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Palladium Complexes of a $P_2C{=}$ Ligand Containing a Central Carbene Moiety

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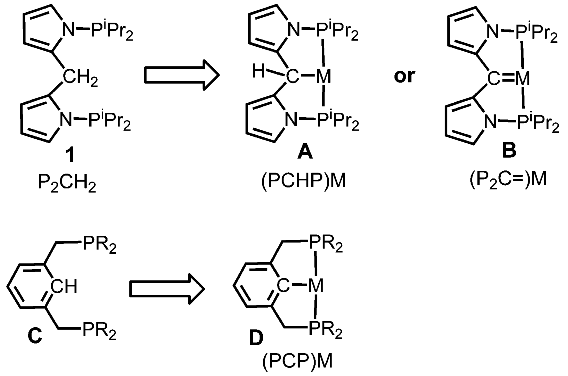
Palladium(II) complexes of the PCHP pincer ligand were prepared from $PdCl_2$, a "proto-pincer" P_2CH_2, and base. The resulting (PCHP)PdCl was converted to (PCHP)PdOTf. (PCHP)PdCl did not react with $NaN(SiMe_3)_2$ but produced (PCHP)PdR (R = Me, Et, Ph) upon reaction with the corresponding organolithium, Grignard, or organozinc reagent. Trityl cation abstracted a hydride from (PCHP)PdCl to yield cationic Pd carbene complex ($P_2C{=}$)PdCl. Analysis of the structural data points to minimal π-interaction between the carbene center and palladium.

Introduction

We have recently reported the preparation of a new pincer "proto-ligand" P_2CH_2 (**1**, Chart 1).[1] Unlike the conventional PCP ligands (**C**),[2] P_2CH_2 can give rise to pincer complexes of both a "phosphine-alkyl-phosphine" (PCHP, **A**) and a "phosphine-carbene-phosphine" ($P_2C{=}$, **B**) types. In the sense of this duality, the P_2CH_2 "proto-pincer" can be likened to bis(dialkylphosphino)pentane.[3] However, the framework of the $P_2C{=}$ ligand is much more rigid and more strongly prearranged for the formation of pincer-type complexes. We have reported examples of both PCHP and $P_2C{=}$ types of ruthenium complexes in an earlier contribution.[1] In the present report, we describe the synthesis and structural characterization of both types of complexes arising from **1** with palladium.

Chart 1



Results and Discussion

Synthesis of (PCHP)PdCl. By analogy with the syntheses of a number of Pd complexes with other PCP ligands,[2] we anticipated that the combination of $PdCl_2$ and base will react with P_2CH_2 via C−H activation and result in formation of a (PCHP)PdCl complex, **2**. One-pot reaction of P_2CH_2 with $(COD)PdCl_2$ and Et_3N afforded **2** as the main product in a 65% isolated yield (Scheme 1). Alternatively, allowing P_2CH_2 to react with $(COD)PdCl_2$ first, followed by removal of volatiles, and subsequent thermolysis of the residue in toluene in the presence of 2 equiv of 2,6-lutidine afforded (PCHP)PdCl (**2**) in a 72% isolated yield.

Complex **2** is soluble in ether and toluene and slightly soluble in pentane. It has been fully characterized by multinuclear NMR

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[21] (a) The lower π-basicity of Pd(II) vs Ru(II) is likely owing to the increase in the effective nuclear charge left to right in the periodic table and can be illustrated by the difference in the stretching frequencies of coordinated CO in $[Cl(Et_3P)_2Pd(CO)]^+$ (2130 cm^{-1})[21b] and in $(^iPr_3P)_2Ru(H)(Cl)(CO)$ (1910 cm^{-1}).[21d] These two examples are particularly relevant to the discussion at hand since these are related to **9** and **15** by formal replacement of the $P_2C{=}$ ligand with two phosphines and a CO. Clearly, the much lower ν_{CO} in a Ru(II) complex testifies to its greater back-donating ability (i.e., π-basicity). (b) Clark, H. C.; Dixon, K. R. *J. Am. Chem. Soc.* **1969**, *91*, 596. (c) Esteruelas, M. A.; Werner, H. *J. Organomet. Chem.* **1986**, *303*, 221.

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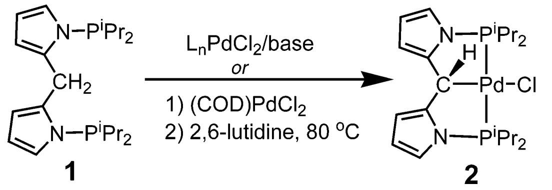
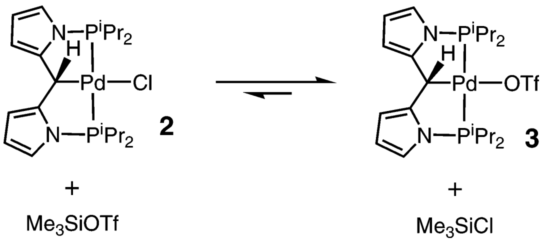
Scheme 1



Scheme 2



in solution and X-ray crystallography in the solid state (vide infra). Two methine resonance and four methyl resonances were observed for the $Pr^i{}_2P$ groups in the ^1H NMR spectrum of **2**, indicating C_s symmetry in solution. The presence of a Pd−CH moiety in **2** was evidenced by a singlet at δ 5.61 ppm in the ^1H NMR spectrum and a triplet at δ 32.8 ppm in the $^{13}C\{^1H\}$ NMR spectrum. The ^{31}P NMR chemical shift of **2** (δ 101.7), considerably downfield from that of free ligand (δ 56.8), is indicative of coordination of the phosphine arms to the metal center.

Synthesis of (PCHP)Pd(OTf). (PCHP)PdOTf (**3**) was prepared using Me_3SiOTf as the Cl/OTf metathesis reagent. This metathesis results in an observable equilibrium (Scheme 2). Repeated application of Me_3SiOTf followed by removal of volatiles afforded clean conversion to **3**. The OTf group is directly coordinated to the metal center, which was deduced from its characteristic ^{19}F NMR resonance (δ −79.9 ppm in C_6D_6), distinct from that of a free OTf anion (δ −80.6 ppm in C_6D_6).[22] Similarly to **2**, (PCHP)PdOTf also displays C_s symmetry in solution.

