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L₂=dmpe and dppe

Brian Dearman

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SYNTHESIS AND CHARACTERIZATION OF $[(C_5R_5)M(CO)_2(L_2)]^+$: R=H,
Me, and Ph; M=Cr and Mo; L_2 =dmpe and dppe

**Thesis submitted to
The Graduate College of
Marshall University**

**In partial fulfillment of the
Requirements for the degree of
Master of Science
Program**

by

**Brian Dearman
Marshall University**

04/10/2002

This thesis was accepted on 2002 April 10 as meeting the research requirements for the master's degree.

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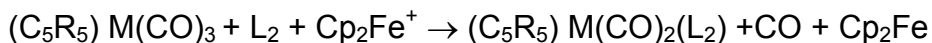
ABSTRACT

SYNTHESIS AND CHARACTERIZATION OF
[(C₅R₅)M(CO)₂(L₂)⁺: R=H, ME, AND PH;
M=CR AND MO; L₂=DMPE AND DPPE

by Brian Dearman

For two decades much research has been concentrated on open-shell transition metal complexes as chemical intermediates. To date, most efforts have concentrated on electron deficient, 17-electron (17e) compounds; however past research has shown that electronically supersaturated, 19-electron (19e) complexes can also participate as intermediates in many reactions. Yet, excluding (C₅H₅)Fe(C₆H₆) type complexes, very few of these compounds have been prepared.^{2,3} To better understand the nature of 19e, the preparation of another series of compounds is desirable.

The addition of the bidentate Lewis bases 1,2- bis(dimethylphosphino)ethane (dmpe) or 1,2-bis(diphenylphosphino)ethane (dppe) to a mixture of [(C₅R₅)M(CO)₃]_x (X= 2 for R= H, Me, Ph; M = Cr, Mo and X=1 for M=Cr, R=Ph) and [Cp₂Fe]PF₆, produces [(C₅R₅)M(CO)₂dmpe]⁺ or [(C₅R₅)M(CO)₂dppe]⁺ except for M=Cr, R=Ph, respectively (eq 4).



DEDICATION

The author wishes to dedicate this thesis to my mother and father for all their help and guidance.

ACKNOWLEDGMENTS

The author wishes to thank my advisor Dr. Michael Castellani for all his help and guidance and help over the past three year. I would also like my research group and the Chemistry department.

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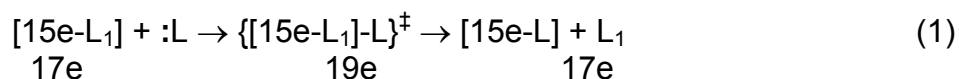
LIST OF SYMBOLS / NOMENCLATURE

CHAPTER I

Introduction

For two decades much research has been concentrated on open-shell transition metal complexes as chemical intermediates.¹ To date, most efforts have concentrated on electron deficient, 17-electron (17e) compounds; however past research has shown that electronically supersaturated, 19-electron (19e) complexes can also participate as intermediates in many reactions. Yet, excluding (C₅H₅)Fe(C₆H₆) type complexes, very few of these compounds have been prepared.^{2,3} To better understand the nature of 19e, the preparation of another series of compounds is desirable.

Seventeen-electron complexes containing CO ligands frequently undergo substitution reactions via associative mechanisms⁴ using an incompletely filled bonding molecular orbital.⁵ This partially filled orbital allows 17e complexes to react at a much faster rates than 18e analogs because it is energetically low lying and available to accept electron density. To understand the relevance of this to 19e complexes consider treating of a 17e species as a 15e species with a 2e donating ligand.



In an associative reaction a new “species” forms when a ligand binds to the parent molecule. This middle species can either be thought of as either a 19e intermediate or transition state, but either way the species formally has a 19e count. The reaction is fast because the electron deficient 17e species possesses a low activation barrier to accept a ligand. Then in step two the electron supersaturated 19e species loses a ligand. This process has a low activation barrier that is caused by the extra electron residing in the antibonding orbital of the metal. The 19e species will usually lose the ligand that donates the lesser amount of electron density because the product molecule will again carry an electron deficient 17e count. The use of monodentate ligands is problematic because, once the ligand is released, the 19e species cannot be reformed. Using bidentate ligands allows 19e complexes to reform because the chelate effect ensures the presence of all ligands necessary to regenerate a 19e complex.

Mechanisms of reactions incorporating transition metal complexes frequently included open-shell intermediates. This makes examination of similar compounds valuable. Among the difficulties in studying 19e intermediates are their high reactivities and short lifetimes. In thermal reactions, 19e complexes exist in such low concentrations that it is nearly impossible to study them directly. NMR is not applicable because paramagnetic compounds usually give such broad spectra that most, if not all, fine detail is lost. This is why crystallography is virtually the only method of generating structural data, but without a stable 19e

species no crystals can be grown to study.

Even though the first 19e complex, Cp_2Co , was prepared over forty years ago, it was not until the 1980s that the role of such complexes as reaction intermediates was investigated.^{2,6,7} Nineteen-electron complexes are powerful reducing agents because the extra electron resides in an antibonding orbital.⁸ Though there are many commercially available oxidants, such as AgBF_4 and $[\text{Cp}_2\text{Fe}]\text{PF}_6$, there are few commercially available organometallic reducing agents. The most common organometallic reducing agent is cobaltocene, $[\text{Cp}_2\text{Co}]$, which decomposes slowly in the solid state and must be purified regularly.⁹ Because there are so few soluble, stoichiometric reducing agents, further investigation into these species is needed.

