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Gold Hydride Complexes

Reactions of a Stable Monomeric Gold(I) Hydride Complex**

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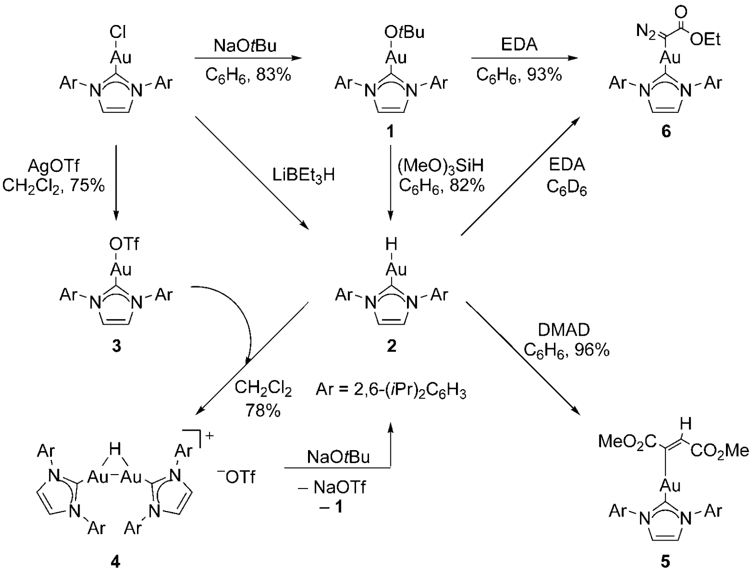
Gold hydride complexes have been postulated as intermediates in a number of homogeneous gold-catalyzed reactions,[1] but relatively little is known about these compounds.[2] The simplest gold hydride, AuH, has been observed in the gas phase[3,4] and trapped in an inert matrix,[5] but has been extensively studied through theoretical calculations.[4b] Complexes with hydride bridges between gold and other metals are well known,[6] but gold-only hydride-bridged complexes have been observed solely in the gas phase.[7]

The N-heterocyclic carbene (NHC) ligand IPr (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) stabilizes a copper(I) hydride of low nuclearity, dimeric [{(IPr)CuH}$_2$], synthesized from [(IPr)CuCl] in two steps.[8] Since NHC ligands have been shown to effectively support many unusual gold species,[9] we believed the same methodology could yield an analogous gold complex. Herein, we present the structure of a stable gold(I) hydride complex and some of its reactions.



Scheme 1. Preparation and reactions of **2**. OTf = CF$_3$SO$_3$, DMAD = dimethyl acetylenedicarboxylate, EDA = ethyl diazoacetate.

The reaction of the known compound [(IPr)AuCl][10] with sodium *tert*-butoxide generated [(IPr)AuO*t*Bu] (**1**), the unsaturated analogue of [(SIPr)AuO*t*Bu] (SIPr = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene).[9b] Treatment of **1** in benzene or dichloromethane with trimethoxysilane yielded [(IPr)AuH] (**2**) after 1.5 h at room temperature (Scheme 1). A new singlet resonance in the ^{1}H NMR spectrum, appearing at $\delta = 5.11$ ppm (C$_6$D$_6$) or $\delta = 3.38$ ppm (CD$_2$Cl$_2$), is assigned as the hydride resonance. This assignment was confirmed through the preparation of the corresponding deuteride complex by reaction of [(IPr)AuCl] with LiDBEt$_3$ [Eq. (1)].

$$[(\mathrm{IPr})\mathrm{AuCl}] \xrightarrow[\mathrm{CH_2Cl_2,\ RT}]{\mathrm{LiDBEt_3}} [(\mathrm{IPr})\mathrm{AuD}]\ (\mathbf{2_D}) + [(\mathrm{IPr})\mathrm{AuEt}] \qquad (1)$$

The ^{1}H NMR spectrum of the reaction product mixture shows ligand-derived resonances identical to those of **2** for the major (ca. 90%) component, assigned as **2$_\mathbf{D}$**, but no hydride resonance. The ^{2}H NMR spectrum of this product in CH$_2$Cl$_2$ gives rise to a singlet resonance at 3.34 ppm. A minor byproduct (ca. 10%) of this reaction is assigned as [(IPr)AuEt]. The IR spectrum of **2** displays a sharp, intense band at 1976 cm^{-1}, a plausible value in light of the 2305.01 cm^{-1} band measured for AuH in the gas phase[11] and the strong σ-donor characteristics of NHC ligands.[12] In the IR spectrum of **2$_\mathbf{D}$**, no band is observed at 1976 cm^{-1}, and the expected Au–D stretch at 1407 cm^{-1} appears to be obscured by bands resulting from ligand-derived stretching modes.

