Gold(III) Alkyne Complexes: Bonding and Reaction Pathways
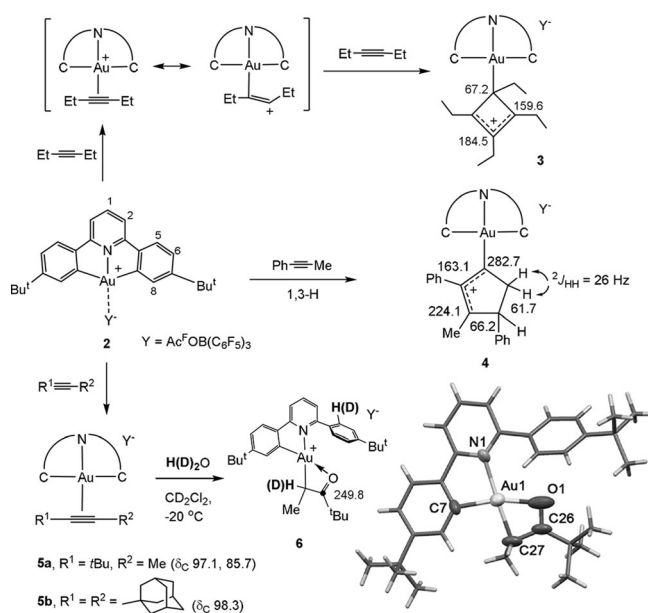
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Abstract: *The synthesis and characterization of hitherto hypothetical Au^{III} π-alkyne complexes is reported. Bonding and stability depend strongly on the trans effect and steric factors. Bonding characteristics shed light on the reasons for the very different stabilities between the classical alkyne complexes of Pt^{II} and their drastically more reactive Au^{III} congeners. Lack of back-bonding facilitates alkyne slippage, which is energetically less costly for gold than for platinum and explains the propensity of gold to facilitate C−C bond formation. Cycloaddition followed by aryl migration and reductive deprotonation is presented as a new reaction sequence in gold chemistry.*

*T*he reactions of gold complexes with alkynes form the basis of a multitude of organic catalytic transformation involving starting materials with C≡C triple bonds.[1] Invariably these reactions are initiated by coordination of the alkyne to the metal, which induces polarization and susceptibility towards nucleophilic attack. Remarkably, unlike alkyne adducts of gold(I), which have been known since the 1970s,[2–4] alkyne π-complexes of gold(III) have remained unknown.[4] This is in sharp contrast to alkyne compounds of isoelectronic platinum(II), which were first reported over 50 years ago and provide textbook examples of the Dewar–Chatt–Duncanson π-bonding model.[5,6] Elucidating the reaction chemistry of gold(III) has provided major challenges and has highlighted that drawing mechanistic analogies between gold(III) and the isolectronic Pd and Pt systems is often not valid.[7–9] We show herein that the hitherto elusive Au^{III} alkyne complexes can in fact readily be generated and have Au–alkyne bond energies comparable to those of platinum, but are drastically more reactive. The results have enabled the

first experiment-based comparison of alkyne bonding in Au^{III} and Pt^{II} systems and shed light on their reactivity differences, which helps explain the superior performance of gold in alkyne catalysis.

The reaction of (C^N^C)AuOAc^F (**1-OAc^F**; OAc^F = trifluoroacetate) with B(C$_6$F$_5$)$_3$ in dry dichloromethane generates the ion pair [(C^N^C)Au···Y] [Y = Ac^{F}OB(C$_6$F$_5$)$_3$][9a] (**2**; Scheme 1). Internal alkynes were added to these solutions at

