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Self-Assembled Cyclophane-Type Copper(I) Complexes of 2,4,6-Tris(diphenylphosphino)-1,3,5-triazine and Their Catalytic Application

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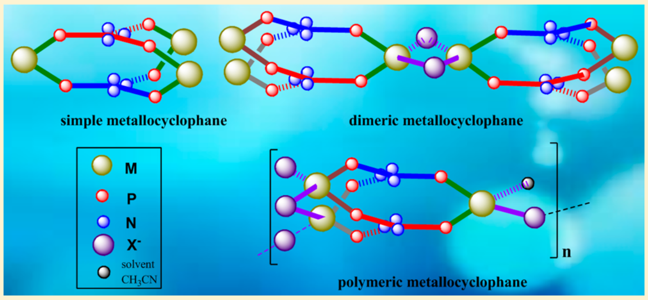
Supporting Information



ABSTRACT: The triazine-based trisphosphine, 2,4,6-tris(diphenylphosphino)-1,3,5-triazine (**1**) was prepared in improved yield by reacting cyanuric chloride with 3 equiv of trimethylsilyldiphenylphosphine. The solid-state structure of **1** showed short intermolecular P···P contacts of 3.362 Å, which is significantly shorter than the sum of the van der Waals radii of phosphorus atoms (3.6 Å). The reaction of 2,4,6-tris(diphenylphosphino)-1,3,5-triazine (**1**) with copper(I) salts in a 2:3 molar ratio yielded various cyclophane-type complexes in quantitative yield. The solid-state structures of these clusters have been found to depend on the size of the halide ions, the solvent employed, and the reaction conditions. Copper(I) chloride formed a monomeric metallocyclophane, whereas copper(I) bromide and copper(I) iodide derivatives preferred dimeric and 1D-polymeric structures, respectively. The tricationic complexes derived from Cu^I ion and 2,4,6-tris(diphenylphosphino)-1,3,5-triazine also adopted monomeric metallocyclophane structures. These complexes have been employed in the A^3 coupling reaction under microwave irradiation. The copper(I) iodide derivative showed excellent catalytic efficiency.

■ INTRODUCTION

Metal-assisted self-assembly for the construction of supramolecular architectures with specific functions has become an attractive approach in recent years.[1−5] These supramolecular systems find numerous applications in catalysis,[6−8] photovoltaics,[9,10] therapeutic agents,[11−13] storage,[14,15] and chemical sensors.[2,16,17] The most used building blocks for the construction of transition-metal-based self-assemblies are platinum group metals.[18−20] Recently, extensive studies have focused on group 11 metal complexes because of their rich photophysical properties.[21,22] Copper(I) halides readily form complexes with soft donor ligands in which the coordination number of the metal center can be varied between two to four. Because of this geometrical flexibility, copper(I) ion adopts various coordinating architectures.[23]

The ligating topologies of the organic ligands and highly directional and predictable nature of the metal−ligand coordination sphere determine the structural outcome and properties of supramolecular systems.[4,24,25] Therefore, rationalization of the ligand design for controlling the geometries and properties of the resulting metal−ligand assemblies have been given much attention in recent years. A large number of supramolecular assemblies derived from rigid, multidentate phosphine ligands have been reported in the literature.[26,27] To form a three-dimensional metal−ligand assembly, either metal or ligand should possess a connectivity of at least three. The ligand 2,4,6-tris(diphenylphosphino)-1,3,5-triazine and related C_3 symmetrical tris(phosphine) ligands are ideally suited candidates for this purpose.[28−32] These ligands have been extensively explored by James and others to form extended networks through multiple ligand coordination to metal centers or through additional bridging ligands to form chains,[33] cyclophane,[28,34,35] and tetrahedral[27,30,36] clusters.[31,36]

Simple monomeric cyclophanes derived from tris(phosphine) ligands with copper(I) and platinum(II) metal centers have been reported in the literature.[28,34,35] Here, we present a novel series of cyclophane-type copper(I) complexes derived from 2,4,6-tris(diphenylphosphino)-1,3,5-triazine. These are the first examples of di- and polymeric structures consisting of cyclophane scaffolds as monomeric units. The application of some of these copper(I) complexes in the A^3 coupling reaction is also discussed.

■ RESULTS AND DISCUSSION

The tris(phosphine), 2,4,6-tris(diphenylphosphino)-1,3,5-triazine (**1**) was prepared by the reaction of cyanuric chloride with Ph_2PSiMe_3 in THF at 0 °C in 59% yield. Previously, **1** was prepared by the reaction of cyanuric fluoride and $KPPh_2$ in 41% yield.[36,37]

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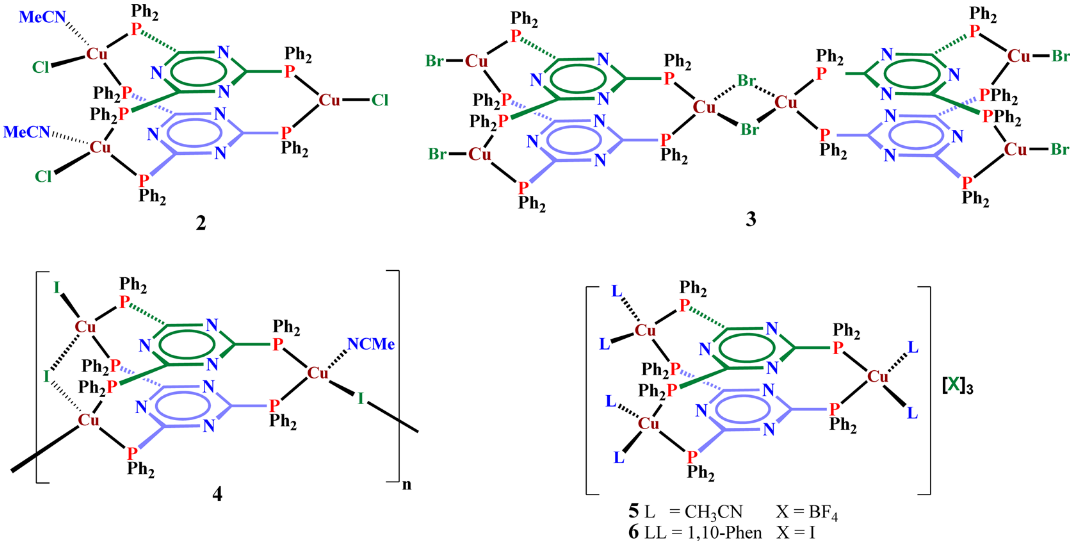
Chart 1. Copper Complexes of Trisphosphine 1



