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Di- and Tetranuclear Copper(I) Complexes Containing Phenylaminobis(phosphonite), PhN{P(OC$_6$H$_4$OMe-*o*)$_2$}$_2$, and Their Reactivity toward Bipyridyl Ligands

Chelladurai Ganesamoorthy,[†] Maravanji S. Balakrishna,*[,†] Paulose P. George,[†] and Joel T. Mague[‡]

Phosphorus Laboratory, Department of Chemistry, Indian Institute of Technology Bombay,
Powai, Mumbai 400 076, India, and Department of Chemistry, Tulane University,
New Orleans, Lousiana 70118

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The aminobis(phosphonite) PhN(P(OC$_6$H$_4$OMe-*o*)$_2$)$_2$ (PNP; **1**) reacts with 2 equiv of CuI to give a binuclear complex, Cu$_2$(μ_2-I)$_2$(NCCH$_3$)$_2$(μ-PNP) (**2**), whereas similar reactions with CuCl and CuBr furnish tetranuclear "ladder"-type complexes, Cu$_4$(μ_2-X)$_2$(μ_3-X)$_2$(μ-PNP)$_2$ (**3**, X = Cl; **4**, X = Br), in excellent yield. The complex **2** when heated under vacuum turns into the tetranuclear complex **5** in a reversible fashion. Similarly, the complexes **3** and **4** on dissolution in CH$_3$CN dissociate reversibly into the corresponding binuclear complexes from which the tetrameric complexes can be readily regenerated. Treatment of **2** with excess of pyridine produces the heterosubstituted derivative, Cu$_2$(μ_2-I)$_2$(C$_5$H$_5$N)$_2$(μ-PNP) (**6**). The interaction of **2** with 2,2′-bipyridine in 1:1 and 1:2 ratios produces the mono- and disubstituted derivatives, Cu$_2$(μ_2-I)I(C$_{10}$H$_8$N$_2$)(μ-PNP) (**7**) and [Cu$_2$(μ_2-I)(C$_{10}$H$_8$N$_2$)$_2$(μ-PNP)]I (**8**), respectively. The chloro and bromo analogues of **7** are prepared by treating the tetranuclear derivatives **3** and **4** with 2,2′-bipyridine. Reaction of **2** with 4,4′-bipyridine in the presence of AgOTf gives the cationic complex [Cu$_4$(NCCH$_3$)$_4$(C$_{10}$H$_8$N$_2$)$_2$(μ-PNP)$_2$](OTf)$_4$ (**9**), whereas the complex [Cu$_2$(NCCH$_3$)$_2$(μ-PNP)$_2$](OTf)$_2$ (**10**) was obtained from the reaction of **2** with 1 equiv of **1** and AgOTf. The reactions of **3** and **4** with 2 equiv of 4,4′-bipyridine in acetonitrile afford one-dimensional copper(I) coordination polymers [Cu$_2$(μ_2-X)$_2$(μ-PNP)(C$_{10}$H$_8$N$_2$)]$_n$ (**13**, X = Cl; **14**, X = Br). The molecular structures of **2**–**4**, **6**–**8**, **12**, and **14** are confirmed by X-ray crystallography.

Introduction

Reactions of copper(I) halides with tertiary phosphines have yielded a variety of complexes with diverse structural types—monomers, oligomeric units, one-dimensional (1D) chain stair-step polymers, and two-dimensional (2D) sheet structures—as a result of the geometric flexibility of copper(I) and also its ability to adopt two-, three-, or four-coordination numbers.[1] Phosphines with moderate steric properties form cubane-type complexes,[2] whereas bis(phosphines) prefer ladder-type structures.[3] The tetranuclear ladder or steplike molecules can dissociate in the presence of solvent molecules to provide useful precursors for coordination polymers when treated with appropriate linkers. Interest in their coordination behavior with these systems arises because of their potential application in catalysis,[4] bio systems,[5] and photochemical areas.[6] The rich photochemistry exhibited by some mixed-ligand copper(I) complexes (phosphines with heteroaromatic ligands) has triggered numerous studies on clarifying the relationship between the structural and optical

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* To whom correspondence should be addressed. E-mail: krishna@chem.iitb.ac.in. Tel.: +91 22 2576 7181. Fax: +91 22 2576 7152/2572 3480.

[†] Indian Institute of Technology Bombay.

[‡] Tulane University.

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properties.[7] Among the various bis(phosphine) ligands, bis(diphenylphosphino)methane (dppm) is an important bridging ligand for making polynuclear species with most metals and particularly with copper(I).[8] Similar types of bis(phosphines), with an "RN<" spacer in place of the methylene group, are known as acyclic diphosphazanes.

The transition-metal chemistry of acyclic diphosphazanes and their bis(chalcogenide) derivatives have attracted considerable attention in recent years because of the versatile coordination behavior of the former, because it is similar to dppm,[9] and the potential application of the latter as single-source precursors of various metal−, nonmetal−, and metalloid−telluride thin films and nanoparticles.[10] Although several groups have studied the coordination behavior of aminobis(phosphines) and related phosphonite derivatives, the copper(I) chemistry of this class of ligands is scant despite their ability to form interesting complexes through their versatile coordination behavior.[8c,11]

As a part of our interest in phosphorus-based ligands and their catalytic applications,[12] we describe here the copper(I) chemistry of aminobis(phosphonite) $PhN(P(OC_6H_4OMe\text{-}o)_2)_2$ (PNP; **1**). The crystal and molecular structures of several di- and tetranuclear complexes including a novel coordination polymer are also described.

Results and Discussion

Reactions with Copper(I) Halides. Treatment of the aminobis(phosphonite) **1** with 2 equiv of CuI in acetonitrile leads to the formation of a dinuclear complex $Cu_2(\mu_2\text{-I})_2(NCCH_3)_2(\mu\text{-PNP})$ (**2**) in good yield (Scheme 1). In contrast, the reactions of **1** with 2 equiv of CuX (X = Cl, Br) in acetonitrile afforded tetranuclear complexes $Cu_4(\mu_2\text{-X})_2(\mu_3\text{-X})_2(\mu\text{-PNP})_2$ (**3**, X = Cl; **4**, X = Br) in quantitative yield. The ^{31}P NMR spectra of complexes **2**−**4** show single resonances at 88.5, 101.3, and 98.2 ppm, respectively. The ^1H NMR spectrum of **2** shows single resonances at 1.94 and 3.57 ppm, respectively, for coordinated CH_3CN and *o*-methoxy groups present in the phenyl rings. The ^1H NMR spectra of **3** and **4** confirm the absence of coordinated acetonitrile, whereas the *o*-methoxy groups on the phenyl rings appear as singlets around 3.7 ppm. Interestingly,

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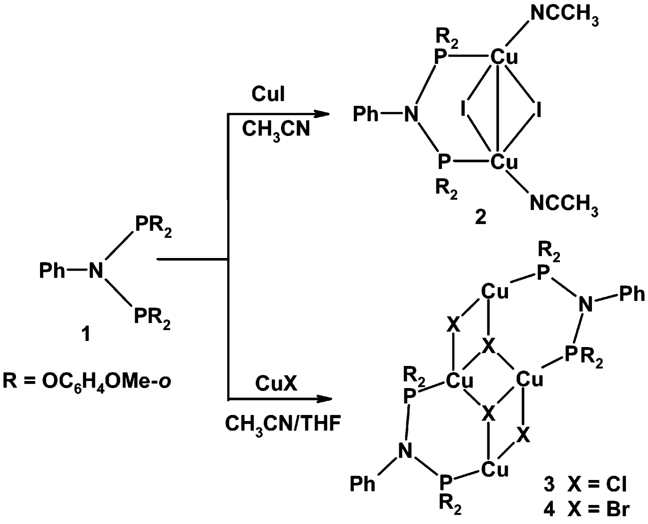
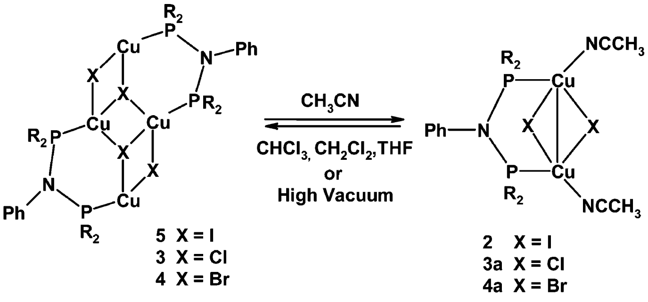
Scheme 1



Scheme 2



complex **2** dimerizes into the tetranuclear complex **5**, analogous to the complexes **3** and **4**, when crystallized from solvents other than acetonitrile such as tetrahydrofuran (THF), dichloromethane, chloroform, etc., or upon sublimation under vacuum. Similarly, compounds **3** and **4** when dissolved in acetonitrile dissociate into dinuclear complexes **3a** and **4a**, respectively, as shown in Scheme 2. The attempts to isolate complexes **3a** and **4a** have been unsuccessful because they dimerize easily during removal of acetonitrile under reduced pressure. However, the formation of **3a** and **4a** was confirmed by reactions of the corresponding tetramers with 2,2′- and 4,4′-bipyridine in an acetonitrile medium, which lead to the formation of complexes having a puckered $P_2Cu_2(\mu_2\text{-}X)_2$ core analogous to that in **2** (Scheme 4). Interestingly, the ^{31}P NMR chemical shifts observed for **2** and **5** (X = I) differ by only 0.4 ppm, indicating that the formation of the dimer apparently does not significantly affect the phosphorus environment. However, the ^1H NMR spectrum of the dinuclear complex shows a resonance due to coordinated acetonitrile that is absent in the spectrum of the tetranuclear derivative. Compounds **2**−**5** are colorless, air-stable, crystalline solids that highly soluble in acetonitrile and moderately soluble in chloroform and acetone. The molecular structures of **2**−**4** are confirmed by the single-crystal X-ray diffraction studies.

