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Article

Heterometallic Chains and Clusters with Gold-Transition Metal Bonds: Synthesis and Interconversion

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Anionic, metal−metal bonded heterotrinuclear chain complexes of the type $[M\{MoCp(CO)_3\}_2]^-$ with M = Cu(I), Ag(I), and Au(I) have been prepared by reaction between a d^{10} metal precursor complex and the carbonylmetalate $[MoCp(CO)_3]^-$. These complexes have been structurally characterized by X-ray diffraction and used as precursors to neutral 2-D hexa- or octanuclear mixed-metal clusters of the general formula $[MMoCp(CO)_3]_n$ (M = Cu, n = 3; M = Ag or Au, n = 4), which are characterized by a central core constituted of interacting d^{10} metal ions, surrounded by the molybdenum atoms. When M = Cu, the six metal atoms form a ν_2-triangular core whereas when M = Ag or Au, a ν_2-square structure is observed for the octanuclear metal core. It is shown in the case of M = Cu and Ag that interconversion between the metal chain complexes of stoichiometry $M[m]_2$ and the clusters $\{M[m]\}_n$ is possible, and the position of the equilibrium depends solely on the respective stoichiometry of the reagents. The new ν_2-square, octanuclear, trimetallic complexes $[CuAg_3\{MoCp(CO)_3\}_4]$ (**7**) and $[CuAu_3\{MoCp(CO)_3\}_4]$ (**8**) have also been obtained and characterized in the solid-state by X-ray diffraction, as well as the unexpected double pentanuclear complex $[\{Na(dme)\}\{Cu_2[MoCp(CO)_3]_3\}]_2$ (**9**).

Introduction

Following the publication by Nyholm and co-workers of the first heterometallic complexes containing a metal−metal bond between a group 11 d^{10} ion M and another transition metal M′,[1] numerous heterometallic complexes containing at least one metal−metal bond between a group 11 d^{10} ion (M = Cu(I), Ag(I), or Au(I)) and another transition metal have been prepared, and a wide range of structural types have been encountered.[2−4] Characterization of the metal core usually requires structural investigations by X-ray diffraction, but in the case of the linear, heterometallic Au(I) anionic complexes $[M'\text{-}Au\text{-}M']^-$, with M′ = $CrCp(CO)_3$, $MoCp(CO)_3$, $WCp(CO)_3$, $Mn(CO)_5$, $FeCp(CO)_2$, or $Co(CO)_4$, far-infrared spectroscopy was used to identify the asymmetric metal−metal stretching vibration and compare the strength of the Au−M′ bond with that of related systems.[5−7] Comparative electroreduction was also performed on these systems.[8]

In addition to the direct metal−metal bonding established in these molecules between M and M′, $d^{10}-d^{10}$ interactions sometimes occur between the metal centers M, and such closed shell interactions have become of increasing interest in experimental and theoretical chemistry.[9−17] The use of precursor complexes containing bare d^{10} ions allows the number of metal−metal bonds these ions can form to be maximized. The simplest heterometallic complexes with bare d^{10} ions from the group 11 metals are the trinuclear, linear or bent chains of the type M′−M−M′ where M′ is a transition metal (M = Cu, M′ = Cr,[18] Mo,[18] W,[18] Co;[19−21] M = Ag,

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M′ = Cr,[18] Mo,[18,22−25] W,[18,22,23] Re,[26] Co,[19] Rh,[27,28] Ir,[29−33] Pt;[34,35] M = Au, M′ = Cr,[6] Mo,[5,6,36,37] W,[6,36] Mn,[5,6,36] Fe,[5,6] Co[5,6,36]) or a post-transition metal (M = Cu, M′ = Ge,[38] M = Au, M′ = Ga,[39,40] Ge,[41] Sn[41]). In this paper, we first describe the new anionic, heterometallic chain complexes $[Na(dme)_2][Cu\{MoCp(CO)_3\}_2]$ (**1**) (dme = 1,2-dimethoxyethane) and $[Na(dme)][Ag\{MoCp(CO)_3\}_2]$ (**2**) (Cp = η^5-C_5H_5) and report the crystal structure of the known[5] Au−Mo−Au chain complex $[NEt_4][Au\{MoCp(CO)_3\}_2]$ (**3**). We then show that these $[M\{MoCp(CO)_3\}_2]^-$ anions (M = Cu(I), Ag(I), and Au(I)) react further with 1 equiv of the d^{10} complex M to afford the neutral planar, 2-D bimetallic clusters $[MMoCp(CO)_3]_n$ (**4**, M = Cu, *n* = 3; **5**, M = Ag, *n* = 4; **6**, M = Au, *n* = 4)[42] and the new trimetallic, octanuclear clusters $[CuAg_3\{MoCp(CO)_3\}_4]$ (**7**) and $[CuAu_3\{MoCp(CO)_3\}_4]$ (**8**), which all contain a coinage metal/Mo ratio of 1. The unexpected double Cu−Mo pentanuclear cluster $[Na(dme)\{Cu_2[MoCp(CO)_3]_3\}]_2$ (**9**) was also obtained from **1**, although in an irreproducible manner, and structurally characterized in the solid-state.

Results and Discussion

1. Synthesis and Structures of the Heterometallic Anionic Chain Complexes $[M\{MoCp(CO)_3\}_2]^-$ with M = Cu(I), Ag(I), and Au(I).

1.1. Copper−Molybdenum Complex. The reaction of $[Cu(NCMe)_4]PF_6$ with 2 equiv of the nucleophilic reagent $[Na(dme)_2][MoCp(CO)_3]$ in toluene at −30 °C afforded the yellow, anionic complex $[Na(dme)_2][Cu\{MoCp(CO)_3\}_2]$ (**1**) which has been characterized by single-crystal X-ray diffraction (Figure 1).

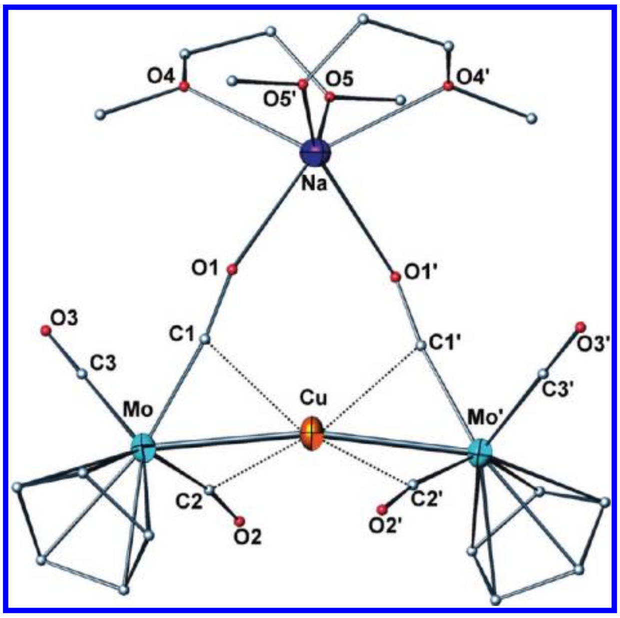

Figure 1. View of the crystal structure of **1**. Selected bond lengths [Å] and angles [deg]: Mo−Cu 2.5810(4), O1−Na 2.432(4), O4−Na 2.371(4), O5−Na 2.411(5); Mo−Cu−Mo′ 168.25(4), C1−O1−Na 137.3(3).

