Supporting Information

Frustrated Lewis Pair-Like Splitting of Aromatic C-H bonds and Abstraction of Halogen Atoms by a Cationic [(^F_PNP)Pt]^+ Species

Jessica C. DeMott, Nattamai Bhuvanesh and Oleg V. Ozerov*

Department of Chemistry, Texas A&M University, 3255 TAMU, College Station, TX 77842.

ozarov@chem.tamu.edu
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. General considerations</td>
<td>S3</td>
</tr>
<tr>
<td>II. Synthetic methods and characterization</td>
<td>S5</td>
</tr>
<tr>
<td>A. Syntheses of starting and auxiliary materials.</td>
<td>S5</td>
</tr>
<tr>
<td>B. Syntheses of neutral (PNP)Pt-R complexes from (PNP)PtCl.</td>
<td>S18</td>
</tr>
<tr>
<td>C. C-H Activation of arenes with 1/NEt3.</td>
<td>S28</td>
</tr>
<tr>
<td>D. Reactions of 1 with K-BARF in arene solvents.</td>
<td>S29</td>
</tr>
<tr>
<td>E. Syntheses of [(PN(H)P)Pt-R]+ by protonation of (PNP)Pt-R.</td>
<td>S48</td>
</tr>
<tr>
<td>F. Syntheses of (PNP)Pt-R by deprotonation of [(PN(H)P)Pt-R]+.</td>
<td>S56</td>
</tr>
<tr>
<td>G. Activation of dichloromethane.</td>
<td>S61</td>
</tr>
<tr>
<td>H. Crossover and competition studies.</td>
<td>S63</td>
</tr>
<tr>
<td>I. Probing the interconversion of isomers of tolyl isomers 3b-d.</td>
<td>S66</td>
</tr>
<tr>
<td>III. DFT Studies</td>
<td>S70</td>
</tr>
<tr>
<td>IV. Details of X-Ray diffractometry studies.</td>
<td>S73</td>
</tr>
<tr>
<td>V. Supporting information references</td>
<td>S78</td>
</tr>
</tbody>
</table>
I. General considerations.

Unless otherwise noted, all manipulations and reactions were performed under argon, using standard glovebox and Schlenk line techniques. Toluene, triethylamine, pentane, C<sub>6</sub>H<sub>6</sub> and C<sub>6</sub>D<sub>6</sub> were dried over NaK/Ph<sub>2</sub>CO/18-crown-6, distilled and stored over molecular sieves in an Ar-filled glovebox. Diethyl ether was dried and deoxygenated (by purging) using a solvent purification system and stored over molecular sieves in an Ar-filled glovebox. Fluorobenzene, 1,4-dioxane, acetonitrile, chlorobenzene, bromobenzene, CH<sub>2</sub>Cl<sub>2</sub> and CD<sub>2</sub>Cl<sub>2</sub> were dried over CaH<sub>2</sub>, distilled or vacuum transferred and stored over molecular sieves in an Ar-filled glovebox. 2-Bromotoluene, 3-bromotoluene and 4-bromotoluene were degassed and stored over molecular sieves in an Ar-filled glovebox. Triflic acid (HOTf) was vacuum transferred before use. Potassium tetrakis(pentafluorophenyl)borate (K-BARF) was dried under vacuum overnight at ambient temperature and stored in an Ar-filled glovebox. (FPNP)PtCl, (FPNP)PtH and (FPNP)PtMe were prepared according to literature procedures. All other chemicals were used as received from commercial vendors. NMR spectra were recorded on a Varian iNova 300 (H NMR, 299.951 MHz; C NMR, 75.426 MHz; P NMR, 121.422 MHz; F NMR, 282.211 MHz), a Varian NMRS 500 (H NMR, 499.682 MHz; C NMR, 125.660 MHz; P NMR, 202.265 MHz; F NMR, 470.111 MHz) or a Varian iNova 400 (H NMR, 399.532 MHz; C NMR, 100.473 MHz). Chemical shifts are reported in δ (ppm). For H and C NMR, the residual solvent peak was used to reference the spectra. H NMR spectra in C<sub>6</sub>D<sub>5</sub>Br were referenced by setting the most downfield signal to 7.30 ppm. C{H} NMR spectra in C<sub>6</sub>D<sub>5</sub>Br were referenced by setting the most downfield signal to 130.9 ppm. F NMR signals (-134.3, -164.8, -168.7 ppm) and C{H} NMR signals (149.5, 147.6, 139.6, 137.6, 135.7, 124.3 ppm) for [BARF]<sup>-</sup> were consistent between spectra and are not included below. P NMR spectra were
referenced using 85% H₃PO₄ at δ 0 ppm. ¹⁹F NMR spectra were referenced using CF₃CO₂H at δ -78.5 ppm. ¹H-¹H COSY experiments were used in the assignment of ¹H NMR signals. Elemental analysis was performed by Complete Analysis Laboratories Inc., Parsippany, NJ, USA. FT-IR spectra were collected using a Bruker ALPHA-P FT-IR spectrometer with a diamond ATR.
II. Synthetic Methods and Characterization.

II-A. Syntheses of starting and auxiliary materials.

(^(P)NP)PtOTf (1). In a 50 mL Teflon screw-capped round-bottomed flask, (^(P)NP)PtH (1.69 g, 2.67 mmol) was dissolved in 20 mL of toluene, forming a clear, yellow solution. MeOTf (332 μL, 2.94 mmol) was added via syringe, and the flask was placed in an oil bath at 110°C for 24 h. During the course of the reaction, a brown solid precipitate formed that is believed to be [(^(P)PN(Me)P)PtH][OTf]. With continued heating, this intermediate loses methane to generate the final product. The resulting orange solution was filtered over Celite, and the volatiles were removed, yielding an oily yellow residue. The residue was redissolved in a minimal amount of toluene and layered with pentane. After recrystallization at -35°C, yellow-orange crystals were collected, washed with cold pentane and dried under vacuum, yielding a yellow solid. Isolated yield: 1.88 g, 90%. 1H NMR (C₆D₆): δ 7.22 (m, 2H, Ar-H), 6.70 (m, 2H, Ar-H), 6.52 (m, 2H, Ar-H), 2.50 (m, 4H, CHMe2), 1.26 (vtd, J_P-H = 8.7 Hz, J_H-H = 7.0 Hz, 12H, CHMe2), 0.90 (vtd, J_P-H = 8.1 Hz, J_H-H = 7.2 Hz, 12H, CHMe2). 13C{¹H} NMR (C₆D₆): δ 160.3 (vt, J_P-C = 9.4 Hz, C_Ar-N), 155.7 (d, J_F-C = 240 Hz, C_Ar-F), 119.0 (m, C_Ar-P), 118.8 (q, J_F-C = 318 Hz, CF₃), 118.4 (d, J_F-C = 23 Hz, C_Ar-H), 118.1 (d, J_F-C = 22 Hz, C_Ar-H), 116.4 (m, C_Ar-H), 25.2 (vt, J_P-C = 15 Hz, CHMe2), 18.1 (CHMe2), 17.5 (CHMe2). 19F NMR (C₆D₆): δ -77.7, -126.9. 31P{¹H} NMR (C₆D₆): δ 45.8 (J_{195Pt-P} = 2,713 Hz).
Figure S1. $^1$H NMR spectrum of 1 in C$_6$D$_6$ at RT measured on a 500 MHz Varian NMRS.
Figure S2. $^{19}$F NMR spectrum of 1 in C$_6$D$_6$ at RT measured on a 300 MHz Varian iNova.
Figure S3. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of 1 in C$_6$D$_6$ at RT measured on a 300 MHz Varian iNova.

(PNP)PtBr (12). In a J. Young NMR tube, 1 (17.9 mg, 0.0229 mmol) was dissolved in C$_6$D$_6$. Me$_3$SiBr (3.0 μL, 0.023 mmol) was added via syringe, and the solution remained clear yellow with full conversion to 12 observed by NMR. $^1$H NMR (C$_6$D$_6$): δ 7.38 (m, 2H, Ar-H), 6.75 (m, 2H, Ar-H), 6.63 (vtd, J$_{P-H}$ = 8.5 Hz, J$_{H-H}$ = 3 Hz, 2H, Ar-H), 2.35 (m, 4H, CHMe$_2$), 1.31 (vtd, J$_{P-H}$ = 8 Hz, J$_{H-H}$ = 7 Hz, 12H, CHMe$_2$), 0.96 (app q (dvt), J = 8 Hz, 12H CHMe$_2$). $^{19}$F NMR (C$_6$D$_6$): δ -128.5. $^{31}\text{P}\{^1\text{H}\}$ NMR (C$_6$D$_6$): δ 40.65 ($J_{195\text{Pt-P}}$ = 2,635 Hz).
Figure S4. $^1$H NMR spectrum of 12 in C$_6$D$_6$ at RT measured on a 300 MHz Varian iNova.

Figure S5. $^{19}$F NMR spectrum of 12 in C$_6$D$_6$ at RT measured on a 300 MHz Varian iNova.
Independent synthesis of \([\text{FPN(H)P}][\text{PtOTf}]\) \([\text{BARF}] (8)\). 1 (26.2 mg, 0.0335 mmol) was dissolved in about 4 mL of pentane and 1 mL of Et₂O, forming a clear yellow solution. \([\text{H(OEt}_2\text{)}][\text{BARF}]\) (24.2 mg, 0.0292 mmol) was added, and a solid immediately precipitated out of the solution. The volatiles were removed, and the pale blue solid was washed 3 times with pentane and then redissolved in CD₂Cl₂. This solution was filtered over Celite into a J. Young NMR tube and characterized by NMR. Please note that 8 is believed to decompose over time in CD₂Cl₂, resulting in the formation of 9. \(^1\text{H}\text{NMR (CD}_2\text{Cl}_2\text{): }\delta 8.31 \text{ (s, J}_{\text{195Pt-H}} = 114\text{Hz, 1H, N-H}), 7.52 \text{ (m, 2H, Ar-H), 7.45-7.35 \text{ (m, 4H, Ar-H), 3.12 \text{ (m, 2H, CHMe}_2\text{), 2.98 \text{ (m, 2H, CHMe}_2\text{), 1.47 \text{ (app q (dvt), J = 8 Hz, 6H, CHMe}_2\text{), 1.45 \text{ (app q (dvt), J = 8 Hz, 6H, CHMe}_2\text{), 1.25 \text{ (app q (dvt), J}}}

Figure S6. \(^{31}\text{P} \{^{1}\text{H}\\} \text{NMR spectrum of 12 in C}_6\text{D}_6 \text{ at RT measured on a 300 MHz Varian iNova.}

= 9 Hz, 6H, CHMe2), 1.24 (app q (dvt), J = 9 Hz, 6H, CHMe2). $^{19}$F NMR (CD2Cl2): δ -77.3, -107.5. $^{31}$P\{H\} NMR (CD2Cl2): δ 47.1 ($J_{195Pt-P} = 2,474$ Hz).

**Independent synthesis of \[(^5PN(H)P)PtCl][BARF]\] (9).** ($^5$PNP)PtCl (32.7 mg, 0.0491 mmol) was dissolved in CD2Cl2 in a J. Young NMR tube, forming a clear yellow solution. [H(OEt2)2][BARF] (41.2 mg, 0.0498) was added, and upon shaking, the solution became a clear, very pale blue. After a few minutes, a small amount of white precipitate was also observed. $^1$H NMR (CD2Cl2): δ 8.01 (s, $J_{195Pt-H} = 86$ Hz, 1H, N-H), 7.44 (m, 2H, Ar-H), 7.40 (m, 2H, Ar-H), 7.36 (m, 2H, Ar-H), 3.05 (m, 2H, CHMe2), 2.88 (m, 2H, CHMe2), 1.50 (vtd, $J_{P-H} = 9$ Hz, $J_{H-H} = 7$ Hz, 6H, CHMe2), 1.42 (vtd, $J_{P-H} = 9$ Hz, $J_{H-H} = 7$ Hz, 6H, CHMe2), 1.33 (vtd, $J_{P-H} = 9$ Hz, $J_{H-H} = 7$ Hz, 6H, CHMe2). $^{19}$F NMR (CD2Cl2): δ -109.4. $^{31}$P\{H\} NMR (CD2Cl2): δ 41.7 ($J_{195Pt-P} = 2,445$ Hz).

![Figure S7. $^1$H NMR spectrum of 9 in CD2Cl2 at RT measured on a 500 MHz Varian NMRS.](image-url)
Figure S8. $^{19}$F NMR spectrum of 9 in CD$_2$Cl$_2$ at RT measured on a 500 MHz Varian NMRS.

