Synthesis and *X*-Ray Crystal and Molecular Structure of $[\{RhFe(\mu\text{-}PPh_2)_2(\mu\text{-}CO)(CO)_3\}_2]$, an Unusual Tetranuclear Compound with a Straight-chain Structure

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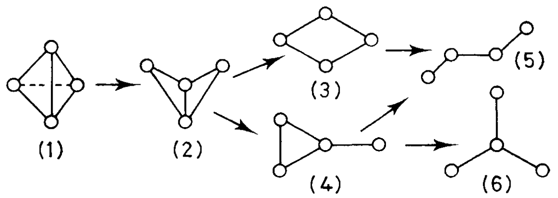
Summary Treatment of $[\{Rh(\eta\text{-}C_3H_5)_2Cl\}_2]$ with $[Fe(CO)_4(PPh_2H)]$ in benzene in the presence of CO affords the mixed metal tetranuclear derivative $[\{RhFe(\mu\text{-}PPh_2)_2(\mu\text{-}CO)(CO)_3\}_2]$, the structure of which has been determined *X*-ray crystallographically.



Scheme

Tetranuclear derivatives of transition metals can adopt a number of different structures[1] 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 (**1**), *e.g.* $[Rh_4(CO)_{12}]$[2] and $[Fe_4(CO)_{13}]^{2-}$,[3] but an increasing number of compounds with the 'butterfly' structure (**2**) are currently being reported, *e.g.* $[Os_4H(CO)_{13}]^-$[4] and $[Rh_4(PPh_2)_5(CO)_5]^-$.[5] Compounds with metal framework structures (**3**) and (**4**) have also been reported, *e.g.* $[Co_4(PPh)_2(CO)_{10}]$[6] and $[Re_4H_4(CO)_{15}]^{2-}$,[7] although in both cases the range is not extensive. Surprisingly however, compounds of type (**5**) and (**6**), in which all the metal atoms are transition elements, do not appear to have been reported.‡ We now describe a representative example of structure (**5**).

Reaction of $[\{Rh(\eta\text{-}C_3H_5)_2Cl\}_2]$[10] with a four-fold molar amount of $[Fe(CO)_4(PPh_2H)]$[11] in benzene at room temperature in the presence of carbon monoxide affords as major

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† Only those compounds in which each transition metal is formally bonded to at least one other are being considered.

‡ Tetranuclear species of type (**5**) and (**6**) containing both transition and main-group elements are known, *e.g.* $[\{Ru(SiMe_3)(CO)_4\}]^8{}_2$ and $[\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2\{Mo(\eta\text{-}C_5H_5)(CO)_3\}SnCl]$.[9]

product a red compound characterised as $[Rh_2Fe_2(PPh_2)_4(CO)_8]$ (A) which contains bridging as well as terminal carbonyl groups according to spectroscopic evidence [ν(C–O): 2027s, 1975s, 1960s, and 1830ms cm^{-1} (Nujol mull)]. The molecular structure of (A) was established *X*-ray crystallographically.

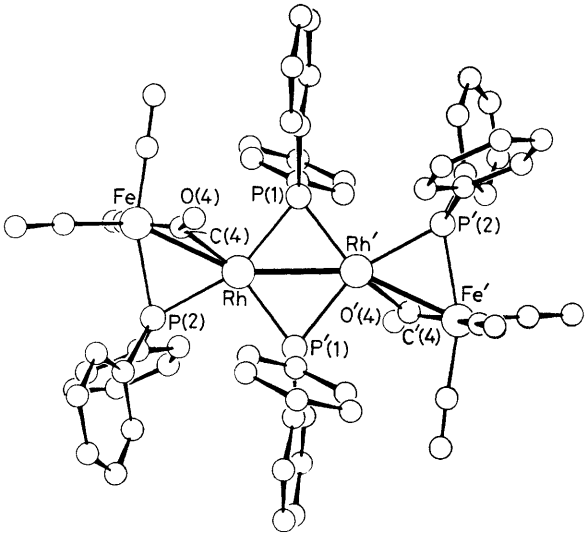

FIGURE. The molecular stereochemistry of $[\{RhFe(\mu\text{-}PPh_2)_2(\mu\text{-}CO)(CO)_3\}_2]$. Bond lengths: Rh–Rh', 2·723(2); Rh–Fe, 2·623(2); Rh–P(1), 2·263(3); Rh'–P(1), 2·301(3); Rh–P(2), 2·262(4); Fe–P(2), 2·237(4); Fe–C(4), 1·890(16); Rh–C(4), 2·148(15) Å.

Crystal data: $C_{56}H_{40}Fe_2O_8P_4Rh_2$, *M* 1282·3, monoclinic, space group $P2_1/c$, a = 12·468(5), b = 13·354(5), c = 17·293(5) Å, β = 95·43(5)°, U = 2866·3 $Å^3$, Z = 2, D_m = 1·50, D_c = 1·49 g cm^{-3}, $F(000)$ = 1284, $\mu(\text{Mo-}K_\alpha)$ = 1·13 mm^{-1}. Data were collected on a Philips PW1100 4-circle diffractometer (N.P.R.L., C.S.I.R., Pretoria) using graphite-monochromated Mo-K_α radiation in the range $6 < 2\theta < 46°$. 3894 reflections were collected and of these 3750 had $I > \sigma(I)$. The structure was solved by standard Patterson and Fourier methods and refined by blocked least squares to R = 0·084 and R_w = 0·080 ($w = 1/\sigma^2F$).§

The molecular geometry of (A) is illustrated in the Figure. The compound adopts a non-closed centrosymmetric chain-like configuration with the two iron atoms in the terminal positions and *trans* disposed with respect to the rhodium–rhodium vector [Fe–Rh–Rh' = 154·3(1)°]. The Fe–Rh and Rh–Rh distances correspond to formal metal–metal bonds. The rhodium atoms are bridged, slightly asymmetrically, by two diphenylphosphino groups [Rh–P(1) = 2·263(3), Rh'–P(1) = 2·301(3) Å] while the rhodium and iron atoms are bridged by both diphenylphosphino and carbonyl ligands. The latter are also slightly asymmetric as evidenced by the Rh–C(4)–O(4) and Fe–C(4)–O(4) bond angles of 124·1 and 155·1° respectively. The RhPFeC rings are puckered [dihedral angle between the RhP(2)Fe and RhC(4)Fe planes is 110°] while the Rh_2P_2 ring is planar.

The ^{31}P n.m.r. spectrum of (A) contains four sets of resonances of complex pattern, one of which could be described as two partially overlapping doublets of doublets. These data are interpreted in terms of the presence of both the *cis*- and *trans*-isomers of $[\{RhFe(\mu\text{-}PPh_2)_2(\mu\text{-}CO)(CO)_3\}_2]$ in solution. The asymmetry of the bridging carbonyl stretching peak in the solution i.r. spectrum of (A) is consistent with this proposal.

We thank the South African Council for Scientific and Industrial Research and the Universities of Natal and South Africa for financial support, the National Institute for Metallurgy for a studentship (N. D. C. T. S.), Dr. J. Coetzer, N.P.R.L., C.S.I.R., Pretoria, for the *X*-ray data collection, and Johnson Matthey Limited for the loan of rhodium salts.

(*Received*, 9*th February* 1981; *Com.* 144.)

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§ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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