

INVESTIGATION OF LOW-VALENT RUTHENIUM AQUO COMPLEXES

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Thanks go to the Bercaw group for help and solace when I was confronted with Ruthenium Road Tar.

Thanks, Stew, for being my best friend.

Abstract

The work presented in this thesis investigates the synthesis of low oxidation state coordination complexes of ruthenium incorporating the anionic ligand, $[\text{CpCo}(\text{P}(\text{O})(\text{OMe})_2)_3]^-$, (LOMe). Several routes to $\text{RuLOMe}(\text{H}_2\text{O})_3^+$ are outlined. These routes produced two major products, possibly related by acid-base chemistry.

A new dimeric ruthenium aquo species with the proposed structure $[\text{Ru}(\text{III})\text{LOMe}(\text{H}_2\text{O})(\mu\text{-OH})]_2\text{OTs}_2$ was isolated. This complex does not provide a straightforward route to the target monomeric oxo compounds, but could conceivably provide a entry into synthesis of ruthenium dimers containing amines and other ligands.

Finally, a new route to $[\text{Ru}(\text{IV})(\text{H}_2\text{O})(\mu\text{-O})]_2\text{OTf}_2$ was discovered which is more convenient and is higher yielding than the previously published procedure.

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Introduction

Oxidation of organic compounds by metal oxo compounds is one of the most fundamental processes in organic chemistry, and has been known for over two hundred years! In this light perhaps it is surprising that this topic is still fertile ground for research. However, there is still a need for more active and selective oxidants. A great deal of research in the past decade has been focused on achieving the selective functionalization of unactivated carbon-hydrogen bonds. As well as being of general chemical interest, the oxidation of alkanes would have obvious practical significance. Of particular interest is the oxidation of methane, which is abundant but unwieldy, to methanol, for fuel.

Previous research in this area by the Bercaw group centered on oxo complexes of early transition metals such as Ta and W. However, these metals proved too oxophilic to serve as oxidation catalysts. For this reason, investigations of oxo complexes of the later transition metals, which form weaker metal oxygen bonds, were undertaken. Ruthenium, in particular was chosen, because its high oxidation states are easily accessible. These high oxidation states (Ru(VI- VII)) help stabilize terminal oxo groups, while imparting considerable oxidation potential to the complex. A premiere example is RuO_4 , an extremely active oxidant that can cleave carbon-carbon double bonds and will even oxidize alkanes.¹ Unfortunately, it is also unstable, photosensitive, volatile, and prone to reaction with common solvents. It has been found that by addition of suitable ancillary ligand, the ruthenyl group, RuO_2 , can be stabilized while retaining much of its formidable oxidation potential. The most important examples in the literature have been compounds of the type $\text{Ru(VI)L}_4\text{O}_2$, which are generally active oxidants.

These d^2 Ru(VI) or Os(VI) dioxo species preferentially exhibit a trans disposition of terminal oxo groups. For example, $[\text{RuO}_2\text{Cl}_4]^{2-}$, $[\text{RuO}_2\text{py}_4]^{2+}$, and $\text{RuO}_2(\text{py})_2(\text{OAc})_2$ exist only in the trans configuration.^{2a-c} Only one complex, $\text{OsO}_2(\text{bpy})_2$ has been synthesized in both the *cis* and the *trans* forms;³ the *cis* form was found to be unstable and isomerized to the trans form in refluxing acetonitrile. Various molecular orbital arguments

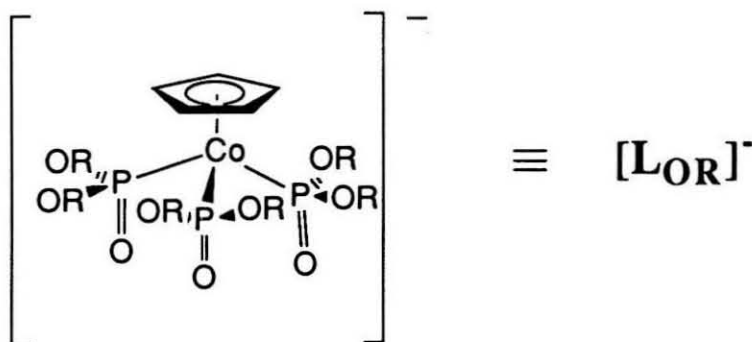
have been advanced to explain the tendency of Ru(VI) to adopt the trans configuration. In simple terms, in the trans case the highest occupied molecular orbital is non-bonding with respect to the oxygen pi orbitals, whereas in the *cis* case, all the d orbitals are slightly destabilized by the oxo groups. Since the *cis* oxo derivatives are expected in general to be thermodynamically less stable than the corresponding trans derivatives, it is believed that the *cis* dioxo species will be more reactive. For this reason, we decided to synthesize a *cis* dioxo species, with the goal of finding a well defined and stable system which could be studied easily.

Some stable Ru(VI) *cis* dioxo complexes have been reported in the literature. In general these fall into two classes. The first contains two molecules of the type *cis*-RuO₂L₂ where L= 6, 6' dichloro-2,2' bipyridine or 6, 6' dimethyl-2,2' bipyridine. The complexes are kinetically trapped in the *cis* form, since the bulky substituents at the ortho positions of the bipyridine present a high barrier to isomerization to the trans compound.⁴ The dichloro-substituted complex is reported to be a very active oxidant of alkenes and even alkanes; no data is available about its selectivity of reaction with alcohols.

The other type of *cis* oxo complex that has been documented is one in which the oxo groups are trans to another oxygen-containing ligand. One example is RuCl₂(η²-CH₃CO₂)(O)₂,⁵ which is reported to be an efficient two electron oxidant of alcohols, alkyl halides, and phosphines.

The work reported herein uses a different approach. It is proposed that the *cis* conformation of the oxo groups in a Ru(VI) compound be enforced by using a facially coordinating tridentate ancillary ligand. Cyclopentadienyl (Cp) and related compounds have been used extensively in such a manner with early transition metals, but the Cp* ligand has been shown to be susceptible to oxidation.⁶ Thus, for use with ruthenium, our attention turned to the formally analogous [CpCo(P(OR)₂O)₃]⁻, [L_{OR}]⁻ (OR=OCH₃, OCH₂CH₃), shown in Figure 1.

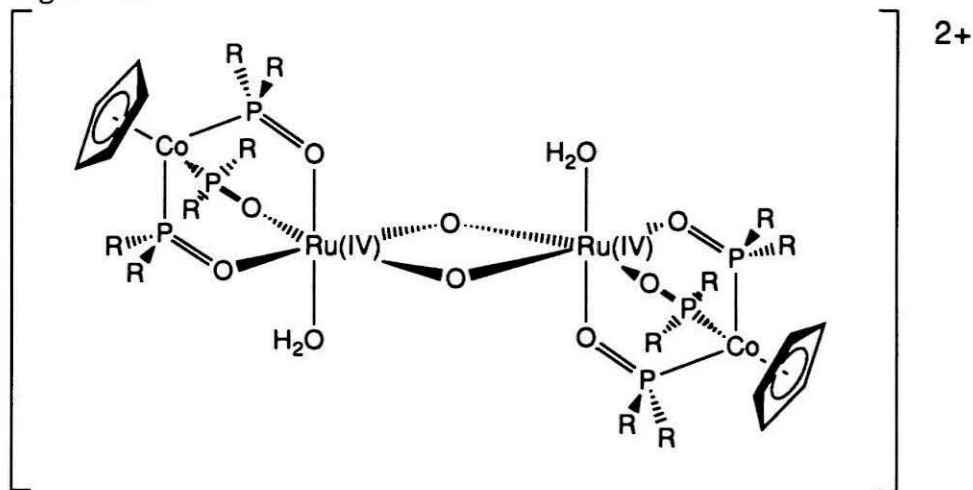
Figure 1.



