Supplementary Information

Experimental Procedures…………………………………………………………………………………S2
Experimental Procedures

General Considerations

Unless otherwise specified, reactions were carried out under an argon or nitrogen atmosphere, and on either a Schlenk line or in a glovebox. Solvents unless otherwise stated were dried by the use of Glass Contour solvent columns. Deuterated solvents were used as received (Cambridge Isotopes). NMR spectra were obtained on one of the following Bruker NMR spectrometers: AC300, AV300, AV301, AV500 (all kinetics runs), DRX499, or DPX200 (2H NMR). All 1H NMR characterization data reported were obtained at 300.0 MHz, and all 13C {1H} NMR spectra at 75.5 MHz. Chemical shifts are given in ppm downfield of TMS, and spectra were referenced to residual proteated solvent (1H) or the solvent carbon (13C).

Synthesis of (κ-N,C,N-2,6-bis(diethylaminomethyl)-phenyl)methyl platinum(II) ([NCN]PtMe, 1)

An oven-dried round bottomed flask with stirbar was charged, dry toluene (50 mL), and (κ-N,C,N-2,6-bis(diethylaminomethyl)-phenyl)chloro platinum(II) (2) (786 mg, 1.72 mmol). Methyl magnesium bromide (3.0 mL, 3.0 M in diethyl ether, 9.0 mmol) was added dropwise over the course of several minutes, during which time the reaction became cloudy and dark orange. After ca. 1 hr, the reaction had turned brown, and was volatiles were removed in vacuo. The residue was thrice extracted with dry pentane (20 mL each) and filtered through oven-dried Celite. Evaporation of the filtrate afforded 507 mg (73% yield) of a white, crystalline material. 1H NMR (C6D6), δ = 0.031 (s w/Pt sat., 2JPtH = 46.8, 3H, Pt-C6H3), 1.325 (t, 3JHH = 7.1 Hz, 12H, NCH2C6H3), 2.368 (m, Pt sat apparent, but unresolved, 4H, NCHH'CH3), 2.879 (m, 4H, NCHH'CH3), 3.647 (s w/Pt sat, 3JPtH = 37.5 Hz, 4H, NCH2Ar), 6.905 (d, 3JHH = 6.9 Hz, 2H, 3,5-ArH), 7.122 (t, 3JHH = 7.5 Hz, 1H, 4-ArH). 13C {1H} (CD2Cl2) δ = 4.43 (Pt-CH3 1JPC = 624), 13.63 (NCH2CH3, 3JPC = 39), 59.76 (NCH2CH3, 2JPC + 3JPC = 14), 75.06 (Ar-CH2-N, 3JPC = 29), 117.59 (3,5-Ar 2JPC = 17), 121.45 (4-Ar), 146.15 (2,6-Ar, 2JPtC + 3JPtC = 60), 173.55 (1-Ar, 1JPtC = 636). Analysis: Calc’d: C: 44.63, H: 6.61, N: 6.12; Found: C: 44.35, H: 6.59, N: 6.21. Attempts to synthesize 1 from 2 with SnMe4 or ZnMe2 resulted in no reaction at room temperature. When these reactions were heated, no reaction was seen below the threshold at which decomposition to intractable mixtures occurred. Reaction of 2 with MeLi results in decomposition even at low temperature. In contrast to the reaction of 2 with methyl magnesium bromide, 2 reacts with methyl magnesium iodide to form [NCN]PtI, which does not further react with the Grignard reagent.

Synthesis of (κ-N,N'-2,6-bis diethylaminomethyl toluene) methyl platinum (II) triflate ([[NC(Me)N]PtMe][OTf], 4) and (κ-N,C,N-2,6-bis(diethylaminomethyl)-phenyl)triflato platinum(II) ([NCN]Pt(OTf), 3):