The addition of an acetonitrile solution of copper(I) halide (CuCl, CuBr, or CuI) to a dichloromethane solution of **1** (L) in a 3:2 molar ratio at room temperature resulted in the formation of copper(I) complexes, $[(CuCl)_3(L)_2(NCMe)_2]$ (**2**), $[(CuBr)_3(L)_2]_2$ (**3**), and $[(CuI)_3(L)_2(NCMe)]_n$ (**4**) (Chart 1). Similar reaction of **1** with $[Cu(NCMe)_4]BF_4$ afforded the tricationic metallocyclophane $[\{(Cu(NCMe)_2)_3(L)_2\}(BF_4)_3]$ (**5**) in quantitative yield. Addition of 1,10-phenanthroline to a solution of **4** in dichloromethane resulted initially in the formation of $[\{(Cu(Phen))_3(L)_2\}(I)_3]$ (**6**) in quantitative yield, as confirmed by spectroscopic and analytical data. Complex **6** consists of a cyclophane structure similar to that of **5**. The crystallization of complex **6** from a mixture of dichloromethane and petroleum ether produced yellow crystals of $[(CuI(Phen))_3(L)]$ (**6a**) along with **1**. It is assumed that, during the crystallization, complex **6** decomposed to form crystals of **6a** and the ligand **1**. The complexes **2**–**6** are moderately air-stable yellow solids, readily soluble in polar organic solvents.

Slow diffusion of acetonitrile into a saturated solution of **2** (in 1,2-dichloroethane) and **4** (in dichloromethane) gave crystals suitable for single-crystal X-ray diffraction studies. The molecular structures of all complexes with atom numbering schemes are shown in Figures 1–6. Selected bond lengths and bond angles are given in Tables 1–5, while crystal data and the details of the structure determinations are given in Table 6.

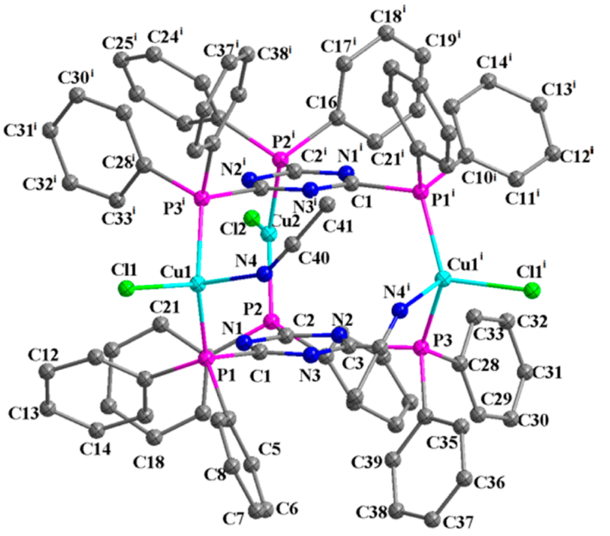


Figure 1. Molecular structure of $[(CuCl)_3(L)_2(MeCN)_2]$ (**2**). All hydrogen atoms and lattice solvents are omitted for clarity.

Single crystals of complex **3** were obtained by layering petroleum ether over a saturated solution of **3** in 1,2-dichloroethane. The core structures of **2**–**4** consist of two triazine rings held together by three copper(I) atoms to form metallocyclophanes. The size of the halide ions appears to control the solid-state structure of these copper complexes. The copper(I) chloride derivative **2** is a monomeric metallocyclophane, whereas the copper(I) bromide derivative **3** is dimeric, formed by dimerization of two metallocyclophane fragments bridged by a $Cu_2(\mu\text{-}Br)_2$ unit (Chart 1). The copper iodide derivative **4** is polymeric in nature. The larger size of the iodide ion facilitates the formation of $[Cu(\mu\text{-}I)Cu]$ links to form a 1D polymer. The two triazine rings in **2**–**4** are separated by a distance of 4.01, 3.90, and 4.37 Å, respectively. The separation between the two triazine rings in **2**–**4** is significantly larger than that observed in the platinum complex of tris(diphenylphosphino)benzene (L), $[(PtCl_2)_3L_2]$ (3.12 Å),[35] which is essentially due to the tetrahedral (~109.5°) or trigonal planar (~120°) geometry adopted by copper compared to square planar (~90°) platinum centers. The separation between the two triazine rings in **2**–**4** is also larger than the corresponding distance in pure organic paracyclophane (3.25 Å), because of longer Cu–P bond distances (2.23–2.27 Å) compared to a typical C–C bond distance of 1.54 Å.[38] The two triazine rings in **2**–**4** are inclined to each other at an angle of 2.66, 5.44, and 18.06°, respectively. The inclination in **4** is significantly higher because of the intracyclophane $[Cu(\mu\text{-}I)Cu]$ bridge. The intracyclophane $[Cu(\mu\text{-}I)Cu]$ bridge is observed only in **4** due to the larger size of iodide. The P···P separations in **2** [4.012–4.083 Å] are larger than those in both **3** [3.878–3.933 Å] and **4** [3.937–4.048 Å]. The geometry around two of the copper atoms in **2** is tetrahedral, whereas the third copper atom is trigonal planar and is surrounded by two phosphorus atoms and a chloride ion. Crystallization of **2** in the absence of acetonitrile led to the isolation of a symmetrical cyclophane cluster with all the copper centers being