This ligand has been shown to be stable at least to one electron oxidation, since it can form a stable complex with Ce(IV).⁷ In addition, its electronic properties are quite favorable. It is a hard oxygen-donor ligand, electronically comparable to F⁻ or OH⁻,⁸ which should help to stabilize high oxidation state complexes. Finally, the solubility of the ligand can be altered greatly by choice of OR substituent. The work described herein uses the LOMe ligand exclusively, because it is water soluble. It was hoped that this property would transfer to complexes incorporating the ligand, which would facilitate their electrochemical analysis.

In designing a synthetic route to terminal oxo complexes of ruthenium containing the LOMe ligand, one encounters a major problem-- the tendency of oxo and hydroxo complexes of ruthenium to form dimers, oligomers and polymers. High oxidation states [Ru(VI-VIII)] stabilize hydroxo and oxo groups by providing strong pi bonding. However, pi bonding in lower oxidation states [Ru (II-V)] results in population of antibonding molecular orbitals. For this reason the low oxidation state complexes have weak metal - oxygen pi bonding, and the oxygen atoms have more basic character, which leads to the formation of oxo- or hydroxo-bridged polymeric species. The tendency of lower oxidation state ruthenium to dimerize is demonstrated by early attempts in our group to synthesize oxo complexes from a mixture of RuO₄ and NaLOR in acid solution.⁹ Under these conditions, RuO₄ is believed to be reduced to Ru(IV).¹⁰ This reaction yielded [Ru(IV)LOR(μ-O)(OH)]₂ (Figure 2) as the major Ru containing species.

Figure 2.



This dimer has shown promise as a two electron oxidant of alcohols, and its reactions are a current topic of research in the Bercaw group. It has an extremely stable $\text{Ru}(\mu\text{-O})_2\text{Ru}$ core, and up to this time no method has been found to convert it to a monomeric species.

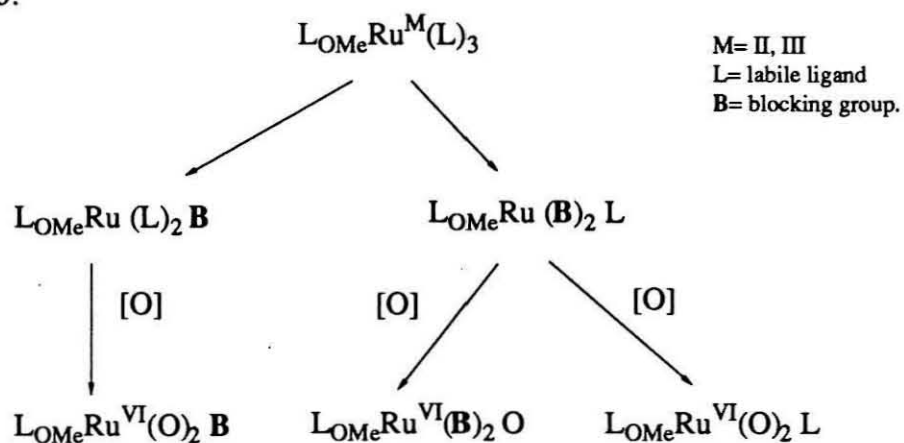
Therefore, to synthesize a monomeric ruthenium oxo complex, a route must be found that does not allow dimers to form in the process.

One obvious strategy would be to avoid the lower oxidation states altogether by using high oxidation state Ru(VI) and Ru(VII) complexes as starting materials. Unfortunately, this does not seem to be a viable option, since most readily available high oxidation state complexes feature a trans disposition of the oxo groups. These complexes have never been reported to isomerize to the corresponding *cis* compounds. Attempts in our lab to add L_{OR} to $[\text{Ru(VI)O}_3(\text{OH})_2]^{2-}$, $[\text{Ru(VII)O}_4]^-$ or $[\text{Os(O)}_2(\text{OH})_4]^{2-}$ proved fruitless.

For that reason we were forced to adopt a different synthetic strategy. The guiding principle was to begin with low oxidation state ruthenium materials that could be substituted with a variety of sterically bulky “blocking” groups. These groups would prevent dimerization until the ruthenium center was brought to a high oxidation state which should be less likely to dimerize. The blocking groups could then be altered or removed

from the molecule if necessary. Figure 3 outlines several general synthetic routes based upon this strategy.

Figure 3.



The work presented in this thesis describes the first step of the project, which is to find low oxidation state starting materials which provide a general route to high oxidation state ruthenium oxo complexes that contain facially coordinating tridentate ligands.

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Results and Discussion

In accordance with the synthetic scheme outlined in the introduction, we wished to find a starting material incorporating $[\text{CpCo}(\text{P}(\text{O})(\text{OCH}_3)_2)_3]^-$, $[\text{LOMe}]$ which was monomeric, well-defined, substitutionally labile, and easily prepared in large quantities. Unfortunately, the most commonly available starting materials are $\text{RuCl}_3 \cdot \text{H}_2\text{O}$, an amorphous solid which probably contains $\text{Ru}(\text{IV})$ and oxo ligands,¹ and RuO_4 , which is rather indiscriminate in its reactivity. In our search for alternative starting materials, one compound which seemed promising was $[\text{RuLOMe}(\text{C}_6\text{H}_6)]^+\text{PF}_6^-$, a crystalline, well-characterized complex previously synthesized by Kläui, et al.² This compound was interesting in light of studies done on the analogous cyclopentadienyl compound, $[\text{RuCp}(\text{C}_6\text{H}_6)]\text{PF}_6$.³ It was shown that the cyclopentadienyl complex could be photolyzed cleanly to replace the benzene with a coordinating solvent such as acetonitrile. In hopes that the LOMe complex would display analogous chemistry, an investigation of its photolytic behavior was undertaken.

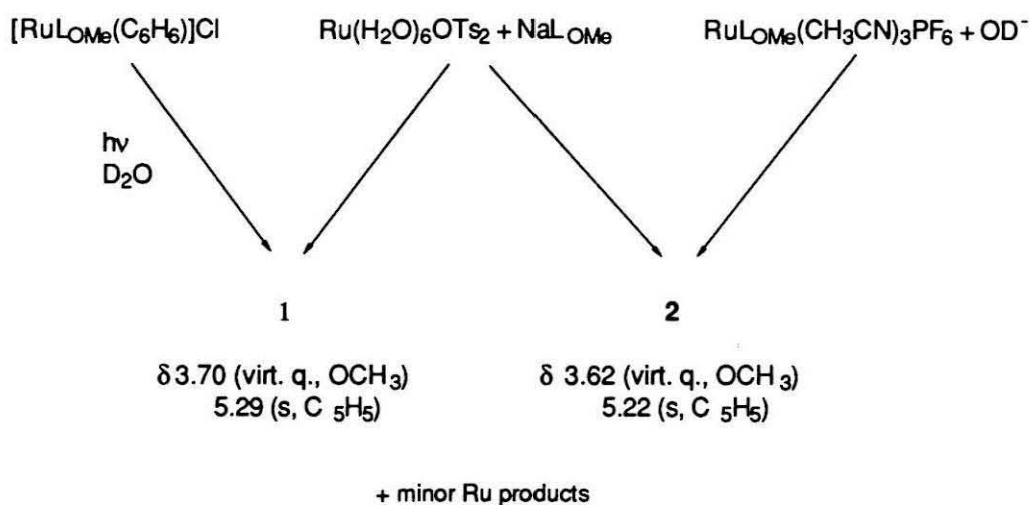
Synthesis of $[\text{RuLOMe}(\text{CH}_3\text{CN})_3]\text{PF}_6$

