

Supporting Information

“Copper-in-Charcoal” Revisited: Delineating the Nature of the Copper Species and its Role in Catalysis

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General experimental

All infrared spectra were obtained using a Perkin-Elmer Paragon 1000 FT-IR spectrophotometer; thin film spectra were acquired using sodium chloride plates.

All ^1H and ^{13}C NMR spectra were measured at 400.13 and 100.62 MHz using a Bruker DPX 400 MHz spectrometer or a Bruker Avance 400 MHz spectrometer. The solvent used for NMR spectroscopy was CDCl_3 (unless stated otherwise) using TMS (tetramethylsilane) as the internal reference. Chemical shifts are given in parts per million (ppm) and J values are given in Hertz (Hz).

Analysis by GCMS utilised a Fisons GC 8000 series (AS 800), using a 15 m x 0.25 mm DB-5 column and an electron impact low resolution mass spectrometer.

Melting points were recorded using a Stuart Scientific melting point apparatus SMP3 and are uncorrected.

All chromatographic manipulations used silica gel as the adsorbent. Reactions were monitored using thin layer chromatography (TLC) on aluminium backed plates with Merck Kiesel 60 F254 silica gel. TLC visualised by UV radiation at a wavelength of 254 nm, or stained by exposure to an ethanolic solution of phosphomolybdic acid (acidified with concentrated sulphuric acid), followed by charring where appropriate. Purification by column chromatography used Merck Kiesel 60 H silica adsorbent.

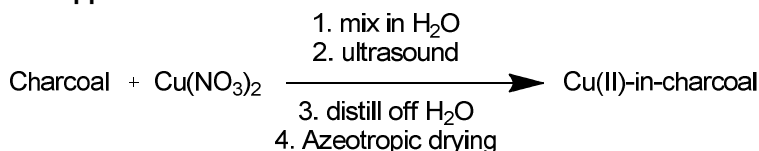
Reaction solvents were obtained commercially dry, except light petroleum (b.p. 40-60 °C) which was distilled from calcium chloride prior to use. Ethyl acetate was distilled over calcium sulfate or chloride. Dichloromethane was distilled over calcium hydride.

Microwave reactions were performed in a Biotage Initiator EXP 8 reactor in 2–5 mL crimped vials.

X-Ray Diffraction Data:

A Bruker D8 powder diffractometer operating with $\text{Cu}_{\text{K}\alpha 1}$ (1.5406 Å) radiation, using a 2θ range of 5° – 60° , with a step size of 0.0147° with a step time of 1s for 1 hour was used for the collection of the X-ray data presented here in this work. The detectors used in the collection of data were a mBraun position sensitive detector and a Lynxeye position sensitive detector that allows a range of scattering angles to be measured increasing signal detection and reducing noise. The collected data were then analysed in the EVA program using ICDD to identify and determine sample purity.

