Synthesis and Structural Characterisation of $[Ag_6\{Fe(CO)_4\}_3\{(Ph_2P)_3CH\}]$: a Distorted Tricapped Octahedral Silver–Iron Cluster

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$[Ag_6\{Fe(CO)_4\}_3\{(Ph_2P)_3CH\}]$ has been synthesised from $[Fe(CO)_4]^{2-}$ and $[Ag_3Cl_3\{(Ph_2P)_3CH\}]$ in tetrahydrofuran and shown to have a distorted tricapped octahedral cluster geometry by a single crystal *X*-ray crystallographic determination; the capping positions are occupied by the iron atoms and the tripodal ligand is co-ordinated to three silver atoms on a face of the octahedron.

Compared with copper and gold the cluster chemistry of silver is poorly developed,[1] and this presumably reflects the lower thermal stabilities of Ag–Ag bonds.[2] Nyholm *et al.*[3] established that silver was capable of forming simple heterometallic compounds, *e.g.* $[Co(CO)_4Ag(o\text{-triars})]$ [*o*-triars = bis(*o*-dimethylarsinophenyl)methylarsine] if the silver atoms are co-ordinatively saturated. More recently, Stone *et al.*[4] have utilised the capping properties of the $AgPPh_3^+$ fragment towards metal carbonyl cluster anions to form the bicapped tetrahedral $[Ru_4Ag_2(CO)_{12}H_2(PPh_3)_2]$ cluster which has an Ag–Ag bond of length 2.857 Å. These observations suggested that it might prove possible to synthesise high nuclearity heterometallic cluster compounds of silver by the reaction of co-ordinatively unsaturated silver(I) complexes with mononuclear transition metal carbonyl anions.

Tetrahydrofuran (thf) solutions of $Na_2[Fe(CO)_4](dioxane)_{3/2}$ and $[Ag_3Cl_3\{(Ph_2P)_3CH\}]$ react rapidly to give a deep red solution from which a dark red powder was isolated in *ca.*

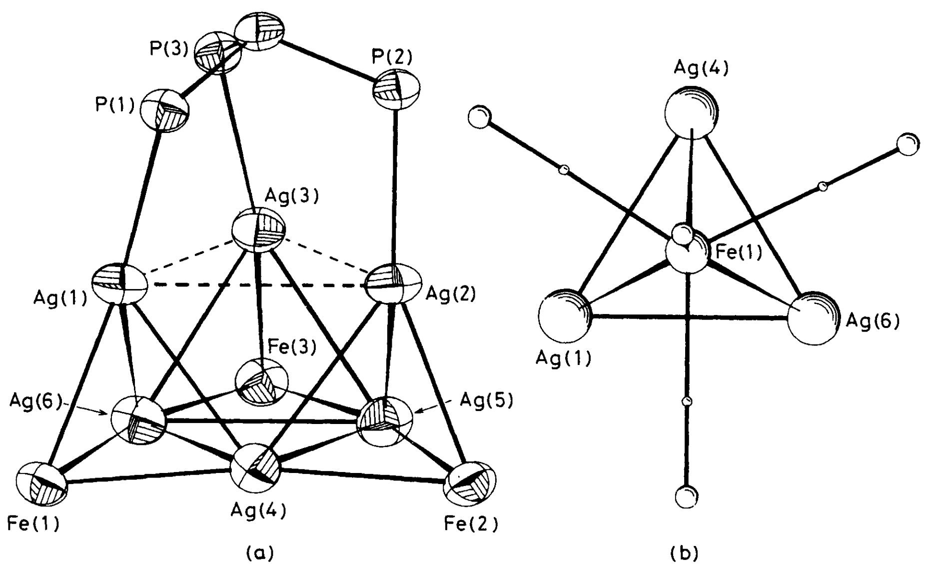

Figure 1. In (a) the skeletal geometry of $[Ag_6\{Fe(CO)_4\}_3\{(Ph_2P)_3CH\}]$ (**1**) is shown. For reasons of clarity the phenyl rings and carbonyls have been omitted. Important interatomic distances include: Ag(1)–Ag(2) 3.415, Ag(1)–Ag(3) 3.292, Ag(1)–Ag(4) 2.851, Ag(1)–Ag(6) 2.960, Ag(2)–Ag(3) 3.288, Ag(2)–Ag(4) 2.861, Ag(2)–Ag(5) 2.980, Ag(3)–Ag(5) 2.869, Ag(3)–Ag(6) 2.817, Ag(4)–Ag(5) 2.921, Ag(4)–Ag(6) 2.854, Ag(5)–Ag(6) 3.065; Fe(1)–Ag(1) 2.679, Fe(1)–Ag(4) 2.682, Fe(1)–Ag(6) 2.710, Fe(2)–Ag(2) 2.655, Fe(2)–Ag(4) 2.668, Fe(2)–Ag(5) 2.720, Fe(3)–Ag(3) 2.664, Fe(3)–Ag(5) 2.710, Fe(3)–Ag(6) 2.703 Å (all e.s.d.s 0.001 Å).

