THERMAL AND FLASH PHOTOLYSIS STUDIES OF LIGAND-EXCHANGE REACTIONS OF SUBSTITUTED METAL CARBONYL COMPLEXES OF Cr AND Mo

DISSERTATION

Presented to the Graduate Council of the University of North Texas in Partial Fulfillment of the Requirements For the Degree of

DOCTOR OF PHILOSOPHY

By

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May, 1989
Thermal and flash photolysis studies of ligand-substitution reactions of cis-\((\text{pip})(\text{L})\text{M(CO)}_4\) by \(\text{L}'\) (pip = piperidine; \(\text{L}, \text{L}' = \text{CO, phosphines, phosphites; M = Cr, Mo}\) implicate square-pyramidal \([\text{L}\text{M(CO)}_4]\), in which \(\text{L}\) occupies a coordination site in the equatorial plane, as the reactive species. In chlorobenzene (= CB) solvent, the predominant species formed after flash photolysis and a steady-state intermediate for the thermal reaction is cis-
\([\text{CB}(\text{L})\text{M(CO)}_4]\), for which rates of CB-dissociation increase with increasing steric demands of coordinated \(\text{L}\). Rates of CB-dissociation from trans-\([\text{CB}(\text{L})\text{M(CO)}_4]\) intermediates, formed after photolysis but not thermally, exhibit no observable dependence on the steric properties of the coordinated \(\text{L}\).
TABLE OF CONTENTS

LIST OF TABLES ............................................. v
LIST OF ILLUSTRATIONS ................................. viii
LIST OF ABBREVIATIONS ................................. xii

Chapter

I. INTRODUCTION ............................................. 1

Reactivity and Bonding of Metal Carbonyls
Problem

II. THE FLASH PHOTOLYSIS SYSTEM ..................... 22

III. EXPERIMENTAL SECTION ............................... 49

Purification of Solvents and Ligands
Synthesis of the Compounds
Thermal Kinetics
Photochemical Kinetics
The Products of the Thermal and Photochemical Reactions

IV. PARALLEL THERMAL AND PULSED LASER FLASH
PHOTOLYSIS STUDY OF cis-(pip)(L)M(CO)₄ (PIP = PIPERIDINE, L = PHOSPHINES AND PHOSPHITES,
M = Mo, Cr) .............................................. 60

Introduction
The Thermal Reactions Studies
Pulsed Laser and Flash Photolysis Studies
Reaction of the cis Photochemically Generated Species in Chlorobenzene (CB) Solution
The Reaction of the trans Photochemically Generated Species in CB Solution
The Photochemical Reaction in Cyclohexane
The Reaction of the trans Photochemically Generated Species in Cyclohexane (CH) Solution

APPENDIX A ............................................... 128
## TABLE OF CONTENTS—Continued

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>APPENDIX B</td>
<td>131</td>
</tr>
<tr>
<td>BIBLIOGRAPHY</td>
<td>171</td>
</tr>
</tbody>
</table>
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. Steric and electronic properties of phosphines and phosphites</td>
<td>6</td>
</tr>
<tr>
<td>II. The values of line increments for the corresponding voltage range selected on the digital oscilloscope</td>
<td>33</td>
</tr>
<tr>
<td>III. The rate constants obtained from the flash photolysis of Cr(CO)₆ in the presence of pip in CB at 31.1 °C</td>
<td>41</td>
</tr>
<tr>
<td>IV. The rate constants obtained from the flash photolysis of cis-(pip)(CP)Mo(CO)₄ in the presence of pip in CB at 31.1 °C</td>
<td>42</td>
</tr>
<tr>
<td>V. The IR stretching frequencies of cis-(pip)(L)-M(CO)₄ in cyclohexane</td>
<td>54</td>
</tr>
<tr>
<td>VI. Elemental analysis of cis-(pip)(L)M(CO)₄</td>
<td>55</td>
</tr>
<tr>
<td>VII. IR-stretching frequencies of (L)(L')M(CO)₄ in CB</td>
<td>58</td>
</tr>
<tr>
<td>VIII. The pseudo first-order rate constants for the reaction of cis-(pip)(L)Mo(CO)₄ with P(O-i-Pr)₃ in the presence of pip and P(O-i-Pr)₃ in CB at 31.1 °C</td>
<td>62</td>
</tr>
<tr>
<td>IX. The pseudo first-order rate constants for the reaction of cis-(pip)(L)Cr(CO)₄ with P(O-i-Pr)₃ in the presence of pip and P(O-i-Pr)₃ in CB at 31.1 °C</td>
<td>63</td>
</tr>
<tr>
<td>X. The rate constant (k₁) for pip dissociation from cis-(pip)(L)Mo(CO)₄ in CB</td>
<td>70</td>
</tr>
<tr>
<td>XI. The rate constants (k₁) for pip dissociation from cis-(pip)(L)Cr(CO)₄ in CB</td>
<td>70</td>
</tr>
<tr>
<td>XII. Values of k₁ at 31.1 °C, competition ratio and activation parameters for k₁ for the reaction of cis-(pip)(L)Mo(CO)₄ with P(O-i-Pr)₃ in the presence of pip and P(O-i-Pr)₃ in CB</td>
<td>71</td>
</tr>
</tbody>
</table>
LIST OF TABLES—Continued

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>XIII. Values of $k_1$, competition ratios and the activation parameters for $k_1$ for the reaction of cis-(pip)(L)Cr(CO)$_4$ with P(O-i-Pr)$_3$ in the presence of pip and P(O-i-Pr)$_3$ in CB at 31.1 °C</td>
<td>71</td>
</tr>
<tr>
<td>XIV. The steric and electronic parameters for the rate constant of pip dissociation from cis-(pip)(L)M(CO)$_4$</td>
<td>75</td>
</tr>
<tr>
<td>XV. The rate constants ($k_1$) of pip dissociation for cis-(pip)(L)M(CO)$_4$ at 31.1 °C in CB solution. (M = W, Cr, Mo)</td>
<td>76</td>
</tr>
<tr>
<td>XVI. Rate constants for the thermal reaction taking place after flash photolysis of cis-(pip)(L)Mo(CO)$_4$ in the presence of pip or P(O-i-Pr)$_3$ in CB at 31.1 °C</td>
<td>84</td>
</tr>
<tr>
<td>XVII. Rate constant for the thermal reaction taking place after flash photolysis of cis-(pip)(L)Cr(CO)$_4$ in the presence of pip or P(O-i-Pr)$_3$ in CB at 31.1 °C</td>
<td>86</td>
</tr>
<tr>
<td>XVIII. The rate constants for the thermal reaction taking place after pulse laser flash photolysis of cis-(pip)(L)Cr(CO)$_4$ in the presence of L’in CB solution at 31.1 °C. L’ = pip, P(O-i-Pr)$_3$</td>
<td>92</td>
</tr>
<tr>
<td>XIX. The rate constants for the thermal reaction taking place after pulsed laser flash photolysis of cis-(pip)(L)Mo(CO)$_4$ in the presence of L’in CB solution at 31.1 °C</td>
<td>92</td>
</tr>
<tr>
<td>XX. The steric and electronic parameters for the rate constants of $(k_3k_2)/k_3(CB)$</td>
<td>93</td>
</tr>
<tr>
<td>XXI. The rate constants $k_3k_2/k_3(CB)$ ($k'$) obtained for the photochemical reactions of cis-(pip)(L)M(CO)$_4$ with pip at 31.1 °C</td>
<td>95</td>
</tr>
<tr>
<td>XXII. The thermal reaction of the photochemically generated trans-[(CB)(L)M(CO)$_4$] with pip in CB at 31.1 °C</td>
<td>98</td>
</tr>
<tr>
<td>Table</td>
<td>Description</td>
</tr>
<tr>
<td>-------</td>
<td>-----------------------------------------------------------------------------</td>
</tr>
<tr>
<td>XXIII</td>
<td>The rate constants for the reaction of ((\text{CB})(\text{L})\text{M(CO)}_4) with pip at 31.1 °C</td>
</tr>
<tr>
<td>XXIV</td>
<td>The Cr-PPh\textsubscript{3} bond lengths of ((\text{PPh}_3)(\text{L})\text{Cr(CO)}_4)</td>
</tr>
<tr>
<td>XXV</td>
<td>The rate constants for the reaction of ((\text{CB})(\text{P(O-i-Pr)}_3)\text{M(CO)}_4) with pip in CH at 31.1 °C</td>
</tr>
<tr>
<td>XXVI</td>
<td>The rate constants for the reaction of ((\text{CB})(\text{P(O-i-Pr)}_3)\text{Mo(CO)}_4) with pip in CH</td>
</tr>
<tr>
<td>XXVII</td>
<td>The rate constants for the reaction of ((\text{CB})(\text{P(O-i-Pr)}_3)\text{Mo(CO)}_4) with pip and \text{CB in CH}</td>
</tr>
</tbody>
</table>
LIST OF ILLUSTRATIONS

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. The σ-donation and π back-bonding of CO with the metal d orbitals</td>
<td>2</td>
</tr>
<tr>
<td>2. Cone angle for tri-substituted phosphorus ligand as defined by Tolman</td>
<td>4</td>
</tr>
<tr>
<td>3. Electronic excitation effect on ligand loss from M(CO)₅(L)</td>
<td>11</td>
</tr>
<tr>
<td>4. The voltage divider construction for the PMT R298</td>
<td>24</td>
</tr>
<tr>
<td>5. The PMT output signal recorded by the oscilloscope a) when no back-off is used, b) when back-off is used</td>
<td>26</td>
</tr>
<tr>
<td>6. The triggering sequence of the slow and fast shutter, back-off, oscilloscope and the xenon lamps</td>
<td>28</td>
</tr>
<tr>
<td>7. The computer to oscilloscope line connection for data transfer</td>
<td>30</td>
</tr>
<tr>
<td>8. Line increments on the digital oscilloscope screen</td>
<td>32</td>
</tr>
<tr>
<td>9. Flash photolysis data of cis-(pip)-(P(O-i-Pr)₃)W(CO)₄ in the presence of pip in CB solution at 31.1 °C. a) plot of absorbance vs. time before and after the flash, b) plot of ln(A₀ - A∞) vs. time, c) plot of ln(A₀ - A∞) vs. time for the slow decay, d) plot of absorbance vs. time for the fast decay, and e) plot of ln(A₀ - A∞) vs. time for the fast decay</td>
<td>36</td>
</tr>
<tr>
<td>10. The flash photolysis system consists of high energy photolyzing micropulser (MP), two power supplies (P₁, P₂), fast and slow shutters (S₁, S₂), sample (S), xenon flash lamps (L₁, L₂), back-off (BO), monochromater (M), PMT (P), oscilloscope (SC), computer (CMF), lotter (FL) and printer (PR)</td>
<td>38</td>
</tr>
<tr>
<td>Figure</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>------</td>
</tr>
<tr>
<td>11. Plot of $k_{\text{obs}}$ (s$^{-1}$) vs. [pip] (M) for the photochemical reaction of Cr(CO)$_6$ and pip in CB at 31.1 °C</td>
<td>43</td>
</tr>
<tr>
<td>12. Plot of $k_{\text{obs}}$ (s$^{-1}$) vs. [pip] (M) for the photochemical reaction of cis-(pip)(CP)-M(CO)$_4$ and pip in CB at 31.1 °C</td>
<td>44</td>
</tr>
<tr>
<td>13. Plots of $k_{\text{obs}}$ (s$^{-1}$) vs. [P(O-i-Pr)$_3$/[pip] for the reaction of cis-(pip)(L)Mo(CO)$_4$ with P(O-i-Pr)$_3$ in the presence of pip in CB at 31.1 °C</td>
<td>64</td>
</tr>
<tr>
<td>14. Plots of $1/k_{\text{obs}}$ (s) vs. [pip]/[P(O-i-Pr)$_3$] for the reaction of cis-(pip)(L)Mo(CO)$_4$ with P(O-i-Pr)$_3$ in the presence of pip and P(O-i-Pr)$_3$ in CB at 31.1 °C</td>
<td>66</td>
</tr>
<tr>
<td>15. a) Plots of $1/k_{\text{obs}}$ (s) vs. [pip]/[P(O-i-Pr)$<em>3$], b) Plots of $k</em>{\text{obs}}$ (s$^{-1}$) vs. [P(O-i-Pr)$_3$]/[pip] for the reaction of cis-(pip)(L)Cr(CO)$_4$ with P(O-i-Pr)$_3$ in the presence of pip in CB at 31.1 °C</td>
<td>67</td>
</tr>
<tr>
<td>16. The mechanism for the thermal reaction of cis-(pip)(L)M(CO)$_4$ with P(O-i-Pr)$_3$(L') in the presence of pip in CB solution</td>
<td>68</td>
</tr>
<tr>
<td>17. The Eyring plots of ln($k_1/T$) vs. 1/T for the rate constants for pip loss from cis-(pip)(L)Cr(CO)$_4$</td>
<td>73</td>
</tr>
<tr>
<td>18. Plot of absorbance vs. time before and after pulsed laser flash photolysis of cis-(pip)-(P(O-i-Pr)$_3$)Mo(CO)$_4$ in the presence of pip in CB solution at 31.1 °C</td>
<td>79</td>
</tr>
<tr>
<td>19. Plot of absorbance vs. time before and after pulsed laser flash photolysis of cis-(pip)-(P(O-i-Pr)$_3$)Mo(CO)$_4$ in the presence of pip in CH solution at 20.2 °C</td>
<td>80</td>
</tr>
<tr>
<td>20. The products formed after the pulsed laser flash photolysis of cis-(pip)(L)M(CO)$_4$.</td>
<td>81</td>
</tr>
</tbody>
</table>
## LIST OF ILLUSTRATIONS--Continued

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>21.</td>
<td>Plots of $k_{\text{obs}} \ (s^{-1})$ vs. $[L'] \ (M)$ for the reaction of cis-$[(\text{CB})(L)\text{Mo(CO)}_4]$ with $L'$ in CB at 31.1 °C. $L' = \text{pip, P(O-i-Pr)}_3$</td>
<td>88</td>
</tr>
<tr>
<td>22.</td>
<td>Plots of $k_{\text{obs}} \ (s^{-1})$ vs. $[L'] \ (M)$ for the reaction of cis-$[(\text{CB})(L)\text{Cr(CO)}_4]$ with $L'$ in CB at 31.1 °C. $L' = \text{pip, P(O-i-Pr)}_3$</td>
<td>89</td>
</tr>
<tr>
<td>23.</td>
<td>The mechanism for the thermal reaction of photochemically generated cis-$[(\text{CB})(L)\text{M(CO)}_4]$ with $L'$ ($L' = \text{pip, P(O-i-Pr)}_3$) in CB solution</td>
<td>90</td>
</tr>
<tr>
<td>24.</td>
<td>The mechanism for the thermal reaction of photochemically generated trans-$[(\text{CB})(L)\text{M-(CO)}_4]$ with $L'$ ($L' = \text{pip}$)</td>
<td>99</td>
</tr>
<tr>
<td>25.</td>
<td>Plots of $k_{\text{obs}} \ (s^{-1})$ vs. $[\text{pip}] \ (M)$ for the reaction of trans-$[(\text{CB})(L)\text{M(CO)}_4]$ with $L'$ in CB at 31.1 °C</td>
<td>100</td>
</tr>
<tr>
<td>26.</td>
<td>Plots of $k_{\text{obs}} \ (s^{-1})$ vs. $[\text{pip}]/[\text{CB}]$ for the reaction of cis-$[(\text{CB})(\text{P(O-i-Pr)}_3)\text{Mo(CO)}_4]$ with pip in the presence of CB in CH solution. * at 11.0 °C; +, at 20.8 °C, at 31.1 °C</td>
<td>109</td>
</tr>
<tr>
<td>27.</td>
<td>Plots of $k_{\text{obs}} \ (s^{-1})$ vs. $[\text{pip}]/[\text{CB}]$ for the reaction of cis-$[(\text{CB})(\text{P(O-i-Pr)}_3)\text{Cr(CO)}_4]$ with pip in the presence of CB in CH solution. * at 10.9 °C; +, at 20.8 °C, at 31.1 °C</td>
<td>110</td>
</tr>
<tr>
<td>28.</td>
<td>Plots of $1/k_{\text{obs}} \ (s)$ vs. $[\text{CB}]/[\text{pip}]$ for the reaction of cis-$[(\text{CB})(\text{P(O-i-Pr)}_3)\text{Mo(CO)}_4]$ with pip in the presence of CB in CH solution. * at 11.0 °C; +, at 20.8 °C; o, at 31.1 °C</td>
<td>111</td>
</tr>
<tr>
<td>29.</td>
<td>Plots of $1/k_{\text{obs}} \ (s)$ vs. $[\text{CB}]/[\text{pip}]$ for the reaction of cis-$[(\text{CB})(\text{P(O-i-Pr)}_3)\text{Cr(CO)}_4]$ with pip in the presence of CB in CH solution. * at 10.9 °C; +, at 20.8 °C; o, at 31.1 °C</td>
<td>112</td>
</tr>
</tbody>
</table>
## LIST OF ILLUSTRATIONS—Continued

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>30.</td>
<td>The mechanism for the thermal reaction of photochemically generated cis-((\text{CB})(\text{L})\text{M(CO)}_4) with pip and CB in CH</td>
<td>113</td>
</tr>
<tr>
<td>31.</td>
<td>Plots of (1/k_{\text{obs}}) vs. ([\text{CB}]/[\text{pip}]) for the reaction of trans-((\text{CB})(\text{P(O-i-Pr)}_3)\text{M(CO)}_4) with pip in the presence of CB in CH solution. *, at 31.1 °C; o, at 20.8 °C</td>
<td>117</td>
</tr>
<tr>
<td>32.</td>
<td>The mechanism for the thermal reaction of photochemically generated trans-((\text{CB})(\text{P(O-i-Pr)}_3)\text{M(CO)}_4) with pip in the presence of CB in CH solution</td>
<td>118</td>
</tr>
<tr>
<td>33.</td>
<td>The overall mechanism for the thermal and photochemical reaction of cis-((\text{pip})(\text{L})\text{M(CO)}_4) with L'</td>
<td>120</td>
</tr>
<tr>
<td>34.</td>
<td>Plot of enthalpy vs. reaction coordinate for conversion of cis-((\text{pip})(\text{P(O-i-Pr)}_3)\text{M(CO)}_4) to cis-((\text{CB})(\text{P(O-i-Pr)}_3)\text{M(CO)}_4). a) M = Cr, b) M = Mo</td>
<td>121</td>
</tr>
</tbody>
</table>
LIST OF ABBREVIATIONS

1. PMT = Photomultiplier tube
2. pip = Piperidine
3. CB = Chlorobenzene
4. CH = Cyclohexane
5. P(OEt)₃ = Triethyl phosphite
6. P(O-i-Pr)₃ = Triisopropyl phosphite
7. PPh₃ = Triphenylphosphine
8. CP = 4-Methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane
9. P(OMe)₃ = Trimethyl phosphite
10. AsPh₃ = Triphenylarsine
11. SbPh₃ = Triphenylstibine
12. Py = Pyridine
CHAPTER I
INTRODUCTION
REACTIVITY AND BONDING OF METAL CARBONYLS

In 1890 Mond, Carl Langer and Quinke discovered the metal carbonyl Ni(CO)$_4$ by accident. The firm of Mond prepared chlorine from ammonium chloride which was obtained from the ammonia-soda process. One of the obstacles in the production of chlorine was the rapid corrosion of nickel valves on the tanks in which ammonium chloride was vaporized. The corrosion was later found to be the result of carbon monoxide which was present in the carbon dioxide used to sweep ammonia from the vaporizing tanks. The reaction of CO with nickel formed Ni(CO)$_4$. Later on Mond used this reaction to separate nickel from cobalt.

The discovery of Ni(CO)$_4$ opened an area of chemistry which led to the preparation of a large number of metal carbonyls, such as Fe(CO)$_5$, Fe$_2$(CO)$_9$, Mo(CO)$_6$, W(CO)$_6$ and Cr(CO)$_6$. Some of the metal carbonyls have been shown to be useful. For example, Fe(CO)$_5$ was used as an antiknock agent in motor fuels, even though lead tetraethyl is a better antiknock agent. Iron carbonyls are less poisonous.

A well-known feature of metal carbonyls is their adherence to the Effective Atomic Number or rare gas rule,
that is, the central atom accepts a number of additional electrons furnished by the ligands so that the total number of electrons surrounding the metal gives it a formally closed-shell configuration.\(^2\)

The nature of carbonyl bonding to the metal has been discussed in detail in several books.\(^3,4\) The carbonyl group possesses an sp-hybrid lone pair of electrons which will form \(\sigma\)-bond by the overlap with the transition metal d orbitals as shown in Figure 1.

\[\text{Figure 1. The } \sigma\text{-donation and } \pi\text{ back-bonding of CO with the metal d orbitals}\]
The carbonyl group has low-lying \( \pi \)-antibonding orbitals which overlap with filled nonbonding d orbitals of appropriate symmetry on the metal atom as shown in Figure 1. The \( \sigma \) bond donates electron density to the metal, but the \( \pi \) bond removes electron density from the metal atom, therefore, causing an increase in the bond order between the metal atom and the carbon atom, but reducing the bond order between the carbon atom and the oxygen atom. The bond order reduction between carbon and oxygen lowers the CO IR stretching frequencies from 2145 cm\(^{-1}\) to between 2100 cm\(^{-1}\) and 1700 cm\(^{-1}\).

Another feature of metal carbonyls is the ease of monitoring their reaction and identifying products by infrared spectroscopy. Furthermore, a great number of metal carbonyl complexes are colored, which makes monitoring their reaction by visible spectroscopy feasible.

Before discussing the reaction of metal carbonyls it is important to understand the bonding ability of other ligands. For example, Horrocks and Taylor\(^5\) described a series of ligands in descending order of \( \pi \)-acceptor ability. Some of these ligands are listed below:

\[
\text{CO} > \text{PF}_3 > \text{SbCl}_3 > \text{PCl}_3 > \text{P(OR)}_3 > \text{PPh}_3
\]

Unlike the ligands listed above, nitrogen in amines and oxygen in ethers have no \( \pi \)-acceptor properties,\(^6\) only \( \sigma \)-donating properties. The study of the effect of ligands on the environment about the metal has occupied a central place
in inorganic chemistry.\textsuperscript{7} Often a change of ligands bonded to the metal will change the metal's reactivity. For example, tris(triphenylphosphine)rhodium(I) chloride is an active catalyst for the hydrogenation of alkenes, whereas the triphenylarsine analogue is less active, and the triphenyl phosphite analogue is inactive.\textsuperscript{8,9} Tolman\textsuperscript{7} has shown that the steric and electronic properties of ligands influence the reactivity of transition metal complexes. The effect of the steric properties on the reactivity of metal carbonyls results from non-bonding forces between parts of a molecule. The steric factor was defined by Tolman for the tri-substituted phosphorus ligand as the ligand cone angle ($\theta$), that is "the apex angle of a cylindrical cone, centered 2.28 Å from the center of the phosphorus atom, which just touches the Vander Waals radii of the

![Figure 2. Cone angle of tri-substituted phosphorus ligand as defined by Tolman](image-url)
outer most atoms." The 2.28 Å was based on the assumption that the metal-phosphorus bond length remains constant at 2.28 Å. Figure 2 shows the cone angle for symmetric ligands. The cone angle for some of the phosphines and phosphites ligands used in this study are listed in Table I.

