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Large Cu¹₈ Chalcogenone Cubic Cages with Non-interacting Counter Ion

Katam Srinivas^a and Ganesan Prabusankar*^a

Two mega size copper(I) cubic cages, $[\{Cu(Bptp)\}_3(PF_6^-)_7 (1) \text{ and } [\{Cu(Bpsp)\}_3(PF_6^-)_7 (2) \text{ supported by imidazole-2-chalcogenone ligands (Bptp = 2,6-bis(1-isopropylimidazole-2-thione)pyridine or Bpsp = 2,6-bis(1-isopropylimidazole-2-selone)pyridine) have been synthesized and characterized. The formation of ionic salts 1 and 2 were confirmed by FT-IR, multinuclear (¹H, ¹³C, ³¹P and ¹⁹F) NMR, UV-vis, TGA, CHN analysis, BET, single crystal X-ray diffraction and powder X-ray diffraction techniques. To the best of our knowledge, these are the first examples of octanuclear copper(I) cluster in a perfect cubic architecture with copper-copper distances of 8.413 Å or 8.593 Å. Interestingly, these anion-centered Cu¹₈ cubic arrangements are not supported by cubic centered ions or face centered molecules. Formation of cationic cubic cages were accompanied by the association of twelve ligands (Bptp or Bpsp) with eight trigonal planar [CuSe₃] vertex. The cationic charge of cubic cages were satisfied by eight PF₆⁻ counter anions, in which one of the PF₆⁻ anion occupies at the centre of Cu₈ cube without any interaction. The copper(I) cubic cages are found to be highly active catalysts in click chemistry as well as hydroamination reactions. The scope of the catalytic reactions have been investigated with thirty five different combinations in click reactions and six different combinations in hydroamination of alkynes.$

Introduction

The chemistry of copper-NHC (NHC = N-heterocyclic carbene) has attracted much attention in the past two decades with invoking requirements in catalysis.¹ The most of the known copper-NHC molecules are mononuclear, dinuclear, trinuclear or tetranuclear.² Though, more than twelve hundred articles have been reported (according to the SciFinder search on "Copper Carbene") related to the copper carbene chemistry, the NHC-Cu clusters are rare.³ Unlike phosphine based copper clusters,⁴ the penta⁵ or higher nuclear copper-NHC derivatives and their catalytic applications are limited due to strong σ donor and poor π accepting nature of NHC along with steric hindrance.⁶ The search for the suitable NHC or analogues of NHC type ligands to isolate the polynuclear copper clusters or cages are in great demand.⁷ Therefore it is one of the most challenging task to design the synthetic strategy using NHC or NHC analogues for clusters or cages of specific nuclearity with shape.^{7d-I} Recently, the NHC analogues of imidazole-2chalcogenone copper(I) complexes have been reported with

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promising features in catalysis due to the tunable σ -donor and π -accepting nature of imidazole-2-chalcogenone.⁸ Surprisingly, the catalytic efficiency of copper-imidazole-2-chalcogenone complexes is better than copper-NHC complexes. Herewith we first perfect Cu₈ cubic report the cages $[{Cu(Bptp)}_{8}(PF_{6})](PF_{6})_{7}$ (1) and $[{Cu(Bpsp)}_{8}(PF_{6})](PF_{6})_{7}$ (2) supported by imidazole-2-chalcogenone ligands (Bptp = 2,6bis(1-isopropylimidazole-2-thione)pyridine or **Bpsp** = 2,6-bis(1isopropylimidazole-2-selone)pyridine). To the best of our knowledge, 1 and 2 are the large copper cubic cages isolated as of now.

