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Mononuclear and Binuclear Metal Complexes of 1,3-Bis(2-pyridylimino)isoindolines

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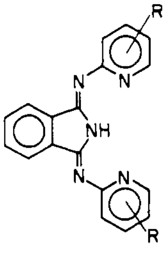
Condensation of 1,2-dicyanobenzene and 2-amino-4-methylpyridine resulted in the formation of a ligand, 4′-MeLH, which in its anionic form functions as a tridentate chelate. Metal complexes were prepared with metal to ligand ratios of 1:1 and 1:2. The 1:1 complexes also contain acetate as a ligand while in the 1:2 complex the two tridentate ligands provide a pseudooctahedral environment about the metal ion. An analogous binucleating ligand was prepared by reaction of 1,2,4,5-tetracyanobenzene and 2-amino-4-*sec*-butylpyridine. This ligand, as a dianion, is capable of binding two metal ions, providing three coordination sites for each. Complexes were prepared in which the remaining coordination sites are occupied either by 4′-MeLH, resulting in two six-coordinate metal ions, or by an acetate ligand. Mononuclear and binuclear complexes were prepared with Mn(II), Fe(II), Co(II), Co(III), Ni(II), Cu(II), and Zn(II). Magnetic, spectral, and electrochemical properties of these molecules were investigated.

Introduction

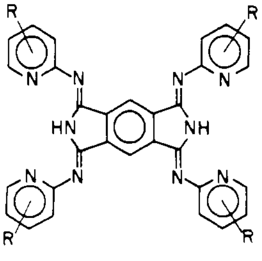
Stable metal complexes of the ligand **1** have been prepared



1

LH,[3] R = H
4′-MeLH, R = 4-CH$_3$

with ligand to metal ion ratios of 2:1 and 1:1.[2] The ligand functions as an anionic tridentate chelate capable of occupying three coplanar sites about the metal ion and forming a pseudooctahedral environment around the metal ion in the bis(ligand) complex, ML$_2$.[3] Metal complexes with M = Fe(II), Co(II), Ni(II), Zn(II), and Cd(II) have been reported, but little has been done to characterize these molecules. These complexes became of greater interest after the synthesis of the conjugated organic molecule **2**, which may function as a bridging ligand between two metal ions.[4] This molecule made it possible to prepare not only binuclear metal complexes but also polymeric metal species. The polymeric complexes were of great interest for two reasons: polynuclear complexes offer a chance to study metal–metal interactions via electrochemistry and magnetic measurements and complexes of this type are interesting candidates for reactions involving multielectron transfer. We report here the preparation and certain physical properties of mononuclear and binuclear metal complexes with Mn(II), Fe(II), Co(II), Co(III), Ni(II), Cu(II), and Zn(II).

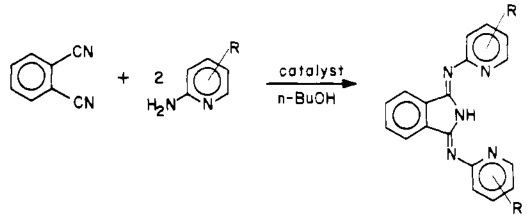


2

HL-LH,[3] R = 4′-*sec*-butyl

Results and Discussion

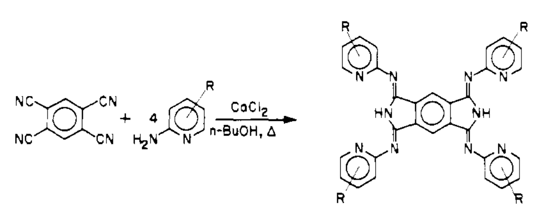
Synthesis and Characterization of the Ligands. Two general syntheses of mononucleating 1,3-bis(arylimino)isoindoline ligands RLH (**1**) involving metal ion-assisted condensation of phthalonitrile with a 2-aminopyridine or other 2-amino heterocycles were described earlier[5] (eq 1).



(1)

1

The binucleating ligand **2** was prepared in a similar manner by these methods as shown in eq 2 and 3. The method of choice afforded the binucleating ligand in good yield from a one-flask synthesis utilizing an alkaline-earth salt (anhydrous CaCl$_2$) to catalyze the condensation of tetracyanobenzene with 4 equiv of aromatic amine. A second method, a template-type



(2)

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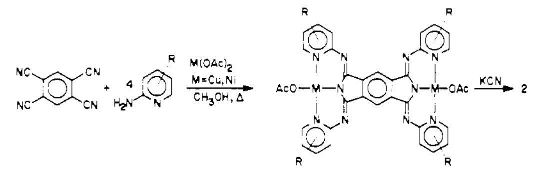

(3)

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(1) (a) California Institute of Technology, Pasadena, CA. (b) Ford Motor Co., Dearborn, MI.

(2) (a) Elvidge, J. A.; Linstead, R. P. *J. Chem. Soc.* **1952**, 5000. (b) Robinson, M. A.; Trotz, S. I.; Hurley, T. J. *Inorg. Chem.* **1967**, *6*, 392.

(3) Mononucleating ligands, **1**, will be denoted as RLH; substituents on the pyridine ring precede the abbreviation, e.g. 4′-MeLH, where the prime designates the position on the pyridine ring. Mononuclear metal complexes are of two types: complexes with metal to ligand ratio of 1:1, ML(OAc), where L is the anion of the ligand LH and OAc also is bound to the metal, and complexes with metal to ligand ratio 1:2, ML$_2$, with two anionic tridentate ligands. HL–LH denotes the binucleating ligand, **2**, with *sec*-butyl groups on the 4-position of the pyridine rings. Binuclear complexes containing the dianion of the ligand are denoted (OAc)ML–LM(OAc) or (4′-MeL)ML–LM(4′-MeL) depending on the other ligands bound to the metals.

(4) Siegl, W. O. *Inorg. Chim Acta* **1977**, *25*, L65.

(5) Siegl, W. O. *J. Org. Chem.* **1977**, *42*, 1872.

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Table I. Yields, Melting Points, and Relative Solubilities for the Binucleating Ligands **2**

compd	derived from (amine)	yield	mp, °C	rel solubility
2a	2-aminopyridine	90	324–326	2.6
2b	2-amino-4-methylpyridine[a]	59	340–341	1
2c	2-amino-5-methylpyridine	79	345–348 dec	ND
2d	2-amino-3,5-dimethylpyridine	ND[b]	375–377	ND
2e	2-amino-4-ethylpyridine	45	353–355	72
2f	2-amino-4-*n*-propylpyridine[a]	58	357–359	52
2g	2-amino-4-*sec*-butylpyridine	83	369–371	105
2h	2-amino-4-*tert*-butylpyridine[a]	44	435–437	1.7
2i	2-amino-4-*n*-amylpyridine	49	317–318	11

[a] Ligand isolated as a monohydrate. [b] ND = not determined.

synthesis, utilized Ni(II) or Cu(II) acetate to facilitate the condensation, affording initially the metal complex **3**, which was subsequently treated with KCN to produce free binucleating ligand, **2**. Attempts to prepare ligand **2** via alkoxide catalysis resulted in the production of significant amounts of blue-purple pigment, possibly phthalocyanine impurities.

A series of binucleating ligands was prepared from tetracyanobenzene and various alkyl-substituted 2-aminopyridines for the purpose of obtaining a ligand with acceptable solubility in organic solvents. The bridging ligands are all high-melting, yellow crystalline solids and with the exception of the 4′-*n*-propyl and 4′-*tert*-butyl derivatives, which are somewhat hygroscopic, have long shelf lives. Solubilities vary over a range of 2 orders of magnitude as shown in Table I, with the 4′-*sec*-butyl derivative being the most soluble; unless indicated otherwise, all work described in this paper was carried out with the 4′-*sec*-butyl-substituted ligand, HL–LH.