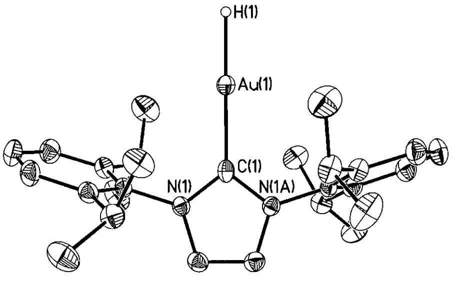


Figure 1. Solid-state structure of **2**·(C$_5$H$_{12}$); thermal ellipsoids are set at the 50% probability level. For clarity, hydrogen atoms (except for that bound to the gold atom) and solvent molecule are omitted. Selected bond lengths [Å] and angles [°]: Au(1)–C(1) 2.045(3), C(1)–N(1) 1.362(3); N(1)-C(1)-Au(1) 127.98(14), N(1)-C(1)-(N1A) 104.0(3). N(1A) is a crystallographic symmetry equivalent of N(1), generated by the operator $-x+2, y, -z+1/2$.

The X-ray crystal structure[13] confirms that **2** is monomeric in the solid state (Figure 1), with the shortest gold–gold separations in the crystal measured at 8.9174(7) Å. When

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exposed to air and moisture, **2** decomposed slowly in solution at room temperature ($t_{1/2} = 6$ h). In the solid state, **2** was stable for weeks under ambient conditions. In contrast, $[\{(\mathrm{IPr})\mathrm{CuH}\}_2]$ decomposes within seconds after exposure to air in the solid state.[8]

We first explored the hydridic character of **2** toward a strong Lewis acid. The trityl salt $[\mathrm{Ph_3C}]^+[\mathrm{BF_4}]^-$, a known hydride acceptor, reacted readily with **2** in $\mathrm{CD_2Cl_2}$. The ^{1}H NMR spectrum of the reaction mixture indicates the formation of a new species (**4**) associated with a hydride resonance at $\delta = 0.42$ ppm. Integration of this resonance relative to ligand resonances suggests a ratio of two IPr ligands per hydride ligand. This result suggested a cationic hydride-bridged species related to known heterometallic examples,[6] which led us to believe that an alternative method for preparing **4** could be found through the reaction of complex **2** with a gold(I) cation. Indeed, treatment of [(IPr)AuCl] with AgOTf in $\mathrm{CH_2Cl_2}$ afforded [(IPr)AuOTf] (**3**), which reacted with **2** in benzene to form a white precipitate. The ^{1}H NMR spectrum of the precipitate is identical to that of the gold complex formed by reaction of $[\mathrm{Ph_3C}]^+$ with **2**, and the resonance at $\delta = 0.42$ ppm is assigned to the bridging hydride ligand.

Analysis of the complex by X-ray crystallography (Figure 2)[13] revealed that **4**, the isolobal analogue of $\mathrm{H_3}^+$, has a triangular structure[7] with a notably short intramolecular $\mathrm{Au^I}$–$\mathrm{Au^I}$ separation (2.7099(4) Å) compared to typical Au–Au distances in aurophilic interactions or in metallic gold.[14] Complex **4** is stable to air and water in the solid state. Preliminary attempts to deprotonate **4** and obtain a dimeric gold(0) complex were unsuccessful. Complex **4** underwent nucleophilic attack by sodium *tert*-butoxide to form **1** and **2**, and the reaction of **4** with *n*-butyllithium resulted in the precipitation of colloidal gold.

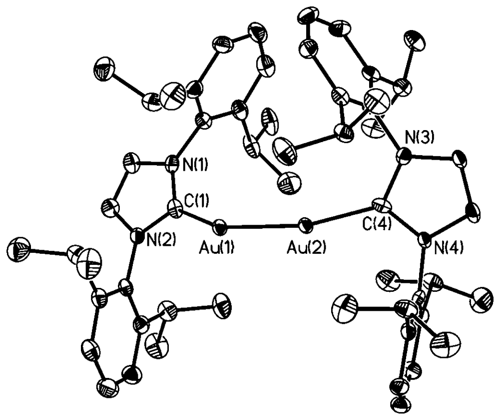

Figure 2. Solid-state structure of **4**·($\mathrm{C_4H_{10}O}$); thermal ellipsoids are set at the 50% probability level. Hydrogen atoms, solvent, and $\mathrm{OTf^-}$ counterion are omitted for clarity, and only one crystallographically independent molecule is shown. Selected bond lengths [Å] and angles[°]: Au(1)–C(1) 2.018(4), Au(1)–Au(2) 2.7099(4), Au(2)–C(4) 2.004(4); C(1)-Au(1)-Au(2) 158.25(12), C(4)-Au(2)-Au(1) 154.22(11).

Alkyne insertion into transition metal hydride complexes is well established.[15] Although **2** displayed no reactivity toward alkynes such as 3-hexyne and diphenylacetylene at room temperature, it reacted cleanly with 1.05 equivalents dimethyl acetylenedicarboxylate (DMAD) in benzene to form the vinylgold complex **5**. The crystal structure of **5** (Figure 3)[13] reveals a *trans* orientation of the gold and hydrogen atoms about the double bond. The *trans* insertion of alkynes into various transition metal hydride complexes has been proposed to occur through a variety of mechanisms.[16] For example, the analogous formation of a *trans*-vinylic product from a platinum(II) hydride complex has been ascribed to the participation of a radical intermediate.[17] Such a mechanism, in this case, would suggest the intriguing possibility of $[(\mathrm{IPr})\mathrm{Au^0}]$ as an intermediate. However, we cannot rule out other mechanisms, such as *syn* insertion followed by isomerization of the resulting vinyl complex.[18,19]

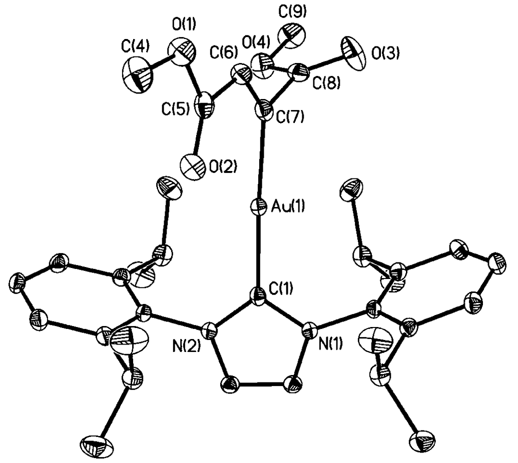

Figure 3. Solid-state structure of **5**; thermal ellipsoids are set at the 50% probability level. For clarity, hydrogen atoms are omitted. Selected bond lengths [Å] and angles [°]: Au(1)–C(1) 2.0178(18), Au(1)–C(7) 2.037(2), C(6)–C(7) 1.340(3), C(5)–C(6) 1.482(3), C(7)–C(8) 1.494(3); C(1)-Au(1)-C(7) 173.59(7), C(6)-C(7)-Au(1) 131.02(15), C(8)-C(7)-Au(1) 113.55(13), C(7)-C(6)-C(5) 123.23(18), C(6)-C(7)-C(8) 115.42(17).

