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### Synthesis and structural characterization of [NEt<sub>4</sub>][Fe<sub>3</sub>( $\mu_3$ -O)( $\mu_3$ -AuPPh<sub>3</sub>)( $\mu$ -CO)<sub>3</sub>(CO)<sub>6</sub>], the new [Au<sub>6</sub>( $\mu_3$ -S)<sub>2</sub>(PPh<sub>3</sub>)<sub>6</sub>][Fe<sub>3</sub>( $\mu_3$ -S)( $\mu$ -AuPPh<sub>3</sub>)(CO)<sub>9</sub>]<sub>2</sub> and [Au<sub>6</sub>( $\mu_3$ -S)<sub>2</sub>(PPh<sub>3</sub>)<sub>6</sub>][Fe<sub>5</sub>( $\mu_3$ -S)<sub>2</sub>(CO)<sub>14</sub>] ionic solids containing assemblages of cluster-cations and cluster-anions

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#### Abstract

The new  $[Fe_3(\mu_3-O)(\mu_3-AuPPh_3)(\mu-CO)_3(CO)_6]^-$  and  $[Fe_3(\mu_3-S)(\mu-AuPPh_3)(CO)_9]^-$  monoanionic congeners have been obtained by reacting the  $[Fe_3(\mu_3-E)(CO)_9]^2^-$  (E = O, S) dianions with one equivalent of Au(PPh\_3)Cl. The gold adduct of the oxygen derivative has been crystallized as tetraethylammonium and trimethylbenzylammonium salt either from THF and n-hexane or acetone and isopropyl alcohol, and structurally characterized in its tetraethylammonium salt (monoclinic, C2/c (No. 15), a = 15.859(2), b = 12.859(2), c = 40.217(8) Å,  $\beta = 96.41(1)^{\circ} Z = 8$ ). The  $[Fe_3(\mu_3-S)(\mu-AuPPh_3)(CO)_9]^-$  gold adduct, in contrast, partially reverts to the parent dianion upon crystallization under the above experimental conditions, and could be precipitated only as the  $[Au_6(\mu_3-S)_2(PPh_3)_6][Fe_3(\mu_3-S)(\mu-AuPPh_3)(CO)_9]_2$  salt (triclinic,  $P\bar{1}$  (No. 2), a = 18.998(8), b = 19.933(8), c = 22.94(1) Å,  $\alpha = 99.91(4)$ ,  $\beta = 98.91(4)$ ,  $\gamma = 107.42(3)^{\circ}$ , Z = 2), by addition of an equivalent of the  $[Au_3(\mu_3-S)(PPh_3)_3]^+$  sulfonium cation to the reaction mixture. The  $[Fe_5(\mu_3-S)_2(CO)_{14}]^2^-$  dianion does not form a gold adduct even in the presence of the sulfonium cation and only the corresponding  $[Au_6(\mu_3-S)_2(PPh_3)_6][Fe_5(\mu_3-S)_2(CO)_{14}]$  salt could be obtained. The  $[Fe_3(\mu_3-O)(\mu_3-AuPPh_3)(\mu-CO)_3(CO)_6]^$ and  $[Fe_3(\mu_3-S)(\mu-AuPPh_3)(CO)_9]^-$  gold adducts are not isostructural and the possible factors leading to their structural diversities are discussed. The  $[Au_6(\mu_3-S)_2(PPh_3)_6][Fe_3(\mu_3-S)(\mu-AuPPh_3)(CO)_9]_2$  and  $[Au_6(\mu_3-S)_2(PPh_3)_6][Fe_5(\mu_3-S)((\mu-AuPPh_3)(CO)_9]_2$  and  $[Au_6(\mu_3-S)_2(PPh_3)_6][Fe_5(\mu_3-S)_2(CO)_{14}]$  salts represent further examples of ionic solids assembled from cluster-cations and cluster-anions. © 1999 Elsevier Science S.A. All rights reserved.

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#### 1. Introduction

Gold exhibits pronounced oxo- and thio-philicity as shown by the existence of  $[(PR_3Au)_3E]^+$  (R = alkyl or aryl substituent; E = O [1], S [2]) cations and hypercoordinated tetrahedral  $[(P(o-Tol)_3Au)_4O]^{2+}$ [3] and square-pyramidal  $[(PPh_3Au)_4S]^{2+}$  [4] dications. Their unexpected stability has been interpreted in terms of *auriophilicity*, that is formation of intramolecular subvan der Waals Au–Au contacts [5]. These studies were originally inspired by the LAu<sup>+</sup>–H<sup>+</sup> isolobal analogy [6].

In view of the existence of the above oxonium and sulfonium cations and the different reactivity of  $[Fe_3(\mu_3-E)(CO)_9]^{2-}$  (E = O [7], S [8], Se [8h,9,10], Te [8h,11,12]) with the isolobal H<sup>+</sup> and CH<sub>3</sub><sup>+</sup> fragments, we became interested in examining the reaction of  $[Fe_3(\mu_3-O)(CO)_9]^{2-}$  and  $[Fe_3(\mu_3-S)(CO)_9]^{2-}$  with

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 $[Au(PPh_3)]^+$ . Indeed, the proton attacks the  $\mu_3$ -O capping heteroatom in  $[Fe_3(\mu_3-O)(CO)_9]^2$  to give  $[Fe_3(\mu_3-O)(CO)_9]^2$ OH)(CO)<sub>0</sub>]<sup>-</sup> [7], at difference of the  $[Fe_3(\mu_3-E)(CO)_0]^2$ <sup>-</sup> (E = S [8], Se [9,10], Te [11,12]) congeners, where it has been shown to span an Fe-Fe edge. On the other side, carbocations such as  $CH_3^+$  bind to E=O and S [7,8g,h], but give rise to iron  $\sigma$ -alkyls when E is a Se or a Te heteroatom [8h]. Such differential reactivity is in keeping with the expected relative strength of the E-R and Fe-R $(R = H, CH_3)$  bonds, as well as the nucleophilicity of the  $\mu_3$ -E capping heteroatom. Indeed, the lone pair increasingly becomes more diffuse and the fractional negative charge delocalized onto the heteroatom decreases on descending the group. That is inferable from the progressive shortening of the Fe-C and lengthening of the C-O bond distances, which point out a progressively increasing back-donation onto the CO ligands on going from  $[Fe_3(\mu_3-O)(CO)_9]^2$  to its heavier congeners [7,8d,e,10].