Structures of 2 and 3. Solid-state X-ray diffraction studies (Figures 1 and 2) confirmed the proposed identities of **2** and **3**. In both structures, the environment about the Pd center is close to an idealized square-planar geometry, with the deviations arising primarily from the chelate constraint. The “pincer bite” angles (P−Pd−P) of ca. 164° and 168° in **2** and **3**, respectively, are roughly similar to those in related (PNP)PdCl (**4**)[4] and (PCP)PdCl (**5**)[5] complexes (Chart 2). The Pd−Cl distance in **2** (ca. 2.40 Å) resembles that in **5** and is substantially longer than its counterpart in **4**. This difference can likely be traced to the weaker trans influence of the amido ligand in **4**. The Pd−P distances in **2** and **3** are unremarkable.

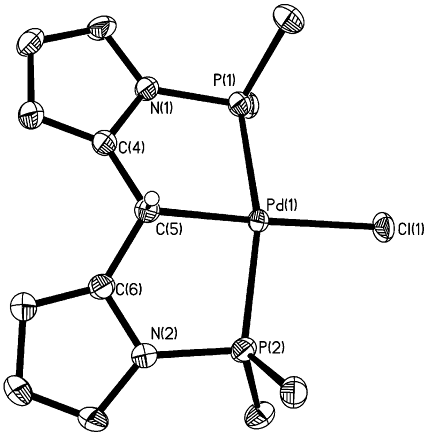


Figure 1. ORTEP drawing (50% thermal ellipsoids) of (PCHP)-Pd(Cl) (**2**) showing selected atom labeling. Hydrogen atoms and methyl groups are omitted for clarity. The Cl atom, Pd atom, and the bridging carbon C5 between two pyrrole rings were found to be disordered over two adjacent positions with refined occupancy factors of 0.83 and 0.17, respectively. Only the molecular structure with the higher occupancy factor is shown. Selected bond distances (Å) and angles (deg): Pd1−Cl1 2.4011(11); Pd1−P1 2.2715(8); Pd1−P2 2.3101(9); Pd1−C5 2.076(2); Cl1−Pd1−P1 94.62(5); Cl1−Pd1−P2 97.82(4); P1−Pd1−P2 163.95(4); Cl1−Pd1−C5 175.41(10); P1−Pd1−C5 84.88(7); P2−Pd1−C5 83.52(7); Cl1−Pd1−C51 155.0(3); P1−Pd1−C51 82.8(2); P2−Pd1−C51 81.7-(3).

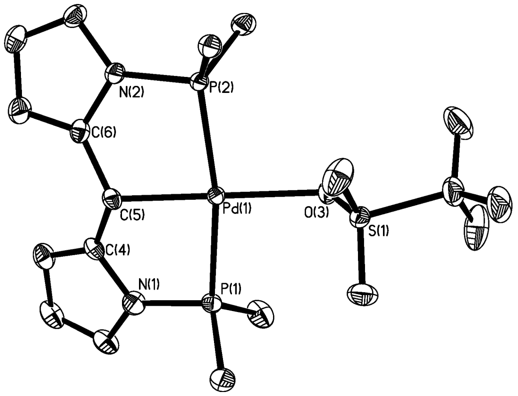


Figure 2. ORTEP drawing (50% thermal ellipsoids) of (PCHP)-Pd(OTf) (**3**) showing selected atom labeling. Hydrogen atoms and methyl groups are omitted for clarity. P atoms and the Pd atom and atoms C4, C5, C6, and N2 were found to be disordered over two adjacent positions with refined occupancy factors of 0.92 and 0.08, respectively. Only the molecular structure with the higher occupancy factor is shown. Selected bond distances (Å) and angles (deg): Pd1−O3 2.1921(15); Pd1−P1 2.3072(8); Pd1−P2 2.2860-(7); Pd1−C5 2.059(2); O3−Pd1−P1 96.45(5); O3−Pd1−P2 94.65-(4); P1−Pd1−P2 167.76(3); O3−Pd1−C5 177.22(8); P1−Pd1−C5 84.52(6); P2−Pd1−C5 84.63(6).

Attempts at Deprotonation of (PCHP)PdX Complexes and Syntheses of (PCHP)PdR (R = Me (6), Et (7), Ph (8)). We were interested in exploring the possibility of accessing Pd complexes of the carbenic $P_2C{=}$ ligand. At first we sought to prepare complexes containing the $(P_2C{=})Pd^0$ fragment; we believed that such species might possess unusual reactivity. One ostensible route to such derivatives is through elimination of HX from the (PCHP)PdX complexes. However, attempts to dehydrochlorinate **2** or dehydrotriflate **3** using $NaN(SiMe_3)_2$ as a strong base were unsuccessful. No reaction was observed upon mixing $NaN(SiMe_3)_2$ with **2** (NMR evidence). The reaction of $NaN(SiMe_3)_2$ with **3** did not lead to dehydrotriflation either: while new unidentified products were formed, no significant amount of $HN(SiMe_3)_2$ was produced and the characteristic Pd−C*H* signal was still detectable by ^1H NMR.