Experimental

Materials

All manipulations were carried out under argon atmosphere using standard Schlenk techniques. The solvents were purchased from commercial sources and purified according to standard procedures and freshly distilled under argon atmosphere prior to use.⁹ Unless otherwise stated, the chemicals were purchased from commercial sources. 1,1'- (pyridine-2,6-diyl)bis(3-isopropyl-1*H*-imidazol-3-ium)bromide, 2,6-Bis(1-isopropylimidazole-2-thione)pyridine (**Bptp**)¹⁰ and 2,6-bis(1-isopropylimidazole-2-selone)pyridine (**Bpsp**) ligands were synthesized as reported.¹¹ 2,6-dibromo pyridine, Sulphur powder, selenium powder and [Cu(CH₃CN)₄]PF₆ were purchased from Sigma Aldrich and used as received. **Instrumentation**

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FT-IR measurement (neat) was carried out on a Bruker Alpha-P Fourier transform spectrometer. The UV-vis spectra were measured on a T90+ UV-visible spectrophotometer. Thermogravimetric analysis (TGA) was performed using a TASDT Q600, Tzero-press. NMR spectra were recorded on Bruker Ultrashield-400 spectrometers at 25 °C unless otherwise stated. Chemical shifts are given relative to TMS and were referenced to the solvent resonances as internal standards. Elemental analyses were performed by the Euro EA-300 elemental analyser. The crystal structures of 1 and 2 were measured on an Oxford Xcalibur 2 diffractometer. Single crystals of complexes suitable for the single crystal X-ray analysis were obtained from their reaction mixture at room temperature and the suitable single crystals for X-ray structural analysis were mounted at room temperature (298 K) in inert oil under an argon atmosphere. Using Olex2,¹² the structure was solved with the ShelXS¹³ structure solution program using Direct Methods and refined with the olex2.refine refinement package using Gauss-Newton minimization. Absorption corrections were performed on the basis of multi-scans. Non-hydrogen atoms were anisotropically refined. Hydrogen atoms were included in the refinement in calculated positions riding on their carrier atoms. No restraint has been made for any of the compounds. CCDC 1573682 and 1573683 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif 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.

Synthesis of 1. [Cu(CH₃CN)₄]PF₆ (0.069 g, 0.185 mmol) was dissolved in acetonitrile (3 mL) in an oven dried Schlenk flask under inert atmosphere, to which Bptp (0.100 g, 0.278 mmol) in chloroform was added dropwise and was allowed to stir for 12 h. Yield: 93% (0.128 g, based on [Cu(CH₃CN)₄]PF₆). M.p.: 220-223 °C (melting). Elemental analysis calcd (%) for $C_{23.5}H_{32.5}N_{7.5}S_3Cu_1P_1F_6$ (724.76): C, 38.94; H, 4.52; N, 14.49; S, 13.27; Found: C, 38.8; H, 4.5; N, 14.7; S, 13.3. ¹H NMR (DMSOd₆, 400 MHz): 1.37-1.39 (d, 2((CH₃)₂CH), 12H), 4.90-4.94 (m, 2(CH₃)₂CH, 2H), 7.74 (d, imidazole, 2H), 7.86 (d, imidazole, 2H), 8.07-8.08 (d, pyridine, 2H), 8.39-8.43 (t, pyridine, 1H) ppm. ¹³C NMR (DMSO-d₆, 100 MHz): 21.03 ((CH₃)₂CH), 49.40 ((CH₃)₂CH), 116.88 (pyridine), 119.99 (imidazole), 120.36 (imidazole), 142.97 (pyridine), 147.56 (pyridine), 155.87 (C=S) ppm. ³¹P NMR (DMSO-*d*₆, 161 MHz): -157.36 to -131.02 (sept, *P*F₆) ppm. ¹⁹F NMR (DMSO-*d*₆, 376 MHz): -71.05 to -69.16 (d, P*F*₆) ppm. FT-IR (neat): \bar{v} 3156(w), 2978(w), 1671(w), 1596(m), 1459(s), 1400(s), 1342(m), 1279(w), 1221(s), 1130(m) (C=S), 1070(w), 995(w), 828(vs) (P–F), 730(m), 682(m), 553(s) (P–F) cm⁻¹.

