Novel (C^C) Zwitterionic Gold(III) Complexes: Synthesis and Insight into the Mechanism of the Cycloauration Step

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In the last years, gold(III) complexes have gained great attention due to their steadily increasing applications in a variety of fields, including catalysis, material science, and biomedicine. [1] Due to the tendency of Au(III) to be reduced to Au(I) or Au(0), stable Au(III) are often prepared in the form cyclometalated species based on pincer or bidentate ligands bearing aryl carbanions and pyridine moieties (e.g. [C^N^C], [C^N] and [N^N] type of ligands).[2] Some of these mono- or bis-cyclometalated species have been used for studying elementary steps in gold-catalyzed transformations, such as in transmetalation, insertion or reductive eliminations. Unfortunately, stable examples of precursors of carboauracycles of type [C^C]Au(III), which could be used to further unveil mechanistic intricacies of gold-promoted C–C bond-forming processes, are very scarce, and essentially limited to systems bearing biphenyl and other $C(sp^2)$-based ligands.

As part of our investigations on the reactivity of Au(III) with alkylidenecyclopropanes (ACPs) equipped with pyridine ligands[3], we have now discovered that substrates in which the ACP and the pyridine are connected through 1,2-phenyl tether exhibit a novel type of reactivity with Au(III) salts to deliver intriguing zwitterionic [C^C]Au(III) carboauracycles. These interesting spirocyclic auracycles result from a cascade process involving the nucleophilic addition of the pyridine moiety to the Au(III)-activated alkene and an intramolecular aromatic metalation of the resulting $C(sp^3)$-gold(III) intermediates.

Importantly, the isolation of the alkyl gold(III) intermediates that precede the cyclometallation, allowed us to use them as a proxy for carefully studying the subsequent aromatic auration. Importantly, our collected data allowed us to rule out a CMD process, previously proposed in related systems, while is fully compatible with a two-step S_EAr pathway in which the Au(III)- arene complexation, rather than the direct formation of the Wheland intermediate, is the rate-limiting step. This study provides a detailed insight into how the Au-C(sp2) bond formation step takes places and the factors that affect this process, which is an elementary step for gold-catalyzed oxidate cross-couplings.

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[3] Jorge A. González, Felipe Verdugo, José L. Mascareñas, Fernando López, Cristina Nevado, *Angew. Chem. Int. Ed.* **2020**, 59, 20049–20054.