In (b) the geometry of a single $Ag_3Fe(CO)_4$ tetrahedron is illustrated in order to show the trigonal bipyramidal nature of the $Fe(CO)_4$ fragment. The C–Fe(x)–C bond angles fall into two groups of three with the following averages: C–Fe(1)–C 91(2) and 120(2), C–Fe(2)–C 92(1) and 120(2), and C–Fe(3)–C 91(1) and 120(2)°.

50% yield by the addition of toluene. Analytical data suggested that phosphine loss had occurred and the stoicheiometry $[Ag_2Fe(CO)_4\{(Ph_2P)_3CH\}_{1/3}]_n$. I.r. and $^{31}P\{^1H\}$ n.m.r. data confirmed the presence of $Fe(CO)_4$ fragments and the chemical equivalence of the phosphorus environments,† but did not define the nuclearity of the cluster. Single crystals of the compound were grown from acetone–hexane and an X-ray crystallographic analysis confirmed that a high nuclearity cluster had resulted from the reaction.‡ The structure of $[Ag_6\{Fe(CO)_4\}_3\{(Ph_2P)_3CH\}]$ (**1**) is illustrated in Figure 1. The molecule has no crystallographically imposed symmetry, but the skeletal atoms have approximately C_3 symmetry. The silver atoms define a distorted octahedron with the tripodal ligand co-ordinated to three silver atoms on the face of the octahedron. These silver atoms [Ag(1), Ag(2), and Ag(3)] are separated by distances which are greater than 3.288(1) Å and therefore fall outside the range where significant Ag · · · Ag bonding has been considered to occur, *i.e.* 2.76—*ca.* 3.05 Å.[5] The remaining Ag · · · Ag distances lie in the range 2.817(1)—3.065(1) Å and have a mean value of 2.909(27) Å, which is close to that found in the metal [2.889(7) Å].[6]

The three $Fe(CO)_4$ fragments cap three of the faces of the octahedron in a symmetrical fashion. The Ag–Fe distances lie in a narrow range, *i.e.* 2.664(1)—2.720(1) Å, and correspond approximately to the sum of the covalent radii for iron and silver (2.68 Å).[7] It is more common for $Fe(CO)_4$ to function as a two-electron edge-bridging fragment isolobal with CH_2 rather than as a capping four-electron fragment isolobal with CH^-.[8,9] In (**1**) the adoption of the triply bridging mode can be attributed to steric effects since the more conventional edge-bridging mode would have required the co-ordination of an additional tripodal ligand to satisfy the 84 electron requirement for octahedral copper and silver clusters, *e.g.* $[Cu_6H_6(PPh_3)_6]$, $[Cu_6Cl_2(C_6H_4\text{-}NMe_2\text{-}2)_4]$, and $[Ag_6\{S_2C{=}C(CN)_2\}_6]^{6-}$.[10]

The adoption of the triply bridging mode by the $Fe(CO)_4$ fragment is associated with a change in the local geometry from *cis*-divacant octahedral to one based on a trigonal bipyramid with an axial ligand missing. This change in geometry leads to a degenerate set of metal d_{xz} and d_{yz} orbitals and symmetrical bonding to the triangular face of silver atoms.

In view of the long Ag · · · Ag distances associated with the silver atoms co-ordinated to the tripodal ligand, the cluster geometry can be described as a triangle of vertex linked Ag_3Fe tetrahedra. The observed electron count of 120 is consistent with the electron counting rules recently developed for condensed polyhedra if the common vertex atoms are characterised by 14 electrons.[11]

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† Spectroscopic data: i.r. ν(CO) (Nujol mull) 2000sh, 1990sh, 1981s, 1900s, and 1882s cm^{-1}; $^{31}P\{^1H\}$ n.m.r. in thf (to high frequency of trimethyl phosphate) δ 9.58 p.p.m. [m, $^1J(^{109}Ag\text{–}P)$ 414 and $^1J(^{107}Ag\text{–}P)$ 334 Hz].

‡ *Crystal data*: $C_{49}H_{31}Ag_6Fe_3P_3O_{12}\cdot 2(C_3H_6O)$ (**1**), $M = 1835.6$, monoclinic, space group $P2_1/c$, $a = 12.168(2)$, $b = 20.473(4)$, and $c = 24.425(3)$ Å, $\beta = 91.65(2)°$, $U = 6082.1$ Å^3, $Z = 4$, $D_c = 2.00$ g cm^{-3}, $\mu(Mo\text{-}K_\alpha) = 26.87$ cm^{-1}, $F(000) = 3560$ electrons. Intensity data were collected at *ca.* 291 K on an Enraf-Nonius CAD4F diffractometer using graphite-monochromated Mo-K_α ($\lambda = 0.71069$ Å) X-radiation. Of 7918 unique reflections ($1.5 < \theta < 22.5°$) 6165 with $I \geqslant 3\sigma(I)$ were used for structure solution (Patterson and Fourier methods) and refinement by blocked-matrix least-squares methods, leading to a final $R = 0.033$ ($R_w = 0.038$). The Ag, P, Fe, C, and O (carbonyl), and methyne carbon atoms were refined anisotropically. The asymmetric unit also contains two molecules of acetone of crystallisation.

The atomic co-ordinates for this structure 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.

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