Synthesis and Properties of the First Ferrocene-Functionalized Ligand in Which All the Donor Atoms Are Cyclopentadienyl-Conjugated

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The synthesis of a new type of ferrocene-functionalized ligand for transition-metal binding is described. The ligand is the first electroactive ferrocene receptor to possess complete conjugation between all the donor atoms and the cyclopentadienyl moiety to which they are attached. ^{1}H and natural-abundance ^{15}N NMR studies indicate that a complex of 2:1 stoichiometry (ligand:Cu^+ ion) is formed, in which the Cu^+ ion is surrounded tetrahedrally by a bipyridyl-like pair of donor nitrogen atoms from each of two ligands. Electrochemical data show that the conjugation of each of the donor atoms with the cyclopentadienyl ring results in an enhanced electrochemical response of the ferrocene moiety to Cu^+ ion binding relative to a similar ligand in which the donor atoms are not conjugated with the cyclopentadienyl ring.

Introduction

The coupling of metallocenes to a variety of ligands has enabled a large number of host−guest interactions to be observed electrochemically.[1] To maximize the response of the metallocene to guest binding, efforts are being made to design host systems in which the chelating atoms are conjugated with the cyclopentadienyl ring for enhanced electronic interaction.[2] Several approaches to host design have been taken, including one consisting of hosts containing ferrocenecarboxylic acid derivatives, so that the electron density on the carbonyl group (and thus the cyclopentadienyl ring also) is perturbed by the presence of a guest metal ion.[3] In another approach, two of the oxygen atoms of a crown ether ligand were attached to a ferrocene unit at the 1- and 1′-positions, thus affording a close proximity effect through bond polarization.[4] A further approach involved linking a crown ether to a ferrocene moiety with a conjugated linker.[5] In each case, the ligand was designed to bind "hard" metal ions such as those belonging to the alkali-metal, alkaline-earth-metal, and lanthanide families. To date, enhanced responsiveness of a ferrocene reporter group to transition-metal ions has been achieved only once, by means of a family of ligands derived from aminoferrocenes.[6]

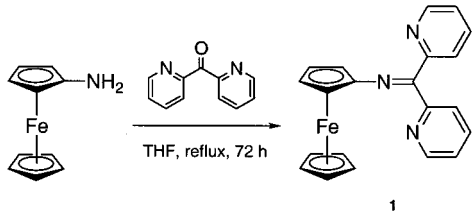

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Figure 1.

In all the examples mentioned above, only some of the chelating atoms within the ligand are cyclopentadienyl-conjugated, and in principle, it is desirable that as many of the chelating atoms as possible afford a conjugated interaction with the metallocene. We wish to report a new type of ligand, designed for transition-metal binding, in which all the nitrogen donor atoms are cyclopentadienyl-conjugated. The ligand (**1**; Figure 1) is a derivative of aminoferrocene, thus furnishing a potential nitrogen donor atom which is conjugated with the cyclopentadienyl ring for enhanced "through-bond" interaction. This nitrogen atom is linked to a 2,2′-bipyridyl moiety via an imine bond, so that the remaining two nitrogen donor atoms are also conjugated with the cyclopentadienyl ring, thus potentially enhancing the through-bond interaction still further. In terms of chelation, ligand **1** affords versatility in that coordination can be envisaged to take place through both pyridyl nitrogen atoms or through the imino nitrogen atom and one of the two pyridyl nitrogen atoms. Having synthesized the ligand, we used a combination of cyclic voltammetry and ^{1}H and natural-abundance ^{15}N NMR to elucidate the structure of the complex of ligand **1** with Cu^+ in solution.

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Results and Discussion

Synthesis of Ligand 1. Very few functionalized aminoferrocenes have been reported, presumably because of the perception that the synthesis of aminoferrocene is not particularly straightforward or that the amine itself is not stable.[7] However, we found aminoferrocene to be much more stable than expected and encountered no significant problems with decomposition, provided reasonable precautions were taken to keep the material under an inert atmosphere during long-term storage. To prepare the aminoferrocene, we employed two literature procedures, each of which has an advantage over the other.[8] The first gave a good yield of aminoferrocene but suffers from the disadvantage that the synthesis of an azide intermediate is necessary.[9] The second gave a lower yield of aminoferrocene but is free from the minor risk of explosion associated with the first.[10] Ligand **1** was synthesized in good yield and purity by the straightforward condensation of equimolar quantities of aminoferrocene and 2,2′-bipyridyl ketone in refluxing THF containing 3 Å molecular sieves. The ligand is reasonably stable to atmospheric oxygen and moisture, and storage of the solid at room temperature under an inert atmosphere resulted in no decomposition after several months. Recrystallization of the ligand may be carried out using chloroform/ether, but column chromatography should be avoided, since it appeared to induce decomposition.

