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Single-Step Substitution of all the α, β-Positions in Pyrrole: Choice of Binuclear versus Multinuclear Complex of the Novel Polydentate Ligand

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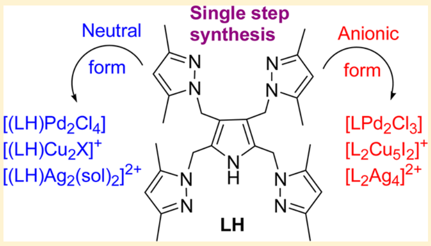
Supporting Information



ABSTRACT: The α and β-positions of pyrrole were substituted with 3,5-dimethylpyrazolylmethyl groups in a single step that involved the reaction between 2,5-dimethylaminomethylpyrrole and 3,5-dimethylpyrazole-1-carbinol, affording 2,3,4,5-tetrakis(3,5-dimethylpyrazol-1-ylmethyl)pyrrole **LH** in 40% yield. The coordination chemistry of this new polydentate ligand **LH** was explored by synthesizing several Pd(II), Cu(I), and Ag(I) complexes. When **LH** was used as a neutral ligand with $[Pd(COD)Cl_2]$, $AgBF_4$, and CuX (X = Cl and I), compartmental type binuclear Pd(II) and Ag(I) complexes such as $[Pd_2Cl_4(\mu\text{-}C_4HN\text{-}2,3,4,5\text{-}(CH_2Me_2pz)_4\text{-}N,N,N,N)]$ and $[Ag_2(\mu\text{-}C_4HN\text{-}2,3,4,5\text{-}(CH_2Me_2pz)_4\text{-}N,N,N,N)(CH_3CN)_2]^{2+}[BF_4^-]_2$ and cage-like copper(I) complexes $[Cu_2(\mu\text{-}X)(\mu\text{-}C_4HN\text{-}2,3,4,5\text{-}(CH_2Me_2pz)_4\text{-}N,N,N,N)]^+[CuX_2]^-$ (X = Cl and I) containing a halide ion bridging in a bent fashion were obtained, respectively. Conversely, when the same metal precursors were treated with **LH** in the presence of *n*-BuLi, the multinuclear complexes $[Pd_2Cl_3(\mu\text{-}C_4N\text{-}2,3,4,5\text{-}(CH_2Me_2pz)_4\text{-}N,N,N,N,N)]$, $[(Cu_2(\mu\text{-}I)\{\mu\text{-}C_4N\text{-}2,3,4,5\text{-}(CH_2Me_2pz)_4\text{-}N,N,N,N,N\})_2Cu]^+I^-$, and $[Ag_4(\mu\text{-}C_4N\text{-}2,3,4,5\text{-}(CH_2Me_2pz)_4\text{-}N,N,N,N,N)_2]^{2+}[BF_4^-]_2$ were obtained. In addition, the treatment of **LH** with $[Pd(OAc)_2]$ gave the mononuclear complex, $[Pd(OAc)(C_4N\text{-}2,3,4,5\text{-}(CH_2Me_2pz)_4\text{-}N,N,N)]$. The chloride analogue of this complex was obtained by the reaction of **LH** with $[Pd(COD)Cl_2]$ in the presence of triethylamine. The structures of all complexes were determined by single-crystal X-ray diffraction analyses, which revealed interesting structural features, including pyrazole arms adopting different conformations with respect to the pyrrole ring plane and linear two- and three-coordinated copper(I) and silver(I) atoms exhibiting weak interactions between the metal and the pyrrolic carbon atoms and Ag(I)···Ag(I) interactions. The observed shorter metal pyrrolide nitrogen (M−N) bond distances and the elongation of the C−C double and single bond distances of the pyrrole ring in these complexes probably indicates the presence of π-donation/π-back bonding between the metal and the pyrrole ring. These multinuclear complexes are novel, and their formations are favored by the multidentating nature of the ligand **LH**.

■ INTRODUCTION

The α-positions of pyrrole is more reactive toward electrophiles than its β-positions. This property has extensively been used for synthesis of porphyrins and a myriad array of products.[1] In fact, nature also used this property to build its molecules. Nonetheless, the β-positions are also sufficiently reactive but remain very difficult for selective substitution over the α-positions.[2] Generally, β-positions or 3,4-disubsituted pyrrole derivatives have been synthesized by the Piloty−Robinson pyrrole synthesis with appropriate starting compounds[3] and other methods.[4]

Metal complexes containing polydentate ligand have been shown to mimic metallo-enzymes and act cooperatively to activate small molecules.[5] Polydentate ligands increase the stability of metal complexes because of their chelating bonding modes. Usually they can be synthesized by tethering ligating groups to the mainframe of a molecule. The pyrazole molecule has been shown to coordinate metal atoms in 20 different modes and has demonstrated its versatile nature of bonding.[6] Hence, pyrazole-based polydentate ligands, such as poly(pyrazolyl)borates[7] and poly(pyrazolyl)alkanes,[8] are a fascinating class of ligand systems as shown by their metal complexes exhibiting novel electronic and magnetic properties. We therefore became interested in attaching 3,5-dimethylpyrazolate groups to the pyrrole ring, which could become a polydentate ligand for metals. Herein, we report the serendipitous finding that the first single-step synthesis of α,β-position-substituted pyrrole, 2,3,4,5-tetrakis(3,5-dimethylpyrazol-1-ylmethyl)pyrrole and the ligating property difference between its neutral and anionic forms with palladium(II), copper(I) and silver(I) metals leads to structural characterization of binuclear and multinuclear palladium(II), copper(I), and silver(I) complexes. These complexes showed interesting structural features such as short contacts between metal and pyrrole carbons, Ag(I)··· Ag(I) interactions, and shorter metal pyrrolide nitrogen bond distances, suggesting π-donation/π-back bonding.

■ RESULTS AND DISCUSSION

Synthesis of Polydentate Ligand. Earlier, we reported the α,α'-substituted pyrrole, 2,5-bis(3,5-dimethylpyrazolyl-

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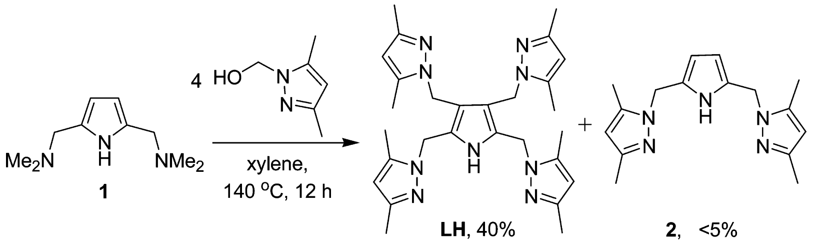
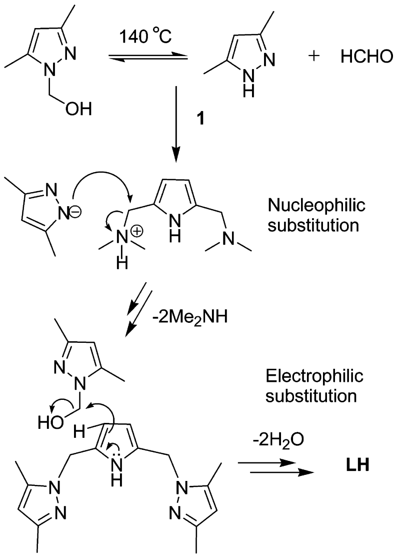
Scheme 1. Synthesis of the $\alpha\alpha'\beta\beta'$-Tetrasubstituted Pyrrole, LH.



methyl)pyrrole, **2** by the reaction between 2,5-bis-(dimethylaminomethyl)pyrrole and 3,5-dimethylpyrazole at an elevated temperature.[9] Using the same strategy, when the reaction was carried out with 4 equiv of 3,5-dimethylpyrazole-1-carbinol, the unprecedented $\alpha\alpha'\beta\beta'$-tetrasubstituted pyrrole, 2,3,4,5-tetrakis(3,5-dimethylpyrazol-1-ylmethyl)pyrrole (**LH**), was isolated in 40% yield along with **2** after workup procedure (Scheme 1). Attempts to synthesize **LH** directly from pyrrole failed and yielded inseparable polymeric products. This suggests that protection of the more reactive α-positions of pyrrole by the dimethylaminomethyl groups is important and facilitates the alkylation of the β-positions. As a result, **LH** is formed by replacing not only the dimethylamino groups in 2,5 positions of **1** but also both the β-CH protons, likely resulting in concomitant formation of water molecules. This reaction is a new simple method and involves two steps from pyrrole. However, the acidic pyrrolic NH group was not alkylated even in the presence of 6 equiv of 3,5-dimethylpyrazole-1-carbinol, as shown by the HRMS analysis of the reaction mixture.

The mechanism of formation of **LH** could involve the steps shown in Chart 1. It is likely that 3,5-dimethylpyrazole-1-carbinol is dissociated at this elevated temperature to give its starting compounds, 3,5-dimethylpyrazole and formaldehyde, which are in equilibrium. The freed 3,5-dimethylpyrazole could protonate both the amine groups of 2,5-bis(dimethylaminomethyl)pyrrole, and subsequently, the resulting ammonium salt undergoes the nucleophilic attack by the 3,5-dimethylpyrazolate anion to give initially 2,5-bis(3,5-dimethylpyrazolylmethyl)pyrrole, **2**. Subsequently, **2** undergoes the electrophilic attack by the carbinol in the β-positions to give the product **LH** with the formation of two water molecules.

Chart 1Proposed mechanism of formation of LH from 2,5-bis(dimethylaminomethyl)pyrrole at elevated temperature.



