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Structural Diversity of Copper(I) Complexes Formed by Pyrrole- and Dipyrrolylmethane-Based Diphosphine Ligands with Cu−X···HN Hydrogen Bonds

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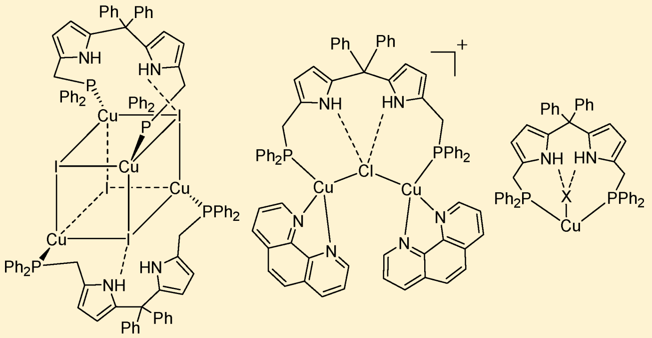
Supporting Information

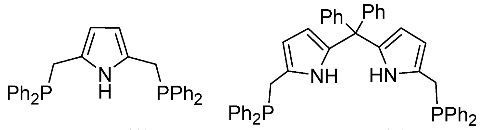
ABSTRACT: Metal complexes containing hydrogen bond donor/acceptor groups are interesting because of their applications in several areas. In the course of our investigation on the synthesis of metal complexes using newly developed pyrrole-based diphosphine ligands, a few structurally interesting copper(I) complexes containing the pyrrolic NH hydrogen bond donors were synthesized. The reaction of 2,5-bis-(diphenylphosphinomethyl)pyrrole (PNP) with an equimolar quantity of CuX (X = Cl, Br, and I) afforded the binuclear copper(I) complexes $[Cu(\mu\text{-}X)(\mu\text{-PNP-}P,P)]_2$ (**1**−**3**) in very good yields (87−90%). Conversely, the analogous reaction between 1,9-bis(diphenylphosphinomethyl)diphenyldipyrrolylmethane (PNNP) and CuX (X = Cl, Br, and I) yielded the mononuclear Cu(I) complexes [CuX(PNNP-*P,P*)] (**4**−**6**) in very good yields (~88%), in which the diphosphine ligand is chelated to the copper metal atom. Interestingly, when this reaction was carried out with a 1:2 mol ratio of ligand/metal, the cubane-like tetranuclear Cu(I) complex, $[Cu_4I_4\{\mu\text{-}Ph_2C(C_4H_3N)_2\text{-}1,9\text{-}(CH_2PPh_2)_2\text{-}P,P\}_2]$ **7**, was isolated in 68% yield. In addition, the reaction between the dipyrrolyldiphosphine ligand (PNNP) and CuCl in the presence of 1 equiv of 1,10-phenanthroline monohydrate and $NaBF_4$ afforded a novel ionic binuclear mixed-ligand Cu(I) complex, $[Cu_2(\mu\text{-}X)(\mu\text{-PNNP-}P,P)(NN)_2]BF_4$ **8**, where NN = 1,10-phenanthroline in 57% yield. The structures of all these complexes were confirmed by the single-crystal X-ray diffraction method and are supported by spectroscopic data. In contrast to the PNP pincer ligand, the dipyrrolyl−diphosphine ligand (PNNP) adopts chelation as well as bridging coordination modes with Cu(I) atoms, indicating its flexibility of bonding. In all the structures, the Cu−X···HN type of hydrogen bonds involving the metal halide ion as acceptor and the pyrrolic NH as donor are present with the Cu−X···H angles, which deviate from the favored 90°, as observed in their solid state structures. Further, the presence of this type of hydrogen bond was confirmed by NBO, AIM, and Hirshfeld analyses.



INTRODUCTION

Copper(I) complexes have attracted attention in the past and continue to be an active area of research because of their diverse structural and photophysical properties;[1] they have potential applications in areas such as optoelectronics[2] and catalysis,[3] among others. Pincer ligands have been used to modify and control the property of metal complexes. As a result, pincer metal complexes have found several applications in areas such as catalysis, sensors, and switches.[4] However, among several types of pincer ligands, PNP-pincer ligands, which have both soft and hard donors, have scarcely been used for synthesizing multinuclear Cu(I) complexes.[5] Peter and co-workers have reported highly emissive Cu(I) complexes bearing an anionic PNP pincer ligand.[6] Van der Vlugt and co-workers studied thiolate bridged binuclear Cu(I) complexes containing a pyridine-based PNP pincer ligand.[5e,7] In this potential area of research, we recently introduced a new type of pyrrole-based NNN,[8] PNP-pincer,[9] and dipyrrolylmethane-based PNNP-type ligands.[9a] The diphosphine ligands PNP and PNNP (Chart 1) are potential tridentate and polydentate ligands, respectively, when deprotonated. On the other hand, as a neutral ligand they can chelate to a metal atom to give a metal complex containing the pyrrolic NH groups. The presence of NH groups in the structure of metal complexes are potential hydrogen bond donors and can stabilize structures via a hydrogen bond to a metal-bound hydrogen acceptor.

Chart 1. Pyrrole(A)- and Dipyrrolylmethane(B)-Based Diphosphine Ligands



PNP(A) **PNNP(B)**

Metal complexes containing hydrogen bond donor/acceptor groups are interesting because of their applications in areas such

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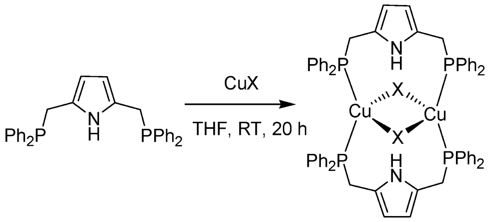
as molecular receptor,[10] switches,[11] supramolecular catalysis,[12] self-assembly,[13] and other reactions.[14] It can be noted from these studies that these hydrogen-bonding groups are useful for orienting substrates to have an optimal interaction with a metal atom that leads to substrate activation and conversion.[15] For example, in nature, carboxypeptidase A performs hydrolysis of peptide bonds with assistance from its hydrogn-bonding groups. Recently, metal complexes containing hydrogen bond groups have been reported as a catalyst for hydrogenation of CO_2,[16] dioxygen activation,[17] and transfer hydrogenation of ketones[18] in which the M−X···H hydrogen bond plays a very important role.

Herein, we report the syntheses and structural characterizations of a series of three-coordinate mononuclear, homoleptic, and heteroleptic binuclear and tetranuclear Cu(I) complexes bearing neutral PNP(**A**) and PNNP(**B**) ligand systems. In addition, the presence of the Cu−X···HN type of hydrogen bond in their structures are confirmed by NBO, AIM, and Hirshfeld analyses.