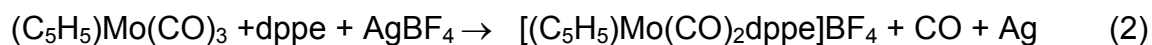
There are many reasons why so few 19e complexes exist compared to 17e complexes. Seventeen-electron complexes tend to attain a closed 18e shell by oxidizing some other species in solution, dimerizing, or disproportionating. These transformations can be controlled by careful experimental design because most are not internal processes. On the other hand, the 19e complexes will attempt to lower its electron count by reducing some other species, rearranging, or through losing a ligand by dissociation. The isolation of the 19e complexes is much more difficult because molecular rearrangement and ligand dissociation are internal processes, which make for difficult control.

Nineteen-electron species are usually formed by the associative addition of 2e ligands to 17e complexes or the reduction of 18e complexes.¹⁰ Unstable 19e species will dissociate, losing a ligand, unless there is some factor to prevent

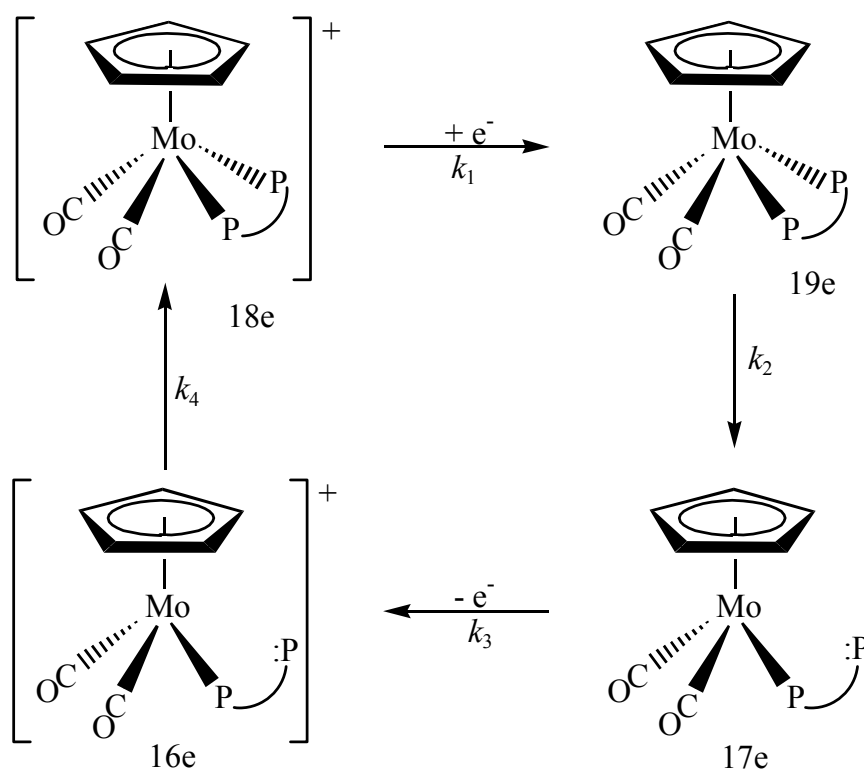
it. For the 19e species to be formed and to be stable the amount of energy released from the new metal-ligand bond formation has to overcome the sum of the entropy cost and the energy required to populate an anti-bonding molecular orbital with one electron. This bond can also be weakened by steric factors such as adding a large ligand to the metal or using a small metal center. Two ways to stabilize the 19e species are using large second row transition series metal centers to reduce steric strain and using strong π -acceptor ligands, such as CO, to remove electron density from the metal.

The R = H and Me complexes of the $(C_5R_5)Cr(CO)_3$ family exist in equilibrium between 17e monomers and 18e dimers in solution and as dimers in the solid state.¹¹ The complex R = Ph exists solely as a 17e monomer both in solution and the solid state due to the small size of the Cr metal and the large size of the phenyl groups.¹² The small size of the Cr metal makes seven-coordinate centers uncommon and unstable.¹³ $[CpCr(CO)_3]_2$, which contains two seven-coordinate centers, is easily made but undergoes reversible homolytic bond cleavage in solution.¹⁴ However, $[(C_5Ph_5)Cr(CO)_3]_2$ cannot form since the C_5Ph_5 ligand occupies more than one-half of the coordination sphere, thus not allowing sufficient room for dimerization.^{15, 16}

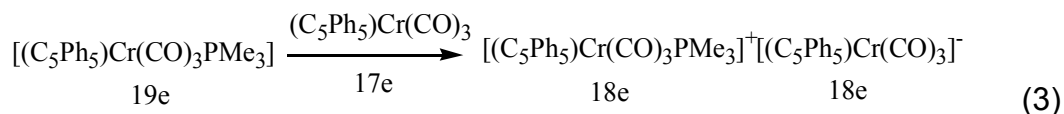
By replacing the small chromium atom with the larger molybdenum, steric crowding is relieved and this allows the C_5H_5 , C_5Me_5 , and C_5Ph_5 dimers to be synthesized. These dimers are used as starting materials in many reactions such as the example in eq 2.¹⁷



The cyclic voltammogram of $\text{CpMo}(\text{CO})_2(\text{dppe})^+$ shows a single, irreversible reduction and a single, irreversible oxidation on the return sweep. The reduction occurs at a very negative potential, while the oxidation occurs at a potential much more positive than expected, unless a significant molecular change occurred. Neither the oxidative or reductive wave shows any sign of reversibility up to 10 V/s.¹⁵ Scheme 1 presents a plausible mechanism consistent with this electrochemical data.