As expected for a Cu(I) complex, the heterotrinuclear sequence Mo−Cu−Mo is almost linear (168.25(4)°) and the Cu center is located on a C_2 axis of symmetry, like the Na^+ cation which is chelated by two dme molecules. This cation is hexacoordinated because it further interacts with the oxygen atoms of the carbonyl ligands C(1)O(1) and C(1′)O(1′), which carry a significant fraction of the negative charge of the complex $[Cu\{MoCp(CO)_3\}_2]^-$. The Na-OC-metal distance (2.432(4) Å) is in agreement with the literature values reported for such interactions (median value from CCSD Nov. 2008: 2.373 Å, σ = 0.13 for 779 samples).[43−56] The C(1)O(1) distance of 1.174(5) Å is not significantly longer than the values for the other carbonyls, (C(2)O(2) = 1.169(6) Å and C(3)O(3) = 1.148(5) Å), which is consistent with the electrostatic nature of the Na-OC interactions. The Cu−Mo distance is in agreement with the literature values reported for this bond (values from CCSD Nov. 2008: median 2.705 Å, mean 2.728 Å,

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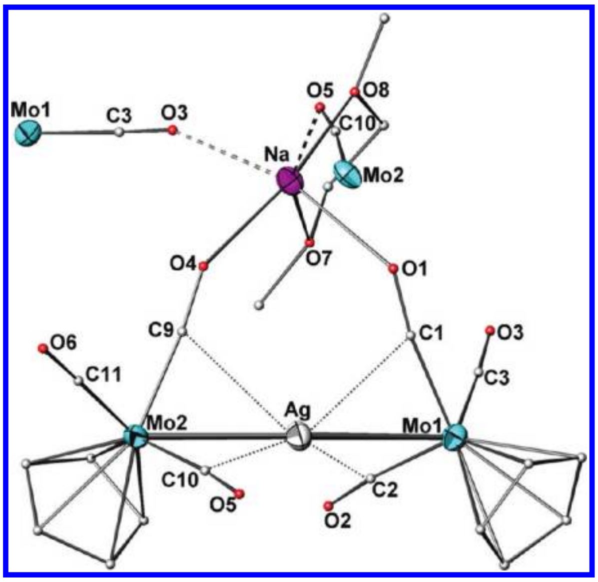

Figure 2. View of the crystal structure of **2**. Selected bond lengths [Å] and angles [deg]: Mo1−Ag 2.7891(9), Mo2−Ag 2.7846(11), O1−Na 2.441(6), O3−Na 2.369(3), O4−Na 2.313(6), O5−Na 2.336(6), Na−O7 2.316(6), Na−O8 2.277(7); Mo1−Ag−Mo2 171.02(3), C1−O1−Na 131.1(5), C3−O3−Na 153.6(6), C9−O4−Na 147.9(6), C10−O5−Na 127.9(5).

σ = 0.11 for 378 samples). The (semi)-bridging bonding situation[57−61] of the CO ligands in complexes **1**−**3** and **7**−**9** is discussed in the Supporting Information.

1.2. Silver−Molybdenum Complex. The reaction of AgBF$_4$ with 2 equiv of [Na(dme)$_2$][MoCp(CO)$_3$] in toluene at −30 °C afforded colorless, light-sensitive crystals of the anionic complex [Na(dme)][Ag{MoCp(CO)$_3$}$_2$] (**2**) which have been characterized by single-crystal X-ray diffraction (Figure 2).

In the crystalline state, the metal core of the anion [Ag{MoCp(CO)$_3$}$_2$]$^-$ adopts an almost linear structure, the Mo(1)−Ag−Mo(2) angle being 171.02(3)°. The Ag−Mo distances are in agreement with the literature values reported for this bond (values from CCSD Nov. 2008: median 2.961 Å, mean 2.955, σ = 0.07 for 85 samples). Like in **1**, the sodium cation interacts with the oxygen atoms of the carbonyl ligands C(1)O(1) and C(9)O(4) to form an eight-membered ring. The Na-OC-metal distances are similar to that in **1** and are in agreement with the literature values reported for this bond (values from CCSD Nov. 2008: median 2.373 Å, mean 2.390 Å, σ = 0.13 for 779 samples).[43−56] Like in **1**, the C(1)O(1) and C(9)O(4) distances of 1.187(8) and 1.165(8) Å, respectively, are comparable with those of the other carbonyl ligands, which are in the range 1.146(10)−1.176(10)Å. Contrary to **1**, the sodium cation of **2** is chelated by only one molecule of dme, and further develops intermolecular interactions with the oxygen atom of two other carbonyls, C(3)O(3) and C(10)O(5), from adjacent molecules (Figure 3). The Mo-CO···Na$^+$ interactions indicate that a significant amount of the negative charge carried by the trinuclear complex is located on the oxygen atoms of the carbonyl ligands, as observed for **1**. This translates into relatively low ν(CO) values in the IR spectra. The bonding situation of the CO ligands is discussed in the Supporting Information.

1.3. Gold−Molybdenum Complex. The reaction of [NEt$_4$][AuBr$_2$] with 2 equiv of [Na(dme)$_2$][MoCp(CO)$_3$] in tetrahydrofuran (THF) at −30 °C afforded the yellow heterotrinuclear complex [NEt$_4$][Au{MoCp(CO)$_3$}$_2$] (**3**). The synthesis of this anionic complex was reported in 1984,[6] but yellow single crystals have now been obtained by slow diffusion of pentane into a THF solution of the product at room temperature and analyzed by single-crystal X-ray diffraction for comparison with **1** and **2** (Figure 4). In the crystalline state, isolated [Au{MoCp(CO)$_3$}$_2$]$^-$ anions have C_2 symmetry and adopt a linear structure, with the Au atom occupying a center of symmetry for the molecule.

The Au−Mo distance is in agreement with the literature values reported for this bond (values from CCSD Nov. 2008: median 2.803 Å, mean 2.840 Å, σ = 0.12 for 76 samples). A similar structure has been observed for the chromium analogue [Au{CrCp(CO)$_3$}$_2$]$^-$.[6]

The parameter [(m−M)$_{\text{exp}}$ − (r_{m} + r_{M})] shows that the shortening of Mo−Au distance with the respect to the sum of the covalent radii of the metals is more pronounced than for the Cr−Au bond, which suggests a stronger bond (Table 1).

2. Transformations of the Heterometallic, Anionic Chain Complexes [M{MoCp(CO)$_3$}$_2$]$^-$ (M = Cu(I), Ag(I), and Au(I)) in Cu$_3$Mo$_3$, Ag$_4$Mo$_4$, or Au$_4$Mo$_4$ Clusters. Neutral, oligomeric 2-D raft-type clusters [MMoCp(CO)$_3$]$_n$ (M = Cu, n = 3; M = Ag or Au, n = 4) were recently obtained by reaction of the metalate [m] = [MoCp(CO)$_3$]$^-$ with the corresponding d^{10}-metal complex M in a 1:1 ratio.[42] In view of the very fast reaction kinetics involving d^{10}-metal centers, it is difficult to know whether a dinuclear M[m] entity is formed first and rapidly oligomerizes or if formation of these clusters occurs via the intermediate formation of trinuclear {M[m]$_2$}$^-$ complexes, which we have shown form readily.[5,6] We thus wondered whether the latter, described above, could be converted into the raft-type clusters by addition of 1 equiv of M to reach a [m]/M ratio of 1. We shall see that this hypothesis is consistent with the following reactions and the reversible transformations observed with the copper and silver complexes.

The reaction of [Cu(NCMe)$_4$]PF$_6$ with 1 equiv of the chain complex **1** in toluene at −30 °C afforded, after slow diffusion of pentane into a toluene solution of the product at −25 °C, yellow, monoclinic crystals of composition 2(**4**)·3C$_7$H$_8$ (Scheme 1). This cluster was recently obtained by the 1:1 reaction between [Cu(NCMe)$_4$]PF$_6$ and [Na(dme)$_2$][MoCp(CO)$_3$] and shown to contain a planar 2-D raft-type core structure constituted by a copper triangle inscribed within a Mo$_3$ triangle.[42] This results in a ν_2-triangular metal core with a Mo/Cu ratio of 1:1.