We then resorted to using stronger, hydrocarbyl bases with **2**. However, instead of dehydrochlorination, preparation of (PCHP)PdR (**6**−**8**) was accomplished by the action of alkyllithium, alkylzinc, or alkylmagnesium reagent on **2** (Scheme 3). The alkylating agents were used in excess with no detriment to the yield of product. The Pd products **6**−**8** can be easily separated from the excess of the alkylating agent by passing the reaction mixture through silica gel. Complexes **6**−**8** were fully characterized by solution NMR spectroscopic methods, and all displayed C_s symmetry in solution when probed by ^1H

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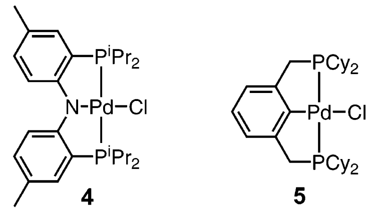
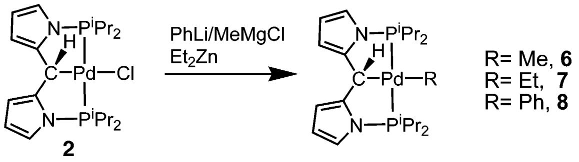
Chart 2. Comparison of the Structural Features (bond distances in Å and the P−Pd−P angle in deg) of Compounds 4 and 5[4,5]

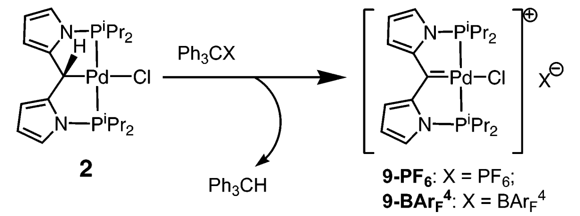


	4	5
Pd-Cl	2.32	2.43
P-Pd-P	163.5	165.5

Scheme 3



Scheme 4



NMR and ^{13}C NMR. The Pd−*CH* of the PCHP ligand in **6**−**8** resonates at ca. δ 4.7 ppm as a singlet in the ^1H NMR spectrum and at ca. δ 34.0 as a triplet (J_{C-P} = 2 Hz) in the $^{13}C\{^1H\}$ NMR spectrum. The α-carbons of the Pd-bound R groups in **6**−**8** gave rise to characteristic triplet resonances in the $^{13}C\{^1H\}$ NMR spectra (**6**, d −17.3 (t, J_{CP} = 12 Hz, Pd−CH_3); **7**, d −3.8 (t, J_{CP} = 10 Hz, Pd−CH_2CH_3); **8**, d 151.8 (t, J_{CP} = 10 Hz, *ipso*-Ph); all in C_6D_6).

Complexes **6**−**8** are all stable in solution at ambient temperature, which is particularly surprising for **7**, where the obvious decomposition pathway via β-hydrogen elimination (BHE) can be envisioned. Remarkably robust Pd alkyls supported by a PNP pincer system have recently been reported by our group elsewhere.[6] The stability of **7** toward BHE in the present work can probably be explained using similar reasoning: the rigidity of the PCHP pincer backbone prevents dissociation of the phosphine arms and thus blocks the BHE pathway. We have tested the stability of **6** at elevated temperature as well. Thermolysis of C_6D_6 solutions of **6** at 100 °C for 2 days did not result in any change observable by NMR spectroscopy. Thus, it appears that $P_2C=$ complexes of Pd^0 are not readily synthetically available. It is likely that the stereoelectronic requirements of a Pd^0 center are incompatible with the geometry imposed by the rigid $P_2C=$ ligand.

Preparation of Carbenic $P_2C=$ Complexes of Pd^{II}. Since removal of the α-H in the (PC*H*P)PdX complexes formally as a *proton* was not at all successful, we conceived that it may be amenable to abstraction as a formal *hydride*. Indeed, the reaction of **2** (Scheme 4) with an archetypal hydride abstraction agent $[Ph_3C][An]$ (An = PF_6, BAr_4^F)[7] afforded the cationic Pd^{II} carbene/phosphine pincer complex $[(P_2C=)PdCl][An]$ (**9-An**) with the corresponding counterion (PF_6 or BAr_4^F). Abstraction of a hydride form the α-C of a metal-bound alkyl has previously been used by others to prepare carbene complexes,[8] including a diarylcarbene of Ta(V) in a pincer-like context.[9] Ph_3CH was observed in both reactions by ^1H NMR spectroscopy. These cationic Pd carbene complexes are not soluble in pentane, only slightly soluble in toluene, but dissolve well in CH_2Cl_2. **9-PF$_6$** and **9-BAr$_4$^{F}** exhibit nearly identical ^1H and ^{13}C NMR spectra for the C_{2v}-symmetric cation **9** (CD_2Cl_2 solution). The ligated carbene carbon resonates at δ 189.6 ppm in the $^{13}C\{^1H\}$ NMR spectrum of **9**. This chemical shift is comparable to those observed for Pd^{II} complexes of N-heterocyclic carbenes (NHC).[10] Schuster and Raubenheimer recently reported “remote NHC” complexes of Pd^{II} (**10** and **11**, Chart 3) in which the carbon attached to Pd resonates at δ 187.0 (**10**) and 180.7 ppm (**11**) in the $^{13}C\{^1H\}$ NMR spectra.[11]

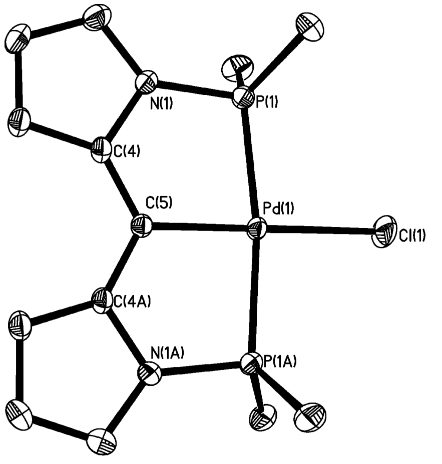
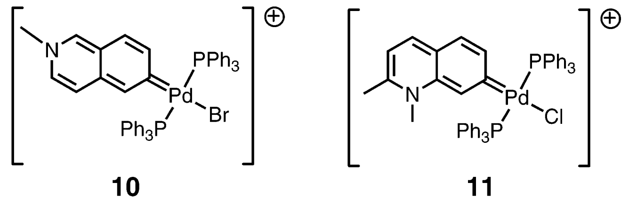


Figure 3. ORTEP drawing (50% thermal ellipsoids) of **9**-PF_6 showing selected atom labeling. Hydrogen atoms, methyl groups, and the counteranion (PF_6) are omitted for clarity. Selected bond distances (Å) and angles (deg): Pd1−P1A 2.2730(7); Pd1−P1 2.2730(7); Pd1−Cl1 2.3337(11); Pd1−C5 1.999(4); P1A−Pd1−P1 171.30(4); P1A−Pd1−Cl1 94.35(2); P1−Pd1−Cl1 94.35(2); P1A−Pd1−C5 85.65(2); P1−Pd1−C5 85.65(2); Cl1−Pd1−C5 179.99(4).

