Experimental Section

$DC_{8,9}PC$ was obtained from Avanti Polar Lipids and used without further purification. TEOS was obtained from Aldrich and used as received. Mineralized lipid tubules were prepared in situ as follows. Typically, $DC_{8,9}PC$ (40 mg) was dissolved in ethanol (2 mL) by sonication (lipid concentration, 0.044 mM), and TEOS (82.4 μL) was added to give a TEOS:lipid molar ratio of 8.3:1. A solution (0.38 g) prepared from H_2O (0.8 g) and 48 wt% aqueous HBr (3.0 g) was added to the lipid/TEOS mixture (final pH 0.5) and a white precipitate formed instantly. The sample was stirred for 5 min, left sealed overnight, and then centrifuged at 5000 rpm for 10 min and the supernatant decanted. Similar preparations were undertaken at TEOS:lipid molar ratios between 4:1 and 1:4. Polydiacetylenic derivatives were prepared by leaving samples of the dried mineralized lipid tubules for two days under ambient conditions in the laboratory. Unmineralized lipid tubules were prepared by addition of H_2O (1 mL) to a solution of $DC_{8,9}PC$ (0.0044 mM) in ethanol (1 mL). Lipid microstructures were also coated externally with silica by addition of TEOS (82.4 μL) to a suspension (20 mg mL^{-1}) of preformed tubules.

Samples were characterized by TEM (JEOL 1200EX), SEM (JEOL JSM 5600 LV), EDXA (Oxford Instruments, ISIS300), and XRD (Siemens D500 diffractometer, $Cu_{K\alpha}$ radiation, $\lambda = 0.15405$ nm). Samples were prepared either as a suspension in ethanol in a quartz cuvette or evaporated from ethanol onto a quartz slide for UV/Vis (800–200 nm) and diffuse reflectance UV/Vis spectroscopy (Perkin Elmer Lambda II with Labsphere titania mirrors), respectively. FT-IR spectroscopy (Perkin Elmer Spectrum 1) was carried out using KBr discs. Raman spectra (Renishaw System 2000) were recorded using a 35 mW HeNe laser at an excitation frequency of 632.8 nm, and probe size of about 1 μm. TGA (Netzsch TG409EP) was carried out at a heating rate of 5 K min^{-1} from room temperature to 600 °C in air with a flow rate of 90 mL min^{-1}. Calcined samples were prepared at 410 °C for 2 h using a heating rate of 3 K min^{-1}.

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Aryl C–H Activation by Cu^{II} To Form an Organometallic Aryl–Cu^{III} Species: A Novel Twist on Copper Disproportionation**

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Selective activation of hydrocarbon C–H bonds by metals under mild conditions is an important pursuit in the functionalization of organic substrates.[1] While such oxidative trans-

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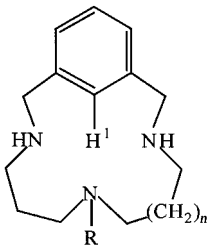
formations are complicated, the fact that the C–H-activation step often determines the selectivity and the rate of the reaction provides ample motivation for understanding the mechanistic details of this step.[2] Assuming the intermediacy of an initial weak C–H adduct with the metal, two limiting mechanisms of C–H activation are possible:[3,4] direct heterolytic C–H-bond cleavage ($M^{n+} + R{-}H \rightarrow M^{n+}{-}R + H^+$), which requires an exogenous base and no change in the formal oxidation state of the metal atom, and oxidative addition ($M^{n+} + R{-}H \rightarrow H{-}M^{n+2}{-}R$), which involves a high-valent metal–hydrido complex.[2,5,6] Activation of C–H bonds by first-row transition metals under mild conditions is generally limited to intramolecular reactions in which the decrease in entropy can potentially compensate for the weaker M–C bonds formed with first-row metals relative to heavier metals.[3,7]

Herein we present three related Cu^{II} coordination complexes that activate an aryl C–H bond of a ligand at room temperature (RT) to form a stable organoaryl–Cu^{III} complex. Spectral and structural characterization of these Cu^{III} species are presented along with mechanistic insight into the activation process.



L^1: R = H $n = 0$
L^2: R = Me $n = 1$
L^3: R = H $n = 1$

Scheme 1. Triazamacrocyclic ligands.