Figure S9. $^{31}$P{$^1$H} NMR spectrum of 9 in CD$_2$Cl$_2$ at RT measured on a 500 MHz Varian NMRS.
[(FNP)Pt-NCMe][BARF] (6). 1 (14.6 mg, 0.0187 mmol) and K BARF (13.4 mg, 0.0187 mmol) were added to a J. Young NMR tube. MeCN was added, forming an orange solution containing some undissolved K-BARF. The NMR tube was placed on an NMR tube rotator overnight, after which the $^{19}$F NMR spectrum showed full conversion to the product. The contents were transferred to a 10 mL Schlenk flask, and the volatiles were removed. The resulting oily solid was washed with isooctane and dried, yielding a yellow solid that was somewhat soluble in C$_6$D$_6$. $^1$H NMR (C$_6$D$_6$): $\delta$ 7.06-7.02 (m, 2H, Ar-H), 6.58-6.53 (m, 4H, Ar-H), 1.96 (m, 4H, CHMe$_2$), 1.41 (s, 3H, NCMe), 0.92 (vtd, J$_{P-H}$ = 9 Hz, J$_{H-H}$ = 7 Hz, 12H, CHMe$_2$), 0.76 (vtd, J$_{P-H}$ = 9 Hz, J$_{H-H}$ = 7 Hz, 12H, CHMe$_2$). $^{13}$C {$^1$H} NMR (C$_6$D$_6$): $\delta$ 159.8 (vt, J$_{P-C}$ = 10 Hz, C$_{Ar-N}$), 156.1 (dvt, J$_{F-C}$ = 242 Hz, J$_{P-C}$ = 5 Hz, C$_{Ar-F}$), 137.7 (t, J$_{P-C}$ = 14 Hz), 119.7 (d, J$_{F-C}$ = 23 Hz, C$_{Ar-H}$), 118.0 (d, J$_{F-C}$ = 23 Hz, C$_{Ar-H}$), 116.8 (m), 116.6 (app q, J = 6.4 Hz, C$_{Ar-H}$), 25.3 (vt, J$_{P-C}$ = 16 Hz, CHMe$_2$), 17.6 (CHMe$_2$), 17.2 (CHMe$_2$), 1.29 (NCMe). $^{19}$F NMR (C$_6$D$_6$): $\delta$ -125.1. $^{31}$P {$^1$H} NMR (C$_6$D$_6$): $\delta$ 48.9 (J$_{195P-P}$ = 2,474 Hz).
Figure S10. $^1$H NMR spectrum of 6 in C$_6$D$_6$ at RT measured on a 300 MHz Varian iNova.

Figure S11. $^{19}$F NMR spectrum of 6 in C$_6$D$_6$ at RT measured on a 300 MHz Varian iNova.
**o-Tollylithium.** 2-bromotoluene (173 mg, 1.01 mmol) was transferred to a small vial. About 5 mL of pentane was added, and the solution was chilled to -35°C in a glovebox freezer. nBuLi (310 μL, 2.5 M solution in hexanes, 0.775 mmol) was added via syringe. The solution was allowed to stir at RT overnight, resulting in the formation of a white precipitate. The solvent was decanted off of the solid, and the solid was washed with 3x 3 mL of pentane and then dried under vacuum. The solid was stored at -35°C. For NMR characterization, an aliquot of the solid was transferred to an NMR tube and mixed with a ∼4:1 C₆D₆:Et₂O solution. Isolated yield: 62 mg, 81%. ¹H NMR (C₆D₆/Et₂O): δ 8.19 (m, 1H, Ar-H), 7.32-7.23 (m, 3H, Ar-H), 2.74 (s, 3H, CH₃).

**m-Tollylithium.** 3-bromotoluene (154 mg, 0.901 mmol) was transferred to a small vial. About 5 mL of pentane was added, and the solution was chilled to -35°C in a glovebox freezer. nBuLi (280 μL, 2.5 M solution in hexanes, 0.700 mmol) was added via syringe. The solution was allowed to stir at RT overnight, resulting in the formation of a white precipitate. The solvent was decanted off of the solid, and the solid was washed with 3x 3 mL of pentane and then dried under vacuum. The solid was stored at -35°C. For NMR characterization, an aliquot of the solid was transfered to an NMR tube and mixed with a ∼4:1 C₆D₆:Et₂O solution. Isolated yield: 62 mg, 81%. ¹H NMR (C₆D₆/Et₂O): δ 8.19 (m, 1H, Ar-H), 7.32-7.23 (m, 3H, Ar-H), 2.74 (s, 3H, CH₃).
transferred to an NMR tube and mixed with a ~4:1 C₆D₆:Et₂O solution. Isolated yield: 59.7 mg, 87%. ¹H NMR (C₆D₆/Et₂O): δ 8.04 (br s, 1H, Ar-H), 8.00 (d, J = 6.6 Hz, 1H, Ar-H), 7.18 (overlapping with C₆D₆ signal, 1H, Ar-H), 6.97 (d of multiplets, J = 7.5 Hz, 1H, Ar-H), 2.30 (s, 3H, CH₃).

*p-Tolyllithium.* 4-bromotoluene (208 mg, 1.22 mmol) was transferred to a small vial. About 5 mL of pentane was added, and the solution was chilled to -35°C in a glovebox freezer. nBuLi (370 μL, 2.5 M solution in hexanes, 0.925 mmol) was added via syringe. The solution was allowed to stir at RT overnight, resulting in the formation of a white precipitate. The solvent was decanted off of the solid, and the solid was washed with 3x 3 mL of pentane and then dried under vacuum. The solid was stored at -35°C. For NMR characterization, an aliquot of the solid was transferred to an NMR tube and mixed with a ~4:1 C₆D₆:Et₂O solution. Isolated yield: 77 mg, 85%. ¹H NMR (C₆D₆/Et₂O): δ 8.04 (d, J = 7 Hz, 2H, Ar-H), 7.08 (d, J = 7 Hz, 2H, Ar-H), 2.24 (s, 3H, CH₃).

[H(OEt₂)₂][BARF]. This procedure was modified from the one reported in the literature.² K-BARF (412 mg, 0.574 mmol) was dissolved in approximately 10 mL of dry Et₂O under Ar. A 100 mL Schlenk flask was filled with HCl gas, and the K-BARF solution was transferred into this flask via syringe. The flask was opened to an Ar atmosphere and allowed to stand in an ice bath. After 30 min, the clear colorless supernatant was cannula transferred through a filter away from the precipitated KCl. Washes were also cannula transferred into the final vessel containing the product solution. The volatiles were removed, and the flask was transferred into a glovebox. The resulting white solid was collected, dried under vacuum and stored at -35°C. Isolated yield: 378 mg, 79.5%. ¹H NMR (CD₂Cl₂): δ 16.4 (br s, 1H, Et₂O-H), 4.06 (br s, 8H, CH₂), 1.42 (t, J = 6.5 Hz, 12H, CH₃).
II-B. Syntheses of neutral (PNP)Pt-R complexes from (PNP)PtCl.

("^F\text{FPNP}\)PtC_6H_5 (2a). ("^F\text{FPNP}\)PtCl (40.7 mg, 0.0610 mmol) was dissolved in C_6D_6 in a J. Young NMR tube. PhLi (41 μL, 1.8 M solution in Et_2O, 0.077 mmol) was added via syringe. After 10 min, the \textsuperscript{19}F NMR spectrum showed full conversion to the product. The solution was filtered over a pad of Celite and silica gel and washed through with toluene. The volatiles were then removed, and the resulting yellow solid was redissolved in C_6D_6 for characterization. Isolated yield: 35 mg, 82%. \textsuperscript{1}H NMR (C_6D_6): \(\delta 7.64 (dd, J = 7.6 \text{ Hz, } 1.9 \text{ Hz, } J_{195\text{Pt-H}} = 54 \text{ Hz, } 2\text{H, o-Ph-H}), 7.55 (m, 2\text{H, Ar-H}), 7.14 (m, 2\text{H, } m\text{-Ph-H}), 6.98 (td, J = 7.6 \text{ Hz, } 1.9 \text{ Hz, } 1\text{H, } p\text{-Ph-H}), 6.75 (m, 4\text{H, Ar-H}), 2.08 (m, 4\text{H, CHMe}_2), 0.90-0.83 (m, 24\text{H, CHMe}_2). \textsuperscript{13}C \{\textsuperscript{1}H\} NMR (C_6D_6): \(\delta 160.7 \text{ (vt, } J_{P\cdot C} = 9 \text{ Hz, } C_{\text{Ar-N}}), 154.5 \text{ (dvt, } J_{F\cdot C} = 236 \text{ Hz, } J_{P\cdot C} = 5 \text{ Hz, } C_{\text{Ar-F}}), 139.5 \text{ (t, } J_{P\cdot C} = 2.3 \text{ Hz, } J_{195\text{Pt-C}} = 28 \text{ Hz}), 136.9 \text{ (t, } J_{P\cdot C} = 9 \text{ Hz), 127.9 (overlapping with } C_6D_6 \text{ signal), 122.1 (t, } J_{P\cdot C} = 1.3 \text{ Hz), 121.4 (vtd, } J_{P\cdot C} = 21 \text{ Hz, } J_{F\cdot C} = 4.5 \text{ Hz, } C_{\text{Ar-P}}), 118.6 \text{ (d, } J_{F\cdot C} = 21 \text{ Hz, } C_{\text{Ar-H}}), 118.2 \text{ (d, } J_{F\cdot C} = 22 \text{ Hz, } C_{\text{Ar-H}}), 115.2 \text{ (app q, } J = 6 \text{ Hz, } C_{\text{Ar-H}}), 24.1 \text{ (vt, } J_{P\cdot C} = 15 \text{ Hz, } \text{CHMe}_2), 17.7 \text{ (CHMe}_2), 17.0 \text{ (CHMe}_2). \textsuperscript{19}F NMR (C_6D_6): \(\delta -130.5. \textsuperscript{31}P \{\textsuperscript{1}H\} NMR (C_6D_6): \(\delta 40.1 \text{ (} J_{195\text{Pt-P}} = 2,848 \text{ Hz).} \)
Figure S13. $^1$H NMR spectrum of 2a in C$_6$D$_6$ at RT measured on a 500 MHz Varian NMRS.
Figure S14. $^{19}$F NMR spectrum of 2a in C$_6$D$_6$ at RT measured on a 500 MHz Varian NMRS.

Figure S15. $^{31}$P{$^1$H} NMR spectrum of 2a in C$_6$D$_6$ at RT measured on a 500 MHz Varian NMRS.
(FPNP)Pt-o-C₆H₄Me (2b). (FPNP)PtCl (52.2 mg, 0.0783 mmol) and o-tollyllithium (9.8 mg, 0.10 mmol) were combined in a 10 mL Schlenk flask and stirred overnight in about 4 mL of toluene. The solution was then filtered over a pad of Celite and silica gel, the volatiles were removed and the resulting oily yellow solid was redissolved in pentane. The solution was filtered a second time over Celite and silica gel and eluted with pentane. The resulting pale blue solid was recrystallized from pentane at -35°C, washed with cold pentane and dried under vacuum. Isolated yield: 32 mg, 57%. ¹H NMR (C₆D₆): δ 7.65 (m, J₁₉⁵Pt-H = 52.9 Hz, 1H, ortho C-H of C₆H₄Me), 7.48 (dquint, J = 9.2 Hz, 2.3 Hz, 2H, Ar-H), 7.13 (m, 1H, meta C-H of C₆H₄Me), 7.03 (m, 2H, meta and para C-H of C₆H₄Me), 6.73 (m, 4H, Ar-H), 2.68 (s, 3H, C₆H₄Me), 2.06 (m, 4H, CHMe₂), 0.83 (m, 24H, CHMe₂). ¹³C{¹H} NMR (C₆D₆): δ 160.2 (vt, Jₚ-C = 9 Hz, CAr-N), 154.5 (dvt, JF-C = 236 Hz, Jₚ-C = 5 Hz, CAr-F), 143.4 (t, Jₚ-C = 2.3 Hz), 138.8 (t, Jₚ-C = 2.4 Hz), 136.5, 125.0 (J₁₉⁵Pt-C = 55 Hz), 122.5, 121.5 (vt, Jₚ-C = 22 Hz, CAr-P), 118.4 (d, Jₚ-C = 22 Hz, CAr-H), 118.3 (d, Jₚ-C = 22 Hz, CAr-H), 115.2 (app q, J = 6 Hz, CAr-H), 28.0 (C₆H₄CH₃), 24.9 (vt, Jₚ-C = 15 Hz, CHMe₂), 23.4 (vt, Jₚ-C = 15 Hz, CHMe₂), 17.37 (CHMe₂), 17.35 (CHMe₂), 17.0 (CHMe₂), 16.5 (CHMe₂). ¹⁹F NMR (C₆D₆): δ -130.5. ³¹P{¹H} NMR (C₆D₆): δ 40.3 (J₁₉⁵Pt-P = 2,901 Hz).
Figure S16. $^1$H NMR spectrum of 2b in C$_6$D$_6$ at RT measured on a 300 MHz Varian iNova.

