Syntheses and Structural Characterization of Ferrocene-Containing Double-Helicate and Mononuclear Copper(II) and Silver(I) Complexes

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The self-assembly and structural characterization of the new ferrocene-containing dicopper-(II) double helicate $[Cu_2L^1_2]$ (**1**) and related copper(II) complex $[CuL^2(CH_3CN)][ClO_4]_2$ (**2**) and silver(I) complexes $[AgL^2(CH_3CN)][BF_4]$ (**3**) and $[AgL^2][BF_4]$ (**4**) have been achieved. These complexes are derived from inexpensive and easy-to-prepare ferrocene-containing bisbidentate Schiff-base ligands H_2L^1, $[(C_6H_4)(OH)CHNNC(CH_3)(C_5H_4)]_2Fe$, and L^2, $[(C_5H_4N)-CHNNC(CH_3)(C_5H_4)]_2Fe$. The neutral double-helical dicopper(II) complex **1** crystallizes in a polar space group. The two ferrocene-containing ligands strand interwined about each other and around the two tetrahedral copper ions in a double-helical fashion, with the Cu···Cu separation being 9.45 Å. The four metal centers are coplanar and form a slightly distorted rhombus with sides of ca. 5.8 Å. Reaction of the ligand L^2 and copper(II) constructed a mononuclear copper complex, **2**. X-ray structural analysis reveals that the copper(II) atom is coordinated in a distorted square pyramidal geometry, with four nitrogen atoms from the two bidentate bind sites forming the basal plane; the acetonitrile nitrogen atom occupies the apical position. The molecular structure of the silver(I) complex **3** is quite similar to that of copper complex **2**, with the silver(I) surprisingly coordinated in a square pyramidal geometry. The silver(I) atom in mononuclear silver complex **4** is coordinated in a new square planar fashion. The result presented here shows that while the ligand $(L^1)^{2-}$ can bridge two metal ions to give a double helicate with Cu(II), the ligand L^2 acts as a tetradentate ligand chelate to a single metal center in its structurally characterized complexes with Cu(II) and Ag(I). Crystal structures of the free ligand H_2L^1 and L^2 are also reported for comparison.

1. Introduction

Within the field of supramolecular inorganic chemistry, self-assembly provides direct access to complex architectures comprising spatially and geometrically well-defined arrays of metal ions.[1−5] The double-helical structures generated by the complexation of two ligands around metal ions lying on the helical axis retain a unique fascination since life itself is encoded within double-helical architecture. While the basic features of the design necessary to assemble a double helix are now fairly well established,[6−8] challenges in defining the precise topography or conformation of the helical superstructure remain. To design species presenting helicates with specific functional features, it is of great importance to establish the rules by which control of the self-assembly process can be achieved through chemical programming by means of suitable components and assembling algorithms.[9]

As part of our studies of metal helicates and boxes derived from Schiff-base multidentate ligands via self-assembly,[10] we became interested in designing new inexpensive and easy-to-prepare ferrocenyl-containing bisbidentate Schiff-base ligands. In our previous work,[11]

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Chart 1

L   **L¹**   **L²**
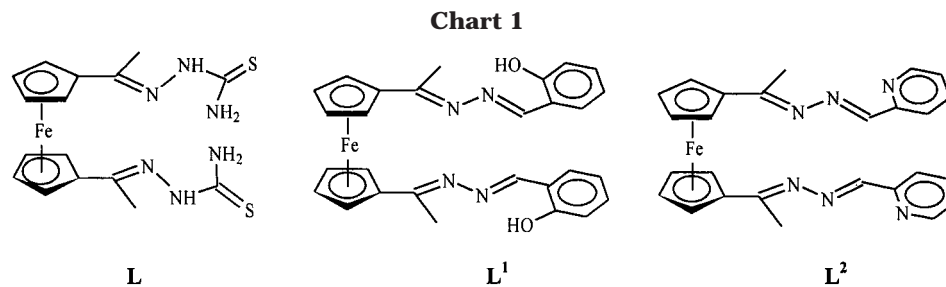
a double-helical architecture generated from easy-to-prepare ferrocene-containing bisthiosemicarbazone ligand (**L**; Chart 1) was constructed via self-assembly. It is postulated that the ferrocene group was chosen as a spacer to separate the two metal binding sites, not only because such a spacer is suitable to assemble a double helix,[8] but also because the molecules containing metallocene units could accommodate a particular metal ion at its coordination site and undergo a concurrent redox change.[12] In addition, the use of organometallic molecules in the construction of crystals with predefined architectures is a means to introduce into the crystals the spin states of metal atoms as well as the specific topological requirements of coordination bonds.[13] In this paper, we design two new bisbidentate Schiff-base ligands, H_2L^1 and L^2. It is suggested[14] that the flexible ligands either can coordinate to a single metal ion as a tetradentate chelate or can coordinate each bidentate arm to a separate metal center to give bridged polynuclear species such as double helicates. To test this approach, dinuclear double-helical copper(II) complex **1**, mononuclear copper(II) complex **2**, and silver(I) complexes **3** and **4** were synthesized and structurally characterized.

2. Results and Discussion

2.1. Synthesis and Structure of Free Ligand H_2L^1. The new Schiff-base ligand H_2L^1 was readily prepared by the reaction of 1,1′-diacetylferrocene dihydrazone with salicylaldehyde in a 1:2 ratio. Elemental analysis and spectroscopic characterization support the formation of a bisbidentate Schiff-base ligand of the expected formula. X-ray-quality crystals of the free ligand were obtained by slowly evaporating a chloroform–diethyl ether solution of H_2L^1. Crystallographic data are presented in Table 1, important bond lengths and angles are depicted in Table 2, and an ORTEP[15] diagram of the ligand is shown in Figure 1.

