Digold Complexes | Hot Paper

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Methyl-, Ethenyl-, and Ethynyl-Bridged Cationic Digold Complexes Stabilized by Coordination to a Bulky Terphenylphosphine Ligand

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Abstract: *Reactions of the gold(I) triflimide complex $[Au(NTf_2)(PMe_2Ar^{Dipp_2})]$ (**1**) with the gold(I) hydrocarbyl species $[AuR(PMe_2Ar^{Dipp_2})]$ (**2a–2c**) enable the isolation of hydrocarbyl-bridged cationic digold complexes with the general composition $[Au_2(\mu\text{-}R)(PMe_2Ar^{Dipp_2})_2][NTf_2]$, where $Ar^{Dipp_2} = C_6H_3\text{-}2,6\text{-}(C_6H_3\text{-}2,6\text{-}iPr_2)_2$ and R = Me (**3**), CH=CH$_2$ (**4**), or C≡CH (**5**). Compound **3** is the first alkyl-bridged digold complex to be reported and features a symmetric $[Au(\mu\text{-}CH_3)Au]^+$ core. Complexes **4** and **5** are the first species of their kind that contain simple, unsubstituted vinyl and acetylide units, respectively. In the series of complexes **3–5**, the bridging carbon atom systematically changes its hybridization from sp^3 to sp^2 and sp. Concomitant with this change, and owing to variations in the nature of the bonding within the $[Au(\mu\text{-}R)Au]^+$ unit, there is a gradual decrease in aurophilicity, that is, the strength of the Au···Au bonding interaction decreases. This change is illustrated by a monotonic increase in the Au–Au distance by approximately 0.3 Å from R = CH$_3$ (2.71 Å) to CH=CH$_2$ (3.07 Å) and C≡CH (3.31 Å).*

The seminal work of Teles and co-workers[1] on the highly efficient addition of MeOH to alkynes catalyzed by $[Au(PPh_3)]^+$, which was generated in situ from $[AuMe(PPh_3)]$ and methanesulfonic acid (HO_3SMe), marked the beginning of homogeneous gold catalysis in 1998. Countless reports on gold-catalyzed electrophilic activations of alkynes, alkenes, allenes, and other molecules with C–C multiple bonds have appeared ever since.[2] Fundamental information on the constitution, structure, and bonding of key intermediates in the proposed mechanistic cycles was, however, gained at a slower pace. For instance, the first structurally characterized alkene and alkyne complexes of $[Au(L)]^+$ cations were not reported until recently.[3,4]

However, the past few years have witnessed remarkable developments in fundamental aspects of gold chemistry, for example, with respect to complexes in different oxidation states[5] as well as the analysis of elementary reaction steps, such as oxidative addition and reductive elimination, α- and β-H abstractions from gold alkyl species, and formal insertions of unsaturated molecules into various gold–heteroatom σ bonds.[6–8] Furthermore, advances have also been made in the important fields of gold carbonyls[9] and hydrides.[5c,10] Likewise, relevant, commonly proposed intermediates, such as cationic gold(I) alkylidene, vinylidene, allenyl, and other species, have been structurally characterized.[11,12] Two comprehensive review articles on organometallic intermediates in gold catalysis were published in 2014.[2g,13]

Cationic digold species of the type $[Au_2(\mu\text{-}R)L_2]^+$, where L represents a neutral ligand, commonly a tertiary phosphine or an N-heterocyclic carbene (NHC), and R is a formally monoanionic hydrocarbon-derived group such as phenyl,[10c,14] alkenyl,[15] or acetylide,[16] have been known for many years (Figure 1, structure **A**). Surprisingly, the related

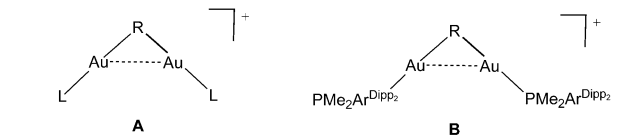

Figure 1. Previously reported hydrocarbyl-bridged digold compounds with the general formula $[Au_2(\mu\text{-}R)L_2]^+$ (**A**) and complexes reported in this work (**B**), where R represents a non-aromatic hydrocarbyl radical.