In keeping with an increased negative charge delocalized on the Fe<sub>3</sub> triangle, the corresponding attack of  $[Au(PPh_3)]^+$  also occurs at an Fe–Fe edge for E = Te [11]. On the contrary, the coordination site of gold for the lighter  $[Fe_3(\mu_3-E)(CO)_9]^{2-}$  (E = O, S and Se) congeners is yet unknown. Only the reaction of  $[Fe_3(\mu_3-S)(CO)_9]^{2-}$  with Au(PPh\_3)Cl has previously been investigated; the neutral Fe<sub>3</sub>( $\mu_3$ -S)( $\mu_3$ -AuPPh\_3)( $\mu_4$ -Au-PPh\_3)(CO)<sub>9</sub> bis-adduct was isolated with no evidence of the intermediate formation of the mono-gold adduct [8c].

It was, therefore, of interest to verify whether the greatest nucleophilicity of the oxygen heteroatom and the oxophilicity of gold could lead to the formation of a  $[Fe_3(\mu_3-O \rightarrow AuPPh_3)(CO)_9]^-$  adduct with a dangling AuPPh<sub>3</sub> moiety, or a butterfly  $[Fe_3Au(\mu_4-O)(CO)_9-$ (PPh<sub>3</sub>)]<sup>-</sup> and, eventually, a capped square-pyramidal  $Fe_3Au_2(\mu_4-O)(CO)_9(PPh_3)_2$ , related to  $[Fe_3Mn(\mu_4 O(CO)_{12}^{-1}$  [13] and  $[Fe_2Ru_3(\mu_4-O)(CO)_{14}^{-1}]^{-1}$ , respectively, [14]. These studies resulted in the synthesis and structural characterization of the new  $[Fe_3(\mu_3-O)(\mu_3 AuPPh_3(\mu-CO)_3(CO)_6]^$ and  $[Fe_3(\mu_3-S)(\mu-AuPPh_3)-$ (CO)<sub>9</sub>]<sup>-</sup> monoanionic congeners. The latter is isostructural with the previously reported  $[Fe_3(\mu_3-Te)(\mu_3-Te)]$  $AuPPh_3(CO)_9$  derivative [11]. As a corollary, we have isolated and characterized the  $[Au_6(\mu_3-S)_2(PPh_3)_6]$ - $[Fe_3(\mu_3-S)(\mu-AuPPh_3)(CO)_9]_2$  and  $[Au_6(\mu_3-S)_2(PPh_3)_6]_ [Fe_5(\mu_3-S)_2(CO)_{14}]$  salts, which represent new examples of ionic solids assembled from cluster-cations and clusteranions [15-17].

#### 2. Results and discussion

## 2.1. Synthesis of $[Fe_3(\mu_3-O)(\mu_3-AuPPh_3)(CO)_6 (\mu-CO)_3]^-$ and $[Fe_3(\mu_3-S)(\mu-AuPPh_3)(CO)_9]^-$

The  $[Fe_3(\mu_3-E)(CO)_9]^{2-}$  (E = O, S) salts readily react with Au(PPh\_3)Cl in a 1:1 molar ratio in most organic

solvents such as THF, acetone and acetonitrile. The formation of the  $[Fe_3(E)(AuPPh_3)(CO)_9]^-$  adducts is signaled by a darkening of the solution, which turns dark red from orange-red, and a shift of ca.  $40 \text{ cm}^{-1}$  to higher wavenumbers of the infrared carbonyl absorptions. The conversion of  $[Fe_3(\mu_3-O)(CO)_0]^2$  into the  $[Fe_3(O)-$ (AuPPh<sub>3</sub>)(CO)<sub>9</sub>]<sup>-</sup> adduct is quantitative, as inferable from the infrared spectrum at the end of the reaction, which shows complete disappearance of absorptions attributable to the starting material. The reaction solution of the  $[Fe_3(O)(AuPPh_3)(CO)_9]^-$  (v(CO) in THF at 2017 mw, 1970 s, 1960 sh, 1939 sh, 1912 mw cm<sup>-1</sup>) adduct displays an IR pattern and absorption wavenumbers very similar to those featured by the butterfly  $[Fe_3(\mu_3-Te)(\mu-AuPPh_3)(CO)_9]^-$  (v(CO) in THF at 2016 mw, 1975 s, 1962 sh, 1931 sh cm<sup>-1</sup>) [11] congener. The [NEt<sub>4</sub>]<sup>+</sup> and [NMe<sub>3</sub>CH<sub>2</sub>Ph]<sup>+</sup> salts of the [Fe<sub>3</sub>(O)-(AuPPh<sub>3</sub>)(CO)<sub>9</sub>]<sup>-</sup> anion have been isolated in a pure crystalline state in 70-80% yields by evaporation in vacuum of the reaction solution, extraction in THF and precipitation with n-hexane.

