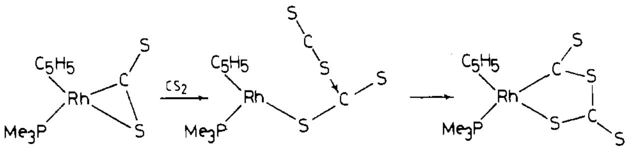
becomes understandable if the mechanism outlined above is considered: the nucleophilic attack at the carbon atom of the linear CS_2 bends the CS_2 fragment, because the electrons donated enter a $\pi_u{}^*$ orbital that is stabilized on bending. The coordination of X to the metal ensues.

The presence of intermediates of type **9** gains greater credibility if the reactions leading to head-to-tail coordination of C_2X_4 clusters,[27,28] **23**, are examined. Referring to the end-on/side-on interconversion mechanism, the formation of compound **11** from the complex $(C_5H_5)Rh(Me_3P)CS_2$ and excess CS_2 seems reasonable. The three steps are depicted in **30**.



30

The examples reported above are just a few from the rich and diverse chapter of the reactivity of complexed CS_2 and CO_2 molecules. It is clear that much deeper insight into the mechanism of each specific reaction is needed. Theoretical investigation is still scarce in this field.

Acknowledgment. C.M. and R.H. are grateful to NATO for awarding a research grant (No. 200.81) through which this collaborative project was made possible. R.H. acknowledges National Science Foundation support (Grant CHE 7828048). Thanks are due to Franco Cecconi for assistance in making drawings. C.M. thanks his CNR colleagues for continuous and helpful discussions.

Appendix

The extended Hückel calculations[6] utilized a modified version of the Wolfsberg–Helmholz formula;[32] see ref 23 for information relative to the atomic parameters used.

The PH_3 molecules had P–H bonds of 1.4 Å and H–P–H angles of 109.5°. In NH_3 molecules the N–H distances were fixed at 1.1 Å. In the $(PH_3)_3Ni$ fragment, the P–Ni–P angle was 90°. In the $(PH_3)_2Ni$ fragment the P–Ni–P angle was 107° unless otherwise specified in the text. All the Ni–P distances were kept fixed at 2.25 Å. In the model $(NH_3)_4CoCO_2{}^+$, the Ni–N distances were 2.0 Å.

Registry No. $(PH_3)_3NiCS_2$, 87761-75-9; $(PH_3)_2NiCS_2$, 87761-76-0; $(PH_3)_2NiCO_2$, 79953-45-0; CO_2, 124-38-9; CS_2, 75-15-0.

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(32) Ammeter, J. H.; Bürgi, H.-B.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 3686.

Contribution No. 6540 from the Division of Chemistry and Chemical Engineering,
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Ruthenium Complexes of 1,3-Bis(2-pyridylimino)isoindolines as Alcohol Oxidation Catalysts

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Received January 21, 1983

The ruthenium complex (1,3-bis(4-methyl-2-pyridylimino)isoindoline)trichlororuthenium(III) catalyzes the autoxidation and electrochemical oxidation 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 autoxidation is affected by the strength of the base used and its coordinating ability. The best results were obtained with sodium ethoxide as a base. Turnover numbers of 10–30 per day were observed in 1 atm 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. The catalyzed electrochemical oxidation was carried out in an alcoholic solution containing 2,6-lutidine with a carbon electrode at 0.8–1.0 V vs. NHE. In the absence of catalyst, negligible current was observed. 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 non-alcoholic solvents in the presence or absence of 2,6-lutidine. Possible pathways for the catalytic autoxidation and electrochemical oxidation are presented.

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 that 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**, $(4'\text{-MeLH})RuCl_3$. In addition the Ru(III) complex catalyzes the electrochemical oxidation of both primary and secondary alcohols. The catalytic oxidations were studied to define the scope and possible mechanism of these reactions.

Results and Discussion

Characterization of $(4'\text{-MeLH})RuCl_3$. The synthesis of $(4'\text{-MeLH})RuCl_3$ has been reported earlier.[9] The Ru(III)

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(1) House, H. O. "Modern Synthetic Reactions", 2nd ed.; W. A. Benjamin: Reading, MA, 1972.

(2) Tang, R.; Diamond, S. E.; Neary, N.; Mares, F. *J. Chem. Soc., Chem. Commun.* **1978**, 562.

(3) Dobson, A.; Robinson, S. D. *Inorg. Chem.* **1977**, *16*, 137.

(4) Murakata, M.; Nishibayashi, S.; Sakamoto, H. *J. Chem. Soc., Chem. Commun.* **1980**, 219.

(5) Blackburn, T. F.; Schwartz, J. *J. Chem. Soc., Chem. Commun.* **1977**, 157.

(6) Roundhill, D. M.; Dickson, M. K.; Dixit, N. S.; Sudha-Dixit, B. P. *J. Am. Chem. Soc.* **1980**, *102*, 5538.

(7) Bibby, C. E.; Grigg, R.; Price, R. *J. Chem. Soc., Dalton Trans.* **1977**, 872.

(8) Tovrog, B. S.; Diamond, S. E.; Mares, F.; Szalkiewicz, A. *J. Am. Chem. Soc.* **1981**, *103*, 3522.

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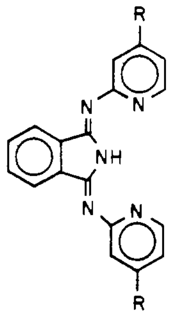


1
LH, R = H
4′-MeLH, R = CH_3
4′-*s*-BuLH, R = *sec*-butyl

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 associated with the pyrrole nitrogen or, more likely, whether it is bound to one of the imine nitrogens.

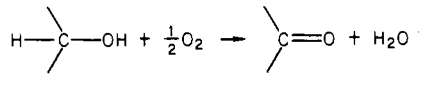
Infrared spectra of metal complexes with deprotonated ligand vs. nondeprotonated ligand show substantial differences in the region 1450–1650 cm^{-1} (Figures 1 and 2). The infrared spectrum of (4′-MeLH)$RuCl_3$ has two strong absorptions above 1600 cm^{-1}, characteristic of a coordinated nondeprotonated isoindoline ligand. Complexes that 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 considerably more soluble in organic solvents when base is added, and it is the basic alcoholic solutions that show the catalytic oxidation of alcohols by electrochemical means and in the presence of oxygen.

