KINETICS AND MECHANISM OF REACTIONS OF DISUBSTITUTED

OCTAHEDRAL METAL CARBONYLS WITH PHOSPHORUS

DONOR LIGANDS AND GERMANIUM TETRAIODIDE

DISSERTATION

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By

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<u>Donor</u> <u>Ligands</u> <u>and</u> <u>Germanium</u> <u>Tetraiodide</u>. Doctor of Philosophy
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The kinetics and mechanism of the reactions of $(tmpa)W$-
$(CO)_4$ and $(tmen)W(CO)_4$ (tmpa = N,N,N',N'-tetramethyl-1,3-di-
aminopropane and tmen = N,N,N',N'-tetramethylethylenediamine)
with four phosphorus donor ligands (triisopropyl phosphite,
triphenyl phosphite, triphenylphosphine and "constrained phos-
phite", 4-methyl-2,6,7-trioxa-1-phosphabicylo[2.2.2]octane)
in xylene have been investigated in detail. These reactions
were found to take place by the ring-opening of the bidentate
ligand in a reversible step which leads to the formation of a
five-coordinate intermediate of the type $[(h^1-tmpa)W(CO)_4]$ or
$[(h^1-tmen)W(CO)_4]$. The intermediate then reacts with one
molecule of phosphorus ligand, L, to form a six-coordinate in-
termediate, which can either expel the bidentate ligand and
react with another molecule of L leading to the formation of
a new disubstituted tungsten tetracarbonyl or go through a
ring-reclosure step to form a seven-coordinate activated com-
plex or intermediate of the type $[(h^2-tmpa)W(CO)_4(L)]$ or $[(h^2-
tmen)W(CO)_4(L)]$ which then regenerates the substrate through the
expulstion of the L molecule. This mechanism is consistent with
the observed rate behavior in these systems. For the reaction

of (tmpa)W(CO)$_4$ with the "constrained phosphite", an intermediate of the type [(h^1-tmpa)W(CO)$_4$P(OCH$_2$)$_3$CCH$_3$] was isolated and identified.

The "competition ratios", k$_2$/k$_{-1}$, which represent the ratios of the second-order rate constant for the reactions of [(h^1-tmpa)W(CO)$_4$] or [(h^1-tmen)W(CO)$_4$] with a phosphorus ligand, k$_2$, to the ring-reclosure rate constant, k$_{-1}$, indicate that the nucleophilicity of the phosphorus ligand is mainly dictated by the steric effect. This trend, however, is not observed for the reactions of these ligands with [(h^1-tmpa)W(CO)$_4$].

The "discrimination ratios", k$_{2L}$/k$_{2P(C_6H_5)_3}$, indicate that intermediates of the type [(h^1-tmpa)W(CO)$_4$] and [(h^1-tmen)W(CO)$_4$] do not discriminate significantly among various phosphorus donor ligands.

The kinetic studies together with the product analysis for the reaction of (tmpa)W(CO)$_4$ with triphenylphosphine provide evidence for the fluxional character of the square-pyramidal five-coordinate intermediate, [(OC)$_4$WP(C$_6$H$_5$)$_3$]. That is, this intermediate with the triphenylphosphine occupying an equatorial position of the basal plane is in equilibrium with its isomer in which the triphenylphosphine group is occupying the axial position, with the equilibrium shifted heavily toward the thermodynamically more stable intermediate (with triphenylphosphine in the equatorial position).

It should also be mentioned that these studies lead to the synthesis of (2,5-norbornadiene)W(CO)$_4$ by the reaction of (tmpa)W(CO)$_4$ with this ligand at 50°C. The former complex is known to be an important source for the preparation of a variety of complexes.

Kinetic studies involving the oxidative elimination reaction of (o-phenanthroline)Mo(CO)$_4$ with germanium tetraiodide at 25°C indicated that this reaction which is very fast (stopped-flow kinetics were employed) takes place through the formation of a 1:1 adduct of the type (o-phen)-Mo(CO)$_4$·GeI$_4$, followed by the expulsion of a carbon monoxide molecule in some fast step(s) forming (o-phen)Mo(CO)$_3$(I)-(GeI$_3$) as the reaction product.

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CHAPTER I

INTRODUCTION

The field of metal carbonyl chemistry is over 100 years old. The first compound of this series, $(PtCl_2CO)_2$, was reported by Schützenberger [1] in 1868. Twenty-two years later, Mond et al. [2] discovered $Ni(CO)_4$, which was the corrosion product of nickel valves in reaction vessels for the Solvay process in producing sodium bicarbonate. A year later, in 1891, Berthelot (working alone) [3], and co-workers, Mond and Quincke [4], simultaneously synthesized $Fe(CO)_5$. In 1904, Dewar and Jones reported reactions of $Ni(CO)_4$ with inorganic [5] and organic [6] compounds. The following year, they [7] synthesized $Fe_3(CO)_{12}$.

These early independent studies triggered continuing interest which mushroomed into a serious work effort begun about 1930 when Hieber [8] and his group launched their extensive studies in the field of metal carbonyl chemistry.

Hieber's efforts sparked phenomenal interest as evidenced by the continuous publication of papers in this field, now amounting to tens of thousands of articles. From the outset, review articles covering these studies began appearing in the respected journals. These reviews have continued into the hundreds at the present time. The most important

periodical containing review articles of metal carbonyls on an annual basis is the Journal of Organometallic Chemistry.

The catalytic properties of metal carbonyl compounds make them an excellent tool for the synthesis of many compounds. The "hydroformylation reaction" is a good example of a catalytic application of the metal carbonyls. This is simply the conversion of an olefin into an aldehyde by the reaction with "synthesis gas", a mixture of carbon monoxide and hydrogen (9), in the presence of $Co_2(CO)_8$.

$$RCH=CH_2 + CO + H_2 \xrightarrow{\quad Co_2(CO)_8 \quad} RCH(CHO)CH_3 + RCH_2CH_2CHO \qquad (I-1)$$
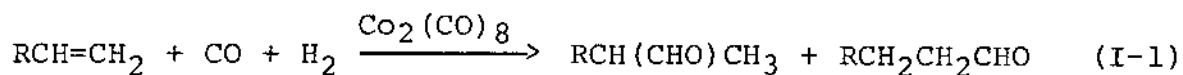
Even though metal carbonyls are generally toxic, bis(aziridino)morpholinophosphine molybdenum pentacarbonyl, $(C_2H_4N)_2P(N\,C_4H_8O)Mo(CO)_5$, is a notable exception. Its nontoxic nature permits its use as an anti-leukemia agent. Doses of 400 mg/kg of this compound have been known to lengthen the mean survival time by 9-48% in laboratory experiments carried out on mice (10).

Among their varied uses, metal carbonyl compounds are important to the fuel industry. As gasoline additives, iron pentacarbonyl and methylcyclopentadienyl manganese tricarbonyl possess anti-knock properties which are equal to, or better than, that of tetraethyl lead (11-13). Moreover, these two compounds are much less poisonous than tetraethyl lead, and their combustion products are relatively non-toxic.

The majority of metal carbonyl compounds are diamagnetic, electronically neutral, volatile and soluble in a wide range or organic solvents (14). Among other advantages, the last two properties facilitate the purification of these compounds.

Bonding

The overwhelming majority of the metal carbonyl compounds obey Sidgwick's rule (15,16). This rule states that the number of electrons from the metal added to the number of bonding electrons from the ligands will equal the number of electrons in the next rare gas in the periodic table. It has been found that the desire to obtain a closed shell of electrons for metals is a more important factor in determining the coordination number of the metal than is the formation of a particular geometrical configuration (17).

Since both carbon and oxygen atoms in carbon monoxide possess unshared pairs of electrons, one might think that bond formation could be possible through either carbon or oxygen. The higher electronegativity of oxygen, however, inhibits the formation of a metal-oxygen bond to the central atom in these complexes (18). Indeed, in all cases for which experimental evidence exists, M-CO bonds, rather than, M-OC bonds (M is the central atom) have been found (19).

In recent years, a number of complexes have been prepared from substituted metal carbonyls and electron-deficient metal-containing species (Lewis acids), e.g., trialkylaluminums,

which have been formulated as containing bonds between the carbonyl oxygen and the electropositive metal (20-25).

Surprisingly, in spite of very high heats of atomization ($\sim$400 KJ mol^{-1}) and low positive, zero or low negative oxidation state, transition metals can make very stable bonds with carbon monoxide, although it is a very poor base. This can be explained on the basis of the multiple nature of the M-CO bond, for which there is much evidence.

Although the bonding of metal carbonyl compounds could be explained in terms of a resonance hybrid of 1a and 1b (See Fig. 1), a molecular-orbital formulation approach is more detailed and probably more accurate. This approach envisions a dative overlap of the filled carbon sigma orbital forming a sigma bond (See Fig. 2a), and a dative overlap of d_π metal orbital with an anti-bonding p_π orbital of the carbon monoxide, forming a π bond (See Fig. 2b). This type of bonding mechanism is called "synergic"; that is, the two types of bonding, carbon to metal sigma bonding, and metal to carbon pi bonding, are mutually reinforcing. Thus, the drift of metallic electrons into carbon monoxide orbitals will make CO as a whole negative and, consequently, increase its basicity via the sigma orbital of carbon. At the same time, the drift of electrons to the metal in the sigma bond makes the CO positive, thus increasing the π accepting ability of the carbon. Therefore, up to a point, the effect of sigma bond formation strengthens the pi bonding and vice versa.

$:\overset{-}{M}-C\equiv\overset{+}{O}: \longleftrightarrow M=C=\overset{..}{\overset{..}{O}}:$

(a)   (b)

Fig. 1--Resonance hybrid representation of the transition metal-carbon monoxide bond.

(a)

(b)
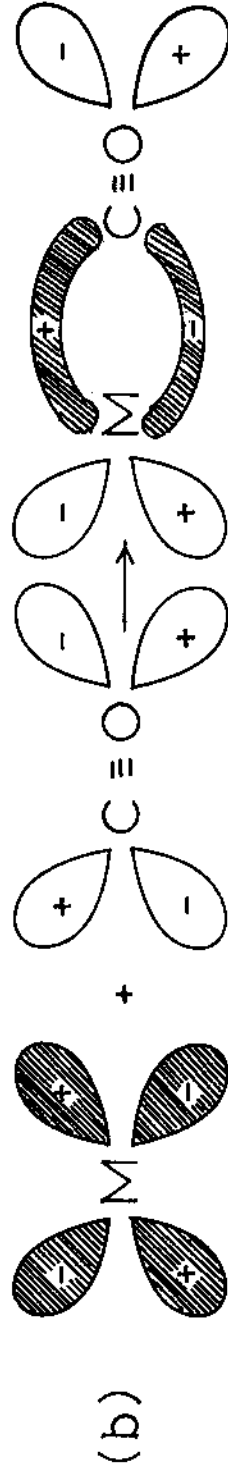
Fig. 2--Molecular orbital representation of the transition metal-carbon monoxide bond.

The most important evidence for the existence of the multiple nature of M-CO bonds is bond length determination. The electron diffraction studies carried out by Brockway and his group (26-29) on various metal carbonyl compounds indicated that metal-carbon bond lengths were shorter than expected for a pure sigma bond.

Infrared spectroscopy, especially that involving the carbonyl stretching modes of these complexes, is very useful for investigation of these compounds. Since these vibrational modes are very distinct, and appear in a range of spectrum, 2200-1800 cm^{-1}, clear of other vibrational modes, they could be used for the following: monitoring the reactions of the metal carbonyl complexes with a variety of other compounds, estimating the purity of derivatives, identifying the fractions obtained from separation procedures, making inferences concerning relative bonding properties of the ligand, and ascertaining the degree of substitution and stereochemistry of the derivatives.

The existence and extent of M-C multiple bonding can be investigated by studying the carbonyl stretching modes rather than M-C stretching or MCO bening modes, since the last two are in the same range with other bands. This makes the assignment of the bands very difficult. The M-C bond order can be inferred from carbonyl stretching modes, on the basis of the assumption that the valence of carbon is constant, so that an increase in M-C bond order must cause an

equal decrease in the C-O bond order. This, in turn, will cause a drop in the carbonyl stretching frequency. For example, the free carbon monoxide has a vibrational stretch at 2143 cm^{-1}, while, the terminal CO groups in neutral carbonyls are found to have carbonyl stretching modes between 2125 and 1850 cm^{-1} (19). It is appropriate to mention, however, that the above point has been oversimplified (30).

Employing group theoretical procedures, the number of infrared active carbonyl stretching modes, based on the "local symmetry" of the carbonyl groups, can be predicted. The symmetry of the carbonyl groups, when the non-carbonyl ligands are considered as point charges, is referred to as the "local symmetry". In cases where the number of predicted and observed carbonyl stretching bands do not agree, one can conclude that the complex, if completely pure, is of lower symmetry (except for the solid state).

Kinetics and Mechanism

In recent years, the emphasis has been shifted from spectroscopic investigation to studies of the kinetics and mechanism of the reactions of metal carbonyl compounds. This enables one to gain a better insight into the nature of bonding in metal carbonyls, as well as the relationship between reactivity and electronic and stereochemical properties of these series of compounds and the species with which metal carbonyls react. A very comprehensive review article

covering the kinetic and mechanistic investigations of metal
carbonyls, up to 1967, has been published by Angelici (31).
Basolo and Pearson (32) reviewed the kinetic studies of car-
bon monoxide exchange with metal carbonyl complexes. A
recent review article by Dobson (33) covers the kinetics and
mechanism of octahedral metal carbonyls in latest years. In
addition, the Journal of Organometallic Chemistry publishes
review articles which cover specific areas of metal carbonyl
chemistry on an annual basis.

The most important group of reactions involving metal
carbonyl compounds are the substitution reactions, where a
ligand replaces either a carbonyl group or another ligand
(if any) in the molecule.

$$M(CO)_n(L)_x + Y \longrightarrow (Y)M(CO)_{n-1}(L)_x + CO \qquad (I-2)$$

$$M(CO)_n(L)_x + Y \longrightarrow (Y)M(CO)_n(L)_{x-1} + L \qquad (I-3)$$
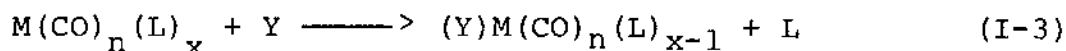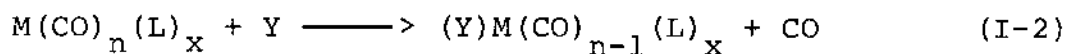
In recent years, the reactions of octahedral carbonyl
complexes have been of special interest to many research
groups for the following reasons: (a) the high degree of
symmetry in these compounds facilitates interpretation of
their infrared spectra; (b) the octahedral metal carbonyl
complexes are typically "inert", thus, their substitution
reactions are slow enough to be measured at ambient and
higher temperatures with conventional techniques; (c) the
substitution reactions can be studied in nonpolar organic

solvents, thus eliminating the solvation effect on the reactivity and avoiding the theoretical and experimental problems which arise in the study of ionic species; (d) the studies done on these complexes may be used as a model for a larger class of compounds; (e) the presence of very intense characteristic carbonyl stretching bands in substrates and products and the color change associated with the progress of such reactions provide the basic tools in monitoring the kinetics and product identification of these systems. Commonly known carbonyl complexes of Cr(O), W(O) and Mo(O) are six-coordinate octahedral complexes (28,23).