The triazamacrocyclic ligands used in this study are presented in Scheme 1.[9,10] Structurally, these ligands are analogous to the tetraazamacrocyclic ligands synthesized from α,α'-2,6-dibromomethylpyridine rather than α,α'-1,3-dibromomethylbenzene, as the latter ligands readily adopt a square-planar binding conformation. Reaction of equimolar amounts of $Cu^{II}(ClO_4)_2 \cdot 6H_2O$ with L^2 in CH_3CN at RT under anaerobic conditions resulted in a rapid decay of the initially formed paramagnetic $[Cu^{II}L^2]^{2+}$ complex to equimolar amounts of two diamagnetic products (Scheme 2). One product is consistent with $[Cu^{I}L^2H]^{2+}$, which could be independently prepared and characterized (^{1}H NMR, ESI MS). An anaerobic optical titration of the final reaction mixture with an excess of phenanthroline confirmed an overall conversion of the initial Cu^{II} into Cu^{I} of about 50%, and this suggests a disproportionation of Cu^{II}. The second diamagnetic product selectively crystallizes in about 50% yield, and is indefinitely stable in protic media (MeOH, H_2O) under aerobic conditions. Analytical data support a 1:1 Cu:ligand complex with two counteranions, **2**-$(ClO_4)_2$, fully consistent with a robust, low-spin Cu^{III} complex. However, Cu^{III} complexes are generally stabilized in square-planar, anionic coordination environments, a ligation mode not initially envisioned for L^1–L^3. The reactions of L^1–L^3 with $Cu^{II}(ClO_4)_2$ or $Cu^{II}(CF_3SO_3)_2$ result in analogous crystalline products, **1**-$(ClO_4)_2$–**3**-$(ClO_4)_2$ or **1**-$(CF_3SO_3)_2$–**3**-$(CF_3SO_3)_2$, respectively, in similar overall yields.

$$2\,[Cu^{II}L](X)_2 \xrightarrow[298\ K]{MeCN} [Cu^{III}L'](X)_2 + [Cu^{I}(LH)](X)_2$$

$L = L^1, L^2, L^3$
$X = ClO_4^-, CF_3SO_3^-$

1•X_2: L^1'
2•X_2: L^2'
3•X_2: L^3'

Scheme 2. Disproportionation reaction.

Crystallographic characterization of **1**-$(ClO_4)_2$ and **2**-$(ClO_4)_2$[11] showed that each copper atom is coordinated by six ligands, although the two perchlorate anions are only weakly associated in axial positions (Cu–O ca. 2.4–2.7 Å). An ORTEP plot of **2** shows the nearly planar coordination environment provided by the macrocyclic ligand (Figure 1).

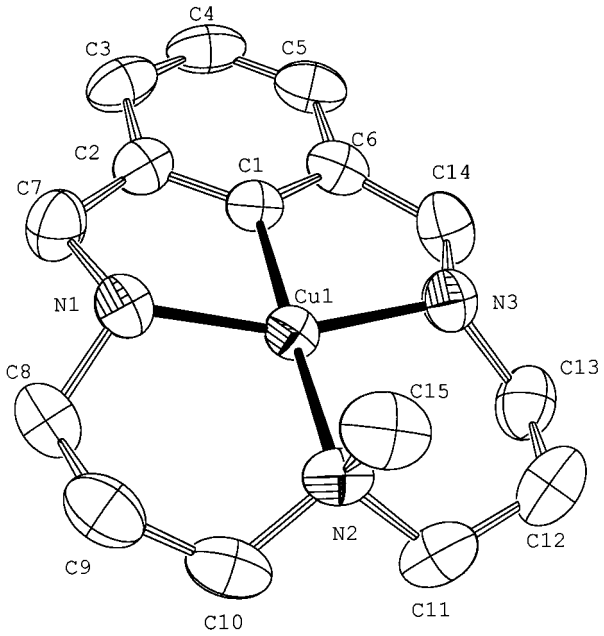


Figure 1. ORTEP plot of **2**-$(ClO_4)_2$ with 50% probability thermal ellipsoids, excluding the two perchlorate anions. Selected bond lengths [Å] and angles [°] of **2**-$(ClO_4)_2$ (corresponding values of **1**-$(ClO_4)_2$ in brackets): Cu1–C1 1.905(3) [1.848(4)], Cu1–N1 1.965(3) [1.899(4)], Cu1–N2 2.031(3) [2.000(8)], Cu1–N3 1.961(3) [1.911(3)]; N1-Cu1-C1 82.9(2) [84.6(2)], C1-Cu1-N3 82.3(2) [84.4(2)], N1-Cu1-N2 96.9(1) [105.6(2)], N2-Cu1-N3 97.4(1) [85.1(2)], C1-Cu1-N2 177.6(1) [163.5(2)], N1-Cu1-N3 160.7(2) [169.0(2)], Cu1-O1 2.442(4) [2.428(6)], Cu1-O8 2.736(4) [2.584(6)].