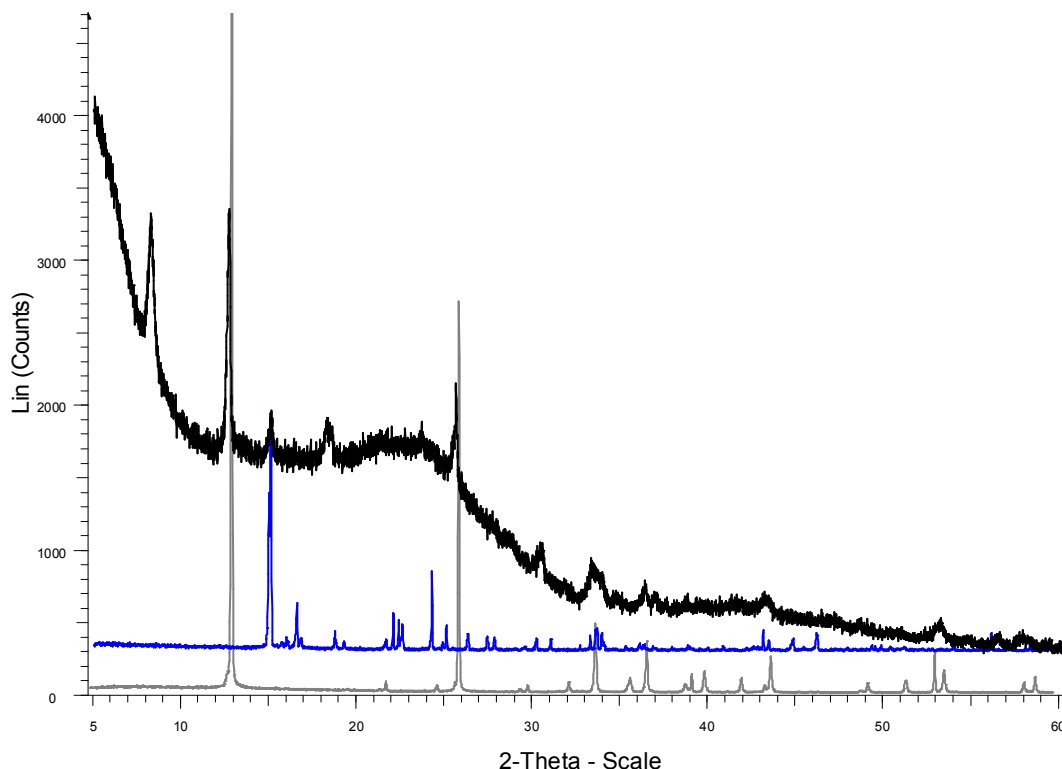
Preparation of Copper-in-Charcoal



Darko KB activated carbon (15.2 g) was added to a 500 mL RBF fitted with stirrer bar. A solution of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (3.3 g, 13.8 mmol) in water (100 mL) was added to the flask, along with an additional (125 mL) water to rinse the sides of the flask. The reaction vessel was then purged with nitrogen for 30 min with vigorous stirring. The flask was then submerged in an ultrasonic bath fitted with a nitrogen balloon for 1 hour. The reaction mixture was then distilled at 175 -180°C with stirring. After the majority of the water was removed, toluene (75 mL) was added and the mixture was dried under Dean-Stark conditions overnight. A further distillation was carried out to remove the remaining solvent. A fine black powder was obtained. This solid was dried overnight in a vacuum oven at 100°C, and then stored in a desiccator. The material was then characterised by powder XRD.

Preparation of Gerhardite

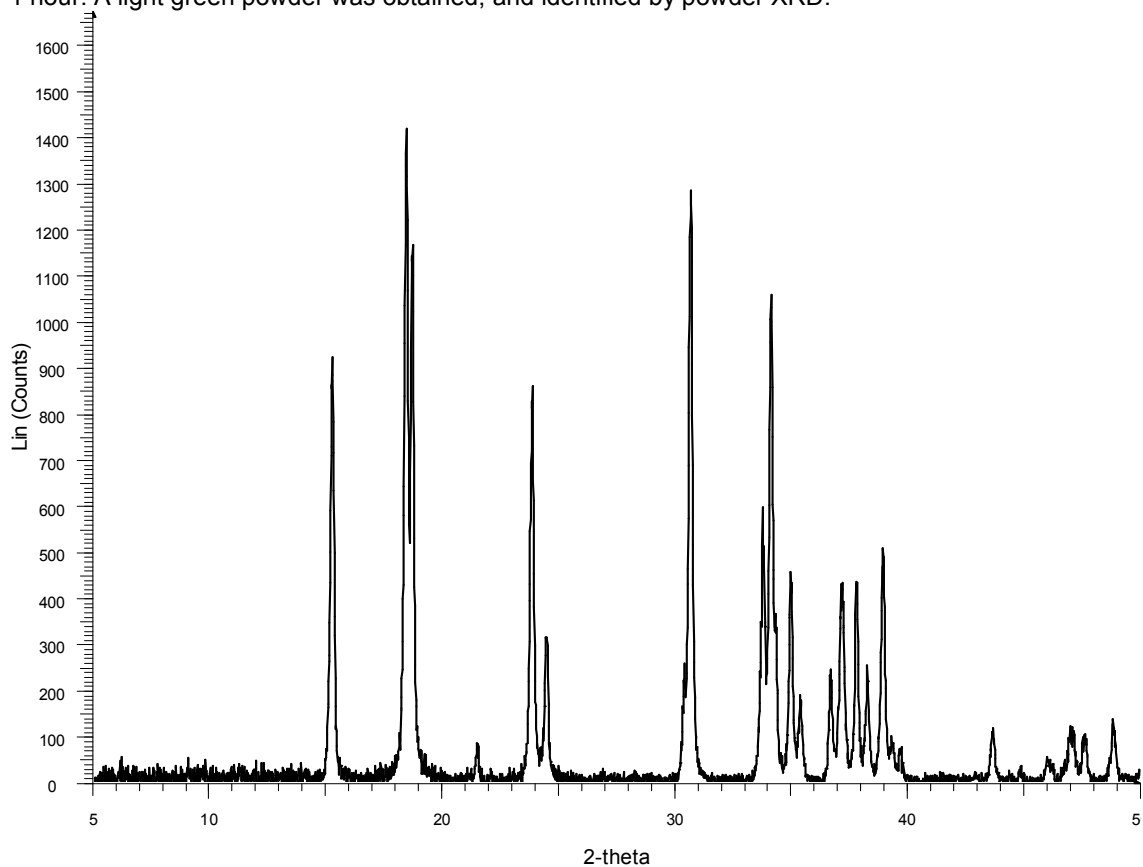
$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (3.3 g, 13.8 mmol) was added to a 500 mL RBF fitted with stirrer bar, water (100 mL) was added to the flask, along with an additional (125 mL) water to rinse the sides of the flask. The reaction vessel was then purged with nitrogen for 30 min with vigorous stirring. The flask was then submerged in an ultrasonic bath fitted with a nitrogen balloon for 1 hour. The reaction mixture was then distilled at 175-180°C with stirring. After the majority of the water was removed, toluene (75 mL) was added and the mixture was dried under Dean-Stark conditions overnight. A further distillation was carried out to remove the remaining solvent. A fine green powder was obtained. This solid was dried overnight in a vacuum oven at 100°C, and then stored in a desiccator. The material was then characterised by powder XRD.