Changing the molecular parts of a ligand changes its electronic properties. These properties account for the electronic effect of ligands. For example, triethyl phosphite will have a different electronic effect on the metal center than triethylphosphine. Strohmeier showed that phosphorus ligands can be arranged in a series based on CO stretching frequencies. His arrangement was based on the hypothesis that the CO stretching frequency depends upon the CO bond order, which depends upon the nature of other ligands bonded to the metal center. As the ligand donates electrons to the metal center, the metal, to keep its d electrons constant, will donate electrons to the CO π* orbitals causing a reduction in the CO bond order and hence a reduction in the IR stretching frequency. In a later study, Tolman equated the A1 stretching frequencies of Ni(CO)3L with the electronic effect (ν).
Table I. Steric and electronic properties of phosphines and phosphites

<table>
<thead>
<tr>
<th>L</th>
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<th>( \nu(A_1 \text{ (cm}^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CP</td>
<td>101</td>
<td>2087.3</td>
</tr>
<tr>
<td>P(OMe)_3</td>
<td>107</td>
<td>2079.5</td>
</tr>
<tr>
<td>P(OEt)_3</td>
<td>109</td>
<td>2076.3</td>
</tr>
<tr>
<td>P(O-i-Pr)_3</td>
<td>130</td>
<td>2075.9</td>
</tr>
<tr>
<td>PPh_3</td>
<td>145</td>
<td>2068.9</td>
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</tbody>
</table>

Clearly, different ligands have different electronic properties, which cause them to bond differently to the metal center. As shown earlier, carbonyls bond by both \( \sigma \) bonding and \( \pi \) back-bonding. However, there is a great deal of controversy about the nature of back-bonding of phosphines or phosphites (L) with transition metals. The conventional rationale suggests that the back-bonding of \( L \) with the metal d orbitals takes place via the empty d orbitals of the phosphorus. Molecular orbital calculations on free ligands done by Ellis\(^{12}\) and co-workers indicate that back-bonding takes place through the empty 3p phosphorus orbitals. Most recently, Marynick's\(^{13}\) molecular orbital calculations for ligands bonded to the metal indicate that back-bonding takes place through the \( \sigma^* \) orbitals of the \( P-X \) bond for ligands such as PF_3 and PH_3.
The effect of ligands on the substitution reactions of metal carbonyls has interested many researchers. Brown\textsuperscript{14} interpreted the thermal substitution reaction of six-coordinate transition metal carbonyls in terms of the ability of a ligand to labilize dissociative loss of CO or other ligands cis to itself. For example, the substitution reaction of Mn(CO)\textsubscript{5}Br shown below always leads to the formation of cis-(Br)(L)Mn(CO)\textsubscript{4},\textsuperscript{14,15} as shown in Reaction 1.

\[
\text{BrMn(CO)\textsubscript{5}} \rightarrow \text{BrMn(CO)\textsubscript{4}} \rightarrow \text{cis-(Br)(L)Mn(CO)\textsubscript{4}}
\]  

(1)

The order of rate of CO dissociation with different ligands bonded to the metal is listed below:

NO\textsubscript{3}\textsuperscript{-} > Cl\textsuperscript{-} > CH\textsubscript{3}CN > Br\textsuperscript{-} > PPh\textsubscript{3} > P(OPh)\textsubscript{3} > CO

The loss of cis CO is attributed to two factors. The first is the ground state effect. The trans CO is more strongly bound than the cis CO. For example, the distance from the metal to the carbon of the trans CO is 1.845 Å in PPh\textsubscript{3}Cr(CO)\textsubscript{5}, but the metal to carbon distance is 1.893 Å for the cis CO. Normally shorter bond is stronger.\textsuperscript{35,36,37}

The second factor which accounts for the loss of cis CO is the stabilization of the transition state. For example, the electron-releasing group o-phenanthroline of Cr(CO)\textsubscript{3}(o-phenanthroline) has been postulated to stabilize the transition state.\textsuperscript{16} In a study of Mn(CO)\textsubscript{5}X (X = Cl, Br, I) substitution reaction, Basolo\textsuperscript{17} concluded that the four
carbonyls cis to X dissociate faster than the trans carbonyl. In contrast with the finding of Basolo, Johnson observed the substitution reaction of \(\text{Mn(CO)}_5X\) by IR spectroscopy and concluded that the cis and trans substitution reaction occur at the same rate. Brown suggested that Johnson's results could be interpreted in terms of ground state isomerization of the cis product. Darensbourg studied \(L\) replacement from \(\text{trans-} (L)_2\text{M(CO)}_4\) by \(^{13}\text{CO}\) to produce \(\text{cis-} (L)(^{13}\text{CO})\text{M(CO)}_4\). In a similar study Atwood examined the ligand dissociation of \(L\) from \(\text{trans-} (L)_2\text{M(CO)}_4\), which led to the five-coordinated intermediate \([\{L\}\text{M(CO)}_4]\) with the vacant site trans to \(L\). Both concluded that the intermediate \([\{L\}\text{M(CO)}_4]\) rearranges to the intermediate with the vacant site cis to \(L\) as shown in Reaction 2.

Furthermore, Atwood concluded that the rate of trans \(\text{PPh}_3\) displacement increases as the size of \(L\) increases in the reaction shown below:
The order of PPh₃ dissociation as a function of L is PPh₃ > PBu₃ > P(OPh)₃ > P(OMe)₃ > CO. This order is opposite to the well-known trans ligand effect order in square planar complexes of d⁸ metals, such as Pt(II), Pd(II), Ni(II), Rh(I) and Ir(II). The following trans effect order, CO > CN > PR₃ > NO₂ > Py > NH₃, has been developed for the substitution reaction shown in Reaction 4.

\[
\text{trans-}(L)(PPh₃)Cr(CO)_4 + CO \rightarrow Cr(CO)_3L + PPh₃ \tag{3}
\]

Although the cis labelization effect is not completely clear, the effect of ligands on transition metal complexes is well documented (see references 7 and 22). Tolman⁷ related the rate constant (k) of the ligand substitution reaction with the ligand cone angle (v) and the ligand electronic effect (θ), as shown in Equation 1.

\[
\log (k) = aθ + bv + c \tag{1}
\]

Most recently Giering and co-workers²³ quantified the heats of reaction in terms of the ligand σ-electronic (ΔH₂σ), σ-
steric (ΔH_σ), π-electronic (ΔH_π) and π-steric (ΔH_πσ), as shown in Equation 2.

\[ ΔH_{RX} = ΔH_σ + ΔH_σ + ΔH_π + ΔH_πσ \] (2)

The ligands were then divided into three classes:
1) σ-donors, 2) σ-donors/π-donors and 3) σ-donors/π-acceptors. For the σ-donor ligands, only ΔH_σ and ΔH_σ will contribute to the heat of reaction. After solving for ΔH_σ and ΔH_σ for class 1 ligands, the solution is then used to solve for Class 2 ligands and so on.

Up to this point, the thermal substitution reaction of metal carbonyls has been discussed, but substitution reactions in metal carbonyls are known to proceed photochemically as well. Organometallic compounds show many electronic transitions, such as metal-to-ligand charge-transfer (MLCT), ligand-to-metal charge-transfer (LMCT), and low-lying ligand field or metal-centered excited state (Lf) transitions. The LF type of excitation brings about efficient ligand dissociation as shown in Figure 3. This electronic transition in organometallic complexes is normally observed in the ultraviolet and visible regions.

For example, the spin-allowed transition for Cr(CO)_6, A_{1g} (t_{2g}^6 e_g^0) \rightarrow T_{1g} (T_{2g}^5 e_g^1) appears at 317 nm. Irradiation of M(CO)_6 (M = W, Mo, Cr) at between 350-400 nm in the presence of a coordinating ligand will form M(CO)_5L,
Figure 3. Electronic excitation effect on ligands loss from $\text{M(CO)}_5(L)$
but irradiation of $\text{M(CO)}_5\text{L}$ could result in the loss of CO as shown in Reaction 5, or the loss of L as shown in Reaction 6.

$$\text{M(CO)}_5\text{L} \xrightarrow{\text{hv}} \text{M(CO)}_4\text{L} + \text{CO} \quad (5)$$

$$\text{M(CO)}_5\text{L} \xrightarrow{\text{hv}} \text{M(CO)}_5 + \text{L} \quad (6)$$

but irradiation of $\text{M(CO)}_5\text{L}$ could result in the loss of CO as shown in Reaction 5, or the loss of L as shown in Reaction 6. Both reactions have been found to be sensitive to the nature of L. When the bonding properties of L and CO are similar, the release of CO becomes competitive with the release of L. Furthermore, both reactions are wavelength dependent. Higher energy excitation leads to the population of $d_{x^2-y^2}$ orbitals and causes a CO loss, but low energy excitation populates the $d_{z^2}$ orbital and causes L loss,$^{24}$ as shown in Figure 3.

Reaction 5 has been shown$^{25,26,27}$ to form the coordinatively unsaturated $[\text{M(CO)}_4\text{L}]$ species, which was found to exist in two isomeric forms, as shown in Reaction 7.

$$\text{C}_{4v} \quad \text{C}_s$$
Matrix isolation studies, thermal kinetic studies of reactions, and flash photolysis with UV-vis or IR detection have been used in identifying organometallic intermediates. Generally, it has been easier to use low temperature techniques to prolong the lifetime of metal carbonyl reaction intermediates so that conventional spectrophotometers can be used. Fast time-resolved techniques have made it possible to detect metal carbonyl intermediates at room temperature in both the solution and gas phase. Furthermore, kinetic study of the recombination of metal carbonyl intermediates with incoming nucleophiles on the time scale of $10^{-3}$ to $10^{-9}$ seconds has made it possible to obtain a better understanding of the chemical reactivity of metal carbonyls.

The flash photolysis technique was first developed by George Porter and Weyforth Norrish. Both were awarded the Nobel prize in 1968 for their development. Flash photolysis is now widely used for the study of fast photochemical reactions. A great deal of development has taken place in the area of electronics, fast computers and lasers which make it possible to measure fast reactions which occur on the order of picoseconds. A typical flash photolysis system consists of a photolyzing light source, analyzing light source, detector, monochromator, sample holder, and a computer for the analysis of data.
The photolyzing light source should have high light intensity in a short period of time, from a nanosecond to picosecond pulse width. The light source is usually in the visible or ultraviolet region. If a laser is used as the photolyzing source, the wavelength must be selected in the region where the sample absorbs light.

The choice of the analyzing light source may vary from one given system of photochemical reactions to another, depending on the particular application. The most widely used light sources are tungsten or xenon lamps. The tungsten lamp is stable and emits a steady light intensity for a long period of time. It is useful for monitoring slow reactions, that is, those occurring on the order of milliseconds. The xenon light source, although more intense, is unstable and recommended for faster reactions. IR (infrared) light sources have also been used. The Glowbar, CO laser and, most recently, the diode laser have been used as an IR source.

When the sample is flashed by the high intensity photolyzing light source, the absorption of this light by the sample will produce an activated chemical species that will undergo a chemical reaction. The reaction is monitored by the analyzing light. Any change in the optical density of the sample will cause a change in the transmitted light which subsequently is sensed by a detector. The obtained electrical signal is then digitized and sent to the computer
for analysis. When setting up the flash photolysis system, it is important to keep the photolyzing light source perpendicular to the analyzing light so that none of the high intensity photolyzing light will pass to the detector and subsequently cause damage. Furthermore, shutters should be used between the sample and the analyzing light. The shutters should open only when data are collected. This is done to prevent photolysis of the sample by the analyzing light source.

Problem

The thermal substitution reactions of six-coordinate metal carbonyls have been extensively studied. Several reaction pathways for ligand substitution are feasible and are described in several books. The dissociative (D) mechanism, associative (A) mechanism and interchange (I) mechanism are possible pathways for ligand substitution reactions. The D mechanism in six-coordinated metal carbonyls is the most common pathway, because the metal center is too crowded to proceed readily by an A mechanism. For example, Darenbourg reported the reaction of cis-(amine)(PPh₃)Mo(CO)₄ with L' (amine = NC₅H₅, NHC₅H₁₀; L' = Lewis bases) to proceed via initial fission of the Mo-N bond to form the five-coordinate [(PPh₃)M(CO)₄] intermediate which reacts with L' to form cis-(L')(PPh₃)Mo(CO)₄.

The study of photochemical reactions of metal carbonyls using pulsed laser flash photolysis has been shown by Dobson.
and co-workers\textsuperscript{30} to compliment the thermal study and shed more light on metal carbonyl substitution reactions. They have reported thermal and pulsed laser photochemical ligand-substitution reaction for (NP)Mo(CO)\textsubscript{4} (NP = 1-(diethylamino)-2-(diphenylphosphino ethane) with L (L = phosphines and phosphites). Both thermal and photochemical reactions proceed via initial fission of the Mo-N bond to form the five-coordinated monohapto [(NP)Mo(CO)\textsubscript{4}] intermediates. In Dobson's pulsed laser flash photolysis experiments, two intermediates have been identified. One has the vacant site cis to the coordinated phosphorus, and the second has the vacant site trans to the phosphorus. The reaction of the trans photochemically generated intermediate with L is slower than that of the cis intermediate. Similar study by Dobson and co-workers\textsuperscript{39} on the thermal and photochemical reaction of cis-(pip)(L)W(CO)\textsubscript{4} with L' (L,L' = phosphine and phosphites) proceed to form cis- and trans-(L)(L')W(CO)\textsubscript{4}.

Earlier Dobson and co-workers\textsuperscript{31} reported that during thermal ligand substitution reaction of (tmpa)W(CO)\textsubscript{4} (tmpa = N,N,N',N' tetramethyl-1,3-diaminopropane) with L, cis- and trans-(L)\textsubscript{2}W(CO)\textsubscript{4} products were obtained. He then concluded that the five-coordinate intermediates [LM(CO)\textsubscript{4}] formed during the thermal reaction are fluxional. However, later on Dobson and co-workers\textsuperscript{32} monitored the same thermal
reaction using $^{31}$P NMR, as shown in Reaction 8. The growth of cis-$(L)_2W(CO)_4$ was seen at the earlier stages of the

$$\text{tmpa}W(CO)_4 + 2L \rightarrow (L)_2W(CO)_4 + \text{tmpa} \quad (8)$$

reaction, but the trans-$(L)_2W(CO)_4$ appears only after an induction period. Furthermore, the pulsed laser flash photolysis of cis-(pip)(PPh$_3$)$_2W(CO)_4$ in the presence of L led to the formation of cis and trans intermediates, each of which decay independently of the other, which indicates no rearrangement between them. Dobson, Poliakoff and Turner$^{40}$ have identified the cis and trans five-coordinated intermediate using pulsed laser flash photolysis with time-resolved IR detection. They found that both intermediates are solvated with the solvent occupying the vacant site. The solvation reactions have been studied. For example, Simon$^{33}$ determined the solvation of five-coordinate [Cr(CO)$_5$] photochemically generated from Cr(CO)$_6$ to take place within 2.5 ps. Lanford and co-workers$^{34}$ measured the rate constant of solvent recombination with [W(CO)$_5$] to be $5 \times 10^{10}$ s$^{-1}$ at 20 °C.

A series of complexes of cis-(pip)(L)M(CO)$_4$ (M = Mo, Cr) were prepared to identify the cis intermediates created by thermal and photochemical reactions. Their reactions as a function of L bonded to the metal center were studied and compared with the results of those obtained for the tungsten analogue. Studying the trans reactivity as a function of L
will permit the study of the trans effect in six-coordinate metal carbonyls. The solvent effect will be studied and the strength of the solvent-metal will be measured. In order to perform this research, a flash photolysis system had to be constructed.
CHAPTER REFERENCES


CHAPTER II

THE FLASH PHOTOLYSIS SYSTEM

The flash photolysis system constructed in our laboratory consists of the following parts:

High energy photolyzing micropulser (MP).—The MP function is to send a high voltage discharged from capacitors to the xenon lamps. The MP from Xenon Corporation, Model 720-A has an output energy of 100-2000 joules and a maximum operating voltage of 10 KV. The output pulse width is 10-100 μs.

Trigger Module (TM).—The TM is used to bring about the initial ionization of the gas in the flash lamps so that the high voltage from the MP will cause the flash. The TM module C from Xenon Corporation has a maximum output of 40 KV. This unit can be operated either by remote control or push-button panel triggering.

The monitoring light source (W).—The W is a 40 watt tungsten lamp connected to a Harrison 627 DC power supply.

The monochromator (M).—The M is a Bausch and Lomb monochromator whose grating contains 1350 grooves per mm.

Photomultiplier Tube (PMT).—The PMT is a multi-alkali photo-cathode tube from Hamamatsu, Model R928. This PMT has UV glass and nine stages (dynodes). It has a range of
185-930 nm with the peak wavelength at 400 nm. The maximum anode to cathode voltage that can be used is 1400 volts. It has a 0.1 mA average anode current with a 22 ns electron transit time and a 2.2 µs rise time. The photomultiplier has been modified as shown in Figure 4. Only four of the dynodes are used (dynode 1 to dynode 4). Dynode 5 is used as an anode for signal output. All others are grounded. Resistors and capacitors were added as shown in Figure 4. The capacitors installed in the photomultiplier provide current to replace the electrons depleted by the light from the dynodes. This setup will provide a linear output up to 10 mA, with 1 ns rise time.

Photomultiplier power supply (P2).—The P2 is from Bertan, Model PMT-2.0A-PN. The output range is from zero to 2000 volts.

Digital oscilloscope (SC).—The SC is from Nicolet, Model 2090 IIIA. It has 4K memory. Its maximum digitizing rate is 50 ns per point and the minimum is 20 seconds per point. The oscilloscope can be triggered internally or externally. The voltage range is 100 mv to 40 v with two channels for signal input.

Computer (CMP).—The CMP is a personal computer (NT-AT) which is IBM compatible with 30 MB and two drives.
Figure 4. The voltage divider construction for the PMT R298
Refrigerated and heated bath circulator.—The circulator is a Forma-Temp Jr. Model 2095 constant temperature bath (+/- 0.02 °C). The bath capacity is 7.5 gallons with maximum temperature operation of 98 °C.

Sample cells.—The cell was constructed by the UNT chemistry glass shop. It is 127 mm long with 13 mm OD and is made of Pyrex glass.

The back-off and sequence generator (BO).—The generator unit was built by the Kinetics Instruments Incorporation.

a) The back-off.

Normally, the voltage obtained from the photomultiplier is larger than the voltage which is due to the change in optical density as a result of photochemical reaction. The function of the back-off is to offset this voltage as shown in Figure 5. Offsetting this voltage brings the signal which is due to the photo-chemical reaction to the center of the oscilloscope. The signal is then easily amplified. Figure 5a shows the signal obtained without using the back-off. Before the shutter is opened, no light will pass to the PMT and zero voltage will be generated. But after the shutter is opened, the light will hit the PMT, which gives off a signal. When the shutter is closed, the voltage goes back to zero. When the
Figure 5. The PMT output signal recorded by the oscilloscope a) when no back-off is used, b) when back-off is used
back-off is used, an offset voltage brings the signal to zero voltage, as shown in Figure 5b. The part of the signal that has been offset is called the baseline.

b) The sequence generator.

The timing for the laser or xenon flash lamp triggering, the opening of the fast and slow shutters, the oscilloscope trigger and the back-off trigger are controlled by the sequence generator, as shown in Figure 6. However, the trigger timing of the individual components can be varied by dials on the front panel. Normally, the sequence starts by opening the slow shutter, which remains open for 1.3 seconds. Then the fast shutter opens. The time the fast shutter is open varies from 2 to 120 ms. After the fast shutter is opened, the back-off is triggered. The oscilloscope is then triggered so as to start data collection. Finally, the laser or the flash lamp is triggered, which usually takes place 180 μs after the back-off is triggered.

Computer interface.—The computer is interfaced with the digital oscilloscope employing a Metra Byte P1012, 24 bit (line connection) digital I/O board. The board consists of three ports, an 8 bit PA port, an 8 bit PB port and an 8 bit PC port. The 2090 111A oscilloscope board is a binary
Figure 6. The triggering sequence of the slow and fast shutter, back-off, oscilloscope and the xenon lamps.
digital I/O, high speed parallel interface, capable of bidirectional data transfer. A total of 56 individual lines are used on the interface. Lines 1A through 28A are used for output, 1B through 28B are used for input. Lines 22B (I/O step), 23B (AC1) and 24B (AC2) are used to control data transfer as shown in Figure 7. They are connected to PC4, PC5 and PC6 of the PI012 board. Lines 2A through 13A are connected to PA0 through PB3. These lines transfer the data from the oscilloscope to the computer. Since the oscilloscope is an 8 bit digitizer, only lines 6A through 13A carry data, as shown in Figure 7. So a digital mask is applied to the PA and PB ports so that the computer will read only the desired 8 bits (PA3 - PB2). Since the oscilloscope works in a negative logic where 1 = true = zero volts and 0 = false = 5 volts, a line driver and inverter 74LS244 is used between the PI012 and the oscilloscope boards. The commands to transfer data are simple and are initiated by a three-step sequence. First, the AC1, AC2 and 22B are all brought to false (5 volts) by sending the number 112 to the PI012 board. This is done by the ASYST command 112 DIGITAL.OUT (see next sections for ASYST). This sets the load address AC1 and AC2 both to false. By using the ASYST command 80 DIGITAL.OUT, AC1 is set to true and AC2 to false. This command will set the oscilloscope to the automatic advance mode starting at the far left of the oscilloscope screen. When I/O step (22B) is pulsed true,
Figure 7. The computer to oscilloscope line connection for data transfer
the oscilloscope will advance one address. The computer reads the data point and advances the oscilloscope to transfer the next data point. This loop is repeated until all of 4K data points are transferred to the computer and stored in an array for analysis. More details about the analysis program will be provided later in the chapter.

Data analysis.--The computer reads the data from the oscilloscope and stores it in an array. The value of each data point depends on its location on the oscilloscope's screen. The oscilloscope screen has 256 horizontal lines divided into two areas. The upper part of the screen displays lines 127 to zero; the lower part of the screen displays lines 255 to 128, as shown in Figure 8. The program FLASH.HA will change the values of the lines so that they will start at 1 on the top of the screen and end at 256 at the lower part of the screen, as shown on the left side of Figure 8. This change was effected so that data points exhibit a continuous decrease from the top to the bottom of the screen. Other information such as time per point, voltage offset and voltage range will be fed to the computer through the keyboard. The time per point will be used to form an array that contains the time for each data point. The voltage range is used to relate the values of each data point obtained from the oscilloscope to voltage. Table II shows the relationship between the selected voltage range and the volts per level increments.
Figure 8. Line increments on the digital oscilloscope screen
The voltage offset is added to each data point after dividing the voltage by the voltage level increments.

