

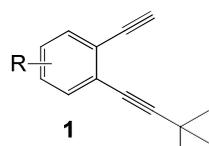


Gem-Diauration and its Significance in Gold-Catalysis

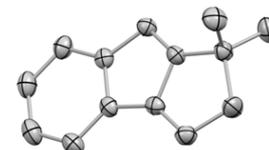
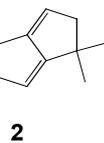
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R = OR, Hal, Alkyl



Crystal structure of 9 (thermal ellipsoids at 25% probability)

Gem-diaurated compounds have been known in literature for over two decades.^[1] 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.

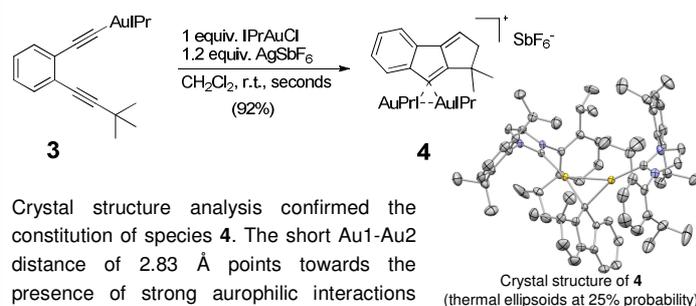
Our results outline the crucial role of diaurated compounds in gold-catalyzed cyclization reactions of aromatic 1,5-diyne.

Furthermore, we found evidence for vinylidene-like reactivity accompanied by a new mode of σ/π -dual activation of the triple bonds in such systems.^[2,3]

The test system we investigated consisted of a simple *tert*-butyl-substituted aromatic diyne which can be transformed with 5 mol% of a Au(I)-NHC catalyst into the corresponding fulvene derivative in a specific reaction with excellent yields.

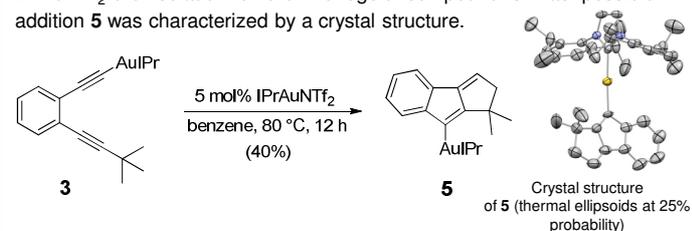
Stable Organo-Gold Intermediates

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



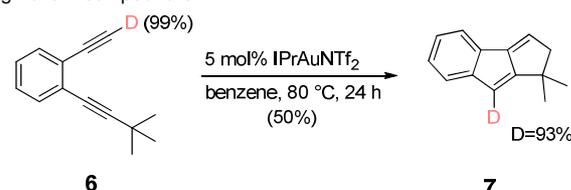
Crystal structure analysis confirmed the constitution of species **4**. The short Au1-Au2 distance of 2.83 Å points towards the presence of strong aurophilic interactions most likely responsible for the high stability of **4** towards protodeauration.

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.

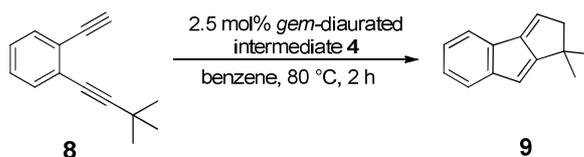


Isotopic Labeling Experiments

The monogold species **5** proved to be much more unstable than the diaurated compound **4** towards protodemetalation. A corresponding experiment with the deuterated substrate **6** lead to a nearly quantitative incorporation of deuterium in the fulvene product **7**. In isolobal analogy the deuterium label is located at the same position as the gold-NHC fragment in compound **5**.



Additionally the diaurated compound **4** proved to be catalytically active by itself. Using 2.5 mol% of the diaurated species leads to full conversion of the substrate **8** within 2 hours which was thrice as fast than the same reaction with 5 mol% IPrAuNTf₂ as catalyst.



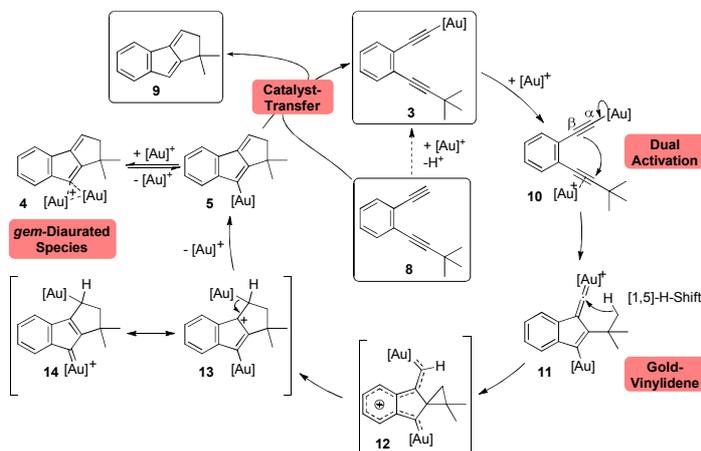
Therefore, *gem*-diaurated compounds may be used as ideal precatalysts for instant σ/π -dual activation.

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 σ/π -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 vinylgold 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.^[4] In case of a stoichiometric approach the reaction stops at the digold compound since no free substrate is available for protodeauration.

References

- [1] E. G. Perevalova, E. I. Symtslova, V. P. Dyachenko, K. I. Grandberg, *Russ. Chem. Bull.* **1984**, *33*, 956-957.
- [2] A. S. K. Hashmi, I. Braun, P. Nösel, J. Schädlich, M. Wietek, M. Rudolph, F. Rominger, *Angew. Chem.* **2012**, *124*, 4532-4536; A. S. K. Hashmi, I. Braun, P. Nösel, J. Schädlich, M. Wietek, M. Rudolph, F. Rominger, *Angew. Chem. Int. Ed.* **2012**, *51*, 4456-4460.
- [3] A. S. K. Hashmi, M. Wietek, I. Braun, P. Nösel, L. Jongbloed, M. Rudolph, F. Rominger, *Adv. Synth. Catal.* **2012**, *354*, 555-562.
- [4] D. Weber, T. D. Jones, L. L. Adduci, M. R. Gagné, *Angew. Chem. Int. Ed.* **2012**, *124*, 2502-2506.