

Unprecedented double migratory insertion of phenyl isocyanide into cyclopentadienyl C-H bonds

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1 Synthesis and Spectroscopic Characterisation of 1-3

1.1 General Considerations

All reactions and manipulations were carried out under an atmosphere of dry argon or dinitrogen gas using standard Schlenk and glove box techniques. The starting material $[\text{ClCu}(\text{CNPh})_2]_2$ was prepared from commercially available starting materials according to a modified literature procedures. NaC_5H_5 was purchased from Aldrich chemicals as a 2M solution in THF and was used as received. For the preparation and characterisation of complexes, all reactions and manipulations were performed under an inert atmosphere of argon or nitrogen using standard Schlenk or glove-box techniques and all solvents were freshly distilled over suitable drying agents and degassed prior to use. ^1H and ^{13}C spectra were recorded on a Brüker Advance 300 MHz spectrometer, using internal references. Coupling constants are given in hertz. Elemental analysis was performed “*in-house*” at the Department of Chemistry, University of Bath.

1.2 Synthesis of $[(\eta^5\text{-C}_5\text{H}_5)\text{Cu}(\text{CNPh})]$, 1.

$[\text{ClCu}(\text{CNPh})_2]_2$ (3.66 g, 6.00 mmol) was dissolved in 20 ml of THF, in a dry and degassed Schlenk under inert atmosphere. To this a 2M solution sodium

cyclopentadienide in THF (6 ml, 12.0 mmol) was added, at room temperature. The reaction mixture was allowed to stir for 2 h. Removal of solvent under reduced pressure resulted in the precipitation of a dark residue, which was slurried, in a minimum (10 ml) of fresh hexane. After 15 minutes the hexane was removed under reduced pressure, and a fresh aliquot of hexane added to the reaction mixture. This process was repeated with a final 10ml of fresh hexane in order to remove residual THF. Fresh hexane (20 ml) was added and the suspension was filtered through celite to remove any insoluble materials, followed by removal of the volatiles *in-vacuo*. This resulted in a dark yellow crude solid that was purified by recrystallisation (hexane) to afford **23** as yellow crystals Yield: 2.36g, 85 %. Anal. Calcd for: C₁₀H₁₂CuN C, 62.19; H, 4.36; N, 6.04: Found: C, 63.04; H, 4.49; N, 6.02; ¹H NMR (300 MHz, 23°C), CDCl₃ (ppm): δ 5.95 (s, 5H, C₅H₅), 7.45-7.28 (m, 5H, C₆H₅); ¹³C{¹H} NMR (75.50 MHz, 23°C) CDCl₃ (ppm): δ 94.8, 126.4, 129.6, 129.8.

1.3 Synthesis of [(CNPh)Cu{κ²-N,N-C₅H₃-1,2-(CHNPh)₂}], **2**.

[ClCu(CNPh)₂]₂ (1.22 g, 2.00 mmol) was placed in a dry and degassed Schlenk under inert atmosphere, into which THF (20 ml) was added. To this a 2M solution sodium cyclopentadienide in THF (2 ml, 4.00 mmol) was added, at room temperature. The reaction mixture was allowed to stir for 72 h at room temperature. The volatiles were removed under reduced pressure to give a brown solid, which was slurried, in a minimum (10 ml) of fresh hexane. After 15 minutes the hexane was removed under reduced pressure, and a fresh aliquot of hexane added to the reaction mixture. This process was repeated with a final 10ml of fresh hexane in order to remove residual THF. The residue was finally extracted hot hexanes (50 ml) and filtered through celite to give a dark yellow solution. Concentration of the solution and storage at -28 °C afforded **2** as yellow crystals. Yield; 0.63g, 36% Anal. Calcd. for: C₂₆H₂₀N₃Cu C, 71.30 ; H, 4.60; N, 9.59: Found: C, 63.04; H, 4.49; N, 6.02; ¹H NMR (300 MHz, 23°C), δ 6.40 (triplet, J = 3.60 Hz, 1H, CHCHCH), δ 7.01 (doublet, J = 3.58 Hz, 2H, CHCHCH), δ 7.12-

7.42 (complex multiplet, 15H, Ph), δ 8.35 (s, 2H, PhNCH) $^{13}\text{C}\{^1\text{H}\}$ NMR (75.50 MHz, 23°C) CDCl_3 (ppm): δ 118.5, 119.5, 120.7, 123.0, 124.3, 126.7, 129.1, 129.9, 135.7, 149.6, 156.4, 162.9.

1.4 Synthesis of $[(\text{CNPh})_2\text{Cu}\{\kappa^2\text{-N,N-C}_5\text{H}_3\text{-1,2-(CHNPh)}_2\}]$, **3**.

Method 1: $[\text{ClCu}(\text{CNPh})_2]_2$ (1.22 g, 2.00 mmol) and PhNC (0.41 g, 4.00 mmol) was placed in a dry and degassed Schlenk under inert atmosphere, into which THF (20 ml) was added. To this a 2M solution sodium cyclopentadienide in THF (2 ml, 4.00 mmol) was added, at room temperature. The reaction mixture was allowed to stir for 72 h at room temperature. The volatiles were removed under reduced pressure to give a brown solid, which was slurried, in a minimum (10 ml) of fresh hexane. After 15 minutes the hexane was removed under reduced pressure, and a fresh aliquot of hexane added to the reaction mixture. This process was repeated with a final 10ml of fresh hexane in order to remove residual THF. The residue was finally extracted hot hexanes (50 ml) and filtered through celite to give a dark yellow solution. Concentration of the solution and storage at -28 °C afforded **3** as dark yellow crystals. (Yield 1.32g, 61%).

Method 2: To a solution of CpCuCNPh (0.23 g, 1.0 mmol) or CpCuCN^tBu (0.21 g, 1.0 mmol) in THF (10 ml), PhNC (0.44 g, 4.30 mmol) was added. The reaction mixture was left to stir for 16 hours and the volatiles were then removed under reduced pressure. The resultant black solid was washed with diethyl ether (20 ml) and filtered. Further concentration and storage at -28 °C resulted in the formation of **3** as dark yellow crystals. (Yield 0.30g, 56%).

Anal. Calcd. for: $\text{C}_{33}\text{H}_{25}\text{N}_4\text{Cu}$ C, 73.25; H, 4.66; N, 10.35: Found: C, 73.92; H, 5.04; N, 10.15; ^1H NMR (300 MHz, 23°C), δ 6.32 (triplet, $J = 3.57$ Hz, 1H, CHCHCH), δ 6.90 (doublet, $J = 3.54$ Hz, 2H, CHCHCH), δ 7.09-7.44 (complex multiplet, 15H, Ph), δ 8.28 (s, 2H, PhNCH) $^{13}\text{C}\{^1\text{H}\}$ NMR (75.50 MHz, 23°C)

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CDCl₃ (ppm): δ 115.6, 118.7, 1122.8, 123.9, 126.5, 128.8, 129.6, 129.8, 134.8,
150.3, 156.5, 162.7.