VIP Gold(III) Hydrides

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A Thermally Stable Gold(III) Hydride: Synthesis, Reactivity, and Reductive Condensation as a Route to Gold(II) Complexes**

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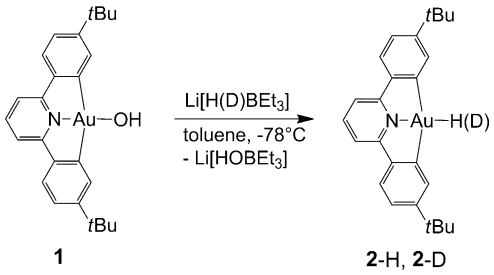
Transition-metal hydride complexes are well-established as key intermediates in numerous homogeneously and heterogeneously catalyzed reactions.[1] Hydride complexes of platinum(II), for example, have been known for over 50 years.[2] Analogous complexes of the isoelectronic gold(III), on the other hand, appear to be unknown.[3] This is all the more surprising as gold complexes have attracted much attention as catalysts and catalyst precursors in recent years.[4] For example, heterogeneous gold catalysts are used for selective hydrogenations;[5] for zirconia-supported gold hydrogenation catalysts, surface Au^{3+} ions have been proposed as active sites.[6] Both gold(I) and gold(III) hydrides have been postulated as intermediates in numerous homogeneously catalyzed hydrogenations,[7,8] hydrosilylations,[9] dehydrogenative alcohol silylations,[10] hydroborations,[11] and other organic transformations.[12] Corma and co-workers used immobilized gold(III) chelate complexes as hydrogenation catalysts and explored the possible involvement of Au^{III} hydride intermediates in detail by kinetic and computational methods.[13] On the other hand, the highly positive standard redox potentials for gold ($Au^{3+}/Au^{+} = 1.36$ V; $Au^{3+}/Au^{0} = 1.52$ V)[14] might suggest facile reduction of Au^{III} in the presence of hydride. Binary hydrides, including AuH, $(H_2)AuH$, $(H_2)AuH_3$, and $[AuH_4]^-$, have been detected in frozen gas matrices below 5 K.[15] We report herein the synthesis and reactions of a thermally stable gold(III) hydride, [(C^N^C)*AuH], wherein (C^N^C)* is a doubly cyclometalated 2,6-bis(4′-*tert*-butylphenyl)pyridine ligand.

The reaction of [(C^N^C)*AuOH][16] (**1**) with $LiHBEt_3$ in toluene at −78 °C followed by stirring at room temperature for 15 min rapidly yielded [(C^N^C)*AuH] (**2**-H), which was isolated as a yellow crystalline complex [Eq. (1)]. The ^{1}H NMR spectrum showed a broad singlet resonance at $\delta = -6.51$ in CD_2Cl_2 and at $\delta = -5.73$ in C_6D_6, while the protons attached to the carbon atom in the β position with respect to the gold center give rise to a pseudo triplet multiplicity, suggesting a ^4J coupling (1 Hz) to the hydride ligand. This assignment was confirmed by the preparation of the corresponding gold deuteride complex **2**-D by treating **1** with $LiDBEt_3$. The ^{1}H NMR spectrum of **2**-D shows the resonances for the C^N^C* ligand that are identical to those of **2**-H, without the hydride resonance, and the phenyl β proton shows the expected doublet multiplicity (see the Supporting Information). The ^{2}H NMR spectrum of **2**-D in CH_2Cl_2 shows a singlet at $\delta = -6.58$.



1 **2**-H, **2**-D (1)

The IR spectrum of **2**-H shows a strong, sharp band at 2188 cm^{-1}, which is higher than the Au–H stretch in [(IPr)AuH] (1976 cm^{-1})[3a] but comparable to that found for AuH and $(H_2)AuH$ in a frozen argon matrix (2226.6 and 2173.6 cm^{-1}, respectively).[15] The Au–D stretching frequency of **2**-D (expected at ca. 1550 cm^{-1}) was not found and is likely to be obscured by other ligand bands in this region.