($^{5}$PNP)Pt-m-C$_6$H$_4$Me (2c). ($^{5}$PNP)PtCl (50.2 mg, 0.075 mmol) and m-tollyllithium (9.0 mg, 0.10 mmol) were combined in a 10 mL Schlenk flask and stirred overnight in about 4 mL of toluene. The solution was then filtered over a pad of Celite and silica gel, the volatiles were removed and the resulting oily yellow solid was redissolved in pentane. The solution was filtered a second time over Celite and silica gel and eluted with pentane. The resulting pale blue solid was recrystallized from pentane at -35°C, washed with cold pentane and dried under vacuum. Isolated yield: 36 mg, 66%. $^1$H NMR (C$_6$D$_6$): $\delta$ 7.57 (br s, $J_{195Pt-H} = 54.6$ Hz, 1H, C-H ortho to Pt and Me), 7.56 (m, 2H, Ar-H), 7.48 (d, $J = 7.4$ Hz, $J_{195Pt-H} = 53.6$ Hz, 1H, C-H ortho to Pt, para to Me), 7.10 (t, $J = 7.4$ Hz, 1H, meta C-H of C$_6$H$_4$Me), 6.82 (d, $J = 7.4$ Hz, 1H, para C-H of C$_6$H$_4$Me), 6.76 (m, 4H, Ar-H), 2.31 (s, 3H, C$_6$H$_4$Me), 2.11 (m, 4H, CHMe$_2$), 0.89 (m, 24H,
CHMe₂).¹³C{¹H} NMR (C₆D₆): δ 160.7 (vt, Jₚ-C = 10 Hz, Cₐr-N), 154.5 (dvt, Jₚ-C = 231 Hz, Jₚ-C = 5 Hz, Cₐr-F), 140.3 (t, Jₚ-C = 2.5 Hz), 136.7 (t, Jₚ-C = 9 Hz), 136.6 (t, Jₚ-C = 2.4 Hz), 136.4, 123.0, 121.5 (vtd, Jₚ-C = 22 Hz, Jₚ-C = 4 Hz, Cₐr-P), 118.7 (d, Jₚ-C = 22 Hz, Cₐr-H), 118.3 (d, Jₚ-C = 22 Hz, Cₐr-H), 115.2 (app q, J = 6 Hz, Cₐr-H), 24.2 (vt, Jₚ-C = 16 Hz, CHMe₂), 22.7 (C₆H₅CH₃), 17.8 (CHMe₂), 17.0 (CHMe₂).¹⁹F NMR (C₆D₆): δ -130.3.³¹P{¹H} NMR (C₆D₆): δ 40.0 (J₁₉₅Pt-P = 2,855 Hz).

Figure S17. ¹H NMR spectrum of 2c in C₆D₆ at RT measured on a 500 MHz Varian NMRS.

(℉PNP)Pt-p-C₆H₄Me (2d). (℉PNP)PtCl (118 mg, 0.177 mmol) and p-tolylithium (19.5 mg, 0.199 mmol) were combined in a 25 mL Schlenk flask and stirred overnight in about 7 mL of toluene. The solution was then filtered over a pad of Celite and silica gel, the volatiles were removed and the resulting oily yellow solid was redissolved in pentane. The solution was filtered
a second time over Celite and silica gel and eluted with pentane. The resulting pale blue solid was recrystallized from pentane at -35°C, washed with cold pentane and dried under vacuum. Isolated yield: 94 mg, 72%. $^1$H NMR (C$_6$D$_6$): $\delta$ 7.56 (m, $J_{195\text{Pt-H}} = 51.9$ Hz, 4H, ortho C-H of C$_6$H$_4$Me and Ar-H), 7.04 (d, $J = 7.6$ Hz, 2H, meta C-H of C$_6$H$_4$Me), 6.76 (m, 4H, Ar-H), 2.27 (s, 3H, C$_6$H$_4$Me), 2.10 (m, 4H, CHMe$_2$), 0.88 (m, 24H, CHMe$_2$). $^{13}$C{$^1$H} NMR (C$_6$D$_6$): $\delta$ 160.8 (vt, $J_{\text{P-C}} = 8.8$ Hz, C$_{\text{Ar-N}}$), 154.5 (dvt, $J_{\text{F-C}} = 237$ Hz, $J_{\text{P-C}} = 5$ Hz, C$_{\text{Ar-F}}$), 139.2 (t, $J_{\text{P-C}} = 9.3$ Hz, $J_{195\text{Pt-C}} = 30$ Hz), 132.0 (t, $J_{\text{P-C}} = 9$ Hz), 130.5 (t, $J_{\text{P-C}} = 1.5$ Hz), 129.0 ($J_{195\text{Pt-C}} = 60$ Hz, C$_{\text{Ar-Pt}}$), 121.6 (vtd, $J_{\text{P-C}} = 22.4$ Hz, $J_{\text{F-C}} = 4$ Hz, C$_{\text{Ar-P}}$), 118.7 (d, $J_{\text{F-C}} = 21$ Hz, C$_{\text{Ar-H}}$), 118.3 (d, $J_{\text{F-C}} = 23$ Hz, C$_{\text{Ar-H}}$), 115.2 (app q, $J = 6$ Hz, C$_{\text{Ar-H}}$), 24.2 (vt, $J_{\text{P-C}} = 15.4$ Hz, CHMe$_2$), 21.2 (C$_6$H$_4$CH$_3$), 17.8 (CHMe$_2$), 17.0 (CHMe$_2$). $^{19}$F NMR (C$_6$D$_6$): $\delta$ -130.6. $^{31}$P{$^1$H} NMR (C$_6$D$_6$): $\delta$ 40.0 ($J_{195\text{Pt-P}} = 2,853$ Hz).
Figure S18. $^1$H NMR spectrum of 2d in C$_6$D$_6$ at RT measured on a 500 MHz Varian NMRS.

$(^{2}$PNP)PtCH$_2$C$_6$H$_5$ (2g). $(^{2}$PNP)PtCl (40.8 mg, 0.0612 mmol) was dissolved in C$_6$D$_6$ in a J. Young NMR tube, producing a clear yellow solution. About 0.5 mL of dioxane was added, followed by BnMgCl (73 μL, 1.0 M solution in Et$_2$O, 0.073 mmol). A white precipitate was immediately generated. The NMR tube was covered with Al foil and placed on an NMR tube rotator for 16 h, after which the $^{19}$F NMR spectrum showed full conversion to the product. The solution was filtered through a pad of Celite and silica gel, yielding a clear yellow solution. The volatiles were removed, and the product was recrystallized from pentane at -35°C. The resulting yellow solid was collected and dried under vacuum. Isolated yield: 18.6 mg, 42.1%. $^1$H NMR (C$_6$D$_6$): δ 7.52 (t, J = 9 Hz, 2H, Ar-H), 7.49 (d, J = 7.5 Hz, 2H, Ar-H), 7.17 (t, J = 7.6 Hz, 2H, Ar-H), 6.97 (t, J = 7.5 Hz, 1H, CH$_2$C$_6$H$_5$), 6.81 (m, 2H, CH$_2$C$_6$H$_5$), 6.73 (m, 2H, CH$_2$C$_6$H$_5$), 3.32
(t, $J_{P,H} = 6$ Hz, $J_{195Pt-H} = 95$ Hz, 2H, $CH_2C_6H_5$), 1.94 (m, 4H, $CHMe_2$), 1.02 (app q (dvt), J = 8 Hz, 12H, $CHMe_2$), 0.90 (app q (dvt), J = 7.7 Hz, 12H, $CHMe_2$). $^{13}$C ($^1$H) NMR (C$_6$D$_6$): δ 160.3 (vt, $J_{P,C} = 10$ Hz, $C_{Ar-N}$), 154.5 (dvt, $J_{F,C} = 236$ Hz, $J_{P,C} = 5$ Hz, $C_{Ar-F}$), 152.5 (t, $J_{P,C} = 2$ Hz, $J_{195Pt-C} = 39$ Hz), 130.6 ($J_{195Pt-C} = 46$ Hz), 127.6, 123.6, 121.9 (vtd, $J_{P,C} = 23$ Hz, $J_{F,C} = 5$ Hz, $C_{Ar-P}$), 118.2 (d, $J_{F,C} = 11$ Hz, $C_{Ar-H}$), 117.9 (d, $J_{F,C} = 22$ Hz, $C_{Ar-H}$), 115.3 (app q, J = 6 Hz, $C_{Ar-H}$), 24.9 (vt, $J_{P,C} = 15$ Hz, $CHMe_2$), 18.3 ($CHMe_2$), 17.6 ($CHMe_2$), -3.4 (t, $J_{P,C} = 6$ Hz, $J_{195Pt-C} = 602$ Hz, $CH_2C_6H_5$). $^{19}$F NMR (C$_6$D$_6$): δ -130.6. $^{31}$P ($^1$H) NMR (C$_6$D$_6$): δ 38.7 ($J_{195Pt-P} = 2,910$ Hz).

Figure S19. $^1$H NMR spectrum of 2g in C$_6$D$_6$ at RT measured on a 500 MHz Varian NMRS.
**Figure S20.** $^{19}$F NMR spectrum of 2g in C$_6$D$_6$ at RT measured on a 500 MHz Varian NMRS.

**Figure S21.** $^{31}$P{$^1$H} NMR spectrum of 2g in C$_6$D$_6$ at RT measured on a 500 MHz Varian NMRS.
II-C. C-H Activation of arenes with 1/NEt₃.

1 plus NEt₃ in C₆D₆. 1 (22.0 mg, 0.0280 mmol) was transferred to a J. Young NMR tube and dissolved in toluene, forming a clear, yellow solution. NEt₃ (5.0 μL, 0.036 mmol) was added via syringe, and the NMR tube was placed in an oil bath at 115°C. The reaction was monitored by ¹⁹F NMR. After 2 weeks, about 17% of the original (¹⁵PNP)PtOTf remained, with approximately 79% conversion of the total starting material to (¹⁵PNP)PtC₆D₅ (2a-D) and 4% conversion to (¹⁵PNP)PtH.

1 plus NEt₃ in toluene. 1 (23.0 mg, 0.0294 mmol) was transferred to a J. Young NMR tube and dissolved in toluene, forming a clear, yellow solution. NEt₃ (5.0 μL, 0.036 mmol) was added via syringe, and the NMR tube was placed in an oil bath at 115°C. The reaction was monitored by ¹⁹F NMR. After 7 days, the complete disappearance of (¹⁵PNP)PtOTf was noted, with about 90% conversion to (¹⁵PNP)PtC₆H₄Me (2b-d) and 10% conversion to (¹⁵PNP)PtH. The volatiles were removed, and the residual solid was redissolved in C₆D₆, filtered over Celite and silica gel and characterized by NMR. The ¹H NMR spectrum showed an 2b:2c:2d tolyl isomeric ratio of approximately 1%:68%:31%.
II-D. Reactions of 1 with K-BARF in arene solvents.

\[ ([\text{FPN(H)P})\text{PtC_6H_5}][\text{BARF}] \text{ (3a). 1 (18.1 mg, 0.0232 mmol) and K-BARF (17.1 mg, 0.0238 mmol) were added to a 5 mL round-bottomed Teflon screw-capped flask. C_6H_6 (2 mL) was added, forming an orange solution containing some undissolved K-BARF. The solution was left to stir at RT. After 24 h, the solution had become a brownish green, and after 4 days, the solution had become a pale green. The complete disappearance of starting material was confirmed by }^{19}\text{F NMR. The volatiles were removed, yielding a pale blue-green solid. The solid was washed with pentane, dried, extracted with CD_2Cl_2 and filtered through a pad of Celite into a J. Young NMR tube for characterization. }^{1}\text{H NMR (CD_2Cl_2): } \delta \text{ 7.52 and 7.51 (overlapping br signals, 2H, Ar-H), 7.38 (td, } J = 8.4 \text{ Hz, 3 Hz, 2H, o-Ph-H, }^{195}\text{Pt coupling buried), 7.36 (t, } J = 7.5 \text{ Hz, 2H, Ar-H), 7.35 (d, } J = 7.5 \text{ Hz, 2H, Ar-H), 7.26 (br s, } J_{195\text{Pt-H}} = 37 \text{ Hz, 1H, N-H), 7.05 (t, } J = 7.8 \text{ Hz, 2H, m-Ph-H), 6.94 (t, } J = 7.2 \text{ Hz, 1H, p-Ph-H), 2.81 (m, 2H, CHMe_2), 2.68 (m, 2H, CHMe_2), 1.20 (m, 12H, CHMe_2), 1.07 (vtd, } J_{\text{P-H}} = 9 \text{ Hz, } J_{\text{H-H}} = 7.5 \text{ Hz, 6H, CHMe_2), 0.88 (vtd, } J_{\text{P-H}} = 9 \text{ Hz, } J_{\text{H-H}} = 7.3 \text{ Hz, 6H, CHMe_2). }^{19}\text{F NMR (CD_2Cl_2): } \delta -111.7. }^{31}\text{P}\{^{1}\text{H}\} \text{ NMR (CD_2Cl_2): } \delta 41.3 (J_{195\text{Pt-P}} = 2,819 \text{ Hz). IR (solid): 3240 cm}^{-1} \text{ (N-H).} \]
Figure S22. $^1$H NMR spectrum of 3a in CD$_2$Cl$_2$ at RT measured on a 400 MHz Varian iNova.