In general, when a substrate, S, reacts with a ligand, L, the rate law falls in one of the following categories:

(I) The rate of disappearance of substrate is independent of the ligand concentration, and is first-order with respect to the substrate. This is observed in a dissociative type mechanism (See Fig. 3), where the rate law is expressed as:

$$ - \frac{d[S]}{dt} = k_1[S] \qquad (I-4)$$

A positive entropy of activation is supportive evidence for such a reaction mechanism. The larger positive entropy of activation, the more bond breaking in the transition state, and thus the activated complex would more closely resemble the intermediate, I, (See Fig. 3). In such a case, the enthalpy of activation approximates the M-C or M-L bond dissociation energy, depending on whether the M-C or M-L bonds breaks.
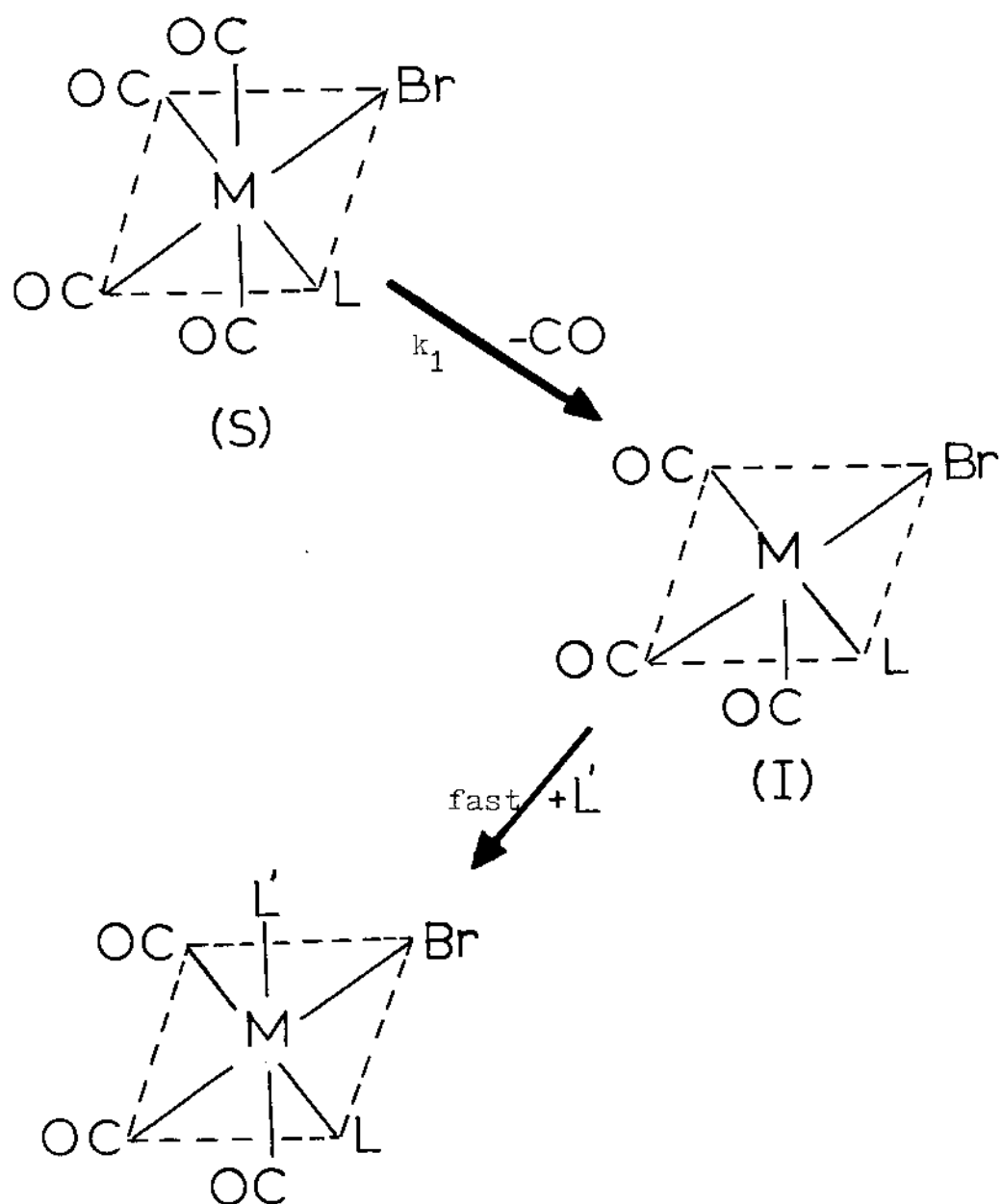
Fig. 3--Unimolecular substitution mechanism involving rate-determining dissociation of carbon monoxide.

Moreover, the rate of disappearance of the substrate for such a reaction mechanism should be independent of the identity of the ligand.

Even though examples of pure dissociative mechanisms are hard to find, one can cite the mechanism of the reactions of $Mn(CO)_4LBr$ with L', studied by Angelici and Basolo (35). They carried out kinetic measurements of the reactions of $Mn(CO)_4LBr$ with a variety of phosphorus and arsenic ligands. The observed rate law for these reactions is consistent with a dissociative type mechanism. Similar results were obtained by Zingales et al. (36), for the reactions of $Re(CO)_4XL$ with various ligands. Atwood and Brown (37) recently studied ^{13}CO exchange and substitution reactions of cis-$M(CO)_4LBr$ (M=Mn, Re) compounds, and observed an identical rate behavior.

(II) The rate of disappearance of the substrate is first-order with respect to both ligand and substrate concentrations, and is second-order overall. This is mainly observed in an associative mechanism, where the rate is expressed as:

$$- \frac{d[S]}{dt} = k_2 [S] [L] \qquad (I-5)$$

A negative entropy of activation provides strong evidence for such a mechanism. It is appropriate to mention, however, that no evidence of the inversion of configuration at an optically active center has been obtained in support of this type of reaction mechanism (31). A second-order rate law is observed

when the rate-determining step involves the formation of a
seven-coordinate intermediate, or activated complex through
the nucleophilic attack at the central metal atom (Fig. 4),
or at the carbonyl carbon (Fig. 5). Examples of nucleo-
philic attack at the central metal are the reactions of
tungsten and molybdenum hexacarbonyls with tetrabutylammonium
halides. In these reactions, a seven-coordinate intermediate or
activated complex is formed by the attack of the halide on the
metal in the rate-determining step. This is followed by the
expulsion of one molecule of carbon monoxide in a fast step (38).

Fenske and Caulton (39) have shown through an orbital
population analysis, that the carbonyl carbon is a favored
site for nucleophilic attack in the hexacarbonyls of vanadium,
chromium, and manganese. It is now well established that
reactions of strongly nucleophilic reagents, such as organo-
lithiums (40), the azide ion (41), and benzylmagnesium
chloride (42), proceed via an attack at a carbonyl carbon.
Furthermore, it has long been known that the carbonylation
products can arise intramolecularly (Fig. 6). Thus, for
example, the acylation of $CH_3Mn(CO)_5$ employing CO to afford
$CH_3COMn(CO)_5$ occurs via a "methyl migration" (43).

$$(OC)_4Mn \begin{array}{c} \delta^+ \\ C\equiv O \\ \uparrow \\ CH_3 \\ \delta^- \end{array} \longrightarrow (OC)_4-Mn(COCH_3) \xrightarrow{*CO} (OC)_4(O*C)Mn(COCH_3)$$
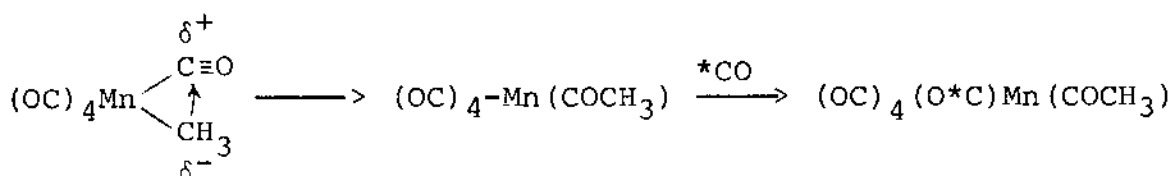
Fig. 6 — Methyl migration mechanism
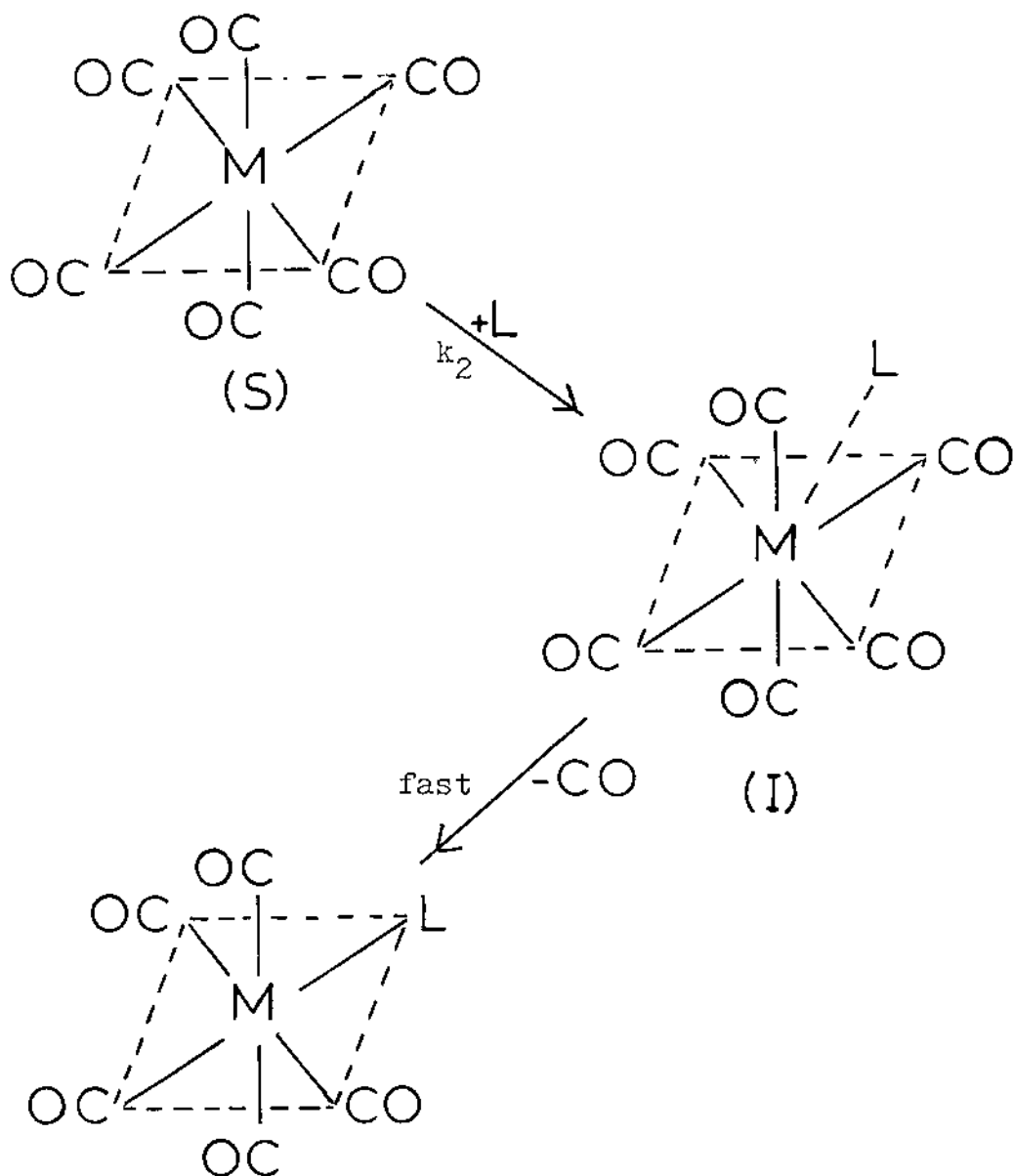
Fig. 4--Bimolecular associative mechanism involving rate-determining attack of L at the central atom.
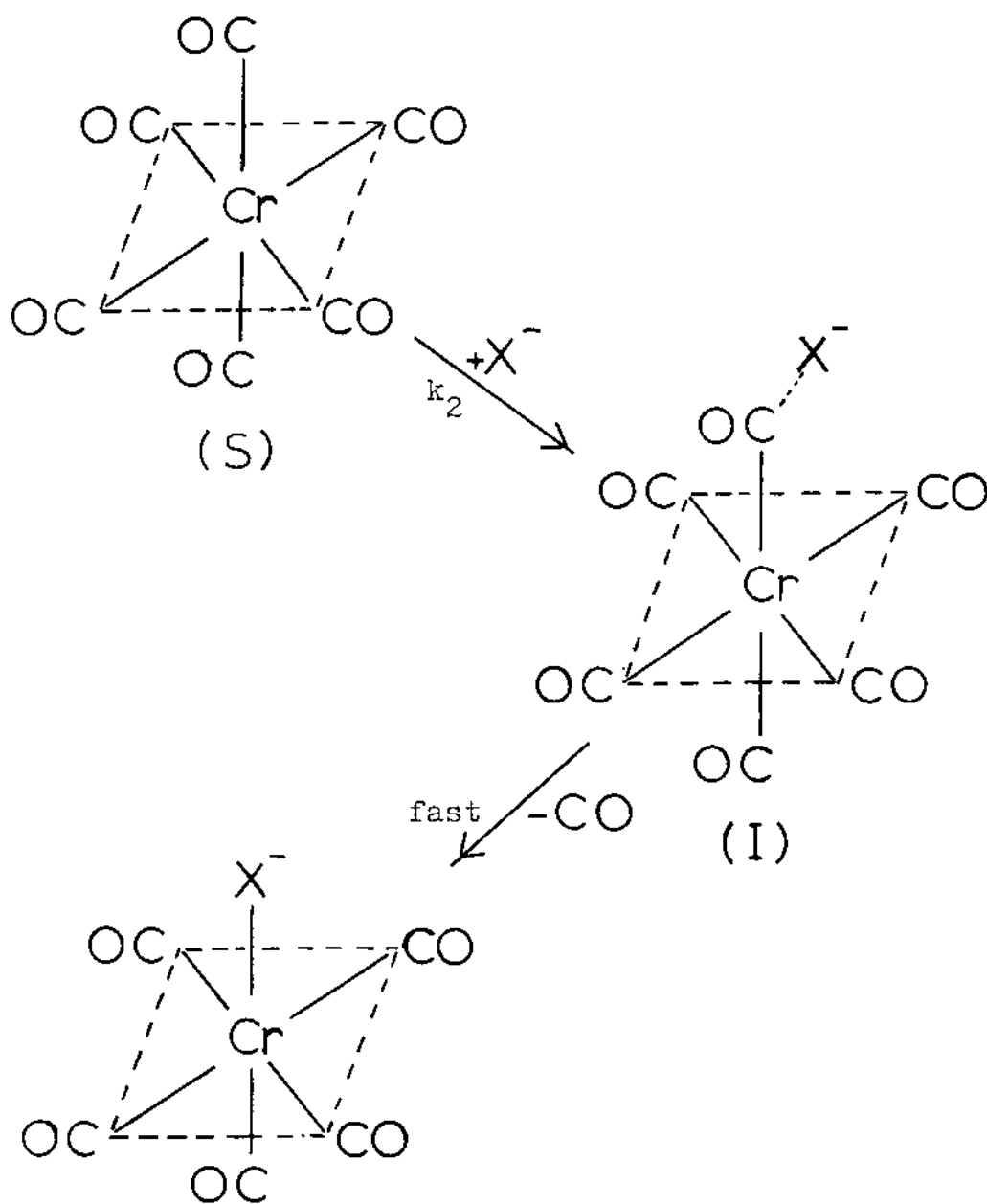
Fig. 5--Bimolecular association mechanism involving
rate-determining attack of the ligand at the carbonyl carbon.

Recent rate studies for the reactions of methyllithium with metal carbonyls and derivatives, together with analyses of the stereochemistries of the acylate reaction products, have supported the proposal that the attack is at the carbonyl group possessing the highest carbonyl stretching force constant, F(CO). This indicates a higher positive charge on the carbon belonging to that carbonyl group (44). The kinetic results for the reactions of $LM(CO)_5$ with benzylmagnesium chloride (45) and with methyllithium (46) indicated that the nucleophilic attack takes place at the carbonyl carbon cis to the L group.

(III) The rate of disappearance of the substrate is a combination of the above two terms. This takes place when there is a competition between the associative and dissociative mechanisms.

$$- \frac{d[S]}{dt} = k_3[S] + k_4[S][L] \qquad (I-6)$$

It follows for such a mechanism that $\Delta S_3^{\ddagger}$ should be positive, while $\Delta S_4^{\ddagger}$ is expected to be negative. There are a large number of reactions which obey such a rate law. For example, the substitution reactions of $M(CO)_6$ (where M = W, Mo, and Cr) with a wide variety of phosphorus and arsenic donor ligands are shown to proceed via this mechanism (47-49).

(IV) The rate of disappearance of the substrate depends on a complex equation. A rate law, such as Eqn. I-7, is one

of the simplest rate laws observed (50). An example of this type are the reactions of (bidentate)$W(CO)_4$ with triethyl and triisopropyl phosphite (Fig. 7).

$$- \frac{d[S]}{dt} = \frac{k_5 k_6 [S][L]}{(k_{-5} + k_6 [L])} \qquad (I-7)$$

In order to avoid complicated mathematical calculations and difficult experimental techniques, the kinetic studies are carried out under pseudo first-order conditions. That is, the concentration of the ligand used is at least ten times as much as the concentration of the substrate. Under this condition, which some people call "flooding", one can assume that when the reaction is completed, the concentration of the ligand has remained essentially the same. Thus, the ligand concentration term, along with the other rate constant(s), can be incorporated in a term designated as k_{obsd}. Employing this method, k_{obsd} for each of the above cases respectively, is equal to k_1, $k_2[L]$, $k_3 + k_4[L]$, and $k_5 k_6 [L]/(k_{-5} + k_6 [L])$, and the rate law is simplified as:

$$- \frac{d[S]}{dt} = k_{obsd}[S] \qquad (I-8)$$

This is first-order with respect to the substrate concentration.

