Journal of Organometallic Chemistry, 66 (1974) 279—288

THE CRYSTAL AND MOLECULAR STRUCTURE OF BIS(μ-DIPHENYLPHOSPHIDOμ'-CARBONYL-π-METHYLCYCLOPENTADIENYLCARBONYLIRON)RHODIUM HEXAFLUOROPHOSPHATE (2Rh—Fe)

R. MASON and J.A. ZUBIETA

School of Molecular Sciences, University of Sussex, Brighton, BN1 9QJ (Great Britain)

(Received June 29th, 1973)

Summary

The structure of the title compound was determined from three-dimensional X-ray diffractometer data. The compound crystallizes in space group *Pbca* with $Z = 8$ and cell dimensions: $a = 19.92$ Å, $b = 25.96$ Å, $c = 15.82$ Å. The structural analysis, based on 2541 independent reflections, has converged to a final R_1 of 0.062. The structure consists of a trinuclear non-closed rhodium—iron complex with μ-diphenylphosphido and carbonyl groups bridging the rhodium and iron atoms. The Rh—Fe distances are 2.659(2) and 2.674(1) Å. Each iron atom is additionally bonded to a methylcyclopentadienyl group and a terminal carbonyl group. The closed structure (2Rh—Fe)-(Fe—Fe), predicted on the basis of the "18 electron rule" and observed in related molecules, is suggested as being unstable with respect to the open structure as a result of the substitution of carbonyl ligands by the highly basic μ-phosphido groups.

Reactions involving the formation of polynuclear complexes based on $[Rh(PPh_3)_3Cl]$ are of interest because of the potential of these species as homogeneous catalysts [1 - 3]. The complex which forms upon treatment of $RhCl_3 \cdot 3H_2O$ with $[Fe(\pi\text{-}CH_3C_5H_4)(CO)_2PPh_2]_2$ in the presence of hexafluorophosphate was characterized as $[Rh\{Fe(\pi\text{-}CH_3C_5H_4)(CO)_2(PPh_2)\}_2]\ PF_6$. The similar trinuclear complexes, $[RhFe_2(\pi\text{-}C_5H_5)(CO)_9]$ and $[Rh_2Fe(\pi\text{-}C_5H_5)_2(CO)_6]$ [4], appear to have closed triangular structures on the basis of Mössbauer and IR spectroscopy. The present complex was shown by IR spectroscopy to contain both terminal and bridging carbonyl groups [5] but its general stereochemistry was sufficiently uncertain to justify a crystallographic analysis.

(Continued on p. 282)

