Mechanism of C–H bond activation of alkyl-substituted benzenes by cationic platinum(II) complexes

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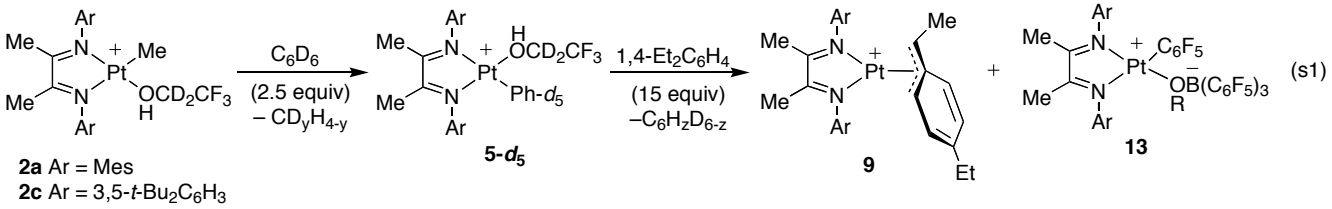
Supporting Information

Contents:

General. ^{1}H NMR and ^{13}C NMR spectra were recorded at ambient temperature using Varian 600 or 300 spectrometers. The data are reported as follows: chemical shift in ppm from internal tetramethylsilane on the δ scale, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. Mass spectra were acquired on a Finnigan LCQ ion trap or Agilent 5973 *Network* Mass Selective detector, and were obtained by peak matching. All reactions were carried out under an atmosphere of nitrogen in glassware, which had been oven-dried. Unless otherwise noted, all reagents were commercially obtained and, where appropriate, purified prior to use. Tris(pentafluorophenyl)borane [$B(C_6F_5)_3$] was purified by sublimation (90 °C, 0.5 mmHg). Trifluoroethanol-d_3 was dried over 3Å molecular sieves for at least 5 d and then was vacuum distilled onto $B(C_6F_5)_3$. After 6 h, the trifluoroethanol-d_3 was vacuum distilled to, and stored in a valved reaction vessel. The platinum dimethyl complexes were synthesized following earlier reported procedures.[1,2] Trifluoroethanol-d_3, $B(C_6F_5)_3$, and platinum dimethyl complexes were stored in a Vacuum Atmosphere nitrogen atmosphere dry box.

I. Properties of the η^3-complex

a. Thermodynamic product determination

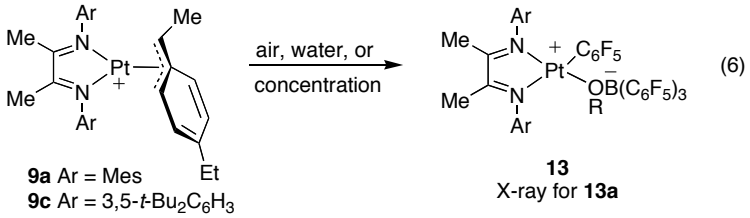


2a Ar = Mes
2c Ar = 3,5-*t*-$Bu_2C_6H_3$

To a solution of **2a** (0.700 mL of a 0.026 M solution of **2a**) was added 0.007 mL of benzene-d_6 (0.08 mmol). After 13 h, visualization of the reaction progress using ^{1}H NMR spectroscopy revealed consumption of **2a** and formation of **5a-*d*$_5$**[1] in 96% yield. The % yield was determined through comparison of diagnostic peaks of **2a** (prior to addition of benzene-d_5) and **5a-*d*$_5$** to the $CF_3C\mathbf{H}_2OH$ resonance (3.88 ppm, qt). To the resulting orange solution was added 0.072 mL of 1,4-diethylbenzene (0.47 mmol). The reaction mixture was heated to 45 °C. After 10 h, analysis of the reaction progress using ^{1}H NMR spectroscopy revealed complete consumption of platinum benzene complex **5a-*d*$_5$** and formation of η^3-complex **9a**[3] in 50% yield along with decomposition product **13a**. For characterization data of **5a-*d*$_5$** see ref 1.

To a solution of **2c** (0.700 mL of a 0.026 M solution of **2c**) was added 0.007 mL of benzene-d_6 (0.08 mmol). After 6 h, visualization of the reaction progress using ^{1}H NMR spectroscopy revealed consumption of **2c** and formation of **5c-*d*$_5$**[1] in 83% yield. To the resulting orange solution was added 0.073 mL of 1,4-diethylbenzene (0.47 mmol). After 13 h, analysis of the reaction progress using ^{1}H NMR spectroscopy revealed complete consumption of platinum benzene complex **5c-*d*$_5$** and formation of η^3-complex **9c**[3] in 63% yield along with decomposition product **13c**. For characterization data of **5c-*d*$_5$** see ref 1. Platinum η^3-complex **9c.** ^{1}H NMR (600 MHz, CF_3CD_2OD) δ 7.61 (s, 1H), 7.59 (s, 1H), 7.24 (br s, 1H), 7.45 (s, 1H), 6.96 (br s, 2H), 6.80 (br s, 1H), 6.47 (s, 1H), 6.39 (s, 1H), 5.88 (d, *J* = 6.6 Hz, 1H), 2.82 (q, *J* = 6.6 Hz, 1H), 2.08 (dd, *J* = 14.7, 7.5 Hz, 1H), 2.02 (s, 3H), 2.00 (dd, *J* = 14.7, 7.5 Hz, 1H), 1.93 (s, 3H), 1.44 (s, 9H), 1.39 (br s, 9H), 1.36 (br s, 9H), 1.30 (s, 9H), 0.93 (t, *J* = 7.5 Hz, 3H), 0.29 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (150.8 MHz, CF_3CD_2OD) δ 179.3, 177.6, 156.1, 155.5, 155.3, 155.2, 155.0, 150.9, (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 149.3 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 148.0, 143.9, 139.8 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 138.1 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 137.8, 136.2, 129.4, 126.9, 125.1, 123.98, 123.93, 121.0 (br m, $\mathbf{C}F_3CD_2OB(C_6F_5)_3$, 117.1, 116.8, 116.6, 115.8, 43.2 (br m), 36.7, 36.6, 32.1, 31.93, 31.96 (2C), 31.8, 31.7, 30.4, 29.7, 20.0, 19.7, 14.6.
LRMS (ESI) *m* / *z* calcd for $C_{42}H_{59}D_2N_2Pt^+$ [M – {$CF_3CD_2OB(C_6F_5)_3$} + 2D + H]$^+$ 792, found 792. The observed isotopic distribution pattern was consistent with the simulation.

b. Isolation of pentafluorophenyl transfer product



9a Ar = Mes
9c Ar = 3,5-*t*-$Bu_2C_6H_3$

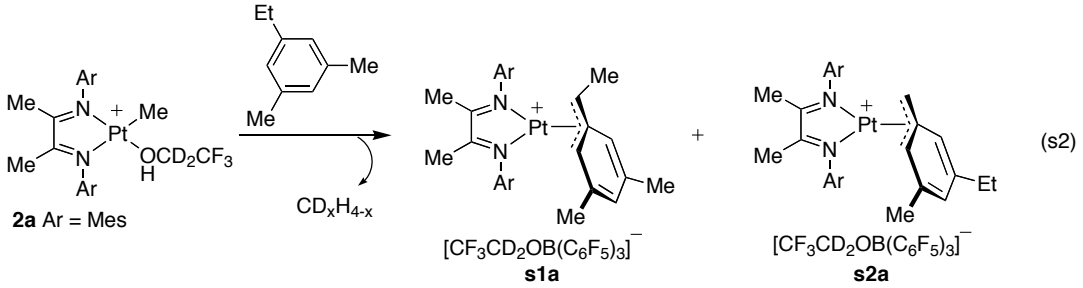
13
X-ray for **13a**

Pentafluoro-transfer product 13a: ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.08 (s, 2H), 6.71 (s, 2H), 2.39 (s, 6H), 2.21 (s, 3H), 2.05 (s, 6H), 1.97 (s, 3H), 1.85 (s, 3H), 1.73 (s, 3H).

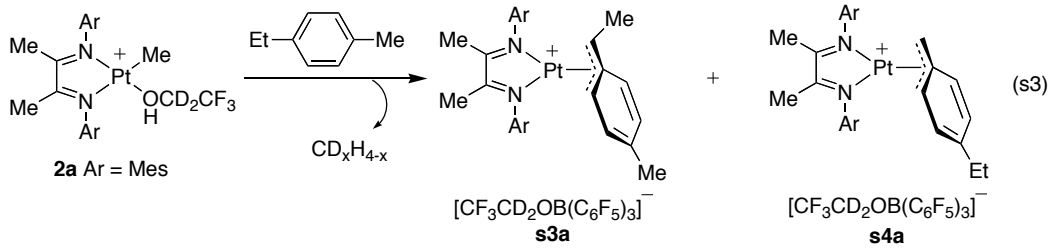
LRMS (ESI) *m* / *z* calcd for $C_{29}H_{31}F_5N_2Pt^+$ [M – {$CF_3CD_2OB(C_6F_5)_3$}]$^+$ 682, found 682. The observed isotopic distribution pattern was consistent with the simulation.
X-Ray quality crystals of **13a** were formed in an NMR tube after slow evaporation of the reaction mixture. For tabular presentation of the crystallographic data, refer to page *s-28*.

Pentafluoro-transfer product 13c: ^{1}H NMR (600 MHz, CF_3CD_2OD) δ 7.70 (t, *J* = 1.7 Hz, 1H), 7.36 (t, *J* = 1.8 Hz, 1H), 7.18 (d, *J* = 1.8 Hz, 2H), 6.74 (s, 2H), 2.22 (s, 3H), 1.99 (s, 3H), 1.39 (s, 18H), 1.26 (s, 18H); ^{13}C NMR (150.8 Mhz, CF_3CD_2OD) δ 184.8, 178.8, 155.8, 155.3, 150.8 (br m), 149.3 (br m), 148.8, 144.9, 140.1 (m), 139.6 (m), 138.3 (m), 137.9 (m), 124.9, 124.7, 122.4, 117.8, 117.0, 116.5, 36.7, 36.5, 31.8, 31.7, 20.8, 20.0.
LRMS (ESI) *m* / *z* calcd for $C_{39}H_{52}N_2F_5OPt^+$ [M – {$CF_3CD_2OB(C_6F_5)_3$} + CH_3OH + H]$^+$ 854, found 854. The observed isotopic distribution pattern was consistent with the simulation.

II. Regioselectivity of benzyl C–H bond activation: methyl- vs ethyl-substituents



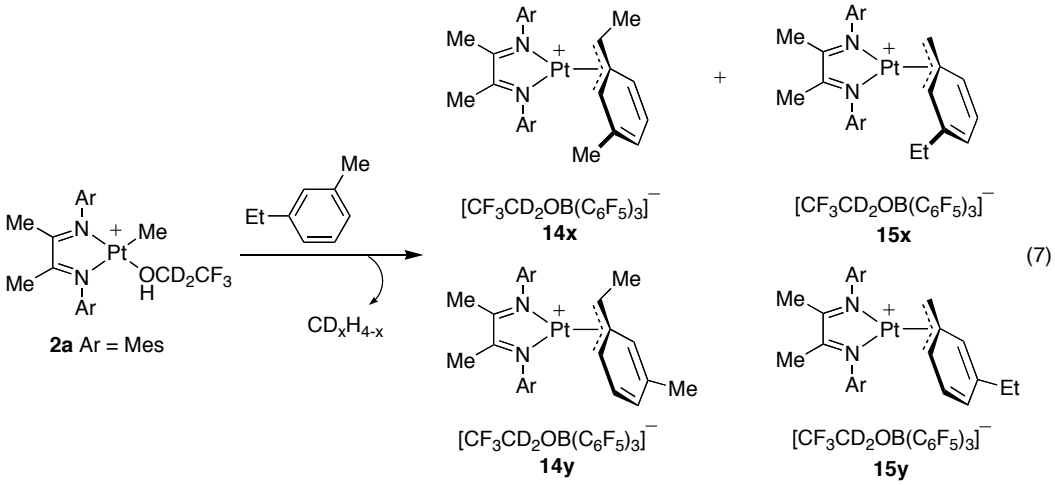
a. Representative procedure:
To a light orange solution of platinum methyl cation **2a** (prepared by dissolving 0.010 g of platinum dimethyl complex **1a** (0.018 mmol) and 0.017 g of $B(C_6F_5)_3$ in 0.700 mL of trifluoroethanol-d_3) was added 0.010 mL of 3,5-dimethyl-ethylbenzene (0.064 mmol). The progress of the reaction was monitored periodically using ^{1}H NMR spectroscopy. After 18 h, the reaction mixture was heated to 45 °C. After 13 h, the reaction mixture was cooled. Analysis using ^{1}H NMR spectroscopy revealed that the η^3-product had been formed as a 13:87 mixture of **s1a** : **s2a**. The isomer ratios were determined from comparison of the methyl group resonances: 0.24 (d, H_a) for **s1a** and 0.98 (t, *aryl ethyl group*) for **s2a**. The major η^3-product, **s2a**, appeared to be formed as a single positional isomer. Platinum η^3-complex **s1a.** ^{1}H NMR (600 MHz CF_3CD_2OD) δ 7.14 (s, 1H), 7.12 (s, 1H), 6.99 (s, 1H), 6.85 (s, 1H), 6.76 (s, 1H), 6.52 (s, 1H), 5.37 (br s, 1H), 2.68 (q, *J* = 6.2 Hz, 1H), 2.38 (s, 3H), 2.25 (s, 3H), 2.20 (s, 3H), 2.15 (s, 3H), 2.08 (s, 3H), 2.01 – 2.05 (m, 2H), 1.98 (s, 3H), 1.83 (s, 3H), 1.77 (s, 3H), 1.67 (s, 3H), 1.53 (s, 3H), 0.24 (d, *J* = 6.6 Hz, 3H); selected data from ^{13}C NMR (150.8 MHz, CF_3CD_2OD) δ 179.86, 178.2, 152.8, 152.3, 150.1, 143.1, 130.0, 129.6, 93.4, 33.1, 32.9, 30.1, 30.05, 30.0, 29.9, 29.7, 21.8, 21.3, 18.9, 17.6, 14.8.
Platinum η^3-complex **s2a.** ^{1}H NMR (600 MHz, CF_3CD_2OD) δ 7.06 (br s, 1H), 7.02 (s, 1H), 7.01 (s, 1H), 6.81 (s, 1H), 6.69 (s, 1H), 5.99 (s, 1H), 5.77 (br s, J_{PtH} = 26 Hz at 300 MHz, 1H), 2.36 (d, *J* = 4.2 Hz 1H) 2.35 (s, 3H), 2.34 (s, 3H), 2.29 (d, *J* = 4.2 Hz, 1H). 2.21 (s, 3H), 2.16 (s, 3H), 1.90 (s, 3H), 1.86 (s, 3H), 1.82 (s, 3H), 1.78 (s, 3H), 1.76 (s, 3H), 0.98 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (150.8 MHz, CF_3CD_2OD) δ 179.8, 178.9, 157.4, 152.4, 150.9 (br s), 149.3 (br s) 145.8, 144.9, 144.6, 143.9, 141.9 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$, 140.3 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 139.5 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 137.9 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 133.3, 131.1, 130.6, 130.4, 123.3, 120.2, 118.3, 101.0, 100.9, 94.2, 43.0, 30.0, 29.8, 21.5, 21.3, 21.1, 18.8, 18.6, 17.5, 17.4, 14.7, 14.6.



Platinum η³-complexes s3a and s4a. The representative procedure was followed using platinum methyl complex **2a** (0.020 mmol) and 0.011 mL of 4-ethyltoluene (0.079 mmol) to afford a 77:23 mixture of **s3a** : **s4a**. The isomer ratios were determined from comparison of the methyl group resonances: 0.33 (d, H_a) for **s3a** and 1.04 (t, *aryl ethyl group*) for **s4a**. Platinum η³-complex **s3a:** ^{1}H NMR (600 MHz, CF_3CD_2OD) δ 7.15 (br s, 2H), 7.09 (br s, 2H), 6.95 (s, 1H), 6.94 (s, 1H), 5.97 (d, J = 5.5 Hz, 1H), 5.58 (d, J = 5.5 Hz, 1H), 2.78 (q, J = 6.6 Hz, 1H), 2.42 (s, 3H), 2.36 (s, 3H), 2.35 (s, 3H), 2.19 (s, 3H), 1.97 (s, 3H), 1.90 (s, 3H), 1.87 (s, 3H), 1.81 (s, 3H), 1.47 (s, 3H), 0.33 (d, J = 6.6 Hz, 3H). ^{13}C NMR (150 MHz, CF_3CD_2OD) δ 180.3, 177.6, 150.9 (br s), 149.3 (br s), 144.6, 142.8, 141.7 (m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 140.1 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 140.4, 139.7, 139.5 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 139.6, 139.0, 137.9 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 137.5, 131.4, 131.2 (br s), 131.1, 129.8, 129.4, 129.0, 128.3, 113.7, 102.3, 101.9 (qm, J = 22.5 Hz, $\mathbf{C}F_3CD_2OB(C_6F_5)_3$) 43.0, 22.3, 21.2, 19.1, 19.0, 18.1, 17.8, 17.43, 16.8, 13.9, 12.6.