Since the straight line plots are easier to manipulate, it is preferable to apply the following procedure: employ the flooding technique and from first-order rate behavior determine the values of k_{obsd}. Then plots of k_{obsd} vs. ligand
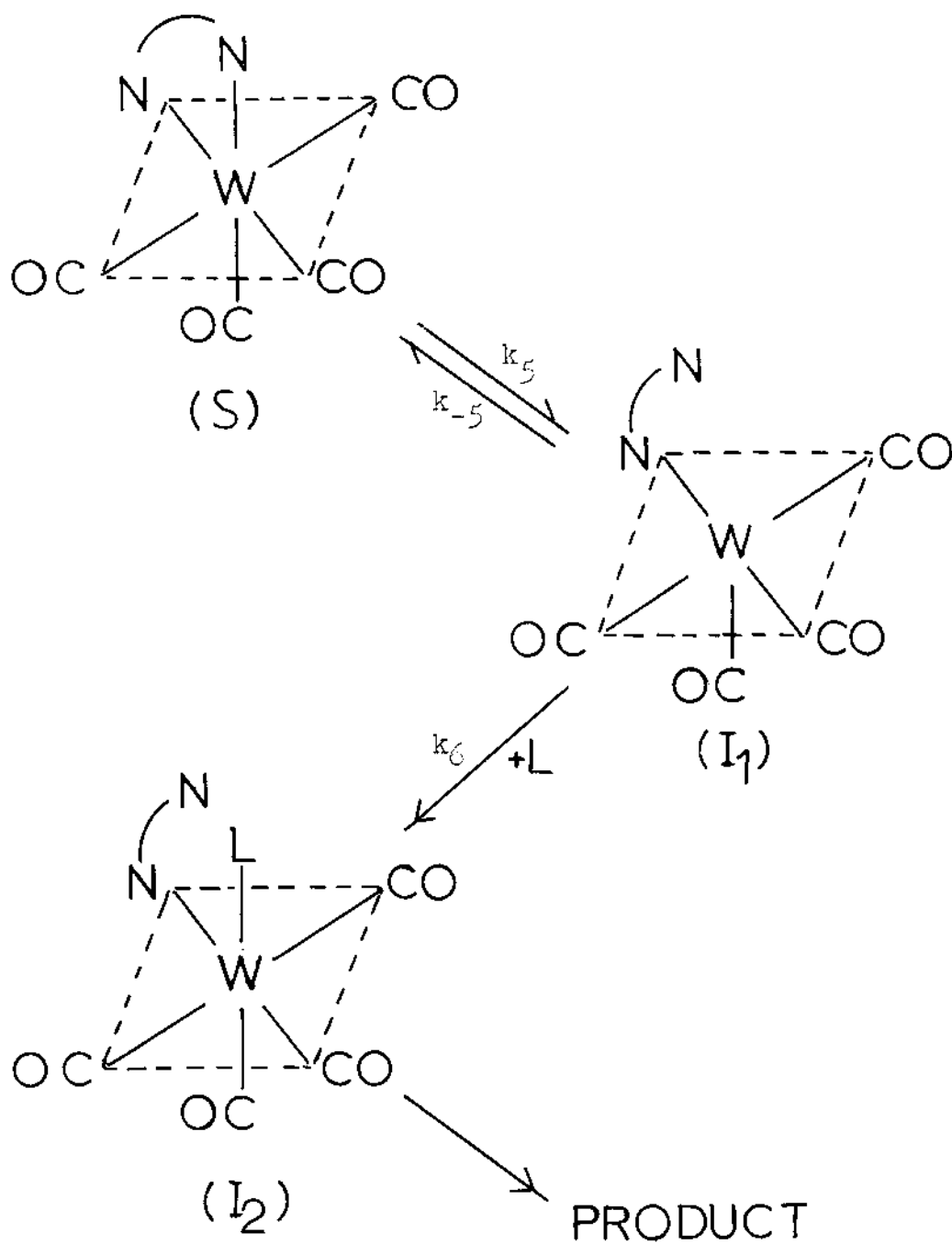
Fig. 7--Simple ring-opening mechanism

concentration would be linear for the above three cases. The observed intercepts and slopes of these plots represent true rate constants. For the fourth case described above, a non-linear plot of k_{obsd} vs. [L] and a linear plot of $1/k_{obsd}$ vs. $1/[L]$ is expected. The intercept and slope of such a plot represent $1/k_5$ and $k_{-5}/k_5 k_6$, respectively.

CHAPTER II

KINETICS AND MECHANISM OF LIGAND-EXCHANGE

REACTIONS OF METAL CARBONYL DERIVATIVES CONTAINING

BIDENTATE AMINE LIGANDS

In the early 60's, it was a common belief (51) that octa-
hedral metal complexes, when the central atom is in the zero oxi-
dation state, do not react by an S_N2 type mechanism due to
steric hinderance and electrostatic repulsion between the
filled d orbitals and the attacking nucleophile. Despite
this, $Mo(CO)_6$ has been found to react with phosphites and
phosphines at a rate which is dependent on the first-order
concentration of the ligand (52). The most plausible mech-
anism which explains the overall second-order character of
these reactions, is a bimolecular associative mechanism. In
this line of investigation, studies of the kinetics and mech-
anism of the reaction of $M(CO)_4(N-N)$ (where M = Mo or W and
N-N = 2,2'-dipyridyl) with various phosphites were undertaken
by Angelici and Graham (53). Since 2,2'-dipyridyl is a non-
rigid molecule, a ring opening mechanism was considered.
That is, one end of the bidentate ligand, via a reversible
step, opens to form a five-coordinate intermediate, $(OC)_4M(N-N)$,
which then reacts with a phosphite ligand to produce $(OC)_4M(L)-$
(N-N). This is followed by ring-reclosure and the loss of a
carbon monoxide molecule to yield the observed product $(OC)_3M(L)(N-N)$.

However, the authors rejected this mechanism in favor of an S_N2 (bimolecular nucleophilic substitution) type mechanism (53).

In 1967, Zingales and Sartorelli (54) adopted the ring-opening mechanism to explain the rate behavior observed for the reactions of $[Mn(CO)_4X]_2$ (X = Cl, Br, or I) with various amines. Dobson and his group (55-61) have studied several reaction systems for which the observed rate behavior is consistent with the ring-opening mechanism. Angelici and Knebel have adopted this mechanism to explain the observed rate behavior for CO exchange reactions of $M(CO)_4(P-N)$ complexes, where M = Cr, Mo, and W, and P-N is a phosphorus-nitrogen donor bidentate ligand (62). The ring-opening mechanism is also consistent with the rate law observed for CO exchange reactions of $Mo(CO)_4(P-N)$, where P-N is a pyridyl-phosphine bidentate ligand (63).

Of special interest was the mechanism of the reactions of $(tmpa)W(CO)_4$ with triisopropyl and triethyl phosphite in xylene (tmpa = N,N,N',N'-tetramethyl-1,3-diaminopropane). Dobson and Faber (50) investigated these two systems and proposed a mechanism (Fig. 7) which included a reversible ring-opening step to form a five-coordinate intermediate, $[(h^1-tmpa)W(CO)_4]$, where the bidentate ligand is attached to the central metal atom by only one nitrogen (64), followed by an S_N2 attack by the phosphorus donor ligand at the metal to form a second intermediate, I_2, which in other fast steps leads to the observed product $L_2W(CO)_4$. Employing a steady-state approximation

for $[(h^1-tmpa)W(CO)_4]$, the following rate law can be derived (See Appendix I for derivation).

$$-\frac{d[S]}{dt} = \frac{k_5k_6[S][L]}{k_{-5} + k_6[L]} \qquad (II-1)$$

Under pseudo first-order reaction conditions (that is, when $[L] > 10[S]$), the following expression can be obtained.

$$k_{obsd} = \frac{k_5k_6[L]}{k_{-5} + k_6[L]} \qquad (II-2)$$

A closer look at the k_{obsd} term shows that a plot of k_{obsd} vs. $[L]$ should pass through the origin and at low ligand concentration, where $k_6[L] << k_{-5}$, the k_{obsd} expression can be reduced to $k_{obsd} = k_5k_6[L]/k_{-5}$. Under this condition a plot of k_{obsd} vs. $[L]$ should be linear. However, over a large range of ligand concentration, this plot (as expected) is not linear.

Upon the rearrangement of Eqn. II-2, one would find the following equation to be true.

$$\frac{1}{k_{obsd}} = \frac{k_{-5}}{k_5k_6[L]} + \frac{1}{k_5} \qquad (II-3)$$

This expression indicates that plots of $1/k_{obsd}$ vs. $1/[L]$ for different ligands are expected to be linear, if the proposed mechanism holds. Moreover, one would expect that these plots have a common intercept, because k_5 is expected to be independent of the identity of the ligand. The experimental

results, however, showed otherwise (50). That is, the k_5 values for the reactions of (tmpa)W(CO)$_4$ with triisopropyl phosphite and triethyl phosphite were recalculated (using weighting factors) and were found to be $(18.5 \pm 1.0) \times 10^{-4}$ and $(145.7 \pm 111.4) \times 10^{-4}$ sec^{-1}, respectively (See Page 36).

In order to rationalize this discrepancy, a ligand-substrate interaction was proposed. This would affect the ring-opening of the substrate to various degrees for different ligands, and therefore, k_5 would be dependent on the identity of the ligand (See Fig. 8).

Attempts to obtain evidence for the existence of such an interaction were unsuccessful; no observable effect of the presence of ligand on the infrared or UV-visible spectra of the substrate in xylene was detected.

Moreover, only two ligands were employed to study the reactions of (tmpa)W(CO)$_4$ with phosphorus donor ligands.

In order to clarify this mechanism, it was desirable to reinvestigate these reactions in greater detail employing other phosphorus donor ligands.
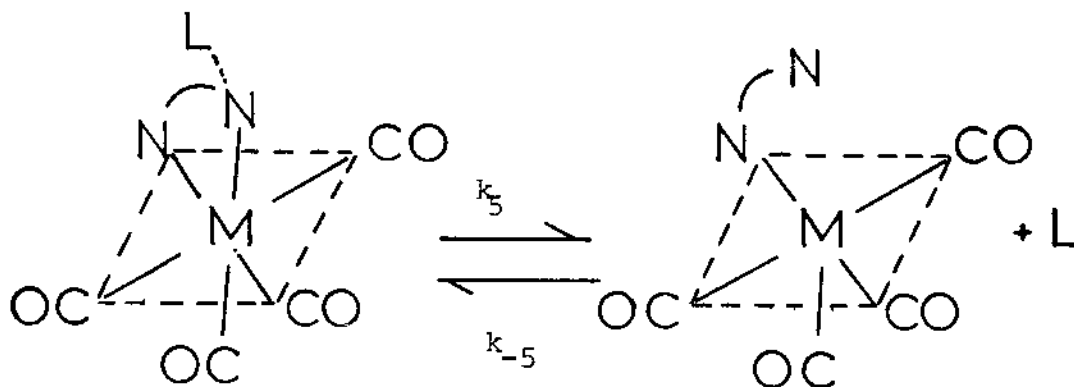
Fig. 8 — Substrate-ligand interaction

Having the stability of the ring in mind, the reactions of $(tmen)W(CO)_4$ (where tmen = N,N,N',N'-tetramethylethylenediamine) with these ligands were studied to see the effect of five and six-membered chelate rings on the ring-opening mechanism.

EXPERIMENTAL SECTION

General

The infrared spectra of all the substrates, intermediate(s) (if stable enough), and products were monitored on a Perkin-Elmer 621 grating spectrophotometer, and were calibrated against water vapor at 1869.4 cm^{-1} (65) every time a spectrum was obtained. Ultraviolet and visible spectra were obtained employing a Cary Model 14 recording spectrophotometer. Melting points were taken on samples in open capillary tubes on a Hoover capillary melting point apparatus, and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

Kinetic runs in the visible region were monitored on a Beckman Model DU-2 direct reading spectrophotometer. The runs carried out in the infrared region of the spectra were monitored on a Perkin-Elmer 621 grating spectrophotometer. The kinetic data were anlyzed by a least-squares curve fitting program on an IBM 360, Model 50 Computer at the NTSU Computing Center.

Preparation and Purification of the Materials

Tungsten hexacarbonyl, which was the starting material for preparation of both (tmpa)W(CO)$_4$ and (tmen)W(CO)$_4$, was purchased from Pressure Chemical Co., Pittsburgh, Pa., and was used without further purification. 2-hydroxymethyl-2-methyl-1,3-propanediol, (HOH$_2$C)$_3$CCH$_3$, was obtained from Aldrich Chemical Co., Milwaukee, Wis., and was used as obtained.

Bidentate Ligands: Both N,N,N',N'-tetramethylethylenedi-amine, (tmen), and N,N,N',N'-tetramethyl-1,3-propanediamine, (tmpa), were purchased from Aldrich Chemical Co., and used as obtained. Bicyclo[2.2.1]hepta-2,5-diene, (NBD), was obtained from Aldrich Chemical Co., and was used without further purification.

Phosphorus Donor Ligands: Triphenyl phosphite was pur-chased from Eastman Kodak Company, Rochester, N.Y. and was fractionally distilled three times over sodium under high vacuum (0.025 torr, 156°C). The distillate was redistilled three additional times under the same pressure, until no odor of phenol could be detected. This purified ligand was used within 24 hr of distillation.

Triisopropyl phosphite was obtained from Aldrich Chemical Co., and was fractionally distilled over sodium under high vacuum (0.05 torr, 29°C), and was analyzed by Mr. James E. Henderson on a Finnigan Corporation Model 3200 Gas Chromato-graph/Mass Spectrometer with a Model 6100 data system utilizing

a Zeta Research, Inc. Model 130 Zeta Plotter, series 100, and
a Texas Instruments, Inc. Silent 700 Electronic Terminal for
data output. The column used was a 5 foot x 2 mm. id. glass
U column with Silicone OV-1 packing on chromosorb W-HP, 80/100
mesh. The chromatogram and peak analysis, as shown on Figures
9 and 10, insured the purity of the distillate.

Triphenylphosphine was purchased from Cincinnati Milacron,
Reading, Ohio, was recrystallized from absolute alcohol three
times, was dried under vacuum in the dark (M.P. = 80°C), and
was stored in a brown bottle.

Trimethyl phosphite was obtained from Aldrich Chemical
Company, and was fractionally distilled over sodium under one
atmospheric pressure of nitrogen.

The "constrained phosphite", 4-methyl-2,6,7-trioxa-1-
phosphabicyclo[2.2.2]octane $P(OCH_2)_3CCH_3$, was prepared by
the modified method of Verkade et al. (66), and was sublimed
seven times at 45°C and 0.2 torr.

$P(O_3C_6H_9)$, 1-phospha-2,8,9-trioxaadamantane, was prepared
by the method of Verkade, et al. (67), and was sublimed twice
under vacuum at 70°C. It then was triturated with small quan-
tities of n-hexane, and was resublimed. The trituration-sub-
limation process was repeated two additional times, after
which the ligand was finally sublimed under vacuum three addi-
tional times. The preparation and purification of this ligand
was carried out by Dr. Melvin N. Memering.

