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A Tris(pyrazolyl) η^6-Arene Ligand That Selects Cu(I) over Cu(II)

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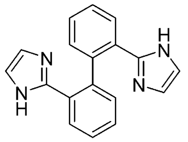
1,3,5-Tris{2′-[(pyrazol-1-yl)methyl]phenyl}benzene, **4**, and its complexes with Cu(I) and Ag(I) have been prepared and characterized. Both Cu^I(**4**) and Ag^I(**4**) triflate crystallize in the rhombohedral space group $R\bar{3}$, with the cations and anions each exhibiting crystallographically imposed 3-fold (C_3) symmetry. In both complexes, **4** behaves as a tris(pyrazolyl) η^6-arene ligand whose arms act as three-pronged tweezers to form chiral, propeller-like cations with pyramidal MN(pyrazole)$_3$ coordination geometries. Centers of symmetry in the space group ensure that the crystals are racemates, with equal numbers of *P*,*P*,*P* and *M*,*M*,*M* enantiomers. In broad outline, each cation is shaped like a three-legged stool, with the metal ion centered at the top and pointed downward from a triangular N(pyrazole) plane toward the center of gravity (Cg) of the central benzene ring (a metal-endo conformation), which constitutes the bottom shelf of the stool. The Cu(I)···Cg and Ag(I)···Cg distances, 3.195(2) and 3.165(2) Å, respectively, support the existence of an η^6 bonding interaction with Ag(I) and, to a lesser extent, with Cu(I). NMR data for Ag^I(**4**) suggest rapid interconversion of this cation in solution between *P*,*P*,*P* and *M*,*M*,*M* enantiomers. Our inability to prepare any Cu(II) complexes with **4** is consistent with cyclovoltammetric results, which suggest that the ligand is more easily oxidized than Cu(I).

Introduction

Small molecule metal-containing complexes having atypical coordination geometries can show useful catalytic, spectroscopic, and kinetic properties. For example, such complexes have found use as polymerization catalysts[1,2] and as structural/spectroscopic models for type 1 sites in copper-containing metalloproteins.[3] The bis(imidazole) biphenyl-based ligand **1** gives rise to nearly isostructural Cu(I)/Cu(II) tetrakis(imidazole) chromophores that have been used to probe electron self-exchange and also to elucidate electronic spectroscopic and EPR features of the structurally novel Cu(II) chromophore.[4] Benzimidazole analogues of **1**, such as **2**, form even more nearly tetrahedral complexes with divalent first-row transition metal ions ranging from Cr(II) to Zn(II).[5] Even a single bis(benzimidazole) unit is sufficient to generate a D_{2d}-flattened, distorted tetrahedral Cu(II) coordination geometry.[6] The 2,2′-biphenyl spacer in **2** also serves



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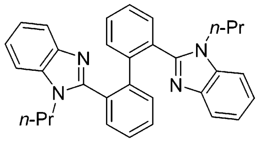

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to position the N-donor groups such that free ligands of this type act as potent proton sponges.[7]

We have chosen to study tridentate structurally constraining ligands with the aim of preparing other approximately tetrahedral Cu(II)/Cu(I) redox couples. Such ligands would supply three out of the four ligand donor sites. Noteworthy prior reports of tridentate structurally constraining ligands include those describing Cu(I) and Cu(II) complexes of *tris*-pyrazolylborates and 1,4,7-triazacyclononanes.[8] However, the relatively small bite angles of these ligands restrict the observed N−Cu−N bond angles to approximately 85 ± 2° and 94 ± 4°, respectively.[8] More recent reports of tripodal, tridentate ligands include the family of benzenes elaborated at the 1,3,5-ring positions with pyrazoles, imidazoles, benzimidazoles, and other ligands.[9] However, these ligands form 2-dimensional network structures with transition metal ions such as Cu(II), Zn(II), Ni(II), and Ag(I) in which the metal ions are ligated in structurally conventional ways by donor groups supplied by three or four different ligands.

We report here the synthesis of two ligands, each of which has nine torsional degrees of freedom, and each of which, on the basis of the examination of molecular models, might be expected to present three suitably oriented convergent pyrazole N-donor ligands. Structural characterizations of the ligands and their complexes with Cu(I) and Ag(I) also are detailed. The structural and supporting electrochemical studies indicate why these particular ligands afford unexpectedly poor complexation of Cu(II).

Experimental Section

1. General Procedures. Melting points were measured on a Thomas-Hoover capillary melting apparatus and are uncorrected. Proton and carbon NMR spectra were obtained with Varian UNITY 300 and 400 spectrometers. Chemical shifts (δ) are reported in parts per million downfield from tetramethylsilane (TMS) with either TMS or the solvent signal as the internal reference. Coupling constants (J) are in hertz. Fast atom bombardment mass spectra (FABMS) were obtained from the Washington University Research Resource in Mass Spectroscopy. Positive ion peaks are given in units of m/z. All reagents were used as received or were purified by using standard methods.[10] Precoated silica gel plates (Merck 60) were used for analytical thin-layer chromatography. E. Merck silica gel (230−400 mesh) was employed for column chromatography. Compound **3** was prepared by using a literature procedure.[11] An alternate preparation of **3** utilizing a Suzuki coupling has also been reported.[12]

2. Syntheses. The preparation of ligands **4** and **5**, and of complexes of **4** with Cu(I) and Ag(I), is described below and outlined in Scheme 1.