The rather complex infrared spectra of the bridging ligands contain characteristic bands in the 1650–1500-cm^{-1} region, ca. 1640 (m–s) and 1590 (s) (also a band at ca. 1540 (m) observed for the 4′-alkyl-substituted ligands), which undergo changes upon chelation of a metal ion. The infrared spectrum of the chelated ligand exhibits only a much weaker band at 1640 cm^{-1} and a shift of the 1590-cm^{-1} band to lower energy; two new bands appear at ca. 1610 and 1525–1515 cm^{-1}. These generalizations appear to be true for a variety of substituted ligands and metal ions.

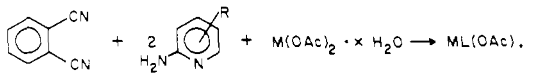
Proton NMR spectra were obtained only for the most soluble of the 4′-alkyl-substituted ligands. The benzo protons appear as a singlet at 8.60–8.70 ppm ($CDCl_3$), and the pyridyl protons are shifted in the general order of $H_5 < H_3 < H_6$ as reported earlier for the mononucleating ligands **1**.[5]

Synthesis and Characterization of Mononuclear Metal Complexes

Mononuclear divalent metal complexes of the type ML(OAc)[3] (M = Mn, Fe, Co, Ni, Cu, and Zn) are readily formed upon treatment of the free ligand with excess metal acetate in alcohol (eq 4). The reaction is rapid at ambient temperature, affording highly colored crystalline solids. All were air stable and thermally stable in the solid state, although Mn(II), Fe(II), and Co(II) complexes were, to some extent, air sensitive in solution; the latter were prepared under an inert atmosphere.

$$\mathbf{1} + M(OAc)_2{\cdot}xH_2O \rightarrow ML(OAc) \qquad (4)$$

The Co(II), Ni(II), Cu(II), and Zn(II) complexes were also prepared by a template reaction directly from phthalonitrile, amine, and metal salt (eq 5).[6]



(5)

With the exception of the Zn(II) complex, all of the complexes, ML(OAc), were paramagnetic. The infrared spectra are dominated by ligand bands; changes observed in the spectrum of the mononucleating ligand upon coordination to a metal ion are analogous to those described above for the bridging ligand.

Treatment of a divalent transition metal salt (Mn, Fe, Co, Ni, Cu, Zn) with 2 equiv of chelating ligand afforded the neutral complex ML_2 in high yields, as indicated in eq 6. For metal salts with very poor bases as counterions, e.g., ClO_4^-, an amine base was usually added to facilitate deprotonation of the ligand; however, with Cl^- or OAc^-, no external base was required.

$$MX_2 + 2LH \rightarrow ML_2 + 2HX \qquad (6)$$

Alternatively, the ML_2-type complexes could be prepared in a two-step process by subsequently treating the product of eq 4 with a second equivalent of chelating ligand, as shown in eq 7. The two-step approach allows the preparation of complexes with two different ligands, as indicated in eq 8. The synthesis of such unsymmetrically substituted (chelated) complexes was usually carried out under conditions whereby the product precipitated from solution, thus minimizing the possibility of ligand scrambling. Evidence that asymmetric synthesis (eq 8) could be carried out for Co(II) without ligand scrambling was obtained from cyclic voltammetric measurements on the mixed-ligand complex Co(4′-MeL)(5′-ClL). The complex Co(4′-MeL)(5′-ClL) exhibited a single wave at 0.081 V vs. NHE, whereas a mixture would have given two waves at −0.094 V vs. NHE for $Co(4'\text{-MeL})_2$ and at 0.235 V vs. NHE for $Co(5'\text{-ClL})_2$.

$$ML(OAc) + LH \rightarrow ML_2 \qquad (7)$$

$$ML(OAc) + L'H \rightarrow MLL' \qquad (8)$$

The observation that ligand exchange could occur in solution, even at room temperature, was made from a series of metal-exchange experiments. Cupric ion readily replaces substitution-labile metal ions such as Co(II), Ni(II), and Zn(II) from complexes of types ML(OAc) and ML_2. However, no exchange occurs with cupric ion and substitution-inert Co(III) in $Co(4'\text{-MeL})_2PF_6$.

The ML_2 complexes of metal ions with unfilled d shells are all dark, intensely colored crystalline solids. In general, the ML_2 complexes have much greater solubilities in organic solvents than the corresponding ML(OAc) complexes; typically, they are soluble in solvents of low polarity such as cyclohexane or toluene but only sparingly soluble in very polar solvents such as methanol.[7] Infrared spectra are essentially identical with spectra of the corresponding ML(OAc) complexes. The NMR spectra, magnetic properties, and electrochemistry are discussed in a later section.

The Co(II) complex $Co(4'\text{-MeL})_2$ was oxidized with ceric ion to the corresponding Co(III) complex, diamagnetic $Co(4'\text{-MeL})_2^+$, and isolated as its BF_4^-, BPh_4^-, and PF_6^- salts. Attempts to similarly prepare $Mn(4'\text{-MeL})_2^+$ were unsuccessful. Complexes of Fe(III) could be prepared by ferricinium oxidation of $Fe(4'\text{-MeL})_2$; however, they were unstable in polar solvents, apparently dissociating one of the tridentate ligands.

Synthesis and Characterization of Binuclear Complexes. The preparation of homonuclear complexes with the binucleating ligand HL–LH, **2**, parallels the preparation of mononuclear

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(6) Siegl, W. O. *Inorg. Nucl. Chem. Lett.* **1974**, *10*, 825.

(7) The Cu(II) complex, $Cu(4'\text{-MeL})_2$, is considerably more soluble in organic solvents than other $M(4'\text{-MeL})_2$ complexes. Solid samples of $Cu(4'\text{-MeL})_2$ usually contained small amounts of the ligand 4′-MeLH because the solubility of the ligand was similar to that of the metal complex. For this reason, the more soluble *sec*-butyl-substituted ligand 4′-*sec*-butylLH was used in order to avoid coprecipitation of the Cu(II) complex and unreacted ligand.

Table II. Magnetic Susceptibility Data for Mononuclear and Binuclear Complexes per Metal Ion

complex	μ_{eff}, μ_B (298 K)	complex	μ_{eff}, μ_B (298 K)
Mn(4′-MeL)$_2$	5.92	(4′-MeL)MnL–LMn(4′-MeL)	5.66
Fe(4′-MeL)$_2$	5.12	(4′-MeL)FeL–LFe(4′-MeL)	5.13
Co(4′-MeL)$_2$	4.85	(4′-MeL)CoL–LCo(4′-MeL)	4.65
Ni(4′-MeL)$_2$	3.10	(4′-MeL)NiL–LNi(4′-MeL)	3.07
Cu(4′-MeL)$_2$	1.85	(4′-*sec*-butylL)CuL–LCu(4′-*sec*-butylL)	1.83

complexes with the mononucleating ligand **1**. The simplest binuclear complexes were obtained by treatment of the bridging ligand with an excess of metal acetate, as shown in eq 9 [M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II), and Zn(II)].[3]

$$\text{HL–LH} + \text{excess } \text{M(OAc)}_2 \rightarrow \text{(AcO)ML–LM(OAc)} \quad (9)$$

The same binuclear complexes of Ni(II) and Cu(II) were obtained via the template route shown in eq 3, although the purity of complexes obtained via the template route was lower. The relatively low solubility of the (AcO)ML–LM(OAc) complexes made purification using solution techniques impractical, and accordingly eq 9 was the preferred route. The new complexes are intensely colored and have high thermal stability. The characteristic changes observed in the infrared spectrum upon coordination of ligand **2** with metal ions was discussed earlier.

