Heterogeneous Catalysis Hot Paper

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Trinuclear Gold Clusters Supported by Cyclic (alkyl)(amino)carbene Ligands: Mimics for Gold Heterogeneous Catalysts**

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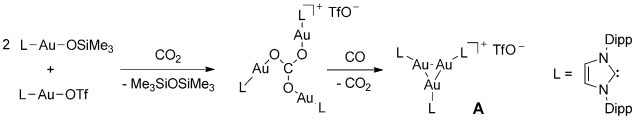
Abstract: *The synthesis of air- and moisture-stable trinuclear mixed-valence gold(I)/gold(0) clusters is described. They promote the catalytic carbonylation of amines under relatively mild conditions. The synthetic route leading to the trinuclear clusters involves a simple ligand exchange from the readily available μ^3-oxo-$[(Ph_3PAu)_3O]^+$ complex. This synthetic method paves the way for the preparation of a variety of mixed-valence gold(I)/gold(0) polynuclear clusters. Moreover, the well-defined nature of the complexes demonstrates that the catalytic process involves a rare example of a definite change of oxidation state of gold from $Au^0{}_2Au^I$ to $Au^I{}_3$.*

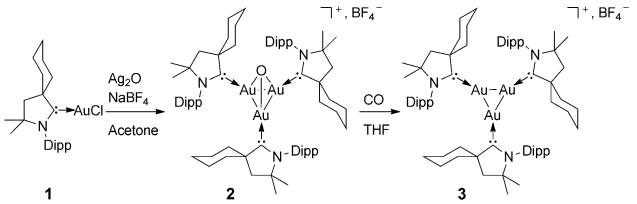
Gold nanoparticles have attracted a great deal of interest owing to their potential applications, not only for nanoelectronic devices[1] and medical science,[2] but also for catalysis.[3] Interestingly, Corma et al.[4] have recently shown that very small metallic gold clusters (3 to 10 atoms) could display catalytic activities that are much higher than those obtained with gold nanoparticles and mononuclear homogeneous gold catalysts.[5] This striking discovery led to the question of whether very small, well-defined clusters, capped with ligands, could mimic the behavior of heterogeneous catalysts. One benefit, among other obvious advantages, would be the possibility of characterizing intermediates in catalytic reactions.

Examination of the literature shows a large number of mixed-valence gold(I)/gold(0) complexes with the formula $(L_nAu_m)^{x+}$.[6] However, there is a single example of the smallest member of the family, namely the tris(gold) cluster **A**, which was recently isolated by Sadighi et al.[7] (Scheme 1). Herein we report two straightforward syntheses of triangular gold complexes ligated by three cyclic (alkyl)(amino)carbenes (CAAC)[8,9] or two CAACs and a phosphine. To demonstrate the possibility of using small well-defined clusters for studying catalytic mechanisms, we investigated a carbonylation reaction, which had previously been studied using supported metallic gold, and gold nanoparticles.[10]



Scheme 1. Synthesis of the only known trinuclear gold complex **A**.[7]

One of the most classical routes for the preparation of small phosphine-supported gold clusters, such as $[(R_3PAu)_6]^{2+}$,[11] $[(R_3P)_6Au_8]^{2+}$,[12] and $[(R_3PAu)_4]^{2+}$,[13] is the reduction of the corresponding μ^3-oxo complexes $[(R_3PAu)_3O]^+X^-$.[14] Although it has been reported that the analogous NHC-supported μ^3-oxo species cannot be prepared,[7] we found that treatment of the $(CAAC_{c\text{-}Hex})AuCl$ complex **1**[15] with Ag_2O, in presence of $NaBF_4$, afforded the desired cluster **2** as an off-white powder in 62% yield (Scheme 2). Subsequent reduction with carbon monoxide[16]



Scheme 2. Synthesis of trinuclear gold clusters **2** and **3**.

produced the trinuclear complex **3** as a pale yellow powder (75% yield). Compound **3** was characterized by ^1H and ^{13}C NMR spectroscopy as well as by high-resolution mass spectrometry. The ^{13}C NMR signal corresponding to the carbene carbon appears at 262.5 ppm, which is half-way between those observed for gold(I) complexes **1** and **2** (237.4 and 230.4 ppm, respectively) and the recently reported neutral $(CAAC_{menthyl})Au{-}Au(CAAC_{menthyl})$ complex[17] (287.2 ppm), as is expected for a mixed-valence gold(I)/gold(0) compound. Cluster **3** was found to be indefinitely stable in air and moisture both in the solid state and in solution; its melting point (240 °C (dec.)) is another indication of its high stability.

