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Preliminary communication

SYNTHESIS AND STRUCTURAL CHARACTERISATION OF THE MIXED-METAL CARBIDO CLUSTER $Fe_5C(\mu_2\text{-}CO)_3(CO)_{11}(\mu_2\text{-}AuPEt_3)(\mu_4\text{-}AuPEt_3)$ AND THE OXIDATION OF Fe—Au CLUSTERS

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Summary

Reaction of $[Fe_5C(CO)_{14}]^{2-}$ with excess $(PEt_3)AuCl/Tl(PF_6)$ affords the mixed-metal cluster $Fe_5C(\mu_2\text{-}CO)_3(CO)_{11}(\mu_2\text{-}AuPEt_3)(\mu_4\text{-}AuPEt_3)$ which has been shown by an X-ray structural analysis to exhibit a novel coordination for one of the $AuPEt_3$ groups. This and another Fe—Au cluster, $Fe_4H(CO)_{12}C(AuPEt_3)$ undergo unusual oxidative rearrangements.

There is evidence to suggest that carbido species may be involved in catalytic processes [1]. Transition metal carbido clusters have been used as models for catalytic reactions on metal surfaces but in many of these complexes the carbide atom is relatively inert. Recently several research groups have successfully activated the carbide atom in tetrairon carbonyl clusters to yield species such as $[Fe_4C(CO)_{12}CO_2CH_3]^-$ [2] and $[Fe_4(\mu\text{-}H)(CO)_{12}(\mu^2\text{-}COCH_3)]$ [3]. In an alternative approach, the carbide has been made to interact with additional metal atoms by polyhedral expansion of $[Fe_4C(CO)_{12}]^{2-}$ or $[Fe_5C(CO)_{14}]^{2-}$ by reactions with coordinately unsaturated complexes to yield anions with general formula $[Fe_5MC(CO)_x]^{y-}$, $[Fe_4M_2C(CO)_x]^{y-}$, or $[Fe_4MC(CO)_x]^{y-}$ [4]. We have recently combined the two techniques by activating the capping carbonyl group in $[Fe_4(CO)_{13}]^{2-}$ and treating it with $AuClPR_3$ (R = Et, Ph) to produce the carbido complexes $Fe_4AuC(H)(CO)_{12}(PR_3)$ and $Fe_4Au_2C(CO)_{12}(PR_3)_2$ [5] under relatively mild conditions. In these two species the encapsulated carbide atom is involved in bonding to both the iron and the gold atoms. In this communication we report an extension of this work to produce a new heptametal cluster, $Fe_5C(CO)_{14}(AuPEt_3)_2$, by the reaction of $[Fe_5C(CO)_{14}]^{2-}$ with $AuClPEt_3$.

The reaction of $[(Ph_3P)_2N][Fe_5C(CO)_{14}]$ with one mole of $AuClPEt_3$ in

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the presence of excess $Tl[PF_6]$ gave a brown anion. The infrared spectrum of this anion exhibited ν(CO) (CH_2Cl_2) bands at 2038w, 1979s, 1961m, 1922w(sh), and 1909w(sh) cm^{-1}. With excess $AuClPEt_3$ a black neutral compound which showed infrared carbonyl stretching frequencies, in CH_2Cl_2, at 2051m, 2009(sh), 1999s, 1984s, 1960m(sh), 1930w(sh), and 1831m(br) cm^{-1} was obtained. This neutral complex was obtained as octahedral-shaped black crystals by recrystallisation from hexane/dichloromethane, and characterised as $Fe_5C(\mu_2\text{-}CO)_3(CO)_{11}(\mu_2\text{-}AuPEt_3)(\mu_4\text{-}AuPEt_3)$ by a single crystal X-ray analysis.

$$[Fe_5C(CO)_{14}]^{2-} \xrightarrow[TlPF_6/CH_2Cl_2]{AuClPEt_3} \text{anion} \xrightarrow[AuClPEt_3]{\text{excess}} Fe_5C(CO)_{14}(AuPEt_3)_2$$

(80% yield)

Crystal data: $C_{27}H_{30}Au_2Fe_5O_{14}P_2$, M 1313.64, monoclinic, $P2_1/c$, a 12.934(5), b 18.879(6), c 16.425(9) Å, β 106.86(4)°, U 3838 $Å^3$, D_c 2.273 g cm^{-3}, $Z = 4$, $\mu(\text{Mo-}K_\alpha)$ 98.75 cm^{-1}.