1,3,5-Tris{2′-[(pyrazol-1-yl)methyl]phenyl}benzene (4). This ligand was prepared by following the procedure of Hartshorn and Steel.[13] A solution of 174.6 mg (0.3 mmol) of 1,3,5-tris[2′-(bromomethyl)phenyl]benzene (**3**), 102 mg (1.5 mmol) of pyrazole, 6 mL of benzene, 1.5 mL of 40% aqueous sodium hydroxide, and 4 drops of 40% aqueous tetrabutylammonium hydroxide was heated at reflux for 4 h. The organic layer was separated out and washed sequentially with 4 mL of 1 M aqueous hydrochloric acid and 4 mL of saturated brine, dried over sodium sulfate, and then concentrated. Chromatography on silica gel using petroleum ether/ethyl acetate (2:1 v/v) as the eluant gave **4** as a yellow oil, which was dissolved in 2 mL of 1:1 petroleum ether/dichloromethane and then concentrated to afford 132 mg (81%) of a white powder, mp 114−116 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.13−7.44 (m, 21 H), 6.15 (t, $J = 2$ Hz, 3 H), 5.33 (s, 6 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 140.9, 140.7, 139.6, 134.0, 130.6, 129.6, 129.1, 128.9, 128.4, 128.3, 105.9, 54.1. $R_f = 0.27$ (ethyl acetate). FABMS: 547 (MH^+).

1,3,5-Tris{2′-[(3,5-dimethylpyrazol-1-yl)methyl]phenyl}benzene (5). This ligand was prepared by following the method of Chin et al.[14] A suspension of 43 mg of sodium hydride (60% in mineral oil, 1.07 mmol) in 2 mL of anhydrous THF was treated with 102 mg (1.07 mmol) of 3,5-dimethylpyrazole, which was added in small portions at room temperature. The mixture was stirred for 20 min until the evolution of hydrogen gas ceased. A solution of 208 mg (0.356 mmol) of 1,3,5-tris[2′-(bromomethyl)-phenyl]benzene (**3**) in 1 mL of THF was added slowly, and the solution was stirred for 4 h. Workup as for **4** gave a residue, which was chromatographed on silica gel by using petroleum ether/ethyl acetate (2:1) as the eluant to give 200 mg (95%) of **5** as a white solid, mp 136−138 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.36 (s, 3 H), 7.32−7.34 (m, 9 H), 6.75 (d, $J = 6.3$ Hz, 3 H), 5.80 (s, 3 H), 5.25 (s, 6 H), 2.20 (s, 9 H), 1.98 (s, 9 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 147.9, 141.1, 139.8, 139.5, 135.0, 130.2, 129.0, 128.5, 127.6, 127.0, 105.7, 51.0, 13.9, 11.4. FABMS: 637 (MLi^+), 631 (MH^+). Single crystals of **5** suitable for X-ray diffraction were obtained by slow evaporation of a filtered solution of 5 mg of **5** in 2 mL of hexane and 1 mL of dichloromethane: rectangular-based prisms, mp 139−140 °C.

1,3,5-Tris{2′-[(pyrazol-1-yl)methyl]phenyl}benzene Copper(I) Triflate·Hexane Solvate, Cu^I(4) CF_3SO_3·Hexane. Hexane vapor was allowed to diffuse into a filtered solution containing 10 mg (0.018 mmol) of ligand **4** and 4.73 mg (0.009 mmol) of Cu(I)$_2$(OTf)$_2$·toluene in 2 mL of acetone, providing colorless crystals of Cu^I(**4**) CF_3SO_3·hexane.

1,3,5-Tris{2′-[(pyrazol-1-yl)methyl]phenyl}benzene Silver(I) Triflate·0.5 Acetone·0.5 Diethyl Ether Solvate, Ag^I(4) CF_3SO_3·0.5 Acetone·0.5 Diethyl Ether Solvate. Ethyl ether was allowed to diffuse into a filtered solution of 10 mg (0.018 mmol) of **4** and 4.07 mg (0.018 mmol) of AgOTf in 2 mL of acetone, giving

