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Synthesis of $[Au_3Fe_2(CO)_8(dppm)]^-$ and $[Au_5Fe_2(CO)_8(dppm)_2]^+$: X-ray Structures of $[NEt_4][Au_3Fe_2(CO)_8(dppm)]$ and $[Au_5Fe_2(CO)_8(dppm)_2][BF_4]$

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Summary: The $[Au_3Fe_2(CO)_8(dppm)]^-$ cluster anion has been isolated from the reaction of either $[AuFe_2(CO)_8]^{3-}$ or $[Fe(CO)_4]^{2-}$ with $Au_2(dppm)Cl_2$ in THF, whereas the $[Au_5Fe_2(CO)_8(dppm)_2]^+$ cluster cation has been obtained by oxidation of the former; both new compounds have been characterized by X-ray studies on their $[NEt_4][Au_3Fe_2(CO)_8(dppm)]$ and $[Au_5Fe_2(CO)_8(dppm)_2][BF_4]$ salts, respectively.

We have recently reported the synthesis and characterization of two bimetallic clusters: $[MFe_2(CO)_8]^{3-}$ and $[M_4Fe_4(CO)_{16}]^{4-}$ (M = Ag,Au).[1,2] The latter has been envisaged to be formally derived from complexation of an M_2^{2+} moiety with two $[MFe_2(CO)_8]^{3-}$ cluster ligands, which are isolobal[3] with bis(diphenylphosphino)methane (dppm). As a consequence of this analogy between $[M_4Fe_4(CO)_{16}]^{4-}$ and $[M_2(dppm)_2]^{2+}$,[4,5] substitution of a dppm ligand for an $[MFe_2(CO)_8]^{3-}$ moiety in $[M_4Fe_4(CO)_{16}]^{4-}$ was expected to afford an $[M_3Fe_2(CO)_8(dppm)]^-$ derivative. The synthesis and structural characterization of such a species (for M = Au) are reported. Further exploitation of the bonding capability of $[Au_3Fe_2(CO)_8(dppm)]^-$ has resulted in the synthesis of the $[Au_5Fe_2(CO)_8(dppm)_2]^+$ cluster cation, which has been characterized by X-ray studies as its tetrafluoroborate salt.

The orange-red $[Au_3Fe_2(CO)_8(dppm)]^-$ (ν_{CO} in THF at 1980 (mw), 1960 (m), and 1890 (s) cm^{-1}) has been obtained either from reaction of $Au_2(dppm)Cl_2$ with $[AuFe_2(CO)_8]^{3-}$ as suggested by isolobal analogy concepts (eq 1) or directly from the $[Fe(CO)_4]^{2-}$ dianion as shown in eq 2.

$$[AuFe_2(CO)_8]^{3-} + Au_2(dppm)Cl_2 \rightarrow [Au_3Fe_2(CO)_8(dppm)]^- + 2Cl^- \quad (1)$$

$$4[Fe(CO)_4]^{2-} + 4Au_2(dppm)Cl_2 \rightarrow 2[Au_3Fe_2(CO)_8(dppm)]^- + [Au_2(dppm)_2]^{2+} + 8Cl^- \quad (2)$$

The tetraethylammonium salt of $[Au_3Fe_2(CO)_8(dppm)]^-$ has been isolated by evaporation of the THF reaction solution and metathesis in methanol with NEt_4Cl.[6]

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(6) Solid $Na_2[Fe(CO)_4]\cdot xTHF$ (0.85 g; $x \sim 2$) and $Au_2(dppm)Cl_2$ (1.69 g) were charged in a Schlenk tube under nitrogen. Anhydrous THF (30 mL) was added. After 1 h of stirring, the resulting orange suspension was filtered and the solution was evaporated to dryness *in vacuo*. The residue was dissolved in methanol. Red crystals of $[NEt_4][Au_3Fe_2(CO)_8(dppm)]$ separated out from the above solution upon addition of NEt_4Cl (2 g) and water (10 mL) and upon standing; yields 62% (based on gold).

