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N−H Cleavage as a Route to Palladium Complexes of a New PNP Pincer Ligand

Lei Fan, Bruce M. Foxman, and Oleg V. Ozerov*

Department of Chemistry, Brandeis University, MS015, 415 South Street,
Waltham, Massachusetts 02454

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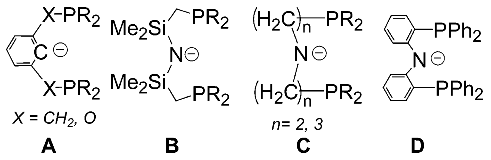
Summary: Pd halide and hydride complexes of a new PNP pincer ligand with a central diarylamido moiety can be prepared via N−H cleavage in a neutral amine/diphosphine PNP ligand. The solid-state structure of (PNP)PdCl shows a meridional PNP ligand about an approximately square-planar Pd center. (PNP)PdH hydrodehalogenates alkyl and certain aryl halides, while (PNP)PdX (X = Cl, I, H, OAc) complexes catalyze Heck coupling of ethyl acrylate with aryl halides.

Utilization of tridentate PCP pincer ligands (**A**), pioneered by Shaw in the 1970s,[1] has been increasing in recent years, owing to their potential for supporting unusual chemical transformations on transition-metal centers.[2] These complexes have been found to be efficient catalysts for alkane dehydrogenation[3] and Heck coupling,[4−6] in addition to providing a platform for seminal mechanistic studies of C−C,[7] C−N,[8] and C−O[9] bond activation.[2] The realm of *anionic* PNP ligands has been mostly limited to the family of Fryzuk's ligands (**B**).[10,11] An anionic *amido*-PNP ligand may be viewed not only as a component of an organometallic chemist's "pincer toolbox" complementary to the PCP ligands but also as a chelate version of the ubiquitous *mer,trans*-Cl(R$_3$P)$_2$ motif. A combination of soft phosphines and hard π-base amido on the same metal is often difficult to achieve without linking these into a chelate, and such a hybrid environment has been shown to lead to unusual structures and reactivity in complexes of **B**.[10] However, **B** suffers from the high oxophilicity of Si in its backbone, leading to high sensitivity to OH and other O-containing groups.[10d,11] Cyclometalation of the Si−CH$_2$−P group has also been described.[10f] PNP ligands featuring aliphatic linkers (**C**) between N and P have been reported,[12−15] yet, for these, few metal complexes utilizing a **C**-type ligand in its anionic form are known.[14] In addition, pincers **B** and **C** are more flexible than **A** and therefore do not have as strong a preference, if any, for the meridional geometry.



We were attracted to the ligand construction wherein *o*-arylene units link the amido and phosphine sites, because it offers increased rigidity and is devoid of β-hydrogens and moisture-sensitive functionalities. At the time of writing, reports were published presenting synthesis of the ligand **D** and its Ni[16a] and Rh[16b] complexes, as well as similar reasoning behind the

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* To whom correspondence should be addressed. E-mail: ozerov@brandeis.edu.

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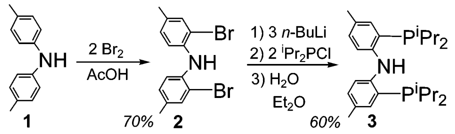
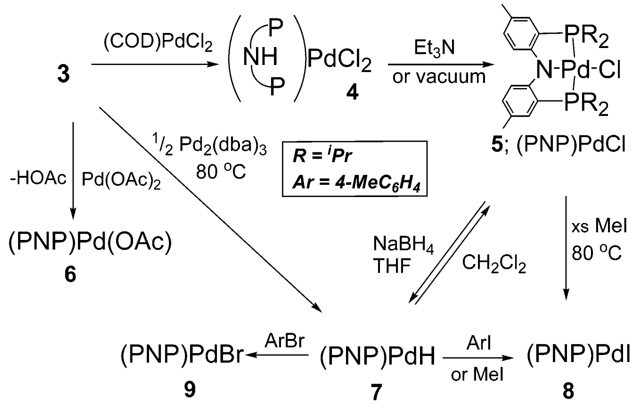
Scheme 1



Scheme 2



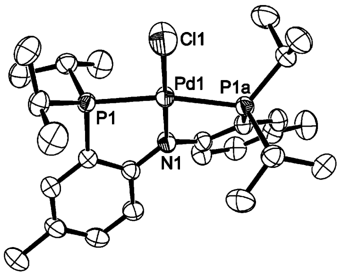


Figure 1. ORTEP drawing (50% thermal ellipsoids) of (PNP)PdCl (**5**) showing selected atom labeling. Hydrogen atoms are omitted for clarity.