Conversely, formation of the trinuclear complex **1** resulted from the reaction of 2(**4**)·3C$_7$H$_8$ with 3 equiv of [Na(dme)$_2$][MoCp(CO)$_3$] in THF at −30 °C (Scheme 1). IR-monitoring in the ν(CO) region showed that the reaction of 2(**4**)·3C$_7$H$_8$ with only 1 equiv of [Na(dme)$_2$][MoCp(CO)$_3$] in THF at −30 °C resulted in a mixture of complexes **1** and **4** (Supporting Information).

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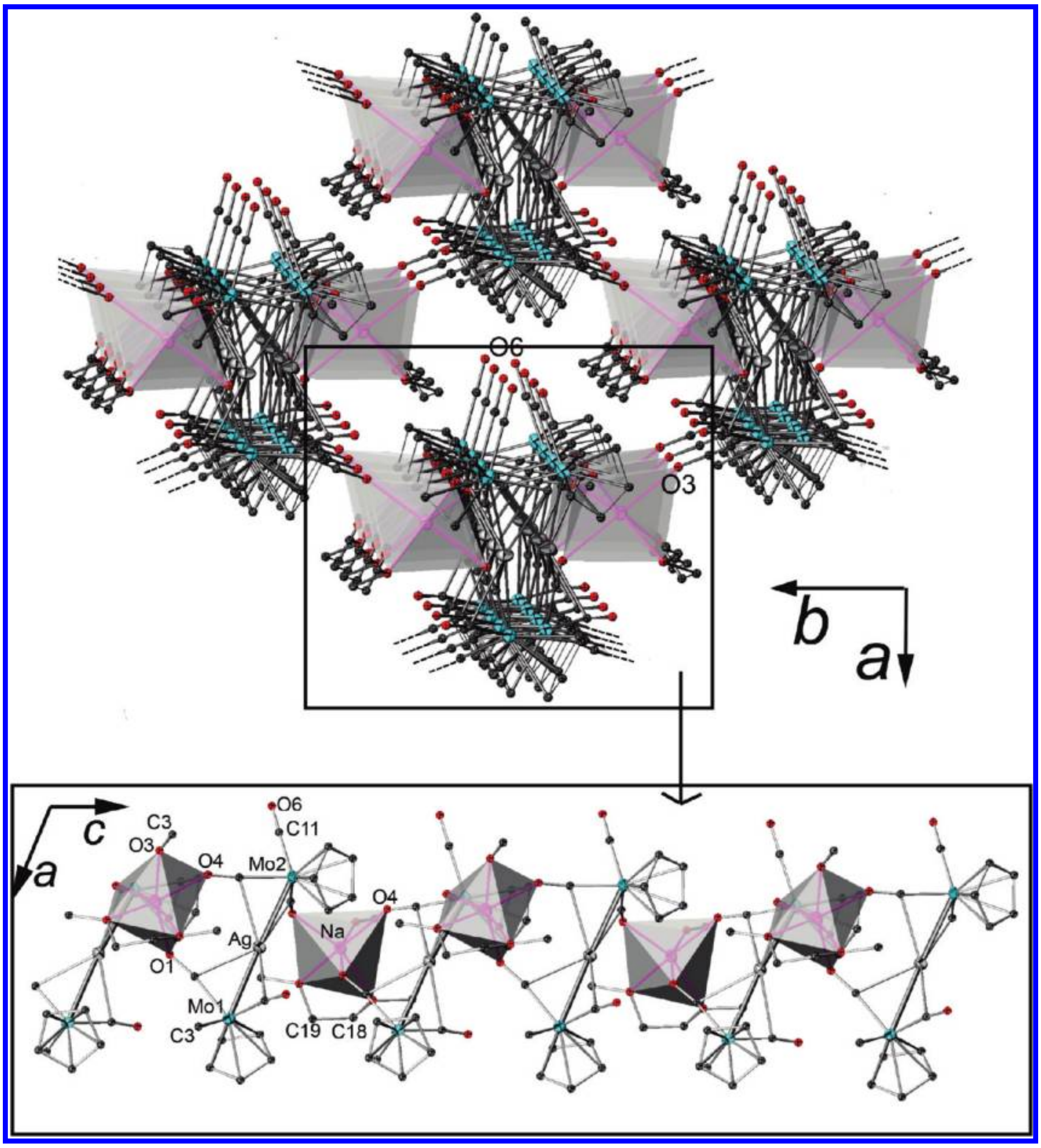


Figure 3. View of the projection of the crystal packing of **2** in two orthogonal planes.

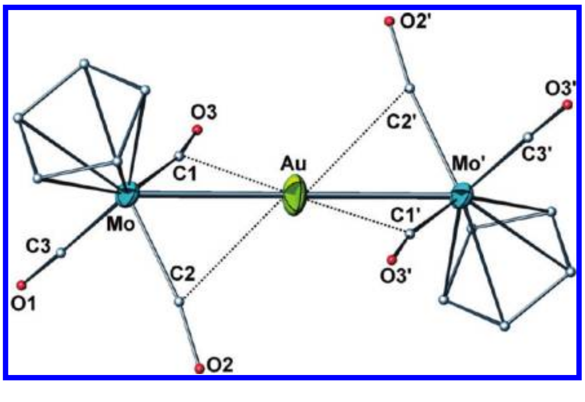


Figure 4. View of the crystal structure of **3**. Selected bond lengths [Å] and angles [deg]: Mo−Au 2.7216(11), C1−O3 1.161(5), C2−O2 1.164(5), C3−O1 1.163(5); Mo−Au−Mo′ 180°.

Table 1. Comparison between Cr−Au and Mo−Au Bond Lengths (Å)

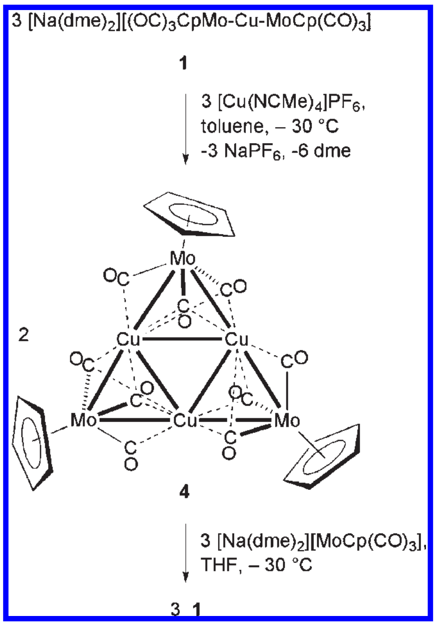
m−M	$(r_m + r_M)$[62]	$(m-M)_{exp}$ aver. values	$(m-M)_{exp} - (r_m + r_M)$
Cr−Au	2.46	2.638	0.178
Mo−Au	2.62	2.722	0.102

r_M and r_m: covalent radii of M and m, respectively.