Synthesis of 2. $[Cu(CH_3CN)_4]PF_6$ (0.055 g, 0.146 mmol) was dissolved in acetonitrile (3 mL) in an oven dried Schlenk flask under inert atmosphere, to which **Bpsp** (0.100 g, 0.220 mmol) in chloroform was added dropwise and was allowed to stir for 12 h. Yield: 81% (0.105 g, based on $[Cu(CH_3CN)_4]PF_6$). M.p.: 215-216 °C (melting). Elemental analysis calcd (%) for $C_{23.5}H_{32.5}N_{7.5}Se_3Cu_1P_1F_6$ (865.45): C, 32.61; H, 3.79; N, 12.14;

Found: C, 32.7; H, 3.8; N, 12.8. ¹H NMR (DMSO- d_6 , 400 MHz): 1.36-1.37 (d, 2((CH₃)₂CH), 12H), 4.92 (m, 2(CH₃)₂CH, 2H), 7.88 (d, imidazole, 2H), 8.01 (d, imidazole, 2H), 8.14-8.15 (d, pyridine, 2H), 8.45 (t, pyridine, 1H) ppm. ¹³C NMR (DMSO- d_6 , 100 MHz): 21.20 ((CH₃)₂CH), 51.57 ((CH₃)₂CH), 118.79 (pyridine), 122.26 (imidazole), 122.71 (imidazole), 143.71 (pyridine), 148.51 (pyridine), 154.19 (*C*=Se) ppm. ³¹P NMR (DMSO- d_6 , 161 MHz): -157.32 to -130.98 (sept, *P*F₆) ppm. ¹⁹F NMR (DMSO- d_6 , 376 MHz): -71.06 to -69.17 (d, *PF*₆) ppm. FT-IR (neat): $\bar{\nu}$ 3156(w), 2977(w), 1692(w), 1574(m), 1458(s), 1420(s), 1341(m), 1217(w), 1116(m) (C=Se), 1073(w), 1045(w), 829(vs) (P–F), 758(m), 732(m), 677(m), 586(m), 554(s) (P–F) cm⁻¹.

Cu(I) catalysts catalysed azide–alkyne cycloaddition reactions (**CuAAC**). Catalyst 1 or 2 (1 mol%), azide (1 mmol) and terminal alkyne (1.2 mmol) were placed in an oven dried schlenk flask. The reaction mixture was then allowed to stir at room temperature and the progress of the reaction was monitored by thin layer chromatography. The solid mass obtained was dissolved in ethyl acetate and passed through silica gel column. The solvent has been removed by rotary evaporator and the residue washed several times with n-hexane yielded pure desired products. All the isolated products were well characterized by ¹H and ¹³C NMR and few products (**Ia**, **Ib**, **IIa** and **IIb**) were also characterized by single crystal X-ray diffraction analysis.

Cu(I) catalysts mediated hydroamination of terminal alkynes with substituted anilines. Catalysts 1 or 2 (1 mol %) and AgBF4 (1 mol %) were placed together in an oven dried schlenk flask. The schlenk flask was then evacuated and refilled with nitrogen two to three times. Subsequently, acetonitrile (1 mL) was added to the mixture and was allowed to stir at room temperature for 5-10 minutes. After which, the corresponding arylamine (0.6 mmol) and terminal alkyne (0.50 mmol) were added successively. The resulting mixture was allowed to stir at 70 °C for the appropriate time and the progression of the reactions were determined by thin layer chromatography. And the isolated imines were well characterized by ¹H and ¹³C NMR spectroscopy.

Results and discussion

Synthesis and characterization

The octanuclear copper(I) cubic clustes **1** and **2** were isolated in excellent yield by treating $[Cu(CH_3CN)_4]PF_6$ with an appropriate amount of **Bptp** or **Bpsp** in acetonitrile/chloroform mixture (Scheme 1). Pyridine-based organo dichalcogenone ligands **Bptp** and **Bpsp** were synthesized in a single step *via* the reactions of pyridine bridged imidazolium dibromide derivatives with elemental chalcogen powder in the presence of K₂CO₃ in good yield.

