*Inorg. Chem.* **2006**, *45*, 8465–8467

Inorganic Chemistry
Communication

# A Traditional Synthetic Method, and a New Structural Motif, for Molybdenum–Gold Clusters: Synthesis and Solid-State Structure of $Au_8\{Mo(CO)_5\}_4(PPh_3)_4$

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Received March 28, 2006

The neutral cluster $[Au_8Mo_4(CO)_{20}(PPh_3)_4]$ was synthesized in low yield from $[AuCl(PPh_3)]$ and $[Mo_2(CO)_{10}]^{2-}$ in acetonitrile at room temperature. The cluster was characterized by X-ray analysis, IR, and $^{31}P$ NMR spectroscopy. Its solid-state structure consists of four $Au_3Mo$ tetrahedral units, fused by four Au atoms in a ring. The average bond lengths are Au–Au 2.77 Å and Mo–Au 2.93 Å. The internal angles of the planar square ring are very close to 90°.

Since the pioneering work of Malatesta et al.,[1] molecular Au clusters have attracted a large scientific interest, mainly devoted to understanding the factors that govern their bonding. For Au, the ability to form a large number of interactions, apparently unsupported by conventional covalent bonds, was named "aurophilicity"[2] and theoretically examined.[3]

More recently, several M−Au heterometallic clusters have been obtained, and they can be conveniently classified into at least two categories: clusters centered by $M(CO)_x$ fragments (usually with an early-transition-metal element such as V,[4] Mo,[5] W,[6] Mn,[7] or Re[8]) and clusters containing a late (or post)-transition-metal element (here including Pd,[9] Pt,[10] Ag,[11] or Hg[12]). The subject was reviewed several years ago by Mingos,[13,14] by Salter[15] and, more recently, by Strähle.[16]

All of these experiences have been applied to the preparation of ultrasmall Au nanoparticles, so that, nowadays, the two fields overlap to a substantial extent.[17] Homo- and heterometallic quasi-molecular clusters find potential application in several fields of nanosciences,[18] such as nanoelectronic,[19] catalysis,[20] and analytical chemistry.[21]

On the other end, the fragment $[Au(PR_3)]^+$ has been widely used to test the nucleophilic reactivity of anionic carbonyl clusters and probe the sites accessible to the isolobal $H^+$.[22]

Exactly for this last reason, to verify if the electrophilic fragment $[AuPPh_3]^+$ was able to add across the unsupported

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10.1021/ic060524l CCC: $33.50

Mo−Mo single bond of $[Mo_2(CO)_{10}]^{2-}$ and to see if the $Mo_2Au$[23] unit was as structurally flexible as the "protonated" Mo−H−Mo bond in $[HMo_2(CO)_{10}]^-$, whose conformation, in the solid state, is strongly dependent on the counterion,[24] we tested the reaction between $(NEt_4)_2[Mo_2(CO)_{10}]$ and $AuPPh_3Cl$.

In contrast to what was expected, adding small portions of the Au complex to an acetonitrile solution of the molybdenum carbonyl anion produces a complex reaction.[25] IR monitoring showed a continuous shifting of the IR bands, suggesting that no single stable compound was formed. However, at approximately a 1:1.5 ratio between the two reagents, some sharp new bands appeared in the spectrum. The reaction was thus stopped, and the mixture was fractionated by solvent extraction. The tetrahydrofuran (THF) fraction was layered with 2-propanol, and the compound $[Au_8Mo_4(CO)_{20}(PPh_3)_4]$ crystallized in low (<10%) yield. Among the other products of the same reaction, the homometallic Au cluster $Au_{11}(PPh_3)_7Cl_3$ was isolated and identified, after an X-ray determination. This product is consistent with a mild reduction of $Au(PPh_3)Cl$, which typically yields homometallic Au clusters.[1] Thus, the synthetic approach to $[Au_8Mo_4(CO)_{20}(PPh_3)_4]$ can be related to the traditional redox condensation, a reaction between coordinatively saturated species in different oxidation states.[26] To the contrary, the other reported heterometallic Mo−Au clusters have been prepared by photolysis of $Ph_3PAuN_3$ in the presence of $Mo(CO)_6$, a method that induces also the decarbonylation of the Mo complex.[4]

The solid-state structure[27] of $[Au_8Mo_4(CO)_{20}(PPh_3)_4]$ is shown in Figure 1 and consists of four $Au_3Mo$ tetrahedral units, mutually sharing a Au vertex, so as to form a square arrangement.