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 1 atm 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.

The only products identified in the oxidation of the secondary alcohols were ketones. Ketones showed no further oxidation and, indeed, could be used as inert solvents. Aldehydes, however, were susceptible to further oxidation and other reactions in basic solution of (4′-MeLH)$RuCl_3$. Except in methanol, the major products of the oxidation of 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.

The catalyzed reaction taking place is shown in eq 1, while



$$\mathrm{H{-}C{-}OH} + \tfrac{1}{2}O_2 \rightarrow \mathrm{C{=}O} + H_2O \qquad (1)$$

Table I lists the alcohols examined and the oxidation products observed. In the absence of catalyst no oxidation products were observed.

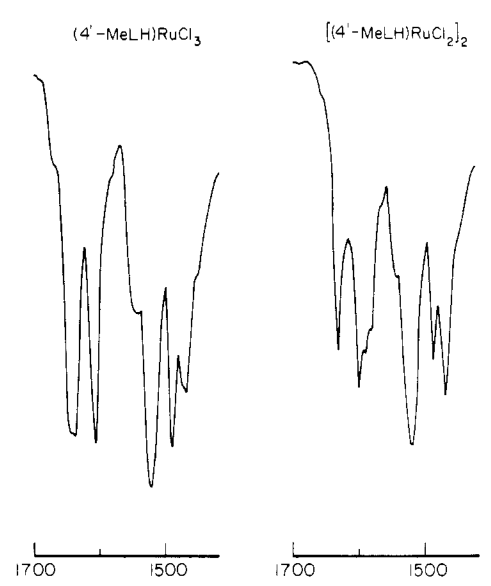


Figure 1. Infrared spectra (KBr) of ruthenium complexes containing nondeprotonated isoindoline ligands. The two strong absorptions in the range 1600–1650 cm^{-1} are characteristic of the presence of a chelated neutral isoindoline ligand.

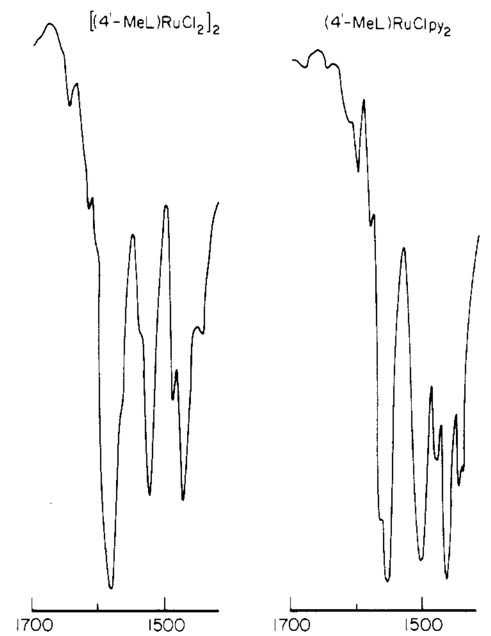


Figure 2. Infrared spectra (KBr) of ruthenium complexes containing deprotonated isoindoline ligands. Note the absence of strong bands in the range 1600–1650 cm^{-1}.

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-h period, usually in the range 20–60 (Table I). 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 1 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)$FeCl_2$ was examined in basic ethanol under 1 atm of oxygen. Hydrated ruthenium trichloride produced very small amounts of acetaldehyde.[11] Catalytic

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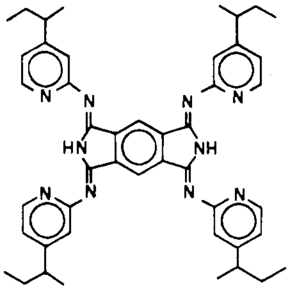
(9) Gagné, R. R.; Marks, D. N.; Siegl, W. O. *Inorg. Chem.* **1982**, *21*, 3140.
(10) Gagné, R. R.; Marritt, W. A.; Marks, D. N.; Siegl, W. O. *Inorg. Chem.* **1981**, *20*, 3260.

Table I. 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	h
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	h
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[f]
ethanol	$NaOC_2H_5$	O_2	70	100	h
1-propanol	$NaOC_2H_5$	O_2	25	30	propionaldehyde, 1,1-dipropoxypropane[g]
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] O_2 or air at 1 atm, 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] The presence of the strong base may result in disproportionation of the aldehyde. [g] Product distribution was 50% aldehyde and 50% acetal. [h] The products identified were the same as in the preceding entry.

activity was observed in basic alcoholic solutions of each of the following complexes: (LH)$RuCl_3$, (4'-s-BuLH)$RuCl_3$, and Cl_3RuHL–$LHRuCl_3$ (where HL–LH is the ligand **2**), with turnover numbers comparable to that of (4'-MeLH)$RuCl_3$.



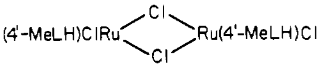
2 ≡ HL-LH

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)$RuCl_3$ as shown by the fact that pyridine slowed the catalytic oxidation considerably.

The use of a strong base, sodium ethoxide, enhanced the reaction (Table I). Under 1 atm of oxygen at ambient temperature approximately 10–30 turnovers were observed in 1 day in the case of 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. At higher temperatures, turnover numbers greater than 100/day were observed in ethanol. The catalyst, (4'-MeLH)$RuCl_3$, at the ambient temperature, showed little or no degradation after 6 days and more than 200 turnovers in ethanol containing several equivalents of sodium ethoxide.

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.

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 2 h in an inert atmosphere. During the reaction ethanol was oxidized stoichiometrically. No gas was evolved, eliminating the possibility that the oxidation product was formed from the dehydrogenation of the alcohol. 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 (Figure 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 μ_B. Analytical data were consistent with the empirical formula (4'-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.[12–14] Indeed, the Ru(II) dimer reacts readily with carbon monoxide, and a monomeric carbonyl complex was isolated (eq 2). The infrared spectrum of the carbonyl complex indicated that the bound isoindoline ligand is neutral. A monomeric neutral pyridine complex, (4'-MeL)$RuCl(py)_2$, was formed upon reaction of the Ru(II) dimer with pyridine, suggesting that pyridine is a strong enough base to deprotonate the ligand.