Chart 3. “Remote” NHC Complexes of Pd



Analysis of the Structural Features of 9-PF$_6$. An X-ray diffraction study of a suitable crystal of **9**-PF_6 revealed an approximately square-planar geometry about Pd with two phosphine arms trans to each other and carbene trans to Cl (Figure 3). The remarkable feature of the structure of **9**-PF_6 is that the pyrrolyl rings are almost perfectly coplanar with the coordination plane of the carbenic carbon and the coordination plane of Pd. Figure 4 provides a convenient side view of the cation of **9**-PF_6 in contrast to the puckered structure of **2**. The “pincer bite” P−Pd−P angle in **9**-PF_6 is greater than that in **2**, consistent with the flattening of the whole ligand framework.

The Pd−$C_{carbenic}$ bond distance in **9**-PF_6 of 1.999(4) Å is only ca. 0.08 Å shorter than the Pd−CH distance in **2** (2.076(2) Å). The hybridization change from C(sp^3) in **2** to C(sp^2) in **9**-PF_6 probably accounts for a portion of this difference. Indeed, the Pd−C(carbene) distance in **9**-PF_6 is very similar to the (presumably single bond) Pd−C(aryl) distances in (PCP)PdCl complexes (**5**,[5] **13**,[14] **14**,[15] Chart 4). The observed Pd−C distance in **9**-PF_6 is also similar to the Pd−C distance in the NHC-containing

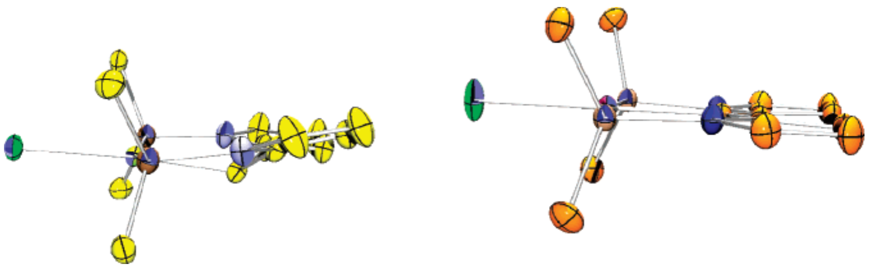
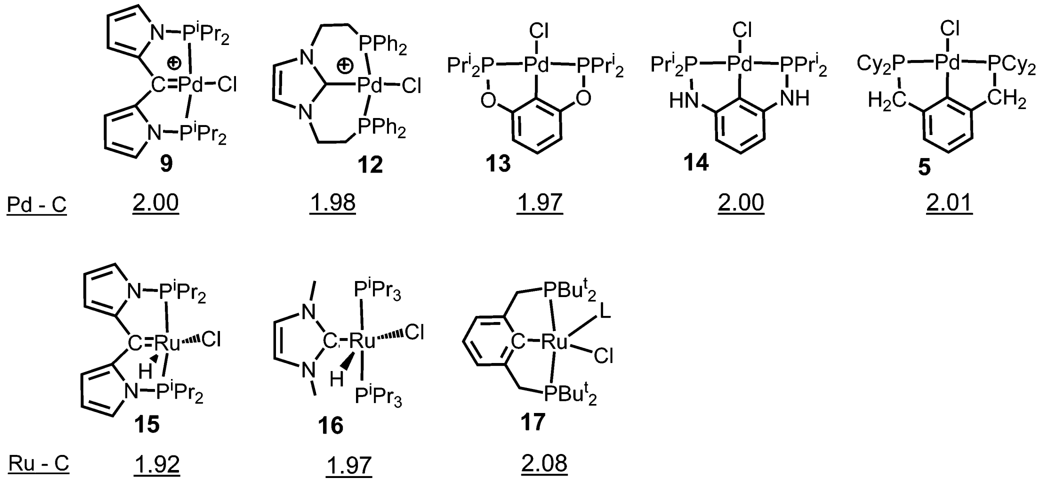


Figure 4. POV-Ray[12] renditions of the Ortep drawings[13] (50% probability ellipsoids) of **2** (left) and **9**-PF_6 (right) viewed along the P−Pd−P axis. Omitted for clarity: H atoms, methyls of the ^iPr groups, PF_6^- group.

Chart 4. Data on the Metal−Carbon Distances (in Å) in Complexes 9 (this work), 5,[5] 12,[16] 13,[14] 14,[15] 15,[1] 16,[18] and 17[19]



pincer complex **12**.[16] N-Heterocyclic carbenes are usually thought of as only weakly π-acidic.[17] The metric data thus suggest little π-interaction in **9**-PF_6, indicating the dominant σ-donor characteristics of the $P_2C{=}$ carbene moiety in this complex. This is consistent with the planarization of the pincer system that presumably takes place to increase the overlap of the pyrrolyl π-systems with what essentially is a carbocationic center.[19] A similar planarization of a diarylcarbene/bis(phenoxide) ligand attached to a Ta(V) center was observed by Kawaguchi et al.[9] In contrast, the reported Ru−carbene distance in $(P_2C{=})Ru(H)(Cl)$ (**15**, Chart 4)[1] is (a) noticeably smaller than that in the structurally similar NHC complex **16**,[18] (b) much shorter than the Pd−C distance in **9**-PF_6 despite the larger size of Ru, and (c) much shorter than the Ru−C(aryl) distance in the pincer complex **17**.[20] As well, the pyrrolyl rings in **15** are significantly twisted out of coplanarity (and therefore conjugation) with the carbene center. Consistent with the lower degree of conjugation in **15**, the $C_{ring}-C_{carbene}$ distance in **15** is ca. 1.45 Å, while it is ca. 1.41 Å in **2**.