Table II. The value of line increments for the corresponding voltage range selected on the digital oscilloscope

<table>
<thead>
<tr>
<th>Selected voltage</th>
<th>Volts per level increments</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 mV</td>
<td>0.8 mV</td>
</tr>
<tr>
<td>200 mV</td>
<td>1.6 mV</td>
</tr>
<tr>
<td>400 mV</td>
<td>3.2 mV</td>
</tr>
<tr>
<td>1 V</td>
<td>8.0 mV</td>
</tr>
<tr>
<td>2 V</td>
<td>16.0 mV</td>
</tr>
<tr>
<td>4 V</td>
<td>32.0 mV</td>
</tr>
<tr>
<td>10 V</td>
<td>80.0 mV</td>
</tr>
<tr>
<td>20 V</td>
<td>160.0 mV</td>
</tr>
<tr>
<td>40 V</td>
<td>320.0 mV</td>
</tr>
</tbody>
</table>

The data obtained are converted to absorbance by dividing the minimum value of the array by each value in the array and then taking the logarithm of all points in the array. In other words, the minimum value is assumed to have a transmittance of one. This assumption is valid because the analysis is done using the values of \([A_i - A^\infty]\). \(A_i\) is the absorbance at some time and \(A^\infty\) is the absorbance at infinite time. If \(Y_1\) is the minimum value and \(Y_i\) is the value of the data at some time (\(Y_i\) is the value obtained from the digital oscilloscope), \(Y^\infty\) is the value of the data at time infinite (\(A^\infty = \) the baseline) and \(T_i\) is the real,
transmittance for any $Y_i$. $T_i$ will be directly proportional to $Y_i$ so that $T_i = bY_i$ ($b$ = constant). Then

$$T_i/Y_1 = bY_i/Y_1$$
(3)

$$Y_i/Y_1 = T_i/Y_1b$$
(4)

$$\log(Y_i/Y_1) = \log (T_i/Y_1b)$$
(5)

$$\log (Y_\infty/Y_1) = \log (T_\infty/Y_1b)$$
(6)

$$(A_i - A_\infty) = -\log (Y_i/Y_1) + \log (Y_\infty/Y_1)$$
(7)

$$= -\log (T_i/Y_1b) + \log (T_\infty/Y_1b)$$
(8)

$$= -\log (T_i) + \log (T_\infty)$$
(9)

Thus, even though $-\log Y_i/Y_1$ does not equal the real absorbance, the value of $[-\log(Y_i/Y_1) + \log (Y_\infty/Y_1)]$ will equal $[A_i - A_\infty]$.

**Analysis of first-order reactions.**—Usually the first-order reaction data are an exponential function of the type $Y = e^{(ax + b)}$. A least-squares fit is performed on the linear function $\ln Y = ax + b$ for the $x,y$-data set $X(x_1, \ldots, x_n), Y(y_1, \ldots, y_n)$. So, it is possible to determine the parameters $a$ and $b$ by the least squares method. The only problem is that the transformation of $Y$ to $\ln(Y)$ changes the error tolerances for the measured data. For instance, if the error brackets for the outcome of the $i$-th experiment are $[Y_i - e_i, Y_i + e_i]$, then it can be shown that the error brackets for $\ln(Y_i)$ are approximately $[\ln(Y_i) - e_i \frac{d\ln Y_i}{dy}, \ln(Y_i) + e_i \frac{d\ln Y_i}{dy}]$. Thus, when $Y_i$ is small, the experimental accuracy of $\ln(Y_i)$ is much poorer...
than the experimental accuracy of \( Y_i \). The variance of the quantity \( \ln(Y_i) \) will be approximately equal to \( 1/(Y_i)^2 \) times the variance of \( Y_i \). For this reason the additional factors \( (Y_i)^2 \) are incorporated in the least squares minimization term used to determine \( a \) and \( b \). Both \( a \) and \( b \) are selected so as to minimize \( [(Y_i)^2 (ax_i + b - \ln Y_i)^2] \).

**Second-order reaction.**—A plot of \( [(A_i - A_0)/(A_i - A_\infty)] \) vs. time should be linear for a second-order reaction, as shown in Equation 10.

\[
(A_i - A_0)/(A_i - A_\infty) = -[A]_0 \ k t
\]

The analysis of the second-order reaction is not used to find the rate constant, but is used to determine whether the data fits as a second-order reaction. Evaluation of the rate constant requires the value of \( [A]_0 \). \( [A]_0 \) is the concentration of \( A \) at time zero.

**Two first-order analyses.**—When two exponential decays are observed, as shown in Figure 9a, the slow decay is fitted first by taking the baseline value (\( A_\infty \)) and then plotting \( \ln(A_i - A_\infty) \) vs. \( t \). Figure 9b shows that the plot of the data for the slow decay of the photochemical reaction of cis-\((\text{pip})(P(\text{O-i-Pr})_3)W(\text{CO})_4 \) with pip in CB at 31.1 °C is linear. The linear part is selected and fitted as a first-order decay, as shown in Figure 9c. The fitted data for the slow reaction are then subtracted from the original data. The result is shown in Figure 9d.
Figure 9. Flash photolysis data of cis-(pip)(P(O-i-Pr)₃)W(CO)₄ in the presence of pip in CB solution at 31.1 °C. a) plot of absorbance vs. time before and after the flash, b) plot of ln(Aₜ - A∞) vs. time, c) plot of ln(Aₜ - A∞) vs. time for the slow decay, d) plot of absorbance vs. time for the fast decay, and e) plot of ln(Aₜ - A∞) vs. time for the fast decay
This data is then fitted as a first-order reaction, as shown in Figure 9e.

**Operation of the flash photolysis system.**—Figure 10 shows the complete setup of the flash photolysis system. A warm up time of 20-30 minutes is recommended before operating the equipment. The power supply of the tungsten lamp (P1), the power supply of the PMT (P2), the oscilloscope (SC), the back-off box (BC), the high energy photolyzing micropulser (MP), the trigger module (TM) are turned on, and the program FLASH.HA is loaded into the computer. No special order is required. (Consult the manual of each component before operation.) The sample is loaded in the jacketed sample cell and is placed in the sample holder. The sample and the width of the slit of the monochromator must be adjusted to allow maximum light to pass to the PMT by getting the maximum voltage ($I_{O}$) at the back-off box digital reading. $I_{O}$ should not exceed more than 2 volts. The oscilloscope cursor is moved to the left of the screen and the cursor is locked into position by pressing the CURSOR and LOCK buttons. This position is where the flash pulse will be recorded. The selection of the time scale and voltage scale depends on the experimental conditions. To collect data, the oscilloscope storage control is set on LIVE and HOLD NEXT. Now the system is ready to collect data. The sequence is
Figure 10. The flash photolysis system consists of high energy photolyzing micro pulser (MP), two power supplies (P1, P2), fast and slow shutters (S1, S2), sample (S), xenon flash lamps (L1, L2), back-off (BO), monochromator (M), PMT (P), oscilloscope (SC), computer (CMP), plotter (PL) and printer (PR).
started by pushing the START button located at the back-off box.

**Electrostatic and magnetic radiation.**—The first problem encountered is that the signal obtained upon flash photolysis of Cr(CO)$_6$ in the presence of pip was a large signal with a rate constant $4 \times 10^4$ sec$^{-1}$. This signal did not change by changing the concentration of pip, and it was obtained even when no sample was in the sample cell. This signal was reduced when the flash lamps’ housing was shielded with copper sheets.

This problem was clearly the result of electrostatic and magnetic radiation caused by the high voltage discharge to the flash lamps that somehow is being picked up by the wires connected to the digital oscilloscope. Therefore, a large box with copper sheets covering all sides was constructed to contain the flash lamps, the trigger module and the tungsten lamp as shown in Figure 10. The box is grounded by wires to a tap water pipe. In addition, all the wires from the PMT to the oscilloscope and the back-off box were shielded by wrapping copper sheets around them. This shielding was found to work best when all the wires and the box are grounded to the same pipeline.

**The PMT saturation.**—Even though the flash lamps are perpendicular to the analyzing light and the PMT, as shown in Figure 10, some of the light from the flash lamps passes
to the PMT and causes saturation of the PMT. This problem was minimized by using black tape on the side of the sample cell and a collimator to prevent any scattered light from the flash lamps from hitting the PMT.

The first data set.—The objective at this point was to obtain data for reactions that are known or could be checked at CFKR (Center for Fast Kinetics Research at the University of Texas at Austin). If the flash photolysis system and the data analysis program work, the data obtained by our system should agree with the data obtained at CFKR. The complexes \( \text{Cr(CO)}_6 \) and \( \text{cis-}(\text{pip})(\text{CP})\text{Mo(CO)}_4 \) were selected to test the flash photolysis system. About \( 10^{-4} \) mole of complex dissolved in CB that contains pip was transferred to the cell for flash photolysis. \( \text{Cr(CO)}_6 \) was used first because upon flash photolysis a big change in absorbance is expected. Because \( \text{Cr(CO)}_6 \) is colorless but the product is yellow, as shown in Reaction 9, the change is easily detected. Table III lists the rate constants obtained for Reaction 9.

\[
\text{Cr(CO)}_6 + \text{pip} \xrightarrow{\text{hv}} \text{Cr(CO)}_3\text{pip} + \text{CO}
\] (9)

<table>
<thead>
<tr>
<th>Colorless</th>
<th>Yellow</th>
</tr>
</thead>
</table>

The fact that the rate increases as the pip concentration increases indicates that the signal obtained is due to a change in the optical density of the solution as a result of the photochemical reaction. Furthermore, the data
obtained at CFKR and listed in Table III fall on the same line, as seen from the plot of \( k_{obs} \) vs. [pip] shown in Figure 11. \( k_{obs} \) is the slope of the line obtained from the plot of \( \ln(A_t - A_\infty) \) vs. time. As will be shown in Chapter IV, the plot of \( k_{obs} \) vs. [pip] is linear. The data obtained after photolysis of the complex cis-(pip)(CP)Mo(CO)_4 with pip as the incoming nucleophile in CB solution are listed in Table IV. There is good agreement between the data obtained from our system and the data obtained at CFKR. A plot of \( k_{obs} \) vs. [pip] is shown in Figure 12. All of the above mentioned data clearly indicate that the system and the data analysis work well.

Table III. The rate constants obtained from the flash photolysis of Cr(CO)_6 in the presence of pip in CB at 31.1 °C

<table>
<thead>
<tr>
<th>[pip]</th>
<th>10^{-4} k_{obs}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6818^a</td>
<td>1.98(2)</td>
</tr>
<tr>
<td></td>
<td>1.995(1)</td>
</tr>
<tr>
<td>0.4615^a</td>
<td>1.37(1)</td>
</tr>
<tr>
<td></td>
<td>1.359(9)</td>
</tr>
<tr>
<td>1.078^a</td>
<td>3.09(5)</td>
</tr>
<tr>
<td></td>
<td>3.10(3)</td>
</tr>
<tr>
<td>0.2094^b</td>
<td>0.586(7)</td>
</tr>
<tr>
<td>0.2012^b</td>
<td>0.570(3)</td>
</tr>
<tr>
<td>0.1047^b</td>
<td>0.2972(1)</td>
</tr>
<tr>
<td>0.1006^b</td>
<td>0.275(6)</td>
</tr>
<tr>
<td>0.05235^b</td>
<td>0.154(2)</td>
</tr>
</tbody>
</table>

^a At CFKR  ^b From the flash photolysis system
Table IV. The rate constants obtained from the flash photolysis of cis-(pip)(CP)Mo(CO)₄ in the presence of pip in CB at 31.1 °C

<table>
<thead>
<tr>
<th>[pip]</th>
<th>10⁻⁴×k_{obs}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0873ᵃ</td>
<td>0.278(4)</td>
</tr>
<tr>
<td>0.2990ᵃ</td>
<td>0.839(5)</td>
</tr>
<tr>
<td>0.5540ᵃ</td>
<td>1.428(7)</td>
</tr>
<tr>
<td>0.9720ᵃ</td>
<td>2.50(1)</td>
</tr>
<tr>
<td>0.0761ᵇ</td>
<td>0.201(4)</td>
</tr>
<tr>
<td>0.1350ᵇ</td>
<td>0.348(1)</td>
</tr>
<tr>
<td>0.1739ᵇ</td>
<td>0.438(4)</td>
</tr>
<tr>
<td>0.2778ᵇ</td>
<td>0.635(3)</td>
</tr>
</tbody>
</table>

ᵃ At CFKR
ᵇ From the flash photolysis system
Figure 11. Plot of $k_{\text{obs}} \, (s^{-1})$ vs. $[\text{pip}]$ (M) for the photochemical reaction of Cr(CO)$_6$ and pip in CB at 31.1 °C

- Data obtained at CFKR
- Data obtained by the system
Figure 12. Plot of $k_{\text{obs}}$ (s$^{-1}$) vs. [pip] (M) for the photochemical reaction of cis-(pip)(CP)M(CO)$_4$ and pip in CB at 31.1 °C

- Data obtained at CFKR
- Data obtained by the system
ASYST software and FLASH.HA.—ASYST was developed by Adaptable Laboratory Software, Inc. Peter Helmers and Jeff Astheimer used the combination of Forth and Apl software concepts in the development of Asyst. Both joined forces with Robert Kreilick, a professor of chemistry at the University of Rochester. The software was developed especially for chemists needing to interface laboratory instruments with computers. The data analysis program was written using ASYST. An attempt was made to make running the program as simple as possible. The commands are divided into two sets:

1) Function key commands (F1 - F10)

The function keys F1 through F10 will perform specific operations as defined below:

F1 - Acquires information about the experiment such as time per point, voltage range, etc. It will transfer the data from the oscilloscope and store it in the computer

F2 - Used to average data files

F3 - Reads stored data

F4 - Used when the actual data analysis needs to be performed

F5 - Stores data file

F6 - Plots absorbance vs. time

F7 - Plots ln(A_t - A_∞) vs. time.
F8 - Reads the indices specified by the left cursor
F9 - Will analyze the fast process. F9 is used only after the slow process analysis is complete
F10 - Reads the right and the left indices specified by the right and left cursors

2) Word commands

Few words are used in the analysis of data to keep the analysis as simple as possible.

Slow: Analyze two exponential decays
KT: Analyze one exponential decay or a second-order decay
get: Select the baseline that best fits the data

First- and second-order reactions.--After loading the data file by F1 or F3, KT is typed into the computer. The data are displayed on the computer screen with two cursors. The two cursors can be moved left or right by the arrow keys. The baseline (A∞) is selected to be between the left and the right cursors and F10 was pressed. The data range (Aₜₕₛ) is selected to be between the two cursors and F10 was pressed. Thus, the computer has the value of A∞ and all the Aₜₕₛ. When F4 is pressed, two kinds of analysis can be performed. The key for numeral one is pressed for a first-
order reaction, and numeral 2 is pressed for a second-order reaction.

Two first-order reactions.—After the data file is loaded, SLOW is typed into the computer. The data is displayed on the computer screen. First, the baseline and then the data range are selected in a manner similar to that described above. The computer displays a logarithmic plot, as shown in Figure 9b. The slow reaction is selected by moving the left cursor to the upper linear part of the slow reaction and pressing F8. The computer performs a least-squares analysis for that part only. The data is plotted at this point using F6 and F7. The analysis of the fast part of the data is done by pressing F9 and then selecting the new baseline and the new data range. A listing of this program is given in Appendix B.
CHAPTER REFERENCES


CHAPTER III

Experimental

Infrared spectra were obtained employing a Perkin-Elmer Model 621 grating or 1710 FT-IR or Nicolet 20 SXB FT-IR Spectrophotometer. The thermal reaction rates were monitored following a decrease in absorbance using a Beckman DU-2 UV-Visible spectrophotometer or Perkin-Elmer 124 spectrophotometer. The photochemical reaction rates were obtained using an in-house built flash photolysis system (see Chapter II) or the pulsed laser flash photolysis system at CFKR. Haake D8 and Forma-temp Jr., Model 2095 bath circulators were employed as temperature control devices. Elemental analyses were performed by Midwest Microlab, Indianapolis, Indiana.

Materials

Purification of solvents and ligands. Chlorobenzene (Fisher) was stirred and refluxed over phosphorus pentoxide and fractionally distilled under nitrogen. Reagent grade cyclohexane (Fisher) was stirred over sodium and fractionally distilled under nitrogen. Piperidine (Aldrich) was fractionally distilled from KOH under nitrogen. Tri(isopropyl) phosphite was fractionally distilled over sodium under reduced pressure (0.4 torr 32 °C). The
triphenylphosphine (Fluka), trimethyl phosphite (Aldrich),
triethyl phosphite (Aldrich), molybdenum hexacarbonyl
(Pressure Chemical), chromium hexacarbonyl (Pressure
Chemical) and CH₃C(CH₂OH)₃ (Aldrich) were used without any
purification in the synthesis of the Cr and Mo complexes.

Synthesis of the compounds

4-methyl-2,6,7-trioxa-1-phosphabicyclo-[2.2.2]octane
(CP) was prepared through use of the published procedure.¹
In a round-bottom flask, 24 g of CH₃C(CH₂OH)₃ and 52 mL of
P(O-i-Pr)₃ were stirred at 50 °C under nitrogen for five
days. The ethanol formed was distilled off leaving a
viscous clear solution. The CP was sublimed under reduced
pressure into a wide-mouthed condenser and was crystallized
from hot n-hexane. A white product was obtained which had a
melting point of 91-92 °C (mp = 91-93)¹. A 54% (20 g) yield
was obtained.

Cis-(pip)₂Mo(CO)₄ was prepared according to
Darensbourg’s method.² Ten grams of Mo(CO)₆ and 25 mL of
piperidine were refluxed in 200 mL of n-heptane for five
hours under nitrogen. The yellow product obtained was
collected by suction filtration and washed with hot n-
heptane to give a 90% yield (9.5g).

Cis-(pip)(CP)Mo(CO)₄ was prepared by the reaction of
4.0 g of cis-(pip)₂Mo(CO)₄ and 2.0 g of CP in 250 mL of 1,2-
dichloroethane. The solution was refluxed for five minutes,
after which the solvent was removed under vacuum. The
complex was redissolved in 100 mL of toluene. The solution was then filtered through Celite-545 to which 50 mL of hexanes were added to cause crystallization of the yellow product. The product was collected by suction filtration and then dried under vacuum to afford an 80% yield (3.7 g).

Cis-(pip)(P(OEt)₃)Mo(CO)₄ was prepared by the reaction of 2.0 g of cis-(pip)₂Mo(CO)₄ and 2.0 mL of P(OEt)₃ in 150 mL of 1,2-dichloroethane. The solution was refluxed for five minutes. The solvent was removed under vacuum, and the product was crystallized from a 50 mL chloroform/MeOH solution (1:1 v/v mixture) to give a 50% yield (1.2 g). The product was collected by suction filtration and then dried under vacuum.

Cis-(pip)(PPh₃)Mo(CO)₄ was prepared by the reaction of 3.0 g of Mo(CO)₄(pip)₂ and 3.0 g of PPh₃ in 150 mL of 1,2-dichloroethane. The solution was refluxed for five minutes. The solvent was removed under vacuum, and the product was crystallized from 50 mL chloroform/ethanol to give a 36% yield (1.6 g). The same method was used to prepare cis-(pip)(P(O-i-Pr)₃)-Mo(CO)₄ which gave a yield of 60% from the reaction of 4.0 g cis-(pip)₂Mo(CO)₄ and 3.5 mL of P(O-i-Pr)₃. The products were collected by suction filtration and then dried under vacuum.

Pip Cr(CO)₅ was prepared according to a published method.³ Ten mL of piperidine and 3.0 g of Cr(CO)₆ in THF were irradiated with a 450 W Hanovia medium pressure mercury
lamp for 30 minutes. The THF solution was removed under vacuum. Cr(CO)₅pip was recrystallized from n-heptane solution to give an 80% yield (3.0 g). The product was collected by suction filtration and then dried under vacuum.

_Cis-(pip)(CP)Cr(CO)₄_ was prepared by reacting 3.0 g of Cr(CO)₅pip in a 1:1 mole ratio with CP (1.6 g) in 150 mL hexanes. The solution was filtered and 120 mL of hexanes that contained 7 mL of pip were added. The solution was then irradiated with a medium pressure mercury lamp 450 W Hanovia for 30 minutes. A yellow powder was filtered and then recrystallized from toluene/hexane solution to give a 70% yield (3.0 g). The product was collected by suction filtration and then dried under vacuum.

_Cis-(pip)(P(O-i-Pr)₃)Cr(CO)₄_ was prepared from 3.0 g of Cr(CO)₅pip and 2.8 mL of P(O-i-Pr)₃ in 150 mL hexanes for one hour. The solution was diluted with 120 mL of hexanes to which 10 mL of pip had been added, and was irradiated for 30 minutes. The solution was reduced under vacuum to 20 mL and stored in the refrigerator to give a 55% yield (2.7 g). The product was collected by suction filtration and then dried under vacuum.

_Cis-(pip)(P(OEt)₃)Cr(CO)₄_ was prepared by the reaction of 3.6 g of Cr(CO)₅pip and 2.5 mL of P(OEt)₃ in n-heptane. The reaction mixture was refluxed for two hours. The solvent was removed, and the product was dissolved in 270 mL THF to which 10 mL of pip were added. The solution was
irradiated for 30 minutes and the solvent was removed. The product was crystalized by adding 100 mL of methanol. The solution was stored in the refrigerator. A 44.6% yield was obtained. The solution was further reduced to obtain more of the product, which made the yield 70% (3.8 g).

The compounds cis-(pip)(CP)Mo(CO)$_4$ and cis-(pip)(CP)Cr(CO)$_4$ gave high yields because they are easily crystallized from toluene/hexanes solution. However, the other cis-(pip)(L)M(CO)$_4$ complexes are highly soluble in most solutions and are not easily crystallized. A great deal of compound was left in the solution. Tables V and VI list the carbonyl stretching frequencies and the elemental analyses.

**Thermal kinetics.**—About $1 \times 10^{-4}$ mole of the substrate was placed in a 100 mL volumetric flask, which was wrapped in aluminum foil and placed in a constant temperature bath. The foil was used to protect the solution from any light in the room. An excess (more than 25/1 mole ratio of ligand to substrate) of P(O-i-Pr)$_3$ and pip were dissolved in 50 mL of CB. The solution was brought to thermal equilibrium before mixing with the substrate. The CB solution was added to the substrate in the 100 mL volumetric flask equipped with a stopcock and rubber sptum. The flask was then flushed with nitrogen. Samples were withdrawn periodically from the 100 mL flask by means of a
Table V. The carbonyl stretching frequencies of cis-(pip)(L) M(CO)$_4$ in cyclohexane

<table>
<thead>
<tr>
<th>M</th>
<th>L</th>
<th>$A'$ (cm$^{-1}$)</th>
<th>$A''$ (cm$^{-1}$)</th>
<th>$A''$ (cm$^{-1}$)</th>
<th>$A''$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo</td>
<td>P(OMe)</td>
<td>2025(m)</td>
<td>1927(m)</td>
<td>1905(s)</td>
<td>1876(m)</td>
</tr>
<tr>
<td></td>
<td>P(OEt)</td>
<td>2023(m)</td>
<td>1923(m)</td>
<td>1902(s)</td>
<td>1873(m)</td>
</tr>
<tr>
<td></td>
<td>P(O-i-Pr)</td>
<td>2022(m)</td>
<td>1921(m)</td>
<td>1900(s)</td>
<td>1870(m)</td>
</tr>
<tr>
<td></td>
<td>PPh$_3$</td>
<td>2017(m)</td>
<td>1911(m)</td>
<td>1899(s)</td>
<td>1868(m)</td>
</tr>
<tr>
<td></td>
<td>CP$^a$</td>
<td>2031(m)</td>
<td>1913(m)</td>
<td>1909(s)</td>
<td>1868(m)</td>
</tr>
<tr>
<td>Cr</td>
<td>CO</td>
<td>2066(m)</td>
<td>1932(s)</td>
<td></td>
<td>1915(m)</td>
</tr>
<tr>
<td></td>
<td>P(OEt)</td>
<td>2015(m)</td>
<td>1918(m)</td>
<td>1893(s)</td>
<td>1866(m)</td>
</tr>
<tr>
<td></td>
<td>P(O-i-Pr)</td>
<td>2013(m)</td>
<td>1915(m)</td>
<td>1891(s)</td>
<td>1862(m)</td>
</tr>
<tr>
<td></td>
<td>PPh$_3$$^b$</td>
<td>2008(m)</td>
<td>1906(m)</td>
<td>1889(s)</td>
<td>1862(m)</td>
</tr>
<tr>
<td></td>
<td>Cp$^a$</td>
<td>2030(m)</td>
<td>---</td>
<td>1908(s)</td>
<td>1866(m)</td>
</tr>
</tbody>
</table>

$^a$ In chloroform solution
$^b$ The complex was not isolated
m = medium, s = strong
Table VI. Elemental analysis of cis-(pip)(L) M(CO)$_4$

<table>
<thead>
<tr>
<th>M</th>
<th>L</th>
<th>Theory %</th>
<th>Found %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo</td>
<td>CP</td>
<td>C = 38.12</td>
<td>C = 38.45</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H = 4.57</td>
<td>H = 4.80</td>
</tr>
<tr>
<td></td>
<td>P(OEt)$_3$</td>
<td>C = 39.23</td>
<td>C = 38.93</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H = 4.83</td>
<td>H = 5.05</td>
</tr>
<tr>
<td></td>
<td>P(O-i-Pr)$_3$</td>
<td>C = 43.13</td>
<td>C = 43.15</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H = 6.44</td>
<td>H = 6.64</td>
</tr>
<tr>
<td>Cr</td>
<td>P(O-i-Pr)$_3$</td>
<td>C = 47.26</td>
<td>C = 47.25</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H = 7.05</td>
<td>H = 6.99</td>
</tr>
<tr>
<td></td>
<td>P(OEt)$_3$</td>
<td>C = 43.38</td>
<td>C = 43.37</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H = 6.31</td>
<td>H = 6.51</td>
</tr>
<tr>
<td></td>
<td>CP</td>
<td>C = 42.33</td>
<td>C = 42.42</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H = 5.08</td>
<td>H = 5.21</td>
</tr>
</tbody>
</table>

syringe and were placed in a 1 cm quartz cell. The absorbance readings were taken immediately. Plots of \( \ln(A_t - A_\infty) \) vs. time were linear. \( A_t \) is the absorbance at some time, and \( A_\infty \) is the absorbance at infinite time. The slopes of the plots were calculated using a linear least-squares program. Most data gave a correlation coefficient of 0.999 or better. A 90% confidence limit (1.65 standard deviations) for rejection of data points was used.