[NCN]PtMe (1) (80.8 mg, 0.161 mmol) was dissolved in dry toluene (10 mL) with a stirbar. Methyl triflate (0.719 mL, 0.2238 M in toluene, 0.161 mmol) was added via
syringe and the solution was allowed to stir overnight. After 12 hours, 4 had formed as a bright yellow precipitate (45.8 mg, 55.3 % yield) which was collected over a frit. The filtrate was evaporated to dryness in vacuo to afford NCN-Pt-OTf (39.9 mg, 38.9% isolated yield, combined isolated yield of 3 + 4 = 94.2%) (3) as an oily brown solid. 1H NMR of 4 (CD2Cl2) δ = 0.684 (s w/satellites, 3H, J$_{PtH}$ = 91.8 Pt-CH$_3$), 1.067 (t, 6H, J$_{HH}$ = 7.2, NCH$_2$CH$_3$), 1.593 (t, 6H, J$_{HH}$ = 7.1, NCH$_2'$CH$_3$'), 2.45-2.9 (m, 8H, NCH$_2$CH$_3$ + NCH$_2'$CH$_3$'), 3.051 (s, 3H), 3.839 (d w/satellites, 2H, J$_{HH}$ = 12.9, J$_{PtH}$ = 48.8 NCHH'Ar), 4.653 (d, 2H, J$_{HH}$ = 13.2, J$_{PtH}$ NCHH'Ar), 7.291 (d, J$_{HH}$ = 7.2, 3,5-Ar), 7.621 (t, J$_{HH}$ = 7.4, 4-Ar). 13C {1H} (CD2Cl2) δ = -12.15 (Pt-C$_3$H$_3$, J$_{PtC}$ = 982), 10.24 (NCH$_2$C$_3$H$_3$), 12.89 (NCH$_2$CH$_3$), 52.83, (Ar-C$_3$H$_2$N, J$_{PtC}$ = 47) 114.33 (1 Aryl, J$_{PtC}$ = 14) 129.80 (3.5-Aryl), 129.80 (4-Aryl), 134.81 (2,6-Aryl). Analysis: Calc’d: C: 36.71, H: 5.35, N: 4.51; Found: C: 36.55, H: 5.37, N: 4.47.

Independent Synthesis of [NCN]Pt(OTf) 3 from (κ-N,C,N-2,6-bis(diethylaminomethyl)-phenyl)chloro platinum(II) (2, [NCN]PtCl):

[NCN]PtCl (2) (300 mg, 0.574 mmol) was added to a recovery flask with a stirbar and dry ether (15 mL) in an oven dried round bottom flask which had been covered with aluminum foil. This was then charged with AgOTf (0.160 mg, 0.574 mmol) and allowed to stir overnight. The next day the precipitate (AgCl) was filtered off on a frit and the product, 3, was collected as an oily brown solid by removal of the ether in vacuo (325.2 mg, 89.1 % yield). 1H (CD$_2$Cl$_2$) δ = 1.489 (t, 12H, J$_{HH}$ = 14.1, NCH$_2$CH$_3$), 2.7-3.0 (m w/satellites, 4H, J$_{PtH}$ unresolved NCHH'CH$_3$), 3.2-3.5 (m, 4H, NCHH'CH$_3$), 4.016 (s w/satellites, 4H, J$_{PtH}$ = 39.3, NCHH'Ar), 6.710 (d, 2H, J$_{HH}$ = 7.5), 6.896 (t, 1H, J$_{HH}$ = 7.5). 13C {1H} (CD$_2$Cl$_2$) δ = 13.467 (NCH$_2$CH$_3$, J$_{PtC}$ = 30), 59.734 (NCH$_2$CH$_3$), 70.472 (ArCH$_2$N, J$_{PtC}$ + J$_{PtC}$ = 66), 118.207 (3.5 Aryl, J$_{PtC}$ = 33), 122.820 (4 Aryl) 144.414 (1 Aryl, J$_{PtC}$ = 1014), 145.599 (2.6 Aryl, J$_{PtC}$ + J$_{PtC}$ = 85). Combustion Analysis: Calc’d: C: 34.52, H: 4.60, N: 4.74; Found: C: 34.49, H: 4.51, N: 4.61.

Reaction of 1 with MeI

A medium-walled J. Young NMR tube charged with 1 (5.9 mg, 12.9 µmol) was cooled to -195 °C and MeI (500 µmol) and CD$_2$Cl$_2$ (350 µL) were added via vacuum transfer. The tube was warmed to room temperature. 1H NMR spectroscopy indicated the slow (minutes to hours) conversion of 1 to 4 (presumably with I$^-$ as the counter-ion) and [NCN]PtI (analogous to 3). No intermediates were observed. The reaction was repeated in C$_6$D$_6$ with identical results. Product ratios corresponded to those observed in the reaction of 1 with MeOTf.

