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

Oleg V. Ozerov *, Chengyun Guo, Bruce M. Foxman

Department of Chemistry, Brandeis University, MS015, 415 South Street, Waltham, MA 02454, United States

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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.
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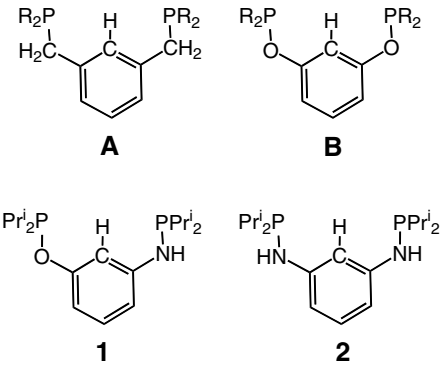
Keywords: Palladium; Pincer; PCP; Phosphine

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.



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-

* Corresponding author.
E-mail address: ozerov@brandeis.edu (O.V. Ozerov).

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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

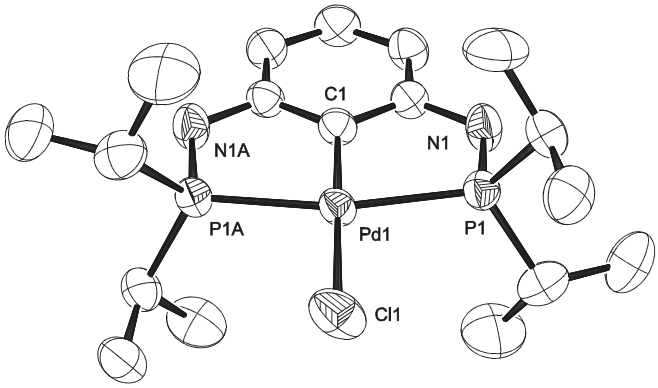
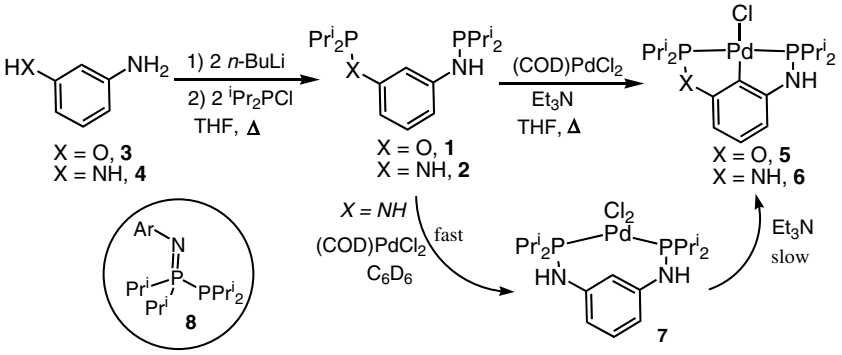
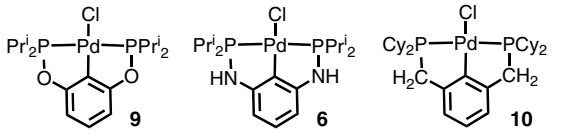


Fig. 1. ORTEP drawing (50% thermal ellipsoids) of (PCP)PdCl (**6**) showing selected atom labeling. Hydrogen atoms and the acetonitrile molecule are omitted for clarity.



Scheme 1.



	9	6	10
Pd - P	2.28	2.2832(5)	2.28
Pd - C	1.97	2.000(3)	2.01
Pd - Cl	2.37	2.3941(9)	2.43
P - Pd - P	160.1	163.85(3)	165.5

Fig. 2. Comparison of the structural features (bond distances in angstrom (Å) and the P–Pd–P angle in degrees) of the (PCP)PdCl compounds **4** (this work), **9** [3b], and **10** [11] (Cy = cyclohexyl). Average and/or rounded values are given for **9** and **10**.

bonds become progressively longer in the same series (see Fig. 2).