The equatorial Cu ligation is composed of three nitrogen atoms of the triazamacrocycle and one aryl C donor. Activation of the aryl C–H^1 bond (Scheme 1) creates a C ligand and allows the macrocycle to adopt a square-planar metal-binding conformation akin to the analogous pyridine-derived tetraazamacrocyclic ligand (see above). The Cu–C distances in **1** and **2** are the shortest in the coordination sphere at 1.848 Å and 1.905 Å, respectively. The Cu–N bond lengths systematically vary within each structure; the two benzylic Cu–N distances in **1** and **2** average 1.90 Å and 1.96 Å, respectively, and are shorter than the nonbenzylic Cu–N distances of 1.96 Å and 2.03 Å, respectively. The lack of extremely short Cu–ligand distances and the hexacoordinate ligation, albeit weak in the axial direction, is unusual for low-spin Cu^{III} complexes.[12] Regarding the C ligand as an anionic donor, designation as Cu^{III} is appropriate with two counteranions.[13] Furthermore, Cu K-edge X-ray absorption spectra[14] of solid

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samples of **1**-$(ClO_4)_2$–**3**-$(ClO_4)_2$ and **1**-$(CF_3SO_3)_2$ clearly exhibit an intense pre-edge feature at 8981 ± 0.5 eV, characteristic of a $1s \rightarrow 3d_{x^2-y^2}$ transition in a low-spin Cu^{III} center.[15] The spectra also indicate that this transition is sensitive to the size of the azamacrocycle, but not to the nature of the coordinating counteranions (Figure 2). The higher energy pre-edge transition for **1**-$(ClO_4)_2$ (8981.2 eV) compared to **2**-$(ClO_4)_2$ (8980.7 eV) correlates with the more compact

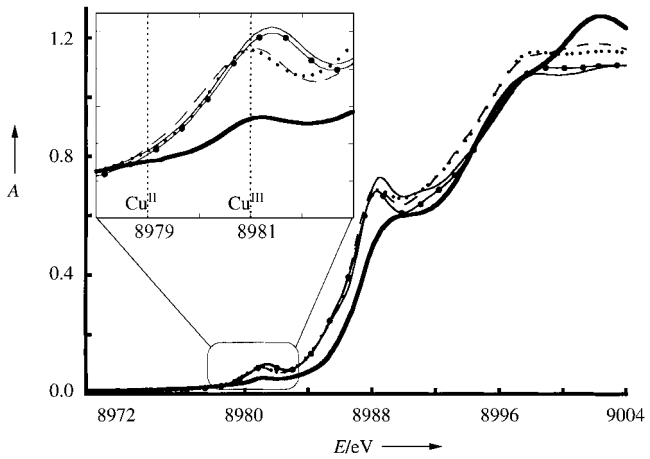

Figure 2. Cu K-edges for Cu^{III} complexes **1**-$(CF_3SO_3)_2$ (——), **1**-$(ClO_4)_2$ (•–•–), **2**-$(ClO_4)_2$ (– – –), **3**-$(ClO_4)_2$ (••••), and $[Cu^{III}(H_{-3}Aib_3)]$[14] (▬▬). The amplified inset shows the pre-edge region ($1s \rightarrow 3d_{x^2-y^2}$ transition, 8978–8983 eV). A = normalized absorption, E = energy.

equatorial ligation; the average equatorial bond lengths in **1** are about 0.05 Å shorter than in **2**. Comparison of **1** with **2** suggests that the difference in the transition energies results primarily from destabilization of the $3d_{x^2-y^2}$ level of **1** relative to **2**. The more unfavorable $Cu^{III} \rightarrow Cu^{II}$ reduction potential of **1** compared to either **2** or **3** (> 0.250 V)[16] further supports this notion. A consistent interpretation of this data is that the more compact ligation afforded by the smaller macrocyclic ligand in **1** better stabilizes a Cu^{III} center.