The [NEt<sub>4</sub>][Fe<sub>3</sub>(S)(AuPPh<sub>3</sub>)(CO)<sub>9</sub>] adduct shows infrared carbonyl absorptions (v(CO) in THF at 2019 mw, 1971 s, 1962 sh, 1933 m, 1915 mw cm<sup>-1</sup>) almost identical to those of [Fe<sub>3</sub>(O)(AuPPh<sub>3</sub>)(CO)<sub>9</sub>], but different from the latter as it undergoes a dissociation equilibrium in solution, as a function of the polarity of the solvent. As a result, its crystallization in analogous conditions, as well as in other solvents, gives rise to mixtures of orange and red crystals of the starting  $[NEt_4]_2[Fe_3(S)(CO)_9]$ material and [NEt<sub>4</sub>][Fe<sub>3</sub>(S)(AuPPh<sub>3</sub>)(CO)<sub>9</sub>], respectively. The above equilibrium shifts almost completely toward dissociation upon crystallization of the corresponding  $[NMe_4]^+$  and  $[NMe_3CH_2Ph]^+$  salts, as a result of the lower solubility of these salts of  $[Fe_3(S)(CO)_9]^2$  with respect to [Fe<sub>3</sub>(S)(AuPPh<sub>3</sub>)(CO)<sub>9</sub>]-; this may explain previous failures in observing the formation of this mono-gold adduct [8c]. It has been, therefore, necessary to modify the reaction conditions in order to isolate the butterfly  $[Fe_3(\mu_3-S)(\mu-AuPPh_3)(CO)_9]^-$  monoanion as a pure salt (see later). The mechanically separated crystals of [NEt<sub>4</sub>][Fe<sub>3</sub>(S)(AuPPh<sub>3</sub>)(CO)<sub>9</sub>] show an infrared spectrum in nujol mull very similar to that of the mother liquor solution (v(CO) at 2018 mw, 1960 s, 1953 sh, 1930 sh, 1910 sh cm $^{-1}$ ).

In contrast, it was immediately apparent that an isomer different from the one present in solution was obtained upon crystallization of both the  $[NEt_4]^+$  and  $[NMe_3CH_2Ph]^+$  salts of the  $[Fe_3(O)(AuPPh_3)(CO)_9]^-$  adduct. Indeed, their crystals in nujol mull show infrared carbonyl absorptions both in the terminal (2010 mw, 1954 s and 1910 s cm<sup>-1</sup>) and bridging (1790 ms cm<sup>-1</sup>) region. The bridging carbonyl absorptions were unequivocally absent in the mother liquor solution before crystallization. Accordingly, the determination

by X-ray diffraction studies (see later) of the structure of the  $[NEt_4]^+$  salt has disclosed a trigonal bipyramidal  $[Fe_3(\mu_3-O)(\mu_3-AuPPh_3)(\mu-CO)_3(CO)_6]^-$  geometry, the apices of which are the oxygen atom and the  $[Au(PPh_3)]^+$  moiety.

The  $[Fe_3(\mu_3-O)(\mu_3-AuPPh_3)(\mu-CO)_3(CO)_6]^-$  monoanion re-isomerizes to the butterfly  $[Fe_3(\mu_3-O)(\mu-$ AuPPh<sub>3</sub>)(CO)<sub>9</sub>]<sup>-</sup> upon dissolving its salts in most organic solvents (e.g. CH<sub>3</sub>CN, THF, acetone and CH<sub>2</sub>Cl<sub>2</sub>), as shown by the almost complete disappearance of absorptions around 1790 cm<sup>-1</sup>. Besides, evaporation of the solvent under vacuum gives a dark red solid material which in nujol mull does not exhibit bridging carbonyl absorptions, the IR pattern being very similar to that of  $[Fe_3(\mu_3-E)(\mu-AuPPh_3)(CO)_9]^-$  (E = S, Te [11]). Moreover, it has been observed that further isomerization can occur by dissolving and drying the same sample under vacuum. After a few cycles a yet different IR spectrum is observed, which could be interpreted as arising from the presence of the  $[Fe_3(\mu_3 - O \rightarrow AuPPh_3)(CO)_9]^-$  (v(CO) in THF at 2039 mw, 1970 s, 1944 ms, 1916 m cm<sup>-1</sup>) isomer and trace amounts of the starting  $[Fe_3(\mu_3 O(CO)_{9}^{2}$  dianion. A related dangling adduct of  $[Fe_3(\mu_3-S)(CO)_9]^2$  with the isolobal Re(CO)<sub>5</sub> fragment has already been reported [18]. The above suggestion stems from the close similarity, both in pattern and wavenumbers, between the above IR spectrum and that of the  $[Fe_3(\mu_3-OR)(CO)_9]^-$  (R = H, Me, SiMe<sub>3</sub>) [7] derivative. In conclusion, there are unequivocal IR spectroscopic evidences that the mono-gold  $[Fe_3(O)(AuPPh_3)(CO)_9]^-$  adduct can exist in three different isomers, that is  $[Fe_3(\mu_3-O \rightarrow AuPPh_3)(CO)_9]^-$ ,  $[Fe_3(\mu_3-O)(\mu-AuPPh_3)(CO)_9]^$ and  $[Fe_{3}(\mu_{3}-O)(\mu_{3}-$ AuPPh<sub>3</sub>)( $\mu$ -CO)<sub>3</sub>(CO)<sub>6</sub>]<sup>-</sup>; the former two are stable in solution and the latter in the solid state. The stabilization of the most compact and symmetrical isomer in the solid state is not fortuitous. Very likely a higher steric regularity allows a more efficient packing and consequent lower solubility of this isomer that can selectively crystallize even if it is present in minor amounts in solution.

It was of interest to confirm the above isomerization equilibria in solution by variable temperature <sup>13</sup>C NMR studies. Unfortunately, isotopic exchange of  $[Fe_3(O)(AuPPh_3)(CO)_9]^-$  with <sup>13</sup>CO was hindered by its rapid degradation under a carbon monoxide atmosphere, which leads to a mixture of the well-known  $Au_2Fe(CO)_4(PPh_3)_2[19,20]$  and  $[HFe_3(CO)_{11}]^-$  [21] compounds.