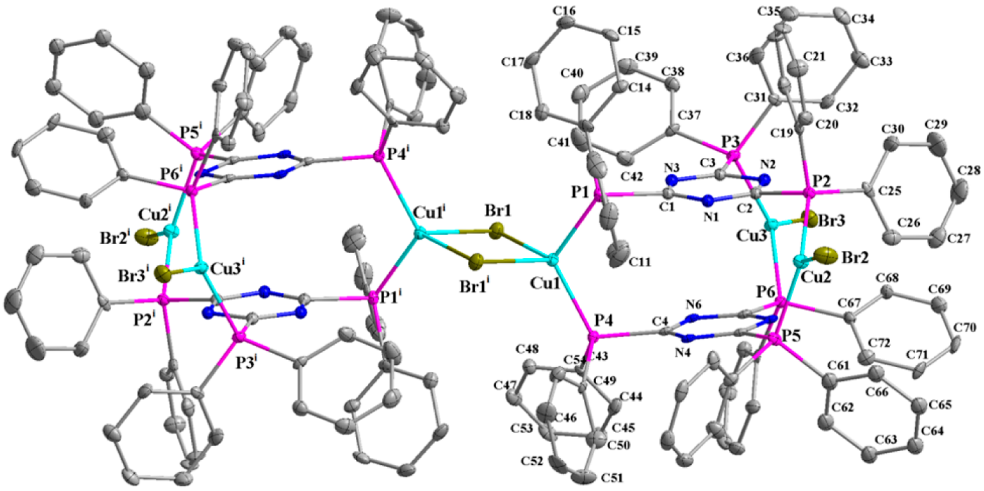


Figure 2. Molecular structure of $[(CuBr)_3(L)_2]_2$ (**3**). All hydrogen atoms and lattice solvents are omitted for clarity.

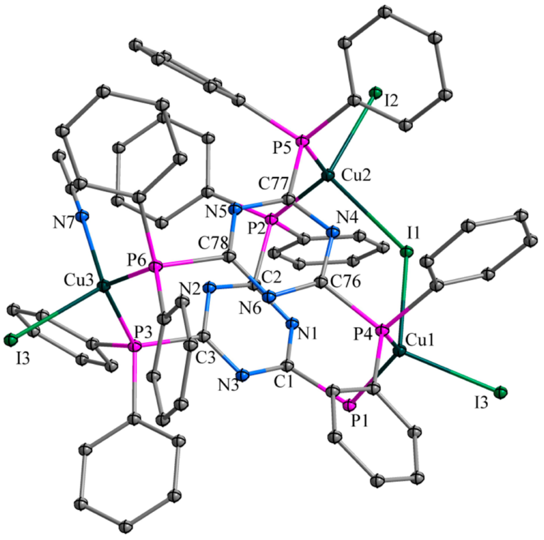


Figure 3. Molecular structure of $[(CuI)_3(L)_2(MeCN)]_n$ (**4**). All hydrogen atoms and lattice solvents are omitted for clarity.

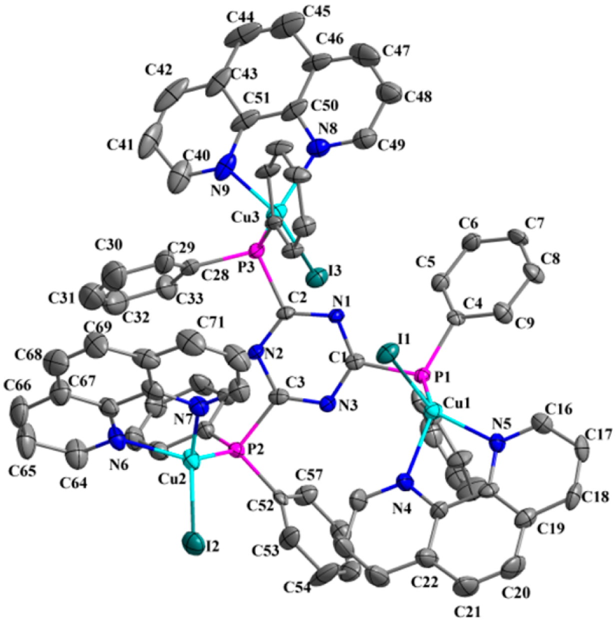


Figure 4. Molecular structure of $[(CuI(Phen))_3(L)]$ (**6a**). All hydrogen atoms and lattice solvents are omitted for clarity.

tricoordinated (see Figure S1 in the Supporting Information). All the copper centers in **4** are tetracoordinated and adopt a distorted tetrahedral geometry. The P−Cu−P bond angles around the copper atoms in **3** do not deviate much from ideal trigonal planar geometry [118.32(6)−122.61(6)°], but significant deviations from tetrahedral geometry are observed for **4** [121.62(3)−127.39(5)°]. The average metal−phosphorus distances in **2**−**4** are 2.24, 2.25, and 2.26 Å, respectively, and are in good agreement with those in $[(R_3P)_2CuX]$.[28,39,40] In **3**, the average Cu−Br bond distances for the tetrahedral copper (2.566 Å) is larger than those in the tricoordinated centers (2.335 Å). In the case of **4**, all the four Cu−I bond distances differ significantly from one another and fall in the range of 2.5821(8)−2.7297(7) Å.