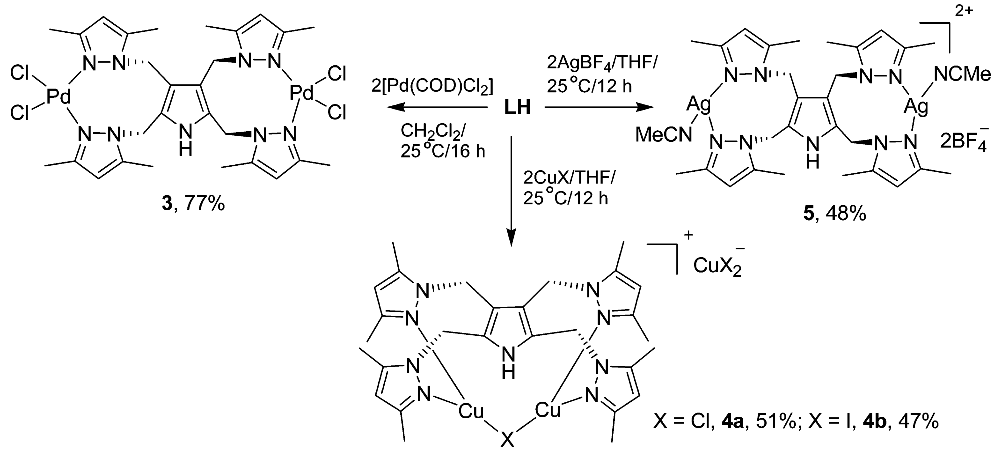
The structure of **LH** was confirmed by NMR, IR, and HRMS analyses. The ^{1}H NMR spectrum of **LH** in $CDCl_3$ shows a broad signal at δ 8.94 ppm for the pyrrolic NH proton; the two diastereotopic methylene protons resonate at δ 5.06 and 4.73 ppm as two sharp singlets together with other signals whose integrated intensities are in accord with the structure.

Synthesis and Characterization of Binuclear Complexes. Having synthesized a new polydentate ligand containing four nucleophilic nitrogen donors and the pyrrolic NH group, which can be deprotonated to become an anionic ligand, we have investigated its coordination chemistry. Besides, it is interesting to compare its coordination chemistry with that of the NNN-pincer ligand **2** (see ref 9) and with that of the tetrapyrazolylmethyl substituted benzene, $C_6H_2(CH_2Me_2pz)_4$.[10] The compartmental binuclear palladium(II) (**3**) and silver(I) (**5**) complexes were synthesized by treating 2 equiv of their respective metal precursors with **LH** (Scheme 2). As a result of the relatively smaller copper atom, the cage-like binuclear copper(I) complex (**4**) was obtained. In all these complexes, the pyrrolic NH proton is intact, and all the pyrazole nitrogens are coordinated. The structures of all these complexes were determined by single-crystal X-ray diffraction analyses, which are supported by NMR, HRMS, and elemental analyses.

The ^{1}H NMR spectrum of **3** in $CDCl_3$ is drastically different from that of the free **LH**. Although **LH** displays two separate broad resonances for the two methylene groups, **3** gives two AB pattern resonances with J = 15.2 Hz for its diastereotopic methylene protons. In addition, the spectrum shows well-separated resonances for the pyrazolyl methyl groups and a broad singlet at δ 9.41 ppm for the pyrrolic NH proton. These contrasting features are attributed to the constraints with which **LH** is coordinated; in the free **LH**, the pyrazolylmethylene groups are free to move. The ^{1}H NMR spectrum of **4a** or **4b** in $CDCl_3$ displays a broad signal for its methylene protons. Conversely, the same complex in a strongly hydrogen bonding solvent DMSO-d_6 gives well-resolved signals for the methylene groups. Complex **5** was obtained after crystallization from acetonitrile/diethyl ether mixture. Although complex **3** and **5** have similar conformations (vide infra), in contrast to the palladium complex **3**, the silver(I) complex **5** in DMSO-d_6 gives broad signals for its methylene groups, probably indicating dynamic behavior in solution. In addition, this spectrum showed the presence of coordinated acetonitrile molecules in **5**. The HRMS spectrum of **5** showed a peak m/z at 713.1203 (calcd 713.1274) corresponding to the ion, $[M{-}2MeCN{-}2BF_4]^+$.

The X-ray structure of **3** (Figure 1 and Table 2) revealed that the pyrazole arms present on both sides of the pyrrole ring are

Scheme 2. Synthesis of Binuclear Complexes Using LH as a Neutral Ligand



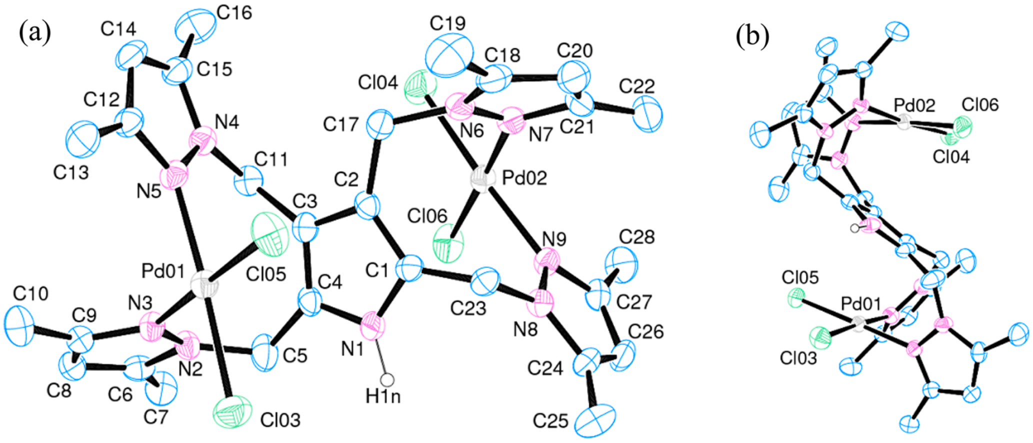


Figure 1. Molecular structure of the binuclear palladium(II) complex **3** (30% thermal ellipsoids) (a) front view and (b) side view. All hydrogen atoms except the pyrrolic NH and the solvent of crystallization water molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): N3−Pd01 2.033(5), N5−Pd01 2.051(6), Cl03−Pd01 2.278(2), Cl05−Pd01 2.302(2), N7−Pd02 2.030(6), N9−Pd02 2.045(5), Cl04−Pd02 2.297(2), Cl06−Pd02 2.279(2), N3−Pd01−N5 91.7(2), N3−Pd01−Cl03 87.19(17), N5−Pd01−Cl03 177.03(17), N3−Pd01−Cl05 178.69(17), N5−Pd01−Cl05 89.57(16), Cl03−Pd01−Cl05 91.55(9), N7−Pd02−N9 89.4(2), N7−Pd02−Cl06 175.11(18), N9−Pd02−Cl06 89.44(17), N7−Pd02−Cl04 91.10(17), N9−Pd02−Cl04 176.15(16), Cl06−Pd02−Cl04 90.42(9), N1···O2 2.845(14), H1n···O2 1.89(7), N1−H1n···O2 158(6), N1···O2^i 2.998(14), H1n···O2^i 2.00(7), N1−H1n···O2^i 171(6). The symmetry operation used to generate equivalent atoms: $-x + 2.5, y, -z + 1.5$.

twisted above and below the plane formed by the pyrrole ring together with its methylene carbon atoms and chelated to two "PdCl$_2$" units one on each side. It is a neutral binuclear compartmental type complex. The side view of the structure shows an "S"-shaped conformation, which minimizes steric crowding. The geometry around each palladium atom is a slightly distorted square plane. The Pd−N(pz) and Pd−Cl bond distances fall within the range reported for the pyrazole-nitrogen-coordinated palladium complexes.[11] The pyrrolic NH group is hydrogen bonded to the water molecules present in the lattice.

The structure of copper(I) complex **4** is formulated as [(LH)Cu$_2$X]$^+$[CuX$_2$]$^-$ (X = Cl (**4a**) and I (**4b**)) in which the two copper atoms are bridged by one neutral ligand **LH** and one halide ion, forming a cage-like cation whose charge is neutralized by the CuX$_2^-$ anion (Figure 2 and Figure 3, respectively). The formation of this product may be due to the smaller size of the copper atom relative to the palladium atom. The three-coordinated copper(I) atom exhibits either a distorted trigonal pyramidal or planar geometry. In addition, the two copper(I) atoms are bridged by the halide ion unsymmetrically, as shown by their distances. The Cu1−Cl1−Cu2 angle of 92.89(5)° in **4a** and the acute angle, Cu2−I1−Cu1 = 75.17(3)°, in **4b** are probably the result of steric constraint of **LH** with which it bridges the two metal atoms. However, the Cu···Cu distance in **4a** or **4b** (3.383(1) Å or 3.127(1) Å, respectively) suggests that there can be no copper−copper bonding.

Interestingly, the two copper atoms in each structure are slightly different. For example, in the case of **4b**, the summation of the three angles is 357.8(1)° at Cu1, whereas the sum is 352.5(1)° at Cu2. The slightly pyramidalized copper(I) atom is in close proximity to two of the pyrrole ring carbon atoms: Cu1−C7 = 2.704(5) Å and Cu1−C8 = 2.693(4) Å in **4a**; Cu2−C2 = 2.519(5) Å and Cu2−C1 = 2.654(6) Å in **4b**. These distances are shorter than the sum of the van der Waals radii of the two atoms (1.7 Å (C) + 1.40 Å (Cu) = 3.10 Å) and hence can represent a weak η^2 interaction involving the pyrrolic π-electrons. Similar close contacts involving arene ring carbons have been reported for a few Cu(I), Ag(I), and Hg(II) complexes.[12] However, Braunstein and co-workers have concluded that such close proximities do not correspond to bonding interactions as shown by DFT calculations.[13] Further, the Cu−N(pz) and Cu−X bond distances are in the range

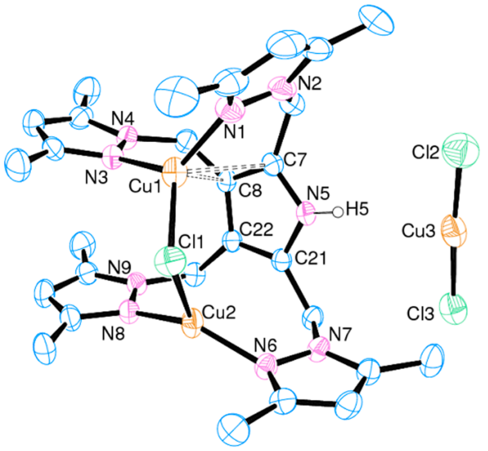


Figure 2. Molecular structure of the binuclear copper(I) chloride complex **4a** (30% thermal ellipsoids). All hydrogen atoms except the pyrrolic NH and one THF solvent molecule are omitted for clarity. The dotted line indicates short contact. Selected bond lengths (Å) and angles (deg): N1−Cu1 1.989(4), N3−Cu1 1.957(4), N6−Cu2 1.928(4), N8−Cu2 1.911(4), Cl1−Cu1 2.2793(15), Cl1−Cu2 2.3874(14), Cl2−Cu3 2.081(2), Cl3−Cu3 2.0951(19), Cu1−Cl1−Cu2 92.89(5), N3−Cu1−N1 126.52(17), N3−Cu1−Cl1 120.52(12), N1−Cu1−Cl1 109.20(13), N8−Cu2−N6 148.89(16), N8−Cu2−Cl1 107.95(12), N6−Cu2−Cl1 102.83(11), Cl2−Cu3−Cl3 176.05(8).