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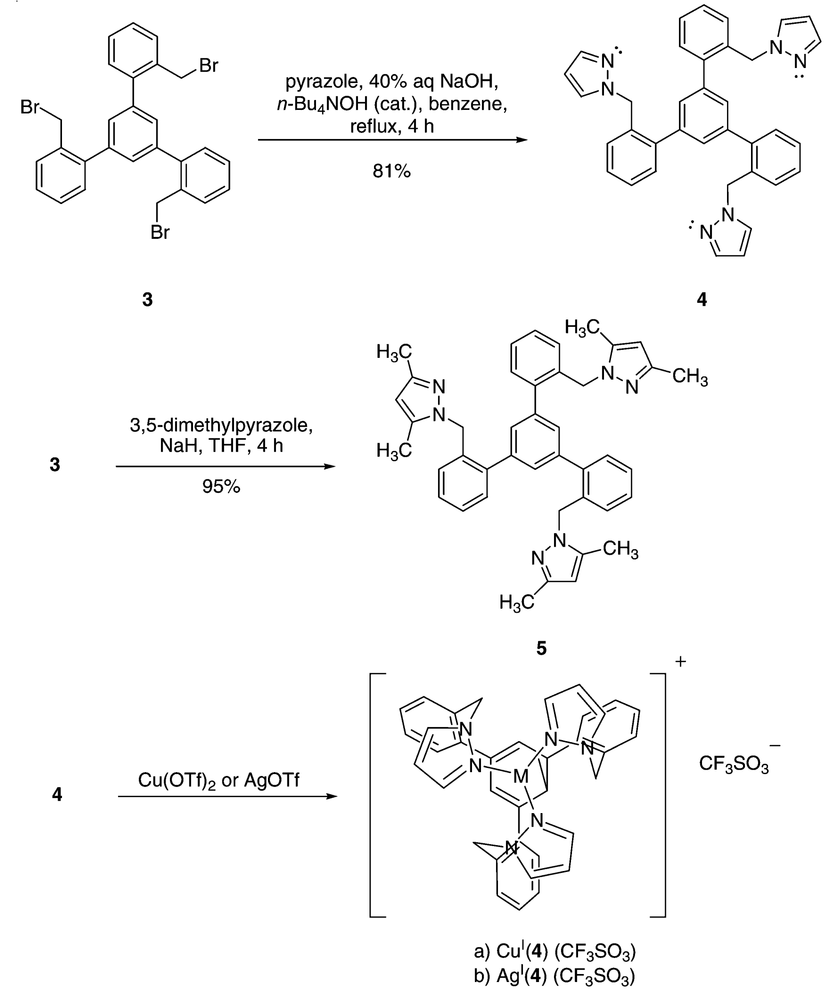
Scheme 1. Preparation of Ligands **4** and **5** and of Complexes of **4** with Cu(I) and Ag(I)



colorless crystals of Ag^I(**4**) CF_3SO_3·0.5 acetone·0.5 diethyl ether. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.59 (s, 3 H), 7.42 (m, 15 H), 6.83 (s, 3 H), 6.28 (s, 3 H), 5.44 (s, 6 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 141.7, 141.1, 140.3, 132.2, 131.7, 130.6, 130.0, 129.3, 129.0, 128.7, 107.0, 54.5.

3. Electrochemical Studies. All electrochemical measurements were carried out with a conventional three-electrode system. A glassy carbon disk of approximately 0.28 cm^2 surface area served as the working electrode. The reference electrode was a commercial saturated-calomel electrode (SCE), and a platinum wire was used as the counter electrode. Cyclic voltammetry was performed by using a BAS 100B electrochemical analyzer interfaced to a personal computer (PC). All measurements were performed on solutions kept under a nitrogen atmosphere. Cyclic voltammetry measurements were made at scan rates of 40−200 mV/s. Calibration was checked against the ferrocene/ferrocenium couple, for which the redox potential was +0.11 V vs SCE. Solutions were made from HPLC-grade dichloromethane that was distilled from CaH_2. A stock dichloromethane solution that was 0.05 M in (n-Bu_4N)(BF_4) was prepared. Solutions of the complexes were prepared at concentrations of 1×10^{-4} to 2×10^{-4} M.

4. Crystal Growth and Structure Determination. Diffraction quality crystals of the ligands and of their complexes with silver and copper ions proved difficult to obtain by using evaporation or vapor diffusion crystallization techniques, despite numerous attempts in a variety of solvents and solvent mixtures. In our hands, it was not possible to obtain crystals of **4** suitable for X-ray diffraction studies. Ligand **5**, however, afforded the unsolvated rhombohedral form reported here (Table 1, Figure 1), as well as two different triclinic forms in the space group $P\bar{1}$, each of which contained disordered solvate molecules.

Three crystalline samples containing Ag^I(**4**) (CF_3SO_3) were obtained in space group $R\bar{3}$, each of which contained severely disordered solvent molecules in spaces between the anions and cations centered about the 3-fold axes in space group $R\bar{3}$. Attempts to prepare crystals of Ag^I(**4**) with perchlorate counterions yielded no useful crystalline material. A similar situation occurred for mixtures containing Cu(I) and ligand **4**: the only crystals obtained that were suitable for diffraction were those containing severely disordered solvent molecules.

Diffraction measurements were made with a Bruker SMART charge-coupled device (CCD) area detector system using ϕ and ω scans. In all cases, a hemisphere of data was collected. Cell parameters were determined by using SMART software.[15a] The SAINT package[15a] was used for integration of data, for Lorentz,

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Table 1. Crystallographic Data for the Several Species Studied

