Supporting Information for

Copper and Silver Benzoate and Aryl Complexes and Their Implications for Oxidative Decarboxylative Coupling Reactions

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I. General Considerations.

All manipulations were performed under N_2 using standard Schlenk or inert-atmosphere glovebox techniques, unless otherwise noted. DMF- d_7 (Cambridge Isotopes) was stored over 4Å molecular sieves. Solvents were taken from a Glass Contours solvent system, in which the solvent is passed through a column of activated alumina with a pressure of Argon. Commercial reagents were used without further purification unless otherwise stated.

¹H and ¹³C{¹H} NMR spectra were recorded on an Agilent 400 MHz spectrometer or a Varian INOVA 600 MHz spectrometer at room temperature, unless otherwise noted. Chemical shifts (δ) are given in parts per million and referenced to the residual solvent signal¹ (DMF- d_7 is referenced to the solvent peaks at 8.02 and 163.15 for ¹H and ¹³C spectra respectively); and all coupling constants (*J*) are reported in Hz. High resolution mass spectra were obtained on a Thermo Finnigan Linear Trapping Quadrupole mass spectrometer. IR spectra were recorded on a Perkin Elmer (Spectrum 100) FT-IR spectrometer. Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA. X-Ray diffraction data was collected on a Bruker AXS D* Venture fixed-chi X-ray diffractometer equipped with a Triumph monochromator, a Mo K α radiation source and a PHOTON 100 CMOS detector at 100 K.

II. Synthesis and Characterization of Copper and Silver Complexes



(phen)Cu(2-nitrobenzoate)₂ (1). To a stirred solution of copper(II) triflate (908.9 mg, 2.51 mmol) in ethanol (30 mL) was added a solution of phenanthroline (452 mg, 2.51 mmol) in ethanol (15 mL). After about one minute, a solution of 2-nitrobenzoic acid (838.9 mg, 5.02 mmol) and sodium hydroxide (201 mg, 5.03 mmol) in water (3 mL) was added slowly; a blue precipitate formed. The reaction mixture was stirred for 2 hours. The next day, ethanol was added (250 mL) and the mixture was brought to a boil and filtered while hot. Upon cooling the title compound crystalized. The product was collected by filtration and washed with ethanol to yield 384.1 mg (0.667 mmol, 26.6 %) as dark blue needles. A second crop of product was obtained by returning the crude product from the hot filtration to the filtrate. bringing it to a boil and filtering hot. After 10 days at room temperature the product was collected by filtration and washed with ethanol to yield 604 mg (1.05 mmol, 41.8 %) of 1 as dark blue needles. IR (ATR, cm⁻¹):.3062 (w), 1642 (s), 1573 (m), 1521 (s), 1428 (m), 1368 (m), 1328 (s), 1265 (m), 1140 (m), 850 (s), 828 (m), 741 (s), 720 (s), 696 (s). HRMS (ESI, 1 % TFA methanol) calculated: 409.01183, found: 409.01267 in $[(\text{phen})\text{Cu}(\text{O}_2\text{CC}_6\text{H}_4\text{NO}_2)]^+$. Elemental Analysis: calculated C₂₆H₁₆CuN₄O₈ C 54.22; H 2.80; N 9.73; Measured C 54.17, H 2.73, N 9.72.



(phenanthroline)Cu(O₂CC₆H₄-*o*-NO₂) (2). To a solution of (CuO⁷Bu)₄ (131 mg, 0.959 mmol) in THF (30 mL) was added a solution of 1,10-phenanthroline (154 mg, 0.855 mmol) in THF (15 mL). The mixture turned brown and was allowed to stir for 5 min. A solution of 2-nitrobenzoic acid (144 mg, 0.859 mmol) in THF (12 mL) was then added. After stirring for 5 min, dark purple solids precipitated from solution. Hexane (20 mL) was added to further precipitation and the dark purple solids were collected by filtration and washed with additional hexane (20 mL) before they were dried and collected yielding 326 mg (0.796 mmol, 93% yield) of **2** as a purple solid.¹H NMR (400 MHz, DMF-*d*₇): δ = at 25°C: 9.19 (2H), 8.94 (2 H), 8.37 (2H), 8.11 (2 H), 7.81 (2H), 7.70 (1H), 7.52 (1H). At -30°C: 9.26 (d, J = 4.2 Hz, 2H), 8.99 (d, J = 7.8 Hz, 2H), 8.42 (s, 2H), 8.14 (dd, J = 7.8, 4.8, 2H), 7.81 (br, 2H), 7.67 (br, 1H), 7.60 (br, 1H). ¹³C NMR (100 MHz, DMF-*d*₇): δ = at 25°C (only 11 C signals could be identified): 151.64, 150.77, 144.75, 138.53, 133.17, 132.23, 131.03, 130.55, 128.31, 126.96, 124.12. IR (ATR, cm⁻¹): 1626.96 (str), 1572.88 (med), 1524.97 (str), 1421.51