The Au and Fe atom positions were determined by Σ_2 sign expansion, and all the remaining non-hydrogen atoms were located by subsequent electron-density difference syntheses. The structure was refined by blocked-cascade least squares (Au, Fe, P, O, and carbide C atoms anisotropic, carbonyl and phosphine C atoms isotropic). The carbon atoms of the phosphine ligands showed some positional disorder, and several atoms were refined with partial occupancies between two sites. No hydrogen atoms were included in the refinements. 4231 Intensities were measured on a Syntex $P2_1$ diffractometer with an $w/2\theta$ scan technique, these were averaged and corrected for absorption to give 3334 unique observed reflections $[F > 3\sigma(F)]$. The final residuals are $R = 0.048$ and $R' = [\Sigma w^{1/2}\Delta/\Sigma w^{1/2}|F_o|] = 0.053$. The weighting scheme employed was $w = [\sigma^2(F) + 0.002|F|^2]$.

The molecular structure of $Fe_5C(\mu_2\text{-}CO)_3(CO)_{11}(\mu_2\text{-}AuPEt_3)(\mu_4\text{-}AuPEt_3)$ is shown in Fig. 1, together with some important bond parameters. The cluster core showing the coordination of the carbido atom, C(1), is illustrated in Fig. 2. The structure is unusual in that it contains two $AuPEt_3$ groups which display different bonding modes. The five Fe atoms lie at the vertices of a square-based pyramid with the carbide atom lying 0.11 Å below the square base. One $AuPEt_3$ group symmetrically bridges the Fe(1)—Fe(4) basal edge, the other three basal edges being asymmetrically bridged by carbonyl ligands. The Au atom of the second $AuPEt_3$ groups caps the square base of the Fe_5 square pyramid to give a distorted octahedral metal arrangement and is also within bonding distance of the carbide atom. The remaining eleven carbonyls are terminally coordinated, two to each of the basal Fe atoms and three to the apical Fe atom.

The Fe—Fe distances in the Fe_5 square pyramid in $Fe_5C(CO)_{14}(AuPEt_3)_2$ are similar in length to the average Fe—Fe distance of 2.64 Å in $Fe_5C(CO)_{15}$ [6], except that in the former complex the $AuPEt_3$ bridged Fe(1)—Fe(4) edge is ca. 0.3 Å longer. The arrangement of the carbonyl ligands differs between the two structures. In the mixed-metal cluster, carbonyl groups bridge the basal Fe—Fe edges while in the $Fe_5C(CO)_{15}$ cluster all the carbonyl groups