cationic alkyl complexes have never been isolated, even though neutral alkyl species, [Au(R)L], are isolable intermediates in gold catalysis.[13,17] The bonding in the model complex $[Au_2(\mu\text{-}CH_3)(PH_3)_2]^+$ was studied in 1994,[18] and cationic gold(III) alkyl complexes were reported recently.[7c]

Herein, we describe the synthesis and structure of the first methyl-bridged digold complex along with the corresponding compounds that contain vinyl and acetylide bridging groups, CH=CH$_2$ and C≡CH, respectively (Figure 1, compound **B**). The new digold cations have the general formula $[Au_2(\mu\text{-}R)(PMe_2Ar^{Dipp_2})_2]^+$ and feature $\{Au(\mu\text{-}R)Au\}^+$ cores that are stabilized by gold coordination to the bulky terphenylphosphine $PMe_2Ar^{Dipp_2}$ ($Ar^{Dipp_2} = C_6H_3\text{-}2,6\text{-}(C_6H_3\text{-}2,6\text{-}iPr_2)_2$).

We originally investigated the low-temperature protonation ($[H(OEt_2)_2][BAr_F]$, CD_2Cl_2, −80 °C; $BAr_F^- = [B(3,5\text{-}$

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$C_6H_3(CF_3)_2)_4]^-$) of the methyl complex $[Au(CH_3)(PMe_2Ar^{Dipp_2})]$ (**2a**), with the expectation of detecting a transient cationic gold σ-CH_4 complex[19] or a CD_2Cl_2 adduct, in the latter case a species perhaps related to Teles' active catalyst.[1] Instead, NMR studies indicated the formation of the dinuclear methyl-bridged complex $[Au_2(\mu\text{-}CH_3)(PMe_2Ar^{Dipp_2})]^+$ with liberation of CH_4. As identical results were obtained using 1:1 and 2:1 ratios of **2a** and the acid, it is evident that the highly electrophilic $[Au(PMe_2Ar^{Dipp_2})]^+$ protonation product competed successfully with $[H(OEt_2)_2]^+$ for unreacted **2a**. We also intended to generate a gold methylidene complex, $[Au(=CH_2)(PMe_2Ar^{Dipp_2})]^+$, by α-hydride abstraction from **2a** with $[Ph_3C]^+$,[6a,20] but once more, complex **3** was the only detectable product of the reaction.[21] We therefore developed the more conventional synthesis of **3** shown in Scheme 1,

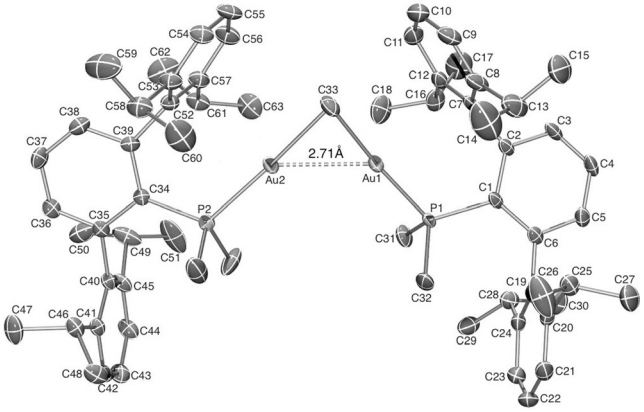
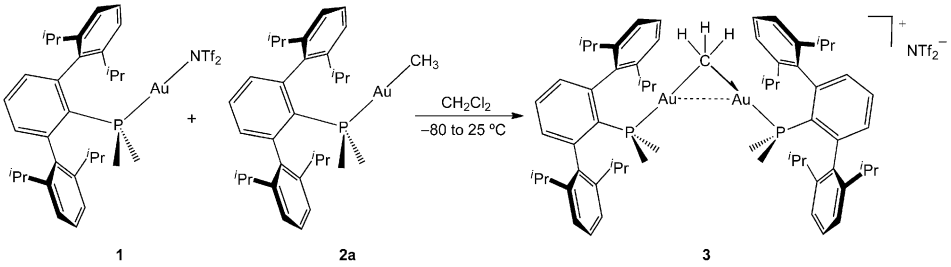


Figure 2. ORTEP view of complex **3**; hydrogen atoms are omitted for clarity, and thermal ellipsoids are set at 50% probability.



