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Communication

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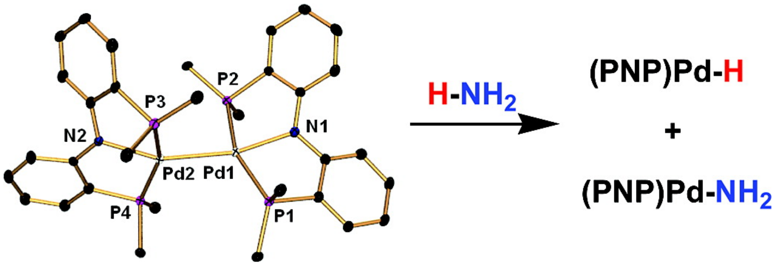

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COMMUNICATIONS

Addition of Ammonia, Water, and Dihydrogen Across a Single Pd−Pd Bond

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Catalytic utilization of ammonia in olefin hydroamination and in coupling with arenes were listed among the top ten challenges for catalysis over a decade ago, and these remain unsolved today.[1a] Transformation of ammonia (NH_3) into a hydride (H) and an amido (NH_2) ligand on a transition metal center is an attractive first step toward its incorporation of elements of NH_3 into higher value chemicals.[1b] In this report, we present an intriguing example of such activation of ammonia (as well as water and dihydrogen) by a photochemically synthesized bimetallic complex. We have previously described a variety of (^{F}PNP)Pd−alkyl compounds and their unusual thermal stability.[2] We now report that, in contrast to their thermal stability, (PNP)Pd−alkyl compounds[3] such as $\mathbf{1}^{F}$ are photolytically unstable. Exposure of solutions of (${}^{R'}$PNP)PdEt ($\mathbf{1}^{F}$/$\mathbf{1}^{Me}$) to sunlight or artificial UV light ($\lambda = 350$ nm) results in the formation of the $Pd^{I}-Pd^{I}$ dimers $\mathbf{2}^{F}$/$\mathbf{2}^{Me}$ (Figure 1, top). In situ NMR monitoring indicated >90% yield of $\mathbf{2}^{F}$ or $\mathbf{2}^{Me}$; isolated yields were in excess of 70%.

We propose that the formation of **2** proceeds via photolytic homolysis of Pd−C bonds[4] with generation of monomeric (PNP)-Pd fragments (which dimerize to form **2**) and alkyl radicals. In accord with this hypothesis, GC−MS analysis of the organic products of photolysis of (^{F}PNP)Pd(n-C_8H_{17}) ($\mathbf{3}^{F}$) in pentane revealed the presence of octane, 1-octene, and hexadecane, as would be expected if n-octyl radical were generated (Figure 1, top).

The solid-state structure of $\mathbf{2}^{Me}$ (Figure 1, middle) reveals that each Pd center is four-coordinate with a distorted square-planar environment and an unbridged Pd−Pd bond. The Pd−Pd bond length in $\mathbf{2}^{Me}$ (2.5758(4) Å) corresponds very well with the Pd−Pd distance calculated from covalent radii, (2.58 Å).[5] This distance is within the range (2.43−2.81 Å)[6] of Pd−Pd distances in other compounds that contain a single Pd−Pd σ-bond and square planar geometry about each Pd center.[7] The deviation from higher symmetry in $\mathbf{2}^{Me}$ can be illustrated by the nonzero dihedral N1−Pd1−Pd2−N2 angle of ca. 32°. However, in solution the compounds **2** display D_{2d} symmetry on the NMR time scale at ambient temperature (C_{2v} symmetry for each (PNP)Pd moiety),[8] presumably owing to fast conformational equilibration. Notably, the structure of $\mathbf{2}^{Me}$ is distinctly different from the structure of "$[(PCP)Pd]_2$" reported by Milstein et al.[9] The latter contains a Pd^0 and a Pd^{II} center and the arms of the PCP pincer are connected to different Pd centers.

