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Gold(I) Chloride Coordinated 3-Hexyne

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A linear gold(I) complex featuring a simple, unstrained alkyne has been synthesized using AuCl and 3-hexyne and characterized using X-ray crystallography. Density functional theory calculations show that σ donation from alkyne → Au dominates over the Au → alkyne π back-donation.

Gold was long considered to be chemically inert and a poor catalyst.[1] However, during the past few years, novel reactions mediated by gold have been reported in the literature on a regular basis and in ever-increasing numbers.[2−5] Alkynes are some of the most commonly used substrates in gold-catalyzed organic synthetic processes. Furthermore, alkyne complexes of gold are believed to be key intermediates in numerous homogeneous and heterogeneous processes. However, isolable gold alkyne complexes are rare. Structurally authenticated gold alkyne compounds that have been described in the literature (Figure 1) have strained alkynes like 3,3,6,6-tetramethyl-1-thiacyclohept-4-yne 1,1-dioxide (**1**)[6] and 3,3,6,6-tetramethyl-1-thiacyclohept-4-yne (**2**)[6] or an alkyne in a tethered framework (**3**).[7] A limited number of gold(I)-coordinated metal acetylides and spectroscopically detected gold alkynes are also known.[8]

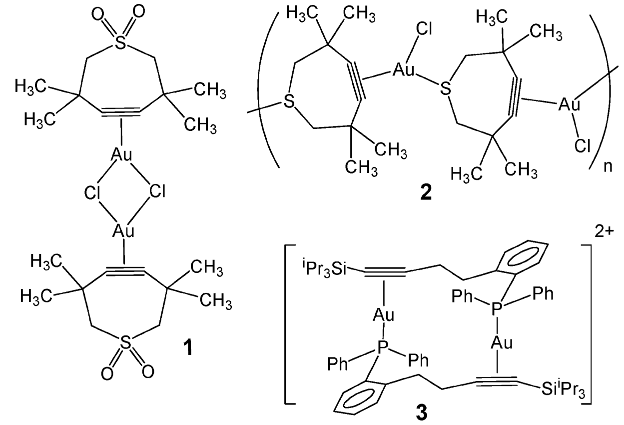

Figure 1. Structurally characterized gold(I) alkyne complexes.

In this paper, we report the isolation and structural characterization of $Au(EtC{\equiv}CEt)Cl$ (**4**), a metal coordination complex featuring *a simple unstrained alkyne* bonded to AuCl (gold chlorides are used routinely in catalytic homogeneous processes mediated by gold). First attempts at the isolation of simple gold(I) alkynes including $Au(EtC{\equiv}CEt)Cl$ were reported by Hüttel and Forkl in 1972.[9] However, they have not been able to characterize them in detail.

The treatment of AuCl with 3-hexyne ($EtC{\equiv}CEt$) in methylene chloride at −20 °C led to $Au(EtC{\equiv}CEt)Cl$, which could be crystallized to obtain colorless, needle-shaped crystals (Scheme 1).[10] $Au(EtC{\equiv}CEt)Cl$ is an air-sensitive solid and decomposes easily and rapidly at room temperature, forming black deposits. $Au(EtC{\equiv}CEt)Cl$ is stable in solution for hours at low temperature but decomposes slowly at room temperature, as is evident from the deposition of dark solids,

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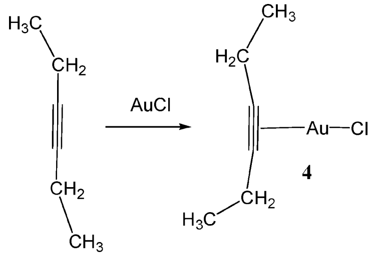
Scheme 1. Synthesis of Au(EtC≡CEt)Cl



