Regiospecific Oximato Coordination at the Oxygen Site: Ligand Design and Low-Spin Mn^{II} and $Fe^{II/III}$ Species

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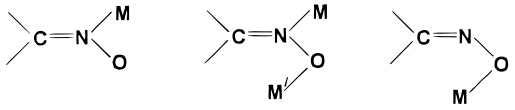
The (pyridylazo)oxime ligand $(C_5H_4N)N{=}NC(=NOH)C_6H_4R(p)$, HRL (R = H, Me), has been synthesized with the objective of promoting the very rare mononuclear oximato-*O* coordination. The synthesis involves hydrazone nitrosation. HRL reacts with $M(ClO_4)_2{\cdot}6H_2O$, affording $[M(RL)_2]$ (M = Mn, Fe), and X-ray structure determinations have indeed revealed the presence of the desired oximato-*O* coordination mode in the distorted octahedral MN_4O_2 sphere characterized by a 2-fold axis of symmetry relating the two tridentate ligands, all chelate rings being five-membered. The M−N and M−O distances are relatively short (1.84−1.99 Å), consistent with spin-pairing (M = Mn, $S = {}^1/_2$; M = Fe, $S = 0$). The M−N bond length trend, $Mn^{II} > Fe^{II}$, is in accord with the larger radius of the low-spin Mn^{II} atom. The M−O length order is, however, $Mn^{II} < Fe^{II}$. This reversal occurs because of the rigidity of the ligand skeleton. Significant M−azo back-bonding is present (N=N length ∼1.30 Å). $[Mn(RL)_2]$ displays hyperfine-split axial EPR spectra ($g_{\|} \sim 1.98$, $g_{\perp} \sim 2.06$, $A_{\|} \sim 170$ G, $A_{\perp} \sim 65$ G) in frozen solution as well as in polycrystalline $[Fe(RL)_2]$ lattices. The quasireversible Fe(III)/Fe(II) couple of $[Fe(RL)_2]$ has $E_{1/2} \sim 0.7$ V. The oxidized complex $[Fe(RL)_2]PF_6$ has been electrosynthesized. It is low-spin ($S = {}^1/_2$) and displays axial EPR spectra ($g_{\|} \sim 1.98$, $g_{\perp} \sim 2.14$) in frozen solution. The Mn(II) → Mn(III) oxidation (∼1.0 V) in $[Mn(RL)_2]$ is irreversible. Crystal data for $[Mn(HL)_2]{\cdot}CH_2Cl_2$: crystal system monoclinic, space group *I*2/*a*, $a = 14.142(7)$ Å, $b = 10.721(7)$ Å, $c = 16.933(10)$ Å, $\beta = 93.01(4)°$, $Z = 4$. Crystal data for $[Fe(HL)_2]{\cdot}CH_2Cl_2$: crystal system monoclinic, space group *I*2/*a*, $a = 14.254(6)$ Å, $b = 10.742(6)$ Å, $c = 16.719(8)$ Å, $\beta = 92.35(4)°$, $Z = 4$.

Introduction

Oximes, like Schiff bases, have persistently played a notable role in the development of transition metal coordination chemistry,[1] and unabated activity is current in this area.[2−6] In mononuclear systems, oximes bind metal ions virtually universally via the N site only, as in **1**. In contrast, the best known



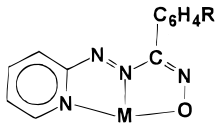
1 **2** **3**

examples of O-binding occur in multinuclear assemblies incorporating the two-atom bridging mode **2** wherein the N site is also engaged.[7−9] Regiospecific mononuclear binding at the O site as in **3** remains a matter of curiosity.[10]

The present work was undertaken with the objective of realizing the coordination mode **3** in a rational manner. For this purpose, a suitable ligand system was designed. It afforded manganese(II) and iron(II,III) chelates wherein the presence of O-binding was authenticated by structure determinations. A notable magnetic feature is the efficacy of **3** in sustaining low-spin character even in the case of bivalent manganese.

