Synthesis and Crystal and Molecular Structure of $[Fe_2Rh_2(\mu\text{-}PPh_2)_4\text{-}(\mu\text{-}CO)_2(CO)_6]$,† an Unusual Straight-chain Tetranuclear Compound

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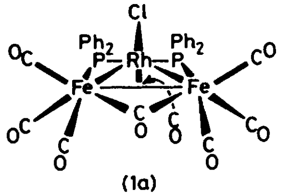
Reaction of $[\{Rh(\eta^3\text{-}C_3H_5)_2Cl\}_2]$ with $[Fe(CO)_4(PPh_2H)]$ in alcohol in the presence of carbon monoxide affords an unusual straight-chain compound, $[Fe_2Rh_2(\mu\text{-}PPh_2)_4(\mu\text{-}CO)_2(CO)_6]$, the structure of which has been determined by *X*-ray methods. The complex crystallizes in space group $P2_1/c$ with $a = 12.468(5)$, $b = 13.354(5)$, $c = 17.293(7)$ Å, $\beta = 95.43(1)°$, and $Z = 2$. The metal-atom skeleton is a centrosymmetric Fe–Rh–Rh–Fe chain with the metal atoms being linked through *closed* Fe–P–Rh and Rh–P–Rh bridge bonds. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectral data for the compound have been interpreted in terms of the presence of two isomeric forms in solution.

The utilisation of co-ordinated or unco-ordinated secondary phosphines and arsines, *e.g.* $[Fe(CO)_4(PPh_2H)]$ and $AsMe_2H$, and of thiols, *e.g.* EtSH, in the synthesis of metal cluster compounds has led to the discovery of a wide range of highly unusual complexes of this type, the stability of which can be associated with the presence of the bridging phosphido-, arsenido-, and thio-ligands. While the majority of these polynuclear compounds adopt closed or semi-closed structures with the bridging ligands linking the metal atoms through *closed* ‡ M–X–M bridge bonds (M = metal, X = bridging unidentate ligand), *e.g.* $[Rh_3(\mu\text{-}PPh_2)_3(CO)_5]$,[1] $[Co_3(\mu\text{-}PMe_2)_3(CO)_6]$,[2] $[Fe_3(\mu\text{-}H)_2(\mu\text{-}PMe_2)_2(CO)_8]$,[3] $[Rh_4(\mu\text{-}PPh_2)_4(CO)_6]$,[4] $[Rh_4(\mu\text{-}PPh_2)_5(CO)_5]^-$,[5] and $[Co_5(\mu\text{-}PMe_2)_3(CO)_{11}]$,[6] a number have open, ring or chain-like structures in which the bridging groups are co-ordinated to the metal atoms through *open* bridge bonds as in $[Fe_2Co(\mu\text{-}AsMe_2)_2(cp)_3(CO)_3]$ [7] (cp = $\eta\text{-}C_5H_5$), $[Rh_3(\mu\text{-}PPh_2)_3(CO)_6(PPh_2H)]$,[8] $[(CO)_5Mn(\mu\text{-}AsMe_2)W(CO)_4(\mu\text{-}AsMe_2)Mn(CO)_5]$,[9] and $[(CO)_4Fe(\mu\text{-}AsMe_2)Co(CO)_3(\mu\text{-}AsMe_2)Cr(cp)(CO)_2(\mu\text{-}AsMe_2)Cr(cp)(CO)_3]$.[10] We have previously reported in a preliminary communication [11] that treatment of $[\{Rh(\eta^3\text{-}C_3H_5)_2Cl\}_2]$ with $[Fe(CO)_4(PPh_2H)]$ in alcohol in the presence of CO affords an unusual straight-chain compound, $[Fe_2Rh_2(\mu\text{-}PPh_2)_4(\mu\text{-}CO)_2(CO)_6]$, in which the metal atoms are linked through *closed* M–P–M bridge bonds. The details of the synthesis and crystal and molecular structure of this compound are reported herein.

Results and Discussion

It has been previously established that reaction of metal allyl compounds with metal complexes containing co-ordinated secondary phosphines leads to the elimination of propene and the formation of polynuclear products containing bridging phosphorus ligands.[2,12,13] On this basis it was assumed that treatment of $[\{Rh(\eta^3\text{-}C_3H_5)_2Cl\}_2]$ with a four-fold molar amount of $[Fe(CO)_4(PPh_2H)]$ would lead to the formation of the trinuclear complex $[Fe_2Rh(\mu\text{-}PPh_2)_2Cl(CO)_8]$ (1) of possible structure (1a), (1b), or (1c) according to the reaction sequence: $[\{Rh(\eta^3\text{-}C_3H_5)_2Cl\}_2] + 4[Fe(CO)_4(PPh_2H)] \longrightarrow 2[Fe_2Rh(\mu\text{-}PPh_2)_2Cl(CO)_8] + 4C_3H_6$. The addition of $[Fe(CO)_4(PPh_2H)]$ in ethanol to a CO-saturated ethanolic solution of $[\{Rh(\eta^3\text{-}C_3H_5)_2Cl\}_2]$ at room temperature in the above molar ratio was indeed found to result in a slow darkening of the reaction mixture over a 24 h period from yellow to red, while addition of a large excess of hexane to this solution led