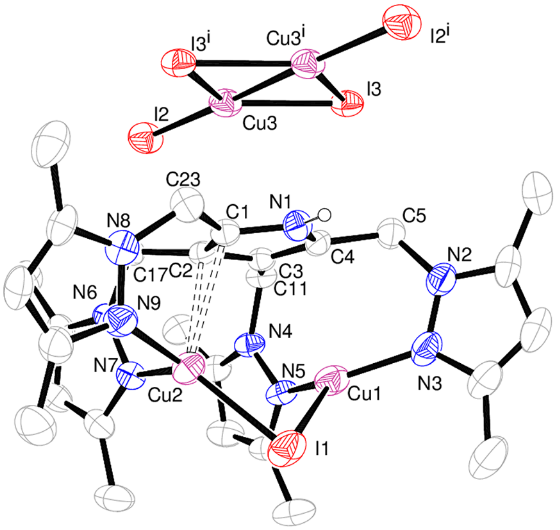


Figure 3. Molecular structure of the binuclear copper(I) iodide complex **4b** (30% thermal ellipsoids) along with the anion $Cu_2I_4^{2-}$. All hydrogen atoms except the pyrrolic NH and one THF are omitted for clarity. The dotted line indicates short contact. Selected bond lengths (Å) and angles (deg): N3−Cu1 1.973(6), N5−Cu1 1.946(5), N7−Cu2 1.996(5), N9−Cu2 2.047(5), Cu1−I1 2.6446(10), Cu2−I1 2.4772(9), C2−Cu2 2.520(5), Cu3−I2 2.4885(9), Cu3−I3 2.5615(10), Cu3−$I3^i$ 2.6087(10), Cu3−$Cu3^i$ 2.6122(16), I3−$Cu3^i$ 2.6087(10), N5−Cu1−N3 134.6(2), N5−Cu1−I1 117.78(14), N3−Cu1−I1 105.44(16), N7−Cu2−N9 104.3(2), N7−Cu2−I1 128.76(14), N9−Cu2−I1 119.43(15), Cu2−I1−Cu1 75.17(3), N7−Cu2−C2 76.17(18), N9−Cu2−C2 89.29(18), I1−Cu2−C2 126.15(13), I2−Cu3−I3 124.98(4), I2−Cu3−$I3^i$ 115.68(4), I3−Cu3−$I3^i$ 119.31(3), I2−Cu3−$Cu3^i$ 174.23(6), I3−Cu3−Cu^i 60.55(3), $I3^i$−Cu3−$Cu3^i$ 58.76(3), Cu3−I3−$Cu3^i$ 60.69(3). The symmetry operation used to generate equivalent atoms: $-x + 1$, $-y$, $-z + 2$.

reported for other copper(I) complexes containing the pyrazolate ligand.[14,15] Furthermore, these complexes are unique and join with the scarcely reported linear[16] and bent[17] monohalide ion bridged binuclear Cu(I) complexes.

The symmetry-generated $[Cu_2I_4]^{2-}$ anion has been reported for several other Cu(I) complexes.[18] In locations where there is a possibility of C−H···I interactions, the observed C···I distances are higher than the sum of their van der Waals radii. Hence, there are no significant C−H···I interactions with which the $[Cu_2I_4]^{2-}$ anion is held in place with the cation in the asymmetric unit. The same applies to the $CuCl_2^-$ anion in **4a**. However, in **4a**, the pyrrolic NH group is hydrogen bonded to the lattice THF molecule, N5···O1 = 2.878(6) Å, H···O1 = 2.09(5) Å, ∠N5−H5...O1 = 152(4)°. Each copper atom of the anion $[Cu_2I_4]^{2-}$ adopts the trigonal planar geometry, and the Cu···Cu distance is 2.6128(16) Å, which is similar to the reported values.[19]

The X-ray structure of complex **5**, given in Figure 4, revealed a compartmental type binuclear three-coordinate silver(I) cationic complex formed by a single neutral ligand **LH.** In the structure, ligand **LH** is twisted such that its pyrazole groups are oriented up and down to the pyrrole ring, in contrast to the structure of **4** in which these groups are on the same side. As a result, the molecule adopts an "S"-shaped conformation, which is similar to the structure of **3.** In addition to the chelation formed by the pyrazole nitrogens conferring a bite angle of 138.1(2)° at Ag1 and 141.0(2)° at Ag2, each silver(I) atom is coordinated by one acetonitrile molecule. The geometry around each metal atom is trigonal planar. Both BF_4^- anions are severely disordered; one of them is located in the direction of the pyrrolic NH group and hydrogen bonded. The Ag−N(pz) distances range from 2.160(5) to 2.229(6) Å, which are similar to the values observed in other three-coordinate silver(I) complexes containing pyrazolate units.[20]

Synthesis and Characterization of Multinuclear Complexes. On the contrary, the treatment of **LH** with the same metal precursors ([Pd(COD)Cl_2], CuI, and $AgBF_4$) in the presence of *n*-BuLi in THF afforded interesting multinuclear complexes **6**, **7**, and **8**, respectively (Scheme 3). Besides, complex **8** was also synthesized by treating **LH** with $AgBF_4$ in the presence of triethylamine. As can be noticed in all complexes, upon deprotonation, **LH** becomes a pentadentate ligand which helps form the multinuclear complexes in which the pyrrolide nitrogen is *σ*-bonded to the metal atoms. Complex **6** is formed by a metathesis reaction that involves the metal-to-ligand mole ratio of 2:1. As a result, all chlorine atoms are not replaced, and the resulting complex contains chloride ions bonded to palladium atoms. Complex **8** was obtained from the reaction involving metal-to-ligand mole ratio of 2:1, as crystals containing two acetonitrile molecules as a solvent of crystallization in poor yields. As silver(I) metal prefers two-coordinate linear geometry and the metal-to-ligand mole ratio is 2:1, the dicationic linearly coordinated silver(I) complex **8** containing two anionic ligands was obtained. Instead of forming a polymeric chain which would be sterically crowded and unfavorable, the presence of five potential ligating atoms (four pyrazolyl and one pyrrolic nitrogen atoms per ligand) force the silver atom to form this tetranuclear complex with linear coordination, in which all the basic pyrazolyl nitrogen atoms are involved in bonding. As to the copper(I) complex **7**, the copper metal can form two-, three-, four-, and other coordinate complexes. Even though the mole ratio is 1:1, which could replace the iodide ion from CuI, the complex containing undisplaced iodide ion bonded to copper(I) metal was obtained in poor yield due to its coordination flexibility. The crystals of

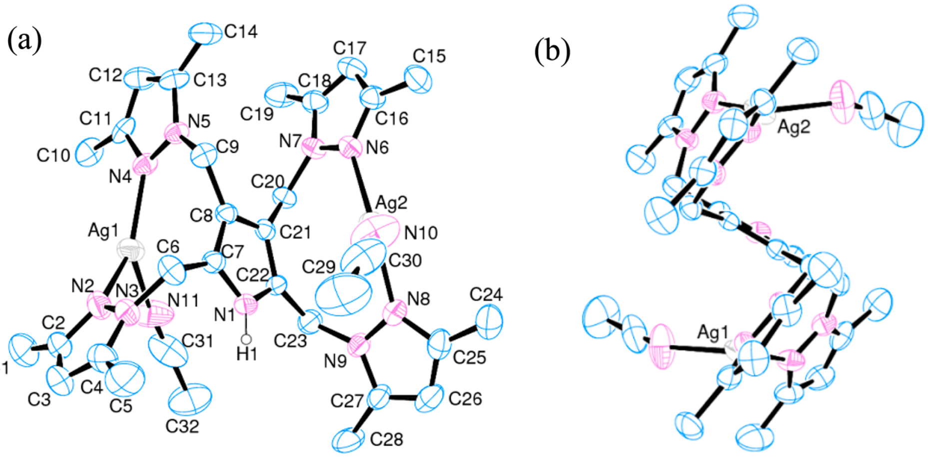
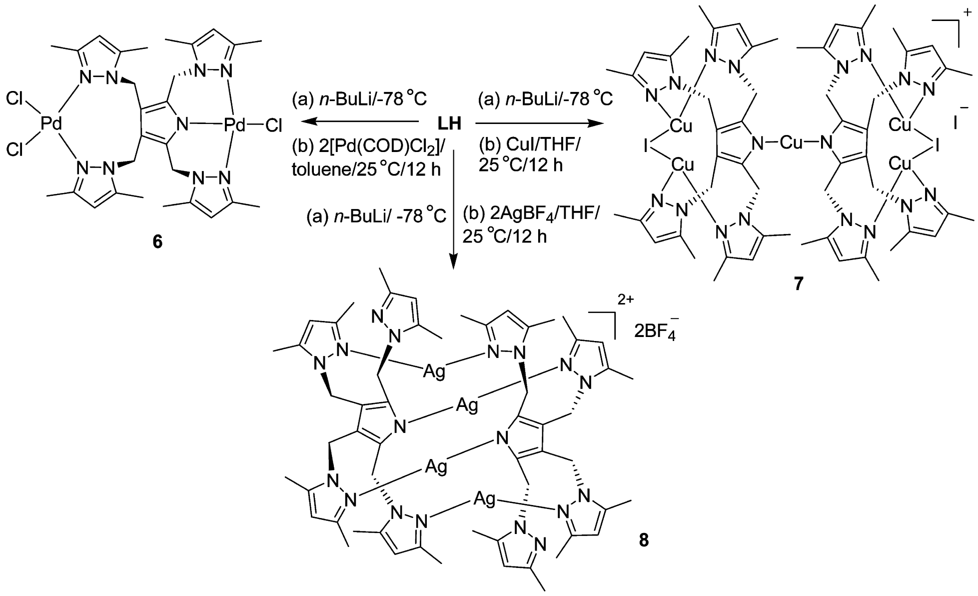


Figure 4. Molecular structure of the binuclear silver(I) complex **5** (30% thermal ellipsoids) (a) front view and (b) side view. All hydrogen atoms except the pyrrolic NH and the two disordered BF_4^- anions are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ag1−N11 2.273(8), N10−Ag2 2.326(10), N2−Ag1 2.226(7), N4−Ag1 2.182(5), N6−Ag2 2.160(5), N8−Ag2 2.229(6), C30−N10−Ag2 154.4(12), N4−Ag1−N2 138.1(2), N4−Ag1−N11 122.3(3), N2−Ag1−N11 99.5(3), N6−Ag2−N8 141.0(2), N6−Ag2−N10 121.2(3), N8−Ag2−N10 97.7(3).

