ORGANOMETALLICS

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Binuclear Palladium Complexes Supported by Bridged Pincer Ligands

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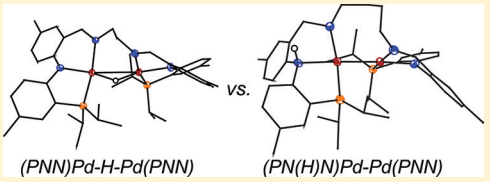
Supporting Information

ABSTRACT: A series of binucleating ligands each containing two tridentate pincer sites based on a central, monoanionic aryl (C) donor flanked by neutral phosphinito (P) and imino (N) donors, [(PCN)-$(CH_2)_n$-(PCN)] (**1**), or a central, monoanionic amido (N) flanked by neutral phosphine (P) and imino donors (N), [(PNN)-$(CH_2)_n$-(PNN)] (**4**), are presented. The metalating sites were linked through the condensation of two equivalents of *m*-hydroxybenzaldehyde or the purposively built asymmetric diarylamine [(H)N(2-C(O)H-4-Me-C_6H_3)(2-P(*i*Pr)$_2$-4-Me-C_6H_3)] (**3**) with primary α,ω-diamines (1,2-diaminoethane, n = 2; 1,4-diaminobutane, n = 4), which simultaneously constructed the imino arms and bridged the pincer cores. Ligands **1** and **4** were then used in the synthesis of neutral, square-planar palladium(II) complexes **5** and **6**, [(PCN-C_n)Pd_2X_2, (PNN-C_n)Pd_2X_2; n = 2, 4; X = Cl, OAc, OTf]. The difference in the *trans* influence of the central donor was demonstrated through X-ray crystal structures of **5b-Cl**, (PCN-C_4)Pd_2Cl_2, and **6b-Cl**, (PNN-C_4)Pd_2Cl_2. The (PNN-C_n)Pd_2X_2 complexes (**6**) proved to be redox-active, presumably via oxidation of the ligand, and cyclic voltammetry illustrated the extent to which electronic communication between the two pincer sites is mediated by the length of the bridge between them. (PCN-C_n)Pd_2OTf_2 (**5-OTf**) and (PNN-C_n)Pd_2OTf_2 (**6-OTf**) complexes reacted with hydride donors such as Et_3SiH or β-hydride-containing alkoxides such as NaO*i*Pr to generate bridging-hydride monocations [(PCN)Pd-H-Pd(PCN)-C_n][OTf] (**5-H**, n = 2, 4) and [(PNN)Pd-H-Pd(PNN)-C_2][OTf] (**6a-H**), where the supported Pd−Pd separation was also found to be affected by the bridge length. In the case of the $(CH_2)_4$-bridged (PNN-C_4)PdOTf (**6b-OTf**), a bridging-hydride monocation was not observed. Instead, the formation of [(PN(H)N)Pd-Pd(PNN)-C_4][OTf] (**6b-H**), protonated at the amido N of the ligand with a direct Pd(I)−Pd(I) bond, was recorded.



INTRODUCTION

Tridentate "pincer" ligands by now represent a ligand archetype in transition-metal chemistry.[1] Metal complexes of these robust, tunable scaffolds have been used as platforms for studies of bond activation,[2] in the identification of transient intermediates,[3] and to support unusual chemical transformations at both highly electron-rich[4,5] and electron-deficient[6] transition-metal centers. We are interested in the construction of bridged, binucleating ligands based on pincer frameworks to explore cooperativity between metal centers.[7] Reports of "poly-pincer" ligands in the literature largely describe systems bridged by rigid groups,[8] designed for coordination polymer synthesis[9] or exploration of electronic communication,[10,11] with some exceptions. Binucleating CNS pincers, derived from thioether-substituted bis-azobenzenes joined by $(CH_2)_3$ units, and their cyclopalladated Pd(II) complexes were reported by Chakravorty and co-workers.[12] Tsubomura et al. prepared a binucleating macrocyclic ligand that coordinates Pd(II) centers through the NCN donor atoms of two 2,6-bis(diaminomethyl)-phenyl units bridged by two flexible $(CH_2)_3$ linkers.[13] Suess and Peters recently detailed a series of nitrogen-rich polydentate ligands containing monoanionic, bis(quinolinyl)-amide pincer-type binding sites.[14] We sought to build binucleating ligands that bring two metal centers into relative proximity that may allow for simulatenous interaction of both metal centers with the same molecule of substrate. To execute this general design principle, we envisioned connecting the two side donors, one in each pincer core, with a flexible and easily variable linker. We were particularly interested in adapting the well-known $P^{\circ}C^{O}P$[15] and PNP[16,17] pincers for this task. $P^{\circ}C^{O}P$ and PNP combine neutral phosphine (or phosphinite) L-type donor "arms" with either an aryl or an amido anionic X-type central site. However, linking the phosphine or phosphinite sites would be synthetically difficult. In contrast, an imine as an L donor seemed well suited to this task because it can be reliably fabricated from aldehyde (or ketone) starting materials and α,ω-diamines, available with many different linkers (Figure 1). Here, we report the implementation of this approach and the exploration of the coordination chemistry of new binucleating PCN and PNN ligands (Figure 1) with palladium. The mononuclear PCN (phosphinite-aryl-imino) pincer ligands have been reported by Gong, Song, and co-workers, but the design of the PNN ligand (phosphine-diarylamido-imine) is new in itself.[18−20] The binucleating pincer platforms complement (and are inspired by) the "Pacman" bis(porphyrin)[21] design, but are synthetically much more easily accessible and tunable.

Received: August 27, 2011
Published: November 18, 2011

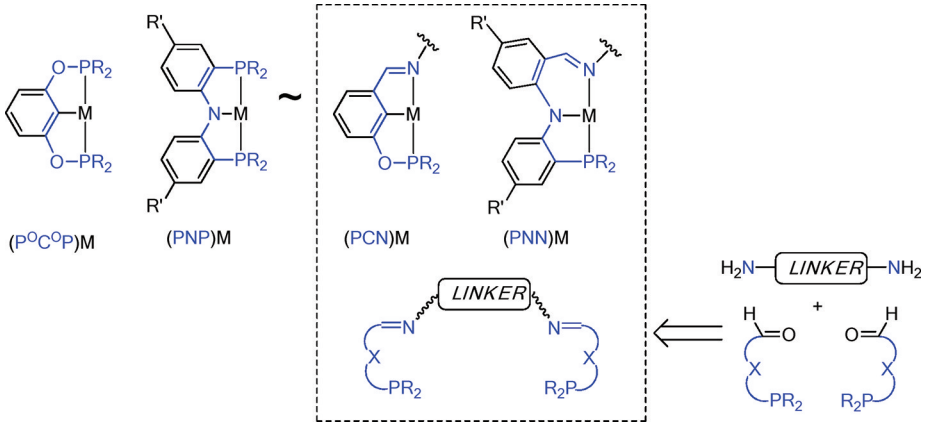
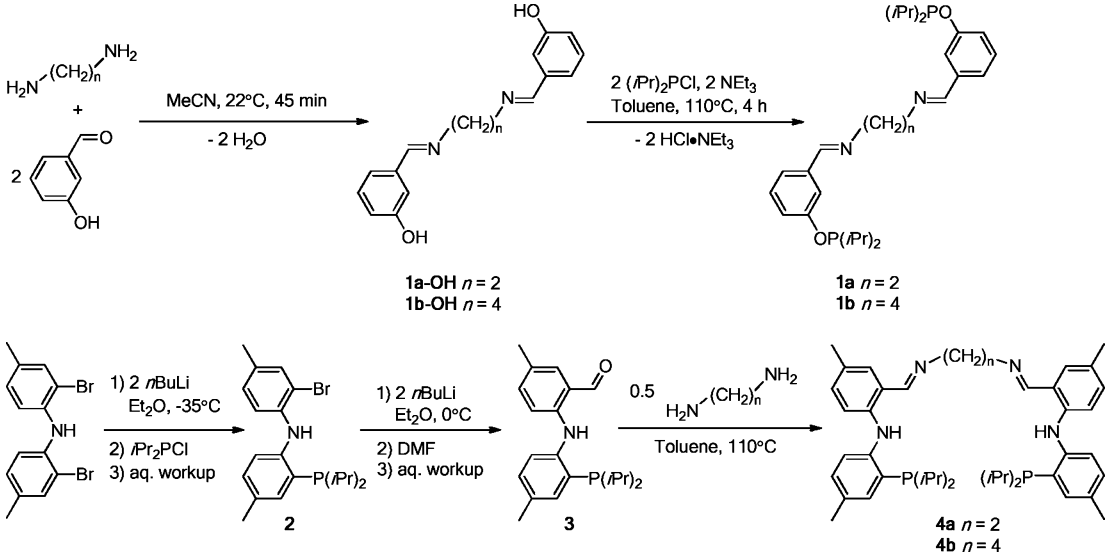


Figure 1. Retrosynthetic deconstruction of imine synthesis and the relationship between P°C°P/PNP and PCN/PNN pincer motifs.

Scheme 1. Synthesis of (PCN-C$_n$) and (PNN-C$_n$) Ligands 1 and 4



RESULTS AND DISCUSSION

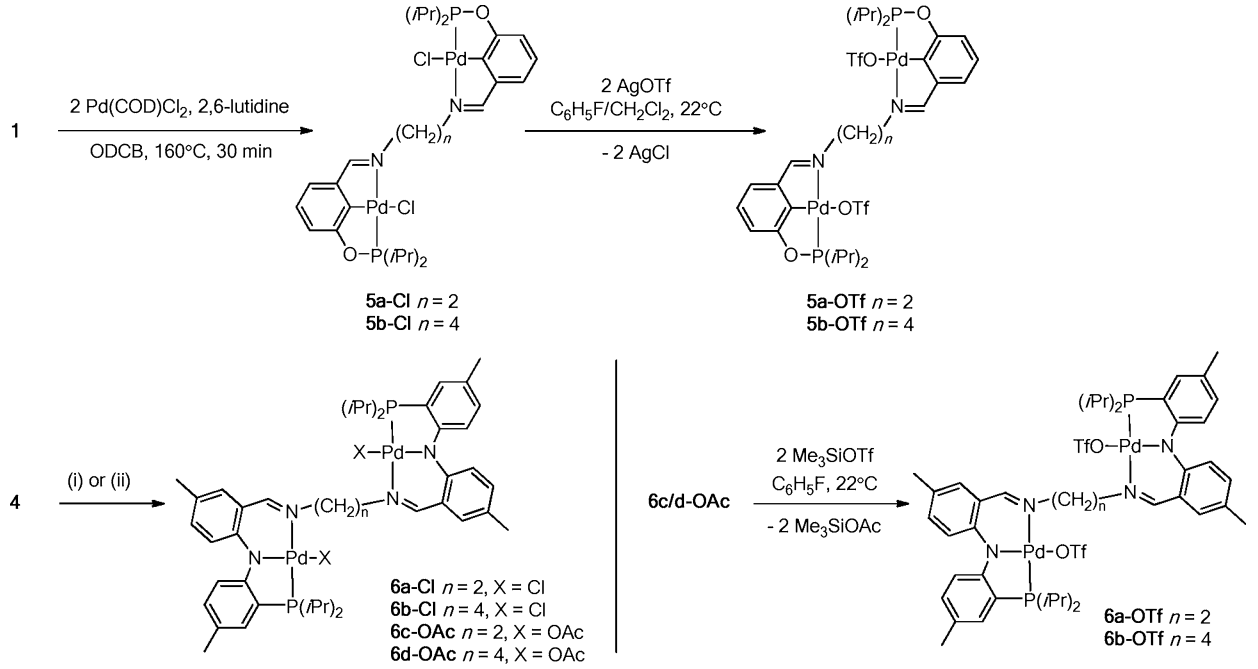
Ligand Synthesis. Using Fryzuk's notation[22] to describe a pincer framework based on the size of the two chelate rings formed, the identity of the donor atoms, and the overall charge of the tridentate ligand, we have constructed a series of binucleating {[5,5]-PCN}$^-$ and {[5,6]-PNN}$^-$ pincer ligands bearing phosphino/phosphinito and imino arms flanking central aryl (C) or amido (N) donors. For the synthesis of ligand **1**, addition of 1,2-diaminoethane or 1,4-diaminobutane to an acetonitrile solution containing two equivalents of *meta*-hydroxybenzaldehyde at room temperature formed the *meta*-substituted ligand precursors (**1-OH**), which precipitated from solution (Scheme 1).[23] These were isolated as moderately soluble white powders and characterized by ^{1}H NMR spectroscopy. Reflux of a mixture of the respective *m*-hydroxybenzaldimine **1a/b-OH**, (iPr)$_2$PCl and a base (Et_3N) in toluene installed the phosphinito arms. The binucleating [(PCN)-(CH$_2$)$_n$-(PCN)] ligands were isolated following work-up in decent yields (**1a**, 69%; **1b**, 57%; 95% purity) as colorless or pale yellow oils, which were further dried in vacuo to remove residual (iPr)$_2$PCl. In each case, downfield singlet resonances assigned to the two *H*C═N hydrogens were located in the ^{1}H NMR spectra of **1a,b** at 8.22 and 8.21 ppm, respectively, while single peaks were observed by ^{31}P{^{1}H} NMR spectroscopy at 149.5 and 148.9 ppm.

A modified strategy was employed in the synthesis of [(PNN)-(CH$_2$)$_n$-(PNN)] ligands **4a,b** (Scheme 1). In this case, the phosphine arm was first installed by direct formation of a P−C bond, followed by introduction of the aldehyde functionality and, in the last step, condensation of two monophosphinated, benzaldehyde derivatives of di-*tolyl*-amine with the desired diamine. First, the monophosphinated intermediate **2** (δ_P = −13.8 ppm) was prepared in 79% isolated yield by reacting bis(2-bromo-4-methylphenyl)amine[24] with two equivalents of *n*BuLi at −40 °C, followed by quenching the dilithiated intermediate with one equivalent of iPr$_2$PCl.[25] Lithium−halogen exchange and addition of dimethylformamide gave the desired aldehyde **3** in high isolated yield (87%; δ_P = −8.8 ppm). As **2** precipitated from more concentrated ethereal solutions at lower temperatures, care was taken to ensure suitable dilution of the reaction mixture in this step ([**2**] < 0.05 M). Condensation of two equivalents of **3** with the respective α,ω-diamines in boiling toluene led to formation of **4a** (81%, δ_P = −5.8 ppm) and **4b** (87%, δ_P = −4.6 ppm), which were isolated as yellow solids.

Synthesis of Neutral Bis(Pd-X) Complexes (X = Cl, OAc, OTf). Forcing conditions (*ortho*-dichlorobenzene, 160

dx.doi.org/10.1021/om2008056 | *Organometallics* 2011, 30, 6641−6654

Scheme 2. Synthesis and Reactivity of (PCN-C$_n$)PdX and (PNN-C$_n$)PdX Complexes[a]



[a]Conditions: (i) 2 equiv Pd(COD)Cl$_2$, 2 equiv 2,6-lutidine, THF, 15 h, 22 °C; (ii) 2 equiv Pd(OAc)$_2$, THF, 1 h, 22 °C.

°C) were necessary for activation of the aryl C(sp^2)−H bond in **1** upon reaction with Pd(COD)Cl$_2$ with 2,6-lutidine as the base in order to generate **5-Cl**. Once formed, the (PCN-C$_n$)Pd$_2$Cl$_2$ complexes were isolated by recrystallization from CH$_2$Cl$_2$/Et$_2$O as bright yellow solids in moderate yields (Scheme 2: **5a-Cl**, 57%; **5b-Cl**, 53%). Metalation was accompanied by a downfield shift in the ^{31}P{^{1}H} NMR signal of the ligands (**1a**, 149.5; **1b**, 148.5 → **5a-Cl**, 202.5; **5b-Cl**, 202.6 ppm), while when complexed, the imine *HC*═N proton showed diagnostic coupling to the *trans* phosphorus [**5a-Cl**, 8.38 (d, $^4J_{HP}$ = 4.8 Hz); **5b-Cl**, 8.26 (d, $^4J_{HP}$ = 5.0 Hz)]. The robustness of the PCN fragment toward oxidation allowed the use of AgOTf to exchange chloride in **5a/b-Cl**, for less strongly bound triflate (OTf) in **5a/b-OTf**. The multinuclear NMR spectra of **5a/b-OTf** showed only minor differences from the chloride-containing precursors, with the exception of the appearance of a signal in the ^{19}F NMR spectrum at −79 ppm (see Table 1).

Table 1. Selected NMR Data (ppm) for 5-Cl/OTf and 6-Cl/OAc in CD$_2$Cl$_2$

	HC═N	HC═N	^{31}P{^{1}H}	^{19}F
5a-Cl	8.38 (d, 4.8 Hz)	176.8 (d, 3.8 Hz)	202.5	
5b-Cl	8.26 (d, 5.0 Hz)	174.4 (d, 4.3 Hz)	202.6	
5a-OTf	8.36 (d, 4.5 Hz)	177.0 (d, 3.9 Hz)	203.2	−78.8
5b-OTf	8.13 (d, 5.0 Hz)	173.7 (d, 3.8 Hz)	202.7	−79.0
6a-Cl	7.95 (d, 13.4 Hz)[a]	162.4[a]	71.3 (71.9)	
6b-Cl	7.79 (d, 13.2 Hz)[a]	161.7 (161.4)	70.8 (70.9)	
6a-OAc	7.95 (d, 12.4 Hz)[a]	162.5 (163.9)	66.2 (66.8)	
6b-OAc	7.66 (d, 12.0 Hz)	161.4 (161.3)	65.3	

[a]Resonances for minor isomer not included.

In comparison, activation of the N−H bond in **4** by Pd(COD)Cl$_2$/2,6-lutidine or [Pd(OAc)$_2$]$_3$ proceeded in a much more facile manner, and (PNN-C$_n$)Pd$_2$X$_2$ (X = Cl, OAc) complexes **6-Cl,OAc** formed at 22 °C and were isolated in good yields (>70%, Scheme 2). Cleavage of the N−H bond led to the disappearance of the downfield resonance in the ^{1}H NMR spectrum assigned to the N-*H* proton. As electrochemical studies established the susceptibility of the (PNN-C$_n$) ligands to oxidation (vide infra), we sought a synthetic route to the palladium triflates that did not involve the potentially oxidizing AgOTf. Me$_3$SiOTf proved capable of abstracting acetate from **6-OAc**, and following the reaction in C$_6$H$_5$F, the triflato species **6-OTf** were isolated as sparingly soluble, deep purple solids in good yields.

