Journal of Organometallic Chemistry, 231 (1982) C59—C64
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

SYNTHESES AND STRUCTURAL CHARACTERISATIONS OF SOME NOVEL MIXED-METAL IRON-GOLD CARBIDO CLUSTERS; X-RAY CRYSTAL STRUCTURES OF $Fe_4AuC(\mu\text{-}H)(CO)_{12}(PPh_3)$ AND $Fe_4Au_2C(CO)_{12}(PEt_3)_2$

BRIAN F.G. JOHNSON, DAVID A. KANER, JACK LEWIS, PAUL R. RAITHBY and
MARIA J. ROSALES
University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain)

(Received February 15th, 1982)

Summary

The reaction of the anion $[Fe_4(CO)_{13}]^{2-}$ with $AuClPR_3$ (R = Et, Ph) yields an anion which upon protonation gives the cluster $Fe_4AuC(H)(CO)_{12}(PR_3)$. This complex is reversibly deprotonated in the presence of base and the resultant anion upon treatment with $AuClPR_3$ (R = Et, Ph) gives $Fe_4Au_2C(CO)_{12}(PR_3)_2$; the formation of the latter involves attack at the carbido centre by the gold phosphine group. Both neutral carbido species were characterised by single-crystal X-ray analyses.

The high yield syntheses of several mixed-metal clusters by the reaction of cluster anions with mononuclear halides or cations have been reported recently [1,2]. Such species are of interest as they may show novel chemical reactivity and are possibly catalytically active [3].

X-ray structure analyses have shown that in the clusters $Os_4Au(H)(CO)_{13}(PEt_3)$ [2], $Os_4Au(H_3)(CO)_{12}(PEt_3)$ [2], and $Os_3FeAu(H)(CO)_{13}(PEt_3)$ [4] the phosphinegold unit bridges an edge of the Os_4 or Os_3Fe polyhedron in a similar way to that of a μ_2-hydride.

We now report the reaction of the anion $[Fe_4(CO)_{13}]^{2-}$ (I) with $AuClPR_3$ (R = Et, Ph) under mild conditions, which gives a purple anion II, and upon protonation of this ion, accompanied by oxidation of some of the cluster, the brown neutral carbido cluster $Fe_4AuC(H)(CO)_{12}(PR_3)$ (R = Et, Ph) (III) is produced. Spectroscopic data for the complexes II and III are presented in

0022-328X/82/0000—0000/$02.75

$$\underset{\text{(I)}}{[Fe_4(CO)_{13}]^{2-}} \xrightarrow[CH_2Cl_2]{AuClPR_3/TlPF_6} \underset{\text{(II)}}{\text{anion}} \xrightarrow[CH_2Cl_2]{HBF_4 \cdot Et_2O} \underset{\text{(III)}}{\underset{47\%}{Fe_4AuC(H)(CO)_{12}(PR_3)}}$$

Table 1. Crystals of III were obtained by recrystallisation from CH_2Cl_2/hexane.

Crystal data: $Fe_4AuC(H)(CO)_{12}(PPh_3)$ (III). $C_{31}H_{16}AuFe_4O_{12}P$, M = 1031.78, triclinic, a 9.855(4), b 12.495(6), c 14.898(7) Å, α 103.46(2), β 98.47(2), γ 99.74(2)°, U 1724.7 Å^3, D_c 1.986 g cm^{-3}, Z = 2, $F(000)$ = 992, μ(Mo-K_α) 59.42 cm^{-1}, space group $P\bar{1}$. The Au atom position was determined from a Patterson synthesis and the remaining non-hydrogen atoms from subsequent electron density difference syntheses. The structure was refined by blocked-cascade least squares (Au, Fe, P, carbonyl C, and O anisotropic, phenyl C isotropic). The hydride ligand was located directly from a difference synthesis while the phenyl H atoms were placed in idealised positions and constrained to ride on the relevant C atom (C—H, 1.08 Å; C—C—H, 120°); the phenyl H atoms were assigned a common isotropic temperature factor. 7233 Intensities were recorded on a Syntex $P2_1$ diffractometer with an $\omega/2\theta$ scan technique, these were averaged and corrected for absorption to give 6741 unique observed reflections [$F > 3\sigma(F)$]. The final residuals are R = 0.037 and $R' = [\Sigma w^{1/2}\Delta/\Sigma w^{1/2}|F_o|]$ = 0.041. The weighting scheme employed was $w = [\sigma^2(F) + 0.001F^2]^{-1}$.

