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Copper(I) Coordination Polymers $[\{Cu(\mu\text{-}X)\}_2\{RP(\mu\text{-}N^tBu)\}_2]_n$ (R = OC_6H_4OMe-*o*; X = Cl, Br, and I) and Their Reversible Conversion into Mononuclear Complexes $[CuX\{(RP(\mu\text{-}N^tBu))_2\}_2]$: Synthesis and Structural Characterization

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The reactions of cyclodiphosphazane *cis*-$[^tBuNP(OC_6H_4OMe\text{-}o)]_2$ (**1**) with 2 equiv of CuX in acetonitrile afforded one-dimensional Cu^I coordination polymers $[Cu_2X_2\{^tBuNP(OC_6H_4OMe\text{-}o)\}_2]_n$ (**2**, X = Cl; **3**, X = Br; **4**, X = I). The crystal structures of **2** and **4** reveal a zigzag arrangement of $[P(\mu\text{-}N)_2P]$ and $[Cu(\mu\text{-}X)_2Cu]$ units in an alternating manner to form one-dimensional Cu^I coordination polymers. The reaction between **1** and CuX in a 2:1 ratio afforded mononuclear tricoordinated copper(I) complexes of the type $[CuX\{(^tBuNP(OC_6H_4OMe\text{-}o))_2\}_2]$ (**5**, X = Cl; **6**, X = Br; **7**, X = I). The single-crystal structures were established for the mononuclear copper(I) complexes **5** and **6**. When the reactant ratios are 1:1, the formation of a mixture of polymeric and mononuclear products was observed. The Cu^I polymers (**2**–**4**) were converted into the mononuclear complexes (**5**–**7**) by reacting with 3 equiv of **1** in dimethyl sulfoxide. Similarly, the mononuclear complexes (**5**–**7**) were converted into the corresponding polymeric complexes (**2**–**4**) by reacting with 3 equiv of copper(I) halide under mild reaction conditions.

Introduction

While the chemistry of cyclodiphosphazanes or diazadiphosphetidines has been an active field of research for the last 3 decades,[1] this saturated P_2N_2 ring system has attracted increased attention in recent years because of its excellent synthetic utility in the design of macrocyles, in coordination chemistry as neutral[2] and anionic ligands,[3] and also as catalysts in ethene polymerization reactions.[4] Because of the preferential cis orientation of the substituents on the P atoms of the cyclodiphosphazane ring, treatment with appropriate linkers (Q) facilitates the formation of simple monomeric (**I**) derivatives[5] or dimeric[6] to pentameric macrocycles (**II**−**V**)[7] through a "coiling process", thus preventing the linear propagation of a P_2N_2 chain that would have led to the formation of very interesting poly(phosph(III)azanes) of the type **VI** (see Chart 1). Although the relationship between the monomer/dimer of P−N compounds ($RN{=}PR'{\equiv}[RP(\mu\text{-}NR')]_2$) with bulky R groups is compared to that between ethene/cyclobutane,[8] cyclodiphosphazanes forming the polymers (type **VII**) similar to polyethenes or polyphosphazenes (**VIII**) are unlikely because coordinatively unsatur-

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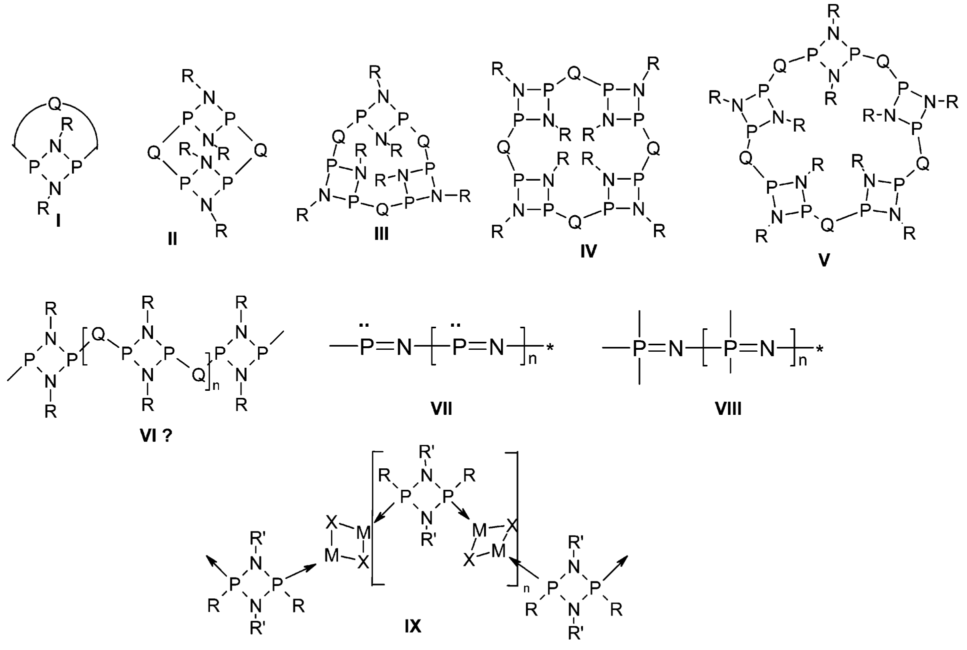
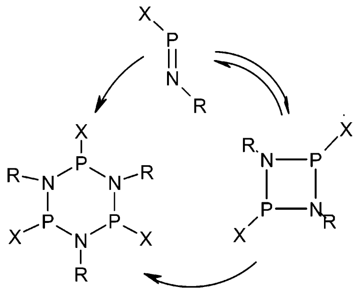
10.1021/ic060464j CCC: $33.50