Complexation of Ligand 1 with Cu^+. Observation by ^1H NMR. The ^1H NMR spectra of ligand **1** alone and ligand **1** treated with 0.5 equiv of Cu^+ are reproduced in parts a and b of Figure 2, respectively. In the case of ligand **1** alone, the inequivalence of each of the eight pyridyl protons is evident, and each signal is well-defined. The two signals due to protons 2,5 and 3,4 on the substituted cyclopentadienyl ring are apparent together with the singlet due to the protons on the unsubstituted cyclopentadienyl ring. The ^{13}C NMR spectrum (see the Experimental Section) confirms the inequivalence by the appearance of 10 ^{13}C signals from the two pyridine rings and the X-ray crystallographic structure (see the Supporting Information) of **1** emphasizes the nonequivalence and the almost orthogonal disposition of the pyridine rings in the solid state.

The ^1H NMR spectrum recorded in the presence of 0.5 equiv of $Cu(CD_3CN)_4^+BF_4^-$ clearly indicates the complexation of Cu^+ by ligand **1**. Eight signals due to the pyridyl protons are still visible, each of which has undergone broadening, this being particularly marked in four of the signals. This suggests formation of a complex in which the imino nitrogen atom and one pyridyl moiety are coordinated to the metal ion in a bipyridyl-like fashion, whereas the other pyridyl moiety is free to rotate rapidly on the NMR time scale, giving sharper signals. The signal due to the unsubstituted cyclopentadienyl ring appears as a slightly broadened singlet. The signal due to the 3,4-protons of the substituted cyclopentadienyl ring is broadened slightly, which is probably due to reduced rate of rotation about the cyclopentadienyl−N bond. The signal due to the 2,5-protons of the substituted cyclopentadienyl ring is almost invisible (having been broadened almost beyond definition), which is attributed to Cu^+ ion induced through-space relaxation of these protons.

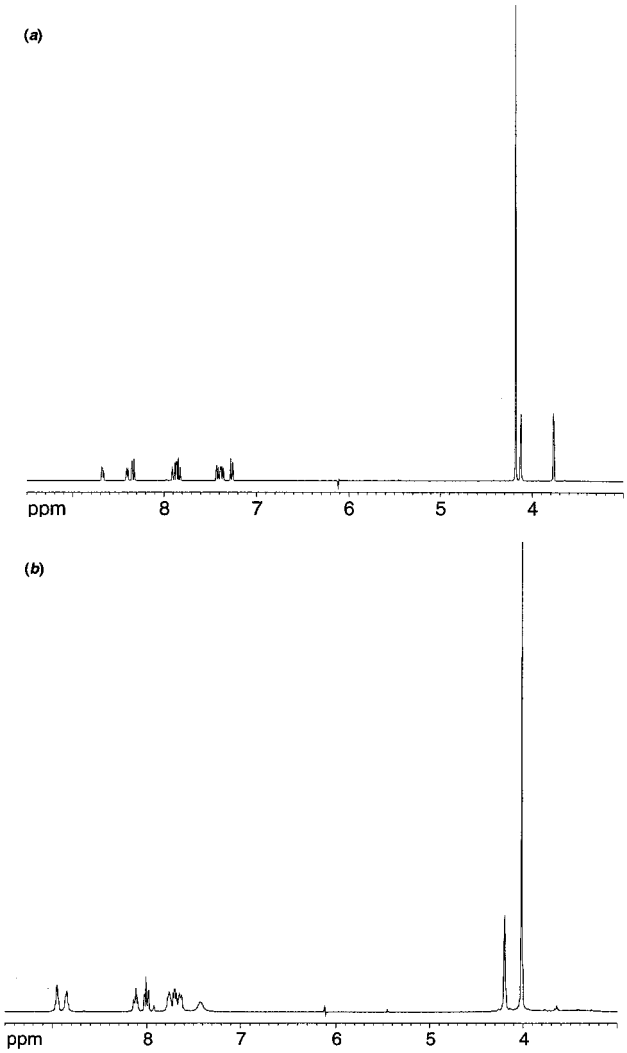

Figure 2. ^1H NMR spectra of ligand **1** in (a) the absence and (b) the presence of 0.5 equiv of Cu^+ (solvent, CD_3CN; standard, Me_4Si 0 ppm; (a), [**1**] = 20.7 mM; (b), [**1**] = 20.7 mM, $[Cu(CD_3CN)_4^+BF_4^-]$ = 10.4 mM).

