1-1-1995

Isomerization and Chelation Studies of Dangling Phosphine Complexes of Group 6

Zhongjiang Jia
Eastern Illinois University

This research is a product of the graduate program in Chemistry at Eastern Illinois University. Find out more about the program.

Recommended Citation
http://thekeep.eiu.edu/theses/1957

This Thesis is brought to you for free and open access by the Student Theses & Publications at The Keep. It has been accepted for inclusion in Masters Theses by an authorized administrator of The Keep. For more information, please contact tabruns@eiu.edu.
THESIS REPRODUCTION CERTIFICATE

TO: Graduate Degree Candidates (who have written formal theses)

SUBJECT: Permission to Reproduce Theses

The University Library is receiving a number of requests from other institutions asking permission to reproduce dissertations for inclusion in their library holdings. Although no copyright laws are involved, we feel that professional courtesy demands that permission be obtained from the author before we allow theses to be copied.

PLEASE SIGN ONE OF THE FOLLOWING STATEMENTS:

Booth Library of Eastern Illinois University has my permission to lend my thesis to a reputable college or university for the purpose of copying it for inclusion in that institution's library or research holdings.

[Signature]

[Date]

I respectfully request Booth Library of Eastern Illinois University not allow my thesis to be reproduced because:

[Blank Line]

[Signature]

[Date]
Isomerization and Chelation Studies of

Dangling Phosphine Complexes of Group 6

(TITLE)

BY

Zhongjiang Jia

THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF

Master of Science in Chemistry

IN THE GRADUATE SCHOOL, EASTERN ILLINOIS UNIVERSITY
CHARLESTON, ILLINOIS

1995

YEAR

I HEREBY RECOMMEND THIS THESIS BE ACCEPTED AS FULFILLING
THIS PART OF THE GRADUATE DEGREE CITED ABOVE

July 27, 1995

DATE

ADVISER

July 27, 1991

DATE

DEPARTMENT HEAD
Isomerization and Chelation Studies of Dangling Phosphine Complexes of Group 6

By Zhongjiang Jia
Adviser: Dr. Richard L. Keiter
Submitted date: July 17, 1995

Approved by the thesis committee:

Dr. R.L. Keiter
July 25, 1995

Dr. E.A. Keiter
July 27, 1995

Dr. J.G. Ellis
July 25, 1995

Dr. D.J. Sheeran
July 25, 1995
ABSTRACT

Vinyl addition reactions, catalyzed by 2,2′-azobis(isobutyronitrile) (AIBN), have been used to prepare six pentacarbonyl complexes of group 6, each of which contains a dangling Ph₂PCH₂CH₂P(p-tol)₂ ligand.

(OC)₅M(PPh₂CH=CH₂) + P(p-tol)₂H → (OC)₅M[PPh₂CH₂CH₂P(p-tol)₂]
(OC)₅M[P(p-tol)₂H] + PPh₂CH=CH₂ → (OC)₅M[P(p-tol)₂CH₂CH₂PPh₂]
M = Cr, Mo, W

Each of the six complexes undergoes slow isomerization and chelation at 55 °C in perdeuterated toluene:

\[
\begin{align*}
\text{(DC)}_5M\text{PPH}_2\text{CH}_2\text{CH}_2\text{P}(p\text{-tol})_2 & \rightleftharpoons \text{(DC)}_5M\text{P}(p\text{-tol})_2\text{CH}_2\text{CH}_2\text{PPH}_2 \\
\kappa_1 & \kappa_1 \\
\text{A} & \text{B} \\
\kappa_2 & \kappa_3 \\
\text{C} & \\
\end{align*}
\]

The reactions were monitored by \(^{31}\text{P}\{^1\text{H}\} \) NMR spectroscopy. The isomerization reactions are reversible in solution, while the chelated products form irreversibly with the loss of carbon monoxide. The rate constants, \( \kappa_1 \) and \( \kappa_1 \), have
been determined for the three pairs of linkage isomers. Equilibrium constants for the chromium and tungsten isomerization reactions were determined from the rate constants. The molybdenum isomerization reactions were sufficiently fast to allow the equilibrium constant to be determined directly. In addition, rate constants $\kappa_2$ and $\kappa_3$, were determined for the chromium and molybdenum chelation reactions. The rate of chelation for the tungsten complexes was too slow to determine. Rate constants and equilibrium constants are shown below:

<table>
<thead>
<tr>
<th>M</th>
<th>$\kappa_1$</th>
<th>$\kappa_1$</th>
<th>$\kappa_2$</th>
<th>$\kappa_3$</th>
<th>$K_{eq}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$10^8 \text{ s}^{-1}$</td>
<td>$10^8 \text{ s}^{-1}$</td>
<td>$10^8 \text{ s}^{-1}$</td>
<td>$10^8 \text{ s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>1.22</td>
<td>0.65</td>
<td>1.15</td>
<td>1.24</td>
<td>1.88</td>
</tr>
<tr>
<td>Mo</td>
<td>759</td>
<td>387</td>
<td>29.6</td>
<td>30.3</td>
<td>1.96</td>
</tr>
<tr>
<td>W</td>
<td>2.31</td>
<td>0.97</td>
<td>---</td>
<td>---</td>
<td>2.38</td>
</tr>
</tbody>
</table>

Rate constants for the isomerization and chelation of the chromium complexes are nearly the same, consistent with dissociative (D) mechanisms for each reaction. Rate constants for isomerization of the molybdenum and tungsten complexes are much larger than those for chelation, suggestive of an associative component in the former reaction. Even so, bond-breaking would appear to be more important than bond-making. Thus, the isomerization is best described as proceeding through an interchange dissociative mechanism ($I_0$).
Dedication

To my parents, my wife, and my son.
Acknowledgements

I would like to thank Dr. Richard L. Keiter for his knowledgeable guidance and kind encouragement.

I would also like to thank Dr. John W. Benson for doing almost all of the NMR experiments and Dr. Ellen A. Keiter for obtaining some of the NMR spectra.

I wish to thank Dr. D.W. Ebdon and Dr. D. Brandt for the helpful discussion about the kinetic plot.

I extend my thanks to the faculty and staff of the Chemistry Department at Eastern Illinois University for their support.

Finally, I would like to thank my wife, Tao Zhang, for typing this thesis.
# Table of Contents

Abstract .................................................................................. i
Dedication ............................................................................... iii
Acknowledgements ................................................................. iv
Table of Contents ................................................................... v
List of Tables ........................................................................... vii
List of Figures .......................................................................... viii

## I. Introduction ........................................................................ 1

1. Metal-Phosphine Bonding .................................................... 1
2. Electronic Effects of Phosphine Ligands ............................... 3
3. Steric Effects of Phosphine Ligands ..................................... 5
4. Mechanism of Chelation and Substitution ......................... 6
5. Isomerization ....................................................................... 8
6. Unsymmetrical Diphosphines ............................................. 10
7. Synthesis of Dangling Diphosphine Complexes ................. 16
8. Purpose of This Work ......................................................... 21

## II. Results and Discussion ..................................................... 23

1. Synthesis of Phosphine Ligands .......................................... 23
2. Synthesis of (OC)$_5$ML
   (M=Cr, Mo, W; L=PPh$_2$H, P(p-tol)$_2$H, PPh$_2$CH=CH$_2$) .... 25
3. Disubstituted Complexes ................................................... 26
4. Dangling Diphosphine Complexes ..................................... 28
5. Diphosphine Oxide Complexes .......................................... 29
6. Chelated Complexes ........................................... 29
7. Variable Temperature $^{31}$P-$^1$H NMR Experiments of
   Compounds $(OC)_5W(dppe)$ and $(OC)_5W(dpmm)$ .......... 30
8. Isomerization Studies of Compounds
   $(OC)_5MPPh_2CH_2CH_2P(p-tol)_2$ and
   $(OC)_5MP(p-tol)_2CH_2CH_2PPh_2 (M=Cr, Mo, W)$ .......... 32

III. Experimental Section ........................................ 104
   1. Materials .................................................... 104
   2. Physical Measurements .................................... 104
   3. Isomerization Studies ..................................... 105
   4. Synthesis .................................................... 105

Reference ......................................................... 116

Appendix I ......................................................... 123
List of Tables

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Properties of Tritolylphosphine Analogues</td>
<td>40</td>
</tr>
<tr>
<td>2. Properties of Ditolylphosphine Analogues</td>
<td>40</td>
</tr>
<tr>
<td>3. Properties of Some Diphosphines</td>
<td>41</td>
</tr>
<tr>
<td>4. Properties of $(OC)_5ML$</td>
<td>41</td>
</tr>
<tr>
<td>5. IR Data of $(OC)_5ML$</td>
<td>42</td>
</tr>
<tr>
<td>6. IR Data of $cis-(OC)_4ML_2$</td>
<td>42</td>
</tr>
<tr>
<td>7. Properties of Disubstituted Complexes</td>
<td>43</td>
</tr>
<tr>
<td>8. Properties of Dangling Diphosphine Complexes</td>
<td>44</td>
</tr>
<tr>
<td>9. IR Data of Dangling Diphosphine Complexes</td>
<td>45</td>
</tr>
<tr>
<td>10. $^{31}P{^1H}$ NMR Data of Diphosphine Oxide Complexes</td>
<td>45</td>
</tr>
<tr>
<td>11. Properties of Chelated Complexes</td>
<td>46</td>
</tr>
<tr>
<td>12. IR Data of Chelated Complexes</td>
<td>46</td>
</tr>
<tr>
<td>13. Variable Temperature $^{31}P{^1H}$ NMR Data of $(OC)_5W(dppe)$</td>
<td>47</td>
</tr>
<tr>
<td>14. Variable Temperature $^{31}P{^1H}$ NMR Data of $(OC)_5W(dpdm)$</td>
<td>47</td>
</tr>
<tr>
<td>15. Kinetic Data of Isomerization and Chelation</td>
<td>48</td>
</tr>
</tbody>
</table>
## List of Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. $^{31}\text{P}$$^{1\text{H}}$ NMR Spectrum of $\text{P}(\text{p-tol})_3$</td>
<td>49</td>
</tr>
<tr>
<td>2. $^{31}\text{P}$$^{1\text{H}}$ NMR Spectrum of $\text{P}(\text{p-tol})_2\text{H}$</td>
<td>50</td>
</tr>
<tr>
<td>3. $^{31}\text{P}$$^{1\text{H}}$ NMR Spectrum of $(\text{p-tol})_2\text{PCH}_2\text{CH}_2\text{P}(\text{p-tol})_2$</td>
<td>51</td>
</tr>
<tr>
<td>4. $^{31}\text{P}$$^{1\text{H}}$ NMR Spectrum of $\text{PPh}_2\text{CH}_2\text{CH}_2\text{P}(\text{p-tol})_2$</td>
<td>52</td>
</tr>
<tr>
<td>5. $^{31}\text{P}$$^{1\text{H}}$ NMR Spectrum of $(\text{OC})_5\text{CrP}(\text{p-tol})_2\text{H}$</td>
<td>53</td>
</tr>
<tr>
<td>6. $^{31}\text{P}$$^{1\text{H}}$ NMR Spectrum of $(\text{OC})_5\text{MoP}(\text{p-tol})_2\text{H}$</td>
<td>54</td>
</tr>
<tr>
<td>7. $^{31}\text{P}$$^{1\text{H}}$ NMR Spectrum of $(\text{OC})_5\text{WP}(\text{p-tol})_2\text{H}$</td>
<td>55</td>
</tr>
<tr>
<td>8. IR Spectrum of $(\text{OC})_5\text{CrP}(\text{p-tol})_2\text{H}$</td>
<td>56</td>
</tr>
<tr>
<td>9. IR Spectrum of $(\text{OC})_5\text{MoP}(\text{p-tol})_2\text{H}$</td>
<td>57</td>
</tr>
<tr>
<td>10. IR Spectrum of $(\text{OC})_5\text{WP}(\text{p-tol})_2\text{H}$</td>
<td>58</td>
</tr>
<tr>
<td>11. $^{31}\text{P}$$^{1\text{H}}$ NMR Spectrum of cis-$(\text{OC})_4\text{W}[\text{P}(\text{p-tol})_2\text{H}]_2$</td>
<td>59</td>
</tr>
<tr>
<td>12. $^{31}\text{P}$$^{1\text{H}}$ NMR Spectrum of cis-$(\text{OC})_4\text{Mo}(\text{PPh}_2\text{CH}=\text{CH}_2)_2$</td>
<td>60</td>
</tr>
<tr>
<td>13. $^{31}\text{P}$$^{1\text{H}}$ NMR Spectrum of cis-$(\text{OC})_4\text{W}(\text{PPh}_2\text{Et})(\text{PPh}_2\text{H})$</td>
<td>61</td>
</tr>
<tr>
<td>14. IR Spectrum of cis-$(\text{OC})_4\text{W}[\text{P}(\text{p-tol})_2\text{H}]_2$</td>
<td>62</td>
</tr>
<tr>
<td>15. IR Spectrum of cis-$(\text{OC})_4\text{Mo}(\text{PPh}_2\text{CH}=\text{CH}_2)_2$</td>
<td>63</td>
</tr>
<tr>
<td>16. IR Spectrum of cis-$(\text{OC})_4\text{W}(\text{PPh}_2\text{Et})(\text{PPh}_2\text{H})$</td>
<td>64</td>
</tr>
<tr>
<td>17. $^{31}\text{P}$$^{1\text{H}}$ NMR Spectrum of $(\text{OC})_5\text{WPPh}_2\text{CH}_2\text{CH}_2\text{P}(\text{p-tol})_2$</td>
<td>65</td>
</tr>
<tr>
<td>18. IR Spectrum of $(\text{OC})_5\text{WPPh}_2\text{CH}_2\text{CH}_2\text{P}(\text{p-tol})_2$</td>
<td>66</td>
</tr>
<tr>
<td>19. $^{31}\text{P}$$^{1\text{H}}$ NMR Spectrum of $(\text{OC})_5\text{WP}(\text{p-tol})_2\text{CH}_2\text{CH}_2\text{PPh}_2$</td>
<td>67</td>
</tr>
<tr>
<td>20. IR Spectrum of $(\text{OC})_5\text{WP}(\text{p-tol})_2\text{CH}_2\text{CH}_2\text{PPh}_2$</td>
<td>68</td>
</tr>
</tbody>
</table>
21. $^{31}$P{$^1$H} NMR Spectrum of
(OC)$_5$CrPPh$_2$CH$_2$CH$_2$P(p-tol)$_2$  

22. IR Spectrum of (OC)$_5$CrPPh$_2$CH$_2$CH$_2$P(p-tol)$_2$  

23. $^{31}$P{$^1$H} NMR Spectrum of
(OC)$_5$CrP(p-tol)$_2$CH$_2$CH$_2$PPh$_2$  

24. IR Spectrum of (OC)$_5$CrP(p-tol)$_2$CH$_2$CH$_2$PPh$_2$  

25. $^{31}$P{$^1$H} NMR Spectrum of
(OC)$_5$MoPPh$_2$CH$_2$CH$_2$P(p-tol)$_2$  

26. IR Spectrum of (OC)$_5$MoPPh$_2$CH$_2$CH$_2$PPh$_2$  

27. $^{31}$P{$^1$H} NMR Spectrum of
(OC)$_5$MoP(p-tol)$_2$CH$_2$CH$_2$PPh$_2$  

28. IR Spectrum of (OC)$_5$MoP(p-tol)$_2$CH$_2$CH$_2$PPh$_2$  

29. $^{31}$P{$^1$H} NMR Spectrum of (OC)$_5$WPPh$_2$CH$_2$CH$_2$PPh$_2$  

30. IR Spectrum of (OC)$_5$WPPh$_2$CH$_2$CH$_2$PPh$_2$  

31. $^{31}$P{$^1$H} NMR Spectrum of
(OC)$_5$MoPPh$_2$CH$_2$CH$_2$P(p-tol)$_2$  

32. IR Spectrum of (OC)$_5$MoPPh$_2$CH$_2$CH$_2$P(p-tol)$_2$  

33. $^{31}$P{$^1$H} NMR Spectrum (upfield) of
(OC)$_5$WPPh$_2$CH$_2$CH$_2$PPh$_2$ at 30 °C  

34. $^{31}$P{$^1$H} NMR Spectrum (upfield) of
(OC)$_5$WPPh$_2$CH$_2$CH$_2$PPh$_2$ at 80 °C  

35. $^{31}$P{$^1$H} NMR Spectrum (upfield) of
(OC)$_5$WPPh$_2$CH$_2$CH$_2$P(O)Ph$_2$ at 80 °C  

36. $^{31}$P{$^1$H} NMR Spectrum of
(OC)$_5$WPPh$_2$CH$_2$PPh$_2$ at -50 °C
37. $^{31}$P{$^1$H} NMR Spectrum of

$(OC)_5 WPPh_2 CH_2 PPh_2$ at 70 °C ........................................... 85

38. $^{31}$P{$^1$H} NMR for the isomerization of

$(OC)_5 MoPPh_2 CH_2 CH_2 P(p\text{-tol})_2$ at various times

at 55 °C in perdeuterated toluene ................................. 86

39. Plot of $\ln([A]/[A]_o-[A]_{eq}/[A]_o)$ vs $t$

$[A=(OC)_5 MoPPh_2 CH_2 CH_2 P(p\text{-tol})_2]$ .................. 87

40. Plot of $[A]/[A]_o$ vs $t$

$[A=(OC)_5 CrPPh_2 CH_2 CH_2 P(p\text{-tol})_2]$ .................. 88

41. Plots of $[B]/[A]_o$ or $[C]/[A]_o$ vs $t$

$[B=(OC)_5 CrP(p\text{-tol})_2 CH_2 CH_2 PPh_2; C=(OC)_4 Cr(dpdt)]$ ................... 89

42. Plot of $[B]/[B]_o$ vs $t$

$[B=(OC)_5 CrP(p\text{-tol})_2 CH_2 CH_2 PPh_2]$ .................. 90

43. Plots of $[A]/[B]_o$ or $[C]/[B]_o$ vs $t$

$[A=(OC)_5 CrPPh_2 CH_2 CH_2 P(p\text{-tol})_2; C=(OC)_4 Cr(dpdt)]$ ................... 91

44. Plot of $[C]/[A]_o$ vs $t$ $[C=(OC)_4 Mo(dpdt)]$ ................... 92

45. Plot of $[C]/[B]_o$ vs $t$ $[C=(OC)_4 Mo(dpdt)]$ ................... 93

46. Plot of $[A]/[A]_o$ vs $t$ $[A=(OC)_5 WPPh_2 CH_2 CH_2 P(p\text{-tol})_2]$

in perdeuterated toluene ........................................... 94

47. Plot of $\ln([A]/[A]_o)$ vs $t$ in perdeuterated toluene

$[A=(OC)_5 WPPh_2 CH_2 CH_2 P(p\text{-tol})_2]$ .................. 95

48. Plot of $[B]/[A]_o$ vs $t$ $[B=(OC)_5 WP(p\text{-tol})_2 CH_2 CH_2 PPh_2]$

in perdeuterated toluene ........................................... 96

49. Plot of $\ln([B]/[A]_o)$ vs $t$ in perdeuterated toluene

$[B=(OC)_5 WP(p\text{-tol})_2 CH_2 CH_2 PPh_2]$ .................. 97
50. Plot of \([B]/[B]_0\) vs \(t\) \([B=(\text{OC})_5\text{WP}(\text{p-tol})_2\text{CH}_2\text{CH}_2\text{PPh}_2]\)
    in perdeuterated toluene ........................................ 98

51. Plot of \([A]/[B]_0\) vs \(t\) \([A=(\text{OC})_5\text{WPPh}_2\text{CH}_2\text{CH}_2\text{P}(\text{p-tol})_2]\)
    in perdeuterated toluene ........................................ 99

52. Plot of \([A]/[A]_0\) vs \(t\) \([A=(\text{OC})_5\text{WPPh}_2\text{CH}_2\text{CH}_2\text{P}(\text{p-tol})_2]\)
    in perdeuterated chloroform ..................................... 100

53. Plots of \([B]/[A]_0\) or \([C]/[A]_0\) vs \(t\)
    \([B=(\text{OC})_5\text{WP}(\text{p-tol})_2\text{CH}_2\text{CH}_2\text{PPh}_2; C=(\text{OC})_4\text{W(dptd})]\)
    in perdeuterated chloroform ..................................... 101

54. Plot of \([B]/[B]_0\) vs \(t\) \([B=(\text{OC})_5\text{WP}(\text{p-tol})_2\text{CH}_2\text{CH}_2\text{PPh}_2]\)
    in perdeuterated chloroform ..................................... 102

55. Plots of \([C]/[B]_0\) vs \(t\) \([C=(\text{OC})_4\text{W(dptd})]\)
    in perdeuterated chloroform ..................................... 103
I. Introduction

Even though the first tertiary phosphine complexes were made in 1857 by Hofmann¹, phosphine coordination chemistry did not begin to boom until the 1960s. Several reasons accounted for the development of this area:

1. Phosphine complexes were found to play a major role in homogeneous catalysis and organic synthesis.
2. Phosphines are soft ligands capable of stabilizing low oxidation state transition metal complexes.
3. New bonding theories were developed to describe the metal-phosphine bond.
4. Many new phosphine ligands and their complexes were synthesized.
5. Sophisticated $^{31}$P NMR techniques were developed that allowed easy characterization of new compounds.