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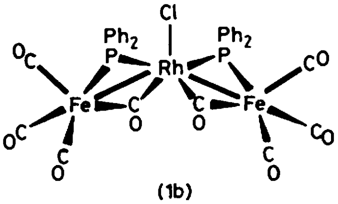

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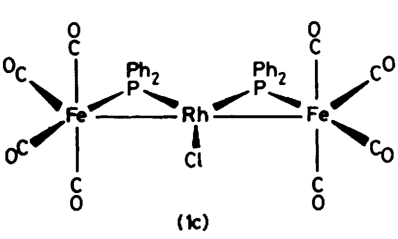

(1c)

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† 1,2;3,4-Di-μ-carbonyl-1,1,1,4,4,4-hexacarbonyl-1,2;2,3;2,3;3,4-tetra-μ-diphenylphosphido-dirhodiumdi-iron(*Fe–Rh–Rh–Fe*).

Supplementary data available (No. SUP 23613, 24 pp.): structure factors, thermal parameters, H-atom co-ordinates. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

‡ A *closed* M–P–M bridge bond is defined as the bond between two metal atoms, M, which are linked through a bridging phosphorus atom and in which the metal–metal distance corresponds to a formal metal–metal bond. The bonding interaction between the metals may be direct, or through the bridging atom or both. An *open* M–P–M bridge bond is one in which the metal–metal distance is appreciably larger than those normally associated with metal–metal bonds.

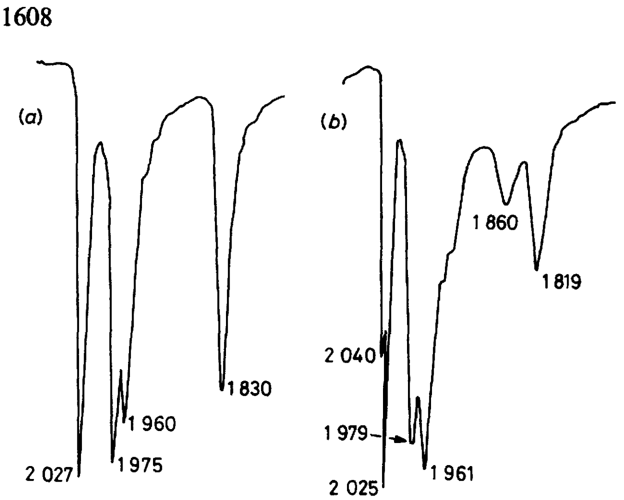

Figure 1. Solid-state (Nujol mull) i.r. spectra of $[Fe_2Rh_2(\mu\text{-}PPh_2)_4(\mu\text{-}CO)_2(CO)_6]$ in the C–O stretching region: (*a*) crystal form (I); (*b*) crystal form (II)

to the precipitation of a red solid, the solid-state i.r. spectrum of which contained three terminal and one bridging carbonyl stretching peaks [ν(C–O) at 2 032s, 1 972s, 1 966s, and 1 816s cm^{-1} measured as a Nujol mull]. Crystallisation of this complex from dichloromethane–hexane afforded red crystals, [2; crystal form (I)], with a slightly modified band pattern in the C–O stretching region of its solid-state i.r. spectrum from that of the crude product [ν(C–O) at 2 027s, 1 975s, 1 960s, and 1 830s cm^{-1}, measured as a Nujol mull, Figure 1(*a*)]. These differences can be ascribed to solid-state effects as at no stage could a recrystallised product with an identical solid-state C–O stretching peak pattern to that of the crude product be isolated. The elemental analyses for the crystallised compound were consistent with the formulation $FeRh(PPh_2)_2(CO)_4$, with the rhodium–iron ratio being 1 : 1 and not 1 : 2 as expected, while a molecular mass measurement of 1 356 (vapour pressure osmometry) was indicative of the species being dimeric, *viz.* $[Fe_2Rh_2(PPh_2)_4(CO)_8]$.