On storing complex **6** in a mixture of dichloromethane and petroleum ether at room temperature, X-ray quality crystals of both **6a** and ligand **1** were formed. The asymmetric unit in **1** contains two molecules with one of them showing strong intermolecular $\pi-\pi$ stacking and nonbonding P···P contacts. The intermolecular $\pi-\pi$ stacking is observed between the central triazine rings of two molecules to form a dimeric structure with an interplane distance of 3.44 Å. The centroids of the two triazine rings exhibit a parallel displacement of approximately 2.57 Å. Interestingly, two short intermolecular P···P contacts of 3.362 Å between P1 and P3 atoms of two independent molecules of **1** are observed. The P···P contact is significantly shorter than the sum of the van der Waals radii of phosphorus atoms (3.6 Å),[41] but larger than that observed in phospha[1]ferrocenophane derivatives.[42,43] The average P−$C_{triazine}$ (1.842 Å) bond distance in **1** is longer than the average P−C_{phenyl} (1.829 Å) bond distance. The structure of **6a** consists of a three tetracoordinated copper centers, being coordinated by 1,10-phenanthroline, iodide, and one phosphorus atom (Figure 4). The average Cu−I (2.606 Å) bond distance in **6a** is similar to that of $[Ph_3PCuI(1,10\text{-phen})]$ (2.6157(6) Å), whereas the average Cu−P (2.179 Å) bond distance is slightly shorter than the same in $[Ph_3PCuI(1,10\text{-phen})]$ (Cu−P = 2.1977(9) Å).[44] To confirm the persistence of the solid-state structures in solution, ^1H, $^{31}P\{^1H\}$, and ESI-MS spectra were recorded for **2**−**6**. The ^1H NMR spectra of **2**−**6** in $CDCl_3$ solution are similar to that of ligand **1** and showed multiplets in

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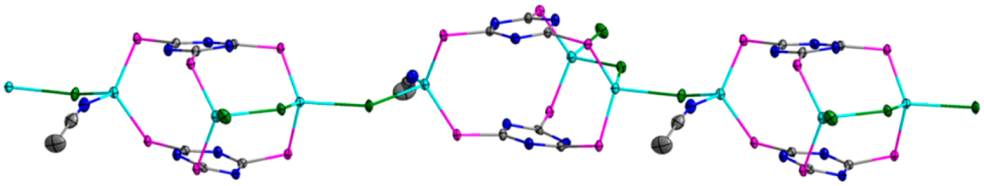
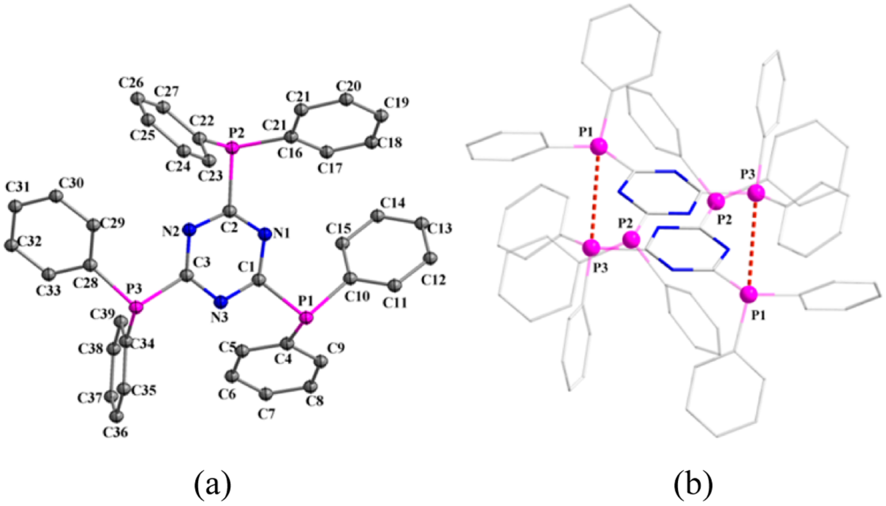


Figure 5. Core of 1D polymer $[(\mathrm{CuI})_3(\mathrm{L})_2(\mathrm{MeCN})]_n$ (**4**).



(a) (b)

Figure 6. (a) Molecular structure of 2,4,6-tris(diphenylphosphino)-1,3,5-triazine (**1**). (b) Intermolecular P···P interaction in **1**.

Table 1. Selected Bond Lengths [Å] and Bond Angles [deg] for 1

bond length [Å]		bond angle [deg]	
P1−C1	1.837(2)	C1−P1−C4	103.43(11)
P1−C4	1.839(3)	C4−P1−C10	100.93(12)
P1−C10	1.829(3)	C2−P2−C22	99.99(12)
P2−C2	1.844(2)	C2−P2−C16	103.22(12)
N1−C1	1.341(3)	C1−N1−C2	114.87(19)
N1−C2	1.340(3)	C2−N2−C3	115.05(19)

Table 2. Selected Bond Lengths [Å] and Bond Angles [deg] for 2

bond length [Å]		bond angle [deg]	
Cu1−Cl1	2.215(5)	P1−Cu1−P1^{i}	132.71(6)
Cu2−Cl2	2.253(3)	P2−Cu2−P2^{i}	126.39(1)
Cu3−Cl3	2.253(4)	P3−Cu3−P3^{i}	126.39(1)
Cu1−P1	2.228(3)	P1−Cu1−Cl1	113.63(5)
Cu2−P2	2.237(4)	P2−Cu2−Cl2	112.88(7)
Cu3−P3	2.258(4)	P3−Cu3−Cl3	116.87(3)

