

The Synthesis and X-Ray Structure of the Heterometallic Tetranuclear Butterfly Cluster Complex, $[\text{Fe}_2\text{Rh}_2(\text{CO})_8\{\mu\text{-Ph}_2\text{PC}(\text{=CH}_2)\text{PPh}_2\}_2]$

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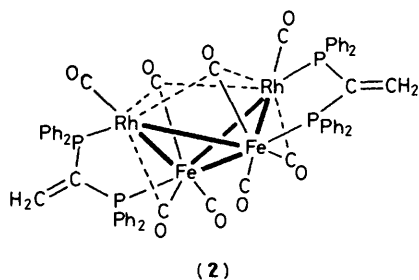
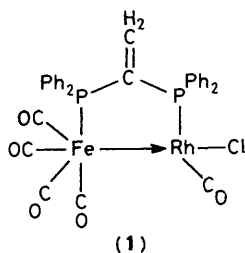
Treatment of the heterometallic complex $[(\text{OC})_4\text{Fe}\{\mu\text{-Ph}_2\text{PC}(\text{=CH}_2)\text{PPh}_2\}\text{RhCl}(\text{CO})]$ with Me_3NO affords the tetranuclear cluster $[\text{Fe}_2\text{Rh}_2(\text{CO})_8\{\mu\text{-Ph}_2\text{PC}(\text{=CH}_2)\text{PPh}_2\}_2]$ which has been characterised by X-ray crystallography as having a butterfly structure with wing-tip Rh atoms.

The synthesis of heterometallic complexes and the study of their chemical properties are of great interest in relation to the possible design of new bifunctional catalysts. The use of multidentate phosphine ligands to achieve heterobimetallic synthesis is a popular and convenient route which can lead to stable heterometallic bonds owing to the presence of the bridging phosphine ligand.¹ For example, a number of complexes containing the $\text{M}(\mu\text{-dppm})_2\text{M}'$ moiety [dppm = bis(diphenylphosphino)methane] have been reported in recent years.² It has recently been shown that the heterobimetallic complex $[(\text{OC})_4\text{Fe}(\mu\text{-dppee})\text{RhCl}(\text{CO})]$ (**1**) [dppee = 1,1-bis(diphenylphosphino)ethene, $\text{Ph}_2\text{PC}(\text{=CH}_2)\text{PPh}_2$] may be prepared by treating $[\text{Fe}(\text{CO})_3(\text{dppee-}P,P')]$ or $[\text{Fe}(\text{CO})_4(\text{dppee-P})]$ with $[\text{RhCl}(\text{CO})_2]_2$.^{3,4} This communication describes the conversion of complex (**1**) into the heterometallic tetranuclear complex $[\text{Fe}_2\text{Rh}_2(\text{CO})_8(\mu\text{-dppee})_2]$ (**2**).

Treatment of a toluene solution of complex (**1**) with one equivalent of a methanol solution of $\text{Me}_3\text{NO}\cdot 2\text{H}_2\text{O}$ at room

temperature slowly affords a dark green solution from which may be isolated in good (50%) yield dark-green diamond-shaped crystals of complex (**2**) on recrystallisation from cold tetrahydrofuran. The spectroscopic data of complex (**2**) [$\nu(\text{CO})$ (in CH_2Cl_2) 1960s, 1936m, 1918w, 1860w cm^{-1} ; n.m.r. $^{31}\text{P}\{^1\text{H}\}$ (C_6D_6): δ 73.5 (d, J_{PP} 98 Hz) and 34.5 (dd, J_{PP} 98, J_{PRh} 179 Hz) p.p.m.] did not allow a full structural characterisation to be made, so an X-ray crystallographic study was carried out.[†] The structure of complex (**2**) is shown in Figure 1.