The above observations allow for tentative conclusions regarding the electronic properties of the carbene donor in the $P_2C{=}$ ligand. The carbene ligand in $P_2C{=}$ possesses variable π-acidity that is moderated by the conjugation with the pyrrolyl rings. With a weakly π-basic metal (Pd^{II}), it acts as a weak π-acceptor at best. However, with a stronger π-base (Ru^{II}),[21] it behaves as a stronger π-acceptor. This variability is more pronounced than for the NHC carbenes.

Conclusion

In summary, we have been able to prepare Pd(II) complexes of the previously reported PCHP ligand. The α-CH moiety in the (PCHP)PdX complexes resists abstraction of H as a *proton*, but permits abstraction of H as a *hydride*. Hydride abstraction leads to the formation of Pd(II) complexes of the rigid carbene/bis(phosphine) pincer ligand $P_2C{=}$. Analysis of the structural data leads to the conclusion that the $P_2C{=}$ ligand is only weakly π-acidic toward Pd(II).

Experimental Section

General Considerations. Unless specified otherwise, all manipulations were performed under an argon atmosphere using standard Schlenk line or glovebox techniques. Toluene, pentane, Et_2O, C_6D_6, C_6H_6, THF, and iso-octane were dried over NaK/Ph_2CO/18-crown-6, distilled or vacuum transferred, and stored over molecular sieves in an Ar-filled glovebox. CD_2Cl_2 was dried over CaH_2 and then vacuum transferred. Ligand P_2CH_2 was prepared according to the published procedure,[1] as was $(COD)PdCl_2$.[22] All other chemicals were used as received from commercial vendors. NMR spectra were recorded on a Varian iNova 400 (^1H NMR, 399.755 MHz; ^{13}C NMR, 100.518 MHz; ^{31}P NMR, 161.822 MHz; ^2H, 61.365 MHz) spectrometer. For ^1H and ^{13}C NMR spectra, the residual solvent peak was used as an internal reference. ^{31}P NMR spectra were referenced externally using 85% H_3PO_4 at δ 0 ppm. Elemental analyses were performed by CALI Labs, Inc. (Parsippany, NJ). GC/MS spectra were recorded on a Hewlett-Packard G1800C GCD system (GCD Plus gas chromatograph electron ionization detector) employing HP-5MS from Agilent Technologies (30 m (column length) × 0.25 mm (i.d.)) and 1227032 from J & W Scientific (30 m × 0.250 mm). Helium was used as a carrier gas.

(PCHP)PdCl (2). Method 1. A mixture of $PdCl_2$ (308 mg, 1.74 mmol Pd), P_2CH_2 (**1**, 658 mg, 1.74 mmol), and Et_3N (731 μL, 5.22 mmol) in 15 mL of toluene was stirred for 18 h at 80 °C. (PCHP)PdCl (**2**) and **1** were observed in the resulting mixture by ^{31}P NMR in a ratio of 10:1. Then, the mixture was filtered and all volatiles were removed under vacuum. The resulting dark red solid was extracted with toluene, and the toluene solution was concentrated to ~5 mL. Pentane was added to further precipitate the product. The yellowish solid was collected and dried under vacuum. Yield: 656 mg (65%).

Method 2. To a solution of P_2CH_2 (**1**, 1.60 g, 4.233 mmol) in toluene was added $(COD)PdCl_2$ (1.183 g, 4.15 mmol). A yellow precipitate was observed. The mixture was stirred for 20 min. ^{31}P NMR analysis showed the absence of NMR resonances of **1**. The immediate release of free COD was observed via GC/MS analysis of an aliquot. The yellow solid was collected by filtration and thoroughly washed with pentane and then toluene, followed by drying under vacuum. This solid was then suspended in toluene, 2,6-lutidine (2 equiv) was added, and the mixture was heated at 80 °C. NMR analysis indicated the clean formation of **2** (>96% by NMR). The mixture was filtered, and all volatiles were removed under vacuum from the filtrate. The resulting dark red residue was extracted with toluene, and the toluene solution was concentrated. Pentane was then added to precipitate the product. The yellowish solid was collected and dried under vacuum to give 1.55 g (72%) of **2**. Both method 1 and method 2 result in the formation of some Pd black, but method 2 results in apparently much less of it. ^1H NMR (CD_2Cl_2): δ 6.49 (t, *J* = 3 Hz, 2H, py-*H*), 6.39 (t, *J* = 2 Hz, 2H, py-*H*), 6.18 (d, *J* = 3 Hz, 2H, py-*H*), 5.61 (s, 1H, PdC*H*), 2.29 (m, 2H, C*H*Me$_2$), 2.09 (m, 2H, C*H*Me$_2$), 1.36 (dvt, J_{H-P} = 9 Hz, J_{H-H} = 7 Hz, 6H, CH*Me*$_2$), 1.22 (dvt, J_{H-P} = 9 Hz, J_{H-H} = 7 Hz, 6H, CH*Me*$_2$), 0.99 (dvt, app. quartet, J_{H-P} = 8 Hz, J_{H-H} = 8 Hz, 6 H, CH*Me*$_2$), 0.89 (dvt, app. quartet, J_{H-P} = 8 Hz, J_{H-H} = 8 Hz, 6 H, CH*Me*$_2$). ^1H NMR (C_6D_6): δ 6.49 (t, *J* = 3 Hz, 2H, py-*H*), 6.39 (t, *J* = 2 Hz, 2H, py-*H*), 6.18 (d, *J* = 3 Hz, 2H, py-*H*), 5.61 (s, 1H, PdC*H*), 2.29 (m, 2H, C*H*Me$_2$), 2.09 (m, 2H, C*H*Me$_2$), 1.36 (dvt, J_{H-P} = 9 Hz, J_{H-H} = 7 Hz, 6H, CH*Me*$_2$), 1.22 (dvt, J_{H-P} = 9 Hz, J_{H-H} = 7 Hz, 6H, CH*Me*$_2$), 0.99 (dvt, app. quartet, J_{H-P} = 8 Hz, J_{H-H} = 8 Hz, 6H, CH*Me*$_2$), 0.89 (dvt, app. quartet, J_{H-P} = 8 Hz, J_{H-H} = 8 Hz, 6H, CH*Me*$_2$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 150.1 (t, *J* = 10 Hz), 118.0 (s), 116.7 (s), 105.0 (t, *J* = 7 Hz), 32.8 (t, *J* = 2 Hz, Pd*C*H), 28.3 (t, *J* = 11 Hz, *C*HMe$_2$), 27.9 (t, *J* = 10 Hz, *C*HMe$_2$), 18.1 (t, *J* = 4 Hz, CH*Me*$_2$), 17.7 (s, CH*Me*$_2$), 17.4 (s, CH*Me*$_2$, two signals overlap). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 101.7 (s). Anal. Calcd for $C_{21}H_{35}ClN_2P_2Pd$: C, 48.57; H, 6.79. Found: C, 48.68; H, 6.91.

