

# Synthesis and some Reactions of Binuclear $\eta$ -Cyclopentadienyl Rhodium Complexes containing Bis(diphenylphosphino)methane and Small Molecules (CO, SO<sub>2</sub>, or SnCl<sub>2</sub>) as Bridging Ligands. Crystal and Molecular Structure of [Rh<sub>2</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>( $\mu$ -CO)( $\mu$ -Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>)] †

Felice Faraone,\* Giuseppe Bruno, Sandra Lo Schiavo, and Gabriella Bombieri

Dipartimento di Chimica Inorganica e Struttura Molecolare, Università di Messina, Piazza S. Pugliatti, 98100 Messina, Italy

The compound [Rh<sub>2</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>( $\mu$ -CO)( $\mu$ -dppm)] (1) was obtained from the reaction of [Rh<sub>2</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>( $\mu$ -CO)(CO)<sub>2</sub>] with bis(diphenylphosphino)methane (dppm). The X-ray structure determination of (1) shows it to crystallize in the space group C2/c with unit-cell dimensions  $a = 23.738(7)$ ,  $b = 11.731(3)$ ,  $c = 26.883(7)$  Å,  $\beta = 123.2(1)^\circ$ , and  $Z = 8$ . On the basis of 2 809 reflections with  $I \geq 3\sigma(I)$ , the structure has been refined to  $R = 0.050$  and  $R' = 0.045$ . The molecule consists of two rhodium atoms bridged by a carbonyl group and a dppm ligand; a terminal  $\eta$ -C<sub>5</sub>H<sub>5</sub> ligand completes the co-ordination sphere of each rhodium atom. The Rh(1)-CO-Rh(2) and P(1)-CH<sub>2</sub>-P(2) fragments are folded on the same side. The cyclopentadienyl ligands are in *cis* position with an interplanar angle of 82.1°. Compound (1) reacts with SO<sub>2</sub> to give [Rh<sub>2</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>( $\mu$ -SO<sub>2</sub>)( $\mu$ -dppm)] and with SnCl<sub>2</sub> to give [Rh<sub>2</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>( $\mu$ -CO)( $\mu$ -SnCl<sub>2</sub>)( $\mu$ -dppm)]. For these reactions the possible site of attack at (1) is discussed. The oxidative addition of Br<sub>2</sub> and I<sub>2</sub> to (1) changes the CO bonding from bridging to terminal. From the reaction with Br<sub>2</sub> the cationic complex [( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Br<sub>2</sub>Rh( $\mu$ -dppm)Rh(CO)Br( $\eta$ -C<sub>5</sub>H<sub>5</sub>)]Br<sub>3</sub> was isolated; in solution it releases CO to form the neutral complex [Rh<sub>2</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Br<sub>4</sub>( $\mu$ -dppm)]. Initial oxidative addition to one rhodium atom occurs in the reaction of I<sub>2</sub> with (1) and [Rh<sub>2</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(CO)I<sub>2</sub>( $\mu$ -dppm)] was isolated. Compound (1) does not react with MeI or with diphenylacetylene in diethyl ether.

We have been interested recently in the reactions of [Rh( $\eta$ -C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>] with the chelating diphosphines Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>n</sub>PPh<sub>2</sub> ( $n = 1-4$ ) and found that the nature of the products obtained depends on the chelate diphosphine chain length.<sup>1,2</sup> The mononuclear complex [Rh( $\eta$ -C<sub>5</sub>H<sub>5</sub>)(CO)(dppm)] [dppm = bis(diphenylphosphino)methane], in which the dppm behaves as a monodentate two-electron donor ligand, has been found as the only product of the reaction of [Rh( $\eta$ -C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>] with dppm. The interest of this finding, due to the fact that in the rhodium complexes dppm acts as a bridging<sup>3-9</sup> or chelating<sup>10-12</sup> ligand, has prompted us to investigate other reactions involving dppm and  $\eta$ -cyclopentadienyl rhodium complexes.

Here we report the synthesis of a new series of binuclear  $\eta$ -cyclopentadienyl rhodium complexes of the type [Rh<sub>2</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>( $\mu$ -X)( $\mu$ -dppm)] (X = CO or SO<sub>2</sub>) and [Rh<sub>2</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>( $\mu$ -CO)( $\mu$ -SnCl<sub>2</sub>)( $\mu$ -dppm)], containing dppm and small molecules as bridging ligands, and the oxidative addition of Br<sub>2</sub> and I<sub>2</sub> on one member of this series, [Rh<sub>2</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>( $\mu$ -CO)( $\mu$ -dppm)]. For this compound the X-ray structure determination is also reported and some comparisons with the 'A-frame' type molecules<sup>3</sup> have been made tentatively.

## Results and Discussion

The addition, at room temperature, of dppm to a diethyl ether solution of [Rh<sub>2</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>( $\mu$ -CO)(CO)<sub>2</sub>] affords the compound [Rh<sub>2</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>( $\mu$ -CO)( $\mu$ -dppm)] (1) as a brown solid, non-electrolyte in benzene solution, and stable in the

solid state for about a week. Its solutions in diethyl ether or benzene are yellow and stable for several hours; acetone and chlorinated solvents decompose the complex more rapidly. A factor complicating this reaction is the formation of a violet product when the mixture is left to stand until the starting rhodium complex has completely reacted. Thus (1), in a pure form, can be obtained only in low yield, interrupting the reaction before the formation of the violet product. This latter complex has not been characterized fully; however, i.r. and <sup>1</sup>H n.m.r. spectral data do not show the presence of carbonyl or cyclopentadienyl groups. Most likely this compound derives from (1), as it forms slowly also when (1) is dissolved in acetone or in chlorinated solvents.

Complex (1) shows, in the i.r. spectrum, a low stretching frequency for the bridging carbonyl ligand at 1 730 cm<sup>-1</sup> and, in the <sup>1</sup>H n.m.r. spectrum, the cyclopentadienyl protons resonance at  $\delta$  5.22 (CDCl<sub>3</sub>), as doublet of doublets [ $J(\text{HP}) = 0.8$ ,  $J(\text{HRh}) = 0.5$  Hz]. For this and the other compounds here reported [except compound (3)] the CH<sub>2</sub> group of the  $\mu$ -dppm ligand gives rise to one broad multiplet. This could be due to time averaging of PCH<sub>2</sub>P protons, rather than to a real equivalence.

