

Electronic Supplementary Information For:

**Generation of [(IPr)Pd(PR₂Cl)] Complexes via P-Cl Reductive
Elimination**

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General Experimental Considerations. All manipulations were conducted at ambient temperature in the absence of oxygen and water under an atmosphere of dinitrogen, either by use of standard Schlenk methods or within an mBraun glovebox apparatus, utilizing glassware that was oven-dried (130 °C) and evacuated while hot prior to use. Celite (Aldrich) was oven-dried for 5 d and then evacuated for 24 h prior to use. Pentane and benzene were deoxygenated and dried by sparging with dinitrogen gas, followed by passage through a double-column solvent purification system purchased from mBraun Inc (one alumina-packed column and one column packed with copper-Q5 reactant). THF and diethyl ether were each dried over Na/benzophenone followed by distillation under an atmosphere of dinitrogen. Benzene-*d*₆ (Cambridge Isotopes) was degassed by using at least three repeated freeze-pump-thaw cycles and stored over 4 Å molecular sieves for 24 h prior to use. All solvents used within the glovebox were stored over activated 4 Å molecular sieves. [(IPr)Pd(Cl)₂]₂^{S1} and P(1-Ad)₂H^{S2} were prepared according to literature procedures, while NaN(SiMe₃)₂ (Aldrich), PCy₂H (Cytec), and P(tBu)₂H (Strem) were purchased. Prepared and purchased solid reagents were evacuated under reduced pressure for 24 h prior to use and were stored in an inert atmosphere glovebox; otherwise chemicals were used as received. ¹H, ¹³C, and ³¹P NMR characterization data were collected at 300K on a Bruker AV-500 spectrometer operating at 500.1, 125.8, and 202.5 MHz (respectively) with chemical shifts reported in parts per million downfield of SiMe₄ (for ¹H and ¹³C) and 85% H₃PO₄ in D₂O (for ³¹P). Elemental analyses were performed by Canadian Microanalytical Service Ltd., Delta, BC (Canada) and Midwest Microlab, LLC, Indianapolis, IN (USA).

Synthesis of 1a. To a magnetically stirred suspension of [(IPr)Pd(Cl)₂]₂ (143 mg, 0.126 mmol) in THF (2 mL) was added P(1-Ad)₂H (77 mg, 0.252 mmol) at room temperature. After one hour, ³¹P NMR analysis of the crude reaction mixture indicated consumption of P(1-Ad)₂H and the formation of a new phosphorus-containing species (**1a**). The solvent was removed under reduced pressure followed by trituration of the resulting crude solid with pentane (3 x 2 mL). The remaining solid was dried in vacuo to

afford **1a** as an analytically pure off-white solid in 94% yield (206 mg, 0.237 mmol). Anal Calcd for $C_{47}H_{67}N_2Cl_2P_1Pd_1$: C 65.01; H 7.78; N 3.23. Found: C 64.82; H 7.56; N 3.31. 1H NMR (C_6D_6): δ 7.39-7.23 (m, 6H, ArH), 6.66 (d, $J = 1.2$ Hz, 2H, NCH=CHN), 3.52 (d, $^1J_{PH} = 350.3$ Hz, 1H, PH), 3.48 (m, 4H, $CHMe_2$), 2.20-2.09 (m, 6H, Ad), 1.98-1.89 (m, 6H, Ad), 1.81-1.73 (m, 6H, Ad), 1.64 (d, $^3J_{HH} = 6.8$ Hz, 12H, $CHMe_2$), 1.56-1.53 (m, 12H, Ad), 1.08 (d, $^3J_{HH} = 7.0$ Hz, $CHMe_2$); $^{13}C\{^1H\}$ NMR (C_6D_6): δ 174.8 (d, $^2J_{PC} = 189.2$ Hz, NCN), 146.4 (ArC), 135.2 (ArC), 129.1 (ArC), 123.1 (d, $J_{PC} = 5.2$ Hz, NCH=CHN), 122.8 (ArC), 41.2 (Ad), 37.4 (d, $J_{PC} = 13.9$ Hz, Ad), 35.7 (Ad), 28.0 ($CHMe_2$), 27.9 (d, $J_{PC} = 8.8$ Hz, Ad), 25.7 ($CHMe_2$), 22.1 ($CHMe_2$); ^{31}P NMR (C_6D_6): δ 56.3. Crystals suitable for X-ray crystallographic analysis were grown by vapor diffusion of pentane into a concentrated solution of **1a** in benzene.

