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.

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