	5, $C_{42}H_{42}N_6$	Cu^I(**4**) CF_3SO_3·solvate[a]	Ag^I(**4**) CF_3SO_3·solvate[a]
fw	630.82	759.28[d]	803.60[d]
a, Å	24.6155(15)	12.7358(4)	13.1505(4)
b, Å	24.6155(15)	12.7358(4)	13.1505(4)
c, Å	10.1554(8)	44.271(3)	44.152(3)
α, deg	90.	90.	90.
β, deg	90.	90.	90.
γ, deg	120.	120.	120.
V, Å^3	5329.0(6)	6218.8(5)	6612.5(6)
space group	$R\bar{3}$	$R\bar{3}$	$R\bar{3}$
crystal system	rhombohedral	rhombohedral	rhombohedral
Z	6	6	6
P_{calcd}, g/cm^3	1.179	1.216[d]	1.211[d]
μ, mm^{-1}	0.071	0.630	0.554
trans factor	0.80−1.00	0.93−0.95	1.00
T, K	273(2)	100(2)	223(2)
data/parameters/restraints	1256/147/0	2358/194/0	2476/154/0
largest diff peak and hole, e/Å^3	0.14, −0.14	0.30, −0.25	1.29, −1.36
R_F[b], R_{wF^2}[c]	0.050, 0.107	0.040, 0.087	0.056, 0.163

[a] Solvate species are identified in the Experimental Section. [b] $R_F = \sum||F_o| - |F_c||/\sum|F_o|$; selection criterion $I > 2\sigma(I)$. [c] $R_{wF^2} = \{[\sum[w(F_o^2 - F_c^2)^2/\sum[w(F_o^2)^2]\}^{1/2}$; selection criterion all F_o^2. [d] This value does not include the mass of the disordered solvent molecules.

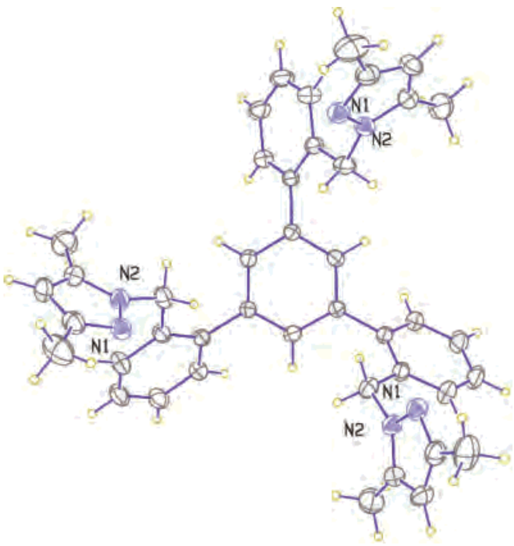

Figure 1. View of **5**.

polarization, and decay corrections, and for merging data. Absorption corrections were applied by using SADABS.[15b]

Structures were solved and refined on F^2 by using the SHELX system and all data.[15c,d] Partial structures were obtained by direct methods; the remaining non-hydrogen atoms in each structure were located by using difference Fourier techniques. H atoms were located on difference Fourier maps or placed at calculated positions. For H atoms whose thermal parameters were not refined, isotropic temperature factors were set equal to 1.2−1.5U_N, where N is the atom bonded to H. Because the solvent disorder is severe in crystals containing either Ag^I(**4**) or Cu^I(**4**), the solvent regions could not be modeled effectively. Consequently, data sets in which the electron density in the regions corresponding to the solvent molecules was removed from the structure factors were generated by using the SQUEEZE algorithm,[16] and the remainder of the structures, consisting of the cations and anions, were refined smoothly to convergence. When removed from the structure as described above, the solvent species left voids of 269 and 323 Å^3 for the solvates of Cu^I(**4**) CF_3SO_3 and Ag^I(**4**) CF_3SO_3, respectively. Views of the structures were prepared by using ORTEP32 for Windows.[15e,f] Additional details of the data collection and refinement for the crystals studied are given in Table 1 and in the Supporting Information.[17]

Although solvated crystalline triflate salts of Cu^I(**4**) were prepared directly from their component parts, all attempts to prepare a corresponding Cu(II) complex of **4** proved fruitless. Solutions containing **4** and Cu(II) triflate in polar organic solvents such as acetone, methylene chloride, or acetonitrile turned blue immediately, suggesting the formation of Cu(II)−ligand bonds. These solutions remained stable over periods of time as long as 3 weeks; however, attempts to obtain crystals, either by evaporation or by solvent diffusion, resulted only in the isolation of species containing Cu(I), suggesting that, as the solutions approached saturation, Cu(II) oxidizes ligand **4**, a supposition that is supported by the electrochemical results presented below. In this sense, ligand **4** selects Cu(I) over Cu(II) for complexation.

Results and Discussion

Description of the Structures. Cu(I) and Ag(I) Complexes of 4. Solvated crystals of Cu^I(**4**) CF_3SO_3 and Ag^I(**4**) CF_3SO_3 are nearly isostructural. Each contains M^I(**4**) cations (M^I = Cu^I, Ag^I), nonligating triflate counterions, and disordered solvate molecules. Both the cations and anions exhibit crystallographically imposed 3-fold symmetry (site 6c in $R\bar{3}$), with the 3-fold axis passing through the metal ion, the center of the central benzene ring of the cations (Figures 2 and 3), and the C and S atoms of the $CF_3SO_3^-$ anions. Apart from any metal ion coordination to the central arene rings, the metal ions are ligated by three pyrazole (pz) nitrogen atoms to afford pyramidal coordination geometries with the Cu(I) and Ag(I) metal ions removed 0.232(2) and 0.254(2) Å, respectively (Table 2, Figure 4), from the planes of the three pz nitrogen atoms in the direction of the central arene rings (metal-endo conformation). Our examination of molecular models suggests that strain-free endo, exo, or trigonal-planar conformations are possible, but only the metal-endo conformation is observed. An endo−exo "mo-

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(17) Crystallographic details for the three structures reported, tabulated electrochemical data, and NMR data for Ag^I(**4**) CF_3SO_3 are given as Supporting Information.