The ionic salts **1** and **2** were confirmed by FT-IR, multinuclear (¹H, ¹³C, ³¹P and ¹⁹F) NMR, UV-vis, TGA, CHN analysis, BET, single crystal X-ray diffraction and powder X-ray diffraction techniques. **1** and **2** are stable under ambient conditions for

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several months and soluble in polar solvents such as acetonitrile and DMSO. In ¹H NMR, the isopropyl CH signal is upfield shifted by around 0.3 ppm, while imidazole CH signals are downfield shifted by 0.4 to 0.9 ppm. The hydrogen at 4th position in the pyridine unit appeared to be downfield shifted by 0.4 ppm, while the other protons at 3^{rd} and 5^{th} position in pyridine moiety appears to be upfield shifted by 0.4 to 0.6 ppm compared to free ligands. The ¹³C NMR spectra of the copper(I) complexes 1 and 2 are mostly the same with very little shift in the resonances when compared to the respective ligand precursors. In ¹³C NMR, the C=S and C=Se signal in 1 and 2 appeared to be upfield shifted (5 ppm for 1 and 1 ppm for 2 compared to corresponding ligand), respectively. This can be attributed to the strong σ donor and poor π accepting nature of the carbone carbon upon complexation with copper(I). The 31 P NMR spectra shows a septet for the presence of PF₆ counter ions in 1 and 2. The ¹⁹F NMR spectra depicts a doublet for PF₆ counter ions in **1** and **2**.



The ionic salts 1 and 2 crystallized in the cubic space group, Pn-3n. The crystallographic data for 1 and 2 are furnished in table S1 (see Supporting information-1). The solid-state structures with selected bond lengths and bond angles are reported in figures 1. Liu and co-workers have reported several octanuclear copper(I) clusters using phosphorus-chalcogenide as suitable ligand, where the presence of interacting elementary ion into the center of a centerosymmetric copper cluster or cubic cage is very essential to retains the original symmetry of the cluster.¹⁴ Notably, a tremendous efforts have been made to alter the size of the octanuclear copper core.¹⁵ The size of the metal core can be altered based on the size and charge of anion present in the center of cage.¹⁶ In all these aforementioned Cu₈(I) cubic cages, the edge length between Cu(I)…Cu(I) in octanuclear copper cubic cage ranges from 2.859 Å to 3.225 Å.^{16c} Surprisingly, the known $Cu_8(I)$ cubic cages were isolated only using $[(^{i}PrO)_{2}PE_{2}]^{-}$ (E = Se or S) ligands. However it appears that the (i) similar such cages have never been reported with any other ligands; (ii) octanuclear copper cubic cages with larger than Cu(I)....Cu(I) edge length of 3.225 Å have never been isolated. Thus, the neutral donor ligand,

imidazole-2-chalcogenone can be an ideal replacement for anionic ligand [('PrO)₂PSe₂]⁻ to generate octanuclear copper(I) clusters. Though several copper(I) cubic cages have been isolated with centered atom (mainly halogen or chalcogen or hvdride etc), only one copper(I) cubic cage. $[Cu_8{Se_2P(O'Pr)_2}_6](PF_6)_2$ has been reported without centered atom,16a where the Cu…Cu seperations are not equal (3.216(1) and 3.220(1) Å). 1 and 2 are the first examples of perfect copper(I) cubic cages known without non-interacting centered atom or molecule.

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Fig. 1 (I) The solid state structure of 1 and 2. Hydrogen atoms and PF₆ counter anions have been omitted for the clarity. Dotted lines between copper centres are imaginary lines. (II) Core structure of cubic cage. Hydrogen atoms, carbon atoms and PF₆ counter anions have been omitted for the clarity. Dotted lines between copper centres are imaginary lines. (III) Coordination environment of copper(I) in 1 and 2. Selected bond lengths (Å) and angles (°) for 1: C(1)–S(1), 1.700(2), S(1)–Cu(1), 2.249 (6), S(1)–Cu(1)–S(1), 120.0, N(1)–C(1)–N(2), 105.07(19), N(1)–C(1)–S(1), 125.17(18), N(2)–C(1)–S(1), 129.74(18), C(1)–S(1), -Cu(1), 12.72(8). Selected bond lengths (Å) and angles (°) for 2: C(1)–Se(1), 1.856(5), Se(1)–Cu(1), 2.338(5), Se(1)–Cu(1)–Se(1), 120.0, N(1)–C(1)–N(2), 105.0(4), N(1)–C(1)–Se(1), 124.5(4), N(2)–C(1)–Se(1), 130.4(4), C(1)–Se(1)–Cu(1), 109.45(14).

