Palladium-Catalyzed Cyclization via Carbopalladation and Acylpalladation

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1 Introduction and General Discussion

Over the past two decades, cyclic carbopalladation and related cyclic acylpalladation of alkenes, allenes, alkynes, and related π complexes including the cyclic Heck reaction have been developed into new and attractive synthetic methods. This chapter mainly discusses catalytic cyclization reactions via cyclic carbopalladation and cyclic acylpalladation, which may not be classified under the cyclic Heck reaction.

Keywords Acylpalladation · Cascade Carbopalladation · Cyclic Acylpalladation · Cyclic Carbopalladation

1 Introduction and General Discussion

Alkenes and alkynes represent some of the most reactive classes of functional groups toward Pd. They are generally more reactive than various
carbonyl functionalities including ketones, esters, amides and even aldehydes [1]. Their presence also makes otherwise relatively unreactive functional groups, such as halogens, in their vicinity much more reactive. Thus, alkenyl, alkynyl, allyl, propargyl, as well as aryl and benzyl halides and related electrophiles are generally more reactive than the corresponding ordinary alkyl halides toward Pd.

Those interactions mentioned above lead to π-complexation and oxidative addition, representing two of the several most widely employed routes to organopalladium derivatives along with transmetallation with Pd, hydropalladation, and heteropalladation defined as addition of Pd – X bonds to π-bonds, where X is any element other than C or H [2].

Organopalladium derivatives obtained by any of the methods indicated above can undergo carbometallation which may be defined as a process of addition, generally syn-addition, of a C–Pd bond to alkenes and alkynes (Schemes 1 and 2). The regiochemistry of carbometallation can be affected by mutually competing factors and is therefore often somewhat unpredictable.

Scheme 1

Scheme 2