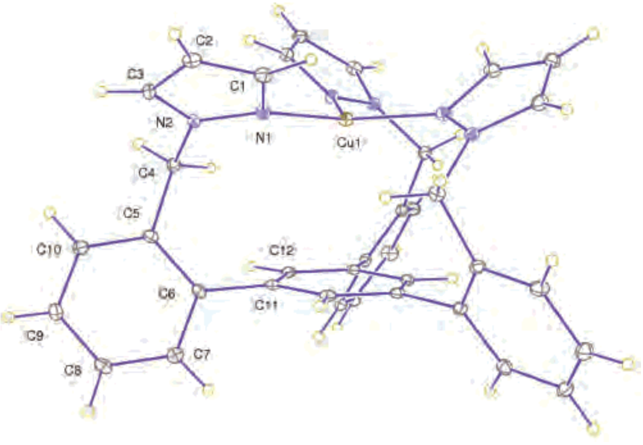


Figure 2. View of Cu^I(**4**).

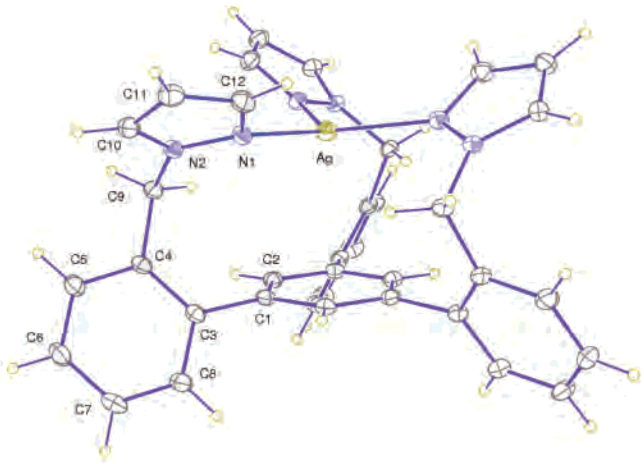


Figure 3. View of Ag^I(**4**).

Table 2. Selected Metric Parameters for the Species Studied (Å, deg)

	Cu^I(**4**)$^+$	Ag^I(**4**)$^+$	**5**
M−N1	1.987(2)	2.235(6)	
M···Cg^a	3.195(2)	3.165(2)	
N1−M−N1′	118.66(2)	118.72(2)	
N1···N1′	3.418(3)	3.846(3)	7.862(4)
M···C11	3.488(2)	3.459(3)	
M···C12	3.482(3)	3.459(3)	
Ar/Ar^b	59.85(6)	62.14(8)	54.31(7)
N_3 plane···M	0.232(2)	0.254(2)	

^{a} Cg corresponds to the center of gravity of the central arene ring. ^{b} The dihedral angle between the planes of the central arene ring and the arene ring bonded to it.

lecular switch” transition has been reported for the endocyclic Cu^I(**7**) monocation, which reacts with phosphines to form the corresponding exocyclic complexes.[18]

For a given metal, the M−N(pz) distances are crystallographically required to be equal, as are the N(pz)−Cu−N(pz) angles. Although the N(pz)−M−N(pz) angles are equal for the copper and silver cations, the Ag−N(pz) distance [2.235(6) Å] is approximately 0.25 Å longer than the corresponding Cu−N(pz) distance [1.987(2) Å)], consistent with the larger size of the Ag(I) ion. In both the Cu(I) and Ag(I) cations, the pz rings and the noncentral arene rings are each canted in the same direction with respect to the central arene ring, giving the cations a propeller shape and conferring chirality to them in the solid state. Because the space group $R\bar{3}$ is centrosymmetric, half of the cations have *P*,*P*,*P* stereochemistry and half have *M*,*M*,*M* stereochemistry; consequently, crystals of Cu^I(**4**)$^-$ and Ag^I(**4**) CF_3SO_3·solvate are racemic.

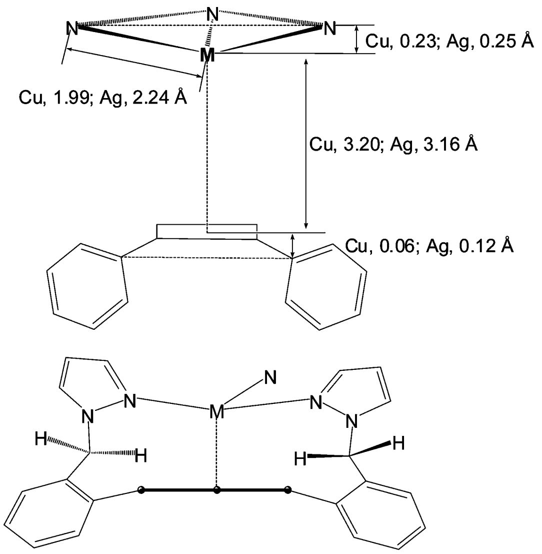
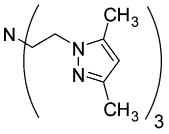


Figure 4. Key structural parameters for Cu^I(**4**) and Ag^I(**4**).