Reaction of 1 with [Me$_3$O][BF$_4$]

A medium-walled J. Young NMR tube charged with 1 (4.5 mg, 9.8 µmol) and [Me$_3$O][BF$_4$] (17.7 mg, 120 µmol) was cooled to -195 °C and CD$_2$Cl$_2$ (350 µL) was added via vacuum transfer. The tube was warmed to -70 °C in the NMR probe, at which point a spectrum showed no reaction. Progressive warming of the solution in 20 °C intervals to room temperature revealed no intermediates, but reaction chemistry analogous to that observed with MeOTf and MeI.
Kinetics of the reaction of 1 with MeOTf

Standard solutions were prepared in a glove box of 1 and TMS$_2$O (0.116 M and 0.235 M, respectively, the latter as an internal standard) in CD$_2$Cl$_2$ and MeOTf (1.20 M) in CD$_2$Cl$_2$. Screw-cap NMR tubes were charged with 150 µL of the solution of 1 and TMS$_2$O. The NMR tube was brought out of the glove box and chilled to -78 °C in a dry ice/acetone bath. Variable amounts of the MeOTf solution (50 µL to 350 µL) were added via syringe, and enough CD$_2$Cl$_2$ was added to bring the total volume to 500 µL (0 µL to 300 µL), thereby assuring pseudo-first order conditions (5-37 equiv. MeOTf). The solutions were shaken at -78 °C to establish good mixing and homogeneity. The NMR tubes were inserted into a pre-cooled NMR probe at -40.0 °C (temperature calibrated with MeOH). Pulses were spaced by one minute to allow for full relaxation. Reactions were followed for either two half lives (2 runs) or three half-lives (6 runs) by integrating the disappearance of the Pt-Me group of 1 relative to the TMS$_2$O standard. In all cases, good first order kinetic behavior was observed ($r^2 > 0.998$), indicating that the reaction was first order in 1. A plot of $k_{obs}$ vs. [MeOTf] indicated that the reaction was first order in MeOTf ($r^2 = 0.97$), with a second-order rate constant of $k = 2.05(15) \times 10^{-4}$ M$^{-1}$s$^{-1}$. In all tubes, a small amount of a side reaction was observed in which methane and 3 were produced, presumably a result of trace HOTf. As this reaction was instantaneous at -40 °C, this did not interfere with kinetic measurements. In one kinetic run, the rate of consumption of 1 to the rate of production of 4 was carefully monitored, and throughout the reaction, the rate of 4 formation was found to be 88% ± 2% that of the disappearance of 1. While no peaks of 3 were sufficiently separated from those of 1 to allow for integration, mass balance requires that the rate of formation of 3 be 12% ± 2% that of the disappearance of 1, for a rate ratio of 7 ± 2 : 1 for Me-Ar to Me-Me coupling.

Reaction of 1 with CD$_3$OTf (NMR characterization)

Two NMR tubes were prepared, one in deuterio- the other in protio-solvent. In the first, 8.1 mg (17.7 µmol) of 1 was loaded into a medium-walled J. Young tube which was cooled to 77K. CD$_3$OTf (50 µmol) and CD$_2$Cl$_2$ (350 µL) were added via vacuum transfer. The reaction was allowed to warm to room temperature and the degree of scrambling was determined by integrating ratio of the Pt-CH$_3$ peak to the Ar-CH$_3$ methyl of 4-d$_3$ in the $^1$H NMR spectrum. This ratio, 4:1, was in keeping with that measured in the second experiment, in which 7.4 mg of 1 (16 µmol) was loaded into a medium-walled J. Young tube which was cooled to 77K. CD$_3$OTf (500 µmol) and CD$_2$Cl$_2$ (350 µL) were added via vacuum transfer. The reaction was allowed to warm to room temperature and the degree of scrambling was determined by integrating ratio of the Pt-CH$_3$ peak to the Ar-CH$_3$ methyl of 4-d$_3$ in the $^2$H NMR spectrum, which ratio was determined to be 1:4.
Reaction of 1 with CD$_3$OTf (GC/MS characterization)

In a gas-tight screwcap vial, 45 mg of 1 (98 µmol) and 1.5 mL of CD$_2$Cl$_2$ were enclosed under argon. MeOTf (14 µL, 99 µmol) was added via syringe. After several minutes, 250 µL of the vial headspace was injected into an HP 5971 GC-MS with the solvent cutoff disabled. Ethane-$h_6$ was identified by the prominence of a peak at 28 g/mol (CH$_2$CH$_2^+$) and an isotopic distribution pattern matching the instrument library. Repeating the experiment with 1 (25.6 mg, 56 µmol), 0.5 mL of CH$_2$Cl$_2$, and CD$_3$OTf (6 µL, 42 µmol), the diagnostic peak at 28 g/mol was replaced by one at 30 g/mol (CD$_2$CH$_2^+$). Other isotopic peaks such as the M$^+$ peak (CH$_3$CD$_3^+$) were also observed at the same retention time, but significant peaks attributable to C$_2$D$_6^+$ (36), C$_2$H$_4^+$ (28), or C$_2$D$_4^+$ (32) were not.