[(FPN(D)P)PtC$_6$D$_5$][BARF] (3a-D). 1 (100 mg, 0.128 mmol) and K-BARF (93.0 mg, 0.130 mmol) were added to a round-bottomed Teflon screw-capped flask. About 3 mL of C$_6$D$_6$ was added, forming an orange solution containing some undissolved K-BARF. The flask was then placed in an oil bath at 80°C. After 2 h, the solution had a cloudy orange appearance, and after 16 h, the reaction became a cloudy green. Conversion to the product was confirmed by NMR. The solution was filtered over a pad of Celite and rinsed through with CH$_2$Cl$_2$. The volatiles were removed under vacuum, yielding a pale green solid that was recrystallized from a CH$_2$Cl$_2$ solution layered with pentane at -35°C. The crystals were collected, washed with pentane and dried under vacuum, yielding a pale blue solid. Conversion to the final product was also
achieved by performing this reaction at RT for 4 days. Isolated yield: 111 mg, 61%. $^1$H NMR (CD$_2$Cl$_2$): $\delta$ 7.52 and 7.51 (overlapping br signals, 2H, Ar-H), 7.36 (t, J = 7.5 Hz, 2H, Ar-H), 7.35 (d, J = 7.5 Hz, 2H, Ar-H), 2.81 (m, 2H, CHMe$_2$), 2.68 (m, 2H, CHMe$_2$), 1.23 (m, 12H, CHMe$_2$), 1.07 (app q (dvt), J = 8 Hz, 6H, CHMe$_2$), 0.88 (app q (dvt), J = 8 Hz, 6H, CHMe$_2$). $^{13}$C($^1$H) NMR (CD$_2$Cl$_2$): $\delta$ 162.4 (dvt, $J_{F-C}$ = 256 Hz, $J_{P-C}$ = 4 Hz, C$_{Ar}$-F), 144.6 (vtd, $J_{P-C}$ = 7 Hz, $J_{F-C}$ = 3 Hz, C$_{Ar}$-N), 136.2 (overlapping with BARF signal), 132.3 (vtd, $J_{P-C}$ = 18 Hz, $J_{F-C}$ = 6 Hz, C$_{Ar}$-P), 128.4 (br s), 126.1, 124.5 (t, $J_{P-C}$ = 8 Hz), 121.5 (d, $J_{F-C}$ = 23 Hz, C$_{Ar}$-H), 120.0 (d, $J_{F-C}$ = 23 Hz, C$_{Ar}$-H), 26.5 (vt, $J_{P-C}$ = 14 Hz, CHMe$_2$), 23.6 (vt, $J_{P-C}$ = 15 Hz, CHMe$_2$), 18.0 (CHMe$_2$), 17.8 (CHMe$_2$), 17.6 (CHMe$_2$), 16.9 (CHMe$_2$). $^{19}$F NMR (CD$_2$Cl$_2$): $\delta$ -111.7. $^{31}$P($^1$H) NMR (CD$_2$Cl$_2$): $\delta$ 41.2 ($J_{195Pt-P}$ = 2,820 Hz). Elemental analysis, found (calculated) for C$_{54}$H$_{34}$D$_6$BF$_{22}$NP$_2$Pt: C, 46.25 (46.50); H, 2.09 (2.34). IR (solid): 2405 cm$^{-1}$ (N-D).
Figure S23. $^1$H NMR spectrum of 3a-D in CD$_2$Cl$_2$ at RT measured on a 500 MHz Varian NMRS.
Figure S24. $^{13}$C{$^1$H} NMR spectrum of 3a-D in CD$_2$Cl$_2$ at RT measured on a 500 MHz Varian NMRS.

Figure S25. $^{19}$F NMR spectrum of 3a-D in CD$_2$Cl$_2$ at RT measured on a 500 MHz Varian NMRS.
Figure S26. $^{31}$P{H} NMR spectrum of 3a-D in CD$_2$Cl$_2$ at RT measured on a 500 MHz Varian NMRS.

$[\text{F}(\text{P}(\text{H})\text{P})\text{PtC}_6\text{H}_4\text{Me}][\text{BARF}]$ (3b-d). 1 (107 mg, 0.137 mmol) and K-BARF (98 mg, 0.14 mmol) were added to a 10 mL round-bottomed Teflon screw-capped flask. Approximately 5 mL of C$_6$H$_5$Me was added, forming a yellow solution containing some undissolved K-BARF. The flask was then placed in an oil bath at 80°C. After 2 h, the solution had become cloudy brown, and after 16 h, the solution had become cloudy blue. The solution was then filtered over a pad of Celite and washed through with CH$_2$Cl$_2$. The volatiles were removed under vacuum, yielding an oily blue residue. A minimal amount of CH$_2$Cl$_2$ was used to redissolve the solids, and the solution was layered with pentane. After recrystallization at -35°C, the resulting pale blue solid was washed with pentane and dried under vacuum. Isolated yield: 165 mg, 84%. The ratio of 3b:(3c plus 3d) in the product mixture was approximately 8%:92% (3c and 3d signals overlap). Characterization was achieved by comparing the $^1$H NMR and $^{13}$C{H} NMR spectra of the product mixture to those of the independently synthesized isomers (see below). $^{19}$F NMR (CD$_2$Cl$_2$): δ -111.7. $^{31}$P{H} NMR (CD$_2$Cl$_2$): δ 41.1 (br, J$_{195P-P}$ = 2,840 Hz). Elemental analysis,
found (calculated) for C$_{55}$H$_{41}$BF$_{22}$NP$_2$Pt: C, 47.07 (47.13); H, 3.02 (2.95). IR (solid): 3240 cm$^{-1}$ (N-H).

Figure S27. $^1$H NMR spectrum of the 3b-d product mixture in CD$_2$Cl$_2$ at RT measured on a 500 MHz Varian NMRS.
Figure S28. $^{13}$C$^{1}$H NMR spectrum of the 3b-d product mixture in CD$_2$Cl$_2$ at RT measured on a 500 MHz Varian NMRS.

Figure S29. $^{19}$F NMR spectrum of the 3b-d product mixture in CD$_2$Cl$_2$ at RT measured on a 500 MHz Varian NMRS.
Figure S30. $^{31}$P$^{[1]}$H NMR spectrum of the 3b-d product mixture in CD$_2$Cl$_2$ at RT measured on a 500 MHz Varian NMRS.

$\text{(F}_{5}\text{PN(H)P})\text{PtC}_6\text{H}_4\text{F}\text{][BARF]}$ (3e). 1 (99 mg, 0.13 mmol) and K-BARF (91 mg, 0.13 mmol) were added to a round-bottomed Teflon screw-capped flask. C$_6$H$_5$F was added, forming a yellow solution containing some undissolved K-BARF. The flask was then placed in an oil bath at 80°C. After 2 h, the solution had a pale green appearance. The solution was filtered over a pad of Celite and eluted with CH$_2$Cl$_2$ and C$_6$H$_5$F. The volatiles were removed under vacuum, yielding an oily blue residue along with a white solid. A minimal amount of CH$_2$Cl$_2$ was used to redissolve the solids, and the solution was layered with pentane. The resulting blue crystals were collected and washed with cold pentane. After drying under vacuum, a pale blue solid was collected. Isolated
yield: 120 mg, 71%. ¹H NMR (CD₂Cl₂): δ 7.52 (m, Ar-H overlapping with N-H signal and o-H of minor rotamer), 7.47 (br s, J₁₉₅Pt-H = 40 Hz, N-H, major rotamer), 7.37 (m, Ar-H), 7.26 (ddd, J = 7.4 Hz, 4.5 Hz, 1.1 Hz, J₁₉₅Pt-H = 74 Hz, o-aryl-H, major rotamer), 7.06 (app q, J = 7.3 Hz, m-aryl-H, major rotamer), 7.02 (app q, J = 7.0 Hz, m-aryl-H, minor rotamer), 6.94 (t, J = 7.4 Hz, m-aryl-H, major rotamer), 6.92 (t, J = 7.4 Hz, m-aryl-H, minor rotamer), 6.87 (td, J = 8.2 Hz, 1.3 Hz, p-aryl-H, major rotamer), 6.86 (td, J = 8.2 Hz, 1.3 Hz, p-aryl-H, minor rotamer), 2.83 (m, 2H, CH₂Me₂), 2.71 (m, 2H, CH₂Me₂), 1.18 (m, CH₂Me₂), 1.17 (vtd, J₃₁₉₅Pt-H = 9 Hz, J₁₉₅H-H = 7 Hz, CH₂Me₂), 1.10 (vtd, J₃₁₉₅Pt-H = 9 Hz, J₁₉₅H-H = 7 Hz, CH₂Me₂), 0.89 (vtd, J₃₁₉₅Pt-H = 9 Hz, J₁₉₅H-H = 7 Hz, CH₂Me₂), 0.84 (vtd, J₃₁₉₅Pt-H = 9 Hz, J₁₉₅H-H = 7 Hz, CH₂Me₂). ^¹³C{¹H} NMR (CD₂Cl₂): δ 162.3 (dvt, J₁₉₅C-H = 254 Hz, J₃₁₉₅C-H = 5 Hz, C₁₉₅F), 144.7 (vtd, J₃₁₉₅C-H = 8 Hz, J₁₉₅C-H = 2.5 Hz, C₁₉₅N, major rotamer), 144.4 (vt, J₃₁₉₅C-H = 8 Hz, C₁₉₅N, minor rotamer), 137.4, 131.8 (vtd, J₃₁₉₅C-H = 18 Hz, J₁₉₅C-H = 6 Hz, C₁₉₅P), 126.3 (d, J₁₉₅C-H = 8 Hz), 126.1 (d, J₁₉₅C-H = 8 Hz), 125.9 (m), 125.2, 124.9, 121.6 (d, J₁₉₅C-H = 24 Hz, C₁₉₅H), 121.2, 120.2 (d, J₁₉₅C-H = 23 Hz, C₁₉₅H), 115.4 (d, J₁₉₅C-H = 27 Hz, C₁₉₅H), 114.7 (d, J₁₉₅C-H = 27 Hz, C₁₉₅H), 26.7 (vt, J₃₁₉₅C-H = 15 Hz, CH₂Me₂), 26.0 (vt, J₃₁₉₅C-H = 14 Hz, CH₂Me₂), 24.9 (vt, J₃₁₉₅C-H = 14 Hz, CH₂Me₂), 23.3 (vt, J₃₁₉₅C-H = 15 Hz, CH₂Me₂), 18.1 (CH₂Me₂, major rotamer), 17.9 (CH₂Me₂, minor rotamer), 17.7 (CH₂Me₂, major rotamer), 17.7 (CH₂Me₂, minor rotamer), 17.5 (CH₂Me₂, minor rotamer), 17.3 (CH₂Me₂, major rotamer), 17.1 (CH₂Me₂, minor rotamer), 16.8 (CH₂Me₂, major rotamer). ^¹⁹F NMR (CD₂Cl₂): δ -92.7 (J₁₉₅Pt-F = 390 Hz, major rotamer), -94.7 (J₁₉₅Pt-F = 317 Hz, minor rotamer), -111.3 (major rotamer), -111.4 (minor rotamer). ^³¹P{¹H} NMR (CD₂Cl₂): δ 43.4 (J₁₉₅P-H = 2,716 Hz, minor rotamer), 43.0 (J₁₉₅P-H = 2,700 Hz, major rotamer). Elemental analysis, found (calculated) for C₅₄H₃₉BF₂₃NP₂Pt: C, 46.04 (46.11); H, 2.71 (2.79). IR (solid): 3233 cm⁻¹ (N-H).
Figure S31. $^1$H NMR spectrum of 3e in CD$_2$Cl$_2$ at RT measured on a 500 MHz Varian NMRS.

Figure S32. $^{13}$C{${}^1$H} NMR spectrum of 3e in CD$_2$Cl$_2$ at RT measured on a 500 MHz Varian NMRS.
Figure S33. $^{19}$F NMR spectrum of 3e in CD$_2$Cl$_2$ at RT measured on a 500 MHz Varian NMRS.
**Figure S34.** $^{31}$P{$^1$H} NMR spectrum of 3e in CD$_2$Cl$_2$ at RT measured on a 500 MHz Varian NMRS.

**Table S1.** $^{19}$F NMR VT study monitoring the ortho fluorine resonances of rotamer A and rotamer B for 3e in C$_6$D$_5$Br from -20°C to 120°C.