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Scheme 1. Formation and reactivity of Au^{III} alkyne complexes, including ^{13}C NMR chemical shifts of the product complexes (CD$_2$Cl$_2$, −20°C). The structure of **2** indicates the numbering system used for NMR assignments. Crystal structure of **6**[SbF$_6$]·CH$_2$Cl$_2$, selected bond lengths [Å] and angles [°]: N1–Au 2.13(1), C7–Au 2.06(2), Au–O1 2.09(2), Au–C27 2.07(2), O1–C26 1.23(2); N1-Au-C7 81.8(7), C7-Au-C27 100.6(9), C7-Au-O1 166.7(7), N1-Au-C27 174.9(8), C27-Au-O1 66.2(8), O1-Au-N1 111.2(6), O1-C26-C27 110(2). The angle through the best planes of pyridine and the C$_6$H$_4$tBu ring is 46°.[20]

−78°C and the mixture was monitored by ^{1}H NMR spectroscopy at −20°C. The outcome of the reactions proved to be dramatically affected by nature of the substituents at the triple bond (Scheme 1). With sterically less hindered alkynes, [2+2] cyclodimerization occurs. In the case of 3-hexyne, this leads to the gold-bound cyclobutenyl cation **3**, the structure and intermolecular contacts of which were elucidated by 2D NMR methods (see the Supporting Information). By contrast, the interaction of 1-phenyl-1-propyne with **2** leads to a complex NMR spectrum consistent with the formation of the cyclopentenyl complex **4**, which is apparently produced by

a combination of cyclodimerization and 1,3-H shifts.[10,11] The observed ^{13}C NMR data are in excellent agreement with the calculated NMR chemical shifts for complexes **3** and **4** (see the Supporting Information). These cyclizations are an expression of the vinyl cation character of Au^{III} alkynes and reflect the tendency toward C−C bond formation that typifies gold-catalyzed alkyne reactions.

Cycloaddition is suppressed by steric hindrance. For example, mixing **2** with around 2.5 molar equiv of ^{t}BuC≡CMe or AdC≡CAd resulted in the reaction of only 1 equiv of alkyne to give the π-complexes **5a** and **5b**, respectively, without cyclodimerization.[11,12] Complexation was confirmed by ^{13}C NMR and the selective dipolar interactions of the Me and ^{t}Bu substituents with the pincer ligand in the ^{1}H NOESY NMR spectrum. Alkyne coordination induces only modest ^{13}C NMR shifts [**5a**: C(Me) $\delta_C = 85.7$ ($\Delta\delta_C = 11.9$ ppm), C-(^{t}Bu) $\delta_C = 97.1$ ($\Delta\delta_C = 9.4$); **5b**: $\delta_C = 98.3$ ($\Delta\delta_C = 10.6$)] very similar to the values observed for $[(R_3P)Au(\text{alkyne})]BF_4$.[13] Solutions of **5a** show no exchange between free and coordinated alkyne and are stable for hours at −30°C but decompose at 25°C within minutes. By contrast, the even more bulky bis(1-adamantyl)acetylene complex **5b** is stable for days in solution at room temperature and can be isolated as a yellow microcrystalline solid.[11]

Gold(III) is well known for its ability to catalyze alkyne hydration.[2a] This process is modelled by **5**, which reacts with water at −20°C to give the ketonyl complex **6**. Evidently the proton released after nucleophilic attack of H_2O at the alkyne cleaves the pincer. The same complex was obtained directly from **1-Cl**, AgSbF$_6$, ^{t}BuC≡CMe, and H_2O (D_2O), in more than 90% yield. The structure was confirmed by X-ray diffraction (Scheme 1).