Returning to the  $[Fe_3(\mu_3-S)(\mu-AuPPh_3)(CO)_9]^-$  adduct, in the attempt to isolate its pure salts, we decided to carry out the crystallization in the presence of the  $[Au_3(\mu_3-S)(PPh_3)_3]^+$  sulfonium cation, [2,22] hopping that this could behave as an effective source of  $[Au(PPh_3)]^+$  fragments and depress dissociation of the former. Indeed, it is well known that its corresponding

 $[Au_3(\mu_3-O)(PPh_3)_3]^+$  oxonium cation is a good alternative to Au(PPh<sub>3</sub>)Cl or Au(PPh<sub>3</sub>)Cl-TlPF<sub>6</sub> mixtures for the addition of [Au(PPh<sub>3</sub>)]<sup>+</sup> fragments to cluster compounds [23,24]. In doing that, we have isolated pure crystals of a salt-like compound in which both cations and anions are molecular clusters, that is  $[Au_6(\mu_3-S)_2 (PPh_3)_6$ [[Fe<sub>3</sub>( $\mu_3$ -S)( $\mu$ -AuPPh<sub>3</sub>)(CO)<sub>9</sub>]<sub>2</sub> salt. Several examples of such ionic solids are already known [15-17]. These have been obtained serendipitously [15-17] or by charge-transfer reaction between the parent neutral species [16]. Most of them are constituted by  $M_4Cp_4X_4$ (M = Cr, Mo, Fe; X = S, Se) cubane mono-cations and  $Fe_4(NO)_4S_4$  cubane mono-anions. Cluster salts involving a carbonyl cluster anion, e.g. the  $[Os_6(CO)_{18}]^{2-}$  dianion [16], or both a carbonyl cluster cation and a carbonyl cluster anion [15] are also documented. To the best of our knowledge, however, the  $[Au_6(\mu_3-S)_2(PPh_3)_6][Fe_3(\mu_3-S)_2(PPh_3)][Fe_3(\mu_3-S)_2(PPh_3)][Fe_3(\mu_3-S)_2(PPh_3)][Fe_3(\mu_3-S)_2(PPh_3)][Fe_3(\mu_3-S)_2(PPh_3)][Fe_3(\mu_3-S)_2(PPh_3)][Fe_3(\mu_3-S)_2(PPh_3)][Fe_3(\mu_3-S)_2(PPh_3)][Fe_3(\mu_3-S)_2(PPh_3)][Fe_3(\mu_3-S)_2(PPh_3)]$  $S(\mu-AuPPh_3)(CO)_9]_2$  and the related  $[Au_6(\mu_3-S)_2(PPh_3)_6]$  $[Fe_5(\mu_3\text{-}S)_2(CO)_{14}]$  salt described below are the first examples of ionic compounds assembled from preformed cluster-cations and cluster-anions. Reactions of cluster cations (e.g.  $[Au_3(\mu_3-O)(PPh_3)_3]^+$ ) with cluster anions have previously been investigated. However, they were aimed at increasing the cluster nuclearity either by condensation or addition of single  $[Au(PPh_3)]^+$  moieties, and the observed results were in keeping with the objectives [23,24]. Evidently, the  $[Au_3(\mu_3-S)(PPh_3)_3]^+$  is much less effective than  $[Au_3(\mu_3-O)(PPh_3)_3]^+$  in releasing  $[Au(PPh_3)]^+$ fragments  $[Fe_{3}(\mu_{3}-S)(\mu_$ and  $AuPPh_3)(CO)_9]^$ is little prone to give the di-gold derivatives under the above experimental conditions.

To better exploit the possibility of isolating ionic solids made by a cluster cation and a cluster anion, we investigated the reaction of the  $[Au_3(\mu_3-S)(PPh_3)_3]^+$ sulfonium cation with the  $[Fe_5(\mu_3-S)_2(CO)_{14}]^2^-$  dianion [8d,f], in the presence or not of an equimolar amount of Au(PPh\_3)Cl. In all cases we succeeded in isolating only  $[Au_6(\mu_3-S)_2(PPh_3)_6][Fe_5(\mu_3-S)_2(CO)_{14}]^1$  No evidence was obtained for the possible formation of a mono-gold adduct of  $[Fe_5(\mu_3-S)_2(CO)_{14}]^2^-$ , corresponding to  $[HFe_5(\mu_3-S)_2(CO)_{14}]^-$  [8f]. Likewise, we do not have any evidence of a charge transfer from the anion to the cation, which could lead to the oxidized  $[Fe_5(\mu_3-S)_2(CO)_{14}]^n - (n = 0, 1)$  congener [8f]. This stems from the low redox propensity of the  $[Au_6(\mu_3-S)_2(PPh_3)_6]^2^+$ dication.

In any case, the isolation of  $[Au_6(\mu_3-S)_2(PPh_3)_6]$ - $[Fe_3(\mu_3-S)(\mu-AuPPh_3)(CO)_9]_2$  and  $[Au_6(\mu_3-S)_2(PPh_3)_6]$ -

<sup>&</sup>lt;sup>1</sup> The dimeric nature of the gold cation in  $[Au_6(\mu_3-S)_2-(PPh_3)_6][Fe_5(\mu_3-S)_2(CO)_{14}]$  has been determined by an X-ray diffraction study (triclinic, space group  $P\bar{1}$ , a = 13.234(4), b = 20.56(1), c = 22.267(9) Å,  $\alpha = 90.53(4)$ ,  $\beta = 96.59(3)$ ,  $\gamma = 98.54(3)^{\circ}$ . Z = 2). Because of the poor quality of the crystal, only the positions of the heavier atoms were determined with reasonable accuracy and therefore details of the structural study are not reported.

 $[Fe_5(\mu_3-S)_2(CO)_{14}]$  shows that preparation of ionic solids assembled from cluster-cations and cluster-anions is more general than expected, and its exploitation could lead to interesting new materials.

2.2. The X ray molecular structures of  $[NEt_4][Fe_3(\mu_3-O)(\mu_3-AuPPh_3)(\mu-CO)_3(CO)_6]$  and  $[Au_6(\mu_3-S)_2(PPh_3)_6][Fe_3(\mu_3-S)(\mu-AuPPh_3)(CO)_9]_2$ 