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Table 1. Crystallographic Data of H_2L^1 and 1

	H_2L^1	1
empirical formula	$C_{28}H_{26}N_4O_2Fe$	$C_{61}H_{59}Cl_3Cu_2Fe_2N_8O_5$
fw	506.38	1329.30
cryst syst	tetragonal	orthorhombic
space group	$I4_1/a$	$P2_12_12_1$
a/Å	9.4702(13)	14.286(2)
b/Å	9.4702(13)	15.364(5)
c/Å	54.108(11)	27.226(3)
V/Å³	4852.6(14)	5976.0(2)
Z	8	4
T/K	293(2)	293(2)
μ/mm⁻¹	0.655	1.368
no. of unique reflns	2134 [R(int) = 0.164]	6773 [R(int) = 0.091]
R1	0.0657	0.0711
wR2 [$I > \sigma 2(I)$]	0.1110	0.0982
goodness of fit	1.055	0.956

Table 2. Selected Bond Lengths (Å) and Angles (deg) of Compounds H_2L^1 and 1

H_2L^1			
C(8)−N(2)	1.282(4)	N(1)−C(7)	1.278(4)
N(2)−N(1)	1.398(4)	C(1)−O(1)	1.352(4)

| 1			
Cu(1)−O(1)	1.880(7)	Cu(2)−O(2)	1.866(8)
Cu(1)−O(3)	1.884(7)	Cu(2)−O(4)	1.906(7)
Cu(1)−N(5)	1.958(8)	Cu(2)−N(8)	1.933(9)
Cu(1)−N(1)	1.967(8)	Cu(2)−N(4)	1.988(9)
C(7)−N(1)	1.338(13)	C(35)−N(5)	1.313(13)
C(1)−O(1)	1.296(13)	C(29)−O(3)	1.334(13)
N(4)−C(22)	1.255(14)	N(8)−C(50)	1.312(14)
C(24)−O(2)	1.268(13)	C(52)−O(4)	1.266(13)
N(1)−Cu(1)−O(1)	93.2(3)	N(4)−Cu(2)−O(2)	92.1(4)
N(1)−Cu(1)−O(3)	146.0(3)	N(4)−Cu(2)−O(4)	149.6(4)
N(1)−Cu(1)−N(5)	99.6(3)	N(8)−Cu(2)−N(4)	100.1(3)
O(1)−Cu(1)−O(3)	91.4(3)	O(2)−Cu(2)−O(4)	88.8(3)
O(1)−Cu(1)−N(5)	149.9(4)	O(2)−Cu(2)−N(8)	151.7(4)
O(3)−Cu(1)−N(5)	93.0(3)	O(4)−Cu(2)−N(8)	93.1(3)
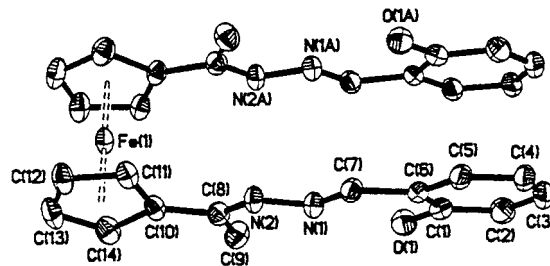
Figure 1. ORTEP plot of the ligand H_2L^1, showing the non-hydrogen atoms as 50% probability thermal ellipsoids. Symmetry code A: $-x$, $3/2 - y$, z.

Since the iron(II) atom is localized in the C_2 axis, half of the molecule is found in an unsymmetric unit. The two equivalent moieties associated with salicylaldene adopt a *cis*-conformation about ferrocene, in which the imine nitrogen atom N(1) acts as an acceptor and the hydroxyl group acts as a donor forming a H bond with
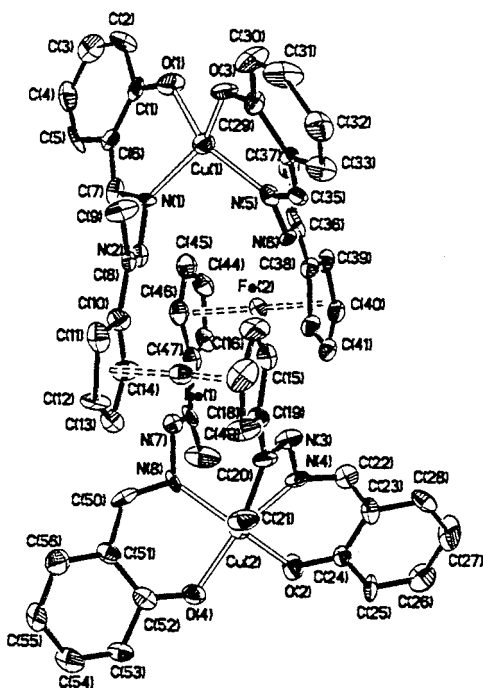
Figure 2. ORTEP plot of the coordinated copper(II) complex **1**, showing the non-hydrogen atoms as 50% probability thermal ellipsoids. The solvent molecules and hydrogen atoms are omitted for clarity.

a N−O distance of 2.87 Å. All the bond distances in the two arms are intermediate between the corresponding single bond and double bond, indicating extensive delocalization over the entire molecular skeleton. The two arms are almost parallel with each other (dihedral angle ca. 0.2°) with the interplanar separation ca. 3.4 Å, indicative of strong intramolecular face-to-face $\pi-\pi$ stacking interactions between them.[16] There are also extensive edge-to-face interactions between the cyclopentadienyl ring and the benzene ring of the adjacent molecule. The dihedral angle between the interacting pair is 73.4°. The shortest interacting atom···atom separation of C(11)···C(5B) (symmetric code B: −1.25 + y, 0.25 − x, 0.25 − z) is 3.57 Å. These edge-to-face interactions might not rank very high on the basis of specific interaction strengths; however, it is known that they play an important role in determining stable crystal packing arrangements.[17]

2.2. Structural Characterization of the Double Helicate 1. Interaction of the $Cu(Ac)_2 \cdot 2H_2O$ with H_2L^1 in boiling methanol gave a dark-brown compound whose elemental analysis indicates the stoichiometry [CuL^1], i.e., a 1:1 metal:ligand ratio as would be expected for a complex between a ligand with four donor atoms and a metal ion with a preference for four-coordination.

The crystal structure of the complex reveals (Figure 2) that it indeed forms a 2:2 (ligand:metal) coordination stoichiometry. The solid state is best described as a double-stranded helix with two copper(II) cations lying

at a center-to-center separation of 9.45 Å and two iron centers separated by a distance of 6.75 Å. The four metal centers are coplanar and form a slightly distorted rhombus with sides of 5.71−5.92 Å, two acute interior angles of 71° and 72°, and two interior angles of 107° and 111°. Each ligand wraps around the two copper(II) cations, two salicylaldene rings belonging to the same metallosynthon being twisted by ca. 74°. Each copper center occupies a four-coordinated distorted tetrahedral environment bound to O and N atoms, with each ligand anion (L^1)$^{2-}$ providing a pair of O and N atoms. Angles O−Cu(1)−O, N−Cu(1)−N, and N−Cu(1)−O [O−Cu(2)−O, N−Cu(2)−N, and N−Cu(2)−O] are in the range of 91.4(3)°, 99.6(3)°, and 146.0(3)−149.9(4)° [88.8(3)°, 100.1-(3)°, and 149.6(4)−151.7(4)°], respectively, which show a distorted tetrahedral geometry around Cu(1) and Cu-(2). The Cu−O distances of 1.866(8)−1.906(7) Å and Cu−N lengths of 1.933(9)−1.988(9) Å agree well with those of the related compounds.[18] Coordination to the metal center also forces the twisting within each ligand. The torsion angles C(36)−C(38)···(47)−C(48) and C(8)−C(10)···C(19)−C(20) are −110.2° and −102.1°, respectively.