The addition of another 0.5 equiv of Cu^+ (1.0 equiv cumulatively, not shown) results in a broadening of the signals due to the protons of the uncomplexed pyridyl moieties. The broadening is attributed to the formation of a weak oligomeric complex. The addition of a third 0.5 equiv of Cu^+ (1.5 equiv cumulatively, not shown) results in further broadening, together with a broadening of the 3,4-protons of the substituted cyclopentadienyl ring beyond definition. These changes are also consistent with the formation of an oligomeric complex.

The distinct signals in Figure 2b result from a single complex which does not undergo ligand exchange on the NMR time scale. Two other reports have described Cu^+ complexation by bipyridyl-like ligands functionalized

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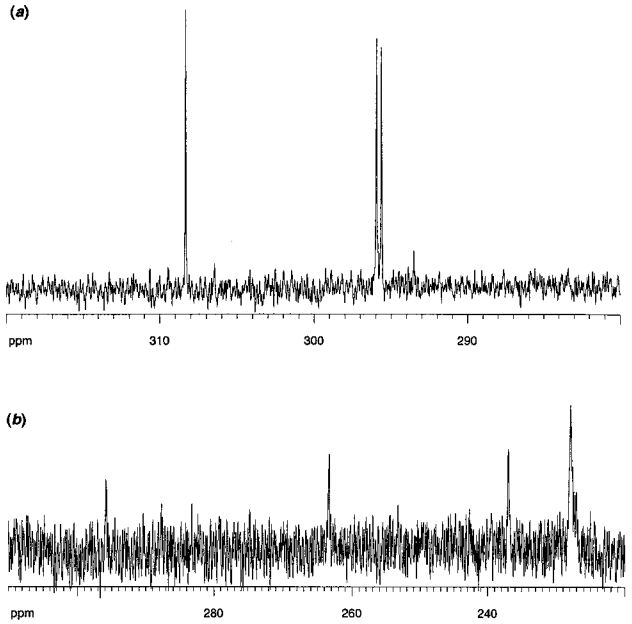

Figure 3. ^{15}N NMR spectra of ligand **1** in (a) the absence and (b) the presence of 0.5 equiv of Cu^+ (solvent, 50% v/v DMSO-d_6/$CDCl_3$; standard, 5 M $^{15}NH_4NO_3$ (NH_4 99% ^{15}N) in 2 M nitric acid, made up with D_2O, NH_4 0 ppm; (a), [**1**] = 164.0 mM; (b), [**1**] = 164.0 mM, [$Cu(CH_3CN)_4^+BF_4^-$] = 82.0 mM).

with ferrocenyl moieties. In one, a similar inertness to exchange on the NMR time scale was observed[11] and it was noted that complexation of Cu^+ caused a restriction in the rotational freedom of the ferrocene moiety with respect to the ligand, as shown by the inequivalence of each of the cyclopentadienyl α- and β-protons in the ^{1}H NMR spectrum of the complex. This behavior differs markedly from that observed on complexation of Cu^+ by ligand **1**, in which complex formation does not significantly affect rotation about the cyclopentadienyl−N bond. In comparison, ^{1}H NMR data presented in the second report[12] reveal a dynamic interconversion between multiple complexes on the NMR time scale.

Observation by ^{15}N NMR. ^{15}N NMR experiments were conducted to confirm the formation of a complex of 2:1 (ligand **1**:Cu^+) stoichiometry in which a Cu^+ ion is chelated by the imino nitrogen atom and one of the pyridine nitrogen atoms of each of two ligands. It was expected that the imino and pyridyl nitrogen atoms of ligand **1** would be well-separated in the ^{15}N NMR spectrum of the ligand and that changes in the ^{15}N NMR chemical shifts induced by Cu^+ ion binding would reveal which nitrogen atoms were involved in complex formation.