<table>
<thead>
<tr>
<th>T, (°C)</th>
<th>Integration A</th>
<th>Integration B</th>
</tr>
</thead>
<tbody>
<tr>
<td>-20</td>
<td>1</td>
<td>0.49</td>
</tr>
<tr>
<td>RT</td>
<td>1</td>
<td>0.51</td>
</tr>
<tr>
<td>40</td>
<td>1</td>
<td>0.52</td>
</tr>
<tr>
<td>60</td>
<td>1</td>
<td>0.54</td>
</tr>
<tr>
<td>80</td>
<td>1</td>
<td>0.56</td>
</tr>
<tr>
<td>100</td>
<td>1</td>
<td>0.58</td>
</tr>
<tr>
<td>120</td>
<td>1</td>
<td>0.59</td>
</tr>
</tbody>
</table>
[(FNP(H)P)PtC₆H₄Cl][BARF] (3f). 1 (21.8 mg, 0.0279 mmol) and K-BARF (19 mg, 0.026 mmol) were added to a 10 mL round-bottomed Teflon screw-capped flask. About 5 mL of C₆H₅Cl was added, forming a yellow solution. An aliquot was taken after 15 min, and 2 new signals were observed by ¹⁹F NMR. The signal at -110.8 ppm corresponded to a C-H activation product, and the signal at -122.8 ppm is believed to be indicative of a Pt-chlorobenzene adduct (4). After 1 h at RT, the signal at -122.8 ppm was the major peak. After 48 h at RT, this signal was no longer visible by ¹⁹F NMR, and full conversion to the C-H activation product was observed. The formation of (FNPN)PtCl was not observed upon addition of decamethyl ferrocene (6 mg, 0.02 mmol). Conversion to the C-H activation product could also be achieved by heating the sample overnight at 80°C. [(FNP)Pt-ClC₆H₅][BARF] (4). ¹⁹F NMR (C₆H₅Cl): δ -122.8.

³¹P{¹H} NMR (C₆H₅Cl): δ 48.6 (J₁₉₅Pt-P = 2,515 Hz). [(FPN(H)P)PtC₆H₄Cl][BARF] (3f). ¹H NMR (CD₂Cl₂): δ 7.51 (m, 2H, Ar-H), 7.45 (br s, 1H, N-H, ¹⁹⁵Pt coupling buried), 7.36 (m, 4H, Ar-H), 7.23 (dd, J = 6.7 Hz, 2.5 Hz, 1H, ortho C-H of C₆H₄Cl, ¹⁹⁵Pt coupling buried), 7.19 (dd, J = 6.8 Hz, 2.5 Hz, 1H, meta C-H of C₆H₄Cl), 7.01 (m, 2H, meta and para C-H of C₆H₄Cl), 2.80 (m, 4H, CHMe₂), 1.19 (app q (dvt), J = 8 Hz, 12H, CHMe₂), 1.10 (app q (dvt), J = 8.5 Hz, 6H, CHMe₂), 0.87 (vtd, Jₚ-H = 9.5 Hz, J_H-H = 7.7 Hz, 6H, CHMe₂). ¹³C{¹H} NMR (CD₂Cl₂): δ 162.4 (d, J₁₉₅Pt-C = 233 Hz, C_Ar-F), 144.7, 140.3 (t, J₁₉₅Pt-C = 3 Hz), 138.3 (J₁₉₅Pt-C = 38 Hz), 131.5 (m), 128.9 (J₁₉₅Pt-C = 33 Hz), 127.2 (J₁₉₅Pt-C = 69 Hz), 126.1, 123.9 (t, J₁₉₅Pt-C = 9 Hz), 122.5, 121.5 (d, J₁₉₅Pt-C = 24 Hz, C_Ar-H), 120.2 (d, J₁₉₅Pt-C = 23 Hz, C_Ar-H), 26.9 (vt, J₁₉₅Pt-C = 14.3 Hz, CHMe₂), 23.1 (vt, J₁₉₅Pt-C = 15 Hz, CHMe₂), 18.0 (CHMe₂), 17.4 (CHMe₂), 17.2 (CHMe₂), 16.6 (CHMe₂). ¹⁹F NMR (CD₂Cl₂): δ -111.3. ³¹P{¹H} NMR (CD₂Cl₂): δ 41.5 (J₁₉₅Pt-P = 2,775 Hz). IR (solid): 3235 cm⁻¹ (N-H).
Figure S35. $^1$H NMR spectrum of 3f in CD$_2$Cl$_2$ at RT measured on a 500 MHz Varian NMRS.

Figure S36. $^{13}$C-$^1$H NMR spectrum of 3f in CD$_2$Cl$_2$ at RT measured on a 500 MHz Varian NMRS.
Figure S37. $^{19}$F NMR spectrum of 3f in CD$_2$Cl$_2$ at RT measured on a 500 MHz Varian NMRS.
Activation of bromobenzene and observation of \([\{^6\text{PNP}\}\text{Pt-BrC}_6\text{D}_5][\text{BARF}]\) (10). 1 (21.4 mg, 0.0274 mmol) and K-BARF (19 mg, 0.026 mmol) were transferred to a J. Young NMR tube. C\(_6\)D\(_5\)Br was added, forming a yellow-orange solution. A capillary containing 1-fluoroctane in C\(_6\)D\(_6\) was used to track the conversion of \([^6\text{PNP}]\text{PtOTf}\) to the products. After 2 h, a new signal was observed in the \(^{19}\text{F}\) NMR spectrum at -122.9 ppm, corresponding to what is believed to be \([[^6\text{PNP}]\text{Pt-BrC}_6\text{D}_5][\text{BARF}]\) (10). After a total of 12 h, 1 was no longer observed by NMR. Continued monitoring of the reaction mixture showed no C-H activation products, even after 2 weeks at RT. The addition of MeCN led to the formation of 6. A decrease in the BARF signals relative to the \(^{19}\text{F}\) NMR signals of the ligand was noted after 2 weeks. Reduction of the reaction
mixture with decamethyl ferrocene led to the formation of (FPNP)PtBr (12) (20% conversion).

[(FPNP)Pt-BrC₆D₅][BARF] (10). ¹H NMR (C₆D₅Br): δ 7.24 (br s, 2H, Ar-H), 6.75 (t, J = 8 Hz, 2H, Ar-H), 6.67 (m, 2H, Ar-H), 2.05 (m, 4H, CHMe₂), 0.99 (vtd, Jₚ-H = 9 Hz, Jₚ-H = 8 Hz, 12H, CHMe₂), 0.89 (app q (dvt), J = 7 Hz, 12H, CHMe₂). ¹³C{¹H} NMR (C₆D₅Br): δ 158.3 (vt, Jₚ-C = 10 Hz, Cₐr-N), 156.0 (d, Jₚ-C = 244 Hz, Cₐr-F), 119.6 (d, Jₚ-C = 22.5 Hz, Cₐr-H), 117.2 (d, Jₚ-C = 21.5 Hz, Cₐr-H), 116.4 (m, Cₐr-P), 116.3 (m, Cₐr-H), 25.3 (vt, Jₚ-C = 29 Hz, CHMe₂), 17.5 (CHMe₂), 16.9 (CHMe₂). ¹⁹F NMR (C₆D₅Br): δ -122.9. ³¹P{¹H} NMR (C₆D₅Br): δ 46.9 (J₁⁹Pt-P = 2,490 Hz). (FPNP)PtBr (12). ¹⁹F NMR (C₆D₅Br): -128.5. ³¹P{¹H} NMR (C₆D₅Br): δ 40.8 (J₁⁹Pt-P = 2,623 Hz).

Figure S39. ¹H NMR spectrum of 10 in C₆D₅Br at RT measured on a 300 MHz Varian iNova.
**Figure S40.** $^{19}$F NMR spectrum of 10 in C$_6$D$_5$Br at RT measured on a 300 MHz Varian iNova.

**Figure S41.** $^{31}$P{$^1$H} NMR spectrum of 10 in C$_6$D$_5$Br at RT measured on a 500 MHz Varian NMRS.
II-E. Syntheses of [(PN(H)P)Pt-R]^+ by protonation of (PNP)Pt-R.

[(PN(H)P)Pt-C₆H₅][BARF] (3a). 2a (21 mg, 0.030 mmol) was dissolved in about 3 mL of pentane in a small vial, forming a clear yellow solution. HOTf (15.4 μL, 1.88 M solution in Et₂O, 0.0290 mmol) was added, and a white precipitate immediately crashed out of the solution. The solvent was decanted off, and the solid was washed with 3x 3 mL of pentane, dried under vacuum and then dissolved in 3 mL of CH₂Cl₂. K-BARF (21 mg, 0.029 mmol) was added, and the solution was stirred overnight at RT. The solution was filtered over Celite, the volatiles were removed and the residual oily blue solid was redissolved in CD₂Cl₂ for characterization. The NMR spectra matched those of the compound synthesized via the C-H activation experiment described above.

Protonation of (FPNP)PtC₆H₄Me isomers. The protonated tolyl isomers were independently synthesized to help confirm the characterization of the products from the toluene C-H activation reactions. The neutral (FPNP)PtC₆H₄Me species were reacted with a substoichiometric amount of [H(OEt₂)₂][BARF] (0.9 eq). The mixtures were dissolved in approximately 5 mL of a 3:1 mixture of pentane and diethyl ether and stirred for 30 min. The resulting solids were loaded onto a bed of Celite, rinsed with pentane and diethyl ether and then washed through with CH₂Cl₂. The volatiles were removed and the isolated solids were redissolved in CD₂Cl₂ for characterization.

[(FPN(H)P)Pt-o-C₆H₄Me][BARF] (3b). Isolated yield: 36 mg, 59%. ¹H NMR (CD₂Cl₂): δ 7.49 (m, 2H, Ar-H), 7.37 (m, 2H, Ar-H), 7.32 (m, 2H, Ar-H), 7.27 (br s, J₁₉₅Pt-H = 32.6 Hz, 1H, N-H), 7.21 (d, J = 7.4 Hz, J₁₉₅Pt-H = 66.8 Hz, 1H, o-tolyl-H), 6.99 (d, J = 7.4 Hz, 1H, m-tolyl-H), 6.92 (t, J = 7.2 Hz, 1H, tolyl-H), 6.87 (td, J = 7.4 Hz, 1.3 Hz, 1H, tolyl-H), 2.82 (m, 2H, CHMe₂), 2.68 (m, 2H, CHMe₂), 2.63 (s, 3H, C₆H₄Me), 1.20 (app q (dvt), J = 8 Hz, 6H, CHMe₂), 1.14 (app
q (dvt), J = 8 Hz, 6H, CHMe₂), 1.05 (app q (dvt), J = 8 Hz, 6H, CHMe₂), 0.83 (app q (dvt), J = 8 Hz, 6H, CHMe₂). $^{13}$C$\text{_{1}{H}}$ NMR (CD₂Cl₂): δ 162.3 (d, $J_{F-C} = 257$ Hz, CAr-F), 144.5, 141.2 (t, $JP-C = 2.3$ Hz), 136.1 (t, $JP-C = 2.4$ Hz, $J_{195Pt-C} = 42$ Hz), 131.7 (m), 129.5 ($J_{195Pt-C} = 40$ Hz), 126.2 (br s), 126.1 ($J_{195Pt-C} = 66$ Hz), 124.5, 124.4, 121.5 (d, $J_{F-C} = 23$ Hz, CAr-H), 120.1 (d, $J_{F-C} = 23$ Hz, CAr-H), 27.4 (C₆H₄CH₃), 26.7 (vt, $JP-C = 14.3$ Hz, CHMe₂), 23.1 (vt, $JP-C = 15.2$ Hz, CHMe₂), 18.0 (CHMe₂), 17.6 (CHMe₂), 17.2 (CHMe₂), 16.5 (CHMe₂). $^{19}$F NMR (CD₂Cl₂): δ -111.6. $^{31}$P$\text{_{1}{H}}$ NMR (CD₂Cl₂): δ 40.3 ($J_{195Pt-P} = 2,848$ Hz).