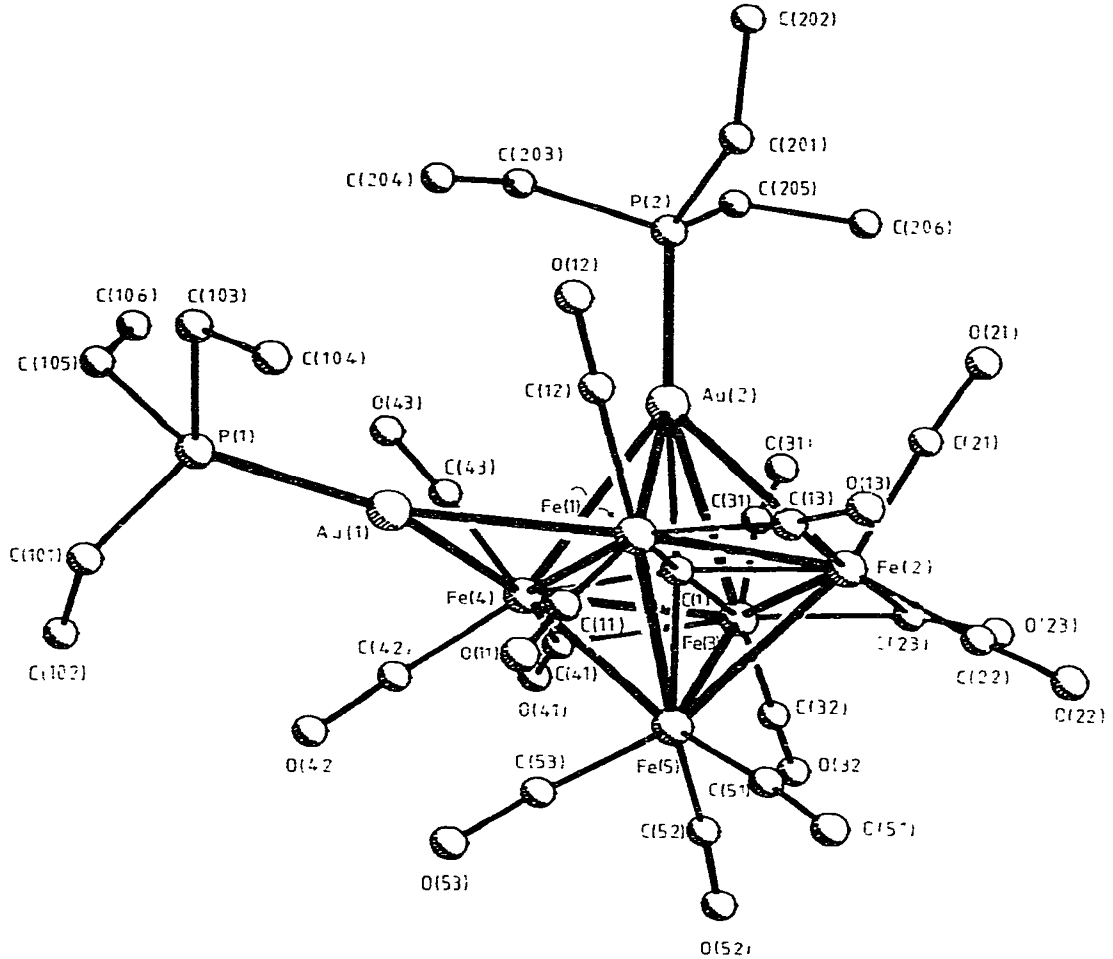


Fig. 1. The molecular structure of $Fe_5C(\mu_2\text{-}CO)_3(CO)_{11}(\mu_2\text{-}AuPEt_3)(\mu_4\text{-}AuPEt_3)$, only one orientation of the disordered phosphine is shown for clarity. Bond lengths: Au(1)—Fe(1), 2. 696(2); Au(1)—Fe(4), 2.701(3); Au(1)—P(1), 2.276(5); Au(2)—Fe(1), 2.828(3); Au(2)—Fe(2), 3.007(2); Au(2)—Fe(3), 3.036(3); Au(2)—Fe(4), 2.871(2); Au(2)—C(1), 2.117(14); Au(2)—P(2), 2.268(4); Fe(1)—Fe(2), 2.623(3); Fe(1)—Fe(4), 2.941(3); Fe(1)—Fe(5), 2.612(3); Fe(1)—C(1), 1.876(18); Fe(2)—Fe(3), 2.573(5); Fe(2)—Fe(5), 2.660(3); Fe(2)—C(1), 1.912(14); Fe(3)—Fe(4), 2.628(3); Fe(3)—Fe(5), 2.686(4); Fe(3)—C(1), 1.936(18); Fe(4)—Fe(5), 2.652(3); Fe(4)—C(1), 1.916(14); Fe(5)—C(1), 1.951(14) Å. Bond angles: Fe(1)—Au(1)—P(1), 145.1(2); Fe(4)—Au(1)—P(1), 148.8(2); Fe(1)—Au(1)—Fe(4), 66.0(1); P(2)—Au(2)—C(1), 176.7(4)°

are terminal. An analogy has been drawn between the bonding modes of $AuPPh_3$ and the hydride ligand [7] and there are many examples of bridging hydrides being associated with the lengthening of metal—metal bonds. This would seem to be the situation in the case of the long Fe(1)—Fe(4) bond. The gold atom, Au(1), may be considered as *sp* hybridized with the orbital directed towards the midpoint of the Fe(1)—Fe(4) bond resulting in a three-centre multi-electron bonding arrangement. Although the three bridging carbonyl groups are somewhat asymmetric each formally donates one electron to each of the metal atoms to which they are bonded.

