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Aurophilic Self-Assembly of a Mo_4Au_2 Phosphinidene Complex with an Unprecedented H-Shaped Planar Metal Core

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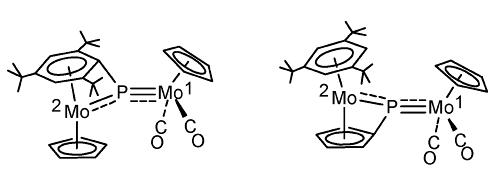
The isomers $[Mo_2Cp_2(\mu\text{-}\kappa^1{:}\kappa^1,\eta^6\text{-}PR^*)(CO)_2]$ (**1**) and $[Mo_2Cp(\mu\text{-}\kappa^1{:}\kappa^1,\eta^5\text{-}PC_5H_4)(CO)_2(\eta^6\text{-}HR^*)]$ (**2**) (Cp = η^5-C_5H_5; R* = 2,4,6-$C_6H_2{}^tBu_3$) react with [AuCl(THT)] and with the cation $[Au(THT)_2]^+$ (THT = tetrahydrothiophene) to give phosphinidene-bridged Mo_2Au complexes resulting from the addition of an AuCl or $Au(THT)^+$ electrophile to their multiple P−Mo bonds. Removal of the Cl^- or THT ligand from these derivatives causes a dimerization of the trinuclear structures to give the cationic derivative $[\{AuMo_2Cp(\mu_3\text{-}\kappa^1{:}\kappa^1{:}\kappa^1,\eta^5\text{-}PC_5H_4)(CO)_2(\eta^6\text{-}HR^*)\}_2]^{2+}$, which displays a novel H-shaped metal core held by strong Mo−Au dative bonds [2.768(1) Å] and an aurophilic interaction [Au−Au = 3.022(1) Å].

Interest in gold chemistry has grown enormously in recent times. There are many reasons for this, ranging from the theoretical aspects concerning the structure and bonding in gold complexes and clusters, including the *aurophilic interactions*,[1] to their remarkable photophysical and photochemical properties,[2] as well as their catalytic activity,[3] a property also exhibited by gold nanoparticles.[4] The last 2 decades have also seen an intense activity concerning the preparation of mixed transition metal−gold compounds and the study of their properties.[5] Gold−gold interactions are a relevant factor contributing to the structure and properties of all of these polynuclear compounds.[1,5,6]

Chart 1



1

2

Recently, we reported the selective synthesis of the phosphinidene complexes $[Mo_2Cp_2(\mu\text{-}\kappa^1{:}\kappa^1,\eta^6\text{-}PR^*)(CO)_2]$ (**1**) and $[Mo_2Cp(\mu\text{-}\kappa^1{:}\kappa^1,\eta^5\text{-}PC_5H_4)(CO)_2(\eta^6\text{-}HR^*)]$ (**2**) (Cp = η^5-C_5H_5; R* = 2,4,6-$C_6H_2{}^tBu_3$),[7] which display unprecedented coordination modes of their P-donor ligands. Both products have a phosphinidene group connecting 17-electron (Mo2) and 15-electron (Mo1) metal fragments, and there is considerable multiplicity in the short P−Mo1 bond, with a bond order intermediate between 2 and 3 (Chart 1).[7,8] As a result, a singular reactivity is shown by these molecules, especially for the less hindered compound **2**, which displays a behavior that can be related to that of both the carbene and carbyne complexes, to give novel molecules displaying unusual coordination environments around the P atom.[8] In developing the chemistry of these unsaturated molecules, we considered their reactions with suitable gold(I) complexes as a synthetic route to novel heterometallic derivatives having Au−Mo and possibly also Au−Au bonds. These reactions were likely to occur because we had found previously that compound **1** could add a molecule of CuCl at its short P−Mo bond.[7] At the same time, it has been shown in recent years that many cationic phosphine−gold(I) complexes or even AuCl and $AuCl_3$ are powerful and selective homogeneous catalysts for the activation of π bonds,[3] a property derived from the interaction of the Au atom with the multiple C−C