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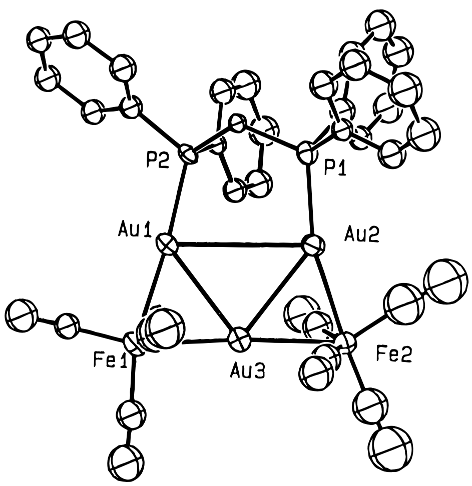

Figure 1. Molecular geometry of the $[Au_3Fe_2(CO)_8(dppm)]^-$ monoanion. Selected bond distances (Å) and angles (deg): Au(1)−Au(3), 2.921(2); Au(2)−Au(3), 2.921(2); Au(1)···Au(2), 3.578(2); Au(2)−Fe(2), 2.545(4); Au(3)−Fe(1), 2.572(4); Au(3)−Fe(2), 2.576(4); Au(1)−Fe(1), 2.554(4); Au(1)−P(2), 2.274(6); Au(2)−P(1), 2.267(7); Au(1)−Au(3)−Au(2), 75.53(4); Fe(1)−Au(3)−Fe(2), 172.7(2); P(2)−Au(1)−Fe(1), 170.8(2); P(1)−Au(2)−Fe(2), 165.7(2).

The $[Au_3Fe_2(CO)_8(dppm)]^-$ anion,[7] as shown in Figure 1, is roughly planar and consists of an isosceles Au_3 triangle with two shorter edges, spanned by $Fe(CO)_4$ groups, and a longer one bridged by a dppm ligand (Au(1)−Au(3) and Au(2)−Au(3) = 2.921(2) Å, Au(1)··· Au(2) = 3.578(2) Å). The opening up of the metal triangle cannot be ascribed to the strain imposed by the rather flexible dppm ligand. In fact shorter Au−Au bond distances have been reported for the $Au_2(\mu_2\text{-dppm})$ unit in $[Au_2Fe_2(CO)_8(\mu\text{-dppm})]$[10] and $[Au_2Fe(CO)_4(dppm)]_2$[11] (2.915(1) and 3.163(1) Å, respectively). The lengthening of the Au(1)···Au(2) contact seems dictated by the preference for the linear coordination of the Au(I) complexes. The idealized molecular symmetry is C_s.

Reaction 2 has previously been reported to afford $[Au_2Fe(CO)_4(dppm)]_2$.[11] We have obtained red crystals of the latter by layering toluene on the nonmetathesized THF solution of reaction 2. These results stem from the occurrence in solution of equilibrium 3, which is strongly influenced by the dielectric constant of the solvent and is completely shifted to the left in several organic solvents such as THF, acetone, and acetonitrile. Related comproportionation−disproportionation equilibria are documented in copper chemistry (e.g. $Cu_2Fe(CO)_4(PPh_3)_4$ and $Cu_2Fe(CO)_4(dppe)_2$; dppe = bis(diphenylphosphino)ethane),[12] but not for gold compounds (e.g. $Au_2Fe(CO)_4(PcHex_3)_2$,[13] $Au_2Fe(CO)_4(PPh_3)_2$,[14,15] $[AuFe_2(CO)_8(PPh_3)]^-$,[16] $[AuFe_3(CO)_{11}(PPh_3)]^-$,[17] and $Au_2Fe_2(CO)_8(dppm)$[10]).

$$2[Au_3Fe_2(CO)_8(dppm)]^- + [Au_2(dppm)_2]^{2+} \rightleftarrows 2[Au_2Fe(CO)_4(dppm)]_2 \quad (3)$$

