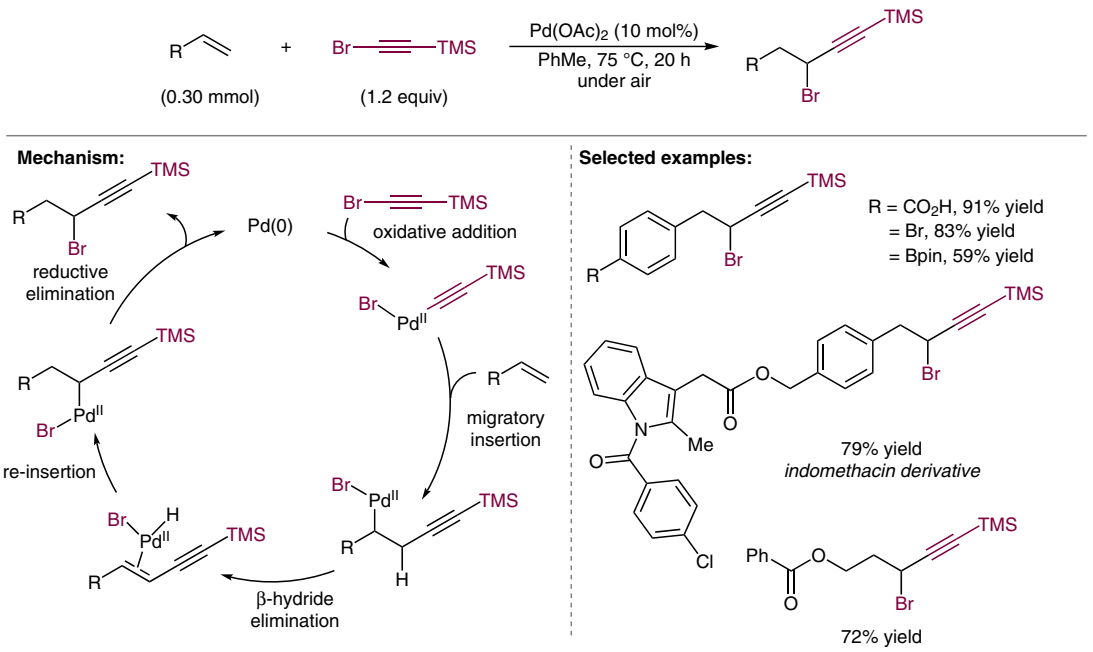
Y. ANO*, N. KAWAI, N. CHATANI (OSAKA UNIVERSITY, JAPAN)
Palladium-Catalyzed 1,1-Alkynylbromination of Alkenes with Alkynyl Bromides
Chem. Sci. **2021**, *12*, 12326–12332, DOI: 10.1039/d1sc02873a.

Palladium-Catalyzed Intermolecular 1,1-Carbobromination of Alkenes with Alkynyl Bromides



Significance: The Chatani group reports a novel method for the synthesis of propargylic bromides via a palladium-catalyzed 1,1-alkynylbromination of alkenes with alkynyl bromides. Notably, in sharp contrast to other carbohalogenations, the reaction does not require any specialized ligand to induce reductive elimination to form the C–X bond; it occurs under ligandless conditions with $Pd(OAc)_2$ as the palladium precursor.

Comment: Although the reaction occurs under air with a Pd(II) source, an induction time was observed under the standard conditions, whereas no induction time was observed with $Pd_2dba_3{\cdot}CHCl_3$. Accordingly, the authors propose Pd(0) as being the active catalyst. The proposed mechanism is comprised of oxidative addition and migratory insertion. β-Hydride elimination is favored over reductive elimination, followed by reinsertion of the alkene. Reductive elimination then affords the final propargylic bromide product.

SYNFACTS Contributors: Mark Lautens, Jeanne Masson-Makdissi
Synfacts 2021, 17(11), 1219 Published online: 19.10.2021
DOI: 10.1055/s-0040-1720667; **Reg-No.:** L12921SF

Category
Metals in Synthesis

Key words
carbohalogenation
carbobromination
palladium catalysis

Synfact of the Month