As a solid, **2**-H is stable to air and moisture at room temperature. Although the hydride is *cis* to two phenyl ligands, and although we do observe Au–C cleavage reactions of this pincer system under acidic conditions,[17] the rigidity of the C^N^C pincer implies that reductive elimination is not favorable. On the other hand, toluene and CH_2Cl_2 solutions of **2**-H darkened rapidly when exposed to light, even though little change was noticeable in the ^{1}H NMR spectrum. However, prolonged exposure to sunlight of CH_2Cl_2 solutions of **2**-H gave [(C^N^C)*AuCl] ($t_{1/2} \approx 4$ h), while heating **2**-H in C_6D_6 for 12 h generated a mixture of products consisting of about 30 % free ligand, with the loss of the hydride resonance. The structure of **2**-H was confirmed by X-ray diffraction (Figure 1).[18]

Complex **2**-H proved unreactive towards ethylene, 3-hexyne, phenylacetylene, and even dimethyl acetylenedicarboxylate. There was also no reaction with CO_2 or with benzaldehyde in the dark or under photolysis. Also no reaction was observed between **2**-H and weak acids such as acetic acid; however, **2**-H reacts instantaneously with the stronger trifluoroacetic acid ($HOAc^F$) to give a mixture of products, with the expected complex [(C^N^C)*AuOAc^F] not being observed among the reaction products. The results suggest that the hydridic character of **2**-H is less pronounced than in the case of Au^I hydrides stabilized by strong NHC donor ligands.[3a] The hydride does however react with 1,1-

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Supporting information for this article (synthetic, spectroscopic, and crystallographic details) is available on the WWW under http://dx.doi.org/10.1002/anie.201206468.

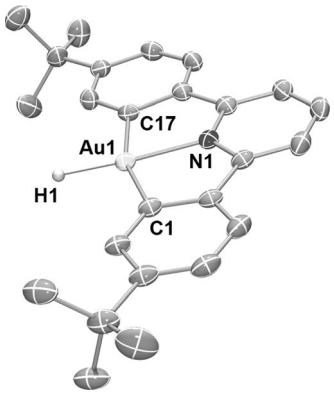
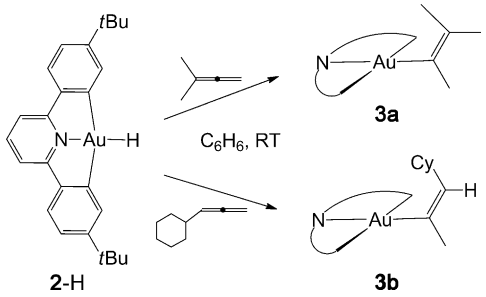


Figure 1. Molecular structure of [(C^N^C)*AuH] (**2**-H) in the solid state. Ellipsoids are set at 50% probability. Hydrogen atoms (except for that bound to the gold atom) are omitted. The hydrogen atom attached to the gold center was located on the density map. Selected bond distances [Å] and angles [°]: Au–N1 2.035(3), Au–C17 2.073(4), Au–C1 2.074(4); C17-Au-C1 161.63(16).

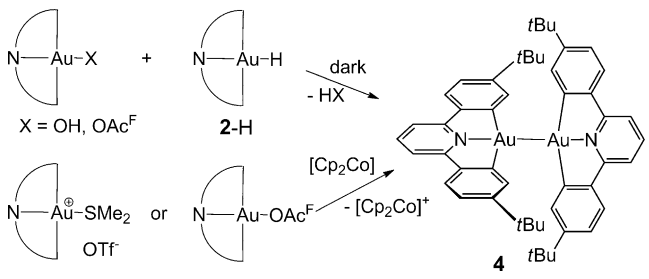
dimethylallene and cyclohexylallene regiospecifically to give single insertion products, the vinyl complexes **3a** and **3b**, respectively (Scheme 1).



Scheme 1. Allene insertion reactions of [(C^N^C)*AuH].

