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Note

Missing link: PCP pincer ligands containing P–N bonds and their Pd complexes

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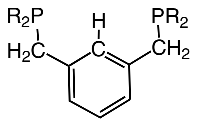
Abstract

New PCP ligands in which the phosphine donor arms are connected to the central aromatic ring via NH moieties and their (PCP)PdCl complexes have been prepared. One such (PCP)PdCl complex was characterized by X-ray diffractometry in the solid state. The (PCP)PdCl complexes are exceptionally robust towards oxygen and water despite the presence of P–N bonds.

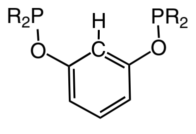
Keywords: Palladium; Pincer; PCP; Phosphine

1. Introduction

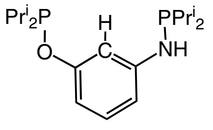
PCP pincer ligands were first introduced by Moulton and Shaw in the 1970's [1]. This class of ligands has attracted a considerable amount of attention. A comprehensive review appeared in 2003 [2]. The major attraction of the PCP ligands (indeed, of many other pincer ligands as well) is their ability to give rise to exceptionally robust metal complexes. The outstanding stability of pincer-ligated complexes permits their use as catalysts under drastic conditions [2]. Examples of applications that have benefited from the use of PCP ligands include the Heck coupling [3], alkane dehydrogenation [4], and transfer hydrogenation [5]. The first PCP ligands had the structure **A**, in which the phosphine donor arms were connected to the central aromatic ring via CH_2 groups [1]. Carbon-based linkers other than CH_2 have also been used since [6]. A more recent modification is the bis(phosphinite) PCP ligands (**B**) in which the phosphine donor arms are connected to the central aromatic ring via O links [3b,3c,4a]. A mixed PCP ligand with one CH_2 and one O link has also been synthesized [7]. Conspicuously missing from this array are PCP ligands in which the phosphine donor arms are connected to the central aromatic ring via NH or NR linkers. Here we present a straightforward synthesis of two such new PCP ligands **1** and **2** and their Pd complexes.



A



B



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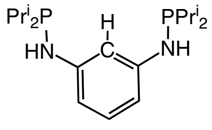

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2. Results and discussion

2.1. Ligand synthesis

Ligands of type **B** are prepared starting from resorcinol and their syntheses are generally more facile and econom-

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ical than the syntheses of **A** because P–O bonds can be made more dependably than the P–C bonds. P–N bonds can also be made in a straightforward fashion from amines, base, and R_2P–Cl. We surmised that ligands **1** and **2** should be easily accessible starting from the commercially available *m*-aminophenol (**3**) and *m*-phenylenediamine (**4**).

Deprotonation of **3** or **4** with *n*-BuLi in THF at ambient temperature, followed by addition of $^{i}Pr_2PCl$ and heating at 85 °C for 12 h resulted in >95% of **1** or **2** with >95% purity (NMR evidence in situ) [8]. Thermolysis is necessary to ensure maximum conversion to the desired products. In some of the crude mixtures at intermediate stages of the reaction, we have observed impurities displaying large J_{PP} values (270–300 Hz) that we tentatively ascribe to compounds containing substructure **8** (Scheme 1) [9]. Compound **2** was isolated in 75% yield as a colorless solid upon work-up. Compound **1** could only be obtained as an oil but of sufficient purity (>95% pure by NMR) for subsequent use.

2.2. Preparation of Pd complexes

Ligand **2** reacted with (COD)$PdCl_2$ in C_6D_6 in the time of mixing at 22 °C liberating 1,5-COD and resulting in a new product tentatively identified as **7**. Subsequent addition of Et_3N had no immediate effect on the composition of the mixture. At 22 °C, even 24 h after the addition of Et_3N, only <5% of **6** was observed. Thermolysis of this mixture at 90 °C for 2 h resulted in only ca. 25% conversion to **6**. Finally, further thermolysis of this mixture for 3 d at 100 °C resulted in the near-quantitative conversion to **6**.

