Gold Clusters

DOI: 10.1002/ange.201206712

Synthesis of a Trigold Monocation: An Isolobal Analogue of $[H_3]^+$**

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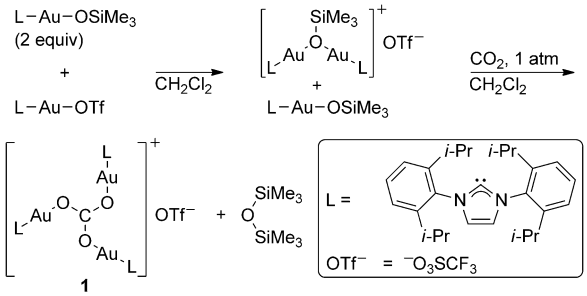
The ion $[H_3]^+$ represents a classic case in molecular orbital theory, the simplest three-center, two-electron bond.[1] The proton affinity of dihydrogen in the gas phase, at 4.4 eV,[2] is nearly equal to the bond enthalpy of H_2 itself.[3] The $[H_3]^+$ ion has been studied spectroscopically in the laboratory;[4] it has been detected in planetary atmospheres,[5a] and is notably abundant in interstellar space.[5b] The concept of isolobality has been used extensively to draw analogies between $[LAu]^+$ and $[H]^+$,[6] and after the discovery of isolable $[(LAu)_2H]^+$ complexes,[7,8] we became interested in the synthesis of an all-gold analogue of $[H_3]^+$.

Complexes of gold(I) with atoms such as oxygen and the heavier chalcogens, nitrogen, and carbon, often exhibit weak but important aurophilic interactions between the d^{10} metal centers.[9] Multicenter covalent bonding is observed in formally mixed-valent gold(I)/gold(0) clusters.[10] These include edge-sharing bitetrahedral clusters of the general formula $[(LAu)_6]^{2+}$,[11] and tetrahedral clusters of the formula $[(LAu)_4]^{2+}$.[12] Clusters such as $[(LAu)_6]^{2+}$, $(L_6Au_8)^{2+}$, and $[(LAu)_4]^{2+}$, have been synthesized by the reduction of phosphine-supported μ_3-oxo or μ_3-imido cations with carbon monoxide.[13] Whereas gold(II) dimers form covalent gold–gold bonds through the interaction of half-filled d-orbitals,[14] the gold–gold bonding in mixed-valent gold(I)/gold(0) clusters $[(LAu)_n]^{x+}$ arises to an important extent from symmetry-adapted combinations of partially filled gold 6s orbitals.[10b]

The interaction of small gold clusters and nanoparticles with O_2 has been studied as a key step in aerobic oxidation catalysis.[15] The $[Au_3]^+$-catalyzed oxidation of CO has been studied theoretically,[16] and $[Au_3]^+$ in the gas phase has been shown to mediate the oxidation of CO by N_2O.[17] Mass spectrometry studies suggest that a transient $[L_2Au_3]^+$ ion, where L_2 is a bridging bisphosphine, undergoes oxidative addition with aryl iodides.[18] Cluster complexes featuring the *cyclo*-Au_3 moiety bonded to tungsten[19] or to main-group elements[20] are known, as are triangular $[Au_2M]$ clusters.[21] We now report the characterization of a stable $[(LAu)_3]^+$ complex, where L is the N-heterocyclic carbene (NHC) 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IDipp). Density functional theory (DFT) lends insight into the bonding among gold centers. Preliminary studies demonstrate sluggish reactivity with oxygen-atom-transfer agents, but facile reactivity with soft electrophiles.

Initially, we planned to obtain $[(LAu)_3]^+$ through the reduction of a corresponding μ_3-oxo complex $[(LAu)_3O]^+$. A wide range of phosphorus-based donor ligands support complexes of this type.[22] Our efforts to obtain an analogous NHC-supported species by the established routes gave rise to mixtures of products, including the hydroxide-bridged digold cation $[(LAu)_2OH]^+$.[23]

Reasoning that the formation of strong silicon–heteroatom bonds could facilitate the synthesis of a μ_3-oxo complex, we generated a cationic siloxide-bridged digold complex from [LAuOTf][7b] and $[LAuOSiMe_3]$, and examined in situ its reactivity toward $[LAuOSiMe_3]$. By ^{1}H NMR spectroscopy we detected the generation of $(Me_3Si)_2O$, but these reactions were incomplete after many days at ambient temperature, and the mixtures decomposed on heating. In contrast, $[(LAu)_2OSiMe_3]^+OTf^-$ ($OTf^- = {}^-O_3SCF_3$) reacts readily with $[LAuOSiMe_3]$ under an atmosphere of CO_2,[24] forming $Me_3SiOSiMe_3$ and $[(LAu)_3CO_3]^+OTf^-$ (**1**) as outlined in Scheme 1. Despite some crystal disorder, single-crystal X-ray diffraction data establish the structure of **1** (see Supporting Information) unambiguously: as a μ_3-carbonato complex[25] with linear geometry about gold, and the expected bent geometry about oxygen. In the presence of moisture, **1** is partially hydrolyzed to $[(LAu)_2OH]^+$ as judged by ^{1}H NMR spectroscopy. Curiously, this hydrolysis remains incomplete in the presence of a large excess of water.[26]



Scheme 1. Preparation of a cationic trigold(I) carbonate.