The molecular structure of III is shown in Fig. 1, together with some important bond parameters. The four Fe atoms define a "butterfly" configuration while the Au atom bridges the two "wingtip" metal atoms, Fe(1) and Fe(4), to give an overall "bridged-butterfly" metal framework which has previously been observed in monometal clusters such as $[Os_5C(CO)_{15}I]^-$ [5]. The dihedral angle between the Fe(1)Fe(2)Fe(3) and Fe(2)Fe(3)Fe(4) planes is 71.7°. The carbido carbon atom, C(1), lies at the centre of the cluster approximately over the midpoint of the Fe(2)—Fe(3) "hinge" bond. The C(carbido)—Fe(wingtip) distances are ca. 0.1 Å shorter than the distances to the "hinge" Fe atoms. The Fe(1)—C(1)—Fe(4) angle is 173.1(2)° with the carbide displaced slightly towards the Au(1) atom. The geometry of this $Fe_4C(\mu\text{-}H)$ unit is generally similar to that observed in $Fe_4H(\eta^2\text{-}CH)(CO)_{12}$ [6] where it may be considered that the η^2-CH group replaces the $CAuPPh_3$ grouping in III. The Fe—Fe distances in $Fe_4H(\eta^2\text{-}CH)(CO)_{12}$ [6] are marginally shorter and the bridging C atom closer to one Fe atom than in III. The bond parameters in the $Fe_4C(\mu\text{-}H)$ unit in these two clusters are in close agreement with those in $[Fe_4C(H)(CO)_{12}]^-$ [7] where there is no other group coordinating to the capping C atom. Each Fe atom in III is also coordinated to three terminal carbonyl ligands. The hydride atom, H(1) was located directly in the structure determination and bridges the Fe(2)—Fe(3) edge. The Au(1) atom sits directly above the carbido atom C(1) and the C(1)—Au(1)—P(1) angle of 177.6(1)° is consistent with this metal being regarded as *sp* hybridized Au^I, as appears to be the case in some mixed Au—Os clusters [1,2,4]. However, in addition to there being a bonding interaction between the Au(1) atom and the carbide the Au(1)—Fe(1) and Au(1)—Fe(4) distances are short enough to indicate bond