Scheme 3. Synthesis of Multinuclear Complexes Using LH as an Anionic Ligand



6, **7**, and **8** are poorly or not soluble in common organic solvents and hence they are characterized primarily by CHN, IR, and X-ray diffraction methods.

The X-ray structure of **6** (Figure 5) revealed that two palladium(II) atoms are bound to one anionic ligand **L**, which adopts the *mer* κ^3-NNN and chelation bonding modes. These bonding features result in a conformation in which three of the pyrazole arms are projected above, while the fourth pyrazole arm is projected below the pyrrole plane. Further, this conformation is different from that found for the neutral ligand complex **3** but remains the same as that found in complex **8** (vide infra). Furthermore, each palladium atom has a distorted square plane, and their Pd−Cl and Pd−N(pz) distances are in the range reported.[11] The Pd−N(pyrrole) bond distance is close to the value found in the 2,5-bis(diphenylphosphinomethyl)pyrrole-coordinated Pd(II) complex [(PNP)PdCl](1.981(4))[21] but is lower than those found in other pyrrolide nitrogen-bonded Pd(II) complexes.[22]

Complex **7** was obtained as crystals containing toluene as a solvent of crystallization in 28% yield. The ^{1}H NMR spectrum of **7** in dmso-d_6 showed broad signals, and there is no peak corresponding to a pyrrolic NH proton. The molecular structure of **7** given in Figure 6 consists of two anionic ligands bridged by one central copper(I) atom. The four pyrazole nitrogens of each ligand bridges the two copper(I) atoms of the moiety "Cu(μ-I)Cu" located on both sides of the molecule, and the pyrrolic nitrogen of each ligand is σ-bonded to the central copper(I) atom. The resulting cationic complex $[L_2Cu_5I_2]^+$ is neutralized by one iodide anion. Interestingly, the central copper(I) atom is almost linearly coordinated by the pyrrolide nitrogen atoms with the N1−Cu1−N1^i angle of 171.5(4)°, which is larger than those found for the two-coordinate copper(I) complexes containing pyrrolides (168.5°)[23] or pyrazolyl rings (167.9(1)°).[24] Further, this observed angle is similar to the angle found in the copper(I) complex containing 3,5-di-*tert*-butylpyrazolyl ligands (171.2(2)°)[25] but is lower than that (180.0(2)°) reported for $[Cu(MeCN)_2]^+$,[26] those

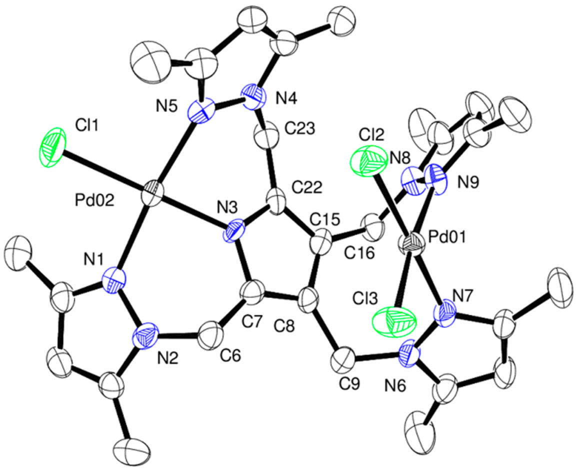


Figure 5. Molecular structure of the **6** (30% thermal ellipsoids). All hydrogen atoms and the solvent of crystallization dichloromethane are omitted for clarity. Selected bond lengths (Å) and angles (deg): N3−Pd02 1.971(5), N1−Pd02 2.058(5), N5−Pd02 2.033(5), Cl1−Pd02 2.3169(19), Cl2−Pd01 2.2870(18), Cl3−Pd01 2.286(2), N7−Pd01 2.014(5), N9−Pd01 2.061(6), N3−Pd02−Cl1 179.06(17), N3−Pd02−N5 86.8(2), N3−Pd02−N1 86.5(2), N5−Pd02−N1 173.3(2), N5−Pd02−Cl1 93.22(16), N1−Pd02−Cl1 93.41(16), N7−Pd01−N9 89.5(2), N7−Pd01−Cl3 89.12(17), N9−Pd01−Cl3 174.06(17), N7−Pd01−Cl2 178.77(17), N9−Pd01−Cl2 90.84(17), Cl3−Pd01−Cl2 90.66(7).

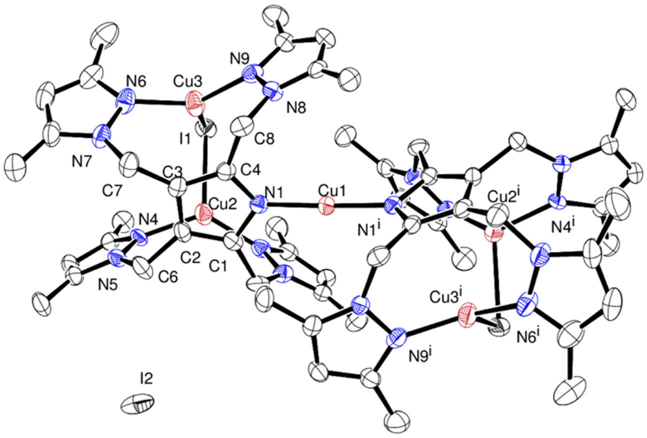


Figure 6. Molecular structure of the pentanuclear copper(I) iodide complex **7** (30% thermal ellipsoids). All hydrogen atoms and one disordered toluene solvent molecule are omitted for clarity. Selected bond lengths (Å) and angles (deg): N1−Cu1 1.858(7), N2−Cu2 1.965(8), N4−Cu2 1.983(6), N6−Cu3 1.956(8), N9−Cu3 1.957(7), Cu2−I1 2.6195(14), Cu3−I1 2.6055(16), Cu1−N1^i 1.858(7), N1−Cu1−N1^i 171.5(4), N2−Cu2−N4 128.6(3), N2−Cu2−I1 115.6(2), N4−Cu2−I1 110.1(2), N6−Cu3−N9 132.7(3), N6−Cu3−I1 110.1(2), N9−Cu3−I1 114.4(2), Cu3−I1−Cu2 85.44(4). The symmetry operations used to generate equivalent atoms: −*x* + 1, *y*, −*z* + 0.5; −*x* + 0.5, −*y* + 0.5, −*z* + 1.

(173.8° and 178.2°) reported for $[CuL_2]^+$ complexes containing the ligated 1,3,5-trimethylpyrazole and 1-methylpyrazole, respectively,[27] and others.[28] In contrast to the nearly coplanar arrangement of the imidazole- or pyrazole-ring-coordinated copper(I) complexes,[24,27,28a,b] the two pyrrole ring planes are almost perpendicular to each other, which probably reduces steric hindrance between the two ligands and can support the presence of π-bonding between the pyrrolide nitrogen and copper atoms. The central copper(I) atom does not exhibit any short contact in contrast to a few of the above two-coordinate copper(I) complexes reported. The bridging nature of each ligand in this complex is similar to that found in **4** containing the neutral ligand. However, the Cu−I−Cu angle of 85.44(4)° is larger than that (75.2(1)°) found in **4b**. Accordingly, the nonbonded Cu···Cu distance of 3.545(2) Å in **7** is larger than that (3.127(1) Å) found in **4b**. The pyrazolyl N−Cu bond distances range from 1.956(8) to 1.983(6) Å, and the Cu−I bond distances are similar to those found in **4b**. The pyrrolic N−Cu bond distance of 1.858(7) Å is slightly shorter than those (1.865 Å) reported for the two-coordinate copper(I) complex containing the pyrrolide ring,[23] indicating a relatively stronger bond.

