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Rearrangement of a Transient Gold Vinylidene into Gold Carbenes

Wouter Debrouwer and Alois Fürstner*

***Abstract**: The gold acetylide complex **20** endowed with a biaryl backbone provides opportunities for a study on the formation and fate of gold vinylidenes. While the formyl group in **20** per se is not sufficiently electrophilic to get attacked by the acetylide in proximity, its activation with TBSOTf at low temperature triggered instantaneous formation of a gold vinylidene (**21**). This metastable species evolved into the cationic gold carbene complex **22** bearing a phenanthrene unit and a hydroxyl group at the aurated center; the recorded data suggest that this product might be better viewed as an acylgold species protonated by triflic acid. The use of [$Me_3O\cdot BF_4$] as the activating agent also led to formation of the analogous Fischer-type carbene **24**, whereas replacement of gold by the [$CpRu(PPh_3)_2]^+$ fragment allowed the ruthenium vinylidene **27** to be isolated, which closely resembles the proposed gold intermediate **21**. The starting gold complex **20**, the derived products **22** and **24**, as well as vinylidene **27** were characterized by X-ray diffraction.*

During the course of comprehensive studies on the synthesis of phenanthrenes and related polycyclic arenes by π-acid catalyzed cycloisomerization,[1,2,3] we noticed that haloalkynes **1** (X = Br, I) rearrange on treatment with catalytic amounts of Au^I to give product **3** in which the halide has migrated by one C-atom (Scheme 1). Intervention of a gold vinylidene of type **2** formed by 1,2-halide shift provided the best explanation for this unusual outcome,[1,4] although such intermediates had never been invoked before. This mechanistic proposal was confirmed by related observations subsequently made in other laboratories[5] and by a first set of DFT calculations.[6,7]