Ligands **1** and **2** can be successfully used without isolation (as-prepared solutions in THF) for the synthesis of **5** or **6**. Addition of (COD)$PdCl_2$ and Et_3N to the crude THF solutions of **1** or **2** followed by thermolysis (105 °C, 13 h) results in high-yield formation of **5** or **6**.

2.3. Stability towards hydrolysis

While P–N bonds are easy to construct, they are also more susceptible to cleavage via hydrolysis, compared with P–C and P–O bonds. The free ligands **1** and **2** are without doubt air- and/or moisture-sensitive. We have not pursued the characterization of the decomposition products, but it is clear that these ligands rapidly degrade in wet solvents in the air from the appearance of new (unidentified) resonances in the ^{31}P NMR spectra. On the other hand, the Pd complexes **5**/**6** are extremely robust. Solutions of **5** or **6** in wet $CDCl_3$ showed no decomposition in the air for 3 days. Furthermore, thermolysis of **5** or **6** in CD_3CN in the presence of 35-fold molar excess of water at 110 °C for 12 h did not lead to any detectable signs of decomposition either. It is rather remarkable how the coordination to the metal and the tight pincer backbone prevent the normally facile P–N hydrolysis [10].

2.4. Structural analysis

The structure of **6** (Fig. 1) was determined in an X-ray diffraction study of a crystal obtained by slow cooling of a hot, wet acetonitrile solution of **6**. The geometry about Pd is approximately square-planar. The structure of **6** can be compared to the structures of **9** [3b] and **10** [11] (the structure of the $^{i}Pr_2P$ analogue is not available). The average Pd–P distances in all three compounds are approximately the same within the error of measurement. The pincer bite angle (P–Pd–P) increases from **9** to **6** and **10**. This is likely a consequence of the size of the linker ($O < NH < CH_2$). Interestingly, the Pd–C and Pd–Cl

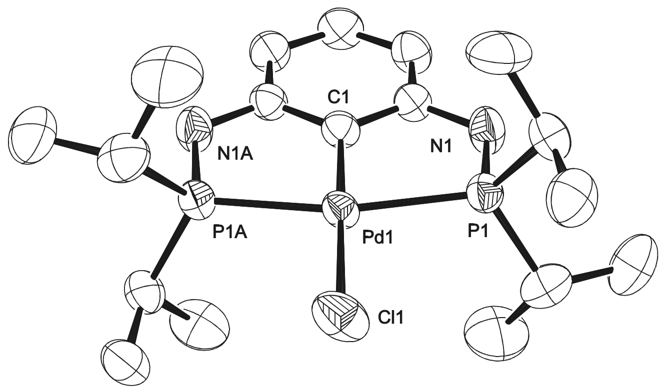
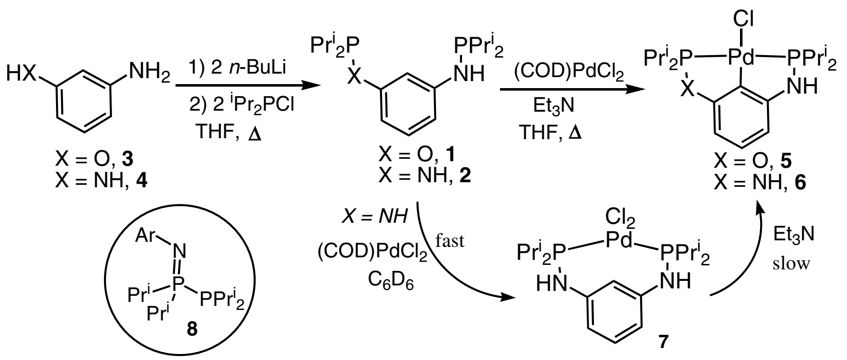


Fig. 1. ORTEP drawing (50% thermal ellipsoids) of (PCP)PdCl (**6**) showing selected atom labeling. Hydrogen atoms and the acetonitrile molecule are omitted for clarity.



Scheme 1.