

Gold Hydride Complexes: Synthesis, Structure, and Reactivity

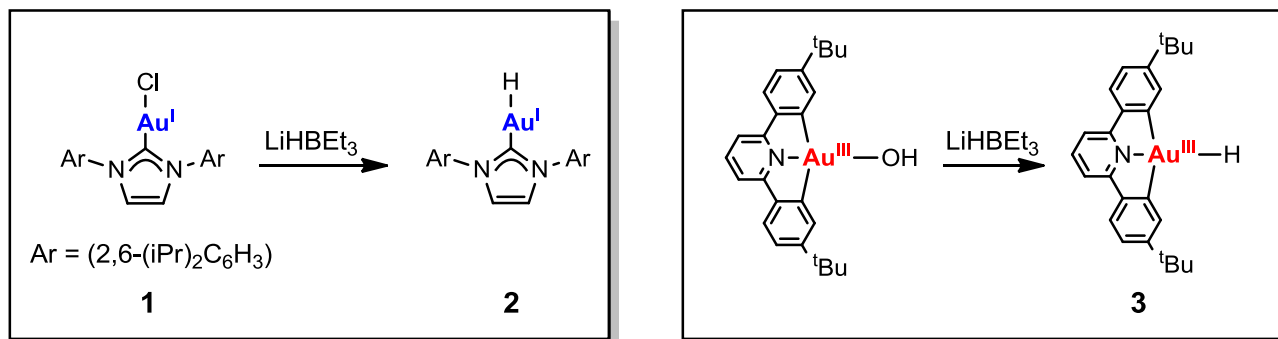
Geoffrey Chambers

Literature Seminar

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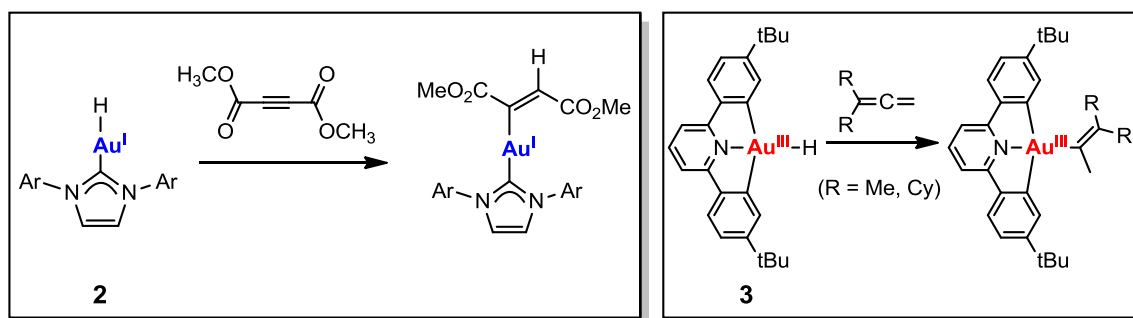
The preparation of transition metal hydride complexes is well established for most of the transition elements. However, isolation of gold hydride complexes has been especially elusive and, compared to the other transition metal hydrides, are sparsely represented in the literature despite being invoked in catalytic cycles.¹ Cationic gold is quite oxidizing ($\text{Au}^{3+/1+} = 1.36 \text{ V}$, $\text{Au}^{3+/0} = 1.52 \text{ V}$, $\text{Au}^{+/0} = 1.83 \text{ V}$),² and it has long been presumed that gold hydride bonds are labile due to the apparent mismatch of an oxidizing metal and a reducing ligand. The binary gold hydrides are known but are unstable with respect to the formation of gold metal and dihydrogen. These complexes have been detected only by the means of the codeposition of gold vapor with hydrogen in an argon matrix at 5 K.³

Gold complexes are known to catalyze a vast array of reactions, but the metal center typically functions merely as a Lewis acid.⁴ In a few cases however, gold hydride species are proposed as intermediates.⁵ Prior to the syntheses of the first gold hydride complexes, there was no evidence that these species were stable enough to exist in solution.



