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 Et₃N was obtained by distillation from CaH₂. 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/¹³C NMR) in CDCl₃ 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 (CDCl₃: δ 7.261/77.0, ¹H/¹³C NMR). ³¹P NMR signals are in ppm and referenced to external 85% H₃PO₄. 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 8¹ and 9² and complexes 10 and 12³ were prepared according to previously reported procedures.

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. ³¹P{¹H} NMR showed

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

\[ \text{1H NMR (CDCl}_3\text{)} \delta: 4.92 (2H, d, J_{HP} = 10.5 \text{ Hz}), 6.47 (2H, s), 6.57 (2H, d, J_{HP} = 7.8 \text{ Hz}), 7.35-8.55 (24H, br s). \]

\[ \text{13C NMR (DMF-d}_7\text{)} \delta: 6.0, 29.6 (d, J_{CP} = 40.6 \text{ Hz}), 44.2, 55.2 (d, J_{CP} = 46.5 \text{ Hz}), 114.0, 116.9, 121.1, 122.3, 123.6, 127.0, 127.1, 127.8, 127.9, 128.1, 129.6, 130.1, 131.0, 131.5, 131.7, 131.9, 135.3, 182.2. \]

\[ \text{19F NMR (CD}_3\text{CN)} \delta: -64.2, -79.9. \]

\[ \text{31P NMR (CDCl}_3\text{)} \delta: 30.7 \text{ (1P, d, } J_{PP} = 317 \text{ Hz)}, 44.5 \text{ (1P, d, } J_{PP} = 317 \text{ Hz). IR } \nu_{\text{CO}} = 2124 \text{ cm}^{-1}. \]

\[ m/z \text{ (HRMS-ESI) } M-\text{CO}+\text{OTf} 967.1053, \text{ C}_{37}\text{H}_{30}\text{N}_{3}\text{F}_{6}\text{P}_{2}\text{S}_{2}\text{Pt calcd: 967.1035. Anal. Calcd: C, 40.92; H, 2.64. Found: C, 41.47; H, 2.32.} \]

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. \[ \text{31P\{1H\} NMR showed quantitative formation of 16 as a single product. The solvent was evaporated to give 16 as a yellowish solid (45 mg, 100%).} \]

\[ \text{1H NMR (CD}_3\text{CN)} \delta: 4.10 (2H, d, J_{HP} = 10 \text{ Hz}), 5.66 (2H, d, J_{HP} = 8 \text{ Hz}), 5.84 (2H, s, CH}_2\text{-Ar), 7.3-8.0 (24H, br m). \]

\[ \text{13C NMR (CD}_3\text{CN)} \delta: 8.0, 29.6 (d, J_{CP} = 39 \text{ Hz}), 46.7, 55.0 (d, J_{CP} = 45 \text{ Hz), 125.9, 128.4, 129.7, 129.8, 129.9, 132.9, 133.0, 133.4, 133.5, 133.6, 163.0 (C-ipso). 19F NMR (CD}_3\text{CN)} \delta: -62.6, -78.6. \]

\[ \text{31P NMR (CD}_3\text{CN)} \delta: 44.2 (1P, d, J_{PP} = 380 \text{ Hz), 31.0 (1P, d, J_{PP} = 380 Hz). m/z \text{ (HRMS-ESI) } M-\text{CH}_3\text{CN}+\text{OTf} 967.1053, \text{ C}_{37}\text{H}_{30}\text{N}_{3}\text{F}_{6}\text{P}_{2}\text{S}_{2}\text{Pt calcd: 967.1035. Anal. Calcd: C, 41.49; H, 2.87. Found: C, 42.23; H, 2.98.} \]