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Covalent Palladium-Zinc Bonds and Their Reactivity

*Claudia M. Fafard, Chun-Hsing Chen, Bruce M. Foxman, and Oleg V. Ozerov**

Department of Chemistry, Brandeis University, MS015, 415 South Street, Waltham,
Massachusetts 02454. ozerov@brandeis.edu

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Experimental.

General Considerations. Unless specified otherwise, all manipulations were performed under an argon atmosphere using standard Schlenk line or glove box techniques. Toluene, ethyl ether, THF, pentane, and isooctane were dried and deoxygenated (by purging) using a solvent purification system[1] by MBraun and stored over molecular sieves in an Ar-filled glove box. C_6D_6 was dried over and distilled from NaK/Ph_2CO/18-crown-6 and stored over molecular sieves in an Ar-filled glove box. MeI was degassed by the freeze-pump-thaw technique. (^{F}PNP)PdEt (**1**)[2] [(^{F}PNP)Pd]$_2$ (**3**)[3], (^{F}PNP)PdH (**6**)[4], (^{F}PNP)PdMe (**7**)[2], (^{F}PNP)PdCl (**9**)[5] and (^{F}PNP)PdOH (**10**)[2] have been reported previously. UV experiments were performed in a Rayonet-type photochemical reactor which contained 19 light sources at 350 nm. Samples were hung in the center of the reaction chamber for the specified amount of time. All other chemicals were used as received from commercial vendors. NMR spectra were recorded on a Varian iNova 400 (^{1}H NMR, 399.755 MHz; ^{13}C NMR, 100.518 MHz; ^{31}P NMR, 161.822 MHz; ^{19}F NMR, 375.912 MHz) spectrometer. Chemical shifts are reported in δ (ppm). For ^{1}H 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. ^{19}F NMR spectra were referenced externally using 1.0 M CF_3CO_2H in $CDCl_3$ at -78.5 ppm. Elemental analyses were performed by CALI Labs, Inc. (Parsippany, NJ).

Preparative isolation of [(^{F}PNP)Pd]$_2$Zn (5). In a reaction flask with a Teflon screw cap (^{F}PNP)PdEt (**1**) (72 mg, 0.126 mmol) was dissolved in THF and Et_2O (0.5 mL and 4 mL respectively). Et_2Zn (170.1 µL, 0.189 mmol of a 15% wt solution in hexane) was added and the mixture was irradiated for 18 h. The solution became dark brown with orange crystals deposited. The supernatant was decanted and the crystals washed with pentane. 54 mg (74% yield) of **5** as orange crystals was collected. ^{1}H NMR (C_6D_6): δ 7.53 (m, 4H, Ar-*H*), 6.82 (m, 8H, Ar-*H*), 2.06 (m, 8H, PC*H*Me$_2$), 1.20 (app. q. (dvt), 24H, 9 Hz, PCH*Me$_2$*), 0.89 (app. q. (dvt), 24H, 8 Hz, PCH*Me$_2$*). ^{13}C{^{1}H} NMR (C_6D_6): δ 158.5 (t, J = 10 Hz, *C*-N), 153.8 (d, J = 234 Hz, C-F), 123.4 (*C*-P), 119.2 (d, J = 21 Hz, C_{Ar}), 118.7 (d, J = 22 Hz, C_{Ar}), 114.6 (C_{Ar}), 25.3 (t, J = 12 Hz, P*C*HMe$_2$), 20.2 (PCH*Me$_2$*), 18.4 (PCH*Me$_2$*). ^{31}P{^{1}H} NMR (C_6D_6): δ 53.9. ^{19}F NMR (C_6D_6): δ -134.2. Elem. Anal. Calc. for $C_{52}H_{80}N_2P_4Pd_2$: C, 50.08; H, 5.95. Found: C, 49.98; H, 5.83%.