Today, phosphines are among the most important ligands in organometallic chemistry.

1. Metal-Phosphine Bonding

Following bonding theory that had been proposed for metal carbonyl complexes,² Chatt³,⁴ offered the first accepted scheme for the metal-phosphorus bond. He suggested that the lone pair of the phosphorus ligand is donated into an empty metal orbital to form a $\sigma$ bond, while the filled metal d orbitals donate electron density to the empty phosphorus 3d orbitals ($\pi$ back-bonding). For metal
carbonyls, $\pi$ back-bonding is formed between the filled metal d orbitals and the empty antibonding orbitals ($\pi^*$) of the carbonyl.

The metal-phosphine bonding theory was supported by several observations. First, no complex formation takes place when PF$_3$ is mixed with BF$_3$ or AlCl$_3$, Lewis acids that do not possess d electrons.$^3$ Two stable compounds, (PF$_3$)$_2$PtCl$_2$ and (PF$_3$PtCl$_2$)$_2$, were obtained, however, with PtCl$_2$. Second, PF$_3$, but not NF$_3$ which has no empty d orbitals of low energy, combines with hemoglobin in a way that is analogous to CO.$^5$ The $\pi$ back-bonding mechanism also accounted for the trans-influence of phosphine ligands.

However, the nature of $\pi$ back-bonding theory has been modified in recent times. It has been argued that the 3d orbitals on phosphorus are too high in energy and too diffuse to engage in directional bonding.$^6$ Ellis et al$^7$ examined the electronic structures of PH$_3$, P(CH$_3$)$_3$, and PF$_3$ with the aid of self-consistent multipolar X$\alpha$ calculations and concluded that the $\pi$-acceptor orbital on phosphorus mostly consists of phosphorus 3p character which has the effect of directing the empty $\pi$ orbital in the direction of the lone pair. For qualitative understanding, Marynick$^8$ demonstrated that d orbitals on phosphorus are not necessary for $\pi$ back-bonding by using approximate and ab initio molecular orbital theory. Structural evidence that P-X bond lengths increase with decreasing M-P distances supported a
new proposal that the phosphorus 3d and P-X σ* orbitals hybridize to form the π-acceptor orbitals. However, Ernst et al. observed that the Ti-P(OEt)₃ bond length (2.472 Å) is significantly shorter than the Ti-PMe₃ bond length (2.550 Å), while the bond strengths follow the opposite order, a result which can not be explained by the π-bonding mechanism alone. Therefore, a possible explanation for the observed trend in M-P bond lengths (M-PF₃ < M-P(OR)₃ < M-PR₃) seems to be that increasing electronegativity of the phosphine substituents causes contraction of the phosphorus lone pair orbital. This explanation allows bond shortening without involving additional bonding interactions.

2. Electronic Effects of Phosphine Ligands

It was of great interest to determine how the electron donor-acceptor properties of phosphine ligands would change with different substituents on phosphorus. Infrared spectroscopy of phosphine substituted metal carbonyls has enabled the study of electronic effects based on the carbonyl frequencies and force constants. The donor strengths of various ligands have been compared. Tolman has proposed a substitutent additivity rule based on the A₁ carbonyl stretching frequency of Ni(CO)₃L.

The C-O stretching frequency shifts in substituted metal carbonyl complexes were interpreted in terms of the π-bonding ability of L. ³¹P NMR studies of ¹⁸³W-³¹P coupling
constants in $\text{R}_3\text{PW(CO)}_5$ complexes also have been interpreted in terms of the W-P $\pi$ bonding. However, Angelici suggested that $\sigma$ bonding, not $\pi$ bonding, is largely responsible for the strength of the W-L bond based on the results of infrared studies\textsuperscript{11} and equilibrium studies\textsuperscript{18}.

It is clear that the more electron-withdrawing substituents give higher CO stretching frequencies, while the better $\sigma$ donor phosphine ligands will lead to a greater W(d$\pi$) $\rightarrow$ CO($\pi'$) back-donation and lower CO stretching frequencies. However, it is very difficult to say to what extent the $\pi$- or $\sigma$-bonding properties of phosphine ligands are responsible for the C-O frequency shift.

Some researchers have attempted to separate $\sigma$ and $\pi$ effects indirectly by using the different CO stretching force constants for carbonyls cis and trans to L in $\text{LM(CO)}_5$\textsuperscript{,19} or directly by using photoelectron spectroscopy (PES)\textsuperscript{20,21}. The $\sigma$ donor ability of phosphine ligands can be quantitatively measured in terms of the basicity of the phosphine as the equilibrium constant in the reaction of H$^+$ with PR$_3$, which is determined by $\sigma$ bonding not $\pi$ bonding. The pK$_a$ values of a number of phosphine ligands have been determined by titration.\textsuperscript{22-24} However, the employment of pK$_a$ values as a measure of $\sigma$-donor ability faces two problems. First, pK$_a$ values are dependent upon the interactions between the phosphorus and the hard acid, H$^+$, rather than a soft acid such as a low-valent metal center.\textsuperscript{25} Second, pK$_a$
values are sensitive to solvation energies of the phosphine ligands. In addition, the pKₐ values were challenged by the results from the gas-phase photoelectron spectroscopy (PES). In the gas phase, the order of the electron donor ability is: \( \text{PPh}_3 > \text{PPh}_2\text{Me} > \text{PPhMe}_2 > \text{PMe}_3 \), while the order of basicity is reversed in solution. The lower basicity of \( \text{PPh}_3 \) was rationalized in terms of the lower solvation energy of the bulkier ion \([\text{PPh}_3\text{H}]^+\) compared to \([\text{PMe}_3\text{H}]^+\) and is therefore due primarily to steric rather than electronic effects. It has also been observed that the binding strength of the \( \text{PX}_3 \) ligands to the titanium centers correlated well with the steric effects of the \( \text{PX}_3 \) groups. Considering \( \sigma, \pi, \) and steric properties of phosphine ligands, Giering et al. developed an analytical method—the quantitative analysis of ligand effects (QALE). They separated the phosphine ligands into two classes, pure \( \sigma \)-donor ligands and \( \sigma \)-donor/\( \pi \) acceptor ligands, and concluded that pKₐ values are still reasonable measures of the \( \sigma \)-donor ability for those ligands that are pure \( \sigma \)-donor ligands.

3. Steric Effects of Phosphine Ligands

As mentioned above, some experimental results can not be explained by electronic effects alone. The steric effects must be taken into account. However, not much attention was devoted to steric effects until the 1970s. By conducting ligand-competition experiments, Tolman ranked
24 ligands to give a stability series which did not correlate with the electronic properties of the phosphine ligands. Thereafter, Tolman used atomic models to define a quantitative steric effect parameter— the ligand cone angle, \( \theta \), which did correlate well with the stability data. The ligand cone angle was measured by the apex angle of a cone centered on the metal. Since the introduction of the cone angle, it has been shown that many chemical and spectroscopic properties of organometallic complexes correlate with ligand cone angles.\(^{30}\) However, there are some limitations in the measurement of the cone angles. First, even symmetric ligands do not have cylindrical symmetry. The ligands are not rigid, and can mesh into one another. Second, the measurement of the cone angles is based on a 2.28 Å M-P bond length and on tetrahedral angles about phosphorus both of which vary in real molecules.\(^{10}\) Other definitions and arguments about the ligand cone angle have been presented but will not be discussed here.\(^ {31,32} \)

4. Mechanism of Chelation and Substitution

Conventionally there are two extreme mechanisms, dissociative and associative (corresponding to SN1 and SN2 reactions), for chelation and ligand substitution. A number of investigations\(^ {33} \) have shown that the reaction of \( \text{M(CO)}_6 \) with monodentate ligands involves a rate-determining dissociative step and the enthalpy of the activation has
been found to correlate with the mean M-CO bond energy. For the reactions of NiL₄ with L' and of Ni(CO)₄ with L, Tolman suggested that the mechanism is probably a dissociative process involving three-coordinate intermediates. The purported reason for a dissociative process is that a five-coordinate intermediate would require nickel to exceed an 18-electron inert gas configuration and be more crowded with too many ligands. The mechanism of the chelation process was also shown to be primarily dissociative. The existence of the five-coordinate ion LM(CO)₄⁺ (M=Cr, Mo, W) in mass spectra and the synthesis of a five-coordinate complex (OC)Mo(PH₂PCH₂CH₂PPh₂)₂ seem to support the SN1 process in six-coordinate group 6 metal complexes.

In summary, there are some trends for the chelation of R₂P(CH₂)ₙPR₂M(CO)₅ (M=Cr, Mo, W; n=1-3).

1. The rate of chelation decreases as the chain length increases.

2. Bulky phosphorus substituents, R, favor chelation.

3. The rate of chelation decreases in the order Mo > Cr > W.

4. The principal enthalpy requirement for activation is M-CO bond stretching, although the ring strain in the complex formed contributes.

5. The principal entropy contribution to activation appears to come from the entropy change associated with the free end of the phosphine ligand, although steric effects
also contribute.

5. Isomerization

Isomerization in phosphine complexes is an old topic. The most familiar example is the cis-trans isomerism in MX$_2$L$_2$ complexes of Pd and Pt.$^{37}$

Some geometrical isomers can also be formed by the chelation of two unsymmetrical diphosphine ligands.$^{38-40}$ The isomerization can be easily followed by $^1$H NMR or $^{31}$P$^{(1)}$H NMR.

(Taken from reference 40)
However, only a few examples of linkage isomerism involving non-ring systems have been studied. Verkade et al.\textsuperscript{41} have synthesized both linkage isomers, Fe(CO)\textsubscript{4}P(OCH\textsubscript{2})\textsubscript{3}P and Fe(CO)\textsubscript{4}P(CH\textsubscript{2}O)\textsubscript{3}P, by irradiation of Fe(CO)\textsubscript{5} with the bicyclic phosphorus ligand P(OCH\textsubscript{2})\textsubscript{3}P. In this instance chelation is not possible because of the rigid geometry of the ligand. Only one isomer, with the smaller PO\textsubscript{3} end coordinated, was obtained from the reaction of P(OCH\textsubscript{2})\textsubscript{3}P with (C\textsubscript{6}H\textsubscript{5}NH\textsubscript{2})W(CO)\textsubscript{5} [or with Cr(CO)\textsubscript{6} or Mo(CO)\textsubscript{6} under uv radiation].\textsuperscript{42} Grim et al.\textsuperscript{43} have observed linkage isomers of the type (OC)\textsubscript{5}WP—P' and (OC)\textsubscript{5}WP′—P from the reaction of Ph\textsubscript{2}PCH\textsubscript{2}CH\textsubscript{2}PMePh or Ph\textsubscript{2}PCH\textsubscript{2}CH\textsubscript{2}PPh(i-Pr) with (C\textsubscript{6}H\textsubscript{5}NH\textsubscript{2})W(CO)\textsubscript{5}, but no evidence was reported for them existing in equilibrium. In addition, the isomers were not separated. In general, the favored order of stability for phosphorus group coordination is R\textsubscript{2}P > RPhP > Ph\textsubscript{2}P (R = alkyl), which is both the steric order and the order of ligand basicity. Groups such as i-Pr that have large steric requirement can lead to a reversal: Ph\textsubscript{2}P > Ph(i-Pr)P.

More recently, Keiter et al.\textsuperscript{44} have reported the isomerization of (OC)\textsubscript{5}WPPh\textsubscript{2}CH\textsubscript{2}CH(PPh\textsubscript{2})\textsubscript{2}, which was believed to be the first experimental evidence for exchange of the terminal and coordinated phosphorus groups in pentacarbonyl complexes of group 6 metals. The -PPh\textsubscript{2} groups on the end of -CH(PPh\textsubscript{2})\textsubscript{2} are more favorable for coordination than the -PPh\textsubscript{2} group on the other end, in a ratio of 5:1 at 25 °C. The
mechanism of the isomerization was suggested to be a 1,4-metal-phosphorus shift involving a pseudo-seven-coordinate transition state because a five-coordinate intermediate could not be trapped with PPh₃. The latest work⁴⁵ on the kinetics and equilibrium of this isomerization reaction has shown that

\[ (OC)₅WPPh₂CH₂CH(PPh₂)₂ \overset{K₁}{\rightleftharpoons} (OC)₅WPPh₂CH(PPh₂)CH₂PPh₂ \quad (1) \]

\( \Delta H = -13.6 \text{ kJ/mol}, \Delta S = -32.5 \text{ J/mol·K}; K₁ = 1.20 \times 10^{-6} \text{ sec}^{-1}, K₁ = 1.92 \times 10^{-7} \text{ sec}^{-1} \) at 10 °C. The forward process is enthalpy driven, while the reverse process is entropy driven. Isomerization reactions for Cr and Mo complexes are under investigation.⁴⁵

Connor et al.³⁵ found that dangling diphosphine complexes \((\text{Me₂PCH₂CH₂PMe₂})_5 \text{(CO)}_5 \) (M=Cr, Mo, W) do not undergo rapid intramolecular exchange between the two phosphorus groups. So far, no work has been done on the isomerization of dangling diphosphine pentacarbonyl complexes of group 6 metals.

6. Unsymmetrical Diphosphines

Diphosphine ligands can be classified roughly into two types: symmetrical \( R₂P(CH₂)ₙPR₂ \) and unsymmetrical \( R₂P(CH₂)ₙPR'R'' \). By the nature and the length of the backbone connecting the two phosphorus groups, they can be further divided into four classes: (a) one-carbon backbones (n=1);
(b) two-and three-carbon backbones \((n=2, 3)\); (c) longer backbones \((n \geq 4)\); and (d) rigid backbones, such as \(R_2PC\equiv CPR_2\), which prevent chelation.

The first diphosphine complexes contained \(Et_2PCH_2CH_2PET_2\) and were synthesized by Wymore and Bailar in 1960.\(^{46}\) After that, many diphosphine ligands and their complexes were prepared. Among them \(PPh_2CH_2CH_2PPh_2\) (dppe) is the most widely used chelating ligand. Because of its ability to form bridged binuclear complexes, \(PPh_2CH_2PPh_2\) (dppm) has also been widely investigated in catalysis studies.\(^{36}\)

The electronic and steric properties of diphosphines can be modified systematically by changing the substituents on the phosphorus. Unsymmetrical diphosphines have been of interest for several reasons: (a) solubilities of the complexes\(^{38}\) may be increased; (b) mechanistic studies are easier to monitor with \(^{31}\)P\{\(^1\)H\} NMR\(^{34, 40}\); and (c) homogeneous catalysis and asymmetric synthesis can be studied.\(^{47}\) In this thesis we will mainly focus on the synthesis of unsymmetrical diphosphine ligands and their complexes.

a. Synthesis of Unsymmetrical Ligands

Most of the symmetrical diphosphines are synthesized by the reaction\(^{48}\):

\[
2R_2PM + X(CH_2)_nX \rightarrow R_2P(CH_2)_nPR_2 + 2MX
\]  
\((R=\text{alkyl or aryl}; M=\text{alkali metal}; X=\text{halogen}; \text{and } n=1-5)\)
The metal organophosphides can be made by metallation of a secondary phosphine\textsuperscript{46} or by cleavage of triphenylphosphine\textsuperscript{49}. The synthesis of unsymmetrical diphosphines has proved to be more difficult. In 1967, Keiter\textsuperscript{50} synthesized bis-(1,2-diphenylphosphino)ethane (dppe) with a new method:

\[ \text{Ph}_2\text{PLi} + \text{Ph}_2\text{PCH=CH}_2 \rightarrow \text{Ph}_2\text{PCHLiCH}_2\text{PPh}_2 \quad (3) \]

\[ \text{Ph}_2\text{PCHLiCH}_2\text{PPh}_2 + \text{H}_2\text{O} \rightarrow \text{PPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2 + \text{LiOH} \quad (4) \]

This method was used to synthesize some new unsymmetrical diphosphine ligands by changing the metal organophosphide.\textsuperscript{51} Grim et al\textsuperscript{43} have employed a similar method to produce many unsymmetrical diphosphine ligands, \( \text{PPh}_2\text{CH}_2\text{CH}_2\text{PBU}_2 \) and \( \text{PPh}_2\text{CH}_2\text{CH}_2\text{PRPh} \), where \( R=\text{methyl, ethyl, n-propyl, isopropyl, sec-butyl, isobutyl, and n-amyl} \). The complexes of group 6 metal carbonyls with these unsymmetrical diphosphine ligands have been synthesized and characterized by \( ^1\text{H NMR, } ^{31}\text{P}\{^1\text{H}\} \text{MNR, and IR} \).\textsuperscript{43,52}

By a variation of Keiter's method, King et al\textsuperscript{53-55} synthesized many novel polytertiary phosphate and arsine ligands by the direct addition of phosphorus-hydrogen and arsenic-hydrogen bonds across the carbon-carbon double bonds of vinylphosphines or the carbon-carbon triple bonds of ethynylphosphines in the presence of a base catalyst such as phenyllithium or potassium tert-butoxide. Some metal
complexes of polytertiary phosphines have been synthesized and characterized by $^{31}{P}^1{H}$ NMR. Meek et al. found that the addition reaction is equally productive when a free-radical catalyst is used instead of the base catalyst. The free-radical catalyzed addition has the advantage of not requiring a solvent and can be carried out at modest temperature.

$$\begin{align*}
P-H + \text{PCH=CH}_2 \xrightarrow{\text{AIBN} \text{ or base}} \text{PCH}_2\text{CH}_2\text{P} \\
\end{align*}$$

(AIBN = 2,2'-azobisisobutyronitrile)

Other methods have also been developed to synthesize the unsymmetrical diphosphine ligands. Grim et al. have synthesized the unsymmetrical diphosphines, $\text{Ph}_2\text{P(CH)}_2\text{PR}'\text{R}^2$, by two routes: reaction of 3-chloropropylidiphenylphosphine with lithium diorganophosphides; or, reaction of the Grignard reagent, $\text{Ph}_2\text{P(CH)}_2\text{MgCl}$, with diorganochlorophosphines. This was the first example of the synthesis a Grignard reagent of a phosphinoalkyl compound.

McAuliffe et al. have prepared the ligand, $\text{Ph}_2\text{P(CH)}_2\text{P(Et)}\text{Ph}$, by a novel synthetic route shown in eq 6-9.

$$\begin{align*}
\text{Br(CH)}_2\text{Br} + \text{Ph}_3\text{P} \xrightarrow{\text{benzene}} [\text{Ph}_3\text{P(CH)}_2\text{Br}]\text{Br}
\end{align*}$$
The key step in the synthesis is the formation of the phosphonium salt with triphenylphosphine in a nonpolar solvent. This method allows the synthesis of novel diphosphines with long backbones, such as \( \text{Ph}_2\text{P(CH}_2)_n\text{PR}_2 \), \( \text{Ph}_2\text{P(CH}_2)_n\text{P(R)Ph} \), and \( \text{Ph(R)P(Ch}_2)_n\text{P(R)Ph} (\text{R} = \text{alkyl}) \). Some of these have been ligands of interest in homogeneous catalysis and asymmetric synthesis.\(^{47}\)

b. Ditolyl Derivatives

Because 1-(diphenylphosphino)-2-(di-p-tolylphosphino)-ethane, \( \text{Ph}_2\text{PCH}_2\text{CH}_2\text{P(p-CH}_3\text{C}_6\text{H}_4)\) \(_2\) (dpdt) was used in our work, a special survey of this ligand has been conducted.