Interaction of Complexes 2−4 with Pyridine and Bipyridyl Ligands. The dinuclear iodo derivative **2** was used for further reactions with strong Lewis bases, such as pyridine, 2,2′-bipyridine, and 4,4′-bipyridine, which resulted in the formation of several mixed-ligand complexes, as shown in Scheme 3. The reports of such types of mixed-ligand copper(I) complexes containing both bis(phosphines) and aromatic amines are scarce.[13] Several groups have studied copper(I) chemistry of numerous diamine bridging ligands such as diazabicyclo[2.2.2]octane (DABCO), pyrimidine, piperazine, *N*,*N*′-dimethylpiperazine (DMP), 4,4′-bipyridyl (Bpy), pyrazine (Pyz), quinoxaline (Quin), phenazine (Phz), and 1,3,5-triazine.[1b−g,14] When the amine is a bifunctional bridging ligand, an extended chain structure is formed. On the other hand, monodentate nitrogen ligands afford simple substituted derivatives. When an additional monodentate phosphorus ligand (L) is introduced into these reactions, the product invariably is $[(CuX)_2L_2(biL)]_n$ (biL: DABCO, DMP, Bpy, Pyz, Quin, Phz). In most of the above reports, the various reactants are added in a consecutive manner and most of the time the products obtained were not anticipated or planned. In view of all of these interesting features, we wanted to *first* isolate discrete copper(I) complexes of bis(phosphines) and *then* interact them with strong Lewis bases in a controlled manner in an attempt to develop a better defined and more systematic reaction chemistry for these systems.

The substitution of coordinated solvent molecules in complex **2** with pyridine in acetonitrile or dichloromethane did not take place, so that the desired complex, $Cu_2(\mu_2\text{-}I)_2(C_5H_5N)_2(\mu\text{-PNP})$ (**6**), was prepared as a white crystalline solid by stirring compound **2** in an excess of pyridine. The ^{31}P NMR spectrum of compound **6** consists of a single broad peak at 102.8 ppm, which is significantly shifted downfield as compared to **2** [coordination shift ($\delta_{P(pyridine)} - \delta_{P(MeCN)}$) = 14.3 ppm]. The ^1H NMR and analytical data are consistent with the proposed structure of compound **6.** Treatment of complex **2** with 2,2′-bipyridine in 1:1 and 1:2 molar ratios afforded the complexes $Cu_2(\mu_2\text{-}I)I(C_{10}H_8N_2)(\mu\text{-PNP})$ (**7**) and $[Cu_2(\mu_2\text{-}I)(C_{10}H_8N_2)_2(\mu\text{-PNP})]I$ (**8**) as bright-yellow crystalline solids in good yield. In the formation of complex **7**, two acetonitrile groups were removed and one of the coordinate bonds of iodine with copper was broken by 2,2′-bipyridine to give both three- and four-coordinated copper centers. The ^{31}P NMR spectrum of complex **7** shows a single broad peak at 101.5 ppm with the broadening due to the presence of quadrupolar nuclei (^{63}Cu and ^{65}Cu, $I = {}^3/_2$). The ^1H NMR spectrum of **7** shows a single resonance at 3.70 ppm due to the *o*-methoxy groups on the phenyl rings. In complex **8**, one of the bridging iodides is completely

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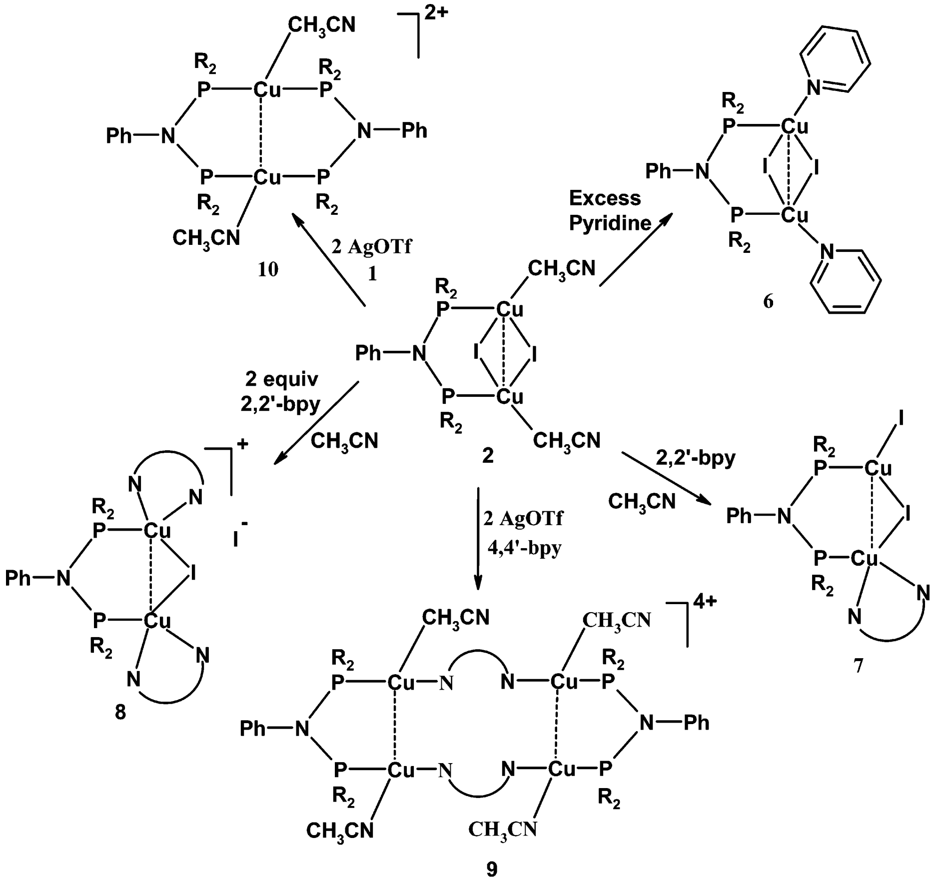
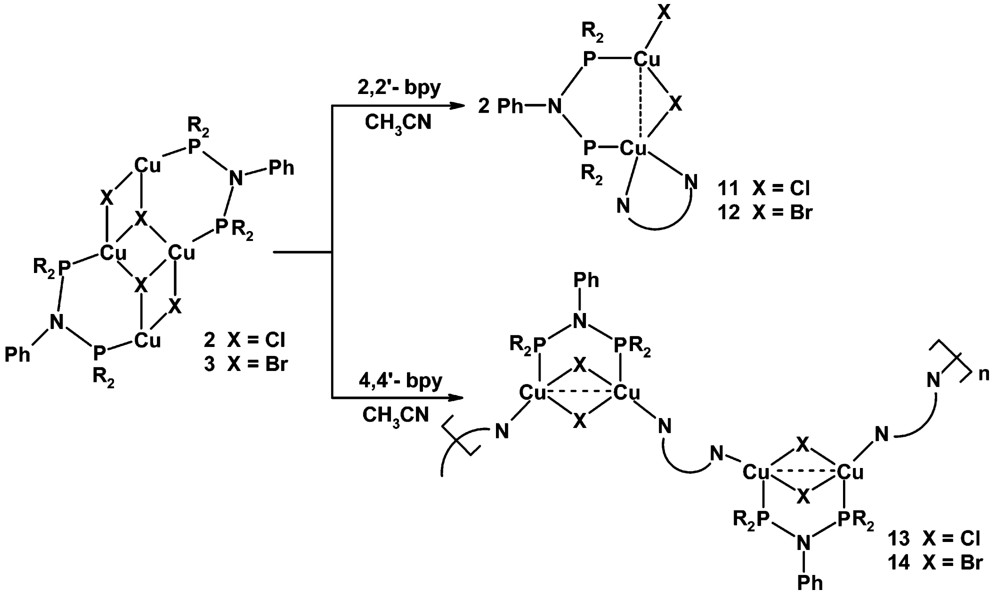
Scheme 3