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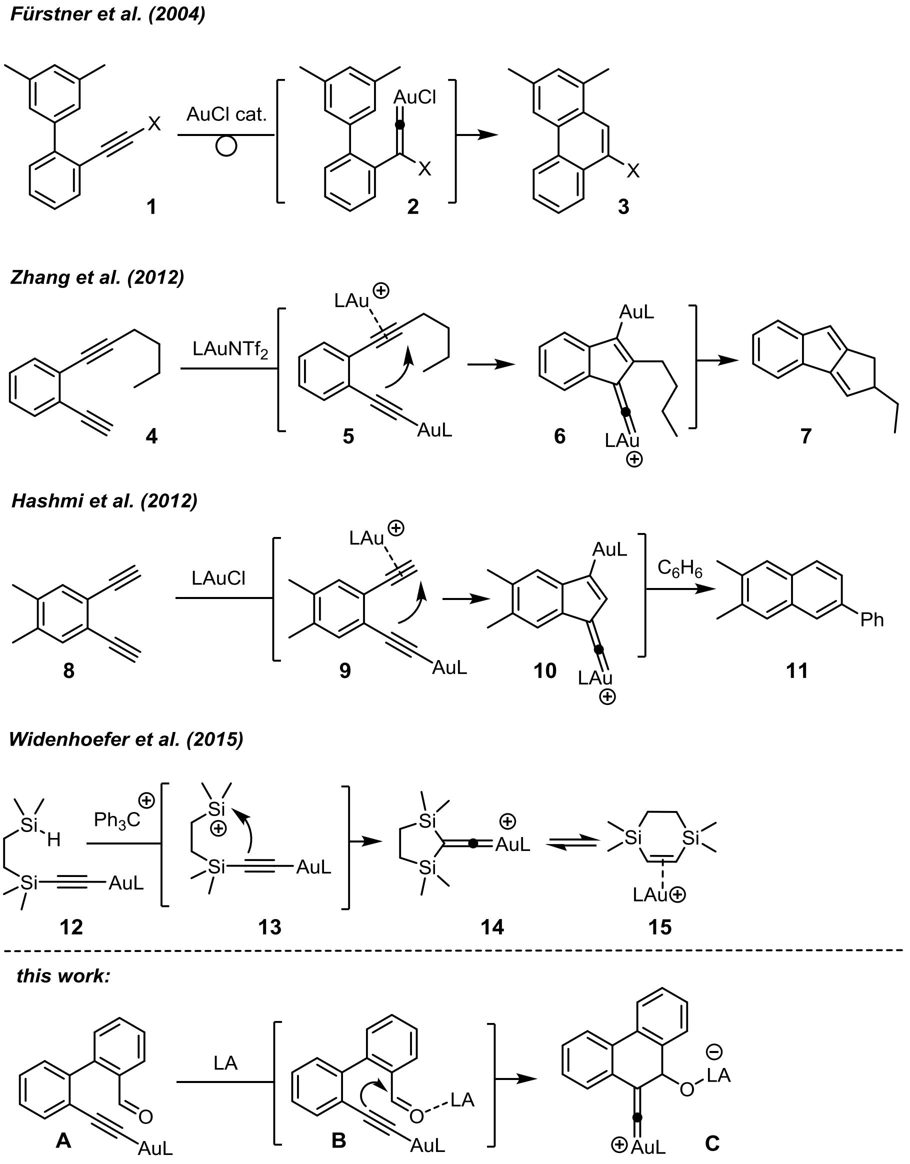
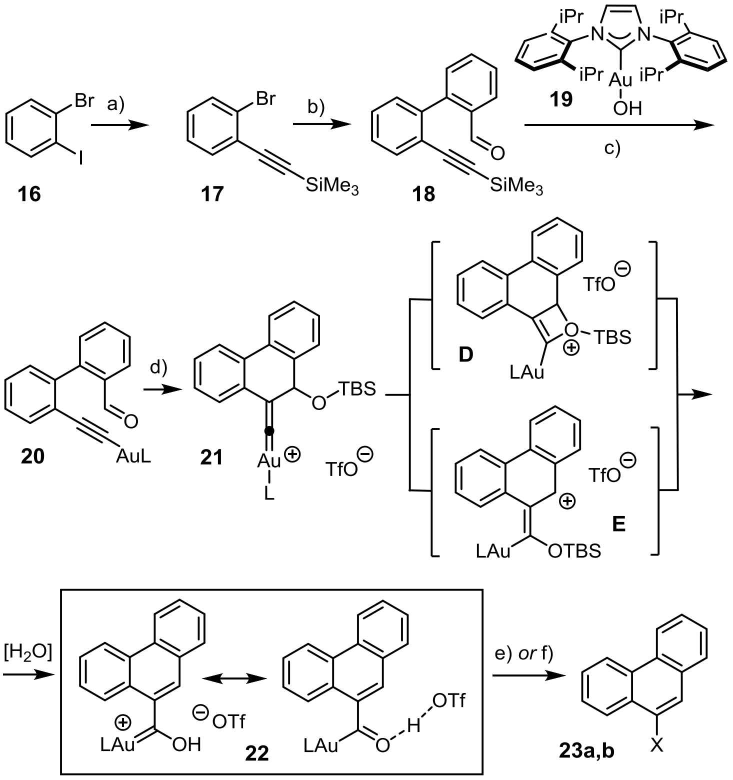


Scheme 1. Gold vinylidenes: prior art and project outline; counterions are not shown for clarity; L = neutral two-electron donor ligand; LA = Lewis acid.

This research area gained momentum when the groups of Zhang[8] and Hashmi[9] independently suggested that gold acetylides such as **5** and **9** react with tethered gold-alkyne π-complexes to form the gold vinylidenes **6** and **10**, respectively (Scheme 1). In its essence, such "dual σ/π activation"[10,11] represents an innovative extension of the arguably most general entry into metal vinylidenes by reaction of a transition metal acetylide with various kinds of electrophiles, including H$^+$, R$^+$ or X$^+$.[4] If this approach pertains to the gold series, it is reasonable to expect that electrophilic partners other than gold-alkyne π-complexes[12] can be used for the same purpose. In fact, Harris and Widenhoefer cleverly used this strategy to generate the gold vinylidene **14**, which is the first and so far only species of its kind to be fully characterized by NMR.[13] Complex **14** was derived from **12** upon in situ release of a tethered silylium cation (**13**); its vinylidene carbon atom resonates at a surprisingly high field (δ (–90°C, CD_2Cl_2) = 206 ppm), likely as a consequence of the stabilizing effect exerted by the two silyl groups onto the polarized vinylidene unit. Such stabilization is arguably necessary to give a gold vinylidene a discrete lifetime: one can safely extrapolate from the growing body of secured information on structure and bonding in gold carbenes[14,15,16] that gold vinylidenes in general must be exceptionally reactive species unless they are tempered by an appropriate ligand framework and/or substitution pattern. Specifically, a vinylcation resonance extreme makes a substantial contribution to their ground state structure;[17] this qualitative picture is well in line with the available experimental and computational data.[10,18,19]

