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Elementary Steps in Gold Catalysis: The Significance of *gem*-Diauration**

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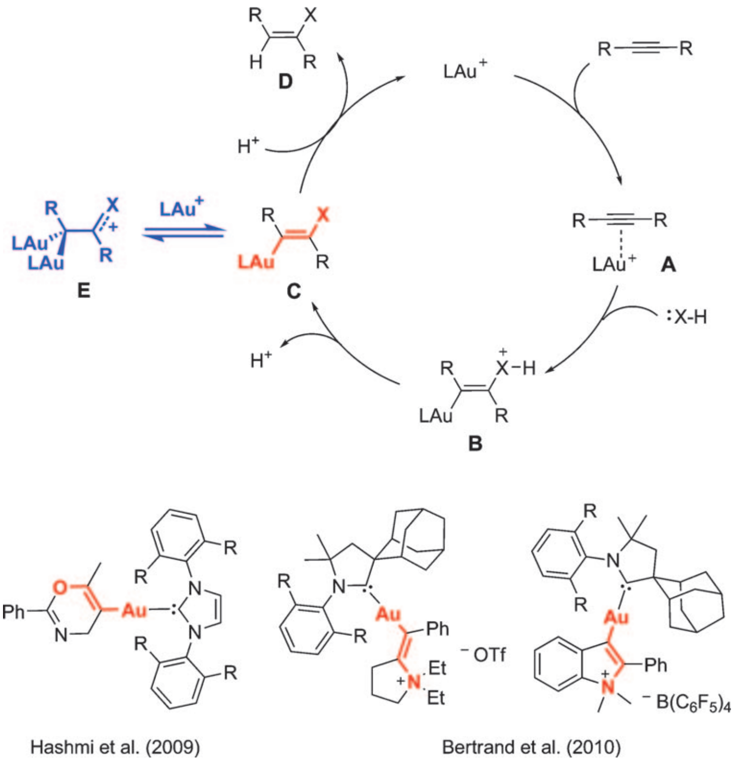
Despite an impressive range of structural manifestations, all the transformations of alkynes induced by carbophilic noble metal catalysts are thought to proceed by a generic mechanism (Scheme 1).[1,2] Coordination of the substrate to a Pt^{II} or Au^{I} center followed by attack of the nucleophile on the resulting π-complex **A** generates an alkenylmetal species **B** by net *trans* addition of the reactants.[3] Loss of H^+ followed by rapid protodeauration releases product **D** and regenerates the catalyst. The efficacy of these latter steps thwarted attempts to isolate complexes of type **C**, which are largely unknown despite their central role within the standard catalytic cycle. Only recently have selected examples of alkenylgold species bearing a vicinal heteroatom substituent X been structurally characterized (see Scheme 1).[4–7]



Scheme 1. Generic catalytic cycle for the gold-catalyzed *trans* addition of a protic nucleophile X–H to an alkyne substrate. Structurally characterized complexes of type **C** comprising a X-C=C-Au substructure are shown;[4,5] R = *i*Pr; X = heteroelement.

By considering the isolobal relationship between a proton and a LAu^+ fragment,[8] however, one may speculate that the catalyst itself could also (reversibly) react with **C** to give complexes of type **E**; this pathway might seriously compete with protodeauration given the affinity of the carbophilic late transition metal to π bonds.[1] A recent report by Gagné and co-workers lent credence to this notion. These authors showed that the ordinary vinylgold compound **2** is capable of intercepting a second gold fragment to form the *gem*-diaurated complex **3** during the catalytic hydroarylation of allene **1** (Scheme 2).[9] Despite a three-center two-electron bonding mode, the “noncanonical” complex **3** was found to be relatively stable, but it reverted to intermediate **2** on treatment with PPh_3, Br^-, or alumina. The constitution of **3** was inferred from mass spectrometry and NMR data, even though the signal of its *gem*-dimetalated carbon atom could not be detected in the ^{13}C NMR spectrum.[9] Related *gem*-digold species were calculated to be competent intermediates in gold-catalyzed cycloisomerization reactions of 1,5-allenynes.[10,11] As part of our investigations on the elementary steps of noble metal catalysis,[2,12,13] we now present the first two fully characterized species of this type, the remarkable stability of which may have implications for gold catalysis in general. Moreover, it is shown that the bias of an alkyne substrate to undergo geminal diauration is strongly correlated with the nature of the incoming nucleophile and the chosen gold source.

