# Copper and Silver Complexes of Tris(triazole)amine and Tris(benzimidazole)amine Ligands: Evidence that Catalysis of an Azide−Alkyne Cycloaddition ("Click") Reaction by a Silver Tris(triazole)amine Complex Arises from Copper Impurities

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Ⓢ *Supporting Information*

ABSTRACT: The synthesis and characterization of a silver complex of the tripodal triazole ligand, tris(benzyltriazolylmethyl)-amine (TBTA, L^1), that is used as promoter to enhance Cu^I-catalyzed azide−alkyne cycloaddition (CuAAC) reactions is reported. X-ray analysis of the silver(I) complex with L^1 reveals a dinuclear cation, $[Ag_2(L^1)_2]^{2+}$, that is essentially isostructural to the copper(I) analogue. While the $[Ag_2(L^1)_2](BF_4)_2$ complex provides catalysis for the azide−alkyne cycloaddition process, evidence is presented that this arises from trace copper contamination. The synthesis of silver(I), copper(II), and copper(I) complexes of a second tripodal ligand, tris(2-benzimidazolylmethyl)amine (L^2), which is used to enhance the rate of CuAAC reactions, is also reported. X-ray crystallography of the Cu^I complex $[Cu^I_3(L^2)_2(CH_3CN)_2](BF_4)_3$ offers structural insight into previous mechanistic speculation about the role of this ligand in the CuAAC reaction.
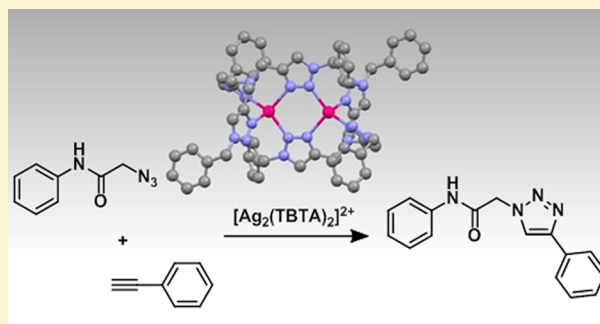
INTRODUCTION

The Cu^I-catalyzed azide−alkyne cycloaddition (CuAAC) reaction affords 1,4-disubstituted 1,2,3-triazoles (Figure 1A).[1−3] The high yield and tolerance for a variety of functional groups has resulted in CuAAC reactions being deployed across the fields of chemistry,[4] materials science,[5,6] and the life sciences.[7,8] Polytriazoles were identified as useful ligands for the CuAAC reaction through the observation of autocatalytic effects with multivalent substrates. Screening of a diverse range of mono-, bis-, and tristriazoles revealed tris-(benzyltriazolylmethyl)amine (TBTA) (L^1, Figure 1B) as the progenitor of a class of effective tripodal triazole ligands for promotion of the reaction in the presence of air.[9−12] The heterocyclic 1,2,3-triazolyl rings synthesized using the CuAAC reaction can themselves act as N donor ligands through both N^2 and N^3, and this has been exploited in the design of polydentate ligand architectures and metal complexes.[13−32] A different type of tripodal ligand, tris(2-benzimidazolylmethyl)-amine (L^2, Figure 1B), provides useful rate enhancements over the "ligand-free" case, but reactions typically exhibit greater sensitivity to oxygen.[33,34] In this work the synthesis and characterization of a Cu^I complex of L^2 is reported as well as its activity as a catalyst in CuAAC reactions. As part of a study of the structure and reactivity of group 11 metal ions with tripodal ligands, the synthesis, isolation, and stuctural characterization of Ag^I complexes of L^1 and L^2 are also presented. The structural
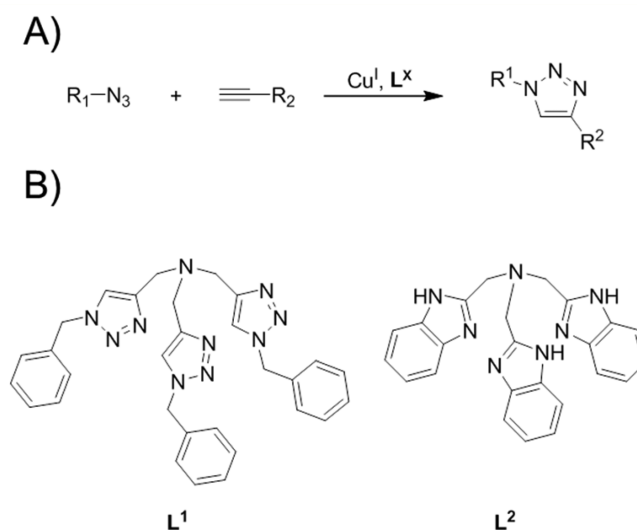

Figure 1. (A) Copper(I)-catalyzed azide-terminal alkyne cycloaddition (CuAAC). (B) Yield/rate accelerating CuAAC additives.

similarity of the Ag^I complex of $\mathbf{L^1}$ to the isoelectronic Cu^I analogue and recent reports of a Ag^I-catalyzed azide/alkyne cycloaddition (AgAAC) reaction[35−40] encouraged an investigation into the catalytic activity of the isolated Ag^I complexes in azide−alkyne cycloaddition reactions.

■ RESULTS AND DISCUSSION

Synthesis of [Cu(L^2)(CH$_3$CN)]$^{2+}$ and [Cu$_3$(L^2)$_2$(CH$_3$CN)$_2$]$^{3+}$. Complexes of Cu^{II} with tripodal tris(benzimidazole)amine ligands such as $\mathbf{L^2}$ have been prepared and investigated as models for the active sites of metalloproteins. Ligand $\mathbf{L^2}$ binds Cu^{II} as a tetradentate donor through the apical nitrogen atom and a benzimidazolyl nitrogen on each of the three limbs. The final coordination site of the five-coordinate complexes can be occupied by either an anion,[41−44] a solvent molecule,[45] or small organic molecules acting as a monodentate ligand.[46−48] The coordination geometry about the Cu^{II} atom is typically square pyramidal or trigonal bipyramidal. N-Alkylation of the benzimidazole heterocycle with an alkyl carboxylic acid substituent affords larger supramolecular structures.[49,50] Complexes of $\mathbf{L^2}$ with Cu^I are less common and are typically stabilized against oxidation using coligands with "soft" donor atoms such as triphenylphosphine or iodide.[41] In these examples $\mathbf{L^2}$ does not coordinate Cu^I as a tetradentate ligand. An isolated Cu^I complex with a tetradentate benzimidazole ligand exhibited a stoichiometry of 2:1 metal to ligand with the metal atoms in a disorted linear geometry.[51]

