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## STRUCTURAL STUDIES OF $\text{Rh}_4(\text{CO})_{12}$ DERIVATIVES IN SOLUTION AND IN THE SOLID STATE \*

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### Summary

The crystal structures of  $\text{Rh}_4(\text{CO})_{10}(\text{PPh}_3)_2$  and  $\text{Rh}_4(\text{CO})_9\{\text{P}(\text{OPh})_3\}_3$  are reported.  $^{31}\text{P}$ - $\{^1\text{H}\}$  NMR studies on  $\text{Rh}_4(\text{CO})_{12-x}\{\text{P}(\text{OPh})_3\}_x$  ( $x = 1, 2$  and  $3$ ) show that each derivative exists as only one isomer in solution whereas the analogous triphenylphosphine derivatives can exist as different isomers. A quantitative redistribution of triphenylphosphites occurs on mixing  $\text{Rh}_4(\text{CO})_{12-x}\text{L}_x$  with  $\text{Rh}_4(\text{CO})_{12-y}\text{L}_y$  ( $\text{L} = \text{P}(\text{OPh})_3$ ;  $x = 0, 1, 2, y = x + 2$ ;  $x = 0, y = x + 4$ ) to give  $\text{Rh}_4(\text{CO})_{12-z}\text{L}_z$  [ $z = \frac{1}{2}(x + y)$ ]; a related rapid intermolecular randomisation of carbonyls occurs on mixing  $\text{Rh}_4(^{12}\text{CO})_{12}$  with  $\text{Rh}_4(^{13}\text{CO})_{12}$ .

### Introduction

Tetranuclear dodecarbonyls and their derivatives have played an important part in the development of cluster chemistry and there is still much interest in the stereochemistry of their substituted derivatives, their intramolecular fluxional behaviour and the mechanism of ligand substitution [1]. We now report the solid state structures of  $\text{Rh}_4(\text{CO})_{12-x}\text{L}_x$  ( $\text{L} = \text{PPh}_3, x = 2$ ;  $\text{L} =$

\* Dedicated to the memory of Professor Paolo Chini.

This collaborative work results directly from the close association of B.T.H., L.L., D.M.P.M., L.G. and U.S. with Paolo Chini to whom we are most grateful for stimulating our interest in carbonyl cluster chemistry.

$P(OPh)_3$ ,  $x = 3$ ) and a  $^{31}P$ - $\{^1H\}$  NMR study of  $Rh_4(CO)_{12-x}L_x$  ( $x = 1, 2, 3$ ) in solution. Evidence is also presented for facile inter-ligand exchange involving both CO and L.

## Experimental

### A. Synthetic procedures

$Rh_4(CO)_{12}$  was prepared as described previously [2]. Triphenylphosphite, from Merck-Suchard, was vacuum-distilled before use and triphenylphosphine (B.D.H.) was used as received. Solvents were dried and stored under nitrogen and all operations were under nitrogen atmosphere. C and H analyses were carried out at the University of Kent by Mr. A.J. Fassam and at the University of Oxford; rhodium was determined by atomic absorption. IR spectra were recorded with a Perkin-Elmer 457 spectrophotometer using 0.1 mm path length  $CaF_2$  cells.  $^{31}P$ - $\{^1H\}$  NMR spectra in  $CD_2Cl_2$  were obtained as described previously [3].

#### Reactions of $Rh_4(CO)_{12}$ with $P(OPh)_3$

(a) *Undecacarbonyl(triphenylphosphite)tetrarhodium*,  $Rh_4(CO)_{11}\{P(OPh)_3\}$ . Triphenylphosphite (0.515 ml, 1.95 mmol) in hexane (20 ml) was added dropwise to a stirred solution of  $Rh_4(CO)_{12}$  (1.459 g, 1.95 mmol) in hexane (250 ml) at room temperature, [i.e.  $P(OPh)_3 : Rh_4(CO)_{12} = 1 : 1$ ]. The colour of the solution changed from orange-red to dark red during the addition and, after 12 hours, a brown precipitate was filtered under nitrogen atmosphere. This compound was identified as  $Rh_4(CO)_{10}\{P(OPh)_3\}_2$  (0.2 g, 7.8%). The volume of the filtered solution was reduced to 75 ml. A dark-red compound,  $Rh_4(CO)_{11}\{P(OPh)_3\}$ , was obtained by standing overnight at  $-20^\circ C$ , collected by filtration, washed with cold hexane and dried in vacuum (0.8 g, 40%). This compound is sparingly soluble in isopropanol and soluble in all common organic solvents. Found: C, 33.81; H, 1.47; Rh, 39.45.  $C_{29}H_{15}O_{14}PRh_4$  calcd.: C, 33.81; H, 1.46; Rh, 39.96%.

(b) *Decacarbonylbis(triphenylphosphite)tetrarhodium*,  $Rh_4(CO)_{10}\{P(OPh)_3\}_2$ . Triphenylphosphite (0.420 ml, 1.59 mmol) in toluene (20 ml) was added dropwise to a stirred solution of  $Rh_4(CO)_{12}$  (0.59 g, 0.79 mmol) in toluene (60 ml) at room temperature for 12 hours (i.e.  $P(OPh)_3 : Rh_4(CO)_{12} = 2 : 1$ ). During this time the colour of the solution changed from orange-red to dark red. Evaporation of the solvent to the dryness gave a crude red product,  $Rh_4(CO)_{10}\{P(OPh)_3\}_2$  which was crystallised by liquid diffusion from dichloromethane and isopropanol (0.8 g, 77%). The compound is insoluble in isopropanol and aliphatic hydrocarbons but soluble in all other common organic solvents. Found: C, 41.82; H, 2.30; Rh, 30.75.  $C_{46}H_{30}O_{16}P_2Rh_4$  calcd.: C, 42.10; H, 2.28; Rh, 31.36%.

(c) *Nonacarbonyltris(triphenylphosphite)tetrarhodium*,  $Rh_4(CO)_9\{P(OPh)_3\}_3$ . Triphenylphosphite (1.16 ml, 4.42 mmol) in tetrahydrofuran (20 ml) was added dropwise to a stirred solution of  $Rh_4(CO)_{12}$  (1.05 g, 1.41 mmol) in tetrahydrofuran (100 ml) at room temperature for 6 hours (i.e.  $P(OPh)_3 : Rh_4(CO)_{12} = 3.1 : 1$ ). During this time the colour of the solution changed immediately from red-orange to red-brown. The volume of the solution was

reduced to 40 ml and isopropanol (50 ml) was slowly added. From liquid diffusion of the two solvents, red crystals of  $Rh_4(CO)_9 [P(OPh)_3]_3$  were obtained (1.35 g, 60%). This compound is insoluble in isopropanol and aliphatic hydrocarbons but soluble in all other common organic solvents. Found: C, 47.39; H, 3.08; Rh, 25.98;  $C_{63}H_{45}O_{18}P_3Rh_4$  calcd.: C, 47.45; H, 2.84; Rh, 25.81%.

#### Reactions of $Rh_4(CO)_{12}$ with $PPh_3$

Preparations carried out according to Whyman's procedure [4] using hexane as solvent, gave only one isomer of  $Rh_4(CO)_{12-x}(PPh_3)_x$  ( $x = 1$  and  $2$ ) whereas the same reactions in toluene solution, with stirring overnight at room temperature, gave products which  $^{31}P$ - $\{^1H\}$  NMR showed to be a mixture of isomers, (see below).

(a) *Undecacarbonyl(triphenylphosphine)tetrarhodium*,  $Rh_4(CO)_{11}(PPh_3)$ . To a stirred solution of  $Rh_4(CO)_{12}$  (0.38 g, 0.51 mmol) in hexane (100 ml) was added dropwise a solution of triphenylphosphine (0.13 g, 0.51 mmol) in hexane. After stirring for a further 10 min, the reaction mixture was reduced in volume under vacuo, until slightly cloudy, filtered and then placed in a freezer. A red crystalline product separated and was filtered off and dried in air (0.41 g, 82%). Found: C, 35.5; H, 1.6;  $C_{29}H_{15}O_{11}PRh_4$  calcd.: C, 35.4; H, 1.5%.

(b) *Decacarbonylbis(triphenylphosphine)tetrarhodium*,  $Rh_4(CO)_{10}(PPh_3)_2$ . To  $Rh_4(CO)_{12}$  (0.5 g, 0.67 mmol) dissolved in the minimum volume of hexane at room temperature was added drop-wise a solution of triphenylphosphine (0.35 g, 1.34 mmol) in hexane with constant stirring. The product, which quickly separated as a red powder, was filtered and dried in air (0.76 g, 94%). Found: C, 45.2; H, 2.8;  $C_{46}H_{30}O_{10}P_2Rh_4$  calcd.: C, 45.4; H, 2.5%.

IR spectra are summarized in Table 1. They are consistent with the presence of both terminal and bridging carbonyls and there is a regular decrease in frequency with increasing substitution.