Chart 1



Scheme 1



ated p-block elements require bulky substituents to stabilize π bonds. In the absence of π bonding, they prefer to form cyclic oligomers (Scheme 1).[8] However, the rigid cis isomers can form coordination polymers of the type **IX** when treated with the appropriate transition metals.

The main advantage of using such rigid units is their ability to form macrocyclic and polymeric structures with metal centers.[9] Many more rigid N-donor ligands such as bis(pyridines) and S-donor ligands such as poly(thiophenes) than rigid P-donor ligands have been utilized for constructing polynuclear metal complexes because of the lack of availability of the latter.[10] Among the transition metals, $\mathrm{Cu^I}$ exhibits many interesting coordination architectures ranging from simple complexes to multinuclear cages and coordination polymers by the formation of dimeric and trimeric $[\mathrm{Cu}(\mu\text{-X})]_n$ units.

Recently, we have exploited the cis conformation of these saturated $\mathrm{P_2N_2}$ rings to make di-, tri-, or tetranuclear metallomacrocycles with cyclodiphosphazanes exhibiting monodentate, bridged bidentate, and chelating tetradentate coordination modes.[11,12] In this paper, we report the first examples of coordination polymers of cyclodiphosphazanes (type **IX**) using $[\mathrm{Cu}(\mu\text{-X})]_2$ as a template. We also describe the formation of mononuclear $\mathrm{Cu^I}$ complexes containing two monodentate cyclodiphosphazanes and their reversible transformation into the corresponding coordination polymers.

Results and Discussion

Synthesis. Treatment of *cis*-$[{}^t\mathrm{BuNP}(\mathrm{OC_6H_4OMe}\text{-}o)]_2$ (**1**) with 2 equiv of CuX (X = Cl, Br, and I) in acetonitrile leads to the formation of $\mathrm{Cu^I}$ coordination polymers **2**−**4**, respectively, in good yield (Scheme 2). The chloro and bromo derivatives are precipitated from the reaction mixture as insoluble white solids, whereas the corresponding iodo complex **4** is soluble in acetonitrile and crystallizes from the

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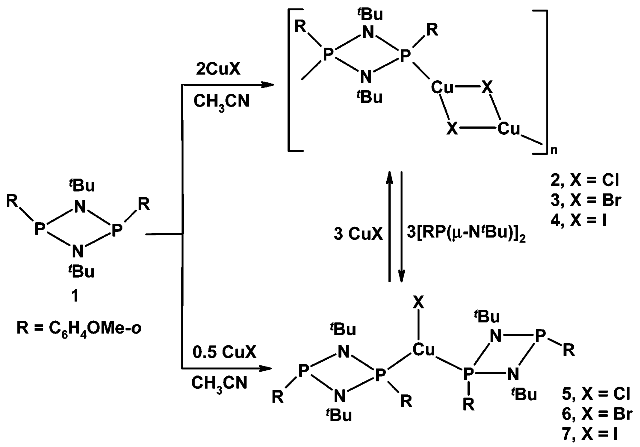
Scheme 2



mother liquor at room temperature. However, these complexes are soluble in hot dimethyl sulfoxide (DMSO), which allowed us to record their NMR spectra. The ^{31}P NMR spectra of complexes **2**−**4** show single resonances at 119.1, 115.4, and 114.2 ppm, respectively.