In 1981, Kapoor et al\(^6^0\) first synthesized the ligand dpdt by the reaction of diphenylvinylphosphine with di(p-tolyl)phosphine in the presence of potassium tert-butoxide. A number of chelated complexes of the types \( (\text{OC})_4\text{M(dpdt)} \) (\( \text{M} = \text{Cr, Mo, W} \)) and \( \text{M(dpdt)X}_2 \) (\( \text{M} = \text{Ni(II), Pd(II), Pt(II); X} = \text{Cl,} \)
Br, I, NCS) have been synthesized. However, no $^{31}\text{P}\{^1\text{H}\}$ NMR data were reported.

The ligand dpdt has not been used frequently. The second case, which was also the last, is found in Cotton and Kilagawa's work.\textsuperscript{38} Because of the insolubility of $\alpha$- and $\beta$-Mo$_2$X$_4$(dppe)$_2$, it is very difficult to investigate the isomerization of $\alpha$- to $\beta$-Mo$_2$X$_4$(dppe)$_2$. Therefore, dpdt was used to synthesize anti- and syn-$\alpha$-Mo$_2$X$_2$(dpdt)$_2$ which are very soluble in CH$_2$Cl$_2$. In addition to increasing the solubility, dpdt also creates more isomers: syn-$\alpha$-, anti-$\alpha$-, syn-$\beta$-, and anti-$\beta$-, instead of only $\alpha$- and $\beta$- isomers for dppe.

Other analogous ligands of dpdt have also been synthesized. 1-(diphenylphosphino)-2-(di-$m$-tolylphosphino)ethane, Ph$_2$PCH$_2$CH$_2$P($m$-CH$_3$C$_6$H$_4$)$_2$ (pmt-pf), was first synthesized by King and Kapoor\textsuperscript{61} in 1972 by a base catalyzed addition of di-$m$-tolyporphosphate to diphenylvinylphosphine. Later on, Kapoor et al\textsuperscript{62} synthesized the same kind of chelated complexes analogous to
those described on page 14 (see reference 60) using the ligand pmt-pf. Again, no $^{31}$P{$^1$H} NMR data were reported.

In addition three diphosphine ligands of the type $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PR}_2$ ($R = \text{m-FC}_6\text{H}_4$, $\text{p-FC}_6\text{H}_4$, $\text{m-CF}_3\text{C}_6\text{H}_4$) have been synthesized by Kapoor et al$^{63}$ using King’s vinyl addition method$^{52}$. These ligands improve the solubility characteristics of transition metal complexes and allow the use of $^{19}$F NMR in characterization of the complexes.

7. Synthesis of Dangling Diphosphine Complexes

Because diphosphine ligands can form chelated and bridged complexes readily, the synthesis of dangling diphosphine complexes becomes more difficult. Potential methods are summarized as follows:

a. Strohmeier’s Method (Photolysis)

Starting materials can be prepared by the method of Strohmeier, first used in 1969.$^{64}$ By irradiation of group 6 metal hexacarbonyls in the presence of excess tetrahydrofuran (THF), a mono-substituted intermediate complex can be formed, in which the THF can be easily substituted by the phosphine ligand.

\[
\text{M(CO)}_6 \xrightarrow{\text{uv}} \text{(OC)}_5\text{M(THF)} + \text{CO} \quad (10)
\]

\[
\text{(OC)}_5\text{M(THF)} + L \xrightarrow{\text{THF}} \text{(OC)}_5\text{ML} + \text{THF} \quad (11)
\]
Keiter et al\textsuperscript{65,66} have synthesized the complexes
\((\text{OC})_5\text{MPPh}_2\text{H}\) and \((\text{OC})_5\text{MPPh}_2\text{CH}=\text{CH}_2\) (M=Cr and W) by Strohmeier's
method in very good yields. Strohmeier's method has not
been used directly for the synthesis of the dangling
diphosphine complexes.

b. Angelici's Method (Aniline substitution)

Anilinepentacarbonyltungsten(O), \text{PhNH}_2\text{W(CO)}_5\text{ can be}
prepared by the irradiation of \text{W(CO)}_6\text{ and a three- to
fivefold excess of aniline in tetrahydrofuran.}\textsuperscript{11} The method
has not been shown to be useful for the synthesis of
\((\text{PhNH}_2)\text{Cr(CO)}_5\) or \((\text{PhNH}_2)\text{Mo(CO)}_5\).

The displacement of aniline from \((\text{PhNH}_2)\text{W(CO)}_5\) by
phosphine ligands occurs readily in a stirred solution of
benzene or toluene at room temperature.\textsuperscript{18a}

\[
(\text{PhNH}_2)\text{M(CO)}_5 + L \rightarrow (\text{OC})_5\text{ML} + \text{PhNH}_2
\]  \hspace{1cm} (12)

Keiter and Shah\textsuperscript{67} prepared the complexes \((\text{OC})_5\text{WPPh}_2(\text{CH}_2)_n\text{PPh}_2\)
(n=1,2) by this method. The complex \((\text{OC})_5\text{W(dppe)}\) was
prepared from a 3:1 mole ratio of dppe and \((\text{Ph}_2\text{NH}_2)\text{W(CO)}_5\),
while a 1:1 mole ratio gives the dimetallic complex
\((\text{OC})_5\text{WPPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2\text{W(CO)}_5\) as the dominant product.

Grim et al have used the method with unsymmetrical
diphosphines.\textsuperscript{43} The dangling phosphine product is a mixture
of two linkage isomers.\textsuperscript{43} The ratio of the two isomers
depends on the electronic and steric differences of the two phosphorus groups.

c. Oxidative Decarbonylation of M(CO)₆

\[
\text{M(CO)₆} + (\text{CH₃})₃\text{NO} \cdot 2\text{H₂O} + \text{L} \xrightarrow{\text{CH₂Cl₂}} \text{(OC)}₅\text{ML} + 2\text{H₂O} + (\text{CH₃})₃\text{N} + \text{CO₂} \quad (13)
\]

The carbonyl groups in M(CO)₆ can be removed by oxidation with trimethylamine N-oxide [(CH₃)₃NO].⁶⁸ For monodentate phosphine ligands, some di- and tri-substituted complexes may form in this reaction.

Hor et al⁶⁹ have prepared the complexes \((\text{OC})₅\text{M[PPH₂(CH₂)}ₙ\text{PPh₂] (n=2, 3, 4; M=Cr, Mo)}\) in low yields (13-42%) by adding \((\text{OC})₅\text{M(CH₃CN)}\) prepared in situ from M(CO)₆ and (CH₃)₃NO in CH₃CN or a CH₃CN/THF mixture. The monobridged dimer is the major by-product. The use of a slight excess of the diphosphine improves the yield of the dangling diphosphine complexes.

d. Lewis Acid-Assisted Nucleophilic Substitution

\[
(\text{OC})₅\text{MX}^- + \text{L} + (\text{R₃O})(\text{BF₄})^- \rightarrow (\text{OC})₅\text{ML} + \text{RX} + \text{R₂O} + \text{BF₄}^- \quad (14)
\]

( X= halogen; R= alkyl )

These reactions were carried out by adding a solution of
[(Et)_3O]BF_4 in CH_2Cl_2 to a stirred mixture of Et_4N[(CO)_5MI] and diphosphine ligand dissolved in CH_2Cl_2 in a mole ratio of 1:1:1. This reaction occurs very rapidly at room temperature. The starting materials Et_4N[(CO)_5MI] (M=Cr, Mo, W) and (R_3O)(BF_4) (R=Me or Et) are established chemical reagents.

This method was originally designed to provide specific syntheses of complexes containing neutral monodentate ligands, such as PH_3Cr(CO)_5. Connor et al. extended this method to the synthesis of dangling diphosphine and phosphine/arsine complexes LM(CO)_5 [M= Cr, Mo, W; L= Me_2PCH_2CH_2PMe_2 (dmpe), PPh_2(CH_2)_nPPh_2 (n=1-3), PPh_2CH_2CH_2AsPh_2 (ape)] and reported yields of >70%. In a 1977 paper from our research group it was shown that this method does not work well. For ape, the only product reported by Connor is the one in which the ligand is bonded through the phosphorus atom.

e. Thermal Reactions

\[
M(CO)_6 + xL \xrightarrow{\text{diglyme}} \text{(OC)}_{6-x}ML_x + xCO
\] (15)

(L= phosphine; diglyme=bis-2-methoxyethyl ether)

The reactions were carried out by refluxing a mixture of the starting materials in diglyme. The value of x depends primarily on the product desired and, to a lesser extent, on
the nature of ligand and the reaction time. A slight deficiency of ligand favors the formation of monosubstituted complexes. Other solvents can also be used, such as monoglyme, n-hexane, n-heptane, and n-decane. This method seems very useful for the synthesis of (OC)₅MoPPh₂CH=CH₂ (97%) and (OC)₅MoPPh₂H (73%) which are the key starting materials in method (f). However, when diphosphine ligands were used, chelated complexes were the dominant products.

f. Vinyl Addition Reaction (Keiter’s Method)

All the methods mentioned above have limitations for synthesizing dangling diphosphine complexes. In particular, phosphine-bridged complexes tend to form if vacant coordination sites become available. In addition, reactions at higher temperatures tend to give chelated products. Further, these methods do not allow control of which end of an unsymmetrical diphosphine ligand becomes coordinated to the metal. This problem arises when one uses an already synthesized unsymmetrical diphosphine ligand. Keiter has resolved this problem by reversing the procedure that was generally used before, i.e. one phosphorus group is coordinated before the other is connected to the carbon backbone.

\[
(OC)₅MPR'₂CH=CH₂ + HPR''₂ \xrightarrow{\text{AIBN or base}} (OC)₅MPR'₂CH₂CH₂PR''₂
\]  

(16)
The former reaction can be carried out under free-radical or base-catalyzed conditions. However, the latter reaction can only proceed under free-radical conditions. In the presence of base, the latter reaction will only give the chelated complex. The mechanism proposed to account for this observation involves the formation of the intermediate cis-\((\text{OC})_n\text{M(PR}_2\text{CH=CH}_2\text{)}(\text{PR}_2')\) followed by intramolecular cyclization.\(^{44,65}\)

8. Purpose of This Work

Following the interesting discovery that \((\text{OC})_5\text{WPPh}_2\text{CH}_2\text{CH(PPh}_2)\text{)}_2\) undergoes isomerization readily at room temperature, the question arose as to how general such reactions are. In particular, we wanted to find out whether simpler systems such as \((\text{OC})_5\text{WPPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2\) undergo equally rapid exchange. We have used variable temperature \(^{31}\text{P\{^1\text{H}\}}\) NMR experiments to look for evidence of exchange of bound and unbound phosphorus groups.

We have employed the unsymmetrical diphosphine, \(\text{PPh}_2\text{CH}_2\text{CH}_2\text{P(p-tol)}_2\) (dpdt), to make the two phosphorus ends nonequivalent. The ligand dpdt was used because \(\text{P(p-tol)}_2\) and \(\text{PPh}_2\) are different electronically, but are the same sterically (same cone angle). We have prepared six novel dangling phosphine complexes of the types
Mo, W). This allowed us to monitor the isomerization of each linkage isomer.

\[
(\text{OC})_5\text{MPPh}_2\text{CH}_2\text{CH}_2\text{P}(p\text{-tol})_2 \rightleftharpoons (\text{OC})_5\text{MP}(p\text{-tol})_2\text{CH}_2\text{CH}_2\text{PPh}_2 \quad (18)
\]

\( (\text{M} = \text{Cr, Mo, W}) \)

We have attempted to obtain equilibrium constants and rate constants of isomerization for these complexes.

One can envision two basic mechanisms for isomerization. A dissociative mechanism (D) involves the formation of a five-coordinate intermediate.

\[
(\text{OC})_5\text{ML}\text{L'} \rightarrow (\text{OC})_5\text{M} + \text{L-L'} \rightarrow (\text{OC})_5\text{ML'}\text{L} \quad (19)
\]

If there is some rate dependence on the incoming nucleophile, but bond-breaking is more important than bond-making the mechanism is called interchange dissociative, \( I_D \).

The other basic mechanism is associative (A) and is analogous to an \( \text{SN}_2 \) reaction.

\[
(\text{OC})_5\text{ML}\text{L'} \rightarrow (\text{OC})_5\text{M} \rightarrow (\text{OC})_5\text{ML'}\text{L} \quad (20)
\]

If bond-making is more important than bond-breaking the mechanism is called interchange associative, \( I_A \).

In this work we have attempted to determine the mechanism of isomerization from the kinetic data collected.
II. Results and Discussion

1. Synthesis of Phosphine Ligands

Tri-(p-tolyl)phosphine was synthesized by the general method of the Grignard reaction.\(^{1b,77}\)

\[
p-\text{MeC}_6\text{H}_4\text{Br} + \text{Mg} \rightarrow p-\text{MeC}_6\text{H}_4\text{MgBr} \quad (21)
\]

\[
3(p-\text{MeC}_6\text{H}_4)\text{MgBr} + \text{PCl}_3 \rightarrow (p-\text{MeC}_6\text{H}_4)_3\text{P} + 3\text{MgBrCl} \quad (22)
\]

The addition of I\(_2\) activates the Mg surface and the MgI\(_2\) thus formed will bind the last traces of water in the reaction mixture.\(^{78}\) The melting point of tri-(p-tolyl)phosphine in this work (145-146 °C) is similar to that reported by Allman and Goel's work (145-148 °C).\(^{24}\) For comparison, the properties of some tritolylphosphine analogues taken from Allman and Goel's work\(^{24}\) are summarized in Table 1. The \(^{31}\text{P}\{^1\text{H}\}\) NMR spectrum of \((p-\text{MeC}_6\text{H}_4)_3\text{P}\) is shown in Figure 1.

The cleavage of tri-(p-tolyl)phosphine to lithium di-(p-tolyl)phosphide and p-tolyllithium, followed by hydrolysis and distillation, gave di-(p-tolyl)phosphine in good yield.

\[
(p-\text{MeC}_6\text{H}_4)_3\text{P} + 2\text{Li} \rightarrow (p-\text{MeC}_6\text{H}_4)\text{Li} + (p-\text{MeC}_6\text{H}_4)_2\text{PLi} \quad (23)
\]

\[
(p-\text{MeC}_6\text{H}_4)_2\text{PLi} + \text{H}_2\text{O} \rightarrow (p-\text{MeC}_6\text{H}_4)_2\text{PH} + \text{LiOH} \quad (24)
\]

The properties of some ditolylphosphine analogues from the literature are summarized in Table 2. The \(^{31}\text{P}\{^1\text{H}\}\) NMR
spectrum of \((p-MeC_6H_4)_2PH\) is shown in Figure 2.

The reaction of lithium di-(p-tolyl)phosphide with 1,2-dichloroethane gave the symmetrical diphosphine, \((p-tol)_2PCH_2CH_2P(p-tol)_2\), in low yield (11.8%). The \(^{31}\text{P}\{^1\text{H}\}\) NMR spectrum is shown in Figure 3.

\[
P(p-tol)_2H + Li \xrightarrow{\text{THF}} P(p-tol)_2Li + \frac{1}{2}H_2
\]

\[
2P(p-tol)_2Li + ClCH_2CH_2Cl \xrightarrow{0 \, ^\circ \text{C}} (p-tol)_2PCH_2CH_2P(p-tol)_2 + 2LiCl
\]

The free-radical addition of di-(p-tolyl)phosphine to diphenylvinylphosphine gave a high yield (94.4%) of unsymmetrical diphosphine \((dpdt)\). The \(^{31}\text{P}\{^1\text{H}\}\) NMR spectrum of \((p-tol)_2PCH_2CH_2PPh_2\) (dpdt) is shown in Figure 4.

\[
\text{AIBN} \xrightarrow{\text{Ph}_2\text{PCH=CH}_2 + HP(p-tol)_2} \text{Ph}_2\text{PCH}_2\text{CH}_2\text{P}(p-tol)_2
\]

The melting point of dpdt in our work (108-109 °C) is similar to that in reference [38] (112.0-112.5 °C), but is very different from that in reference [60] (81-82 °C). The properties of some relatives of dpdt are summarized in Table 3.

For the above mentioned phosphines, the \(^{31}\text{P}\) chemical shift depends mainly on the electronic properties and the
position of the substituents on the phenyl group. In general, the CH₃C₆H₄ group makes the ligand more basic, causes an upfield ³¹P chemical shift, and makes the boiling and melting points higher than does a C₆H₅ group. For the same kind of substituent, it seems that the order of basicity is: para- > meta- > ortho-, while the ³¹P chemical shift is in the order of meta- > para- > ortho-. For diphosphines, the ³¹P chemical shift of one phosphorus does not vary much when the substituents of the phenyl group of the other phosphorus group are changed. Likewise, the P-P coupling constants show little variation, indicating that the two phosphorus groups, separated by three bonds, do not have much electronic influence on each other.

2. Synthesis of (OC)₅ML (M=Cr, Mo, W; L=PPh₂H, P(p-tol)₂H, PPh₂CH=CH₂)

Three methods, photolysis,⁶⁵,⁶⁶ oxidative decarbonylation, and thermal substitution,⁸¹ were used for the synthesis of monosubstituted tungsten and chromium complexes (see Introduction). However, oxidative decarbonylation, using Me₃NO as an initiator, gave disubstituted molybdenum complexes, M(CO)₄L₂, as dominant products. Monosubstituted molybdenum complexes were synthesized by thermal reaction in monoglyme or toluene⁸¹. Diglyme was avoided to avoid formation of trans-M(CO)₄L₂.⁶⁵. The ³¹P{¹H} NMR spectra of (OC)₅MP(p-tol)₂H (M=Cr, Mo, W) are shown in Figures 5-7.
The properties of \((\text{OC})_5\text{ML}\) complexes are given in Table 4. The \(^{31}\text{P}\) chemical shifts of complexes \((\text{OC})_5\text{ML}\) with the same phosphine ligand are in the order \(\text{Cr} > \text{Mo} > \text{W}\).

The infrared spectra of complexes \((\text{OC})_5\text{ML}\) are characterized by the \(A_1^{(1)}, A_1^{(2)},\) and \(E\) modes expected for local \(C_{4v}\) symmetry.\(^{14}\) The \(A_1^{(1)}\) and \(E\) modes show in the same \(C\text{-O}\) absorption band because of accidental degeneracy or near degeneracy. Because the molecule is not rigorously of \(C_{4v}\) symmetry, the forbidden \(B_1\) mode was also observed as a weak band. The IR spectra of \((\text{OC})_5\text{MP(p-tol)}_2\text{H}\) (\(M=\text{Cr, Mo, W}\)) are shown in Figures 8-10. The IR data are given in Table 5.

3. Disubstituted Complexes

The compound \(\text{cis-}(\text{OC})_4\text{W[P(p-tol)}_2\text{H)}_2\) was obtained as a by-product from the synthesis of \((\text{OC})_5\text{WP(p-tol)}_2\text{H}\). The \(^{31}\text{P}{^1\text{H}}\) NMR spectrum is shown in Figure 11. In addition, \(\text{cis-}(\text{OC})_4\text{Mo(PPh}_2\text{CH=CH}_2)_2\) was the dominant product obtained by oxidation decarbonylation, a method frequently used for the synthesis of monosubstituted complexes. The \(^{31}\text{P}{^1\text{H}}\) NMR spectrum of \(\text{cis-}(\text{OC})_4\text{Mo(PPh}_2\text{CH=CH}_2)_2\) is shown in Figure 12. Keiter et al\(^{65}\) have synthesized the complexes \(\text{trans-}(\text{OC})_4\text{M(PPh}_2\text{CH=CH}_2)_2\) (\(M=\text{Cr, Mo, W}\)) and \(\text{cis-}(\text{OC})_4\text{W(PPh}_2\text{H)}_2\) by thermal reactions in diglyme, but the complex \(\text{cis-}(\text{OC})_4\text{W(PPh}_2\text{CH=CH}_2)_2\) was not synthesized successfully. Smith and Thompson\(^{81}\) have synthesized \(\text{cis-}(\text{OC})_4\text{Mo(PPh}_2\text{H)}_2\) (mp 95-98 °C) which was found to exist in two configurations in the
solid state: symmetric and asymmetric.