XRD results for the copper on carbon material (top) compared to copper nitrate starting material (blue) and $\text{Cu}_2(\text{OH})_3(\text{NO}_3)$ (grey)

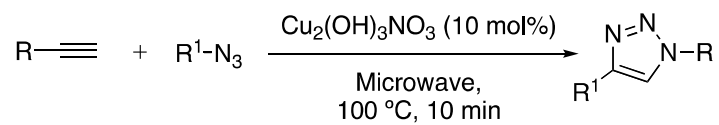
Preparation of Libethenite ($\text{Cu}_2(\text{PO}_4)\text{OH}$)


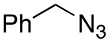
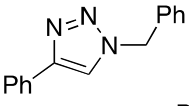
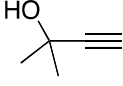
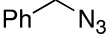
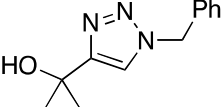
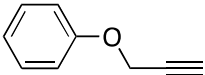
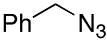
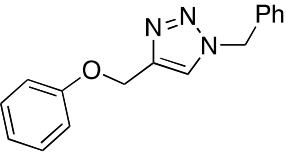
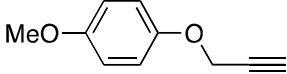
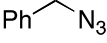
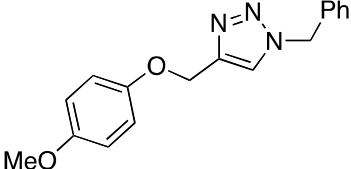
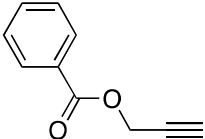
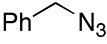
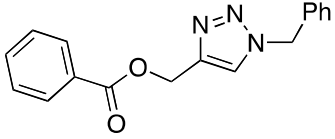
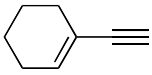

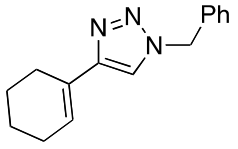
$\text{CuSO}_4 \cdot \text{H}_2\text{O}$ (1.1 g, 6.2 mmol) was added to a conical flask, water (20 mL) was then added in a separate conical flask $(\text{NH}_4)_2\text{HPO}_4$ (0.42 g, 3.2 mmol) dissolved in water (20 mL). The ammonium phosphate solution was then added to the copper sulphate solution, in a single addition, and neutralised with NH_3 (4-5 drops). The mixture was then heated to 70°C until the solution turned a light green colour. The mixture was allowed to cool, then filtered under suction and washed with H_2O (100 mL). The solid was then vacuum oven dried at 120°C for 1 hour. A light green powder was obtained, and identified by powder XRD.