(PCHP)Pd(OTf) (3). To a solution of **2** (230 mg, 0.444 mmol) in 15 mL of toluene was added Me_3SiOTf (104 μL, 0.577 mmol). Then, the mixture was stirred for 10 min. All volatiles were removed under vacuum. The resulting residue was dissolved in 10 mL of toluene, and Me_3SiOTf (104 μL, 0.577 mmol) was added again. The mixture was stirred for another 10 min, and the solution was pumped to dryness. The resulting residue was extracted with toluene, and the toluene solution was concentrated under vacuum to almost dryness. About 20 mL of pentane was added to precipitate **3**. **3** was collected by filtration and dried under vacuum. Yield: 264 mg (94%). ^1H NMR (C_6D_6): δ 6.37 (t, *J* = 3 Hz, 2H, py-*H*), 6.33 (s, 2H, py-*H*), 6.11 (d, *J* = 3 Hz, 2H, py-H), 5.90 (s, 1H, PdC*H*), 2.56 (m, 2H, C*H*Me$_2$), 1.98 (m, 2H, C*H*Me$_2$), 1.25 (dvt, J_{H-P} = 10 Hz, J_{H-H} = 8 Hz, 6H, CH*Me*$_2$), 1.19 (dvt, app. quartet, J_{H-P} = 9 Hz, J_{H-H} = 9 Hz, 6H, CH*Me*$_2$), 0.87 (dvt, app. quartet, J_{H-H} = 9 Hz, J_{H-P} = 9 Hz, 6H, CH*Me*$_2$), 0.79 (dvt, app. quartet, J_{H-H} = 7 Hz, J_{H-P} = 7 Hz, 6H, CH*Me*$_2$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 148.7 (t, *J* = 10 Hz), 117.9 (s), 117.8 (s), 105.7 (t, *J* = 7 Hz), 30.5 (t, *J* = 2 Hz, Pd*C*H), 28.2 (t, *J* = 11 Hz, *C*HMe$_2$), 27.7 (t, *J* = 10 Hz, *C*HMe$_2$), 18.5 (t, *J* = 3 Hz, CH*Me*$_2$), 17.9 (t, *J* = 2 Hz, CH*Me*$_2$), 17.1 (s, CH*Me*$_2$), 16.3 (t, *J* = 4 Hz, CH*Me*$_2$). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 103.1 (s). ^{19}F NMR (C_6D_6): δ −79.9 (s). Anal. Calcd for $C_{22}H_{35}F_3N_2O_3P_2SPd$: C, 41.75; H, 5.57. Found: C, 41.95; H, 5.71.

(PCHP)Pd(Me) (6). **2** (143 mg, 0.276 mmol) was dissolved in ether. To the stirred solution was added 260 μL (0.422 mmol) of MeLi in hexane. The reaction mixture was stirred over 2 h. ^{31}P NMR in situ indicated quantitative formation of **6**. The solution was quenched with methanol. Then the volatiles were evaporated under reduced pressure. The solid residue was extracted with ether and then passed through a pad of silica gel. The filtrate was pumped to dryness. The resulting residue was washed with a small quantity of pentane and dried under vacuum. Yield: 75 mg (55%). ^1H NMR (C_6D_6): δ 6.64 (t, *J* = 3 Hz, 2H, py-*H*), 6.49 (s, 2H, py-*H*), 6.28 (d, *J* = 2 Hz, 2H, py-H), 4.72 (s, 1H, PdC*H*), 2.17 (m, 2H, C*H*Me$_2$), 2.04 (m, 2H, C*H*Me$_2$), 1.10 (dvt, app. quartet, J_{H-P} = 8 Hz, J_{H-H} = 8 Hz, 6H, CH*Me*$_2$), 1.06 (dvt, app. quartet, J_{H-P} = 8 Hz, J_{H-H} = 8 Hz, 6H, CH*Me*$_2$), 0.94 (m, 12H, two CH*Me*$_2$ signals overlap), 0.18 (t, app. quartet, J_{H-P} = 6 Hz, 3H, Pd*Me*). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 152.1 (t, *J* = 10 Hz), 117.6 (s), 115.3 (s), 104.3 (t, *J* = 6 Hz), 36.0 (t, *J* = 2 Hz, Pd*C*H), 28.2 (m, two *C*HMe$_2$ signals overlap), 18.6 (t, *J* = 4 Hz, *C*HMe$_2$), 17.8 (s, CH*Me*$_2$), 17.7 (s, CH*Me*$_2$), 17.4 (t, *J* = 3 Hz, CH*Me*$_2$), −17.3 (t, *J* = 12 Hz, Pd*Me*). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 104.3 (s). Anal. Calcd for $C_{22}H_{38}N_2P_2Pd$: C, 52.96; H, 7.68. Found: C, 52.87; H, 7.82.