More evidence for this mechanism is provided by examining the synthesis of $(C_5Ph_5)Cr(CO)_3PMe_3$ and the reduction of 18e $(C_5Ph_5)Cr(CO)_2depe^+$. The reaction of $(C_5Ph_5)Cr(CO)_3$ and PMe_3 initially yields the 18e/18e salt $[(C_5Ph_5)Cr(CO)_3PMe_3]^+[(C_5Ph_5)Cr(CO)_3]^-$ at low temperature.¹⁵ The most reasonable method of generating the $(C_5Ph_5)Cr(CO)_3PMe_3^+$ involves a 19e intermediate.



The most stable 19e complexes would be ones with ligands that remove some of the electron density from the metal, but not as to entirely localize the unpaired electron on the ligands. Past electrochemical studies have shown complexes that incorporate the C_5Ph_5 ligand have reduction potentials approximately 0.25 V more positive than C_5H_5 .¹⁶ Similar C_5Me_5 analogs have a potential 0.25 V more negative than C_5H_5 .¹⁷ Thus, formation of 19e complexes should be favored in the order $C_5Ph_5 > C_5H_5 > C_5Me_5$, based on the electronic contributions of these ligands. In principle, a complex with three CO ligands and an electron rich phosphine should stop the loss of CO and stabilize the 19e complex. As of now no 19e complexes with standard alkyl or aryl phosphines or phosphites have been isolated.^{18,19} Using bidentate phosphines, such as $R_2PCH_2CH_2PR_2$, along with 2 CO ligands, allows for a more reasonable set of electronically supersaturated complexes because the chelate effect will ensure the presence of all ligands necessary to generate a 19e total. Though the

ligands will provide more electron density to the metal, the amount of donation can be regulated by having an electron donating or electron withdrawing group as the substituent on the phosphine.

Synthesis of $(C_5R_5)M(CO)_2(L_2)^+$ complexes offers convenient starting reagents for the generation of 19e $(C_5R_5)M(CO)_2(L_2)$ radical complexes.

Towards that end, we report herein the synthesis of a variety of new $(C_5R_5)M(CO)_2(L_2)^+$ complexes and their spectral and electrochemical characterization. Their potential use as starting materials for the synthesis of new 19e complexes is also examined.

CHAPTER II

Experimental Section

General Procedures

Unless otherwise stated, all reactions were performed under a nitrogen atmosphere using standard Schlenk techniques. Solids were manipulated under argon in a Vacuum Atmospheres glovebox equipped with a HE-493 dri-train. Hexane (Ashland Oil) was distilled from sodium under nitrogen. Benzene and tetrahydrofuran (THF) were distilled from potassium /benzophenone ketyl under nitrogen (Fisher). Dichloromethane and acetonitrile (Fisher) were heated to reflux over CaH_2 and distilled under nitrogen. NMR solvents (Cambridge Isotope) were vacuum distilled over CaH_2 and placed under nitrogen atmosphere. 1,2- Bis(dimethylphosphino)ethane (dmpe), 1,2-bis(diphenylphosphino)ethane (dppe), and $[\text{CpMo}(\text{CO})_3]_2$ were purchased (Strem) and used as received. $[\text{CpCr}(\text{CO})_3]_2$, $[\text{Cp}^*\text{M}(\text{CO})_3]_2$ ($\text{M}=\text{Cr}, \text{Mo}$)²¹, and $[\text{C}_5\text{Ph}_5\text{Cr}(\text{CO})_3]\cdot\text{C}_6\text{H}_6$ ¹² were prepared according to literature procedures.

Infrared spectra were recorded on a Nicolet 20 DXB FTIR spectrometer. Melting points were obtained in the Vacuum Atmospheres glovebox and are uncorrected. NMR spectra were obtained using a 500 MHz Varian spectrometer. UV-visible spectra were obtained using Hewlett Packard 8452A Diode Array

Spectrophotometer . Electrochemical data were obtained on an EG&G PAR VersaStat Model 250-1 Electrochemical Analysis system. Freshly distilled CH₃CN was employed as the solvent, with a supporting electrolyte of 0.1 M n-Bu₄NPF₆ (recrystallized from 95% ethanol). Solutions were ca. 1 mM in complex. All data were obtained with a Pt disk working electrode and an Ag/Ag⁺ reference electrode. Elemental analyses were performed by Mickroanalytisches Labor Pascher, Remagen, Germany.

Synthesis of [(C₅H₅)Cr(CO)₂dmpe]PF₆ (1)

[(C₅H₅)Cr(CO)₃]₂ (0.500 g, 1.24 mmol) and [(C₅H₅)₂Fe]PF₆ (0.850 g, 2.57 mmol) were dissolved in dichloromethane (40 mL). Dmpe (0.5 mL, 3 mmol) was added to the reaction flask, resulting in the formation of a white gas. The initial reaction color was dark-green, The reaction mixture was heated to reflux overnight to yield a yellow-orange solution. The mixture was filtered via cannula and dried *in vacuo*. Hexane (20 mL) was added and solution was filtered via cannula and the resulting yellow solid was dried *in vacuo* to yield 0.41 g (0.88 mmol, 71%) of [(C₅H₅)Cr(CO)₂dmpe]PF₆. Mp: 152-153 °C (dec). Anal. Calcd for C₁₃H₂₁CrF₆O₂P₃: C, 33.35; H, 4.52. Found: C, 33.32; H, 4.55.