The complex cis-(OC)₄W(PPh₂Et)(PPh₂H) was prepared by the base catalyzed reaction as described in the literature. The ³¹P{¹H} NMR spectrum is shown in Figure 13.

\[
\text{(OC)₅WPPh₂H + PPh₂Et} \xrightarrow{\text{THF, KOBu}^+ \text{ reflux 2h}} \text{cis-(OC)₄W(PPh₂Et)(PPh₂H)} + \text{CO} \quad (28)
\]

The cis complexes have C₂ᵥ symmetry and the infrared spectra are characterized by the B₁, B₂, A₁(¹), and A₁(²) vibrational modes. B₁ and B₂ modes overlap to form one band (Figures 14-16). The A₁(¹) band often appears as a shoulder on the very strong B₁ and B₂ bands and as a result the frequency of this band is often difficult to measure. The IR data are listed in Table 6. Other properties of these complexes are given in Table 7.

The melting points and ³¹P chemical shifts of the complexes are in the order of trans- > cis- > mono-.
infrared spectra can also be used to distinguish between di- and mono-substituted or cis- and trans- complexes which have different symmetries and different CO stretching frequencies.

From Tables 4 and 7, the $^{183}$W-31P coupling constants decrease in the order PPh$_2$CH=CH$_2$ > PPh$_2$H > P(p-tol)$_2$H, which corresponds with the decreasing electronegativity order of the substituents on phosphorus. The Fermi contact term is believed to be the main contributor to the coupling interactions.

4. Dangling Diphosphine Complexes

Six novel dangling diphosphine complexes were synthesized by Keiter's free-radical vinyl addition reaction (see introduction). The $^{31}$P($^1$H) NMR and IR spectra are shown in Figure 17-30. The melting points and $^{31}$P($^1$H) NMR data are given in Table 8. The IR data are listed in Table 9.

The melting points of the diphosphine complexes with the PPh$_2$ group coordinated are higher than those of the complexes with the P(p-tol)$_2$ group coordinated, which is the reverse of that found for (OC)$_5$MPPh$_2$H and (OC)$_5$MP(p-tol)$_2$H (M=Cr, Mo, W). The $^{31}$P chemical shifts of the coordinated phosphorus groups are in the order of Cr > Mo > W, while those of the uncoordinated phosphorus groups are insensitive to the metals. The phosphorus-phosphorus coupling constants
are in the order of W > Mo > Cr, which is opposite to that of the chelated complexes of diphenylphosphinite, \( \text{PPh}_2(CH_2)_n\text{OPPh}_2 \) (\( n=1 \) or 2).\(^87\) Among the complexes the molybdenum one has the highest CO stretching frequency.

5. Diphosphine Oxide Complexes

Keiter et al\(^88\) have isolated the complex, \((\text{OC})_5\text{WPPh}_2\text{CH}_2\text{CH}_2\text{P(O)}\text{Ph}_2\), which decomposes at 170-175 °C.

Three diphosphine dioxides of the type \( \text{PPh}_2\text{P(O)}\text{CH}_2\text{CH}_2\text{P(O)}\text{PhR} \) (\( \text{R}=\text{Me, Et, i-Pr} \)) were synthesized by Grim et al.\(^{43}\) Some \(^{31}\text{P}\{^1\text{H}\} \) NMR data of diphosphine oxide complexes, which were not isolated, were obtained in the course of our experimentations and are included in Table 10 for completeness. The diphosphine oxide complexes have large downfield \(^{31}\text{P} \) chemical shifts and large phosphorus-phosphorus coupling constants. The large phosphorus-phosphorus coupling constants, compared to non-oxides, were accounted for by consideration of the change in oxidation state (+3 to +5) and by the increasing s character in the phosphorus bonds.\(^{43}\)

6. Chelated Complexes

The chelated complexes can be prepared easily by refluxing a mixture of \( \text{M(CO)}_6 \) and diphosphine in a solvent.\(^{43,60,62}\) In preparing the dangling diphosphine complexes by Keiter's free-radical vinyl addition
reaction, the chelated complex of molybdenum formed at high temperature. The $^{31}$P{$^1$H} NMR and IR spectra of (OC)$_4$Mo(dpdt) are shown in Figure 31 and 32. The melting points and $^{31}$P{$^1$H} NMR data are summarized in Table 11. The IR data are summarized in Table 12.

The unusual large downfield $^{31}$P chemical shifts of the chelated complexes were explained by ring strain. However, the much more strained four-membered rings show much less downfield $^{31}$P chemical shifts. Grim et al. also observed that the phosphorus-phosphorus coupling constants in chelated complexes of Ph$_2$PCH$_2$OPPh$_2$ and Ph$_2$P(CH$_2$)$_n$PPhR (n= 1, 2; R= Me, Et, i-Pr) contain contributions of coupling both through the backbone and through the metal center ($|J_{pp}| = J^{bp}_{pp} + J^{mp}_{pp}$). The sign of $J^{bp}_{pp}$ is opposite to that of $J^{mp}_{pp}$ and this fact accounts for the observed small coupling constants. The average observed values of $J_{pp}$ for [Ph$_2$P(CH$_2$)$_2$PPhR]M(CO)$_4$ are 12, 5, and 4 Hz for M= Cr, Mo, and W, respectively, which is similar to our results.

7. Variable Temperature $^{31}$P{$^1$H} NMR Experiments of Compounds (OC)$_5$W(dppe) and (OC)$_5$W(dppm)

If the exchange between the coordinated and uncoordinated phosphorus groups in (OC)$_5$WPPh$_2$CH$_2$CH$_2$PPh$_2$ is fast enough, a time-averaged spectrum will be observed, in which the tungsten-phosphorus satellites disappear or become
much smaller in magnitude, and the two doublets may collapse into a single line. However, the variable temperature $^{31}P\{^1H\}$ NMR experiments (Table 13) show that the pattern and chemical shifts of the $^{31}P\{^1H\}$ NMR spectrum at room temperature (Figure 33) remains the same as those at high temperature (Figure 34). Therefore, it can be concluded that the exchange between the two phosphorus groups is too slow to be detected over the temperature range of 30-80 °C.

It needs to be pointed out that oxidation of the terminal phosphine took place during the experiment because the NMR tube was not sealed completely (Figure 35). In addition, the reaction of compound (OC)$_5$W(dppe) with the solvent (or some impurity in the solvent) was also significant. However, chelation was not observed below 80 °C.

In contrast, the $^2J_{pp}$ values of (OC)$_5$WPPh$_2$CH$_2$PPh$_2$ change from 122.4 to 110.6 Hz over the range of -50 to 70 °C, while the $^1J_{wp}$ values change insignificantly (Figures 36 and 37, Table 14). In addition, the $^{31}P$ chemical shifts of the two phosphorus groups move downfield somewhat with increasing temperature. The change of $^2J_{pp}$ with temperature does not mean that the two phosphorus groups are undergoing exchange. It has been shown that the temperature can affect $^2J_{pp}$ by changing the conformation of diphosphine ligands. The compound (OC)$_5$W(dppm) may exist in two conformations A and B.

31
Conformation A, in which the phosphorus lone pair is directed toward the W-P bond, may give rise to larger value of $^{3}J_{pp}$ than B in which the phosphorus lone pair is directed away from the W-P bond. The phosphorus lone pair in A may interact with the C group which is close to it to make conformation A more stable at room temperature. When the temperature is increased, the weak interaction between the phosphorus lone pair and CO will be broken allowing the C-P bond to rotate freely.

8. Isomerization Studies of Compounds

$\text{(OC)}_{6}M\text{PPh}_{2}\text{CH}_{2}\text{CH}_{2}P(p\text{-tol})_{2}$ and $\text{(OC)}_{6}M\text{P}(p\text{-tol})_{2}\text{CH}_{2}\text{CH}_{2}\text{PPh}_{2}$

$\text{(M=Cr, Mo, W)}$

Even though rapid exchange between the two phosphorus groups in compounds $\text{(OC)}_{6}W\text{PPh}_{2}\text{(CH}_{2}\text{)}_{n}\text{PPh}_{2}$ ($n=1,2$) was not observed, isomerization of the title compounds in solution could be followed with $^{31}\text{P}\left\{^{1}\text{H}\right\}$ NMR spectroscopy (Figure 38). In addition, the chromium and molybdenum compounds undergo chelation to some extent. Chelation of tungsten complexes in $(\text{CD})_{6}$C$_{4}$D$_{5}$ was insignificant within the time of investigation. The reactions, carried out at 55 °C, are shown in Scheme 1.
For the reaction \( \text{A} \rightleftharpoons \text{B} \)

the rate of disappearance of \( \text{A} \) is given by

\[
- \frac{d[A]}{dt} = \kappa_1[A] - \kappa_1[B]
\]

(29)

From stoichiometry: \( [A]_o + [B]_o = [A] + [B] = [A]_{eq} + [B]_{eq} \)

(30)

at equilibrium:

\[
\frac{[B]_{eq}}{[A]_{eq}} = K = \frac{\kappa_1}{\kappa_1}
\]

(31)

Substitution of equation (30) and (31) into the differential equation (29) gives

\[
- \frac{d[A]}{dt} = (\kappa_1 + \kappa_1) ([A] - [A]_{eq})
\]

(32)

Integration of equation (32) gives

\[
\ln([A] - [A]_{eq}) = -(\kappa_1 + \kappa_1)t + \ln([A]_o - [A]_{eq})
\]

(33)

To solve this problem, the equilibrium constant \( K \) should be known. For molybdenum compounds, the isomerization is relatively fast and the equilibrium constant can be easily
measured: 1.96 ([B]_{eq}/[A]_{eq}) at 55 °C in (CD_3)C_6D_5. The plot of ln([A]/[A]_0-[A]_{eq}/[A]_0) vs time for molybdenum compound is shown in Figure 39. For tungsten and chromium compounds, however, it takes a very long time to reach equilibrium because the isomerizations are extremely slow. In addition, the occurrence of chelation for the chromium complex makes the analysis more complicated. It is possible, however, to obtain all rate constants and equilibrium constants from a detailed analysis.

For the general reaction

\[
\begin{array}{ccc}
 A & \xleftarrow{k_1} & B \\
 & k_2 \rightarrow & \ \ \ C \\
 & k_3 \leftarrow & \\
\end{array}
\]

The rate equations are

\[
\frac{d[A]}{dt} = -(k_1 + k_2)[A] + k_{-1}[B]
\]

(34)

\[
\frac{d[B]}{dt} = k_1[A] - (k_{-1} + k_3)[B]
\]

(35)

\[
\frac{d[C]}{dt} = k_2[A] + k_3[B]
\]

(36)

which can be solved by the literature method.\textsuperscript{92}

From eq (35), [A] can be solved as

\[
[A] = \frac{1}{k_1} \frac{d[B]}{dt} + \frac{k_{-1} + k_3}{k_1} [B]
\]

(37)

Differentiation followed by substitution into eq (34) gives

\[
\frac{d^2[B]}{dt^2} + (k_1 + k_{-1} + k_2 + k_3) \frac{d[B]}{dt} + (k_1k_3 + k_2k_{-1} + k_2k_3)[B] = 0
\]

(38)
It is assumed that \([B]\) is of the form \(e^{rt}\); thus substitution of \([B]=e^{rt}\) into eq (38) generates the characteristic equation

\[
\begin{align*}
  r^2 + (\kappa_1 + \kappa_{-1} + \kappa_2 + \kappa_3)r + \kappa_1\kappa_3 + \kappa_2\kappa_{-1} + \kappa_2\kappa_3 &= 0 \\
  \text{in which } 2r_1 &= -((\kappa_1 + \kappa_{-1} + \kappa_2 + \kappa_3) \pm [(\kappa_1 + \kappa_{-1} + \kappa_2 + \kappa_3)^2 \\
  &\quad - 4(\kappa_1\kappa_3 + \kappa_2\kappa_{-1} + \kappa_2\kappa_3)]^{1/2} 
\end{align*}
\]

(39)

The general solution for \([B]\) is given as

\[
[B] = C_+ e^{rt} + C_- e^{-rt} \tag{41}
\]

where \(C_+\) and \(C_-\) are arbitrary constants.

Substitution of eq (41) into eq (37) gives

\[
\kappa_1[A] = C_+(r_+ + \kappa_{-1} + \kappa_3)e^{rt} + C_-(r_- + \kappa_{-1} + \kappa_3)e^{-rt} \tag{42}
\]

in which \(C_+\) and \(C_-\) can be found from the simultaneous solution of equations (43) and (44).

\[
[B]_0 = C_+ + C_- \tag{43}
\]

\[
\kappa_1[A]_0 = C_+(r_+ + \kappa_{-1} + \kappa_3) + C_-(r_- + \kappa_{-1} + \kappa_3) \tag{44}
\]

If \([B]_0 = 0\) and \([C]_0 = 0\), the exact solutions are given as

\[
[A] = \frac{-(r_+ + \kappa_1 + \kappa_2)[A]_0}{r_+ - r_-} e^{rt} + \frac{(r_+ + \kappa_1 + \kappa_2)[A]_0}{r_+ - r_-} e^{-rt} \tag{45}
\]

\[
[B] = \frac{\kappa_1[A]_0}{r_+ - r_-} (e^{rt} - e^{-rt}) \tag{46}
\]

\[
[C] = \frac{[(r_+ + \kappa_1)\kappa_2 - \kappa_1\kappa_3]}{r_+(r_+ - r_-)} [A]_0(1 - e^{rt}) \\
  + \frac{[\kappa_1\kappa_3 - (r_+ + \kappa_1)\kappa_2]}{r_+(r_+ - r_-)} [A]_0(1 - e^{-rt}) \tag{47}
\]

35
As \( r_{+}t \) and \( r_{-}t \) are very small in our case, the terms of \( e^{r_{+}t} \) and \( e^{r_{-}t} \) can be simplified as \( 1 + r_{+}t \) and \( 1 + r_{-}t \), respectively. Substitution of \( e^{r_{+}t} = 1 + r_{+}t \) and \( e^{r_{-}t} = 1 + r_{-}t \) into equations (45), (46), and (47) followed by rearrangement gives the simpler forms

\[
\frac{[A]}{[A]_0} = 1 - (\kappa_1 + \kappa_2) t \tag{48}
\]

\[
\frac{[B]}{[A]_0} = \kappa_1 t \tag{49}
\]

\[
\frac{[C]}{[A]_0} = \kappa_2 t \tag{50}
\]

If the isomerization is started with pure isomer B, similarly the equations of concentration vs time are given as

\[
\frac{[B]}{[B]_0} = 1 - (\kappa_{-1} + \kappa_3) t \tag{51}
\]

\[
\frac{[A]}{[B]_0} = \kappa_{-1} t \tag{52}
\]

\[
\frac{[C]}{[B]_0} = \kappa_3 t \tag{53}
\]

Therefore, the rate constants, \( \kappa_1, \kappa_2, \kappa_{-1}, \) and \( \kappa_3 \), can be obtained for the isomerization and chelation reactions if one starts with pure isomer A and with pure isomer B. The plots of concentration with time give good straight lines (Figures 40-46, 48, 50-55; \( r \geq 0.9 \)). When the Naperian logarithm of concentration is used, the disappearance of the starting isomer with time is a straight line (Figure 47), while the appearance of the product isomer with time follows a curve (Figure 49). In eq (48), the term \( 1 - (\kappa_1 + \kappa_2) t \) approximately equals \( e^{-(\kappa_1 + \kappa_2) t} \), while the term in eq (49), \( \kappa_1 t \), can be written as \( e^{\kappa_1 t} - 1 \). Therefore, when the logarithm is applied, eq (48) will give a straight line and eq (49) will
generate a curve. The rate constants are given in Table 15.

The rates of isomerization follow the order of Mo >> W >> Cr, while the rates of chelation are in the order of Mo >> Cr >> W which is consistent with the order of the first CO dissociation energy in M(CO)$_6$ [W(47.8) > Cr(45.3) > Mo(40.3)]: kcal/mol]$^{93}$ This provides evidence for a dissociation pathway for chelation. Such a pathway is consistent with Connor's chelation studies$^{34}$ involving (OC)$_5$ML [L= ((cyclo-C$_6$H$_{11}$)PCH)$_2$].

In all of the cases, the rate of isomerization of A, (OC)$_5$MPPh$_2$CH$_2$CH$_2$P(p-tol)$_2$, is faster than that of B, (OC)$_5$MP(p-tol)$_2$CH$_2$CH$_2$PPh$_2$ (M=Cr, Mo, W) because the p-tol group is a better σ-donor than the Ph group [e.g. P(p-tol)$_3$, pKa= 3.84; and PPh$_3$, pKa= 2.73]$^{24}$ In other words the less stable (OC)$_5$MPPh$_2$CH$_2$CH$_2$P(p-tol)$_2$ dissociates faster than the more stable (OC)$_5$MP(p-tol)$_2$CH$_2$CH$_2$PPh$_2$. In addition, the tolyl end is more nucleophilic than the phenyl end of the phosphorus and therefore any contribution from an associative mechanism would be consistent with the observed rates.

The rates of isomerization of compounds A and B (M=Cr, W; $10^{-8}$ s$^{-1}$ at 55 °C) are very much slower than those of compounds (OC)$_5$WPPh$_2$CH$_2$CH(PPh$_2$)$_2$ and (OC)$_5$WPPh$_2$CH(Ph)$_2$CH$_2$PPh$_2$ ($10^{-4}$ and $10^{-5}$ s$^{-1}$ at 55 °C)$^{45}$ which are believed to have a significant associative component.
The question arises, why is the above reaction four orders of magnitude faster than the isomerization of \((\text{OC})_5\text{WPPh}_2\text{CH}_2\text{CH}_2\text{P(p-tol)}_2\)? The answer may lie in the number of dangling phosphine arms. In the tri-tertiary phosphine one arm may interact with the carbon of a metal carbonyl which in turn weakens the M-P bond, allowing the third phosphorus group to swing in and displace the bound phosphorus.

The complex, \((\text{OC})_5\text{WPPh}_2\text{CH}_2\text{CH}_2\text{P(p-tol)}_2\), does not have a third arm to displace the bound phosphorus or interact with the metal carbonyl. Thus, the bound metal-phosphorus bond is not weakened and dissociation or exchange with another phosphine is not favorable.

By plotting the equation, \(\ln \kappa = -(E_a/R) \cdot T^{-1} + b\), it can be estimated that the first-order rate constants at 55 °C for the dissociation\(^9\) of \(\text{PPh}_3\) from \(\text{Cr(CO)}_5\text{PPh}_3\) and the chelation\(^9\) of \((\text{OC})_5\text{Cr(dcppe)}\) [dcppe = \(((\text{cyclo-C}_6\text{H}_{11})\text{PCH})_2\)] are \(2 \times 10^{-9} \text{ s}^{-1}\) and \(2.4 \times 10^{-8} \text{ s}^{-1}\) respectively, which are similar to those of the isomerization and the chelation of compounds.
Therefore, the isomerization and chelation for compound (OC)$_5$CrPPh$_2$CH$_2$CH$_2$P(p-tol)$_2$ and (OC)$_5$CrP(p-tol)$_2$CH$_2$CH$_2$PPh$_2$ may also proceed by the dissociative mechanism. For molybdenum and tungsten compounds, however, the isomerization is an order of magnitude faster than chelation, suggesting an associative component.

The rate of chelation for compound (OC)$_5$MPPhCH$_2$CH$_2$P(p-tol)$_2$ is slower than that for compound (OC)$_5$MP(p-tol)$_2$CH$_2$CH$_2$PPh$_2$ (M=Cr, Mo, W) because the P(p-tol)$_2$ group, with its greater basicity, can make the transition state more stable than can the PPh$_2$ group.  

