

On Gold Adventures and Beyond

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Gold-catalyzed oxidative cross-couplings have bloomed in the past few years postulating gold(III) fluorides as productive reactive intermediates. However, experimental support for these species is to-date scarce due to their labile nature, and thus the reactivity of Au-F bonds remains largely unexplored. In order to address these challenges, novel 3,5-disubstituted phenylpyridine based ligands have been developed. Interestingly, these (N[^]C[^]C)Au^{III}-F complexes reacted with different terminal alkynes under mild reaction conditions resulting in the formation of gold-alkynyl species which exhibit striking luminescent properties compared to their analogous (C[^]N[^]C)Au^{III} complexes. Further, these newly stabilized gold(III) fluorides interact with boronic acids. Aryl boron reagents have been typically used as reaction partners in gold oxidative couplings with Selectfluor as stoichiometric oxidant. Au^{III}-F species have been invoked as the key partners of boron species towards the formation of new C-C bonds. However, the nature of the interaction Au^{III}-F/B is still unclear. Taking advantage of fine-tuned C[^]N type ligands, we were able to access monocyclometalated (C[^]N)Au^{III}(R)F (R = F, alkyl, aryl) complexes in monomeric form that were used to probe the interaction Au^{III}-F with aryl boronic acids. We showed that a direct transmetalation precedes reductive elimination to produce the coupling product thus ruling out a bimolecular reductive elimination pathway.