The crystal of **6** contained one equivalent of CH_3CN per each Pd. The CH_3CN molecule lies on a crystallographic symmetry element and the N of CH_3CN is equidistant from the two NH units of two different molecules of **6**. However, the (MeC)N···N(H) separation is ca. 3.2 Å; too long for a certifiable hydrogen bond.

3. Conclusion

In summary, we have prepared new PCP ligands in which the phosphine donor arms are connected to the central aromatic ring via NH moieties. New (PCP)PdCl complexes were prepared and **6** was structurally characterized in the solid state. Similar to other (PCP)PdCl complexes, the Pd complexes of the new PCP ligands are exceptionally robust towards oxygen and water despite the presence of P–N bonds.

4. Experimental

4.1. General considerations

Unless specified otherwise, all manipulations were performed under an argon atmosphere using standard Schlenk line or glovebox techniques. Toluene, ethyl ether, C_6D_6, THF, and isooctane were dried over NaK/Ph_2CO/18-crown-6, distilled or vacuum transferred and stored over molecular sieves in an Ar-filled glovebox. PhF and CH_2Cl_2 were dried with and distilled from CaH_2. Diisopropylchlorophosphine (Aldrich) was vacuum transferred, leaving a small amount of yellow oil behind. All other chemicals were used as received from commercial vendors. NMR spectra were recorded on a Varian iNova 400 (^{1}H NMR, 399.755 MHz; ^{13}C NMR, 100.518 MHz; ^{31}P NMR, 161.822 MHz) spectrometer. Chemical shifts are reported in δ (ppm). For ^{1}H and ^{13}C NMR spectra, the residual solvent peak was used as an internal reference. ^{31}P NMR spectra were referenced externally using 85% H_3PO_4 at δ 0 ppm. Elemental analyses were performed by CALI Labs, Inc. (Parsippany, NJ).

Caution! In our extensive experience, heating screw-capped or J. Young NMR tubes (Wilmad) or screw-capped (PTFE liner) glass tubes containing C_6D_6 or THF solutions as described throughout up to 100–110 °C has not led to tube failure. However, heating volatile flammable liquids in closed glass vessels should be done with utmost caution. We use silicon oil baths for heating and only allow for partial (< 1/3) immersion of the vessel. This should be done only in a fume hood, away from other flammable materials.