The faces of the cubanes **1** and **2** are open. Notably, the distance between copper atoms in **1** (8.413 Å) and **2** (8.593 Å) are equal. The diagonal distance between Cu····Cu is 14.571 Å (for **1**) and 14.883 Å (for **2**). The Cu····Cu diagonal distance found in **1** and **2** are nearly 50% shorter than the diagonal Fe····Fe distance found in the large Fe^{II}/Ni^{II} face capped cubic box (25.622 Å).¹⁷ The solid-state structures of complexes **1** and **2** consists of one cubic $[Cu_8(Bptp/Bpsp)_{12}]^{8+}$ cation and eight $[PF_6]^-$ anions, in which each copper center is linked by three ligands. The E–Cu–E bond angles around copper centers in **1** and **2** are in favour of trigonal planar arrangement.

The carbon–sulfur bond lengths in **1** is 1.700(2) Å, which is closer to that of (C=S, 1.61 Å) double bond^{18a} than a single bond distance (C–S, 1.83 Å).^{18b} The carbon–selenium bond length in **2** is 1.856(5) Å, which is closer to that of a C–Se single bond distance (1.94 Å)^{19a} than a C=Se double bond distance (1.74 Å).^{19b} The S–Cu distance (2.249 (6) Å) in complex **1** is slightly shorter than that of dichloro-[(η^3 -S,S,N)(2,6-bis){[N-isopropyl]imidazole-1-ylidene-2-thione}-pyridine copper(II)] (2.30-2.32 Å).²⁰ The Se–Cu bond length (2.338(5) Å) found in **2** is slightly elongated than that of [(IPr=Se)₂Cu]X and [(IMes=Se)₂Cu]X (Where X = BF₄ and ClO₄) (2.24-2.27 Å).^{8c}

PXRD and Thermogravimetric analysis

The PXRD pattern of bulk crystalls of **1** and **2** are nearly comparable with calculated PXRD pattern of corresponding single crystal data (See supporting information 1, Figure S16 and S17), which clealy supports the phase purity of bulk samples of **1** and **2**.



Fig. 2 TGA curves of **1** and **2** from 30 to 550 °C under a nitrogen atmosphere with a heating rate of 10 °C min⁻¹. For **1**: residual wt 26%, calc. wt 23%; For **2**: residual wt 39%, calc. wt 40%.

Moreover, the theremal stability of **1** and **2** is not comparable (Figure 2). The thermal decomposition pathway of **1** is much clear than **2**. **1** and **2** depicted enough stability until 200 °C. Then compound **1** shows a little weight loss (5%), which can be attributed to the phase change in **1**. Subsequently **1** shows enough stability until 305 °C then observed a sudden weight loss in a single step to give Cu_2S residue (26%, Calcd. 23%), which can be attributed to the decomposition of organic moieties in **1**. Besides, **2** depicts gradual weight loss from its melting point (210 °C) through minor phase transformations along with the organic moieties decomposition to yield Cu_3Se_2 residue (39%, Calcd. 40%).

UV-visible absorption studies

The solution state and solid state UV-visible absorption spectra of **1** and **2** are compared with **Bptp** and **Bpsp**, respectively (Figure 3). Almost similar absorption patterns for $\pi \rightarrow \pi^*$ (200-300 nm) and $n \rightarrow \pi^*$ (300–350 nm) transitions are observed in the solution state UV-vis spectroscopy for both the ligands and their copper(I) complexes (**1** and **2**). Bathchromic shift was noticeed for **Bpsp** and **2** compared to **Bptp** and **1**. Interestingly, in the solid state UV-vis study, complexes **1** and **2** depicted the bathochromic shift along with broadening of absorption band due to a strong molecular association in solid state form compared to their solution state study.



Fig. 3 UV-vis spectra of Bptp, Bpsp, 1 and 2 (Solution state in acetonitrile at 25 °C, 2.8 x 10^{-5} M).