3

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

Oxygen uptake, at the ambient temperature, by the solid **3** or of acetone slurries of the solid **3** gave a stoichiometry of 0.25 O_2/Ru. This suggests a simple one-electron oxidation of each ruthenium. Stoichiometric reaction of a suspension of **3** in ethanol under 1 atm of oxygen at 25 °C gave the golden brown insoluble material **4**. The product could be isolated since the catalytic reaction is slow at 25 °C. Characterization

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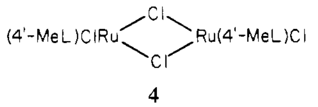
(11) Hydrated ruthenium trichloride has been reported to catalyze the autoxidation of secondary alcohols at 2–3 atm of oxygen.[2]

(12) Benedetti, E.; Braca, G.; Salvetti, F.; Grassi, B. *J. Organomet. Chem.* **1972**, *37*, 361.

(13) Nicholson, J. K. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 264.

(14) Ruiz-Ramirez, L.; Stephenson, T. A.; Switkes, E. S. *J. Chem. Soc., Dalton Trans.* **1973**, 1770.



$$\mathrm{(4'\text{-}MeL)ClRu}\overset{\mathrm{Cl}}{\underset{\mathrm{Cl}}{\diamond}}\mathrm{Ru(4'\text{-}MeL)Cl}$$

4

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 (Figure 2). Magnetic measurements yielded a value of 1.95 μ_B/ruthenium, consistent with a low-spin d^5 Ru(III) ion.[15] 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 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.[16]

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 also was made directly from the starting Ru(III) complex, (4′-MeLH)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**.

Ethanolic slurries of **4** formed the Ru(II) dimer **3** upon heating at reflux in ethanol for 20 h in the absence of oxygen. Taking the reaction to completion required an extended period of time, presumably due to the low solubility of [(4′-MeL)-RuCl$_2$]$_2$. Insoluble dimeric complexes were observed for the reaction of (LH)RuCl$_3$ in ethanol containing 2,6-lutidine. Reactions of (4′-*s*-BuLH)RuCl$_3$ in basic ethanol, however, gave no readily isolable products. It is not known whether the dimers do not form in this case or whether thay 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** 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.

Catalytic Electrochemical Oxidation of Alcohol. Both complexes, (4′-MeLH)RuCl$_3$ and (4′-*s*-BuLH)RuCl$_3$, exhibit electrocatalytic behavior in alcoholic solutions. The electrochemistry and products formed from the catalyzed electrochemical oxidation of alcohols are identical for the two complexes. Long-term electrochemical experiments, such as constant-potential electrolyses, were perfomed with use of (4′-*s*-BuLH)RuCl$_3$ preferentially to avoid precipitation of the Ru(III) dimeric complex **4**.

Electrochemistry in Ethanol. Cyclic voltammograms of basic ethanolic solutions of (4′-MeLH)RuCl$_3$ were obtained with 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 at 0.7–0.9 V vs. NHE. This current was much larger than the current that would be associated with oxidizing the complex alone. In the absence of catalyst the voltammograms showed negligible current to approximately 1.2 V (Figure 3). 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. It was also desirable to use a weak base to minimize deprotonation of the alcohol. Alkoxides exhibit different electrochemical behavior from alcohols.[17]

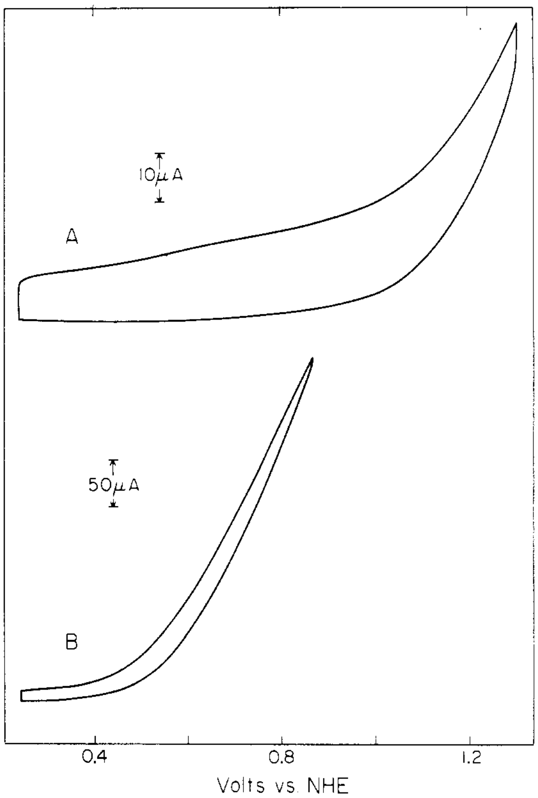


Figure 3. Cyclic voltammograms of an ethanol solution containing 2,6-lutidine before (A) and after (B) addition of (4′-MeLH)RuCl$_3$. Note the different current scales for each voltammogram.

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 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.[17]

The effect of chloride ion on the electrochemistry in ethanol was also investigaed because chloride is lost from the complex in basic ethanolic solution. 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 mmol solutions of (4′-*s*-BuLH)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

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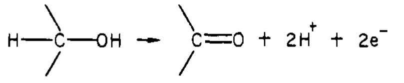
(15) The magnetic moment is consistent with little or no magnetic coupling between the two Ru(III) ions. A Ru(III) chloro-bridged dimer studied previously, with a magnetic moment of 1.93 μ_B/Ru, also shows no magnetic coupling.[13]

(16) Nakamoto, K. "Infrared Spectra of Inorganic and Coordination Compounds", 2nd ed.; Wiley-Interscience: New York, 1970.

(17) Sundholm, G. *J. Electroanal. Chem. Interfacial Electrochem.* **1971**, *31*, 265.

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*-BuLH)-$RuCl_3$ in ethanol containing 0.5 mL of 2,6-lutidine was electrolyzed at 0.75 V vs. NHE with an initial current of 2.0 mA. After 20 h of electrolysis 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 it was initially. Addition of base causes a shift of the catalytic wave to lower potentials again (a shift from approximately 1.0 to 0.8 V vs. NHE). Protons produced in the electrochemical reaction (eq 3) may protonate



$$\mathrm{H{-}C(-)(-){-}OH} \rightarrow \mathrm{{>}C{=}O} + 2H^+ + 2e^- \qquad (3)$$

the active ruthenium–isoindoline complex and thus increase the electrochemical potential for oxidation. More than 20 two-electron oxidations were completed with the curent 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.