■ RESULTS AND DISCUSSION

Homoleptic Binuclear Cu(I) Complexes 1, 2, and 3. As shown in Scheme 1, the reaction between an equimolar quantity of the PNP-pincer ligand, **A**, and CuX (X = Cl, Br, and I) afforded the binuclear copper(I) complexes **1**, **2**, and **3**, bearing two bridging diphosphine ligands, respectively. These complexes were isolated in very good yields (87−90%) and are characterized by spectroscopic, elemental analysis, and single-crystal X-ray diffraction methods.[19] The ^1H NMR spectra of complexes **1**−**3** in toluene-d_8 feature broad singlets for their NH, CH_2, and the pyrrolic β-CH protons, indicating a symmetrical structure for them. The $^{31}P\{H\}$ NMR spectra of **1**−**3** recorded in the same solvent show singlets at $\delta = -13.0$, -15.9, and -21.9 ppm, respectively, indicating that all four phosphorus centers of each complex are in equivalent environments. Further, the ^{31}P chemical shifts of complex **1** and **2** are downfield shifted by 3.3 and 0.4 ppm, respectively, while that of **3** is upfield shifted by 5.6 ppm, as compared to the free ligand (^{31}P: $\delta = -16.3$ ppm). This trend of the chemical shift moving to the shielded region as the electronegativity of the halide ion decreases is opposite to the trend shown by the Ni(II) pincer metal complexes containing the same ligand $[NiX\{C_4H_2N\text{-}2,5\text{-}(CH_2PPh_2)_2\text{-}\kappa^3PNP\}]$ (X = Cl, Br, and I) reported earlier.[9a]

Scheme 1. Synthesis of Homoleptic Binuclear Cu(I) Complexes 1−3 Bearing the PNP-Pincer Ligand A



X = Cl, **1**; Br, **2**; I, **3**

The structures of **1** and **3** were determined by X-ray diffraction.[19] The ORTEP diagram of **1** is given in Figure 1 along with selected bond lengths and angles, and their refinement data are summarized in Table 2. These complexes crystallize in the monoclinic system with one molecule in their asymmetric unit. The X-ray structure revealed that each diphosphine ligand is twisted and bridges the planar rhombic "$Cu(\mu\text{-}X)_2Cu$" core in a *trans* fashion such that the plane formed by Cu_2X_2 core and the plane formed by the pyrrole ring together with the methylene carbons of each diphosphine ligand are orthogonal to each other. The two Cu(I) atoms are not equally bridged by the halide ions, for instance, Cu1−Cl1 = 2.500(2) Å and Cu2−Cl1 = 2.463(2) Å, having a difference of 0.037 Å. The Cu···Cu distances are 3.615(2) Å (**1**) and 3.610(1) Å (**3**), which are substantially longer than that found in the Cu metal (2.56 Å) and hence indicate no bonding interaction between the copper atoms. These nonbonding distances fall in the range reported for similar rhombic "$Cu(\mu\text{-}X)_2Cu$" core structures containing two bridging diphosphine ligands.[20] Their average X−Cu−X angles (86.34(7)° (Cl) and 97.56(3)° (I)) are smaller than those found in the respective Cu(I) dimer complexes of the type $[L_2Cu(\mu\text{-}X)_2CuL_2]$ containing monodentate and chelating diphosphine ligands,[16b,21] but the average I−Cu−I angle (97.56(3)°) is higher than that found [94.06(6)°] in $[Cu_2(\mu\text{-}I)_2\{\mu\text{-}Ph_2P(CH_2)_2CONH(CH_2)_2NHCO(CH_2)_2PPh_2\}_2]$.[20a]

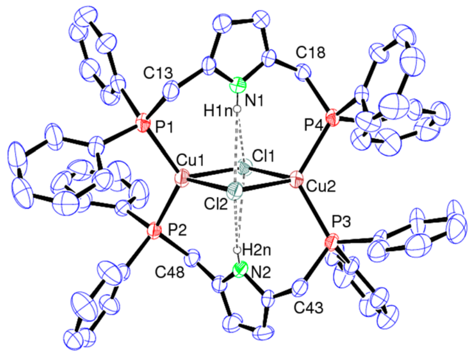


Figure 1. ORTEP diagram of **1** with 30% probability ellipsoids; most H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): P1−Cu1 2.314(2), P2−Cu1 2.293(2), P3−Cu2 2.275(2), P4−Cu2 2.258(2), Cl1−Cu2 2.463(2), Cl1−Cu1 2.500(2), Cl2−Cu2 2.452(2), Cl2−Cu1 2.497(2), Cu2−Cl1−Cu1 93.50(7), Cu2−Cl2−Cu1 93.82(7), P2−Cu1−P1 124.48(8), P2−Cu1−Cl2 122.48(8), P1−Cu1−Cl2 97.61(8), P2−Cu1−Cl1 97.85(8), P1−Cu1−Cl1 124.20(8), Cl2−Cu1−Cl1 85.45(7), P4−Cu2−P3 119.75(8), P4−Cu2−Cl2 122.14(8), P3−Cu2−Cl2 101.52(8), P4−Cu2−Cl1 100.78(8), P3−Cu2−Cl1 122.32(8), Cl2−Cu2−Cl1 87.23(7), N1···Cl2 3.383(7), H1n···Cl2 2.74(8), N1−H1n···Cl2 145(8), N1···Cl1 3.509(7), H1n···Cl1 2.89(8), N1−H1n···Cl1 141(8), N2···Cl2 3.341(7), H2n···Cl2 2.65(8), N2−H2n···Cl2 162(9), Cu1−Cl2···H1n 66(2), Cu2−Cl2···H1n 68(2), Cu1−Cl1···H1n 64(2), Cu2−Cl1···H1n 65(2), Cu1−Cl2···H2n 68(2), Cu2−Cl2···H2n 70(2), Cu1−Cl1···H2n 62(2), Cu2−Cl1···H2n 64(2).

Each Cu(I) atom exhibits a pseudotetrahedral geometry. In the chloride complex **1**, both arms of each ligand are almost equally twisted as indicated by the dihedral angles, P4−C18−C17−N1 = −56.3(9)° and P1−C13−C14−N1 = −48.0(9)°, which assisted the pyrrolic NH groups to form two bifurcated hydrogen bonds. In the case of the iodide complex **3**, the twist angles differ drastically, for instance, P1−C13−C14−N1 = −69.4(7)° and P4−C18−C17−N1 = −24.2(9)°, and hence the pyrrolic NH groups are not able to form bifurcated hydrogen bonds, in contrast to the chloride structure. However, the Cu···Cu distance (3.610(1) Å) found in **3** does not differ much from that (3.615(2) Å) of **1**. Complex **3** exhibits the I1···I2 distance of 4.1217(6) Å, which is longer than that reported for the binuclear Cu(I) complex containing bridging diphosphine

Scheme 2. Synthesis of Cu(I) Complexes of the Dipyrrolylmethane-Based Diphosphine Ligands B: Three Coordinate, 4–6, and the Cubane-Like Tetranuclear, 7, complexes

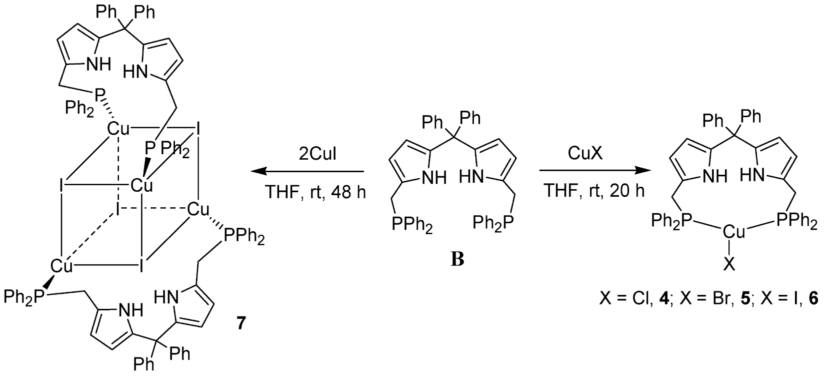


Table 1. Selected Bond Lengths (Å) and Angles (°) for the Three-Coordinate Cu(I) Complexes, 4–6

complex	P1–Cu	P2–Cu	Cu–X	P1–Cu–P2	P1–Cu–X	P2–Cu–X
4	2.2391(7)	2.2511(7)	2.2927(7)	142.13(3)	109.34(3)	108.36(3)
5	2.238(2)	2.251(2)	2.4208(15)	141.88(7)	109.54(7)	108.43(7)
6	2.2456(14)	2.2500(14)	2.5404(7)	131.28(5)	115.00(4)	113.15(4)

ligand $[Cu_2(\mu\text{-}I)_2(Ph_2P(CH_2)_2CONH(CH_2)_2NHCO\text{-}(CH_2)_2PPh_2)_2]$ (I···I = 3.96 Å).[20a]