Platinum η³-complex **s4a:** ^{1}H NMR (600 MHz, CF_3CD_2OD) δ 7.18 (s, 1H), 7.06 (s, 2H), 7.03 (s, 2H), 7.01 (s, 1H), 6.53 (d, J = 2.1 Hz, 1H), 6.24 (d, J = 2.4 Hz, 1H), 2.39 (s, 3H), 2.37 (s, 3H), 2.36 (s, 3H), 2.29 (s, 3H), 2.26 (s, 3H), 2.20 (s, 3H), 2.18 – 2.12 (m, 2H), 1.88 (s, 1H), 1.87 (s, 1H), 1.85 (s, 3H), 1.47 (s, 3H), 1.04 (t, J = 7.8, 3H). Selected data from ^{13}C NMR (150 MHz, CF_3CD_2OD) δ 180.4, 178.3, 151.1, 146.8, 145.5, 144.6, 140.3, 139.9, 137.4, 137.0, 130.9, 130.0, 129.2, 128.7, 128.4, 126.6, 126.4, 122.8, 117.9, 114.7, 30.2, 29.7, 29.6, 22.3, 21.6, 21.1, 19.1, 18.8, 18.3, 16.3, 16.0.

LRMS (ESI) m / z calcd for $C_{31}H_{39}N_2Pt^+$ [M – {$CF_3CD_2OB(C_6F_5)_3$}]$^+$ 634, found 634. The observed isotopic distribution pattern was consistent with the simulation.



Platinum η³-complexes 14a and 15a. The representative procedure was followed using platinum methyl complex **2a** (0.019 mmol) and 0.009 mL of 3-ethyltoluene (0.065 mmol) to afford a 79:21 mixture of **14a** : **15a**. η³-Complex **14a** was formed as a 66:33 mixture of positional isomers and η³-complex **15a** was formed as a 93:7 mixture of position isomers. The isomer ratios were determined from comparison of the methyl group resonances between 0.25 – 0.35 (d, H_a) for **14a** and 0.95 – 1.05 (t, *aryl ethyl group*) for **15a**. Platinum η³-complex **14a** (major positional isomer): ^{1}H NMR (600 MHz, CF_3CD_2OD) δ 7.15 (br s, 2H), 7.06 (br s, 2H),

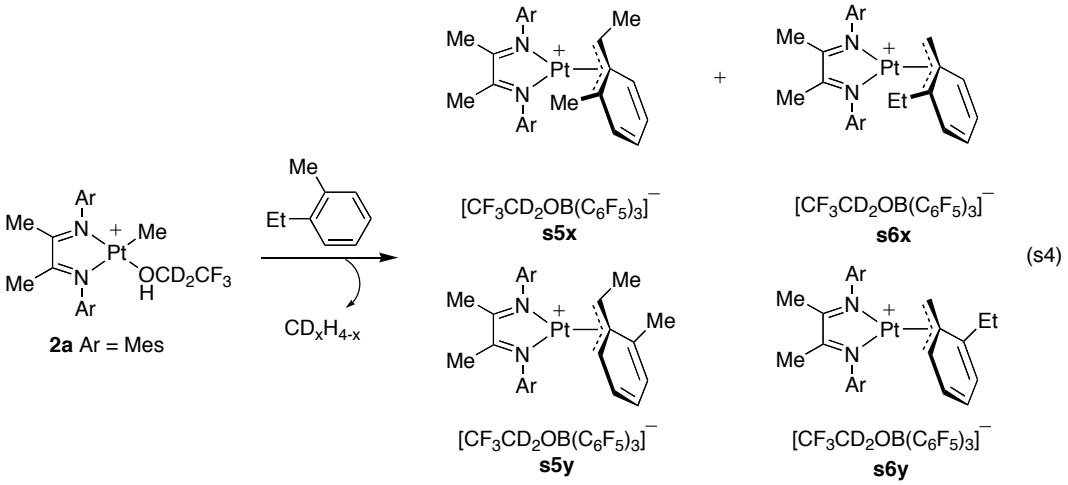
7.01 (m, 1H), 6.98 (s, 1H), 6.77 (s, 1H), 5.34 (d, J_{PtH} = 44 Hz, 1H), 2.77 (q, J = 6.6 Hz, J_{PtH} = ~60 Hz, 1H), 2.379 (s, 3H), 2.376 (s, 3H), 2.35 (s, 3H), 2.31 (s, 3H), 2.25 (s, 3H), 1.93 (s, 3H), 1.89 (s, 3H), 1.86 (s, 3H), 1.41 (s, 3H), 0.32 (d, J = 6.6 Hz, 3H). ^{13}C NMR (150 MHz, CF_3CD_2OD) δ 180.3, 177.5, 150.9 (br s), 149.3 (br s), 144.4, 143.1, 141.7 (m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 140.4, 139.9, 139.6, 139.5 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 138.7 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 137.9 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 131.4, 131.1 (br s), 131.0, 130.8, 129.9, 129.7, 129.4, 128.8, 124.6, 118.9 (m, $\mathbf{C}F_3CD_2OB(C_6F_5)_3$), 117.7, 43.0, 32.6, 30.1, 21.2, 21.1, 18.1, 17.8, 17.4, 16.8, 15.0, 12.3.

Platinum η^3-complex **14a** (minor positional isomer): ^{1}H NMR (600 MHz, CF_3CD_2OD) δ 7.11 (s, 2H), 7.08 (br s, 2H), 7.03 (br s, 1H), 6.86 (s, 1H), 6.06 (dd, J = 8.4, 6.6 Hz, 1H), 5.77 (J_{PtH} = ~30 Hz, 1H), 2.86 (q, J = 6.6 Hz, J_{PtH} = ~54 Hz, 1H), 2.36 (s, 3H), 2.35 (s, 3H), 2.34 (s, 3H), 2.31 (s, 3H), 2.33 (s, 3H), 2.14 (s, 3H), 2.04 (s, 3H), 1.98 (s, 3H), 1.82 (s, 3H), 0.29 (d, J = 6.6 Hz, 3H). ^{13}C NMR (150 MHz, CF_3CD_2OD) δ 180.4, 178.3, 156.4, 149.1, 146.7, 145.9, 144.6, 143.2, 140.5, 140.3, 140.1, 131.4, 131.0, 129.9, 129.5, 129.1, 128.6, 128.4, 116.7, 112.2, 43.9, 32.5, 21.8, 21.0, 19.0, 18.8, 17.8, 17.7, 17.6, 17.34, 13.0.

Platinum η^3-complex **15a** (selected data for major positional isomer): ^{1}H NMR (600 MHz, CF_3CD_2OD) δ 6.36 (t, J = 7.8 Hz, 1H), 5.71 (d, J = 7.6 Hz, J_{PtH} broadening observed, 1H), 2.33 (s, 3H), 2.11 (s, 3H), 2.10 (s, 3H), 1.98 (s, 3H), 1.87 (m, 2H), 1.663 (s, 3H), 1.658 (s, 3H), 1.61 (s, 3H), 1.04 (t, J = 7.8, 3H); selected data from ^{13}C NMR (150 MHz, CF_3CD_2OD) δ 180.2, 178.2, 156.3, 146.6, 144.7, 143.5, 143.2, 142.9, 139.7, 132.2, 131.4, 130.9, 130.8, 129.7, 129.5, 129.3, 129.2, 128.6, 122.8, 116.7, 42.9, 30.1, 22.1, 21.6, 20.98, 19.9, 19.1, 18.97, 17.5, 17.4, 17.30.

Platinum η^3-complex **15a** (selected data for minor positional isomer): 0.97 (t, J = 7.8 Hz, 3H).

LRMS (ESI) m / z calcd for $C_{31}H_{39}N_2Pt^+$ [M – {$CF_3CD_2OB(C_6F_5)_3$}]$^+$ 634, found 634. The observed isotopic distribution pattern was consistent with the simulation.



(s4)

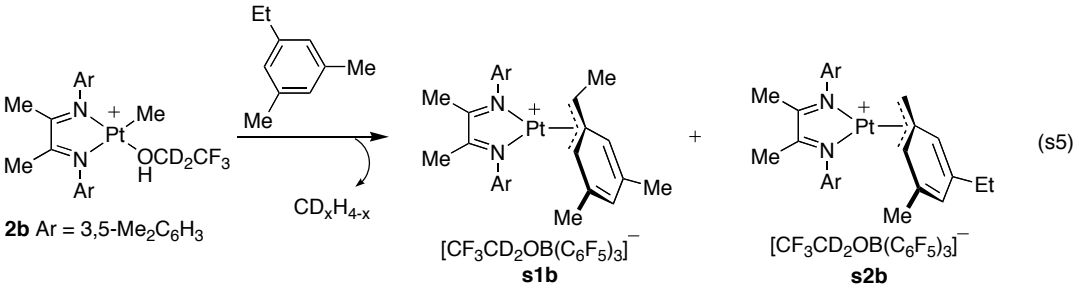
Platinum η^3-complexes s5a and s6a. The representative procedure was followed using platinum methyl complex **2a** (0.019 mmol) and 0.009 mL of 2-ethyltoluene (0.065 mmol) to afford a 78:22 mixture of **s5a** : **s6a**. η^3-Complex **s5a** was formed as a >95:5 mixture of positional isomers and η^3-complex **s6a** was formed as a 84:16 mixture of position isomers. The isomer ratios were determined from comparison of the methyl group resonances between 0.25 – 0.35 (d, H_a) for **s5a** and 0.95 – 1.05 (t, *aryl ethyl group*) for **s6a**. Platinum η^3-complex **s5a** (major positional isomer): ^{1}H NMR (600 MHz, CF_3CD_2OD) δ 7.10 (br s, 1H), 7.05 (s, 1H), 6.99 (t, J = 3.0 Hz, 1H), 6.96 (s, 1H), 6.77 (s, 1H), 6.67 (t, J = 7.8 Hz, 1H), 6.10 (t, J = 7.2 Hz, 1H), 5.80 (t, J = 3.0 Hz, J_{PtH} = 48 Hz, 1H), 3.65 (q, J = 6.6 Hz, J_{PtH} broadening observed, 1H), 2.38 (s, 3H), 2.37 (s, 3H), 2.31 (s, 3H), 2.30 (s, 3H), 2.14 (s, 3H), 2.11 (s, 3H), 1.97 (s, 3H), 1.88 (s, 3H), 1.33 (s, 3H), 0.44 (d, J = 6.6 Hz, 3H); ^{13}C NMR (150.8 MHz, CF_3CD_2OD) δ 180.3, 177.7, 150.9 (br s), 149.3 (br s), 145.2, 142.6, 141.7 (br m,

$CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 140.5, 140.2 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 139.8, 139.6, 139.5 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 137.9 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 136.9, 136.1, 135.4, 131.2, 131.1, 130.9, 130.8, 129.6, 129.2, 128.5, 124.1 (br m, $\mathbf{C}F_3CD_2OB(C_6F_5)_3$), 115.1, 44.11, 30.1, 21.2, 21.1, 20.0, 19.2, 19.1, 18.8, 18.0, 17.9, 17.8.

Platinum η^3-complex **s6a** (selected data for major positional isomer): ^{1}H NMR (600 MHz, CF_3CD_2OD) δ 7.25 (m, 1H), 7.04 (m, 1H), 6.91 (m, 1H), 6.72 (t, J = 7.2 Hz, 1H), 6.02 (t, J = 7.2 Hz, 1H), 5.84 (m, 1H), 5.76 (m, 1H), 5.71 (t, J = 3.3 Hz, J_{PtH} = ~50 Hz, 1H), 2.95 (d, J = 4.8 H, J_{PtH} broadening observed, 1H), 2.344 (s, 3H), 2.341 (s, 3H), 2.33 (s, 3H), 2.25 – 2.19 (m, 2H), 2.16 (s, 3H), 2.03 (s, 3H), 1.88 (s, 3H), 1.87 (s, 3H), 1.34 (s, 3H), 1.12 (t, J = 7.8, 3H); ^{13}C NMR (150 MHz, CF_3CD_2OD) δ 180.8, 178.1, 145.8, 143.6, 142.7, 142.8, 142.0, 140.8, 140.4, 139.9, 137.1, 136.0, 135.3, 132.0, 130.7, 130.4, 129.6, 128.8, 127.5, 117.5, 44.09, 30.1, 29.8, 27.4, 22.1, 21.0, 20.0, 19.1, 18.9, 17.6, 14.4.

Platinum η^3-complex **s6a** (selected data for minor positional isomer): 0.96 (t, J = 7.8 Hz, 3H).

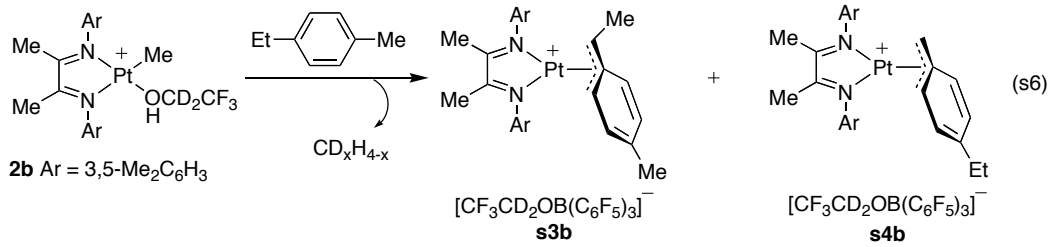
LRMS (ESI) m / z calcd for $C_{31}H_{39}N_2Pt^+$ [M – {$CF_3CD_2OB(C_6F_5)_3$}]$^+$ 634, found 634. The observed isotopic distribution pattern was consistent with the simulation.



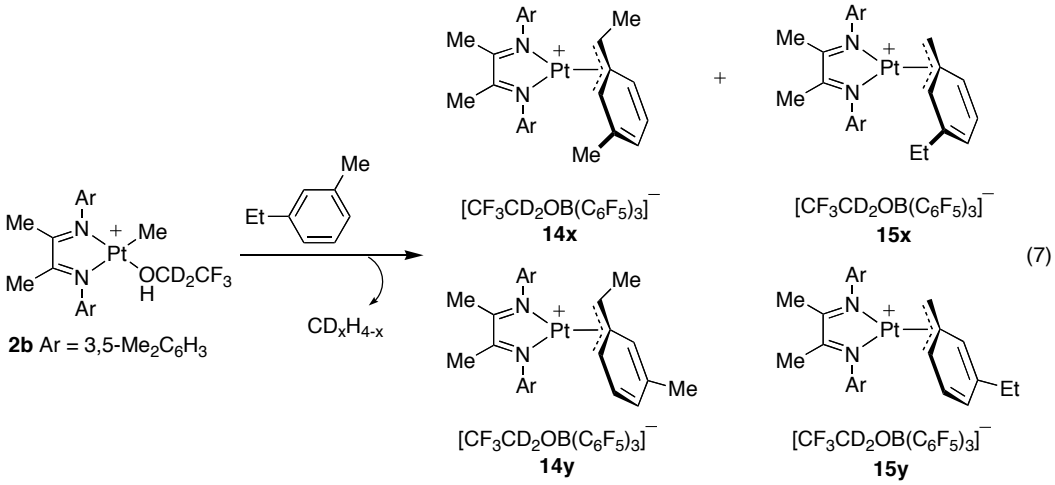
Platinum η^3-complexes s1b and s2b. The representative procedure was followed using platinum methyl complex **2b** (0.029 mmol) and 0.018 mL of 3,5-dimethyl-ethylbenzene (0.115 mmol) to afford a 20:80 mixture of **s1b** : **s2b**. η^3-Complex **s2b** was formed as a >95:5 mixture of positional isomers. The isomer ratios were determined from comparison of the methyl group resonances: 0.32 (d, H_a) for **s1b** and 1.04 (t, *aryl ethyl group*) for **s2b**. Platinum η^3-complex **s1b:** ^{1}H NMR (600 MHz, CF_3CD_2OD) δ 7.25 (s, 1H), 7.07 (s, 1H), 6.89 (s, 1H), 6.71 (s, 1H), 6.63 (s, 1H), 6.46 (s, 1H), 6.22 (m, 1H), 5.56 – 5.70 (br s, 1H), 5.43 (s, 1H), 2.66 (q, J = 6.6 Hz, 1H), 2.46 (s, 3H), 2.38 (s, 3H), 2.32 (s, 3H), 2.28 (s, 3H), 2.19 (s, 3H), 2.03 (s, 3H), 1.88 (s, 3H), 1.65 (s, 3H), 0.32 (d, J = 6.6 Hz, 3H); ^{13}C NMR (150.8 MHz, CF_3CD_2OD) δ 179.40, 178.5, 152.4, 151.6, 149.6, 149.1, 148.5, 147.89, 143.0, 142.7, 142.2, 138.7, 131.4, 131.0, 130.5, 128.7, 128.3, 126.9, 120.5, 117.5, 42.3, 30.1, 29.92, 22.1, 21.6 (2C), 21.2, 21.1, 21.0, 12.9

Platinum η^3-complex **s2b:** ^{1}H NMR (600 MHz, CF_3CD_2OD) δ 7.04 (s, 1H), 6.99 (s, 1H), 6.90 (s, 1H), 6.75 (br s, 2H), 6.13 (s, 1H), 6.04 – 6.22 (br s, 1H), 5.84 – 6.04 (br s, 1H), 5.76 (s, J_{PtH} = 30 Hz at 300 MHz, 1H), 2.58 (d, J = 7.8 Hz, 1H), 2.43 (d, J = 7.8 Hz, 1H), 2.34 (s, 6H), 2.32 (s, 6H), 1.95 (s, 3H), 1.89 (s, 3H), 1.86 (s, 3H), 1.04 (t, J = 7.8 Hz, 3H); ^{13}C NMR (150.8 MHz, CF_3CD_2OD) δ 179.38, 177.8, 156.5, 151.7, 150.9 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 150.6, 149.3 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 147.95, 146.8, 146.7, 146.6, 142.4, 142.1, 140.1, 139.6 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 137.9 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 131.6, 131.2, 128.8, 127.0, 119.0, 118.6, 102.6, 93.6 (br), 33.1, 29.93 (2C), 21.8, 21.7, 21.5 (2C), 21.4, 20.0, 14.9.