TABLE 1

ATOMIC POSITIONS AND THERMAL[a] PARAMETERS WITH STANDARD DEVIATIONS IN PARENTHESES

Atom	*x/a*	*y/b*	*z/c*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rh	0.06939(4)	0.13256(3)	0.19395(5)	5.12(4)	5.24(4)	6.76(5)	0.39(4)	0.29(5)	0.60(5)
Fe(1)	0.05042(6)	0.23450(5)	0.19184(9)	5.83(9)	4.91(9)	5.09(8)	0.12(7)	−0.28(9)	0.51(9)
Fe(2)	0.14918(6)	0.05615(5)	0.14369(9)	4.29(8)	5.04(9)	7.50(10)	0.45(8)	0.77(8)	0.44(9)
P(1)	−0.0253(1)	0.1744(1)	0.2279(2)	5.3(2)	5.0(2)	5.3(2)	0.2(1)	−0.1(1)	0.4(1)
P(2)	0.0685(1)	0.0513(1)	0.2422(2)	4.4(1)	5.4(2)	6.3(2)	−0.2(2)	−0.1(2)	0.4(2)
P(3)	0.2903(2)	0.3546(1)	0.2597(2)	8.8(2)	6.4(2)	8.7(2)	0.3(2)	0.7(2)	−0.2(2)
F(1)	0.2734(5)	0.3100(3)	0.1985(7)	21.0(9)	14.3(7)	21.9(9)	−1.9(7)	−4.7(8)	−6.5(8)
F(2)	0.3390(4)	0.3720(4)	0.1877(6)	15.5(6)	21.1(9)	14.9(7)	−9.8(7)	3.2(6)	1.7(8)
F(3)	0.3130(6)	0.4008(4)	0.3148(7)	33(1)	19.5(9)	18.6(9)	−8.3(9)	2.7(9)	−9.0(9)
F(4)	0.3425(4)	0.3214(4)	0.3025(6)	17.5(7)	25(1)	14.9(7)	9.5(7)	−3.6(7)	2.3(8)
F(5)	0.2400(5)	0.3403(4)	0.3314(7)	16.7(8)	26(1)	22(1)	2.9(8)	10.2(8)	7.5(9)
F(6)	0.2330(4)	0.3848(4)	0.2127(7)	12.6(7)	21.4(9)	28(1)	5.9(6)	−2.2(8)	7.9(9)
O(1)	0.0661(4)	0.2711(3)	0.3674(5)	12.1(3)					
O(2)	0.1889(3)	0.1975(2)	0.2206(4)	8.4(2)					
O(3)	0.0732(3)	−0.0024(3)	0.0169(3)	7.5(2)					
O(4)	0.1204(3)	0.1358(3)	0.0161(4)	6.8(2)					
C(1)	0.0583(5)	0.2532(4)	0.2992(7)	8.0(4)					
C(2)	0.1294(4)	0.1952(3)	0.2034(6)	5.3(2)					
C(3)	0.1010(5)	0.0203(4)	0.0690(6)	5.4(3)					
C(4)	0.1209(5)	0.1155(4)	0.0850(6)	5.5(3)					
C(5a)[b]	−0.0668(5)	0.1808(3)	0.3302(5)	4.7(3)					
C(6a)	−0.0674(5)	0.1395(4)	0.3897(6)	5.5(3)					
C(7a)	−0.1034(5)	0.1430(4)	0.4684(7)	6.5(3)					
C(8a)	−0.1417(5)	0.1873(4)	0.4829(6)	6.7(3)					
C(9a)	−0.1408(5)	0.2288(4)	0.4276(7)	6.5(3)					
C(10a)	−0.1027(4)	0.2261(4)	0.3513(7)	5.6(3)					
C(11b)	−0.0934(4)	0.1602(3)	0.1521(6)	4.4(2)					

C(12b)	−0.0758(5)	0.1355(4)	0.0759(6)	5.5(3)
C(13b)	−0.1262(5)	0.1264(4)	0.0122(7)	6.3(3)
C(14b)	−0.1919(5)	0.1418(4)	0.0272(7)	6.4(3)
C(15b)	−0.2086(5)	0.1655(4)	0.1004(6)	6.2(3)
C(16b)	−0.1610(5)	0.1777(4)	0.1681(6)	5.7(3)
C(17c)	0.0882(4)	0.0478(3)	0.3573(6)	4.7(3)
C(18c)	0.0738(6)	0.0027(4)	0.4075(7)	7.1(3)
C(19c)	0.0859(5)	0.0055(4)	0.4971(7)	7.5(3)
C(20c)	0.1118(5)	0.0479(4)	0.5342(7)	6.6(3)
C(21c)	0.1274(5)	0.0927(4)	0.4864(7)	7.1(3)
C(22c)	0.1159(5)	0.0903(4)	0.3956(6)	5.7(3)
C(23d)	0.0041(5)	0.0022(3)	0.2256(5)	4.3(2)
C(24d)	−0.0639(5)	0.0160(4)	0.2257(6)	5.6(3)
C(25d)	0.1111(5)	−0.0229(4)	0.2084(7)	6.8(3)
C(26d)	0.0929(5)	0.0717(4)	0.1843(8)	6.9(4)
C(27d)	0.0230(5)	0.4145(4)	0.3175(7)	7.2(3)
C(28d)	0.0246(5)	−0.0487(4)	0.2037(7)	6.1(3)
C(29e)	0.0981(4)	0.3065(4)	0.1437(6)	5.8(3)
C(30e)	0.0833(5)	0.3065(4)	0.1437(6)	6.2(3)
C(31e)	0.0090(5)	0.3052(4)	0.1596(7)	6.2(3)
C(32e)	−0.0187(5)	0.2662(4)	0.1040(6)	5.6(3)
C(33e)	0.0355(4)	0.2420(4)	0.0561(7)	5.8(3)
C(34e)	0.1652(5)	0.2598(4)	0.0401(7)	7.5(4)
C(35f)	0.2399(5)	0.0429(4)	0.0807(7)	5.6(3)
C(36f)	0.2465(5)	0.0883(4)	0.1313(7)	6.1(3)
C(37f)	0.2337(5)	0.0733(4)	0.2186(6)	6.2(3)
C(38f)	0.2212(5)	0.0188(4)	0.2203(6)	5.5(3)
C(39f)	0.2246(4)	0.0008(4)	0.1328(7)	5.7(3)
C(40f)	0.2481(6)	0.0405(5)	−0.0196(8)	9.5(5)

