Gold Complexes

DOI: 10.1002/anie.201200080

Isolable Tris(alkyne) and Bis(alkyne) Complexes of Gold(I)**

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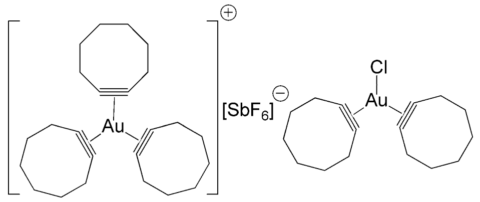
Gold has been one of the best metal ions to activate and mediate reactions involving alkynes. Among the different types of gold-catalyzed reactions, cycloaddition chemistry involving alkynes and addition of nucleophiles to alkynes are quite common and have been very useful in synthesis.[1–8] Most of these processes are believed to be initiated by the π complexation of alkyne to the electrophilic gold(I) center. Therefore, a detailed understanding of the gold–alkyne interaction, including the structures and bonding of gold(I)–alkyne π adducts, is of significant importance.[9–11] Our efforts in this area led to the isolation of gold(I) (mono)alkyne compounds such as [Au(EtC≡CEt)Cl] and $[(N\{(C_3F_7)C(Dipp)N\}_2)Au(EtC{\equiv}CEt)]$.[12,13] A few other structurally authenticated alkyne π complexes of gold are also known.[14–17]

In contrast, molecules with more than one π-bonded alkyne moiety on gold are extremely rare.[9] A limited number of structurally characterized gold complexes with more than one alkynyl metal moiety, also commonly referred to as σ acetylides, are known, but they represent a different category.[18–24] Wittig and Fischer reported a gold π alkyne complex $[Au(coct)_2Br]$ in 1972 (coct = cyclooctyne) featuring two alkyne units on a gold center, but structural data are not available.[25] Hüttel and Forkl also reported some gold adducts possibly involving more than one simple alkyne unit on gold, but the compounds were thermally unstable and poorly characterized.[26] Herein, we present the synthesis, spectroscopy, and first structural details of a tris(alkyne) and a bis(alkyne) gold complex, $[(coct)_3Au][SbF_6]$ and $[Au(coct)_2Cl]$ (Scheme 1). Optimized geometries of $[(coct)_3Au]^+$ and $[Au(coct)_2Cl]$ using density functional theory (DFT) at the BP86/def2-TZVPP level of theory and a detailed analysis of the gold–alkyne bonding interactions are also presented. We also show that Au^+ mediates the cyclotrimerization of alkynes leading to arenes.



Scheme 1. Tris(alkyne) and bis(alkyne) complexes of gold: $[(coct)_3Au][SbF_6]$ and $[Au(coct)_2Cl]$.

The treatment of $AuSbF_6$ (prepared in situ from AuCl and $AgSbF_6$) with slightly more than four equivalents of cyclooctyne in dichloromethane led to the tris(alkyne) adduct $[(coct)_3Au][SbF_6]$, which was isolated in 60% yield. It is a moderately light- and air-sensitive solid. The $^{13}C\{^1H\}$ NMR spectrum of $[(coct)_3Au][SbF_6]$ in CD_2Cl_2 at room temperature showed a broad singlet at $\delta = 102.15$, which can be assigned to the carbon resonance of the gold-bound alkyne moiety. The corresponding signal of free cyclooctyne was observed at $\delta = 94.90$. The methylene protons on the α carbons of the alkyne moiety appear as a multiplet at $\delta = 2.64$ in the ^1H NMR spectrum, which also exhibit a downfield shift (compared to $\delta = 2.13$ peak of the free alkyne) as a result of gold(I) coordination. The IR spectrum of $[(coct)_3Au][SbF_6]$ displays a weak band at 2116 cm^{-1}, which can be assigned to the C≡C stretch of the alkyne moieties. This is about 100 cm^{-1} decrease upon coordination. For comparison, the corresponding band of the free cyclooctyne was observed at 2216 cm^{-1}. Overall, there are notable changes in the alkyne moiety upon coordination to the cationic gold center.