Results and Discussion

Syntheses. Ligands and Complexes. The concerned ligand system HRL (H refers to the dissociable oxime hydrogen) is a (pyridylazo)oxime synthesized from 2-hydrazinopyridine as in shown Scheme 1, which also outlines the synthesis of $[Mn^{II}(RL)_2]$, $[Fe^{II}(RL)_2]$, and $[Fe^{III}(RL)_2]PF_6$. The binding mode (vide infra) of RL^- in these chelates is depicted in **6**.



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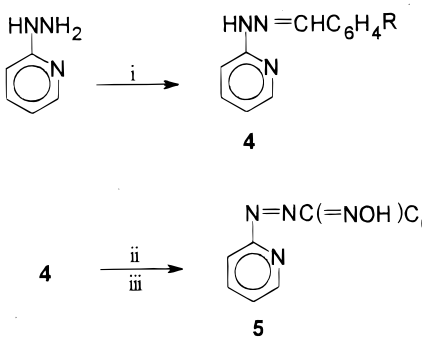
Scheme 1

A. Ligand



B. Complexes

$$M(ClO_4)_2 + 2\,HRL \xrightarrow{iv} [M^{II}(RL)_2] + 2\,HClO_4\ (M = Mn, Fe)$$

$$[Fe^{II}(RL)_2] + PF_6^- \xrightarrow{v} [Fe^{III}(RL)_2]PF_6$$

i. RC_6H_4CHO, ethanol-water mixture, stir, 25°C.
ii. *n*-$C_4H_9NO_2$, NaOMe, MeOH, boil.
iii. Dilute NaOH, 25°C, extract with Et_2O, neutralize the aqueous part with 1N H_2SO_4, 0°C.
iv. MeOH, stir, 25°C.
v. MeCN, NH_4PF_6 / TEAP, 0.90 V *vs* SCE, stir, 25°C.

Table 1. Electrochemical[a] Data in Acetonitrile Solution at 298 K

compd	M^{III}/M^{II} $E_{1/2}$,[b] V (ΔE_p,[c] mV); n[d,e]	$[-N{=}N-]/[-N\cdots N-]^-$ $E_{1/2}$,[b] V (ΔE_p,[c] mV)
$[Mn(HL)_2]$	1.00[f]	−0.58 (70)
$[Mn(MeL)_2]$	0.98[f]	−0.62 (60)
$[Fe(HL)_2]$	0.70 (90); 1.02	−0.72 (100)
$[Fe(MeL)_2]$	0.68 (80); 0.98	−0.76 (100)
$[Fe(HL)_2]PF_6$	0.70 (90); 1.01	−0.71 (90)
$[Fe(MeL)_2]PF_6$	0.68 (90); 0.99	−0.74 (90)

[a] At a platinum disk electrode; supporting electrolyte tetraethylammonium perchlorate (TEAP, 0.1 M); scan rate 50 mV s^{-1}; reference electrode SCE; solute concentration $\sim 10^{-3}$ M. [b] $E_{1/2}$ is calculated as the average of anodic (E_{pa}) and cathodic (E_{pc}) peak potentials. [c] $\Delta E_p = E_{pa} - E_{pc}$. [d] $n = Q/Q'$, where Q is the observed coulomb count and Q' is the calculated electron count for one-electron transfer. [e] Constant-potential electrolysis was performed at 200 mV below E_{pc} for reduction and at 200 mV above E_{pa} for oxidation. [f] E_{pa} values.