XRD pattern for the Libethenite sample prepared in our laboratory independently from the support materials.

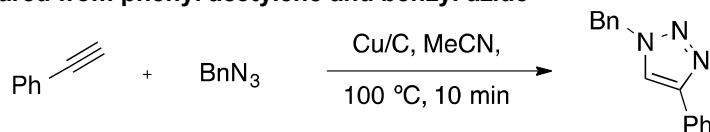
Table S1:



Entry	Alkyne	Azide	Product	Yield (%)
1				97
2				97
3				88
4				92
5				99
6				87

General conditions: Alkyne (2.6 mmol), benzyl azide (1.7 mmol), $\text{Cu}_2(\text{OH})_3\text{NO}_3$ (10 mol%), dioxane (2 mL), microwave 100 $^\circ\text{C}$, 10 min.

Table 1: Representative triazole click reaction using copper on support material catalyst
Triazole prepared from phenyl acetylene and benzyl azide



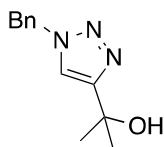
Benzyl azide (0.23g 1.7mmol) and phenylacetylene (0.26g 2.6mmol) were added to a 5 mL microwave tube fitted with magnetic stirrer bar. Copper-in-Charcoal (DarkoKB, prepared above) (0.05g) was added and the mixture suspended in acetonitrile (5 mL). The reaction was then heated in the microwave for 10 min at 100°C. The reaction was then allowed to cool to room temperature, the solid support material removed by gravity filtration, and washed with EtOAc (3 x 10 mL). The solvent was removed under reduced pressure to afford a pale off white solid that was purified by column chromatography eluting with Light petroleum/ethyl acetate to afford the product as colourless crystals (0.34g, 85%). mp °C 126-129 °C, (lit. m.p. 127-128 °C).¹ IR (CDCl₃): ν_{max} 734.4, 908.8, 2253.0, 3035.1, 3583.9 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 5.58 (s, 2H), 7.19-7.35 (m, 8H), 7.60 (s, 1H), 7.74 (d, 2H, J = 1.4 Hz); ¹³C NMR (400 MHz, CDCl₃): δ = 54.2, 119.6, 125.7, 127.5, 128.1, 128.2, 128.8, 129.2, 130.6, 134.7, 148.3.

Table 1 and S1: Representative triazole click reaction using Gerhardite

Triazole prepared from phenyl acetylene and benzyl azide

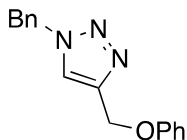
Benzyl azide (0.23g 1.7mmol) and phenylacetylene (0.26g 2.6mmol) were added to a 5 mL microwave tube fitted with magnetic stirrer bar. Gerhardite (0.021g, 0.17 mmol, w.r.t. Cu content) was added and the mixture suspended in 1,4-dioxane (5 mL). The reaction was then heated in the microwave for 10 min at 100°C. The reaction was then allowed to cool to room temperature, the solid support material removed by gravity filtration, and washed with EtOAc (3 x 10 mL). The solvent was removed under reduced pressure to afford a pale off white solid that was purified by column chromatography eluting with Light petroleum/ethyl acetate to afford the product as colourless crystals (0.39g, 97%).

Table S1 Entry 2: Triazole prepared from 2-methyl-3-butyn-2-ol and benzyl azide:²



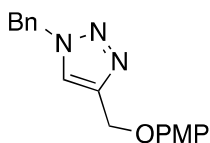
Colourless crystals. ¹H NMR (400 MHz, CDCl₃, 25°C, TMS) δ = 7.27 – 7.41 (6 H, m), 5.49 (2 H, s), 1.63 (6 H, s). ¹³C NMR (400 MHz, CDCl₃, 25°C, TMS) δ = 156.1, 134.6, 129.1, 128.8, 128.2, 119.1, 68.5, 54.2, 30.5.