A new Cu^{II} complex of $\mathbf{L^2}$ was prepared by combining $\mathbf{L^2}$ and Cu(BF$_4$)$_2$·6H$_2$O in acetonitrile followed by precipitation with diethyl ether to give a light green solid. Crystals of [Cu(L^2)(CH$_3$CN)](BF$_4$)$_2$·5CH$_3$CN suitable for X-ray crystallography were grown by evaporation of an acetonitrile solution at ambient temperature. The metal atom is five-coordinate and in a distorted trigonal bipyramidal coordination environment with the ligand acting as a N$_4$ tetradentate donor with the final coordination site occupied by a molecule of acetonitrile (Figure 2). The Cu−N-*heterocyclic* distances (Cu−N3 2.042(4) Å, Cu−N5 2.051(4) Å, Cu−N6 2.027(4) Å) are slightly shorter than
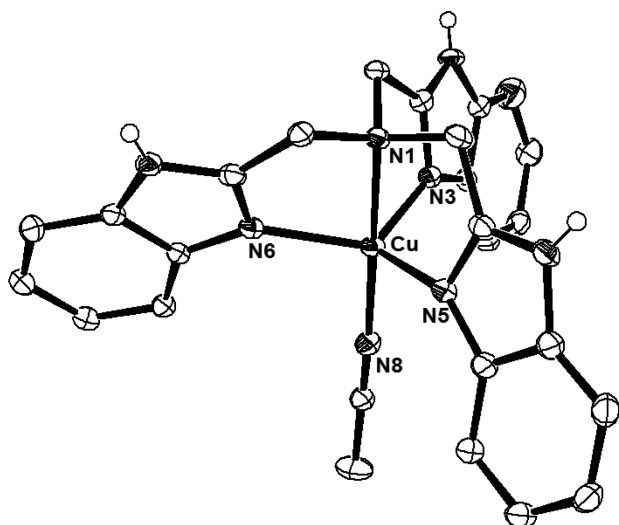

Figure 2. ORTEP representation, with ellipsoids at the 40% probability level, of [Cu(L^2)(CH$_3$CN)](BF$_4$)$_2$·5CH$_3$CN. Anions, solvent molecules, and hydrogen atoms, except the benzimidazole hydrogens, are omitted for clarity.

the Cu−N-*tertiary amine* distance (Cu−N1 2.070(4) Å). Similar complexes where water or iodide occupies the final coordination site typically have a longer Cu−N-*tertiary amine* distance (∼2.10−2.12 Å).[41,45,48] The major signal in the positive ion high-resolution electrospray ionization (HR-ESI) mass spectrum of this complex was at m/z 235.0588, corresponding to [Cu(L^2)]$^{2+}$ ([C$_{24}$H$_{21}$N$_7$Cu]$^{2+}$ requires 235.0577), and a smaller signal was observed at m/z 255.5700, corresponding to [Cu(L^2)(CH$_3$CN)]$^{2+}$ ([C$_{26}$H$_{24}$N$_8$Cu]$^{2+}$ requires 255.5710).

The active catalyst of CuAAC reactions is a Cu^I species, and the electrochemical behavior of [Cu(L^2)(CH$_3$CN)]$^{2+}$ was investigated by cyclic voltammetry in acetonitrile. The complex exhibits a quasi-reversible one-electron redox process centered at $E_{1/2}$ = 0.14 V (vs SCE, where $E_{1/2}$ = [E_{pc} + E_{pa}]/2 and Fc/Fc$^+$ = 0.38 V) attributed to a Cu^{II}/Cu^I couple (E_{pa} − E_{pc} = 94 mV, under the same conditions for Fc/Fc$^+$ E_{pa} − E_{pc} = 70 mV) (Figure 3). A Cu^I complex of $\mathbf{L^2}$ was prepared by the addition
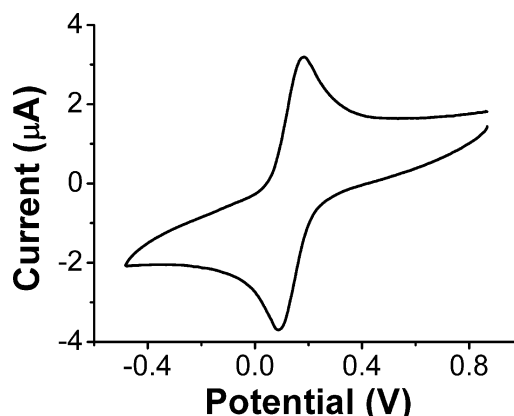

Figure 3. Cyclic voltammogram of [Cu(L^2)(CH$_3$CN)](BF$_4$)$_2$ in acetonitrile, 0.1 mol L^{-1} (Bu$_4$N)(BF$_4$), scan rate = 0.2 V s^{-1}. Potentials are quoted vs SCE assuming $E_{1/2}$(Fc/Fc$^+$) = 0.38 V.