In contrast to the 1,1′-conformation of the cyclopentadienyl rings of the ligand H_2L^1 in which the substitutes are eclipsed, the conformation of the cyclopentadienyl rings in the coordinated complex **1** is 1,3′-disubstituted, which is favored for most ferrocene derivatives in the crystal structure.[19] No significant deformation of the almost parallel cyclopentadienyl ring is observed. The skeletal ferrocenes are found to have ordinary Fe−C bond distances. Both the chloroform and ether molecule lie outside the cavity. Since the compound crystallizes in a polar space group, $P2_12_12_1$, only one enantiomer was found in the structure.

A comparison of this structure to the crystal structure of the zinc(II) complex of diacetylferrocenyl bisthiosemicarbazone, Zn_2L_2,[11] indicates that the linkage methods of ferrocene in the molecules are different. In Zn_2L_2, ferrocene acts as a bridge group linking two salicylaldenes, while it acts as a hinge in $Cu_2L^1_2$. The axis through the centers of two cyclopentadienyl rings of the same ferrocene molecule is almost perpendicular to that of Cu(1)···Cu(2) in $Cu_2L^1_2$, but parallel to that of Zn-(1)···Zn(2) in Zn_2L_2. It is attributed to the length of the chain between two coordinating sites in a strand to satisfy the formation of helical architecture. From the structures of the free ligand H_2L^1 and $Cu_2L^1_2$, it is clearly not possible for two bidentate sites of one ligand to coordinate to a single metal ion in such a way that the two Cu(NO) planes are mutually perpendicular, which would confer the required pseudotetrahedral geometry on the metal in a mononuclear complex.

2.3. Synthesis and Characterization of Ligand L^2. To explore further the conformational preferences of the ferrocenyl group, which may serve as a bridge, and to generate a well-defined cavity for possible host−guest investigation, the new ligand L^2 was designed and investigated. The new Schiff-base ligand L^2 was readily prepared by the reaction of 1,1′-diacetylferrocene dihy-

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Table 3. Crystallographic Data of L² and 2−4

	L²	2	3	4
empirical formula	$C_{26}H_{24}FeN_6$	$C_{28}H_{27}Cl_2CuFeN_7O_8$	$C_{28}H_{27}AgBF_4FeN_7$	$C_{27}H_{25}AgBCl_3F_4FeN_6$
fw	476.36	779.86	712.10	790.41
cryst syst	orthorhombic	monoclinic	triclinic	monoclinic
space group	Pbca	$P2_1/c$	$P\text{-}1$	$P2_1/c$
a/Å	12.152(3)	20.924(3)	10.412(2)	10.806(2)
b/Å	18.930(5)	8.583(5)	11.202(1)	27.372(4)
c/Å	19.876(3)	17.478(2)	13.167(1)	10.916(3)
V/Å³	4572.3(2)	3138(2)	1438.1(3)	3123.9(2)
Z	8	4	2	4
T/K	293(2)	293(2)	293(2)	293(2)
μ/mm⁻¹	0.686	1.372	1.243	1.401
no. of unique reflns	3966 [R(int) = 0.0754]	5523 [R(int) = 0.0459]	4978 [R(int) = 0.0451]	5156 [R(int) = 0.0944]
R1	0.0721	0.0764	0.0720	0.0711
wR2 [$I > \sigma2(I)$]	0.1693	0.1454	0.1923	0.1760
goodness of fit	1.015	1.026	1.061	1.020

Table 4. Selected Bond Lengths (Å) and Angles (deg) of Compounds L² and 2−4^a

L²			2	3	4
C(6)−N(2)	1.241(7)	M(1)−N(1)	1.993(8)	2.365(6)	2.277(7)
C(7)−N(3)	1.277(7)	M(1)−N(2)	2.024(7)	2.500(5)	2.521(8)
C(19)−N(4)	1.300(7)	M(1)−N(5)	1.998(7)	2.500(6)	2.308(7)
C(21)−N(5)	1.265(7)	M(1)−N(6)	2.004(7)	2.383(6)	2.472(8)
N(2)−N(3)	1.406(6)	M(1)−N(7)	2.581(9)	2.345(8)	
N(4)−N(5)	1.411(6)				
		N(1)−M(1)−N(2)	80.6(3)	69.1(2)	70.2(3)
		N(2)−M(1)−N(5)	100.9(3)	96.2(2)	106.4(2)
		N(1)−M(1)−N(6)	102.1(3)	104.0(2)	111.6(3)
		N(2)−M(1)−N(6)	166.7(3)	143.5(2)	165.7(2)
		N(1)−M(1)−N(5)	160.1(3)	144.8(2)	174.8(3)
		N(5)−M(1)−N(6)	81.1(3)	68.4(2)	70.6(2)
		N(1)−M(1)−N(7)	89.0(5)	110.9(2)	
		N(2)−M(1)−N(7)	82.7(5)	117.6(2)	
		N(6)−M(1)−N(7)	84.3(6)	98.5(2)	
		N(5)−M(1)−N(7)	110.9(5)	104.3(2)	

^{a} M = Cu for **2** and M = Ag for **3** and **4**.

drazone with 2-pyridinecarboxaldehyde in a 1:2 ratio. The ¹H NMR of **L²** in d_6-acetone was recorded at 298 K, in which the protons at 4.5−5.0 and 7.4−8.6 ppm reveal the presence of the ferrocene moiety, the pyridyl ring, and the CH=N group. Elemental analysis and other spectroscopic characterization also support the formation of bisbidentate Schiff-base ligand **L²** of the expected formula. Recrystallization from diethyl ether provided crystals suitable for X-ray determination.