Three-Coordinate 4–6 and the Cubane-Like Tetranuclear 7 Cu(I) Complexes. As shown in Scheme 2, the reaction between the dipyrrolylmethane-based diphosphine ligand **B** and CuX (X = Cl, Br, and I) in a 1:1 mol ratio afforded the mononuclear Cu(I) complexes **4**, **5**, and **6** in very good yields (~88%), respectively. Interestingly, when the mole ratio of **B** and CuI is changed to 1:2, the cubane-like tetranuclear Cu(I) complex **7** was isolated in 68% yield. These mononuclear complexes **4**, **5**, and **6** in toluene-d_8 possess almost the same ^{31}P chemical shift values, which appear as singlets at $\delta = -5.7$, −5.8, and −6.6 ppm, respectively. Similarly, the ^{31}P{H} NMR spectrum of **7** in dichloromethane gives a singlet at $\delta = -6.2$ ppm. All these ^{31}P chemical shifts are downfield shifted as compared to that of the free ligand (^{31}P: $\delta = -15.5$ ppm), and they indicate that the two phosphorus centers in each complex are in equivalent environments. Further, none of these complexes exhibit emission in toluene or dichloromethane solution, but their structures are interesting with Cu–X···HN hydrogen bonds among other features described below (Table 1.

The X-ray structure of **4** and its selected bond lengths and angles are given in Figure 2. The structures of **5** and **6** are given in SI (Figure S33 and Figure S34, respectively). Complexes **4**–**6** crystallize in the triclinic $P\bar{1}$ space group with one molecule in their asymmetric unit. The structure of each complex [CuX(PNNP)], where X = Cl, Br, and I, consists of one chelated diphosphine ligand **B** and one halide atom, resulting in a three-coordinate Cu(I) complex. The geometry around the copper atom in each complex is a planar distorted equilateral triangular with the P1–Cu–P2 angles (X = Cl, 142.13(3)°, Br, 141.88(7)°, and I, 131.28(5)°) higher than the corresponding other two angles, P1–Cu–X and P2–Cu–X, and the sum of the angles around copper ranges from 359.4 to 359.8°. The two phosphorus atoms and Cu–X unit form a plane, and the dipyrrolylmethane moiety is located above this plane with both the pyrrolic NH groups oriented toward the halide ion and hydrogen bonded to the halide ion, as shown in Figure 2.

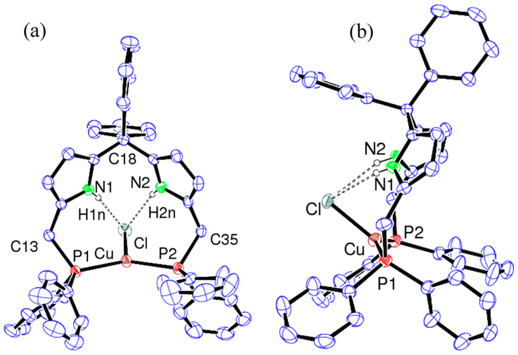


Figure 2. (a) ORTEP diagram of **4** with 30% probability ellipsoids; most H atoms are omitted for clarity; (b) side view. Hydrogen bonding distances (Å) and angles (°): N1···Cl 3.374(2), H1n···Cl 2.57(3), N1–H1n···Cl 170(3), N2···Cl 3.283(2), H2n···Cl 2.50(3), N2–H2n···Cl 160(2), Cu–Cl···H1n 73.1(6), Cu–Cl···H2n 78.3(6).

All the Cu–P bond distances are shorter than those reported for an analogous tricoordinate Cu(I) pincer complex, [PNPCuBr][5c] (2.3104(5) Å and 2.3150(5) Å), and those for the complexes of the formula $[CuXL_2]$ containing monodentate phosphine ligands (L = PPh_3,[22] or PCy_3[23]) or a chelating diphosphine ligand.[24] However, certain Cu–P bond distances are slightly higher than that found in the $[CuXL_2]$ complex when L = $P(CH_2Ph)_3$.[25] This can be because of steric factors associated with the dipyrrolydiphosphine ligand **B**. Consequently, the Cu–X bond distances (Cl, 2.2927(7) Å or Br, 2.4208(15) Å) are longer than the corresponding value reported for the $[CuXL_2]$ complexes containing monodentate phosphine ligands (L = PPh_3, PCy_3, PPh_2(*o*-tol),[26] or PCy_2Ph[27]) or a bidentate phosphine ligand.[20] Conversely, the Cu–I bond distance (2.5404(7) Å) in **6** is lower than that reported for the $[CuXL_2]$ complexes containing the phosphine ligand such as PCy_3 or $P(CH_2Ph)_3$, but it is longer when this copper complex contains PPh_3 or PPh_2(*o*-tol). Further, since the two phosphorus atoms of the diphosphine ligand **B** are connected via nine atoms, the P–Cu–P angles in **4**–**6** are higher than those reported for the [PNPCuBr] complex containing (2,6-bis[(diphenylphosphino)methyl]pyridine) and

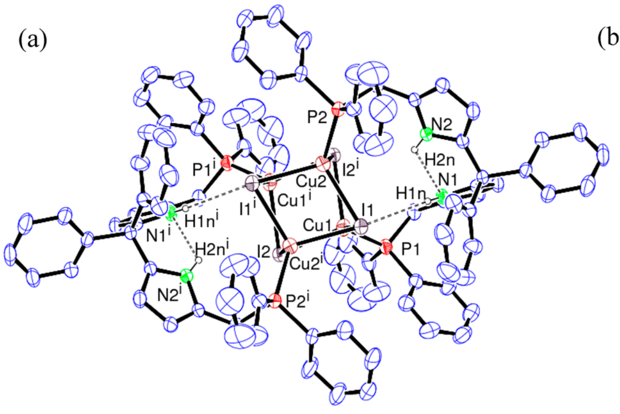


Figure 3. (a) ORTEP diagram of **7** with 30% probability ellipsoids; most H atoms are omitted for clarity; (b) shows only the "$Cu_4I_4P_4$" skeleton of the distorted cubane structure. Selected bond lengths (Å) and angles (°): P1−Cu1 2.2552(16), P2−Cu2 2.2434(16), Cu1−I1 2.6393(9), Cu1−I2 2.6807(8), Cu1−I2^{i} 2.7954(9), Cu1⋯Cu2^{i} 2.972(1), Cu1⋯Cu2 3.252(1), Cu1⋯Cu1^{i} 3.248(1), Cu2⋯Cu2^{i} 3.195(1), Cu2−I1 2.6745(8), Cu2−I1^{i} 2.6831(8), Cu2−I2^{i} 2.7347(9), I1⋯I2 4.458, I1⋯I2^{i} 4.195, I1⋯I1^{i} 4.205, I2⋯I2^{i} 4.273, I2⋯I1^{i} 4.195, P1−Cu1−I1 115.15(5), P1−Cu1−I2 114.54(5), I1−Cu1−I2 113.86(3), P1−Cu1−I2^{i} 107.68(5), I1−Cu1−I2^{i} 101.02(3), I2−Cu1−I2^{i} 102.54(3), P2−Cu2−I1 121.14(5), P2−Cu2−I1^{i} 111.97(4), I1−Cu2−I1^{i} 103.42(3), P2−Cu2−I2^{i} 107.29(5), I1−Cu2−I2^{i} 101.71(3), I1^{i}−Cu2−I2^{i} 110.74(3), Cu1−I1−Cu2 75.45(3), Cu1−I1−Cu2^{i} 67.87(2), Cu2−I1−Cu2^{i} 73.21(3), Cu1−I2−Cu2^{i} 66.55(2), Cu1−I2−Cu1^{i} 72.72(3), Cu2^{i}−I2−Cu1^{i} 72.02(2), N1⋯I1 3.947(4), H1n⋯I1 3.17(5), N1−H1n⋯I1 174(5), N2⋯N1 3.011(6), H2n⋯N1 2.43(5), N2−H2n⋯N1 124(4), Cu1−I1⋯H1n 70.0(9), Cu2−I1⋯H1n 94.2(9).