Isomerism of (PNN-C$_n$)Pd$_2$X$_2$ Complexes. The ^{1}H NMR spectra of **6** also contained imine proton resonances split into doublets with slightly larger $^4J_{HP}$ (∼12−13 Hz) than observed for **5** (Table 1). The ^{31}P{^{1}H} NMR resonances of the coordinated phosphines were found considerably downfield of the free ligands and in regions characteristic of the X group (Table 1: X = Cl, ≈ 71 ppm; X = AcO, = 65−66 ppm; X = OTf, = 77−78 ppm). The multinuclear NMR spectra of analytically pure samples of **6** showed two sets of signals in different ratios depending on the bridge length and the nature of the X ligand (see Supporting Information). For example, with the shorter (CH$_2$)$_2$ bridge separating the two (PNN)PdX halves, an 8:1 ratio was observed by ^{31}P{^{1}H} NMR for **6a-Cl**, while a 5:1 ratio was observed for **6a-OAc** in CD$_2$Cl$_2$ at 22 °C. For the longer (CH$_2$)$_4$-bridged complexes, two peaks were registered in a more balanced ratio of 1.4:1 for **6b-Cl**, while a single peak was observed in the ^{31}P{^{1}H} NMR spectrum of **6b-OAc** in CD$_2$Cl$_2$ at 22 °C. In C$_6$D$_5$CD$_3$ solution at 22 °C, a ratio of 2.7:1 (**6a-Cl**) was observed, while the ratio of the two peaks observed for **6b-Cl** did not change appreciably in C$_6$D$_5$CD$_3$ solution at 22 °C.

Variable-temperature NMR spectroscopic studies of **6a-Cl** were used to investigate the stability of the ratio of peaks with respect to temperature (see Figures SI-2 and SI-3 in the Supporting Information). At 65 °C, the two resonances in the ^{31}P{^{1}H} NMR spectrum, which were baseline separated at 25

dx.doi.org/10.1021/om2008056 | *Organometallics* 2011, 30, 6641−6654

°C, broadened and overlapped. Very broad resonances for both sets of major and minor peaks were still visible in the ^{1}H NMR spectrum. At 85 °C, the resonances for the methyl groups of the *i*Pr substituents began to coalesce into two broad peaks, and a single, broad phosphorus resonance was observed. At the high-temperature limit of the solvent (105 °C), the phosphorus resonance had sharpened, while the four *i*Pr methyl resonances collapsed into two broad peaks and a single *i*Pr methine resonance was observed. The aromatic region (and two methyl groups of the ligand backbone) contained relatively sharp signals compared with those assigned to the *i*Pr groups, including a single doublet for the imino proton ($^4J_{HP}$ = 13.2 Hz). Our observations indicate that while the compounds giving rise to these separate sets of peaks are distinct by NMR spectroscopy at ambient temperature, the rate of interconversion is too fast for the persistence of the individual compounds on the time scale of experimental handling.

The two similar sets of resonances observed for the coordinated (PNN-C$_n$) ligands in **6** suggested the presence of isomers. Although the origin of the isomerism is not yet fully certain, we tentatively attribute the pairs of resonances to the presence of diasteromers based on the orientation of the two aryl rings of the PNN backbone with respect to one another,[26] akin to atropisomers such as the representative biaryl binapthyl systems.[27] As each binuclear molecule contains two (PNN)PdX moieties, if the two orientations within the same molecule are the same (Figure 2, *R*,*R* or *S*,*S*), a set of *rac* confomers lacking

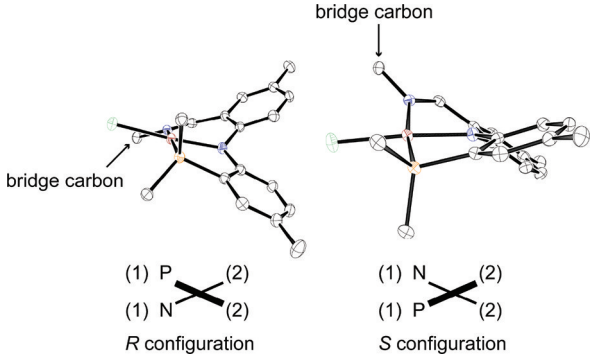


Figure 2. Depictions of the two possible orientations of the aryl rings of the PNN backbone: *R* and *S*. Phosphorus is shown in orange and nitrogen in blue. Simplified depictions with the chiral axis viewed end-on used to designate *R* and *S* in accordance with binapthyl atropisomers are shown below, with Cahn–Ingold–Prelog priorities in parentheses.[28]

an internal mirror plane can be drawn. Different pairings (*R*/*S* or *S*/*R*) would represent the *meso* confomer.

In contrast, most chiral pincer ligand systems known are based on *m*-xylyl {(5,5)-ECE}$^-$ pincer frameworks and carry their stereogenic centers on the arms, not the backbone, of the ligand.[29] These are typically incorporated via an auxiliary chiral site[20,30] and include substituents exhibiting axial chirality.[31] Other positions available for generating stereogenic centers are the benzylic methylene groups or the two –ER^{1}R^2 donor arms when the substituents on E differ (E = N, P; R^1 ≠ R^2).[32] While diarylamido-based pincer complexes are generally C_2-symmetric in the solid state, bis(phosphine)diarylamido (PNP)PdX complexes are all C_{2v}-symmetric in solution, even at low temperatures.[33] The process by which the configuration of a single pincer site can be inverted (and thus the diastereomers interconverted) is the "flipping" of the two aromatic rings past each other, and it is apparently significantly slower in the {[5,6]-PNN}$^-$ pincer complexes than in the {[5,5]-PNP}$^-$ analogues. Rigid, terphenyl-based PCP and NCN systems

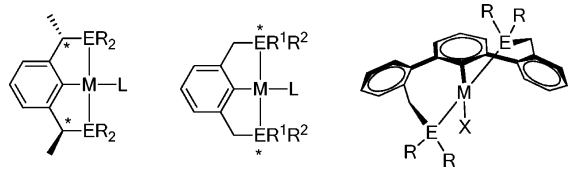


Figure 3. Representative examples of chiral pincer complexes.

that exhibit atropisomerism have also been reported (Figure 3).[26,34]

Solid-State Structures of Neutral (PCN-C$_n$)Pd$_2$X$_2$ and (PNN-C$_n$)Pd$_2$X$_2$ Complexes. To examine the arrangement of the binuclear complexes in the solid state, X-ray crystallographic studies were undertaken. Yellow, X-ray quality crystals of **5b-Cl** were grown by diffusing Et$_2$O into a CH$_2$Cl$_2$ solution at room temperature. The two pincer cores are crystallographically distinct, and each contains a palladium in a typical, distorted square-planar coordination environment with the phosphinito and imine arms pulled back slightly to an N–Pd–P angle of 158°. The bond distances to Pd resemble those of previously reported mononuclear analogues[18] and related systems.[35,19] The Pd–Cl distances [2.359(3) Å] do not significantly differ from similar {[5,5]-PCP}$^-$ PdCl complexes such as the symmetric bis(phosphinito)aryl compound (^{iPr}P°C^{O}P^{iPr})PdCl [2.370(2) Å],[36] consistent with the strong *trans* influence of the central aryl donor. Despite numerous attempts, issues with crystal twinning prevented structural characterization of the (CH$_2$)$_2$-bridged derivative **5a-Cl**.

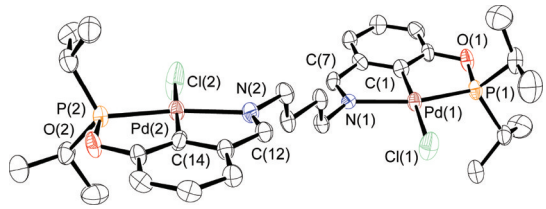


Figure 4. ORTEP of **5b-Cl** with thermal ellipsoids shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Pd(1)–Cl(1) 2.359(2), Pd(1)–N(1) 2.141(6), Pd(1)–P(1) 2.208(2), Pd(1)–C(1) 1.954(7), N(1)–C(7) 1.280(10), Pd(2)–Cl(2) 2.359(3), Pd(2)–N(2) 2.152(7), Pd(2)–P(2) 2.203(2), Pd(2)–C(14) 1.956(8), N(2)–C(12) 1.263(9); N(1)–Pd(1)–P(1) 158.4(2), C(1)–Pd(1)–Cl(1) 177.3(2), N(2)–Pd(2)–P(2) 158.5(2), C(14)–Pd(2)–Cl(2) 177.2(2).

For comparison, structural determinations of (PNN-C$_n$)Pd compounds **6-Cl** and **6a-OAc** were carried out on block-shaped red crystals grown from 1:4 C$_6$H$_6$/pentane mixtures at 0 °C. Each asymmetric unit contains one pincer core or half of a molecule. As can be seen in Figures 5 and 6, in both **6a-Cl** and **6a-OAc**, the C_2-bridged bimetallic pincer folds back on itself in the solid state, whereas **6b-Cl** is fully extended, similar to the structure of **5b-Cl**. Each pincer core contains a palladium in distorted square-planar geometry, with typical ligand–metal distances.[17] **6a-Cl** and **6a-OAc** crystallized in the space group

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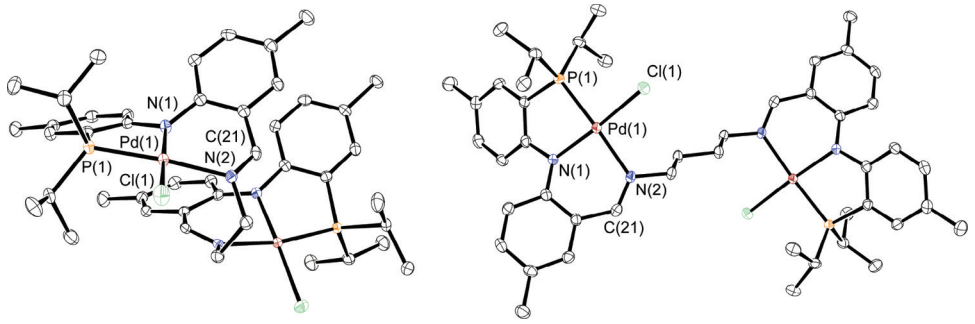


Figure 5. ORTEPs of **6a-Cl** and **6b-Cl** with ellipsoids shown at the 50% probability level. Hydrogens and solvent molecule (1/2 C_6H_6, **6b-Cl**) are omitted for clarity. Selected bond distances (Å) and angles (deg): **6a-Cl**: Pd(1)−N(1) 2.013(2), Pd(1)−N(2) 2.091(2), Pd(1)−P(1) 2.2233(9), Pd(1)−Cl(1) 2.321(1), C(15)−N(2) 1.282(2); N(1)−Pd(1)−Cl(1) 174.93(4), N(2)−Pd(1)−P(1) 168.69(4). **6b-Cl**: Pd(1)−N(1) 2.018(2), Pd(1)−N(2) 2.093(2), Pd(1)−P(1) 2.2189(9), Pd(1)−C(1) 2.3197(9), C(21)−N(2) 1.273(3); N(1)−Pd(1)−Cl(1) 174.17(6), N(2)−Pd(1)−P(1) 171.57(6).

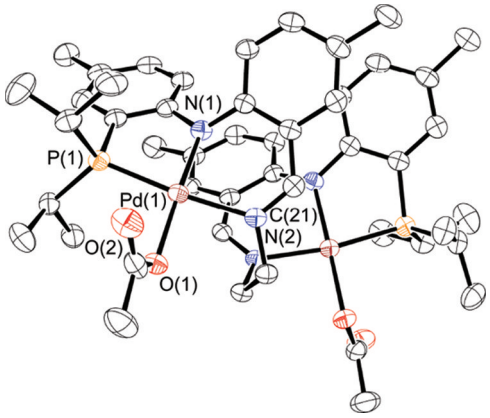


Figure 6. ORTEP of **6a-OAc** with ellipsoids shown at the 50% probability level. Hydrogens are omitted for clarity. Selected bond distances (Å) and angles (deg): Pd(1)−P(1) 2.224(1), Pd(1)−N(1) 1.986(4), Pd(1)−N(2) 2.073(3), Pd(1)−O(1) 2.069(4), N(2)−C(23) 1.285(6); P(1)−Pd(1)−N(2) 171.8(1), N(1)−Pd(1)−O(1) 176.4(2).

*C*2/*c* as a mixture of *rac* isomers, (*S*,*S*, shown in Figures 5 and 6) and (*R*,*R*), as the molecule does not contain the center of crystallographic symmetry. **6b-Cl** crystallized as the *meso* isomers (*R*,*S*) and (*S*,*R*) with the center of crystallographic symmetry coinciding with the center of symmetry of the molecule. Unlike the {(5,5)-PCN}$^-$ ligands, which form two five-membered rings once bound to a metal, the {(5,6)-PNN}$^-$ core forms both a five- and six-membered ring. Accordingly, the P−Pd−N angles are relaxed compared with those in **5b-Cl** [168.69(4)° (**6a-Cl**), 171.57(6)° (**6b-Cl**), and 171.8(1)° (**6b-OAc**), respectively], but not as much as in the (NNN)PdCl complex we recently reported [176.77(17) Å], which contained a {(6,6)-NNN}$^-$ pincer.[37] The central amido donor would be expected to exert less of a *trans* influence on the chloride in **6-Cl** than an aryl donor, and the shorter Pd−Cl distances reflect this [**6a-Cl**, 2.321(1) Å; **6b-Cl**, 2.3197(9) Å; **5b-Cl**, 2.359(2) Å].

Anodic Electrochemistry of (PNN-C_n)Pd_2X_2 Complexes. Inspired by the similarity between the (PNN) pincer cores in **6-Cl** and the known redox-active bis(phosphine)-diarylamido (PNP) ligand (PNP = N[2-P(*i*Pr)$_2$-4-methylphenyl]$_2$),[38] we decided to probe the oxidation of **6-Cl** using cyclic voltammetry in CH_2Cl_2 at ambient temperature. The anodic region of the voltammogram of **6a-Cl** shows two well-separated one-electron oxidation steps. The current response of each peak depended linearly on $\nu^{1/2}$, indicating reversible, diffusion-controlled redox events. Figure 7 shows cyclic voltammograms of approximately equimolar amounts of **6a-Cl** and **6b-Cl** in CH_2Cl_2. The current response of **6b-Cl** (Figure 7, right) is twice as large as the individual peaks evident in the CV of **6a-Cl** (Figure 7, left), as both pincer cores in **6b-Cl** were oxidized at overlapping potentials. Mixed-valence Ru(II)/Ru(III) complexes supported by {(5,5}-PCP)$^-$ pincer ligands have been

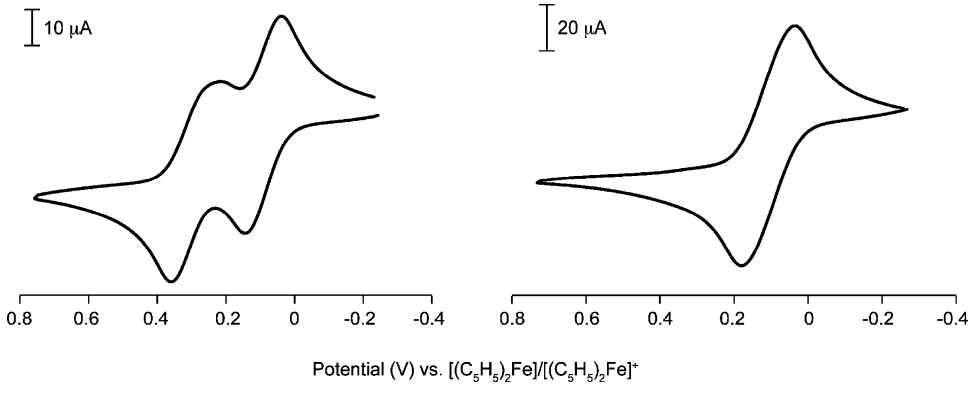


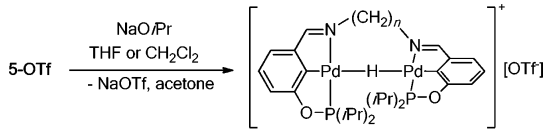
Figure 7. Cyclic voltammograms of **6a-Cl** (left) and **6b-Cl** (right) in CH_2Cl_2 at 22 °C. The scan rate was 100 mV/s in the positive direction. The concentration of analyte was [**6a-Cl**] = 3.0 × 10^{-3} M; [**6b-Cl**] = 3.5 × 10^{-3} M, respectively, with 0.3 M nBu$_4$NPF$_6$ as supporting electrolyte. Measured potentials: **6a-Cl**, $E_{1/2}$ = 0.09, 0.30 V; **6b-Cl**, $E_{1/2}$ = 0.11 V.

dx.doi.org/10.1021/om2008056 | *Organometallics* 2011, 30, 6641−6654

reported where electronic communication is mediated by a rigid, π-conjugated link joining the two cyclometalated fragments.[11] In comparison, the short, saturated hydrocarbon bridge in **6a-Cl** simply brings the two pincer cores close enough that the second oxidation occurred at a higher potential due to Columbic repulsion and a two-wave pattern results. It is not clear whether the stacking of the two pincer cores observed in the solid-state structure of **6a-Cl** plays a special role in the apparent communication between the two oxidation sites. The (PCN-C_n) complexes **5-Cl** did not exhibit any electrochemical response in the anodic region under the same conditions (−1.5 to 1.5 V vs $[(C_5H_5)_2Fe]/[(C_5H_5)_2Fe]^+$), which supports the notion of ligand-based redox events in **6-Cl**.