Alternatively, the structure can be described as a square Au cluster, whose edges are all bridged by $Mo(CO)_5$ and $Au(PPh_3)$ units, with alternate orientation. Therefore, the idealized symmetry of the molecule is $D_{2d}$.

Thus, the four Au atoms that define the square are unsupported by ligands (a feature quite uncommon in Au cluster chemistry[28]) and connected to six metal atoms. The unshared four Au atoms are three-connected and carry a $PPh_3$ ligand. Despite this strong structural difference, the Au−Au distances are very similar, with no significant differences within the two groups. The average Au−Au separation is 2.77 ± 0.02 Å. Also, the Au−Mo edges fall within a short range, and the mean distance is 2.93 ± 0.03 Å. The first value is normal for these cluster species, but the latter appears slightly longer than other known values, which are typically shorter than 2.85 Å.[16] The internal polygon is a really undistorted square with internal angles very close to 90° and deviations from the mean plane smaller than 0.01 Å.

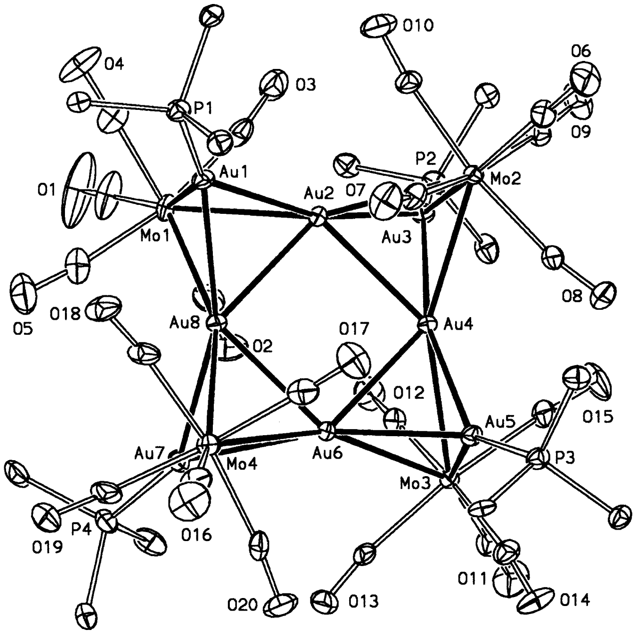

**Figure 1.** Solid-state structure of $Au_8Mo_4(CO)_{20}(PPh_3)_4$. The ellipsoids are drawn at 30% probability. Average bond lengths are Au−Au 2.77 Å, P−Au 2.31 Å, Mo−Au 2.93 Å.

The carbonyl ligands around the Mo centers define slightly distorted square-based pyramids, with axial−equatorial angles always smaller than 90°. The axial carbonyls deviate from linearity as a consequence of a weak interaction with Au: the Mo−C−O angles are in the range 169.4−174.6°, and the corresponding Au−C separations are in the range 2.69−2.89 Å. However, this effect is common to both types of structurally different Au atoms and is typically found in carbonyl clusters containing the $[Au-PPh_3]$ fragment;[22] therefore, they can hardly be considered as semibridging ligands. In agreement with the local $C_{4v}$ symmetry of the carbonyl groups, the IR spectrum of the compound, in a THF solution, shows only two bands in the zone of the terminal ligands.[25]

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(25) $(NEt_4)_2[Mo_2(CO)_{10}]$ (27 mg, 0.04 mmol) and $AuClPPh_3$ (32 mg, 0.064 mmol) were dissolved in 5 mL of MeCN and stirred at room temperature for 1 h. The solvent was dried in a vacuum, and the residue was washed with 2-propanol (2 × 5 mL) and extracted with 3 mL of THF. The solution was layered with 2-propanol, and when the solvents were mixed, well-shaped crystals of the product were recovered. IR (CO stretching, THF solution): 2029s, 1933vs, br. $^{31}P$ NMR in $CD_2Cl_2$: 58 ppm.

