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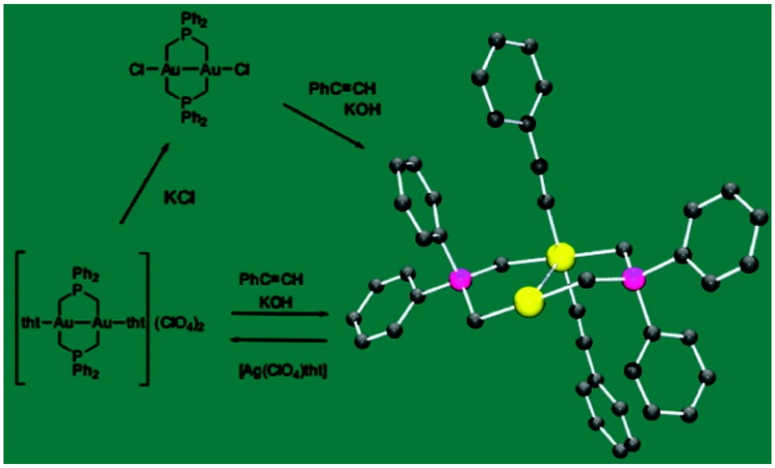

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A Family of Alkynylgold(III) Complexes $[Au^{I}(\mu\text{-}\{CH_2\}_2PPh_2)_2Au^{III}(C{\equiv}CR)_2]$ (R = Ph, ^{t}Bu, Me_3Si): Facile and Reversible Comproportionation of Gold(I)/Gold(III) to Digold(II)

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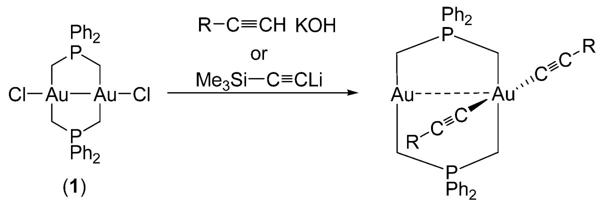
Ever since the first report of an explosive gold carbide complex in 1900,[1] various groups have explored the structures and chemistry of this class of gold compounds.[2] Gold(I) acetylide complexes with phosphine ligands have been extensively studied for their interesting luminescence properties by Yam and Che and co-workers.[3] The Puddephatt group has published elegant work on gold(I) acetylide polymers as well as on the self-assembly of macrocycles and [2]catenanes containing gold(I) acetylide units.[4] Humphrey and co-workers have presented detailed studies on nonlinear optical (NLO) properties of gold(I) acetylide complexes.[5] Gold(I) acetylides have also recently been explored as potential molecular wires.[6] In marked contrast, there are only very few examples of gold(III) acetylide complexes reported in the literature. Complexes of the type *cis*-$[Au(C{\equiv}CCF_3)Me_2(L)]$ (L = PMe_2Ph, PPh_3) were reported by the groups of Puddephatt and Komiya.[7−9] Very recently, the Schmidbaur group reported the synthesis and X-ray structures of the dimethyl gold(III) acetylide complexes $[Au(C{\equiv}CR)Me_2(PPh_3)]$ (R = H, Me).[10] A gold(III) complex containing a side-on-coordinated alkyne has also been proposed as an intermediate in the gold(III)-catalyzed addition of water to terminal alkynes; however, this compound has only been characterized spectroscopically in situ.[11]

Binuclear gold(II) complexes containing the phosphorus bis(ylide) ligand, $(CH_2)_2PPh_2$, have been studied extensively over the last 30 years.[12] In continuing these studies, we wished to examine reactions of the binuclear digold(II)dichloride complex $[Au_2Cl_2(\mu\text{-}\{CH_2\}_2PPh_2)_2]$ with various alkynes in the hope that digold(II) acetylide complexes of the type $[Au_2(C{\equiv}CR)_2(\mu\text{-}\{CH_2\}_2PPh_2)_2]$ could be obtained. The rather unexpected reactivity of this system and the isolation and molecular structure of the first binuclear gold(III) alkyne complex are reported herein. Although it is known that binuclear gold(II) complexes can afford heterovalent gold(I)/gold(III) complexes by disproportionation,[13] the inverse reaction, that is, formation of digold(II) complexes by comproportionation of gold(I)/gold(III) complexes, has so far never been observed.