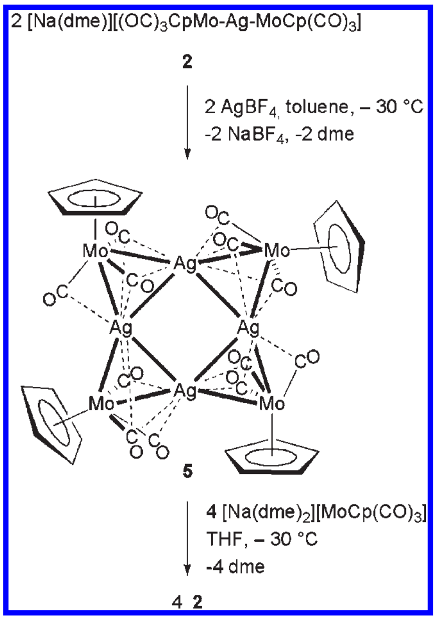
The reaction of $AgBF_4$ with 1 equiv of **2** in toluene −30 °C afforded after slow diffusion of pentane into a toluene solution of the product at −25 °C yellow, orthorhombic crystals of the light-sensitive product **5** (Scheme 2). This cluster has been recently obtained by the 1:1 reaction of $AgBF_4$ with $[Na(dme)_2][MoCp(CO)_3]$ and shown to contain an octanuclear metal core constituted by a silver square inscribed within a distorted molybdenum square, thus forming a v_2-square with a Mo/Ag ratio of 1:1.[42]

Reformation of complex **2** was observed when **5** was reacted with 4 equiv of $[Na(dme)_2][MoCp(CO)_3]$ in THF at −30 °C (Scheme 2). IR-monitoring showed that the reaction of **5** with only 2 equiv of $[Na(dme)_2]$-$[MoCp(CO)_3]$ in THF at −30 °C led to a mixture of complexes **2** and **5** (Supporting Information). This indicates

Scheme 1. Interconversion between the Linear Complex **1** and Cluster **4**



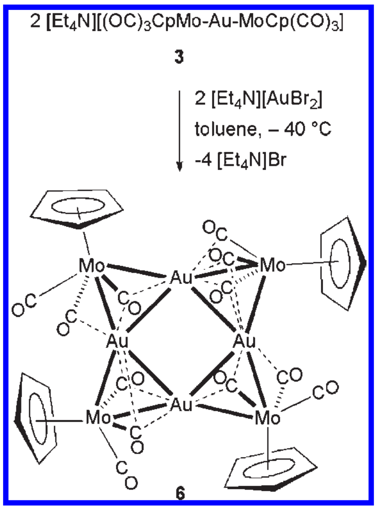
Scheme 2. Interconversion between the Linear Complex **2** and Cluster **5**



that the reversibility of the transformations between the trinuclear, linear complex and the cluster solely depends on the stoichiometry of the reagents used.

The reaction of $[NEt_4][AuBr_2]$ with 1 equiv of **3** in toluene −40 °C afforded, after slow diffusion of pentane into a toluene solution of the product at −25 °C, red, triclinic crystals of **6**, which has also been obtained by the 1:1 reaction between $[NEt_4][AuBr_2]$ and $[Na(dme)_2][MoCp(CO)_3]$ and found to have a structure similar to that of **5**, the metal core forming a ν_2-square with a Mo/Au ratio of 1:1 (Scheme 3).[42] The transformation of **6** back to **3** was not examined but is likely to proceed as in the case of M = Cu and Ag.

Scheme 3. Conversion of the Linear Complex **3** in Cluster **6**



3. Synthesis and Structures of the Trimetallic, Octanuclear Clusters $[CuAg_3\{MoCp(CO)_3\}_4]$ and $[CuAu_3\{MoCp(CO)_3\}_4]$. The results described above for M = Cu(I) and Ag(I) clearly show that interconversion between the metal chain complexes of stoichiometry $M_2[m]$ and the clusters $\{M[m]\}_n$ is possible in the presence of an equivalent of a suitable mononuclear complex M. The position of the equilibrium depends solely on the respective quantities of reagents present. These observations encouraged us to try to associate two different group 11 metals within the same cluster and extend the above series of 2-D raft-type heterometallic clusters to systems containing three different metals.

The reaction of $AgBF_4$ with 1 equiv of **1** in toluene at −30 °C afforded the yellow-orange, temperature sensitive (decomposition) cluster $[CuAg_3\{MoCp(CO)_3\}_4]$ (**7**) which was characterized by single-crystal X-ray diffraction in $\mathbf{7}\cdot C_7H_8$. The same complex was obtained by the reaction of $[Cu(NCMe)_4]PF_6$ with 1 equiv of **2** in toluene at −30 °C. Although the stoichiometry of the reagents used was Mo/Cu = 2 and Mo/Ag = 2, **7** was the only product isolated by crystallization, in which these ratios are 4:1 and 4:3, respectively.

The X-ray single crystal analysis revealed an ordered structure which contains a square metal core, formed by three Ag(I) and one Cu(I) centers (Figure 5). Each edge of this square is bridged by a metalloligand $MoCp(CO)_3$, and the four Mo centers form a distorted square (Mo1−Mo2, 5.449(5) Å, Mo2−Mo3 5.476(5) Å, Mo3−Mo4 5.199(8), Mo4−Mo1 5.406(7) Å). Like **5** and **6**, this cluster has a ν_2-square structure. However, the molybdenum atoms are not coplanar with the silver and copper atoms, since a slight tetrahedral distortion leads the Mo3 and Mo4 atoms to be located on opposite sides of the $CuAg_3$ plane (Figure 7).

The Ag−Ag, Ag−Cu, Mo−Ag, and Mo−Cu distances are in the range of those found in the literature (median and mean values from CCSD Nov. 2008: 3.016 Å, 3.052 Å, σ = 0.20 for 3343 samples; 2.864 Å, 2.857 Å, σ = 0.14 for 103 samples; 2.961, 2.955 Å, σ = 0.07 Å for 85 samples and 2.705 Å, 2.728 Å, σ = 0.11 for 378 samples, respectively). The bonding situation of the CO ligands is discussed in the Supporting Information.

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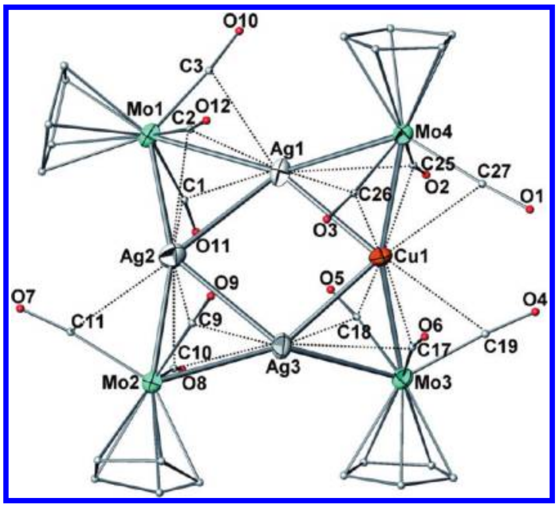

Figure 5. View of the crystal structure of **7** in $\mathbf{7}\cdot C_7H_8$. Selected bond lengths [Å] and angles [deg]: Ag1−Ag2 2.9093(8), Ag2−Ag3 2.9351(11), Ag3−Cu1 2.8143(9), Cu1−Ag1 2.7339(11), Ag1···Ag3 3.7110(8), Ag2···Cu1 4.3141(13), Mo1−Ag1 2.8302(11), Mo1−Ag2 2.7548(7), Mo2−Ag2 2.7781(7), Mo2−Ag3 2.8454(7), Mo3−Ag3 2.8419(9), Mo3−Cu1 2.6372(8), Mo4−Cu1 2.6412(9), Mo4−Ag1 2.8333(8); Cu1−Ag1−Ag2 99.68(3), Ag1−Ag2−Ag3 78.83(2), Ag2−Ag3−Cu1 97.22(2), Ag3−Cu1−Ag1 83.94(3), Mo1−Ag1−Mo4 145.26(3), Mo1−Ag2−Mo2 160.07(3), Mo2−Ag3−Mo3 148.61(2), Mo3−Cu1−Mo4 160.09(4).

