Heterometallic Clusters

A Gallium-Coated Gold Cluster**

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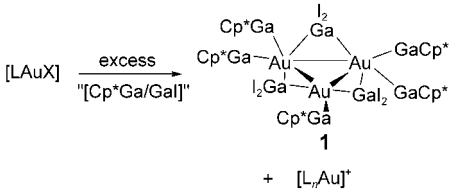
There is much interest in the properties of gold in heterogeneous catalysis,[1–3] supramolecular chemistry,[4] nanochemistry,[1] cluster-complex chemistry,[5] luminescent complexes,[6] and intermetallic compounds and alloys.[7–12] Much of this interest centers on gold–gold and gold–other metal interactions. For applications in catalysis and intermetallic chemistry, the combination of gold—the most electronegative metal—with electropositive metals yields gold in formal negative oxidation states (aurides) or materials with strongly polarized gold–electropositive metal bonds.[2,9–13] In this report, we describe the first complex that contains a Au–Ga bond which is also the first gold cluster complex in which the gold atoms are bonded only to an electropositive main-group metal.[14]

Recent advances in group 13 chemistry have provided reagents of low-valent electropositive group 13 metals that can function as ligands and as reducing agents.[15–19] With these properties in mind, we investigated reactions of gold(I) complexes with Cp*M (Cp* = pentamethylcyclopentadienyl; M = Ga, Al) reagents to prepare gold cluster complexes of gold–electropositive metals.

First, "[Cp*Ga/GaI]", which was prepared by the addition of Cp*K·DME (DME = 1,2-dimethoxyethane) to GaI[20] in a ratio of ≈1:2, was added to a solution of [(Ph_3P)AuCl] in dichloromethane. The resulting orange solution contained the known[21,22] gold cluster $[(Ph_3P)_6Au_6]^{2+}$, which indicated that the gallium reagent had reduced the gold(I) centers but failed to coordinate the resulting reduced Au species. In contrast, reversing the order of addition of the components such that [(Ph_3P)AuCl] was added to excess "[Cp*Ga/GaI]" instead yielded a yellow solution from which air-sensitive orange-yellow crystals of the phosphine-free gold–gallium cluster complex $[Au_3(\mu\text{-}GaI_2)_3(Cp^*Ga)_5]$ (**1**, see Scheme 1) were isolated.[23]



Scheme 1. Isolation of the gold–gallium cluster complex $[Au_3(\mu\text{-}GaI_2)_3(Cp^*Ga)_5]$ (**1**).

A yellow solid **2** was also isolated which spectroscopic data suggested was $[(Ph_3P)_nAu]^+$ (n = 2–3)[24–26] The addition of PCy_3 (Cy = cyclohexyl) to solutions of **2** gave rise to peaks in the ^{31}P NMR spectrum which were associated with free PPh_3 and $[(Cy_3P)_2Au]^+$; PCy_3 does not form *tris* adducts.[27] The nature of the anion in **2** in solution was more difficult to define. The data obtained indicated the presence of several different Cp*Ga-containing ions at ambient temperatures that were exchanging rapidly on the ^1H and ^{13}C NMR timescale. At ambient temperature, ^1H and ^{13}C NMR spectra showed a single peak for Cp*, whereas ^1H NMR spectra at low temperature showed several peaks for Cp*, and ^{71}Ga NMR measurements at ambient temperature displayed several peaks for Ga. To eliminate the possibility of a contribution from chloride ion to this mixture, [(Ph_3P)AuI] was used instead of [(Ph_3P)AuCl] in the preparation of **1**. The yield of **1** was improved, but the properties of the side product **2** were not significantly altered. Finally, the use of [(Cy_3P)AuI] in the preparation yielded a mixture of crystals of **1** and $[(Cy_3P)_2Au]^+[Cp^*GaI_3]^-$ (**3**) from NMR spectroscopic and X-ray crystal structural analysis.[23] These results point to the presence of several different $[(Cp^*)_xGa_yI_z]^-$ anions (x, y, z = integers) in solutions of **2**. Although anions that comprise polynuclear Ga complexes with Cp* have not been reported, anions which consist of polynuclear Ga complexes with $Si(SiMe_3)_3$ have been isolated.[28] Cluster **1** was also prepared in a similar yield from [(Ph_3P)AuI] and a mixture of Cp*Ga and GaI_3, but in this case, **2** was not formed and the co-products were not isolated or identified.[29]