(med), 1347.38 (str), 140.83 (med), 828.71 (med), 783.25 (w), 722.32 (str), 697.04 (med). HRMS (ESI, CH₃CN): positive mode: 409.01209 [(phen)Cu(O₂CC₆H₄NO₂)]⁺, 423.06686 [(phen)₂Cu]⁺, 589.08092 [(phen)₂Cu(O₂CC₆H₄NO₂)]⁺, negative mode: 394.96031 [Cu(O₂CC₆H₄NO₂)₂]⁻. Elemental Analysis: calculated C₁₉H₁₂CuN₃O₄ C 55.68, H 2.95; N 10.25, Measured: C 54.85, H 3.11, N 10.14.



Figure S1. Aromatic regions of the ¹H NMR spectra of **2** acquired at (a) 25° C and (b) -30° C in DMF- d_7 . The phen resonances are indicated with filled squares (\blacksquare) and the benzoate resonances with open circles (**O**). The full room temperature spectrum in Section VI, p S17.

(CuOtBu)₄. The title compound was synthesized following a modification of a literature procedure.² In a nitrogen filled glove box, THF (30 mL) was added to CuCl (2.0 g, 20.2 mmol) and NaOtBu (1.78 g, 17.7 mmol). The mixture was allowed to stir for 5 h before the solvent was removed under vacuum. The crude material was purified by sublimation (60 mtorr, 100 °C, ice water cooled cold finger) in batches to yield the title compound as a light yellow solid in 72% yield (1.74 g, 12.7 mmol). ¹H NMR (400 MHz, C₆D₆): $\delta = 1.306$ (s). The spectral data are consistent with the literature characterization.²



5,5-dimethyl-2-(2-nitrophenyl)-[1,3,2]dioxaborinane. The title compound was prepared by modification of the literature synthesis.³ 2-Nitrophenylboronic acid (1.00 g, 6.00 mmol) and neopentyl glycol (0.620 g, 5.95 mmol) were combined in a mortar and pestle until a homogenous brown oil was formed. Silica gel (~4 g) was added and the mixture was combined until a free-flowing powder was obtained. The powder was transferred to a frit

containing a silica gel pad. The product was eluted with hexanes/ethyl acetate (8:2 (v/v), about 500 mL). The solvent was removed under vacuum to yield the product as a red oil (1.39 g, 5.91 mmol, 99%). ¹H NMR (400 MHz, CDCl₃): δ = 1.11 (s, 6 H), 3.79 (s, 4 H), 7.45 – 7.50 (m, 1 H), 7.52 – 7.58 (m, 1 H), 7.58 - 7.65 (m, 1 H), 8.09 (d, J=7.8 Hz, 1 H). The spectroscopic data are consistent with the literature values.⁴