The reaction of $[NEt_4][AuBr_2]$ with 1 equiv of **1** in toluene at −30 °C afforded the red, temperature-sensitive cluster $[CuAu_3\{MoCp(CO)_3\}_4]$ (**8**) which was characterized by single-crystal X-ray diffraction in $\mathbf{8}\cdot C_7H_8$. This complex was also obtained from the reaction of $[Cu(NCMe)_4]PF_6$ with 1 equiv of **3** in toluene at −30 °C and was the only product isolated by crystallization.

This cluster contains a central square metal core, two opposite positions being occupied by Au(I) centers, and the other two containing a mixture of gold and copper (Figure 6). The best fit for the structure refinement was obtained when assuming an 80:20 Cu/Au occupation for one of these two sites, 20:80 Cu/Au for the other. Each edge of the square is bridged by the metalloligand $[MoCp(CO)_3]$, and the molybdenum atoms are not coplanar with the gold and copper atoms, as a result of a slight tetrahedral distortion which leads the Mo3 and Mo4 atoms to be situated on the opposite sides of the $CuAu_3$ plane (Figure 7). Like in **7**, the eight metal atoms in this cluster form a ν_2-square type arrangement. The bonding situation of the CO ligands is discussed in the Supporting Information.

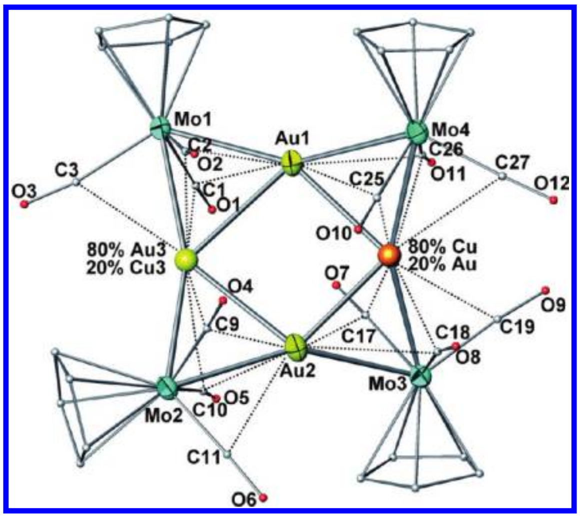

Figure 6. View of the crystal structure of **8** in $\mathbf{8}\cdot C_7H_8$. Selected bond lengths [Å] and angles [deg]: Au1-(80% Cu/20% Au) 2.7250(15), (80% Cu/20% Au)-Au2 2.6657(15), Au2-(80% Au3/20% Cu3) 2.862(1), (80% Au3/20% Cu3)-Au1 2.9037(9), Au1···Au2 3.7658(11), (80% Cu/20% Au)···(80% Au3/20% Cu3) 4.1106(14), Mo1−Au1 2.7915(14), Mo1-(80% Au3/20% Cu3) 2.7775(16), Mo2-(80% Au3/20% Cu3) 2.7583(16), Mo2−Au2 2.7838(14), Mo3−Au2 2.7774(14), Mo3-(80% Cu/20% Au) 2.695(2), Mo4-(80% Cu/20% Au) 2.671(2), Mo4−Au1 2.7906(15); (80% Au3/20% Cu3)-Au1-(80% Cu/20% Au) 93.77(4), Au1-(80% Cu/20% Au)-Au2 88.62(4), (80% Cu/20% Au)-Au2-(80% Au3/20% Cu3) 96.02(4), Au2-(80% Au3/20% Cu3)-Au1 93.77(4), Mo1−Au1−Mo4 150.14(5), Mo2−Au2−Mo3 149.02(5), Mo3-(80% Cu/20% Au)−Mo4 154.50(7), Mo1-(80% Au3/20% Cu3)−Mo2 159.98(5).

The Mo−Au distances are in the range 2.7774(14)−2.7915(14) Å, values which are in agreement with those reported for this bond (values from CCSD Nov. 2008: median 2.803 Å, mean 2.840 Å, σ = 0.12 for 76 samples). The Mo−Au/Cu distances are in the range 2.671(2)−2.7775(16) Å and are shorter than the Mo−Au distances. The average M−M distances Au−Au/Cu are in the range 2.6657(15)−2.9037(9) Å and are comparable with the median values found for Au−Cu and Au−Au bonds (median and mean values from CCSD November 2008: 2.762 Å, 2.788 Å, σ = 0.14 for 83 samples; 2.918 Å, 2.944 Å, σ = 0.19 for 2940 samples, respectively) (Table 2).

We report in Table 2 a comparison between the experimental values for the $d^{10}-d^{10}$ metal−metal distances and the corresponding covalent, atomic, metal atom, and van der Waals radii. The most appropriate reference for the $d^{10}-d^{10}$ interactions is the sum of the van der Waals radii.

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The average M−M distances in **7** and **8** are significantly shorter than the sum of the van der Waals radii.[67] This, together with the inward bending of the Mo−M−Mo bonds in the ν_2-squares, suggests the existence of attractive intramolecular $d^{10}-d^{10}$ interactions between the group 11 metals. Examples of Cu−Ag,[68−79] Cu−Au,[77,80−98] and Ag−Au[73,77,78,87−90,99−151] interactions have been reported in the literature.

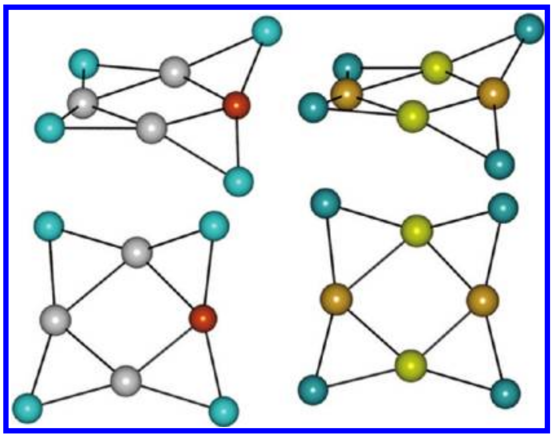

Figure 7. Views of the metal cores of **7** (left) and **8** (right).

4. Structure of an Unexpected Cu_4Mo_6 Complex. The reaction between of **1** with 0.33 equiv of $[Cu(NCMe)_4]PF_6$ in toluene at −50 °C afforded a few yellow crystals which were shown by X-ray diffraction to correspond to the general formula $[Na(dme)\{Cu_2[MoCp(CO)_3]_3\}]_2$ (**9**).

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Table 2. Covalent, Atomic, van der Waals Radii and Experimental M−M distances (in Å)

	Cu−Cu	Ag−Ag	Au−Au	Ag−Cu	Au−Cu
experimental M−M average values for $\{M[m]\}_n$	2.627(8)	2.870(1)	2.774(1)		
experimental M−M average values in **7**		2.922 (1)		2.774(1)	
sum of the single-bond covalent radii[62]	2.24	2.56	2.48	2.40	2.36
sum of the covalent radii[63]	2.64	2.90	2.72	2.77	2.68
sum of the covalent radii (two-coordinated univalent M)[64]	2.26	2.66	2.50	2.46	2.38
sum of the covalent radii (four-coordinated univalent M)[65]	2.58	2.92	2.74	2.75	2.66
sum of the atomic radii[66]	2.346	2.678	2.672	2.512	2.509
sum of the metal atom radii[66]	2.556	2.89	2.884	2.723	2.720
sum of the van der Waals radii[67]	2.80	3.44	3.32	3.12	3.38
[sum of the van der Waals radii − experimental M−M average values]	0.168	0.57	0.546	0.331	