The crystallographic data are presented in Table 3, and important bond lengths and angles are depicted in Table 4. The ORTEP diagram of the ligand **L²** shown in Figure 3 reveals that two pyridyl ring moieties adopt a *cis*-conformation about ferrocene, as in **H₂L¹**; however, there are no obvious intramolecular $\pi-\pi$ stacking interactions between the two arms. As an alternation, one pyridyl ring [N(6), C(22) to C(26)] stacks with the symmetry-related ring [N(6A), C(22A) to C(26A)] (symmetry code A: $2 - x$, $1 - y$, $-z$) of the adjacent molecule with an interplane separation of 3.58 Å and the shortest interplane atom···atom separation C(22)···C(26A) of 3.59 Å. The other pyridyl ring [N(1), C(1) to C(5)] stacks with one of the cyclopentadienyl rings [C(14B) to C(18B)] (symmetry code B: $1.5 - x$, $0.5 + y$, z) of the adjacent molecule with the dihedral angle of the stacked pair ca. 9.5° and the shortest interplane atom···atom separation C(4)···C(18B) ca. 3.54 Å.[16] In contrast to the *cis*-conformation of N_{imine},O-coordinating sites in **H₂L¹**, the coordinated sites N_{imine},$N_{pyridyl}$ in **L²** adopt a *trans*-conformation. From the conformation of the molecule, it is apparent that the two C=N−N=C bonds allow a
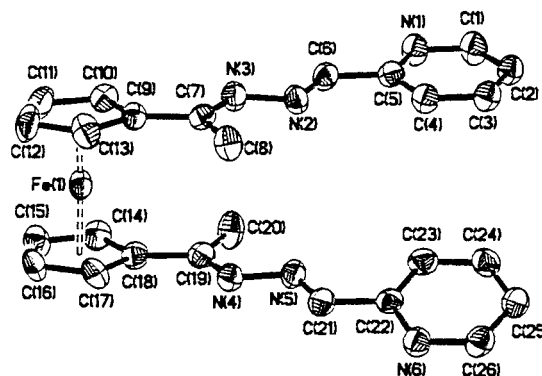

Figure 3. ORTEP plot of the ligand **L²**, showing the non-hydrogen atoms as 50% probability thermal ellipsoids. The solvent molecules and hydrogen atoms are omitted for clarity.

substantial degree of flexibility, such that the two bidentate fragments can vary their separation, which will be of significance for determining the mode of coordination of the ligand.[20]

2.4. Structural Characterization of Cu(II) Complex 2. Stirring the mixture of **L²** and copper(II) diperchlorate gave dark-red Cu(II) complex with empirical formula (from elemental analysis) [CuL²(CH₃CN)][ClO₄]₂. In this case, however. the mass spectrum (Figure 4) was consistent with a monomeric complex rather than a dimeric one.

Crystal stucture analysis (Figure 5) exhibits unexpectedly that there is no formation of the double-helical structure; instead a monomeric complex formed. The ligand **L²** acts as a tetradentate chelate, coordinating all four donors to a single metal center, giving an approximately square pyramidal symmetry. According to the method of Addison et al. for classifying five-coordinate geometries intermediate between square pyramidal (C_{4v}) and trigonal bipyramidal (D_{3h}),[21] the parameter $\tau = 0.11$ (where a value of 1 denotes perfect trigonal bipyramidal symmetry and 0 denotes perfect square pyramidal symmetry) indicates an intermediate structure but one that lies more toward the square pyramidal limit. The basal donors are therefore the N(1), N(2), N(5), and N(6) atoms, and the apical position is occupied by the acetonitrile nitrogen atom N(7). The

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(21) Addison, A. W.; Rao, T. N.; Reedijk, J.; Rijn, J. Van. Verschoor, G. C. *J. Chem. Soc., Dalton Trans.* **1984**, 1349.
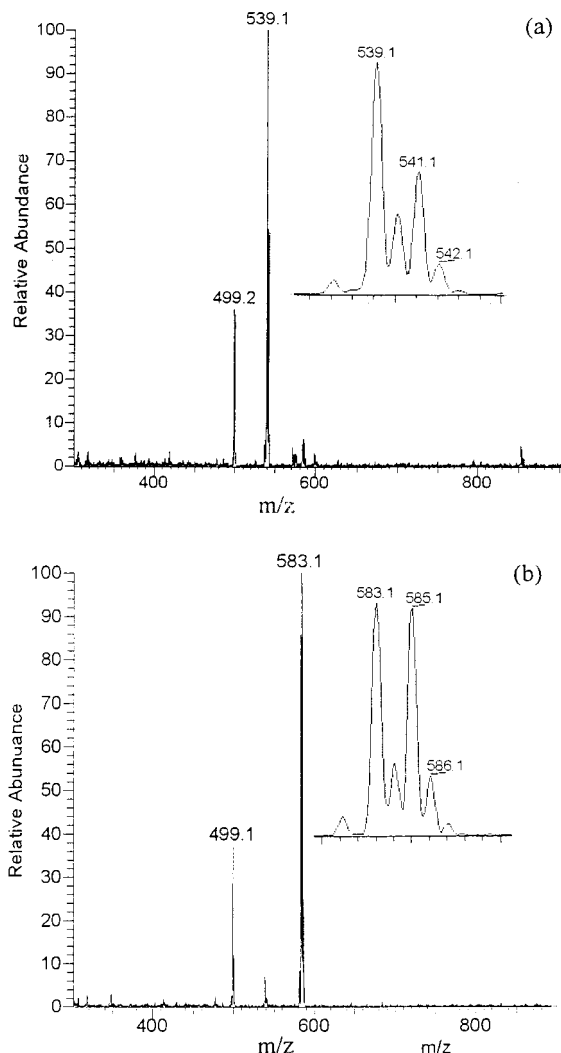
Figure 4. Electrospray mass spectrum of the copper(II) complex **2** (a) and silver(I) complex **4** (b).
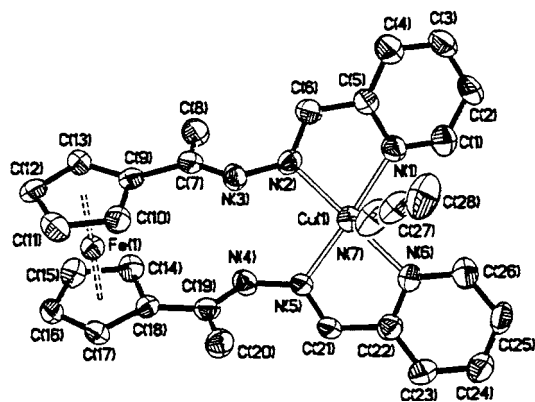