In a few instances crystallisation of the crude product yielded crystals of a different morphology from those described above. This compound was also characterised as $[Fe_2Rh_2(PPh_2)_4(CO)_8]$ but whereas the band pattern of the terminal carbonyl stretching peaks in its solid-state i.r. spectrum is very similar to that of the more common crystalline form, the bridging carbonyl stretching region of its spectrum [2; crystal form (II)] contains two peaks and not one as found for the latter [ν(C–O) at 2 040 (sh), 2 025s, 1 979s, 1 961s, 1 860mw, and 1 819m cm^{-1}, measured as a Nujol mull, Figure 1(*b*)]. On the other hand, the solution i.r. spectra of the two crystalline forms in the C–O stretching region are identical [ν(C–O) at 2 033 (sh), 2 027s, 1 985s, 1 970s, and 1 843m br cm^{-1}, measured in CCl_4]. With the aim of ascertaining whether these two crystalline forms are of different or of the same isomer and, more important, of establishing the structure of either or both of these isomers, crystallographic studies were attempted on both crystalline forms.

X-Ray Structural Studies.—Crystals of suitable quality for *X*-ray diffraction studies could only be obtained for the crystalline form with a single bridging carbonyl stretching band in its i.r. spectrum *viz.* [2; crystal form (I)]; all attempts to obtain suitable crystals of the second, less common crystalline form, proved unsuccessful. The molecular structure of $[Fe_2Rh_2(PPh_2)_4(CO)_8]$ [2; crystal form (I)] is illustrated in Figure 2. The molecule has a centrosymmetric straight-chain configuration with two iron atoms in terminal positions and *trans*-disposed with respect to the central Rh–Rh vector [Fe–Rh–Rh′ = 154.3(1)°]. The rhodium atoms are bridged, slightly asymmetrically, by two diphenylphosphido-groups [Rh–P(1) = 2.263(3), Rh′–P(1) = 2.301(3) Å] while the rhodium and iron atoms are bridged by both diphenylphosphido and carbonyl ligands; the bridging is markedly asymmetric in the case of the latter as evidenced by the Rh–C(4)–O(4) and Fe–C(4)–O(4) bond angles of 124.1(1.1) and 155.1(1.2)° respectively. The Fe–Rh and Rh–Rh distances correspond with those normally associated with formal Fe–Rh and Rh–Rh bonds indicating that the Fe–P–Rh and Rh–P–Rh bridge bonds are of the *closed* and not of the *open* type. The RhPFeC rings are puckered [the dihedral angle between the RhP(2)Fe and RhC(4)Fe planes is 110(1)°] while the Rh_2P_2 ring is planar (crystallographically imposed). The three terminal carbonyl ligands are bonded in the usual way to each of the Fe atoms, completing the octahedral coordination around these atoms.

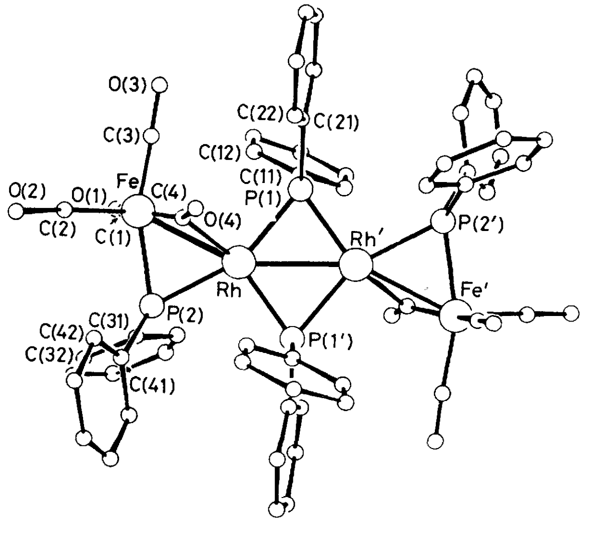

Figure 2. The molecular stereochemistry of $[Fe_2Rh_2(\mu\text{-}PPh_2)_4(\mu\text{-}CO)_2(CO)_6]$ (2)