of [Cu(CH$_3$CN)$_4$]BF$_4$ to a solution of the tris(benzimidazole) ligand $\mathbf{L^2}$ in dimethylformamide (DMF), followed by precipitation with diethyl ether. Recrystallization of the colorless solid from DMF−acetonitrile−ether resulted in the formation of colorless, cube-shaped crystals of [Cu$_3$(L^2)$_2$(CH$_3$CN)$_2$](BF$_4$)$_3$·5DMF, which were characterized by X-ray crystallography (Figure 4A). The complex contains three copper atoms coordinating two tris(benzimidazole) ligands despite the use of a 1:1 (Cu:L^2) ratio in the synthesis. Both ligands within the molecule act as a bidentate donor through two of the limbs of the tripodal ligand to a copper atom to give an eight-membered chelate ring (Figure 4B). This copper atom is three-coordinate distorted trigonal planar, with the final coordination site occupied by acetonitrile. The remaining limb of each tripodal ligand acts as a bridging monodentate ligand to the second copper atom, which is two-coordinate with a distorted linear geometry, N9−Cu1−N6 167.54(8)°. The Cu−N-*heterocylic* distances are shorter for this two-coordinate copper (Cu1−N9 1.8826(19) Å, Cu1−N6 1.8849(19) Å) when compared to the three-coordinate copper (for example, Cu2−N2 1.999(2) Å). This Cu^I complex is unstable in both solution and the solid state, rapidly decomposing on exposure to air and under vacuum to give green Cu^{II} complexes. This crystal structure adds structural support to speculation on the role of $\mathbf{L^2}$ as an accelerating
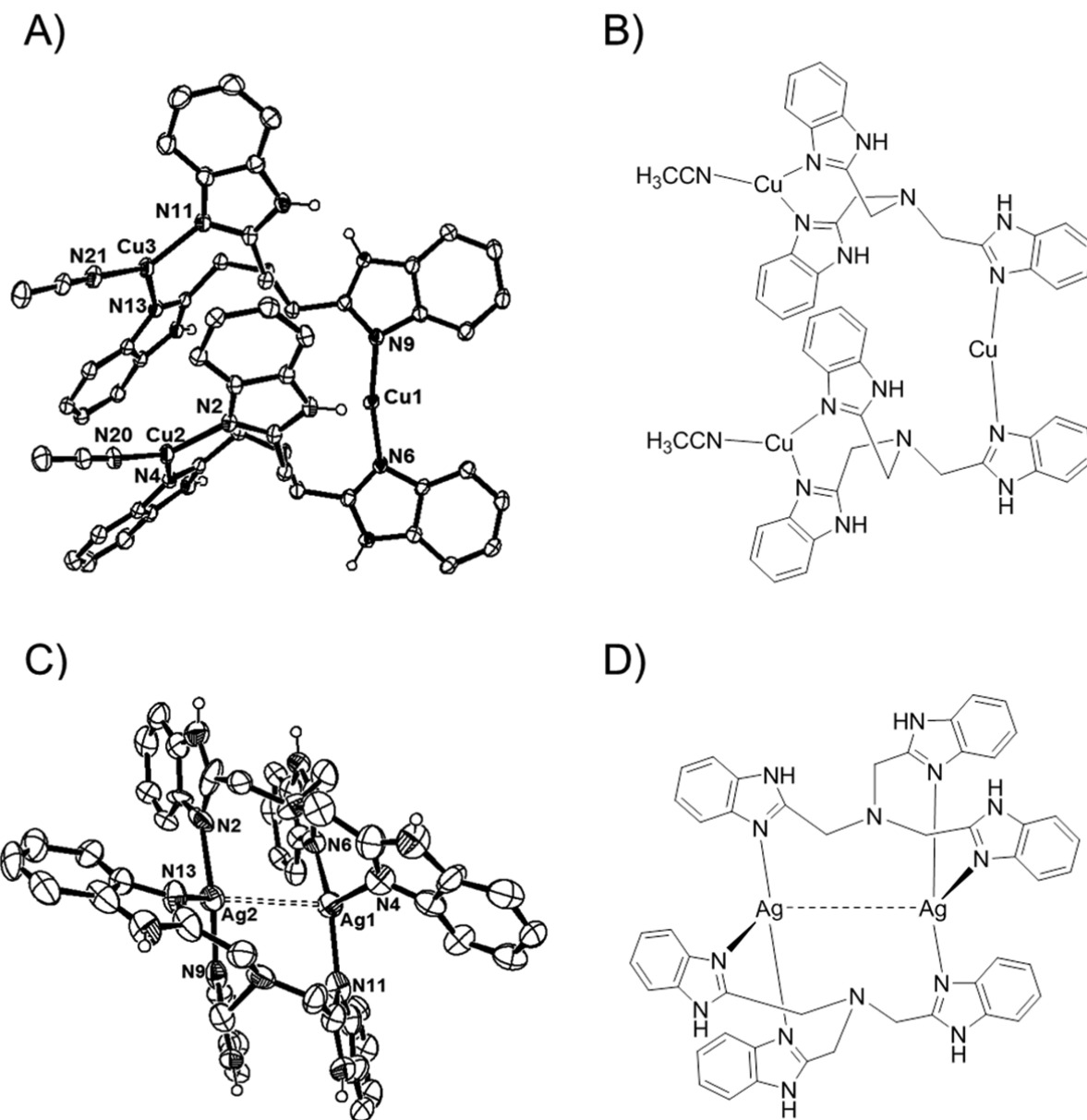
Figure 4. (A) ORTEP representation, with ellipsoids at the 40% probability level, of $[Cu_3(L^2)_2(CH_3CN)_2](BF_4)_3 \cdot 5DMF$, (B) schematic representation of the cation $[Cu_3(L^2)_2(CH_3CN)_2]^{3+}$, (C) ORTEP represenatation, with ellipsoids at the 40% probability level, of $[Ag_2(L^2)_2](BF_4)_2 \cdot 1^1/_2Et_2O$, (D) schematic representation of the cation $[Ag_2(L^2)_2]^{2+}$. Anions, solvent molecules, and hydrogen atoms, except the benzimidazole hydrogens, are omitted for clarity.

ligand in CuAAC reactions. It has been argued that the tripodal nature of L^2 may provide a high local concentration of weakly coordinated limbs at the copper atom and allow access to open coordination sites.[34] Furthermore, the involvement of complexes consisting of two Cu^I ions coordinated to two ligands has been invoked.[34] The bridging Cu^I provides an overall complex where the remaining two essentially equivalent Cu^I ions are held in close proximity, and this could be of some significance given recent mechanistic insight that identified two interchangeable copper atoms in a CuAAC reaction promoted by an N-heterocyclic carbene copper complex.[52] It is plausible that the coordinated acetonitrile molecules could be exchanged for either σ- or π-bound acetylides or organic azides as part of the catalytic cycle. It is also of interest to note that in $[Cu_3(L^2)_2(CH_3CN)_2](BF_4)_3 \cdot 5DMF$ the tertiary nitrogen atoms of L^2 are not coordinated to Cu^I despite evidence

suggesting that electron richness at the metal provided by coordination to a tertiary apical nitrogen aids triazole formation; analogous ligands lacking a central tertiary nitrogen are less effective at accelerating CuAAC reactions.[34]

Synthesis of $[Ag_2(L^2)_2]^{2+}$ and $[Ag_2(L^1)_2]^{2+}$. Complexes of L^2 with Ag^I with different stoichiometry are possible, and $[Ag_3(L^2)_2]^{3+}$- and $[Ag_4(L^2)_2(CF_3CO_2)_2(CH_3CN)_2]^{2+}$-containing complexes have been isolated.[53,54] By altering the stoichiometry of the reagents a new silver complex of L^2, $[Ag_2(L^2)_2](BF_4)_2$, was prepared by the addition of one molar equivalent of $AgBF_4$ to a solution of L^2 in acetonitrile. The X-ray crystal structure reveals a dication with two ligands bridging two silver atoms (Figure 4C). The tripodal ligand adopts the *endo* conformation with three imine N atoms pointing in toward the lone pair of electrons on the apical nitrogen. Each Ag^I is coordinated to two benzimidazole limbs from one ligand

Table 1. Crystal Data and Data Collection and Refinement Parameters

	$[Cu(L^2)(CH_3CN)](BF_4)_2 \cdot 5CH_3CN$	$[Cu_3(L^2)_2(CH_3CN)_2](BF_4)_3 \cdot 5C_3H_7NO$	$[Ag_2(L^2)_2]_2(BF_4)_4 \cdot 3(CH_3CH_2)_2O$	$[Ag(L^1)]BF_4 \cdot CH_3CN$
formula	$C_{36}H_{39}N_{14}CuB_2F_8$	$C_{67}H_{83}N_{21}O_5Cu_3B_3F_{12}$	$C_{108}H_{114}N_{28}O_3Ag_4B_4F_{16}$	$C_{32}H_{31}N_{11}AgBF_4$
M	892.96	1713.59	2630.99	764.36
color and habit	yellow block	colorless block	colorless plate	colorless block
cryst size (mm^3)	$0.4154 \times 0.2722 \times 0.1278$	$0.2700 \times 0.1485 \times 0.0720$	$0.30 \times 0.08 \times 0.02$	$0.4661 \times 0.2064 \times 0.1200$
system	triclinic	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
T (K)	130.00(10)	130.0(2)	130.0(1)	130.0(2)
a (Å)	12.537(5)	14.1830(4)	14.2453(11)	11.8407(5)
b (Å)	12.735(5)	15.9565(4)	16.5697(15)	12.2913(5)
c (Å)	14.852(5)	18.5552(6)	26.1993(18)	14.6737(5)
α (deg)	108.124(5)	79.598(2)	93.610(6)	108.487(3)
β (deg)	103.591(5)	71.313(3)	97.437(6)	96.896(3)
γ (deg)	106.069(5)	73.709(3)	113.695(8)	117.111(4)
$U/Å^3$	2027.3(13)	3799.1(2)	5569.9(8)	1712.01(14)
Z	2	2	2	2
D_{calcd} (Mg m^{-3})	1.463	1.498	1.569	1.483
wavelength (Å)	0.7107 (Mo Kα)	1.541 84 (Cu Kα)	1.541 84 (Cu Kα)	1.541 84 (Cu Kα)
absorp coeff (mm^{-1})	0.622	1.776	6.315	5.261
$F(000)$	916	1764	2668	776
reflns measd	17 327	28 851	32 038	12 409
indep reflns	7112 [$R_{int} = 0.0286$]	14 883 [$R_{int} = 0.0292$]	18 709 [$R_{int} = 0.1649$]	6716 [$R_{int} = 0.0192$]
R [$I > 2\sigma(I)$]	0.0662	0.0407	0.0716	0.0317
$wR(F^2)$ (all data)	0.1805	0.1174	0.1791	0.0870