4.2. Preparation of *m*-$C_6H_4(NHPPr^i_2)(OPPr^i_2)$ (*1*)

m-Aminophenol (26.4 mg, 242 μmol) was dissolved in 5 mL of THF in a culture tube equipped with a PTFE-lined cap and was treated with *n*-BuLi (313 μL of 1.6 M solution in hexanes, 500 μmol) at 22 °C. A slightly turbid red-colored solution formed rapidly. To this, ^{i}Pr$_2$PCl (95 μL, 600 μmol) was added. The color dissipated and apparently clear yellow solution formed. This was heated in an 85 °C oil bath for 12 h. ^{31}P NMR analysis of an aliquot showed complete conversion to **1** (with some small excess of ^{i}Pr$_2$PCl observed). The volatiles were removed in vacuo, the residue was dissolved in 1 mL of isooctane and then the volatiles were removed in vacuo again. The residue was dissolved in pentane and filtered through a plug of Celite. The volatiles were removed from the filtrate in vacuo leaving behind a colorless oil. It was dissolved in $CDCl_3$ for NMR characterization (>95% pure). ^{1}H NMR ($CDCl_3$): δ 6.99 (apparent t, 1H, $J_{HH} = 8$ Hz, *para*-CH_{Aryl}), 6.73 (apparent t, 1H, $J_{HP} = 1.5$ Hz, *ipso*-CH_{Aryl}), 6.58 (d, 1H, $J_{HH} = 8$ Hz, *meta*-CH_{Aryl}), 6.48 (d, 1H, $J_{HH} = 8$ Hz, *meta*-CH_{Aryl}), 3.67 (d, 1H, $J_{HP} = 11$ Hz, NH), 1.89 (septet of doublets, 2H, $J_{HH} = 7$ Hz, $J_{HP} = 2$ Hz, OP–C*H*Me$_2$), 1.71 (septet of doublets, 2H, $J_{HH} = 7$ Hz, $J_{HP} = 1.5$ Hz, HNP–C*H*Me$_2$), 1.16 (dd, 6H, $J_{HP} = 11$ Hz, $J_{HH} = 7$ Hz, OP–CH*Me*$_2$), 1.09 (dd, 6H, $J_{HP} = 13$ Hz, $J_{HH} = 7$ Hz, OP–H*Me*$_2$), 1.06 (dd, 6H, $J_{HP} = 1.5$ Hz, $J_{HH} = 7$ Hz, HNP–CH*Me*$_2$), 1.04 (dd, 6H, $J_{HP} = 3$ Hz, $J_{HH} = 7$ Hz, OP–CH*Me*$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 160.1 (d, $J_{CP} = 9$ Hz, *ortho*-*C*–OP), 150.1 (d, $J_{CP} = 16$ Hz, *ortho*-*C*-NHP), 129.4 (s, *para*-*C*H$_{Aryl}$), 109.3 (d, $J_{CP} = 12$ Hz, *meta*-*C*H$_{Aryl}$), 108.4 (d, $J_{CP} = 11$ Hz, *meta*-*C*H$_{Aryl}$), 106.1 (t, $J_{CP} = 12$ Hz, *ipso*-CH$_{Aryl}$), 28.2 (d, $J_{CP} = 17$ Hz, *C*HMe$_2$), 26.6 (d, $J_{CP} = 11$ Hz, *C*HMe$_2$), 18.7 (d, $J_{CP} = 19$ Hz, CH*Me*$_2$), 17.7 (d, $J_{CP} = 20$ Hz, CH*Me*$_2$), 17.0 (two doublets overlapping, 8 Hz, CH*Me*$_2$). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 147.5 (s, O*P*), 48.9 (s, HN*P*).

4.3. Preparation of *m*-$C_6H_4(NHPPr^i_2)_2$ (*2*)

m-Phenylenediamine (1.00 g, 9.26 mmol) was dissolved in 40 mL of THF in a flask equipped with a PTFE vacuum valve. *n*-BuLi (7.6 mL of 1.6 M solution in hexanes, 19.0 mmol) was added to it. The yellow mixture was stirred for 10 min, then some 10% of the volume was removed by