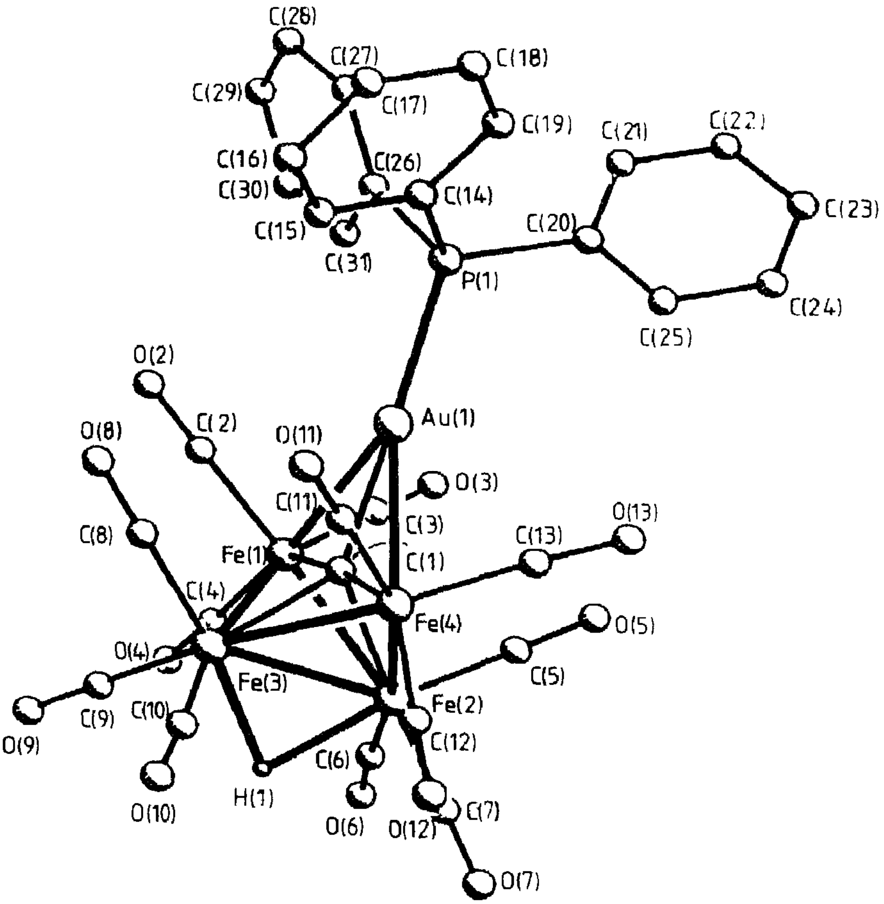

Fig. 1. The molecular structure of $Fe_4AuC(\mu\text{-}H)(CO)_{12}(PPh_3)$. Bond lengths: Au(1)—Fe(1), 2.880(1); Au(1)—Fe(4), 2.854(1), Fe(1)—Fe(2), 2.626(1); Fe(1)—Fe(3), 2.638(1); Fe(2)—Fe(3), 2.618(1); Fe(2)—Fe(4), 2.644(1); Fe(3)—Fe(4), 2.628(1); Au(1)—C(1), 2.077(5); Fe(1)—C(1), 1.844(5); Fe(2)—C(1), 1.957(4), Fe(3)—C(1), 1.951(5); Fe(4)—C(1) 1.868(5); Fe(2)—H(1), 1.92(8); Fe(3)—H(1), 1.89(7) Å. Bond angles: Fe(1)—Au(1)—Fe(4), 80.5(1); Au(1)—C(1)—Fe(1), 94.4(2); Au(1)—C(1)—Fe(4), 92.5(2); Fe(2)—H(1)—Fe(3), 87(3)°.

TABLE 1

SPECTROSCOPIC DATA (for R = Et only)

	IR (ν(CO)) (CH_2Cl_2)			NMR (hydride ^1H)	Mass spectrum (m/e)
II	2104w,	2069w,	2040(sh)	—	—
	2032m,	1997m,	1967vs		
	1923m(br),	1600m			
III	2080m,	2038s,	2032vs	−24.1 δ(s)	888
	2008s,	2004s,	1969w		
	1951w				
IV	2038w,	2013w,	1989s	—	—
	1964vs,	1939(sh),	1914(sh)		
V	20[illegible]0w,	2009s,	2001(sh)	—	1202 (weak)
	1978m,	1958w(sh),	1933w		

formation. If the Au atom is *sp* hybridized then a *p* orbital on the Au could interact with available orbitals on the Fe atoms to give a delocalised Fe—Au—Fe bond.

In the related Fe_4Rh carbido cluster $[Fe_4RhC(CO)_{14}]^-$ [8] the metal atoms define a square pyramid, similar to that in the pentanuclear iron carbide $Fe_5C(CO)_{15}$ [9], and not the "bridged-butterfly" geometry observed for III.

The cluster $Fe_4AuC(H)(CO)_{12}(PR_3)$ (III) may be reversibly deprotonated in the presence of base to yield a brown anion IV, which forms a green/brown neutral compound, $Fe_4Au_2C(CO)_{12}(PR_3)_2$ (R = Et, Ph) (V) upon reaction with $AuClPR_3$ (R = Et, Ph). The spectroscopic data for compounds IV and V are listed in Table 1. Crystals of V were obtained by recrystallisation from CH_2Cl_2/hexane.

$$Fe_4AuC(H)(CO)_{12}(PR_3) \xrightarrow[HBF_4 \cdot Et_2O]{NEt_3} \text{anion} \xrightarrow[CH_2Cl_2]{AuClPR_3/TlPF_6}$$

(III) (IV)

$$Fe_4Au_2C(CO)_{12}(PR_3)_2$$

(V) 90%

Crystal data: $Fe_4Au_2C(CO)_{12}(PEt_3)_2$ (V). $C_{25}H_{30}Au_2Fe_4O_{12}P_2$, $M = 1201.77$ monoclinic, a 21.502(9), b 11.457(5), c 17.679(9) Å, β 125.977(32)°, U 3524.5 Å^3, D_c 2.264 g cm^{-3}, $Z = 4$, $F(000) = 2272$, $\mu(\text{Mo-}K_\alpha)$ 99.85 cm^{-1}, space group $C2/c$. 2246 Intensities were recorded on a Syntex P2_1 diffractometer using graphite-monochromated Mo-K_α radiation and an $\omega/2\theta$ scan technique. The data were averaged and corrected for absorption to give 2231 observed reflections $[F > 3\sigma(F)]$. The structure was solved and refined using the same techniques as for (III). All non-hydrogen atoms were assigned anisotropic thermal parameters while the ethyl H atoms were assigned a common isotropic temperature factor and were constrained to ride in idealised positions (C—H, 1.08 Å). The final residuals are $R = 0.033$ and $R' = 0.035$. The weighting scheme employed was $\omega = [\sigma^2(F) + 0.002\,F^2]^-$.

