SUPPORTING INFORMATION

Olefin Hydroarylation Catalyzed by (Pyridyl-Indolate)Pt(II) Complexes: Catalytic Efficiencies and Mechanistic Aspects

Benjamin A. Suslick, Allegra L. Liberman-Martin, Truman C. Wambach, T. Don Tilley*

Department of Chemistry, University of California, Berkeley, California 94720, United States
Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States

*Corresponding Author E-mail: tdtiley@berkeley.edu
TABLE OF CONTENTS

EXPERIMENTAL SECTION ............................................................................................................. S3-S21
  General Considerations .............................................................................................................. S3
  Scheme S1 ..................................................................................................................................... S4
  Synthesis of Ligands and Pt(II) Complexes ............................................................................. S4-S17
  Catalytic Methods ...................................................................................................................... S17-S21

EXPERIMENTAL FIGURES ........................................................................................................... S22-S37
  Figure S1 ...................................................................................................................................... S22
  Figure S2 ...................................................................................................................................... S22
  Figure S3 ...................................................................................................................................... S23
  Figure S4 ...................................................................................................................................... S24
  Figure S5 ...................................................................................................................................... S25
  Figure S6 ...................................................................................................................................... S26
  Figure S7 ...................................................................................................................................... S27
  Figure S8 ...................................................................................................................................... S28
  Figure S9 ...................................................................................................................................... S29
  Figure S10 ................................................................................................................................. S30
  Figure S11 .................................................................................................................................... S31
  Figure S12 .................................................................................................................................... S32
  Figure S13 .................................................................................................................................... S33
  Figure S14 .................................................................................................................................... S34
  Figure S15 .................................................................................................................................... S35
  Figure S16 .................................................................................................................................... S36
  Figure S17 .................................................................................................................................... S37
  Figure S18 .................................................................................................................................... S38
  Figure S19 .................................................................................................................................... S39

TABLES .......................................................................................................................................... S40-S41
  Table S1 ....................................................................................................................................... S40
  Table S2 ....................................................................................................................................... S41

NMR SPECTRA OF COMPOUNDS ............................................................................................ S42-S117

REFERENCES ............................................................................................................................... S118
EXPERIMENTAL SECTION

General Considerations. All reactions and experiments, unless otherwise noted, were performed using standard Schlenk techniques under N\(_2\) atmosphere or inside a N\(_2\) glovebox. Schlenk glassware was oven dried overnight before use and N-N\(^-\) ligated metal complexes were stored at ambient temperature in a N\(_2\) glovebox. Solvents were stored over 3 Å molecular sieves after drying with a JC Meyers Phoenix SDS solvent purification system. Solvents for organic syntheses were used without further purification. Deuterated NMR solvents were purchased from Cambridge Isotope Laboratory. Benzene-\(d_6\) was degassed by three freeze/pump/thaw cycles and then dried over 3 Å molecular sieves.

Ethylene (99.9\%) was purchased in a gas cylinder from Praxair Technology and used as received. \(o\)-Ethyltoluene, \(m\)-ethyltoluene, \(p\)-ethyltoluene, NaO\(\text{tBu}\), AgOTf, PhLi, 2,6-di-\(tert\)-butyl-4-methylpyridine, and tridecane were purchased from commercial sources and used without further purification. Si(SiMe\(_3\))\(_4\) was purchased from a commercial source, sublimed before use, and stored in a N\(_2\) glovebox. Phenyl hydrazine (S\(2a\)), 4-methoxyphenyl hydrazine hydrochloride (S\(2f\)), 4-methylphenyl hydrazine hydrochloride (S\(2h\)), 4-fluorophenyl hydrazine hydrochloride (S\(2g\)), 4-bromophenyl hydrazine hydrochloride (S\(2i\)), and 2-chloro-4-methylphenylhydrazine hydrochloride (S\(2j\)) were purchased from commercial sources and used without further purification. 2,5-Difluorophenyl hydrazine (S\(2b\)), \(1^\text{2},3,4,5\)-tetrafluorophenyl hydrazine (S\(2c\)), \(4^\text{2}\)-tert-butyl-2-acetylpyridine, \(\text{cis-}(\text{SMe}_2)_2\text{PtPh}_2\), [(\(\mu\text{-Et}_2\))PtPh\(_2\)]\(_2\), and [(\(\text{C}_2\text{H}_4\))Pt(\(\mu\text{-Cl})\text{Cl})]\(_2\) (Zeise’s Dimer\(^5\)) were prepared according to published literature procedures.

All \(^1\text{H}, ^{13}\text{C}\{^1\text{H}\}, \) and \(^{19}\text{F}\) NMR experiments were carried out using Bruker AV-300, AVB-400, AVQ-400, AV-500, AV-600 MHz, or AV-900 MHz (equipped with a TCI cryoprobe) spectrometers at ambient temperatures (unless otherwise noted). \(^1\text{H}\) and \(^{13}\text{C}\{^1\text{H}\}\) NMR experiments were internally calibrated to residual solvents relative to tetramethyldisilane. \(^{19}\text{F}\) NMR was calibrated externally to hexafluorobenzene. Quantitative GC experiments were performed on an Agilent 7890 GC equipped with an HP-5 column (25 m x 0.20 mm x 0.33 µm film) and an FID detector. High resolution mass spectrometry (HRMS) experiments were carried out by the QB3/Chemistry Mass Spectrometry Facility at the University of California, Berkeley. ESIHR experiments were performed on a LTQ-FT instrument (from Thermo-Finnigan) with direct injection using Excalibur software. EIHR experiments were performed on an Autospec Premier instrument (from Waters) using MassLynx software.

Elemental analyses were performed at the Microanalytical Laboratory at the University of California, Berkeley using a Perkin Elmer 2400 Series II combustion analyzer equipped for determination of %C, %H and %N (as well as %S). Single crystal X-ray diffraction experiments were performed on the CheXray crystallography facility at the University of California, Berkeley with a Bruker APEX-II CCD area detector using Mo K\(\alpha\) radiation (\(\lambda = 0.71073\) Å) monochromated by QUAZAR multilayer mirrors. Crystals were kept at 100(2) K during data collection. Data collection was performed using Bruker APEX2 software. Unit cell refinement and data reduction were performed using Bruker SAINT software. Structures were solved in WinGX using SHELXT-2014 software and refined with SHELXL-2014 software using anisotropic parameters. All thermal ellipsoid graphics were rendered using ORTEP-32 software.
Synthesis of Ligands and Pt(II) Complexes.

Scheme S1. General N-N' Ligand Synthetic Route.

Synthesis of \((E)-4-(\text{tert}-\text{butyl})-2-(1-(2\text{-phenylhydrazono})\text{ethyl})\text{pyridine} \text{ (S3a)}\). Aryl hydrazine S2a (0.60 mL, 5.7 mmol, 1 equiv) and 4-\text{tert}-\text{butyl}-2-acetylpyridine (1.0 g, 5.7 mmol, 1 equiv) were dissolved in absolute ethanol (10 mL) with catalytic glacial acetic acid (ca. 2 pipette drops) and refluxed at 90 °C for 4 h under air until judged complete by TLC (10% ethyl acetate/hexanes). Upon completion, the reaction mixture was cooled to ambient temperature and then diluted with water (50 mL). The crude mixture was extracted with dichloromethane (3 x 50 mL). The organic layers were combined, washed with brine (50 mL), dried over Na\(_2\)SO\(_4\), and filtered. Volatile components were removed under reduced pressure yielding the title compound as an orange solid (1.3 g, 87 %). \(^1\)H NMR (dichloromethane-\(d_2\), 600.1 MHz): \(\delta 8.44 \text{ (d, } J = 5.3 \text{ Hz, 1H)}, 8.19 \text{ (s, 1H, N–H)}, 7.63 \text{ (s, 1H)}, 7.30 \text{ (t, } J = 7.7 \text{ Hz, 2H)}, 7.22 \text{ (d, } J = 7.4 \text{ Hz, 3H)}, 6.90 \text{ (t, } J = 7.2 \text{ Hz, 1H)}, 2.38 \text{ (s, 3H, N=CCH}3\), 1.37 \text{ (s, 9H, 'Bu)}). \(^{13}\)C\({^{1}\text{H}}\) NMR (dichloromethane-\(d_2\), 150.9 MHz): \(\delta 160.5, 156.5, 148.4, 143.4, 129.7, 120.8, 120.3, 116.8, 113.6, 112.9, 35.1, 30.7, 10.3\) HRMS (EI) \(m/z\): [M] \(^+\) Calcd for C\(_{17}\)H\(_{21}\)N\(_3\) 267.1735; Found 267.1729.

Synthesis of 2-(4-(\text{tert}-\text{butyl})pyridin-2-yl)-1\text{H}-\text{indole} \text{ (1a, 'BuPyInd)}. Hydrazine S3a (1.3 g, 4.9 mmol, 1 equiv) was heated to 140 °C in neat polyphosphoric acid (3 mL) under air for 1.5 h using a large stir bar to ensure thorough mixing. After completion, the reaction mixture was cooled to ambient temperature and quenched with NaOH\textsubscript{(aq)} (150 mL, 20 wt%). The crude
mixture was extracted with dichloromethane (4 x 50 mL). The organic layers were combined, washed with brine (50 mL), dried over MgSO₄, and filtered. Volatile components were removed under reduced pressure to afford an orange solid. Purification by SiO₂ column chromatography (eluting with 10% ethyl acetate/hexanes) afforded the title compound as an off-white powder (0.59 g, 48%). ¹H NMR (benzene-d₆, 400.1 MHz): δ 9.57 (s, 1H), 8.42 (dd, J = 5.3, 0.6 Hz, 1H), 7.76 – 7.71 (m, 1H), 7.69 (dd, J = 1.8, 0.6 Hz, 1H), 7.21 – 7.18 (m, 2H), 7.08 – 7.02 (m, 1H), 6.95 (dd, J = 2.0, 0.8 Hz, 1H), 6.77 (dd, J = 5.3, 1.9 Hz, 1H), 1.08 (s, 9H). ¹H NMR (dichloromethane-d₂, 400.1 MHz): δ 9.83 (s, 1H, N–H), 8.48 (d, J = 5.3 Hz, 1H), 7.82 (d, J = 1.9 Hz, 1H), 7.64 (d, J = 7.9 Hz, 1H), 7.43 (d, J = 8.3 Hz, 1H), 7.23 – 7.16 (m, 2H), 7.09 (t, J = 7.8 Hz, 1H), 7.05 (d, J = 2.1 Hz, 1H), 1.38 (s, 9H, 'Bu). ¹³C {¹H} NMR (dichloromethane-d₂, 150.9 MHz): 161.3, 150.6, 149.4, 137.7, 136.9, 129.6, 123.3, 121.4, 120.4, 120.1, 117.1, 111.7, 100.2, 35.2, 30.7. HRMS (EI) m/z: [M]⁺ Calcd for C₁₇H₁₈N₂ 250.1470; Found 250.1470.

Synthesis of (BuPyInd)PtPh(SMe₂) (2a). Cis-(SMe₂)₂PtPh₂ (200 mg, 0.42 mmol, 1.1 equiv) and 1a (100 mg, 0.40 mmol, 1 equiv) were dissolved in benzene (20 mL). The reaction mixture was allowed to stir at ambient temperature for 5 h. Volatile components were then removed under reduced pressure. Under ambient atmosphere, SiO₂ column chromatography (eluting with 10% ethyl acetate/hexanes) provided the title compound as a yellow solid (220 mg, 95%). X-Ray quality crystals were obtained by slow diffusion of pentane into toluene at -35 °C. ¹H NMR (benzene-d₆, 600.1 MHz): δ 8.31 (d, J = 8.3 Hz, 1H), 8.03 (d, J = 7.8 Hz, 1H), 7.74 (d with ¹⁹⁵Pt satellites, d_JHH = 7.2 Hz, J_PtH = 33 Hz, 2H), 7.67 (d, J = 6.3 Hz, 1H), 7.55 (s, 1H), 7.45 (t, J = 7.4 Hz, 1H), 7.33 (t, J = 7.2 Hz, 1H), 7.27 – 7.17 (m, 3H), 7.15 – 7.12 (m, 1H), 5.83 (d, J = 5.9 Hz, 1H), 1.54 (s with ¹⁹⁵Pt satellites, d_JPtH = 53 Hz, 6H, SMe₂), 0.84 (s, 9H, 'Bu). ¹H NMR (dichloromethane-d₂, 400.1 MHz): δ 7.88 (dd, J = 8.3, 0.8 Hz, 1H), 7.78 (d, J = 2.0 Hz, 1H), 7.62 – 7.56 (m, 3H), 7.53 (d, J = 6.6 Hz, 1H), 7.10 (t, J = 7.2 Hz, 2H), 7.05 – 6.97 (m, 3H), 6.89 (t, J = 7.7 Hz, 1H), 6.80 (dd, J = 6.4, 2.2 Hz, 1H), 2.31 (s with ¹⁹⁵Pt satellites, d_JPtH = 56 Hz, 6H, SMe₂), 1.31 (s, 9H, 'Bu). ¹³C {¹H} NMR (benzene-d₆, 150.9 MHz): δ 162.0, 160.0, 149.9, 148.6, 147.1, 146.8, 139.1, 138.0, 132.6, 123.7, 122.6, 122.3, 118.3, 118.1, 116.4, 115.1, 103.2, 34.7, 29.8, 22.9. Anal. Calcd for C₂₅H₂₈N₂PtS: C, 51.45; H, 4.84; N, 4.80; S, 5.49. Found: C, 51.13; H, 4.92; N, 4.55; S, 5.35.

Synthesis of (E)-4-(tert-butyl)-2-(1-(2-(2,5-difluorophenyl)hydrazono)ethyl) pyridine (S3b). Aryl hydrazine S2b (0.66 g, 4.5 mmol, 1.3 equiv) and 4-tert-butyl-2-acetylpyridine (0.64 g, 3.6 mmol, 1 equiv) were dissolved in absolute ethanol (10 mL) with catalytic glacial acetic acid (ca. 2 pipette drops) and refluxed at 90 °C for 4 h under air until judged complete by TLC (10% ethyl acetate/hexanes). Upon completion, the reaction mixture was cooled to ambient temperature. Volatile components were removed under reduced pressure to afford an orange solid. Recrystallization from hexanes yielded the title compound as a yellow solid (0.88 g, 81%). ¹H NMR (dichloromethane-d₂, 600.1 MHz): δ 8.47 (dd, J = 5.2, 0.6 Hz, 1H), 8.18 (d, J = 1.3 Hz, 1H), 7.68 (s, 1H, N–H), 7.37 (ddd, J = 10.0, 6.6, 3.1 Hz, 1H), 7.26 (dd, J = 5.3, 1.9 Hz, 1H), 7.02

---

S5
(ddd, J = 11.1, 8.9, 4.9 Hz, 1H), 6.55 – 6.44 (m, 1H), 2.41 (s, 3H, N=CCH₃), 1.38 (s, 9H, "Bu).

