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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

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ENTITLED.....Synthesis of Some Cyclopentadienyl and Pentamethylcyclo-

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**SYNTHESIS OF SOME CYCLOPENTADIENYL AND
PENTAMETHYLCYCLOPENTADIENYL MOLYBDENUM OXO COMPOUNDS**

BY

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Thesis

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Chapter 1

Route to and Synthesis of Some

Cyclopentadienyl Molybdenum Alkoxides

A. Introduction

The study of the mechanism of oxidation of organic substrates over MoO_3 may be important in developing industrial processes as well as understanding oxidation over metal oxide surfaces. The oxidation of organic substrates can be broken down into three basic steps: 1) the binding of the substrate at the surface site, 2) the oxidation and desorption of the product, and 3) uptake of dioxygen to replenish the site left by the desorption of the product. ¹ Due to the difficulty of studying surface bound intermediates, some compounds modeling these intermediates have been synthesized. Polyoxoanion derivatives containing organic subunits have been synthesized and characterized in the past. ² These polyoxoanions were synthesized to model intermediates suggested by Machiels and Grasselli ^{3,4} and to provide information about the chemistry involved in high oxidation state molybdenum alkoxide reactions. ⁵

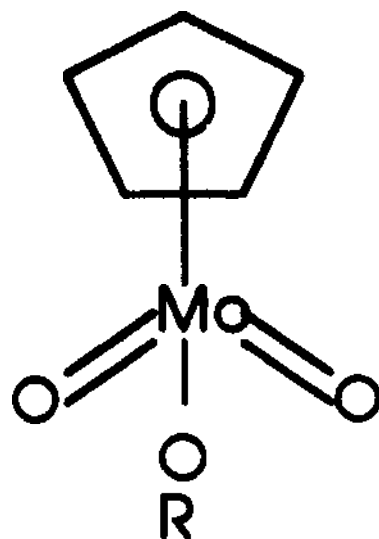


Figure 1

Wang has synthesized the compounds $P_3O_9MoO_2(OR)^{-2}$ (which are soluble, homogenous models of the surface bound intermediates on MoO_3) and has studied their thermal decomposition.⁵ The synthesis of $CpMoO_2OBU^t$ ($Cp = (n^5-C_5H_5)$) has also been carried out to model these surface bound intermediates. This compound, $CpMoO_2OBU^t$, and other materials which I have synthesized, were used in on going studies of oxidation mechanisms. The cyclopentadienyl molybdenum dioxo alkoxides (see Figure 1) will enable us to see changes in reactivity due to changes in the ligand trans to the alkoxide.

B. Experimental Section

Reagents, Solvents, and General Procedures. All glassware was oven dried at 120 °C for reactions that were performed under nitrogen

or in vacuo. The following were purchased from commercial sources and used without further purification: SnClBu^n_3 (Aldrich), molybdenum trioxide (Aldrich), 1,2-dichloroethane (Mallinckrodt), cyclohexane (Fisher), bromoform (Aldrich). $\text{CpMo}(\text{CO})_3$ and NaCp were supplied by Frank Rosenberg. A solution of 1% bromine in dichloromethane by volume was prepared by adding 5.88 mmoles of bromine to 50 mL of dichloromethane.

Thionyl chloride (Aldrich) was freshly distilled before use. Chlorobenzene (Fisher) and dichloromethane (Fisher) were refluxed over P_2O_5 under nitrogen and freshly distilled before use. Anhydrous diethyl ether (Mallinckrodt) was refluxed over benzophenone/sodium under nitrogen and freshly distilled before use. Pentane (Phillips 66) was refluxed over sodium/potassium alloy under nitrogen and freshly distilled before use. Toluene (Baker) was refluxed over sodium under nitrogen and freshly distilled before use. Benzene (Fisher) was refluxed over potassium under nitrogen and freshly distilled before use. *t*-Butanol (Aldrich) was distilled under nitrogen from sodium onto activated 3-angstrom molecular sieves and stored in a desiccator. Proton sponge (Aldrich) was sublimed 2 x at 50 °C at 0.003 torr and stored under nitrogen in a dry box protected from light.