The molecule consists of a butterfly arrangement of metal atoms with rhodium at the wing-tip sites and iron at the 'hinge' sites. Two Fe–Rh bonds are bridged both by the dppee ligands and by semi-bridging carbonyl ligands [Fe(1)–C(5) 182(1), Rh(1)–C(5) 247(1) pm, Fe(1)–C(5)–O(5) 169.5(8)°; Fe(2)–C(8) 179(1), Rh(2)–C(8) 251(1) pm, Fe(2)–C(8)–O(8) 169.2(8)°]. These bond lengths and angles indicate only a very weak, but significant, interaction between the rhodium atoms and the carbonyl ligands. Two carbonyl ligands [C(6)O(6) and C(7)O(7)] are involved in semi-face bridging but again the interactions with the rhodium atoms are very weak [Fe(1)–C(6) 181(1), Rh(1)–C(6) 261(1), Rh(2)–C(6) 243(1) pm, Fe(1)–C(6)–O(6) 167.8(7)°; Fe(2)–C(7) 180(1), Rh(1)–C(7) 253(1), Rh(2)–C(7) 265(1) pm, Fe(2)–C(7)–O(7) 170.7(7)°]. The four remaining carbonyl ligands are essentially linear [mean M–C–O 176(1)°]. The Fe–Rh bond lengths show significant differences, with the phosphine-bridged Fe–Rh distances being shorter than the unbridged Fe–Rh distances. The Fe–Fe bond [270.7(1) pm] is longer than the Fe–Rh bond lengths, and indicates a weak Fe–Fe bond {cf. Fe–Fe 253.9(7) pm in the 60-electron tetrahedral cluster $[\text{Fe}_2\text{Rh}_2(\text{cp})_2(\text{CO})_8]$



[†] Crystal data. $[\text{Fe}_2\text{Rh}_2(\text{CO})_8\{\text{Ph}_2\text{PC}(\text{=CH}_2)\text{PPh}_2\}_2]$ (**2**), $\text{C}_{60}\text{H}_{44}\text{O}_8\text{Fe}_2\text{P}_4\text{Rh}_2$, $M = 1334$, monoclinic, space group $P2_1/n$, $a = 1995.7(2)$, $b = 1399.3(4)$, $c = 2079.3(2)$ pm, $\beta = 96.83(1)^\circ$, $U = 5.765(1)$ nm³, $Z = 4$, Mo- K_α radiation, $\lambda = 71.069$ pm, $\mu(\text{Mo-}K_\alpha) = 11.86$ cm⁻¹, $F(000) = 2680$, $3 < 2\theta < 48^\circ$. The structure was solved by Patterson and heavy atom methods (SHELX⁵) using 6648 reflections with $F > 6\sigma(F)$. Least squares refinement with anisotropic thermal parameters for Fe, Rh, P, and carbonyl atoms, constrained phenyl groups, and hydrogens in calculated positions converged to $R = 6.0\%$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