TRIISOPROPYL PHOSPHITE
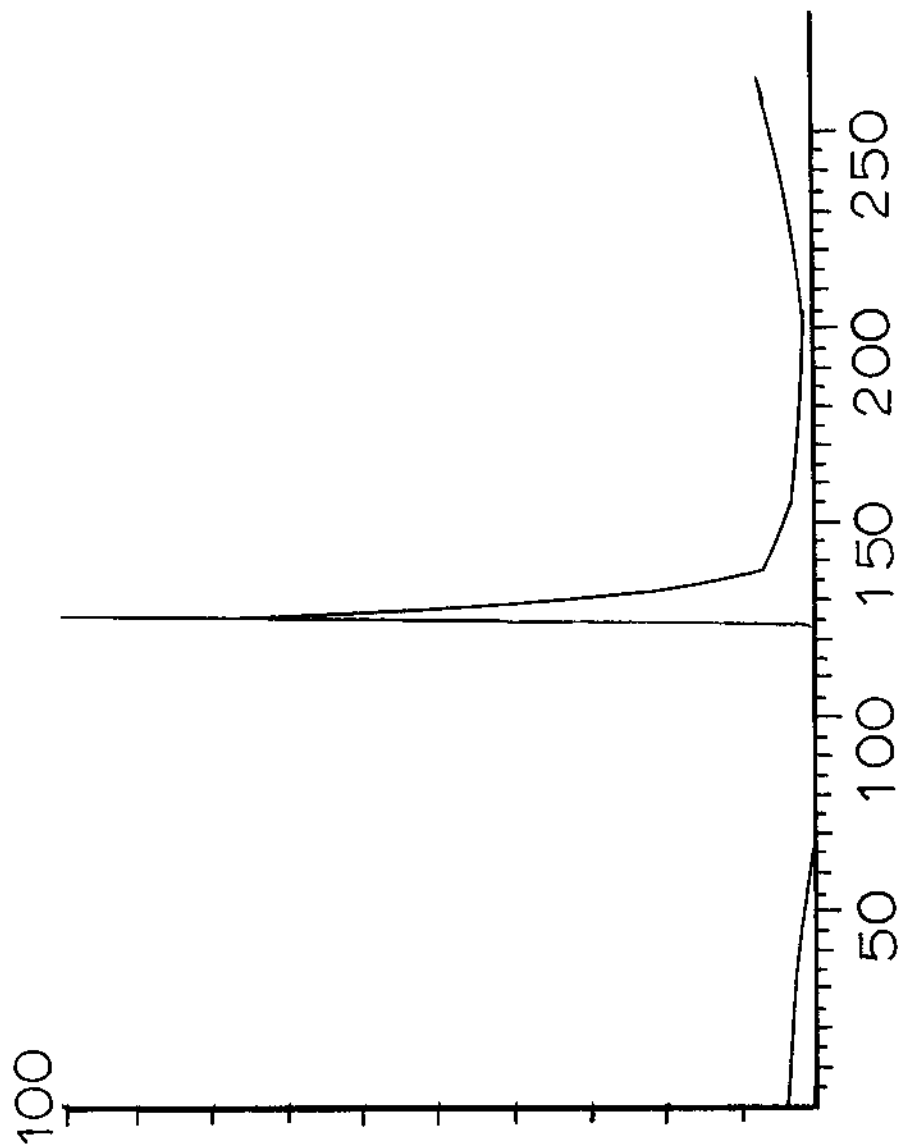
Fig. 9--Gas chromatogram of purified triisopropyl phosphite (Ordinate and Abscissa have arbitrary units).

TRIISOPROPYL PHOSPHITE
#131
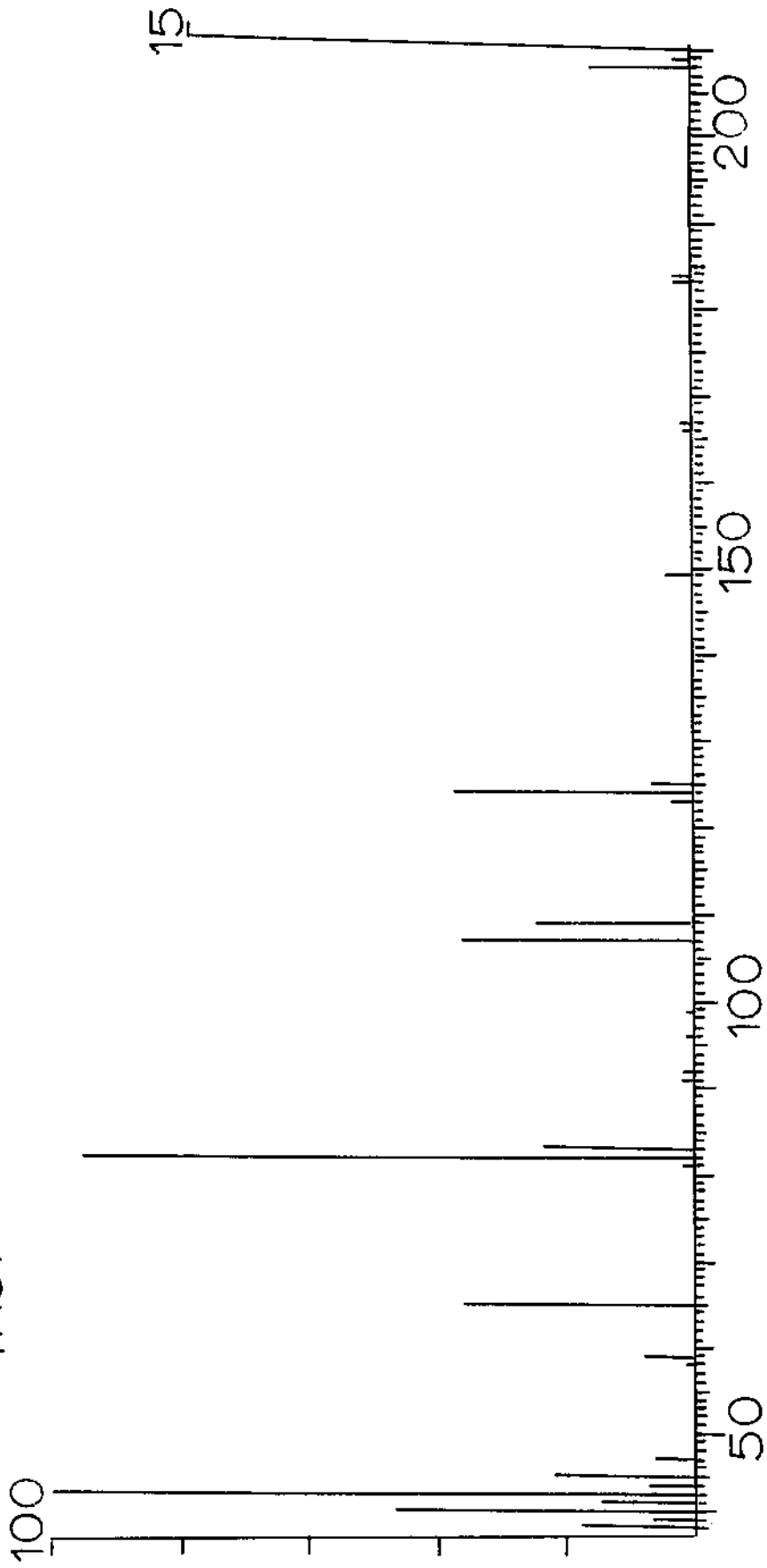
Fig. 10—Mass spectrum of the purified triisopropyl phosphite

(Ordinate = % of base peak, Abscissa = m/e).

All liquid phosphorus donor ligands were stored under one nitrogen atmosphere in foil-wrapped flasks equipped with stopcocks and rubber septa, and were used within 2-3 days.

Complexes

(Tmen)W(CO)$_4$ — This compound was prepared by a method similar to that of Poilblanc (68). A three-neck flask equipped with a bubbler, a rubber septum, and a magnetic stirrer, was charged with 35.2 g of tungsten hexacarbonyl and 80 ml of tmen. The flask had been purged with purified nitrogen for five minutes before and after charging it with the starting materials. The solution was then refluxed and samples were withdrawn periodically. The progress of the reaction was monitored by the infrared spectra. The sampling was continued until the reaction was completed (ca. 76 hr). The solution was then cooled to room temperature and filtered. The residue was extracted with dichloromethane and recrystallized by the "solvent-differential technique" with dichloromethane/hexane (69). The product was filtered, washed with hexane, and dried under vacuum. The final product weighed 12 g (29.1% yield).

(Tmpa)W(CO)$_4$ — This complex was prepared by the method of Dobson and Faber, described elsewhere (50).

Solvent

Purified grade xylene was obtained from Matheson, Coleman & Bell, was refluxed over sodium for an hour, and was fractionally

distilled using a 75 cm Vigreaux column. The fraction ob-
tained at 138°C was stored under nitrogen at atmospheric
pressure and was used within 2-3 days.

Identification of the Reaction Products

For every system under investigation, a preliminary run
was monitored by scanning through the carbonyl stretching
region of the spectra (2200-1800 cm^{-1}) as a function of time.
The carbonyl stretching frequencies for $W(CO)_4[P(OCH_2)_3CCH_3]_2$,
$W(CO)_4[P(OC_6H_5)_3]_2$, and $W(CO)_4[P(C_6H_5)_3]_2$ had been reported
elsewhere (70-72). $W(CO)_4[P(OCH(CH_3)_2)_3]_2$, however, had not
been synthesized. Therefore, this product was made and was
isolated as described below.

$\underline{W(CO)_4[P(OCH(CH_3)_2)_3]_2}$ — 2 g of (tmpa)$W(CO)_4$ and 10 ml
(ca. 9.7 g) of triisopropyl phosphite were dissolved in 100
ml xylene in a three-neck flask equipped with a condenser, a
bubbler, and a rubber septum. The solution in the reaction
flask was kept in a constant-temperature oil bath at 90°C and
was stirred magnetically under nitrogen atmosphere. Samples
were withdrawn periodically with the help of a syringe with
a long needle, and the infrared spectra were monitored (car-
bonyl stretching region) to check the progress of the reaction.
After 20 min, the reaction was completed. The solution was
then cooled and its volume was reduced to about 5 ml under
vacuum. 50 ml of heptane was added, and the mixture was left
in the freezer overnight. It was then filtered in a cold room.

The pale yellow crystals obtained were washed with cold heptane and were dried under vacuum. The final product weighed about 0.3 g (m p = 92-94°C). The infrared spectrum of this product in chloroform showed the following carbonyl stretching bands: 2037(w), 1953(m), and 1900(vs) cm^{-1}. Anal. Calc'd for $C_{22}H_{42}O_{10}WP_2$: C, 37.09; H, 5.94. Found: C, 37.24; H, 6.02.

Reaction Intermediates

A three-neck flask equipped with a bubbler, a condenser, a rubber septum, and a magnetic stirrer was purged with purified nitrogen for five minutes. The flask was then charged with the appropriate starting materials and was placed in a constant-temperature water bath at 43°C. Samples were withdrawn periodically and their carbonyl stretching frequencies were monitored. In order to prepare $(h^1-tmpa)W(CO)_4[P(OCH_2)_3-CCH_3]$, 4 g of $(tmpa)W(CO)_4$ and 14 g of $P(OCH_2)_3CCH_3$ were dissolved in 60 ml of xylene. After one hour of reaction time, no trace of $(tmpa)W(CO)_4$ was detected. The solution was then cooled and the solvent was removed under vacuum. The residue was sublimed at 50°C/0.1 torr for three days, and 9.7 g of unreacted $P(OCH_2)_3CCH_3$ was recovered. The residue was dissolved in 30 ml of xylene, cooled in a dry ice-acetone bath, and filtered to separate $W(CO)_4[P(OCH_2)_3CCH_3]_2$. The filtrate was evaporated to dryness under vacuum and weighed (1.5 g). The infrared spectrum of this intermediate in xylene showed the following

bands: 2030(m), 1913(s), 1900(vs), and 1880(s) cm^{-1}. Anal. Calc'd for $C_{16}H_{27}O_7WN_2P$: C, 33.47; H, 4.74. Found: C, 33.29; H, 4.75.

For the synthesis of $(h^1$-tmpa$)W(CO)_4[P(O_3C_6H_9)]$, 0.63 g of (tmpa)$W(CO)_4$ and 0.65 g of $P(O_3C_6H_9)$ were dissolved in xylene. After 3200 seconds, this intermediate reached its maximum concentration. After five hours, it was completely converted to $W(CO)_4[P(O_3C_6H_9)]_2$. ν(CO)(xylene) for $[h^1$-tmpa]-$W(CO)_4[P(O_3C_6H_9)]$ are: 2029(m), 1915(s), 1902(vs), and 1874(m) cm^{-1}, where m = medium, s = strong, and vs = very strong.

Preparation of (NBD)$W(CO)_4$

(Tmpa)$W(CO)_4$ (1.2 g) and NBD (15 ml) were placed in a three-neck flask fitted with a bubbler, a condenser, and a rubber septum. The solution was stirred under nitrogen at atmospheric pressure, and the flask was kept in a constant-temperature oil bath at 50°C. A periodic sample analysis was carried out by monitoring the carbonyl stretching frequencies of (tmpa)$W(CO)_4$. After 4 hr., the solution was cooled to room temperautre. The excess norbornadiene was then removed under vacuum, and the residue was extracted with 120 ml of hexane in several portions. The volume of the hexane extract was reduced to 20 ml under vacuum, affording a yellow precipitate, which was filtered and was dried under vacuum. This crude, yellow product was sublimed at high vacuum (0.1 torr and 80°C), to give 0.56 g of product (51.3%). This is

comparable to the yield obtained by the method of King and Fronzaglia (73), and is preferred to their method, due to the fact that (tmpa)$W(CO)_4$, used here as starting material, is much more stable and easier to prepare than $(CH_3CN)_3W(CO)_3$, which was used by them.

Determination of the Optimum Conditions
for Kinetic Studies

For every system under investigation, a preliminary run was monitored by scanning the carbonyl stretching region of the spectrum (2200-1800 cm^{-1}). This insured the identification of product(s) and intermediate(s) (if stable enough). When the reaction was completed, a visible spectrum of the resulting solution was obtained by superimposing this spectrum on a visible spectrum recorded from substrate solution with the same concentration. The optimum wavelength (where there is a maximum difference in abosrbance of the substrate and the product solutions) was obtained.

In the case of triphenylphosphine, all of the kinetic runs were monitored by a Beckman DU-2 direct reading spectrophotometer. In other cases, a few of the runs were monitored by the DU-2, while the majority of the kinetic data was obtained in the infrared region of the spectra.

The dark points shown on the graphs (See Figs. 12-15) represent the runs monitored by infrared, and the others represent runs monitored on the visible region of the spectra.

A close look at these graphs show that there is good agreement between the two techniques. Even though both instruments produced comparable results, the Perkin-Elmer 621 spectrophotometer was preferred because of the following advantages:

(1) A great deal of solution (ca. 80%) can be saved by using the infrared cells which are much smaller in size than the quartz cells used in the visible region of the spectra.

(2) Having the chart paper on the Perkin-Elmer 621 spectrophotometer enables a person to obtain a permanent record of the runs. Moreover, faster reactions (half-lives as low as 400 sec) can be monitored.

(3) The Perkin-Elmer 621 spectrophotometer is a double beam instrument and once it is adjusted for zero and 100% transmittance, the reaction may be conveniently followed with no further adjustment. Since the Beckman DU-2 is a single beam instrument and 100% transmittance should be adjusted prior to every reading, this might be a barrier for monitoring faster reactions.

The majority of runs, therefore, were carried out monitoring the disappearance of carbonyl stretching frequencies of 1834 cm^{-1} for (tmpa)W(CO)$_4$ and 1840 cm^{-1} for (tmen)W(CO)$_4$.

Determination of Reaction Rates

For every kinetic run, two volumetric flasks were purged with nitrogen. One flask was charged with a small amount of the substrate (ca. $1.3 \times 10^{-3} M$) and was equipped with a teflon stopcock having a ground glass male joint on one end, and a rubber spetum on the other. The second flask was charged with a calculated amount of ligand (enough to make a ligand concentration at least ten times that of the substrate to insure pseudo first-order conditions) and stoppered. Both flasks were placed in a constant-temperature oil or water bath (depending on the reaction temperature) equipped with a Haake Model R21 constant temperature circulator (which maintained the reaction temperatures to within $\pm$ 0.05 degree C). The temperature was checked periodically by an auxiliary Haake precision thermometer, graduated to a tenth of a degree C. The volume of the flask containing the ligand was brought up to the mark, gradually, by adding the solvent. After 20 minutes, the ligand solution was added under a stream of nitrogen to the flask containing the substrate. The substrate was dissolved completely and the flask was replaced in the bath. Depending on the half-life of the reaction, a period of about 200-400 seconds was allowed to insure thermal equilibrium before the first sample was withdrawn employing a glass syringe fitted with a 10-inch long needle. At this moment, an electrical timer (Precision

Scientific Co.) was turned on. The time of the withdrawal of the first sample was taken as zero time. The sampling was continued at timed intervals, which were chosen in such a way that at least four to five samplings could be made in each half-life.

The samples were quenched as soon as they were withdrawn (by allowing them to cool) and placed in appropriate cells. A pair of sodium chloride cells with 0.2 mm lead spacers were used to monitor the disappearance of the appropriate carbonyl stretching frequency of the substrates. The small amount of sample required to fill up the infrared sample cell made it possible to obtain as many as eighteen withdrawals per 10 ml of ligand solution. A quartz cell with 1 cm path length was employed to monitor the disappearance of the absorption band of the substrate in the visible region of the spectra. Because of the large amount of sample required to fill the quartz cell, only thirteen withdrawals could be obtained from 50 ml of ligand solution.