The binuclear complexes, (OAc)ML–LM(OAc) (**3**), react readily with mononucleating ligand, LH (**1**), as shown in eq 10, a procedure analogous to the formation of MLL′ described by eq 8.

$$\text{(AcO)ML–LM(OAc)} + 2\text{LH} \rightarrow \underset{\mathbf{4}}{\text{LML–LML}} \quad (10)$$

The preparation of this new series of binuclear complexes, **4**, can also be approached by treating the bridging ligand with two equivalents of ML(OAc) according to eq 11.

$$\text{HL–LH} + 2\text{ML(OAc)} \rightarrow \underset{\mathbf{4}}{\text{LML–LML}} \quad (11)$$

The two metal ions in the complexes LML–LML (**4**) are encapsulated by organic ligands similar to ML$_2$ and accordingly have significantly increased solubility in organic solvents when compared with the binuclear complexes **3**, allowing the application of solution techniques for characterization. The monomeric nature of these complexes is suggested by a molecular weight determination (in toluene) on ((4′-*sec*-butyl)L)NiL–LNi((4′-*sec*-butyl)L) which yielded a value of 1699 compared with a calculated value of 1680.

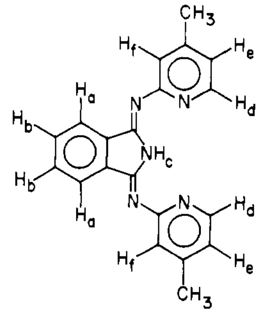
Attempts to prepare (4′-MeL)FeL–LFe(4′-MeL) by the approaches outlined above (eq 10 and 11) were unsuccessful. The mononuclear metal complex Fe(4′-MeLH)Br$_2$ (coordinated 4′-MeLH is protonated presumably at one of the imine nitrogens), obtained from the reaction of 4′-MeLH with excess ferrous bromide in alcohol, proved a useful starting material for preparing (4′-MeL)FeL–LFe(4′-MeL). Treatment of deprotonated binucleating ligand with an excess of Fe(4′-MeLH)Br$_2$ yielded the desired binuclear Fe(II) complex.

The infrared spectra of binuclear M(II) complexes are very similar to those of ML$_2$. Proton NMR spectra and magnetic and electrochemical properties are discussed below.

The cobalt complex (4′-MeL)CoL–LCo(4′-MeL) was successfully oxidized with ceric ion to the corresponding Co(III) complex and isolated as its BPh$_4^-$ and PF$_6^-$ salts.

Magnetic Susceptibility. Table II gives values of μ_{eff} for both mononuclear and binuclear M(II) complexes, all of which are high spin. Magnetic measurements have been made on (AcO)CuL–LCu(OAc) over a range of temperatures from liquid helium to room temperature. The results of these measurements show a very slight metal–metal interaction with $J = -1$ cm^{-1}.[8] In general, the magnetic moments of binuclear complexes are slightly lower per metal ion than the moments of the corresponding mononuclear complexes. It is unlikely that these lower values result from magnetic coupling but are probably attributable to trace impurities.

Table III. Proton NMR Data for Mononuclear Complexes in CDCl$_3$^{a}



proton	4′-MeLH	Zn(II)	Co(III)	Co(II)	Ni(II)	Fe(II)
H$_a$	8.01	8.04	8.13	26.5	13.0	11.0
H$_b$	7.54	7.55	7.76	26.0	11.9	9.0
H$_c$	13.97					
H$_d$	8.40	7.93	7.37	106		
H$_e$	6.83	6.35	6.62	35.6	33.1	31.6
H$_f$	7.23	7.07	7.10	43.7	51.1	41.5
CH$_3$	2.30	2.07	2.31	−15.7	−6.3	−24.8

^{a} Values are given in ppm vs. Me$_4$Si at 34 °C.

Electronic Absorption Spectra. The visible spectra of all mononuclear and binuclear complexes show intense (ϵ ~20–50 000) ligand absorptions in the range 400–450 nm. All of the complexes are yellow in dilute solution as is the ligand. For the metal complexes, the high-energy ligand absorptions are fairly broad so that concentrated solutions (~10 mM) are nearly black, and ligand field absorptions could not be identified.

The mononuclear iron(II) complex shows two broad absorptions at 650 and 740 nm (ϵ ~800) in addition to the ligand absorptions. These bands may be assigned, due to their position and intensity, as Fe(II) → L charge-transfer bands.

Proton NMR Spectra. Proton NMR spectra were obtained for the mononuclear Fe(II), Co(II), Co(III), Ni(II), and Zn(II) complexes, M(4′-MeL)$_2$, to identify the complexes and to test their purity (Table III). Spectra of the Mn(II) and Cu(II) complexes are severely broadened due to the slow electron-relaxation times of these metals. In the diamagnetic complexes, the protons could be assigned with no ambiguity from the splitting pattern of the peaks. In contrast, peak widths for the paramagnetic complexes of approximately 0.2 ppm totally overwhelmed any splitting. For this reason assignment was more difficult and less reliable. In general, NMR spectra of all the paramagnetic complexes are very similar. The protons in the paramagnetic species were assigned by using integration data and trends observed in the diamagnetic complexes and in other similar paramagnetic complexes.[9] The magnitude of the shift of the paramagnetic molecules was found to be dependent on the metal involved. Among the paramagnetic complexes, the protons α to the nitrogen of the pyridine ring, H$_d$, were observed only for the Co(II) complex and appear far downfield at 106 ppm. This resonance is extremely broad due to the nearness of these protons to the paramagnetic center. Similar behavior was reported for Co(phen)$_3^{2+}$.[10]

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(8) Hendrickson, D. N., unpublished results.
(9) Cramer, R. E.; Drago, R. S. *J. Am. Chem. Soc.* **1970**, *92*, 66.
(10) LaMar, G. N.; Van Hecke, G. R. *Inorg. Chem.* **1970**, *9*, 1546.

Table IV. Electrochemical Potentials for Mononuclear and Binuclear Complexes As Measured in DMF (vs. NHE)

complex	M(II/III) E^f	M(II/III) $E_{pa} - E_{pc}$[a]	n[b]	ligand waves, E^f
Mn(4′-MeL)$_2$	0.310	90	1.00	−1.438, −1.652
Fe(4′-MeL)$_2$	0.130	65	0.99	−1.460, −1.680
Co(4′-MeL)$_2$	−0.094	90	0.95	−1.420, −1.680
Ni(4′-MeL)$_2$	0.954	90	1.01	−1.435, −1.664
Zn(4′-MeL)$_2$				−1.470, −1.660
(4′-MeL)MnL–LMn(4′-MeL)	0.323	240	2.04	−1.173, −1.418, −1.600
(4′-MeL)FeL–LFe(4′-MeL)	0.182	100	2.04	−1.204, −1.494, −1.642, −1.758
(4′-MeL)CoL–LCo(4′-MeL)	−0.045	160	1.90	−1.185, −1.455, −1.640
(4′-MeL)NiL–LNi(4′-MeL)	0.976[c]		2.10	−1.190, −1.477, −1.650

[a] Anodic peak to cathodic peak separation of metal wave in cyclic voltammetry given in millivolts. [b] Number of electrons involved in metal oxidation determined by constant-potential electrolysis. [c] Potentials were obtained by differential-pulse voltammetry due to low solubility.

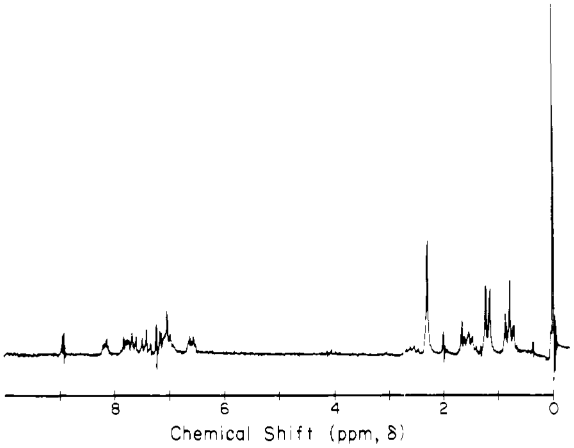

Figure 1. Proton NMR spectrum of (4′-MeL)CoL–LCo(4′-MeL)(ClO$_4$)$_2$ in CDCl$_3$ at 34 °C. Integration of the *sec*-butyl protons (0.8 and 1.1 ppm) and the methyl protons (2.3 ppm) provide evidence for describing the complex as binuclear.