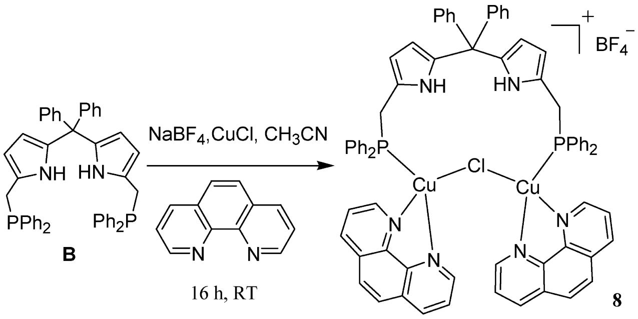
those found in [$CuXL_2$] complexes (L = PPh_3, PCy_3, $P(CH_2P)_3$, PPh_2(*o*-tol), or PCy_2Ph).

The tetranuclear Cu(I) complex **7** crystallizes in the monoclinic *P*2/*n* space group with one-half of the molecule in the asymmetric unit. The whole molecule was generated by C_2 symmetry operation and is given in Figure 3. The X-ray structure revealed that four Cu(I) and four I^- atoms are arranged alternatively in the corners of a distorted cubane structure. Each face of this distorted cube consists of a "Cu_2I_2" unit, and their copper atoms are bridged by two diphosphine ligands in a *trans* fashion. Each Cu atom is coordinated to three iodine atoms and one phosphorus donor, exhibiting a distorted tetrahedral geometry. Cu−P, Cu−I, Cu⋯Cu, and I⋯I distances and their angles are in the range reported for other distorted Cu(I) cubane structures containing monodentate[28] or bidentate phosphine[20a] ligands. The Cu⋯Cu distances vary from 2.972(1) to 3.252(1) Å, averaging to 3.167(1) Å. The Cu−I bond lengths vary from 2.6393(9) Å to 2.7954(9) Å about Cu1 and from 2.6745(8) Å to 2.7347(9) Å about Cu2. The Cu−I−Cu angles range from 66.55(2)° to 75.45(3)°, showing the distortion of cubane structure, which is probably caused by repulsion between the iodine atoms. Both the pyrrolic NH groups are projected toward the "Cu_4I_4" core, and one of the NH groups of each ligand is hydrogen bonded to the iodine atom.

Further, in contrast to several Cu(I) cubane clusters with reported different Cu⋯Cu distances that affect their luminescence properties, complex **7** is not emissive probably because of its relatively longer nonbonding Cu⋯Cu distances.[29] To the best of our knowledge, this structure represents only the third copper−iodide cubane containing a bidentate phosphine ligand.

Heteroleptic Binuclear Cu(I) Complex 8. Because we observed the Cu−X⋯H hydrogen bonding in the solid-state structures of homoleptic Cu(I) complexes, we set the synthesis of heteroleptic Cu(I) complex to observe this type of hydrogen bonding. A novel binuclear ionic Cu(I) complex **8** was obtained in 57% yield from the one-pot reaction between the dipyrrolyldiphosphine ligand **B** and CuCl in the presence of 1 equiv of 1,10-phenanthroline monohydrate and $NaBF_4$ (Scheme 3). The ^{31}P NMR spectrum of **8** in CH_2Cl_2 gives a singlet at δ −6.4 ppm, which is downfield shifted as compared with that of the free ligand and indicating that the phosphorus centers are in equivalent environments. This complex in CH_2Cl_2 exhibits an absorption band (λ_{max}) at 439 nm, falling in the region characteristic for a metal-to-ligand charge-transfer transition (see Supporting Information, Figure S31). This wavelength is longer than the λ_{max} values reported for the mononuclear mixed-ligand Cu(I) complexes containing a simple phenanthroline ligand, [Cu(NN)(P−P)]BF_4 (P−P = bis[2-(diphenylphosphino)phenyl]ether) (λ_{max} = 391 nm)[30] and [Cu(NN)$(PPh_3)_2$]BF_4 (λ_{max} = 365 nm).[31]

Scheme 3. Synthesis of a Mixed-Ligand Cu(I) Complex 8 Containing the Bridging Dipyrrolyldiphosphine Ligand B



Complex **8** is not emissive in toluene or dichloromethane solution, like the previous copper complexes. This observation is consistent with the report of McMillin[1a,32] and others[33] that homoleptic or heteroleptic Cu(I) complexes containing one 2,9-disubstituted phenanthroline molecule are emissive, while Cu(I) complexes containing simplex 1,10-phenanthroline are not emissive, because the substituents at the 2,9-positions of the phenanthroline molecule sterically inhibit the structural distortion of Cu(I) complex from the tetrahedral to the flattened structure in the excited state. Further, the structure of **8** as determined by X-ray diffraction given in Figure 4 is interesting with the bent chloride ion bridging and Cu−X···H hydrogen bonds.

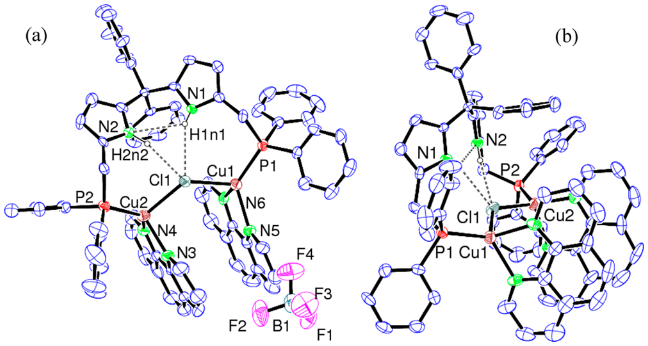


Figure 4. (a) ORTEP diagram of **8** with BF$_4^-$ with 30% probability ellipsoids; most H atoms are omitted for clarity; (b) a view along the Cu···Cu vector. Selected bond lengths (Å) and angles (°): N3−Cu2 2.060(7), N4−Cu2 2.062(7), N5−Cu1 2.143(8), N6−Cu1 2.043(7), P1−Cu1 2.198(2), P2−Cu2 2.177(2), Cl1−Cu1 2.403(2), Cl1−Cu2 2.404(3), N6−Cu1−N5 79.3(3), N6−Cu1−P1 131.1(2), N5−Cu1−P1 126.3(2), N6−Cu1−Cl1 95.6(2), N5−Cu1−Cl1 108.0(2), P1−Cu1−Cl1 110.37(9), N3−Cu2−N4 81.4(3), N3−Cu2−P2 119.9(2), N4−Cu2−P2 128.4(2), N3−Cu2−Cl1 97.5(2), N4−Cu2−Cl1 111.9(2), P2−Cu2−Cl1 110.75(9), N1···Cll 3.228(7), H1n1···Cl1 2.56(8), N1−H1n1···Cl1 155(9), N2···Cll 3.259(7), H2n2···Cl1 2.34(7), N2−H2n2···Cl1 164(6), N1···N2 3.005(10), H1n1···N2 2.53(8), N1−H1n1···N2 125(9), Cu1−Cl1···H1n1 91(2), Cu1−Cl1···H2n2 136(2), Cu2−Cl1···H1n1 128(2), Cu2−Cl1···H2n2 85(2).