Scheme 1. Synthesis of the *gem*-σ,σ-diaurated methyl complex **3**.

which involves the reaction of gold triflimide complex **1** (see the Supporting Information, Figure S2 for an ORTEP view of this compound) and neutral methyl derivative **2a**.[15c,16f,22] Complex **3** was isolated as a white crystalline solid (ca. 90% yield).

Complex **3** possesses fair thermal stability at 25°C. It appears that the isopropyl substituents of the flanking aryl rings of $PMe_2Ar^{Dipp_2}$ are essential for the kinetic stabilization of **3**, as the analogous $PMe_2Ar^{Xyl_2}$ complex ($Ar^{Xyl_2} = C_6H_3$-2,6-$(C_6H_3$-2,6-$Me_2)_2$) could only be safely manipulated in solution below −20°C. At somewhat higher temperatures (−10°C, CD_2Cl_2), it decomposed in a bimolecular process that produced $[Au(PMe_2Ar^{Xyl_2})_2][NTf_2]$, metallic gold, and ethane.[15c,21] Complex **3** decomposed after several days at room temperature by a similar path.

The bridging methyl ligand of complex **3** gives rise to ^1H and ^{13}C NMR resonances at 0.34 (s) and −0.1 ppm (t, $^2J_{CP}$ = 53 Hz), respectively, the measured coupling constant being almost half the value found in neutral **2a** (102 Hz). It also features a one-bond ^{13}C–^1H coupling of 129 Hz, which indicates symmetric Au–CH_3–Au coordination, void of any agostic interactions. A three-center-two-electron (3c-2e) bond is also in accord with single-crystal X-ray analysis and DFT studies (see below).

Figure 2 shows the molecular structure of the $[Au_2(\mu\text{-}CH_3)(PMe_2Ar^{Dipp_2})_2]^+$ cation of complex **3** (see also Table S10 for some relevant metric parameters). The central $\{Au_2(\mu\text{-}CH_3)\}$ unit forms a nearly isosceles triangle, with two very similar Au–CH_3 bonds (2.210(5) and 2.227(4) Å) and a Au–Au separation of 2.7120(8) Å. The latter is shorter than the average value found in other *gem*-digold compounds[10c,14–16] and than the Au–Au distance of 2.878 Å in metallic gold,[18] indicating an important contribution of aurophilicity to the bonding within the $\{Au(CH_3)Au\}^+$ triangular core of **3**.[23] For comparison, this Au–Au distance is similar to the aurophilic contacts in $\{Au_2(\mu\text{-}H)\}^+$ structures (ca. 2.71–2.75 Å).[10] In close analogy to gold complexes of biarylphosphine ligands,[16c,24] each Au atom of complex **3** exhibits a weak Au···C_{arene} secondary interaction with the *ipso* carbon atom of a flanking aryl ring of the terphenylphosphine. However, the distances seem to be too long (3.027(3) and 3.102(4) Å) to be meaningful in terms of bonding.[24]

Transition-metal complexes with methyl bridging ligands, $\{M(\mu\text{-}CH_3)M\}$, have been known for many years,[25] but as briefly mentioned above, this conspicuous structure had previously not been known for gold. Complex **3** constitutes the simplest model reported to date for the isolobal CH_5^+ ion, that is, protonated methane (compare, for instance, **3** with the $[C(AuPPh_3)_5]^+$ cation[26] and other related species).[27] Protonated methane was postulated a long time ago by Olah and co-workers to understand some features of the NMR spectra of solutions of CH_4 in strongly acidic media.[28]