### 2.2.1. Molecular structure of $[Fe_3(\mu_3-O)(\mu_3-AuPPh_3)-(\mu-CO)_3(CO)_6]^-$ as its $[NEt_4]^+$ salt

The solid state structure of the anion of  $[Fe_3(\mu_3 -$ O)( $\mu_3$ -AuPPh<sub>3</sub>)( $\mu$ -CO)<sub>3</sub>(CO)<sub>6</sub>]<sup>-</sup> is shown in Fig. 1 and relevant bond lengths and angles are reported in Table 1. The anion contains a  $Fe_3$  triangle whose edges are spanned by three bridging CO ligands; the remaining six CO groups are terminally bonded in a  $C_{3v}$  array of the fragment. A  $\mu_3$ -O<sup>2-</sup> anion and a  $\mu_3$ -Au(PPh<sub>3</sub>)<sup>+</sup> cation cap the faces of the Fe<sub>3</sub> triangle. The idealized symmetry of the anion is  $C_{3v}$  if only the *ipso* atoms of the phenyl rings are considered; a  $C_3$  symmetry is a good approximation of the anion as a whole. The Fe-Fe interactions are very close each other (2.528, 2.528, 2.488(4) Å) and slightly longer than those observed in the parent  $[Fe_3(\mu_3-O)(CO)_9]^{2-}$  dianion (2.480, 2.480, 2.492(1) Å) [7]. The slight lengthening of the Fe-Fe distances upon decreasing the overall molecular charge probably means that bonding electron density is



Fig. 1. ORTEP drawing of the anion  $[Fe_3(\mu_3-O)(\mu_3-AuPPh_3)(\mu-CO_3(CO)_6]^-$  (thermal ellipsoids are drawn at 30% probability level).

Table 1

Selected bond lengths (Å) and angles (°) for  $[Fe_3(\mu_3-O)(\mu_3-AuPPh_3)(\mu-CO)_3(CO)_6]\cdot 0.5C_4H_8O$ 

Au–Fe(1)	2.736(2)	Fe(2)–O(10)	1.89(1)
Au-Fe(2)	2.708(2)	Fe(3)–O(10)	1.90(1)
Au-Fe(3)	2.720(2)	Fe-C(bridging)(avg.)	2.05
Au–P	2.293(2)	Fe-C(avg.)	1.76
Fe(1)-Fe(2)	2.528(3)	C-O(bridging)(avg.)	1.14
Fe(1)– $Fe(3)$	2.489(3)	C–O(avg.)	1.14
Fe(1)-O(10)	1.89(1)	$Au \cdots C(1)$	2.78(2)
Au…C(9)	2.77(2)	Au…C(5)	2.78(2)
Fe(1)-C(1)-O(1)	178(2)	Fe(1)-C(2)-O(2)	178(2)
Fe(3)-C(9)-O(9)	174(2)	Fe(2)-C(4)-O(4)	175(2)
Fe(2)-C(5)-O(5)	174(2)	Fe(3)-C(8)-O(8)	177(2)
Fe(1)-C(3)-O(3)	140(2)	Fe(2)–C(3)–O(3)	144(2)
Fe(1)-C(7)-O(7)	145(2)	Fe(3)-C(7)-O(7)	141(2)
Fe(2)-C(6)-O(6)	143(2)	Fe(3)-C(6)-O(6)	140(2)

removed from the Fe<sub>3</sub> triangle in establishing the interaction with the acidic [Au(PPh<sub>3</sub>)]<sup>+</sup> fragment. The Fe-O distances are equivalent (1.89, 1.89, 1.90(1) Å) and identical to those reported for the aforementioned dianion. Noteworthy the  $[Au(PPh_3)]^+$  fragment, different from what was observed in other chalcogen-containing clusters of the type  $[Fe_3(\mu_3-E)(\mu-AuPPh_3)(CO)_9]^-$  (E = S, Te [11]), is triply bridging the Fe<sub>3</sub> unit (Au-Fe distances 2.736, 2.708 and 2.720(3), average 2.72 Å) instead of doubly bridging one Fe-Fe bond (see also Section 2.2.2). This bonding mode of the  $Au(PPh_3)$ has been reported only in  $[Fe_6C(\mu_3$ group  $AuPPh_{3}(CO)_{16}]^{-}$  [25] (Au-Fe 2.733, 2.732, 2.785(2), avg. 2.75 Å). It should be noted that gold, as usual when favorable stereochemical conditions occur, exhibits secondary bonding interactions with the facing CO ligands (average Au...CO contact 2.77 Å). The attractive nature of this interaction is demonstrated by the fact that the V shaped terminal carbonyl groups are not symmetrically placed above and below the Fe<sub>3</sub> plane. Those involved in the Au…CO attraction are farther from this plane (avg. 1.35 Å) than those on the opposite side (avg. 1.17 Å). The latter have normal contacts with the  $\mu_3$ -O atom (avg.  $\mu_3$ -O···CO 2.66 Å).

#### 2.2.2. Molecular structure of $[Au_3(\mu_3-S)(PPh_3)_3]_2$ - $[Fe_3(\mu_3-S)(\mu-AuPPh_3)(CO)_9]_2$

The crystals of the title compound are made up of dimeric  $[Au_3(\mu_3-S)(PPh_3)_3]_2^{2+}$  cluster cations and  $[Fe_3(\mu_3-S)(\mu-AuPPh_3)(CO)_9]^-$  cluster anions; the independent part is one formula unit.

2.2.2.1.  $[Au_3(\mu_3-S)(PPh_3)_3]_2^{2+}$ . The cluster dication is shown in Fig. 2 and relevant bond lengths and angles are reported in Table 2. The solid state structure of the  $[Au_3(\mu_3-S)(PPh_3)_3]_2^{2+}$  cation is an assemblage of two  $Au_3(\mu_3-S)$  triangles facing each other edge-to-edge, thus realizing two additional Au…Au contacts. Was not for the asymmetry of these two additional contacts (see Fig. 2), the two units would have been related by inversion. These auriophilic interactions are non-equivalent (Au(2)···Au(4) 2.985 and Au(1)···Au(6) 4.194(2) Å) and generate a weakly bonded supramolecule. The Au-Au and Au-S distances in the sulfur-capped triangles fall in the expected ranges: Au-Au 3.055-3.238(2), average 3.162 Å, Au-S 2.310-2.362(3), average 2.331 Å. Each Au atom bears one PPh<sub>3</sub> ligand realizing an almost linear S-Au-P coordination (average S-Au-P angle 177°). This dimeric motif is not unusual and has already been reported in its  $[PF_6]^-$  salt [26]. In the latter cluster the gold aggregation between the two monomers is more symmetric than in the case under study (Au-Au contacts 3.236 and 3.361(3) Å). However, upon changing the counterion the monomeric cation  $[Au_3(\mu_3-S)(PPh_3)_3]^+$ has been found in its  $[BF_4]^-$  salt [27]. The above described structural variations in the solid state on one hand give an idea of the weakness of the auriophilic interactions and on the other hand confirm the relevance of the secondary valence forces in influencing the stereochemistry of gold(I) compounds.