13C{¹H} NMR (dichloromethane-d₂, 150.9 MHz): δ 161.2, 160.7, 159.6, 156.2, 148.9, 147.7, 147.0, 146.2, 135.2, 135.1, 135.0, 121.0, 117.2, 116.1, 116.0, 115.9, 105.8, 105.7, 105.6, 102.3, 102.1, 35.3, 30.9, 10.8 (fluorinated carbons difficult to observe and assign due to complicated C–F couplings). 19F NMR (dichloromethane-d₂, 376.4 MHz): δ -116.23 (br s), -141.45 (br s). HRMS (EI) m/z: [M]⁺ Calcd for C₁₇H₁₉N₃F₂, 303.1547; Found, 303.1549.

Synthesis of 2-(4-(tert-butyl)pyridin-2-yl)-4,7-difluoro-1H-indole (1b, "BuPyInd-4,5-F₂). Hydrazone S3b (0.75 g, 2.5 mmol, 1 equiv) was heated to 110 °C in neat polyphosphoric acid (10 mL) for 4 h under air using a large stir bar to ensure thorough mixing. After completion, the reaction mixture was cooled to ambient temperature and quenched with NaOH (aq) (200 mL, 20 wt%). The crude mixture was extracted with diethyl ether (3 x 100 mL). The organic layers were combined, washed with brine (50 mL), dried over MgSO₄, and filtered. Volatile components were removed under reduced pressure to afford an orange/yellow solid. Purification by SiO₂ column chromatography (eluting with 10% ethyl acetate/hexanes) afforded the title compound as a yellow powder (0.11 g, 15%).

Hydrazone S3b (110 mg, 0.39 mmol, 1.1 equiv) were reacted with 19F NMR (dichloromethane-d₂, 376.4 MHz): δ -127.61 (dd, J = 22.5, 9.5 Hz), -139.43 (dd, J = 22.2, 10.3 Hz). HRMS (EI) m/z: [M]⁺ Calcd for C₁₇H₁₆N₂F₂ 286.1282; Found, 286.1284.

Synthesis of ("BuPyInd-4,7-F₂)PtPh(SMe₂) (2b). In a manner similar to that used above for 2a, cis-(SMe₂)₂PtPh₂ (175 mg, 0.37 mmol, 1 equiv) and 1b (110 mg, 0.39 mmol, 1 equiv) were dissolved in benzene (20 mL). Purification by SiO₂ column chromatography (eluting with 10% ethyl acetate/hexanes) yielded the title compound as a yellow solid (202 mg, 88%). X-Ray quality crystals were obtained by slow diffusion of pentane into toluene at -35 °C. 1H NMR (dichloromethane-d₂, 600.1 MHz): δ 7.85 (d, J = 1.5 Hz, 1H), 7.56 (d, J = 7.2 Hz, 2H), 7.52 (d, J = 6.3 Hz, 1H), 7.19 (d, J = 2.6 Hz, 1H), 7.10 (t, J = 7.4 Hz, 2H), 6.03 (t, J = 7.3 Hz, 1H), 6.87 (dd, J = 6.2, 1.9 Hz, 1H), 6.63 (ddd, J = 12.2, 8.3, 3.9 Hz, 1H), 6.47 (td, J = 9.2, 2.5 Hz, 1H), 2.18 (s with 195Pt satellites, Jpₚt = 58 Hz, 6H, SMe₂). 1.32 (s, 9H, "Bu). 13C{¹H} NMR (dichloromethane-d₂, 150.9 MHz): δ 163.8, 158.5, 154.6, 153.0, 152.9, 149.9, 149.8, 148.8, 148.5, 148.2, 148.1, 143.5, 137.5, 136.9, 136.8, 136.7, 136.76, 128.8, 124.0, 123.8, 123.7, 123.6, 123.5, 119.8, 117.5, 105.8, 105.7, 105.6, 101.04, 100.99, 100.90, 100.8, 99.0, 35.8, 30.4, 24.3 (fluorinated carbons difficult to observe and assign due to complicated C–F couplings). 19F NMR (dichloromethane-d₂, 376.4 MHz): δ -127.70 (ddd, J = 23.3, 9.5, 4.0 Hz), -129.99 (dd, J = 23.3, 12.3 Hz). Anal. Calcd for C₂₅H₂₀F₂₃N₃PtS: C, 48.46; H, 4.23; N, 4.52. Found: C, 48.66; H, 4.31; N, 4.50.
Synthesis of (E)-4-(tert-butyl)-2-(1-(2,3,4,5-tetrafluorophenyl)hydrazono)ethyl pyridine (S3c). Aryl hydrazine S2c (1.8 g, 9.7 mmol, 1.3 equiv) and 4-tert-butyl-2-acetylpyridine (1.4 g, 7.8 mmol, 1 equiv) were dissolved in absolute ethanol (40 mL) with catalytic glacial acetic acid (ca. 2 pipette drops) and refluxed under air at 110 °C for 4 h. Volatile components were removed under reduced pressure to afford an orange/yellow solid. Purification by SiO₂ column chromatography (eluting with 10% ethyl acetate/hexanes and then 50% ethyl acetate/hexanes) afforded the title compound as a yellow powder (0.25 g, 27%).

Synthesis of 2-(4-(tert-butyl)pyridin-2-yl)-4,5,6,7-tetrafluoro-1H-indole (1c, 'BuPyInd-4,5,6,7-F₄). Hydrazine S3c (1.0 g, 2.9 mmol, 1 equiv) was heated to 110 °C in neat polyphosphoric acid (7 mL) for 4 h under air using a large stir bar to ensure thorough mixing. After completion, the reaction mixture was cooled to ambient temperature and quenched with NaOH(aq) (150 mL, 10 wt%). The crude mixture was extracted with dichloromethane (4 x 50 mL). The organic layers were combined, washed with brine (100 mL), dried over MgSO₄, and filtered. Volatile components were removed under reduced pressure to afford an orange/yellow solid. Purification by SiO₂ column chromatography (eluting with 5% ethyl acetate/hexanes) afforded the title compound as a yellow powder (0.25 g, 27%).

Synthesis of ('BuPyInd-4,5,6,7-F₄)PtPh(SMe₂) (2c). In a manner similar to that used above for 2a, cis-(SMe₂)₂PtPh₂ (121 mg, 0.26 mmol, 1.1 equiv) and 1c (75 mg, 0.23 mmol, 1 equiv) were dissolved in benzene (20 mL). Purification by SiO₂ column chromatography (eluting with 10%...
ethyl acetate/hexanes) yielded the title compound as a yellow solid (131 mg, 86%). X-Ray quality crystals were obtained by slow diffusion of pentane into toluene at -35 °C. $^1$H NMR (benzene-$d_6$, 600.1 MHz): $\delta$ 7.58 (d, $J = 7.4$ Hz, 2H), 7.53 (d, $J = 6.3$ Hz, 1H), 7.40 (s, 1H), 7.21 (s, 1H), 7.17–7.10 (m, 3H), 7.07 (t, $J = 7.1$ Hz, 1H), 5.86 (d, $J = 5.8$ Hz, 1H), 1.49 (s with $^{195}$Pt satellites, $J_{PtH} = 55$ Hz, 6H, SMe$_2$), 0.80 (s, 9H, tBu).

$^{13}$C{$^1$H} NMR (benzene-$d_6$, 150.9 MHz): $\delta$ 162.3, 157.9, 149.0, 148.9, 148.8, 148.2, 143.2, 137.0, 136.5, 136.4, 134.4, 134.3, 134.2, 132.8, 132.7, 132.6, 131.5, 131.4, 123.6, 119.9, 118.7, 117.8, 117.7, 117.6, 117.6, 116.3, 99.3, 34.4, 29.3, 22.6. (fluorinated carbons difficult to observe and assign due to complicated couplings).

$^{19}$F NMR (dichloromethane-$d_2$, 376.4 MHz): $\delta$ -151.69 (td, $J = 20.6, 18.6, 4.6$ Hz), -153.35 (dd, $J = 20.8, 15.2$ Hz), -169.26 (td, $J = 20.2, 3.9$ Hz), -173.48 (td, $J = 20.1, 4.0$ Hz).

Anal. Calcd for C$_{25}$H$_{24}$F$_4$N$_2$PtS: C, 45.80; H, 3.69; N, 4.27; S, 4.89. Found: C, 45.99; H, 3.69; N, 4.08; S, 5.05.

Synthesis of (E)-2-(1-(2-phenylhydrazono)ethyl)pyridine (S3d). A mixture of aryl hydrazine S2a (2.0 mL, 20 mmol, 1 equiv) and 2-acetylpyridine (2.3 mL, 20 mmol, 1 equiv) in absolute ethanol (20 mL) with catalytic glacial acetic acid (ca. 2 pipette drops) was heated to 90 °C for 2 h under air until reaction was judged complete by TLC (10% ethyl acetate/hexanes). Upon completion, the reaction mixture was cooled to 0 °C, resulting in the formation of orange needles. The solution was filtered and the solid was washed with cold absolute ethanol. Residual volatile components were removed under reduced pressure to afford the title compound as orange needles (3.1 g, 73%). $^1$H NMR (dimethyl sulfoxide-$d_6$, 600.1 MHz): $\delta$ 9.49 (s, 1H, NH), 8.52 (d, $J = 4.7$ Hz, 1H, Py), 8.11 (d, $J = 8.1$ Hz, 1H, Py), 7.76 (td, $J = 7.7, 1.9$ Hz, 1H, Py), 7.31 – 7.22 (m, 5H, C$_6$H$_5$), 6.80 (tt, $J = 7.2, 1.3$ Hz, 1H, Py), 2.34 (s, 3H, N=CCH$_3$).

$^{13}$C{$^1$H} NMR (dimethyl sulfoxide-$d_6$, 150.9 MHz): $\delta$ 156.2, 148.3, 145.5, 141.4, 136.1, 128.9, 122.2, 119.4, 119.2, 113.0, 11.0. HRMS (ESI) m/z: [M + H]$^+$ Calcd for C$_{13}$H$_{14}$N$_3$212.1182; Found 212.1177.

Synthesis of 2-(pyridin-2-yl)-1H-indole (1d, PyInd). Hydrazone S3d (1.0 g, 4.7 mmol, 1 equiv) was heated to 140 °C in neat polyphosphoric acid (3 mL) for 2 h under air using a large stir bar to ensure thorough mixing. After completion, the reaction mixture was cooled to ambient temperature and quenched with NaOH (aq) (50 mL, 20 wt%). The crude mixture was extracted with dichloromethane (4 x 50 mL). The organic layers were combined, washed with brine (50 mL), dried over MgSO$_4$, and filtered. Volatile components were removed under reduced pressure to afford an orange solid. Purification by SiO$_2$ column chromatography (eluting with 10% ethyl acetate/hexanes) afforded the title compound as a yellow powder (0.32 g, 35%). $^1$H NMR (dichloromethane-$d_2$, 600.1 MHz): $\delta$ 9.68 (s, 1H, N–H), 8.58 (d, $J = 4.8$ Hz, 1H, Py), 7.63 (d, $J = 8.0$ Hz, 1H, Py), 7.15 (t, $J = 7.7, 1.8$ Hz, 1H, Py), 7.42 (d, $J = 8.2$ Hz, 1H, Py), 7.15 – 7.10 (m, 2H), 7.09 (t, $J = 7.5$ Hz, 1H), 7.04 – 7.03 (m, 1H). $^{13}$C{$^1$H} NMR (dichloromethane-$d_2$, 150.9 MHz): $\delta$ 151.0, 149.4, 137.2, 137.0, 136.9, 129.6, 123.5, 122.5, 121.5, 120.5, 120.2, 111.7, 100.7. HRMS (ESI) m/z: [M + H]$^+$ Calcd for C$_{13}$H$_{11}$N$_2$ 195.0917; Found 195.0913.
Synthesis of (PyInd)PtPh(SMe$_2$) (2d). In a manner similar to that used above for 2a, cis-(SMe$_2$)$_2$PtPh$_2$ (75 mg, 0.16 mmol, 1 equiv) and 1d (39 mg, 0.20 mmol, 1.3 equiv) were dissolved in benzene (20 mL). The crude product was washed with 10% ethyl acetate/hexanes solution (20 mL) to afford the title compound as a yellow solid (81 mg, 97%). $^1$H NMR (dichloromethane-d$_2$, 600.1 MHz): $\delta$ 7.88 (d, $J = 8.4$ Hz, 1H), 7.81 (d, $J = 8.1$ Hz, 1H), 7.71 (td, $J = 7.7$, 1.6 Hz, 1H), 7.67 (dd, $J = 5.9$, 1.3 Hz, 1H), 7.65 – 7.55 (m, 3H), 7.11 (t, $J = 7.4$ Hz, 2H), 7.05 – 6.96 (m, 3H), 6.90 (ddd, $J = 7.9$, 6.7, 1.0 Hz, 1H), 6.77 (ddd, $J = 7.3$, 6.0, 1.6 Hz, 1H), 2.31 (s with $^{195}$Pt satellites, $J_{PtH} = 61$ Hz, 6H), SMe$_2$).

$^{13}$C{$^1$H} NMR (dichloromethane-d$_2$, 150.9 MHz): $\delta$ 159.9, 149.3, 149.1, 147.9, 147.6, 138.6, 137.6, 134.6, 128.6, 123.8, 122.3, 121.7, 121.0, 120.4, 117.9, 114.7, 102.7, 23.8. Anal. Calcd for C$_{21}$H$_{20}$N$_2$PtS: C, 47.81; H, 3.82; N, 5.31. Found: C, 47.99; H, 3.56; N, 5.29.

Synthesis of (E)-2-(1-(2-(4-methoxyphenyl)hydrazono)ethyl)pyridine (S3e). A mixture of aryl hydrazine S$_2$e (as the HCl salt, 3.6 g, 20 mmol, 1 equiv) and 2-acetylpyridine (2.3 mL, 20 mmol, 1 equiv) in absolute ethanol (20 mL) with catalytic glacial acetic acid (ca. 2 pipette drops) was heated to 90 °C for 3 h under air until reaction was judged complete by TLC (10% ethyl acetate/hexanes). Upon completion, the reaction mixture was cooled to 0 °C, resulting in the formation of an orange/red solid. The solution was filtered and the solid was washed with cold absolute ethanol. Residual volatile components were removed under reduced pressure to afford the title compound as a dark orange powder (4.2 g, 85%).