---

[a] Temperature Factor = $\exp[-2\pi^2(U_{11}\cdot h^2\cdot a^{*2} + U_{22}\cdot k^2\cdot b^{*2} + U_{33}\cdot l^2\cdot c^{*2} + 2U_{12}\cdot h\cdot k\cdot a^{*}\cdot b^{*} + 2U_{13}\cdot h\cdot l\cdot a^{*}\cdot c^{*} + 2U_{23}\cdot h\cdot l\cdot b^{*}\cdot c^{*})]$, U_{ij} and U (for all C atoms) in Å^2 X 10^2. [b] The notation a...d refers to carbon atoms of phenyl rings of the diphenyl phosphido groups, phenyl groups a and b being attached to P(1) and c and d to P(2); e refers to the methyl cyclopentadienyl groups bonded to Fe(1) and f to that bonded to Fe(2).

Experimental

Crystal data

$C_{40}H_{34}RhFe_2O_4F_6P_3$, $M = 1018.3$, orthorhombic, $a = 19.92(1)$, $b = 25.96(1)$, $c = 15.82(1)$ Å, $U = 8180.8$ Å^3, $D_m = 1.65 \pm 0.02$ g.cm^{-3}, $Z = 8$, $D_c = 1.68$. Space group *Pbca* from systematic absences: $\{0kl\}$ for $k = 2n + 1$, $\{h0l\}$ for $l = 2n + 1$, and $\{hk0\}$ for $h = 2n + 1$. Mo-K_α radiation, $\lambda = 0.7107$ Å, $\mu = 13.6$ cm^{-1}.

Measurement of intensities

Red-brown, needle shaped crystals of $[Rh\{Fe(\pi\text{-}CH_3C_5H_4)(CO)_2(PPh_2)\}_2]PF_6$ were prepared as previously reported [5]. Preliminary unit cell dimensions were determined from precession photographs, and final cell data obtained by least squares refinement of 12 reflections which had been centered on a Hilger and Watts four-circle diffractometer (Mo-K_α radiation).

A crystal of dimensions 0.14 × 0.30 × 0.13 mm was mounted along its long axis and used for data collection. The 600, 006, and 115 reflections were used to monitor crystal and instrument stability. Their intensities varied by no more than ± 1.2% of the mean value for the entire collection procedure. Intensity measurements were based on an ω—2θ scan routine with background measurements of 15 s made at the extremeties of each scan. Each reflection count was accumulated over 100 steps of 0.01° with 1 s counting time at each step. Diffracted rays were collected using a circular aperture of 2.5 mm diameter, 250 mm from the crystal.

Corrections were applied for background, attenuators, Lorentz and polarization effects but not for absorption ($\mu = 13.6$ cm^{-1}) or extinction effects.

A total of 2541 independent reflections with $I \geqslant 3\sigma(I)$ were collected within the sphere defined by $2.0° \leqslant \theta \leqslant 24.0°$.

