Electronic Supplementary Information
for

Benzene C-H Activation by Platinum(II) Complexes of Bis(2-diphenylphosphinophenyl)amide

Experimental

General procedures. Unless otherwise specified, all experiments were performed under nitrogen using standard Schlenk or glovebox techniques. All solvents were reagent grade or better and purified by standard methods. The NMR spectra were recorded on Varian instruments. Chemical shifts (δ) are listed as parts per million downfield from tetramethylsilane and coupling constants (*J*) in hertz. ^{1}H NMR spectra are referenced using the residual solvent peak at δ 7.16 for C_6D_6 and δ 7.27 for $CDCl_3$. ^{13}C NMR spectra are referenced using the residual solvent peak at δ 128.39 for C_6D_6 and δ 77.23 for $CDCl_3$. The assignment of the carbon atoms for all new compounds is based on the DEPT ^{13}C NMR spectroscopy. ^{19}F and ^{31}P NMR spectra are referenced externally using $CFCl_3$ in $CHCl_3$ at δ 0 and 85% H_3PO_4 at δ 0, respectively. Routine coupling constants are not listed. All NMR spectra were recorded at room temperature in specified solvents unless otherwise noted. Elemental analysis was performed on a Heraeus CHN-O Rapid analyzer.

Materials. Compounds H[PNP],[1] [PNP]Li(THF)$_2$,[1] $PtCl_2(SMe_2)_2$,[2] $[PtMe_2(\mu\text{-}SMe_2)]_2$,[2] and $PtPh_2(SMe_2)_2$[3,4] were prepared according to the procedures reported previously. All other chemicals were obtained from commercial vendors and used as received.

X-ray crystallography. Data for compounds [PNP]PtCl, [PNP]PtMe, and {[PNP]Pt(pyridine)}(OTf) were collected on a Bruker-Nonius Kappa CCD diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.7107 Å). Structures were solved by direct methods and refined by full matrix least squares procedures against F^2 using maXus or WinGX crystallographic software package. All full-weight non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions.

Synthesis of [PNP]PtCl. A yellow solution of [PNP]Li(THF)$_2$ (191.2 mg, 0.278 mmol) in THF (4 mL) was added dropwise to a yellow suspension of $PtCl_2(SMe_2)_2$ (108.5 mg, 0.278 mmol, cis/trans ratio ca. 1:2) in THF (6 mL) at –35 °C. After being stirred at room temperature for 18 h, the reaction mixture was stripped to dryness in vacuo. The residue thus obtained was extracted with CH_2Cl_2 (12 mL). The CH_2Cl_2 solution was passed through a pad of Celite and the solvent was removed in vacuo, affording the product as a yellow solid; yield 208.9 mg (98%). ^{1}H NMR ($CDCl_3$, 499.767 MHz) δ 7.801 (m, 8, Ar), 7.717 (m, 2, Ar), 7.463 (m, 12, Ar), 7.154 (m, 2, Ar), 7.078 (t, 2, Ar), 6.568 (t, 2, Ar). ^{1}H NMR (C_6D_6, 199.979 MHz) δ 7.921 (m, 10, Ar), 7.192 (m, 2, Ar), 6.999 (m, 12, Ar), 6.879 (t, 2, Ar), 6.443 (t, 2, Ar). ^{31}P{^{1}H} NMR ($CDCl_3$, 202.310 MHz) δ 26.099 ($^{1}J_{PPt}$ = 2759 Hz). ^{31}P{^{1}H} NMR (THF, 121.416 MHz) δ 25.000 ($^{1}J_{PPt}$ = 2769 Hz). ^{31}P{^{1}H} NMR (C_6D_6, 80.952 MHz) δ 25.430 ($^{1}J_{PPt}$ = 2751 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$, 125.679 MHz) δ 161.925 (t, J_{CP} = 11.37 Hz, C), 135.059 (s, CH), 133.641 (t, J_{CP} = 6.35 Hz, CH), 131.571 (s, CH), 130.862 (s, CH), 130.146 (t, J_{CP} = 29.09 Hz, C), 128.720 (t, J_{CP} = 5.47 Hz, CH), 121.333 (t, J_{CP} = 27.71 Hz, C), 118.677 (s, CH), 116.818 (s, CH). Anal. Calcd. for $C_{36}H_{28}ClNP_2Pt$: C, 56.37; H, 3.68; N, 1.83. Found: C, 56.08; H, 4.00; N, 1.90.