Photochemical kinetics.—Some of the data were obtained at the Center for Fast Kinetics Research at the University of Texas at Austin (CFKR). Others were obtained in the UNT laboratory. CFKR's pulsed laser flash photolysis system$^{10}$
employs an Nd:YAG Laser (Quantel YG 481) with a pulse width of 11 ns at 355 nm (100 mJ).

Five mg of the substrate were dissolved in 10 mL of solvent solution that contained an excess (more than 25/1 mole ratio of ligand to substrate) of ligand. The mixture was then transferred to a 1 cm quartz jacketed cell. The solution was brought to thermal equilibrium and was kept under nitrogen. The obtained signal was the average of at least four flashes using the same solution. However, the data obtained in our laboratory using the flash photolysis system described in Chapter 2 was obtained from a single flash. Temperature at the jacketed observation cell was maintained through use of an external circulating bath (+/- 0.02 °C).

The products of the thermal and photochemical reactions.--Both thermal and photochemical reactions of cis-(pip)(L)M(CO)₄ (with incoming L' (L, L' = phosphine and phosphite) proceed to replace pip in the complexes as shown below:

\[
\text{cis-(pip)(L)M(CO)₄ + L'} \stackrel{hv \text{ or } \Delta}{\longrightarrow} (L')(L)M(CO)₄ + \text{pip}
\]

The loss of pip in the thermal reaction is due to the fact that pip is more weakly held than the other ligands bonded to the metal. Several studies² performed on six-coordinated metal carbonyls in which one of the ligands is a σ-donor only show that the reactions proceed by the thermal
replacement of this ligand.\(^4,5,6\) Since ligands such as pip containing nitrogen are \(\sigma\)-donors only, their photochemical reaction as a result of populating the \(\sigma^*\) (\(d_{z^2}\)) will lead to the loss of pip. The reactions of the \(\text{cis-}(\text{pip})(\text{L})\text{M(CO)}_4\) (\(\text{M} = \text{Cr, MO}\)) complexes with \(\text{P(O-i-Pr)}_3\) showed the same behavior, where pip is lost and is replaced by \(\text{P(O-i-Pr)}_3\). This fact is supported by the carbonyl stretching frequencies. For example, the thermal reaction of \(\text{cis-}(\text{pip})(\text{P(OEt)}_3)\text{M(CO)}_4\) with \(\text{P(O-i-Pr)}_3\) in CB was monitored by FT-IR. The reactant \(\text{A'}\) mode of vibration is at 2020 cm\(^{-1}\), but the product \(\text{A'}\) mode of vibration is at 2029 cm\(^{-1}\), a strong indication of pip replacement with the \(\pi\)-accepting ligand \(\text{P(O-i-Pr)}_3\). Table VII shows the reactants' and products' carbonyl stretching frequencies for some of the Cr and Mo complexes in CB solution. The products of the photochemical reaction showed the same spectra as the products of thermal reaction. Both thermal and photochemical reactions led to the formation of \(\text{trans-}(\text{L})(\text{L'})\text{M(CO)}_4\), indicated by the growth of the \(\text{E}\) mode of vibration listed in Table VII. The \(\text{trans}\) product formed thermally is believed to be formed from the thermal isomerization of \(\text{cis-}(\text{L})(\text{L'})\text{M(CO)}_4\). But the \(\text{trans}\) complex is believed to be formed from the relaxation of the vibrationally and electronically excited five-coordinated intermediate caused by the pulse of the laser or flash lamps.\(^7,8,9\) For more details see Chapter 4.
Table VII. IR-stretching frequencies of \((L)(L')M(CO)\_4\) in CB

<table>
<thead>
<tr>
<th>M</th>
<th>L</th>
<th>L'</th>
<th>(A'(\text{cm}^{-1}))</th>
<th>(A'(\text{cm}^{-1}))</th>
<th>(A''(\text{cm}^{-1}))</th>
<th>(A''(\text{cm}^{-1}))</th>
<th>Trans E(\text{cm}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo</td>
<td>pip</td>
<td>P(OEt)</td>
<td>2020 (m)</td>
<td>---</td>
<td>1897 (s)</td>
<td>1852 (m)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>P(O-i-Pr)_3</td>
<td>P(OEt)</td>
<td>2029 (m)</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>1912 (vs)</td>
</tr>
<tr>
<td></td>
<td>pip</td>
<td>P(O-i-Pr)_3</td>
<td>2019 (m)</td>
<td>---</td>
<td>1896 (s)</td>
<td>1850 (m)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>P(O-i-Pr)_3</td>
<td>P(O-i-Pr)_3</td>
<td>2028 (m)</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>1910 (vs)</td>
</tr>
<tr>
<td></td>
<td>pip^a</td>
<td>CF</td>
<td>2031 (m)</td>
<td>1913</td>
<td>1909 (s)</td>
<td>1868 (m)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>P(O-i-Pr)_3^a</td>
<td>CF</td>
<td>2039 (m)</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>pip^a</td>
<td>CF</td>
<td>2030 (m)</td>
<td>---</td>
<td>1908 (s)</td>
<td>1866 (m)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>P(O-i-Pr)_3^a</td>
<td>CF</td>
<td>2035 (m)</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td></td>
<td>pip</td>
<td>P(OEt)_3</td>
<td>2012 (m)</td>
<td>1905.5</td>
<td>1889.9 (s)</td>
<td>1848 (m)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>P(O-i-Pr)_3</td>
<td>P(OEt)_3</td>
<td>2018.7 (m)</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>901 (vs)</td>
</tr>
<tr>
<td></td>
<td>pip</td>
<td>P(O-i-Pr)_3</td>
<td>2010 (m)</td>
<td>1904</td>
<td>1889 (s)</td>
<td>1844 (m)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>P(O-i-Pr)_3</td>
<td>P(O-i-Pr)_3</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>1899 (vs)</td>
</tr>
</tbody>
</table>

\^a In chloroform solution
m = medium, s = strong, vs = very strong
CHAPTER IV

PARALLEL THERMAL AND PULSED LASER FLASH PHOTOLYSIS STUDY OF

CIS-(PIP)(L)M(CO)₄ (PIP = PIPERIDINE, L = PHOSPHINES

AND PHOSPHITES M = Mo, Cr)

Introduction

In this chapter the results of thermal and pulsed laser

flash photolysis of cis-(pip)(L)M(CO)₄ reactions with

incoming nucliphiles will be discussed. The thermal

reactions in CB solution will be discussed first.

Discussion of the photochemical reactions in CB and in

cyclohexane (CH) solution will follow.

Recently, Dobson and co-workers¹,² have reported that

parallel flash photolysis and thermal investigation of

ligand exchange in octahedral metal carbonyl complexes can

offer information about the ligand-substitution process. In

their study, they concluded that both photochemically and

thermally generated intermediates were identical. The rates

of reaction of photochemically generated intermediates with

incoming nucleophiles were found to be solvent dependent³,

which indicates that these intermediates are solvated.

Additional evidence that these intermediates are solvated

was obtained by using flash photolysis with infrared

detection.⁴
The thermal reactions studies.

Earlier, Hyde and Darensbourg\(^5\) reported the thermal reactions of \(\text{cis-}(\text{pip})(\text{PPh}_3)\text{Mo(CO)}_4\) with \(L, L = \text{Lewis bases}\) proceeded by the mechanism shown in Reaction 11.

\[
\begin{align*}
\text{cis-}(\text{pip})(\text{PPh}_3)\text{Mo(CO)}_4 & \xrightleftharpoons[k_{-1}(\text{pip})]{k_1} (\text{PPh}_3)\text{Mo(CO)}_4 + \text{L} \\
& \xrightarrow[k_2(\text{L})]{(\text{PPh}_3)\text{Mo(CO)}_4} \text{L}(\text{PPh}_3)\text{Mo(CO)}_4
\end{align*}
\] (11)

They found the rate of reaction to be independent of \([L]\).

In the present study the reaction rates of \(\text{cis-}(\text{pip})(L)\text{M(CO)}_4\) in the presence of large excesses of both \text{pip} and \(\text{P(O-i-Pr)}_3\) in \(\text{CB}\) solution were monitored at 430 nm using a Beckman DU-2 direct-reading spectrophotometer. Plot of \(\ln(A_t - A^\infty)\) vs. time was linear up to at least 2 half-lives. \(A_t\) is the absorbance at time \(t\), and \(A^\infty\) is the absorbance at infinite time (The absorbance of a \(\text{CB}\) solution that contained \text{pip} and \(\text{P(O-i-Pr)}_3\)). The slopes of the lines \(k_{\text{obs}}\) were obtained using the least squares method. A 90% confidence limit was used to reject points. The values of \(k_{\text{obs}}\) obtained for the reactions of \(\text{cis-}(\text{pip})(L)\text{Mo(CO)}_4\) and \(\text{cis-}(\text{pip})(L)\text{Cr(CO)}_4\) at 31.1 °C are listed in Tables VIII and IX, respectively. Plots of \(k_{\text{obs}}\) vs. \([\text{P(O-i-Pr)}_3]/[\text{pip}]\) are curved. Figure 13 shows typical curved plots for the data obtained from the reactions of molybdenum complexes. However, plots of \(1/k_{\text{obs}}\) vs. \([\text{pip}]/[\text{P(O-i-Pr)}_3]\) were linear.
Table VIII. The pseudo first-order rate constants for the reactions of cis-(pip)(L)Mo(CO)₄ with P(O-i-Pr)₃ in the presence of pip and P(O-i-Pr)₃ in CB at 31.1 °C

<table>
<thead>
<tr>
<th>L</th>
<th>[pip]/[P(O-i-Pr)₃]</th>
<th>10⁴ * k_{obs} (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPh₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0000</td>
<td></td>
<td>2.99 (1)</td>
</tr>
<tr>
<td>0.1981</td>
<td></td>
<td>2.039 (4)</td>
</tr>
<tr>
<td>0.3172</td>
<td></td>
<td>1.715 (9)</td>
</tr>
<tr>
<td>0.5039</td>
<td></td>
<td>1.27 (1)</td>
</tr>
<tr>
<td>0.6119</td>
<td></td>
<td>1.123 (8)</td>
</tr>
<tr>
<td>0.8338</td>
<td></td>
<td>0.947 (9)</td>
</tr>
<tr>
<td>1.0612</td>
<td></td>
<td>0.804 (8)</td>
</tr>
<tr>
<td>P(O-i-Pr)₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0000</td>
<td></td>
<td>0.269 (4)</td>
</tr>
<tr>
<td>0.2640</td>
<td></td>
<td>0.174 (3)</td>
</tr>
<tr>
<td>0.4960</td>
<td></td>
<td>0.133 (1)</td>
</tr>
<tr>
<td>0.7219</td>
<td></td>
<td>0.1123 (7)</td>
</tr>
<tr>
<td>0.9070</td>
<td></td>
<td>0.099 (1)</td>
</tr>
<tr>
<td>1.222</td>
<td></td>
<td>0.080 (1)</td>
</tr>
<tr>
<td>P(OEt)₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0000</td>
<td></td>
<td>0.1681 (1)</td>
</tr>
<tr>
<td>0.2379</td>
<td></td>
<td>0.1140 (3)</td>
</tr>
<tr>
<td>0.4979</td>
<td></td>
<td>0.0843 (2)</td>
</tr>
<tr>
<td>0.7230</td>
<td></td>
<td>0.0706 (3)</td>
</tr>
<tr>
<td>0.9734</td>
<td></td>
<td>0.0580 (4)</td>
</tr>
<tr>
<td>CP</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0000</td>
<td></td>
<td>0.1002 (6)</td>
</tr>
<tr>
<td>0.2250</td>
<td></td>
<td>0.0755 (6)</td>
</tr>
<tr>
<td>0.4440</td>
<td></td>
<td>0.0568 (4)</td>
</tr>
<tr>
<td>0.6760</td>
<td></td>
<td>0.0488 (4)</td>
</tr>
<tr>
<td>1.0902</td>
<td></td>
<td>0.0372 (4)</td>
</tr>
<tr>
<td>1.397</td>
<td></td>
<td>0.0323 (4)</td>
</tr>
</tbody>
</table>
Table IX. The pseudo first-order rate constants for the reactions of cis-(pip)(L)Cr(CO)$_4$ with P(O-i-Pr)$_3$ in the presence of pip and P(O-i-Pr)$_3$ in CB at 31.1 °C

<table>
<thead>
<tr>
<th>L</th>
<th>[pip]/[P(O-i-Pr)$_3$]</th>
<th>$10^5 \times k_{obs}$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(O-i-Pr)$_3$</td>
<td>0.0000</td>
<td>5.61 (1)</td>
</tr>
<tr>
<td></td>
<td>0.3371</td>
<td>3.49 (1)</td>
</tr>
<tr>
<td></td>
<td>0.6148</td>
<td>2.64 (1)</td>
</tr>
<tr>
<td></td>
<td>0.7022</td>
<td>2.451 (9)</td>
</tr>
<tr>
<td></td>
<td>0.9341</td>
<td>2.060 (8)</td>
</tr>
<tr>
<td>P(OEt)$_3$</td>
<td>0.0000</td>
<td>2.167 (9)</td>
</tr>
<tr>
<td></td>
<td>0.3890</td>
<td>1.299 (6)</td>
</tr>
<tr>
<td></td>
<td>0.5070</td>
<td>1.148 (6)</td>
</tr>
<tr>
<td></td>
<td>0.9672</td>
<td>0.814 (7)</td>
</tr>
<tr>
<td></td>
<td>1.242</td>
<td>0.682 (5)</td>
</tr>
<tr>
<td>CP</td>
<td>0.0000</td>
<td>0.378 (2)</td>
</tr>
<tr>
<td></td>
<td>0.1463</td>
<td>0.313 (2)</td>
</tr>
<tr>
<td></td>
<td>0.2374</td>
<td>0.294 (1)</td>
</tr>
<tr>
<td></td>
<td>0.3109</td>
<td>0.268 (2)</td>
</tr>
<tr>
<td></td>
<td>0.3646</td>
<td>0.268 (2)</td>
</tr>
<tr>
<td></td>
<td>0.4303</td>
<td>0.243 (2)</td>
</tr>
<tr>
<td></td>
<td>0.6801</td>
<td>0.213 (2)</td>
</tr>
</tbody>
</table>
Figure 13. Plots of $k_{obs}$ (s$^{-1}$) vs. $[P(O-i-Pr)_3]/[pip]$ for the reaction of cis-(pip)(L)Mo(CO)$_4$ with $P(O-i-Pr)_3$ in the presence of pip in CB at 31.1 °C. *, L = CP; o, L = P(OEt)$_3$; +, L = P(O-i-Pr)$_3$
as shown in Figures 14 and 15. This behavior is typical of reactions in which competition for intermediates is taking place.

The data obtained in this study are in good agreement with the mechanism proposed by Hyde and Daresbourg. However, the mechanism proposed in this study and in an earlier study of the tungsten analogue involves the formation of the solvated intermediates [(CB)(L)M(CO)₄], (I₂) as shown in Figure 16. The reaction of cis-(pip)(L)M(CO)₄ in the presence of pip and P(O-i-Pr)₃ in CB solution proceeds by the initial dissociation of pip and the formation of the five-coordinated intermediate [(L)M(CO)₄], (I₁). I₁ will react with P(O-i-Pr)₃, pip or CB. The reaction will proceed to form the thermodynamically stable product (P(O-i-Pr)₃)(L)M(CO)₄. The rate law derived in Appendix A and shown in Equations 11 and 12 is similar to the rate law derived by Daresbourg. Nonetheless; the

\[
k_{\text{obs}} = \frac{k_1 k_2 [P(O-i-Pr)_3]}{(k_{-1} [\text{pip}] + k_2 [P(O-i-Pr)_3])} \quad (11)
\]

\[
1/k_{\text{obs}} = (k_{-1}/k_1k_2) \times ([\text{pip}]/[P(O-i-Pr)_3]) + 1/k_1 \quad (12)
\]

thermal data do not demonstrate the formation of the solvated intermediate I₂ where CB occupies the vacant site. The flash photolysis experiments discussed in the next section will establish the formation of I₂.
Figure 14. Plots of \( \frac{1}{k_{\text{obs}}}(s) \) vs. \([\text{pip}]/[\text{P(O-i-Pr)}_3] \) for the reaction of cis-(pip)(L)Mo(CO)_4 with P(O-i-Pr)_3 in the presence of pip and P(O-i-Pr)_3 in CB at 31.1 °C. *, L = CP; o, L = P(OEt)_3; +, L = P(O-i-Pr)_3; #, L = PPh_3
Figure 15. Plots of $1/k_{\text{obs}}$ (s) vs. $[\text{pip}]/[\text{P}(\text{O-i-Pr})_3]$, for the reaction of cis-(pip)$(L)\text{Cr(CO)}_4$ with $\text{P}(\text{O-i-Pr})_3$ in the presence of pip in CB at 31.1 °C. +, $L = \text{CP}$; *, $L = \text{P(OEt)}_3$; o, $L = \text{P(O-i-Pr)}_3$
Figure 16. The mechanism for the thermal reaction of cis-(pip) (L)M(CO)₄ with P(O-i-Pr)₃ (L') in the presence of N = pip in CB solution.
As can be seen in Figures 14 and 15, the plots of $1/k_{\text{obs}}$ vs. $[\text{pip}]/[\text{P}(\text{O-i-Pr})_3]$ are linear with intercepts. The intercept equals $1/k_1$, and the slope equals $k_{-1}/k_1k_2$. The rate constant for pip loss from the cis-(pip)(L)M(CO)$_4$ is $k_1$. The competition ratios ($\text{CR} = k_2/k_{-1}$) are obtained by dividing the intercept by the slope of each line. The competition ratio is the ratio of the rate constant of P(O-i-Pr)$_3$ and pip attacking the five-coordinate intermediate $I_1$. The values of $k_1$ and $k_2/k_{-1}$ are listed in Tables XII and XIII.

Before discussing the data in Tables XII and XIII, the enthalpies and entropies of activation for pip loss ($k_1$) from cis-(pip)(L)M(CO)$_4$ will be addressed. The values of the $k_1$'s were obtained from the intercepts of the linear plots of $1/k_{\text{obs}}$ vs. $[\text{pip}]/[\text{P}(\text{O-i-Pr})_3]$ at 31.1°C. However, the values of $k_1$'s at other temperatures were obtained for the reactions of cis-(pip)(L)M(CO)$_4$ with P(O-i-Pr)$_3$, where the ratio of $[\text{pip}]/[\text{P}(\text{O-i-Pr})_3]$ equals zero. The $k_1$ values which were used to calculate the activation parameters are listed in Tables X and XI.