(PCHP)Pd(Et) (7). A screw-cap test tube was charged with **2** (100 mg, 0.193 mmol), EtMgBr in ether (100 μL, 0.30 mmol, 3 M), 60 μL of dioxane, and 15 mL of ether. After 3 days at ambient temperature, ^{31}P NMR in situ indicated quantitative formation of **7**. The reaction was quenched with methanol. Then the volatiles were evaporated under reduced pressure. The solid residue was extracted with ether and then passed through a pad of silica gel. The filtrate was pumped to dryness. The resulting residue was washed with pentane and dried under vacuum. Yield: 49 mg (50%). ^1H NMR (C_6D_6): δ 6.63 (t, *J* = 3 Hz, 2H, py-*H*), 6.49 (s, 2H, py-*H*), 6.29 (d, *J* = 3 Hz, 2H, py-H), 4.65 (s, 1H, PdC*H*), 2.20 (m, 2H, C*H*Me$_2$), 2.07 (m, 2H, C*H*Me$_2$), 1.60 (t, *J* = 8 Hz, 3H, PdCH$_2$C*H*$_3$), 1.32 (q, *J* = 8 Hz, 2H, PdC*H*$_2$CH$_3$), 1.13 (dvt, J_{H-P} = 9 Hz, J_{H-H} = 8 Hz, 6H, CH*Me*$_2$), 1.04 (dvt, app. quartet, J_{H-P} = 8 Hz, J_{H-H} = 8 Hz, 6H, CH*Me*$_2$), 0.96 (m, 12H, two CH*Me*$_2$ signals overlap). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 152.0 (t, *J* = 7 Hz), 117.3 (s), 115.3 (s), 104.2 (t, *J* = 6 Hz), 34.7 (t, *J* = 2 Hz, Pd*C*H), 28.2 (t, *J* = 10 Hz, *C*HMe$_2$), 27.7 (t, *J* = 11 Hz, *C*HMe$_2$), 18.6 (t, *J* = 4 Hz, CH*Me*$_2$), 18.4 (t, *J* = 2 Hz, PdCH$_2$*C*H$_3$), 17.8 (s, CH*Me*$_2$), 17.6 (s, CH*Me*$_2$), 17.3 (t, *J* = 4 Hz, CH*Me*$_2$), −3.8 (t, *J* = 10 Hz, Pd*C*H$_2$CH$_3$). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 102.7 (s). Anal. Calcd for $C_{23}H_{40}N_2P_2Pd$: C, 53.85; H, 7.86. Found: C, 53.85; H, 7.73.

(PCHP)Pd(Ph) (8). A screw-cap tube was charged with **2** (110 mg, 0.212 mmol), PhLi in ether (160 μL, 0.32 mmol, 2 M), and 10 mL of ether. ^{31}P NMR in situ indicated quantitative formation of **8** less than 10 min after mixing. A few drops of methanol were added to the reaction mixture, and then all volatiles were evaporated under reduced pressure. The solid residue was extracted with toluene and then passed through a pad of silica gel. The filtrate was pumped to dryness. The resulting residue was washed with a pentane and dried under vacuum. Yield: 60 mg (50%). ^1H NMR (C_6D_6): δ 7.66 (d, *J* = 7 Hz, 2H, Ph-*H*), 7.24 (t, *J* = 8 Hz, Ph-*H*), 7.06 (t, *J* = 7 Hz, 1H, Ph-*H*), 6.62 (d, *J* = 3 Hz, 2H, py-H), 6.52 (s, 2H, py-H), 6.24 (d, *J* = 2 Hz, 2H, py-*H*), 4.87 (s, 1H, PdC*H*), 2.14 (m, 2H, C*H*Me$_2$), 1.94 (m, 2H, C*H*Me$_2$), 0.93 (m, 18H, three CH*Me*$_2$ signals overlap), 0.77 (dvt, app. quartet, J_{H-P} = 8 Hz, J_{H-H} = 8 Hz, 6H, CH*Me*$_2$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 160.0 (t, *J* = 15 Hz), 151.8 (t, *J* = 10 Hz, *ipso*-Ph), 139.8 (s), 127.2 (s), 122.6 (s), 117.5 (s), 115.5 (s), 104.6 (t, *J* = 6 Hz), 33.1 (t, *J* = 2 Hz, Pd*C*H), 27.5 (t, *J* = 11 Hz, *C*HMe$_2$), 26.6 (t, *J* = 12 Hz, *C*HMe$_2$), 18.2 (t, *J* = 4 Hz, CH*Me*$_2$), 17.6 (s, CH*Me*$_2$), 17.1 (s, CH*Me*$_2$), 16.9 (t, *J* = 3 Hz, CH*Me*$_2$). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 102.1 (s). Anal. Calcd for $C_{27}H_{40}N_2P_2Pd$: C, 57.81; H, 7.19. Found: C, 57.98; H, 7.21.

$[(P_2C{=})PdCl]^+PF_6^-$ (9-PF$_6$). **2** (147 mg, 0.283 mmol) was dissolved in ca. 10 mL of CH_2Cl_2. To the stirred solution was added 109 mg (0.281 mmol) of $Ph_3C^+PF_6^-$. The reaction mixture was stirred at room temperature for 30 min. Formation of a yellow precipitate was observed. The yellow solid was collected by filtration, washed with toluene, and dried over vacuum. Yield: 123 mg (66%). Triphenylmethane was observed in the filtrate by NMR and GC/MS. ^{1}H NMR (CD_2Cl_2): δ 7.84 (s, 2H, py-*H*), 7.62 (d, $J = 4$ Hz, 2H, py-*H*), 7.18 (dd, $J = 4$ Hz, $J = 2$ Hz, 2H, py-*H*), 2.91 (septet, $J = 7$ Hz, 4H, C*H*Me$_2$), 1.46 (dvt, $J_{H-P} = 10$ Hz, $J_{H-H} = 7$ Hz, 12H, CH*Me*$_2$), 1.34 (dvt, $J_{H-P} = 8$ Hz, $J_{H-H} = 7$ Hz, 12H, CH*Me*$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 189.6 (s, Pd=C), 153.8 (t, $J = 11$ Hz), 141.2 (s), 127.8 (s), 125.1 (t, $J = 4$ Hz), 28.7 (t, $J = 10$ Hz, *C*HMe$_2$), 17.9 (s, two CH*Me*$_2$ signals overlap). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 125.5 (s), −143.9 (septet, $J_{P-F} = 711$ Hz). ^{19}F NMR (CD_2Cl_2): δ −76.0 (d, $J_{P-F} = 711$ Hz). Anal. Calcd for $C_{21}H_{34}ClF_6N_2P_3Pd$: C, 38.03; H, 5.17. Found: C, 37.96; H, 5.03.