Scheme 4



displaced to produce a cationic complex with the iodide now present as the counterion. The ^{31}P NMR spectrum of complex **8** consists of a single broad peak at 101.1 ppm, and the ^{1}H NMR spectrum shows a single resonance at 3.68 ppm corresponding to the *o*-methoxy groups on the phenyl rings. The compositions of **7** and **8** as 1:1 and 1:2 complexes of **2** and 2,2′-bipyridine were verified by elemental analysis and the structures of complexes **7** and **8** confirmed by single-crystal X-ray diffraction studies. The tetranuclear complex $[Cu_4(NCCH_3)_4(C_{10}H_8N_2)_2(\mu\text{-PNP})_2](OTf)_4$ (**9**) was obtained as a pale-yellow crystalline solid when **2** was treated with 1 equiv of 4,4′-bipyridine in the presence of 2 equiv of AgOTf in acetonitrile. In a similar manner, the complex $[Cu_2(NCCH_3)_2(\mu\text{-PNP})_2](OTf)_2$ (**10**) was prepared by treating complex **2** with 2 equiv of AgOTf and 1 equiv of **1** in acetonitrile. Complex **10** undergoes facile dissociation in the presence of air and moisture. The ^{31}P NMR spectra of complexes **9** and **10** consist of broad single peaks at 104.6

Table 1. NMR Data for Compounds **1**−**12**

compound	^{31}P NMR (in ppm)	^{1}H NMR (in ppm)		
		CH$_3$CN	OCH$_3$	aryl protons
1	132.2 (s)		3.62 (s)	6.76−7.60 (m)
2	88.5 (s)	1.94 (s)	3.57 (s)	6.60−7.72 (m)
3	101.3 (s)		3.67 (s)	6.61−7.66 (m)
4	98.2 (s)		3.67 (s)	6.56−7.73 (m)
5	88.9 (s)		3.64 (s)	6.64−7.79 (m)
6	102.8 (s)		3.64 (s)	6.68−8.12 (m)
7	101.5 (s)		3.70 (br s)	6.64−7.99 (m)
8	101.1 (s)		3.68 (s)	6.68−8.10 (m)
9	104.6 (s)	2.04 (s)	3.76 (s)	6.87−7.87 (m)
10	111.7 (s)	1.97 (s)	3.70 (s)	6.82−7.71 (m)
11	101.9 (s)		3.68 (br s)	6.68−7.74 (m)
12	101.4 (s)		3.69 (br s)	6.67−7.79 (m)

and 111.7 ppm, respectively. The ^{1}H NMR spectra consist of two singlets at 2.06 and 3.74 ppm respectively for acetonitrile and *o*-methoxy groups of the phenyl rings. The analytical data are consistent with the proposed structures for complexes **9** and **10**.

The reactions of complexes **3** and **4** with 2 equiv of 2,2′-bipyridine in acetonitrile afforded the dinuclear complexes $Cu_2(\mu_2\text{-}X)X(C_{10}H_8N_2)(\mu\text{-PNP})$ (**11**, X = Cl; **12**, X = Br) in good yield, whereas similar reactions with 4,4′-bipyridine led to the formation of 1D zigzag copper(I) coordination polymers $[Cu_2(\mu_2\text{-}X)_2(\mu\text{-PNP})(C_{10}H_8N_2)]_n$ (**13**, X = Cl; **14**, X = Br). Because of the poor solubility of complexes **13** and **14** in almost all solvents, NMR spectroscopic studies could not be carried out. However, the molecular compositions were confirmed from elemental analysis data. The ^{31}P NMR spectra of complexes **11** and **12** show single resonances at 101.9 and 101.4 ppm, respectively, whereas the ^{1}H NMR spectra show broad single peaks around 3.7 ppm corresponding to the *o*-methoxy groups. The ^{1}H NMR and analytical data are consistent with the proposed structures of compounds **11** and **12**. The structures of complexes **12** and **14** are confirmed by single-crystal X-ray diffraction studies. For comparison, the ^{1}H and ^{31}P NMR spectral data for complexes **1**−**12** are given in Table 1.

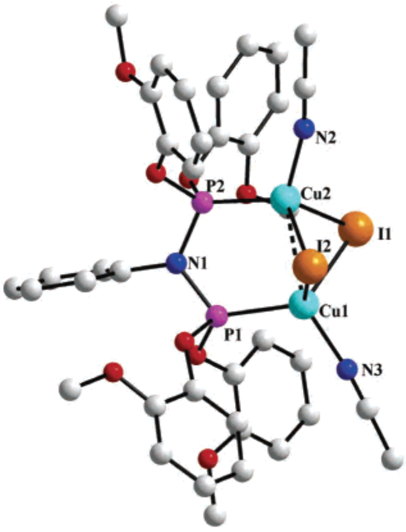


Figure 1. Molecular structure of **2**. All hydrogen atoms and the lattice solvent have been omitted for clarity.

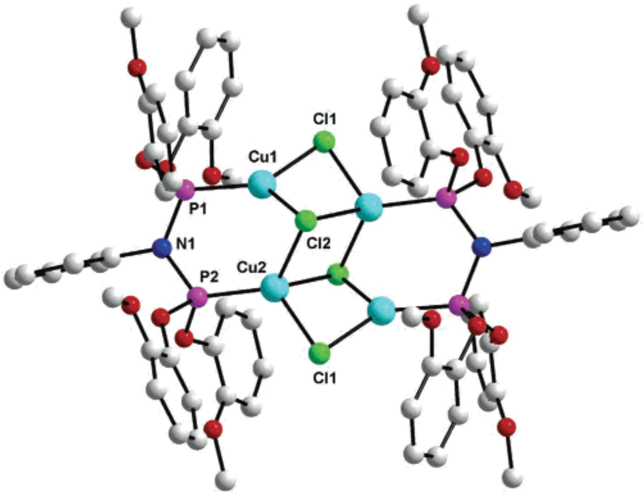


Figure 2. Molecular structure of **3**. All hydrogen atoms and the lattice solvent have been omitted for clarity.

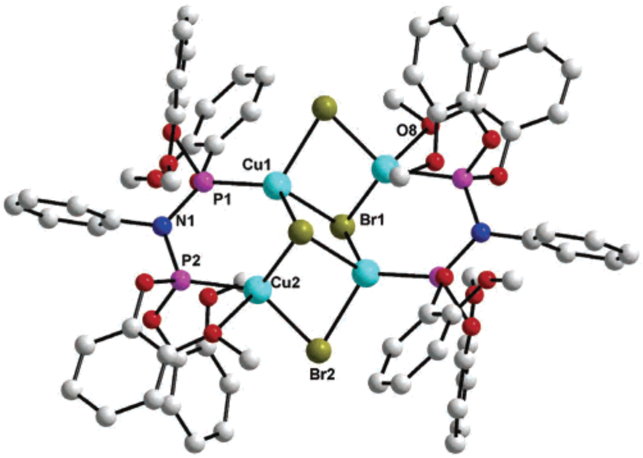


Figure 3. Molecular structure of **4**. All hydrogen atoms and the lattice solvent have been omitted for clarity.

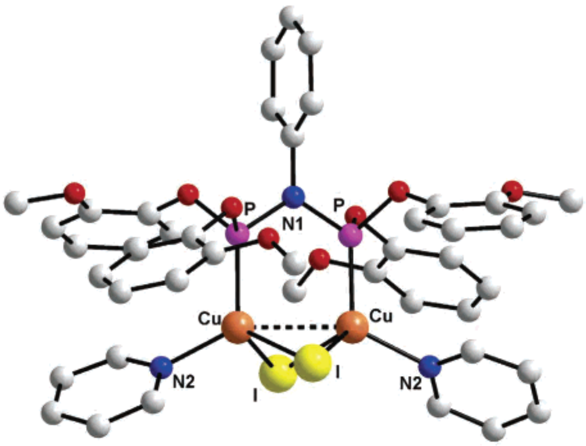


Figure 4. Molecular structure of **6**. All hydrogen atoms have been omitted for clarity.

Crystal and Molecular Structures of 2−4, 6−8, 12, and 14. Perspective views of the molecular structures of compounds **2**−**4**, **6**−**8**, **12**, and **14** with atom-numbering schemes are shown in Figures 1−8, respectively. Crystal data and the details of the structure determinations are given in Table 2, while selected bond lengths and bond angles are given in Tables 3−5. The X-ray crystal structure determination of complex **2** shows that it exists as a monomeric complex.