Indeed, the ^{15}N NMR spectrum of ligand **1** shows three signals in two distinct environments (Figure 3a). Clearly, the signal at lowest field (308.3 ppm) is that due to the imino nitrogen atom, whereas the two higher field signals (295.9 and 295.6 ppm) are those due to the nitrogen atoms of the two distinct pyridine moieties, either cis or trans to the lone pair of the imino nitrogen. The sum of the integrals of the pyridine signals is twice the integral of the imino signal, and all the signals lie within the expected chemical shift ranges.[13] The addition of 0.5 equiv of Cu^+ (as $Cu(CH_3CN)_4^+BF_4^-$) results in a dramatic change in the appearance of the spectrum (Figure 3b). (The prominent, broad signal at highest field (227.9 ppm) is that due to acetonitrile liberated from $Cu(CH_3CN)_4^+BF_4^-$.) The chemical shift of one of the pyridine signals remains unchanged at 295.9 ppm, whereas the other two signals have undergone pronounced upfield shifts to 263.3 and 236.9 ppm.[14] The upfield shifts of two of the three signals confirms chelation of the metal ion by the imino nitrogen atom and one of the pyridine nitrogen atoms, since chelation by both pyridine nitrogen atoms would be manifested as a displaced pair of signals with very similar chemical shifts, together with a relatively unperturbed signal due to the imino nitrogen atom. The observation of the chelating atoms themselves therefore affords ^{15}N NMR a clear advantage over other analytical techniques. The narrow line width of ^{15}N NMR signals, coupled with the large chemical shift range (ca. 1500 ppm) of the ^{15}N nucleus, facilitates the discrimination of nuclei in multiple environments, and we suggest that ^{15}N NMR could be more widely used in contexts such as this.

Table 1. Electrochemical Parameters[a] for Ligand 1 in the Absence and Presence of Cu^+

amt of Cu^+, equiv[b]	$E_{1/2}$	E_{pa}	E_{pc}	ΔE_p	ΔE_{pa}	ΔE_{pc}
0	420	465	370	95		
0.5	490	575	400	175	110	30
1.0	530	590	470	120	125	100
2.0	540	600	485	115	135	115

[a] Electrochemical parameters are quoted in mV: $E_{1/2}$, redox potential (vs SCE); E_{pa}, anodic current peak potential (vs SCE); E_{pc}, cathodic current peak potential (vs SCE); ΔE_p, peak-to-peak potential splitting ($E_{pa} - E_{pc}$); ΔE_{pa}, the change in E_{pa} (with respect to that of the ligand alone) following the addition of Cu^+; ΔE_{pc}, the change in E_{pc} (with respect to that of the ligand alone) following the addition of Cu^+; SCE, standard calomel electrode. [b] Equivalents of Cu^+ with respect to ligand **1**.

Observation by Cyclic Voltammetry. The reversible oxidation and reduction of ligand **1** (2 mM; Figure 4a) was observed by cyclic voltammetry (data and abbreviations listed in Table 1) (Fe^{2+}/Fe^{3+} $E_{1/2}$ = +420 mV, vs SCE, ΔE_p = 95 mV). The addition of 0.5 equiv of Cu^+ (Figure 4b) resulted in a wave which was quasi-reversible (ΔE_p = 175 mV) but with an anodic shift in E_{pa} of 110 mV and an anodic shift in E_{pc} of only 30 mV. This may represent an E_{pa}/E_{pc} ratio of about 3.7 but is more likely to indicate an exchanging mixture of ligand and complex at the concentration of the experiment (2 mM). Additional Cu^+ (Figure 4c,d) drives the equilibrium toward a 2:1 (ligand **1**:Cu^+) complex, which at a ratio of 2:1 (Cu^+:ligand **1**) appears to be fully formed and gives rise to a quasi-reversible wave (ΔE_p = 115 mV) with shifts in E_{pa} and E_{pc} of similar magnitude (135 and 115 mV, respectively).