The molecular structure of V is illustrated in Fig. 2, together with some important bond parameters. The molecule lies on a crystallographic 2-fold axis which bisects the Au(1)—Au(1') and Fe(2)—Fe(2') bonds and passes through the carbido carbon atom, C(1). The four Fe atoms again define a "butterfly" geometry with a dihedral angle between the "wings" of 72.9°. The two Au atoms lie above but slightly skewed with respect to the Fe(2)—Fe(2') "hinge" bond and bridge the "wingtip" Fe(1) and Fe(1') atoms. The six metal atoms define a distorted octahedron with the carbido carbon, C(1), lying approximately at its centre. A carbide at the centre of an octahedral array has been observed in a number of monometal clusters [10] and in these the C atom is approximately equidistant from all six metal atoms. However, in V, because of the two types of metal atoms present the carbide is closer to the Fe atoms, having similar Fe—C(carbide) distances to those in III. The Fe_4C core is similar to that in $[Fe_4(\mu_4\text{-}C)(CO)_{12}]^{2-}$ [11] although the Fe—Fe distances are ca. 0.03 Å longer, and the main difference in Fe—Fe bond lengths between III

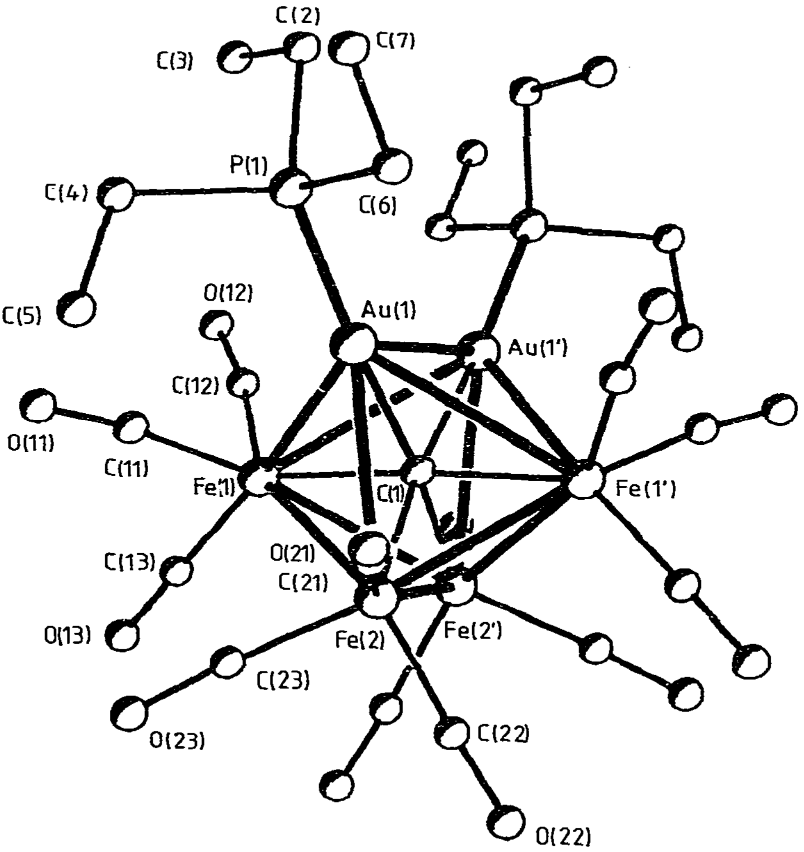

Fig. 2. The molecular structure of $Fe_4Au_2C(CO)_{12}(PEt_3)_2$. Bond lengths: Au(1)—Fe(1), 2.770(1); Au(1)—Fe(1'), 2.999(2); Au(1)—Fe(2'), 2.982(2); Au(1)—Au(1'), 3.017(1); Fe(1)—Fe(2), 2.679(3); Fe(1)—Fe(2'), 2.690(2); Fe(2)—Fe(2'), 2.562(2); Au(1)—C(1), 2.119(11); Fe(1)—C(1), 1.900(2); Fe(2)—C(1), 1.958(12) Å. Bond angles: Fe(1)—Au(1)—Fe(1') 82.2(1); Fe(1)—C(1)—Fe(1'), 175.2(9); Au(1)—C(1)—Fe(1), 87.0(3)°.