The molecular structure of cluster **1** in the solid-state[23] is shown in Figure 1. The structure consists of a triangle of gold atoms which is bridged by GaI_2 units on its edges. A two-fold

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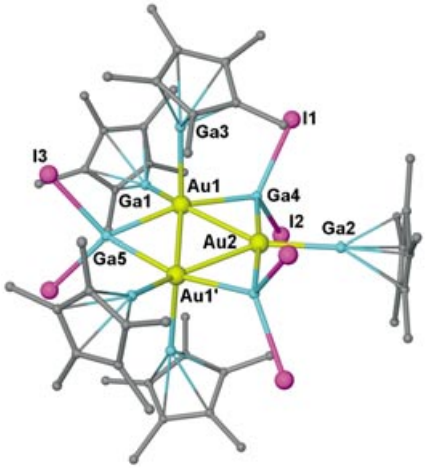

Figure 1. Drawing of $[Au_3(\mu\text{-}GaI_2)_3(Cp^*Ga)_5]$ **1**. Hydrogen atoms are omitted for clarity. Only one orientation of the twofold disordered Cp* of Ga2 is shown. Selected distances [Å] and angles [°]: Au1-Au2 2.7256(6), Au1-Au1′ 2.8045(8), Au1-Ga1 2.3840(12), Au1-Ga3 2.6199(13), Au2-Ga2 2.3773(17), Au1-Ga5 2.5325(13), Au1-Ga4 2.5322(12), Au2-Ga4 2.5280(12); Au2-Au1-Au1′ 59.04(1), Au1-Au2-Au1′ 61.93(2), Ga1-Au1-Ga3 101.93(5), Au2-Ga4-Au1 65.18(3), Au1-Ga5-Au1′ 67.24(4).

axis along the Ga2–Au2–Ga5 vector relates the two halves of the molecule. The two symmetry-related Au atoms (Au1 and Au1′) are each coordinated by two Cp*Ga units, whereas the third unique gold atom (Au2), which lies on the two-fold axis, is coordinated by only one Cp*Ga unit (Ga2). This Cp*Ga unit also lies on the two-fold axis and results in the disorder of the Cp* group over two positions. The Cp*Ga units are arranged around the Au_3 triangle in approximately axial and equatorial positions. The unique Cp*Ga unit (Ga2) and the Cp*Ga units of Ga1 and Ga1′ occupy axial positions in, or nearly in, the Au_3 plane. The other two Cp*Ga units (Ga3 and Ga3′) are nearly perpendicular to the plane in opposite axial positions to Au1 and Au1′. The absence of an axial Cp*Ga unit on Au2 may result from steric crowding because with three axial ligands, two must be on the same side of the Au_3 plane. The axial Cp*Ga groups lie at a greater distance (Au1–Ga3 = 2.6199(13) Å) from the gold atoms than the equatorial Cp*Ga groups (Au1–Ga1 = 2.3840(12) Å, Au2–Ga2 = 2.3773(17) Å) which suggests a weaker interaction with the former. The axial distance is close to the sum of the single-bond covalent radii of 2.58 Å for Au–Ga.[30] The shorter equatorial distances are comparable to the Pt–Ga bond lengths (average = 2.335 Å) in $[Pt(Cp^*Ga)_4]$ after correction for the slightly larger (0.04 Å) covalent radius of Au.[31]

The Cp*(centroid)–Ga distance in Cp*Ga–metal complexes is thought to correlate with the degree of charge transfer from the Ga center to the metal atom.[32] Greater charge transfer results in a smaller radius for gallium and a smaller Cp*(centroid)–Ga distance. The axial Cp*(centroid)–Ga distance of 2.01(1) Å is somewhat smaller than those of Cp*Ga in the solid state (2.081 Å)[33] or in the gas phase (2.081(5) Å)[34] and is similar to $[(Cp^*Ga)_4Ni]$ (2.003(4) Å)[32]—a complex which is thought to involve relatively little charge transfer from the Cp*Ga ligand. The corresponding equatorial distances of 1.89(1) and 1.88(1) Å indicate a greater degree of charge transfer to the gold centers and are similar to that found in $[Cp^*GaFe(CO)_4]$ (1.863(4) Å).[35] The two Au–Au distances in **1** (2.7256(6) and 2.8045(8) Å) are shorter than those found in metallic gold (2.884 Å) and are well within the range associated with Au–Au cluster bonds.[5] DFT (density functional theory) calculations also support the presence of Au–Au bonds (see below). The three other known Au_3 clusters have, on average, similar Au–Au distances, although $[(dppe)_2Au_3In_3Br_7(thf)]^-$ and $[(dppe)_2Au_3In_3Cl_6(thf)_6]$ (dppe = 1,2-bis(diphenylphosphino)ethane) show much greater variation with one very short distance (2.575(1) and 2.562(1) Å, respectively) and two longer distances (2.860(1) and 2.858(1), and 2.939(1) and 2.931(1) Å, respectively).[36,37] The Au–Au distances (2.764(2), 2.780(3), and 2.757(2) Å) for the symmetric Au_3 cluster $[(Cp'Nb)_3Au_3(\mu\text{-}H)_6]$ ($Cp' = C_5H_4SiMe_3$) are very regular and lie between the two values for **1**.[38]