The interaction of **1** with CuX in a 2:1 ratio in acetonitrile affords highly soluble tricoordinated Cu^{I} complexes **5** (X = Cl), **6** (X = Br), and **7** (X = I), with cyclodiphosphazane showing a monodentate mode of coordination. The ^{31}P NMR spectra of complexes **5**−**7** consist of two broad signals due to the presence of both coordinated and uncoordinated P centers. The signals due to the coordinated P appear at 110.3, 108.6, and 107.2 ppm, whereas the uncoordinated P centers resonate at 134.9, 139.6, and 142.5 ppm, respectively. Surprisingly, in all of these complexes (**5**−**7**), no $^{2}J_{PP}$ was observed even at −50 °C and only two sharp singlets were observed. Similar results were also observed in the previously reported Pd^{II} and Rh^{I} complexes of the same ligand.[12] The ^{1}H NMR spectra of **5**−**7** recorded at room temperature show a single resonance for the OMe groups around 3.80 ppm, while at low temperature (−50 °C), the ^{1}H NMR spectrum of **7** shows two different signals at 3.84 and 3.79 ppm for the OMe groups. The mass spectral data show a peak at m/z 963.33 for all three complexes as a base peak, which corresponds to a M−X ion (X = Cl, Br, and I). Single-crystal X-ray structure determinations established the structures of complexes **2** and **4**−**6**.

The reaction of **1** with 1 equiv of CuX afforded a mixture of both polymeric and tricoordinated complexes in all cases (X = Cl, Br, and I), as indicated by their ^{31}P NMR spectral data. Wright and co-workers have reported[13] an exo-metalated tetranuclear Cu^{I} complex obtained in a reaction of CuCl with in situ generated dimer [(2-C$_5$H$_4$N)NP}$_2$O}]$_2$, in the presence of an excess of pyridine, which by blocking the two coordination sites on the Cu^{I} centers probably would have terminated the possibility of the formation of similar polymeric products.

Crystal Structures of Complexes 2 and 4−6. Molecular structures of Cu^{I} complexes **2** and **4**−**6** with their atom numbering schemes are shown in Figures 1−4, respectively.

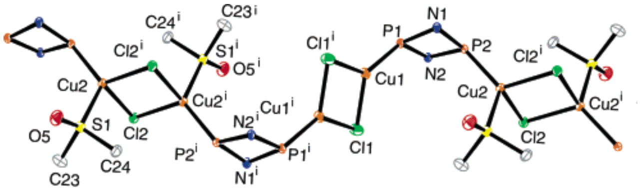


Figure 1. Molecular structure of **2**. Thermal ellipsoids are drawn at the 50% probability level. Uncoordinated solvent molecules, H atoms, and substituents on P and N have been omitted for clarity.

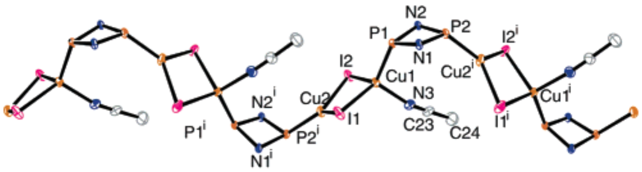


Figure 2. Molecular structure of **4**. Thermal ellipsoids are drawn at the 50% probability level. Uncoordinated solvent molecules, H atoms, and substituents on P and N have been omitted for clarity.

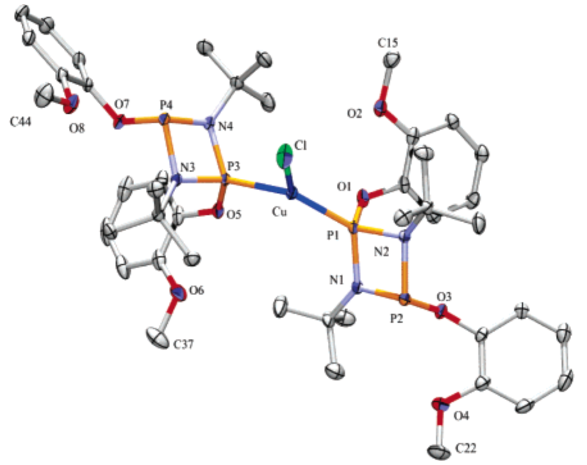


Figure 3. Molecular structure of **5.** Thermal ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity.

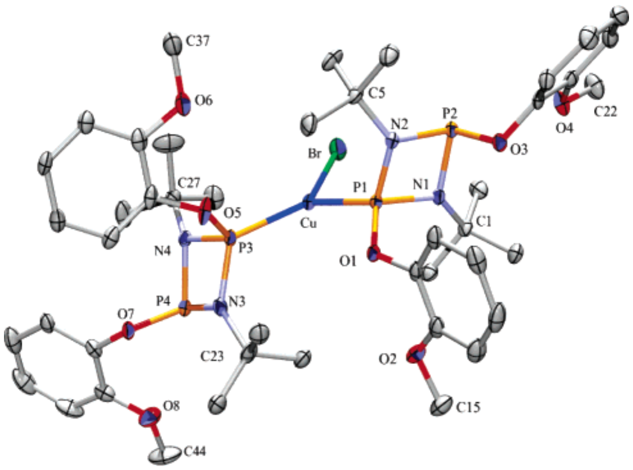


Figure 4. Molecular structure of **6**. Thermal ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity.