Synthesis of 2a. To a magnetically stirring solution of **1a** (0.107 g, 0.123 mmol) in benzene (2 mL) was added $NaN(SiMe_3)_2$ (24 mg, 0.129 mmol). After three hours of stirring at room temperature, ^{31}P NMR analysis of the crude reaction mixture indicated complete consumption of **1a**, and formation of a single phosphorus-containing product (**2a**). The reaction mixture was diluted with pentane (4 mL) and filtered through Celite. The eluent was collected and the solvent was removed under reduced pressure. The crude solid was then triturated with pentane (3 x 2 mL) and diethyl ether (3 x 2 mL), and dried in vacuo to give **2a** as an analytically pure dark yellow solid in 75% yield (77 mg, 0.092 mmol). Anal Calcd for $C_{47}H_{66}N_2Cl_1P_1Pd_1$: C 67.84; H 8.00; N 3.37. Found: C 67.52; H 7.72; N 3.41. 1H NMR (C_6D_6): δ 7.31-7.26 (m, 2H, ArH), 7.17-7.14 (m, 4H, ArH), 6.46 (s, 2H, NCH=CHN), 2.83 (m, 4H, $CHMe_2$), 2.10-1.98 (m, 12H, Ad), 1.91-1.84 (m, 6H, Ad), 1.68 (d, $^3J_{HH} = 7.0$ Hz, 12H, $CHMe_2$), 1.66-1.59 (m, 12H, Ad), 1.20 (d, $^3J_{HH} = 7.9$ Hz, 12H, $CHMe_2$); $^{13}C\{^1H\}$ NMR (C_6D_6): δ 197.2 (d, $^2J_{PC} = 224.2$ Hz, NCN), 145.4 (ArC), 136.4 (ArC), 128.3 (ArC), 122.5 (ArC), 120.1 (NCH=CHN), 42.4 (d, $J_{PC} = 8.8$ Hz, Ad), 39.2 (d, $J_{PC} = 9.8$ Hz, Ad), 36.3 (Ad), 28.2 (d, $J_{PC} = 9.8$ Hz, Ad), 28.1 ($CHMe_2$), 24.5 ($CHMe_2$), 22.9 ($CHMe_2$); ^{31}P NMR

(C₆D₆): δ 159.6. Crystals suitable for X-ray crystallographic analysis were grown by vapor diffusion of pentane into a concentrated solution of **2a** in benzene.

Synthesis of 2b. To a magnetically stirring solution of [(IPr)Pd(Cl)₂]₂ (80 mg, 0.071 mmol) in benzene (1.5 mL) was added P(tBu)₂H (25 μ L, 0.138 mmol). After one hour, ³¹P NMR analysis of the crude reaction mixture indicated consumption of P(tBu)₂H and the formation of a new phosphorus-containing species (58.5 ppm, the presumptive intermediate **1b**). The reaction mixture was diluted with pentane (4 mL), and filtered through Celite. The eluent was collected and the solvent was removed under reduced pressure to afford a yellow solid. This solid was dissolved in benzene (1.5 mL) and magnetic stirring was initiated. To this solution was added NaN(SiMe₃)₂ (25 mg, 0.138 mmol). After three hours of stirring at room temperature, ³¹P NMR analysis of the crude reaction mixture indicated clean conversion to a single phosphorus-containing product (**2b**). The reaction mixture was diluted with pentane (4 mL) and filtered through Celite. The eluent was collected and the solvent was removed under reduced pressure. The crude solid was then triturated with pentane (3 x 2 mL) and diethyl ether (3 x 2 mL), and dried in vacuo to give **2b** as an analytically pure orange-brown solid in 68% yield (64 mg, 0.094 mmol). Anal Calcd for C₃₅H₅₄N₂Cl₁P₁Pd₁: C 62.22; H 8.06; N 4.15. Found C 61.97; H 8.12; N 3.89. ¹H NMR (C₆D₆): δ 7.27 (m, 2H, ArH), 7.16-7.15 (m, 4H, ArH), 6.45 (s, 2H, NCH=CHN), 2.85 (m, 4H, CHMe₂), 1.66 (d, ³J_{HH} = 6.5 Hz, 12H, CHMe₂), 1.19-1.15 (m, 30H, CHMe₂ and CMe₃); ¹³C{¹H} NMR (C₆D₆): δ 146.9 (ArC), 137.9 (ArC), 130.0 (ArC), 124.2 (NCH=CHN or ArC), 121.9 (ArC or NCH=CHN), 39.8 (d, ¹J_{PC} = 7.5 Hz, CMe₃), 29.6-29.5 (m, CHMe₂ and CMe₃), 26.0 (CHMe₂), 24.5 (CHMe₂), the carbene NCN resonance could not be identified unambiguously; ³¹P NMR (C₆D₆): δ 163.7. Crystals suitable for X-ray diffraction were grown from a concentrated solution of **2b** in pentane that was stored at -30 °C.