Determination of the structure

A three-dimensional Patterson synthesis revealed the positions of the rhodium and iron atoms. A difference Fourier synthesis, based on the three heavy atom-phased structure factors, then provided the positions of all remaining non-hydrogen atoms in the $[Rh\{Fe(\pi\text{-}CH_3C_5H_4)(CO)_2(PPh_2)\}_2]PF_6$ unit. Unit weights—least-squares refinement of positional and isotropic temperature parameters converged to a discrepancy index, $R_1 = 0.11$. Further block-diagonal least-squares refinement of position and anisotropic (for Rh, Fe, P and F atoms) and isotropic carbon and oxygen temperature factors gave a value of $R_1 = 0.063$. Two final cycles of least-squares refinement on all parameters were accomplished assigning to each reflection a weight of $1/\sigma^2$ where σ is the standard deviation in F_o, calculated during the data processing and based on counting statistics only. This led to a significant improvement in the standard deviations of the bond lengths and angles and final discrepancy indices $R_1 = 0.062$, $R_2 = 0.064$. The terminal difference density syntheses, calculated on the basis of the refined parameters, showed no excursions of electron density greater than 0.3 e/Å^3.

The atomic scattering factors used were those for Rh, Fe, P, F^-, O and C. The effects of anomalous dispersion from iron were included in the calculations [17].

TABLE 2

SELECTED BOND LENGTHS[a] (Å) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

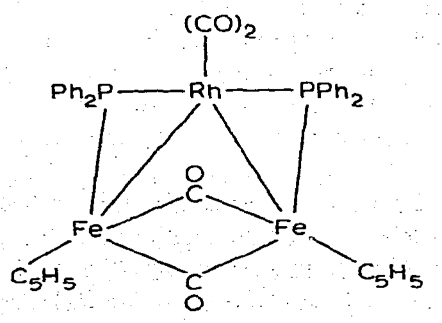
Rh—Fe(1)	2.674(1)	P(3)—F(1)	1.53(1)
Rh—Fe(2)	2.659(2)	P(2)—F(2)	1.55(1)
Rh—C(2)	2.023(9)	P(3)—F(3)	1.54(1)
Rh—C(4)	2.025(10)	P(3)—F(4)	1.51(1)
Rh—P(1)	2.239(3)	P(3)—F(5)	1.54(1)
Rh—P(2)	2.238(3)	P(3)—F(6)	1.56(1)
Fe(1)—P(1)	2.241(3)	C(1)—O(1)	1.17(1)
Fe(1)—C(1)	1.74(1)	C(2)—O(2)	1.21(1)
Fe(1)—C(2)	1.89(9)	C(3)—O(3)	1.15(1)
Fe(1)—C(29)	2.14(1)	C(4)—O(4)	1.19(1)
Fe(1)—C(30)	2.12(1)		
Fe(1)—C(31)	2.07(1)	C(29)—C(34)	1.50(1)
Fe(1)—C(32)	2.10(1)	C(35)—C(40)	1.57(2)
Fe(1)—C(33)	2.14(1)	C(29)—C(30)	1.41(1)
		C(29)—C(33)	1.47(1)
Fe(2)—P(2)	2.222(3)	C(30)—C(31)	1.50(1)
Fe(2)—C(3)	1.77(1)	C(31)—C(32)	1.43(1)
Fe(2)—C(4)	1.88(1)	C(32)—C(33)	1.46(1)
Fe(2)—C(35)	2.08(1)	C(35)—C(36)	1.41(1)
Fe(2)—C(36)	2.12(1)	C(35)—C(39)	1.45(1)
Fe(2)—C(37)	2.09(1)	C(36)—C(37)	1.44(1)
Fe(2)—C(38)	2.10(1)	C(37)—C(38)	1.44(1)
Fe(2)—C(39)	2.08(1)	C(38)—C(39)	1.43(1)
P(1)—C(5)	1.799(9)		
P(1)—C(11)	1.827(9)		
P(2)—C(17)	1.830(10)		
P(2)—C(23)	1.831(9)		

[a] The carbon—carbon distances within the phenyl groups of the diphenylphosphido residues vary from a minimum bond length of 1.33(1) to a maximum of 1.44(1)Å with an average value of 1.40(1)Å.

The final positional and thermal parameters are presented in Table 1. The relevant bond lengths and angles, together with estimated standard deviations are presented in Tables 2 and 3. Figure 1 is a perspective view giving the labelling at the atoms and Fig. 2a is a stereo pair of the $[Rh\{Fe(\pi\text{-}CH_3C_5H_4)(CO)_2(PPh_2)\}_2]^+$ unit. Figure 2b is a view of the PF_6^- anion with a representation of its thermal vibrations (25% probability ellipsoids). A list of observed and calculated structure factor moduli may be obtained from the authors.