The activation parameters for the rate constants of dissociation of pip ($k_1$) were obtained using the Eyring equation shown below:

$$\ln(k_1/T) = \ln(R/\text{Nh}) + (\Delta S^\# / R) - (\Delta H^\# / RT)$$ (13)
Table X. The rate constant ($k_1$) for pip dissociation from $\text{cis-}(\text{pip})(L)\text{Mo(CO)}_4$ in CB

<table>
<thead>
<tr>
<th>L</th>
<th>T(°C)</th>
<th>$10^5 \times k_1$ (sec$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPh$_3$</td>
<td>31.1</td>
<td>30. (1)</td>
</tr>
<tr>
<td></td>
<td>34.1</td>
<td>43.1 (2)</td>
</tr>
<tr>
<td></td>
<td>36.9</td>
<td>63.1 (4)</td>
</tr>
<tr>
<td></td>
<td>39.9</td>
<td>104.8 (8)</td>
</tr>
<tr>
<td>P(O-i-Pr)$_3$</td>
<td>31.1</td>
<td>2.62 (6)</td>
</tr>
<tr>
<td></td>
<td>39.9</td>
<td>9.34 (2)</td>
</tr>
<tr>
<td></td>
<td>50.0</td>
<td>39.9 (1)</td>
</tr>
<tr>
<td>P(OEt)$_3$</td>
<td>31.1</td>
<td>1.66 (2)</td>
</tr>
<tr>
<td></td>
<td>39.9</td>
<td>6.30 (5)</td>
</tr>
<tr>
<td></td>
<td>50.2</td>
<td>27.1 (1)</td>
</tr>
<tr>
<td>CP</td>
<td>31.1</td>
<td>1.00 (2)</td>
</tr>
<tr>
<td></td>
<td>39.9</td>
<td>3.90 (1)</td>
</tr>
<tr>
<td></td>
<td>50.2</td>
<td>15.78 (8)</td>
</tr>
</tbody>
</table>

Table XI. The rate constants ($k_1$) for pip dissociation from $\text{cis-}\text{pip(L)}\text{Cr(CO)}_4$ in CB

<table>
<thead>
<tr>
<th>L</th>
<th>T(°C)</th>
<th>$10^5 \times k_1$ (sec$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(O-i-Pr)$_3$</td>
<td>31.1</td>
<td>5.65 (3)</td>
</tr>
<tr>
<td></td>
<td>40.0</td>
<td>24.3 (2)</td>
</tr>
<tr>
<td></td>
<td>51.3</td>
<td>125. (9)</td>
</tr>
<tr>
<td>P(OEt)$_3$</td>
<td>31.1</td>
<td>2.18 (2)</td>
</tr>
<tr>
<td></td>
<td>40.6</td>
<td>10.35 (5)</td>
</tr>
<tr>
<td></td>
<td>51.3</td>
<td>50.9 (2)</td>
</tr>
<tr>
<td>CP</td>
<td>31.1</td>
<td>0.378 (2)</td>
</tr>
<tr>
<td></td>
<td>39.9</td>
<td>1.511 (9)</td>
</tr>
<tr>
<td></td>
<td>51.3</td>
<td>8.70 (3)</td>
</tr>
</tbody>
</table>
Table XII. A list of $k_1$, competition ratio and activation parameters of $k_1$ for the reaction of cis-(pip)(L)Mo(CO)$_4$ with P(O-i-Pr)$_3$ in the presence of pip and P(O-i-Pr)$_3$ in CB at 31.1 °C

<table>
<thead>
<tr>
<th>L</th>
<th>$\theta^b$</th>
<th>$10^5 \cdot k_1$ (s$^{-1}$)$^a$</th>
<th>$k_2/k_{-1}$</th>
<th>$\Delta H_1$ (kcal/mol)</th>
<th>$\Delta S_1$ (e.u)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CP</td>
<td>101</td>
<td>1.00 (2)</td>
<td>0.67 (2)</td>
<td>27.4 (3)</td>
<td>10 (1)</td>
</tr>
<tr>
<td>P(OMe)$_3$</td>
<td>107</td>
<td>1.51 (3)</td>
<td>0.65 (2)</td>
<td>27.9 (5)</td>
<td>12 (1)</td>
</tr>
<tr>
<td>P(OEt)$_3$</td>
<td>109</td>
<td>1.67 (2)</td>
<td>0.51 (1)</td>
<td>27.78 (3)</td>
<td>11.99 (9)</td>
</tr>
<tr>
<td>P(O-i-Pr)$_3$</td>
<td>130</td>
<td>2.61 (6)</td>
<td>0.54 (2)</td>
<td>27.4 (4)</td>
<td>12 (1)</td>
</tr>
<tr>
<td>P(Ph)$_3$</td>
<td>145</td>
<td>3.0 (1)</td>
<td>0.38 (2)</td>
<td>26 (2)</td>
<td>10 (5)</td>
</tr>
</tbody>
</table>

$^a$ At 31.1 °C
$^b$ $\theta$ cone angle from Reference 7

Table XIII. A list of $k_1$s, competition ratios and the activation parameters for $k_1$ for the reaction of cis-(pip)(L)Cr(CO)$_4$ with P(O-i-Pr)$_3$ in the presence of pip and P(O-i-Pr)$_3$ in CB at 31.1 °C

<table>
<thead>
<tr>
<th>L</th>
<th>$\theta^b$</th>
<th>$10^5 \cdot k_1$ (s$^{-1}$)$^a$</th>
<th>$k_2/k_{-1}$</th>
<th>$\Delta H_1$ (kcal/mol)</th>
<th>$\Delta S_1$ (e.u)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CP</td>
<td>101</td>
<td>3.78 (2)</td>
<td>0.90 (5)</td>
<td>29.8 (2)</td>
<td>16.1 (8)</td>
</tr>
<tr>
<td>P(OEt)$_3$</td>
<td>109</td>
<td>21.9 (2)</td>
<td>0.67 (1)</td>
<td>30.0 (2)</td>
<td>19.9 (7)</td>
</tr>
<tr>
<td>P(O-i-Pr)$_3$</td>
<td>130</td>
<td>56.5 (3)</td>
<td>0.538 (6)</td>
<td>29.4 (4)</td>
<td>20 (1)</td>
</tr>
</tbody>
</table>

$^a$ At 31.1 °C
$^b$ From Reference 7
The plots of $\ln(k_1/T)$ vs. $1/T$ are linear. Figure 17 shows typical plots. The enthalpies of activation ($\Delta H_1^\ddagger$) for the rate constants of pip dissociation were obtained from the slopes, and the entropies ($\Delta S_1^\ddagger$) were obtained from the intercepts of the Eyring plots. The enthalpies and entropies of activation are listed in Tables XII and XIII.

The entropy of activation for the rate constant of pip loss is about 10 e.u. for the molybdenum complexes, and about 19 e.u. for the chromium complexes, indicating a dissociative loss of pip from the metal carbonyl complexes, which leads to the formation of $[(L)M(CO)_4]$ intermediates, as shown in Figure 16. The competition ratios ($k_2/k_1$) listed in Tables XII and XIII are small and very close to one, indicating little discrimination (if any, it is small) between pip and $P(O-i-Pr)_3$ attacking the five-coordinated intermediate $[(L)M(CO)_4]$. In both tables, the $k_1$ values increase as the size of L bonded to the metal center increases or as the cone angle, as defined by Tolman,$^7$ increases. It is tempting to conclude that the steric factor (cone angle) is causing this effect, but the electronic properties of the ligands bonded to the metal must also have an effect on the rate constant of pip dissociation. For example, a $20^\circ$ increase in the cone angle between $P(OEt)_3$ and $P(O-i-Pr)_3$ caused an increase in the rate constant by a factor of 1.5; however, a $15^\circ$
Figure 17. The Eyring plots of $\ln (k_1/T)$ vs. $1/T$ for the rate constants of pip loss from cis-(pip)(L)Cr(CO)$_4$

o, $L = \text{P(\text{O-i-Pr})}_3$

$, L = \text{P(\text{OEt}})_3$

+, $L = \text{CP}$
increase in the cone angle between P(0-i-Pr)\textsubscript{3} and PPh\textsubscript{3} caused an increase in rate constant by a factor of 11.5, as shown in Table XII.

The electronic and steric effect of ligands on the rate constants (k\textsubscript{1}) can be separated using Equation 13 shown below:

\[
\log (k_1) = a \theta + b \upsilon + c
\]

\theta and \upsilon, as defined in the introduction, are the steric and the electronic factors, where a, b and c are constants. Using a multi-linear regression, one will be able to solve for the values of a, b and c. The values obtained are listed in Table XIV. The positive values of a indicate an increase of k\textsubscript{1} which results from the increase of the cone angle, but negative b values indicate a decrease in k\textsubscript{1} as the electronic factor increases, or as the back-bonding ability of the ligand bonded to the metal center increases. The steric effect on the rate constant for pip loss occurs because larger ligands will force pip to dissociate faster. As the back-bonding ability of L increases, the metal center becomes more acidic, thus enhancing the bonding between the metal and the electron donor, pip. This is a ground state effect. Furthermore, ligands which are weaker π-acceptors are known to be better donors\textsuperscript{9,10} and will stabilize the transition state.\textsuperscript{8}
The metal center also affects the rate of pip dissociation as shown in Table XV. For small ligands such as CP (cone angle = 101°), the order for the rate constant $k_1$ as a function of the metal center is Mo > Cr >> W. This order is in disagreement with the effective nuclear charge order Cr < Mo << W\textsuperscript{28}. However, for larger ligands, as shown for P(0Et)\textsubscript{3} and P(0-i-Pr)\textsubscript{3} in Table XIV, the order is Cr > Mo >> W. Therefore, when the size of the ligand is small and the steric effect is less important, the rate constants ($k_1$) order as function of the metal is Mo > Cr > W. However, when the size of the ligand is large and the steric effect is important, the increase in the rate constant of pip loss for the smaller metal Cr will be larger than the increase in the rate constant of pip loss for the larger metals Mo and W.
Table XV. The rate constants of pip dissociation ($k_1$) for $\text{cis-pip(L)M(CO)}_4$ at 31.1 °C in CS solution

<table>
<thead>
<tr>
<th>L</th>
<th>$10^5\cdot k_1(M=\text{Cr})$</th>
<th>$10^5\cdot k_1(M=\text{Mo})$</th>
<th>$10^8\cdot k_1(M=\text{W})^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CP</td>
<td>0.378(2)</td>
<td>1.00(2)</td>
<td>2.06</td>
</tr>
<tr>
<td>$\text{P(OEt)}_3$</td>
<td>2.18(2)</td>
<td>1.67(2)</td>
<td>1.88</td>
</tr>
<tr>
<td>$\text{P(O-i-Pr)}_3$</td>
<td>5.65(3)</td>
<td>2.62(6)</td>
<td>54.2</td>
</tr>
</tbody>
</table>

$^a$ Values estimated from Reference 3

Pulsed laser and flash photolysis studies.

The characterization of the five-coordinated intermediates of Group 6 metal carbonyls were first observed by Sheline and co-workers$^{11,12}$. The photolysis of $\text{M(CO)}_6$ at 77 °K in methylcyclohexane glasses produced $\text{M(CO)}_5$ intermediates, which were identified by IR to have a $C_{4v}$ geometry. In a similar study, Turner and co-workers$^{13,14}$ generated $[\text{M(CO)}_5]$ in a variety of matrices from the photolysis of $[\text{M(CO)}_6]$. The UV-vis spectra of $[\text{M(CO)}_5]$ were found to be sensitive to the nature of the matrix. They concluded that the matrix species interact with the vacant coordination site on the metal.

The photolysis of $\text{M(CO)}_5L$ has been shown by matrix isolation to form two intermediates. For example, Poliakoff's$^{16}$ photolysis of $\text{W(CO)}_5\text{CS}$ led to the formation $[\text{W(CO)}_4\text{CS}]$, which was found to exist in two isomeric forms,
as shown in Reaction 12. He then presented evidence that the photochemically generated species \([\text{W(CO)}_4\text{CS}]\) is in a vibrationally or electronically excited state. In this excited state, the rearrangement of \([\text{W(CO)}_4\text{CS}]\) intermediates takes place as shown in Reaction 13.

\[
\begin{align*}
\text{CO} & \quad \text{CO} \\
\text{CO} & \quad \text{CO} \\
\text{CO} & \quad \text{CO}
\end{align*}
\quad \text{Matrix} \quad \text{hw}
\]

\[
\begin{align*}
\text{CS} & \quad \text{CS} \\
\text{CO} & \quad \text{CO} \\
\text{CO} & \quad \text{CO}
\end{align*}
\]

(12)

\[
\begin{align*}
\text{C}_4\nu & \quad \text{C}_s
\end{align*}
\]

In the discussion of the thermal reactions, the competition ratios \((k_2/k_{-1})\) of pip and \(\text{P(O-i-Pr)}_3\) attacking the five-coordinate intermediates \(\text{LM[(CO)}_4\) were calculated. By using the flash photolysis technique the hope was to generate these intermediates in predominant quantities, thereafter measuring the rate constants of the pip attacking the five-coordinate intermediates \((k_{-1} \text{ in Figure 16})\) and \(\text{P(O-i-Pr)}_3 \) attacking the five-coordinate intermediates \((k_2 \text{ in Figure 16})\). As will be seen, the flash photolysis experiments were not as straightforward as expected.
In this study, pulsed laser flash photolysis was performed on \( \text{cis-}(\text{pip})(\text{L})\text{M(CO)}_4 \) (\( \text{M} = \text{Cr}, \text{Mo}; \text{L} = \text{phosphines and phosphites} \)) in the presence of incoming nucleophile. Figure 18 shows a typical plot of absorbance vs. time before and after pulsed laser flash photolysis of \( \text{cis-}(\text{pip})(\text{L})\text{M(CO)}_4 \) in the presence of \( \text{pip} \) in CB solution. Figure 19 shows similar plot for the same experiment in cyclohexane (CH) solution. The photochemical data for the experiment using CB solution fits as a first-order reaction (decay); however, the photochemical data obtained using CH solution fits as two first-order reaction (decays).

Earlier Dobson and co-workers\(^1\) observed the same behavior in the flash photolysis of \( \text{NP} \text{M(CO)}_4 \) in the presence of \( \text{L} \) (NP = 1-(diethylamino)-2-(diphenylphosphino)ethane). This photochemical reaction proceeds via initial fission of the Mo-N bond and the formation of two intermediates. The vacant site for one is \text{cis}, and the vacant site for the other is \text{trans} to the coordinated phosphorus. Upon pulsed laser flash photolysis of \( \text{cis-}(\text{pip})(\text{L})\text{W(CO)}_4 \), Dobson and co-workers\(^4\) also identified the \text{cis} and \text{trans} intermediates using IR detection. In both studies, the \text{cis} generated intermediates react faster with incoming nucleophiles than the \text{trans} intermediate. Furthermore, both intermediates are solvated, with the solvent occupying the vacant site on the metal, as shown in Figure 20.
Figure 18. Plot of absorbance vs. time before and after pulsed laser flash photolysis of cis-(pip)-(P(O-i-Pr)₃)Mo(CO)₄ in the presence of pip in CB solution at 31.1 °C.
Figure 19. Plot of absorbance vs. time before and after pulsed laser flash photolysis of cis-(pip)(P(O-i-Pr)₃)Mo(CO)₄ in the presence of pip in CH solution at 20.2 °C. [pip] = 0.0813 M
Figure 20. The photochemical products formed after the pulsed laser flash photolysis of cis-(pip)(L)M(CO)$_4$. 
$N = \text{pip, solv = solvent}$
Based on their finding it is reasonable to conclude that the two first-order reactions (decays) shown in Figure 19 resulted from the reaction of pip with the cis-

\[(\text{CH})(\text{L})\text{Mo}()\text{CO}_4\] and trans-\[(\text{CH})(\text{L})\text{M}()\text{CO}_4\] photochemically generated species, and that the cis species react faster than the trans species.

**Reaction of the cis photochemically generated species in CB solution.**

As mentioned earlier, two decays resulted from the flash photolysis of the cis-(pip)(L)M(CO)\(_4\) in the presence of incoming ligands (L'), which means that two intermediates have been generated. After the laser or the flash lamps pulse, pip is lost from the complex, which leads to the formation of the five-coordinate intermediates [(L)M(CO)\(_4\)]. The solvation of these intermediates takes place at a rate too fast to be detected by the instruments used in this study; however, Simon and Peters\(^{18}\) determined that solvation of the photochemically generated [Cr(CO)\(_5\)] is complete within 2.5 ps. Langford and co-workers\(^{19}\) reported a rate constant of 5 \(\times\) 10\(^{10}\) s\(^{-1}\) for the solvation of [W(CO)\(_5\)] by perfluoromethylcyclohexane. The cis-[(CB)(L)M(CO)\(_4\)], (I\(_2\)) (see Figure 16), the intermediate which was previously proposed, was generated in large amounts by the flash photolysis of the cis-(pip)(L)M(CO)\(_4\) in CB solution. The bimolecular rate constants (k\(_{obs}\)) for the reactions of I\(_2\) with excesses of incoming ligands (L') are listed in Tables
XVI and XVII. Plots of $k_{\text{obs}}$ vs. $[L']$ are linear with zero intercepts, as shown in Figures 21 and 22.

The mechanism proposed for the reaction of $\text{I}_2$ with incoming ligands is shown in Figure 23. This mechanism involves initial loss of CB to form the five-coordinated intermediates $[(L)\text{M(CO)}_4]$, ($I_1$). $I_1$ combines with $L'$ to form $(L)(L')\text{M(CO)}_4$. Derivation of the rate law needed to obtain Equation 15 is shown in Appendix A.

$$k_{\text{obs}} = \frac{(k_3k_2[L'])}{(k_3[\text{CB}] + k_2[L'])} \quad (15)$$

Since CB is present in much larger amounts than $L'$, $k_3[\text{CB}] \gg k_2[L']$, so Equation 15 becomes equation 16.

$$k_{\text{obs}} = \left[(k_3k_2)/(k_3[\text{CB}])\right] \times [L'] \quad (16)$$

As seen in Figures 22 and 23, the plots of $k_{\text{obs}}$ vs. $[L']$ are linear with zero intercepts, which is in agreement with Equation 16. The slope of each line equals the composite rate constant divided by [CB], $(k_3k_2/k_3[\text{CB}])$. Values of $k_3k_2/k_3[\text{CB}]$ are listed in Tables XVIII and XIX. In both tables the values of $k_3k_2/k_3[\text{CB}]$ increase as the cone angle of the ligand bonded to the metal increases. This is true because $k_2 = k_3$, as will be shown later. Hence, the value of $k_3k_2/k_3[\text{CB}]$ reflects the rate constant of CB dissociation ($k_3$) from the metal complex. Furthermore, when
Table XVI. Rate constants for the thermal reaction taking place after flash photolysis of cis-\text{pip}\text-(L)\text{Mo}{(\text{CO})}_4\text{ in the presence of pip or }\text{P(O-i-Pr)}_3\text{ in CB at }31.1\ ^\circ\text{C}

<table>
<thead>
<tr>
<th>L</th>
<th>[L'], (M)</th>
<th>(10^{-3} \times k_{\text{obs}} \text{ (s}^{-1}\text{)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>\text{L'} = \text{pip}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>0.1045</td>
<td>11.35 (6)</td>
</tr>
<tr>
<td></td>
<td>0.2734</td>
<td>11.7 (1)</td>
</tr>
<tr>
<td></td>
<td>0.4615</td>
<td>28.6 (3)</td>
</tr>
<tr>
<td></td>
<td>0.6818</td>
<td>48.7 (4)</td>
</tr>
<tr>
<td></td>
<td>0.9032</td>
<td>71.5 (8)</td>
</tr>
<tr>
<td>CP</td>
<td>0.0873</td>
<td>2.78 (4)</td>
</tr>
<tr>
<td></td>
<td>0.2990</td>
<td>8.39 (5)</td>
</tr>
<tr>
<td></td>
<td>0.5540</td>
<td>14.28 (7)</td>
</tr>
<tr>
<td></td>
<td>0.9720</td>
<td>25.0 (1)</td>
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<td>0.0761</td>
<td>2.01 (4)</td>
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<tr>
<td></td>
<td>0.1350</td>
<td>3.48 (1)</td>
</tr>
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<td>0.1739</td>
<td>4.38 (4)</td>
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<td>0.2778</td>
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<td>\text{P(OEt)}_3</td>
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<td>0.1407</td>
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<td>28.1 (2)</td>
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<td></td>
<td>1.0328</td>
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<tr>
<td>\text{P(O-i-Pr)}_3</td>
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<td></td>
<td>0.0764</td>
<td>8.7 (2)</td>
</tr>
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<td>0.5162</td>
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<td></td>
<td>1.0328</td>
<td>128. (1)</td>
</tr>
<tr>
<td>\text{PPh}_3</td>
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<td></td>
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<tr>
<td></td>
<td>0.2139</td>
<td>80.5 (1)</td>
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<td>0.4178</td>
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</tr>
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<td></td>
<td>0.6140</td>
<td>207. (6)</td>
</tr>
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<td></td>
<td>1.1234</td>
<td>376. (5)</td>
</tr>
<tr>
<td>$L''$</td>
<td>$[L''], ,(M)$</td>
<td>$10^3 \times k_{obs} ,(s^{-1})$</td>
</tr>
<tr>
<td>-------</td>
<td>----------------</td>
<td>----------------------------------</td>
</tr>
<tr>
<td>$L'' = P(O-i-Pr)_3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CP</td>
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<tr>
<td>0.0760</td>
<td>1.45 (2)</td>
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<td>$P(OEt)_3$</td>
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<td>1.0925</td>
<td>37.0 (6)</td>
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<td>0.9241</td>
<td>32.9 (2)</td>
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<tr>
<td>0.4577</td>
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<tr>
<td>$P(O-i-Pr)_3$</td>
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<tr>
<td>0.9241</td>
<td>82. (8)</td>
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<td>0.7305</td>
<td>68.5 (5)</td>
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<td>0.6648</td>
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<td>0.5427</td>
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<td>0.4577</td>
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<td>$PPh_3$</td>
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<td>0.2893</td>
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<tr>
<td>0.1350</td>
<td>42. (3)</td>
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</table>
Table XVII. Rate constant for the thermal reaction taking place after flash photolysis of cis-(pip)(L)Cr(CO)\textsubscript{4} in the presence of pip or P(O-i-Pr)\textsubscript{3} in CB at 31.1 °C

<table>
<thead>
<tr>
<th>L</th>
<th>[L'], (M)</th>
<th>10\textsuperscript{-3} * k\textsubscript{obs} (s\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>L' = pip</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CP</td>
<td>0.6486</td>
<td>7.17 (5)</td>
</tr>
<tr>
<td></td>
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<td>5.69 (2)</td>
</tr>
<tr>
<td></td>
<td>0.3850</td>
<td>4.40 (4)</td>
</tr>
<tr>
<td></td>
<td>0.3243</td>
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<tr>
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<td>0.2543</td>
<td>2.93 (5)</td>
</tr>
<tr>
<td></td>
<td>0.1621</td>
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</tr>
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<td></td>
<td>0.0984</td>
<td>1.14 (2)</td>
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<tr>
<td>P(OEt)\textsubscript{3}</td>
<td>0.1045</td>
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<td></td>
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<td>P(O-i-Pr)\textsubscript{3}</td>
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Table XVII - Continued

<table>
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<tr>
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<th>([L'], \text{ (M)})</th>
<th>(10^{-3} \times k_{obs} \text{ (s}^{-1}))</th>
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<tbody>
<tr>
<td>(L' = \text{P(O-i-Pr)}_3)</td>
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<td>(\text{P(O-i-Pr)}_3)</td>
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<tr>
<td>(\text{P(OEt)}_3)</td>
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<tr>
<td></td>
<td></td>
<td>17.9 (2)</td>
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</table>
Figure 21. Plots of $k_{obs}$ (s$^{-1}$) vs. [L'] (M) for the reaction of cis-(CB)(L)Mo(CO)$_4$ with L' in CB at 31.1 °C. a) L' = pip; #, L = CP; +, L = P(OEt)$_3$; *, L = P(O-i-Pr)$_3$; O, L = PPh$_3$, b) L' = P(O-i-Pr)$_3$; #, L = CP; +, L = P(OEt)$_3$; O, L = P(O-i-Pr)$_3$; *, L = PPh$_3$
Figure 22. Plots of $k_{\text{obs}}$ (s$^{-1}$) vs. $[L']$ (M) for the reaction of cis-(CB)(L)Cr(CO)$_4$ with $L'$ in CB at 31.1 °C. a) $L' = \text{pip}; +, L = \text{CP}; *, L = P(\text{OEt})_3$; $O, L = P(\text{O-i-Pr})_3$; b) $L' = P(\text{O-i-Pr})_3; +, L = \text{CP}; O, L = P(\text{OEt})_3; *, L = P(\text{O-i-Pr})_3$
Figure 23. The mechanism for the thermal reaction of photochemically generated cis-(CB)(L)M(CO)$_4$ with L' (L' = pip, P(O-i-Pr)$_3$) in CB solution.
P(O-i-Pr)$_3$ is the incoming nucleophile, $k_3$ (the rate constant for CB dissociation) and $k_{-3}$ (the rate constant for CB combination with $I_1$) are similar to the $k_3$ and $k_{-3}$ when pip is the incoming nucleophile. Therefore, the competition ratios for the photochemical reactions of each complex listed in Tables XVIII and XIX can be obtained by dividing the values of $k_3k_2/k_{-3}[CB]$ when P(O-i-Pr)$_3$ is the incoming nucleophile by the values of $k_3k_2/k_{-3}[CB]$ when pip is the incoming nucleophile. The competition ratios listed in Tables XVIII and XIX are similar to the competition ratios obtained thermally and listed in Tables XII and XIII, which indicates that similar intermediates, namely the five-coordinated intermediates [(L)M(CO)$_4$, ($I_1$), are being generated in both the thermal and photochemical reactions.

