

Homogeneous gold catalysis: The role of protons

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Abstract

Recent reports have shown that some homogeneous gold catalyzed reactions might in fact be proton-catalyzed. Here, the knowledge on the role of Bronsted acids in gold-catalyzed reactions is summarized.

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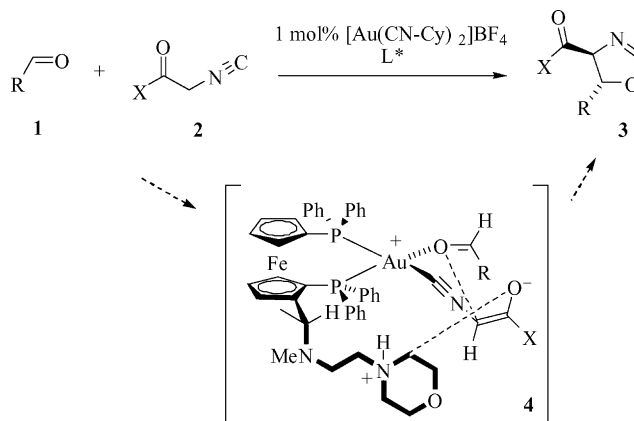
1. Introduction

Bond's [1], Haruta's [2] and Hutching's [3] pioneering work from the 1970s and 1980s caused an avalanche of publications on heterogeneous gold catalysis. In homogeneous catalysis, the development was delayed by about 10 years, early work between 1986 and 2000 of Ito and Hayashi [4], Utimoto [5], Teles [6] as well as the Hashmi group [7,8] also initiated an impressive growth of activity, which in terms of the total numbers of publications per year has yet only reached 5% of the total numbers of publications on heterogeneous gold catalysis. Recent reviews have summarized this development of homogeneous gold catalysis [9–13].

Parallel to the progress in homogeneous gold catalysis there has always been a discussion on the role of protons in these reactions, occasionally the protons were suspected to be the true catalyst. Here we want to discuss today's knowledge on that critical issue.

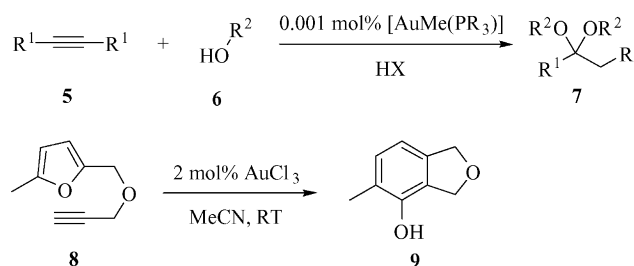
2. Proton transfer, protic media, aqueous media

Already the first examples mentioned above involved a proton transfer, in the Ito–Hayashi asymmetric aldol reaction [4] it is assumed that the isocyanoacetate 2 is converted to the nucleophile by a deprotonation.



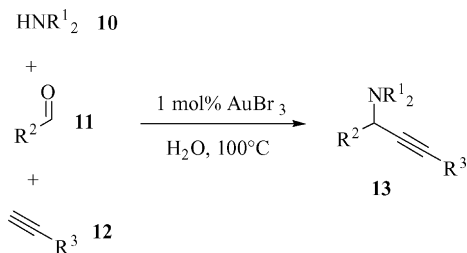
Hydrogen bonds of the ammonium-group in the intermediate 4 are assumed to be a crucial factor for the chirality transfer from the enantiomerically pure phosphane ligand to the product [14,15].

The nucleophilic additions to alkynes 5 proceeded in alcohols or even aqueous solvents [5]. Teles used acidic conditions to convert in situ the pre-catalyst [AuMeL] to the cationic active gold species by loss of methane [6] and non-absolute solvents, occasionally with added alcohol or water, were used in the synthesis of phenols 9 [8].