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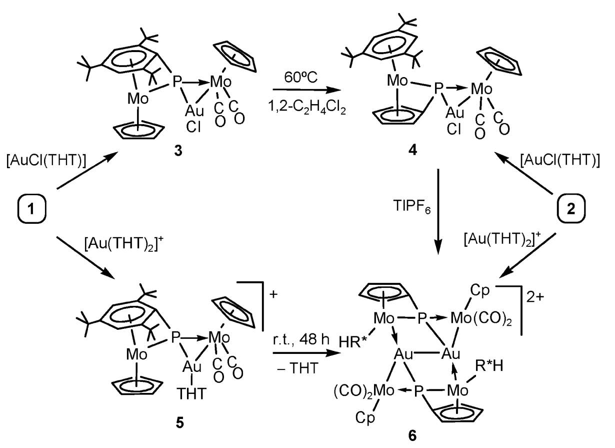
10.1021/ic8011487 CCC: $40.75

Scheme 1



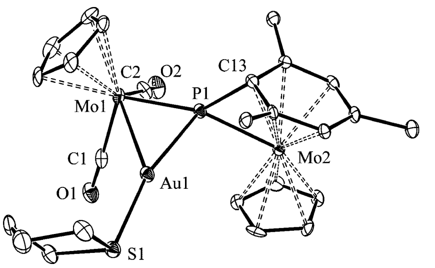


Figure 1. ORTEP drawing (30% probability) of the cation in **5**, with H atoms and Me groups of ^{t}Bu substituents omitted for clarity. Selected bond lengths (Å): Mo1−Au1 = 2.7690(8), Mo1−P1 = 2.335(2), Au1−P1 = 2.397(2), Au1−S1 = 2.357(2), P1−Mo2 = 2.348(2), P1−C13 = 1.84(1). Bond angles (deg): Mo1−P1−Mo2 = 157.9(1), P1−Au1−S1 = 165.5(1).

bonds, even if full structural evidence for the coordination of cationic gold(I) complexes to alkenes or alkynes has been limited to a few examples.[9]

We here report some unexpected results concerning the interaction of the multiple P−Mo bonds present in compounds **1** and **2** with several gold(I) compounds (Scheme 1). As will be shown below, this interaction not only allows for the rational formation of new MoAu phosphinidene complexes but also induces the activation of C−H and C−P bonds as required to transform the PR* and Cp ligands into an HR*/PC$_5$H$_4$ pair. Moreover, in the absence of other ligands, the naked Au$^+$ cation forces a condensation of the new Mo$_2$Au complexes by overriding unfavorable electrostatic repulsions and involving the formation of new and strong Au−Mo and Au−Au bonds, to yield an almost planar H-shaped metal core. As far as we know, this metal arrangement has not been previously reported, and it can be directly related here to the presence of a strong aurophilic interaction.

Compound **1** reacts easily with [AuCl(THT)] in a CH$_2$Cl$_2$ solution at room temperature to give the red complex [AuMo$_2$ClCp$_2$(μ-κ^1:κ^1:κ^1,η^6-PC$_6$H$_2{}^t$Bu$_3$)(CO)$_2$] (**3**) (THT = SC$_4$H$_8$; Scheme 1).[10] Spectroscopic data for **3** are similar to those reported for the CuCl adduct of **1**, structurally characterized by us previously.[7] Thus, we assume a similar structure for **3**, with an AuCl unit bound to the multiple P−Mo bonds of **1**. In agreement with the resulting change in the coordination mode of the phosphinidene ligand (from μ_2 to μ_3), the phosphorus nucleus in **3** (δ_P 400.2 ppm) appears now to be more shielded than that in the starting material, as was found for the CuCl adduct (δ_P 439.1 ppm).[7] In contrast to this copper analogue, however, the gold complex **3** cannot be isolated as a pure material because in solution it transforms progressively into a violet isomer identified as the cyclopentadienylidene−phosphinidene complex [AuMo$_2$ClCp(μ-κ^1:κ^1:κ^1,η^5-PC$_5$H$_4$)(CO)$_2$(η^6-HR*)] (**4**).[11] The ^{31}P NMR shift of this compound (δ_P 377.5 ppm) suggests the retention of a μ_3-bridging phosphinidene ligand, but its ^{1}H NMR spectrum reveals that a substantial rearrangement in the hydrocarbon groups has taken place, to give η^6-HR* and η^5-C$_5$H$_4$ ligands (see the Supporting Information). The corresponding spectroscopic changes are similar to those occurring during the isomerization of compound **1** into **2**, so we conclude that **4** indeed has a PC$_5$H$_4$ ligand. In agreement with this, compound **4** can be directly prepared from **2** and [AuCl(THT)], a reaction taking place almost instantaneously at room temperature (Scheme 1). We have shown previously that the substantial rearrangement required to transform the aryl−phosphinidene complex **1** into the cyclopentadienylidene−phosphinidene derivative **2** is acid-catalyzed and most likely involves the intermediacy of the phosphide cation [Mo$_2$Cp$_2$(μ-P)(CO)$_2$(η^6-HR*)]$^+$. This transformation is completed in ca. 2 h when carried out in a wet CH$_2$Cl$_2$ solution at 313 K.[7] Compared to this, an independent experiment showed that the transformation of **3** into **4** is completed in ca. 10 min at 333 K, thus proving that the coordination of AuCl to the multiple P−Mo bond in **1** also imposes substantial activation on several bonds (P−C and C−H) of the molecule. However, further studies will be needed to check the synthetic potential of these effects.