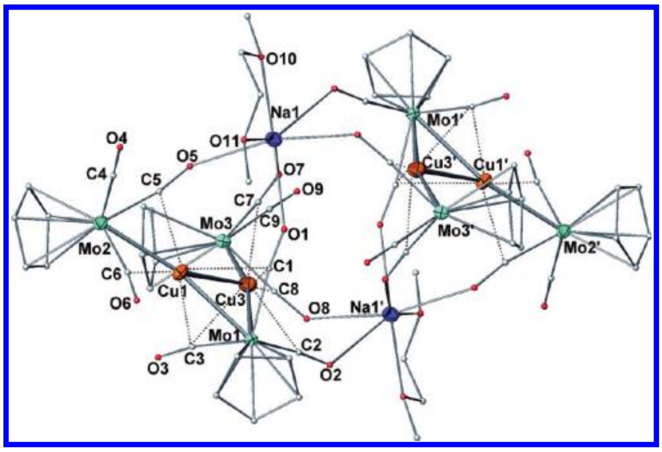

Figure 8. View of the pseudo-dimeric structure of **9** in the solid-state. Selected bond lengths [Å] and angles [deg]: Cu1−Cu3 2.8946(8), Cu1···Cu3′ 7.1628(7), Cu3···Cu1′ 7.1628(7), Mo1−Cu1 2.641(6), Mo2−Cu1 2.6029(6), Mo1−Cu3 2.5933(6), Mo3−Cu3 2.5796(6), O1−Na 2.464(3), O2−Na 2.620(3), O5−Na 2.438(3), O7−Na 2.454(4), O8−Na 2.480(3), O10−Na 2.349(3), O11−Na 2.404(3); Mo1−Cu1−Mo2 164.38(3), Mo1−Cu3−Mo3 165.15(3), C1−O1−Na1 145.0(3), C2−O2−Na1 131.6(3), C5−O5−Na1 137.1(3), C7−O7−Na1 141.1(3), C8−O8−Na1 124.6(3).

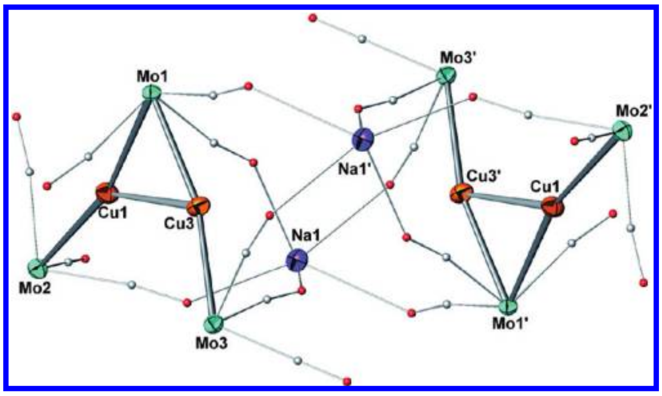

Figure 9. View of the metallic core of **9**.

Two identical pentanuclear fragments [Na(dme)]-[$Cu_2\{MoCp(CO)_3\}_3$] (Figures 8 and 9) are connected, centrosymmetrically, by Mo-CO···Na^+ interactions, similar to those in complexes **1** and **2**, to form a pseudo-dimeric Cu_4Mo_6 complex in the solid-state. Each Cu_2Mo_3 moiety resembles a Cu_3Mo_3 ν_2-triangular cluster **4** with a missing copper center. The structure of this cluster therefore suggests that the Cu_2Mo_3 moiety may be an intermediate in the formation of the Cu_3Mo_3 core of **4**. Unfortunately, despite numerous attempts, including changes in the reagent stoichiometry and reaction temperature, we could not devise a rational synthesis for this complex, and all attempts to generate this complex only led, after crystallization, to the yellow monoclinic crystals of 2(**4**)·$3C_7H_8$. The Na···OC-metal distances of **9** are in range 2.349(3)−2.620(3) Å and are in agreement with the literature values reported for such interactions (median value from CCSD 2.373 Å, σ = 0.13 for 779 samples).[43−56] The bonding situation of the CO ligands is discussed in the Supporting Information. The Cu1−Cu3 bond length of 2.8946(8) Å, longer than in **4** (which ranged from 2.6167(13) to 2.6594(13) Å)[42] and the Cu−Mo distances in the range 2.5796(6)−2.641(6) Å, similar to those in **4**, are in agreement with the literature values reported for these bonds (median values from CCSD Nov. 2008: 2.701 Å, σ = 0.21 for 3946 samples and 2.705 Å, σ = 0.11 for 378 samples, respectively).

Conclusion

The synthesis and full characterization of the trinuclear chain complexes of the type $\{[m]\text{-}M\text{-}[m]\}^-$ containing the metalloligand [m] = $MoCp(CO)_3$ (**1**, M = Cu; **2**, M = Ag; **3**, M = Au) has confirmed the possibility of surrounding a bare d^{10} metal ion with two organometallic moieties through direct metal−metal bonding. When these complexes are associated with Na^+ as counterion, Na···OC electrostatic interactions occur in the solid-state, which is consistent with the significant electron density carried by their oxygen atom and readily accounts for the rather low ν(CO) values observed in the IR spectrum. Reaction of these trinuclear complexes with 1 equiv of the d^{10} metal precursor complex afforded the 2-D clusters $[MMoCp(CO)_3]_n$ (**4**, M = Cu, n = 3; **5**, M = Ag, n = 4; **6**, M = Au, n = 4) in which the metal ratio is 1:1. Such transformations were shown in the case of M = Cu, Ag to be reversible and to depend solely on the stoichiometry of the reagents present. It is therefore possible that the very fast reactions, in a 1:1 stoichiometry, between the d^{10} metal complexes $[Cu(NCMe)_4]PF_6$, $AgBF_4$ and $[NEt_4][AuBr_2]$ and $[MoCp(CO)_3]^-$, which afford the clusters $[MMoCp(CO)_3]_n$, occur either by "oligomerization" of a

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hypothetical dinuclear unit [MMoCp(CO)$_3$], as suggested in related systems[152] or by the intermediacy of the chain complexes {[m]-M-[m]}$^-$ which would then react, very rapidly, with the second half equivalent of the complex M present. This stepwise synthesis via isolable intermediates was used to incorporate a second d^{10} metal ion into the octanuclear clusters by reaction of **1** with AgBF$_4$ or [NEt$_4$][AuBr$_2$], and afforded the trimetallic ν_2-square clusters [CuAg$_3${MoCp(CO)$_3$}$_4$] (**7**) and [CuAu$_3${MoCp(CO)$_3$}$_4$] (**8**), respectively. It remains important to collect more data on intramolecular d^{10}−d^{10} interactions based on X-ray diffraction studies to gain a better knowledge of their range and scope and to appreciate their structural consequences.

Experimental section

General Procedures. All reactions were carried out under an atmosphere of nitrogen using conventional Schlenk techniques. Solvents were dried according to standard procedures. Elemental analyses were performed by the Service de Microanalyse, Université de Strasbourg and the Service Central d'Analyse du CNRS, Solaize. NMR spectra were recorded on a Bruker Avance 300 instrument (^{1}H, 300 MHz; ^{13}C{^{1}H}, 75.47 MHz). Chemical shifts (in ppm) were measured at ambient temperature or at −30 °C and are referenced to TMS. IR spectra were recorded in the region 4000−400 cm^{-1} on a FT-IR Nicolet spectrometer (Nicolet 67000 FT-IR Smart Orbit Ge and Nicolet 380 FT-IR). [Na(dme)$_2$][MoCp(CO)$_3$] was synthesized according to literature procedures.[153] The compounds [Cu(NCMe)$_4$]PF$_6$ and AgBF$_4$ were purchased from Strem Chemicals and Sigma-Aldrich, respectively and [NEt$_4$][AuBr$_2$] was synthesized according to literature procedures.[154] A different synthesis of complexes **4**−**6** has been reported elsewhere which afforded similar yields.[42] The reaction mixtures were generally filtered over CaF$_2$ to help remove the inorganic salts.