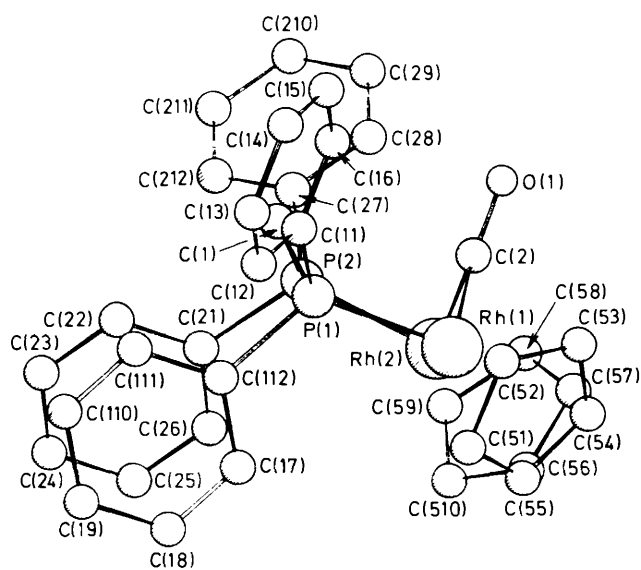
In order to define fully the molecular structure of complex (1) a single-crystal X-ray diffraction study has been undertaken. A view of the structure of (1) down the *c* axis, including the numbering scheme, is presented in Figure 1. Final positional parameters are given in Table 1, bond lengths and angles in Table 2. The molecule consists of two rhodium atoms bridged by a carbonyl group and a dppm ligand; the terminal cyclopentadienyl ligand completes the co-ordination sphere of each rhodium atom. Although the molecule approximates idealized C<sub>s</sub> symmetry, with a mirror plane passing through the methyl and carbonyl groups, this is destroyed by the non-symmetrical orientation of the phenyl and cyclopentadienyl groups, as is shown in Figure 2. While the co-ordination number of Rh is five, the parameters listed in Table 1 indicate a trigonal co-ordination geometry if the  $\eta$ -cyclopentadienyl ligand is

†  $\mu$ -[Bis(diphenylphosphino)methane]- $\mu$ -carbonyl-bis( $\eta$ -cyclopentadienyl)dirhodium(I) (Rh-Rh).

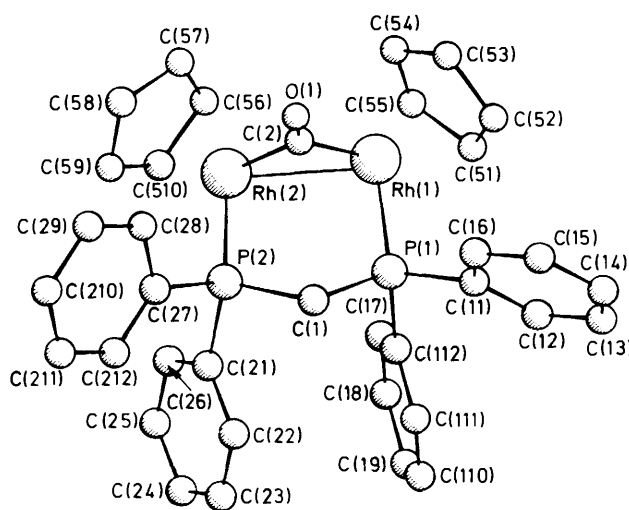
Supplementary data available (No. SUP 23808, 22 pp.): observed and calculated structure factors, thermal parameters, least-squares planes. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii-xix.

**Table 1.** Final fractional atomic co-ordinates ( $\times 10^4$ ) for non-hydrogen atoms, with estimated standard deviations in parentheses

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Rh(1)	2 949(0)	2 466(1)	1 572(0)	C(16)	3 850(4)	977(6)	3 165(3)
Rh(2)	1 604(0)	2 259(1)	915(0)	C(11)	3 836(4)	532(6)	2 677(3)
P(1)	3 071(1)	727(2)	1 929(1)	C(18)	3 032(4)	-1 156(6)	628(2)
P(2)	1 576(1)	590(2)	1 288(1)	C(19)	3 211(4)	-2 245(6)	876(2)
C(1)	2 374(4)	288(7)	2 002(3)	C(110)	3 344(4)	-2 440(6)	1 442(2)
O(1)	2 226(4)	3 135(6)	2 138(3)	C(111)	3 298(4)	-1 547(6)	1 761(2)
C(2)	2 247(5)	2 766(7)	1 739(4)	C(112)	3 119(4)	-458(6)	1 513(2)
C(51)	3 808(7)	2 687(11)	1 426(8)	C(17)	2 986(4)	-263(6)	947(2)
C(52)	4 002(6)	3 131(13)	1 996(6)	C(22)	1 644(3)	-1 766(5)	1 117(2)
C(53)	3 599(7)	4 076(10)	1 888(6)	C(23)	1 518(3)	-2 736(5)	770(2)
C(54)	3 135(7)	4 157(10)	1 282(7)	C(24)	1 159(3)	-2 644(5)	152(2)
C(55)	3 254(7)	3 343(12)	974(6)	C(25)	926(3)	-1 582(5)	-118(2)
C(56)	1 406(6)	3 365(11)	134(6)	C(26)	1 053(3)	-613(5)	228(2)
C(57)	1 193(7)	3 963(9)	461(5)	C(21)	1 412(3)	-705(5)	846(2)
C(58)	663(6)	3 376(11)	427(6)	C(28)	832(3)	1 479(4)	1 719(3)
C(59)	560(5)	2 386(9)	91(5)	C(29)	346(3)	1 475(4)	1 859(3)
C(510)	998(6)	2 414(10)	-111(4)	C(210)	-35(3)	497(4)	1 763(3)
C(12)	4 408(4)	9(6)	2 756(3)	C(211)	69(3)	-478(4)	1 526(3)
C(13)	4 993(4)	-69(6)	3 323(3)	C(212)	555(3)	-474(4)	1 386(3)
C(14)	5 007(4)	376(6)	3 811(3)	C(27)	936(3)	504(4)	1 482(3)
C(15)	4 436(4)	899(6)	3 732(3)				
$M_A^*$	3 560	3 479	1 513	$M_B^*$	964	3 101	200

**Figure 1.** View of the molecule down *c*

regarded as occupying a single triangular vertex, the other two being occupied by one carbon and one phosphorus of the two bridging ligands. The Rh(1)-CO-Rh(2) and P(1)-CH<sub>2</sub>-P(2) fragments are folded on the same side; this results from the steric requirement to have the two cyclopentadienyl ligands in the less hindered side of the molecule. The coordination of the cyclopentadienyl ligands seems to orientate the distribution of the other ligands *trans* to them. In this respect it is interesting to compare the structural features of the complex considered here with those of [Rh<sub>2</sub>(η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(μ-CO)<sub>2</sub>(PPh<sub>3</sub>)].<sup>13</sup> In the latter a folding of the two bridging CO groups in *cis* positions with an interplanar angle 145.6° is observed, while between the cyclopentadienyl groups, also in *cis* positions, the angle is 66°. This could be correlated to the folding of the CO bridging group and the P(1)-C(1)-P(2) fragment corresponding to an angle of 44.1° and to the inter-

**Figure 2.** View of the molecule down *a*

planar angles between the two cyclopentadienyl ligands of 82.1° in the present complex.