Figure 5. ORTEP plot of the coordinated copper(II) complex **2**, showing the non-hydrogen atoms as 50% probability thermal ellipsoids. The solvent molecules and hydrogen atoms are omitted for clarity.

principal distortion from ideal square pyramidal geometry arises from a distortion in the basal plane (mean deviations of ca. 0.30 Å), which has an expanded angle N(2)−Cu(1)−N(5) of 101°. The mean planes of the two bidentate binding arms are inclined at an angle of 34° to one another. It is clear from the structure that the ferrocene-containing spacer is sufficiently flexible to
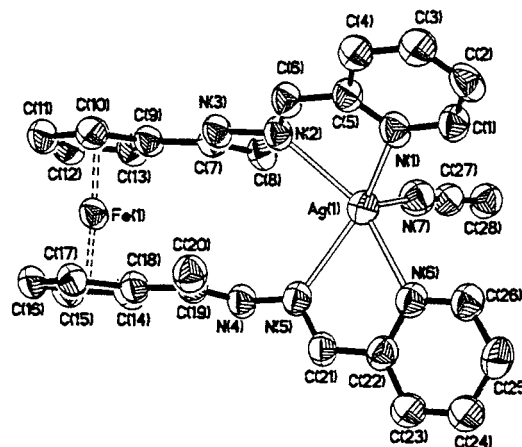

Figure 6. ORTEP plot of the coordinated silver(I) complex **3**, showing the non-hydrogen atoms as 50% probability thermal ellipsoids. The solvent molecules and hydrogen atoms are omitted for clarity.

allow the two bidentate arms to chelate to one metal ion. The formation of the mononuclear complex and the forcing of the five-coordinate geometry on the copper center are indicative of the stability of the nonhelical structure.

Twisting between the two side chains is induced by coordination to the metal center with a torsion angle C(7)−C(9)···C(18)−C(19) of 42.3°. Another feature is that the staggered orientation of two cyclopentadienyl rings is accompanied by the coordination to the Cu(II) atom. The degree of stagger, 53.5°, is defined here as the dihedral angle between the mean planes through the atoms Fe(1)−C(9)−C(7) and Fe(1)−C(18)−C(19). Two pyridyl rings of complex **2** are almost perpendicular to the cyclopentadienyl ring planes to which they are attached.

While the copper(II) in **1** is coordinated in a tetrahedral geometry, the copper(II) in **2** is coordinated in a square pyramidal geometry, with the two binding sites of the ligand forming the basal plane. From the structures mentioned above, it is clearly not possible for the two bidentate sites of both ligands to coordinate to a single metal with tetrahedral geometry in such a way that the two chelate planes are mutually perpendicular. In this case, it seems that the square pyramidal coordination geometry of the copper(II) in complex **2** is the main factor causing the molecule to be formed in a mononuclear fashion. To test this approach, we therefore use an usually tetrahedrally coordinated metal ion, silver(I), to construct the double-helicate compound.

2.5. Structural Characterization of Ag(I) Complexes 3 and 4. Reaction of AgBF$_4$ with **L**^{2} in methanol leads to the formation of a red compound that is moisture-sensitive in solution but stable in the solid state. Following crystallization of the complex in acetonitrile, crystals of **3** were isolated whose elemental analysis was consistent with formation of [AgL^2(CH$_3$CN)](BF$_4$). X-ray structure determination (Figure 6) confirms the mononuclear [FcAg]$^+$ cation with four coordination donors of the ligand and an acetonitrile molecule coordinated to a single silver(I) center. The coordination geometry is surprisingly square pyramidal, with the four nitrogen atoms of the Schiff-base ligand forming the basal plane (mean deviation of the best
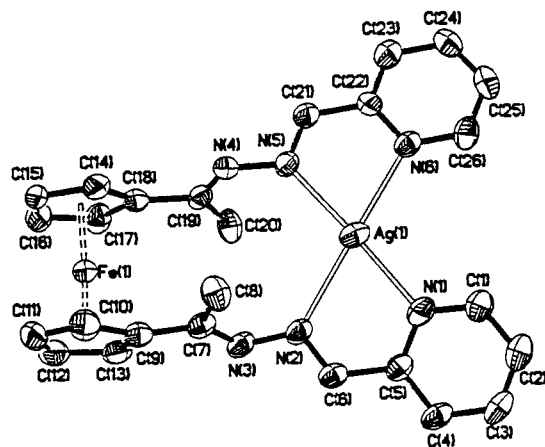
Figure 7. ORTEP plot of the coordinated silver(I) complex **4**, showing the non-hydrogen atoms as 50% probability thermal ellipsoids. The solvent molecules and hydrogen atoms are omitted for clarity.

plane of ca. 0.03 Å) and the acetonitrile nitrogen atom occupying the apical position.

The topological parameter $\tau = 0.02$ indicates an almost ideal square pyramidal geometry. The silver(I) atom is outside the basal plane ca. 0.75 Å toward the apical atom. Such coordination is quite novel for silver-(I) complexes. Although no further proof supports the postulation that the square pyramidal geometry of Cu-(II) and silver(I) complexes **2** and **3** is the main factor causing the molecules not to be formed in a dinuclear fashion, it seems possible that the relatively simple mononuclear complex [AgL(CH$_3$CN)] arises in part from the presence of the coordinated acetonitrile.[20,22] We therefore investigated the reaction of ligand **L²** with silver(I) in dichloromethane following the recrystallization of the complex in chloroform as its BF$_4^-$ salt, whose elemental analysis is consistent with formation of [AgL²](BF$_4$). However, the ESI-MS spectrum also confirms the mononuclear formation of complex **4**. Crystal structure analysis (Figure 7) reveals that two binding sites bond to a single silver atom, forming a mononuclear [FcAg]$^+$ cation. The coordination geometry is surprisingly square planar with the four nitrogen atoms of the Schiff-base ligand coordinated in a plane (mean deviation of the best plane of ca. 0.03 Å).

While the Ag−N distances for the two silver complexes are quite similar, the difference induced by the coordination geometry is noteworthy. The degrees of stagger between the cyclopentadienyl rings for **4** and **3** are 6.9° and 72.3°, respectively. Compared with that of **2**, the smaller stagger angle between the cyclopentadienyl rings is due to the difference in coordination geometry. The dihedral angles between two chelating planes of AgNNCC for **4** and **3** are 18.2° and 46.5°, respectively. Coordination to the metal center also forces twisting between the two side chains with a torsion angle C(7)−C(9)···C(18)−C(19) of 18.3° and 10.7° for **4** and **3**, respectively.

