu-dppm)_2]$ species could be suggested also for the dppm derivative.⁸ This explanation is supported by the ¹H NMR spectrum (Table 2), in which two signals assigned to the -CH₂- group of the dppm ligand were observed. An analogous behaviour has been described in the [Rh(π -allyl) (dppm)] complex.²³

In conclusion, we have established that the substitution of the two CO ligands in $[Rh(quin)(CO)_2]$ is produced by aryldiphosphine ligands, in contrast with the behaviour observed with monotriarylphosphines.⁶ The monomeric [Rh(quin)(P-P)]complexes obtained show a dynamic behaviour in solution.

$[Rh_2(I)_2(X)_2(quin)_2(CO)_2(\mu-P-P)] (X = I, CH_3; P-P = dppe, dppm) complexes$

Reactions of $[Rh_2(quin)_2(CO)_2(\mu-P-P)]$ (P-P = dppe, dppm) with an excess of I_2 or CH_3I yield the oxidative additions products $[Rh_2(I)_2(X)_2$ $(quin)_2(CO)_2(\mu-P-P)]$ (X = I, CH₃) (Table 1).

 $[Rh_2(I)_4(quin)_2(CO)_2(\mu-P-P)]$ are stable and insoluble orange-brown solids, but the related $[Rh_2(I)_2(CH_3)_2(quin)_2(CO)_2(\mu-P-P)]$ are yellow species soluble in polar organic solvents, in which a slow decomposition is observed; they are neutral in freshly prepared CH_2Cl_2 solutions.

The IR spectra in KBr discs of these new compounds (Table 1) show only one $v(C \equiv O)$ band at 2070–2050 cm⁻¹, indicating relative *trans* positions of the two terminal CO ligands¹⁵ as well as the absence of isomers in the solid state. The $v(C \equiv O)$ values are shifted by 118–88 cm⁻¹ to higher frequencies than those of the starting compounds, in agreement with the formation of octahedral rhodium(III) oxidative addition products.^{12,24} As expected, this shift is higher for the iodine derivatives than the methyl iodide derivatives.¹² The position of $v_{as}(OCO)$ and $v_{sym}(OCO)$ bands is consistent with the (N—O) bidentate coordination of the 2quinaldinate ligand.^{6,12}

The ³¹P NMR spectra of the $[Rh_2(I)_2(CH_3)_2]$ $(quin)_2(CO)_2(\mu - P - P)] (P - P = dppe, dppm) com$ plexes (Table 2) show two signals, with 3:1 and 2:1 relative intensity, respectively, attributed to two isomeric forms in solution. The spectra, monitored by time-scanning, did not show changes in the pattern or the relative intensity of the signals, indicating the simultaneous formation and invariance in the ratio of the two isomers formed. The spectrum of the $[Rh_2(I)_2(CH_3)_2(quin)_2(CO)_2(\mu-dppe)]$ derivative shows two AA'XX' spin system with J(X-X') 0.0 Hz,¹³ both signals showing identical coupling constants (Fig. 1b). This fact suggests the equivalence of the dppe ligands in the two isomers. The ³¹P NMR spectrum of the $[Rh_2(I)_2(CH_3)_2]$ $(quin)_2(CO)_2(\mu$ -dppm)] shows the same pattern, but only one AA'XX' (J(X-X') 0.0 Hz) spin system was observed for the most intense signal, the other one appearing as a broad doublet with only the P-Rh coupling being observed. From the above data a + 3 formal oxidation state for the rhodium atoms¹² as well as no metal-metal bond is proposed for the oxidative addition products. The δ values are consistent with a similar electron-donation of the diphosphine ligands in both parent and oxidative addition products, in contrast with the behaviour observed for the analogous mononuclear species [Rh(I)(CH₃)(quin) $(CO)|P(R-C_6H_4)_3|$.¹² It suggests Rh-CH₃ and Rh-I bonds are weaker in the binuclear rhodium(III) than in the related mononuclear species. This fact is also supported by the higher shielding of the CH₃-protons observed in their ¹H NMR spectra (Table 2) of the former complexes relative to the latter and even to free CH₃I (δ 2.16 ppm).

The existence of the two isomeric forms of $[Rh_2(I)_2(CH_3)_2(quin)_2(CO)_2(\mu-dppm)]$ in solution is confirmed by the ¹H NMR spectrum of this complex. Two signals at δ 1.38 and 1.24 ppm (relative intensity 2:1) assigned to the CH₃ protons indicated the equivalence of the two methyl groups in each isomer. The ¹H NMR spectrum of the dppe derivative (Table 2) shows two sets of signals, the first one consisting in three singlets in the methyl region, and the second one with three signals in the $-CH_2$ - region of the dppe ligand, one of them having lower intensity in each set. We have tentatively assigned the most intense signals to the same isomer, having the two CH₃ ligands no equivalent. In contrast, the disposition of the CH₃ groups in the minor isomer could be related to that in the dppm derivative. It

seems that the larger chain of the bridging dppe ligand permits a different and less constrained disposition of the added groups. This fact is reflected in its relatively higher stability.