In contrast to the results obtained for **1** in the solid state that indicate three different types of Cp*Ga groups, ^1H and ^{13}C NMR spectra of **1** in CD_2Cl_2 show only one signal for the Cp*Ga ligands at 25 °C. Lowering the temperature down to −90 °C leads to increased broadening of the peak without the resolution of the 1:2:2 pattern expected for the three different Cp* groups. This most likely indicates rapid exchange of the different Cp*Ga groups. No signals were detected in the ^{71}Ga NMR spectrum at 25 °C or at −70 °C; the absence of signals in the ^{71}Ga NMR spectra for several Cp*Ga–Pt complexes has also been reported.[39] Addition of free Cp*Ga to a solution of **1** at 25 °C yielded a single peak in the ^1H NMR spectrum which lies between the values for **1** and Cp*Ga. This indicates exchange of free and coordinated Cp*Ga groups. Fluxional behavior and exchange with free Cp*M units has been observed with the linear Pd_3 cluster $[Pd_3(Cp^*In)_4(\mu\text{-}Cp^*In)_4]$,[40] but not with dinuclear $[Pt_2(Cp^*Ga)_2(\mu\text{-}Cp^*Ga)_3]$ complexes.[31,41]

The above data show the presence of a Au_3 triangular cluster with neutral electron-donor Cp*Ga ligands. However, the presence of the bridging GaI_2 units allows an alternative interpretation of the structure as a six-membered Au–Ga ring without Au–Au bonds.[42] Furthermore, there is ambiguity in the assignment of the oxidation states of the Au centers. With neutral Cp*Ga ligands, the GaI_2 units may be assigned a positive, neutral, or negative charge which corresponds to the oxidation states +3, +2, or +1 of gallium. Corresponding oxidation states for the Au centers would then be −1, 0, or +1. To assist in the resolution of these ambiguities, DFT calculations with the LAN2DZ basis set, which has been shown to be effective for Au clusters,[43] were performed on an analogue of **1** with Cp ligands (Cp = cyclopentadienyl).[29] The optimized structure (no symmetry constraints) corresponded closely to the structure for **1** showing the same axial–equatorial distribution of the CpGa ligands. Isodensity surfaces of the electron-density distribution show the topological features expected for Au_3 and Au_2Ga rings (see Figure 2). Ring critical points in the centers and bond paths[44a] along the Au–Au and Au–Ga bonds are clearly visible and support the view of **1** as a Au_3 cluster ligated by Ga centers. Natural population analysis[44b] atom charges are