The compounds SnCpBu^n_3 ⁶, MoOCl_4 ⁷, MoOCl_3 ⁸, CpMoCl_4 ⁶, $(\text{CpMoO}(\mu\text{-O}))_2$ ⁶, and CpMoO_2Br ⁶ were prepared by literature procedures. Nonetheless, our performance of these preparations is detailed in the following section.

Analytical Procedures. Infrared Spectra were measured from mineral oil (Nujol) mulls between KBr plates on a Perkin-Elmer 1330 spectrophotometer and were referenced to the 1028 cm^{-1} band of a 0.05 mm thick polystyrene film. An Oriel high pressure mercury lamp operated at 200 watt was used for photolysis.

Synthesis of $\text{Sn}(\text{n}^5\text{-C}_5\text{H}_5)\text{Bu}^{\text{n}}_3$. In a dry box, 27.03 g (0.307 moles) of NaCp was placed in a 500 mL schlenk flask. 200 mL of toluene and 100 g (0.307 moles) of $\text{SnClBu}^{\text{n}}_3$ were added via cannula and solution was stirred under nitrogen for two days. The tan-brown liquid was then filtered off and toluene was removed in vacuo. The remaining bright yellow liquid was then fractionally distilled, under vacuum at 0.01 torr and at 115 $^{\circ}\text{C}$, yielding a light yellow liquid. The product was stored under nitrogen in the refrigerator. (84.7 g, 0.239 moles, 78% yield).

Synthesis of MoOCl_4 . The following procedure was performed under dry nitrogen. 50.0 g (0.347 moles) of MoO_3 was refluxed in 750 mL of SOCl_2 for 12 hours, or until no white solid remained in the flask. The resulting purple solution was then cooled and filtered through a sintered-glass filter. The solvent was then removed, using a double cold trap, under vacuum yielding a dark green solid. This solid was held in vacuo overnight to ensure thorough removal of the thionyl chloride. The dark green solid (MoOCl_4) was then pulverized. A low yield in this procedure was a result of breaking the flask containing the MoOCl_4 , it was later found that the best way to avoid this was to break up the dark green solid when about 10 mL of thionyl chloride was remaining. 300 mL of chlorobenzene was then added and the mixture was refluxed for 4.5 hours. The reaction flask was then cooled and the chlorobenzene was

filtered away from the thick, dark brown solid. This solid was washed with 2 x 50 mL of chlorobenzene and dried in vacuo overnight. The product was stored at room temperature under nitrogen for 3 months with no apparent decomposition. (73.5 g, 0.337 moles, 48.5% yield).

Synthesis of $(\text{CpMoO}(\mu\text{-O}))_2$. The following procedure was performed under dry nitrogen. 750 mL of diethyl ether and 10.7 g (0.05 moles) of MoOCl_3 were combined in a 1000 mL schlenk flask. 18.5 g (0.05 moles) of SnCpBu^n_3 was added dropwise over 20 minutes and stirred 15 hours. The resulting dark solution was then filtered via cannula and the remaining residue washed with 2 x 200 mL of diethyl ether. The combined extracts were concentrated in vacuo to about 700 mL and hydrogen chloride gas was bubbled into the stirred solution for one half hour. This produced a green solution with red microcrystals precipitated out. The green solution was then filtered via cannula leaving the red microcrystals in the bottom of the flask. These crystals were washed 2 x 200 mL with diethyl ether then dried in vacuo for 30 minutes. Deionized water was degassed by bubbling nitrogen through boiling water for 5 minutes and cooled to room temperature under nitrogen. Then 250 mL of degassed water was poured into the flask over a heavy nitrogen flow. The red crystals turned yellow upon addition of the degassed water and the resulting mixture was stirred for 2 days. The water was then filtered off via cannula leaving a dark tan solid and which was dried in vacuo for 1 hour. The dark tan solid ($(\text{CpMoO}(\mu\text{-O}))_2$) was recrystallized from hot-cold dichloromethane yielding a tan-brown powder (1.9 g, 7.0 mmol, 26% yield).

