ORGANOMETALLICS

Fluorinated Anions Promoted "on Water" Activity of Di- and Tetranuclear Copper(I) Catalysts for Functional Triazole Synthesis

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S Supporting Information

ABSTRACT: A set of di- and tetra-copper(I) compounds $[Cu_2(L^1H)_2]$ - $[BAr^{F}]_{2}$ (1) (L¹H = bis(5,7-dimethyl-1,8-naphthyridin-2-yl)amine; BAr^{F} = $[B\{C_6H_3(CF_3)_2\}_4])$ and $[Cu_4(L^1)_2(L^2)_2][BNB^F]_2$ (2) $(L^2 = 5,7$ -dimethyl-1,8-naphthyridin-2-amine; $BNB^F = [NH_2\{B(C_6F_5)_3\}_2])$, stabilized by naphthyridine-based ligands and containing fluorinated anions, is synthesized. Their catalytic utility for copper(I)-catalyzed azide-alkyne coupling (CuAAC) reactions in organic solvents and "on water" is evaluated. The dimer analogue $[Cu_2(L^1H)_2][BPh_4]_2$ (3) with nonfluorinated anion is synthesized for the purpose of comparison. All three compounds show CuAAC activity in organic solvents, although the performance of 3 is considerably lower. Remarkable rate enhancement is displayed by compounds containing fluorinated anions (1 and 2) under "on water" conditions for the model reaction involving benzyl azide, affording 98%



conversions in 15-20 min, where compound 3 gives 76% conversions in 50 min. Kinetic experiments reveal the involvement of two coppers in the cycloaddition process. Employing a host of substrates, the usefulness of fluorinated anions to dramatically improve the catalytic activity of Cu(I) compounds under "on water" conditions is demonstrated.

INTRODUCTION

The application of organic solvents for organic reactions stems from solubility and reactivity considerations. Access of light organics from petrochemicals accompanied by a rapid growth of organometallic chemistry fueled the use of organic solvents as a medium for chemical reactions. Environmental and safety concerns, however, have forced researchers to develop green and sustainable methods.¹ One of the important elements to pursue green chemistry is to employ cheap and nonhazardous solvents. Water is obviously an ideal choice.² Besides being cheap and nontoxic, water with its the high heat capacity allows exothermic reactions to be carried out safely. Further, the product isolation is simpler. Despite all these benefits, the low water solubility of organics has prevented widespread use of water in organic reactions. Designing water-soluble catalysts and reagents is not a viable solution since it cripples the range, tolerance, and effectiveness of the reactions.³

There has been continued efforts to use water as solvent for organic reactions. In 1980, Breslow observed significant rate acceleration of the Diels-Alder reaction in homogeneous aqueous solution.⁴ Since then a number of reports have appeared where organic reactions are accelerated in water.^{2b,5} The selectivity too is reported to improve in aqueous medium.⁶ The most interesting discovery was made by Sharpless in 2005. Unusual rate acceleration of a $[2\sigma + 2\sigma + 2\pi]$ cycloaddition of quadricyclane and dimethylazodicarboxylate was observed even when the reactants are not soluble in water.⁷ The rate enhancement in aqueous suspension was found significantly

higher than in neat conditions, prompting Sharpless to ascribe this as an "on water" effect.⁸

The Cu(I)-catalyzed azide and alkyne coupling (CuAAC) reaction is the most convenient method for the synthesis of functional triazole, which is shown to be an effective linker between building units of biological relevance and resembles certain characteristics of a peptide bond.9 The cycloaddition reaction rate is enhanced and the regioselectivity (1,4regioisomer) is improved by Cu(I). The CuAAC reaction tolerates most functional groups, exhibits wide substrate scope with respect to both azides and alkynes, and operates in a variety of solvents and a wide range of pH.¹⁰ Different Cu(I) sources are successfully used in this reaction including Cu(I) salt (CuI), in situ reduction of Cu(II) (particularly CuSO₄ and the reducing agent ascorbic acid), and comproportionation of Cu(II) and Cu(0).^{10b,11} Although ligand-free reactions are fairly effective, nitrogen donor ligands are recognized to play many significant roles, for example, stabilizing Cu(I) from undesired oxidation, acting as a base for alkyne deprotonation, and generating catalytically active clusters from metal aggregates.¹² Kinetic, calorimetric, isotope crossover experiments, and DFT calculations clearly suggest a second-order rate with respect to Cu.¹³ It is now well accepted that the reaction proceeds through a stepwise mechanism where alkyne and azide bind to two different but closely spaced Cu ions. The second Cu