More surprisingly perhaps, **2**-H also reacts slowly with the hydroxide **1** to give the gold(II) dimer **4**. Compound **4** is formed at room temperature in benzene or dichloromethane solutions in the dark over a period of several days and was isolated as yellow crystals. The reaction of [(C^N^C)*AuOAc^F] with **2**-H is faster, occurring within a few minutes, and gives **4** in 75% yield, together with some unidentified side products (Scheme 2).

The reaction of a metal hydride and a metal hydroxide (or carboxylate) to eliminate water (or acid) with concomitant



Scheme 2. Formation of the Au^{II}–Au^{II} dimer **4** by various routes.

reduction of the two metal centers thus amounts to reductive condensation. Dimeric metal–metal-bonded gold(II) complexes are typically made by oxidation of Au^I precursors[19–21] or comproportionation;[22] we are not aware of a precedent for the reductive route observed. We note however that the inverse of reductive condensation, the oxidative addition of H_2O and NH_3 across a Pd^I–Pd^I bond, has recently been reported.[23]

To confirm its identity, product **4** was also independently synthesized by the one-electron reduction of [(C^N^C)*Au(SMe$_2$)]$^+$ or of [(C^N^C)*AuOAc^F] with cobaltocene. In fact, the formation of **4** is observed as a side reaction in several transformations of **2**-H and is possibly indicative of competing one-electron reaction pathways. The crystal structure of **4** confirmed the complex as a dinuclear Au^{II} complex (Figure 2). The gold–gold bond length of 2.4941(4) Å is among the shortest separations for an unsupported Au^{II}–Au^{II} bond.[24]

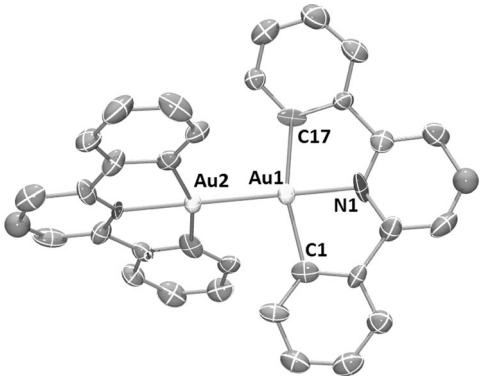


Figure 2. Molecular structure of [(C^N^C)*$_2$Au$_2$] (**4**) in the solid state. Hydrogen atoms and *tert*-butyl groups have been omitted for clarity. Ellipsoids are set at 50% probability. Selected bond distances [Å] and angles [°]: Au1–Au2 2.4941(4); N1-Au1-Au2 179.4(2), C1-Au1-C17 162.3(5).

Complex **4** emits green photoluminescence in the solid state ($\lambda_{emiss} = 444, 457, 479$ nm). The compound is stable to air and moisture in the solid state and in dichloromethane solution in air at −25 °C for long periods of time. No reaction was observed between a mixture of **4** and elemental sulfur in toluene (60 °C, 12 h). The lack of reactivity is most probably a reflection of the steric shielding provided by the four *tert*-butyl substituents that envelope the Au–Au bond. On the other hand, the Au–Au bond is oxidatively cleaved by iodine to give [(C^N^C)*AuI]. Photolytic bond homolysis is also possible, and **4** decomposes slowly in CH_2Cl_2 at room temperature under ambient light.

In conclusion, gold(III) hydrides, which have long been postulated as catalytic intermediates, are indeed isolable and thermally stable, given a suitable ligand environment. Reactivity studies show that the Au–H bond is highly covalent and undergoes regioselective insertion reactions with allenes to give gold(III) vinyl compounds, while there was no reaction with simple noncyclic alkynes. A contributory factor to the stability of the Au–H bond in the present case is probably the

rigid (C^N^C)* pincer framework, which only permits associative reactions that are not favorable for square-planar d^8 Au^{III}. The hydride does however react with $[(C^N^C)^*Au^{III}X]$ ($X = OH$, OAc^F) to give a binuclear Au^{II} complex by HX elimination in a reductive condensation process.

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