Synthesis of CpMoO₂Br. 2.4 g (6.22 mmol) of ((CpMoO(u-O))₂) and 250 mL of dichloromethane were combined in a 500 mL schlenk flask. A solution of 1% bromine in dichloromethane by volume was prepared. 40 mL of the 1% bromine solution (6.22 mmol) was added dropwise under nitrogen over 10 minutes and stirred for 15 minutes. The resulting dark green solution was filtered via cannula under nitrogen and pumped dry in vacuo. The dark green solid was then extracted under nitrogen with 3 x 50 mL of benzene. 50 mL of cyclohexane was added and dioxygen was bubbled in for 12 hours. The remaining solution was removed under reduced pressure. The dark green-yellow solid was recrystallized twice with 100 mL diethyl ether and 50 mL pentane and then sublimed at 60 °C and 0.003 torr. The bright yellow solid was collected in a dry box and stored in the freezer in the dry box for 2 weeks without apparent decomposition (1.4 g, 5.13 mmol, 41% yield).

Synthesis of CpMoO₂OBut. The following procedure was performed under nitrogen and all solvents were transferred via a vacuum line. All glassware was flame-dried in vacuo in addition to oven dried prior to use. Pentane and toluene were stored over t-butyl lithium, diethyl ether was stored over n-butyl lithium.

A 50 mL schlenk flask containing 0.80 g (3.7 mmol) of proton sponge and a 250 mL schlenk flask containing 1.0 g (3.7 mmol) of CpMoO₂Br and a stir bar were prepared in a dry box. 25 mL and 60 mL of toluene were added to the 50 mL schlenk flask and 250 mL schlenk flask, respectively. 0.36 mL (3.8 mmol) of t-butanol was then syringed into the 250 mL schlenk flask. The solution in the 50 mL flask was added via cannula to the 250 mL flask which was stirred and cooled with ice. The

reaction was stirred for 1.5 hours at 0 °C, then filtered, yielding a red-brown filtrate. The toluene was removed in vacuo and 80 mL of diethyl ether was added to the resulting purple solid. This solution was then warmed to room temperature while stirring and 20 mL of pentane was added to the mixture. The solution was once again warmed to room temperature then placed in the freezer for 4 hours. The solution was filtered, leaving a gray sludge, and 70 mL of pentane was added to the filtrate. The solution was warmed to room temperature and then was cooled to -15 °C overnight. The dark orange-red solution contained some powder but no crystals. Therefore the solution was filtered and the golden orange-red liquid was placed in dry-ice overnight. The resulting yellow microcrystals were collected and dried in vacuo. The nmr of this product showed it to be the t-butoxide. Yield was not measured but was estimated to be about 10%.

$^1\text{H NMR}$ (C_6D_6 , 20°C): 1.225 ppm (9 H, singlet), 5.894 ppm (5 H, singlet).

Attempted Synthesis of CpMoOBr_2 .

(A) An attempt was made to reproduce the procedure described by Cousins.¹ 4.0 g (16.3 mmol) of $\text{CpMo}(\text{CO})_3$ was recrystallized, hot-cold, from 100 mL of 1,2-dichloroethane. Purple crystals were collected and stored in air at room temperature (2.6 g, 10.6 mmol, 65% yield). 1.0 g (4.1 mmol) of $\text{CpMo}(\text{CO})_3$ and 20 mL of bromoform were placed in an open crystallizing dish and quickly heated directly on a preheated hot plate. The originally purple solution turned black upon boiling and was heated until only a black solid