LRMS (ESI) m / z calcd for $C_{30}H_{37}N_2Pt^+$ [(M – {$CF_3CD_2OB(C_6F_5)_3$}]$^+$ 620, found 620. The observed isotopic distribution pattern was consistent with the simulation.



Platinum η³-complexes s3b and s4b. The representative procedure was followed using platinum methyl complex **2b** (0.019 mmol) and 0.008 mL of 4-ethyltoluene (0.06 mmol) to afford a 78:22 mixture of **s3b** : **s4b**. The isomer ratios were determined from comparison of the methyl group resonances: 0.38 (d, H_a) for **s3b** and 0.98 (t, *aryl ethyl group*) for **s4b**. Platinum η³-complex **s3b**. ^{1}H NMR (600 MHz, CF_3CD_2OD) δ 7.16 (m, 1H), 7.07 (s, 1H), 7.06 (br s, 2H), 6.88 (s, 1H), 6.84 (s, 1H), 6.55 – 6.63 (m, 2H), 6.48 (s, 1H), 5.87 – 5.98 (br s, 1H), 2.80 (q, J = 6.6 Hz, J_{PtH} broadening observed, 1H), 2.38 (s, 3H), 2.18 (s, 3H), 2.15 (s, 3H), 2.04 (s, 3H), 1.98 (s, 3H), 1.91 (s, 3H), 1.77 (s, 3H), 0.38 (d, J = 6.6 Hz, 3H).
Platinum η³-complex **s4b**: ^{1}H NMR (600 MHz, CF_3CD_2OD) δ 7.22 (s, 1H), 7.00 (s, 1H), 6.97 (s, 1H), 6.89 (s, 1H), 6.69 (m, 1H), 6.45 (s, 1H), 6.32 (s, 1H), 6.28 (m, 1H), 6.21 (s, 1H), 5.75 (d, J = 6.6 Hz, 1H), 2.35 (s, 3H), 2.34 (s, 3H), 2.29 (s, 3H), 2.26 (s, 3H), 2.09 (s, 3H), 2.07 (s, 3H), 2.06 – 2.10 (m, 2H), 1.87 (d, J = 7.8 Hz, 1H), 1.81 (d, J = 7.8 Hz, 1H), 0.98 (t, J = 7.8 Hz, 3H).
Combined data for complexes **s3b** and **s4b**: ^{13}C NMR (150.8 MHz, CF_3CD_2OD) δ 185.4, 184.4, 179.4, 177.2, 155.4, 150.9 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 149.6, 149.3 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 148.5, 147.9, 145.6, 145.2, 144.2, 143.6, 143.1, 142.2, 142.1, 141.4, 140.3, 139.7 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 138.1 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 137.2, 134.0, 132.9, 132.0, 131.7, 131.3, 130.6, 130.5, 129.9, 129.6, 129.2, 127.9, 126.5, 126.1, 125.1, 124.2, 121.5 (br m, $\mathbf{C}F_3CD_2OB(C_6F_5)_3$), 120.5, 120.4, 120.1, 120.0, 119.8, 119.5, 119.2, 42.5 (br), 30.2, 30.1, 29.7, 29.57, 29.55, 29.47, 29.41, 22.1, 22.0, 21.5, 21.4, 21.1, 21.0, 20.1, 20.04, 19.97, 19.6.
LRMS (ESI) *m* / *z* calcd for $C_{29}H_{35}DN_2Pt^+$ [M – {$CF_3CD_2OB(C_6F_5)_3$} + D + H]$^+$ 609, found 609. The observed isotopic distribution pattern was consistent with the simulation.



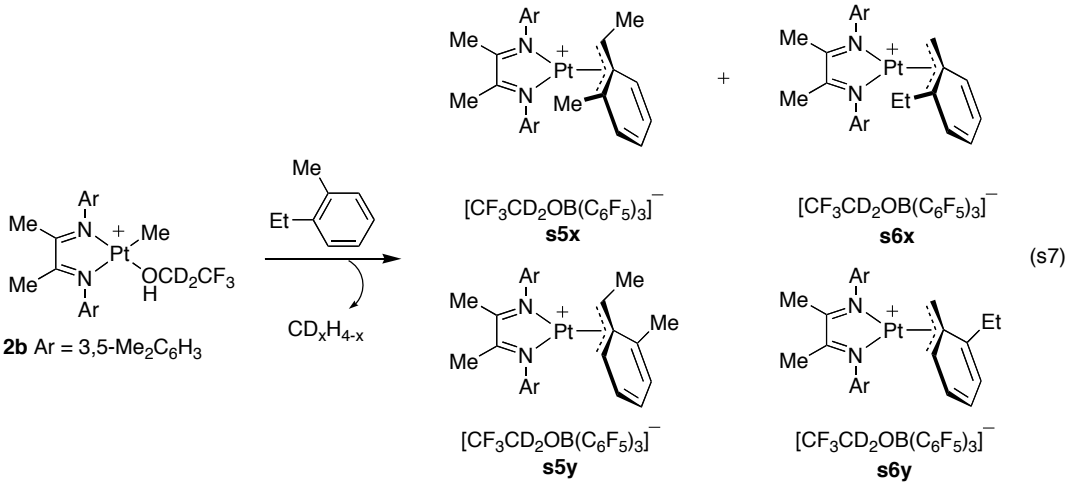
Platinum η³-complexes 14b and 15b. The representative procedure was followed using platinum methyl complex **2b** (0.019 mmol) and 0.011 mL of 3-ethyltoluene (0.079 mmol) to afford a 51:49 mixture of **14b** : **15b**. η³-Complex **14b** was formed as a 50:50 mixture of positional isomers, and η³-complex **15b** was formed as a 79:21 mixture of positional isomers. The isomer ratios were determined from comparison of the methyl group resonances: 0.23 (d, H_a) for **14b** and 0.99 (t, *aryl ethyl group*) for **15b**. Platinum η³-complex **14b** (combined data for both positional isomers): ^{1}H NMR (600 MHz, CF_3CD_2OD) δ 7.18 (m, 1H), 7.13 (m, 1H), 7.10 (s, 1H),

6.93 (m, 1H), 6.86 (s, 1H), 6.85 (s, 1H), 6.81 (m, 1H), 6.78 (s, 1H), 6.76 (s, 1H), 6.74 (s, 1H), 6.73 (s, 1H), 6.68 (s, 1H), 6.67 (s, 1H), 6.59 (s, 1H), 6.57 (s, 1H), 6.54 (s, 1H), 6.35 (m, 1H), 6.14 (s, 1H), 5.97 (s, 1H), 5.57 (d, J = 6.6 Hz, 1H), 2.84 (q, J = 6.6 Hz, J_{PtH} broadening observed, 1H), 2.69 (q, J = 6.6 Hz, J_{PtH} broadening observed, 1H), 2.37 (s, 3H), 2.36 (s, 3H), 2.34 (s, 3H), 2.32 (s, 3H), 2.27 (s, 3H), 2.26 (s, 3H), 2.17 (s, 3H), 1.99 (s, 3H), 1.98 (s, 3H), 1.95 (s, 3H), 1.93 (s, 3H), 1.92 (s, 3H), 1.89 (s, 3H), 1.69 (s, 3H), 0.37 (d, J = 6.6 Hz, 3H), 0.35 (d, J = 6.6 Hz, 3H); the benzylic methylene protons were not distinguishable. ^{13}C NMR (150.8 MHz, CF_3CD_2OD) δ 179.7, 179.64, 179.60, 179.56, 156.1, 150.9 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 150.6, 149.6, 149.3 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 147.74, 147.72, 147.6, 145.2, 143.0, 142.44, 142.2, 142.1, 141.5, 140.7, 140.2, 139.7 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 138.8, 138.1 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 132.9, 131.99, 131.96, 131.7, 131.5, 131.4, 131.1, 131.0, 130.7, 129.65, 129.63, 127.8, 127.6, 126.40, 126.38, 126.1, 125.1, 121.8 (br m, $\mathbf{C}F_3CD_2OB(C_6F_5)_3$), 121.5, 120.3, 119.8, 118.9, 42.71, 42.7, 22.08, 22.04, 21.9, 21.2, 21.05, 20.20, 20.18, 20.14, 20.04, 20.01, 19.96, 19.82, 19.77, 19.7, 14.9, 14.7.

Platinum η^3-complex **15b** (major positional isomer): ^{1}H NMR (600 MHz, CF_3CD_2OD) δ 7.16 (m, 1H), 7.15 (s, 1H), 6.84 (s, 1H), 6.61 (s, 1H), 6.56 (m, 1H), 6.31 (s, 1H), 6.27 (m, 1H), 5.95 (s, 1H), 5.78 (br s, 1H), 5.63 (s, 1H), 3.60 (s, 1H), 2.66 (d, J = 7.8 Hz, 1H), 2.54 (d, J = 7.8 Hz, 1H), 2.38 (s, 6H), 2.19 (s, 6H), 2.15 (s, 3H), 2.04 (s, 3H), 1.01 (t, J = 7.8 Hz, 3H); ^{13}C NMR (150 MHz, CF_3CD_2OD) δ 185.4, 184.4, 147.7, 147.8, 145.5, 144.1, 142.38, 134.0, 132.8, 129.8, 129.2, 128.8, 127.4, 126.9, 125.5, 125.11, 123.7, 123.3, 120.5, 120.0, 30.1, 30.0, 21.7, 21.52, 21.50, 21.4, 21.08, 20.09, 20.03.

Selected data for platinum η^3-complex **15b** (minor positional isomer): ^{1}H NMR (600 MHz, CF_3CD_2OD) δ 1.05 (t, J = 7.8 Hz, 3H).

LRMS (ESI) m / z calcd for $C_{29}H_{36}N_2Pt^+$ [(M – {$CF_3CD_2OB(C_6F_5)_3$} + H]$^+$ 607, found 607. The observed isotopic distribution pattern was consistent with the simulation.



(s7)

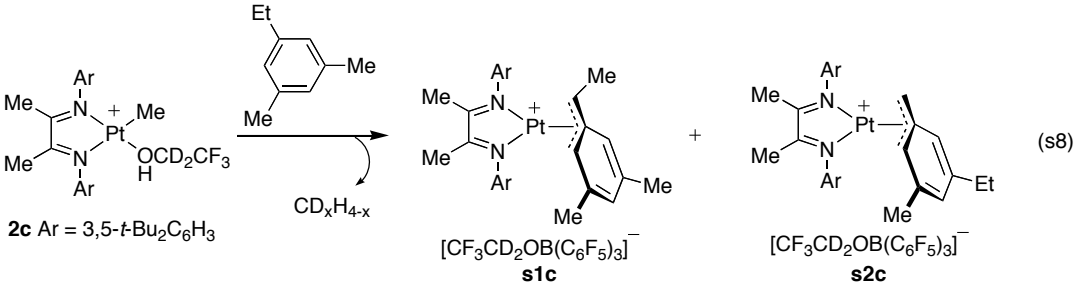
Platinum η^3-complexes s5b and s6b. The representative procedure was followed using platinum methyl complex **2b** (0.019 mmol) and 0.011 mL of 2-ethyltoluene (0.078 mmol) to afford a 69:31 mixture of **s5b** : **s6b**. η^3-Complex **s5b** was formed as a >95:5 mixture of position isomers, and η^3-complex **s6b** was formed as a 76:24 mixture of position isomers. The isomer ratios were determined from comparison of the methyl group resonances: 0.50 (d, H_a) for **s5b** and 1.04 – 1.14 (t, *aryl ethyl*) for **s6b**. Platinum η^3-complex **s5b**: ^{1}H NMR (600 MHz, CF_3CD_2OD) δ 6.89 (d, J = 7.2 Hz, 1H), 6.80 – 6.84 (m, 2H), 6.50 – 6.82 (m, 3H), 6.47 (s, 1H), 6.15 (t, J = 7.2 Hz, 1H), 5.75 (d, J = 6.6 Hz, J_{PtH} broadening observed, 1H), 5.5 – 5.8 (br s, 1H), 3.77 (q, J = 6.6 Hz, J_{PtH} broadening observed, 1H), 2.38 (br s, 6H), 2.19 (s, 3H), 2.15 (s, 3H), 1.98 (s, 3H), 1.96 (br s, 6H), 0.50 (d, J = 6.6 Hz, 3H); ^{13}C NMR (150.8 MHz, CF_3CD_2OD) δ 184.4, 179.4, 150.9 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 150.2, 149.3 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 147.45, 145.5, 144.1, 142.2, 139.7 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 138.0 (br m,

$CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 136.6, 134.9, 134.0, 131.6, 131.5, 130.7, 129.6, 127.5, 127.4, 127.0, 121.6 (br m, $\mathbf{C}F_3CD_2OB(C_6F_5)_3$), 120.0, 119.6, 118.9, 45.48, 27.4, 21.4, 21.09, 20.1, 19.8, 19.7, 19.0, 15.2.

Platinum η^3-complex **s6b** (major positional isomer): ^{1}H NMR (600 MHz, CF_3CD_2OD) δ 6.89 (d, J = 7.2 Hz, 1H), 6.54 – 6.9 (m, 5H), 6.34 (m, 1H), 6.08 (t, J = 7.2 Hz, 1H), 5.64 – 5.84 (br s, 1H), 5.44 (d, J = 6.6 Hz, 1H), 3.12 (d, J = 4.8Hz, 2H), 2.50 – 2.54 (m, 2H), 2.36 (s, 3H), 2.15 (br s, 6H), 2.03 (s, 3H), 1.99 (s, 3H), 1.94 (s, 3H), 1.15 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150.8 MHz, CF_3CD_2OD) δ 179.8, 177.4, 150.6, 149.3, 147.39, 144.7, 143.0, 140.8, 137.5, 136.4, 132.9, 132.0, 130.9, 129.5, 129.2, 128.9, 128.8, 126.1, 120.5, 120.4, 45.43, 22.1, 21.8, 21.6, 21.14, 20.04, 20.0, 19.9, 19.3.

Selected data for platinum η^3-complex **s6b** (minor positional isomer): ^{1}H NMR (600 MHz, CF_3CD_2OD) δ 1.04 (t, J = 7.2Hz, 3H).

LRMS (ESI) m / z calcd for $C_{29}H_{36}N_2Pt^+$ [M – {$CF_3CD_2OB(C_6F_5)_3$} + H]$^+$ 607, found 607. The observed isotopic distribution pattern was consistent with the simulation.