We conjectured that a ligand architecture as shown in **A** might also lend itself to an investigation into gold vinylidenes (Scheme 1). The aromatic backbone was thought to be a robust and well accessible platform that ensures proximity of the nucleophilic and electrophilic sites; if necessary, the reactivity of the carbonyl can be tuned by activation with an appropriate Lewis-acid as shown in **B**, whereas substituents on the arene rings might ultimately help to stabilize the resulting complex **C**. In a first foray, we prepared the parent compound of this series by a sequence of palladium catalyzed cross coupling reactions exploiting the differential in the reactivity of the C-I and C-Br bond of **16** (Scheme 2).[2c] Treatment of **18** with the gold hydroxide complex **19**[20] afforded the corresponding gold acetylide **20** in essentially quantitative yield.[21] Even though this reaction was carried out in alcoholic medium at 60°C, spontaneous cyclization with formation of a gold vinylidene did not occur. The aldehyde per se is obviously not sufficiently electrophilic to succumb to spontaneous attack by the acetylide unit of **20**, despite the fact that the two sites supposed to react with each other are fairly close in space – at least in the solid state (C5····C18 3.02 Å) – and the biaryl is only slightly twisted (C6-C11-C12-C17 58.5°) (Figure 1).



Scheme 2. a) HC≡CSiMe$_3$, [(Ph$_3$P)$_2$PdCl$_2$] (1 mol%), CuI (3 mol%), Et$_3$N, 84%; b) 2-formylphenylboronic acid, Pd$_2$(dba)$_3$ (5 mol%), RuPhos (10 mol%), K$_3$PO$_4$, toluene, reflux, 82%; c) **19**, MeOH/EtOH (1:1), 60°C, quant.; d) TBSOTf, CH$_2$Cl$_2$, –78°C, 75%; e) CD$_2$Cl$_2$, RT, **23a** (X = H), quant. (NMR); f) CD$_2$Cl$_2$, MeOH, **23b** (X = COOMe), quant. (NMR); dba = bisbenzylideneacetone, TBS = *tert*-butyldimethylsilyl; L = 1,3-bis(2,6-diisopropyl)imidazole-2-ylidene.

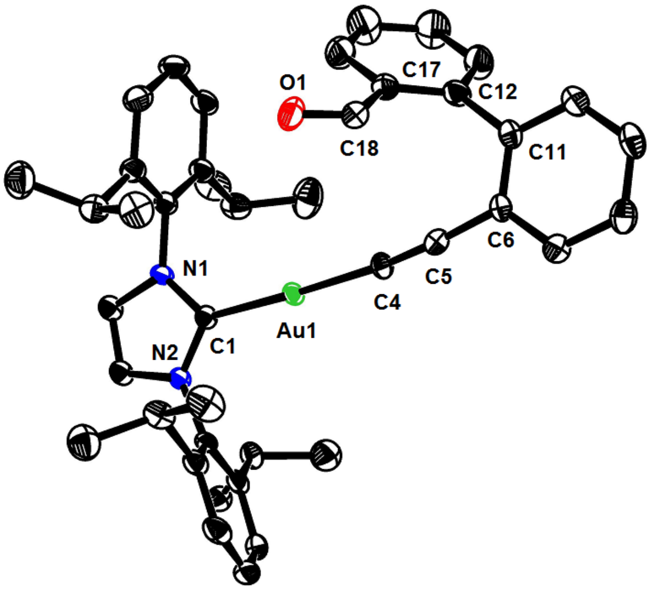


Figure 1. Structure of the gold acetylide complex **20** in the solid state; anisotropic displacement parameters are shown at the 50% probability level. Selected bond lengths (Å) and angles (°): C5–C4 1.207(6), C4–Au1 1.983(5), Au1–C1 2.012(5), C5-C4-Au1 173.8(4).