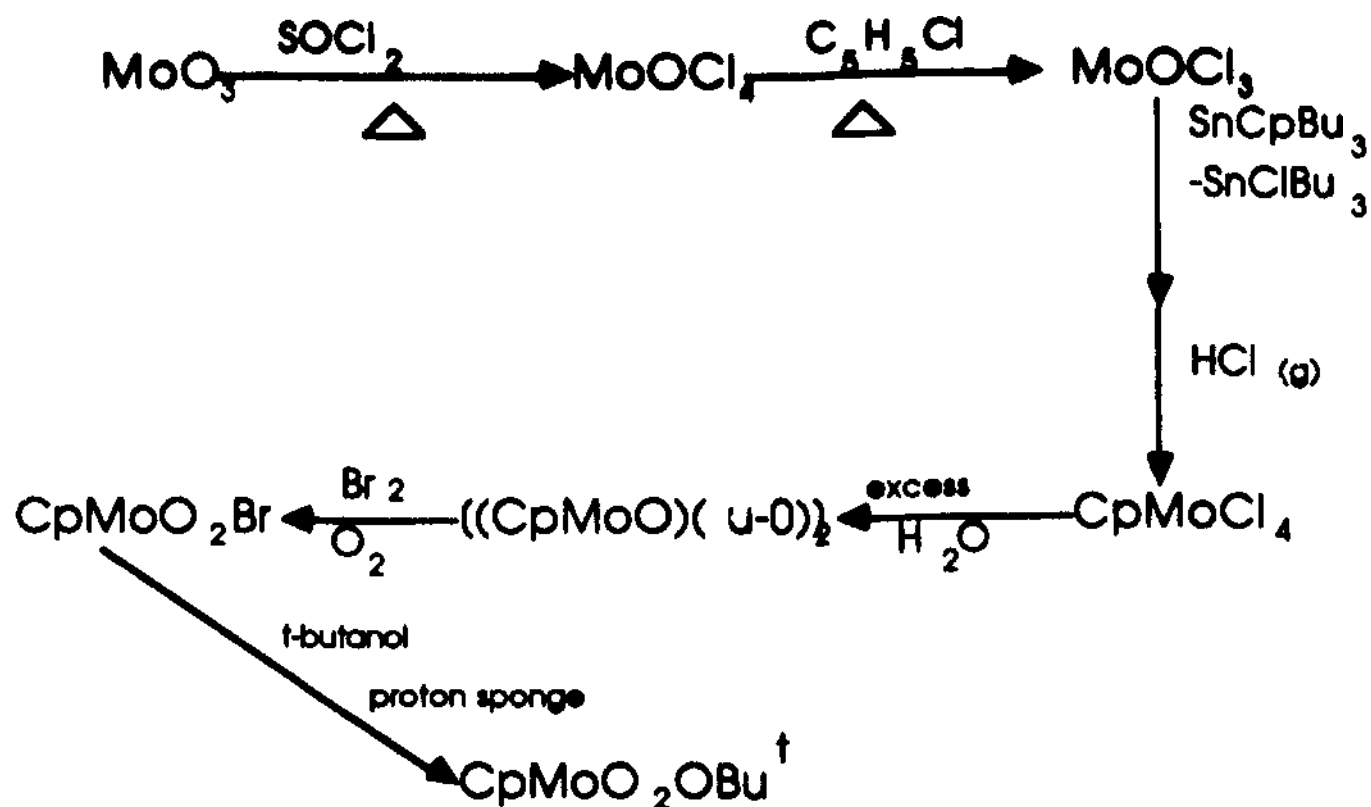
remained. This solid was extracted with 20 mL of diethyl ether. The solvent was removed from the extract under reduced pressure (on a rotary evaporator) leaving a brown-yellow oil. In an attempt to obtain a crystalline product this oil was dissolved in 20 mL of pentane then the solvent was removed under reduced pressure leaving a red-brown oil. This oil was redissolved in 20 mL of pentane and the solvent removed under reduced pressure leaving a black solid.

(B) The procedure is the same as above except the reaction was run in a 100 mL three-necked flask, fitted with a reflux condenser and a dry dioxygen inlet. Dioxygen was dried by passing it through a sulfuric acid bubbler. Also the solvent from the ether extraction was removed in vacuo rather than by reduced pressure from water aspiration. The ether extraction resulted in an oil which was discarded.

(C) 0.6 g $\text{CpMo}(\text{CO})_3$, 12.6 mL of 1% bromine solution and 15 mL of 1,2-dichloroethane were combined in a 50 mL flask and stirred at room temperature for 20 minutes while bubbling in dioxygen. The reaction was monitored by IR Spectroscopy at 20 minute intervals by removing an aliquot of solution from the reaction vessel and removing the solvent in vacuo. The resulting solid was then made into a nujol mull. After the first IR Spectrum was acquired, 12.6 mL of the 1% bromine solution was added and the dioxygen flow was slowed. After a total of 60 minutes no solvent remained. The resulting black solid was dried in vacuo and a final IR Spectrum was obtained. All 3 IR Spectra showed a carbonyl stretch while none showed the desired terminal oxygen stretch.