Formation of Cationic Bridging Hydride Complexes. We next investigated the possibility of using a binucleating pincer platform to prepare complexes with metal centers in electronically different environments, for example, combining an electrophilic metal center on one side with a metal hydride on the other. Upon addition of one equivalent of NaO*i*Pr to CD_2Cl_2 solutions of **5-OTf**, the production of acetone was noted in the appearance of a singlet in the ^{1}H NMR spectrum at 2.12 ppm (CD_2Cl_2). This was accompanied by a downfield shift in the $^{31}P\{^1H\}$ NMR to 207 ppm and the growth of a triplet far upfield in the hydride region of the ^{1}H NMR spectrum (J = 13.5 Hz). The generation of acetone and the appearance of a palladium-bound hydride in a symmetric molecule (one set of ligand resonances was observed) is consistent with *i*PrO$^-$ having displaced OTf at Pd, followed by β-hydride elimination or intramolecular abstraction of a hydride from [Pd]-O*i*Pr and collapse of the two palladium cores to form a symmetric bridging-hydride **5-H** (Scheme 3).[39] In the

Scheme 3. Reactivity of 5a/b-OTf



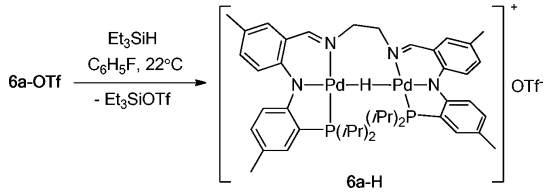
5a-H n = 2
5b-H n = 4

formation of **5-H**, the pincer framework likely retards β-hydride elimination at the isopropoxide-bound metal center, as has been demonstrated for (PNP)Pd alkyls and alkoxides.[40] Therefore, in the reaction of **5-OTf** with NaO*i*Pr, it is possible that β-hydride elimination is a binuclear process, with the second palladium abstracting a hydride from a coordinated O*i*Pr. Alternatively, the hydride may be transferred to Pd directly from an external isopropoxide, without the intermediate formation of a Pd−O bond.[41]

The ^{19}F NMR spectra of **5-H** showed a slightly upfield-shifted resonance of an outer-sphere triflate (−80 ppm). Interestingly, a broad absorption corresponding to the bridging hydride was observed in the expected region[42] of the IR spectrum of **5a-H** (1702 cm^{-1}), while only a very weak absorption was observed for **5b-H** (1713 cm^{-1}). This is likely reflective of the differences between the structure of the Pd−H−Pd cores resulting from the relative flexibility imparted by the different hydrocarbon bridge lengths, as further discussed below. Complexes with hydrides bridging two palladium centers have been reported.[43−47] Examples involving Pd(II) centers include "A-frame" complexes with the metal−metal distance predictated by bridging bis(phosphine) ligands.[44,48,49] The reduction of Pd(II) complexes to form binuclear compounds,[43] clusters,[47] or chains[46] containing reduced Pd(I or 0) centers is also common. In **5-H**, the hydride (H$^-$) bridges two Pd(II) centers. Alternatively, this may be viewed as a Pd−H bond serving as a 2e$^-$ donor to a pincer-supported Pd$^+$.[39] Either formulation involves two Pd(II) centers.

Addition of one equivalent of Et_3SiH to a fluorobenzene solution of the Pd-OTf **6a-OTf** at 22 °C caused the color of the solution to change drastically from purple to a deep green over a 15 min period (Scheme 4). The green color (λ_{max} = 632 nm)

Scheme 4. Formation of the Bridging-Hydride-Containing Monocation 6a-H



is distinct from the typical orange-yellow of known (PNP)PdH complexes.[17] Only a single set of ligand resonances was observed by ^{1}H and $^{31}P\{^1H\}$ NMR spectroscopy (δ_P = 83.4 ppm), suggesting the presence of a single isomer in solution. In addition, a triplet was registered in the hydride region of the ^{1}H NMR spectrum (δ_H = −20.08 ppm, J = 15.2 Hz). This suggested that, as in the formation of **5-H**, a hydride had been abstracted by one of the palladium centers of **6a-OTf**. This may have occurred via generation of a mixed Pd-H/Pd-OTf complex wherein displacement of the second triflate by the Pd-H led to the bridging-hydride monocationic **6a-H**. The ^{19}F NMR spectrum of the isolated product contained an appropriately upfield-shifted resonance for the now outer-sphere OTf counterion (δ_F = −80.2 ppm). The protons of the $(CH_2)_2$ bridge in **6a-H** are diastereotopic, and two broadened doublets were observed. The two methine protons and all four methyl groups of each phosphine arm are chemically inequivalent. The imino arm of each pincer core is still bound to a metal center, and a single doublet for the imino proton was observed slightly upfield at 7.70 ppm and showed coupling to phosphorus ($^4J_{HP}$ =12.5 Hz). As for **5a-H**, the IR spectrum of **6a-H** contained a broad absorption in the expected region (1735 cm^{-1}). Addition of a second equivalent of Et_3SiH left **6a-H** unaffected.

Solid-State Structures of Cationic Bridging-Hydride Complexes. Single crystals of **5-H** and **6a-H** were studied by X-ray diffraction, and the solid-state structures exhibited interesting differences (Figures 8 and 9). The shorter $(CH_2)_2$

Table 2. Selected NMR Data (ppm) for Bridging Hydrides 5-H and 6a-H in CD_2Cl_2

	*H*C═N	HC═N	$^{31}P\{^1H\}$	^{19}F	Pd-*H*-Pd
5a-H	8.32 (d, 4.0 Hz)	178.3 (d, 3.3 Hz)	207.1	−79.8	−9.19 (t, 13.5 Hz)
5b-H	8.34 (d, 4.0 Hz)	178.7 (d, 3.3 Hz)	207.5	−79.7	−8.42 (t, 13.5 Hz)
6a-H	7.70 (d, 12.5 Hz)	161.7	83.4	−80.2	−20.08 (t, 15.2 Hz)

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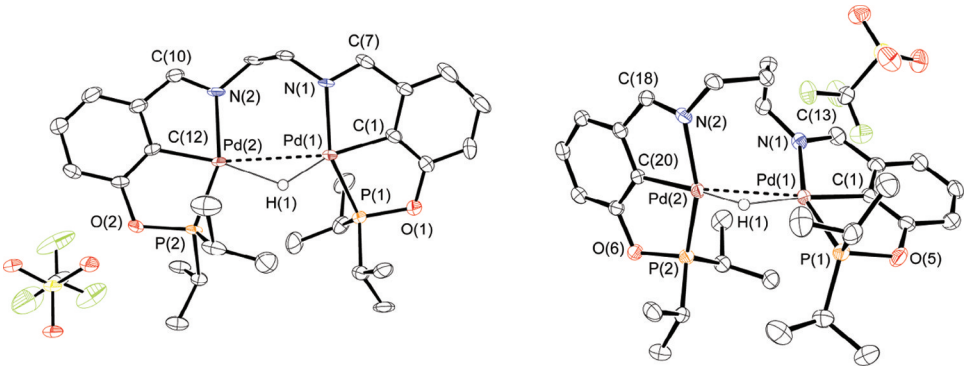


Figure 8. ORTEP of **5a-H** and one of two ion pairs in the asymmetric unit of **5b-H** with thermal ellipsoids shown at the 50% probability level. With the exception of H(1), hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): **5a-H**: Pd(1)−Pd(2) 3.2612(12), Pd(1)−P(1), 2.220(2), Pd(2)−P(2) 2.219(2), Pd(1)−N(1) 2.153(5), Pd(2)−N(2) 2.125(5), Pd(1)−C(1) 1.988(6), Pd(2)−C(12) 1.980(6), N(1)−C(7) 1.285(8), N(2)−C(21) 1.306(8), Pd(1)−H(1) 1.66, Pd(1)−H(2) 1.98; C(1)−Pd(1)−Pd(2) 166.5(2), C(12)−Pd(2)−Pd(1) 166.0(2), N(1)−Pd(1)−P(1) 156.7(2), N(2)−Pd(2)−P(2) 157.4(2). **5b-H**: Pd(1)−Pd(2) 2.9602(8), Pd(1)−P(1) 2.208(1), Pd(2)−P(2) 2.220(1), Pd(1)−N(1) 2.172(4), Pd(2)−N(2) 2.152(3), Pd(1)−C(1) 1.987(4), Pd(2)−C(20) 1.978(4), N(1)−C(13) 1.287(6), N(2)−C(18) 1.285(5), Pd(1)−H(1) 1.79, Pd(1)−H(2) 1.58; C(1)−Pd(1)−Pd(2) 157.2(1), C(20)−Pd(2)−Pd(1) 154.6(1), N(1)−Pd(1)−P(1) 156.5(1), N(2)−Pd(2)−P(2) 157.2(1).

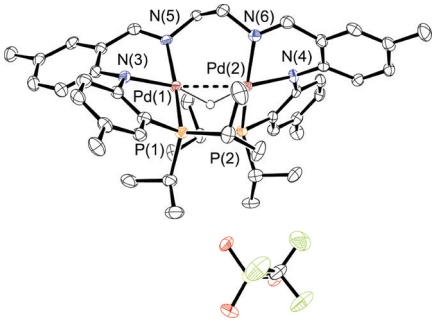


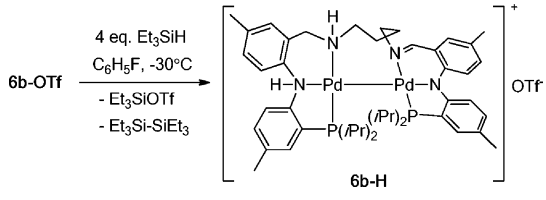
Figure 9. ORTEP of **6a-H** with ellipsoids shown at the 50% probability level. Hydrogens are omitted for clarity. Selected bond distances (Å) and angles (deg): Pd(1)−Pd(2) 2.9774(8), N(3)−Pd(1), 2.035(3), N(4)−Pd(2) 2.033(3), N(5)−Pd(1) 2.092(3), N(6)−Pd(2) 2.085(3), P(1)−Pd(1) 2.2269(12), P(2)−Pd(2) 2.2196(12), Pd(1)−H(1) 1.63, Pd(2)−H(1) 1.64; N(5)−Pd(1)−P(1) 169.1(1), N(3)−Pd(1)−Pd(2) 170.0(1), N(6)−Pd(2)−P(2) 167.89(10), N(4)−Pd(2)−Pd(1) 170.09(10).

bridge in **5a-H** prevented overly close approach of the two metal centers, and the Pd−Pd distance is quite long, at 3.2612(12) Å. Conversely, the longer $(CH_2)_4$ bridge allowed for a much closer Pd−Pd interaction of 2.9602(8) and 2.9710(8) Å for the two molecules in the asymmetric unit of **5b-H**. The more flexible {(5,6)-PNN}$^-$ pincer core in **6a-H** (with the imino arm forming a six-membered ring when bound to the metal) enabled the two palladium centers to approach more closely than in the $(CH_2)_2$-bridged PCN analogue **5a-H**. Indeed, the Pd−Pd distance in **6a-H** [2.9774(8) Å] is only slightly longer than in the C_4-bridged **5b-H** [2.9602(8) Å]. All three supported Pd−Pd distances are long compared with that of the formally (PNP)Pd(I)−Pd(I)(PNP) dimer, $[(PNP)Pd]_2$, 2.5758(4) Å,[4] and other compounds with unambiguous Pd(I)−Pd(I) bonds.[50] **6a-H** crystallized in the orthorhombic space group *Pbca* as a mixture of *rac* isomers (*R,R*) and (*S,S*, shown in Figure 9).

The bridging-hydride structures may alternatively be viewed as having protonated Pd(I)−Pd(I) bonds. The collective bond distances are comparable with those found in A-frame $[Pd_2R_2(\mu\text{-H})(\mu\text{-dppm})_2]^+$ cations (~2.93−3.08 Å),[44,49] open "clam-shell",[51] and related bridged Pd(II) dimers.[52] While, like in **5b-H** and **6a-H**, such systems exhibit Pd−Pd separations shorter than sum of the van der Waals radii (3.26 Å),[53] there has been no agreement on the definitive presence of a metal−metal bond,[54] although in some acetate-bridged "clam-shell" complexes, d^8−d^8 Pd−Pd bonding interactions have been identified by computational analysis.[51]

Aberrant Reactivity of C_4-Bridged $(PNN)_2Pd_2(OTf)_2$ (6b-OTf). Unlike in the formation of **6a-H**, the addition of 1−3 equivalents of Et_3SiH led to complex mixtures. The deep-green product (**6b-H**, λ_{max} = 604 nm) isolated from the addition of four equivalents of Et_3SiH to a fluorobenzene solution of the C_4-bridged triflato species **6b-OTf** did not contain a hydride resonance in the ^{1}H NMR. The product exhibited an upfield-shifted ^{19}F NMR signal (δ_F = −79.9 ppm), suggesting a cationic product with a triflate counterion; however the two phosphines were observed to be inequivalent by $^{31}P\{^1H\}$ NMR spectroscopy and showed weak coupling to one another [δ_P = 64.2 (d, $^3J_{PP}$ = 5 Hz), 49.6 ppm (d, $^3J_{PP}$ = 5 Hz)], indicating a compound with two inequivalent pincer cores. The combination of a new downfield resonance in the ^{1}H NMR spectrum (9.7 ppm) and a broad peak at 3152 cm^{-1} in the IR spectrum of **6b-H** indicated protonation at nitrogen. Careful integration of the ^{1}H NMR spectrum revealed the presence of two more hydrogens than would be expected for a bridging-hydride complex analogous to **6a-H**, or its isomer.

Scheme 5. Proposed H-Migration and Formation of a Pd−Pd Bond with Concomitant Reduction of One Imine Arm in the Formation of 6b-H



An X-ray diffraction study of single crystals grown from fluorobenzene allowed us to establish the molecular structure of **6b-H** (Figure 10). The two Pd centers are connected by a

dx.doi.org/10.1021/om2008056 | *Organometallics* 2011, 30, 6641−6654

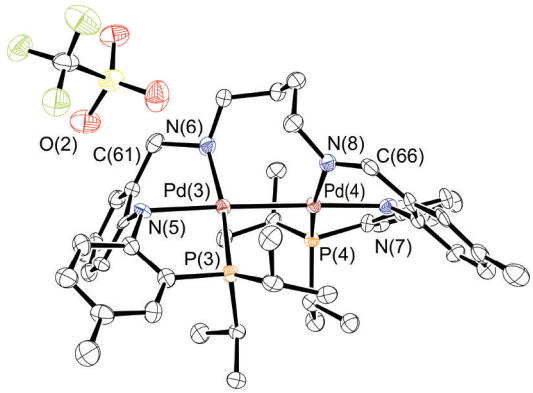


Figure 10. ORTEP of **6b-H** with ellipsoids shown at the 50% probability level. One of two ion pairs in the asymmetric unit is shown; hydrogens and fluorobenzene solvent molecules are omitted for clarity. Selected bond distances (Å) and angles (deg): Pd(3)−Pd(4) 2.5578(12), Pd(3)−P(3) 2.214(2), Pd(4)−P(4) 2.223(2), Pd(3)−N(5) 2.241(6), Pd(3)−N(6) 2.150(7), Pd(4)−N(7) 2.104(6), Pd(4)−N(8) 2.086(7), C(61)−N(6) 1.512(10), C(66)−N(8) 1.278(9); N(5)−Pd(3)−Pd(4) 177.5(2), N(7)−Pd(4)−Pd(3) 175.0(2), N(6)−Pd(3)−P(3) 172.9(2), N(8)−Pd(4)−P(4) 168.0(2).

direct bond; the Pd−Pd distance of 2.5578(12) Å is comparable to that in the (PNP)Pd−Pd(PNP) dimer.[4] The two "halves" of **6b-H** are indeed distinct. Hydrogenation of the one imine arm was evident in the lengthened N−C bond [N(6)−C(61) 1.511(11) Å] compared with the other [N(8)−C(66) 1.285(10) Å], while both N(5) and N(6) exhibited pronounced pyramidalization (Figure 10). The now protonated diarylamine N(5)-H is engaged in a hydrogen bond with O(2) of a nearby triflate counterion [N(5)···O(2) 2.930(9) Å; N(5)−H···O(2) 161°]. The product of the addition of H_2 across the N−Pd bond of (PNP)PdOTf, [(PN(H)P)PdH][OTf] also contains a protonated diarylamido PN(H)P ligand, which in the solid state is similarly engaged in a hydrogen bond with a triflate anion [N···O 2.833(6) Å; N−H···O 172(4)°].[55] Reduction of the imine arms was also noted when **6-Cl** was treated with borohydride reducing agents such as $NaBH_4$ or $LiBEt_3H$, followed by decomposition to unidentified products. If the bridging-hydride complexes **5a-H**, **5b-H**, and **6a-H** may be formally viewed as products of protonation of a Pd(I)−Pd(I) bond, **6b-H** can be instead regarded as a product of protonation of a Pd(I)−Pd(I) complex at the N atom of the amido ligand.

CONCLUSION

A series of binucleating pincer ligands and their palladium complexes have been prepared and fully characterized. The bridge length separating the two metal cores modulates their electronic communication, as observed by cyclic voltammetry, and influences their reactivity. The formation of bridging-hydride monocations from the respective bimetallic triflato species was investigated, and the resultant metal−metal distance was also found to be dictated by the bridge length. In one case, the flexibility imparted by the long four-carbon bridge allowed the two palladium centers to approach one another close enough to form a direct metal−metal bond upon deprotonation of the presumed bridging-hydride intermediate by an opportunistic amide. Current investigations further examining cooperative reactivity between two metal centers are ongoing.

EXPERIMENTAL SECTION

Unless otherwise noted, all procedures were carried out under argon in a glovebox or using standard Schlenk techniques. $Me_3SiOSO_2CF_3$ (Gelest), 3-hydroxybenzaldehyde (Alfa Aesar), 1,2-diaminoethane and 1,4-diaminobutane (Aldrich), and $[Pd(OAc)_2]_3$ (Strem) were purchased and used without special purification. Mesitylene and xylenes were deoxygenated by four freeze−pump−thaw cycles prior to use. 2,6-Lutidine (Aldrich) was dried over CaH_2 under Ar. Bis(2-bromo-4-methylphenyl)amine[24] and $Pd(COD)Cl_2$[56] were prepared according to published procedures. Solvents were dried and distilled from an appropriate drying agent (NaK/Ph_2CO or CaH_2) and deoxygenated prior to use. NMR spectra were recorded on a Mercury 300 MHz, Inova 300 MHz, or Inova 500 MHz spectrometer. ^1H and $^{13}C\{^1H\}$ NMR spectra were referenced to residual solvent peaks.[57] ^1H NMR in C_6D_5Br were referenced setting the most upfield signal to 7.00 ppm.[58] $^{31}P\{^1H\}$ and ^{19}F spectra were externally referenced to H_3PO_4 (85%, 0 ppm) and CF_3COOH (−78.5 ppm). ^{13}C NMR spectra were assigned with the help of ^{13}C DEPT experiments. ^1H NMR spectra were assigned using selective $^1H\{^{31}P\}$ decoupling and $^1H-^1H$ COSY experiments. Elemental analyses were performed by CALI Laboratories, Parsippany, NJ. FT-IR spectra were collected using a Bruker ALPHA-P FT-IR spectrometer with a diamond ATR.