In conclusion we have measured the rates of isomerization and chelation of three pairs of linkage isomers. These rates suggest that isomerization and chelation proceed by a dissociative mechanism (D) in the case of the chromium isomers. Reactions for molybdenum and tungsten are best described as taking place by a dissociative interchange mechanism (ID). Equilibrium constants (Table 15) in all cases establish that (OC)$_5$MP(p-tol)$_2$CH$_2$CH$_2$PPh$_2$ is more stable than (OC)$_5$MPPh$_2$CH$_2$CH$_2$P(p-tol)$_2$. Variable temperature studies are underway to determine $\Delta H$ and $\Delta S$ for these reactions as well as activation parameters.
### Table 1. Properties of Tritolylphosphine Analogues (from Allman and Goel's work\textsuperscript{24})

<table>
<thead>
<tr>
<th>Ligand</th>
<th>pK\textsubscript{a}</th>
<th>mp (°C)</th>
<th>δ\textsubscript{p} (ppm)\textsuperscript{a}</th>
</tr>
</thead>
<tbody>
<tr>
<td>P[4-(CH\textsubscript{3})\textsubscript{2}NC\textsubscript{6}H\textsubscript{4}]\textsubscript{3}</td>
<td>8.65</td>
<td>265-270</td>
<td>-11.7</td>
</tr>
<tr>
<td>P(4-CH\textsubscript{3}OC\textsubscript{6}H\textsubscript{4})\textsubscript{3}</td>
<td>4.57</td>
<td>135-137</td>
<td>-10.6</td>
</tr>
<tr>
<td>P(4-CH\textsubscript{3}C\textsubscript{6}H\textsubscript{4})\textsubscript{3}</td>
<td>3.84</td>
<td>145-148 (145-146)\textsuperscript{b}</td>
<td>-8.3 (-7.5)\textsuperscript{c}</td>
</tr>
<tr>
<td>P(3-CH\textsubscript{3}C\textsubscript{6}H\textsubscript{4})\textsubscript{3}</td>
<td>3.30</td>
<td>103-104</td>
<td>-5.3</td>
</tr>
<tr>
<td>P(2-CH\textsubscript{3}C\textsubscript{6}H\textsubscript{4})\textsubscript{3}</td>
<td>3.08</td>
<td>125-127</td>
<td>-27.8</td>
</tr>
<tr>
<td>P(C\textsubscript{6}H\textsubscript{5})\textsubscript{3}</td>
<td>2.73</td>
<td>80</td>
<td>-6.3</td>
</tr>
<tr>
<td>P(4-FC\textsubscript{6}H\textsubscript{4})\textsubscript{3}</td>
<td>1.97</td>
<td>80-81</td>
<td>-9.3</td>
</tr>
<tr>
<td>P(4-ClC\textsubscript{6}H\textsubscript{4})\textsubscript{3}</td>
<td>1.03</td>
<td>100-101</td>
<td>-8.7</td>
</tr>
</tbody>
</table>

\textsuperscript{a} CH\textsubscript{2}Cl\textsubscript{2}/C\textsubscript{6}D\textsubscript{6} 9:1 (v/v) \textsuperscript{b} this work \textsuperscript{c} this work (CDC\textsubscript{13}) except where noted

### Table 2. Properties of Ditolylphosphine Analogues

<table>
<thead>
<tr>
<th>Ligand</th>
<th>b.p (°C)</th>
<th>δ\textsubscript{p} (ppm)</th>
<th>\textsuperscript{1}\textsubscript{J}\textsubscript{PH} (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HP(2-CH\textsubscript{3}C\textsubscript{6}H\textsubscript{4})\textsubscript{2} \textsuperscript{a}</td>
<td>104-106/0.1 mmHg</td>
<td>-59.1</td>
<td>219</td>
</tr>
<tr>
<td>HP(3-CH\textsubscript{3}C\textsubscript{6}H\textsubscript{4})\textsubscript{2} \textsuperscript{a}</td>
<td></td>
<td>-40.3</td>
<td>214</td>
</tr>
<tr>
<td>HP(4-CH\textsubscript{3}C\textsubscript{6}H\textsubscript{4})\textsubscript{2}</td>
<td>(110/0.1 mmHg)\textsuperscript{b}</td>
<td>-43.0\textsuperscript{a} (-42.0)\textsuperscript{b}</td>
<td>212\textsuperscript{a} (218.4)\textsuperscript{b}</td>
</tr>
<tr>
<td>HP[4-(CH\textsubscript{3})\textsubscript{3}CC\textsubscript{6}H\textsubscript{4}]\textsubscript{2} \textsuperscript{a}</td>
<td></td>
<td>-43.9</td>
<td>212</td>
</tr>
<tr>
<td>HP(p-FC\textsubscript{6}H\textsubscript{4})\textsubscript{2} \textsuperscript{d}</td>
<td>110-113/2.0 mmHg</td>
<td>-44.0</td>
<td>219.7</td>
</tr>
<tr>
<td>HP(m-FC\textsubscript{6}H\textsubscript{4})\textsubscript{2} \textsuperscript{d}</td>
<td>115-118/2.5 mmHg</td>
<td>-40.9</td>
<td>220.4</td>
</tr>
<tr>
<td>HP(C\textsubscript{6}H\textsubscript{5})\textsubscript{2}</td>
<td>150-154/11 mmHg\textsuperscript{e}</td>
<td>-40.7\textsuperscript{f}</td>
<td>216\textsuperscript{f}</td>
</tr>
</tbody>
</table>

\textsuperscript{a} reference 79 (neat solution) \textsuperscript{b} this work (CDC\textsubscript{13}) \textsuperscript{c} reference 38 \textsuperscript{d} reference 63 (CDC\textsubscript{13}) \textsuperscript{e} reference 49 \textsuperscript{f} reference 80 (neat solution)
Table 3. Properties of Some Diphosphines

<table>
<thead>
<tr>
<th>Ligand</th>
<th>mp (°C)</th>
<th>$\delta_{PPh2}$ (ppm)</th>
<th>$\delta_{PR}$ (ppm)</th>
<th>$^3J_{PP}$ (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPh$_2$CH$_2$CH$_2$PPh$_2$</td>
<td>139-140</td>
<td>-13.2$^b$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PPh$_2$CH$_2$CH$_2$P(p-tol)$_2$ $^c$</td>
<td>108-109</td>
<td>-12.1</td>
<td>-14.2</td>
<td>34.6</td>
</tr>
<tr>
<td>(p-tol)$_2$PCH$_2$CH$_2$P(p-tol)$_2$ $^c$</td>
<td>148-149</td>
<td></td>
<td>-14.0</td>
<td></td>
</tr>
<tr>
<td>PPh$_2$CH$_2$CH$_2$P(m-CH$_3$C$_6$H$_4$)$_2$</td>
<td>95$^d$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PPh$_2$CH$_2$CH$_2$P(m-FC$_6$H$_4$)$_2$ $^e$</td>
<td>92-93</td>
<td>-12.1</td>
<td>-11.1</td>
<td>34.8</td>
</tr>
<tr>
<td>PPh$_2$CH$_2$CH$_2$P(p-FC$_6$H$_4$)$_2$ $^e$</td>
<td>93-94</td>
<td>-12.2</td>
<td>-14.5</td>
<td>35.0</td>
</tr>
<tr>
<td>PPh$_2$CH$_2$CH$_2$P(m-CF$_3$C$_6$H$_4$)$_2$</td>
<td>88-89</td>
<td>-12.2</td>
<td>-11.2</td>
<td>35.1</td>
</tr>
</tbody>
</table>

$^a$ reference 53  $^b$ reference 51  $^c$ this work  $^{31}$P($^1$H) NMR in CDCl$_3$  $^d$ reference 61  $^e$ reference 63  $^{31}$P($^1$H) NMR in C$_6$H$_6$

Table 4. Properties of (OC)$_5$ML

<table>
<thead>
<tr>
<th>Complex</th>
<th>mp (°C)</th>
<th>$\delta_P$ (ppm)$^a$</th>
<th>$J_{PH}$ (Hz)</th>
<th>$J_{WP}$ (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(OC)$_5$CrPPPh$_2$H</td>
<td>60-61$^b$</td>
<td>32.9$^b$</td>
<td>340$^c$</td>
<td></td>
</tr>
<tr>
<td>(OC)$_5$MoPPh$_2$H</td>
<td>74-75.5$^b$</td>
<td>6.7$^b$</td>
<td></td>
<td>330$^c$</td>
</tr>
<tr>
<td>(OC)$_5$WPPh$_2$H</td>
<td>90-91</td>
<td>-13.2$^d$</td>
<td>345.3$^d$</td>
<td>229.3$^d$</td>
</tr>
<tr>
<td></td>
<td>(91-93)$^d$</td>
<td>(-13.7)$^d$</td>
<td>(334.9)$^d$</td>
<td>(229.6)$^d$</td>
</tr>
<tr>
<td>(OC)$_5$CrP(p-tol)$_2$H</td>
<td>91-92</td>
<td>30.9</td>
<td>338.2</td>
<td></td>
</tr>
<tr>
<td>(OC)$_5$MoP(p-tol)$_2$H</td>
<td>81-82</td>
<td>4.5</td>
<td>332.3</td>
<td></td>
</tr>
<tr>
<td>(OC)$_5$WP(p-tol)$_2$H</td>
<td>89-90</td>
<td>-15.5</td>
<td>332.3</td>
<td>227.5</td>
</tr>
<tr>
<td>(OC)$_5$CrPPPh$_2$CH=CH$_2$</td>
<td>54-55</td>
<td>47.9$^b$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(58-59)$^b$</td>
<td>(47.4)$^b$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(OC)$_5$MoPPPh$_2$CH=CH$_2$</td>
<td>57-58$^b$</td>
<td>29.3$^b$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(OC)$_5$WPPh$_2$CH=CH$_2$</td>
<td>59-60$^d$</td>
<td>11.9$^d$</td>
<td>239.3$^d$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(64-65)$^d$</td>
<td>(11.4)$^d$</td>
<td>(239.4)$^d$</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ CDCl$_3$  $^b$ reference 66  $^c$ reference 81  $^d$ reference 65
### Table 5. IR Data of (OC)$_5$ML ($\text{CH}_2\text{Cl}_2$, cm$^{-1}$)

<table>
<thead>
<tr>
<th>Complex</th>
<th>$A_1^{(2)}$</th>
<th>$B_1$</th>
<th>$(E+A_1^{(1)})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(OC)$_5$CrPPh$_2$H$^a$</td>
<td>2078</td>
<td>1993</td>
<td>1953</td>
</tr>
<tr>
<td>(OC)$_5$MoPPh$_2$H$^a$</td>
<td>2074</td>
<td>1992</td>
<td>1950</td>
</tr>
<tr>
<td>(OC)$_5$WPPh$_2$H</td>
<td>2075</td>
<td>1985$^b$</td>
<td>1942 $^b$</td>
</tr>
<tr>
<td></td>
<td>2077$^b$</td>
<td></td>
<td>1947$^b$</td>
</tr>
<tr>
<td>(OC)$_5$CrP(p-tol)$_2$H</td>
<td>2066</td>
<td>1984</td>
<td>1943</td>
</tr>
<tr>
<td>(OC)$_5$MoP(p-tol)$_2$H</td>
<td>2075</td>
<td></td>
<td>1948</td>
</tr>
<tr>
<td>(OC)$_5$WP(p-tol)$_2$H</td>
<td>2074</td>
<td></td>
<td>1940</td>
</tr>
<tr>
<td>(OC)$_5$CrPPh$_2$CH=CH$_2$</td>
<td>2064</td>
<td>1983</td>
<td>1941</td>
</tr>
<tr>
<td>(OC)$_5$MoPPh$_2$CH=CH$_2$</td>
<td>2074</td>
<td>1991</td>
<td>1949</td>
</tr>
<tr>
<td>(OC)$_5$WPPh$_2$CH=CH$_2$</td>
<td>2072</td>
<td>1979</td>
<td>1939</td>
</tr>
</tbody>
</table>

$^a$ reference 82 (CHCl$_3$)  
$^b$ reference 65 (CHCl$_3$)  
$^c$ reference 66 (CHCl$_3$)

### Table 6. IR Data of cis-(OC)$_4$ML$_2$ ($\text{CH}_2\text{Cl}_2$, cm$^{-1}$)

<table>
<thead>
<tr>
<th>Complex</th>
<th>$A_1^{(2)}$</th>
<th>$A_1^{(2)}$</th>
<th>$(B_1+B_2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-(OC)$_4$W(PPh$_2$H)$_2$</td>
<td>2020</td>
<td>1917</td>
<td>1903</td>
</tr>
<tr>
<td>cis-(OC)$_4$W[P(p-tol)$_2$H]$_2$</td>
<td>2021</td>
<td></td>
<td>1906</td>
</tr>
<tr>
<td>cis-(OC)$_4$Mo(PPh$_2$CH=CH$_2$)$_2$</td>
<td>2022</td>
<td></td>
<td>1907,1883</td>
</tr>
<tr>
<td>cis-(OC)$_4$W(PPh$_2$Et)(PPh$_2$H)</td>
<td>2019 (2023)$^b$</td>
<td>(1922)$^b$</td>
<td>1901, 1877 (1903)$^b$</td>
</tr>
</tbody>
</table>

$^a$ reference 65 (CHCl$_3$)  
$^b$ reference 83 (CHCl$_3$)
Table 7. Properties of Disubstituted Complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>mp (°C)</th>
<th>δ_p (ppm)</th>
<th>1^J_{PH} (Hz)</th>
<th>2^J_{pp} (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-(OC)₄W(PPh₂H)₂</td>
<td>88-90</td>
<td>-2.8</td>
<td>342</td>
<td>224.1</td>
</tr>
<tr>
<td>cis-(OC)₄W[P(p-tol)₂H]₂</td>
<td>138-139</td>
<td>-4.4</td>
<td>336.6</td>
<td>223.8</td>
</tr>
<tr>
<td>cis-(OC)₄Mo(PPh₂CH=CH₂)₂</td>
<td>93-94</td>
<td>29.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>trans-(OC)₄Mo(PPh₂CH=CH₂)₂</td>
<td>148-150</td>
<td>41.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>cis-(OC)₄W(PPh₂Et)(PPh₂H)</td>
<td>130-130.5 (128-129)</td>
<td>2.4 (1.4)⁰ (PPh₂H) 14.8 (14.1)⁰ (PPh₂Et) 335⁰ 230.1 (230)⁰ [1^J_{PP}(PPh₂H)] 225.7 (226)⁰ [1^J_{PP}(PPh₂Et)]</td>
<td>16.7 (17)³</td>
<td></td>
</tr>
</tbody>
</table>

⁰ CDCl₃  
³ reference 83

refs
Table 8. Properties of Dangling Diphosphine Complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>mp (°C)</th>
<th>$\delta_{W-P}$ (ppm)</th>
<th>$\delta_P$ (ppm)$^a$</th>
<th>$^3J_{PP}$ (Hz)</th>
<th>$^1J_{2WP}$ (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(OC)$_5$WPPh$_2$CH$_2$CH$_2$PPh$_2$</td>
<td>112-115 (116-117)$^b$</td>
<td>13.4 (11.4)$^c$</td>
<td>-12.2 (13.7)$^c$</td>
<td>37.5 (37.2)$^c$</td>
<td>239.4 (240.0)$^c$</td>
</tr>
<tr>
<td>(OC)$_5$CrPPh$_2$CH$_2$CH$_2$P(p-tol)$_2$</td>
<td>133-134</td>
<td>50.5</td>
<td>-13.6</td>
<td>35.1</td>
<td></td>
</tr>
<tr>
<td>(OC)$_5$MoPPh$_2$CH$_2$CH$_2$P(p-tol)$_2$</td>
<td>130</td>
<td>31.7</td>
<td>-13.6</td>
<td>37.0</td>
<td></td>
</tr>
<tr>
<td>(OC)$_5$WPPh$_2$CH$_2$CH$_2$P(p-tol)$_2$</td>
<td>143-144</td>
<td>13.6</td>
<td>-13.7</td>
<td>37.6</td>
<td>239.3</td>
</tr>
<tr>
<td>(OC)$_5$CrP(p-tol)$_2$CH$_2$CH$_2$PPh$_2$</td>
<td>103-104</td>
<td>48.4</td>
<td>-11.8</td>
<td>35.0</td>
<td></td>
</tr>
<tr>
<td>(OC)$_5$MoP(p-tol)$_2$CH$_2$CH$_2$PPh$_2$</td>
<td>90-91</td>
<td>29.7</td>
<td>-11.8</td>
<td>35.9</td>
<td></td>
</tr>
<tr>
<td>(OC)$_5$WP(p-tol)$_2$CH$_2$CH$_2$PPh$_2$</td>
<td>111-112</td>
<td>11.5</td>
<td>-12.0</td>
<td>38.0</td>
<td>238.4</td>
</tr>
</tbody>
</table>

$^a$ CDCl$_3$  $^b$ reference 67  $^c$ reference 86
Table 9. IR Data of Dangling Diphosphine Complexes
(CH$_2$Cl$_2$, cm$^{-1}$)

<table>
<thead>
<tr>
<th>Complex</th>
<th>A$_1^{(1)}$</th>
<th>B$_1$</th>
<th>(E+A$_1^{(1)}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(OC)$_5$WPPh$_2$CH$_2$CH$_2$PPh$_2$</td>
<td>2071 (2074)$^a$</td>
<td>1982 (1986)$^a$</td>
<td>1937 (1940)$^a$</td>
</tr>
<tr>
<td>(OC)$_5$CrPPh$_2$CH$_2$CH$_2$P(p-tol)$_2$</td>
<td>2063</td>
<td>1983</td>
<td>1939</td>
</tr>
<tr>
<td>(OC)$_5$MoPPh$_2$CH$_2$CH$_2$P(p-tol)$_2$</td>
<td>2073</td>
<td>1989</td>
<td>1945</td>
</tr>
<tr>
<td>(OC)$_5$WPPh$_2$CH$_2$CH$_2$P(p-tol)$_2$</td>
<td>2071</td>
<td>1981</td>
<td>1937</td>
</tr>
<tr>
<td>(OC)$_5$CrP(p-tol)CH$_2$CH$_2$PPh$_2$</td>
<td>2062</td>
<td>1982</td>
<td>1937</td>
</tr>
<tr>
<td>(OC)$_5$MoP(p-tol)$_2$CH$_2$CH$_2$PPh$_2$</td>
<td>2072</td>
<td>1989</td>
<td>1943</td>
</tr>
<tr>
<td>(OC)$_5$WP(p-tol)$_2$CH$_2$CH$_2$PPh$_2$</td>
<td>2071</td>
<td>1981</td>
<td>1936</td>
</tr>
</tbody>
</table>

$^a$ reference 67 (CHCl$_3$)

Table 10. $^{31}$P-$^1$H NMR Data of Diphosphine Oxide Complexes
(CDCl$_3$)

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\delta_{P-W}$ (ppm)</th>
<th>$\delta_{P-O}$ (ppm)</th>
<th>$^3$J$_{PP}$ (Hz)</th>
<th>$^1$J$_{WP}$ (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(OC)$_5$WPPh$_2$CH$_2$CH$_2$P(O)Ph$_2$</td>
<td>13.6$^a$ 13.3$^b$</td>
<td>33.1$^a$ 31.6$^b$</td>
<td>47.5$^a$ 48.8$^b$</td>
<td>239.9$^a$ 241.5$^b$</td>
</tr>
<tr>
<td>(OC)$_5$WPPh$_2$CH$_2$CH$_2$P(O)(p-tol)$_2$</td>
<td>13.8</td>
<td>32.4</td>
<td>48.1</td>
<td></td>
</tr>
<tr>
<td>(OC)$_5$WP(p-tol)$_2$CH$_2$CH$_2$P(O)Ph$_2$</td>
<td>11.8</td>
<td>32.2</td>
<td>48.0</td>
<td></td>
</tr>
<tr>
<td>(OC)$_5$CrPPh$_2$CH$_2$CH$_2$P(O)P(p-tol)$_2$</td>
<td>50.8$^c$</td>
<td>28.1$^c$</td>
<td>46.4$^c$</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ in (CDCl$_3$)$_2$  $^b$ reference 86  $^c$ in C$_6$D$_5$(CD$_3$)
Table 11. Properties of Chelated Complexes (CDCl₃)