The cationic part of this complex consists of two Cu(I) atoms bridged by one diphosphine and one chlorine ligand. In addition, each copper atom is chelated by one phenanthroline molecule, resulting in a monocationic binuclear Cu(I) complex whose charge is neutralized by the disordered BF$_4^-$ ion. The chlorine atom bridges the two copper atoms by being on the bridging side of the dipyrrolydiphosphine ligand so that the pyrrolic NH groups are able to form hydrogen bonds. The dipyrrolylmethane moiety of the ligand is bent toward the chlorine atom. The two phenanthroline molecules exhibiting $\pi-\pi$ interactions are parallel to each other when viewing along the Cu•••Cu vector and are perpendicular to an approximate plane formed by the two Cu, P, methylene carbon atoms together with the chloride ion in the center. The geometry around each copper atom is a distorted tetrahedral with almost equal P1−Cu1−Cl1 and P2−Cu2−Cl1 angles of 110.37(9)° and 110.75(9)°, respectively. The Cu1−P1 and Cu2−P2 bond distances are almost equal and smaller than those found for the mononuclear **4** and the tetranuclear **7** Cu(I) complexes. Similarly, the Cu−Cl bond distances [2.403(2) Å and 2.404(3) Å] are slightly shorter than the average Cu−Cl distance (2.478(2) Å) found in complex **1** but are longer than those (2.2927(7) Å) found in the mononuclear complex **4**. The Cu1···Cu2 distance of 4.332(2) Å indicates no bonding interaction between the two copper atoms and is longer than that (3.310 Å) reported for the similar dinuclear Cu(I) complex containing 2,2′-bipyridine.[34] Each copper atom in the structure of **8** possesses 18 valence electrons, and the complex is air stable.

Hydrogen Bonding Discussion. In all the structures **1**, **3**, and **4**−**8**, the pyrrolic NH groups form hydrogen bonds with the metal halide ion whose metric parameters are given in their figure captions. In addition, the structures of **7** and **8** showed one of the pyrrolic NH groups hydrogen bonded to the adjacent pyrrolide nitrogen atom, that is, the N−H···N type of hydrogen bond. All the H···X (X = Cl, Br, and I) distances are well below the sum of the van der Waals radii of the corresponding atoms with their N−H···X angles greater than 140°. This type of M−X···HN hydrogen bonding has been analyzed particularly by Crabtree,[35] Brammer,[36] Bernstein[37] and co-workers and has been reported for several structures.[38] The interesting aspect of this type of hydrogen bond is the directional preference of M−X···HN interaction, and its angle falls in the range of 90−130°, as observed in many structures.[34] However, analysis of the Cu−X···H angles in the structures of

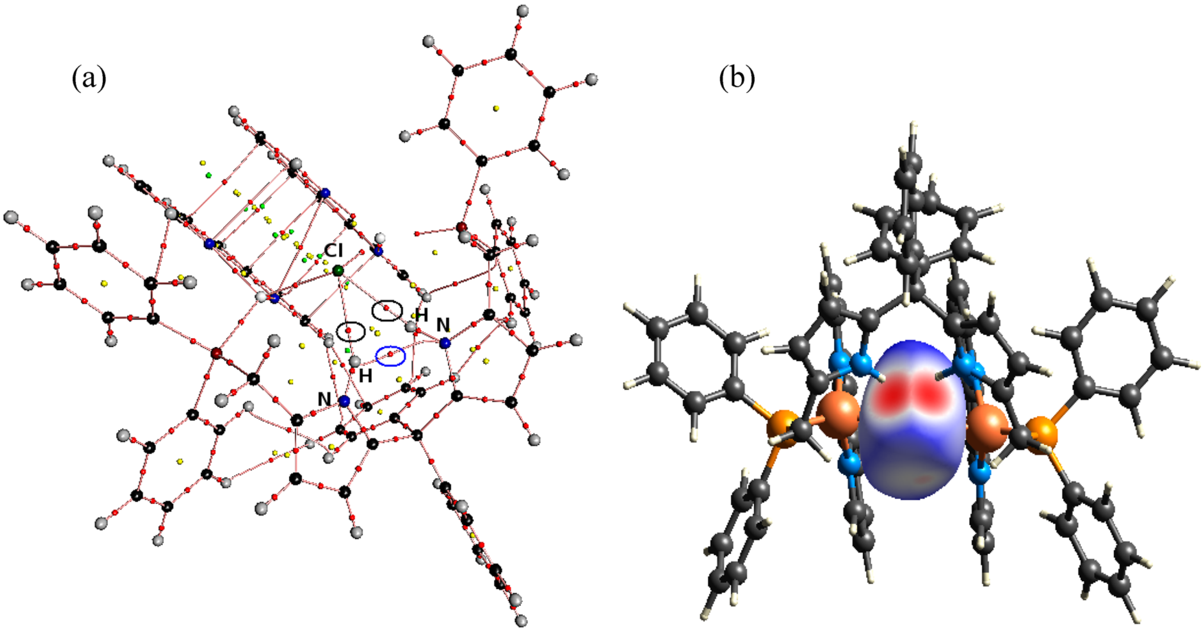


Figure 5. (a) Optimized structure of **8**. The bond critical points between the pyrrolic hydrogen atom and the Cu−Cl unit, signifying hydrogen bonds, are highlighted with black circles. (b) Hirshfeld[43] surface analysis of the observed Cu−X···HN interactions in complex **8**.

1, **3**, and **4**−**8** showed some anomalies. The tetranuclear **7** and the mixed ligand complex **8** showed most of the Cu−X···H angles above 90° (ranging from 70.0(9) to 136(2)°), complying with the directionally preferred angular value. In contrast to this, the Cu−X···H angles displayed by the dinuclear (**1** and **3**) and the mononuclear (**4**−**6**) complexes range from 56.51(2)° to 78.3(6)°, which are drastically lower than 90° that is expected for the more basic p-lone pair orbital of metal bound halide ion involved.[33] Steric constraints of the ligand systems that form mono-, di-, and tetranuclear complexes containing bridging and terminal halide ions, electron rich Cu(I)-d^{10}, and packing forces could contribute to these observed angles in the solid state. In addition, these angles are similar to the values found for a Cu(I) dimer complex of the type containing bridging chloride ions, $[LCu(\mu\text{-}Cl)_2CuL]$[39] (Cu1−Cl1···H8 = 81.85(2)°, $Cu1^i$−Cl1···H8 = 155.61(3)°), for a Cu(I) dimer complex containing terminally bonded chloride ions (Cu1−Cl2···$H2N^i$ = 87.8(7)°),[40] and for a mononuclear Cu(I) complex containing a terminally bonded chloride ion (Cu1−Cl1···H1 = 83(1)°);[41] these angles are obtained by viewing their cif files by Mercury 3.1 software.