Metric parameters for the $CuN(pz)_3$ substructure in Cu^I-(**4**) lie within the ranges reported for the trigonal-pyramidal complex Cu^I(**6**): Cu−N, 1.976(4)−2.038(4) Å; N−Cu−N′, 115.63(18)−119.21(17)°.[19] The Ag−N(pz) distance is also typical for its type and is very nearly equal to the shortest of those reported[20] (2.243−2.299 Å) for three, three-coordinate silver(I) complexes containing substituted pyrazole ligands.



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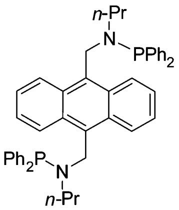

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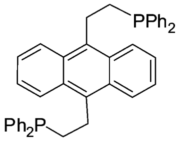

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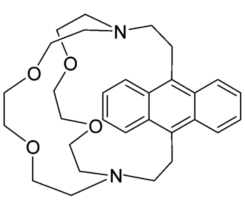

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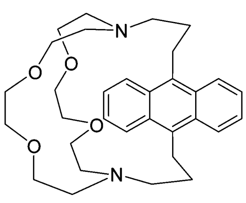

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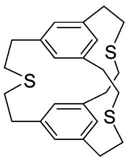

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In Cu^I(**4**), the distance between the copper ion and the centroid of the central arene ring is 3.195(2) Å, a value very nearly equal to the corresponding distance of 3.165(2) Å in Ag^I(**4**). To what extent do these distances imply η^6 bonding

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Table 3. M⋯Cg(arene) η^6 Geometries [M = Ag(I), Cu(I)][a]

	Ag(I)⋯Cg(arene), Å	arene	conformation	coord no.[b]	ref
Ag$^{\mathrm{I}}$(**7**)	2.79	anthracene	endo	2, tweezers	18, 22
Ag$^{\mathrm{I}}$(**8**)	3.148	anthracene	endo	2, tweezers	18
Ag$^{\mathrm{I}}$(**4**)	3.165(2)	benzene	endo	3, 3-prong tweezers	this work
Ag$^{\mathrm{I}}$(**9**)	3.01	anthracene	endo	4, encapsulated	24
Ag$^{\mathrm{I}}$(**10**)[c]	4.46	anthracene	endo	6, encapsulated	24
Ag$^{\mathrm{I}}$(**10**)[c]	5.14	anthracene	endo	6, encapsulated	24

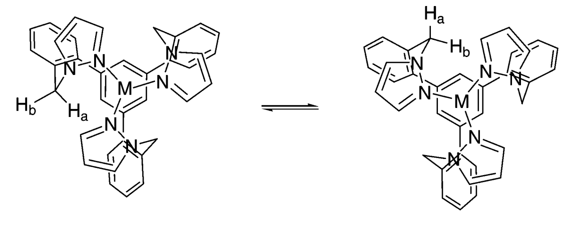
	Cu(I)⋯Cg(arene)	arene	conformation	coord no.[b]	ref
Cu$^{\mathrm{I}}$(**7**)	2.498	anthracene	endo	2, tweezers	18
Cu$^{\mathrm{I}}$(**11**)	2.97	bis(benzene)	planar	3, encapsulated	21
Cu$^{\mathrm{I}}$(**4**)	3.195(2)	benzene	endo	3, 3-prong tweezers	this work

[a] Cg corresponds to the center of gravity of the arene ring of interest. [b] This number excludes coordination to the arene. [c] Two forms of this cation were reported.

interactions? Such interactions are rare, particularly for Cu(I), although several have been reported for both ions in the past few years (Table 3). For Ag(I) systems, a hapticity of six has been observed in several systems involving the central ring of anthracene, and possibly in the present instance, involving the central arene ring. Mascal et al.[21] concluded, on the basis of NMR data and an analysis of arene centroid-to-metal distances derived from the Cambridge Structural Database,[23] that Ag(I)⋯arene centroid distances in the range 2.89−3.37 Å for η^6 arenes constitute weak bonding interactions in which the arenes coordinate the silver ions. Fluorescence emission spectroscopic evidence is consistent with a bonding interaction in Ag$^{\mathrm{I}}$(**9**), which has an Ag⋯centroid distance of 3.01 Å, but not in either conformer of Ag$^{\mathrm{I}}$(**10**), both of which exhibit much longer Ag(I)⋯arene centroid distances.[24] On the basis of these data, the Ag(I)⋯arene interaction in Ag$^{\mathrm{I}}$(**4**) in the solid state may be described as a weak η^6 bonding interaction, a conclusion consistent with the metal-endo conformation of the cation.