For the runs montiored by the Beckman DU-2, 100% transmittance was set against air prior to each measurement. For the runs monitored by infrared, however, zero and 100% transmittance were set when both cells were filled with the solvent, while the transmittance recordings of the samples taken were carried out when the reference cell contained the solvent and the other cell was filled with the sample withdrawn at a timed interval. It is appropriate to mention that the reactions

performed with the reference cell containing the ligand solutions were consistent with the measurements carried out where the reference cell contained the solvent alone, indicating that the ligands were transparent in the frequencies where the reactions were monitored.

In order to obtain the transmittance at infinite time, the final sample was withdrawn after at least eight half-lives (99.6% completion) had elapsed. Each transmittance recorded was converted to absorbance employing the equation $A = \log 1/T$. The absorbance values were then corrected for A_∞, according to the relationship $A_{corr} = A_t - A_\infty$, where A_t is the absorbance at time t, and A_∞ is the absorbance at infinite time (74). Since the reactions were carried out under pseudo first-order conditions, plots of $\ln A_{corr}$ vs. t were obtained. The half-life was determined for each run from the best straight line drawn through the points. These plots were linear to at least two half-lives.

The k_{obsd} values were calculated by employing a semi-logarithmic least-squares program. This program was designed to line fit $\ln A_{corr}$ vs. time values, keep the points which fell within two standard deviations and reject the rest.

Statistical Analysis of Data

For each kinetic run, the k_{obsd} value was calculated from the semi-logarithmic least-squares program as $k_{obsd} = a \pm S$, where a represents the value of k_{obsd} determined from

the best straight line and S represents the corresponding limit of error for that individual run. The $1/k_{obsd}$ value was then computed according to the following equation:

$$\frac{1}{k_{obsd}} = \frac{1}{a} \pm (\frac{S}{a})(\frac{1}{a}) \qquad (II-4)$$

where $(S/a)(1/a)$ represents the error limit for $1/k_{obsd}$ value.

For every system of substrate and ligand, several different sets of $1/[L]$ and $1/k_{obsd}$, with their individual limits of error, were obtained. A weighted linear least-squares program was employed to fit these data with a weighting factor of $1/S_1^2$, where $S_1 = (S/a)(1/a)$, for each individual point (75). This procedure assured putting less weight on the points with higher error limits. From this program, a slope of $b \pm S_2$ and intercept of $c \pm S_3$ were obtained for each line, where S_2 and S_3 represent limits of error in slope and intercept, respectively. As is shown in Appendix II, the following relationship holds:

$$\frac{intercept}{slope} = \frac{k_2}{k_{-1}} = \frac{(c \pm S_3)}{(b \pm S_2)} \qquad (II-5)$$

That is, one can divide intercept by slope to calculate k_2/k_{-1}, the "competition ratio", for intermediate, I_1. The statistical calculations can be carried out by either one of the following two methods:

Method I

$$\frac{k_2}{k_{-1}} = \frac{c \pm S_3}{b \pm S_2} = \frac{c}{b} \pm (\frac{c}{b}) \; (\frac{S_3}{c} + \frac{S_2}{b}) \tag{II-6}$$

Method II

$$d_1 = \frac{c + S_3}{b - S_2} \tag{II-7}$$

$$d_2 = \frac{c}{b} \tag{II-8}$$

$$d_3 = \frac{c - S_3}{b + S_2} \tag{II-9}$$

$$d_4 = \frac{[(d_1 - d_2) + (d_2 - d_3)]}{2} = \frac{d_1 - d_3}{2} \tag{II-10}$$

$$\frac{k_2}{k_{-1}} = d_2 \pm d_4 \tag{II-11}$$

That is, one can determine the highest limit, d_1, the median, d_2, and the lowest limit, d_3, then compute the average deviation from d_2.

The results calculated from the two techniques are in a very good agreement for all of the systems studied.

Results

The products of the reaction of $(tmpa)W(CO)_4$ with different phosphorus ligands have been shown to be mainly cis and trans disubstituted tungsten tetracarbonyls (76). The kinetic results for every system investigated indicate that the rate of disappearance of the substrate is dependent both on the substrate and on the ligand. Under flooding conditions,

the rate of disappearance of the substrate was first-order in the substrate. Figure 11 shows a typical first-order plot of $\ln A_{corr}$ <u>vs</u>. t.

As mentioned previosuly, a semi-logarithmic least-squares program was used to calculate k_{obsd} values. The results are listed for the reactions of various phosphorus ligands, with $(tmen)W(CO)_4$, in Table I and with $(tmpa)W(CO)_4$ in Table II. The numbers in parenthesis are the limits of error for each individual k_{obsd}, and are within one standard deviation. Figures 12 and 13 represent plots of k_{obsd} <u>vs</u>. [L] for $(tmen)$-$W(CO)_4$ and $(tmpa)W(CO)_4$, respectively, while their corresponding reciprocal plots of $1/k_{obsd}$ <u>vs</u>. $1/[L]$ are shown on Figures 14 and 15.

As was mentioned in the experimental section, one can calculate the values for the k_2/k_{-1} ratio, which is simply the competition ratio for the intermediate, I_1, reacting with phosphorus ligands, k_2, to the ring-reclosure, k_{-1}. Table III shows these values for the reactions of $(tmen)W(CO)_4$ with various phosphorus ligands, while Table IV contains these ratios for the reactions of $(tmpa)W(CO)_4$ with the same ligands.

Discussion

A close look at the plots of $1/k_{obsd}$ <u>vs</u>. $1/[L]$ for the reactions of phosphorus ligands with $(tmen)W(CO)_4$ (See Fig. 14) or $(tmpa)W(CO)_4$ (See Fig. 15) shows that they are linear but they do not have a common intercept. This is consistent
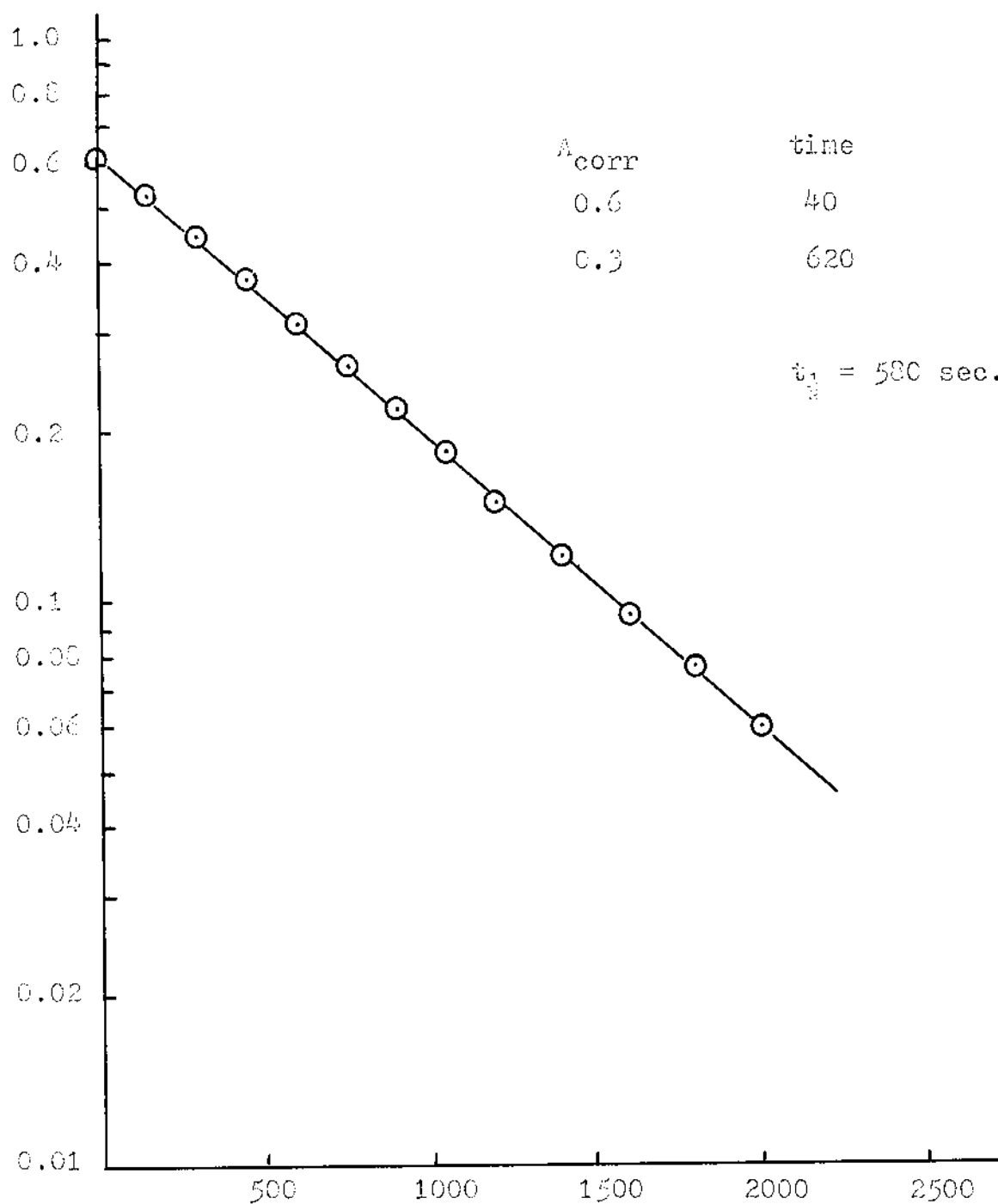
Fig. 11--A typical plot of ln A_{corr} vs. t. (ordinate = A_{corr}; abscissa = time, sec.).

TABLE I

RATE DATA FOR THE REACTION OF $(TMEN)W(CO)_4$

WITH PHOSPHORUS LIGANDS IN XYLENE*

$10^2[L]$ M	$10^4 k_{obsd}$ sec^{-1}	$1/[L]$ M^{-1}	$1/k_{obsd}$ sec	$**\Delta(1/k_{obsd})$ sec
Ligand = $P(OCH_2)_3CCH_3$		Temperature = 120.00(5)°C		
Slope = 150.8 ± 3.1		Intercept = 313.6 ± 9.7		
7.52	4.62(8)	13.298	2165(39)	-154
10.24	5.70(2)	9.766	1754(7)	-32
14.25	7.14(2)	7.018	1401(8)	+30
22.82	9.95(4)	4.382	1005(4)	+31
27.33	11.76(6)	3.659	850(4)	-15
30.31	12.20(4)	3.299	820(3)	+9
33.87	13.49(13)	2.952	741(7)	-17
34.48	13.22(4)	2.900	756(2)	+5
43.64	15.78(11)	2.292	634(4)	-25
43.98	15.22(7)	2.274	657(3)	+1
46.98	15.84(5)	2.129	631(2)	-3
50.96	16.46(6)	1.962	607(2)	-2
Ligand = $P(OC_6H_5)_3$		Temperature = 120.00(5)°C		
Slope = 1787.9 ± 60.5		Intercept = 581.5 ± 50.1		
7.63	0.43(1)	13.106	23289(544)	-725
38.80	1.91(4)	2.577	5241(109)	+52

TABLE I--<u>Continued</u>

$10^2[L]$ M	$10^4 k_{obsd}$ sec^{-1}	$1/[L]$ M^{-1}	$1/k_{obsd}$ sec	**$\Delta(1/k_{obsd})$ sec
45.61	2.24(4)	2.192	4469(80)	-33
52.30	2.48(4)	1.912	4030(68)	+30
73.49	3.19(4)	1.361	3136(44)	+122
87.37	3.79(6)	1.145	2637(42)	+9
97.48	4.34(13)	1.026	2302(70)	-113
117.03	4.78(6)	0.854	2091(25)	-18
134.36	5.11(4)	0.744	1958(14)	+46
143.50	5.79(5)	0.697	1726(15)	-101
152.10	5.59(9)	0.657	1788(29)	+31
166.86	5.78(27)	0.599	1728(80)	+75
178.44	6.14(7)	0.560	1629(19)	+46
186.48	6.34(12)	0.536	1578(30)	+38

Ligand = $P(C_6H_5)_3$ Temperature = 120.00(5)°C

Slope = 415.7 $\pm$ 27.4   Intercept = 589.6 $\pm$ 83.8

3.12	0.58(2)	32.051	17177(456)	+3263
6.23	1.22(1)	16.051	8226(48)	+964
8.58	1.58(3)	11.655	6325(108)	+890
15.32	2.97(3)	6.527	3366(31)	+63
20.23	4.03(5)	4.943	2482(30)	-162
23.89	4.61(3)	4.186	2168(14)	-162
26.98	5.15(4)	3.706	1941(17)	-190

TABLE I—Continued

$10^2[L]$ M	$10^4 k_{obsd}$ sec^{-1}	1/[L] M^{-1}	$1/k_{obsd}$ sec	**$\Delta(1/k_{obsd})$ sec
31.83	5.65(4)	3.142	1770(13)	-126
35.26	5.61(6)	2.836	1781(18)	+12
41.83	6.45(4)	2.391	1550(9)	-34
61.16	7.07(5)	1.636	1415(9)	+145
72.41	8.16(8)	1.381	1226(12)	+62
82.68	8.38(15)	1.210	1194(21)	+101

Ligand = $P(OCH(CH_3)_2)_3$ Temperature = 110.00(5)°C

Slope = 1407.6 $\pm$ 58.4   Intercept = 705.4 $\pm$ 98.1

$10^2[L]$ M	$10^4 k_{obsd}$ sec^{-1}	1/[L] M^{-1}	$1/k_{obsd}$ sec	**$\Delta(1/k_{obsd})$ sec
***12.53	1.01(2)	7.981	9881(178)	-1212
13.11	0.90(2)	7.628	11169(264)	-273
16.50	1.10(1)	6.061	9082(98)	-154
18.80	1.21(1)	5.319	8236(61)	+43
20.74	1.31(2)	4.822	7627(92)	+134
***25.10	1.72(2)	3.985	5826(60)	-409
27.54	1.80(1)	3.631	5540(26)	-276
39.82	2.37(2)	2.511	4226(27)	-14
56.98	2.99(1)	1.775	3347(13)	+171
66.02	3.36(2)	1.515	2973(16)	+135
77.33	3.80(2)	1.293	2635(16)	+109
96.91	4.84(2)	1.032	2065(9)	-92

TABLE I--Continued

$10^2[L]$ M	$10^4 k_{obsd}$ sec^{-1}	$1/[L]$ M^{-1}	$1/k_{obsd}$ sec	**$\Delta(1/k_{obsd})$ sec

Ligand = $P(OCH(CH_3)_2)_3$ Temperature = 120.00(5)°C

Slope = 459.5 ± 11.3   Intercept = 361.8 ± 35.5

10.18	1.95(5)	9.823	5126(127)	+125
10.68	2.16(5)	9.363	4617(109)	−165
11.46	2.28(3)	8.726	4389(52)	−90
14.10	2.90(3)	7.092	3447(33)	−255
14.18	2.94(5)	7.052	3402(58)	−280
17.21	3.30(2)	5.811	3028(23)	−64
18.77	3.08(10)	5.328	3251(107)	+389
18.77	3.58(5)	5.328	2797(38)	−65
30.27	5.23(2)	3.304	1913(8)	+15
47.29	7.08(3)	2.115	1414(7)	+81
51.13	7.86(3)	1.956	1272(5)	+16
61.83	9.07(3)	1.617	1102(3)	+7
81.21	11.44(5)	1.231	874(4)	−38

Ligand = $P(OCH(CH_3)_2)_3$ Temperature = 130.00(5)°C

Slope = 150.2 ± 5.3   Intercept = 155.1 ± 11.9

11.64	7.34(11)	8.591	1362(21)	−84
13.62	8.36(7)	7.342	1196(10)	−62

TABLE I--<u>Continued</u>

$10^2[L]$ M	$10^4 k_{obsd}$ sec^{-1}	$1/[L]$ M^{-1}	$1/k_{obsd}$ sec	**$\Delta(1/k_{obsd})$ sec
16.17	9.29(9)	6.184	1076(10)	−8
17.88	10.41(6)	5.593	960(6)	−35
21.53	12.06(14)	4.644	829(10)	−24
26.06	13.30(8)	3.837	752(4)	+20
30.08	15.08(9)	3.324	663(4)	+8
38.47	18.43(6)	2.599	543(2)	−3
45.78	19.85(10)	2.184	504(3)	+20
52.43	22.26(5)	1.907	449(1)	+8
65.65	25.71(16)	1.523	389(2)	+5
82.83	32.01(17)	1.207	312(2)	−24