As a representative example for each type of stucture, the chloro derivative complexes **1**, **4**, **8** and the cubane structure **7** were analysized by NBO and AIM calculation methods to ascertain the presence of H-bonds in the above-mentioned complexes. The NBO analysis of the bond between the pyrrolide nitrogen and its hydrogen atom showed an increased s-orbital character for the pyrrolide nitrogen atom as compared to the same in the free ligands **A** and **B** (see Supporting Information, Table S8). This increase in s-orbital character (suggesting an increase in electgronegativity of the N atom) is a characteristic feature of the presence of the H-bond in these structures. Further, upon comparison of the ν(NH) stretching frequency of the free ligands **A** and **B** (Chart 1) with that of the corresponding optimized geometry of complex, the ν(NH) stretching frequency for each structure is red shifted, suggesting the weakening of the N−H bonds in these complexes (see Supporting Information, Table S8). This could be because of the presence of H-bonds between the pyrrolic NH and chlorine atom. This is further supported by the AIM analysis for the presence of an electron density path linking the pyrrolic NH proton with acceptor (Cl−Cu) and a bond critical point for each H-bond. For example, the optimized structure of complex **8** with all bond critical points is given in Figure 5. The bond critical points between the pyrrolic hydrogen atom and Cu−Cl unit, signifying hydrogen bonds, are highlighted by black circles in Figure 5. At each of these critical points, the electron density is more than 0.002 au, and the Laplacian of electron density is higher than 0.004 au (see Supporting Information, Table S9), thus fulfilling the criteria for H-bond.[42]

In addition, to check the propensity of the pyrrole ring NH toward hydrogen bonding, the corresponding structures containing furan rings instead of pyrrole rings were optimized (see Supporting Information, Figure S37). These furan ring optimized structures were found to be adopting the same conformation as do the pyrrole ring structures **1**, **4**, **7**, and **8**. However, the existence of H-bonds in these structures is supported by the O···X distances in the optimized furan derivative structures. The O···X distances are much longer than the sum of the van der Waals radii of the oxygen and chlorine atoms and are longer than the N···X distances of the corresponding pyrrole ring structures. Therefore, it is comprehensible that because of the formation of NH···X hydrogen bonds in **1**, **4**, **7**, and **8**, N···X distances are shorter and fall within the sum of the van der Waals radii of the nitrogen and chlorine atoms. In addition, Hirshfeld analysis clearly confirms the presence of Cu−X···HN interactions in these complexes (see Figure 5b for **8** and Supporting Information, Figure S38 for other structures).

■ CONCLUSION

The monopyrrolyldiphosphine PNP-pincer ligand **A** gave the dimeric Cu(I) complexes in which the ligand adopts a bridging mode of coordination, while the dipyrrolyldiphosphine PNNP ligand **B** afforded the mono-, di- and tetranuclear Cu(I) complexes, in which it exhibits the chelating and bridging coordination modes. This shows that ligand **B** is more flexible than **A** probably because of the chain length difference between them. It is interesting to note that the formation of the mononuclear Cu(I) complex **6** against the tetranuclear complex **7** was controlled by changing the mole ratio of the PNNP ligand **B**. In addition, although none of the Cu(I) complexes formed by these diphosphine ligands are emissive, they represent rarely reported and structurally interesting complexes with multiple Cu−X···HN type of hydrogen bonds with the majority of Cu−X···H angles below 90° in contrast to the preferred 90−130° value. The presence of H-bonds involving metal halide ion as acceptor and the pyrrolic NH as donor was confirmed by the NBO and AIM analyses, which are supported by Hirshfeld analysis. All these are further contributing to the existing structural diversity of Cu(I) complexes. In particular, the binuclear heteroleptic complex **8** represents a novel structure of its type. Synthesis of other mixed−ligand Cu(I) and Ag(I) complexes for their photophysical properties and other metal complexes are underway.

■ EXPERIMENTAL SECTION

All reactions and manipulations were carried out under a nitrogen atmosphere using standard Schlenk-line techniques. Petroleum ether (bp 40−60 °C) and other solvents were distilled according to the standard procedures. The PNP (**A**) and PNNP (**B**) ligands were prepared as per the procedure reported in the literature.[14] CuX (X = Cl, Br, and I), toluene-d_8, $CDCl_3$, and $NaBF_4$ were purchased from Aldrich. The compound 1,10-phenanthroline, solvents and other chemicals were purchased from local commercial sources. ^1H NMR (200 and 400 MHz), ^{13}C NMR (50.3 and 100.6 MHz), and ^{31}P (161.9 MHz) spectra were recorded on Bruker ACF200 and AV400 spectrometers at room temperature. ^1H NMR chemical shifts are referenced with respect to the chemical shift of the residual protons present in the deuterated solvents. For ^{31}P NMR measurements, 85% H_3PO_4 was used as an external standard. FTIR spectra were recorded using Perkin−Elmer Spectrum Rx. High-resolution mass spectra (ESI) were recorded using the Xevo G2 Tof mass spectrometer (Waters). Elemental analyses were carried out using a Perkin−Elmer 2400 CHN analyzer. UV−vis spectra were recorded using a quartz cuvette on a Shimadzu spectrophotometer.

Computational Method. The crystal structure of complexes **1**, **4**, **7**, and **8** were used as the starting point of geometry optimization employing the M06-2X functional[44] and 6-31G(d,p) basis set. Frequency calculation was carried out for these complexes by employing the BLYP[45] functional and 6-31G(d,p) basis set. Natural bond orbital (NBO) analysis[46] and atoms in molecules (AIM) analysis[47] were carried out to check the existence of hydrogen bonds in these complexes. For NBO analysis, the B3LYP[48] functional and 6-31+G(d,p) basis set was used. For complex 7, a smaller basis set (3-21G) was used. While the AIM analysis was performed using AIM2000 program,[49] the geometry optimization, frequency calculations, and NBO analysis were carried out using Gaussian09 program.[50]

Synthesis of [Cu(*μ*-Cl){*μ*-C_4H_2NH-2,5-$(CH_2PPh_2)_2$-*P,P*}]$_2$, 1. To a THF (~50 mL) solution of monopyrrolic diphosphine ligand **A** (0.234 g, 0.505 mmol) was added solid CuCl (0.050 g, 0.505 mmol), and the solution was stirred for 16 h at room temperature, giving a clear solution. The solution was layered with petroleum ether and allowed to stand for about 2 weeks to give colorless crystals of complex **1**. The crystals were separated by decanting the mother liquor and dried under vacuum (0.250 g, 0.222 mmol, 88% yield). ^1H NMR (toluene-*d*$_8$, 400 MHz, ppm): δ = 3.55 (s, 8H, C*H*$_2$), 5.42 (s, 4H, pyrrole *β*-C*H*), 6.83−7.25 (m, 40H, phenyl C*H*), 12.00 (br s, 2H, N*H*). $^{31}P\{^1H\}$NMR (161.9 MHz, toluene-*d*$_8$, ppm): δ = −13.0(s). FT-IR (KBr, cm^{-1}): ν = 3319 (s), 3051 (m), 1584 (m), 1483 (m), 1434 (s), 1398 (w), 1271 (w), 1182 (w), 1100 (m), 1029 (m), 998 (w), 827 (m), 741 (vs), 693 (vs), 639 (w), 508 (m), 477 (m), 444 (w), 403 (w). HRMS (+ESI) *m*/*z*: $[M - Cl^-]^+$ calcd for $C_{60}H_{54}Cl_2Cu_2N_2P_4$, 1087.1718; found, 1087.1440. Anal. Calcd for $C_{60}H_{54}Cl_2Cu_2N_2P_4$: C, 64.06; H, 4.84; N, 2.49. Found: C, 64.26; H, 4.96; N, 2.37.

The bromide (**2**) and the iodide (**3**) analogues of complex **1** were synthesized by following the synthetic procedure of **1**. For the synthesis of **2**, CuBr (0.050 g, 0.350 mmol) and ligand **A** (0.162 g, 0.350 mmol) were used. The yield is 90% (0.190 g, 0.160 mmol). For the synthesis of **3**, CuI (0.100 g, 0.525 mmol) and ligand **A** (0.244 g, 0.525 mmol) were used. The yield is 87% (0.3 g, 0.230 mmol).