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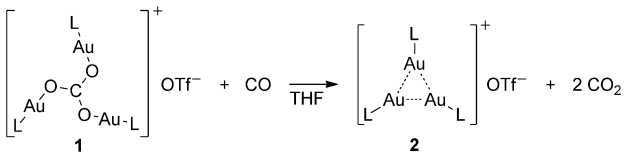
[**] We thank the Georgia Institute of Technology and the U.S. National Science Foundation (CHE-1057659 to T.G.G.) for support. We thank Prof. Dr. Jake Soper and Michael Bayless (GATech) for the use of their potentiostat and for invaluable help with electrochemical measurements; Prof. Dr. Seth Marder and his group kindly allowed us the use of their infrared spectrometer.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201206712.



Scheme 2. Reduction of **1** by carbon monoxide (1 atm, room temperature, 3 days).

Under an atmosphere of carbon monoxide, **1** undergoes slow reduction in THF solution to form $[(LAu)_3]^+OTf^-$ (**2**; Scheme 2). Certain metal complexes react with carbon dioxide to form metal carbonates plus carbon monoxide; the reduction of a trigold(I) carbonate by carbon monoxide represents the reverse of this process.[27] The reduction might proceed through displacement of a carbonate oxygen from one gold center, forming the known[28] cation $[LAuCO]^+$ and a Lewis basic $[(LAu)_2CO_3]$; however, no intermediates were detected by ^{1}H NMR spectroscopy while the reaction was in progress. Complex **2** is remarkably robust, being stable in $[D_8]$THF, CD_2Cl_2, or CD_3CN solution for days at ambient temperature. Exposure of CD_2Cl_2 solutions of **2** to humid air for several hours, or addition of excess water or methanol, resulted in no decomposition discernible by ^{1}H NMR spectroscopy.

Crystallization of **2** from a mixture of THF and toluene afforded colorless needles suitable for X-ray diffraction. The resulting crystal structure revealed that the $[(LAu)_3]^+$ ion is of approximate D_3 symmetry, with the imidazolylidene rings canted by 63.1(4)° to 77.7(4)° (Figure 1). The Au_3 ring is nearly equilateral, with bond angles between 59.603(9)° and 60.331(8)°, and Au–Au distances from 2.6438(5) to 2.6633(5) Å. These distances, similar to those calculated for free $[Au_3]^+$ (2.63–2.64 Å),[29] fall within the range found for clusters of $[Au_3]$ bound to main-group elements (2.562(1)–3.010(1) Å).[20] The gold-bound carbon atoms are essentially coplanar with the Au_3 ring, the sum of angles about each Au center ranging from 359.8(2)° to 360.0(2)°, but the C-Au-Au angles vary from the ideal 150° by up to 7.4(1)°. The Au–C distances, between 2.039(4) Å and 2.064(4) Å, are slightly longer than those in $[(LAu)_2H]^+$ (2.004(4), 2.018(4) Å).[7b]

Density-functional theory calculations were applied to **2′**, a model compound in which *N*-methyl groups replace the 2,6-diisopropylphenyl moieties. Geometry optimization converged on a potential-energy minimum with rough D_3 symmetry. The Au_3 triangle is calculated to be nearly equilateral: Au–Au distances range from 2.705–2.706 Å, and no Au-Au-Au angle deviates from 60° by more than 0.02°. Gold–carbon bond lengths range from 2.804–2.805 Å. For all three Au–Au bonds, the average Wiberg bond order in the Löwdin basis[30] is 0.86. In contrast, the bond order between gold atoms in the geminally diaurated aryl complex $[(Me_3PAu)_2$-(phenyl)$]^+$ is 0.71.[31,32] This comparison suggests that Au–Au bonding in mixed-valence gold(0/I) triangles exceeds that in aurophilically linked gold(I).