Next, we focused our attention on the reactions of triflimide complex **1** with the neutral vinyl and acetylide complexes **2b** and **2c**, respectively (see Figures S3 and S4 for ORTEP views of these compounds). As shown in Scheme 2, these reactions provided the σ,π-vinyl and σ,π-acetylide complexes **4** and **5**, respectively, which are the first members of these families of compounds that contain unsubstituted ethenyl or ethynyl bridges. The vinyl complex **4** exhibits $^{13}C\{^1H\}$ resonances at 154 (t, $^2J_{CP}$ = 60 Hz) and 142.2 ppm ($^3J_{CP}$ ≈ 0 Hz), which are due to the CH and CH_2 moieties of the bridging ethenyl ligand. For the mononuclear precursor $[Au(CH{=}CH_2)(PMe_2Ar^{Dipp_2})]$ (**2b**), the corresponding signals

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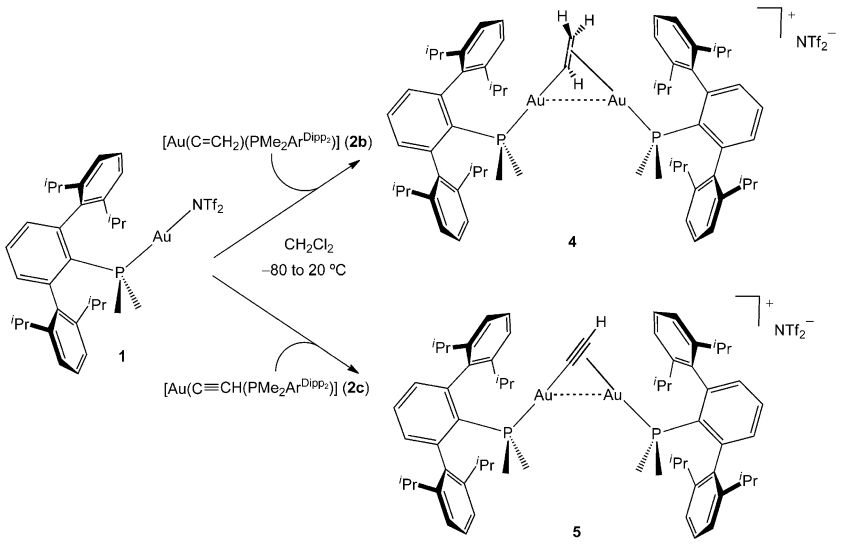

Scheme 2. Synthesis of the dinuclear vinyl and acetylide complexes **4** and **5**.

appeared at $\delta = 168.4$ ($^2J_{CP} = 125$ Hz) and 128.4 ppm ($^3J_{CP} \approx 0$ Hz). Hence, upon coordination to the $[Au(PMe_2Ar^{Dipp_2})]^+$ ion, the resonances of the two olefinic carbon atoms shift in opposite directions by about 14 ppm, while $^2J_{CP}$ is reduced to roughly half its original magnitude. Unfortunately, comparison of these data with those reported for substituted alkenyl species (see below) reveals that they are of little value to discriminate between the possible σ,σ- and σ,π-alkenyl coordination modes.[15] In the σ,π-acetylide complex **5**, the C_α and C_β ^{13}C NMR resonances are found at 132.1 (t, $^2J_{CP} = 72$ Hz) and 97.3 ppm (t, $^3J_{CP} = 16$ Hz), respectively. Complexes **4** and **5** are fluxional in solution and exhibit a single $^{31}P\{^1H\}$ resonance in the temperature interval from −60 to 25 °C (0.24 and −2.3 ppm for **4** and **5**, respectively). Plausible mechanisms for related exchange reactions have been advanced in the literature[15,16] (see Figures S13 and S14).

ORTEP representations of the molecular structures of complexes **4** and **5** are shown in Figure 3 and Figure 4, respectively. Selected bond lengths and angles are given in Tables S12 and S14. In the two compounds, carbon atom C1 is bonded to the two gold atoms in a non-symmetric fashion,

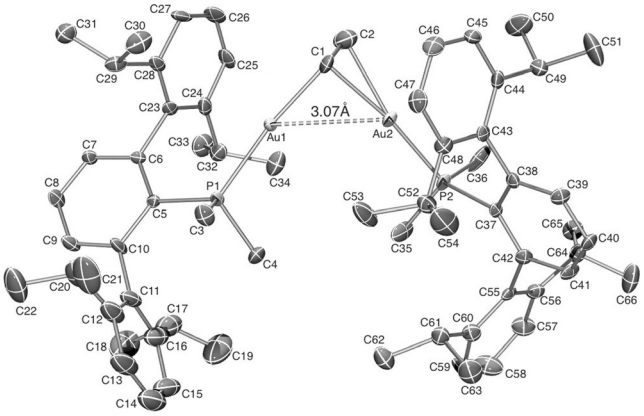

Figure 3. ORTEP view of complex **4**; hydrogen atoms are omitted for clarity, and thermal ellipsoids are set at 50% probability.