The binuclear products gave very complex spectra. The diamagnetic Co(III) complex, however, gave a particularly well-resolved spectrum (Figure 1), permitting analysis. Integrations of *sec*-butyl protons and methyl protons gave the expected ratio for one binucleating ligand and two mononucleating ligands per complex, helping to substantiate that this complex is binuclear and not a higher order polymer. The aromatic protons were difficult to assign due to overlapping peaks in this region of the spectrum.

The use of NMR spectroscopy to investigate intramolecular electron transfer in the mixed-valent Co^{II}Co^{III} complex was attempted. Equilibrium concentrations of (4′-MeL)CoL–LCo(4′-MeL)$^+$ were generated by mixing equimolar amounts of (4′-MeL)CoL–LCo(4′-MeL) and (4′-MeL)CoL–LCo(4′-MeL)$^{2+}$. The mixture gave a spectrum that is very similar to the composite spectrum of (4′-MeL)CoL–LCo(4′-MeL) plus (4′-MeL)CoL–LCo(4′-MeL)$^{2+}$ but with several additional peaks. One of the peaks, which is very broad, sharpens into a single peak at −1.5 ppm at higher temperatures (∼50 °C) and resolves into two peaks at 4.3 and −10.7 ppm as the temperature is lowered (∼−50 °C). This behavior is typical of a process whose rate is on the order of the NMR time scale. However, due to the complexity of these spectra and the chemical structures involved, it was not possible to assign this process to intramolecular electron transfer.

Electrochemistry. Electrochemical measurements have been made on all mononuclear and binuclear complexes (Table IV). Most complexes exhibited quasi-reversible behavior except for Cu(4′-*sec*-butyl L)$_2$ and all complexes having a single tridentate ligand, M(4′-MeL)OAc, for which both anodic and cathodic cyclic voltammetric waves could not be obtained. Cyclic voltammograms of mononuclear complexes, M(4′-MeL)$_2$ (e.g., Figure 2) consist of a metal oxidation wave and two reductions attributable to the ligand. The anodic and cathodic peak currents for the M(II/M(III) couple are equal, but the peak potential separation is larger than the expected 58 mV for a reversible one-electron process.[11] Coulometry at potentials anodic of the metal oxidations verify that these are one-electron processes with $n = 1.0 \pm 0.05$.

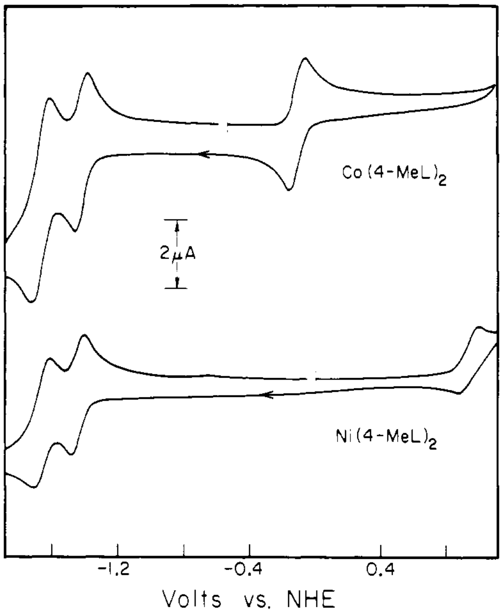

Figure 2. Cyclic voltammograms of DMF solutions: upper figure Co(4′-MeL)$_2$; lower figure Ni(4′-MeL)$_2$.

The metal reduction potentials of the binuclear complexes are very similar to potentials measured for the mononuclear complexes. The metal oxidations in the binuclear complexes are quite broad (Figure 3) and constant-potential electrolysis anodic of these waves yields n values of 2.0 ± 0.1. This behavior is consistent with two closely spaced one-electron oxidations resulting in one broad wave. Similar behavior has been observed for some ruthenium dimers.[12] In general, the factors determining the potential difference between two consecutive redox processes in binuclear complexes are complex.[13] A separation of the two one-electron waves by 100 mV or less sets a range for the constant describing the comproportionation equilibrium (eq 12; $4 \leq K_{com} \leq 50$). The lower limit of 4 corresponds to completely noninteracting metal centers, in which case one would expect a single electrochemical wave with $E_{pa} - E_{pc} = 58$ mV.[14]

$$\mathrm{M(II)M(II)} + \mathrm{M(III)M(III)}^{2+} \rightleftharpoons \mathrm{M(II)M(III)}^{+} \qquad (12)$$

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(11) Nicholson, R. S.; Shain, I. *Anal. Chem.* **1964**, *36*, 706.

(12) (a) Tom, G. M.; Creutz, C.; Taube, H. *J. Am. Chem. Soc.* **1974**, *96*, 7827. (b) Powers, M. J.; Meyer, T. J. *Inorg. Chem.* **1978**, *17*, 1785.

(13) Gagné, R. R.; Spiro, C. L. *J. Am. Chem. Soc.* **1980**, *102*, 1443.

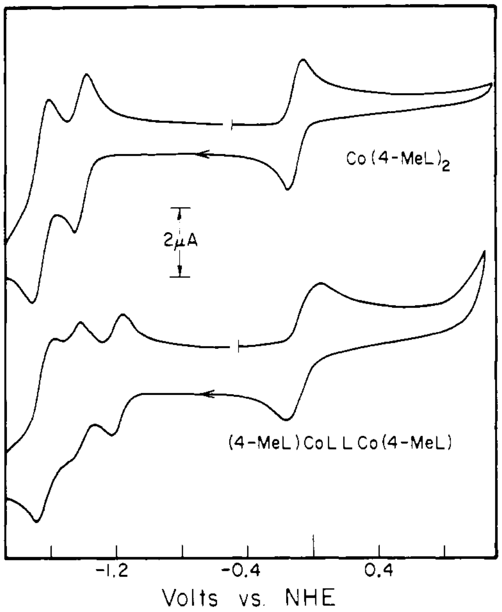

Figure 3. Cyclic voltammograms of DMF solutions: upper figure Co(4′-MeL)$_2$; lower figure (4′-MeL)CoL–LCo(4′-MeL).

Table V. Cobalt(III)/Cobalt(II) Reduction Potentials, E^f, for Several Co(RL)$_2$[a]

complex	E^f, V	complex	E^f, V
Co(4′-MeL)$_2$	−0.094	Co(5′-ClL)$_2$	0.235
CoL$_2$	−0.031	Co(5′-NO$_2$L)$_2$	0.589
Co(4′-MeL)(5′-ClL)	0.081		

[a] Potentials were measured in DMF and are reported vs. NHE.

The electrochemical results indicate that the binuclear complexes undergo a two-electron metal oxidation with the two electrons being transferred at nearly the same potential. One would then expect longer chain polymers to undergo multielectron oxidation with all of the electrons transferred at approximately the same potential. This may be a very desirable property for utilization of these complexes as multielectron-transfer catalysts.

Cyclic voltammograms of the binuclear complexes also show three ligand reductions. Two of these reductions appear at approximately the same potential as reductions observed for the mononuclear complexes. The third ligand reduction appears at a more positive reduction potential and is presumably due to reduction of the bridging ligand. The binuclear Fe(II) complex shows a fourth reduction at even more negative potentials than the ligand reductions. The product of this reduction has not been investigated.

A series of mononuclear Co(II) complexes containing various substituents on the pyridine ring of the ligand were prepared in order to determine the effect of these substituents on the metal reduction potential (Table V). The results of these measurements show that the effect of the substituents is significant. A shift of nearly 700 mV is observed in going from a 4′-methyl to a 5′-nitro substituent. A plot of the reduction potential vs. the Hammett parameter of the substituent is approximately linear (Figure 4), as has been observed in certain other ligand systems.[15]

Thus, by changing the substituents, a large shift in reduction potential can be produced, making it possible to design a complex having specific redox chemistry. Accordingly, the reactivity of these complexes with various substrates might be significantly altered by the effects of these substituents on the reduction potential.