The situation with Cu$^{\mathrm{I}}$(**4**), which exhibits the longest Cu(I)⋯Cg distance in Table 3, is less clear. For the Cu$^{\mathrm{I}}$(**7**) cation, the short Cu(I)⋯Cg distance compared with that in Ag$^{\mathrm{I}}$(**7**), and the results of theoretical studies, which indicate greater electron density between Cu⋯C atoms compared with the Ag⋯C atoms, were taken reasonably to indicate Cu(I)⋯C bonds stronger than those in the silver analogue.[18] Indeed, the Cu(I)⋯Cg distance in Cu$^{\mathrm{I}}$(**7**) is shorter than a Cu(I)⋯Cg distance of 2.528 Å attributed to η^2-phenyl ligation,[25] implying reasonably strong coordination in Cu$^{\mathrm{I}}$(**7**). In Cu$^{\mathrm{I}}$(**11**), the copper cation is encapsulated in the S-cylindrophane with a trigonal CuS(thioether)$_3$ unit capped on the top and bottom by arene rings. NMR data[21] imply a bonding interaction between the metal and the arene rings, and the geometry is consistent with a hapticity of 6. On the basis of the above analysis, the Cu$^{\mathrm{I}}$(**4**) cation, with its endo conformation and nearly perfect geometry for η^6 bonding, but with a Cu(I)⋯Cg distance approximately 0.2 Å longer than that in Cu$^{\mathrm{I}}$(**11**), most likely contains a weakly coordinating η^6 bonding interaction.

Scheme 2



M(**4**): (*P*, *P*, *P*) M(**4**): (*M*, *M*, *M*)

Solution Behavior of Ag $^{\mathrm{I}}$(4). Although the structures of the Ag(I) and Cu(I) complexes of **4** in solution are unproven, several observations are worthy of comment. The Ag(I) complex [from crystals of Ag$^{\mathrm{I}}$(**4**) CF$_3$SO$_3$] is soluble in, and recoverable from, chloroform, dichloromethane, acetone, acetonitrile, and ethyl acetate. The ^{1}H NMR spectrum of the complex in deuteriochloroform solution reveals a symmetric structure in which signals assignable to protons of the three pyrazoles and the three methylenes are apparently respectively equivalent and are qualitatively similar to the corresponding signals in the spectrum of ligand **4**. The three equivalent protons of the central aryl ring in the Ag(I) complex move 0.4 ppm upfield from their position in the spectrum of ligand **4**, suggesting that coordination to Ag(I) is occurring, and that the central ring is affected upon complexation, possibly by its proximity to the metal cation.[17]

The six methylene protons of the Ag(I) complex appear as a singlet in deuteriochloroform solution, and when examined in CD$_2$Cl$_2$ solution, the singlet only broadens slightly upon cooling to − 46 °C. Thus, an equilibration process, such as M(**4**) (*P*,*P*,*P*) ⇆ M(**4**) (*M*,*M*,*M*) (Scheme 2), might be interconverting H$_a$ and H$_b$ of the methylenes. Examination of Dreiding molecular models of a triply pyrazole-coordinating Ag(I) complex of **4** does not indicate a clear steric preference for positioning the metal cation endo (close to the central aryl ring), exo (away from the central aryl ring), or trigonal planar (with the metal cation and three coordinating pyrazole N's coplanar). Although the position of the metal in the crystalline state is clearly endo, a situation that may reflect the stability gained by coordination of the central aryl ring as a fourth ligand, the configuration in solution might be different. In particular, a global equilibra-

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tion process such as M(**4**) (*P*,*P*,*P*) $\leftrightarrows$ M(**4**) (*M*,*M*,*M*) does not appear to be possible with the complex rigidly held in either the endo or exo configuration unless a Ag(I)−N bond is temporarily broken, or unless all three Ag(I)−N bonds are stretched, perhaps into a trigonal-planar coordination geometry. It is noteworthy in this regard that attempts to introduce an additional ligand, such as acetonitrile, iodide, thiocyanate, or benzyl mercaptide, into solutions of complexes Ag^I(**4**) or Cu^I(**4**), did not lead to characterizable crystalline complexes.

Structure of 5. Molecule **5** (Figure 1) crystallizes in space group $R\bar{3}$ without solvate species. As with the metal-containing complexes described above, **5** adopts a conformation with a 3-fold axis perpendicular to the plane of the central arene ring and passing through its center of mass. Compared with the cations above, **5** exhibits a more open conformation as measured, for example, by the distances between the potentially ligating N(pz) atoms N22 in **5** [7.862(4) Å] and the ligating N(pz) atoms in both Cu^I(4) [3.418(3) Å] and Ag^I(4) [3.846(3] Å). In **5**, as in the metal complexes, the aryl substituents on the central arene ring are canted in the same helical sense, conveying chirality on individual cations, and the centers of symmetry in the space group ensure that the crystals are racemic. Despite the gross similarities between **4** and **5**, we have thus far been unable to prepare metal complexes of **5**, possibly owing to steric hindrance among its methyl groups, which are located adjacent to the potentially ligating nitrogen atoms. In Cu^I(**4**), for example, the nonbonding H(C1)···H′(C1) distance of 4.72 Å would be expected to be shortened considerably by replacing H with CH_3, possibly reducing H···H′ distances to values well below the nominal van der Waals radius of the methyl group (ca. 4 Å). In this context, complexation of **5** with larger metals might be considered possible.