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activates the azide and further engages in π -interaction with terminal acetylide bound to the first copper. The overall activation barrier is computed to be substantially lower than a single Cu pathway.¹⁴

We recently demonstrated that fluorinated anion BAr^F [tetrakis(3,5-bis(trifluoromethyl))phenyl borate] (Scheme 1a)





induces "on water" activity of the Ag(I) salt for the hydration of terminal alkynes.¹⁵ To widen the scope of this chemistry for reactions that do not necessarily utilize water as one of the substrates, metal complexes containing fluorinated anions are examined for "on water" CuAAC reaction. Since the active catalysts are known to involve at least two copper ions, a 1.8naphthyridine-based ligand, capable of stabilizing bimetallic systems, is used.¹⁶ A discrete dinuclear Cu(I) compound is synthesized containing nitrogen donor ligands bis(5,7-dimethyl-1,8-naphthyridin-2-yl)amine (L1H) (Scheme 1c) and two BAr^F anions (Scheme 1a). Use of the ditris-(pentafluorophenyl)borane amide (BNB^F) (Scheme 1b) anion resulted in the formation of a tertanuclear compound. A dinuclear analogue with a nonfluorinated BPh₄ anion is also synthesized for the sake of comparison. Di- and tetranuclear Cu complexes exhibit higher "on water" activity than in organic solvents. However, complexes containing fluorinated anions are evidently more effective than complexes containing nonfluorinated anions. This work thus demonstrates the utility of fluorinated anions to dramatically improve "on water" activity of organometallic catalysts.

RESULTS AND DISCUSSION

Synthesis and Structures. Room-temperature reaction of $L^{1}H$ with one equivalent of $[Cu(CH_{3}CN)_{4}][OTf]$ in acetonitrile afforded a red solid, which was characterized as $[Cu_{2}(L^{1}H)_{2}][OTf]_{2}$ by ESI-MS, IR spectroscopy, and CHN analysis. A signal at an m/z ratio of 392 (z = 2) is attributed to the dicationic unit $[Cu_{2}(L^{1}H)_{2}]^{2+}$ on the basis of the mass and isotopic distribution pattern. The IR spectrum exhibits an absorption at $\nu = 1070 \text{ cm}^{-1}$ for the triflate anion. Poor solubility in common organic solvents hindered further characterization.

The solubility was considerably improved by exchanging the anions. Mixing a solution of $[Cu(CH_3CN)_4][OTf]$, L^1H ligand, and NaBAr^F in acetonitrile afforded $[Cu_2(L^1H)_2][BAr^F]_2$ (1) in high yield (90%). The molecular structure of 1 revealed a discrete dicopper(I) complex (Figure 1) where two L^1H ligands span two copper atoms. The asymmetric unit contains half of



Figure 1. Dicationic unit of 1 with selective atom labeling. Displacement ellipsoids are set at 30% probability, and hydrogen atoms are omitted for clarity. The prime character (') indicates atoms at the symmetrically equivalent positions. Selected bond distances (Å) and angles (deg): Cu1-Cu1' 2.4813(13), Cu1-N2 1.982(5), Cu1-N4 2.034(4), Cu1-N5' 1.935(4), N5'-Cu1-N2 129.1(2), N5'-Cu1-N4 139.1(2), N2-Cu1-N4 89.46(19), N5'-Cu1-Cu1 88.56(14), N2-Cu1-Cu1 119.67(13), C11-N3-C10 127.8(5).

the molecule related to the other half by a C_2 axis bisecting the Cu…Cu vector. One naphthyridine unit of each ligand bridges two copper atoms and additionally chelate one copper utilizing the proximal nitrogen atom of the second naphthyridine. The geometry around each copper center is distorted trigonal planar. The Cu…Cu distance is 2.4813(13) Å. The N–Cu–N angles imposed by three nitrogens of two ligands at Cu are 89.46(19)°, 129.1(2)°, and 139.1(2)°. The Cu–N bond lengths vary within a range of 1.935(4)-2.034(4) Å. The ESI-MS spectrum shows a signal at m/z ratio of 392 (where z = 2) assigned for the dicationic unit $[Cu_2(L^1H)_2]^{2+}$. The IR spectrum confirms the absence of triflates for the bulk solid.