Cyclic voltammetry was carried out using a CH Instruments model 700D Series electrochemical analyzer/workstation in conjunction with a three-electrode cell. The working electrode was a CHI 104 glassy carbon disk (3.0 mm diameter), and the auxiliary electrode a platinum wire. The reference electrode was a $Ag/AgNO_3$ electrode separated from the test solution by a fine-porosity frit and 0.3 M nBuPF$_6$ solution. CVs were conducted in solutions of CH_2Cl_2 with 0.3 M NBu_4PF_6 as supporting electrolyte at scan rates of 100 mV/s. The concentration of analyte was 3.0×10^{-3} M (**6a-Cl**) and 3.5×10^{-3} M (**6b-Cl**), respectively. CVs were referenced to the $Fe(\eta^5\text{-}C_5H_5)_2/Fe(\eta^5\text{-}C_5H_5)_2^+$ redox couple using $Fe(\eta^5\text{-}C_5Me_5)_2/Fe(\eta^5\text{-}C_5Me_5)_2^+$ as an internal standard and whose redox potential was measured to be −0.53 V vs $Fe(\eta^5\text{-}C_5H_5)_2/Fe(\eta^5\text{-}C_5H_5)_2^+$. No electrochemical response was measured for **5-Cl** under the same conditions.

Synthesis of 1a-OH. 1,2-Diaminoethane (1.10 mL, 16.4 mmol) was added by syringe to a stirring solution of 3-hydroxybenzaldehyde (4.00 g, 32.7 mmol) in 50 mL of acetonitrile. After ∼5 min, a white precipitate formed. The suspension was stirred at room temperature for an additional 45 min. The solid was then collected on a ground glass frit and washed with 3 × 50 mL of cold acetonitrile. Isolated yield = 3.97 g (91%). The solid is soluble in dimethylsulfoxide or acetone. ^1H NMR (DMSO-d_6, 300 MHz, 22 °C): δ 9.32 (br, O*H*), 8.23 (s, 2H, *H*C═N), 7.21 (m, 2H, Ar C*H*), 7.10 (m, 4H, Ar C*H*), 6.82 (m, 2H, Ar C*H*), 3.83 ppm (s, 4H, CH_2). $^{13}C\{^1H\}$ NMR (DMSO-d_6, 75 MHz, 22 °C): δ 162.0 (*H*C═N), 157.6 (COH), 137.5 (Ar CH), 129.7 (Ar *C*H), 119.3 (Ar CH), 117.8 (Ar CH), 113.6 (Ar *C*H), 60.9 ppm (CH_2).

Synthesis of 1a: PCN-C_2. The bridged *m*-hydroxybenzaldimine **1a-OH** (1.93 g, 7.19 mmol), triethylamine (2.10 mL, 15.1 mmol), and diisopropylchlorophosphine (2.40 mL, 15.1 mmol) were combined in toluene (10 mL) and heated at reflux for 4 h. The solution was pumped dry, extracted with pentane/diethyl ether, and filtered over a short plug of silica to give a colorless oil. Isolated yield = 2.47 g (69%). ^1H NMR ($CDCl_3$, 300 MHz, 22 °C): δ 8.22 (s, 2H, *H*C═N), 7.42 (br s, 2H, Ar C*H*), 7.28 (overlapped with solvent, Ar C*H*), 7.24 (br, 2H, Ar C*H*), 7.16 (m, 2H, Ar C*H*), 3.93 (s, 4H, CH_2), 1.90 (m, 4H, *i*Pr C*H*Me$_2$), 1.14 (dd, J = 10.8, 7.1 Hz, 12H, *i*Pr CH*Me*), 1.07 ppm (dd, J = 16.0, 7.2 Hz, 12H, *i*Pr CH*Me*). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz, 22 °C): δ 162.4 (HC═N), 159.7 (d, J = 9.0 Hz, CO), 137.7 (Ar CH), 129.5 (Ar CH), 121.6 (Ar CH), 120.7 (d, J = 11.6 Hz, Ar CH), 118.0 (d, J = 9.5 Hz, Ar CH), 61.7 (CH_2), 28.4 (d, J = 17.6 Hz, *i*Pr CHMe), 17.81 (d, J = 20.2 Hz, *i*Pr CH*Me*), 17.1 ppm (d, J = 8.5 Hz, *i*Pr CH*Me*). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121 MHz, 22 °C): δ 149.5 ppm (s).

Synthesis of 1b-OH. This was prepared in a similar fashion to **1a-OH**. 1,2-Diaminobutane (1.65 mL, 16.4 mmol) was added by syringe to a stirring solution of 3-hydroxybenzaldehyde (4.00 g, 32.7 mmol) in 50 mL of acetonitrile. Isolated yield of *m*-hydroxybenzaldimine = 4.25

dx.doi.org/10.1021/om2008056 | *Organometallics* 2011, 30, 6641−6654

g (87%). ^{1}H NMR (DMSO-d_6, 300 MHz, 22 °C): δ 8.23 (s, 2H, *H*C═N), 7.21−7.12 (m, 6H, Ar C*H*), 6.84 (dd, J_{HH} = 2.7, 0.9 Hz, 2H, Ar C*H*), 3.56 (s, 4H, CH_2), 1.64 ppm (s, 4H, CH_2). ^{13}C{^{1}H} NMR (DMSO-d_6, 75 MHz, 22 °C): δ 160.7 (HC═N), 157.7 (COH), 137.6 (Ar CH), 129.7 (Ar CH), 119.3 (Ar CH), 117.8 (Ar CH), 113.7 (Ar CH), 60.3 (CH$_2$), 28.4 ppm (CH$_2$).

Synthesis of 1b: PCN-C$_4$. This was prepared in a similar fashion to **1a**, using triethylamine (0.988 mL, 7.09 mmol), diisopropylchlorophosphine (1.13 mL, 7.09 mmol), C$_4$-bis-*m*-hydroxybenzaldimine (1.00 g, 3.37 mmol), 10 mL of toluene. Isolated yield of **2** = 1.19 g (67%). ^{1}H NMR (CDCl$_3$, 300 MHz, 22 °C): δ 8.21 (s, 2H, *H*C═N), 7.43 (m, 2H, Ar C*H*), 7.30 (m overlapped with solvent, 4H, Ar C*H*), 7.16 (m, 2H, Ar C*H*), 3.63 (br, 4H, NCH_2) 1.91 (m, 4H, *i*Pr C*H*Me), 1.76 (br m, 4H, CH_2), 1.15 (dd, J = 10.8, 6.9 Hz, 12H, *i*Pr CH*Me*), 1.07 ppm (dd, J = 16.0, 7.3 Hz, 12H, *i*Pr CH*Me*). ^{13}C{^{1}H} NMR (CDCl$_3$, 75 MHz, 22 °C): δ 160.9 (*H*C═N), 159.8 (d, J = 8.7 Hz, *C*O), 137.8 (Ar *C*H), 129.6 (Ar *C*H), 121.5 (Ar *C*H), 120.7 (d, J = 11.42 Hz, Ar *C*H), 118.1 (d, J = 9.1 Hz, Ar *C*H), 61.6 (NCH$_2$), 28.7 (d, J = 19.0 Hz, *i*Pr *C*HMe), 28.3 (CH$_2$), 17.9 (d, J = 20.2 Hz, *i*Pr CH*Me*), 17.2 ppm (d, J = 8.5 Hz, *i*Pr CH*Me*). ^{31}P{^{1}H} NMR (CDCl$_3$, 121 MHz, 22 °C): δ 148.9 ppm (s).

Synthesis of 2. A solution of bis(2-bromo-4-methylphenyl)amine (5.46 g, 15.4 mmol) in diethyl ether (160 mL) was cooled to −40 °C, and *n*BuLi (12.30 mL, 30.8 mmol; 2.5 M in hexanes) was added portionwise. The reaction was warmed to room temperature over 1 h and stirred for an additional 15 min. *i*Pr$_2$PCl (2.45 mL, 15.4 mmol) was added dropwise at 0 °C. After 15 h of stirring, the mixture was quenched with 5 mL of degassed 1:1 ethanol/water, stirred for 1 h, dried, extracted with 35 mL of an ether/pentane mixture (6:1), filtered over Celite, and redried. The off-white solid was washed with 3 × 5 mL portions of cold pentane to leave a crystalline, white solid. Yield = 4.76 g (79%). ^{1}H NMR (C$_6$D$_6$, 500 MHz, 22 °C): 7.69 (d, J = 9.7 Hz, 1H, N*H*), 7.23 (overlapping m, 3H, Ar C*H*), 7.17 (overlapped with solvent, 1H, Ar C*H*), 6.90 (d, J = 8.7 Hz, 1H), 6.71 (d, J = 8.7 Hz, 1H, Ar C*H*), 2.18 (s, 3H, CH_3), 1.96 (m overlapped with methyl, J = 6.8, 1.7 Hz, 2H, *i*Pr C*H*Me), 1.93 (s, 3H, CH_3), 1.06 (ddd J = 15.4, 7.0 Hz, 6H, *i*Pr CH*Me*), 0.92 ppm (dd, J = 11.7, 6.9 Hz, 6H, *i*Pr CH*Me*). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 126 MHz, 22 °C): δ 146.1 (d, J = 18.7 Hz, *C*P), 139.7 (*C*Br), 133.9 (Ar *C*H), 133.8 (d, J = 2.3 Hz, Ar *C*H), 131.0 (*C*Me), 130.7 (Ar *C*H), 130.0 (*C*Me), 128.9 (Ar *C*H), 123.6 (d, J = 16.1 Hz, *C*N), 118.5 (d, J = 2.6 Hz, Ar *C*H), 116.5 (Ar *C*H), 114.0 (*C*N), 23.2 (d, J = 11.2 Hz, *i*Pr *C*HMe), 21.0 (CH$_3$), 20.4 (CH$_3$), 20.2 (d, J = 9.8 Hz, *i*Pr CH*Me*), 19.0 ppm (d, J = 8.8 Hz, *i*Pr CH*Me*). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 202 MHz, 22 °C): δ −13.8 ppm (s).

Synthesis of 3. Two equivalents of *n*BuLi (2.24 mL, 5.60 mmol; 2.5 M solution in hexanes) was added dropwise to a solution of **2** (1.00 g, 2.55 mmol) in diethyl ether (50 mL) at 0 °C (ice bath). The cooling bath was then removed, and the mixture was stirred for 2 h. The cooling bath was replaced, and dimethylformamide (0.59 mL, 7.62 mmol) was added dropwise by syringe. The solution turned orange over the course of 1 h and was stirred at room temperature for 12 h. Ethanol and water (1:1, 10 mL) were added, and stirring was continued for 2 h. The flask was dried in vacuo, and the resulting orange solid extracted with 20 mL of THF and 5 mL of CH$_2$Cl$_2$, which was passed through a plug of silica to give a bright yellow solution, which upon drying gave a similarly colored solid. Yield = 0.837 g (87%). ^{1}H NMR (C$_6$D$_6$, 500 MHz, 22 °C): δ 10.69 (br d, J = 4.1 Hz, 1H, N*H*), 9.72 (s, 1H, (O)C*H*), 7.31 (dd, J = 8.0, 4.1 Hz, 1H, Ar C*H*), 7.26 (m, J = 2.4 Hz, 1H, Ar C*H*), 7.07 (d, J = 8.1 Hz, 1H, Ar C*H*), 6.91 (dd, J = 8.2, 2.1 Hz, 1H, Ar C*H*), 6.84−6.80 (overlapping m, 2H, Ar C*H*), 2.17 (s, 3H, CH_3), 1.99 (m, 2H, *i*Pr C*H*Me), 1.97 (s overlapped with C*H*, 3H, CH_3), 1.08 (dd, J = 15.0, 7.2 Hz, 6H, *i*Pr CH*Me*), 0.93 ppm (dd, J = 11.6, 6.8 Hz, 6H, *i*Pr CH*Me*). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 126 MHz, 22 °C): δ 193.5 ((O)CH), 146.3 (CC(O)H), 143.7 (d, J = 20.6 Hz, *C*P), 136.5 (Ar *C*H), 136.2 (Ar *C*H), 134.5 (Ar *C*H), 133.1 (Ar *C*), 130.4 (Ar *C*H), 129.8 (d, J = 21.3 Hz, Ar *C*), 125.8 (Ar *C*), 124.1 (d, J = 2.6 Hz, Ar *C*H), 120.5 (Ar *C*), 113.4 (Ar *C*H), 23.5 (d, J = 14.3 Hz, *i*Pr CHMe), 21.1 (CH$_3$), 20.3 (d, J = 19.4 Hz, *i*Pr CH*Me*), 20.0 (CH$_3$), 19.2 ppm (d, J = 9.9 Hz, *i*Pr CH*Me*). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 202 MHz, 22 °C): δ −8.8 ppm (s).

Synthesis of 4a: PN(H)N-C$_2$. 1,2-Diaminoethane (0.0293 mL, 0.437 mmol) was added to a solution of **6** (0.300 g, 0.879 mmol) in toluene (10 mL) and refluxed for 20 h. The mixture was then pumped dry, and the product extracted with CH$_2$Cl$_2$, passed through a short plug of silica, and redried. The pale yellow solid was recrystallized from CH$_2$Cl$_2$/pentane at −35 °C. Isolated yield = 0.251 g (81%). ^{1}H NMR (C$_6$D$_6$, 500 MHz, 22 °C): δ 11.44 (d, J = 3.4 Hz, 2H, N*H*), 8.37 (s, 2H, *H*C═N), 7.42 (dd, J = 8.2, 4.0 Hz, 2H, Ar C*H*), 7.30 (br, 2H, Ar C*H*), 7.24 (d, J = 9.1 Hz, 2H, Ar C*H*), 6.90 (dd, J = 8.5, 1.1 Hz, 2H, Ar C*H*), 6.81−6.79 (overlapped m, 4H, Ar C*H*), 4.07 (s, 4H, CH$_2$), 2.20 (s, 6H, CH_3), 2.09 (m overlapped with Me, 4H, *i*Pr C*H*Me), 2.05 (s, 6H, CH_3), 1.14 (dd, J = 14.9, 7.0 Hz, 12H, *i*Pr CH*Me*), 1.01 ppm (dd, J = 11.7, 7.2 Hz, 12H, *i*Pr CH*Me*). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 126 MHz, 22 °C): δ 165.6 (HC═N), 145.4 (d, J = 19.9 Hz, *C*P), 144.6 (Ar *C*), 134.5 (Ar CH), 131.7 (Ar CH), 131.5 (Ar *C*), 130.4 (Ar CH), 128.3 (Ar *C*), 125.5 (Ar *C*), 122.9 (two peaks overlapped Ar CH), 119.8 (Ar *C*), 113.5 (Ar CH), 61.8 (CH$_2$), 23.6 (d, J = 14.0 Hz, *i*Pr CHMe), 21.1 (CH$_3$), 20.7 (d, J = 19.3 Hz, *i*Pr CH*Me*), 20.3 (CH$_3$), 19.6 ppm (d, J = 9.9 Hz, *i*Pr CH*Me*). ^{31}P{^{1}H} NMR (CDCl$_3$, 202 MHz, 22 °C): δ −5.8 ppm (br s).

Synthesis of 4b: PN(H)N-C$_4$. The procedure was like that for **4a** using 1,2-diaminobutane (0.221 mL, 2.20 mmol) and **6** (1.50 g, 4.40 mmol) in toluene. Isolated yield of pale yellow solid = 1.405 g (87%). ^{1}H NMR (CDCl$_3$, 500 MHz, 22 °C): δ 10.70 (d, J = 3.2 Hz, 2H, N*H*), 8.28 (s, 2H, *H*C═N), 7.29 (dd, J = 8.2, 3.9 Hz, 2H, Ar C*H*), 7.22 (m overlapped with solvent, 2H, Ar C*H*), 7.05 (dd, J = 8.1, 1.9 Hz, 2H, Ar C*H*), 7.01 (d, J = 1.9 Hz, 2H, Ar C*H*), 6.96 (d, J = 8.4 Hz, 2H, Ar C*H*), 6.91 (dd, J = 8.4, 1.6 Hz, 2H, Ar C*H*), 3.60 (br, 4H, CH_2), 2.31 (s, 6H, CH_3), 2.23 (s, 6H, CH_3), 2.08 (m, 4H, *i*Pr C*H*Me), 1.81 (br, 4H, CH_2), 1.05 (dd, J = 14.9, 7.0 Hz, 12H, *i*Pr CH*Me*), 0.89 ppm (dd, J = 11.6, 6.8 Hz, 12H, *i*Pr CH*Me*). ^{13}C{^{1}H} NMR (CDCl$_3$, 126 MHz, 22 °C): δ 163.5 (HC═N), 144.6 (d, J = 19.3 Hz, *C*P), 144.3 (Ar *C*), 134.6 (d, J = 2.7 Hz, Ar CH), 133.8 (Ar CH), 131.8 (d, J = 2.0 Hz, Ar *C*), 131.3 (Ar CH), 130.0 (Ar CH), 128.9 (d, J = 19.2 Hz, Ar CH), 125.4 (Ar *C*), 123.2 (d, J = 3.1 Hz, Ar CH), 119.1 (Ar *C*), 113.4 (Ar *C*), 61.7 (CH$_2$), 28.9 (CH$_2$), 23.4 (d, J = 13.0 Hz, *i*Pr CHMe), 21.1 (CH$_3$), 20.5 (CH$_3$), 20.4 (*i*Pr CHMe), 19.5 ppm (d, J = 10.3 Hz, *i*Pr CH*Me*). ^{31}P{^{1}H} NMR (CDCl$_3$, 202 MHz, 22 °C): δ −4.6 ppm (br s).

Synthesis of 5a-Cl: (PCN-C$_2$)PdCl. A solution of **1a** (0.323 g, 0.645 mmol) in 10 mL of *ortho*-dichlorobenzene was added to a suspension of Pd(COD)Cl$_2$ (0.368 g, 1.29 mmol) and 2,6-lutidine (0.149 mL, 1.29 mmol) in 5 mL of the same. The mixture was heated at reflux for 30 min. Cooling the mixture led to the formation of a pale yellow precipitate, which was collected, washed with diethyl ether (3 × 50 mL), and extracted with dichloromethane. A yellow powder was precipitated from solution upon addition of diethyl ether, collected, redissolved in dichloromethane, and passed through a plug of silica. Concentration and recrystallization from dichloromethane/diethyl ether at −20 °C yielded pale yellow crystals (0.287 g, 57%). ^{1}H NMR (CD$_2$Cl$_2$, 300 MHz, 22 °C): δ 8.38 (d, $^4J_{HP}$ = 4.8 Hz, 2H, *H*C═N), 6.94 (m, 4H, Ar C*H*), 6.75 (dt, J = 7.4, 1.3 Hz, 2H, Ar C*H*), 4.40 (br, 4H, CH_2), 2.43 (m, 4H, *i*Pr C*H*Me), 1.38 (dd, J = 19.3, 7.3 Hz, *i*Pr CH*Me*), 1.28 ppm (dd, J = 16.2, 7.0 Hz, *i*Pr CH*Me*). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 75 MHz, 22 °C): δ 176.8 (d, J = 3.8 Hz, HC═N), 163.6 (d, J = 6.2 Hz, *C*O), 153.0 (*C*Pd), 145.8 (*C*C═N), 126.7 (Ar CH), 122.2 (Ar CH), 114.3 (d, J = 15.6 Hz, Ar CH), 58.4 (CH$_2$), 29.5 (d, J = 25.5 Hz, *i*Pr CHMe), 17.5 (d, J = 5.8 Hz, *i*Pr CH*Me*), 16.9 ppm (*i*Pr CH*Me*). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 121 MHz, 22 °C): δ 202.5 ppm (s). Anal. Calcd for C$_{28}$H$_{40}$Cl$_2$N$_2$O$_2$P$_2$Pd$_2$: C, 42.99; H, 5.15; N, 3.58. Found: C, 42.95; H 5.08; N, 3.49. Mp: 191 °C.