Synthesis of [Na(dme)$_2$][Cu{MoCp(CO)$_3$}$_2$] (1). Solid [Cu(NCMe)$_4$]PF$_6$ (0.220 g, 0.59 mmol) was added to a suspension of [Na(dme)$_2$][MoCp(CO)$_3$] (0.529 g, 1.18 mmol) in toluene (20 mL) at −30 °C. The mixture was stirred for 15 min, and the resulting orange solution was filtered over CaF$_2$ and then concentrated under reduced pressure. Precipitation with pentane afforded a pale yellow powder which was washed with pentane (0.225 g, 50%). Yellow crystals were obtained by slow diffusion of pentane into a toluene solution of the product at −25 °C. This compound is temperature sensitive in the solid-state and in solution, which prevented collection of satisfactory elemental analysis data. IR (solid) ν(CO): 1951 vw sh, 1904 s, 1810 vs, 1763 vs, 1738 s cm^{-1}. IR (KBr) ν(CO): 1930 s, 1900 m, 1837 vs, 1799 m, 1756 w cm^{-1}. IR (THF) ν(CO): 1928 s, 1917 s, 1827 vs, 1798 m sh cm^{-1}. ^{1}H NMR (C$_6$D$_6$): δ 3.09 (s, 12H, CH$_3$, dme), 3.17 (s, 8H, CH$_2$, dme), 5.26 (s, 10H, Cp). ^{13}C{^{1}H} (C$_6$D$_6$): δ 58.42 (CH$_3$, dme), 71.33 (CH$_2$, dme), 88.59 (Cp).

Synthesis of [Na(dme)][Ag{MoCp(CO)$_3$}$_2$] (2). Solid AgBF$_4$ (0.130 g, 0.67 mmol) was added to a suspension of [Na(dme)$_2$][MoCp(CO)$_3$] (0.600 g 1.34 mmol) in toluene at −30 °C in the dark. The mixture was stirred for 15 min, and the resulting red solution was filtered over CaF$_2$ and then concentrated under reduced pressure. Precipitation with pentane afforded a white powder which was washed with pentane (0.200 g, 42%). Colorless crystals were obtained by slow diffusion of pentane into a toluene solution of the product at −25 °C. This compound is light- and temperature-sensitive, which prevented collection of satisfactory elemental analysis data. IR (solid) ν(CO): 1925 w, 1908 s, 1830 m, 1808 w, 1776 w sh, 1757 vs cm^{-1}. IR (KBr) ν(CO): 1926 s, 1909 s, 1833 m, 1808 w, 1777 w sh, 1758 vs cm^{-1}. IR (THF) ν(CO): 1963 vw, 1931 w sh, 1917 vs, 1832 s, 1812 s cm^{-1}. ^{1}H NMR (acetone-d_6): δ 3.30 (s, 6H, CH$_3$), 3.48 (s, 4H, CH$_2$), 5.32 (s, 10H, Cp). ^{13}C{^{1}H} (acetone-d_6): δ 57.88 (CH$_3$, dme), 71.58 (CH$_2$, dme), 85.74 (Cp).

Synthesis of [NEt$_4$][Au{MoCp(CO)$_3$}$_2$] (3). Solid [NEt$_4$][AuBr$_2$] (0.195 g, 0.40 mmol) was added to a solution of (Na(dme)$_2$][MoCp(CO)$_3$] (0.358 g, 0.80 mmol) in THF (20 mL) at −30 °C. The temperature was slowly raised to ambient temperature. The mixture was stirred for 15 min, the resulting yellow solution was filtered over CaF$_2$, and the solvent was evaporated under reduced pressure. The solid was dissolved in toluene (2 × 20 mL), and the solution was concentrated under reduced pressure. Precipitation with pentane afforded a pale yellow powder which was washed with pentane (0.157 g, 48% yield). Yellow crystals were obtained by slow diffusion of pentane into a THF solution of the product at room temperature. No better analysis could be obtained than reported in the literature.[6] IR (solid) ν(CO): 1924 sh, 1906 s, 1808 vs cm^{-1}. IR (KBr) ν(CO): 1898 vs br, 1819 vs, br cm^{-1}. IR (THF) ν(CO): 1936 w, 1912 s, 1832 s br cm^{-1}. ^{1}H NMR (C$_6$D$_6$): δ 5.30 (s, 10H, Cp), 3.45−3.53 (q, J = 7.3 Hz, 8H, NCH$_2$CH$_3$), 1.37−1.42 (m, 12H, NCH$_2$CH$_3$). ^{13}C{^{1}H} (C$_6$D$_6$): δ 6.14 (CH$_3$, NEt$_4$), 51.50 (CH$_2$, NEt$_4$), 86.56 (Cp).

Synthesis of [Cu$_3${MoCp(CO)$_3$}$_3$] (4). Solid [Cu(NCMe)$_4$](PF$_6$) (0.100 g, 0.27 mmol) was added to a solution of **1** (0.204 g, 0.27 mmol) in toluene (10 mL) at −30 °C. The mixture was stirred for 10 min, and the resulting orange solution was filtered over CaF$_2$ and then concentrated under reduced pressure. Precipitation with pentane afforded a pale yellow powder which was washed with pentane (0.075 g, 39% yield). Yellow, monoclinic crystals of 2(**4**)·3C$_7$H$_8$ were obtained by slow diffusion of pentane into a toluene solution of the product at −25 °C. Analytical data for this cluster were as reported elsewhere.[42]

Synthesis of [Ag$_4${MoCp(CO)$_3$}$_4$] (5). Solid AgBF$_4$ (0.055 g, 0.28 mmol) was added to a solution of **2** (0.200 g, 0.28 mmol) in toluene (10 mL) at −30 °C in the dark. The temperature was slowly raised to ambient. The mixture was stirred for 10 min, and the resulting yellow solution was filtered over CaF$_2$ and then concentrated under reduced pressure. Precipitation with pentane afforded a pale yellow powder which was washed with pentane (0.080 g, 40%). Yellow crystals of **5** were obtained by slow diffusion of pentane into a THF solution of the product at −25 °C. This compound is light-sensitive. Analytical data for this cluster were as reported elsewhere.[42]

Synthesis of [Au$_4${MoCp(CO)$_3$}$_4$] (6). [NEt$_4$][AuBr$_2$] (0.090 g, 0.18 mmol) was dissolved in acetone (1 mL), and the solution was added to a solution of **3** (0.147 g, 0.18 mmol) in toluene (10 mL) at −40 °C. The mixture was stirred for 10 min, and the resulting orange-red solution was filtered over CaF$_2$ and concentrated under reduced pressure. Temperature-sensitive red crystals of **6**·C$_7$H$_8$ were obtained by slow diffusion of pentane into a toluene solution of the product at −25 °C (0.050 g, 30%). Analytical data for this cluster were as reported elsewhere.[42]

Synthesis of [CuAg$_3${MoCp(CO)$_3$}$_4$] (7). Two different procedures were applied successfully:

- Solid AgBF$_4$ (0.040 g, 0.20 mmol) was added to a solution of complex **1** (0.151 g, 0.20 mmol) in toluene (10 mL) at −30 °C. The mixture was stirred for 10 min, and the resulting orange solution was filtered over CaF$_2$ and concentrated under reduced pressure. Yellow-orange crystals of **7** (0.050 g, 17%) were obtained by slow diffusion of pentane into a toluene solution of the product at −25 °C.
- Solid [Cu(NCMe)$_4$]PF$_6$ (0.075 g, 0.20 mmol) was added to a solution of **2** (0.142 g, 0.20 mmol) in toluene (10 mL) at −30 °C. The mixture was stirred for 10 min, and the resulting orange solution was filtered over CaF$_2$ and concentrated under reduced pressure. Yellow-orange