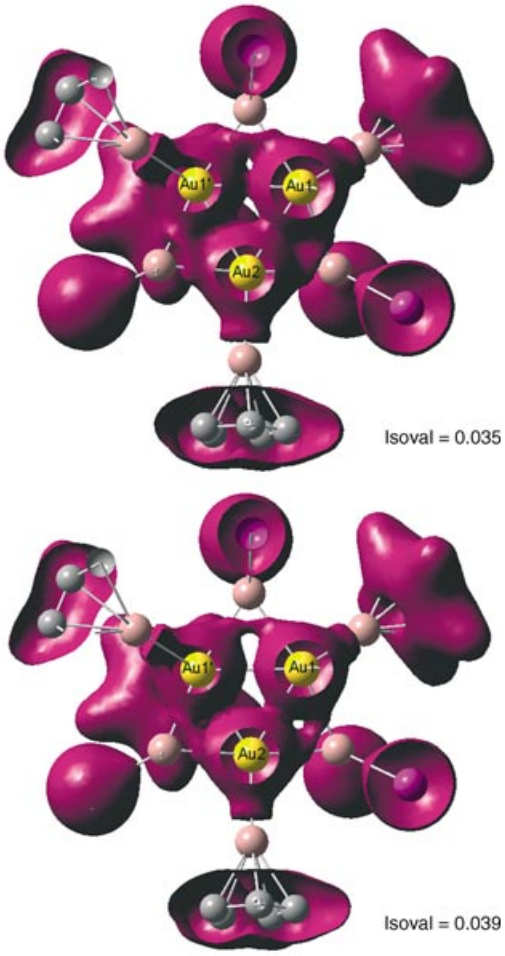

Figure 2. Isodensity surfaces of the electron-density distribution (0.035 e a.u.^{3} (top) and 0.039 e a.u.^{3}). Hydrogen atoms are not shown. Atoms and density from slightly above the Au_3 plane have been removed for clarity.

provided in Table 1. A small positive charge is assigned to the gold atoms. This charge is nearly equal to those of the bridging gallium atoms (Ga4 and Ga5) which indicates an essentially nonpolar covalent bond and suggests the oxidation assignment of +2 for the Ga centers of the GaI_2 units and 0 for the Au atoms. Large positive charges are assigned to the Ga atoms of the CpGa ligands (Ga1, Ga2, Ga3) and indicate substantial bond polarization for these Ga–Au bonds. Negative charges reside on the Cp groups and the iodine centers.[29] The polarity of the axial CpGa–Au bond is somewhat less than those of the equatorial bonds; this observation is consistent with the Cp*(centroid)–Ga distances discussed above.

Table 1: Calculated atom charges in the Cp analogue of **1**.

Atom	Charge	Atom	Charge
Au1	0.12	Ga1	0.86
Au2	0.16	Ga2	0.90
		Ga3	0.78
		Ga4	0.11
		Ga5	0.11

In conclusion, low-valent Ga species are effective reducing reagents for [LAuX] (L = ligand, X = anion) and, when present in excess, they effectively trap the reduced gold centers by ligation. Given the large number of phosphine–gold cluster complexes reported,[22,45] this bodes well for the synthesis of a new family of group 13 ligated gold cluster complexes. DFT calculations on the Cp analogue of **1** show a Au_3 cluster with Au–Au bonds with near-charge-neutral gold atoms and strongly polarized CpGa–Au bonds. Efforts are now underway to prepare the aluminum analogue of **1** and other Au–electropositive metal cluster complexes through a similar approach.

Experimental Section

All manipulations were performed under N_2 atmosphere in a dry box (Vacuum Atmospheres Co.) with anhydrous, dioxygen-free solvents.

[Cp*Ga/GaI]:[46] A mixture of Ga metal particles (0.50 g, 7.17 mmol) and I_2 (0.91 g, 3.58 mmol) in benzene (10 mL) was sonicated for 12 h at 50 °C. KCp*·DME (0.983 g, 3.71 mmol) was added to the resulting pale green suspension of GaI,[20] and the mixture was stirred for 48 h to give a yellow solution and a light gray precipitate. After filtration, the solid was washed with benzene (20 mL), and the combined yellow filtrates were concentrated to yield the title compound as a green-yellow solid, which was used without any further purification (Cp*Ga was not obtained on attempted sublimation of the solid). ^{1}H NMR (C_6D_6, 250 MHz, 25 °C): $\delta = 1.93$ (s, Cp*), 3.01 (s, DME), 3.10 ppm (s, DME); integration ratio of 10:3:2, respectively; ^{71}Ga NMR (C_6D_6, 91.5 MHz, −70 °C): $\delta = -645.6$ ppm (br s, $\omega_{1/2} = 9800$ Hz); no signal was observed at 25 °C.

1: [(Ph_3P)AuI] (12.5 mg, 21.3 mmol) in CH_2Cl_2 (4 mL) was added dropwise to [Cp*Ga/GaI] (35.2 mg) in CH_2Cl_2 (2 mL). Small amounts of gray solid formed and the initial yellow color faded. The reaction mixture was stirred for 5 h and was then passed through diatomaceous earth. The volatiles were removed in vacuo. Addition of diethyl ether to the resulting oily residue gave a pale yellow solid, **2**, and a dark yellow-colored solution, which were separated by filtration. Solid **2** was washed several times with ether until the washings were colorless, and then dried (20.6 mg). The dark yellow filtrate and the ether washings were combined; on standing overnight at room temperature, orange-yellow crystals of **1**, which were suitable for X-ray crystal structure analysis, formed (8.5 mg, 47 % based on Au). (The same procedure repeated with [(Ph_3P)AuCl] gave similar results.)