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.[18] 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 butylaldehyde, 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 methanol oxidation products by evaporation or by production of a nonvolatile component.[19]

The catalyzed electrochemical oxidation in neat ethanol favors the production of acetaldehyde.[20] In order to study the specificity of the catalyst for production of acetaldehyde, the electrochemistry of (4′-MeLH)$RuCl_3$ was examined in a non-alcoholic solvent containing ethanol. In acetone or acetonitrile containing 2,6-lutidine, approximately 10% ethanol, and (4′-MeLH)$RuCl_3$, an irreversible anodic current was observed, but at potentials 0.3–0.4 V more positive than those that had been observed in neat ethanol. Because of the dissimilar electrochemical behavior found, the electrochemical oxidations of alcohols in non-alcoholic solvents were not studied further.

Electrochemistry in Non-Alcohols. The cyclic voltammogram of (4′-MeLH)$RuCl_3$ in dichloromethane (Figure 4) shows a quasi-reversible oxidation wave and is nearly identical with that of (4′-*s*-BuLH)$RuCl_3$. The anodic and cathodic peak currents for these oxidation waves are equal, but the peak potential separation is slightly larger (60–80 mV depending on the solvent) than the 58 mV expected for a reversible one-electron process.[21] The results of electrochemistry in various solvents are presented in Table II.

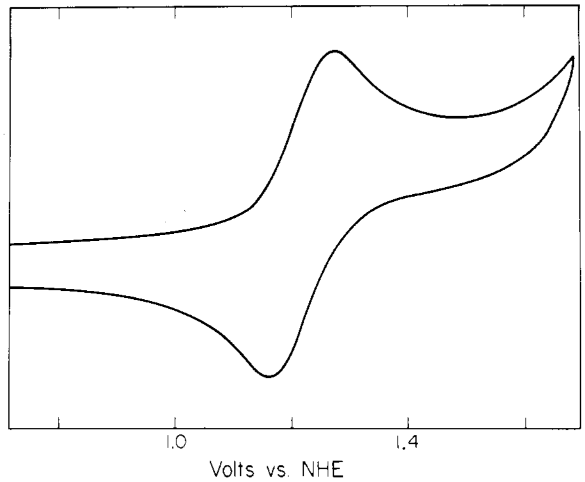


Figure 4. Cyclic voltammogram of (4′-MeLH)$RuCl_3$ in dichloromethane.

Table II. Electrochemical Potentials for (4′-MeLH)$RuCl_3$ As Measured in Various Solvents (vs. NHE)

	E_f, V	
solvent	(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

Coulometry was unable to determine the number of electrons involved in the oxidation since the product of the oxidation was not stable as evidenced by the cyclic voltammograms after electrolysis. The instability of the oxidized product was observed in all solvents used: *N,N*-dimethylformamide, acetonitrile, acetone, and dichloromethane. However, addition of an equimolar amount of tris(acetylacetonato)ruthenium(III), $Ru(acac)_3$(a one-electron standard),[22] to the solution of (4′-MeLH)$RuCl_3$ resulted in two oxidation waves with equal currents. 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*-BuLH)$RuCl_3$ in acetonitrile or dichloromethane gave no immediate precipitation of AgCl, another indication that the chlorides are bound to ruthenium in solution.

Cyclic voltammograms were obtained 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 II). For example,

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(18) The less than quantitative determination of acetone may be due to loss of acetone by diffusion and evaporation.

(19) Polymeric material has been observed in the electrochemical oxidation of alcohols: Sundholm, F.; Sundholm, G.; Suontama, K. *Suom. Kemistil. B* **1972**, *45*, 383.

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(22) Patterson, G. S.; Holm, R. H. *Inorg. Chem.* **1972**, *11*, 2285.

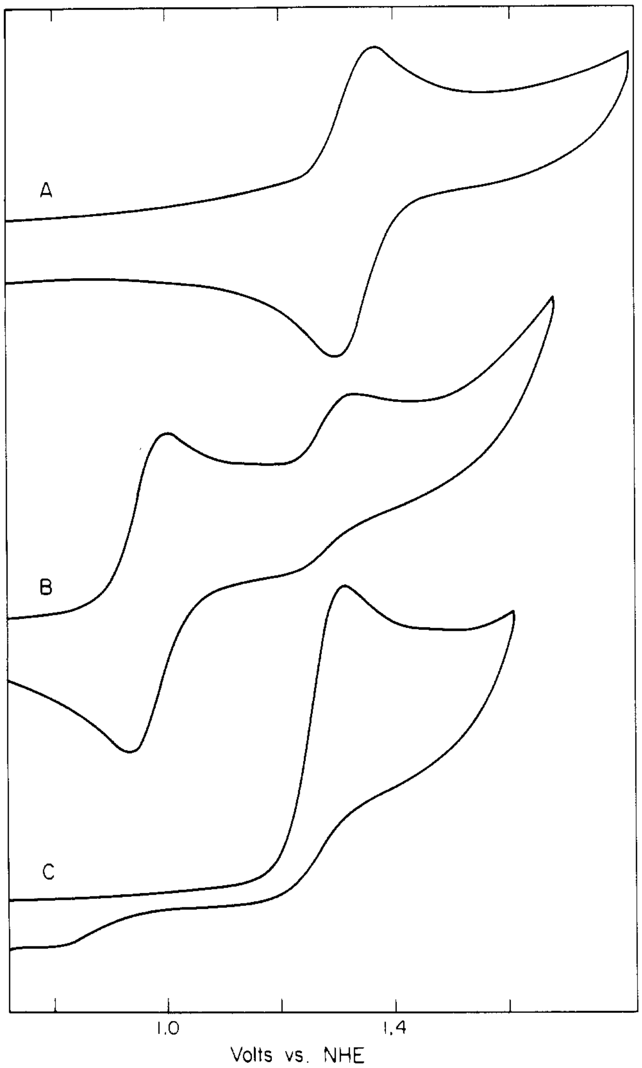


Figure 5. Cyclic voltammograms of acetonitrile solutions: (A) (4′-*s*-BuLH)RuCl$_3$; (B) (4′-*s*-BuLH)RuCl$_3$ + 2,6-lutidine after several minutes of stirring; (C) (4′-*s*-BuLH)RuCl$_3$ + 2,6-lutidine + 1 equiv of Ag$^+$.