The molecular structure of **8**, given in Figure 7, consists of two anionic ligands coordinated to four silver(I) metal atoms in a different fashion compared to any of the structures presented here, which is formulated as the dication $[L_2Ag_4]^{2+}$ and neutralized by the two disordered BF_4^- anions. Three of the four pyrazole arms of each ligand are twisted to one side of the pyrrole ring plane, while the fourth arm is twisted to the opposite direction; one of them remains uncoordinated or as a spectator ligand. The pyrrolide nitrogen atom of each ligand is σ-bonded to one silver atom which is bonded to one of the pyrazole nitrogens of the other ligand with the N1−Ag1−N6 angle of 172.4(2)°. Conversely, the angles around the other two silver(I) atoms which are coordinated only by the remaining pyrazole nitrogens are rather bent, for example, N3−Ag2−N8 = 147.1(2)°. This bent angle could be due to the short contacts that the Ag2 and Ag2^i atoms have with the nitrogen atoms of the spectator position pyrazole arms (e.g., Ag2···N5^i = 2.534(7) Å, which is much less than the sum of the van der Waals radii (3.25 Å) of the nitrogen and silver atoms). Conversely, the Ag1and Ag1^i atoms have close contacts only to the pyrrole ring carbon atoms C3 and C4 (Ag1···C4^i = 2.894(7) Å and Ag1···C3^i = 3.080(6) Å), which are also less

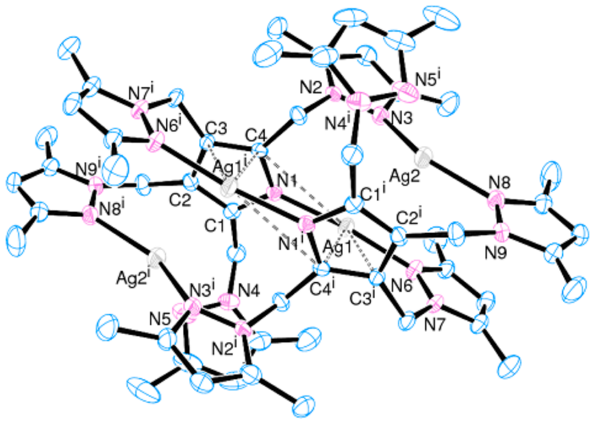
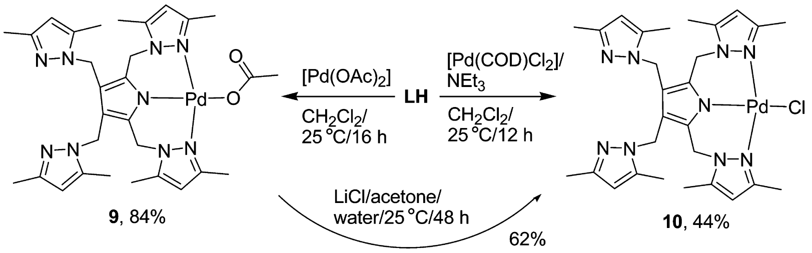


Figure 7. Molecular structure of the tetranuclear silver(I) complex **8** (30% thermal ellipsoids). All hydrogen atoms, two acetonitrile molecules as solvent of crystallization and the two disordered BF_4^- anions are omitted for clarity. The dotted line indicates short contact. Selected bond lengths (Å) and angles (deg): N1−Ag1 2.117(5), N3−Ag2 2.205(5), N8−Ag2 2.177(5), N5−Ag2^i 2.534(6), N6−Ag1 2.135(5), Ag1−Ag2 3.1151(9), Ag2−N5^i 2.534(6), N1−Ag1−N6 172.4(2), N1−Ag1−Ag2 110.40(14), N6−Ag1−Ag2 77.17(15), N8−Ag2−N3 147.1(2), N8−Ag2−N5^i 106.2(2), N3−Ag2−N5^i 97.2(2), N8−Ag2−Ag1 111.35(15), N3−Ag2−Ag1 68.35(14), N5−Ag2−Ag1 128.12(15). The symmetry operation used to generate equivalent atoms: −*x*, −*y*, −*z* + 1.

Scheme 4. Synthesis of Mononuclear Complexes Using LH.



than the sum of the van der Waals radii, 3.40 Å,[29] and are similar to complex **4** and to other silver complexes reported.[30] The pyrrolide N−Ag distance (2.117(5) Å) is shorter than any of the pyrazole N−Ag distances in the structure. Furthermore, the structure showed a metal−metal contact; the Ag1···Ag2 distance of 3.1150(9) Å is less than the sum of the van der Waals radii of silver atoms, 3.40 Å, but is longer than that found in silver metal, 2.884 Å,[31] and closer to other reported silver complexes.[32]

Synthesis and Characterization of Mononuclear Complexes. The ligating property of **LH** was also explored with metal precursors containing a leaving group that can abstract a proton from the ligand. Thus, the reaction of **LH** with 1 equiv of [Pd(OAc)$_2$] afforded the mononuclear cyclopalladated complex **9** containing the η^1-coordinated acetate group and two spectator position pyrazole arms in 84% yield (Scheme 4). The chloride analogue complex **10** was obtained when **LH** was treated with 1 equiv of [Pd(COD)Cl$_2$] in the presence of triethylamine. The structure of **10** was confirmed by comparing its ^{13}C NMR spectrum, which displayed 14 peaks with that of **9** in CDCl$_3$. In addition, the (+)ESI-MS spectra of **9** and **10** showed the same molecular ion peak m/z at 604.2151, which corresponds to the $[M - OAc]^+$ and $[M - Cl]^+$ ions, respectively. In addition, complex **9** was transformed to **10** by treating **9** with lithium chloride in acetone/water. The ^{1}H NMR spectrum of **9** or **10** in CDCl$_3$ gives overlapped multiplets for the methylene protons belonging to the coordinated and uncoordinated arms, indicating dynamic behavior involving movement of pyrazole groups in solution that could be similar to the dynamic property shown by the palladium complex formed by 2,5-bis(3,5-dimethylpyrazolylmethyl)pyrrole **2** (see ref 9) and other complexes.[10]

The structure of complex **9** was confirmed by the X-ray diffraction method (Figure 8 and Table 2). In this structure, the ligand **LH** adopts the monoanionic *mer* κ^3-NNN coordination mode to coordinate to the palladium atom and left the other two pyrazole arms in a spectator position. Further, each pyrazole arm is twisted alternatively up and down to the pyrrole plane; that is, pyrazolyl groups of every pair attached to any two adjacent positions on the pyrrole ring are oriented opposite to each other. This configuration could be an effort to reduce the steric crowding, which is probably not retained in solution as shown by the overlapped multiplets for the methylene protons in its ^{1}H NMR spectrum at room temperature. The twist angles, C1−N1−Pd1−N3 = 37.4(5)° and C4−N1−Pd1−N4 = 36.0(5)° are almost the same as those in the structure of $[Pd(OAc)\{C_4H_2N\text{-}2,5\text{-}(CH_2Me_2pz)_2\text{-}N,N,N\}]$.[9] The palladium atom adopts a distorted square planar geometry defined by the two neutral pyrazolyl nitrogen atoms, lying trans to each other with the "pincer bite" angle of 174.3°, and the two anionic donors—nitrogen and oxygen atoms of the pyrrole and the acetate groups, respectively. All the pyrazolyl and pyrrole N−Pd bond distances are within the reported range.[33]

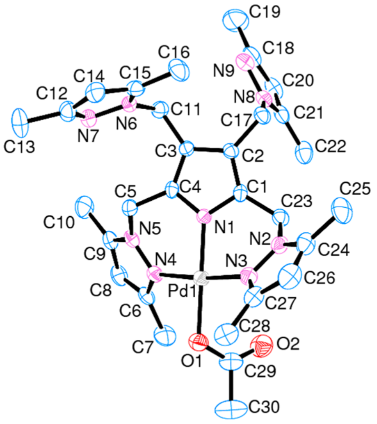


Figure 8. Molecular structure of the mononuclear palladium(II) complex **9** (30% thermal ellipsoids). All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): N1−Pd1 1.963(5), N3−Pd1 2.038(5), N4−Pd1 2.048(5), O1−Pd1 2.022(4), C29−O2 1.224(8), C29−O1 1.266(9), C29−C30 1.513(9), N1−Pd1−O1 178.43(18), N1−Pd1−N3 87.27(19), O1−Pd1−N3 91.56(19), N1−Pd1−N4 87.42(19), O1−Pd1−N4 93.72(19), N3−Pd1−N4 174.3(2), C29−O1−Pd1 116.8(4).

Structure Comparison. A considerable amount of theoretical work has been done to understand the nature of the metal pyrrolide nitrogen (M−N) bond in metal complexes, which showed the existence of π-donation/π-back bonding synergism.[34] In several X-ray structures, the pyrrolide nitrogen metal bond distance is shorter than the value expected if there is only σ bonding, indicating some π-bonding character.[35] This interaction also affects the pyrrole ring C−C double and single bond distances.[34c] In view of these studies (see Table 1), it is conceivable that the observed pyrrolide nitrogen metal bond distances are considerably shorter than the neutral pyrazolyl nitrogen metal bond distances. In **6**, **9**, **7**, and **8**, the difference in distance between the average M−N(pyrazolyl) and the M−N(pyrrolide) bonds is 0.074, 0.070, 0.107, and 0.046 Å, respectively. This could be because of π-back bonding from the metal to empty MO of the pyrrole ring, as reported for other pyrrolide nitrogen-bonded metal complexes.[34b,c] The copper(I) complex **7** showed the highest difference. Further, the presence of π-back bonding can also be inferred from the elongation of both the C−C double and single bonds of the pyrrole ring in comparison with uncoordinated ligand. Because an X-ray structure of **LH** is not available, the pyrrole ring bond distances are compared with the closely related free ligand **2**, for which a crystal structure has been reported.[9] For example, the average pyrrole ring C−C double bond distance in **6** or **9**, which contains the anionic ligand, is 1.382(9) or 1.386(8) Å,

Table 1. Comparison of the Metal Nitrogen (M−N) and the Pyrrole Ring C−C Bond Distances (Å) Observed in 3−9 with the Free Ligand 2

			pyrrole ring distances			
	M−N (pyrrolide)	ave. M−N (pyrazolyl)	C=C	C=C	C−C	N−C
free ligand **2**			C9−C10 1.360(6)	C7−C8 1.359(6)	C8−C9 1.415(7)	N3−C7 1.354(5) N3−C10 1.365(6)
3		2.039(5)	C1−C2 1.377(9)	C3−C4 1.369(9)	C2−C3 1.408(9)	N1−C1 1.369(8) N1−C4 1.359(9)
4a		1.946(4)	C7−C8 1.380(6)	C21−C22 1.383(6)	C8−C22 1.430(6)	N5−C7 1.359(6) N5−C21 1.355(5)
4b		1.990(5)	C1−C2 1.377(7)	C3−C4 1.376(8)	C2−C3 1.432(7)	N1−C1 1.369(7) N1−C4 1.350(7)
5		2.199(6)	C7−C8 1.394(8)	C21−C22 1.387(8)	C8−C21 1.412(8)	N1−C7 1.360(8) N1−C22 1.364(8)
6	N3−Pd02 1.971(5)	2.045(5)	C7−C8 1.387(9)	C15−C22 1.378(9)	C8−C15 1.422(9)	N3−C22 1.340(8) N3−C7 1.373(8)
7	N1−Cu1 1.858(7)	1.965(7)	C1−C2 1.404(12)	C3−C4 1.396(12)	C2−C3 1.420(12)	N1−C1 1.371(10) N1−C4 1.358(10)
8	N1−Ag1 2.117(5) N6−Ag1 2.135(5)	2.172(5)	C1−C2 1.391(8)	C3−C4 1.393(8)	C2−C3 1.416(8)	N1−C1 1.375(7) N1−C4 1.365(7)
9	N1−Pd1 1.963(5)	2.043(5)	C1−C2 1.382(8)	C3−C4 1.391(8)	C2−C3 1.419(8)	N1−C4 1.341(7) N1−C1 1.373(7)

respectively, which are longer than those found in the free ligand **2**. Similarly, the C−C single bond distance in the same complexes is slightly longer than that shown by **2**. A similar trend, with even greater elongation, was also observed for the copper(I) (**7**) and silver(I) (**8**) complexes, as shown in Table 1.