<table>
<thead>
<tr>
<th>Complex</th>
<th>mp  (°C)</th>
<th>δ_PPh₂ (ppm)</th>
<th>δ_P(tol)₂ (ppm)</th>
<th>J_PP (Hz)</th>
<th>J_W (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(OC)_4Cr(dpdt)</td>
<td>(118-119)</td>
<td>80.8</td>
<td>78.6</td>
<td>11.3</td>
<td></td>
</tr>
<tr>
<td>(OC)_4Mo(dpdt)</td>
<td>147-148</td>
<td>55.8</td>
<td>53.6</td>
<td>5.7</td>
<td></td>
</tr>
<tr>
<td>(OC)_4W(dpdt)</td>
<td>(165)</td>
<td>41.1</td>
<td>39.1</td>
<td>5.6</td>
<td></td>
</tr>
<tr>
<td>(OC)_4W(dppe)</td>
<td>(206-207)</td>
<td>41.3</td>
<td>(40.1)</td>
<td></td>
<td>230.2</td>
</tr>
</tbody>
</table>

a reference 60  b in C₆D₆(CD₃)  c reference 87

Table 12. IR Data of Chelated Complexes (cm⁻¹)

<table>
<thead>
<tr>
<th>Complex</th>
<th>A₁(2)</th>
<th>A₁(1)</th>
<th>B₁</th>
<th>B₁</th>
</tr>
</thead>
<tbody>
<tr>
<td>(OC)_4Cr(dpdt)</td>
<td>2030</td>
<td>1898</td>
<td>1890</td>
<td>1855</td>
</tr>
<tr>
<td>(OC)_4Mo(dpdt)</td>
<td>2021</td>
<td>1909</td>
<td>1882</td>
<td>(1840)</td>
</tr>
<tr>
<td>(OC)_4W(dpdt)</td>
<td>2005</td>
<td>1930</td>
<td>1910</td>
<td>1880</td>
</tr>
<tr>
<td>(OC)_4W(dppe)</td>
<td>2019</td>
<td>1922</td>
<td>1909</td>
<td>1897</td>
</tr>
</tbody>
</table>

a reference 60 (KBr)  b this work (CH₂Cl₂)  c reference 87 (ClCH₂CH₂Cl)
Table 13. Variable Temperature $^{31}\text{P}^{1\text{H}}$ NMR Data of (OC)$_5$W(dppe) [(CDCl$_2$)$_2$]

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>$\delta_{p-w}$ (ppm)</th>
<th>$\delta_p$ (ppm)</th>
<th>$^1J_{WP}$ (Hz)</th>
<th>$^3J_{PP}$ (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>13.3</td>
<td>-11.6</td>
<td>238.5</td>
<td>36.7</td>
</tr>
<tr>
<td>50</td>
<td>13.3</td>
<td>-11.5</td>
<td>237.2</td>
<td>36.7</td>
</tr>
<tr>
<td>65</td>
<td>13.3</td>
<td>-11.3</td>
<td>239.3</td>
<td>35.9</td>
</tr>
<tr>
<td>80</td>
<td>13.4</td>
<td>-10.9</td>
<td>241.6</td>
<td>36.6</td>
</tr>
</tbody>
</table>

Table 14. Variable Temperature $^{31}\text{P}^{1\text{H}}$ NMR Data of (OC)$_5$W(dppe) [C$_6$D$_5$(CD$_3$)]

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>$\delta_{p-w}$ (ppm)</th>
<th>$\delta_p$ (ppm)</th>
<th>$^2J_{PP}$ (Hz)</th>
<th>$^1J_{WP}$ (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-50</td>
<td>11.2</td>
<td>-23.7</td>
<td>122.4</td>
<td>245.5</td>
</tr>
<tr>
<td>-30</td>
<td>11.2</td>
<td>-23.6</td>
<td>121.0</td>
<td>245.3</td>
</tr>
<tr>
<td>-10</td>
<td>11.2</td>
<td>-23.6</td>
<td>119.0</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>11.2</td>
<td>-23.6</td>
<td>116.6</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>11.2</td>
<td>-23.5</td>
<td>114.0</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>11.3</td>
<td>-23.4</td>
<td>111.7</td>
<td>246.9</td>
</tr>
<tr>
<td>70</td>
<td>11.4</td>
<td>-23.2</td>
<td>110.6</td>
<td>246.5</td>
</tr>
<tr>
<td>room a</td>
<td>10.0</td>
<td>-24.8</td>
<td>106.2</td>
<td>245.6 (3J$_{WP}$ 6.3)</td>
</tr>
</tbody>
</table>

* a reference 86 (CDCl$_3$)
Table 15. Kinetic Data of Isomerization and Chelation at 55°C.

\[
\begin{align*}
\text{(OC)}_5\text{MPh}_2\text{CH}_2\text{CH}_2\text{P(p-tol)}_2 & \xrightleftharpoons{K_1}{\kappa_2} \text{(OC)}_5\text{MP(p-tol)}_2\text{CH}_2\text{CH}_2\text{PPh}_2 \\
& \xrightleftharpoons{K_1}{\kappa_3} \text{(OC)}_4\text{M(dpdt)}
\end{align*}
\]

<table>
<thead>
<tr>
<th>M</th>
<th>solvent</th>
<th>$K_1$ (10^8) s(^{-1})</th>
<th>$K_2$ (10^8) s(^{-1})</th>
<th>$K_3$ (10^8) s(^{-1})</th>
<th>$K_{eq}=K_1/K_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>(CD(_3))C(_6)D(_5)</td>
<td>1.22</td>
<td>0.65</td>
<td>1.15</td>
<td>1.24</td>
</tr>
<tr>
<td>Mo</td>
<td>(CD(_3))C(_6)D(_5)</td>
<td>759</td>
<td>387</td>
<td>29.6</td>
<td>30.3</td>
</tr>
<tr>
<td>W</td>
<td>(CD(_3))C(_6)D(_5)</td>
<td>2.31</td>
<td>0.97</td>
<td></td>
<td></td>
</tr>
<tr>
<td>W</td>
<td>CDC(_2)_3</td>
<td>2.03</td>
<td>1.25</td>
<td>0.32</td>
<td>0.46</td>
</tr>
</tbody>
</table>
Figure 1. $^{31}$P{$^1$H} NMR Spectrum of P(p-tol),

<table>
<thead>
<tr>
<th>HEIGHT</th>
<th>HEIGHT(L)</th>
<th>FREQ(Hz)</th>
<th>PPM</th>
</tr>
</thead>
<tbody>
<tr>
<td>108.27</td>
<td>108.36</td>
<td>-1784.94</td>
<td>-14.665</td>
</tr>
<tr>
<td>187.74</td>
<td>190.24</td>
<td>-923.62</td>
<td>-7.588</td>
</tr>
<tr>
<td>248.32</td>
<td>250.97</td>
<td>-918.92</td>
<td>-7.330</td>
</tr>
<tr>
<td>3730.15</td>
<td>------</td>
<td>-915.52</td>
<td>-7.322</td>
</tr>
<tr>
<td>600.63</td>
<td>702.01</td>
<td>-907.03</td>
<td>-7.432</td>
</tr>
<tr>
<td>103.36</td>
<td>119.54</td>
<td>3632.12</td>
<td>29.843</td>
</tr>
</tbody>
</table>
Figure 2. $^{31}\text{P}^{1\text{H}}$ NMR Spectrum of $\text{P}(p\text{-tol})_2\text{H}$
Figure 3. $^{31}P{(^1H)}$ NMR Spectrum of

$(p$-tol)$_2$PCH$_2$CH$_2$P(p-tol)$_2$, (dpdt)
Figure 4. $^{31}\text{P}[^1\text{H}]$ NMR Spectrum of

$\text{PPh}_3\text{CH}_2\text{CH}_2\text{P(p-tol)}_2$
Figure 5. $^{31}\text{P}'{\text{H}} \text{ NMR Spectrum of}$

$\text{(OC)}_2\text{CrP(p-tol)}_2\text{H}$
Figure 7. $^{31}$P$\{$H$\}$ NMR Spectrum of

$\text{(OC)}_5\text{WP(p-tol)}_2\text{H}$

<table>
<thead>
<tr>
<th>HEIGHT</th>
<th>HEIGHT(L)</th>
<th>FREQ(HZ)</th>
<th>PPM</th>
</tr>
</thead>
<tbody>
<tr>
<td>106.30</td>
<td>185.37</td>
<td>-1995.98</td>
<td>-16.399</td>
</tr>
<tr>
<td>1289.27</td>
<td></td>
<td>-1995.98</td>
<td>-16.399</td>
</tr>
<tr>
<td>76.05</td>
<td></td>
<td>-1766.32</td>
<td>-14.512</td>
</tr>
</tbody>
</table>
Figure 9. IR Spectrum of (OC)₅MoP(p-tol)₂H
Figure 11. $^{31}\text{P}^{1\text{H}}$ NMR Spectrum of

cis-$(\text{OC})_4\text{W}[\text{P}(\text{p-tol})_2\text{H}]_2$
Figure 12. $^{31}\text{P}^{1\text{H}}$ NMR Spectrum of

cis-$(\text{OC})_2\text{Mo}(\text{PPh}_2\text{CH}=$CH$_2)_2$,
Figure 13. $^3$P($^2$H) NMR Spectrum of cis-(OC)$_5$(PPh$_2$H)$_2$W(PPh$_2$Et)$_2$(PPh$_2$H)
Figure 14. IR Spectrum of cis-(OC)₄W[P(p-tol)₃]₂
Figure 15. IR Spectrum of cis-(OC)_4Mo(PPh_2CH=CH)_2
Figure 16. IR Spectrum of cis-(OC)$_4$W(PPh$_2$Et)(PPh$_2$H)
Figure 17. $^{31}\text{P}\{^1\text{H}\}$ NMR Spectrum of

$(\text{OC})_2\text{WPPh}_2\text{CH}_2\text{CH}_2\text{P}(\text{p-tol})_2$
Figure 18. IR Spectrum of \((\text{OC})_5\text{WPPh}_2\text{CH}_2\text{CH}_2\text{P}(p\text{-tol})_2\)
Figure 19. $^1{H}^1$ NMR Spectrum of (OC)WP(p-tol), CH, CH2PPh,
Figure 20. IR Spectrum of \( (\text{OC})_5\text{WP(p-tol)}_2\text{CH}_2\text{CH}_2\text{PPh}_2 \)
Figure 21. $^{31}$P{$^1$H} NMR Spectrum of

$$(OC)_2CrPPh_2CH_2CH_2P(p\text{-tol})_2$$
Figure 22. IR Spectrum of \((\text{OC})_2\text{CrPPh}_2\text{CH}_2\text{CH}_2\text{P(p-tol)}_2\)
Figure 23. $^{31}$P{$^1$H} NMR Spectrum of

$\text{(OC)}_5\text{CrP}(p$-tol)$_2\text{CH}_2\text{CH}_2\text{PPh}_2$
Figure 24. IR Spectrum of (OC)₅Cr₆P₆ (p-tol), (CH₃)₂P₅B₃H₃
Figure 26. IR Spectrum of \((OC)_2\text{MoPPh}_2\text{CH}_2\text{CH}_2\text{P(p-tol)}_2\)
Figure 29. $^{31}$P\textsuperscript{1H} NMR Spectrum of

$$(\text{OC})_3\text{WPPh}_3\text{CH}_2\text{CH}_2\text{PPh}_2$$
Figure 31. $^{31}\text{P}^{'}\text{H}$ NMR Spectrum of

$\text{(OC)}_2\text{MoPPh}_2\text{CH}_2\text{CH}_2\text{P}\text{(p-tol)}_2$
Figure 32. IR Spectrum of \((\text{OC})_4\text{MoPPh}_2\text{CH}_2\text{CH}_2\text{P}(p\text{-tol})_2\).
Figure 33. $^{31}\text{P}^1\text{H}$ NMR Spectrum (upfield) of $(\text{OC})_3\text{WPPh}_3\text{CH}_2\text{CH}_2\text{PPh}_3$ at 30 °C
Figure 34. $^{31}$P$^1$H NMR Spectrum (upfield) of

$\text{(OC)}_3\text{WPPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2$ at 80 °C
Figure 35. $^{31}{\text{P}}

$^{[1]{\text{H}}}$ NMR Spectrum (upfield) of

$(\text{OC})_2\text{WPPh}_2\text{CH}_2\text{CH}_2\text{P(O)}\text{Ph}_2$, at 80 °C.

12.0 PPM
14
16
18
Figure 36. $^{31}\text{P}^{1}\text{H}$ NMR Spectrum of

$\text{(OC)}_{5}\text{WPPh}_{2}\text{CH}_{2}\text{PPh}_{2}$ at -50 °C

<table>
<thead>
<tr>
<th>LINE</th>
<th>HEIGHT(L)</th>
<th>FREQ(Hz)</th>
<th>PPM</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>87.76</td>
<td>1820.82</td>
<td>12.494</td>
</tr>
<tr>
<td>2</td>
<td>1327.46</td>
<td>1698.11</td>
<td>11.452</td>
</tr>
<tr>
<td>3</td>
<td>1391.17</td>
<td>1575.74</td>
<td>10.012</td>
</tr>
<tr>
<td>4</td>
<td>128.79</td>
<td>1457.97</td>
<td>9.970</td>
</tr>
<tr>
<td>5</td>
<td>104.69</td>
<td>344.68</td>
<td>2.502</td>
</tr>
<tr>
<td>6</td>
<td>122.74</td>
<td>3307.91</td>
<td>-23.247</td>
</tr>
<tr>
<td>7</td>
<td>1165.62</td>
<td>3397.27</td>
<td>-23.311</td>
</tr>
<tr>
<td>8</td>
<td>141.10</td>
<td>3440.65</td>
<td>-23.309</td>
</tr>
<tr>
<td>9</td>
<td>1872.74</td>
<td>3519.66</td>
<td>-24.151</td>
</tr>
<tr>
<td>10</td>
<td>84.74</td>
<td>3529.57</td>
<td>-24.219</td>
</tr>
</tbody>
</table>
Figure 37. $^{31}$P{^1}H NMR Spectrum of

$(OC)_2WPPh_2CH_2PPh_2$ at 70 °C

<table>
<thead>
<tr>
<th>LTEN</th>
<th>HEIGHT(1)</th>
<th>FREQ(1Z)</th>
<th>PPM</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>132.39</td>
<td>2943.53</td>
<td>20.198</td>
</tr>
<tr>
<td>2</td>
<td>100.40</td>
<td>1846.58</td>
<td>12.471</td>
</tr>
<tr>
<td>3</td>
<td>365.72</td>
<td>1735.67</td>
<td>11.910</td>
</tr>
<tr>
<td>4</td>
<td>1710.52</td>
<td>1723.01</td>
<td>11.823</td>
</tr>
<tr>
<td>5</td>
<td>1732.16</td>
<td>1612.47</td>
<td>11.064</td>
</tr>
<tr>
<td>6</td>
<td>164.74</td>
<td>1489.52</td>
<td>10.220</td>
</tr>
<tr>
<td>7</td>
<td>1117.91</td>
<td>-3303.42</td>
<td>-22.667</td>
</tr>
<tr>
<td>8</td>
<td>170.52</td>
<td>-3310.08</td>
<td>-22.714</td>
</tr>
<tr>
<td>9</td>
<td>1548.53</td>
<td>-3326.98</td>
<td>-22.829</td>
</tr>
<tr>
<td>10</td>
<td>165.96</td>
<td>-3343.19</td>
<td>-22.940</td>
</tr>
<tr>
<td>11</td>
<td>1424.74</td>
<td>-3407.51</td>
<td>-23.507</td>
</tr>
</tbody>
</table>
Figure 38. \(^{31}\text{P}[^1\text{H}]\) NMR for the isomerization of 

(OC)_5MoPPh_2CH_2CH_2P(p-tol)_2 at various 
times at 55 °C in perdeuterated toluene.
Figure 39. Plot of ln([A]/[A]₀ - [A]ₜ/[A]₀) vs t

[A=(OC)₅MoPPh₂CH₂CH₂P(p-tol)₂]

at 55 °C in perdeuterated toluene.
Figure 40. Plot of $[A]/[A]_0$ vs $t$ for $[A=(OC)_3CrPPh_2CH_2CH_2P(p-tol)_2]$ at 55 °C in perdeuterated toluene.
Figure 41. Plots of \([B]/[A]_0\) or \([C]/[A]_0\) vs \(t\)

\[B=(OC)_3CrP(p-tol)_2CH_2CH_2PPh_2;\ C=(OC)_4Cr(dpdt)\]

at 55 °C in perdeuterated toluene.
Figure 42. Plot of $[B]/[B_0]$ vs $t$ for $[B=(OC)CrP(p-tol),CH,CH,Ph]$ at 55 °C in perdeuterated toluene.
Figure 43. Plots of $[A]/[B]_0$ or $[C]/[B]_0$ vs $t$
$[A]=(OC)\text{CrPPh}_2\text{CH}_2\text{CH}_2\text{P}_{(p\text{-tol})}$; $C=(OC)\text{Cr(dpdt)}$
at 55 °C in perdeuterated toluene.
Figure 44. Plot of $[\text{C}]/[\text{A}]_0$ vs $t$ [$\text{C}=(\text{OC})_2\text{Mo(dpdt)}$]

at 55 °C in predeuterated toluene.
Figure 45. Plot of \([\text{C}] / [\text{B}]_0\) vs. \(t\) \([\text{C}=(\text{OC})_2\text{Mo(dpdt)}]\)

at 55 °C in predeuterated toluene.
Figure 46: Plot of $[A]/[A]_0$ vs $t$ for $[A]=\text{OC}\text{WPPh}_2\text{CH}_2\text{P}(\text{p-tol})_2$ at 55°C in perdeuterated toluene.
Figure 47. Plot of $\ln \left( \frac{[A]}{[A]_0} \right)$ vs $t$ at 55 °C in perdeuterated toluene $\left( [A] = \text{PhCH}_2\text{CH}_2\text{Ph}, [p\text{-tol}] \right)$. 
Figure 48. Plot of $[\text{B}] / [\text{A}]_o$ vs $t$ for $[\text{B}=(\text{OC})_2\text{WP}(\text{p-tol})_2\text{CH}_2\text{CH}_2\text{PPh}_2]$ at $55^\circ\text{C}$ in perdeuterated toluene.
Figure 49. Plot of $\ln([B]/[A])$ vs $t$ at 55 °C in perdeuterated toluene $[B=(OC)\text{WP}_{p-\text{tol}},]CH_2CH_2PPh_2$. 

$0$ $500$ $1000$ $1500$ $2000$ $2500$ $t$ (h) 

$-1.5$ $-2.1$ $-2.7$ $-3.3$ $-3.9$ $-4.5$ 

$\ln([B]/[A])$ vs $t$
Figure 50. Plot of $[B]/[B_0]$ vs $t$ for $[B=(OC)_3 WP (p-tol)]_2 CH_2 PH_2$ at 55 °C in perdeuterated toluene.
Figure 51. Plot of $[A]/[B]_0$ vs $t$ for $[A=\{(OC)\_2WP\_2CH\_2CH\_2P(p\text{-tol})\}]$ at 55 °C in perdeuterated toluene.
Figure 52. Plot of $[A]/[A]_0$ vs $t$ \([A=\text{(OC)\_5 WPPh\_2CH\_2CH\_2P(p-tol)}_2]\)

at 55 °C in perdeuterated chloroform.
Figure S3. Plots of $[B]/[A]$ or $[C]/[A]$ vs $t$ at 55 °C in perdeuterated chloroform.

$[B] = (OC)_5WP(p$-tol)$_2CH_2CH_2PPh_2$; $C = (OC)_5WP(dpdt)$.
Figure 54. Plot of $[\text{B}] / [\text{B}_0]$ vs $t$ [B=$\text{(OC)}_2\text{WP(p-tol)}_2\text{CH}_2\text{CH}_2\text{PPh}_2$] at 55 °C in perdeuterated chloroform.
Figure 55. Plot of \([C]/[B]_0\) vs \(t\) \([C=(OC)_nW(dpdt)]\) at 55 °C in perdeuterated chloroform.
III. Experimental Section

1. Materials

Tetrahydrofuran (THF) was predried over calcium hydride and was freshly distilled from sodium and benzophenone as needed. All other solvents were used without further purification. Metal hexacarbonyls and phosphines were purchased from Strem Chemicals Inc. and Aldrich Chemical Co., respectively, and used without further purification.

2. Physical Measurements

$^{31}$P{$^1$H} NMR spectra of all synthesized compounds were recorded with a General Electric QE-300 spectrometer. Deuteriochloroform, CDCl$_3$, and phosphoric acid, H$_3$PO$_4$ (85%), were used as solvent and reference, respectively. The IR spectra were obtained with a Nicolet 20 DXB spectrometer with dichloromethane as a solvent. All melting points were taken with an Arthur H. Thomas Unimelt apparatus without correction.