Discussion

It is the non-closed form of the observed structure that deserves most comment for the alternative arrangements shown below.



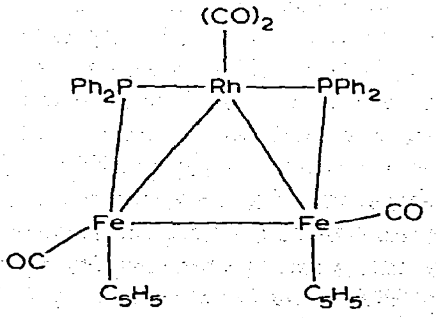


TABLE 3

SELECTED BOND ANGLES[a] (°) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Fe(1)—Rh—Fe(2)	145.03(5)	F(1)—P(3)—F(4)	89.5(5)
Fe(1)—Rh—P(1)	53.39(7)	F(1)—P(3)—F(5)	97.1(5)
Fe(1)—Rh—C(2)	44.9(3)	F(1)—P(3)—F(6)	86.0(5)
Fe(1)—Rh—P(2)	159.34(8)	F(2)—P(3)—F(3)	89.4(6)
Fe(1)—Rh—C(4)	106.1(3)	F(2)—P(3)—F(4)	93.0(5)
Fe(2)—Rh—P(1)	159.11(8)	F(2)—P(3)—F(5)	176.8(6)
Fe(2)—Rh—P(2)	53.13(7)	F(2)—P(3)—F(6)	88.5(5)
Fe(2)—Rh—C(2)	105.4(3)	F(3)—P(3)—F(4)	89.9(6)
Fe(2)—Rh—C(4)	44.7(3)	F(3)—P(3)—F(5)	88.7(6)
P(1)—Rh—P(2)	111.8(1)	F(3)—P(3)—F(6)	94.8(6)
P(1)—Rh—C(2)	95.4(3)	F(4)—P(3)—F(5)	89.6(5)
P(1)—Rh—C(4)	136.7(3)	F(4)—P(3)—F(6)	175.1(6)
P(2)—Rh—C(2)	137.4(3)	F(5)—P(3)—F(6)	89.1(5)
P(2)—Rh—C(4)	94.4(3)	F(1)—C(1)—O(1)	171.8(9)
P(1)—Rh—Fe(1)	53.39(7)	Rh—C(2)—Fe(1)	86.1(6)
P(1)—Rh—Fe(2)	159.11(8)	Rh—C(2)—O(2)	129.7(6)
P(2)—Rh—Fe(1)	159.34(8)	Fe(1)—C(2)—O(2)	143.5(7)
P(2)—Rh—Fe(2)	53.13(7)	Fe(2)—C(3)—O(3)	175.3(9)
Rh—Fe(1)—P(1)	53.33(7)	Rh—C(4)—Fe(2)	85.8(4)
Rh—Fe(1)—C(1)	104.6(4)	Rh—C(4)—O(4)	130.5(7)
Rh—Fe(1)—C(2)	49.0(3)	Fe(2)—C(4)—O(4)	143.0(8)
P(1)—Fe(1)—C(1)	90.8(4)	C(30)—C(29)—C(33)	109.8(8)
P(1)—Fe(1)—C(2)	99.2(3)	C(30)—C(29)—C(34)	125.2(9)
C(1)—Fe(1)—C(2)	89.2(5)	C(33)—C(29)—C(34)	124.7(9)
Rh—Fe(2)—P(2)	53.72(7)	C(29)—C(30)—C(31)	107.5(8)
Rh—Fe(2)—C(3)	105.0(3)	C(30)—C(31)—C(32)	107.3(8)
Rh—Fe(2)—C(4)	49.4(3)	C(31)—C(32)—C(33)	108.9(8)
P(2)—Fe(2)—C(3)	91.6(3)	C(29)—C(33)—C(32)	106.6(8)
P(2)—Fe(2)—C(4)	99.3(3)	C(36)—C(35)—C(39)	110.6(9)
C(3)—Fe(2)—C(4)	87.2(4)	C(36)—C(35)—C(40)	125.4(9)
Rh—P(1)—Fe(1)	73.28(8)	C(39)—C(35)—C(40)	124.0(9)
Rh—P(1)—C(5)	129.8(3)	C(35)—C(36)—C(37)	106.3(9)
Rh—P(1)—C(11)	112.1(3)	C(36)—C(37)—C(38)	108.2(8)
Fe(1)—P(1)—C(5)	117.7(3)	C(37)—C(38)—C(39)	107.3(8)
Fe(1)—P(1)—C(11)	118.5(3)	C(35)—C(39)—C(38)	107.5(8)
C(5)—P(1)—C(11)	104.2(4)	P(1)—C(5)—C(6)	120.7(7)
Rh—P(2)—Fe(2)	73.20(9)	P(1)—C(5)—C(10)	121.1(7)
Rh—P(2)—C(17)	111.8(3)	P(1)—C(11)—C(12)	117.0(7)
Rh—P(2)—C(23)	128.0(3)	P(1)—C(11)—C(16)	121.3(7)
Fe(2)—P(2)—C(17)	121.3(3)	P(2)—C(17)—C(18)	121.6(7)
Fe(2)—P(2)—C(23)	116.8(3)	P(2)—C(17)—C(22)	118.0(7)
C(17)—P(2)—C(23)	104.7(4)	P(2)—C(23)—C(24)	120.1(7)
F(1)—P(3)—F(2)	84.8(6)	P(2)—C(23)—C(28)	118.5(7)
F(1)—P(3)—F(3)	174.2(6)		

