

II.2 Pd(0) and Pd(II) Compounds Without Carbon—Palladium Bonds

II.2.1 Metallic Palladium and Its Mixtures

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Palladium (Pd) without any ligands are Pd—Pd bonded three-dimensional network polymers that are essentially insoluble in organic solvents and water. Many different forms of Pd including Pd evaporation slug, foil, granule, powder (or black), rod, shot, sponge, and wire of over 99.9% purity (up to 99.999%) are commercially available. One of the principal uses of Pd in organic synthesis is in catalytic hydrogenation and hydrogenolysis. In many cases, however, the use of mixtures of Pd and some suitable support materials is recommended for Pd-catalyzed reduction. Some representative and commercially available supported Pd catalysts are listed in **Table 1**, and they include (i) Pd on activated carbon (Pd on C or Pd/C), (ii) Pd on alumina (Pd on Al₂O₃), and (iii) Pd on various alkaline earth metal salts, such as CaCO₃, BaCO₃, BaSO₄, and SrCO₃ with the Pd content up to 30 wt% (typically 1–10 wt%).

Although metallic Pd may be used to prepare Pd(0) complexes containing various neutral ligands, these compounds are usually prepared either by the reduction of Pd(II) compounds containing halogens or oxygen ligands, such as PdCl₂, Li₂PdCl₄, Cl₂Pd(PPh₃)₂, and Pd(OAc)₂, or by ligand displacement of other Pd(0) complexes, such as Pd(dba)_n, as discussed later in this part. For solubility and other reasons, metallic Pd is often not the most convenient source of Pd in laboratories. In fact, even metallic Pd compounds without nonmetallic ligands have been prepared by treating the Pd(II) compounds mentioned above with various reducing agents, such as NaBH₄.^[1] In such reactions, however, the exact product structures may not have been well established. In the reaction mentioned above, Pd species containing Pd—B bonds is likely.

In some cases, Pd catalysts of reduced activity are desired. Partial hydrogenation of alkynes to alkenes without producing significant amounts of alkanes is a representative example, and partially poisoned Pd catalysts, most notably Lindlar's catalyst^[2] consisting of Pd on CaCO₃ deactivated by PbO or some other Pb compounds, have been widely used.

Since the use of metallic Pd and its mixtures or more specifically their applications in heterogeneous catalytic reductions are discussed in **Sect. VII.2** as well as **Sects. III.3.1**,

TABLE 1. Some Commercially Available Palladium on Supports^a

Supported Pd	Pd Content (wt%)
Pd on activated C	1–30
Pd on Al ₂ O ₃	0.5–10
Pd on BaCO ₃	5
Pd on CaCO ₃	5
Pd on SrCO ₃	2
Pd on BaSO ₄	5
Pd on polyethyleneimine/SiO ₂	1–3
Pd on CaCO ₃ poisoned with PbO (Lindlar catalyst) ^b	5

^a(i) *Aldrich Catalog Handbook of Fine Chemicals*, **1998–1999**. (ii) *Strem Chemicals, Inc. Catalog* (No. 17) **1997–1999**.

^bH. Lindlar and R. Dubois, *Org. Synth.*, **1966**, 46, 89.

V.2.3.1, and **VI.2.4**, these sections and references cited therein should be consulted for additional discussion of metallic Pd and its mixtures.

REFERENCES

- [1] H. C. Brown and C. A. Brown, *J. Am. Chem. Soc.*, **1962**, 84, 1492.
- [2] H. Lindlar and R. Dubois, *Org. Synth.*, **1966**, 46, 89.