Redox-active ligands which are capable of binding Cu^+ are very rare,[11,12,15] but one (reported by Buda et al.)[11]

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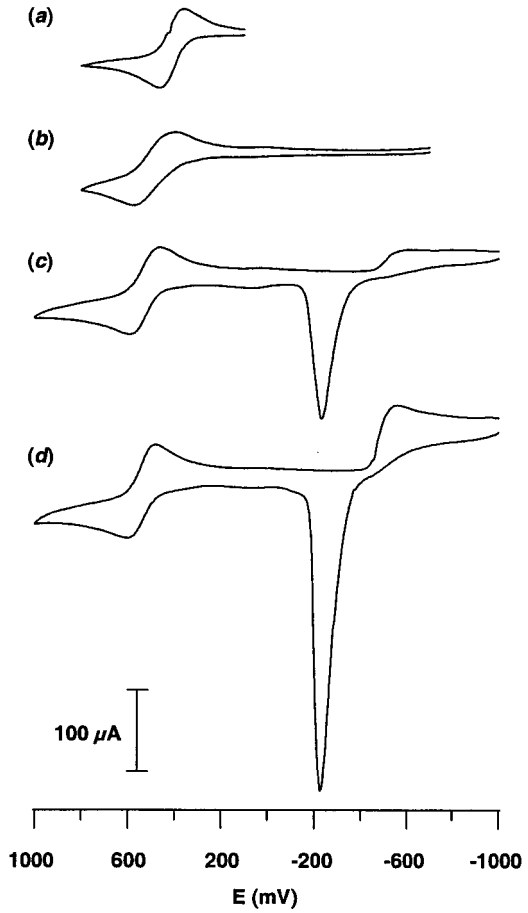

Figure 4. Cyclic voltammograms (vs SCE) obtained for ligand **1** in (a) the absence and the presence of (b) 0.5, (c) 1.0, and (d) 2.0 equiv of Cu^+ (solvent, CH_3CN; [**1**] = 2.0 mM; [*n*-$Bu_4{}^+ClO_4{}^-$] = 0.1 M; scan rate 10 mV s^{-1}).

is somewhat similar to ligand **1** with regard to chelation moiety and mode of ferrocene substitution. The ligand was shown to chelate Cu^+ by means of a bipyridyl moiety (linked to ferrocene via a methylene/ester bridge) in a complex of stoichiometry 2:1 (ligand:Cu^+). The presence of the methylene group effectively insulates the ligand electronically from the ferrocene unit, but nonetheless an anodic shift in $E_{1/2}$ of 50 mV was observed following complexation of Cu^+. The corresponding shift resulting from the addition of 2.0 equiv of Cu^+ to ligand **1** is 120 mV, which represents a significant enhancement. The proposal of a 2:1 (ligand **1**:Cu^+) stoichiometry is given further support by the observation of the oxidation of free Cu^+ at higher ratios of Cu^+ (Figure 4c,d), but evidently the complex is not formed completely at lower concentrations of Cu^+.

Experimental Section

General Comments. ^{15}N (40.55 MHz) NMR spectra were recorded at 300 K using a Bruker AMX400 spectrometer with 2.5 mL samples in 10 mm tubes. Inverse-gated ^1H decoupling was used with a relaxation delay of 3.0 s (total recycle time 7.1 s) and 30° pulse flip angle; 22 756 and 31 200 transients for the ligand and complex, respectively, were obtained. Line broadening of 1 Hz was applied during Fourier transformation. 2,2′-Bipyridyl ketone was obtained from Fluka. $Cu(CH_3CN)_4{}^+BF_4{}^-$ was prepared according to a literature procedure.[12] THF was dried by distillation from sodium/benzophenone onto 3 Å molecular sieves; acetonitrile was dried by distillation from calcium hydride onto 3 Å molecular sieves.

Synthesis of Ligand 1. Aminoferrocene (0.951 g, 4.73 mmol) and 2,2′-bipyridyl ketone (0.872 g, 4.73 mmol), together with 3 Å molecular sieves (3.0 g), were heated under reflux for 72 h in dry THF (20 mL). The mixture was then cooled, diluted with THF (30 mL), and filtered. The residue was washed with THF (2 × 20 mL), and the filtered washings were combined with the filtrate. Evaporation gave ligand **1** (1.60 g, 92%) as a dark red oily solid, which crystallized in almost analytically pure form on standing.