A second type of alkyne complex could be generated after Au−C bond cleavage of **1-C$_6$F$_5$** with $[H(OEt_2)_2][H_2N\{B-(C_6F_5)_3\}_2]$ in C_6D_5Cl, followed by removal of associated Et$_2$O.[14] Ether-free **7** reacts with 3-hexyne at −78°C in CD_2Cl_2 to generate **8a** (Scheme 2). Alkyne coordination was
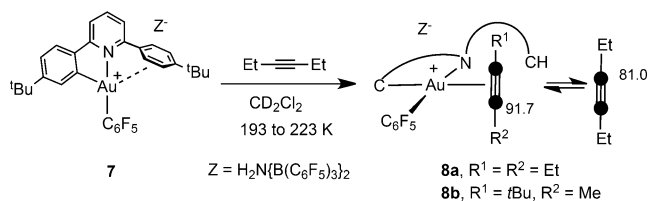

Scheme 2. Generation of C^N-chelated alkyne complexes.

indicated by a significant shift in the ligand signals. In this type of compound, the π-ligand is *trans* to an anionic C atom, which, unlike the pyridine donors in **3–5**, exerts a strong *trans* influence, resulting in substantial weakening of the Au−alkyne bond.

At −50°C, 3-hexyne coordination to **8a** is strong enough to allow separate observation of the ethyl signals of bound and free alkyne. The ^{13}C NMR signal of the coordinated triple bond was located at $\delta_C = 91.7$ ($\Delta\delta_C = 10.7$ ppm). ^{1}H NOESY NMR experiments revealed the presence of chemical

exchange, thus indicating that the complex is still fluxional at −50°C. Raising the temperature broadens the resonances, and coalescence between free and bound 3-hexyne occurs at about −30°C. The simulation of the VT ^{1}H NMR spectra of **8a** allowed the activation parameters of alkyne exchange to be estimated ($\Delta H^{\pm} = 19.9$ kcal mol^{-1} and a positive $\Delta S^{\pm} = 34$ cal mol^{-1} K^{-1}), and the results suggest that the exchange has a dissociative character. For the ^{t}BuC≡CMe complex **8b**, well-resolved spectra were obtained at −60°C, thereby allowing complete NMR characterization and a direct comparison with complex **5**, where the alkyne is *trans* to a pyridine donor. The alkyne ^{13}C signals of **8b** are very similar to those of **5**; there is no detectable *trans* influence on the ^{13}C NMR chemical shifts.

While these alkyne complexes have so far resisted all attempts at crystallization, structural confirmation of alkyne bonding was unexpectedly obtained from the reaction of **9**[15] with AgC≡C^{t}Bu, which gives the thermally stable crystalline products **10** and **11**. The latter, a product of partial reduction, contains a π-bonded Au(C≡CtBu)$_2$ anion, which, probably due to packing effects, displays two types of Au^{III}-alkynyl interactions: one symmetrical Au^{III}–alkynyl bond with an elongated C≡C distance of 1.23(3) Å, and one asymmetric alkynyl bridge that shows two very different Au^{III}−C distances (2.29(2) and 2.52(2) Å) and lacks the C≡C bond elongation (Scheme 3).
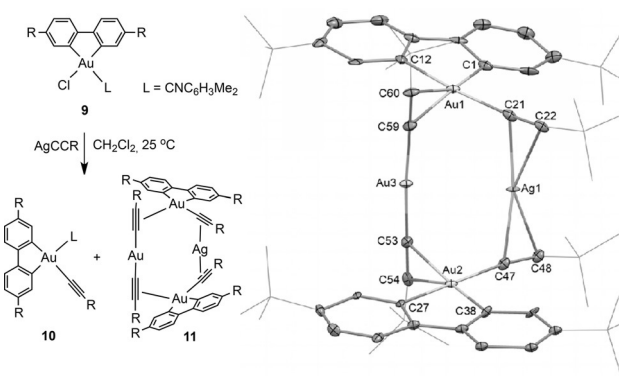
Scheme 3. Formation of the *p*-bonded Au^{III} alkynyl complex **11**. Hydrogen bonds are omitted for clarity; ellipsoids are drawn at 50%. Selected bond lengths [Å] and angles [°]: Au1–C59 2.33(2), Au1–C60 2.40(2), Au1–C21 1.98(3), Au2–C53 2.29(2), Au2–C54 2.52(2), Au2–C47 2.07(2), C53–C54 1.17(3), C59–C60 1.23(3); C53-Au3-C59 175.6-(9), Au1-C60-C59 72(1), Au1-C59-C60 78(1), Au2-C53-C54 87(2), Au2-C54-C53 65(2).[20]