The complexes are uniformly low spin in nature (vide infra) and display characteristic allowed transitions in the 400−750 nm region (see Experimental Section). They are electroactive and display two one-electron responses. Reduction potential data are listed in Table 1. In $[Fe(RL)_2]$, the Fe(III)/Fe(II) couple near 0.7 V forms the basis for the electrosynthesis of $[Fe^{III}(RL)_2]^+$. The voltammograms of $[Fe(RL)_2]$ (initial scan anodic) and $[Fe(RL)_2]^+$ (initial scan cathodic) are virtually superposable, suggesting gross structural similarities. The couple near −0.7 V for the complexes is assigned to azo reduction, $[-N{=}N-]/[-N\cdots N-]^-$.[11] In $[Mn(RL)_2]$, metal oxidation occurs irreversibly at ~1.0 V.

A note on the choice of HRL for achieving binding mode **3** is in order. Azooxime and azopyridine ligands always bind metal ions in the form of five-membered (N^a, N^o)$M^{2,6-8}$ and (N^a, N^p)-M^{12} chelate rings (N^a = azo N; N^o = oximato N; N^p = pyridine N). In HRL, the azooxime and azopyridine functions have been juxtaposed. If coordination via N sites alone was to take place in the tridentate bicyclic chelation of RL^-, only one chelate ring would be five-membered, the other being four-membered and presumably unstable. This difficulty is circumvented via a one-atom shift of the oximato coordination from the N^o to the O^o site, and both chelate rings become five-membered.

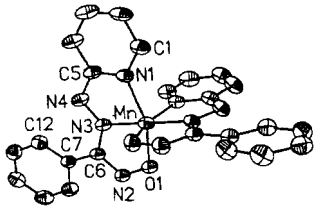


Figure 1. Perspective view and atom-labeling scheme for $[Mn(HL)_2]$ with all the atoms being represented by 30% probability ellipsoids.

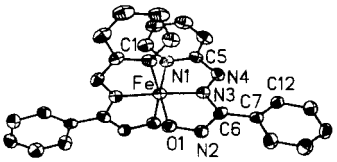


Figure 2. Perspective view and atom-labeling scheme for $[Fe(HL)_2]$ with all the atoms being represented by 30% probability ellipsoids.

Structures. Both $[Mn(HL)_2]\cdot CH_2Cl_2$ and $[Fe(HL)_2]\cdot CH_2Cl_2$ afforded single crystals, thus providing a rare opportunity for observing the subtle differences between bond parameters of low-spin Mn^{II} and Fe^{II} held in the same coordination environment. As expected, the two structures are isomorphous and nearly isometric. Molecular views and atom-numbering schemes are shown in Figures 1 and 2. Selected bond parameters are listed in Table 2. The metal atom, as well as the dichloromethane carbon atom, lies on a crystallographic 2-fold axis. The two ligands are thus equivalent by symmetry. The HL^- ligand binds in a meridional tridentate fashion via O^o, N^a, and N^p atoms, forming the distorted octahedral MN_4O_2 coordination sphere as in **6**.

This work provides the first quantitation of Mn−N^p, 1.990(3) Å, and Mn−O^o, 1.891(3) Å, lengths in a low-spin manganese(II) complex. The Mn−N^a length, 1.873(3) Å, is significantly shorter than the average values (1.92−1.96 Å) observed in two structurally characterized low-spin azooxime complexes incorporating (N^a, N^o)Mn chelation.[13] There is a large radial contraction[14] due to spin-pairing (range of Mn^{II}−N and Mn^{II}−O distances in high-spin species is 2.1−2.3 Å).

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Table 2. Selected Bond Distances (Å) and Angles (deg) and Their Estimated Standard Deviations for $[M(HL)_2]\cdot CH_2Cl_2$

	M = Mn	M = Fe
	Distances	
M−N1	1.990(3)	1.968(6)
M−N3	1.873(3)	1.841(7)
M−O1	1.891(3)	1.912(5)
N2−O1	1.357(4)	1.333(8)
N3−N4	1.322(4)	1.298(8)
	Angles	
N3−M−N3A	179.5(2)	177.4(4)
N3−M−O1	80.3(1)	81.2(3)
N3−M−O1A	100.1(1)	96.9(3)
N3−M−N1A	101.9(1)	103.0(3)
N3−M−N1	77.7(1)	78.9(3)
O1−M−O1A	93.6(2)	92.7(4)
O1−M−N1	157.9(1)	160.0(3)
N1−M−N1A	89.7(2)	89.9(4)
O1A−M−N1	92.6(1)	92.1(2)