Even though the reaction sequence from **1** to **3** proved to be efficient, the starting material **1** can only be made in 41% yield.[15] Therefore, we decided to investigate the possibility of ligand exchange, using the readily available phosphine-

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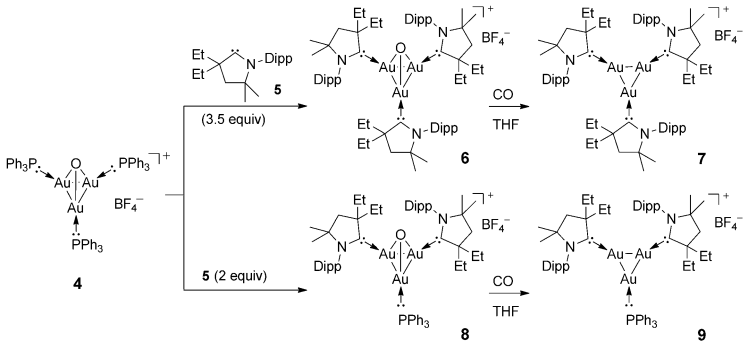


Scheme 3. Synthesis of trinuclear complexes **6**–**9** from the phosphine-supported μ^3-oxo complex **4**.

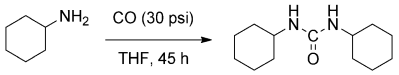
supported μ^3-oxo complex **4**[14] as a precursor (Scheme 3). Addition of 3.5 equivalents of $CAAC_{diEt}$ **5**[18] to **4** proceeded smoothly, and the μ^3-oxo complex **6** was isolated in 86% yield as an off-white solid. Subsequent treatment of **6** with carbon monoxide yielded the desired trinuclear gold complex **7** as a pale yellow solid in almost quantitative yield. Very interestingly, this reaction sequence is very flexible. Indeed, the addition of two equivalents of $CAAC_{diEt}$ **5** to **4** allows, after reduction with CO, the preparation of the mixed (CAAC)(phosphine)-supported complex **9**.

Single-crystal X-ray diffraction studies of **6**, **7**, and **9** were carried out (Figure 1).[19] Similar to the analogous cluster bearing P(*o*-Tol)$_3$ ligands,[20] **6** has a pseudo-tetrahedral geometry, and can be viewed as three [CAAC-Au]$^+$ units, with strong aurophilic interactions,[21] bound to a central O^{2-}. In **7**, the Au–Au distances (2.6324(8)–2.6706(8) Å) are much shorter than in **6** (3.1669(3)–3.3149(3) Å), which is indicative of true covalent bonds; for comparison, a gold–gold distance of 2.552 Å was observed for the neutral (CAAC)Au–Au-(CAAC) complex.[17] In **9**, the distance between the two gold atoms bearing CAACs (2.6604(4) Å) is slightly longer than the other Au–Au bonds (2.6191(4) and 2.6219(4) Å), arguing for the stronger σ-donor properties of CAACs, compared to triphenyl phosphine.[9]

Owing to our ongoing interest in the gold-catalyzed functionalization of amines,[22] we chose to investigate the behavior of cluster **7** for the carbonylation of this class of compounds. Such a reaction is the simplest and most environmentally friendly route for the preparation of urea derivatives.[23,24]

We were at first very disappointed to observe that with 2.5 mol% of **7**, cyclohexylamine did not react with carbon monoxide (30 psi) even after four days at 70°C under strict anaerobic conditions (Table 1, entry 1). However, we quickly found that under the same experimental conditions, but in air, *N*,*N*′-dicyclohexylurea was formed in 30% yield after two days (entry 2). Increasing the temperature to 90°C appeared to be beneficial for the conversion (entry 3), but further increase above 90°C did not improve the yields, certainly due to the degradation of the catalyst. Interestingly, under 10 psi of oxygen, the yield improved drastically (entry 4). Noteworthy, under the same conditions, the more bulky cluster **3**, and the μ^3-oxo complex **6** (entry 5 and 6) proved to be less efficient than **7**, and the $CAAC_{menthyl}$–AuCl complex[22a] failed to produce any *N*,*N*′-dicyclohexylurea.

Table 1: Catalytic carbonylation of cyclohexylamine.