A reaction identical to that of 1 but with NaBNB^F afforded a tetranuclear complex, $[Cu_4(L^1)_2(L^2)_2][BNB^F]_2$ (2), where L² is 5,7-dimethyl-1,8-naphthyridin-2-amine (NP-NH₂), a ligand that is presumably generated by hydrolysis of L¹H under reaction conditions. The X-ray structure of 2 (Figure 2) confirms a tetranuclear structure spanned by two L¹ and two L² ligands. The deprotonated ligand L1 bridges two independent dicopper units as shown in Figure 2 utilizing two naphthyridine nitrogens to bridge one dicopper unit and an amido nitrogen and one naphthyridine nitrogen to bridge the second pair of copper. Each L^2 bridges two copper atoms through naphthyridine nitrogens, and the amine unit remains free. The asymmetric unit contains one-half of the tetramer connected to the other half by a center of inversion. The Cu1-Cu2 and Cu2-Cu2' distances are 2.4559(6) and 2.7064(8) Å, respectively.

Use of NaBPh₄ under identical conditions resulted in a dinuclear complex, $[Cu_2(L^1H)_2][BPh_4]_2$ (3), in moderate yield (55%). The relatively lower yield is due to partial anion exchange. Analytically pure product is isolated by extraction with dichloromethane, in which the triflate analogue is insoluble. IR absorption reveals the absence of triflates in the product. ESI-MS is identical to 1, suggesting a dinuclear composition (Figure S1).



Figure 2. Dicationic unit of 2 with selective atom labeling. Displacement ellipsoids are set at 50% probability, and hydrogen atoms are omitted for clarity. The prime character (') indicates atoms at the symmetrically equivalent positions. Selected bond distances (Å) and angles (deg): Cu1-Cu2 2.4559(6), Cu2-Cu2' 2.7064(8), Cu1-N2 1.978(3), Cu1-N5' 1.996(3), Cu1-N7 2.038(3), Cu2-N3 2.006(3), Cu2-N4' 2.025(3), Cu2-N6 2.065(3), N2-Cu1-N5' 128.48(12), N2-Cu1-N7 115.82(12), N5'-Cu1-N7 115.65(11), N2-Cu1-Cu2 87.20(8), N3-Cu2-N4' 130.05(12), N3-Cu2-N6 115.71(12), N4'-Cu2-N6 113.20(11), N3-Cu2-Cu1 88.37(9).

Although BAr^F and BPh₄ anions afforded dinuclear complexes 1 and 3, BNB^F gave tetranuclear complex 2. This is most likely due to adventitious moisture, which breaks down the ligand L¹H to generate L², and subsequent self-assembly of Cu(I) and the ligands results in 2. The NaBAr^F and NaBPh₄ are dried well, but NaBNB^F is highly hygroscopic and could not be made completely moisture free. As a result, the ligand is hydrolyzed, causing formation of the tetranuclear complex.¹⁷

Catalytic Studies. In Organic Solvents. To evaluate the catalytic efficiency of 1 for the azide-alkyne cycloaddition reaction, initial experiments were carried out using phenylacetylene (1 mmol), benzyl azide (1 mmol), and catalyst 1 (0.01 mmol) in tetrahydrofuran (THF) at room temperature. Without any additives such as nitrogen bases, full conversion to 1-benzyl-4-phenyl-1H-1,2,3-triazole was observed after 5 h. Purification of the product by silica gel column chromatography with petroleum ether/ethyl acetate (3:2 v/v) provided 95% isolated yield (Table 1, entry 1a). The solvent effect was examined using model substrates. No significant change was observed in other organic solvents including dichloromethane and acetonitrile. In neat conditions only 42% product was obtained after 5 h.18 Under optimal conditions, the functional group tolerance and substrate scope were examined in THF. Aromatic alkynes (1a-f, 1t, Table 1) as well as heteroaromatic alkynes (1g, 1h, Table 1) afforded excellent yields (85–98%) of the corresponding triazoles with the exception of 1-ethynyl-3,5bis(trifluoromethyl)benzene (entry 1i), which did not react under identical conditions. In general, aromatic alkynes with electron-withdrawing groups reacted faster than the same bearing electron-donating groups. Aromatic alkyne 2-ethynyl-6methoxynaphthalene with a bulky substituent (entry 1j) gave a moderate yield (60%). All aliphatic alkynes (1k-s, 1u, 1y, Table 1) gave products with moderate to good yields (58-80%), and a relatively longer reaction time was required in comparison to aromatic alkynes. Reactions of phenylacetylene with other organic azides, such as tosyl azide, trimethylsilyl