Observations and Comparisons. When equimolar amounts of Cu(II) triflate and **4** were mixed in acetone, blue solutions resulted, suggesting the possibility of a bonding interaction between the Cu(II) ions and the *tris*-pyrazolyl ligand **4**. However, during a period of several days at room temperature, the color slowly faded, and colorless crystals of the Cu(I) product, Cu^I(**4**) CF_3SO_3·solvate, were obtained. Apparently, slow reduction of Cu(II) had occurred. Solvated Cu^I(**4**) CF_3SO_3 crystals were also obtained directly from Cu(I) triflate and **4**. A similar autoreduction was observed previously with the ligand trpyn(*n*-Bu)$_6$.[19] Attempts to prepare a Cu(II) complex of trpyn(*n*-Bu)$_6$, which contains bulky *n*-butyl groups, afforded only colorless Cu(I) derivatives. In contrast, Cu(II) complexes were readily obtained by using less-hindered, unsubstituted, or methyl-substituted analogues.[19] Redox instability has also been observed for a modified yeast Cu(II) superoxide dismutase whose Cu(II)−imidazolate bridge is broken, resulting in the formation of a reduced, approximately trigonal Cu(I)(N(imidazole)$_3$ unit, which was characterized crystallographically and spectroscopically.[26]

Ligand **5** differs from *tris*-pyrazolylborate, whose 3,5-ring disubstitution increases the oxidative stability of its metal complexes and allows pseudotetrahedral coordination to be achieved by additional metal ion ligation to thiolate or peroxide.[8a,b] As noted above, **4** should permit apical coordination to a trigonal CuN_3 unit more easily than **5** because ligand **4** is less hindered sterically than ligand **5**.

In general, pyrazoles and imidazoles are good ligands for both Cu(II) and Cu(I) and normally do not promote the autoreduction of Cu(II). The unexpected autoreduction of Cu(II) in solutions containing ligand **4** may be related to the instability of trigonally coordinated Cu(II) lacking a thiolate or selenolate ligand. Such ligands form highly covalent bonds that appear to allow Cu(I) or Cu(II) to share structurally similar, trigonal-based coordination geometries related to those observed for type 1 Cu(I)/Cu(II) protein sites.[27,28]

The strong S(thiolate)−Cu(II) π-bonding present in blue copper active sites and in model complexes has been characterized by comprehensive structural, spectroscopic, and calculational studies.[28] One important consequence of this large covalency is that the Cu(II) ion acquires substantial Cu(I) character, allowing otherwise unfavorable trigonal-based coordination. In contrast, trigonal three-coordination is an easily accessible geometry for Cu(I) and Ag(I). Cu(I) shows linear, trigonal, and tetrahedral coordination with pyrazole N-donors[29] and may easily "hop" between such coordination sites in inorganic lattices such as $CuVP_2S_6$.[30]

Electrochemical Studies. A cyclic voltammogram of ligand **4** (scan rate, 50 mV/s) exhibited irreversible oxidations at 464 mV and 664 mV, with no corresponding reduction peaks. For Cu^I(**4**) CF_3SO_3, at scan rates of 50 and 500 mV/s, a single quasi-reversible redox couple, likely corresponding to the Cu(I)/Cu(II) couple, was observed at 750 mV, along with several irreversible oxidations. These results suggest that ligand **4** is oxidized at a potential below that required to oxidize Cu(I) to Cu(II) in Cu^I(**4**), consistent with our inability to isolate a stable, pyramidal Cu^{II}(**4**) species. In a different experiment, we were unable to isolate a Cu(I) complex with *N*-benzylpyrazole, obtaining instead, by the redox fixation of CO_2, a stable Cu(II) oxalate complex containing coordinated *N*-benzylpyrazole.[31] We are unaware of any stable three-coordinate Cu(II) complexes with neutral ligands; one such complex with an anionic ligand has been isolated.[3b]

Conclusions. With Cu(I) and Ag(I), ligand **4** acts as tridentate three-pronged tweezers to form chiral, propeller-like cations that exhibit N(pyrazole)$_3$ coordination, and whose triflates crystallize as racemates. Interaction of the metal atoms with the central arene ring is likely. In the solid state, the Cu^I(**4**) and the Ag^I(**4**) cations exhibit crystallographically

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imposed C_3 symmetry with the metal ions positioned on the 3-fold axes in the rhombohedral space group $R\bar{3}$. The coordination geometries of the metal ions are exclusively endo, with the metal ions directed inward toward and situated over the center of mass of the central arene fragment of the tridentate ligand. Crystallographic and NMR data support the existence of an η^6 bonding interaction with Ag(I) and, to a lesser extent, with Cu(I). Our inability to prepare any Cu(II) complexes with **4** is consistent with cyclovoltammetric results, which suggest that the ligand is more easily oxidized than Cu(I).

Supporting Information Available: Crystallographic details in CIF format for the three structures described in the manuscript; HETCOR NMR data and assignments for Ag^I(**4**) triflate; and tabulated electrochemical data are available free of charge via the Internet at http://pubs.acs.org.

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