The bonding of alkynes to Au^{III} was explored by Density Functional Theory (DFT) calculations (Gaussian 09, TPSSh/cc-pVTZ//B3LYP/SVP), and compared to bonding in structurally related Pt^{II} fragments (Table 1).[16] Surprisingly, the dissociation energies of Au^{III} and Pt^{II} with pyridine ligands in a *trans* position were remarkably similar, thus suggesting that the observed differences in reactivity are not due to thermodynamic effects. Alkyne bonding to $[(C\text{^}N\text{-}CH)Au(C_6F_5)]^+$ was weaker by 30–40 kcal mol^{-1} compared to $[(C\text{^}N\text{^}C)Au]^+$ for both electronic and steric reasons: the empty coordination

***Table 1:*** Calculated alkyne-dissociation free energies from gold(III) and platinum(II) fragments [kcal mol^{-1}].[a, 11]

| Ligand	[(C^N^C)Au]$^+$	[(C^N^N)Pt]$^+$	[(C^N^CH)Au(C$_6$F$_5$)]$^+$
CO	46.5	55.7	8.5
HC≡CH	38.9	41.7	4.3
MeC≡CMe	48.7	47.6	12.3
EtC≡CEt	53.0	50.8	15.0
MeC≡C^{t}Bu	53.1	51.0	13.4
MeC≡CPh	50.6	49.7	13.8

[a] C^N^N = 2,2'-bipyridyl-6-C$_6$H$_4$.

site in [(C^N-CH)Au(C$_6$F$_5$)]$^+$ is *trans* to a strong Au−C bond, and it is shielded by the dangling aryl arm. General bonding trends are very similar between the two types of complexes, with the more π-donating alkynes binding most strongly.

The Au^{III}−C(alkyne) bond lengths calculated for the model [(C^N^C)Au(2-butyne)]$^+$ correspond remarkably closely to those found for the π-bonded alkynyl ligand in **11** (Figure 1).
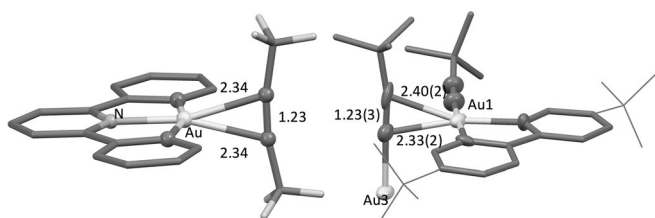
Figure 1. Comparison of Au−C and C−C distances [Å] in the calculated model [(C^N^C)Au(2-butyne)]$^+$ (left) and the π-alkynyl fragment of the crystal structure of **11**.[20]

In order to assess the *trans* influence on back-donation, charge-decomposition analysis was carried out.[17] Back-donation for all gold(III) compounds is very low and is further reduced by strong *trans* ligands; for example, **5** shows a back- donation/donation (B/D) ratio of 0.43. This drops to B/D = 0.17 for **8a**, which is much less than in structurally analogous [(C^N^N)Pt^{II}(3-hexyne)]$^+$ (B/D = 0.77). The stability of alkyne complexes depends almost entirely on π-donation from the triple bond. We ascribe the relative stability of **8** and the reduced tendency of this complex to undergo [2+2] cycloaddition to the steric shielding provided by the "Pacman"-type C^N-aryl ligand structure, which provides a kinetically protected binding pocket and thus enables the detection of these thermodynamically labile species.