#### Ligand redistribution reactions

(a)  $P(OPh)_3$  redistribution. The following reactions:



$$x = 0, 1, 2 \quad y = x + 2 \quad z = \frac{1}{2}(x + y)$$

TABLE 1  
IR SPECTRA

Compound	CO terminal ( $cm^{-1}$ )			CO bridging ( $cm^{-1}$ )	
$Rh_4(CO)_{12}$ <sup>a</sup>	2074vs	2069vs	2043s	1885s	
$Rh_4(CO)_{11} \{P(OPh)_3\}_1$ <sup>a</sup>	2093m	2063vs	2040s	2035(sh)	1875m 1860m
$Rh_4(CO)_{10} \{P(OPh)_3\}_2$ <sup>b</sup>	2070s	2050vs	2025vs	1850s 1840(sh)	
$Rh_4(CO)_9 \{P(OPh)_3\}_3$ <sup>b</sup>	2060s	2040vs	2020vs	1890vw 1845s	
$Rh_4(CO)_{11} \{PPh_3\}_1$ <sup>c</sup>	2080s	2053vs	2020s	1902w	1867ms 1852ms(sh)
$Rh_4(CO)_{10} \{PPh_3\}_2$ <sup>d</sup>	2067s	2042s	2017s	1850ms 1825m(sh)	

<sup>a</sup> In hexane solution. <sup>b</sup> In tetrahydrofuran solution. <sup>c</sup> In 1,2-dichloroethylene solution. <sup>d</sup> In dichloro-methane solution.



were carried out by mixing equimolar amounts of reactants in  $\text{CD}_2\text{Cl}_2$  solution at room temperature and monitoring the course of the reaction by  $^{31}\text{P}\{-^1\text{H}\}$  NMR.

(b)  $^{12}\text{CO}/^{13}\text{CO}$  redistribution. The reaction:



$$x = 0, 1-12$$

was carried out by mixing equimolar amounts of unenriched and highly enriched samples of  $\text{Rh}_4(\text{CO})_{12}$  in  $\text{CH}_2\text{Cl}_2$  and monitoring the reaction by IR spectroscopy.

### B. Crystallographic analyses

Crystals of  $\text{Rh}_4(\text{CO})_{10}(\text{PPh}_3)_2$ , (I), and  $\text{Rh}_4(\text{CO})_9\{\text{P}(\text{O}^i\text{Ph})_3\}_3$ , (II), suitable for X-ray analysis, were obtained in both cases, by recrystallisation from

(continued on p. 340)

TABLE 2

CRYSTAL DATA AND DETAILS OF STRUCTURE ANALYSES OF  $\text{Rh}_4(\text{CO})_{10}(\text{PPh}_3)_2$  (I) AND  $\text{Rh}_4(\text{CO})_9\{\text{P}(\text{O}^i\text{Ph})_3\}_3 \cdot \text{THF}$  (II)

Crystal Data	$\text{Rh}_4\text{C}_{46}\text{H}_{30}\text{O}_{10}\text{P}_2$ (I)	$\text{Rh}_4\text{C}_{67}\text{H}_{53}\text{O}_{19}\text{P}_3$ (II)
Formula	$\text{Rh}_4\text{C}_{46}\text{H}_{30}\text{O}_{10}\text{P}_2$ (I)	$\text{Rh}_4\text{C}_{67}\text{H}_{53}\text{O}_{19}\text{P}_3$ (II)
<i>M</i>	1215.7	1666.7
Crystal system	Monoclinic	Triclinic
<i>a</i> (Å)	17.903(3)	14.626(8)
<i>b</i> (Å)	17.933(3)	14.965(7)
<i>c</i> (Å)	14.228(3)	16.630(8)
$\alpha$ (°)	90	106.80(4)
$\beta$ (°)	95.75(2)	104.43(4)
$\gamma$ (°)	90	93.73(4)
$\mu$ (Å <sup>3</sup> )	4545.2	3338
Space group	$P2_1/a$	$P\bar{1}$
<i>z</i>	4	2
$D_c$ (g cm <sup>-3</sup> )	1.55	1.67
$F(000)$	2384	3064
Linear absorption coefficient (Mo- $K_\alpha$ )	8.5 cm <sup>-1</sup>	10.8 cm <sup>-1</sup>
Crystal size	0.3 × 0.15 × 0.15 mm	
Data Collection using Mo- $K_\alpha$ radiation ( $\lambda = 0.71069$ Å)		
$\theta_{\text{min}}, \theta_{\text{max}}$	1.5–20.0°	1.5–20.0°
$\omega$ -Scan width parameters		
$A, B(0)$ in width = $A + B \tan \theta$	1.0 0.35	1.0 0.35
Total Data	3604	6355
Observed data $I_0 > 3\sigma(I_0)$	2745	3304
Merging <i>R</i> factor	0.0259	0.0262
Refinement Block refinement		
No. of parameters	268	397
Weighting scheme Chebyshev (see text for details)		
Final $R = \Sigma \Delta F / \Sigma (F_0)$	0.0433	0.0469
$R' = (\Sigma \omega \Delta F^2 / \Sigma \omega F_0^2)^{1/2}$	0.0520	0.0581

TABLE 3

FRACTIONAL ATOMIC COORDINATES ( $\times 10^4$ ) AND ISOTROPIC TEMPERATURE FACTORS ( $\times 10^4$ ) FOR  $\text{Rh}_4(\text{CO})_{10}(\text{PPh}_3)_2$

Atom	$x/a$	$y/b$	$z/c$	$U(\text{ISO})$
Rh(1)	1020.0(6)	375.2(7)	-3178.0(8)	
Rh(2)	1777.0(6)	601.0(6)	-1471.0(7)	
Rh(3)	1769.5(7)	1662.6(6)	-2904.4(8)	
Rh(4)	2563.8(6)	398.4(6)	-3033.1(7)	
C(11) <sup>a</sup>	805(9)	494(10)	-4500(12)	583(45)
O(11)	670(8)	552(8)	-5317(10)	881(49)
C(12)	862(8)	-673(9)	-3031(10)	401(47)
O(12)	759(6)	-1286(7)	-2915(8)	592(52)
C(13)	106(11)	714(11)	-2734(13)	655(51)
O(13)	-458(9)	930(9)	-2484(11)	984(46)
C(21)	1093(9)	79(9)	-863(11)	425(51)
O(21)	645(7)	-271(7)	-526(8)	684(47)
C(231) <sup>b</sup>	1294(9)	1639(11)	-1592(8)	439(51)
O(231)	885(7)	2032(10)	-1223(9)	686(47)
C(241)	2322(8)	-326(8)	-1945(10)	360(48)
O(241)	2420(6)	-951(6)	-1740(7)	466(47)
C(31)	1005(9)	2251(10)	-3528(11)	602(51)
O(31)	518(8)	2567(9)	-3940(10)	911(52)
C(32)	2462(10)	2441(9)	-2678(12)	467(49)
O(32)	2896(11)	2926(10)	-2563(13)	843(50)
C(341)	2266(8)	1149(8)	-4061(11)	414(49)
O(341)	2284(6)	1305(7)	-4854(8)	634(50)
C(41)	3547(9)	729(9)	-2764(11)	450(49)
O(41)	4143(7)	990(7)	-2652(9)	742(50)
P(1)	2973(2)	-597(2)	-3910(2)	318(9)
C'(111) <sup>c</sup>	2284(8)	-1328(8)	-4237(10)	388(37)
C'(112)	1733(9)	-1211(9)	-4995(11)	451(40)
C'(113)	1183(10)	-1761(10)	-5273(12)	633(50)
C'(114)	1214(10)	-2424(10)	-4813(12)	603(48)
C'(115)	1745(9)	-2548(9)	-4054(12)	535(44)
C'(116)	2297(9)	-2011(9)	-3745(11)	509(43)
C'(121)	3359(8)	-353(9)	-5023(10)	446(38)
C'(122)	3817(9)	277(9)	-5033(11)	544(44)
C'(123)	4185(10)	436(10)	-5829(12)	637(49)
C'(124)	4096(10)	-32(10)	-6615(12)	621(49)
C'(125)	3629(10)	-652(11)	-6616(13)	649(50)
C'(126)	3256(9)	-810(9)	-5838(11)	472(41)
C'(131)	3772(8)	-1128(9)	-3320(10)	437(39)
C'(132)	4078(10)	-1693(10)	-3833(12)	572(45)
C'(133)	4697(11)	-2118(10)	-3409(13)	665(52)
C'(134)	4980(11)	-1969(11)	-2494(14)	751(58)
C'(135)	4661(11)	-1409(12)	-1987(14)	759(58)
C'(136)	4040(10)	-984(10)	-2380(12)	597(48)
P(2)	2518(2)	829(2)	-48(2)	325(9)
C'(211)	3157(8)	72(9)	304(12)	366(48)
C'(212)	2847(9)	-648(9)	370(11)	504(50)
C'(213)	3320(10)	-1273(10)	635(13)	637(48)
C'(214)	4068(9)	-1161(10)	842(13)	553(53)
C'(215)	4383(8)	-461(9)	798(11)	671(48)
C'(216)	3945(8)	172(8)	506(11)	469(45)
C'(221)	2008(8)	931(9)	1004(12)	441(45)
C'(222)	1296(9)	1253(10)	932(13)	558(48)
C'(223)	914(9)	1389(11)	1736(13)	738(50)
C'(224)	1277(9)	1202(11)	2616(13)	652(53)
C'(225)	1982(8)	858(10)	2716(11)	700(51)
C'(226)	2374(8)	734(9)	1900(11)	624(50)
C'(231)	3120(8)	1666(8)	-17(10)	406(43)

TABLE 3 (continued)

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> (ISO)
C'(232)	3598(8)	1729(8)	-724(10)	493(45)
C'(233)	4074(9)	2347(9)	-759(11)	600(51)
C'(234)	4052(10)	2897(10)	-78(13)	608(50)
C'(235)	3591(9)	2856(9)	600(12)	632(51)
C'(236)	3090(8)	2222(9)	668(11)	547(45)

<sup>a</sup> Terminal carbonyl ligands may be identified by the first digit in parenthesis which indicates the rhodium atom to which they are attached. <sup>b</sup> For bridging carbonyl ligands the first two digits refer to the rhodium atoms being bridged by the carbonyl ligand. <sup>c</sup> The carbon atoms of the phenyl rings attached to phosphorus are primed and the first digit in parenthesis indicates the phosphorus atom to which they are attached and the second the number of the ring (i.e. 1-3).

