Transition Metal Complexes of 1,3-bis(2′-pyridylimino)Isoindolines and Their Use as Alcohol Oxidation Catalysts

Thesis by

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Abstract

Condensation of 1,2-dicyanobenzene and 2-amino-4-methylpyridine resulted in the formation of a ligand, 4′-MeLH, which in its anionic or neutral 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 or chlorides as ligands 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-s-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 either occupied 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), Zn(II), Ru(II), and Ru(III). Mixed-metal complexes containing Ru(II) were also prepared. Magnetic, spectral and electrochemical properties of these molecules were investigated.

The ruthenium complex, (4′-MeLH)RuCl$_3$, catalyzes the autoxidation of alcohols in basic alcoholic solution. The reaction is general, resulting in the oxidation of primary and secondary alcohols, with the principal products being aldehydes and ketones. The catalytic reaction is affected by the strength of the base used and its coordinating ability. The best results were obtained using sodium ethoxide as a base. Turnover numbers of 10-30 per day were observed in one atmosphere of oxygen at ambient temperature; with larger turnover numbers at higher temperatures. More than 200 turnovers were observed in the oxidation of ethanol at the ambient temperature with little or no loss of catalytic activity. Dimeric complexes of Ru(II) and Ru(III) were isolated from ethanolic solutions. These complexes were characterized and their role in the catalytic reaction is discussed.

The Ru(III) complex, (4′-MeLH)RuCl$_3$, also catalyzes the electrochemical oxidation of alcohols in basic alcoholic solution. The best results were obtained with 2,6-lutidine as the base. The electrochemical oxidation was carried out at a carbon electrode immersed in an alcoholic solution at 0.8-1.0 V *vs.* nhe. In the absence of catalyst, negligible current was observed. The catalyzed electrochemical oxidation was general, oxidizing primary and secondary alcohols, with the principal products being aldehydes and ketones. More than 20 catalytic cycles were completed with the current remaining at 75% of its initial value. The Ru(III) complex exhibits reversible one-electron oxidation waves in nonalcoholic solvents in the presence or absence of 2,6-lutidine. The electrochemistry in alcohols and nonalcohols is discussed, and a possible pathway for the catalytic electrochemical oxidation is presented.

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CHAPTER 1

Introduction

INTRODUCTION

Reactions involving the transfer of two or more electrons from a complex to a small molecule substrate are of great interest and importance. Reactions of this type are being investigated for use in chemical synthesis, solar energy conversion and fuel cells.

Nature has utilized multi-metallic enzymes to perform the multi-electron transfer reactions needed for energy conversion and chemical synthesis. The multi-metallic system nitrogenase effects the six-electron reduction of nitrogen to ammonia.[1] The active site of nitrogen reduction in nitrogenase is believed to contain one or two molybdenum atoms and several iron atoms.[2,3] An iron-sulfur cluster containing molybdenum or coupled to molybdenum has been implicated by some of the physical studies of the enzyme.[4-6]

Cytochrome oxidase and laccase are enzymes which catalyze the four electron reduction of O_2 to H_2O. Laccase contains four Cu(I) ions in its reduced state which are all oxidized to Cu(II) as O_2 is reduced to H_2O.[7] Reduced cytochrome oxidase has two Fe(II) and two Cu(I) ions which are oxidized by one electron upon reduction of oxygen.[8] Both of these enzymes demonstrate the ability of multi-metal systems to effect multi-electron transfer.

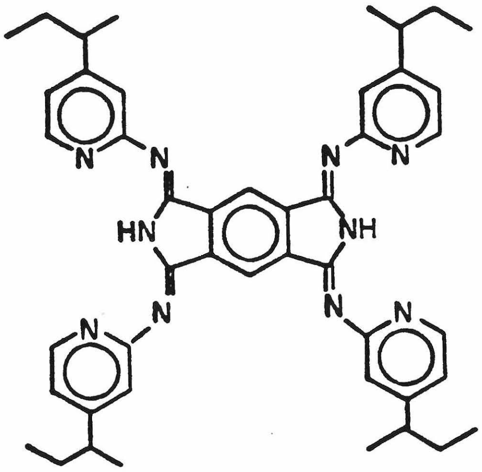
The development of synthetic systems that catalyze the four electron reduction of oxygen is a major obstacle in the design of electrochemical fuel cells. One approach to this problem has been to utilize polynuclear metal complexes as catalysts.[9] The difficulty in converting the chemical energy of oxygen to electrical energy by reduction of oxygen to water, is to avoid the unstable intermediates produced by the transfer of one or two electrons; eq. 1. Production

$$\begin{array}{llll} & \xrightarrow{4e^-,\ 4H^+} & 2H_2O & E = 1.23\ V \\ O_2 & \xrightarrow{2e^-,\ 2H^+} & H_2O_2 & E^0 = 0.68\ V \\ & \xrightarrow{e^-,\ H^+} & HO_2 & E^0 = -0.13\ V \end{array} \qquad (1)$$

of these unstable intermediates will limit the potential which can be drawn from the system. A successful demonstration of the reduction of O_2 to H_2O has been made using dimeric metalloporphyrin molecules.[10,11] A dicobalt cofacial porphyrin was observed to catalyze the electrochemical reduction of oxygen and at quite positive potentials.

Other multi-metal systems have been studied for the photocatalytic splitting of water.[12-14] A binuclear rhodium isocyanide complex has demonstrated the ability to reduce protons to molecular hydrogen upon solar irradiation.[12,13] Multi-metal complexes have also been exploited as catalysts in chemical synthesis. Polynuclear metal clusters are prime candiates as catalysts for the reduction of CO by H_2.[15,16]

The basis for using multi-metal complexes to effect multi-electron transfer has a firm foundation in nature and in synthetic systems. The work presented in this thesis involves the synthesis and characterization of polynuclear metal complexes containing the bridging ligand **1**, HL-LH, and their possible use as multi-electron transfer reagents. The ligand **1** bridges two metal ions providing



= HL–LH

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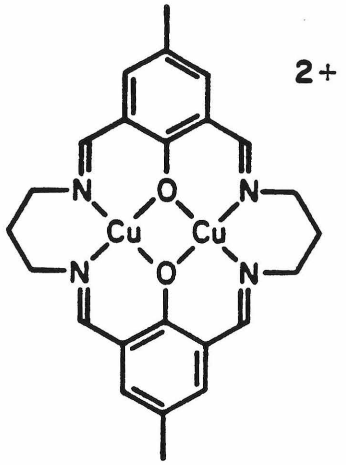
three coordination sites for each. The ligand is normally present as a dianion due to loss of the two pyrrole protons. The bridging ligand **1** not only made it possible to prepare binuclear metal complexes, but also polymeric species containing octahedral metal ions. Adjacent metal ions in these polynuclear complexes are quite distant, but are bridged by a conjugated π system. The metal-metal interactions in the complexes were expected to be small, but the presence of the flat conjugated bridging ligand suggested that electron transfer between the metals might be facile.

The weak metal-metal interaction in these complexes was considered to be an advantage in their possible use as multi-electron transfer reagents. Binuclear complexes with strong interactions between the metals typically exhibit two one-electron reductions at distinctly different potentials. For example, the binuclear Cu(II) complex **2** exhibits two one-electron reductions at -0.52 V and -0.91 V



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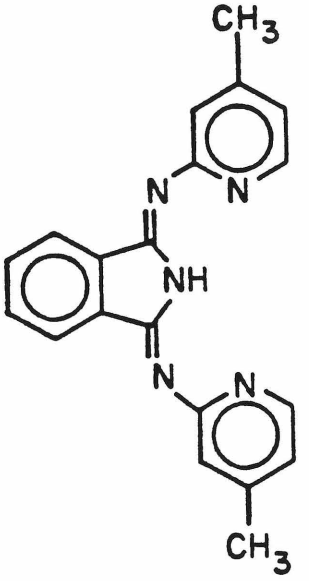
vs. nhe.[17] This complex may transfer two electrons to a substrate, but in a stepwise fashion because of its strong metal-metal interactions. In contrast, polynuclear complexes containing the bridging ligand 1 have reduction potentials for each metal that are nearly equivalent. The complexes have the capability of transferring several redox equivalents at a single electrochemical potential.

Multiple coordination sites are potentially available for substrate binding in these complexes. A metal bound to the ligand 1 leaves several coordination sites open for interaction with a substrate. Metal complexes were prepared where the metal ion is bound to 1 and to one or more readily dissociable ligands.

The first investigations of these molecules involved the synthesis and characterization of mononuclear and binuclear isoindoline complexes containing first-row transition metals; Chapter 2. Mononuclear, $M(4'\text{-MeL})_2$, and binuclear complexes, (4′-MeL)ML-LM(4′-MeL), were prepared using the tridentate mononucleating ligand 3, resulting in a pseudooctahedral environment about the metal ions. Complexes of this type were important in characterizing the electrochemical properties of these molecules.



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Analogous mononuclear and binuclear complexes of ruthenium were prepared; Chapter 3. The primary objective in making the ruthenium complexes was to take advantage of the information available from the spectroscopic properties of mixed-valent ruthenium binuclears. Mixed-valent complexes of ruthenium normally exhibit an intervalence transfer (IT) band at low energy; usually in the near infrared.[18-20] The properties of the IT band of mixed-valent complexes where the valences are localized and the metal-metal interactions are weak, are described by a theory developed by Hush.[21,22] From this theory, the properties of the IT band can be used to obtain detailed information concerning thermal intramolecular electron transfer in the binuclear complex. This approach has been exploited in the study of many ruthenium mixed-valent binuclear complexes.[18-20]

The reactivity of the metal-isoindoline complexes with substrates was explored. Isoindoline complexes of Ru(III) were observed to undergo reduction in the presence of alcohols. In particular, the complex (4′-MeLH)$RuCl_3$ was found to catalyze the autoxidation of alcohols; Chapter 4. This reaction was investigated to determine how the two-electron oxidation of alcohol was catalyzed by a monometal species.

The Ru(III) complex, (4′-MeLH)$RuCl_3$, was also found to catalyze the electrochemical oxidation of alcohols. Chapter 5 presents the results of the study of this electrocatalytic oxidation.

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CHAPTER 2

Mononuclear and Binuclear Metal Complexes of 1, 3-bis(2′-pyridylimino)Isoindolines

Mononuclear and Binuclear Metal Complexes of 1,3-bis(2′-pyridylimino) Isoindolines

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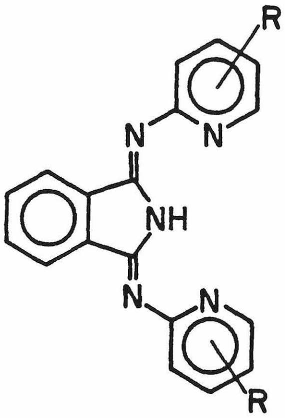
David N. Marks,[1a] and Walter O. Siegl[1b]

Abstract

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-s-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 either occupied 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 with ligand to metal ratios of 2:1 and 1:1.[2] The ligand functions as an

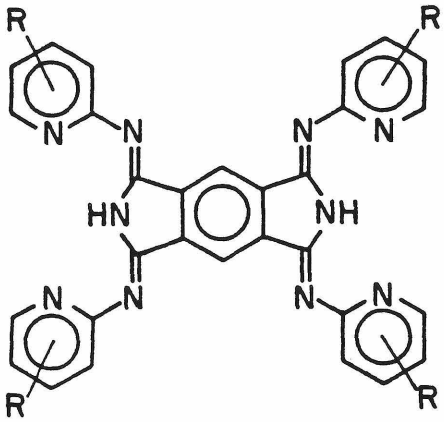


LH,[3] R = H

4′-MeLH, R = 4′-CH_3

1

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 not only made it possible to prepare 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 electro-



HL-LH,[3] R = 4′-s-butyl

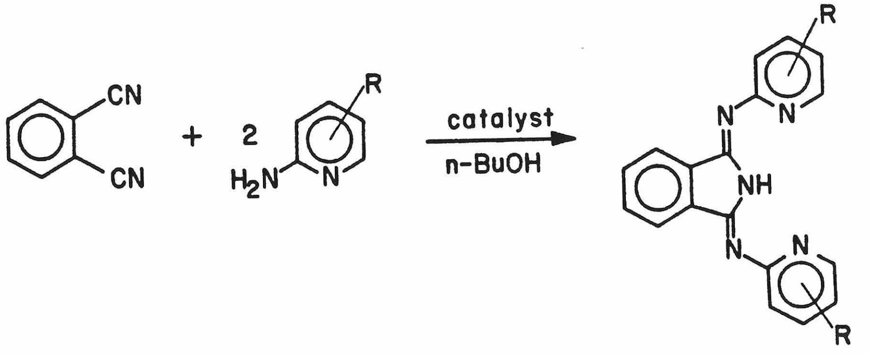
2

chemistry and magnetic measurements, and complexes of this type are interesting candidates for reactions involving multi-electron 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).

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).

The binucleating ligand 2 was prepared in a similar manner by these methods as shown in eqs. 2 and 3. The method of choice afforded



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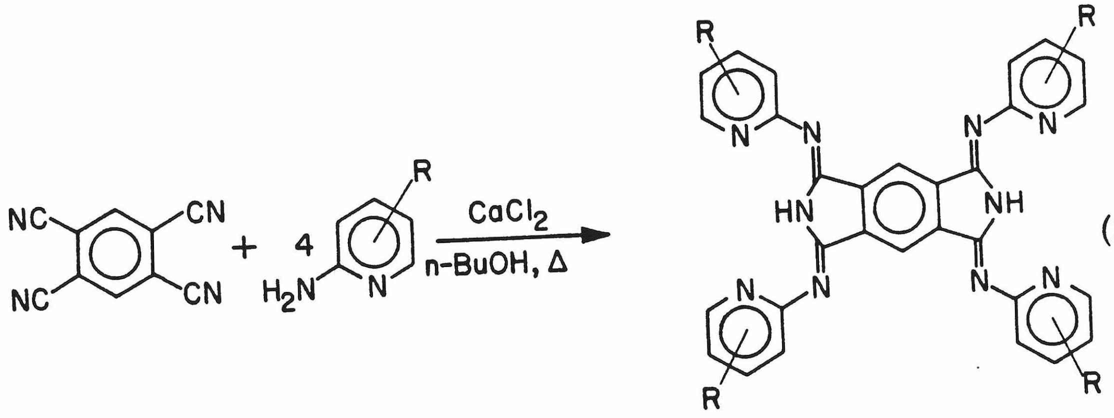
the binucleating ligand in good yield from a one flask synthesis utilizing an alkaline earth salt (anhydrous $CaCl_2$) to catalyze the condensation of tetracyanobenzene with four equivalents of aromatic amine. A second method, a template-type synthesis, utilized Ni(II) or Cu(II) acetate to facilitate 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



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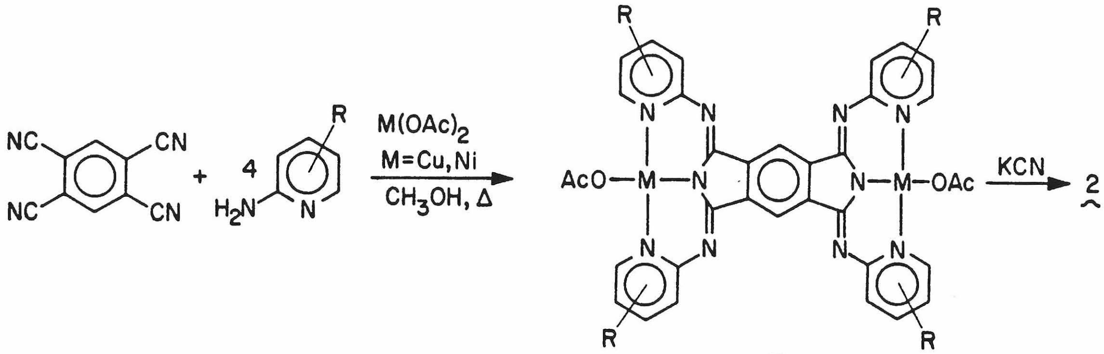


(3)

3

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′-*t*-butyl derivatives, which are somewhat hygroscopic, have long shelf lives. Solubilities vary over a range of two orders of magnitude as shown in Table 1, with the 4′-*s*-butyl derivative being the most soluble; unless indicated otherwise, all work described in this paper was carried out with the 4′-*s*-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}

TABLE 1. Yields, Melting Points, and Relative Solubilities for the Binucleating Ligands, 2.

Cpd.	Derived from (amine)	Yield	Melting Point (°C)	Relative Solubility
2a	2-aminopyridine	90	324-6	2.6
2b	2-amino-4-methylpyridine[a]	59	340-1	1
2c	2-amino-5-methylpyridine	79	345-8 (dec)	ND
2d	2-amino-3,5-dimethylpyridine	ND[b]	375-7	ND
2e	2-amino-4-ethylpyridine	45	353-5	72
2f	2-amino-4-n-propylpyridine[a]	58	357-9	52
2g	2-amino-4-s-butylpyridine	83	369-71	105
2h	2-amino-4-t-butylpyridine[a]	44	435-7	1.7
2i	2-amino-4-n-amylpyridine	49	317-18	11

[a] Ligand isolated as a monohydrate.

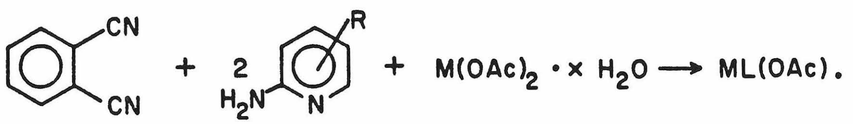
[b] ND = not determined.

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 mono-nucleating 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 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. 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]

$$\mathbf{1} + M(OAc)_2 \cdot x\,H_2O \rightarrow ML(OAc) \qquad (4)$$



(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 two equivalents of chelating ligand afforded the neutral complex ML_2 in high yields, as indicated in eq. 6

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

For metal salts with very poor bases as counter ions, 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.

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

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

approach allows the preparation of complexes with two different ligands, as indicated in eq. 8:

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

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′-MeL)$_2$ and at 0.235 V vs. nhe for Co(5′-ClL)$_2$.

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′-MeL)$_2$PF$_6$.

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 to 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′-MeL)$_2$, was oxidized with ceric ion to the corresponding Co(III) complex, diamagnetic Co(4′-MeL)$_2^+$, isolated as its BF$_4^-$, BPh$_4^-$, and PF$_6^-$ salts. Attempts to similarly prepare Mn(4′-MeL)$_2^+$ were unsuccessful. Complexes of Fe(III) could be prepared by ferricinium oxidation of Fe(4′-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 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] The same binuclear complexes of Ni(II) and Cu(II) were

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

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. The preparation

$$\underset{\mathbf{3}}{\text{(AcO)ML-LM(OAc)}} + \text{2LH} \rightarrow \underset{\mathbf{4}}{\text{LML-LML}} \qquad (10)$$

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

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.

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′-*s*-butyl L)NiL-LNi(4′-*s*-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 (eqs. 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 2 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.

Electronic Absorption Spectra. The visible spectra of all mononuclear and binuclear complexes show intense ($\epsilon \sim$ 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.

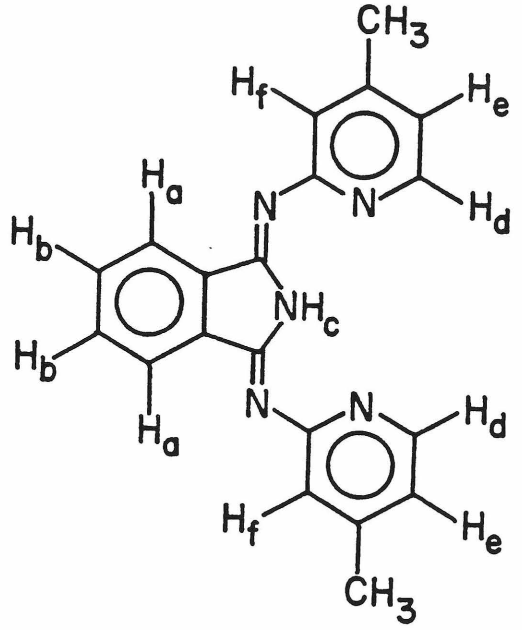
The mononuclear iron (II) complex shows two broad absorptions at 650 nm and 740 nm ($\epsilon \sim$ 800) in addition to the ligand absorptions. These bands may be assigned, due to their position and intensity, as Fe(II) → L charge transfer bands.

Proton NMR Spectra. Proton nmr spectra were obtained for the mononuclear Fe(II), Co(II), Co(III), Ni(II), and Zn(II) complexes, $M(4'\text{-MeL})_2$, to identify the complexes and to test their purity (Table 3). Spectra of the Mn(II) and Cu(II) complexes are severely broadened due to the slow electron relaxation times of these metals. In the diamag-

TABLE 2. Magnetic Susceptibility Data for Mononuclear and Binuclear Complexes per Metal Ion.

Complex	μ_{eff} (B.M. 298 K)
Mn(4′-MeL)$_2$	5.92
Fe(4′-MeL)$_2$	5.12
Co(4′-MeL)$_2$	4.85
Ni(4′-MeL)$_2$	3.10
Cu(4′-s-butylL)$_2$	1.85
(4′-MeL)MnL-LMn(4′-MeL)	5.66
(4′-MeL)FeL-LFe(4′-MeL)	5.13
(4′-MeL)CoL-LCo(4′-MeL)	4.65
(4′-MeL)NiL-LNi(4′-MeL)	3.07
(4′-MeL)CuL-LCu(4′-MeL)	1.83

TABLE 3. Proton NMR Data for Mononuclear Complexes in $CDCl_3$. Values are given as δ, ppm, vs. TMS at 34° C.



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

netic 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 by trends observed in the diamagnetic complexes and in other similar paramagnetic complexes.[9] The magnitude of the shift in 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]

The binuclear products gave very complex spectra. The diamagnetic Co(III) complex, however, gave a particularly well resolved spectrum (Fig. 1), permitting analysis. Integrations of s-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 $(4'\text{-MeL})CoL\text{-}LCo(4'\text{-MeL})^+$ were

FIGURE 1. Proton nmr spectrum of (4′-MeL)CoL-LCo(4′-MeL)-$(ClO_4)_2$ in $CDCl_3$ at 34°C. Integration of the s-butyl protons (0.8 and 1.1 ppm) and the methyl protons (2.3 ppm) provide evidence for describing the complex as binuclear.

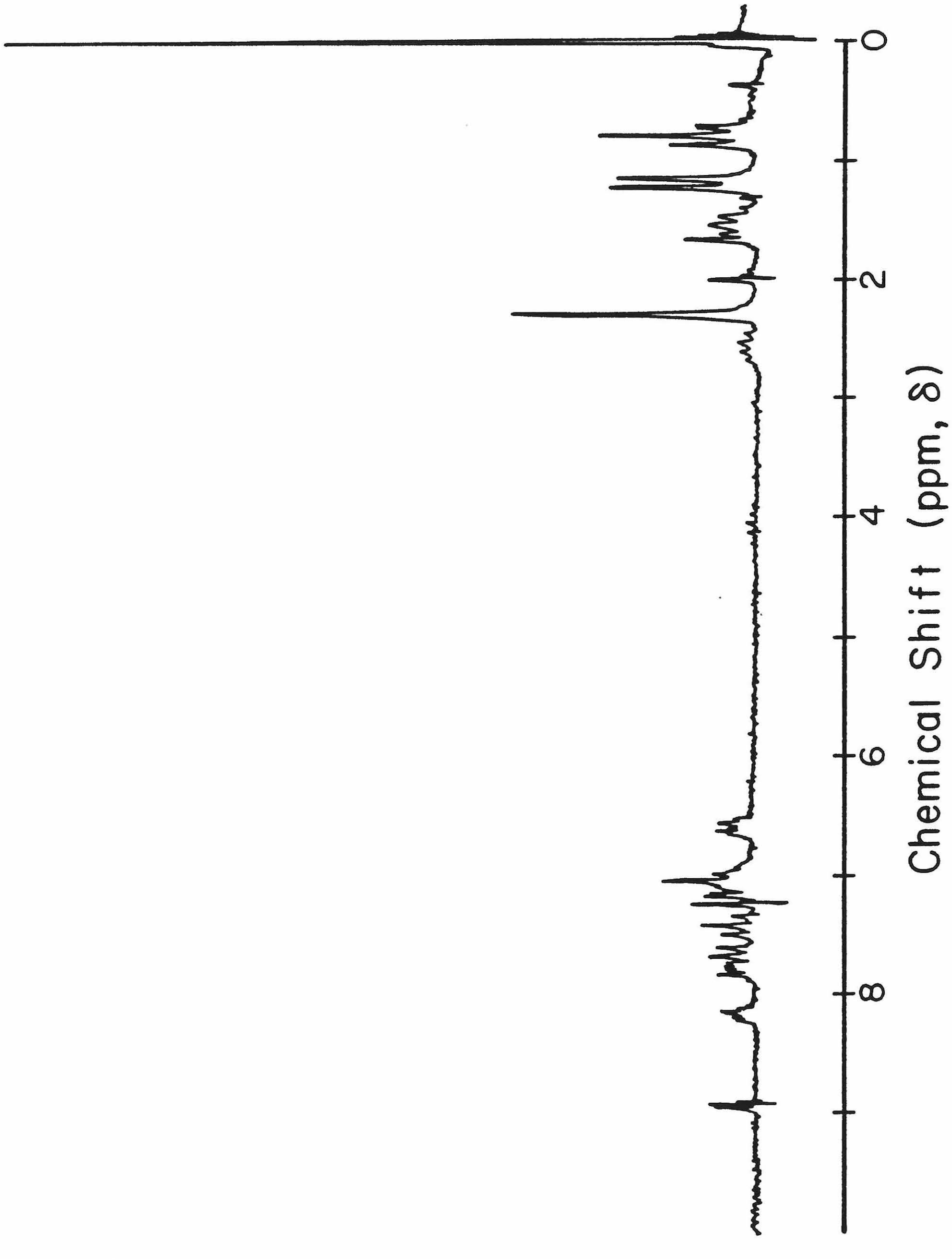


Figure 1

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 ppm 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 4). Most complexes exhibited quasi-reversible behavior except for Cu(4′-*s*-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., Fig. 2, consist of a metal oxidation wave and two reductions attributable to the ligand. The anodic and cathodic peak currents for the M(II/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 $n = 1.0 \pm 0.05$.

The metal reduction potentials of the binuclear complexes are very similar to potentials measured for the monuclear complexes.

TABLE 4. Electrochemical Potentials for Mononuclear and Binuclear Complexes as Measured in DMF (*vs.* NHE).

	M(II/III)			Ligand Waves, E^f			
Complex	E^f	$E_{p_a}-E_{p_c}$[a]	n[b]				
$Mn(4'\text{-}MeL)_2$	0.310	90	1.00		-1.438	-1.652	
$Fe(4'\text{-}MeL)_2$	0.130	65	0.99		-1.460	-1.680	
$Co(4'\text{-}MeL)_2$	-0.094	90	0.95		-1.420	-1.680	
$Ni(4'\text{-}MeL)_2$	0.954	90	1.01		-1.435	-1.664	
$Zn(4'\text{-}MeL)_2$	--	--	--		-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 2. Cyclic voltammograms of DMF solutions: upper figure $Co(4'\text{-MeL})_2$, lower figure $Ni(4'\text{-MeL})_2$.

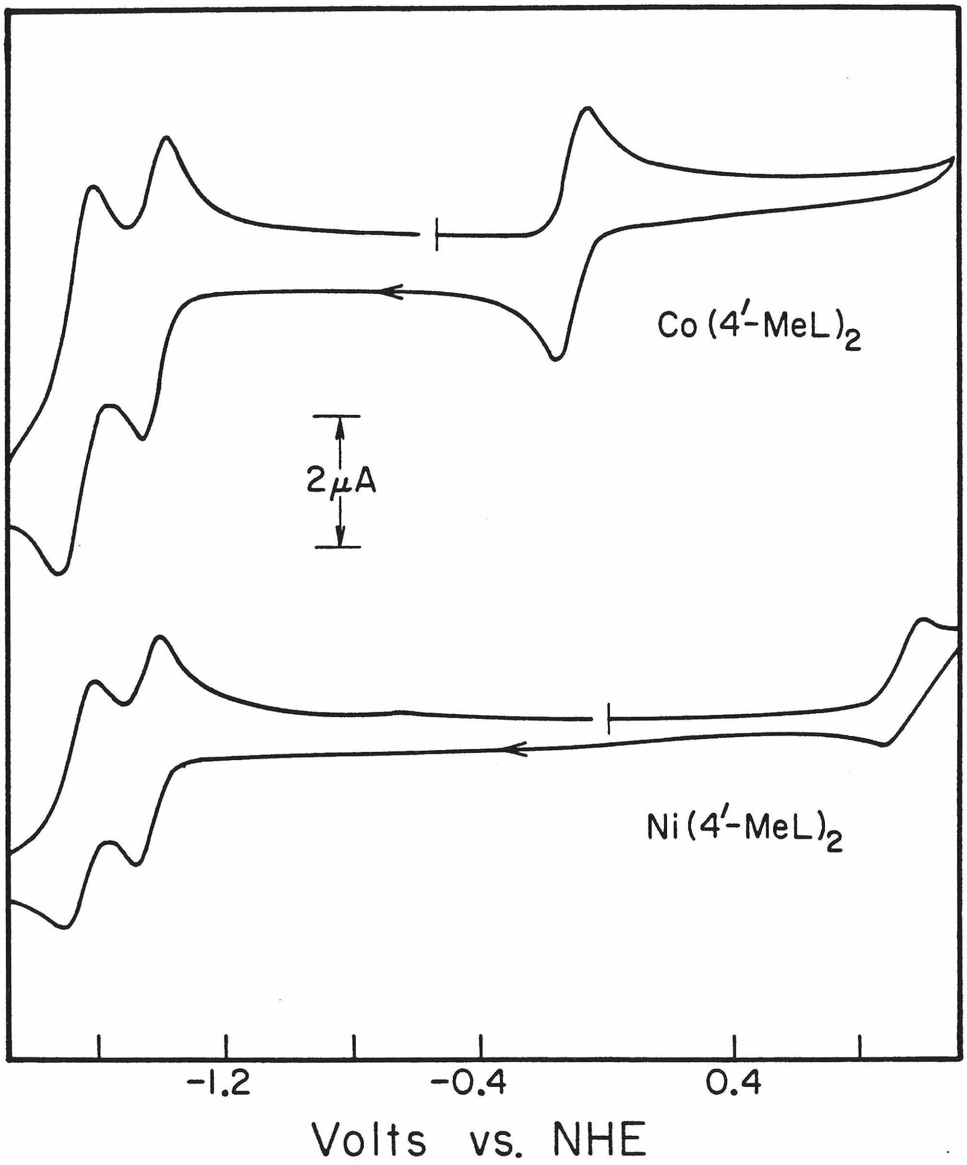


Figure 2

The metal oxidation in the binuclear complexes are quite broad, Fig. 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) of $4 \leq K_{com} \leq 50$. The lower limit of 4 corresponds to completely noninteracting metal

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

centers, in which case one would expect a single electrochemical wave with $E_{p_a} - E_{p_c} = 58$ mV.[14]

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 multi-electron 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 multi-electron 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

FIGURE 3. Cyclic voltammograms of DMF solutions: upper figure $Co(4'\text{-}MeL)_2$, lower figure $(4'\text{-}MeL)CoL\text{-}LCo(4'\text{-}MeL)$.

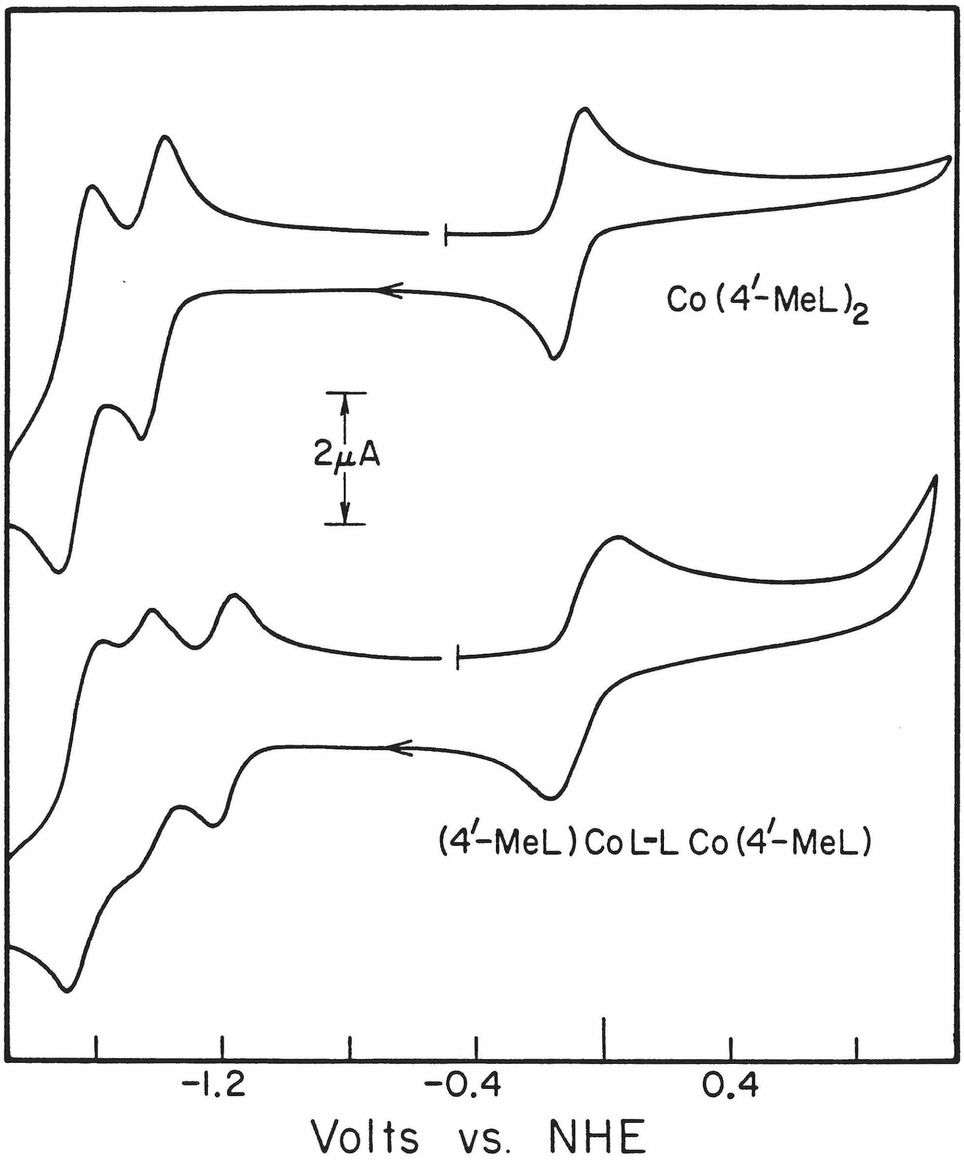


Figure 3

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 5). 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 (Fig. 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.