Rather than trying to obtain alkenylgold species of type **C** by the route depicted in Scheme 1, we aimed to prepare such intermediates by exchanging gold for boron (Scheme 3). Although such reactions are usually performed in 2-propanol,[14] nonprotic media were found to be equally suitable. Specifically, 1-ethoxypropyne (**5**)[15] was hydroborated with catecholborane and the resulting alkenylboronate **6**[16] treated with the Gagosz complex $[(Ph_3P)AuNTf_2]$ (1 equiv)[17] in THF in the presence of Cs_2CO_3. Much to our surprise, the ^{11}B NMR spectrum of an aliquot of the reaction mixture indicated that only half of the starting boronate ester was consumed. The high-resolution

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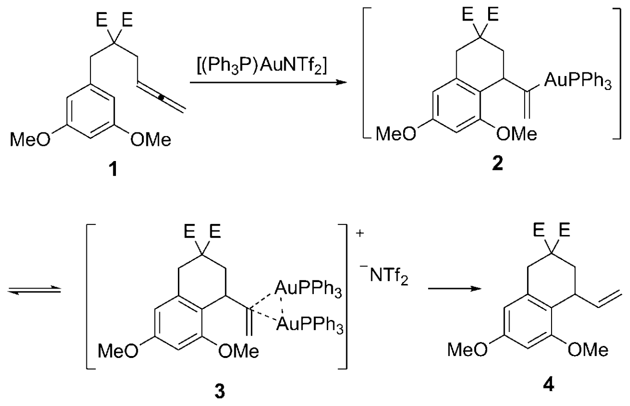
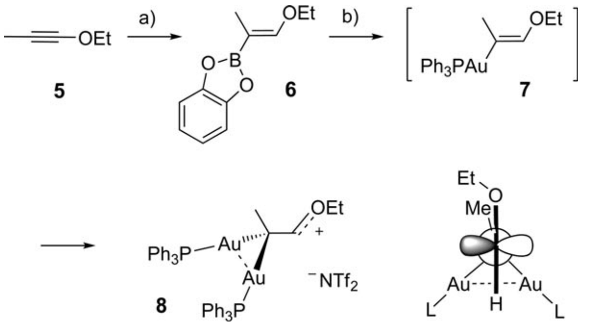


Scheme 2. A *gem*-diaurated compound with a three-center two-electron bond as a competent intermediate in the hydroarylation of allenes, see Ref. [9].



Scheme 3. Preparation of an air-stable *gem*-diaurated complex and Newman projection along its C2⋯C1 axis, which illustrates the oxocarbenium center at C2 as well as the eclipsing orientation of the EtO and Me substituents (the torsion angle O1-C2-C1-C5 is only 1.7°): a) catecholborane, neat, 70 °C, 55 %; b) [(Ph$_3$P)AuNTf$_2$], Cs$_2$CO$_3$, THF, RT, 85 %.

electrospray mass spectrum of the resulting product showed a signal at $m/z = 1003.1801$, consistent with the presence of the diaurated cation **8**. At no time could the expected monometalated species **7** be detected, irrespective of the Au/B ratio chosen. This finding implies that the interception of the second gold fragment is faster than the formation of the monoaurated complex. With this information in hand, the exchange reaction was repeated with two equivalents of [(Ph$_3$P)AuNTf$_2$], which afforded complex **8** in 85 % yield after purification by routine flash chromatography on silica gel.[18] Thus, **8** is even more stable than Gagné's complex **3**, which was reported to rapidly decompose on silica or Florisil.

The diauration manifests in significant spectral changes. Thus, the signal for the metalated atom C1 shifts from $\delta_C = 96.5$ ppm in boronate **6** to $\delta_C = 116.6$ ppm (t, $^2J_{PC} = 60.6$ Hz) in the gold complex **8**; likewise, the signal for the alkoxylated atom C2 experiences a pronounced downfield shift from $\delta_C = 159.9$ ppm in **6** to $\delta_C = 174.8$ ppm in **8**. This significant deshielding may reflect a build-up of an appreciable level of positive charge at C2. Further information was sought to corroborate this interpretation. After many attempted crystallizations, a sample of **8** suitable for X-ray diffraction analysis was obtained.