[Cu(*μ*-Br){*μ*-C_4H_2NH-2,5-$(CH_2PPh_2)_2$-*P,P*}]$_2$, 2. ^1H NMR (toluene-*d*$_8$, 400 MHz, ppm): δ = 3.66 (s, 8H, C*H*$_2$), 5.51 (s, 4H, pyrrole *β*-C*H*), 6.87−7.22 (m, 40H, phenyl C*H*), 11.60 (br s, 2H, N*H*). $^{31}P\{^1H\}$NMR (161.9 MHz, toluene-*d*$_8$, ppm): δ = −16.0 (s). FT-IR (KBr, cm^{-1}): ν = 3323 (s), 3050 (m), 1584 (m), 1483 (m), 1434 (s), 1397 (m), 1166 (m), 1100(s), 1030 (m), 808 (m), 742 (s), 693 (vs), 635 (w), 507 (s), 478 (m). HRMS (+ESI) *m*/*z*: $[M - Br^-]^+$ calcd for $C_{60}H_{54}Br_2Cu_2N_2P_4$, 1131.1213; found, 1131.0908. Anal. Calcd for $C_{60}H_{54}Br_2Cu_2N_2P_4$: C, 59.37; H, 4.48; N, 2.31. Found: C, 58.62; H, 4.69; N, 2.15.

[Cu(*μ*-I){*μ*-C_4H_2NH-2,5-$(CH_2PPh_2)_2$-*P,P*}]$_2$, 3. ^1H NMR (toluene-*d*$_8$, 400 MHz, ppm): δ = 3.75 (s, 8H, C*H*$_2$), 5.55 (s, 4H, pyrrole *β*-C*H*), 6.88−7.21 (m, 40H, phenyl C*H*), 11.45 (br s, 2H, N*H*). $^{31}P\{^1H\}$NMR (161.9 MHz, toluene-*d*$_8$, ppm): δ = −21.9(s). FT-IR (KBr, cm^{-1}): ν = 3330 (vs), 3050 (w), 1583 (w), 1482 (m), 1434 (s), 1395 (m), 1098 (m), 1030 (m), 832 (w), 742 (vs), 693 (vs), 633 (w), 506 (s), 478 (m). HRMS (+ESI) *m*/*z*: $[M - I^-]^+$ calcd for $C_{60}H_{54}I_2Cu_2N_2P_4$, 1179.1074; found, 1179.0767. Anal. Calcd for $C_{60}H_{54}Cu_2I_2N_2P_4$: C, 55.10; H, 4.16; N, 2.14. Found: C, 55.69; H, 4.43; N, 1.92.

Synthesis of Complex [CuCl{$Ph_2C(C_4H_2NH)_2$-1,9-$(CH_2PPh_2)_2$-*P,P*}], 4. To a THF (50 mL) solution of dipyrrolyldiphosphine ligand **B** (0.352 g, 0.510 mmol) was added solid CuCl (0.050 g, 0.505 mmol), and the solution was stirred for 20 h at room temperature, giving a clear solution. The solution was layered with petroleum ether and then allowed to stand for 2 weeks to give colorless crystals of complex **4**. The crystals were separated by decanting the solution and then dried under vacuum (0.350 g, 0.440 mmol, 87% yield). ^1H NMR (toluene-*d*$_8$, 400 MHz, ppm): δ = 3.49 (s, 4H, C*H*$_2$), 5.57 (s, 2H, pyrrole *β*-C*H*), 5.89 (t, *J* (HH) = 2.8 Hz, 2H, pyrrole *β*-C*H*), 6.88−7.42 (m, 30H, phenyl C*H*), 10.81 (br s, 2H, N*H*). $^{31}P\{^1H\}$NMR (161.9 MHz, toluene-*d*$_8$, ppm): δ = −5.7(s). FT-IR (KBr, cm^{-1}): ν =3298 (s), 3054 (m), 1587 (m), 1482 (m), 1434 (s), 1393 (m), 1261 (w), 1214 (w), 1185 (w), 1121 (w), 1098 (m), 1043 (w), 873 (w), 793 (s), 773 (s), 756 (s), 697 (vs), 647 (w), 578 (w), 508 (m), 476 (w), 448 (w). HRMS (+ESI) *m*/*z*: $[M - Cl^-]^+$ calcd for $C_{47}H_{40}ClCuN_2P_2$, 757.2063; found, 757.1982. Anal. Calcd for $C_{47}H_{40}ClCuN_2P_2$: C, 71.12; H, 5.08; N, 3.53. Found: C, 71.46; H, 5.20; N, 3.31.

The bromide (**5**) and the iodide (**6**) analogues of complex **4** were synthesized by following the synthetic procedure of **4**. For the synthesis of **5**, CuBr (0.050 g, 0.350 mmol) and dipyrrolydiphosphine ligand **B** (0.242 g, 0.350 mmol) were used. The yield is 88% (0.215 g, 0.260 mmol). For the synthesis of **6**, CuI (0.100 g, 0.525 mmol) and ligand **B** (0.365 g, 0.525 mmol) were used. The reaction mixture was concentrated to ~20 mL, and then ~20 mL of petroleum ether was added. After the solution was cooled to −15 °C for 1 week, colorless crystals of **6** were formed. The yield is 87% (0.405 g, 0.460 mmol).

[CuBr{$Ph_2C(C_4H_2NH)_2$-1,9-$(CH_2PPh_2)_2$-*P,P*}], 5. ^1H NMR (toluene-*d*$_8$, 400 MHz, ppm): δ = 3.54 (s, 4H, C*H*$_2$), 5.57 (s, 2H, pyrrole *β*-C*H*), 5.90 (t, *J* (HH) = 2.8 Hz, 2H, pyrrole *β*-C*H*), 6.89−7.43 (m, 30H, phenyl C*H*), 10.50 (br s, 2H, N*H*). $^{31}P\{^1H\}$NMR (161.9 MHz, toluene-*d*$_8$, ppm): δ = −5.8(s). FT-IR (KBr, cm^{-1}): ν = 3306 (s), 3054 (w), 1586 (m), 1482 (m), 1434 (s), 1393 (m), 1260 (w), 1184 (m), 1097 (s), 1043 (m), 791 (s), 771 (s), 755 (s), 697 (vs), 508 (s). HRMS (+ESI) *m*/*z*: $[M - Br^-]^+$ calcd for $C_{47}H_{40}BrCuN_2P_2$, 757.2063; found, 757.1982.

[CuI{$Ph_2C(C_4H_2NH)_2$-1,9-$(CH_2PPh_2)_2$-*P,P*}], 6. ^1H NMR (toluene-*d*$_8$, 400 MHz, ppm): δ = 3.60 (s, 4H, C*H*$_2$), 5.55 (s, 2H, pyrrole *β*-C*H*), 5.90 (s, 2H, pyrrole *β*-C*H*), 6.87−7.44 (m, 30H, phenyl C*H*), 10.12 (br s, 2H, N*H*). $^{31}P\{^1H\}$NMR (161.9 MHz, toluene-*d*$_8$, ppm): δ = −6.6(s). FT-IR (KBr, cm^{-1}): ν = 3400 (m), 3294 (s), 3052 (m), 1580 (m), 1484 (s), 1444 (m), 1434 (s), 1394 (m), 1309 (w), 1262 (w), 1217 (w), 1180 (w), 1156 (w), 1101 (s), 1082 (m), 1037 (m), 998 (w), 899(w), 874 (w), 835 (w), 812 (w), 783 (m), 762 (s), 741 (s), 692 (vs), 634 (w), 593 (w), 539 (w), 507 (s), 495 (m), 484 (m), 460 (w), 444 (w). HRMS (+ESI) *m*/*z*: $[M - I^-]^+$ calcd for $C_{47}H_{40}CuIN_2P_2$, 757.2063; found, 757.1926.