The X-ray crystal structure of $[(coct)_3Au][SbF_6]$ (Figure 1) shows that the cationic $[(coct)_3Au]^+$ moiety adopts a distorted spoke-wheel structure. Steric congestion perhaps prevents achieving the coplanar geometry of the three alkyne groups. The torsion angles between the six alkyne carbon atom and gold (Au-C1-C2-C9-C10-C17-C18) mean plane and Au-C1-C2, Au-C9-C10, Au-C17-C18 planes are 6.3°, 43.9°, and 3.0°, respectively. As evident from these angles, one of the cyclooctynes shows noticeable out-of-plane twist. The Au−C bond distances involving this alkyne (that is, Au−C9 and Au−C10) are significantly longer compared to the corresponding distances involving the other two cyclooctynes. However, the C≡C distances are essentially the same for all three units. These distances (av. 1.216(7) Å) are at the shorter end of the reported C≡C bond lengths of cationic and neutral gold mono(alkyne) adducts, which range from 1.206(11) Å to 1.259(12) Å,[12–17] and are shorter than C=C distances reported for (tris)alkene adducts such as $[(H_2C{=}CH_2)_3Au][SbF_6]$ (av. 1.364(7) Å)[27] and $[(norbornene)_3Au][SbF_6]$ (av.

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[**] This work was supported by the National Science Foundation (CHE-0845321) and the Robert A. Welch Foundation (Grant Y-1289).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201200080.

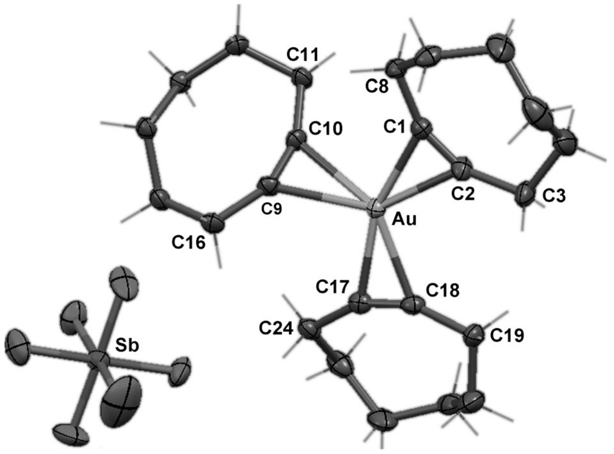


Figure 1. Molecular structure of [(coct)$_3$Au][SbF$_6$]. Ellipsoids are set at 50% probability. Calculated values at the BP86/def2-TZVPP level are given in brackets. Selected bond lengths [Å] and angles [°]: Au–C1 2.205(4) [2.197], Au–C2 2.216(5) [2.229], Au–C9 2.341(5) [2.407], Au–C10 2.336(4) [2.407], Au–C17 2.198(5) [2.197], Au–C18 2.218(5) [2.229], C1–C2 1.217(7) [1.255], C9–C10 1.213(7) [1.236], C17–C18 1.217(7) [1.255]; C1-Au-C2 31.96(17) [32.93], C9-Au-C10 30.07(16) [29.74], C17-Au-C18 32.00(17) [32.93], C1-C2-C3 152.9(5) [152.71], C2-C1-C8 151.9(4) [151.09], C9-C10-C11 155.7(5) [155.82], C10-C9-C16 154.0(5) [155.82], C17-C18-C19 152.5(5) [152.71], C18-C17-C24 151.8(5) [151.08].

1.378(5) Å).[28] [(coct)$_3$Au][SbF$_6$] does not have close Au···F or Au···Au contacts in the solid state.

The calculated bond lengths and angles of [(coct)$_3$Au]$^+$ (see Figure 1) agree well with the experimental data except for the theoretical Au–C distances of the out-of-plane cyclooctyne ligand, which are somewhat larger than the observed value. This may be due to intermolecular forces, which tend to shorten weaker bonds in the solid state.[29] The calculated structure of [(coct)$_3$Au]$^+$ was determined together with the optimized structure of [(acetylene)$_3$Au]$^+$ for comparison (Supporting Information, Figure S6). This structure of [(acetylene)$_3$Au]$^+$ has also two nearly coplanar acetylene ligands with short Au–C bonds and one out-of-plane twisted ligand that has longer Au–C bonds. In these tris(alkyne) gold(I) complexes, a planar spoke-wheel arrangement is not the lowest energy configuration as a result of steric repulsions between the alkyne moieties. Computed structures show that gold-bound cyclooctyne molecules (most notably, the in-plane cyclooctyne moieties) of [(coct)$_3$Au]$^+$ have relatively longer C≡C bond distances and smaller C≡C–C angles (that is, greater deviation from linearity) compared to the C≡C distance (1.214 Å) and the C≡C–C angles (157.6°) of the free cyclooctyne.