2.2.2.2.  $[Fe_3(\mu_3-S)(\mu-AuPPh_3)(CO)_9]^-$ . The overall molecular geometries of the two independent anions are substantially equivalent and therefore only one is shown in Fig. 3. Relevant bond lengths and angles are reported in Table 2. The anions consist of a triangle of iron atoms with a face-capping sulfur atom and an Au(PPh<sub>3</sub>) group bridging one Fe-Fe edge and lying below the Fe<sub>3</sub>S tetrahedron. Each iron carries three terminal carbonyls at variance with what has been observed in  $[Fe_3(\mu_3-O)(\mu_3-AuPPh_3)(\mu-CO)_3(CO)_6]^-$ , where there are three edge bridging COs (previous section). The anions conform to an idealized  $C_s$  symmetry with a mirror plane passing through S, Au, P and one Fe atom, if the orientations of the phenyl rings are ignored. The Fe-Fe interactions define isosceles triangles (2.592, 2.586, 2.704(2) and 2.758, 2.597, 2.596(3) Å) in which the longer edges are those spanned by the Au(PPh<sub>3</sub>) groups, as it has been found in the related  $[Fe_3(\mu_3-Te)(\mu-AuPPh_3)(CO)_9]^-$ (2.836,2.620 and 2.622(4) Å, respectively) [11] and in the neutral [Fe<sub>3</sub>( $\mu_3$ - $SPr^{i}(\mu-AuPPh_{3})(CO)_{9}$  (2.800, 2.644 and 2.631(8) Å, respectively) [28]. The Fe-S bonds (2.188, 2.185, 2.177(3), average 2.18 Å, and 2.188, 2.184, 2.176(3) Å,



Fig. 2. ORTEP drawing of the dication  $[Au_6(\mu_3-S)_2(PPh_3)_6]^{2+}$  (thermal ellipsoids are drawn at 30% probability level). Hydrogen atoms have been omitted for clarity.

Table 2

Selected bond lengths (Å) and angles (°) for  $[Au_6(\mu_3\text{-}S)(PPh_3)_6]\text{-}[Fe_3(\mu_3\text{-}S)(\mu\text{-}AuPPh_3)(CO)_9]_2$ 

$[Au_6(\mu_3-S)_2(PPh_3)_6]$	2+		
Au(1)–Au(2)	3.238(2)	Au(4)–Au(5)	3.055(2)
Au(2)–Au(3)	3.064(2)	Au(5)–Au(6)	3.162(2)
Au(1)–Au(3)	3.193(2)	Au(4)–Au(6)	3.259(2)
Au(1)–P(1)	2.261(3)	Au(4)–P(4)	2.281(3)
Au(2)–P(2)	2.277(3)	Au(5) - P(5)	2.257(3)
Au(3)–P(3)	2.263(3)	Au(6)–P(6)	2.260(3)
Au(1)–S(2)	2.310(3)	Au(2)–S(2)	2.358(3)
Au(3)–S(2)	2.326(3)	Au(4)-S(1)	2.362(3)
Au(5)–S(1)	2.316(3)	Au(6) - S(1)	2.315(3)
Au(2)–Au(4)	2.985(2)	Au(1)Au(6)	4.194(2)
S(2)-Au(2)-P(2)	174.3(1)	S(1)-Au(4)-P(4)	175.5(1)
S(2)–Au(3)–P(3)	177.3(1)	S(1)-Au(5)-P(5)	177.3(1)
S(2)–Au(1)–P(1)	176.8(1)	S(1)-Au(6)-P(6)	178.4(1)
[Fe <sub>3</sub> (µ <sub>3</sub> -S)(µ-AuPPh	n <sub>3</sub> )(CO) <sub>9</sub> ] <sup>-</sup>		
Anion 1		Anion 2	
Fe(1)-Fe(2)	2.592(2)	Fe(4)-Fe(5)	2.758(3)
Fe(2)-Fe(3)	2.586(2)	Fe(5)–Fe(6)	2.596(3)
Fe(1)-Fe(3)	2.704(2)	Fe(4)– $Fe(6)$	2.597(3)
Fe(1)-S(3)	2.188(3)	Fe(4)-S(4)	2.188(4)
Fe(2)–S(3)	2.177(3)	Fe(5)-S(4)	2.184(3)
Fe(3)–S(3)	2.185(3)	Fe(6)-S(4)	2.176(4)
Fe(1)-Au(7)	2.648(2)	Fe(4)-Au(8)	2.659(2)
Fe(3)-Au(7)	2.710(2)	Fe(5)-Au(8)	2.657(2)
Au(7)–P(7)	2.275(3)	Au(8)–P(8)	2.295(3)
Fe-C(avg.)	1.76	Fe-C(avg.)	1.15
C–O(avg.)	1.15	C–O(avg.)	1.15
Au(7)…C(7)	2.72(1)	Au(8)…C(15)	2.62(2)
Au(7)…C(1)	2.70(1)	Au(8)…C(11)	2.60(1)
Au(7)…C(2)	2.63(1)	Au(8)–C(10)	2.99(1)
Au(7)…C(9)	2.77(1)		