$^1$H NMR (dimethyl sulfoxide-d$_6$, 600.1 MHz): $\delta$ 10.47 (s, 1H, N–H), 8.69 (d, $J = 5.6$ Hz, 1H), 8.41 (t, $J = 7.7$ Hz, 1H), 8.21 (d, $J = 8.3$ Hz, 1H), 7.73 (t, $J = 6.5$ Hz, 1H), 7.60 (d, $J = 8.8$ Hz, 2H), 6.88 (d, $J = 8.9$ Hz, 2H), 3.72 (s, 3H, OMe), 2.39 (s, 3H, N=CCH$_3$).

$^{13}$C{$^1$H} NMR (dimethyl sulfoxide-d$_6$, 150.9 MHz): $\delta$ 154.4, 149.7, 144.9, 142.0, 137.9, 136.4, 128.6, 123.8, 122.3, 121.7, 121.0, 120.4, 117.9, 114.7, 102.7, 23.8. HRMS (EI) m/z: [M]$^+$ Calcd for C$_{14}$H$_{15}$N$_3$O 241.1215; Found 241.1212.

Synthesis of 5-methoxy-2-(pyridin-2-yl)-1H-indole (1e, PyInd-5-MeO). Hydrazine S3e (0.70 g, 2.9 mmol, 1 equiv) was dissolved in glacial acetic acid (10 mL). The reaction mixture was heated to 115 °C under a flow of N$_2$ for 28 h, after which the reaction mixture was cooled to ambient temperature. The reaction mixture was quenched with KOH (aq) (100 mL, 20 wt%). The crude mixture was extracted with dichloromethane (3 x 50 mL). The organic layers were combined, washed with brine, dried over MgSO$_4$, and filtered. The crude mixture was purified by SiO$_2$ column chromatography (eluting with 50% chloroform/toluene and then chloroform) to afford the title compound as a yellow solid (0.084 g, 13%). $^1$H NMR (dichloromethane-d$_2$, 600.1 MHz): $\delta$ 9.65 (s, 1H, N–H), 8.57 (dt, $J = 4.9$, 1.3 Hz, 1H), 7.80 (dt, $J = 8.1$, 1.1 Hz, 1H), 7.74 (td, $J = 7.7$, 1.8 Hz, 1H), 7.29 (d, $J = 8.8$ Hz, 1H), 7.18 (ddd, $J = 7.4$, 4.8, 1.2 Hz, 1H), 7.09 (d, $J = 2.4$ Hz, 1H), 6.96 (dd, $J = 2.0$, 0.9 Hz, 1H), 6.85 (dd, $J = 8.8$, 2.4 Hz, 1H), 3.84 (s, 3H, OMe).

$^{13}$C{$^1$H} NMR (dichloromethane-d$_2$, 150.9 MHz): $\delta$ 154.9, 150.7, 149.6, 137.8, 137.0, 132.2,
130.0, 122.4, 120.1, 114.1, 112.5, 102.6, 100.5, 56.0. HRMS (EI) m/z: [M]^+ Calcd for C_{14}H_{22}N_{2}O 224.0950; Found 224.0951.

**Synthesis of (PyInd-5-MeO)PtPh(SMe$_2$) (2e).** Cis-(SMe$_2$)$_2$PtPh$_2$ (40 mg, 0.08 mmol, 1 equiv) and 1e (19 mg, 0.08 mmol, 1 equiv) were dissolved in benzene (20 mL). The reaction mixture was allowed to stir at 50 °C for 20 h. Volatile components were then removed under reduced pressure. The crude product was triturated with 10% ethyl acetate/hexanes solution (20 mL) to afford the title compound as a yellow solid (36 mg, 77%).

**1H NMR** (dichloromethane-d$_2$, 600.1 MHz): δ 7.77 (d, J = 9.0 Hz, 1H), 7.75 (d, J = 8.6 Hz, 1H), 7.68 (ddd, J = 8.5, 5.8, 1.5 Hz, 1H), 7.64 (d, J = 6.0 Hz, 1H), 7.62 – 7.57 (m, 2H), 7.10 (t, J = 7.5 Hz, 2H), 7.05 – 7.01 (m, 1H), 7.00 (d, J = 2.6 Hz, 1H), 6.93 (s, 1H), 6.74 (ddd, J = 8.9, 2.6 Hz, 1H), 3.82 (s, 3H, OMe), 2.30 (s with 195Pt satellites, J$_{PtH}$ = 58 Hz, 6H, SMe$_2$).

**13C{$_1$H} NMR** (dichloromethane-d$_2$, 150.9 MHz): δ 153.1, 149.2, 147.0, 146.9, 146.6, 145.8, 138.5, 137.5, 137.0, 128.5, 123.7, 120.6, 120.2, 115.5, 113.9, 102.2, 101.5, 55.8, 23.7. Anal. Calcd for C$_{22}$H$_{22}$N$_2$OPtS • 0.5 CD$_2$Cl$_2$: C, 44.96; H, 4.02; N, 4.66. Found: C, 45.15; H, 3.74; N, 4.40.

**Synthesis of (E)-2-(1-(2-(p-tolyl)hydrazono)ethyl)pyridine (S3f).** A mixture of aryl hydrazine S$_2$f (as the HCl salt, 2.2 g, 14 mmol, 1 equiv) and 2-acetylpyridine (1.6 mL, 14 mmol, 1 equiv) in absolute ethanol (30 mL) with catalytic glacial acetic acid (ca. 2 pipette drops) was heated to 90 °C for 2 h under air until reaction was judged complete by TLC (10% ethyl acetate/hexanes). Upon completion, the reaction mixture was cooled to 0 °C, resulting in the formation of an orange solid. The solution was filtered and the solid was washed with cold absolute ethanol. Residual volatile components were removed under reduced pressure to afford the title compound as an orange powder (2.5 g, 78%).

**1H NMR** (dimethyl sulfoxide-d$_6$, 600.1 MHz): δ 10.26 (s, 1H, N–H), 8.67 (d, J = 5.6 Hz, 1H), 8.37 (t, J = 8.1 Hz, 1H), 8.23 (d, J = 8.2 Hz, 1H), 7.71 (t, J = 6.6 Hz, 1H), 7.45 (d, J = 8.0 Hz, 2H), 7.11 (d, J = 8.0 Hz, 2H), 2.37 (s, 3H, N=CCH$_3$), 2.25 (s, 3H, Me).

**13C{$_1$H} NMR** (dimethyl sulfoxide-d$_6$, 150.9 MHz): δ 149.9, 144.7, 142.4, 141.9, 131.8, 130.1, 129.4, 123.4, 122.4, 114.4, 20.4, 11.9. HRMS (ESI) m/z: [M + H]^+ Calcd for C$_{22}$H$_{22}$N$_3$ 226.1334; Found 226.1339.

**Synthesis of 5-methyl-2-(pyridin-2-yl)-1H-indole (1f, PyInd-5-Me).** Hydrazone S3f (1.0 g, 4.4 mmol, 1 equiv) was heated to 140 °C in neat polyphosphoric acid (3 mL) for 1 h under air using a large stir bar to ensure thorough mixing. After completion, the reaction mixture was cooled to ambient temperature and quenched with NaOH$_{aq}$ (150 mL, 10 wt%). The crude mixture was extracted with dichloromethane (4 x 50 mL). The organic layers were combined, washed with brine (50 mL), dried over MgSO$_4$, and filtered. Volatile components were removed under
reduced pressure to afford an orange solid. Purification by SiO\textsubscript{2} column chromatography (eluting with 10% ethyl acetate/hexanes) afforded the title compound as a white powder (0.31 g, 33%). \textsuperscript{1}H NMR (dichloromethane-\textit{d}\textsubscript{2}, 600.1 MHz): \(\delta\) 9.49 (s, 1H, N–H), 8.56 (dt, \(J = 5.0, 1.4\) Hz, 1H), 7.80 (dt, \(J = 8.3, 1.2\) Hz, 1H), 7.73 (td, \(J = 7.7, 1.8\) Hz, 1H), 7.42 (d, \(J = 8.3\) Hz, 1H), 7.18 (ddd, \(J = 7.4, 4.9, 1.3\) Hz, 1H), 7.04 (d, \(J = 8.3\) Hz, 1H), 6.94 (d, \(J = 1.8\) Hz, 1H), 2.43 (s, 3H, Me). \textsuperscript{13}C\{\textsuperscript{1}H\} NMR (dichloromethane-\textit{d}\textsubscript{2}, 150.9 MHz): \(\delta\) 150.8, 149.6, 137.3, 137.0, 135.3, 129.9, 129.8, 125.3, 122.3, 121.0, 120.1, 111.4, 100.2, 21.6. HRMS (ESI) m/z: [M + H]\textsuperscript{+} Calcd for C\textsubscript{14}H\textsubscript{13}N\textsubscript{2} 209.1073; Found 209.1069.

Synthesis of (PyInd-5-Me)PtPh(SMe\textsubscript{2}) (2f). In a manner similar to that used above for 2a, cis-(SMe\textsubscript{2})\textsubscript{2}PtPh\textsubscript{2} (75 mg, 0.16 mmol, 1 equiv) and 1f (42 mg, 0.20 mmol, 1.3 equiv) were dissolved in benzene (10 mL). The crude product was triturated with 10% ethyl acetate/hexanes solution (20 mL) to afford the title compound as a yellow solid (75 mg, 88%). \textsuperscript{1}H NMR (dichloromethane-\textit{d}\textsubscript{2}, 600.1 MHz): \(\delta\) 7.76 (dd, \(J = 8.9, 2.2\) Hz, 2H), 7.72 – 7.64 (m, 2H), 7.60 (d with \(\textsuperscript{195}Pt\) satellites, \(J_{\text{HH}} = 6.7\) Hz, \(J_{\text{PhH}} = 31\), 2H), 7.35 (s, 1H), 7.11 (t, \(J = 7.5\) Hz, 2H), 7.02 (td, \(J = 7.2, 1.5\) Hz, 1H), 6.92 (s, 1H), 6.86 (dd, \(J = 8.4, 1.8\) Hz, 1H), 6.73 (ddd, \(J = 7.2, 5.8, 1.5\) Hz, 1H), 2.38 (s, 3H, Me), 2.30 (s with \(\textsuperscript{195}Pt\) satellites, \(J_{\text{PhH}} = 59\) Hz, 6H, SMe\textsubscript{2}). \textsuperscript{13}C\{\textsuperscript{1}H\} NMR (dichloromethane-\textit{d}\textsubscript{2}, 150.9 MHz): \(\delta\) 159.9, 149.2, 147.6, 146.3, 146.0, 138.5, 137.6, 132.2, 128.6, 126.9, 124.5, 123.8, 121.0, 120.7, 120.3, 114.4, 102.2, 23.8, 21.7. Anal. Calcd for C\textsubscript{22}H\textsubscript{22}N\textsubscript{2}PtS: C, 48.79; H, 4.09; N, 5.17. Found: C, 49.07; H, 3.89; N, 4.80.

Synthesis of (E)-2-(1-(2-(4-fluorophenyl)hydrazono)ethyl)pyridine (S3g). A mixture of aryl hydrazine S2g (as the HCl salt, 2.0 g, 12 mmol, 1 equiv) and 2-acetylpyridine (1.4 mL, 12 mmol, 1 equiv) in absolute ethanol (30 mL) with catalytic glacial acetic acid (ca. 2 pipette drops) was heated to 90 °C for 3 h under air until reaction was judged complete by TLC (10% ethyl acetate/hexanes). Upon completion, the reaction mixture was cooled to 0 °C, resulting in the formation of an orange/yellow solid. The solution was filtered and the solid was washed with cold absolute ethanol. Residual volatile components were removed under reduced pressure to afford the title compound as a yellow powder (2.7 g, 83%). \textsuperscript{1}H NMR (dimethyl sulfoxide-\textit{d}\textsubscript{6}, 600.1 MHz): \(\delta\) 10.48 (s, 1H, N–H), 8.71 (d, \(J = 5.3\) Hz, 1H), 8.41 (t, \(J = 8.3\) Hz, 1H), 8.25 (d, \(J = 8.3\) Hz, 1H), 7.75 (t, \(J = 6.6\) Hz, 1H), 7.63 (dd, \(J = 8.8, 4.7\) Hz, 2H), 7.13 (t, \(J = 8.9\) Hz, 2H), 2.40 (s, 3H, N=CCH\textsubscript{3}). \textsuperscript{13}C\{\textsuperscript{1}H\} NMR (dimethyl sulfoxide-\textit{d}\textsubscript{6}, 150.9 MHz): \(\delta\) 158.1, 156.5, 149.9, 144.5, 142.8, 140.8, 132.9, 123.7, 122.7, 115.6, 115.5, 115.4, 12.0 (fluorinated carbons difficult to observe and assign due to complicated C–F couplings). \textsuperscript{19}F NMR (dimethyl sulfoxide-\textit{d}\textsubscript{6}, 376.4 MHz, DMSO): \(\delta\) -122.5 (br s). HRMS (ESI) m/z: [M + H]\textsuperscript{+} Calcd for C\textsubscript{13}H\textsubscript{13}N\textsubscript{3}F 230.1088; Found 230.1084.
Synthesis of 5-fluoro-2-(pyridin-2-yl)-1H-indole (1g, PyInd-5-F). Hydrazone S3g (1.0 g, 4.4 mmol, 1 equiv) was heated to 140 °C in neat polyphosphoric acid (3 mL) for 1.5 h under air using a large stir bar to ensure thorough mixing. After completion, the reaction mixture was cooled to ambient temperature and quenched with NaOH (aq) (150 mL, 10 wt%). The crude mixture was extracted with dichloromethane (4 x 50 mL). The organic layers were combined, washed with brine (50 mL), dried over MgSO₄, and filtered. Volatile components were removed under reduced pressure to afford a tan solid. Purification by SiO₂ column chromatography (eluting with 10% ethyl acetate/hexanes) afforded the title compound as a white powder (0.58 g, 62%).

**1H NMR** (dichloromethane-d₂, 600.1 MHz): δ 9.73 (s, 1H, N–H), 8.59 (d, J = 4.7 Hz, 1H), 7.82 (d, J = 7.9 Hz, 1H), 7.76 (td, J = 7.8, 1.8 Hz, 1H), 7.25 – 7.19 (m, 1H), 7.00 (d, J = 2.1 Hz, 1H), 6.96 (td, J = 9.1, 2.5 Hz, 1H).