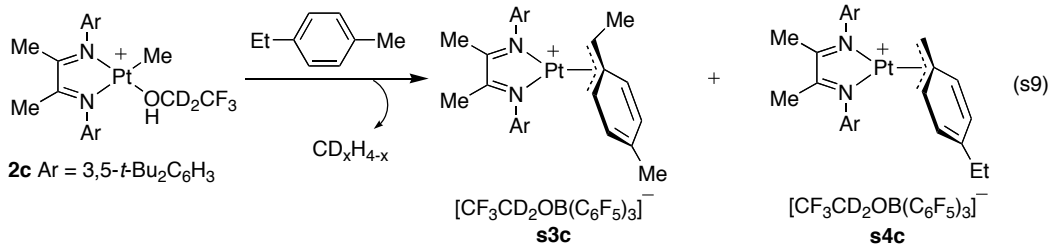


Platinum η^3-complexes s1c and s2c. The representative procedure was followed using platinum methyl complex **2c** (0.013 mmol) and 0.009 mL of 3,5-dimethyl-ethylbenzene (0.06 mmol) to afford a 55:45 mixture of **s1c** : **s2c**. η^3-Complex **s2c** was formed as a >95:5 mixture of position isomers. The isomer ratio was determined from comparison of the methyl group resonances: 0.23 (d, H_a) for **s2c** and 0.99 (t, *aryl ethyl group*) for **s2c**. Platinum η^3-complex **s1c**: ^{1}H NMR (600 MHz, CF_3CD_2OD) δ 7.57 (t, J = 1.8 Hz, 1H), 7.56 (t, J = 1.8 Hz, 1H), 7.36 (t, J = 1.8 Hz, 1H), 7.25 (br s, 1H), 7.02 (br s, 1H), 7.00 (d, J = 1.8 Hz, 1H), 6.48 (t, J = 1.8 Hz, 1H), 6.05 (br s, 1H), 5.47 (br s, J_{PtH} broadening observed, 1H), 2.69 (q, J = 6.6 Hz, J_{PtH} broadening observed, 1H), 2.25 (s, 3H), 1.99 (s, 3H), 1.81 (s, 3H), 1.59 (s, 3H), 1.39 (s, 9H), 1.370 (s, 9H), 1.35 (s, 9H), 1.33 (s, 9H), 0.23 (d, J = 6.6 Hz, 3H).

Platinum η^3-complex **s2c**: ^{1}H NMR (600 MHz, CF_3CD_2OD) δ 7.71 (t, J = 1.8 Hz, 1H), 7.531 (t, J = 1.8 Hz, 1H), 7.525 (t, J = 1.8 Hz, 1H), 7.25 (br s, 1H), 6.78 (br s, 1H), 6.63 (br s, 1H), 6.42 (t, J = 1.8 Hz, 1H), 6.06 (t, J = 1.8 Hz, 1H), 5.89 (br s J_{PtH} broadening observed, 1H), 2.52 (d, J = 4.6 Hz, 1H), 2.50 (d, J = 4.6 Hz, 1H), 2.25 – 2.16 (m, 2H), 2.13 (s, 3H), 1.97 (s, 3H), 1.80 (s, 3H), 1.372 (s, 9H), 1.36 (s, 9H), 1.34 (s, 9H), 1.24 (s, 9H), 0.99 (t, J = 7.8 Hz, 3H).

Combined data for complexes **s1c** and **s2c**: ^{13}C NMR (150 MHz, CF_3CD_2OD) δ 179.6, 179.04, 178.95, 178.8, 157.7, 155.8, 155.6, 155.2, 150.9 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 149.3 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 149.0, 148.9, 146.8, 146.73, 146.66, 140.2, 140.1, 139.7 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 138.1 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 130.22, 130.24, 129.2, 128.8, 128.3, 127.4, 126.94, 126.90, 126.0, 125.5, 125.1, 124.5, 124.2, 124.0, 123.7, 123.3, 121.6 (br m, $\mathbf{C}F_3CD_2OB(C_6F_5)_3$), 119.4, 117.0, 116.83, 116.77, 115.3, 115.01, 114.95, 114.7, 98.8, 47.5, 42.9, 37.0, 36.7, 36.64, 36.60, 36.49, 34.2, 31.9, 31.87, 31.84, 31.78, 31.7, 31.6, 30.04, 29.98, 29.92, 29.88, 22.2, 21.9, 21.8, 21.5, 21.4, 21.3, 20.9, 20.3, 14.8, 12.9.

LRMS (ESI) m / z calcd for $C_{42}H_{61}N_2Pt^+$ [(M – {$CF_3CD_2OB(C_6F_5)_3$} + H]$^+$ 789, found 789. The observed isotopic distribution pattern was consistent with the simulation.

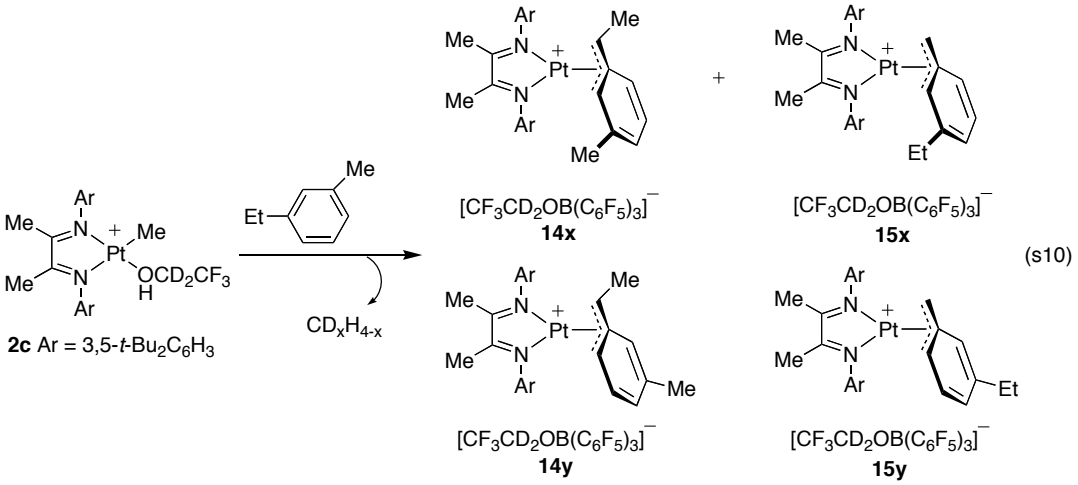


Platinum η³-complexes s3c and s4c. The representative procedure was followed using platinum methyl complex **2c** (0.015 mmol) and 0.008 mL of 4-ethyltoluene (0.06 mmol) to afford a 79:21 mixture of **s3c** : **s4c**. The isomer ratio was determined from comparison of the methyl group resonances: 0.23 (d, H_a) for **s3c** and 0.99 (t, *aryl ethyl group*) for **s4c**. Platinum η³-complex **s3c**: ^{1}H NMR (600 MHz, CF_3CD_2OD) δ 7.59 (t, *J* = 1.8 Hz, 1H), 7.57 (t, *J* = 1.8 Hz, 1H), 7.24 (br s, 1H), 7.15 (d, *J* = 1.8 Hz, 1H), 6.96 (s, 1H), 6.90 – 6.88 (m, 1H), 6.77 (br s, 1H), 6.74 (s, 1H), 6.29 (s, 1H), 5.81 (d, *J* = 7.2 Hz, J_{PtH} broadening observed, 1H), 2.77 (q, *J* = 6.6 Hz, 1H), 2.01 (s, 3H), 1.90 (s, 3H), 1.67 (s, 3H), 1.44 (s, 9H), 1.39 (br s, 9H), 1.35 (br s, 9H), 1.30 (s, 9H), 0.30 (d, *J* = 6.6 Hz, 3H).

Platinum η³-complex **s4c**: ^{1}H NMR (600 MHz, CF_3CD_2OD) δ 7.71 (t, *J* = 1.8 Hz, 1H), 7.36 (t, *J* = 1.8 Hz, 1H), 7.26 (m, 1H), 7.12 (s, 1H), 7.07 (s, 1H), 7.04 – 7.03 (m, 1H), 7.00 (br s, 1H), 6.83 (m, 1H), 6.41 (s, 1H), 5.38 (m, 1H), 2.18 (m, 2H), 2.13 (s, 3H), 1.98 – 1.95 (m, 2H), 1.99 (s, 3H), 1.29 (br s, 9H), 1.37 (s, 9H), 1.35 (br s, 9H), 1.24 (s, 9H), 0.89 (t, *J* = 7.5 Hz, 3H).

Combined data for complexes **s3c** and **s4c**: ^{13}C NMR (150 MHz, CF_3CD_2OD) δ 179.6, 179.0, 178.94, 178.84, 157.7, 157.2, 156.7, 156.0, 155.85, 155.81, 155.6, 155.5, 155.2, 150.9 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 149.3 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 149.0, 148.9, 147.9, 146.8, 146.73, 146.66, 140.17, 140.1, 139.7 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 138.1 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 130.2, 129.2, 128.5, 128.4, 128.3, 127.0, 125.1, 124.5, 124.2, 124.0, 121.6 (br m, $\mathbf{C}F_3CD_2OB(C_6F_5)_3$), 119.3, 117.0, 116.8, 116.3, 115.3, 115.03, 114.94, 114.7, 98.8, 47.5, 42.9, 37.0, 36.7, 36.6, 36.5, 34.3, 31.9, 31.87, 31.84, 31.78, 31.73, 31.68, 31.6, 30.0, 29.9, 22.2, 21.9, 21.8, 21.5, 21.4, 21.3, 20.9, 20.3, 14.8, 12.9.

LRMS (ESI) *m* / *z* calcd for $C_{41}H_{57}D_2N_2Pt^+$ [M – {$CF_3CD_2OB(C_6F_5)_3$} + 2D]$^+$ 776, found 776. The observed isotopic distribution pattern was consistent with the simulation.



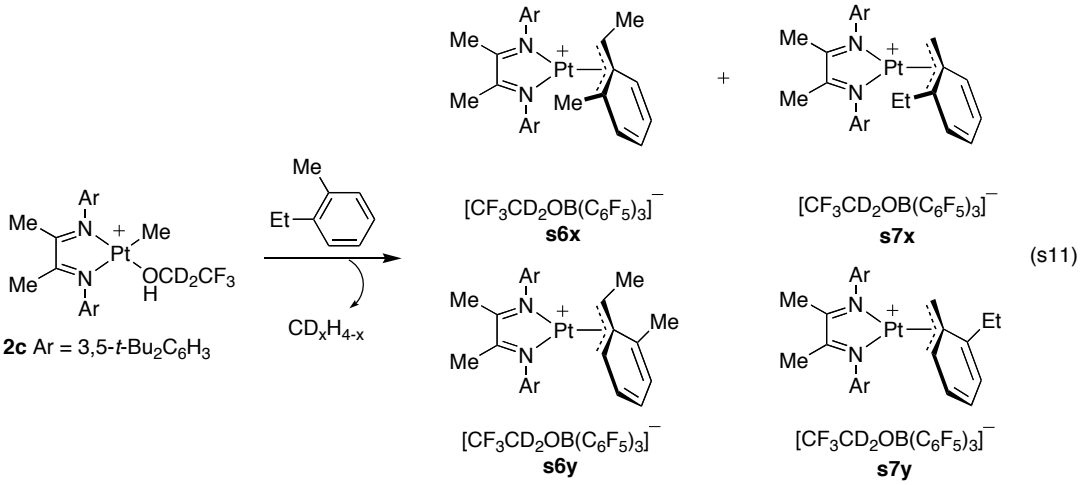
Platinum η³-complexes 14c and 15c. The representative procedure was followed using platinum methyl complex **2c** (0.014 mmol) and 0.009 mL of 3-ethyltoluene (0.065 mmol) to afford a 47:53 mixture of **14c** : **15c**. η³-Complex **14c** was formed as a 52:48 mixture of position isomers; and η³-complex **15c** was formed as a 70:30 mixture of position isomers. The isomer ratios were determined from comparison of the methyl group

resonances: 0.25 – 0.30 (d, H_a) for **14c** and 0.97 – 1.05 (t, *aryl ethyl group*) for **15c**. Platinum η^3-complex **14c** (combined data for both positional isomers): ^{1}H NMR (600 MHz, CF_3CD_2OD) δ 7.71 (t, *J* = 1.8 Hz, 1H), 7.58 (t, *J* = 1.8 Hz, 1H), 7.534 (t, *J* = 1.8 Hz, 1H), 7.525 (br s, 1H), 7.363 (t, *J* = 1.8 Hz, 1H), 7.34 (s, 1H), 7.25 (br s, 1H), 6.92 (s, 1H), 6.90 (s, 1H), 6.81 (br s, 1H), 6.77 (s, 1H), 6.75 (s, 1H), 6.74 (s, 1H), 6.72 (s, 1H), 6.62 (m, 1H), 6.56 (s, 1H), 6.52 (m, 2H), 6.07 (s, 1H), 5.69 (s, J_{PtH} broadening observed, 1H), 2.83 (q, *J* = 6.6 Hz, 1H), 2.73 (q, *J* = 6.6 Hz, 1H), 2.27 (s, 3H), 2.13 (s, 3H), 1.99 (s, 3H), 1.90 (s, 3H), 1.88 (s, 3H), 1.84 (s, 3H), 1.42 (s, 9H), 1.39 (br s, 18H), 1.36 (s, 9H), 1.33 (s, 9H), 1.26 (s, 9H), 1.25 (s, 9H), 1.18 (s, 9H), 0.29 (d, *J* = 6.6 Hz, 3H), 0.26 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, CF_3CD_2OD) δ 185.5, 185.3, 184.0, 181.6, 156.6, 156.1, 155.5, 155.4, 150.9 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 149.3 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 148.6, 148.4, 147.9, 145.8, 145.5, 141.4, 139.7 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 139.0, 138.1 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 137.2, 137.1, 130.7, 129.6, 129.2, 128.6, 128.4, 126.90, 126.4, 125.06, 124.0, 123.71, 123.68, 123.26, 123.21, 121.1 (br m, $\mathbf{C}F_3CD_2OB(C_6F_5)_3$), 118.5, 117.1, 117.0, 116.6, 116.8, 116.3, 115.3, 115.1, 85.2 (br m, 2C), 43.2, 43.1, 36.62, 36.59, 36.56, 36.5, 32.00, 31.95, 31.87, 31.78, 31.75, 31.68, 31.62, 29.99, 29.95, 30.04, 29.98, 29.88, 29.1, 22.5, 20.9, 20.4, 20.0, 19.8, 14.8, 12.9.

Platinum η^3-complex **15c** (major positional isomer): ^{1}H NMR (600 MHz, CF_3CD_2OD) δ 7.57 (br s, 2H), 7.29 (t, *J* = 1.8 Hz, 1H), 7.25 (br s, 1H), 6.86 (br s, 1H), 6.52 (br s, 1H), 6.52 (s, 1H), 6.23 (dd, *J* = 8.4, 6.0 Hz, 1H), 6.15 (s, 1H), 5.56 (d, *J* = 6.6 Hz, J_{PtH} broadening observed, 1H), 2.24 (s, 3H), 2.18 (m, 2H), 2.06 (m, 2H), 1.77 (s, 3H), 1.39 (br s, 9H), 1.37 (s, 9H), 1.32 (br s, 9H), 1.24 (s, 9H), 0.99 (t, *J* = 7.8 Hz, 3H); ^{13}C NMR (150 MHz, CF_3CD_2OD) δ 179.4, 177.5, 155.7, 155.5, 148.1, 146.8, 140.2, 131.3, 129.8, 127.8, 127.4, 125.5, 125.11, 124.4, 124.1, 116.8, 116.0, 115.0, 114.9, 76.4, 43.1, 36.74, 36.61, 36.55, 31.9, 30.1, 30.04, 22.2, 22.0, 21.5, 20.1, 19.7, 12.8.

Platinum η^3-complex **15c** (minor positional isomer): ^{1}H NMR (600 MHz, CF_3CD_2OD) δ 7.69 (t, *J* = 1.7 Hz, 1H), 7.63 (t, *J* = 1.8 Hz, 1H), 7.54 (t, *J* = 1.7 Hz, 1H), 7.28 (br s, 1H), 7.18 (m, 1H), 6.96 (t, *J* = 1.8 Hz, 1H), 6.56 (br s, 1H), 6.40 (t, *J* = 1.8 Hz, 1H), 6.31 (br s, 1H), 5.96 (d, *J* = 6.6 Hz, J_{PtH} broadening observed, 1H), 2.00 (s, 3H), 2.24 (m, 2H), 1.98 – 1.96 (m, 2H), 1.68 (s, 3H), 1.44 (s, 9H), 1.24 (s, 9H), 1.35 (br s, 9H), 1.34 (br s, 9H), 1.03 (t, *J* = 7.8 Hz, 3H).