evaporation in vacuo (to remove butane). Then $^{i}Pr_2PCl$ was added. The PTFE vacuum valve was closed and the mixture was heated at 80 °C overnight. ^{31}P NMR analysis of an aliquot showed <5% excess of $^{i}Pr_2PCl$ and **2** only. The volatiles were removed in vacuo, and the residue was twice triturated with isooctane. The solid was then extracted with C_6H_6 and filtered (ca. 20 mL used). Ca. 5 mL of toluene was added to this mixture and the volatiles were removed in vacuo to yield an oily mass. To this oily residue, ca. 3 mL Et_2O and ca. 20 mL of pentane was added and the flask was placed into the freezer (−35 °C). The next day the solids were filtered off, washed with pentane at 22 °C on the glass frit and dried in vacuo to yield 0.49 g (15%) of **2**. Compound **2** is moderately soluble in pentane. The combined washings were reduced in volume to ca. 20 mL in vacuo and placed into the freezer. After 4 h, the solid precipitate was quickly filtered off, washed with *cold* pentane, and dried in vacuo to give 1.44 g (45%) of **2**. Analogously, the third fraction was obtained (0.45 g, 15%). Total isolated yield: 2.42 g (75%). The obtained material was colorless and >95% pure by NMR. ^1H NMR ($CDCl_3$): δ 6.90 (t, 1H, $J_{HH} = 8$ Hz, *para*-CH_{Aryl}), 6.61 (apparent quintet (tt), 1H, $J_{HP} \approx J_{HH} = 2$ Hz, *ipso*-CH_{Aryl}), 6.34 (apparent dt, 2H, $J_{HP} = 8$ Hz, $J_{HP} \approx J_{HH} = 2$ Hz, *meta*-CH_{Aryl}), 3.60 (d, 2H, $J_{HP} = 11$ Hz, NH), 1.70 (septet of doublets, 4H, $J_{HH} = 7$ Hz, $J_{HP} = 2$ Hz, HNP–C*H*Me_2), 1.06 (dd, 12H, $J_{HP} = 2$ Hz, $J_{HH} = 7$ Hz, CH*Me*$_2$), 1.03 (dd, 12H, $J_{HP} = 3$ Hz, $J_{HH} = 7$ Hz, CH*Me*$_2$). ^1H NMR (C_6D_6): δ 7.04 (t, 1H, $J_{HH} = 8$ Hz, *para*-CH_{Aryl}), 6.97 (br t, 1H, $J_{HP} = 2$ Hz, *ipso*-CH_{Aryl}), 6.52 (br d, 2H, $J_{HP} = 8$ Hz, *meta*-CH_{Aryl}), 3.33 (d, 2H, $J_{HP} = 11$ Hz, NH), 1.42 (septet of doublets, 4H, $J_{HH} = 7$ Hz, $J_{HP} = 2$ Hz, HNP–C*H*Me_2), 0.96 (dd, 12H, $J_{HP} = 16$ Hz, $J_{HH} = 7$ Hz, CH*Me*$_2$), 0.90 (dd, 12H, $J_{HP} = 11$ Hz, $J_{HH} = 7$ Hz, CH*Me*$_2$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 150.4 (d, $J_{CP} = 16$ Hz, *ortho*-*C*-NHP), 130.0 (s, *para*-*C*H_{Aryl}), 107.3 (d, $J_{CP} = 12$ Hz, *meta*-*C*H_{Aryl}), 103.9 (t, $J_{CP} = 13$ Hz, *ipso*-CH_{Aryl}), 26.9 (d, $J_{CP} = 13$ Hz, *C*HMe_2), 19.0 (d, $J_{CP} = 21$ Hz, CH*Me*$_2$), 17.2 (d, 8 Hz, CH*Me*$_2$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 48.0 (s, HN*P*). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 47.3 (s, HN*P*).