TABLE 4

FRACTIONAL ATOMIC COORDINATES AND ISOTROPIC TEMPERATURE FACTORS FOR Rh<sub>4</sub>(CO)<sub>9</sub>(P(OPh)<sub>3</sub>)<sub>3</sub>

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> (ISO)
Rh(1)	2066(1)	3404(1)	1395(1)	
Rh(2)	-1226(1)	8282(1)	8670(1)	
Rh(3)	1054(1)	3290(1)	2546(1)	
Rh(4)	2762(1)	2642(1)	2679(1)	
C(11) <sup>a</sup>	1876(16)	3166(16)	0194(17)	0543(69)
O(11)	8287(13)	7071(13)	0559(13)	0833(57)
C(131) <sup>b</sup>	0718(15)	3718(15)	1455(15)	0412(60)
O(131)	0082(10)	3969(10)	1016(10)	0512(43)
C(31)	1279(15)	4478(16)	3346(15)	0428(60)
O(31)	1466(11)	5208(12)	3894(12)	0726(52)
C(341)	1755(16)	2651(16)	3364(16)	0484(65)
O(341)	1726(11)	2413(11)	4006(11)	0622(48)
C(141)	3301(15)	2783(15)	1683(14)	0416(61)
O(141)	3926(11)	2579(11)	1375(11)	0605(47)
C(41)	3640(17)	3597(17)	3603(17)	0550(69)
O(41)	4077(12)	4226(12)	4174(12)	0712(52)
C(21)	0874(17)	0816(18)	1791(17)	0594(73)
O(21)	0638(12)	0222(12)	2078(12)	0774(54)
C(22)	1903(18)	1067(18)	0606(18)	0656(77)
O(22)	2337(13)	0710(13)	0111(13)	0847(58)
C(23)	0104(17)	1628(16)	0494(16)	0522(67)
O(23)	0606(13)	8451(12)	0070(12)	0806(56)
O'(33) <sup>c</sup>	0972(9)	6459(10)	6850(9)	0452
P(3)	0434(4)	7170(4)	7465(4)	0371
O'(31)	0683(10)	8089(11)	7221(10)	0584(45)
O'(43)	-3558(10)	9261(10)	8044(10)	0517(41)
P(4)	-3407(4)	8624(4)	7153(4)	0382
O'(41)	-4418(10)	8514(10)	6437(10)	0542(43)
O'(32)	1162(10)	7422(10)	8410(10)	0496(41)
O'(42)	2824(9)	0637(9)	3129(9)	0427(38)
P(1)	2883(4)	4871(4)	1868(4)	0434
O'(11)	3899(10)	4911(10)	2539(10)	0536(43)
O'(12)	2515(10)	5732(10)	2470(10)	0545(43)
C'(13)	3120(9)	5380(10)	1185(9)	0452(39)
C'(116)	4738(16)	5640(17)	2915(16)	0548(67)
C'(111)	5526(20)	5237(20)	3214(20)	0832(89)
C'(112)	6330(23)	5991(24)	3635(23)	1050(108)
C'(113)	6340(24)	6909(24)	3701(23)	1067(110)
C'(115)	4608(17)	6542(18)	2921(17)	0641(74)
C'(114)	5515(19)	7196(18)	3308(18)	0734(82)

TABLE 4 (Continued)

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> (ISO)
C'(126)	1881(16)	6319(16)	2206(16)	0515(65)
C'(121)	1257(16)	6092(16)	1389(16)	0558(69)
C'(122)	0645(19)	6762(19)	1220(19)	0755(84)
C'(123)	0736(20)	7629(20)	1836(20)	0813(88)
C'(124)	1391(19)	7825(19)	2598(20)	0793(87)
C'(125)	2045(18)	7172(19)	2882(18)	0708(79)
C'(136)	3363(15)	4902(16)	0433(15)	0472(63)
C'(131)	4028(16)	4309(16)	0474(15)	0508(65)
C'(132)	4257(19)	5835(19)	-0328(20)	0817(88)
C'(133)	3818(18)	4036(18)	-1072(18)	0685(78)
C'(134)	3146(19)	4639(19)	-1091(19)	0746(84)
C'(135)	2899(17)	5118(17)	-0323(17)	0590(71)
C'(326)	2173(14)	7744(14)	8625(14)	0384(57)
C'(321)	2755(16)	7075(16)	8635(16)	0543(67)
C'(322)	6259(18)	2675(18)	1160(18)	0694(78)
C'(333)	5902(18)	1747(19)	0877(18)	0682(78)
C'(334)	6500(21)	1020(21)	0906(20)	0903(94)
C'(326)	2464(17)	8681(17)	8847(17)	0625(73)
C'(316)	0730(17)	8216(18)	6447(15)	0684(78)
C'(311)	1481(17)	7910(18)	6121(17)	0800
C'(312)	1630(16)	8198(18)	5412(17)	0800
C'(313)	0899(18)	8543(18)	4950(15)	0800
C'(314)	0198(17)	8901(18)	5305(17)	0800
C'(315)	0075(16)	8680(18)	6035(17)	0800
C'(331)	0960(17)	5049(18)	5841(17)	0646(74)
C'(332)	0918(21)	4030(22)	5625(22)	0960(100)
C'(333)	0825(21)	3632(21)	6277(22)	0923(97)
C'(334)	0810(20)	4063(20)	7111(21)	0847(90)
C'(335)	0910(15)	5106(16)	7320(15)	0502(64)
C'(336)	9099(16)	4500(16)	3308(16)	0523(66)
C'(416)	-5182(14)	7762(14)	6191(13)	0352(55)
C'(411)	-5438(15)	7277(15)	5321(15)	0464(62)
C'(412)	-6236(17)	6515(18)	5004(17)	0663(76)
C'(413)	-6663(18)	6358(18)	5646(19)	0704(79)
C'(414)	-6359(18)	6837(18)	6504(19)	0738(81)
C'(415)	-5586(16)	7622(16)	6815(16)	0538(67)
C'(426)	3133(15)	0309(15)	3845(15)	0440(60)
C'(421)	-3666(17)	10423(17)	6221(17)	0613(72)
C'(422)	3895(20)	9261(20)	4510(21)	0881(95)
C'(423)	6415(20)	0381(20)	4766(20)	0827(89)
C'(424)	6986(23)	9689(23)	4744(23)	1040(107)
C'(426)	-2773(21)	9320(21)	5472(21)	0906(96)
C'(436)	-3713(15)	10225(15)	8232(15)	0456(61)
C'(431)	-2952(16)	10911(16)	8587(16)	0527(67)
C'(432)	-3119(18)	11864(18)	8791(18)	0684(77)
C'(433)	-4024(19)	12105(19)	8651(18)	0739(82)
C'(434)	-4812(20)	11358(20)	8286(20)	0862(92)
C'(435)	-4656(19)	10373(19)	8068(18)	0761(83)
C(100) <sup>d</sup>	7216(38)	8629(38)	2589(37)	1404(78)
C(101) <sup>d</sup>	7986(41)	8283(37)	2891(37)	1404(78)
C(102) <sup>d</sup>	8750(39)	8781(38)	2805(37)	1404(78)
C(103) <sup>d</sup>	8472(39)	9237(36)	2103(38)	1404(78)
O(104) <sup>d</sup>	7428(24)	9209(23)	2066(24)	1404(78)

<sup>a</sup> Terminal carbonyl ligands may be identified by the first digit in parenthesis which indicates the rhodium atom to which they are attached. <sup>b</sup> For bridging carbonyl ligands the first two digits refer to the rhodium atoms being bridged by the carbonyl ligand. <sup>c</sup> The phosphite oxygen and carbon atoms are primed and the first digit indicates the phosphorus atom with which they are associated. <sup>d</sup> The THF of crystallization atomic coordinates and temperature factors.