LRMS (ESI) *m* / *z* calcd for $C_{41}H_{62}N_2Pt^+$ [M – {$CF_3CD_2OB(C_6F_5)_3$} + H]$^+$ 775, found 775. The observed isotopic distribution pattern was consistent with the simulation.



(s11)

Platinum η³-complexes s6c and s7c. The representative procedure was followed using platinum methyl complex **2c** (0.014 mmol) and 0.008 mL of 2-ethyltoluene to afford a 54:46 mixture of **s6c** : s7c. Both η^3-complexes **s6c** and s7c were formed as a >95:5 mixtures of position isomers. The isomer ratio was determined from comparison of the methyl group resonances: 0.48 (d, H_a) for **s6c** and 1.10 (t, *aryl ethyl group*) for **s7c**.

Combined data for complexes **s6c** and **s7c**: ^{1}H NMR (600 MHz, CF_3CD_2OD) δ 7.59 (t, *J* = 1.8 Hz, 1H), 7.57 (t, *J* = 1.8 Hz, 1H), 7.52 (dt, *J* = 9.6, 1.2 Hz, 2H), 7.34 (s, 1H), 7.10 (br s, 2H), 7.05 (d, *J* = 1.2 Hz, 1H), 7.02 (br s, 1H), 6.98 (s, 1H), 6.96 (d, *J* = 7.2 Hz, 1H), 6.93 (br d, *J* = 7.2 Hz, 1H), 6.76 (t, *J* = 7.2 Hz, 1H), 6.69 (t, *J* = 7.8 Hz, 1H), 6.20 (t, *J* = 7.8 Hz, 1H), 6.10 (t, *J* = 7.2 Hz, 1H), 6.06 (dt, *J* = 9.6, 1.8 Hz, 2H), 5.78 (d, *J* = 6.6 Hz, J_{PtH} broadening observed, 1H), 5.46 (d, *J* = 6.6 Hz, J_{PtH} broadening observed, 1H), 3.76 (q, *J* = 6.6 Hz, J_{PtH} broadening observed, 1H), 3.08 (d, *J* = 6.6 Hz, J_{PtH} broadening observed, 2H), 2.38 (q, *J* = 7.8 Hz, 2H), 2.02 (s, 3H), 2.00 (s, 3H), 1.98 (s, 3H), 1.95 (s, 3H), 1.92 (s, 3H), 1.43 (s, 18H), 1.39 (s, 18H), 1.37 (s, 18H), 1.30 (s, 18H), 1.11 (t, *J* = 7.8 Hz, 3H), 0.48 (d, *J* = 6.6 Hz, 3H).
Specific data for platinum η^3-complex **s6c**: ^{1}H NMR (600 MHz, CF_3CD_2OD) δ 3.76 (q, *J* = 6.6 Hz, 1H, J_{PtH} broadening observed, 1H), 0.48 (d, *J* = 6.6 Hz, 3H).
Specific data for platinum η^3-complex **s7c**: ^{1}H NMR (600 MHz, CF_3CD_2OD) δ 3.08 (d, *J* = 6.6 Hz, J_{PtH} broadening observed, 2H), 2.38 (q, *J* = 7.8 Hz, 2H), 1.11 (t, *J* = 7.8 Hz, 3H).
^{13}C NMR (150 MHz, CF_3CD_2OD) δ 179.3, 177.7, 156.7, 155.8, 155.5, 155.2, 150.9 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 150.4, 150.0, 149.3 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 147.73, 147.67, 144.9, 147.9, 139.7 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 138.13, 138.1 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 137.3, 136.2, 136.1, 136.0, 134.8, 129.6, 128.8, 127.3, 128.4, 126.90, 126.89, 125.5, 125.11, 125.06, 124.1, 123.7, 123.6, 123.3, 121.1 (br m, $\mathbf{C}F_3CD_2OB(C_6F_5)_3$), 117.0, 116.5, 116.1, 116.0, 115.4, 114.9, 114.4, 72.8 (br m, 2C), 45.73, 45.67, 36.74, 36.70, 36.68, 36.65, 36.61, 36.59, 36.55, 36.53, 36.49, 32.0, 31.88, 31.8, 31.7, 22.2, 22.0, 21.5, 20.9, 20.4, 20.1, 19.9, 19.7, 19.6, 13.0, 12.8.
LRMS (ESI) *m* / *z* calcd for $C_{41}H_{59}N_2Pt^+$ [M – {$CF_3CD_2OB(C_6F_5)_3$}]$^+$ 774, found 774. The observed isotopic distribution pattern was consistent with the simulation.

III. General Comments about the study of different alkyl-substituted benzene isotopologs

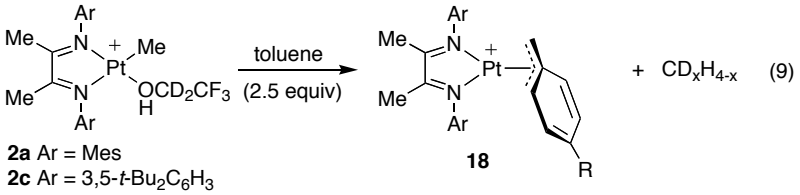
a. Representative Procedure

A light orange solution of platinum methyl cation **2a** (prepared by dissolving 0.010 g of platinum dimethyl complex **1a** (0.018 mmol) and 0.017 g of $B(C_6F_5)_3$ (0.033 mmol) in 0.700 mL of trifluoroethanol-d_3) was analyzed using ^{1}H NMR spectroscopy. At this time the amount of deuterium incorporation into the Pt-Me resonance was determined by comparison of its peak area to the average peak area of both the aryl protons and methyl groups present on the diimine ligand. After spectroscopic analysis, 2.5 equivalents of substrate were added. The progress of the reaction was monitored periodically using ^{1}H NMR spectroscopy. After 10 h, the reaction mixture was heated to 45 °C. After 13 h, the reaction mixture was cooled and ^{1}H NMR spectroscopy analysis revealed complete consumption of the aryl complexes and formation of the η^3-product. The amount of deuterium incorporation into the η^3-product was determined by comparison of the average signal intensity of the methyl groups present on the diimine ligand with the resonances associated with H_a, H_b, and H_c respectively. After spectroscopic analyses, the reaction mixture was filtered through SiO_2; and the resulting clear filtrate, containing recovered substrate, was analyzed by GCMS.

IV. Examination of *p*-xylene and toluene isotopologs

a. Toluene isotopologs

i. Representative procedure

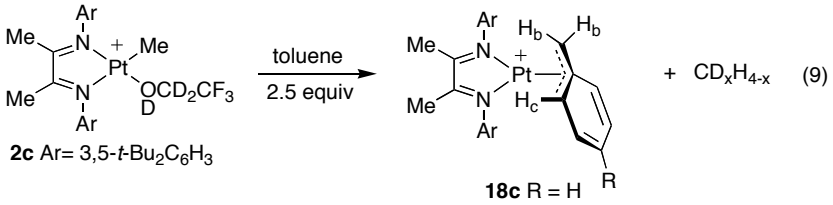


2a Ar = Mes
2c Ar = 3,5-*t*-$Bu_2C_6H_3$

Platinum η^3-complex 18a (R = H). To a light orange solution of platinum methyl cation **2a** (prepared by dissolving 0.010 g of platinum dimethyl complex **1a** (0.018 mmol) and 0.017 g of $B(C_6F_5)_3$ (0.033 mmol) in 0.700 mL of trifluoroethanol-d_3) was added 0.005 mL of toluene (0.05 mmol). The progress of the reaction was monitored periodically using ^{1}H NMR spectroscopy. After 14 h, the reaction mixture was analyzed to reveal the starting platinum methyl cation **1a** (13%) and a mixture of aryl complexes. The ratio of aryl complexes was not determined. After spectroscopic analysis, the reaction mixture was heated to 45 °C. After 13 h, the reaction mixture was cooled, and ^{1}H NMR spectroscopy analysis revealed complete consumption of the aryl complexes and formation of η^3-product **18a** (R=H) in 75% yield. After spectroscopic analyses, the reaction mixture was filtered through SiO_2; and the resulting clear filtrate, containing recovered substrate, was analyzed by GCMS. Platinum η^3-complex **18a** (R=H): ^{1}H NMR (600 MHz, CF_3CD_2OD) δ 7.14 (s, 1H), 7.12 (m, 1H), 7.08 (s, 2H), 6.81 (m, 1H), 6.78 (s, 2H), 6.65 (m, 1H), 6.25 (d, J = 6.6 Hz, 1H), 2.34 (s, 3H), 2.39 (s, 6H), 2.17 (s, 3H), 2.15 (s, 6H), 2.10 (s, 3H), 2.00 (s, 3H), 1.90 (d, J = 6.6 Hz, 1H), 1.86 (s, 1H); ^{13}C NMR (150.8 MHz, CF_3CD_2OD) δ 180.9, 178.2, 150.9 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 149.2 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 145.8, 143.7, 142.8, 141.9, 141.8, 140.9, 140.4, 140.3, 140.1, 139.5 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 138.5, 137.9, 131.7, 131.1, 130.9, 130.7, 130.4, 129.8, 117.2, 101.4, 32.3, 21.2, 21.1, 21.0, 20.9, 19.2, 18.1, 17.7, 17.3.
LRMS (ESI) m / z calcd for $C_{29}H_{35}N_2Pt^+$ [M – $\{CF_3CD_2OB(C_6F_5)_3\}$]$^+$ 606, found 606. The observed isotopic distribution pattern was consistent with the simulation.

η^3-Complex 18c (R=H). The representative procedure was followed using platinum methyl complex **2c** (0.018 mmol) and 0.005 mL of toluene (0.05 mmol) to afford η^3-complex **18c** (R=H) in 50% yield: ^{1}H NMR (600 MHz, CF_3CD_2OD) δ 7.10 (br s, 1H), 7.69 (br s, 1H), 7.37 (br s, 1H), 7.14 (s, 1H), 7.12 (m, 1H), 7.05 (m, 1H), 6.85 (m, 1H), 6.75 (s, 1H), 6.65 (m, 1H), 6.56 (m, 1H), 6.30 (d, J = 6.6 Hz, 1H), 2.15 (s, 3H), 2.06 (s, 1H), 2.00 (s, 3H), 1.95 (s, 1H), 1.38 (s, 9H), 1.26 – 1.34 (br s, 18H), 1.25 (s, 9H); ^{13}C NMR (150.8 MHz, CF_3CD_2OD) δ 182.1, 176.6, 156.6, 156.4, 155.6, 155.5, 155.2, 154.4, 150.9 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 149.3 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 147.0, 140.3, 139.7 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 138.2 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 134.4, 130.6, 129.8, 126.8, 124.5, 121.3 (br m, $\mathbf{C}F_3CD_2OB(C_6F_5)_3$), 117.9, 117.0, 116.7, 116.3, 115.5, 36.8, 36.7, 36.5, 36.3, 32.0, 31.9, 31.8, 31.7, 21.8, 20.4, 19.8.
LRMS (ESI) m / z calcd for $C_{39}H_{55}N_2Pt^+$ [M – $\{CF_3CD_2OB(C_6F_5)_3\}$]$^+$ 746, found 746. The observed isotopic distribution pattern was consistent with the simulation.

ii. Composite data for toluene isotopolog study with $Ar_2(NN)PtMe^+$ (Ar = 3,5-*t*-$Bu_2C_6H_3$)



2c Ar= 3,5-*t*-$Bu_2C_6H_3$ **18c** R = H

Table s1. Toluene isotopolog study

Entry	Substrate	CH_4 : CDH_3 : CD_2H_2 : CD_3H[a]	MS analysis of recovered substrate[b] $\frac{[M+1]^+}{[M]^+}$	$\frac{[M-1]^+}{[M]^+}$
1	$CH_3C_6H_5$	66:32:2:0	0.50	...
2	$CD_3C_6D_5$	9:43:38:10	...	0.20
3	$CH_3C_6D_5$	18:42:32:8	...	0.32
4	$CD_3C_6H_5$	68:32:0:0	0.84	...

[a] The reported ratio includes the methane isotopologs produced from the protonation of the starting platinum dimethyl complex as determined using ^{1}H NMR spectroscopy. [b] Ion ratios corrected by corresponding values for unexchanged starting substrate.

iii. Summary of GCMS data from recovered substrate

Table s2. GCMS data for toluene isotopologs

Identity	M+ (abundance)	M+1 (abundance)	M-1 (abundance)	(M+1)/M	(M-1)/M
PhMe-d_0 (91)	233889	158842	105	0.6791	0.0004
PhMe-d_8 (98)	373776	43341	3363	0.1160	0.0090
PhMe-d_5 (97)	337567	26066	229590	0.0772	0.6801
PhMe-d_3 (94)	362117	336140	166721	0.9283	0.4604

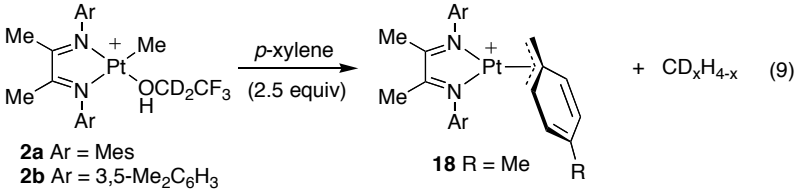
$Mes(NN)_2PtMe$ (TFE-d_3, silylated NMR tube)

Identity	M+ (abundance)	M+1 (abundance)	M-1 (abundance)	(M+1)/M	|Δ std|	(M-1)/M	|D std|
PhMe-d_0 (91)	183328	171653	235	0.9363	0.2572	0.0013	0.0008
PhMe-d_8 (98)	863079	225054	219410	0.2607	0.1448	0.2542	0.2452
PhMe-d_5 (97)	260212	304101	109644	1.1687	1.0914	0.4214	0.2588
PhMe-d_3 (94)	291783	21789	319986	0.0747	0.8536	1.0967	0.6363

$Ar_2(NN)PtMe$ (Ar = 3,5-*t*-$Bu_2C_6H_3$, TFE-d_3, silylated NMR tube)

Identity	M+ (abundance)	M+1 (abundance)	M-1 (abundance)	(M+1)/M	|Δ std|	(M-1)/M	|D std|
PhMe-d_0 (91)	183544	216869	594	1.1816	0.5024	0.0032	0.0028
PhMe-d_8 (98)	1390529	353055	296456	0.2539	0.1379	0.2132	0.2042
PhMe-d_5 (97)	142681	170372	50914	1.1941	1.1168	0.3568	0.3233
PhMe-d_3 (94)	261880	21345	288215	0.0815	0.8467	1.1005	0.6401

b. *p*-xylene isotopologs



i. Representative procedure

Platinum η³-complex product 18a (R=Me). To a light orange solution of platinum methyl cation **2a** (prepared by dissolving 0.022 g of platinum dimethyl complex **1a** (0.040 mmol) and 0.049 g of $B(C_6F_5)_3$ (0.096 mmol) in 0.700 mL of trifluoroethanol-d_3) was added 0.012 mL of *p*-xylene (0.092 mmol). The progress of the reaction was monitored periodically using ^{1}H NMR spectroscopy. After 14 h, the reaction mixture heated to 45 °C. After 13 h, the reaction mixture was cooled and ^{1}H NMR spectroscopy analysis revealed complete consumption of the aryl complexes and formation of η³-product **18a** (R=Me) in 95% yield. After spectroscopic analyses, the reaction mixture was filtered through SiO_2 and the resulting clear filtrate, containing recovered substrate, was analyzed by GCMS. Platinum η³-complex **18a** (R=Me): ^{1}H NMR (600 MHz, CF_3CD_2OD) δ 6.91 (s, 1H), 6.81 (s, 2H), 6.54 (s, 1H), 6.21 (d, *J* = 7.8 Hz, 2H), 5.96 (d, *J* = 7.8 Hz, 2H), 2.16 (br s, 6H), 1.96 (br s, 6H), 1.87 (s, 1H), 1.77 (s, 1H), 1.66 (s, 3H), 1.65 (s, 3H), 1.61 (s, 6H), 1.57 (s, 3H); ^{13}C NMR (150.8 MHz, CF_3CD_2OD) δ 180.5, 178.2, 150.9 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 149.3 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 145.9, 142.7, 140.3, 139.9, 139.6, 139.5 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 139.5, 138.8, 138.4, 137.9 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 136.9, 131.5, 131.4 (br s, 2C), 130.5, 126.4, 124.6, 123.7, 114.4, 102.3, 31.6, 22.2, 21.14, 21.10, 21.0, 19.9, 19.2, 19.1, 18.8, 18.2.