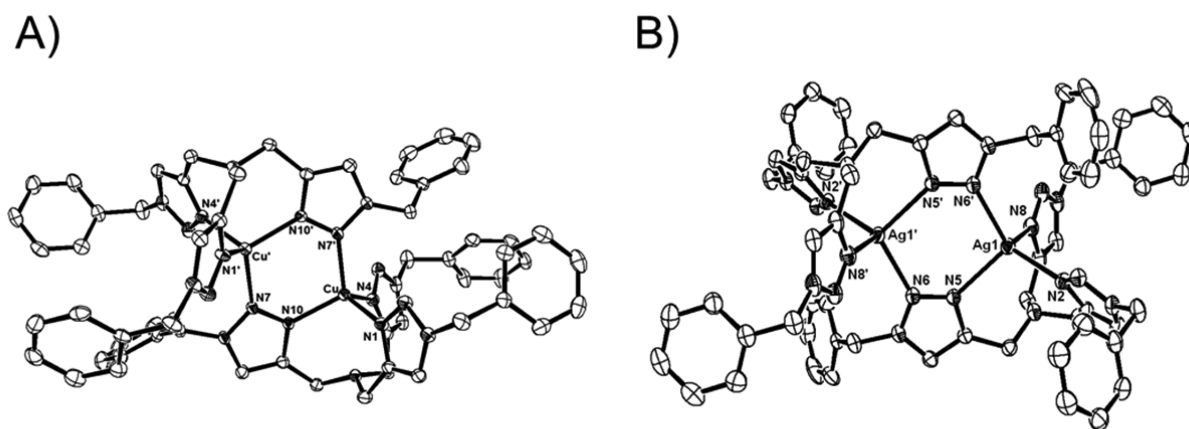**Figure 5.** ORTEP representations, with ellipsoids at the 40% probability level, of (A) $[Cu_2(L^1)_2](BF_4)_2$ from ref 13 and (B) $[Ag_2(L^1)_2](BF_4)_2 \cdot CH_3CN$. Anions, solvent molecules, and hydrogen atoms are omitted for clarity.

and a benzimidazole limb from the other ligand. The Ag^I is in a distorted Ag–N$_3$ trigonal planar environment but with an additional short Ag···Ag contact of 3.095(2) Å, which is shorter than the sum of van der Waals radii (3.44 Å), suggesting a weak argentophilic interaction.[55,56] The structure of $[Ag_2(L^2)_2]^{2+}$ is similar to that of the disilver complex of the N-methylated benzimidazole ligand, but the Ag···Ag distance of that complex is significantly shorter at 2.88 Å.[53] Analysis of $[Ag_2(L^2)_2](BF_4)_2$ by ^{1}H NMR spectroscopy revealed that the resonance due to the benzimidazolyl proton shifts downfield from δ 12.44 ppm in the free ligand to δ 12.91 ppm upon coordination to Ag^I and is accompanied by a small shift in the signals attributed to the methylene protons to δ 4.20 ppm. The complex was not sensitive to ambient light, as the tetrafluoroborate salt in either the solid state or solution and the major signal in positive ion HR-ESI MS was at m/z 514.0902, corresponding to $[Ag^IL^2]^+$
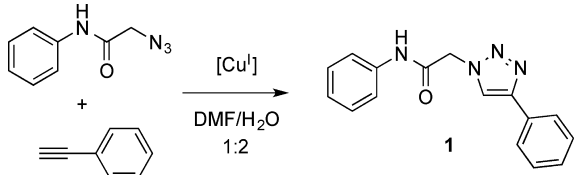
($[C_{24}H_{21}N_7Ag]^+$ requires 514.0909) with no evidence for the dimer observed in the solid state.

The silver complex $[Ag_2(L^1)_2](BF_4)_2$ was prepared by the addition of AgBF$_4$ to a solution of L^1 in acetonitrile followed by precipitation with diethyl ether and was characterized by ^{1}H and ^{13}C NMR spectroscopy, HRMS, and microanalysis. Crystals suitable for single-crystal X-ray crystallography grown from acetonitrile–diethyl ether revealed the colorless crystals to be the dinuclear dication $[Ag_2(L^1)_2]^{2+}$ as the tetrafluoroborate salt and essentially isostructural to the $[Cu_2(L^1)_2]^{2+}$ complex reported previously (Figure 5A and B).[13] $[Ag_2(L^1)_2](BF_4)_2$ is stable with respect to light in both the solid and solution states, with no precipitation of colloidal silver observed upon extended exposure to light. Within the complex, each silver atom is four-coordinate with distorted tetrahedral geometry. Each L^1 ligand is a tridentate donor that binds each Ag^I atom through the proximal nitrogen atoms of the three triazole functional groups,

and the fourth donor atom to Ag^I is provided by a medial nitrogen atom from a triazole group attached to a second bridging ligand to give an overall $[Ag_2(\mu\text{-}(L^1\text{-}\kappa^4\text{-}N^2N^3N^{3'}N^{3''})_2]^{2+}$ dimeric structure (abbreviated as $[Ag_2(L^1)_2]^{2+}$). In the ^1H NMR spectrum of $[Ag_2(L^1)_2]^{2+}$ the resonance attributed to the triazolyl proton is shifted downfield (δ 8.22 ppm) when compared to the free ligand (δ 8.08 ppm), as is the resonance associated with the methylene protons adjacent to the tripodal tertiary amine. The HR-ESI MS reveals a signal for the monomer, $[Ag^IL^1]^+$ m/z = 637.1692 ($[C_{30}H_{30}N_{10}Ag]^+$ requires 637.1706).