4.4. Preparation of (m-$C_6H_3(NHPPr^i_2)(OPPr^i_2)$)PdCl (5)

It is possible to use isolated **1** for the synthesis of **5**, however it is not necessary. *m*-Aminophenol (300 mg, 2.75 mmol) was dissolved in 10 mL of THF in a culture tube equipped with a PTFE-lined cap and was treated with *n*-BuLi (2.20 mL of 1.6 M solution in hexanes, 5.50 mmol) at 22 °C. A copious amount of precipitate formed rapidly. To this mixture, $^{i}Pr_2PCl$ (0.95 mL, 6.0 mmol) was added. The resultant mixture was heated in a 60 °C oil bath for 12 h. Then, (COD)$PdCl_2$ (0.74 g, 2.6 mmol), Et_3N (0.45 mL, 3.2 mmol), and 10 mL of toluene was added. This mixture was heated in a closed culture tube at 105 °C for 13 h. NMR analysis of an aliquot showed primarily **5** and an excess (~10%) of **1**. Ca. 5 mL of pentane was added to the mixture and it was filtered through a layer of Celite on a glass frit. The residue was extracted with ether and the washings filtered as well. The volatiles were removed in vacuo from the combined washings, and the residue was dissolved in PhF/CH_2Cl_2. This solution was filtered to remove a small amount of insolubles and then the volatiles were removed in vacuo. The residue was treated with 2 mL of Et_2O, 1 mL of PhF and then CH_2Cl_2in small portions until complete dissolution. The resultant solution was placed into the freezer (−35 °C). The next day the white precipitate was filtered off, washed with ether on the glass frit, and dried in vacuo to give 0.96 g (76% based on Pd) of **5**. ^1H NMR (C_6D_6): δ 6.91 (apparent t, 1H, $J_{HH} = 8$ Hz, *para*-CH_{Aryl}), 6.61 (d, 1H, $J_{HH} = 8$ Hz, *meta*-CH_{Aryl}), 6.17 (d, 1H, $J_{HH} = 8$ Hz, *meta*-CH_{Aryl}), 3.25 (br s, 1H, NH), 2.17 (m, 2H, C*H*Me_2), 1.93 (m, 2H, HNP–C*H*Me_2), 1.34 (dd, 6H, $J_{HP} = 4$ Hz, $J_{HH} = 7$ Hz, OP–CH*Me*$_2$), 1.30 (dd, 6H, $J_{HP} = 3$ Hz, $J_{HH} = 7$ Hz, HNP–CH*Me*$_2$), 1.11 (dd, 6H, $J_{HP} = 14$ Hz, $J_{HH} = 7$ Hz, OP–CH*Me*$_2$), 0.90 (dd, 6H, $J_{HP} = 14$ Hz, $J_{HH} = 7$ Hz, HNP–CH*Me*$_2$). ^1H NMR ($CDCl_3$): δ 6.82 (apparent t, 1H, $J_{HH} = 8$ Hz, *para*-CH_{Aryl}), 6.31 (d, 1H, $J_{HH} = 8$ Hz, *meta*-CH_{Aryl}), 6.30 (d, 1H, $J_{HH} = 8$ Hz, *meta*-CH_{Aryl}), 4.18 (br s, 1H, NH), 2.41 (m(9), 2H, $J_{HP} \approx J_{HH} = 7$ Hz, C*H*Me_2), 2.33 (m, 2H, C*H*Me_2), 1.18 – 1.39 (four dd overlapping, 24H, CH*Me*$_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 166.6 (dd, $J_{CP} = 9$ Hz and 3 Hz, *ortho*-*C*–OP), 157.2 (dd, $J_{CP} = 23$ Hz and 2 Hz, *ortho*-*C*–NHP), 127.4 (s, *para*-*C*H_{Aryl}), 126.5 (s, *ipso*-C_{Aryl}–Pd), 104.2 (d, $J_{CP} = 16$ Hz, *meta*-*C*H_{Aryl}), 103.1 (d, $J_{CP} = 15$ Hz, *meta*-*C*H_{Aryl}), 28.6 (dd, $J_{CP} =$ 18 Hz and 5 Hz, *C*HMe_2), 27.2 (dd, $J_{CP} = 21$ Hz and 4 Hz, *C*HMe_2), 18.0 (d, $J_{CP} = 7$ Hz, CH*Me*$_2$), 17.3 (d, $J_{CP} = 7$ Hz, CH*Me*$_2$), 17.0 (s, CH*Me*$_2$), 16.7 (s, CH*Me*$_2$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 187.1 (d, $J_{PP} = 405$ Hz, O*P*), 113.0 (d, $J_{PP} = 405$ Hz, HN*P*). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 186.8 (d, $J_{PP} = 415$ Hz, O*P*), 112.4 (d, $J_{PP} = 415$ Hz, HN*P*). Elemental Anal. Calc. (Found) for $C_{18}H_{32}ClNOP_2Pd$: C, 44.83 (45.13); H, 6.69 (6.61); N, 2.90 (3.25)%.

4.5. Preparation of (m-$C_6H_3(NHPPr^i_2)_2$)PdCl (6)

It is possible to use isolated **2** for the synthesis of **6**, however it is not necessary. *m*-Phenylenediamine (297 mg, 2.75 mmol) was dissolved in ca. 20 mL of THF in a culture tube. *n*-BuLi (2.20 mL of 1.6 M solution in hexanes, 5.50 mmol) was added while stirring vigorously. Upon the completion of addition, the mixture was stirred for 3 min, followed by addition of $^{i}Pr_2PCl$ (0.95 mL, 6.0 mmol). The tube was closed and placed in a 105 °C oil bath for 30 min. Then, (COD)$PdCl_2$ (0.74 g, 2.6 mmol), Et_3N (two drops), anhydrous K_2CO_3 (0.76 g, 5.5 mmol) and 10 mL of toluene was added. This mixture was heated in a closed culture tube at 105 °C for 13 h. The resultant mixture was filtered with the aid of Celite and the volatiles were removed from the filtrate in vacuo. The residue was dissolved in CH_2Cl_2 (cloudy solution). The insolubles were