Table 3. Magnetic Moment and EPR Spectral Data (X-band)

compd	magnetic moment[a] μ_{eff}, μ_B		EPR $g_{\|}$	$g_{\perp}$	$A_{\|}$, G	$A_{\perp}$, G
$[Mn(HL)_2]$[b]	1.93	*c*	1.982	2.065	170	60
		d	1.980	2.063	160	65
$[Mn(MeL)_2]$[e]	1.89	*c*	1.977	2.062	170	60
		d	1.978	2.060	170	65
$[Fe(HL)_2]PF_6$	1.98	*c*	1.987	2.137		
$[Fe(MeL)_2]PF_6$	2.01	*c*	1.982	2.141		

[a] In solid state (298 K). [b] In dichloromethane−toluene solution (298 K), $g_{iso} = 2.035$, $A_{iso} = 94$ G. [c] In 1:1 dichloromethane−toluene solution at 77 K. [d] In polycrystalline $[Fe(RL)_2]$ host with 1% $[Mn(RL)_2]$ as dopant. [e] In dichloromethane−toluene solution (298 K), $g_{iso} = 2.041$, $A_{iso} = 90$ G.

The Fe−N[a], 1.841(7) Å, and Fe−N[p], 1.968(6) Å, distances are ∼0.03 Å shorter than Mn−N[a] and Mn−N[p] distances. In effect, the iron(II) atom is drawn closer to the azopyridine fragment and this is also reflected in the larger N[a]−M−N[p] bite angle for iron (M = Fe, 78.9(3)°; M = Mn, 77.7(1)°). These observations are consistent with the trend in low-spin radii:[14] $Mn^{II} > Fe^{II}$. However, the Fe−O[o] distance, 1.912(5) Å, is slightly longer than the Mn−O[o] distance. The reason for this is the inflexibility of the conjugated ligand frame, the frames of the two complexes being nearly exactly superposable. As the smaller iron(II) atom adjusts to N[p], N[a] chelation, it becomes distanced from O[o].

There is a significant $t_2 \rightarrow \pi^*$(azo) back-bonding component[11a] to the strong N[p], N[a] affinity for the bivalent d^5 and d^6 ions as seen in the relatively long, ∼1.30 Å, azo N=N length (∼1.25 Å in uncoordinated state).[15] The ready accessibility of the π^*-(azo) orbital for back-bonding is consistent with its relatively low energy as reflected in the reduction potential data; vide supra.

Spin States and EPR Spectra. The $[Fe(RL)_2]$ complexes are diamagnetic while $[Mn(RL)_2]$ and $[Fe(RL)_2]^+$ have a low-spin d^5 configuration ($S = {}^1/_2$). Magnetic moments and EPR spectral data are listed in Table 3. In dichloromethane−toluene solution at room temperature, $[Mn(RL)_2]$ displays a six-line (^{55}Mn, $I = 5/2$) isotropic EPR spectrum with $A_{iso} \sim 90$ G. When the solution is frozen at 77 K, the spectrum becomes axial, both components being hyperfine-split. A virtually identical spectrum is furnished by polycrystalline $[Fe(RL)_2]$ doped with 1% $[Mn(RL)_2]$ (Figure 3, Table 3).

In principle, $[Mn(RL)_2]$ has rhombic symmetry, but in practice, the rhombic component of the ligand field is not resolved. The EPR spectrum of $[Fe(RL)_2]PF_6$ in frozen glass is also axial,[16] Figure 3.