Upon addition of TBSOTf at –78°C, however, the almost colorless solution of **20** in CH_2Cl_2 instantaneously turned orange-red; ^{13}C NMR spectra recorded at this temperature showed the presence of an intermediate with a distinctive low-field resonance at δ_C = 293 ppm, which proved metastable and evolved within minutes into a new compound with a characteristic resonance at δ_C = 283.5 ppm; concurrently, the intense orange-red color faded away, giving rise to a yellow solution. The constitution of the resulting complex **22** was unambiguously established by NMR and X-ray diffraction (Figure 2).

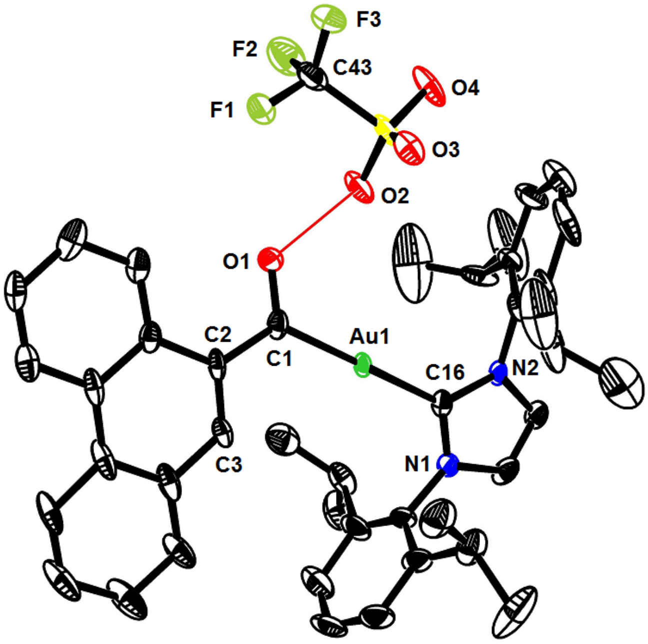
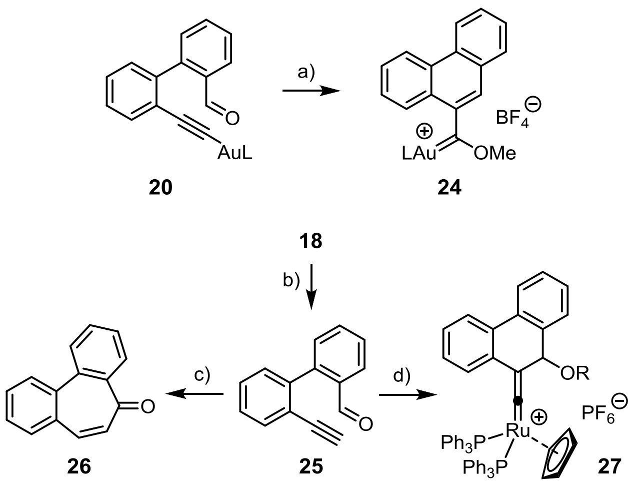


Figure 2. Structure of the gold carbene complex **22** in the solid state; anisoptropic displacement parameters are shown at the 50% probability level; the thin red line indicates the O1··(H)··O2 hydrogen bonding array. Selected bond lengths (Å): Au1–C1 2.010(9), Au1–C16 2.011(9), C1–C2 1.467(9), C2–C3 1.337(8), C1–O1 1.274(9).