the oxidation of (4′-*s*-BuLH)RuCl$_3$ in acetone occurs at 1.17 V vs. NHE (eq 4), but upon addition of base the wave shifts

$$\begin{gathered}(4'\text{-}s\text{-BuLH})\text{RuCl}_3{}^+ + e^- \rightarrow (4'\text{-}s\text{-BuLH})\text{RuCl}_3 \\ E_f = 1.17\ \text{V}\end{gathered} \tag{4}$$

to 0.88 V. The new wave is ascribed to the oxidation of the anionic trichloro complex formed by deprotonation of the isoindoline ligand (eq 5). The oxidation waves observed in

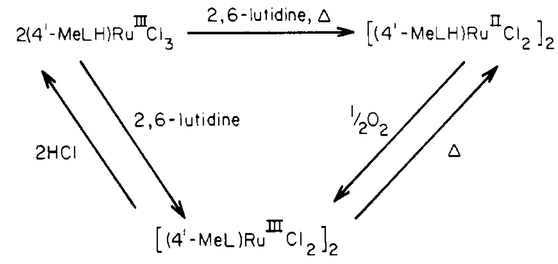
$$\begin{gathered}(4'\text{-}s\text{-BuL})\text{RuCl}_3 + e^- \rightarrow (4'\text{-}s\text{-BuL})\text{RuCl}_3{}^- \\ E_f = 0.88\ \text{V}\end{gathered} \tag{5}$$

N,*N*-dimethylacetamide and *N*,*N*-dimethylformamide show very little shift in potential upon addition of base (Table II). 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 1 h. However, 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. This electrochemical behavior is consistent with the loss of chloride ion from the anionic complex, resulting in a neutral species.

Similar electrochemical behavior is observed in acetonitrile but chloride ion may be displaced much more readily. The Ru(III)/Ru(IV) oxidation of (4′-*s*-BuLH)RuCl$_3$ in acetonitrile occurs 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 (Figure 5). 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$_3$CN), in which acetonitrile has displaced a chloride ion. Addition of 1 equiv 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 5).

Scheme I[a]



[a] Ethanol is the solvent

Discussion of Possible Mechanisms

Catalyzed Autoxidation. 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 is 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 coproduct of the oxidation of alcohols. No hydrogen gas is produced. The species and reactions observed in ethanol are presented in Scheme I.

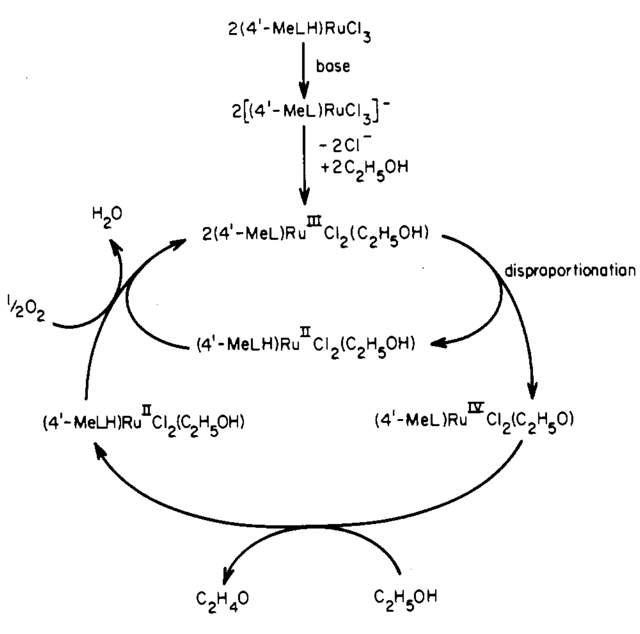
The presence of the dimer **3**, formed in the oxidation of ethanol, may give some indication of the reactive species. The oxidation states of ruthenium in the dimeric complexes suggest a one-electron change per metal, Ru(II/III), while the oxidation of ethanol to acetaldehyde is formally a two-electron 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 termination steps in the catalytic process because of their low solubility.

One can write a possible pathway involving as intermediates the dimeric complexes isolated. This pathway, while 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 II (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.

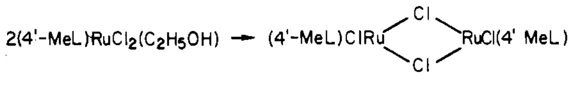
The dissolution of (4′-MeLH)RuCl$_3$ in basic ethanol involves initially the deprotonation of the isoindoline ligand. These complexes were observed electrochemically in nonalcoholic solvents. Cyclic voltammograms of solutions of (4′-MeLH)-RuCl$_3$ in acetonitrile also indicate that chloride ion may be displaced readily by a solvent molecule. One would expect behavior in ethanol similar to that observed in acetonitrile, with ethanol also a reasonable ligand for Ru(III). The negative

Scheme II



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, $(4'\text{-MeL})RuCl_2(C_2H_2OH)$, may be the precursor to the insoluble Ru(III) dimer **4**, formed in ethanol with 2,6-lutidine at ambient temperature (eq 6).



$$2(4'\text{-MeL})RuCl_2(C_2H_5OH) \rightarrow (4'\text{-MeL})ClRu\begin{matrix}Cl\\ \\ Cl\end{matrix}RuCl(4'\ MeL) \quad (6)$$

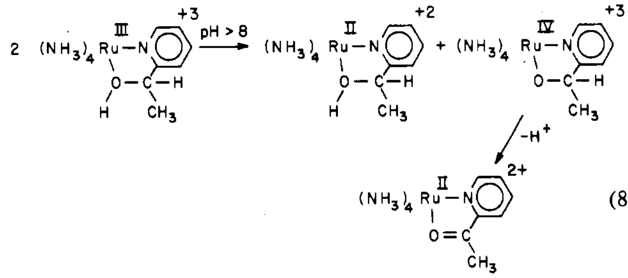
4

The first step in the proposed catalytic cycle (Scheme II), the disproportionation of $(4'\text{-MeL})RuCl_2(C_2H_5OH)$, 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.[23,24] Rudd and Taube have ascribed the base dependence to proton removal from NH_3 coordinated to Ru(IV)[23] (eq 7). The coupling of a Ru^{III} disproportionation

$$2(NH_3)_5Ru^{III}py^{3+} \rightleftharpoons (NH_3)_5Ru^{II}py^{2+} + (NH_3)_4(NH_2)Ru^{IV}py^{3+} + H^+ \quad (7)$$

with the subsequent oxidation of bound alcohol by Ru^{IV} has been observed stoichiometrically by Tovrog et al.[24] The pathway proposed for the reaction is shown in eq 8. This reaction was also found to be favored in basic solution.