As evident from Figure 1, the two gold atoms bind almost equidistantly to the same C atom; the C1−Au1 and C1−Au2 bonds at 2.130(14) Å and 2.181(16) Å, respectively, are only slightly longer than an average C−Au single bond.[20] The conceivable alternative mode, in which only one LAu$^+$ fragment is σ bonded, while the second one engages in side-on coordination, does not make any substantial contribution to the ground-state structure of **8**. As a consequence, the former C=C bond in **6** has lost much of its double-bond character, as can be gleaned from the C1−C2 bond length of 1.41(2) Å. Rather, the C2−O1 bond is very short (1.32(2) Å) compared with the reference bond length for -CH$_2$−OR: 1.426 Å,[21] thus confirming the build-up of considerable charge density at this site. In the extreme, one can interpret the structure of **8** as an oxocarbenium cation flanked by a dimetalated center (see the Newman projection in Scheme 3). These data indicate that complex **8**—in contrast to Gagné's compound **3**—does not rely on a three-center two-electron bond, but rather comprises two almost regular carbon–gold σ bonds, one of which is formed at the expense of the π system of the precursor complex. Overall, the formation of **8** is reminiscent of the reactivity pattern of organosilicon compounds, in which metalation is directed toward the α position and positive charge is stabilized at the β carbon atom by hyperconjugation with the C−Si bond.[22] To what degree the Au⋯Au interaction in **8** (Au1−Au2 2.7591(8) Å)[23] contributes to the unusual stability of this complex remains to be elucidated.

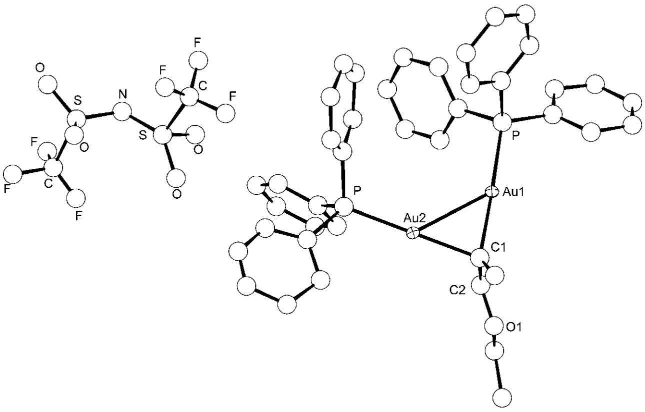
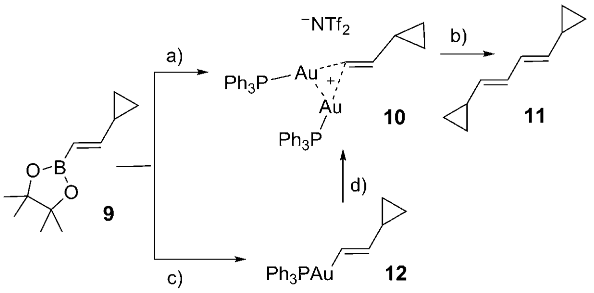


Figure 1. Structure of **8** in the solid state; disordered THF in the crystal is omitted for clarity.[19]

Rendering the double bond of a vinylgold species of type **C** less electron rich and/or reducing the ability of the heteroelement to stabilize adjacent positive charge should have an impact on its propensity to undergo such a diauration. To probe this notion, the readily available compounds **9**, **13**, and **15** were subjected to the gold-for-boron swap (Schemes 4 and 5). Most interestingly, the commercial pinacol boronate **9** with a cyclopropyl substituent rather than a heteroatom closely mimicked the reaction behavior of its alkoxylated cousin **6**. On treatment with [(Ph$_3$P)AuNTf$_2$] in THF at low



Scheme 4. a) [$(Ph_3P)AuNTf_2$], Cs_2CO_3, THF, −78 °C→RT, 51 %; b) CD_2Cl_2, 90 % (NMR), see text; c) [$(Ph_3P)AuBr$], 2-PrOH, Cs_2CO_3, 50 °C, 76 %; d) [$(Ph_3P)AuNTf_2$], CD_2Cl_2, quantitative (NMR).

temperature, **9** converted into the corresponding diaurated species **10**, irrespective of the B/Au ratio. However, **10** was found to be more fragile than its analogue **8**. When kept in CD_2Cl_2 solution, it readily decomposed to diene **11**, with concomitant formation of [$Au(PPh_3)_2$]NTf_2[19] and colloidal gold as the inorganic by-products.