Data for **1**: ^{1}H NMR (CD_2Cl_2, 250 MHz, 25 °C): $\delta = 1.15$ (t, 6H, $(CH_3CH_2)_2O$), 2.12 (s, 75H, Cp*), 3.45 ppm (q, 4H, $(CH_3CH_2)_2O$); ^{13}C NMR (CD_2Cl_2, 75.47 MHz, 25 °C): $\delta = 10.17$ (Cp*-CH_3), 14.98 ($(CH_3CH_2)_2O$), 65.54 ($(CH_3CH_2)_2O$), 114.79 ppm (Cp*-ring); at −70 °C, the peaks broaden slightly; Far-IR (Nujol mull, polyethylene plates): $\tilde{\nu} = 468$ cm^{-1} (br, Au–GaCp*); elemental analysis: calcd for $C_{50}H_{75}Au_3Ga_8I_6 \cdot C_4H_{10}O$: C 24.38, H 3.22; found: C 24.65, H 3.22.

Data for **2**: ^{1}H NMR (CD_2Cl_2, 250 MHz, 25 °C.): $\delta = 1.79$ (s), 7.53–7.22 ppm (m); relative integrations 1.7:1.0; ^{1}H NMR (CD_2Cl_2, 250 MHz, −70 °C): $\delta = 1.74$ & 1.71 (s), 1.63 (s), 7.50–7.06 ppm (m); relative integrations 0.8:0.9:1.0; ^{13}C NMR (CD_2Cl_2, 62.9 MHz, 25 °C): $\delta = 9.16$ (Cp*-CH_3), 113.93 (Cp*-ring), 128.88 (t, $J_{C\text{-}P} = 15$ Hz), 130.08 (s), 133.17 ppm (d, $J_{C\text{-}P} = 50$ Hz); ^{31}P NMR (CD_2Cl_2, 101.25 MHz, −70 °C): $\delta = 19.45$ ppm (s); no signal is observed at 25 °C. ^{71}Ga NMR (CH_2Cl_2, 91.5 MHz, 25 °C): $\delta = -457.74$ (s, $\omega_{1/2} = 164$ Hz), −236.53 (s, $\nu_{1/2} = 401$ Hz), −40.81 (s, $\omega_{1/2} = 328$ Hz), 123.15 ppm (s, $\omega_{1/2} = 255$ Hz).

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[23] X-ray diffraction data for **1**: $M_f = C_{50}H_{75}Au_3Ga_8I_6 \cdot C_4H_{10}O$, $T = 173$ K, $\lambda = 0.71073$ Å, monoclinic, $C2/c$, $a = 24.5902(13)$ Å, $b = 14.3255(7)$ Å, $c = 23.9938(13)$ Å, $\beta = 119.3630(10)°$, $Z = 4$, no. refl = 8167 ($5062 > 2\sigma(I)$), refinement on F^2, $R_1(> 2\sigma(I)) = 0.0528$, R_w(all data) = 0.1215, $GOF = 1.003$. Data for **3**: $M_f = C_{46}H_{81}AuGaI_3P_2$, $T = 173$ K, $\lambda = 0.71073$ Å, triclinic, $P\bar{1}$, $a = 11.2723(4)$ Å, $b = 11.7563(4)$ Å, $c = 19.9135(7)$ Å, $\alpha = 83.9070(10)$, $\beta = 89.1700(10)$, $\gamma = 77.3550(10)°$, $Z = 4$, no. refl = 11107 ($8862 > 2\sigma(I)$), refinement on F^2, $R_1(> 2\sigma(I)) = 0.0652$, R_w(all data) = 0.1946, $GOF = 1.038$. A drawing of the structure is available in the Supporting Information. ^{1}H NMR (CD_2Cl_2, 250 MHz, 25 °C): $\delta = 1.78$ (s, 15H, Cp*), 1.94 (m, 24H, PCy_3), 1.79 (m, 6H, PCy_3), 1.38 ppm (m, 36H, PCy_3); ^{31}P NMR (CD_2Cl_2, 101 MHz, 25 °C): $\delta = 64.4$ (s). CCDC 244293 (**1**) and 244294 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).
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