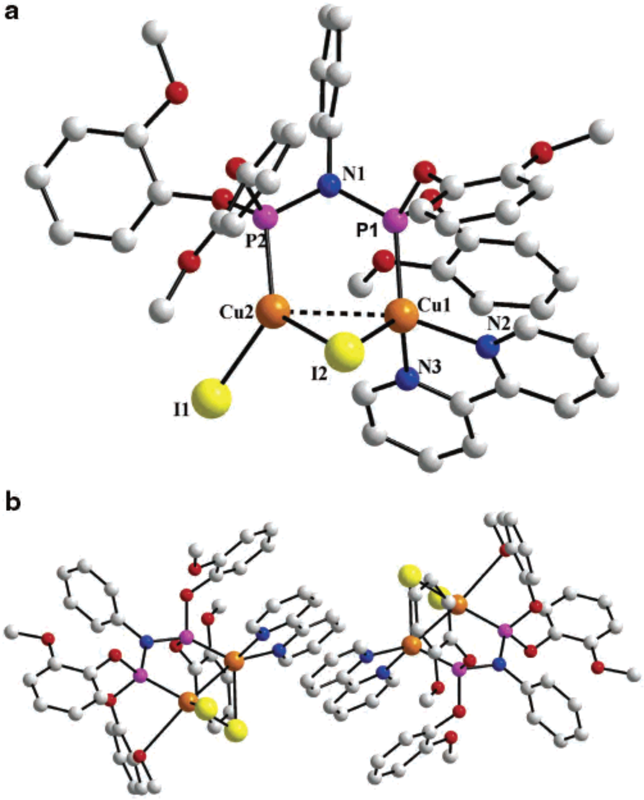


Figure 5. (a) Molecular structure of **7**. All hydrogen atoms and the lattice solvent have been omitted for clarity. (b) $\pi-\pi$ stacking in complex **7**.

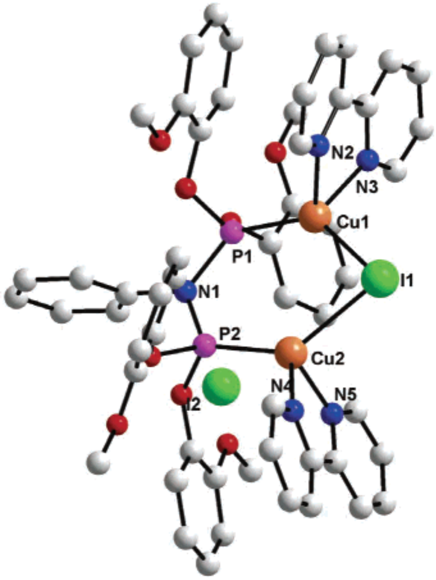


Figure 6. Molecular structure of **8**. All hydrogen atoms and the lattice solvent have been omitted for clarity.

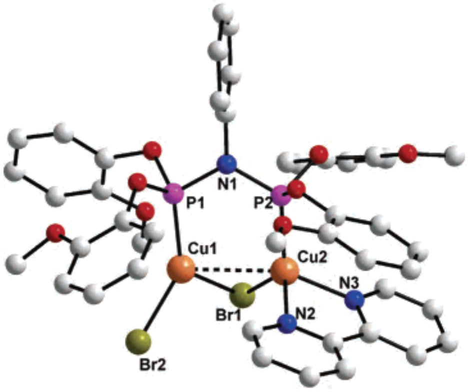


Figure 7. Molecular structure of **12**. All hydrogen atoms and the lattice solvent have been omitted for clarity.

Both of the copper(I) centers are tetrahedrally coordinated to a phosphorus atom, two bridging iodine atoms, and a solvent molecule. The Cu_2I_2 core adopts a butterfly shape with the iodine atoms at the wingtips. The four Cu−I bond lengths differ significantly from one another but can be seen (Table 3) to fall roughly into a "longer" pair and a "shorter" pair, with each copper atom forming a "long" and a "short" Cu−I bond. The distance between the two copper centers is Cu1···Cu2 = 2.721(1) Å, which indicates the presence of ligand-supported Cu···Cu interactions. Such types of interactions between formally closed-shell metal centers are well documented.[15] The body of evidence is especially large in the case of gold(I) complexes;[16] the term "aurophilicity" is used to describe the Au−Au bonding interactions, which can be as strong as 11 kcal mol^{-1}.[17] These metallophilic interactions are due to the combination of correlation and relativistic effects with added ionic contributions.[18] In the molecular structure of **2**, the two independent Cu−P distances are virtually the same [Cu1−P1 = 2.219(1) Å and Cu2−P2 = 2.204(1) Å] while the I−Cu−I angles [I1−Cu1−I2 = 101.14(1)° and I1−Cu2−I2 = 100.77(1)°] show distortion in the tetrahedral environment around copper. The angles about the iodine atoms [Cu1−I2−Cu2 = 59.92(1)°; Cu1−I1−Cu2 = 61.66(1)°] are considerably smaller.

The molecular structures of both **3** and **4** consist of neutral $Cu_4(\mu_2\text{-}X)_2(\mu_3\text{-}X)_2(\mu\text{-PNP})_2$ cores having crystallographically imposed centrosymmetry. The Cu_4X_4 cores have a "step"like structure, with each of the 10 edges of the Cu_4X_4 "step" defined by a Cu−X bond. In **3**, Cu2 has a distorted tetrahedral geometry, being bonded to one phosphorus and three chlorine atoms, whereas Cu1 exhibits trigonal coordination, with only two chlorines and one phosphorus atom bonded to it. The Cu−P distances differ only slightly [2.142(1) to 2.152(1) Å], while the Cu−Cl bond lengths vary appreciably, ranging from 2.254(1) Å (Cu1−Cl1) to 2.520(1) Å (Cu2−Cl2_a). As expected, the Cu−Cl distances involving the triply bridging chlorines (Cl2 and Cl2_a) are longer than those to the doubly bridging chlorines (Cl1 and

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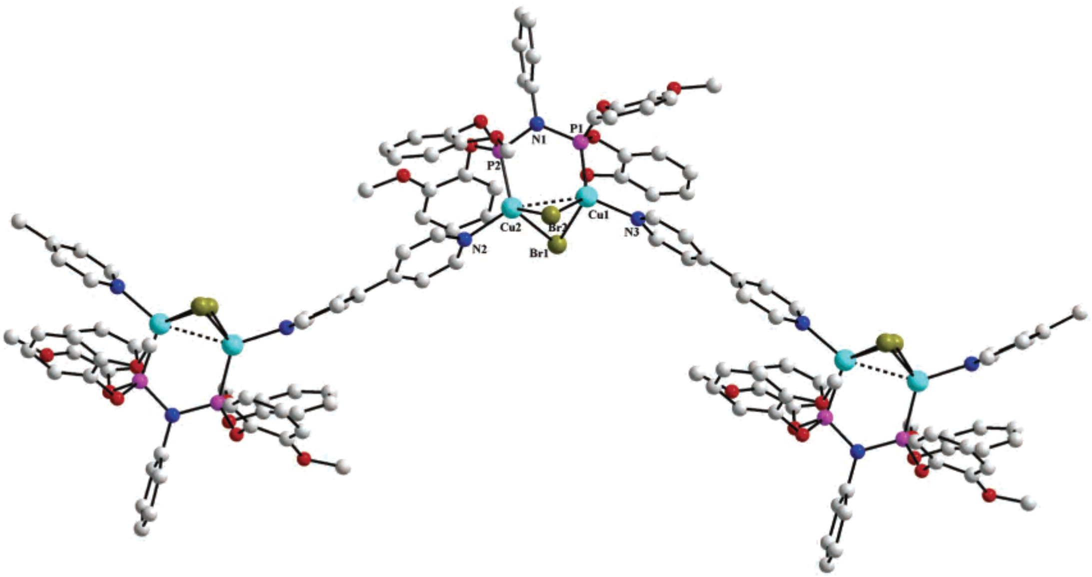

Figure 8. Molecular structure of **14**. All hydrogen atoms and the lattice solvent have been omitted for clarity.

Cl1_a). The four copper atoms are precisely coplanar, and the Cu···Cu distances, in order of increasing length, are Cu1···Cu2′ = Cu1′···Cu2 = 2.819(1) Å and Cu1···Cu2 = Cu1′···Cu2′ = 2.939(1) Å. The Cl−Cu−Cl angles [Cl1−Cu1−Cl2 = 99.86(2)° and Cl2−Cu2−Cl1_a = 99.25(2)°] are larger than the Cu−Cl−Cu angles, which range from 73.29(2)° to 86.08(2)°.

