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The First Uncharged Heterotrimetallic “Wing-bridged” Butterfly

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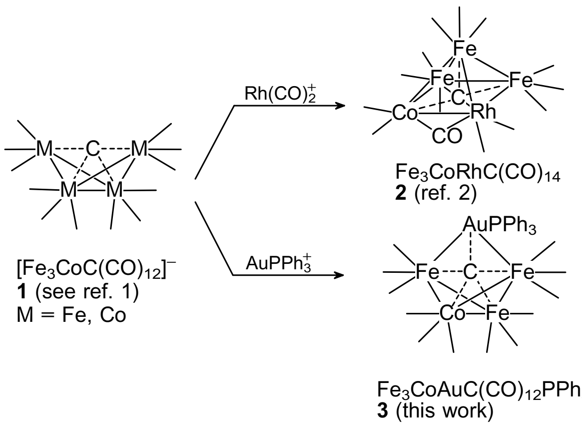
The reaction of $[Fe_3CoC(CO)_{12}]^-$ with $AuPPh_3^+$ leads to the new heterotrimetallic $Fe_3CoAuC(CO)_{12}PPh_3$ cluster with a wing-bridged butterfly geometry.

There is considerable interest in the synthesis and structure of heteropolymetallic clusters.[1] Many studies have been made in chemistry of heterobimetallic molecules of different nuclearity. However, known examples of heterotrimetallic clusters are relatively rare. Recently we reported[2] that bimetallic carbido carbonyl butterfly $[Fe_3CoC(CO)_{12}]^-$ **1** reacts with an electron-deficient $Rh(CO)_2^+$ group to form new heterotrimetallic $Fe_3CoRhC(CO)_{14}$ cluster **2**. A single crystal X-ray structure determination of the PPh_3-substituted derivative of the cluster **2** showed that its cluster core is a square pyramid with Co and Rh atoms *cis*-positioned in the basal plane with an interstitial "carbide" C atom bonded to all five metal atoms.

To extend this cluster series, we have investigated the addition of an $AuPPh_3^+$ group, isoelectronic with $Rh(CO)_2^+$, to the same anion **1**.



Scheme 1

The reaction (Scheme 1) leads to the same type of uncharged cluster $Fe_3CoAuC(CO)_{12}PPh_3$ **3**,[†] with composition and properties similar to **2** (taking into account the existence of one triphenylphosphine fragment ligand at the Au atom in **3** instead of two carbonyls at the Rh atom in **2**). However, the IR spectra of the clusters **2** and **3** in the regions ν_{CO} and ν_{M-C} differ dramatically from each other both by the position of the bands and by their shapes. The disagreement was much greater than one could expect for isostructural clusters. It was therefore suggested that the metal cores in **2** and **3** have different geometries, notwithstanding the same number of cluster valence electrons (CVE), 74, therein. This hypothesis has now been proved by a single crystal X-ray study of **3**.[‡]

The Fe_3Co asymmetric butterfly moiety in **3** with a carbide atom C(1) inside it is linked to an Au atom by two Fe–Au bonds through the wing-tip Fe atoms (Fig. 1). In accordance with the decrease of coordination abilities in late transition metals, the Au atom in **3** forms only two metal–metal bonds, whereas the Rh atom in **2** forms three such bonds. The closest coordination environment of the Au atom in **3** [C(1), P(1), Fe(1) and Fe(2)] is almost planar: the sum of the bonding angles at the Au atom equals 359.7°. Coordination of Au in **3** may be described alternatively as linear [C(1) and P(1) atoms, bond angle C(1)–Au–P(1) 177.1(3)°] with two symmetrically placed additional bonds Au–Fe(1) and Au–Fe(2). As compared to the Au atom in **3**, the Rh atom in **2** has a more uniform environment close to a distorted octahedral (three transition metal atoms and three CO ligands) with a carbide C atom as an asymmetric cap.