The binuclear digold(II)dichloride complex $[Au_2Cl_2(\mu\text{-}\{CH_2\}_2PPh_2)_2]$ (**1**) reacts with alkynes $RC{\equiv}CH$ (R = ^{t}Bu, Ph) in the presence of KOH or with $Me_3SiC{\equiv}CLi$ (prepared in situ from $Me_3SiC{\equiv}CH$ and ^{n}BuLi) to give the pale-yellow complexes $[Au^{I}(\mu\text{-}\{CH_2\}_2PPh_2)_2Au^{III}(C{\equiv}CR)_2]$ [R = Ph (**2**), ^{t}Bu (**3**), and $SiMe_3$ (**4**)] in good yields (Scheme 1).

Scheme 1



R = Ph (**2**), ^{t}Bu (**3**), Me_3Si (**4**)

All three complexes show singlet resonances in their $^{31}P\{^1H\}$ NMR spectra, and their ^1H NMR spectra consist of two doublets ($^2J_{PH}$ = ca. 12 Hz) for the two inequivalent CH_2 groups, as well as signals for the PPh_2 groups. In addition, singlet resonances at δ = 1.00 and −0.03 ppm are observed for the ^{t}Bu and Me_3Si groups of complexes **3** and **4**, respectively. The IR spectra of complexes **2**−**4** show bands at ca. 2100 and 571 cm^{-1} due to $\nu(C{\equiv}C)$ and $\nu(Au{-}C_{ylide})$ stretches, respectively. Molecular ion peaks were observed in the FAB mass spectra for complexes **2** and **3**, while complex **4** displayed peaks corresponding to the loss of one and two Me_3Si groups. The heterovalent gold(I)/gold(III) structure was confirmed by an X-ray diffraction study of complex **2**.

The molecular structure of **2** (Figure 1) consists of two $(CH_2)_2PPh_2$ units bridging a linearly coordinated gold(I) and a square-planar-coordinated gold(III) atom, forming an eight-membered organometallic ring. In addition, two phenylacetylide ligands coordinate to the gold(III) center in a trans arrangement. The Au···Au distance in **2** [2.9687(2) Å] is considerably longer than that of the starting digold(II)dichloride complex **1** [2.600(1) Å],[14] confirming the absence of a formal gold−gold bond. It is however, similar to the gold−gold separation in the gold(I) bis(ylide) complex $[Au_2(\mu\text{-}\{CH_2\}_2PPh_2)_2]$ [2.977(1) Å],[15] indicative of aurophilic attractions. The $Au^{I}{-}C_{ylide}$ distances [ca. 2.1 Å] are also similar to those in $[Au_2(\mu\text{-}\{CH_2\}_2PPh_2)_2]$ [2.091(7) Å]. The $Au^{III}{-}C_{alkyne}$ as well as the C≡C distances in **2** [2.002(3), 2.003(3) Å and 1.208(4), 1.206(4) Å, respectively] are slightly longer than those observed in a typical gold(I) alkynyl complexes, such as

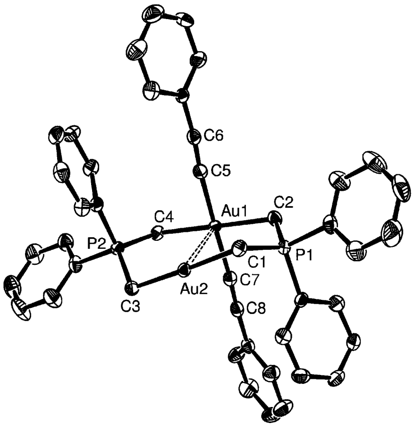


Figure 1. Molecular structure of **2**. Thermal ellipsoids show 50% probability levels, and hydrogen atoms have been omitted for clarity. Selected bond distances (Å): Au(1)···Au(2) 2.9687(2), Au(1)−C(4) 2.119(3), Au(1)−C(2) 2.123(3), Au(2)−C(3) 2.089(3), Au(2)−C(1) 2.080(3), Au(1)−C(5) 2.002(3), Au(1)−C(7) 2.003(3), C(5)−C(6) 1.208(4), C(7)−C(8) 1.206(4). Selected bond angles (deg): C(2)−Au(1)−C(4) 178.44(11), C(1)−Au(2)−C(3) 175.75(11), C(5)−Au(1)−C(7) 177.49(11).