TABLE 5  
SOME IMPORTANT INTRAMOLECULAR BOND LENGTHS FOR  $\text{Rh}_4(\text{CO})_{10}(\text{PPh}_3)_2$  (Å)

Rh(1)—Rh(2)	2.692(1)	Rh(1)—Rh(3)	2.679(2)
Rh(1)—Rh(4)	2.751(2)	Rh(2)—Rh(3)	2.788(2)
Rh(2)—Rh(4)	2.771(2)	Rh(3)—Rh(4)	2.692(2)
Rh(1)—C(11) <sup>a</sup>	1.893(17)	Rh(2)—C(231) <sup>a</sup>	2.051(14)
Rh(1)—C(12)	1.916(16)	Rh(2)—C(241)	2.075(14)
Rh(1)—C(13)	1.911(19)	Rh(3)—C(341)	2.154(15)
Rh(2)—C(21)	1.829(16)	Rh(3)—C(231)	2.128(15)
Rh(3)—C(31)	1.880(12)	Rh(4)—C(241)	2.099(14)
Rh(3)—C(32)	1.873(13)	Rh(4)—C(341)	2.020(15)
Rh(4)—C(41)	1.861(16)	C(11)—O(11)	1.168(18)
Rh(4)—P(1)	2.337(4)	C(12)—O(12)	1.130(17)
Rh(2)—P(2)	2.341(3)	C(13)—O(13)	1.170(20)
C(231)—O(231)	1.178(17)	C(21)—O(21)	1.159(17)
C(241)—O(241)	1.167(16)	C(31)—O(31)	1.150(17)
C(341)—O(341)	1.166(16)	C(32)—O(32)	1.166(17)
		C(41)—O(41)	1.160(17)

<sup>a</sup> See footnotes to Table 3.

THF/isopropanol. The crystals used for the X-ray work were sealed in 0.5 mm Lindemann capillaries. Unit cell parameters were initially determined from oscillation and Weissenberg photographs and later refined using setting angles for 25 (for I) and 24 (for II) high angle reflections automatically centred on a CAD 4 diffractometer. The crystal data and details of the data collection and structure refinement are summarised in Table 2. Intensity data were recorded on the CAD 4 diffractometer using graphite monochromated  $\text{Mo-K}_\alpha$  radiation and an  $\omega-2\theta$  scan technique in the manner described previously [5]. During data collection the crystals showed no indications of decomposition. The data were corrected for Lorentz and polarization effects and absorption.

The structures were solved via Patterson and electron density, Fourier syntheses and refined by blocked matrix least-squares techniques, anisotropic temperature factors being assigned to the non-carbon atoms. II contained a molecule of THF of crystallisation, which showed slight disorder, and for the THF carbon atoms positional and a common isotropic temperature factor were refined. Hydrogen atoms were not refined, but were positioned in idealised positions ( $\text{C-H} = 1.0 \text{ \AA}$ ) and assigned isotropic temperature factors of  $0.05 \text{ \AA}^3$  before each cycle of refinement. The final cycle of least-squares refinement for I led to a conventional  $R$  value of 0.0433 and a weighted  $R$  factor of 0.0520.

The weighting scheme used was based on  $\omega = \frac{1}{\sum_{r=1}^n A_r T_r(X)}$  where  $n$  is the number

of coefficients,  $A_r$ , for a Chebyshev series,  $T_r$  is the polynomial function and  $X$  is  $F_0/F_0(\text{max})$ . Four coefficients were used and the final parameters were equal to 14.30, 21.07, 10.98 and 3.11 giving a flat agreement analysis [6]. For II the final cycles of least squares refinement converged to a conventional  $R$  factor equal to 0.0469; the coefficients in the Chebyshev series were found



TABLE 6

SOME IMPORTANT INTRAMOLECULAR BOND ANGLES FOR  $\text{Rh}_4(\text{CO})_{10}(\text{PPh}_3)_2$  ( $^\circ$ )

<i>Rh—Rh—Rh</i>			
Rh(2)—Rh(1)—Rh(3)	62.53(4)	Rh(1)—Rh(3)—Rh(2)	58.95(4)
Rh(2)—Rh(1)—Rh(4)	61.20(4)	Rh(1)—Rh(3)—Rh(4)	61.62(4)
Rh(3)—Rh(1)—Rh(4)	59.42(4)	Rh(2)—Rh(3)—Rh(4)	60.73(4)
Rh(1)—Rh(2)—Rh(3)	58.51(4)	Rh(1)—Rh(4)—Rh(2)	58.34(4)
Rh(1)—Rh(2)—Rh(4)	60.46(4)	Rh(1)—Rh(4)—Rh(3)	58.96(4)
Rh(3)—Rh(2)—Rh(4)	57.93(4)	Rh(2)—Rh(4)—Rh(3)	61.34(4)
<i>Rh—Rh—P</i>			
Rh(1)—Rh(4)—P(1)	108.34(1)	Rh(1)—Rh(2)—P(2)	175.5(1)
Rh(2)—Rh(4)—P(1)	137.8(1)	Rh(3)—Rh(2)—P(2)	118.4(1)
Rh(3)—Rh(4)—P(1)	151.1(1)	Rh(4)—Rh(2)—P(2)	115.3(1)
<i>Rh—Rh—CO<sub>terminal</sub></i>		<i>Rh—Rh—CO<sub>bridging</sub></i>	
Rh(2)—Rh(1)—C(11)	156.0(5)	Rh(1)—Rh(2)—C(231)	83.7(4)
Rh(3)—Rh(1)—C(11)	95.5(5)	Rh(3)—Rh(2)—C(231)	49.3(3)
Rh(4)—Rh(1)—C(11)	100.1(5)	Rh(4)—Rh(2)—C(231)	107.2(5)
Rh(2)—Rh(1)—C(12)	96.7(4)	Rh(1)—Rh(2)—C(241)	78.2(4)
Rh(3)—Rh(1)—C(12)	155.1(4)	Rh(3)—Rh(2)—C(241)	106.1(4)
Rh(4)—Rh(1)—C(12)	99.5(4)	Rh(4)—Rh(2)—C(241)	48.8(4)
Rh(2)—Rh(1)—C(13)	91.4(4)	Rh(1)—Rh(3)—C(231)	82.6(4)
Rh(3)—Rh(1)—C(13)	96.4(6)	Rh(2)—Rh(3)—C(231)	47.0(3)
Rh(4)—Rh(1)—C(13)	149.0(6)	Rh(4)—Rh(3)—C(231)	107.6(5)
Rh(1)—Rh(2)—C(21)	92.7(5)	Rh(1)—Rh(3)—C(341)	76.1(4)
Rh(3)—Rh(2)—C(21)	137.8(5)	Rh(2)—Rh(3)—C(341)	107.1(4)
Rh(4)—Rh(2)—C(21)	136.9(5)	Rh(4)—Rh(3)—C(341)	47.7(4)
Rh(1)—Rh(3)—C(31)	94.9(5)	Rh(1)—Rh(4)—C(241)	76.5(4)
Rh(2)—Rh(3)—C(31)	132.8(6)	Rh(2)—Rh(4)—C(241)	48.0(4)
Rh(4)—Rh(3)—C(31)	143.7(6)	Rh(3)—Rh(4)—C(241)	108.8(4)
Rh(1)—Rh(3)—C(32)	168.6(7)	Rh(1)—Rh(4)—C(341)	76.4(4)
Rh(1)—Rh(3)—C(32)	115.3(6)	Rh(2)—Rh(4)—C(341)	112.0(4)
Rh(1)—Rh(3)—C(32)	107.1(6)	Rh(3)—Rh(4)—C(341)	52.1(4)
Rh(1)—Rh(4)—C(41)	160.5(5)		
Rh(2)—Rh(4)—C(41)	109.8(5)		
Rh(3)—Rh(4)—C(41)	102.3(5)		
<i>OC<sub>terminal</sub>—Rh—CO<sub>terminal</sub></i>		<i>OC<sub>bridge</sub>—Rh—CO<sub>bridge</sub></i>	
C(11)—Rh(1)—C(12)	101.6(7)	C(231)—Rh(2)—C(241)	155.2(4)
C(11)—Rh(1)—C(13)	101.4(7)	C(231)—Rh(2)—C(341)	147.7(4)
C(12)—Rh(1)—C(13)	97.8(7)	C(241)—Rh(4)—C(341)	152.6(6)
C(31)—Rh(2)—C(32)	95.81(5)		
<i>OC<sub>terminal</sub>—Rh—CO<sub>bridging</sub></i>		<i>P—Rh—CO<sub>terminal</sub></i>	
C(21)—Rh(2)—C(231)	95.8(6)	P(2)—Rh(2)—C(21)	91.6(5)
C(21)—Rh(2)—C(241)	102.0(5)	P(1)—Rh(4)—C(41)	90.7(5)
C(31)—Rh(2)—C(231)	95.1(5)		
C(31)—Rh(2)—C(341)	102.5(4)	<i>P—Rh—CO<sub>bridging</sub></i>	
C(32)—Rh(2)—C(231)	100.4(5)	P(2)—Rh(2)—C(231)	96.5(4)
C(32)—Rh(2)—C(341)	97.7(4)	P(2)—Rh(2)—C(241)	100.2(4)
C(41)—Rh(4)—C(241)	107.9(6)	P(1)—Rh(4)—C(241)	91.2(4)
C(41)—Rh(4)—C(341)	52.1(4)	P(1)—Rh(4)—C(341)	101.3(4)
<i>Rh—C—O<sub>terminal</sub></i>		<i>Rh—C—O<sub>bridging</sub></i>	
Rh(1)—C(11)—O(11)	178.7(17)	Rh(2)—C(231)—O(231)	141.4(13)
Rh(1)—C(12)—O(12)	177.6(13)	Rh(2)—C(241)—O(241)	138.8(12)
Rh(1)—C(13)—O(13)	178.2(17)	Rh(3)—C(231)—O(231)	134.5(13)
Rh(2)—C(21)—O(21)	176.2(14)	Rh(3)—C(341)—O(341)	133.7(13)
Rh(3)—C(31)—O(31)	175.3(14)	Rh(4)—C(241)—O(241)	137.9(11)
Rh(3)—C(32)—O(32)	178.1(14)	Rh(4)—C(341)—O(341)	146.1(13)
Rh(4)—C(41)—O(41)	173.7(14)		