(phenanthroline) $Cu(C_6H_4-o-NO_2)$ (3). All starting materials and solvents (THF, pentanes) were pre-measured and cooled in a -30°C freezer for 3 hours. The reaction was performed at room temperature (78 °F) with the materials being removed from the freezer just before use. To a stirred solution (40-mL screw-top vial) of 1,10-phenanthroline (77 mg, 0.43 mmol) and 5,5-dimethyl-2-(2-nitrophenyl)-1,3,2-dioxaborinane (106 mg, 0.45 mmol) in THF (10 mL), (CuO^tBu)₄ (63 mg, 0.46 mmol Cu) in THF (5 mL) was quickly added in roughly 1-mL portions. The mixture was allowed to stir for 2.5 minutes before pentanes were quickly added in roughly 1-mL portions to a total volume of 40 mL to precipitate the product. The precipitate was filtered, washed with pentanes (20 mL), and dried under vacuum for 30 minutes to yield 115 mg (0.314 mmol, 73% yield) of the title complex as a brown solid. The product was stored at -30°C under N₂ to prevent decomposition. ¹H NMR (600 MHz, DMF d_7): $\delta = 9.10$ (d, J = 3.6, 2H), 8.88 (d, J = 7.9, 2H), 8.30 (s, 2H), 8.08 (dd, J = 8.2, 4.7, 2H), 8.01 (d, J = 6.9, 1H), 7.95 (d, J = 8.2, 1H), 7.37 (t, J = 7.0, 1H), 7.11 (t, J = 7.1, 1H). ¹³C NMR (100 MHz, DMF- d_7): $\delta = 159.84$, 150.97, 144.79, 143.17, 138.99, 132.34, 130.98, 130.40, 128.24, 126.88, 124.52, 122.80. IR (ATR, cm⁻¹): 1573 (w), 1485 (m), 1423 (m), 1292 (m), 1229 (w), 843 (s), 725 (s). Elemental Analysis: calculated C₁₉H₁₂CuN₃O₄ C 59.09, H 3.31; N 11.49, Measured: C 59.09, H 3.45; N 10.23. Satisfactory analysis could not be obtained due to the instability of complex 3.



(phenanthroline)Ag($O_2CC_6H_4$ -o-NO₂) (4). This synthesis was performed on the benchtop protected from light. To a mixture of Ag₂O (194 mg, 1.67 mmol Ag) in CH₃CN (20 mL) was added a solution of 2-nitrobenzoic acid (278 mg, 1.66 mmol) in CH₃CN (20 mL). The mixture was allowed to stir at room temperature. After about 2 h, the silver oxide had dissolved to leave a colorless solution, which was then filtered through a pad of celite. A solution of 1,10-phenanthroline (304 mg, 1.68 mmol) in CH₃CN (20 mL) was added slowly to the filtrate with rapid stirring. Upon addition, the title compound precipitated from solution as a white solid. The product was collected, washed with CH₃CN (5 mL) and ether (~ 100 mL), and dried to yield 652 mg (1.44 mmol, 87 % yield) of the title compound. ¹H

NMR (600 MHz, DMF- d_7): $\delta = 9.31$ (dd, J = 4.4, 1.4, 2H), 8.84 (dd, J = 8.1, 1.5, 2H), 8.26 (s, 2H), 8.08 (dd, J = 8.1, 4.5, 2H), 7.90 (dd, J = 7.6, 1.3, 1H), 7.73 (d, J = 8.0, 1H), 7.64 (td, J = 7.8, 0.8, 1H), 7.55 (td, J = 7.7, 1.3, 1H). ¹³C NMR (125 MHz, DMF- d_7): $\delta = 152.71$, 151.09 (CO), 143.41, 139.68 (2C), 132.58, 131.43, 130.47, 130.19, 128.38, 126.12 (2C), 23.65. IR (ATR, cm⁻¹): 1620 (s), 1602 (s), 1567 (m), 1526 (s), 1509 (m), 1421 (m), 1367 (s), 1221 (w), 1262 (w), 1142 (w), 1100 (w), 861 (w), 840 (s), 785 (m), 743 (m), 725 (s), 696 (m). Elemental Analysis: calculated C₁₉H₁₂AgN₃O₄ C 50.25; H 2.66; N 9.25; measured C 50.06, H 2.67, N 9.11.

$$Ag \longrightarrow O_2N$$

5

Ag(C₆H₄–*o*-NO₂) (5). To a mixture of AgF (269.3 mg, 2.12 mmol) and anhydrous CH₃CN (20 mL) in the glovebox, was added a solution of 5,5-dimethyl-2-(2-nitrophenyl)-[1,3,2]dioxaborinane (499 mg, 2.12 mmol) in CH₃CN (20 mL). The mixture was allowed to stir for 24 h while being protected from light with aluminum foil. During the course of the reaction, the AgF dissolved and the title compound precipitated as a bright yellow solid. The solid was collected by filtration and washed with ether (~50 mL), to yield 343 mg (1.49 mmol, 70% yield) of the title compound as a bight yellow powder. ¹H NMR (600 MHz, DMF-*d*₇): $\delta = 8.10$ (m, 2H), 7.60 (dt, *J* = 10.9, 1.7, 1H), 7.48 (m, 1H). ¹³C NMR (125 MHz, DMF-*d*₇): $\delta = 146.47$, 140.42, 132.87, 130.95, 124.06. IR (ATR, cm⁻¹): 1577 (w), 1550 (w), 1511 (m), 1490 (s), 1436 (w), 1414 (w), 1337 (m), 1320 (s), 1298 (m), 1239 (w), 1073 (m), 856 (m), 798 (m), 790 (m), 719 (s), 688 (m). Elemental Analysis: calculated C₆H₄AgNO₂ C 31.34; H 1.75; N 6.09; Measured C 31.25, H 1.59, N 5.98.

III. General Methods and Results for the Coupling Reactions

Catalytic Reactions with CuCl (Scheme 8). 2-nitrobenzoic acid (33 mg, 0.2 mmol) was combined with CuCl (2 mg, 0.02 mmol), phen (4 mg, 0.02 mmol), Cs₂CO₃ (65 mg, 0.2 mmol), Ag₂O (93 mg, 0.4 mmol if included), and 4Å molecular sieves (200 mg) in a 25 mL Schlenk tube fitted with a septum and a stir bar. The tube was evacuated and backfilled with N₂ three times before a solution of benzoxazole (36 mg, 0.3 mmol) in dry DMF (2.0 mL, 0.15 M) was added. The reaction mixture was stirred under N₂ at 110°C for 23 h. Upon completion, the mixture was cooled to room temperature and diluted with ethyl acetate (40 mL). The mixture was filtered through celite and the filtrate was added to a roundbottom flask containing hexamethylbenzene standard (5 mg, 0.03 mmol). The solvent was removed (by rotary evaporation to ~2mL, then by vacuum line), a 1,1,2,2-tetrachloroethane standard (3 μ L, 0.28 mmol) was added and the crude mixture dissolved in CDCl₃ for ¹H NMR analysis.



 Table S1. Yields of Catalytic Reactions with Benzoxazole (Scheme 8)

Reactions with (phen)Cu^{II}(O₂CC₆H₄-*o*-NO₂)₂ (1) (Scheme 9). In a nitrogen filled glovebox, (phen)Cu(O₂CC₆H₄-*o*-NO₂)₂ (115 mg, 0.20 mmol) was added to a 25 mL Schlenk tube containing Cs₂CO₃ (65 mg, 0.2 mmol), Ag₂O (93 mg, 0.4 mmol if included), and 4Å molecular sieves (200 mg). A solution of benzoxazole (36 mg, 0.3 mmol) in dry DMF (1.0 mL, 0.30 M) was added, followed by 1 mL of dry DMF to ensure all solids are in solution. The Schlenk tube was fitted with a septum and a stir bar and transferred to Schlenk line and 110°C oil bath. The reaction mixture was stirred under N₂ at 110°C for 23 h. Upon completion the mixture was cooled to room temperature and diluted with ethyl acetate (50 mL) and let sit from 30 minutes to overnight to allow any remaining copper(I) species to oxidize. The mixture was filtered through a silica gel pad (2 cm) and rinsed with ethyl acetate (150 mL). The solvent was removed under vacuum and the crude mixture dissolved in CDCl₃. After the addition of 1,1,2,2-tetrachloroethane standard (3 µL, 0.28 mmol) the solution was analyzed by ¹H NMR spectroscopy.



Table S2. Yields of Stoichiometric Reactions of 1 with Benzoxazole (Scheme 9).

Reactions with (phen)Cu(O₂CC₆H₄-*o***-NO₂) (2) (Scheme 10). In a nitrogen filled glovebox, (phen)Cu(O₂CC₆H₄-***o***-NO₂) 2 (82 mg, 0.20 mmol) was added to a 25 mL Schlenk tube containing Cs₂CO₃ (65 mg, 0.2 mmol), Ag₂O (93 mg, 0.4 mmol if included), and 4Å molecular sieves (200 mg). A solution of benzoxazole (36 mg, 0.3 mmol) in dry DMF (1.0 mL, 0.30 M) was added, followed by 1 mL of dry DMF to ensure all solids are in solution. The Schlenk tube was fitted with a septum and a stir bar and transferred to Schlenk line and 110°C oil bath. The reaction mixture was stirred under N₂ at 110°C for 23 h. Upon completion the mixture was cooled to room temperature and diluted with ethyl acetate (50 mL) and let sit from 30 minutes to overnight to allow any remaining copper(I) species to oxidize. The mixture was filtered through a silica gel pad (2 cm) and rinsed with ethyl acetate (150 mL). The solvent was removed under vacuum and the crude mixture dissolved in CDCl₃. After the addition of 1,1,2,2-tetrachloroethane standard (3 µL, 0.028 mmol) the solution was analyzed by ¹H NMR spectroscopy.**





Reactions with (phen)Cu(C₆H₄-*o***-NO₂) (3) (Scheme 10). In a nitrogen filled glovebox, (phen)Cu(C₆H₄-***o***-NO₂) 3** (73 mg, 0.2 mmol) was added to a 25 mL Schlenk tube containing Cs₂CO₃ (65 mg, 0.2 mmol), Ag₂O (93 mg, 0.4 mmol if included), and 4Å molecular sieves (200 mg). A solution of benzoxazole (36 mg, 0.3 mmol) in dry DMF (1.0 mL, 0.30 M) was added, followed by 1 mL of dry DMF to ensure all solids are in solution. The Schlenk tube was fitted with a septum and a stir bar and transferred to Schlenk line and 110°C oil bath. The reaction mixture was stirred under N₂ at 110°C for 23 h. Upon completion the mixture was cooled to room temperature and diluted with ethyl acetate (50 mL) and let sit from 30 minutes to overnight to allow any remaining copper(I) species to oxidize. The mixture was filtered through a silica gel pad (2 cm) and rinsed with ethyl acetate (150 mL). The solvent was removed under vacuum and the crude mixture dissolved in CDCl₃. After the addition of 1,1,2,2-tetrachloroethane standard (3 µL, 0.28 mmol) the solution was analyzed by ¹H NMR spectroscopy.



Table S4. Yields of Stoichiometric Reactions of 3 with Benzoxazole (Scheme 10).

Procedure and Yields for Reaction of (phen)Cu(C₆H₄-o-NO₂) (3) with Phenyliodide.

In a nitrogen filled glovebox, iodobenzene (23 uL, 41 mg, 0.20 mmol) was added to a GC vial containing a stir bar, (phen)Cu(C₆H₄-*o*-NO₂) **3** (36 mg, 0.097 mmol) and DMF (200 uL). The vial was tightly closed, sealed using electrical tape and stirred at room temperature for 40 minutes. After removal from the glovebox the vial was heated to 120 °C with a pre-heated aluminum block for 22 hours. Upon completion the bright-red mixture was cooled to room temperature and diluted with ethyl acetate (30 mL), sonicated, filtered through a silica gel pad (2 cm) and rinsed with ethyl acetate (170 mL). The solvent was removed under vacuum and the crude mixture dissolved in CDCl₃. After the addition of 1,1,2,2-tetrachloroethane standard (10 μ L, 0.094 mmol) the solution was analyzed by ¹H NMR spectroscopy. The reaction yielded 2-nitrobiphenyl (50%) and 2,2'-dinitrobiphenyl (11%).

Reactions with (phen)Ag(O₂CC₆H₄-*o***-NO₂) (4) (Scheme 11). On the benchtop, Cs_2CO_3 (65 mg, 0.2 mmol), (phen)Ag(2-NO₂C₆H₄) 4 (91 mg, 0.2 mmol), Ag₂O (70 mg, 0.3 mmol if included), CuCl (2 mmg, 0.02 mmol, if included) and 4Å molecular sieves (200 mg) were combined in a 25 mL Schlenk tube fitted with a septum and a stir bar. The Schlenk tube was connected to a Schlenk line and evacuated/backfilled with N₂ three times. A solution of benzoxazole (36 mg, 0.3 mmol) in dry DMF (1.0 mL, 0.30 M) was added, followed by 1.0 mL of DMF and the reaction mixture was stirred under N₂ at 110°C for 23 h. Upon completion, the mixture was cooled to room temperature and diluted with ethyl acetate (40 mL). The mixture was filtered through celite and to the filtrate was added hexamethylbenzene standard (5 mg, 0.03 mmol) before the filtrate was washed with water (1 x 100 mL), the aqueous layer was extracted with ethyl acetate (2 x 100 mL) and the combined organics were washed with brine, dried over Na₂SO₄. A small portion of the solution (1 mL) was removed for analysis by GC, and for the remainder of the mixture, the solvent was removed (by rotary evaporation to ~2mL, then by vacuum line) and the crude mixture dissolved in CDCl₃ for ¹H NMR analysis.**

 Table S5. Yields of Stoichiometric Reactions of 4 with Benzoxazole (Scheme 11)



Reactions with Ag(C₆H₄-*o***-NO₂) (5) (Scheme 11). In a nitrogen filled glovebox, Ag(C₆H₄-***o***-NO₂) 5 (46 mg, 0.20 mmol) was added to a 25 mL Schlenk tube containing Cs₂CO₃ (65 mg, 0.2 mmol), Ag₂O (70 mg, 0.3 mmol if included), CuCl (2 mg, 0.02 mmol, if included) and 4Å molecular sieves (200 mg). A solution of benzoxazole (36 mg, 0.3 mmol) in dry DMF (1.0 mL, 0.30 M) was added, followed by 1 mL of dry DMF to ensure all solids were in solution. The Schlenk tube was fitted with a septum and a stir bar and transferred to Schlenk line and 110°C oil bath. The reaction mixture was stirred under N₂ at 110°C for 23 h. Upon completion, the mixture was filtered through celite and to the filtrate was added hexamethylbenzene standard (5 mg, 0.03 mmol) before the filtrate was washed with water (1 x 100 mL), the aqueous layer was extracted with ethyl acetate (2 x 100 mL) and the combined organics were washed with brine, dried over Na₂SO₄. A small portion of the solution (1 mL) was removed for analysis by GC, and for the remainder of the mixture, the solvent was removed (by rotary evaporation to ~2mL, then by vacuum line) and the crude mixture dissolved in CDCl₃ for ¹H NMR analysis.**

Table S6. Yields of Stoichiometric Reactions of 5 with Benzoxazole (Scheme 11).



IV. X-Ray Crystallographic Data for Complex 1

Single crystals of **1** were obtained from the following synthesis:

To a stirred solution of copper(II) triflate (908 mg, 2.51 mmol) in ethanol (100 mL) was added a solution of 2-nitrobenzoic acid (419 mg, 2.51 mmol) and sodium hydroxide (99.6 mg, 2.49 mmol) in water (10 mL). After about 2 minutes, the solution was filtered and a solution of phenanthroline (452 mg, 2.51 mmol) in ethanol (20 mL) was added to the filtrate. The reaction mixture was stirred for 30 minutes and then cooled on ice for 2 hours. The precipitate was filtered off and a few milliliters of the filtrate were stored in a freezer. After several days, crystals suitable for x-ray diffraction were obtained.