■ CONCLUSION

A single-step synthesis of the $\alpha\alpha'\beta\beta'$-tetrasubstituted pyrrole was developed starting from the Mannich base. As a polydentate ligand, the ligating property of **LH** depends on the size of metal atom and what form of **LH** is used—neutral or anionic. When **LH** was used as a neutral ligand, the compartmental type binuclear palladium(II) and silver(I) complexes were isolated; with the relatively smaller size copper atom, it afforded cage-like binuclear copper(I) complexes. Conversely, when **LH** was used as an anionic ligand, the multinuclear copper(I) and silver(I) complexes were isolated and structurally characterized. Thus, it gives us the option of choosing either binuclear or multinuclear complexes, and their structures were established by X-ray diffraction. Although two-coordinate copper(I) complexes have been reported,[36] these multinuclear complexes exhibit interesting structural features including short contacts, and their formations are strongly favored by the multidentating nature of the ligand **LH**. Consequently, for example in **7**, the copper(I) atom possesses two different geometries—linear and trigonal. Upon comparison of the M−N and the pyrrole ring C−C bond distances with the free ligand **2**, within the group 11 metals studied, the relatively shorter M−N bond distance in the copper(I) complex **7** probably indicates the presence of more pronounced π-donation and back bonding than that in the silver(I) complex **8**. Synthesis of other ligands using this method and metal complexes across the periodic table is under progress.

■ 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. 2,5-Bis-[(dimethylamino)methyl]pyrrole,[37] 3,5-dimethylpyrazole-1-carbinol,[38] and [Pd(COD)Cl_2][39] were prepared according to the literature procedures. Other chemicals were obtained from commercial sources and used without further purification. ^{1}H NMR (200 and 400 MHz) and ^{13}C NMR (50.3 and 100.6 MHz) spectra were recorded on a Bruker ACF200 spectrometer. Chemical shifts are referenced with respect to the chemical shift of the residual protons present in the deuterated solvents. FTIR spectra were recorded using PerkinElmer 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. Melting points were determined in open capillaries and are corrected using benzophenone as a reference.

Synthesis of 2,3,4,5-Tetrakis(3,5-dimethylpyrazol-1-ylmethyl)pyrrole, LH. A xylene (20 mL) solution of 3,5-dimethylpyrazole-1-carbinol (5.57 g, 44.2 mmol) and 2,5-bis(dimethylaminomethyl)pyrrole (2.00 g, 11.05 mmol) was refluxed for about 12 h. The solution was cooled to room temperature and then concentrated to ~7 mL. Addition of petroleum ether (50 mL) to this solution gave **LH** as a crude dark brown precipitate. The precipitate was separated and washed with petroleum ether (3 × 25 mL). The precipitate was loaded onto a silica gel column chromatography. Elution using ethyl acetate/methanol (50:1, v/v) gave the first fraction from which the solvent was removed under vacuum to give **LH** as a colorless solid (2.20 g, 4.41 mmol, 40%), mp 174 °C. ^{1}H NMR ($CDCl_3$, 200 MHz, 25 °C): δ = 8.94 (br s, 1H, NH), 5.78 (s, 2H, pyrazole CH), 5.73 (s, 2H, pyrazole CH), 5.06 (s, 4H, CH_2), 4.73 (s, 4H, CH_2), 2.19(s, 12H, CH_3), 2.06 (s, 6H, CH_3), 2.04 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$, 50.3 MHz, 25 °C): δ = 148.1, 147.1, 139.3, 139.1, 124.8, 113.7, 105.7, 105.4, 44.5, 43.3, 13.6, 11.2, 10.9. FT-IR (KBr, cm^{-1}): ν = 3402 (m), 2923 (m), 1652 (w), 1550 (s), 1458 (s), 1427 (s), 1382 (m), 1283 (m), 1225 (w), 1028 (w), 985 (w), 855 (w), 775 (m), 685 (w), 620 (w), 550 (w). HRMS (−ESI) m/z: $[M - H^+]^-$ calcd for $C_{28}H_{36}N_9$, 498.3094; found, 498.3089.

Synthesis of [Pd_2Cl_4(μ-C_4HN-2,3,4,5-(CH_2Me_2pz)$_4$-*N*,*N*,*N*,*N*)], 3. To a solution of [Pd(COD)Cl_2] (0.1 g, 0.35 mmol) in dichloromethane (15 mL) was added **LH** (0.09 g, 0.175 mmol). The solution was stirred for 16 h at room temperature. The solvent was removed under vacuum and the residue was washed with diethyl ether (3 × 10 mL) and then dried under vacuum to give **3** as red solid (0.12 g, 0.135 mmol, 77% based on Pd). A saturated solution of **3** in toluene/dichloromethane mixture was allowed to stand for slow evaporation at room temperature to give **3** as red-colored needle-shaped crystals. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ = 9.41 (br s, 1H, NH), 5.92 (s, 2H, pyrazole CH), 5.88 (s, 2H, pyrazole CH), 5.41 (d, $J(H_AH_B)$ = 15.2 Hz, 2H, CH_2), 5.29 (d,

$J(H_AH_B)$ = 15.2 Hz, 2H, CH_2), 4.48 (overlapped doublets, $J(H_AH_B)$ = 15.2 Hz, 4H, CH_2), 2.73 (s, 6H, CH_3), 2.59 (s, 6H, CH_3), 2.32 (s, 6H, CH_3), 2.28 (s, 6H, CH_3). FT-IR (KBr, cm^{-1}): ν = 3245 (m), 3128 (w), 2926 (m), 1627 (w), 1554 (s), 1459 (s), 1422 (s), 1263 (m), 1155 (w), 1056 (w), 991 (w), 793 (m), 657 (w), 621 (w). HRMS (+ESI) *m/z*: $[M - 2Cl]^+$ calcd for $C_{28}H_{37}Cl_2N_9Pd_2$, 781.0619; found, 781.0622. Anal. Calcd for $C_{28}H_{40}Cl_4N_9O_{1.5}Pd_2$: C, 38.16; H, 4.57; N, 14.30. Found: C, 38.11; H, 4.59; N, 13.79.

Synthesis of $[Cu_2(\mu\text{-}X)(\mu\text{-}C_4HN\text{-}2,3,4,5\text{-}(CH_2Me_2pz)_4\text{-}N,N,N,N)]^+[CuX_2]^-$ (X = Cl for 4a and I for 4b). To a solution of CuX (X = Cl or I) in THF (~50 mL) was added **LH**. The solution was stirred for 12 h at room temperature. The solvent was removed under vacuum, and the residue was dissolved in THF. The THF solution was layered with petroleum ether to give **4a** or **4b** as colorless crystals after 3 days.

For 4a (X = Cl). CuCl (0.1 g, 1.01 mmol), **LH** (0.25 g, 0.50 mmol). Yield: 0.15 g, 0.17 mmol, 51% based on Cu. ^1H NMR ($CDCl_3$, 400 MHz, 25 °C): δ = 11.79 (br s, 1H, NH), 5.82 (s, 2H, pyrazole CH), 5.64 (s, 2H, pyrazole CH), 4.95 (br s, 8H, CH_2), 2.43 (s, 6H, CH_3), 2.28 (s, 6H, CH_3), 2.25 (s, 6H, CH_3), 2.21 (s, 6H, CH_3). ^1H NMR (DMSO-d_6, 400 MHz, 25 °C): δ = 11.95 (br s, 1H, NH), 6.06 (s, 2H, pyrazole CH), 5.71 (s, 2H, pyrazole CH), 5.34 (d, $J(H_AH_B)$ = 14.0 Hz, 2H, CH_2), 5.19 (s, 4H, CH_2), 4.96 (d, $J(H_AH_B)$ = 14.0 Hz, 2H, CH_2), 2.38 (s, 6H, CH_3), 2.28 (s, 6H, CH_3), 2.19 (s, 6H, CH_3), 2.12 (s, 6H, CH_3). ^{13}C NMR (DMSO-d_6, 100.6 MHz, 25 °C): δ = 146.7, 145.5, 140.1, 138.7, 127.2, 116.4, 105.7, 104.8, 66.8, 41.4, 40.8, 24.9, 13.6, 13.6, 10.8. FT-IR (KBr, cm^{-1}): ν = 3116 (m), 3018 (m), 2924 (m), 2734 (w), 1620 (w), 1552 (s), 1460 (s), 1425 (s), 1266 (m), 1093 (w), 1048 (m), 788 (m), 680 (w), 620 (w). HRMS (+ESI) *m/z*: $[M - CuCl_2]^+$ calcd for $C_{28}H_{37}ClCu_2N_9$, 660.1647; found, 660.1434.