**13C{¹H} NMR** (dichloromethane-d₂, 150.9 MHz): δ 158.8, 157.2, 149.8, 149.2, 138.5, 136.7, 133.0, 129.4, 129.3, 122.3, 119.8, 112.1, 111.4, 111.2, 105.5, 105.3, 100.2, 100.1 (fluorinated carbons difficult to observe and assign due to complicated C–F couplings).

**19F NMR** (dichloromethane-d₂, 376.4 MHz): δ -124.2 (br s). HRMS (ESI) m/z: [M + H]+ Calcd for C₁₃H₁₀F₂N₂ 213.0823; Found 213.0817.

Synthesis of (PyInd-5-F)PtPh(SMe₂) (2g). In a manner similar to that used above for 2a, cis-(SMe₂)₂PtPh₂ (75 mg, 0.16 mmol, 1 equiv) and 1g (42 mg, 0.20 mmol, 1.3 equiv) were dissolved in benzene (10 mL). The crude product was triturated with hexanes (10 mL) then 10% ethyl acetate/hexanes solution (15 mL) to afford the title compound as a yellow solid (63 mg, 73%).

**1H NMR** (dichloromethane-d₂, 600.1 MHz): δ 7.84 (dd, J = 9.1, 4.8 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.76 – 7.70 (m, 1H), 7.67 (d with 195Pt satellites, J₁HH = 6.9 Hz, J₁PH = 37, 2H), 7.20 (dd, J = 10.2, 2.7 Hz, 1H), 7.11 (t, J = 7.4 Hz, 2H), 7.03 (t, J = 7.4 Hz, 1H), 6.98 (s, 1H), 6.82 – 6.75 (m, 2H), 2.31 (s with 195Pt satellites, J₁PH = 60 Hz, 6H, SMe₂).

**13C{¹H} NMR** (dichloromethane-d₂, 150.9 MHz): δ 159.5, 157.8, 156.3, 149.3, 147.9, 145.8, 145.3, 138.7, 137.5, 128.6, 123.9, 121.3, 120.5, 115.4, 111.0, 110.8, 105.1, 104.9, 102.5, 102.4, 23.7 (fluorinated carbons difficult to observe and assign due to complicated C–F couplings).


Synthesis of (E)-2-(1-(2-(4-chlorophenyl)hydrazono)ethyl)pyridine (S3h). A mixture of aryl hydrazine S2h (as the HCl salt, 3.6 g, 20 mmol, 1 equiv) and 2-acetylpyridine (2.3 mL, 20 mmol, 1 equiv) in absolute ethanol (20 mL) with catalytic glacial acetic acid (ca. 2 pipette drops) was heated to 90 °C for 2 h under air until the reaction was judged complete by TLC (10% ethyl acetate/hexanes). Upon completion, the reaction mixture was cooled to 0 °C, resulting in the formation of an orange solid. The solution was filtered and the solid was washed with cold absolute ethanol. Residual volatile components were removed under reduced pressure to afford the title compound as a light orange powder (3.9 g, 77%).

**1H NMR** (dimethyl sulfoxide-d₆, 600.1 MHz): δ 9.73 (s, 1H, N–H), 8.59 (d, J = 4.7 Hz, 1H), 8.48 (d, J = 8.0 Hz, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.76 – 7.70 (m, 1H), 7.67 (d, J = 5.9 Hz, 1H), 7.59 (d with 195Pt satellites, J₁HH = 6.9 Hz, J₁PH = 37, 2H), 7.20 (dd, J = 10.2, 2.7 Hz, 1H), 7.11 (t, J = 7.4 Hz, 2H), 7.03 (t, J = 7.4 Hz, 1H), 6.98 (s, 1H), 6.82 – 6.75 (m, 2H), 2.31 (s with 195Pt satellites, J₁PH = 60 Hz, 6H, SMe₂).

HRMS (ESI) m/z: [M + H]+ Calcd for C₁₉H₁₃FN₂O₂: C, 308.0823; Found: C, 308.0817.
1H NMR (dichloromethane-d2, 600.1 MHz): δ 9.97 (s, 1H, N–H), 8.59 (d, J = 4.7 Hz, 1H), 7.82 (d, J = 7.9 Hz, 1H), 7.76 (td, J = 7.7, 1.8 Hz, 1H), 7.61 (d, J = 2.2 Hz, 1H), 7.32 (d, J = 8.6 Hz, 1H), 7.23 (dd, J = 7.4, 4.9 Hz, 1H), 7.15 (dd, J = 8.7, 2.0 Hz, 1H), 6.98 (d, J = 2.3 Hz, 1H). 13C{1H} NMR (dichloromethane-d2, 150.9 MHz): δ 150.2, 149.7, 138.7, 137.2, 135.3, 130.6, 125.9, 123.6, 122.9, 120.7, 120.4, 112.9, 100.2. HRMS (EI) m/z: [M]+ Calcd for C13H9N2Cl 228.0454; Found 228.0455.

Synthesis of (PyInd-5-Cl)PtPh(SMe2) (2h). In a manner similar to that used above for 2a, cis-(SMe2)2PtPh2 (45 mg, 0.10 mmol, 1 equiv) and 1h (27 mg, 0.12 mmol, 1.2 equiv) were dissolved in benzene (10 mL). The crude product was triturated with 10% ethyl acetate/hexanes solution (15 mL) to afford the title compound as a yellow solid (50 mg, 94%). 1H NMR (dichloromethane-d2, 600.1 MHz): δ 7.85 (d, J = 8.9 Hz, 1H), 7.81 (dd, J = 7.7, 1.4 Hz, 1H), 7.73 (td, J = 7.7, 1.6 Hz, 1H), 7.68 (d, J = 5.7 Hz, 1H), 7.59 (d with 195Pt satellites, JHH = 6.8 Hz, JPtH = 36 Hz, 2H), 7.54 (d, J = 2.2 Hz, 1H), 7.15 – 7.09 (m, 2H), 7.05 – 7.00 (m, 1H), 6.97 (s, 1H), 6.95 (dd, J = 8.9, 2.1 Hz, 1H), 6.81 (ddd, J = 7.5, 5.9, 1.5 Hz, 1H), 2.30 (s with 195Pt satellites, JPH = 60 Hz, 6H, SMe2). 13C{1H} NMR (dichloromethane-d2, 150.9 MHz): δ 159.3, 149.4, 147.8, 147.3, 145.2, 138.8, 137.4, 132.7, 128.7, 123.9, 123.2, 122.4, 121.5, 120.6, 120.5, 115.8, 102.0, 23.7. Anal. Calcd for C21H19ClN2PtS • 1.2CD2Cl2: C, 40.02; H, 3.60; N, 4.20. Found: C, 40.01; H, 3.60; N, 4.22.

Synthesis of (E)-2-(1-(2-(4-bromophenyl)hydrazono)ethyl)pyridine (S3i). A mixture of aryl hydrazine S2i (as the HCl salt, 3.2 g, 14 mmol, 1 equiv) and 2-acetylpyridine (1.6 mL, 14 mmol, 1 equiv) in absolute ethanol (30 mL) with catalytic glacial acetic acid (ca. 2 pipette drops) was heated to 90 °C for 2 h under air until reaction was judged complete by TLC (10% ethyl
acetate/hexanes). Upon completion, the reaction mixture was cooled to 0 °C, resulting in the formation of a light orange solid. The solution was filtered and the solid was washed with cold absolute ethanol. Residual volatile components were removed under reduced pressure to afford the title compound as an orange powder (3.6 g, 87%). $^1$H NMR (dimethyl sulfoxide-$d_6$, 600.1 MHz): $\delta$ 10.59 (s, 1H, N–H), 8.74 (d, $J = 5.0$ Hz, 1H), 8.42 (t, $J = 7.0$ Hz, 1H), 8.26 (d, $J = 6.7$ Hz, 1H), 7.78 (t, $J = 5.3$ Hz, 1H), 7.60 (d, $J = 6.0$ Hz, 2H), 7.43 (d, $J = 6.4$ Hz, 2H), 2.42 (s, 3H, N=C(CH$_3$)$_3$). $^{13}$C{${^1}$H} NMR (dimethyl sulfoxide-$d_6$, 150.9 MHz): $\delta$ 148.7, 148.5, 144.6, 143.6, 142.9, 131.5, 123.9, 122.9, 116.3, 112.4, 12.2. HRMS (ESI) m/z: [M + H]$^+$ Calcd for C$_{13}$H$_{13}$N$_3$Br 290.0287; Found 290.0286.

**Synthesis of 5-bromo-2-(pyridin-2-yl)-1H-indole (1i, PyInd-5-Br).** Hydrazine S3i (1.0 g, 3.5 mmol, 1 equiv) was heated to 140 °C in neat polyphosphoric acid (3 mL) for 1.5 h under air using a large stir bar to ensure thorough mixing. After completion, the reaction mixture was cooled to ambient temperature and quenched with KOH (aq) (100 mL, 20 wt%). The crude mixture was extracted with dichloromethane (4 x 50 mL). The organic layers were combined, washed with brine (50 mL), dried over MgSO$_4$, and filtered. Volatile components were removed under reduced pressure to afford an orange oily solid. Purification by SiO$_2$ column chromatography (eluting with 10% ethyl acetate/hexanes) afforded an oily white solid. Recrystallization from hexanes layered onto a benzene solution afforded the title compound as a white solid (0.19 g, 20%). $^1$H NMR (benzene-$d_6$, 600.1 MHz): $\delta$ 9.42 (s, 1H, N–H), 8.30 (d, $J = 4.6$ Hz, 1H), 7.85 – 7.74 (m, 1H), 7.25 (dd, $J = 8.6$, 1.9 Hz, 1H), 7.22 (d, $J = 7.9$ Hz, 1H), 7.01 (td, $J = 7.7$, 1.7 Hz, 1H), 6.61 (d, $J = 8.6$ Hz, 1H), 6.57 (d, $J = 1.6$ Hz, 1H), 6.55 (dd, $J = 7.5$, 4.8 Hz, 1H). $^{13}$C{${^1}$H} NMR (benzene-$d_6$, 150.9 MHz): $\delta$ 150.3, 149.2, 138.1, 136.4, 135.5, 131.4, 126.4, 124.0, 122.1, 120.0, 113.8, 113.3, 100.4. HRMS (ESI) m/z: [M + H]$^+$ Calcd for C$_{13}$H$_{10}$N$_2$Br 273.0022; Found 273.0018.

**Synthesis of (PyInd-5-Br)PtPh(SMe$_2$) (2i).** In a manner similar to that used above for 2a, cis-(SMe$_2$)$_2$PtPh$_2$ (63 mg, 0.13 mmol, 1 equiv) and 1i (36 mg, 0.13 mmol, 1 equiv) were dissolved in benzene (10 mL). The crude product was triturated with 10% ethyl acetate/hexanes solution (15 mL) to afford the title compound as a yellow solid (60 mg, 75%). $^1$H NMR (dichloromethane-$d_2$, 600.1 MHz): $\delta$ 7.82 – 7.79 (m, 2H), 7.74 (td, $J = 7.7$, 1.5 Hz, 1H), 7.70 (d, $J = 2.1$ Hz, 1H), 7.68 (dd, $J = 6.1$, 1.3 Hz, 1H), 7.59 (dd with $^{195}$Pt satellites, $J_{HH} = 7.7$, 1.4 Hz, $J_{PH} = 31$ Hz, 2H), 7.11 (t, $J = 7.6$ Hz, 2H), 7.07 (dd, $J = 8.9$, 2.1 Hz, 1H), 7.03 (tt, $J = 7.3$, 1.2 Hz, 1H), 6.97 (d, $J = 1.0$ Hz, 1H), 6.82 (dd, $J = 7.4$, 6.0, 1.5 Hz, 1H), 2.30 (s with $^{195}$Pt satellites, $J_{PH} = 59$ Hz, 6H, SMe$_2$). $^{13}$C{${^1}$H} NMR (dichloromethane-$d_2$, 150.9 MHz): $\delta$ 159.3, 149.4, 147.6, 147.4, 138.8, 137.4, 133.5, 128.6, 124.8, 123.9, 123.7, 121.5, 120.7, 120.6, 116.2, 110.9, 101.9, 23.7. Anal. Calcd for C$_{21}$H$_{19}$BrN$_2$PtS • 0.7CD$_2$Cl$_2$: C, 39.06; H, 3.29; N, 4.20. Found: C, 39.24; H, 3.02; N, 4.09.
Synthesis of (E)-2-(1-(2-chlorophenyl)hydrazono)ethyl)pyridine (S3j). A mixture of aryl hydrazine S2j (as the HCl salt, 3.1 g, 20 mmol, 1 equiv) and 2-acetylpyridine (2.3 mL, 20 mmol, 1 equiv) in absolute ethanol (20 mL) with catalytic glacial acetic acid (ca. 2 pipette drops) was heated to 90 °C for 2 h under air until reaction was judged complete by TLC (10% ethyl acetate/hexanes). Upon completion, the reaction mixture was cooled to 0 °C, resulting in the formation of a light yellow solid. The solution was filtered and the solid was washed with cold absolute ethanol. Residual volatile components were removed under reduced pressure to afford the title compound as a light yellow powder (3.8 g, 77%).

$^1$H NMR (dimethyl sulfoxide-d$_6$, 600.1 MHz): δ 8.90 (s, 1H, N–H), 8.74 (d, $J$ = 5.4 Hz, 1H), 8.34 – 8.28 (m, 2H), 7.98 (d, $J$ = 8.3 Hz, 1H), 7.73 (t, $J$ = 7.0 Hz, 1H), 7.44 (d, $J$ = 8.0 Hz, 1H), 6.98 (t, $J$ = 7.7 Hz, 1H), 2.46 (s, 3H, N=CCH$_3$).

$^{13}$C{ $^1$H} NMR (dimethyl sulfoxide-d$_6$, 150.9 MHz): δ 144.5, 140.1, 129.3, 128.1, 124.3, 123.1, 122.8, 122.3, 118.5, 117.6, 116.4, 11.2. HRMS (EI) m/z: [M]$^+$ Calcd for C$_{13}$H$_{12}$N$_3$Cl 245.0720; Found 245.0717.

Synthesis of 7-chloro-2-(pyridin-2-yl)-1H-indole (1j, PyInd-7-Cl). Hydrazone S3j (1.0 g, 4.1 mmol, 1 equiv) was heated to 140 °C in neat polyphosphoric acid (3 mL) for 1.5 h under air using a large stir bar to ensure thorough mixing. After completion, the reaction mixture was cooled to ambient temperature and quenched with KOH (aq) (100 mL, 20 wt%). The crude mixture was extracted with dichloromethane (4 x 50 mL). The organic layers were combined, washed with brine (50 mL), dried over MgSO$_4$, and filtered. Volatile components were removed under reduced pressure to afford an orange solid. Purification by SiO$_2$ column chromatography (eluting with 10% ethyl acetate/hexanes) afforded the title compound as a white powder (0.18 g, 19%).