In compound **4**, the Cu1 center is four-coordinated, being bonded to three bromines and one phosphorus atom, whereas Cu2 is trigonal planar, with two bromines and one phosphorus surrounding it. The Cu−P distances vary from 2.155(2) to 2.180(2) Å. The four Cu···Cu distances, in order of increasing length, are Cu1···Cu2 = Cu1′···Cu2′ = 2.931(1) Å and Cu1···Cu2′ = Cu1′···Cu2 = 2.980(2) Å. The Cu−Br bond lengths range from 2.372(1) Å (Br2−Cu2_a) to 2.640(1) Å (Br1−Cu1_a). The angles Br1−Cu1−Br2 and Br1−Cu2−Br2_a are 101.66(3)° and 102.04(3)°, respectively. In complex **4**, the oxygen atom (O8) of the methoxy group of one of the phenyl rings makes a close approach to Cu2 (Cu2−O8 = 2.765 Å). Because Cu2 is formally three-coordinate and because this distance is less than the sum of the van der Waals radii of oxygen and copper (2.90 Å), it is likely that this represents a weak bonding interaction with the copper center. As in **3**, the Cu−Br distances involving the triply bridging bromines are longer than those involving the doubly bridging bromines.[3]

Complex **6** has crystallographically imposed 2-fold rotational symmetry, with the unique copper(I) center exhibiting distorted tetrahedral coordination geometry, as indicated by the interligand angles, which range from 103.28(2)° to 118.89(4)°, with the metal atom being surrounded by one phosphorus, one nitrogen, and two iodine ligands. The Cu_2I_2 core has a butterfly shape like that of **2**, but while there are two different Cu−I bond lengths [Cu_a-I = 2.657(1) Å and Cu−I = 2.693(1) Å], this difference is considerably less than that found for the Cu−I distances in **2**. The distance between the two copper centers (Cu1···Cu2) is 2.708(1) Å, which is shorter compared to that in complex **2** [2.721(1) Å]. The Cu−P distance is 2.187(1) Å, while the Cu1−I−Cu1_a angle is 60.82(2)°.

The crystals of **7** suitable for X-ray diffraction analysis were grown from an acetonitrile solution. In complex ′**7**, Cu1 is four-coordinated [one phosphorus, one iodine, and two nitrogen (from the bipyridine moiety) atoms], whereas the Cu2 center is three-coordinated, being bound to one phosphorus and two iodine centers. The two Cu−P distances differ significantly [Cu1−P1 = 2.1684(9) Å; Cu2−P2 = 2.1868(6) Å] as do the Cu−I distances to the bridging iodine atom [Cu2−I2 = 2.5745(5) Å and Cu1−I2 = 2.6447(5) Å]. While the asymmetry in the iodide bridge is not unusual, it is surprising that the shorter Cu−P distance is to the four-coordinated copper. Possibly this is the result of the proposed $\pi-\pi$ interaction between one of the *o*-methoxyphenoxy groups on P1 and the 2,2′-bipyridyl ligand (vide infra). The Cu−N bond lengths [Cu1−N2 = 2.060(3) Å and Cu1−N3 = 2.061(3) Å] are identical, while the terminal Cu2−I1 bond distance is 2.5410(5) Å. The distance between two copper centers is 2.877(1) Å. The I1−Cu2−I2 angle is 108.86(2)°, while the Cu1−I2−Cu2 angle is 66.88(1)°. These angles obviously indicate a distortion of the copper coordination sphere, which is occasioned primarily by the small bite angle of the 2,2′-bipyridine [N2−Cu1−N3 = 79.78(11)°]. The three-coordinated Cu2 atom shows a weak interaction with an oxygen atom (O6) of one of the *o*-methoxy groups (Cu2−O6 = 2.784 Å) similar to that found in compound **4** (2.765 Å) and less than the sum of the van der Waals radii of copper and oxygen (2.90 Å). In addition, compound **7** shows noncovalent intermolecular $\pi-\pi$ interactions between two 2,2′-bipyridine moieties and intramolecular $\pi-\pi$ interactions between one of the phenyl groups and the 2,2′-bipyridine moiety (Figure 5). The 2,2′-bipyridine moieties and phenyl rings have offset or slipped stacking $\pi-\pi$ alignment (i.e., the rings are parallel-displaced), with the minimum distance between the two 2,2′-bipyridine rings being 3.691 Å.[19]

Complex **8** contains a NP_2Cu_2I core having an irregular hexagonal shape with two different Cu−P and Cu−I

Table 2. Crystallographic Information for Compounds **2**−**4**, **6**−**8**, **12**, and **14**

	2	**3**	**4**	**6**	**7**	**8**	**12**	**14**
empirical formula	$C_{40}H_{42}Cu_2I_2N_4O_8P_2$	$C_{76}H_{82}Cl_4Cu_4N_2O_{18}P_4$	$C_{71}H_{69}Br_4Cl_9Cu_4N_2O_{16}P_4$	$C_{44}H_{43}Cu_2I_2N_3O_{10}P_2$	$C_{46}H_{44}Cu_2I_2N_4O_8P_2$	$C_{58}H_{53}Cl_{12}Cu_2I_2N_5O_8P_2$	$C_{45}H_{42}Br_2Cl_3Cu_2N_3O_8P_2$	$C_{52}H_{53}Br_2Cu_2N_7O_8P_2$
fw	1149.62	1831.32	2103.70	1216.66	1223.69	1816.30	1208.01	1252.85
cryst syst	orthorhombic	triclinic	triclinic	tetragonal	monoclinic	orthorhombic	orthorhombic	monoclinic
space group	*Pbca*	$P\bar{1}$	$P\bar{1}$	$P4_12_12$	$P2_1/c$	*Pbca*	$P2_12_12_1$	$P2_1/n$
a, Å	21.358(2)	10.8096(7)	11.6883(8)	16.612(1)	13.177(1)	21.648(2)	11.7794(8)	11.7184(8)
b, Å	18.497(1)	11.2597(8)	13.4616(9)	16.612(1)	21.533(2)	23.023(2)	18.399(1)	22.114(1)
c, Å	22.614(2)	16.097(1)	15.865(1)	20.530(2)	17.116(2)	28.375(2)	22.135(2)	20.745(1)
α, deg	90	90.985(1)	75.309(1)	90	90	90	90	90
β, deg	90	93.765(1)	89.169(1)	90	98.129(1)	90	90	94.063(1)
γ, deg	90	90.897(1)	69.062(1)	90	90	90	90	90
V, Å^3	8934(1)	1954.4(2)	2247.2(3)	5665.4(7)	4807.7(8)	14142(2)	4797.3(6)	5362.4(5)
Z	8	1	1	4	4	8	4	4
ρ_{calc}, g cm^{-3}	1.709	1.556	1.642	1.426	1.691	1.706	1.673	1.552
μ(Mo Kα), mm^{-1}	2.459	1.362	3.110	1.946	2.291	2.027	2.841	2.402
F(000)	4544	940	1105	2408	2424	7184	2424	2544
T (K)	293	293	100	100	100	100	100	100
2*θ* range, deg	1.7−28.3	1.3−28.3	1.3−27.8	2.3−28.4	1.5−28.3	2.1−24.0	2.0−28.4	2.1−28.4
total no. reflns	77 036	17 567	20 056	10 0412	42 752	173 551	86 062	94 570
to. of indep reflns	10 955 [R_{int} = 0.045]	9078 [R_{int} = 0.020]	10 260 [R_{int} = 0.030]	7059 [R_{int} = 0.057]	11 606 [R_{int} = 0.036]	10 992 [R_{int} = 0.096]	11 959 [R_{int} = 0.061]	13 373 [R_{int} = 0.045]
GOF (F^2)	1.05	1.04	1.05	1.16	1.04	1.08	1.04	1.04
R1[a]	0.0345	0.0308	0.0553	0.0466	0.0413	0.0643	0.0391	0.0304
wR2[b]	0.0793	0.0807	0.1744	0.1454	0.0943	0.1702	0.0945	0.0739

[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 $P = (F_o^2 + 2F_c^2)/3$.

distances [Cu1−P1 = 2.211(2) Å, Cu2−P2 = 2.146(2) Å and Cu1−I1 = 2.439(1) Å, Cu2−I1 = 2.763(1) Å, respectively]. The copper(I) atoms both exhibit distorted tetrahedral geometry, being coordinated to the bridging iodine, one end of the bridging bis(phosphine) ligands, and the two nitrogen atoms from the 2,2′-bipyridine moiety. The small N−Cu−N′ angles [N2−Cu1−N3 = 78.2(2)° and N4−Cu2−N5 = 83.1(2)°] are primarily responsible for these distortions and are comparable with those observed in **7** and **12**. The distance between the two copper centers is 3.310 Å, which is considerably larger than the Cu•••Cu distances found in most of the other complexes in the present investigation.