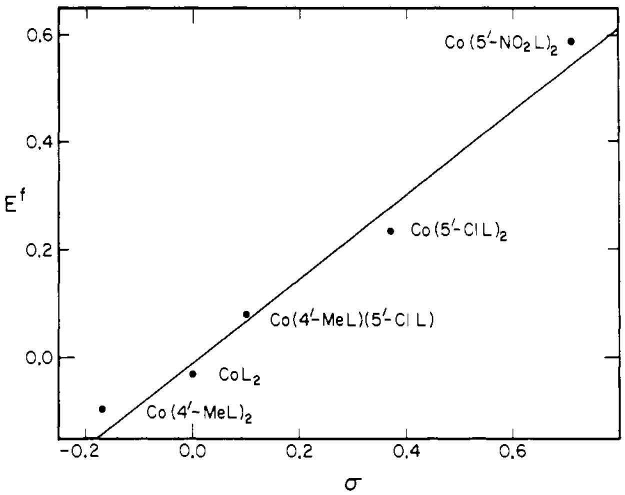

Figure 4. Half-wave potentials vs. σ_p for mononuclear Co(II) complexes containing various substituents on the isoindoline ligand.

Experimental Section

Synthesis. All organic ligands gave satisfactory carbon, hydrogen, and nitrogen analyses, while metal complexes gave satisfactory carbon, hydrogen, nitrogen, and metal analyses.

Mononuclear Chelating Ligands, RLH. The synthesis and physical and spectral data for all the mononuclear chelating isoindoline ligands, RLH, employed in this study were reported earlier.[5]

Binucleating Ligands. All of the binucleating ligands reported in Table I were prepared by the general procedure illustrated below for the 4′-*sec*-butylpyridyl derivative **2g**. Ligands with significantly lower solubility were purified by recrystallization from nitrobenzene or quinoline.

1,3,5,7-Tetrakis(2-(4-*sec*-butylpyridyl)imino)benzodipyrrole (2g). A 1 L round-bottom flask was charged with 5.81 g (0.033 mol) of 1,2,4,5-tetracyanobenzene, 22.5 g (0.15 mol) of 2-amino-4-*sec*-butylpyridine,[5] 2.61 g of anhydrous calcium chloride, and 500 mL of methanol. The mixture was stirred at ambient temperature for 7 days and then warmed gradually to reflux temperature. After 2 days at reflux, the methanol was allowed to distill off and the solvent volume was maintained by the gradual addition of *n*-butyl alcohol. The suspension in butyl alcohol was heated at reflux for an additional 7 days. The mixture was allowed to cool and then filtered. The green crystalline solid was washed with methanol and dried in vacuo to a weight of 21.35 g. The crude solid was dissolved in methylene chloride, treated with activated charcoal, Norit A, overnight, and passed through a column of Celite (top) and silica gel (bottom). After the volume of the eluate was reduced, 17.10 g of yellow crystalline product, mp 369–371 °C, was obtained. With further volume reduction and addition of hexane, an additional 1.70 g of less pure ligand was also obtained for a yield of 76%.

NMR analysis of the product gave the following peaks: *sec*-butyl protons 0.90 (t), 1.31 (d), 1.65 (quintet), 2.64 (sextet); pyridine protons 6.92 (d), 7.31 (s), 8.5 (d); benzene protons 8.77 (s); pyrrole protons 14.08 (br, s).

Template Synthesis of the Binucleating Ligand (2). A mixture of 89 mg (0.5 mmol) of 1,2,4,5-tetracyanobenzene, 330 mg (2.2 mmol) of 2-amino-4-*sec*-butylpyridine, 200 mg (1.0 mmol) of cupric acetate hydrate, and 10 mL of methanol was stirred at ambient temperature for 5 days followed by 3 days at reflux. After the solution was cooled, the solvent was allowed to evaporate and the residue was washed with water and dried to afford 430 mg of green powder. To this was added 5 mmol of KCN (325 mg), 20 mL ethanol, and 10 mL of chloroform, and gentle heating, keeping the mixture from boiling, was applied for 2 days. Upon being cooled, the green suspension was filtered and the insoluble material washed with chloroform. The combined filtrate washes were evaporated to dryness and the residue extracted with chloroform. The chloroform extract was passed through a minicolumn of alumina which removed most of the green pigment. From the eluant, a 45% yield (167 mg) of greenish yellow crystals was obtained

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[14] Flanagan, J. B.; Margel, S.; Bard, A. J.; Anson, F. C. *J. Am. Chem. Soc.* **1978**, *100*, 4248.

[15] See, for example: Addison, A. W.; Stenhouse, J. H. *Inorg. Chem.* **1978**, *17*, 2161.

which were identical spectroscopically with the ligand obtained via the $CaCl_2$-catalyzed route.

Solubility of Binucleating Ligands. An excess of binucleating ligand was added to 25 mL of benzene and warmed gently. The supersaturated solutions were allowed to stand at ambient temperature (23 ± 0.5 °C) for at least 1 week before analysis. Aliquots were removed periodically, were passed through a filter (Millipore LS, 5.0 μM), and, after appropriate dilution, were analyzed spectrophotometrically on a Cary 17D spectrophotometer. With use of previously determined molar extinction coefficients, concentrations were calculated. Analyses were repeated periodically until concentrations had stabilized; relative solubility values are reported in Table I.

Preparation of (Acetato)[1,3-bis(2-pyridylimino)isoindolinato]-metal(II) Complexes [M(RL)OAc]. The following method was employed for the preparation of M(RL)OAc complexes of divalent Mn, Fe, Co, Ni, Cu, and Zn. The preparation of the Mn(II), Fe(II), and Co(II) complexes was carried out under an argon atmosphere; no effort was made to exclude air from the other preparations. One millimole of chelating ligand and 2 mmol of metal(II) acetate hydrate in 15 mL of methanol was stirred at ambient temperature for 24 h. After this time the suspension was filtered and the solid washed with methanol and dried in vacuo. Yields of complexes were generally 90% or higher. The colors of the M(4′-MeL)OAc complexes are as follows: Mn(II) tan, Fe(II) green, Co(II) gold-tan, Ni(II) green, Cu(II) brown, and Zn(II) yellow.

Preparation of Fe(4′-MeLH)Br$_2$. Under a helium atmosphere, a solution of 2.0 g (6.1 mmol) of 4′-MeLH in 40 mL of warm methanol was added to a solution of 2.6 g (9.0 mmol) for $FeBr_2\cdot4H_2O$ in 10 mL of methanol. The reaction mixture was heated with stirring for 10 min. After the mixture was cooled to ambient temperature, 20 mL of diethyl ether was added to the mixture and stirred for 5 min. The green crystalline product (65% yield) was collected by vacuum filtration, washed with diethyl ether, and dried under a stream of helium.

Preparation of Mononuclear Metal(II) Complexes, M(RL)$_2$. The following general procedure was used to prepare mononuclear complexes of Mn(II), Fe(II), Co(II), Ni(II), and Zn(II) with RL = 4′-MeL. Preparations of iron and cobalt complexes were conducted in an inert atmosphere.

A solution of 0.7 mmol of the metal(II) perchlorate in 5 mL of methanol was added to a solution containing the mononucleating ligand (1.5 mmol) and 0.5 mL of triethylamine in 40 mL of hot methanol. The reaction was heated at reflux for 30 min during which time dark microcrystalline solid had formed. After being cooled, the mixture was filtered and the product was washed with hot methanol. The complexes CoL_2 and Co(5′-NO$_2$L) were prepared in the same fashion. The yields were Mn(4′-MeL)$_2$ 74%, Fe(4′-MeL)$_2$ 77%, Co(4′-MeL)$_2$ 79%, Ni(4′-MeL)$_2$, 75%, Zn(4′-MeL)$_2$ 83%, CoL_2 91%, and Co(5′-NO$_2$L)$_2$ 12%.