*[S] $\simeq$ 1.3 x 10^{-3} M

**Deviation from the line determined by the least-squares fit of $1/k_{obsd}$ <u>vs</u>. $1/[L]$.

***Points rejected on the basis of equal weighting.

TABLE II

RATE DATA FOR THE REACTION OF $(TMPA)W(CO)_4$

WITH PHOSPHORUS LIGANDS IN XYLENE*

$10^2[L]$ M	$10^4 k_{obsd}$ sec-1	$1/[L]$ M^{-1}	$1/k_{obsd}$ sec	**$\Delta(1/k_{obsd})$ sec
Ligand = $P(OCH(CH_3)_2)_3$		Temperature = 43.00(5)°C		
Slope = 775.5 $\pm$ 11.7		Intercept = 50.06 $\pm$ 14.56		
7.42	0.96(1)	13.477	10417(84)	-84
16.36	2.12(1)	6.112	4720(23)	-70
36.76	4.59(3)	2.720	2179(12)	+19
49.05	6.32(3)	2.039	1584(8)	-47
57.63	7.08(5)	1.735	1412(10)	+16
65.04	8.23(7)	1.538	1215(10)	-27
81.96	9.81(3)	1.220	1020(3)	+24
86.24	10.29(8)	1.160	972(7)	+23
140.52	17.00(9)	0.712	588(3)	-14
145.98	17.63(16)	0.685	567(5)	-14
171.73	20.52(24)	0.582	487(6)	-14
Ligand = $P(C_6H_5)_3$		Temperature = 43.00(5)°C		
Slope = 1113.7 $\pm$ 86.3		Intercept = 770.6 $\pm$ 120.3		
21.98	1.56(1)	4.550	6415(47)	+578
32.00	2.38(2)	3.125	4198(28)	-52

TABLE II--Continued

$10^2[L]$ M	$10^4 k_{obsd}$ sec^{-1}	$1/[L]$ M^{-1}	$1/k_{obsd}$ sec	$**\Delta(1/k_{obsd})$ sec
40.03	2.62(3)	2.498	3814(41)	+261
50.58	3.41(2)	1.977	2930(19)	-43
64.82	4.46(2)	1.543	2240(12)	-248
80.05	4.60(2)	1.249	2172(7)	+10
80.06	4.61(4)	1.249	2168(20)	+6
93.71	5.23(4)	1.067	1913(16)	-46
99.63	4.87(3)	1.004	2052(13)	+164
106.58	5.40(3)	0.938	1851(9)	+36

Ligand = $P(OC_6H_5)_3$ Temperature = 43.00(5)°C

Slope = 2186.8 $\pm$ 31.0   Intercept = 1550.0 $\pm$ 39.9

$10^2[L]$ M	$10^4 k_{obsd}$ sec^{-1}	$1/[L]$ M^{-1}	$1/k_{obsd}$ sec	$**\Delta(1/k_{obsd})$ sec
12.73	0.53(0)	7.856	18792(85)	+63
17.98	0.73(1)	5.562	13680(137)	-33
24.25	0.92(1)	4.124	10881(74)	+312
35.12	1.31(1)	2.847	7635(36)	-142
39.55	1.47(2)	2.528	6812(74)	-268
77.67	2.24(3)	1.288	4469(52)	+102
123.22	2.90(2)	0.812	3446(26)	+121
146.79	3.16(3)	0.681	3169(28)	+129
179.33	3.64(1)	0.558	2747(9)	-24

TABLE II--Continued

$10^2[L]$ M	$10^4 k_{obsd}$ sec^{-1}	$1/[L]$ M^{-1}	$1/k_{obsd}$ sec	$**\Delta(1/k_{obsd})$ sec
Ligand = P(OCH$_2$)$_3$CCH$_3$			Temperature = 43.00(5)°C	
Slope = 327.4 $\pm$ 13.0			Intercept = 484.2 $\pm$ 36.1	
Fast Reaction				
8.08	2.18(1)	12.376	4596(27)	+60
10.12	2.68(1)	9.881	3725(14)	+6
11.22	3.01(1)	8.913	3320(15)	-82
13.94	3.56(2)	7.174	2808(16)	-24
27.56	5.58(6)	3.628	1794(18)	+121
32.68	6.35(3)	3.060	1574(7)	+88
43.79	8.26(4)	2.284	1211(5)	-21
44.11	7.05(4)	2.267	1418(8)	+192
50.38	9.16(3)	1.985	1092(4)	-42
50.42	9.43(4)	1.983	1060(4)	-73
67.32	10.02(3)	1.485	998(3)	+28
74.00	10.86(9)	1.351	921(8)	-5
Slow Reaction				
8.84	1.08(1)	-----	-------	---
32.91	0.95(2)	-----	-------	---
43.08	0.87(4)	-----	-------	---
51.20	0.81(4)	-----	-------	---

TABLE II--<u>Continued</u>

$10^2[L]$ M	$10^4 k_{obsd}$ sec-1	1/[L] M-1	$1/k_{obsd}$ sec	**$\Delta(1/k_{obsd})$ sec
56.68	0.75(2)	-----	-------	---
64.17	0.81(1)	-----	-------	---
72.70	0.87(1)	-----	-------	---

*[S] $\simeq 1.2 \times 10^{-3}$M

**Deviation from the line determined by the least-squares fit of $1/k_{obsd}$ <u>vs</u>. 1/[L].
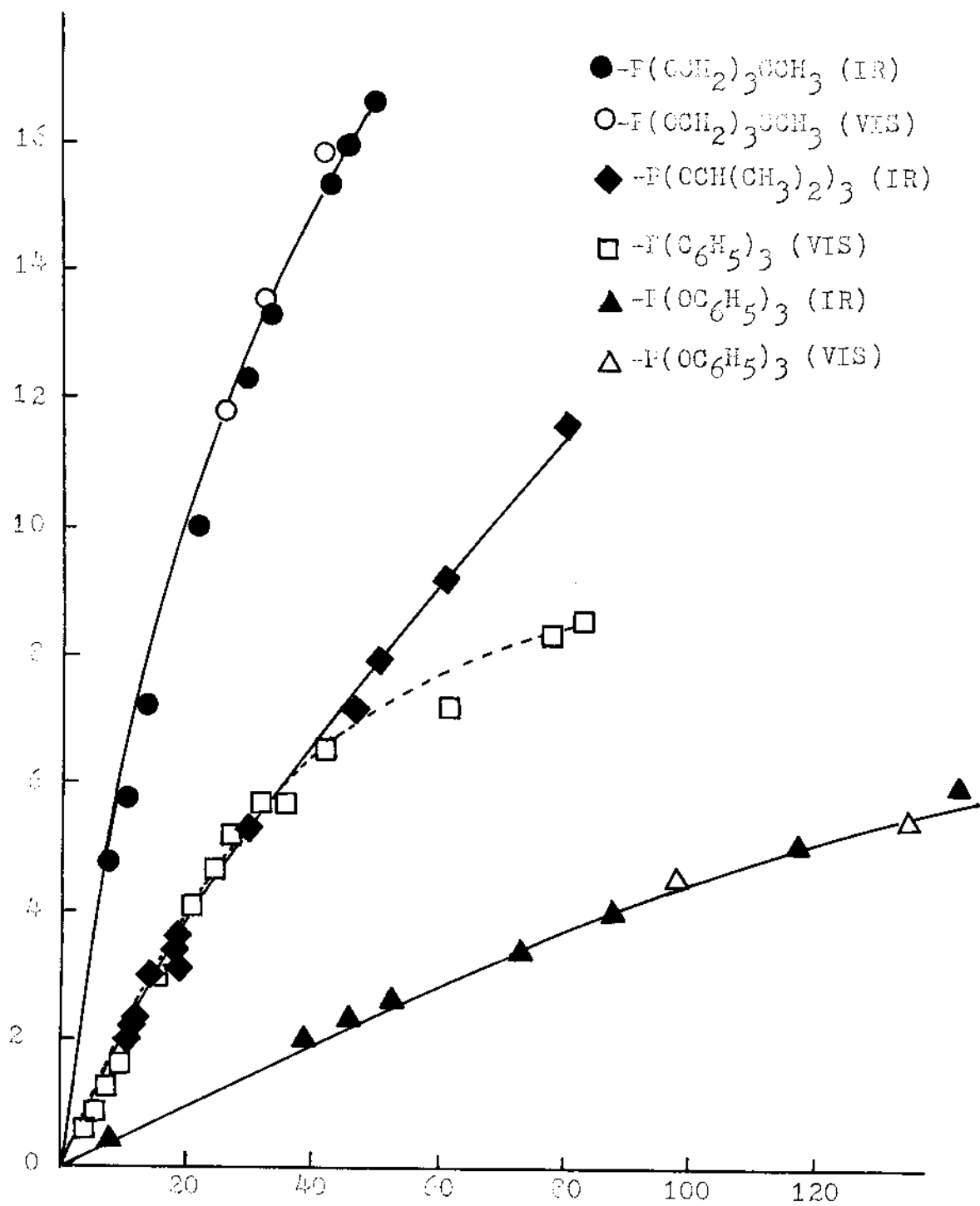
Fig. 12--Plot of k_{obsd} vs. [L] for reaction of various phosphorus ligands with (tmen)W(CO)$_4$ in xylene at 120°C (Ordinate = k_{obsd} x 10^4 sec^{-1}, Abscissa = [L] x 10^2 moles/l).

Fig. 13--Plot of k_{obsd} vs. [L] for reactions of various phosphorus ligands with (tmpa)W(CO)$_4$ in xylene at 43°C   (Ordinate = $k \times 10^4$ sec^{-1}, Abscissa = [L] $\times 10^2$ moles/l).
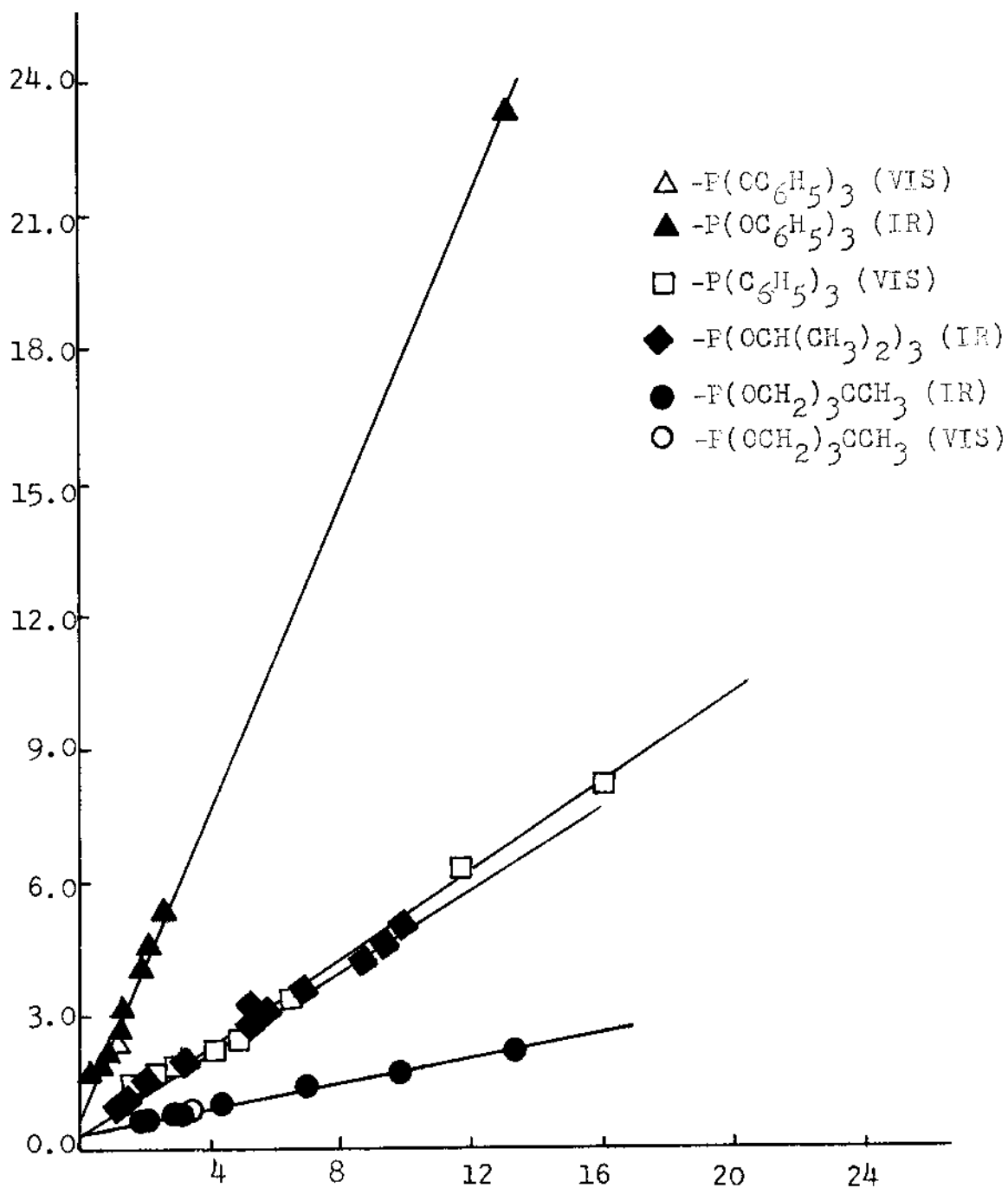
Fig. 14—Plot of $1/k_{obsd}$ vs. $1/[L]$ for reaction of various phosphorus ligands with $(tmen)W(CO)_4$ in xylene at 120°C (Ordinate = $1/k_{obsd}$ x 10^{-3} sec, Abscissa = $1/[L]$ l/mole).
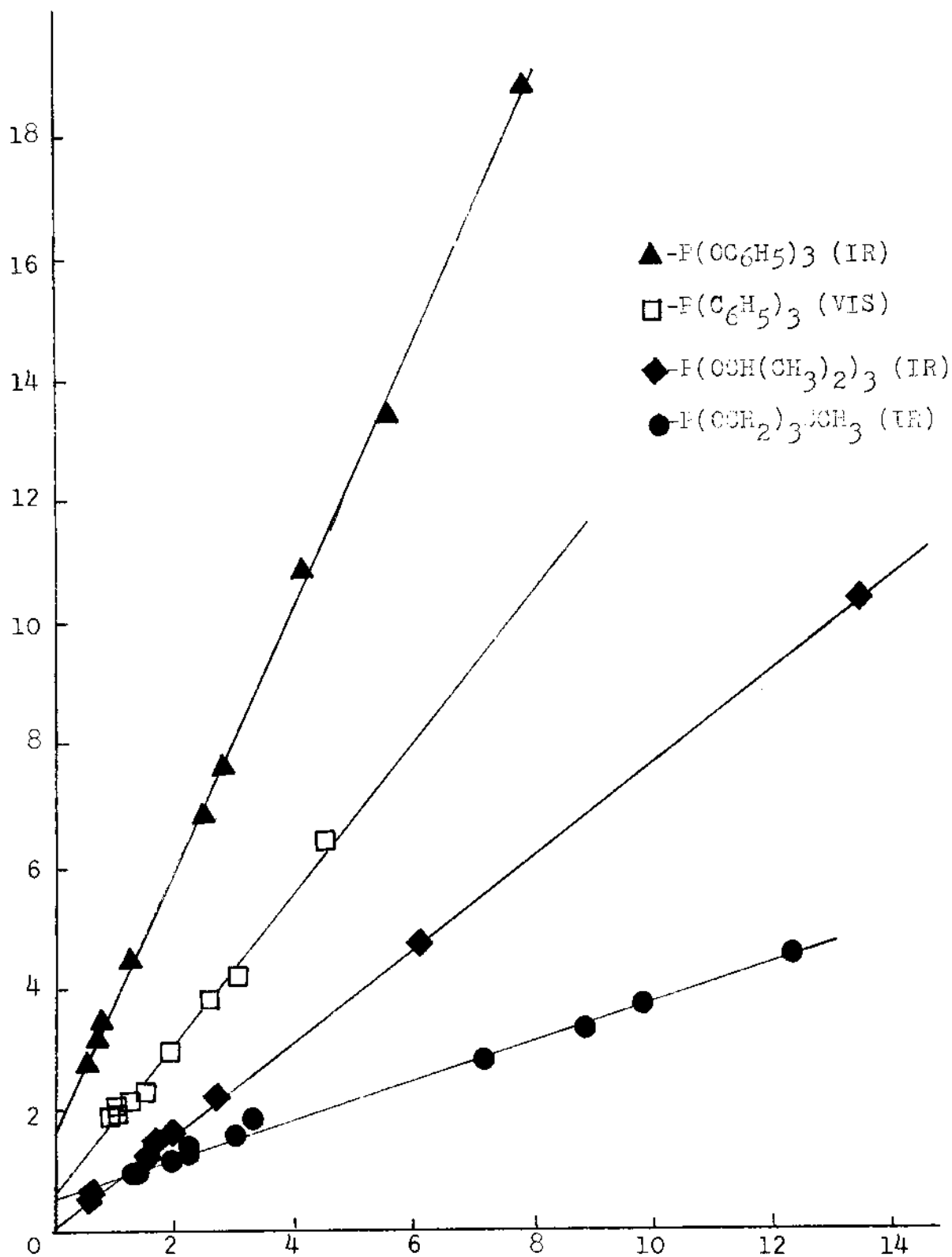
Fig. 15--Plot of $1/k_{obsd}$ vs. $1/[L]$ for reaction of (tmpa)-
W(CO)$_4$ with various phosphorus ligands in xylene at 43°C (Or-
dinate = $1/k \times 10^{-3}$ sec, Abscissa = $1/[L]$ 1/mole).