azide, and hexyl azide, afforded corresponding functionalized triazoles (**1v**, **1w**, **1x**) in good yields. The catalytic performance of **1** compares well with other copper(I) catalysts under homogeneous conditions^{10a-c,14d} with a notable exception of Straub's N-heterocyclic carbene based dicopper(I) catalyst,^{13c} which displays higher activity in dichloromethane.

"On Water" Condition. A dramatic increase in the rate was noticed when the model reaction was carried out under "on water" conditions (phenylacetylene/benzyl azide/catalyst = 1/ 1/0.01 mmol; 4 mL of water), affording 98% yield within 20 min (Figure S2). This is despite the fact that both substrates and catalyst 1 are immiscible with water. Changing the solvent to D₂O drastically lowered the yield, providing a maximum conversion of 50% in 20 min. For a wide range of substrates studied in this work (aliphatic or aromatic), the CuAAC reactions proceeded much faster under "on water" conditions than in THF. Aromatic alkynes with electron-withdrawing groups such as *p*-F and *o*-CHO reacted readily with benzyl azide "on water" to form the desired products in nearquantitative yields (98-100%) within 10 min (Table 1, 1b and 1c). Electron-rich aromatic alkynes bearing electron-donating groups such as 2,5-Me, p-OMe, and p-Me gave comparatively lower yields (87-92%) in 30 min (Table 1, 1d, 1e, 1f). Although 1-ethynyl-3,5-bis(trifluoromethyl)benzene (Table 1, 1i) did not react in THF, 99% yield was obtained within 10 min under "on water" conditions. The ethynyl group on a heterocyclic ring such as 3-ethynylthiophene and 2-ethynylpyridine "on-water" afforded 92% and 95% yields within 30 min, respectively (Table 1, 1g and 1h). The bulkier 2-ethynyl-6methoxynaphthalene (Table 1, 1j) gave a moderate yield of 72% after 45 min. Aliphatic alkynes (Table 1, 1k–1s and 1u) are less reactive and took more time to reach completion, a trend similar to that observed in THF. 1,3-Diethynylbenzene gave the monoaddition product with one equivalent of benzyl azide but gave a mixture of mono- and diaddition products in 80:20 ratio with two equivalents of benzyl azide. 1.7-Dioctadyene gave exclusively the diaddition product (Table 1, It and Iu). Tosyl azide, trimethylsilyl azide, and hexyl azide gave corresponding triazoles (1v, 1w, 1x) in good yields with phenylacetylene "on water" in a short reaction time. Cycloaddition of terminal alkyne, attached to a purine base, gave the corresponding triazole (92%, 30 min) (Table 1, 1y). A scaledup reaction with 5 mmol of benzyl azide and phenylacetylene each in 10 mL of water did not cause any appreciable loss of yield and purity of the product (96%, 20 min).

The catalytic efficiencies of all three compounds are compared both "on water" and in THF for the model reaction (Figure 3). Consumptions of alkyne were measured in regular time intervals by GC-MS using dodecane as internal standard. All three compounds display remarkably enhanced activity "on water" than in THF. Compounds 1 and 2, containing fluorinated anions, are highly active "on water" and give nearquantitative yields in 15-20 min. Compound 3, containing BPh₄, is the least active under both conditions, but affords product up to 76% in 50 min "on water". Compound 2 is found to be slightly better "on water" than 1, but the difference is more pronounced in THF. The relative performances of 1, 2, and 3 are compared with a selected set of substrates, and the general trends are found to be the same as that of the model reaction (Table 2). The "on water" protocol with Cu(I) complexes containing fluorinated anions appears highly efficient compared to other heterogeneous methods and aqueous and solvent-free CuAAC reactions.¹⁹

