Heterobimetallic Synthesis using the Tripod Ligand, $HC(PPh_2)_3$: the *X*-Ray Structure of $[(CO)_5FeRh(tripod)]^+$

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The tripod ligand, $HC(PPh_2)_3$, can be used to construct heterobimetallic complexes such as $[(CO)_5FeRh(tripod)]^+$, the *X*-ray structure of which shows the presence of a metal–metal bond.

Heterobimetallic complex synthesis has elicited some recent interest in view of the catalytic potential of such bifunctional systems. In particular complexes involving the use of heterodifunctional ligands (*e.g.* $Ph_2PCH_2^-$,[1] $Ph_2PC_5H_4^-$ [2]) and bridging or constraining ligands (PR_2^-,[3] $Ph_2PCH_2PPh_2$,[4] $Ph_2PC_5H_4N$ [5]) are of special concern since proximity effects involved in bifunctional behaviour can be maintained even in the absence of any metal–metal bond. We have previously shown that the tripod ligand, $HC(PPh_2)_3$ can assemble[6a] and stabilise[6b] triangular arrays of metal atoms in molecular clusters. We describe here an example of the use of tripod to construct heterobimetallic complexes in *stepwise* reactions.

$HC(PPh_2)_3$ reacts with $Fe_3(CO)_{12}$ or $Fe(CO)_5$ in toluene to yield several products among which the major complexes produced $[HC(PPh_2)_3]Fe(CO)_4$, $[HC(PPh_2)_3]Fe(CO)_3$, and $[HC(PPh_2)_3]Fe_2(CO)_7$ are easily distinguished by ^{31}P n.m.r.

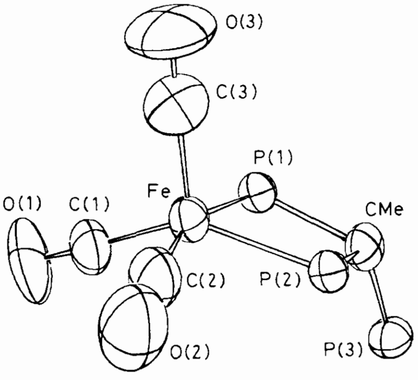

Figure 1. Molecular structure of $Fe(CO)_3[HC(PPh_2)_3]$. Phenyl groups omitted for clarity.

spectroscopy and can be separated by fractional crystallisation. Notably the ^{31}P n.m.r. spectrum of the complex [HC(PPh$_2$)$_3$]Fe(CO)$_3$ shows that two phosphorus nuclei are bound to iron [CH$_2$Cl$_2$, δ +32.8 p.p.m. (d, 2P, $^2J_{P-P}$ 13 Hz)], the third remaining unco-ordinated [δ −18.8 p.p.m. (t, 1P)]. In the *X*-ray structure†‡ of this complex (Figure 1), there is a pendant phosphine arm of the tripod ligand poised to bind a second metal.

For example, [HC(PPh$_2$)$_3$]Fe(CO)$_3$ reacts with [Rh(CO)$_2$Cl]$_2$ (molar ratio 1 : 1) in tetrahydrofuran at 25 °C to yield a yellow crystalline complex, [(CO)$_5$FeRh{HC(PPh$_2$)$_3$}]$^+$[Rh(CO)$_2$Cl$_2$]$^-$. Significantly whereas the ^{31}P n.m.r. signals (in CD$_2$Cl$_2$) of the phosphorus nuclei bound to iron are in the same region at +32.65 p.p.m. (dd, $^2J_{P-P}$ 19 Hz, $^2J_{Rh-P}$ 1.8 Hz), the third nucleus now appears at 7.1 p.p.m. (dt, $^1J_{P-Rh}$ 125 Hz, $^2J_{P-P}$ 19 Hz) showing complexation to rhodium has occurred.

The *X*-ray structure†‡§ of [(CO)$_5$FeRh{HC(PPh$_2$)$_3$}]$^+$-[Rh(CO)$_2$Cl$_2$]$^-$ (Figure 2) shows that complexation has occurred with the formation of a Rh–Fe bond [2.776(2) Å] in a cationic complex, the metals clasped together by the tripod ligand. The iron atom in a quasi-octahedral ligand environment is linked to a square planar rhodium atom with two phosphorus atoms attached to iron [Fe–P, 2.229(3) and 2.228(3) Å] and the other to rhodium [Rh–P, 2.328(3) Å]. Extension of this apparently general approach¶ to the synthesis of other heterobimetallic systems as well as studies on the reactivity of such complexes will be reported elsewhere.

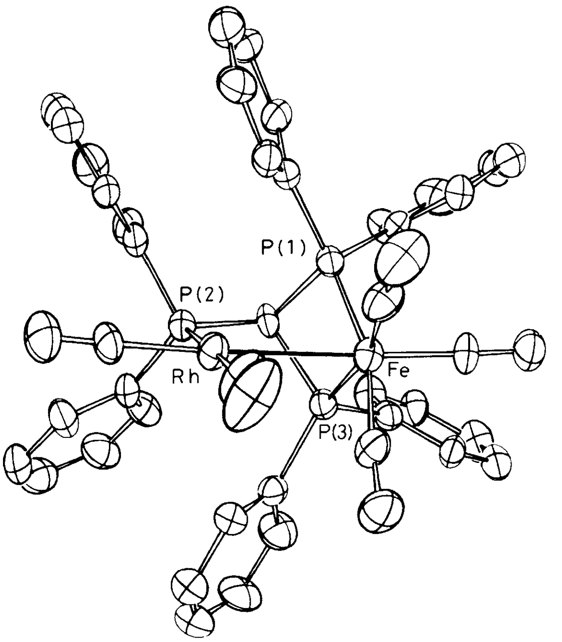

Figure 2. Molecular structure of the [(CO)$_5$FeRh{HC(PPh$_2$)$_3$}]$^+$ cation.

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† *Crystal data* for (CO)$_3$Fe[HC(PPh$_2$)$_3$]: monoclinic, space group *Cc* (No. 9), a = 12.535(5), b = 26.84(1), c = 12.146(4) Å, β = 103.53(1)°, Z = 4, U = 3973.3 Å, D_c = 1.145, D_o = 1.13(1) g cm^{-3}. The structure was solved by conventional Patterson methods and refined by full-matrix least-squares using 2436 reflections with $I > 3\sigma(I)$. The phenyl rings were refined as rigid groups with isotropic thermal parameters for each atom, while the remaining atoms were refined anisotropically. The final discrepancy indices arc R = 8.4 and R_w = 11%.

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

§ *Crystal data* for [(CO)$_5$FeRh{HC(PPh$_2$)$_3$}]$^+$[Rh(CO)$_2$Cl$_2$]$^-$: monoclinic, space group $P2_1/c$, a = 20.208(7), b = 11.544(5), c = 21.066(8) Å, β = 102.60(3)°, Z = 4, U = 4795.86 Å^3, D_c = 1.608, D_o = 1.59 g cm^{-3}. Data were collected on a Picker-Nuclear FACS-1 diffractometer controlled using the N.R.C. crystallographic system (ref. 7). A total of 4545 reflections were measured in the range 2.5 < 2θ < 40.0°, and 3335 with $I > 3\sigma(I)$ were used in the structure solution by statistical phasing refinement. Final discrepancy indices are R = 5.8 and R_w = 7.9%. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were placed at calculated positions.

¶ For example, the reaction of Ru$_3$(CO)$_{12}$ with tripod also yields the analogous complex Ru(CO)$_3$(tripod).

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