(D) This procedure is analogous to the previous procedure except that a quartz reaction flask was used and the reaction run under UV light. After 15 minutes the IR Spectrum still showed carbonyl stretch. After 30 minutes the IR Spectrum showed no carbonyl stretch and a terminal oxygen stretch. At this point the solvent was removed in vacuo leaving a black oil with some orange crystals. This solid was extracted with 20 mL of toluene and 15 mL of pentane was added to the extract. This solution was cooled to $-15\text{ }^{\circ}\text{C}$ overnight. Since no precipitate formed the solvent was removed in vacuo yielding a black oil that was discarded.

C. Results and Discussion



Scheme 1

The reactions covered in this work are summed in scheme 1, and detailed in the experimental section and discussed below. The reaction of MoO_3 with SOCl_2 under nitrogen affords the dark green solid MoOCl_4 , which is then refluxed with chlorobenzene to yield dark brown MoOCl_3 . When MoOCl_3 is treated with SnCpBu^n_3 followed by hydrogen chloride gas and then degassed water the tan dimer, $((\text{CpMoO})(\mu\text{-O}))_2$, 1 is produced. The dimer, 1, is then reacted with a 1% bromine solution and dioxygen gas to yield the yellow bromide CpMoO_2Br , 2. The bromide, 2, is then treated with one equivalent of proton sponge and t-butanol in toluene, yielding the moisture-sensitive alkoxide, $\text{CpMoO}_2\text{OBu}^t$, 3. The ^1H NMR of 3 shows a Cp resonance at 5.89 ppm and a methyl resonance at 1.23 ppm. This spectrum also showed a resonance due to the anhydride and a methyl resonance at 1.05 ppm due to t-butanol which were believed to have been produced by wet C_6D_6 .

We made several unsuccessful attempts to make CpMoOBr_2 because it appeared to be a shorter path to the dimer, 1, with higher yield.¹ Cousins and Green reported that CpMoOBr_2 could be made by quickly heating $\text{CpMo}(\text{CO})_3$ and bromoform in a open crystallizing dish until the solution turned dark orange and an sticky orange product formed in the bottom of the dish. The bromoform was then removed on a steam bath by blowing a stream of air over the surface of the solvent. The resulting black solid was extracted with diethyl ether and upon removal of the diethyl ether orange crystals formed. When this procedure was attempted in our hands (see experimental section, method A) the original solution of $\text{CpMo}(\text{CO})_3$ and bromoform turned

black upon boiling, never observing an orange sticky product, then when extracting with diethyl ether an oil formed which when dissolved in pentane yielded a black solid. When the attempt to reproduce the literature procedure failed, alternate syntheses were attempted. The next attempt (method B) was to put the reaction into a flask under dry dioxygen and follow the same procedure, but this resulted in the formation of an oil which was discarded.

Bromoform was then replaced with a 1% bromine solution and the room temperature reaction (method C) was monitored by IR Spectroscopy. The IR Spectrum from this reaction never showed the disappearance of the carbonyl absorption band or the appearance of the desired terminal oxygen absorption band (at 945 cm^{-1}).¹ The final attempt (method D) to synthesize and isolate CpMoOBr_2 was performed under UV light and in a manner similar to the above procedure. The final IR Spectrum showed the desired terminal oxygen absorption band and no carbonyl absorption band, indicating the reaction was completed. The resulting black oil with orange crystals was treated with toluene then pentane only to yield a black oil which was discarded.

D. Conclusion

The preparation of CpMoO_2Br from MoOCl_4 was found to work as reported by Bunker.⁶ $\text{CpMoO}_2\text{O}^-\text{Bu}^+$ can be synthesized from equimolar quantities of CpMoO_2Br , proton sponge, and t-butanol.