The first photolysis of $[\text{RuLOMe}(\text{C}_6\text{H}_6)]^+\text{PF}_6^-$ was done in acetonitrile, as was reported for the Cp compound. This reaction is quite slow, requiring 46 hr. to go to 95% completion under the reaction conditions. The reaction was extremely clean, leading to $\text{RuLOMe}(\text{CH}_3\text{CN})_3\text{PF}_6$, with no decomposition of starting material or product observed by NMR spectroscopy. Unfortunately, the tris acetonitrile complex was exceedingly inert to substitution. No substitution of the acetonitrile ligands by water was apparent in aqueous solution by ^1H NMR spectroscopy. In addition, oxidations attempted with H_2O_2 , *tert*-butyl hydroperoxide, or 3-chloroperbenzoic acid yielded either no reaction, or ill-defined products. This lack of reactivity is consistent with the exceptional stability of related acetonitrile complexes of $\text{Ru}(\text{II})$. For example, the reported rate constant for acetonitrile exchange onto $\text{Ru}(\text{CH}_3\text{CN})_6^{2+}$ is $8.9 \pm 2 \times 10^{-11} \text{ s}^{-1}$.⁴ For this reason, $[\text{RuLOMe}(\text{CH}_3\text{CN})_3]^+$ was abandoned as a direct precursor to $\text{Ru}(\text{VI})$ oxo complexes.

Routes to $[\text{RuL}_{\text{OMe}}(\text{H}_2\text{O})_3]^+$

Instead, our attention was turned to the synthesis of ruthenium aquo species containing L_{OMe} . A complex such as $[\text{RuL}_{\text{OMe}}(\text{H}_2\text{O})_3]^+$ was expected to be more labile to substitution.⁵ In addition, it was possible that the aquo ligands could be oxidized directly to oxo groups, thus simplifying the synthesis of our target compounds. Three routes to $\text{Ru(II)L}_{\text{OMe}}(\text{H}_2\text{O})_3^+$ were investigated, the results of which are summarized in Fig. 1.

Figure 1

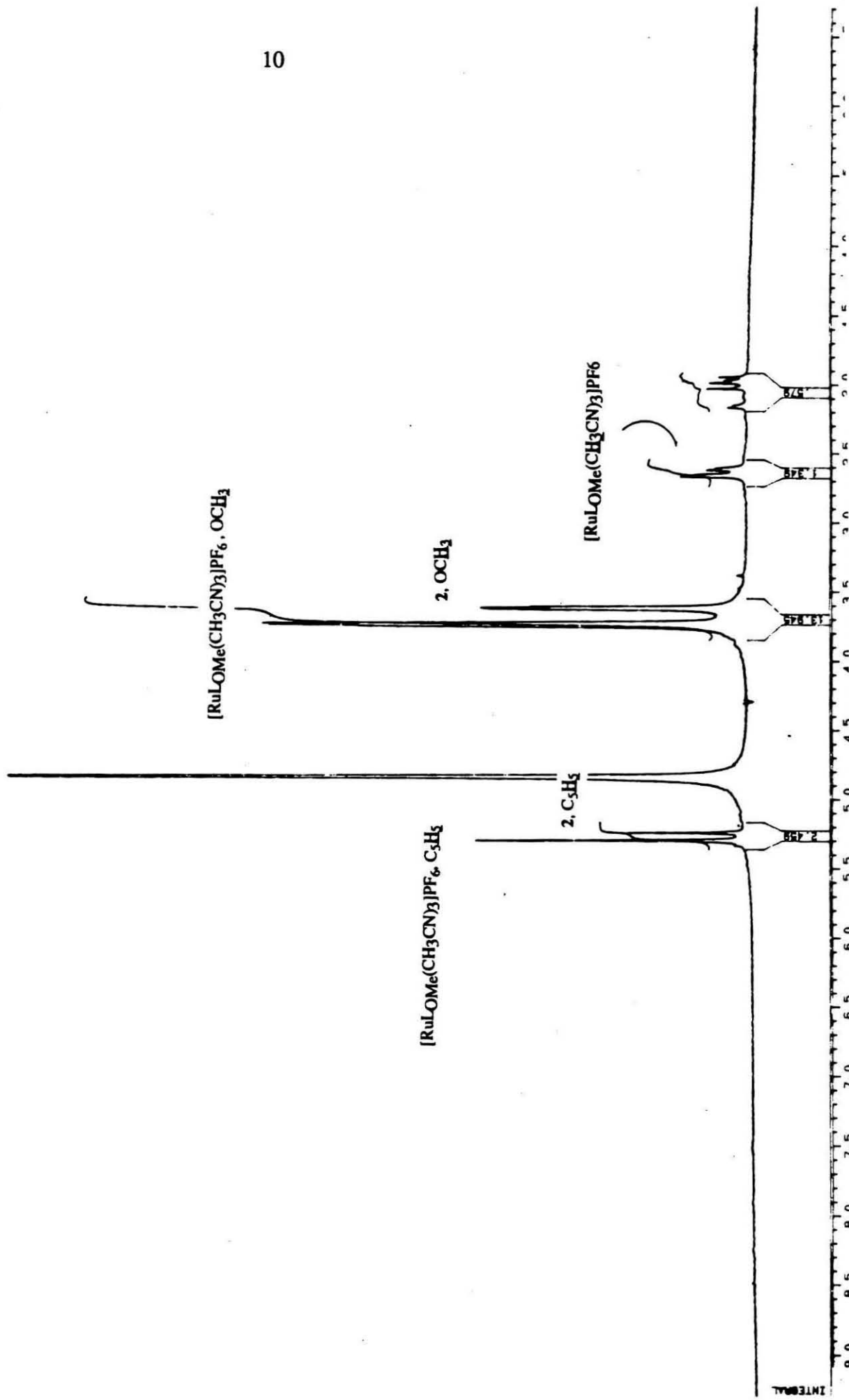


The first reaction attempted was the photolysis of $\text{RuL}(\text{C}_6\text{H}_6)\text{Cl}$ in unbuffered D_2O . This was done at the NMR tube scale under Ar. As was the case in acetonitrile, the photolysis was quite slow, at best going to about 40% completion after 17 hr as calculated from the ratios of ligand resonances in the ^1H NMR spectrum. The major species in solution, **1**, exhibited ^1H NMR (500 MHz) resonances at δ 3.70 (virt. q, OCH_3) and 5.29 (s, C_5H_5). In addition, a minor species at δ 3.59 (virt. q, OCH_3) and 5.45 (s, C_5H_5) was present which could not be assigned. A smaller amount of a species later identified as $[\text{Ru}^{\text{III}}\text{L}_{\text{OMe}}(\mu\text{-OH})(\text{H}_2\text{O})]_2$ (**3**) was also present. Because the reaction products seemed confusing at the time, another route was investigated.

The second route was the reaction of $[\text{Ru}(\text{H}_2\text{O})_6]\text{OTs}_2$ with NaL_{OMe} in D_2O at the NMR tube scale under argon. When the two were mixed in 0.1 M *p*-toluenesulfonic acid, no reaction was observed by ^1H NMR spectroscopy after 3 hr. However, when the reaction was done in unbuffered D_2O , a reaction was observed, with the formation of a small amount of precipitate. The major species observed by ^1H NMR spectroscopy was **1**, the same complex produced by the photolysis of $\text{RuL}_{\text{OMe}}(\text{C}_6\text{H}_6)\text{Cl}$. A small amount of **2** was formed, with resonances at δ 5.22 (s, 5H, C_5H_5) and 3.62 (virt. q, 18H, OCH_3). Minor resonances which could be assigned to (**3**) were also present, which might have originated from $\text{Ru}(\text{III})(\text{H}_2\text{O})_6^{3+}$ present in the starting material.

