Communications

Gold Complexes

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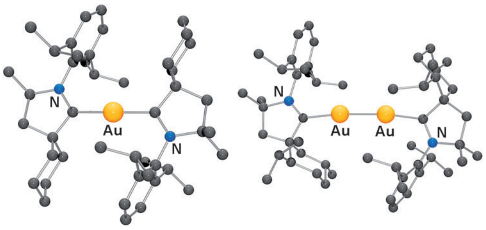
Isolation of Neutral Mono- and Dinuclear Gold Complexes of Cyclic (Alkyl)(amino)carbenes



The smallest pieces of gold! Thanks to the presence of two π-accepting cyclic (alkyl)(amino)carbenes (CAACs), complexes featuring one and two atoms of gold in the formal oxidation state of zero can be isolated.

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Isolation of Neutral Mono- and Dinuclear Gold Complexes of Cyclic (Alkyl)(amino)carbenes**

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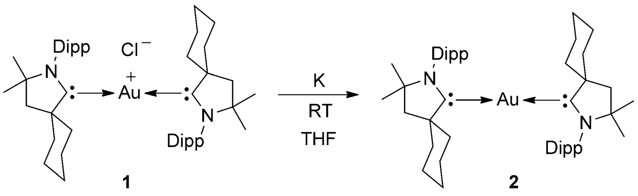
The common oxidation states of gold are -I, +I, and +III, with rare complexes featuring a gold +II, +IV, and +V.[1] To date, apart in elemental gold,[2] the zero oxidation state has been mentioned in mixed gold(0)/gold(I) complexes of the general formula $[(\mathrm{LAu})_n]^{m+}$, $m\mathrm{X}^-$ as exemplified by the classical $[(\mathrm{Ph_3PAu})_6]^{2+}$ $2(\mathrm{BF_4}^-)$[3a] and $[(t\mathrm{Bu_3PAu})_4]^{2+}$ $2(\mathrm{BF_4}^-)$,[3b] and the recently reported $\{[(\mathrm{NHC})\mathrm{Au}]_3\}^+$ $(\mathrm{TfO})^-$ complex.[4] There are also a few examples of multinuclear mixed-metal clusters,[5] such as $[cis\text{-}\eta^2\text{-}\{(\mathrm{Ph_3P})\mathrm{Au{-}Au}(\mathrm{PPh_3})\}\mathrm{Ph_3PCr(CO)_4}]$,[6] in which the Au atom can be considered to have an oxidation state of zero. However, mononuclear ($\mathrm{L}_n\mathrm{Au}$), binuclear (LAu−AuL), and polynuclear $[(\mathrm{LAu})_n]$ neutral complexes in which atoms of gold are coordinated end-on by L ligands have never been isolated.[7,8] Earlier claims of the preparation of $[(\mathrm{Ph_3P})\mathrm{Au{-}Au}(\mathrm{PPh_3})]$[9] have not been confirmed, and calculations by Schwerdtfeger and Boyd[10] on the model compound $(\mathrm{H_3P})\mathrm{Au{-}Au}(\mathrm{PH_3})$ leave serious doubts about the structural assignment. In fact, this type of dinuclear gold(0) species supported by phosphines[11] has been postulated as intermediates to rationalize the formation of gold nanoparticles. In their recent review, Raubenheimer and Schmidbaur[7] wrote that "*it is very likely that N-heterocyclic carbenes (NHCs) may be the right choice to prepare the much sought-after complexes of the* Au_2 *molecule*". Unfortunately, Sadighi et al.[12] have shown that the (NHC)Au−Au(NHC) complex, generated by the deprotonation of the corresponding cationic hydride-bridged species, was also unstable and led to colloidal gold.

We reasoned that for stabilizing electron-rich gold(0) centers, the most suitable ligands should be π-electron accepting while also capable of forming strong bonds with gold. Cyclic (alkyl)(amino)carbenes (CAACs)[13,14] feature the desired properties,[15] and furthermore they strongly stabilize paramagnetic centers.[16] Herein we report the synthesis and single-crystal X-ray diffraction study of neutral mononuclear and dinuclear gold complexes, which are stable for days at room temperature, both in solution and in the solid state.