TABLE III

THE COMPETITION RATIOS FOR THE REACTION OF

$(TMEN)W(CO)_4$ WITH PHOSPHORUS LIGANDS IN XYLENE

LIGAND	TEMPERATURE	k_2/k_{-1}
	degree C.	liter/mole
$P(C_6H_5)_3$	120.00(5)	1.42(30)
$P(OC_6H_5)_3$	120.00(5)	0.32(04)
$P(OCH_2)_3CCH_3$	120.00(5)	2.08(11)
$P(OCH(CH_3)_2)_2$	120.00(5)	0.68(08)
	110.00(5)	0.50(09)
	130.00(5)	1.03(12)

TABLE IV

THE COMPETITION RATIOS FOR THE REACTION OF

$(TMPA)W(CO)_4$ WITH PHOSPHORUS LIGANDS IN XYLENE

LIGAND	TEMPERATURE	k_2/k_{-1}
	degree C.	liter/mole
$P(C_6H_5)_3$	43.00(5)	0.69(16)
$P(OC_6H_5)_3$	43.00(5)	0.71(03)
$P(OCH(CH_3)_2)_3$	43.00(5)	0.06(02)
$P(OCH_2)_3CCH_3$	43.00(5)	1.48(17)

with the results obtained by Faber and Dobson (50), indicating that, indeed, as it was suspected, the simple ring-opening mechanism (See Fig. 7) does not fully explain the experimental results. One can include, however, a ring-reclosure step for the intermediate, I_2, followed by the expulsion of L to form the starting material (See Fig. 16), to modify the mechanism to fit the kinetic data. The ring-reclosure is not uncommon and has been observed in several instances to afford final products containing a chelate ring in the structure (77,78).

Employing the steady-state approximation for the three intermediates, I_1, I_2, and I_3 (as is shown in Appendix II) in the modified mechanism, the following rate law can be derived:

$$-\frac{d[S]}{dt} = \frac{k_1 k_2 k_3 [S][L]}{(k_3 + k_4)(k_{-1} + k_2[L])} \qquad \text{(II-12)}$$

Under pseudo first-order reaction conditions, all of the terms (except [S]) on the right hand side of the above equation remain constant throughout the reaction, and can be incorporated into the k_{obsd} term, shown below:

$$k_{obsd} = \frac{k_1 k_2 k_3 [L]}{(k_3 + k_4)(k_{-1} + k_2[L])} \qquad \text{(II-13)}$$

This equation requires that plots of k_{obsd} vs. [L] pass through the origin, be linear at the low ligand concentration (first-order in ligand), gradually curve, and finally, at
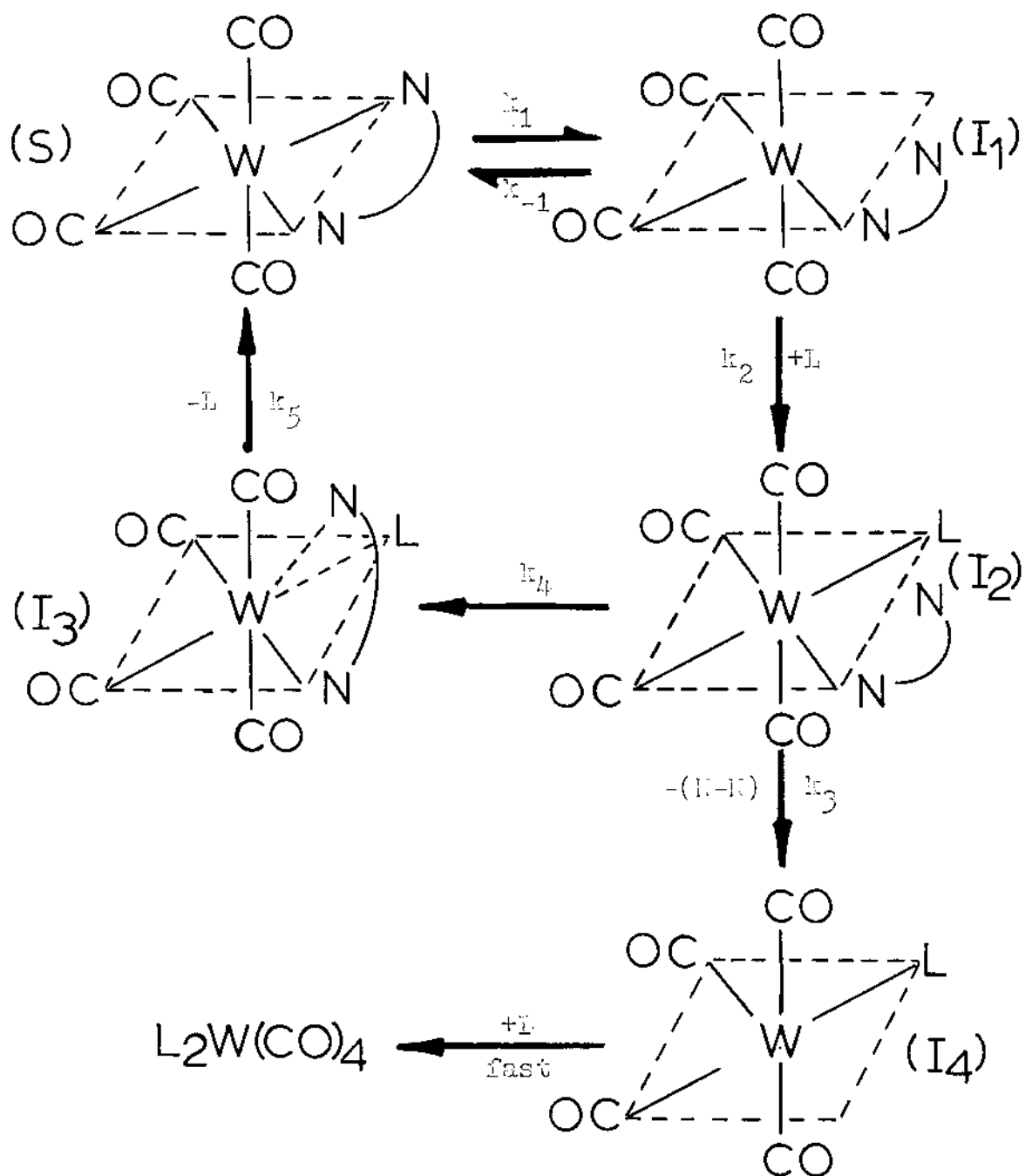
Fig. 16--The modified ring-opening mechanism

high enough ligand concentrations (if the ligand is soluble enough and if the rate is slow enough to measure with the technique employed), turn to a straight line parallel to the abscissa (ligand independent). Indeed, this behavior is observed for both $(tmen)W(CO)_4$ (See Fig. 12) and $(tmpa)W(CO)_4$ (See Fig. 13).

One would rather deal with straight lines than with complex curves. Eqn. II-13 can be rearranged to give the following equation:

$$\frac{1}{k_{obsd}} = \frac{k_3 + k_4}{k_1 k_3} + \frac{k_{-1}(k_3 + k_4)}{k_1 k_2 k_3 [L]} \qquad (II-14)$$

Consequently, plots of $1/k_{obsd}$ $\underline{vs}$. $1/[L]$ should be straight lines with intercepts of $(k_3 + k_4)/(k_1 k_3)$. Since the values of both k_3 and k_4 depend on the identity of the ligand, non-common intercepts are expected for such a mechanism.

In the case of the reaction of $(tmpa)W(CO)_4$ with the "constrained phosphite", $P(OCH_2)_3CCH_3$, an intermediate of the type I_2, $(h^1\text{-}tmpa)W(CO)_4[P(OCH_2)_3CCH_3]$, was isolated and identified. Monitoring the disappearance of this intermediate as a function of time in the infrared region of the spectrum demonstrated that its rate of disappearance is independent of the ligand concentration (See Fig. 13), a point in support of the modified mechanism. A similar behavior had been observed for the reaction of this ligand with $(DTN)W(CO)_4$ and an intermediate, $(h^1\text{-}DTN)W(CO)_4[P(OCH_2)_3CCH_3]$, had been isolated and identified (61). It is appropriate to say that

intermediates similar to those mentioned above have been proposed before (60), even though not isolated.

Since the intermediate, I_2, for the reaction of (tmpa)-$W(CO)_4$ with $P(OCH_2)_3CCH_3$ is stable enough to be isolated, one might question the validity of the application of steady-state approximation for this case. The following relation-ship can be derived (as shown in Appendix III) without assu-ming a steady-state approximation for the intermediate, I_2:

$$- \frac{d[S]}{dt} = \frac{k_1 k_2 k_3 [S][L] + k_4(k_{-1} + k_2[L])d[I_2]/dt}{(k_3 + k_4)(k_{-1} + k_2[L])} \qquad (II-15)$$

The only way that the plot of $1/k_{obsd}$ vs. $1/[L]$ for the re-action of (tmpa)$W(CO)_4$ with $P(OCH_2)_3CCH_3$ could be linear is for the second term on the numerator of the above equation to be negligible.

Another question which comes to mind is why in the re-actions of (tmpa)$W(CO)_4$ with various phosphorus ligands which were employed, only $P(OCH_2)_3CCH_3$ forms a stable inter-mediate and not the other ligands. This could be attributed in part to the size of the "constrained phosphite". More-over, $P(OCH_2)_3CCH_3$ with its caged structure is an "unusual" ligand and is capable of forming a number of coordination compounds which are not formed by similar, nonconstrained phosphites (79). The dipole moment for the "constrained phosphite" is unusually high (4.15D) in comparison to the values known for triphenylphosphine (1.34D) or triphenyl

phosphite (2.03D) (80). This along with chemical shift and coupling constant data indicate that a change in hybridization occurs on constraining the molecule into a bicyclic structure (79). This change of hybridization should increase the s character of the lone pair on the phosphorus atom, which leads to a more stable intermediate of type $(h^1\text{-tmpa})W(CO)_4[P(OCH_2)_3CCH_3]$.

It was suspected that a compound such as $P(O_3C_6H_9)$, which is similar to $P(OCH_2)CCH_3$ in structure, would behave similarly. Indeed, this ligand in reaction with $(tmpa)W(CO)_4$ in xylene, produced a very stable intermediate.

One might also ask why a stable intermediate is not observed in the case of the reaction of $(tmen)W(CO)_4$ with the "constrained phosphite". This may be because tmpa with a pK_{a1} value of 10.08, compared to 8.97 for tmen (81) is a stronger base. Therefore, it would be more difficult to break the W-N bond for tmpa than for tmen (82). There is also another factor involved, which is the higher sensitivity of step 3 (See Fig. 16) to temperature. The reaction of $(tmen)W(CO)_4$ with the "constrained phosphite" is carried out at 120°C, compared to 43°C for $(tmpa)W(CO)_4$. The intermediate, I_2, for $(tmen)W(CO)_4$ probably does not live long enough to be detected.

The kinetic results show that $(tmen)W(CO)_4$ does not react with phosphorus ligands at 43°C, and that the reactions proceed with a measurable rate only at above 100°C. This is

consistent with the idea that five-membered chelate ring is more stable than a six-membered one (83). In light of this observation, it is not surprising that attempts by Fronzaglia and King (73) to synthesize (norbornadience)$W(CO)_4$ from the reaction of (tmen)$W(CO)_4$ with 2,5-norbornadiene in boiling hexane (b.p. = 68°C) for 20 hours were unsuccessful. Since norbornadiene polymerizes at higher temperatures, this reaction could not have been carried out at 100°C in a different solvent. (NBD)$W(CO)_4$, which is an important starting material for the preparation of a large variety of compounds (84-87), can be prepared by the reaction of $(CH_3CN)_3W(CO)_3$ with NBD, but an alternate route for its synthesis was needed. This is mainly because $(CH_3CN)_3W(CO)_3$ is a very unstable and difficult compound to prepare and to handle. As is described in the experimental section, (NBD)$W(CO)_4$ can be synthesized by the reaction of (tmpa)$W(CO)_4$ with 2,5-norbornadiene at 43°C with a comparable yield. This method, therefore, is a preferred route because (tmpa)$W(CO)_4$ is air-stable, whereas $(CH_3CN)_3W(CO)_3$ is not.

Another point worthy of elaboration is raised by the competition ratios shown on Tables III and IV. Since k_{-1} should be independent of the identity of the ligand (See Fig. 16), k_2/k_{-1} for the reactions of a substrate with various ligands should reflect the relative rates of attack of L upon the five-coordinate intermediate (I_1). These ratios for the

reactions of $(tmen)W(CO)_4$ with various phosphorus ligands vary in the order of $P(OCH_2)_3CCH_3$ > $P(C_6H_5)_3$ > $P(OCH(CH_3)_2)_3$ > $P(OC_6H_5)_3$. Since the nucleophilicity depends on both steric and electronic properties, the observed series is reasonable. A parameter which indicates the degree of steric crowding, is the cone angle determined by Tolman (88). Table V shows the cone angles for the ligands which were used in the kinetic studies.

TABLE V

CONE ANGLES OF PHOSPHORUS LIGANDS

LIGAND	CONE ANGLE DEGREE
$P(OCH_2)_3CCH_3$	101(2)
$P(OCH(CH_3)_2)_3$	114(2)
$P(OC_6H_5)_3$	121(10)
$P(C_6H_5)_3$	145(2)

Tolman (89) has also determined a parameter which is a measure of electron donating ability of the phosphorus ligands that decreases as $P(C_6H_5)_3$ > $P(OCH(CH_3)_2)_3$ > $P(OC_6H_5)_3$ > $P(OCH_2)_3CCH_3$. From the observed k_2/k_{-1} values (See Fig. 16), it might be concluded that the steric effect is the dictating factor in the nucleophilicty except for the case of triphenyl-phosphine. The values of k_2/k_{-1} for the reactions of (tmpa)-$W(CO)_4$ with the same ligands follow a similar trend seen for

the reactions of (DTN)W(CO)$_4$ with the above four phosphorus

ligands (61) (which is not clearly understood).

Another interesting point is that, one can divide the

competition ratios of various ligands for a given intermed-

iate, by a k_2/k_{-1} standard value to obtain a term designated

as $k_{2L}/k_{2P(C_6H_5)_3}$, which simply represents the ability of a

given intermediate to "discriminate" among various nucleo-

philes. Table VI presents "discrimination abilities", of a

few intermediates and coordinatively-saturated metal carbonyl

substrates toward various ligands. Based on Hammond's

Postulate (90,91), this ability should be related to the

extent of bond-making in the transition state leading to the

product formation. For metal carbonyls, substrates of lower

coordination number generally exhibit the greater discrimi-

nation abilities (31) as is indicated by the data (Table VI)

for four-coordinate Co(CO)$_3$NO (92). It is of interest to

note that discriminating abilities of intermeidates,

$[(C_6H_5)_3PMo(CO)_4]$ (93) and $[(h^1-DTO)W(CO)_4]$ (61), do not

differ too greatly from those of the hexacarbonyls, although,

based upon limited data, [Mo(CO)$_5$] (94) may be less discrimi-

nating. This observation is suggestive of significant bond-

making in the intermediate and of appreciable bond-breaking

accompanying interaction of substrate and nucleophile for the

hexacarbonyls. It is appropriate to mention that this con-

clusion is reached based on the assumption that the ground

TABLE VI

DISCRIMINATION ABILITIES $k_{2L}/k_{2P(C_6H_5)_3}$ FOR ASSOCIATIVE REACTIONS OF METAL CARBONYLS[a]

Metal Carbonyl	LIGAND		
	$P(n-C_4H_9)_3$	$P(OR)_3$	$P(C_6H_5)_3$
[b] $[Mo(CO)_5]$	....	1.15	1.00
[c] $[(PPh_3)Mo(CO)_4]$	0.46	....	1.00
[d] $[(h^1\text{-DTO})W(CO)_4]$	....	1.09	1.00
[e] $Mo(CO)_6$	11.6	3.78	1.00
[e] $W(CO)_6$	8.0	1.91	1.00
[f] $Co(CO)_3NO$	90.0	1.8	1.00
[g] $[(h^1\text{-tmen})W(CO)_4]$	....	....	1.00
[g] $[(h^1\text{-tmpa})W(CO)_4]$	....	....	1.00

[a] Error limits omitted.