The orange-red $[Au_3Fe_2(CO)_8(dppm)]^-$ anion contains two cis-divacant octahedral $Fe(CO)_4$ moieties of C_{2v} symmetry that are capable of further bonding. A slight stereochemical rearrangement of the above moiety, for instance that derived from an equatorially trivacant pentagonal bipyramid, should make available a further filled σ orbital on each iron, as found in $[M_5Fe_4(CO)_{16}]^{3-}$ (M = Cu, Ag).[1,18] Therefore, $[Au_3Fe_2(CO)_8(dppm)]^-$ is potentially a bidentate cluster ligand isolobal with dppm. This consideration led us to investigate the further condensation of $[Au_3Fe_2(CO)_8(dppm)]^-$ with $Au_2(dppm)Cl_2$ to give a $[Au_5Fe_2(CO)_8(dppm)_2]^+$ cluster cation. Reaction 4 occurs in $CHCl_3$ upon addition of $Au_2(dppm)Cl_2$ in slight excess.[19] The red $[Au_5Fe_2(CO)_8(dppm)_2]^+$ (ν_{CO} at 2005 (s) and 1950 (s) cm^{-1}) cation has been alternatively obtained in good yields by oxidation in acetonitrile solution of $[Au_3Fe_2(CO)_8(dppm)]^-$ with tropylium tetrafluoroborate.[20] The resulting $[Au_5Fe_2(CO)_8(dppm)_2][BF_4]$ salt has been crystallized by layering of diisopropyl ether, and its molecular structure has been determined by X-ray crystallography.[21]

$$[Au_3Fe_2(CO)_8(dppm)]^- + Au_2(dppm)Cl_2 \rightarrow [Au_5Fe_2(CO)_8(dppm)_2]^+ + 2Cl^- \quad (4)$$

The structure of the cation $[Au_5Fe_2(CO)_8(dppm)_2]^+$ is shown in Figure 2. The unit cell contains two cations positioned around nonequivalent inversion centers, and therefore, each cation conforms to a precise C_i symmetry. The idealized symmetry of each cation is C_{2h},

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[7] Crystal data for $[NEt_4][Au_3Fe_2(CO)_8(dppm)]$: M_r = 1441.30, monoclinic, space group $P2_1/c$ (No. 14), a = 17.720(4) Å, b = 11.785(4) Å, c = 23.837(6) Å, β = 111.60(2)°, V = 4628(2) Å^3, Z = 4, D_c = 2.068 Mg m^{-3}, $F(000)$ = 2712, λ = 0.710 73 Å, T = 298 K, μ(Mo Kα) = 10.205 mm^{-1}. Data were collected on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo Kα radiation (ω scan mode). A total of 4296 independent reflections were collected to $2\theta_{max}$ = 40° and corrected for the effects of decay and absorption. Direct methods (SHELXS 86)[8] identified the positions of the metal atoms, and iterative cycles of least-squares refinement (on F^2) and difference Fourier synthesis located the remaining non-hydrogen atoms. The metal atoms were refined anisotropically, and the hydrogen atoms were placed in calculated positions (C−H = 0.96 Å). Refinement on F^2 (SHELXL 93)[9] against 4256 data led to final convergence with R1 = 0.0599, wR2 = 0.1175, and S = 1.072 ($F_o > 4\sigma(F_o)$) for 212 refined parameters.

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[15] As deduced from IR monitoring, only very minor amounts of a related $[Au_3Fe_2(CO)_8(PPh_3)_2]^-$ intermediate were detectable in the corresponding reaction of $Au(PPh_3)Cl$ with the $[Fe(CO)_4]^{2-}$ dianion.

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[19] In spite of the stability of $[Au_5Fe_2(CO)_8(dppm)_2]^+$ in most solvents with both high and low dielectric constant, reaction 4 is strongly affected by the nature of the solvent and affords several other products, which are currently under investigation.

[20] $[NEt_4][Au_3Fe_2(CO)_8(dppm)]$ (1.2 g) was dissolved in acetonitrile (30 mL), and solid tropylium tetrafluoroborate (0.2 g) was added with stirring. After 1 h of stirring, the resulting red reaction mixture was evaporated to dryness. The residue was dissolved in acetonitrile (20 mL), and the suspension was filtered. $[Au_5Fe_2(CO)_8(dppm)_2][BF_4]$ was precipitated as red crystals by layering diisopropyl ether (30 mL) on top of the solution; yield 73% (based on gold).

[21] Crystal data for $[Au_5Fe_2(CO)_8(dppm)_2][BF_4]$: M_r = 2182.20, triclinic, space group $P\bar{1}$ (No. 2), a = 10.051(4) Å, b = 10.086(2) Å, c = 33.284(6) Å, α = 87.79(1)°, β = 111.60(2)°, γ = 82.17(2)°, V = 3318(2) Å^3, Z = 2, D_c = 2.185 Mg m^{-3}, $F(000)$ = 2020, λ = 0.710 73 Å, T = 298 K, μ(Mo Kα) = 11.592 mm^{-1}. Data collection, refinement, and solution were carried out as above.[7] A total of 11 672 independent reflections were collected ($2\theta_{max}$ = 54°). Refinement on F^2 against 11 607 data led to final convergence with R1 = 0.0794, wR2 = 0.1770, and S = 1.076 ($F_o > 4\sigma(F_o)$) for 316 refined parameters.