$^1$H NMR (dichloromethane-d$_2$, 600.1 MHz): δ 9.74 (s, 1H, N–H), 8.61 (d, $J$ = 4.7 Hz, 1H), 7.81 (d, $J$ = 7.9 Hz, 1H), 7.75 (td, $J$ = 7.8, 1.8 Hz, 1H), 7.52 (ddd, $J$ = 8.0, 3.2, 1.2 Hz, 2H), 7.13 (s, 1H), 7.10 – 7.00 (m, 2H), 13$^3$C{ $^1$H} NMR (dichloromethane-d$_2$, 150.9 MHz): δ 150.1, 149.7, 138.1, 137.1, 134.2, 131.0, 122.9, 122.7, 121.3, 120.3, 120.2, 117.1, 101.5. HRMS (ESI) m/z: [M + H]$^+$ Calcd for C$_{13}$H$_{10}$N$_2$Cl 229.0527; Found 229.0527.

Synthesis of (PyInd-7-Cl)PtPh(SMe$_2$) (2j). Cis-(SMe$_2$)$_2$PtPh$_2$ (40 mg, 0.08 mmol, 1 equiv) and 1j (23 mg, 0.10 mmol, 1.2 equiv) were dissolved in benzene (10 mL). The reaction mixture was stirred at 50 °C for 22 h. Volatile components were removed under reduced pressure. The crude product was triturated with 25% ethyl acetate/hexanes solution (15 mL) to afford the title compound as a white powder (23 mg, 49%).

$^1$H NMR (dichloromethane-d$_2$, 600.1 MHz): δ 7.80 (d, $J$ = 8.6 Hz, 1H), 7.75 (td, $J$ = 7.7, 1.5 Hz, 1H), 7.57 – 7.54 (m, 2H), 7.52 (ddd, $J$ = 8.0, 3.2, 1.2 Hz, 2H), 7.13 (s, 1H), 7.10 – 7.04 (m, 3H), 7.03 – 6.98 (m, 1H), 6.86 (t, $J$ = 7.6 Hz, 1H), 6.82 (ddd, $J$ = 7.4, 5.9, 1.6 Hz, 1H), 2.15 (s with $^{195}$Pt satellites, $J$$_{PH}$ = 62 Hz, 6H, SMe$_2$). $^{13}$C{ $^1$H} NMR (dichloromethane-d$_2$, 150.9 MHz): δ 160.9, 159.5, 149.6, 149.1, 139.2, 138.8, 137.7, 134.4, 128.6, 124.0, 123.0, 121.5, 120.8, 120.7, 120.4, 118.9, 103.7, 24.6. Anal. Calcd for C$_{21}$H$_{19}$ClN$_2$PtS: C, 44.88; H, 3.41; N, 4.98. Found: C, 44.85; H, 3.37; N, 4.67.
Synthesis of (PyInd)PtPh(SEt)₂ (2k). [([µ-SEt]PtPh₂)_2 (45 mg, 0.05 mmol, 1 equiv) and 1d (42 mg, 0.10 mmol, 2 equiv) were dissolved in benzene (10 mL). The reaction mixture was stirred at 50 °C for 20 h. Volatile components were removed under reduced pressure. The crude product was triturated with hexanes (10 mL) then 15% ethyl acetate/hexanes solution (15 mL) to afford the title compound as a yellow solid (41 mg, 72%). ³¹H NMR (dichloromethane-d₂, 600.1 MHz): δ 8.11 (d, J = 8.5 Hz, 1H), 7.81 (d, J = 8.1 Hz, 1H), 7.70 (td, J = 7.7, 1.6 Hz, 1H), 7.66 – 7.55 (m, 4H), 7.10 (t, J = 7.5 Hz, 2H), 7.03 (s, 1H), 7.03 – 6.98 (m, 2H), 6.89 (t, J = 7.4 Hz, 1H), 6.75 (ddd, J = 7.3, 5.9, 1.6 Hz, 1H), 2.75 (dq with ¹⁹⁵Pt satellites, J_{HH} = 14.8, 7.6 Hz, J_{PtH} = 60 Hz, 2H, SCH₂CH₃), 2.55 (dq with ¹⁹⁵Pt satellites, J_{HH} = 14.1, 7.4 Hz, J_{PtH} = 71 Hz, 2H, SCH₂CH₃), 1.43 (t, J = 7.4 Hz, 6H, SCH₂CH₃). ¹³C {¹H} NMR (dichloromethane-d₂, 150.9 MHz): δ 160.8, 150.3, 150.0, 147.5, 145.9, 139.5, 138.5, 133.0, 129.5, 124.6, 123.0, 122.5, 121.8, 118.8, 116.5, 103.6, 32.6, 14.2. Anal. Calcd for C₂₃H₂₄N₂PtS • 0.4 CD₂Cl₂: C, 47.61; H, 4.37; N, 4.75. Found: C, 47.85; H, 4.02; N, 4.71.

Synthesis of (BuPyInd)PtPh(C₂H₄) (3) via Ligand Exchange with 2a. Inside a glovebox, 2a (30 mg, 0.05 mmol) was dissolved in benzene-d₆ (0.7 mL) in a low pressure/vacuum J. Young NMR tube (4 mm outer diameter, 3 mL). On a Schlenk line, the solution was thoroughly degassed by three freeze/pump/thaw cycles after which ethylene (1 atm) was added at ambient temperature. After 1 day at ambient temperature, the volatile components were removed under reduced pressure to remove SMe₂ in order to prevent back reactions. Inside a glovebox, fresh benzene-d₆ was added and degassed as described previously. Additional ethylene (1 atm) was added and the mixture was left for 1 day. This process was repeated a total of four times. The reaction mixture was concentrated under reduced pressure and passed through a SiO₂ column under ambient atmosphere (eluting with 5% ethyl acetate/hexanes and then 10% ethyl acetate/hexanes) to yield the title compound as a yellow solid (8 mg, 29%). Recrystallization by slow diffusion of pentane into a toluene solution of 3 yielded X-ray quality crystals. ¹H NMR (benzene-d₆, 600.1 MHz): δ 7.76 (t, J = 6.4 Hz, 1H), 7.69 (t, J = 6.5 Hz, 1H), 7.56 – 7.43 (m, 2H), 7.31 – 7.22 (m, 3H), 7.10 – 7.02 (m, 2H), 6.94 (d, J = 5.1 Hz, 1H), 6.76 (t, J = 5.7 Hz, 1H), 6.45 (t, J = 6.8 Hz, 1H), 6.31 (dt, J = 5.9, 2.9 Hz, 1H), 3.40 (s with ¹⁹⁵Pt satellites, J_{PtH} = 59 Hz, 4H, C₂H₄), 0.99 (s, 9H, 'Bu). ¹³C {¹H} NMR (dichloromethane-d₂, 400.1 MHz): δ 7.87 (d, J = 1.7 Hz, 1H), 7.69 (d, J = 6.0 Hz, 1H), 7.55 – 7.40 (m, 3H), 7.23 (dd, J = 6.0, 2.0 Hz, 1H), 7.15 – 7.04 (m, 3H), 7.01 (d, J = 0.8 Hz, 1H), 6.78 (tt, J = 7.5, 0.9 Hz, 1H), 6.56 (ddd, J = 8.3, 6.9, 1.3 Hz, 1H), 5.64 (dd, J = 8.6, 0.7 Hz, 1H), 3.83 (s with ¹⁹⁵Pt satellites, J_{PtH} = 59 Hz, 4H, C₂H₄), 1.39 (s, 9H, 'Bu). ¹³C {¹H} NMR (benzene-d₆, 150.9 MHz): δ 162.1, 157.5, 153.9, 148.8, 147.8, 142.2, 139.1, 137.7, 128.9, 124.6, 124.0, 121.0, 120.0, 118.8, 117.5, 116.3, 104.0, 63.9, 34.8, 29.9. Anal. Calcd for C₂₅H₂₆N₂Pt: C, 54.64; H, 4.77; N, 5.10. Found: C, 54.98; H, 4.54; N, 5.09.

Synthesis of (BuPyInd)PtPh(C₂H₄) (3) via Ligation and Phenylation of Zeise’s Dimer. A mixture of Zeise’s dimer (91 mg, 0.15 mmol, 1 equiv), 1a (77 mg, 0.31 mmol, 2 equiv), and NaO’Bu (35 mg, 0.31 mmol, 2 equiv) were dissolved in benzene (20 mL). A bright orange solid readily precipitated from solution. The mixture was stirred for 16 h at ambient temperature. Volatile components were removed under reduced pressure. Recrystallization from hexanes afforded cis/trans-(PyInd)PtCl(C₂H₄) as an orange solid (114 mg, 72%) which was identified by ¹H NMR spectroscopy and used without further purification. ¹H NMR (dichloromethane-d₂,
300.1 MHz): δ 8.60 (d, J = 8.5 Hz, 1H), 7.78 (d, J = 2.3 Hz, 1H), 7.56 (d, J = 8.1 Hz, 1H), 7.41 (d, J = 6.6 Hz, 1H), 7.19 – 7.06 (m, 2H), 7.04 – 6.93 (m, 2H), 4.67 – 4.36 (m, 2H, C₂H₄), 4.42 – 3.97 (m, 2H, C₂H₄), 1.38 (s, 9H, tBu).

In THF (10 mL), cis/trans-(PyInd)PtCl(C₂H₄) (114 mg, 0.22 mmol, 1 equiv) was treated with AgOTf (60 mg, 0.24 mmol, 1 equiv) at ambient temperature and stirred for 1 h. A solution of PhLi in THF (5 mL, 0.24 mmol, 47 mM, 1.1 equiv) was slowly added. The reaction mixture was then heated to 50 °C for 20 h in the dark. The reaction mixture was filtered over Celite and the filtrate was concentrated under reduced pressure, and purification by SiO₂ column chromatography (eluting with 5% ethyl acetate/hexanes) afforded the title compound as a yellow solid (25 mg, 20% yield).

Synthesis of (tBuPyInd)Pt(CH₂CH₂Ph)(C₂H₄) (4). Caution: working with high pressures is a potential safety hazard, and the reaction vessel should be tested above working pressures prior to usage. Inside a glovebox, 2a (140 mg, 0.24 mmol) was dissolved in benzene (10 mL) in a 50 mL Teflon stoppered Schlenk flask equipped with a stir bar. On a Schlenk line, the solution was thoroughly degassed by three freeze/pump/thaw cycles, and ethylene (1 atm) was added. The reaction vessel was brought back into a glovebox and fresh benzene (0.7 mL), or 3.00 (s with ¹⁹⁵Pt satellites, Jₚₜ = 60 Hz, 4H, C₂H₄), 1.39 (s, 9H, tBu).

Catalytic Methods

General Procedure for Ethylene Hydroarylation with Benzene-d₆ Using Catalysts 2a-k, 3, and 4. Inside a glovebox, catalysts 2a-k, 3, or 4 (0.0026 mmol, 3.7 mM), benzene-d₆ (0.7 mL), and a known amount of Si(SiMe₃)₄ as an internal standard, were added to a low pressure/vacuum (4 mm outer diameter, 3 mL) J. Young NMR tube. On a Schlenk line, the solution was thoroughly degassed by three freeze/pump/thaw cycles and ethylene (1 atm) was added at ambient temperature. The reaction vessel was submerged in a 100 °C bath. Product formation was monitored over a 24 h by ¹H NMR spectroscopy after 50, 100, 150, 200, 250, 300, 1370 min of heating. Product formation was determined by identifying new benzylic and methyl resonances in the ¹H NMR spectrum and comparing them to literature values.* Overall TON was
determined by comparing the benzylic peak to the internal standard peak. Selected \textsuperscript{1}H NMR resonances for benzylic/methyl protons for \text{C}_{6}\text{D}_{5}\text{CH}_{2}\text{CH}_{3}\text{D}: \text{\textsuperscript{1}H NMR (benzene-}\text{d}_6, 400.1 \text{ MHz}): \delta 2.44 (\text{tt}, J_{HH} = 7.5 \text{ Hz}, J_{HD} = 1.1 \text{ Hz, } 2\text{H}), 1.06 (\text{tt}, J_{HH} = 7.5 \text{ Hz}, J_{HD} = 2.0 \text{ Hz, } 2\text{H}). Polyethylbenzene formation was qualitatively identified by GC-MS after filtering through Al\textsubscript{2}O\textsubscript{3} (Figure S16).

High Pressure Ethylene Hydroarylation with Benzene Using Catalyst 2a. Caution: working with high pressures is a potential safety hazard, and the reaction vessel should be tested above working pressures prior to usage. In a glovebox, a Fischer-Porter apparatus (50 mL) equipped with a stir bar was charged with catalyst 2a (4.5 mg, 7.7 µmol, 3.7 mM) in benzene-\text{d}_6 (2.1 mL) with a known amount Si(SiMe\textsubscript{3})\textsubscript{4} as an internal standard. The apparatus was transferred onto a Schlenk line and attached to a high pressure ethylene inlet. The reaction vessel was then purged with ethylene, pressurized to 3 atm, and then heated to 100 °C with vigorous stirring for 6 h. After this time, the reaction vessel was depressurized and cooled to ambient temperature. A \textsuperscript{1}H NMR spectrum of the reaction mixture was acquired to determine ethylbenzene turnovers.

