

GOLD-CATALYZED CROSS-COUPLING-TYPE REACTION OF BROMOALKYNES WITH ALLYLSILANES THROUGH A CONCEALED REARRANGEMENT

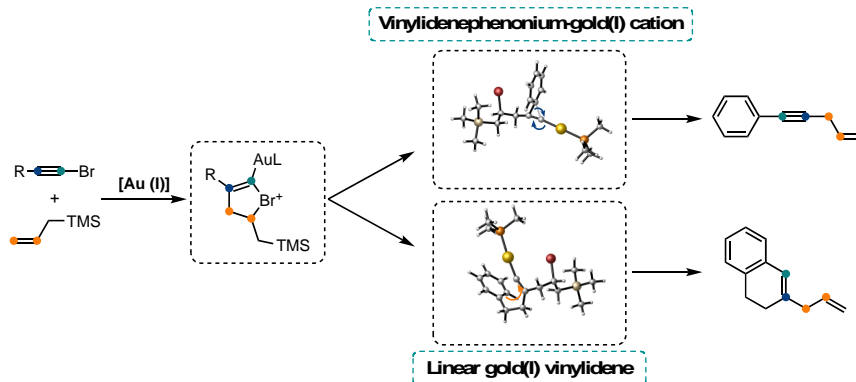
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Recent advances in homogeneous gold(I) catalysis show the versatility of vinylidenes intermediates. These species are usually formed starting from a gold(I) acetylide precursors or *via* alkyne-vinylidene isomerization.^[1]

Our group reported the gold(I)-catalyzed [2+2] intermolecular cycloaddition of terminal alkynes with alkenes to form cyclobutenes.^[2] In contrast, the gold(I)-catalyzed reaction of bromoalkynes with alkenes leads to a novel way of access to gold(I) vinylidenes. The reaction occurs *via* transformation of the cyclopropyl gold(I) carbene into an unprecedented cyclic bromonium intermediate and a subsequent bromine migration. Mechanistic studies revealed that linear gold(I) vinylidenes can be involved in hydroarylation reaction, while aryl substituted gold(I) vinylidene are distorted towards a vinylidenephonium-gold(I) cation allowing a concealed 1,2-aryl-migration to form 1,4-enynes in a cross-coupling-type reaction.



[1] Gagosz, F., *Synthesis* **2019**, *51*, 1087–1099.

[2] Lopez-Carrillo, V.; Echavarren, A. M., *J. Am. Chem. Soc.* **2010**, *132*, 9292–9294.