Synthesis of [PNP]PtMe. Method 1. The platinum dimethyl complex, $[PtMe_2(\mu\text{-}SMe_2)]_2$, was prepared in situ as follows. A finely ground solid of $PtCl_2(SMe_2)_2$ (72.59 mg, 0.186 mmol, cis/trans ratio ca. 1:2) was suspended in diethyl ether (3 mL) and chilled to –35 °C. To this cold, yellow suspension was added dropwise a solution of methyl lithium (0.24 mL, 1.6 M in diethyl ether, Acros, 0.379 mmol, 2.04 equiv). The reaction mixture was

naturally warmed with stirring at room temperature until the yellow solid of $PtCl_2(SMe_2)_2$ disappeared (ca. 20 min after addition of MeLi). At this moment, the quantitative formation of the platinum dimethyl complex was assumed. The reaction mixture was then chilled to –35 °C again. To this was added dropwise a colorless solution of H[PNP] (100 mg, 0.186 mmol) in THF (2 mL). After being stirred at room temperature overnight, the reaction mixture was stripped to dryness in vacuo. The residue thus obtained was extracted with benzene (10 mL) and filtered through a pad of Celite. Solvent was removed in vacuo to afford the desired product as a yellow solid; yield 108.7 mg (78%). **Method 2.** Yellow [PNP]PtCl (100 mg, 0.13 mmol) was dissolved in THF (6 mL) and cooled to –35 °C. To this was added MeMgCl (0.04 mL, 3 M in THF, Aldrich, 0.12 mmol) dropwise. The reaction mixture was stirred at room temperature overnight and evaporated to dryness under reduced pressure. The solid residue was triturated with pentane (2 mL x 2) and dissolved in benzene (6 mL). The benzene solution was filtered through a pad of Celite, which was further washed with benzene (3 mL x 2). The combined benzene solution was evaporated to dryness in vacuo to afford the product as a yellow solid in quantitative yield (105 mg). Slow evaporation of a concentrated benzene solution at room temperature afforded yellow crystals suitable for X-ray crystallography. ^{1}H NMR (C_6D_6, 499.767 MHz) δ 7.978 (d, 2, Ar), 7.705 (m, 8, Ar), 6.970 (m, 16, Ar), 6.448 (t, 2, Ar), 1.367 (t, 3, CH_3, $^3J_{HP}$ = 5.5 Hz). ^{31}P{^{1}H} NMR (C_6D_6, 202.310 MHz) δ 30.571 ($^1J_{PPt}$ = 2983 Hz). ^{31}P{^{1}H} NMR (THF, 80.953 MHz) δ 30.410 ($^1J_{PPt}$ = 2989 Hz). ^{31}P{^{1}H} NMR (CH_2Cl_2, 121.416 MHz) δ 30.010 ($^1J_{PPt}$ = 2969 Hz). ^{13}C{^{1}H} NMR (C_6D_6, 125.677 MHz) δ 162.729 (t, J_{CP} = 10.93 Hz, C), 136.346 (s, CH), 134.209 (t, J_{CP} = 6.60 Hz, CH), 132.861 (t, J_{CP} = 26.96 Hz, C), 132.432 (s, CH), 130.708 (s, CH), 129.143 (t, J_{CP} = 4.71 Hz, CH), 124.310 (t, J_{CP} = 27.96 Hz, C), 117.844 (s, CH), 117.287 (s, CH), –22.711 (t, $^2J_{CP}$ = 5.70 Hz, CH_3). Anal. Calcd. for $C_{37}H_{31}NP_2Pt$: C, 59.52; H, 4.18; N, 1.88. Found: C, 59.46; H, 4.45; N, 1.78.