The Rh-P(dppm) distances in (1) are comparable to those found in a related dppm-bridged dimer.<sup>14</sup> It is worthwhile comparing the parameters of the bridged dppm framework with those of the unbridged dppm in the monomeric complex [Rh(η-C<sub>5</sub>H<sub>5</sub>)(CO)(dppm)].<sup>2</sup> The two independent Rh-P distances [2.218(2) and 2.205(2) Å] in the dimer are slightly different, but this is probably a consequence of packing effects, and both are significantly shorter than the Rh-P distance (2.240 Å) in the monomer. The P-C-P angle (114.4°) in the monomer rhodium compound is reduced to 107.8(4)° in (1) and the configuration of the dppm ligand is the same in the two compounds, with *cis* related P atoms in both cases. The P-C(methylene) distances are not influenced by the chelation being equal, within experimental error, to those of the unbridged dppm and are again comparable with the P-C(phenyl) distances. The symmetrically bridging carbonyl

Table 2. Molecular geometry

(a) Intramolecular distances (Å)			
Rh(1)-Rh(2)	2.683(1)		
Rh(1)-P(1)	2.205(2)	Rh(2)-P(2)	2.218(2)
Rh(1)-C(2)	1.978(9)	Rh(2)-C(2)	1.971(9)
Rh(1)-C(51)	2.295(10)	Rh(2)-C(56)	2.288(11)
Rh(1)-C(52)	2.245(11)	Rh(2)-C(57)	2.266(10)
Rh(1)-C(53)	2.288(10)	Rh(2)-C(58)	2.285(11)
Rh(1)-C(54)	2.262(10)	Rh(2)-C(59)	2.250(10)
Rh(1)-C(55)	2.334(11)	Rh(2)-C(510)	2.318(10)
average Rh(1)-C	2.285(10)	average Rh(2)-C	2.281(10)
P(1)-C(1)	1.843(8)	P(2)-C(1)	1.849(8)
P(1)-C(11)	1.843(7)	P(2)-C(21)	1.835(6)
P(1)-C(112)	1.828(6)	P(2)-C(27)	1.858(6)
C(2)-O(1)	1.182(9)		
C(51)-C(52)	1.44(2)	C(56)-C(57)	1.42(2)
C(51)-C(55)	1.43(2)	C(56)-C(510)	1.38(2)
C(52)-C(53)	1.39(2)	C(57)-C(58)	1.39(2)
C(53)-C(54)	1.38(2)	C(58)-C(59)	1.41(2)
C(54)-C(55)	1.39(2)	C(59)-C(510)	1.41(1)
average C-C	1.41(2)	average C-C	1.40(2)
Rh-M <sub>A</sub> *	1.947(10)	Rh-M <sub>B</sub> *	1.945(10)
(b) Intramolecular angles (°)			
C(2)-Rh(1)-P(1)	89.6(3)	C(2)-Rh(2)-P(2)	87.4(3)
C(1)-P(1)-Rh(1)	113.1(3)	C(21)-P(2)-Rh(2)	119.1(2)
C(11)-P(1)-C(1)	104.8(3)	C(21)-P(2)-C(1)	104.3(3)
C(11)-P(1)-Rh(1)	113.9(2)	C(27)-P(2)-Rh(2)	114.0(2)
C(112)-P(1)-Rh(1)	118.4(2)	C(27)-P(2)-C(1)	103.3(3)
C(112)-P(1)-C(1)	102.3(3)	C(27)-P(2)-C(21)	102.7(3)
C(112)-P(1)-C(11)	102.6(3)	P(2)-C(1)-P(1)	107.8(4)
O(1)-C(2)-Rh(1)	136.8(8)	O(1)-C(2)-Rh(2)	137.5(8)
Rh(2)-C(2)-Rh(1)	85.6(4)	C(1)-P(2)-Rh(2)	111.8(3)
M <sub>A</sub> *-Rh(1)-C(2)	131.8(3)	M <sub>B</sub> *-Rh(2)-C(2)	131.5(3)
M <sub>A</sub> *-Rh(1)-P(1)	132.3(3)	M <sub>B</sub> *-Rh(2)-P(2)	134.0(3)

group has an average Rh-C distance of 1.974(9) Å and the Rh-C(CO)-Rh angle is 85.6(4)°, as expected.<sup>15</sup> The observed Rh-C distance is comparable with the values of 1.960(8) and 1.974(7) Å reported for [Rh<sub>2</sub>Br<sub>2</sub>(μ-CO)(μ-dppm)<sub>2</sub>]<sup>9</sup> and [Rh<sub>2</sub>Cl<sub>2</sub>(μ-CO)(μ-dema)(dppm)<sub>2</sub>]<sup>16</sup> (dema = dimethyl acetylenedicarboxylate) respectively, and is significantly shorter than the values observed in other rhodium complexes containing bridging carbonyl ligands. The geometrical features of (1) (Figures 1 and 2) suggest the possibility of a comparison with those of 'A-frame' complexes<sup>3,17</sup> having dppm ligands. The metal square-planar geometry of the 'A-frame' molecules is replaced by a trigonal geometry in (1), but the two metal centres are still tied together through the common ligand CO at the apex; the terminal ligands are cyclopentadienyls, rather than the more typical halogen, CO, or CNR. The Rh-Rh bond distance in (1) is significantly shorter than that [2.756(9) Å] reported for the 'A-frame' complex [Rh<sub>2</sub>Br<sub>2</sub>(μ-CO)(μ-dppm)<sub>2</sub>]<sup>9</sup> also the Rh-C-Rh bond angle of 85.6(4)° is smaller than the value [89.4(4)°] for the latter. However, the P...P separation, 2.983(3) Å, is comparable with the values [3.026(3) and 2.994(3) Å] reported for the above 'A frame' complex. This suggests that the sub-