[a] Internal phenyl angles have been omitted. The variation for all C—C—C angles within the four phenyl groups lies within the limits of 115.0(83)° and 123.8(90)° with an average value of 120.0°.

They are identical in conforming to the eighteen-electron "rule" and in being *closo*-complexes such as are typically observed in $Os_3(CO)_{12}$ [6], $(Re_3Cl_{12})^{3-}$ [7] and $Fe_3(CO)_{12}$ [8]. Open triangular arrangements are, however, uncommon in such fifty-valence electron trinuclear complexes as $Fe_3(CO)_9S_2$ [9] and $Mn_2Fe(CO)_{14}$ [10] where it is phenomenologically presumed that orbitals which are strongly antibonding with respect to metal—metal bonds are now populated, a conclusion which is much strengthened by the structural observations on $Co_3(\pi\text{-}C_5H_5)_3(CO)S$, $[Co_3(\pi\text{-}C_5H_5)_3S_2]^+$ and $Co_3(\pi\text{-}C_5H_5)_3S$ where the metal—metal distances average 2.45, 2.59 and 2.69 Å [11]. That the highest filled orbitals, in even the 48 valence electron trinuclear complexes, are antibonding with respect to the cluster is also nicely illustrated by the metal—metal bond lengths in $Ru_3(CO)_{12}$ [12] and $Ru_3(CO)_4(C_8H_8)_2$

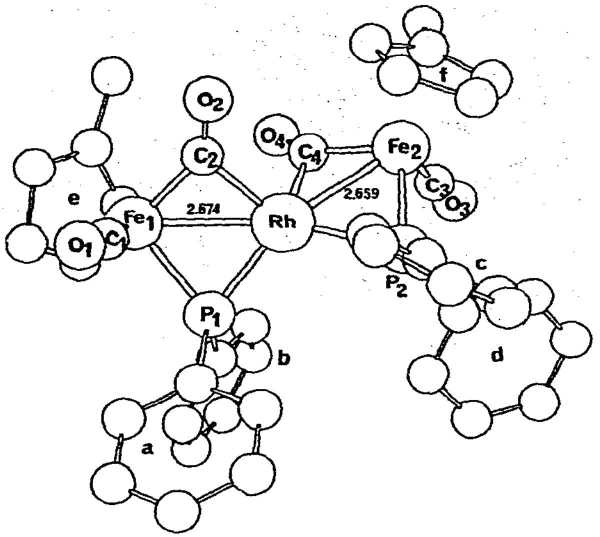


Fig. 1. Schematic representation of the $[Rh\{Fe(PPh_2)(CO)_2(\pi\text{-}CH_3C_5H_4)\}_2]^+$ moiety, indicating atom labelling.