To check our hypothesis, we first carried out the cyclic voltammetry of a tetrahydrofuran solution of the known $(\mathrm{CAAC})_2\mathrm{Au}^{\mathrm{I}}$ complex **1** (Scheme 1),[17] containing 0.1 M $n\mathrm{Bu_4NPF_6}$ as electrolyte (Figure 1a). A reversible one-electron reduction was observed at $E_{1/2} = -2.24$ V versus $\mathrm{Fc^+/Fc}$, which prompted us to perform the chemical synthesis of $(\mathrm{CAAC})_2\mathrm{Au}$ complex **2**. A benzene solution of **1** was stirred at room temperature for 4 h in a Schlenk flask coated with a potassium mirror. After filtration and evaporation of the solvent under vacuum, a green solid was obtained. Recrystallization from a THF solution stored at −78 °C under argon afforded **2** (Scheme 1) as thermally stable (m.p. 110 °C), highly air- and water-sensitive, light green single crystals (yield: 44 %).



Scheme 1. Synthesis of $[(\mathrm{CAAC})_2\mathrm{Au}]$ complex **2**. Dipp = 2,6-diisopropylphenyl.

An X-ray diffraction study[18] (Figure 1c) first confirmed that complex **2** is neutral, and features a linear geometry (C1-Au-C1′ 180.0°), with the five-membered ring ligands being coplanar (N1-C1-C1′-N1′ dihedral angle 180°). The Au−C1 (1.991(2) Å) and C1−N1 (1.344(3) Å) bonds of **2** are slightly shorter and longer, respectively, than in the gold(I) precursor **1** (2.0321(11) and 1.304(2) Å), indicating a significant π-back-donation of the unpaired electron from gold to the ligands. As expected, solutions of **2** are NMR-silent and EPR-active. The room-temperature EPR spectrum of **2** in benzene shows a broad signal at $g = 1.9607$, while in the solid state (Figure 1b) the anisotropic tensors are $g_{xx} = 1.9410$, $g_{yy} = 1.9543$, and $g_{zz} = 1.9864$.[19] Calculations at the (U)M05-2X/def2-SVP level using the NBO method show that the spin density in **2** is mainly localized on the carbene carbons (60 %) and the nitrogen atoms (20 %), while only 17 % stays at gold. The

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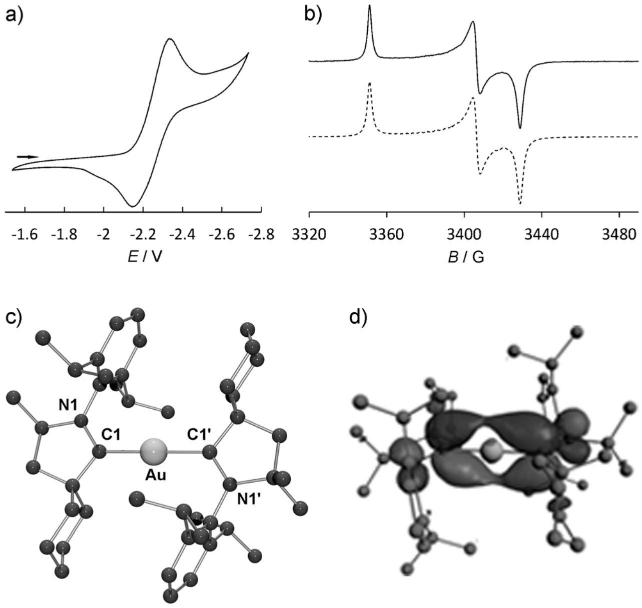


Figure 1. a) Cyclic voltammogram of **1** (nBu_4NPF_6 as electrolyte, potential versus Fc^+/Fc, scan rate 100 mVs^{-1}). b) Experimental (——) and simulated (-----) EPR spectrum of **2** in a frozen benzene solution at 235 K. B = magnetic field. c) Solid-state structure of **2** (hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (°), with calculated values at (U)M05-2X/def2-SVP in square brackets: Au1–C1 1.991(2) [2.006], C1–N1 1.344(3) [1.348]; C1-Au1-C1′ 180 [180]; N1-C1-C1′-N1′ 180 [180]; d) Graphical representation of the SOMO of **2**.