Scheme 1: Syntheses of the first monomeric gold hydride complexes

The first Au^{I} hydride complex (2) was synthesized by the treatment of the chloride complex (1) with LiHBET_3 (scheme 1). The complex was confirmed to be a monomeric Au hydride in the solid state through X-ray crystallography.⁶ The stability of 2 is attributed to the strong σ -donor N-heterocyclic carbene (NHC) ligand and its synthesis was inspired by the dimeric copper hydride NHC complex $[(\text{IPr})\text{CuH}]_2$.⁷ The hydridic character of the complex was established by ligand abstraction with half an equivalent of $[\text{Ph}_3\text{C}]\text{BF}_4$ to generate the bridging hydride salt $\{[(\text{IPr})\text{Au}]_2\text{H}\}\text{OTf}$. Hydride 2 does not readily undergo insertion reactions and is unreactive toward many alkynes, but it does react with dimethyl acetylenedicarboxylate to form a *trans* alkene product (scheme 2).



Scheme 2: Reactions of the hydrides 2 and 3 with electrophiles

More recently, the synthesis of the first Au^{III} hydride complex (**3**) was reported. As with the synthesis of **2**, LiHBEt₃ is used to install the hydride (scheme 1).⁸ Strong carbon σ -donors deter reduction of the metal center by the hydride ligand. Reductive elimination is also curbed through the use of a rigid CNC-pincer which disfavors C–H bond formation because of the resulting unfavorable bent Au^I complex that would result.⁹ The hydride **3** is protonated by trifluoroacetic acid to produce (CNC)Au–O₂CCF₃ and dihydrogen. Similar to **2**, **3** does not readily undergo hydride insertion reactions and is unreactive toward many alkynes and alkenes. Surprisingly, **3** regioselectively adds hydride to the terminal olefin in reactions with 1,1-dimethylallene and 1,1-dicyclohexylallene (scheme 2).

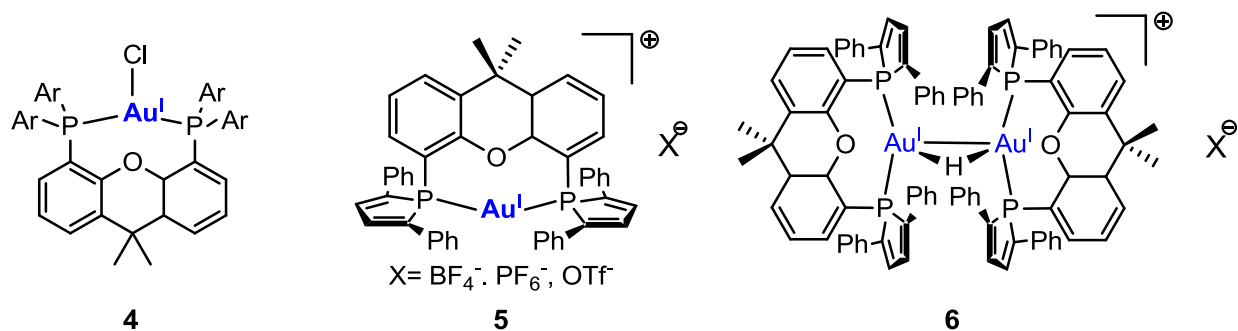
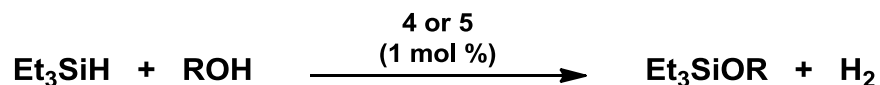


Figure 1: Catalytically active gold complexes and bridging hydride intermediate

Although the first hydride complexes show only stoichiometric reactivity with a limited number of substrates, the xantphos gold complex **4** and phosphole analog **5** have been shown to efficiently and selectively catalyze the dehydrogenative silylation of alcohols (eq. 1).^{10,11}



Equation 1: dehydrogenative silylation of an alcohol

The bimetallic bridging hydride complex **6** has been shown to be a key intermediate in the catalytic cycle for **5**.¹² The mechanism of this catalytic process has been studied thoroughly utilizing DFT calculations, which predict a strong counterion effect in [5]X ($X^- = \text{BF}_4^-, \text{PF}_6^-, \text{OTf}^-$) in agreement with experimental observation.

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