Synthesis of [(C₅H₅)Cr(CO)₂dppe]PF₆ (2)

[(C₅H₅)Cr(CO)₃]₂ (1.00 g, 2.48 mmol), dppe (2.18 g, 5.48 mmol) and [(C₅H₅)₂Fe]PF₆ (1.81 g, 5.47 mmol) were dissolved in THF (40 mL). The initial color of the reaction mixture was green. The reaction was heated to reflux overnight yielding a brown-yellow solution with a yellow precipitate. The mixture

was filtered via cannula and the resulting yellow solid was washed with 10 mL of THF. The mixture was filtered via cannula and the resulting yellow solid was dried *in vacuo* to yield 2.94 g (4.11 mmol, 82%) of $[(C_5H_5)Cr(CO)_2dppe]PF_6$. Mp: 187-190°C (dec).

Synthesis of $[(C_5H_5)Mo(CO)_2dmpe]PF_6$ (3)

$[(C_5H_5)Mo(CO)_3]_2$ (0.500 g, 1.02 mmol) and $[(C_5H_5)_2Fe]PF_6$ (0.700 g, 2.11 mmol) were dissolved in dichloromethane (40 mL). Dmpe (0.40 mL, 2.4 mmol) was added to the reaction flask yielding an initially red mixture. The reaction was heated to reflux overnight producing an orange solution, which was filtered via cannula and dried *in vacuo*. Hexane (20 mL) was added the solution was filtered via cannula and the resulting yellow solid was dried *in vacuo* to yield 0.411 g (1.43 mmol, 70%) of $[(C_5H_5)Cr(CO)_2dppe]PF_6$. Mp: 170-173 °C (dec). Anal. Calcd for $C_{13}H_{21}MoF_6O_2P_3$: C, 30.49; H, 4.13. Found: C, 30.27; H, 4.29.

Synthesis of $[(C_5H_5)Mo(CO)_2dppe]PF_6$ (4)

$[(C_5H_5)Mo(CO)_3]_2$ (1.00 g, 2.04 mmol), dppe (1.63 g, 4.10 mmol) and $[(C_5H_5)_2Fe]PF_6$ (1.35 g, 4.08 mmol) were dissolved in THF (40 mL). The initial color of the reaction mixture was red. The reaction was heated to reflux overnight yielding a orange-yellow solution with a yellow precipitate. The mixture was filtered via cannula and the resulting yellow solid was washed with 10 mL of THF. The mixture was filtered via cannula and the resulting yellow solid was

dried *in vacuo* to yield 2.08 g (2.74 mmol, 70%) of $[(C_5H_5)Cr(CO)_2dppe]PF_6$.

Mp: 182-184 °C (dec).

Synthesis of $[(C_5Me_5)Cr(CO)_2dmpe]PF_6$ (5)

$[(C_5Me_5)Cr(CO)_3]_2$ (0.500 g, 0.92 mmol) and $[(C_5H_5)_2Fe]PF_6$ (0.610 g, 1.84 mmol) were dissolved in dichloromethane (40 mL). Dmpe (0.40 mL, 2.40 mmol) was added to the reaction flask yielding a black mixture. The reaction was heated to reflux overnight producing a green solution. The mixture was filtered via cannula and dried *in vacuo*. Hexane (20 mL) was added and filtered via cannula and the resulting green solid was dried *in vacuo* to yield 0.72 g (1.33 mmol, 73%) of $[(C_5Me_5)Cr(CO)_2dppe]PF_6$. Mp: 145-147 °C.

Synthesis of $[(C_5Me_5)Cr(CO)_2dppe]PF_6$ (6)

$[(C_5Me_5)Cr(CO)_3]_2$ (0.500 g, 0.92 mmol), dppe (0.630 g, 1.58 mmol) and $[(C_5H_5)_2Fe]PF_6$ (0.53 g, 1.60 mmol) were dissolved in THF (40 mL). The initial color of the reaction mixture was deep red. The reaction was heated to reflux overnight yielding a brown-yellow solution with a yellow precipitate. The mixture was filtered via cannula and the resulting yellow solid was washed with 10 mL of THF. The mixture was filtered via cannula and the resulting yellow solid was dried *in vacuo* to yield 1.12 g (1.42 mmol, 77%) of $[(C_5Me_5)Cr(CO)_2dppe]PF_6$. Mp: 196-198 °C (dec).

Synthesis of $[(C_5Me_5)Mo(CO)_2dmpe]PF_6$ (7)

$[(C_5Me_5)Mo(CO)_3]_2$ (0.30 g, 0.47 mmol) and $[(C_5H_5)_2Fe]PF_6$ (0.38 g, 1.15 mmol) were dissolved in dichloromethane (30 mL). Dmpe (0.20 mL, 1.20 mmol) was added to the reaction flask yielding a deep red mixture. The reaction was heated to reflux overnight yielding a brown-orange solution. The mixture was filtered via cannula and dried *in vacuo*. Hexane (20 mL) was added and then filtered via cannula and the resulting yellow solid was dried *in vacuo* to yield 0.95 g (1.21 mmol, 77%) of $[(C_5Me_5)Mo(CO)_2dmpe]PF_6$. Mp: 135-137°C (dec).

Synthesis of $[(C_5Me_5)Mo(CO)_2dppe]PF_6$ (8)

$[(C_5Me_5)Mo(CO)_3]_2$ (0.500 g, 0.79 mmol), dppe (0.630 g, 1.58 mmol) and $[(C_5H_5)_2Fe]PF_6$ (0.53 g, 1.60 mmol) were dissolved in THF (40 mL). The initial color of the reaction mixture was red. The reaction was heated to reflux overnight yielding a brown-yellow solution with a yellow precipitate. The mixture was filtered via cannula and the resulting yellow solid was washed with 10 mL of THF. The mixture was filtered via cannula and the resulting yellow solid was dried *in vacuo* to yield 1.01 g (1.22 mmol, 77%) of $[(C_5Me_5)Cr(CO)_2dppe]PF_6$. Mp: 148-150°C (dec).