2.6. Electrochemistry Studies. Molecules containing metallocene units could accommodate a particular metal ion at its coordination site and undergo a concurrent redox change.[12] Polyferrocenes generally undergo
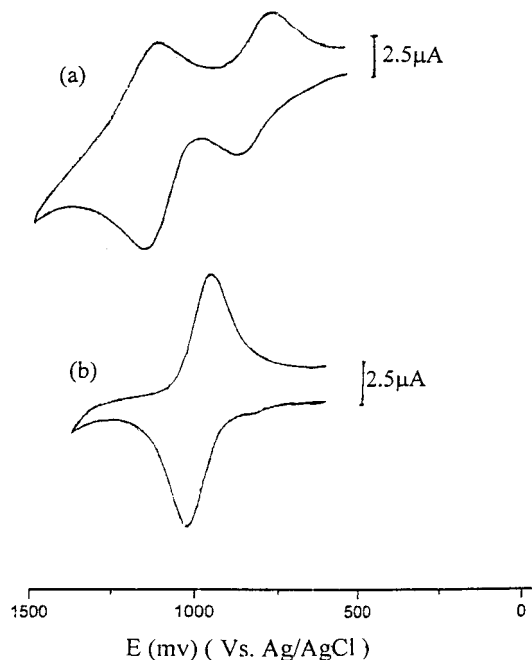

Figure 8. Cyclic voltammogram of complexes **1** (0.25 × 10^{-3} M) (a) and **2** (~1.0 × 10^{-3} M) in CH$_2$Cl$_2$ containing *n*-Bu$_4$NClO$_4$ (0.1 M) at a scanning rate of 35 mV s^{-1} (vs AgCl/Ag).

reversible one-electron oxidations, with the number of waves being determined by the number of ferrocenyl units.[23,24] The half-wave potentials of the redox processes and the separation between consecutive waves vary over a wide range depending on the nature of the compound. Cyclic voltammograms of complexes **1** and **2** are presented in Figure 8. As expected, the complex **1** undergoes two sequential one-electron ferrocene-based oxidations (0.83 and 1.00 V) in the scan range 0.5−1.5 V, while complex **2** undergoes one-electron oxidation at 0.99 V, providing convincing evidence for the presence of two ferrocene moieties in **1** and one ferrocene in **2**.

Pulse voltammetry measurement of the silver(I) complexes **3** and **4** (Figure 9) exhibits one peak at 0.89 and 0.87 V, respectively, corresponding to the one-electron metal-based oxidation Fc/Fc$^+$, suggesting a mononuclear character of the silver complexes **3** and **4**. The peaks corresponding to Ag/Ag$^+$ oxidation in **3** and **4** appear at 0.46 and 0.45 V, respectively.

3. Conclusion

The structural studies of the Cu(II) and Ag(I) complexes with ferrocene-containing ligands bearing podant N,O- and N,N-coordination sites give insight into the factors favoring self-assembly of the mixed organometallic coordination complexes. A match between the geometry of the ligand binding sites and the preferred geometry of the metal ion would force the ligands to bind their coordination sites to separate metal ions. The results here demonstrate that it is possible for the ferrocene-containing ligand systems to operate in multimode fashion when two different sets of metal ion coordination geometries are brought into operation in

(22) Wei, G.; Lawreance, G. A.; Richens, D. T.; Hambley, T. W.; Turner, P. *J. Chem. Soc., Dalton Trans.* **1998**, 623.

(23) Brown, G. M.; Meyer, T. J.; Cowan, D. O.; LeVanda, C.; Kaufman, F. P.; Roling, V.; Rausch, M. D. *Inorg. Chem.* **1975**, *14*, 507.
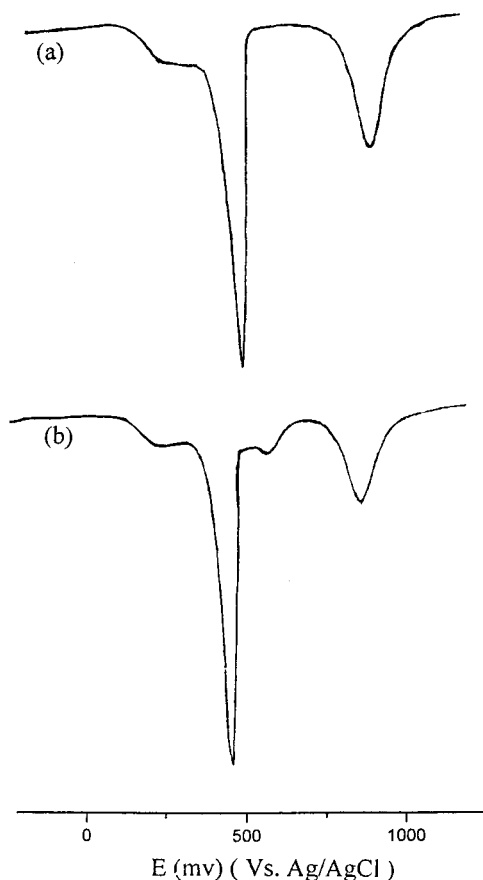(24) Gorton, J. E.; Lentzner, H. L.; Watts, W. E. *Tetrahedron* **1971**, *27*, 4353.

Figure 9. Differential pulse voltammogram of complexes **3** (a) and **4** (~1.0×10^{-3} M) (b) in CH_2Cl_2 containing n-Bu$_4$-NClO$_4$ (0.1 M) at a scanning rate of 35 mV s^{-1} (vs AgCl/Ag).

self-assembly. The role of spacer is fundamental. The double-helical complex derived here from an inexpensive and readily prepared ferrocene-containing ligand is interesting in that it provides an unusual example in the choice of spacer. The development of new ligand systems containing the functional ferrocene group is in progress.

4. Experimental Section

4.1. General Procedures. All chemicals were of reagent grade quality obtained from commercial sources and used without further purification. Elemental analyses (C, H, and N) were carried out on a Perkin-Elmer 240 analyzer. IR spectra were recorded on a Nicolet 170SX FT-IR spectrophotometer with KBr pellets in the 4000–400 cm^{-1} region, ^{1}H NMR spectra on AM5600 Bruker spectrometers at 298 K using TMS as internal standard, and electrospray mass spectra on a LCQ system (Finnigan MAT) using methanol as the mobile phase. Electronic absorption spectra were obtained on a Shimmadzu 3100 spectrophotometer in dichloromethane solution.