Ability of $[Cu_3(L^2)_2(CH_3CN)_2](BF_4)_3$ To Catalyze the Azide-Terminal Alkyne Cycloaddition. The complex $[Cu_3(L^2)_2(CH_3CN)_2](BF_4)_3$ was investigated for its ability to catalyze the cycloaddition of α-azidoacetanilide and phenylacetylene in DMF−water (1:2) (Table 2). Relatively dilute

Table 2. Effect of Copper Source on the Cycloaddition Synthesis of Triazoles[a]

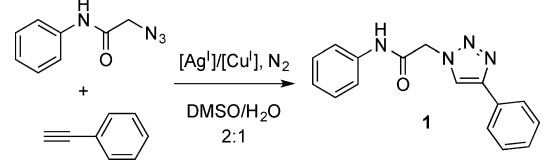| entry	Cu source (1 mol %)	L^2 (mol %)	NaAsc (mol %)	yield[b] (%)
1	CuSO$_4$			0
2	CuSO$_4$		10	9
3	CuSO$_4$	1	10	64
4	[Cu(L^2)(CH$_3$CN)](BF$_4$)$_2$		10	61
5	[Cu(CH$_3$CN)$_4$]BF$_4$			0
6	[Cu(CH$_3$CN)$_4$]BF$_4$	1		0
7	[Cu(CH$_3$CN)$_4$]BF$_4$	1	10	60
8	[Cu$_3$(L^2)$_2$(CH$_3$CN)$_2$] (BF$_4$)$_3$[c]			19

[a]Reactions were carried out in DMF−water (1:2) for 24 h. [b]Yields were determined by ^1H NMR analysis of solids isolated by filtration following dilution of reaction mixtures with water. [c]$[Cu_3(L^2)_2(CH_3CN)_2](BF_4)_3$ was prepared in deoxygenated DMF under an inert atmosphere and added directly to azide and alkyne reagents.

concentrations of the azide and alkyne starting materials (ca. 35 mmol L^{-1}) were used. Copper catalyst and reducing agent (sodium ascorbate) were present at 1 and 10 mol %, respectively (to give final concentrations of Cu of ca. 350 μmol L^{-1}). The reactions were conducted in vials open to the air, and under these relatively challenging conditions the reaction catalyzed by CuSO$_4$ in the presence of sodium ascorbate in the absence of L^2 results in a 9% yield of triazole **1** (entry 2). In comparison the Cu^{II} complex $[Cu(L^2)(CH_3CN)](BF_4)_2$ and sodium ascorbate gave the triazole in 61% yield (entry 4). The isolated Cu^I complex $[Cu_3(L^2)_2(CH_3CN)_2](BF_4)_3$ afforded **1** in a 19% yield (entry 8), highlighting the air sensitivity of CuAAC reactions accelerated with L^2.[33,34] Notably, CuSO$_4$ and L^2 in the presence of ascorbate gave yields similar to that of $[Cu(L^2)(CH_3CN)](BF_4)_2$ as well as $[Cu(CH_3CN)_4]BF_4$ and L^2 both in the presence of ascorbate (entries 3, 4, and 7), suggesting that identical species are responsible for the catalysis.

Catalytic Activity of $[Ag_2(L^1)_2](BF_4)_2$ and $[Ag_2(L^2)_2]$-$(BF_4)_2$ in Azide−Alkyne Cycloaddition Reactions. Mechanistic proposals for the CuAAC reaction invoke stepwise activation of alkyne substrates through the formation of mono-, di-, or polymetallic Cu-η^1 and Cu-η^2 acetylide complexes, resulting in polarization and activation of the alkyne triple bond.[34,57−62] The resulting multicopper complexes are also believed to coordinate to the terminal N of the azide substrate, prior to cycloaddition. The second-row congener Ag^I, like Cu^I, has the ability to act as a σ- and π-Lewis acid, as demonstrated by an extensive array of Ag acetylide complexes.[63−73] Considering the chemical and structural similarity of the isoelectronic $[M_2(L^1)_2]^{2+}$, M = Cu^I or Ag^I, complexes and recent reports of the AgAAC reaction,[35−40] an investigation of the potential of the presented silver complexes to act as catalysts in azide−alkyne cycloaddition reactions was warranted.

The ability of $[Ag_2(L^1)_2](BF_4)_2$ and $[Ag_2(L^2)_2](BF_4)_2$ to catalyze the reaction of phenylacetylene with α-azidoacetanilide at room temperature in DMSO−H$_2$O (2:1) was investigated (Table 3). When compared to the previous reactions used to

Table 3. Effect of Silver Source on the Cycloaddition Synthesis of Triazoles[a]

entry	complex	L^1 (mol %)	NaAsc (mol %)	yield[b] (%)
1	[Ag$_2$(L^1)$_2$](BF$_4$)$_2$ 1 mol %[c]			40
2	[Ag$_2$(L^2)$_2$](BF$_4$)$_2$ 1 mol %			5
3	AgBF$_4$ 1 mol %	1		39
4	AgBF$_4$ 1 mol %			1.2
5		5		0
6			10	0
7		5	10	12
8	CuSO$_4$ 0.03 mol %[c]		10	68
9	CuSO$_4$ 0.03 mol %			10
10	[Cu$_2$(L^1)$_2$](BF$_4$)$_2$ 1 mol %			quant.
11	[Ag$_2$(L^1)$_2$](BF$_4$)$_2$ 1 mol %[c] (using >99.99% AgBF$_4$)			1.1
12	[Ag$_2$(L^2)$_2$](BF$_4$)$_2$ 1 mol % (using >99.99% AgBF$_4$)			0

[a]Reactions were carried out in DMSO−water (2:1) for 72 h in the dark under an inert atmosphere. [b]Yields were determined by ^1H NMR analysis of solids isolated by filtration following dilution of reaction mixtures with water. [c]1 mol % of $[Ag_2(L^1)_2](BF_4)_2$ with 560 ppm copper (as determined by microanalysis) is equivalent to 0.03 mol % CuSO$_4$.

test the Cu^I complexes of L^2, less challenging conditions were applied; the concentration of the organic azide and alkyne starting materials was increased (to ca. 380 mmol L^{-1}), the reaction mixtures were sparged with dinitrogen prior to addition of the catalyst, and the reactions were conducted in sealed vials under an inert atmosphere. The use of $[Ag_2(L^1)_2]$-$(BF_4)_2$ at a catalyst loading of 1 mol % furnished triazole **1** in 40% yield (entry 1). Addition of AgBF$_4$ (1 mol %) by itself did not promote cycloaddition, with only neglible yields of triazole isolated (entry 4), but adding both AgBF$_4$ and L^1 (1 mol %) to

the reaction mixture gave similar yields (entry 3) of triazole **1** to those for the isolated complex $[Ag_2(L^2)_2](BF_4)_2$. The silver complex of the tripodal benzimidazole ligand $[Ag_2(L^2)_2](BF_4)_2$ gave only negligible yields of the triazole **1** (entry 2).

