Gem-Diauration and its Significance in Gold-Catalysis

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Gem-diaurated compounds have been known in literature for over two decades. However, their mechanistic significance and role in gold-catalyzed cyclization reactions have not been clearly elucidated so far. Although the preparation from monogold organyls is possible, very few examples exist on the isolation of those compounds from actual catalytic processes.

Our results outline the crucial role of diaurated compounds in gold-catalyzed cyclization reactions of aromatic 1,5-dienes.

Stable Organo-Gold Intermediates

Conducting the same reaction with the corresponding gold acetylide 3 and stochiometric amounts of the gold catalyst lead to the immediate formation of the air-stable gem-diaurated compound 4.

Crystal structure analysis confirmed the constitution of species 4. The short Au1-Au2 distance of 2.83 Å points towards the presence of strong aurophilic interactions most likely responsible for the high stability of 4 towards protodeauration.

In return, when the gold acetylide 3 was subjected to catalytic amounts of IPrAuNTf2, the isolation of the monogold compound 5 was possible. In addition 5 was characterized by a crystal structure.

Mechanism

Putting the above findings together we propose the following mechanism for the gold-catalyzed formation of fulvenes:

The initial step of the catalytic cycle proceeds via the formation of the gold(I) acetylide 3. The non-terminal system proved to be unreactive under the same conditions, thus emphasizing the importance of the acetylide for this transformation.

Once the acetylide is formed a second [Au]−-fragment facilitates the activation of the internal triple bond. This α/β-dual activation leads in a 5-endo-dig cyclization step to a vinylidene-like intermediate 11. The latter then undergoes a fast [1,5]-hydride shift furnishing cation 12 which is stabilized by a gold-NHC fragment. Attack of the vinyldene double bond generates intermediates 13 and 14 which give the monogold compound 5 after elimination of [Au]−. Upon cleavage of the gold NHC moiety by a catalyst transfer step the product 9 is released and the gold catalyst is ready to form new gold acetylide. The proposed equilibrium between mono- and diaurated species is much dependent on the corresponding counterion and the amount of free substrate.

In case of a stochiometric approach the reaction stops at the digold compound since no free substrate is available for protodeauration.

References: