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Synthesis, Characterization, X-Ray Crystallography Analysis, and Catalytic Activity of *bis*(2-pyridylmethyl)amine Copper Complexes Containing Coupled Pendent Olefinic Arms in Atom Transfer Radical Addition (ATRA) Reactions

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ABSTRACT

The synthesis, characterization, and catalytic activity of *bis*(2-pyridylmethyl)amine (BPMA) copper complexes incorporating olefinic pendent arms are reported. Four copper(I) and four copper(II) complexes were synthesised employing four different counterions [chloride (Cl⁻), perchlorate (ClO₄-), trifluoromethanesulfonate (CF₃SO₃-), and tetraphenylborate (BPh₄-)]. The counterions used ranged from coordinating (Cl⁻) to non-coordinating (BPh₄-), producing different coordination modes in respective complexes. Solid state results obtained for the copper(I) complex incorporating the non-coordinating (BPh₄-) counterion displayed an associative bond between the metal center and the C=C group in the olefinic arm of a neighbouring complex. This interaction led to augmentation of the C=C bond due to back-bonding from the metal center. Five solid state structures were obtained for the copper(II) complexes with two also displaying

- 20 metal center. Five solid state structures were obtained for the copper(II) complexes with two also displaying intermolecular associative bonding between olefinic pendent arms and the metal center. X-ray crystallography studies showed that the olefinic arm motifs incorporated were hemilabile. Solution studies indicated that the copper complexes had some inherent reducing power and could be potential candidates for use as catalysts in atom transfer radical processes. However, only moderate conversions and yields were obtained in atom transfer radical addition (ATRA) reaction studies performed utilizing the copper complexes due to the presence of a competing reaction.
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KEYWORDS

Metal-Organic Frameworks, Radicals, Carbon–Carbon Activation, X-Ray Crystallography, and Electrochemistry

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1. INTRODUCTION

Copper(I)–olefin interactions play an important biological role and have been investigated as the resting state of several copper-catalyzed reactions.^[1,2] Complexes employing these interactions have been utilized as active species in homogeneous catalysis and serve as important intermediates in a variety of chemical processes such as; aziridination, cyclopropanation, and conjugate addition to α , β -unsaturated ketones.^[3-6]

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More recently, supramolecular motifs incorporating these interactions have become a topic of interest due to their luminescent properties with respect to quenching of guest-host exchanges.^[7] Many studies investigating analogous copper-olefin systems utilize the biological structure model reported for ethylene coordination,^[8] while others employ multi-dentate electron-rich nitrogen donor ligands.^[9-11] The first stable copper(I)-olefin complex reported by Thompson *et al.* utilized the tridentate ligand motif hydro-*tris*(3,5-dimethyl pyrazolyl)borate [HB (3,5-Me₂PZ)₃],^[12] while more recent studies employ neutral nitrogen donor based heterocyclic ligands such as; *bis*(pyrazolyl)methanes,^[13] dipyridylamines,^[14] phenanthroline,^[15] *bis*(2pyridyl)amine^[16] and bipyridine^[17] (Scheme 1). The tridentate *N*-(3-indolyethyl)-*N*,*N*'-bis(6-methyl-2-pyridyl methyl)amine (Me₂IEP) and macrocyclic N-[2-(1-naphthyl)ethyl]-1-aza-4,8-dithiacyclo-decane ligands have also been used to stabilize copper- η^2 -indole and copper- η^2 -naphthyl complexes.^[18] In addition, Hoffman *et al.* successfully synthesized a stable copper–olefin complex (up to 180 °C) utilizing iminophosphanamide ligand derivatives as chelating stabilizers to affix olefin motifs incorporated in those structures.^[19]



Scheme 1. Some common multi-dentate nitrogen donor based ligands used to study Copper-Olefin coordinations.[22]

The catalytic function of copper in the aforementioned examples can be attributed to its capacity to engage olefins in both σ - and π -interactions; and ability to rapidly exchange these and other ligands present in its coordination sphere especially in aqueous conditions.^[20] Furthermore, the Dewar-Chatt-Duncason 55 model describing olefins as σ -donors and concomitant π -acceptors has been used to explain most features observed in olefin bonding.^[21] According to the model, π -bond interactions consists of two components: (i) the (Cu¹ \leftarrow L), donor-acceptor component due to overlap of the occupied olefin π *p*-orbital and the unoccupied $(4s^0)$ orbital of the Cu¹ atom, which is the dominant species in the bond; and (ii) the (Cu¹ \rightarrow L) *p*-dative component, which is formed upon electron-density withdrawal from the $(3d^{10})$ Cu¹ orbitals to the unoccupied anti-bonding orbital of the C=C group.^[21] Studies show that different ancillary ligands bound to copper affect the relative energy of the σ - and π - type metal orbitals, subsequently exerting a certain influence on the metal-olefin bond present.^[22] Of interest to this study are chemical reactions incorporating copper complexes with olefin substrates such as; cyclopropanation,^[23] aziridination,^[24] epoxidation,^[25] atom transfer radical addition,^[26] and atom transfer radical cyclization.^[27] Given the importance of these studies, we hereby report 65 on the synthesis, characterization, electrochemical study, and catalytic activity of copper bis(2pyridylmethyl)amine (BPMA) complexes containing coupled pendent olefinic arms for use in atom transfer radical addition (ATRA) reactions.

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2. MATERIALS AND METHODS 70

with care and in small quantities.

2.1.1. General Methods and Procedures: All reagents were purchased from commercial sources and used as received. The ligand precursor bis(2-pyridylmethyl)amine (BPMA) was synthesized according to literature procedures,^[28] and B-BPMA ligand was synthesized according to modified literature procedures.^[29,30] All manipulations involving copper(I) complexes were performed under argon in a drybox (<1.0 ppm 0_2 and <0.5 ppm H₂O) or using standard Schlenk line techniques. Solvents (acetonitrile, diethyl ether, and pentane) were degassed and deoxygenated using an Innovative Technology solvent purifier. Methanol solvent was vacuum distilled and deoxygenated by bubbling in argon gas for thirty minutes prior to use. Copper(II) complexes were all synthesized under ambient conditions using solvents as purchased. Important Safety <u>Note</u>: Perchlorate salts such as $[Cu^{I}(ClO_{4})]$ used in this study are potentially explosive and should be handled

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2.1.2. Instrumentation and Equipment: ¹H and ¹³C NMR spectra were obtained using a Bruker Avance 400 MHz spectrometer with chemical shifts given in (ppm) relative to residual solvent peaks [CDCl₃ δ 7.26 ppm, CD₃CN δ 1.96 ppm, and (CD₃)₂CO δ 2.09 ppm). MestReNova and iNMR software were used to generate 85 images of NMR spectra. A Nicolet Smart Orbit 380 FT-IR spectrometer (Thermo Electron Corporation) was used to collect IR spectra utilizing 16 scans from 500 nm to 4000 nm at a resolution of 2.00 cm⁻¹. A DuPont Instruments Sorvall RC-5B Refrigerated Superspeed Centrifuge was used to separate ultra-fine particles of sodium chloride after salt metathesis reactions. Cyclic voltammetry experiments were conducted on a NuVant EZstat-HV potentiostat using a standard three-electrode system: Pt-disc working electrode, Ag/AgNO₃ 90 reference electrode, and Pt-wire auxiliary electrode. Complex solutions (2.0 mM) were prepared in dry acetonitrile containing 0.1 M tetrabutylammonium hexafluorophosphate (NBu₄PF₆) as supporting electrolyte with measurements carried out under N₂ atmosphere at a scanning rate (v) of 0.05 V s⁻¹. Potentials were measured relative to a ferrocenium/ferrocene couple ($E^{\circ}_{Fc+/Fc} = 0.07 \text{ V vs } Ag/AgNO_3 \text{ in } CH_3CN)^{[31]}$ which was used as an internal standard. This allowed for conversion of potentials to the aqueous saturated calomel 95 electrode (SCE) scale that used to reference all potentials. UV-Vis spectra were obtained using a Varian Cary 100 Bio-Spectrometer in 1.0 cm path-length quartz cuvettes. High resolution electrospray ionization spectra were acquired on an Agilent Technologies 650 Accurate-Mass time of flight mass spectrometer operating in positive (+) mode. Spectra were acquired over the mass range of 50 to 3000 m/z accumulating data at 2 Hz. MassHunter Workstation operating software equipped with Qualitative Analysis software was used to

- 100 interpret all acquired data. Samples were diluted in spectroscopic grade acetonitrile or methanol and presented to the instrument through direct injection. Elemental analysis results for carbon, hydrogen, and nitrogen were obtained from Midwest Microlabs, LLC.
- **2.1.3. General Procedure for Atom Transfer Radical Addition Reactions:** (For reactions utilizing AIBN); 105 Into a glass vial, carbon tetrachloride (0.677 g, 4.40 mmol), AIBN (0.033 g, 0.20 mmol), p-dimethoxybenzene

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(internal standard), and alkene of choice (4.00 mmol) were added. Acetonitrile was introduced to the mixture until a total volume of 2018 µL was obtained. (For reactions utilizing ascorbic acid); Into a glass vial, carbon tetrachloride (0.677 g, 4.40 mmol), 0.25 M ascorbic acid (0.80 mL, 0.20 mmol), internal standard p-110 dimethoxybenzene, and alkene of choice (4.00 mmol) were added. Methanol was introduced to the mixture until a total volume of 2018 µL was obtained. In each case, the total solution volume was divided into five aliquots (400 µL) and placed in separate NMR tubes. A zero-time sample was obtained from residual solution left in each glass vial. Stock catalyst solutions (0.05 M and 0.01 M) were prepared by dissolving a catalyst of choice in either acetonitrile or methanol (depending on the ATRA reaction investigated). Catalyst solutions were added to corresponding NMR tubes as follows: blank tube (0 µL), [100]:[1] tube (160 µL of 0.05M), 115 [500]:[1] tube (160 µL of 0.01M), and [1000]:[1] tube (80 µL of 0.01M). Total volume in each tube was adjusted by adding acetonitrile (AIBN reactions) or methanol (ascorbic acid reactions) to achieve a total of 560 μ L as follows: blank tube (160 μ L), [100]:[1] tube (160 μ L), [500]:[1] tube (0 μ L), and [1000]:[1] tube (80 µL). NMR tubes with AIBN were sealed under argon with standard polyethylene caps and wrapped in 120 Teflon tape to ensure a tight seal. NMR tubes with ascorbic acid were not sealed under argon as ascorbic acid

is activated by oxygen present in the tubes. Reaction tubes were placed in a thermostatted oil bath set at 60 °C for 24 hours. Alkene conversions and monoadducts yields were determined *via* ¹H NMR spectroscopy.

2.1.4. Crystallography Structure Determination: X-ray intensity data were collected at 150 K using graphite-monochromated Mo-K radiation (0.71073 Å) with a Bruker Smart Apex II CCD diffractometer. Data reduction included absorption corrections by the multi-scan method using SADABS.^[32] Structures were solved by direct methods and refined by full matrix least-squares using SHELXTL 6.1 bundled software package.^[33] Hydrogen atoms were positioned geometrically (aromatic C-H 0.93, methylene C-H 0.97, and methyl C-H 0.96) and treated as riding atoms during subsequent refinements, with U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(methyl C). Methyl groups are allowed to rotate about their local 3-fold axes but not to tip to best fit the experimental electron density. ORTEP-3 for windows,^[34] Crystal Maker 7.2, an Olex2 version 1.2 were used to generate molecular graphics. For detailed crystallographic data tables, please refer to supporting information.

2.2.1. Synthesis of (but-3-en-1-yl)-bis(2-pyridylmethyl)amine [B-BPMA]: Precursor BPMA (8.064 g, 40.50 mmol) was dissolved in 15 mL acetonitrile followed by slow addition of triethylamine (4.098 g, 40.50 mmol) and 4-bromobutene (5.468 g 40.50 mmol). The reaction was allowed to mix for four days to ensure complete deprotonation and coupling. Generation of a triethylamine hydrogen bromide salt [Et₃NH]+[Br]⁻ was observed as white crystals in a brown colored solution. The solution was filtered and desired product extracted from the filtrate using a hexane/water solvent combination. The hexane layers were isolated and solvent was removed using a rotary evaporator. The final product was dried under vacuum for two hours to produce the ligand as a yellow colored oil (8.516 g, 83%). ¹H NMR (CDCl₃, 400 MHz): δ 2.31 (dd, *J* = 8.0 and 21.6 Hz, 2H), 2.64 (t, *J* = 7.2 Hz, 2H), 3.83 (s, 4H), 4.97 (d, *J* = 10.4 Hz, 1H), 5.01 (d, *J* = 18.8 Hz, 1H), 5.75 (m, *J* = 10.4 Hz, 1H), 7.13 (t, *J* = 6.4 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.64 (t, *J* = 7.6 Hz, 2H), 8.51 (d, *J* = 4.4 Hz, 2H). ¹³C

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NMR (CDCl₃, 400 MHz): δ 159.75, 149.01, 136.38, 135.38, 122.80, 121.88, 117.93, 77.13, 59.90, 57.32. FT-IR (liquid): *v* (cm⁻¹) = 3066 (w), 2922 (w), 2816 (w), 2158 (s), 1639 (s), 1588 (s), 1361 (s), 994 (w), 756 (s).

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2.2.2. Synthesis of [Cu¹(B-BPMA)(Cl)], 1: In a drybox, B-BPMA (1.000 g, 3.950 mmol) was dissolved in 10 mL acetonitrile in a 50 mL Schlenk flask. CuCl (0.391 g, 3.95 mmol) was added to give a yellowish-red colored solution. The reaction was allowed to mix for 6 hours then 15 mL of pentane was added to generate a bright yellow precipitate. Solvent was removed from the flask using a Schlenk line. Precipitate obtained was washed twice with 20 mL aliquots of pentane and vigorous stirring for thirty minutes. Solvent was then removed and precipitate dried under vacuum for two hours to yield a bright yellow solid (1.308 g, 94%). ¹H NMR (CD₃CN, 400 MHz): δ 2.29 (dd, *J* = 6.4 and 20.8 Hz, 2H), 2.71 (t, *J* = 6.8 Hz, 2H), 3.89 (s, 4H), 4.82 (d, *J* = 4.8 Hz, 1H), 4.86 (d, *J* = 11.6 Hz, 1H), 5.55 (m, *J* = 5.6 Hz, 1H), 7.34 (d, *J* = 4.8 Hz, 2H), 7.39 (t, *J* = 7.2 Hz, 2H), 7.78 (t, *J* = 7.2 Hz, 2H), 8.61 (d, *J* = 4.8 Hz, 2H). ¹H NMR (CD₃OD, 400 MHz): δ 2.25 (dd, *J* = 6.0 and 18.4 Hz, 2H), 3.03 (t, *J* = 6.4 Hz, 2H), 4.15 (s, 4H), 4.63 (d, *J* = 8.4 Hz, 1H), 4.68 (d, *J* = 15.2 Hz, 1H), 5.34 (m, *J* = 8.8 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.47 (t, *J* = 8.0 Hz, 2H), 7.89 (t, *J* = 7.6 Hz, 2H), 8.69 (d, *J* = 5.2 Hz, 2H). FT-IR (solid): v (cm⁻¹) = 3271 (w), 3083 (w), 2923 (w), 2818 (w), 2325 (s), 2303 (s), 1602 (s), 1477 (s), 1437 (s), 1287 (s). TOF-ESI-MS: (*m*/*z*) [M - (Cl)]+ calculated for C₁₆H₁₉N₃Cu 316.0875, found 316.0897 (7 ppm).

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2.2.3. Synthesis of [Cuⁱ(B-BPMA)][ClO₄], 2: In a drybox, B-BPMA ligand (1.000 g, 3.950 mmol) was dissolved in 10 mL acetonitrile in a 50 mL Schlenk flask. Cu(ClO₄) (1.292 g, 3.950 mmol) was added to the flask to give a yellow colored solution. The reaction was allowed to mix for six hours then 15 mL of pentane was slowly added to the solution generating a yellow precipitate. Solvent was removed from the Schlenk flask utilizing a vacuum line. The precipitate obtained was washed twice by transferring two 20 mL aliquots of pentane into the flask and stirring vigorously for thirty minutes. Solvent was then removed and final precipitate dried under vacuum for two hours to yield a yellow colored solid (2.109 g, 92%). ¹H NMR (CD₃CN, 400 MHz): δ 2.45 (dd, *J* = 8.8 and 22.4 Hz, 2H), 2.77 (t, *J* = 8.0 Hz, 2H), 3.87 (s, 4H), 4.92 (d, *J* = 10.0 Hz, 1H), 4.98 (d, *J* = 16.8 Hz, 1H), 5.70 (m, *J* = 10.4 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.38 (t, *J* = 6.0 Hz, 2H), 7.80 (t, *J* = 7.6 Hz, 2H), 8.63 (d, *J* = 4.8 Hz, 2H). FT-IR (solid): v (cm⁻¹) = 3271 (w), 3083 (w), 2923 (w), 2818 (w), 2325 (s), 2303 (s), 1602 (s). TOF-ESI-MS: (*m*/*z*) [M – (ClO₄)]⁺ calculated for C₁₆H₁₉N₃Cu 316.0875, found 316.1344 (148 ppm).

- 2.2.4. Synthesis of [Cu¹(B-BPMA)][CF₃SO₃], 3: In a drybox, B-BPMA ligand (1.000 g, 3.950 mmol) was dissolved in 10 mL acetonitrile in a 50 mL Schlenk flask. Cu(CF₃SO₃) (2.044 g, 3.950 mmol) was added to the flask to give a yellowish-brown colored solution. The reaction was allowed to mix for six hours then 15 mL of pentane was slowly added to the solution to generate a yellowish-brown precipitate. Solvent was removed from the Schlenk flask utilizing a vacuum line. The precipitate obtained was washed twice by transferring two 20 mL aliquots of pentane into the flask and stirring vigorously for thirty minutes. Solvent was then removed and precipitate obtained dried under vacuum for two hours to vield a vellowish brown colored.
- and precipitate obtained dried under vacuum for two hours to yield a yellowish-brown solid (2.740 g, 90%).

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¹H NMR (CD₃CN, 400 MHz): δ 2.26 (dd, *J* = 6.8 and 20.4 Hz, 2H), 2.89 (t, *J* = 6.8 Hz, 2H), 3.96 (s, 4H), 4.80 (d, *J* = 9.6 Hz, 1H), 4.83 (d, *J* = 16.4 Hz, 1H), 5.55 (m, *J* = 9.6 Hz, 1H), 7.38 (d, *J* = 7.6 Hz, 2H), 7.43 (t, *J* = 6.0 Hz, 2H), 7.86 (t, *J* = 7.6 Hz, 2H), 8.61 (d, *J* = 5.6 Hz, 2H). ¹H NMR ((CD₃)₂CO, 400 MHz): δ 2.30 (dd, *J* = 5.6 and 17.6 Hz, 2H), 3.18 (t, *J* = 5.6 Hz, 2H), 4.17 (d, *J* = 16.8 Hz, 2H), 4.47 (d, *J* = 16.4 Hz, 2H), 4.61 (d, *J* = 8.4 Hz, 1H), 4.71 (d, *J* = 15.2 Hz, 1H), 5.38 (m, *J* = 6.4 Hz, 1H), 7.51 (t, *J* = 6.4 Hz, 2H), 7.53 (d, *J* = 7.6 Hz, 2H), 7.95 (t, *J* = 7.6 Hz, 2H),

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- $= 15.2 \text{ Hz}, 11\text{ H}, 5.38 \text{ (m, } J = 6.4 \text{ Hz}, 11\text{ H}, 7.51 \text{ (t, } J = 6.4 \text{ Hz}, 21\text{ H}), 7.53 \text{ (d, } J = 7.6 \text{ Hz}, 21\text{ H}), 7.95 \text{ (t, } J = 7.6 \text{ Hz}, 21\text{ H}), 8.81 \text{ (d, } J = 4.8 \text{ Hz}, 21\text{ H}). FT-IR (solid): v (cm⁻¹) = 3579 (w), 3070 (w), 2924 (w), 2825 (w), 2325 (s), 2305 (s), 1605 (s), 1483 (s), 1442 (s), 1256 (s), 763 (s), 634 (s), 572 (s), 516 (s), 503 (s). TOF-ESI-MS: (m/z) [M (CF_3SO_3)]^+ calculated for C_{16}H_{19}N_3Cu 316.0875, found 316.0916 (12 ppm).$
- 2.2.5. Synthesis of [Cuⁱ(B-BPMA)][BPh₄], 4: In a drybox, complex 1 (1.000 g, 3.950 mmol) was dissolved in 10 mL of methanol in a 50 mL Schlenk flask. NaBPh₄ (1.352 g, 3.950 mmol) was added to the flask generating a yellowish-cream colored precipitate in a light yellow solution. The reaction was allowed to mix for six hours then filtered to isolate the precipitate. The precipitate was washed twice with 20 mL aliquots of methanol and dried under vacuum for two hours to yield a cream colored solid (2.281 g, 97%). ¹H NMR (CD₃CN, 400 MHz):
 δ 2.28 (dd, *J* = 7.2 and 22.0 Hz, 2H), 2.87 (t, *J* = 7.2 Hz, 2H), 3.95 (s, 4H), 4.81 (d, *J* = 10.4 Hz, 1H), 4.84 (d, *J* =
- 16.4 Hz, 1H), 5.55 (m, J = 6.8 Hz, 1H), 6.84 (t, J = 7.2 Hz, 1H), 6.99 (t, J = 7.6 Hz, 1H), 7.27 (m, J = 2.8 Hz, 1H), 7.37 (d, J = 7.6 Hz, 2H), 7.41 (t, J = 4.9 Hz, 2H), 7.84 (t, J = 7.6 Hz, 2H), 8.61 (d, J = 5.2 Hz, 2H). ¹H NMR ((CD₃)₂CO, 400 MHz): δ 2.28 (dd, J = 6.0 and 18.4 Hz, 2H), 3.12 (t, J = 5.6 Hz, 2H), 4.25 (s, 4H), 4.57 (d, J = 9.2 Hz, 1H), 4.69 (d, J = 14.8 Hz, 1H), 5.36 (m, J = 6.4 Hz, 1H), 6.76 (t, J = 7.2 Hz, 1H), 6.91 (t, J = 7.6 Hz, 1H), 7.31 (m, J = 4.0 Hz, 1H), 7.48 (d, J = 8.0 Hz, 2H), 7.92 (t, J = 7.6 Hz, 2H), 8.74 (d, J = 4.4 Hz, 2H). FT-IR (solid): v (cm⁻¹) = 3055 (s), 3025 (s), 3000 (s), 2885 (s), 2360 (s), 2320 (w), 1607 (s), 1579 (s), 1480 (s), 751 (s), 706 (s). Single crystals suitable for X-ray crystallography analysis were obtained by slow diffusion of diethyl ether

into a complex solution made in acetonitrile at room temperature.

- 2.2.6. Synthesis of [Cu^u(B-BPMA)(Cl₂)], 5: B-BPMA ligand (4.000 g, 15.80 mmol) was dissolved in 20 mL acetonitrile in a 50 mL round bottom flask. CuCl₂ (2.124 g, 15.80 mmol) was added to the flask producing a green colored solution. The reaction was allowed to mix for six hours then 20 mL of pentane was slowly added to the solution and vigorously mixed to generate a bright green precipitate. The mixture was filtered and precipitate washed twice with two 20 mL aliquots of pentane. Solvent was removed from the precipitate by drying under vacuum for two hours to yield a green solid (5.818 g, 95%). TOF-ESI-MS: (*m*/*z*) [M Cl]⁺ calculated for C₁₆H₁₉N₃Cl₁Cu 351.0564, found 351.0602 (10 ppm). Elemental Analysis for C₁₆H₁₉N₃Cu₁Cl₂ (387.7942 g/mol): calculated C 49.55, H 4.94, N 10.84; found C 49.66, H 4.93, N 10.82. Single crystals suitable for X-ray analysis were obtained by slow diffusion of diethyl ether into a complex solution made in acetonitrile.
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2.2.7. Synthesis of [Cu^{II}(B-BPMA)(Cl)(ClO₄)], 6: Complex 5 (1.000 g, 2.580 mmol) was dissolved in 10 mL acetonitrile in a 50 mL round bottom flask. NaClO₄ (0.316 g, 2.58 mmol) was added to the flask to give a green

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colored solution. The reaction was allowed to mix for six hours generating a white sodium chloride precipitate in a green colored solution. The mixture was filtered and solute centrifuged to separate any fine
particles of sodium chloride from solution. Solvent was removed using a rotary evaporator producing a green solid. The precipitate obtained was washed twice by transferring 20 mL of pentane into the flask and stirring vigorously for thirty minutes. The solvent was then removed by filtration and final precipitate dried under vacuum for two hours to yield a green colored solid (1.072 g, 92%). TOF-ESI-MS: (*m/z*) [M – (ClO₄)]⁺ calculated for C₁₆H₁₉N₃Cl₁Cu 351.0564, found 351.0639 (21 ppm), [M – Cl]⁺ calculated for C₁₆H₁₉N₃O₄Cl₁Cu
415.0360, found 415.0352 (19 ppm). Elemental Analysis for C₁₆H₁₉N₃O₄Cu₁Cl₂ (451.7918 g/mol): calculated C 42.54, H 4.24, N 9.30; found C 42.23, H 4.26, N 9.28. Single crystals suitable for X-ray analysis were obtained by slow diffusion of diethyl ether into a complex solution made in acetonitrile generating structure **6-A**, and slow diffusion of pentane into a complex solution made in dichloromethane generating structure **6-B**.

2.2.8. Synthesis of [Cu^{II}(B-BPMA)(Cl)(CF₃SO₃)], 7: Complex 5 (1.000 g, 2.580 mmol) was dissolved in 10 mL of acetonitrile in a 50 mL round bottom flask. Na(CF₃SO₃) (0.444 g, 2.58 mmol) was added to the flask to give a green colored solution. The reaction was allowed to mix for six hours generating a white sodium chloride precipitate in a green colored solution. The mixture was filtered and solute centrifuged to separate fine particles of sodium chloride from the solution. The solvent was removed using a rotary evaporator producing a green solid. The precipitate obtained was washed twice by transferring 20 mL of pentane into the flask and stirring vigorously for thirty minutes. Solvent was removed and precipitate dried under vacuum for 2 hours to yield a green colored solid (1.203 g, 93%). TOF-ESI-MS: (*m/z*) [M - (OTf)]⁺ calculated for C₁₆H₁₉N₃Cl₁Cu 351.0564, found 351.0757 (54 ppm). Elemental Analysis for C₁₇H₁₉N₃F₃O₃S1Cu₁Cl₁ (501.4103 g/mol): calculated C 40.72, H 3.82, N 8.38; found C 40.69, H 3.86, N 8.50. Single crystals suitable for X-ray analysis were obtained by slow diffusion of diethyl ether into a complex solution made in acetonitrile at room temperature.

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2.2.9. Synthesis of [Cu^u(B-BPMA)(Cl)][BPh₄], 8: Complex **5** (1.000 g, 2.580 mmol) was dissolved in 10 mL of methanol in a 50 mL round bottom flask. NaBPh₄ (0.883 g, 2.58 mmol) was added to the flask to give a greenish-blue precipitate in a green colored solution. The reaction was allowed to mix for 6 hours generating a greenish-blue colored precipitate in a clear solution. Solvent was removed utilizing a rotary evaporator. Precipitate obtained was washed twice by transferring 20 mL aliquots of methanol into the flask and stirring vigorously for thirty minutes. Solvent was removed and final precipitate dried under vacuum for two hours to yield a green solid (1.663 g, 96%). Elemental Analysis for C₄₀H₃₉N₃B₁Cu₁Cl₁ (671.5678 g/mol): calculated C 71.54, H 5.85, N 6.26; found C 71.20, H 5.82, N 6.03. Single crystals suitable for X-ray analysis were obtained by slow diffusion of diethyl ether into a complex solution made in acetonitrile at room temperature.

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3. SYNTHESIS AND SOLUTION STUDIES

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Ligand precursor *bis*(2-pyridylmethyl)amine (BPMA) was synthesized according to established literature procedures,^[28] and (but-3-en-1-yl)-*bis*(2-pyridylmethyl)amine ligand (B-BPMA) was synthesized utilizing modified literature procedures.^[29,30]. As presented in Scheme 2, three copper(I) complexes were synthesized by reacting one equivalent of a copper(I) salt (Cl⁻, ClO₄⁻, and CF₃SO₃⁻) with one equivalent of B-BPMA generating the following complexes; [Cu^I(B-BPMA)(Cl)] **1**, [Cu^I(B-BPMA)][ClO₄] **2**, and [Cu^I(B-BPMA)][CF₃SO₃] **3**. The final copper(I) complex [Cu^I(B-BPMA)][BPh₄] **4**, was synthesized via salt metathesis by reacting one equivalent of complex **1** with one equivalent of Na(BPh₄). A copper(II) complex was prepared by reacting one equivalent of copper(II) chloride with one equivalent of B-BPMA in acetonitrile producing [Cu^{II}(B-BPMA)(Cl₂)] **5**. Salt metathesis reactions employing one equivalent of complex **5** and one equivalent of Na(ClO₄), Na(CF₃SO₃), and Na(BPh₄) were then used to generate the copper (II) complexes [Cu^{II}(B-BPMA)(Cl)(ClO₄)] **6**, [Cu^{II}(B-BPMA)(Cl)(CF₃SO₃)] **7**, and [Cu^{II}(B-BPMA)(Cl)[[BPh₄] **8**.

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Scheme 2. Synthesis of: (I) B-BPMA ligand from BPMA ligand precursor; (II) [Cuⁱ(B-BPMA)(Cl)] **1**, [Cuⁱ(B-BPMA)][ClO₄] **2**, and [Cuⁱ(B-BPMA)][CF₃SO₃] **3**; (III) Salt metathesis reaction between Complex **1** and Na(BPh₄)to produce [Cuⁱ(B-BPMA)][BPh₄] **4**; (IV) Synthesis of copper(II) complex [Cuⁱ(B-BPMA)(Cl₂)] **5** and salt metathesis reactions used to generate [Cuⁱ(B-BPMA)(Cl)(ClO₄)] **6**, [Cuⁱⁱ(B-BPMA)(Cl)(CF₃SO₃)] **7**, and [Cuⁱⁱ(B-BPMA)(Cl)][BPh₄] **8**.

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Figure 1 shows the progressive ¹H NMR spectrum obtained for BPMA (**A**), B-BPMA (**B**), and [Cu¹(B-BPMA)][X] (X⁻ = Cl⁻ (**C**), ClO₄⁻ (**D**), CF₃SO₃⁻ (**E**) and BPh₄⁻ (**F**)). Pyridyl proton signals appear as two doublets and two triplets between 7.00 and 9.00 ppm corresponding to four protons. Methylene protons (**H**₆) appear as a singlet at 3.75 ppm. Proton resonances corresponding to the olefinic arm are located between 2.00 ppm and 6.00 ppm; accounting for seven protons. The characteristic methine proton in the olefinic arm (**H**₉) for the ligand is displayed as a multiplet at 5.78 ppm and around 5.50 ppm for the copper(I) complexes. Although counterions of the copper(I) complexes become less coordinating from (Cl⁻) to (BPh₄⁻), which could lead to



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Figure 1. ¹H NMR spectra (400 MHz, CD₃CN) for; [A] BPMA precursor, [B] B-BPMA ligand, [C] [Cu¹(B-BPMA)(Cl)] **1**, [D] [Cu¹(B-BPMA)][ClO₄] **2**, [E] [Cu¹(B-BPMA)][CF₃SO₃] **3**, and [F] [Cu¹(B-BPMA)][BPh₄] **4**. CD₃CN solvent peak has been omitted for clarity purposes, tetraphenylborate (BPh₄⁻) proton signals denoted as (**P**₁) to (**P**₃) and CH₂Cl₂ solvent as (**S**₁).

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different structural arrangements in solution; no significant proton shifts were observed in the aromatic region of spectra corresponding to those complexes [Figure 1, (C) to (F)]. Slight shifts were observed in the 285 aliphatic region of the copper(I) complexes, specifically proton (H_7), as the counterion became progressively non-coordinating. This could be attributed to motion in the olefinic arm that might be occurring to accommodate a desired tetrahedral geometry for the copper(I) metal center. Mass spectrometry experiments performed on the copper(I) complexes all displayed corresponding signals (m/z) and isotope patterns for the [Cu¹(B-BPMA)]⁺ ion. There were no indications of doubly charged species or dimer structures as determined 290 by mass spectrometry. Copper(II) complexes were characterized using UV-Vis spectroscopy, elemental analysis, and mass spectrometry. UV-Vis spectroscopy results displayed a blue shift as the counterion became less coordinating from complex 5 to complex 8. Elemental analyses were consistent with theoretical calculations. Finally, TOF-ESI mass spectrometry experiments revealed signals (m/z) and isotope patterns corresponding to the $[Cu^{II}(B-BPMA)(CI)]^+$ ion for each complex (spectroscopy results are presented in the 295 supporting information).

4. X-RAY CRYSTALLOGRAPHY RESULTS

Single crystals suitable for X-ray analysis were obtained for complexes 4, 5, 6, 7, and 8. Complex 4
crystallized in a monoclinic system with a C 2/c space group, producing the dimer structure shown in Figure
2. The metal center adopted a distorted tetrahedral geometry forming an associative bond with the olefinic arm of a neighboring complex. Further examination revealed elongation of the C=C bond which, considering the non-coordinating nature of counterion, may be occurring to accommodate the preferred geometry of the metal. Typical bond lengths reported for free C=C moieties range from 1.309 Å to 1.337 Å,^[35] with C=C bond
lengths in planar ethylene reported at 1.336 Å.^[32] In comparison, a bond length of 1.376(3) Å was obtained for the C=C moiety in complex 4. Similar bond lengths have been observed in transition metal-olefin complexes incorporating platinum (1.375(4) Å)^[37] and ruthenium (1.376(10) Å),^[38] with reports of lengths as



Figure 2. Molecular structure for complex 4 [Cu¹(B-BPMA)][BPh₄], collected at 150 K and shown with 50% probability ellipsoids. Hydrogen atoms and one tetraphenylborate (BPh₄-) counterion have been omitted for clarity purposes. Selected bond distances [Å] and angles [deg] are: Cu1–N1 2.046(2), Cu1–N2 2.287(2), Cu1–N3 2.034(2), Cu1–C15 2.078(2), Cu1–C16 2.031(5), C14–C15 1.507(3), C15–C16 1.376(3); N2–Cu1–C15 127.1(4), N3–Cu1–C15 101.2(3), N1–Cu1–C15 141.0(3), N2–Cu1–C15 129.9(2), N3–Cu1–C15 138.9(1), N1–Cu1–C15 103.0(4) and Cu1–C15–C16 68.9(6).

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- long as 1.477(4) Å in some tantalum complexes.^[39] With respect to C=C bond lengths observed in similar copper(I) olefin coordinations, a study by Oguadinma & Schaper report similar elongations with lengths ranging from 1.385(4) Å to 1.391(2) Å.^[40] Elongation of the C=C bond in complex 4 can also be attributed to a sigma-type donation from the C=C π-orbital into copper metal's *s*-orbital or *hybrid*-orbital, which is concomitant with π back-bonding from the copper metal's *d*-orbital into the empty π*-orbital of the C=C bond.^[21,40] This transfer increases hybridization of the C=C bond making it more *sp*³ like resulting in an augmentation of that bond. Our observations are in line with the *Dewar-Duncanson-Chatt* model which provides a bonding picture for metal–olefin coordinations similar to those seen in carbonyl–metal bonds.^[21]
- Alternatively, hybridization increases for carbon atoms in the C=C bond can be observed in bond angles obtained for protons located on the terminal carbon. Displacement of hydrogen atoms from planar positions observed in free ethylene, a convention developed by Stalick & Libers, is routinely used to measure the 325 degree of hybridization for carbon atoms in metal-olefin coordination.^[41] The angle (α) obtained between normals of the C-H-H planes serves as a measure for "bending" of hydrogen atoms away from the metal center. Figure 3 shows the (α) angle of 72.2° obtained in complex 4, which is comparable to other electron rich metal ethylene compounds reported in the literature.^[42] For comparison, the (α) value reported for sp² hybridized carbon atoms in free ethylene is zero (0), while that for sp^3 hybridized carbon atoms in ethane is 330 roughly 108°.^[43] A deviation from planarity is indicative of the formation of hybrid orbitals with higher *p*character which is observed in the olefinic group of complex 4. Separate structural studies by our group, utilizing copper(I) complexes incorporating a shorter propene olefinic arm (P-BPMA), highlight the effect of counterion coordination on complex geometry attained.^[44] In that study, metallation reactions employing the coordinating chloride ligand produced a molecular structure with no metal-olefin associative bonding. 335 Rather, the metal center adopted a distorted tetrahedral geometry, characteristic of copper(I) d^{10} complexes. Substituting the chloride ligand with a less coordinating perchlorate counterion (ClO₄) produced a crystal
- structure displaying identical metal-olefin coordination as observed in this study. The metal center adopted a similar distorted tetrahedral geometry, forming an associative bond with the olefinic arm of a neighboring
 complex, leading to similar elongation of the C=C bond in the olefinic arm.