Entry	Catalyst	*T* [°C]	O_2	Yield [%][a]
1	**7** (2.5%)	70	none	0
2	**7** (2.5%)	70	air	30
3	**7** (2.5%)	90	air	51
4	**7** (2.5%)	90	10 psi	69
5	**3** (2.5%)	90	10 psi	29
6	**6** (2.5%)	90	10 psi	34

[a] Yields determined by GC, using biphenyl as internal standard.

Using the optimized conditions, we performed preliminary experiments to study the scope of this catalytic process. As shown in Table 2, benzyl amine and 2-phenylethylamine could be converted into the corresponding urea in good yields of 74% and 72%, respectively (entries 1 and 3). No decomposition of catalyst could be observed during the reaction with benzylamine as the substrate, which encouraged us to decrease the catalyst loading to 0.5 mol%; the urea was obtained with 52% yield after extending the reaction time to four days (entry 2). In the case of more sterically hindered amines, the conversion was significantly decreased (entry 4–6), while no reaction was observed with the less nucleophilic aniline (entry 7).

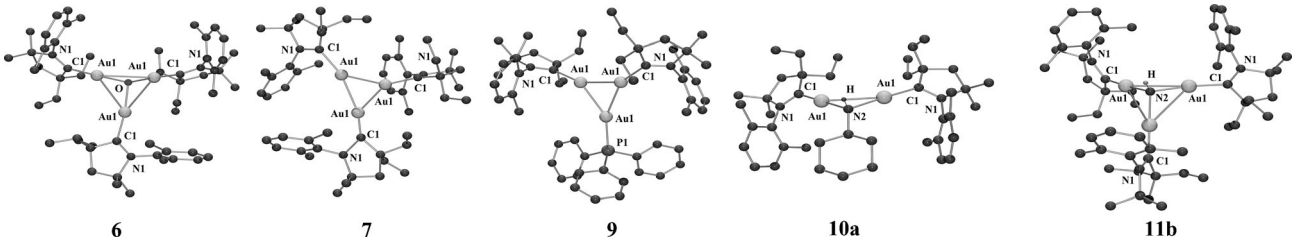
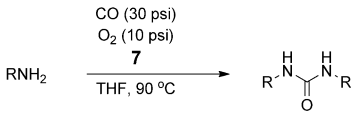


Figure 1. Solid-state structures of **6**, **7**, **9**, **10a**, and **11b**. BF_4^- anions, solvent molecules, and hydrogen atoms, except on the amine nitrogen of **10a** and **11b**, are omitted for clarity. Isopropyl substituents on the aryl groups were limited to the connecting carbon atoms.

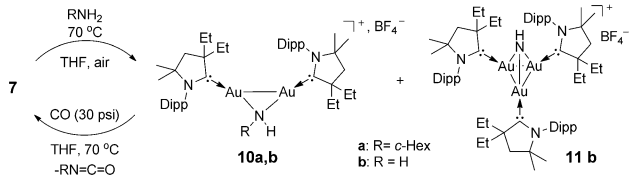
Table 2: Catalytic carbonylation of amines.



Entry	Substrate	**7** (mol%)	*t* [h]	Yield [%][a]
1	benzylamine	2.5	45	74
2	benzylamine	0.5	96	52
3	2-phenylethylamine	2.5	45	72
4	α-methylbenzylamine	2.5	45	40
5	α-methylbenzylamine	2.5	72	55
6	2-adamantylamine	2.5	45	10
7	aniline	2.5	45	0

[a] Yields determined by NMR with triphenylmethane as the internal standard.

Examination of the literature shows that several other transition-metal catalysts are efficient for this transformation, but generally at higher CO pressures and temperatures.[10,23,24] More importantly, the well-defined nature of **7** allowed for an investigation of the intermediates involved in the catalytic process. We first found that **7** does not react with carbon monoxide (30 psi) at 90 °C. Similarly, in the absence of air, no reaction occurs with cyclohexylamine at 90 °C. In contrast, in aerobic condition, or under 10 psi of oxygen, **7** reacts with cyclohexylamine, leading after two days at 70 °C to the dinuclear complex **10a**, which was isolated in 63% yield (Scheme 4). Interestingly, under the same experimental conditions, but using ammonia, a mixture of the dinuclear and trinuclear complexes **10b** and **11b** was obtained. The structures of **10a/b** and **11b** were ascertained by X-ray diffraction (Figure 1). In all of these complexes, the Au–Au bond distances (3.16 to 3.31 Å) are typical for gold(I)–gold(I) aurophilic interactions,[21] and are similar to those observed in the μ^3-oxo complex **6**.



Scheme 4. Addition of amines to trinuclear cluster **7** to afford dinuclear and trinuclear complexes **10a,b** and **11b**, and subsequent reaction with CO to return **7**, along with isocyanates.