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Table 3. Crystallographic Data, Data Collection Parameters, and Refinement Results for **1**, **2**, **3**, **7**·C_7H_8, **8**·C_7H_8, and **9**

	1	**2**	**3**
formula	$C_{24}H_{30}CuMo_2NaO_{10}$	$C_{20}H_{20}AgMo_2NaO_8$	$C_{24}H_{30}AuMo_2NO_6$
Fw (g·mol^{-1})	756.89	711.10	817.34
cryst system	monoclinic	monoclinic	monoclinic
space group	$C2/c$	Cc	$P2_1/c$
a (Å)	20.7774(7)	15.9681(5)	7.948(3)
b (Å)	10.8479(4)	16.4950(6)	11.473(5)
c (Å)	14.3734(6)	11.9423(4)	14.781(7)
α (deg)	90.00	90.00	90.00
β (deg)	114.164(2)	129.984(2)	90.72(2)
γ (deg)	90.00	90.00	90.00
V (Å^3)	2955.77(19)	2410.18(14)	1347.7(10)
Z	4	4	2
crystal size (mm)	0.15 × 0.08 × 0.07	0.12 × 0.09 × 0.08	0.10 × 0.09 × 0.08
color	yellow	colorless	yellow
D_{calc} (g·cm^{-3})	1.701	1.960	2.014
μ (mm^{-1})	1.613	1.888	6.382
T (K)	173(2)	173(2)	173(2)
F(000)	1512	1384	784
Θ limits (deg)	2.15/29.98	2.07/27.48	2.25/30.01
reflections collected	11405	7803	11250
no. of independent data	4276	4010	3926
no. of data ($I > 2\sigma(I)$)	2410	3085	2879
no. of parameters	173	289	170
R_1	0.0512	0.0397	0.0354
wR_2	0.1390	0.0831	0.0890
GOF	0.961	0.984	1.010
max/min res. dens. (e·Å^{-3})	1.117/-1.449	0.865/-1.196	1.286/ −1.322
R_{int}	0.0665	0.0542	0.0541

	7·C_7H_8	**8**·C_7H_8	**9**
formula	$C_{32}H_{20}Ag_3CuMo_4O_{12}\cdot C_7H_8$	$C_{32}H_{20}Au_3CuMo_4O_{12}$	$C_{56}H_{50}Cu_4Mo_6Na_2O_{22}$
Fw (g·mol^{-1})	1459.52	1726.81	1950.74
cryst system	monoclinic	monoclinic	triclinic
space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a (Å)	17.5163(5)	17.4767(8)	11.3840(4)
b (Å)	12.3964(4)	12.4192(7)	12.0860(4)
c (Å)	22.1469(7)	22.1282(8)	12.3210(6)
α (deg)	90.00	90.00	85.3970(12)
β (deg)	120.54(2)	119.917(2)	68.4860(15)
γ (deg)	90.00	90.00	89.3140(12)
V (Å^3)	4141.8(9)	4162.9(3)	157.74(11)
Z	4	4	1
crystal size (mm)	0.10 × 0.10 × 0.10	0.09 × 0.08 × 0.07	0.12 × 0.09 × 0.09
color	yellow, orange	orange	yellow
D_{calc} (g·cm^{-3})	2.341	2.755	2.061
μ (mm^{-1})	3.121	12.255	2.567
T (K)	173(2)	173(2)	173(2)
F(000)	2784	3168	952
Θ limits (deg)	1.35/30.02	1.34/27.48	1.69/30.05
reflections collected	25862	26178	13079
no. of independent data	12097	9523	9182
no. of data ($I > 2\sigma(I)$)	7188	5236	6041
no. of parameters	532	522	406
R_1	0.0504	0.0724	0.0443
wR_2	0.1314	0.1902	0.1108
GOF	1.108	0.983	0.987
max/min res. dens. (e·Å^{-3})	1.456/-2.287	3.950/-3.589	1.594/-1.535
R_{int}	0.0534	0.1254	0.0319

crystals of **7** (0.043 g, 15%) were obtained by slow diffusion of pentane into a toluene solution of the product at −25 °C.

This compound is temperature-sensitive, which prevented collection of satisfactory elemental analysis data. IR (solid) ν(CO): 1941 s, 1889 s sh, 1857 vs cm^{-1}. IR (THF) ν(CO): 1944 s, 1897 vs, 1867 vs cm^{-1}. ^{1}H NMR (C_7D_8 at −30 °C): δ 4.82 (s, 20H, Cp), ^{13}C{^{1}H} (C_6D_6, 75.47 MHz): δ 86.82 (Cp).

Synthesis of [CuAu$_3${MoCp(CO)$_3$}$_4$] (8). Two different procedures were applied successfully:

- Solid [NEt$_4$][AuBr$_2$] (0.050 g, 0.10 mmol) was dissolved in acetone (1 mL), and the solution was added to a solution of **1** (0.076 g, 0.10 mmol) in toluene (10 mL) at −30 °C. The mixture was stirred for 10 min, and the resulting orange solution was filtered over CaF_2 and concentrated under reduced pressure. Red crystals of **8** (0.020 g, 11%) were obtained by slow diffusion of pentane into a toluene solution of the product at −25 °C.
- Solid [Cu(NCMe)$_4$]PF$_6$ (0.104 g, 0.28 mmol) was added to a solution of **3** (0.229 g, 0.28 mmol) in toluene (10 mL) at −30 °C. The mixture was stirred for 10 min, and the resulting orange solution was filtered over CaF_2 and concentrated under reduced pressure. Red crystals of **8** (0.045 g, 9%) were obtained by slow diffusion of pentane into a toluene solution of the product at −25 °C.

This compound is temperature sensitive, which prevented collection of satisfactory elemental analyses and $^{13}C\{^1H\}$ NMR data. IR (solid) ν(CO) = 1978 w sh, 1948 w, 1882 s. IR (THF) ν(CO) = 1981 sh, 1951 s br, 1912 w sh, 1890 s. ^1H NMR (C_7D_8): δ 4.88 (s, 20H, Cp).

Synthesis of $[Na(dme)\{Cu_2[MoCp(CO)_3]_3\}]_2$ (9) and $2(\mathbf{4})\cdot 3C_7H_8$. Solid $[Cu(NCMe)_4]PF_6$ (0.082 g, 0.22 mmol) was added to a solution of the heterotrinuclear complex **1** (0.50 g, 0.66 mmol) in 10 mL of toluene at −50 °C. The mixture was stirred for 5 min, and pentane was slowly added directly to the resulting orange solution. Two types of yellow crystals were obtained: **9** and $2(\mathbf{4})\cdot 3C_7H_8$. Only a few crystals of complex **9** were obtained on one occasion, which prevented more complete characterization of this complex, but these crystals were suitable for X-ray diffraction. Despite several attempts, only compound $2(\mathbf{4})\cdot 3C_7H_8$ was obtained when this experiment was repeated.

Crystal Structure Determinations. The data were collected on a Nonius Kappa-CCD area detector diffractometer (Mo−Kα, λ = 0.71073 Å, ϕ scan). The relevant data are summarized in Table 3.

The cell parameters were determined from reflections taken from one set of 10 frames (1.0° steps in ϕ angle), each at 20 s exposure. The structures were solved using direct methods (SHELXS97) and refined against F^2 using the SHELXL97 software.[155] The absorption was corrected empirically (with Sortav) for the area detector data. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in their calculated positions and refined with a riding model in SHELXL97.

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Supporting Information Available: Crystallographic details for all structures in the form of CIF files, experimental details and analysis of the (semi)-bridging bonding situation of the CO ligands in complexes **1**−**3** and **7**−**9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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