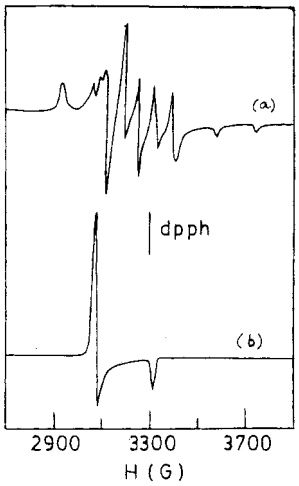
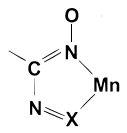


Figure 3. (a) X-band EPR spectrum of polycrystalline $[Fe(HL)_2]$ doped with 1% $[Mn(HL)_2]$ at 298 K. (b) X-band EPR spectrum of $[Fe(HL)_2]$-PF_6 in frozen 1:1 dichloromethane−toluene solution at 77 K.

Among bivalent 3d ions, manganese(II) has the highest spin-pairing energy,[17] and only very strong-field ligands can induce low-spin character. Such species are therefore relatively uncommon.[13a] It has been argued that chelate rings of type **7**[10c,13a,18] incorporating oximato-*N* binding can induce low-spin



X = NPh, O

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character in manganese(II), consistent with the large ligand field splitting associated with such binding.[19] A notable finding of the present work is that oximato-*O* coordination can also be strong enough (note the short M−O distances) and as effective in sustaining spin-pairing.

Concluding Remarks

It is demonstrated that the rare mononuclear oximato-*O* coordination is achievable via juxtaposition of azopyridine and azooxime functions. In spite of O-binding, bischelation of RL^- is able to induce a low-spin configuration for manganese(II) in an axial ligand field. The rigidity of the ligand skeleton finds expression in the bond length trends: M−N, $Mn^{II} > Fe^{II}$ but M−O, $Mn^{II} < Fe^{II}$.

Facile one-electron azo reduction characterizes coordinated RL^-. The reduced ligand can be stabilized via binding to Co^{III}. With 4d and 5d elements, HRL affords mono- and multinuclear species with variable azo reduction levels. These and other findings are under scrutiny and will be reported in the future.

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Experimental Section

Physical Measurements. A Hitachi 330 spectrophotometer was used to record UV−vis spectra. EPR spectra were recorded in the X-band on a Varian E-109 spectrometer fitted with a quartz dewar. The spectra were calibrated with respect to DPPH ($g = 2.0037$). Magnetic susceptibilities were measured with a model 155 PAR vibrating-sample magnetometer fitted with a Walker Scientific L75FBAL magnet. A Perkin-Elmer 2400 Series(II) elemental analyzer was used to collect microanalytical data (CHN). Electrochemical measurements were performed under a nitrogen atmosphere on a PAR 370-4 electrochemistry system using solvents and supporting electrolytes purified/prepared as before.[20] All potentials are referenced to the saturated calomel electrode (SCE). Solution electrical conductivities were measured with the help of a Philips PR 9500 bridge, the solute concentrations being $\sim 10^{-3}$ M.

Synthesis of Ligands, HRL, 5. The details of the synthesis are given below for the R = H ligand (the R = Me ligand was prepared similarly).

2-(Pyridylazo)benzaldoxime, HHL, 5 (R = H). To a 1:1 ethanolic solution (yellow) of 2.50 g (0.023 mol) of 2-hydrazinopyridine was added dropwise 2.43 g (0.022 mol) of benzaldehyde. The contents were allowed to stir for 2 h, and a white precipitate of the hydrazone, **4** (R = H), separated out. This was collected, washed with 1:1 aqueous ethanol, and then dried in vacuo over fused $CaCl_2$. Yield: 3.60 g (80%).