There are various possibilities of isomeric compounds to perform the requirements of equivalence between the CO, diphosphine and $-CH_3$ ligands deduced from the spectroscopic data, and in order to deduce the formed isomers their crystalline structures had to be solved. Unfortunately, the instability and low solubility of the compounds studied prevented the isolation of crystals.

Finally, it is noted that dirhodium(I) complexes with two *trans* bridging dppm ligands ("face to face") add generally only one ligand to each rhodium atom giving rise to oxidative addition products with metal-metal bond.²⁴⁻²⁶ This behaviour is different from those observed in our cases. The presence of only one (P---P) bridging ligand makes a less rigid structure allowing the addition of two ligands to each rhodium atom and then no metalmetal bond is required to complete the coordination around the metals.

EXPERIMENTAL

IR spectra were recorded on a 1300 Perkin–Elmer spectrophotometer (over the 4000–200 cm⁻¹ range) with KBr pellets and CH₂Cl₂ solutions. Analyses (C, H, N) were carried out by the Servicio de Microanálisis de la Universidad Complutense de Madrid (Spain). ¹H, ³¹P and ¹³C NMR spectra were recorded on a Varian XR-300 spectrometer at room temperature, using TMS and 85% H₃PO₄ as standards. Mass spectra were recorded on a VG Micromass 7070 spectrometer. Conductance measurements were performed in 10⁻⁴ M CHCl₃ or CH₂Cl₂ solution with a Philips PR 9500 conductimeter. Complex [Rh(quin)(CO)₂] was prepared by our published methods.⁶ Commercial dppe, dppm, I₂ and CH₃I were used.

Solution and refinement of the crystal structure

The crystals were black and fibrous. One of the crystals was mounted on a kappa diffractometer. The cell dimensions refined by least-squares fitting of the θ values of 25 reflections. A summary of the fundamental crystal data is given in Table 5.

The intensities were corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections for rhodium and phosphorus were taken from International Tables for X-ray Crystallography.²⁷ The structure was solved by Patterson and Fourier methods. An empirical absorption correction was

Table 5. Crystal and refinement data for $[Rh_2(quin)_2 (CO)_2(\mu$ -dppm)]

Formula	Rh ₂ P ₂ N ₂ O ₄ C ₄₇ H ₁₄
M,	990.55
Crystal system	Orthorhombic
Space group	$P2_{1}2_{2}2_{1}$
a(Å)	10.123(5)
$b(\mathbf{A})$	20.24(2)
c (Å)	24.067(3)
$V(\dot{A}^3)$	4931(5)
Z	4
<i>F</i> (000)	1992
D_{calc} (g cm ⁻³)	1.33
Temp (K)	295
μ (cm ⁻¹)	7.6
Cryst. dimens., mm	$0.5 \times 0.4 \times 0.5$
Diffractometer	Enraf–Nonius CAD4
Radiation	graphite-monochromated
	Mo- K_{α} ($\lambda = 0.71069$ Å)
Scan technique	ω-2θ
Data collected	(-12,0,0) to $(12,23,28)$
θ	$1 < \theta < 25$
Unique data	4743
Unique data (I) $\geq 2\sigma(I)$	2129
$R_{\rm int}$ (%)	5.4
Std rflns	3/188
Decay (%)	26
$R_{\rm F}$ (%)	8.3
$Rw_{F}(\%)$	9.7
Average shift/error	0.39

applied at the end of isotropic refinement.²⁸ The maximum and minimum absorption correction factors were 1.399 and 0.630, respectively.

In order to prevent bias on $\Delta(F)$ vs (F_o) or sin θ/λ , the last steps of the refinement were calculated by PESOS Program²⁹ with w = $1/(a+b|F_o|)^2$ and the following coefficients: $|F_o| < 59$, a = 16.67 and b = -0.20; $59 < |F_o| < 380$, a = 2.50 and b = 0.03.

A final mixed refinement employing anisotropic factors only for the heavy atoms, due to poor diffraction spectra, and fixed coordinates for the hydrogen atoms lead to R(%) = 8.3 and $R_w = 9.7$.