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presumably metallic gold, on the walls of the container.[11] The ^{1}H NMR spectrum of Au(EtC≡CEt)Cl in CD_2Cl_2 at −20 °C displays a quartet and a triplet at δ 2.61 and 1.23, respectively. These values did not change significantly upon warming to room temperature. The corresponding signals of the free 3-hexyne were observed at δ 2.15 (qt) and 1.11 (t), respectively (indicating that AuCl coordination leads to a downfield shift of both signals). The ^{13}C NMR signal of the acetylenic carbons also shows a downfield shift (δ 81.1 peak of the free ligand shifts to δ 86.4, upon coordination). The corresponding signals of $[HC\{(F_3C)CO\}_2Ag]_2$(EtC≡CEt),[12] $Cu_2(\mu\text{-}O_2CCF_3)_2$(EtC≡CEt)$_2$,[13] $(Ph_3P)_2$Ni(EtC≡CEt),[14] and [K(18-crown-6)[$PtCl_3$(EtC≡CEt)]][15] were observed at δ 81.5, 88.3, 126.0, and 72.6, respectively. Note that, in contrast to the observation with the alkyne adduct Au(EtC≡CEt)Cl, alkene carbons show large upfield ^{13}C NMR shifts upon coordination of Au^I centers to olefins.[16,17] For example, the ^{13}C NMR signal of the coordinated ethylene in $[N\{(C_3F_7)C(2,6\text{-}Cl_2C_6H_3)N\}_2]Au(C_2H_4)$ appears at δ 59.1, while the corresponding peak of the free ethylene appears at δ 123.5.[18]

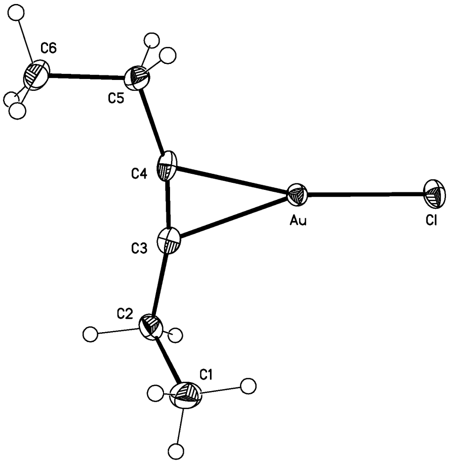

Figure 2. Molecular structure of Au(EtC≡CEt)Cl. Selected bond lengths (Å) and angles (deg): Au−C4 2.152(4), Au−C3 2.172(5), Au−Cl 2.2703(11), C1−C2 1.530(7), C2−C3 1.472(7), C3−C4 1.224(6), C4−C5 1.470(6), C5−C6 1.526(6); C4−Au−C3 32.88(17), C4−Au−Cl 167.13(13), C3−Au−Cl 159.99(12), C3−C2−C1 112.4(4), C4−C3−C2 166.9(5), C4−C3−Au 72.7(3), C2−C3−Au 120.3(3), C3−C4−C5 163.0(5), C3−C4−Au 74.4(3), C5−C4−Au 122.6(3), C4−C5−C6 111.6(4).

Table 1. Selected Bond Lengths (Å) and Angles (deg) of Au(EtC≡CEt)Cl[a]

Parameter	experimental	computed
C3≡C4	1.224(6)	1.247
Au−C4	2.152(4)	2.206
Au−C3	2.172(5)	2.231
Au−Cl	2.2703(11)	2.304
C4−C3−C2	166.9(5)	165.7
C3−C4−C5	163.0(5)	163.0

[a] See Figure 2 for the atom numbering scheme. The calculated C≡C distance of free 3-hexyne is 1.215 Å.

