

Palladium complexes of a new phosphine-amido-siloxide pincer ligand with variable degrees of protonation



Jillian J. Davidson^a, C.M. Nagaraja^{b,1}, Chun-Hsing Chen^{b,2}, Bruce M. Foxman^b, Oleg V. Ozerov^{a,*}

^a Department of Chemistry, Texas A&M University, 3255 TAMU, College Station, TX 77842, USA

^b Department of Chemistry, Brandeis University, 415 South Street, Waltham, MA 02454, USA

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ABSTRACT

This manuscript describes the preparation of a new PN(H)SiO(H) pincer-type ligand that is based on the diarylamine backbone and links together phosphine, amine, and silanol donor sites. Treatment of PN(H)SiO(H) with Pd(acac)₂, (COD)PdCl₂, or Pd(OAc)₂ resulted in the formation of (κ²-PNSiO(H))Pd(acac) (**3**), (κ²-PN(H)SiO(H))PdCl₂ (**4**), and (κ³-PNSiO(H))PdOAc (**5**), in which the supporting ligand displays different degrees of coordination and protonation. In complex **5**, the PNSiO(H) ligand functions as a tridentate phosphine-amido-silanol pincer ligand, with additional strong hydrogen bonding between the silanol OH and one of the oxygens of the Pd-bound acetate. Complex **5** cleanly exchanged acetate for a triflate upon treatment with Me₃SiOTf, yielding (κ³-PNSiO(H))PdOTf (**6**). Analogous treatment with Me₃SiCl did not lead cleanly to the expected (κ³-PNSiO(H))PdCl (**7**), but instead ultimately to (κ²-PN(H)SiO(SiMe₃))PdCl₂ (**8**). The dianionic PNSiO ligand was accessed by reactions of **5** with base in the presence of pyridine or PMe₃ to give (κ³-PNSiO)Pd(py) (**9**) and (κ³-PNSiO)Pd(PMe₃) (**10**), respectively. Solid-state structures of **5** and **9** were established by single-crystal X-ray diffractometry and revealed square-planar geometry about Pd with tridentate coordination of the pincer ligand.

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1. Introduction

The term “pincer” has become reserved for tridentate ligands binding to a transition metal in a meridional fashion. Pincer ligands have become a staple for studies of organometallic structure and reactivity since their introduction by Shaw and coworkers in the 1970's [1]. The frequently praised advantage of this ligand class is the high thermal stability of their transition metal complexes. Perhaps equally important is the ability to introduce modular variations that preserve the overall binding mode, but can offer both steric and electronic control. Pincer ligands with a central anionic (X-type) ligand flanked by two neutral (L-type) donors are by far the most common type with a great variety of LXL combinations in the literature [2,3]. Our group has dedicated a considerable amount of effort to the studies of complexes bearing diarylamido/bis(phosphine) PNP ligands [4], as have others [5,6]. The diarylamido backbone is particularly attractive because side donor arms

connected to the *ortho*-positions are prearranged in a semi-rigid meridional binding motif. In addition to a variety of PNP ligands, symmetric monoanionic NNN [7] and SNS [8] ligands have been utilized. At the same time, Veige et al. have developed robust chemistry of trianionic, diarylamido-based ONO ligands which carry alkoxide donors in place of phosphines of PNP [9]. Of additional relevance are trianionic and redox non-innocent diarylamido-based NNN ligands [10] by Heyduk et al. The ligands of Veige and Heyduk have been applied to early transition metals, which complement the three hard, anionic donors well. We became interested in incorporating a negatively charged side donor into a diarylamido-based pincer, while retaining a phosphine as the other side donor to produce a hybrid ligand with more affinity for late transition metals. Over the last few years, convenient synthetic procedures appeared for preparing diarylamido-based pincers with different side donors. Goldberg, Kemp, and co-workers have reported PNP' ligands with different phosphine donors [11] and our group disclosed syntheses of monoanionic PNN ligands [12]. Utilizing an analogous synthetic approach we have been able to prepare a “PNSiO” ligand, in which one of the phosphines of PNP has been “replaced” with a silanol/siloxide donor. Here, we report Pd(II) coordination chemistry which showcases the capacity of the new ligand to switch between neutral, mono- and dianionic forms. Pincer complexes containing central siloxy donors with flanking

* Corresponding author.