For 4b (X = I). CuI (0.10 g, 0.52 mmol), **LH** (0.13 g, 0.30 mmol). Yield: 0.10 g, 0.08 mmol, 47% based on Cu. ^1H NMR ($CDCl_3$, 200 MHz, 25 °C): δ = 9.33 (br s, 1H, NH), 5.86 (s, 2H, pyrazole CH), 5.80 (s, 2H, pyrazole CH), 5.21 (br s, 4H, CH_2), 4.67 (br s, 4H, CH_2), 2.36 (s, 6H, CH_3), 2.32 (s, 6H, CH_3), 2.30 (s, 6H, CH_3), 2.11 (s, 6H, CH_3). ^1H NMR (DMSO-d_6, 400 MHz, 25 °C): δ = 12.10 (br s, 1H, NH), 6.05 (s, 2H, pyrazole CH), 5.76 (s, 2H, pyrazole CH), 5.18 (br s, 8H, CH_2), 2.39 (s, 6H, CH_3), 2.26 (s, 6H, CH_3), 2.19 (s, 6H, CH_3), 2.16 (s, 6H, CH_3). ^{13}C NMR (DMSO-d_6, 100.6 MHz, 25 °C): δ = 146.7, 145.8, 140.2, 138.9, 126.9, 116.4, 106.1, 105.2, 66.9, 41.5, 41.2, 25.0, 14.4, 14.1, 10.8. FT-IR (KBr, cm^{-1}): ν = 3239 (w), 2928 (m), 2868 (m), 1650 (w), 1625 (w), 1553 (s), 1458 (s), 1422 (s), 1387 (m), 1265 (m), 1115 (w), 1045 (w), 920 (w), 888 (w), 788 (w), 682 (w). HRMS (+ESI) *m/z*: $[M - CuI_2]^+$ calcd for $C_{28}H_{37}Cu_2IN_9$, 752.1009; found, 752.0784. Anal. Calcd for $C_{32}H_{45}Cu_3I_3N_9O$: C, 33.62; H, 3.97; N, 11.03. Found: C, 33.41; H, 3.75; N, 11.26.

Synthesis of $[Ag_2(\mu\text{-}C_4HN\text{-}2,3,4,5\text{-}(CH_2Me_2pz)_4\text{-}N,N,N,N)(CH_3CN)_2]^{2+}[BF_4^-]_2$, 5. To a tetrahydrofuran (~50 mL) solution of $AgBF_4$ (0.05 g, 0.26 mmol) was added **LH** (0.06 g, 0.13 mmol). The solution was stirred for 12 h at room temperature in the dark, resulting in the formation of colorless precipitate. The solution was filtered to remove the precipitate. The solvent was removed from the filtrate under vacuum, and the residue was washed with THF (10 mL) followed by petroleum ether twice (2 × 20 mL) and then dried under vacuum, giving a colorless solid. This solid was dissolved in acetonitrile and then layered with diethyl ether to give colorless crystals of **5** over a period of 7 days (0.06 g, 0.06 mmol, 48% based on Ag). ^1H NMR (DMSO-d_6, 200 MHz, 25 °C): δ = 11.39 (br s, 1H, NH), 6.08 (s, 2H, pyrazole CH), 6.02 (s, 2H, pyrazole CH), 5.15 (s, 4H, CH_2), 4.84 (s, 4H, CH_2), 2.37 (s, 6H, CH_3), 2.21 (s, 12H, CH_3), 2.07 (s, 6H, CH_3), 2.05 (s, 6H, CH_3). ^{13}C NMR (DMSO-d_6, 50.3 MHz, 25 °C): δ = 148.4, 148.0, 142.2, 141.7, 127.3, 114.9, 105.8, 105.7, 99.5, 42.0, 41.8, 14.2, 11.2, 10.6. FT-IR (KBr, cm^{-1}): ν = 3402 (m), 3324 (m), 2922 (m), 1633 (w), 1552 (s), 1462 (s), 1426 (s), 1387 (m), 1273 (m), 1229 (w), 1080 (vs), 1032 (vs), 890 (w), 807 (m), 774 (m), 689 (w), 617 (w), 524 (w), 467 (w). HRMS (+ESI) *m/z*: $[M - 2MeCN - 2BF_4]^+$ calcd for $C_{28}H_{37}Ag_2N_9$, 713.1274; found, 713.1203.

Synthesis of $[Pd_2Cl_3(\mu\text{-}C_4N\text{-}2,3,4,5\text{-}(CH_2Me_2pz)_4\text{-}N,N,N,N,N)]$, 6. To a toluene solution of **LH** (0.25 g, 0.50 mmol) was added *n*-BuLi (1.6 M in hexanes, 0.5 mL, 0.75 mmol) at −78 °C. The solution was allowed to warm to room temperature and stirred for an additional 1 h. Then this solution was added to the tetrahydrofuran solution of $[Pd(COD)Cl_2]$ (0.285 g, 1.00 mmol) at room temperature. After stirring for 12 h, all volatiles were evaporated, and the residue was dissolved in dichloromethane (~100 mL). The solution was layered with petroleum ether, and orange crystals of **6** were formed over a period of 1 week (~0.09 g, 0.10 mmol, 20% yield). FT-IR (KBr, cm^{-1}): ν = 3121 (w), 2954 (w), 2922 (m), 1626 (w), 1554 (s), 1464 (s), 1424 (s), 1390 (s), 1263 (m), 1228 (m), 1058 (w), 1002 (w), 887 (w), 833 (w), 793 (m), 735 (w), 623 (w). Anal. Calcd for $C_{29}H_{38}Cl_5N_9Pd_2$: C, 38.58; H, 4.24; N, 13.96. Found: C, 38.15; H, 4.23; N, 13.67.

Synthesis of $[(Cu_2(\mu\text{-}I)\{\mu\text{-}C_4N\text{-}2,3,4,5\text{-}(CH_2Me_2pz)_4\text{-}N,N,N,N,N\})_2Cu]^+I^-$, 7. To a toluene solution of **LH** (0.25 g, 0.50 mmol) was added *n*-BuLi (1.6 M in hexanes, 0.5 mL, 0.75 mmol) at −78 °C. The solution was allowed to warm to room temperature and stirred for an additional 1 h. This solution was added to the THF solution of CuI (0.10 g, 0.5 mmol) at room temperature. After stirring for 12 h, the solution was layered with petroleum ether to give colorless crystal of **7** over a period of 7 days (0.05 g, 0.03 mmol, 28% based on Cu). ^1H NMR (DMSO-d_6, 400 MHz, 25 °C): δ = 5.86 (s, 2H, pyrazole CH), 5.70 (s, 2H, pyrazole CH), 5.23−4.77 (m, 8H, CH_2), 2.30 (s, 12H, CH_3), 2.26 (s, 12H, CH_3), 2.17 (s, 12H, CH_3), 2.13 (s, 12H, CH_3). ^{13}C NMR (DMSO-d_6, 100.6 MHz, 25 °C): δ = 146.4, 145.2, 139.7, 134.8, 125.3, 114.3, 105.7, 105.0, 45.7, 42.3, 14.5, 14.3, 11.4, 10.9. FT-IR (KBr, cm^{-1}): ν = 2921 (m), 2868 (w), 1551 (s), 1457 (s), 1423 (s), 1385 (w), 1266 (m), 1228 (m), 1046 (m), 985 (w), 954 (w), 881 (w), 780 (m), 682 (w), 621 (w), 509 (w). Anal. Calcd for $C_{63}H_{80}Cu_5I_3N_{18}$: C, 42.32; H, 4.51; N, 14.10. Found: C, 41.82; H, 4.45; N, 14.23.

Synthesis of $[Ag_4(\mu\text{-}C_4N\text{-}2,3,4,5\text{-}(CH_2Me_2pz)_4\text{-}N,N,N,N)_2]^{2+}[BF_4^-]_2$, 8. *Method A.* To a toluene solution of **LH** (0.25 g, 0.50 mmol) was added *n*-BuLi (1.6 M in hexanes, 0.5 mL, 0.75 mmol) at −78 °C. The solution was allowed to warm to room temperature and stirred for an additional 1 h. This solution was added to a THF solution of $AgBF_4$ (0.20 g, 1.00 mmol) at room temperature. After stirring for 12 h in the dark, all volatiles were evaporated under vacuum, and the residue was dissolved in acetonitrile (~20 mL). The solution was filtered and layered with diethyl ether (~50 mL), which was allowed to stand for slow evaporation to give a few colorless crystals of **8**.

Method B. To an acetonitrile (~40 mL) solution of **LH** (0.25 g, 0.50 mmol) and triethylamine (0.278 mL, 2.00 mmol) was added $AgBF_4$ (0.195 g, 1.00 mmol). The solution was stirred for 12 h at room temperature in dark, resulting in the formation of suspension. The solution was filtered, and the filtrate was evaporated under vacuum. The residue was washed with diethyl ether (3 × 10 mL) and extracted with acetonitrile (∼50 mL). The acetonitrile solution was layered with diethyl ether (∼100 mL) to give tiny colorless crystals of **8**. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ = 6.02 (s, 2H, pyrazole CH), 5.90 (s, 2H, pyrazole CH), 5.31 (s, 4H, CH_2), 5.21 (s, 4H, CH_2), 2.46 (s, 12H, CH_3), 2.32 (s, 12H, CH_3), 2.30 (s, 12H, CH_3), 2.23 (s, 12H, CH_3). FT-IR (KBr, cm^{-1}): ν = 2927 (m), 1626 (w), 1552 (s), 1460 (s), 1424 (s), 1383 (m), 1336 (w), 1269 (w), 1226 (w), 1056 (vs), 949 (w), 884 (w), 831 (w), 779 (w), 731 (w), 680 (w), 626 (w). Anal. Calcd for $C_{60}H_{78}Ag_4B_2F_8N_{20}$: C, 42.78; H, 4.67; N, 16.63. Found: C, 42.52; H, 4.68; N, 16.32.

Synthesis of [Pd(OAc)(C_4N-2,3,4,5-($CH_2Me_2pz)_4$-*N*,*N*,*N*)], 9. To a solution of [Pd(OAc)$_2$] (0.20 g, 0.90 mmol) in dichloromethane (30 mL) was added **LH** (0.44 g, 0.90 mmol). The solution was stirred for 16 h at room temperature. The solvent was removed under vacuum, and the residue was dissolved in a minimum quantity (∼5−10 mL) of dichloromethane. Addition of hexanes (∼150 mL) results in the precipitate of some solid, which was separated by filtration. The solvent was removed from the filtrate under vacuum to give **9** as a pale yellow solid (0.50 g, 0.75 mmol, 84% based on Pd). Suitable single crystals of **9** for X-ray diffraction study were grown from a dichloromethane/hexane (1/15, v/v) solution upon slow evaporation at room temperature. ^{1}H NMR ($CDCl_3$, 200 MHz, 25 °C): δ = 5.75 (s, 4H, pyrazole CH), 5.08−4.91 (m, 8H, CH_2), 2.30 (s, 6H, CH_3), 2.18 (s, 12H, CH_3), 2.03 (s, 6H, CH_3), 1.93 (s, 3H, acetate-CH_3). ^{13}C NMR ($CDCl_3$, 50.3 MHz, 25 °C): δ = 177.8, 151.0, 146.8, 141.2, 138.9, 126.1, 112.0, 107.1, 105.7, 45.2, 44.9, 23.3, 13.7, 13.6, 11.7, 11.3. FT-IR (KBr, cm^{-1}): ν = 2925 (m), 2863 (w), 2574 (w), 1715 (m), 1623 (m), 1554 (s), 1460 (s), 1423 (s), 1387 (s), 1327 (m), 1259 (s), 1060 (w), 1034 (w), 876 (w), 797 (m), 680 (w), 615 (w). HRMS (+ESI) *m*/*z*: [M − OAc]$^+$ calcd for $C_{28}H_{36}N_9Pd$, 604.2128; found, 604.2151.