The size of the macrocycle and derivatization dramatically influence the rate of disproportionation of $[Cu^{II}L]^{2+}$. Optical monitoring of the progress of the reaction (300–800 nm) suggests a complex mechanism for the formation of **1**–**3**. Starting with a 1:1 Cu^{II}:L stoichiometry ($L = L^1$–L^3), the disappearance of each initially formed $[Cu^{II}L]^{2+}$ complex exhibits an induction period followed by an exponential decay suggestive of an autocatalytic reaction. While a slight excess of Cu^{II} completely inhibits the disproportionation reaction, a slight excess of ligand (Cu^{II}:L 1:1.3) accelerates the reaction by elimination of the induction period. Under such conditions, the process is first order in $[Cu^{II}]$ from 0.5 to 2.5 mM, and the observed rate constants for $[Cu^{II}L^1]^{2+}$ and $[Cu^{II}L^2]^{2+}$ of $2.1(1) \times 10^{-2}$ and $1.9(1) \times 10^{-1}$ s^{-1}, respectively, clearly show that the complex of the larger, more flexible L^2 ligand reacts faster.[17] The rate of disproportionation of $[Cu^{II}L^3]^{2+}$ is comparable to that of $[Cu^{II}L^2]^{2+}$.

Assuming similar mechanisms for the formation of **1**–**3**, the rate-determining step (RDS) involves C–H^1 bond cleavage; a large primary kinetic isotope effect (KIE) was measured with selectively monodeuterated L^3.[18] The combined data suggests that the RDS in the disproportionation reaction is a base-assisted, heterolytic C–H bond cleavage to give a $[Cu^{II}L']^+$ complex, where L′ represents the deprotonated ligand (Scheme 2). The inhibition of the disportionation reaction by excess Cu^{II} suggests that free ligand can act as the exogenous base. Subsequent fast electron transfer from $[Cu^{II}L']^+$ to another $[Cu^{II}L]^{2+}$ complex would result in the observed diamagnetic Cu^{III} and Cu^{I} products. The ability of an amine such as the free ligand to readily deprotonate an aryl C–H bond in the RDS is potentially explained by an enhanced σ_{CH}–Cu interaction. Such interactions can significantly reduce the pK_a of an aryl C–H group.[3,19] The macrocyclic constraints of L^1–L^3 ligated to Cu^{II} through all three nitrogen atoms requires the aryl C–H^1 bond to be in close, if not intimate, contact with the Cu^{II} center.[20] Deprotonation and formation of a $[Cu^{II}L']^+$ complex would then lead to products.[19]

While aryl C–H-insertion chemistry and formation of stabilized Cu^{III}–aryl complexes in these simple triazamacrocyclic ligands is intriguing, their subsequent reactivity with hydroxide to yield Cu^{II}–phenoxoazamacrocyclic complexes is perhaps more interesting.[21] Most remarkable is that the same Cu^{II} phenoxo products result from exposing the Cu^{I} triazamacrocyclic complexes to dioxygen, and this reaction proceeds through an intermediate observed in the Cu^{III}/hydroxide reaction. This oxidative chemistry is reminiscent of the aromatic hydroxylation performed by tyrosinase, a binuclear copper enzyme.[22] While the generally accepted enzymatic mechanism does not involve direct aryl C–H activation by a Cu^{II} center, no current data precludes it. Further studies on these complexes are necessary to highlight the mechanistic similarities to or differences from the biological systems.

Experimental Section

The synthesis of **1**-$(ClO_4)_2$ is representative of all complexes prepared in this study.

Equimolar amounts of L^1 (30 mg, 1.4×10^{-4} mol) and $Cu^{II}(ClO_4)\cdot 6H_2O$ (51 mg, 1.4×10^{-4} mol) were dissolved in CH_3CN (3 mL) under Ar. The resulting yellow solution was stirred for 30 min and filtered through Celite. Slow diffusion of diethyl ether into the filtered solution resulted in the formation of yellow crystals of $[Cu^{III}L^{1\prime}](ClO_4)_2$ (**1**-$(ClO_4)_2$) in 50% yield of isolated product (32 mg, 7×10^{-5} mol) after 24 h. The analogous procedure with $Cu^{II}(CF_3SO_3)_2$ resulted in nearly identical yields of isolated **1**-$(CF_3SO_3)_2$. X-ray quality crystals of **1**-$(ClO_4)_2$ and **2**-$(ClO_4)_2$ were obtained by recrystallization from CH_3CN/diethyl ether.