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Complex **5** crystalized in a monoclinic system with a $P2_1/n$ space group, producing the structure shown in Figure 4. No coordination was observed with the olefinic arm in this case, as the metal adopted a distorted square pyramidal geometry with two chloride ligands and three nitrogen donor atoms. The olefinic C=C bond measured at 1.268(7) Å, which is slightly lower but still within the range reported for some free C=C groups. The length obtained could be due to thermal motion observed in the olefinic arm during refinement cycles.



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Figure 4. Molecular structure for complex **5** [Cu^{II}(B-BPMA)(Cl₂)], collected at 150 K and shown with 50% probability ellipsoids. Hydrogen atoms have been omitted for clarity purposes. Selected bond distances [Å] and angles [deg]: Cu1–N1 1.978(7), Cu1–N2 2.121(5), Cu1–N3 1.993(4), Cu1–Cl1 2.277(2), Cu1–Cl2 2.405(2), N2–C13 1.482(4), C14–C15 1.576(6), C15–C16 1.268(7); N1–Cu1–Cl1 95.35(9), N2–Cu1–Cl1 132.01(8), N3–Cu1–Cl1 95.41(7), N1–Cu1–Cl2 92.24(9), N2–Cu1–Cl2 105.15(8), N1–Cu1–N2 81.93(8), N1–Cu1–N3 162.70(2), C14–C15–C16 114.277(5).

Two polymorph structures were obtained for complex 6 as presented in Figure 5. Vapor diffusion crystallization methods utilizing acetonitrile and diethyl ether produced structure **6-A**, while methods using methanol and diethyl ether produced structure 6-B. Their arrangement difference is most likely due to the nature of solvent used; acetonitrile (aprotic) versus methanol (protic). Complex 6-A crystallized in a 360 monoclinic system with a $P_{1/c}$ space group, while **6-B** crystallized in a triclinic system with a P_{1} space group. Both complexes displayed bridging dimer structures containing symmetry related elements connecting the two molecular units incorporated. The metal center in 6-A adopted a distorted octahedral geometry by forming axial bonds to one oxygen atom in the perchlorate counterion and a chloride ligand from a neighboring complex. Structure 6-B also displayed a distorted octahedral geometry but the metal 365 center now makes what appears to be an associative axial bond with the C=C olefinic group of the ligand in order to accommodate that geometry. A second axial bond is made with the chloride ligand from a neighboring complex as observed in 6-A, but in this case no bonding was observed with the perchlorate counterion. The associative bond between the metal center and the olefinic arm is similar to that observed in complex 4. Bond distances obtained from this coordination (Cu1–C15: 2.955(6) Å and Cu1–C16: 2.873(5) Å) 370 are longer than those reported in complex 4 (Cu1-C15: 2.078(2) Å and Cu1-C16: 2.031(5) Å), but within

range of the distance obtained for the second axial bond (Cu1-Cl1': 2.946(7) Å). We did not observe any

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elongation in the C=C bond present in structure **6-B** measuring at 1.260(2) Å; in comparison the C=C bond in structure **6-A** measured at 1.305(2) Å. The shorter length obtained in **6-B** is most likely due to the significant thermal motion observed for the olefinic arm during structure solution refinement cycles, requiring the use of restraints to model C---C bond distances. Attempts were made to reduce the thermal motion observed by collecting X-ray diffraction data at lower temperatures (100 K), but similar disorders were still obtained requiring the use of restraints to model atom position and bonds.

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The molecular structure obtained for complex **7** is also shown in Figure 5. Similar to **6-A**, it crystallized in a monoclinic system with $P 2_1/n$ space group and displayed a bridging structure with symmetry related elements. The metal center adopted a distorted octahedral geometry with axial bonds to one oxygen atom in the triflate counterion and a chloride ligand from a neighboring complex. The olefinic arm is retracted away from the metal center with some distortion observed in ellipsoid displacements of carbon atoms in the C=C group. As discussed earlier, this can be attributed to motion of the terminal carbon atom (C16) as its position most likely fluctuates between "*trans*" and "*cis*" orientations with respect to (C13). Complex **8** displayed a similar bridging structure and also crystallized in a monoclinic system with $P 2_1/n$ space group (Figure 6). Taking into consideration the non-coordinating nature of the tetraphenylborate counterion incorporated, the olefinic arm is once again pulled down towards the metal center, presumably to facilitate a six-coordinate distorted octahedral geometry as observed in structure **6-B**. Distortions due to thermal motion were also detected in the ellipsoid displacement parameters for the C=C group, as reported in complex **7**. Axial bond distances measured in complex **8** were similar to those observed in complex **6-B** (Cu1–C15: 3.034(5) Å, Cu1–

C16: 3.050(2) Å, and Cu1–Cl1': 2.945(3) Å) with a C=C bond length of 1.284(9) Å.





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Axial elongations were observed in the molecular geometry obtained for complex 8 which could be due
to the presence of Jahn-Teller effects. For example, the equatorial Cu1–Cl1 bond distance measured at 2.2505(6) Å, while the axial Cu1–Cl1' bond distance measured at 2.9450(6) Å. Alternatively, some studies suggest that copper(II) complexes with apical Cu-L bonds significantly longer than basal ones may be due to the result of a double electron occupancy of the anti-bonding *a*₁ orbital and single occupancy of the *b*₁ orbital, leading to increased anti-bonding electron density along the apical Cu-L axis.^[45] Similar copper(II) complexes with a square plane of ligand donors and one or two axial Cu-L interactions with bond lengths in the range of 2.1-2.8 Å are well documented in the literature.^[46] With respect to the copper(II) complexes presented in this study, taking into consideration the covalent and van der Waals radii of copper (1.4 Å), axial Cu-Cl bond distances of less than 2.8 Å can be viewed as genuine bonds while distances between 2.8-3.2 Å represent a weaker secondary interaction that is predominantly electrostatic in nature and distances greater than 3.2 Å



Figure 6. Molecular structure obtained for complex **8** [Cu^{II}(B-BPMA)(Cl)][BPh4] collected at 150 K and shown with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity purposes. Selected bond distances [Å] and angles [deg]: Cu1–N1 1.9864(12), Cu1–N2 2.0520(11), Cu1–N3 1.9810(12), Cu1–Cl1 2.2505(6), Cu1–Cl1' 2.945(6), N3–C8 1.346(7), N2–C13 1.506(3), C13–C14 1.4853(5), C14–C15 1.556(5), C15–C16 1.284(11); N1–Cu1–Cl1 97.53(4), N2–Cu1–Cl1 178.06(2), N3–Cu1–Cl1 96.65(7), N1–Cu1–N2 83.66(4), N1–Cu1–N3 165.47(5), and C14–C15–C16 122.06(4).