Table 1. Compound 1-Catalyzed [3 + 2] Cycloaddition of Benzyl azide with Various Alkynes^{*a,b*}

R————Н + ∬

$$la (95\%, 5 h)^{e}, (98\%, 20 min)^{d}$$

$$lb (99\%, 2 h)^{e}, (100\%, 10 min)^{d}$$

$$lc (90\%, 8 h)^{e}, (87\%, 30 min)^{d}$$

$$le (90\%, 8 h)^{e}, (90\%, 30 min)^{d}$$

$$le (90\%, 8 h)^{e}, (90\%, 30 min)^{d}$$

$$lg (90\%, 8 h)^{e}, (92\%, 30 min)^{d}$$

$$lh (95\%, 8 h)^{e}, (95\%, 30 min)^{d}$$

$$li (60\%, 12 h)^{e}, (72\%, 45 min)d$$

$$lk (80\%, 12 h)^{e}, (78\%, 60 min)^{d}$$

$$ln (65\%, 12 h)^{e}, (72\%, 60 min)^{d}$$

$$ln (65\%, 12 h)^{e}, (71\%, 60 min)^{d}$$

$$lq (70\%, 6 h)^{e}, (73\%, 50 min)^{d}$$

$$lr (65\%, 12 h)^{e}, (71\%, 60 min)^{d}$$

$$lq (70\%, 6 h)^{e}, (73\%, 50 min)^{d}$$

$$lr (65\%, 12 h)^{e}, (71\%, 60 min)^{d}$$

$$lq (70\%, 6 h)^{e}, (73\%, 50 min)^{d}$$

$$lr (65\%, 12 h)^{e}, (71\%, 60 min)^{d}$$

1s (60%, 12 h)^c, (58%, 60 min)^a

1v (92%, 6 h)^c, (90%, 30 min)^a



1 mol% Cat.1

1t (92%, 6 h)^c, (95%, 30 min)^d

1w (75%, 10 h)^c, (68%, 60 min)^c



1y (88%, 6 h)^c, (92%, 30 min)^d

^aAzide (1 mmol), alkyne (1 mmol), and catalyst 1 (0.01 mmol) at room temperature. ^bIsolated yields. ^cIn THF (4 mL). ^dOn water (4 mL). ^eTwo equivalents of azide were used.

D

Kinetic Studies. The initial rate of reaction was monitored (up to $\sim 10-15\%$ conversion) to determine the order with respect to catalyst 1. Reactions were performed with varying concentrations of 1 and equimolar amounts of phenylacetylene, benzyl azide, and dodecane (internal standard). The initial rate varied linearly with catalyst concentration, and the reaction was found to be first-order with respect to 1 (Figure S3a). Further, equimolar amounts of azide, alkyne, and dodecane (n_{azide} = $n_{\text{alkyne}} = n_{\text{dodecane}}$) were mixed with 1 mol % of catalyst 1 in 4 mL of THF. Each aliquot of 0.2 mL was taken out at a regular time interval and immediately quenched by flash column chromatography, and the amount of unreacted phenylacetylene was measured using GC-MS against an internal standard.

According to the integrated rate law for the reaction of the type $A + B \rightarrow C$ with the restriction [A] = [B] at t = 0, the 1/ [alkyne], vs time plot fit well to a second-order kinetics (Figure S4). Both of these experiments thus suggest the involvement of catalyst 1, azide, and alkyne, one molecule each, in the ratedetermining step. As one molecule of catalyst 1 consists of two copper centers, it can be argued that the reaction is taking place on the bimetallic platform. The effect of temperature on the rate of the reaction of 1 was also examined. The activation parameters were determined from the plot of $\ln(k/T)$ vs 1/T, which was linear over the temperature range studied (303-333 K) (Figure S5). The estimated entropy of activation (ΔS^{\ddagger}) is -42.50 ± 1.89 cal mol⁻¹ K⁻¹, and the enthalpy of activation

8%, 2 h)^c, (98%, 10 min)^d



%. 24h)^c. (99%. 10 min)^d

2%, 12 h)^c, (75%, 60 min)^a



55%, 12 h)^c, (70%, 60 min)^d



52%, 12 h)^c, (65%, 60 min)^d



1u^e (68%, 12 h)^c, (65%, 60 min)^a



1x (70%, 12 h)^c, (76%, 60 min)^d



Figure 3. Conversion vs time plots for catalysts 1, 2, and 3 in THF and "on water" at 30 $^\circ$ C for the model reaction.