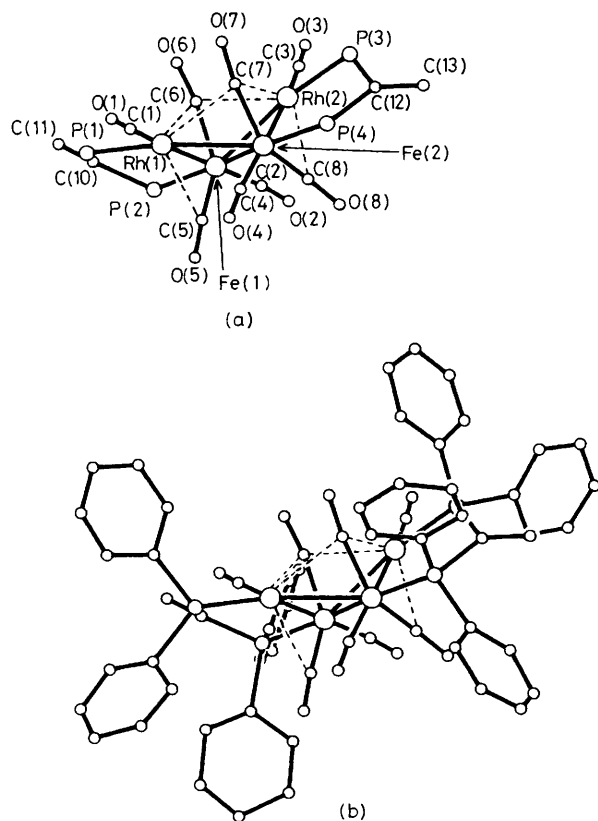


Figure 1. The structure of $[\text{Fe}_2\text{Rh}_2(\text{CO})_8(\mu\text{-Ph}_2\text{PC(=CH}_2\text{)PPh}_2)_2]$; (a) with phenyl rings omitted, and (b) with H atoms omitted. Important bond lengths (pm) and angles ($^\circ$) are: Rh(1)–Fe(1) 254.5(1), Rh(1)–Fe(2) 267.6(1), Rh(1)···Rh(2) 375.7(1), Rh(1)–P(1) 223.1(2), Rh(1)–C(1) 185.0(9), Rh(1)–C(5) 247.1(9), Rh(1)–C(6) 251.2(9), Rh(1)–C(7) 252.8(8), Fe(1)–Rh(2) 263.9(1), Fe(1)–Fe(2) 270.7(1), Fe(1)–P(2) 219.3(2), Fe(1)–C(2) 176.5(9), Fe(1)–C(5) 182.2(9), Fe(1)–C(6) 180.7(8), Rh(2)–Fe(2) 256.0(1), Rh(2)–P(3) 222.9(2), Rh(2)–C(3) 184.3(10), Rh(2)–C(6) 242.7(9), Rh(2)–C(7) 258.1(8), Rh(2)–C(8) 250.8(9), Fe(2)–P(4) 218.9(2), Fe(2)–C(4) 179.5(9), Fe(2)–C(7) 179.6(8), Fe(2)–C(8) 178.7(9); Rh(1)–Fe(1)–Rh(2) 99.8(1), Rh(1)–Fe(2)–Rh(2) 98.5(1), Fe(1)–C(5)–O(5) 169.5(8), Fe(1)–C(6)–O(6) 167.8(7), Fe(2)–C(7)–O(7) 170.7(7), Fe(2)–C(8)–O(8) 169.2(8), P(1)–C(10)–P(2) 114.4(4), P(3)–C(12)–P(4) 114.2(4).

(cp = $\eta^5\text{-C}_5\text{H}_5$),⁶ and Fe–Fe 262.7(5) pm for the ‘hinge’ bond in the 62 electron butterfly cluster⁷ $[\text{Fe}_4(\text{CO})_{13}\text{H}]^-$.

Complex (2) is a 58-valence-electron species for which simple electron accounting suggests that, as in the heterobinuclear precursor complex (1), the Fe atoms attain an 18-electron configuration and each provide two electrons for a donor–acceptor bond to an Rh atom thus enabling each Rh atom to achieve a 16-electron configuration (ignoring the effects of the semi-bridging carbonyl ligands). In this way, complex (2) may be envisaged as being formed by the addition of one $[\text{FeRh}(\text{CO})_4(\text{dppee})]$ moiety to another by the formation of one Fe–Fe and two Fe–Rh bonds.

We have not been able to determine the fate of the chlorine in this reaction. However, the formation of (2) is accompanied by an Fe–Rh bond cleavage reaction since a $\text{Rh}(\mu\text{-dppee})_2\text{Rh}$ containing species is detected (³¹P n.m.r.) in the crude product solution. It may also be significant that a small amount of (2) is formed on treatment of (1) with KPF_6 , indicating that ionisation of the chlorine ligand may be a first step in the formation of (2). The analogous product, $[\text{Fe}_2\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_8]$, is formed on treatment of $[(\text{OC})_4\text{Fe}(\mu\text{-dppm})\text{Rh}(\text{CO})\text{Cl}]$ with Me_3NO .

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