Complex **22** turned out to be a cationic Fischer-type gold carbene bearing a phenanthrene entity and a hydroxyl group as the substituents flanking the carbene center, even though the proton of the –OH group has not been localized on the Fourier map. The gold "carbene" Au1–C1 bond is as long (2.010(9) Å) as the gold-NHC distance Au1–C16 (2.011(9) Å), in line with a very low bond order in either case.[22] In contrast, the C1–O1 distance (1.274(9) Å) is remarkably short, thus indicating substantial carbonyl character. **22** can therefore rightfully be viewed as an acylgold species protonated by triflic acid. This interpretation is reinforced by the tight ion pairing of the cationic entity with the escorting triflate anion, which manifests itself in a very short O1··(H)··O2 distance (2.551 Å). In line with the notion that **22** shows substantial acyl metal character, this compound was found to decarbonylate to give **23a** (X = H) when kept in solution,[23] whereas treatment with MeOH at low temperature afforded the corresponding ester **23b** (X = COOMe). To the best of our knowledge, **22** is the first isolated gold complex of its kind.

We propose that **22** is formed upon attack of the alkynylgold group of **20** onto the activated formyl substituent in vicinity, which gives rise to a transient gold vinylidene species **21** that likely manifests itself in the δ_C = 293 ppm signal observed at the outset of the reaction. Whether the subsequent conversion into **22** proceeds in a metathesis fashion via a discrete oxete intermediate **D** or in a stepwise manner passing through a stabilized benzylic cation such as **E** cannot be decided at this point, although some preliminary data speak for an ionic pathway (see below). In any case, aromatization of the backbone certainly drives this formal alkyne/carbonyl metathesis reaction.[24]



Scheme 3. a) $Me_3O{\cdot}BF_4$, CH_2Cl_2, –78°C → RT, 55%; b) TBAF, MeOH/THF, 0°C → RT, 95%; c) TBSOTf, CH_2Cl_2, –78°C → RT, 82%; d) $[CpRu(PPh_3)_2Cl]$, NH_4PF_6, MeOH, reflux, 88% (R = H, Me); Cp = cyclopentadienyl; TBAF = tetra-*n*-butylammonium fluoride

Although the significant carbonyl character of the emerging [LAu–C(=O)R] unit in **22** explains why the silyl group derived from TBSOTf used to activate the aldehyde is not

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retained in the resulting gold complex but was cleaved off in situ or during product isolation by adventitious water, we explored whether a more "sticky" activating agent stays on. To this end, compound **20** was treated with [$Me_3O{\cdot}BF_4$]; while no spontaneous reaction was observed at –78°C, gentle warming of the mixture led to the formation of the corresponding methoxycarbene **24** (Scheme 3). Its structure in the solid state also features the characteristic pattern of a distinctively long Au1–C1 but a notably short Au1–O1 bond and is hence similar to that of **22** (Figure 3).

Another control experiment proved that the gold atom attached to the alkyne unit plays a crucial role in determining the course of the reaction. Specifically, the terminal alkyne **25** derived from **18** was exposed to TBSOTf in CH_2Cl_2 at low temperature. In line with our expectation, no phenanthrene system was formed in this case; rather, the known seven-membered enone **26** could be isolated in good yield.[25]