Tetranuclear derivatives of transition metals can adopt a number of different configurations,[14] all of which can be considered as being based on the tetrahedron by cleavage of one or more metal–metal bonds as illustrated in the Scheme.* The majority of known tetranuclear species adopt the tetrahedral structure (A), examples being provided by $[Rh_4(CO)_{12}]$,[16] $[Fe_4(CO)_{13}]^{2-}$,[17] and $[Re_4H_6(CO)_{12}]^{2-}$ [18] but an increasing number of compounds with the 'butterfly' structure (B) are currently being reported, *e.g.* $[Fe_4H(CO)_{13}]^-$,[19] $[Rh_4(\mu\text{-}PPh_2)_5(CO)_5]^-$,[5] and $[FeRh_3(\mu\text{-}PPh_2)_3(\mu\text{-}CO)_2(CO)_6]$.[20] Examples of tetranuclear compounds with configurations (C) and (D) are far more limited but are known, with $[Co_4(\mu\text{-}PPh)_2(\mu\text{-}CO)_2(CO)_8]$ [21] and $[Ir_4(CO)_8(MeCO_2CCCO_2Me)_4]$ [22] having planar metal atom skeletons as in (C) and with $[Re_4H_4(CO)_{15}]^{2-}$ [23] and $[Os_3ReH(CO)_{15}(MeCN)]$ [24] adopting structure (D). Representative examples of structure (E) and (F) are more limited still and in fact at the time of the crystal-structure determination of $[Fe_2Rh_2(\mu\text{-}PPh_2)_4(\mu\text{-}CO)_2(CO)_6]$ no example of a purely transition-metal tetranuclear cluster

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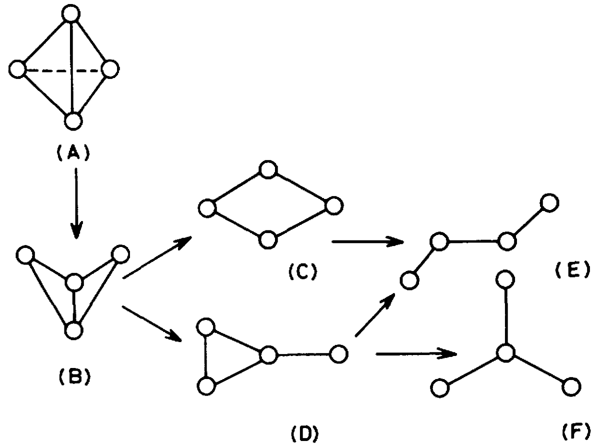
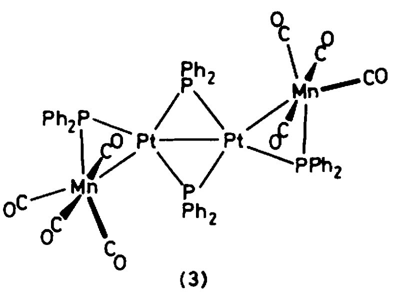
* Only those compounds in which each transition metal is *formally* bonded to at least one other by metal–metal bonds are being considered; this classification includes complexes in which the metal atoms are linked through *closed* three-centre bridge bonds as in $[\{Fe(\mu\text{-}PPh_2)(cp)(CO)\}_2]^{2+}$ [15] and $[Co_3(\mu\text{-}PMe_2)_3(CO)_6]$.[2]



Scheme.

of either configuration (E) or (F) had been reported.* However, since then Braunstein *et al.*[27] have established that $[Mn_2Pt_2(\mu\text{-}PPh_2)_4(CO)_8]$ (3) has a centrosymmetric straight-chain structure very similar to that described above for $[Fe_2Rh_2(\mu\text{-}PPh_2)_4(\mu\text{-}CO)_2(CO)_6]$ while Mann and co-workers[28] have shown that $[Rh_2\{CNC(CH_3)_2C_2H_4(CH_3)_2NC\}_4Mn_2(CO)_{10}][PF_6]_2$ adopts a structure in which the two rhodium and two manganese atoms are essentially collinear. The



(3)

complex $[Fe_2Rh_2(\mu\text{-}PPh_2)_4(\mu\text{-}CO)_2(CO)_6]$ thus provides, together with the two tetranuclear compounds just described, the first example of an all-transition metal tetranuclear compound with structure (E).

In the crystal structure of the complex, centrosymmetric molecules of $[Fe_2Rh_2(\mu\text{-}PPh_2)_4(\mu\text{-}CO)_2(CO)_6]$ lie with the mid-point of the Rh–Rh vector located at $(0,0,\frac{1}{2})$ and symmetry-related positions. No intermolecular close contacts were observed. The crystal packing is depicted in Figure 3.