The X-ray crystal structure of Au(EtC≡CEt)Cl is illustrated in Figure 2. 3-Hexyne coordinates to gold in a η^2 fashion with Au−C bond lengths of 2.152(4) and 2.172(5) Å (Table 1). The gold adopts a linear coordination environment (Cl−Au−centroid$_{C≡C}$ angle of 176.3°). These distances are shorter than the Au−C distances of cationic species **3** [2.197(5) and 2.270(5) Å] reported by Shapiro and Toste.[7] Gold complexes of angle-strained alkynes **1** and **2** from Behrens group feature shorter (and presumably stronger) Au−C bonds [2.050(7)−2.100(8) Å].[6] The C≡C bond length of the bonded alkyne in Au(EtC≡CEt)Cl [1.224(6) Å] is only marginally longer than the typical alkyne C≡C bond distance of 1.202(5) Å[19] [e.g., ^{t}BuC≡C^{t}Bu, 1.2022(15) Å].[20] Note that often changes in the C−C bond distance upon coordination of coinage metals to alkyne (or alkene) moieties are harder to discern using routine X-ray crystallography because relatively small lengthenings are often overshadowed by high estimated standard deviations (esd's).[17] However, the average C≡C−C angle of 165.0(5)° indicates a significant deviation from linearity. The Au−Cl bond distance of 2.2703(11) Å is similar to the corresponding distance in two-coordinate compounds like Au(PPh_3)Cl [2.279(3) Å],[21] Au(*cis*-cyclooctene)Cl [2.266(4) Å],[22] and Au(CO)Cl [2.261(6) Å].[23]

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(10) **Au(EtC≡CEt)Cl**: ^{1}H NMR (CD_2Cl_2, 258 K) δ 1.23 (t, J = 7.2 Hz, 6H, CH_3), 2.61 (q, J = 7.2 Hz, 4H, CH_2); ^{13}C{^{1}H} NMR (CD_2Cl_2, 258 K) δ 14.7, 15.2, 86.4 (C≡C). Crystal data: empirical formula $C_6H_{10}AuCl$, fw = 314.56, T = 100(2) K, crystal system = tetragonal, space group = $P4_1$, a = 8.3936(4) Å, b = 8.3936(1) Å, c = 11.2283(5) Å, V = 791.06(5) Å^3, Z = 4, final R indices [$I > 2\sigma(I)$] R1 = 0.0145, wR2 = 0.0343; R indices (all data) R1 = 0.0149, wR2 = 0.0345.

(11) A mixture of 3-hexyne and gold(I) chloride (1:4 molar ratio) in CH_2Cl_2, upon warming to room temperature, generates metallic gold and various decomposition products after about 2 h. Filtering of this mixture, upon cooling to −20 °C, produced few crystals. X-ray analysis (see Figure S1 in the Supporting Information, CCDC 703381) revealed this to be a dimer of a gold(III) complex, 1-chloroaura-2,5-*trans*-dichloro-2,3,4,5-tetraethylcyclopent-3-ene (see Figure S3 in the Supporting Information), presumably formed by a cycloaddition pathway. This could be an intermediate during the gold chloride mediated formation of *trans*-3,4-dichloro-tetraalkyl-1-cyclobutenes from alkynes (because reductive elimination of the organic ligand fragment from this gold(III) adduct would lead to such compounds and AuCl). See: Hűttel, R.; Forkl, H. *Chem. Ber.* **1972**, *105*, 2913–2921, and ref 9.

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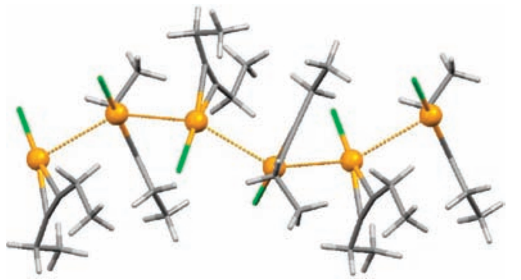

Figure 3. Diagram showing the formation of chains via Au···Au contacts.

There are weak aurophilic interactions[24] [Au···Au separations of 3.26260(15) Å and Au···Au···Au angles of 137.753(4)°] between the neighboring Au(EtC$\equiv$CEt)Cl molecules, leading to the formation of helical chains (Figure 3). Helices lie on a 4-fold screw axis (see Figure S1 in the Supporting Information).