and V is due to the bridging hydride across the Fe—Fe "hinge" bond in III. Each Fe atom is also coordinated to three terminal carbonyl groups. As in III the C(1)—Au(1)—P(1) units are approximately linear, with an angle at Au of 176.6(3)°, while the Au(1)—C(1) bond length is ca. 0.11 Å longer. The Au(1)—Au(1') distance is considerably longer than the value of 2.793(4) Å in $Os_4Au_2(H_2)(CO)_{12}(PPh_3)_2$ [12] but similar to Au—Au distances in larger gold clusters such as $[Au_6\{P(p\text{-}MeC_6H_4)_3\}_6]^{2+}$ [13] (2.932(2)—3.091(2) Å) and $Au_{11}I_3[P(C_6H_4Cl)_3]_7$ [14] (2.861(6)—3.165(9) Å). The Au(1)—Fe(1) "wingtip" distance is shorter than in III but the interactions with Fe(1') and Fe(2') are longer. The bond parameters involving the Au atoms are consistent with the view that these metals are formally *sp* hybridized and form σ-bonds with the carbide. There are then two empty *p* orbitals potentially available on each Au atom to form delocalised multicentre bonds with the "wingtip" Fe atoms and the other Au atom. It is probably the orientation of the *p* orbitals on the Au atom, which are involved in metal—metal bonding, which causes the skewing of the Au(1)—Au(1') bond relative to the Fe(2)—Fe(2') bond, as there is no apparent crowding of the groups within the molecule which may otherwise cause this rotation.

There are no other examples of M_4M_2' neutral carbido clusters but anionic species with general formula $[Fe_5MC(CO)_x]^{y-}$ and $[Fe_4M_2C(CO)_x]^{y-}$ [8,15] are known. These adopt an octahedral geometry with the carbide close to the centre of the metal polyhedron.

These reactions emphasise the ease of the formation of mixed metal-iron carbido cluster complexes under relatively mild conditions, starting with non-carbido iron carbonyl cluster units.

We thank the S.E.R.C. for financial support and the Universidad Nacional Autónoma de México for a grant (to M.J.R.).

References

1 B.F.G. Johnson, D.A. Kaner, J. Lewis and P.R. Raithby, J. Organometal. Chem., 215 (1981) C33.
2 B.F.G. Johnson, D.A. Kaner, J. Lewis, P.R. Raithby and M.J. Taylor, J. Chem. Soc. Chem. Commun., (1982) in the press.
3 R.L. Pruett and J.S. Bradley, European Patent Application No. 81301398.4.
4 D.A. Kaner and P.R. Raithby, unpublished work.
5 P.F. Jackson, B.F.G. Johnson, J. Lewis, J.N. Nicholls, M. McPartlin and W.J.H. Nelson, J. Chem. Soc. Chem. Commun., (1980) 564.
6 M.A. Beno, J.M. Williams, M. Tachikawa and E.L. Muetterties, J. Am. Chem. Soc., 120 (1980) 4542.
7 E.M. Holt, K.H. Whitmire and D.F. Shriver, J. Organometal. Chem., 213 (1981) 125.
8 M. Tachikawa, A.C. Sievert, E.L. Muetterties, M.R. Thompson, C.S. Day and V.W. Day, J. Am. Chem. Soc., 102 (1980) 1725.
9 E.H. Braye, L.F. Dahl, W. Hübel and D.L. Wampler, J. Am. Chem. Soc., 84 (1962) 4633.
10 A. Sirigu, M. Bianchi, and E. Benedetti, J. Chem. Soc. Chem. Commun., (1969) 596; G.B. Ansell and J.S. Bradley, Acta Crystallogr., B, 36 (1980) 726.
11 R.F. Boehme and P. Coppens, Acta Crystallogr., B, 37 (1981) 1914.
12 B.F.G. Johnson, D.A. Kaner, J. Lewis, P.R. Raithby and M.J. Taylor, Polyhedron, (1982) in the press.
13 P. Bellon, M. Manassero and M. Sansoni, J. Chem. Soc. Dalton Trans., (1973) 2423.
14 V.G. Allano, B.L. Bellon, M. Manassero and M. Sansoni, J. Chem. Soc. Chem. Commun., (1970) 1210.
15 M. Tachikawa, R L. Geerts and E.L. Muetterties, J. Organometal. Chem., 213 (1981) 11.