[(coct)$_3$Au][SbF$_6$] decomposes in refluxing hexane/CH$_2$Cl$_2$ to produce a mixture of compounds from which tris(hexamethylene)benzene can be isolated as a major component (47% yield of isolated product; see the Supporting Information, Figure S5 for the X-ray structure). Tris(hexamethylene)benzene can also be synthesized using cyclooctyne and a much smaller amount of AuSbF$_6$ generated in situ. Use of 3-hexyne with a catalytic amount of AuSbF$_6$ in refluxing CH$_2$Cl$_2$ gave hexaethylbenzene as the sole cycloaddition product, which was isolated in 48% yield. Although we are yet to optimize the yields of these cycloaddition products, it is clear from these preliminary data that gold(I) is a competent catalyst for [2+2+2] cycloaddition. To our knowledge, there are no reports of analogous gold mediated [2+2+2] cycloaddition of alkynes leading to arenes.[30–33]

Treatment of AuCl with about 5 equiv of cyclooctyne in dichloromethane led to [Au(coct)$_2$Cl], which was isolated as a colorless crystalline solid in 52% yield. Reaction of AuCl with cyclooctyne in a 1:1 molar ratio also produced the same product, but at a much lower yield. The ^{1}H and ^{13}C NMR spectra of [Au(coct)$_2$Cl] in CD$_2$Cl$_2$ at room temperature do not show large changes in chemical shift values compared to the corresponding signals of the free cyclooctyne, but the changes are more noticeable at 193 K. This perhaps indicates a relatively weak alkyne–AuCl interaction in solution. IR and Raman data of crystalline material however show a large reduction (180–190 cm^{-1}) in C≡C stretch indicating strong gold–alkyne bond. IR spectra of [Au(coct)$_2$Br][25] and a related copper complex [Cu(coct)$_2$Cl][34] have been reported and the C≡C stretch in these adducts appears at 2035 and 2073 cm^{-1}, respectively. The shift of cyclooctyne $\nu_{C\equiv C}$ to a much lower wave number in the gold complex [Au(coct)$_2$Cl] compared to that of the copper analogue suggests much stronger alkyne–metal interaction in the gold adduct.

The crystal structure of [Au(coct)$_2$Cl] from X-ray diffraction is shown in Figure 2. The two alkyne moieties and AuCl adopt essentially a coplanar geometry. The C≡C bond lengths are slightly longer and Au–C bond distances shorter in [Au(coct)$_2$Cl] compared to those observed for [(coct)$_3$Au][SbF$_6$]. However, some of these differences, in particular the differences in C≡C length, are not significant at the 3σ level of esd. [Au(coct)$_2$Cl] does not have close intermolecular Au···Cl or Au···Au contacts in the solid state. There are no structurally

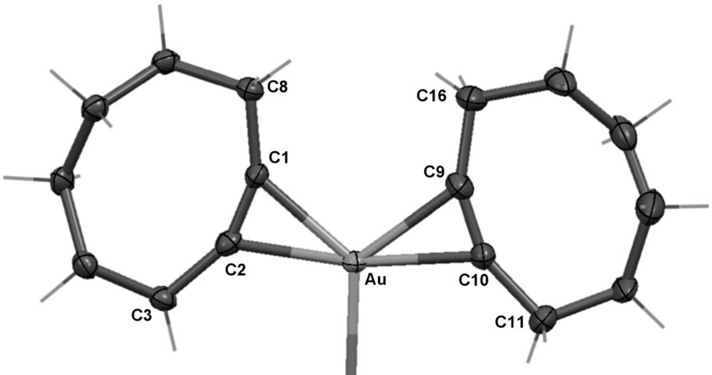


Figure 2. Molecular structure of [Au(coct)$_2$Cl]. Ellipsoids are set at 50% probability. Calculated values at the BP86/def2-TZVPP level are given in brackets. Selected bond distances [Å] and angles [°]: Au–Cl 2.4225(8) [2.429], Au–C1 2.187(3) [2.196], Au–C2 2.153(3) [2.161], Au–C9 2.189(3) [2.196], Au–C10 2.164(3) [2.161], C1–C2 1.238(4) [1.258], C9–C10 1.230(5) [1.258]; C1-Au-C2 33.13(12) [33.54], C9-Au-C10 32.81(12) [33.54], C1-C2-C3 153.4(3) [152.90], C2-C1-C8 153.1(3) [150.51], C9-C10-C11 154.7(3) [152.90], C10-C9-C16 154.0(3) [150.51].