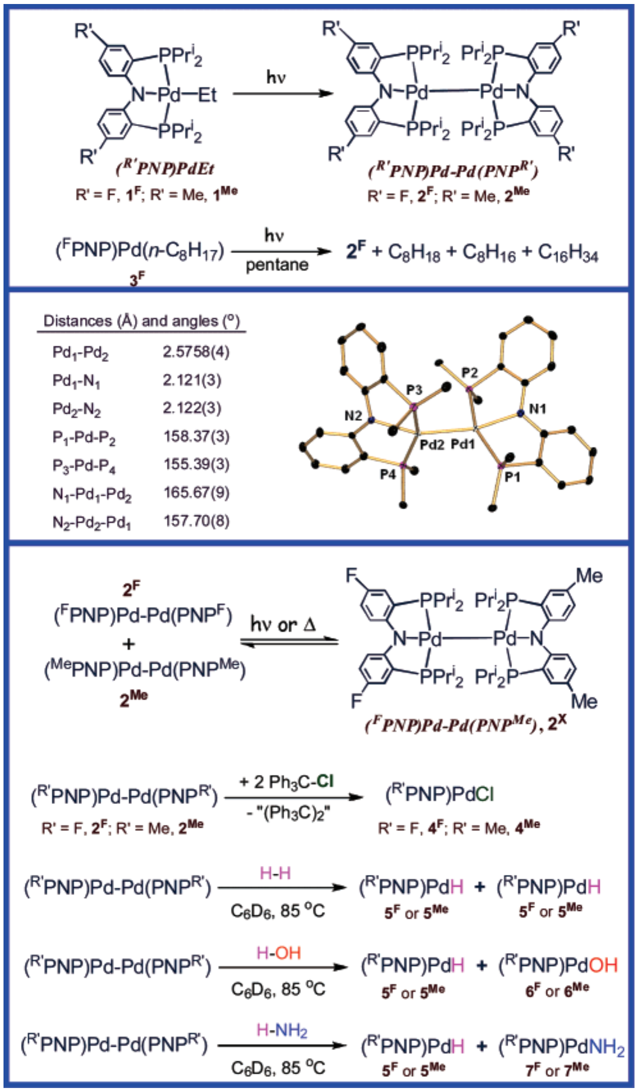

Figure 1. Synthesis (top), structure (middle), and reactivity (bottom) of the (PNP)Pd−Pd(PNP) dimers $\mathbf{2}^{F}$ and $\mathbf{2}^{Me}$. In the ORTEP graphic of the X-ray structure of $\mathbf{2}^{Me}$ (middle, 50% thermal ellipsoids), all hydrogen atoms and Me group have been omitted for clarity.

We were intrigued by whether the reversible homolytic cleavage of the Pd−Pd bond in **2** may generate a finite concentration of a monomeric (PNP)Pd species. The X-band solution EPR spectrum of compound $\mathbf{2}^{F}$ (solutions of $\mathbf{2}^{Me}$ were EPR silent) revealed a weak g_{iso} value of 2.005 with a line width of 16 G thus consistent with an organic-centered radical. It is possible that this reflects a monomeric (PNP)Pd species with a Pd^0 center and an oxidized ligand radical.[10] The concentration of (PNP)Pd, however, is small enough that the solution NMR spectra are consistent with diamagnetism of **2**, and the resonances display no dependence of chemical shifts on temperature in the 22−85 °C range.

We surmised that if (PNP)Pd monomers are reversibly produced in solution, a mixture of $\mathbf{2}^{F}$ and $\mathbf{2}^{Me}$ should produce a mixed dimer ($\mathbf{2}^{X}$). Indeed, thermolysis (75 °C, 87 h, in the dark) or photolysis ($\lambda = 350$ nm, 18 h)[11] of a 1:1 mixture of $\mathbf{2}^{F}$/$\mathbf{2}^{Me}$ in C_6D_6 results in the formation of a ca. 1:1:2 mixture of $\mathbf{2}^{F}$/$\mathbf{2}^{Me}$/$\mathbf{2}^{X}$, corresponding to

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a statistical distribution of the two different (PNP)Pd fragments (Figure 1, bottom). **2**^{X} gives rise to a set of ^{F}PNP and a set of ^{Me}PNP resonances of equal intensity. Solutions of **2**^{F}/**2**^{Me} in C_6D_6 (kept in the dark) generate **2**^{X} even at room temperature, albeit slowly (ca. 5% in 4 d).

A metal−metal bond may be viewed as a potential two-electron reductant. We expected that **2** would tend to undergo reactions resulting in the ultimate formation of monomeric (PNP)PdX compounds. This can be accomplished by outer-sphere oxidation, such as in a reaction with Ph_3CCl where **2**^{F} and **2**^{Me} react to give (^{F}PNP)PdCl (**4**^{F}) and (^{Me}PNP)PdCl (**4**^{Me}), correspondingly, along with Gomberg's dimer[12] (Figure 1, bottom). Notably, oxidation of a 1:1:2 mixture of **2**^{F}/**2**^{Me}/**2**^{X} with Ph_3CCl produces **4**^{F} and **4**^{Me} in a 1:1 ratio as the only PNP species.

Alternatively, addition of X−Y across the Pd−Pd bond can give (PNP)PdX and (PNP)PdY in what can be referred to as binuclear oxidative addition[13] (Figure 1, bottom). Thermolysis of **2** under 1 atm of H_2 in C_6D_6 at 85 °C leads to the formation of **5**. Thermolysis of **2** in the presence of 10 equiv of water in THF at 90 °C for 1−4 d leads to the formation of equimolar amounts of **5** and **6**. Thermolysis of **2** under 1 atm of NH_3 in C_6D_6 at 95 °C for 18 h leads to the formation of approximately equimolar amounts of **5** and **7**.[14] The identities of complexes **7** were verified by alternative syntheses.[15]

The mechanism of the reactions of **2** with H_2, H_2O, and NH_3 is not yet clear. It is possible that dissociation into (PNP)Pd monomers is required. However, given the small size of all three reactants in question, one cannot rule out initial attack of these reagents on a Pd center and/or a concerted σ-bond metathesis pathway.