The crystallographic data and the details of structure determination are given in Table 1. The selected bond distances and bond angles are listed in Tables 2 and 3.

The colorless crystals of **2** were obtained from a DMSO solution at room temperature. The core structure of **2** consists of four-membered [RP(μ-N^{t}Bu)]$_2$ and [Cu(μ-Cl)$_2$Cu] units

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Table 1. Crystallographic Data for **2** and **4**−**6**

	2·DMSO	**4**·CH_3CN	**5**	**6**
formula	$C_{24}H_{38}Cl_2Cu_2N_2O_5P_2S$	$C_{24}H_{35}Cu_2I_2N_3O_4P_2$	$C_{44}H_{64}ClCuN_4O_8P_4$	$C_{44}H_{64}BrCuN_4O_8P_4$
fw	804.71	913.44	999.87	1044.32
cryst syst	triclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	Cc	$P2_1$	$P2_1$
a, Å	10.3726(8)	13.4780(10)	9.5024(7)	9.6070(10)
b, Å	12.2730(10)	18.1040(10)	18.7330(10)	18.694(2)
c, Å	15.4980(10)	15.015(10)	14.0920(10)	14.084(2)
α, deg	68.3010(10)	90	90	90
β, deg	85.1400(10)	108.4950(10)	96.2170(10)	96.547(2)
γ, deg	77.5260(10)	90	90	90
V, Å^3	1789.8(2)	3474.5(4)	2493.7(3)	2512.9(5)
Z	2	4	2	2
$\rho_{calc,}$ g cm^{-3}	1.493	1.746	1.332	1.380
μ(Mo Ka), mm^{-1}	1.582	3.128	0.672	1.409
F(000)	832	1792	1052	1088
cryst size (mm^3)	0.12 × 0.14 × 0.26	0.16 × 0.16 × 0.26	0.13 × 0.15 × 0.16	0.06 × 0.12 × 0.14
T (K)	293	100	100	100
2θ range, deg	1.4−27.8	2.0−28.3	1.5−28.3	1.5−28.3
total no. of reflns	15 924	15 345	22 382	22 523
no. of indep reflns	8159 [$R_{int} = 0.017$]	7781 [$R_{int} = 0.021$]	11 579 [$R_{int} = 0.028$]	11 429 [$R_{int} = 0.038$]
GOF (F^2)	1.05	1.04	1.00	0.98
R1^a	0.0307	0.0311	0.0351	0.0418
wR2^b	0.0840	0.0752	0.0793	0.0844

^{a} $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $wR2 = \{[\sum w(F_o{}^2 - F_c{}^2)/\sum w(F_o{}^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o{}^2) + (xP)^2]$, where $P = (F_o{}^2 + 2F_c{}^2)/3$.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for **2** and **4**

bond distance (Å)		bond angle (deg)	
		Complex **2**	
Cu1−P1	2.141(1)	P1−Cu1−Cl1	130.37(2)
Cu2−P2	2.192(1)	P1−Cu1−Cl1^i	129.63(2)
Cu1−Cl1	2.279(1)	Cl1−Cu1−Cl1^i	99.73(2)
Cu1−Cl1^i	2.294(1)	Cu1−Cl1−Cu1^i	80.27(2)
Cu2−Cl2	2.363(2)	P2−Cu2−S1	122.31(2)
Cu2−Cl2^i	2.376(5)	S1−Cu2−Cl2	98.54(2)
Cu2−S1	2.358(1)	Cl2−Cu2−Cl2^i	93.74(2)
S1−O5	1.486(2)	P(2)−Cu2-Cl2^i	117.32(2)
P1−N1	1.698(2)	Cl2−Cu2−P2	119.30(2)
P1−N2	1.691(2)	Cu2−S1−O5	119.97(7)
P2−N1	1.696(2)	Cu2−Cl2−Cu2^i	86.26(2)
P2−N2	1.699(2)	P1−N1−P2	96.32(8)
Cu1···Cu1^i	2.947	P1−N2−P2	96.50(8)
Cu2···Cu2^i	3.240	N1−P1−N2	82.69(8)
		N1−P2−N2	82.52(8)
		Complex **4**	
Cu1−P1	2.206(1)	P1−Cu1−N3	106.13(11)
Cu2−P2^i	2.198(2)	P1−Cu1−I2	115.32(4)
Cu1−I1	2.643(1)	P1−Cu1−I1	117.31(4)
Cu1−I2	2.669(2)	I1−Cu1−I2	102.54(2)
Cu2−I1	2.552(1)	I1−Cu2−I2	108.47(2)
Cu2−I2	2.555(1)	N3−Cu1−I1	113.85(12)
Cu1−N3	2.041(4)	Cu1−I1−Cu2	73.74(2)
P1−N1	1.705(3)	Cu1−I2−Cu2	73.25(2)
P1−N2	1.706(4)	Cu1−N3−C23	162.17(43)
P2−N1	1.687(4)	P2^i−Cu2−I1	127.61(4)
P2−N2	1.690(3)	P2^i−Cu2−I2	123.75(4)
Cu1···Cu2	3.118	P1−N1−P2	96.5(2)
		P1−N2−P2	96.3(2)
		N1−P1−N2	81.76(18)
		N1−P2−N2	82.74(18)