TABLE 5. Cobalt (III/II) Reduction Potentials, E^f, for Several $Co(RL)_2$. Potentials were Measured in DMF and are Reported *vs*. NHE.

Complex	Co(III)/Co(II)
$Co(4'\text{-}MeL)_2$	-0.094 V
CoL_2	-0.031 V
$Co(4'\text{-}MeL)(5'\text{-}ClL)$	0.081 V
$Co(5'\text{-}ClL)_2$	0.235 V
$Co(5'\text{-}NO_2L)_2$	0.589 V

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

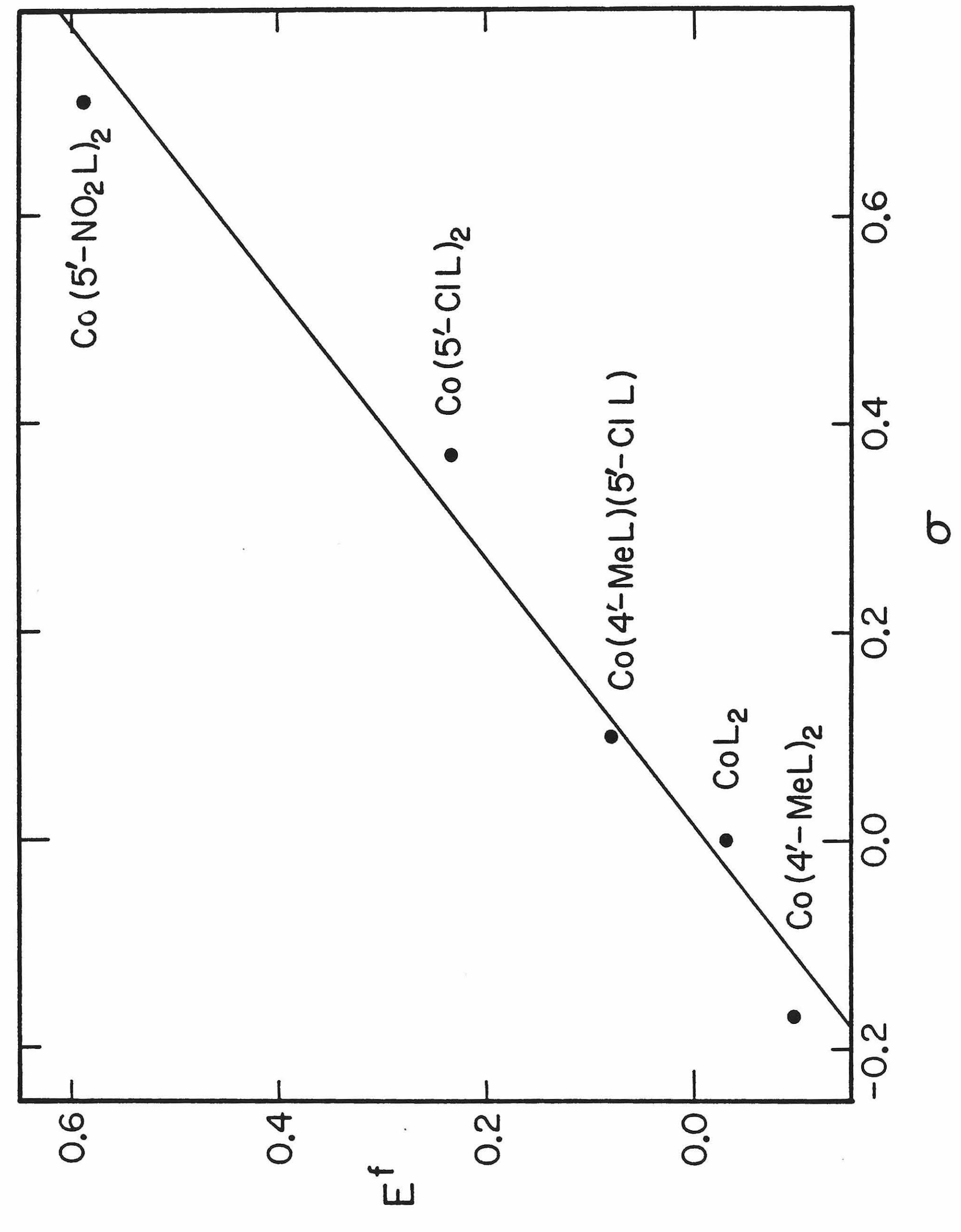

Co(5'-NO$_2$L)$_2$
Co(5'-Cl L)$_2$
Co(4'-MeL)(5'-Cl L)
CoL$_2$
Co(4'-MeL)$_2$
E^f
0.6
0.4
0.2
0.0
σ
-0.2
0.0
0.2
0.4
0.6

Figure 4

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 1 were prepared by the general procedure illustrated below for the 4′-s-butylpyridyl derivative, **2g**. Ligands with significantly lower solubility were purified by recrystallization from nitrobenzene or quinoline.

1,3,5,7-Tetra(2′-(4′-s-butylpyridyl)imino)benzodipyrrole, **2g**. A 1L roundbottom flask was charged with 5.81 g (0.033 mol) of 1,2,4,5-tetracyanobenzene, 22.5 g (0.15 mol) 2-amino-4-s-butylpyridine,[5] 2.61 g anhydrous calcium chloride, and 500 ml of methanol. The mixture was stirred at ambient temperature for seven days and then warmed gradually to reflux temperature. After two days at reflux, the methanol was allowed to distill off and the solvent volume was maintained by the gradual addition of n-butanol. The suspension in butanol was heated at reflux for an additional seven 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). Upon reducing the volume of the eluate, 17.10 g of yellow crystalline product, mp 369-71 °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: s-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) 1,2,4,5-tetracyanobenzene, 330 mg (2.2 mmol) 2-amino-4-s-butylpyridine, 200 mg (1.0 mmol) cupric acetate hydrate, and 10 ml methanol was stirred at ambient temperature for five days followed by three days at reflux. After cooling, the solvent was allowed to evaporate and the residue was washed with water and dried to afford 430 mg of green powder. Five mmol KCN (325 mg), 20 ml ethanol, and 10 ml chloroform was added to the green powder and gentle heating, keeping the mixture from boiling, was applied for two days. Upon cooling, 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 mini-column of alumina which removed most of the green pigment. From the eluant, a 45% yield (167 mg) of greenish-yellow crystals was obtained which were identical spectroscopically to 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 one week before analysis. Aliquots were removed periodically, passed through a filter (Millipore LS, 5.0 μM), and, after appropriate dilution, were analyzed spectrophotometrically on a Cary 17D spectrophotometer. Using previously determined molar extinction coefficients, concentrations were calculated. Analyses were repeated periodically until concentrations had stabilized; relative solubility values are reported in Table 1.

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 mmol of chelating ligand and 2 mmol of metal(II) acetate hydrate in 15 ml of methanol was stirred at ambient temperature for 24 hours. 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) 4′-MeLH in 40 ml warm methanol was added to a solution of 2.6 g (9.0 mmol) $FeBr_2 \cdot 4H_2O$ in 10 ml methanol. The reaction mixture was heated with stirring for 10 minutes. After cooling to ambient temperature, 20 ml diethyl ether was added to the mixture and stirred for five minutes. 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 mmole of the metal(II) perchlorate in 5 ml methanol was added to a solution containing the mononucleating ligand (1.5 mmoles) and 0.5 ml triethylamine in 40 ml hot methanol. The reaction was heated at reflux for 30 minutes during which time dark microcrystalline solid had formed. After cooling, the mixture was filtered and the product was washed with hot methanol. The complexes CoL_2 and $Co(5'\text{-}NO_2L)$, were prepared in the same fashion. Yields: $Mn(4'\text{-}MeL)_2$ 74%, $Fe(4'\text{-}MeL)_2$ 77%, $Co(4'\text{-}MeL)_2$ 79%, $Ni(4'\text{-}MeL)_2$ 75%, $Zn(4'\text{-}MeL)_2$ 83%, CoL_2 91%, and $Co(5'\text{-}NO_2L)_2$ 12%.

Preparation of Bis(1,3-bis(2′-(5′-chloro)pyridylimino)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 stirring for 16 hours 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, m.p. > 350° C.

Preparation of Bis(1, 3-bis(2′-(4′-s-butyl)pyridylimino)isoindolinato)copper(II), Cu(4′-s-butylL)$_2$. A solution of 34 mg (0.25 mmol) anhydrous cupric chloride in 10 ml methanol was added to 210 mg (0.51 mmol) of the chelating ligand, 4′-*s*-butylLH; and stirred at ambient temperature.[7] The initial green solution changed to a yellow-brown suspension after a few minutes. After 15 minutes, 0.2 ml of triethylamine was added and the stirring was continued. After 45 minutes 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) Co(4′-MeL)OAc, 88 mg (0.27 mmol) of chelating ligand, and 5 ml pyridine. The dark red solution was stirred under argon at ambient temperature for 24 hours. 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 337-8 °C.

Preparation of [1, 3-bis(2′-(4′-methylpyridyl)imino)isoindolinato]-[1, 3-bis(2′-(5′-chloropyridyl)imino)isoindolinato]cobalt(II), Co(4′-MeL)(5′-ClL). To 184 mg (0.5 mmol) 5′-ClLH and 222 mg (0.5 mmol) Co(4′-MeL)OAc in a Schlenk tube under argon was added 10 ml methanol and 1 ml triethylamine. The mixture was stirred at ambient temperature for two 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(2′-(4′-methylpyridyl)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 stirring at ambient temperature for 16 hours, the solution was transferred 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) 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$_6$ · 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(2′-(4′-methylpyridyl)imino)isoindolinato)cobalt(III) tetraphenylborate, Co(4′-MeL)$_2$ (ϕ_4B). A mixture of 44 mg (0.1 mmol) Co(4′-MeL)OAc, 36 mg (0.11 mmol) chelating ligand, 4′-MeLH, 41 mg (0.12 mmol) sodium tetraphenylboron, and 6 ml of methanol was stirred for 24 hours under argon at ambient temperature. Then 77 mg (0.14 mmol) ceric ammonium nitrate was added and the red-brown solution immediately changed to a brown suspension. After an additional five hours at 25° C, the suspension was filtered in the air and the solid was washed with methanol and with water. After drying in vacuo, an 84% yield (87 mg) of gold-brown microcrystals was obtained.

Metal Exchange Studies: Ni(4′-MeL)OAc and $Cu(OAc)_2 \cdot H_2O$. To 55 mg (0.125 mmol) Ni(4′-MeL)OAc and 250 mg (1.25 mmol) cupric acetate hydrate was 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 hours. 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.

Metal Exchange Studies: $Ni(4'\text{-}MeL)_2$ and $Cu(OAc)_2 \cdot H_2O$. To 71 mg (0.1 mmol) $Ni(4'\text{-}MeL)_2$ and 200 mg (1.0 mmol) 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 hours 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 to that of Cu(4′-MeL)OAc. Analysis by thin layer chromatography (SiO_2, EtOAc) of the powder showed no remaining $Ni(4'\text{-}MeL)_2$. The yield of Cu(4′-MeL)OAc was 93%.

Metal Exchange Studies: $[Co(4'-MeL)_2]PF_6$ and $Cu(OAc)_2 \cdot H_2O$. A solution of 86 mg (0.1 mmol) $[Co(4'-MeL)_2]PF_6$ and 200 mg (1.0 mmol) $Cu(OAc)_2 \cdot H_2O$ in 3 ml chloroform and 2 ml methanol was stirred at ambient temperature for 24 hours. 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 to that of the starting material. Thin layer chromatographic 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 methanol, followed by 10 ml chloroform. The suspension was stirred at ambient temperature for 72 hours. The suspension was filtered and the solid was washed repeatedly with methanol until the washes were no longer green. After drying 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) Co(4′-MeL)OAc, 74 mg (0.1 mmol) HL-LH, and 5 ml methanol in a Schlenk tube under argon was added 0.5 ml triethylamine. After the dark brown suspension was stirred at ambient temperature for 20 hours, an additional 10 ml 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. TMS at 34° C): aromatic protons: 48.6, 45.7, 37.0, 30.6, 29.1, and 27.5; *s*-butyl protons: -4.3 and -7.6; and methyl protons: -13.7.

Alternate Preparation of (4′-MeL)CoL-LCo(4′-MeL). A Schlenk tube was charged with 98 mg (0.1 mmol) (AcO)CoL-LCo(OAc), 65 mg (0.2 mmol) 4′-MeLH, and 5 ml methanol; the mixture was stirred under argon at ambient temperature. After 15 minutes, 0.5 ml triethylamine was added to the brown suspension and the stirring was continued for an additional 16 hours. An additional 10 ml 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 to 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) $AgClO_4$ was added to a slurry of

430 mg (0.79 mmol) Fe(4′-MeLH)Br_2 in 35 ml 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) sodium methoxide in 20 ml 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) HL-LH and 29 mg (0.54 mmol) sodium methoxide in 5 ml methanol and 15 ml toluene. After stirring for one hour, 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, 33 mg (0.06 mmol) of ceric ammonium nitrate was added and the mixture was stirred for 0.5 hour 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 stirring for 0.5 hour 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′-s-butylL)NiL-LNi(4′-s-butylL) and Molecular Weight Determination. To 245 mg (0.25 mmol) (AcO)NiL-LNi(OAc) and 226 mg (0.55 mmol) 4′-*s*-butylLH was added 20 ml chloroform and the resulting solution was stirred at ambient temperature for 72 hours. 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) (AcO)CuL-LCu(OAc) and 22 mg (0.066 mmol) 4′-MeLH was added 5 ml methanol and 0.2 ml triethylamine. The resulting suspension was stirred at 25° C, as the color gradually changed from olive-green to yellow-gold. After three hours the suspension was filtered and the solid was washed with methanol and dried *in vacuo*. A 48% yield (27 mg) of gold-colored powder was obtained; mp $>$ 390° C.

Attempted Preparation of (4′-MeL)ZnL-LZn(4′-MeL). To 450 mg (1 mmol) Zn(4′-MeL)OAc and 272 mg (0.5 mmol) of binucleating ligand, HL-LH, was added 200 ml methanol and 20 ml triethylamine; the resulting suspension was stirred at ambient temperature for seven 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 4A 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 a 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 assuming a value of +0.400 V for the ferrocene/ferricinium couple. When the ferrocene oxidation wave overlapped with the wave under investigation, the cobaltocene/cobalticinium couple, -0.936 V vs. the NHE, was used as an internal standard.

Formal reduction potentials, E^f, were measured by cyclic voltammetry using the formula $E^f = (E_{p_a} + E_{p_c})/2$. 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 using Pascal's constants.

Proton nmr spectra were obtained on Varian EM-390 and Jeol FX90Q nmr spectrometers with $CDCl_3$ as the solvent and tetramethylsilane as a reference.

Electronic spectra were recorded on a Cary 14 spectrophotometer. Solution spectra were obtained using one centimeter matched quartz cells.

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s-butyl substituted ligand, 4′-s-butylLH was used in order to avoid coprecipitation of the Cu(II) complex and unreacted ligand.

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CHAPTER 3

Synthesis and Characterization of Mononuclear and Binuclear Ruthenium Complexes of 1, 3-bis(2′-pyridylimino)Isoindolines

Synthesis and Characterization of Mononuclear and Binuclear Ruthenium Complexes of 1,3-bis(2'-pyridylimino)Isoindolines

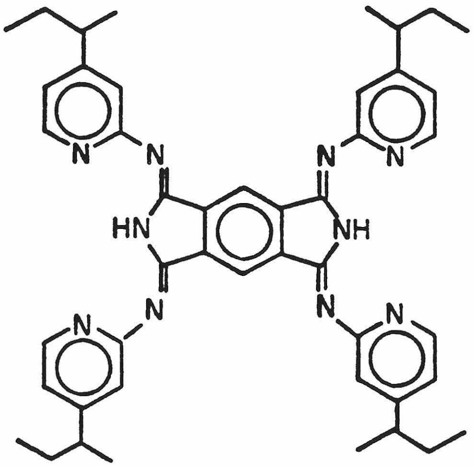
David N. Marks,[1a] Walter O. Siegl[1b] and Robert R. Gagné[1a]

Abstract

Ruthenium complexes were prepared containing the ligand, 4'-MeLH, resulting from the condensation of 1,2-dicyanobenzene and 2-amino-4-methylpyridine. The ligand functions as a tridentate chelate in its anionic or neutral form. Ruthenium complexes were prepared with metal to ligand ratios of 1:1 and 1:2. The 1:1 complex of Ru(III) also contains three chlorides as ligands, Ru(4'-MeLH)Cl_3, while in the 1:2 complex, Ru$(4'\text{-MeL})_2$, the two tridentate ligands provide a pseudooctahedral environment about the metal ion. Binuclear complexes were prepared in which the metals are bridged by the ligand made from the reaction of 1,2,4,5-tetracyanobenzene and 2-amino-4-s-butylpyridine. The binucleating ligand binds two metal ions, providing three coordination sites for each, with the remaining coordination sites occupied by $4'\text{-MeL}^-$. Binuclear Ru(II), Ru(III) and mixed-metal complexes were prepared. Spectral and electrochemical properties of these molecules were investigated.

INTRODUCTION

Binuclear transition metal complexes, in which the two metals are bridged by the ligand 1, have been prepared and characterized.[2] The ligand 1, HL-LH, binds two metal ions, functioning as a tridentate

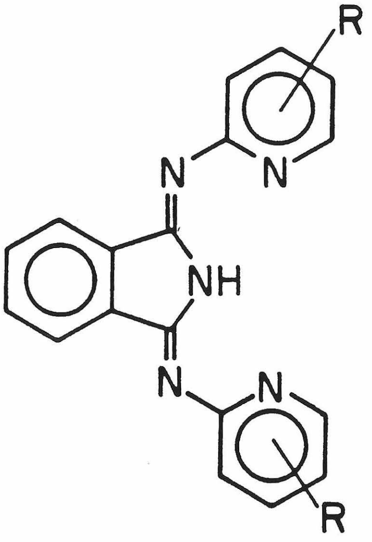


= HL-LH[3]

1

chelate for each metal. In the metal complexes the bridging ligand is normally present as a dianion due to deprotonation of the two pyrrole nitrogens. Binuclear complexes were prepared in which the remaining metal coordination sites are occupied by the anion of the isoindoline ligand 2, 4′-MeL$^-$, resulting in two six-coordinate metal ions, (4′-MeL)ML-LM(4′-MeL).

The bridging ligand 1 also made it possible to prepare polymeric metal species containing octahedral metal ions. These oligomeric complexes were of interest because of their possible use as multi-



4′-MeLH, R = 4-CH_3 [3]

5′-ClLH, R = 5-Cl

2

electron transfer reagents. Adjacent metal ions in the complex are quite distant from one another, at approximately 11 Å.[4] The presence of the flat conjugated bridging ligand, however, suggested that electron transfer between the metal ions might be facile.

Mononuclear and binuclear complexes of first-row transition metals have previously been prepared and characterized.[2] Electrochemical and magnetic measurements of the binuclear species indicated little interaction between the metal ions.

Numerous studies involving ruthenium mixed-valent binuclear complexes have been made.[5,6] The results of these studies suggest that information concerning the rate of intramolecular electron transfer in polynuclear complexes containing the bridging ligand **1**, might be obtainable by investigating the spectroscopic properties of the mixed-valent ruthenium binuclear complex. Mononuclear, binuclear, and trinuclear ruthenium complexes were prepared. The electrochemical and spectroscopic properties of these species are reported.

RESULTS AND DISCUSSION

The syntheses of the ligands have been described elsewhere.[2,7]

Synthesis and Characterization of Mononuclear Ruthenium Complexes. The mononuclear bis(isoindoline)Ru(II) complex **3**, $Ru(4'\text{-}MeL)_2$, was prepared by reaction of the free ligand in a basic alcoholic solution with either tetrakis(dimethylsulfoxide)dichlororuthenium(II), $Ru(DMSO)_4Cl_2$, or hydrated ruthenium trichloride (eq. 1 and 2). The Ru(II) starting material was preferred because the

$$Ru(DMSO)_4Cl_2 + 2\ 4'\text{-}MeLH \xrightarrow{\text{base}} \underset{\mathbf{3}}{Ru(4'\text{-}MeL)_2} \tag{1}$$

$$RuCl_3 \cdot xH_2O + 2\ 4'\text{-}MeLH \xrightarrow{\text{base}} \underset{\mathbf{3}}{Ru(4'\text{-}MeL)_2} \tag{2}$$

yield of the product was much improved. A greater than 60% yield was attained in this reaction, compared to approximately 15% yield when starting with hydrated ruthenium trichloride.

The preparation of $Ru(4'\text{-}MeL)_2$ from hydrated ruthenium trichloride is analogous to the synthesis of $Ru(bpy)_3^{2+}$.[8] In both these syntheses, the initial Ru(III) species is reduced during the reaction to Ru(II) with, presumably, the coincident oxidation of alcohol.

The mononuclear Ru(II) complex **3** is a dark-blue crystalline solid, dissolving in nonpolar solvents such as methylene chloride and toluene to produce dark-green solutions. Although air stable in the solid state, methylene chloride solutions of **3** are moderately air sensitive. The corresponding Ru(III) complex **4**, $Ru(4'\text{-}MeL)_2^+$, was isolated from a methylene chloride solution which had been exposed to air for several hours. The complex **3** was more conveniently oxidized with silver ion to the Ru(III) complex **4**, isolated as its ClO_4^- salt (eq. 3). The dark red-brown Ru(III) complex **4** is paramagnetic with a magnetic moment of 1.85 B.M., indicative of a d^5 low-spin complex having one unpaired electron. Attempts to prepare $Ru(4'\text{-}MeL)_2^+$ directly from the reaction of hydrated ruthenium trichloride and 4'-MeLH were unsuccessful.

$$\underset{\mathbf{3}}{Ru(4'\text{-}MeL)_2} + AgClO_4 \rightarrow \underset{\mathbf{4}}{Ru(4'\text{-}MeL)_2ClO_4} + Ag \qquad (3)$$

The infrared spectra of the metal complexes exhibit strong bands due to the presence of the deprotonated isoindoline ligand.[2] The proton nmr spectra, electronic spectra, and electrochemistry are discussed in a later section.

Synthesis and Characterization of $(RLH)RuCl_3$. To avoid polymerization problems in the synthesis of the binuclear complex, it was necessary to isolate a ruthenium complex containing one chelated isoindoline ligand and several readily dissociable ligands. For the first-row transition metals, M(II) complexes of the type, M(4'-MeL)OAc, could be easily isolated, and they proved useful as intermediates in the synthesis of the binuclear species (eq. 4). Attempts to prepare a

$$2M(4'\text{-}MeL)OAc + HL\text{-}LH \rightarrow (4'\text{-}MeL)ML\text{-}LM(4'\text{-}MeL) \qquad (4)$$

mono(isoindoline) complex of Ru(II) were unsuccessful. Complexes containing Ru(III) of the type $(RLH)RuCl_3$, were prepared for various substituted isoindoline ligands. These complexes were utilized as the intermediate species necessary in the synthesis of the binuclear ruthenium complex.

The complexes (RLH)$RuCl_3$, 5, were made from the reaction of hydrated ruthenium trichloride and the isoindoline ligand in ethanol with no added base, eq. 5. The Ru(III) complexes 5 were obtained as

$$RuCl_3 \cdot xH_2O + RLH \rightarrow \underset{5}{(RLH)RuCl_3} \qquad (5)$$

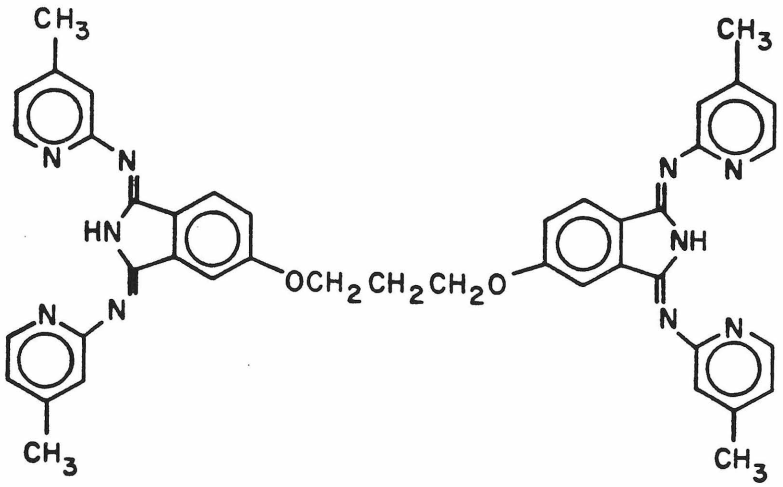
dark-brown crystals which usually contained one molecule of ethanol per ruthenium as a solvate. The Ru(III) ions in these complexes are bound to a neutral isoindoline ligand, consistent with the analytical data, magnetic measurements and the infrared spectrum of the complex. The infrared spectrum of (4'-MeLH)$RuCl_3$ has strong bands in the region 1600-1650 cm^{-1} which are characteristic of a chelated nondeprotonated isoindoline ligand.[9] The proton, presumably, is not still associated with the pyrrole nitrogen, since this would likely interfere with bonding to the metal. The proton may be associated with one of the imine nitrogens. Treatment of complex 5 with a second equivalent of ligand in the presence of a tertiary amine base, led to the formation of the Ru(II) complex 3, $Ru(RL)_2$.

Synthesis and Characterization of Binuclear Ruthenium Complexes. A binuclear Ru(II) complex 6, was prepared by treating the bridging ligand 1, HL-LH, with two equivalents of (4'-MeLH)$RuCl_3$ in basic ethanol, according to eq. 6. The binuclear complex 6 is intensely

$$2(4'\text{-MeLH})RuCl_3 + HL\text{-}LH \xrightarrow{\text{base}} \underset{6}{(4\ \text{-MeL})RuL\text{-}LRu(4'\text{-MeL})} \qquad (6)$$

colored and has high solubility in organic solvents such as toluene. Although air stable in the solid state the complex is moderately air sensitive in solution. The binuclear Ru(II) complex 6 was successfully oxidized with silver ion to the corresponding Ru(III) binuclear species which was isolated as its ClO_4^- salt, (4′-MeL)RuL-LRu(4′-MeL)$(ClO_4)_2$. Magnetic measurements indicate the presence of two isolated Ru(III) ions with a magnetic moment at ambient temperature of 1.83 Bohr magnetons per ruthenium in the complex. The infrared spectra of the binuclear Ru(II) and Ru(III) complexes are very similar to those of the mononuclear complexes containing deprotonated isoindoline ligands. Proton nmr spectra, electronic spectra, and electrochemical properties are discussed below.

A binuclear Ru(II) complex was prepared with the ligand 7, HL-$O(CH_2)_3O$-LH, bridging the two metal ions. The ligand was treated with two equivalents of (4′-MeLH)$RuCl_3$ to prepare the binuclear complex 8, eq. 7. The binuclear complex 8 was obtained as a dark-green



7

$$2(4'\text{-MeLH})\text{RuCl}_3 + \text{HL-O(CH}_2)_3\text{O-LH} \rightarrow \underset{8}{(4'\text{-MeL})\text{RuL-O(CH}_2)_3\text{O-LRu}(4'\text{-MeL})} \quad (7)$$

solid; the infrared spectrum indicated that both ends of the bridging ligand were complexed.

The preparation of heteronuclear bimetal complexes necessitated the addition of metal ions to the bridging ligand in a stepwise fashion. The ruthenium ion was added first, since both Ru(II) and Ru(III) are rather substitution inert. Ruthenium in either oxidation state was unlikely to undergo ligand exchange during the addition of the second metal ion. The reaction of the Ru(III) complex 5 with a large excess of bridging ligand (eq. 8) afforded a mixture of products from which the desired mononuclear complex 9, in which one end of the bridging ligand remained unchelated, was isolated after chromatography. The complex

$$\underset{5}{(4'\text{-MeLH})\text{RuCl}_3} + \text{excess HL-LH} \xrightarrow{\text{base}} \underset{9}{(4'\text{-MeL})\text{RuL-LH}} \quad (8)$$

9 was obtained as a dark-green powder which was quite soluble in non-polar solvents including cyclohexane. The infrared spectrum exhibited a relatively strong band at approximately 1635 cm^{-1} characteristic of the unchelated end of the bridging ligand, in addition to bands at lower energy characteristic of the complexed end of the molecule.[2]

The characterization of complex 9 was further confirmed by its conversion to the previously isolated binuclear ruthenium complex 6, (4′-MeL)RuL-LRu(4′-MeL). Treatment of 9 with an equivalent of (4′-MeLH)RuCl_3 converted it to the binuclear complex 6 in good yield. Alternatively, treatment of 9 with (5′-ClLH)RuCl_3 yielded a binuclear complex, 10, in which the two ruthenium ions were in essentially identical coordination environments but in somewhat different electronic environments (eq. 9).

$$\underset{9}{(4'\text{-MeL})\text{RuL-LH}} + (5'\text{-ClLH})\text{RuCl}_3 \xrightarrow{\text{base}} \underset{10}{(4'\text{-MeL})\text{RuL-LRu}(5'\text{-ClL})} \qquad (9)$$

The complex 9 was also readily converted to various heteronuclear bimetallic complexes using conditions developed earlier for mononuclear complexes. For example, complex 9 reacted with cupric acetate to form the (Ru, Cu) complex 11 and with dichlorobis(benzonitrile)palladium(II) to form the (Ru, Pd) complex 12 in good yield; eqs. 10 and 11. No evidence for metal ion exchange was observed in either reaction.

$$\underset{9}{(4'\text{-MeL})\text{RuL-LH}} + \text{Cu(OAc)}_2 \rightarrow \underset{11}{(4'\text{-MeL})\text{RuL-LCu(OAc)}} \qquad (10)$$

$$\underset{9}{(4'\text{-MeL})\text{RuL-LH}} + \text{PdCl}_2(\text{NCC}_6\text{H}_5)_2 \rightarrow \underset{12}{(4'\text{-MeL})\text{RuL-LPdCl}} \qquad (11)$$

Synthesis and Characterization of a Trinuclear Ru(II) Complex.

The first step in the synthesis of the trinuclear complex was the preparation of the mononuclear complex 13. Tetrakis(dimethylsulfoxide)dichlororuthenium(II) reacted with a large excess of bridging ligand to form a mixture of products from which the mononuclear complex 13 was isolated after chromatography; eq. 12. The complex

$$\text{RuCl}_2(\text{DMSO})_4 + \text{excess HL-LH} \xrightarrow{\text{base}} \underset{13}{\text{HL-LRuL-LH}} \qquad (12)$$

13 is dark green in color and exhibited a moderately strong band in the infrared spectrum at approximately 1635 cm^{-1} characteristic of the uncomplexed ends of the bridging ligands. The mononuclear complex 13 reacted with two equivalents of $(4'\text{-MeLH})RuCl_3$ according to eq. 13 to afford the trinuclear Ru(II) complex 14 in good yield. The trinuclear

$$\underset{13}{\mathrm{HL\text{-}LRuL\text{-}LH}} + 2(4'\text{-}\mathrm{MeLH})\mathrm{RuCl_3} \xrightarrow{\text{base}} \underset{14}{(4'\text{-}\mathrm{MeL})\mathrm{RuL\text{-}LRuL\text{-}LRu}(4'\text{-}\mathrm{MeL})} \tag{13}$$

complex was also dark green, and gave an elemental analysis consistent with its formulation. In the infrared, the 1635 cm^{-1} band had disappeared, indicating that both ends of the bridging ligand were now complexed in the product. The infrared spectrum was otherwise quite similar to that of the binuclear Ru(II) complex 6, (4′-MeL)RuL-LRu-(4′-MeL).

Proton NMR Spectra. The proton nmr spectra of the diamagnetic Ru(II) complexes were useful in identifying the complexes and testing their purity. Very broadened spectra were observed for the Ru(III) complexes and consequently were of no use in characterization.

The Ru(II) mononuclear complex 3, $Ru(4'\text{-MeL})_2$, gives a well resolved spectrum, and peak assignments can be made from the integration and splitting pattern of the peaks (see Experimental Section). The spectrum of the binuclear Ru(II) complex 6, (4′-MeL)RuL-LRu-(4′-MeL), provides evidence for its description as a discrete binuclear species. Integrations of *s*-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.

Electronic Absorption Spectra. The visible spectra of mononuclear and binuclear ruthenium complexes have intense ($\epsilon \sim$ 20-50,000) ligand absorptions in the range 400-450 nm. These high-energy ligand absorptions are fairly broad, so that concentrated solutions ($\sim$ 10 mM) are very dark.