420 5. ELECTROCHEMICAL STUDIES

Cyclic voltammetry experiments are typically used to predict the activity of complexes employed in ATRA reactions.^[48-50] The equilibrium constant for a given alkyl halide in ATRA ($K_{ATRA} = k_a/k_d$) is directly correlated to $E_{1/2}$ values obtained from cyclic voltammetry experiments; provided the halidophilicity of transition metal complex (X⁻ + [Cu^{II}L_m]²⁺ \leftrightarrow [Cu^{II}L_mX]⁺; K_X , X = Br or Cl) remains constant.^[51] Generally, equilibrium constants are larger for complexes that better stabilize the higher oxidation (Cu^{II}) state of the metal species corresponding to a more reducing complex.^[52] Therefore, linear correlations are typically observed between

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COMPLEX	<i>E</i> _{1/2} (mV) ^{<i>a</i>}	$\Delta E_{\rm p}$ (mV)	<i>İ</i> pa/ <i>İ</i> pc
[Cu(Me ₆ TREN)(Cl)][Cl]	- 440	80	1.10
[Cu(TPMA)(Cl)][Cl]	- 353	70	1.07
[Cu(B-BPMA)][Cl ₂]	- 168	102	1.10
[Cu(B-BPMA)(Cl)][ClO ₄]	- 100	202	1.20
[Cu(B-BPMA)(Cl)][OTf]	- 108	224	1.13
[Cu(B-BPMA)(Cl)][BPh4]	- 109	228	1.16
[Cu(P-BPMA)(Cl ₂)]	- 187	151	1.08
[Cu(P-BPMA)(Cl)][ClO ₄]	- 113	244	1.15
[Cu(P-BPMA)(Cl)][BPh4]	- 114	244	1.02

Table 1. Cyclic Voltammetry Data for Cu Complexes Incorporating Me₆TREN, TPMA, B-BPMA, and P-BPMA Ligand Motifs.

^aComplex solutions (2.0 mM) were prepared in dry acetonitrile containing 0.10 M NBu₄PF₆ as supporting electrolyte with measurements carried out under N₂ atmosphere at a scanning rate (v) of 50 mV/s. Potentials were measured relative to a ferrocenium/ferrocene couple.

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In(K_{ATRA}) and $E_{1/2}$ values for copper complexes incorporating neutral nitrogen-based ligands.^[53,54] Structural studies show that redox potentials for copper complexes used in atom transfer radical processes are strongly correlated to the ligand structure employed in their design.^[51] As a result, reducing power of complexes has been observed to increase with the number of nitrogen donor atoms incorporated in their ligand design (tetradentate > tridentate > bidentate). Aliphatic amines have also been found to be more nucleophilic compared to aromatic amines, and are more efficient at stabilizing the Cu^{II} species generated in atom transfer radical processes.^[52] Finally, for a given ligand, $E_{1/2}$ values vary with respect to the halide utilized, with CuBr complexes usually having higher redox potentials compared to CuCl complexes. This variance is even more pronounced in complexes made with tridentate and tetradentate ligands.^[52]

Due to the olefinic arm motion observed in B-BPMA complexes presented, we can consider ligand denticity to be pseudo-tetradentate with possibility to bind to a metal at four points (three N-donor atoms and the olefinic C=C bond) depending on reaction conditions. As such, reducing power of these complexes should not be greater than those reported for complexes employing true tetradentate ligands such as *tris*[2 445 (dimethylamino)ethyl)amine (Me₆TREN) and tris(2-pyridylmethyl)amine (TPMA). Furthermore, the reducing power for B-BPMA complexes should be lower than those obtained for complexes with analogous ligand denticity incorporating aliphatic motifs or bromide ligands. Table 1 summarizes the $E_{1/2}$ potentials obtained from cyclic voltammetry experiments comparing complexes 5, 6, 7, and 8 to two of the most active tripodal complexes reported for ATRA and ATRP, [Cu(ME₆TREN)(Cl)][Cl] and [Cu(TPMA)(Cl)][Cl]. As expected, $[Cu(ME_6TREN) (Cl)][Cl]$ was the most reducing, with a $E_{1/2}$ potential of (- 440 mV), due to its denticity and 450 aliphatic ligand motif. In comparison, [Cu(TPMA)(Cl)][Cl] was the second most reducing due to its denticity and aromatic ligand motif. Complexes made with B-BPMA all displayed single quasi-reversible redox behavior with i_{pa}/i_{pc} values varying from 1.02 to 1.16 and peak separations ranging from 80 mV to 244 mV (Figure 7, left). The counterion species incorporated affected the reducing power obtained as a transition to

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Comparative studies performed on copper complexes made with the shorter propene olefinic arm (P-BPMA),^[44,55] displayed the same trend with less coordinating counterions producing complexes with lower reducing power (Figure 7, right).



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Figure 7. (Left): CV results for Cu complexes incorporating the Me₆TREN (A), TPMA (B), and B-BPMA (C) ligand motifs. (Right): CV results for Cu complexes employing the P-BPMA ligand motif with counterions becoming less coordinating (A) Cl, (B) ClO₄, and (C) BPh₄. All measurements were conducted in CH₃CN with 0.1 M TBAPF₆ at a scan rate of 50 mV/s.

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6. ATOM TRANSFER RADICAL ADDITION REACTIONS

Electrochemical studies indicate that Cu(B-BPMA) complexes would not be able to facilitate the conversion of alkene substrates as efficiently as those reported for [Cu(ME₆TREN)(Cl)][Cl] and [Cu(TPMA)(Cl)][Cl].^[56,57] Nonetheless, the E_{1/2} values obtained for Cu(B-BPMA) complexes showed that they do possess some inherent reducing power and should be able to catalyze ATRA reactions. Cyclic voltammetry 470 studies also suggested that Cu(B-BPMA) complexes incorporating the chloride counterion should be more active (up to 68 mV), compared to others made with less coordinating counterions. Subsequently, complexes presented in this study were investigated as catalysts in ATRA reactions employing carbon tetrachloride (CCl₄) and select alkenes with varying propagation rate constants (1-hexene, 1-octene, 1-decene, styrene, methylacrylate, methyl methacrylate, acrylonitrile, and vinylacetate). Conversion of alkene to monoadduct 475 was monitored utilizing ¹H NMR spectroscopy, with yields determined relative to the internal standard p-dimethoxybenzene. ATRA results are summarized in Table 2, with complete results provided in the supporting information. Reactions utilizing AIBN as the reducing agent were carried out in acetonitrile, while reactions employing ascorbic acid were performed in methanol. Our desire for a monophasic system and poor solubility of ascorbic acid in acetonitrile were reasons for the solvent change.^[58]

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Reactions proceeded at 60 °C utilizing catalyst loadings as low as 0.04 mol % relative to alkene with moderate conversions and yields. These values were even lower with respect to styrene, methyl acrylate, and methyl methacrylate in ATRA reactions incorporating AIBN reducing agents. This decrease can be attributed to the formation of oligomers and polymers during the reaction as a result of; (i) insufficient trapping of