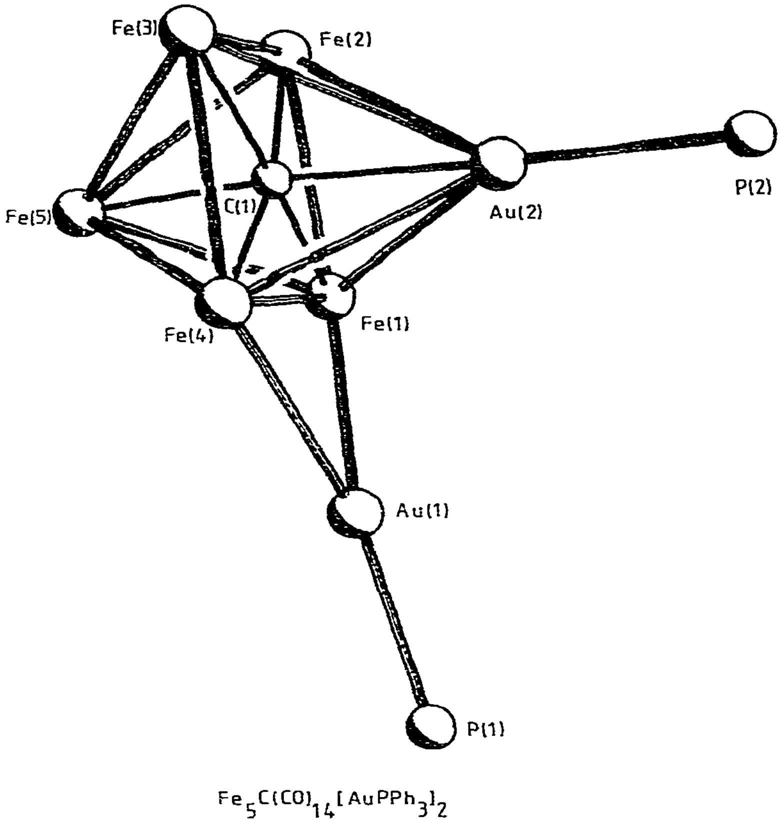
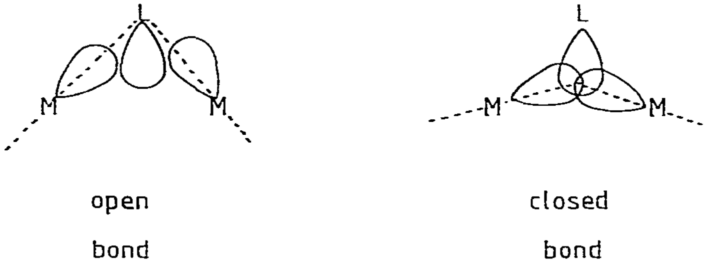


Fig. 2. The cluster core in $Fe_5C(\mu_2\text{-}CO)_3(CO)_{11}(\mu_2\text{-}AuPEt_3)(\mu_4\text{-}AuPEt_3)$.