Synthesis of $[(C_5Ph_5)Cr(CO)_2dmpe]PF_6$ (9)

$[(C_5Ph_5)Cr(CO)_3] \cdot C_6H_6$ (0.60 g, 0.91 mmol) and $[(C_5H_5)_2Fe]PF_6$ (0.32 g, 0.97 mmol) were dissolved in dichloromethane (30 mL). Dmpe (0.20 mL, 1.20 mmol) was added to the reaction flask yielding a green mixture. The reaction

was stirred overnight yielding a green solution. The mixture was filtered via cannula and dried *in vacuo*. Hexane (20 mL) was added, then the mixture was filtered via cannula, and the resulting green solid was dried *in vacuo* to yield 0.55 g (0.66 mmol, 73%) of $[(C_5Me_5)Mo(CO)_2dmpe]PF_6$. Mp: 135-137°C (dec).

Purification of Compounds

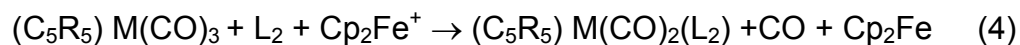
All solids were recrystallized by dissolving the powder in 5 mL or 10 mL dichloromethane and layering with equal amounts of hexane. The two layers were allowed to mix over a period of 1 week and crystals were formed. The only compound that was unable to be purified by recrystallization was $[(C_5Me_5)Mo(CO)_2dmpe]^+$. This compound was dissolved in dichloromethane and excess hexane was added to precipitate the product out. All compounds were further purified by washing with ether, dissolving in dichloromethane, filtering via cannula, and finally removal of solvent *in vacuo*.

CHAPTER III

Results and Discussion

Synthesis

The addition of the bidentate Lewis bases 1,2- bis(dimethyl-phosphino)ethane (dmpe) or 1,2-bis(diphenylphosphino)ethane (dppe) to a mixture of $[(C_5R_5)M(CO)_3]_x$ ($X= 2$ for $R= H, Me, Ph$; $M = Cr, Mo$ and $X=1$ for $M=Cr, R=Ph$) and $[Cp_2Fe]PF_6$, produces $[(C_5R_5)M(CO)_2dmpe]^+$ or $[(C_5R_5)M(CO)_2dppe]^+$ except for $M=Cr, R=Ph$, respectively (eq 4).



All of the compounds except $[(C_5Ph_5)Cr(CO)_2dmpe]PF_6$ were prepared at reflux. In compounds **1-8**, the starting materials were $[(C_5R_5)M(CO)_3]_2$ and require heat to cleave the dimer into the 17e monomers that react with the ligands. The reaction that yielded $[(C_5Ph_5)Cr(CO)_2dmpe]PF_6$ occurs at room temperature because the starting carbonyl complex is a monomer. All dmpe reactions were carried out in dichloromethane, while reactions with dppe were conducted in THF. The ionic dppe materials were synthesized in THF because 50% of product precipitated from solution, making isolation and purification of compounds simpler. Unfortunately, not all of the compound precipitated unless a twofold excess of hexane was added to the reaction solution. This technique of adding excess hexane to the reaction solution was used on all compounds

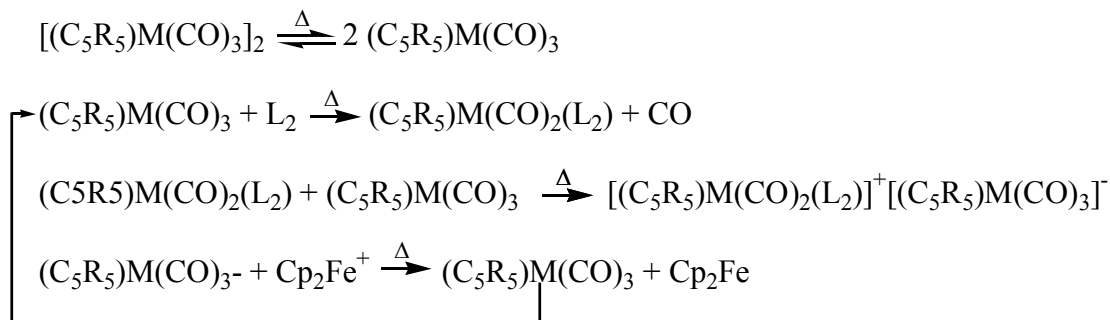
(dmpe and dppe) to maximize yields. If the twofold excess of hexane was not added to the reaction mixture the yields decreased by 5-10% with the dmpe or by 20-30% with the dppe compounds. THF was also used as a solvent for dmpe reactions but yields for $[(C_5H_5)Cr(CO)_2dmpe]PF_6$ and $[(C_5H_5)Mo(CO)_2dmpe]PF_6$ were significantly lower, 55% and 51% compared to 71% and 70% in dichloromethane. Dichloromethane was also used for dppe reactions but yields were lower for $[(C_5H_5)Cr(CO)_2dppe]PF_6$ and $[(C_5H_5)Mo(CO)_2dppe]PF_6$ 45% and 59% respectively compared to 82% and 70% in THF. These trends were also seen in compounds **5** vs. **7** and **6** vs. **8**. Purification was also more difficult when using THF for the dmpe reactions and Dichloromethane for the dppe reactions.