Synthesis of 2c. To a magnetically stirring solution of [(IPr)Pd(Cl)₂]₂ (70 mg, 0.062 mmol) in benzene (1.5 mL) was added PCy₂H (25 μ L, 0.121 mmol). After one hour, ³¹P NMR analysis of the crude reaction

mixture indicated consumption of PCy₂H and the formation of a new phosphorus-containing species (25.9 ppm, the presumptive intermediate **1c**). The reaction mixture was diluted with pentane (4 mL), and filtered through Celite. The eluent was collected and the solvent was removed under reduced pressure to afford a yellow solid. This solid was dissolved in benzene (1.5 mL) and magnetic stirring was initiated. To this solution was added NaN(SiMe₃)₂ (22 mg, 0.121 mmol). After one hour of stirring at room temperature, ³¹P NMR analysis of the crude reaction mixture indicated clean conversion to a single phosphorus-containing product (**2c**). The reaction mixture was diluted with pentane (4 mL) and filtered through Celite. The eluent was collected and the solvent was removed under reduced pressure. The crude solid was then triturated with pentane (3 x 2 mL) and diethyl ether (3 x 2 mL), and dried in vacuo to give **2c** as an orange-brown solid in 74% yield (65 mg, 0.089 mmol). ¹H NMR (C₆D₆): δ 7.05 (m, 2H, ArH), 6.95-6.93 (m, 4H, ArH), 6.21 (s, 2H, NCH=CHN), 2.62 (m, 4H, CHMe₂), 1.70-0.95 (m, 46H, Cy and CHMe₂; distinct CHMe₂ resonances observed at 1.44 (d, ³J_{HH} = 6.5 Hz) and 0.97 (d, ³J_{HH} = 7.0 Hz)); ¹³C{¹H} (C₆D₆): δ 146.3 (ArC), 137.3 (ArC), 129.5 (ArC), 123.6 (NCH=CHN or ArC), 121.5 (ArC or NCH=CHN), 42.3 (Cy), 29.1-28.8 (m, Cy and CHMe₂), 28.0-26.9 (m, Cy), 26.7 (Cy), 25.6 (CHMe₂), 23.9 (CHMe₂), the carbene NCN resonance could not be identified unambiguously; ³¹P NMR (C₆D₆): δ 138.4. Crystals suitable for X-ray diffraction were grown from a concentrated solution of **2c** in pentane that was stored at -30 °C.