In addition to the ligand absorptions, lower energy absorptions are observed in the complexes of Ru(II) and Ru(III), Table 1. An intense Ru(II) → L charge transfer band is observed (Figure 1) at approximately 650-700 nm in the mononuclear and binuclear complexes, $Ru(4'\text{-}MeL)_2$ and (4′-MeL)RuL-LRu(4′-MeL). The band is composed of overlapping absorptions, with a band shape quite similar to the Ru(II) → L charge transfer band in tris(bipyridine)ruthenium(II), $Ru(bpy)_3^{2+}$.[10] The multiple absorption bands observed for $Ru(bpy)_3^{2+}$ have been ascribed to charge transfer into different antibonding ligand orbitals.

The Ru(III) complexes, $Ru(4'\text{-}MeL)_2ClO_4$ and (4′-MeL)RuL-LRu-$(4'\text{-}MeL)(ClO_4)_2$, show absorptions in the near infrared at approximately 770 nm and 860 nm. These absorptions may be assigned as L → Ru(III) charge transfer due to the similarity of the spectrum with that of $Ru(bpy)_3^{3+}$. Overlapping absorption bands are observed for $Ru(bpy)_3^{3+}$ at low energy (675 nm) of similar intensity (ϵ = 410) that have been assigned as L → Ru(III) charge transfer.[11]

Table 1. Electronic Spectral Data in Methylene Chloride

Complex	λ_{max} (nm)	ϵ
Ru(4′-MeL)$_2$	665	9,800
(4′-MeL)RuL-LRu(4′-MeL)	710	21,300
Ru(4′-MeL)$_2$ClO$_4$	770	400[a]
	847	400[a]
(4′-MeL)RuL-LRu(4′-MeL)(ClO$_4$)$_2$	770	1,100[a]
	865	1,100[a]

[a] These are maximum values of extinction coefficients. The bands observed appear as peaks on the tail of the visible absorption.

FIGURE 1. Visible - near IR spectrum of (4′-MeL)RuL-LRu(4′-MeL) in methylene chloride.

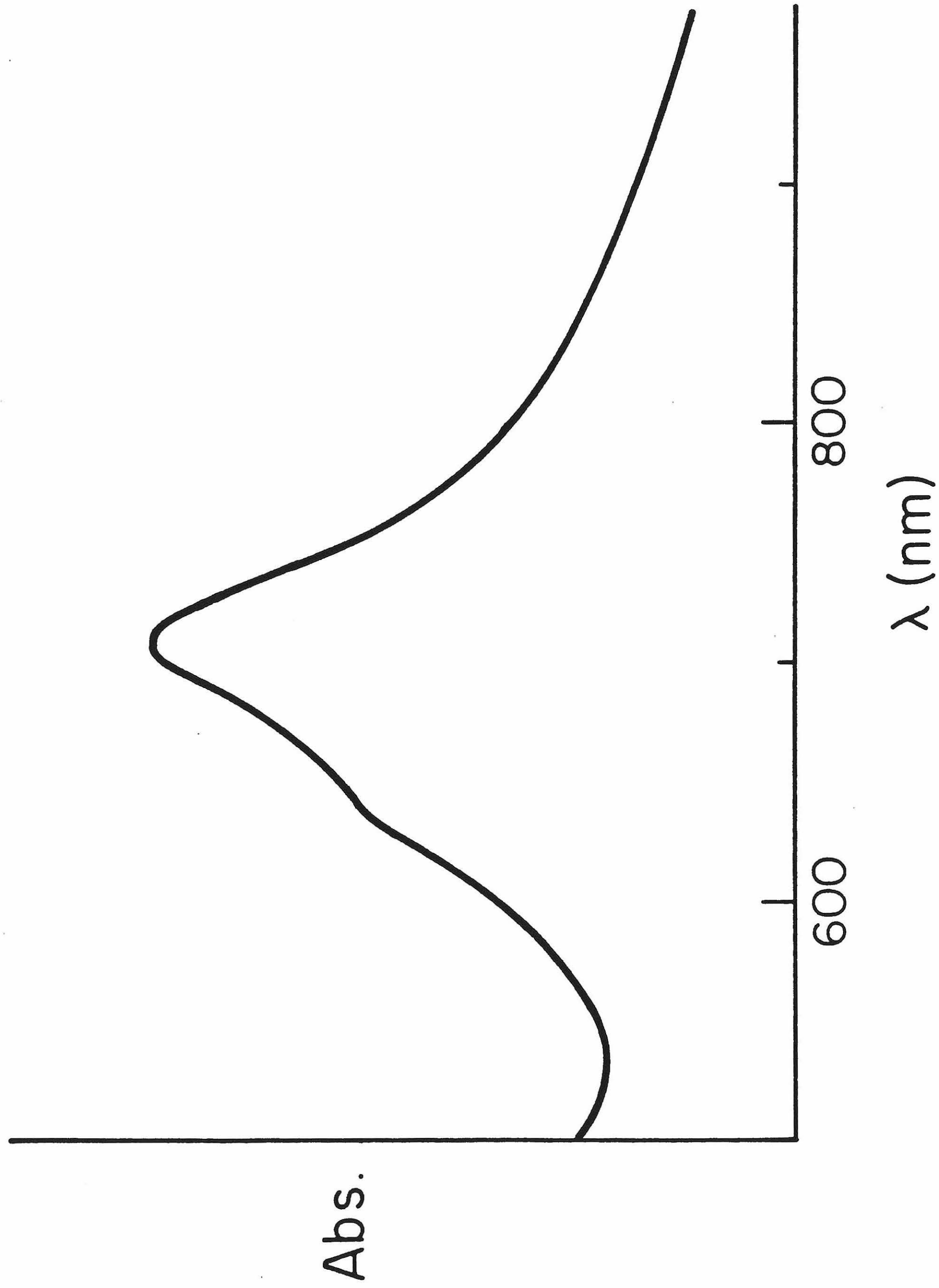


Figure 1.

Electrochemistry. Electrochemical measurements were made on solutions of Ru(4′-MeL)$_2$, **3**, and (4′-MeL)RuL-LRu(4′-MeL), **6**, in N,N-dimethylformamide (DMF). Cyclic voltammograms of the metal oxidation waves are presented in Figure 2. Identical electrochemistry is observed for the Ru(III) complexes. The cyclic voltammogram of the mononuclear complex exhibits a single reversible oxidation wave with anodic current equal to cathodic current. The anodic to cathodic peak potential separation of 65 mV is independent of scan rate over the range 20-500 mV/sec. Coulometry at a potential anodic of the oxidation wave verifies that this is a one-electron process.

The cyclic voltammogram of the binuclear complex, **6**, has a broad oxidation wave at approximately the same potential as observed for the mononuclear complex. The electrochemical wave has equal anodic and cathodic current. The anodic to cathodic peak potential separation is independent of scan rate indicating two reversible overlapping oxidation waves rather than an irreversible process. Coulometry at a potential anodic of the metal oxidations confirms a two-electron process.

The electrochemistry observed for the mononuclear and binuclear complexes is essentially reversible. Anodic to cathodic peak potential separations were always observed to be greater than the expected 58 mV for a reversible process;[12] however, the separation of 65 mV seen for Ru(4′-MeL)$_2$ was identical to the separation observed for the reversible couple ferrocene/ferricinium[13] under the same conditions. The increased broadening of the wave is likely due to uncompensated solution resistance. Because of the greater breadth of the electro-

FIGURE 2. Cyclic voltammograms of DMF solutions:
(A) Ru(4′-MeL)$_2$ and (B) (4′-MeL)RuL-LRu(4′-MeL).

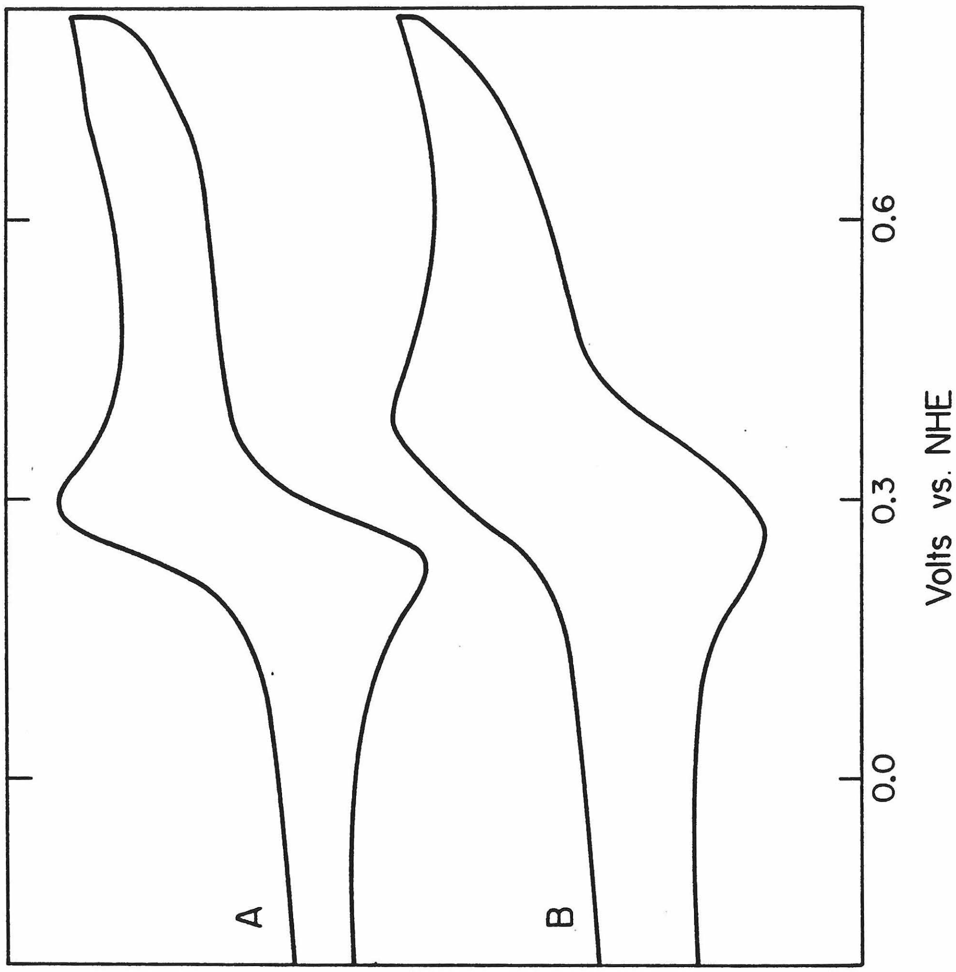


Figure 2.

chemical waves it was not possible to use the equations of Richardson and Taube[14] to calculate the separation between the two oxidation waves of the binuclear complex.

The separation of the two oxidation waves was estimated by a graphical approach. The electrochemistry observed for the binuclear complex 6 was simulated by the addition of two one-electron waves separated by varying amounts. The electrochemistry observed for the mononuclear complex, $Ru(4'\text{-}MeL)_2$, was used as the one-electron model. Using a differential pulse voltammogram obtained for $Ru(4'\text{-}MeL)_2$, a good recreation of the oxidation wave observed for the binuclear complex was found at a separation of the two waves of 75 mV ± 5 mV; Figure 3.

Ligand reductions similar to those seen for complexes of Mn(II), Fe(II), Co(II), Ni(II) and Zn(II) are observed for these mononuclear and binuclear complexes of ruthenium.[2] The mononuclear complex, $Ru(4'\text{-}MeL)_2$, has two reduction waves (Table 2). The binuclear species has two reductions at approximately the same potentials as the mononuclear complex. A third ligand reduction appears at a more positive potential which is presumably due to reduction of the bridging ligand. In addition, a fourth reduction wave is observed at very negative potentials. For binuclear complexes of the first row transition metals, only iron shows four reduction waves and this most negative reduction has not been studied further.

The electrochemical behavior of the trinuclear ruthenium complex 14, (4'-MeL)RuL-LRuL-LRu(4'-MeL), was studied. Over-

FIGURE 3. Observed differential pulse voltammogram of (4′-MeL)RuL-LRu(4′-MeL) in DMF (solid line). The dotted lines represent the two one-electron oxidation waves which constitute the observed voltammogram. The positions of the two oxidation waves were determined by graphically simulating the observed voltammogram.

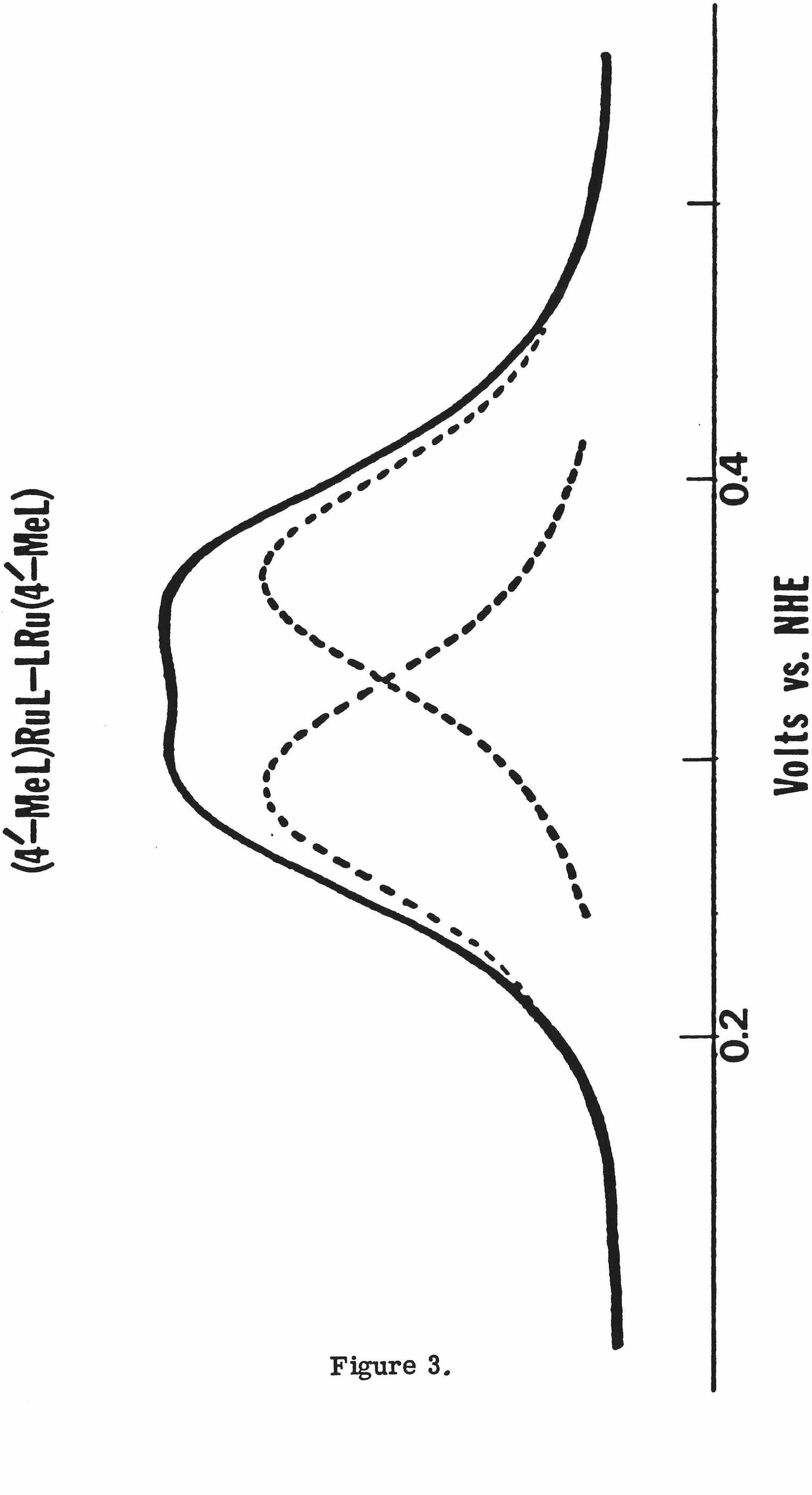


Figure 3.

Table 2. Electrochemical Potentials for Mononuclear and Binuclear Ruthenium Complexes as measured in DMF (vs. nhe).

Complex	M(II/III)		n^b	Ligand Waves, E^f
	E^f	$E_{p_a}-E_{p_c}$ [a]		
$Ru(4'\text{-}MeL)_2$	0.278	65	0.98	-1.381
				-1.662
(4'-MeL)RuL-LRu(4'-MeL)	0.325	120	2.02	-1.128
	(0.288, 0.363)[c]			-1.401
				-1.644
				-1.805

[a] Anodic peak to cathodic peak potential 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 of the two one-electron oxidation waves determined graphically.

lapping metal oxidation waves were observed in the same region as in the mononuclear and binuclear complexes, approximately 0.3 V vs. nhe. The detail of the differential pulse voltammogram indicated initial oxidation of the two terminal Ru(II) ions at nearly the same potential, followed by oxidation of the middle Ru(II) ion at slightly higher potential.

The electrochemistry of two other ruthenium binuclear complexes was also investigated. The binuclear complex **10**, (4′-MeL)RuL-LRu-(5′-ClL), contained the two metal ions in different chemical environments. The difference in the environments of the metal ions was great enough that two separate one-electron waves were observed (Table 3).

The electrochemical behavior of the binuclear Ru(II) complex **8**, (4′-MeL)RuL-O$(CH_2)_3$O-LRu(4′-MeL) was also explored. In this complex, the bridging ligand, **7**, is not conjugated, and the metal ions should be totally isolated from one another. The binuclear Ru(II) complex **8** shows one reversible oxidation wave in cyclic voltammetry. This oxidation wave has the shape of a one-electron wave with an anodic to cathodic peak separation of 65 mV, (Table 3). Coulometry confirmed that this is a two-electron oxidation.

The electrochemistry of the three binuclear complexes, (4′-MeL)RuL-LRu(5′-ClL), (4′-MeL)RuL-LRu(4′-MeL), and (4′-MeL)RuL-O$(CH_2)_3$O-LRu(4′-MeL), illustrates the different types of behavior that may be expected for binuclear complexes; Figure 4. For binuclear complexes in which the metals are in different environments, or where there is sufficient interaction between the two metals,[15]

Table 3. Electrochemical Potentials (measured in DMF vs. nhe).

No.	Complex	Ru(II/III)	
		E^f	$E_{p_a}-E_{p_c}$[a]
10	(4′-MeL)RuL-LRu(5′-ClL)	0.310, 0.480	65[b]
6	(4′-MeL)RuL-LRu(4′-MeL)	0.325 (0.288, 0.363)[c]	120
8	(4′-MeL)RuL-O$(CH_2)_3$O-LRu(4′-MeL)	0.265	65
9	(4′-MeL)RuL-LH	0.324	70
12	(4′-MeL)RuL-LPdCl	0.323	65
11	(4′-MeL)RuL-LCu(OAc)	0.308	70
3	Ru$(4'\text{-MeL})_2$	0.278	65

[a] Anodic peak to cathodic peak separation of metal wave in cyclic voltammetry, at a scan rate of 200 mV/sec. given in millivolts.

[b] Anodic peak to cathodic peak separation of both waves are equal.

[c] Potentials of the two one-electron oxidation waves determined graphically.

FIGURE 4. Cyclic voltammograms of DMF solutions:
(A) (4′-MeL)RuL-O$(CH_2)_3$O-LRu(4′-MeL),
(B) (4′-MeL)RuL-LRu(4′-MeL), and
(C) (4′-MeL)RuL-LRu(5′-ClL).

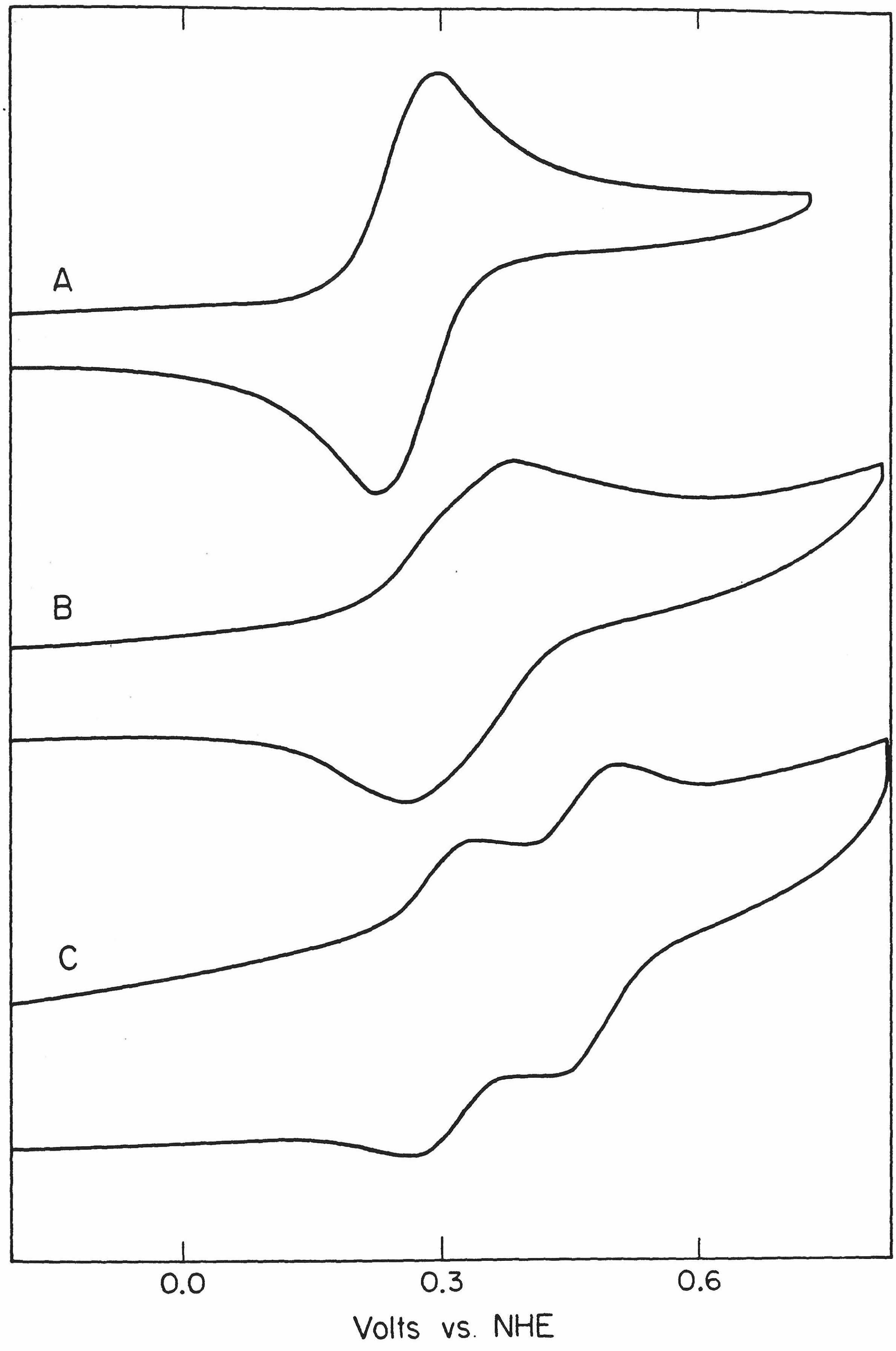


Figure 4.

one observes two separate one-electron waves. As the interaction between identical metals in a binuclear complex decreases, as in (4′-MeL)RuL-LRu(4′-MeL), the two one-electron waves overlap, producing a single broadened electrochemical wave. In the extreme case where the metals are isolated from one another, a single two-electron electrochemical wave with the shape of a one-electron wave is observed.[16]

In order to quantify the extent of metal-metal interaction in the binuclear ruthenium complex, 6, (4′-MeL)RuL-LRu(4′-MeL), the electrochemistry of mixed-metal complexes was investigated; Table 3. In a previous study the delocalization energy of a mixed-valent $Cu^{II}Cu^{I}$ macrocyclic complex was estimated by studying the electrochemistry of some mixed-metal binuclear complexes having the same charge and structure as the homobinuclear complex.[15] Cyclic voltammograms of the mixed metal complexes, (4′-MeL)RuL-LPdCl, 12, and (4′-MeL)RuL-LCu(OAc), 11, exhibit reversible ruthenium oxidation waves. [The complex 9, (4′-MeL)RuL-LH may also be considered if charge is the primary concern (H^+ = Pd-Cl^+).] These complexes have ruthenium oxidation waves more positive than the first oxidation of (4′-MeL)RuL-LRu(4′-MeL). Since other effects such as charge and coordination environment are the same for ruthenium, the change in the electrochemical potential between the heterobinuclear and homobinuclear complexes can be ascribed to the delocalization energy in the mixed-valent ruthenium species. The mixed-valent ruthenium complex can delocalize the odd electron over both metals. This delocalization is not energetically favorable when the two metals are not identical.

The Ru(II/III) oxidation is at a higher electrochemical potential for the mixed-metal complexes, as expected, if the mixed-valent ion, (4′-MeL)RuL-LRu(4′-MeL)$^{+}$, is stabilized by electron delocalization. However, the magnitude of the shift is small (20-30 mV). Accounting for the statistical contribution to the shift of the oxdiation wave, approximately 18 mV,[17] makes the stabilization energy, if any, even smaller.

Preparation of the Mixed-Valent Ion (4′-MeL)RuL-LRu(4′-MeL)$^{+}$. Equilibrium solutions containing the mixed-valent ion, (4′-MeL)RuL-LRu(4′-MeL)$^{+}$, were prepared by mixing solutions of the reduced Ru(II)Ru(II) complex with the oxidized Ru(III)Ru(III) binuclear complex. Spectroscopic measurements of the mixed-valent ion were complicated by the presence of the Ru(II)Ru(II) and Ru(III)Ru(III) binuclear species in solution, related by the equilibrium in eq. 14. The constant

$$\mathrm{Ru(II)Ru(II)} + \mathrm{Ru(III)Ru(III)}^{+2} \rightleftharpoons 2\mathrm{Ru(II)Ru(III)}^{+} \qquad (14)$$

describing this comproportionation equilibrium can be calculated knowing the separation of the two one-electron waves as determined graphically. A value of 75 ± 5 mV for the electrochemical potential separation of the two waves yields a comproportionation equilibrium constant of 19 ± 4. A pure sample of the mixed-valent complex was not isolable in the solid state.

Comparisons may be made between the ruthenium isoindoline binuclear complex 6, (4′-MeL)RuL-LRu(4′-MeL), and the ruthenium ammine binuclear species where the metals are bridged by

4,4′-bipyridine (Table 4). The properties of the two complexes are quite similar, indicating that the interaction between the metals may also be similar. The properties of the intervalence transfer (IT) band for ruthenium mixed-valent complexes containing 4,4′-bipyridine may give an indication of what to expect for (4′-MeL)RuL-LRu(4′-MeL)$^+$. The mixed-valent complexes, $(NH_3)_5Ru(4,4'\text{-bpy})Ru(NH_3)_5^{5+}$ and $(bpy)_2ClRu(4,4'\text{-bpy})Ru(bpy)_2Cl^{3+}$, exhibit broad absorptions in the near infrared between 900 and 1200 nm (depending on the solvent), with extinction coefficients ranging from 100 to 1000.[5,18,19] In these cases the position of the IT band shows the solvent dependence predicted by Hush for weakly coupled binuclear complexes.[20] From the Hush theory, a rate of thermal intramolecular electron transfer can be calculated to be in the range 10^7-10^8 sec^{-1} for these complexes.

A distinct band was not observed in the near infrared region of the spectrum of the mixed-valent ion, (4′-MeL)RuL-LRu(4′-MeL)$^+$, in methylene chloride. This was due to the tailing of the very intense Ru(II) → L charge transfer band present for the Ru(II)Ru(II) binuclear species, Figure 1, as well as the mixed-valent ion. (The charge transfer band may be slightly shifted in the mixed-valent complex, but because of the weak metal-metal interaction it is expected to be very similar to the band observed for the Ru(II)Ru(II) complex.[5]) The charge transfer band in the binuclear Ru(II) complex has an extinction coefficient of 420 at 1000 nm. This makes it impossible to observe a broad relatively weak intervalence transfer band in this region of the spectrum.

Table 4. Comparison of Data for Ruthenium Binuclear Complexes

Complex	d (Å)[a]	E_1-E_2[b]	K_{com}[c]
(4'-MeL)RuL-LRu(4'-MeL)	11[d]	75	19
$(NH_3)_5Ru(4,4'\text{-bpy})Ru(NH_3)_5$	11.1[e]	82[f]	24[f]

[a] Distance between the metals in binuclear complex.

[b] Separation of the two one-electron oxidation waves.

[c] Comproportionation equilibrium constant.

[d] Ref. 4.

[e] Ref. 5.

[f] Ref. 18.

CONCLUSIONS

Discrete binuclear and trinuclear ruthenium complexes containing the bridging ligand **1** were prepared by a stepwise synthesis. The binuclear ruthenium complex, (4′-MeL)RuL-LRu(4′-MeL), undergoes a two-electron oxidation with the two electrons being transferred at approximately the same potential. The analogous trinuclear complex shows similar behavior, with three closely spaced one-electron oxidations. The ability of these complexes to undergo multi-electron oxidation with all of the electrons transferred at approximately the same potential, may be a very desirable property for their possible use as multi-electron transfer reagents. An estimate of the rate of intramolecular electron transfer in the polynuclear complexes was not obtainable from spectroscopic measurements.

EXPERIMENTAL SECTION

Synthesis of Ligands. The synthesis of the mononuclear chelating isoindoline ligands **2**,[7] and the binucleating ligand **1**[2] have been reported previously.

Preparation of Ru(4′-MeL)$_2$, 3, from RuCl$_3$ · xH$_2$O. A solution containing 325 mg (1.2 mmol) of hydrated ruthenium trichloride, 900 mg (2.7 mmol) of 4′-MeLH and 160 mg (3 mmol) of sodium methoxide in 50 ml of methanol was heated at reflux for 48 hours in air. After cooling, a fine blue powder was collected from the solution and dried *in vacuo.* The yield of the product was 15%.

The reaction time could be reduced by addition of 450 mg (12 mmol) of sodium borohydride to the refluxing solution of hydrated ruthenium trichloride and 4′-MeLH after 30 minutes. The solution was refluxed for two hours and cooled. A 19% yield of the product was obtained.

The complex, Ru(4′-MeL)$_2$, gave a ^{1}H NMR spectrum in $CDCl_3$ with the following peaks in ppm (vs. TMS at 34° C): benzene protons: 8.25 (mult) and 7.66 (mult); pyridine protons: 7.33 (d), 7.26 (s), and 5.99 (d); and methyl protons: 2.02 (s).

Anal: Calcd. for $C_{40}H_{32}N_5Ru$: C, 63.74; H, 4.28; N, 18.58. Found: C, 63.35; H, 4.6; N, 18.15.

Preparation of Ru(4′-MeL)$_2$, 3, from Ru(DMSO)$_4$Cl$_2$. To 50 mg (0.1 mmol) of tetrakis(dimethylsulfoxide)dichlororuthenium(II) (Strem) and 66 mg (0.2 mmol) of 4′-MeLH in 7 ml of methanol was added 0.5 ml of triethylamine. The mixture was heated with stirring at reflux for 10 hours. After cooling to the ambient temperature the dark-blue crystalline solid was collected by filtration, washed with methanol, and dried. Yields of the analytically pure complex ranged from 60-80%. The product was identical to the solid prepared from hydrated ruthenium trichloride.

Preparation of (4′-MeLH)RuCl$_3$ · C$_2$H$_5$OH, 5. A solution containing 0.5 g (2.1 mmol) of hydrated ruthenium trichloride dissolved in 150 ml of ethanol was heated at reflux with nitrogen bubbling through the solution. After an hour, 0.5 g (1.5 mmol) of 4′-MeLH was added. The solution continued heating with nitrogen passing through it for an additional 1½ hours. After cooling, a dark microcrystalline solid was collected, washed with ethanol and dried *in vacuo.* The yield of the product was 60%.

Anal: Calcd for $C_{20}H_{17}N_5RuCl_3 \cdot C_2H_5OH$: C, 45.49; H, 3.99; N, 12.06. Found: C, 45.3; H, 4.05; N, 12.0.

Preparation of (5′-ClLH)$RuCl_3 \cdot C_2H_5OH$. To 270 mg (1.0 mmol) of hydrated ruthenium trichloride and 370 mg (1.0 mmol) of 5′-ClLH was added 15 ml of ethanol. The mixture was heated with stirring at reflux for 39 hours. After cooling to the ambient temperature, the brown suspension was filtered and the solid was washed with ethanol and dried. The product was obtained as dark brown microcrystals in 36% yield.

Anal: Calcd for $C_{18}H_{11}N_5Cl_5Ru \cdot C_2H_5OH$: C, 38.63; H, 2.76; N, 11.27. Found: C, 38.2; H, 2.5; N, 11.4.

Preparation of Ru(4′MeL)$_2$, 3, from (4′-MeLH)$RuCl_3 \cdot C_2H_5OH$. To 58 mg (0.10 mmol) of (4′-MeLH)$RuCl_3 \cdot C_2H_5OH$ and 39 mg (0.12 mmol) of 4′-MeLH was added 10 ml of dioxane and 1 ml of triethylamine. The mixture was heated with stirring at reflux for 42 hours. After cooling to the ambient temperature the solvent was allowed to evaporate. The residue was washed several times with methanol leaving behind a 37 mg (49%) yield of dark-blue crystals which were spectroscopically identical to the complex prepared by other routes.

Preparation of (4′-MeL)RuL-LRu(4′-MeL), 6. A solution containing 300 mg (0.52 mmol) of (4′-MeLH)$RuCl_3 \cdot C_2H_5OH$ and 190 mg (0.26 mmol) of HL-LH in 80 ml of ethanol was heated at reflux for three hours. During this time the solution became dark green. To this solution was added 70 mg (1.3 mmol) of sodium methoxide, and the solution stirred at the ambient temperature for 45 minutes. The solution was filtered and a dark solid was collected. Methylene chloride (10 ml) was added to the solid resulting in a dark-green solution. The solution was filtered to remove undissolved NaCl. To the filtrate was added 5 ml of methanol. After slow evaporation of the methylene chloride, dark-green microcrystalline solid formed. The solid was washed with methanol and dried in vacuo. Calculated yield was 10-15%.