The initial excitement of successful cycloaddition using $[Ag_2(L^1)_2](BF_4)_2$ as a catalyst and thus an apparent AgAAC reaction was tempered by the relatively low yields of triazole formed as well as variations in yields between experiments. Each of the attempted cycloaddition experiments was performed using crystals of the silver complexes that were of sufficient quality for structure determinations, and the consistent molecular structure of isolates from different synthetic preparations was confirmed by X-ray crystallography. To investigate if the low yields of triazole could be a result of catalysis due to trace copper contamination, crystalline samples of $[Ag_2(L^1)_2](BF_4)_2$ were analyzed by microanalysis including determinations of Cu composition. Surprisingly the crystalline samples of $[Ag_2(L^1)_2](BF_4)_2$ were found to contain 560 ± 11 mg kg^{-1} of copper (0.056%, 560 ppm). Obtaining elemental analysis results that were in accordance with the calculated values was difficult due to both the copper contaminant and solvent molecules likely present in the crystal lattice. The source of this trace level of copper is unknown but perhaps is not surprising given the chemical similarities of copper and silver (reagent grade AgBF$_4$ (>98% purity) was used in the synthesis of $[Ag_2(L^1)_2](BF_4)_2$). The trace copper contamination of L^1 itself is possible as the ligand is prepared by a CuAAC reaction between tripropargylamine and benzyl azide[9] and is itself a ligand for Cu^I and Cu^{II}.[13] To minimize copper contamination L^1 was isolated by a modified procedure that included multiple washes with disodium ethylenediaminetetraacetic acid to remove trace copper. This procedure resulted in the preparation of L^1 with a copper concentration of 200 ± 20 mg kg^{-1} (0.02%, 200 ppm). The ability of a very low loading of copper to catalyze the CuAAC reaction of phenylacetylene and α-azidoacetanilide was demonstrated by the use 0.03 mol % Cu(SO$_4$)·5H$_2$O (approximately equal to the trace copper concentration using 1 mol % of $[Ag_2(L^1)_2](BF_4)_2$ (assuming a 0.056% copper contamination)), and sodium ascorbate gave a 68% yield of the triazole **1** (entry 8, Table 3). This suggests that the trace quantities of copper present in $[Ag_2(L^1)_2](BF_4)_2$ are sufficient to account for the low yields of triazole observed. Reactions with L^1 (entry 5) or sodium ascorbate (entry 6) alone were unsuccessful, but a combination of both (entry 7) gave a modest yield of **1**, suggesting that copper contamination is the source of the catalytic activity and that the addition of sodium ascorbate generates catalytically active Cu^I.

The syntheses of $[Ag_2(L^1)_2](BF_4)_2$ and $[Ag_2(L^2)_2](BF_4)_2$ were repeated using high-purity AgBF$_4$ (trace metals basis AgBF$_4$ ($\geq$99.99% purity)). This resulted in Ag$_2(L^1)_2](BF_4)_2$ with a significantly reduced copper content (8 ± 0.8 mg kg^{-1}, 0.0008%, 8 ppm) and a drastic reduction in catalytic activity, with 1.1% yield of **1** for $[Ag_2(L^1)_2](BF_4)_2$ (the residual catalytic activity most likely arises from residual copper present in L^1), and no reaction using $[Ag_2(L^2)_2](BF_4)_2$ as catalyst (entries 11 and 12).

In summary, new Cu^{II} and Cu^I complexes of the tris(benzimidazole)amine ligand L^2 have been isolated and structurally characterized. The Cu^I complex $[Cu_3(L^2)_2(CH_3CN)_2](BF_4)_3$ is an effective catalyst for the CuAAC reaction, both under oxygen-rich conditions in the presence of sodium ascorbate and under oxygen-free conditions in the absence of sodium ascorbate. The structure of

$[Cu_3(L^2)_2(CH_3CN)_2](BF_4)_3$ offers structural insight into the mechanism by which L^2 acts as an accelerating ligand in CuAAC reactions. A Ag^I complex of the tripodal triazole ligand, TBTA (L^1), was isolated that is essentially isostructural to a Cu^I complex reported previously.[13] A new silver complex of L^2 was prepared, and the crystal structure reveals a disilver cation with two ligands bridging two silver atoms. Although a successful cycloaddition of an azide and terminal alkyne is catalyzed by the isolated $[Ag_2(L^1)_2](BF_4)_2$ complex, careful analysis supports the conclusion that catalysis most likely results from trace amounts of copper despite considerable efforts to minimize this contamination. In this context it is noteworthy that polymeric σ-bonded silver acetylides react with azides only in the presence of Cu^I catalysis[70] and that a molecular Ag$_8$Cu$_6$ acetylide complex yields a triazole simply upon exposure to benzyl azide.[73] The importance of trace metal contaminants was highlighted recently in homogeneous cross-coupling reactions that were originally thought to be catalyzed by iron, but later work revealed a ppm trace impurity of Cu in the Fe to be the active catalyst.[74] The present work adds another example to a growing list of instances whereby very low concentrations of contaminating metals can result in catalysis artifacts that can be problematic and misleading.[75,76]

■ EXPERIMENTAL SECTION

General Procedures. Reagents and solvents were purchased from various commercial sources and used without further purification unless otherwise stated. ^{1}H NMR spectra were recorded at 500 MHz, and ^{13}C NMR spectra were collected at 125 MHz on a Varian FT-NMR 500 spectrometer. All chemical shifts are referenced to residual solvent peaks and are quoted in ppm relative to TMS. ESI-MS spectra were recorded on an Agilent 6510 ESI-TOF LC/MS mass spectrometer. Cyclic voltammograms were recorded on an AUTOLAB PGSTAT100 electrochemical workstation using GPES V4.9 software and employed a glassy carbon working electrode, a platinum counter electrode, and a Ag/Ag$^+$ reference electrode (silver wire in acetonitrile (AgNO$_3$ (0.01 mol L^{-1})). All measurements were carried out in HPLC grade acetonitrile that was dried over 3 Å sieves before use. All solutions were 5 mmol L^{-1} of analyte in 0.1 mol L^{-1} tetrabutylammonium tetrafluoroborate solution. Each solution was purged with N$_2$ prior to analysis and measured at ambient temperature under a N$_2$ atmosphere. Microanalyses for C, H, N, Ag, and Cu were carried out by CMAS Chemical & Microanalytical Services Pty. Ltd., Belmont, Vic. Syntheses of L^2,[33] $[Cu_2(L^1)_2](BF_4)_2$,[13] and α-azidoacetanilide[13] were performed according to literature procedures.

Synthesis of L^1. This compound was prepared by modification of a literature procedure.[9] [Cu(MeCN)$_4$]BF$_4$ (89 mg, 0.28 mmol) was added to a solution of tripropargylamine (1 mL, 7.07 mmol), benzyl azide (4.23 g, 31.8 mmol), and 2,6-lutidine (0.82 mL, 0.925 g/mL, 7.07 mmol) in acetonitrile (10 mL) at 0 °C. The reaction was warmed to ambient temperature and stirred for 3 days, during which time precipitate formed. The precipitate was collected by filtration and washed with cold acetonitrile. The solid was suspended in 1 M EDTA solution (pH 9, 150 mL) and stirred vigorously for 2 h, then collected by filtration. The solid was redissolved in ethyl acetate (150 mL), washed with additional 1 M EDTA solution (pH 9, 3 × 100 mL), dried over MgSO$_4$, and then concentrated before hexane (20 mL) was added and the reaction mixture was cooled to 0 °C followed by −20 °C. The precipitate was collected by filtration, washed with hexane, and dried *in vacuo* to afford L^1 (1.88 g, 3.54 mmol, 50%) as a colorless microcrystalline solid. An analytical sample was obtained by recrystallization from ethyl acetate−hexane. NMR spectra were as reported previously.[9] ^{1}H NMR (d_6-DMSO, 500 MHz): δ 8.08 (s, 3H, triazole-*H*), 7.27−7.37 (m, 15H, phenyl-*H*), 5.59 (s, 6H, phenyl-C*H$_2$*), 3.63 (s, 6H, N-C*H$_2$*-triazole). HRMS (ESI$^+$): *m/z* 531.2750 (calcd for $[C_{30}H_{31}N_{10}]^+$ 531.2728). Anal. Calcd for C$_{30}$H$_{30}$N$_{10}$: C, 67.90; H,

5.70; N, 26.40. Found: C, 67.98; H, 5.72; N, 26.36; Cu 200 ± 20 mg kg^{-1}.