Table 3. Selected Bond Lengths [Å] and Bond Angles [deg] for 3

bond length [Å]		bond angle [deg]	
Cu1−Br1	2.5720(11)	P1−Cu1−P4	118.32(6)
Cu1^{i}−Br1	2.4597(11)	P2−Cu2−P5	119.67(7)
Cu2−Br2	2.3322(12)	P3−Cu3−P6	122.61(6)
Cu3−Br3	2.3389(11)	P1−Cu1−Br1	97.65(5)
Cu1−P1	2.2669(19)	P1−Cu1−Br1^{i}	114.07(5)
Cu1−P4	2.2718(18)	P2−Cu2−Br2	120.72(6)
Cu2−P2	2.2391(18)	P5−Cu2−Br2	119.43(5)
Cu2−P5	2.2465(19)	P3−Cu3−Br3	120.61(5)
Cu3−P3	2.2304(18)	P6−Cu3−Br3	116.60(5)
Cu3−P6	2.2528(18)	Br−Cu1−Br1^{i}	93.41(3)

Table 4. Selected Bond Lengths [Å] and Bond Angles [deg] for 4

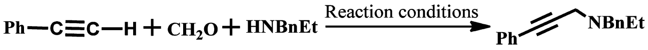
bond length [Å]		bond angle [deg]	
Cu1−I3	2.6509(7)	P1−Cu1−P4	127.39(5)
Cu2−I2	2.5821(8)	P2−Cu2−P5	124.73(5)
Cu3−I3	2.6386(7)	P3−Cu3−P6	121.62(5)
Cu1−I1	2.6727(8)	Cu1−I1−Cu2	130.535(19)
Cu2−I1	2.7297(7)	P1−Cu1−I3	100.04(4)
Cu1−P1	2.2616(13)	P1−Cu1−I1	106.68(3)
Cu1−P4	2.2538(12)	P2−Cu2−I1	103.93(4)
Cu2−P2	2.2736(13)	P2−Cu2−I2	112.62(4)
Cu2−P5	2.2631(13)	I1−Cu1−I3	102.209(19)
Cu3−P3	2.2724(13)	I1−Cu2−I2	108.06(2)
Cu3−P6	2.2376(13)		
Cu3−N7	2.020(4)		

the region of 7.46−7.10 ppm. The ^{1}H NMR spectrum of **5** and **6** showed additional signals from acetonitrile and 1,10-phenthroline, respectively. The ^{31}P{^{1}H} NMR spectra of **2**−**6** consist of single resonances in the range of 1.7 to −3.3 ppm, indicating the presence of single species in solution. The ESI-MS spectra of **2** showed a base peak at 1527.06 corresponding to the $[\mathrm{M} - \mathrm{Cl}]^{+}$ ion. Surprisingly, the ESI-MS spectra of **3** and **4** also showed base peaks of monomeric units at 1616.85 and 1710.93 corresponding to $[\mathrm{M}_{\mathrm{monomer}} - \mathrm{X}]^{+}$ fragments, respectively. The mass spectrum of **5** showed a weak peak at 485.70 corresponding to the $[\mathrm{M} - (\mathrm{CH_3CN})_6 - (\mathrm{BF_4})_3]^{3+}$ ion. The mass spectral data and solution NMR studies show that the complexes adopt a monomeric structure in solution. The weak halide bridges in **3** and **4** break down in solution to form monomeric entities. However, the solid-state ^{31}P NMR (CP-MAS) spectrum of **4** showed a multiplet in the region of −24.0

Table 5. Selected Bond Lengths [Å] and Bond Angles [deg] for 6a

bond length [Å]		bond angle [deg]	
Cu1−I1	2.5939(10)	I1−Cu1−P1	105.75(6)
Cu2−I2	2.6124(11)	I1−Cu1−N4	103.02(16)
Cu3−I3	2.6134(10)	P1−Cu1−N4	122.58(16)
Cu3−N8	2.070(5)	N4−Cu1−N5	80.72(19)
Cu1−N4	2.075(5)	I2−Cu2−P2	121.74(6)
Cu2−N6	2.068(6)	I2−Cu2−N6	101.83(16)
Cu1−P1	2.1719(19)	I2−Cu2−N7	100.87(16)
Cu2−P2	2.1781(19)	I3−Cu3−P3	109.51(6)
Cu3−P3	2.1862(19)	I3−Cu3−N8	107.26(16)

Table 7. Optimization of Reaction Conditions[c]



Sl. no.	catalyst	solvent	conv[a] (%)
1	**2** (0.33 mol %)	MeCN (5% H_2O)	89
2	**3** (0.33 mol %)	MeCN (5% H_2O)	93
3	**4** (0.33 mol %)	MeCN (5% H_2O)	100 (95[b])
4	**4** (0.33 mol %)	MeCN	83
5	no catalyst	MeCN (5% H_2O)	32
6	**4** (0.33 mol %)	toluene	31
7	**4** (0.33 mol %)	neat	56
8	**4** (0.33 mol %)	THF	72
9	**4** (0.33 mol %)	H_2O	78
10	**4** (0.1 mol %)	MeCN (5% H_2O)	99 (95[b])
11	**4** (0.01 mol %)	MeCN (5% H_2O)	94

[a]Conversion is based on amines by GC analysis using dodecane as internal standard. [b]Isolated yield. [c]The reaction was carried at 100 °C, under microwave irradiation (5 min) in a closed vessel.

to 6.4 ppm, thus confirming the polymeric structure in the solid state.

Multicomponent coupling of an alkyne, an aldehyde, and an amine leading to the formation of synthetically useful propargylamines is referred as the A^3 coupling reaction.[45−48] Several transition-metal catalysts, including copper, silver, gold, ruthenium, cobalt, and iridium, have been tested for the A^3 coupling reaction.[49−52] Copper salts, such as CuCl, $CuCl_2$, CuBr, and CuI, in the presence $RuCl_3$ as cocatalyst have been successfully utilized in the A^3 coupling reaction.[52] In order to assess the catalytic utility of copper clusters **2**−**4**, A^3 coupling reactions have been performed under microwave irradiation.