A consistent picture was beginning to form, which became more complete after examination of the third route, which utilized $[\text{RuL}_{\text{OMe}}(\text{CH}_3\text{CN})_3]^+$ as a starting material. Despite its discouraging inertness to substitution by water, it was thought that the acetonitrile ligands might be displaced by a stronger nucleophile than water, such as hydroxide ion. Indeed, when $[\text{RuL}_{\text{OMe}}(\text{CH}_3\text{CN})_3]^+$ was dissolved in 0.1 or 1.0 M OD^- in D_2O under Ar, complex **2** was seen in the 500 MHz ^1H NMR spectrum, with peaks at δ 5.22 (s, 5H, C_5H_5) and 3.62 (virt. q, 18H, OCH_3). A representative spectrum of the reaction in progress appears in Fig. 2. During the reaction the bound acetonitrile resonance at δ 2.63 was replaced by several resonances between 1.9 and 2.2 ppm that are characteristic of the products of base-catalyzed hydrolysis of acetonitrile. During the course of the reaction two additional peaks were seen in the bound acetonitrile region. These are tentatively assigned to intermediates in the stepwise replacement of the three acetonitrile ligands by hydroxide, where one or two acetonitrile ligands have been replaced. A slight shift in the methoxy peak of the L_{OMe} ligand was also observed. It could not be determined from the NMR data whether the mechanism of reaction was straightforward displacement of the acetonitrile with OH^- , followed by hydrolysis of free acetonitrile, or rather hydrolysis of the coordinated acetonitrile followed by substitution with water.

Fig. 2. $[\text{RuLOMe}(\text{CH}_3\text{CN})_3]\text{PF}_6 + 1\text{M KOH/D}_2\text{O}$, 1 day under Ar.



It is believed that both **1** and **2** are ruthenium aquo or hydroxo species, since the same products are formed from widely varying starting materials. Because **2** formed at high pH, and **1** was found at more neutral conditions, it seems likely that the two are related by acid-base reactions. This is not an unreasonable supposition, since pK_a s for related Ru(II) tris aquo species range from 7.9 for $[\text{Ru}(\text{C}_6\text{H}_6)(\text{H}_2\text{O})_3]^{2+}$ to 12.3 for $[\text{Ru}(\text{tpm})(\text{H}_2\text{O})_3]$ (tpm = tris(1-pyrazolyl)methane).⁷ Structures for **1** and **2** are suggested in Fig. 3.

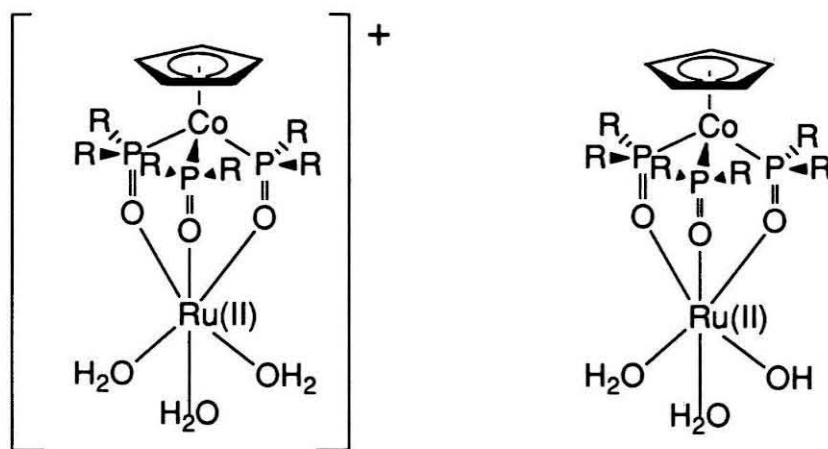
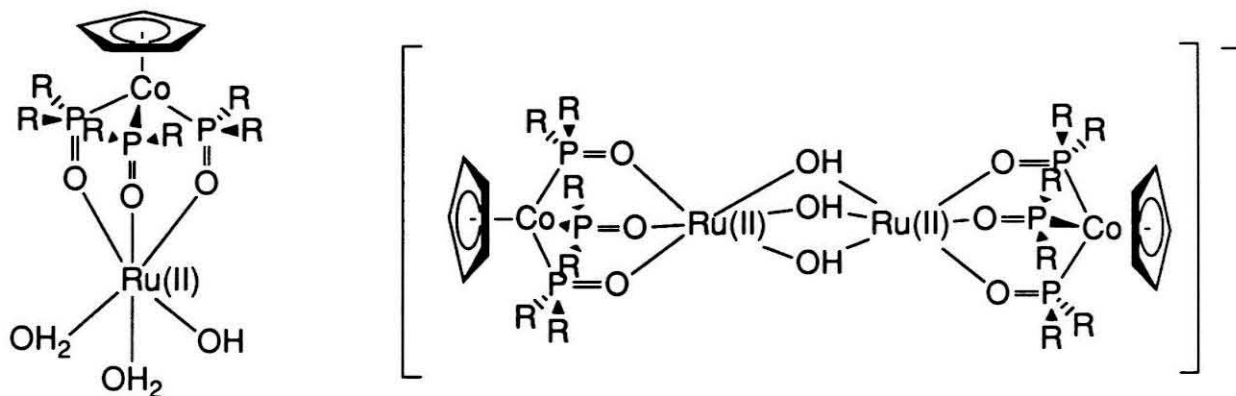


Fig. 3. Possible structures for **1**(above) and **2** (below)



All structures are consistent with the available NMR data if fast proton exchange between the aquo and hydroxo ligands is occurring.

In the presence of air, **2** is converted to a new product with a green color, which displays a splitting pattern in the NMR spectrum that indicates C_{3v} symmetry about the ligand. During every attempt at isolation of a clean product, whether by precipitation, extraction, or neutralization, this product decomposed to $NaLOMe$ and a black intractable solid (presumably $Ru(OH)_3$ or $RuO_2 \cdot nH_2O$). Because of this behavior, it seems likely that the green product is actually polymeric $Ru(OH)_x$. This result is not really a surprising one, since ruthenium(III) and ruthenium(IV) aquo and oxo complexes have been shown to polymerize under basic conditions.¹ Keeping this in mind, it would be interesting to treat $RuLOMe(CH_3CN)_3^+$ with strong acid. If indeed its decomposition in base relies upon hydrolysis of coordinated acetonitrile, hydrolysis of $[RuLOMe(CH_3CN)_3]PF_6$ in acid solution in air may produce a stable Ru(III) tris aquo species.

Reactions of $(RuLOMeCl_2)_2O$

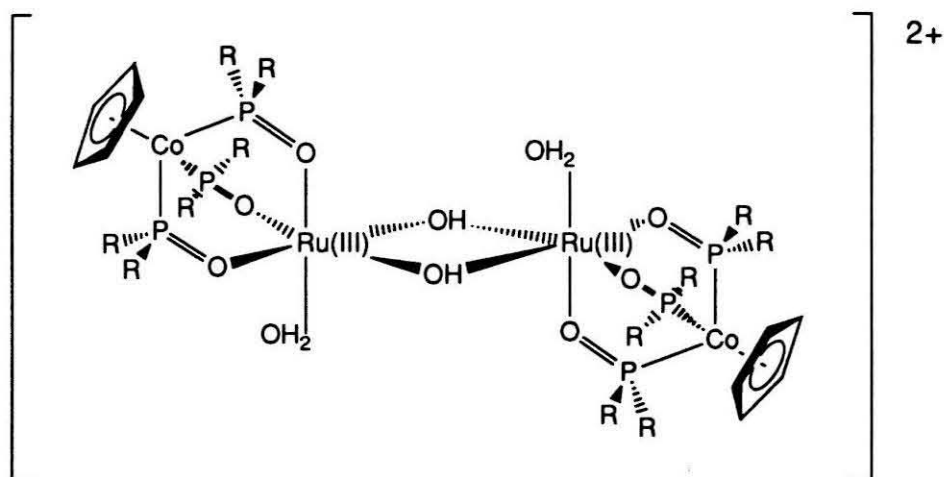
An investigation was begun of the possibilities of using $(RuLOMeCl_2)_2O$ ($R=Me, Et$) as a starting material for synthesis of Ru(VI) oxo complexes. This compound was synthesized and structurally characterized by Kaspar Evertz. Its advantage as a starting material is its ease of synthesis; $NaLOMe$ is simply stirred with commercial $RuCl_3$ in ethanol in air. Its disadvantage is obvious: the compound is already an oxo-bridged dimer, which was to be avoided.