The structure of **12** is similar to the structure of **7**. In both of the structures, the 2,2′-bipyridine moiety and the terminal halogen atom are displaced to the same side of the Cu_2P_2 plane while the $Cu_2(\mu_2\text{-}X)$ bridge is folded away from the terminal halogen atom. The patterns of bond lengths and bond angles in **12** are similar to those in **7**.

The yellow crystals of **14** were obtained from an acetonitrile solution at room temperature. The core structure of **14** consisted of repeating $[P_2Cu_2(\mu\text{-}Br)_2]$ and 4,4′-bipyridine units arranged in an alternating fashion to form a 1D zigzag coordination polymer. The coordination geometry around the copper atom is tetrahedral considering one nitrogen atom of 4,4′-bipyridine, one phosphorus atom of **1**, and two bromine atoms. The Cu−P distances [Cu1−P1 = 2.1593(6) Å and Cu2−P2 = 2.1696(6) Å] are slightly different. The Br1−Cu1−Br2 and Br1−Cu2−Br2 angles are 96.06(1)° and 95.70(1)°, respectively, while the Cu1−Br1−Cu2 and Cu1−Br2−Cu2 angles are 63.18(1)° and 65.45(1)°. The Cu•••Cu distance of 2.695(1) Å is longer than that in the polymer $[Cu_2(\mu\text{-}I)_2(\mu\text{-phenazine})]_n$ [2.525(1) Å][1g] but shorter than the same one in $[(PPh_3)_2Cu_2(\mu\text{-}I)_2(\mu\text{-}4,4'\text{-bpy})]_n$ (3.143 Å),[1a] $[(Ph_3P)_2Cu_2(\mu\text{-}Cl)_2(\mu\text{-pyrazine})]_n$ [3.059(1) Å],[7a] and $[(PPh_3)_2Cu_2(\mu\text{-}Cl)_2(\mu\text{-}4,4'\text{-bpy})]_n$ [2.997(1) Å].[20] The dihedral angle between the two pyridine rings is 31.1(3)°. In all of these complexes, the geometry around the nitrogen center that bridges the two phosphonite centers is planar, with the sum of the angles around nitrogen close to 360°.

Conclusion

The aminobis(phosphonite) **1** readily reacts with copper(I) halides to give either dinuclear or steplike tetranuclear complexes depending upon the reaction conditions and the stoichiometry of the reactants. Interestingly, the dimeric and tetrameric complexes undergo reversible interconversion, which is also reflected in their reactivity toward nitrogen donor aromatic amines. Both di- and tetranuclear complexes react with pyridine, 2,2′-bipyridine, and 4,4′-bipyridine to give mixed-donor complexes. 2,2′-Bipyridine affords simple substitution products, whereas 4,4′-bipyridine produces novel coordination polymers with zigzag structures. Most of these complexes show good ligand-supported Cu•••Cu interactions.

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Table 3. Selected Bond Distances and Bond Angles for Complexes **2**−**4**

complex **2**				complex **3**				complex **4**			
bond distances (Å)		bond angles (deg)		bond distances (Å)		bond angles (deg)		bond distances (Å)		bond angles (deg)	
P1−N1	1.691(2)	P1−N1−P2	117.76(14)	P1−N1	1.676(2)	P1−N1−P2	120.13(9)	P1−N1	1.680(4)	P1−N1−P2	119.8(3)
P2−N1	1.678(2)	N1−P1−Cu1	120.01(9)	P2−N1	1.691(2)	N1−P1−Cu1	115.60(5)	P2−N1	1.675(5)	N1−P1−Cu1	120.39(17)
P1−O1	1.627(2)	N1−P2−Cu2	116.04(9)	P1−O1	1.608(1)	N1−P2−Cu2	121.16(5)	P1−O1	1.621(4)	N1−P2−Cu2	118.73(16)
P1−O3	1.617(2)	P1−Cu1−I1	123.18(2)	P1−O3	1.623(1)	P2−Cu2−Cl1	120.33(2)	P1−O3	1.626(4)	P2−Cu2−Br1	120.96(5)
P2−O5	1.624(2)	P1−Cu1−I2	100.20(2)	P2−O5	1.612(1)	P2−Cu2−Cl2	124.06(2)	P2−O5	1.618(4)	P2−Cu2−Br2	136.64(5)
P2−O7	1.618(2)	P2−Cu2−I1	114.09(2)	P2−O7	1.609(2)	P1−Cu1−Cl1	130.86(2)	P2−O7	1.619(4)	P1−Cu1−Br1	126.21(5)
P1−Cu1	2.219(1)	P2−Cu2−I2	115.61(2)	P1−Cu1	2.1416(5)	P1−Cu1−Cl2	129.28(2)	P1−Cu1	2.180(1)	P1−Cu1−Br2	118.62(5)
P2−Cu2	2.204(1)	P1−Cu1−N3	114.41(8)	P2−Cu2	2.1523(5)	Cl1−Cu1−Cl2	99.86(2)	P2−Cu2	2.155(1)	Br1−Cu1−Br2	101.66(3)
Cu1−I1	2.6584(4)	P2−Cu2−N2	112.10(8)	Cu1−Cl1	2.2536(5)	Cl1−Cu2−Cl2	99.25(2)	Cu1−Br1	2.4913(8)	Br1−Cu2−Br2	102.04(3)
Cu1−I2	2.7136(4)	Cu1−I1−Cu2	61.66(1)	Cu1−Cl2	2.3241(5)	Cu1−Cl1−Cu2	79.98(2)	Cu1−Br2	2.4850(8)	Cu1−Br1−Cu2	72.32(3)
Cu2−I1	2.6510(4)	Cu1−I2−Cu2	59.92(1)	Cu2−Cl1	2.3180(5)	Cu1−Cl2−Cu2	73.29(1)	Cu2−Br1	2.4761(8)	Cu1−Br2−Cu2	75.66(3)
Cu2−I2	2.7349(4)	I1−Cu1−I2	101.14(1)	Cu2−Cl2	2.3977(5)			Cu2−Br2	2.3719(8)		
Cu1−N3	2.006(3)	I1−Cu2−I2	100.77(1)								
Cu2−N2	1.984(3)										

Table 4. Selected Bond Distances and Bond Angles for Complexes **6**−**8**

complex **6**				complex **7**				complex **8**			
bond distances (Å)		bond angles (deg)		bond distances (Å)		bond angles (deg)		bond distances (Å)		bond angles (deg)	
P−N1	1.682(3)	P−N1−P_a	116.7(2)	P1−N1	1.689(3)	P1−N1−P2	118.7(2)	P1−N1	1.765(7)	P1−N1−P2	119.7(4)
P−O1	1.63 (1)	Cu−P−N1	118.3 (1)	P2−N1	1.678(3)	Cu1−P1−N1	123.2(1)	P2−N1	1.584(7)	Cu1−P1−N1	129.3(2)
P−O3	1.64(1)	P−Cu−N2	116.3(2)	P1−O1	1.607(4)	Cu2−P2−N1	115.5(1)	P1−O3	1.608(6)	Cu2−P2−N1	120.3(3)
P−Cu	2.187(1)	I_a−Cu−P	118.89(4)	P1−O3	1.608(3)	P1−Cu1−N2	114.66(8)	P1−O1	1.552(5)	I1−Cu1−P1	132.53(6)
I−Cu	2.6932(7)	I−Cu−P	104.33(4)	P2−O5	1.631(3)	P1−Cu1−N3	118.65(8)	P2−O7	1.661(5)	I1−Cu2−P2	136.32(6)
I−Cu_a	2.6567(7)	I−Cu−N2	109.0(2)	P2−O7	1.615(3)	I2−Cu1−P1	117.81(3)	P2−O5	1.677(5)	N2−Cu1−N3	78.2(2)
Cu−N2	2.038(5)	I−Cu−I_a	103.28(2)	P1−Cu1	2.1684(9)	I2−Cu2−P2	126.42(3)	P1−Cu1	2.211(2)	N4−Cu2−N5	83.1(2)
		Cu−I−Cu_a	60.82(2)	P2−Cu2	2.1873(9)	I1−Cu2−P2	124.72(3)	P2−Cu2	2.146(2)	I1−Cu1−N2	105.6(2)
				Cu1−N2	2.060(3)	I2−Cu1−N2	102.85(8)	Cu1−N2	2.102(7)	I1−Cu1−N3	98.1(2)
				Cu1−N3	2.061(3)	I2−Cu1−N3	115.35(8)	Cu1−N3	2.105(6)	I1−Cu2−N4	105.7(2)
				I1−Cu2	2.5410(5)	I1−Cu2−I2	108.86(2)	Cu2−N4	1.977(6)	I1−Cu2−N5	101.0(2)
				I2−Cu1	2.6447(5)	Cu1−I2−Cu2	66.88(1)	Cu2−N5	2.010(6)	P1−Cu1−N2	112.8(2)
				I2−Cu2	2.5745(5)	N2−Cu1−N3	79.8(1)	I1−Cu1	2.439(1)	P1−Cu1−N3	115.8 (2)
								I1−Cu2	2.763(1)	P2−Cu2−N4	108.2(2)
										P2−Cu2−N5	109.7(2)
										Cu1−I1−Cu2	78.76(3)