Propylene Hydroarylation with Benzene-\text{d}_6 Using Catalysts 2a-k. In a similar manner to that described in the general procedure above, catalysts 2a-k (0.0026 mmol, 3.7 mM), benzene-\text{d}_6 (0.7 mL), propylene (1 atm), and a known amount of Si(SiMe\textsubscript{3})\textsubscript{4} as an internal standard were added to a low pressure/vacuum (4 mm outer diameter, 3 mL) J. Young NMR tube. The reaction vessel was submerged in a 100 °C bath. Product formation was monitored over a 24 h period by \textsuperscript{1}H NMR spectroscopy after 50, 100, 150, 200, 250, 300, 1370 min of heating. Product formation was determined by identifying new benzylic and methyl resonances in the \textsuperscript{1}H NMR spectrum and comparing them to literature values of cumene-\text{d}_6 (\text{C}_{6}\text{D}_{5}\text{CHCH}_{2}\text{CH}_{2}\text{D})\textsuperscript{2} and n-propylbenzene-\text{d}_6 (\text{C}_{6}\text{D}_{5}\text{CH}_{2}\text{CHDCH}_{3})\textsuperscript{8}. For product selectivity ratios, the ratio of the benzylic peaks for the two isomers was calculated by \textsuperscript{1}H NMR spectroscopy. Overall TON was determined by comparing the benzylic peak to the internal standard peak for Si(SiMe\textsubscript{3})\textsubscript{4}. Selected \textsuperscript{1}H NMR resonance for the benzylic proton for cumene-\text{d}_6 (\text{C}_{6}\text{D}_{5}\text{CH(CH}_{3})(\text{CH}_{2}\text{D})): \text{\textsuperscript{1}H NMR (benzene-}\text{d}_6, 400.1 \text{ MHz): } \delta 2.70 (\text{h}, J_{HH} = 6.6 \text{ Hz, } J_{HD} = 1.3 \text{ Hz}). Selected \textsuperscript{1}H NMR peak for the benzylic protons for n-propylbenzene-\text{d}_6 (\text{C}_{6}\text{D}_{5}\text{CHH}_{2}\text{CHDCH}_{3}): \text{\textsuperscript{1}H NMR (benzene-}\text{d}_6, 400.1 \text{ MHz): } \delta 2.42 (\text{dt}, J_{HH} = 7.3 \text{ Hz, } J_{HD} = 1.0 \text{ Hz}).

Hydroarylation of tert-Butylethylene with Benzene-\text{d}_6 Using Catalyst 2a. Inside a glovebox, catalyst 2a (0.0026 mmol, 0.3 mol% catalyst loading relative to olefin, 3.7 mM), benzene-\text{d}_6 (0.7 mL), tert-butylethylene (100 µL, 0.78 mmol), and a known amount of Si(SiMe\textsubscript{3})\textsubscript{4} as an internal standard, were heated to 100 °C for 24 h. A \textsuperscript{1}H NMR spectrum was acquired and new benzylic peaks were identified for tert-butylethylenebenzene and 1-tert-butyl-1-phenylethane. These peaks were in agreement with literature values.\textsuperscript{9} The overall TON was determined by comparing the integration of the benzylic peaks to the standard peak, and product selectivity was determined as the ratio of the two new benzylic peaks. Selected \textsuperscript{1}H NMR resonances for the benzylic protons for tert-butylethylenebenzene and 1-tert-butyl-1-phenylethane: \textsuperscript{1}H NMR (300.1 MHz): \delta 2.46 (dt, J_{HH} = 9.2 \text{ Hz, } J_{HD} = 1.4 \text{ Hz}), 2.41 (tt, J_{HH} = 6.3 \text{ Hz, } J_{HD} = 1.3 \text{ Hz}).

Attempted Hydroarylation of Cyclohexene with Benzene-\text{d}_6 Using Catalyst 2a. The general procedure was followed with 2a (0.0026 mmol, 0.3 mol% catalyst loading relative to olefin, 3.7 mM), benzene-\text{d}_6 (0.7 mL), cyclohexene (8.0 µL, 0.082 mmol), and a known amount of
Si(SiMe)_3 as a standard were heated to 100 °C for 24 h. A ^1H NMR spectrum was acquired. No new products were identified and cyclohexene was not consumed.

**Attempted Hydroarylation of 1-Octene with Benzene-d_6 Using Catalyst 2a.** Catalyst 2a (0.0026 mmol, 0.3 mol% catalyst loading relative to olefin, 3.7 mM), benzene-d_6 (0.7 mL), 1-octene (100 µL, 0.64 mmol), and a known amount of Si(SiMe)_3 as a standard were added to a low pressure/vacuum (4 mm outer diameter, 3 mL) J. Young NMR tube. The reaction vessel was submerged in a 100 °C bath for 24 h. The reaction mixture was then cooled to ambient temperature and an aliquot of the reaction mixture was diluted in chloroform-d_4. Product formation was determined by identifying new benzylic and methyl resonances in the ^1H NMR spectrum and comparing them to known literature values in chloroform-d_4. TON was determined by comparing the benzylic peak to the internal standard peak. Selected ^1H NMR resonances for benzyl/methyl protons for C_6H_5CH_2CH_3: ^1H NMR (chloroform-d_4, 400.1 MHz): δ 2.65 (q, J = 7.6 Hz, 2H), 1.22 (t, J = 7.6, 3H).

**Ethylene Hydroarylation with Benzene Using Catalyst 2a.** In a similar manner to that described in the general procedure above, catalyst 2a (1.5 mg, 0.0026 mmol, 3.7 mM), benzene (0.7 mL), ethylene (1 atm), and a known amount of Si(SiMe)_3 as a standard were added to a low pressure/vacuum (4 mm outer diameter, 3 mL) J. Young NMR tube. The reaction vessel was submerged in a 100 °C bath for 24 h. The reaction mixture was then cooled to ambient temperature and an aliquot of the reaction mixture was diluted in chloroform-d_4. Product formation was determined by identifying new benzylic and methyl resonances in the ^1H NMR spectrum and comparing them to known literature values in chloroform-d_4. TON was determined by comparing the benzylic peak to the internal standard peak. Selected ^1H NMR resonances for benzyl/methyl protons for C_6H_5CH_2CH_3: ^1H NMR (chloroform-d_4, 400.1 MHz): δ 2.65 (q, J = 7.6 Hz, 2H), 1.22 (t, J = 7.6, 3H).

**Competitive Ethylene Hydroarylation with Equimolar Benzene and Benzene-d_6 Using Catalyst 2a.** In a similar manner to that described in the general procedure above, catalyst 2a (1.5 mg, 0.0026 mmol, 3.3 mM), benzene (0.4 mL), benzene-d_6 (0.4 mL), ethylene (1 atm), and a known amount of Si(SiMe)_3 as a standard were added to a low pressure/vacuum (4 mm outer diameter, 3 mL) J. Young NMR tube. The reaction vessel was submerged in a 100 °C bath for 24 h. The ratio of C_6H_5CH_2CH_3 to C_6D_5CH_2CH_2D was determined by ^1H and ^13C{^1H} NMR spectroscopy (Figure S15). In the ^1H NMR spectrum, the ratio was calculated by integration of the benzylic proton resonances. In ^13C{^1H} NMR spectrum, the ratio was calculated by integration of the methyl CH_3 and CH_2D resonances [selected NMR value for mixture of C_6D_5CH_2CH_3 and C_6D_2CH_2CH_2D: ^13C{^1H} NMR (benzene-d_6, 226.4 MHz, D_1 = 60.0 s, temp = 298.0 K): δ 15.9 (s, measure T_1 = 3.9 s), 15.5 (t, J_CD = 19.2 Hz, measured T_1 = 4.3 s)].

**Hydroarylation of Ethylene with Toluene Using Catalyst 2a.** Inside a glove box, catalyst 2a (0.0026 mmol, 3.7 mM), toluene (0.7 mL) and tridecane as an internal standard (7 µL, 0.029 mmol) were added to a low pressure/vacuum (4 mm outer diameter, 3 mL) J. Young NMR tube. On a Schlenk line, the solution was thoroughly degassed by three freeze/pump/thaw cycles and then ethylene (1 atm) was added at ambient temperature. The reaction vessel was submerged in a 100 °C bath for 24 h. GC calibration curves and response factors were generated for authentic samples of o-ethyltoluene, m-ethyltoluene, and p-ethyltoluene versus a tridecane standard using known concentrations in ethyl acetate. The signals corresponding to m- and p-ethyltoluene could not be resolved and were integrated as a single peak. A 300 µL aliquot of the reaction mixture was dissolved in 1.5 mL ethyl acetate and filtered over a short plug of Al_2O_3 to remove any residual metal complexes. Using the response factor, this sample was then analyzed by GC to determine overall TON and product selectivity for o-ethyltoluene versus the mixture of m- and p-ethyltoluene.
Ethylene Hydroarylation with Mesitylene Using Catalyst 2a. In a similar manner to that described in the general procedure above, catalyst 2a (0.0026 mmol, 3.7 mM), mesitylene (0.7 mL), ethylene (1 atm), and a known amount of Si(SiMe$_3$)$_4$ were added to a low pressure/vacuum (4 mm outer diameter, 3 mL) J. Young NMR tube. The reaction vessel was submerged in a 100 °C bath for 24 h. The reaction mixture was cooled to ambient temperature and an aliquot was diluted in chloroform-$d_1$. Product formation was determined by identifying new benzylic and methyl resonances in the $^1$H NMR spectrum and comparing them to known literature values of 1-ethyl-2,4,6-trimethylbenzene.$^{12}$ Overall TON was determined by comparing the benzylic peak to the internal standard peak for Si(SiMe$_3$)$_4$. Selected $^1$H NMR resonances for benzylic/methyl protons for 1-ethyl-2,4,6-trimethylbenzene: $^1$H NMR (chloroform-$d_1$, 400.1 MHz): δ 2.60 (q, $J$ = 7.4 Hz, 2H), 2.29 (s, 6H), 2.25 (s, 3H), 1.08 (t, $J$ = 7.6 Hz, 3H).

Ethylene Hydroarylation with Benzene-$d_6$ Using 2a with Added Base. In a similar manner to that described in the general procedure above, catalyst 2a (0.0026 mmol, 3.7 mM), benzene-$d_6$ (0.7 mL), 2,6-di-tert-butyl-4-methylpyridine (11 mg, 0.054 mmol, 20 equiv relative to 2a), ethylene (1 atm) and a known amount of Si(SiMe$_3$)$_4$ as an internal standard were added to a low pressure/vacuum (4 mm outer diameter, 3 mL) J. Young NMR tube. The reaction vessel was submerged in a 100 °C bath. Product formation was monitored over a 24 h period by $^1$H NMR spectroscopy after 50, 100, 150, 200, 250, 300, 1370 min of heating.

Ethylene Hydroarylation with Benzene-$d_6$ Using Catalysts 2a or 4 with Added Dimethyl Sulfide. In a similar manner to that described in the general procedure above, 2a or 4 (0.0026 mmol, 3.7 mM), benzene-$d_6$ (0.7 mL), dimethyl sulfide (2.0 µL, 0.026 mmol, 10 equiv. relative to [Pt]), ethylene (1 atm), and a known amount of a Si(SiMe$_3$)$_4$ internal standard were added to a low pressure/vacuum (4 mm outer diameter, 3 mL) J. Young NMR tube. The reaction vessel was submerged in a 100 °C bath. Product formation was monitored over a 24 h period by $^1$H NMR spectroscopy after 50, 100, 150, 200, 250, 300, 1370 min of heating.

Ethylene Hydroarylation with Benzene-$d_6$ Using Catalysts 2a or 3 in the Presence of Hg(0). In a similar manner to that described in the general procedure above, catalyst 2a or 3 (0.0026 mmol, 3.7 mM), benzene-$d_6$ (0.7 mL), ethylene (1 atm), a known amount of Si(SiMe$_3$)$_4$ as an internal standard, and Hg(0) (ca. 1 pipette drop) were added to a low pressure/vacuum (4 mm outer diameter, 3 mL) J. Young NMR tube. The reaction mixture was submerged in a 100 °C bath. Product formation was monitored over a 24 h period by $^1$H NMR spectroscopy after 50, 100, 150, 200, 250, 300, 1370 min of heating.

Ethylene Hydroarylation with Benzene-$d_6$ Using Catalysts 2a or 3, Pre-Stirring with Hg(0). In a glovebox, catalyst 2a or 3 (0.0026 mmol, 3.7 mM) and a known amount Si(SiMe$_3$)$_4$ as a standard were dissolved in benzene-$d_6$ (0.7 mL). This solution was stirred at ambient temperature with Hg(0) (ca. 1 pipette drop) for 30 min. The solution was decanted and then filtered over Celite to remove residual Hg(0) from the reaction mixture. This solution was then added to a low pressure/vacuum (4 mm outer diameter, 3 mL) J. Young NMR tube. On a Schlenk line, the solution was thoroughly degassed by three freeze/pump/thaw cycles and then ethylene (1 atm) was added at ambient temperature. The reaction vessel was submerged in a 100 °C bath. Product
formation was monitored over a 24 h period by \(^1\)H NMR spectroscopy after 50, 100, 150, 200, 250, 300, 1370 min of heating.

**Thermolysis Reactions using Compounds 2a, 3 or 4 in Benzene-\(d_6\).** Inside a glovebox, 2a, 3, or 4 (0.0086 mmol, 8.6 mM) and a known amount of Si(SiMe\(_3\))\(_4\) as an internal standard were dissolved in benzene-\(d_6\) (1 mL) and added to a low pressure/vacuum (4 mm outer diameter, 3 mL) J. Young NMR tube. The reaction vessel was submerged in a 100 °C bath for 48 h. The reaction mixture was monitored by \(^1\)H NMR spectroscopy after 50, 100, 1370, 2810 min of heating.

**Thermolysis of 2a in Benzene-\(d_6\) in the Presence of Hg(0).** In a glovebox, catalyst 2a (0.0026 mmol, 3.7 mM), benzene-\(d_6\) (0.7 mL), a known amount of Si(SiMe\(_3\))\(_4\) as a standard, and Hg(0) (ca. 1 pipette drop) were added to a low pressure/vacuum (4 mm outer diameter, 3 mL) J. Young NMR tube. The reaction vessel was submerged in a 100 °C bath. Product formation was monitored over a 24 h period by \(^1\)H NMR spectroscopy after 50, 100, 150, 200, 250, 300, 1370 min of heating.

**Variable Temperature \(^1\)H NMR Spectroscopy with Compounds 2a, 3 or 4.** In a similar manner to that described in the general procedure above, catalysts 2a, 3 or 4 (0.0026 mmol, 3.7 mM), benzene-\(d_6\) (0.7 mL), ethylene (1 atm), and a known amount of Si(SiMe\(_3\))\(_4\) as a standard were added to a low pressure/vacuum (4 mm outer diameter, 3 mL) J. Young NMR tube. An NMR spectrometer (500.2 MHz) was preheated to 80 °C. The temperature was separately calibrated using the peak-to-peak separation of resonances in neat ethylene glycol (measured temp = 353 K). Once the spectrometer reached temperature, the J. Young reaction vessel was injected into the spectrometer. Scans were taken every 10 min over a 3 h time span. Products were quantified versus the internal standard. The identity of Pt based species was identified versus authentic samples (*vide supra*).