Synthesis of [PNP]PtOTf. Method 1: From [PNP]PtMe. Neat trifluoromethanesulfonic acid (0.01 mL, Lancaster, 0.133 mmol) was added to a yellow solution of [PNP]PtMe (99.1 mg, 0.133 mmol) in benzene (10 mL) at room temperature. The solution became orange in color in 2 h. After being stirred at room temperature for 15 h, the reaction mixture was evaporated to dryness in vacuo. The residue was extracted with benzene (10 mL) and filtered through a pad of Celite. Solvent was removed in vacuo, affording the product as an orange solid; yield 72 mg (61%). **Method 2: From [PNP]PtCl.** A Teflon-capped J. Young tube was charged with a benzene solution (0.7 mL) of [PNP]PtCl (3 mg, 0.004 mmol) and silver triflate (1.0 mg, 0.004 mmol) at room temperature. The reaction was monitored by ^{31}P{^{1}H} NMR spectroscopy which indicated formation of [PNP]PtOTf quantitatively in 19 h. ^{1}H NMR (C_6D_6, 499.767 MHz) δ 7.851 (m, 6, Ar), 7.624 (m, 2, Ar), 7.004 (m, 16, Ar), 6.738 (t, 2, Ar), 6.351 (t, 2, Ar). ^{31}P{^{1}H} NMR (C_6D_6, 202.308 MHz) δ 27.757 ($^1J_{PPt}$ = 2809 Hz). ^{31}P{^{1}H} NMR (THF, 80.953 MHz) δ 27.23 ($^1J_{PPt}$ = 2792 Hz). ^{31}P{^{1}H} NMR ($CHCl_3$, 80.953 MHz) δ 27.340 ($^1J_{PPt}$ = 2808 Hz). ^{13}C{^{1}H} NMR (C_6D_6, 125.678 MHz) δ 162.654 (t, J_{CP} = 10.87 Hz, C), 135.330 (s, CH), 134.352 (t, J_{CP} = 6.60 Hz, CH), 132.455 (s, CH), 131.785 (s, CH), 129.850 (t, J_{CP} = 29.35 Hz, C), 129.496 (t, J_{CP} = 5.72 Hz, CH), 129.241 (t, J_{CP} = 5.72 Hz, CH), 120.404 (s, CH), 117.731 (s, CH). ^{19}F NMR (C_6D_6, 188.146 MHz) δ –78.697.

Synthesis of {[PNP]Pt(pyridine)}OTf. Pyridine (0.4 mL, 0.142 M stock solution in benzene, 0.0568 mmol) was added to a solution of [PNP]PtOTf (50 mg, 0.0568 mmol) in benzene (10 mL) at room temperature. Yellow solid began to precipitate in ca. 2 h. The reaction mixture was stirred at room temperature for 18 h. The yellow solid was collected by filtration and dried in vacuo; yield 52 mg (95.4%). Crystals suitable for X-ray diffraction analysis were grown from a concentrated toluene/acetone (ca. 10:1) solution at room

temperature. ^{1}H NMR ($CDCl_3$, 499.767 MHz) δ 8.067 (m, 2, Ar), 7.877 (t, 1, Ar), 7.764 (m, 2, Ar), 7.567 (m, 4, Ar), 7.498 (t, 8, Ar), 7.438 (m, 8, Ar), 7.250 (m, 6, Ar), 6.719 (t, 2, Ar). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125.678 MHz) δ 162.242 (t, J_{CP} = 10.6 Hz, C), 152.014 (s, CH), 140.146 (s, CH), 134.569 (s, CH), 132.899 (s, CH), 132.593 (t, J_{CP} = 6.7 Hz, CH), 132.251 (s, CH), 129.779 (t, J_{CP} = 5.3 Hz, CH), 127.665 (s, CH), 127.235 (t, J_{CP} = 28.8 Hz, C), 120.003 (t, J_{CP} = 4.4 Hz, CH), 119.049 (t, J_{CP} = 28.8 Hz, C), 117.343 (t, J_{CP} = 5.8 Hz, CH). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 202.310 MHz) δ 28.924 ($^{1}J_{PPt}$ = 2660 Hz). $^{31}P\{^{1}H\}$ NMR (acetone, 80.953 MHz) δ 29.028 ($^{1}J_{PPt}$ = 2657 Hz). ^{19}F NMR (acetone, 188.151 MHz) δ –79.633.