Photolysis of (^{F}PNP)PdEt (1) with varying amounts of Et_2Zn. *Experiment A*. **1** (20 mg, 0.035 mmol) was dissolved in C_6D_6 and Et_2Zn (23.4 µL of 15% wt solution in hexanes, 0.026 mmol) was added. The solution was irradiated for 18 h. By ^{31}P NMR the solution contained **5** and **3** in an 79:11 ratio. The solution contained approximately 10% other compounds. *Experiment B*. **1** (20 mg, 0.035 mmol) was dissolved in C_6D_6 and Et_2Zn (31.5 µL of 15% wt solution in hexanes, 0.035 mmol) was added. The solution was irradiated for 18 h. By ^{31}P NMR the solution contained >85% **5**. No **3** was observed by NMR.

Reaction of [(^{F}PNP)Pd]$_2$ (3) with Et_2Zn. **3** (20 mg, 0.037 mmol) was dissolved in C_6D_6. Et_2Zn (33.2 µL of 15% wt solution in hexanes, 0.037 mmol) was added and the solution was irradiated for 18 h. The solution had gone from dark green to dark brown. The solution contained >88% of **5** (NMR evidence).

Reaction of [(^{F}PNP)Pd]$_2$ (3) with Zn dust. **3** (100mg, 0.092 mmol) was dissolved in THF, Zn dust (6 mg, 0.092 mmol) was added, and the mixture was stirred for 18 h at ambient temperature. No change was observed by NMR. Additional Zn dust (30 mg, 0.458 mmol) was added and the mixture was heated for 18 h in a 65 °C oil bath. No change was observed by NMR.

Thermolysis of 5. **5** was heated in C_6D_6 for 18 h at 80 °C. No change was observed by NMR.

Reaction of 5 with MeI. 5 (20 mg, 0.017 mmol) was dissolved in C_6D_6. MeI (2.2 μL, 0.036 mmol) was added. The solution was allowed to stand at ambient temperature for 1 h. The color of the solution turned from orange to red. NMR spectra showed a ratio of 89:5:4 for (^{F}PNP)PdI (**11**) : (PNP)PdMe (**7**) : **5** (with <2% unidentified compounds). The ^1H NMR spectra also revealed formation of Me_2Zn (^1H NMR: δ -0.68 ppm in C_6D_6). After 5 d at ambient temperature the solution had become more orange in color. NMR spectra showed a 40:57 ratio of **11** to **7** (<3% unidentified compounds). For comparison, **11** was generated in a reaction of (^{F}PNP)PdCl (**9**) and MeI (we have previously shown that (^{Me}PNP)PdCl reacts with MeI to produce (^{Me}PNP)PdI).[6] Heating at 95 °C for two hours gave a 1:1 mixture of **9** and **11** (Data for **11** follow. ^{31}P NMR (C_6D_6): δ 51.8; ^{19}F NMR (C_6D_6): δ -130.6.).

Reaction of 5 with H_2. In a J. Young tube, **5** (19 mg, 0.017 mmol) was dissolved in C_6D_6. The NMR tube was freeze-pump-thaw degassed and refilled with 1 atm of H_2. The solution was heated for 6 h at 95 °C. No (^{F}PNP)PdH (**6**) was observed. Only **5** was observed by NMR.

Reaction of 5 with H_2O. 2 (18.7 mg, 0.016 mmol) was dissolved in THF and H_2O (10 μL, 0.555 mmol) added. ^{19}F and $^{31}P\{^1H\}$ NMR analysis revealed the presence of **5**, (^{F}PNP)PdH **(6)** and another unidentified compound. Heating the solution for 6 h at 95 °C lead to complete conversion to **6**.

Reaction of 5 with air. 5 (10 mg, 0.0087 mmol) was dissolved in C_6D_6 and exposed to air. After 24 h at ambient temperature **5** and (^{F}PNP)PdOH **(10)** were observed by ^{19}F and $^{31}P\{^1H\}$ NMR in a 1:3 ratio as well as small quantities of other unidentified compounds.