To a suspension of 3.60 g (0.018 mol) the hydrazone **4** in 25 mL of dry ethanol was added 1.85 g (0.018 mol) of freshly prepared *n*-$BuNO_2$. To this mixture was added a solution of sodium methoxide (prepared by refluxing 0.85 g of metallic sodium in 25 mL of dry methanol). The mass was heated to reflux for 2 h, affording an intensely red solution, which was cooled and filtered into an ice-cold solution of sodium hydroxide (prepared by dissolving 1.0 g of NaOH in 100 mL of water). After 12 h, the solution was extracted with diethyl ether. The aqueous layer was separated from the mixture, cooled to 0 °C, and finally acidified with a 1 N ice-cold solution of sulfuric acid to neutral pH when the HHL ligand separated out as a yellow precipitate. This was filtered off, washed with water, and dried in vacuo over fused $CaCl_2$. Yield: 1.80 g (44%). Anal. Calcd for **5** (R = H), $C_{12}H_{10}N_4O$: C, 63.72; H, 4.42; N, 24.77. Found: C, 63.65; H, 4.38; N, 24.68. Mp: 103−105 °C.

Anal. Calcd for **5** (R = Me), $C_{13}H_{12}N_4O$: C, 65.00; H, 5.00; N, 23.33. Found: C, 64.91; H, 5.05; N, 23.26. Mp: 100−102 °C.

Synthesis of Complexes. Dichloromethane Adduct of Bis[(2-pyridylazo)-1-benzaldoximato]manganese(II), $[Mn(HL)_2]\cdot CH_2Cl_2$. The complex was prepared by adding a methanolic solution (10 mL) of HHL (0.066 g, 0.29 mmol) to a solution containing $Mn(ClO_4)_2\cdot 6H_2O$ (0.050 g, 0.14 mmol), and the deep violet solution so formed was stirred for 2 h. The deposited dark violet crystalline solid was filtered off, washed several times with 1:1 aqueous methanol, and dried in vacuo over fused $CaCl_2$. It was finally recrystallized from dichloromethane−hexane. Yield: 0.062 g (84%). Anal. Calcd for $C_{25}H_{20}N_8O_2Cl_2Mn$: C, 50.85; H, 3.59; N, 18.98. Found: C, 50.78; H, 3.56; N, 18.90. UV−vis (CH_2Cl_2; λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 650 (4200); 550 (5200); 490 (4400); 420 (5200).

The complex $[Mn(MeL)_2]\cdot CH_2Cl_2$ was prepared similarly. Anal. Calcd for $C_{27}H_{22}N_8O_2Cl_2Mn$: C, 52.68; H, 3.57; N, 18.21. Found: C, 52.59; H, 3.54; N, 18.27. UV−vis (CH_2Cl_2; λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 640 (4400); 550 (5500); 480 (4800); 410 (5300).

Dichloromethane Adduct of Bis[(2-pyridylazo)-1-benzaldoximato]iron(II), $[Fe(HL)_2]\cdot CH_2Cl_2$. The dark green complex was prepared by the same procedure as above, replacing $Mn(ClO_4)_2\cdot 6H_2O$ by $Fe(ClO_4)_2\cdot 6H_2O$. Yield: 0.062 g (90%). Anal. Calcd for $C_{25}H_{20}N_8O_2Cl_2Fe$: C, 50.77; H, 3.38; N, 18.96. Found: C, 50.69; H, 3.33; N, 18.88. UV−vis (CH_2Cl_2; λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 700 (6600); 540 (5000); 475 (5600); 400 (10 600).

Anal. Calcd for $[Fe(MeL)_2]\cdot CH_2Cl_2$, $C_{27}H_{24}N_8O_2Cl_2Fe$: C, 52.36; H, 3.88; N, 18.10. Found: C, 52.29; H, 3.83; N, 18.15. UV−vis (CH_2Cl_2; λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 700 (6300); 550 (4900); 475 (5200); 400 (10 100).