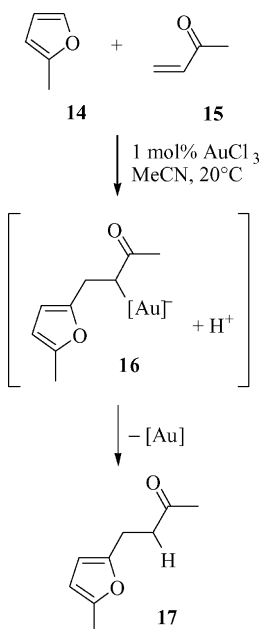
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Homogeneous gold catalyzed reactions can even be conducted in water, Li et al. have well documented that for the three-component reaction of amine 10, aldehyde 11 and alkyne 12 to the propargylic amine 13 [16–18], work which was confirmed by work of Wong and Che [19].



Toste coined the term “open flask conditions” for these types of catalysts that are not dependent on the exclusion of humidity or oxygen [20].

Still, one should be aware that in any catalysis proceeding through organogold-intermediates with carbon-gold single bonds, at some point the latter has to be cleaved by a proto-deauration step [10,13], which for example, in enolate complex intermediates 16 is faster than a β-hydrogen elimination [21].



This is in accordance with earlier reports by Baker and Westcott on the diborylation of styrenes [22]. The instability of gold hydrides [23,24] is probably responsible for the low tendency for a β-hydrogen elimination in such organogold intermediates.

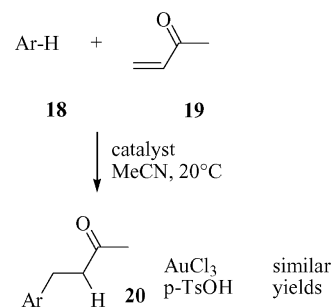
3. Catalysis by gold versus catalysis by protons

The isolobal analogy of Lewis, Stone, Hoffmann and others early pointed out the equivalency of R₃PAu⁺ and H⁺ [25–28]. This was successfully used in the synthesis of the gold analogues of different protonated molecules like (R₃PAu)₃O⁺, the “gold form” of H₃O⁺ [29].

Does this analogy mean that in gold catalyzed reactions the gold catalyst can be replaced by the significantly cheaper proton? Recent reports in the literature seem to support that assumption, but a closer look shows that for other reactions the investigators have done their homework and conducted the proper control experiments.

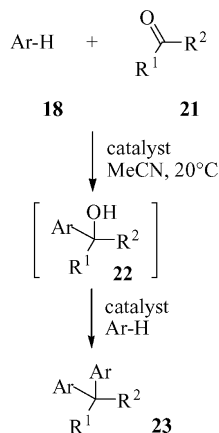
3.1. Reactions with protons as the active species

The first result of similar catalytic activity of gold-complexes and strong acids concerned the hydroarylation of α,β-unsaturated ketones 18, as Dyker and Hashmi reported [30]. It is conceivable that AuCl₃ and water form a strong Bronsted acid with a gold-complex as the counter ion. But not for every arene both types of catalysts provided the same yield [31].



Carbonyl:

The next reports concerning such system by Nair on the reaction of the three-fold reaction of α,β-unsaturated aldehydes [32] and the two-fold reaction of aryl aldehydes with electron-rich arenes [33] claimed AuCl₃ to be the catalyst. But experiments of Hashmi et al. have proven that a catalytic amount of *p*-toluenesulphonic acid shows an identical activity. Furthermore, not only aldehydes but also ketones like acetone react. The investigation proved that the initially formed benzylic alcohol 22 reacts faster with the second equivalent of the electron-rich arene than the carbonyl group of the starting material. This shows that different “gold-catalyzed” reactions of activated benzylic alcohols [34,35] might be Bronsted acid-catalyzed, too.



The latest observation of that kind comes from the groups of He [36] and Hartwig [37]. Both groups found, that instead of the previously used gold catalyst [38], for hydroamination of

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