filtered off and the volatiles were removed from the filtrate. The residue was dissolved in ca. 20 mL of an Et_2O/CH_2Cl_2 mixture and set to the −35 °C freezer. The next day the yellowish solid was collected and dried (0.84 g, 60%). Similar treatment of supernatant produced an additional 0.20 g (15%). However, this material was contaminated by traces of Et_3NHCl. In the air, the solids were placed in a culture tube and treated with 20 mL of CH_3CN and 1 mL of H_2O. Upon heating to ca. 90 °C (closed tube), the solids completely dissolved. This was allowed to stand at ambient temperature for 2 h, and then was placed into a −25 °C freezer overnight. The next day 0.64 g (49%) of large regular shaped crystals was collected. Similar treatment of the supernatant yielded an additional 0.25 g (19%). One of these crystals was selected for an X-ray diffraction study. The material thus obtained contains 1 equiv of CH_3CN per Pd.

^1H NMR (C_6D_6): δ 6.97 (t, 1H, $J_{HH} = 8$ Hz, *para*-CH_{Aryl}), 6.12 (d, 2H, $J_{HH} = 8$ Hz, *meta*-CH_{Aryl}), 3.23 (br s, 2H, NH), 1.42 (m, 4H, HNP–C*H*Me_2), 1.35 (apparent quartet (dvt), 12H, 8 Hz, CH*Me*$_2$), 0.93 (apparent quartet (dvt), 12H, 8 Hz, CH*Me*$_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 157.6 (br s, *ortho*-*C*-NHP), 127.1 (br s, *para*-*C*H_{Aryl}), 123.8 (s, *ipso*-C_{Aryl}-Pd), 102.0 (br s, *meta*-*C*H_{Aryl}), 27.2 (vt, $J_{CP} = 13$ Hz, *C*HMe_2), 18.0 (vt, $J_{CP} = 3$ Hz, CH*Me*$_2$), 17.0 (s, CH*Me*$_2$). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 112.5 (s, HN*P*). Elemental Anal. Calc. (Found) for $C_{18}H_{33}ClN_2P_2Pd(CH_3CN)$: C, 45.99 (46.00); H, 6.95 (7.06); N, 8.04 (7.81)%.

4.6. Observation of (m-$C_6H_4(NHPPr^i_2)_2$)$PdCl_2$ (7) and its conversion to 6

A J. Young NMR tube was charged with **2** (17.0 mg, 50 μmol), (COD)$PdCl_2$ (14.3 mg, 50 μmol) and 0.6 mL of C_6D_6. A yellow solution was formed. NMR analysis after 1 h at 22 °C showed the predominant formation of **7** and free 1,5-cyclooctadiene. Only a small amount (<3%) of **6** was observed. To this solution Et_3N (8.3 μL, 60 μmol) was added. After 18 h at 22 °C, there was little change in the composition of the resultant solution. The NMR tube was then placed into a 90 °C oil bath for 2 h. ^{31}P NMR analysis revealed ca. 25% conversion to **6**. The heating was continued for 3 d at 110 °C and after that time the conversion to **6** was >98% by ^{31}P NMR. NMR data for **7** follow. ^1H NMR (C_6D_6): δ 6.87 (br s, 1H, *ipso*-CH_{Aryl}), 6.86 (t, 1H, $J_{HH} = 8$ Hz, *para*-CH_{Aryl}), 6.56 (d, 2H, $J_{HH} = 8$ Hz, *meta*-CH_{Aryl}), 6.43 (t, 2H, 6 Hz, NH), 2.86 (m, 4H, HNP–C*H*Me_2), 1.44 (apparent quartet (dvt), 12H, 8 Hz, CH*Me*$_2$), 1.23 (apparent quartet (dvt), 12H, 8 Hz, CH*Me*$_2$). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 74.1 (s, HN*P*).

