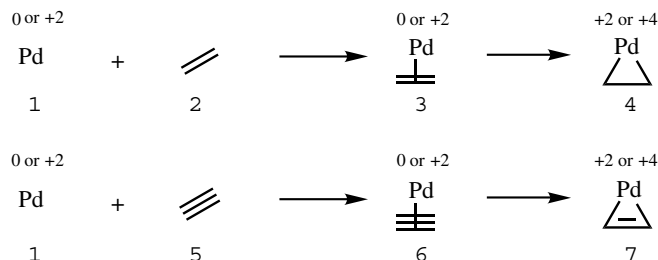


IV.10.3 Other Reactions Involving Palladacyclopropanes and Palladacycloprenes

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Although palladacyclopropanes and palladacycloprenes can be postulated as intermediates when palladium in the oxidation state 0 or +2 interacts with an alkene or an alkyne, there is very little evidence that Pd-catalyzed reactions of alkenes and alkynes actually proceed this way.

In principle, a palladacyclopropane might be generated starting from palladium(0) or palladium(II) **1** and an alkene **2** (Scheme 1): after coordination to form a π -complex **3**, oxidative addition would yield a σ -complex **4**, a pallada(II)- or pallada(IV)cyclopropane. Likewise, the analogous reaction with an alkyne **5** would lead to a palladacycloprenene **7**.



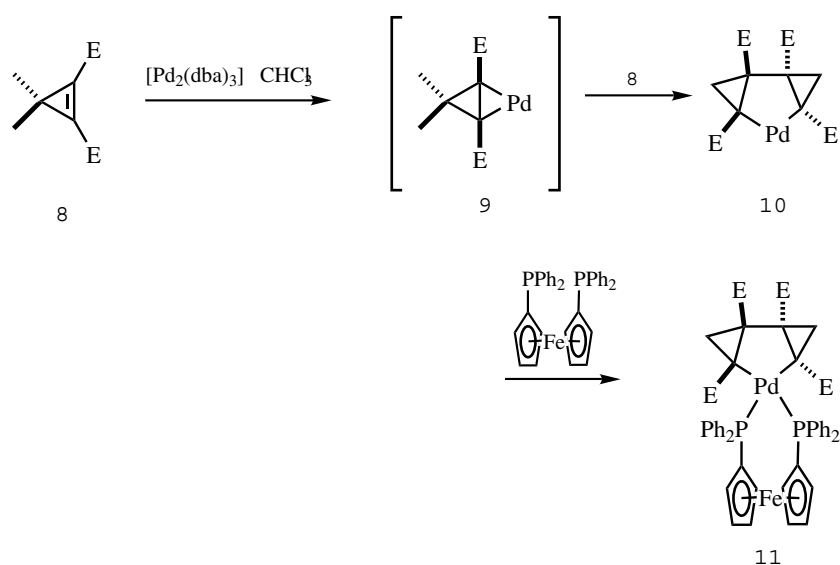
Scheme 1

Conclusive evidence for palladacyclopentanes^[1] and palladacyclopentadienes^{[2],[3]} as potentially stable intermediates has been put forward, and they have a close analogy to such metallacycles with other metals.^{[4],[5]} They frequently are intermediates in metal-catalyzed or -mediated formal $[2 + 2 + 2]$ cyclotrimerizations of alkynes and strained alkenes. It is plausible to assume that palladacyclopropanes or -cycloprenes also play a role in such formal $[2 + 2 + 2]$ processes catalyzed by palladium(0), for example, in the type of Pd-catalyzed cyclotrimerization of 3,3-dimethylcyclopropene reported by Binger et al.^[6] (see also **Sect. IV.2.4**), for which a palladacyclopentane as intermediate was already isolated.^[7] Moreover, dimethyl 3,3-dimethylcyclopropenedicarboxylate **8** has recently been shown to form the tricyclic palladacyclopentane derivative **10**, the structure

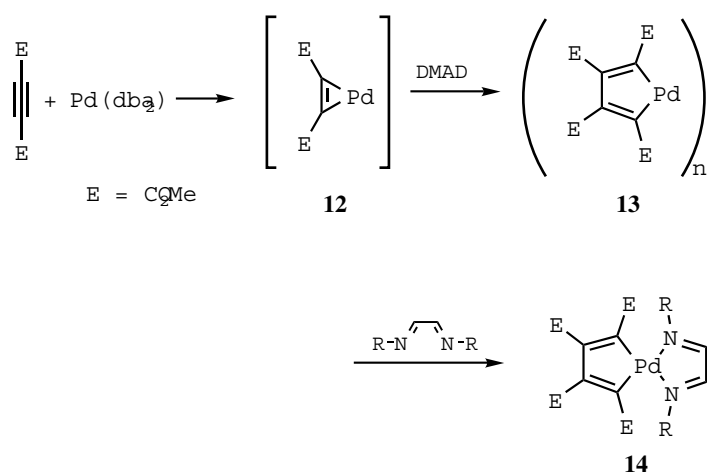
of which was proved by X-ray analysis of its 1,1'-bis(diphenylphosphinyl)ferrocene adduct **11** (Scheme 2).^[1] It is most reasonable that **10** is formed via carbopalladation of **8** by the palladacyclopropane derivative **9**.

$\text{Pd}(\text{dba})_2$ reacts rapidly with dimethyl acetylenedicarboxylate (DMAD) to form the polymeric palladacyclopentadiene TCPC(**13**),^[2] which could be fully characterized as diazadiene complexes **14** (Scheme 3).^[3]

The palladacyclopentadiene **12** would most probably be an intermediate en route to **13**, and, indeed, 1:1 complexes of palladium and DMAD have been obtained and characterized by ^1H NMR and IR spectroscopy with stabilizing ligands such as triphenylphosphine^[2] and *N,N'*-di-*tert*-butyl-1,4-diaza-1,3-diene^[3] present (Scheme 4). Unfortunately, however, it was



Scheme 2



Scheme 3



In enyne cycloisomerizations developed by Trost (see **Sect. IV.2.5** and **IV.3.1**), palladacycles are also likely intermediates (**Scheme 5**).^[9] In the palladium(II)-initiated cyclization of an enyne **19**, the palladacyclopentene **21** has been postulated, requiring palladium to adopt the formal oxidation state +4. Catalytic cycles involving Pd(II)–Pd(IV) are not well precedented; however, by now several reactions have been reported in which Pd(IV) intermediates are most likely,^{[10]–[16]} and one palladium(IV)



complex has been fully characterized by an X-ray crystal structure analysis.^[17] Most probably, **21** would be formed from the π -complex **22** via the palladacyclopropene **20** by intramolecular carbopalladation of the double bond.

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