The second gold atom, Au(2), may also be considered as *sp* hybridized Au^I. The C(1)—Au(2)—P(2) angle of 176.7(4)° is in keeping with this suggestion, and the Au(2)—C(1) distance is similar to the distance of 2.077(5) Å in $Fe_4AuC(H)(CO)_{12}(PPh_3)$ [5] where direct interaction between these atoms has been proposed. The Au(2)—Fe distances range from 2.828(3) to 3.036(3) Å the two longer Au—Fe bonds, Au(2)—Fe(2) and Au(2)—Fe(3), are significantly longer than either of the Au—Fe distances in the "bridged-butterfly" arrangement in $Fe_4AuC(H)(CO)_{12}(PPh_3)$, but are similar to several of the Au—Fe distances in the octahedral cluster $Fe_4Au_2C(CO)_{12}(PEt_3)_2$ [5]. All these Au—Fe distances are indicative of some bonding interaction and the asymmetry of the $AuPEt_3$ cap is in keeping with the electron imbalance in the Fe_4 square base; the shorter Au(2)—Fe distances are with the Fe atoms involved in the Au(1) bridged bond and which formally have 17½ electrons each. There is no bond between the two Au atoms in this complex unlike two other cluster complexes containing two Au atoms, $Fe_4Au_2C(CO)_{12}(PEt_3)_2$ [5] and $Os_4Au_2H_2(CO)_{12}(PPh_3)_2$ [8] where the metal polyhedron is in keeping with direct Au—Au interaction. It may be that in the case of $Fe_5C(CO)_{14}(AuPEt_3)_2$ there is a driving force to form a closed polyhedron about the carbide which favours the observed edge bridged octahedral metal arrangement rather than a polyhedron in which there is an additional Au—Au interaction. However the structure of $Fe_5C(CO)_{14}(AuPEt_3)_2$ represents the third member of the series where the first two members are $Fe_4AuC(H)(CO)_{12}(PPh_3)$ and $Fe_4Au_2C(CO)_{12}$-$(PEt_3)_2$, the number of metal atoms being increased by one in each case.

One possible bonding scheme for the structure may be developed if the iron atoms are considered to be d^2sp^3 hybridised and the gold atoms *sp* hybridised. The geometry around the four basal Fe atoms is close to octahedral if the basal Fe—Fe interactions are not considered. The *trans*-L—Fe(basal)—L angles, where L may be CO, Au, or Fe(5), all lie in the range 159.8(7)—172.0(7)° which is in keeping with the d^2sp^3 hybridisation of the Fe atoms with the orbitals directed at the ligands. Since the angles all show considerable deviations from linearity this may indicate that the bonds are "closed" multicentre bonds in which there is some direct overlap between orbitals on adjacent Fe atoms. If the carbide is considered to use a spherically symmetrical orbital the one lobe of the *sp* orbital on the capping Au(2) atom would interact with this carbide orbital and with the lobes of four d^2sp^3 orbitals from the Fe atoms at a point along the C(1)—Au(2) vector. If the fifth Fe atom, Fe(5), is also d^2sp^3 hybridised a multicentre bond involving three lobes of this hybrid with four lobes from the four basal Fe atoms and the orbital from the carbide could occur.



SCHEME 1

The air oxidation of $Fe_5C(CO)_{11}(AuPEt_3)_2$ in toluene or dichloromethane affords the brown anion in fair yield. This presumably involves the loss of an Fe atom, probably as Fe^{2+}, and a structural rearrangement, Au(1) moving to the now vacant octahedral site.

$$Fe_5Au_2C(CO)_{14}(PEt_3)_2 \xrightarrow[100\text{ h, }4^\circ C]{\text{air}}$$

$$\underset{(25\%\text{ of Au})}{Fe_4Au_2C(CO)_{12}(PEt_3)_2} + \underset{(68\%\text{ of Au})}{\text{anion} + Fe^{2+} + 2CO}$$

The oxidative loss of an iron atom from an Fe_5C or Fe_5CM cluster has been previously observed [4,9], but without the accompanying rearrangement. A similar oxidation is observed for $Fe_4AuC(H)(CO)_{12}(PEt_3)$, but with an inter- rather than intra-molecular gold migration.

$$\mathrm{Fe}\ 2\ \mathrm{Fe_4AuC(H)(CO)_{12}(PEt_3)}\ \xrightarrow[\substack{100\text{ h, }4^\circ\text{C}\\ \mathrm{CH_2Cl_2}}]{\text{AIR}}$$

$$\underset{(12\%\text{ of Au})}{\mathrm{Fe_4Au_2C(CO)_{12}(PEt_3)_2}} + 3\mathrm{Fe^{2+}} + \mathrm{H^+} + \underset{(85\%\text{ of Au})}{\mathrm{Fe_4AuC(H)(CO)_{12}(PEt_3)}} + 12\mathrm{CO}$$

This oxidative disproportionation occurs not only in solution, but also in the solid state over a period of months. Thus, the migrating "$\mathrm{AuPEt_3}$" unit is not only labile in solution, but it is also free to diffuse, or at least to reorientate itself in a solid matrix.

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