E-mail address: ozarov@chem.tamu.edu (O.V. Ozerov).

¹ Current address: Department of Chemistry, Indian Institute of Technology Ropar, Rupnagar 140001, Punjab, India.

² Current address: Department of Chemistry, Indiana University, 800 E. Kirkwood Ave., Bloomington, IN 47405, USA.

phosphines have been previously reported [13–15]. These P(Si)OP pincer ligands were not synthesized directly but rather arose from reactions of metal-silyl bonds in silyl/bis(phosphine)PSiP complexes with water and/or O₂. Monoanionic PNO pincer complexes of Pd have been recently reported by Vigalok and co-workers [16] (see Fig. 1).

2. Results and discussion

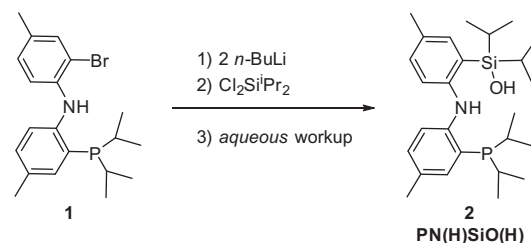
2.1. Synthesis and characterization of **2**

Compound **1** is a convenient precursor from which several types of C_s symmetric PNL ligands have been prepared [12] and it worked for the synthesis of the desired PN(H)SiO(H) ligand (**2**), as well. Treatment of **1** with two equivalents of *n*-butyllithium, followed by addition of one equivalent of Cl₂SiⁱPr₂ and subsequent aqueous workup allowed isolation of **2** as a colorless solid in a moderate yield of 66% after recrystallization from ether (see Scheme 1).

Multinuclear NMR analysis of **2** indicated C_s symmetry in solution on the NMR time scale. By ¹H NMR spectroscopy **2** shows a broad singlet at 2.80 ppm for the SiOH proton. Also in evidence were two resonances (each a doublet of doublets) belonging to the methyl groups of the isopropyl arms bound to phosphorus and an additional pair of doublets correspond to the methyl groups of the isopropyl arms bound to silicon. Additionally, six aromatic signals and one singlet corresponding to the amine proton were observed. These features indicate that the two aryl groups are “flipping” faster than the NMR timescale, resulting in time averaged C_s symmetry in solution. A singlet in the ³¹P{¹H} NMR spectrum at δ –13.7 ppm was observed, a similar chemical shift to those of free PNP or PNN ligands with a PPr₂ group reported previously [4,12].

2.2. Synthesis of Pd complexes of **2**

At first, we set out to investigate the reactions of **2** (Scheme 2) with three common PdX₂ precursors: Pd(OAc)₂, (COD)PdCl₂, and Pd(acac)₂ (COD = 1,5-cyclooctadiene, acac = acetylacetonate). The reaction between **2** and Pd(acac)₂ resulted in N–H bond activation and loss of one equivalent of acetylacetonate to form complex **3** with a [κ²-PNSiO(H)] ligand. The NMR spectroscopic features of **3** are consistent with the proposed structure. The ¹H NMR spectrum of **3** featured a broad singlet in ¹H NMR at 5.27 ppm assigned to the silanol proton which differs substantially from the chemical shift



Scheme 1.