LRMS (ESI) *m* / *z* calcd for $C_{30}H_{37}N_2Pt^+$ [M – {$CF_3CD_2OB(C_6F_5)_3$}]$^+$ 620, found 620. The observed isotopic distribution pattern was consistent with the simulation.

For the characterization data for η³-complex **18b** (R=Me) see ref 3.

Table s3. GCMS data for *p*-xylene isotopologs

p-xylene-d_4

Identity	M (abundance)	M+1 (abundance)	M-1 (abundance)	(M+1)/M	(M-1)/M
parent ion (110)	91642	8468	29622	0.092	0.3232
[M–Me]$^+$ (95)	102698	7567	53617	0.0737	0.5221

p-xylene-d_6

Identity	M (abundance)	M+1 (abundance)	M-1 (abundance)	(M+1)/M	(M-1)/M
parent ion (112)	26734	3767	5665	0.1409	0.2119
[M–Me]$^+$ (94)	28432	18933	898	0.6659	0.0316

Mes_2(NN)PtMe + *p*-xylene-d_4 (TFE-d_3, silylated NMR tube)

Identity	M (abundance)	M+1 (abundance)	M-1 (abundance)	(M+1)/M	|Δ std|	(M-1)/M	|Δ std|
parent ion (110)	86852	8274	39301	0.0953	0.0029	0.4525	0.1293
$[M–Me]^+$ (95)	95861	7417	62468	0.0774	0.0037	0.6517	0.1296

Mes_2(NN)PtMe + *p*-xylene-d_6 (TFE-d_3, silylated NMR tube)

Identity	M (abundance)	M+1 (abundance)	M-1 (abundance)	(M+1)/M	|Δ std|	(M-1)/M	|Δ std|
parent ion (112)	92419	46780	22255	0.5062	0.3653	0.2408	0.0289
$[M–Me]^+$ (94)	83050	87932	695	1.0587	0.3929	0.0084	0.0232

Ar_2(NN)PtMe + *p*-xylene-d_4 (Ar = 3,5-dimethylbenzene, TFE-d_3, silylated NMR tube)

Identity	M (abundance)	M+1 (abundance)	M-1 (abundance)	(M+1)/M	|Δ std|	(M-1)/M	|Δ std|
parent ion (110)	74207	11479	48129	0.1547	0.0623	0.6486	0.3253
$[M–Me]^+$ (95)	85722	9636	74290	0.1124	0.0387	0.8666	0.3446

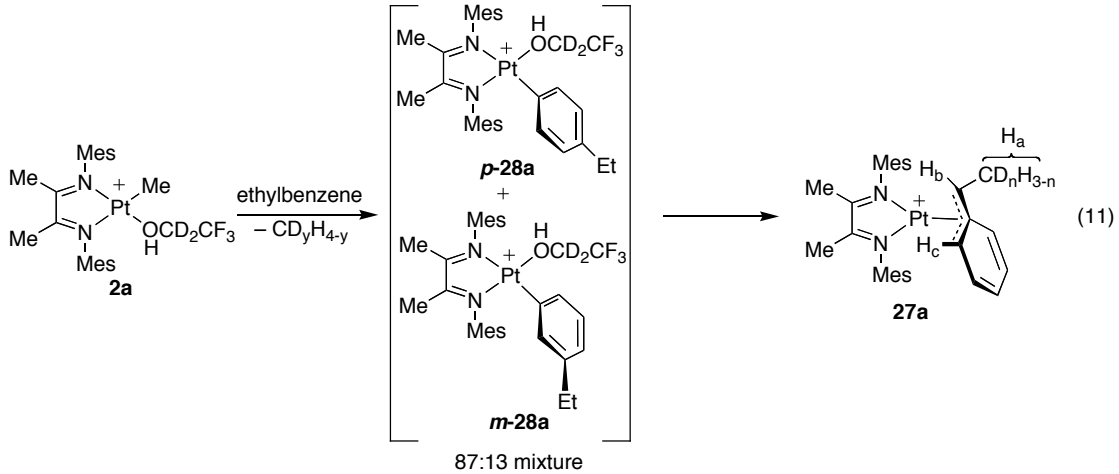
Ar_2(NN)PtMe + *p*-xylene-d_6 (Ar = 3,5-dimethylbenzene, TFE-d_3, silylated NMR tube)

Identity	M (abundance)	M+1 (abundance)	M-1 (abundance)	(M+1)/M	|Δ std|	(M-1)/M	|Δ std|
parent ion (112)	126681	61136	6053	0.4826	0.3417	0.0478	0.1641
$[M–Me]^+$ (94)	118741	124458	3931	1.0481	0.3822	0.0331	0.0015

V. Examination of ethyl-substituted benzene isotopologs

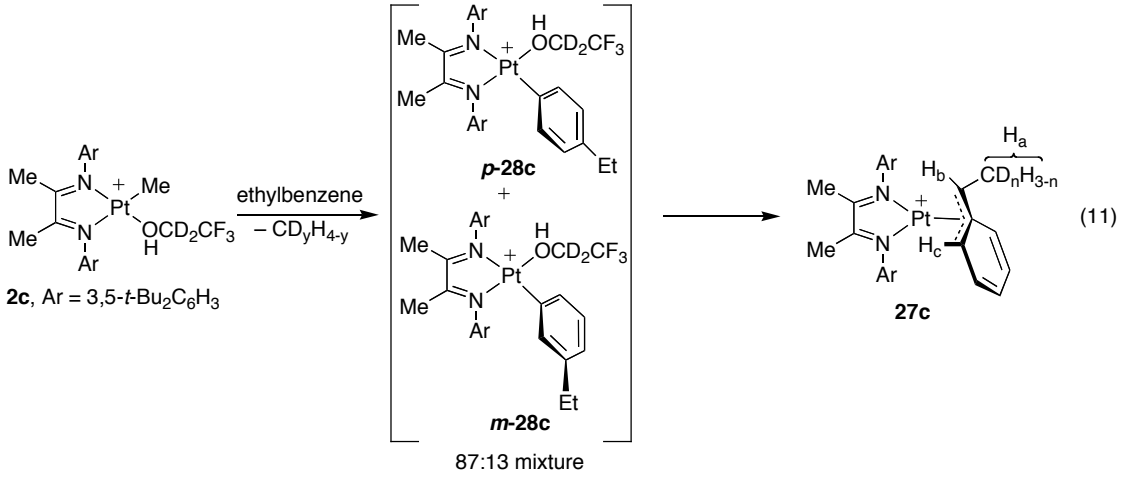
a. Ethylbenzene isotopologs

i. Representative procedure



(11)

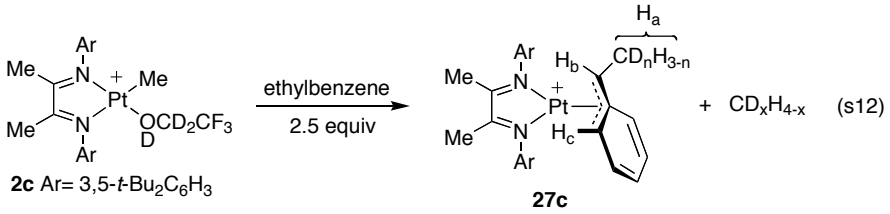
Platinum η³-complex product 27a. Representative procedure:
To a light orange solution of platinum methyl cation **2a** (prepared by dissolving 0.010 g of platinum dimethyl complex **1a** (0.018 mmol) and 0.017 g of $B(C_6F_5)_3$ (0.033 mmol) in 0.700 mL of trifluoroethanol-d_3) was added 0.056 mL of ethylbenzene (0.46 mmol). The progress of the reaction was monitored periodically using ^{1}H NMR spectroscopy. After 14 h, the reaction mixture was analyzed to reveal the starting platinum methyl cation **1a** (13%) and a mixture of aryl complexes, ***m*-28a** and ***p*-28a**, and η³-complex **27a** had been formed in 72% yield (65:35, **28a**:**27a**). The ratio of aryl complexes **28a** was determined to be 87:13 from analysis of the methyl triplet peaks at 1.06 and 1.04 ppm. After spectroscopic analysis, the reaction mixture was heated to 45 °C. After 13 h, the reaction mixture was cooled and ^{1}H NMR spectroscopy analysis revealed complete consumption of the aryl complexes and formation of η³-product **27a**. After spectroscopic analyses, the reaction mixture was filtered through SiO_2; and the resulting clear filtrate, containing recovered substrate, was analyzed by GCMS.
Selected ^{1}H NMR data for aryl complexes **28a** (major isomer): ^{1}H NMR (600 MHz, CF_3CD_2OD) δ 7.10 (s, 1H), 7.08 (s, 1H), 7.05 (s, 1H), 7.02 (s, 1H), 6.50 – 6.76 (m, 4H), 2.36 (s, 6H), 2.33 (s, 3H), 2.14 (s, 6H), 2.10 (s, 3H), 2.04 (s, 3H), 1.84 (s, 3H), 1.06 (t, J = 7.8 Hz, 3H), the expected dd of the benzylic protons were not distinguishable; minor isomer: 1.04 (t, J = 7.8 Hz, 3H).
Platinum η³-complex **27a**: ^{1}H NMR (600 MHz, CF_3CD_2OD) δ 7.17 (m, 1H), 7.10 (m, 1H), 7.08 (s, 1H), 7.03 (d, J = 7.8 Hz, 1H), 7.01 (s, 1H), 6.82 (m, 1H), 6.78 (s, 1H), 6.22 (m, 1H), 5.61 (d, J = 6.6 Hz, J_{PtH} broadening observed, 1H), 2.86 (q, J = 6.6 Hz, J_{PtH} = 60 Hz, 1H), 2.39 (s, 3H), 2.34 (s, 3H), 2.22 (s, 3H), 2.15 (s, 3H), 1.97 (s, 3H), 1.92 (s, 3H), 1.90 (s, 3H), 1.47 (s, 3H), 0.35 (d, J = 6.6 Hz, 3H). ^{13}C NMR (150 MHz, CF_3CD_2OD) δ 180.7, 177.6, 150.9 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 149.3 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 144.4, 143.0, 140.5, 139.6, 137.9 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 139.5 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 137.1, 131.4, 131.1, 131.0, 130.9, 129.9, 129.8, 129.5, 129.4, 128.9, 127.1, 126.4, 124.6, 117.4 (br m, $\mathbf{C}F_3CD_2OB(C_6F_5)_3$), 116.3, 43.7, 21.2, 21.1, 21.0, 19.2, 19.1, 18.2, 17.7, 17.4, 17.0
LRMS (ESI) m / z calcd for $C_{30}H_{38}N_2Pt^+$ [M – {$CF_3CD_2OB(C_6F_5)_3$} + H]$^+$ 621, found 621. The observed isotopic distribution pattern was consistent with the simulation.



Platinum η³-complex 27c. The representative procedure was followed using platinum methyl complex **2c** (0.018 mmol) and 0.006 mL of ethylbenzene (0.05 mmol) to afford η³-complex **27c** in 50% yield: ^{1}H NMR (600 MHz, CF_3CD_2OD) δ 7.72 (t, J = 1.8 Hz, 1H), 7.37 (t, J = 1.8 Hz, 1H), 7.35 (s, 1H), 7.05 (d, J = 7.8 Hz, 1H), 7.03 (s, 1H), 6.89 (br s, 1H), 6.84 (m, 1H), 6.78 (br s, 1H), 6.36 (m, 1H), 6.16 (s, 1H), 5.75 (d, J = 6.6 Hz, J_{PtH} broadening observed, 1H), 2.86 (q, J = 6.6 Hz, J_{PtH} broadening observed, 1H), 2.15 (s, 3H), 2.01 (s, 3H), 1.42 (s, 9H), 1.40 (br s, 9H), 1.36 (br s, 9H), 1.33 (s, 9H), 0.33 (d, J = 6.6 Hz, 3H); ^{13}C NMR (150.8 MHz, CF_3CD_2OD) δ 179.7, 177.5, 155.7, 155.4, 150.9 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 149.3 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$),

147.9, 146.8, 139.8 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 139.4, 138.2 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 136.6, 130.9, 129.9, 129.5, 129.3, 127.1, 126.9, 124.1, 123.6, 121.1 (br m, $\mathbf{C}F_3CD_2OB(C_6F_5)_3$), 117.0, 116.8, 115.9, 115.1, 36.6, 32.03, 31.99, 31.95, 31.79, 31.75, 31.69, 30.2, 30.0, 19.9, 19.6, 12.9.
LRMS (ESI) *m / z* calcd for $C_{40}H_{58}N_2Pt^+$ [M – {$CF_3CD_2OB(C_6F_5)_3$} + H]$^+$ 761, found 761. The observed isotopic distribution pattern was consistent with the simulation.

ii. Composite data for 1,4-diethylbenzene isotopolog study with $Ar_2(NN)PtMe^+$ (Ar = 3,5-*t*-$Bu_2C_6H_3$)



2c Ar= 3,5-*t*-$Bu_2C_6H_3$ **27c**

Table s4. Ethylbenzene isotopolog study

Entry	Substrate	CH_4 : CDH_3 : CD_2H_2 : CD_3H[a]	MS analysis of recovered substrate[b]				% Deuterium in **27c**		
			$\frac{[M+1]^+}{[M]^+}$	$\frac{[M-1]^+}{[M]^+}$	$\frac{[(M+1)-Me]^+}{[M-Me]^+}$	$\frac{[(M-1)-Me]^+}{[M-Me]^+}$	H_a	H_b	H_c
1	$CH_3CH_2C_6H_5$	66:34:0:0	0.71	...	0.63	...	38	0	31
2	$CD_3CD_2C_6D_5$	19:48:28:5	...	0.19	...	0.16	>95	>95	>95
3	$CH_3CH_2C_6D_5$	18:47:30:5	...	0.44	...	0.60	60	0	49
4	$CH_3CD_2C_6H_5$	67:33:0:0	0.89	...	0.71	...	37	>95	44
5[c]	$CH_3CD_2C_6H_5$	100:0:0:0	<0.01	...	<0.01	...	0	>95	0
6	$CD_3CH_2C_6H_5$	67:33:0:0	0.81	...	1.10	...	37	0	77

[a] The reported ratio includes the methane isotopologs produced from the protonation of the starting platinum dimethyl complex as determined using ^{1}H NMR spectroscopy. [b] Ion ratios corrected by corresponding values for unexchanged starting substrate. [c] CF_3CH_2OH employed as solvent.

iii. Summary of GCMS data from recovered substrate

Table s5. GCMS data for ethylbenzene isotopologs

EtPh-d_0 std

Identity	M (abundance)	M+1 (abundance)	M-1 (abundance)	(M+1)/M	(M-1)/M
parent ion (106)	117033	10522	18463	0.0899	0.1578
$[M-Me]^+$ (91)	352879	27658	10802	0.0784	0.0306

EtPh-d_{10} std

Identity	M (abundance)	M+1 (abundance)	M-1 (abundance)	(M+1)/M	(M-1)/M
parent ion (116)	218921	18666	25590	0.0853	0.1169
$[M-Me]^+$ (98)	713889	53652	53462	0.0752	0.0749

EtPh-d_5 std

Identity	M (abundance)	M+1 (abundance)	M-1 (abundance)	(M+1)/M	(M-1)/M
parent ion (111)	62633	9851	7635	0.1573	0.1219
$[M\text{-}Me]^+$ (96)	188828	22460	11773	0.1189	0.0623

EtPh-α-d_2 std

Identity	M (abundance)	M+1 (abundance)	M-1 (abundance)	(M+1)/M	(M-1)/M
parent ion (108)	73196	6522	7245	0.0891	0.0990
$[M\text{-}Me]^+$ (93)	219883	17339	9047	0.0789	0.0411

EtPh-β-d_3 std

Identity	M (abundance)	M+1 (abundance)	M-1 (abundance)	(M+1)/M	(M-1)/M
parent ion (109)	48377	7073	10803	0.1462	0.2233
[M-Me]+ (91)	149560	25200	50	0.1685	0.0003

Mes_2(NN)PtMe EtPh-d_0 (TFE-d_3, silylated NMR tube)