Synthesis of [PNP]PtPh. Method 1: From cis-$PtPh_2(SMe_2)_2$. The platinum diphenyl complex, cis-$PtPh_2(SMe_2)_2$, was prepared in situ as follows. A finely ground solid of $PtCl_2(SMe_2)_2$ (72.59 mg, 0.186 mmol, cis/trans ratio ca. 1:2) was suspended in THF (3 mL) and chilled to –35 °C. To this cold, yellow suspension was added dropwise a solution of phenyl lithium (0.24 mL, 2 M in cyclohexane/ ether solution, Acros, 0.48 mmol, 2.55 equiv). After being stirred at room temperature for 5 h, the reaction was quenched by addition of one drop of distilled water and stripped to dryness in vacuo. The residue was redissolved in THF (3 mL) and cooled to –35 °C. A colorless solution of H[PNP] (100 mg, 0.186 mmol) in THF (3 mL) at –35 °C was added. The reaction mixture was stirred at room temperature for 18 h and stripped to dryness in vacuo. The residue thus obtained was extracted with diethyl ether (2 mL x 5) and filtered through a pad of Celite. The solvent was removed in vacuo to afford the product as a yellow solid; yield 71.6 mg (48%). **Method 2: From [PNP]PtCl.** To a THF solution (0.7 mL) of [PNP]PtCl (10 mg, 0.013 mmol) was added PhMgCl (0.06 mL, 0.205 M stock solution in THF, 0.012 mmol) at room temperature. The reaction solution was transferred to a Teflon-capped NMR tube and the reaction was monitored by $^{31}P\{^{1}H\}$ NMR spectroscopy, which showed complete conversion of [PNP]PtCl to [PNP]PtPh in 37 h. **Method 3: From [PNP]PtMe.** A Teflon-capped J. Young tube was charged with a benzene solution (0.5 mL) of [PNP]PtMe (3.0 mg, 0.004 mmol) and $B(C_6F_5)_3$ (2.0 mg, 0.004 mmol, 1 equiv) at room temperature. The reaction was monitored by $^{31}P\{^{1}H\}$ NMR spectroscopy which indicated quantitative formation of [PNP]PtPh in 31 h. **Method 4: From [PNP]PtOTf.** A Teflon-capped J. Young tube was charged with a benzene solution (0.5 mL) of [PNP]PtOTf (3.0 mg, 0.003 mmol) and DABCO (0.04 mL, 0.085 M in C_6H_6, 0.003 mmol) and immersed to a prescribed oil bath at 150 °C. The reaction was monitored by $^{31}P\{^{1}H\}$ NMR spectroscopy which indicated quantitative formation of [PNP]PtPh in 2.5 h. ^{1}H NMR (499.767 MHz, C_6D_6) δ 8.058 (m, 2, Ar), 7.509 (m, 7, Ar), 7.395 (d, 2, Ar), 7.107 (m, 2, Ar), 7.026 (t, 2, Ar), 6.932 (m, 14, Ar), 6.821 (t, 2, Ar), 6.452 (t, 2, Ar). $^{31}P\{^{1}H\}$ NMR (C_6D_6, 202.310 MHz) δ 27.897 ($^{1}J_{PPt}$ = 2967Hz). $^{31}P\{^{1}H\}$ NMR (diethyl ether, 80.953 MHz) δ 28.010 ($^{1}J_{PPt}$ = 2967Hz). $^{31}P\{^{1}H\}$ NMR (THF, 121.415 MHz) δ 27.850 ($^{1}J_{PPt}$ = 2979Hz). $^{31}P\{^{1}H\}$ NMR ($CHCl_3$, 80.953 MHz) δ 27.420 ($^{1}J_{PPt}$ = 2945Hz). $^{13}C\{^{1}H\}$ NMR (C_6D_6, 125.677 MHz) δ 163.272 (t, J_{CP} = 10.49 Hz, C), 139.431 (t, J_{CP} = 8.17 Hz, C), 138.686 (t, J_{CP} = 2.70 Hz, CH), 136.906 (s, CH), 134.156 (t, J_{CP} = 6.41 Hz, CH), 132.506 (s, CH), 131.602 (t, J_{CP} = 28.15 Hz, C), 130.719 (s, CH), 128.975 (t, J_{CP} = 5.47 Hz, CH), 127.738 (s, CH), 124.004 (t, J_{CP} = 28.41 Hz, C), 122.622 (s, CH), 118.151 (t, J_{CP} = 4.08 Hz, CH), 117.442 (t, J_{CP} = 5.03 Hz, CH). Anal. Calcd. for $C_{42}H_{33}NP_2Pt$: C, 62.37; H, 4.11; N, 1.73. Found: C, 62.75; H, 4.39; N, 1.62.

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