Compound **1** also reacts instantaneously with stoichiometric amounts of [Au(THT)$_2$](PF$_6$) to give the red complex [AuMo$_2$Cp$_2$(μ_3-κ^1:κ^1:κ^1,η^6-PR*)(CO)$_2$(THT)](PF$_6$) (**5**), resulting from the addition of the Au(THT)$^+$ electrophile to the multiple P−Mo bond in **1**.[12] The molecular geometry of the cation in **5** (Figure 1)[13] is comparable to that of the copper analogue of **3**.[7] The Au(THT) unit here attains its preferred two-coordinated 14-electron configuration by accepting an electron pair from a P−Mo π-bonding orbital in **1**, thus resembling the coordination of alkyne or alkene ligands to gold(I) centers.[9] A strong parallelism can also be established between **5** and some gold derivatives of metal carbene complexes, such as [AuWCp{μ-CH(C$_6$H$_4$Me)}(CO)$_2$-

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(10) Selected data for **3**. ν(CO) (CH$_2$Cl$_2$): 1932 (vs), 1864 (s) cm^{-1}. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ 400.2 (s, br, μ_3-PR*).

(11) Selected data for **4**. ν(CO) (CH$_2$Cl$_2$): 1942 (vs), 1870 (s) cm^{-1}. ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 370.1 (s, br, μ_3-PC$_5$H$_4$).

(12) Selected data for **5**. ν(CO) (CH$_2$Cl$_2$): 1937 (vs), 1869 (s) cm^{-1}. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ 420.0 (s, br, μ_3-PR*).

(13) X-ray data for **5**·CH$_2$Cl$_2$: red crystals, monoclinic ($P2_1/c$), a = 8.5381(2) Å, b = 26.1255(5) Å, c = 19.6161(1) Å, β = 112.056(1)°, V = 4055.4(1) Å^3, T = 100 K, Z = 4, R = 0.0508, GOF = 1.065.

$(PPh_3)]$.[14] As a result of the coordination to the gold fragment, the short P−Mo bond in **1** is considerably elongated [from 2.248(1) to 2.335(2) Å]. Yet both Mo−P lengths in **5** are relatively short (for single bonds), with this possibly indicating the presence of residual multiplicity in these interactions. Besides this, the Au−P [2.397(2) Å] and Au−Mo [2.769(1) Å] distances are somewhat longer than the reference single bond lengths [cf. Au−P = 2.309(2) Å in $[\{Cp(CO)_2Mo\}_2(\mu\text{-H})(\mu_3\text{-PH})Au(PPh_3)]$,[15] and Au−Mo = 2.710(1) Å in $[Mo(AuPPh_3)Cp(CO)_3]$,[16]], as is expected from the tricentric nature of the P−Mo−Au interaction in **5**.

Compound **5** evolves slowly in a CH_2Cl_2 solution to give the dicationic and poorly soluble green complex $[\{AuMo_2Cp(\mu_3\text{-}\kappa^1\text{:}\kappa^1\text{:}\kappa^1,\eta^5\text{-PC}_5H_4)(CO)_2(\eta^6\text{-HR*})\}_2](PF_6)_2$ (**6**), with the transformation being complete in ca. 2 days at room temperature.[17] The formation of **6** requires the dissociation of a THT ligand and dimerization of the resulting cation, coupled at some intermediate stage to a PR*/Cp rearrangement similar to that observed for **3**. Apparently, these rearrangements are especially favored by the coordination of gold(I) electrophiles to the phosphinidene **1** because CuCl does not induce this transformation. It is thus likely that **5** first undergoes a slow isomerization similar to that observed for **3**, then dissociating the THT ligand and undergoing dimerization, whereby the metallocene center in one monomer occupies the vacant position left at gold in a second molecule and the reverse. Indeed, the highest occupied molecular orbital in **2** is a nonbonding orbital essentially centered on the arene-bound Mo atom.[8] In agreement with all of this, compound **6** can also be synthesized by halide extraction from **4** with $TlPF_6$ or through the reaction of **2** with stoichiometric amounts of $[Au(THT)_2](PF_6)$ (Scheme 1).