stitution of the second dppm ligand and of the two terminal halogens by the two cyclopentadienyl ligands allow a shorter Rh-Rh bond; the length of this bond is therefore influenced by the number and the steric hindrance of the ligands. In the idealized 'A-frame' the (terminal ligand)-metal-(apex bridge ligand) angle is about 180°;<sup>3,17</sup> in the present case the terminal ligands are substituted by the cyclopentadienyls and the angles C(2)-Rh(1)-M<sub>A</sub>\* and C(2)-Rh(2)-M<sub>B</sub>\* are respectively 131.8(3) and 131.5(3)°, substantially different from the ideal value of 180° [M<sub>A</sub>\* and M<sub>B</sub>\* represent the centroids of cyclopentadienyl rings C(51)-C(55) and C(56)-C(510) respectively].

The unit-cell contents of [Rh<sub>2</sub>(η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(μ-CO)(μ-dppm)] are shown in Figure 3.

The compound (1) reacts with sulphur dioxide to give the complex [Rh<sub>2</sub>(η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(μ-SO<sub>2</sub>)(μ-dppm)] (2) as an orange solid, a non-electrolyte in solution, and soluble in benzene and chlorinated solvents. Its i.r. spectrum is similar to that of (1), except for the lack of a band associated with a carbonyl group and the presence of bands at 1160 and 1040 cm<sup>-1</sup> which are due to the symmetric and asymmetric S-O stretching frequencies. These values are at frequencies lower than those generally observed for other SO<sub>2</sub> ligands bridging metal-metal bonded centres.<sup>7,18-23</sup> Low ν(SO) frequencies, have already been observed<sup>9,23,24</sup> for SO<sub>2</sub>-bridged compounds for which the parent μ-CO complex exhibits a low ν(CO) value. The low ν(CO) and ν(SO) values for (1) and (2) can result from the fact that rhodium atoms in these complexes are both electron rich. Consequently the bond with the acceptor ligands CO and SO<sub>2</sub> is particularly strong, as evidenced by the short rhodium-carbonyl distance in (1). The <sup>1</sup>H n.m.r. spectrum shows a single resonance at δ 5.19 (CDCl<sub>3</sub>) due to the cyclopentadienyl protons as a doublet of doublets [*J*(HP) = 0.9, *J*(HRh) = ca. 0.6 Hz], indicating that (2) is a symmetric species. The i.r. spectra obtained during the slow stepwise addition of SO<sub>2</sub> to (1) do not show new bands assignable to bridging or terminal carbonyl species. Once the reaction has reached completion only the symmetric SO<sub>2</sub>-bridged species, [Rh<sub>2</sub>(η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(μ-SO<sub>2</sub>)(μ-dppm)] remains in solution. Thus the i.r. spectra seem to exclude the SO<sub>2</sub> attack at a terminal position, remote from the bridging site. On the other hand, the possibility of an SO<sub>2</sub> attack directly at the bridging site is supported by the isolation of the complex [Rh<sub>2</sub>(η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(μ-CO)(μ-SnCl<sub>2</sub>)(μ-dppm)] (3), in which the bridging site is occupied by the SnCl<sub>2</sub> group. Compound (3) is the product of the reaction of (1) with SnCl<sub>2</sub>; it is an orange solid, non-conducting in benzene solution, soluble in benzene, acetone, and chlorinated solvents, and insoluble in diethyl ether and saturated hydrocarbons. In agreement with its formulation the i.r. spectrum shows ν(CO) at 1795 cm<sup>-1</sup> and ν(Sn-Cl) at 290 and 320 cm<sup>-1</sup>; in the <sup>1</sup>H n.m.r. spectrum the cyclopentadienyl resonance is observed at δ 5.40 (CDCl<sub>3</sub>) as a not well resolved multiplet, due to the coupling of the hydrogens with the phosphorus, tin, and rhodium atoms.

The formation of (3) is evidence for the presence of the metal-metal bond in (1); thus the SnCl<sub>2</sub> can approach the metal centres to give insertion. The insertion of SnCl<sub>2</sub> in the metal-metal bond of organometallic complexes is a well known reaction.<sup>25</sup> SO<sub>2</sub>, which does not undergo the same process, forms a different product in the analogous reaction. Recently it has been reported that while [Rh<sub>2</sub>(η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(μ-CO)(CO)<sub>2</sub>] reacts with SO<sub>2</sub>, giving [Rh<sub>2</sub>(η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(μ-SO<sub>2</sub>)(CO)<sub>2</sub>],<sup>20</sup> the analogous reaction with SnCl<sub>2</sub> yields the trimer [{Rh(η-C<sub>5</sub>H<sub>5</sub>)(CO)(SnCl<sub>2</sub>)<sub>3</sub>].<sup>26</sup>

The addition of bromine to a benzene solution of (1) affords an orange compound, which, on the basis of analytical, spectroscopic and conductivity data must be formulated as [(η-C<sub>5</sub>H<sub>5</sub>)Br<sub>2</sub>Rh(μ-dppm)Rh(CO)Br(η-C<sub>5</sub>H<sub>5</sub>)]Br<sub>3</sub> (4). Ac-

