Gold Hydrides

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Fire and Ice: A Gold(III) Monohydride

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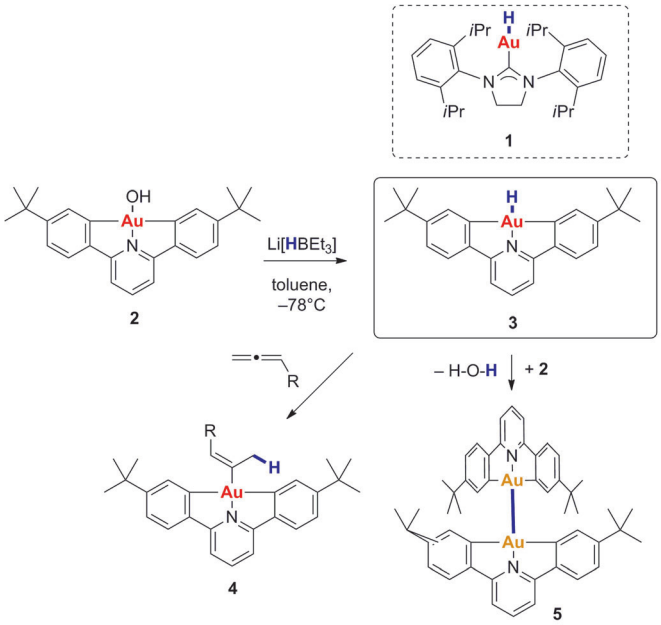
For a long time gold hydride complexes, compounds with a direct bond between a strongly oxidizing metal center ($Au^{3+}/Au^{1+} = 1.36$ V; $Au^{3+}/Au^{0} = 1.52$ V; $Au^{1+}/Au^{0} = 1.69$ V)[1] and an electron-rich hydride ligand, were assumed to be unstable.[2] In the context of the topical field of homogeneous gold catalysis, the lack of β-H elimination reactions, which are one common reaction pathway for other transition metals, was assigned to this instability.[3–5] Thus early reports of binary hydrides like AuH, $(H_2)AuH$, $(H_2)AuH_3$ and $[AuH_4]$ were limited to detection in frozen gas matrices below 5 K[2b–e,6] or, for gold(I) hydride, in the gas phase.[7]

The recent isolation of the stable N-heterocyclic carbene (NHC) gold(I) monohydride **1**[8] (Scheme 1) and a stable dinuclear gold(I) hydride[9] disproves the generally assumed low stability of gold hydride complexes in a spectacular manner. In a subsequent publication,[10] a gold(I) hydride species, which could be characteriszd by ^{1}H and ^{31}P NMR measurements and ESI mass spectrometry, was reported; NMR and kinetic studies indicated that the reaction mechanism of the gold-catalyzed dehydrogenative silylation indeed involves a gold(I) hydride species as a key intermediate.

This finding supported mechanisms that propose the active participation of gold(I) hydrides in the dehydrogenative silylation of alcohols[10,11] [the hydrolysis of IPrAuH[8] (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) would nicely fit into that picture], the formation of hexabutyldistannane by intermolecular dehydrogenative dimerization,[12] the hydrosilylation of ketones and imines,[11,13] the hydroboration of imines,[14] C–H activation,[15] and the enantioselective hydrogenation of alkenes and imines.[16] And it also could explain reactions for which the intermediacy of gold hydrides could be assumed, like the first reported homogeneous gold-catalyzed hydrogenation[17] and the gold-catalyzed synthesis of pyridines, in which the final step is the dehydrogenation of the initially formed dihydropyridine intermediate.[18]

Corma et al. have suggested gold(III) monohydrides as intermediates in homogeneous gold-catalyzed hydrogenation reactions, a pathway supported by DFT calculations.[19] Lately, supported by calculations at the PCM(CH_2Cl_2)-B3LYP/def2-SVP level, Alcaide et al. proposed a β-H elimination as an elemental step in a gold(III)-catalyzed reaction forming strained oxetenes.[20]



Scheme 1. Synthesis and reactions of a gold(III) monohydride.

Now, Bochmann and co-workers have reported the synthesis of a stable gold(III) monohydride **3**[21] bearing a C-N-C pincer ligand. The gold hydroxide **2**[22] was treated with $LiHBEt_3$ in toluene at −78 °C and subsequent stirring of the reaction mixture at room temperature for 15 min provided **3** as a dark yellow crystalline complex in 75% yield. The structural assignment was confirmed by an X-ray crystal structure analysis (Au–H 1.616(16) Å; the hydride was located in a difference density map and refined; bond length to the *trans* ligand: Au–N 2.035(3) Å).

At room temperature and in the solid state **3** is stable to air and moisture. The rigidity of the pincer ligand prevents the reductive elimination of **3** to form a phenyl–H bond. Solutions of **3**, when exposed to light or heated, decomposed.

In the ^{1}H NMR spectrum of **3**, a broad singlet resonance at $\delta = 6.51$ ppm in CD_2Cl_2 and at $\delta = 5.73$ ppm in C_6D_6 was assigned to the hydride ($\delta = 3.38$ (CD_2Cl_2) and 5.11 ppm (C_6D_6) for IPrAuH). At 2188 cm^{-1} the Au–H IR stretching vibration is comparable to those reported for AuH (2227 cm^{-1}) and $(H_2)AuH$ (2174 cm^{-1}) in an argon matrix,[2] but significantly higher than in (IPr)AuH (1976 cm^{-1}).[8a]

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The chemical properties of this gold hydride with the formal oxidation state +III indeed differ from these of the gold(I) hydride:

1) The hydridic reactivity in **3** is less pronounced than that of IPrAuH; **3** does not react with acetic acid. In the reaction with trifluoroacetic acid a mixture of products is obtained instead of the corresponding trifluoroacetate complex.
2) Interestingly, **3** did not insert ethylene, 3-hexyne, phenylacetylene, dimethyl acetylenedicarboxylate, CO_2, or benzaldehyde. This again is different from the reactivity of IPrAuH, which reacts with dimethyl acetylenedicarboxylate (but forms the product of a *trans* addition, which excludes a concerted one-step mechanism).[8a] However, **3** does react with 1,1-dimethylallene and cyclohexylallene and delivers the vinylgold(I) complexes **4** in high chemo- and regioselectivity.
3) Compound **3** also reacts with the hydroxide **2** (slow, 75% yield) and with the corresponding trifluoroacetate (fast, quantitative yield) to give the unique gold(II) dimer **5** as yellow crystals; again the connectivity was confirmed by X-ray crystal structure analysis (Au–Au 2.4941(4) Å).

These exciting results and this new reactivity shows that in the near future we can expect new and important impulses from gold(III) hydrides for inorganic and organometallic chemistry as well as homogeneous gold catalysis. This demonstration of the accessibility will encourage chemists to explore new catalytic cycles and new stoichiometric reactions of these species.

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