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 $(4'\text{-MeL})RuCl_2(C_2H_5OH)$ 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.



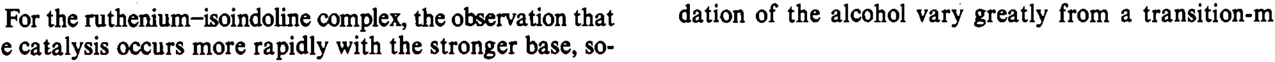
(8)

In the proposed catalytic cycle, (Scheme II), 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

$$(4'\text{-MeL})Cl_2Ru^{IV}OCH_2CH_3 \rightarrow (4'\text{-MeL})Cl_2Ru^{IV}H + CH_3CHO \xrightarrow{C_2H_5OH} [(4'\text{-MeL})Cl_2Ru^{II}(C_2H_5OH)]^- + H^+ \rightarrow (4'\text{-MeLH})Cl_2Ru^{II}(C_2H_5OH) \quad (9)$$

metal alkoxides or metal amides to give metal hydrides and oxidized ligand has been well documented.[3,25,26] Hydride transfer 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).

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 II). The reaction of the dimer $[(4'\text{-MeLH})RuCl_2]_2$ (**3**) 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 $(4'\text{-MeLH})RuCl_3$ in ethanol containing hydrogen peroxide and 2,6-lutidine showed formation of acetaldehyde when stirred at ambient temperature under nitrogen. The Ru(II) dimeric complex **3** that forms from the reaction with ethanol under an inert atmosphere may result from dimerization of the proposed Ru(II) intermediate (eq 10).



$$2(4'\text{-MeLH})RuCl_2(C_2H_5OH) \rightleftharpoons (4'\text{-MeLH})ClRu\begin{matrix}Cl\\ \\ Cl\end{matrix}RuCl(4'\text{-MeLH}) \quad (10)$$

Catalyzed Electrochemical Oxidation. The mediated electrochemical oxidation of alcohols is significant in that the oxidation takes place at much lower potentials than the direct oxidation of alcohols at a carbon electrode[27] 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.[28-33] The electroactive species that control the oxidation of the alcohol vary greatly from a transition-metal

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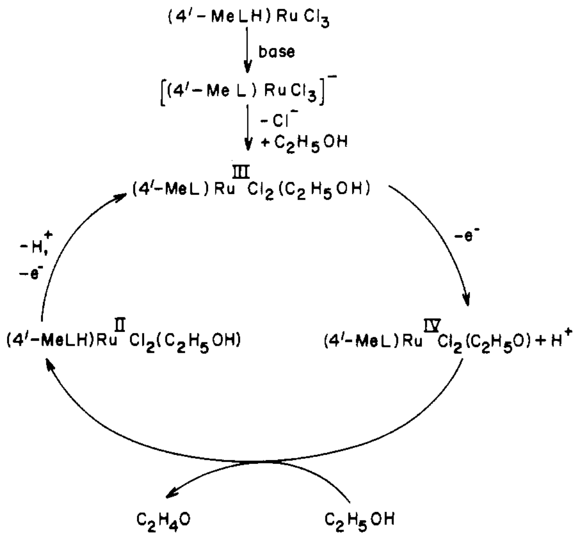
Scheme III



complex to organic molecules. Most of these reported catalytic systems suffer from one or more of the following problems: the catalyst oxidizes only secondary alcohols; few catalytic cycles (5–10) are completed before the catalyst degrades; there is poor specificity for production of aldehydes in the oxidation of primary alcohols; the oxidation occurs at relatively high potentials (>1 V vs. SCE).

The most efficient of these catalytic systems is the Ru(IV) oxo complex $(trpy)(bpy)RuO^{2+}$ (trpy is 2,2′,2″-terpyridine and bpy is 2,2′-bipyridine), which oxidized primary and secondary alcohols.[28] The catalyst is long lived and functions electrochemically in the range 0.6–0.8 V vs. SCE. The product of the reaction of the oxo complex with alcohol is the Ru(II) aquo complex $(trpy)(bpy)Ru(OH_2)^{2+}$.

The ruthenium–isoindoline catalytic system has similar characteristics and apparently also involves Ru(IV) as the active species. Indirect evidence for this comes from the reversible oxidation waves observed in non-alcoholic solvents. Unfortunately, a Ru(IV) complex could not be isolated by electrolysis of the Ru(III) species.

This is the first example of a molecule that 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 a possible reaction pathway for the electrochemical oxidation, as illustrated in Scheme III.

As described above, the dissolution of $(4'\text{-MeLH})RuCl_3$ 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 chemistry of $(4'\text{-MeLH})RuCl_3$ 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, it is difficult to ascertain the identity of the electroactive complex.

Loss of chloride ion from $(4'\text{-MeL})RuCl_3^-$ probably results in solvent coordination. Moreover, electrochemical oxidation of the resulting species during catalytic oxidation is dependent on the acid concentration. These observations suggest that electrochemical oxidation may be accompanied by deprotonation of coordinated alcohol (eq 11). The electrochemical

$$(4'\text{-MeL})RuCl_2(C_2H_5OH) \rightarrow (4'\text{-MeL})RuCl_2(C_2H_5O) + H^+ + e^- \quad (11)$$

potential for the oxidation in eq 11 will be dependent on the concentration of acid in the ethanolic solution, shifting positive as the acid concentration increases. This behavior is found for the catalyzed electrochemical oxidation; however, it cannot be quantified because the oxidation is irreversible.