The cation in **6** displays an almost planar H-shaped Mo_4Au_2 core (Figure 2),[18] which seems to have no precedent within the currently characterized hexanuclear compounds. This skeletal geometry is also unusual for clusters having flat metal skeletons of any size, with these being generally built up from edge-shared triangular faces.[19] The former Mo_2Au units are held together by the new and strong Mo−Au donor bonds [2.768(1) Å], complemented with a considerably strong aurophilic interaction, as judged from the short Au−Au separation [3.022(1) Å].[1] This is accompanied by a relaxation of the Mo1−Au [to 2.880(1) Å] and P−Mo2 [to 2.462(2) Å] bonds, while the P−Mo1 bond remains quite short [2.308(2) Å], with this suggesting the retention of substantial multiplicity here.

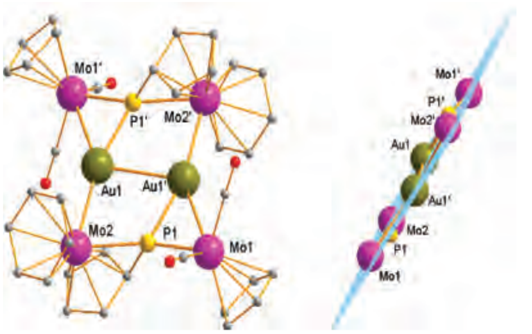

Figure 2. Molecular structure of the cation in **6**, with H atoms and ^{t}Bu groups omitted for clarity (left), and a lateral view of the average Mo_4Au_2 plane (blue), with all ligands (except the P atoms) omitted for clarity (right).

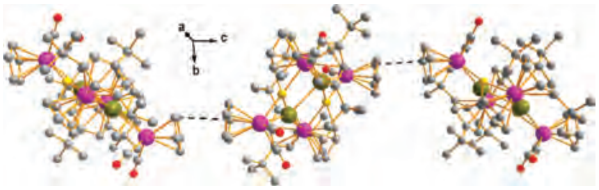

Figure 3. View of the 1D supramolecular chain in **6** (along the *c* axis) with H atoms, anions, and solvent molecules omitted for clarity.

The crystal packing in compound **6** is also remarkable because the cations are ordered along one of the crystallographic axes as a result of the presence of strong $\pi-\pi$-stacking interactions[20] between adjacent Cp ligands (Figure 3). These involve interligand approaches (shortest C−centroid distance of ca. 3.34 Å) comparable to the interlaminar spacing in graphite (3.35 Å), in spite of unfavorable electrostatic repulsions.

The structure of the cation in **6** seems to be retained in an acetone solution. Thus, the molar conductivity of this salt (176 Ω^{-1} cm^2 mol^{-1}) falls within the expected range for 2:1 electrolytes,[21] while the NMR data suggest restricted rotation of the η^6-HR* arene ligand, a phenomenon not observed previously for tri- or tetranuclear derivatives of compound **2**. Further studies are now in progress to examine the physical and chemical properties of this unusual compound and related gold and silver species.

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Supporting Information Available: Preparative and spectroscopic data for new complexes (PDF) and crystallographic data for compounds **5** and **6** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) Selected data for **6**. ν(CO) (MeCN): 1942 (vs), 1880 (s) cm^{-1}. $^{31}P\{^1H\}$ NMR ($Me_2CO\text{-}d_6$): δ 347.9 (s, br, μ_3-PC_5H_4).

(18) X-ray data for $\mathbf{6}\cdot 2CH_2Cl_2$: green crystals, monoclinic (*C*2/*c*), a = 29.4219(8) Å, b = 10.1898(2) Å, c = 26.2038(7) Å, β = 116.100(4)°, V = 7054.9(4) Å^3, T = 100 K, Z = 4, R = 0.0435, GOF = 1.057.

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