The desired propargylamines are obtained in excellent yields by the reaction of aldehyde, amine, and alkyne in the presence of copper catalysts (**2**−**4**). Initially, a mixture of phenyl acetylene, formaldehyde, and *N*-benzylethanamine was used as a model substrate to optimize the reaction conditions. The conversions were excellent when **4** (0.33 mol %) was used as a catalyst (Table 7, entry 3) under microwave irradiation in wet acetonitrile. The yield was lowered considerably in other solvents (Table 7, entries 5−8). A moderate conversion of 32% was observed even in the absence of the catalyst (Table 7, entry 5). It was observed that the presence of water was necessary for the higher yields (Table 7, entry 9). Further, catalyst loading was decreased to 0.1 mol % without affecting the conversion significantly (Table 7, entry 10). Under the optimized reaction conditions, various combinations of substituted amines and alkynes with *para*-formaldehyde were subjected to the coupling reaction. For example, the reaction of pentyne with formaldehyde and *N*-benzylethanamine gave 87% yield (Chart 2, entry b). Similarly, the reaction of morpholine or *N*-methylpiperazine with formaldehyde and alkynes gave good to excellent yield (Chart 2, entries c−g). The results of the coupling reaction are summarized in Chart 2. In comparison to the literature methods, the present protocol involves only 0.1 mol % catalyst loading without any additives.[45] The

Table 6. Crystallographic Data of 1−4 and 6a[a]

	1	2	3	4	6a
formula	$C_{39}H_{30}N_3P_3$	$C_{82}H_{66}Cl_3Cu_3N_8P_6 \cdot C_2H_4Cl_2$	$C_{78}H_{60}Br_3Cu_3N_6P_6 \cdot 0.5(C_2H_4Cl_2)$	$C_{80}H_{63}Cu_3I_3N_7P_6 \cdot C_2H_3N$	$C_{75}H_{54}Cu_3I_3N_9P_3$
formula weight	633.57	1745.17	1746.94	1920.57	1745.50
crystal system	triclinic	trigonal	monoclinic	monoclinic	triclinic
space group	$P\bar{1}$ (No. 2)	$P3_121$ (No. 152)	$P2_1/n$ (No. 14)	Cc (No. 9)	$P\bar{1}$ (No. 2)
a [Å]	10.2469(2)	17.5311(3)	17.192(4)	13.303(3)	11.5209(12)
b [Å]	13.8978(3)	17.5311(3)	18.254(4)	27.703(7)	15.8765(17)
c [Å]	23.3456(4)	23.1240(4)	24.392(5)	21.447(5)	24.201(3)
α [deg]	89.790(1)	90	90	90	75.258(1)
β [deg]	79.542(1)	90	101.724(3)	98.274(3)	86.507(1)
γ [deg]	84.910(1)	120	90	90	74.065(1)
V [Å^3]	3256.25(11)	6154.77(18)	7495(3)	7822(3)	4116.3(8)
Z	4	3	4	4	2
ρ_{calc} [g cm^{-3}]	1.292	1.413	1.548	1.631	1.408
μ[mm^{-1}]	1.927	3.893	2.654	2.165	1.994
$F(000)$	1320	2676	3508	3800	1716
T (K)	150	100	100	100	150
2θ range [deg]	3.2−72.4	5.82−133.2	2.6−25.0	1.9−29.4	1.7−28.3
total no. of reflns	25 575	40 344	56 156	69 004	19 957
no. of indep reflns	12 205	7220	10 269	18 868	10 476
R_{int}	0.051	0.047	0.108	0.043	0.144
R	0.0468	0.0417	0.0662	0.0282	0.0657
wR	0.1145	0.1048	0.1144	0.0662	0.1477
S	1.03	1.10	1.12	1.02	0.89

[a]$w = 1/[s^2(F_o^2) + (0.0241P)^2 + 1.2733P]$, where $P = (F_o^2 + 2F^2)/3$.

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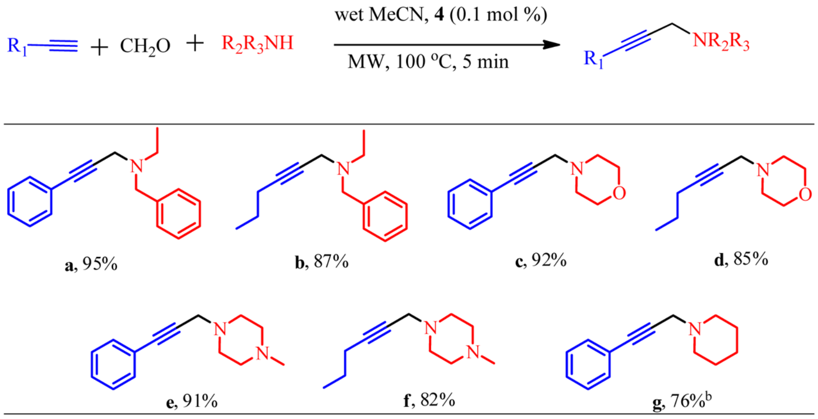
Chart 2. Substrate Scope for A^3 Coupling Reaction[a,c]



[a]Isolated yield. [b]Conversion is based on amine by GC analysis. [c]A^3 coupling of alkyne, aldehyde, and amine using catalyst **4** (0.1 mol %) in wet acetonitrile (4 mL) at 100 °C, under microwave irradiation (5 min).

experimental procedure was simple and produced good to excellent yield within 5 min. However, similar coupling reactions of *N*-benzylethanamine and morpholine in the presence of 0.1 mol % of [Cu(PPh$_3$)$_2$I] also produced the corresponding products in 86% and 79% yields. On increasing the [Cu(PPh$_3$)$_2$I] loading to 0.2 mol %, the yields improved to 96% and 85%, respectively.