Similar behavior has been observed involving deprotonation of hydroxide ligand upon oxidation of Ru(III) to Ru(IV)[34] (eq 12). The oxidation was reversible, with the pH dependence

$$(bpy)_2pyRu(OH)^{2+} \rightarrow (bpy)_2pyRuO^{2+} + H^+ + e^- \quad (12)$$

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

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. Indeed, the formation of ruthenium alkoxides has been invoked as an intermediate step in several studies of catalytic oxidations of alcohols.[2,3,26]

The proposed product of the oxidation at the electrode, $(4'\text{-MeL})RuCl_2(OC_2H_5)$, is also the complex that was proposed as the active oxidant in the autoxidation of alcohols. From oxidation of the coordinated alkoxide, a Ru(II) complex forms that 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 mechanisms proposed are consistent with all of the observations of the catalytic reaction. 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.

Experimental Section

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*-BuLH, LH, and HL–LH, has been described previously.[10]

Catalytic Oxidation of Ethanol. To a slurry of 45 mg (0.08 mmol) of $(4'\text{-MeLH})RuCl_3\cdot C_2H_5OH$ in 30 mL of ethanol was added 0.5 mL of 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 $(4'\text{-MeLH})CoBr_2$, $(4'\text{-MeL})FeCl_2$, $Cl_3RuHL\text{–}LHRuCl_3$ + 2,6-lutidine, $(LH)RuCl_3$ + 2,6-lutidine, $(4'\text{-}s\text{-BuLH})RuCl_3$ + 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 also was carried out 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 $(4'\text{-MeLH})RuCl_3$ 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) of $(4'\text{-MeLH})RuCl_3\cdot C_2H_5OH$ and 0.5 mL of 2,6-lutidine in 30 mL of ethanol. This solution was stirred overnight at 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

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(34) Moyer, B. A.; Meyer, T. J. *Inorg. Chem.* **1981**, *20*, 436.

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) of (4′-MeLH)RuCl$_3$·C$_2$H$_5$OH and 12 mg (0.17 mmol) of sodium ethoxide in 30 mL of ethanol was stirred under oxygen at 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$_2$]$_2$ ((3–4) × 10^{-5} mol) 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 ambient temperature for 6 days, during which time the solid in the flask turned red-brown. The gas over the sample was transferred with use of 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) of hydrated ruthenium trichloride dissolved in 150 mL of ethanol was heated at reflux with nitrogen bubbling through the solution. After 1 h, 0.5 g (1.5 mmol) of 4′-MeLH was added. The solution continued to be heated with nitrogen passing through it for an additional 1$^1/_2$ h. 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*-BuLH)RuCl$_3$ and (LH)RuCl$_3$ were prepared from hydrated ruthenium trichloride and either 4′-*s*-BuLH or LH. Each product was collected in 45% yield. Anal. Calcd for C$_{20}$H$_{17}$N$_5$RuCl$_3$·C$_2$H$_5$OH: C, 45.49; H, 3.99; N, 12.06. Found: C, 45.3; H, 4.05; N, 12.0. Calcd for C$_{26}$H$_{29}$N$_5$RuCl$_3$: C, 50.45; H, 4.72; N, 11.31. Found: C, 50.15; H, 4.7; N, 11.3. Calcd for C$_{18}$H$_{13}$N$_5$RuCl$_3$: 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) of hydrated ruthenium trichloride in 50 mL of ethanol was heated at reflux with nitrogen passing through the solution. After 1 h, 0.22 g (0.3 mmol) of HL–LH was added with an additional 10 mL of ethanol. The solution continued to be refluxed with nitrogen passing through it for 1$^1/_2$ h. After the mixture cooled, 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$_2$Cl$_6$: 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). Under a helium atmosphere 80 mg (0.14 mmol) of (4′-MeLH)RuCl$_3$·C$_2$H$_5$OH was slurried in 40 mL of ethanol and 1 mL of 2,6-lutidine. After 15 min of stirring at the ambient temperature the undissolved solid was filtered off. The red-brown filtrate was heated at reflux for 2 h, during which time the solution became green with green solid forming. After cooling, the solid was collected, washed with ethanol, and dried in vacuo. The solid was stored under helium. The yield of the product based on the amount of (4′-MeLH)RuCl$_3$·C$_2$H$_5$OH dissolved was 60% (30 mg). Anal. Calcd for C$_{40}$H$_{34}$N$_{10}$Ru$_2$Cl$_4$: 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*-BuLH)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) of (4′-MeLH)RuCl$_3$·C$_2$H$_5$OH and 0.5 mL of 2,6-lutidine in 15 mL of 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 with use of 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) of [(4′-MeLH)RuCl$_2$]$_2$ in 20 mL of ethanol was stirred for 3 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$_5$RuCl$_2$O: 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 of [(4′-MeLH)RuCl$_2$]$_2$ was added to 5 mL of pyridine. With stirring, the green solid gradually dissolved over a period of 4 days, producing a dark green solution. The solution was concentrated by slow evaporation, and a 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$_7$RuCl: 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 of [(4′-MeLH)RuCl$_2$]$_2$ (3) in 20 mL of ethanol was stirred in air for 3 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$_2$Cl$_4$·C$_2$H$_5$OH·2H$_2$O: 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$_2$Cl$_4$·C$_2$H$_5$OH·2H$_2$O: 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. Under a helium atmosphere 70 mg (0.12 mmol) of (4′-MeLH)RuCl$_3$·C$_2$H$_5$OH was slurried in 40 mL of ethanol and 1 mL of 2,6-lutidine. After 15 min of stirring at ambient temperature, the undissolved solid was filtered off. The filtrate was stirred for 2 h, 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$_2$Cl$_4$·3C$_2$H$_5$OH: C, 48.68; H, 4.44; N, 12.34. Found: C, 48.45; H, 4.5; N, 12.35.