Calculations were performed using the X-ray 80 program.³⁰ Final atomic positional and thermal parameters, bond lengths and angles, and F_o/F_c values have been deposited as supplementary material with the Editor, from whom copies are available on request. Atomic coordinates have also been submitted to the Cambridge Crystallographic Data Centre.

Preparation of the complexes

The reactions and purification methods were carried out at room temperature, under oxygenfree nitrogen. [Rh₂(quin)₂(CO)₂(μ -dppm)]. Dppm (0.058 g, 0.15 mmol) was added to a suspension in the darkness of [Rh(quin)(CO)₂] (0.100 g, 0.30 mmol) in acetone. A red-black solution was formed, from which a green-black solid gradually precipitated. After 17 h, the solid was filtered off, washed with acetone, recrystallized from CH₂Cl₂/Et₂O-hexane and dried *in vacuo*. Yield : 70%.

A layer of Et_2O /hexane 1:2 over a CH_2Cl_2 solution of $[Rh_2(quin)_2(CO)_2(\mu$ -dppm)] under oxygenfree nitrogen in the darkness gave rise to filiform crystals after 1 day, which were filtered off, washed with Et_2O /hexane and dried *in vacuo*.

[Rh₂(quin)₂(CO)₂(μ -dppe)]. Sixty milligrams of dppe (0.15 mmol) were added to a solution of [Rh(quin)(CO)₂] (0.100 g, 0.30 mmol) in CH₂Cl₂. The colour of the solution changed from redorange to brown, and a yellow solid gradually precipitated. After 17 h stirring the solid was filtered off, washed with cold CH₂Cl₂ and dried *in vacuo*. Yield: 80%.

[Rh(quin)(dppm)]. Method (a): to a cold suspension of dppm (0.081 g, 0.21 mmol) in acctone, [Rh(quin)(CO)₂] (0.063 g, 0.19 mmol) was added. An orange solution was formed, and after 20 min an orange solid began to precipitate. The reaction's mixture was stirred for 16 h and then the solid was filtered off, washed with acetone and dried *in vacuo*. Yield: 60%.

Method (b): to a suspension in the darkness of $[Rh_2(quin)_2(CO)_2(\mu$ -dppm)] (0.090 g, 0.09 mmol) in acetone 0.038 g (0.10 mmol) of dppm were added. After 5 h the orange solid formed was filtered off, washed with acetone and dried *in vacuo*. Yield: 65%.

[Rh(quin)(dppe)]. Method (a): the addition of dppe (0.132 g, 0.33 mmol) to a solution of [Rh(quin)(CO)₂] (0.100 g, 0.30 mmol) in CH₂Cl₂ caused a change in the colour from red-orange to brown. The colour became yellow with evolution of the reaction. After 48 h, the addition of Et₂O precipitated a yellow solid which was filtered off, recrystallized from CH₂Cl₂/Et₂O, washed with Et₂O and dried *in vacuo*. Yield: 58%.

Method (b): the addition of dppe (0.052 g, 0.13 mmol) to a suspension of $[\text{Rh}_2(\text{quin})_2(\text{CO})_2(\mu-\text{dppe})]$ (0.120 g, 0.12 mmol) in CH₂Cl₂ caused slow redissolution and after 28 h a yellow solution was obtained. The complex was precipitated and purified as above. Yield : 62%.

[Rh₂(I)₄(quin)₂(CO)₂(μ -P—P)] (P—P = dppe, dppm). 0.040 g of I₂ (0.16 mmol) in CH₂Cl₂ solution was added in the darkness to [Rh₂(quin)₂(CO)₂(μ -P—P)] (P—P = dppe, dppm; 0.070 g, 0.07 mmol) in CH₂Cl₂. An orange-brown precipitate was formed. After 1 h the solid was filtered off, washed with CH_2Cl_2 and dried in vacuo. Yield: P-P = dppe, 85%; P-P = ddpm, 80%.

[Rh₂(I)₂(CH₃)₂(quin)₂(CO)₂(μ -P—P)] (P—P = dppe, dppm). Excess CH₃I (2 cm³) was added in the darkness to the complexes [Rh₂(quin)₂ (CO)₂(μ -P—P)] (P—P = dppe, dppm; 0.100 g, 0.10 mmol) in CH₂Cl₂. A yellow (P—P = dppe) or red (P—P = dppm) solution was formed. The solutions were stirred for 1 h and a faint precipitate that appeared (P—P = dppm) was separated by filtration. After concentration of the solutions under reduced pressure and addition of Et₂O/n-hexane (1/4) the yellow solid compounds were obtained. They were filtered off, recrystallized from CH₂Cl₂/Et₂O-hexane and dried *in vacuo*. Yield: P—P = dppe, 70%; P—P = dppm, 60%.

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