Acknowledgements

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Appendix. Supporting information available

Crystallographic data for the structural analysis of **6** · CH_3CN have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 606911. This information is available free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk). Graphical representations of the ^1H NMR spectra of **1** and **2** are available as Supporting Information online. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.07.018.

References

[1] C.J. Moulton, B.L. Shaw, J. Chem. Soc., Dalton Trans. (1976) 1020.
[2] M.E. van der Boom, D. Milstein, Chem. Rev. 103 (2003) 1759.
[3] (a) D. Morales-Morales, R. Redon, C. Yung, C.M. Jensen, Chem. Commun. (2000) 1619;
(b) D. Morales-Morales, C. Grause, K. Kasaoka, R. Redon, R.E. Cramer, C.M. Jensen, Inorg. Chim. Acta 300–302 (2000) 958;
(c) F. Miyazaki, K. Yamaguchi, M. Shibasaki, Tetrahedron Lett. 40 (1999) 7379;
(d) M. Ohff, A. Ohff, M.E. van der Boom, D. Milstein, J. Am. Chem. Soc. 119 (1997) 11687.
[4] (a) I. Gottker-Schnetmann, P. White, M. Brookhart, J. Am. Chem. Soc. 126 (2004) 1804;
(b) K. Krogh-Jespersen, M. Czerw, K. Zhu, B. Singh, M. Kanzelberger, N. Darji, P.D. Achord, K.B. Renkema, A.S. Goldman, J. Am. Chem. Soc. 124 (2002) 10797;
(c) F. Liu, E.B. Pak, B. Singh, C.M. Jensen, A.S. Goldman, J. Am. Chem. Soc. 121 (1999) 4086;
(d) M.W. Haenel, S. Oevers, K. Angermund, W.C. Kaska, H.-J. Fan, M.B. Hall, Angew. Chem., Int. Ed. Engl. 40 (2001) 3596.
[5] P. Dani, T. Karlen, R.A. Gossage, S. Gladiali, G. van Koten, Angew. Chem., Int. Ed. Engl. 39 (2000) 743.
[6] (a) P. Dani, M. Albrecht, G.P.M. van Klink, G. van Koten, Organometallics 19 (2000) 4468;
(b) F. Gorla, A. Togni, L.M. Venanzi, A. Albinati, F. Lianza, Organometallics 13 (1994) 1607.
[7] M.R. Eberhard, S. Matsukawa, Y. Yamamoto, C.M. Jensen, J. Organomet. Chem. 687 (2003) 185.
[8] In our experience, ligand **B** where R = ^{i}Pr can be prepared from resorcinol, $^i Pr_2PCl$ and Et_3N in THF at 70–80 °C in ca. 15 min. An analogous approach (Et_3N instead of *n*-BuLi as base) to **1** or **2** resulted only in incomplete conversion.
[9] (a) For other cases where reactions of deprotonated aminophosphines with phosphorus electrophiles led to iminophosphorane products, see: Z. Fei, R. Scopelliti, P.J. Dyson, Dalton Trans. (2003) 2772;
(b) V.L. Foss, Y.A. Veits, T.E. Chernykh, I.F. Lutsenko, Zh. Obshch. Khim 54 (1984) 2670;
(c) V.L. Foss, Y.A. Veits, T.E. Tret'yakova, I.F. Lutsenko, Zh. Obshch. Khim. 47 (1977) 954.
[10] For an example of an aminophosphine complex stable to alcoholysis, see: P.W. Dyer, J. Fawcett, M.J. Hanton, R.D.W. Kemmitt, R. Padda, N. Singh, Dalton Trans. (2003) 104.
[11] R.J. Cross, A.R. Kennedy, K.W. Muir, J. Organomet. Chem. 487 (1995) 227.