■ CONCLUSIONS

In summary, self-assembled cyclophane-type metal−ligand clusters based on tritopic tris(phosphine) and copper(I) salts have been synthesized. The solid-state structures of these complexes depend on the size of the halide ions. The copper(I) chloride derivative is a monomeric metallocyclophane, whereas the copper bromide derivative is dimeric. The large iodide ions act as a bridge between individual metallocyclophane units to form a 1D polymeric chain. The tricationic clusters, as expected, adopt monomeric metallocyclophane structures. The study suggests that the size of these cyclophane clusters can be controlled by varying the size of the halide ions or by making cationic complexes. Preliminary application of copper(I) metallocyclophanes toward catalytic A^3 coupling reactions suggests that they might serve as useful scaffolds for new catalyst design. The work in this direction in progress in our laboratory.

■ EXPERIMENTAL SECTION

General Procedures. All manipulations were performed under rigorously anaerobic conditions using Schlenk techniques. All the solvents were purified by conventional methods[53] and distilled prior to use. The compounds, PPh$_2$SiMe$_3$,[54] CuCl,[55] CuBr,[55] and [Cu(CH$_3$CN)$_4$]BF$_4$[56] were prepared according to the published procedures. Cyanuric chloride, CuI, and 1,10-phenthroline were purchased from Aldrich Chemicals and used as such without further purification. Other chemicals were obtained from commercial sources and purified prior to use.

Instrumentation. The solution ^{1}H, ^{13}C, and ^{31}P{^{1}H} NMR (δ in ppm) spectra were recorded using a Bruker AV 400 spectrometer operating at frequencies of 400, 100, and 162 MHz, respectively. The spectra were recorded in CDCl$_3$ solutions with CDCl$_3$ as internal lock. Solid-state ^{31}P NMR spectra were recorded on a Bruker AV 500 MHz spectrometer operating at a frequency of 200 MHz with magic-angle spinning (MAS) at 15 kHz. NMR shifts are given in δ with positive values downfield of tetramethylsilane (^{1}H and ^{13}C{^{1}H}), external H$_3$PO$_4$ in D$_2$O (^{31}P), and external ammonium dihydrogen phosphate reference (solid state ^{31}P, δ 0). The microanalyses were performed using a Carlo Erba Model 1112 elemental analyzer. The mass spectra were recorded using a Waters Q-Tof micro (YA-105). The melting points were observed in capillary tubes and are uncorrected.

Synthesis of 2,4,6-Tris(diphenylphosphino)-1,3,5-triazine, [C$_3$N$_3$(PPh$_2$)$_3$] (1).[35] To a solution of cyanuric chloride (3.5 g, 19.14 mmol) in tetrahydrofuran (30 mL) was added a solution of trimethylsilyldiphenylphosphine (16.3 g, 63.15 mmol) in the same solvent (40 mL) at 0 °C. The reaction mixture was stirred for 2 h at room temperature. The solvent and trimethylsilyl chloride formed were removed under reduced pressure. The white sticky solid was triturated with dry ethanol to obtain pure **1** as a white solid. Yield: 59% (7.2 g). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.35−7.31 (m, Ar, 18H), 7.23−7.19 (m, Ar, 12H). ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$): δ 0.7 (s).

Synthesis of {(C$_3$N$_3$(PPh$_2$)$_3$)$_2$(CuCl)$_3$} (2). To a dichloromethane solution (10 mL) of CuCl (0.0141 g, 0.142 mmol) was added dropwise a solution of **1** (0.06 g, 0.0947 mmol) in the same solvent (10 mL) at room temperature with stirring. The clear yellow solution was further stirred for 4 h, and the solvent was reduced to 3 mL under reduced pressure and layered with petroleum ether (3 mL) to obtain a yellow precipitate. The precipitate was isolated by filtration, washed with diethyl ether (5 mL), and dried under reduced pressure. The X-ray quality crystals were obtained by layering a concentrated solution of **2** in 1,2-dichloroethane with acetonitrile. Yield: 90% (0.067 g). mp: 255 °C (dec.). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.40−7.11 (m, Ar, 60H). ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$): δ −2.1 (s). CP-MAS ^{31}P{^{1}H} NMR (200 MHz): δ −1.0 (br s). MS (EI): m/z = 1527.06 [M − Cl]$^+$. Anal. Calcd. for $C_{82}H_{66}Cl_3Cu_3N_8P_6\cdot C_2H_4Cl_2$: C, 57.80; H, 4.04; N, 6.42%. Found: C, 57.61; H, 3.79; N, 6.23%.

Synthesis of {(C$_3$N$_3$(PPh$_2$)$_3$)$_2$(CuBr)$_3$}$_2$ (3). A solution of **1** (0.1 g, 0.1578 mmol) in dichloromethane (10 mL) was added dropwise to a solution of CuBr (0.034 g, 0.2367 mmol) in acetonitrile (5 mL). The yellow solution was stirred for 4 h, and the solvent was removed under reduced pressure to afford a yellow solid. The crude product was recrystallized from a mixture of dichloromethane and petroleum ether. The X-ray quality crystals were obtained by layering a concentrated solution of **3** in 1,2-dichloroethane with petroleum ether. Yield: 92% (0.124 g). mp: 246 °C (dec.). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.41−7.10 (m, Ar, 60H). ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$): δ −2.7 (s). MS (EI): m/z = 1616.85 [M$_{\text{monomer}}$ − Br]$^+$. Anal. Calcd. for $C_{156}H_{120}Br_6Cu_6N_{12}P_{12}\cdot C_2H_4Cl_2$: C, 54.31; H, 3.58; N, 4.81%. Found: C, 54.16; H, 3.55; N, 4.59%.