Synthesis of 5b-Cl: (PCN-C$_4$)PdCl. The synthesis was like that for **5a-Cl** using Pd(COD)Cl$_2$ (0.304 g, 1.06 mmol), **1b** (0.281 g, 0.532 mmol), and 2,6-lutidine (0.123 mL, 1.06 mmol). Isolated yield = 0.229 g (53%). ^{1}H NMR (CD$_2$Cl$_2$, 500 MHz, 22 °C): δ 8.26 (d, J = 5.0 Hz, 2H, *H*C═N), 7.04 (d, J = 7.0 Hz, 2H, Ar C*H*), 7.17 (app t, J = 7.5 Hz, 2H, Ar C*H*), 6.78 (d, J = 7.5 Hz, 2H, Ar C*H*), 3.80 (br m, 4H, CH_2), 2.42 (m, 4H, *i*Pr C*H*Me), 1.94 (m, 4H, CH_2), 1.37 (dd, J = 19.5, 7.5 Hz, 12H, *i*Pr CH*Me*), 1.29 ppm (dd, J = 16.5, 7.0 Hz). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 126 MHz, 22 °C): δ 174.4 (d, J = 4.3 Hz, HC═N), 163.7

dx.doi.org/10.1021/om2008056 | *Organometallics* 2011, 30, 6641−6654

(d, J = 6.3 Hz, *C*O), 153.1 (*C*Pd), 146.6 (*C*C=N), 126.6 (Ar *C*H), 122.2 (Ar *C*H), 114.0 (d, J = 15.6 Hz, Ar *C*H), 58.5 (CH_2), 29.6 (d, J = 25.3 Hz, *i*Pr CHMe), 27.6 (CH_2), 17.5 (d, J = 5.8 Hz, *i*Pr CH*Me*), 16.9 ppm (*i*Pr CH*Me*). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 202 MHz, 22 °C): δ 202.6 ppm (s). Anal. Calcd for $C_{30}H_{44}Cl_2N_2O_2P_2Pd_2$: C, 44.46; H, 5.47; N, 3.46. Found: C, 44.56; H 5.44; N, 3.54. Mp: 203 °C.

Synthesis of 5a-OTf: (PCN-C$_2$)PdOTf. Solid silver trifluoromethanesulfonate (AgOTf: 0.066 g, 0.256 mmol) was added to a bright yellow solution of **5a-Cl** (0.100 g, 0.128 mmol in 10 mL of a ~3:1 mixture of C_6H_5F/CH_2Cl_2). After 15 min of vigorous stirring, a white suspension had formed. After 1 h, the mixture was filtered and pumped to dryness, and the product was extracted with toluene, filtered over Celite, and dried to give a white powder, which was recrystallized from pentane/toluene. Yield = 0.110 g (85%). ^1H NMR (CD_2Cl_2, 500 MHz, 22 °C): δ 8.36 (d, $^4J_{HP}$ = 4.5 Hz, 2H, *H*C=N), 7.08 (d, J = 8.0 Hz, 2H, Ar C*H*), 7.04 (dd, J = 7.5, 6.5 Hz, 2H, Ar C*H*), 6.79 (d, J = 8.0 Hz, 2H, Ar C*H*), 4.11 (s, 4H, CH_2), 2.59 (m, 4H, *i*Pr *CH*Me), 1.38 (dd, J = 20.5, 7.5 Hz, 12H, *i*Pr CH*Me*), 1.28 ppm (dd, J = 15.5, 7.0 Hz, 12 H, *i*Pr CH*Me*). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 126 MHz, 22 °C): 176.9 (d, J = 3.9 Hz, HC=N), 164.3 (d, J = 6.2 Hz, *C*O), 146.2 (d, J = 3.1 Hz, *C*Pd), 145.8 (*C*C=N), 127.9 (Ar CH), 123.6 (Ar *C*H), 115.4 (d, J = 14.6 Hz, Ar *C*H), 58.0 (CH_2), 29.5 (d, J = 25.2 Hz, *i*Pr *CH*Me), 17.7 (d, J = 6.0 Hz, *i*Pr CH*Me*), 16.8 ppm (d, J = 2.3 Hz, *i*Pr CH*Me*). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 202 MHz, 22 °C): δ 203.2 (s) ppm. ^{19}F NMR (CD_2Cl_2, 470 MHz, 22 °C): δ −78.8 (s) ppm. Anal. Calcd for $C_{30}H_{40}F_6N_2O_8P_2Pd_2S_2$: C, 35.69; H, 3.99; N, 2.77. Found: C, 35.55; H 3.75; N, 2.63.

Synthesis of 5b-OTf: (PCN-C$_4$)PdOTf. The synthesis was like that for **5a-OTf**, using AgOTf (0.250 g, 0.975 mmol), **5b-Cl** (0.395 g, 0.487 mmol), and CH_2Cl_2 (10 mL). Isolated yield = 0.442 g (87%). ^1H NMR (CD_2Cl_2, 500 MHz, 22 °C): δ 8.13 (d, $^4J_{HP}$ = 5.0 Hz, 2H, *H*C=N), 7.07 (m, 4H, Ar C*H*), 6.79 (d, J = 7.0 Hz, 2H, Ar C*H*), 3.71 (br, 4H, CH_2), 2.57 (m, 4H, *i*Pr *CH*Me), 1.84 (br, 4H, CH_2), 1.36 (dd, J = 20.0, 7.0 Hz, 12H, *i*Pr CH*Me*), 1.28 ppm (dd, J = 16.0, 7.0 Hz, 12 H, *i*Pr CH*Me*). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 126 MHz, 22 °C): δ 173.7 (d, J = 3.8 Hz, HC=N), 164.3 (d, J = 5.4 Hz, *C*O), 146.3 (*C*CH=N), 146.1 (d, J = 3.1 Hz, *C*Pd), 127.7 (Ar CH), 123.1 (Ar *C*H), 114.9 (d, J = 15.3 Hz, Ar *C*H), 59.1 (NCH_2), 29.5 (d, J = 24.5 Hz, *i*Pr CHMe), 27.2 (CH_2), 17.7 (d, J = 6.2 Hz, *i*Pr CH*Me*), 16.8 ppm (d, J = 2.3 Hz, *i*Pr CH*Me*). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 202 MHz, 22 °C): δ 202.7 (s) ppm. ^{19}F NMR (CD_2Cl_2, 470 MHz, 22 °C): δ −79.0 (s) ppm. Anal. Calcd for $C_{32}H_{44}F_6N_2O_8P_2Pd_2S_2$: C, 37.04; H, 4.27; N, 2.70. Found: C, 36.93; H 4.07; N, 2.49.

Synthesis of 5a-H: [(PCN)Pd-H-Pd(PCN)-C$_2$][OTf]. Solid NaO*i*Pr (0.0080 g, 0.097 mmol) was added in two portions to a rapidly stirring dichloromethane solution of **5a-OTf** (0.0970 g, 0.0961 mmol; 5 mL) at room temperature, which darkened from light yellow to orange-brown. The mixture was stirred for 1 h, and an aliquot was checked by ^{31}P NMR to ensure complete conversion to **5a-H**. The solution was then filtered over a short plug of Celite, dried in vacuo, and washed with 3 × 2 mL of Et_2O. The remaining pale tan solid was dried again in vacuo. Isolated yield = 0.0562 g (68%). X-ray quality crystals were grown from CH_2Cl_2/Et_2O at −30 °C. ^1H NMR (CD_2Cl_2, 499 MHz, 22 °C): δ 8.32 (d, $^4J_{HP}$ = 4.0 Hz, 2H, *H*C=N), 7.20 (d, J = 7.0 Hz, 2H, Ar C*H*), 7.16 (t, J = 7.7 Hz, 2H, Ar C*H*), 6.93 (d, J = 7.5 Hz, 2H, Ar C*H*), 4.12 (br, 4H, CH_2), 2.32 (br m, 4H, *i*Pr *CH*Me), 1.33 (dd, J = 7.5, 2.0 Hz, 12H, *i*Pr CH*Me*), 1.30 (pseudo t, J = 6.5 Hz, 12H, *i*Pr CH*Me*), −9.19 ppm (t, J = 13.5 Hz, 1H, Pd-*H*-Pd). $^{13}C\{^1H\}$ (CD_2Cl_2, 126 MHz, 22 °C): δ 178.3 (d, J = 3.3 Hz, HC=N), 162.9 (d, J = 6.2 Hz, Ar *C*), 158.2 (Ar *C*), 146.5 (Ar *C*), 128.4 (Ar *C*H), 123.2 (Ar *C*H), 115.1 (d, J = 15.3 Hz, Ar *C*H), 64.6 (CH_2), 30.6 (d, J = 26.9 Hz, *i*Pr *CH*Me), 18.7 ppm (d, J = 4.9 Hz, *i*Pr CH*Me*). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 202 MHz, 22 °C): δ 207.1 ppm. ^{19}F NMR (CD_2Cl_2, 470 MHz, 22 °C): δ −79.8 ppm. UV−vis (CH_2Cl_2): λ (ε) shoulder at 370 nm (6420 $M^{-1}cm^{-1}$). Anal. Calcd for $C_{29}H_{41}F_3N_2O_5P_2Pd_2S_1$: C, 40.43; H, 4.80; N, 3.25. Found: C, 40.35; H, 4.81; N, 3.09.

Synthesis of 5b-H: [(PCN)Pd-H-Pd(PCN)-C$_4$][OTf]. A precooled THF solution of NaO*i*Pr (0.0065 g, 0.079 mmol; 5 mL) was added to a solution of **5b-OTf** (0.0412 g, 0.0397 mmol) at −30 °C and left to stand for 1 h. After warming to room temperature, the solution was dried in vacuo, extracted with CH_2Cl_2, filtered over a short plug of Celite, and redried. The resulting tan solid was washed with Et_2O (3 × 1 mL) and dried. X-ray quality crystals were grown from CH_2Cl_2/Et_2O at −30 °C. Isolated yield = 31.9 g (90%). ^1H NMR (CD_2Cl_2, 499 MHz, 22 °C): δ 8.34 (d, J = 4.0 Hz, 2H, *H*C=N), 7.20 (overlapped d, J = 5.5 Hz, 2H, Ar C*H*), 7.17 (overlapped dd, J = 7.0, 5.5 Hz, 2H, Ar C*H*), 6.95 (d, J = 7.0 Hz, 2H, Ar C*H*), 4.40 (br m, 2H, CH_2), 3.62 (br m, 2H, CH_2), 2.50−2.43 (overlapped m, 4H, CH_2 and *i*Pr *CH*Me), 2.32 (h, J = 7.5 Hz, 2H, *i*Pr *CH*Me), 1.90 (br m, 2H, CH_2), 1.37 (dd, J = 15.0, 7.0, 6H, *i*Pr CH*Me*), 1.34−1.30 (overlapped m, 12H, *i*Pr CH*Me*), 1.23 (dd, J = 17.2, 6.7 Hz, 6H, *i*Pr CH*Me*), −8.42 ppm (t, $^2J_{HP}$ = 13.5 Hz, 1H, Pd-*H*-Pd). $^{13}C\{^1H\}$ (CD_2Cl_2, 126 MHz, 22 °C): δ 178.7 (d, J_{CP} = 3.3 Hz, HC=N), 162.6 (d, J_{CP} = 5.5 Hz, Ar *C*), 157.9 (Ar *C*), 146.5 (Ar *C*), 128.5 (Ar CH), 122.9 (Ar *C*H), 115.0 (d, J_{CP} = 15.7 Hz, Ar CH), 62.3 (NCH_2), 30.7 (d, J_{CP} = 26.7 Hz, *i*Pr CHMe), 30.3 (d, J_{CP} = 27.1 Hz, *i*Pr CHMe), 27.1 (CH_2), 18.7 (d, J_{CP} = 7.3 Hz, *i*Pr CH*Me*), 18.6 (d, J_{CP} = 2.8 Hz, *i*Pr CH*Me*), 16.1 ppm (d, J_{CP} = 4.1 Hz, *i*Pr CH*Me*). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121 MHz, 22 °C): δ 207.5 ppm. ^{19}F NMR (CD_2Cl_2, 282 MHz, 22 °C): δ −79.7 ppm. UV−vis (CH_2Cl_2): λ (ε) shoulder at 360 nm (6090 M^{-1} cm^{-1}). Anal. Calcd for $C_{31}H_{45}F_3N_2O_5P_2Pd_2S_1$: C, 41.86; H, 5.10; N, 3.15. Found: C, 41.78; H, 5.26; N, 2.99.

Synthesis of 6a-Cl: (PNN-C$_2$)PdCl. In a 50 mL Schlenk flask, **4a** (0.0492 g, 0.0696 mmol), Pd(COD)Cl_2 (0.0397 g, 0.139 mmol), and 2,6-lutidine (16.1 mL, 0.139 mmol) were dissolved in THF (10 mL). The mixture was stirred at room temperature for 15 h. The orange suspension turned a deep wine-red. The reaction mixture was dried, and the residue was extracted and passed through a short plug of silica using CH_2Cl_2 and dried in vacuo. The resulting dark red solid was recrystallized from benzene/pentane. Isolated yield = 0.056 g (81%). ^1H NMR (CD_2Cl_2, 500 MHz, 22 °C): δ 7.95 (d, J = 13.4 Hz, 2H, *H*C=N), 7.93 (shoulder, minor *H*C=N), 7.31 (m, minor C*H*), 7.20 (m, minor C*H*), 7.09 (overlapped m, minor C*H*), 7.07 (overlapped d, J = 8.7 Hz, 2H, Ar C*H*), 7.05 (overlapped d, J = 13.0 Hz, 2H, Ar C*H*), 6.98 (overlapped m, minor C*H*), 6.84 (m, minor C*H*), 6.71 (br t, J = 7.6 Hz, 4H, Ar C*H*), 6.37 (s, 4H, Ar C*H*), 5.11 (d, J = 6.9 Hz, 2H, CH_2), 4.71 (br, minor CH_2), 4.22 (br, minor CH_2), 4.02 (d, J = 6.8 Hz, 2H, CH_2), 2.75 (h, J = 6.7 Hz, 2H, *i*Pr *CH*Me), 2.37 (overlapped m, minor *i*Pr *CH*Me), 2.31 (overlapped m, 2H, *i*Pr *CH*Me), 2.27 (overlapped s, 6H, CH_3), 2.11 (s, minor CH_3), 1.96 (s, 6H, CH_3), 1.58 (overlapped dd, J = 16.8, 6.6 Hz, *i*Pr CH*Me*), 1.52 (overlapped dd, J = 16.5, 7.3 Hz, *i*Pr CH*Me*), 1.44−1.34 (overlapped m, minor *i*Pr CH*Me*), 1.29 (dd, J = 18.2, 7.0 Hz, *i*Pr CH*Me*), 1.24−1.18 (m, minor *i*Pr CH*Me*), 1.15 ppm (dd, J = 15.6, 6.7 Hz, *i*Pr CH*Me*). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 126 MHz, 22 °C): δ (major isomer) 162.4 (HC=N), 162.2 (d, J = 19.9 Hz, *C*N), 149.6 (br, Ar *C*P), 134.5 (d, J = 2.8 Hz, Ar *C*H), 133.5 (Ar *C*H), 132.8 (Ar *C*H), 131.0 (Ar *C*H), 128.7 (Ar *C*), 125.8 (Ar *C*), 121.2 (d, J = 14.3 Hz, Ar *C*H), 120.1 (Ar *C*), 119.7 (Ar *C*), 118.2 (Ar *C*H), 60.4 (CH_2), 27.0 (d, J = 24.1 Hz, *i*Pr CHMe), 23.5 (d, J = 30.4 Hz, *i*Pr CHMe), 20.5 (CH_3), 20.1 (*i*Pr CH*Me*), 19.0 (d, J = 3.9 Hz, *i*Pr CH*Me*), 18.6 (CH_3), 17.9 (*i*Pr CH*Me*), 17.6 ppm (*i*Pr CH*Me*). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 202 MHz, 22 °C): δ 71.9 (s, minor), 71.3 ppm (s, major, 8:1 ratio). UV−vis (C_6H_5F): λ (ε) 336 (16 320), 440 (6650), 531 nm (8850 M^{-1} cm^{-1}). Anal. Calcd for $C_{44}H_{58}N_4Cl_2P_2Pd_2$: C, 53.45; H, 5.91; N, 5.67. Found: C, 53.57; H, 6.02; N, 5.63. Mp: 280 °C (dec).