^1H NMR (360 MHz, $CDCl_3$, Me_4Si δ 0; δ (ppm), J (Hz)): 3.87 (2 H, t, J = 2, substituted cyclopentadienyl), 4.09 (2 H, t, J = 2, substituted cyclopentadienyl), 4.21 (5 H, s, unsubstituted Cp), 7.20 (1 H, d, J = 8, Py), 7.30 (1 H, t, J = 6, Py), 7.34 (1 H, t, J = 6, Py), 7.74 (1 H, t, J = 8, Py), 7.79 (1 H, t, J = 8, Py), 8.30 (1 H, d, J = 8, Py), 8.53 (1 H, d, J = 6, Py), 8.78 (1 H, d, J = 6, Py). ^{13}C NMR (90 MHz, $CDCl_3$, Me_4Si δ 0; δ (ppm)): 66.2 (CH, substituted cyclopentadienyl), 67.6 (CH, substituted cyclopentadienyl), 69.8 (CH, unsubstituted Cp), 101.6 (C_{quat}, cyclopentadienyl−N), 122.4 (CH, Py), 123.3 (CH, Py), 123.8 (CH, Py), 124.0 (CH, Py), 136.4 (CH, Py), 136.4 (CH, Py), 149.0 (CH, Py), 150.0 (CH, Py), 157.1 (C_{quat}, Py), 157.6 (C_{quat}, Py), 163.4 (C_{quat}, N═CPy(Py)). UV−vis (λ_{max} (nm) (ϵ (dm^3 mol^{-1} cm^{-1})); CH_3CN)): 261 (12 460), 300 (11 160), 488 (1730). Anal. Calcd for $C_{21}H_{17}N_3Fe$: C, 68.68; H, 4.67; N, 11.44. Found: C, 67.99; H, 4.59; N, 11.26. High-resolution mass spectrometry (FAB): *m/e* calcd for $C_{21}H_{17}N_3Fe$ 367.0772, found 367.0760.

Cyclic Voltammetry. The data were acquired with an EG&G Princeton Applied Research "VersaStat" apparatus and are quoted with reference to a standard calomel electrode. Cu^+ was added as aliquots of a solution of $Cu(CH_3CN)_4{}^+BF_4{}^-$ in dry, Ar-purged acetonitrile to a solution of ligand **1** (2 mM) in dry, Ar-purged acetonitrile containing tetra-*n*-butylammonium perchlorate (0.1 M) as the supporting electrolyte. Anhydrous, anaerobic conditions were maintained by the use of an argon atmosphere. Before each scan was recorded, the working electrode (a Pt disk of surface area ca. 20 mm^2) was rinsed in methanol, air-dried, dipped in concentrated nitric acid, followed by water and methanol, and held in the flame of a Bunsen burner for a few seconds. The counter electrode consisted of a Pt wire (4 × 0.5 mm). A scan rate of 10 mV s^{-1} was employed, with a sweep from −1.0 to +1.0 to −1.0 V.

Preparation of Samples for ^1H NMR Complexation Study. Using Schlenk techniques, a solution of ligand **1** (20.7 mM) in dry, degassed (by freeze−thaw cycling with Ar) CD_3CN was prepared. An aliquot (500 μL) of the solution was transferred to an Ar-flushed 5 mm NMR tube equipped with a rubber septum cap, and the ^1H NMR spectrum recorded. $Cu(CH_3CN)_4{}^+BF_4{}^-$ (1.6 mg, 0.5 mol equiv with respect to ligand **1**) was dissolved in dry, degassed CD_3CN (200 μL) and the solution evaporated to dryness. The residue was treated with an aliquot (500 μL) of the solution of ligand **1** ([**1**] = 20.7 mM, [Cu^+] = 10.4 mM), and the ^1H NMR spectrum obtained as above.

Preparation of Samples for ^{15}N NMR Complexation Study. The solutions of ligand and complex were prepared according to a procedure analogous to that described for ^1H NMR, but with 50% v/v DMSO-d_6/$CDCl_3$ employed as the solvent to afford [**1**] = 164.0 mM and [$Cu(CH_3CN)_4{}^+BF_4{}^-$] = 82.0 mM. (The exchange of $Cu(CH_3CN)_4{}^+$ $BF_4{}^-$ with CD_3CN was not carried out.)

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College, London) is thanked for the crystal structure determination of ligand **1**, which was obtained using a diffractometer funded by the EPSRC and King's College, London. Mrs. J. E. Hawkes and Mr. J. Cobb (King's College, London) are thanked for expert assistance with the NMR spectroscopy. The purchase and operation of the Bruker AMX400 spectrometer used in this study was supported in part by the University of London Intercollegiate Research Service (ULIRS).

Supporting Information Available: A figure giving the X-ray crystallographic structure of ligand **1** and tables of crystal data and structure refinement details, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates and isotropic displacement parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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