4.2. Electrochemical Measurements. Differential pulse voltammetry was done with an EG and GPAR model 273 instrument, which has a 50 ms pulse width, with current sample 40 ms after the pulse was applied. A sweep rate of 25 mV s^{-1} was used in all pulse experiments. Cyclic voltammetry was also performed using EG and GPAR model 273 potentiostats in a three-electrode cell with a purged Ar gas inlet and outlet. The cell comprises a platinum wire working electrode, a platinum auxiliary electrode, and a Ag wire reference electrode. Current–potential curves were displayed on an IBM computer using model 270 electrochemical analysis

software. The voltammograms of the complexes were obtained in dichloromethane with n-Bu$_4$NClO$_4$ (0.1 mol·dm^{-3}) as the electrolyte. The ferrocene (1.0×10^{-3} mol·dm^{-3}), as external standard, undergoes a reversible one-electron oxidation as expected (E_{pa} = 0.63 V vs Ag/AgCl electrode, E_{pc} = 0.70 V vs Ag/AgCl electrode, scanning rate 50 mV s^{-1}).

Caution! *Although no problems were encountered in this work, the salt perchlorates are potentially explosive. They should be prepared in small quantities and handled with care.*

4.3. Crystallography. Parameters for data collection and refinement of ligand **H$_2$L^1** and complex **1** are summarized in Tables 1 and 2 and those for ligand **L^2** and complexes **2**−**4** in Tables 3 and 4. The intensities of **H$_2$L^1** were collected on an Enraf-Nouris CCD system[25] with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Data were reduced using the HKL Denzo and maXus program,[26] and a semiempirical absorption correction from ψ scans was applied.[27] The intensities of **L^2** and complexes **1**−**4** were collected on a Siemens P4 four-circle diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) using the ω−2θ scan mode. Data were corrected for Lorenz polarization effects during data reduction using XSCANS,[28] and a semiempirical absorption correction from ψ scans was applied. The structures were solved by direct methods and refined on F^2 using full-matrix least-squares methods using SHELXTL version 5.0.[29] Anisotropic thermal parameters were refined for non-hydrogen atoms. For complex **2**, oxygen atoms of the two ClO$_4^-$ anions were refined disordered over two positions, O(12) to O(14) and O(22) to O(24) as well as O(12′) to O(14′) and O(22′) to O(24′), respectively; these two positions were refined to occupancies of 0.56(3) and 0.45(2) as well as 0.44(3) and 0.55(2), respectively. For **3**, the BF$_4^-$ anion was disordered over two positions, F(1), F(2), F(3), and F(4) and F(1′), F(2′), F(3′), and F(4′); these two atom positions were refined to occupancies of 0.62(4) and 0.38(4), respectively. For **4**, the BF$_4^-$ anion was also disordered over two positions, F(11), F(12), F(13), and F(14) and F(11′), F(12′), F(13′), and F(14′); these two positions were refined to occupancies of 0.53(4) and 0.47(4), respectively. To assist the refinement, several restraints were applied: (1) all B−F and Cl−O bonds were restrained to be similar; (2) thermal parameters on adjacent atoms in disordered moieties were restrained to be similar.

4.4. Preparation. 1,1′-Diacetylferrocene Dihydrazone. To a solution of hydrazine hydrate (5 mL) in ethanol (10 mL) was added slowly diacetylferrocene (1.35 g, 5 mmol) in ethanol. After the resulting solution was refluxed for 2 h, most of the solvent was evaporated. The orange crystalline solid formed after cooling was isolated and dried under vacuum. Yield: 85% (relative to diacetylferrocene).

H$_2$L^1. The mixture of 1,1′-diacetylferrocene dihydrazone (1.2 g, 4 mmol) and salicylaldehyde (0.96 g, 8 mmol) in methanol was warmed to 50 °C and allowed to stir for 1 h. The red precipitate was filtered and recrystallized from methanol−acetonitrile (1:1) solution. Yield: 93%. Anal. Found: C, 65.1; H, 5.2; N, 11.6. Calcd for C$_{28}$H$_{26}$N$_4$O$_2$Fe(CH$_3$OH)$_{0.5}$(CH$_3$CN)$_{0.5}$: C, 65.3; H, 5.5; N, 11.6. ^{1}H NMR (500 MHz, CD$_3$OCD$_3$): δ 8.62

(25) "Collect" data collection software, Nonius B.V., Delft, The Netherlands, 1998.

(26) (a) Otwinowski, Z.; Minor, W. *Processing of X-ray Diffraction Data Collected in Oscillation Mode*; Carter, C. W., Jr., Sweet, R. M., Eds.; Methods in Enzymology, Vol. 276: Macromolecular Crystallography, Part A; Academic Press: New York, 1997; pp 307−326. (b) Mackay, S.; Gilmore, C. J.; Tremayne, M.; Stuart, N.; Shankland, K. maXus: a computer program for the solution and refinement of crystal structures from diffraction data, University of Glasgow, Scotland, U.K., Nonius B.V., Delft, The Netherlands, and MacScience Co. Ltd., Yokohama, Japan, 1998.

(27) (a) Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33. (b) Blessing, R. H. *J. Appl. Crystallogr.* **1997**, *30*, 421.

(28) XSCANS, Version 2.1, Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1994.

(29) SHELXTL, Version 5.0, Siemens Industrial Automation, Inc. Analytical Instrumentation, Madison, WI, 1995.

(2H, s, CH=N), 7.40 (2H, d, J = 7.4 Hz, phenyl H^3), 7.33 (2H, t, J = 11.3, 7.5 Hz, phenyl H^4), 6.89 (2H, t, J = 7.4, 7.4 Hz, phenyl H^5), 6.82 (2H, d, J = 8.1 Hz, phenyl H^6), 4.94 (4H, cyclopentadienyl H$_\alpha$), 4.58 (4H, cyclopentadienyl H$_\beta$), 2.35 (6H, s, CH$_3$). IR (cm^{-1}, KBr disk): 3052 (v_{C-H}), 1610, 1580, 1478, 1449 ($v_{C=C}$, $v_{C=N}$), 1271 (v_{N-N}), 753 (δ_{C-H}). Electronic spectra in CH$_2$Cl$_2$, λ_{max} (log ϵ): 288 nm (4.65), 344 nm (4.49). Crystals suitable for X-ray structural determination were obtained by slowly evaporating a chloroform−diethyl ether solution in air.