As mentioned earlier the rate of CB dissociation ($k_1$) increases as the cone angle of the ligand bonded to the metal center increases. Using Equation 17, the electronic and steric effect on the rate constants ($k_3k_2/k_{-3}[CB]$) were separated by solving for $a$, $b$ and $c$. The data obtained are

$$\log(k_3k_2/k_{-3}[CB]) = a\theta + b\nu + c$$  \hspace{1cm} (17)$$

listed in Table XX. The positive steric parameters ($a$) indicate an increase in the rate constants (rate constants of CB dissociation from the metal), as the cone angle of $L$ bonded to the metal increases. However, the negative
Table XVIII. The rate constants of the thermal reaction taking place after pulse laser flash photolysis of cis-(pip)(L)Cr(CO)_4 in the presence of L'in CB solution at 31.1 °C

<table>
<thead>
<tr>
<th>L</th>
<th>L' = P(O-i-Pr)_3</th>
<th>L' = pip</th>
</tr>
</thead>
<tbody>
<tr>
<td>CP</td>
<td>0.87 (3)</td>
<td>1.10 (1)</td>
</tr>
<tr>
<td>P(OEt)_3</td>
<td>5.75 (11)</td>
<td>7.83 (7)</td>
</tr>
<tr>
<td>P(O-i-Pr)_3</td>
<td>20.6 (4)</td>
<td>31.7 (3)</td>
</tr>
<tr>
<td>CO</td>
<td>---</td>
<td>2.89 (2)</td>
</tr>
</tbody>
</table>

Table XIX. The rate constants of the thermal reaction taking place after pulse laser flash photolysis of cis-(pip)(L)Mo(CO)_4 in the presence of L' in CB solution at 31.1 °C

<table>
<thead>
<tr>
<th>L</th>
<th>L' = P(O-i-Pr)_3</th>
<th>L' = pip</th>
</tr>
</thead>
<tbody>
<tr>
<td>CP</td>
<td>1.6 (1)</td>
<td>2.55 (4)</td>
</tr>
<tr>
<td>P(OEt)_3</td>
<td>3.5 (2)</td>
<td>5.75 (15)</td>
</tr>
<tr>
<td>CO</td>
<td>---</td>
<td>10.40 (5)</td>
</tr>
<tr>
<td>P(O-i-Pr)_3</td>
<td>9.9 (8)</td>
<td>12.4 (5)</td>
</tr>
<tr>
<td>PPh_3</td>
<td>19.2 (9)</td>
<td>32.5 (3)</td>
</tr>
</tbody>
</table>
Table XX. The steric and electronic parameters for the rate constants of \( \frac{k_3k_2}{k_3(CB)} \) for the reaction of \( \text{cis-}[(CB)(L)M(CO)_4] \) with \( L' \)

<table>
<thead>
<tr>
<th>M</th>
<th>10^2*a</th>
<th>10^2*b</th>
<th>10^2*c</th>
<th>L'</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo</td>
<td>1.87</td>
<td>-1.46</td>
<td>32.8</td>
<td>P(O-i-Pr)_3</td>
</tr>
<tr>
<td></td>
<td>1.62</td>
<td>-2.11</td>
<td>46.8</td>
<td>pip</td>
</tr>
<tr>
<td>Cr</td>
<td>2.78</td>
<td>-5.72</td>
<td>120.7</td>
<td>pip</td>
</tr>
<tr>
<td></td>
<td>2.53</td>
<td>-5.61</td>
<td>118.6</td>
<td>P(O-i-Pr)_3</td>
</tr>
</tbody>
</table>

electronic parameters (b) indicate a decrease in rate constants as the back-bonding of \( L \) increases. This is similar to the data obtained from the thermal reactions as listed in Table XIV. However, when \( L \) bonded to the metal center is CO, the rate constants deviate from the patterns of the other ligands, so these were not included in the calculation for the electronic and steric parameters. Even though the cone angle of CO is 98°, which is smaller than the cone angle of CP (cone angle = 101°), the rate constant for CB dissociation when \( L \) is CO is larger than the rate constant when \( L \) is CP, as shown in Table XVIII. In Table XIX the rate of CB dissociation when \( L \) is CO is faster than the rate of CB dissociation when \( L \) is P(OEt)_3 or CP.
What makes CB dissociate faster than expected for the complexes when L is CO is not clear. An explanation of this phenomenon is presented below. In the ligands used in this study, the π back-bonding and the σ-donating ability are shown below.

\[
PPh_3 > \text{P(O-i-Pr)}_3 > \text{P(0Et)}_3 > \text{CP} \quad \text{σ-donation}
\]

\[
\text{CO} > \text{CP} > \text{P(OEt)}_3 > \text{P(O-i-Pr)}_3 > \text{PPh}_3 \quad \text{π back-bonding}
\]

The electronic effect of a ligand is most likely caused by its σ-donating and the π back-bonding abilities of the ligands. The better donor ligands will stabilize the transition state and therefore increase the rate of CB dissociation. The better π-acceptor ligands will make the metal more acidic, enhancing the bonding between the metal and CB, which decreases the rate of CB dissociation. It is clear from the above discussion that the electronic effect on the rate of CB dissociation is due to both the σ-donating and π-accepting ability of the ligand bonded to the metal. The CO is well known to be a good π-acceptor but its σ-donating ability is unclear. For example, Graham determined CO to be a better σ-donor than PF₃. However, Hall disagrees with Graham's results, but he concluded that CO's act as electron reservoirs and keep the overall metal d electron delocalization constant. In other words,
the CO's will donate electrons whenever the metal needs them. This may cause a stabilization of the transition state and increase the rate of CB dissociation.

The effect of the metal center on the rate constants of CB dissociation can be seen in the data listed in Table XXI.

Table XXI. The rate constants $k_3 k_2 / k_3 [CB] (k')$ obtained for the photochemical reactions of cis-(pip) (L)M(CO)$_4$ with pip at 31.1 °C

<table>
<thead>
<tr>
<th>L</th>
<th>$10^{-4} k' (M = Cr)$</th>
<th>$10^{-4} k' (M = Mo)$</th>
<th>$10^{-4} k' (M = W)$ $^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CP</td>
<td>1.10(1)</td>
<td>2.55(4)</td>
<td>0.184(7)CP</td>
</tr>
<tr>
<td>CO</td>
<td>2.89(2)</td>
<td>10.4(5)</td>
<td>0.0</td>
</tr>
<tr>
<td>P(OEt)$_3$</td>
<td>7.83(7)</td>
<td>5.75(15)</td>
<td>0.423(6)</td>
</tr>
<tr>
<td>P(O-i-Pr)$_3$</td>
<td>31.7(3)</td>
<td>12.4(5)</td>
<td>1.00(5)</td>
</tr>
</tbody>
</table>

The pattern seen in this table is similar to that seen in Table XIV for the thermal dissociation of pip from the metal complexes. For small ligands bonded to the metal (CP and CO), the order for the rate constants $(k_3 k_2 / k_3 [CB])$ as a function of the metal center is Mo > Cr > W. This order changes to Cr > Mo > W for larger ligands. As mentioned earlier, when the ligand is small so that the steric factor is not important, the order is Mo > Cr > W. However, when the ligand bonded to the metal is large the
steric effect becomes important, especially for the small metal Cr, which causes the order to be Cr > Mo > W.

The reaction of the trans photochemically generated species in CB solution.

After the pulsed laser flash photolysis of cis-(pip)(P(O-i-Pr)_3)Mo(CO)_4 in the presence of pip in CB solution, one first-order decay was observed, as shown in Figure 19. While monitoring the reaction using a longer time scale, a second and slower first-order decay was observed. This decay was attributed\textsuperscript{3,4,17} to the reaction of photochemically generated trans-[(CB)(L)M(CO)_4] with incoming nucliphile (L'). The slow data obtained from the photochemical substitution reaction of cis-(pip)(L)Mo(CO)_4 and cis-(pip)(L)Cr(CO)_4 with incoming nucleophile are listed in Table XXII. The data obtained when L = CO are listed in Tables XXVI and XVII.

Plots of k_{obs} vs. [L'] (L' = pip) are linear with zero intercepts, as shown in Figure 25. The mechanism proposed for the reaction of trans-[(CB)(L)M(CO)_4] is similar to that of the cis analogue shown in Figure 24. The rate law derived in Appendix A gives Equation 17.

\[
k_{obs} = \frac{k_5 k_6 [\text{pip}]}{k_5 [\text{CB}] + k_6 [\text{pip}]}
\]

but since \( k_5 [\text{CB}] \gg k_6 [\text{pip}] \), Equation 17 becomes Equation 18.
\[ k_{obs} = \left( \frac{k_5 k_6}{k_5 [CB]} \right) \times [\text{pip}] \quad (18) \]

Therefore, plots of \( k_{obs} \) vs. [pip] are expected to be straight lines, as shown in Figure 26. The slopes of the lines \( \left( \frac{k_5 k_6}{k_5 [CB]} \right) \) are listed in Table XXIII.

As will be seen in the next sections, \( k_6 = k_5 \); therefore, the rate constants \( \frac{k_5 k_6}{k_5 [CB]} \) largely reflect the values of the rate constants for the CB dissociation from \( \text{trans-}(CB)(L)M(CO)_4 \). In Table XXIII the order of the ligand effect on the rate constants of CB dissociation is CO > P(OEt)_3 > P(0-i-Pr)_3 > PPh_3. This order is opposite to the order given for the rate constants of CB dissociation from the \( \text{cis-}[(CB)(L)M(CO)_4] \). The rate constants of CB dissociation from \( \text{trans-}[(CB)(L)M(CO)_4] \), as expected, are not influenced by the size of \( L \) bonded to the metal center, but increase as the \( \pi \) back-bonding ability of \( L \) increases. These facts are in disagreement with the results of Atwood and coworker's\(^{20,21,22}\) for the displacement of \( L' \) from \( \text{trans-}(L')(L)M(CO)_4 \) (\( L' \) and \( L \) are phosphines and phosphites). Their results indicate that the rate of displacement of \( L' \) increases as the size of \( L \) increases. For example, he measured the rate of PPh_3 dissociation from \( \text{trans-PPh}_3(L')Cr(CO)_4 \), as shown in Reaction 14. The order of dissociation of the \( \text{trans PPh}_3 \) to \( L \) is PPh_3 > PBu_3 > P(0Ph)_3 > P(0Me)_3 > CO. This order is similar to that
Table XXII. The thermal reaction of the photochemically generated trans-[\((\text{CB})(L)\text{M(CO)}_4\)] with pip in CB at 31.1 °C

<table>
<thead>
<tr>
<th>M</th>
<th>L</th>
<th>[pip]</th>
<th>$10^{-3} \times k_{\text{obs}}$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>P(\text{O-i-Pr})$_3$</td>
<td>0.2960</td>
<td>3.61 (4)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.2219</td>
<td>2.67 (1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.19065</td>
<td>2.23 (1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.1417</td>
<td>1.71 (5)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.0487</td>
<td>0.555 (2)</td>
</tr>
<tr>
<td></td>
<td>P(\text{OEt})$_3$</td>
<td>0.3991</td>
<td>7.02 (7)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.3888</td>
<td>6.1 (4)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.2519</td>
<td>4.46 (12)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.1996</td>
<td>3.54 (3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.1260</td>
<td>2.025 (5)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.06032</td>
<td>0.97 (8)</td>
</tr>
<tr>
<td>Mo</td>
<td>PPh$_3$</td>
<td>0.5926</td>
<td>4.04 (6)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.4491</td>
<td>3.04 (3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.2926</td>
<td>2.1 (1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.2245</td>
<td>1.64 (1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.1482</td>
<td>1.07 (2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.1234</td>
<td>0.90 (3)</td>
</tr>
<tr>
<td></td>
<td>P(\text{O-i-Pr})$_3$</td>
<td>0.2217</td>
<td>4.82 (7)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.1776</td>
<td>3.92 (5)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.1250</td>
<td>2.83 (5)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.0764</td>
<td>1.75 (4)</td>
</tr>
</tbody>
</table>

Table XXIII. The rate constants for the reactions of trans-[\((\text{CB})\text{M(CO)}_4\)] with pip in CB at 31.1 °C

<table>
<thead>
<tr>
<th>M</th>
<th>L</th>
<th>$10^{-4} \times (k_5k_6/k_{-5}[\text{CB}])$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>P(\text{O-i-Pr})$_3$</td>
<td>1.23 (2)</td>
</tr>
<tr>
<td></td>
<td>P(\text{OEt})$_3$</td>
<td>1.80 (4)</td>
</tr>
<tr>
<td></td>
<td>CO</td>
<td>2.89 (2)</td>
</tr>
<tr>
<td>Mo</td>
<td>P(\text{O-i-Pr})$_3$</td>
<td>2.12 (3)</td>
</tr>
<tr>
<td></td>
<td>PPh$_3$</td>
<td>0.67 (1)</td>
</tr>
<tr>
<td></td>
<td>CO</td>
<td>10.40 (5)</td>
</tr>
</tbody>
</table>
Figure 24. The mechanism for the thermal reaction of photochemically generated trans-[(CB)(L)M(CO)$_4$] with L' (L' = pip)
Figure 25. Plots of $k_{obs}$ (s$^{-1}$) vs. [pip] (M) for the reaction of trans-(CB)(L)M(CO)$_4$ with L' in CB at 31.1 °C. a) M = Cr; o, L = P(O-i-Pr)$_3$; #, L = P(O-i-Pr)$_3$; *, L = CO, b) M = Mo; o, L = PPh$_3$; #, L = P(O-i-Pr)$_3$; *, L = CO
expected for the cis complexes where the larger ligands increase the rate of PPh$_3$ dissociation. It is difficult to conceive of a steric interaction from a trans ligand.

The crystal structures$^{21}$ showed no correlation between the Cr-PPh$_3$ bond lengths and rates of PPh$_3$ dissociation from trans-(PPh$_3$)(L)Cr(CO)$_4$ complexes as shown in Table XXIV. The Cr-PPh$_3$ bond lengths increase as the π-accepting

Table XXIV. The Cr-PPh$_3$ bond lengths of trans-Cr(CO)$_4$(L)(PPh$_3$) from Reference 21

<table>
<thead>
<tr>
<th>L</th>
<th>Cr-PPh$_3$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBu$_3$</td>
<td>2.345 (3)</td>
</tr>
<tr>
<td>P(OMe)$_3$</td>
<td>2.362 (2)</td>
</tr>
<tr>
<td>P(OPh)$_3$</td>
<td>2.393 (1)</td>
</tr>
<tr>
<td>CO</td>
<td>2.422 (1)</td>
</tr>
</tbody>
</table>

ability of the trans ligands increases. Schenk and Buchner$^{23}$ measured the coupling constant ($J(W-P)$) for different trans-(L)(L'W(CO)$_4$. He concluded that a ligand forming a strong bond to the metal also demands more s and d character from the bond, leaving less s and d character for
the bond to the trans ligand. Since $J(W-P)$ directly reflects the contribution of the tungsten s orbital to the W-P bond, $J(W-P)$ is a measure of the trans influence of the ligand opposite to itself. They arranged the following ligands according to their increasing trans influence on tungsten:

$$\text{SbPh}_3 < \text{AsPh}_3 < \text{PPh}_3 < \text{CO}$$

The $^{31}$P-NMR and the crystal structure data are in good agreement with the results presented in the present study for the rate of CB dissociation from trans-$(\text{CB})(\text{L})\text{M(CO)}_4$. The trans influence in this case is similar to the well-known trans effect in square-planar complexes.$^{24}$ It is most likely that the trans influence is a ground state effect; that is, the better $\pi$-acceptor ligand reduces the bonding between CB and the metal center. As the $\pi$-acceptor ability of L increases, the electron density between L and the metal center increases. As the electron density between L and the metal center increases, the electron density between the metal center and CB decreases. This weakens the bond between CB and the metal, resulting in an increase in the rate of CB dissociation. Finally, it is worth noting that the data in Table XXIII show the rate of CB dissociation order is Mo > Cr for a given ligand bonded to the metal. This is another indication that the size of the ligands is not important in the trans-$(\text{CB})(\text{L})\text{M(CO)}_4$ complexes. Data for the reaction of photochemically
generated trans-[(CB)(L)W(CO)₄] are not presented, because it was not possible to obtain reproducible data since a small signal was obtained in the flash photolysis experiment using the tungsten complexes. Furthermore, the complexes with L = CP showed one decay. This could be due to the fact that the cis- and trans-[(CB)(CP)M(CO)₄] react with L' at the same rate.

The photochemical reaction in cyclohexane.—The reactions of the photochemically generated species with incoming ligand in cyclohexane (CH) solution are about 1000 times faster than in chlorobenzene (CB) solution. This is true for both the cis and trans photochemically generated intermediates, which is a good indication that these intermediates are solvated. A typical plot of absorbance vs. time before and after the pulsed laser flash photolysis of cis-(pip)(P(O-i-Pr)₃)Mo(CO)₄ in the presence of pip as the incoming nucleophile in CH solution is shown in Figure 19. A similar plot was obtained when pip was replaced by CB. This indicates that CB is behaving like any ligand where kinetically stable cis- and trans-[(CB)(P(O-i-Pr)₃)M(CO)₄] intermediates are formed, as identified by Dobson and co-workers⁴ for the tungsten analogue.

A pulsed laser flash photolysis experiment was performed on cis-(pip)(L)M(CO)₄ in the presence of CB and pip in CH solution. As would be expected, the photochemically generated intermediated [LM(CO)₄],(I₁) will
react with CH, CB and pip. This process takes place in a picosecond$^{18,19}$ to form cis-$[(CH)(L)M(CO)_4]$, (CH$_1$), cis-[(CB)LM(CO)$_4$], (CB$_1$), and cis-(pip)(L)M(CO)$_4$, (pip)$_1$. In a separate experiment using pulsed laser flash photolysis of cis-(pip)(P(O-i-Pr)$_3$)Mo(CO)$_4$, the pseudo-first order rate constants were measured for the reaction of the photochemically generated cis and trans species with pip or with CB at 20.2 °C in CH solution. When CB was the incoming nucleophile, the rate constants for the fast and slow decays were 6(3) $\times$ 10$^7$ s$^{-1}$ and 8(5) $\times$ 10$^6$ s$^{-1}$, respectively. But when pip was the incoming nucleophile, the rate constants for the fast and slow decays were 8(2) $\times$ 10$^7$ s$^{-1}$ and 1.2(1) $\times$ 10$^7$ s$^{-1}$, respectively. Thus, after 1 µs the reaction solution will contain the cis- and trans-[(CB)(P(O-i-Pr)$_3$)Mo(CO)$_4$]. The cis and trans reactions with pip were then monitored as they proceeded to form the cis- and trans-(pip)(P(O-i-Pr)$_3$)Mo(CO)$_4$.

The data obtained from the pulsed laser flash photolysis of cis-(pip)(L)M(CO)$_4$ in the presence of pip and CB in CH solution at three different temperatures are listed in Table XXV. Plots of $k_{obs}$ vs. [pip]/[CB], as shown in Figures 26 and 27, are curved.
Table XXV. The rate constants of cis-[(CB)P(O-i-Pr)₃M(CO)₄] reaction with pip in CH at 31.1 °C

<table>
<thead>
<tr>
<th>M</th>
<th>T °C</th>
<th>[CB]/[pip]</th>
<th>10⁻⁴ * k_{obs} (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo</td>
<td>11.0</td>
<td>0.83</td>
<td>12.0 (2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.30</td>
<td>12.1 (2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.82</td>
<td>10.5 (1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.74</td>
<td>10.3 (1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.42</td>
<td>6.9 (2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.36 (2)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>10.5 (1)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.36 (2)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.82</td>
<td>6.6 (1)</td>
</tr>
<tr>
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<td></td>
<td>3.36 (2)</td>
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<td>5.69 (4)</td>
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<tr>
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<td>3.36 (2)</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>7.42</td>
<td>5.79 (9)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.36 (2)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>18.68</td>
<td>3.44 (5)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.36 (2)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20.8</td>
<td>0.83</td>
<td>6.6 (3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.30</td>
<td>6.5 (3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.82</td>
<td>6.6 (3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.74</td>
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### Table XXV - Continued

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However, plots of $1/k_{obs}$ vs. [CB]/[pip] are linear, as shown in Figures 28 and 29. The mechanism proposed is
shown in Figure 30. The kinetically stable cis-
[(CB)(L)M(CO)₄] will decay by the reversible loss of CB to
form [LM(CO)₄], (I₁), which is in equilibrium with cis-
[(CH)(L)M(CO)₄], (I₃), and finally the I₁ reaction with pip
formed cis-(pip)(L)M(CO)₄. A steady state approximation for
I₁ and I₃ was used to derive the rate law (see Appendix A)
to obtain Equations 19 and 20.

\[ k_{\text{obs}} = \frac{k_3k_2[pip]}{k_3[CB] + k_2[pip]} \] (19)

\[ \frac{1}{k_{\text{obs}}} = \frac{k_3}{k_3k_2} * \left( \frac{[CB]}{[pip]} \right) + \frac{1}{k_3} \] (20)

As seen in Figures 28 and 29, the plots of 1/k_{obs} vs.
[CB]/[pip] are linear with intercepts, which is in good
agreement with the mechanism proposed. The intercept equals
1/k₃ and the slope equals k⁻³/k₃k₂. The values of the rate
constants of CB dissociation from cis-[(CB)(L)M(CO)₄] k₃,
k₃k₂/k⁻³ and the competition ratios (k⁻³/k₂) are listed in
Table XXVI. As demonstrated by Dobson and co-workers³,⁴ and
this study, the solvent molecules occupy a specific site in
the octahedral coordination sphere. In the above study, the
replacement of the solvent (CB) by pip, or the disolvation
process, proceeds by a dissociative mechanism. This fact is
supported by the non-linear plots of k_{obs} vs. [pip]/[CB]
shown in Figures 26 and 27. In the associative or
interchange mechanisms shown in Reaction 15, plots of

\[ \text{cis-}(\text{CB})(\text{L})\text{M(CO)}₄ \xrightarrow{k_4[pip]} [\text{CCB}(\text{pip})(\text{L})(\text{M(CO)}₄] \xrightarrow{\text{fast}} \text{cis-}(\text{pip})(\text{L})\text{M(CO)}₄ \] (15)
$k_{\text{obs}}$ vs. $[\text{pip}]/[\text{CB}]$ should be linear provided that $[\text{CB}]$ is constant. Furthermore, the entropies of activation (Table XXVI) for CB dissociation are positive, a further evidence of a dissociative mechanism. The competition ratios reported here and those of other workers$^{2,3,4}$ are close to one, and different from the competition ratio given by Lees and Adamson.$^{24}$ They

Table XXVI. The rate constants for the cis-[(CB)-(P(O-i-Pr)$_3$)M(CO)$_4$] reaction with pip in CH

<table>
<thead>
<tr>
<th>M</th>
<th>T</th>
<th>$10^{-5} \times k_3$</th>
<th>$10^{-5} \times (k_3k_2/k_{-3})$</th>
<th>CR = $k_{-3}/k_2$</th>
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<tbody>
<tr>
<td>Mo</td>
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<td>8.06 (7)</td>
<td>10.1 (2)</td>
<td>0.80 (2)</td>
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<td>20.8</td>
<td>4.0 (3)</td>
<td>5.8 (2)</td>
<td>0.69 (7)</td>
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<tr>
<td></td>
<td>11.0</td>
<td>1.82 (3)</td>
<td>3.10 (4)</td>
<td>0.59 (2)</td>
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</tbody>
</table>

$\Delta H_3^\# = 12.1$ (3) kcal/mol \hspace{2cm} $\Delta S_3^\# = 8.7$ (9) (e.u.)

$\Delta H_3^\# + \Delta H_2^\# - \Delta H_{-3}^\# = 9.5$ (2) kcal/mol

<table>
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<tr>
<th>M</th>
<th>T</th>
<th>$10^{-5} \times k_3$</th>
<th>$10^{-5} \times (k_3k_2/k_{-3})$</th>
<th>CR = $k_{-3}/k_2$</th>
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<tr>
<td>Cr</td>
<td>31.1</td>
<td>18.5 (3)</td>
<td>43.1 (6)</td>
<td>0.43 (1)</td>
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<td>20.8</td>
<td>11.1 (2)</td>
<td>22.3 (2)</td>
<td>0.50 (1)</td>
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<td>10.9</td>
<td>5.7 (3)</td>
<td>11.9 (4)</td>
<td>0.48 (4)</td>
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$\Delta H_3^\# = 12.1$ (3) kcal/mol \hspace{2cm} $\Delta S_3^\# = 8.7$ (9) (e.u.)