 (ΔH^{\ddagger}) is 6.24 \pm 0.59 kcal mol⁻¹. A large and negative ΔS^{\ddagger} value is consistent with a concerted cycloaddition in the ratelimiting step.

Similar experiments were carried out with catalyst **2**. The plot of initial rate vs [catalyst **2**] revealed that the order with respect to **2** is 1.49, a value in between first-order and second-order. The $1/[alkyne]_t$ vs time plot is also not linear (Figure S3b). It appears that two dicopper units in **2** do not act independently, and reaction on one dicopper impedes the activity of the second unit.

"On-Water" Effect. The remarkable increase in rate and yield of the CuAAC reaction under "on water" conditions deserves an explanation. The Cu(I) catalysts and alkynes are dissolved in benzyl azide, creating an organic phase. It is pertinent to mention here that the solubility of compounds 1 and 2 is higher than that of 3 in common organic solvents. Nonpolar organic molecules when placed in water are brought together out of mutual repulsions. The high surface tension of water favors minimal contact between hydrophobic molecules and polar water, allowing all components to mix intimately, causing the reaction rate to accelerate. Furthermore, to explain

enhanced "on water" activity, Marcus and Jung proposed a model where one OH group out of four water molecules protrudes out at the organic-aqueous interface (Figure S6).⁸ The free surface hydroxyl groups favor "docking" of insoluble organic molecules via a hydrogen-bonding interaction at the interface as on a catalyst surface. This water arrangement at the oil-water interface is attributed to a higher reaction rate. It is argued that catalysts containing fluorinated anions interact with the surface hydroxyl hydrogen via hydrogen bond interactions²⁰ and thus accelerate the reaction rate compared to homogeneous or neat conditions. Such an interaction is absent with nonfluorinated anions. In accordance with this model, a vigorous mixing is needed to achieve the highest efficiency of the catalyst by maximizing the surface area. Indeed, the reaction is slow when carried out in D₂O due to its higher viscosity affecting efficient mixing. It is our assertion that both enforced hydrophobic interactions and enhanced surface interactions contribute to the improved "on water" activity promoted by the fluorinated anions.

CONCLUSIONS

In conclusion, we report here three active di- and tetranuclear copper(I) catalysts with fluorinated BAr^F and BNB^F as well as nonfluorinated BPh4 for CuAAC reactions. Although these catalysts are effective in organic solvents, the reaction rate was greatly enhanced under "on water" conditions. More importantly, compounds with fluorinated anions display clear superiority "on water" compared to the one with a nonfluorinated anion. Enforced hydrophobic interactions between organic components on the water surface and enhanced interaction of a fluorinated catalyst with a free hydroxyl group at the oil-water interface are tentatively attributed to higher activity. Inclusion of fluorinated anions in cationic complexes to achieve improved catalytic activity "on water" is an attractive option in terms of simplicity, short reaction time, easy product isolation, and sustainability. Further studies are being carried out with catalysts containing fluorinated anions for a variety of reactions to establish a general trend and decipher the underlying reasons for enhanced "on water" activity.





^aAzide (1 mmol), alkynes (1 mmol), and catalysts 1 (0.01 mmol), 2 (0.005 mmol), and 3 (0.01 mmol) on water (4 mL) at room temperature. ^bIsolated yields.

EXPERIMENTAL SECTION

General Procedures. All reactions with metal complexes were carried out under an atmosphere of purified nitrogen using standard Schlenk vessel and vacuum line techniques. The crystallized compounds were powdered, washed several times with dry petroleum ether, and dried under vacuum for at least 48 h prior to elemental analyses. ¹H NMR spectra were obtained on a JEOL JNM-LA 500 MHz spectrometer. ¹H NMR chemical shifts were referenced to the residual hydrogen signal of the deuterated solvents. The chemical shift is given as dimensionless δ values and is frequency referenced relative to TMS for ¹H and ¹³C NMR spectroscopy. Elemental analyses were performed on a Thermoquest EA1110 CHNS/O analyzer. The GC-MS experiment was performed on an Agilent 7890A GC and 5975C MS system. Infrared spectra were recorded in the range 4000-400 cm⁻¹ on a Vertex 70 Bruker spectrophotometer on KBr pellets. ESI-MS were recorded on a Waters Micromass Quattro Micro triplequadrupole mass spectrometer.