Optimization of complex Au(EtC$\equiv$CEt)Cl at the B3LYP/LANL2DZ(Au), ccpVDZ(C,H), and AUG-ccpVDZ(Cl) levels of theory reproduces the experimental geometry (Table 1). Interestingly, the computed structure predicts a partial slippage of the gold(I) away from the symmetrical η^2 coordination.[4] However, the calculated energy difference between the slipped and symmetric structures is very small, about 1 kJ/mol. Moreover, we found no barrier between the two geometries. The experimentally observed Au−C bond distances show slight asymmetry, but the difference is not significant at the 3σ level of esd. Nevertheless, the close correspondence between the computed and experimental structures suggests that crystal packing factors do not significantly influence the geometry of the complex.

The optimized geometry was used to analyze the energetics of the complex, bonding between the metal center and the alkyne, and to compute the NMR chemical shift. Molecular orbital and natural bond orbital analysis corroborate the expected σ donation from the occupied in-plane alkyne π orbital to the empty metal−chlorine σ^* orbital and Au → alkyne back-donation from the occupied d orbital of gold to the π^* orbital of the alkyne.

Second-order perturbation analysis indicates that the magnitude of σ donation from alkyne → Au (319 kJ/mol) dominates over the Au → alkyne π back-donation (111 kJ/mol). For comparison, corresponding values reported for the simplified version of cationic gold alkyne complex **3** are 237 and 55.6 kJ/mol.[7] Lower values for the latter species are not surprising because it has a relatively bulkier and somewhat weakly donating alkyne,[25] a competing phosphine donor, and a cationic gold center. We also find a formation enthalpy of Au(EtC$\equiv$CEt)Cl with reference to molecular AuCl and 3-hexyne at -157 kJ/mol (this is in good agreement with calculated acetylene and propyne binding energies to AuCl of -142.8 and -151.4 kJ/mol, respectively).[5]

In order to understand the difference between AuCl adducts of strained alkynes and simple unstrained EtC$\equiv$CEt, we examined the bonding and energetics of the AuCl complex of 1-thiacyclohept-4-yne (C_6H_8S). The optimized structure shows that C_6H_8S coordinates to AuCl in a symmetrical fashion. The adduct Au(C_6H_8S)Cl has an enthalpy of formation of -204.9 kJ/mol. The activation barrier for adduct formation between AuCl and C_6H_8S or EtC$\equiv$CEt is essentially zero. Thus, the enthalpy of formation data of AuCl adducts indicate that the dissociation of C_6H_8S from Au(C_6H_8S)Cl is significantly more unfavorable relative to EtC$\equiv$CEt dissociation from Au(EtC$\equiv$CEt)Cl. Second-order perturbation analysis of bonding in Au(C_6H_8S)Cl shows that the magnitude of σ donation from alkyne → Au (419 kJ/mol) dominates over the Au → alkyne π back-donation (185 kJ/mol). Comparison to the corresponding values in Au(EtC$\equiv$CEt)Cl shows that Au(C_6H_8S)Cl features much stronger gold alkyne σ and π components. The Au−C distances are also relatively short in the Au(C_6H_8S)Cl adduct (see the Supporting Information).

We also calculated a downfield shift of the ^{13}C NMR signal of the acetylenic carbons of Au(EtC$\equiv$CEt)Cl upon coordination, which is consistent with the experimental observation. However, the calculated downfield shift of δ 11.6 for the symmetrical arrangement (shifts of δ 8.5 and 13.8 for the slipped geometry) is somewhat larger than the δ 5.3 shift observed in the experiment.

In summary, we describe the first X-ray structural data of a simple, unconstrained alkyne complex of gold(I). Density functional theory calculations show that σ donation from alkyne → Au dominates over the Au → alkyne π back-donation. Gold chlorides are widely used as effective π-activation catalysts for alkynes, and Au(η^2-EtC$\equiv$CEt)Cl may be viewed as a good model for the likely intermediate in some of these processes.

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Supporting Information Available: Further details of the synthesis and characterization, additional data, and figures. This material is available free of charge via the Internet at http://pubs.acs.org. CCDC 703380 contains the supplementary crystallographic data for Au(EtC$\equiv$CEt)Cl. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, U.K.).

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