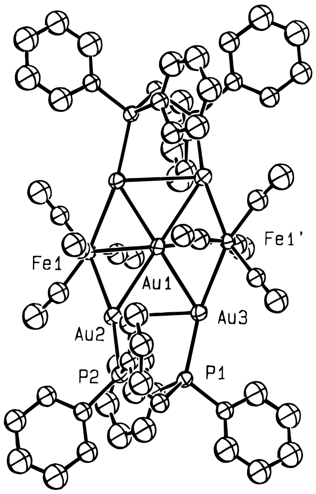

Figure 2. Structure of one of the two independent cations (**A**) of $[Au_5Fe_2(CO)_8(dppm)_2]^+$. The cations sit on inversion centers. Selected bond distances (Å) and angles (deg) for **A** and **B** (in brackets): Au(1)−Au(2), 2.924(1) [2.630(1)]; Au(1)−Au(3), 2.717(1) [2.840(1)]; Au(2)−Au(3), 3.051(2) [3.312(2)]; Au(1)−Fe(1), 2.533(3) [2.751(3)]; Au(2)−Fe(1), 2.607(3) [2.650(4)]; Au(3)−Fe(1′), 2.750(4) [2.438(3)]; Au(2)−P(1), 2.329(6) [2.277(7)]; Au(3)−P(2), 2.398(6) [2.139(6)]; Fe(1)−Au(2)−P(1), 166.2(2) [165.9(2)]; Fe(1′)−Au(3)−P(2), 170.0(2) [168.9(2)].

with the mirror plane containing the iron atoms. The two independent half-molecules have the same overall conformations, and therefore, they are chemically equivalent. The metal frameworks of the cations consist of a "bow tie" of gold atoms whose tips are bridged by dppm ligands, whereas the $Fe(CO)_4$ units are triply bridging the central and two apical gold atoms. The central Au atoms sit on inversion centers, and the gold frames are therefore planar. The $Fe(CO)_4$ units adopt idealized C_s symmetry with the two iron atoms pointing upward and downward with respect to the Au_5 plane (distance from the plane ±0.92 Å). One axial carbonyl in each $Fe(CO)_4$ group is leaning on the central gold, while the other is almost orthogonal to the metal frame. The Au−Fe (range 2.438(3)−2.750(3) Å) and Au−Au interactions are rather scattered (Au(center)−Au(periphery) range, 2.630−2.924(1) Å; Au(periphery)−Au(periphery), 3.051 and 3.312(2) Å). Nevertheless, the average values of all Au−Fe and Au−Au interatomic separations in the two independent cations are very close. A similar effect was found for the two deformation isomers of $[Au_4Fe_4(CO)_{16}]^{4-}$.[2] The Au−P distances are in the range 2.139−2.398(6) Å. The figures quoted above show great variability within each set of chemically equivalent bonds; therefore, the solid-state structures of these soft molecules are valuable only to assess the general stereogeometry, since the bond distances are intrinsically ill-defined to tenths of an angstrom.

A simple rationalization of the molecular structures of $[Au_3Fe_2(CO)_8(dppm)]^-$ and $[Au_5Fe_2(CO)_8(dppm)_2]^+$ is in terms of relatively strong Au−Fe and Au−P bonds around linearly coordinated Au(I) units, in addition to secondary aurophilic[22] interactions. The above features enable a Tinkertoy construction of clusters according to isolobal analogy concepts. Finally, it is worth noting that substitution of dppm for PPh_3 as ancillary ligand in the Au−Fe clusters triggers the occurrence in solution of disproportionation equilibria (e.g. equilibrium 3), which appear to be tunable as a function of the dielectric constant of the solvent and/or the phosphine ligand.

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Supporting Information Available: Tables of crystal data and data collection details, fractional coordinates and *U* values, bond distances and angles, and anisotropic thermal parameters for $[NEt_4][Au_3Fe_2(CO)_8(dppm)]$ and $[Au_5Fe_2(CO)_8(dppm)_2][BF_4]$ (29 pages). Ordering information is given on any current masthead page.

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