Preparation of Bis(1,3-bis((5-chloro-2-pyridyl)imino)isoindolinato)cobalt(II). To 368 mg (1.0 mmol) of ligand and 119 mg (0.5 mmol) of cobaltous chloride hexahydrate under argon was added 10 mL of methanol and 1 mL of triethylamine. After being stirred for 16 h at 25 °C, the mixture was filtered in the air and the product was washed with methanol and dried in vacuo. A 97% yield (383 mg) of red-brown microcrystals was obtained; mp >350 °C.

Preparation of Bis(1,3-bis((4-*sec*-butyl-2-pyridyl)imino)isoindolinato)copper(II) [Cu(4′-*sec*-butylL)$_2$]. A solution of 34 mg (0.25 mmol) of anhydrous cupric chloride in 10 mL of methanol was added to 210 mg (0.51 mmol) of the chelating ligand, 4′-*sec*-butylLH, and stirred at ambient temperature.[7] The initial green solution changed to a yellow-brown suspension after a few minutes. After 15 min, 0.2 mL of triethylamine was added and the stirring was continued. After 45 min, the suspension was filtered and the solid was washed with methanol and dried in vacuo. An 84% yield (186 mg) of gold microcrystals was obtained; mp 263–264.5 °C.

Conversion of Co(4′-MeL)OAc to Co(4′-MeL)$_2$. A Schlenk tube was charged with 110 mg (0.25 mmol) of Co(4′-MeL)OAc, 88 mg (0.27 mmol) of chelating ligand, and 5 mL of pyridine. The dark red solution was stirred under argon at ambient temperature for 24 h. Water (4 × 5 mL) was added, and the resulting precipitate was collected, washed with water, and dried in vacuo to afford a quantitative yield of red-brown crystalline Co(4′-MeL)$_2$; mp 337–338 °C.

Preparation of [1,3-Bis((4′-metbyl-2-pyridyl)imino)isoindolinato][1,3-bis((5-chloro-2-pyridyl)imino)isoindolinato]cobalt(II) [Co(4′-MeL)(5′-ClL)]. To 184 mg (0.5 mmol) of 5′-ClLH and 222 mg (0.5 mmol) of Co(4′-MeL)OAc in a Schlenk tube under argon was added 10 mL of methanol and 1 mL of triethylamine. The mixture was stirred at ambient temperature for 2 days and then filtered in the air. The solid was washed with methanol and dried in vacuo to afford a 92% yield (348 mg) of brown microcrystalline powder.

Preparation of Bis(1,3-bis((4-methyl-2-pyridyl)imino)isoindolinato)cobalt(III) Hexafluorophosphate [Co(4′-MeL)$_2$PF$_6$]. To 71 mg (0.1 mmol) of Co(4′-MeL)$_2$ and 57 mg (0.104 mmol) of ceric ammonium nitrate, $(NH_4)_2Ce(NO_3)_6$, in a Schlenk tube under argon was added 5 mL of methanol. After a few minutes a clear red-brown solution was obtained. After being stirred at ambient temperature for 16 h, the solution was transformed to an open beaker and the solvent was allowed to evaporate. The solid residue was washed with water. Methanol (5 mL) and 25 mg (0.15 mmol) of NH_4PF_6 were added to the residue, and the mixture was stirred until the solvent had evaporated. The residue was extracted with methylene chloride, and heptane was added in small amounts to the filtered extract. On standing dark crystals of the hexafluorophosphate salt were obtained as the methylene chloride solvate: Co(4′-MeL)$_2$PF$_6\cdot$2CH$_2$Cl$_2$, mp 256.5–257.5 °C, 89% yield.

Anal. Calcd for $C_{42}H_{36}N_{10}CoCl_2PF_6$: C, 49.14; H, 3.53; N, 13.65; Cl, 13.82; P, 3.02. Found: C, 49.5; H, 3.45; N, 13.7; Cl, 13.75; P, 3.0.

Preparation of Bis(1,3-bis((4-methyl-2-pyridyl)imino)isoindolinato)cobalt(III) Tetraphenylborate [Co(4′-MeL)$_2$(Ph$_4$B)]. A mixture of 44 mg (0.1 mmol) Co(4′-MeL)OAc, 36 mg (0.11 mmol) of chelating ligand, 4′-MeLH, 41 mg (0.12 mmol) of sodium tetraphenylboron, and 6 mL of methanol was stirred for 24 h under argon at ambient temperature. Then 77 mg (0.14 mmol) of ceric ammonium nitrate was added, and the red-brown solution immediately changed to a brown suspension. After an additional 5 h at 25 °C, the suspension was filtered in the air and the solid was washed with methanol and with water. After the suspension was dried in vacuo, an 84% yield (87 mg) of gold-brown microcrystals was obtained.

Metal-Exchange Studies. (a) Ni(4′-MeL)OAc and Cu(OAc)$_2\cdot$H$_2$O. To 55 mg (0.125 mmol) of Ni(4′-MeL)OAc and 250 mg (1.25 mmol) of cupric acetate hydrate as added 3 mL of chloroform and 2 mL of methanol. After a few minutes a clear dark green solution was obtained and was stirred at ambient temperature for 24 h. The solvent was then allowed to evaporate, and the residue was washed with water and dried. The solid was extracted with methylene chloride and heptane was added in small aliquots to the extract. On standing, beautiful brown needles deposited. The crystals were collected, washed with heptane and ether, and dried to afford an 88% yield of Cu(4′-MeL)OAc.

(b) Ni(4′-MeL)$_2$ and Cu(OAc)$_2\cdot$H$_2$O. To 71 mg (0.1 mmol) of Ni(4′-MeL)$_2$ and 200 mg (1.0 mmol) of cupric acetate hydrate was added 3 mL of chloroform and 2 mL of methanol. The resulting dark green solution was stirred at ambient temperature for 24 h and then evaporated under a stream of argon. The residue was extracted with methylene chloride and the solvent removed from the extract. The extract residue was extracted with benzene. From the benzene extract, 100 mg of green powder was obtained. The IR (KBr) spectrum was identical with that of Cu(4′-MeL)OAc. Analysis by thin-layer chromatography (SiO_2, EtOAc) of the powder showed no remaining Ni(4′-MeL)$_2$. The yield of Cu(4′-MeL)OAc was 93%.

(c) [Co(4′-MeL)$_2$]PF$_6$ and Cu(OAc)$_2\cdot$H$_2$O. A solution of 86 mg (0.1 mmol) of [Co(4′-MeL)$_2$]PF$_6$ and 200 mg (1.0 mmol) of Cu(OAc)$_2\cdot$H$_2$O in 3 mL of chloroform and 2 mL of methanol was stirred at ambient temperature for 24 h. The solvent was evaporated under a stream of argon, and the residue was extracted with methylene chloride. After the methylene chloride was evaporated from the extract, the new residue was extracted with tetrahydrofuran. After addition of heptane to the tetrahydrofuran extract, dark crystals gradually deposited. The crystals (86 mg) were collected and dried in vacuo. The IR (KBr) spectrum was identical with that of the starting material. Thin-layer chromatography analysis (SiO_2; $CHCl_3$–EtOH 10:1) of the product showed the absence of any Cu(4′-MeL)OAc, the potential exchange product.

Preparation of (AcO)ML–LM(OAc) (3). The general procedure for the preparation of (AcO)ML–LM(OAc) complexes (3) is illustrated below for the binuclear Cu(II) complex. The preparation of the Mn(II), Fe(II), and Co(II) complexes was carried out under an inert atmosphere.

To 745 mg (1.0 mmol) of binucleating ligand, HL–LH, and 1 g (5.0 mmol) of cupric acetate hydrate was added 50 mL of methanol followed by 10 mL of chloroform. The suspension was stirred at ambient temperature for 72 h. The suspension was filtered, and the solid was washed repeatedly with methanol until the washes were no longer green. After the suspension was dried in vacuo, a 97% yield (959 mg) of greenish yellow powder was obtained.

Preparation of LML–LML (4). Binuclear complexes of Mn(II), Co(II), and Ni(II) were prepared by two different methods. The two different preparations are illustrated below for Co(II).

