Catalytic Alkenylation of Neopentyl Palladium Species Using N-Tosyl Hydrazones

Significance: Palladium-catalyzed Heck-type cascades have long been used to install molecular complexity in a single transformation. In early pioneering work, Negishi and Grigg have reported cascade processes involving carbonylation sequences, Stille and Suzuki couplings, as well as C−H functionalization as terminating steps. However, despite these advances, terminations involving palladium carbenes have been far less explored. Gu and co-workers report the combination of N-tosyl hydrazone derived carbenes and in situ generated alkyl palladiums in a new alkenylation reaction.

Comment: The authors present a palladium-catalyzed Heck-type cascade reaction en route to alkenes by terminating the cyclization sequence with a reaction with N-tosyl hydrazones, products can be obtained with high E/Z ratios. The method benefits from the ability to generate diverse hetero- and carbocycles in good to excellent yields under relatively mild conditions, using a simple palladium(II) pre-catalyst. Cyclization onto electron-deficient alkenes was shown to be preferred in a competition experiment involving a diene substrate.