The *gem*-diaurated character of **10** was evident from the high-resolution mass spectrum (ESI$^+$) and the characteristic fingerprints in the NMR data. C2 is even more deshielded ($\delta_C = 192.2$ ppm) in this compound than in **8**.[24] Surprisingly though, the integrity of the cyclopropyl ring indicates that insufficient charge density resides at this position to trigger ring opening/rearrangement, as expected for an emergent "cyclopropylmethyl cation".[25] Therefore, it was of particular interest to compare the structure of **10** in the solid state (Figure 2) with that of **8** described above. Whereas the overall constitution of both complexes is similar and dominated by the conspicuous *gem*-digold unit, the pattern of the bond lengths in the backbone is strikingly different: thus, the C1–C2 bond in **8** (1.41(2) Å) is notably elongated, whereas the C1–C2 bond in **10** (1.366(8) Å) is short and fairly close to that of a regular olefin. In contrast, the C2–O1 bond in **8** is significantly contracted by virtue of the oxocarbenium character of this site, whereas the corresponding C2–C3 bond in complex **10** (1.462(8) Å) is hardly affected and falls into the range of a regular single bond between a cyclopropyl ring and an olefin.[26] Hence, we conclude that **10** is more adequately described by a three-center two-electron bonding motif of the kind previously proposed by the research groups of Gagné and Toste[9,10] rather than as a cation flanked by a *gem*-dimetalated center, as is the case in **8**. The distinctly different character of **8** and **10** shows that the charge density resulting from the second auration step can either be "kept within" the resulting {Au_2C} entity or largely accumulated at the adjacent position if a sufficiently stabilizing heteroelement is present. This surprising modularity in the bonding character suggests that *gem*-diauration might occur in many structural environments of different chemical nature.

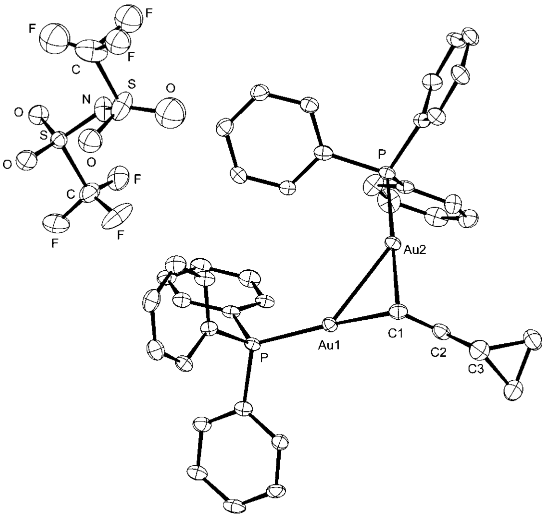
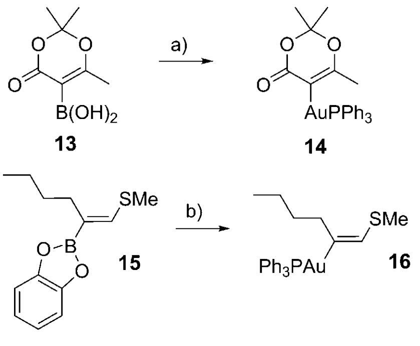


Figure 2. Structure of complex **10** in the solid state.[19]