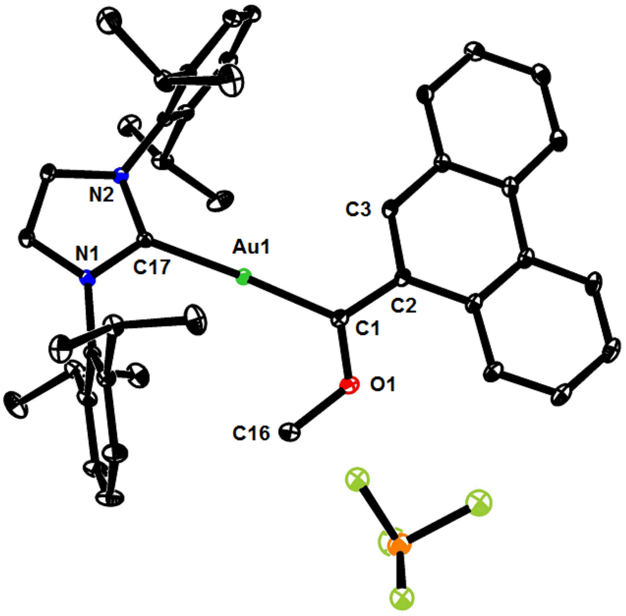

Figure 3. Structure of the gold carbene complex **24** in the solid state; anisoptropic displacement parameters are shown at the 50% probability level; solute CH_2Cl_2 and the disorder of the $[BF_4]^-$ counterion are not shown for clarity. Selected bond lengths (Å): Au1–C1 2.018(2), Au1–C17 2.017(2), C1–C2 1.457(2), C1–O1 1.296(2), O1–C16 1.466(2), C2–C3 1.374(2).

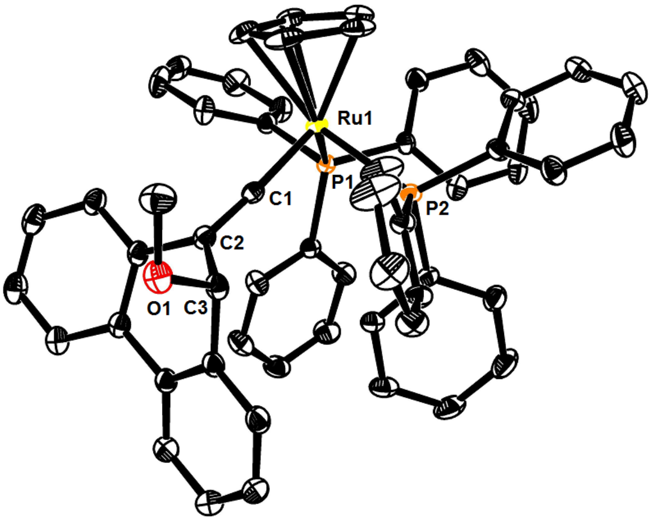

Figure 4. Structure of the ruthenium vinylidene complex **27b** (R = Me) in the solid state; anisoptropic displacement parameters are shown at the 60% probability level, the PF_6 counterion and cocrystallized water are not shown for clarity. Selected bond lengths (Å) and angles (°): Ru1–C1 1.844(1), C1–C2 1.322(2), C2–C3 1.529(2), Ru1-C1-C2 174.0(1), C1-C2-C3-O1 124.3(2)

Finally, the proposed intervention of a metal vinylidene of type **B** was corroborated by an experiment in which the terminal alkyne **25** was treated with $[CpRu(PPh_3)_2Cl]$ and NH_4PF_6; ruthenium vinylidenes in general are well behaved and many members of this series had been characterized in the past.[4,26] In fact, substrate **25** readily furnished the expected ruthenium vinylidene **27**, in which the new C-C-bond has already formed by attack of the aldehyde onto the (transient) metal acetylide but the subsequent rearrangement resulting in aromatization and concomitant Fischer carbene formation has not yet taken place (Scheme 3). As the reaction was carried out in MeOH at elevated temperature, product **27a** (R = H) was admixed with the corresponding methyl ether **27b** (R = Me) formed by solvolysis. This latter compound could be isolated in pure form by recrystallization; its structure in the solid state is shown in Figure 4. The ready –OH for –OMe exchange indicates facile ionization at the benzylic position adjacent to the vinylidene β-C-atom; this reactivity profile, in turn, suggests that an ionic scenario might also govern the conversion of the gold vinylidene **21** into the final carbene complex **22**. The fact that the –OMe substituent on the puckered backbone of **27b** points away from the electrophilic vinylidene C1-atom also renders oxete formation unlikely. Yet, we emphasize that this mechanistic aspect needs further scrutiny.

In any case, the preliminary results outlined above on the intramolecular reaction of a gold acetylide with an activated aldehyde partner provide evidence for the transient formation of gold vinylidenes as discrete yet highly reactive species; the spectroscopic signature of one representative was recorded at low temperature. The particular ligand design used in this study, however, allowed this particular type of intermediate to escape by an unprecedented rearrangement to a gold carbene. Attempts to refine the approach with the hope of being able to fully characterize such an exceedingly rare gold vinylidene complex of immediate relevance for catalysis are in progress.

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