average 2.18 Å) are slightly asymmetric and in both anions the shorter Fe-S distance is that to the iron atoms not involved in the bonding to the Au(PPh<sub>3</sub>) unit. The Au(PPh<sub>3</sub>) groups make an asymmetric and a symmetric bridge in the two independent anions (2.648, 2.710(2) Å and 2.659, 2.657(2) Å, respectively), the Fe-Au distances being comparable to those reported for the aforementioned  $[Fe_3(\mu_3-Te)(\mu-AuPPh_3)(CO)_9]^-$  (2.681 and 2.652(3) Å) [11]. A major difference between the two anions lies in the Fe<sub>3</sub>Au butterfly (dihedral angles between the planes Fe-Fe-Fe and Fe-Fe-Au 147.30 and 118.04°, respectively). This effect and the already mentioned asymmetry in the Fe-Au distances are consequences of asymmetry in the packing forces. As described above the oxygen derivative in the family of anions  $[Fe_3(E)(AuPPh_3)(CO)_9]^-$  (E = O, S, Te) exhibits a more regular  $C_{3v}$  structure than the heavier congeners whose stereogeometries conform to a  $C_s$  symmetry. The steric factors involved in the structural differences can be appreciated if a structural model is built in which a  $\mu_3$ -S ligand replaces the oxygen (Fe-S distances 2.18 Å) keeping the CO ligands where found in the oxygen derivative. S…CO contacts as short as 2.7 Å are calculated, much shorter than the sum of the van der Waals

radii (3.2 Å) [29]. It is therefore evident that a  $C_{3v}$  structure is destabilized in the anions of the heavier chalcogenides. In fact in the all terminal CO arrangement adopted by the S and Te derivatives, the CO ligands remain far from the  $\mu_3$ -E ligand. More subtle electronic factors are probably involved in the stabilization of the  $\mu_2$  bonding mode of the AuPPh<sub>3</sub> fragment when the edges of the Fe<sub>3</sub> triangle are free from CO ligands.

#### 3. Experimental

All reactions including sample manipulations were carried out using standard Schlenk techniques under nitrogen and in carefully dried solvents. The  $[Fe_3O(CO)_9]^{2-}$  [7];  $[Fe_3S(CO)_9]^{2-}$  [8a,f];  $[Fe_5S_2(CO)_{14}]^{2-}$  [8f] and  $[Au_3S(PPh_3)_3]CI$  [22] salts have been prepared according to the literature. Analyses of Fe and Au were performed by atomic absorption on a Pye-Unicam instrument. Infrared spectra were recorded on a Perkin Elmer 1605 interferometer using CaF<sub>2</sub> cells.

3.1. Synthesis of  $[NEt_4][Fe_3(\mu_3-O)(\mu_3-AuPPh_3)(CO)_9]$ 

Solid  $[NEt_4]_2[Fe_3(\mu_3-O)(CO)_9]$  (1.51 g, 2.17 mmol) and



Fig. 3. ORTEP drawing of one of the anions  $[Fe_3(\mu_3-S)(\mu-AuPPh_3)(CO)_9]^-$  (thermal ellipsoids are drawn at 30% probability level).

Table 3

378

 $Crystal \ data \ and \ experimental \ details \ for \ [NEt_4][Fe_3(\mu_3-O)(\mu_3-AuPPh_3)(\mu-CO)_3(CO)_6] \cdot 0.5C_4H_8O \ and \ [Au_6(\mu_3-S)_2(PPh_3)_6][Fe_3(\mu_3-S)(\mu-AuPPh_3)(CO)_9]_2 = 0.5C_4H_8O \ and \ [Au_6(\mu_3-S)_2(PPh_3)_6][Fe_3(\mu_3-S)(\mu-AuPPh_3)(\mu-CO)_3(CO)_9]_2 = 0.5C_4H_8O \ and \ [Au_6(\mu_3-S)_2(PPh_3)_6][Fe_3(\mu_3-S)(\mu-AuPPh_3)($ 

Empirical formula	$C_{35}H_{35}AuFe_{3}NO_{10}P \cdot 0.5C_{4}H_{8}O$	$C_{162}H_{120}Au_8Fe_6O_{18}P_8S_4$
Formula weight	1061.18	4641.41
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71069	0.71069
Crystal symmetry	monoclinic	triclinic
Space group	C2/c (No. 15)	<i>P</i> 1 (No. 2)
a (Å)	15.859(2)	18.998(8)
b (Å)	12.859(2)	19.933(8)
c (Å)	40.217(8)	22.94(1)
α (°)	90	99.91(4)
β (°)	96.46(1)	98.41(4)
γ (°)	90	107.42(3)
Cell volume ( $Å^3$ )	8149(3)	7982(6)
Ζ	8	2
$D_{\rm c}  ({\rm Mg}  {\rm m}^{-3})$	1.730	1.931
$\mu$ (Mo K $\alpha$ ) (mm <sup>-1</sup> )	4.731	8.040
F(000)	4192	4416
Crystal size (mm)	$0.40 \times 0.40 \times 0.50$	$0.12 \times 0.20 \times 0.23$
$\theta$ Range (°)	2.5–30	2.5–25
Scan mode	ω	ω
Reflections collected	$12\ 240\ (+h,\ +k,\ \pm l)$	28 703 $(\pm h, \pm k, +l)$
Unique observed reflections $[F_{o} > 4\sigma(F_{o})]$	11 499	27 907
Goodness-of-fit on $F^2$	1.229	0.908
$R_1 (F)^{\rm a}, w R_2 (F^2)^{\rm b}$	0.0922, 0.2390	0.0347, 0.0822
Weighting scheme	$a = 0.0620, \ b = 401.0833^{\text{b}}$	$a = 0.0589, \ b = 0.2926^{\rm b}$
Largest difference peak and hole (e $Å^{-3}$ )	1.916 and -2.560	0.958 and -1.897

<sup>a</sup>  $R_1 = \Sigma \parallel F_o \mid - \mid F_c \mid / \Sigma \mid F_o \mid.$ 

<sup>b</sup>  $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$  where  $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$  where  $P = (F_o^2 + 2F_c^2)/3$ .