Crystallographic Solution and Refinement Details. Crystallographic data were obtained at 173(±2) K on either a Bruker D8/APEX II CCD or a Bruker PLATFORM/APEX II CCD diffractometer using a graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation, employing samples that were mounted in inert oil and transferred to a cold gas stream on the diffractometer. Programs for diffractometer operation, data collection, and data reduction (including SAINT) were supplied by Bruker. Gaussian integration (face-indexed) was employed as the absorption correction method and the structures were each solved by

use of direct methods (*SHELXS-97*^{S3} for **1a**, **2a**·**0.5C₅H₁₂**, and **2c**; *SIR-97*^{S4} for **2b**). The structures were refined by use of full-matrix least-squares procedures (on F^2 ; *SHELXL-97*^{S3}) with R_1 based on $F_o^2 \geq 2\sigma(F_o^2)$ and wR_2 based on $F_o^2 \geq -3\sigma(F_o^2)$. Anisotropic displacement parameters were employed for all the non-hydrogen atoms; during the structure solution process for **2a**, half of an equivalent of pentane was located in the asymmetric unit and was refined anisotropically. All hydrogen atoms were added at calculated positions and refined by use of a riding model employing isotropic displacement parameters based on the isotropic displacement parameter of the attached atom. Additional crystallographic information is provided in Table S1 and in the accompanying CIF (CCDC 847279 - 847282).

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Table S1. Crystallographic Data for **1a**, **2a·0.5C₅H₁₂**, **2b**, and **2c**.

	1a	2a·0.5C₅H₁₂	2b	2c
Empirical formula	C ₄₇ H ₆₇ Cl ₂ N ₂ PPd	C _{49.50} H ₇₂ ClN ₂ PPd	C ₃₅ H ₅₄ ClN ₂ PPd	C ₃₉ H ₅₈ ClN ₂ PPd
Formula weight	868.30	867.91	675.62	727.69
Crystal dimensions	0.23 x 0.19 x 0.15	0.50 × 0.31 × 0.27	0.35 × 0.14 × 0.10	0.42 × 0.08 × 0.04
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>C</i> 2/ <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	16.2112 (16)	21.4934 (7)	18.2945 (11)	12.3612 (6)
<i>b</i> (Å)	12.1097 (12)	13.5722 (5)	18.0530 (10)	21.7925 (10)
<i>c</i> (Å)	22.836 (2)	31.6794 (11)	22.0271 (13)	14.5546 (7)
α (deg)	90	90	90	90
β (deg)	106.2460 (10)	95.8069 (4)	96.3508 (7)	96.2170 (10)
γ (deg)	90	90	90	90
<i>V</i> (Å ³)	4304.0 (7)	9193.9 (6)	7230.3 (7)	3897.7 (3)
<i>Z</i>	4	8	8	4
ρ_{calcd} (g cm ⁻³)	1.340	1.254	1.241	1.240
μ (mm ⁻¹)	0.627	0.531	0.655	0.613
Range of transmission	0.9102–0.8671	0.8691–0.7768	0.9350–0.8031	0.9747–0.7816
2θ limit (deg)	55.04	50.98	52.84	53.02
	-20 ≤ <i>h</i> ≤ 21	-26 ≤ <i>h</i> ≤ 26	-22 ≤ <i>h</i> ≤ 22	-15 ≤ <i>h</i> ≤ 15
	-15 ≤ <i>k</i> ≤ 15	-16 ≤ <i>k</i> ≤ 16	-22 ≤ <i>k</i> ≤ 22	-27 ≤ <i>k</i> ≤ 27
	-29 ≤ <i>l</i> ≤ 29	-38 ≤ <i>l</i> ≤ 38	-27 ≤ <i>l</i> ≤ 27	-18 ≤ <i>l</i> ≤ 18
Total data collected	37222	33027	28604	31101
Independent reflections	9881	8574	7417	8058
<i>R</i> _{int}	0.0667	0.0156	0.0366	0.0784
Observed reflections	8010	8131	6018	5491
Data/restraints/parameters	9881 / 0 / 478	8574 / 0 / 492	7417 / 0 / 361	8058 / 0 / 397
Goodness-of-fit	1.019	1.033	1.029	1.007
<i>R</i> ₁ [<i>F</i> _o ² ≥ 2σ(<i>F</i> _o ²)]	0.0420	0.0467	0.0298	0.0426
<i>wR</i> ₂ [<i>F</i> _o ² ≥ -3σ(<i>F</i> _o ²)]	0.1139	0.1267	0.0745	0.1023
Largest peak, hole (eÅ ⁻³)	1.551, -1.537	3.996, -0.642	0.533, -0.434	1.009, -0.704