TABLE 7

SOME IMPORTANT INTRAMOLECULAR BOND LENGTHS (Å) FOR  $\text{Rh}_4(\text{CO})_9(\text{P}(\text{O}^i\text{Ph})_3)_3$ 

Rh(1)—Rh(2)	2.691(2)	Rh(2)—Rh(3)	2.696(3)
Rh(1)—Rh(3)	2.727(3)	Rh(2)—Rh(4)	2.695(2)
Rh(1)—Rh(4)	2.715(2)	Rh(3)—Rh(4)	2.715(3)
Rh(1)—P(1)	2.247(6)	Rh(1)—C(131)	2.072(21)
Rh(4)—P(4)	2.230(6)	Rh(1)—C(141)	2.096(21)
Rh(3)—P(3)	2.236(6)	Rh(3)—C(131)	2.052(23)
Rh(1)—C(11)	1.868(26)	Rh(3)—C(341)	1.998(21)
Rh(2)—C(21)	1.837(25)	Rh(4)—C(341)	2.069(23)
Rh(2)—C(22)	1.847(26)	Rh(4)—C(141)	2.058(23)
Rh(2)—C(23)	1.834(25)	P(4)—O'(41)	1.613(15)
Rh(3)—C(31)	1.836(23)	P(4)—O'(42)	1.595(16)
Rh(4)—C(41)	1.886(23)	P(4)—O'(43)	1.589(16)
C(11)—O(11)	1.155(21)	P(1)—O'(11)	1.604(15)
C(31)—O(31)	1.166(23)	P(1)—O'(12)	1.600(16)
C(41)—O(41)	1.139(24)	P(1)—O'(13)	1.627(16)
C(21)—O(21)	1.191(26)	P(3)—O'(31)	1.586(16)
C(22)—O(22)	1.188(27)	P(3)—O'(32)	1.585(15)
C(23)—O(23)	1.184(26)	P(3)—O'(33)	1.635(15)
C(131)—O(131)	1.183(22)		
C(341)—O(341)	1.224(25)		
C(141)—O(141)	1.169(22)		

to take up the following values, 7.28, 8.35, 3.96 and gave flat agreement analyses [6].

The fractional coordinates for I and II are given in Tables 3 and 4 respectively,

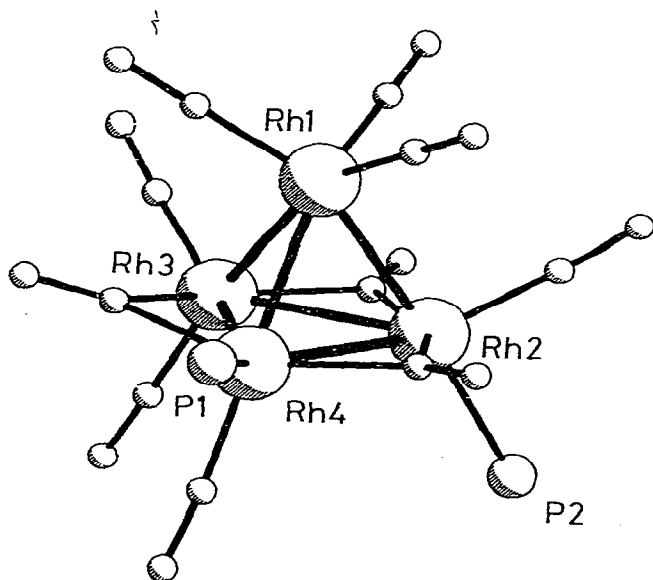


Fig. 1. Structure of  $\text{Rh}_4(\text{CO})_{10}(\text{PPh}_3)_2$ . (The phenyl rings have been omitted for clarity.)

TABLE 8  
SOME IMPORTANT BOND ANGLES (°) FOR  $\text{Rh}_4(\text{CO})_9(\text{P}(\text{OPh})_3)_3$

<i>Rh-Rh-Rh</i>			
Rh(2)-Rh(1)-Rh(3)	59.04(6)		
Rh(2)-Rh(1)-Rh(4)	59.84(6)		
Rh(3)-Rh(1)-Rh(4)	59.85(6)		
Rh(1)-Rh(2)-Rh(3)	60.88(6)		
Rh(1)-Rh(2)-Rh(4)	60.43(6)		
Rh(3)-Rh(2)-Rh(4)	60.46(5)		
Rh(1)-Rh(3)-Rh(2)	59.48(6)		
Rh(1)-Rh(3)-Rh(4)	59.73(6)		
Rh(2)-Rh(3)-Rh(4)	59.75(5)		
Rh(1)-Rh(4)-Rh(2)	59.73(6)		
Rh(1)-Rh(4)-Rh(3)	60.42(6)		
Rh(2)-Rh(4)-Rh(3)	59.79(5)		
<i>Rh-Rh-P</i>			
Rh(2)-Rh(1)-P(1)	103.61(16)		
Rh(3)-Rh(1)-P(1)	107.85(16)		
Rh(4)-Rh(1)-P(1)	105.42(15)		
Rh(1)-Rh(3)-P(3)	139.39(16)		
Rh(4)-Rh(3)-P(3)	96.89(14)		
Rh(2)-Rh(3)-P(3)	139.55(15)		
Rh(1)-Rh(4)-P(4)	139.52(16)		
Rh(2)-Rh(4)-P(4)	97.16(15)		
Rh(3)-Rh(4)-P(4)	139.34(15)		
<i>Rh-Rh-CO<sub>terminal</sub></i>		<i>Rh-CO<sub>bridging</sub>-Rh</i>	
Rh(2)-Rh(1)-C(11)	97.9(7)	Rh(1)-C(131)-Rh(3)	82.5(8)
Rh(3)-Rh(1)-C(11)	140.2(6)	Rh(1)-C(141)-Rh(4)	82.4(8)
Rh(4)-Rh(1)-C(11)	140.1(7)	Rh(3)-C(341)-Rh(4)	80.8(7)
Rh(1)-Rh(3)-C(31)	105.6(6)		
Rh(2)-Rh(3)-C(31)	163.1(6)	<i>Rh-Rh-CO<sub>bridging</sub></i>	
Rh(4)-Rh(3)-C(31)	106.9(6)	Rh(2)-Rh(1)-C(131)	80.6(6)
Rh(1)-Rh(4)-C(41)	106.8(7)	Rh(3)-Rh(1)-C(131)	49.0(6)
Rh(2)-Rh(4)-C(41)	162.5(7)	Rh(4)-Rh(1)-C(131)	108.8(6)
Rh(3)-Rh(4)-C(41)	104.6(7)	Rh(2)-Rh(1)-C(141)	81.6(5)
Rh(1)-Rh(2)-C(21)	156.4(8)	Rh(3)-Rh(1)-C(141)	108.4(5)
Rh(1)-Rh(2)-C(22)	92.3(6)	Rh(4)-Rh(1)-C(141)	48.6(5)
Rh(1)-Rh(2)-C(23)	98.8(7)	Rh(1)-Rh(3)-C(131)	48.4(6)
Rh(3)-Rh(2)-C(21)	100.6(8)	Rh(2)-Rh(3)-C(131)	80.1(6)
Rh(3)-Rh(2)-C(22)	150.3(6)	Rh(4)-Rh(3)-C(131)	108.1(6)
Rh(3)-Rh(2)-C(23)	98.3(7)	Rh(1)-Rh(3)-C(341)	109.2(6)
Rh(4)-Rh(2)-C(21)	98.6(7)	Rh(2)-Rh(3)-C(341)	49.6(6)
Rh(4)-Rh(2)-C(22)	96.5(6)	Rh(4)-Rh(3)-C(341)	82.4(6)
Rh(4)-Rh(2)-C(23)	155.0(1)	Rh(1)-Rh(4)-C(341)	108.4(6)
		Rh(2)-Rh(4)-C(341)	81.5(6)
		Rh(3)-Rh(4)-C(341)	48.0(6)
		Rh(1)-Rh(4)-C(131)	50.7(5)
		Rh(2)-Rh(4)-C(141)	82.7(5)
		Rh(3)-Rh(4)-C(141)	111.0(5)
<i>P-Rh-CO<sub>terminal</sub></i>			
P(1)-Rh(1)-C(11)	98.3(7)		
P(3)-Rh(3)-C(31)	99.9(6)		
P(4)-Rh(4)-C(41)	100.2(6)		
<i>OC<sub>terminal</sub>-Rh-CO<sub>terminal</sub></i>		<i>OC<sub>bridging</sub>-Rh-CO<sub>bridging</sub></i>	
C(21)-Rh(2)-C(22)	101.3(10)	C(131)-Rh(1)-C(141)	156.7(8)
C(21)-Rh(2)-C(23)	98.3(10)	C(131)-Rh(3)-C(341)	156.9(8)
C(22)-Rh(2)-C(23)	98.2(9)	C(341)-Rh(4)-C(141)	158.6(8)
<i>P-Rh-CO<sub>bridging</sub></i>		<i>OC<sub>terminal</sub>-Rh-CO<sub>bridging</sub></i>	
P(1)-Rh(1)-C(131)	99.2(6)	C(11)-Rh(1)-C(131)	98.2(9)