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Chapter 2

The Reaction of tris(2,4,6-trimethoxyphenyl) Phosphine and u-Oxo-bis((η^5 -pentamethylcyclopentadienyl)dioxomolybdenum)

A. Introduction

The goal of our research project was to find an alternate synthesis method for making $((\text{Cp}^*\text{MoO})(\text{u-O}))_2$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{H}_5$). The currently employed procedure involves the use of trimethyl phosphine.¹ Trimethyl phosphine is a pyrophoric liquid which has a terrible odor, making it difficult and unpleasant to handle. Trimethyl phosphine is also expensive and difficult to prepare. It has been reported by Holm that tris(2,4,6-trimethoxyphenyl) phosphine is a good oxygen acceptor.² Therefore, we thought this reported phosphine might be a better choice to make $((\text{Cp}^*\text{MoO})(\text{u-O}))_2$. Tris(2,4,6-trimethoxyphenyl) phosphine is a solid which is easily prepared from relatively cheap starting materials: 1,3,5-trimethoxybenzene, n-butyl lithium and triphenyl phosphite. The solid phosphine is also stable in air for short periods of time.

We observed that the reaction of tris(2,4,6-trimethoxyphenyl) phosphine and $((\text{Cp}^*\text{MoO})_2(\text{u-O}))$ is not a high yield preparation for $((\text{Cp}^*\text{MoO})(\text{u-O}))_2$. However, the NMR Spectrum of the product showed the presence of a singlet hydrogen resonance which was interpreted as a new pentamethylcyclopentadienyl molybdenum oxide species.

Organometallic oxo compounds are of interest because so many more compounds can be made from them. The oxo ligand can easily be replaced with a halide or removed by triphenyl phosphine. Reduction of the oxo compounds is also a promising route to organometallic clusters containing oxygen atoms.³

B. Experimental Section

Reagents, Solvents, and General Procedures. All glassware was oven dried at 120 °C for reactions that were performed under nitrogen or in vacuo. The following were purchased from commercial sources and used without further purification: 1.6 M n-butyl lithium in hexanes (Aldrich), triphenyl phosphite (Aldrich), ethanol (Midwest Grain Products), 1,3,5-trimethoxybenzene (Aldrich), and neutral alumina, Brockman activity 1, 80-200 mesh (Fisher). ((Cp*MoO)₂(μ-O)) was supplied by Frank Rosenberg.

Dichloromethane (Fisher) was refluxed over P₂O₅ under nitrogen and freshly distilled before use. Anhydrous diethyl ether (Mallinckrodt) and tetrahydrofuran (American Burdick and Jackson) were refluxed over benzophenone/sodium under nitrogen and freshly distilled before use. Pentane (Phillips 66) was refluxed over sodium/potassium alloy under nitrogen and freshly distilled before use. Toluene (Baker) was refluxed over sodium under nitrogen and freshly distilled before use.

The compounds 2,4,6-trimethoxyphenyl lithium ⁴ and tris(2,4,6-methoxyphenyl) phosphine ⁵ were prepared by literature procedures. Nonetheless, our performance of these preparations is detailed in the following section.

Analytical procedures. Infrared Spectra were measured from mineral oil (Nujol) mulls between KBr plates on a Perkin-Elmer 1330 spectrophotometer and were referenced to the 1028 cm^{-1} band of a 0.05 mm thick polystyrene film.

Synthesis of 2,4,6-trimethoxyphenyl lithium. The following procedure was performed under dry nitrogen. 20.9 g (0.125 moles) of 1,3,5-trimethoxybenzene and 80 mL of diethyl ether were combined in a 250 mL schlenk flask. 83 mL (0.125 moles) of n-butyl lithium in hexanes was syringed into the flask and the solution was refluxed for 12 hours. Half of the solution was removed in vacuo and the other half filtered off via cannula. The remaining white solid was washed with 2 x 100 mL of pentane and then dried in vacuo yielding a pale yellow solid (20.6 g, 0.118 moles, 95% yield).

Synthesis of tris(2,4,6-trimethoxyphenyl) phosphine. The following procedure was performed under dry nitrogen. 20.6 g (0.118 moles) of 2,4,6-trimethoxyphenyl lithium and 300 mL diethyl ether were combined in a 500 mL schlenk flask. 10.5 mL (0.04 moles) of triphenyl phosphite was syringed into the ice cooled flask and the solution was stirred for 12 hours. The solvent was filtered off via cannula leaving a white solid which was then dried in vacuo. The tris(2,4,6-trimethoxyphenyl) phosphine was

recrystallized, hot-cold, with 200 mL of ethanol yielding a tan solid (10.4 g, 0.0195 moles, 50% yield).