perceived advantages of *o*-arylene linkers in PNP ligands. This report reflects our focus on Pd chemistry and on a PNP ligand with *alkyl* and not aryl substituents on P, with the intent to avoid the potential problem of ortho-PPh metalation, obtain a more donating ligand, confer higher solubility, and facilitate ^{1}H NMR analysis. Our synthetic approach, complementary to that of Liang et al.,[16a] uses a chlorophosphine instead of the generally more expensive and less accessible anionic bis(hydrocarbyl)phosphide reagents.

Preparation of **1**[17] and its bromination[18] have been carried out in our laboratories on a >50 g scale (Scheme 1). One-pot deprotonation and lithium−bromine exchange generates the trilithio derivative (confirmed by deuteriolysis) of **2** in situ, which is then selectively C-phosphinated with ^{i}Pr$_2$PCl to provide (PNP)H (**3**) upon hydrolysis (see the Supporting Information). We make note of the guiding examples of selective C-silylation of *ortho-C,N*-dilithioanilines and of *ortho-C,O*-dilithiophenols.[19] NMR data for **3** are consistent with an average C_{2v} symmetry in solution. The ^{31}P NMR resonance is found at −12.9 ppm, and the ^{1}H NMR resonance for the NH proton is a triplet (J_{HP} = 8 Hz) at 8.28 ppm.

The reaction between (PNP)H and (COD)PdCl$_2$ done in the presence of Et$_3$N or followed by removal of volatiles in vacuo produces **5** in good yield (Scheme 2). The solid-state structure of **5** was determined in the course of an X-ray diffraction study (Figure 1 and Supporting Information). The geometry about Pd is approximately square planar, with the P−Pd−P angle of 163.54(2)° being a consequence of the chelate constraint. Pd, N, and Cl lie on a crystallographic axis of symmetry. The Pd−P (2.2914(4) Å) and Pd−Cl (2.3157(7) Å) distances are unremarkable and are similar to those found in (**B**)PdCl.[10d,e] The Pd−N distance in **5** (2.0258(19) Å) is shorter than that in (**B**)PdCl (2.063(2) Å)[10d,e] but longer than the Pd−N(amido) distance in (NNN)PdCl (1.962(2) Å; NNN = bis(quinolinyl)amido).[20] The two aromatic rings in **5** are distinctly nonparallel, with an angle of ca. 46.6°. The environment about N is trigonal planar; this plane deviates from the coordination plane of Pd by ca. 29.2°. The twist in the chelate backbone presumably arises from the preference for a staggered conformation of phosphine donors and from repulsion between ortho hydrogens on the aromatic rings.

Solution NMR studies in C$_6$D$_6$ indicate that cyclooctadiene (COD) is displaced from (COD)PdCl$_2$ by **3** upon mixing to form a solution of **4**. Whereas vacuum or base is needed to convert **4** to **5**, reaction of **3** with Pd(OAc)$_2$ proceeds with immediate loss of HOAc and formation of **6**. HCl loss in the absence of base occurs in the reactions of neutral forms of **A** with PdCl$_2$ sources,[1,2,5,6] but this is unlike the reactivity known for the neutral (amino) forms of **C**, which form [(Ph$_2$P−NH−PPh$_2$)PdCl]Cl species that do not spontaneously lose HCl.[15] It is likely that the more basic phosphine donors and/or weaker diarylamine N−H bond are responsible for facile HCl loss from **4**. The NMR data for **4**−**6** are consistent with an average C_{2v} symmetry in solution (^{31}P NMR: δ 46.9 (**4**), 48.2 (**5**), 48.4 (**6**) ppm). The observed higher symmetry of **5** in solution (compared to C_2 in the solid state) implies a fast flipping motion of the chelate backbone that makes axial and equatorial ^{i}Pr groups equivalent on the NMR time scale. Observation of virtual triplet substructures and of a broad singlet at 10.00 ppm (N−*H*) in the ^{1}H NMR spectrum of **4** is consistent with a "PNHP" ligand with trans phosphines (large J_{PP}).[21] However, these data are insufficient to unambiguously determine the binding mode (e.g., κ^3-*P,N,P*, κ^2-*P,P*, or fast equilibrium) of the "PNHP" ligand in **4**.