Materials. Solvents were dried by conventional methods, distilled under nitrogen, and deoxygenated prior to use. $B(C_6F_5)_3$, NaNH₂, 1-bromo-3,5-bis(trifluoromethyl)benzene, and all alkynes used in the catalysis reaction were purchased from Sigma-Aldrich. NaBPh₄ was purchased from Spectrochem Pvt. Ltd. L^1H , 21 [Cu-(CH₃CN)₄(OTf)], 22 NaBAr^{F,23} and Na[NH₂{B(C₆F₅)₃}₂] were synthesized according to the literature procedures.

Synthesis of $[Cu_2(L^1H)_2](OTf)_2$. To a stirring suspension of L¹H (60 mg, 0.18 mmol) in 15 mL of acetonitrile was added one equivalent of $[Cu(CH_3CN)_4(OTf)]$ (69 mg, 0.18 mmol). The reaction mixture was allowed to stir for 1 h at room temperature under a N₂ atmosphere. The solvent was reduced to 1 mL. A 10 mL amount of diethyl ether was added to induce precipitation. The solid precipitate was washed and filtered. This process was repeated three times, and the red-colored solid product was dried under vacuum. Yield: 174 mg (88%). ESI-MS, m/z: 392 $[Cu_2(L^1H)_2]^{2+}$. IR (KBr, cm⁻¹): ν (OTf) 1070. Anal. Calcd for $C_{42}H_{38}Cu_2F_6N_{10}S_2O_6$: C, 46.57; H, 3.54; N, 12.94. Found: C, 46.53; H, 3.50; N, 12.91.

Synthesis of [Cu₂(L¹H)₂][BAr^F]₂ (1). To a stirring suspension of L¹H (50 mg, 0.15 mmol) in 15 mL of acetonitrile was added one equivalent of [Cu(CH₃CN)₄(OTf)] (59 mg, 0.15 mmol). The reaction mixture was allowed to stir for 1 h at room temperature under a N₂ atmosphere. Subsequently one equivalent of NaBAr^F (134 mg, 0.15 mmol) was added, and stirring was continued for an additional 4 h. The deep red reaction mixture was filtered through a small pad of Celite. The solvent was evaporated under vacuum, and the resultant solid mass was dissolved in 1 mL of dichloromethane. A 10 mL amount of petroleum ether was added to induce precipitation. The solid precipitate was washed and filtered. This process was repeated three times, and the red-colored solid product was dried under vacuum. X-ray quality crystals were grown by layering petroleum ether onto a saturated dichloromethane solution of 1 inside an 8 mm o.d. vacuum-sealed glass tube. Yield: 353 mg (90%). ¹H NMR (500 MHz, CD₃CN, 292 K): δ 11.99 (br, 2H), 7.46-8.21 (m, 36H), 2.51 (s, 12H), 2.44 (s, 12H). ¹³C NMR (125 MHz, CD₃CN, 294 K): δ 161.9, 134.7, 128.8, 127.8, 125.6, 123.5, 121.3, 117.5, 22.5 17.5. ¹⁹F NMR (500 MHz, CD₃CN, 292 K): δ –62.37 (s, 48F). ESI-MS, m/z: 392 $[Cu_2(L^1H)_2]^{2+}$. Anal. Calcd for C₁₀₄H₆₂B₂Cu₂F₄₈N₁₀: C, 49.71; H, 2.49; N, 5.58. Found: C, 49.67; H, 2.45; N, 5.53.