The binuclear complex gave a ^{1}H NMR spectrum in $CDCl_3$ with the following peaks in ppm (vs. TMS at 34° C): s-butyl protons: 0.70 (t), 0.97 (d), 1.50 (mult), and 2.40 (mult); and methyl protons: 2.07 (s). The aromatic protons showed many overlapping peaks from 6.1-9.2 ppm.

Anal: Calcd for $C_{86}H_{82}N_{20}Ru_2$: C, 64.65; H, 5.17; N, 17.53. Found: C, 64.15; H, 5.05; N, 17.55.

Without the addition of sodium methoxide a product of composition (4′-MeL)RuL-LRu(4′-MeL) · 4HCl was isolated. This corresponds to the binuclear complex which contains all nondeprotonated isoindoline ligands.

Anal: Calcd for $C_{86}H_{82}N_{20}Ru_2 \cdot 4HCl$: C, 59.24; H, 4.97; N, 16.07. Found: C, 59.2; H, 5.0; N, 16.4.

Preparation of (4′-MeL)RuL-LRu(4′-MeL)(ClO_4)$_2$. To a slurry containing 33 mg (0.02 mmol) of (4′-MeL)RuL-LRu(4′-MeL) in 25 ml of toluene was added a toluene solution containing 65 mg (0.3 mmol) of silver perchlorate. The blue-green solution turned red-brown, with dark solid forming. After stirring for an hour, the solid was collected and washed with toluene. The solid was dissolved in 10 ml of methylene chloride and filtered through a fine frit to remove silver metal. Red-brown crystalline solid was collected from the filtrate, in 90% yield, after addition of 2 ml of toluene and slow evaporation of the solution. The solid was dried in vacuo. Multiple analyses were consistent with toluene present in the product.

Anal: Calcd for $C_{80}H_{82}N_{20}Ru_2Cl_2O_8 \cdot 1.5\ C_7H_8$: C, 59.90; H, 4.90; N, 14.48. Found: C, 60.1; H, 4.75; N, 14.4.

Preparation of $Ru(4'\text{-}MeL)_2ClO_4$, 4. The mononuclear Ru(III) complex was prepared by oxidation of $Ru(4'\text{-}MeL)_2$ with $AgClO_4$. The procedure used was the same as described above for the binuclear complex. Dark red-brown crystals were isolated in 70% yield. The proton nmr spectrum of the product in $CDCl_3$ showed the presence of toluene and methylene chloride; consistent with the analytical data.

Anal: Calcd for $C_{40}H_{32}N_{10}RuClO_4 \cdot C_7H_8, \frac{3}{4}CH_2Cl_2$: C, 56.84; H, 4.15; N, 13.88. Found: C, 56.55; H, 4.45; N, 13.9.

Alternatively the Ru(III) complex, isolated as its PF_6^- salt, was prepared by oxidation of $Ru(4'\text{-}MeL)_2$ with oxygen. A solution containing 53 mg (0.07 mmol) of $Ru(4'\text{-}MeL)_2$ in 7 ml of methylene chloride was added to a suspension of 16 mg (0.1 mmol) ammonium hexafluorophosphate in 2 ml of acetonitrile. The mixture was allowed to stand at the ambient temperature until the solvent had evaporated. The residue was extracted with methylene chloride and the extract was filtered. Toluene was added to the filtrate and upon standing dark crystals deposited. The crystals were collected, washed with toluene, and dried to afford a 52% yield of the Ru(III) salt.

Anal. Calcd for $C_{40}H_{32}N_{10}RuPF_6 \cdot 5/4CH_2Cl_2$: C, 49.29; H, 3.46; N, 13.94. Found: C, 49.37; H, 3.33; N, 13.52.

Preparation of (4′-MeL)RuL-$O(CH_2)_3O$-LRu(4′-MeL), **8**. To 73 mg (0.10 mmol) of HL-$O(CH_2)_3O$-LH[21] and 116 mg (0.20 mmol) of (4′-MeLH)$RuCl_3 \cdot C_2H_5OH$ was added 10 ml of dioxane. The mixture was heated at reflux with stirring, and after 20 minutes, 1 ml of triethylamine was added. Heating was continued for 24 hours. The dark-green suspension was allowed to cool and the solvent was allowed to evaporate. The residue was extracted with toluene and the extract was passed over a column of silica gel. With additional toluene a green band was eluted. Evaporation of the toluene yielded 35 mg (22%) of green microcrystalline powder which was a single compound by TLC (SiO_2, $CHCl_3$).

Anal. Calcd for $C_{83}H_{68}N_{20}O_2Ru_2$: C, 63.10; H, 4.34; N, 17.74. Found: C, 62.95; H, 4.4; N, 17.35.

Preparation of (4′-MeLH)RuL-LH, **9**. To 120 mg (0.20 mmol) of (4′-MeLH)$RuCl_3 \cdot C_2H_5OH$ and 550 mg (0.74 mmol) of bridging ligand HL-LH was added 25 mg (0.22 mmol) of 1,4-diazobicyclo[2.2.2]octane, Dabco, and 10 ml of dioxane. The mixture was heated with stirring at reflux for 24 hours and the solvent was then allowed to evaporate at the ambient temperature in the dark. The residue was extracted with cyclohexane and the extract was passed through a column of neutral alumina. The column was eluted with toluene and the first green band was collected. The solvent was evaporated and the residue was recrystallized from methylene chloride-heptane to give dark-green crystals. Yields ranged from 15-35%.

Anal: Calcd for $C_{66}H_{67}N_{15}Ru \cdot H_2O$: C, 66.64; H, 5.85; N, 17.67. Found: C, 66.95; H, 5.7; N, 17.5.

Preparation of (4′-MeL)RuL–LRu(4′-MeL), **6**, from (4′-MeL)-RuL-LH, **9**. A mixture of 34 mg (0.029 mmol) of (4′-MeL)RuL-LH and 50 mg (0.087 mmol) of (4′-MeLH)$RuCl_3 \cdot C_2H_5OH$ in 7 ml of dioxane was heated with stirring at reflux. Once the mixture was refluxing, 0.5 ml of triethylamine was added; heating was continued for 44 hours. The reaction mixture was allowed to cool, a few drops of methanol were added, and the solvent was allowed to evaporate in the dark. The residue was extracted with toluene and the extract was passed over a column of neutral alumina. Elution with additional toluene removed a green band from which 27 mg (79% yield) of dark-green powder were obtained. The powder was spectroscopically identical to material obtained by the alternate route.

Preparation of (4′-MeL)RuL-LRu(5′-ClL), **10**. A mixture of 108 mg (0.092 mmol) of (4′-MeL)RuL-LH and 86 mg (0.14 mmol) of (5′-ClLH)$RuCl_3 \cdot C_2H_5OH$ in 10 ml of dioxane was heated with stirring to reflux; 1 ml of triethylamine was added and the heating was continued for 42 hours. The reaction mixture was transferred to a beaker and the solvent was allowed to evaporate at the ambient temperature. The residue was washed with cyclohexane and then extracted with toluene. The toluene extract was placed on a column of neutral alumina and the column was eluted with additional toluene. A green material was eluted first which gave a single spot by TLC(SiO_2, $CHCl_3$). The toluene was evaporated at the ambient temperature and the residue was recrystallized from CH_2Cl_2-heptane to afford a 61% yield of dark-green crystals which exhibited an ir spectrum similar to that of (4′-MeL)-RuL-LRu(4′-MeL).

Anal. Calcd for $C_{84}C_{76}Cl_2N_{20}Ru_2 \cdot H_2O$: C, 60.91; H, 4.74; N, 16.91. Found: C, 61.1; H, 4.9; N, 16.65.

Preparation of (4′-MeL)RuL-LCu(OAc), ***11.*** To 40 mg (0.034 mmol) of (4′-MeL)RuL-LH and 14 mg (0.068 mmol) of cupric acetate hydrate was added 10 ml of methylene chloride. The suspension was stirred at the ambient temperature for 3.5 hours after which time none of the starting Ru(II) complex was detectable by TLC(SiO_2, EtOAc). The mixture was filtered and the residue was washed with methylene chloride. Heptane was added to the combined washes and filtrate and they were allowed to stand in the dark. After partial evaporation of the solvent dark-green microcrystals deposited. A yield of 36 mg (82%) was obtained.

Anal. Calcd for $C_{68}H_{70}N_{15}O_2RuCu$: C, 63.11; H, 5.45; N, 16.24. Found: C, 63.15; H, 5.4; N, 16.1.

Preparation of (4′-MeL)RuL-LPdCl, ***12.*** To 37 mg (0.032 mmol) of (4′MeL)RuL-LH in 6 ml of methylene chloride was added an equimolar amount (12.1 mg) of dichlorobis(benzonitrile)palladium(II) in 5 ml of methylene chloride. After stirring for 30 minutes at the ambient temperature the starting Ru(II) complex had disappeared, TLC(SiO_2, $CHCl_3$). The reaction mixture was allowed to stand overnight at the ambient temperature and was then filtered. The filtrate was placed on a column of neutral alumina. Elution with methylene chloride-ethyl acetate removed a green band from the column from which a dark-green microcrystalline powder was obtained, 26 mg (61%). The 1640 cm^{-1} band characteristic of the unchelated end of the starting material was greatly diminished in the product.

Anal. Calcd for $C_{66}H_{66}N_{15}ClPdRu \cdot H_2O$: C, 59.60; H, 5.15; N, 15.79. Found: C, 59.7; H, 5.25; N, 15.4.

Preparation of HL-LRuL-LH, 13. To 49 mg (0.10 mmol) of tetrakis(dimethylsulfoxide)dichlororuthenium(II) and 447 mg (0.60 mmol) of the bridging ligand 1, HL-LH, was added 15 ml of dioxane and 1 ml of triethylamine. The mixture was heated, with stirring, at reflux for 31 hours. After cooling, the solvent was allowed to evaporate at the ambient temperature. The residue was extracted with cyclohexane and the extract was placed on a column of neutral alumina. The column was eluted with toluene to remove a green band which contained a single component, TLC (SiO_2, $CHCl_3$). Evaporation of the solvent yielded 35 mg (22%) of dark-green microcrystalline powder.

Anal. Calcd for $C_{92}H_{102}N_{20}Ru$: C, 69.54; H, 6.47; N, 17.63. Found: C, 69.65; H, 6.4; N, 17.55.

Preparation of (4′-MeL)RuL-LRuL-LRu(4′-MeL), 14. To 70 mg (0.044 mmol) of HL-LRuL-LH and 52 mg (0.11 mmol) of (4′-MeLH)-$RuCl_3 \cdot C_2H_5OH$ was added 10 ml of dioxane and 1 ml of triethylamine; the mixture was heated at reflux with stirring for 24 hours. The solvent was allowed to evaporate at the ambient temperature and the residue was extracted with cyclohexane and with toluene. The combined extracts were chromatographed over neutral alumina. A green band was eluted with toluene which produced a single spot on TLC (SiO_2, $CHCl_3$). A 70% yield of dark-green microcrystals was obtained from cyclohexane-diethylether.

Anal. Calcd for $C_{132}H_{134}N_{30}Ru_3$: C, 64.87; H, 5.53; N, 17.20. Found: C, 64.55; H, 5.2; N, 17.2.

Physical Measurements. Procedures for making electrochemical measurements have been described previously.[2] Potentials for the complexes were measured *vs.* ferrocene.[13] The formal potentials were then adjusted to potentials *vs.* nhe assuming a value of 0.400 V for the ferrocene/ferricinium couple. When ferrocene overlapped with the wave under investigation, the cobaltocene/cobalticinium couple, -0.936 V *vs.* nhe, was used as an internal standard. 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 using 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. Electronic spectra were recorded on a Cary 14 spectrophotometer. Solution spectra were obtained using one centimeter matched quartz cells. Elemental analyses were performed by the California Institute of Technology analytical facility and by Galbraith Laboratories, Knoxville, Tennessee.

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3. The binucleating ligand with s-butyl groups on the pyridine rings, 1, is denoted as HL-LH. Mononucleating ligands, 2, are denoted as RLH where substituents on the pyridine ring precede the abbreviation, e.g., 4′-MeLH. The organic molecule RLH, 2, may function as a tridentate chelate in its neutral form, or in its anionic form upon deprotonation of the pyrrole nitrogen.
4. Estimated from data in the following two references; Gagné, R. R.; Gall, R. S.; Lisensky, G. C.; Marsh, R. E.; Speltz, L. M. Inorg. Chem. 1979, 18, 771; Stynes, H. C.; Ibers, J. A. Inorg. Chem. 1971, 10, 2304.
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21. The preparation of this and related ligands will be discussed in a separate publication.

CHAPTER 4

Ruthenium Complexes of 1, 3-bis(2′-pyridylimino)Isoindolines as Alcohol Autoxidation Catalysts

Ruthenium Complexes of 1,3-bis(2′-pyridylimino)Isoindolines as Alcohol Autoxidation Catalysts

Robert R. Gagné and David N. Marks

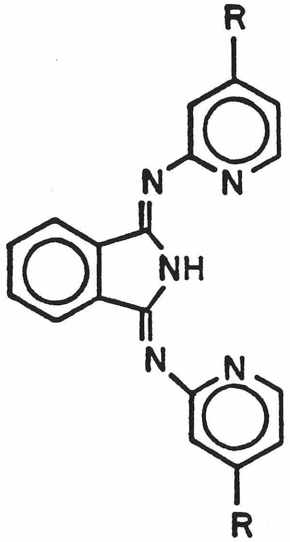
Abstract

The ruthenium complex, 1,3-bis(2′-(4′-methylpyridyl)imino)-isoindolinetrichlororuthenium(III), catalyzes the autoxidation of alcohols in basic alcoholic solution. The reaction is general, resulting in the oxidation of primary and secondary alcohols, with the principal products being aldehydes and ketones. The catalytic reaction is affected by the strength of the base used and its coordinating ability. The best results were obtained using sodium ethoxide as a base. Turnover numbers of 10-30 per day were observed in one atmosphere of oxygen at ambient temperature, with larger turnover numbers at higher temperatures. More than 200 turnovers were observed in the oxidation of ethanol at the ambient temperature with little or no loss of catalytic activity. Dimeric complexes of Ru(II) and Ru(III) were isolated from ethanolic solutions. These complexes were characterized and their role in the catalytic reaction is discussed.

INTRODUCTION

High oxidation state transition metal complexes, such as MnO_4^- and CrO_3, are commonly used reagents for the oxidation of alcohols. These complexes, however, often show limited selectivity in their reactions and function, in normal use, as stoichiometric oxidizing agents.[1]

Few transition metal complexes are known which catalyze the oxidation of alcohols and, in most cases, the reaction mechanisms are not well understood.[2-8] We report the oxidation of alcohols to aldehydes or ketones by molecular oxygen, as mediated by a ruthenium catalyst in homogeneous solution. The oxidation takes place in a basic alcoholic solution of the Ru(III) complex containing ligand 1, (4′-MeLH)$RuCl_3$. The catalytic oxidation was studied to define the scope and possible mechanism of the reaction.



LH, R = H
4′-MeLH, R = CH_3
4′-s-butylLH, R = s-butyl

1

RESULTS AND DISCUSSION

Characterization of (4′-MeLH)$RuCl_3$. The synthesis of (4′-MeLH)$RuCl_3$ has been reported earlier.[9] The Ru(III) ion is bound to a neutral tridentate isoindoline ligand, 1, and to three chloride ions, forming a pseudooctahedral environment around the metal ion. Analytical data, magnetic measurements and the infrared spectrum of the complex are all consistent with the presence of a neutral nondeprotonated isoindoline ligand. It is not known whether the proton is still associated with the pyrrole nitrogen or, more likely, whether it is bound to one of the imine nitrogens.

Infrared spectra were very useful in determining whether the bound isoindoline ligand was neutral or deprotonated. Infrared spectra of metal complexes with deprotonated ligand vs. nondeprotonated ligand show substantial differences in the region 1450-1650 cm^{-1} (Figs. 1 and 2). The infrared spectrum of (4′-MeLH)$RuCl_3$ has two strong absorptions above 1600 cm^{-1}, characteristic of a coordinated nondeprotonated isoindoline ligand. Complexes which contain deprotonated isoindoline ligands, only exhibit weak bands above 1600 cm^{-1}. The infrared spectra of complexes of this type have been discussed previously.[10] These absorptions cannot be readily assigned to a specific vibration but may be coupled modes involving the imines and the pyridine groups.

The complex (4′-MeLH)$RuCl_3$ is sparingly soluble in most organic solvents but insoluble in alcohols. The complex is

FIGURE 1. Infrared spectra (KBr) of ruthenium complexes containing nondeprotonated isoindoline ligands. The two strong absorptions in the range 1600-1650 cm^{-1} are characteristic of the presence of a chelated neutral isoindoline ligand.

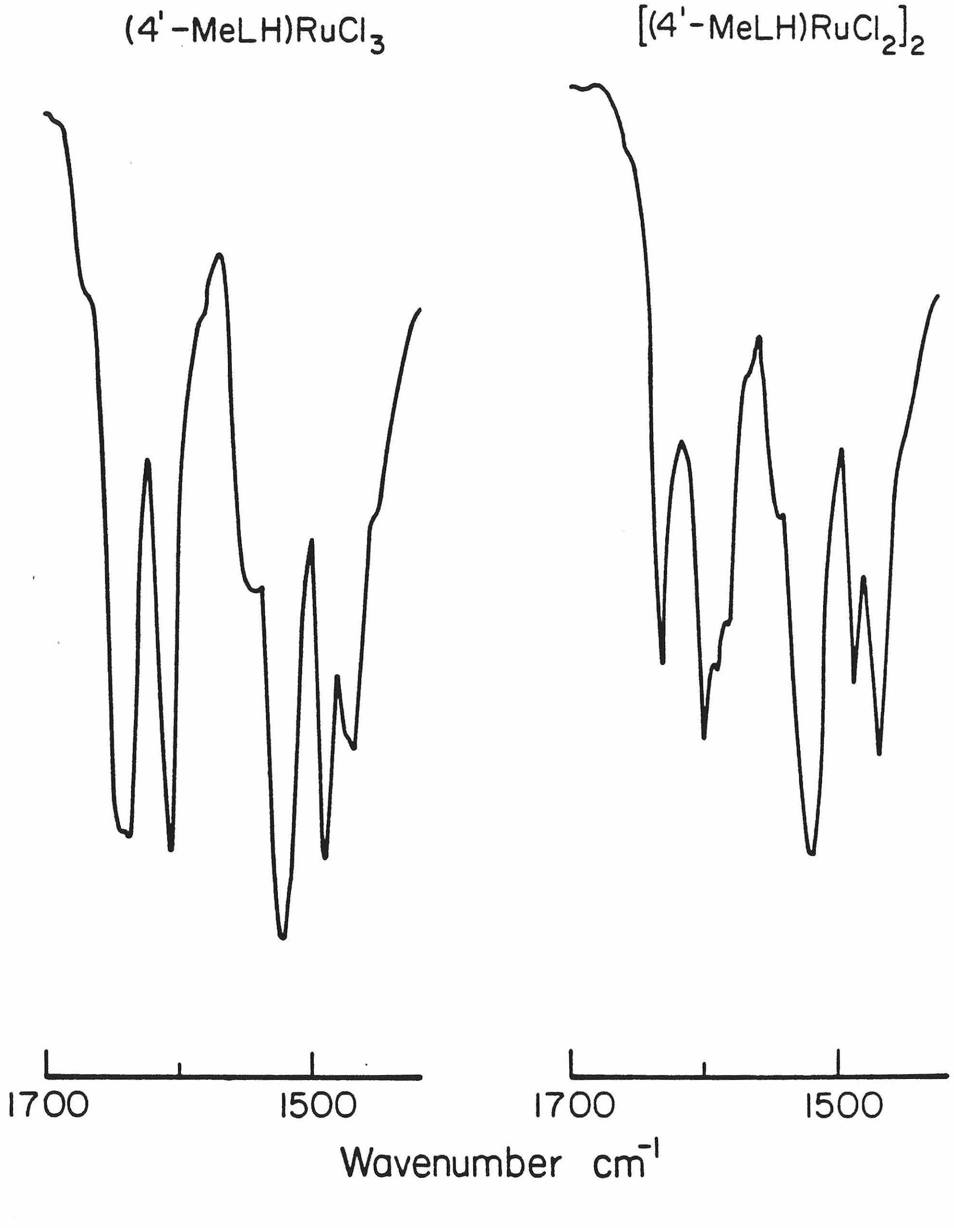

(4'-MeLH)RuCl3
[(4'-MeLH)RuCl2]2
1700
1500
1700
1500
Wavenumber cm-1

Figure 1.

FIGURE 2. Infrared spectra (KBr) of ruthenium complexes containing deprotonated isoindoline ligands. Note the absence of strong bands in the range 1600-1650 cm^{-1}.

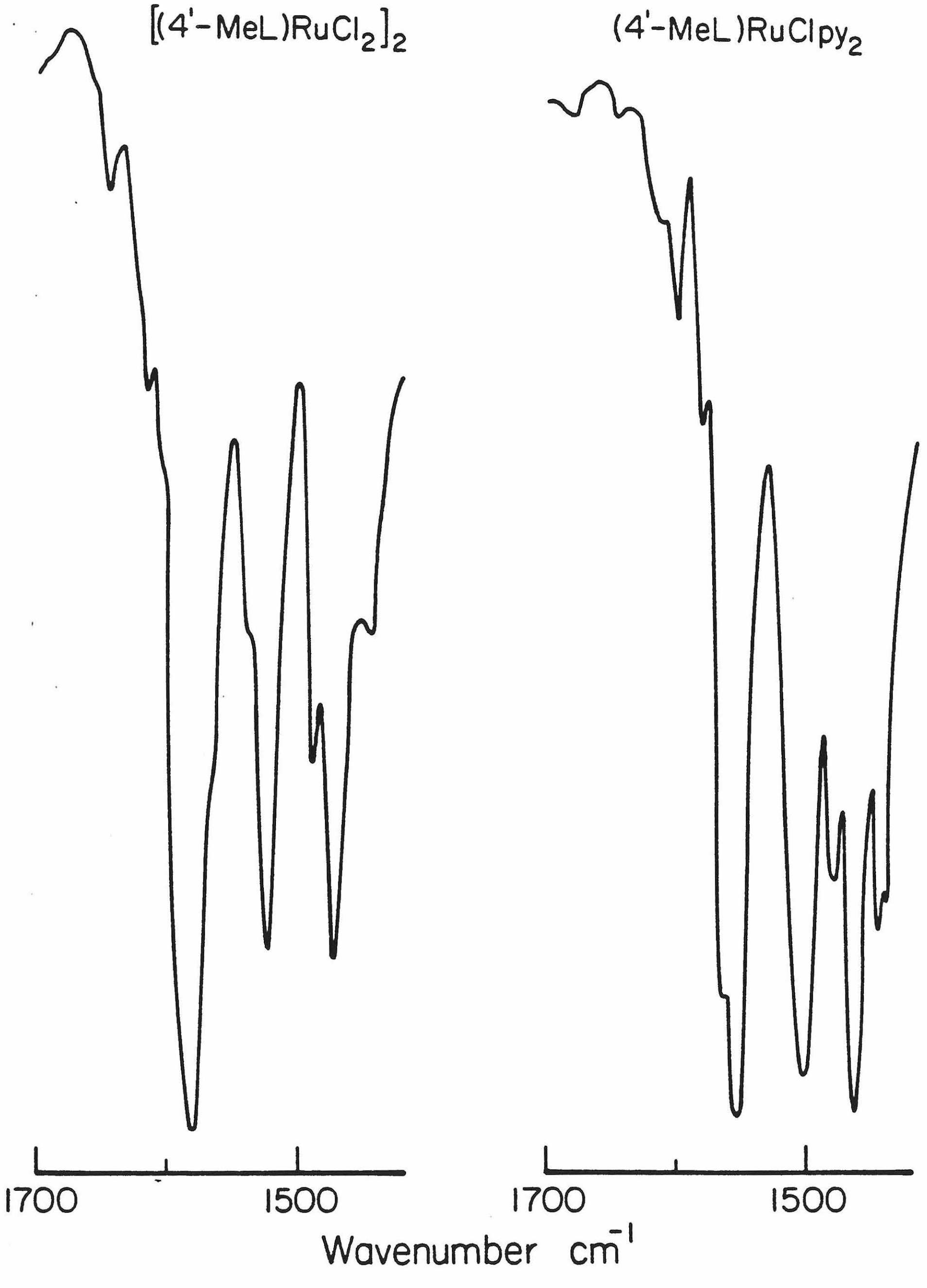

[(4'-MeL)RuCl2]2
(4'-MeL)RuClpy2
1700
1500
1700
1500
Wavenumber cm-1

Figure 2.

considerably more soluble in organic solvents when base is added, and it is the basic alcoholic solutions, in the presence of oxygen, that show the catalytic alcohol oxidation.

Catalytic Oxidation of Alcohols. Catalytic reactions were observed when alcoholic solutions of (4′-MeLH)$RuCl_3$ were stirred and heated to 60-75°C with the base 2,6-lutidine under one atmosphere of oxygen. The catalytic oxidation of alcohols was quite general, resulting in the oxidation of all alcohols used: methanol, ethanol, 1-butanol, 2-butanol and cyclohexanol.

Products from the catalytic oxidation were identified by gas chromatography, mass spectral analysis and UV spectroscopy. The only products identified in the oxidation of the secondary alcohols were ketones. In contrast, several products were observed in the oxidation of primary alcohols, apparently resulting from further oxidation and reactions of the aldehydes initially formed. The catalyzed reaction taking place is shown in eq. 1, while Table 1 lists the alcohols examined and the oxidation products observed. In the absence of catalyst no oxidation products were observed.

$$\mathrm{H-\overset{\backslash}{\underset{/}{C}}-OH} + \tfrac{1}{2}\mathrm{O_2} \rightarrow \mathrm{\overset{\backslash}{\underset{/}{C}}{=}O} + \mathrm{H_2O}\ . \tag{1}$$

Except in methanol, the major products of the oxidation of the primary alcohols are the corresponding aldehydes and their acetals. The ethyl acetate that was observed in the oxidation of ethanol was formed in small amounts and only after several days of reaction. Ketones showed no oxidation in the presence of the catalyst and could be used as inert solvents for the oxidation of alcohols. Aldehydes

Table 1. Results of Alcohol Oxidations Catalyzed by (4′-MeLH)RuCl$_3$

Alcohol	Base	Oxidant[a]	Temp(°C)	Turnover Number[b]	Products Identified
methanol	2, 6-lutidine	O_2	60	5	methyl formate
ethanol	2, 6-lutidine	O_2	70	25	acetaldehyde, 1, 1-diethoxyethane, ethyl acetate[c]
ethanol	2, 6-lutidine	air	70	10	"
ethanol	2, 6-lutidine	H_2O_2	25	5	acetaldehyde
ethanol	2, 6-lutidine	O_2	25	trace[d]	acetaldehyde
1-butanol	2, 6-lutidine	O_2	90	100	butyraldehyde, 1, 1-dibutoxybutane[e]
1-butanol	pyridine	O_2	90	5	"
2-butanol	2, 6-lutidine	O_2	75	60	2-butanone
2-butanol	2, 6-lutidine	O_2	90	100	2-butanone
cyclohexanol	2, 6-lutidine	O_2	90	25	cyclohexanone
ethanol	$NaOC_2H_5$	O_2	25	30	acetaldehyde, 1, 1-diethoxyethane, ethyl acetate
ethanol	$NaOC_2H_5$	O_2	70	100	"
1-propanol	$NaOC_2H_5$	O_2	25	30	propionaldehyde, 1, 1-dipropoxypropane[f]
1-butanol	$NaOC_2H_5$	O_2	25	35	butyraldehyde
2-propanol	$NaOC_2H_5$	O_2	25	15	acetone
2-butanol	$NaOC_2H_5$	O_2	25	10	2-butanone

a. Oxidant - O_2 or air at one atmosphere, H_2O_2 as a 30% aqueous solution.

b. Turnover number = number of moles of two-electron oxidized species per mole of catalyst on the first day of reaction.

c. Product identified was > 90% acetaldehyde.

d. Trace = stoichiometric or less.

e. Product distribution was 20% aldehyde and 80% acetal.

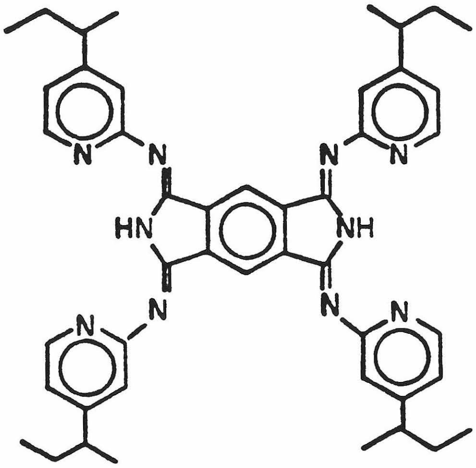
f. Product distribution was 50% aldehyde and 50% acetal.

were susceptible to further oxidation and other reactions in basic solutions of (4′-MeLH)RuCl$_3$.

Turnover numbers for the catalyst (i.e., number of moles of two-electron oxidized species produced per mole of catalyst) were less than 100 per 24-hour period; usually in the range 20-60 (Table 1). Turnover numbers of 100 were attained in 1-butanol and 2-butanol where reactions were run at higher temperatures.

The catalytic oxidation of ethanol was monitored daily over a period of a week. The catalytic activity of (4′-MeLH)RuCl$_3$ remained fairly constant for several days but then steadily declined. After a week of heating at 70° C in ethanol with 2,6-lutidine, little oxidation was occurring.

Other similar metal complexes were studied for potential catalytic activity. No reactivity was observed when (4′-MeLH)CoBr$_2$ or (4′-MeL)FeCl$_2$ were examined in basic ethanol under one atmosphere of oxygen. Hydrated ruthenium trichloride produced very small amounts of acetaldehyde, perhaps functioning as a stoichiometric oxidant.[11] Catalytic activity was observed in basic alcoholic solutions of each of the following complexes: (LH)RuCl$_3$, (4′-*s*-butylLH)RuCl$_3$, and Cl$_3$RuHL-LHRuCl$_3$, where HL-LH is the ligand **2**. These three complexes catalyze the autoxidation of alcohols, yielding turnover numbers comparable to (4′-MeLH)RuCl$_3$.



= HL-LH

2

The base, 2,6-lutidine, used in order to solubilize the Ru(III) complex, was chosen for its weak basicity and its poor ligating properties. The choice of the base was found to be critical to the catalytic behavior of (4′-MeLH)RuCl$_3$. The use of pyridine as a base slowed the catalytic oxidation considerably. Pyridine may be hindering the oxidation by binding to the metal, indicating that the noncoordinating nature of 2,6-lutidine is important.

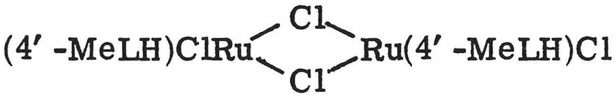
The use of a strong base, sodium ethoxide, enhanced the reaction. An alcoholic solution of (4′-MeLH)RuCl$_3$ containing several equivalents of sodium ethoxide was stirred under one atmosphere of oxygen at the ambient temperature,and products of alcohol oxidation were observed (Table 1). Approximately 10-30 turnovers were observed in one day upon reaction with ethanol, 1-propanol, 2-propanol, 1-butanol, or 2-butanol. The principal products of the oxidation were aldehydes or ketones as observed with 2,6-lutidine. With heating, turnover numbers of greater than 100 per day were observed in ethanol. The catalyst, (4′-MeLH)RuCl$_3$, at the ambient temperature, showed little or no degradation after six days and more than 200 turnovers in ethanol containing several equivalents of sodium ethoxide.

Oxidation of Amines. Reactions with amines were also investigated. The complex, (4′-MeLH)RuCl$_3$, was reduced rapidly in n-propylamine but no organic oxidation products were observed by gas chromatography. It is likely that the reaction of the Ru(III) complex with amines is stoichiometric, with the oxidized organic product, an imine or nitrile, remaining bound to the metal. The oxidation of amines by ruthenium has been observed for several ruthenium complexes,[12-14] but in only one case was it found to be catalytic.[2]

Isolation and Characterization of Ruthenium Complexes Obtained from Reactions in Ethanol. Several ruthenium complexes were isolated from reactions of (4′-MeLH)RuCl$_3$ in ethanol under various conditions. These derivatives were studied in order to help identify possible steps in the catalytic reaction.

To prevent the catalytic oxidation of ethanol, (4′-MeLH)RuCl$_3$ was stirred and heated in ethanol with 2,6-lutidine in an oxygen-free atmosphere. Under these conditions ethanol was oxidized stoichiometrically and a precipitate formed. The reaction was monitored on a vacuum line for gas evolution. No gas was evolved during the reaction, eliminating the possibility that the oxidation product was formed from the dehydrogenation of the alcohol.