| | 1 | | |
|-----------------------------------|---|--|--|
| Empirical formula | C ₂₆ H ₁₆ CuN ₄ O ₈ | | |
| Emp. formula weight | 575.97 g/mol | | |
| Temperature | 00(2) K | | |
| Wavelength | 0.71073 Å | | |
| Crystal size | 0.076 x 0.107 x 0.376 mm | | |
| Crystal system | monoclinic | | |
| Space group | $P 2_1/c$ (No. 14) | | |
| Unit cell dimensions | $a = 11.1134(5) \text{ Å} \ \alpha = 90^{\circ}$ | | |
| | $b = 21.1702(9) \text{ Å} \beta = 101.1894(13)^{\circ}$ | | |
| | $c = 9.8578(4) \text{ Å} \gamma = 90^{\circ}$ | | |
| Volume | 2275.19(17) Å ³ | | |
| Z | 4 | | |
| Density (calculated) | 1.681 g/cm^3 | | |
| Absorption coefficient | 1.025 mm ⁻¹ | | |
| F(000) | 1172 | | |
| Theta range for data used | in 3.18 to 30.13° | | |
| Index ranges | $-15 \le h \le 15, -29 \le k \le 29, -13 \le l \le 13$ | | |
| Reflections | 52150 | | |
| Independent reflections | 6694 [R(int) = 0.0550] | | |
| Coverage of independent | 99.8% | | |
| Absorption correction | multi-scan | | |
| Max. and min. transmissi | on 0.926 and 0.699 | | |
| Refinement method | Full-matrix least-squares on F ² | | |
| Refinement program | SHELXL-2014 (Sheldrick, 2014) | | |
| Data / restraints / | 6694 / 0 / 352 | | |
| Goodness-of-fit on F ² | 1.053 | | |
| Final R indices | 5123 data; I>2 σ (I) R1 = 0.0370, wR2 = 0.0780 | | |
| | all data $R1 = 0.0616$, $wR2 = 0.0858$ | | |
| Largest diff. peak and ho | le 0.517 and -0.478 e^{-1}/A^{3} | | |

 Table S7. Crystallographic Data for Complex 1

Interatomic Distances (Å) for Complex 1

| Cu1-O1 | 1.9507(12) | Cu1-O3 | 1.9655(13) | | | | |
|-------------------------------|------------|------------|------------|--|--|--|--|
| Cu1-N2 | 2.0032(15) | Cu1-N1 | 2.0138(15) | | | | |
| O1-C13 | 1.294(2) | O2-C13 | 1.222(2) | | | | |
| O3-C20 | 1.280(2) | O4-C20 | 1.226(2) | | | | |
| O5-N3 | 1.218(2) | O6-N3 | 1.225(2) | | | | |
| O7-N4 | 1.234(2) | O8-N4 | 1.223(2) | | | | |
| N1-C3 | 1.326(2) | N1-C1 | 1.362(2) | | | | |
| N2-C12 | 1.328(2) | N2-C2 | 1.356(2) | | | | |
| N3-C19 | 1.467(3) | N4-C26 | 1.464(2) | | | | |
| C1-C6 | 1.401(2) | C1-C2 | 1.429(2) | | | | |
| C2-C9 | 1.403(2) | C3-C4 | 1.400(3) | | | | |
| C4-C5 | 1.372(3) | C5-C6 | 1.411(3) | | | | |
| C6-C7 | 1.434(3) | C7-C8 | 1.358(3) | | | | |
| C8-C9 | 1.435(3) | C9-C10 | 1.407(3) | | | | |
| C10-C11 | 1.376(3) | C11-C12 | 1.405(3) | | | | |
| C13-C14 | 1.519(2) | C14-C19 | 1.389(3) | | | | |
| C14-C15 | 1.390(3) | C15-C16 | 1.393(3) | | | | |
| C16-C17 | 1.377(3) | C17-C18 | 1.373(3) | | | | |
| C18-C19 | 1.389(3) | C20-C21 | 1.530(3) | | | | |
| C21-C26 | 1.390(3) | C21-C22 | 1.393(3) | | | | |
| C22-C23 | 1.387(3) | C23-C24 | 1.385(3) | | | | |
| C24-C25 | 1.384(3) | C25-C26 | 1.382(3) | | | | |
| Bond Angles (°) for Complex 1 | | | | | | | |
| 01-Cu1-O3 | 92.18(5) | O1-Cu1-N2 | 175.97(6) | | | | |
| O3-Cu1-N2 | 91.66(6) | O1-Cu1-N1 | 94.21(6) | | | | |
| O3-Cu1-N1 | 173.49(6) | N2-Cu1-N1 | 81.98(6) | | | | |
| C13-O1-Cu1 | 121.99(11) | C20-O3-Cu1 | 120.09(12) | | | | |
| C3-N1-C1 | 117.94(16) | C3-N1-Cu1 | 129.67(13) | | | | |
| C1-N1-Cu1 | 112.34(12) | C12-N2-C2 | 118.41(16) | | | | |
| C12-N2-Cu1 | 128.71(13) | C2-N2-Cu1 | 112.88(12) | | | | |
| O5-N3-O6 | 122.87(19) | O5-N3-C19 | 118.82(16) | | | | |
| O6-N3-C19 | 118.27(18) | 08-N4-07 | 124.62(18) | | | | |
| O8-N4-C26 | 117.84(17) | O7-N4-C26 | 117.43(16) | | | | |
| N1-C1-C6 | 123.71(16) | N1-C1-C2 | 116.25(15) | | | | |
| C6-C1-C2 | 120.02(16) | N2-C2-C9 | 123.36(16) | | | | |
| N2-C2-C1 | 116.41(15) | C9-C2-C1 | 120.21(16) | | | | |