Figure 2a shows a frontier-orbital energy-level diagram of **2′**. Plots of the highest occupied and lowest unoccupied Kohn–Sham orbitals (HOMO and LUMOs) appear in Figure 2b;

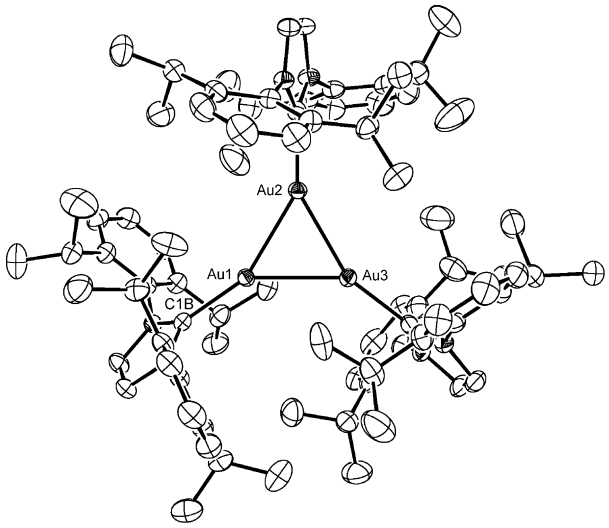


Figure 1. Thermal ellipsoid plot (ellipsoids set at 50% probability) of **2**·C_4H_8O. For clarity, hydrogen atoms, OTf anion and solvent are omitted. Selected bond lengths [Å] and angles [°]: Au1–Au2 2.6563(6), Au2–Au3 2.6438(5), Au1–Au3 2.6633(5), Au1–C1B 2.048(3), Au2–C1C 2.064(4), Au3–C1 2.039(4); Au2-Au1-Au3, 59.603(9), Au3-Au2-Au1 60.331(8), Au2-Au3-Au1, 60.066(15).

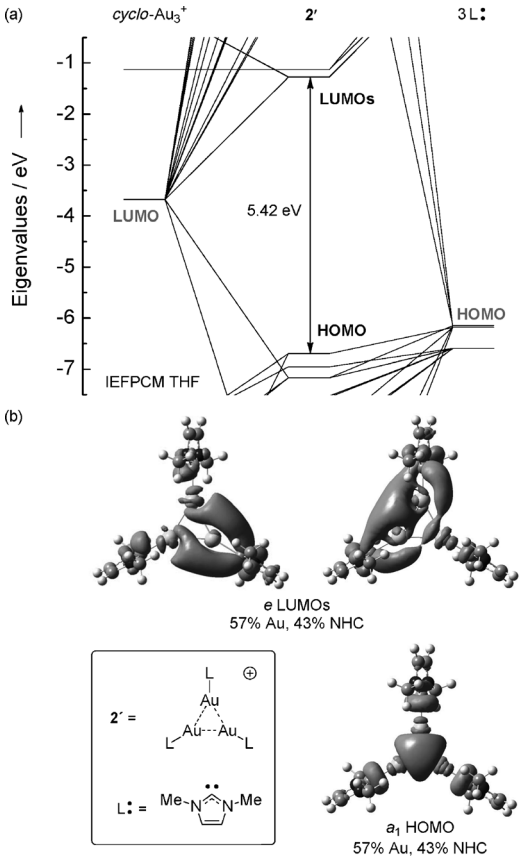


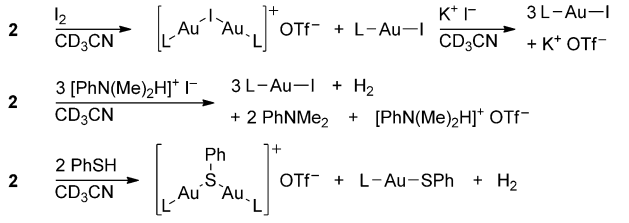
Figure 2. a) Partial Kohn–Sham orbital energy diagram of **2′**. b) Plots of selected orbitals (0.02 a.u.) and percentage compositions in terms of electron densities of fragments. Implicit THF solvation is included with the integral equation formalism of the polarizable continuum model (IEFPCM THF); see Supporting Information for details.

percentages are of electron density. The frontier orbitals are reminiscent of those in $[H_3]^+$. The HOMO is a singly degenerate a_1 combination mainly of s-type orbitals on gold. The LUMOs are doubly degenerate and built preponderantly of gold *p*-functions. Fortuitously, both sets of orbitals derive approximately 57% of their electron density from gold and approximately 43% from the NHC ligands. A large HOMO–LUMO gap is calculated: 5.42 eV.

Electrochemical oxidation of **2** requires high potentials. The cyclic voltammogram of **2** in CH_3CN solution (see Supporting Information) shows an irreversible oxidation wave, with maximum current density at +1.5 V relative to $Cp_2Fe/[Cp_2Fe]^+$ ($Cp = \eta$-C_5H_5). No reduction wave was observed within the electrochemical window of CH_3CN or THF.[33] In attempts at chemical oxidation, treatment of **2** with the oxygen-atom-transfer agent Me_3NO resulted in the very slow and incomplete appearance of a single new set of IDipp resonances in the ^{1}H NMR spectrum, which we tentatively ascribe to the formation of a Nesmeyanov-type complex $[(LAu)_3O]^+$. Efforts to drive this reaction to completion have so far resulted in decomposition. The more kinetically active oxidant [PhIO], alone or in combination with Me_3NO, gave no reaction.