The lability of Au^{III} alkyne complexes and their high reactivity contrasts sharply with the thermal and chemical stability of their Pt^{II} analogues. Surprisingly, the alkyne binding energies for Au^{III} are comparable to or slightly higher than those for Pt^{II}: −50.3 kcal mol^{-1} for [(C^N^C)Au-(3-hexyne)]$^+$, versus −42.6 kcal mol^{-1} for [(C^N^N)Pt(3-hexyne)]$^+$. However, the reduced back-bonding permits more facile alkyne slippage, with consequent accumulation of positive charge on the β-carbon atom and an increase in its susceptibility to nucleophilic attack.
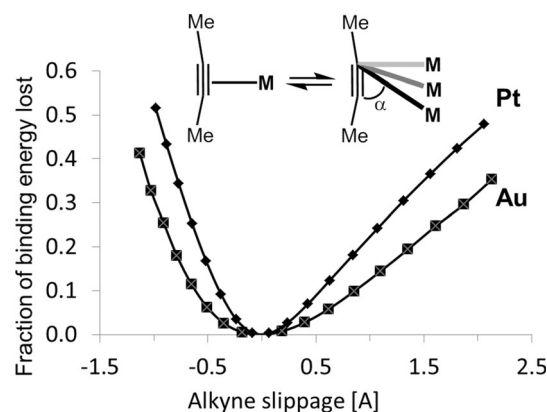
Figure 2. Fraction of binding energy lost vs. 2-butyne slippage [Å] for AuCl$_3$ (■) and PtCl$_2$(H$_2$O) (◆).

Alkyne slippage was probed by using 2-butyne adducts of AuCl$_3$ and PtCl$_2$(H$_2$O) as models and varying the angle α in the range 35–120° with steps of 5°, resulting in slippage values of approximately −1 to +2 Å (Figure 2).[18] In the (non-slipped) π-complexes, this angle is close to 75° and 73° for Cl$_3$Au(butyne) and *trans*-Cl$_2$(H$_2$O)Pt(butyne), respectively. Back-bonding can be expected to increase the barrier to geometric deformation, and indeed, at a slippage of +1 Å, the Au complex has lost only 13% of its acetylene binding energy, while the Pt complex has lost 23% (Figure 2). We believe this easier deformation of Au complexes contributes significantly to the higher reactivity of gold(III) acetylene complexes.

Warming a mixture of **8a** and 3-hexyne to room temperature gives the thermally stable product **12** (Scheme 4). Its formation involves [2+2] cycloaddition, followed by C$_6$F$_5$
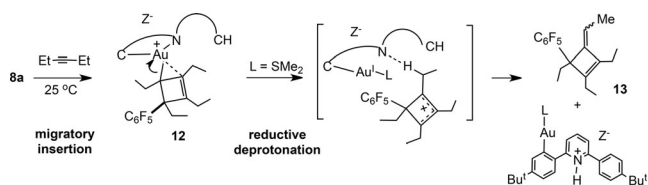
Scheme 4. Reactivity of the alkyne complexes: C−C coupling and alkene release.

migration to the resulting cyclobutenyl cation. The C=C bond is significantly polarized due to a weak interaction with the gold center (δ_C = 138.0 and 185.1; cf. calculated values (Me model): δ_C = 131.4 and 189.3). This reaction sequence—alkyne cycloaddition followed by migratory insertion into an Au-C(aryl) bond—is to the best of our knowledge unprecedented in gold chemistry.

Alkenes are typically released from metal alkyls by β-H elimination, as recently shown for gold(III) *n*-alkyls.[8c] This process requires a vacant site in a *cis* position and is suppressed by donor ligands. By contrast, alkene release from **12** is actually induced by donors (SMe$_2$ or xylylNC). Monitoring **12**/SMe$_2$ mixtures at −30°C, where the reaction is quite slow, showed no evidence for the formation of a transient Au^{III}−H species,[9b–d] nor was there evidence for

a C(aryl)−H coupling product resulting from such an intermediate. On the other hand, a broad signal at $\delta_H = 13.4$ appeared, typical of a protonated pyridine. These findings suggest that **12** may follow an alternative path: reductive deprotonation, involving dissociation into a gold(I) aryl and a cyclobutenyl cation (Scheme 4), and likely assisted by stabilizing SMe$_2$ coordination to Au^I, followed by deprotonation of the cyclobutenyl cation by pyridine to give **13** as an E/Z mixture.