| N1-C3-C4 | 122.30(17) | C5-C4-C3 | 120.01(17) |
|-------------|------------|-------------|------------|
| C4-C5-C6 | 119.24(17) | C1-C6-C5 | 116.79(17) |
| C1-C6-C7 | 118.69(16) | C5-C6-C7 | 124.46(17) |
| C8-C7-C6 | 121.57(17) | C7-C8-C9 | 120.44(17) |
| C2-C9-C10 | 117.15(17) | C2-C9-C8 | 119.03(17) |
| C10-C9-C8 | 123.80(17) | C11-C10-C9 | 119.28(17) |
| C10-C11-C12 | 119.66(17) | N2-C12-C11 | 122.14(17) |
| O2-C13-O1 | 127.00(17) | O2-C13-C14 | 119.37(16) |
| O1-C13-C14 | 113.41(15) | C19-C14-C15 | 116.72(17) |
| C19-C14-C13 | 126.25(17) | C15-C14-C13 | 116.90(16) |
| C14-C15-C16 | 121.3(2) | C17-C16-C15 | 120.1(2) |
| C18-C17-C16 | 120.10(19) | C17-C18-C19 | 119.0(2) |
| C14-C19-C18 | 122.66(19) | C14-C19-N3 | 119.92(17) |
| C18-C19-N3 | 117.32(18) | O4-C20-O3 | 126.87(17) |
| O4-C20-C21 | 117.79(16) | O3-C20-C21 | 115.22(16) |
| C26-C21-C22 | 115.83(17) | C26-C21-C20 | 125.66(16) |
| C22-C21-C20 | 118.36(16) | C23-C22-C21 | 121.70(19) |
| C24-C23-C22 | 120.35(19) | C25-C24-C23 | 119.66(19) |
| C26-C25-C24 | 118.49(19) | C25-C26-C21 | 123.92(18) |
| C25-C26-N4 | 116.15(17) | C21-C26-N4 | 119.82(17) |

(1) Gottlieb, H. E.; Kotlyar, V.; Abraham, N. J. Org. Chem. 1997, 62, 7512-7515.

⁽²⁾ Lemmen, T. H.; Goeden, G. V.; Huffman, J. C.; Geerts, R. L.; Caulton, K. G. *Inorg. Chem.* **1990**, *29*, 3680-2685.

⁽³⁾ Schnürch, M.; Holzweber, M.; Mihovilovic, M. D.; Stanetty, P. Green Chem. 2007, 9, 139-145.

⁽⁴⁾ Fang, H.; Kaur, G.; Yan, J.; Wang, B. Tetrahedron Lett. 2005, 46, 1671-1674.

¹H and ¹³C NMR Spectra of Copper and Silver Complexes V.







¹H NMR spectrum of (phen)Cu(C₆H₄-o-NO₂) (3) in DMF- d_7 at 600 MHz.





¹H NMR spectrum of (phen)Ag($O_2CC_6H_4$ -*o*-NO₂) (4) in DMF- d_7 at 600 MHz.





¹H NMR spectrum of $Ag(C_6H_4-o-NO_2)$ (5) in DMF- d_7 at 600 MHz.