TABLE 8 (continued)

<i>P-Rh-CO bridging</i>		<i>OCterminal-Rh-CO bridging</i>	
P(1)-Rh(1)-C(141)	93.7(6)	C(11)-Rh(1)-C(141)	99.1(8)
P(3)-Rh(3)-C(131)	98.5(6)	C(131)-Rh(3)-C(31)	95.8(8)
P(3)-Rh(3)-C(341)	98.4(6)	C(341)-Rh(4)-C(41)	93.6(9)
P(4)-Rh(4)-C(341)	99.3(6)	C(141)-Rh(4)-C(41)	97.2(9)
P(4)-Rh(4)-C(141)	97.0(5)	C(341)-Rh(3)-C(31)	96.6(8)
<i>OCterminal-Rh-P</i>		<i>OCbridging-Rh-P</i>	
C(11)-Rh(1)-P(1)	98.3(7)	C(131)-Rh(1)-P(1)	99.2(7)
C(31)-Rh(3)-P(3)	99.9(6)	C(141)-Rh(1)-P(1)	93.7(5)
C(41)-Rh(4)-P(4)	100.2(7)	C(131)-Rh(1)-P(3)	98.5(6)
		C(341)-Rh(3)-P(3)	98.4(6)
		C(341)-Rh(4)-P(4)	99.3(6)
		C(141)-Rh(4)-P(4)	97.0(6)
<i>Rh-C-O terminal</i>		<i>Rh-C-O bridging</i>	
Rh(1)-C(11)-O(11)	174.1(20)	Rh(1)-C(131)-O(131)	138.6(17)
Rh(2)-C(21)-O(21)	177.0(20)	Rh(1)-C(141)-O(141)	135.6(15)
Rh(2)-C(22)-O(22)	175.5(20)	Rh(3)-C(131)-O(131)	138.6(17)
Rh(2)-C(23)-O(23)	177.3(20)	Rh(3)-C(341)-O(341)	141.5(16)
Rh(3)-C(31)-O(31)	175.2(18)	Rh(4)-C(341)-O(341)	135.9(16)
Rh(4)-C(41)-O(41)	171.9(20)	Rh(4)-C(141)-O(141)	143.4(15)
<i>Phosphite bond angles</i>			
Rh(1)-P(1)-O'(11)	109.7(6)	Rh(3)-P(3)-O'(31)	120.2(3)
Rh(1)-P(1)-O'(12)	120.6(6)	Rh(3)-P(3)-O'(32)	112.1(3)
Rh(1)-P(1)-O'(13)	121.2(6)	Rh(3)-P(3)-O'(33)	120.7(3)
Rh(4)-P(4)-O'(41)	120.9(3)		
Rh(4)-P(4)-O'(42)	117.5(3)		
Rh(4)-P(4)-O'(43)	111.1(3)		

anisotropic thermal parameters and lists of observed and calculated structure factors are available from the authors.

In the structure factor calculations described above neutral scattering factors were taken from ref. 7 and corrected for anomalous dispersion using  $\Delta f'$  and  $\Delta f''$  values from ref. 8. All the calculations were performed on the Oxford University ICL2980 computer using CRYSTALS computer programmes [9].

The important intramolecular bond lengths and bond angles for  $\text{Rh}_4(\text{CO})_{10}$ -( $\text{PPh}_3$ )<sub>2</sub> are given in Tables 5 and 6 and for  $\text{Rh}_4(\text{CO})_{10}\{\text{P}(\text{O}^i\text{Ph})_3\}_3$  in Tables 7 and 8; perspective drawings of the structures of I and II are shown in Figs. 1 and 2, respectively.

#### Discussion of the solid state molecular structure of $\text{Rh}_4(\text{CO})_{12}$ derivatives

The crystal structures of  $\text{Rh}_4(\text{CO})_{10}(\text{PPh}_3)_2$  and  $\text{Rh}_4(\text{CO})_9\{\text{P}(\text{O}^i\text{Ph})_3\}_3$  reported in this paper, together with those previously reported for  $\text{Rh}_4(\text{CO})_8\{\text{P}(\text{O}^i\text{Ph})_3\}_4$  [10] and  $\text{Rh}_4(\text{CO})_8(\text{dppm})_2$  \* [11], are all based on the  $\text{Rh}_4(\text{CO})_{12}$  structure illustrated in Fig. 3. In  $\text{Rh}_4(\text{CO})_{12}$  the terminal CO ligands fall into three distinct symmetry types, described as apical, radial and axial as shown in Fig. 3. In  $\text{Rh}_4(\text{CO})_{10}(\text{PPh}_3)_2$ , which is isomorphous with  $\text{Ir}_4(\text{CO})_{10}(\text{PPh}_3)_2$  [12],

\* dppm = bis(diphenylphosphino)methane,  $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ .

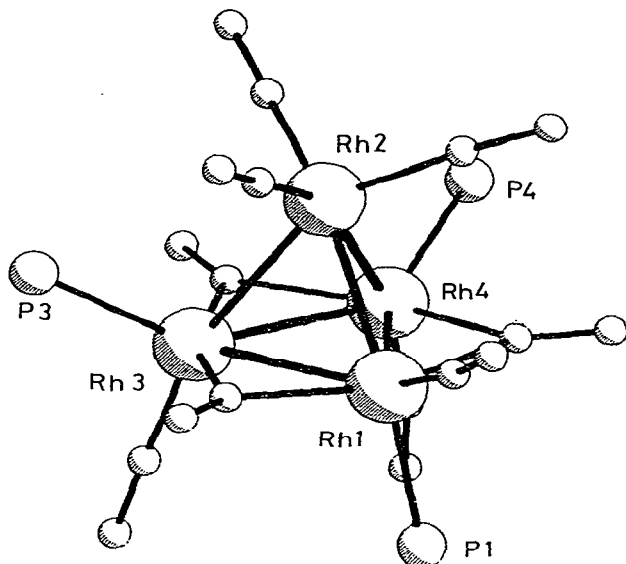


Fig. 2. Structure of  $\text{Rh}_4(\text{CO})_9\{\text{P}(\text{OPh})_3\}_3$ . (The OPh groups have been omitted for clarity.)

the phosphine ligands occupy radial and axial sites on adjacent metal atoms (Fig. 1). In  $\text{Rh}_4(\text{CO})_9\{\text{P}(\text{OPh})_3\}_3$  the third phosphite ligand occupies a radial site (Fig. 2), as in  $\text{Ir}_4(\text{CO})_9(\text{PPh}_3)_3$ , [12] and in  $\text{Rh}_4(\text{CO})_8\{\text{P}(\text{OPh})_3\}_4$  the phosphite ligands are coordinated to each of the rhodium atoms with two phosphites occupying axial and one phosphite radial sites [10]. These site preferences for phosphine and phosphite ligands in the solid state presumably reflect the gross steric/electronic requirements of the bulky phosphorus-containing ligands.