Miscellaneous investigations

Considering the size of these cages, **1** was subjected to BET analysis. The maximum quantity adsorbed at STP is 1.45 cm³/g, which is not very impressive (See Supporting Information, Figure S15). Besides, the attempts to transmetallate copper in **1** by gold using (dms)AuCl were unproductive (See Supporting Information 2, Note 1). Both **1** and **2** undergoes dissociation to result the starting materials by depositing gold metal on the surface of the flask. In order to understand the host-guest property of these cages, the preliminary studies were carried out between **1** and pyrene or perylene (See supporting

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information 2, Note 2). 1 act as a host for both perylene and pyrene to result 1@perylene and 1@pyrene, respectively. Notably the perylene uptake by 1 is much faster than pyrene. Attempt to introduce C_{60} into 1 was not successful.

Catalytic examinations

Subsequently, **1** and **2** were employed for azide-alkyne cycloaddition reactions to produce 1,2,3-triazoles under mild conditions (Scheme 2, Table 1). Though, the catalytic reactions were promising both in water medium (entry 1) and under neat conditions (entry 2), the less reaction time was noticed for the solvent free reaction over the water media reaction.



Scheme 2 Catalysts 1 and 2 mediated one-pot synthesis of triazoles.

 Table 1 Optimization studies for CuAAC reaction mediated by Copper(I) catalysts 1 and

 2.^a

Entry	Catalyst	Cat.	Solvent	Time (min)	Yield
		(110178)		(11111)	(70)
1	1	1	water	30	>99
2	1	1	neat	15	>99
3	1	0.5	neat	60	98
4	1	0.1	neat	180	94
5	1	2	neat	15	>99
6	2	1	neat	20	>99
7	[Cu(CH₃CN)]PF ₆	1	neat	60	45

 $^a\!\rm Reaction$ conditions: phenyl acetylene (0.6 mmol), benzyl azide (0.5 mmol) and solvent (2 mL). $^b\!\rm Isolated$ yield

Besides, the yield of la was decreased, when the catalyst mol% was decreased (for 0.5 mol%, see entry 3 and for 0.1 mol%, see entry 4). However, the extension of time led to the isolation of quantitative yield of Ia. On the other hand, not much improvement in the yield was observed by reducing the time or increasing catalyst loading (2 mol%, entry 5). Notably, catalyst 2 requires little longer time than the catalyst 1 (entry 6). In addition, less amount of product formation (la) was observed under solvent free conditions using only $[Cu(CH_3CN)_4](PF_6)$ (entry 7). Further, we have explored the scope of the reactions using benzyl azide, 4-nitrobenzylazide, 4-bromobenzylazide, phenylazide and 2,4,6-trimethyl phenylazide with a varieties of terminal alkynes using 1 mol% of 1 and/or 2 as catalysts under solvent free conditions. The yield of the product was excellent (>95%, Chart 1).



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Chart 1 a Reaction conditions: alkyne (1.2 mmol), azide (1 mmol), Catalyst 1 and/or 2 (1 mol%), neat, isolated yield.

The isolated products were characterized by ${}^{1}H$ and ${}^{13}C$ NMR spectroscopy. The solid state structures of isolated products **Ia**, **Ib**, **IIa**, and **IIb** were additionally evaluated by single crystal X-ray diffraction analysis.

In addition to this the catalysts longevity has been investigated using 1 mol% of catalyst **1** with benzyl azide and phenyl acetylene in neat conditions at room temperature and it was found that the same catalyst can produce appreciable yields for eight successive cycles. Moreover, PXRD studies on reused catalyst revealed that the catalyst exists as an intact octanuclear cage rather than dissociated molecules (Figure 4 and also See supporting information-2, Note 3).

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mmol) and phenyl acetylene (1.2 mmol) under neat conditions at room temperature.

Since the copper catalyzed one-pot synthesis of triazoles, by a three-component reaction (organic bromide, sodium azide and an alkyne; in order to avoid azide isolation) is very much demanding,²¹ the **1** and **2** mediated one-pot reactions were performed in water (Scheme 3).