Synthesis of 6b-Cl: (PNN-C$_4$)PdCl. The procedure/workup was like that for **6a-Cl**, using **4b** (0.203 g, 0.276 mmol), Pd(COD)Cl_2 (0.158 g, 0.553 mmol), and 2,6-lutidine (64 μL, 0.55 mmol). Isolated yield = 0.204 g (72%). ^1H NMR (CD_2Cl_2, 500 MHz, 22 °C): δ 7.79 (d, J = 13.2 Hz, 2H, major *H*C=N), 7.72 (d, J = 13.2 Hz, minor *H*C=N, 1:1.4 ratio), 7.29−7.26 (overlapped m, 2H, Ar C*H*), 7.15−7.04 (overlapped m, 4H, Ar C*H*), 6.95−6.90 (overlapped, 4H, Ar CH), 6.85 (overlapped d, J = 8.4 Hz, 2H, major Ar C*H*), 6.84 (overlapped d, J = 8.4 Hz, minor Ar C*H*), 4.76 (br, 2H, major CH_2), 4.63 (br, minor CH_2), 3.35 (br, 2H, major CH_2), 3.28 (br, 2H, minor CH_2), 2.71 (m, 2H, *i*Pr *CH*Me), 2.31 (m, 2H, *i*Pr *CH*Me), 2.26 (br s, CH_3), 2.18 (s, CH_3), 2.00 (overlapped br, 4H, major CH_2), 1.92 (br, minor CH_2), 1.47 (m, minor *i*Pr CH*Me*), 1.43 (m, minor *i*Pr CH*Me*),

dx.doi.org/10.1021/om2008056 | *Organometallics* 2011, 30, 6641−6654

1.39 (m, minor *i*Pr CH*Me*), 1.33 (dd, *J* = 18.1, 6.4 Hz, 12H, *i*Pr CH*Me*), 1.18 ppm (dd, *J* = 15.3, 6.8 Hz, 12H, *i*Pr CH*Me*). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 126 MHz, 22 °C): δ 162.6 (d, *J* = 19.8 Hz, *C*N), 161.7 (major HC═N), 161.4 (minor HC═N), 149.7 (Ar *C*P), 134.5 (major Ar *C*H), 134.3 (minor Ar *C*H), 133.9 (Ar *C*H), 132.9 (Ar *C*H), 131.5 (Ar *C*H), 129.2 (Ar *C*), 126.0 (Ar *C*), 125.9 (Ar *C*), 120.9 (d, *J* = 13.9 Hz, Ar *C*H), 120.5 (major Ar *C*), 120.2 (minor Ar *C*), 118.6 (overlapped minor Ar *C*H), 118.5 (overlapped major Ar *C*H), 60.11 (minor CH_2), 59.6 (major CH_2), 29.6 (minor CH_2), 29.2 (major CH_2), 27.0 (d, *J* = 25.5 Hz, *i*Pr *C*HMe), 23.8 (d, *J* = 30.4 Hz, *i*Pr *C*HMe), 20.5 (minor CH_3), 20.1 (major CH_3), 18.9 (d, *J* = 3.2 Hz, major *i*Pr CH*Me*), 18.17 (minor *i*Pr CH*Me*), 18.11 (minor *i*Pr CH*Me*), 18.0 (minor *i*Pr CH*Me*, signal for fourth Me group overlapped), 17.7 ppm (major *i*Pr CH*Me*). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 202 MHz, 22 °C): δ 70.9 (overlapped s, minor), 70.8 ppm (overlapped s, major 1:1.4 ratio). UV−vis (C_6H_5F): λ (ε) 337 (15 180), 435 (5640), 529 nm (6840 M^{-1} cm^{-1}). Anal. Calcd for $C_{46}H_{62}N_4Cl_2P_2Pd_2$: C, 54.34; H, 6.15; N, 5.51. Found: C, 54.13; H, 5.99; N, 5.09. Mp: 171 °C.

Synthesis of 6a-OAc: (PNN-C_2)PdOAc. Solid $[Pd(OAc)_2]_3$ (0.129 g, 0.574 mmol of Pd) was added to a solution of **4a** (0.203 g, 0.287 mmol) in THF (10 mL). The color immediately changed from light yellow to wine-red. The solution was stirred for 1 h at room temperature, then dried in vacuo. The crude product was redissolved in a minimal amount of C_6H_5F, filtered over Celite, and dried. The resulting solid was recrystallized from C_6H_6/pentane to give a wine-red solid. Isolated yield = 0.272 g (91%). ^1H NMR (CD_2Cl_2, 500 MHz, 22 °C): δ 7.95 (d, $^3J_{HP}$ = 12.4 Hz, 2H, major *H*C═N), 7.91 (overlapped d, minor *H*C═N), 7.33 (d, *J* = 8.2 Hz, minor Ar *C*H), 7.18 (d, *J* = 8.2 Hz, minor Ar *C*H), 7.10 (d, *J* = 8.6 Hz, 2H, major Ar *C*H), 7.00 (overlapped m, *J* = 7.9 Hz, minor Ar *C*H), 6.96 (d, *J* = 8.6 Hz, 2H, major Ar *C*H), 6.83 (overlapped m, minor Ar *C*H), 6.70 (apparent t, *J* = 10.1 Hz, 4H, major Ar *C*H), 6.42 (m, *J* = 3.7 Hz, 2H, major Ar *C*H), 6.36 (s, 2H, major Ar *C*H), 4.53 (d, *J* = 6.6 Hz, 2H, major CH_2), 4.31 (m, minor CH_2), 3.90 (br m, d, *J* = 6.6 Hz in $^1H\{^{31}P\}$, 2H, major CH_2), 3.81 (m, minor CH_2), 2.59 (overlapped m, h, *J* = 6.9 Hz in $^1H\{^{31}P\}$, 2H, major *i*Pr *C*HMe), 2.43 (overlapped m, h, *J* = 6.9 Hz in $^1H\{^{31}P\}$, 2H, major *i*Pr *C*HMe), 2.25 (s overlapped with m of minor *i*Pr *C*HMe, 6H, CH_3), 2.08 (s, minor CH_3), 1.97 (s, 6H, AcO CH_3), 1.91 (s, minor CH_3), 1.90 (s, 6H, major CH_3), 1.45 (dd, *J* = 18.2, 7.0 Hz, 6H, major *i*Pr CH*Me*), 1.32 (overlapped m, minor *i*Pr CH*Me*), 1.29 (overlapped dd, *J* = 15.9, 7.0 Hz, 6H, major *i*Pr CH*Me*), 1.24 (overlapped dd, *J* = 19.2, 7.0 Hz, 6H, major *i*Pr CH*Me*), 1.19 (m, minor *i*Pr CH*Me*), 1.14 ppm (dd, *J* = 13.6, 7.0 Hz, 6H, major *i*Pr CH*Me*). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 126 MHz, 22 °C): δ 177.2 (minor, *C*═O), 177.0 (major, *C*═O), 163.9 (minor *H*C═N), 162.5 (major HC═N), 162.4 (major Ar *C*), 149.5 (major Ar *C*), 134.6 (major Ar *C*H), 134.4 (minor Ar *C*), 134.2 (minor Ar *C*), 133.6 (major Ar *C*H), 133.0 (minor Ar *C*), 132.7 (major Ar *C*H), 131.8 (minor Ar *C*), 131.3 (major Ar *C*H), 128.9 (d, *J* = 6.5 Hz, minor Ar *C*), 128.2 (d, *J* = 7.0 Hz, major Ar *C*), 126.3 (minor Ar *C*), 125.8 (minor Ar *C*), 125.6 (d, *J* = 3.7 Hz, major Ar *C*), 120.8 (d, *J* = 13.0 Hz, major Ar *C*H), 120.4 (d, *J* = 14.8 Hz, minor Ar *C*H), 119.6 (major Ar *C*), 119.5 (minor Ar *C*), 119.3 (major Ar *C*), 118.8 (major Ar *C*H), 59.8 (minor CH_2), 59.7 (major CH_2), 27.0 (d, *J* = 22.7 Hz, minor *i*Pr *C*HMe), 26.9 (d, *J* = 23.2 Hz, major *i*Pr *C*HMe), 23.6 (minor CH_3), 23.3 (major CH_3), 22.0 (d, *J* = 29.8 Hz, minor *i*Pr *C*HMe), 21.7 (d, *J* = 29.1 Hz, major *i*Pr *C*HMe), 20.5 (major CH_3), 20.2 (major CH_3), 20.1 (minor CH_3), 19.2 (d, *J* = 4.8 Hz, major *i*Pr CH*Me*), 19.0 (d, *J* = 3.7 Hz, major *i*Pr CH*Me*), 18.6 (br, minor *i*Pr CH*Me*), 16.5 (minor *i*Pr CH*Me*), 16.4 (d, *J* = 2.5 Hz, major *i*Pr CH*Me*), 16.3 ppm (d, *J* = 6.1 Hz, major *i*Pr CH*Me*). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 202 MHz): δ 66.8 (minor), 66.2 ppm (major, 1:5 ratio). UV−vis (C_6H_5F): λ (ε) 334 (10 500), 433 (3230), 523 nm (6380 M^{-1} cm^{-1}). Anal. Calcd for $C_{48}H_{64}N_4O_4P_2Pd_2$: C, 55.66; H, 6.23; N, 5.41. Found: C, 55.61; H, 6.44; N, 5.43. Mp: 174 °C.

Synthesis of 6b-OAc: (PNN-C_4)PdOAc. The procedure was like that for **6a-OAc**, using $[Pd(OAc)_2]_3$ (0.128 g, 0.571 mmol of Pd) and **4b** (0.210 g, 0.286 mmol). Isolated yield = 0.258 g (85%). ^1H NMR (CD_2Cl_2, 500 MHz, 22 °C): δ 7.66 (d, $^3J_{HP}$ = 12.0 Hz, 2H, *H*C═N), 7.32 (dd, *J* = 8.0, 3.5 Hz, 2H, Ar *C*H), 7.12 (m, 2H, Ar *C*H), 6.97 (d, *J* = 8.0 Hz, 2H, Ar *C*H), 6.91 (m, 4H, Ar *C*H), 6.86 (d, *J* = 8.5 Hz, 2H, Ar *C*H), 4.09 (br, 2H, CH_2), 3.27 (br, 2H, CH_2), 2.62 (m, 2H, *i*Pr *C*HMe), 2.36 (m, 2H, *i*Pr *C*HMe), 2.25 (s, 6H, CH_3), 2.18 (s, 6H, CH_3), 2.01 (br, 2H, CH_2) 1.91 (s, 3H, −OC(O)CH_3), 1.86 (s, 3H, −OC(O)CH_3), 1.80 (br, 2H, CH_2) 1.32−1.22 (overlapped m, 18H, *i*Pr CH*Me*), 1.15 ppm (dd, *J* = 14.0, 7.0 Hz, 6H, *i*Pr CH*Me*). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 126 MHz, 22 °C): δ 177.1 (overlapped, *C*═O), 162.8 (Ar *C*), 162.7 (Ar *C*), 161.4 (HC═N), 161.3 (*HC*═N), 149.6 (Ar *C*), 134.4 (Ar *C*H), 134.0 (Ar *C*H), 132.8 (overlapped, Ar *C*H), 131.7 (Ar *C*H), 129.4 (Ar *C*), 128.9 (Ar *C*), 128.8 (Ar *C*), 128.5 (Ar C), 126.0 (Ar *C*), 125.6 (m, Ar *C*), 120.5 (Ar *C*H), 120.4 (Ar *C*H), 119.9 (Ar *C*), 119.5 (Ar *C*), 119.3 (Ar *C*H), 59.6 (NCH_2), 59.5 (NCH_2), 29.6 (CH_2), 26.9 (d, $^1J_{CP}$ = 23.0 Hz, *i*Pr CHMe), 23.5 (overlapped, AcO *Me*), 23.4 (overlapped, AcO *Me*), 21.8 (d, $^1J_{CP}$ = 28.0 Hz, *i*Pr CHMe), 20.5 (CH_3), 20.1 (CH_3), 19.1 (d, *J* = 3.8 Hz, *i*Pr CH*Me*), 18.5 (d, *J* = 3.3 Hz, *i*Pr CH*Me*), 16.5 (*i*Pr CH*Me*), 16.4 ppm (*i*Pr CH*Me*). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 202 MHz, 22 °C): δ 65.3 ppm (s). UV−vis (C_6H_5F): λ (ε) 336 (11 330), 427 (3640), 521 nm (6620 M^{-1} cm^{-1}). Anal. Calcd for $C_{50}H_{68}N_4O_4P_2Pd_2$: C, 56.45; H, 6.44; N, 5.27. Found: C, 56.37; H, 6.54; N, 5.16. Mp: 189 °C.

Synthesis of 6a-OTf: (PNN-C_2)PdOTf. Me_3SiOTf (80 mL, 0.45 mmol) was added to a solution of **6a-OAc** (0.230 g, 0.222 mmol) in C_6H_5F (15 mL). The mixture was stirred for 4 h at room temperature and dried in vacuo. The resulting purple powder was suspended in Et_2O and collected by filtration. Isolated yield = 0.237 g (88%). ^1H NMR (C_6D_6, 300 MHz, 22 °C, peaks for major isomer reported): δ 7.81 (d, $^4J_{HP}$ = 13.2 Hz, 2H, *H*C═N), 7.11 (d, *J* = 9.0 Hz, 2H, Ar *C*H), 6.69 (br d, *J* = 8.4 Hz, 2H, Ar *C*H), 6.53 (overlapped d, *J* = 8.1 Hz, 1H, Ar *C*H), 6.53 (overlapped d, *J* = 9.0 Hz, 1H, Ar *C*H), 6.43 (br d, *J* = 8.4 Hz, 2H, Ar *C*H), 6.23 (d, J = 3.9 Hz, 1H, Ar *C*H), 6.20 (d, J = 3.6 Hz, 1H, Ar *C*H), 6.01 (d, *J* = 1.8 Hz, 2H, Ar *C*H), 5.15 (m, *J* = 7.8 Hz, 2H, CH_2), 4.12 (m, *J* = 7.5 Hz, 2H, CH_2), 2.72 (m, 2H, *i*Pr *C*H), 2.06 (s, overlapped, 6H, *Me*), 2.02 (m, overlapped, 2H, *i*Pr C*H*), 1.79 (s, 6H, *Me*), 1.39 (dd, J = 16.5, 6.9 Hz, 6H, *i*Pr CH*Me*), 1.23 (dd, overlapped, *J* = 18.6, 6.9 Hz, 6H, *i*Pr CH*Me*), 1.17 (dd, overlapped, *J* = 20.1, 6.9 Hz, 6H, *i*Pr CH*Me*), 0.72 ppm (dd, J = 14.1, 6.6 Hz, 6H, *i*Pr CH*Me*). $^{13}C\{^1H\}$ NMR (C_6D_6, 126 MHz, 22 °C, peaks for major isomer reported): δ 162.6 (Ar), 162.1 (d, *J* = 19.2 Hz, HC═N), 149.1 (Ar), 134.8 (Ar), 133.9 (Ar), 132.9 (Ar), 131.1 (Ar), 129.1 (d, J = 7.7 Hz, Ar), 126.8 (d, *J* = 24.6 Hz, Ar), 121.6 (d, *J* = 13.8 Hz, Ar), 119.2 (Ar), 118.9 (Ar), 118.5 (Ar), 60.4 (CH_2), 26.2 (d, *J* = 23.0 Hz, *i*Pr CHMe), 22.4 (d, *J* = 27.6 Hz, *i*Pr CHMe), 20.3 (CH_3), 20.1 (CH_3), 19.3 (d, J = 3.8 Hz, *i*Pr CH*Me*), 19.2 (d, *J* = 3.0 Hz, *i*Pr CH*Me*), 16.7 (d, *J* = 2.3 Hz, *i*Pr CH*Me*), 16.0 ppm (d, *J* = 6.9 Hz, *i*Pr CH*Me*). $^{31}P\{^1H\}$ NMR (C_6D_6, 202 MHz, 22 °C): δ 72.5 (major, 12:1 ratio), 74.1 ppm (minor). ^{19}F NMR (C_6D_6, 202 MHz, 22 °C): δ −77.9 (major), −78.1 ppm (minor). UV−vis (C_6H_5F): λ (ε) 329 (10 950), 446 (5650), 534 nm (4180 M^{-1} cm^{-1}). Anal. Calcd for $C_{46}H_{58}F_6N_4O_6P_2Pd_2S_2$: C, 45.44; H, 4.81; N, 4.61. Found: C, 45.32; H, 4.69; N, 4.59.

Synthesis of 6b-OTf: (PNN-C_4)PdOTf. Me_3SiOTf (50 mL, 0.28 mmol) was added to a solution of **6b-OAc** (0.147 g, 0.138 mmol) in C_6H_5F (10 mL). The mixture was stirred for 4 h at room temperature and dried in vacuo. The resulting purple powder was suspended in Et_2O and collected by filtration. Isolated yield = 0.152 g (88%). The product is sparingly soluble in C_6H_5F. Due to solubility issues, a meaningful ^{13}C NMR spectrum could not be collected. ^1H NMR (C_6D_6, 500 MHz, 22 °C): δ 7.45 (br d, *J* = 12.0 Hz, 2H, *H*C═N), 7.13 (br m, 2H, Ar *C*H), 6.95 (br m overlapped, 4H, Ar *C*H), 6.84 (br, 2H, Ar *C*H), 6.73 (br, 2H, Ar *C*H), 6.59 (br, 2H, Ar *C*H), 4.60 (br, 2H, CH_2), 3.28 (br, 1H, CH_2), 3.16 (br, 1H, CH_2), 2.80 (m, *J* = 8.0 Hz, 2H, *i*Pr *C*HMe), 2.24−2.12 (m overlapped, 2H, *i*Pr *C*HMe), 2.12 (br overlapped, 12H, CH_3),1.94 (br m, 2H, CH_2), 1.82 (br m, 2H, CH_2), 1.38 (dd, *J* = 16.5, 6.5 Hz, 6H, *i*Pr CH*Me*), 1.35 (dd, *J* = 18.5, 6.5 Hz, 6H, *i*Pr CH*Me*), 1.25 (dd, *J* = 20.0, 6.5 Hz, 6H, *i*Pr CH*Me*), 0.96 ppm (dd, *J* = 14.0, 7.5 Hz, 6H, *i*Pr CH*Me*). $^{31}P\{^1H\}$ NMR (C_6D_6, 202 MHz, 22 °C): δ 72.2 (br, minor), 72.1 (br, major 1:0.9 ratio) ppm. ^{19}F NMR (C_6D_6, 202 MHz, 22 °C): δ −77.5 (major), −77.6 ppm (minor). UV−vis (C_6H_5F): λ (ε) 329 (11 780), 440 (5600), 552

dx.doi.org/10.1021/om2008056 | *Organometallics* 2011, 30, 6641−6654

nm (3650 M^{-1} cm^{-1}). Anal. Calcd for $C_{48}H_{62}F_6N_4O_6P_2Pd_2S_2$: C, 46.35; H, 5.02 ; N, 4.50. Found: C, 46.26; H, 5.11; N, 4.36.