Microanalyses were performed by the Microanalytical Laboratory, University of Illinois at Urbana. The variable temperature NMR experiments on (OC)$_5$WPPh$_2$CH$_2$CH$_2$PPh$_2$ and (OC)$_5$WPPh$_2$CH$_2$PPh$_2$ were performed at 30, 50, 65, and 80 °C in (CDCl$_3$)$_2$ and at -50, -30, -10, 10, 30, 50, 70 °C in C$_6$D$_6$, respectively, with a Nicolet NT-360 instrument by Spectral Data Services, Inc., Champaign, IL. The sample was in solution for 15-20 min at each temperature.
3. Isomerization Studies

An NMR tube containing 20-40 mg of one of the isomers (OC)_3M(dpdt) (M= Cr, Mo, W), dissolved in 0.25-0.50 ml of CDCl₃ or C₆D₅(CD₃), was sealed under N₂ and put into a 55 °C water bath. The ³¹P{¹H} NMR spectra were taken of the samples periodically. The amounts of the isomers in the NMR tubes were determined by the integration of the signals from the uncoordinated phosphorus. A delay time of 15 sec provide internal consistency. Appendix I contains the kinetic data obtained from these studies.

4. Synthesis

(1). Preparation of Tri(p-tolyl)phosphine, (p-MeC₆H₄)₃P

A solution of p-bromotoluene (100 ml; 0.813 mol) dissolved into 200 ml of anhydrous ethyl ether, together with a granule of iodine, was added in drops in the course of 3 hours to a stirred mixture of 25.00 g (1.030 mol) of magnesium turnings and 300 ml of anhydrous ethyl ether contained in a 2000 ml 3-neck flask equipped with a condenser, a N₂ inlet, and a dropping funnel. A piece of freshly cut Mg turning was needed to initiate the Grignard reaction. The exothermic reaction was controlled within 35-36 °C by a cold water bath to allow gentle reflux.

A solution of PCl₃ (20.0 ml; 0.229 mol) in anhydrous Et₂O (180 ml) was added in drops in the course of 6 h to the Grignard solution prepared as above and cooled to -6 °C by a
mixture of ice and NaCl. After the completion of addition, the solution was heated to reflux for 1 h.

The resulting solution was cooled with ice, hydrolyzed by drops with 50 ml of highly concentrated NH₄Cl solution, and filtered to remove the solid. The filtrate was dried over anhydrous MgSO₄ overnight, and then filtered. After some of the solvent was removed with a rotary evaporator, to the filtrate was added an equal volume of ethyl alcohol and the solution was cooled to -5 °C. Recrystallization gave 47.6 g (yield 57.7%) of white solid: mp 145-146 °C; ³¹P{¹H} NMR (CDCl₃) δₚ -7.5 ppm (see reference 24).

(2). Preparation of Di(p-tolyl)phosphine, (p-MeC₆H₄)₂PH

To a rapidly stirred solution of 10.14 g (33.31 mmol) of (p-tol)₃P dissolved in 300 ml of dried THF was added 0.943 g (0.136 mol) of finely cut Lithium under N₂. The solution became deep dark within a few minutes. After stirring for 33 h at ambient temperature, the solution was cooled to 0 °C and hydrolyzed with 20-30 ml of highly concentrated aqueous NH₄Cl which was purged with N₂ for 30 min in drops. The dark color of the solution changed to colorless.

Distillation of the resulted solution under vacuum gave 5.4 g (yield 74%) of colorless liquid: bp ~110 °C (0.1 mmHg); ³¹P NMR (CDCl₃) δₚ -42.0 ppm, ¹J_PH 218.4 Hz (see references 38 and 79).
(3). Preparation of 1,2-bis(di-p-tolylphosphino)ethane, (p-tol)$_2$PCH$_2$CH$_2$P(p-tol)$_2$ (dtpe)

To a rapidly stirred solution containing dried THF (30 ml) and P(p-tol)$_2$H (1.0 ml; 4.7 mmol) was added finely cut lithium (0.14 g; 20.2 mmol) under N$_2$. The solution was cooled to 0 °C. Then 0.2 ml (2.5 mmol) of ClCH$_2$CH$_2$Cl dissolved in 2 ml of dried THF was added to the solution as above. The resulting solution was hydrolyzed with 2.5 ml of H$_2$O and filtered to remove the inorganic salt. After removing the solvent from the filtrate, the residue was recrystallized from methanol at -5 °C to give 0.25 g (yield 11.8%) of white solid: mp 148-149 °C; $^{31}$P{H} NMR (CDCl$_3$) δ$_P$ -14.0 ppm. Anal. Calcd. for C$_{30}$H$_{32}$P$_2$: C, 79.28; H, 7.10. Found: C, 77.18; H, 6.93.

(4). Preparation of 1-((diphenylphosphino)-2-(di-p-tolylphosphino)ethane, Ph$_2$PCH$_2$CH$_2$P(p-tol)$_2$ (dpdt)

A mixture of Ph$_2$PCH=CH$_2$ (2.5 ml; 12.6 mmol), P(p-tol)$_2$H (2.5 ml; 12.5 mmol), and AIBN (0.33 g) was heated to 76 °C and stirred for 17 h under N$_2$. The solution solidified after a few hours. The solid was crystallized from 3:1 CH$_3$OH/CH$_2$Cl$_2$ to give 5.01 g (yield 94.4%) of white solid: mp 108-109 °C; $^{31}$P{H} NMR (CDCl$_3$) δ$_{PPh2}$ -12.1 ppm, δ$_{P(p-tol)2}$ -14.2 ppm, $^3$J$_{PP}$ 34.6 Hz; Anal. Calcd for C$_{28}$H$_{28}$P$_2$: C, 78.86; H, 6.62; Found: C, 79.46; H, 6.69 (see references 38 and 60).
(5). Preparation of Pentacarbonyldi(p-tolyl)phosphine-tungsten(0), (OC)$_5$WP(p-tol)$_2$H

To a solution containing 1.839 g (5.228 mmol) of W(CO)$_6$, 0.581 g (5.228 mmol) of Me$_3$N·2H$_2$O, and 50 ml of CH$_2$Cl$_2$ purged with N$_2$ for 20 min was added 1.12 g (5.23 mmol) of P(p-tol)$_2$H and stirred under N$_2$. The initial yellow color of the solution gradually turned to a deep brown color and then changed back to yellow after a few hours. After 72 h, the solvent of the solution was evaporated to dryness under vacuum. To the residue was added 80 ml of 1:3 CH$_2$Cl$_2$/CH$_3$OH and filtered to remove the unreacted W(CO)$_6$. Recrystallization from the filtrate at -5 °C gave 1.21 g of grey solid which showed three triplet signals in the $^{31}$P{$_1^H$} NMR spectrum. The solid was separated by Al$_2$O$_3$ column chromatography with gradient elution from 5:1 to 1:1 (v/v) n-hexane/CH$_2$Cl$_2$. The first yellow band was collected and evaporated to remove the solvent under vacuum. Recrystallization of the residue from methanol at -5 °C gave 0.367 g (yield 13.0%) of white solid which was (OC)$_5$WP(p-tol)$_2$H: mp 89-90 °C; IR[ν(C=O) (CH$_2$Cl$_2$, cm$^{-1}$)] 2074 (m), 1940(vs); $^{31}$P NMR (CDCl$_3$) δ$_p$ -15.5 ppm, $^1$J$_{WP}$ 227.5 Hz, $^1$J$_{PH}$ 332.3 Hz. Anal. Calcd for C$_{19}$H$_{15}$O$_5$PW: C, 42.41; H, 2.81. Found: C, 42.57; H, 2.88.

The second colorless band was collected and recrystallized as above to give 0.048 g (yield 2.5%) of white solid which was showed to be cis-(OC)$_5$W[P(p-tol)$_2$H]$_2$: 108
mp 138-139 °C; IR[ν(C=O)(CH2Cl2, cm⁻¹)] 2021 (m), 1906 (vs, br); 
³¹P NMR (CDCl₃) δₚ -4.4 ppm, ¹JₚH 223.8 Hz, ¹JₚW 336.6 Hz. Anal. Calcd for C₃₂H₃₀O₄P₂W: C, 53.06; H, 4.17. Found: C, 52.90; H, 4.17.

The third compound which showed a triplet in its ³¹P{¹H} NMR spectrum (δₚ = 4.6 ppm, ¹JₚH = 215.9 Hz) was lost.

(6). Preparation of (OC)₅WPPh₂H

The procedure was the same as that for preparing (OC)₅WP(p-tol)₂H except that 6.10 g (17.3 mmol) of W(CO)₆, 3.0 ml (17.3 mmol) of PPh₂H, and 2.01 g (18.1 mmol) of Me₃NO·2H₂O were used. Recrystallization gave 5.01 g (yield 55.3%) of white solid: mp 90-91 °C; IR[ν(C=O)(CH₂Cl₂, cm⁻¹)] 2075 (m), 1942 (vs); ³¹P NMR (CDCl₃) δₚ -13.2 ppm, ¹JₚH 345.3 Hz, ¹JₚW 229.3 Hz (see reference 65).

(7). Preparation of (OC)₅CrP(p-tol)₂H

In a quartz reaction vessel equipped with a 400w uv lamp was added Cr(CO)₆ (4.02 g; 18.3 mmol) and THF (250 ml). After irradiating for 6 h, 4.0 ml (18.6 mmol) of P(p-tol)₂H was injected into the solution. The solution changed from bright orange to light yellow within 10 min, and then to green. After stirring for 1.5 h, the solvent was removed from the solution. By dissolving the residue into 1:1 CH₂Cl₂/CH₃OH, the unreacted Cr(CO)₆ was removed by precipitation. Some other unwanted solids were removed by
further precipitation with CH$_2$OH in several steps. Recrystallization from the solution at -5 °C for several days gave 1.2 g (yield 31.7%) of light yellow crystal: mp 91-92 °C; IR[ν(C=O)(CH$_2$Cl$_2$, cm$^{-1}$)] 2066(m), 1984(w), 1943(vs); $^{31}$P NMR (CDCl$_3$) δ$_p$ 30.9 ppm, $^1$J$_{PH}$ 338.2 Hz. Anal. Calcd for C$_{19}$H$_{15}$O$_5$PCr: C, 56.17; H, 3.72. Found: C, 55.54; H, 3.60.

(8). Preparation of (OC)$_5$MoP(p-tol)$_2$H

A solution of Mo(CO)$_6$ (3.56 g; 0.036 mol) and 1,2-dimethoxyethane (60 ml) was heated to reflux for 1 h. To the resulting solution was added 2.9 ml (0.036 mol) of P(p-tol)$_2$H and the solution was allowed to reflux for 2.5 h. The solvent was removed by the rotary evaporator. The residue was dissolved into a mixture of CH$_3$OH/CH$_2$Cl$_2$ (1:1). Recrystallization from the solution at -5 °C gave 3.6 g (yield 58.3%) of white solid: mp 81-82 °C; IR[ν(C=O)(CH$_2$Cl$_2$, cm$^{-1}$)] 2075(m), 1948(vs); $^{31}$P NMR (CDCl$_3$) δ$_p$ 4.5 ppm, $^1$J$_{PH}$ 332.3 Hz. Anal. Calcd for C$_{19}$H$_{15}$O$_5$PMo: C, 50.69; H, 3.36. Found: C, 50.59; H, 3.25.

(9). Preparation of (OC)$_5$WPPh$_2$CH=CH$_2$

The procedure is the same as that for (OC)$_5$WP(p-tol)$_2$H except that 6.00 g (0.0170 mol) of W(CO)$_6$, 3.4 ml (0.017 mol) of PPh$_2$CH=CH$_2$, and 1.89 g (0.0170 mol) of Me$_3$NO·2H$_2$O were used. Recrystallization gave 3.99 g (yield 43.8%) of white solid: mp 59-60 °C; IR[ν(C=O)(CH$_2$Cl$_2$, cm$^{-1}$)] 2072(m),
1979 (w), 1939 (vs); $^{31}$P{$^1$H} NMR (CDCl$_3$) $\delta_p$ 11.9 ppm, $^1J_{WP}$ 239.3 Hz (see reference 65).

(10). Preparation of (OC)$_5$CrPPh$_2$CH=CH$_2$

**Method A:**

The procedure is the same as that for (OC)$_5$WP(p-tol)$_2$H except that PPh$_2$CH=CH$_2$ (0.95 ml; 4.8 mmol), Cr(CO)$_6$ (1.0 g; 4.8 mmol), and Me$_3$NO·2H$_2$O (0.53 g; 4.8 mmol) were used. Recrystallization at $-5^\circ$C for 7 days gave 1.16 g (yield 60.2%) of light yellow crystal (OC)$_5$CrPPh$_2$CH=CH$_2$; mp 54-55 $^\circ$C; $^{31}$P{$^1$H} NMR (CDCl$_3$) $\delta_p$ 47.9 ppm; IR[$\nu$(C=O)(CH$_2$Cl$_2$, cm$^{-1}$)] 2064 (m), 1983 (w), 1941 (vs) (see reference 66).

**Method B:**

The procedure is the same as that for (OC)$_5$CrP(p-tol)$_2$H except that a mixture of Cr(CO)$_6$ (5.07 g; 23.0 mmol) and THF (250 ml) was irradiated for 2 h followed by the injection of 4.6 ml (23.1 mmol) of PPh$_2$CH=CH$_2$. Recrystallization gave 1.67 g (yield 17.9%) of light yellow crystals; mp 54-55 $^\circ$C.

(11). Preparation of cis-(OC)$_4$Mo(PPh$_2$CH=CH$_2$)$_2$

The procedure is the same as that for (OC)$_5$WP(p-tol)$_2$H except that Mo(CO)$_6$ (7.14 g; 0.0269 mol), PPh$_2$CH=CH$_2$ (5.4 ml; 0.027 mol), and Me$_3$NO·2H$_2$O (2.99 g; 0.0269 mol) were used. Recrystallization gave 2.2 g (yield 25.9%) of white crystal; mp 93-94 $^\circ$C; $^{31}$P{$^1$H} NMR (CDCl$_3$) $\delta_p$ 29.3 ppm; IR[$\nu$(C=O)(CH$_2$Cl$_2$, cm$^{-1}$)] 2022 (m), 1907 (vs), 1883 (vs). Anal. Calcd for
Preparation of \((\text{OC})_5\text{WPPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2\)

A mixture of \((\text{OC})_5\text{WPPh}_2\text{CH}≡\text{CH}_2\) (3.01 g; 5.61 mmol), \(\text{PPh}_2\text{H}\) (0.98 ml; 5.6 mmol), and AIBN (0.11 g) was heated to 80 °C and stirred for 24 h under \(\text{N}_2\). Then the resulting solution was evaporated under vacuum at 80 °C for 1 h. The unreacted materials were removed by precipitation from 3:1 \(\text{CH}_3\text{OH}/\text{CH}_2\text{Cl}_2\) and the solution was recrystallized at -5 °C to give 0.85 g (yield 42.9%) of white solid: mp 112-115 °C; \(^{31}\text{P}\{^1\text{H}\}\text{NMR (CDCl}_3\)} \(\delta_{\text{P-W}} 13.4 \text{ ppm, } \delta_{\text{P}} -12.2 \text{ ppm, } \text{ }^{3}J_{\text{PP}} 37.5 \text{ Hz, } \text{ }^{1}J_{\text{WP}} 239.4 \text{ Hz; IR[\nu(C=O) (CH}_2\text{Cl}_2\text{, cm}^{-1})]} 2071(\text{m}), 1982(\text{w}), 1937(\text{vs})\) (see references 67 and 86).

Preparation of \((\text{OC})_5\text{WPPh}_2\text{CH}_2\text{CH}_2\text{P(p-tol)}_2\)

The procedure is the same as that for \((\text{OC})_5\text{WPPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2\) except that 3.0 g (5.6 mmol) of \((\text{OC})_5\text{WPPh}_2\text{CH}≡\text{CH}_2\), 1.1 g (5.1 mmol) of \((\text{p-tol)}_2\text{PH},\) and 0.13 g of AIBN were used. Recrystallization gave 1.71 g (yield 44.3%) of white solid: mp 143-144 °C; \(\text{IR[\nu(C=O) (CH}_2\text{Cl}_2\text{, cm}^{-1})]} 2071(\text{m}), 1981(\text{w,br)}, 1937(\text{vs}); \text{ }^{31}\text{P}\{^1\text{H}\}\text{NMR (CDCl}_3\)} \(\delta_{\text{PPh}} 13.6 \text{ ppm, } \delta_{\text{P(p-tol)}_2} -13.7 \text{ ppm, } \text{ }^{3}J_{\text{PP}} 37.6 \text{ Hz, } \text{ }^{1}J_{\text{WP}} 239.3 \text{ Hz}\) Anal. Calcd for \(\text{C}_{33}\text{H}_{28}\text{O}_5\text{P}_2\text{W}\): C, 52.82; H, 3.76. Found: C, 52.64; H, 3.75.

Preparation of \((\text{OC})_5\text{WP}(\text{p-tol})_2\text{CH}_2\text{CH}_2\text{PPh}_2\)

The procedure is the same as that for \((\text{OC})_5\text{WPPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2\)

C\text{32H}_{26}\text{O}_4\text{P}_2\text{Mo}: C, 60.77; H, 4.14. Found: C, 60.78; H, 4.02.
except that (OC)$_5$WP(p-tol)$_2$H (0.31 g; 5.69 x $10^{-4}$ mol), PPh$_2$CH=CH$_2$ (0.15 ml; 6.6 x $10^{-4}$), and AIBN (0.12 g) were used. Recrystallization gave 0.33 g (yield 77%) of yellow solid which was a mixture. Further purification by Al$_2$O$_3$ column chromatography with gradient elution of 3:1 to 1:1 n-hexane/CH$_2$Cl$_2$ gave 0.190 g (yield 44.5%) of white solid: mp 111-112 °C; IR[$\nu$(C=O) (CH$_2$Cl$_2$, cm$^{-1}$)] 2071 (m), 1981 (w), 1936 (vs); $^{31}$P{$^1$H} NMR (CDCl$_3$) $\delta_{p(p-tol)}$ 11.5 ppm, $\delta_{PPh_2}$ -12.0 ppm, $^3$J$_{PP}$ 38.0 Hz, $^1$J$_{WP}$ 238.4 Hz. Anal. Calcd for C$_{33}$H$_{28}$O$_5$P$_2$W: C, 52.82; H, 3.76. Found: C, 51.75; H, 3.82.

(15). Preparation of (OC)$_5$CrPPh$_2$CH$_2$CH$_2$P(p-tol)$_2$

The procedure is the same as that for (OC)$_5$WPPh$_2$CH$_2$CH$_2$PPh$_2$ except that (OC)$_5$CrPPh$_2$CH=CH$_2$ (1.10 g; 2.72 mmol), P(p-tol)$_2$H (0.55 ml; 2.57 mmol), and AIBN (0.12 g) were used. Recrystallization gave 0.41 g (yield 25.9%) of white crystal: mp 133-134 °C; $^{31}$P{$^1$H} NMR (CDCl$_3$) $\delta_{PPh_2}$ 50.5 ppm, $\delta_{p(p-tol)}$ -13.6 ppm, $^3$J$_{PP}$ 35.1 Hz; IR[$\nu$(C=O) (CH$_2$Cl$_2$, cm$^{-1}$)] 2063 (m), 1983 (w), 1939 (vs). Anal. Calcd for C$_{33}$H$_{28}$O$_5$P$_2$Cr: C, 64.08; H, 4.56. Found: C, 63.82; H, 4.22.

(16). Preparation of (OC)$_5$CrP(p-tol)$_2$CH$_2$CH$_2$PPh$_2$

The procedure is the same as that for (OC)$_5$WPPh$_2$CH$_2$CH$_2$PPh$_2$ except that (OC)$_5$CrP(p-tol)$_2$H (1.09 g; 2.68 mmol), PPh$_2$CH=CH$_2$ (0.55 ml; 2.60 mmol), and AIBN (0.15 g) were used. Recrystallization gave 0.98 g (yield 58.9%)
of light yellow crystal: mp 103-104 °C; $^{31}$P{$^1$H} NMR (CDCl$_3$)
$\delta_{P(p-tol)2}$ 48.4 ppm, $\delta_{PPh2}$ -11.8 ppm, $^3J_{PP}$ 35.0 Hz;
IR[\nu(C=O)(CH$_2$Cl$_2$, cm$^{-1}$)] 2062 (m), 1982 (w), 1937 (vs). Anal.
Calcd for C$_{33}$H$_{28}$O$_5$P$_2$Cr: C, 64.08; H, 4.56. Found: C, 63.71; H, 4.58.