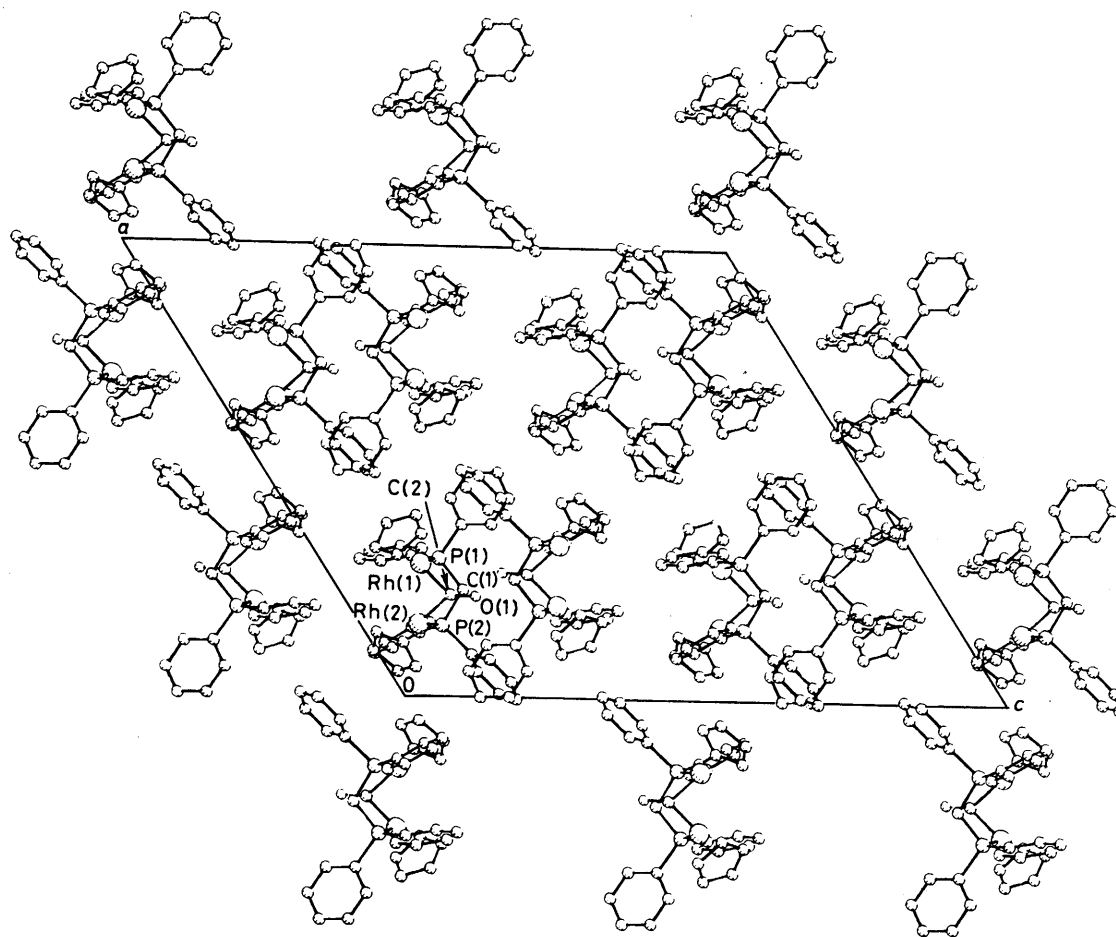


Figure 3. Molecular packing down *b*

cordingly its conductivity in acetone solution is in the range expected for a 1 : 1 electrolyte and its i.r. spectrum shows the carbonyl stretching frequency at  $2100\text{ cm}^{-1}$ , *i.e.* at a value indicative of a terminal CO in a rhodium(III) complex. In agreement with the fact that the co-ordinated cyclopentadienyl ions are not in equivalent environments, two signals, appearing as doublets at  $\delta$  5.38 and 6.07 are observed in the  $^1\text{H}$  n.m.r. spectrum ( $\text{CDCl}_3$ ). The signals at lower field can be assigned to cyclopentadienyl bonded to a rhodium-carbonyl moiety, due to the effect of the charge of the metal on the cyclopentadienyl proton resonance.<sup>27</sup> For complex (4), as well as for the other compounds obtained from the reactions of (1) with halogens, the splitting of the cyclopentadienyl resonance by rhodium atoms appears to be beyond the resolution of the spectrophotometer and not calculable.

The oxidative addition of  $\text{Br}_2$  to (1) implies initial cleavage of the rhodium-carbonyl bond [as confirmed also by the isolation of (6)] and subsequent oxidation by a second  $\text{Br}_2$  molecule of the rhodium(I) associated with the CO group.

As usually found for mononuclear cationic cyclopentadienyl-carbonyl or -thiocarbonyl rhodium(III) species<sup>27,28</sup> complex (4), when left in solution, releases the CO, converting to the neutral complex  $[\text{Rh}_2(\eta\text{-C}_5\text{H}_5)_2\text{Br}_4(\mu\text{-dppm})]$  (5). In the  $^1\text{H}$  n.m.r. spectrum a single resonance at  $\delta$  5.32 [ $J(\text{HP}) = 1.3\text{ Hz}$ ] for the cyclopentadienyl protons, indicating that (5) is a symmetric species, is observed.

The reaction of (1) with iodine is different to the analogous reaction with bromine. The slow stepwise addition of  $\text{I}_2$  to (1) in diethyl ether solution produces the compound  $[\text{Rh}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})\text{I}_2(\mu\text{-dppm})]$  (6) as a brown solid, a non-

electrolyte in benzene solution. The i.r. spectrum of the compound shows a band at  $2000\text{ cm}^{-1}$  due to terminal CO stretching and in the  $^1\text{H}$  n.m.r. two different resonances for the cyclopentadienyl protons at  $\delta$  5.46 [ $J(\text{HP}) = 1.0\text{ Hz}$ ] and 5.70 [ $J(\text{HP}) = 0.8\text{ Hz}$ ] ( $\text{CDCl}_3$ ) are observed. The formation of (6) results from a mononuclear oxidative addition of  $\text{I}_2$  to (1). Initial oxidative addition to one rhodium atom has been proposed for the oxidative addition of  $\text{H}_2$  to  $[\text{Rh}(\text{PPh}_3)_2\text{Cl}]_2$ <sup>29,30</sup> and of MeI and MeBr to  $[\text{Rh}(\text{SBU}^1(\text{CO})(\text{PMe}_2\text{Ph})_2)]_2$ .<sup>31</sup> The value of  $\nu(\text{CO})$  in (6) is rather high for a carbonyl in a rhodium(I) environment; the interaction between one of the iodides with the rhodium(I) (associated with the CO group) can account for the observed value. This interaction can be favoured since the two rhodium atoms are in close proximity owing to the dppm steric requirements. The larger steric bulk of the  $\text{I}^-$  ligand, compared to  $\text{Br}^-$ , certainly favours the formation of (6). An excess of  $\text{I}_2$  reacts with (1) or with (6) to give a mixture of uncharacterized compounds.

Compound (1) does not react with neat MeI or with diphenylacetylene in diethyl ether.