Synthesis of [Ag$_2$(L^1)$_2$](BF$_4$)$_2$. AgBF$_4$ (147 mg, 0.755 mmol) was added to a solution of **L^1** (406 mg, 0.764 mmol) in deoxygenated acetonitrile (70 mL). The colorless solution was stirred at ambient temperature in the dark for 90 min, then concentrated under reduced pressure. The resulting pale yellow oil was dried *in vacuo* to give a pale brown solid. The solid was recrystallized from acetonitrile–diethyl ether to yield the product (412 mg, 75%) as a colorless crystalline solid. ^{1}H NMR (500 MHz; d_6-DMSO): δ 8.18 (s, 3H, triazole-*H*), 7.38–7.29 (m, 15H, phenyl-*H*), 5.60 (s, 6H, phenyl-C*H$_2$*), 3.67 (s, 6H, N-C*H$_2$*-triaozle). ^{13}C NMR (126 MHz; d_6-DMSO): δ 144.4, 135.9, 129.3, 128.8, 128.5, 125.1, 53.8, 47.9. HRMS (ESI$^+$): *m/z* 637.1692 (calcd for $[C_{30}H_{30}AgN_{10}]^+$ 637.1707). Anal. Calcd for Ag$_2$C$_{60}$H$_{60}$N$_{20}$B$_2$F$_8$·3CH$_3$CN·(CH$_3$CH$_2$)$_2$O: C, 51.02; H, 4.83; N, 19.55; Ag, 13.09. Found: C, 51.25; H, 4.65; N, 20.26; Ag 14.67; Cu 560 ± 11 mg kg^{-1}. Crystals suitable for X-ray crystallography were grown by vapor diffusion out of acetonitrile and diethyl ether.

Synthesis of [Ag$_2$(L^1)$_2$](BF$_4$)$_2$ with Analytical Grade Reagents. All glassware was washed with freshly prepared aqua-regia, rinsed with Milli-Q water, and allowed to dry at ambient temperature. Plastic spatulas were used for weighing out all reagents. Trace-metal basis AgBF$_4$ (≥99.99%, 96 mg, 0.49 mmol) was added to a solution of **L^1** (262 mg, 0.493 mmol) as prepared *vide supra* in acetonitrile (spectroscopic grade, 25 mL), and the colorless solution was stirred at ambient temperature for 16 h. The solution was concentrated, and diethyl ether added dropwise until turbidity just persisted. The solution was heated to afford full dissolution and then cooled to ambient temperature, followed by 0 °C, then finally −20 °C for 16 h. The precipitate was collected by filtration, washed with diethyl ether, and dried *in vacuo* to yield the product (302 mg, 84%) as a colorless crystalline solid. ^{1}NMR and HRMS spectra were consistent with that observed *vide supra*. Anal. Calcd for Ag$_2$C$_{60}$H$_{60}$N$_{20}$B$_2$F$_8$: C, 49.68; H, 4.17; N, 19.31; Ag, 14.87. Found: C, 49.75; H, 4.18; N, 19.51; Ag, 14.83; Cu, 8 ± 0.8 mg kg^{-1}.

Synthesis of [Cu(L^2)(CH$_3$CN)](BF$_4$)$_2$. A solution of Cu(BF$_4$)$_2$·6H$_2$O (424 mg, 1.23 mmol) in acetonitrile (3 mL) was added to a suspension of **L^2** (500 mg, 0.982 mmol) in acetonitrile (20 mL). The resulting dark green solution was stirred at ambient temperature for 5 min; then diethyl ether was added until turbid, and the solution cooled to −20 °C overnight. The green precipitate was collected by filtration, washed with diethyl ether, and dried *in vacuo* to yield product as fine light green crystals (612 mg, 91%). HRMS (ESI$^+$): *m/z* 235.0588 (calcd for $[C_{24}H_{21}CuN_7]^{2+}$ 235.0572). Anal. Calcd for CuC$_{24}$H$_{21}$N$_7$B$_2$F$_8$·CH$_3$CN: C, 45.54; H, 3.53; N, 16.34. Found: C, 45.23; H, 3.70; N, 16.48. Crystals suitable for X-ray crystallography were grown from slow evaporation of acetonitrile.

Synthesis of [Cu$_3$(L^2)$_2$(CH$_3$CN)$_2$](BF$_4$)$_3$. A solution of [Cu-(MeCN)$_4$]BF$_4$ (28.5 mg, 0.091 mmol) in deoxygenated acetonitrile (0.5 mL) was added to a solution of **L^2** (25 mg, 0.061 mmol) in deoxygenated dimethylformamide (1 mL) in a Schlenk tube equipped with stirrer bar. The mixture was stirred at ambient temperature for 30 min under an inert atmosphere, and deoxygenated diethyl ether (6 mL) was added to afford a white precipitate. The suspension was cooled at −20 °C for 2 days, and the precipitate was collected by filtration under N$_2$, washed with deoxygenated diethyl ether, and dried *in vacuo* to give [Cu$_3$(**L^2**)$_2$(CH$_3$CN)$_2$](BF$_4$)$_3$ as a white powder (18.6 mg, 46%). ^{1}H NMR (90% CD$_3$CN, 10% d_7-DMF, 500 MHz): δ 12.40 (br s, 6H, imidazole-*H*), 7.84–7.24 (m, 24H, phenyl-*H*), 4.12 (s, 12H, N-C*H$_2$*-benzimidazole). Broad signals in the ^{1}H NMR spectra suggested rapid ligand exchange and instability in solution. Analysis at a lower temperature (−60 °C) resulted in only modest improvement. This ligand exchange and instability in solution prohibited the acquisition of a ^{13}C NMR spectrum. Microanalysis of the complex was not obtained, as the compound decomposed upon drying *in vacuo*, most likely following loss of the coordinated solvent. Crystals suitable for X-ray crystallography were grown from a saturated deoxygenated dimethylformamide–acetonitrile (9:1) solution layered with deoxygenated diethyl ether.

