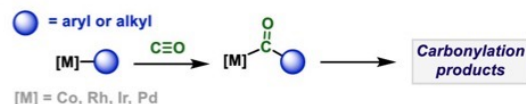


Migratory Insertion of CO into a Au–C Bond

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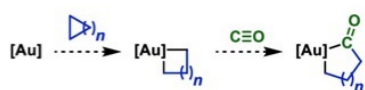
Introduction

(A) Transition-metal mediated carbonylation:



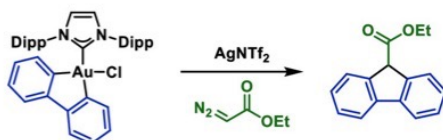
Atom economical Industrially relevant [M] = Au is unknown

(B) Possible route to Au–C migratory insertion:



Strategy: (i) access metallacycles via C–C bond activation
(ii) establish viability of CO insertion

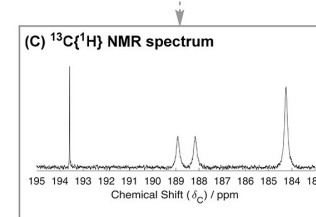
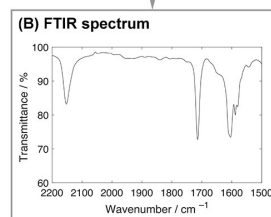
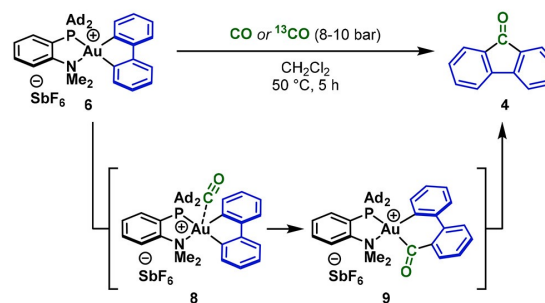
(C) Carbene insertion into a Au–C bond (ref. 18a):



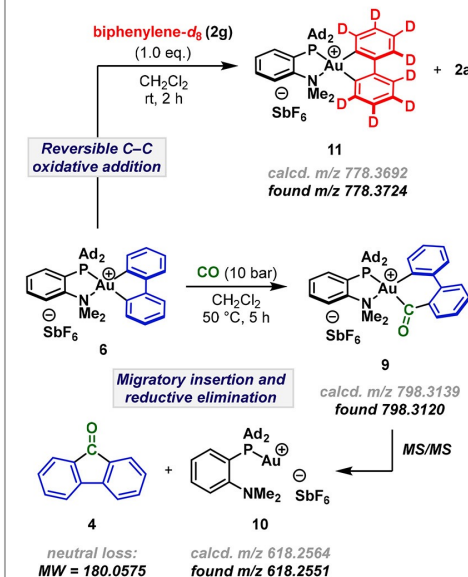
So far, the inserting reactants into Au–C bond are limited, for example a carbene, while CO is not included.

Mechanistic Studies This process is also confirmed by DFT calculation (see the original paper)

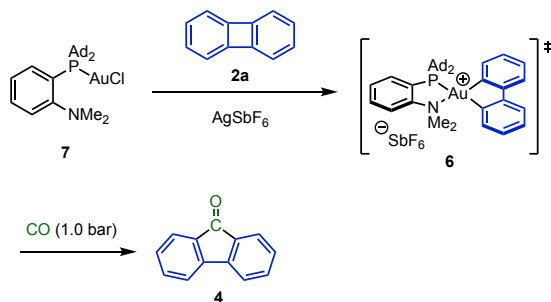
(A) Reaction mixture analysis by FTIR and ¹³C NMR spectroscopies



(D) Mass spectrometry



This work

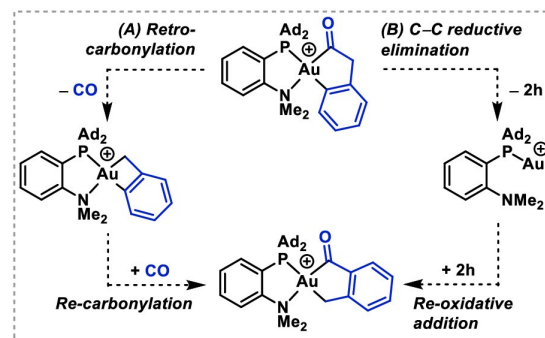


Bidentate ligand (7)-supported Au complex reacts with **2a** to form complex **6** via activating strained C–C bond to form Au–C bonds, where CO could insert into it to finally afford product **4**.

Reaction was monitored by FTIR where three carbonyl signals were observed. The one at 2152 cm⁻¹ is assigned to free CO (of **8**), and the remaining two signals probably belongs to CO-inserted complex **9** and product **4**. ¹³CO gas was used for spectroscopically monitoring the insertion process by ¹³C NMR. Signal at 193.6 ppm is assigned to free CO (of **8**), and the broad singlet signal at 184.3 ppm is the free CO (of **8**), and the doublet signal at 188.5 is suggested to belong to complex **9**.

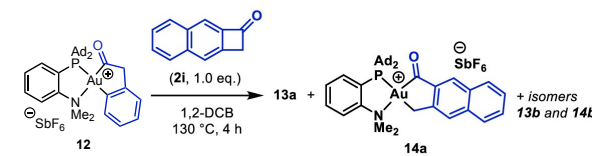
Deuterated biphenylene replacement reveals the C–C oxidative addition to be reversible.

CO-inserted intermediate **9** could also be observed by mass spectrometry, and tandem MS analysis could show the existence of fragment **10** and product **4**.



A rearrangement occurred, and two plausible pathways were proposed.

- 1) Retro-carbonylation, then re-carbonylation (which is like the case of Rh)
- 2) C–C reductive elimination, then Re-oxidative addition



Experimental investigation by mixing **12** with **2i** afforded isomers of both **13** and **14**, which indicated the C–C reductive elimination is much favored.