**Figure S42.** $^{1}$H NMR spectrum of 3b in CD₂Cl₂ at RT measured on a 300 MHz Varian iNova.
\[\text{[\(\text{F}PN(H)P\)Pt-\(m\)-C\(_6\)H\(_4\)Me][BARF]\ (3c)\].\text{ Isolated yield: 51 mg, 73\%.}}\]

\[\text{\(^1\text{H NMR (CD}_2\text{Cl}_2): \delta 7.52 (m, 2H, Ar-}\text{H), 7.36 (m, 5H, Ar-}\text{H and o-CH of tolyl), 7.24 (br s, J}\text{\(_{195Pt-H} = 34.9\ Hz, 1H, N-H), 7.05 (br m, 1H, o-CH), 6.93 (t, J = 7.5 Hz, 1H, m-CH), 6.76 (d, J = 7.5 Hz, 1H, p-CH), 2.80 (m, 2H, CHMe}_2\), 2.68 (m, 2H, CHMe}_2\), 2.25 (s, 3H, C\(_6\)H\(_4\)Me), 1.20 (m, 12H, CHMe}_2\), 1.08 (vtd, J\text{\(_{P-H} = 9\ Hz, J_{H-H} = 7\ Hz, CHMe}_2\), 0.89 (vtd, J\text{\(_{P-H} = 9\ Hz, J_{H-H} = 7\ Hz, CHMe}_2\).}}\]

\[\text{\(^{13}\text{C}\{^1\text{H}\} \text{NMR (CD}_2\text{Cl}_2): \delta 162.3 (dvt, J}\text{\(_F-C = 256\ Hz, J}\text{\(_P-C = 4\ Hz, C\text{Ar-F})}, 144.6 (vtd, J}\text{\(_P-C = 7\ Hz, J}\text{\(_F-C = 3\ Hz, C\text{Ar-N})}, 138.6, 136.9, 133.3, 132.3 (vtd, J}\text{\(_P-C = 17\ Hz, J}\text{\(_F-C = 6\ Hz, C\text{Ar-P})}, 128.7, 126.0, 125.0, 124.5, 121.5 (d, J}\text{\(_F-C = 23\ Hz, C\text{Ar-H})}, 120.0 (d, J}\text{\(_F-C = 23\ Hz, C\text{Ar-H}), 26.4 (vt, J}\text{\(_P-C = 13\ Hz, CHMe}_2\), 23.5 (vt, J}\text{\(_P-C = 15\ Hz, CHMe}_2\), 21.5 (C\(_6\)H\(_4\)CH\(_3\)), 18.0 (CHMe}_2\), 17.9 (CHMe}_2\), 17.6 (CHMe}_2\), 17.0 (CHMe}_2).}}\]

\[\text{\(^{19}\text{F NMR (CD}_2\text{Cl}_2): \delta -111.8.}}\]

\[\text{\(^{31}\text{P}\{^1\text{H}\} \text{NMR (CD}_2\text{Cl}_2): \delta 41.0 (J}\text{\(_{195Pt-P} = 2,838\ Hz).}}\]
Figure S43. $^1$H NMR spectrum of 3c in CD$_2$Cl$_2$ at RT measured on a 500 MHz Varian NMRS.

$[\left(\eta^5\text{PN(H)P}\right)\text{Pt}-p-C_6\text{H}_4\text{Me}]\text{[BARF]}$ (3d). Isolated yield: 49 mg, 80%. $^1$H NMR (CD$_2$Cl$_2$): $\delta$ 7.51 (m, 2H, Ar-H), 7.44-7.0 (very broad signal, 2H, o-CH), 7.36 (m, 4H, Ar-H), 7.22 (br s, J$_{195\text{Pt-H}}$ = 37.6 Hz, 1H, N-H), 6.89 (d, J = 7.7 Hz, 2H, m-CH), 2.80 (m, 2H, CHMe$_2$), 2.67 (m, 2H, CHMe$_2$), 2.23 (s, 3H, C$_6$H$_4$Me), 1.19 (m, 12H, CHMe$_2$), 1.07 (vtd, J$_{\text{P-H}}$ = 9 Hz, J$_{\text{H-H}}$ = 8 Hz, CHMe$_2$), 0.88 (dvt, J$_{\text{H-H}}$ = 9 Hz, J$_{\text{P-H}}$ = 8 Hz, CHMe$_2$). $^{13}$C$_{\text{H}}$$^1$H NMR (CD$_2$Cl$_2$): $\delta$ 162.3 (dvt, J$_{\text{F-C}}$ = 256 Hz, J$_{\text{P-C}}$ = 5 Hz, C$_{\text{Ar-F}}$), 144.6 (vtd, J$_{\text{P-C}}$ = 8 Hz, J$_{\text{F-C}}$ = 3 Hz, C$_{\text{Ar-N}}$), 135.9 (t, J$_{\text{P-C}}$ = 2.4 Hz, overlapping with BARF signal, J$_{195\text{Pt-C}}$ = 42 Hz), 133.6, 132.4 (vtd, J$_{\text{P-C}}$ = 17 Hz, J$_{\text{F-C}}$ = 6 Hz, C$_{\text{Ar-P}}$), 129.9, 126.1, 121.5 (d, J$_{\text{F-C}}$ = 23 Hz, C$_{\text{Ar-H}}$), 120.0 (d, J$_{\text{F-C}}$ = 23 Hz, C$_{\text{Ar-H}}$), 26.4 (vt, J$_{\text{P-C}}$ = 14.7 Hz, CHMe$_2$), 23.6 (vt, J$_{\text{P-C}}$ = 15.2 Hz, CHMe$_2$), 20.8 (C$_6$H$_4$CH$_3$), 18.1 (CHMe$_2$), 17.9
(CHMe₂), 17.6 (CHMe₂), 17.0 (CHMe₂). ¹⁹F NMR (CD₂Cl₂): δ -111.4. ³¹P{¹H} NMR (CD₂Cl₂): δ 41.1 (J₁⁹Pt-P = 2,830 Hz).

Figure S44. ¹H NMR spectrum of 3d in CD₂Cl₂ at RT measured on a 300 MHz Varian iNova.
Figure S45. $^1$H NMR spectra of the tolyl methyl resonances for 3b, 3c and 3d in CD$_2$Cl$_2$ at RT measured on a 500 MHz Varian NMRS.

$[\{^5\text{PN}(\text{H})\text{PtCH}_2\text{C}_6\text{H}_5\}\text{BARF}]$ (3g). In a 25 mL Schlenk flask covered with Al foil, 2g (18.6 mg, 0.0257 mmol) was dissolved in approximately 5 mL of a 1:1 Et$_2$O/pentane solution. [H(OEt)$_2$][BARF] (19.4 mg, 0.0234 mmol, 0.9 eq) was added, and the formation of a white precipitate was noted after 30 min. The solution was stirred overnight, and the formation of additional precipitate was observed after 12 h. The volatiles were removed, and the resulting solid was resuspended in pentane, loaded on a bed of Celite, rinsed with pentane and then washed through with CH$_2$Cl$_2$. The volatiles were removed, and the solid was redissolved in CD$_2$Cl$_2$ for characterization. $^1$H NMR (CD$_2$Cl$_2$): $\delta$ 7.42-7.38 (m, 2H, Ar-H), 7.38-7.32 (m, 6H, Ar-H overlapping with o-CH of benzyl), 7.23 (t, J = 7.5 Hz, 2H, m-CH of benzyl), 7.12 (t, J = 8 Hz, 1H, p-CH of benzyl), 7.09 (br s, J$_{195\text{Pr-H}}$ = 35 Hz, 1H, N-H), 3.46 (t, J = 6.3 Hz, J$_{195\text{Pr-H}}$ = 95 Hz, 2H, CH$_2$C$_6$H$_5$), 2.85 (m, 2H, CHMe$_2$), 2.41 (m, 2H, CHMe$_2$), 1.32 (app q (dvt), J = 8 Hz, 6H, CHMe$_2$), 1.28 (app q (dvt), J = 7.5 Hz, 6H, CHMe$_2$), 1.15 (app q (dvt), J = 8 Hz, 6H,
CHMe₂), 1.10 (vtd, Jₚ-H = 9 Hz, J_H-H = 7 Hz, 6H, CHMe₂). ¹⁹F NMR (CD₂Cl₂): δ -111.5. ³¹P {¹H} NMR (CD₂Cl₂): δ 41.1 (J₁₉₅Pt-P = 2,954 Hz).

Figure S46. ¹H NMR spectrum of 3g in CD₂Cl₂ at RT measured on a 500 MHz Varian NMRS.
Figure S47. $^{19}$F NMR spectrum of 3g in CD$_2$Cl$_2$ at RT measured on a 300 MHz Varian iNova.

Figure S48. $^{31}$P{${}^1$H} NMR spectrum of 3g in CD$_2$Cl$_2$ at RT measured on a 300 MHz Varian iNova.

(FPNP)PtC₆D₅ (2a-D). 3a-D (29 mg, 0.023 mmol) was transferred to a J. Young NMR tube and dissolved in C₆D₆. KOtBu (3 mg, 0.03 mmol) was added, and the NMR tube was shaken, yielding a yellow solution with a colorless precipitate. Full conversion to 2a-D was confirmed by ¹⁹F NMR, using fluorobenzene as an internal standard. The solution was filtered into a 10 mL Schlenk flask, the volatiles were removed and the resulting yellow solid was redisolved in C₆D₆ for characterization. ¹H NMR (C₆D₆): δ 7.55 (m, 2H, Ar-H), 6.75 (m, 4H, Ar-H), 2.08 (m, 4H, CHMe₂), 0.90-0.83 (m, 24H, CHMe₂). ¹⁹F NMR (C₆D₆): δ -130.6. ³¹P{¹H} NMR (C₆D₆): δ 40.1 (J₁⁹Pt-P = 2,848 Hz).

Deprotonation of 3b-d with KOtBu. [(FPN(H)P)PtC₆H₄Me][BARF] (65 mg, 0.047 mmol) was transferred to a J. Young NMR tube and dissolved in C₆D₆. KOtBu (6 mg, 0.05 mmol) was added, and the NMR tube was shaken, yielding a yellow solution with a colorless precipitate. The ¹⁹F NMR spectrum showed full conversion to 2b-d, and the ¹H NMR spectrum showed a 2b:(2c plus 2d) ratio of 8%:92% (2c and 2d signals overlap).

(FPNP)PtC₆H₄F (2e). 3e (19.8 mg, 0.0141 mmol) was transferred to a J. Young NMR tube and dissolved in C₆D₆. KOtBu (2 mg, 0.02 mmol) was added, and the NMR tube was shaken, yielding a yellow solution with a colorless precipitate. The ¹⁹F NMR spectrum showed full conversion to 2e. ¹H NMR (C₆D₆): δ 7.61 (m, J₁⁹Pt-H = 65 Hz, 1H, ortho C-H of C₆H₄F), 7.52 (m, 2H, Ar-H), 6.95-6.91 (m, 3H, meta and para C-H of C₆H₄F), 6.77-6.71 (m, 4H, Ar-H), 2.17 (m, 2H, CHMe₂), 2.04 (m, 2H, CHMe₂), 0.96-0.79 (m, 24H, CHMe₂). ¹³C{¹H} NMR (CD₂Cl₂): δ 166.8 (d, JF-C = 227 Hz, CAr-F), 160.6 (br s, CAr-N), 154.2 (d, JF-C = 237 Hz, CAr-F), 140.5 (dvt, JF-C = 18 Hz, JAr-C = 2 Hz, CAr-H), 124.0 (JPt-C = 58 Hz, CAr-Pt), 123.5 (dvt, JF-C = 7.5 Hz, JAr-C = 1.4 Hz, CAr-H), 121.3 (vt, JPt-C = 18 Hz, CAr-Pt), 120.7 (m, 118.5 (d, JF-C = 21.5 Hz, CAr-H), 117.9
(d, J_{F-C} = 22.5 Hz, C_{Ar-H}), 115.0 (br s, C_{Ar-H}), 113.5 (d, J_{F-C} = 29 Hz, C_{Ar-H}), 25.3 (vt, J_{P-C} = 15 Hz, CHMe_2), 23.8 (vt, J_{P-C} = 15 Hz, CHMe_2), 17.6 (br, CHMe_2), 17.3 (CHMe_2), 17.0 (CHMe_2).

^{19}F\text{ NMR (C}_6\text{D}_6): \delta -92.3 (J_{195Pt-F} = 338 Hz), -131.3. ^{31}P\{^1H\}\text{ NMR (C}_6\text{D}_6): \delta 42.1 (J_{195Pt-P} = 2,770 Hz).

Figure S49. ^1H\text{ NMR spectrum of 2e in C}_6\text{D}_6\text{ at RT measured on a 500 MHz Varian NMRS.}
Figure S50. $^{19}$F NMR spectrum of $2e$ in $C_6D_6$ at RT measured on a 500 MHz Varian NMRS.

Figure S51. $^{31}$P{$_1$H}NMR spectrum of $2e$ in $C_6D_6$ at RT measured on a 500 MHz Varian NMRS.

$^{(FPNP)}PtC_6H_4Cl$ (2f). 3f (24.2 mg, 0.0170 mmol) was transferred to a J. Young NMR tube and dissolved in $C_6D_6$. KO'Bu (2 mg, 0.02 mmol) was added, and the NMR tube was shaken, yielding a yellow solution and a colorless precipitate. The solution was filtered over Celite and silica gel, and the resulting clear yellow solution was used for characterization. $^{1}$H NMR ($C_6D_6$):
δ 7.59 (dd, J = 7.5 Hz, 1.9 Hz, J_{195Pt-H} = 60.6 Hz, 1H, ortho C-H of C₆H₄Cl), 7.47 (br s, 2H, Ar-H), 7.31 (d, J = 7.6 Hz, 1H, meta C-H of C₆H₄Cl), 6.90 (td, J = 7.6 Hz, 1.8 Hz, 1H, meta C-H of C₆H₄Cl), 6.79 (td, J = 7.6 Hz, 1.9 Hz, 1H, para C-H of C₆H₄Cl), 6.72 (m, 4H, Ar-H), 2.29 (m, 2H, CHMe₂), 2.04 (m, 2H, CHMe₂), 0.98-0.77 (m, 24H, CHMe₂). ¹³C{¹H} NMR (CD₂Cl₂): δ 160.3 (vt, J_{P-C} = 10 Hz, C_{Ar-N}), 154.2 (d, J_{F-C} = 233 Hz, C_{Ar-F}), 143.5 (t, J_{P-C} = 3 Hz), 141.1 (t, J_{P-C} = 2 Hz), 137.3 (t, J_{P-C} = 9 Hz), 127.9, 125.6 (J_{195Pt-C} = 56 Hz, C_{Ar-Pt}), 123.5, 121.4 (m, C_{Ar-P}), 118.4 (d, J_{F-C} = 21 Hz, C_{Ar-H}), 117.9 (d, J_{F-C} = 22 Hz, C_{Ar-H}), 115.1 (app q, J = 6 Hz, C_{Ar-H}), 25.5 (vt, J_{P-C} = 15.6 Hz, CHMe₂), 23.6 (vt, J_{P-C} = 15.3 Hz, CHMe₂), 17.5 (CHMe₂), 17.4 (CHMe₂), 17.2 (CHMe₂), 16.8 (CHMe₂). ¹⁹F NMR (C₆D₆): δ -130.2. ³¹P{¹H} NMR (C₆D₆): δ 41.6 (J_{195Pt-P} = 2,809 Hz).