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(27) Crystal data: $C_{92}H_{60}Au_8Mo_4O_{20}P_4$, $M = 3568.88$, monoclinic, space group $P2_1/n$ (No. 14), $a = 16.910(1)$ Å, $b = 26.502(3)$ Å, $c = 21.427(2)$ Å, $\beta = 91.11(1)°$, $V = 9600.7(15)$ Å$^3$, and $Z = 4$. Bruker SMART area detector, $\omega$ scan, $T = 223$ K, full-matrix least-squares refinement on all reflections (23 881), R2 = 0.055 and wR2 = 0.074 on $F^2$, conventional R1 = 0.033 on 16 303 reflections [$I > 2\sigma(I)$]. The atomic coordinates of the structural model have been deposited with the Cambridge Crystallographic Data Centre (deposition number CCDC 602883).

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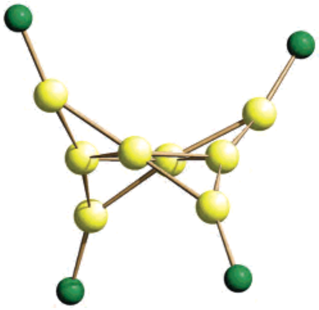

**Figure 2.** Schakal[30] plot of the position of the Au (yellow) and P (green) atoms in $[Au_8Mo_4(PPh_3)_4(CO)_{20}]$.

The description of the bonding in the compound is quite straightforward: because only the electrons of the Au atoms are involved in skeletal bonding, there are eight electrons available for cluster bonds.

The same conclusion can be drawn, considering that both $(AuPPh_3)^+$ and $[Mo(CO)_5]$ are isolobal Lewis acids and therefore participate in the cluster bonding with eight empty orbitals. The electrons are all supplied by the remaining $[Au_4]^{4-}$ fragment, whose edges are indeed supported by eight electrons. Under this assumption, the four Au−Au bonds of the internal square act as the electron donors, the eight $(AuPPh_3)^+$ and $[Mo(CO)_5]$ units as electron acceptors, in four unconventional four-center two-electron $M_3-AuPR_3$ bonds.[13] This description is fully consistent with the long Mo−Au bond distances (a consequence of their low bond order) and also with the essentially linear coordination of all of the Au atoms. As a matter of fact, the angles centered at Au and defined by the geometrical centers (Gc) of the four tetrahedra are about 177° for the Gc−Au−P angle and 162° for the Gc−Au−Gc angle.

The present compound is new by several respects: (i) it is not a heterometal-centered cluster of Au but, instead, a heterometal cluster *centered by a cluster of Au*, which can be conceived as the electron donor toward the $d^6$ $L_5$ metal fragments; (ii) this cluster, which would be classified, according to Mingos, as a toroidal structure,[29] possesses four bonding cluster orbitals; (iii) the arrangement of the eight Au atoms, shown in Figure 2, cannot be reconducted to a fragment of an icosahedron.

Nevertheless, the disposition of the metal atoms in this compound may resemble structural motifs found in other fields of inorganic chemistry. For example, the eight Au atoms, forming a $D_{2d}$ crown, are reminiscent of the eight alternating nonmetallic atoms in $N_4S_4$ or $As_4S_4$[31] rather than the more familiar $S_8$ molecule.[32] Moreover, rings of four tetrahedra are present in some synthetic silicate[33] and in the *cyclo*-tetrametaphosphates.[34]

This last analogy suggests that further work on this subject may possibly lead to the isolation of different oligomeric structures. Larger rings or linear structures imply larger Gc−Au−Gc angles, so they are disfavored by steric hindrance of the ligands on adjacent tetrahedra but favored by more linear coordination at the shared Au atoms.

Additionally, this cluster can be used to model the adsorption and decomposition of $Mo(CO)_6$ on Au surfaces, which may have catalytic implications[20] after the observation that the resulting Mo nanoclusters show surprising reactivity toward S-containing molecules. This distinctive behavior has been ascribed to electronic perturbations originated by the bimetallic bonding.[35]

**Acknowledgment.** This work was funded by Università di Milano Bicocca and by Faculty of Farmacia, Università di Milano.

**Supporting Information Available:** Crystallographic data in the CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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