In hopes of obtaining a monomeric complex, the somewhat counter-intuitive step of reducing $(RuLOMeCl_2)_2O$ was taken. Meyer, et al., set some precedent for this type of reaction in their synthesis of $[(tpm)Ru(H_2O)_3]^{2+}$ by zinc reduction of $[(tpm)Ru^{III}(\mu-O)(\mu-O_2P(O)(OH)_2 Ru^{III}(tpm))]$ ($tpm = \text{tris}(1\text{-pyrazolyl})\text{methane}$).⁷

Reduction of $(RuLOMeCl_2)_2O$ by a large excess of Zn/Hg amalgam in 0.1M p-toluenesulfonic acid under Ar resulted in a purple solution. After oxidation of the solution

by air, a yellow crystalline product, **3**, slowly forms in about 30% yield, assuming an approximate molecular weight of 750 g/mol per Ru center. Unfortunately, crystals suitable for x-ray structure determination were not forthcoming, but based upon the following chemical and spectroscopic evidence, the structure shown in Fig. 4 is proposed.

Figure 4. Proposed structure of **3**



The complex is of the type $\text{RuL}_{\text{OMe}}(\text{A})_2\text{B}$, and contains a mirror plane, as evidenced by the ^1H NMR spectrum of the product, which displayed a quartet:quartet:triplet (1:1:1) pattern in D_2O for the OCH_3 peaks of the ligand. OTs^- resonances were also present and integrated as 1 OTs^- per ligand resonance, indicating that each ruthenium center is singly charged. Addition of silver nitrate to the sample resulted in a color change, but no precipitation of AgCl , suggesting that the Cl^- in the starting material was removed during the reaction. Perhaps the strongest structural evidence comes from cyclic voltammetry experiments. The electrochemistry of **3**⁸ was identical to that of $[\text{Ru}(\text{IV})\text{L}_{\text{OMe}}(\mu\text{-O})(\text{H}_2\text{O})]_2^{2+}$, the so-called (IV-IV) dimer, which suggests that **3** is a reduced form of the (IV-IV) dimer and shares its doubly bridged structure. The electrochemical results could be reproduced chemically; addition of oxidants such as H_2O_2 or 3-chloroperbenzoic acid to **3**,

or heating a neutral aqueous solution of the compound in air resulted in fast, quantitative conversion to the (IV-IV) dimer.

At this point it may be fruitful to reflect on the reason a dimeric species was formed in this case. Ru(III) aquo complexes are generally more acidic than their Ru(II) analogs. Typical pK_a s are between 2 and 3.^{4,7} When Ru(III) complexes are deprotonated, they are prone to formation of polymeric compounds.⁹ Although the reduction of $(RuLOMeCl_2)_2O$ is begun at pH 1, by the end of the reaction the pH is substantially higher, approximately 3 by pH paper. The higher pH could encourage the slow formation of **3**. Possibly, if the solution were acidified after the removal of Zn, the formation of the dimer could be prevented. Alternatively, if higher yields of the dimer were desired the pH could be adjusted accordingly.

Although it is dimeric, **3** is synthetically interesting, because its aquo ligand can be substituted easily by other ligands. This property was first discovered in an NMR tube sample of **3** in methanol. After 24 hr., **3** had been converted partially to a new species with slightly different chemical shift. This suggested that a OCH_3^- complex, perhaps $[RuLOMe(OCH_3)(\mu-OH)]_2$, had formed. This result led us to investigate whether **3** would react with other nucleophilic ligands. Indeed, when **3** was dissolved in neat pyridine, a new yellow complex was formed, which displayed resonances in the 1H NMR spectrum (CD_2Cl_2 , 500 MHz) at δ 2.37 (OTs), 2.69 (OCH_3), 3.43 (OCH_3), 4.11 (OCH_3), 4.96 (C_5H_5), 6.88 (py), 7.16 (py, OTs), 7.71(OTs), and 8.31(py). If this reaction is general, it could be used to prepare amino analogs of $[Ru(IV)(H_2O)(\mu-O)]_2^{2+}$ and perhaps even a mixed oxo-imido complex.

Preparation of $[RuLOMe(OH_2)(\mu-O)]_2OTf_2$

In the course of our investigations of the reactivity of $(RuLOMeCl_2)_2O$ an improved route to $[RuLOMe(OH_2)(\mu-O)]_2OTf_2$, **4**, was discovered. This compound had been prepared previously by reaction of RuO_4 and $NaLOR$ in dilute sulfuric acid,¹⁰ but the yields for the reaction with $NaLOMe$ were quite low (10-25%). It was found that refluxing a

mixture of $(\text{RuLOMeCl}_2)_2\text{O}$ and AgOTf followed by addition of HOTf produced **4** in approximately 55% yield. In addition to the improved yield, the procedure is advantageous in that the starting materials are easier to prepare and handle. The best yield for the procedure is obtained when the mixture is refluxed for 1 hr. and worked up immediately. Longer heating at lower temperatures leads to the production of yellow and brown products instead of the desired dimer. These products were not characterized.

Conclusions

The work presented in this thesis investigates the synthesis of low oxidation state coordination complexes of ruthenium incorporating the anionic ligand, $[\text{CpCo}(\text{P}(\text{O})(\text{OMe})_2)_3]^-$, (LOMe). Several routes to $\text{RuLOMe}(\text{H}_2\text{O})_3^+$ were outlined. These routes produced two major products, possibly related by acid-base chemistry. All of these routes may lead to a monomeric aquo species, if the pH of the reactions is carefully controlled.

A new dimeric ruthenium aquo species with the proposed structure $[\text{RuLOMe}(\text{H}_2\text{O})(\mu\text{-OH})]_2$ was isolated. This complex does not provide a straightforward route to the target monomeric oxo compounds, but could conceivably provide a entry into synthesis of ruthenium dimers containing amines and other ligands.

Finally, a new route to $[\text{Ru}(\text{IV})(\text{H}_2\text{O})(\mu\text{-O})]_2\text{OTf}_2$ was discovered which is more convenient and is higher yielding than the previously published procedure.

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Experimental Section

All solvents were reagent grade and were used as received unless otherwise noted. $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (99.9% metal basis) was purchased from Johnson Matthey. $\text{C}_5\text{H}_5\text{Li}$, $\text{N}(\text{CH}_2\text{CH}_3)_4\text{CN}$, $\text{HPO}(\text{OC}_6\text{H}_5)_2$, KPF_6 , NH_4PF_6 , $\text{CF}_3\text{SO}_3\text{H}$, and AgCF_3SO_3 were purchased from Aldrich Chemical Co. $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3 \cdot \text{H}_2\text{O}$ was obtained from Spectrum Chemical. $(\text{Ru}(\text{C}_6\text{H}_6)\text{Cl}_2)_2^1$ and $\text{RuLOMe}(\text{C}_6\text{H}_6)\text{PF}_6^2$ were prepared by literature methods. NaLOMe was prepared by the literature method³, and could be recrystallized from $\text{CH}_2\text{Cl}_2/\text{acetone}$. $(\text{RuLOMeCl}_2)_2\text{O}$, previously prepared by Kaspar Evertz, was prepared by stirring equimolar amounts of NaLOMe and $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ in absolute ethanol for 24 hr., removing the solvent by rotary evaporation, and washing the resulting brown-red solid with diethyl ether and methanol.