$\Delta H_3^\# + \Delta H_2^\# - \Delta H_{-3}^\# = 10.3$ (3) kcal/mol
Figure 26. Plots of $k_{obs}$ (s$^{-1}$) vs. [pip]/[CB] for the reaction of cis-[(CB)(P(O-i-Pr)$_3$)Mo(CO)$_4$] with pip in the presence of CB in CH solution. *, at 11.0 °C; +, at 20.8 °C; o, at 31.1 °C.
Figure 27. Plots of $k_{obs}$ ($s^{-1}$) vs. [pip]/[CB] for the reaction of cis-[(CB)(P(O-i-Pr)$_3$)Cr(CO)$_4$] with pip in the presence of CB in CH solution. * at 10.9 °C; +, at 20.8; o, at 31.1 °C.
Figure 28. Plots of $1/k_{obs}$ (s) vs. [CB]/[pip] for the reaction of cis-[(CB)(P(O-i-Pr)$_3$Mo(CO)$_4$] with pip in the presence of CB in CH solution. *, at 11.0 °C; +, at 20.8 °C; o, at 31.1 °C
Figure 29. Plots of $1/k_{obs}$ (s) vs. [CB]/[pip] for the reaction of cis-[(CB)(P(O-i-Pr)_3)]Cr(CO)_4 with pip in the presence of CB in CH solution. *, at 10.9 °C; +, at 20.8 °C; o, at 31.1 °C
Figure 30. The mechanism for the thermal reaction of photochemically generated cis-[(CB)\((L)M(CO)\textsubscript{4}\)] with pip and CB in CH.
reported a competition ratio of 270 between 4-acetylpyridine and methylcyclohexane for the photochemically generated [W(CO)₅]. When the experiment of Lees and Adamson was repeated, data different from theirs was obtained.

The values of \( k_3k_2/k_3 \) obtained from the reaction of \( \text{cis-}[(\text{CB})(\text{L})\text{M(CO)}_4] \) with pip in CH solution at 31.1 °C are listed in Table XXVI and the values of \( k_3k_2/k_3[\text{CB}] \) obtained from the reaction of \( \text{cis-}(\text{CB})(\text{L})\text{M(CO)}_4 \) in CB at 31.1 °C (Tables XVIII and XIX) should be the same. The rate constant \( k_3k_2/k_3 \) obtained from the reaction of \( \text{cis-}[(\text{CB})(\text{P(O-i-Pr)}_3)\text{Mo(CO)}_4] \) with pip in CH (31.1 °C) is 10.1(2) \( \times 10^5 \) s⁻¹, and the rate constant of the same reaction in CB solution (31.1 °C) is 12.2(5) \( \times 10^5 \) s⁻¹, which was obtained after multiplying the value of \( k_3k_2/k_3[\text{CB}] \) by the concentration of CB. The rate constant for the \( \text{cis-}[(\text{CB})(\text{P(O-i-Pr)}_3)\text{Cr(CO)}_4] \) reaction in CH and CB solution are 43.1(6) \( \times 10^5 \) s⁻¹ and 31.2(3) \( \times 10^5 \) s⁻¹ respectively. The fact that the \( \Delta S^\#_3 \) for the rate of CB dissociation from the chromium complex is zero is not understood.

The order of the rate constants (\( k_3 \)) of CB dissociation from \( \text{cis-}[(\text{CB})(\text{P(O-i-Pr)}_3)\text{M(CO)}_4] \) at 31.1 °C as a function of the metal is Cr > Mo > W. The \( k_3 \) values are shown in Table XXVI but the rate constant (\( k_3 = 0.426(53) \times 10^5 \)) of
CB dissociation from the tungsten complex was obtained from the study of Dobson and co-workers.

The reaction of the trans photochemically generated species in CH solution.--After the pulsed laser flash photolysis of cis-(pip)(P(O-i-Pr)₃)Mo(CO)₄ in the presence of pip and CB in CH solution two decays were observed. The data obtained from the slow decays are listed in Table XXVII. Plots of \( k_{\text{obs}} \) vs. [pip]/[CB] are curved (not shown here), but plots of \( 1/k_{\text{obs}} \) vs. [CB]/[pip] are linear, as shown in Figure 31. The mechanism proposed for the reaction of trans-[(CB)(P(O-i-Pr)₃)Mo(CO)₄ with pip is similar to the cis analogue, as shown in Figure 32. The rate law derived in the Appendix A obtain Equations 21 and 22.

\[
k_{\text{obs}} = \frac{(k_5k_6[L'])}{k_5[CB]} = k_6[L'] \quad (21)
\]

\[
1/k_{\text{obs}} = \frac{(k_5/k_5k_6)}{([CB]/[pip])} + 1/k_5 \quad (22)
\]

Table XXVII. The rate constants for the reaction of trans-[(CB)(P(-O-i-Pr)₃)Mo(CO)₄] in CH with pip and CB

<table>
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<th>T °C</th>
<th>[CB]/[pip]</th>
<th>( 10^{-4}k_{\text{obs}} ) (s⁻¹)</th>
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<td>18.68</td>
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<td>3.74</td>
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Table XXVII - Continued

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<th>[CB]/[pip]</th>
<th>$10^{-4}k_{\text{obs}}$ (s⁻¹)</th>
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<td>20.8</td>
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<td>7.2 (8)</td>
<td>7.1 (9)</td>
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The competition ratios ($k_6/k_5$) are 0.90(7) and 0.9(1) at 31.1 °C and 20.8 °C, respectively. Clearly, there is no discrimination between CB and pip recombination with the five-coordinated intermediate whose vacant site is trans to P(O-i-Pr)₃. In the early discussion the competition ratio was assumed to be one, and the above data confirm this. From the slope of a plot of $1/k_{\text{obs}}$ vs. [CB]/[pip] a value of 2.04(2) x $10^5$ s⁻¹ ($k_5k_6/k_5$) was obtained, the reaction of trans-[(CB)(P(O-i-Pr)₃)Mo(CO)₄] with pip in CB at 31.1 °C $k_5k_6/k_5$ is 2.08(3) x $10^5$ (see Table XXIII). This provides strong evidence for the formation of trans-[(CB)(P(O-i-Pr)₃)Mo(CO)₄] by the pulsed laser flash photolysis of cis-(pip)(P(O-i-Pr)₃)Mo(CO)₄ in the CB/CH mixture experiment and the experiment in CB solution only.
Figure 31. Plots of $1/k_{obs} (s)$ vs. $[CB]/[pip]$ for the reaction of trans-[$(CB)(P(O-i-Pr))_3$]$\text{Mo(CO)}_4$ with pip in the presence of CB in CH solution. *, at 31.1 °C; o, at 20.8 °C.
Figure 32. The mechanism for the thermal reaction of photochemically generated trans-[(CB)(P(O-i-Pr)₃)Mo(CO)₄] with pip in the presence of CB in CH solution
Conclusion

In this study as in others\textsuperscript{3,4,26} the parallel flash photolysis and thermal investigation of ligand substitution reaction in octahedral metal carbonyls complexes (see Figure 33) offer complementary information. The thermal and photochemical reaction of cis-(pip)(L)M(CO)\textsubscript{4} leads to the formation of the five-coordinated [LM(CO)\textsubscript{4}], which does not discriminate between incoming nucleophiles. This is supported by the fact that the thermally obtained competition ratios of P(O-i-Pr)\textsubscript{3} and pip for the five-coordinated intermediates are similar to the competition ratios obtained photochemically. Furthermore, the competition ratios of CB and pip for the five-coordinated intermediate and those mentioned above are close to one, indicating a diffusion controlled reaction of $L'$ ($L' = CB$, pip and P(O-i-Pr)\textsubscript{3}) with the five-coordinated intermediate which is supported by Langford's and co-worker's\textsuperscript{19} and Simon's and co-worker's\textsuperscript{18} results. The rate of solvation of the photochemically generated [M(CO)\textsubscript{5}] is within the expected rate of diffusion. Therefore, the activation energies for solvation and ligand recombination with the five-coordinated intermediates are small. Based on Hammond's postulate,\textsuperscript{27} the solvated species should resemble the non-solvated species. This conclusion is supported by the fact that the changes in enthalpies of activation between the interaction of pip and CB with the naked five-
Figure 33. The overall mechanism for the thermal and photochemical reaction of cis-(pip)(L)M(CO)₄ with L'.
Figure 34. Plot of enthalpy vs. reaction coordinate for conversion of cis-((pip)(P(O-i-Pr)3)M(CO)4 to cis-(CB)(P(O-i-Pr)3)M(CO)4.
coordinated intermediate are small, as shown in Figure 34. As has been shown, the symmetry of the five-coordinated solvated species is $C_4v$; therefore, it is reasonable to assume the same symmetry for the naked five-coordinated intermediate.

The nature of thermal replacement of pip from cis-(pip)(L)M(CO)$_4$ with L' and that of CB from the photochemically generated cis-[(CB)(L)M(CO)$_4$] is dissociative. As was shown in this study, the loss of pip or CB from the metal complexes is influenced by the electronic and steric properties of the ligand bonded to the metal (L). The order of the ligand's (L) effect on the rate constants of pip and CB dissociation from the cis complexes are shown below:

$$PPh_3 > P(O-i-P)_3 > P(OEt)_3 > CP$$

As the size of L increases, the rate constant of the leaving ligand increases. The electronic effect results from the $\sigma$-donating and $\pi$-accepting ability of L; that is, the more $\sigma$-donating ligand stabilizes the transition state, and the more $\pi$-accepting ligand stabilizes the ground state.

In the pulsed laser flash photolysis of cis-(pip)(L)M(CO)$_4$ in CB solution only and in CB/CH mixtures, cis-[(CB)(L)M(CO)$_4$] is formed. This conclusion is supported by the fact that the values of $k_3k_2/k_3$ obtained
from both experiments are the same because in both experiments the rate determining step is the dissociative loss of CB from the metal complex.

The order of CB and pip dissociation from the metal complexes as a function of the metal center is Mo > Cr > W for complexes with small L bonded to the metal. This order is similar to that observed for dissociation of CO and amine from zero valent metal complexes. However, for complexes with large L bonded to the metal, the order is Cr > Mo > W. Dobson and co-workers observed similar behavior for the rate of chelate ring-closure after the pulse laser flash photolysis of (NP)M(CO)₄. When the size of L is large, the steric effect becomes important, especially for the small metal Cr, which changes the order to Cr > Mo > W.

The order of ligand (L) effect on the rate of CB dissociation from trans-(CB)(L)M(CO)₄ is shown below:

\[ \text{CO} > P(\text{OEt}) > P(\text{O-i-Pr})_3 > \text{PPh}_3 \]

The size of L does not seem to affect the rate of CB dissociation. Therefore, as will be expected, the rate of CB dissociation as a function of the metal is Mo > Cr. The ligand trans effect in octahedral metal carbonyl is similar to the trans effect in square-planar complexes, where the better \( \pi \)-accepting ligand increases the rate of dissociation of the ligand trans to itself.
In the thermal substitution reaction of cis-(pip)(L)M(CO)₄ with L', cis and trans-(L)(L')M(CO)₄ were formed. The thermal study does not provide conclusive evidence of how the trans product was formed. As was seen in Chapter 1, two pathways are possible, either the cis product isomerizes to trans, as shown in Reaction 15, or the five-coordinated intermediate isomerizes before the ligand attack, as shown in Reaction 16.

\[
\text{cis-(L')(L)M(CO)₄} \xrightarrow{\text{trans-(L')(L)M(CO)₄}} \text{trans-(L')(L)M(CO)₄} \quad (16)
\]

\[
\text{cis-(L')(L)M(CO)₄} \xleftrightarrow{\text{trans-(L')(L)M(CO)₄}} \text{trans-(L')(L)M(CO)₄} \quad (17)
\]

However, the pulsed laser flash photolysis experiments in this study and in an earlier published study\textsuperscript{26} demonstrated the formation of cis and trans intermediates, where each independent of the other react with L' to form the cis and trans product. Recently, Hall\textsuperscript{34} calculated the energy barrier for the five-coordinated Cr(CO)₄PH₃ and Mn(CO)₄Cl cis/trans conversion to be 10 kcal. This energy barrier is larger than the energy for L' recombination with the five-
coordinate intermediate. Therefore, it is reasonable to conclude that the thermal generated trans-\((\text{L})(\text{L'})\text{M(CO)}_4\) is formed by the thermal isomerization of the cis-\((\text{L})(\text{L'}\text{M(CO)}_4\), not from the isomerization of the five-coordinated species. In contrast, the photochemically trans-generated complexes are believed to be formed from the relaxation of the vibrationally and electronically excited state of five-coordinated intermediate caused by the laser flash\(^{16}\).
CHAPTER REFERENCES


34. Hall, M. B., unpublished results (obtained with permission).
APPENDIX A

DERIVATION OF THE RATE LAW FOR THE MECHANISMS
1 - For the mechanism shown in Figure 16 one can write the following equation:

\[
\begin{align*}
\frac{d[S]}{dt} &= -k_1[S] + k_{-1}[\text{pip}][I_1] \\
\frac{d[I_1]}{dt} &= k_1[S] - k_{-1}[\text{pip}][I_1] - k_2[L'][I_1] \\
&\quad - k_3[\text{CB}][I_1] + k_{-3}[I_2] \\
\frac{d[I_2]}{dt} &= -k_{-3}[I_2] + k_3[\text{CB}][I_1]
\end{align*}
\]

where \([S], [I_1]\) and \([I_2]\) are the concentrations of cis-(pip)(L)M(CO)\(_4\), (L)M(CO) and cis-(CB)(L)M(CO)\(_4\) respectively. Assuming the steady state approximation for \([I_1]\) and \([I_2]\) so that:

\[
\begin{align*}
\frac{d[I_1]}{dt} &= 0 \\
\frac{d[I_2]}{dt} &= 0
\end{align*}
\]

By adding Equations 24 and 25 and solving for \([I_x]\), Equation 27 will be obtained.

\[
[I_x] = \frac{(k_1[S])}{(k_{-1}[\text{pip}] + k_2[L'])}
\]

Substituting 28 into 23 gives Equation 29.

\[
\frac{d[S]}{dt} = \frac{(k_1k_2[L'][S])}{(k_{-1}[\text{pip}] + k_2[L'])}
\]

Under pseudo first-order reaction conditions, Equation 29 reduces to

\[
\frac{d[S]}{dt} = k_{\text{obs}}[S]
\]

where

\[
k_{\text{obs}} = \frac{(k_1k_2[L'])}{(k_{-1}[\text{pip}] + k_2[L'])}
\]

2 - For the mechanism shown in Figure 23.

\[
\begin{align*}
\frac{d[I_2]}{dt} &= -k_3[I_2] = k_{-3}[\text{CB}][I_1] \\
\frac{d(I_1)}{dt} &= k_3[I] - k_{-3}[\text{CB}][I_1] - k_2[L'][I_1]
\end{align*}
\]
Assuming the steady state approximation for $[I_1]$ so that

$$[I_1] = \frac{k_3[I]}{(k_{-3}[CB] + k_2[L'])}$$

and by substituting 34 into 32, Equation 35 is obtained.

$$\frac{d[I_2]}{dt} = \frac{(k_3k_2[L'][I_2])}{(k_{-3}[CB] + k_2[L'])}$$

or

$$= k_{obs}[I_2]$$

where

$$k_{obs} = \frac{(k_3k_2[L'])}{(k_{-3}[CB] + k_2[L'])}$$

since $k_{-3}[CB] >> k_2[L']$

$$k_{obs} = \frac{(k_3k_2/k_{-3}[CB])*[L']}{37}$$

3 - For the mechanism shown in Figure 24, similar
derivation as in 2. For the mechanism in Figure 30,
similar derivation as in 1.
APPENDIX B

FLASH.HA PROGRAM
This program acquires data from the Nicolet 2090 digital scope, applies scale factors, and stores the data in a file. The interface is currently configured to read data from the 2090. It cannot write to the 2090, but this is not terribly important. The interface is via a Metrabyte PIO12
I/O board and the 2090’s Binary I/O. The PI012 is configured in ASYST as two ports: 8255.PORT (Ports A and B, A0 is LSB, B7 is MSB) and IO.PORT (PORT C). The 8255.PORT reads data, while IO.PORT writes data. Data is transferred from the scope on output lines 1B through 13B. These lines are connected to the PI012 via 74LS240 inverting line drivers, which convert from the scope’s negative logic (true or 1 = 0V, false or 0 = 5V) to positive logic, so that the data is read directly by the computer. (Since the data is in two’s complement code, all numbers greater than 127 represent negative numbers. Conversion from two’s complement to signed decimal numbers is done by the word T in this program). The normalization data, carried on scope output 1A (brown wire) is connected to the PI012 8255 PB7; this data is not used, as normalisation data is entered at the keyboard. Lines 2A - 13A are connected to PA0 - PB3; since the 204A digitizer is an 8 bit digitizer only lines 6A through 13A carry data, so a digital mask is applied to the 8255 PA and PB ports that reads only the desired 8 bits (bit4, PA3 - bit11, PB3, yellow wire). Commands to the 2090 are simple, since the only goal is to transfer a full 4K record to the computer. The lines to the 2090 are passed through a 74LS244 line driver because the sink current of the PI012 is too low. Data transfer is initiated by a three step sequence, and controlled by a a simple loop. Initially, 2090 inputs 22B (I/O step, PC4, white wire), 23B
(AC1, PC5, blue wire) and 24B (AC2, PC6, orange wire) are all brought false (5V, neg. logic) with the command 112 DIGITAL.OUT. This sets the Load Address mode (AC1 and AC2 both false). When the 80 DIGITAL.OUT (AC1 true, AC2 false) command is given the the 2090 is placed in the automatic address advance mode, starting at -2048 (the left edge of the screen). When I/O Step is pulsed true (PULSE.BITS command, with PC masked so only PC4 pulses) the scope advances 1 address. This pulse, and the command to read the new data byte, are given in a BEGIN - UNTIL loop.

\ Variable Declarations:

INTEGER SCALAR #PTS \ Number of data points to calculate
INTEGER SCALAR L \ Left (lower) index from READOUT.
\ INDICES
INTEGER SCALAR R \ Right (higher) index from READOUT.
\ INDICES
INTEGER SCALAR NPTS \ Number of points for calculation =
\ R - L + 1
INTEGER SCALAR IP \ INITIAL DATA POINT
INTEGER SCALAR N \ Integer variable
INTEGER SCALAR XI
INTEGER SCALAR YI
INTEGER SCALAR J1
<table>
<thead>
<tr>
<th>Variable</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>REAL SCALAR D1</td>
<td>\ used in the calc. of STD. CORR COEF \ etc.</td>
</tr>
<tr>
<td>REAL SCALAR C1</td>
<td>\ Time per data point - #PTS*TPP = \ total time</td>
</tr>
<tr>
<td>REAL SCALAR A1</td>
<td>\ mV per voltage increment</td>
</tr>
<tr>
<td>REAL SCALAR M</td>
<td>\ +/- Volts full scale, entered in \ SENSITIVITY</td>
</tr>
<tr>
<td>REAL SCALAR TPP</td>
<td>\ Offset voltage entered in OFFSET</td>
</tr>
<tr>
<td>REAL SCALAR MVPP</td>
<td>\ Experiment temperature</td>
</tr>
<tr>
<td>REAL SCALAR VFS</td>
<td>\ Ligand Concentration</td>
</tr>
<tr>
<td>REAL SCALAR VOFFS</td>
<td>\ Monitoring frequency or wavelength</td>
</tr>
<tr>
<td>REAL SCALAR TEMP</td>
<td>\ Used to specify what fraction of \ []MAX is set as \ the minimum value in array PLOT</td>
</tr>
<tr>
<td>REAL SCALAR CONC</td>
<td>\ Minimum value for data in PLOT ( Y \ []MAX*FRACT)</td>
</tr>
<tr>
<td>REAL SCALAR PMF</td>
<td>\ INT is the value of the intercept \ of a plot.</td>
</tr>
<tr>
<td>REAL SCALAR INT</td>
<td>\ SLOPE is the value of the slope of \ a plot.</td>
</tr>
<tr>
<td>REAL SCALAR SLOPE</td>
<td>\ K1 and K2 are rate constants.</td>
</tr>
<tr>
<td>REAL SCALAR K1</td>
<td>\ ABS at t final</td>
</tr>
<tr>
<td>REAL SCALAR K2</td>
<td></td>
</tr>
<tr>
<td>REAL SCALAR PF</td>
<td></td>
</tr>
</tbody>
</table>
REAL SCALAR STD.DEV
REAL SCALAR RESID.MEAN
1 N :=
\ String Definitions
20 STRING FILENAME \ Name of file to store data in
3 STRING ABS/%T \ Absorbance or per cent
\ transmittance
1 STRING %T? \ Is the data entered or read in %T
\ (Y or N)
20 STRING SUBS \ Substrate
20 STRING LIG \ Ligand
20 STRING SOLV \ Solvent
10 STRING DATE
10 STRING TIME
20 STRING XLBL \ Label for X axis
20 STRING YLBL \ Label for Y axis
1 STRING WGTS \ Weighted fit ? (Y or N, N is \ default)
3 STRING NIC \ Type of data to be analysed (raw \ data, competition
\ ratio, Kobs vs L, activation \ parameters, etc.)
1 STRING FIXAXES
1 STRING +/-
2 STRING UV/IR
40 STRING K12 \ used for labe of plot
20 STRING M1 \ error in slope
20 STRING CO
20 STRING ST1
" N" WGT $ := " N" FIXAXES $ := " %T" ABS/%T $ := " UV"
UV/IR $ :=

\ Array Definitions

INTEGER DIM[ 4096 ] ARRAY YR \ Array for raw data
REAL DIM[ 4096 ] ARRAY X(XY) \ Array for time
0 X(XY) :=
X(XY) CREATE.COPY Y(XY) \ Array for Abs/%T
X(XY) CREATE.COPY W1
X(XY) CREATE.COPY W2
X(XY) CREATE.COPY FITDATA \ Calculated Y values
X(XY) CREATE.COPY RE \ 
REAL DIM[ 2 , 6 ] ARRAY COEF1 \ value (for plots)
REAL DIM[ 2 ] ARRAY COEFF \ Coefficients from
\ fits: K1, K2
REAL DIM[ 15 ] ARRAY CCOF
REAL DIM[ 15 ] ARRAY PFS
\ Window Definitions

0 0 0 79 WINDOW {TOPLINE} \ This is the program top
\ line
3 0 3 79 WINDOW {MENUNAME}
6 0 24 79 WINDOW {MENUS}
0 0 23 79 WINDOW {ALL}
20 8 20 79 WINDOW {PROMPT}
24 38 24 79 WINDOW {TRACER}
0 0 24 79 WINDOW {TOTAL}
24 0 24 79 WINDOW {LAST}

: TOTAL
{TOTAL}
SCREEN.CLEAR
;

: ALL
{ALL}
SCREEN.CLEAR
;

: PROMPT
{PROMPT} SCREEN.CLEAR
;

: LAST
{LAST} SCREEN.CLEAR
;

\ 8255.PORT and IO.PORT define I/O ports on the PIO12 board
\ used to acquire data from the Nicolet 2090.