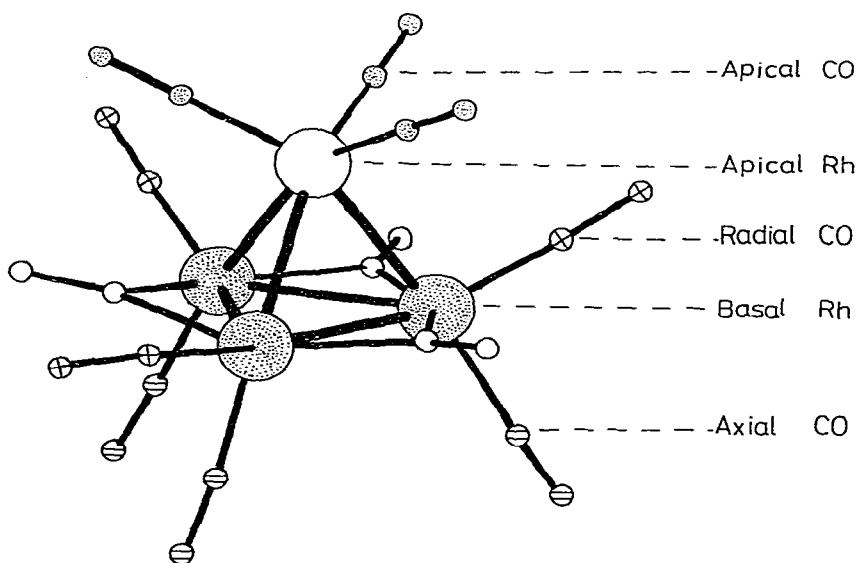


Fig. 3. Nomenclature of ligands and metals based on the  $\text{Rh}_4(\text{CO})_{12}$  structure.

TABLE 9  
A COMPARISON OF BOND LENGTHS (Å) AND BOND ANGLES (°) IN Rh<sub>4</sub>(CO)<sub>12</sub> AND ITS DERIVATIVES

Compound	Rh <sub>4</sub> (CO) <sub>12</sub> <sup>a</sup>	Rh <sub>4</sub> (CO) <sub>10</sub> (PPH <sub>3</sub> ) <sub>2</sub> <sup>b</sup>	Rh <sub>4</sub> (CO) <sub>8</sub> {P(OPh) <sub>3</sub> } <sub>3</sub> <sup>b</sup>	Rh <sub>4</sub> (CO) <sub>8</sub> {P(OPh) <sub>3</sub> } <sub>4</sub> <sup>c</sup>	Rh <sub>4</sub> (CO) <sub>8</sub> (dppm) <sub>2</sub> <sup>d</sup>
Rh <sub>basal</sub> -Rh <sub>basal</sub>	2.750	2.719	2.741	2.752	
Rh <sub>basal</sub> -Rh <sub>apical</sub>	2.707	2.694	2.709	2.716	
Rh-Rh (mean)	2.73	2.71	2.72	2.71	
Rh-P	2.34	2.23-2.25	2.20-2.25	2.27-2.33	
Rh-C (terminal)	1.96 mean	1.829-1.916	1.834-1.886	1.83 mean	1.91 mean
Rh-C (bridging)	1.99 mean	2.020-2.154	1.998-2.096	2.00 mean	2.09 mean
Rh <sub>apical</sub> -Rh <sub>basal</sub> -P <sub>rad</sub>	108.3	97.2 96.9	c	90.4	
Rh <sub>apical</sub> -Rh <sub>basal</sub> -P <sub>ax</sub>	175.5	163.1	c	154.7, 151.9	
Rh <sub>apical</sub> -Rh <sub>basal</sub> -C <sub>rad</sub>	95 mean	97.9	c	105.7, 108.3	
Rh <sub>apical</sub> -Rh <sub>basal</sub> -C <sub>ax</sub>	165 mean	162.5, 163.1	c	169.4	
Rh <sub>basal</sub> -Rh <sub>basal</sub> -P <sub>rad</sub>	f	139.4	c	135.8	
Rh <sub>basal</sub> -Rh <sub>basal</sub> -P <sub>ax</sub>	f	116.8	c	98	

<sup>a</sup> Reference 14. <sup>b</sup> This work. <sup>c</sup> Reference 10. <sup>d</sup> Reference 11. <sup>e</sup> Not reported. <sup>f</sup> Rh<sub>basal</sub>-Rh<sub>basal</sub>-C is 137.7° and 109.2° for radial and axial CO's respectively.

Recent CNDO calculations [13] show that in  $\text{Co}_4(\text{CO})_{12}$  axial carbonyls are the poorest electron acceptors: it therefore seems reasonable that in  $\text{Rh}_4(\text{CO})_{12}$  other ligands first occupy an axial site where the  $\pi$ -back bonding requirement is small (see below). The second ligand goes *trans* to the first because of steric effects and similarly the third ligand does not readily occupy an axial site, since this would put two bulky ligands on the same triangular face of the icosahedral ligand polyhedron, but instead goes into a radial site.

A comparison of the metal-metal bond lengths in the  $\text{Rh}_4(\text{CO})_{12}$  derivatives given in Table 9 indicates that the mean Rh-Rh bond length is rather insensitive to the nature and degree of substitution. The observed mean Rh-Rh bond lengths lie in the range 2.71–2.73 Å which is close to that reported for the parent molecule [14]. In each of the substituted cluster compounds which have been studied, the mean bond lengths for the carbonyl-bridged metal-metal bonds is slightly longer (by 0.03–0.04 Å) than the non-bridged metal-metal bonds. In individual molecules the difference is on the edge of statistical significance, but the fact that the same pattern emerges in each of the four structures leads us to believe that there is a distinct difference in the two types of metal-metal bonds.

The metal-carbon and carbon-oxygen bond lengths and their associated bond angles for the molecules in Table 9, do not show statistically significant variations. Furthermore, even in  $\text{Rh}_4(\text{CO})_{10}(\text{PPh}_3)_2$ , which has an asymmetric distribution of phosphine ligands, there is little evidence for the formation of asymmetric carbonyl bridges. The largest difference in metal-carbon bond lengths is observed for the carbonyls bridging Rh(2)-Rh(3) and Rh(4)-Rh(3) and are equal to 0.077 and 0.134 Å, respectively, which are only 5 and 9 times, respectively, the standard deviations associated with these bond lengths.

The steric constraints imposed by the bulky phosphorus-containing ligands is reflected in the large variation observed for  $\widehat{\text{Rh-Rh-P}}$  bond angles. For radial phosphines and phosphites,  $\widehat{\text{Rh}_{\text{ap}}-\text{Rh}_{\text{bas}}-\text{P}_{\text{rad}}}$  varies from 108° in  $\text{Rh}_4(\text{CO})_{10}(\text{PPh}_3)_2$  to 97° in  $\text{Rh}_4(\text{CO})_9\{\text{P}(\text{OPh})_3\}_3$  and these angles should be compared with the value of  $\widehat{\text{Rh}_{\text{ap}}-\text{Rh}_{\text{bas}}-\text{C}_{\text{rad}}}$  95° in  $\text{Rh}_4(\text{CO})_{12}$ ; corresponding variations are found in  $\widehat{\text{Rh}_{\text{ap}}-\text{Rh}_{\text{bas}}-\text{P}_{\text{ax}}}$ . Similarly, apart from  $\text{Rh}_4(\text{CO})_8(\text{dppm})_2$ , which has small angles because of the small bite angle imposed by the chelating ligand which bridges apical and basal sites within the cluster [11], the largest variations in  $\widehat{\text{Rh}_{\text{bas}}-\text{Rh}_{\text{bas}}-\text{P}}$  angles from the corresponding  $\widehat{\text{Rh}_{\text{bas}}-\text{Rh}_{\text{bas}}-\text{C}}$  angles in  $\text{Rh}_4(\text{CO})_{12}$  are found for  $\text{Rh}_4(\text{CO})_{10}(\text{PPh}_3)_2$  (Table 9); this probably stems in part from the larger cone angle of  $\text{PPh}_3$  compared to  $\text{P}(\text{OPh})_3$  [15] and from the greater degree of flexibility of ligand orientations in the less substituted cluster.

### $^{31}\text{P}\{^1\text{H}\}$ NMR studies

The solution structures of  $\text{Rh}_4(\text{CO})_{12-x}\{\text{P}(\text{OPh})_3\}_x$  ( $x = 1, 2$  and 3) have been shown by  $^{31}\text{P}\{^1\text{H}\}$  NMR studies to be identical to their solid state structure; for all these derivatives there is evidence for only one isomer in solution. As found for the corresponding iridium clusters [16], the radial phosphorus resonance occurs at higher frequency than the axial phosphorus and the numerical value of  $^1J(\text{Rh-P})$  is significantly bigger for  $\text{P}_{\text{rad}}$  than  $\text{P}_{\text{ax}}$ . Coupling between  $\text{P}_{\text{ax}}$  and  $\text{P}_{\text{rad}}$  is not observed and values of  $^2J(\text{Rh-P}_{\text{ax}})$  are small or non-observable

TABLE 10

SUMMARY OF  $^{31}\text{P}$  NMR DATA ON  $\text{Rh}_4(\text{CO})_{12-x}\text{L}_x$  ( $\text{L} = \text{P}(\text{OPh})_3, \text{PPh}_3; x = 1, 2, 3$ ) in  $\text{CD}_2\text{Cl}_2$  ( $\text{L} = \text{P}(\text{OPh})_3$ ) AND IN ACETONE- $d_6$  ( $\text{L} = \text{PPh}_3$ )

