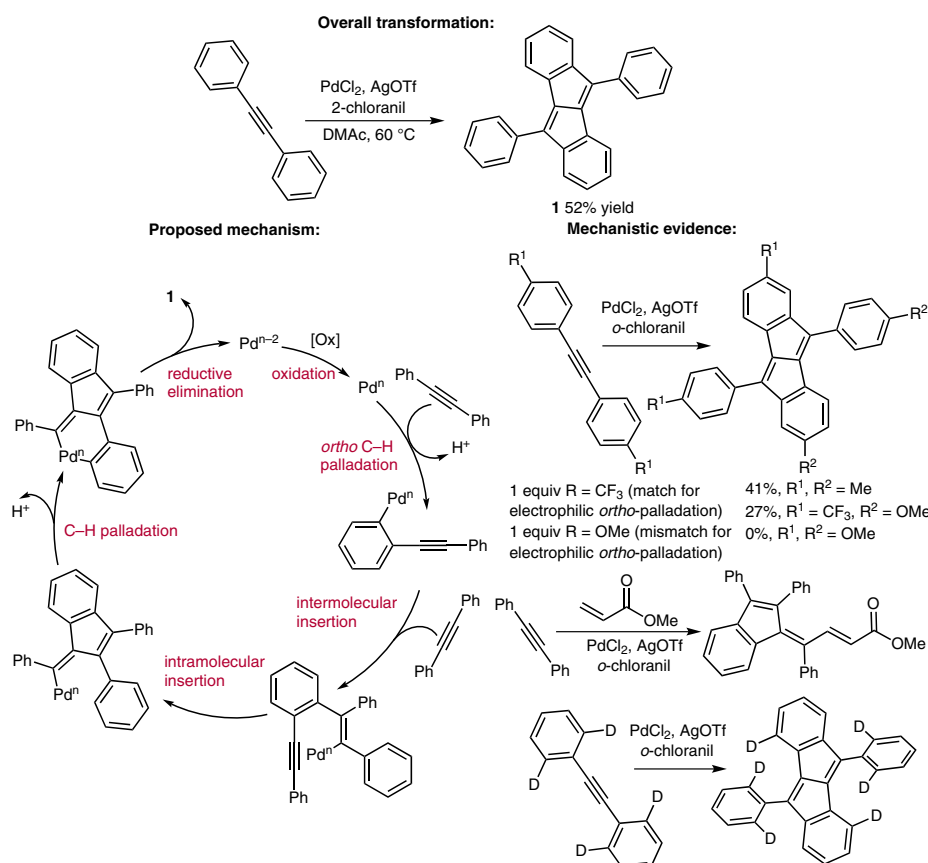


Dibenzo[*a,e*]pentalenes by *ortho* C–H Activation



Significance: Itami and co-workers have devised an elegant synthesis of dibenzo[*a,e*]pentalene (**1**), a classic π -conjugated polycyclic hydrocarbon, through the dimerization of aryl acetylenes. Unlike other approaches to **1**, this method does not require *ortho* functionalization of the aryl group. Instead, this position is activated through an electrophilic palladation/C–H activation. The *ortho* selectivity was demonstrated by a deuterium-labeling experiment and an analysis of substituents effects supports the proposed electrophilic palladation mechanism.

Comment: Following the *ortho* C–H activation, a catalytic cycle is proposed involving two insertion steps (intermolecular followed by intramolecular), another C–H palladation, and reductive elimination to yield the desired dibenzo[*a,e*]pentalenes. The cycle is completed by re-oxidation of the palladium. Trapping and cross-dimerization experiments support the hypothesized catalytic cycle. The authors also demonstrate this method is effective with asymmetric aryl acetylenes.