Synthesis of [Ag$_2$(L^2)$_2$](BF$_4$)$_2$. AgBF$_4$ (140 mg, 0.719 mmol) was added to a solution of **L^2** (301 mg, 0.738 mmol) in deoxygenated acetonitrile (90 mL). The solution was stirred at ambient temperature in the dark for 4 h under an inert atmosphere. The solvent was removed under reduced pressure, and the crude solid residue was recrystallized from acetonitrile–diethyl ether to give [Ag$_2$(**L^2**)$_2$](BF$_4$)$_2$ (346 mg, 77%) as a colorless powder. ^{1}H NMR (d_6-DMSO, 500 MHz): δ 12.92 (s, 6H, imidazole-*H*), 7.37 (m, 6H, phenyl-*H*), 7.23 (m, 6H, phenyl-*H*), 7.11 (m, 6H, phenyl-*H*), 6.99 (m, 6H, phenyl-*H*), 4.24 (s, 12H, N-C*H$_2$*-benzimidazole). ^{13}C NMR (d_6-DMSO, 126 MHz): δ 153.0, 147.8, 133.5, 123.4, 122.6, 117.8, 112.1, 53.2. HRMS (ESI$^+$): *m/z* 514.0902 (calcd for $[C_{24}H_{21}AgN_7]^+$ 514.0909). Anal. Calcd for Ag$_2$C$_{48}$H$_{42}$N$_{14}$B$_2$F$_8$·6H$_2$O: C, 43.93; H, 4.15; N, 14.94. Found: C, 43.45; H, 3.65; N, 14.77. Crystals suitable for X-ray crystallography were grown by vapor diffusion out of acetonitrile and diethyl ether.

Synthesis of [Ag$_2$(L^2)$_2$](BF$_4$)$_2$ with Analytical Grade Reagents. All glassware was washed with freshly prepared aqua-regia, rinsed with Milli-Q water, and allowed to dry at ambient temperature. Plastic spatulas were used for weighing out all reagents. Trace metal basis AgBF$_4$ (≥99.99%, 113 mg, 0.580 mmol) was added to a suspension of **L^2** (236 mg, 0.579 mmol) in acetonitrile (spectroscopic grade, 40 mL), and the mixture was stirred at ambient temperature for 16 h, during which time the majority of solid dissolved. The turbid solution was filtered through Celite and concentrated, and diethyl ether added dropwise until turbidity just persists. The solution was heated to afford full dissolution and then cooled to ambient temperature, followed by 0 °C, then finally −20 °C for 16 h. The precipitate was collected by filtration, washed with diethyl ether, and dried *in vacuo* to yield the product (216 mg, 62%) as a colorless crystalline solid. A second crop was obtained by concentrating the filtrate and adding a large excess of diethyl ether before collecting the colorless solid by filtration. ^{1}NMR and HRMS spectra were consistent with that observed *vide supra*. Anal. Calcd for Ag$_2$C$_{48}$H$_{42}$N$_{14}$B$_2$F$_8$: C, 47.87; H, 3.52; N, 16.28. Found: C, 47.53; H 3.71; N, 16.33.

Procedure for Cycloaddition Reactions. *General Description of Copper-Catalyzed Reactions.* Reactions were carried out in tubes open to ambient atmosphere in a mixture of DMF–Milli-Q water (1:2; 7.5 mL) with stirring at ambient temperature for 24 h. Reactions were carried out using the indicated copper source with the addition or omission of **L^2** (1 mol %) and sodium ascorbate (10 mol %) as shown in Table 2. Reaction mixtures were diluted with water, allowing precipitation of residual azide and triazole product, followed by filtration and drying. The purity of isolated solids was analyzed by ^{1}H NMR spectroscopy to determine final yield by comparing the integration of CH$_2$ protons of α-azidoacetanilide (δ_H 4.04 ppm) with the CH$_2$ protons of the triazole **1** (δ_H 5.38 ppm).

Representative Procedure. Sodium ascorbate (5 mg, 10 mol %) was added to a solution of phenylacetylene (30 μL, 275 μmol), α-azidoacetanilide (44 mg, 250 μmol), and [Cu**L^2**(CH$_3$CN)](BF$_4$)$_2$ (1.7 mg, 1 mol %) in dimethylformamide (2.5 mL) and Milli-Q water (5 mL). The mixture was stirred at ambient temperature for 24 h. The suspension was diluted with water (10 mL), cooled to 0 °C, and stirred for 1 h. The precipitate was collected by filtration and dried *in vacuo* to yield triazole **1** (42 mg, 61%) as a light brown powder. ^{1}H NMR (d_6-DMSO, 500 MHz): δ 10.49 (s, 1H, N*H*), 8.59 (s, 1H, triazole-*H*), 7.88 (d, *J* = 8.0 Hz, 2H, phenyl-*H*), 7.59 (d, *J* = 7.5 Hz, 2H, phenyl-*H*), 7.45 (t, *J* = 8.0 Hz, 2H, phenyl-*H*), 7.33 (t, *J* = 8.0 Hz, 3H, phenyl-*H*), 7.09 (t, *J* = 7.5 Hz, 1H, phenyl-*H*), 5.38 (s, 2H, amide-C*H$_2$*-triazole).

General Description of Silver-Catalyzed Reactions. Reactions were carried out in sealed tubes under an inert atmosphere in a mixture of DMSO–Milli-Q water (2:1) with stirring at ambient temperature for 72 h. The solvent was sparged with N$_2$ for 15 min prior to addition of the catalyst. Reactions were carried out using the indicated metal source with the addition or omission of **L^1** and sodium ascorbate as shown in Table 3. Purity of isolated solids was analyzed by ^{1}H NMR to determine final yields by comparing the integration of CH$_2$ protons of the α-azidoacetanilide (δ_H 4.04 ppm) with the CH$_2$ protons of the product (δ_H 5.38 ppm).

Representative Procedure. A solution of phenylacetylene (125 μL, 1.14 mmol) and α-azidoacetanilide (200 mg, 1.14 mmol) in dimethyl sulfoxide (2.0 mL) and Milli-Q water (1.0 mL) was sparged with N_2 for 15 min; then $[Ag_2(\mathbf{L^1})_2](BF_4)_2$ (8 mg, 1 mol % of Ag) was added. The reaction mixture was stirred at ambient temperature in the dark for 72 h under an inert atmosphere. The suspension was diluted with water (10 mL), cooled to 0 °C, and stirred for 1 h. The precipitate was collected by filtration and dried *in vacuo* to recover the crude product as a brown powder. Integration of the CH_2 protons by ^1H NMR revealed a final yield of triazole **1** (126 mg, 40%).

X-ray Crystallography. Crystals of compounds $[Ag_2(\mathbf{L^1})_2](BF_4)_2$, $[Cu(\mathbf{L^2})(CH_3CN)](BF_4)_2$, $[Cu_3(\mathbf{L^2})_2(CH_3CN)_2](BF_4)_3$, and $[Ag_2(\mathbf{L^2})_2](BF_4)_2$ were mounted in low-temperature oil, then flash cooled. Intensity data were collected at 130 K (unless otherwise stated) on an X-ray diffractometer with a CCD detector using Cu Kα (λ = 1.54184 Å) or Mo Kα (λ = 0.71073 Å) radiation. Data were reduced and corrected for absorption.[77] The structures were solved by direct methods and difference Fourier synthesis using the SHELX[78] suite of programs as implemented within the WINGX[79] software. Thermal ellipsoid plots were generated using the program ORTEP-3.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

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Notes
The authors declare no competing financial interest.

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