The next question was whether CO was able to displace the nitrogen fragment of complexes **10** and **11**. Indeed, when **10a**, **10b**, and **11b** were treated with carbon monoxide (30 psi) at 70 °C, the trinuclear cluster **7** was recovered. In the case of **10a**, we were also able to observe the formation of the cyclohexyl isocyanate, along with traces of urea.

During the first step of the catalytic process (**7** to **10** and **11**), two gold centers are oxidized. We hypothesize that oxygen is necessary to scavenge the hydrogen atoms, but the mechanism remains unclear. During the second step (**10** and **11** to **7**), two gold centers are reduced, and the carbon monoxide is oxidized by two electrons.

Gold catalysts are usually viewed as soft carbophilic Lewis acids,[25] and only a few recent reports postulate redox processes.[26,27] For example, Toste et al.[28] found a catalytic process involving two Au^I complexes giving a dinuclear Au^{II}–Au^{II} intermediate. The carbonylation of amines reported herein is a very rare example of a gold catalyzed process involving a definite change of oxidation state of the metal from $Au_2^0Au^I$ to Au_3^I.

Along with the catalytic interest of this work, the synthesis of trinuclear complexes by ligand exchange paves the way for the preparation of a variety of carbene-supported multinuclear gold clusters, using known well-defined mixed-valence phosphine–gold clusters.

Experimental Section

Synthesis of μ^3-oxo complex **6**: A THF solution (30 mL) of $CAAC_{diEt}$ (1.1 g, 3.5 mmol) was added slowly to a THF solution (90 mL) of $(PPh_3Au)_3O^+BF_4^-$ (1.5 g, 1.0 mmol). After 20 min, volatiles were removed under vacuum and the residue was washed with diethyl ether (3 × 10 mL). After drying, complex **6** was obtained as an off-white solid (1.42 g, 86% yield, m.p. 220 °C (dec.)). ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 7.36$ (t, $J = 7.7$ Hz, 3H), 7.18 (d, $J = 7.7$ Hz, 6H), 2.67 (sept., $CHCH_3$, $J = 7.0$ Hz, 6H), 2.00 (s, 6H), 1.76–1.63 (m, 6H), 1.61–1.49 (m, 6H), 1.29–1.23 (m, 36H), 1.23–1.17 (m, 18H), 0.96 ppm (t, $J = 7.0$ Hz, 18H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): $\delta = 231.0$ (C_{carb}), 145.1 (C_{ortho}), 134.1 (C_{ipso}), 129.7 (C_{para}), 124.7 (C_{meta}), 80.6 (C_{quat}), 62.8 (C_{quat}), 40.3 (C_{H2}), 32.1 (C_{H2}), 29.3, 29.2, 27.7, 22.6, 9.71 ppm; HRMS (ESI-TOFMS): m/z calculated for $C_{66}H_{105}Au_3N_3O^+$ 1546.7254, found 1546.7226. Single crystals of **6** were obtained by vapor diffusion of diethyl ether into a saturated THF solution.

Synthesis of trinuclear cluster **7**: A THF solution (15 mL) of **6** (1.4 g, 0.87 mmol) was stirred under 30 psi of CO for 12 h. The solvent was removed under vacuum and **7** was obtained as a yellow solid (1.28 g, 91% yield, m.p. 232 °C (dec.)). ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 7.37$ (t, $J = 7.8$ Hz, 3H), 7.18 (d, $J = 7.8$ Hz, 6H), 2.68 (sept., $CHCH_3$, $J = 6.6$ Hz, 6H), 1.90 (s, 6H), 1.64–1.53 (m, 6H), 1.45–1.35 (m, 6H), 1.28–1.19 (m, 36H), 1.09 (d, $J = 6.5$ Hz, 18H), 0.89 ppm (t, $J = 7.3$ Hz, 18H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) = 264.8 (C_{carb}), 145.0 (C_{ortho}), 134.0 (C_{ipso}), 129.5 (C_{para}), 124.5 (C_{meta}), 81.7 (C_{quat}), 63.6 (C_{quat}), 41.9 (C_{H2}), 31.5 (C_{H2}), 29.2, 29.1, 28.0, 22.4, 9.80 ppm; HRMS (ESI-TOFMS): m/z calculated for $C_{66}H_{105}Au_3N_3^+$ 1530.7305, found 1530.7312. Single crystals of **7** were obtained by vapor diffusion of diethyl ether into a saturated THF solution.

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