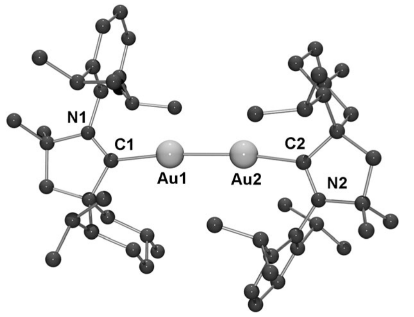
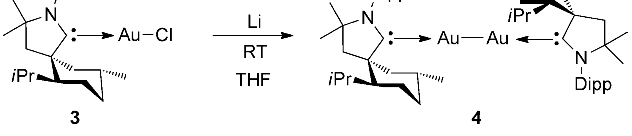


Figure 2. Solid-state structure of **4** with only one rotamer shown (hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (°), with calculated values at M05-2X/def2-SVP in square brackets: Au1–Au2 2.5520(6) [2.579], Au1–C1 2.082(10) [2.123], Au2–C2 2.088(9) [2.133], C1–N1 1.261(12) [1.307], C2–N2 1.337(10) [1.308]; C1-Au1-Au2 173.8(2) [171.3], C2-Au2-Au1 171.3(3) [169.3]; N1-C1-C2-N2 177.65(66) [146.0].

shape of the SOMO (Figure 1 d) shows that the unpaired electron is delocalized over the p(π) AOs of the carbene ligand and the p(π) AO of Au. This means that the electronic reference configuration for the bonding in $(CAAC)_2Au$ is $d^{10}s^0p^1$ but not the ground state configuration $d^{10}s^1p^0$.

From these results, it can be concluded that CAACs behave as redox active ligands, and it could be argued that **2** has only a weak gold(0) character. Thus, the next question was to investigate if a neutral mono-CAAC gold complex would undergo a dimerization into a (CAAC)Au−Au(CAAC) complex, and if the latter would be stable enough to be isolated. For this purpose, the bulkier menthyl-substituted CAAC was chosen.[13] Reduction at room temperature of the (CAAC)AuCl complex **3** with a suspension of lithium sand in THF afforded after work up the dinuclear complex **4**, which was isolated in 20% yield as highly air- and water-sensitive light brown crystals (m.p. 98 °C; Scheme 2). Its non-ionic character was indicated by its solubility in non-polar solvent, such as n-hexane, and its diamagnetic nature apparent from NMR spectroscopy. Interestingly, a ^{13}C NMR signal was observed at $\delta = 286$ ppm, downfield-shifted by $\delta = 50$ ppm compared to the carbene gold(I) precursor **3**; a similar trend has been observed with a variety of metal–NHC complexes when comparing oxidation states zero and one.[20] A single-crystal X-ray diffraction study confirmed the desired (CAAC)Au−Au(CAAC) structure. There are six molecules in the asymmetric unit, three of them are nearly identical (Figure 2), the others differ merely by the respective orientation of the two carbene ligands; in other words these molecules are rotamers. As predicted by Schwerdtfeger and Boyd[10] for $(H_3P)Au-Au(PH_3)$, the C1-Au1-Au2-C2 skeleton is almost linear (C1-Au1-Au2 173.8(2), Au1-Au2-C2: 171.3(3)°), and the gold–gold bond is short (2.5520(6) Å).



Scheme 2. Synthesis of $[(CAAC)_2Au_2]$ complex **4**.