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for **5** and **6**

bond distance (Å)		bond angle (deg)	
		Complex **5**	
Cu−P1	2.197(1)	P1−Cu−Cl	125.58(3)
Cu−P3	2.244(1)	P3−Cu−Cl	104.16(3)
Cu−Cl	2.216(1)	P1−Cu−P3	130.11(2)
P1−O1	1.627(2)	Cu−P1−O1	104.38(6)
P2−O3	1.667(2)	Cu−P3−O5	114.58(6)
P3−O5	1.629(2)	P1−O1−C9	126.43(15)
P4−O7	1.667(2)	P2−O3−C16	117.94(14)
P1−N1	1.692(2)	P3−O5−C31	125.55(16)
P1−N2	1.692(2)	P4−O7−C38	117.96(14)
P2−N1	1.703(2)	P1−N1−P2	97.79(10)
P2−N2	1.729(2)	P1−N2−P2	96.80(10)
P3−N3	1.690(2)	N1−P1−N2	82.92(9)
P3−N4	1.684(2)	N1−P2−N2	81.49(9)
P4−N3	1.704(3)	P3−N3−P4	97.23(10)
P4−N4	1.720(2)	P3−N4−P4	96.85(10)
O1−C9	1.391(3)	N3−P3−N4	83.01(9)
O3−C16	1.394(3)	N3−P4−N4	81.50(9)
O5−C31	1.404(3)		
O7−C38	1.385(3)		
		Complex **6**	
Cu−P1	2.241(1)	P1−Cu−Br	104.81(3)
Cu−P3	2.203(2)	P3−Cu−Br	125.56(3)
Cu−Br	2.350(1)	P1−Cu−P3	129.44(4)
P1−O1	1.628(2)	Cu−P1−O1	113.62(9)
P2−O3	1.668(2)	Cu−P3−O5	104.05(9)
P3−O5	1.623(2)	P1−O1−C9	126.66(19)
P4−O7	1.667(2)	P2−O3−C16	118.61(19)
P1−N1	1.687(3)	P3−O5−C31	126.55(20)
P1−N2	1.688(3)	P4−O7−C38	117.78(18)
P2−N1	1.708(3)	P1−N1−P2	97.32(14)
P2−N2	1.720(3)	P1−N2−P2	96.79(14)
P3−N3	1.685(3)	N1−P1−N2	82.98(13)
P3−N4	1.684(3)	N1−P2−N2	81.42(13)
P4−N3	1.707(3)	P3−N3−P4	97.50(15)
P4−N4	1.727(3)	P3−N4−P4	96.77(15)
O1−C9	1.399(4)	N3−P3−N4	82.69(14)
O3−C16	1.388(4)	N3−P4−N4	80.84(14)
O5−C31	1.397(4)		
O7−C38	1.385(4)		