Synthesis of 6a-H: [(PNN)Pd-H-Pd(PNN)-C_2][OTf]. Et_3SiH (6.2 mL, 0.039 mmol) was added to a solution of **6a-OTf** (0.047 g, 0.039 mmol) in C_6H_5F (1 mL) and then layered with pentane (4 mL). The mixture was placed in a −30 °C freezer and left to stand overnight. A precipitate of a dark green powder was collected and washed with pentane. Isolated yield = 0.033 g (80%). Crystals suitable for X-ray diffraction were obtained through slow evaporation of a dilute benzene solution. ^{1}H NMR (CD_2Cl_2, 500 MHz, 22 °C): δ 7.70 (d, J_{HP} = 12.5 Hz, 2H, *H*C═N), 7.31 (dd, J = 9.0, 3.5 Hz, 2H, Ar C*H*), 7.12 (d, J = 3.5 Hz, 2H, Ar C*H*), 7.10 (br s, 2H, Ar C*H*), 7.07 (d, J = 2.5 Hz, 2H, Ar C*H*), 7.04 (overlapped d, 2H, Ar C*H*), 7.02 (overlapped dd, J = 9.0, 2.5 Hz, 2H, Ar C*H*), 4.73 (d, J = 11.5 Hz, 2H, CH_2), 4.34 (d br, J = 13.0 Hz, 2H, CH_2), 2.48 (h, J = 6.5 Hz, 2H, *i*Pr C*H*Me), 2.31 (s, 6H, CH_3), 2.25 (s, 6H, CH_3), 2.22 (overlapped m, 2H, *i*Pr C*H*Me), 1.36 (dd, J = 17.5, 6.5 Hz, 6H, *i*Pr CH*Me*), 1.28 (dd, J = 13.5, 6.5 Hz, 6H, *i*Pr CH*Me*), 1.14 (dd, J = 19.0, 6.5 Hz, 6H, *i*Pr CH*Me*), 1.08 (dd, J = 19.0, 6.5 Hz, 6H, *i*Pr CH*Me*), −20.08 ppm (t, J_{HP} = 15.2 Hz, 1H, Pd-*H*-Pd). ^{13}C{^{1}H} NMR (CD_2Cl_2, 126 MHz, 22 °C): δ 161.7 (*H*C═N), 160.7 (d, J = 18.7 Hz, Ar *C*), 148.7 (Ar *C*), 135.3 (Ar CH), 134.4 (d, J = 1.4 Hz, Ar CH), 133.4 (Ar CH), 131.9 (Ar CH), 130.4 (d, J = 7.5 Hz, Ar *C*), 127.7 (Ar C), 127.0 (Ar *C*), 119.6 (d, J = 13.6 Hz, Ar CH), 118.2 (Ar CH), 117.7 (d, J = 47.0 Hz, Ar *C*), 68.5 (CH_2), 27.9 (d, J = 24.8 Hz, *i*Pr *C*HMe), 22.4 (d, J = 31.7 Hz, *i*Pr CHMe), 20.5 (CH_3), 20.3 (CH_3), 18.9 (*i*Pr CH*Me*), 18.7 (*i*Pr CH*Me*), 18.4 (d, J = 2.8 Hz, *i*Pr CH*Me*), 16.4 ppm (d, J = 6.5 Hz, *i*Pr CH*Me*). ^{31}P{^{1}H} NMR (CD_2Cl_2, 202 MHz, 22 °C): δ 83.4 ppm. ^{19}F NMR (CD_2Cl_2, 470 MHz, 22 °C): δ −80.2 ppm. UV−vis (C_6H_5F): λ (ε) 334 (15 150), 467 (8550), 632 nm (3420 M^{-1} cm^{-1}). Anal. Calcd for $C_{45}H_{59}F_3N_4O_3P_2Pd_2S_1$: C, 50.62; H, 5.57 ; N, 5.25. Found: C, 50.56; H, 5.62; N, 5.24.

Synthesis of 6b-H: [(PN(H)N)Pd-Pd(PNN)-C_4][OTf]. Excess Et_3SiH (0.101 mmol, 16 μL) was added to a solution of **6b-OTf** (0.032 g, 0.025 mmol) in C_6H_5F (5 mL) at −30 °C. The deep purple solution was allowed to warm to room temperature and gradually changed to a dark green color over 48 h. The reaction mixture was dried in vacuo to remove all volatiles. Redissolution, filtering over Celite, and drying left a forest-green powder. Yield = 0.025 g (90%). Single crystals suitable for X-ray diffraction were obtained by slow evaporation of a C_6H_5F solution. ^{1}H NMR (C_6D_5Br, 500 MHz, 22 °C): δ 9.07 (s, 1H, N*H*), 7.52 (dd, J_{HH} = 7.5 Hz, J_{HP} = 3.0 Hz, 1H, *H*C═N; d in ^{1}H{^{31}P} NMR spectrum, J = 7.5 Hz), 7.39 (d, J = 8.5 Hz, 1H, Ar C*H*), 7.25−7.22 (overlapped m, 3H, Ar C*H*), 7.11 (d, J = 7.5 Hz, 1H, Ar C*H*), 6.96 (d, J = 2.5 Hz, 1H, Ar C*H*), 6.85 (dd, J = 7.5, 2.5 Hz, 1H Ar C*H*), 6.83 (overlapped m, 3H, Ar C*H*), 6.75 (d, J = 7.5 Hz, 1H, Ar C*H*), 6.09 (d, J = 8.0 Hz, 1H, Ar C*H*), 5.80 (t, J = 11.2 Hz, 1H, CH_2), 4.69 (br t, J = 11.5 Hz, 1H, CH_2), 3.89 (t, J = 13.5 Hz, 1H, CH_2), 3.68 (m, 1H, CH_2), 3.53 (m, 1H, CH_2), 3.43 (s, 2H, CH_2), 3.09 (m, 1H, CH_2), 2.29 (s, 3H, *Me*), 2.27 (s, 3H, *Me*), 2.25 (s, 3H, *Me*), 2.24 (s, 3H, *Me*), 2.20 (br m, 2H, *i*Pr C*H*Me), 2.01 (br m, 2H, *i*Pr C*H*Me), 1.83 (br t, J = 14.0 Hz, 1H, CH_2), 1.71 (br m, 1H, CH_2), 1.28 (dd, J = 17.0, 7.0 Hz, 3H, *i*Pr CH*Me*), 1.07 (dd, J = 17.5, 7.5 Hz, 3H *i*Pr CH*Me*), 1.04−0.97 (overlapped m, 6H, *i*Pr CH*Me*), 0.93−0.87 (overlapped m, 6H, *i*Pr CH*Me*), 0.70−0.64 ppm (overlapped m, 6H, *i*Pr CH*Me*). ^{13}C{^{1}H} (CD_2Cl_2, 126 MHz, 22 °C): δ 169.0 (HC═N), 144.9 (d, J = 12.3 Hz, Ar *C*), 144.0 (d, J = 13.0 Hz, Ar *C*), 144.0 (Ar *C*), 142.6 (Ar *C*), 139.7 (d, J = 5.4 Hz, Ar *C*), 139.2 (d, J = 5.4 Hz, Ar *C*), 134.8 (Ar *C*), 134.4 (d, J = 1.2 Hz, Ar *C*), 134.3 (d, J = 1.5 Hz, Ar *C*), 134.0 (Ar *C*), 133.6 (Ar *C*), 133.4 (Ar *C*), 133.1 (Ar *C*), 132.8 (Ar *C*), 132.7 (Ar *C*), 132.1 (Ar *C*), 131.7 (Ar *C*), 131.4 (Ar *C*), 130.4 (Ar *C*), 129.9 (d, J = 7.7 Hz, Ar *C*), 129.7 (d, J = 8.5 Hz, Ar *C*), 129.5 (Ar *C*), 118.7 (Ar *C*), 118.0 (Ar *C*), 68.1 (CH_2), 54.9 (CH_2), 54.8 (CH_2), 32.2 (CH_2), 25.5 (CH_2), 21.4 (d, J = 3.7 Hz, *i*Pr), 21.3 (d, J = 3.8 Hz, *i*Pr), 20.7 (d, J = 4.5 Hz, *i*Pr), 20.5 (d, J = 9.9 Hz, *i*Pr), 19.4 (d, J = 7.7 Hz, *i*Pr), 19.3 (d, J = 6.9 Hz, *i*Pr), 19.1 (d, J = 4.5 Hz, *i*Pr), 17.5 (d, J = 4.5 Hz, *i*Pr), 16.3 (d, J = 7.7 Hz, *i*Pr), 15.9 ppm (d, J = 6.9 Hz, *i*Pr). ^{31}P{^{1}H} NMR (CD_2Cl_2, 202 MHz, 22 °C): δ = 64.2 (d, $^3J_{PP}$ = 5 Hz), 49.6 ppm (d, $^3J_{PP}$ = 5 Hz). ^{19}F NMR (CD_2Cl_2, 282 MHz, 22 °C): δ −79.9 ppm. UV−vis (C_6H_5F): λ (ε) 355 (14 000), 427 (10 150), 495 (shoulder), 604 nm (1760 M^{-1} cm^{-1}). Anal. Calcd for $C_{47}H_{65}F_3N_4O_3P_2Pd_2S_1$: C, 51.42; H, 5.97 ; N, 5.10. Found: C, 51.21; H, 5.79; N, 4.96.

X-ray Crystallography. In each case, multifaceted crystals of suitable size and quality were selected from representative samples of the same habit using an optical microscope and mounted onto a nylon loop. Low-temperature (110 or 120 K) X-ray data were obtained on a Bruker APEXII CCD based diffractometer (Mo sealed X-ray tube, K_α = 0.71073 Å). All diffractometer manipulations, including data collection, integration, and scaling, were carried out using the Bruker APEXII software.[59] Absorption corrections were applied using SADABS.[60] Space groups were determined on the basis of systematic absences and intensity statistics, and structures were solved by direct methods and refined by full-matrix least-squares on F^2. The structure was solved in the space groups noted in each case using XS[61] (incorporated in SHELXTL), and PLATON[62] was used to check for missed symmetry. Except where noted, all non-hydrogen atoms were refined with anisotropic thermal parameters.

Crystal structure data for 5b-Cl: $C_{30}H_{44}Cl_2N_2O_2P_2Pd_2$, 810.31 g/mol, orthorhombic, space group $Pca2_1$; a = 20.096(13) Å, b = 7.401(5) Å, c = 22.203(15) Å, $\alpha = \beta = \gamma$ = 90°, V = 3302(4) Å^3; Z = 4, ρ_{calcd} = 1.630 g cm^{-3}; crystal dimensions 0.18 × 0.08 × 0.06 mm; diffractometer Bruker APEXII CCD; Mo Kα radiation, 150(2) K, $2\theta_{max}$ = 55.58°; 36 780 reflections, 7731 independent (R_{int} = 0.0813), direct methods; absorption coeff (μ = 1.378 mm^{-1}), absorption correction multiscan (SADABS); refinement (against F_o^2) with SHELXTL V6.1, 364 parameters, 1 restraints, R_1 = 0.0556 ($I > 2\sigma$) and wR_2 = 0.1441 (all data), Goof = 1.057, residual electron density 2.801/−1.138 e Å^{-3}.

Crystal structure data for 6a-Cl: $C_{44}H_{58}Cl_2N_4P_2Pd_2$, 988.58 g/mol, monoclinic, space group $C2/c$; a = 23.037(11) Å, b = 13.509(6) Å, c = 14.442(7) Å, β = 103.707(5)°, V = 4367(4) Å^3; Z = 4, ρ_{calcd} = 1.504 g cm^{-3}; crystal dimensions 0.48 × 0.15 × 0.04 mm; diffractometer Bruker APEXII CCD; Mo Kα radiation, 110(2) K, $2\theta_{max}$ = 55.26°; 23 962 reflections, 4994 independent (R_{int} = 0.0379), direct methods; absorption coeff (μ = 1.055 mm^{-1}), absorption correction multiscan (SADABS); refinement (against F_o^2) with SHELXTL V6.1, 250 parameters, 0 restraints, R_1 = 0.0228 ($I > 2\sigma$) and wR_2 = 0.0568 (all data), Goof = 1.058, residual electron density 0.398/−0.424 e Å^{-3}.

Crystal structure data for 6b-Cl: $C_{46}H_{62}Cl_2N_4P_2Pd_2{\cdot}3(C_6H_6)$, 1250.96 g/mol, triclinic, space group $P\bar{1}$; a = 7.757(3) Å, b = 13.319(5) Å, c = 14.878(5) Å, α = 97.967(4)°, β = 96.749(4)°, γ = 98.808(4)°, V = 1489.1(9) Å^3; Z = 1, ρ_{calcd} = 1.395 g cm^{-3}; crystal dimensions 0.21 × 0.18 × 0.11 mm; diffractometer Bruker APEXII CCD; Mo Kα radiation, 110(2) K, $2\theta_{max}$ = 55°; 17 26 reflections, 6767 independent (R_{int} = 0.0533), direct methods; absorption coeff (μ = 0.790 mm^{-1}), absorption correction multiscan (SADABS); refinement (against F_o^2) with SHELXTL V6.1, 340 parameters, 0 restraints, R_1 = 0.0369 ($I > 2\sigma$) and wR_2 = 0.1008 (all data), Goof = 1.054, residual electron density 0.782/−0.526 e Å^{-3}.

Crystal structure data for 6a-OAc: $C_{48}H_{64}N_4O_4P_2Pd_2$, 1035.77 g/mol, monoclinic, space group $C2/c$; a = 22.247(8) Å, b = 21.245(8) Å, c = 14.767(6) Å, β = 128.243(4)°, V = 5482(4) Å^3; Z = 4, ρ_{calcd} = 1.255 g cm^{-3}; crystal dimensions 0.26 × 0.23 × 0.19 mm; diffractometer Bruker APEXII CCD; Mo Kα radiation, 110(2) K, $2\theta_{max}$ = 55.18°; 30 619 reflections, 6282 independent (R_{int} = 0.0337), direct methods; absorption coeff (μ = 0.755 mm^{-1}), absorption correction: multiscan (SADABS); refinement (against F^2_0) with SHELXTL V6.1, 278 parameters, 0 restraints, R_1 = 0.0256 ($I > 2\sigma$) and wR_2 = 0.0701 (all data), Goof = 1.072, residual electron density 0.394/−0.243 e Å^{-3}. The SQUEEZE protocol included in PLATON was used to account for disordered pentane molecules included in the crystal lattice (and confirmed by ^{1}H NMR spectroscopy) that could not be satisfactorily modeled.

Crystal structure data for 5a-H: $C_{29}H_{41}F_3N_2O_5P_2Pd_2S_1$, 861.44 g/mol, monoclinic, space group $P2_1/c$; a = 16.569(6) Å, b = 13.748(5) Å, c = 16.022(6) Å, $\alpha = \gamma$ = 90°, β = 90.617(4)°, V = 3649(2) Å^3; Z = 4, ρ_{calcd} = 1.568 g cm^{-3}; crystal dimensions 0.14 × 0.13 × 0.10 mm; diffractometer Bruker APEXII CCD; Mo Kα radiation, 110(2) K,

dx.doi.org/10.1021/om2008056 | *Organometallics* 2011, 30, 6641−6654

$2\theta_{max}$ = 55.0°; 41 091 reflections, 8379 independent (R_{int} = 0.0873), direct methods; absorption coeff (μ = 1.182 mm^{-1}), absorption correction multiscan (SADABS); refinement (against F_o^2) with SHELXTL V6.1, 393 parameters, 0 restraints, R_1 = 0.0635 ($I > 2\sigma$) and wR_2 = 0.1776 (all data), Goof = 0.981, residual electron density 3.934/−1.394 e $Å^{-3}$. The SQUEEZE protocol included in PLATON was used to account for disordered CH_2Cl_2 solvent molecules found in the crystal lattice (verified by ^1H NMR) that could not be satisfactorily modeled. The large residual is likely due to a small amount of unaccounted for twinning.

Crystal structure data for 5b-H: $C_{31}H_{45}F_3N_2O_5P_2Pd_2S_1$, 889.49 g/mol, monoclinic, space group $P2_1/c$; a = 20.882(5) Å, b = 13.676(3) Å, c = 25.112(6) Å, β = 102.349(3)°, V = 7005(3) $Å^3$; Z = 8, ρ_{calcd} = 1.687 g cm^{-3}; crystal dimensions: 0.15 × 0.06 × 0.04 mm; diffractometer: Bruker APEXII CCD; Mo Kα radiation, 150(2) K, $2\theta_{max}$ = 55.16°; 78 794 reflections, 16 068 independent (R_{int} = 0.0657), direct methods; absorption coeff (μ = 1.235 mm^{-1}), absorption correction: multiscan (SADABS); refinement (against F_o^2) with SHELXTL V6.1, 838 parameters, 1 restraints, R_1 = 0.0431 ($I > 2\sigma$) and wR_2 = 0.1121 (all data), Goof = 1.018, residual electron density 1.761/−1.199 e $Å^{-3}$.

Crystal structure data for 6a-H: $C_{45}H_{59}F_3N_4O_3P_2Pd_2S_1 \cdot 0.5(C_6H_6)$, 1106.82 g/mol, orthorhombic, space group $Pbca$; a = 16.545(6) Å, b = 24.021(9) Å, c = 25.028(9) Å, $\alpha = \beta = \gamma$ = 90°, V = 9947(6) $Å^3$; Z = 8, ρ_{calcd} = 1.478 g cm^{-3}; crystal dimensions 0.10 × 0.07 × 0.04 mm; diffractometer Bruker APEXII CCD; Mo Kα radiation, 110(2) K, $2\theta_{max}$ = 55.72°; 110 280 reflections, 11 725 independent (R_{int} = 0.1419), direct methods; absorption coeff (μ = 0.884 mm^{-1}), absorption correction multiscan (SADABS); refinement (against F_o^2) with SHELXTL V6.1, 580 parameters, 0 restraints, R_1 = 0.0469 ($I > 2\sigma$) and wR_2 = 0.1118 (all data), Goof = 1.020, residual electron density 0.827/−1.098 e $Å^{-3}$.

Crystal structure data for 6b-H: $2(C_{46}H_{65}F_3N_4O_3P_2Pd_2S_1) \cdot 3(C_6H_5F)$, 2483.96 g/mol, monoclinic, space group Cc; a = 31.487(14) Å, b = 10.730(5) Å, c = 33.438(15) Å, β = 102.072(5) °, V = 11047(9) $Å^3$; Z = 4, ρ_{calcd} = 1.493 g cm^{-3}; crystal dimensions 0.43 × 0.12 × 0.08 mm; diffractometer Bruker APEXII CCD; Mo Kα radiation, 110(2) K, $2\theta_{max}$ = 55°; 56 610 reflections, 24 729 independent (R_{int} = 0.0792), direct methods; absorption coeff (μ = 0.809 mm^{-1}), absorption correction multiscan (SADABS); refinement (against F_o^2) with SHELXTL V6.1, 1277 parameters, 34 restraints, R_1 = 0.0594 ($I > 2\sigma$) and wR_2 = 0.1350 (all data), Goof = 0.974, residual electron density 1.288/−0.894 e $Å^{-3}$. Three fluorobenzene solvent molecules were found in the crystal lattice with elongated thermal parameters, likely caused by unresolved disorder. No disorder was observed in the main residue or triflate counterion. No additional symmetry was found using ADDSYMM incorporated within the program PLATON[62] when run on .res or .cif files either containing or omitting the disordered solvent molecules, confirming the space group selection. The Flack parameter indicates that the crystal is a racemate [0.45(2)].