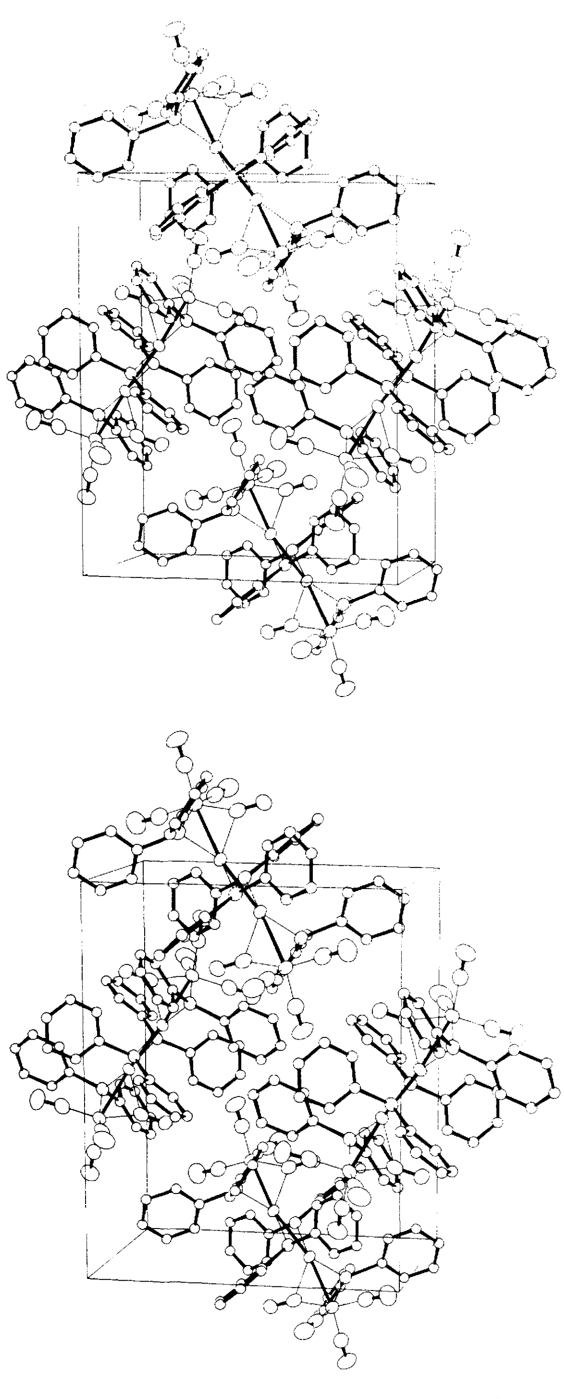


Figure 3. The crystal packing for $[Fe_2Rh_2(\mu\text{-}PPh_2)_4(\mu\text{-}CO)_2(CO)_6]$

Solution Structural Studies.—As described above, the two crystal forms of $[Fe_2Rh_2(\mu\text{-}PPh_2)_4(\mu\text{-}CO)_2(CO)_6]$ afford identical solution i.r. spectra with the bridging carbonyl stretching peak therein being broad and unresolved, even when CCl_4 is utilised as solvent. More important, this peak was found to be distinctly asymmetric which is indicative of the presence of more than one isomer of $[Fe_2Rh_2(\mu\text{-}PPh_2)_4(\mu\text{-}CO)_2(CO)_6]$ in solution. This was confirmed by means of n.m.r. spectroscopic studies. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum contains five resonances, two of which overlap each other at −29.9 p.p.m., relative to $P(OMe)_3$, while the other three are centred at 103.5, 119.4, and 143.2 p.p.m. respectively; two resonances only are expected for the centrosymmetric isomer of $[Fe_2Rh_2(\mu\text{-}PPh_2)_4(\mu\text{-}CO)_2(CO)_6]$. On the basis of this spectral evidence it is proposed that this compound occurs in solution as an isomer in which the two iron atoms are *cis*-disposed with respect to the two rhodium atoms as illustrated in structure (4), as well as the centrosymmetric isomer with *trans*-disposed iron atoms. The two resonances found at *ca.* −29.9 p.p.m. are best described in terms of two overlapping doublets of doublets, arising from $^{103}Rh\text{-}^{31}P$ and $^{31}P\text{-}^{31}P$ coupling, and can be assigned to the phosphorus atoms which bridge the rhodium–iron bonds in the two isomers. The remaining three resonances are shifted

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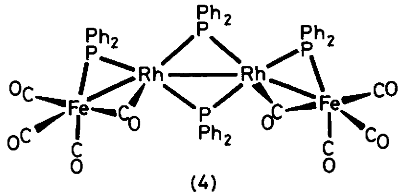
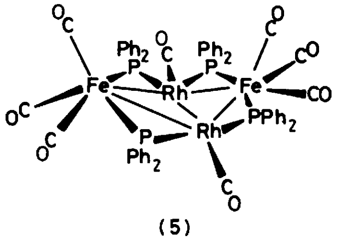
* Tetranuclear species of type (E) and (F) containing both transition and main-group elements are known, *e.g.* $[\{Ru(SiMe_3)(CO)_4\}_2]$[25] and $[SnCl\{Fe(cp)(CO)_2\}_2\{Mo(cp)(CO)_3\}]$.[26]



