

## II.2.2 Palladium Complexes Containing Halogen and Oxygen Ligands

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As indicated in **Sect. II.2.1**, Pd(II) complexes containing halogen and/or oxygen ligands, such as PdCl<sub>2</sub> and Pd(OAc)<sub>2</sub>, are some of the most commonly used starting Pd compounds for the preparation of a wide range of Pd precatalysts and catalysts.

### A. PALLADIUM(II) COMPLEXES CONTAINING HALOGEN LIGANDS

Although PdCl<sub>2</sub> is by far the most widely used palladium halide, there are several other commercially available palladium halides as shown in **Table 1**.

Palladium chloride is prepared by treating Pd metal with Cl<sub>2</sub> at elevated temperatures. It exists as an essentially linear doubly Cl-bridged polymer **1**.<sup>[1]</sup> Palladium bromide is prepared from Pd and Br<sub>2</sub> in the presence of nitric acid, while PdI<sub>2</sub> is normally prepared by treatment of PdCl<sub>2</sub> with iodide ions.<sup>[1]</sup>

One of the inconveniences associated with the use of these palladium halides is their low solubility in aqueous and organic media. Although PdCl<sub>2</sub> is soluble in water, it is insoluble in most of the organic solvents, unless some chemical transformations can readily take place, as in the cases of nitriles (**Scheme 1**). This inconvenience can readily be overcome by addition of alkali metal chlorides (e.g., LiCl). Addition of 2 equiv of LiCl to a suspension of PdCl<sub>2</sub> in a suitable organic solvent (e.g., THF) dissolves PdCl<sub>2</sub> through the formation of Li<sub>2</sub>PdCl<sub>4</sub> (**Scheme 1**), which may then be used as a solubilized form of PdCl<sub>2</sub> for the preparation of various other Pd complexes, as detailed in later sections.

### B. PALLADIUM(II) COMPLEXES CONTAINING OXYGEN LIGANDS

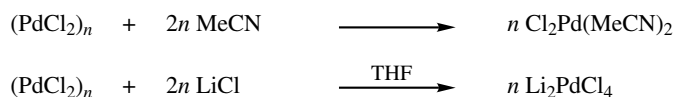
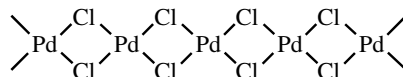
Some of the commercially available Pd(II) complexes containing oxygen ligands are shown in **Table 2**.

Palladium oxide (PdO) can be prepared from Pd and O<sub>2</sub>. It may be obtained as a yellow gelatinous hydrate (PdO · *n* H<sub>2</sub>O) that dries to a brown and less hydrated species. Upon further heating it eventually becomes black, but it cannot be completely dehydrated without loss of oxygen.<sup>[1]</sup>

**TABLE 1. Some Commercially Available Pd(II) Complexes Containing Halogen Ligands<sup>a</sup>**

Compound	Formula Weight	Other Descriptions
PdCl <sub>2</sub>	177.31	Rust-colored solid
PdBr <sub>2</sub>	266.22	Black solid
PdI <sub>2</sub>	360.21	Black solid
Li <sub>2</sub> PdCl <sub>4</sub> · n H <sub>2</sub> O	262.09 + n H <sub>2</sub> O	Hygroscopic
Na <sub>2</sub> PdCl <sub>4</sub>	294.19	
K <sub>2</sub> PdCl <sub>4</sub>	326.41	Brown powder
K <sub>2</sub> PdBr <sub>4</sub>	504.21	Reddish-brown powder
(NH <sub>4</sub> ) <sub>2</sub> PdCl <sub>4</sub>	284.29	Reddish-brown powder

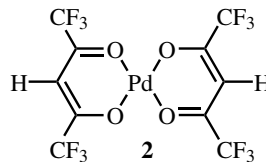
<sup>a</sup>(i) *Aldrich Catalog Handbook of Fine Chemicals* **1998–1999**. (ii) *Strem Chemicals, Inc. Catalog* (No. 17) **1997–1999**.

**Scheme 1****1**

By far the most widely used Pd—O compound is Pd(OAc)<sub>2</sub>. This compound can be prepared by the treatment of Pd sponge or PdO(H<sub>2</sub>O)<sub>n</sub> with HOAc or glacial HOAc. It may also be prepared by the reaction of Pd(NO<sub>3</sub>)<sub>2</sub> with glacial HOAc. Pd(NO<sub>3</sub>)<sub>2</sub> may, in turn, be prepared by the reaction of Pd with HNO<sub>3</sub>. Various other Pd—O compounds [e.g., Pd(acac)<sub>2</sub>] may be prepared from Pd(OAc)<sub>2</sub> and PdX<sub>2</sub> (X = Cl or Br) by appropriate substitution reactions.

**TABLE 2. Some Commercially Available Pd(II) Complexes Containing Oxygen Ligands<sup>a</sup>**

Compound	Formula Weight	Other Descriptions
PdO	122.40	Black Powder, mp 870 °C
Pd(OH) <sub>2</sub> on C	—	Pearlman's catalyst <sup>b</sup>
Pd(OAc) <sub>2</sub>	224.49	Orange-brown solid, mp 205 °C(dec.)
Pd(OCOC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	252.55	
Pd(OCOCF <sub>3</sub> ) <sub>2</sub>	332.43	
Pd(acac) <sub>2</sub>	301.62	
Pd[OC(CF <sub>3</sub> )=CHOCOCF <sub>3</sub> ] <sub>2</sub> ( <b>2</b> )	520.51	
Pd(NO <sub>3</sub> ) <sub>3</sub> in HNO <sub>3</sub>		
PdSO <sub>4</sub>	202.46	



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

Palladium hydroxide on C, typically 20 wt% Pd (dry basis), is commonly called Pearlman's catalyst.<sup>[2]</sup> It has been reported to be particularly active for hydrogenolysis of benzyl–nitrogen bonds and effective even in cases where other Pd/C catalysts are not.

## REFERENCES

- [1] F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 5th ed., Wiley, New York, **1988**, 1455 pp.
- [2] M. Fieser, *Reag. Org. Synth.*, **1992**, 16, 269.