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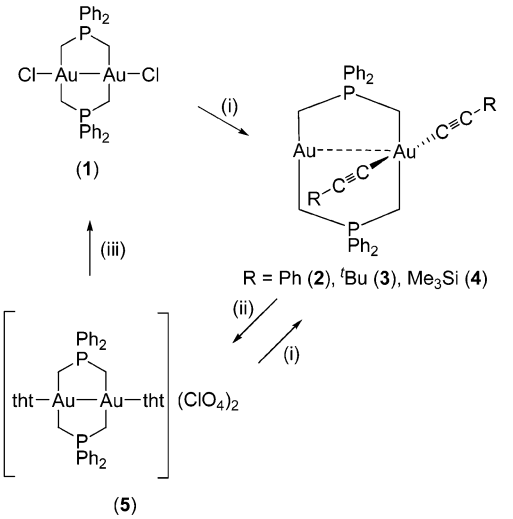
Scheme 2 [a]



[a] (i) RC≡CH (R = Ph, ^{t}Bu)/KOH or LiC≡CSiMe$_3$; (ii) [Ag(ClO$_4$)tht]; (iii) KCl.

[Au(C≡CPh)PPh$_3$] [Au−C = 1.97(2) Å; C≡C = 1.18(2) Å].[16] We propose that complexes **3** and **4** are isostructural to **2**, based on their very similar spectral data; in particular, the presence of two inequivalent CH$_2$ resonances in their ^{1}H NMR spectra is inconsistent with the symmetrical digold(II) structure [Au$_2$(C≡CR)$_2$(μ-{CH$_2$}$_2$-PPh$_2$)$_2$]. Complexes **2**−**4** represent the first fully characterized examples of gold complexes containing two acetylide ligands bound to gold(III). Usually, oxidative addition or ligand metathesis reactions in these types of complexes form symmetrical digold(II) or digold(III) species. Only in two cases has the formation of a mixed-valence dimer been observed previously. Treatment of either the digold(II) dimer [Au$_2$X$_2$(μ-{CH$_2$}$_2$PMe$_2$)$_2$] (X = Cl, Br) or the digold(III) complex [Au$_2$(X$_2$)$_2$(μ-{CH$_2$}$_2$PMe$_2$)$_2$] with MeLi affords the mixed-valence complex [Au(μ-{CH$_2$}$_2$PMe$_2$)$_2$Au(Me)$_2$] in high yields.[17]

The phenyl analogue [Au$^{\mathrm{I}}$(μ-{CH$_2$}$_2$PPh$_2$)$_2$Au$^{\mathrm{III}}$(Me)$_2$] has been isolated as one of the products of the reaction of MeLi with the A-frame gold(III) complex [Au$_2$Br$_2$(μ-CH$_2$)(μ-{CH$_2$}$_2$PPh$_2$)$_2$].[18]

Complex **2** reacts with 2 equiv of [Ag(ClO$_4$)tht] (tht = tetrahydrothiophene) to give the cationic digold(II) complex [Au$_2$(tht)$_2$(μ-{CH$_2$}$_2$PPh$_2$)$_2$](ClO$_4$)$_2$ (**5**)[19] (Scheme 2). Surprisingly, this reaction can be reversed, that is, treatment of **5** with PhC≡CH and KOH reforms the original mixed-valence complex **2**. This facile and reversible comproportionation between gold(I)/gold(III) and digold(II) ylide complexes, to the best of our knowledge, is unprecedented. Complex **5** reacts with KCl to give the starting digold(II)dichloride dimer **1**,[20] thus completing a cycle from digold(II) to gold(I)/gold(III) and back to the original digold(II) complex.

At present, we have limited knowledge about the mechanism of these reactions. It is likely that initially a symmetrical digold(II)-diacetylide compound is formed, which then undergoes an isomerization process to give the mixed-valence complex. Such isomerization reactions have precedence in other binuclear gold systems. Gold(I) complexes containing the cyclometalated phosphine ligand 6-MeC$_6$H$_3$PPh$_2$ react with halogens to give digold(II)dihalide complexes, which rapidly isomerize to gold(I)/gold(III) complexes.[21] The reason for this rapid isomerization has been determined to be due to steric crowding, that is, the *ortho*-Me substituent being “in the way” of the axial halide ligands.[22] In our case, however, the steric argument is clearly not applicable, so electronic effects must be invoked, similarly to what is observed in the mixed-valence methyl analogues [Au(μ-{CH$_2$}$_2$PR$_2$)$_2$Au(Me)$_2$].[17,18] Perhaps it is the fact that the gold(III) center is only coordinated to carbon bonds that favors the gold(I)/gold(III) isomer over the symmetric digold(II) species. The comproportionation from gold(I)/gold(III) to digold(II) in the presence of [Ag(ClO$_4$)tht] probably involves coordination of some silver species to the alkyne triple bond, followed by elimination of the insoluble silver acetylide and subsequent rearrangement and formation of the gold−gold bond.

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Supporting Information Available: Crystallographic data for **2** (CIF), and experimental details (PDF). This material is available free of change via the Internet at http://pubs.acs.org.

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