[13]: the replacement of the eight terminal carbonyl ligands by the weaker Lewis acid, cyclooctatetraene, leads to an increase in the Ru—Ru bond length from 2.85 to 2.94 Å.

A high proportion of carbonyl ligands in $Fe_3Rh(\pi\text{-}C_5H_5)(CO)_{11}$ [14] and $Fe_2Rh_2(\pi\text{-}C_5H_5)_2(CO)_8$ [15] is obviously sufficient to stabilise the cluster with the maximum number of metal—metal bonds. In the present complex, the presence of the strongly basic phosphido-ligands serves to additionally destabilise the *closo* arrangement. Intuitively then, *closo* arrangements are possible for the complexes, $RhFe_2(\pi\text{-}C_5H_5)(CO)_9$ and $Rh_2Fe(\pi\text{-}C_5H_5)(CO)_6$ in accord with the suggestions from spectroscopic data [4].

The Rh—Fe bond distances of 2.659(2) and 2.674(2) Å appear significantly different while being entirely comparable with the values observed in the tetranuclear species [14,15]. Additionally, the stereochemistry around the rhodium atom is unusual as the bond angles of Table 3 illustrate. The dihedral angles between the planes containing Fe(1)C(2)Rh and Fe(1)P(1)Rh (155.6°) and Fe(2)C(4)Rh and Fe(2)P(2)Rh (153.5°) are essentially equivalent. We have no sensible rationalisation of the small difference between the two Rh—Fe bond lengths. There are no unusual features concerning the metal—ligand bond lengths. Unlike the asymmetric carbonyl bridge bonds observed in $Rh_2Fe_2(C_5H_5)_2(CO)_8$, the difference of 0.14 Å between the Rh—C(O) and Fe—C(O) lengths is close to the difference in covalent radii between the two metals. The mean bridge bond angles (Rh—P—Fe, 73.2°; Rh—C—Fe, 85.9°) are consistent with the general bonding scheme [16] for bridged binuclear species in so far as they further illustrate the point that the covalent radius of the bridging atom is much less important than other factors (electronic configuration of the metal; number of terminal metal—ligand bonds and so on) in determining a metal—metal bond length.