of the same proton in **2**. It is likely that the SiOH group serves as a hydrogen bond donor to the nitrogen, one of the oxygens of the acac ligand, or perhaps Pd [17], but we have no firm evidence in support of these interactions. Treatment of **2** with (COD)PdCl₂ resulted in clean formation of a new complex assigned as **4** on the basis of spectroscopic data. The ¹H NMR spectrum of **4** featured singlets at 9.20 ppm and at 4.90 ppm assigned to the NH and SiOH protons, respectively. Complex **4** was also observed as the major product in the reaction of **2** and Pd(COD)Cl₂ in the presence of 2,6-lutidine. The non-activation of the NH bond in **4** stands in contrast to the reactivity of the PNP and PNN ligands where the central NH is easily cleaved with or even without added base [4,12]. **4** was isolated as a bright yellow solid with a yield of 45% upon workup. While in both **3** and **4**, the silanol moiety does not participate in direct bonding to Pd, the reaction of **2** with Pd(OAc)₂ produced complex **5**, in which **2** has been transformed into a monoanionic, tridentate phosphine-amido-silanol ligand. Complex **5** was isolated in 88% yield as an analytically pure purple powder upon workup. The identity of **5** was confirmed by solid-state X-ray analysis (vide infra), elemental analysis, and with NMR spectroscopic data which is fully consistent with the assignment. The key feature of the ¹H NMR spectrum is the resonance at δ ca. 14.9 ppm, arising from the SiOH proton. The downfield chemical shift is suggestive of a hydrogen bonding interaction, which is indeed evident in the solid state structure. Interestingly, the NMR spectra of **5** are indicative of C₁ symmetry in solution. The ¹H NMR spectrum is characterized by four doublets of doublets and four doublets corresponding to the isopropyl groups on P and Si, respectively. A similar loss of symmetry upon coordination was observed in square-planar PNN complexes [12] and was attributed to the increased barrier for “flipping” of the aryl rings past each other when the ligand is locked about the metal with fused 5- and 6-membered metallacycles. In contrast, square-planar complexes of PNP ligands form two 5-membered metallacycles and retain the free ligand’s symmetry.

Next, we wanted to evaluate the potential of **5** to serve as a precursor to other PNSiO(H) complexes. Silyl reagents appeared appropriate for metathesis of the acetate with other anionic ligands. This approach was feasible by use of one equiv of Me₃SiOTf to give complex **6** as a purple solid in moderate yields of 70% upon isolation (Scheme 4). ¹⁹F, ³¹P{¹H}, and ¹H NMR spectra of **6** are consistent with the formation of a square-planar complex featuring coordination of the [PNSiO(H)] ligand in an κ³-fashion to the Pd center. ¹⁹F and ³¹P{¹H} spectra featured singlets at –79.5 ppm and 88.6 ppm, respectively. Seven resonances were observed by ¹H NMR spectroscopy in the aromatic chemical shift region, which include the hydroxyl hydrogen and the aromatic protons of the diarylamido backbone. The upfield ¹H NMR chemical shift of the hydroxyl compared to that observed for **5** suggests that **6** does not exhibit a similar degree of hydrogen bonding between the hydroxyl proton and the adjacent triflate (see Scheme 3).

In contrast to the reaction of **5** with Me₃SiOTf, the analogous reaction with one equivalent of Me₃SiCl did not lead to the formation of a single anticipated product (**7**). However, in the presence of

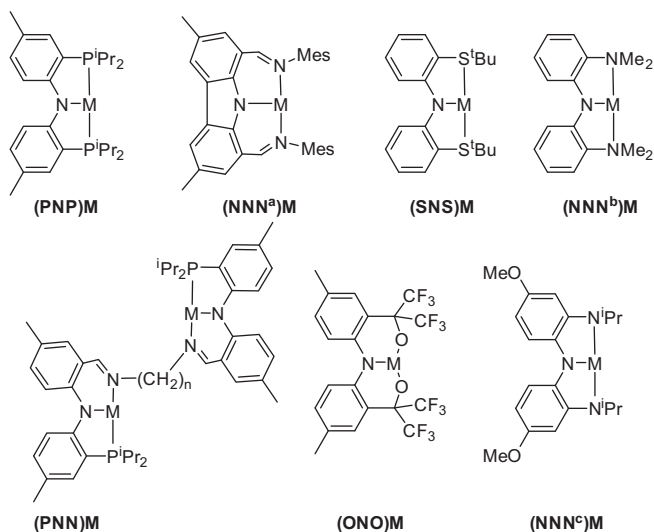


Fig. 1. Representation of various PNP, PNN, NNN, SNS, and ONO Pincer Complexes.

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