When treated with [$(Ph_3P)AuBr$] in 2-PrOH, however, boronate **9** transformed into the regular vinylgold species **12** ($E/Z = 71{:}29$, NMR spectroscopy), with no signs of dimetalation discernible by spectroscopic means.[27] This result shows that the counterion of the chosen gold source critically determines the outcome of the reaction. [$(Ph_3P)AuBr$] is not electrophilic enough to be trapped by the primary intermediate, whereas the second auration is exceedingly fast if the identical gold fragment [$Au(PPh_3)$]$^+$ is escorted by the less-coordinating triflimide. Moreover, this experiment shows that 2-propanol (p$K_a = 17.1$) is not capable of protonating the gold center off complex **12** even at 50 °C.[28]



Scheme 5. a) [$(Ph_3P)AuBr$], 2-PrOH, Cs_2CO_3, 50 °C, 86 %; b) [$(Ph_3P)AuCl$], 2-PrOH, Cs_2CO_3, 50 °C, 60 %.

Next, the characteristic β-alkoxyvinylboronate motif of **6** was embedded in the cyclic frame of compound **13**,[29] in which the double bond is conjugated to the ester carbonyl group and is hence less electron rich (Scheme 5). Compound **13** underwent a clean gold-for-boron exchange with [$(Ph_3P)AuBr$], whereas the use of [$(Ph_3P)AuNTf_2$] led to decomposition. As a result of the less nucleophilic character of the double bond, only the corresponding monoaurated complex **14** was obtained in a respectable 86 % yield, and its constitution was unambiguously confirmed by crystal-structure analysis (Figure 3). Likewise, formal replacement of the oxygen atom by sulfur, as in compound **15**,[16b] afforded the corresponding alkenylgold complex **16**. This outcome is thought to reflect the reduced nucleophilicity of a vinyl sulfide compared to a

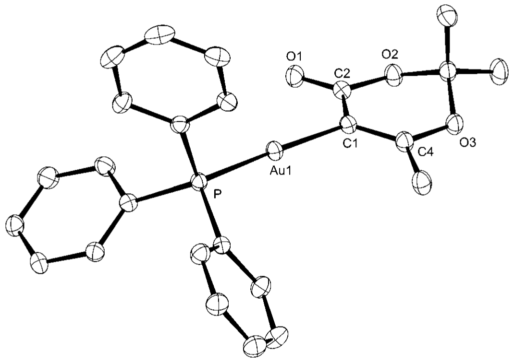


Figure 3. Structure of complex **14** in the solid state.[19] Selected bond lengths [Å]: C1-Au1 2.038(3), C1-C4 1.355(5), C1-C2 1.460(5), C4-O3 1.367(4).

regular enol ether, as well as the lower capacity of sulfur to stabilize an adjacent carbocation.

Overall, this series of experiments has important ramifications for gold catalysis in general. The *gem*-dimetalation of alkyne substrates by highly electrophilic gold complexes is much more favorable than previously recognized;[30] it can materialize either in a three-center two-electron arrangement or in the form of two regular C−Au bonds flanked by a stabilized cationic center. For turnover of a given gold fragment to occur in a catalytic setting, however, protodeauration must outperform this facile side reaction, as the resulting *gem*-digold complexes can be surprisingly resistant to protolytic cleavage. Apparently, protons do not attack the C−Au bonds themselves with ease, at least in cationic species such as **8**, but rather seem to engage the π system of an intermediate of type **C** as the primary site of interaction.[31] Furthermore, our results show that the chosen gold catalyst must be carefully matched with the donor capacity of the incoming nucleophile X−H to avoid such *gem*-dimetalation pathways. The formation of stable *gem*-diaurated intermediates may partly sequester the catalyst and hence have an impact on the necessary loading for a given transformation. Since high turnover numbers are of eminent practical relevance when working with precious noble metal species, this competing process should be taken into consideration in future catalyst optimization studies.

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[19] The anisotropic displacement parameters are drawn at the 50% probability level; hydrogen atoms are omitted for clarity. CCDC-777626 (**8**), 779085 (**10**), 777624 (**14**), and 777625 ($[Au(PPh_3)_2]NTf_2$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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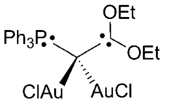

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[31] This conclusion is in line with previous findings, which indicated involvement of the π system in the transition state, see Ref. [28]. Moreover, it might explain why complex **10** with an intact olefinic skeleton is much more susceptible to protonolysis than complex **8** with a largely saturated backbone.