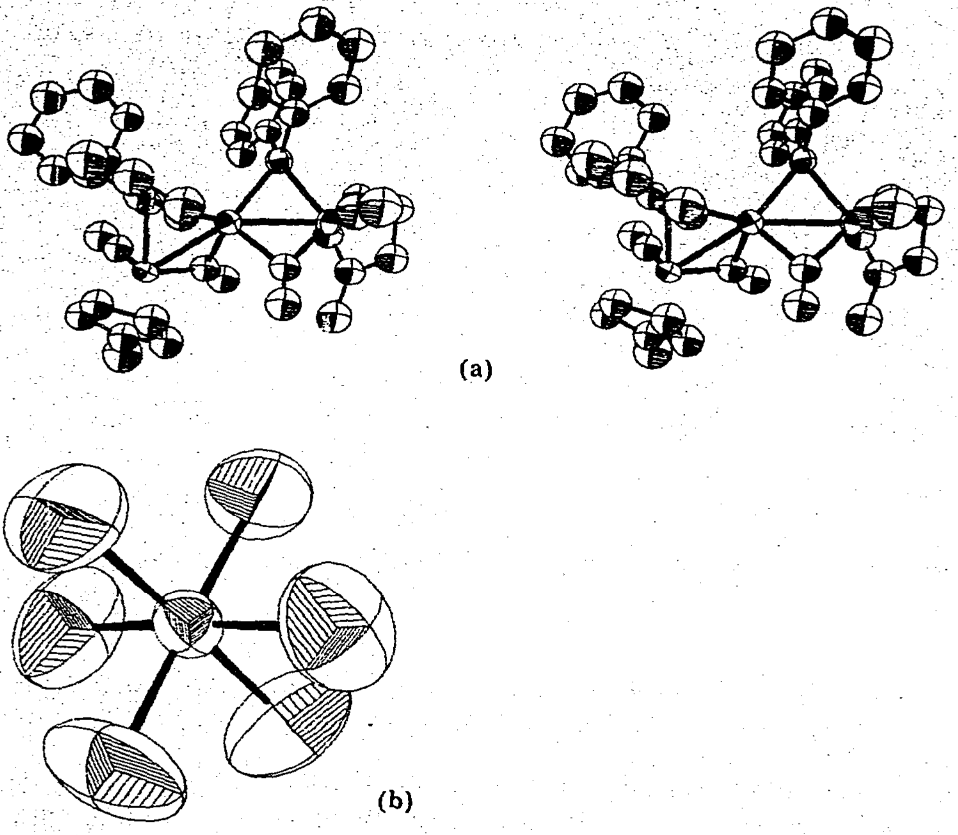


Fig. 2. (a) Stereoscopic view of the [Rh $\{Fe(PPh_2)(CO)_2(\pi\text{-}CH_3C_5H_4)\}_2]^+$ cation; the atomic vibrations are depicted via 50% probability ellipsoids and (b) the envelopes of 25% probability for the hexafluorophosphate anion.

The carbon—oxygen (carbonyl) bond lengths are seen to average 1.16(1) Å and 1.20(1) Å respectively for the terminal and bridging ligands. The carbon—carbon bond lengths within the cyclopentadienyl rings range from 1.41 to 1.51 Å in an apparently significant way but this is much more likely to be a comment on systematic underestimates in the e.s.d.'s of the carbon atoms since the iron—carbon bond length variations do not establish a consistent pattern.

Acknowledgements

We are grateful to the S.R.C. for general support of these studies and to the National Institutes of Health for a fellowship (J.A.Z.).

References

1 J.A. Osborn, F.H. Jardine, J.F. Young and G. Wilkinson, J. Chem. Soc. A, (1966) 1711.
2 D. Evans, J.A. Osborn and G. Wilkinson, J. Chem. Soc. A, (1968) 3133.
3 J.R. Shapley, R.R. Schroch and J.A. Osborn, J. Amer. Chem. Soc., 91 (1969) 2816.
4 J. Knight and M.J. Mays, J. Chem. Soc. A, (1970) 654.
5 R.J. Haines, R. Mason, J.A. Zubieta and C.R. Nolte, J. Chem. Soc., Chem. Commun., (1972) 990.

6 (a) E.R. Corey and L.F. Dahl, J. Amer. Chem. Soc., 83 (1961) 2203;
(b) E.R. Corey and L.F. Dahl, Inorg. Chem., 1 (1962) 521.
7 J.A. Bertrand, F.A. Cotton and W.A. Dollase, Inorg. Chem., 2 (1963) 1166.
8 C.H. Wei and L.F. Dahl, J. Amer. Chem. Soc., 88 (1966) 1821.
9 C.H. Wei and L.F. Dahl, Inorg. Chem., 4 (1965) 493.
10 (a) E.H. Shubert and R.K. Sheline, Z. Naturforsch. B, 20 (1965) 1306;
(b) P.A. Agron, R.D. Ellison and H.A. Levy, Acta Crystallogr., 23 (1967) 1079.
11 P.D. Frisch and L.F. Dahl, J. Amer. Chem. Soc., 94 (1972) 5082.
12 R. Mason and A.I.M. Rae, J. Chem. Soc. A, (1968) 778.
13 M.J. Bennett, F.A. Cotton and P. Legzdins, J. Amer. Chem. Soc., 89 (1967) 6797.
14 (a) M.R. Churchill and M. Veidis, J. Chem. Soc., Chem. Commun., (1970) 1470;
(b) M.R. Churchill and M.V. Veidis, J. Chem. Soc. A, (1971) 2995.
15 (a) M.R. Churchill and M.V. Veidis, J. Chem. Soc., Chem. Commun., (1970) 529;
(b) M.R. Churchill and M.V. Veidis, J. Chem. Soc. A, (1971) 2170.
16 R. Mason and D.M.P. Mingos, J. Organometal. Chem., 50 (1973) 53.
17 International Tables for X-Ray Crystallography, Vol. III, The Kynoch Press, Birmingham, pp. 202, 204, 213 ff.