Figure S52. ¹H NMR spectrum of 2f in C₆D₆ at RT measured on a 500 MHz Varian NMRS.
Figure S53. $^{19}$F NMR spectrum of 2f in C$_6$D$_6$ at RT measured on a 500 MHz Varian NMRS.

Figure S54. $^{31}$P{$^1$H} NMR spectrum of 2f in C$_6$D$_6$ at RT measured on a 500 MHz Varian NMRS.
II-G. Activation of dichloromethane.

\[(\text{FPNP})\text{PtCl}[\text{BARF}] \ (9a)\]. 1 (20.8 mg, 0.0266 mmol) and K-BARF (21 mg, 0.029 mmol) were transferred to a J. Young NMR tube. CD$_2$Cl$_2$ was added, and the solution immediately went from a bright yellow color to a darker brown/green, followed by a more gradual change to a blue solution. NMR spectra provided evidence for a paramagnetic species. Upon the addition of decamethyl ferrocene (10 mg, 0.031 mmol), the solution changed from dark blue to orange/brown. After filtering the solution over Celite, \((\text{FPNP})\text{PtCl}\) (50% conversion) was observed by $^{19}$F NMR.

\[(\text{FPNP})\text{PtCl}[\text{HCB}_{11}\text{Cl}_{11}] \ (9b)\]. The paramagnetic \((\text{FPNP})\text{PtCl}\)^+ species was independently generated by reacting \((\text{FPNP})\text{PtCl}\) (54.3 mg, 0.0814 mmol) with Ag[HC$_{11}$B$_{11}$Cl$_{11}$] (51.3 mg, 0.0815 mmol) in CD$_2$Cl$_2$. The solution was stirred for 5 min in a 10 mL Schlenk flask covered with Al foil and then filtered over Celite through a glass microfiber into a J. Young NMR tube. No product signals were observed by $^{31}$P\{$^1$H\} or $^{19}$F NMR. Broad signals were observed in the $^1$H NMR spectrum along with the C-H signal of the carborane anion. Crystals were obtained from a CH$_2$Cl$_2$ solution that was layered with pentane and cooled to -35°C. One of the crystals was used for X-ray diffraction studies. The remaining crystals were washed with cold pentane and dried under vacuum. Isolated yield of the remaining fraction: 42 mg, 44%. Elemental analysis, found (calculated) for C$_{25}$H$_{35}$B$_{11}$Cl$_{11}$F$_2$NP$_2$Pt: C, 25.18 (25.26); H, 2.98 (2.97).
Figure S55. $^1$H NMR spectrum of 9b in CD$_2$Cl$_2$ at RT measured on a 500 MHz Varian NMRS.
II-H. Crossover and competition studies.

Crossover studies. A solid sample of 3b-d yielded no crossover products when dissolved or suspended in C₆D₆ (minimally soluble) or fluorobenzene in a J. Young NMR tube. The solutions were monitored at RT for up to 48 h, and no changes were observed by ¹⁹F, ³¹P or ¹H NMR. Additionally, no changes were observed after heating at 80°C for up to 48 h. Similar observations were made for 3e in C₆D₆ (minimally soluble) or toluene (minimally soluble) and 3a-D in toluene (minimally soluble) or fluorobenzene.

Thermolysis of 3a-D in the presence of MeCN. 3a-D (26.8 mg, 0.0192 mmol) was transferred to a J. Young NMR tube and dissolved in CD₂Cl₂, forming a pale blue solution. Fluorobenzene (5.0 µL) was added as an internal standard, followed by 300 µL of MeCN. The solution was monitored at RT for 5 days, and no changes were observed by NMR. The volatiles were removed, and the resulting solid was dissolved in neat MeCN. After heating at 80°C for 24 h, the solution had become clear green, and the formation of 6 (approximately 26%) was observed by ¹⁹F and ³¹P NMR.

Competition studies:

Table S2. Arene solvent molar ratios, observed C-H activation product ratios and adjusted molar-weighted ratios for competition studies.

<table>
<thead>
<tr>
<th>Solvent Mixture</th>
<th>Molar Ratio</th>
<th>Observed Ratio of Products</th>
<th>Molar-Weighted Product Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₆D₆:PhF</td>
<td>1.06</td>
<td>3e:3a-D</td>
<td>16:1</td>
</tr>
<tr>
<td>C₆H₆:PhF</td>
<td>1.05</td>
<td>3e:3a</td>
<td>5.3:1</td>
</tr>
<tr>
<td>C₆H₆:C₆D₆</td>
<td>0.994</td>
<td>3a:3a-D</td>
<td>3.2:1</td>
</tr>
<tr>
<td>C₆H₆:toluene</td>
<td>1.19</td>
<td>3a:3b-d</td>
<td>2.3:1</td>
</tr>
</tbody>
</table>

C₆D₆ vs PhF. 1 (20.3 mg, 0.0260 mmol) was combined with K-BARF (20.2 mg, 0.0281 mmol) in a J. Young NMR tube, and a 1:1 (by volume) C₆D₆:C₆H₅F solution (prepared by combining 1.00 mL of C₆D₆ and 1.00 mL of C₆H₅F) was added, forming a cloudy orange
solution. After combining the reagents at RT, the $^{19}$F NMR spectrum showed only starting material. After heating the NMR tube for 30 min at 80°C, 3e was observed to be the major product by $^{19}$F NMR. After 24 h at 80°C, a pale blue solution containing a white precipitate had formed. The $^{19}$F and $^1$H NMR spectra showed a 3e:3a-D ratio of approximately 16:1.

**C$_6$H$_6$ vs PhF.** A 1:1 (by volume) solution of C$_6$H$_6$:C$_6$H$_5$F was prepared by combining 1.00 mL of C$_6$H$_6$ and 1.00 mL of C$_6$H$_5$F in a small vial. 1 (25.0 mg, 0.0320 mmol) and K-BARF (23.3 mg, 0.0325 mmol) were transferred as solids into a Teflon-stoppered round-bottomed flask. The C$_6$H$_6$:C$_6$H$_5$F solution was added, and the reaction flask was placed in an oil bath at 80°C. After 3 h, the solution had become a pale blue with a grey precipitate. The volatiles were removed, and the products were extracted with CD$_2$Cl$_2$ and passed through a layer of Celite into a J. Young NMR tube. The $^{19}$F NMR and $^1$H NMR spectra showed a 3e:3a ratio of approximately 5:1.

**C$_6$H$_6$ vs C$_6$D$_6$.** A 1:1 (by volume) solution of C$_6$H$_6$:C$_6$D$_6$ was prepared by combining 1.00 mL of C$_6$H$_6$ and 1.00 mL of C$_6$D$_6$ in a small vial. 1 (22.4 mg, 0.0287 mmol) and K-BARF (21.2 mg, 0.0295 mmol) were transferred as solids into a Teflon-stoppered round-bottomed flask. The C$_6$H$_6$:C$_6$D$_6$ solution was added, and the reaction flask was placed in an oil bath at 80°C. After 3 h, the solution had become a pale blue with a grey precipitate. The volatiles were removed, and the products were extracted with CD$_2$Cl$_2$ and passed through a layer of Celite into a J. Young NMR tube. The $^1$H NMR spectrum showed a 3a:3a-D ratio of approximately 3:1.

**C$_6$H$_6$ vs C$_6$H$_5$Me.** A 1:1 (by volume) solution of C$_6$H$_6$:C$_6$H$_5$Me was prepared by combining 1.00 mL of C$_6$H$_6$ and 1.00 mL of C$_6$H$_5$Me in a small vial. 1 (21.7 mg, 0.0278 mmol) and K-BARF (20.9 mg, 0.0279 mmol) were transferred as solids into a Teflon-stoppered round-bottomed flask. The C$_6$H$_6$:C$_6$H$_5$Me solution was added, and the reaction flask was placed in an oil bath at 80°C. After 3 h, the solution had become a pale blue with a grey precipitate. The
volatiles were removed, and the products were extracted with CD$_2$Cl$_2$ and passed through a layer of Celite into a J. Young NMR tube. The $^1$H NMR spectrum showed a 3a:3b-d ratio of approximately 2.3:1.
II-I. Probing the interconversion of isomers of tolyl isomers 3b-d.

**Monitoring the isomerization of 3b in CD₂Cl₂.** 3b (36 mg, 0.026 mmol) was dissolved in CD₂Cl₂ in a J. Young NMR tube, forming a pale blue solution. The solution was monitored at RT by ¹H, ¹⁹F and ³¹P NMR spectroscopy for up to 2 weeks. No changes were observed. Addition of neat HOTf (9.0 μL, 0.10 mmol, 4 eq) resulted in the formation of 8 as the major product and a 3b:3c:3d:free toluene ratio of approximately 9%:35%:16%:40%.

**Monitoring the isomerization of 3c in CD₂Cl₂.** 3c (51 mg, 0.036 mmol) was dissolved in CD₂Cl₂ in a J. Young NMR tube, forming a pale blue solution. The solution was monitored at RT by ¹H, ¹⁹F and ³¹P NMR spectroscopy for up to 2 weeks, but no changes were observed. A 0.11 M solution of HOTf was prepared in fluorobenzene. 20 min after the addition of the HOTf solution (33 μL, 0.0036 mmol, 0.1 eq), some 3d was observed along with the appearance of free toluene. After 16 h at RT, the 3b:3c:3d:free toluene ratio was 3%:70%:26%:1%. An additional portion of the HOTf solution (163 μL, 0.0179 mmol, 0.5 eq) was added, and after another 16 h at RT, the 3b:3c:3d:free toluene ratio was 11%:56%:18%:15%. Finally, 19.0 μL of neat HOTf (0.233 mmol total, 6.46 eq) was added to the NMR tube, and the 3b:3c:3d:free toluene ratio became 6%:25%:10%:59%. The major product was identified as 8.

**Monitoring the isomerization of 3d in CD₂Cl₂.** 3d (49 mg, 0.035 mmol) was dissolved in CD₂Cl₂ in a J. Young NMR tube, forming a pale blue solution. The solution was monitored at RT by ¹H, ¹⁹F and ³¹P NMR spectroscopy for up to 2 weeks, but no changes were observed. A 0.11 M solution of HOTf was prepared in fluorobenzene. 20 min after the addition of the HOTf solution (90.0 μL, 0.0099 mmol, 0.28 eq), some formation of 3c was observed along with the appearance of free toluene. After 16 h, the 3b:3c:3d:free toluene ratio was approximately 2%:9%:80%:9%. An additional portion of the HOTf solution (286 μL, 0.0315 mmol, 0.9 eq) was
added, and after another 16 h at RT, the $3b:3c:3d$:free toluene ratio was approximately 3%:24%:59%:14%. Finally, 18.0 μL of neat HOTf (0.235 mmol total, 6.7 eq) was added to the NMR tube, and the $3b:3c:3d$:free toluene ratio became approximately 3%:22%:35%:39%. The major product was identified as 8.

Figure S56. $^1$H NMR spectra showing the isomerization of $3c$ upon addition of HOTf in CD$_2$Cl$_2$ at RT measured on a 500 MHz Varian NMRS.

**Monitoring the isomerization of $3g$ in CD$_2$Cl$_2$.** $3g$ (19.8 mg, 0.0141 mmol) was dissolved in CD$_2$Cl$_2$ in a J. Young NMR tube, forming a pale blue solution. The solution was monitored at RT by $^1$H, $^{19}$F and $^{31}$P NMR spectroscopy for up to 2 weeks, but no changes were observed. Then, 5.0 μL of neat HOTf (0.057 mmol, 4 eq) was added to the NMR tube. After 16 h at RT, the starting material had been completely consumed, and the $3b:3c:3d$:free toluene ratio was approximately 2%:39%:9%:50%. The major product was identified as 8.
Attempted isomerization of 3c in the presence of 2c. 3c (12.8 mg, 9.13 μmol) was dissolved in CD2Cl2 in a J. Young NMR tube, forming a pale blue solution. A 5.33 mM solution of 2c was prepared in CD2Cl2, and 84 μL of this solution (0.45 μmol) was added to the NMR tube. No changes were observed after 12 h at RT. Up to one equivalent of 2c (6.6 mg, 9.1 μmol) was added, but no changes were observed after 24 h.