Reaction of 5 with NH_3. In a J. Young tube, **5** (20 mg, 0.017 mmol) was dissolved in C_6D_6. The NMR tube was freeze-pump-thaw degassed and refilled with 1 atm of NH_3. The solution was heated for 24 h at 95 °C. Only **5** was observed.

Reaction of 5 with Ph_3CCl. **5** (10 mg, 0.0086 mmol) was dissolved in C_6D_6 and Ph_3CCl (11.9 mg, 0.043 mmol) added. Upon mixing a precipitate was observed. Complete conversion to **9** was observed by ^{19}F and ^{31}P NMR.

Reaction of 5 with Et_2Zn. **5** (26 mg, 0.023 mmol) was dissolved in C_6D_6. Et_2Zn (40.7 µL, 0.045 mmol of 15% wt solution in hexanes) was added. NMR spectra were recorded within 10 min after mixing. By ^{31}P NMR two signals were observed; one for compound **5** and the other tentatively assigned as (^{F}PNP)PdZnEt (**8**). The ratio of **5**:**8** was 52:48. Selected NMR data for **8**. ^{19}F NMR (C_6D_6): δ -133.8. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 61.7 ppm.

Reaction of 5 with varying amounts of Et_2Zn. **5** was dissolved in C_6D_6 and reacted with Et_2Zn (15% wt in hexanes) to produce a mixture of **5** and **8**.

Table S1: Amounts of **5** and Et_2Zn in the reaction and the observed ratios of **5** to **8**.

5 (mg, mmol)	Equivalents of Et_2Zn (µL, mmol)	Ratio **5**:**8**[a]
10, 0.0087	2 (15.7, 0.0174)	60:40
10.5, 0.0091	5 (41.0, 0.0456)	49:51
10, 0.00869	10 (77.4, 0.0869)	39:61
10.2, 0.0088	20 (154.7, 0.1774)	30:70

[a] Ratios were determined by ^{31}P NMR.

Reaction of (^{F}PNP)PdH (6) with Et_2Zn. **6** (23 mg, 0.042 mmol) was dissolved in C_6D_6 and Et_2Zn (20 µL, 0.022 mmol) was added. The solution was allowed to stand at ambient temperature for 2 h during which time it had turned brown in color. NMR analysis revealed the presence of **5**, **6** and **8** in a 20:75:5 ratio in the solution. The mixture was heated for 4.5 h at 60 °C, after which **8** was no longer observed. The ratio of **5** to **6** was 47:53 and a trace amount of **1** was also observed. Additional Et_2Zn (20 µL, 0.148 mmol) was added and the solution was allowed to stand for 18 h at ambient temperature. The ratio of **5**, **6** and **8** became 49:40:11 with trace amounts of **1**.

X-Ray data collection, solution, and refinement for 5. Single crystals of **5** suitable for X-ray diffraction measurements were obtained directly from the photolysis reaction, and mounted in a glass capillary. Data collection was carried out at room temperature (low temperature apparatus was not available) on a CAD-4 Turbo diffractometer equipped with MoKα radiation;[7] completeness was 99.9%. The structure was solved by direct methods (SIR92).[8] From the lack of systematic absences, the observed metric constants and intensity statistics, space group *C2/c* was chosen initially; subsequent solution and refinement confirmed the correctness of this choice. Full-matrix least squares refinement was carried out using the Oxford University *Crystals for Windows* system.[9] All nonhydrogen atoms were refined using anisotropic displacement parameters; the hydrogen atoms were allowed to ride on the respective carbon atoms. The final least-squares refinement converged to $R_1 = 0.0395$ ($I > 2\sigma(I)$, 3161 data) and $wR_2 = 0.0666$ (F, 5385 data, 278 parameters). A full report on this structure is available as a CIF file.

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