with the Au1–C1 bond being shorter than the Au2–C1 bond. Thus, the former are 2.066(9) and 2.003(8) Å long in **4** and **5**, respectively, and the latter have lengths of 2.210(8) and 2.245(8) Å. Gold atom Au2 is also bonded to the terminal ethenyl or ethynyl carbon atom C2, with distances of 2.34(1) and 2.23(1) Å, respectively. It is therefore evident that in contrast with the methyl group of complex **3**, the unsaturated hydrocarbyl ligands of **4** and **5** do not form 3c-2e bonds with the gold atoms, but adopt a σ,π coordination mode, thereby forming a normal covalent bond (to Au1) and a dative covalent bond (to Au2).[29] Whereas alkyne coordination to Au2 in **5** is symmetric (Au2–C distances of ca. 2.24 Å), the alkene–gold interaction in **4** is skewed towards the gold-substituted

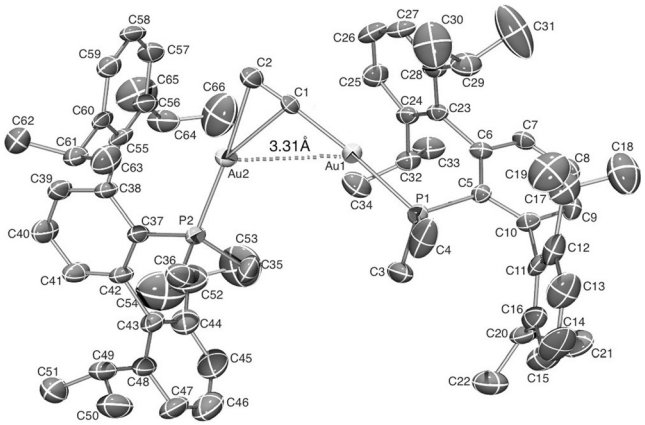

Figure 4. ORTEP view of complex **5**; hydrogen atoms are omitted for clarity, and thermal ellipsoids are set at 50% probability.

atom C1 (ca. 2.21 vs. 2.34 Å), doubtless as a reflection of stronger aurophilic bonding in **4** (ca. 3.07 Å) relative to **5** (3.31 Å). In our view, complexes **3**, **4**, and **5** are thus far the simplest isolable hydrocarbyl derivatives with the $\{Au_2(\mu\text{-}R)\}^+$ core, and nicely illustrate for the first time the changes in the strength of aurophilic bonding that occur when the hybridization of the bridging carbon atom is changed from sp^3 to sp^2 and sp. Thus, the aurophilic interaction decreases monotonically in the series $CH_3 > CH{=}CH_2 > C{\equiv}CH$, as illustrated by an increase in the Au–Au distance of approximately 0.3 Å from one compound to another.

As discussed above, complex **4** features an uncommon σ,π coordination of its bridging vinyl ligand, which contrasts with the σ,σ binding exhibited by the substituted alkenyl ligands in the structurally characterized digold complexes listed in the Cambridge Structural Database (CSD),[30] with the only exceptions being two alkenyl species of the $-C(R){=}CH_2$ type.[15a,d] Some of these structures are shown in Figure 5. It seems that σ,π-alkenyl binding could require an unsubstituted $=CH_2$ terminus, but this hypothesis needs be confirmed