The dmpe ligand reacted rapidly with the $(C_5R_5)M(CO)_3$ complexes at room temperature, but reflux was used to accelerate the reaction. The dppe ligand required 12-24 hours at reflux to complete the reaction. Dmpe reacted with all starting metal complexes, however the larger dppe did not react with $(C_5Ph_5)Cr(CO)_3$, presumably because the steric hindrance of the phenyl groups substituted on the Cp ring, the small atomic size of Cr atom, and the large dppe ligand. The reaction was tried in both solvents with extended reflux (48 hrs) and no reaction occurred.

It is well known that 17e complexes undergo substitution reactions via associative pathways.¹¹ The reactions of dmpe and dppe with the metal complexes yield products and occur at rates consistent with associative pathways. The 17e complexes undergo associative pathways because the complex is electron deficient. This allows the complex to associate with the

incoming ligand before the CO is cleaved thus allowing for possible 19e intermediates.

A plausible mechanism for reaction (4) is shown in Scheme 2 below.



Scheme 2

The syntheses of analogs to compounds **1-9** are accomplished with the bidentate ligands without the use of the oxidant ferrocenium hexafluorophosphate, $[Cp_2Fe]PF_6$, however the resulting compounds have the formula $[CpM(CO)_2L_2]^+[CpM(CO)_3]^-$. Copeland and Castellani first observed this in the reaction of $(C_5Ph_5)Cr(CO)_3$ and bis(1,2-diethylphosphino)ethane (depe).¹⁵



The disadvantage of this procedure is that the $(C_5R_5)M(CO)_3$ starting material disproportionates causing half of the comparatively expensive starting material to be lost in the synthesis of compound. Adding $[Cp_2Fe]PF_6$ as an oxidant causes the 18e $[C_5Ph_5Cr(CO)_3]^-$ to be oxidized back to the 17e starting material, leaving PF_6^- as the counter ion to $[C_5R_5M(CO)_2L]^+$. The regenerated

starting complex can then react with another equivalent of ligand, thus potentially doubling the reaction yields.

IR Spectroscopy

Infrared spectral data are compiled in Table 1. The IR data show complexes incorporating a Mo metal center to always have higher energy CO stretches than corresponding complexes with a Cr metal center. In general, the energy of the CO stretch increases as you move down Group VI because of the increased force constants between the carbon and the oxygen bond.²⁰ Also, the resulting compounds **1-9** should have higher energy CO stretches than the CO stretches in the starting material due to the cationic charge on the species and this is observed in Table 1.²⁰

The lower energy CO stretches of Cp*M(CO)₂(L₂) compared to CpM(CO)₂(L₂) or (C₅Ph₅) M(CO)₂(L₂) are caused by the methyl groups being more electron releasing than the hydrogen or phenyl groups. This greater electron density available to the metal leads to increased π^* backbonding to the CO by the metal. Increased backbonding reduces the strength of the CO bond because backbonding occurs between the metal d orbital and the π^* orbital of the CO.²⁰ This in turn lowers the CO stretching frequency. The dmpe complexes should have lower energy CO stretches than the dppe due to the electron donating of the methyl groups. This trend is observed in Table 1 except for the Cp* series which is, surprisingly, reversed. In general, the Mo complexes should

have higher energy stretches than the corresponding Cr compounds. The Mo has larger and more dispersed d-orbitals, which causes weaker backbonding.

IR spectra were acquired in THF, which is a weakly coordinating solvent and Dichloromethane, which is not. If the solvent coordinated to the complexes, the positions of the CO stretches would change measurably between the two solvents seen in Table 1. No appreciable difference in the CO stretching frequencies between two solvents exists suggesting little or no interaction between the metal and the solvent.

NMR Spectroscopy

The NMR data seen in Table 2 and 3 were acquired in CD_2Cl_2 . H_3PO_4 was used as an external standard for ^{31}P NMR spectra, but PF_6^- was also used as an internal reference. The PF_6^- heptet was centered at -142 ppm in all spectra. As seen in Table 3 the ^{31}P resonances for the CpCr series are further downfield by about 5 ppm than the CpMo series for both the dmpe and dppe series. The same is true for the C_5Me_5 series. The C_5Me_5 series is further upfield because the phosphorus is more shielded by the added electron donation to the metal by the methyl groups. Consistent with this the ^{31}P NMR resonances for the dmpe complexes occur further upfield than the dppe complexes.

The ^1H NMR allows for the observation of the dynamic process associated with the interconversion of different ring conformations of the five membered ring formed by the metal and the bidentate phosphines (Fig. 6).

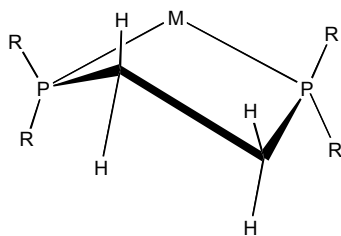


Figure 6

The tetrahedral geometry of the phosphorus and carbon atoms on the ring causes the ring to pucker. As in cyclopentadiene, such rings can twist. For this system, our data suggest they do so at different rates. At the slow limit the four methylene hydrogens are non-equivalent. At the fast limit those above the ring plane will be equivalent, as will those below it, resulting in two resonances. Also seen is an intermediate rate where two sets of singlets are observed.

The ^1H NMR spectra were acquired under the same conditions as the ^{31}P NMR spectra. The resonances for the Cp protons were found to have the expected chemical shifts as well as the phenyl peaks and the methyl peaks on the C_5Me_5 and C_5Ph_5 series, respectively as seen in Table 2.

UV-Visible Spectroscopy

All UV-Visible spectral data are collected in Table 4.