In light of the demonstrated effectiveness of some $(\mathrm{NHC})\mathrm{Au^I}$ complexes for carbene transfer catalysis,[20] we explored the reactivity of **2** with a carbene precursor, expecting possibly to observe a net carbene insertion into the gold–hydrogen bond. Complex **2** reacted slowly with ethyl diazoacetate (EDA) in $\mathrm{C_6D_6}$ to form a yellow product. The ^{1}H NMR spectrum of the crude reaction mixture shows no resonances suggesting the formation of a carboxy alkyl gold complex, but a small singlet observed at $\delta = 4.47$ ppm is consistent with the presence of dihydrogen. The yellow product **6** accounts for 77 % of the total IPr ligand resonances by integration of the ^{1}H NMR spectrum, and the IR spectrum of **6** shows a sharp, intense band at 2040 cm^{-1} characteristic of a diazo moiety. These data are consistent with the deprotonation of EDA to form an α-metalated diazo complex and dihydrogen.

Metalation of diazo compounds by metal amides,[21] by *n*BuLi,[22] by silver(I) oxide,[23] and by mercuric oxide[24] are well known. Although there have been no examples of related gold diazo compounds, to our knowledge, gold alkoxides have been shown to deprotonate carbonyl compounds such as methyl cyanoacetate to form the resulting C-bound gold(I) enolates.[25] In contrast to these highly basic species, however, complex **2** is fairly stable to acids. For example, no reaction occurred between **2** and water or *tert*-butyl alcohol in C_6D_6 under inert atmosphere. The attempted reaction of **2** with the more acidic hexafluoro-*tert*-butyl alcohol in C_6D_6 led to some broadening of the hydride resonance, but no hydrogen evolution was observed. Complex **2** reacted with benzoic acid, but the reaction required several hours and formed a number of unidentified decomposition products. Despite these results, the observed deprotonation and auration of EDA might be more favorable owing to the formation of a stabilized carbanion, rather than a hard oxyanion, bound to gold(I).

To determine whether the auration of EDA is hydride-specific or occurs more generally with Brønsted-basic gold(I) complexes, we examined the reaction of the *tert*-butoxide complex **1** with EDA in benzene. Within 7 h at ambient temperature this reaction formed complex **6** and *tert*-butyl alcohol quantitatively as judged by ^{1}H NMR spectroscopy. A single-crystal X-ray diffraction study of **6**, prepared in this manner, confirmed its structure as an α-metalated diazo compound (Figure 4).[13] The distance between the Au center and the diazoalkyl carbon atom (2.0328(19) Å) is similar to the $\text{Au}-\text{C}_{\text{NHC}}$ distance of 2.0069(16) Å; the diazoalkyl group displays a short N–N bond (1.134(3) Å) and a rather long N–C bond (1.311(3) Å).

In conclusion, a monomeric terminal hydride complex of gold(I) has been synthesized and structurally characterized. This complex undergoes *trans* addition to an electrophilic alkyne and deprotonates a diazo compound to form the α-aurated derivative. A strong Lewis acid can abstract the hydride, generating a gold(I) cation that further reacts to form a binuclear hydride-bridged cationic complex. These results may lead to new opportunities in gold(I) catalysis.

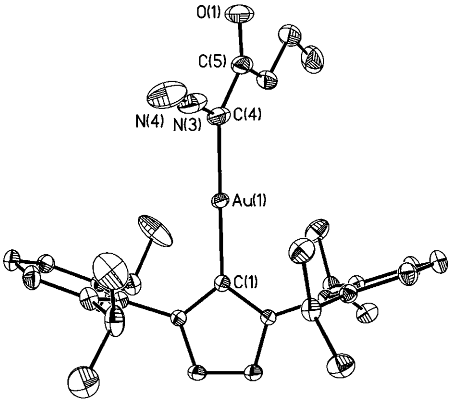

Figure 4. Solid-state structure of **6**; thermal ellipsoids are set at the 50% probability level. For clarity, hydrogen atoms are omitted. Selected bond lengths [Å] and angles [°]: Au(1)–C(1) 2.0069(16), Au(1)–C(4) 2.0328(19), N(3)–N(4) 1.134(3), N(3)–C(4) 1.311(3), C(4)–C(5) 1.449(3); C(1)-Au(1)-C(4) 174.43(7), N(4)-N(3)-C(4) 176.2(2), N(3)-C(4)-C(5) 111.37(18), N(3)-C(4)-Au(1) 116.10(15), C(5)-C(4)-Au(1) 132.49(15).

Experimental Section

See the supporting information for synthetic details.

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