$x$	$\text{L}$	$T$ ( $^\circ\text{C}$ )	$\delta(\text{P}_{\text{ax}})^a$ (ppm)	$\delta(\text{P}_{\text{rad}})^a$ (ppm)	$^1J(\text{Rh}-\text{P}_{\text{ax}})^b$ (Hz)	$^1J(\text{Rh}-\text{P}_{\text{rad}})^b$ (Hz)
1	$\text{P}(\text{OPh})_3$	-52	+100.9		-205	
2	$\text{P}(\text{OPh})_3$	-52	+102.2	+116.6	-212	-260
3	$\text{P}(\text{OPh})_3$	-52	+102.2	+118.0	-215	-263
1	$\text{PPh}_3$	-70	+24.1		-119	
1	$\text{PPh}_3$	-54		+24.9		-134
2	$\text{PPh}_3$	-70	+18.5	+32.6	-127	-138.2
2	$\text{PPh}_3$	-56	+28.2		-125	

<sup>a</sup> From  $\text{H}_3\text{PO}_4$  positive shifts are to high frequency. <sup>b</sup> See text for a discussion of signs; where the sign is not specified it has not been determined. <sup>c</sup>  $^2J(\text{P}_{\text{rad}}-\text{RhL}_{\text{rad}})$ . <sup>d</sup>  $^2J(\text{P}_{\text{rad}}-\text{RhL}_{\text{ax}})$ . <sup>e</sup> Can be interchanged.

whereas  $^2J(\text{Rh}-\text{P}_{\text{rad}})$  values are significant. The assignment of  $^2J(\text{Rh}-\text{P}_{\text{rad}})$  follows from a consideration of the angles in Table 9 and the splittings observed for the radial resonance in  $\text{Rh}_4(\text{CO})_{10}\{\text{P}(\text{OPh})_3\}_2$ , which appears as a doublet  $\{^1J(\text{Rh}_{\text{bas}}-\text{P})\}$  of doublets  $\{^2J(\text{Rh}_{\text{ap}}-\text{P})\}$ .

The simulated and observed resonance for  $\text{Rh}_4(\text{CO})_9\{\text{P}(\text{OPh})_3\}_3$  are shown in Fig. 4. The axial resonance consists of a doublet  $\{^1J(\text{Rh}_{\text{ap}}-\text{P})\}$  of doublets  $\{^2J(\text{Rh}_{\text{ap}}-\text{P})\}$  of triplets  $\{^2J(\text{Rh}_{\text{bas}}-\text{P})\}$  and the analysis of the radial resonance approximates to an AA'XX' spin system, for the two radial phosphites (A) and the rhodium atoms to which they are attached (X), which is further split into a doublet of doublets due to two bond couplings with the other basal and apical rhodium atoms. It has been previously shown that  $^1J(\text{Rh}-\text{P})$  is negative [17]

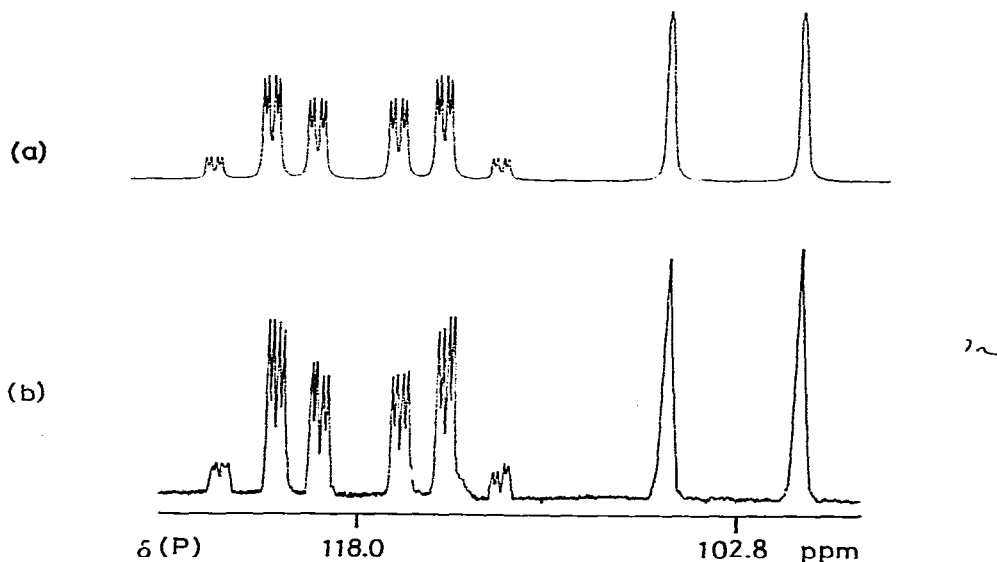


Fig. 4.  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectrum of  $\text{Rh}_4(\text{CO})_9\{\text{P}(\text{OPh})_3\}_3$  in  $\text{CD}_2\text{Cl}_2$  at  $-52^\circ\text{C}$ . (a) Simulated using parameters in Table 10. (b) observed.



${}^2J(\text{Rh}_{\text{bas}}-\text{P}_{\text{rad}})^b$ (Hz)	${}^2J(\text{Rh}_{\text{bas}}-\text{P}_{\text{ax}})^b$ (Hz)	${}^2J(\text{Rh}_{\text{ap}}-\text{P}_{\text{rad}})^b$ (Hz)	${}^2J(\text{Rh}_{\text{ap}}-\text{P}_{\text{ax}})^b$ (Hz)	${}^3J(\text{P}_{\text{rad}}-\text{P}_{\text{rad}})^b$ (Hz)
18	0	8	0	
16 <sup>c</sup> 18 <sup>d</sup>	3 <sup>e</sup>	7	0 <sup>e</sup>	167
	2 <sup>e</sup>		0 <sup>e</sup>	
	0		0	
12	0		0	
	0		0	

and this analysis shows  ${}^2J(\text{AX}')$  to have the same sign as  ${}^1J(\text{AX})$  and gives  ${}^2J(\text{AX}') = -16.2$  Hz; this is very similar to that obtained for the two bond coupling of  $\text{P}_{\text{rad}}$  with  $\text{Rh}_{\text{bas}}(\text{P}_{\text{ax}})$  and suggests that  ${}^2J(\text{P}_{\text{rad}}-\text{Rh}(\text{P}_{\text{ax}}))$  is also negative. These data are summarised in Table 10.

When the reaction of  $\text{Rh}_4(\text{CO})_{12}$  with  $x\text{PPh}_3$  is carried out in hexane and the products,  $\text{Rh}_4(\text{CO})_{12-x}(\text{PPh}_3)_x$  ( $x = 1$  and  $2$ ), isolated quickly, then the resultant complexes are shown to have the same stereochemistry as the triphenylphosphite analogues and there is no evidence for other isomers (see Table 10). Trends, similar to those found in the phosphite derivatives, are found for  $\delta(\text{PPh}_3)$  and  $J(\text{Rh}-\text{PPh}_3)$  with  $J(\text{Rh}-\text{PPh}_3)$  having, as expected, approximately half the value of  $J(\text{Rh}-\text{P}(\text{OPh})_3)$ . However, when the reaction is carried out for longer periods of time in a solvent (toluene) in which the product is soluble, there is evidence for different isomers being formed. This should be contrasted with the stereospecific reaction of  $\text{P}(\text{OPh})_3$  with  $\text{Rh}_4(\text{CO})_{12}$  under similar conditions. Similar results have been obtained for triphenylphosphine/triphenylphosphite substitution on  $\text{Co}_3(\text{CO})_9\text{CX}$  [18]. In both cases the bulkier triphenylphosphine gives mixtures of isomers because of steric destabilisation of the first formed product.

${}^{31}\text{P}\{-^1\text{H}\}$  NMR readily shows that the qualitative redistribution reactions described in eqs. 1 and 2 occur at room temperature over 3–12 h. Statistical effects alone cannot account for these reactions going to completion and it seems probable that destabilisation, resulting on progressive substitution, must be of the order of 4 kcal mol<sup>-1</sup> in order to account for eqs. 1 and 2.

Carbonyl redistribution in eq. 3 was shown to occur by IR spectroscopy; the IR spectrum of  $\text{Rh}_4(\text{CO})_{12}$  (45.5%  ${}^{13}\text{CO}$ ), synthesized by direct exchange with  ${}^{13}\text{CO}$ , was identical to that obtained immediately on mixing equimolar amounts of unenriched  $\text{Rh}_4(\text{CO})_{12}$  and  $\text{Rh}_4(\text{CO})_{12}$  (90%  ${}^{13}\text{CO}$ ) in  $\text{CH}_2\text{Cl}_2$  under a nitrogen atmosphere at room temperature. The mechanism of this surprisingly facile (<30 secs at 25°C) reaction is unlikely to involve CO dissociation from the parent cluster and must therefore occur via cluster agglomeration or fragmentation. Uncharged clusters containing more than 4 rhodium atoms would be expected to be very insoluble and therefore unlikely intermediates. It thus seems

possible that cluster fragmentation is responsible for these facile redistributions even though this has only been previously observed under CO pressure [4].

Finally it should be noted that the  $^{13}\text{C}$  NMR spectra of these complexes are complicated, because of their complex spin systems, and  $^{13}\text{C}$ - $\{^{31}\text{P}\}$  and  $^{13}\text{C}$ - $\{^{103}\text{Rh}\}$  studies of these molecules will be reported separately.

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