Table 5. Selected Bond Distances and Bond Angles for Complexes **12** and **14**

complex **12**				complex **14**			
bond distances (Å)		bond angles (deg)		bond distances (Å)		bond angles (deg)	
P1−N1	1.685(3)	P1−N1−P2	119.3(2)	P1−N1	1.685(2)	P1−N1−P2	118.13(9)
P2−N1	1.677(3)	Cu1−P1−N1	116.1(1)	P2−N1	1.687(2)	P1−Cu1−Br1	107.97(2)
P1−O1	1.612(3)	Cu2−P2−N1	121.7(1)	P1−Cu1	2.1593(6)	P1−Cu1−Br2	121.73(2)
P1−O3	1.619(2)	P2−Cu2−N2	113.3(1)	P2−Cu2	2.1696(6)	P2−Cu2−Br1	115.00(2)
P2−O5	1.664(4)	P2−Cu2−N3	116.8(1)	Cu1−Br1	2.5414(3)	P2−Cu2−Br2	116.36(2)
P2−O7	1.590(6)	Br1−Cu1−P1	124.81(3)	Cu1−Br2	2.5157(3)	P1−Cu1−N3	122.48(5)
P1−Cu1	2.157(1)	Br1−Cu2−P2	120.68(3)	Cu2−Br1	2.6017(4)	P2−Cu2−N2	111.75(5)
P2−Cu2	2.144(1)	Br2−Cu1−P1	130.40(3)	Cu2−Br2	2.4683(4)	Cu1−Br1−Cu2	63.18(1)
Cu2−N2	2.072(3)	Br1−Cu2−N2	116.9(1)	Cu1−N3	2.022(2)	Cu1−Br2−Cu2	65.45(1)
Cu2−N3	2.044(3)	Br1−Cu2−N3	100.8(1)	Cu2−N2	2.029(2)	Br1−Cu1−Br2	96.06(1)
Br1−Cu1	2.4294(6)	Br1−Cu1−Br2	104.77(2)			Br1−Cu2−Br2	95.70(1)
Br1−Cu2	2.4250(6)	Cu1−Br1−Cu2	70.22(2)				
Br2−Cu1	2.3320(6)	N2−Cu2−N3	80.7(1)				

Similar studies of this ligand with silver and gold centers are under way.

Experimental Section

General Procedures. All manipulations were performed under rigorously anaerobic conditions using Schlenk techniques. All of the solvents were purified by conventional procedures and distilled prior to use.[21] The compounds PhN{P(OC$_6$H$_4$OMe-*o*)$_2$}$_2$[22] and CuX (X = Cl, Br)[23] were prepared according to the published procedures. AgOTf, 2,2′-bipyridine, and 4,4′-bipyridine 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 ^{1}H and ^{31}P{^{1}H} NMR (δ in ppm) spectra were recorded using a Varian VXR 300 or VXR 400 spectrometer operating at the appropriate frequencies using tetramethylsilane and 85% H$_3$PO$_4$ as internal and external references, respectively. The

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microanalyses were performed using a Carlo Erba model 1112 elemental analyzer. The melting points were observed in capillary tubes and are uncorrected.

Synthesis of $Cu_2(\mu_2\text{-}I)_2(NCCH_3)_2\{PhN(P(OC_6H_4OMe\text{-}o)_2)_2\}\cdot CH_3CN$ (2). A solution of cuprous iodide (0.089 g, 0.467 mmol) in acetonitrile (5 mL) was added dropwise to a solution of **1** (0.151 g, 0.234 mmol) also in acetonitrile (5 mL). After stirring for 4 h, the solution was concentrated under vacuum and kept at room temperature overnight to give analytically pure product **2** as white crystals. Yield: 89% (0.239 g). Mp: 230−232 °C (dec). Anal. Calcd for $C_{40}H_{42}Cu_2I_2N_4O_8P_2$: C, 41.79; H, 3.68; N, 4.87. Found: C, 41.76; H, 3.61; N, 4.75. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.94 (s, CH_3CN, 6H), 3.57 (s, OCH_3, 12H), 6.60−7.72 (m, Ph, 21H). $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$): δ 88.5 (s).

Synthesis of $Cu_4(\mu_2\text{-}Cl)_2(\mu_3\text{-}Cl)_2\{PhN(P(OC_6H_4OMe\text{-}o)_2)_2\}_2$ (3). A solution of cuprous chloride (0.031 g, 0.314 mmol) in acetonitrile (3 mL) was added dropwise to a solution of **1** (0.102 g, 0.157 mmol) also in acetonitrile (5 mL). The reaction mixture was allowed to stir at room temperature for 4 h. The resulting solution was concentrated to 2 mL followed by the addition of diethyl ether to give **3** as a white precipitate. White crystals were obtained upon recrystallization from a 3:1 THF−petroleum ether mixture. Yield: 90% (0.120 g). Mp: 218−220 °C (dec). Anal. Calcd for $C_{68}H_{66}Cu_4Cl_4N_2O_{16}P_4$: C, 48.41; H, 3.94; N, 1.66. Found: C, 48.38; H, 3.90; N, 1.71. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.67 (s, OCH_3, 24H), 6.61−7.66 (m, Ph, 42H). $^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$): δ 101.3 (s).

Synthesis of $Cu_4(\mu_2\text{-}Br)_2(\mu_3\text{-}Br)_2\{PhN(P(OC_6H_4OMe\text{-}o)_2)_2\}_2$ (4). Compound **4** was synthesized by a procedure similar to that of **3** using cuprous bromide (0.053 g, 0.370 mmol) and **1** (0.120 g, 0.185 mmol). X-ray-quality crystals were obtained from a $CHCl_3$ solution. Yield: 92% (0.159 g). Mp: 244−250 °C (dec). Anal. Calcd for $C_{68}H_{66}Cu_4Br_4N_2O_{16}P_4$: C, 43.79; H, 3.57; N, 1.50. Found: C, 43.77; H, 3.55; N, 1.56. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.67 (s, OCH_3, 24H), 6.56−7.73 (m, Ph, 42H). $^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$): δ 98.2 (s).

Synthesis of $Cu_4(\mu_2\text{-}I)_2(\mu_3\text{-}I)_2\{PhN(P(OC_6H_4OMe\text{-}o)_2)_2\}_2$ (5). The complex **2** (0.050 g, 0.045 mmol) was dissolved in dichloromethane (5 mL), layered with petroleum ether (1 mL), and kept at −30 °C for 1 day to give an analytically pure product of **5** as white crystals. Yield: 91% (0.042 g). Mp: 238−240 °C (dec). Anal. Calcd for $C_{68}H_{66}Cu_4I_4N_2O_{16}P_4$: C, 39.78; H, 3.24; N, 1.36. Found: C, 39.70; H, 3.22; N, 1.30. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.64 (s, OCH_3, 24H), 6.64−7.79 (m, Ph, 42H). $^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$): δ 88.9 (s).

Synthesis of $Cu_2(\mu_2\text{-}I)_2(C_5H_5N)_2\{PhN(P(OC_6H_4OMe\text{-}o)_2)_2\}$ (6). To 5 mL of pyridine was added compound **2** (0.050 g, 0.045 mmol), and the mixture was allowed to stir at room temperature for 3 h. The resulting yellow solution was taken to dryness under vacuum; the residue was dissolved in dichloromethane, layered with petroleum ether, and stored at −30 °C to give white crystals of **6**. Yield: 91% (0.049 g). Mp: 190−192 °C (dec). Anal. Calcd for $C_{44}H_{43}Cu_2I_2N_3O_8P_2$: C, 44.61; H, 3.66; N, 3.55. Found: C, 44.48; H, 3.63; N, 3.47. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.64 (s, OCH_3, 12H), 6.68−8.12 (m, Ph, C_5H_5N, 31H). $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$): δ 102.8 (s).