Copper(II) Complex 1. H$_2$L^1 (0.25 g, 0.5 mmol) and copper acetate (0.12 g, 0.5 mmol) were mixed in 25 mL of methanol. After the resulting mixture was refluxed for 8 h, the dark-brown solid formed was isolated, washed with methanol, and dried under vacuum. Yield: 82%. Anal. Found: C, 58.5; H, 5.0; N, 9.3. Calcd for C$_{56}$H$_{48}$N$_8$O$_4$Fe$_2$Cu$_2$(CH$_3$OH): C, 58.6; H, 4.5; N, 9.6. IR (cm^{-1}): 3016 (v_{C-H}), 1606, 1534, 1467, 1443 ($v_{C=C}$, $v_{C=N}$), 1199 (v_{N-N}), 756 (δ_{C-H}). Electronic spectra in CH$_2$Cl$_2$, λ_{max} (log ϵ): 292 nm (4.56), 342 nm (4.41) 473 nm (3.47). Crystals of **1** suitable for X-ray structural determination were obtained by slow diffusion of diethyl ether into a chloroform solution of **1**.

L^2. The mixture of 1,1′-diacetylferrocene dihydrazone (1.2 g, 4 mmol) and 2-pyridinecarboxaldehyde (0.86 g, 8 mmol) in absolute ethanol was stirred for 1 h at room temperature. The red precipitate was filtered and washed with diethyl ether. Yield: 91%. Anal. Found: C, 65.9; H, 5.3; N, 16.6. Calcd for C$_{26}$H$_{24}$N$_6$Fe(CH$_3$CH$_2$OCH$_2$CH$_3$)$_{0.5}$: C, 65.5; H, 5.7; N, 16.4. ^{1}H NMR (500 MHz, CD$_3$COCD$_3$): δ 8.61 (2H, s, CH=N), 8.36 (2H, s, pyridyl H^6), 8.00 (2H, d, J = 7.6 Hz, pyridyl H^3), 7.74 (2H, t, J =7.1, 7.1 Hz, pyridyl H^5), 7.40 (2H, d, J = 4.9 Hz, pyridyl H^4), 4.94 (4H, cyclopentadienyl H$_\alpha$), 4.54 (4H, cyclopentadienyl H$_\beta$), 2.39 (6H, s, CH$_3$). IR (cm^{-1}, KBr disk): 3052 (v_{C-H}), 2863, 1610, 1580, 1478, 1449 ($v_{C=C}$, $v_{C=N}$), 1271 (v_{N-N}), 753 (δ_{C-H}). Electronic spectra in CH$_2$Cl$_2$, λ_{max} (log ϵ): 295 nm (4.75). Crystals suitable for X-ray structural determination were obtained by slowly evaporating a diethyl ether solution.

Copper(II) Complex 2. L^2 (0.24 g, 0.5 mmol) and copper perchlorate (0.12 g, 0.5 mmol) were mixed in 25 mL of ethanol. After the resulting mixture was stirred for 4 h, the red-brown solid formed was isolated, washed with ethanol, recrystallized from acetonitrile−methanol, and dried under vacuum. Yield: 85%. Anal. Found: C, 44.1; H, 4.6; N, 13.5. Calcd for C$_{26}$H$_{24}$N$_6$FeCu(ClO$_4$)$_2$(CH$_3$CN)$_2$CH$_3$OH: C, 43.7; H, 4.0; N, 13.1. Electrospray mass spectrum, m/z (relative intensity):

539.1(100) [(CuL^2)$^+$]. IR (cm^{-1}, KBr disk): 3052 (v_{C-H}), 2863, 1610, 1580, 1478, 1449 ($v_{C=C}$, $v_{C=N}$), 1271 (v_{N-N}), 1098, 623 (v_{Cl-O}),753 (δ_{C-H}). Electronic spectra in acetonitrile, λ_{max} (log ϵ): 295 nm (4.49), 464 nm (3.16). Crystals of **2** suitable for X-ray structural determination were obtained by slow diffusion of diethyl ether into an acetonitrile solution.

Ag(I) Complex 3. L^2 (0.24 g, 0.5 mmol) and silver tetrafluoroborate (0.12 g, 0.5 mmol) were mixed in 25 mL of methanol. After the resulting mixture was stirred for 2 h, the red solid formed was isolated, washed with methanol, recrystallized from acetonitrile−methanol, and dried under vacuum. Yield: 89%. Anal. Found: C, 45.4; H, 4.3; N, 12.3. Calcd for C$_{26}$H$_{24}$N$_6$FeAgBF$_4$(CH$_3$CN)(CH$_3$OH)(H$_2$O): C, 45.7; H, 4.4; N, 12.8. Electrospray mass spectrum, m/z (relative intensity): 583.1 (100) [(AgL^2)$^+$]. IR (cm^{-1}, KBr disk): 3083 (v_{C-H}), 1617, 1587, 1477, 1435 ($v_{C=C}$, $v_{C=N}$), 1292 (v_{N-N}), 748 (δ_{C-H}). Electronic spectra in CH$_2$Cl$_2$, λ_{max} (log ϵ): 293 nm (4.56), 397 nm (4.02). Crystals of **3** suitable for X-ray structural determination were obtained by slow evaporation of an acetonitrile solution isolating moisture.

Ag(I) Complex 4. L^2 (0.24 g, 0.5 mmol) and silver tetrafluoroborate (0.12 g, 0.5 mmol) were mixed in 25 mL of dichloromethane. After the resulting mixture was stirred for 2 h, most of the solvent was evaporated and the red solid formed was isolated, washed with ethanol, and dried under vacuum. Yield: 84%. Anal. Found: C, 47.9; H, 4.1; N, 12.8. Calcd for C$_{26}$H$_{24}$N$_6$FeAgBF$_4$CH$_3$CH$_2$OH: C, 47.5; H, 4.4; N, 12.9. Electrospray mass spectrum, m/z (relative intensity): 583.1 (100) [(AgL^2)$^+$]. IR (cm^{-1}, KBr disk): 3083 (v_{C-H}), 1617, 1587, 1477, 1435 ($v_{C=C}$, $v_{C=N}$), 1292 (v_{N-N}), 748 (δ_{C-H}). Electronic spectra in CH$_2$Cl$_2$, λ_{max} (log ϵ): 293 nm (4.69), 393 nm (4.15). Crystals of **4** suitable for X-ray structural determination were obtained by slow evaporation of a chloroform solution.

Supporting Information Available: Complete details of the X-ray diffraction study on H$_2$L^1, **1**, L^2, and **2**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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