Synthesis of [Cu_4I_4\{*μ*-$Ph_2C(C_4H_3N)_2$-1,9-$(CH_2PPh_2)_2$-*P,P*}$_2$] 7. To a THF (100 mL) solution of dipyrrolydiphosphine ligand **B** (0.365 g, 0.525 mmol) was added solid CuI (0.200 g, 1.050 mmol). The solution was stirred for 48 h at room temperature and then filtered to remove some insoluble residue. The clear solution was layered with petroleum ether, which then was allowed to stand for 2 weeks to give colorless crystals of complex **7**. Crystals were separated by decanting the mother liquor and dried under vacuum (0.412 g, 0.180 mmol, 68% yield). ^1H NMR (toluene-*d*$_8$, 400 MHz, ppm): δ = 3.58 (br s, 8H, C*H*$_2$), 5.48 (br s, 4H, pyrrole *β*-C*H*), 5.58 (br s, 4H, pyrrole *β*-C*H*), 6.84−7.47 (m, 60H, phenyl C*H*), 8.76 (br s, 4H, N*H*). $^{31}P\{^1H\}$NMR (161.9 MHz, CH_2Cl_2, D_2O as external lock, ppm): δ = −6.2(s). FT-IR (KBr, cm^{-1}): ν = 3433 (m), 3333 (m), 3052 (m), 2953 (w), 1574 (m), 1483 (m), 1434 (s), 1401 (m), 1274 (w), 1181 (m), 1099 (m), 1044(m), 999 (w), 902 (w), 827 (m), 774 (m), 741 (s), 694 (vs), 623 (w), 506 (m), 480 (m), 448 (w). Anal. Calcd. for $C_{102}H_{96}Cu_4I_4N_4O_2P_4$: C, 53.36; H, 4.21; N, 2.44. Found: C, 53.14; H, 3.92; N, 2.49.

Table 2. Crystallographic Data for 1, 4, 7, and 8

	1	4	7	8
empirical formula	$C_{60}H_{54}Cl_2Cu_2N_2P_4$	$C_{47}H_{40}ClCuN_2P_2$	$C_{102}H_{96}Cu_4I_4N_4O_2P_4$	$C_{71}H_{56}BClCu_2F_4N_6P_2$
fw	1124.91	793.74	2295.47	1304.50
wavelength (Å)	0.71073	0.71073	0.71073	0.71073
temp (K)	293(2)	293(2)	293(2)	293(2)
cryst syst	monoclinic	triclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P\bar{1}$	$P2/n$	Cc
a (Å)	9.988(3)	11.0444(7)	17.3607(15)	24.571(8)
b (Å)	18.830(5)	13.7726(9)	12.7387(11)	16.581(5)
c (Å)	29.206(8)	14.0611(9)	22.6008(18)	17.629(5)
α (deg)	90.0	112.505(2)	90.0	90.0
β (deg)	95.846(8)	94.387(2)	104.827(2)	122.542(8)
γ (deg)	90.0	93.330(2)	90.0	90.0
vol (Å^3)	5464(3)	1961.3(2)	4831.8(7)	6055(3)
Z	4	2	2	4
D_{calcd} (mg m^{-3}	1.367	1.344	1.578	1.431
μ (mm^{-1})	1.034	0.743	2.262	0.861
F(000)	2320	824	2280	2680
θ range (deg)	1.29 to 25.00	1.58 to 26.39	1.60 to 25.00	1.57 to 24.72
total/unique no. of reflns	64460/9609	25391/7816	56689/8513	34632/10051
R_{int}	0.1216	0.0375	0.0672	0.1608
data/restr/params	9609/0/637	7816/0/484	8513/0/502	10051/45/800
GOF (F^2)	1.058	1.015	1.036	0.992
$R1$, $wR2$	0.0748, 0.1767	0.0403, 0.0937	0.0472, 0.0948	0.0672, 0.0900
R indices (all data) $R1$, $wR2$	0.1491, 0.2184	0.0634, 0.1054	0.0762, 0.1048	0.1653, 0.1149
largest different peak and hole (e Å^{-3})	1.227 and −0.455	0.447, −0.371	0.635 and −0.576	0.320, −0.402

Synthesis of [$Cu_2(\mu$-Cl)(μ-PNNP-*P,P*)(NN)$_2$]BF_4, 8. The dipyrrolyldiphosphine ligand **B** (0.351 g, 0.505 mmol), CuCl (0.050 g, 0.505 mmol), and $NaBF_4$ (0.060 g, 0.510 mmol) were taken in a Schlenk flask. Eighty milliliters of acetonitrile was added to this flask, and the resultant solution was stirred for 30 min, resulting in the formation of colorless precipitate. To this suspension, 1,10-phenanthroline monohydrate (0.100 g, 0.505 mmol) was added, resulting in a disappearance of the precipitate and a clear solution. The solution was stirred for 16 h and then filtered to remove some insoluble residue. The clear solution was layered with diethyl ether and allowed to stand for 1 week to give yellow crystals of complex **8**. The crystals were separated by decanting the solution and were dried under vacuum (0.190 g, 0.145 mmol, 57% yield). ^{1}H NMR (CD_3CN, 400 MHz, ppm): δ = 3.65 (s, 4H, CH_2), 5.46 (s, 2H, pyrrole β-C*H*), 5.51 (s, 2H, pyrrole β-C*H*), 6.87−7.30 (m, 34H, phenyl and phenanthroline C*H*), 7.76, 8.00, 8.18 (br s, 12H, phenanthroline C*H*), 10.47 (br s, 2H, N*H*). ^{31}P{^{1}H}-NMR (161.9 MHz, CH_2Cl_2, D_2O as external lock, ppm): δ = −6.4(s). FT-IR (KBr, cm^{-1}): ν = 3336 (s), 3063 (m), 1623 (w), 1587 (m), 1511 (m), 1485 (m), 1422 (s), 1186 (w), 1059 (vs), 846 (s), 771 (s), 755 (s), 727 (s), 695 (s), 507 (m), 484 (m). UV−vis: (λ_{max}, CH_2Cl_2, nm) = 439, ε = 5919 M^{-1}cm^{-1}. HRMS (+ESI) *m*/*z*: [M − CuCl − BF_4 − 2phen]$^+$ calcd for $C_{71}H_{56}BClCu_2F_4N_6P_2$, 1304.5417; found, 757.1963.

X-ray Crystallography. Suitable single crystals of **1**−**8** were obtained from solvents mentioned in their respective synthetic procedures. Single-crystal X-ray diffraction data collections for all the compounds were performed at room temperature using Bruker-APEX-II CCD diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å). The structures were solved by SIR-92[51] or SHELXS-97 available in WinGX, which successfully located most of the non-hydrogen atoms. Subsequently, least-squares refinements were carried out on F^2 using SHELXL-97 (WinGX version)[52] to locate the remaining non-hydrogen atoms.

Typically, for all the structures, hydrogen atoms attached to carbons were fixed in calculated positions. For most of the structures, the NH hydrogen atoms were located from the difference Fourier map and freely refined isotropically with their thermal parameters set as equivalent to 1.2 times that of their parent atoms. In the structure of **3**, one of the NH hydrogen atoms was fixed, while the other was located. In case of the structure of **7**, the unit cell contains two molecules of THF which have been treated as a diffuse contribution to the overall scattering without specific atom positions by SQUEEZE/PLATON.[53] The presence of THF is supported by the ^{1}H NMR spectrum recorded for the crystals of **7** in toluene-d_8 showing multiplets at δ = 1.46 ppm and 3.56 ppm. Use of SQUEEZE/PLATON necessarily contributes to the discrepancy between calculated and reported formulas in the cif file for the structure of **7**. In the structure of **8**, the BF_4^- anion is disordered over two positions with occupancy factors of 76 and 24%, which are handled successfully with EADP and SADI options. The refinement data are summarized in Table 2.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

NMR, IR, HRMS, UV, X-ray structures, refinement data, crystallographic data (cif), Hirshfeld analysis, optimized structures and their Cartesian coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(19) The X-ray structure of **3** is given in SI (Figure S32). The X-ray structure of the bromide derivative **2** (Figure S35) could not be solved completely as their phenyl carbons have very large thermal parameter values. However, its ORTEP diagram and refinement data are given in Supporting Information.

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