Reaction of (4′-*s*-BuLH)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) of [(4′-MeL)RuCl$_2$]$_2$ in 15 mL of ethanol. The mixture was stirred at ambient temperature for 1 h. The insoluble brown solid present initially dissolved upon addition of the aqueous HCl. After 1 h of stirring, 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 with the spectrum of (4′-MeLH)RuCl$_3$·C$_2$H$_5$OH. Anal. Calcd for C$_{20}$H$_{17}$N$_5$RuCl$_3$·C$_2$H$_5$OH: C, 45.49; H, 3.99; N, 12.06. Found: C, 45.3; H, 4.1; N, 11.95.

Reaction of [(4′-MeL)RuCl$_2$]$_2$·3C$_2$H$_5$OH (4) with Ethanol and Heat. A slurry of 40 mg (0.035 mmol) of [(4′-MeL)RuCl$_2$]$_2$·3C$_2$H$_5$OH in 20 mL of ethanol was heated at reflux for 20 h under 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′-MeLH)RuCl$_2$]$_2$. Anal. Calcd for C$_{40}$H$_{34}$N$_{10}$Ru$_2$Cl$_4$: C, 48.11; H, 3.43; N, 14.02. Found: C, 47.9; H, 3.6; N, 13.9.

Preparation of (4′-MeLH)CoBr$_2$. Under an inert atmosphere a solution of 1.0 g (3.1 mmol) of 4′-MeLH in 70 mL of hot methanol was added to a solution containing 1.3 g (4.5 mmol) of CoBr$_2$·4H$_2$O in 15 mL of methanol. The solution was heated at relux for 15 min, during which time solid had formed. The reaction mixture continued to be stirred for 3 h. The brown solid was collected and dried in vacuo. The yield of the product was 60%. Anal. Calcd for C$_{20}$H$_{17}$N$_5$CoBr$_2$: C, 43.99; H, 3.14; N, 12.82. Found: C, 43.9; H, 3.2; N, 12.9.

Preparation of (4′-MeL)FeCl$_2$. A solution of 0.5 g (1.5 mmol) of 4′-MeLH in 35 mL of hot methanol was added slowly to a solution containing 0.5 g (1.85 mmol) of FeCl$_3$·6H$_2$O. The solution was heated at reflux for 15 min and then cooled. Dark microcrystalline solid was collected in 43% yield and dried in vacuo. Anal. Calcd for C$_{20}$H$_{16}$N$_5$FeCl$_2$: C, 53.01; H, 3.56; N, 15.46. Found: C, 53.3; H, 3.8; N, 15.5.

Physical Measurements. Infrared spectra were obtained on all compounds with 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 with a Perkin-Elmer Model 180 spectrophotometer. Magnetic measurements were made on samples at room temperature with a Cahn Instruments Faraday balance, with Hg-Co(SCN)$_4$ as a calibrant. Diamagnetic corrections were made with use of Pascal's constants. Elemental analyses were performed by the California Institute of Technology's analytical facility and by Galbraith Laboratories, Knoxville, TN.

Electrochemistry. Tetrabutylammonium perchlorate, TBAP, and tetrabutylammonium tetrafluoroborate, 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, isopropyl alcohol, 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 under a helium atmosphere with identical results.

Constant-Potential Electrolysis. Constant-potential electrolyses in alcoholic and non-alcoholic 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 non-alcoholic solvents.

Solutions containing 23 mg (0.037 mmol) of (4′-*s*-BuLH)RuCl$_3$ and 0.25–0.5 mL of 2,6-lutidine in 20–25 mL of alcohol were electrolyzed at 0.8–1.0 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 it 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 with use of a known amount of *n*-hexane as an internal standard.

Solutions of (4′-*s*-BuLH)RuCl$_3$ or (4′-MeLH)RuCl$_3$·C$_2$H$_5$OH in non-alcoholic 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/mol 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$_3$·C$_2$H$_5$OH or (4′-*s*-BuLH)RuCl$_3$ in the solvent of interest. One drop of 2,6-lutidine was added when the effect of the base was measured. To remove chloride from the complex, a solution containing 1 equiv of AgNO$_3$ in acetonitrile was added. The electrochemical behavior of chloride ion in various solvents was studied by adding tetraethylammonium chloride 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/ferrocenium couple.[35]

Formal reduction potentials, E_f, were measured by cyclic voltammmetry 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.

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*-BuLH)RuCl$_3$. Equimolar amounts of the standard and (4′-*s*-BuLH)RuCl$_3$ were added to the electrochemical solution, and cyclic voltammograms were obtained.

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Registry No. **1** (R = H), 14526-01-3; **1** (R = CH$_3$), 61702-01-0; **1** (R = *sec*-butyl), 61702-07-6; **3**, 87884-75-1; **4**, 87884-74-0; NaOC$_2$H$_5$, 141-52-6; Ag$^+$, 14701-21-4; RuCl$_3$, 10049-08-8; CO, 630-08-0; (4′-MeLH)RuCl$_3$, 82044-85-7; Cl$_3$RuHL-LHRuCl$_3$, 87884-73-9; (4′-*s*-BuLH)RuCl$_3$, 87901-51-7; (4′-MeLH)CoBr$_2$, 87884-76-2; (4′-MeL)FeCl$_2$, 87884-77-3; (LH)RuCl$_3$, 87884-78-4; (4′-MeLH)-RuCl$_2$CO, 87884-81-9; (4′-MeL)RuCl(py)$_2$, 87884-79-5; [(L)RuCl$_2$]$_2$, 87884-80-8; methanol, 67-56-1; ethanol, 64-17-5; 1-butanol, 71-36-3; 2-butanol, 78-92-2; cyclohexanol, 108-93-0; 1-propanol, 71-23-8; 2-propanol, 67-63-0; 2,6-lutidine, 108-48-5; pyridine, 110-86-1; methyl formate, 107-31-3; acetaldehyde, 75-07-0; 1,1-diethoxyethane, 105-57-7; ethyl acetate, 141-78-6; butyraldehyde, 123-72-8; 1,1-dibutoxybutane, 5921-80-2; 2-butanone, 78-93-3; cyclohexanone, 108-94-1; propionaldehyde, 123-38-6; 1,1-dipropoxypropane, 4744-11-0; butyraldehyde, 123-72-8; acetone, 67-64-1.

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[35] Gagné, R. R.; Koval, C. A.; Lisensky, G. C. *Inorg. Chem.* **1980**, *19*, 2854.