(4)

fairly far downfield and, consistent with other ^{31}P n.m.r. data for phosphido-ligands that bridge metal–metal bonds,[29,30] can be assigned to the phosphorus atoms bridging the two rhodium atoms. The resonance at 103.5 p.p.m., a triplet resulting from $^{103}Rh–^{31}P$ coupling only, and the more complex resonance at 119.4 p.p.m., arising from $^{31}P–^{31}P$ as well as $^{103}Rh–^{31}P$ coupling, are assigned to the non-equivalent phosphorus atoms of the *cis* isomer while the considerably coupled resonance at 143 p.p.m. is assigned to the two equivalent phosphorus atoms of the centrosymmetric isomer. Significantly, the ^{31}P n.m.r. spectrum of $[Mn_2Pt_2(\mu\text{-}PPh_2)_4(CO)_8]$ (3) has been found to exhibit only two resonances which is consistent with this compound occurring in one isomeric form in solution and with the solid-state structure being retained; the resonance at 133 p.p.m. [relative to $P(OMe)_3$] was assigned to the phosphorus atoms bridging the two platinum atoms while that at 22 p.p.m. was assigned to the phosphorus atoms bridging the platinum and manganese atoms.[27]

The formation of a product in the reaction of $[\{Rh(\eta^3\text{-}C_3H_5)_2Cl\}_2]$ with $[Fe(CO)_4(PPh_2H)]$ in which the iron–phosphorus ratio is 1 : 2 can no doubt be associated with Rh–P bonds being stronger than corresponding Fe–P bonds in systems of the type under investigation. The same explanation would account for this product adopting the structure established and not the more *closed* butterfly configuration (5), illustrated below, and also for it being inert to decarbonylation and subsequent rearrangement to a more *closed* structure in spite of the fact that its carbonyl groups can be readily substituted by phosphorus donor ligands.[31]



(5)

Experimental

Instrumentation.—Infrared spectra were recorded on Perkin-Elmer 457 and 283 grating spectrophotometers while the ^1H and ^{31}P n.m.r. spectra were measured on Varian FT80A and JEOL PFT 100 instruments.

Synthesis of $[Fe_2Rh_2(\mu\text{-}PPh_2)_4(\mu\text{-}CO)_2(CO)_6]$.—All reactions and manipulations were carried out under an atmosphere of N_2 using Schlenk-tube techniques. Solvents were dried by standard procedures. The complexes $[\{Rh(\eta^3\text{-}C_3H_5)_2Cl\}_2]$ and $[Fe(CO)_4(PPh_2H)]$ were prepared according to literature methods.[32,33] Molecular mass values and elemental analyses were obtained by Mr. M. Martin-Short, Microanalytical Laboratory, University of Natal, Pietermaritzburg, by Elemental Microanalysis Ltd., Beaworthy, Devon, United Kingdom, and by the H. Malissa and G. Reuter Analytical Laboratories, Engelskirchen, West Germany.

Table 1. Fractional atomic co-ordinates (× 10^5 for Rh and Fe, × 10^4 for all other atoms) with e.s.d.s in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Rh	813(8)	6 041(7)	43 741(6)
Fe	−6 588(15)	15 044(15)	30 844(11)
P(1)	1 471(3)	−107(3)	5 114(2)
P(2)	984(3)	1 727(3)	3 701(3)
C(4)	−304(11)	132(12)	3 193(8)
O(4)	−241(8)	−698(8)	2 980(6)
C(1)	−1 037(12)	2 711(12)	3 410(9)
O(1)	−1 308(10)	3 500(9)	3 591(7)
C(2)	−366(12)	1 770(11)	2 115(10)
O(2)	−166(10)	1 956(9)	1 504(7)
C(3)	−2 021(11)	1 127(11)	2 896(8)
O(3)	−2 907(9)	881(9)	2 750(6)
C(11)	2 164(10)	−1 142(10)	4 669(7)
C(12)	2 194(11)	−1 213(11)	3 898(8)
C(13)	2 732(12)	−1 981(11)	3 541(9)
C(14)	3 205(12)	−2 696(12)	4 008(9)
C(15)	3 180(14)	−2 683(14)	4 819(11)
C(16)	2 625(13)	−1 855(12)	5 135(10)
C(21)	2 531(10)	613(10)	5 626(7)
C(22)	2 260(12)	1 359(11)	6 116(8)
C(23)	3 010(13)	1 960(12)	6 522(9)
C(24)	4 075(15)	1 768(14)	6 434(10)
C(25)	4 392(14)	1 026(13)	5 932(10)
C(26)	3 614(11)	463(11)	5 539(8)
C(31)	1 298(10)	2 953(10)	4 108(7)
C(32)	1 720(12)	3 670(12)	3 660(9)
C(33)	1 832(14)	4 677(14)	3 953(10)
C(34)	1 534(14)	4 888(14)	4 693(10)
C(35)	1 067(13)	4 150(13)	5 128(10)
C(36)	960(12)	3 201(12)	4 836(9)
C(41)	2 210(11)	1 371(11)	3 251(8)
C(42)	2 159(12)	793(11)	2 560(9)
C(43)	3 106(13)	472(13)	2 265(10)
C(44)	4 038(15)	658(14)	2 639(10)
C(45)	4 145(15)	1 228(13)	3 340(10)
C(46)	3 200(12)	1 572(11)	3 629(9)