Attempted isomerization of 3c in the presence of BF3. 3c (9.0 mg, 6.4 μmol) was dissolved in CD2Cl2 in a J. Young NMR tube, forming a pale blue solution. A 47.5 mM solution of BF3·SMe2 was prepared in CD2Cl2, and 7.0 μL of this solution (0.33 μmol) was added to the NMR tube. No changes were observed after 12 h at RT. Up to one equivalent of BF3·SMe2 (135 μL, 6.41 μmol) was added, but no changes were observed after 24 h.

Attempted isomerization of 3c in the presence of [H(OEt2)2][BARF]. 3c (9.0 mg, 6.4 μmol) was dissolved in CD2Cl2 in a J. Young NMR tube, forming a pale blue solution. A 0.0128 M solution of [H(OEt2)2][BARF] was prepared in Et2O, and 25 μL of this solution (0.33 μmol) was added to the NMR tube. No changes were observed after 12 h at RT. Up to one equivalent of [H(OEt2)2][BARF] (0.50 mL, 6.4 μmol) was added, but no changes were observed after 24 h.

Attempted isomerization of 3c in the presence of B(C6F5)3. 3d (25.8 mg, 0.0184 mmol) was added to a CD2Cl2 solution of B(C6F5)3 (4.88 μmol, 0.265 eq) in a J. Young NMR tube. The solution was monitored for 3 days, but no changes were observed by NMR.

Attempted isomerization of 3c in the presence of [H(OEt2)2][OTf]. 3c (32.1 mg, 0.0228 mmol) was dissolved in CD2Cl2 in a J. Young NMR tube, forming a pale blue solution. A 1.88 M solution of HOTf was prepared in Et2O, and 12.0 μL of this solution (0.0226 mmol) was added to the NMR tube. After 16h, no changes were observed by 1H, 19F, and 31P NMR. A total of 3.4
equivalents of [H(OEt)_2][OTf] (0.0775 mmol) was added with no isomerization observed after 5 days at RT.
III. DFT Studies.

Computational details. All calculations were carried out in Gaussian 09 \textsuperscript{3} using the PBE1PBE (also known as PBE0)\textsuperscript{4} and M06-L\textsuperscript{5} functionals, tight optimizations, and the ultrafine integration grid (a pruned (99,590) grid). The basis sets\textsuperscript{6} included Def2-QZVPP (with the corresponding ECP) for Pt,\textsuperscript{7} 6-311+G(2df) for the N, F, and P atoms, and 6-31+G(d,p) for all other atoms. The default PCM method (solvent = tetrahydrofurane) was used for all calculations of this work with the UFF radii scaled by 1.1 (explicit hydrogens). The optimized geometries were verified to have no negative harmonic frequencies by frequency calculations which also provided the enthalpies and free energies reported here. The free energies were calculated under $P = 302$ atm in THF.\textsuperscript{68}
<table>
<thead>
<tr>
<th></th>
<th>([\text{(^\text{F}P\text{N}P\text{P})Pt}]^+) Singlet PBE1PBE</th>
<th>([\text{(^\text{F}P\text{N}P\text{P})Pt}]^+) Triplet PBE1PBE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt-P</td>
<td>2.327</td>
<td>2.298</td>
</tr>
<tr>
<td>Pt-N</td>
<td>1.964</td>
<td>2.090</td>
</tr>
<tr>
<td>N-C(_{\text{Ar}})</td>
<td>1.393</td>
<td>1.381</td>
</tr>
<tr>
<td>P-Pt-P</td>
<td>166.59</td>
<td>167.02</td>
</tr>
<tr>
<td>P-Pt-N</td>
<td>83.29</td>
<td>83.51</td>
</tr>
<tr>
<td>C(<em>{\text{Ar}})-N-C(</em>{\text{Ar}})</td>
<td>122.94</td>
<td>124.15</td>
</tr>
<tr>
<td>C(_{\text{Ar}})-N-Pt</td>
<td>118.53</td>
<td>117.93</td>
</tr>
</tbody>
</table>

Table S3. Calculated bond distance data (in Å) and angles (deg) using PBE1PBE functional for \([\text{(^\text{F}P\text{N}P\text{P})Pt}]^+\).

![Figure S57. PBE1PBE optimized geometries for singlet and triplet states of \([\text{(^\text{F}P\text{N}P\text{P})Pt}]^+\).](image)

Figure S57. PBE1PBE optimized geometries for singlet and triplet states of \([\text{(^\text{F}P\text{N}P\text{P})Pt}]^+\).
Table S4. Calculated bond distance data (in Å) and angles (deg) using M06-L functional for \([\text{\(\text{FPNP}\)}\text{Pt}\]⁺

<table>
<thead>
<tr>
<th></th>
<th>([\text{(\text{FPNP})}\text{Pt}]⁺ Singlet M06-L</th>
<th>([\text{(\text{FPNP})}\text{Pt}]⁺ Triplet M06-L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt-P</td>
<td>2.342</td>
<td>2.314</td>
</tr>
<tr>
<td>Pt-N</td>
<td>1.994</td>
<td>2.142</td>
</tr>
<tr>
<td>N-C_&lt;sub&gt;A&lt;/sub&gt;</td>
<td>1.391</td>
<td>1.377</td>
</tr>
<tr>
<td>P-Pt-P</td>
<td>164.11</td>
<td>163.51</td>
</tr>
<tr>
<td>P-Pt-N</td>
<td>82.05</td>
<td>81.75</td>
</tr>
<tr>
<td>C_&lt;sub&gt;A&lt;/sub&gt;-N-C_&lt;sub&gt;A&lt;/sub&gt;</td>
<td>123.69</td>
<td>125.02</td>
</tr>
<tr>
<td>C_&lt;sub&gt;A&lt;/sub&gt;-N-Pt</td>
<td>118.16</td>
<td>117.49</td>
</tr>
</tbody>
</table>

Figure S58. M06-L optimized geometries for singlet and triplet states of \([\text{\(\text{FPNP}\)}\text{Pt}\]⁺

---

Electronic Supplementary Material (ESI) for Chemical Science
This journal is © The Royal Society of Chemistry 2013

S72
IV. Details of X-Ray diffractometry studies.

**X-Ray data collection, solution, and refinement for 3e.** A pale blue, multi-faceted block of suitable size (0.20 x 0.11 x 0.06 mm) was selected from a representative sample of crystals of the same habit using an optical microscope and mounted onto a nylon loop. Low temperature (110 K) X-ray data were obtained on a Bruker APEXII CCD based diffractometer (Mo sealed X-ray tube, $\lambda_{\text{Mo}} = 0.71073$ Å). All diffractometer manipulations, including data collection, integration and scaling were carried out using the Bruker APEXII software. An absorption correction was applied using SADABS. The space group was determined on the basis of systematic absences and intensity statistics and the structure was solved by direct methods and refined by full-matrix least squares on $F^2$. The structure was solved in the monoclinic $P\overline{2}_1/c$ space group using XS (incorporated in SHELXTL). No missed symmetry was reported by PLATON. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in idealized positions and refined using riding model. Deuterium atoms of the solvent molecules were not placed due to solvent disorder. The structure was refined (weighted least squares refinement on $F^2$) and the final least-squares refinement converged to $R_1 = 0.0285$ ($I > 2\sigma(I)$, 10152 data) and $wR_2 = 0.0670$ ($F^2$, 11953 data, 757 parameters, 1 restraints). The fluorine atom on the metallated fluorobenzene residue was found to reside with partial occupancy on C(43) and C(45) and was refined as such.

**X-Ray data collection, solution, and refinement for 3c/d.** A Leica MZ 75 microscope was used to identify a suitable pale blue blocks with very well defined faces with dimensions (max, intermediate, and min) 0.15 mm x 0.13 mm x 0.10 mm from a representative sample of crystals of the same habit. The crystal mounted on a nylon loop was then placed in a cold nitrogen stream (Oxford) maintained at 110 K.

S73
A BRUKER APEX 2 X-ray (three-circle) diffractometer was employed for crystal screening, unit cell determination, and data collection. The goniometer was controlled using the APEX2 software suite, v2008-6.0. The sample was optically centered with the aid of a video camera such that no translations were observed as the crystal was rotated through all positions. The detector was set at 6.0 cm from the crystal sample (APEX2, 512x512 pixel). The X-ray radiation employed was generated from a Mo sealed X-ray tube (\(K_\alpha = 0.70173\)Å with a potential of 40 kV and a current of 40 mA) fitted with a graphite monochromator in the parallel mode (175 mm collimator with 0.5 mm pinholes).

Sixty data frames were taken at widths of 0.5°. These reflections were used in the auto-indexing procedure to determine the unit cell. A suitable cell was found and refined by nonlinear least squares and Bravais lattice procedures. The unit cell was verified by examination of the h k l overlays on several frames of data. No super-cell or erroneous reflections were observed.

After careful examination of the unit cell, a standard data collection procedure was initiated using omega scans.

Integrated intensity information for each reflection was obtained by reduction of the data frames with the program APEX2. The integration method employed a three dimensional profiling algorithm and all data were corrected for Lorentz and polarization factors, as well as for crystal decay effects and were finally merged and scaled to produce a suitable data set. The absorption correction program SADABS was employed to correct the data for absorption effects (as well as systematic errors).

Systematic reflection conditions and statistical tests of the data suggested the space group \(P2_1/n\). A solution was obtained readily using SHELXTL (XS). The tolyl group attached to the
Pt was disordered with para and meta isomers, which was modeled successfully, with a ratio of 53:47 respectively. The hydrogen atoms were placed in idealized positions geometrically and were set riding on the respective parent atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters. The structure was refined (weighted least squares refinement on $F^2$) to convergence.\textsuperscript{11,13}

**Figure S59.** Olex\textsuperscript{2} structure plot of 3c-d showing tolyl group attached to Pt as disordered with para and meta isomers modeled successfully in a ratio of 53:47, respectively.

**X-Ray data collection, solution, and refinement for 9b.** A Leica MZ 75 microscope was used to identify a suitable blue blocks with very well defined faces with dimensions (max, intermediate, and min) 0.60 mm x 0.08 mm x 0.04 mm from a representative sample of crystals
of the same habit. The crystal mounted on a nylon loop was then placed in a cold nitrogen stream (Oxford) maintained at 110 K.

A BRUKER APEX 2 X-ray (three-circle) diffractometer was employed for crystal screening, unit cell determination, and data collection. The goniometer was controlled using the APEX2 software suite, v2008-6.0.\textsuperscript{9} The sample was optically centered with the aid of a video camera such that no translations were observed as the crystal was rotated through all positions. The detector was set at 6.0 cm from the crystal sample (APEX2, 512x512 pixel). The X-ray radiation employed was generated from a Mo sealed X-ray tube (K\textsubscript{\alpha} = 0.70173Å with a potential of 40 kV and a current of 40 mA) fitted with a graphite monochromator in the parallel mode (175 mm collimator with 0.5 mm pinholes).

Sixty data frames were taken at widths of 0.5°. These reflections were used in the auto-indexing procedure to determine the unit cell using CELL\_NOW.* Two components were identified and refined by nonlinear least squares and Bravais lattice procedures. The orientation matrices were verified by examination of the h k l overlays on several frames of data. No super-cell or erroneous reflections were observed.

After careful examination of the unit cell, a standard data collection procedure was initiated using omega scans.

Integrated intensity information for each reflection was obtained by reduction of the data frames with the program APEX2.\textsuperscript{9} The integration method employed a three dimensional profiling algorithm and all data were corrected for Lorentz and polarization factors, as well as for crystal decay effects and were finally merged and scaled to produce a suitable data set. The absorption correction program TWINABS\textsuperscript{10} was employed to correct the data for absorption
effects (as well as systematic errors) and also to separate the twin components. Only the major component was used for structure solution as well as least squares refinement.

Systematic reflection conditions and statistical tests of the data suggested the space group $P2_1/c$. A solution was obtained readily using SHELXTL (XS).\textsuperscript{11} Hydrogen atoms were placed in idealized positions and were set riding on the respective parent atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters. The structure was refined (weighted least squares refinement on $F^2$) to convergence.\textsuperscript{11,13}
V. Supporting Information References.


6 These basis sets are available from the EMSL Basis Set Library (bse.pnl.gov).


9 APEX2 “Program for Data Collection on Area Detectors” BRUKER AXS Inc., 5465 East Cheryl Parkway, Madison, WI 53711-5373 USA.

10 SADABS, Sheldrick, G.M. “Program for Absorption Correction of Area Detector Frames”, BRUKER AXS Inc., 5465 East Cheryl Parkway, Madison, WI 53711-5373 USA.

11 G. M. Sheldrick, M. Acta Cryst., 2008, A64, 112-122. XS, BRUKER AXS Inc., 5465 East Cheryl Parkway, Madison, WI 53711-5373 USA.