Table 1: Energy decomposition analysis (EDA) results of [(coct)$_3$Au]$^+$ and [Au(coct)$_2$Cl].[a]

Compound	[(coct)$_3$Au]$^+$	[(coct)$_3$Au]$^+$	[Au(coct)$_2$Cl]
Interacting fragments	Au(coct)$_2$$^+$ coct-A	Au(coct)$_2$$^+$ coct-B	AuCl(coct) coct
ΔE_{int}	−44.5	−27.9	−40.27
$\Delta E_{\mathrm{pauli}}$	164.6	98.8	185.04
$\Delta E_{\mathrm{elstat}}$[b]	−131.0 (62.7%)	−78.5 (62.0%)	−143.04
$\Delta E_{\mathrm{orbital}}$[b]	−78.1 (37.3%)	−48.2 (38.0%)	−82.26
(1), ΔE_{σ}[c] (−C≡C−)→Au	−36.9 (47.2%)	−29.2 (60.6%)	−33.4 (40.6%)
(2), $\Delta E_{\pi\|}$[c] Au→(−C≡C−)	−31.4 (40.2%)	−12.6 (26.1%)	−40.6 (49.4%)
(3), $\Delta E_{\pi\perp}$[c] (−C≡C−)→Au	−3.6 (4.6%)	−1.9 (3.9%)	−2.6 (3.2%)
rest	−6.2 (7.9%)	−4.5 (9.3%)	−5.7 (6.9%)

[a] At the BP86/TZ2P+//BP86/def2-TZVPP level of theory; values given in kcal mol^{-1}. See Scheme 2 for (1)–(3). [b] Values in parentheses are the percentage contributions to the total attractive interactions $\Delta E_{\mathrm{elsat}} + \Delta E_{\mathrm{orbital}}$. [c] Values in parentheses are the percentage contributions to the total orbital interactions $\Delta E_{\mathrm{orbital}}$.

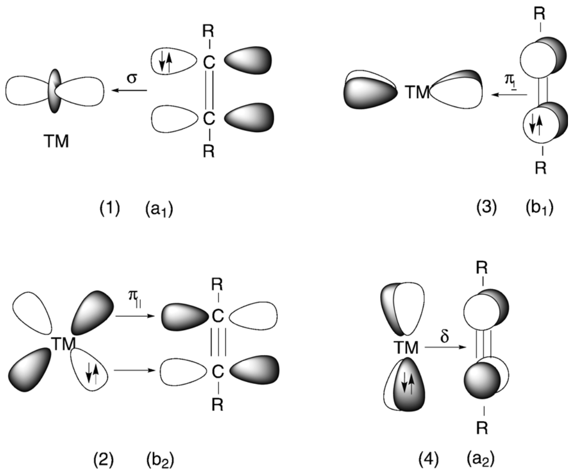
characterized bis(alkyne) gold complexes in the literature for comparing metric parameters, but an analogous copper complex [Cu(coct)$_2$Cl] is known which has shorter M−C bond distances (av. 2.041(2), 2.080(2) Å) as expected for a system involving a smaller metal ion.[34]

The calculated bond lengths and angles of [Au(coct)$_2$Cl] in Figure 2 show a very good agreement with the experimental data. The calculated structures of [Au(coct)$_2$Cl] and [Au(coct)Cl] (Supporting Information, Figure S6) show that gold-bound cyclooctyne molecules have longer C≡C bonds and smaller C≡C−C angles compared to the corresponding C≡C distance (1.214 Å) and C≡C−C angles (157.6°) of free cyclooctyne. Note that free cyclooctyne is a strained molecule with C≡C−C angles that already deviate significantly from 180°. The extent of bending back of the alkyne moiety upon coordination to Au$^{\mathrm{I}}$ is therefore not as high as those observed experimentally for Au(EtC≡CEt)Cl (C≡C−C angles = 166.9(5)°, 163.0(5)°), which is based on a non-angle-strained 3-hexyne.[13] In agreement with experiment, the calculations give lower wavenumbers for the C≡C stretching frequency of the ligands in the metal complexes compared with free cyclooctyne. The calculated frequency shifts are 241 cm^{-1} for [Au(coct)$_2$Cl] using the asymmetric mode, which has a higher intensity, and 115 cm^{-1} for [(coct)$_3$Au]$^+$ (see the Supporting Information).