$\text{RuLOMe}(\text{CH}_3\text{CN})_3\text{PF}_6$. 0.775 g $\text{RuLOMe}(\text{C}_6\text{H}_6)\text{PF}_6$ (0.001 mol) were dissolved in 225 ml CH_3CN . The solution was degassed by bubbling with N_2 for 15 minutes, and irradiated in a 100 W Ace-Hanovia immersion lamp apparatus. The reaction was monitored by ^1H NMR spectroscopy. After 46 hr the reaction was >98% complete and the solvent was removed *in vacuo*. Yield 0.682 g (83%) yellow-brown powder. ^1H NMR (500 MHz, D_2O) δ 5.30 (s, 5H, C_5H_5), 3.72 (virtual quartet, 18H, OCH_3), 2.63 (s, 9H, CH_3CN). IR (nujol mull) 2267 (m), 1601(w), 1617(w), 1174(w), 1120(s), 1107(s), 1040(s), 1006(s), 873(shoulder), 844(s), 777(m), 731(m), 631(shoulder), 601(m), 557(m).

$[\text{Co}(\text{C}_5\text{H}_5)(\text{P}(\text{OC}_6\text{H}_5)_2)_3]^- \text{N}(\text{C}_2\text{H}_5)_4^+$ (NEt_4LOPh). 44.8 g $\text{Co}(\text{C}_5\text{H}_5)_2$ (0.237 mol) was heated with 200 ml (1.04 mol) $\text{HPO}(\text{OPh})_2$ to 120 °C under Ar for 20 hr. The resulting yellow solid was filtered in air and washed with ethanol and *n*-pentane. The solid was dissolved in CH_2Cl_2 and filtered to remove a black residue. Yield of $\text{Co}(\text{LOPh})_2$ after removal of solvent was 24.4 g (18%). 9.35 g (0.055 mol) $\text{Co}(\text{LOPh})_2$ was dissolved in 500 ml CH_2Cl_2 . 5.0 g $\text{N}(\text{C}_2\text{H}_5)_4\text{CN}$ (0.032 mol) were dissolved in 75 ml CH_2Cl_2 and added to the $\text{Co}(\text{LOPh})_2$. The orange mixture was stirred under air for two days. Solid

orange $\text{Co}(\text{CN})_6[\text{N}(\text{C}_2\text{H}_5)_4]$ was removed by filtration. Solvent was removed from the filtrate by rotary evaporation, and the residue was redissolved in acetone, then filtered to remove excess $\text{Co}(\text{L}_{\text{OPh}})_2$. The filtrate was stripped again, then dissolved in toluene. The solution was filtered to remove any remaining $\text{N}(\text{C}_2\text{H}_5)_4\text{CN}$, and the solvent was removed by rotary evaporation to reveal a yellow oil, which was taken up in CH_2Cl_2 and dried over MgSO_4 (Caution! L_{OPh} forms $\text{Mg}(\text{L}_{\text{OPh}})_2$ upon prolonged standing with MgSO_4 !). Removal of the solvent by rotary evaporation yielded a yellow solid soluble in CHCl_3 , CH_2Cl_2 , and toluene. ^1H NMR (500 MHz, CDCl_3) δ 1.34 (t, 12H, $\text{N}(\text{CH}_2\text{CH}_3)_4$), 3.39 (q, 8H, $\text{N}(\text{CH}_2\text{CH}_3)_4$), 5.52 (s, 5H, C_5H_5), 6.65 (m, 18H, C_6H_5), 7.00 (m, 12H, C_6H_5).

$[\text{Ru}^{\text{III}}\text{L}_{\text{OMe}}(\text{H}_2\text{O})(\mu\text{-OH})_2[\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3]_2] \cdot 2$ 7.13 g *p*-

$\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3\cdot\text{H}_2\text{O}$ were added to a Schlenk flask and dissolved in 375 ml distilled H_2O to make a 0.1 M solution, which was degassed by sparging with Ar for 20 min. 1.5 g $(\text{RuL}_{\text{OMe}}\text{Cl}_2)_2\text{O}$ (1262.3 g/mol, 1.2 mmol) was added to the flask under Ar flush. 15 g granular Zn was swirled with 0.75 g HgCl_2 in 50 ml H_2O and rinsed with distilled water. The Zn was added to the Schlenk flask under Ar flush, and the solution was stirred magnetically until bubbling has ceased (*ca.* 10 min.). The purple solution was filtered under air to remove Zn, then stirred under Ar overnight, during which time yellow needle-like crystals had formed. These were filtered and washed with a small amount of H_2O . Yield 0.600 g (%). This material is soluble in water, CH_3OH , CH_2Cl_2 , and THF. It is slightly air-sensitive and should be stored under an inert atmosphere. ^1H NMR (500 MHz, D_2O) δ 2.41 (s, 6H, tos), 3.15 (virtual t, 12H, OCH_3), 4.07 (virtual q, 12H, OCH_3), 4.18 (virtual q, 12H, OCH_3), 5.51 (s, 10H, C_5H_5), 7.38 (d, 4H, tos), 7.70 (d, 4H, tos).

$(\text{RuL}_{\text{OMe}}(\text{OH}_2)\text{O})_2(\text{CF}_3\text{SO}_3)_2$. 0.1000 g $(\text{RuL}_{\text{OMe}}\text{Cl}_2)_2\text{O}$ (1262.3 g/mol, 7.9×10^{-5} mol) and 0.0812 g AgOTf (3.16×10^{-4} mol) were refluxed in 30 ml H_2O for 1 hr, during which time the solution became green and an AgCl precipitate was formed. The solution was filtered while hot to remove the AgCl (0.0297 g, 66%). To the yellow-green