A solution of (4′-MeLH)RuCl$_3$ in ethanol containing 2,6-lutidine, initially red-brown, gave a green precipitate after heating at reflux for two hours in an inert atmosphere. The air-sensitive solid isolated was insoluble in all organic solvents tested and, therefore, proved difficult to characterize. An infrared spectrum of the green solid showed strong bands in the region 1600-1650 cm^{-1}, characteristic of a nondeprotonated isoindoline ligand bound to the metal (Fig. 1). The complex was diamagnetic as determined by magnetic susceptibility, with the magnetic moment increasing upon exposure of the solid sample to oxygen, approaching a value of 1.9 Bohr magnetons. Analytical data were consistent with the empirical formula $(4'\text{-MeLH})RuCl_2$. With only solid state measurements possible on the insoluble material, the complex was formulated as the Ru(II) chloro-bridged dimer, 3. Ruthenium ions bridged by two chlorides are not uncommon and complexes of this type usually react readily with additional ligands to break the dimer and form monomeric complexes.[15-17] Indeed, the



$$(4'\text{-MeLH})ClRu\overset{Cl}{\underset{Cl}{\lessgtr}}Ru(4'\text{-MeLH})Cl$$

3

Ru(II) dimer reacts readily with carbon monoxide, and a monomeric carbonyl complex was isolated (eq. 2). The infrared spectrum of the

$$[(4'\text{-MeLH})RuCl_2]_2 \xrightarrow{CO} 2(4'\text{-MeLH})RuCl_2CO. \qquad (2)$$

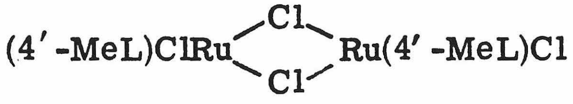
carbonyl complex gave ν_{CO} at 1950 cm^{-1} and indicated that the bound isoindoline ligand is neutral. A monomeric pyridine complex was formed upon reaction of the Ru(II) dimer with pyridine (eq. 3).

$$[(4'\text{-MeLH})RuCl_2]_2 \xrightarrow{\text{Pyridine}} 2(4'\text{-MeL})RuClPy_2 \qquad (3)$$

Apparently pyridine is a strong enough base to deprotonate the ligand, for the neutral bis(pyridine) complex was isolated.

The reaction of the Ru(II) dimer, $[(4'\text{-MeLH})RuCl_2]_2$, 3, with oxygen was investigated. Oxygen uptake measurements, at the ambient temperature, of the solid, and acetone slurries of the solid, gave a stoichiometry of 0.25 O_2/Ru. This represents a simple one-electron oxidation of each ruthenium. Stoichiometric reaction of a suspension of $[(4'\text{-MeLH})RuCl_2]_2$ in ethanol under one atmosphere of oxygen at 25° C gave a golden-brown insoluble material, 4. The product could be isolated since the catalytic reaction is slow at 25° C. Characterization of this product was also hampered by its low solubility.

The infrared spectrum of the oxidation product isolated from ethanol, 4, showed bands in the 1450-1600 cm^{-1} region characteristic of a deprotonated isoindoline ligand (Fig. 2). Magnetic measurements yielded a value of 1.95 Bohr magnetons per ruthenium, consistent with a low-spin d^5 Ru(III) ion.[18] These results and the analytical data suggest that the complex be formulated as a Ru(III) chloro-bridged dimer, 4. Absorption in the far infrared spectrum assignable to



4

bridging Ru-Cl modes could not be identified conclusively; they may be obscured by other absorptions, including those associated with Ru-N stretches, in the 250-300 cm^{-1} region.[19]

The reaction of the Ru(II) dimer, **3**, with oxygen to form the Ru(III) dimer, **4**, involves the oxidation of Ru(II) to Ru(III) and deprotonation of the isoindoline ligand. The Ru(III) dimer, $[(4'\text{-MeL})\text{RuCl}_2]_2$, also was made directly from the starting Ru(III) complex, $(4'\text{-MeLH})\text{RuCl}_3$, simply by stirring a solution of the monomeric complex and 2, 6-lutidine in ethanol for several hours in air at 25° C. The reverse reaction was effected by adding HCl(aq) to an ethanolic slurry of $[(4'\text{-MeL})\text{RuCl}_2]_2$, **4**.

Ethanolic slurries of **4**, $[(4'\text{-MeL})\text{RuCl}_2]_2$, showed formation of the Ru(II) dimer **3** upon heating at reflux in ethanol for 20 hours in the absence of oxygen. Taking the reaction to completion required an extended period of time, presumably due to the low solubility of $[(4'\text{-MeL})\text{RuCl}_2]_2$.

The reactions in ethanol of ruthenium isoindoline complexes containing different substituents on the ligand also were investigated. Insoluble dimeric complexes were observed for the reaction of $(\text{LH})\text{RuCl}_3$ in ethanol containing 2, 6-lutidine. Reactions of $(4'\text{-}\underline{s}\text{-butylLH})\text{RuCl}_3$ in basic ethanol, however, showed no readily isolable products. It is not known whether the dimers do not form in this case or whether they are now more soluble. The visible spectra of these solutions were of little use in determining the presence of the dimeric complexes.

The insoluble Ru(II) dimer, **3**, $[(4'\text{-MeLH})\text{RuCl}_2]_2$, does not form when the base used is sodium ethoxide. This may result because of deprotonation of the isoindoline ligand in the dimeric complex or in a precursor to the dimer.

DISCUSSION OF POSSIBLE MECHANISMS

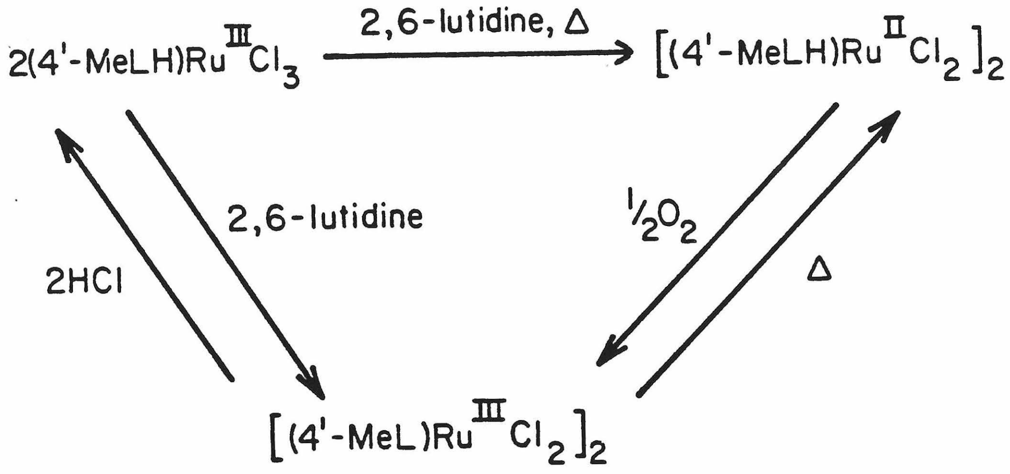
Several observations were made concerning the catalytic oxidation of alcohols by studying the reaction under catalytic conditions and under conditions in which the dimeric complexes were formed. These observations are summarized below.

1. The catalytic reaction is faster when a stronger base was employed.
2. Stoichiometric oxidation of alcohol occurs in an oxygen-free atmosphere.
3. The use of a coordinating base, pyridine, hinders the catalytic oxidation.
4. Oxygen is needed for the catalytic oxidation.
5. Water is, presumably, a co-product of the oxidation of alcohols. No hydrogen gas is produced.

It was hoped that the ruthenium complexes isolated from the reactions of (4'-MeLH)$RuCl_3$ in ethanol under various conditions would help clarify the pathway of the catalytic reaction. The species and reactions observed are presented in Scheme 1.

The presence of the dimer, 3, formed in the oxidation of ethanol, may give some indication of the reactive species. The oxidation states of ruthenium in the dimeric complexes suggest a one-electron change per metal, Ru(II/III), while the oxidation of ethanol to acetaldehyde is formally a two-electron process. To effect the two-electron change, the reduction of a Ru(III) dimer to a Ru(II) dimer may be invoked rather than a two-electron change for a single metal species. However, it is also possible that the formations of the dimeric complexes represent

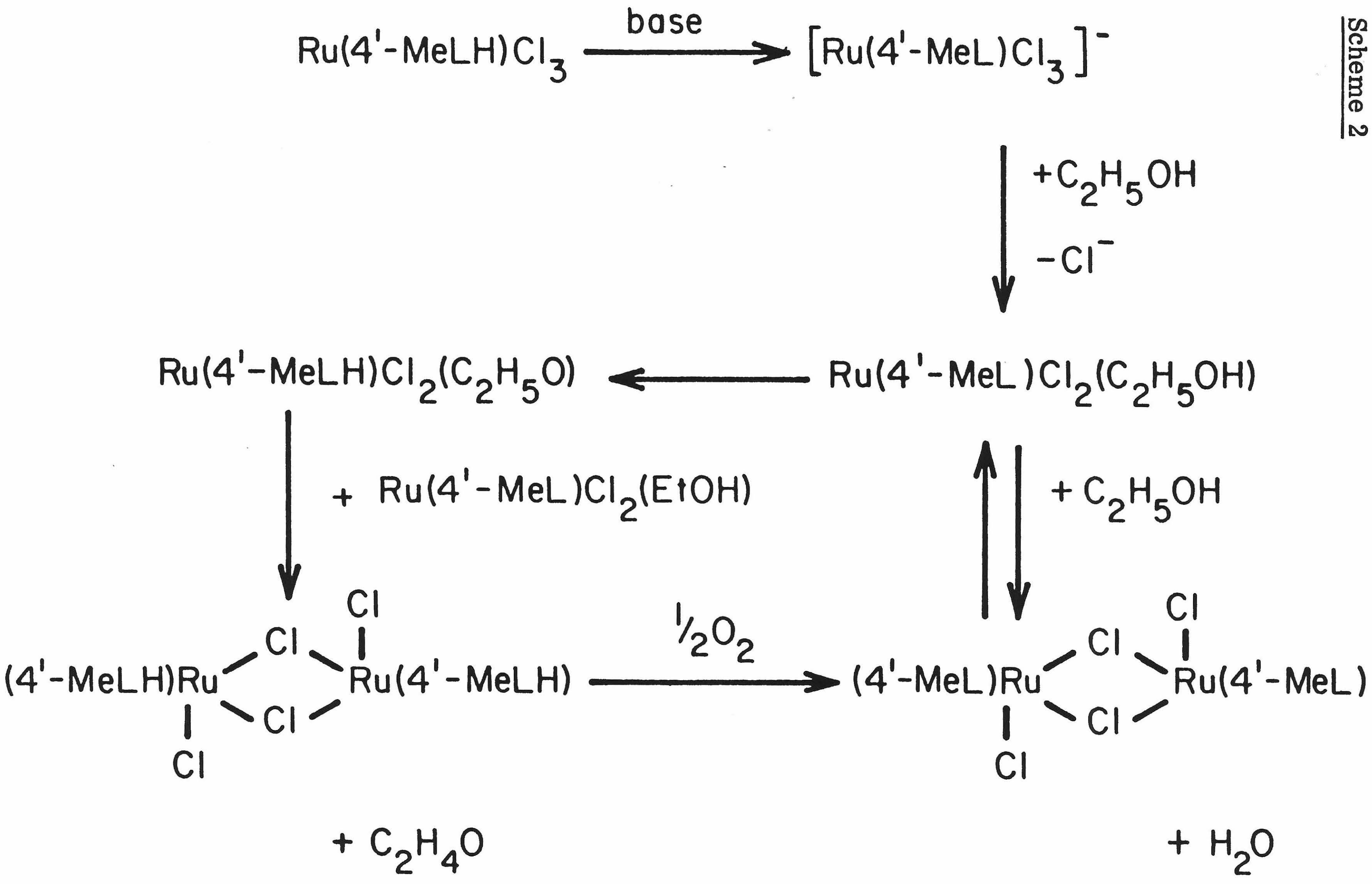
Scheme 1 (ethanol as solvent)



termination steps in the catalytic process because of their low solubility.

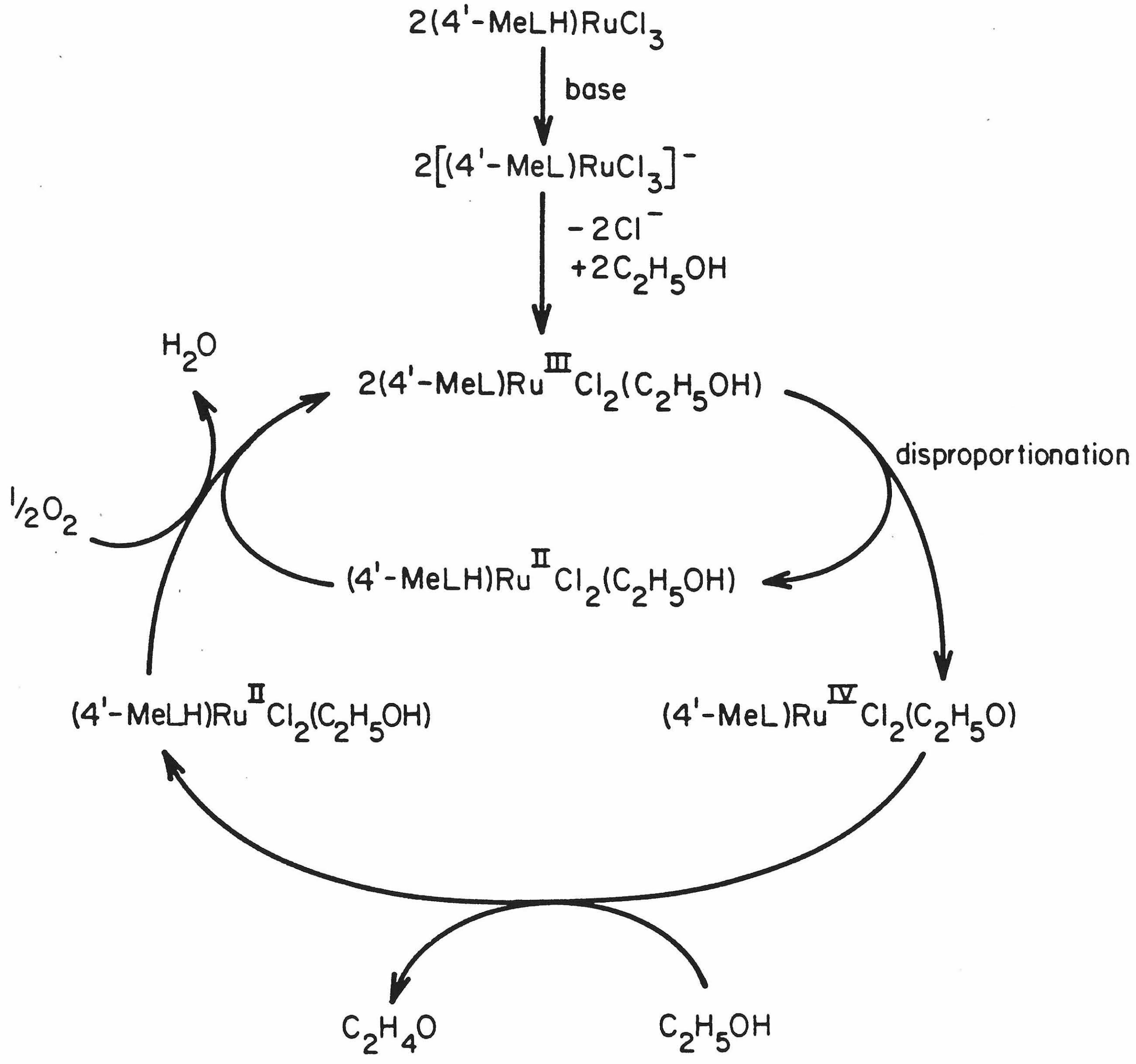
One possible pathway, involving the dimeric complexes isolated as intermediates, is shown in Scheme 2. This scheme, while apparently consistent with the observations of the catalytic system seems unlikely due to involvement of the insoluble dimeric complexes as catalytic intermediates. No insoluble material was observed during the catalytic reaction.

A more likely process for the catalytic oxidation of alcohols is shown in Scheme 3 (illustrated for ethanol). It will be shown that this process is consistent with the observations, and evidence for each step in the mechanism will be discussed in turn.


Ru(4'-MeLH)Cl3
base
[Ru(4'-MeL)Cl3]⁻
+C2H5OH
−Cl⁻
Ru(4'-MeL)Cl2(C2H5OH)
Ru(4'-MeLH)Cl2(C2H5O)
+ Ru(4'-MeL)Cl2(EtOH)
+ C2H5OH
(4'-MeLH)Ru
Cl
Cl
Cl
Cl
Ru(4'-MeLH)
½O2
(4'-MeL)Ru
Cl
Cl
Cl
Cl
Ru(4'-MeL)
+ C2H4O
+ H2O

Scheme 2

Scheme 3


2(4'-MeLH)RuCl3
base
2[(4'-MeL)RuCl3]⁻
-2Cl⁻
+2C2H5OH
2(4'-MeL)RuIIICl2(C2H5OH)
disproportionation
(4'-MeLH)RuIICl2(C2H5OH)
(4'-MeL)RuIVCl2(C2H5O)
(4'-MeLH)RuIICl2(C2H5OH)
H2O
½O2
C2H4O
C2H5OH

The dissolution of (4′-MeLH)$RuCl_3$ in basic ethanol involves initially the deprotonation of the isoindoline ligand. These complexes can be observed electrochemically in nonalcoholic solvents.[20] The protonated complex, (4′-MeLH)$RuCl_3$, exhibits a reversible oxidation wave in several solvents (acetone, propylene carbonate, dichloromethane, and acetonitrile) assignable to the Ru(III)/Ru(IV) oxidation (eq. 4). Upon addition of 2, 6-lutidine to these solutions, the oxidation

$$(4'\text{-MeLH})RuCl_3 \longrightarrow (4'\text{-MeLH})RuCl_3^+ + e^- \qquad (4)$$

wave shifts to much lower potentials (a shift of 0.3-0.4 V). The new wave is ascribed to oxidation of the anionic trichloro complex formed by deprotonation of the isoindoline ligand (eq. 5). The large shift in

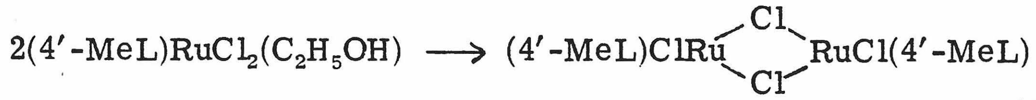
$$(4'\text{-MeL})RuCl_3^- \longrightarrow (4'\text{-MeL})RuCl_3 + e^- \qquad (5)$$

potential can be explained by the charges of the species undergoing oxidation.

Cyclic voltammograms of solutions of (4′-MeLH)$RuCl_3$ in acetonitrile indicate that chloride ion may be displaced by a solvent molecule. Electrochemical measurements of solutions of (4′-MeLH)$RuCl_3$ in acetonitrile with 2, 6-lutidine give an oxidation wave that has been attributed to oxidation of the neutral complex (4′-MeL)$RuCl_2(CH_3CN)$.[20] The electrochemical results indicate that acetonitrile may easily displace chloride from the anionic complex.

One would expect similar behavior in ethanol to that observed in acetonitrile, with ethanol also a reasonable ligand for Ru(III). The negative effect that pyridine has on the reaction can be explained by the importance of the coordination of ethanol to ruthenium on the catalysis. Pyridine was found to slow the catalytic reaction, perhaps because ruthenium binds pyridine preferentially to ethanol. Further evidence for the loss of chloride from the complex in alcoholic solution is suggested by the composition of the dimeric species isolated after reaction in ethanol: each dimer has two chlorides per ruthenium.

The Ru(III) complex formed after loss of chloride, (4′-MeL)RuCl$_2$(C$_2$H$_5$OH), may be the precursor to the insoluble Ru(III) dimer, 4, formed in ethanol with 2,6-lutidine at the ambient temperature (eq. 6).

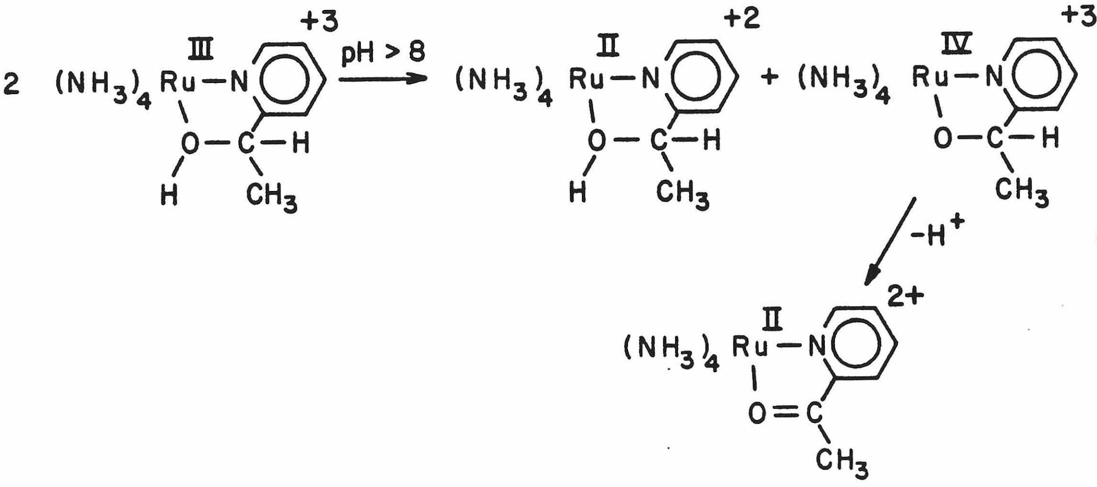


$$2(4'\text{-MeL})\text{RuCl}_2(\text{C}_2\text{H}_5\text{OH}) \longrightarrow (4'\text{-MeL})\text{ClRu}\overset{\text{Cl}}{\underset{\text{Cl}}{\diamond}}\text{RuCl}(4'\text{-MeL}) \qquad (6)$$

The first step in the proposed catalytic cycle (Scheme 3), the disproportionation of (4′-MeL)RuCl$_2$(C$_2$H$_5$OH), accounts for the observation that oxygen is not needed to oxidize ethanol stoichiometrically. The disproportionation of Ru(III) complexes is well precedented. The disproportionation of Ru(III) amines has been studied and found to be dependent on the basicity of the solution.[21,22] Rudd and Taube have ascribed the base dependence to proton removal from NH$_3$ coordinated to Ru(IV)[21] (eq. 7). The coupling of a Ru$^{\text{III}}$ disproportionation with the subsequent

$$2(\text{NH}_3)_5\text{Ru}^{\text{III}}\text{Py}^{+3} \rightleftharpoons (\text{NH}_3)_5\text{Ru}^{\text{II}}\text{Py}^{+2} + (\text{NH}_3)_4(\text{NH}_2)\text{Ru}^{\text{IV}}\text{Py}^{+3} + \text{H}^+ \qquad (7)$$

oxidation of bound alcohol by Ru$^{\text{IV}}$ has been observed stoichiometrically by Tovrog et al.[22] The pathway proposed for the reaction is shown in eq. 8. This reaction was also found to be favored in basic solution.



(8)

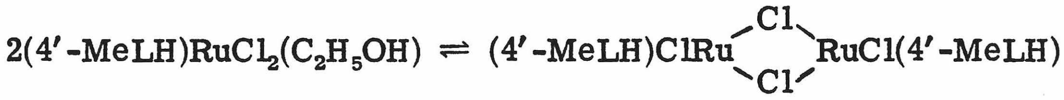
For the ruthenium isoindoline complex, the observation that the catalysis occurs more rapidly with the stronger base, sodium ethoxide, than with 2,6-lutidine can be accounted for by the base dependence of the disproportionation step. The disproportionation of (4′-MeL)RuCl$_2$-(C$_2$H$_5$OH) would be favored in a basic solution in which the alcohol in the Ru(IV) complex would be largely deprotonated. The disproportionation equilibrium would also be enhanced by the protonation of the Ru(II) complex.

In the proposed catalytic cycle, Scheme 3, the Ru(IV) ion functions as a two-electron oxidant, oxidizing the coordinated alkoxide to aldehyde or ketone. The reaction may go through intermediate steps involving β-hydride transfer to the metal to form a ruthenium hydride (eq. 9). This reaction of metal alkoxides or metal amides to give metal hydrides and oxidized ligand has been well documented.[3,23,24] Hydride transfer possibly may occur in the observed catalytic reaction, although no evidence of a hydride intermediate was observed. It is evident from the dimeric species isolated that the oxidation of ethanol produces protons in addition to acetaldehyde. Deprotonation of a hydride intermediate would complete the two-electron reduction of ruthenium (eq. 9).

$$\begin{tikzcd} (4'\text{-MeL})Cl_2Ru^{IV}\text{-}OCH_2CH_3 \arrow[r] & (4'\text{-MeL})Cl_2Ru^{IV}\text{-}H + CH_3CHO \arrow[d, "C_2H_5OH"] \\ (4'\text{-MeLH})Cl_2Ru^{II}(C_2H_5OH) & {[(4'\text{-MeL})Cl_2Ru^{II}(C_2H_5OH)]^- + H^+} \arrow[l] \end{tikzcd} \qquad (9)$$

Meyer *et al.* have studied the electrocatalytic as well as the stoichiometric oxidation of alcohols by a Ru(IV) complex.[25] The Ru(IV) oxo complex, $(bpy)_2pyRuO^{2+}$ (bpy is 2,2′-bipyridine), oxidizes alcohols and the resulting metal species is the Ru(II) aquo complex, $(bpy)_2pyRuOH_2^{2+}$. A study of the catalyzed electrochemical oxidation of alcohols by $(4'\text{-MeLH})RuCl_3$ is also consistent with a Ru(IV) complex as the active species.[20]

The Ru(II) complex, $(4'\text{-MeLH})RuCl_2(C_2H_5OH)$, formed from the disproportionation and from the oxidation of ethanol, may be oxidized by oxygen; completing the catalytic cycle (Scheme 3). The reaction of the dimer, **3**, $[(4'\text{-MeLH})RuCl_2]_2$ with oxygen supports the eventual four-electron reduction of oxygen to water and the oxidation of the monomeric Ru(II) complex should be similar. Hydrogen peroxide may be an intermediate in this reaction. Solutions of (4′-MeLH)RuCl$_3$ in ethanol containing hydrogen peroxide and 2,6-lutidine showed formation of acetaldehyde when stirred at the ambient temperature under nitrogen. The Ru(II) dimeric complex 3 that forms from the reaction with ethanol in an inert atmosphere, may result from dimerization of the proposed Ru(II) intermediate (eq. 10).



$$2(4'\text{-MeLH})\text{RuCl}_2(\text{C}_2\text{H}_5\text{OH}) \rightleftharpoons (4'\text{-MeLH})\text{ClRu}\overset{\text{Cl}}{\underset{\text{Cl}}{\diamond}}\text{RuCl}(4'\text{-MeLH}) \qquad (10)$$

The mechanism proposed is consistent with all of the observations of the catalytic reaction. Unfortunately, more conclusive mechanistic information could not be obtained. Isolation of complexes from solution invariably led to the insoluble dimers since they were the least soluble species. Also methods used to isolate solids from solution, such as concentration of solution or addition of a nonpolar solvent, favored dimer formation. The solution chemistry is complex because there are multiple equilibria with which to be concerned: protonation and deprotonation of isoindoline and alcohol ligands, oxidation and reduction of the metal center, disproportionation equilibrium, solvolysis of chloride ion, and dimerization. The electrochemical oxidation of alcohols catalyzed by (4′-MeLH)RuCl$_3$ in basic solution was also examined as reported elsewhere.[20]

EXPERIMENTAL

All solvents and reagents were purchased from commercial sources and used without further purification with the exception of 2-butanol which was distilled from calcium sulfate. The synthesis of the organic ligands, 4′-MeLH, 4′-s-butylLH, LH, and HL-LH, has been described previously.[10]

Physical Measurements. Infrared spectra were obtained on all compounds using a Beckman IR·4240 spectrophotometer. Samples were examined as KBr pellets. In the case of air-sensitive samples, the KBr pellets were prepared under a helium atmosphere. Far infrared spectra (500-150 cm^{-1}) were run on samples as vaseline films on polyethylene plates using a Perkin-Elmer Model 180 spectrophotometer. Magnetic measurements were made on samples at room temperature using a Cahn Instruments Faraday balance, with $HgCo(SCN)_4$ as a calibrant. Diamagnetic corrections were made using Pascal's constants. Electrochemical measurements were made as described previously.[10] Elemental analyses were performed by the California Institute of Technology's analytical facility and by Galbraith Laboratories, Knoxville, Tennessee.

Catalytic Oxidation of Ethanol. To a slurry of 45 mg (0.08 mmol) $(4'\text{-MeLH})RuCl_3 \cdot C_2H_5OH$ in 30 ml ethanol was added 0.5 ml 2,6-lutidine. The solution was heated at 70° C with air or oxygen passing over it. The gas exited through a U tube immersed in a dry ice/acetone bath which condensed any volatile products. The reaction mixture and the contents of the U tube were analyzed by gas chromatography and it was found that the oxidation products had concentrated in the U tube. The reaction using pyridine as the base was run in the same way.

The same general procedure was used to study the reaction of other complexes with ethanol. These included: (4′-MeLH)$CoBr_2$, (4′-MeL)$FeCl_2$, Cl_3RuHL-LHRuCl_3 + 2,6-lutidine, (LH)RuCl_3 + 2,6-lutidine, (4′-s-butylLH)RuCl_3 + 2,6-lutidine, $RuCl_3 \cdot xH_2O$, $[(4'\text{-MeLH})RuCl_2]_2$, and $[(4'\text{-MeL})RuCl_2]_2$. The catalytic oxidation of methanol was also studied in this manner.

For the reaction in higher boiling alcohols, cyclohexanol, 2-butanol and n-butanol, air or oxygen was kept at atmospheric pressure over the solution. In this way the products remained in the reaction mixture.

The reaction of ethanol with hydrogen peroxide in the presence of (4′-MeLH)RuCl_3 was run at 25 °C under N_2. Four drops of an aqueous 30% H_2O_2 solution was added to a solution containing 40 mg (0.07 mmol) (4′-MeLH)$RuCl_3 \cdot C_2H_5OH$ and 0.5 ml 2,6-lutidine in 30 ml ethanol. This solution was stirred overnight at the ambient temperature under nitrogen and the reaction mixture was analyzed by gas chromatography.

The products of the reactions were subjected to GC analysis with a Hewlett-Packard 5830A gas chromatograph using a Carbowax 20M column and a diethylene glycol succinate column. The identity of the products was checked by comparing retention times for the oxidation product and the pure sample. The identification of the products was further verified in the case of the oxidation of ethanol by GC/MS analysis performed by the California Institute of Technology's analytical facility. The ultraviolet spectrum of methyl formate was used to verify the presence of this product in the oxidation of methanol.

The catalytic oxidation of ethanol using sodium ethoxide as a base was performed in the following way. A solution of 40 mg (0.07 mmol) (4′-MeLH)$RuCl_3 \cdot C_2H_5OH$ and 12 mg (0.17 mmol) sodium ethoxide in 30 ml ethanol was stirred under oxygen at the ambient temperature. The reaction mixture was analyzed by gas chromatography as described above. Other alcohols studied in the same manner were: 1-propanol, 2-propanol, 1-butanol and 2-butanol. Sodium methoxide was also used as a base.

Oxygen Uptake Measurements. An accurately weighed sample of [(4′-MeLH)$RuCl_2]_2$ ($3\text{-}4 \times 10^{-5}$ mole) was placed in a 5 ml round-bottom flask and attached to an 8 ml calibrated volume. The entire assembly was evacuated on a vacuum line. (For reactions of the solid as a suspension in acetone, degassed acetone (4 ml) was distilled onto the sample.) The evacuated sample compartment was closed and dry oxygen was added to the calibrated volume to a pressure of approximately 600 torr. The calibrated volume was opened to the flask containing the sample. The sample was stirred at the ambient temperature for six days during which time the solid in the flask turned red-brown. The gas over the sample was transferred using a Toepler pump to a 14 ml calibrated volume. The quantity of oxygen reacted is the initial amount minus the amount remaining.

Preparation of (4′-MeLH)$RuCl_3$. A solution of 0.5 g (2.1 mmol) hydrated ruthenium trichloride dissolved in 150 ml ethanol was heated at reflux with nitrogen bubbling through the solution. After an hour, 0.5 g (1.5 mmol) 4′-MeLH was added. The solution continued heating with nitrogen passing through it for an additional 1½ hours. After cooling, a dark microcrystalline solid was collected, washed with ethanol and dried in vacuo. The yield of the product was 55%.

In the same manner (4′-s-butylLH)RuCl$_3$ and (LH)RuCl$_3$ were prepared from hydrated ruthenium trichloride and either 4′-s-butylLH or LH. Each product was collected in 45% yield.

Anal: Calcd for $C_{20}H_{17}N_5RuCl_3 \cdot C_2H_5OH$: C, 45.49; H, 3.99; N, 12.06. Found: C, 45.3; H, 4.05; N, 12.0.

Anal: Calcd for $C_{26}H_{29}N_5RuCl_3$: C, 50.45; H, 4.72; N, 11.31. Found: C, 50.15; H, 4.7; N, 11.3.

Anal: Calcd for $C_{18}H_{13}N_5RuCl_3$: C, 42.66; H, 2.59; N, 13.82. Found: C, 42.0; H, 2.3; N, 13.7.

Preparation of Cl$_3$RuHL-LHRuCl$_3$. A solution of 0.3 g (1.2 mmol) hydrated ruthenium trichloride in 50 ml ethanol was heated at reflux with nitrogen passing through the solution. After an hour, 0.22 g (0.3 mmol) HL-LH was added with an additional 10 ml ethanol. The solution continued refluxing with nitrogen passing through it for 1½ hours. After cooling, solid was collected from the solution, washed with ethanol and dried in vacuo. The product was isolated in 50% yield.

Anal: Calcd for $C_{46}H_{52}N_{10}Ru_2Cl_6$: C, 47.64; H, 4.52; N, 12.08. Found: C, 46.95; H, 4.55; N, 11.75.