Procedure. An ethanolic solution (*ca.* 40 cm^3) of $[Fe(CO)_4(PPh_2H)]$ (1.60 g, 4.5 mmol) was added dropwise to a stirred suspension of $[\{Rh(\eta^3\text{-}C_3H_5)_2Cl\}_2]$ (0.4 g, 1.1 mmol) in CO-saturated ethanol (*ca.* 20 cm^3) at room temperature and the reaction mixture stirred for a further 24 h. Hexane (*ca.* 100 cm^3) was then added and the red precipitate which separated from solution was isolated by decantation of the mother-liquor and washed with hexane. Red crystals of $[Fe_2Rh_2(\mu\text{-}PPh_2)_4(\mu\text{-}CO)_2(CO)_6]$ were obtained by crystallisation of the precipitate from dichloromethane–hexane using vapour diffusion techniques [Found: C, 52.3; H, 3.1; Fe, 8.6; Rh, 16.7%; *M*, 1 356 (vapour pressure osmometry in benzene). Calc. for $C_{56}H_{40}Fe_2O_8P_4Rh_2$: C, 52.4; H, 3.1; Fe, 8.7; Rh, 16.1%; *M*, 1 282].

X-Ray Crystallography.—*Crystal data*. $C_{56}H_{40}Fe_2O_8P_4Rh_2$, $M = 1\,282.34$, Monoclinic, space group $P2_1/c$, $a = 12.468(5)$, $b = 13.354(5)$, $c = 17.293(7)$ Å, $\beta = 95.43(1)°$, $U = 2\,866.3$ Å^3, $D_m = 1.50(5)$, $Z = 2$, $D_c = 1.49$ g cm^{-3}, $F(000) = 1\,284$, $\lambda(Mo\text{-}K_\alpha) = 0.7107$ Å, $\mu(Mo\text{-}K_\alpha) = 11.3$ cm^{-1}.

Preliminary photography established the space group and gave the unit-cell parameters which were refined using 25 high-angle reflections measured on a Philips PW1100 four-circle diffractometer using graphite-monochromated Mo-K_α radiation. The crystal used (dimensions 0.4 × 0.32 × 0.2 mm) showed no instability; however it diffracted rather weakly and the relatively high final *R* values reflect the indifferent crystal quality. Diffraction data were collected in the range

Table 2. Selected bond lengths (Å) and angles (°) with e.s.d.s in parentheses

				C–C (phenyl rings)	Average
Rh–Rh′	2.723(2)	Fe–C(4)	1.890(16)	Ring 1: 1.341(18)—1.439(23)	1.380(20)
Rh–Fe	2.623(2)	Rh–C(4)	2.148(15)	Ring 2: 1.358(20)—1.398(22)	1.377(20)
Rh–P(1)	2.263(3)	C(1)–O(1)	1.159(17)	Ring 3: 1.367(18)—1.439(20)	1.395(20)
Rh′–P(1)	2.301(3)	C(2)–O(2)	1.137(16)	Ring 4: 1.299(21)—1.426(23)	1.385(20)
Rh–P(2)	2.262(4)	C(3)–O(3)	1.157(17)		
Fe–P(2)	2.237(4)	C(4)–O(4)	1.173(16)		
Fe–C(1)	1.785(17)	P(1)–C(11)	1.836(13)		
Fe–C(2)	1.784(17)	P(1)–C(21)	1.799(13)		
Fe–C(3)	1.773(15)	P(2)–C(31)	1.811(13)		
		P(2)–C(41)	1.843(14)		