Identity	M (abundance)	M+1 (abundance)	M-1 (abundance)	(M+1)/M	|Δ std|	(M-1)/M	|Δ std|
parent ion (106)	88198	26051	15474	0.2954	0.2055	0.1754	0.0177
$[M\text{-}Me]^+$ (91)	245509	68158	38	0.2776	0.1992	0.0002	0.0305

Mes_2(NN)PtMe EtPh-d_0 (TFE-d_0)

Identity	M (abundance)	M+1 (abundance)	M-1 (abundance)	(M+1)/M	|Δ std|	(M-1)/M	|Δ std|
parent ion (106)	35390	2868	5604	0.0810	0.0089	0.1583	0.0006
$[M\text{-}Me]^+$ (91)	102949	7939	2739	0.0771	0.0013	0.0266	0.0040

Mes_2(NN)PtMe EtPh-d_{10} (TFE-d_3, silylated NMR tube)

Identity	M (abundance)	M+1 (abundance)	M-1 (abundance)	(M+1)/M	|Δ std|	(M-1)/M	|Δ std|
parent ion (116)	104456	9057	35823	0.0867	0.0014	0.3429	0.2261
$[M\text{-}Me]^+$ (98)	325784	24270	95368	0.0745	0.0007	0.2927	0.2178

Mes_2(NN)PtMe EtPh-d_5 (TFE-d_3, silylated NMR tube)

Identity	M (abundance)	M+1 (abundance)	M-1 (abundance)	(M+1)/M	|Δ std|	(M-1)/M	|Δ std|
parent ion (111)	158680	25146	54633	0.1585	0.0012	0.3443	0.2224
$[M\text{-}Me]^+$ (96)	448128	49018	132723	0.1094	0.0096	0.2962	0.2338

Mes_2(NN)PtMe EtPh-α-d_2 (TFE-d_0)

Identity	M (abundance)	M+1 (abundance)	M-1 (abundance)	(M+1)/M	|Δ std|	(M-1)/M	|Δ std|
parent ion (108)	77768	7216	7847	0.0928	0.0037	0.1009	0.0019
$[M\text{-}Me]^+$ (93)	227205	17068	7510	0.0751	0.0037	0.0331	0.0081

Mes_2(NN)PtMe EtPh-α-d_2 (TFE-d_3)

Identity	M (abundance)	M+1 (abundance)	M-1 (abundance)	(M+1)/M	|Δ std|	(M-1)/M	|Δ std|
parent ion (108)	97866	29768	11740	0.3042	0.2151	0.1200	0.0210
$[M-Me]^+$ (93)	286828	83438	11743	0.2909	0.2120	0.0409	0.0002

Mes_2(NN)PtMe EtPh-b-d_3 (TFE-d_3)

Identity	M (abundance)	M+1 (abundance)	M-1 (abundance)	(M+1)/M	|Δ std|	(M-1)/M	|Δ std|
parent ion (109)	15261	4606	3419	0.3018	0.1556	0.2240	0.0007
$[M-Me]^+$ (91)	39824	13417	18	0.3369	0.1684	0.0005	0.0001

Ar_2(NN)PtMe EtPh-d_0 (Ar = 3,5-*t*-$Bu_2C_6H_3$, TFE-d_3, silylated NMR tube)

Identity	M (abundance)	M+1 (abundance)	M-1 (abundance)	(M+1)/M	|Δ std|	(M-1)/M	|Δ std|
parent ion (106)	15647	12550	4020	0.8021	0.7122	0.2569	0.0992
$[M-Me]^+$ (91)	58575	41435	436	0.7074	0.6290	0.0074	0.0232

Ar_2(NN)PtMe EtPh-d_{10} (Ar = 3,5-*t*-$Bu_2C_6H_3$, TFE-d_3, silylated NMR tube)

Identity	M (abundance)	M+1 (abundance)	M-1 (abundance)	(M+1)/M	|Δ std|	(M-1)/M	|Δ std|
parent ion (116)	60029	5065	18485	0.0844	0.0009	0.3079	0.1910
$[M-Me]^+$ (98)	189682	13959	44960	0.0736	0.0016	0.2370	0.1621

Ar_2(NN)PtMe EtPh-d_5 (Ar = 3,5-*t*-$Bu_2C_6H_3$, TFE-d_3, silylated NMR tube)

Identity	M (abundance)	M+1 (abundance)	M-1 (abundance)	(M+1)/M	|Δ std|	(M-1)/M	|Δ std|
parent ion (111)	17586	9161	9819	0.5209	0.3636	0.5583	0.4364
[M-Me]+ (96)	61025	7738	40304	0.1268	0.0079	0.6605	0.5981

Ar_2(NN)PtMe EtPh-α-d_2 (Ar = 3,5-*t*-$Bu_2C_6H_3$, TFE-d_3, silylated NMR tube)

Identity	M (abundance)	M+1 (abundance)	M-1 (abundance)	(M+1)/M	|Δ std|	(M-1)/M	|Δ std|
parent ion (108)	22572	22170	4436	0.9822	0.8931	0.1965	0.0268
[M-Me]+ (93)	94286	74074	5987	0.7856	0.7068	0.0635	0.0632

Ar_2(NN)PtMe EtPh-α-d_2 (Ar = 3,5-*t*-$Bu_2C_6H_3$, TFE-d_0)

Identity	M (abundance)	M+1 (abundance)	M-1 (abundance)	(M+1)/M	|Δ std|	(M-1)/M	|Δ std|
parent ion (108)	84558	8215	8289	0.0972	0.0080	0.0980	0.0010
[M-Me]+ (93)	247392	20114	2306	0.0813	0.0024	0.0093	0.0318

Ar_2(NN)PtMe EtPh-β-d_3 (Ar = 3,5-*t*-$Bu_2C_6H_3$, TFE-d_3, silylated NMR tube)

Identity	M (abundance)	M+1 (abundance)	M-1 (abundance)	(M+1)/M	|Δ std|	(M-1)/M	|Δ std|
parent ion (109)	55464	44679	21382	0.8055	0.6593	0.3855	0.1622
[M-Me]+ (91)	107477	134923	4484	1.2554	1.0869	0.0417	0.0414

b. 1,4-Diethylbenzene isotopologs

i. Composite data for 1,4-diethylbenzene isotopolog study with $Ar_2(NN)PtMe^+$ (Ar = 3,5-*t*-$Bu_2C_6H_3$)

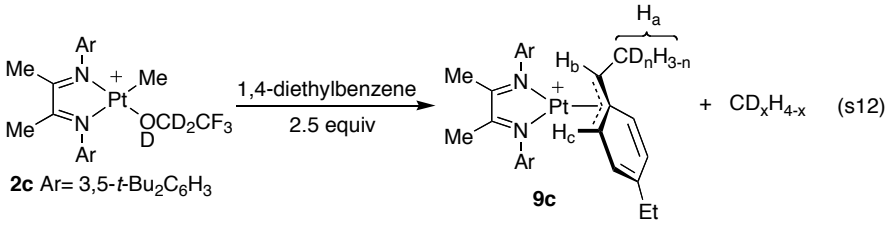


Table s6. 1,4-Diethylbenzene isotopolog study

Entry	Substrate	CH_4 : CDH_3 : CD_2H_2 : CD_3H[a]	Recovered substrate % isotope change				% Deuterium in **9c**		
			$\frac{[M+1]^+}{[M]^+}$	$\frac{[M-1]^+}{[M]^+}$	$\frac{[(M+1)-Me]^+}{[M-Me]^+}$	$\frac{[(M-1)-Me]^+}{[M-Me]^+}$	H_a	H_b	H_c
1	$(CH_3CH_2)_2C_6H_4$	61:35:4:0	0.98	...	1.14	...	71	0	19
2	$(CD_3CD_2)_2C_6H_4$	61:35:4:0	1.62	...	2.30	...	82	>95	94
3	$(CH_3CH_2)_2C_6D_4$	29:45:23:3	...	0.25	...	0.66	63	0	49

[a] The reported ratio includes the methane isotopologs produced from the protonation of the starting platinum dimethyl complex as determined by ^1H NMR spectroscopy. [b] Ion ratios corrected by corresponding values for unexchanged starting substrate. [c] CF_3CH_2OH was employed as the solvent.

ii. Summary of recovered substrate isotopolog isotope exchange

Table s7. GCMS data for 1,4-diethylbenzene isotopologs

1,4-$Et_2C_6H_4$-d_0 std

Identity	M (abundance)	M+1 (abundance)	M-1 (abundance)	(M+1)/M+	(M-1)/M+
parent ion (134)	101488	11383	172	0.1122	0.0017
$[M-Me]^+$ (119)	202315	19344	247	0.0956	0.0012

1,4-$(CD_3CD_2)_2C_6H_4$ std

Identity	M (abundance)	M+1 (abundance)	M-1 (abundance)	(M+1)/M+	(M-1)/M+
parent ion (144)	38913	4347	2557	0.1117	0.0657
$[M-Me]^+$ (126)	90700	9209	3280	0.1015	0.0362

1,4-$(CH_3CH_2)_2C_6D_4$ std

Identity	M (abundance)	M+1 (abundance)	M-1 (abundance)	(M+1)/M+	(M-1)/M+
parent ion (138)	1794	213	535	0.1187	0.2982
$[M-Me]^+$ (123)	2582	259	733	0.1003	0.2839

$Mes_2(NN)PtMe$ $Et_2C_6H_4$ (TFE-d_3, silylated NMR tube)

Identity	M (abundance)	M+1 (abundance)	M-1 (abundance)	(M+1)/M+	|Δ std|	(M-1)/M+	|Δ std|
parent ion (134)	58066	11234	619	0.1935	0.0813	0.0107	0.0090
$[M-Me]^+$ (119)	118063	21391	2480	0.1812	0.0856	0.0210	0.0198

$Mes_2(NN)PtMe\ Et_2C_6H_4$ (TFE-d_0)

Identity	M (abundance)	M+1 (abundance)	M-1 (abundance)	(M+1)/M+	|Δ std|	(M-1)/M+	|Δ std|
parent ion (134)	7198	817	146	0.1135	0.0013	0.0203	0.0186
$[M\text{-}Me]^+$ (119)	14431	1450	308	0.1005	0.0049	0.0213	0.0201

$Mes_2(NN)PtMe\ 1,4\text{-}(CD_3CD_2)_2C_6H_4$ (TFE-d_3, silylated NMR tube)

Identity	M (abundance)	M+1 (abundance)	M-1 (abundance)	(M+1)/M+	|Δ std|	(M-1)/M+	|Δ std|
parent ion (144)	158657	43305	14366	0.2729	0.1612	0.0905	0.0248
$[M\text{-}Me]^+$ (126)	321527	92256	17169	0.2869	0.1854	0.0534	0.0172

$Mes_2(NN)PtMe\ 1,4\text{-}(CH_3CH_2)_2C_6D_4$ (TFE-d_3, silylated NMR tube)

Identity	M (abundance)	M+1 (abundance)	M-1 (abundance)	(M+1)/M+	|Δ std|	(M-1)/M+	|Δ std|
parent ion (138)	1092	208	533	0.1905	0.0717	0.4881	0.1899
$[M\text{-}Me]^+$ (123)	1812	278	888	0.1534	0.0531	0.4902	0.2063

$Ar_2(NN)PtMe\ Et_2C_6H_4$ (Ar =3,5-*t*-$Bu_2C_6H_3$, TFE-d_3, silylated NMR tube)

Identity	M (abundance)	M+1 (abundance)	M-1 (abundance)	(M+1)/M+	|Δ std|	(M-1)/M+	|Δ std|
parent ion (134)	2365	2595	111	1.0973	0.9851	0.0469	0.0452
$[M\text{-}Me]^+$ (119)	7921	9781	2979	1.2348	1.1392	0.3761	0.3749

$Ar_2(NN)PtMe\ 1,4\text{-}(CD_3CD_2)_2C_6H_4$ (Ar =3,5-*t*-$Bu_2C_6H_3$, TFE-d_3, silylated NMR tube)

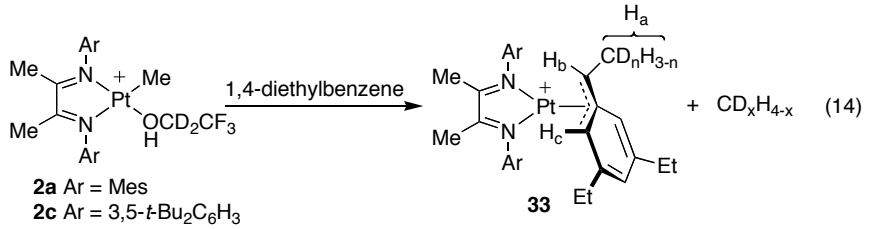
Identity	M (abundance)	M+1 (abundance)	M-1 (abundance)	(M+1)/M+	|Δ std|	(M-1)/M+	|Δ std|
parent ion (144)	5210	9042	1501	1.7355	1.6238	0.2881	0.2224
$[M\text{-}Me]^+$ (126)	6882	16550	3090	2.4048	2.3033	0.4490	0.4128

$Ar_2(NN)PtMe\ 1,4\text{-}(CH_3CH_2)_2C_6D_4$ (Ar =3,5-*t*-$Bu_2C_6H_3$, TFE-d_3, silylated NMR tube)

Identity	M (abundance)	M+1 (abundance)	M-1 (abundance)	(M+1)/M+	|Δ std|	(M-1)/M+	|Δ std|
parent ion (138)	414	215	225	0.5193	0.4006	0.5435	0.2453
$[M\text{-}Me]^+$ (123)	574	316	540	0.5505	0.4502	0.9408	0.6569

c. 1,3,5-Triethylbenzene isotopologs

i. Representative procedure



Platinum η³-complex 33a. Representative procedure:

To a light orange solution of platinum methyl cation **2a** (0.700 mL of a solution containing 0.039 g of platinum dimethyl complex **1a** (0.071 mmol) and 0.075 g of $B(C_6F_5)_3$ (0.146 mmol) in trifluoroethanol-d_3) was added 0.018 mL of 1,3,5-triethylbenzene (0.096 mmol). The progress of the reaction was monitored periodically using ^{1}H NMR spectroscopy. After 14 h, the reaction mixture heated to 45 °C. After 13 h, the reaction mixture was cooled, and ^{1}H NMR spectroscopy analysis revealed formation of η^3-product **33a** in 94% yield. After spectroscopic analyses, the reaction mixture was filtered through SiO_2; and the resulting clear filtrate, containing recovered substrate, was analyzed by GCMS. Platinum η^3-complex **33a**: ^{1}H NMR (600 MHz, CF_3CD_2OD) δ 7.13 (s, 1H), 7.07 (s, 1H), 7.05 (s, 1H), 6.96 (s, 1H), 6.75 (s, 1H), 6.54 (s, 1H), 5.46 (s, J_{PtH} broadening observed, J_{PtH} = 44 Hz at 300 MHz, 1H), 2.73 (q, J = 6.6 Hz, 1H), 2.42 – 2.52 (m, 2H), 2.35 (br s, 6H), 2.33 (s, 3H), 2.07 (s, 3H), 1.99 (s, 3H), 1.94 – 2.01 (m, 1H), 1.83 (s, 3H), 1.80 – 1.86 (m, 1H), 1.77 (s, 3H), 1.53 (s, 3H), 1.10 (t, J = 7.2 Hz, 3H), 0.86 (t, J = 7.2 Hz, 3H), 0.26 (d, J = 6.6 Hz, 3H); ^{13}C NMR (150.8 MHz, CF_3CD_2OD) δ 179.8, 178.4, 158.8, 156.2, 150.9 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 149.3 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 146.7, 144.6, 143.9, 140.5, 140.1, 139.6 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 137.9 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 131.5, 131.4, 131.2, 131.1, 130.0, 129.6, 129.1, 128.5, 124.6, 118.7, 108.9, 43.6, 30.5, 39.6, 21.2, 21,1, 19.2, 18.9, 18.0, 17.7, 17.5, 17.4, 15.1, 14.6, 12.6.
LRMS (ESI) *m* / *z* calcd for $C_{34}H_{46}N_2Pt^+$ [M – $[CF_3CD_2OB(C_6F_5)_3]$ + H]$^+$ 677, found 677. The observed isotopic distribution pattern was consistent with the simulation.