Electrochemistry

All electrochemical data are collected in Table 5. Hexafluorophosphate ion was chosen as the counter ion because it is electrochemically inactive in the voltage regions available in CH_3CN . It is expected that the molybdenum complexes would have approximately the same reduction potential as the

corresponding chromium complexes because they possess similar electron affinities and ionization potentials. This trend is seen in Table 4. In previous research $[(C_5H_5)Cr(CO)_3PMe_3]^+$ was reduced at a potential 0.25 V more positive than the corresponding $[(C_5Me_5)Cr(CO)_3PMe_3]^+$.¹⁵ As seen in Table 5, the addition of more electron density by changing from Cp to Cp* has no significant effect on the electron transfer potentials. This observation is likely because the majority of the electron transfer potential relies on the ligand attached to the phosphine. The dmpe series compared to the dppe series should have a more negative reduction potential due to the increased electron density around the metal atom and the phosphine. This trend is observed in Table 5.

The oxidation sweep of the compounds shows that the oxidative potential derives from a molecular orbital based on the metal, Cp, and phosphine. As seen in Scheme 1, after the reduction, one of the bonds between the bidentate ligand and metal breaks, causing the formation of a 17e complex. As seen in Table 5 the dmpe and the (C_5Me_5) complexes are easier to oxidize than the dppe and the Cp complexes.

There are four different regions in the voltammogram (A, B, C, D) in Fig. 7.

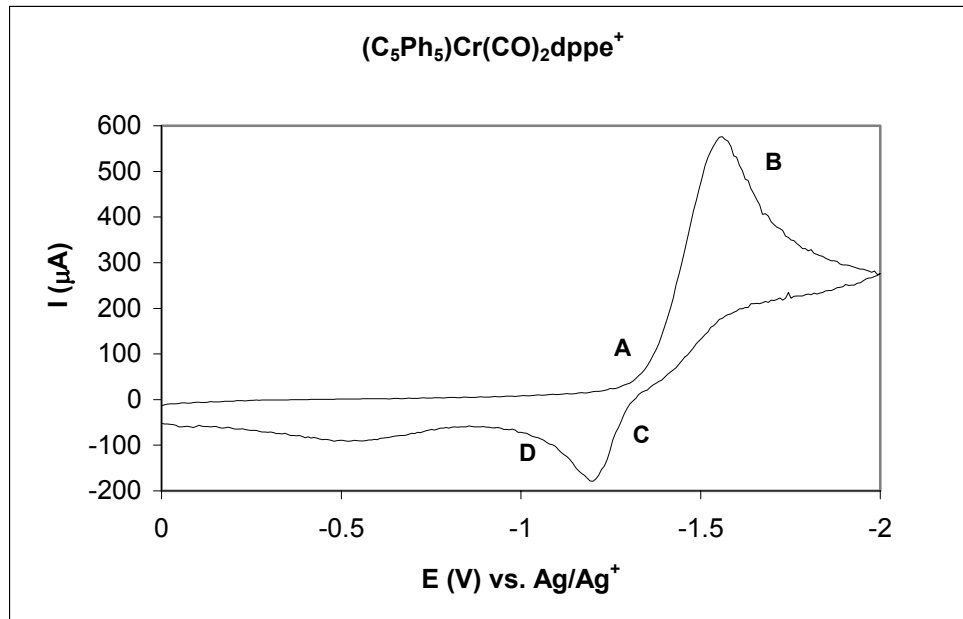


Figure 7

Region A refers to the complex $(C_5R_5)M(CO)_2(\eta^2-L_2)^+$ which is compounds 1-8. Once the compound is reduced it enters region B, $(C_5R_5)M(CO)_2(\eta^2-L_2)$. This is the 19e species that has a very short lifetime as seen in Fig 7. Region C is $(C_5R_5)M(CO)_2(\eta^1-L_2)$ which is a 17e species that is monodentate. The region D is a 16e $(C_5R_5)M(CO)_2(\eta^1-L_2)^+$. As Fig. 3 shows compounds **1-8** have an irreversible oxidation and reduction.

Stability Tests

All compounds were dissolved in Dichloromethane, exposed to the air, and placed in sealed test tubes. Infrared spectra were taken at 0 min, 8 hours, 24 hours, 1 week, 2 weeks, 3 weeks, and 1 month. There was no appreciable change in CO intensity, indicating that the compounds are air-stable. Solid-state

air sensitivity was not tested because compounds that are air-stable in solution are typically air-stable in the solid state.

CHAPTER IV

Conclusion

Compounds **1-8**, air-stable 18e complexes, were synthesized in good yields. ^1H and ^{31}P NMR, IR, and electrochemical data were compiled for the product complexes. The electrochemical data shows a single irreversible reduction and a single irreversible oxidation suggesting in compounds **1-8** the 19e complexes are not isolable or observable at ambient temperatures.

Table 1. Infrared Spectral Data for (C₅R₅)M(CO)₂(L₂) Complexes

Complex	Solvent		reference
	ν(C≡O), cm ⁻¹ , ^a		
	THF	CH ₂ Cl ₂	
(C ₅ H ₅)Cr(CO) ₃	2012, 1948, 1925		21
(C ₅ H ₅)Cr(CO) ₂ dmpe ⁺	1959, 1889	1967, 1909	This work
(C ₅ H ₅)Cr(CO) ₂ dppe ⁺	1965, 1907	1971, 1916	This work
(C ₅ H ₅)Mo(CO) ₃	1959, 1916, 1905		21
(C ₅ H ₅)Mo(CO) ₂ dmpe ⁺	1975, 1908	1980, 1913	This work
(C ₅ H ₅)Mo(CO) ₂ dppe ⁺	1979, 1911	1984, 1919	This work
(C ₅ Me ₅)Cr(CO) ₃	1918, 1877, 1848		21
(C ₅ Me ₅)Cr(CO) ₂ dmpe ⁺	1943, 1884	1951, 1891	This work
(C ₅ Me ₅)Cr(CO) ₂ dppe ⁺	1941, 1880	1947, 1887	This work
(C ₅ Me ₅)Mo(CO) ₃	1940, 1907		21
(C ₅ Me ₅)Mo(CO) ₂ dmpe ⁺	1958, 1887	1967, 1897	This work
(C ₅ Me ₅)Mo(CO) ₂ dppe ⁺	1956, 1889	1964, 1897	This work
(C ₅ Ph ₅)Cr(CO) ₃	1897, 1792		21
(C ₅ Ph ₅)Cr(CO) ₂ dmpe ⁺	1948, 1892	1953, 1900	This work

^aAll absorptions are strong.