Rh′–Rh–Fe	154.3(1)	Rh–Fe–C(1)	103.1(5)	Rh–C(4)–O(4)	124.1(1.1)
Rh′–Rh–P(2)	151.7(1)	Rh–Fe–C(2)	143.4(4)	Fe–C(4)–O(4)	155.1(1.2)
Rh′–Rh–C(4)	123.7(4)	Rh–Fe–C(3)	106.3(4)	Fe–C(1)–O(1)	177.0(1.4)
Rh′–Rh–P(1)	54.0(1)	Rh–Fe–P(2)	54.8(1)	Fe–C(2)–O(2)	178.5(1.5)
Rh′–Rh–P(1′)	52.7(1)	Rh–Fe–C(4)	53.9(4)	Fe–C(3)–O(3)	178.0(1.5)
P(1)–Rh–P(1′)	106.8(1)	P(2)–Fe–C(1)	89.3(5)	Rh–P(1)–C(11)	116.4(4)
P(1)–Rh–Fe	149.5(1)	P(2)–Fe–C(2)	99.3(5)	Rh–P(1)–C(21)	122.8(4)
P(1)–Rh–P(2)	100.2(1)	P(2)–Fe–C(3)	160.7(5)	Rh′–P(1)–C(11)	113.0(4)
P(1)–Rh–C(4)	120.3(4)	P(2)–Fe–C(4)	83.5(4)	Rh′–P(1)–C(21)	124.7(3)
P(1′)–Rh–Fe	102.6(1)	C(4)–Fe–C(1)	155.5(7)	Rh–P(2)–C(31)	119.9(4)
P(1′)–Rh–P(2)	150.1(1)	C(4)–Fe–C(2)	102.7(7)	Rh–P(2)–C(41)	121.3(5)
P(1′)–Rh–C(4)	99.3(4)	C(4)–Fe–C(3)	87.4(6)	Fe–P(2)–C(31)	117.4(4)
Fe–Rh–P(2)	53.9(1)	C(1)–Fe–C(2)	101.6(7)	Fe–P(2)–C(41)	121.6(5)
Fe–Rh–C(4)	45.3(4)	C(1)–Fe–C(3)	92.1(7)	C(11)–P(1)–C(21)	104.9(6)
P(2)–Rh–C(4)	77.4(4)	C(2)–Fe–C(3)	99.3(7)	C(31)–P(2)–C(41)	103.9(6)
Rh–P(1)–Rh′	73.2(1)	Rh–C(4)–Fe	80.8(4)		
Rh–Rh′–P(1)	52.7(1)	Rh–P(2)–Fe	71.3(1)		

				C–C–C (phenyl rings)	Average
P(1)–C(11)–C(12)	121.9(1.1)	P(2)–C(31)–C(32)	119.5(1.1)	Ring 1: 117.1(1.5)—123.4(1.4)	120.0(1.5)
P(1)–C(11)–C(16)	118.4(1.1)	P(2)–C(31)–C(36)	119.3(1.0)	Ring 2: 116.8(1.6)—123.0(1.4)	120.0(1.5)
P(1)–C(21)–C(22)	118.8(1.0)	P(2)–C(41)–C(42)	121.5(1.1)	Ring 3: 118.9(1.5)—121.5(1.5)	120.0(1.5)
P(1)–C(21)–C(26)	123.1(1.0)	P(2)–C(41)–C(46)	119.7(1.1)	Ring 4: 117.6(1.5)—122.2(1.8)	120.0(1.5)

$6 < 2\theta < 46°$ [out of 3 894 reflections collected, 3 750 independent reflections had $I > \sigma(I)$] and were corrected for Lorentz and polarization effects but not for absorption.

Structure solution and refinement. All calculations were carried out on a Burroughs B6800 computer at the University of South Africa. The structure was solved by conventional heavy-atom techniques using SHELX.[34] Table 1 gives the fractional atomic co-ordinates of the non-hydrogen atoms while relevant bond lengths and angles are summarised in Table 2. In three final least-squares cycles, in which a weighting scheme $w = k/\sigma^2$ was employed, all atoms except the phenyl carbons were refined with anisotropic thermal parameters. Hydrogen atoms were positioned geometrically and given a common thermal parameter, U_H. Refinement converged with $R = 0.084$ and $R' = 0.080$ and was considered complete when no shift to error ratio exceeded 1.0; k refined to 0.625 and U_H to 0.09(1) Å^2. In a final difference electron-density map there was no peak higher than 0.8 e Å^{-3}. Scattering factors (except H) were from ref. 35(*a*) and that for H from ref. 35(*b*).

Acknowledgements

We thank the South African Council for Scientific and Industrial Research and the Universities of Natal and South Africa for financial support, the South African Council for Mineral Technology for a studentship (to N. D. C. T. S.), Mr. John Albain, National Physics Research Laboratory of the Council for Scientific and Industrial Research, Pretoria for the intensity data collection and Johnson Matthey for the loan of rhodium salts.

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Received 7th September 1982; *Paper* 2/1541