Supplementary Information

1,2,3-Triazolylidene Based Complexes via Post-modification of Pincer Click Ligands

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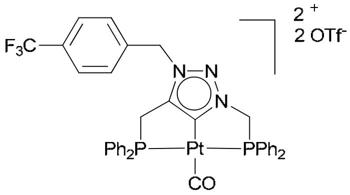
General Methods. Oxygen- and moisture-sensitive reactions were carried out under an atmosphere of purified nitrogen in a glovebox equipped with an inert gas purifier, or by using standard Schlenk techniques. Dry Et_3N was obtained by distillation from CaH_2. Solvents were purified by passing through a column of activated alumina under inert atmosphere. All commercially available reagents were used as received, unless otherwise indicated. NMR spectra were recorded at 300 MHz/75 MHz ($^1H/^{13}C$ NMR) in $CDCl_3$ unless otherwise stated on a Bruker AVANCE 300 MHz spectrometer at 23°C. Chemical shifts (δ) are reported in parts per million and the residual solvent peak was used as an internal standard ($CDCl_3$: δ 7.261/77.0, 1H/13C NMR). ^{31}P NMR signals are in ppm and referenced to external 85% H_3PO_4. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet, b = broad), integration, and coupling constant(s) (Hz).

Ligands **8**[1] and **9**[2] and complexes **10** and **12**[3] were prepared according to previously reported procedures.



14

To a solution of **13** (36 mg, 0.039 mmol) in THF (1 mL) was added silver triflate (19.8 mg, 0.077 mmol, 2 eq) in THF (0.5 mL). After 10 minutes, the mixture was filtered through a plug of celite. Dry CO was bubbled through the reaction mixture for 10 minutes. $^{31}P\{^1H\}$ NMR showed

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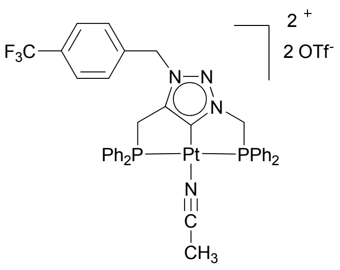
[1] E. M. Schuster, G. Nisnevich, M. Botoshansky and M. Gandelman, *Organometallics*, 2009, **28**, 5025.

[2] E. M. Schuster, M. Botoshansky and M. Gandelman, *Angew. Chem. Int. Ed.*, 2008, **47**, 4555.

[3] E. M. Schuster, M. Botoshansky and M. Gandelman, *Organometallics*, 2009, **28**, 7001.

quantitative formation of **14** as a single product. The solvent was evaporated to give **14** as a grey solid (31 mg, 70%).

^{1}H NMR ($CDCl_3$) δ: 4.92 (2H, d, J_{HP}= 10.5 Hz), 6.47 (2H, s), 6.57 (2H, d, J_{HP}= 7.8 Hz), 7.35-8.55 (24H, br s). ^{13}C NMR (DMF-d_7) δ: 6.0, 29.6 (d, J_{CP} = 40.6 Hz), 44.2, 55.2 (d, J_{CP} = 46.5 Hz), 114.0, 116.9, 121.1, 122.3, 123.6, 127.0, 127.1, 127.8, 127.9, 128.1, 129.6, 130.1, 131.0, 131.5, 131.7, 131.9, 135.3, 182.2. ^{19}F NMR (CD_3CN) δ: -64.2, -79.9. ^{31}P NMR ($CDCl_3$) δ: 30.7 1P, d, J_{PP} = 317 Hz), 44.5 (1P, d, J_{PP} = 317 Hz). IR ν_{CO}= 2124 cm^{-1}. *m/z* (HRMS-ESI) M-CO+OTf 967.1053, $C_{37}H_{30}N_3F_6P_2SPt$ calcd: 967.1035. Anal. Calcd: C, 40.92; H, 2.64. Found: C, 41.47; H, 2.32.



16

To a solution of **13** (36 mg, 0.039 mmol) in THF (1 mL) was added silver triflate (19.8 mg, 0.077 mmol, 2 eq) in acetonitrile (0.5 mL). After 10 minutes, the mixture was filtered through a plug of celite. ^{31}P{^{1}H} NMR showed quantitative formation of **16** as a single product. The solvent was evaporated to give **16** as a yellowish solid (45 mg, 100%).

^{1}H NMR (CD_3CN) δ: 4.10 (2H, d, J_{HP} = 10 Hz), 5.66 (2H, d, J_{HP} = 8 Hz), 5.84 (2H, s, CH_2-Ar), 7.3-8.0 (24H, br m). ^{13}C NMR (CD_3CN) δ: 8.0, 29.6 (d, J_{CP}= 39 Hz), 46.7, 55.0 (d, J_{CP}= 45 Hz), 125.9, 128.4, 129.7, 129.8, 129.9, 132.9, 133.0, 133.4, 133.5, 133.6, 163.0 (C-ipso). ^{19}F NMR (CD_3CN) δ: -62.6, -78.6. ^{31}P NMR (CD_3CN) δ: 44.2 (1P, d, J_{PP}= 380 Hz), 31.0 (1P, d, J_{PP}= 380 Hz). *m/z* (HRMS-ESI) M-CH_3CN+OTf 967.1053, $C_{37}H_{30}N_3F_6P_2SPt$ calcd: 967.1035. Anal. Calcd: C, 41.49; H, 2.87. Found: C, 42.23; H, 2.98.