Platinum η^3-complex 33c. The representative procedure was followed using platinum methyl complex **2c** (0.019 mmol) and 0.018 mL of 1,3,5-triethylbenzene (0.096 mmol) to afford η^3-complex **33c** in 92% yield: ^{1}H NMR (600 MHz, CF_3CD_2OD) δ 7.58 (t, J = 1.8 Hz, 1H), 7.53 (t, J = 1.8 Hz, 1H), 7.36 (s, 1H), 7.00 (d, J = 1.2 Hz, 1H), 6.79 (s, 1H), 6.73 (t, J = 1.8 Hz, 1H), 6.67 (s, 1H), 6.06 (t, J = 1.8 Hz, 1H), 5.58 (s, J_{PtH} broadening observed, 1H), 2.72 (q, J = 6.6 Hz, 1H), 2.52 – 2.56 (m, 2H), 1.94 (s, 3H), 1.82 – 1.86 (m, 1H), 1.77 (s, 3H), 1.72 – 1.78 (m, 1H), 1.40 (s, 9H), 1.39 – 1.42 (br s, 9H), 1.35 – 1.38 (br s, 9H), 1.33 (s, 9H), 1.14 (t, J = 7.2 Hz, 3H), 0.85 (t, J = 7.8 Hz, 3H), 0.25 (d, J = 6.6 Hz, 3H); ^{13}C NMR (150.8 MHz, CF_3CD_2OD) δ 179.0, 178.9, 158.9, 157.7, 156.1, 155.8, 155.5, 155.4, 155.3, 150.9 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 149.3, 149.3 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 148.8, 146.7, 139.8 (br m, $CF_3CD_2OB(\mathbf{C}_6F_5)_3$), 138.1, 126.9, 126.0, 124.3, 124.0, 121.3 (br m, $\mathbf{C}F_3CD_2OB(C_6F_5)_3$), 119.5, 116.9, 115.3, 114.8, 43.0, 37.0, 36.7, 32.0, 31.93, 31.90, 31.7, 30.5, 30.1, 29.6, 20.1, 19.8, 15.2, 14.7, 13.1, 13.0.
LRMS (ESI) *m* / *z* calcd for $C_{44}H_{66}N_2Pt^+$ [M – $\{CF_3CD_2OB(C_6F_5)_3\}$ + H]$^+$ 817, found 817. The observed isotopic distribution pattern was consistent with the simulation.

ii. Summary of recovered substrate isotopolog isotope exchange

Table s8. GCMS data for 1,3,5-triethylbenzene isotopologs

$1,3,5\text{-}(CH_3CH_2)_3C_6H_3$ std

Identity	M (abundance)	M+1 (abundance)	M-1 (abundance)	(M+1)/M	(M-1)/M
parent ion (162)	5721	999	836	0.1746	0.1461
$[M\text{-}Me]^+$ (147)	7694	820	394	0.1066	0.0512

$1,3,5\text{-}(CD_3CD_2)_3C_6H_3$ std

Identity	M (abundance)	M+1 (abundance)	M-1 (abundance)	(M+1)/M	(M-1)/M
parent ion (177)	11030	2700	2183	0.2448	0.1979
$[M\text{-}Me]^+$ (159)	19576	4744	3269	0.2423	0.1670

1,3,5-$(CH_3CH_2)_3C_6D_3$ std

Identity	M (abundance)	M+1 (abundance)	M-1 (abundance)	(M+1)/M	(M-1)/M
parent ion (165)	750	187	528	0.2493	0.7040
$[M\text{-}Me]^+$ (150)	816	0	108	0.0000	0.1324

$Mes_2(NN)PtMe$ + 1,3,5-$(CD_3CD_2)_3C_6H_3$ (TFE-d_3, silylated NMR tube)

Identity	M (abundance)	M+1 (abundance)	M-1 (abundance)	(M+1)/M	|Δ std|	(M-1)/M	|Δ std|
parent ion (177)	11878	2908	2404	0.2448	0.0702	0.2024	0.0563
$[M\text{-}Me]^+$ (159)	21069	5109	3521	0.2425	0.1359	0.1671	0.1159

$Mes_2(NN)PtMe$ + 1,3,5-$(CH_3CH_2)_3C_6D_3$ (TFE-d_3, silylated NMR tube)

Identity	M (abundance)	M+1 (abundance)	M-1 (abundance)	(M+1)/M	|Δ std|	(M-1)/M	|Δ std|
parent ion (165)	1024	117	371	0.1143	0.1351	0.3623	0.3417
$[M\text{-}Me]^+$ (150)	1382	160	339	0.1158	0.1158	0.2453	0.1129

$Ar_2(NN)PtMe$ + 1,3,5-$(CH_3CH_2)_3C_6H_3$ (Ar= 3,5-*t*-$Bu_3C_6H_3$, TFE-d_3, silylated NMR tube)

Identity	M (abundance)	M+1 (abundance)	M-1 (abundance)	(M+1)/M	|Δ std|	(M-1)/M	|Δ std|
parent ion (162)	10034	9856	363	0.9823	0.8076	0.0362	0.1100
$[M\text{-}Me]^+$ (147)	17713	17434	397	0.9842	0.8777	0.0224	0.0288

$Ar_2(NN)PtMe$ + 1,3,5-$(CD_3CD_2)_3C_6H_3$ (Ar= 3,5-*t*-$Bu_3C_6H_3$, TFE-d_3, silylated NMR tube)

Identity	M (abundance)	M+1 (abundance)	M-1 (abundance)	(M+1)/M	|Δ std|	(M-1)/M	|Δ std|
parent ion (177)	18668	14571	4301	0.7805	0.6059	0.2304	0.0843
$[M\text{-}Me]^+$ (159)	35249	26329	4919	0.7469	0.6404	0.1396	0.0883

$Ar_2(NN)PtMe$ + 1,3,5-$(CH_3CH_2)_3C_6D_3$ (Ar= 3,5-*t*-$Bu_3C_6H_3$, TFE-d_3, silylated NMR tube)

Identity	M (abundance)	M+1 (abundance)	M-1 (abundance)	(M+1)/M	|Δ std|	(M-1)/M	|Δ std|
parent ion (165)	455	50	212	0.1099	0.1349	0.4659	0.2381
$[M\text{-}Me]^+$ (150)	611	40	51	0.0655	0.1769	0.0835	0.0489

VI. Kinetic experiments

a. Representative procedure

A stock solution of the platinum methyl cation, **2a**, was generated by diluting a mixture of 0.025 g of platinum dimethyl complex **1a** (0.046 mmol) and 0.050 g of $B(C_6F_5)_3$ (0.094 mmol) to 5.00 mL with trifluoroethanol-d_3. Upon dissolution, 0.700 mL of the resulting 0.009 M solution of the platinum methyl cation **2a** was placed in a 1 mL volumetric flask and 0.025 mL of benzene (0.28 mmol) was added. The resulting mixture was diluted to 1.00 mL with trifluoroethanol-d_3 and vigorously agitated. Upon homogeneity, 0.700 mL of the resulting light

orange solution was transferred to a J. Young NMR tube, and the mixture was cooled to –10 °C to prevent further reaction. The sample was inserted into the NMR probe, which had come to an equilibrium temperature of 20 °C. After briefly shimming on the sample, an array of spectra was acquired over 14 h. After completion of the run, the intensity data for relating the concentrations of reagent 1 and product 2 were obtained from the NMR spectra and were fit to the first-order exponential equations

$$[1] = Ae^{-k_{obs}t}, \text{ and}$$
$$[2] = A(1 - e^{-k_{obs}t}).$$

Second-order rate constants were obtained from a plot of k_{obs} vs $[C_6H_6]$ over the concentration range 0.28 to 1.2 M. The 1,4-diethylbenzene and 1,3,5-triethylbenzene reactions were treated analogously, though not over such a broad concentration range due to lower solubility.

b. Summary of kinetic data

Table s9. Benzene substrate

Entry	L_nPtMe^+	Substrate	T (°C)	[substrate] (M)	k_{obs} (× 10^4 s^{-1})	R^2-value	Error in equation fit (× 10^4 s^{-1})
1	**2a**	C_6H_6	20	0.280	1.56	0.99963	0.01
2	**2a**	C_6H_6	20	0.414	2.12	0.99985	0.01
3	**2a**	C_6H_6	20	0.560	2.78	0.99954	0.02
4	**2a**	C_6H_6	20	0.635	3.06	0.9985	0.04
5	**2a**	C_6H_6	20	1.12	4.98	0.9995	0.04

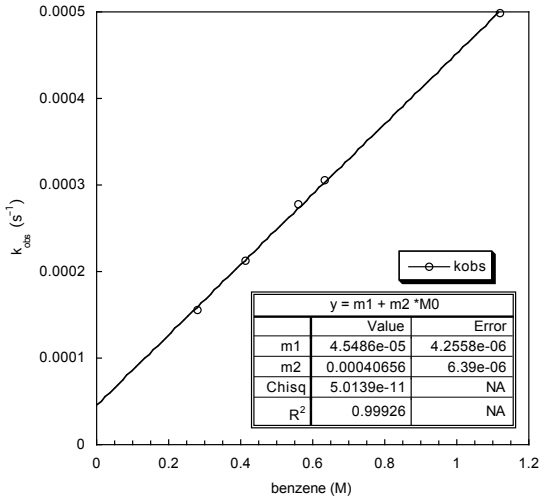


Figure s1. Determination of k_2 for the reaction of **2a** with benzene

Table s10. 1,4-Diethylbenzene substrate

Entry	L_nPtMe^+	Substrate	T (°C)	[substrate] (M)	k_{obs} (× 10^4 s^{-1})	R^2-value	Error in equation fit (× 10^4 s^{-1})
1	**2a**	$(CH_3CH_2)_2C_6H_4$	20	0.276	0.653	0.9995	0.005
2	**2a**	$(CH_3CH_2)_2C_6H_4$	20	0.398	0.987	0.99962	0.007
3	**2a**	$(CH_3CH_2)_2C_6H_4$	20	0.514	1.21	0.999	0.01
4	**2a**	$(CH_3CH_2)_2C_6H_4$	20	0.578	1.41	0.9975	0.03
5	**2a**	$(CH_3CH_2)_2C_6H_4$	25	0.332	1.24	0.99969	0.09
6	**2a**	$(CH_3CH_2)_2C_6D_4$	25	0.330	1.31	0.99954	0.02
7	**2a**	$(CD_3CD_2)_2C_6H_4$	25	0.352	1.25	0.99997	0.03

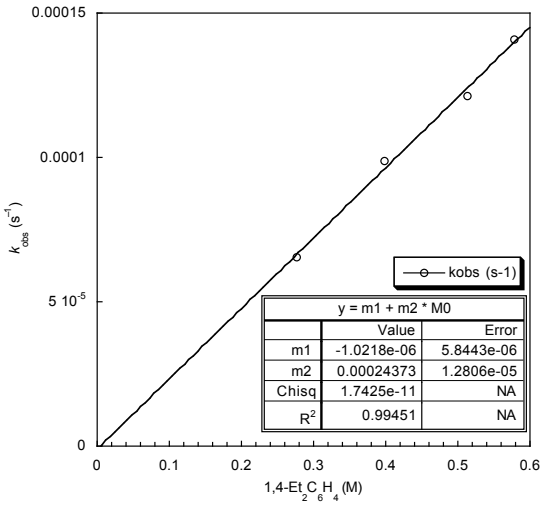


Figure s2. Determination of k_2 for the reaction of **2a** with 1,4-diethylbenzene

Table s11. 1,3,5-Triethylbenzene substrate

Entry	L_nPtMe^+	Substrate	T (°C)	[substrate] (M)	k_{obs} (× 10^4 s^{-1})	R^2-value	Error in equation fit (× 10^4 s^{-1})
1	**2a**	$(CH_3CH_2)_3C_6H_3$	20	0.106	0.147	0.99744	0.006
2	**2a**	$(CH_3CH_2)_3C_6H_3$	20	0.186	0.260	0.99848	0.008
3	**2a**	$(CH_3CH_2)_3C_6H_3$	20	0.249	0.345	0.99955	0.005
4	**2a**	$(CH_3CH_2)_3C_6H_3$	20	0.323	0.439	0.99959	0.004
5	**2a**	$(CH_3CH_2)_3C_6H_3$	40	0.271	3.10	0.99958	0.03
6	**2a**	$(CH_3CH_2)_3C_6D_3$	40	0.268	2.96	0.9994	0.04
7	**2a**	$(CD_3CD_2)_3C_6H_3$	40	0.268	1.00	0.99995	0.01

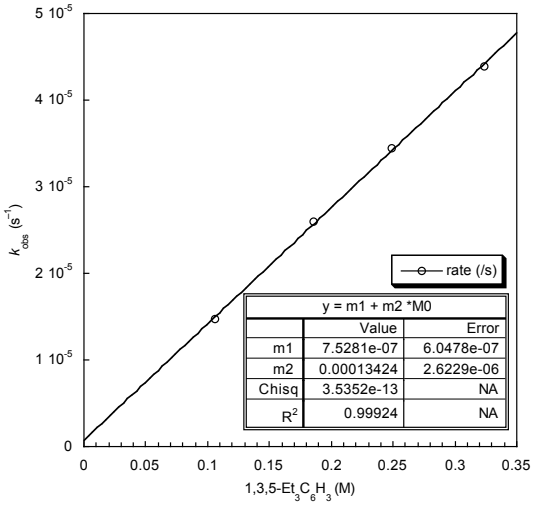


Figure s3. Determination of k_2 for the reaction of **2a** with 1,3,5-triethylbenzene

VII. References

(1) Zhong, H. A.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2002**, *124*, 1378-1399.
(2) Heyduk, A. F.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2003**, *125*, 6366-6367.
(3) Heyduk, A. F.; Driver, T. G.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2004**, *126*, 15034-15035.

VIII. Crystallographic data for **13a**

General Details of X-Ray Data Collection and Reduction. X-ray diffraction data were collected on a Siemens 3-circle platform diffractometer equipped with a CCD detector. Measurements were carried out at 100 K using Mo Kα (λ = 0.71073 Å) radiation, which was wavelength selected with a single crystal graphite monochromator. Four sets of data were collected using ω scans and a –0.3° scan width. The data frames were integrated to *hkl*/intensity and final unit cells were calculated by using the SAINT program v.6.45 from Bruker AXS. The structures were solved and refined with the Bruker SMART v5.054 suite of programs developed by G. M. Sheldrick and Bruker AXS, 2000.

Table s12. Crystal data and structure refinement for **13a** (CCDC 248006).

Empirical formula	$C_{46}H_{28}BF_{20}N_2OPt$	
Formula weight	1210.60	
Crystallization Solvent	Trifluoroethanol	
Crystal Habit	Fragment	
Crystal size	0.37 x 0.31 x 0.18 mm^3	
Crystal color	Orange	
Data Collection		
Type of diffractometer	Bruker SMART 1000	
Wavelength	0.71073 Å MoKα	
Data Collection Temperature	100(2) K	
θ range for 29686 reflections used in lattice determination	2.17 to 44.98°	
Unit cell dimensions	a = 11.8621(3) Å	
	b = 18.2176(4) Å	β= 98.5320(10)°
	c = 20.7937(5) Å	
Volume	4443.77(18) $Å^3$	
Z	4	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Density (calculated)	1.810 Mg/m^3	
F(000)	2356	
Data collection program	Bruker SMART v5.054	
θ range for data collection	1.87 to 48.91°	
Completeness to θ = 48.91°	89.2 %	
Index ranges	$-20 \le h \le 24$, $-38 \le k \le 31$, $-43 \le l \le 40$	
Data collection scan type	ω scans at 2 ϕ settings each of 2θ=-28º and -73º	
Data reduction program	Bruker SAINT v6.45	
Reflections collected	91169	
Independent reflections	39590 [R_{int}= 0.0461]	
Absorption coefficient	3.281 mm^{-1}	
Absorption correction	Integration and multi-scan	
Max. and min. transmission	0.60991 and 0.35867	

Table s12 (cont.)

Structure solution and Refinement

Structure solution program	SHELXS-97 (Sheldrick, 1990)
Primary solution method	Patterson method
Secondary solution method	Difference Fourier map
Hydrogen placement	Geometric positions
Structure refinement program	SHELXL-97 (Sheldrick, 1997)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	39590 / 0 / 648
Treatment of hydrogen atoms	Riding
Goodness-of-fit on F^2	1.199
Final R indices [I>2σ(I), 24712 reflections]	R1 = 0.0446, *w*R2 = 0.0678
R indices (all data)	R1 = 0.0929, *w*R2 = 0.0753
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.003
Average shift/error	0.000
Largest diff. peak and hole	3.855 and -3.460 e.Å^{-3}

Special Refinement Details

All large peaks in the final electron difference Fourier map are within 1Å of Pt and are assumed to arise from an incomplete absorption correction model. Correction for absorption was performed in XPREP using measured crystal faces (resulting in T_{min} and T_{max} shown in Table 1) then additional corrections were made using SADABS where $T_{min}/T_{max} = 0.852466$.

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.