IR (1350-500 cm^{-1}): 1321(m), 1284(w), 1219(m), 1199(m), 1179(w), 1151(m), 1114(m), 1082(m), 1033(m), 946(m), 919(m), 814(m), 804(m), 794(sh), 729(w), 674(w), 634(w). $^1\text{H NMR}$ (CDCl_3 , 20 $^\circ\text{C}$): 3.49 ppm (6H, singlet), 3.78 ppm (3H, singlet), 6.04 ppm (2H, doublet).

Reaction of $(\text{Cp}^*\text{MoO}_2)_2(\mu\text{-O})$ and tris(2,4,6-trimethoxyphenyl) phosphine. The following procedure was performed under dry nitrogen. 2.0 g (3.76 mmol) of tris(2,4,6-trimethoxyphenyl) phosphine, 0.25 g (0.46 mmol) of $(\text{Cp}^*\text{MoO}_2)_2(\mu\text{-O})$ and 50 mL of toluene were combined in a 100 mL schlenk flask and refluxed for 12 hours. Toluene was then removed in vacuo leaving a dark red-brown solid. This solid was dissolved in 10 mL of dichloromethane, allowed to react for 20 minutes, and then the dichloromethane was removed in vacuo. The resulting solid was extracted with 4 x 10 mL of toluene, then the toluene was removed in vacuo from the combined extracts. The resulting solid was dissolved in 5 mL of dichloromethane, allowed to react for 20 minutes, and then the dichloromethane was removed in vacuo leaving a brown oil. The brown oil was dissolved in 3 mL of toluene and ran through a 3 inch alumina column.

C. Results and Discussion

The reaction of 1,3,5-trimethoxybenzene with n-butyl lithium under dry nitrogen affords the pale yellow solid 2,4,6-trimethoxyphenyl lithium. This pale yellow solid is then reacted with triphenyl phosphite at 0 °C to yield a white solid tris(2,4,6-trimethoxyphenyl) phosphine, 1. The white solid, 1, was refluxed with $((\text{Cp}^*\text{MoO}_2)_2(\mu\text{-O}))$ in toluene yielding a red-brown solid.

The red-brown solid was identified by ^1H NMR to contain a mixture of unreacted, 1, unreacted $((\text{Cp}^*\text{MoO}_2)_2(\mu\text{-O}))$, the desired $((\text{Cp}^*\text{MoO}(\mu\text{-O}))_2)$, 2, and an unidentified compound that appears as a singlet at 2.355 ppm in CDCl_3 . Since there was a mixture of products with a low yield of, 2, the idea of using this reaction as a way to prepare, 2, was abandoned. At this point our efforts became diverted toward isolating the compound whose NMR Spectrum is a singlet at 2.355 ppm. Several unsuccessful attempts were made to isolate the unknown compound. The unknown compound appears to decompose in tetrahydrofuran and diethyl ether. There was limited success in isolating the compound through a series of reactions with dichloromethane followed by extraction with toluene (see experimental section). The reaction with dichloromethane produces a phosphonium salt ⁵ which is insoluble in toluene and can be separated more easily than the phosphine. This procedure yields a brown oil which is then dissolved in a minimum of toluene and passed through an alumina column. Two bands separated on the column. The first fraction collected was dark brown and found by ^1H NMR to contain a mixture of the unknown compound and the $((\text{Cp}^*\text{MoO}_2)_2(\mu\text{-O}))$. The second fraction collected was identified by ^1H NMR to contain unreacted, 1, and, 2. The first fraction

was not separated further because the yield was extremely low, ca. 2%. By weighing the brown oil before passing it through the column and comparing that weight to the amount started with, it was found that 75% of the pentamethylcyclopentadienyl molybdenum compounds were lost in the extractions with toluene. A better method might be extraction with a toluene/dichloromethane mixture. The project was not completed because time did not allow for further experimentation.

D. Conclusion

The preparation of $((\text{Cp}^*\text{MoO})(\mu\text{-O}))_2$ from $((\text{Cp}^*\text{MoO}_2)_2(\mu\text{-O}))$ and tris(2,4,6-trimethoxyphenyl) phosphine is not a promising route because of low yield. It appears that a new pentamethylcyclopentadienyl molybdenum oxo compound is being formed, however we have not been able to isolate this as a pure compound.

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