■ ASSOCIATED CONTENT

Supporting Information

^1H and $^{31}P\{^1H\}$ NMR spectra illustrating isomerism in (PNN-C_n)Pd_2X_2 complexes; ^1H NMR and IR spectra of **5-H** and **6-H**. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENTS

Support of this research by the NSF (CHE-0944634), the Dreyfus Foundation (Camille Dreyfus Teacher-Scholar Award to O.V.O.), and the Welch Foundation (grant A-1717) is gratefully acknowledged. We thank Dr. Nattami Bhuvanesh and Dr. Joe Reibenspies for helpful discussions regarding X-ray crystallography and Jillian J. Davidson for assistance in the preparation of compound **2**.

■ REFERENCES

(1) (a) Moulton, C. J.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1976**, 1020. (b) Albrecht, M.; van, K. G. *Angew. Chem., Int. Ed.* **2001**, *40*, 3750. (c) van der Boom, M. E.; Milstein, D. *Chem. Rev.* **2003**, *103*, 1759. (d) *The Chemistry of Pincer Compounds*; Morales-Morales, D.; Jensen, C. M., Eds.; Elsevier: Amsterdam, 2007. (e) Selander, N.; Szabó, K. J. *Chem. Rev.* **2011**, *111*, 2048.

(2) Gozin, M.; Weisman, A.; Ben-David, Y.; Milstein, D. *Nature* **1993**, *364*, 699.

(3) Bernskoetter, W. H.; Schauer, C. K.; Goldberg, K. I.; Brookhart, M. *Science* **2009**, *326*, 553.

(4) Fafard, C. M.; Adhikari, D.; Foxman, B. M.; Mindiola, D. J.; Ozerov, O. V. *J. Am. Chem. Soc.* **2007**, *129*, 10318.

(5) (a) Adhikari, D.; Mossin, S.; Basuli, F.; Dible, B. R.; Chipara, M.; Fan, H.; Huffman, J. C.; Meyer, K.; Mindiola, D. J. *Inorg. Chem.* **2008**, *47*, 10479. (b) Whited, M. T.; Zhu, Y.; Timpa, S. D.; Chen, C.-H.; Foxman, B. M.; Ozerov, O. V.; Grubbs, R. H. *Organometallics* **2009**, *28*, 4560. (c) Whited, M. T.; Grubbs, R. H. *Acc. Chem. Res.* **2009**, *42*, 1607. (d) Tsvetkov, N.; Fan, H.; Caulton, K. G. *Dalton Trans.* **2011**, *40*, 1105.

(6) (a) Fan, L.; Ozerov, O. V. *Chem. Commun.* **2005**, 4450. (b) Fullmer, B. C.; Fan, H.-J.; Pink, M.; Huffman, J. C.; Tsvetkov, N. P.; Caulton, K. G. *J. Am. Chem. Soc.* **2010**, *133*, 2571. (c) Flores, J. A.; Cavaliere, V. N.; Buck, D.; Pinter, B.; Chen, G.; Crestani, M. G.; Baik, M.-H.; Mindiola, D. J. *Chem. Sci.* **2011**, *2*, 1457. (d) Cavaliere, V. N.; Crestani, M. G.; Pinter, B.; Pink, M.; Chen, C.-H.; Baik, M.-H.; Mindiola, D. J. *J. Am. Chem. Soc.* **2011**, *133*, 10700.

(7) (a) Chisholm, M. H. *Polyhedron* **1986**, *5*, 25. (b) Wolczanski, P. T. *Polyhedron* **1995**, *14*, 3335. (c) Ceccon, A.; Santi, S.; Orian, L.; Bisello, A. *Coord. Chem. Rev.* **2004**, *248*, 683. (d) Gavrilova, A. L.; Bosnich, B. *Chem. Rev.* **2004**, *104*, 349. (e) Cowie, M. *Can. J. Chem.* **2005**, *83*, 1043.

(8) (a) Sugimoto, M.; Nonoyama, M. *Inorg. Nucl. Chem. Lett.* **1979**, *15*, 405. (b) Chan, C.-W.; Mingos, M. P.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1996**, 81. (c) Fernandez, A.; Fernandez, J. J.; Lopez-Torres, M.; Suarez, A.; Ortigueira, J. M.; Vila, J. M.; Adams, H. *J. Organomet. Chem.* **2000**, *612*, 85. (d) Sumby, C. J.; Steel, P. J. *Organometallics* **2003**, *22*, 2358.

(9) Zhao, C.-Q.; Jennings, M. C.; Puddephatt, R. J. *Dalton Trans.* **2008**, 1243.

(10) (a) Lagunas, M.-C.; Gossage, R. A.; Spek, A. L.; van Koten, G. *Organometallics* **1998**, *17*, 731. (b) Steenwinkel, P.; Kooijman, H.; Smeets, W. J. J.; Spek, A. L.; Grove, D. M.; van Koten, G. *Organometallics* **1998**, *17*, 5411.

(11) Gagliardo, M.; Amijs, C. H. M.; Lutz, M.; Spek, A. L.; Havenith, R. W. A.; Hartl, F.; van Klink, G. P. M.; van Koten, G. *Inorg. Chem.* **2007**, *46*, 11133.

(12) Chattopadhyay, S.; Sinha, C.; Choudhury, S. B.; Chakravorty, A. *J. Organomet. Chem.* **1992**, *427*, 111.

(13) Tsubomura, T.; Tanihata, T.; Yamakawa, T.; Ohmi, R.; Tamane, T.; Higuchi, A.; Katoh, A.; Sakai, K. *Organometallics* **2001**, *20*, 3833.

(14) Suess, D. L. M.; Peters, J. C. *Chem. Commun.* **2010**, 6554.

(15) (a) Goettker-Schnetmann, I.; White, P.; Brookhart, M. *J. Am. Chem. Soc.* **2004**, *126*, 1804. (b) Goettker-Schnetmann, I.; White, P. S.; Brookhart, M. *Organometallics* **2004**, *23*, 1766.

(16) (a) Liang, L.-C.; Lin, J.-M.; Hung, C.-H. *Organometallics* **2003**, *22*, 3007. (b) Winter, A. M.; Eichele, K.; Mack, H.-G.; Potuznik, S.; Mayer, H. A.; Kaska, W. C. *J. Organomet. Chem.* **2003**, *682*, 149.

(17) Fan, L.; Foxman, B. M.; Ozerov, O. V. *Organometallics* **2004**, *23*, 326.

(18) Zhang, B.-S.; Wang, C.; Gong, J.-F.; Song, M.-P. *J. Organomet. Chem.* **2009**, *694*, 2555.

(19) Zhang, B.-S.; Wang, W.; Shao, D.-D.; Hao, X.-Q.; Gong, J.-F.; Song, M.-P. *Organometallics* **2010**, *29*, 2579.

(20) Niu, J.-L.; Chen, Q.-T.; Hao, X.-Q.; Zhao, Q.-X.; Gong, J.-F.; Song, M.-P. *Organometallics* **2010**, *29*, 2148.
(21) (a) Chang, C. J.; Loh, Z.-H.; Shi, C.; Anson, F. C.; Nocera, D. G. *J. Am. Chem. Soc.* **2004**, *126*, 10013. (b) Givaja, G.; Volpe, M.; Leeland, J. W.; Edwards, M. A.; Young, T. K.; Darby, S. B.; Reid, S. D.; Blake, A. J.; Wilson, C.; Wolowska, J.; McInnes, E. J. L.; Schroeder, M.; Love, J. B. *Chem.—Eur. J.* **2007**, *13*, 3707. (c) Harvey, P. D.; Stern, C.; Gros, C. P.; Guilard, R. *Coord. Chem. Rev.* **2007**, *251*, 401.
(22) Fryzuk, M. D.; MacNeil, P. A. *J. Am. Chem. Soc.* **1981**, *103*, 3592.
(23) Mahon, M. F.; McGinley, J.; Rooney, A. D.; Walsh, J. M. D. *Inorg. Chim. Acta* **2009**, *362*, 2353.
(24) Gilman, H.; Zuech, E. A. *J. Org. Chem.* **1961**, *26*, 3481.
(25) (a) Liang, L.-C.; Chien, P.-S.; Lee, P.-Y. *Organometallics* **2008**, *27*, 3082. (b) Lansing, R. B.; Goldberg, K. I.; Kemp, R. A. *Dalton Trans.* **2011**, *40*, 8950.
(26) Ma, L.; Woloszynek, R. A.; Chen, W.; Ren, T.; Protasiewicz, J. D. *Organometallics* **2006**, *25*, 3301.
(27) Oki, M. *Top. Stereochem.* **1983**, *14*, 1.
(28) Designations are assigned based on ranking "front" then "back" substituents. With the hydrocarbon bridge placed toward the back and the phosphine arm coming out of the page, the aryl rings are twisted with respect to one another in two different ways: *R* or *S*. Each binuclear molecule contains two (PNN)PdX moieties: if the two orientations within the same molecule are the same (*R*,*R* or *S*,*S*), the isomer lacks an internal mirror plane and would be *rac*; if they are different (*R*,*S* or *S*,*R*), the isomer is referred to as *meso*.
(29) Niu, J.-L.; Hao, X.-Q.; Gong, J.-F.; Song, M.-P. *Dalton Trans.* **2011**, *40*, 5135.
(30) (a) Benito-Garagorri, D.; Bocokić, V.; Mereiter, K.; Kirchner, K. *Organometallics* **2006**, *25*, 3817. (b) Nishiyama, H. *Chem. Soc. Rev.* **2007**, *36*, 1133. (c) Stol, M.; Snelders, D. J. M.; Godbole, M. D.; Havenith, R. W. A.; Haddleton, D.; Clarkson, G.; Lutz, M.; Spek, A. L.; Van, K. G. P. M.; Van, K. G. *Organometallics* **2007**, *26*, 3985. (d) Bugarin, A.; Connell, B. T. *Organometallics* **2008**, *27*, 4357. (e) Yang, M.-J.; Liu, Y.-J.; Gong, J.-F.; Song, M.-P. *Organometallics* **2011**, *30*, 3793. (f) El-Zaria, M. E.; Arii, H.; Nakamura, H. *Inorg. Chem.* **2011**, *50*, 4149.
(31) (a) Baber, R. A.; Bedford, R. B.; Betham, M.; Blake, M. E.; Coles, S. J.; Haddow, M. F.; Hursthouse, M. B.; Orpen, A. G.; Pilarski, L. T.; Pringle, P. G.; Wingad, R. L. *Chem. Commun.* **2006**, 3880. (b) Aydin, J.; Kumar, K. S.; Sayah, M. J.; Wallner, O. A.; Szabó, K. J. *J. Org. Chem.* **2007**, *72*, 4689.
(32) (a) Gorla, F.; Togni, A.; Venanzi, L. M.; Albinati, A.; Lianza, F. *Organometallics* **1994**, *13*, 1607. (b) Longmire, J. M.; Zhang, X.; Shang, M. *Organometallics* **1998**, *17*, 4374. (c) Dani, P.; Albrecht, M.; van, K. G. P. M.; van, K. G. *Organometallics* **2000**, *19*, 4468. (d) Morales-Morales, D.; Cramer, R. E.; Jensen, C. M. *J. Organomet. Chem.* **2002**, *654*, 44. (e) Evans, D. R.; Huang, M.; Seganish, W. M.; Fettinger, J. C.; Williams, T. L. *Organometallics* **2002**, *21*, 893. (f) Gosiewska, S.; Martinez Herreras, S.; Lutz, M.; Spek, A. L.; Havenith, R. W. A.; van Klink, G. P. M.; van Koten, G.; Gebbink, R. J. M. K. *Organometallics* **2008**, *27*, 2549.
(33) Fan, L. PNP pincer ligands and their late transition metal complexes in the context of strong bond activation and catalysis. Ph.D. Dissertation, Brandeis University, 2006.
(34) Ma, L.; Imbesi, P. M.; Updegraff, J. B.; Hunter, A. D.; Protasiewicz, J. D. *Inorg. Chem.* **2007**, *46*, 5220.
(35) For related (PCN)NiX systems, see: (a) Spasyuk, D. M.; Zargarian, D.; van, d. E. A. *Organometallics* **2009**, *28*, 653. (b) Spasyuk, D. M.; Zargarian, D. *Inorg. Chem.* **2010**, *49*, 6203.
(36) Morales-Morales, D.; Grause, C.; Kasaoka, K.; Redon, R.; Cramer, R. E.; Jensen, C. M. *Inorg. Chim. Acta* **2000**, *300*−*302*, 958.
(37) Hollas, A. M.; Gu, W.; Bhuvanesh, N.; Ozerov, O. V. *Inorg. Chem.* **2011**, *50*, 3673.
(38) (a) Adhikari, D.; Mossin, S.; Basuli, F.; Huffman John, C.; Szilagyi Robert, K.; Meyer, K.; Mindiola Daniel, J. *J. Am. Chem. Soc.* **2008**, *130*, 3676. (b) Radosevich, A. T.; Melnick, J. G.; Stoian, S. A.; Bacciu, D.; Chen, C.-H.; Foxman, B. M.; Ozerov, O. V.; Nocera, D. G. *Inorg. Chem.* **2009**, *48*, 9214.
(39) Shapley, J. R.; Pearson, G. A.; Tachikawa, M.; Schmidt, G. E.; Churchill, M. R.; Hollander, F. J. *J. Am. Chem. Soc.* **1977**, *99*, 8064.
(40) Fafard, C. M.; Ozerov, O. V. *Inorg. Chim. Acta* **2007**, *360*, 286.
(41) A number of examples are known in the literature where apparent β-hydrogen elimination from a late metal alkoxide proceeds by dissociation of the alkoxide and transfer of the hydride from the dissociated alkoxide. See: (a) Blum, O.; Milstein, D. *J. Am. Chem. Soc.* **1995**, *117*, 4582. (b) Ritter, J. C. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1998**, *120*, 6826. (c) Blum, O.; Milstein, D. *J. Organomet. Chem.* **2000**, *593*−*594*, 479. (d) Smythe, N. A.; Grice, K. A.; Williams, B. S.; Goldberg, K. I. *Organometallics* **2009**, *28*, 277. (e) Fulmer, G. R.; Herndon, A. N.; Kaminsky, W.; Kemp, R. A.; Goldberg, K. I. *J. Am. Chem. Soc.* **2011**, *133*, 17713.
(42) Cooper, C. B., III; Shriver, D. F.; Onaka, S. *Adv. Chem. Ser.* **1978**, *167*, 232.
(43) (a) Fryzuk, M. D.; Lloyd, B. R.; Clentsmith, G. K. B.; Rettig, S. J. *J. Am. Chem. Soc.* **1991**, *113*, 4332. (b) Portnoy, M.; Frolow, F.; Milstein, D. *Organometallics* **1991**, *10*, 3960. (c) Fryzuk, M. D.; Lloyd, B. R.; Clentsmith, G. K. B.; Rettig, S. J. *J. Am. Chem. Soc.* **1994**, *116*, 3804.
(44) Stockland, R. A. Jr.; Anderson, G. K.; Rath, N. P. *Inorg. Chim. Acta* **1997**, *259*, 173.
(45) Zhuravel, M. A.; Moncarz, J. R.; Glueck, D. S.; Lam, K.-C.; Rheingold, A. L. *Organometallics* **2000**, *19*, 3447.
(46) Goto, E.; Begum, R. A.; Zhan, S.; Tanase, T.; Tanigaki, K.; Sakai, K. *Angew. Chem., Int. Ed.* **2004**, *43*, 5029.
(47) Baya, M.; Houghton, J.; Konya, D.; Champouret, Y.; Daran, J.-C.; Almeida Lenro, K. Q.; Schoon, L.; Mul, W. P.; van Oort, A. B.; Meijboom, N.; Drent, E.; Orpen, A. G.; Poli, R. *J. Am. Chem. Soc.* **2008**, *130*, 10612.
(48) (a) Xu, C.; Anderson, G. K. *Organometallics* **1994**, *13*, 3981. (b) Xu, C.; Anderson, G. K. *Organometallics* **1996**, *15*, 1760.
(49) Stockland, R. A. Jr.; Anderson, G. K.; Rath, N. P. *J. Am. Chem. Soc.* **1999**, *121*, 7945.
(50) (a) Kullberg, M. L.; Lemke, F. R.; Powell, D. R.; Kubiak, C. P. *Inorg. Chem.* **1985**, *24*, 3589. (b) Lin, W.; Wilson, S. R.; Girolami, G. S. *Inorg. Chem.* **1994**, *33*, 2265.
(51) Bercaw, J. E.; Durrell, A. C.; Gray, H. B.; Green, J. C.; Hazari, N.; Labinger, J. A.; Winkler, J. R. *Inorg. Chem.* **2010**, *49*, 1801.
(52) (a) Cotton, F. A.; Matusz, M.; Poli, R.; Feng, X. *J. Am. Chem. Soc.* **1988**, *110*, 1144. (b) Yip, H. K.; Lai, T. F.; Che, C. M. *Dalton Trans.* **1991**, 1639. (c) Xia, B.-H.; Che, C.-M.; Zhou, Z.-Y. *Chem.—Eur. J.* **2003**, *9*, 3055. (d) Pan, Q.-J.; Zhang, H.-X.; Zhou, X.; Fu, H.-G.; Yu, H.-T. *J. Phys. Chem. A* **2007**, *111*, 287.
(53) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.
(54) (a) Murahashi, T.; Kurosawa, H. *Coord. Chem. Rev.* **2002**, *231*, 207. (b) Frech, C. M.; Shimon, L. J. W.; Milstein, D. *Angew. Chem., Int. Ed.* **2005**, *44*, 1709.
(55) Gregor, L. C.; Chen, C.-H.; Fafard, C. M.; Fan, L.; Guo, C.; Foxman, B. M.; Gusev, D. G.; Ozerov, O. V. *Dalton Trans.* **2010**, *39*, 3195.
(56) Drew, D.; Doyle, J. R. *Inorg. Synth.* **1990**, *28*, 346.
(57) Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. *Organometallics* **2010**, *29*, 2176.
(58) Benson, S.; Payne, B.; Waymouth, R. M. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 3637.
(59) *APEX2, Version 2 User Manual*, M86-E01078; Bruker Analytical X-Ray Systems: Madison, WI, 2006.
(60) Sheldrick, G. M. *SADABS, Program for Absorption Correction for Data from Area Detector Frames*; University of Göttingen: Göttingen, Germany, 2008.
(61) Sheldrick, G. M. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2008**, *A64*, 112.
(62) Spek, A. L., *PLATON, A Multipurpose Crystallographic Tool*; Utrecht University: Utrecht, The Netherlands, 1998.