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485 **Table 2.** ATRA of CCl₄ to select alkenes employing Cu(B-BPMA) complexes with AIBN and ascorbic acid reducing agents.^a

Entry	Catalyst	Reducing Agent	Alkene	[Alk]:[Cat]	Conversion ^b	Yield ^b	TON
1			1-Hexene	500:1	70	65	325
2				1000:1	68	60	600
3			1 Decene	500:1	90	48	240
4	1		1-Decene	1000:1	87	46	460
5			A angel a nituil a	500:1	100	65	325
6	_	AIDN	Acrylonitrile	1000:1	100	50	500
7	5	AIDN	Styrene	500:1	49	16	80
8				1000:1	12	5	50
9			Methylacrylate	500:1	100	28	140
10				1000:1	100	13	130
11			Mather Mathematic	500:1	100	40	200
12			Methyl Methaci ylate	1000:1	100	35	350
13			1 Havana	500:1	70	80	400
14			1-Hexelle	1000:1	64	80	800
15			1-Docono	500:1	71	53	265
16			1-Decene	1000:1	60	44	440
17			Acrylonitrile	500:1	100	56	280
18	6	AIRN	Act yloniti ne	1000:1	100	40	400
19	0	AIDN	Styrene	500:1	67	63	315
20	_			1000:1	45	31	310
21	-		Methylacrylate	500:1	100	25	125
22	_			1000:1	100	14	140
23	-		Methyl Methacrylate	500:1	100	50	250
24				1000:1	100	34	340
25	-		1-Hexene	500:1	72	84	420
26	-			1000:1	65	66	660
27	-		1-Decene	500:1	57	30	150
28	-			1000:1	51	30	300
29			Acrylonitrile	500:1	100	60	300
30	7	AIBN		1000:1 500:1	100	50	500
31	-		Styrene Methylacrylate Methyl Methacrylate	500:1	59	55 27	275
32	-			E00:1	39	27	270
24				1000.1	100	14	110
25				E00.1	100	14 56	290
26				1000.1	100	25	250
27				E00.1	76		420
20			1-Hexene	1000.1	69	74	740
20	8 AIBN			500.1	75	50	250
40			1-Decene Acrylonitrile	1000.1	63	47	470
41				500.1	100	62	310
42				1000.1	100	44	440
43		AIBN	Styrene	500.1	64	59	295
44	1			1000:1	43	31	310
45	1		Methylacrylate	500:1	100	29	145
46				1000:1	100	14	140
47	1			500:1	100	54	270
48	7		Methyl Methacrylate	1000:1	100	41	410

^{*a*}ATRA reactions were performed in acetonitrile (utilizing AIBN) or methanol (utilizing ascorbic acid as reducing agent) at 60 °C for 24 hours with [alkene]:[CCl4]:[AIBN]/[ascorbic acid] ratios set at [1]:[1.1]:[0.05]. Two trials of each reaction were performed. ^{*b*}Conversions and yields were determined using ¹H NMR spectroscopy (relative errors are ± 10 %).

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radicals generated by the free radical initiator and copper(II) complexes, and (ii) further activation of monoadducts by the copper(I) complex. The moderate activity observed for Cu(B-BPMA) complexes is most likely due to the presence of a competing ATRA reaction between the olefinic arms of the complexes and the intended alkene substrates. This theory is supported by results obtained from an independent study carried out by our group on reactions between isolated copper(I) complexes employing the B-BPMA ligand motif and excess carbon tetrachloride.^[59] Results from that study showed that atom transfer radical addition of carbon tetrachloride (CCl₄) occurs on the C=C bond present in olefinic arms of the copper(I) activator species,



producing new copper(II) analogues with functionalized and elongated olefinic arms as shown in Figure 8.

Cu^I(B-BPMA) Complex

Figure 8. Competing ATRA reaction occurring on C=C bonds located in the olefinic arms of copper(I) BPMA complexes.

7. CONCLUSION

In summary the synthesis, characterization, electrochemical study, and catalytic activity of a series of copper complexes incorporating bis(2-pyridylmethyl)amine (BPMA) ligands with pendent olefinic arms were 505 reported. Solid state studies for complex 4 revealed associative bonding present between the copper metal center and C=C group in the olefinic arm of a neighboring complex. This metal-olefin coordination resulted in elongation of the C=C bond which was attributed to a sigma-type donation from the C=C π -orbital into metal's s-orbital or hybrid-orbital, concomitant with π back-bonding from the metal's d-orbital into the empty π^* orbital of the C=C bond. This transfer increased the hybridization of carbon atoms in the C=C bond, making 510 them more sp^3 like, producing an (α) angle of 72.2° used to denote the degree of bending for hydrogen atoms located on the C=C bond. The associative bonding observed is most likely due to the non-coordinating nature of the tetraphenylborate (BPh_{4}) counterion and a desire for characteristic tetrahedral geometry by the metal center. Independent studies carried out with a similar ligand motif (P-BPMA) showed that copper(I) complexations with coordinating counterions such as chlorine, produce solid state structures lacking 515 associative bonding to the olefinic C=C group.^[44,55] Copper(II) complexes, excluding complex 5, adopted distorted octahedral geometries either through bonding with a counterion or associative bonding with the C=C group in olefinic arms. X-Ray crystallography results provided insight to the deactivator species, or transition states, that might be present during atom transfer radical addition (ATRA) reactions when employing these compounds. 520

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Electrochemical studies showed that copper complexes made with the B-BPMA ligand motif were not as reducing as those incorporating purely tetradentate aromatic or aliphatic nitrogen donor atoms. Comparison studies carried out with the highly active complexes such as $[Cu(ME_6TREN)(Cl)][Cl]$ and [Cu(TPMA)(Cl)][Cl]displayed significant activity change with $E_{1/2}$ value differences as large as 340 mV. Despite that difference, cyclic voltammetry experiments did show that Cu(B-BPMA) complexes do have some inherent reducing power and may be efficient catalysts worth investigating in some atom transfer radical processes. However, ATRA reactions performed with Cu(B-BPMA) complexes showed moderate conversions and poor yields. In addition, no activity difference was observed between complexes employing the coordinating chloride counterion and those incorporating less coordinating counterions, as suggested in electrochemical studies. The counterion effect on reducing power was also observed in copper complexes incorporating ligands with the shorter propene olefinic arm (P-BPMA); where an $E_{1/2}$ activity difference of up to 74 mV was obtained. The moderate activity obtained for Cu(B-BPMA) complexes and the intended alkene substrates. This observation between C=C groups in the olefinic arms of complexes and the intended alkene substrates. This observation was disseminated in independent studies by our group on the effect of excess CCl₄ addition to isolated copper(I) complexes employing the (B-BPMA) ligand motif.

ASSOCIATED CONTENT

Supporting Information: Provided are: complete X-ray crystallographic data tables and CIF files; mass spectrometry results, UV-Vis spectroscopy results, infrared spectroscopy results; detailed ligand synthesis mechanism; and complete ATRA results including all ¹H NMR spectra obtained.

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545 APPENDIX A. Supplementary Data

CCDC 1414532 – 1414537 contain the supplementary crystallographic data for complexes **4** to **8**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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This work highlights the synthesis, characterization, and catalytic activity of bis(2pyridylmethyl)amine (BPMA) copper complexes incorporating olefinic pendent arms in atom transfer radical addition (ATRA) of carbon tetrachloride to select alkenes.

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Synopsis