Synthesis of [Cu₄(L¹)₂(L²)₂][NH₂[B(C₆F₅)₃]₂]₂ (2). The reaction of L¹H (51 mg, 0.15 mmol), [Cu(CH₃CN)₄(OTf)] (57 mg, 0.15 mmol), and NaBNB^F (164 mg, 0.15 mmol) was carried out by following a procedure similar to that described for the synthesis of 1. X-ray quality crystals were grown by layering petroleum ether onto a saturated dichloromethane solution of 2 inside an 8 mm o.d. vacuum-sealed glass tube. Yield: 404 mg (80%). ¹H NMR (500 MHz, CD₃CN, 292 K): δ 8.09 (d, J = 9 Hz, 6H), 7.14 (d, J = 9 Hz, 6H), 7.22 (s, 6H), 5.67 (br, 4H), 2.55 (s, 12H), 2.40 (s, 12H). ¹³C NMR (125 MHz, CD₃CN, 294 K): δ 148.8, 146.9, 140.2, 138.3, 137.9, 137.8, 135.9, 135.8, 135.6, 134.8, 118.2, 116.9, 29.9, 21.9. ¹⁹F NMR (500 MHz, CD₃CN, 292 K): δ 134.38 (s, 12F), 160.38 (s, 6F), 166.32 (s, 12F). Anal. Calcd for

 $\rm C_{132}H_{62}B_4Cu_4F_{60}N_{18}$: C, 47.51; H, 1.87; N, 7.56. Found: C, 47.47; H, 1.84; N, 7.52.

Synthesis of $[Cu_2(L^1H)_2][BPh_4]_2$ (3). To a stirring suspension of $L^{1}H$ (50 mg, 0.15 mmol) in 15 mL of acetonitrile was added one equivalent of [Cu(CH₃CN)₄(OTf)] (57 mg, 0.15 mmol). The reaction mixture was allowed to stir for 1 h at room temperature under a N_2 atmosphere. Subsequently one equivalent of NaBPh₄ (52) mg, 0.15 mmol) was added, and again the reaction mixture was stirred 4 h. The acetonitrile solvent was evaporated under vacuum, and the resultant solid mass was dissolved in 10 mL of dichloromethane. The suspension was filtered through a small pad of Celite. The solvent was evaporated under vacuum, and the resultant solid mass was dissolved in 1 mL of dichloromethane. A 10 mL amount of petroleum ether was added to induce precipitation. The solid precipitate was washed and filtered. This process was repeated three times, and the orange-red solid product was dried under vacuum. Yield: 118 mg (55%). ¹H NMR (500 MHz, CD₃CN, 292 K): δ 8.94 (br, 2H), 6.78–6.79 (m, 12H), 7.25-7.29 (m, 24H), 7.62 (m, 4H), 7.78-7.80 (m, 4H), 7.99-8.01(m, 8H), 3.10 (s, 12H), 2.64 (s, 12H). ¹³C NMR (125 MHz, CD₃CN, 294 Κ): δ 163.8, 161.1, 1473, 135.9, 134.3, 129.9, 129.4, 128.6, 126.7, 125.6, 122.2, 121.7,115.5, 24.1, 18.2. ESI-MS, m/z: 392 [Cu₂(L¹H)₂]²⁺. Anal. Calcd for C₈₈H₇₈B₂Cu₂N₁₀: C, 74.23; H, 5.52; N, 9.84. Found: C, 74.19; H, 5.48; N, 9.81.

General Procedure for the Catalytic Reaction in THF. Catalyst (0.01 mmol for 1 and 3, 0.005 mmol for 2), alkyne (1 mmol), and benzyl azide (1 mmol) were taken in 4 mL of THF. The reaction mixture was stirred at room temperature inside a closed glass tube, and the progress of the reaction was monitored by TLC. After the completion of the reactions the products were purified by chromatography on a silica gel column using hexane/EtOAc (3:2 v/ v) as eluent. The isolated products were characterized by ¹H and ¹³C NMR and ESI-MS spectra.

General Procedure for the Catalytic Reaction Using Water as Solvent. Catalyst (0.01 mmol for 1 and 3, 0.005 mmol for 2), alkyne (1 mmol), and benzyl azide (1 mmol) were taken in 4 mL of water. The reactants are insoluble in water. The mixture was stirred vigorously at room temperature. After completion of the reaction, water was decanted off and the solid products were dried under vacuum. The products were further purified by chromatography on a silica gel column using hexane/EtOAc (3:2 v/v) as eluent. The isolated products were characterized by ¹H and ¹³C NMR and ESI-MS spectra. Alternatively, the solid products were washed with hexane, dried, and recrystallized from methanol. NMR pure products could be obtained without any appreciable loss of yields.

ASSOCIATED CONTENT

S Supporting Information

Crystallographic table and supporting schemes and figures are provided. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/ acs.organomet.Sb00348.

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Notes

The authors declare no competing financial interest.

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