**Styrene Determination in Ethylene Hydroarylation with Benzene Using Catalyst 2a.** In a similar manner to that described in the general procedure above, catalyst 2a (1.5 mg, 0.0026 mmol, 3.7 mM), benzene-\(d_6\) (0.7 mL), ethylene (1 atm), and a known amount of Si(SiMe\(_3\))\(_4\) as a standard were added to a low pressure/vacuum (4 mm outer diameter, 3 mL) J. Young NMR tube. The reaction vessel was submerged in a 100 °C bath for 24 h. The reaction mixture was then cooled to ambient temperature and degassed by three freeze/pump/thaw cycles. Vinlyic resonances for styrene,\(^{13}\) \(\beta\)-(E)-deuterostyrene,\(^{14}\) and \(\beta\)-(Z)-deuterostyrene\(^{14}\) were identified in the \(^1\)H NMR spectrum and were in agreement with reported literature values. Products were quantified versus the internal standard. Selected \(^1\)H NMR resonances for the vinylic protons in styrene (PhCH=CH\(_2\)): \(^1\)H NMR (benzene-\(d_6\), 400.1 MHz): \(\delta 6.57 (dd, J = 18.3, 11.0 \text{ Hz})\), \(5.59 (dd, J = 17.6, 1.3 \text{ Hz})\), \(5.06 (dd, J = 10.9, 1.2 \text{ Hz})\). Selected \(^1\)H NMR resonances for the vinylic protons in \(\beta\)-(E)-deuterostyrene (PhCH=CHD): \(^1\)H NMR (benzene-\(d_6\), 400.1 MHz): \(\delta 6.64 (bd, J = 17.9 \text{ Hz})\), \(5.69 (bd, J = 17.9 \text{ Hz})\). Selected \(^1\)H NMR resonances for the vinylic protons in \(\beta\)-(Z)-deuterostyrene: \(^1\)H NMR (benzene-\(d_6\), 400.1 MHz): \(6.67 (bd, J = 10.5 \text{ Hz})\), \(5.16 (bd, J = 10.9 \text{ Hz})\).

**Determination of Decomposition Products and Organometallic Speciation in Ethylene Hydroarylation with Benzene Using Catalyst 2a.** In a glovebox, catalyst 2a (21 mg, 0.036
mmol, 7.2 mM) was dissolved in benzene (5 mL) in a 100 mL Teflon stoppered Schlenk flask equipped with a stir bar. On a Schlenk line, the solution was thoroughly degassed by three freeze/pump/thaw cycles and then ethylene (1 atm) was added at ambient temperature. The reaction mixture was heated to 100 °C for 20 h. The reaction mixture was then cooled to ambient temperature and volatile components were removed under reduced pressure. Dichloromethane was added to the residue. The resultant solution was spotted onto a preparatory SiO₂ TLC plate (eluting with 10% ethyl acetate/hexanes) in order to separate Pt(0) from organometallic and ligand species. Two broad bands (R_f = 0.40-0.55, and 0.02-0.10) were observed. The top band was physically removed and the products were extracted with dichloromethane (2 x 10 mL). The solution was filtered to remove residual SiO₂. An aliquot of the resultant solution was filtered over Al₂O₃ and a HRMS (ESI-TOF) was acquired. The results are summarized in Table S1.
Figure S1. Crystal structure of 2b, with thermal ellipsoid at 50% probability. For clarity, hydrogen atoms have been omitted. Selected bond length (Å) and angles (°) for 2: C(3)–Pt(1): 2.009(3), N(1)–Pt(1): 2.049(2), N(2)–Pt(1): 2.125(2), S(1)–Pt(1): 2.2611(7), C(3)–Pt(1)–N(1): 93.16(10), C(3)–Pt(1)–S(1): 90.10(8), N(1)–Pt(1)-N(2): 79.19(9), N(2)–Pt(1)–S(1): 97.56(6).

Figure S2. Crystal structure of 2c, with thermal ellipsoid at 50% probability. For clarity, hydrogen atoms have been omitted. Selected bond length (Å) and angles (°) for 3: C(3)–Pt(1): 2.008(2), N(2)–Pt(1): 2.0522(17), N(1)–Pt(1): 2.1244(16), S(1)–Pt(1): 2.2619(5), C(3)–Pt(1)–
N(2): 93.64(7), C(3)–Pt(1)–S(1): 89.83(6), N(2)–Pt(1)–N(1): 79.16(6), N(1)–Pt(1)–S(1): 97.36(5).

**Figure S3.** Monitored hydroarylation of ethylene (1 atm) with benzene-$d_6$ at 100 °C over 46 h by \textsuperscript{1}H NMR spectroscopy using catalysts 2a-k (3.7 mM). Turnovers are given as the average of triplicate experiments with error calculated as the standard deviation.
Figure S4. Representative chromatogram of catalytic ethylene hydroarylation with benzene-$d_6$ using catalysts 2a-k. Ethylbenzene-$d_6$ (6.70-6.79 min) and diethylbenzenes-$d_6$ (6.78-6.84 min) are partially overlapping. Note that the sample was diluted in benzene as a carrier solvent in the GC-MS experiment. Additionally, note that the ortho-, meta-, para-isomers of diethylbenzene could not be resolved.
Figure S5. Monitored hydroarylation of propylene (1 atm) with benzene-$d_6$ at 100 °C over 46 h by $^1$H NMR spectroscopy using catalysts 2a-k (3.7 mM). Turnovers are given as the average of triplicate experiments with error calculated as the standard deviation.
Figure S6. Monitored product regioselectivity during hydroarylation of propylene (1 atm) with benzene-$d_6$ at 100 °C over 46 h by $^1$H NMR spectroscopy using catalysts 2a-k (3.7 mM) [note: catalyst 2j is omitted; error bars have been omitted for clarity]. Selectivities determined as the ratio of TO$\text{Linear}$:TO$\text{Branched}$ and values are given as the average of triplicate experiments.
Figure S7. Plot of total turnovers from the hydroarylation of propylene with benzene-$d_6$ using catalysts 2a-2k (measured at 24 h) vs. the initial product formation rate (measured as the turnovers after 1 h). Turnovers represent the sum of turnovers for cumene-$d_6$ and $n$-propylbenzene-$d_6$. The dashed line is a linear fit of the data.
**Figure S8.** $^{13}$C-$^1$H NMR spectrum of the resulting products [C$_6$H$_5$(CH$_2$CH$_3$) at 15.9 ppm and C$_6$D$_5$(CH$_2$CH$_2$D) at 15.6 ppm] from competitive hydroarylation of ethylene with 2a in an equimolar mixture of benzene and benzene-$d_6$. Note that methyl resonances in ethylbenzene-$d_6$ appear as a t due to C–D coupling ($J_{2H^{13}C} = 19.2$ Hz).
Figure S9. $^1$H NMR spectra of Pt speciation during ligand substitution reaction after exposure of 2a to ethylene (1 atm) at ambient temperature. Resonance a (3.37 ppm, $J_{	ext{PtH}} = 59$ Hz) is the $\text{C}_2\text{H}_4$ fragment of complex 3. Resonance b (3.01 ppm, $J_{	ext{PtH}} = 54$ Hz) is the $\text{C}_2\text{H}_4$ fragment of complex 4. Resonance c (1.54 ppm, $J_{	ext{PtH}} = 53$ Hz) is the SMe$_2$ fragment of complex 2a. Free SMe$_2$ is observed at 1.72 ppm. **Insert A:** Monitored $^1$H NMR spectra of the substitution reaction over the course of 3 days. Note that resonances a, b, and SMe$_2$ grow in intensity over time while resonance c decays. **Insert B:** Expansion of the $^1$H NMR spectra after 66 h of exposure to C$_2$H$_4$. Note the relative ratio of the integrations of resonances c, a, and b are ca. 6.3:4.0:0.8, respectively. This corresponds to the observed product ratio of 2a:3:4 of 1.1:1.0:0.2, respectively.
**Figure S10.** Monitored thermolysis of complex 2a at 100 °C in benzene-$d_6$. Lower: $^1$H NMR spectrum after 1 h of heating. Middle: $^1$H NMR spectrum after 3 h of heating. Upper: $^1$H NMR spectrum after 46 h of heating. Selected resonances shown above for compound 2a: δ 1.54 (s, $J_{PtH} = 60$ Hz, a), 0.84 (s, d). Selected resonances above for compound **cis**-2a: δ 1.50 (s, $J_{PtH} = 52$ Hz, b), 1.01 (s, c). Aryl protons for 2a and **cis**-2a overlap, making individual peak assignment difficult.
Figure S11. Monitored thermolysis of complex 3 at 100 °C in benzene-$d_6$. Lower: initial $^1$H NMR spectrum prior to heating. Middle: $^1$H NMR spectrum after 1 h of heating. Upper: $^1$H NMR spectrum after 24 h of heating. Selected resonances shown above for compound 3: 3.83 (s, $J_{PH} = 59$ Hz, a). Rapid decomposition of 3 occurs with concurrent ethylbenzene formation. Note that H(D) exchange appears to occur to produce a mixture of ethylbenzene-$d_1$ and ethylbenzene-$d_0$. 
Figure S12. Monitored thermolysis of complex 4 at 100 °C in benzene-$d_6$. Lower: $^1$H NMR spectrum after 1 h of heating. Middle: $^1$H NMR spectrum after 3 h of heating. Upper: $^1$H NMR spectrum after 24 h of heating. Selected resonances shown above for compound 4: $\delta$ 3.22 (t, $J = 8.1$ Hz, a), 3.01 (s, $J_{\text{PH}} = 54$ Hz, b), 2.12 (t, $J_{\text{HH}} = 8.2$ Hz, $J_{\text{PH}} = 67$ Hz, c). Ethylene resonance at 5.25 noted during early time points of heating. Ethylbenzene benzylic resonance (d) noted after 1 h and rapidly increased as 4 decomposed.
Figure S13. Monitored hydroarylation of ethylene (1 atm) with benzene-$d_6$ at 100 °C over 144 h by $^1$H NMR spectroscopy using catalysts 2a and 4 (3.7 mM) with and without added SMe$_2$ in the reaction mixture. Turnovers are given as the average of triplicate experiments with error calculated as the standard deviation.
**Figure S14.** Variable temperature $^1$H NMR of 2a at 80 °C in benzene-$d_6$. Scans were taken once every 10 min during the course of the reaction (over a 2 h period). The resonance corresponding to bound ethylene in 3 (b) was observed at the first scan after being heated in the NMR spectrometer. Additionally, free SMe$_2$ was noted as well as bound SMe$_2$ (not shown). Full conversion of 2a to 3, therefore, was not observed. Conversion of ethylene and benzene-$d_6$ to ethylbenzene-$d_6$ was rapidly observed, as noted by the formation of the ethylbenzene-$d_6$ benzylic peak (a). Complex 4 was not observed to a major extent during the course of the variable temperature $^1$H NMR experiment.
Figure S15. Variable temperature $^1$H NMR of 3 at 80 °C in benzene-$d_6$. Scans were taken once every 10 min during the course of the reaction (over a 2 h period). Bound ethylene resonances (b) for complex 3 were noted in every time point of the experiment, and only slowly reduced in intensity over time. Resonances corresponding to complex 4 (c, d, and e) only slowly grew in intensity during the reaction. Rapid formation of ethylbenzene-$d_6$ (a) was noted during the course of the reaction.
Figure S16. Variable temperature $^1$H NMR of 4 at 80 °C in benzene-$d_6$. Scans were taken once every 10 min during the course of the reaction (over a 3 h period). Bound ethylene resonances (b) for complex 3 only slowly grew in intensity during the reaction. Resonances corresponding to complex 4 (c, d, and e) were present during the entirety of the experiment, and only decreased in intensity slowly during the reaction. Slow formation of ethylbenzene-$d_6$ (a) was noted during the course of the reaction.
Figure S17. Monitored hydroarylation of ethylene (1 atm) with benzene-$d_6$ at 100 °C over 46 h by $^1$H NMR spectroscopy using catalyst 2a (3.7 mM) with (blue) and without added 2,6-di-tert-butyl-4-methylpyridine (green). Turnovers are given as the average of triplicate experiments with error calculated as the standard deviation.
Figure S18. Monitored hydroarylation of ethylene (1 atm) with benzene-$d_6$ at 100 °C over 144 h by $^1$H NMR spectroscopy using catalysts 2a and 3 (3.7 mM) with and without the presence of Hg(0) in the reaction mixture. Turnovers are given as the average of triplicate experiments with error calculated as the standard deviation.
Figure S19. Monitored hydroarylation of ethylene (1 atm) with benzene-$d_6$ at 100 °C over 46 h by $^1$H NMR spectroscopy using catalysts 2a and 3 (3.7 mM) with and without prestirring the catalysts with Hg(0) prior to olefin addition. Mercury was removed prior to substrate addition and heating. Turnovers are given as the average of triplicate experiments with error calculated as the standard deviation.
**Table S1.** Decomposition products identified by HRMS (ESI-TOF) after ethylene hydroarylation with catalyst 2a in benzene at 100 °C for 20 h. Masses of proposed structures (as the H⁺ or K⁺ species) are given under the Theoretical m/z.