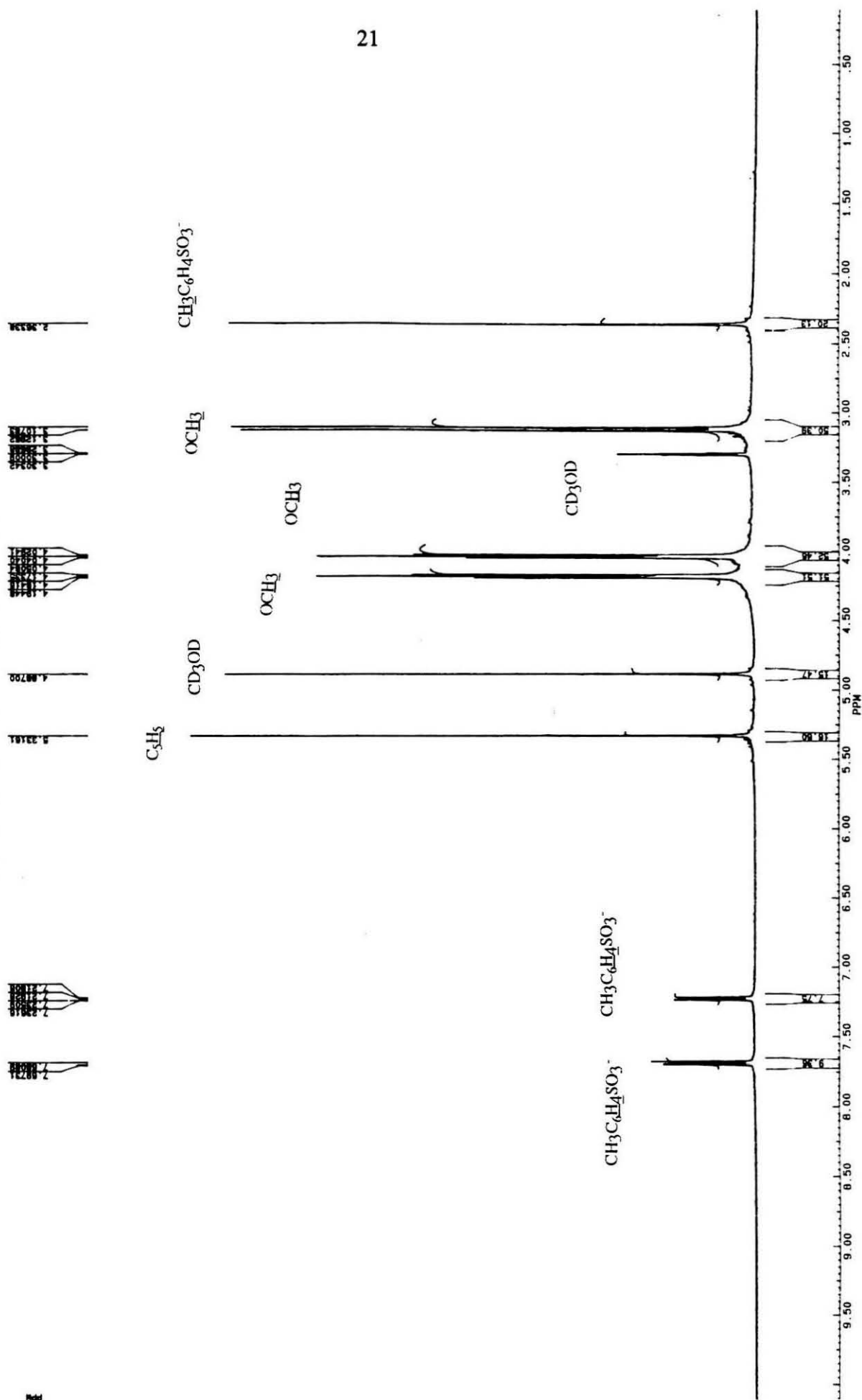
filtrate was added a few drops of $\text{CF}_3\text{SO}_3\text{H}$. A green solid precipitated, leaving a yellow solution. The precipitate was collected on a fine sintered glass frit and washed with a small amount of water. Yield: 0.0692 g green solid. The ^1H NMR spectrum of this material was identical to material prepared according to the published method,⁴ but contained small amounts of **3** and a paramagnetic impurity which was detected as broad humps in the ^1H NMR spectrum.

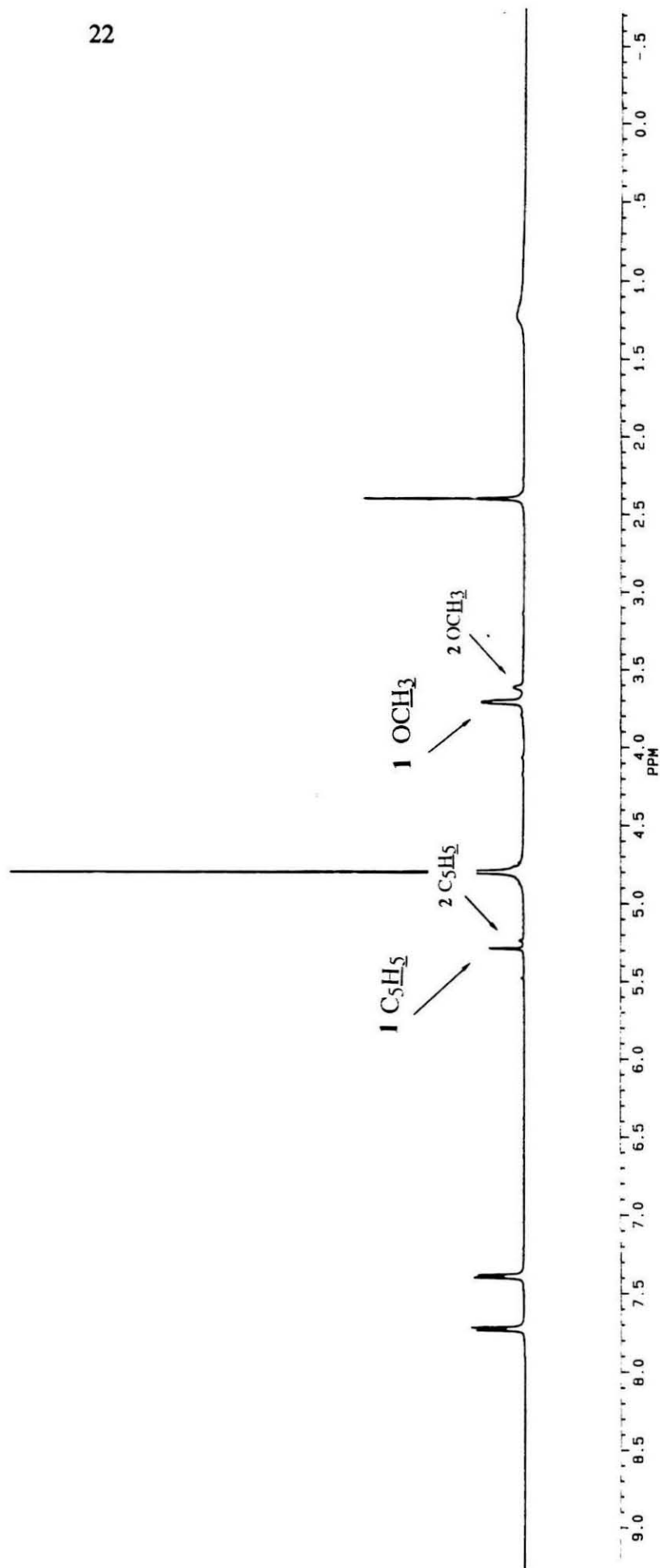
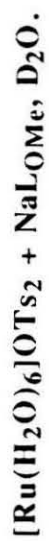
$\text{H}_2\text{LOMePF}_6$. NaLOMe was dissolved in 0.10 M H_2SO_4 . An excess of NH_4PF_6 was added to precipitate $\text{H}_2\text{LOMePF}_6$ as large golden crystals. (The neutral monoprotonated form of this ligand is a yellow oil). ^1H NMR (90 MHz, CDCl_3) δ 13.2 (s, 2H), 5.5 (s, 5H, C_5H_5), 3.8 (virtual quartet, 18 H, OCH_3).