Preparation of [(4′-MeLH)RuCl$_2$]$_2$, **3**. In a helium atmosphere 80 mg (0.14 mmol) (4′-MeLH)RuCl$_3 \cdot C_2H_5OH$ was slurried in 40 ml ethanol and 1 ml 2,6-lutidine. After stirring for 15 minutes at the ambient temperature the undissolved solid was filtered off. The red-brown filtrate was heated at reflux for two hours during which time the solution became green with green solid forming. After cooling, the solid was collected, washed in ethanol and dried *in vacuo.* The solid was stored under helium. The yield of the product based on the amount of (4′-MeLH)$RuCl_3 \cdot C_2H_5OH$ dissolved was 60% (30 mg).

Anal: Calcd for $C_{40}H_{34}N_{10}Ru_2Cl_4$: C, 48.11; H, 3.43; N, 14.02; Cl, 14.20. Found: C, 47.85; H, 3.55; N, 13.65; Cl, 14.35.

A similar green solid is formed upon the reaction of (LH)$RuCl_3$ under the same conditions, while the reaction of (4′-*s*-butylLH)$RuCl_3$ results in a green solution with no solid forming.

The complex **3**, [(4′-MeLH)$RuCl_2$]$_2$, was also prepared on a vacuum line under argon. A solution of 55 mg (0.095 mmol) (4′-MeLH)$RuCl_3 \cdot C_2H_5OH$ and 0.5 ml 2,6-lutidine in 15 ml ethanol was added to a 25 ml flask fitted with a Vigreaux condenser. The condenser and flask were attached to an 8 ml calibrated volume. The entire assembly was evacuated on a vacuum line. The evacuated sample compartment was closed and argon was added to the calibrated volume to a pressure of approximately 600 torr. The calibrated volume was opened to the condenser and flask containing the sample. The sample solution was stirred and heated at reflux overnight. The gas over the sample was transferred using a Toepler pump to a 14 ml calibrated volume. The quantity of gas present after the reaction was equal to the amount of argon initially present.

Reactions of [(4′-MeLH)RuCl$_2$]$_2$, 3, with carbon monoxide. A mixture of 40 mg (0.040 mmol) [(4′-MeLH)RuCl$_2$]$_2$ in 20 ml ethanol was stirred for three days under an atmosphere of carbon monoxide. The green solid present initially, turned brown on reacting. The solid was collected under helium, washed with ethanol and dried in vacuo. The infrared spectrum showed ν_{CO} at 1950 cm^{-1}.

Anal: Calcd for $C_{21}H_{17}N_5RuCl_2O$: C, 47.83; H, 3.25; N, 13.28. Found: C, 47.65; H, 3.5; N, 13.25.

With pyridine. Under a helium atmosphere, 40 mg [(4′-MeLH)RuCl$_2$]$_2$ was added to 5 ml pyridine. With stirring, the green solid gradually dissolved over a period of four days producing a dark-green solution. The solution was concentrated by slow evaporation and dark-green microcrystalline solid formed. The solid was collected and dried in vacuo. The product was stable to air oxidation.

Anal: Calcd for $C_{30}H_{26}N_7RuCl$: C, 58.01; H, 4.22; N, 15.79. Found: C, 58.1; H, 4.45; N, 16.25.

With oxygen. A slurry of 40 mg [(4′-MeLH)RuCl$_2$]$_2$, 3, in 20 ml ethanol was stirred in air for three days. The green solid present initially gradually reacted and a golden-brown microcrystalline solid was collected and dried in vacuo.

Anal: Calcd for $C_{40}H_{32}N_{10}Ru_2Cl_4 \cdot C_2H_5OH, 2H_2O$: C, 46.76; H, 3.92; N, 12.98. Found: C, 46.45; H, 4.25; N, 12.7.

The same procedure was used for the reaction of [(LH)RuCl$_2$]$_2$ with oxygen and a brown solid was collected.

Anal: Calcd for $C_{36}H_{24}N_{10}Ru_2Cl_4 \cdot C_2H_5OH, 2H_2O$: C, 44.63; H, 3.35; N, 13.70. Found: C, 44.45; H, 3.7; N, 13.25.

Reaction of (4′-MeLH)$RuCl_3$ in basic ethanol. In a helium atmosphere 70 mg (0.12 mmol) (4′-MeLH)$RuCl_3 \cdot C_2H_5OH$ was slurried in 40 ml ethanol and 1 ml 2,6-lutidine. After stirring at the ambient temperature for 15 minutes, the undissolved solid was filtered off. The filtrate was stirred for two hours during which time the red-brown Ru(III) dimer, **4**, precipitated from solution. The solid was collected, washed with ethanol and dried *in vacuo.* The yield of the product (35 mg) was 56% based on the amount of (4′-MeLH)$RuCl_3$ dissolved.

Anal: Calcd for $C_{40}H_{32}N_{10}Ru_2Cl_4 \cdot 3C_2H_5OH$: C, 48.68; H, 4.44; N, 12.34. Found: C, 48.45; H, 4.5; N, 12.35.

Reaction of (4′-*s*-butylLH)$RuCl_3$ under the same conditions results in no solid being formed.

Reaction of [(4′-MeL)$RuCl_2$]$_2$, 4, with aqueous HCl. Two drops of 12*M* aqueous HCl was added to 30 mg (0.03 mmol) [(4′-MeL)$RuCl_2$]$_2$ in 15 ml ethanol. The mixture was stirred at the ambient temperature for an hour. The insoluble brown solid present initially, dissolved upon addition of the aqueous HCl. After stirring for an hour, dark microcrystalline solid had formed and the filtrate was nearly colorless. The solid was collected, washed with ethanol and dried *in vacuo.* An IR spectrum of the product was identical to the spectrum of (4′-MeLH)$RuCl_3 \cdot C_2H_5OH$.

Anal: Calcd for $C_{20}H_{17}N_5RuCl_3 \cdot C_2H_5OH$: C, 45.49; H, 3.99; N, 12.06. Found: C, 45.3; H, 4.1; N, 11.95.

Reaction of [(4′-MeL)$RuCl_2$]$_2 \cdot 3C_2H_5OH$, 4, with ethanol and heat. A slurry of 40 mg (0.035 mmol) [(4′-MeL)$RuCl_2$]$_2 \cdot 3C_2H_5OH$ in 20 ml ethanol was heated at reflux for 20 hours in a helium atmosphere.

The brown solid present initially reacted, and when the reaction was complete, green solid had formed. The solid was collected, washed with ethanol and dried *in vacuo.* The IR spectrum of the product was identical with that of $[(4'\text{-MeLH})RuCl_2]_2$.

Anal: Calcd for $C_{40}H_{34}N_{10}Ru_2Cl_4$: C, 48.11; H, 3.43; N, 14.02. Found: C, 47.9; H, 3.6; N, 13.9.

Preparation of $(4'\text{-MeLH})CoBr_2$. In an inert atmosphere a solution of 1.0 g (3.1 mmol) 4'-MeLH in 70 ml hot methanol was added to a solution containing 1.3 g (4.5 mmol) $CoBr_2 \cdot 4H_2O$ in 15 ml methanol. The solution was heated at reflux for 15 minutes during which time solid had formed. The reaction mixture continued stirring for three hours. The brown solid was collected and dried *in vacuo.* The yield of the product was 60%.

Anal: Calcd for $C_{20}H_{17}N_5CoBr_2$: C, 43.99; H, 3.14; N, 12.82. Found: C, 43.9; H, 3.2; N, 12.9.

Preparation of $(4'\text{-MeL})FeCl_2$. A solution of 0.5 g (1.5 mmol) 4'-MeLH in 35 ml hot methanol was added slowly to a solution containing 0.5 g (1.85 mmol) $FeCl_3 \cdot 6H_2O$. The solution was heated at reflux for 15 minutes and then cooled. Dark microcrystalline solid was collected in 43% yield and dried *in vacuo.*

Anal: Calc for $C_{20}H_{16}N_5FeCl_2$: C, 53.01; H, 3.56; N, 15.46. Found: C, 53.3; H, 3.8; N, 15.5.

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CHAPTER 5

Ruthenium Complexes of 1,3-bis(2′-pyridylimino)Isoindolines for the Electrocatalytic Oxidation of Alcohols

Ruthenium Complexes of 1,3-bis(2′-pyridylimino)Isoindolines for the Electrocatalytic Oxidation of Alcohols

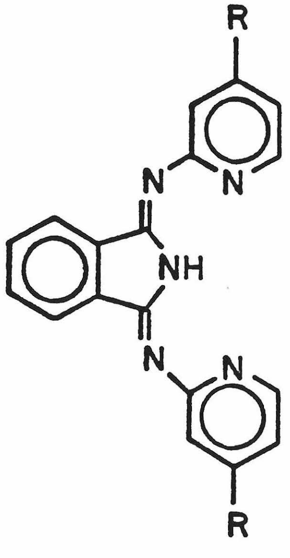
Robert R. Gagné and David N. Marks

Abstract

The ruthenium complex, 1,3-bis(2′-(4′-methylpyridyl)imino)-isoindolinetrichlororuthenium(III) catalyzes the electrochemical oxidation of alcohols in basic alcoholic solution. The best results were obtained with 2,6-lutidine as the base. The electrochemical oxidation was carried out at a carbon electrode immersed in an alcoholic solution at 0.8-1.0 V vs. nhe. In the absence of catalyst, negligible current was observed. The catalyzed electrochemical oxidation was general, oxidizing primary and secondary alcohols, with the principal products being aldehydes and ketones. More than 20 catalytic cycles were completed with the current remaining at 75% of its initial value. The ruthenium(III) complex exhibits reversible one-electron oxidation waves in nonalcoholic solvents in the presence or absence of 2,6-lutidine. The electrochemistry in alcohols and nonalcohols is discussed and a possible pathway for the catalytic electrochemical oxidation is presented.

INTRODUCTION

We have recently observed the autoxidation of alcohols to ketones or aldehydes catalyzed by a ruthenium complex.[1] The complex from which the catalyst is derived, (4'-MeLH)$RuCl_3$, has a Ru(III) ion bound to three chlorides and the tridentate ligand 1, 1,3-bis(2'-(4'-methylpyridyl)imino)isoindoline. The complex functions as a catalyst and becomes soluble in alcohols after the deprotonation of the isoindoline ligand. In the process of studying this reaction, the electrochemistry of (4'-MeLH)$RuCl_3$ was investigated in a basic ethanolic solution. A large anodic current was observed at relatively low potentials, indicating a catalyzed electrochemical oxidation of ethanol. The catalyzed electrochemistry was found to be quite general, oxidizing 2-propanol, methanol and 1-butanol as well as ethanol. The catalytic electrochemical oxidation of alcohols and the electrochemical behavior of (4'-MeLH)$RuCl_3$ in nonalcoholic solvents were studied and are reported herein.



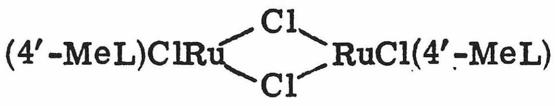
4'-MeLH; R = CH_3
4'-s-butylLH; R = s-butyl

1

RESULTS AND DISCUSSION

Characterization of (4'-MeLH)RuCl$_3$. The synthesis of (4'-MeLH)RuCl$_3$ has been reported earlier.[2] The complex is insoluble in alcoholic solvents, and as a solid has no reactivity with alcohols. Upon addition of base, the complex becomes soluble, and these basic alcoholic solutions catalytically oxidize alcohols in the presence of oxygen. Using 2, 6-lutidine as a base, the catalytic reaction is very slow unless heated to 60-70°C.

The complex, (4'-MeLH)RuCl$_3$, initially dissolves in alcoholic solutions containing the base 2, 6-lutidine, but after stirring for several hours a solid precipitates from solution. The red-brown insoluble material has been characterized as the Ru(III) chloro-bridged dimer 2.[1] The formation of the solid was a difficulty encountered in long-term electrochemical experiments such as constant potential electrolyses. To avoid this problem, a more soluble complex, (4'-s-butylLH)RuCl$_3$, was prepared.[1] This complex was considerably more soluble in organic solvents than (4'-MeLH)RuCl$_3$, although it was still nearly insoluble in ethanol in the absence of base. Additionally, ethanolic solutions of (4'-s-butylLH)RuCl$_3$ containing 2, 6-lutidine give no precipitate upon stirring. It has not been ascertained whether monomeric species are favored in this case or whether the resulting dimer is more soluble.



$$(4'\text{-MeL})\mathrm{ClRu}\begin{smallmatrix}\mathrm{Cl}\\ \\ \mathrm{Cl}\end{smallmatrix}\mathrm{RuCl}(4'\text{-MeL})$$

2

Both complexes, (4′-MeLH)$RuCl_3$ and (4′-s-butylLH)$RuCl_3$, exhibit electrocatalytic behavior in alcoholic solutions. The electrochemistry and products formed from the catalyzed electrochemical oxidations of alcohols are identical for the two complexes. Electrolyses were performed using (4′-s-butylLH)$RuCl_3$ preferentially to avoid precipitation of the Ru(III) dimeric complex **2**.

Electrochemistry in Ethanol. Cyclic voltammograms of basic ethanolic solutions of (4′-MeLH)$RuCl_3$ were obtained using a basal plane pyrolytic graphite working electrode. This electrode was used rather than a platinum electrode because platinum also catalyzes the electrochemical oxidation of ethanol. A large anodic current was observed in the cyclic voltammograms, much larger than the current which would be associated with oxidizing the complex alone. Large anodic currents were observed at 0.7 to 0.9 V vs. nhe, while the solution of 2,6-lutidine in ethanol showed negligible current to approximately 1.2 V; Figure 1. Similar cyclic voltammetric behavior was obtained for methanol and 2-propanol.

The base used for the electrochemical measurements was 2,6-lutidine. It was chosen for its poor ligating properties so that it would not interfere with chemistry occurring at the metal. Also, it was desirable to use a weak base, in order that the alcohol was not deprotonated to any degree which would have altered its electrochemical behavior.[3]

The base used had a major effect on the observed electrochemistry. The addition of pyridine as a base resulted in a shift of the catalytic wave to more positive potentials (a shift of approximately

FIGURE 1. Cyclic voltammograms of an ethanol solution containing 2, 6-lutidine before (A) and after (B) addition of (4′-MeLH)RuCl_3. Note the different current scales for each voltammogram.

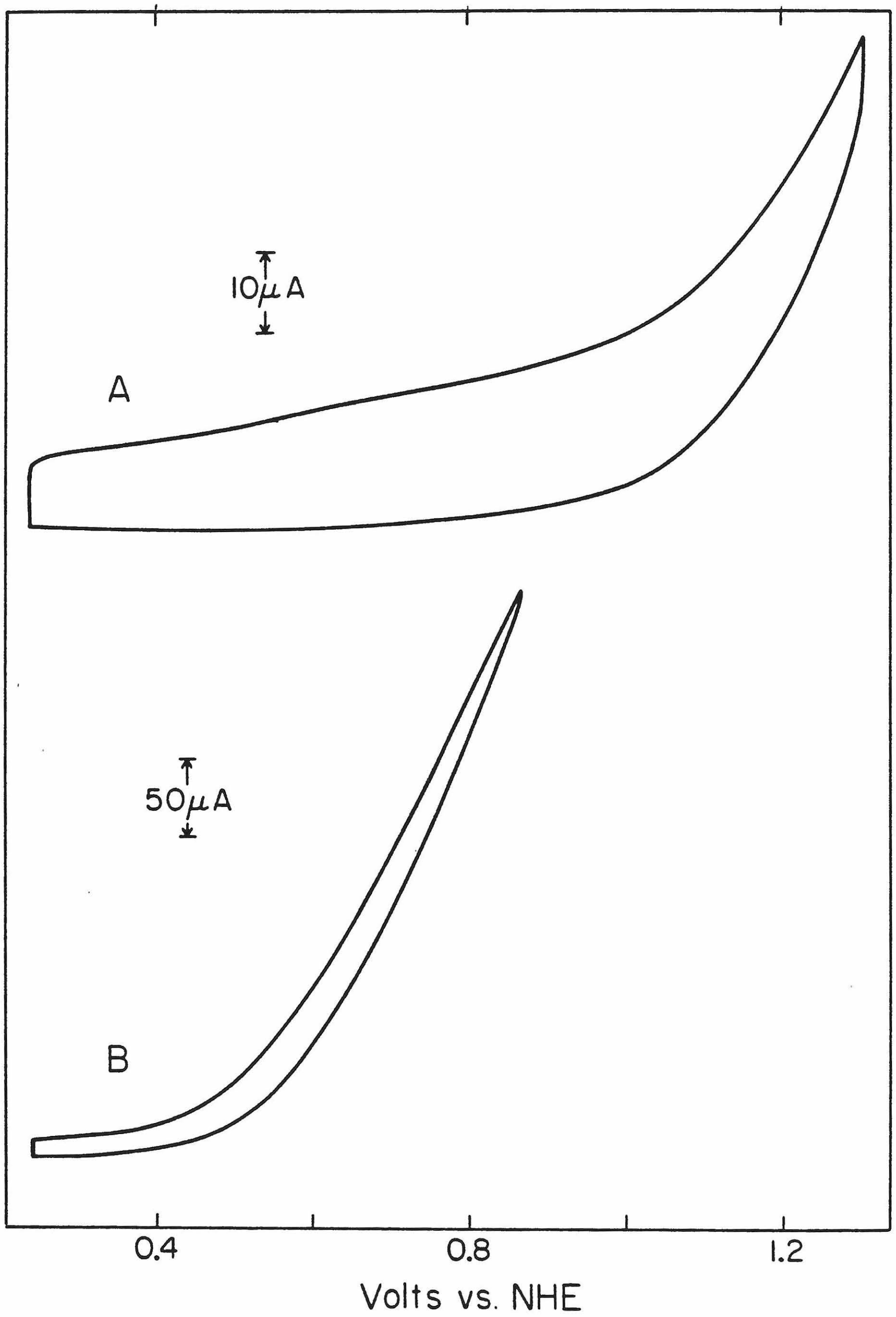


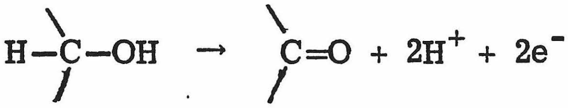
Figure 1.

0.2 V); indicating that pyridine was hindering the catalyzed electrochemical oxidation, probably by binding to the metal ion. Sodium ethoxide could not be used as a base since it was more easily oxidized than ethanol.[3]

The effect of chloride ion on the electrochemistry in ethanol was also investigated because chloride is lost from the complex in basic ethanolic solution.[1] The oxidation of chloride ion in ethanol occurs at greater than 1.2 V vs. nhe on a basal plane pyrolytic graphite electrode. The addition of chloride ion to a basic solution of ethanol was found to have a negligible effect on the current in the working range 0.8-1.0 V vs. nhe.

Electrolysis in Alcohols. The cyclic voltammetric results indicate that (4′-MeLH)$RuCl_3$ is catalyzing the electrochemical oxidation of alcohols. In order to determine the product of the oxidation as well as the lifetime of the catalyst, constant potential electrolyses were conducted. A carbon block electrode with surface area approximately 6.5 cm^2 functioned as the working electrode in these experiments. Typical electrolyses were run on 1-3 millimolar solutions of (4′-s-butylLH)$RuCl_3$ in the alcohol containing 2,6-lutidine. Applied potentials were held constant (0.8-1.0 V vs. nhe) and currents were normally in the range of 1-5 mA. Current in the absence of catalyst was small.

The oxidation current slowly decreased during the electrolysis. The current had dropped significantly after electrolyzing for a long period of time. In these cases, the current could be increased again by addition of several drops of 2,6-lutidine. (For example, a solution of 25 ml of 1.5 mM (4′-s-butylLH)$RuCl_3$ in ethanol containing 0.5 ml 2,6-lutidine was electrolyzed at 0.75 V vs. nhe with an initial current of 2.0 mA. After electrolyzing for 20 hours the current had dropped to 0.6 mA; however, upon addition of several drops of 2,6-lutidine to the solution, the current rose to 1.5 mA.) Cyclic voltammograms of an ethanolic solution where the current has decreased show that the catalytic anodic current is at a higher electrochemical potential than initially. Addition of base causes a shift of the catalytic wave to lower potentials again (a shift from approximately 1.0 V to 0.8 V vs. nhe). Protons are produced in the electrochemical reaction (eq. 1) and the acid may affect the catalysis by protonating the active ruthenium-isoindoline complex, resulting in an increased electrochemical potential for oxidation. Alternatively, protons may be involved in the electrochemical oxidation of the metal complex. More than twenty two-



$$\mathrm{H{-}\overset{\backslash}{\underset{/}{C}}{-}OH} \rightarrow \mathrm{\overset{\backslash}{\underset{/}{C}}{=}O} + 2H^{+} + 2e^{-} \qquad (1)$$

electron oxidations were completed with the current holding at approximately 75% of its initial value. More exhaustive oxidation was not studied because of problems caused by diffusion between the compartments of the electrolysis cell.

Products from the electrochemical oxidation were identified by gas chromatography and mass spectral analysis. Ketones or aldehydes were the predominant products of the electrolysis in various alcohols. Acetone was the sole product of the electrochemical oxidation of 2-propanol. More than 80% of the electrochemical equivalents passed could be accounted for by the acetone formed.[4] Only acetaldehyde was produced during the early stages in the oxidation of ethanol, but as the oxidation continued, 1,1-diethoxyethane and small amounts of acetic acid were observed. An electrolysis in ethanol with 1% acetaldehyde added yielded small quantities of acetic acid being produced immediately. The results of the oxidation of ethanol indicate that acetaldehyde is formed as a product of the oxidation, but the aldehyde can be subsequently oxidized by the catalyst. The electrolysis of n-butanol was very similar to that of the oxidation of ethanol. The product observed initially was butyraldehyde, but as the aldehyde concentration increased, small amounts of additional products were formed. Gas chromatographic analysis of the solution from the electrochemical oxidation of methanol showed only trace amounts of several species. This may be due to loss of oxidation products by evaporation or by production of a nonvolatile component.[5]

The catalyzed electrochemical oxidation in neat ethanol favors the production of acetaldehyde.[6] In order to study the specificity of the catalyst for production of acetaldehyde, the electrochemistry of (4′-MeLH)RuCl$_3$ in a nonalcoholic solvent (acetone or acetonitrile) containing 2,6-lutidine and approximately 10% ethanol was examined. An irreversible anodic current was observed in these solutions but at potentials significantly more positive (0.3 to 0.4 V higher) than had been observed in neat ethanol. Because of the dissimilar electrochemical behavior found, the electrochemical oxidations of alcohols in nonalcoholic solvents were not studied further.

Aldehydes or ketones were also the principal products of the autoxidation of alcohols catalyzed by (4′-MeLH)RuCl$_3$.[1] Turnover numbers for the oxidation of ethanol (i.e., number of moles of two-electron oxidized species produced per mole of catalyst) were found to be approximately 30 per day (sodium ethoxide as a base, ambient temperature, and one atmosphere of oxygen). Turnover numbers for the electrochemical oxidation of ethanol are approximately the same, at a potential of 0.8 V vs. nhe with a graphite electrode of surface area 6.5 cm^2.

Electrochemistry in Nonalcohols. Cyclic voltammograms of (4′-MeLH)$RuCl_3$ in nonalcoholic solvents exhibit a quasi-reversible oxidation wave. The cyclic voltammogram of (4′-MeLH)$RuCl_3$ in dichloromethane is shown in Figure 2. (The electrochemistry observed for (4′-s-butylLH)$RuCl_3$ is nearly identical to that of (4′-MeLH)$RuCl_3$, with electrochemical potentials differing by 0.01 V or less.) The anodic and cathodic peak currents for these oxidation waves are equal, but the peak potential separation is slightly larger than the 58 mV expected for a reversible one-electron process.[7] The peak potential separation was normally in the range 60-80 mV, primarily dependent on the solvent. The results of electrochemistry in various solvents are presented in Table 1.

In order to determine the number of electrons involved in the observed oxidation wave, coulometry was tried. However, the product of the oxidation was not stable over the electrolysis time period as evidenced by the cyclic voltammograms after electrolysis, which usually were very different than those initially observed. The instability of the oxidized product was observed in all solvents used: N,N-dimethylformamide, acetonitrile, acetone, and dichloromethane.

FIGURE 2. Cyclic voltammogram of (4′-MeLH)RuCl$_3$ in dichloromethane.

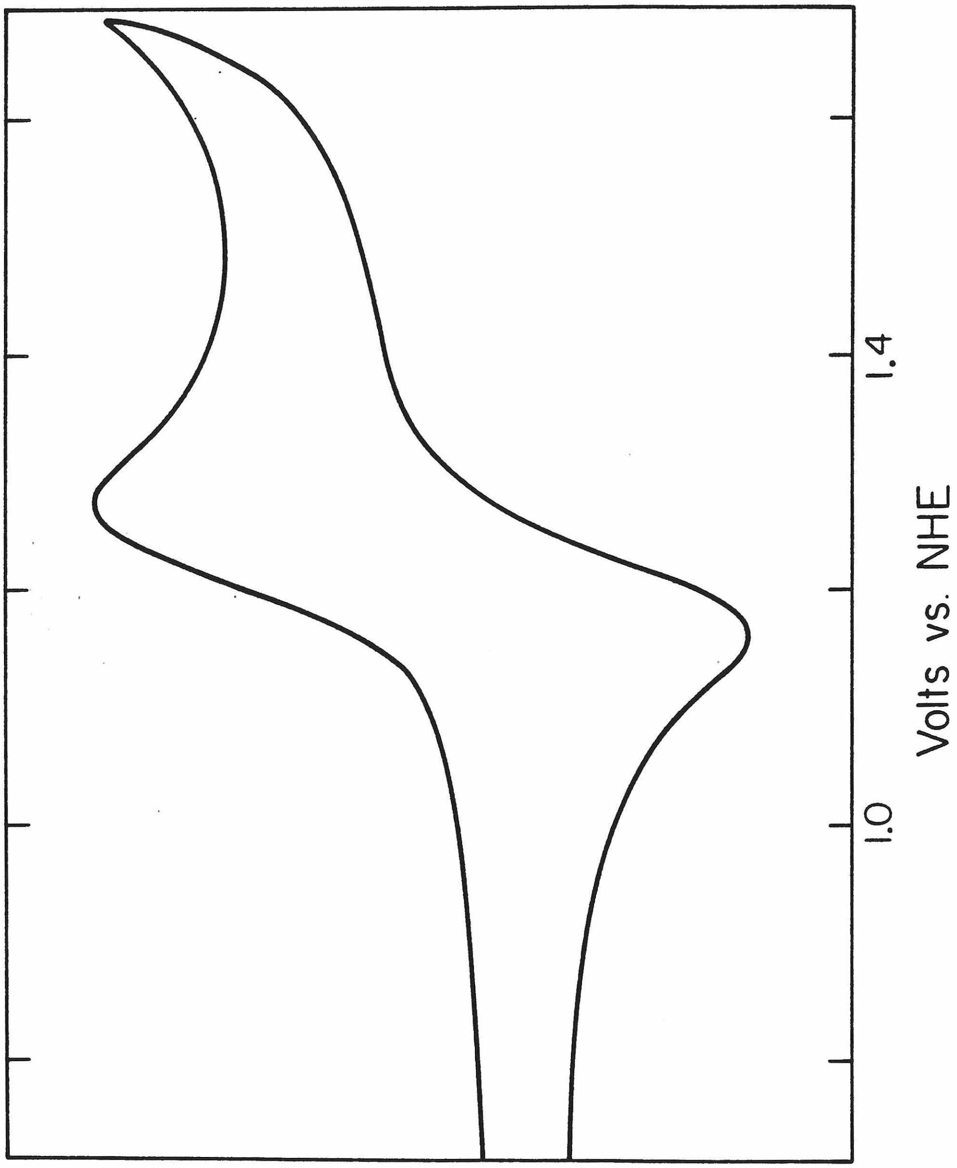


Figure 2.

TABLE 1. Electrochemical Potentials for (4′-MeLH)$RuCl_3$ as Measured in Various Solvents (vs. nhe).

Solvent	E^f	
	(4′-MeLH)$RuCl_3$	(4′-MeLH)$RuCl_3$ + 2, 6-lutidine
Acetonitrile	1.35	0.98
Propylene Carbonate	1.35	1.00
Acetone	1.17	0.88
Dichloromethane	1.25	0.86
N, N-Dimethylformamide	0.95	0.92
N, N-Dimethylacetamide	0.91	0.91

The oxidation wave observed for (4'-MeLH)$RuCl_3$ was found to be a one-electron process by adding an equimolar amount of another electroactive species to a solution of (4'-MeLH)$RuCl_3$ in dichloromethane. Tris(acetylacetonato)ruthenium(III), $Ru(acac)_3$, was used as the one-electron standard.[8] A reversible one-electron oxidation wave is observed for $Ru(acac)_3$ at 0.94 V vs. nhe in dichloromethane. A solution containing equimolar amounts of (4'-MeLH)$RuCl_3$ and $Ru(acac)_3$, exhibit two oxidation waves with equal current. This indicates that the reversible oxidation of (4'-MeLH)$RuCl_3$ is a one-electron process.

Other metal complexes containing first-row metals with neutral and deprotonated isoindoline ligands do not show any ligand oxidations in this region. Therefore the observed electrochemistry is attributed to a Ru(III)/Ru(IV) oxidation in the metal complex.

Chlorides remain bound to the metal in acetone, acetonitrile dichloromethane and propylene carbonate as evidenced by the electrochemical results. The presence of free chloride ion in these solutions would be indicated by an irreversible wave due to chloride oxidation at a potential less than 1.1 V. No anodic waves are observed except for the reversible oxidation of the ruthenium complex at more positive potentials. The addition of Ag^+ to solutions of (4'-s-butylLH)$RuCl_3$ in acetonitrile or dichloromethane gave no immediate precipitation of AgCl; another indication that the chlorides are bound to ruthenium in solution.

Cyclic voltammograms were run with 2,6-lutidine added to determine the effect of base on the electrochemistry. In most cases, the oxidation wave shifts to much lower potentials upon addition of 2,6-lutidine (Table 1). For example, the oxidation of (4′-s-butylLH)-$RuCl_3$ in acetone occurs at 1.17 V vs. nhe (eq. 2), but upon addition of base this wave disappears and a new oxidation wave is present at

$$(4'\text{-}\underline{s}\text{-butylLH})RuCl_3^+ + e^- \rightarrow (4'\text{-}\underline{s}\text{-butylLH})RuCl_3 \quad E_f = 1.17\,V \qquad (2)$$

0.88 V. The new wave is ascribed to the oxidation of the anionic trichloro complex formed by deprotonation of the isoindoline ligand (eq. 3). The large shift in potential may be accounted for by the

$$(4'\text{-}\underline{s}\text{-butylL})RuCl_3 + e^- \rightarrow (4'\text{-}\underline{s}\text{-butylL})RuCl_3^- \quad E_f = 0.88\,V \qquad (3)$$

charges of the species undergoing oxidation. The oxidation waves observed in N,N-dimethylformamide and N,N-dimethylacetamide show very little shift in potential upon addition of base (Table 1). This suggests that the complex is already deprotonated in these solvents.

The anionic trichloro complex appears to be quite stable to loss of chloride in acetone as no changes are observed in the electrochemistry after an hour. When one equivalent of Ag^+ was added to the solution, the change in coordination environment about the metal was observed electrochemically. The oxidation wave at 0.88 V disappears upon addition of Ag^+, and is replaced by an irreversible (anodic current greater than cathodic current) oxidation at approximately 1.20 V vs. nhe. The electrochemical behavior is consistent with the loss of chloride ion from the anionic complex with a solvent molecule binding to the metal. The potential has shifted positive again because the complex being oxidized is uncharged.

Similar electrochemical behavior is observed in acetonitrile but chloride ion may be displaced much more readily by the solvent in this case. The Ru(III)/Ru(IV) oxidation of (4′-s-butylLH)$RuCl_3$ in acetonitrile is at 1.35 V vs. nhe. Deprotonation of the neutral complex upon addition of base results in a shift of the wave to 0.98 V, (Fig. 3). The cyclic voltammogram of the basic acetonitrile solution, however, changes with time. A new irreversible oxidation wave appears at approximately 1.27 V and grows in as the 0.98 V wave diminishes. The new oxidation wave may be assigned to oxidation of the neutral complex, (4′-MeL)$RuCl_2(CH_3CN)$, in which acetonitrile has displaced a chloride ion. Addition of one equivalent of Ag^+ to this solution provides further evidence for this assignment as the 0.98 V oxidation wave completely disappears and the irreversible wave at 1.27 V alone is present, Figure 3. From the electrochemical behavior it is apparent that acetonitrile may easily displace chloride ion from the anionic complex.

DISCUSSION OF THE CATALYTIC PATHWAY

The mediated electrochemical oxidation of alcohols reported is significant in that the oxidation takes place at much lower potentials than the direct oxidation of alcohols at a carbon electrode,[9] and that only a catalytic amount of the metal species is needed to complete the oxidation. Several chemical systems capable of catalyzing the electrochemical oxidation of alcohols have been reported recently.[10-15] The electroactive species which control the oxidation of the alcohol vary greatly from a transition-metal complex to organic molecules.

FIGURE 3. Cyclic voltammograms of acetonitrile solutions: (A) (4′-s-butylLH)RuCl$_3$, (B) (4′-s-butylLH)RuCl$_3$ + 2, 6-lutidine after stirring for several minutes, and (C) (4′-s-butylLH)RuCl$_3$ + 2, 6-lutidine + one equivalent of Ag$^+$.