The free energy pathway for alkyne dimerization and cyclobutenyl–aryl coupling is shown in Scheme 5. Starting with the mono-alkyne π-complex **B1**, the Au atom moves to
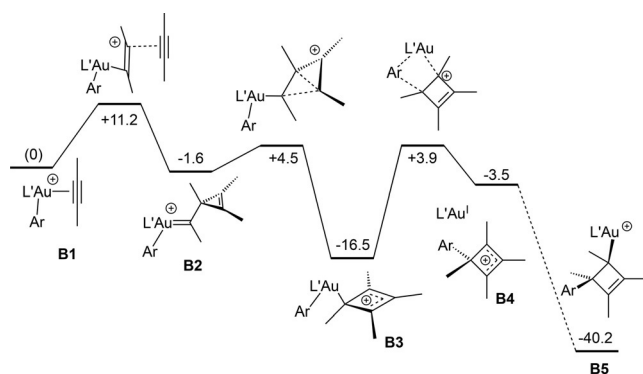
Scheme 5. Free energy profile (298 K, chlorobenzene) for cyclodimerization and formation of **12**.

one of the two *sp*-C atoms, creating a gold-bound vinyl cation, which attacks the π-bond of a second alkyne. The resulting cyclopropenylmethylene cation **B2** is a shallow local minimum. Opening of one of the two ring single bonds leads to the aurated cyclobutenyl cation **B3**. The rate-limiting step is the initial alkyne–alkyne coupling. The transition state for coupling of the C$_6$F$_5$ and cyclobutenyl fragments (**B3** to **B4**/**B5**) looks somewhat like insertion of cyclobutadiene into the Au−C$_6$F$_5$ bond. The calculated barrier of approximately 20 kcal mol^{-1} indicates that this reaction should be rather slow at room temperature, as was indeed observed. The product **B4** formed immediately from the transition state resembles a combination of neutral (η^1-C^N-CH)Au^I (with a long Au····N distance of 3.04 Å) and a cyclobutenyl cation, which would constitute an intramolecular redox reaction. This pair of species easily collapses to rather stable Au^{III} cyclobutenyl complex **B5**. We suspect that a direct route from **B3** to **B5** is avoided because that leads to an unfavorable isomer with the newly formed Au−C bond *trans* to that of the C^N-CH ligand. With additional stabilization by SMe$_2$, intermediate **B4** may also provide a pathway for the release of the organic product through reductive deprotonation (for the possibility of alkene release through β-H elimination, see the Supporting Information).

In conclusion, several distinct types of well-defined gold-(III) alkyne complexes are now accessible and were characterized by spectroscopic, structural, and computational methods. Their synthesis enabled an outline of their reaction pathways. Alkyne bonding is subject to a strong *trans*

influence: ligands *trans* to pyridine-N are bound significantly more strongly than *trans* to an anionic C donor. Although Au^{III} and Pt^{II} alkyne adducts show comparable binding energies, the much lower back-bonding in Au^{III} complexes reduces the energy cost of alkyne slippage and facilitates C≡C bond polarization. This greatly enhances the susceptibility of gold-bound alkynes towards nucleophilic attack and C−C bond formation, which is in line with the behavior of gold catalysts. Overall, gold(III) alkyne complexes display reaction pathways that are unprecedented in gold chemistry and illustrate the drastic reactivity differences between Au^{III} compounds and their Pt^{II} congeners.

Conflict of interest

The authors declare no conflict of interest.

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[20] CCDC 1559726 (**6**) and 1569528 (**11**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.