Preparation of (4′-MeL)CoL–LCo(4′-MeL). To 89 mg (0.2 mmol) of Co(4′-MeL)OAc, 74 mg (0.1 mmol) of HL–LH, and 5 mL of methanol in a Schlenk tube under argon was added 0.5 mL of triethylamine. After the dark brown suspension was stirred at ambient temperature for 20 h, an additional 10 mL of methanol was added. The suspension was filtered in the air, and the solid was washed with methanol and dried in vacuo to afford a 91% (137 mg) yield of red-brown powder which exhibited a single spot on thin-layer chromatography (SiO_2, EtOAc).

The Co(II) binuclear complex gave a ^1H NMR spectrum in $CDCl_3$ with the following peaks (vs. Me_4Si at 34 °C): 48.6, 45.7, 37.0, 30.6, 29.1, and 27.5 (aromatic protons), −4.3 and −7.6 (*s*-butyl protons), and −13.7 (methyl protons).

Alternate Preparation of (4′-MeL)CoL–LCo(4′-MeL). A Schlenk tube was charged with 98 mg (0.1 mmol) of (AcO)CoL–LCo(OAc), 65 mg (0.2 mmol) of 4′-MeLH, and 5 mL of methanol; the mixture was stirred under argon at ambient temperature. After 15 min, 0.5 mL of triethylamine was added to the brown suspension and the stirring was continued for an additional 16 h. An additional 10 mL of methanol was added, and the suspension was filtered in the air. The dark brown powder was washed with methanol and dried in vacuo to afford a 77% yield (116 mg). The IR (KBr) spectrum was identical with that of material prepared by the first method.

Preparation of (4′-MeL)FeL–LFe(4′-MeL). Under a helium atmosphere, 160 mg (0.79 mmol) of $AgClO_4$ was added to a slurry of 430 mg (0.79 mmol) of $Fe(4'\text{-MeLH})Br_2$ in 35 mL of methanol. After stirring briefly, the mixture was filtered to remove precipitated silver bromide. Toluene (15 mL) and a solution of 43 mg (0.79 mmol) of sodium methoxide in 20 mL of methanol were added to the filtrate resulting in a green to reddish brown color change. To this solution was added slowly a solution of 200 mg (0.27 mmol) of HL–LH and 29 mg (0.54 mmol) of sodium methoxide in 5 mL of methanol and 15 mL of toluene. After 1 h of stirring, the dark green solid was collected by vacuum filtration, washed with several portions of methanol, and dried under a stream of helium; 79% yield.

Preparation of [(4′-MeL)CoL–LCo(4′-MeL)](PF_6)$_2$. To a suspension of 45 mg (0.03 mmol) of (4′-MeL)CoL–LCo(4′-MeL) in 5 mL of methanol was added sufficient methylene chloride to produce a homogeneous solution. To this solution was added 33 mg (0.06 mmol) of ceric ammonium nitrate, and the mixture was stirred for 0.5 h at ambient temperature after which time the solvent was evaporated under a stream of argon. The residue was washed with water, dried in vacuo, and then extracted with methylene chloride. To the CH_2Cl_2 extract was added 11 mg (0.07 mmol) of NH_4PF_6 in 3 mL of methanol; after 0.5 h of stirring, the mixture was filtered to remove a small amount of brown precipitate and the solvent was evaporated under a stream of argon. The residue was washed with water and dried in vacuo to afford 45 mg of brown powder. The powder was extracted with ethyl acetate, and heptane was added in small aliquots to the extract. On standing dark brown microcrystals deposited. The crystals were collected, washed with toluene, and dried in vacuo to afford a 67% yield (26 mg) of [(4′-MeL)CoL–LCo(4′-MeL)](PF_6)$_2$.

Preparation of (4′-*sec*-butylL)NiL–LNi(4′-*sec*-butylL) and Molecular Weight Determination. To 245 mg (0.25 mmol) of (AcO)-NiL–LNi(OAc) and 226 mg (0.55 mmol) of 4′-*sec*-butylLH was added 20 mL of chloroform, and the resulting solution was stirred at ambient temperature for 72 h. Heptane was added in small amounts until crystals deposited. A 60% yield (250 mg) of dark red crystals was obtained.

The solution molecular weight determination in toluene was carried out on the red crystals by Dr. M. Zinbo of the Ford Scientific Research Labs using a Hitachi-Perkin Elmer molecular weight apparatus. This vapor-phase osmomimetry method gave an observed value of 1699 compared with a calculated value of 1680.

Preparation of (4′-MeL)CuL–LCu(4′-MeL). To 33 mg (0.033 mmol) of (AcO)CuL–LCu(OAc) and 22 mg (0.066 mmol) of 4′-MeLH was added 5 mL methanol and 0.2 mL of triethylamine. The resulting suspension was stirred at 25 °C, as the color gradually changed from olive-green to yellow-gold. After 3 h the suspension was filtered and the solid was washed with methanol and dried in vacuo. A 48% yield (27 mg) of gold powder was obtained; mp >390 °C.

Attempted Preparation of (4′-MeL)ZnL–LZn(4′-MeL). To 450 mg (1 mmol) of Zn(4′-MeL)OAc and 272 mg (0.5 mmol) of binucleating ligand, HL–LH, was added 200 mL of methanol and 20 mL of triethylamine; the resulting suspension was stirred at ambient temperature for 7 days. The reaction mixture was filtered, washed with methanol, and dried in vacuo to afford a 60% yield (458 mg) of yellow-orange microcrystalline powder; mp >400 °C.

Carbon, hydrogen, and nitrogen analysis of the product was satisfactory for the binuclear Zn(II) complex; however, the proton NMR spectrum of the product gave a mononucleating ligand to binucleating ligand ratio of less than 2:1 expected for a discrete binuclear complex. This suggests that the product isolated contains a higher order polymer.

Electrochemistry. Tetrabutylammonium perchlorate, TBAP (Southwestern Analytical Chemicals), was dried in vacuo before use. Spectroquality acetonitrile and *N*,*N*-dimethylformamide, distilled under reduced pressure over 4-Å molecular sieves, were used for electrochemical measurements.

A Princeton Applied Research Model 173 potentiostat galvanostat coupled with a Model 179 digital coulometer and a ramp generator of our own design were used for constant-potential electrolysis and cyclic voltammetry. A storage oscilloscope and an X-Y recorder were used to display the results. A Princeton Applied Research 174A polarographic analyzer was used in conjunction with an X-Y recorder for differential-pulse polarography.

Constant-potential electrolyses were carried out in a three-compartment H cell. The cell consisted of 25-mL sample and auxiliary compartments separated by a small center compartment. Each compartment was separated by a medium-porosity sintered glass frit. A platinum gauze was used as the working electrode for electrolyses.

Cyclic voltammetry and differential-pulse voltammetry were carried out in a single compartment cell containing approximately 5 mL of solution. The working electrode was a platinum-button electrode. For all electrochemical measurements the supporting electrolyte used was 0.1 M TBAP. The Ag/Ag^+ reference electrode consisted of a silver wire immersed in an acetonitrile solution containing 0.01 M $AgNO_3$ and 0.1 M TBAP. The Ag^+ solution and silver wire were contained in an 8-mm glass tube fitted on the bottom with a fine-porosity sintered glass frit. The auxiliary electrode consisted of a coiled platinum wire. All measurements were made in an helium atmosphere.

Small amounts of ferrocene were added to electrochemical solutions as an internal standard. Potentials for the complexes were measured vs. ferrocene.[16] The formal potentials were then adjusted to potentials vs. the NHE with the assumption of a value of +0.400 V for the ferrocene/ferricinium couple.

Formal reduction potentials, E^f, were measured by cyclic voltammetry with use of the formula $E^f = (E_{pa} + E_{pc})/2$. The potentials determined in this way are approximate in that the systems examined did not display strict reversibility and corrections were not made for diffusion coefficients. Reduction potentials measured by cyclic voltammetry and differential-pulse polarography agreed to within ±10 mV.