Table 4. Crystallographic Data for $[M(HL)_2]\cdot CH_2Cl_2$

	M = Mn	M = Fe
empirical formula	$C_{25}H_{19}N_8O_2Cl_2Mn$	$C_{25}H_{19}N_8O_2Cl_2Fe$
fw	589.32	590.23
space group	*I*2/*a*	*I*2/*a*
a, Å	14.142(7)	14.254(6)
b, Å	10.721(7)	10.742(6)
c, Å	16.933(10)	16.719(8)
β, deg	93.01(4)	92.35(4)
V, Å^3	2570(3)	2558(2)
Z	4	4
T, °C	293(2)	293(2)
λ, Å	0.710 73	0.710 73
ρ_{calcd}, g cm^{-3}	1.523	1.533
μ, cm^{-1}	7.62	8.39
R1[a] [$I > 2\sigma(I)$]	0.0547	0.0821
wR2[b] [$I > 2\sigma(I)$]	0.1251	0.1633
GOF	1.045	1.042

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

Bis[(2-pyridylazo)-1-benzaldoximato]iron(III) Hexafluorophosphate, $[Fe(HL)_2]PF_6$. $[Fe(HL)_2]$ (0.05 g, 0.1 mmol) was dissolved in 25 mL of acetonitrile, and NH_4PF_6 (0.016 g, 0.1 mmol) was added as the supporting electrolyte. The dark green mixture was stirred at room temperature for 0.25 h and then subjected to exhaustive oxidation at 0.9 V vs SCE under nitrogen. The oxidation was stopped when the coulomb count corresponded to one-electron oxidation and the color of the solution became reddish pink. The solvent was evaporated in vacuo to obtain the brown solid in pure form. Yield: 0.059 g (92%). Anal. Calcd for $C_{24}H_{18}N_8O_2PF_6Fe$: C, 42.17; H, 2.64; N, 16.39. Found: C, 42.13; H, 2.63; N, 16.31. UV−vis (CH_2Cl_2; λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 560 (1700); 440 (1800).

The complex $[Fe(MeL)_2]PF_6$ was electrosynthesized in a similar fashion. Anal. Calcd for $C_{26}H_{22}N_8O_2PF_6Fe$: C, 45.95; H, 3.24; N, 16.49. Found: C, 45.88; H, 3.21; N, 16.41. UV−vis (CH_2Cl_2; λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 565 (1800); 445 (1900).

X-ray Structure Determinations. Crystals of $[Mn(HL)_2]\cdot CH_2Cl_2$ (0.3 × 0.4 × 0.3 mm) and $[Fe(HL)_2]\cdot CH_2Cl_2$ (0.4 × 0.3 × 0.3 mm) were grown by slow diffusion of hexane into dichloromethane solutions. For both complexes, cell parameters were determined by the least-squares fit of 30 machine-centered reflections (2θ 15−30°). Data were collected by the ω-scan technique in the 2θ range 3−50° on a Siemens R3m/V four-circle diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å). Two check reflections measured after every 98 reflections showed no intensity reduction. Data were corrected for Lorentz−polarization effects, and an empirical absorption correction was performed on both sets of data on the basis of azimuthal scans[21] of six reflections. For $[Mn(HL)_2]\cdot CH_2Cl_2$, 2453 reflections were collected, of which 2280 were unique and 1673 satisfying $I > 2\sigma(I)$ were used for structure solution. In the case of $[Fe(HL)_2]\cdot CH_2Cl_2$, the corresponding numbers are 2442, 2257, and 1023, respectively.

All calculations for data reduction and structure solution and refinement were done using programs of SHELXTL, Version 5.03.[22] Both the structures were solved by direct methods and were refined by full-matrix least-squares calculations on F^2. All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were included in calculated positions. Significant crystal data are listed in Table 4.

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Supporting Information Available: X-ray crystallographic files, in CIF format, for $[Mn(HL)_2]\cdot CH_2Cl_2$ and $[Fe(HL)_2]\cdot CH_2Cl_2$. The material is available free of charge via the Internet at http://pubs.acs.org.

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