Reaction of **5** with NaBH$_4$ in THF produced, upon protolytic workup, the Pd(II) hydride **7**.[22] The ^{1}H NMR signal corresponding to Pd−H is found at −10.33 ppm (t, J_{HP} = 6 Hz), and the solution NMR data indicate C_{2v} symmetry. No decomposition of **7** was detected by NMR after thermolysis in C$_6$D$_6$ (80 °C, 24 h), nor was it found

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Scheme 3

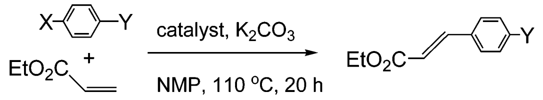

Table 1. Summary of the Heck Reaction Results[a]

	catalyst	amt of Pd (mol %)	Y[a]	X[a]	conversn (%), ^{1}H NMR	isolated yield (%)
1[b]	**8**	1	NO_2	I	>98	
2[b]	**5**	1	NO_2	I	>98	
3[b]	**6**	1	NO_2	I	>98	
4[c]	**6**	0.5	CH_3	I	>98	91
5[b]	**7**	0.5	CH_3	I	>98	95
6[a]	**6**	0.5	NO_2	Br	70	
7[b]	**6**	0.5	F	Br	2[d]	
8[b]	**6**	0.5	CH_3	Br	50	
9[b]	**8**	0.5	CH_3	Br	0	
10[b]	**6**	0.5	NO_2	Cl	20	
11[b]	**6**	0.5	CH_3	Cl	0	

[a] See Scheme 3 and the Supporting Information for experimental details. [b] Reactants mixed under Ar. [c] Reactants mixed in the air. [d] By ^{19}F NMR.

to undergo H/D exchange with solvent under these conditions. The resistance of **7** to reductive N−H elimination is apparently of thermodynamic origin—we found that $Pd_2(dba)_3$ reacts with **3** in C_6D_6 (Pd:PNP ratio 1:1, 80 °C, 10 h) quantitatively (^{31}P NMR) to form **7**. This is a rare example of N−H oxidative addition to Pd^0.[23] The formation of **7** here is likely favored by the product-adapted rigid ligand geometry and by the fact that the diarylamine N−H bond broken is relatively weak.[24]

We investigated the reactivity of **7** with organic halides in C_6D_6. **7** reacted with 1−3 equiv of MeI, CH_2Cl_2, and 4-iodonitrobenzene or 4-iodo- or 4-bromotoluene, quantitatively producing **5**, **8**, or **9**, as appropriate. In each of these reactions the organic product of a replacement of halide by H was also observed. **8** was independently synthesized by thermolysis of **5** in the presence of excess MeI. Hydrodehalogenation of haloarenes by Pd(II) hydrides has been reported.[5b,25] It is plausible that reactions of **7** with organic halides proceed by a radical mechanism,[5b,6a] although the S_N2 oxidative addition/C−H reductive elimination pathway may be more likely for MeI, the more active electrophile.[26] No reaction was observed between **7** and 4-chlorotoluene, benzotrifluoride, or fluorobenzene after 24 h at 100 °C.

Pd complexes of PCP ligands have been successfully used as catalysts in the Heck coupling or alkenes with aryl halides.[2,4−6] We found that their PNP analogues reported here (**5**−**8**) can also be used as catalysts for the Heck coupling of ethyl acrylate and iodo- and bromoarenes (Scheme 3, Table 1), including under aerobic conditions (Table 1, entry 4).

In conclusion, we have developed a new synthetic route to a diarylamine-based PNP ligand and demonstrated the preference of this rigidly meridional PNP ligand for forming square-planar Pd(II) complexes by N−H cleavage. The new (PNP)PdX (X = H, Hal, OAc) complexes catalyze the Heck coupling of iodo- and bromoarenes, including under aerobic conditions. It has been proposed that pincer Pd catalysts operate by a mechanism different from that of conventional Pd(0) catalysts.[2,5,6] Efforts are underway in our laboratories to examine the scope, applicability, and mechanistic details of the catalysis of the Heck reaction by Pd complexes of ligand **3** and related PNP ligands.

Acknowledgment. We are grateful to Brandeis University for support of this research.

Supporting Information Available: Text, figures, and tables giving experimental details, characterization data, and crystallographic information; crystallographic data are also available as CIF files. This material is available via the Internet free of charge at http://pubs.acs.org.

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