The EDA-NOCV results (see the Supporting Information) show that the total interaction energy and the orbital interactions between Au_2 and the CAAC ligands in **4** are much weaker than between Au and the CAACs in **2**. This is because Au_2 binds in **4** to the ligands through its electronic ^2S ($d^{10}s^1p^0$, $J = 1/2$) ground state, while Au binds in **2** through the ^2P ($d^{10}s^0p^1$, $J = 1/2$) excited state, which is 106.8 $kcal\,mol^{-1}$ higher in energy.[21] This explains why the Au−C bond in **2** is significantly shorter than in **4**. The calculated bond dissociation energies D_e for breaking both Au−C bonds in the reactions $\mathbf{2} \rightarrow Au + 2\,CAAC$ (91.2 $kcal\,mol^{-1}$) and $\mathbf{4} \rightarrow Au_2 + 2\,CAAC$ (90.6 $kcal\,mol^{-1}$), which yield the fragments in the electronic ground state, are nearly the same. Naked Au_2 has a calculated Au−Au bond length of 2.546 Å, which is very close to the observed (2.5520(6) Å) and calculated (2.579 Å) gold–gold distance in **4**. The Au−Au bond comes from the coupling of the unpaired electrons in the valence s AO of gold, that is, from the $d^{10}s^1p^0$ ground configuration, which is sd-hybridized. This leaves one vacant sd-hybridized σ* orbital of Au_2 as acceptor MO for donation from the minus combination of the carbon lone-pair donor orbitals of the CAAC ligands. The $CAAC \rightarrow Au_2 \leftarrow CAAC$ donation from the plus combination of the ligand donor orbitals occurs into a vacant σ MO of Au_2, which has mainly p(σ) character. A detailed analysis of the bonding situation in **2** and **4** will be presented elsewhere.

When phosphines are used as ligands, a variety of small and large gold clusters, including nanoparticles, are available, and have found numerous applications;[22] all of these particles possess positive charges. We are currently investigating the synthesis of similar clusters using cyclic (alkyl)(amino)carbenes as ligands. Importantly, as these results demonstrate that CAACs can stabilize gold in the formal zero oxidation state, we believe that neutral clusters of different sizes, mimicking gold surfaces, will be accessible.

Experimental Section

Synthesis of mononuclear gold complex **2**: Gold complex **1**[17] (200 mg) was added to a Schlenk flask with a potassium mirror (ca. 50 mg, excess). Benzene (30 mL) was added, and the solution was stirred for 4 h at room temperature. Subsequently, the solution was filtered and the solvent was removed under vacuum. The residue was extracted with 3 × 20 mL of benzene and the solvent was removed to yield a green solid. Crystals suitable for X-ray diffraction were grown at −78 °C from a concentrated THF solution. Yield: 85 mg (44 %). Mp: 110 °C.

Synthesis of the dinuclear gold complex **4**: In a glove box, gold complex **3**[17] (150 mg) and lithium sand (4.5 mg, 2 equiv) were stirred in THF (20 mL) for 1.2 hours. The solution was subsequently filtered and dried in vacuo. The product was extracted with 3 × 20 mL of hexane, and the solvent evaporated. The solid residue was washed with 3 × 0.5 mL of hexane to yield a pale brown solid. Crystals suitable for X-ray diffraction were grown at −30 °C from a concentrated hexanes solution. Yield: 56 mg (20 %). Mp: 98 °C (dec.); $^{13}C\{^{1}H\}$ NMR (C_6D_6, 500 MHz) = 287.2 ($C_{carbene}$), 145.8 (C_{ortho}), 145.5 (C_{ortho}), 136.0 (C_{ipso}), 128.6 (C_{para}), 124.2 (C_{meta}), 76.5 (C_{quat}), 66.7 (C_{quat}), 53.6 (C_{H2}), 52.5 (C_{H}), 50.3 (C_{H2}), 36.9 (C_{H2}), 29.6, 29.3, 29.2, 29.1, 29.0, 28.6, 28.3, 27.3, 25.6, 25.0 (C_{H2}), 23.5, 23.3, 23.2, 20.0.

Computational details: The geometry optimization of the molecules have been carried out using the DFT functional M05-2X[23] with def2-SVP basis sets[24] and quasi-relativistic effective core potentials for Au[25] using the program package Gaussian 09.[26] The nature of the stationary points was verified by calculation of the vibrational frequencies. The nature of the gold–ligand bonding was analyzed with the EDA-NOCV method[27] at BP86/TZ2P[28,29] where relativistic effects are considered with the ZORA approximation[30] using the program ADF.[31]

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