Synthesis of $Cu_2(\mu_2\text{-}I)I(C_{10}H_8N_2)\{PhN(P(OC_6H_4OMe\text{-}o)_2)_2\}$ (7). To a solution of **2** (0.071 g, 0.064 mmol) in accetonitrile (5 mL) was added dropwise a solution of 2,2′-bipyridine (0.010 g, 0.064 mmol) in the same solvent (5 mL), and the reaction mixture was stirred at room temperature for 4 h. The resulting yellow solution was concentrated and kept at room temperature for 1 day to give analytically pure bright-yellow crystals of **7**. Yield: 87% (0.066 g). Mp: 198−200 °C (dec). Anal. Calcd for $C_{44}H_{41}Cu_2I_2N_3O_8P_2$: C, 44.68; H, 3.49; N, 3.55. Found: C, 44.54; H, 3.43; N, 3.60. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.70 (br s, OCH_3, 12H), 6.64−7.99 (m, Ph, $C_{10}H_8N_2$, 29H). $^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$): δ 101.5 (s).

Synthesis of $[Cu_2(\mu_2\text{-}I)(C_{10}H_8N_2)_2\{PhN(P(OC_6H_4OMe\text{-}o)_2)_2\}]I$ (8). Compound **8** was synthesized by a procedure similar to that of **7** using 2 equiv of 2,2′-bipyridine (0.023 g, 0.149 mmol) and **2** (0.083 g, 0.075 mmol). Yield: 84% (0.084 g). Mp: 118−120 °C (dec). Anal. Calcd for $C_{54}H_{49}Cu_2I_2N_5O_8P_2$: C, 48.44; H, 3.69; N, 5.23. Found: C, 48.54; H, 3.63; N, 5.17. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.68 (s, OCH_3, 12H), 6.68−8.10 (m, Ph, $C_{10}H_8N_2$, 37H). $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$): δ 101.1 (s).

Synthesis of $[Cu_4(NCCH_3)_4(C_{10}H_8N_2)_2\{PhN(P(OC_6H_4OMe\text{-}o)_2)_2\}_2]\ (OTf)_4$ (9). To a vigorously stirred mixture of **2** (0.148 g, 0.133 mmol) and AgOTf (0.068 g, 0.266 mmol) in acetonitrile (7 mL) was added dropwise a solution of 4,4′-bipyridine (0.021 g, 0.133 mmol) in the same solvent (8 mL) at room temperature. The mixture was allowed to stir for a further 1 h. Silver iodide, thus formed, was separated by filtration through Celite. The filtrate was concentrated under vacuum, layered with 1 mL of THF, and kept at −30 °C to give an analytically pure product of **9** as yellow crystals. Yield: 86% (0.150 g). Mp: 142−144 °C (dec). Anal. Calcd for $C_{100}H_{94}Cu_4F_{12}N_{10}O_{28}P_4S_4$: C, 45.87; H, 3.62; N, 5.35; S, 4.90. Found: C, 45.76; H, 3.74; N, 5.45; S, 4.96. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.04 (s, CH_3CN, 12H), 3.76 (s, OCH_3, 24H), 6.87−7.87 (m, Ph, $C_{10}H_8N_2$, 58H). $^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$): δ 104.6 (s).

Synthesis of $[Cu_2(NCCH_3)_2\{PhN(P(OC_6H_4OMe\text{-}o)_2)_2\}_2](OTf)_2$ (10). To a vigorously stirred mixture of **2** (0.042 g, 0.038 mmol) and AgOTf (0.019 g, 0.076 mmol) in acetonitrile (7 mL) was added dropwise a solution **1** (0.024 g, 0.038 mmol) in the same solvent (5 mL), and the mixture was stirred for 3 h. Silver iodide, thus formed, was separated by filtration through Celite. The filtrate was concentrated under vacuum, layered with 1 mL of diethyl ether, and kept at −30 °C to give an analytically pure product of **10**. Yield: 70% (0.047 g). Mp: 150−152 °C. Anal. Calcd for $C_{74}H_{72}Cu_2F_6N_4O_{22}P_4S_2$: C, 49.42; H, 4.04; N, 3.12; S, 3.56. Found: C, 49.56; H, 3.99; N, 3.15; S, 3.36. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.97 (s, CH_3CN, 6H), 3.70 (s, OCH_3, 24H), 6.82−7.71 (m, Ph, 42H). $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$): δ 111.7 (s).

Synthesis of $Cu_2(\mu_2\text{-}Cl)Cl(C_{10}H_8N_2)\{PhN(P(OC_6H_4OMe\text{-}o)_2)_2\}$ (11). This was synthesized by a procedure similar to that of **7** using 2 equiv of 2,2′-bipyridine (0.007 g, 0.047 mmol) and **3** (0.040 g, 0.024 mmol). Yield: 80% (0.038 g). Mp: 180−182 °C (dec). Anal. Calcd for $C_{44}H_{41}Cu_2Cl_2N_3O_8P_2$: C, 52.86; H, 4.13; N, 4.20. Found: C, 52.81; H, 4.06; N, 4.21. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.68 (br s, OCH_3, 12H), 6.68−7.74 (m, Ph, $C_{10}H_8N_2$, 29H). $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$): δ 101.9 (s).

Synthesis of $Cu_2(\mu_2\text{-}Br)Br(C_{10}H_8N_2)\{PhN(P(OC_6H_4OMe\text{-}o)_2)_2\}$ (12). This was synthesized by a procedure similar to that of **7** using 2 equiv of 2,2′-bipyridine (0.009 g, 0.058 mmol) and **4** (0.054 g, 0.029 mmol). Yield: 74% (0.047 g). Mp: 210−212 °C (dec). Anal. Calcd for $C_{44}H_{41}Cu_2Br_2N_3O_8P_2$: C, 48.54; H, 3.80; N, 3.86. Found: C, 48.49; H, 3.73; N, 3.80. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.69 (br s, OCH_3, 12H), 6.67−7.79 (m, Ph, $C_{10}H_8N_2$, 29H). $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$): δ 101.4 (s).

Synthesis of $[Cu_2(\mu_2\text{-}Cl)_2(C_{10}H_8N_2)\{PhN(P(OC_6H_4OMe\text{-}o)_2)_2\}]_n$ (13). To a solution of **3** (0.040 g, 0.024 mmol) in acetonitrile (3 mL) was added dropwise a solution of 4,4′-bipyridine (0.007 g, 0.047 mmol) in the same solvent (1 mL). The resulting yellow solution was kept as such at room temperature for 1 day to give analytically pure yellow crystals of **13**. Yield: 80% (0.038 g).

Mp: 230−232 °C (dec). Anal. Calcd for $C_{44}H_{41}Cl_2Cu_2N_3O_8P_2$: C, 52.86; H, 4.13; N, 4.20. Found: C, 52.80; H, 4.11; N, 4.17.

Synthesis of $[Cu_2(\mu_2\text{-}Br)_2(C_{10}H_8N_2)\{PhN(P(OC_6H_4OMe\text{-}o)_2)_2\}]_n$ (14). Compound **14** was synthesized by a procedure similar to that of **13** using **4** (0.015 g, 0.008 mmol) and 4,4′-bipyridine (0.003 g, 0.016 mmol). Yield: 84% (0.015 g). Mp: 240−242 °C (dec). Anal. Calcd for $C_{44}H_{41}Br_2Cu_2N_3O_8P_2$: C, 48.54; H, 3.80; N, 3.86. Found: C, 48.48; H, 3.83; N, 3.77.

X-ray Crystallography. A crystal of each of the compounds **2**−**4**, **6**−**8**, **12**, and **14** suitable for X-ray crystal analysis was mounted in a Cryoloop with a drop of Paratone oil and placed in the cold nitrogen stream of the Kryoflex attachment of a Bruker APEX CCD diffractometer. Full spheres of data were collected using 606 scans in ω (0.3° per scan) at $\phi = 0$, 120, and 240° for **2**−**4** and **7**, while for **6**, **8**, **12**, and **14**, a combination of three sets of 400 scans in ω (0.5° per scan) at $\varphi = 0$, 90, and 180° plus two sets of 800 scans in φ (0.45° per scan) at $\omega = -30$ and 210° was used, all under the control of the *SMART* software package.[24] The raw data were reduced to F^2 values using the *SAINT+* software,[25] and global refinements of unit cell parameters using 6000−9500 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*[26]). The structures were solved by direct methods (for **2**, **6**−**8**, **12**, and **14**), or the positions of the heavy atoms were obtained from a sharpened Patterson function (for **3** and **4**). All structures were refined by full-matrix least-squares procedures using the *SHELXTL* program package.[27] Hydrogen atoms were placed in calculated positions and included as riding contributions, with isotropic displacement parameters tied to those of the attached non-hydrogen atoms.

In **2** and **12**, disorder in one or more of the *o*-methoxyphenoxy substituents was seen, while in **6**, all of these substituents were disordered, presumably because in this instance their orientations do not conform to the crystallographically imposed 2-fold rotational symmetry of the core. Details of treatments of the disorders are provided in the CIFs.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of **2**−**4**, **6**−**8**, **12**, and **14**. This material is available free of charge via the Internet at http://pubs.acs.org.

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