References

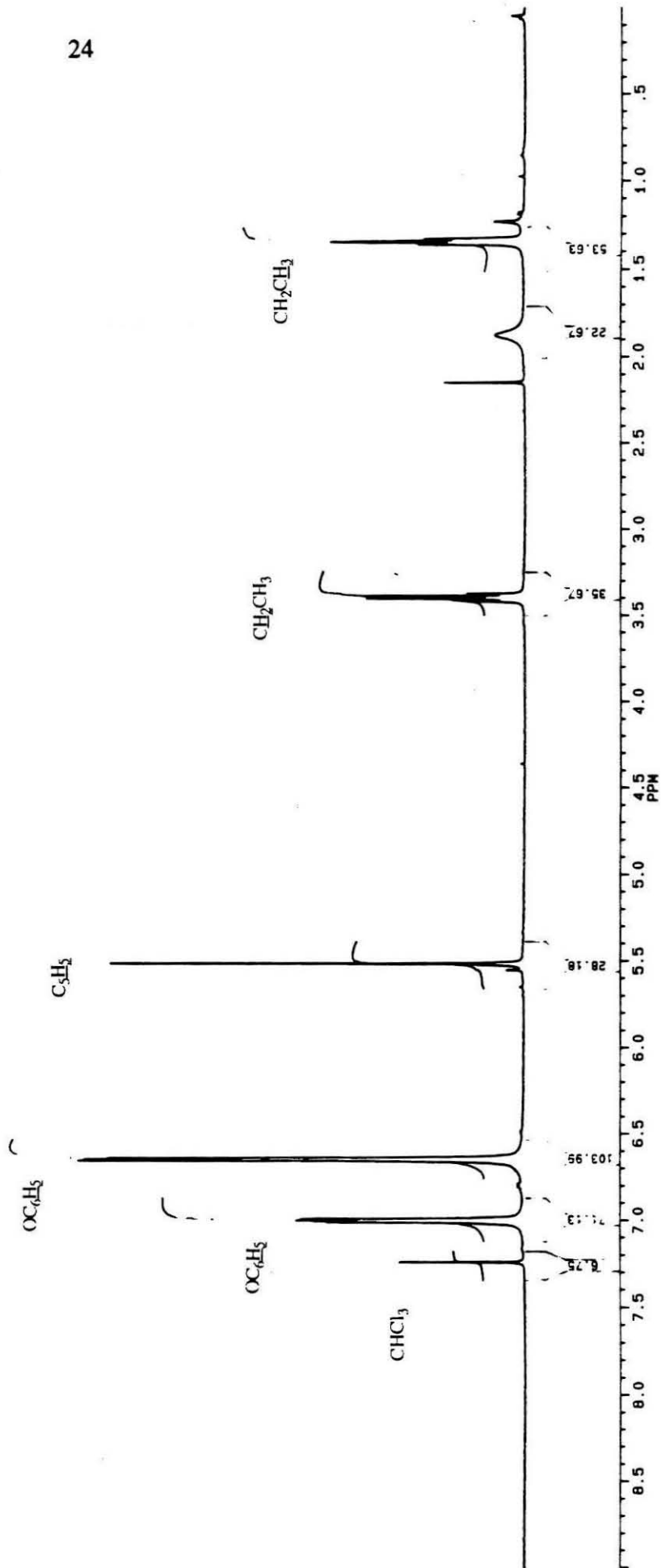
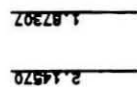
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$[\text{Ru}^{\text{III}}\text{LOMe}(\mu\text{-OH})(\text{H}_2\text{O})]_2$, CD_3OD , 500 MHz.

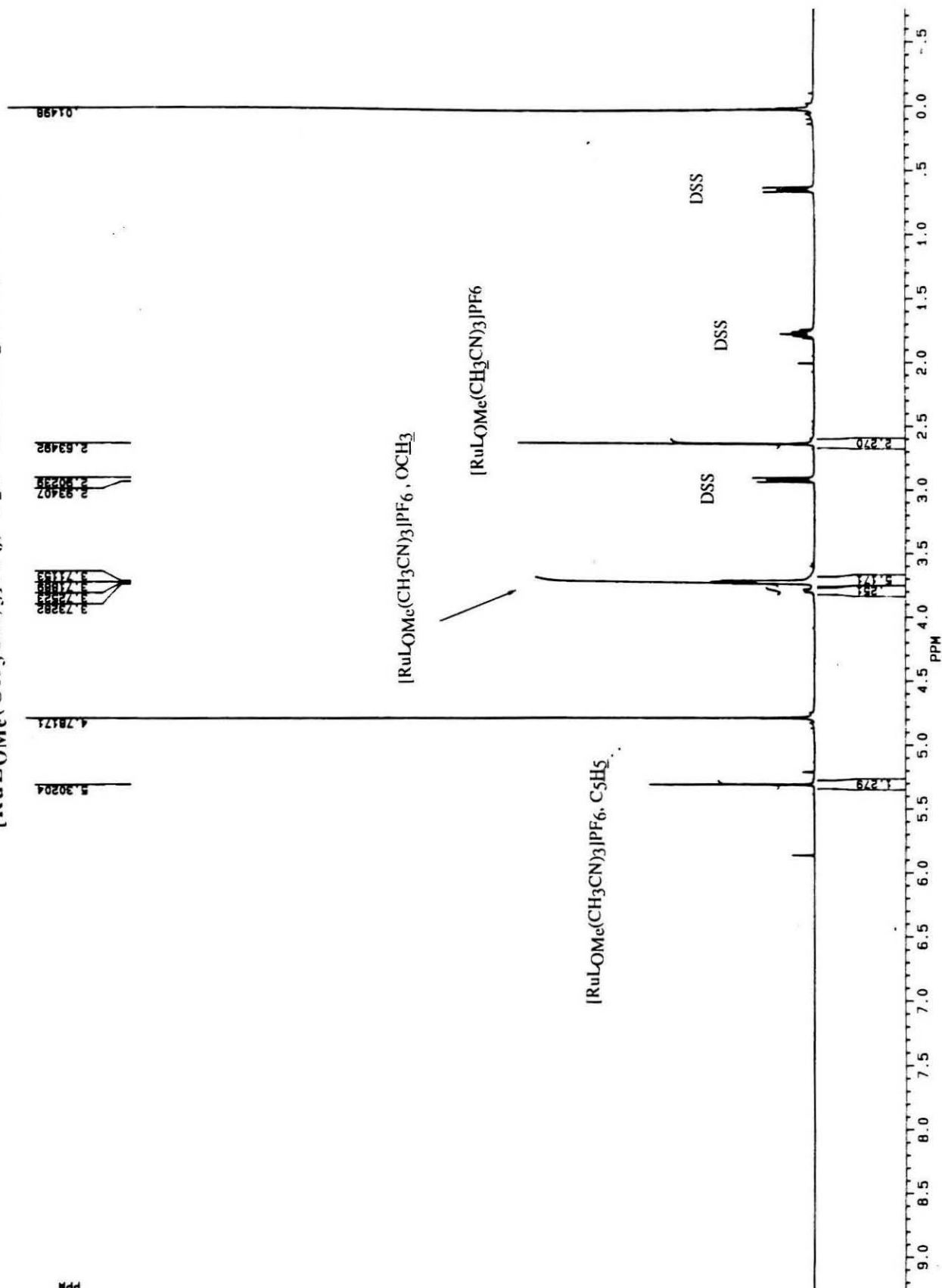




$[(C_5H_5)Co(P(O)(OC_6H_5)_3)]_3[N(CH_2CH_3)_4] \cdot (NEt_4LOPh.)$, $CDCl_3$, 500 MHz.



[RuLOMe(CH₃CN)₃]PF₆, D₂O containing DSS, 500 MHz.



EPCS. 900

SOLVENT	CDCl ₃
SF	500.137
SF0	500.130
SF02	500.130
SF2	500.137
SY	83.0
01	8760.000
SI	16384
TD	16384
SM	5000.000
SM2	5000.000
HZ/PT	0.610
VD	0.0

Label	Value
PW	4.5
PD	5.000
AG	1.638
R6	20
VS	32
TE	297

DE	127.5	25
DA	12	
DN	100	
EW	6300	
02	9000.000	
DP	63L PO	

LB	0.0
6B	0.0
NC	4
2X	35.00
Y	0.0
E1	9.245P
F2	- .751P
MI	.02
OC	1.000
HZ/CM	142.840
PPM/CM	.286
IS	1
SR	6639.46