<table>
<thead>
<tr>
<th>Found m/z</th>
<th>Theoretical m/z</th>
<th>Assignment (Compound Number)</th>
</tr>
</thead>
<tbody>
<tr>
<td>251.1559</td>
<td>[M + H]⁺ Calcd for C₁₇H₁₉N₂, 251.154.</td>
<td>![Structure 1a]</td>
</tr>
<tr>
<td>393.2098</td>
<td>[M + K]⁺ Calcd for C₂₅H₃₆N₂K, 393.1728.</td>
<td>![Structure 5]</td>
</tr>
<tr>
<td>536.1706</td>
<td>[M + H]⁺ Calcd for C₂₁H₂₃N₂PtS, 536.1694</td>
<td>[(tBuPyInd)PtEt(SMe₂)]H⁺ (7)</td>
</tr>
<tr>
<td>550.1831</td>
<td>[M + H]⁺ Calcd for C₂₅H₂₇N₂Pt, 550.1816.</td>
<td>[(tBuPyInd)PtPh(C₂H₄)]H⁺ (3)</td>
</tr>
<tr>
<td>584.1706</td>
<td>[M + H]⁺ Calcd for C₂₃H₂₉N₂PtS, 584.1694.</td>
<td>[(tBuPyInd)PtPh(SMe₂)]H⁺ (2a)</td>
</tr>
<tr>
<td>612.2007</td>
<td>[M + H]⁺ Calcd for C₂₇H₃₃N₂PtS, 612.2007.</td>
<td>[(tBuPyInd)Pt(CH₂CH₂Ph)(SMe₂)]H⁺ (6)</td>
</tr>
<tr>
<td>626.1817</td>
<td>[M + H]⁺ Calcd for C₃₁H₃₁N₂Pt, 626.2129.</td>
<td>[(tBuPyInd)PtPh(H₂C=CHPh)]H⁺ (8)</td>
</tr>
<tr>
<td>Compound</td>
<td>2a</td>
<td>2b</td>
</tr>
<tr>
<td>----------</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td><strong>Empirical Formula</strong></td>
<td>C_{25}H_{28}N_2PtS</td>
<td>C_{25}H_{26}F_2N_2PtS</td>
</tr>
<tr>
<td><strong>Formula Mass</strong></td>
<td>583.64</td>
<td>619.64</td>
</tr>
<tr>
<td><strong>Crystal System</strong></td>
<td>Monoclinic</td>
<td>Triclinic</td>
</tr>
<tr>
<td><strong>Space Group</strong></td>
<td>C2/c</td>
<td>P-1</td>
</tr>
<tr>
<td><strong>a (Å)</strong></td>
<td>25.6857(8)</td>
<td>9.0052(4)</td>
</tr>
<tr>
<td><strong>b (Å)</strong></td>
<td>11.6427(4)</td>
<td>10.3193(5)</td>
</tr>
<tr>
<td><strong>c (Å)</strong></td>
<td>18.7609(6)</td>
<td>13.9951(6)</td>
</tr>
<tr>
<td><strong>α (°)</strong></td>
<td>90</td>
<td>90.135(2)</td>
</tr>
<tr>
<td><strong>β (°)</strong></td>
<td>116.0020(10)</td>
<td>92.418(2)</td>
</tr>
<tr>
<td><strong>γ (°)</strong></td>
<td>90</td>
<td>94.402(2)</td>
</tr>
<tr>
<td><strong>Unit Cell Volume (Å³)</strong></td>
<td>5042.6(3)</td>
<td>1295.52(10)</td>
</tr>
<tr>
<td><strong>Z</strong></td>
<td>8</td>
<td>2</td>
</tr>
<tr>
<td><strong>Reflections Collected</strong></td>
<td>35910</td>
<td>29536</td>
</tr>
<tr>
<td><strong>Independent Reflections</strong></td>
<td>4634</td>
<td>4718</td>
</tr>
<tr>
<td><strong>R_{int}</strong></td>
<td>0.0267</td>
<td>0.0276</td>
</tr>
<tr>
<td><strong>Completeness to θ = 25.000° (%)</strong></td>
<td>100.0</td>
<td>99.4</td>
</tr>
<tr>
<td><strong>Final R indices (I &gt; 2σ(I))</strong></td>
<td>0.0139</td>
<td>0.0172</td>
</tr>
<tr>
<td><strong>Final R indices (all data)</strong></td>
<td>0.0147</td>
<td>0.0178</td>
</tr>
<tr>
<td><strong>Goodness-of-Fit of F²</strong></td>
<td>1.041</td>
<td>1.050</td>
</tr>
</tbody>
</table>

Note: Complete crystallographic data can be found in the CIF files and is available free of charge via the Internet at http://pubs.acs.org.
NMR SPECTRA OF COMPOUNDS

Figure S20. $^1$H NMR of S3a in CD$_2$Cl$_2$. 

![NMR Spectrum of S3a in CD$_2$Cl$_2$.]
Figure S21. $^{13}$C{$^{1}$H} NMR of S3a in CD$_2$Cl$_2$. 
Figure S22. $^1$H NMR of 1a in CD$_2$Cl$_2$. 
Figure S23. $^{13}$C{$^1$H} NMR of 1a in CD$_2$Cl$_2$. 

![NMR spectrum of 1a in CD$_2$Cl$_2$.](image)
Figure S24. $^1$H NMR of 2a in C$_6$D$_6$. Insert: enlargement of aryl resonances.
Figure S25. $^{13}$C{$^1$H} NMR of 2a in C$_6$D$_6$.
Figure S26. $^1$H NMR of S3b in CD$_2$Cl$_2$. 

![Figure S26: $^1$H NMR of S3b in CD$_2$Cl$_2$.]
Figure S27. $\text{^{13}C\{^{1}H\}}$ NMR of S3b in CD$_2$Cl$_2$. 

![NMR spectrum of S3b in CD$_2$Cl$_2$](image_url)
Figure S28. $^{19}$F NMR of S3b in CD$_2$Cl$_2$. Insert: expansion of the ligand based $^{19}$F resonances.
Figure S29. $^1$H NMR of 1b in CD$_2$Cl$_2$. 

![NMR Spectrum Image]
Figure S30. $^{13}$C{$^1$H} NMR of 1b in CD$_2$Cl$_2$. 

![Chemical Structure](image)
Figure S31. $^{19}$F NMR of 1b in CD$_2$Cl$_2$. Insert: expansion of the ligand based $^{19}$F resonances.
Figure S32. $^1$H NMR of 2b in CD$_2$Cl$_2$. 

$\text{(BuPylnd-4,7-F}_2\text{)PtPh(SMe}_2\text{)}$
Figure S33. $^{13}$C\{$^1$H\} NMR of 2b in CD$_2$Cl$_2$. 

(8^BuPyInd-4,7-F$_2$)PtPh(SMe$_2$)
Figure S34. $^{19}\text{F}$ NMR of 2b in CD$_2$Cl$_2$. Insert: expansion of the ligand based $^{19}\text{F}$ resonances.
Figure S35. $^1$H NMR of S3c in CD$_2$Cl$_2$. 
Figure S36. $^{13}$C($^1$H) NMR of S3c in CD$_2$Cl$_2$. Insert: expansion of arene carbons coupling to $^{19}$F.
Figure S37. $^{19}$F NMR of S3c in CD$_2$Cl$_2$. Left insert: expansion of $^{19}$F resonance centered at -139.5 ppm. Right insert: expansion of $^{19}$F resonances centered at -157.7, -162.9, and -170.6 ppm.
Figure S38. $^1$H NMR of 1c in CD$_2$Cl$_2$. 
Figure S39. $^{13}$C($^1$H) NMR of 1c in CD$_2$Cl$_2$. Insert: expansion of arene carbons coupling to $^{19}$F.
Figure S40. $^{19}$F NMR of 1c in CD$_2$Cl$_2$. Left insert: expansion of $^{19}$F resonance centered at -150.1 ppm. Right insert: expansion of $^{19}$F resonances centered at -160.8, -165.1, and -169.6 ppm.
Figure S41. $^1$H NMR of 2c in C$_6$D$_6$.

$^{1}$BuPyInd-4,5,6,7-F$_4$PtPh(SMe$_2$)
Figure S42. $^{13}\text{C}{^1\text{H}}$ NMR of 2c in C$_6$D$_6$. expansion of arene carbons coupling to $^{19}\text{F}$. 

$^{19}\text{F} \text{NMR}$ 

(C$_{Bu}$PyInd-4,5,6,7-$\text{F}_4$)PtPh(SMe$_2$)
Figure S43. $^{19}$F NMR of 2c in $C_6D_6$. Left insert: expansion of $^{19}$F resonances centered at -151.7 and -153.4 ppm. Right insert: expansion of $^{19}$F resonances centered at -169.3 and -173.5 ppm.

(4BuPylnd-4,5,6,7-F_4)PtPh(SMe_2)
Figure S44. $^1$H NMR of S3d in DMSO-$d_6$. 

![NMR spectrum of S3d in DMSO-$d_6$.]
Figure S45. $^{13}\text{C}^{1\text{H}}\text{NMR}$ of S3d in DMSO-$d_6$. 

\[
\text{HN} - \text{N} - \text{Y} - \text{N} - \text{Ph}
\]
Figure S46. $^1$H NMR of 1d in CD$_2$Cl$_2$. 
Figure S47. $^{13}$C($^1$H) NMR of 1d in CD$_2$Cl$_2$. 
Figure S48. $^1$H NMR of 2d in CD$_2$Cl$_2$. 

(PyInd)PtPh(SMe$_2$)
Figure S49. $^{13}$C($^1$H) NMR of 2d in CD$_2$Cl$_2$. Insert: expansion from 165.0 to 130.0 ppm.
Figure S50. $^1$H NMR of S3e in DMSO-$d_6$. 

[Chemical structure image]
Figure S51. $^{13}$C-$^1$H NMR of S3e in DMSO-$d_6$. Insert: expansion from -152.0 ppm to -128.0 ppm.
Figure S52. $^1$H NMR of 1e in CD$_2$Cl$_2$. 
Figure S53. $^{13}$C-$^1$H NMR of 1e in CD$_2$Cl$_2$. 

![NMR Spectrum](image)
Figure S54. $^1$H NMR of 2e in CD$_2$Cl$_2$. 

(PyrInd-5-MeO)PtPh(SMe$_2$)
Figure S55. $^{13}\text{C}'{^1}\text{H}$ NMR of 2e in CD$_2$Cl$_2$. 

(PyInd-5-MeO)PtPh(SMe$_2$)
Figure S56. $^1$H NMR of S3f in DMSO-$d_6$. 

![NMR spectrum of S3f in DMSO-$d_6$]
Figure S57. $^{13}$C($^1$H) NMR of S3f in DMSO-$d_6$. Insert: expansion from 155.0 ppm to 119.0 ppm.
Figure S58. $^1$H NMR of 1f in CD$_2$Cl$_2$. 

![NMR spectrum of 1f in CD$_2$Cl$_2$](image)
Figure S59. $^{13}\text{C}^{1\text{H}}$ NMR of 1f in CD$_2$Cl$_2$. 

[Graph showing a peak at approximately 130 ppm]
Figure S60. $^1$H NMR of 2f in C₆D₆.
Figure S61. $^{13}$C\{$^1$H\} NMR of 2f in C$_6$D$_6$. Insert: expansion from 165.0 to 141.0 ppm.
Figure S62. $^1$H NMR of S3g in DMSO-$d_6$. 
Figure S63. $^{13}\text{C}\{^1\text{H}\}$ NMR of S3g in DMSO-$d_6$. Insert: expansion from 160.0 to 130.0 ppm.
Figure S64. $^{19}$F NMR of S3g in DMSO-$d_6$. Insert: expansion of $^{19}$F resonance centered at -122.5 ppm.
Figure S65. $^1$H NMR of 1g in CD$_2$Cl$_2$. 

![NMR spectrum of 1g in CD$_2$Cl$_2$]
Figure S66. $^{13}$C($^{1}$H) NMR of 1g in CD$_2$Cl$_2$. 
Figure S67. ¹⁹F NMR of 1g in CD₂Cl₂. Insert: expansion of ¹⁹F resonance centered at -124.2 ppm.
Figure S68. $^1$H NMR of 2g in CD$_2$Cl$_2$. 

(PyInd-5-F)PtPh(SMe$_2$)
Figure S69. $^{13}$C($^1$H) NMR of 2g in CD$_2$Cl$_2$. Insert: expansion from 165.0 to 140.0 ppm.
Figure S70. $^{19}$F NMR of 2g in CD$_2$Cl$_2$. Insert: expansion of $^{19}$F resonance centered at -127.0 ppm.
Figure S71. $^1$H NMR of S3h in DMSO-$d_6$. 

![NMR spectrum of S3h in DMSO-$d_6$](image)
Figure S72. $^{13}$C($^1$H) NMR of S3h in DMSO-$d_6$. Insert: expansion form 150.0 to 133.0 ppm.
Figure S73. $^1$H NMR of 1h in CD$_2$Cl$_2$. 
Figure S74. $^{13}$C($^1$H) NMR of 1h in CD$_2$Cl$_2$. 
Figure S75. $^1$H NMR of 2h in CD$_2$Cl$_2$. 

(PyInd-5-Cl)PtPh(SMe$_2$)
Figure S76. $^{13}$C($^1$H) NMR of 2h in CD$_2$Cl$_2$. Insert: expansion from 160.0 to 145.0 ppm.
Figure S77. $^1$H NMR of S3i in DMSO-$d_6$. 
Figure S78. $^{13}$C-$^1$H NMR of S3i in DMSO-$d_6$. Insert: expansion from 150.0 to 141.0 ppm.
Figure S79. $^1$H NMR of 1i in C$_6$D$_6$. 

![NMR Spectrogram](image)
Figure S80. $^{13}\text{C}^{'1\text{H}}$ NMR of 1i in C$_6$D$_6$. 
Figure S81. $^1$H NMR of 2i in CD$_2$Cl$_2$. 

(PyInd-5-Br)PtPh(SMe$_2$)
Figure S82. $^{13}$C-$^1$H NMR of 2i in CD$_2$Cl$_2$. Insert: expansion from 163.0 to 130.0 ppm.
Figure S83. $^1$H NMR of S3j in DMSO-d$_6$. 
Figure S84. $^{13}$C-$^1$H NMR of S3j in DMSO-$d_6$. Insert: expansion from 145.0 to 138.0 ppm and 130.0 to 113.0 ppm.
Figure S85. $^1$H NMR of 1j in CD$_2$Cl$_2$. 

![NMR Spectrum of 1j in CD$_2$Cl$_2$]
Figure S86. $^{13}$C($^1$H)NMR of 1j in CD$_2$Cl$_2$. 

![Chemical Structure](image)
Figure S87. $^1$H NMR of 2j in CD$_2$Cl$_2$. Insert: expansion from 7.90 to 6.70 ppm.
Figure S88. $^{13}$C-{'H} NMR of 2j in CD$_2$Cl$_2$. Insert: expansion from 170.0 to 130.0 ppm.
**Figure S89.** $^1$H NMR of 2k in CD$_2$Cl$_2$. Top insert: expansion of arene $^1$H resonances from 8.40 to 6.50 ppm. Bottom insert: expansion of $^1$H resonances from 2.80 to 1.0 ppm corresponding to SEt$_2$ protons.
Figure S90. $^{13}\text{C}^{1\text{H}}$ NMR of 2k in CD$_2$Cl$_2$. 

(PyInd)PtPh(SEt$_2$)
Figure S91. $^1$H NMR of 3 in CD$_2$Cl$_2$. 
Figure S92. $^{13}$C($^1$H) NMR of 3 in CD$_2$Cl$_2$. Insert: expansion from 165.0 to 133.0 ppm.
Figure S93. $^1$H NMR of 4 in C₆D₆. Insert: expansion of aliphatic $^1$H resonances from 3.30 to 1.80 ppm.
Figure S94. $^{13}\text{C}\{^1\text{H}\}$ NMR of 4 in C$_6$D$_6$. 

![NMR Spectrum](image)

$\text{(tBuPylnd)Pt(CH}_2\text{CH}_2\text{Ph)(C}_2\text{H}_4)$
REFERENCES

8 Compared to benzylic resonance in n-propylbenzene-d0: 1H NMR (benzene-d6, 500 MHz): δ 2.43 (t J = 7.4 Hz, 2H) from Simonneau, A.; Friebel, J.; Oestreich, M. Eur. J. Org. Chem. 2014, 2077–2083.