[(P_2C=)PdCl]$^+$BAr$_4^F$ (9-BAr$_F$^{4}). **2** (60 mg, 0.115 mmol) was dissolved in ca. 10 mL of CH_2Cl_2. To the stirred solution was added 116 mg (0.115 mmol) of $Ph_3C^+BAr_4^F$. The reaction mixture was stirred at room temperature for 30 min. The volatiles were removed under vacuum, and the residue was extracted with CH_2Cl_2. The CH_2Cl_2 was pumped to dryness, and the resulting solid was washed with 1 mL of pentane three times to afford the crude product. Pure form of the title complex was obtained from recrystallization of the crude solid out of a CH_2Cl_2/pentane mixture. Yield: 50 mg (35%). ^{1}H NMR (CD_2Cl_2): δ 7.72 (s, 8H, BAr$_4^F$), 7.70 (s, 2H, py-*H*), 7.56 (s, 4H, BAr$_4^F$), 7.51 (br, s, 2H, py-*H*), 7.08 (dd, $J = 4$ Hz, $J = 2$ Hz, 2H, py-*H*), 2.91 (septet, $J = 7$ Hz, 4H, C*H*Me$_2$), 1.44 (dvt, $J_{H-P} = 10$ Hz, $J_{H-H} = 7$ Hz, 12H, CH*Me*$_2$), 1.31 (dvt, $J_{H-P} = 8$ Hz, $J_{H-H} = 7$ Hz, 12H, CH*Me*$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 190.5 (s, Pd=C), 162.1 (q, $J_{C-B} = 50$ Hz, BAr$_4^F$), 153.7 (t, $J = 11$ Hz), 140.3 (s), 135.1 (s, BAr$_4^F$), 129.2 (q, $^2J_{C-F} = 31$ Hz, BAr$_4^F$), 127.3 (s), 123.9 (s, $^1J_{C-F} = 272$ Hz, CF_3 of BAr$_4^F$), 124.7 (t, $J = 4$ Hz), 117.8 (s, BAr$_4^F$), 28.6 (t, $J = 10$ Hz, *C*HMe$_2$), 17.6 (t, $J = 2$ Hz, CH*Me*$_2$), 17.5 (s, CH*Me*$_2$). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 125.7 (s). ^{19}F NMR (CD_2Cl_2): δ −65.8 (s, BAr$_4^F$).

X-ray Data Collection, Solution, and Refinement for 2, 3, and 9-PF$_6$. All operations were performed on a Bruker-Nonius Kappa Apex2 diffractometer, using graphite-monochromated Mo Kα radiation. All diffractometer manipulations, including data collection, integration, scaling, and absorption corrections, were carried out using the Bruker Apex2 software.[23] Preliminary cell constants were obtained from three sets of 12 frames. Data collection was carried out at 120 K, using a frame time of 10 s (5 s for **68**) and a detector distance of 60 mm. The optimized strategy used for data collection consisted of (four, three, and eight, respectively) phi and omega scan sets, with 0.5° steps in phi or omega; completeness for each structure was high (99.9%, 99.8%, and 98.8%, respectively). A total of 443, 1128, and 1391, respectively, frames were collected. Final cell constants were obtained from the *xyz* centroids of 6889, 6110, and 2901, respectively, reflections after integration.

From the lack of systematic absences, the observed metric constants, and intensity statistics, space groups $P2_1/n$, *Pbca*, and $C2/c$ were chosen initially; subsequent solution and refinement confirmed the correctness of the initial choices. The structures were solved using SIR-92[24] and refined (full-matrix least-squares) using the Oxford University Crystals for Windows program.[25] All ordered non-hydrogen atoms were refined using anisotropic displacement parameters; hydrogen atoms were fixed at calculated geometric positions and allowed to ride on the corresponding carbon atoms.

Each structure contained significant disorder, which was resolved successfully for atoms separated significantly. In all cases the two-component disorder was described with a constraint that the occupancies of the major and minor components sum to 1.0. Major component atoms were refined by using anisotropic displacement parameters, while minor component atoms were refined by using isotropic displacement parameters. For compound **2**, the Pd and Cl atoms, as well as atom C(5), were disordered, with the occupancy of the major component at 0.827(5). If the two components were present in equal amounts, the resultant image would be nearly C_2-symmetric about an axis passing through the midpoints of the disordered Pd, Cl, and C atoms. The final least-squares refinement converged to $R_1 = 0.0275$ ($I > 2\sigma(I)$, 5166 data) and $wR_2 = 0.0559$ (F^2, 6897 data, 257 parameters). For compound **3**, the disorder of the Pd and P atoms, as well as atoms C(4), C(5), C(6), and N(2), could be resolved, with the occupancy of the major component at 0.918(2). If the two components were present in equal amounts, the resultant image would be nearly C_s-symmetric, with the mirror plane normal to the square plane and containing the Pd atom and atom C(5). The final least-squares refinement converged to $R_1 = 0.0255$ ($I > 2\sigma(I)$, 5755 data) and $wR_2 = 0.0559$ (F^2, 8190 data, 336 parameters). For compound **9**-PF$_6$, the Pd complex occupies a site of crystallographic 2 symmetry containing Pd(1), Cl(1), and C(5), with no apparent disorder, while the PF_6^- anion occupies a site of crystallographic −1 symmetry. The anion is disordered, with the two components (atoms F(2) and F(3) and their minor counterparts F(21) and F(31)) related approximately by a rotation of 45° about the F(1)−P(2)−F(1)′ direction, with the occupancy of the major component at 0.760(6). The final least-squares refinement converged to $R_1 = 0.0348$ ($I > 2\sigma(I)$, 3085 data) and $wR_2 = 0.0828$ (F^2, 3979 data, 170 parameters).

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Supporting Information Available: Crystallographic information in the form of CIF files. This material is available via the Internet free of charge at http://pubs.acs.org.

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