Synthesis of [Pd(Cl)(C_4N-2,3,4,5-($CH_2Me_2pz)_4$-*N*,*N*,*N*)], 10. To a solution of [Pd(COD)Cl$_2$] (0.10 g, 0.35 mmol) and **LH** (0.175 g, 0.35 mmol) in dichloromethane (10 mL) was added dropwise triethylamine (0.20 mL, 1.40 mmol) at room temperature. The solution was stirred for 12 h and then washed with water three times. The organic layer was separated and dried over anhydrous Na_2SO_4. The solution was filtered, and the filtrate was concentrated to a minimum amount. Addition of hexanes (200 mL) results in the formation of a light brown precipitate. The solution was again filtered, and the precipitate was washed with diethyl ether two times. The precipitate was dried under vacuum to give **10** as brown solid (0.10 g, 0.16 mmol, 44% yield based on Pd). ^{1}H NMR ($CDCl_3$, 200 MHz, 25 °C): δ = 5.82 (s, 2H, pyrazole CH), 5.78 (s, 2H, pyrazole CH), 5.30−4.90 (m, 8H, CH_2), 2.58 (s, 6H, CH_3), 2.24 (s, 6H, CH_3), 2.22 (s, 6H, CH_3), 2.07 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$, 50.3 MHz, 25 °C): δ = 153.1, 147.0, 141.6, 139.0, 126.0, 111.8, 107.6, 105.8, 45.6, 44.9, 16.3, 13.7, 11.9, 11.5. FT-IR (KBr, cm^{-1}): ν = 2956 (w), 2923 (m), 2857 (w), 1653 (w), 1552 (s), 1458 (s), 1426 (s), 1384 (s), 1336 (w), 1295 (w), 1260 (s), 1220 (w), 1094 (m), 1029 (m), 874 (w), 800 (s), 678 (w), 626 (w). HRMS (+ESI) *m*/*z*: [M − Cl]$^+$ calcd for $C_{28}H_{36}N_9Pd$, 604.2128; found, 604.2151.

Synthesis of 10 from 9. Solid LiCl (0.02 g, 0.375 mmol) was added to a solution of complex **9** (0.05 g, 0.075 mmol) in acetone/water (v/v 3/2, 5 mL). The resultant suspension was stirred at room temperature for 48 h to give a pale yellow precipitate. The solution was filtered, and the precipitate was washed with water twice (3 mL). The precipitate was dissolved in dichloromethane, and the solution was dried over anhydrous Na_2SO_4 and then filtered. The filtrate was evaporated under vacuum to give complex **10** as a brown solid (0.03 g, 0.05 mmol, 62% yield based on Pd). The ^{1}H NMR spectrum of **10** obtained from this procedure is the same as that obtained for **10** synthesized from the above method.

X-ray Crystallography. Suitable single crystals of **3**−**9** were obtained from solvents mentioned in their respective synthetic procedures. Single crystal X-ray diffraction data collections for these crystals were performed using a Bruker-APEX-II CCD diffractometer with graphite monochromated molybdenum Kα radiation (λ = 0.71073 Å). The structures were solved by SIR-92[40] available in the WinGX program which successfully located most of the non-hydrogen atoms. Subsequently, least-squares refinements were carried out on F^2 using SHELXL-97[41] (WinGX version) to locate the remaining non-hydrogen atoms. Typically for all the structures, hydrogen atoms attached to carbon atoms were fixed in calculated positions. The pyrrolic 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.

Complex **3** crystallizes in the monoclinic $P2/n$ space group, and the asymmetric unit contains one molecule of **3** and three water molecules, two of which have half occupancy. Hydrogen atoms attached to these water molecules are neither fixed nor located, as they have not appeared, which results in the discrepancy between the calculated and reported values in its cif file. Complex **4a** crystallizes in the monoclinic space group $P2_1/c$, and the asymmetric unit contains both the cation and anion represented together with one THF molecule; however, complex **4b** crystallizes in the triclinic space group $P\bar{1}$, and the asymmetric unit contains units similar to **4a**. Complex **5** crystallizes in the orthorhombic space group $Pna2(1)$ with the whole molecule of **5** in the asymmetric unit. The pyrrolic NH hydrogen atom could not be located but was fixed. Its BF_4^- ions are severely disordered and were handled successfully using SIMU and SADI. Complex **6** crystallizes in the monoclinic space group $P2_1/c$ with all angle values equal to 90° and the asymmetric unit contains one molecule of **6** together with one dichloromethane molecule in the lattice. Complex **7** crystallizes in the monoclinic centrosymmetric space group $C2/c$, and the asymmetric unit contains one-half of the molecule, in which the central copper(I) atom is located on the inversion center, together with one iodine atom and one toluene molecule as a solvent of crystallization. The whole molecule was generated by the symmetry operation. The toluene molecule is highly disordered and could not be modeled. As a result, there is a discrepancy between the calculated and reported number of hydrogen atoms. Complex **8** crystallizes in the monoclinic $P2_1/n$ space group and the asymmetric unit contains one-half of the molecule, one BF_4^- and one acetonitrile solvent. The whole molecule was generated by the symmetry operation and has an inversion center. The two BF_4^- ions are severely disordered and were handled successfully using EADP and SADI. Complex **9** crystallizes in the monoclinic space group $C2/c$ with one molecule in the asymmetric unit. The refinement data for all the structures are summarized in Table 2.

Table 2. Crystallographic Data for 3−9

	$3 \cdot 3H_2O$	$4a \cdot C_4H_8O$	$4b \cdot C_4H_8O$	5	$6 \cdot CH_2Cl_2$	$7 \cdot C_7H_8$	$8 \cdot 2CH_3CN$	9
empirical formula	$C_{28}H_{43}Cl_4N_9O_3Pd_2$	$C_{32}H_{45}Cl_3Cu_3N_9O$	$C_{32}H_{45}Cu_3I_3$ N_9O	$C_{32}H_{43}Ag_2B_2$ F_8N_{11}	$C_{29}H_{38}Cl_5N_9Pd_2$	$C_{63}H_{80}Cu_5I_3N_{18}$	$C_{60}H_{78}Ag_4B_2F_8N_{20}$	$C_{30}H_{39}N_9O_2Pd$
fw	908.31	868.74	1143.09	971.13	902.73	1787.85	1684.52	664.10
wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
temp (K)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)
cryst syst	monoclinic	monoclinic	triclinic	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2/n$	$P2_1/c$	$P\bar{1}$	$Pna2(1)$	$P2_1/c$	$C2/c$	$P2_1/n$	$C2/c$
a/Å	17.840(3)	17.8756(11)	11.5080(13)	16.546(2)	14.4357(15)	34.062(7)	12.874(3)	25.480(4)
b/Å	8.9328(15)	17.0372(11)	12.0734(14)	13.631(2)	28.482(3)	14.332(3)	16.378(3)	14.7785(17)
c/Å	22.386(4)	12.9493(8)	16.0273(18)	18.377(3)	8.5802(9)	14.568(3)	16.669(4)	17.786(2)
α/degree	90.00	90.00	88.789(4)	90.00	90.00	90.00	90.00	90.00
β/degree	93.429(6)	102.187(2)	79.613(3)	90.00	90.00	95.993(3)	103.524(7)	108.903(7)
γ/degree	90.00	90.00	71.175(3)	90.00	90.00	90.00	90.00	90.00
vol (Å^3)	3561.1(11)	3854.8(4)	2071.5(4)	4144.6(10)	3527.8(6)	7073(2)	3417.3(12)	6336.4(14)
Z	4	4	2	4	4	4	2	8
D_{calcd}, g cm^{-3}	1.694	1.497	1.833	1.556	1.700	1.679	1.637	1.392
μ/mm^{-1}	1.354	1.886	3.798	1.019	1.434	2.840	1.205	0.628
$F(000)$	1832	1784	1108	1952	1808	3552	1696	2752
θ range (deg)	1.82 to 25.00	1.17 to 25.00	1.29 to 25.00	1.86 to 25.30	1.43 to 25.00	1.54 to 25.00	1.77 to 25.00	1.62 to 25.00
total/unique no. of reflns	41430/6277	45623/6798	24984/7266	37606/6597	32557/5169	41407/6224	40434/6016	37405/5585
R_{int}	0.1029	0.0761	0.0396	0.0676	0.0912	0.1062	0.1334	0.1237
data/restr./ params	6277/0/414	6798/0/436	7266/15/446	6597/379/573	5169/0/406	6224/0/407	6016/21/435	5585/0/379
GOF (F^2)	1.033	1.012	1.016	1.000	0.914	1.043	1.000	1.036
$R1$, $wR2$	0.0481, 0.1035	0.0459, 0.1142	0.0377, 0.0926	0.0419, 0.0966	0.0451, 0.0987	0.0572, 0.1302	0.0511, 0.0919	0.0554, 0.1274
$R1$, $wR2$ (all data)	0.0974, 0.1262	0.0950, 0.1432	0.0715, 0.1162	0.0729, 0.1113	0.0891, 0.1124	0.1245, 0.1683	0.1167, 0.1151	0.1103, 0.1533
peak and hole (e Å^{-3})	0.662 and −0.497	0.553 and −0.280	0.772 and −0.613	0.557 and −0.424	0.505 and −0.747	1.177 and −0.768	0.512 and −0.419	0.631 and −0.513

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

NMR, IR spectra, and crystallographic data (CIF). 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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