Synthesis of {(C$_3$N$_3$(PPh$_2$)$_3$)$_2$(CuI)$_3$(NCCH$_3$)}$_n$ (4). This was synthesized by a procedure similar to that of **3**, using **1** (0.056 g, 0.0884 mmol) and CuI (0.0253 g, 0.1326 mmol). The X-ray quality crystals were obtained by layering a concentrated solution of **4** in dichloromethane with acetonitrile. Yield: 94% (0.076 g). mp: 230 °C (dec.). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.42−7.12 (m, Ar, 60H), 1.99 (s, CH$_3$CN, 18H). ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$): δ −3.3 (s).

CP-MAS $^{31}P\{^1H\}$ NMR (200 MHz): δ −24.0 to 6.4 (m). MS (EI): m/z = 1710.93 $[M_{monomer} - (CH_3CN) - I]^+$. Anal. Calcd. for $C_{80}H_{63}I_3Cu_3N_7P_6 \cdot CH_3CN$: C, 51.27; H, 3.46; N, 5.83%. Found: C, 51.14; H, 3.39; N, 5.72%.

Synthesis of $[\{(C_3N_3(PPh_2)_3)_2(Cu(NCCH_3)_2)_3\}(BF_4)_3]$ (5). A solution of **1** (0.1 g, 0.1578 mmol) in dichloromethane (10 mL) was added dropwise to a solution of $[(Cu(NCMe)_4)BF_4]$ (0.075 g, 0.2367 mmol) in acetonitrile (5 mL). The yellow solution was stirred for 4 h, and the solvent was reduced to 2 mL and layered with petroleum ether (3 mL) to obtain a yellow precipitate. The precipitate was isolated by filtration, washed with diethyl ether (5 mL), and dried under reduced pressure. Yield: 81% (0.126 g). mp: 235 °C (dec.). ^1H NMR (400 MHz, $CDCl_3$): δ 7.46 (t, J = 7.4 Hz, 12H), 7.30−7.20 (m, Ar, 48H), 1.99 (s, CH_3CN, 18H). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 1.7 (s). MS (EI): m/z = 485.7 $[M - (CH_3CN)_6 - BF_4]^{3+}$. Anal. Calcd. for $C_{90}H_{78}N_{12}B_3Cu_3F_{12}P_6$: C, 55.02; H, 4.00; N, 8.56%. Found: C, 55.11; H, 3.89; N, 8.12%.

Synthesis of $[\{(C_3N_3(PPh_2)_3)_2(Cu(1,10\text{-phen})_3\}(I)_3]$ (6). To a solution of **4** (0.048 g, 0.026 mmol) in dichloromethane (5 mL) was added dropwise a solution of 1,10-phenanthroline (0.014 g, 0.078 mmol) in the same solvent (5 mL) at room temperature. The reaction mixture was stirred for a further 2 h, concentrated to 2 mL, and layered with petroleum ether (3 mL). The turbid yellow solution was stored at room temperature for 24 h to obtain **6** as a yellow crystalline solid. Yield: 92% (0.057 g). mp: 223 °C (dec.). ^1H NMR (400 MHz, $CDCl_3$): δ 8.55 (br s, 6H), 8.24 (d, 6H, J = 8 Hz), 7.83 (m, 12H), 7.43 (m, 12H), 7.28−7.07 (m, 48H). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 1.3 (s). Anal. Calcd. for $C_{75}H_{54}Cu_3I_3N_9P_3$ $C_{114}H_{84}N_{12}Cu_3I_3P_6$: C, 57.80; H, 4.04; N, 6.42%. Found: C, 57.60; H, 3.79; N, 6.32%.

General Procedure for A^3 Coupling Reactions. The reactions were performed in a closed vessel containing a mixture of alkyne (1 equiv), amine (1.0 equiv), $(CH_2O)_n$ (1.1 equiv), and catalyst (0.1 mol %) in wet acetonitrile (4 mL). An initial microwave power of 80 W was applied to reach 100 °C temperature. After a specified reaction time, the reaction mixture was filtered and dried under reduced pressure. The residual mixture was diluted with H_2O (8 mL) and Et_2O (8 mL), followed by extraction twice with Et_2O (6 mL). The combined organic fractions were dried over $MgSO_4$, and the solvent was evaporated under vacuum. The crude products were purified by silica gel column chromatography using petroleum ether/ethyl acetate as the eluent. Yields were calculated against alkyne.

X-ray Crystallography. A crystal of each of the compounds **1**, **2**, **4**, and **6a** suitable for X-ray crystal analysis was mounted on a Mitegenloop with a drop of Paratone oil and placed in a cold nitrogen stream on the diffractometer. Hemispheres of data for **1** and **2** were collected on a Bruker D8 Venture diffractometer using mirror-monochromated Cu−Kα radiation (λ = 1.54178 Å), while full spheres of data for **4** and **6a** were collected on a Bruker Smart APEX instrument with graphite-monochromated Mo−Kα radiation (λ = 0.71073 Å) using the APEX2[57] program suite. A crystal of **3** was mounted on a glass fiber using epoxy glue and placed on a Rigaku Saturn724 CCD diffractometer equipped with graphite-monochromated Mo−Kα radiation (λ = 0.71073 Å). The raw data were reduced to F^2 values using the SAINT software. Multiple measurements of equivalent reflections provided the basis for an empirical absorption correction as well as a correction for any crystal deterioration during the data collection (SADABS[57]). All the structures were solved by direct methods (SHELXS[58]and SHELXT[58]) and refined by full-matrix least-squares procedures on F^2 using SHELXL[58] (SHELXTL program package[57]). Hydrogen atoms attached to carbon were placed in calculated positions and included as riding contributions with isotropic displacement parameters tied to those of the attached non-hydrogen atoms.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b02075.

Selected NMR and mass spectra, and crystal structures (PDF)
Crystallographic data for **1** (CIF)
Crystallographic data for **2** (CIF)
Crystallographic data for **3** (CIF)
Crystallographic data for **4** (CIF)
Crystallographic data for **6a** (CIF)

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Notes

The authors declare no competing financial interest.

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