arranged alternately in a zigzag fashion to form a one-dimensional coordination polymer. The molecule is made up of two different kinds of [Cu(μ-Cl)$_2$Cu] units, which differ in their coordination number at the Cu^I centers. In the [Cu1(μ-Cl1)$_2$Cu1^i] dimeric unit, the Cu is tricoordinated with the coordination sites occupied by a P atom of the cyclodiphosphazane and two bridging Cl atoms. The geometry around the metal center is trigonal planar. The bond angle P1−Cu1−Cl1 [130.37(2)°] is larger than Cl1−Cu1−Cl1^i [99.73(2)°]. The P1−Cu1−Cl1^i bond angle is almost identical with P1−Cu1−Cl1. In the [Cu2(μ-Cl2)$_2$Cu2^i] dimeric unit, the geometry around the Cu center is distorted tetrahedral, with DMSO occupying the fourth coordination site and the angles about Cu varying from 122.31(2)° for S1−Cu2−P2 to 98.54(2)° for Cl2−Cu2−S1. The nonbonding Cu1⋯Cu1^i distance is 2.947 Å, whereas the Cu2⋯Cu2^i distance is 3.240 Å. This difference arises as a result of the increase in the coordination number from 3 to 4. In both cases, the Cu⋯Cu distances are noticeably greater than the sum of the van der Waals radii for the Cu^I ion, which confirms the nonexistence of metallophilic interactions in polymer **2**. The Cu1−P1 and Cu1−Cl1 bond distances are shorter than Cu2−P2 and Cu2−Cl2, and this difference is again due to the tri- and tetracoordinated nature of the two Cu^I centers. The Cu2−S1 bond distance is 2.358(1) Å, which indicates the coordination of DMSO to the Cu^I center.[14] The weak interaction between Cu1 and O2 atoms was observed for compound **2**, which is evident from the bond distance of 2.677 Å. The [Cu(μ-Cl)$_2$Cu] units are planar, whereas the P_2N_2 ring is slightly puckered ($\varphi_2 = 0.157$ Å)[15] in order to form a strain-free zigzag polymeric structure. Because of the puckering of the P_2N_2 ring, the sum of the angles around N is 354.33(10)°.

The crystals of **4** suitable for X-ray diffraction studies were grown from an acetonitrile solution at room temperature. The core structure of **4** is similar to that of its chloro analogue **2**. The polymer **2** contains two different [Cu(μ-Cl)$_2$Cu] dimeric units, with the Cu centers in a given unit having identical geometry. In the case of **4**, only one type of [Cu(μ-I)$_2$Cu] dimeric unit exists and the two Cu centers have different geometries. In the molecular structure of **4**, Cu1 is in a distorted tetrahedral environment consisting of two bridging I atoms, a P atom from cyclodiphosphazane, and a N atom from the coordinated acetonitrile molecule. The geometry around the Cu2 center is distorted trigonal planar. The nonbonded Cu⋯Cu distance is 3.118 Å. The four-membered [Cu(μ-I)$_2$Cu] unit in **4** is slightly puckered ($\varphi_2 = 0.238$ Å),[15] whereas in the case of **2**, both of the four-membered [Cu(μ-Cl)$_2$Cu] rings are planar. The presence of two different geometries in one dimeric unit in **4** may be responsible for the puckering. The diazadiphosphetidine ring is also puckered ($\varphi_2 = -0.186$ Å).[15] The Cu−P bond distances in **4** are slightly longer as compared to the same in the chloro derivative.

The single crystals of **5** and **6** were grown from an acetonitrile solution at −30 °C. In both complexes, the Cu^I atom occupies the center of a distorted trigonal plane, the corners are occupied by two P atoms from two different cyclodiphosphazane units, the Cl atom in complex **5**, and the Br atom in complex **6**. Of the two different kinds of geometrical arrangements possible for planar tricoordinated Cu^I (T- and Y-shaped), complexes **5** and **6** prefer the latter. The P1−Cu−P3 angles are 130.11(2)° for **5** and 129.44(4)° for **6**, which indicates that the identity of the halogen atom does not have a great influence on the geometry of the molecule. The P1−Cu−P3 bond angles lie between the similar angles reported[16] for tricoordinated complexes of a less bulkier phosphine ligand like PPh_3 [125.48(7)°] and bulkier ligands such as PCy_3 [134.44(8)°] and PBn_3 [136.53(2)°]. The P1−Cu−P3 bond angles are larger than the P1−Cu−Cl and P3−Cl−Cu bond angles in the same molecule. The P−Cu and Cu−X bond distances are in good agreement with the literature values for tricoordinated copper(I) phosphine complexes.[17] In **5**, the puckering parameters (φ_2)[15] for the $P_1N_1P_2N_2$ and $P_3N_3P_4N_4$ rings are respectively −0.112 and +0.132 Å, while in **6**, the corresponding values are +0.137 and −0.166 Å.

The interesting feature of these metal-containing polymers is that they undergo depolymerization (reversible coordination) in the presence of added ligands to give simple complexes, a process that is not facile with covalently bonded polymers.[18] This led to our study of the interconversion between poly- and mononuclear complexes in NMR tube reactions using appropriate reactants. Polymer **4** was dissolved in hot DMSO-d_6 in an NMR tube, 3 equiv of **1** was added, and the reaction was monitored through ^{31}P NMR spectroscopy. Within 1 h, the peak at 114.2 ppm disappeared and two new peaks appeared at 142.5 and 107.2 ppm, indicating the complete conversion of polymer **4** into the mononuclear complex [CuI{(^{t}BuNP(OC$_6$H$_4$OMe-*o*))$_2$}$_2$] (**7**). Similarly, the complete conversion of the mononuclear complex **7** into polymer **2** was also observed upon the addition of 3 equiv of CuI in DMSO-d_6.