Au(PPh<sub>3</sub>)Cl (1.17 g, 2.37 mmol) were mixed in a 100 ml flask under a nitrogen atmosphere. Anhydrous THF (30 ml) was added and the suspension was rapidly stirred for 6 h. After this period of time IR monitoring only showed the presence of the infrared absorptions of  $[Fe_3(\mu_3-O)(\mu_3-AuPPh_3)(CO)_9]^{2-}$ . The suspension was filtered and the resulting red solution was evaporated to dryness under vacuum. The residue was washed with water (20 ml) and toluene (20 ml). Extraction of the residue with THF (30 ml) and precipitation by diffusion of n-hexane (50 ml) gave 1.38 g of  $[NEt_4][Fe_3(\mu_3-O)(\mu_3-AuPPh_3)(CO)_9]$  as dark red crystals. *Anal.* Found: Au, 19.01; Fe, 16.15; C, 41.27; H, 3.66. Calc. for  $[NEt_4][Fe_3(\mu_3-O)(\mu_3-AuPPh_3)(CO)_9]$ : Au, 19.22; Fe, 16.35; C, 40.99; H 3.42%.

### 3.2. Synthesis of $[Au_6(\mu_3-S)(PPh_3)_6][Fe_3(\mu_3-S)(\mu-AuPPh_3)(CO)_9]_2$

Solid  $[NEt_4]_2[Fe_3S(CO)_9]$  (0.86 g, 1.21 mmol) and Au(PPh\_3)Cl (0.62 g, 1.25 mmol) were mixed in a 100 ml flask under a nitrogen atmosphere. Anhydrous THF (30 ml) was added and the suspension was rapidly stirred for 2 h. Solid  $[Au_3S(PPh_3)_3]Cl (1.73 g, 1.2 mmol)$  was added under stirring. The resulting red suspension was evaporated to dryness under vacuum and the residue was washed with water (50 ml in portions) and toluene (20 ml).

Extraction of the residue with acetone (40 ml) and precipitation by diffusion of isopropyl alcohol (70 ml) gave 1.76 g of  $[Au_6(\mu_3-S)_2(PPh_3)_6][Fe_3(\mu_3-S)(\mu-AuPPh_3)(CO)_9]_2$  as dark red crystals. *Anal*. Found: Au, 33.6; Fe, 7.05; C, 41.8; H, 2.63. Calc. for  $[Au_6(\mu_3-S)(PPh_3)_6][Fe_3(\mu_3-S)(\mu-AuPPh_3)(CO)_9]_2$ : Au, 33.97; Fe, 7.22; C, 41.91; H, 2.59%.

#### 3.3. Synthesis of $[Au_6(\mu_3-S)_2(PPh_3)_6][Fe_5(\mu_3-S)_2(CO)_{14}]$

Solid  $[NEt_4]_2[Fe_5S_2(CO)_{14}]$  (0.52 g, 0.52 mmol) and  $[Au_3S(PPh_3)_3]Cl$  (1.56 g, 1.08 mmol) were mixed in a 100 ml flask under a nitrogen atmosphere. Anhydrous THF (30 ml) was added and the suspension was rapidly stirred for 2 h. The resulting red suspension was evaporated to dryness under vacuum and the residue was washed with water (50 ml in portions) and toluene (20 ml). Extraction of the residue with acetone (40 ml) and precipitation by diffusion of isopropyl alcohol (70 ml) gave 0.76 g of  $[Au_6(\mu_3-S)_2(PPh_3)_6][Fe_5(\mu_3-S)_2(CO)_{14}]$  as dark red crystals. *Anal.* Found: Au, 33.1; Fe, 7.62; C, 41.34; H, 2.61. Calc. for  $[Au_6(\mu_3-S)_2(PPh_3)_6][Fe_5(\mu_3-S)_2(CO)_{14}]$ : Au, 33.26; Fe, 7.86; C, 41.20; H, 2.53%.

#### 3.4. Crystallography

Crystal data and details of the data collection for  $[NEt_4][Fe_3(\mu_3 - O)(\mu_3 - AuPPh_3)(\mu - CO)_3(CO)_6] \cdot 0.5C_4H_8O$ 

and  $[Au_6(\mu_3-S)_2(PPh_3)_6][Fe_3(\mu_3-S)(\mu-AuPPh_3)(CO)_9]_2$  are given in Table 3. The diffraction experiments were carried out at room temperature on a fully automated Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo K $\alpha$  radiation. The unit cell parameters were determined by a least-squares fitting procedure using 25 reflections. Data were corrected for Lorentz and polarization effects. No decay correction was necessary. An empirical absorption correction was applied by using the azimuthal scan method [30].

 $[NEt_4][Fe_3(\mu_3 - O)(\mu_3 - AuPPh_3)(\mu - CO)_3(CO)_6] \cdot 0.5C_4$ - $H_8O$ . The space group C2/c was determined on the basis of systematic absences. The positions of the metal atoms were found by direct methods using the SHELXS 86 program [31]. All non-hydrogen atoms were located from Fourier-difference maps. One molecule of tetrahydrofuran placed across a mirror plane was also found in the asymmetric unit. The phenyl groups were refined as rigid hexagons (C-C 1.39, C-H 0.93 Å, C-C-C 120°). The final refinement on  $F^2$  proceeded by full-matrix leastsquares calculations (SHELXL 93) [32] using anisotropic thermal parameters for all the non-hydrogen atoms. The phenyl H atoms were assigned an isotropic thermal parameter 1.2 times  $U_{eq}$  of the pertinent carbon atoms. The final Fourier-difference map showed residual electron density in the  $+1.92 - 2.56 \text{ e}^{-3}$  range in the vicinity of the Au atom.

 $[Au_6(\mu_3-S)_2(PPh_3)_6][Fe_3(\mu_3-S)(\mu-AuPPh_3)(CO)_9]_2$ . The positions of the metal atoms were found by direct methods using the SHELXS 86 program [31]. All non-hydrogen atoms were located from Fourier-difference maps. The phenyl rings were treated as described above. The final refinement on  $F^2$  proceeded by full-matrix least-squares calculations (SHELXL 93) [32] using anisotropic thermal parameters for all the non-hydrogen atoms. The final Fourier-difference map showed residual electron density in the + 0.96 to 1.90 e Å<sup>-3</sup> range in the vicinity of the Au atom

#### 4. Supplementary material

Complete tables of fractional atomic coordinates and equivalent isotropic displacement parameters, anisotropic displacement parameters, bond lengths, bond angles and hydrogen atom coordinates have been deposited at the Cambridge Crystallographic Data Centre.

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