Table S1 Entry 3: Triazole prepared from propargyl phenyl ether and benzyl azide:³



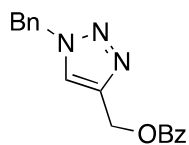
Colourless crystals. ¹H NMR (400 MHz, CDCl₃, 25°C, TMS) δ = 7.53 (1 H, s), 7.29–7.31 (8 H, m), 6.95-6.98 (2 H, m), 5.52 (2 H, s), 5.18 (2H, s); ¹³C NMR (400 MHz, CDCl₃, 25°C, TMS) δ = 158.2, 144.8, 134.5, 129.6, 129.2, 128.8, 128.2, 122.7, 121.3, 114.8, 62.1, 54.3.

Table S1 Entry 4: Triazole prepared from propargyl 4-methoxyphenyl ether and benzyl azide:⁴



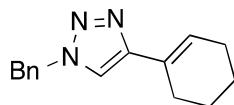
Colourless crystals. ¹H NMR (400 MHz, CDCl₃, 25°C, TMS) δ = 7.52 (1H, s), 7.35 – 7.37 (3 H, m), 7.26 – 7.27 (2 H, m), 6.89 – 6.91 (2 H, m), 6.80 – 6.84 (2 H, m), 5.53 (2 H, s), 5.13 (2 H, s), 3.76 (3 H, s); ¹³C NMR (400 MHz, CDCl₃, 25°C, TMS) δ = 154.2, 152.3, 144.9, 134.5, 129.2, 128.8, 128.1, 122.5, 115.9, 114.7, 62.9, 55.7, 54.2.

Table S1 Entry 5: Triazole prepared from propargyl benzoate and benzyl azide:²



Colourless crystals. ¹H NMR (400 MHz, CDCl₃, 25°C, TMS) δ = 8.02 (2 H, dd, *J* 0.4, .2 Hz), 7.61 (1 H, s), 7.44 – 7.57 (1 H, m), 7.34 – 7.42 (5 H, m), 7.26 – 7.31 (2 H, m), 5.53 (2 H, s), 5.45 (2 H, s). ¹³C NMR (400 MHz, CDCl₃, 25°C, TMS) δ = 166.4, 143.4, 134.4, 133.2, 129.8, 129.2, 128.9, 128.4, 128.2, 123.8, 58.1, 54.3.

Table S1 Entry 6: Triazole prepared from 1-ethynylcyclohexene and benzyl azide:⁵



Colourless crystals. ¹H NMR (400 MHz, CDCl₃, 25°C, TMS) δ = 7.24 – 7.37 (6 H, m), 6.49 – 6.51 (1 H, t, *J* 2.0 Hz), 5.51 (2 H, s), 2.16-2.34 (4 H, m), 1.64-1.75 (4 H, m); ¹³C NMR (400 MHz, CDCl₃, 25°C, TMS) δ = 150.0, 135.0, 129.1, 128.6, 128.0, 127.3, 125.1, 118.2, 54.0, 26.4, 25.3, 22.4, 22.2.

Time elapsed experiments (Figure 3)

Three identical experiments were set-up separately and the insoluble copper species removed by filtration after 2h, 120h and 240h respectively.

The general procedure is outlined below:

Benzyl azide (0.23g 1.7mmol) and phenylacetylene (0.26g 2.6mmol) were added to a 50 mL RBF containing a magnetic stirrer bar. Gerhardite (0.050g, 0.4 mmol, w.r.t. Cu content) and Libethenite 0.048g, 0.4 mmol, w.r.t. Cu content) was added and the mixture suspended in acetonitrile (10 mL). The reaction was then stirred at room temperature for the time indicated. The insoluble copper species was removed by gravity filtration, washed with EtOAc (3 x 10 mL) and dried in air before being analysed by XRD.

References

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- (3) Rostovtsev, V. V.; Green, L. G.; Fokin, V. V.; Sharpless, K. B. *Angew. Chem., Int. Ed.*, **2002**, 41, 2596.
- (4) Buckley, B. R.; Dann, S. E.; Harris, D. P.; Heaney, H.; Stubbs, E. C. *Chem. Commun.* **2010**, 46, 2274.
- (5) Zhao, Y.-B.; Yan, Z.-Y.; Liang, Y.-M. *Tetrahedron Lett.*, **2006**, 47, 1545.