Physical Measurements. Magnetic susceptibility measurements were obtained on samples at the ambient temperature using a Cahn Instruments Faraday balance, with $HgCo(SCN)_4$ as a calibrant. Diamagnetic corrections were made with the use of Pascal's constants.

Proton NMR spectra were obtained on a Varian EM-390 NMR spectrometer with $CDCl_3$ as the solvent and tetramethylsilane as a reference.

Acknowledgment. We appreciate financial assistance from the Department of Energy, the Sloan Foundation (R.R.G.), and the National Science Foundation.

Registry No. 2a, 66096-16-0; **2b**, 66096-17-1; **2c**, 78090-02-5; **2d**, 78090-03-6; **2e**, 66096-18-2; **2f**, 66096-19-3; **2g**, 66096-21-7; **2h**, 66096-20-6; **2i**, 66096-22-8; **3**, M = Cu, 66114-32-7; **3**, M = Mn, 78065-17-5; **3**, M = Fe, 78065-18-6; **3**, M = Co, 78065-19-7; **4**, M = Mn, R = Me, 78065-20-0; **4**, M = Co, R = Me, 78065-21-1; **4**,

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(16) Gagné, R. R.; Koval, C. A.; Lisensky, G. C. *Inorg. Chem.* **1980**, *19*, 2854.

M = Ni, R = Me, 78064-10-5; **4**, M = Fe, R = Me, 78065-22-2; **4**, Me = Cu, R = Me, 78090-06-9; **4**, M = Ni, R = *sec*-butyl, 66114-34-9; **4**, M = Cu, R = *sec*-butyl, 78065-23-3; Mn(4′-MeL)OAc, 78065-24-4; Fe(4′-MeL)OAc, 78065-25-5; Co(4′-MeL)OAc, 78065-26-6; Ni(4′-HMeL)OAc, 78065-27-7; Cu(4′-MeL)OAc, 78065-28-8; Fe(4′-MeLH)Br_2, 78065-29-9; Mn(4′-MeL)$_2$, 78065-30-2; Fe(4′-MeL)$_2$, 78065-31-3; Co(4′-MeL)$_2$, 78065-32-4; Ni(4′-MeL)$_2$, 78065-33-5; Zn(4′-MeL)$_2$, 78065-34-6; CoL_2, 14911-23-0; Co(5′-NO_2L)$_2$, 78090-07-0; Co(5′-ClL)$_2$, 78090-08-1; Cu(4′-*sec*-BuL)$_2$, 78065-35-7; Co(4′-MeL)(5′-ClL), 78065-36-8; Co(4′-MeL)$_2PF_6$, 78065-38-0; Co(4′-MeL)$_2$(Ph_4B), 78065-39-1; [(4′-MeL)CoL-LCo(4′-MeL)]PF_6, 78355-31-4; [(4′-MeL)CoL-LCo(4′-MeL)](ClO_4)$_2$, 78090-10-5; 2-aminopyridine, 504-29-0; 2-amino-4-methylpyridine, 695-34-1; 2-amino-5-methylpyridine, 1603-41-4; 2-amino-3,5-dimethylpyridine, 41995-30-6; 2-amino-4-ethylpyridine, 33252-32-3; 2-amino-4-*n*-propylpyridine, 61702-15-6; 2-amino-4-*sec*-butylpyridine, 61702-16-7; 2-amino-4-*tert*-butylpyridine, 33252-26-5; 2-amino-4-*n*-amylpyridine, 60781-86-4; 1,2,4,5-tetracyanobenzene, 712-74-3.

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Pentamethylcyclopentadienyl Derivatives of the Trivalent Lanthanide Elements Neodymium, Samarium, and Ytterbium

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The anionic complexes of the type $[ML_x][(Me_5C_5)_2M'Cl_2]$, where M is lithium or sodium, L is diethyl ether or *N*,*N*,*N′*,*N′*-tetramethylethylenediamine, and M′ is neodymium, samarium, or ytterbium, have been prepared from the metal trichlorides and the pentamethylcyclopentadienide anion. The neutral species $(Me_5C_5)_2NdCl(THF)$, $(Me_5C_5)_2NdN(SiMe_3)_2$, and $(Me_5C_5)_2YbCl(THF)$ have also been prepared. The mono-ring derivatives $[Na(OEt_2)_2][(C_5Me_5)NdCl_3]$ and $(Me_5C_5)Nd[N(SiMe_3)_2]_2$ are also described.

Cyclopentadienyl derivatives of the lanthanide metals, except europium, of the type Cp_3M were first prepared by Wilkinson in 1956 from sodium cyclopentadienide and the metal trichloride in tetrahydrofuran.[1] The europium derivative, as its tetrahydrofuran complex, $Cp_3Eu(THF)$, was described later.[2] Di- and monocyclopentadienyl compounds, Cp_2MCl and $CpMCl_2$, respectively, have also been prepared.[3,4]

Tris(methylcyclopentadienyl)neodymium, $(MeC_5H_4)_3Nd$, is a tetramer in the solid state, and it is likely that the other binary compounds are also associated into oligomeric units in the solid.[5] The bis(cyclopentadienyl)chloro derivatives are monomeric in refluxing tetrahydrofuran but dimeric in refluxing benzene.[3] A crystal structure of $[(MeC_5H_4)_2YbCl]_2$ shows that it is dimeric by way of chloride bridging groups.[6] A σ-alkyl, $[Cp_2YbMe]_2$, is also dimeric in the solid state.[7] In this case the methyl groups bridge the two ytterbium atoms. An ionic bonding model for cyclopentadienyllanthanide derivatives has been proposed by Raymond.[8] The organometallic chemistry of these elements has been exhaustively reviewed.[9]

A straightforward synthetic scheme for pentamethylcyclopentadiene and its alkali-metal derivatives allows this useful reagent to be prepared in large quantities.[10] This ligand is potentially useful for preparation of substituted derivatives as its steric size limits the degree of substitution that can be obtained. Only two pentamethylcyclopentadienyl groups can be attached to a metal atom even for large metal atoms such as uranium or thorium.[11,12]

We have recently shown that europium trichloride is reduced by sodium pentamethylcyclopentadienide in refluxing tetrahydrofuran to give $(Me_5C_5)_2Eu(THF)$.[13] As a result of this observation, we have investigated the reaction of the pentamethylcyclopentadienide anion with some other lanthanide trichlorides.

Ytterbium trichloride reacts with 2 molar equiv of $LiMe_5C_5$ in tetrahydrofuran to give violet $[Li(OEt_2)_2][(Me_5C_5)_2YbCl_2]$ upon crystallization from diethyl ether. Some physical properties are shown in Table I. The complex is paramagnetic, and the proton nuclear magnetic resonance spectrum is uninformative, as only a broad resonance was observed for the methyl group protons, a phenomenon observed for all the compounds described in this paper. Thus, at least one derivative of each compound was prepared in order to further substantiate the stoichiometry. The diethyl ether in $[Li(OEt_2)_2][(Me_5C_5)_2YbCl_2]$ can be replaced by *N*,*N*,*N′*,*N′*-tetramethylethylenediamine, giving $[Li(tmed)][(Me_5C_5)_2YbCl_2]$. Anionic complexes of samarium and neodymium, $[Li(tmed)][(Me_5C_5)_2SmCl_2]$, $[Li(OEt_2)_2][(Me_5C_5)_2NdCl_2]$, and $[Li(tmed)_2][(Me_5C_5)_2NdCl_2]$, were prepared similarly. It is rather curious that the neodymium compound yields a 2:1 tmed complex whereas the samarium compound yields a 1:1 tmed complex. Another way of saying this is that the former is more thermodynamically stable than the latter (four Li–N bonds rather than two Li–N and two Li–Cl bonds and the associated changes in the relative lattice energies). In absence of thermochemical data we cannot account for this behavior in a reasonable manner.

In contrast to europium trichloride, ytterbium trichloride is not reduced by reaction of 2 molar equiv of $NaMe_5C_5$ in tetrahydrofuran. Instead, two ytterbium(III) products are obtained when diethyl ether is used as a crystallization solvent.

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