Addition of H_2 across an unbridged single metal−metal bond was reported for $Rh^{II}-Rh^{II}$ dimers.[16] Several examples have been reported where a water molecule was converted into a hydride and a hydroxide ligands.[17] *Well-defined*[18] oxidative addition of NH_3 resulting in a terminal hydride and a terminal NH_2 ligands has only been achieved recently in a (PCP)Ir system.[1b,19] The splitting of NH_3 by **2** represents the first example where *two* metal centers cooperate to split NH_3 into terminal M−H and M−NH_2 (examples[20] of conversion of NH_3 to bridging amido and imido ligands exist). As pointed out by Hartwig and Goldman,[1b] the scarcity of N−H oxidative addition reactivity for ammonia is partly due to the usually preferred alternative of simple coordination to the metal via the lone pair at N. This alternative is ever-present for a monometallic oxidative addition of NH_3. Yet, in the present case, NH_3 (as well as H_2O or H_2), being a two-electron donor, is a mismatch for an odd-electron (PNP)Pd fragment and the dimeric **2** itself is not set up to coordinate another two-electron donor either.

In summary, we have discovered that (PNP)Pd−alkyl complexes are susceptible to photochemical homolysis of the Pd−C bond which results in the formation of (PNP)Pd−Pd(PNP) dimers with a single Pd−Pd bond. These dimers can reversibly generate monomeric (PNP)Pd fragments in solution. They react with dihydrogen, water, and ammonia via binuclear oxidative addition cleaving the H−X bond (where X is H, OH, or NH_2). The reaction with ammonia represents a new mode of activation of this important molecule.

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Supporting Information Available: Experimental details, crystallographic information in the form of a CIF file, characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(3) (^{F}PNP)Pd(n-C_4H_9) and (^{F}PNP)Pd(n-C_8H_{17}) react with a similar rate to that of **1**^{F}, (^{F}PNP)PdMe and (^{F}PNP)PdCH_2Ph react more slowly, while (^{F}PNP)PdPh and (^{F}PNP)PdH are not photoreactive under these conditions.

(4) Photolytic scission of transition metal−carbon bonds has been observed previously. See the following examples: (a) Gabrilsson, A.; Blanco-Rodriguez, A. M.; Matousek, P.; Towrie, M.; Vlček, A., Jr. *Organometallics*, **2006**, *25*, 2148. (b) Burns, C. T.; Shen, H.; Jordan, R. F. *J. Organomet. Chem.* **2003**, *683*, 240. (c) Klein, A.; Slageren, J. v.; Záliš, S. *J. Organomet. Chem.* **2001**, 202. (d) Ankianiec, B. C.; Hardy, D. T.; Thomson, S. K.; Watkins, W. N.; Young, G. B. *Organometallics*, **1992**, *11*, 2591.

(5) (a) The covalent radius of Pd was calculated by subtracting 0.77 Å, the covalent radius of carbon in CH_3, from the Pd−C bond length in (^{F}PNP)Pd-CH_3,[5b] 2.06 Å. The resulting covalent radius of (PNP)Pd is 1.29 Å and the calculated Pd−Pd distance is thus twice that, or 2.58 Å. (b) Ozerov, O. V.; Guo, C.; Fan. L.; Foxman, B. M. *Organometallics* **2004**, *23*, 5573.

(6) (a) Allen, F. H. *Acta Crystallogr., Sect. B: Struct. Sci.* **2002**, *58*, 380. (Version 5.27 of the Cambridge Structural Database.) (b) For instance, the Pd-Pd distances in $[(Me_3P)_3Pd\text{-}Pd(PMe_3)_3]^{2+}$ and in $[(\mu\text{-}Me_2PCH_2\text{-}PMe_2)_2Pd_2Br_2]$ are ca. 2.60 Å.[6c,d] (c) Lin, W.; Wilson, S. R.; Girolami, G. S. *Inorg. Chem.* **1994**, *33*, 2265. (d) Kullberg, M. L.; Lemke, F. R.; Powell, D. R.; Kubiak, C. P. *Inorg. Chem.* **1985**, *24*, 3589.

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(8) C_{2v} is the highest symmetry a (PNP)M fragment can attain and is observed (by NMR at 22 °C) for simple (PNP)PdX compounds.

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(10) For an example of a redox non-innocent NNN pincerlike ligand, see Bart, S. C.; Chlopek, K.; Bill, E.; Bouwkamp, M. W.; Lobkovsky, E.; Neese, F.; Wieghardt, K.; Chirik, P. J. *J. Am. Chem. Soc.* **2006**, *128*, 13901.

(11) Exposure of a mixture of **2**^{F} and **2**^{Me} to ambient light caused slow appearance of the signals of **2**^{X}.

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(14) A small (<5%) quantity of **6**^{F}/**6**^{Me} was also observed, presumably from hydrolysis of **7**^{F}/**7**^{Me} by traces of water in NH_3.

(15) (PNP)PdOTf (**8**^{F}/**8**^{Me}) react with NH_3 to give [(PNP)Pd(NH_3)]OTf (**9**^{F}/**9**^{Me}), which upon deprotonation with KN($SiMe_3$)$_2$ yields **7**^{F}/**7**^{Me}.

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