Table 2. ^1H NMR Data for $(\text{C}_5\text{R}_5)\text{M}(\text{CO})_2(\text{L}_2)$ Complexes

Compound	Cp	C_5Me_5	dmpe	dppe
$(\text{C}_5\text{H}_5)\text{Cr}(\text{CO})_2\text{dmpe}^+$	4.97		2.27, 2.12, 1.86, 1.53	
$(\text{C}_5\text{H}_5)\text{Cr}(\text{CO})_2\text{dppe}^+$	4.57			7.70, 7.55, 7.33, 3.68, 3.21, 2.67, 1.82
$(\text{C}_5\text{H}_5)\text{Mo}(\text{CO})_2\text{dmpe}^+$	5.45		1.76, 1.71	
$(\text{C}_5\text{H}_5)\text{Mo}(\text{CO})_2\text{dppe}^+$	4.75			7.61, 7.48, 7.44, 3.69, 2.97, 2.25, 1.83
$(\text{C}_5\text{Me}_5)\text{Cr}(\text{CO})_2\text{dmpe}^+$		1.92		
$(\text{C}_5\text{Me}_5)\text{Cr}(\text{CO})_2\text{dppe}^+$		1.48		7.77, 7.53, 7.31, 3.69, 3.22, 2.94, 1.82
$(\text{C}_5\text{Me}_5)\text{Mo}(\text{CO})_2\text{dmpe}^+$		1.98		
$(\text{C}_5\text{Me}_5)\text{Mo}(\text{CO})_2\text{dppe}^+$		1.47		7.56, 7.27, 7.18, 3.45, 2.69, 2.59, 1.16

Table 3. ^{31}P NMR Data for $(\text{C}_5\text{R}_5)\text{M}(\text{CO})_2(\text{L}_2)$ Complexes

Compound	ppm
$(\text{C}_5\text{H}_5)\text{Cr}(\text{CO})_2\text{dmpe}^+$	84.78
$(\text{C}_5\text{H}_5)\text{Cr}(\text{CO})_2\text{dppe}^+$	101.6
$(\text{C}_5\text{H}_5)\text{Mo}(\text{CO})_2\text{dmpe}^+$	53.47
$(\text{C}_5\text{H}_5)\text{Mo}(\text{CO})_2\text{dppe}^+$	80.62
$(\text{C}_5\text{Me}_5)\text{Cr}(\text{CO})_2\text{dmpe}^+$	80.05
$(\text{C}_5\text{Me}_5)\text{Cr}(\text{CO})_2\text{dppe}^+$	95.10
$(\text{C}_5\text{Me}_5)\text{Mo}(\text{CO})_2\text{dmpe}^+$	58.77, 49.12
$(\text{C}_5\text{Me}_5)\text{Mo}(\text{CO})_2\text{dppe}^+$	75.57
$(\text{C}_5\text{Ph}_5)\text{Cr}(\text{CO})_2\text{dmpe}^+$	78.46, 42.91, 30.40

Table 4. UV-Visible Data for (C₅R₅)M(CO)₂(L₂) Complexes

Compound	Max wavelength λ
(C ₅ H ₅)Cr(CO) ₂ dmpe ⁺	288
(C ₅ H ₅)Cr(CO) ₂ dppe ⁺	288
(C ₅ H ₅)Mo(CO) ₂ dmpe ⁺	274
(C ₅ H ₅)Mo(CO) ₂ dppe ⁺	280
(C ₅ Me ₅)Cr(CO) ₂ dmpe ⁺	282
(C ₅ Me ₅)Cr(CO) ₂ dppe ⁺	288
(C ₅ Me ₅)Mo(CO) ₂ dmpe ⁺	280
(C ₅ Me ₅)Mo(CO) ₂ dppe ⁺	282
(C ₅ Ph ₅)Cr(CO) ₂ dmpe ⁺	302

Table 5. Electrochemistry for (C₅R₅)M(CO)₂(L₂) Complexes

Compound	Volts		
(C ₅ H ₅)Cr(CO) ₂ dmpe ⁺	-2.07	-1.39	
(C ₅ H ₅)Cr(CO) ₂ dppe ⁺	-1.6	-1.18	
(C ₅ H ₅)Mo(CO) ₂ dmpe ⁺	-2.03	-1.22	
(C ₅ H ₅)Mo(CO) ₂ dppe ⁺	-1.73	-1.08	
(C ₅ Me ₅)Cr(CO) ₂ dmpe ⁺	-2.06	-1.48	
(C ₅ Me ₅)Cr(CO) ₂ dppe ⁺	-1.81	-1.32	-0.35
(C ₅ Me ₅)Mo(CO) ₂ dmpe ⁺	-2.08	-1.36	
(C ₅ Me ₅)Mo(CO) ₂ dppe ⁺	-1.79	-1.22	

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