The NBO analysis suggests that the gold atom in [(coct)$_3$Au]$^+$ carries a positive charge of +0.80 e, which means that there is an overall charge donation from the ligands to Au$^+$ of 0.20 e. The partial charge of the AuCl moiety in [Au(coct)$_2$Cl] is +0.16 e, which suggests that each cyclooctyne ligand receives 0.08 e from the metal. The cyclooctyne ligands are thus net electron donors in [(coct)$_3$Au]$^+$ but they are overall electron acceptors in [Au(coct)$_2$Cl]. The calculated bond dissociation energy (BDEs) for loss of one cyclooctyne ligand in [(coct)$_3$Au]$^+$ at BP86-D3/TZ2P+ is $D_{\mathrm{o}} = 18.8$ kcal mol^{-1}. This is higher than the BDE for loss of one acetylene ligand in [(acetylene)$_3$Au]$^+$ ($D_{\mathrm{o}} = 7.3$ kcal mol^{-1}). The calculated BDE for loss of one cyclooctyne ligand in [Au(coct)$_2$Cl] is $D_{\mathrm{o}} = 16.2$ kcal mol^{-1}.

The BDEs for loss of one cyclooctyne ligand from [(coct)$_3$Au]$^+$ do not discriminate between the two types of ligands, because the remaining [(coct)$_2$Au]$^+$ fragment relaxes to the same structure. The different strength of the metal–ligand interactions in the complex can be analyzed in detail with the energy decomposition analysis (EDA) method. Table 1 shows the EDA results for the [(coct)$_2$Au]$^+$-coct(A) and [(coct)$_2$Au]$^+$-coct(B) interactions, where (A) and (B) denotes the ligands with short and long metal–ligand bonds, respectively.

The EDA results of [(coct)$_3$Au]$^+$ (Table 1) show that the intrinsic interaction energy between the gold fragment and coct(A) is clearly stronger ($\Delta E_{\mathrm{int}} = 44.5$ kcal mol^{-1}) than for the coct(B) ligand ($\Delta E_{\mathrm{int}} = 27.9$ kcal mol^{-1}). The breakdown of ΔE_{orb} into contributions of orbitals that have different symmetry shows that the (−C≡C−)→Au σ donation (Scheme 2, (1)) is the largest component for both the more strongly bonded ligand A (47.2%) and particularly for the less strongly bonded ligand B (60.6%). The in-plane Au→(−C≡C−) $\pi_{\|}$ back-donation (Scheme 2, (2)) contributes 40.2% (ligand A) and 26.1% (ligand B) to ΔE_{orb}, respectively. The contribution of the (−C≡C−)→Au out-of-plane $\pi_{\perp}$ donation is very small. This result agrees with previous analyses of the bonding in metal–alkyne complexes.[35] A similar result is obtained for the bonding in [Au(coct)$_2$Cl], but there is one significant difference between the two complexes. The EDA data suggest that in the latter species, the Au→(−C≡C−) π back-donation is stronger than the (−C≡C−)→Au σ donation. This is in agreement with the calculated charge distribution, which indicates that the cyclooctyne ligands in [Au(coct)$_2$Cl] carry a small negative charge and that they



Scheme 2. Bonding orbital interactions between a transition-metal atom (TM) and an alkyne moiety (R−C≡C−R).

serve as overall charge acceptors, whereas the cyclooctyne ligands in $[(\mathrm{coct})_3\mathrm{Au}]^+$ are weak electron donors.

In summary, we have presented the synthesis and complete characterization of tris(alkyne) and bis(alkyne) gold(I) complexes using cyclooctyne as the alkyne moiety. We are in the process of synthesizing the tris(cyclooctyne) complexes of copper and silver, and the results are promising. Catalytic cycloaddition chemistry and other alkyne adducts of gold are also under investigation.

Received: January 4, 2012

Keywords: alkynes · cycloaddition · density functional calculations · gold · X-ray diffraction

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