In contrast, **2** reacts smoothly with I_2 in CD_3CN solution at ambient temperature, giving rise to a ^{1}H NMR spectrum with a single set of resonances arising from IDipp. The signal for the isopropyl methine protons appears broadened, consistent with the formation of $[(LAu)_2I]^+OTf^-$ and [LAuI], followed by rapid degenerate exchange on the NMR timescale.[34] After addition of KI to the solution, only [LAuI] is detected (Scheme 3). The triiodide anion, added as KI_3, also oxidizes **2** rapidly in CD_3OD solution to form [LAuI].[35]

The coordination of soft Lewis bases to the $[(LAu)_3]^+$ ion may be the key to its activation (Scheme 3). For example, **2** shows no reaction with the mild acid $[Ph(Me)_2NH]^+BF_4^-$ in



Scheme 3. Oxidative cleavage of **2** to form Au^I complexes.

CD_3CN solution. It does, however, react with three equivalents of $[Ph(Me)_2NH]^+I^-$, forming [LAuI] and dihydrogen, for which a small resonance appears at $\delta = 4.6$ ppm in the ^{1}H NMR spectrum.[36] In the presence of excess benzenethiol, **2** is converted into [LAuSPh], $[(LAu)_2SPh]^+OTf^-$, and dihydrogen.[36] This reaction is analogous to the surface functionalization of gold metal to form gold(I) thiolate coatings.[37]

In summary, an N-heterocyclic carbene ligand stabilizes a tri-gold cation $[(LAu)_3]^+$, synthesized through the reduction of a cationic trigold(I) carbonate with carbon monoxide. Structural characterization indicates Au–Au bond lengths similar to those predicted for $[Au_3]^+$ in the gas phase. The $[(LAu)_3]^+$ ion is relatively inert, reflecting its large calculated HOMO–LUMO gap, but is readily cleaved by iodine, by a mild source of HI, or by a thiol to form three Au^I centers. Studies of multielectron redox chemistry using this ion and related complexes are ongoing.

Experimental Section

2: In a glovebox under N_2, a resealable Schlenk tube was charged with **1** (0.061 g, 0.0032 mmol) and THF (2 mL). The tube was sealed with a Teflon screwcap and removed from the glovebox; the solution of **1** was degassed and exposed to CO (ca. 1 atm). The tube was resealed and the reaction mixture was stirred for 72 h at ambient temperature. The resulting pale yellow solution was filtered through Celite and evaporated to dryness. The residual solid was washed with benzene, then crystallized from THF/toluene at −35 °C. The product was dissolved in THF, filtered through Celite and evaporated to dryness. The residual solid was crystallized again from THF/toluene at −35 °C, washed with hexanes (3 × 10 mL) and dried in vacuo to give colorless crystals of **2** (0.025 g, 41%). ^{1}H NMR (CD_3CN): $\delta = 7.43$ (t, $J =$ 8.0 Hz, 6H, *para*-CH), 7.20 (d, $J = 8.0$ Hz, 12H, *meta*-CH), 7.11 (s, 6H, NCH), 2.47 (sept., $J = 6.8$ Hz, 12H, $CH(CH_3)_2$), 1.04 (d, $J =$ 6.8 Hz, 36H, $CH(CH_3)_2$), 0.92 ppm (d, $J = 6.8$ Hz, 36H, $CH(CH_3)_2$). ^{13}C NMR (CD_3CN): $\delta = 205.2$ (NCAu), 146.3 (*ortho*-C), 135.7 (*ipso*-C), 131.1 (*para*-C), 125.6 (NCH), 125.3 (*meta*-C), 29.1 ($CH(CH_3)_2$), 25.1 ($CH(CH_3)_2$), 24.7 ppm ($CH(CH_3)_2$). ^{19}F NMR (CD_2Cl_2): $\delta =$ −78.9 ppm. IR (KBr): $\tilde{\nu} = 3161$, 3118, 3088, 2970, 2927, 2868, 1464, 1270, 1151, 1030, 805, 763, 635 cm^{-1}. Elemental analysis (%) calcd for $C_{82}H_{108}Au_3F_3N_6O_3S$: C 51.68, H 5.71, N 4.41; found: C 51.42, H 5.63, N 4.32.

Received: August 19, 2012
Published online: October 4, 2012

Keywords: carbon monoxide · cluster compounds · gold · isolobal relationships · N-heterocyclic carbene ligands

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