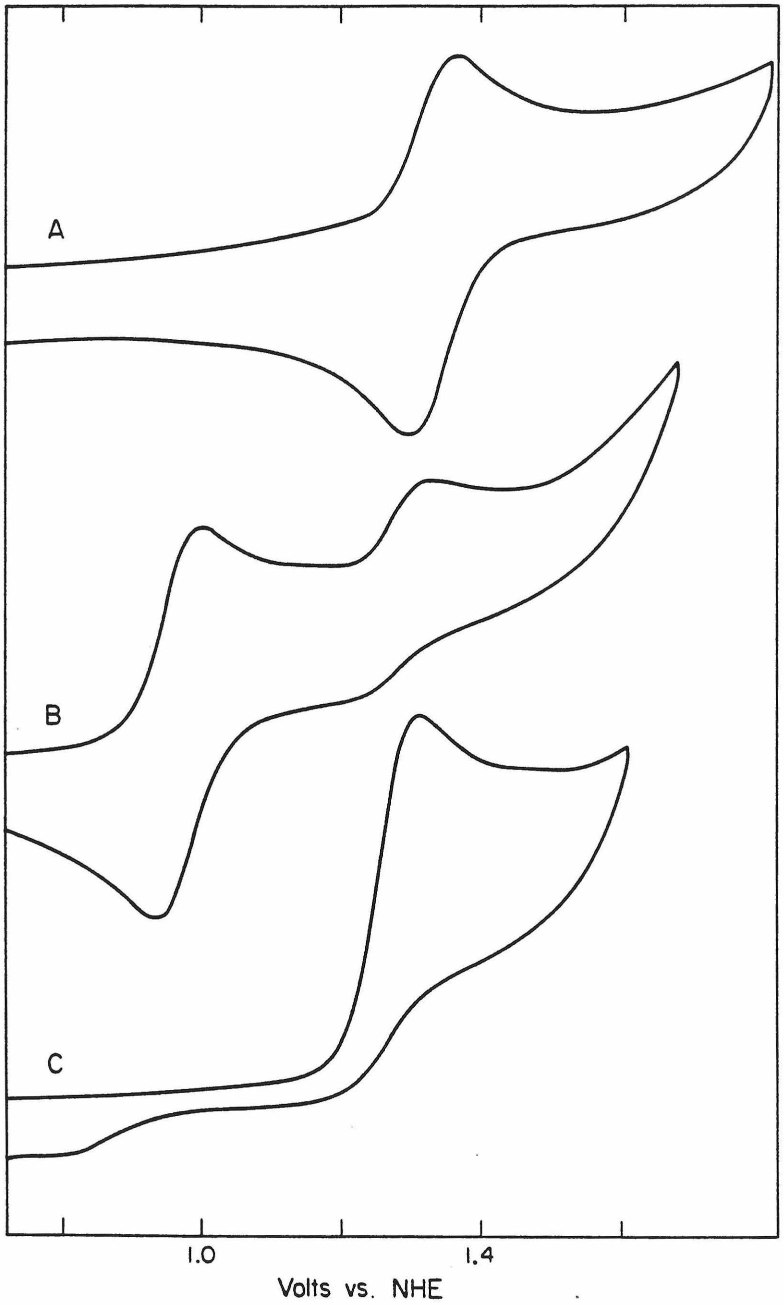


Figure 3.

Most of these reported catalytic systems suffer from one or more of the following problems:

1) The catalyst oxidizes only secondary alcohols.
2) Few catalytic cycles (5-10) are completed before the catalyst degrades.
3) There is poor specificity for production of aldehydes in the oxidation of primary alcohols.
4) The oxidation occurs at relatively high potentials ($>$ 1 V vs. SCE).

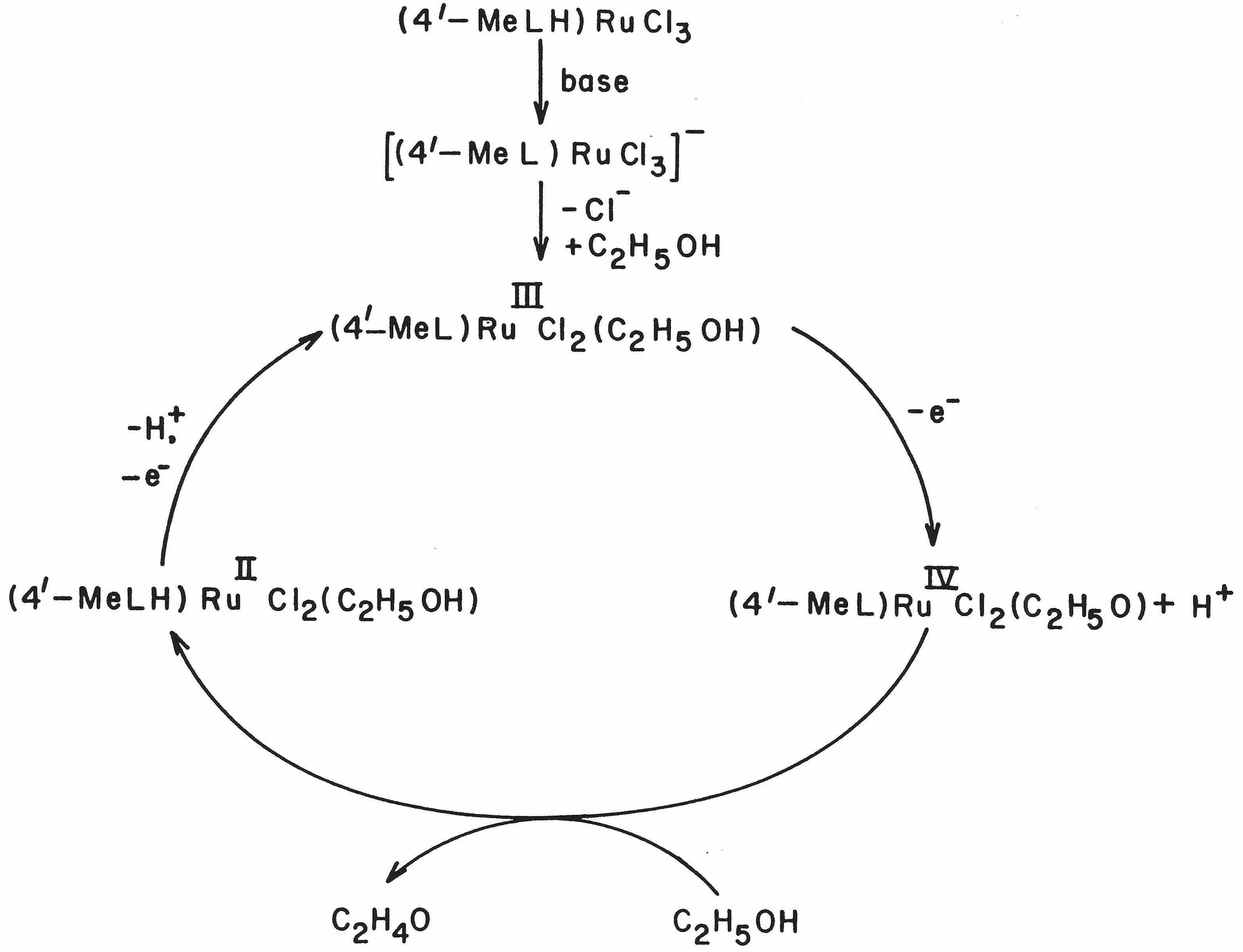
The most efficient of these catalytic systems is the only other report concerning the use of a transition-metal complex as a catalyst. Moyer et al.[10] have observed the electrochemical oxidation of 2-propanol and ethanol catalyzed by the Ru(IV) oxo complex $(trpy)(bpy)RuO^{2+}$ (trpy is 2,2′,2″-terpyridine and bpy is 2,2′-bipyridine). The product of the reaction of the oxo complex with alcohol was the Ru(II) aquo complex $(trpy)(bpy)Ru(OH_2)^{2+}$. The catalyst was long-lived and functioned electrochemically in the range 0.6-0.8 V vs. SCE.

The ruthenium-isoindoline catalytic system has similar characteristics to the ruthenium catalyst reported by Moyer. Our electrochemical results also suggest that the species active in the oxidation of alcohols contains Ru(IV). Indirect evidence for this comes from the reversible oxidation waves observed in nonalcoholic solvents which indicate a Ru(III)/Ru(IV) oxidation of the metal complex. Unfortunately, a Ru(IV) complex could not be isolated by electrolysis of the Ru(III) solutions due to instability of the oxidized complex.

This is the first example of a molecule which catalyzes both the electrochemical oxidation of alcohols and the oxidation of alcohols by molecular oxygen. The electrochemical results in conjunction with the studies of the catalyzed autoxidation of alcohols can be used to propose possible reaction pathways for the electrochemical oxidation. The reaction pathway in Scheme 1 is illustrated for the oxidation of ethanol but can be generalized for other alcohols.

The dissolution of (4′-MeLH)$RuCl_3$ in basic solutions of ethanol involves initially the deprotonation of the isoindoline ligand and then displacement of chloride ion from the anionic complex by ethanol. The electrochemistry of (4′-MeLH)$RuCl_3$ observed in acetonitrile provides evidence for these two steps. As described previously the Ru(III)/Ru(IV) oxidation wave for (4′-MeLH)$RuCl_3$ in acetonitrile shows a marked shift to lower potentials upon addition of base, indicating deprotonation of the isoindoline ligand in the initial complex. Also, a new oxidation wave begins to grow in with time that can be assigned to oxidation of the neutral complex, (4′-MeL)$RuCl_2(CH_3CN)$, in which acetonitrile has displaced a chloride ion. One would expect similar behavior in ethanol to that in acetonitrile, with ethanol also a good ligand for Ru(III). Further evidence for the loss of chloride and coordination of ethanol results from the study of the catalyzed autoxidation of alcohols.[1]

The chemistry of (4′-MeLH)$RuCl_3$ in basic ethanolic solution is complex. Many reactions have been observed in these solutions, including: protonation and deprotonation of the isoindoline and alcohol ligands, dimerization of the Ru(III) complex, and metal based redox reactions. Because of the complicated solution chemistry involved,


(4′–MeLH) RuCl3
base
[(4′–MeL) RuCl3]⁻
-Cl⁻
+C2H5OH
(4′–MeL)Ru III Cl2(C2H5OH)
–e⁻
(4′–MeL)Ru IV Cl2(C2H5O) + H⁺
(4′–MeLH) Ru II Cl2(C2H5OH)
-H.+
–e⁻
C2H4O
C2H5OH

Scheme 1

it is difficult to ascertain the identity of the electroactive complex.

The electrochemical potential at which the oxidation is observed (0.8-0.9 V vs. nhe) provides the only characterization of the electroactive species. The alcohol complex, $(4'\text{-MeL})RuCl_2(C_2H_5OH)$, is a possible candidate as the active species in the catalytic electrochemical oxidation. An electrochemical potential higher than that observed would be expected for the one-electron oxidation of this complex; eq. 4. (Compare the potential observed for the oxidation of

$$(4'\text{-MeL})RuCl_2(C_2H_5OH) \rightarrow (4'\text{-MeL})RuCl_2(C_2H_5OH)^+ + e^- \qquad (4)$$

$(4'\text{-MeL})RuCl_2(CH_3CN) = 1.27$ V). However, a deprotonation of the coordinated ethanol coincident with oxidation of the metal complex would result in a lower electrochemical potential (eq. 5). The potential

$$(4'\text{-MeL})RuCl_2(C_2H_5OH) \rightarrow (4'\text{-MeL})RuCl_2(C_2H_5O) + H^+ + e^- \qquad (5)$$

may be significantly lower due to the change in the charge of the metal complex because of deprotonation.

The electrochemical potential for the oxidation in eq. 5 will be dependent on the concentration of acid in the ethanolic solution; shifting positive as the acid concentration increases. This behavior is observed for the catalyzed electrochemical oxidation. As the concentration of acid increases during the oxidation of alcohol, the catalytic anodic wave shifts positive. The acid dependence of the electrochemical potential cannot be quantified in this case because the oxidation under consideration is irreversible.

Similar behavior has been observed involving deprotonation of a hydroxide ligand upon oxidation of Ru(III) to Ru(IV);[16] eq. 6. Reversible electrochemistry was observed for the oxidation, with the

$$(bpy)_2 py RuOH^{2+} \rightarrow (bpy)_2 py RuO^{2+} + H^+ + e^- \qquad (6)$$

pH dependence expected. The Ru(IV) oxo complex was the product of the oxidation even under very acidic conditions.

By comparison with the chemistry described above, the deprotonation of the alcohol bound to Ru(IV) in the complex $(4'\text{-MeL})RuCl_2(C_2H_5OH)^+$, may be very favorable in basic solution. The formation of ruthenium alkoxides has been invoked as an intermediate step in several studies of catalytic oxidations of alcohols.[17-19]

The proposed product of the oxidation at the electrode, $(4'\text{-MeL})RuCl_2(OC_2H_5)$, is also the complex that has been proposed as the active oxidant in the autoxidation of alcohols.[1] From oxidation of the coordinated alkoxide, a Ru(II) complex forms which can be readily oxidized at the electrode to Ru(III) to complete the two-electron oxidation. The oxidation of the alkoxide ligand may involve intermediate steps but no intermediates have been observed.

The results from the study of the catalyzed autoxidation of alcohols provide some guidelines concerning the electroactive species. The dimeric complex $\underset{\frown}{2}$ was prepared in an ethanolic solution of $(4'\text{-MeLH})RuCl_3$ containing 2, 6-lutidine; however, it seems unlikely that the dimeric complex is the electroactive species because of its low solubility. The catalyzed autoxidation of ethanol containing $(4'\text{-MeLH})RuCl_3$ and 2, 6-lutidine was very slow unless heated. No oxidation product was observed on stirring the solution for one hour in one atmosphere of oxygen at ambient temperature. This observation makes it less likely that complexes which may form as a result of the oxidation of ethanol, such as metal hydrides or Ru(II) complexes, function as the electroactive species.

The factors which make it difficult to study the electrocatalytic reaction, such as coordination of ethanol and acid-base equilibria, are possibly the same factors most influential in the functioning of the catalyst. The coordination of ethanol may be an important part of the reaction. This is suggested by the negative effect that pyridine has on the electrochemistry. The selectivity of the catalyst may also be enhanced when the alcohol must coordinate to the metal before oxidation takes place, instead of the catalyst functioning only as an outer sphere electron-transfer reagent. The protonation and deprotonation of isoindoline and alcohol ligands are very important to the operation of the catalyst. The effects of these reactions are made evident by the electrochemical potential observed for the oxidation. As discussed above, the potential for the catalyzed electrochemical oxidation shifts positive as acid builds up during the reaction. More conclusive information concerning the pathway of the catalyzed electrochemical oxidation of alcohols will be difficult to obtain because of these problems.

EXPERIMENTAL

Synthesis. The syntheses of (4′-MeLH)RuCl$_3$ · C$_2$H$_5$OH and (4′-s-butylLH)RuCl$_3$ were reported earlier.[1,2]

Electrochemistry. Tetrabutylammonium perchlorate, TBAP, and tetrabutylammoniumtetrafluoroborate, TBAB, (Southwestern Analytical Chemicals) were dried in vacuo before use. Propylene carbonate, distilled under reduced pressure and N,N-dimethylformamide, distilled under reduced pressure over 4A molecular sieves, were used for electrochemical measurements. Acetone, acetonitrile, dichloromethane and N,N-dimethylacetamide used for electrochemistry were spectroquality grade. Alcoholic solvents (methanol, ethanol, isopropanol and n-butanol) were reagent grade but showed no electrochemically active impurities over the range of potentials tried. Gas chromatography also showed no impurities down to 0.01 %.

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 voltammetry.

The supporting electrolyte normally used for electrochemical measurements was 0.1 M TBAP. In 2-propanol and 1-butanol, where it was not possible to prepare 0.1 M TBAP solutions due to decreased solubility, either 0.1 M TBAB or 0.05 M TBAP was used as the supporting electrolyte. The 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. Constant potential electrolyses and cyclic voltammetric measurements were made both in air and in a helium atmosphere with identical results.

Constant Potential Electrolysis. Constant potential electrolyses in alcoholic and nonalcoholic solvents 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 block of pyrolytic graphite with surface area approximately 6.5 cm^2 was used as the working electrode in alcohols, while a platinum gauze electrode was used in nonalcoholic solvents.

Solutions containing 23 mg (0.037 mmol) (4′-s-butylLH)$RuCl_3$ and 0.25-0.5 ml of 2,6-lutidine in 20-25 ml of alcohol were electrolyzed at 0.8 to 1.0 V vs. nhe. Currents of 1-5 mA were observed initially but after several equivalents of charge had passed the current had dropped sharply. More 2,6-lutidine (2 drops) was added and the current was restored to nearly its initial value.

The electrolyzed solution was analyzed with a Hewlett-Packard 5830A gas chromatograph using a Carbowax 20 M column and a diethylene glycol succinate column. The identity of the product was checked by comparing retention times for the oxidation product and the pure sample. The identification of the products was further verified in the case of the oxidation of ethanol by GC/MS analysis performed by the California Institute of Technology analytical facility. The amount of acetone produced in the oxidation of 2-propanol was quantitatively determined using a known amount of n-hexane as an internal standard.

Solutions of (4′-s-butylLH)$RuCl_3$ or (4′-MeLH)$RuCl_3 \cdot C_2H_5OH$ in nonalcoholic solvents were electrolyzed anodic of the oxidation wave (1.2 V in acetone, 1.5 V in acetonitrile, 1.4 V in dichloromethane and 1.0 V vs. nhe in N,N-dimethylformamide). The current remained high after passing more than 4 electrons per mole of complex in each case. Cyclic voltammograms after electrolysis were different from the initial ones except for the N,N-dimethylformamide solution.

Cyclic Voltammetry. Cyclic voltammetry was carried out in a single compartment cell containing approximately 5 ml of solution. A platinum button electrode and a basal plane pyrolytic graphite electrode were used as working electrodes.

Cyclic voltammetric solutions were prepared by dissolving (4′-MeLH)$RuCl_3 \cdot C_2H_5OH$ or (4′-s-butylLH)$RuCl_3$ in the solvent of interest. One drop of 2,6-lutidine was added when the effect of base was measured. To remove chloride from the complex, a solution containing one equivalent of $AgNO_3$ in acetonitrile was added. The electrochemical behavior of chloride ion in various solvents was studied by adding tetraethylammonium perchlorate to the electrochemical solution.

Small amounts of ferrocene were added to electrochemical solutions as an internal standard. Potentials for the complexes were measured vs. ferrocene. Formal potentials are reported vs. nhe by assuming a value of 0.400 V for the ferrocene/ferricinium couple.[20]

Formal reduction potentials, E^f, were measured by cyclic voltammetry using the formula $E^f = (Ep_a + Ep_c)/2$. 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.

Tris(acetylacetonato)ruthenium(III), $Ru(acac)_3$, (Matthey Bishop) was used as a one-electron standard with which to compare the heights of the reversible oxidation observed for (4'-s-butylLH)$RuCl_3$. Equimolar amounts of the standard and (4'-s-butylLH)$RuCl_3$ were added to the electrochemical solution and cyclic voltammograms were obtained.

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PROPOSITION 1

Structural Study of V-nitrogenase

A structural study, using X-ray absorption spectroscopy, of nitrogenase in which molybdenum has been replaced by vanadium is proposed. Information will be obtained from this study concerning the environment of vanadium in the substituted enzyme, which may have implications to the native protein.

The facile reduction of N_2 to ammonia by nitrogen-fixing microorganisms has long been an area of fascination to scientists of many fields. Biologists and chemists have worked arduously in this area and yet the process remains largely a mystery.

The enzyme that effects nitrogen reduction, nitrogenase, contains both molybdenum and iron atoms. An iron-molybdenum cofactor has been isolated from the enzyme which is able to restore catalytic activity to an inactive component of the protein.[1] Several techniques have been used to deduce the chemical environment of the iron atoms in the protein. EPR spectroscopy was useful in this regard because the iron atoms are coupled in a paramagnetic fragment.[2] Mössbauer and visible spectroscopy have also been used to determine the oxidation states and coordination environment of the iron.[3] Molybdenum in the protein is not amenable to these techniques. Recently, however, X-ray absorption spectroscopy (XAS) was used to characterize molybdenum in the protein.[4,5] The results of this analysis show mainly sulfur ligands bonded to molybdenum, but also several iron atoms within 3 Å. This determination led to some uncertainty in the molybdenum environment, being interpreted differently by two separate investigators,[4-6] but still provides the best information available concerning molybdenum ligation.

It has been observed that vanadium will replace molybdenum in some nitrogen-fixing bacteria.[7] This is accomplished by growing the bacteria in a medium containing vanadium and no molybdenum. In this manner it is possible to isolate a protein containing vanadium and iron with a small amount of molybdenum impurity.

Two research groups have prepared and studied the V-Fe protein.[7-10] The vanadium substituted protein reduces all nitrogenase substrates tested; N_2, C_2H_2 and various nitriles, although V-nitrogenase proved to be less active than Mo-nitrogenase. Differences in substrate binding, electron transfer reactions and products released were found comparing the reactivity of the two proteins.

Two fundamental questions arise in studying the vanadium substituted protein:

1. Does vanadium occupy the same site as molybdenum?
2. Is the reduction of substrate occurring at vanadium?

It is believed that vanadium is simply substituting into a site that molybdenum normally occupies. The similar physical properties of V-nitrogenase and Mo-nitrogenase suggest that this is true. However, at present there is no conclusive evidence for this assumption.

Two different conclusions were reached concerning the site of substrate reduction in V-nitrogenase. One belief is that the small amount of molybdenum impurity present in V-nitrogenase accounts for its activity.[9] It is claimed that vanadium incorporation leads to stabilization of the enzyme and more effective use of the molybdenum present. In order for this to be correct, a turnover number per molybdenum of more than ten times that of Mo-nitrogenase would be required. The alternate explanation is that substrate reduction is occurring at vanadium which is less effective than molybdenum due to chemical differences between the two metals.[10]

Previous investigators have shown that it is possible to obtain quality X-ray absorption spectra of metalloproteins, including Mo-nitrogenase.[11] It is believed that V-nitrogenase will present no new difficulties. The protein V-nitrogenase is less stable than Mo-nitrogenase but certainly should be stable enough for the spectral analysis.

Vanadium XAS of the protein, and especially the extended fine structure of the X-ray absorption spectrum (EXAFS) will indicate the chemical environment surrounding vanadium. Although it has been assumed that vanadium substitutes into the same site as molybdenum, this analysis will provide the first spectroscopic support for this assumption. The vanadium EXAFS would be expected to show exactly the same environment as the molybdenum EXAFS. Confirmation of the fact that vanadium substitutes for molybdenum in an identical site may lead to a better understanding of the molybdenum EXAFS results. In addition, confirmation of this fact will strengthen the conclusions of Hardy et al., made from their kinetic measurements on V-nitrogenase, that molybdenum is involved in substrate binding and possibly substrate reduction in the native protein.[10] A closer comparison of substrate reduction in the two proteins can reliably be made after it is certain that the environments are the same.

Results of measurements of substrate reduction by V-nitrogenase and Mo-nitrogenase show great differences. These differences provide strong support for the binding of substrate at molybdenum and vanadium in the proteins. (If the substrate were binding to iron one would expect only a small change in the rate of binding due to substitution of vanadium for molybdenum, provided that the conformation of the protein is not significantly altered.) Direct evidence for substrate binding at vanadium may be indicated by EXAFS spectra of the vanadium protein in the presence of substrate. One would expect to see a change in the EXAFS spectra with and without substrate due to a change in the ligands around the metal atom. This effect may be small and difficult to quantify, but if observable, would provide the first direct evidence for substrate binding to vanadium or molybdenum in the protein.[12]

Phase shifts and amplitudes necessary for the EXAFS analysis can be determined empirically, in most cases, by collecting EXAFS spectra of several vanadium compounds where the structures are known from crystallographic work. A recent investigation of vanadium in the blood cells of tunicates by X-ray absorption spectroscopy has provided many of the parameters necessary for a study of V-nitrogenase.[14] The model compounds utilized, contained V–C, V–N, V–S and V–O bonds, from which amplitude and phase parameters were obtained. These parameters also may be calculated from an electron-atom scattering theory with favorable results.[15] The V-Fe contribution to the observed EXAFS spectrum may be dealt with in this manner.

An X-ray absorption study of V-nitrogenase will determine the chemical environment about vanadium. Comparison with the molybdenum environment in Mo-nitrogenase, determined also by XAS, can be made to determine if vanadium has simply substituted for molybdenum in the protein. With a knowledge of the chemical environment of vanadium in the protein, more reliable conclusions can be drawn in comparing the reactivity of the vanadium and molybdenum containing proteins.

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PROPOSITION 2

Linear Trinuclear Metal Complexes

The preparation of a series of linear trinuclear complexes is proposed. These complexes will be used to study the extent of metal-metal interaction between the two terminal metal ions as a function of the central metal ion.

The interactions between metal ions in polynuclear complexes have been studied extensively. Synthetic systems have been investigated as models for multi-metal biological systems. Progress has been made in attempts to reproduce the behavior of various multimetallic proteins by synthetic models.[1-3] The effects of metal-metal interactions are also of industrial interest as metal cluster compounds become of greater importance as catalysts.[4, 5]

Quantitative measurements of the interactions between metals have been made for many binuclear complexes utilizing spectroscopic, electrochemical,and magnetic methods. Magnetic interactions between metal ions have been studied for many binuclear complexes; especially the relationship between the magnetic coupling and the structure of the complex.[6] The mediation of the magnetic effects by various bridging groups also has been examined.[7]

A measure of the extent of interaction between metal ions appears in the magnitude of the constant describing the comproportionation equilibrium (eq. 1). Comparing homobinuclear complexes

$$M^{II}M^{II} + M^{III}M^{III} \rightleftharpoons 2M^{II}M^{III} \qquad (1)$$

containing the same metal in similar coordination environments, a larger comproportionation constant suggests a greater interaction between the metal ions. For example, the binuclear ruthenium complexes $(NH_3)_5RuLRu(NH_3)_5^{+n}$, n = 4, 5, and 6, have comproportionation constants indicative of the mediation of the metal-metal interaction by the bridging ligand; L = NC-CN[8] $K_{com} = 10^{13}$, L = pyrazine[9] $K_{com} = 10^6$, L = 4,4′-bipyridine[10] $K_{com} = 20$.

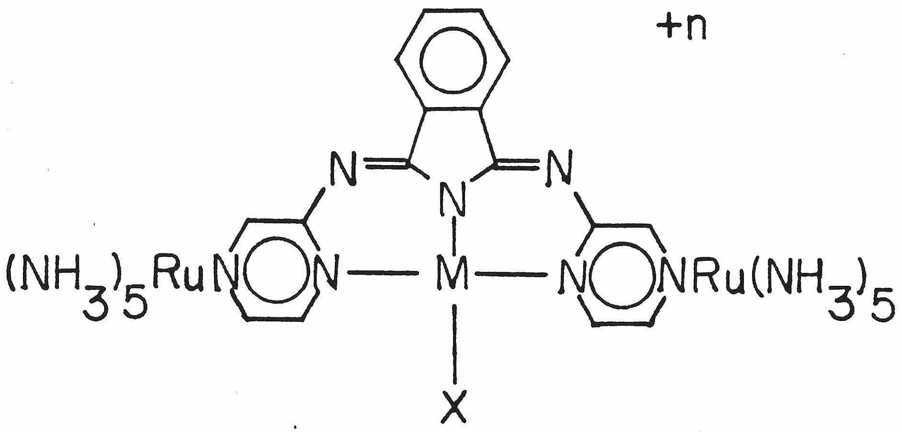
The spectroscopic properties of mixed-valent binuclear complexes have been used to estimate the rate of intramolecular electron transfer in these species. A low-energy absorption is often observed for these complexes which, in some cases, can be assigned to intervalence transfer,[11-13] eq. 2. The theory developed by Hush

$$M^{II}\text{-}L\text{-}M^{III} \xrightarrow{h\nu} M^{III}\text{-}L\text{-}M^{II} \tag{2}$$

describes the properties of the intervalence transfer (IT) band for weakly coupled, valence localized, mixed-valent complexes.[14] Providing that the observed IT absorption exhibits the properties outlined by Hush, detailed information concerning intramolecular thermal electron transfer may be obtained from the position and intensity of the IT band. This approach has been used in the study of many mixed-valent ruthenium complexes.

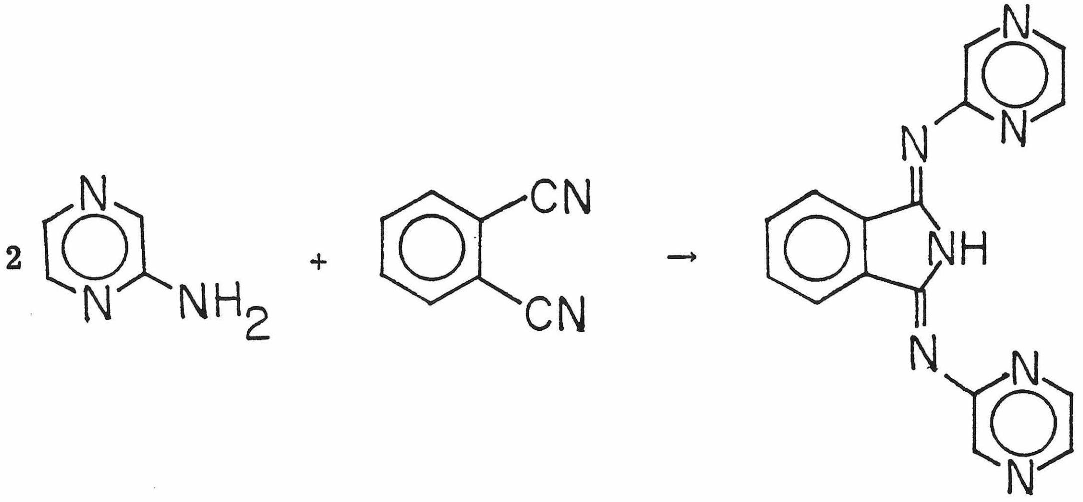
Detailed studies have been made relating the effect of the bridging ligand on the metal-metal interactions. One of the best characterized systems involves the complexes, $(bpy)_2ClRuLRuCl(bpy)_2^{+n}$, or $(NH_3)_5RuLRu(NH_3)_5^{+n}$, where the bridging ligands have been varied extensively. Changes in the bridging ligand showed the effect of distance (L = pyrazine vs. 4,4′-bipyridine) and conjugation (L = 1,2-bis(4′-pyridyl)ethylene vs. 1,2-bis(4′-pyridyl)ethane) on the interaction between the metals.[11] However, in none of these studies involving the bridged ruthenium ammines or any other binuclear complex, has the interaction mediated by a bridging group containing a metal ion been examined. A study of this type would be helpful in determining the utility of linear polynuclear complexes as multi-electron transfer reagents. The characteristics of the central metal ion which permit greater intramolecular communication between the terminal metal ions may be applied to this and other problems.

An investigation of binuclear complexes bridged by a moiety containing a metal ion is proposed; specifically, the preparation of complexes of the type 1. These complexes provide an opportunity to study the effect of the central metal ion on the interaction between the terminal ruthenium ions.



1

The preparation of the ligand 2, pyzLH, is necessary for this study. This ligand is quite similar to other bis(arylimino)isoindoline ligands that have been prepared previously,[15] and should provide no new synthetic difficulties. The ligand 2 may be prepared from aminopyrazine[16] and 1,2-dicyanobenzene as illustrated in eq. 3. It is expected that ligand 2 will have chelating properties similar to

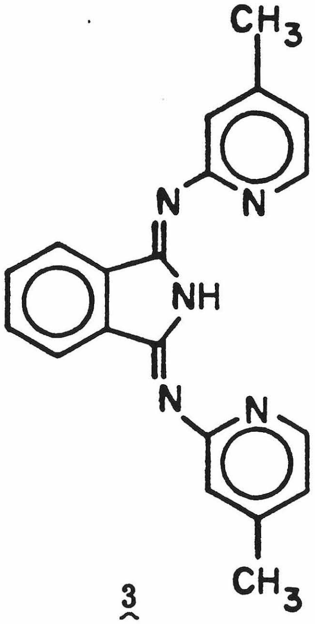


(3)

2

previously prepared ligands; with an ability to function as a tridentate chelate in its neutral form and in its anionic form upon loss of the pyrrole proton.

In order to have a constant coordination environment at the central metal ion, the isoindoline ligand 3 will be utilized to provide

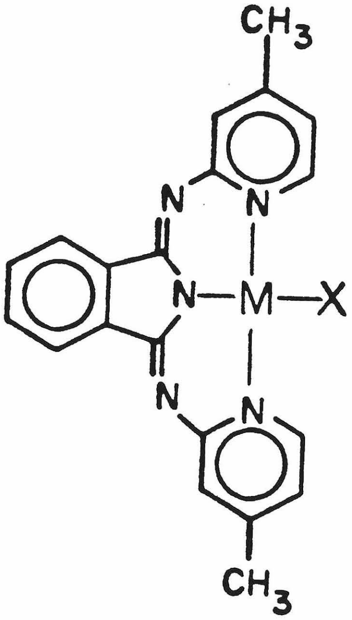


= 4′-MeLH

3

an octahedral environment for the central metal. Equations 4 and 5 outline the preparation of the pseudooctahedral complex 5, M(pyzL)(4′-MeL). The synthesis is identical to procedures which have been used to prepare bis(isoindoline) metal complexes.[17] Complexes of the type 4, M(4′-MeL)X, have been prepared for

MX_2 + 4′-MeLH →



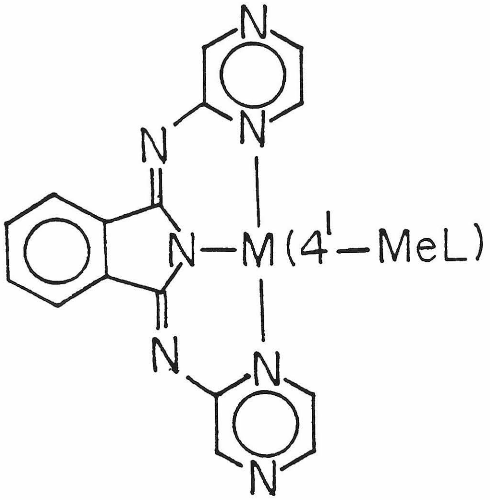
(4)

4

M = Mn, Fe, Cr, Ni, Cu, and Zn, and X = acetate. The reaction of 4 with pyzLH should yield the desired pseudooctahedral mononuclear complex 5. The chelate effect should favor coordination of pyzLH as a tridentate ligand rather than coordinating only pyrazine to the metal.