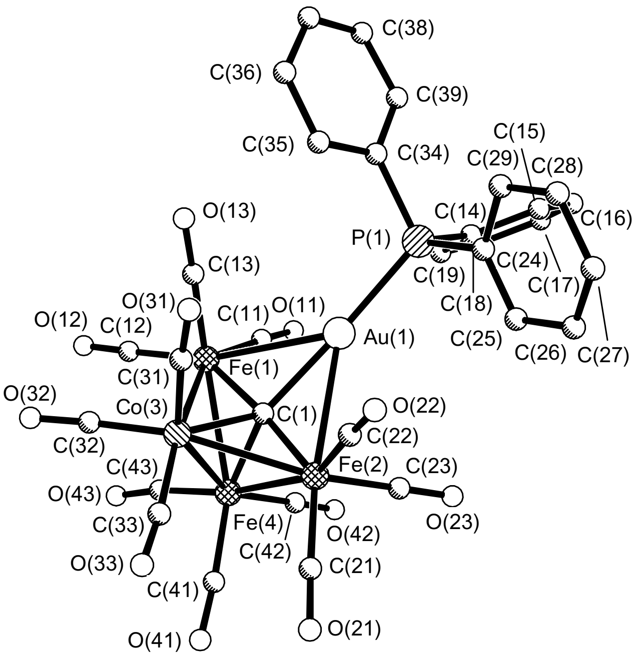


Fig. 1 Molecule **3** (H atoms omitted for clarity). Main interatomic distances/Å: Au–Fe(1) 2.880, Au–Fe(2) 2.813, Fe(1)–Fe(3) 2.616, Fe(1)–Co 2.615, Fe(2)–Fe(3) 2.631, Fe(2)–Co 2.633, Fe(3)–Co 2.517, Au–C(1) 2.086, Fe(1)–C(1) 1.855, Fe(2)–C(1) 1.837, Fe(3)–C(1) 1.921, Co–C(1) 1.941, Au–P 2.276, Fe–C(CO) 1.77–1.84, Co–C(CO) 1.77–1.81; significant bond angles/°: Fe(1)–Au–P 138.4, Fe(2)–Au–P 140.6, C(1)–Au–P 177.1(3), Fe(1)–C(1)–Au 93.7, Fe(1)–C(1)–Fe(3) 87.7, Fe(1)–C(1)–Co 87.08, Fe(2)–C(1)–Au 91.4, Fe(2)–C(1)–Fe(3) 88.8, Fe(2)–C(1)–Co 88.3, Au–C(1)–Fe(3) 150.5, Au–C(1)–Co 128.2, Fe(3)–C(1)–Co 81.3, Fe(1)–C(1)–Fe(2) 174.6. Esds: M–M 0.001, Au–P 0.001, Au–C 0.01, Co–C 0.01, Fe–C 0.01 Å (both for carbide atom and Co ligands); M–C(1)–M′ 0.5.

Each of the Fe and Co atoms in **3** is coordinated by three terminal CO ligands, bond distances M–CO 1.77–1.82(1) A (where M is a transition metal). The carbide C atom inside the open metal core has a distorted trigonal bipyramidal environment of five metal atoms with a noticeable asymmetry in Au–C–Co and Au–C–Fe(3) bond angles [128.2(5) and 150.5(5)°, respectively]. The non-bonded Au–Co [3.623(1) A] and Au–Fe(3) [3.875(1) A] intramolecular contacts are therefore different, and the metal cluster core strongly deviates from the idealised C_{2v} to C_s non-crystallographic symmetry. The Au–P bond distance of 2.276(1) A, together with other geometric parameters of the ligand environment in **3**, agree well with the known structural data.[3]

A similar M_4AuC geometry has been observed, for example, in the bimetallic $Fe_4AuC(\mu\text{-}H)(CO)_{12}(PPh_3)$, isolated in 47% yield from a reaction of the tetrahedral anion $[Fe_4(CO)_{13}]^{2-}$ with $ClAuPPh_3$.[4]

A variable directionality of the addition of different 12-electron metal-containing cations to heterometallic butterflies, mentioned above, provides wide scope for further investigation.

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[†] *Preparation of* **3**: $(Me_4N)[Fe_3CoC(CO)_{12}]$ **1a** (0.1 g, 0.15 mmol) was dissolved in CH_2Cl_2 (10 ml) at 25 °C. Excess $ClAuPPh_3$ was added and the suspension was stirred at room temperature for 5 min until the initially deep red solution turned brown. The solvent was removed and the residual solid extracted with pentane. Filtration followed by evaporation of the solution to dryness yielded $Fe_3CoAuC(CO)_{12}PPh_3$ (0.12 g, 0.12 mmol, 80%). After recrystallization from pentane (−5 °C) a black crystalline compound was obtained: IR, ν_{CO}/cm^{-1} (pentane) 2080m, 2034s, 2015s, 1989w; Nujol ν_{M-C}/cm^{-1} 796, 777sh, 740. Found: C 36.43, H 1.42. Calc. for $C_{31}H_{15}O_{12}PAuCoFe_3$: C 36.01, H 1.46%.

[‡] *Crystal data for* **3**: $C_{31}H_{15}O_{12}AuCoFe_3P$, $M = 1034$, triclinic, space group $P\bar{1}$, $a = 11.039(2)$, $b = 12.725(3)$, $c = 13.647(4)$ A, $\alpha = 79.00(2)$, $\beta = 81.09(2)$, $\gamma = 64.83(2)°$, $V = 1697(1)$ A , $Z = 2$, $D_c = 2.023$ g cm^{-3}. Experimental data were collected with a Syntex $P2_1$ diffractometer at −100 °C (λMoK_α, $\theta/2\theta$ scan, 5051 unique reflections up to $2\theta_{max} = 54°$). The structure was solved by direct methods and refined by full-matrix block-diagonal least-squares, using a PC version of SHELXTL PLUS programs. Absorption was corrected by the DIFABS procedure, all non-hydrogen atoms were refined in anisotropic approximation and H atoms were revealed in a Fourier difference map and refined isotropically. The location of the Co atom in the cluster core was found in the last stages of the refinement by a comparison of R values for each of the four sites in the butterfly moiety. Final values: $R = 0.043$, $R_w = 0.065$ with 4512 non-zero reflections ($I > 4\sigma$).

References

1 S. P. Gubin, *Koord. Khim.*, 1994, **20**, 403 (*Russ. J. Coord. Chem.*, 1994, **20**, 379).

2 S. P. Gubin, T. V. Galuzina, P. A. Kozmin, M. D. Surajskay and T. B. Larina, *Koord. Khim.*, 1994, **20**, 665 (*Russ. J. Coord. Chem.*, 1994, **20**, 627).

3 A. G. Orpen, L. Brammer, F. H. Allen, O. Kennard and D. G. Watson, *J. Chem. Soc., Dalton Trans.*, 1989, S1.

4 B. F. G. Jonson, D. A. Kaner, J. Lewis, P. R. Raithby and M. J. Rosales, *Organometallic Chem.*, 1982, **231**, 59.

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