(17). Preparation of (OC)$_5$MoPPh$_2$CH$_2$CH$_2$P(p-tol)$_2$

The procedure is the same as that for (OC)$_5$WPPh$_2$CH$_2$CH$_2$PPh$_2$
except that (OC)$_5$MoPPh$_2$CH=CH$_2$ (1.52 g; 3.38x10$^{-3}$ mol), P(p-tol)$_2$H (0.8 ml; 3.7 x 10$^{-3}$), and AIBN (0.21 g) were heated at
about 43 °C. Recrystallization gave 0.82 g (yield 36.6%) of
white solid: mp 130 °C; IR[\nu(C=O)(CH$_2$Cl$_2$, cm$^{-1}$)] 2073 (m),
1989 (w), 1945 (vs); $^{31}$P{$^1$H} NMR (CDCl$_3$) $\delta_{PPh2}$ 31.7 ppm,
$\delta_{P(p-tol)2}$ -13.6 ppm, $^3J_{PP}$ 37.0 Hz. Anal. Calcd for C$_{33}$H$_{28}$O$_5$P$_2$Mo:

(18). Preparation of (OC)$_5$MoP(p-tol)$_2$CH$_2$CH$_2$PPh$_2$

The procedure is the same as that for (OC)$_5$WPPh$_2$CH$_2$CH$_2$PPh$_2$
except that (OC)$_5$MoP(p-tol)$_2$H (2.00 g; 4.42 x 10$^{-3}$ mol),
PPh$_2$CH=CH$_2$ (0.94 ml; 4.42 x 10$^{-3}$), and AIBN (0.12 g) were
heated at about 40 °C. Recrystallization gave 2.18 g (yield
74.5%) of white solid: mp 90-91 °C; IR[\nu(C=O)(CH$_2$Cl$_2$, cm$^{-1}$)]
2072 (m), 1989 (w), 1943 (vs); $^{31}$P{$^1$H} NMR (CDCl$_3$) $\delta_{P(p-tol)2}$
29.7 ppm, $\delta_{PPh2}$ -11.8 ppm, $^3J_{PP}$ 35.9 Hz. Anal. Calcd for
C$_{33}$H$_{28}$O$_5$P$_2$Mo: C, 59.83; H, 4.26. Found: C, 59.68; H, 4.16.
Preparation of (OC)$_4$MoPPh$_2$CH$_2$CH$_2$P(p-tol)$_2$

The procedure is the same as that for (OC)$_5$WPPh$_2$CH$_2$CH$_2$PPh$_2$ except that (OC)$_5$WPPh$_2$CH=CH$_2$ (2.50 g; 5.59 x 10$^{-3}$ mol), P(p-tol)$_2$H (1.2 ml; 5.6 x 10$^{-3}$), and AIBN (0.16 g) were heated at about 80 °C. Recrystallization gave 1.5 g (yield 42.3%) of white solid which was chelated compound: mp 147-148 °C; IR[$\nu$(C=O) (CH$_2$Cl$_2$, cm$^{-1}$)] 2021 (m), 1909 (vs), 1882 (s); $^{31}$P{$^1$H} NMR (CDCl$_3$) $\delta_{PPh2}$ 55.8 ppm, $\delta_{P(p-tol)2}$ 53.6 ppm, $J_{PP}$ 5.7 Hz. Anal. Calcd for C$_{32}$H$_{28}$O$_4$P$_2$Mo: C, 60.58; H, 4.45. Found: C, 60.74; H, 4.33.

Preparation of cis-(OC)$_4$W(PPh$_2$Et)(PPh$_2$H)

A solution containing dried THF (50 ml), (OC)$_5$WPPh$_2$H (1.22 g; 2.33 mmol), PPh$_2$Et (0.50 ml; 2.5 mmol), and KOBu (0.21 g; 1.9 mmol) was refluxed for 2 h. Then 1 ml of H$_2$O was added to the solution to quench the reaction. The solution became red. The resulting solution was extracted with 1:1 H$_2$O/CH$_2$Cl$_2$. After removing the solvent from the organic layer, the residue was recrystallized from 4:1 CH$_3$OH/CH$_2$Cl$_2$ to give 0.62 g (yield 38.2%) of white solid: mp 130-130.5 °C; $^{31}$P{$^1$H} NMR (CDCl$_3$) $\delta_{PPh2Et}$ 2.4 ppm ($^1J_{WP}$ 230.1 Hz), $\delta_{PPh2H}$ 14.8 ppm ($^1J_{WP}$ 225.7 Hz), $^2J_{PP}$ 16.7 Hz; IR[$\nu$(C=O) (CH$_2$Cl$_2$, cm$^{-1}$)] 2019(m), 1901(vs), 1877(m) (see reference 83).

A small triplet also appeared on the spectra at -2.1 ppm ($^1J_{WP}$ 224.0 Hz) which was believed to be cis-(OC)$_4$W(PPh$_2$H)$_2$. 
Reference


28. Golovin, M.N.; Rahman, Md.M.; Belmonte, J.E.; Giering,


1976, No.150, 335.


60. Sadanani, N.D.; Walia, A.; Kapoor, P.N.; Kapoor, R.N.


62. Sadanani, N.N.; Watia, A.; Kapoor, P.N.; Kapoor, R.N.

63. Kapoor, P.N.; Pathak, D.D.; Gaur, G.; Kutty, M.


65. Keiter, R.L.; Sun, Y.Y.; Brodack, J.W.; Cary, L.W.


    1993, 460, 197.


71. Meerwein, H.; Hinz, G.; Hofmann, P.; Kroning, E.; Pfeil,


Chem. 1972, 43, 357.

74. Magee, T.A.; Mathews, C.N.; Wang, T.S.; Wotiz, J.H.


Appendix I

(1) \((\text{OC})_5\text{CrPPh}_2\text{CH}_2\text{CH}_2\text{P(p-tol)}_2\rightleftharpoons (\text{OC})_5\text{CrP(p-tol)}_2\text{CH}_2\text{CH}_2\text{PPh}_2\)
\[ \begin{align*}
\text{A} & \rightarrow \text{B} \\
\downarrow & \downarrow \\
(\text{OC})_4\text{Cr(dpdt)} & \text{C}
\end{align*} \]

at 55 °C in perdeuterated toluene

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>([A]/[A]_0)</th>
<th>([B]/[A]_0)</th>
<th>([C]/[A]_0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>52.0</td>
<td>0.9841</td>
<td>0.007996</td>
<td>0.007861</td>
</tr>
<tr>
<td>218.8</td>
<td>0.9621</td>
<td>0.01652</td>
<td>0.01635</td>
</tr>
<tr>
<td>386.9</td>
<td>0.9524</td>
<td>0.02777</td>
<td>0.01987</td>
</tr>
<tr>
<td>554.4</td>
<td>0.9434</td>
<td>0.02904</td>
<td>0.02753</td>
</tr>
<tr>
<td>723.0</td>
<td>0.9194</td>
<td>0.04388</td>
<td>0.03673</td>
</tr>
<tr>
<td>910.1</td>
<td>0.9042</td>
<td>0.05268</td>
<td>0.04318</td>
</tr>
<tr>
<td>1082.4</td>
<td>0.8955</td>
<td>0.05283</td>
<td>0.05166</td>
</tr>
<tr>
<td>1221.8</td>
<td>0.8789</td>
<td>0.06532</td>
<td>0.05581</td>
</tr>
<tr>
<td>1391.0</td>
<td>0.8638</td>
<td>0.07046</td>
<td>0.06576</td>
</tr>
<tr>
<td>1581.6</td>
<td>0.8528</td>
<td>0.07902</td>
<td>0.06817</td>
</tr>
<tr>
<td>2036.3</td>
<td>0.8140</td>
<td>0.09531</td>
<td>0.09071</td>
</tr>
</tbody>
</table>

(2) \((\text{OC})_5\text{CrP(p-tol)}_2\text{CH}_2\text{CH}_2\text{PPh}_2\rightleftharpoons (\text{OC})_5\text{CrPPh}_2\text{CH}_2\text{CH}_2\text{P(p-tol)}_2\)
\[ \begin{align*}
\text{B} & \rightarrow \text{A} \\
\downarrow & \downarrow \\
(\text{OC})_4\text{Cr(dpdt)} & \text{C}
\end{align*} \]

at 55 °C in perdeuterated toluene

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>([B]/[B]_0)</th>
<th>([A]/[B]_0)</th>
<th>([C]/[B]_0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>52.3</td>
<td>0.9786</td>
<td>0.01394</td>
<td>0.007478</td>
</tr>
<tr>
<td>220.2</td>
<td>0.9673</td>
<td>0.01936</td>
<td>0.01330</td>
</tr>
<tr>
<td>387.3</td>
<td>0.9525</td>
<td>0.02538</td>
<td>0.02209</td>
</tr>
<tr>
<td>554.7</td>
<td>0.9468</td>
<td>0.02603</td>
<td>0.02717</td>
</tr>
<tr>
<td>723.3</td>
<td>0.9307</td>
<td>0.03130</td>
<td>0.03799</td>
</tr>
<tr>
<td>910.4</td>
<td>0.9114</td>
<td>0.04053</td>
<td>0.04806</td>
</tr>
<tr>
<td>1081.7</td>
<td>0.9063</td>
<td>0.04108</td>
<td>0.05265</td>
</tr>
<tr>
<td>1222.2</td>
<td>0.8936</td>
<td>0.04553</td>
<td>0.06092</td>
</tr>
<tr>
<td>1391.4</td>
<td>0.8861</td>
<td>0.04702</td>
<td>0.06684</td>
</tr>
<tr>
<td>1581.8</td>
<td>0.8768</td>
<td>0.05010</td>
<td>0.07310</td>
</tr>
<tr>
<td>2037.7</td>
<td>0.8430</td>
<td>0.06152</td>
<td>0.09551</td>
</tr>
</tbody>
</table>
(3) \((\text{OC})_5\text{MoPPh}_2\text{CH}_2\text{CH}_2\text{P}(\text{p-tol})_2\) \(\rightleftharpoons\) \((\text{OC})_5\text{MoP}(\text{p-tol})_2\text{CH}_2\text{CH}_2\text{PPh}_2\)

\(
\text{at } 55 \degree C\text{ in perdeuterated toluene } (K=1.96)
\)

<table>
<thead>
<tr>
<th>Time (sec)</th>
<th>([A]/[A]_0)</th>
<th>(\ln([A]/[A]<em>0 - [A]</em>{eq}/[A]_0))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1813</td>
<td>0.9815</td>
<td>-0.4406</td>
</tr>
<tr>
<td>3626</td>
<td>0.9742</td>
<td>-0.4520</td>
</tr>
<tr>
<td>5439</td>
<td>0.9563</td>
<td>-0.4805</td>
</tr>
<tr>
<td>7252</td>
<td>0.9424</td>
<td>-0.5033</td>
</tr>
<tr>
<td>9065</td>
<td>0.9327</td>
<td>-0.5194</td>
</tr>
<tr>
<td>10878</td>
<td>0.9198</td>
<td>-0.5414</td>
</tr>
<tr>
<td>12691</td>
<td>0.9047</td>
<td>-0.5676</td>
</tr>
<tr>
<td>14504</td>
<td>0.8940</td>
<td>-0.5867</td>
</tr>
<tr>
<td>16317</td>
<td>0.8826</td>
<td>-0.6074</td>
</tr>
<tr>
<td>18130</td>
<td>0.8769</td>
<td>-0.6179</td>
</tr>
</tbody>
</table>

(4) \((\text{OC})_5\text{MoPPH}_2\text{CH}_2\text{CH}_2\text{P}(\text{p-tol})_2\) \(\rightleftharpoons\) \((\text{OC})_5\text{MoP}(\text{p-tol})_2\text{CH}_2\text{CH}_2\text{PPh}_2\)

\((\text{OC})_4\text{Mo(dpdt)}\)

\(
\text{at } 55 \degree C\text{ in perdeuterated toluene}
\)

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>([C]/[A]_0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>52.8</td>
<td>0.0948</td>
</tr>
<tr>
<td>95.0</td>
<td>0.1637</td>
</tr>
<tr>
<td>218.0</td>
<td>0.2967</td>
</tr>
<tr>
<td>388.0</td>
<td>0.4594</td>
</tr>
</tbody>
</table>

(5) \((\text{OC})_5\text{MoP}(\text{p-tol})_2\text{CH}_2\text{CH}_2\text{PPh}_2\) \(\rightleftharpoons\) \((\text{OC})_5\text{MoPPH}_2\text{CH}_2\text{CH}_2\text{P}(\text{p-tol})_2\)

\((\text{OC})_4\text{Mo(dpdt)}\)

\(
\text{at } 55 \degree C\text{ in perdeuterated toluene}
\)

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>([C]/[B]_0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>53.1</td>
<td>0.0884</td>
</tr>
<tr>
<td>95.1</td>
<td>0.1585</td>
</tr>
<tr>
<td>218.4</td>
<td>0.2944</td>
</tr>
<tr>
<td>388.3</td>
<td>0.4612</td>
</tr>
</tbody>
</table>
(6) \((\text{OC})_5\text{WPPh}_2\text{CH}_2\text{CH}_2\text{P(p-tol)}_2 \rightleftharpoons (\text{OC})_5\text{WP}(p\text{-tol})_2\text{CH}_2\text{CH}_2\text{PPh}_2\)

A

at 55 °C in perdeuterated toluene

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>$[A]/[A]_0$</th>
<th>$[B]/[A]_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>219.4</td>
<td>0.9691</td>
<td>0.0309</td>
</tr>
<tr>
<td>387.9</td>
<td>0.9580</td>
<td>0.0420</td>
</tr>
<tr>
<td>555.4</td>
<td>0.9447</td>
<td>0.0553</td>
</tr>
<tr>
<td>724.0</td>
<td>0.9289</td>
<td>0.0711</td>
</tr>
<tr>
<td>911.0</td>
<td>0.9128</td>
<td>0.0872</td>
</tr>
<tr>
<td>1082.4</td>
<td>0.8929</td>
<td>0.1071</td>
</tr>
<tr>
<td>1223.0</td>
<td>0.8867</td>
<td>0.1133</td>
</tr>
<tr>
<td>1392.2</td>
<td>0.8687</td>
<td>0.1313</td>
</tr>
<tr>
<td>1582.4</td>
<td>0.8566</td>
<td>0.1434</td>
</tr>
<tr>
<td>2037.3</td>
<td>0.8178</td>
<td>0.1822</td>
</tr>
<tr>
<td>2396.1</td>
<td>0.7925</td>
<td>0.2075</td>
</tr>
</tbody>
</table>

(7) \((\text{OC})_5\text{WP}(p\text{-tol})_2\text{CH}_2\text{CH}_2\text{PPh}_2 \rightleftharpoons (\text{OC})_5\text{WPPh}_2\text{CH}_2\text{CH}_2\text{P}(p\text{-tol})_2\)

B

A

at 55 °C in perdeuterated toluene

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>$[B]/[B]_0$</th>
<th>$[A]/[B]_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>219.8</td>
<td>0.9480</td>
<td>0.0520</td>
</tr>
<tr>
<td>388.3</td>
<td>0.9438</td>
<td>0.0562</td>
</tr>
<tr>
<td>555.7</td>
<td>0.9318</td>
<td>0.0682</td>
</tr>
<tr>
<td>724.3</td>
<td>0.9222</td>
<td>0.0778</td>
</tr>
<tr>
<td>911.4</td>
<td>0.9227</td>
<td>0.0773</td>
</tr>
<tr>
<td>1082.7</td>
<td>0.9136</td>
<td>0.0864</td>
</tr>
<tr>
<td>1223.5</td>
<td>0.9141</td>
<td>0.0859</td>
</tr>
<tr>
<td>1392.5</td>
<td>0.9002</td>
<td>0.0998</td>
</tr>
<tr>
<td>1583.0</td>
<td>0.9021</td>
<td>0.0979</td>
</tr>
<tr>
<td>2037.8</td>
<td>0.8846</td>
<td>0.1154</td>
</tr>
<tr>
<td>2396.4</td>
<td>0.8686</td>
<td>0.1314</td>
</tr>
</tbody>
</table>
(8) \((\text{OC})_5\text{WPPh}_2\text{CH}_2\text{CH}_2\text{P}(\text{p-tol})_2 \leftrightarrow (\text{OC})_5\text{WP}(\text{p-tol})_2\text{CH}_2\text{CH}_2\text{PPh}_2\)

\[ \text{A} \quad \leftrightarrow \quad \text{B} \]

\((\text{OC})_5\text{W(dpdt)}\)

at 55 °C in perdeuterated chloroform

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>([A]/[A]_0)</th>
<th>([B]/[A]_0)</th>
<th>([C]/[A]_0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>166</td>
<td>0.9679</td>
<td>0.0214</td>
<td>0.0107</td>
</tr>
<tr>
<td>331</td>
<td>0.9471</td>
<td>0.0355</td>
<td>0.0174</td>
</tr>
<tr>
<td>500</td>
<td>0.9361</td>
<td>0.0443</td>
<td>0.0196</td>
</tr>
<tr>
<td>669</td>
<td>0.9138</td>
<td>0.0636</td>
<td>0.0226</td>
</tr>
<tr>
<td>842</td>
<td>0.9014</td>
<td>0.0697</td>
<td>0.0289</td>
</tr>
<tr>
<td>1031</td>
<td>0.8815</td>
<td>0.0874</td>
<td>0.0311</td>
</tr>
<tr>
<td>1657</td>
<td>0.8332</td>
<td>0.1324</td>
<td>0.0344</td>
</tr>
<tr>
<td>1918</td>
<td>0.7902</td>
<td>0.1737</td>
<td>0.0361</td>
</tr>
<tr>
<td>2180</td>
<td>0.7974</td>
<td>0.1636</td>
<td>0.0390</td>
</tr>
<tr>
<td>2680</td>
<td>0.7630</td>
<td>0.2031</td>
<td>0.0339</td>
</tr>
</tbody>
</table>

(9) \((\text{OC})_5\text{WP}(\text{p-tol})_2\text{CH}_2\text{CH}_2\text{PPh}_2 \leftrightarrow (\text{OC})_5\text{WPPh}_2\text{CH}_2\text{CH}_2\text{P}(\text{p-tol})_2\)

\[ \text{B} \quad \leftrightarrow \quad \text{A} \]

\((\text{OC})_5\text{W(dpdt)}\)

at 55 °C in perdeuterated chloroform

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>([B]/[B]_0)</th>
<th>([A]/[B]_0)</th>
<th>([C]/[B]_0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>164</td>
<td>0.9876</td>
<td>0.0265</td>
<td>0.0208</td>
</tr>
<tr>
<td>332</td>
<td>0.9527</td>
<td>0.0308</td>
<td>0.0301</td>
</tr>
<tr>
<td>502</td>
<td>0.9391</td>
<td>0.0397</td>
<td>0.0286</td>
</tr>
<tr>
<td>670</td>
<td>0.9317</td>
<td>0.0290</td>
<td>0.0367</td>
</tr>
<tr>
<td>843</td>
<td>0.9343</td>
<td>0.0473</td>
<td>0.0391</td>
</tr>
<tr>
<td>1032</td>
<td>0.9136</td>
<td>0.0896</td>
<td>0.0431</td>
</tr>
<tr>
<td>1675</td>
<td>0.8673</td>
<td>0.0588</td>
<td>0.0510</td>
</tr>
<tr>
<td>1915</td>
<td>0.8902</td>
<td>0.0556</td>
<td>0.0645</td>
</tr>
<tr>
<td>2179</td>
<td>0.9444</td>
<td>0.0556</td>
<td>0.0645</td>
</tr>
<tr>
<td>2680</td>
<td>0.9355</td>
<td>0.0556</td>
<td>0.0645</td>
</tr>
</tbody>
</table>