Conclusions

We have reported the first examples of Cu^I coordination polymers of cyclodiphosphazanes, which undergo rare reversible transformations into the corresponding mononuclear complexes. Although cis conformers are not kinetically suited for extending the linear propagation to give the coordination polymers, the formation of rhombic [Cu(μ-Cl)]$_2$ units during the reaction and their flexible orientations and variable coordination numbers of Cu^I centers facilitated the formation of coordination polymers.

Experimental Section

General Procedures. All manipulations were performed under rigorously anaerobic conditions using high vacuum manifolds and Schlenk techniques. All of the solvents were purified by conventional procedures and distilled prior to use.[19] The compounds *cis*-[^{t}BuNP(OC$_6$H$_4$OMe-*o*)]$_2$ (**1**),[11] copper(I) chloride, and copper(I) bromide[20] were prepared according to the published procedure. Copper(I) iodide was purchased from commercial sources and used as received.

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Spectroscopy. The ^{1}H and ^{31}P{^{1}H} NMR (δ in ppm) spectra were recorded using a Varian Mercury Plus spectrometer operating at the appropriate frequencies using tetramethylsilane and 85% H_3PO_4 as internal and external references, respectively. Microanalyses were performed on a Carlo Erba model 1112 elemental analyzer. Mass spectrometry experiments were carried out using a Waters Q-Tof micro-YA-105. Melting points were recorded in capillary tubes and are uncorrected.

Synthesis of [Cu_2Cl_2{^{t}BuNP(OC_6H_4OMe-o)}$_2$]$_n$ (2). An acetonitrile solution (10 mL) of CuCl (34 mg, 0.35 mmol) was added dropwise to an acetonitrile (10 mL) solution of **1** (79 mg, 0.175 mmol) at room temperature with stirring. A white precipitate was separated out from the reaction mixture immediately after the addition. Then the stirring was continued for a further 4 h, and the precipitate was isolated by filtration. The solid was washed with 2 × 5 mL of diethyl ether and dried under reduced pressure. Yield: 98 mg (87%). Mp: 260−262 °C (dec). ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.33−6.86 (m, *Ph*, 8H), 3.78 (s, *OMe*, 6H), 1.39 (s, ^{t}*Bu*, 18H). ^{31}P{^{1}H} NMR (121 MHz, DMSO-d_6): δ 119.1 (br s). Anal. Calcd for $C_{22}H_{32}N_2O_4P_2Cu_2Cl_2$: C, 40.74; H, 4.97; N, 4.32. Found: C, 40.83; H, 4.80; N, 4.19.

Synthesis of [Cu_2Br_2{^{t}BuNP(OC_6H_4OMe-*o*)}$_2$]$_n$ (3). The synthesis was the same as that for **2**, except using CuBr (80 mg, 0.559 mmol) and **1** (120 mg, 0.278 mmol). Yield: 180 mg (90%). Mp: 254−256 °C (dec). ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.37−6.87 (m, *Ph*, 8H), 3.78 (s, *OMe*, 6H), 1.41 (s, ^{t}*Bu*, 18H). ^{31}P{^{1}H} NMR (DMSO-d_6, 161 MHz): δ 115.4 (br s). Anal. Calcd for $C_{22}H_{32}N_2O_4P_2Cu_2Br_2$: C, 35.83; H, 4.37; N, 3.79. Found: C, 35.92; H, 4.48; N, 3.83.

Synthesis of [Cu_2I_2{^{t}BuNP(OC_6H_4OMe-*o*)}$_2$]$_n$ (4). An acetonitrile solution (10 mL) of CuI (283 mg, 1.49 mmol) was added dropwise to a 10-mL acetonitrile solution of **1** (335 mg, 0.74 mmol) at room temperature. The reaction mixture was stirred for 6 h and then concentrated to 10 mL. Allowing the mixture to set at room temperature for a day afforded the product as colorless crystals. Yield: 550 mg (89%). Mp: 242−244 °C (dec). ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.43−6.86 (m, *Ph*, 8H), 3.80 (s, *OMe*, 6H), 2.03 (s, CH_3CN, 3H), 1.45 (s, ^{t}*Bu*, 18H). ^{31}P{^{1}H} NMR (161 MHz, DMSO-d_6): δ 114.2 (br s). Anal. Calcd for $C_{24}H_{35}N_3O_4P_2Cu_2I_2$: C, 33.04; H, 4.04; N, 4.81. Found: C, 33.18; H, 3.97; N, 4.67.