$M(4'\text{-}MeL)X$ + pyzLH →

4 2



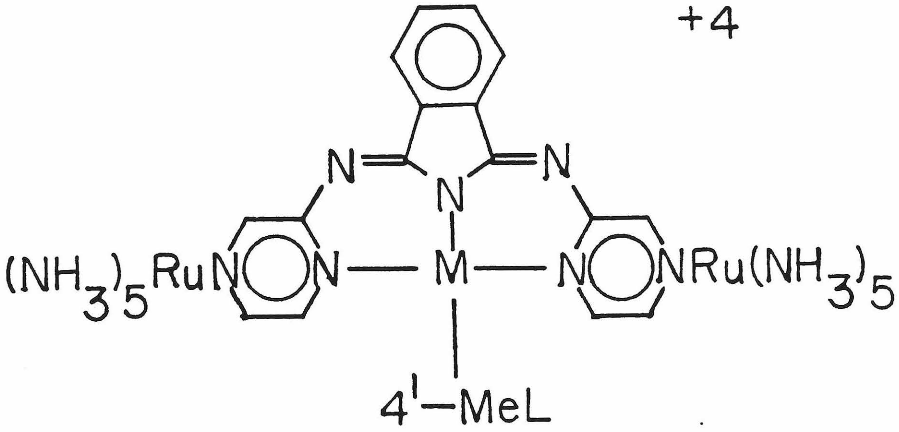
(5)

5

The remote pyrazine nitrogen atoms in complex 5 remain available for bonding to other metal ions. The final trinuclear complex 6 may be prepared by reaction of $(NH_3)_5Ru(H_2O)^{2+}$[18] and M(pyzL)(4′-MeL); eq. 6.

$2(NH_3)_5Ru(H_2O)^{2+} + M(pyzL)(4'\text{-}MeL) \rightarrow$

(6)



6

The trinuclear complexes 6 provide an opportunity to study the interaction between the two terminal ruthenium ions as a function of the central metal ion. This effect may be measured electrochemically by noting changes in the separation of the two one-electron oxidations for the terminal ruthenium ions. From the separation of the two waves, E_2-E_1, the comproportionation constant, K_{com}, can be calculated using eq. 7. The comproportionation constant, as mentioned above,

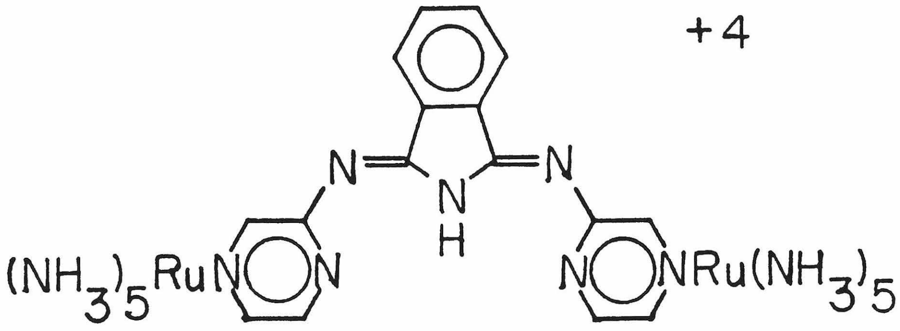
$$\ell n\, K_{com} = \frac{nF}{RT} |E_2 - E_1| \qquad (7)$$

provides a measure of the interaction between the ruthenium ions. The comproportionation constants may be small in some cases, resulting in overlapping oxidation waves. The separation between the two one-electron oxidation waves can be determined, even in this case, by using methods that have been described elsewhere.[19,20]

The trinuclear complex which has the terminal ruthenium ions in different oxidation states may exhibit an intervalence transfer absorption due to transfer of an electron from one end of the molecule to the other. Intervalence transfer bands have been observed for trinuclear ruthenium complexes bridged by pyrazine ligands, $(NH_3)_5RupyzRu(NH_3)_4pyzRu(NH_3)_5^{+7}$. In this trinuclear complex, multiple IT bands have been ascribed to electron transfer between adjacent metals and between the two end metals.[21]

The trinuclear complexes proposed offer a chance to examine several effects. A wide variation in the central metal ion should be possible with M = Mn, Fe, Co, Ni, Cu, Zn and Ru. For comparison purposes, a complex with no central metal ion, 7, could be prepared, eq. 8. The complex 7 should be obtainable since the substitution

$$2(\mathrm{NH}_3)_5\mathrm{Ru}(\mathrm{H}_2\mathrm{O})^{2+} + \mathrm{pyzLH} \rightarrow \qquad (8)$$



7

inert Ru(II) ions will not readily lose ammine ligands to bind to the tridentate chelate. The complex 7 may be isolated either with the neutral ligand or in its anionic form by addition of base. The ruthenium-ruthenium interaction in the complex 7 will illustrate the mediation of the interaction by the conjugated ligand in the absence of a central metal ion.

The effect of the reduction potential of the central metal ion on the interaction between the terminal ruthenium ions can also be investigated with these complexes. The coordination environment of the central metal ion can be held constant and the electrochemical potential changed by altering the substituents on the nonbridging isoindoline ligand. The reduction potential should be affected significantly by a change from a methyl substituent on the pyridine ring to a chloro or nitro substituent.[17] Substituents on the non-bridging isoindoline ligand may also be changed to enhance the solubility of the complex.

In summary, the preparation of a series of linear trinuclear complexes is proposed. The extent of interaction between the two terminal metal ions will be studied. The effect of the central metal ion on the mediation of this interaction will be explored by varying the central metal.

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PROPOSITION 3

A Model for Vanadium Binding in Sea Squirts

A study of the vanadium-binding properties of mucopolysaccharides and simple sulfate-containing carbohydrates is proposed as a model for the binding of vanadium by the marine animals known as sea squirts.

Nature has utilized many different metal ions to perform a wide variety of biochemical processes. Metalloproteins and metalloenzymes have been especially well studied by biologists and chemists to determine the function of these metallic systems.

Certain members of the class of sea animals called Ascidiacea (sea squirts) contain large amounts of vanadium in their blood cells.[1] Despite the discovery of vanadium in the blood of Ascidiacea in the early 1900's and continuous research since then, little is known conclusively about the biochemical function of the vanadium in the animals.

Vanadium is found in the animal as V(III), present in vacuoles (vanadophores) within the blood cells.[2] The aqueous solution within the vanadophore also contains large amounts of sulfuric acid. The exact concentration of acid is not known but has been reported to be as high as 1 M.[3]

The V(III) species found in the vanadophore has been shown to be a powerful reducing agent.[4] It is generally believed that the reducing properties of the complex are the key to its primary biochemical function. Various hypotheses have been proposed concerning the use of the reducing strength of the complex for processing nutrients or in the synthesis of the cellulose-like mantle of the sea animal.[5]

A respiratory function for the vanadium complex has also been suggested. Oxygen uptake measurements on the blood cells indicated a reversible absorption of oxygen, with the blood cells fully saturated at 5 mm Hg.[6] A more recent study, however, refutes this, claiming no reversible oxygen binding by the vanadium-containing blood.[7]

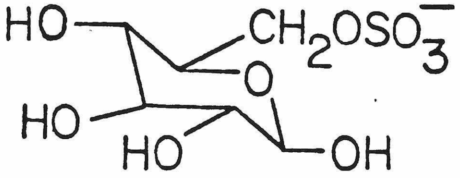
All the physical studies of the V(III) complex found in the blood are hampered by a major problem; since the function of the vanadium complex is unknown, there is no method for assaying the sample to be certain that degradation has not taken place. The vanadium-containing species is also very susceptible to oxidation. These difficulties have led to conflicting conclusions regarding the vanadium complex, such as the oxygen-binding properties discussed above.

More reliable studies have made use of physical measurements on vanadium in intact blood cells. X-ray absorption spectroscopy indicates a coordination environment of six oxygen atoms around the vanadium, with no evidence for the presence of a vanadyl group.[8] A ^{1}H NMR study of vanadium in living blood cells utilized the excellent contact shift properties of V(III). The results of this investigation suggest that most (4 or 5) of the ligands coordinated to vanadium are water.[9] The physical studies of the structure of the vanadium complex indicate that it is a very simple species; perhaps just an aquo-sulfato complex of V(III).

While advances have been made in determining the nature of the vanadium complex in the blood of the sea squirts, little is known about how vanadium is taken up by the organism. Vanadium is acquired by the animal from the aqueous phase. Vanadium is present in sea water as V(V)[10] (probably as $VO_2(OH)_2^-$) at a concentration of approximately 10^{-8} M. The concentration of vanadium in the animal can be up to one million times the concentration in sea water. Biological studies investigating the site and rate of vanadium uptake by various species of tunicates (of which the Ascidiacea are one class) have been made.[6,10,11] Experiments involving the assimilation of radioactive vanadium, and other metal ions, by the tunicates have provided information concerning the site of uptake. The results indicate that vanadium, as well as iron, niobium, tantalum, chromium, and titanium are bound by sulfate groups on the mucopolysaccharides which line the pharynx of the animal.[6] All of these metals are scavenged from sea water but only selected metals are taken into the tissues and blood, with vanadium concentrated more than the other metals. The specificity for vanadium in the blood of members of the class Ascidiacea is very high and remains an intriguing mystery.

This area of study has lacked investigations of model inorganic compounds that have proved helpful in better understanding the metal environments in metalloproteins such as hemoglobin, nitrogenase and many others. A study of the vanadium binding properties of mucopolysaccharides and simple sulfate-containing carbohydrates is proposed. Research on vanadium uptake by sea squirts suggests that these molecules may function as ligands to bind V(V) from sea water.

Studies of the binding properties of various mucopolysaccharides (chondroitin sulfate, dermatan sulfate, and others) with Zn(II) and Cu(II) have been made.[12,13] The formation constant for the complexation of copper was measured by spectroscopic methods while the stoichiometry of zinc binding was measured by uptake of radioactive zinc. A similar investigation with V(V) may help in understanding the assimilation of the metal by the biological system. Comparisons of the binding of other metals, such as Fe, Nb, Cr, etc., may also be made and related to the uptake of these metals by the living system. Simple sulfate-containing monosaccharides and disaccharides, for example 1 or 2, which are individual units of the mucopolysaccharides, may also function as ligands for the metals.[14] The monomeric species resulting from complexation by these groups should be more easily characterizable by spectroscopic methods, and more information concerning the ligating environment of the metal may be obtainable.



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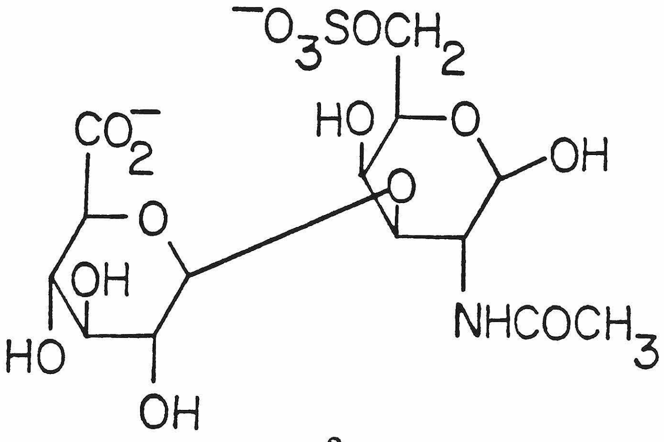

2

If the mucopolysaccharides provide an accurate model of the ligating groups that assimilate metals in the animal, then its binding properties would be expected to be relatively nonselective. The living organism, as described above, is able to bind several metal ions but in many species vanadium is selectively passed onto the blood. Few suggestions as to how this occurs have been made. The model system proposed may provide some insight into this question.

The redox properties of vanadium in the ligating environment of the sulfate-carbohydrate groups may be very informative. Vanadium is initially bound in the organism as V(V) but is present in the blood as V(III). Little is known concerning where in the organism this reduction occurs. The release of vanadium to the blood and tissues may be related to the reduction of the vanadium polysaccharide complex. Similar suggestions have been made concerning the release of iron upon reduction from siderophores in microbial iron transport.[16] A study of the redox properties of other metals ligated by mucopolysaccharides may aid in determining the differences between vanadium and these metals in the animal.

The relationship between the acid-base properties of the ligands and the binding of metal ions may also be important. The variation in the metal-binding properties of the sulfate-carbohydrates can be measured as a function of pH to determine its effect on the model system.

In summary, a study of the vanadium-binding properties of mucopolysaccharides and sulfate-containing mono- and disaccharides is proposed. These ligands are suggested as a model for the binding of vanadium from sea water by marine animals known as sea squirts. With a characterization of the binding properties of the ligands and the redox properties of the complexed metal, information may be obtained which can be related to vanadium binding and selective transfer in the organism.

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PROPOSITION 4

Osmium Ammine Binuclear Complexes

The synthesis of ligand bridged osmium ammine binuclear complexes is proposed.

Research in the area of mixed-valent binuclear complexes has been extensive. Mixed-valent complexes have been particularly useful in evaluating hypotheses involving electron transfer between metal ions. The theoretical treatment proposed by Hush,[1] as well as other theories, have been applied to these systems in order to determine rates of intramolecular electron transfer and parameters related to electron delocalization in binuclear complexes. This information is available for weakly coupled mixed-valent complexes from the properties of the intervalence transfer (IT) absorption. Provided that certain criteria are satisfied (solvent dependence of the position of the IT band and predicted band width for the absorption), the rate of thermal intramolecular electron transfer can be estimated from the position of the IT band. Additionally, the extinction coefficient of the absorption can be related to the extent of electron delocalization in the mixed-valent complex.

Power and Meyer have measured the properties of the intervalence transfer absorption for a series of mixed-valent ruthenium binuclear complexes, $(bpy)_2ClRuLRuCl(bpy)_2^{3+}$ (bpy = 2, 2′-bipyridine), where the bridging ligand L is varied.[2] The results of this study indicate that the energy of the optical transition increases as the distance between the two metal ions increases, Table 1. This effect is also observed for the ruthenium ammine mixed-valent binuclear complexes, $(NH_3)_5RuLRu(NH_3)_5^{5+}$.[3,4] Utilizing the Hush treatment for both of these cases, the results indicate that as the distance between the metal ions increases, the rate of intramolecular electron transfer decreases.

TABLE 1. Properties of Intervalence Transfer Absorptions for Several Mixed-Valent Complexes (in H_2O).[a]

	$(NH_3)_5RuLRu(NH_3)_5^{5+}$	$(bpy)_2ClRuLRuCl(bpy)_2^{3+}$	$(CN)_5FeLFe(CN)_5^{5-}$
Bridging Ligand	$\nu(\epsilon)$[b]	$\nu(\epsilon)$	$\nu(\epsilon)$
Pyrazine	1560 (5000)	1270 (455)	1200 (2200)
4,4′-bipyridine	1030 (880)	890 (100-200)[c]	1200 (1100)
trans-1,2-bis(4′-pyridyl)ethylene	960 (760)	830 (135-270)[c]	1300 (600)

[a] Compiled from data in Ref. 2-5.

[b] ν in nm, ϵ in M^{-1} cm^{-1}.

[c] Extinction coefficients are approximate because the comproportionation constant is unknown.

The only study of mixed-valent complexes with a variable bridging ligand and a metal other than ruthenium involves the iron binuclear complexes $(CN)_5FeLFe(CN)_5^{5-}$.[5] Analogous chemical and spectroscopic behavior had been observed for mononuclear complexes $Fe(CN)_5L^{3-}$ and $Ru(NH_3)_5L^{2+}$, where L is a heterocyclic ligand, and similar properties were expected for the binuclear species. However, in contrast to the trend observed for the ruthenium binuclear complexes,there is no dependence of the energy of the intervalence transfer band on the bridging ligand (Table 1). These results contradict the conclusions of Meyer concerning the role of distance in optical and thermal electron transfer, and suggest that the rate of intramolecular electron transfer in the iron complexes is not dependent on the distance between the metals. Another series of mixed-valent complexes containing a metal other than ruthenium or iron might be helpful in clarifying this discrepancy.

The synthesis of osmium ammine binuclear complexes is proposed. The general synthetic scheme should be amenable to the preparation of osmium binuclear complexes containing a variety of bridging ligands. These complexes may provide a better understanding of the effect of distance between the metal centers on the properties of the intervalence transfer absorption.

Because of synthetic difficulties, the chemistry of Os(II) and Os(III) ammines has not been explored as thoroughly as the ruthenium analogs. It has been only recently that procedures have been discovered for the synthesis of pentaammine complexes of Os(II) and Os(III) containing a heterocyclic ligand.[6] While the Ru(II) aquo complex,

$Ru(NH_3)_5H_2O^{2+}$, has been the key starting material for the synthesis of various pentaammine ruthenium species,the dinitrogen complexes of osmium, $(NH_3)_4Os(N_2)_2^{2+}$ and $(NH_3)_5OsN_2^{2+}$ are important reagents in the preparation of osmium ammine complexes. These two complexes are prepared as illustrated in equations 1 and 2.[7,8] From the reaction

$$(NH_4)_2OsCl_6 + N_2H_4 \cdot H_2O \xrightarrow{\text{heat}} [Os(NH_3)_5N_2]Cl_2 \qquad (1)$$

$$Os(NH_3)_5N_2^{2+} + NaNO_2 \xrightarrow{\text{HCl}} [Os(NH_3)_4(N_2)_2]Cl_2 \qquad (2)$$

chemistry that is known for osmium ammine complexes three potential synthetic schemes for the synthesis of binuclear species may be proposed. They are outlined and discussed below.

Synthetic Scheme 1

$$(NH_3)_4Os^{II}(N_2)_2^{2+} + L \xrightarrow{\text{heat}} (NH_3)_4Os^{II}(N_2)L^{2+} \qquad (3)$$

$$(NH_3)_4Os^{II}(N_2)L^{2+} \xrightarrow[\text{air}]{\text{HCl}} (NH_3)_4ClOs^{III}L^{2+} \qquad (4)$$

$$(NH_3)_4ClOs^{III}L^{2+} + (NH_3)_4Os^{II}(N_2)_2^{2+} \xrightarrow{\text{heat}}$$

$$(NH_3)_4ClOs^{III}LOs^{II}N_2(NH_3)_4^{4+} \qquad (5)$$

$$(NH_3)_4ClOs^{III}LOs^{II}N_2(NH_3)_4^{4+} \xrightarrow[\text{air}]{\text{HCl}}$$

$$(NH_3)_4ClOs^{III}LOs^{III}Cl(NH_3)_4^{4+} \qquad (6)$$

The reactions shown in equations 3 and 4 have been used to prepare mononuclear Os(III) complexes with L = pyrazine, pyridine and other nitrogen heterocycles.[9] The synthesis of the unsymmetrical mixed-valent complex in eq. 5 is dependent on the ligating properties of the uncoordinated heterocyclic nitrogen in the complex $(NH_3)_4ClOs^{III}L^{2+}$. Provided that the binding of osmium does not affect the remote nitrogen of the bridging ligand significantly, this reaction is analogous to the preparation of the mononuclear complex $(NH_3)_4N_2OsL^{2+}$ in eq. 3. Larger bridging groups, such as 4,4′-bipyridine, where the metals are more isolated from one another, should not be greatly affected by the binding of the first metal ion. Difficulties may be encountered with pyrazine as a bridging group, especially for a dimer containing two Os(II) ions which are able to back-bond extensively to the heterocyclic ligand.[6] However, the binuclear complexes prepared in equations 5 and 6, a mixed-valent Os(II)Os(III) species and a binuclear Os(III) complex, may not be a problem even for the smaller bridging ligands.

<u>Synthetic Scheme 2</u>

$$2Os^{II}(NH_3)_4(N_2)_2^{2+} + L \rightarrow (NH_3)_4N_2Os^{II}LOs^{II}(NH_3)_4N_2^{4+} \qquad (7)$$

$$(NH_3)_4N_2Os^{II}LOs^{II}(NH_3)_4N_2^{4+} \xrightarrow[air]{HCl} (NH_3)_4ClOs^{III}LOs^{III}(NH_3)_4Cl^{4+} \qquad (8)$$

The synthesis of the binuclear Os(II) complex, eq. 7, is analogous to the preparation of the mononuclear complex $(NH_3)_4N_2OsL^{2+}$.[9] This synthetic scheme will be particularly subject to the problems discussed above involving two Os(II) ions bound to the bridging group. Therefore the synthesis of binuclear complexes with pyrazine as a bridging ligand will probably be very difficult using this procedure, while with larger bridging groups such as 4,4′-bipyridine there should be much less of a problem. Another potential difficulty with this synthetic scheme is the possibility of oligomerization. This should be a minor problem since monomeric complexes formed from a substitution of both dinitrogen groups of one osmium ion were not observed for the reaction in eq. 3.

Synthetic Scheme 3

$$2(NH_3)_5Os^{II}N_2^{2+} \xrightarrow[(EtO)_3PO]{Ag^+} \xrightarrow{L} (NH_3)_5Os^{III}LOs^{III}(NH_3)_5^{6+} \quad (9)$$

This one-step synthesis of the decaammine complex is analogous to the preparation of the $(NH_3)_5OsL^{3+}$ species.[6] Upon oxidation of the Os(II) complex with Ag^+, dinitrogen is lost and the nitrogen heterocycle binds to the metal.

Utilizing these three general methods, the symmetrical binuclear complexes, $(NH_3)_5OsLOs(NH_3)_5^{6+}$ and $(NH_3)_4ClOsLOsCl(NH_3)_4^{4+}$, as well as the unsymmetrical dimer, $(NH_3)_4ClOs^{III}LOs^{II}N_2(NH_3)_4^{4+}$, may be prepared. Binuclear complexes should be obtainable for a variety of bridging groups, including: 4,4′-bipyridine, trans-1,2-bis(4′-pyridyl)-ethylene, 1,2-bis(4′-pyridyl)ethane, bis(4-pyridyl)amine, bis(4-pyridyl)-methane, and perhaps pyrazine. Complexes of this type have been prepared where the bridging ligand joins two $Ru(NH_3)_5^{2+}$ or two $Fe(CN)_5^{3-}$ units as described above.

The mixed-valent complexes can be generated chemically or electrochemically by reduction of the Os(III) binuclear species. Monomeric Os(II) complexes have been prepared containing heterocyclic ligands, and they are stable in basic solutions in the absence of air.[6] The binuclear osmium species will provide a comparison with the analogous ruthenium complexes which have been studied extensively. Greater overlap with the bridging ligand is expected for osmium and should lead to a greater interaction between the metals. The properties of the intervalence transfer bands for the osmium complexes will be interesting, especially as they relate to the discrepancy in behavior observed for the ruthenium and iron mixed-valent complexes.

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PROPOSITION 5

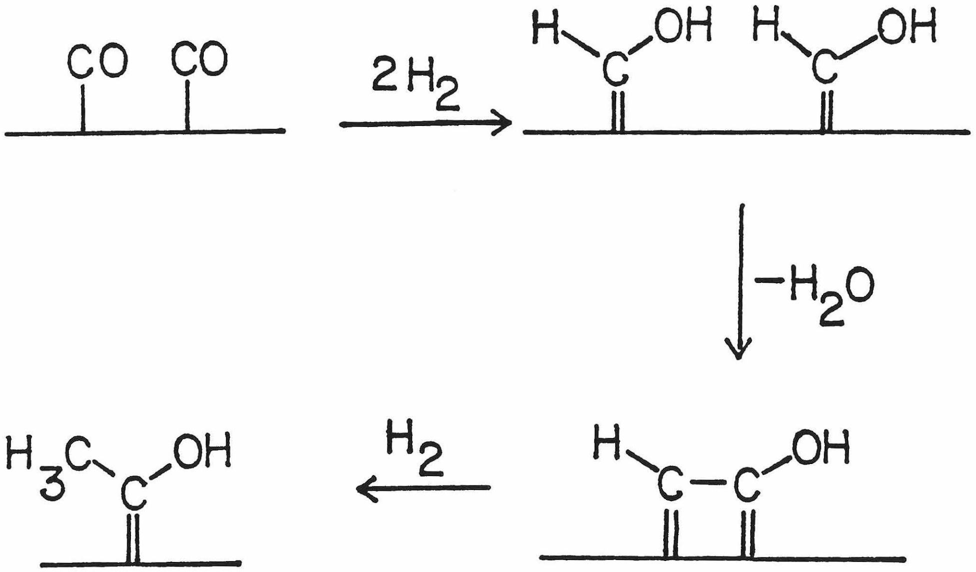
Mixed Catalysts for the Hydrogenation of Carbon Monoxide

An investigation of the products of carbon monoxide hydrogenation over a mixed heterogeneous catalyst is proposed. The catalysts of interest combine a material which catalyzes the hydrogenation of carbon monoxide to hydrocarbons and a material which catalyzes the production of alcohols.

The utilization of CO and H_2, derived from coal, for the synthesis of hydrocarbons and alcohols is currently an area of tremendous industrial and academic interest. Even after many years of extensive investigation of this process, the mechanism of carbon monoxide hydrogenation remains controversial. The majority of the research on the hydrogenation of CO has involved the formation of hydrocarbons. However, in most cases, the mechanistic theories proposed have been equally applicable to alcohol as well as hydrocarbon formation. Several of the more prominent mechanisms are presented below.

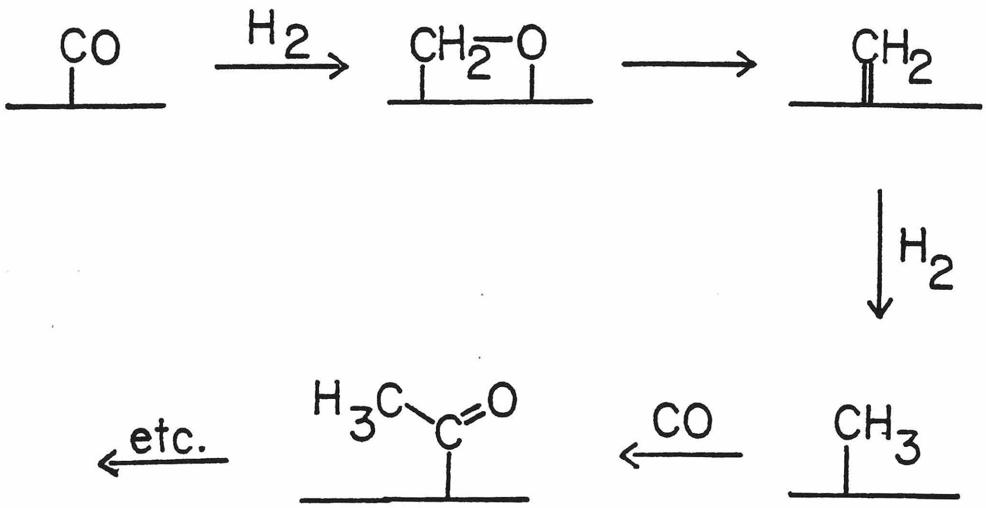
A mechanism for CO hydrogenation suggested by Anderson and Emmett is illustrated in Scheme 1.[1] This proposal suggests that C-C

Scheme 1



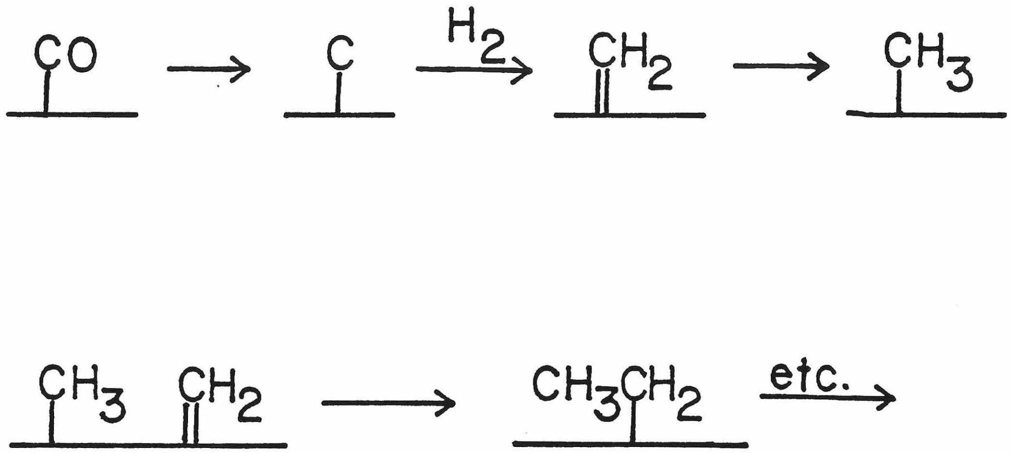
bond formation results from the dehydration of hydroxymethylene groups on the surface of the catalyst. A more recent proposal for the mechanism of CO hydrogenation is shown in Scheme 2.[2] In this

Scheme 2



mechanism the formation of C-C bonds are proposed to take place by carbonyl insertion into a surface metal-alkyl bond. The carbide mechanism suggested by Fischer and Tropsch is outlined in Scheme 3.[3] This mechanism accounts for the production of hydrocarbons, but unlike the mechanisms discussed above, is not applicable to the formation of alcohol products. In the Fischer and Tropsch proposal C-C bonds result from the polymerization of surface methylene groups.

Scheme 3



Some recent experiments have provided evidence for the carbide mechanism. Studies of the dissociative adsorption of carbon monoxide on metal catalysts have been made.[4] Surface carbon deposits are observed when CO is heated over metals which catalyze its hydrogenation to hydrocarbons. The resulting surface carbide is readily hydrogenated at low temperatures. These experiments indicate that the first step in the hydrogenation of carbon monoxide catalyzed by Fe, Co, Ni, and Ru, under conditions at which hydrocarbons are formed, may be cleavage of the C-O bond. Pettit has recently demonstrated that in the presence of H_2, methylene groups do polymerize on metal surfaces to form hydrocarbons.[5]

Increasing evidence supports the initial dissociation of carbon monoxide, and formation of hydrocarbons from polymerization of surface methylene groups. A different mechanism must then be operative for the production of alcohols from CO and H_2, which may involve hydroxymethylene or hydroxymethyl groups on the catalyst surface.

A detailed investigation of the products formed upon hydrogenation of carbon monoxide catalyzed by a mixture of an alcohol production catalyst and a catalyst that favors hydrocarbon formation is proposed. The objective of this study is to monitor the products of CO hydrogenation as a function of catalyst mixture. If two different surface intermediates are involved in the formation of alcohols and hydrocarbons, then new organic products may be observed for the hydrogenation over the mixed catalyst. One might envision the interaction of methylene groups on the surface of the hydrocarbon catalyst with the surface hydroxymethylene groups of the alcohol catalyst, and perhaps, the formation of longer chain alcohols may be observed. New products would not be expected if the formation of hydrocarbons and alcohols were both occurring by either of the mechanisms outlined in Schemes 1 and 2.

It is necessary for this study to combine two different catalysts both of which function at the same temperature, pressure, H_2/CO ratio, etc., but yield different hydrogenation products. This presents some difficulties because the metal catalysts; Fe, Ru, Rh, and others typically used for the formation of hydrocarbons from CO, have also been found to yield alcohols under somewhat different conditions.[6]

However, there appear to be several potential catalyst mixtures for use in this study. Phosphomolybdate catalysts, $P_2Mo_{22}O_{39}$, hydrogenate CO to long chain paraffins while under the same conditions a zinc oxide/chromium oxide catalyst produces methanol.[6] Other possibilities include Ni and other metals as hydrocarbon catalysts, and oxides to catalyze alcohol production.

The desired mixed catalysts can be prepared by methods that have been used previously. Metal catalysts may be deposited on the support material by wetting the support with a solution of the metal salt, followed by heating under hydrogen to reduce the metal tothe elemental state.[7] Variable concentrations of the metal on the support can be attained by changing the initial concentration of the metal salt solution. Subsequently the alcohol catalyst may be combined with the supported metal catalyst by precipitation or mechanical mixing.[8]

A series of control experiments will be necessary for this study. The products of carbon monoxide hydrogenation must be determined for each component of the catalyst mixture separately. These measurements must be performed for each catalyst support and catalyst concentration used, and under the same reaction conditions as the final catalyst mixture. Only recently has the effect of the catalyst support been quantitatively investigated.[7,9] The support was found to have a significant effect on the activity of the catalyst. These results will be helpful in defining the optimum conditions for the experiment.

Previous studies have been made of the effect of salts of cobalt and iron on the formation of alcohols.[8] These studies were conducted not with the reduced metals, which catalyze hydrocarbon formation, but with metal complexes. In addition, the conditions used for the hydrogenation, low temperature and high pressure, favored alcohol formation, and no control experiments were performed.

The effect of combining two metals, both of which are catalytically active for the hydrogenation of CO to hydrocarbons, has been investigated for a variety of metals.[10-12] The activities and products formed by use of the mixed-metallic catalysts were in some cases substantially different than the individual metals under the same conditions. These changes in catalytic behavior have been attributed to alloying of the two metals, resulting in a new catalytic species. Specific interactions between the catalysts in the proposed study; such as formation of ternary oxides or new phases, is also a potential problem. Changes in the catalyst may be monitored by X-ray powder diffraction, X-ray photoelectron spectroscopy and other physical techniques.

In summary, a mixed carbon monoxide hydrogenation catalyst, composed of a material which catalyzes hydrocarbon formation and a catalyst which favors alcohol production, will be studied. From a detailed investigation of the products observed from CO hydrogenation over the mixed catalyst, information may be obtained concerning the possible interaction between organic fragments on the surface of each catalyst.

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