### Experimental

$[\text{Rh}_2(\eta\text{-C}_5\text{H}_5)_2(\mu\text{-CO})(\text{CO})_2]$  was prepared by a modification of a published procedure.<sup>26</sup> Other reagents were used as obtained from commercial sources. Infrared spectra were recorded with a Perkin-Elmer 457 spectrometer using a polystyrene film for calibration. A Perkin-Elmer R 24B spectrometer was used to obtain  $^1\text{H}$  n.m.r. spectra;  $\text{SiMe}_4$  was used as internal standard. Molecular weights were determined

with a Knauer vapour pressure osmometer. Conductivity measurements were made with a Radiometer CDM 3 conductivity meter. Elemental analyses were performed by the Microanalytical Laboratory of the Organic Chemistry Institute of Milan and Analytische Laboratorien Malissa and Reuter, Elbach, Germany.

All the reactions were carried out under an atmosphere of oxygen-free nitrogen.

$\mu$ -[Bis(diphenylphosphino)methane]- $\mu$ -carbonyl-bis( $\eta$ -cyclopentadienyl)dirhodium(I),  $[\text{Rh}_2(\eta\text{-C}_5\text{H}_5)_2(\mu\text{-CO})(\mu\text{-dppm})]$  (1).—To a diethyl ether solution (60 cm<sup>3</sup>) of  $[\text{Rh}_2(\eta\text{-C}_5\text{H}_5)_2(\mu\text{-CO})(\text{CO})_2]$  (0.200 g, 0.5 mmol), dppm (0.192 g, 0.5 mmol) in the same solvent (20 cm<sup>3</sup>) was added dropwise, with stirring. The stoichiometric amount of dppm was not all added, and the brown precipitate which formed (1 h) was removed by filtration, washed with pentane and dried. Additional product was obtained by adding the remaining dppm solution to the filtrate. If the addition of dppm solution is not slow, the product obtained is impure with the presence of a violet product (see Results and Discussion section); yield 56% [Found: C, 57.6; H, 4.3%; M ( $\text{C}_6\text{H}_6$ ), 735.  $\text{C}_{36}\text{H}_{32}\text{O}_2\text{P}_2\text{Rh}_2$  requires C, 57.75; H, 4.3%; M, 748];  $\nu(\text{CO}) = 1\ 730\ \text{cm}^{-1}$  (Nujol);  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 5.22 [dd, 10 H,  $\text{C}_5\text{H}_5$ ,  $J(\text{HP}) = 0.8$ ,  $J(\text{HRh}) = 0.5\ \text{Hz}$ ], 2.70 [m, br, 2 H,  $\text{CH}_2$ ], 7.12—7.45 [m br, 20 H,  $\text{C}_6\text{H}_5$ ].

$\mu$ -[Bis(diphenylphosphino)methane]-bis( $\eta$ -cyclopentadienyl)- $\mu$ -(sulphur dioxide)-dirhodium(I),  $[\text{Rh}_2(\eta\text{-C}_5\text{H}_5)_2(\mu\text{-SO}_2)(\mu\text{-dppm})]$  (2).—Sulphur dioxide was bubbled through a benzene solution (70 cm<sup>3</sup>) of (1) (0.085 g, 0.114 mmol). The solution turned from brown-yellow to orange, while a little orange precipitate was formed. The solution was concentrated to 5 cm<sup>3</sup> by evaporation at reduced pressure. Precipitation was completed by adding pentane. The orange product obtained was recrystallized from dichloromethane-hexane (1:3); yield 0.086 g, 96% [Found: C, 53.65; H, 4.1; S, 4.15%; M ( $\text{C}_6\text{H}_6$ ), 768.  $\text{C}_{35}\text{H}_{32}\text{O}_2\text{P}_2\text{Rh}_2\text{S}$  requires C, 53.6; H, 4.1; S, 4.1%; M, 784];  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 5.19 [dd, 10 H,  $\text{C}_5\text{H}_5$ ,  $J(\text{HP}) = 0.9$ ,  $J(\text{HRh}) = \text{ca. } 0.6\ \text{Hz}$ ], 2.66 [m br, 2 H,  $\text{CH}_2$ ], 7.02—7.64 [m br, 20 H,  $\text{C}_6\text{H}_5$ ].

$\mu$ -[Bis(diphenylphosphino)methane]- $\mu$ -carbonyl-bis( $\eta$ -cyclopentadienyl)- $\mu$ -(dichlorostannio)-dirhodium,  $[\text{Rh}_2(\eta\text{-C}_5\text{H}_5)_2(\mu\text{-CO})(\mu\text{-SnCl}_2)(\mu\text{-dppm})]$  (3).—To a benzene solution (70 cm<sup>3</sup>) of (1) (0.11 g, 0.15 mmol) was added  $\text{SnCl}_2$  (0.028 g, 0.15 mmol). The mixture was stirred at room temperature for ca. 1 h. The solution turned orange. It was filtered and the solvent evaporated off at reduced pressure. The crude product was extracted with benzene and then recrystallized from dichloromethane-hexane (1:3); yield 0.062 g, 45% [Found: C, 45.9; H, 3.3; Cl, 7.7%; M ( $\text{C}_6\text{H}_6$ ), 925;  $\text{C}_{36}\text{H}_{32}\text{Cl}_2\text{OP}_2\text{Rh}_2\text{Sn}$  requires C, 46.1; H, 3.4; Cl, 7.55%; M, 938];  $\nu(\text{CO}) = 1\ 795\ \text{vs}\ \text{cm}^{-1}$  (Nujol);  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 5.40 [m, 10 H,  $\text{C}_5\text{H}_5$ ], 2.74, 2.86 [m, br, 2 H,  $\text{CH}_2$ ], 7.2—7.45 [m br, 20 H,  $\text{C}_6\text{H}_5$ ].

$\mu$ -[Bis(diphenylphosphino)methane]-tribromocarbonylbis( $\eta$ -cyclopentadienyl)dirhodium Tribromide,  $[\text{Rh}_2\text{Br}_3(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\mu\text{-dppm})]\text{Br}_3$  (4).—A solution of bromine in benzene was added dropwise to a solution of (1) (0.130 g, 0.17 mmol) in the same solvent (85 cm<sup>3</sup>). An orange precipitate was immediately formed. This was collected by filtration, washed several times with diethyl ether and dried; yield 0.200 g, 94% (Found: C, 35.2; H, 2.5; Br, 39.2.  $\text{C}_{36}\text{H}_{32}\text{Br}_6\text{OP}_2\text{Rh}_2$  requires C, 35.2; H, 2.6; Br, 39.05%);  $\nu(\text{CO}) = 2\ 100\ \text{vs}\ \text{cm}^{-1}$  (Nujol);  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 5.38 [d, 5 H,  $\text{C}_5\text{H}_5$ ,  $J(\text{HP}) = 1.2$ ], 6.07 [d, 5 H,  $\text{C}_5\text{H}_5$ ,  $J(\text{HP}) = 1.4\ \text{Hz}$ ], 2.28 [m br, 2 H,  $\text{CH}_2$ ], 7.2—7.5 [m br, 20 H,  $\text{C}_6\text{H}_5$ ].