Synthesis of [CuCl{(^{t}BuNP(OC_6H_4OMe-*o*))$_2$}$_2$] (5). An acetonitrile solution (10 mL) of CuCl (12 mg, 0.123 mmol) was added to **1** (111 mg, 0.246 mmol) in 10 mL of acetonitrile with stirring. After 4 h of stirring, the solution was concentrated to 8 mL under reduced pressure and stored at −30 °C for 2 days to obtain the product as colorless crystals. Yield: 103 mg (83%). Mp: 140−142 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37−6.83 (m, *Ph*, 16H), 3.82 (s, *OMe*, 12H), 1.43 (s, ^{t}*Bu*, 36H). ^{31}P{^{1}H} NMR (161 MHz, $CDCl_3$): δ 134.9 (br s), 110.3 (br s). Anal. Calcd for $C_{44}H_{64}N_4O_8P_4CuCl$: C, 52.85; H, 6.45; N, 5.60. Found: C, 52.84; H, 6.35; N, 5.91. MS (EI): *m*/*z* 963.43 (M − Cl).

Synthesis of [CuBr{(^{t}BuNP(OC_6H_4OMe-*o*))$_2$}$_2$] (6). The synthesis was the same as that for **5**, except using CuBr (10 mg, 0.075 mmol) and **1** (67 mg, 0.15 mmol). Yield: 61 mg (79%). Mp: 151−153 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37−6.83 (m, *Ph*, 16H), 3.81 (s, *OMe*, 12H), 1.44 (s, ^{t}*Bu*, 36H). ^{31}P{^{1}H} NMR (161 MHz, $CDCl_3$): δ 139.6 (br s), 108.6 (br s). Anal. Calcd for $C_{44}H_{64}N_4O_8P_4CuBr$: C, 50.60; H, 6.17; N, 5.36. Found: C, 50.62; H, 6.32; N, 5.52. MS (EI): *m*/*z* 963.33 (M − Br).

Synthesis of [CuI{(^{t}BuNP(OC_6H_4OMe-*o*))$_2$}$_2$] (7). The synthesis was the same as that for **5**, except using CuI (34 mg, 0.181 mmol) and **1** (163 mg, 0.363 mmol). Yield: 165 mg (84%). Mp: 156−158 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.25−6.82 (m, *Ph*, 16H), 3.81 (s, *OMe*, 12H), 2.00 (s, CH_3CN, 3H), 1.45 (s, ^{t}*Bu*, 36H). ^{1}H NMR (300 MHz, $CDCl_3$, −50 °C): δ 7.86−6.81 (m, *Ph*, 16H), 3.84 (s, *OMe*, 6H), 3.79 (s, *OMe*, 6H), 2.09 (s, CH_3CN, 3H), 1.48 (s, ^{t}*Bu*, 36H). ^{31}P{^{1}H} NMR (161 MHz, $CDCl_3$, 25 °C): δ 142.5 (br s), 107.2 (br s). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, −50 °C): δ 138.8 (s), 101.9 (s). Anal. Calcd for $C_{44}H_{64}N_4O_8P_4CuICH_3CN$: C, 48.78; H, 5.96; N, 6.18. Found: C, 48.55; H, 6.19; N, 6.08. MS (EI): *m*/*z* 963.4 (M − I).

X-ray Crystallography. Crystals of **2** and **4**−**6** were mounted in a CryoLoop with a drop of Paratone oil and placed in the cold N_2 stream of the Kryoflex attachment of the Bruker APEX CCD diffractometer. For each, a full sphere of data were collected using 606 scans in ω (0.3° per scan) at φ = 0, 120, and 240° using the *SMART* software package.[21] The raw data were reduced to F^2 values using the *SAINT*+ software,[22] and global refinements of unit cell parameters employing 5931−7305 reflections chosen from the full data sets were performed. Multiple measurements of equivalent reflections provided the basis for empirical absorption corrections as well as corrections for any crystal deterioration during the data collection (*SADABS*[23]). The structures were solved by direct methods and refined by full-matrix least-squares procedures using the *SHELXTL* program package.[24] H atoms were placed in calculated positions [C−H = 0.95 Å (aromatic rings) or 0.98 Å (methyl groups)] and included as riding contributions with isotropic displacement parameters 1.2 (aromatic rings) or 1.5 (methyl groups) times those of the attached non-H atoms.

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Supporting Information Available: X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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