

PART II

Palladium Compounds: Stoichiometric Preparation, *In Situ* Generation, and Some Physical and Chemical Properties

II.1 Background for Part II

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Any Pd-catalyzed synthesis must begin with the procurement of Pd-containing catalysts or, more often than not, precatalysts either from commercial and other sources or by their stoichiometric preparation. The great majority of Pd complexes used for this purpose have been Pd(0) and Pd(II) complexes, and their stoichiometric preparation as discrete Pd compounds are discussed in **Sect. II.2**. These Pd compounds may contain various ligands containing practically all nonmetallic and even some metallic atoms. Some of the simplest Pd precatalysts and catalysts used under heterogeneous conditions are metallic Pd and its mixtures with various support compounds (**Sect. II.2.1**), while Pd(II) compounds containing only oxygen and/or halogen ligands represent some of the simplest precatalysts and catalysts used under homogeneous conditions (**Sect. II.2.2**).

In the majority of cases, these Pd(II) compounds containing oxygen and/or halogen groups are either stoichiometrically or under catalytic reaction conditions converted into Pd(0) or Pd(II) complexes containing P and/or other group 15 atom ligands (e.g., N and As) (**Sect. II.2.3**). Although much limited, those Pd(0) and Pd(II) complexes that contain S and heavier group 16 atom ligands have also been used as catalysts and catalyst precursors (**Sect. II.2.4**). Hydrido derivatives of Pd(0) and Pd(II) have played important roles in the Pd-catalyzed hydrogenation and other related reactions (**Sect. II.2.5**). Related to them are Pd(0) and Pd(II) complexes containing various metal ligands, such as those containing B, Si, and Sn (**Sect. II.2.6**). In recognition of the special significance of chiral Pd(0) and Pd(II) complexes in asymmetric synthesis, they are discussed separately in **Sect. II.2.7**. Many of these Pd(0) and Pd(II) compounds exist as doubly bridged dimers, but such dimers are often dissociated into or converted to monomers under the Pd-catalyzed reaction conditions. For this reason, distinction between monomers and dimers is often very loosely made or even ignored in some cases. Therefore, monomers and ligand-bridged dimers are presented together in the same sections.

These inorganic or nonorganometallic Pd(0) and Pd(II) complexes must then be converted either stoichiometrically or under catalytic conditions into organopalladium derivatives for Pd-catalyzed organic synthesis, as outlined in **Sect. II.3**. It is important to note that some carbon ligand-containing Pd(0) and Pd(II) complexes that are preparable stoichiometrically as discrete isolatable complexes are often preferred catalysts and catalyst precursors, some of which are even commercially available. However, the great majority of organopalladium reagents and intermediates are generated *in situ* under catalytic conditions. The terms *reagents* and *intermediates* have been used by some chemists to

describe those reagents that do not incorporate any of their C ligands into the products (*reagents*) and those that do (*intermediate*), respectively. But this practice is only loosely followed in this Handbook.

In many Pd-catalyzed reactions, generation of organopalladium derivatives is often achieved under the Curtin–Hammett conditions, and attempts to prepare them under the stoichiometric conditions in a discrete step may fail as in the case of generation of π -allylpalladium acetate from allyl acetate and Pd(0) complexes.^{[1]–[3]} Although *in situ* generation of organopalladium derivatives is discussed throughout the entire Handbook, a brief discussion of the general methods of the synthesis and generation of organopalladium derivatives would be useful and is therefore presented in **Sect. II.3.1**, while those Pd(0) and Pd(II) complexes containing C ligands that have been obtained as discrete species are summarized in **Sect. II.3.2**.

All of the Pd compounds discussed above are Pd(0) and Pd(II) complexes. Although as yet much more limited in number and synthetic scope, an increasing number of Pd(I) and Pd(III) complexes have been prepared and investigated, and some Pd(IV) complexes have been claimed or suggested mainly as intermediates. The relative rarity of Pd(I) and Pd(III) complexes most probably is an indication of the general reluctance of more ubiquitous Pd(0) and Pd(II) complexes to undergo net one-electron transfer. This, in turn, suggests that Pd-catalyzed reactions may generally proceed without complications due to radical processes. In fact, the great majority of the known organopalladium reactions are thought to involve concerted two-electron processes of Pd(0) and Pd(II) complexes. As Pd(IV) complexes are accessible by two-electron oxidation of Pd(II) complexes, it is possible that many more Pd(IV) complexes may be found to play roles as transient intermediates or even isolatable species. Aside from Pd(I) and Pd(III) radicals, many other spin-paired Pd(I) and Pd(III) species will undoubtedly be synthesized, and explorations of their chemistry are expected to lead to new important branches of organopalladium chemistry. The current scope and significance of these as yet rare Pd complexes are discussed in **Sect. II.4**.

Finally, as in the other parts of this Handbook, a later section within a part is generally, but not always, given a higher priority than an earlier section. Thus, for example, $\text{Cl}_2\text{Pd}(\text{PPh}_3)_2$ is discussed in **Sect. II.2.3** rather than in **Sect. II.2.2** to minimize unnecessary overlaps.

REFERENCES

- [1] B. M. Trost, *Tetrahedron*, **1977**, 33, 2615–2649.
- [2] B. M. Trost, *Acc. Chem. Res.*, **1980**, 13, 385–393.
- [3] R. F. Heck, *Palladium Reagents in Organic Syntheses*, Academic Press, New York, **1985**, 461 pp.