$\mu$ -[Bis(diphenylphosphino)methane]-tetrabromobis( $\eta$ -cyclopentadienyl)dirhodium(III),  $[\text{Rh}_2(\eta\text{-C}_5\text{H}_5)_2\text{Br}_4(\mu\text{-dppm})]$  (5).—An acetone solution (30 cm<sup>3</sup>) of (4) (0.070 g, 0.057 mmol) was left to stand until the i.r. spectrum indicated complete disappearance of the  $\nu(\text{CO})$  band (ca. 5 h). The solvent was partially evaporated at reduced pressure. The product was obtained as an orange solid by adding hexane; yield 0.053 g, 89% [Found: C, 40.55; H, 3.2; Br, 30.9%; M ( $\text{C}_6\text{H}_6$ ), 1 026.  $\text{C}_{35}\text{H}_{32}\text{Br}_4\text{P}_2\text{Rh}_2$  requires C, 40.4; H, 3.1; Br, 30.75%; M, 1 040];  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 5.32 [d, 10 H,  $\text{C}_5\text{H}_5$ ,  $J(\text{HP}) = 1.3\ \text{Hz}$ ], 2.24 [m br, 2 H,  $\text{CH}_2$ ], 7.1—7.5 [m br, 20 H,  $\text{C}_6\text{H}_5$ ].

$\mu$ -[Bis(diphenylphosphino)methane]-carbonylbis( $\eta$ -cyclopentadienyl)di-iododirhodium,  $[\text{Rh}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})\text{I}_2(\mu\text{-dppm})]$  (6).—To a diethyl ether solution (130 cm<sup>3</sup>) of (1) (0.120 g, 0.16 mmol) a solution of iodine (0.041 g, 0.16 mmol) in the same solvent (5 cm<sup>3</sup>) was added dropwise, making sure not to add an excess of iodine. A brown precipitate was immediately formed. This was separated by filtration, washed with diethyl ether and dried; yield 0.100 g, 62% [Found: C, 43.25; H, 3.3; I, 25.65%; M ( $\text{C}_6\text{H}_6$ ), 1 015.  $\text{C}_{36}\text{H}_{32}\text{I}_2\text{OP}_2\text{Rh}_2$  requires C, 43.15; H, 3.2; I, 25.3%; M, 1 002];  $\nu(\text{CO}) = 2\ 000\ \text{vs}\ \text{cm}^{-1}$  (Nujol);  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 5.46 [d, 5 H,  $\text{C}_5\text{H}_5$ ,  $J(\text{HP}) = 1.0$ ], 5.70 [d, 5 H,  $\text{C}_5\text{H}_5$ ,  $J(\text{HP}) = 0.8\ \text{Hz}$ ], 2.16 [m br, 2 H,  $\text{CH}_2$ ], 7.20—7.50 [m br, 20 H,  $\text{C}_6\text{H}_5$ ].

*Attempted Reaction of (1) with MeI.*—Compound (1) (0.070 g, 0.057 mmol) was dissolved in MeI (4 cm<sup>3</sup>) and the mixture stirred for 6 h. After evaporation of the MeI, (1) was recovered unchanged.

*Attempted Reaction of (1) with PhC<sub>2</sub>Ph.*—To a solution of (1) in diethyl ether, an excess of diphenylacetylene was added. The mixture was stirred at room temperature for ca. 6 h. After evaporation of the solvent, the starting materials were recovered.

*X-Ray Data Collection.*—A prismatic single crystal of (1) of dimensions ca. 0.22 × 0.15 × 0.18 mm was lodged in a glass capillary. The X-ray intensity data were collected on a Siemens Stoe four-circle automated diffractometer with graphite-monochromated Mo- $K_{\alpha}$  radiation. The unit cell was determined on the basis of 25 strong reflections found by mounting the crystal at random, varying the orientation angles  $\phi$  and  $\chi$  over a range of 120° each with the detector position varying in the range  $6 \leq \theta \leq 10^\circ$ . For the determination of precise lattice parameters, 20 strong reflections with  $9 \leq \theta \leq 14^\circ$  were considered. Integrated intensities for  $hkl$  reflections with  $k$  and  $l \geq 0$  and  $3 \leq \theta \leq 25^\circ$  were measured using the  $\omega/\theta$  scan method with a scan speed of  $0.03^\circ\ \text{s}^{-1}$ , scan width of 1.2°, and two background counts of 20 s at each of the scans. Of the 3 766 reflections thus considered, 2 809 having a net intensity greater than  $3\sigma(I)$  were used in the structure determination and refinement.

The intensities of three standard reflections, monitored at 100-reflection intervals, showed no greater fluctuations than those expected from Poisson statistics. The intensity data were corrected for Lorentz-polarization effects but not for absorption.

*Crystal Data.*— $\text{C}_{36}\text{H}_{32}\text{OP}_2\text{Rh}_2$ ,  $M = 748.2$ , Monoclinic, space group  $C2/c$ ,  $a = 23.738(7)$ ,  $b = 11.731(3)$ ,  $c = 26.883(7)$  Å,  $\beta = 123.2(1)^\circ$ ,  $U = 6\ 266.2\ \text{\AA}^3$ ,  $Z = 8$ ,  $D_c = 1.59\ \text{g}\ \text{cm}^{-3}$ ,  $F(000) = 3\ 008$ ,  $\mu(\text{Mo-}K_{\alpha}) = 12.35\ \text{cm}^{-1}$ ,  $\lambda(\text{Mo-}K_{\alpha}) = 0.710\ 69\ \text{\AA}$ .

