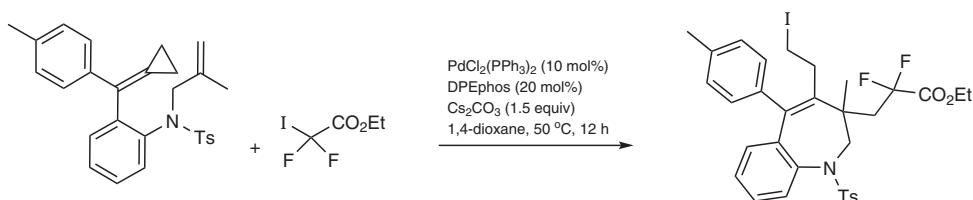


1.14 Palladium(I)-Mediated Reactions

G. Maestri and A. Serafino

Several elegant reactivities can be observed in reactions involving palladium(I) species, allowing access to molecular architectures that are often beyond the capabilities of popular diamagnetic palladium complexes. This review presents three main axes of research in this context, which have mostly emerged in the last decade. Reactions promoted by visible light enable synthetic methods that are unusual in their mild experimental conditions coupled with remarkably broad functional group tolerance. The use of discrete palladium(I) dimers as precatalysts allows one to perform a wide set of cross-coupling protocols, such as Kumada and Negishi reactions, and chalcogenation reactions, with a surgical precision on the carbon–halogen bond that is initially activated. The generation of alkyl radicals and palladium(I) species through a thermal strategy proves useful for the elaboration of substrates with several polyfluorinated fragments, which are otherwise elusive coupling partners for more common two-electron processes.



Keywords: alkenes • alkynes • alkyl halides • aryl compounds • cyclization • electron transfer • heterocycles • palladium catalysts • photochemistry • radicals • radical cyclization • reductive elimination