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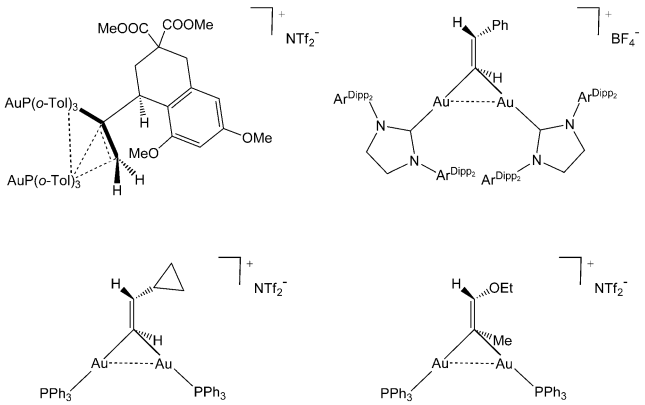

Figure 5. Representative substituted vinyl-bridged complexes previously characterized by single-crystal X-ray diffraction. Moving clockwise from the upper left structure, the compounds were reported in Refs. [15a–c].

by further research. In contrast, all substituted acetylide complexes with a bridging μ-C≡CR unit reported to date have structures of the σ,π-type.[16]

Finally, it is noteworthy that complexes **4** and **5** may be viewed as isolobal analogues to the ethenium ($C_2H_5^+$) and ethynium ($C_2H_3^+$) ions, respectively, that is, protonated ethylene and acetylene. For the two species, there is theoretical consensus on structures in which H^+ interacts with a π-component of the carbon–carbon multiple bond.[31]

DFT calculations (wB97xD/6-31 + (d,g) and SDD) were used to model the *gem*-digold (**3**) and σ,π-activated (**4** and **5**) compounds.[32] PMe_3 replaced the experimentally used terphenylphosphine in the calculations, and was chosen to isolate the interactions within the {Au(μ-R)Au}$^+$ cores of **3**–**5** from secondary interactions with the flanking diisopropylphenyl groups of the real phosphine. Free optimization of the model complexes gave Au–Au distances for the σ,π-activated complexes clearly shorter than for the aurophilic range[23] and longer than those measured experimentally (Figure 6). However, the Au–Au interaction of **3** was retained in the *gem*-diaurated model, and was overestimated by only 0.08 Å. Natural bonding orbital (NBO) analysis[33] showed that the

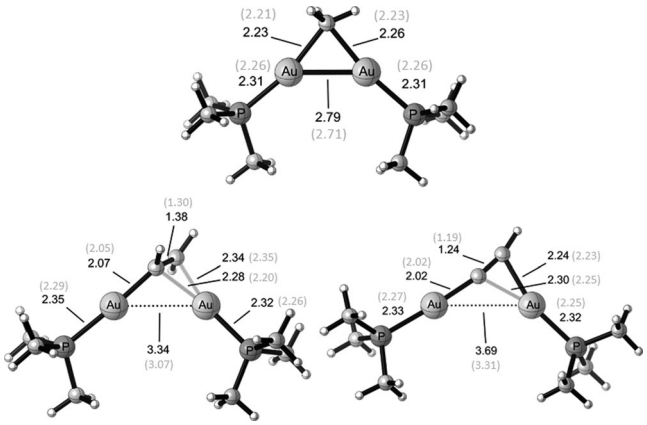

Figure 6. DFT-optimized geometries of the model species **3**-PMe_3, **6**-PMe_3, and **7**-PMe_3.

σ,π-activated complexes **4** and **5** exhibit the expected donor–acceptor interaction between the {Me_3P–Au–R} (R = CH=CH_2 and C≡CH) and {Me_3P–Au}$^+$ fragments, with electron density donation from a π-orbital of the olefin or alkyne fragment to a σ*(Au–P) orbital and back donation from one gold-based orbital to a π* orbital of the C=C or C≡C linkage. The corresponding NBO analysis of the PMe_3-based model favored, however, a 3c-2e bond involving the two gold atoms and the methyl fragment.

In conclusion, we have synthesized and structurally characterized the cationic methyl-bridged complex **3**, which has filled an important gap in the organometallic chemistry of gold(I). This compound and the related vinyl and acetylide complexes **4** and **5**, respectively, form the simplest series of isolable organometallic {Au(μ-R)Au}$^+$ derivatives, and offer the opportunity of experimentally determining the variation in the strength of the aurophilic interaction that accompanies a change in the hybridization of the bridging carbon atom.

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