*Structure Determination.*—The positions of the two crystallographically independent rhodium atoms were determined

from a three-dimensional Patterson function. The Fourier-difference synthesis phased with the heavy-atom positions allowed the location of the non-hydrogen atoms. Full-matrix least-squares refinement of this model was carried out minimizing the function  $\sum w(|F_o| - |F_c|)^2$ , where  $|F_o|$  and  $|F_c|$  are the observed and calculated structure factors. The weighting scheme used in the last refinement cycles was  $w = 2.5407/[\sigma^2(F_o) + 0.000318 F_o^2]$  which showed reasonable consistency in a test of  $w\Delta^2$  for data sectioned with respect both to  $F_o$  and to  $(\sin\theta)/\lambda$ . Anisotropic temperature factors were introduced for all the non-hydrogen atoms except for those belonging to the phenyl rings. These were refined as rigid groups and restricted to their normal geometry ( $D_{6h}$  symmetry, C-C 1.395 Å) using the group refinement procedure. Each ring was assigned six variable positional parameters and each ring carbon atom was assigned an individual isotropic thermal parameter. Hydrogen-atom contributions were used as fixed atoms in calculated positions:  $d(\text{C-H}) = 0.95$  Å and  $B_{\text{iso}} = 6$  Å<sup>2</sup>.

This model reached convergency with values  $R = [\sum(|F_o| - |F_c|)]/\Sigma(F_o) = 0.050$  and  $R' = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.045$ . A difference-Fourier map calculated at this point was practically featureless. The anomalous dispersion terms<sup>32</sup> for Rh and P were taken into account in the refinement. Atomic scattering factors for all non-hydrogen atoms were taken from ref. 33 and for hydrogen atoms from ref. 34. Data processing and computation were carried out using the SHELX 76 program package.<sup>35</sup>

#### Acknowledgements

We thank the C.N.R. and the Public Education Ministry for financial support.

#### References

- 1 F. Faraone, G. Bruno, G. Tresoldi, G. Faraone, and G. Bombieri, *J. Chem. Soc., Dalton Trans.*, 1981, 1651.
- 2 F. Faraone, G. Bruno, S. Lo Schiavo, G. Tresoldi, and G. Bombieri, *J. Chem. Soc., Dalton Trans.*, 1983, 433.
- 3 D. M. Hoffman and R. Hoffmann, *Inorg. Chem.*, 1981, **20**, 3543 and refs. therein.
- 4 J. T. Mague and J. P. Mitchner, *Inorg. Chem.*, 1969, **8**, 119.
- 5 A. L. Balch, *J. Am. Chem. Soc.*, 1976, **98**, 8049.
- 6 A. R. Sanger, *J. Chem. Soc., Dalton Trans.*, 1981, 228.
- 7 C. P. Kubiak, C. Woodcock, and R. Eisenberg, *Inorg. Chem.*, 1980, **19**, 2733.
- 8 M. Cowie and S. K. Dwight, *Inorg. Chem.*, 1980, **19**, 2500.
- 9 M. Cowie and S. K. Dwight, *Inorg. Chem.*, 1980, **19**, 2508 and refs. therein.
- 10 K. W. Chiu, H. S. Rzepa, R. N. Sheppard, G. Wilkinson, and W. K. Wong, *Polyhedron*, 1982, **1**, 809.
- 11 M. Cowie and S. K. Dwight, *Inorg. Chem.*, 1979, **18**, 1209.
- 12 L. H. Pignolet, D. H. Doughty, S. C. Nowicki, and A. L. Casalnuovo, *Inorg. Chem.*, 1980, **19**, 2172.
- 13 F. Faraone, G. Bruno, S. Lo Schiavo, P. Piraino, and G. Bombieri, *J. Chem. Soc., Dalton Trans.*, 1983, 1819.
- 14 M. Cowie and T. G. Southern, *Inorg. Chem.*, 1982, **21**, 246 and refs. therein.
- 15 R. Colton and M. J. McCormick, *Coord. Chem. Rev.*, 1980, **31**, 1.
- 16 M. Cowie and T. G. Southern, *J. Organomet. Chem.*, 1980, **193**, C46.
- 17 C. P. Kubiak and R. Eisenberg, *Inorg. Chem.*, 1980, **19**, 2726.
- 18 S. Otsuku, Y. Tutsuuo, M. Miki, T. Aoke, M. Matsumoto, H. Yoshioka, and K. Nakatsu, *J. Chem. Soc., Chem. Commun.*, 1973, 445.
- 19 L. S. Brenner, M. M. Olmstead, H. Hope, and A. L. Balch, *J. Organomet. Chem.*, 1978, **153**, C31.
- 20 W. A. Hermann, J. Plank, M. L. Ziegler, and P. Wulknitz, *Chem. Ber.*, 1981, **114**, 716.
- 21 A. L. Balch, L. S. Benner, and M. M. Olmstead, *Inorg. Chem.*, 1979, **18**, 2996.
- 22 M. Angoletta, P. L. Bellon, M. Manassero, and M. Sansoni, *J. Organomet. Chem.*, 1974, **81**, C40.
- 23 M. Cowie and S. K. Dwight, *Inorg. Chem.*, 1980, **19**, 209.
- 24 M. Cowie, S. K. Dwight, and A. R. Sanger, *Inorg. Chim. Acta*, 1978, **31**, L407.
- 25 See, for example, F. G. A. Stone, *Rev. Pure Appl. Chem.*, 1967, **17**, 41; F. Bonati and G. Wilkinson, *J. Chem. Soc.*, 1964, 179; F. Bonati, S. Cenini, D. Morelli, and R. Ugo, *J. Chem. Soc. A*, 1966, 1052; D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, 1966, **5**, 1405.
- 26 F. Faraone, S. Lo Schiavo, G. Bruno, P. Piraino, and G. Bombieri, *J. Chem. Soc., Dalton Trans.*, 1983, 1813.
- 27 A. J. Oliver and W. A. G. Graham, *Inorg. Chem.*, 1970, **9**, 243.
- 28 F. Faraone, G. Tresoldi, and G. A. Loprete, *J. Chem. Soc., Dalton Trans.*, 1970, 933.
- 29 J. Halpern, *J. Chem. Soc., Chem. Commun.*, 1973, 629.
- 30 C. A. Tolman, P. Z. Meakin, D. L. Lindner, and J. P. Jesson, *J. Am. Chem. Soc.*, 1974, **96**, 2762.
- 31 A. Mayanza, J. J. Bonnet, J. Galy, P. Kalck, and R. Poiblan, *J. Chem. Res.*, 1980, (S) 146, (M) 2101.
- 32 D. T. Cromer and D. Libermann, *J. Chem. Phys.*, 1970, **53**, 1981.
- 33 D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, 1968, **24**, 321.
- 34 R. F. Stewart, *J. Chem. Phys.*, 1970, **53**, 3175.
- 35 G. M. Sheldrick, SHELX 76 Computing System, University of Cambridge, 1976.

Received 9th May 1983; Paper 3/734