8255.PORT
2 DIGITAL.TEMPLATE RAW
\8255: reads bits 4
YR TEMPLATE.BUFFER
\ PORT A & B ON
\ to 11
\ from Nicolet
\ interface by
\ masking bits

IO.PORT

4 DIGITAL.TEMPLATE PC.OUT
\ PORT C OUTPUTS ON
\ 8255

: ERROR!

PROMPT ." That won't work. ERROR # " ?ERROR# . "." Strike a
key when ready"
BREAK \ KEY DROP MYSELF
;

\ These words read and write data to disk

: WRITE.FILE

FILE.TEMPLATE
14 COMMENTS

INTEGER DIM[ #PTS ] SUBFILE

END

FILENAME DEFER> FILECREATE

FILENAME DEFER> FILEOPEN

ABS/%T             1 >COMMENT
TEMP               2 >COMMENT
SUBS               3 >COMMENT
LIG                4 >COMMENT
CONC               5 >COMMENT
Solv               6 >COMMENT
LAMBDA             7 >COMMENT
"DATE"             8 >COMMENT
TPP                9 >COMMENT
#PTS               10 >COMMENT
MVPP               11 >COMMENT
WGTS               12 >COMMENT
NIC                13 >COMMENT
VOFFS              14 >COMMENT

1 SUBFILE YR     SUB[ 1 , #PTS ] ARRAY>FILE

FILECLOSE
"
: READ.FILE

." Reading file " FILENAME "TYPE
FILENAME DEFER> FILE.OPEN

1 COMMENT> ABS/%T " :=
2 COMMENT> 32 "NUMBER TEMP :=
3 COMMENT> SUBS " :=
4 COMMENT> LIG " :=
5 COMMENT> 32 "NUMBER CONC :=
6 COMMENT> SOLV " :=
7 COMMENT> 32 "NUMBER LAMBDA :=
8 COMMENT> DATE " :=
9 COMMENT> 32 "NUMBER TPP :=
10 COMMENT> 32 "NUMBER #PTS :=
11 COMMENT> 32 "NUMBER MVPP :=
12 COMMENT> WGTS " :=
13 COMMENT> NIC " :=
14 COMMENT> 32 "NUMBER VOFFS :=

1 SUBFILE YR SUB[ 1 , #PTS ] FILE > ARRAY
FILE.CLOSE

; 
\ The following sections set up graphics displays.
\ Vuport definitions
: DATA.VU \ Upper vuport
.050 .050 VUPORT.ORIG

.8 .8 VUPORT.SIZE
HORIZONTAL AXIS.FIT.OFF GRID.OFF

VERTICAL AXIS.FIT.OFF GRID.OFF
1 2 LABEL.POINTS

.180 .210 AXIS.ORIG

.7 .7 AXIS.SIZE

.025 .008 TICK.SIZE

.5 .8 TICK.JUST

; \ Word to setup data vuport axis area
: DATA.VU.SET
  X(XY) SUB[ 1, #PTS ] \ one dimensional
  \ x values
Y(XY) SUB[ 1 , #PTS ]               \ one dimensional
               \ y values

VERTICAL LINEAR
OVER OVER WORLD.COORDS               \ two copies in
                                    \ order
[]MIN/MAX VERTICAL WORLD.SET          \ set vertical
                                      \ scaling
[]MIN/MAX HORIZONTAL WORLD.SET       \ set horizontal
                                      \ scaling
[]MIN SWAP []MIN SWAP WORLD.COORDS AXISS.POINT
                                    \ set axis
                                    \ origin.

: DATA.VU.SET1

X(XY) SUB[ 1 , #PTS ]               \ one dimensional
               \ x values

RE SUB[ 1 , #PTS ]                  \ one dimensional
               \ y values

VERTICAL LINEAR
OVER OVER WORLD.COORDS               \ two copies in
                                    \ order
[]MIN/MAX VERTICAL WORLD.SET          \ set vertical
                                      \ scaling
[]MIN/MAX HORIZONTAL WORLD.SET       \ set horizontal
                                      \ scaling
[]MIN SWAP []MIN SWAP WORLD.COORDS AXISS.POINT
\set axis
\origin.

; DATA.VU.SET2

X(XY) SUB[ L , NPTS ] \ one dimensional
\ x values

RE SUB[ L , NPTS ] \ one dimensional
\ y values

VERTICAL LINEAR

OVER OVER WORLD.COORDS \ two copies in
\ order

[]MIN/MAX VERTICAL WORLD.SET \ set vertical
\ scaling

[]MIN/MAX HORIZONTAL WORLD.SET \ set horizontal
\ scaling

[]MIN SWAP []MIN SWAP WORLD.COORDS AXIS.POINT \ set axis
\ origin.

;

: LOG.VU.SET

X(XY) SUB[ L , NPTS ] \ one dimensional
\ x values

RE SUB[ L , NPTS ] \ one dimensional
\ y values

OVER OVER WORLD.COORDS \ two copies in
\ order
VERTICAL LOGARITHMIC

[MIN/MAX VERTICAL] WORLD.SET \ set vertical
\ scaling

[MIN/MAX HORIZONTAL] WORLD.SET \ set horizontal
\ scaling

[MIN SWAP] [MIN SWAP] WORLD.COORDS AXIS.POINT \ set axis
\ origin.

\ Label plot

: LABEL.PLOT

NORMAL.COORDS

1 LABEL.SCALE.Y / " " YLBL ":=

1 LABEL.SCALE.X / " " sec " " CAT XLBL ":=

.09 .30 POSITION 90 LABEL.DIR \ change label
\ direction

YLBL LABEL \ label y axis

XLBL "LEN 2. / .0175 * .5 SWAP - \ X-position to
\ start label

.05 POSITION 0 LABEL.DIR \ reset label
\ direction

XLBL LABEL

K1 NEG "." K12 ":=
M "." M1 ":= \ label x axis
K12 " +/- " "CAT K12 ":=
K12 M1 "CAT K12 ":=
" Kobs= " K12 "CAT K12 ":=
.1 .97 POSITION 0 LABEL.DIR FILENAME LABEL
.6 .97 POSITION 0 LABEL.DIR SUBS LABEL
.6 .92 POSITION 0 LABEL.DIR LIG CONC "." "CAT LABEL
.45 .87 POSITION 0 LABEL.DIR
K12 LABEL
" Corr Cof= " COEF1 [ 1, 5 ] "." "CAT CO ":=
" STD.= " STD.DEV "." "CAT ST1 ":=
.6 .82 POSITION 0 LABEL.DIR CO LABEL
.6 .77 POSITION 0 LABEL.DIR ST1 LABEL
CURSOR.OFF
;

\ Actual data plotting words.

: PLOT.DATA
   TOTAL
   DATA.VU
   VUPORT.CLEAR \ set up vuport for data
   DATA.VU.SET \ set up and scale axes
   XY.AXIS.PLOT \ PLOT THE AXIS
X(XY) SUB[ 1 , #PTS ] \ x (time) values
Y(XY) SUB[ 1 , #PTS ] \ y (absorbance) values

XY.DATA.PLOT \ plot the data
\ add labels
\ outline the graph
;

: PLOT.FIT
DATA.VU VUPORT.CLEAR
TOTAL
DATA.VU.SET1
XY.AXIS.PLOT
X(XY) SUB[ 1 , #PTS , 10 ]
RE SUB[ 1 , #PTS , 10 ]
1 COLOR
XY.DATA.PLOT
X(XY) SUB[ L , IP , 10 ]
FITDATA SUB[ L , IP , 10 ]
1 COLOR
XY.DATA.PLOT
LABEL.PLOT
;
: PLOT.FIT1
DATA.VU VUPORT.CLEAR
TOTAL
DATA.VU.SET2
XY.AXIS.PLOT
  X(XY) SUB[ L , NPTS ]
RE SUB[ L , NPTS ]
1 COLOR
  XY.DATA.PLOT
X(XY) SUB[ L , NPTS ]
FITDATA SUB[ L , NPTS ]
1 COLOR
XY.DATA.PLOT
LABEL.PLOT
;
: PLOT.LOG
  DATA.VU VUPORT.CLEAR \ set up vuport for data
  TOTAL \ set up and scale axes
LOG.VU.SET
XY.AXIS.PLOT \ plot the axis
  X(XY) SUB[ L , NPTS ] \ x (time) values
RE SUB[ L , NPTS ] \ y (absorbance) values
1 COLOR
XY.DATA.PLOT
X(XY) SUB[ L , NPTS ] \ plot the data
FITDATA SUB[ L , NPTS ]
XY.DATA.PLOT

LABEL.PLOT \ add labels
;

: PLOT.LOG1

DATA.VU VUPORT.CLEAR \ set up vuport for
\ data

TOTAL \ set up and scale
\ axes

LOG.VU.SET

XY.AXIS.PLOT \ plot the axis

X(XY) SUB[ L , NPTS ] \ x (time) values

RE SUB[ L , NPTS ] \ y (absorbance)
\ values

1 COLOR

XY.DATA.PLOT

;

: HP7

HP7470 \ send plot to plotter

PLOT.FIT

;

: HP.LOG

HP7470 \ send log plot to plotter

PLOT.LOG

;

: MAIN.MENU

ALL
The following words are used to check the values of assorted variables, and to change their values. RET keeps the value shown.

: FILE.SIZE

" The number of data points is " #PTS . 3 SPACES ." New value? "
#INPUT IF #PTS := THEN ;

: CONCENTRATION

" The concentration is " CONC . 3 SPACES ." M. New value? "
#INPUT IF CONC := THEN ;
: SUBSTRATE

." The substrate is " SUBS "TYPE  3 SPACES ." Change to: "
SINPUT IF SUBS ":= THEN
;

: TEMPERATURE

." The temperature is " TEMP .  3 SPACES ." New value? "
SINPUT IF TEMP := THEN
;

: SENSITIVITY \ When DASH-16 or other A/D is used to
 \ acquire data this word will have to be
 \ expanded using IF-THEN-ELSE statements and
 \ A/D.SCALE word in a Case Statement.

." The voltage range is +/-" VFS .  3 SPACES ." New value? "
SINPUT IF VFS := THEN VFS
CASE \ Uses VFS to determine MVPP.
 20 OF 160 MVPP := ENDOF
 10 OF  80 MVPP := ENDOF
  4 OF  32 MVPP := ENDOF
  2 OF  16 MVPP := ENDOF
  1 OF   8 MVPP := ENDOF
Valid voltage ranges are 20, 10, 4, 2, 1, 0.4, 0.2, or 0.1.

The offset voltage is +/- VOFFS. New value? 

#INPUT IF VOFFS := THEN 

The time per point is " TPP. New value? "

: OFFSET \ Used to enter values for the offset voltage.
\ This word must be modified when the offset 
\ voltage is read from the backoff box rather 
\ than entered manually.

." The offset voltage is +/-" VOFFS . 3 SPACES ." New 

value? 

#INPUT IF VOFFS := THEN 

;
#INPUT IF TPP := THEN
;

: SOLVENT

." The solvent is " SOLV "TYPE 3 SPACES ." Change to: "
SINPUT IF SOLV ":= THEN
;

: LIGAND

." The ligand is " LIG "TYPE 3 SPACES ." Change to: "
SINPUT IF LIG ":= THEN
;

: WAVELENGTH

." The wavelength is " LAMBDA . 3 SPACES ." Change to: "
#INPUT IF LAMBDA := THEN
;

: FILE

." The filename is " FILENAME "TYPE 3 SPACES ." Change to: "
SINPUT IF FILENAME ":= THEN
"The data is recorded in " UV/IR "TYPE 2 SPACES ."
Change ? (Y or N)"
Y.OR.N
IF
  " IR" UV/IR "=
    IF
      " UV" UV/IR ":=
    ELSE
      " IR" UV/IR ":=
    THEN
THEN
:

: KINCOND  \ Used to enter conditions of a kinetics run.
  \ If data is read
  \ from the 2090, there are 4096 points. RET
  \ defaults to value
  \ shown.

ALL CR CR 5 SPACES
FILE CR 5 SPACES FILE.SIZE CR 5 SPACES TEMPERATURE CR 5
SPACES SOLVENT CR
This section reads data from the Nicolet 2090

\ PREP

\ DIGITAL.INIT

\ DAS.INIT

\ RAW

4080, \ Sets mask to read bits 4 through 11.
\ Uses buffered
\ DIGITAL.MASK \ input for greater speed.
PC.OUT

255, DIGITAL.MASK
\ These commands
\ initialize the
\ memory

112 DIGITAL.OUT
\ address location for
\ the scope

80 DIGITAL.OUT

PC.OUT

16, DIGITAL.MASK
\ Masks PC.OUT so that
PULSE.BITS
\ only pulses I/O STEP
;

: READ

PC.OUT PULSE.BITS
\ Sets 2090 to first
\ (leftmost) bit
BEGIN
\ Actual routine that
\ reads digital data
RAW DIGITAL.IN>ARRAY
\ into the data array
?BUFFER.FULL
PC.OUT
PULSE.BITS
UNTIL

;

: T \ Converts raw data from scope so the data is  \
\ decreasing from
#PTS 1 + 1 DO \ tope to buttom
YR [ I ] 128 < IF
  YR [ I ] 129 + Y(XY) [ I ] :=
ELSE
  YR [ I ] 127 - Y(XY) [ I ] :=
THEN
LOOP
Y(XY) 255 - NEG 2 + Y(XY) :=
;

: GET.DATA \ Reads data from Nicolet as 8 bit twos  \
\ complement binary integers
PREP
READ
;

: TRANS.CALC \ Returns data to array Y(XY) as %T  \
\ values, where Y(XY) []MAX is defined as \
\ 100*T.
VOFFS MVPP / 1000 * Y(XY) + 
Y(XY) := \ Adds offset voltage 
\ to recorded signal, 
\ which gives the 
\ total signal 
\ intensity.

Y(XY) DUP []MIN / 100 * Y(XY) := 
" %T" ABS/%T "="
;
: ACQ.DATA
KINCOND
PROMPT ." Strike any key when ready to read data from the 2090." KEY DROP
PROMPT ." Reading data from scope."
GET.DATA
PROMPT ." Transforming data"
T
TRANS.CALC
X(XY) []RAMP X(XY) TPP * X(XY) :=
WRITE.FILE
MAIN.MENU
;
: %T.TO.ABS \ This converts %T to absorbance using OD =
 \ log(100/%T)
" %T" ABS/%T "=
IF
100 Y(XY) / LOG

Y(XY) :=

"ABS" ABS/%T ":="

THEN
;

: ZERO.ARRAYS
0. RE := 0. FITDATA :=
0 J1 :=
;

: RI \ When F10 is pressed, this word reads out
\ the indices of XYDATA
\ XSECT[ 1 ] that enclose the region of
\ interest.

READOUT.INDICES
ESCAPE
;

: RII
READOUT.INDICES
ESCAPE
;

: RS
ARRAY.READOUT  \ Sets marker lines. See Asyst I-6-15.

INTERPRET.KEYS

ONESCAPE: R := L := R L - 1 + NPTS :=

#PTS L - IP :=

BELL

;

: RS1

--------

ARRAY.READOUT  \ Sets marker lines. See Asyst I-6-15.

INTERPRET.KEYS

ONESCAPE: SWAP L + L := STACK.CLEAR

R L - I + NPTS :=

#PTS L - IP :=

BELL

;

: BAS  \ select the base line

RS

Y(XY) SUB[ L , NPTS ] MEAN PF :=

;

: AL  \ select the range of data

ZERO.ARRAYS

RS

Y(XY) SUB[ L , NPTS ]

RE SUB[ L , NPTS ] :=

;

: RES.CALC
FITDATA SUB[ L , NPTS ] LN RE SUB[ L , NPTS ] LN -
DUP DUP

VARIANCE SQRT

STD.DEV :=
* []SUM C1 :=

X(XY) SUB[ L , NPTS ] DUP DUP

[]SUM DUP * A1 :=
* []SUM D1 :=

C1 NPTS * C1 :=
NPTS D1 * A1 - ABS D1 :=
NPTS 2 - D1 * INV C1 * SQRT M :=

;

: COE1

RE SUB[ L , NPTS ] LN
FITDATA SUB[ L , NPTS ] LN
2 REGRESS.ANOVA

COEF1 :=

;

: KSET \ Sets X and Y arrays in stack prior to
 \ least-squares calculation.

STACK.CLEAR
X(XY) SUB[ L , NPTS ]

RE SUB[ L , NPTS ] \ This fits data to the equation
 \ (PT-PF) = exp(-kt) or (if PF > PO)
 \ (PF - PT) = exp(-kt)
\( Y(\text{XY}) \text{[L]}PF > \)

\begin{verbatim}
IF
   Y(\text{XY}) \text{SUB}[1, \#PTS]PF - RE \text{SUB}[1, \#PTS] :=
ELSE
   PF Y(\text{XY}) \text{SUB}[1, \#PTS] - RE \text{SUB}[1, \#PTS] :=
THEN
;
;
: SMO
   .05 SET.CUTOFF.FREQ
   Y(\text{XY}) SMOOTH Y(\text{XY}) :=
;
: KT \ This fits data to the equation \( (PT - PF) = \exp(-kt) \) or \( \{ \text{if } PF > P0 \} (PF - PT) = \exp(-kt) \)
\end{verbatim}

\%T.TO.ABS
TOTAL
PLOT.DATA
BAS
AL
;
:
FIRST.ORDER.FIT
K+/- PROMPT ." PROCEEDING"
KSET

LEASTSQ.EXP.FIT \ array of 2 coefficients left \[ k_t \ B \]
\ DUP \[ 1 \] SWAP \[ 2 \] separate into
\ elements \[ array -- k \ B \]

OVER OVER \[ k \ B -- k \ B \ k \ B \]

COEFF \[ 1 \] := \ Save the coefficients.
\ A_0 = 1 = B,

COEFF \[ 2 \] := \ A_1 = 2 = k_1.

COEFF \[ 2 \] \ k_1 := \ PF + INT = P_0 (DECAY) OR
\ INT - PF = P_0 (GROWTH)
\ X(XY)

ROT * + EXP \ Compute the fit data
\ array.

FITDATA := \ Save in array FITDATA.

RES.CALC

COl

TOTAL

PLOT.FIT

PROMPT ." Strike a key when ready "

KEY DROP

PLOT.LOG

: SLOW \ will do analysis for the slow data for a
\ tow first order

\ reactions

K+/-
KSET
PLOT.LOG1
RS1
FIRST.ORDER.FIT
;
: RD

{ALL} SCREEN.CLEAR

{MENUS} SCREEN.CLEAR ." What is the filename? " "INPUT
FILENAME ":=

CR ." READING " FILENAME "TYPE READ.FILE {PROMPT}
SCREEN.CLEAR

." File read. "
T
TRANS.CALC
X(XY) []RAMP X(XY) TPP * X(XY) :=

MAIN.MENU
ONERR: {PROMPT} SCREEN.CLEAR ." ERROR ! "
MAIN.MENU

; : SD \ Store data command

{PROMPT} SCREEN.CLEAR ." What filename?"

"INPUT FILENAME ":=
WRITE.FILE
;

: SECOND.ORDER \ will do the analysis for a second order
\ reaction
K+/-
RE RE [ L ] -
RE / RE :=
KSET
1 LEASTSQ.POLY.FIT
COEFF :=
PLOT.FIT1 ;

: AD \ This word is the data analysis menu (FIT MENU)
    ALL {MENUNAME} SCREEN.CLEAR 32 SPACES ." ***FIT
MENU****"
    {MENUS} SCREEN.CLEAR 24 SPACES ." What do you wish to
calculate?" CR
10 SPACES
." 1) First order rates 2) Second order
fit" CR 10 SPACES
." 3) Numerical fit to first order 4) K from Kobs
vs L" CR 10 SPACES
." 5) Competition ratios 6) Activation
Parameters"
PROMPT ." Enter the number of your choice"
KEY PROMPT ." PROCEEDING"
CASE

49 OF FIRST.ORDER.FIT ENDOF
50 OF SECOND.ORDER ENDOF
\ 51 OF FIRST.ORDER.CURVE.FIT ENDOF
\ 52 OF KOB.S.VS.L ENDOF
\ 53 OF COMP.RATIO ENDOF
\ 54 OF ACT.PARAM ENDOF
MYSELF
ENDCASE
;

\ used to average data files
STACK.CLEAR
ALL
FILE
1 J1 + J1 :=
READ.FILE
T
TRANS.CALC

X(XY) \[]RAMP X(XY) TPP * X(XY) :=

Y(XY) FITDATA + FITDATA :=
CR "." MORE FILES TO ADD Y OR N "
Y.OR.N
IF
MYSELF
THEN
FITDATA J1 / Y(XY) :=
: AVE.DATA
ZERO ARRAYS

; : 2ND \ will do the analysis for the fast part of the
\ two
RE W1 := \ first order reaction
FITDATA W2 :=
RE FITDATA - Y(XY) :=
TOTAL
PLOT DATA
BAS
AL
FIRST ORDER FIT
;
: PLOT 2FIRST
FITDATA W2 + W2 :=
X(XY) SUB[ 1 , #PTS , 10 ]
W1 SUB[ 1 , #PTS , 10 ]
XY AUTO PLOT
X(XY) SUB[ L , IP , 10 ]
W2 SUB[ L , IP , 10 ]
XY DATA PLOT
;
: GET1 \ used to fit data and select the base line that
%T.TO.ABS \ best fit the data

TOTAL

PLOT DATA

AL

Y(XY) SUB[ L, NPTS ] [ ] MIN DUP 10 / + PF :=

; : FIRST.ORDER.FIT2

K+/- PROMPT " PROCEEDING"

KSET

LEASTSQ.EXP.FIT \ array of 2 coefficients left [ kt B ]

\ elements [ array -- k B ]

OVER OVER \ [ k B -- k B k B ]

COEFF [ 1 ] := \ Save the coefficients. A0 = 1 = B,


COEFF [ 2 ] K1 := \ PF + INT = P0 (DECAY)
\ OR
\ INT - PF = P0
\ (GROWTH)

X(XY)

ROT * + EXP \ Compute the fit data
\ array.

FITDATA := \ Save in array

FITDATA.

CO1
; : GET2
16 1 DO
FIRST.ORDER.FIT2
   Y(XY) SUB[ L , NPTS ] [ MIN 100 / PF + PF :=
   PF PFS [ I ] :=
   COEF1 [ 1 , 5 ] CCOF [ I ] :=
   K1 . COEF1 [ 1 , 5 ] . PF .
LOOP
;
: RS3
   ARRAY.READOUT
INTERPRET.KEYS
ONESCAPE: R :=
;
: GET
GET1
GET2
PFS
CCOF
XY.AUTO.PLOT
RS3
   PFS [ R ] PF :=
FIRST.ORDER.FIT
;
: MAIN.KEYS
   F1 FUNCTION.KEY.DOES ACQ.DATA \ Read data from
F2 FUNCTION.KEY.DOES AVE.DATA \ Nicolet 2090
\ takes ave of
\ data files

F3 FUNCTION.KEY.DOES RD \ Read data from
\ file

F4 FUNCTION.KEY.DOES AD \ Analyse XYDATA
\ Analyse XYDATA

F5 FUNCTION.KEY.DOES SD \ Store data

F6 FUNCTION.KEY.DOES HP7 \ plot abs vs
\ time

F7 FUNCTION.KEY.DOES HP.LOG \ plot ln(abs) vs
\ time

F8 FUNCTION.KEY.DOES RII \ on the ploter

F9 FUNCTION.KEY.DOES 2ND

F10 FUNCTION.KEY.DOES RI

; INIT \ First word called

CLEAR.FUNCTION.KEYS

-1 4 SCI.FORMAT

MAIN.KEYS

GRAPHICS.DISPLAY

STACK.CLEAR

TOTAL

MAIN MENU
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