The catalysts **1** and **2** gave remarkable yield (> 90%) from reactants with electron-rich or electron-poor azides and alkynes (See Supporting information-2, Chart S1). The catalytic efficiency of **1** and **2** are comparable with cationic $[Cu(NHC)_2]^+$ systems.²² Thus, it was realized that the co-coordinatively unsaturated Cu(I) centers with trigonal planar arrangement along with open face cubic arrangement allow the CuAAC reaction substrates to conveniently approach the metal center on cubic surface to trigger the reaction (See supporting information-2).

Moreover, the catalysts **1** and **2** were highly active and selective (Markovnikov's product) for the hydroamination of terminal alkynes with arylamines (Scheme 4, Table 2). The reaction was performed between phenyl acetylene and 2,6-dimethyl aniline in acetonitrile using 1 mol% catalyst **1** or **2** along with 1 mol% AgBF₄ as cocatalyst.



Table 2 Optimization studies for hydroamination reaction mediated by Copper(I) catalysts 1 and 2.^a

Entry	Catalyst	Cat.	Solvent	Time	Yield
		(mol%)		(h)	(%) ^b
1	1	1	CH₃CN	2	>99
2	2	1	CH₃CN	2	>99
3 ^c	1	1	CH₃CN	3	98
4 ^d	1	1	CH₃CN	12	72
5	1	1	Benzene	2	20
6	1	1	CH₃OH	2	70
7	1	1	THF	2	65
8 ^e	1	1	CH₃CN	2	90
9	AgBF₄	1	CH₃CN	12	30
10	Ag(OTf)	1	CH₃CN	12	25

^aReaction conditions: phenyl acetylene (0.5 mmol), 2,6-dimethylaniline (0.6 mmol) and solvent (2 mL). ^bIsolated yield, ^cwithout AgBF₄, ^dreaction performed at room temperature, ^ewith Ag(OTf).

The reaction proceeds very smoothly with both the catalysts in presence of AgBF₄ in 2 h (entry 1 and 2). Besides the absence of AgBF₄ required slightly longer time (3 h) for the completion of hydroamination reaction (entry 3). On the other hand, moderate yield was noticed for the same reaction performed at RT for 12 h (entry 4). However, benzene (entry 5), methanol (entry 6) and tetrahydrofuran (entry 7) produced moderate yields. The presence of Ag(OTf) along with catalyst 1 gave fairly good yield (entry 8). However, AgBF₄ presence is significant in this transformation. The starting material conversion was not appriciable only with $AgBF_4$ (entry 9) or Ag(OTf) (entry 10) under longer reaction times. Therefore acetonitrile was anticipated to be the best solvent for this transformation with quantitative yields. The catalysts were highly active (yield, from 92 to 99%) with excellent functional group tolerance (Chart 2) and the catalytic efficiency of 1 or 2 are on par with Cu-NHC catalysts.^{22b,23}





 VIIc, 98%, 97%
 VIIc, 92%, 96%

Chart 2 Isolated products of hydroamination reaction catalyzed by copper(I) catalysts 1 and 2.^a aReaction conditions: alkyne (0.5 mmol), substituted aniline (0.6 mmol) and solvent (2 mL).

Conclusions

In summary, the large octanuclear Cu(I) cubic cages (1 and 2) supported by organo dichalcogenones were synthesized and characterized. 1 and 2 are the first examples of perfect Cu(I) cubic cage with Cu(I)·····Cu(I) distance of 8.413 Å (for 1) and 8.593 Å (for 2). Formation of cationic cubic cages were accompanied by the association of twelve ligands (Bptp or Bpsp) with eight trigonal planar [CuSe₃] vertex. The cationic charge of cubic cages were satisfied by eight PF₆⁻ counter anions, in which one of the PF₆⁻ anion occupies at the centre of Cu₈ cube without any interaction. Moreover, 1 and 2 are found to be very active catalysts in click chemistry under mild condition, one pot synthesis of triazoles as well as the selective hydroamination of terminal alkynes.

Conflicts of interest

The authors have no conflicts of interest to declare for this article.

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Table of Contends

Synthesis and applications of two mega size octanuclear copper(I) chalcogenone cages have been reported.



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