1-$(ClO_4)_2$: ESI-MS (CH_3CN): m/z 380 [**1**-(ClO_4)]$^+$; UV/Vis (CH_3CN): $\lambda_{max}(\varepsilon) = 273$ (6900), 409 nm (280); ^{1}H NMR (500 MHz, CD_3CN, 25 °C): $\delta =$ 7.28 (t, 1H), 7.03 (d, 1H), 7.01 (d, 1H), 6.85 (m, 1H), 5.96 (m, 1H), 4.65 (d, 1H), 4.60 (m, 2H), 4.51 (d, 1H), 3.48 (dt, 1H), 3.37 (td, 1H), 3.24 (dd, 1H), 3.13 (m, 3H), 2.97 (qd, 1H), 2.75 (q, 1H), 2.17 (m, 1H), 1.65 ppm (m, 1H); elemental analysis (%) calcd for $C_{13}H_{20}N_3CuCl_2O_8$: C 32.5, H 4.2, N 8.7; found: C 32.9, H 4.0, N 8.6.

2-$(ClO_4)_2$: ESI-MS (CH_3CN): m/z 408 [**2**-(ClO_4)]$^+$; UV/Vis (CH_3CN): $\lambda_{max}(\varepsilon) = 291$ (7500), 440 nm (sh, 250); ^{1}H NMR (500 MHz, CD_3CN, 25 °C): $\delta = 7.27$ (t, 1H), 6.95 (d, 2H), 6.33 (m, 2H), 4.67 (d, 2H), 4.52 (d, 2H), 3.24 (m, 2H), 3.08 (m, 2H), 3.05 (m, 2H), 2.73 (s, 3H), 2.65 (dt, 2H), 2.15 (m, 2H), 1.95 ppm (m, 2H); elemental analysis (%) calcd for $C_{15}H_{24}N_3CuCl_2O_8$: C 35.4, H 4.7, N 8.3; found: C 35.7, H 4.4, N 8.4.

3-$(ClO_4)_2$: ESI-MS (CH_3CN): m/z 394 [**3**-(ClO_4)]$^+$; UV/Vis (CH_3CN): $\lambda_{max}(\varepsilon) = 280$ (8200), 448 nm (sh, 280); ^{1}H NMR (500 MHz, CD_3CN, 25 °C): $\delta = 7.27$ (t, 1H), 6.95 (d,2H), 6.12 (m, 2H), 4.61 (dd, 2H), 4.49 (dd, 2H),

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3.14 (m, 1H), 3.09 (m, 3H), 2.99 (dq, 2H), 2.63 (dq, 2H), 2.04 (m, 2H), 1.77 (m, 2H); elemental analysis (%) calcd for $C_{14}H_{23}N_3CuCl_2O_8$: C 33.9, H 4.7, N 8.5; found: C 34.1, H 4.6, N 8.4.

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[16] Parameters for the cyclic voltammetric measurements of **1**-$(ClO_4)_2$–**3**-$(ClO_4)_2$: scan rate of 100 mV s^{-1}, tetrabutylammonium hexafluorophosphate 0.2 M, CH_3CN, RT, potential reported relative to SSCE. Ferrocene was used as internal reference at $E_{1/2} = 370$ mV. **1**-$(ClO_4)_2$: irreversible reduction with a small returning wave, $E_{1/2} = -380$ mV, $E_{pc} = -445$ mV, $E_{pa} = -315$ mV, $\Delta E = 130$ mV. **2**-$(ClO_4)_2$: reversible wave at $E_{1/2} = -105$ mV, $E_{pc} = -145$ mV, $E_{pa} = -60$ mV, $\Delta E = 85$ mV. **3**-$(ClO_4)_2$: reversible wave at $E_{1/2} = -180$ mV, $E_{pc} = -240$ mV, $E_{pa} = -125$ mV, $\Delta E = 120$ mV.
[17] At 298 K, $[Cu^{II}L^1]_i = 1.25$ mM; $[L^1]_i/[Cu^{II}]_i = 1.28$; $[Cu^{II}L^2]_i = 1.21$ mM, $[L^2]_i/[Cu^{II}]_i = 1.28$.
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Migration of a Phosphane Ligand between the Two Metal Centers in Diruthenium Hydrido Complexes**

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In the coordination sphere of a metal cluster complex, the substrate can often interact with multiple metal centers simultaneously. The bridging coordination of hydride or carbon monoxide is a typical example of such interaction, and the multiple coordination of the ligand seems to be closely related to the dynamic behavior and reactivity of the ligand. Indeed, a carbonyl ligand in a cluster complex often undergoes intramolecular migration between the metal centers by way of an intermediary species with the bridging carbonyl.[1]For a better understanding of the nature of *multimetallic activation*, it is important to elucidate the interaction between the ligand and the multiple metal centers through the

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