[b] Reference 94; $R = CH_3$

[c] Reference 93; $R' = C_2H_5$.

[d] Reference 61; $R = R' = CH_3$.

[e] Reference 47; $R = R' = C_2H_5$.

[f] Reference 92; $R = R' = CH_3$.

[g] This work, $R' = CH_3$.

TABLE VI--<u>Continued</u>

	LIGAND		
$P(OCH_2)_3CR'$	$P(OC_6H_5)_3$	$As(C_6H_5)_3$	$P(OCH(CH_3)_2)_3$
....	....	0.85	....
1.62	....	0.32	....
2.32	0.48	....	1.22
2.01	0.84	0.58	....
1.67	....	....	....
0.65	0.034	0.002	....
1.46	0.22	....	0.48
2.14	1.03	....	0.09

states of the products are not similar in energy, an assumption which is difficult to assess in the absence of the information about the relative ground state energies of the reaction products.

A similar treatment of the second-order rate constants reported by von Gustorf et al. (95) for the reactions of various solvents with $[Cr(CO)_5]$, reveals that they vary 23 fold. This indicates that $[Cr(CO)_5]$ does not discriminate signficantly among various solvents.

Evidence for the Fluxionality of $W(CO)_4(PPh_3)$ Intermediate: A "site preference" model that can explain a considerable body of kinetic data, was recently proposed by Atwood and Brown (96) which simply says that in octahedral metal carbonyl derivatives, $M(CO)_5L$, carbonyls cis to the substituent L are labilized relative to those in the hexacarbonyls themselves when L is a poorer acceptor of metallic d_π electron density relative to CO. This was attributed to a thermodynamic preference by L to adopt a position in the basal plane of the square-pyramidal intermediate arising through the dissociation of a carbonyl group. Thus, the transition state is stabilized by the presence of the equatorial ligand L relative to that with the CO ligand. Even though, at first glance, one might think that the sixteen valance electron, five-coordinate intermediate could take the form of either square-pyramidal or trigonal-bipyramidal

geometry, substantial evidence has been presented that inter-
mediates of this type exhibit square-pyramidal rather than
trigonal-bipyramidal configuration, both in solution and in
inert matrices (97-105). It is appropriate to mention that
in $[M(CO)_4L]$, where L is a better π-accepting ligand than CO,
the predominant square-pyramidal species is expected to
contain L on the axial position (106). The following is
evidence for the preferred geometry of $[W(CO)_4(PPh_3)]$.

As mentioned previously, the kinetics investigations in
some cases were carried out by monitoring the visible absorp-
tion band of the substrate. Especially, in the case of the
reactions of triphenylphosphine with $(tmen)W(CO)_4$ and
$(tmpa)W(CO)_4$, plots of $\ln(A_t - A_\infty)$ were linear to two or more
half-lives for the reactions carried out under pseudo first-
order reaction conditions. Furthermore, it was determined
that the final reaction products were trans- and cis-$(PPh_3)_2$-
$W(CO)_4$, with the trans isomer predominant (ca. 80%). It is
also known that the substrates and the trans isomer are
yellow. Thus, non-linear plots of $\ln(A_t - A_\infty)$ vs. t are to be
expected, unless the ratio of the molar concentrations of the
product isomers, [trans]/[cis], remains constant over the
course of the reaction (see Appendix IV). Furthermore, the
analysis of the carbonyl stretching spectra of the reaction
solutions, as a function of time, for both of these systems,
also, confirmed that no isomerization occurs on the time scale

of the ligand-substitution process. Consequently, the formation of both cis and trans isomeric products with a constant ratio must involve a process rapid on the time scale of the reaction. One might suggest that a very rapid, intramolecular, non-dissociative isomerization of $L_2W(CO)_4$ takes place on the time scale of the reaction. Darensbourg, however, has confirmed that no such isomerization takes place under the above reaction conditions (107). A fluxional five-coordinate intermediate, such as $[W(CO)_4(PPh_3)]$, could be responsible for this observation.

The results of a series of enrichment experiments, carried out by Darensbourg on cis-$(C_5H_{10}NH)(PPh_3)W(CO)_4$ similar to those previously performed on analogous cis-(amine)-$(PPh_3)Mo(CO)_4$ complexes (93), provide further supportive evidence for the fluxionality of $[W(CO)_4(PPh_3)]$. It was demonstrated that cis-$(C_5H_{10}NH)(PPh_3)W(CO)_4$ undergoes stereospecific enrichment with ^{13}CO to afford cis-$(^{13}CO)(PPh_3)W(CO)_4$. On the other hand, cis-$(C_5H_{10}NH)(PPh_3)W(CO)_4$ reacts with triphenylphosphine in xylene also affording a mixture of cis- and trans-$(PPh_3)_2W(CO)_4$ products, with cis to trans ratio similar to that observed for the reaction of $(tmpa)W(CO)_4$. Both processes, the stereospecific enrichment and the ligand substitution, in all probability proceed via the same intermediate, I_4 (See Fig. 16), in which the phosphorus ligand initially is in the equatorial plane. Based upon the detailed

kinetic results for ligand replacement reactions of (amine)-
$Mo(CO)_5$ (94) and cis-(amine)$(PPh_3)Mo(CO)_4$ (93) substrates,
it is probable that the formation of equatorially-substituted
$[W(CO)_4(PPh_3)]$ involves essentially complete breaking of the
amine-tungsten bond.

The mechanism shown on Fig. 17 explains the dual nature
of the five-coordinate intermediate in its reaction with ^{13}CO
and triphenylphosphine. Since the equatorially-substituted
five-coordinate intermediate (I_4) is the predominant species,
reaction with ^{13}CO affords cis-$(^{13}CO)(PPh_3)W(CO)_4$, while the
steric hinderance dictates that a larger ligand (such as
triphenylphosphine) react mainly with the axially-substi-
tuted intermediate (I_5) to account for the observed products.
Thus, as was proposed by Atwood and Brown (96), these results
are interpretable in terms of a thermodynamically more stable
equatorially-substituted square-pyramidal intermediate (I_4).

A similar mechanistic pathyway has been invoked by Dobson
and Ross (108) to explain the stereochemical outcome of the
reactions of $Ph_3E-Mn(CO)_5$ (E = Ge, Sn) with phosphines and
amines, although no evidence for the fluxionality of the
presumed $[Ph_3E-Mn(CO)_4]$ intermediate was obtained.

In summary, the mechanisms of the reactions of (N-N)-
$W(CO)_4$ (where N-N = tmpa and tmen) with various phosphorus
donor ligands were studied in detail. It was found that the
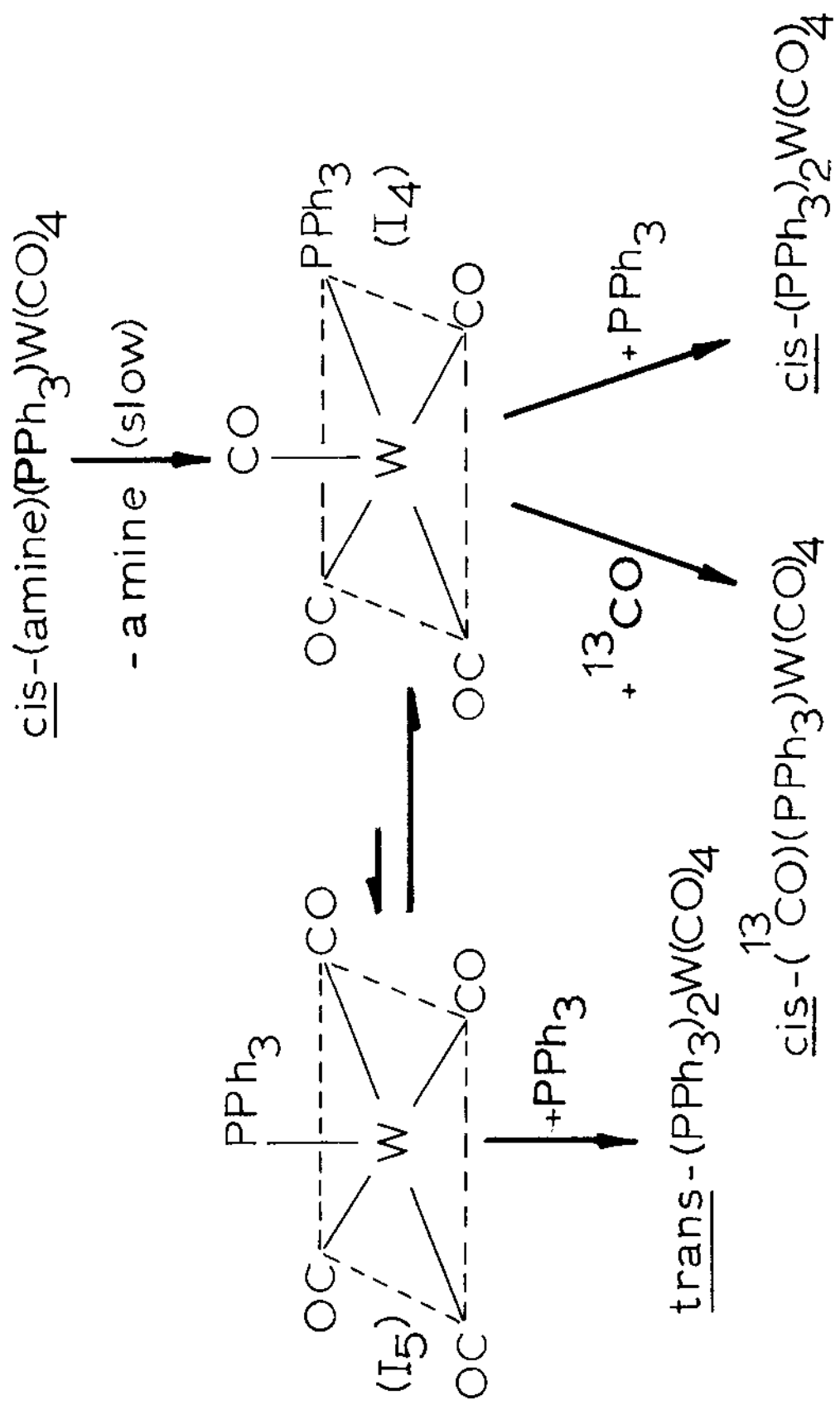simple ring-opening mechanism (See Fig. 7) does not fully explain

Fig. 17--Proposed mechanism for fluxional behavior of $(PPh_3)_2W(CO)_4$

the kinetic data. The modified ring-opening mechanism (See Fig. 16), however, is consistent with the observed rate behavior. Isolation and identification of the intermediates such as $[(h^1\text{-tmpa})(OC)_4WP(OCH_2)_3CCH_3]$ or $[(h^1\text{-tmpa})(OC)_4WP(O_3C_6H_9)]$ is consistent with this mechanism.

The fact that the reactions of $(\text{tmpa})W(CO)_4$ with the phosphorus ligands take place with an appreciable rate at 43°C while the rates of the reactions of $(\text{tmen})W(CO)_4$ become measurable only at temperatures above 100°C is in agreement with the idea that six-membered chelate rings are less stable than the five-membered ones. This difference in the stability of the chelate rings lead to the synthesis of $(\text{NBD})W(CO)_4$ by the direct reaction of $(\text{tmpa})W(CO)_4$ with 2,5-norbornadiene at 50°C.

Another interesting aspect of the problem was determination of the "discrimination ratios" for the reactions of the five-coordinate intermediates, $[(h^1\text{-tmpa})W(CO)_4]$ and $[(h^1\text{-tmen})W(CO)_4]$ with various phosphorus donor ligands. The results shown in Table VI indicate that these intermediates do not discriminate significantly among the various ligands.

The "competition ratios" determined for the reactions of $(\text{tmpa})W(CO)_4$ with the phosphorus ligands indicate that the nucleophilicity of these ligands is dictated by the steric effect except for triphenylphosphine. The ratios obtained for the reactions of $(\text{tmen})W(CO)_4$ with the same ligands, however, do not follow this trend.

Finally, a great deal of convincing evidence is presented which indicates that the five-coordinate intermediate, $[(OC)_4-WP(C_6H_5)_3]$ has a fluxional character. That is, due to the "site preference" model, the triphenylphosphine group is thermodynamically expected to occupy an equatorial position in the basal plane of this square-pyramidal intermediate. This intermediate, however, undergoes a reversible non-dissociative intramolecular rearrangement to form another square-pyramidal isomer which contains the triphenylphosphine group in an axial position. The equilibrium between the two isomers is expected to shift heavily toward the former isomer with the triphenylphosphine group in an equatorial position. The observed data are consistent with the fluxional character of $[(OC)_4WP(C_6H_5)_3]$.

It is appropriate to mention that the intercept obtained in this work for the reaction of $(tmpa)W(CO)_4$ with triisopropyl phosphite at $43.00(5)°C$, 50.06 ± 14.56, is in reasonable agreement with the recalculated intercept from Dobson and Faber's work (50) for this system, which is determined to be 68.64 ± 52.49.

CHAPTER III

KINETICS AND MECHANISM OF THE

OXIDATIVE ELIMINATION REACTION OF

(o-PHENATHROLINE)Mo(CO)$_4$ WITH GeI$_4$

In recent years, a new class of reaction called "oxidative elimination" has been added to the reactions of metal carbonyl chemistry. In this type of reaction, usually, a carbon monoxide ligand is replaced by two univalent ligands derived from the oxidizing agent.

$$M(CO)_n + TX \longrightarrow M(CO)_{n-1}(T)(X) + CO \qquad (III-1)$$
$$(X = Cl, Br, I)$$
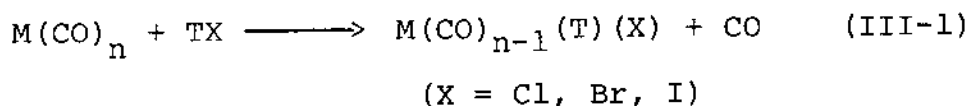
In such reactions, the formal oxidation state of the central metal atom is increased by two, while its coordination number is increased by one. Thus, a metal carbonyl such as (o-phenanthroline)Mo(CO)$_4$, undergoing this type of reaction with GeI$_4$, yields a seven-coordinate complex like (o-phen)Mo(CO)$_3$-(GeI$_3$)(I). Although the synthetic studies of a versatile series of the oxidants including Group IV-A halides and their organic derivatives (TX = R$_n$M'$_{4-n}$; R= alkyl; M' = Sn, Ge; X = Cl, Br, I; n= 0-2) with metal carbonyls such as cis-L$_2$M(CO)$_4$ (L$_2$ = 2,2'-dipyridyl) have been reported (109,110), only the kinetics and mechanism of L$_2$M(CO)$_4$ (where L$_2$ = dipy

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or o-phen) with HgX_2 had been investigated (111,112). An interesting aspect of these reactions is that oxidants (TX) yield two stereochemically different isomeric products of the type $L_2M(CO)_3(T)(X)$, depending on the identity of X, R, and M'. The structures of these isomers are known to be capped octahedral, or capped trigonal prismatic by x-ray crystallographic studies done on the representative complexes (113-115).

In order to gain a better insight into the kinetics and mechanism of oxidative elimination reactions, and to find out whether or not the formation of the two isomeric products took place by the same or through different mechanisms, studies of the kinetics of the reactions of (o-phen)Mo(CO)$_4$ with GeI$_4$ as part of a larger system of reactions of (dipy)W(CO)$_4$ with $(C_6H_5)SnCl_3$, $(n-C_4H_9)SnCl_3$, and $(C_6H_5)_2SnCl_2$, was undertaken. The products of the last three systems were exclusively capped octahedral.

EXPERIMENTAL SECTION

Molybdenum hexacarbonyl was purchased from Climas Molbdenum Company, New York, N.Y. and was used as obtained. 1,10-phenanthroline (o-phen) was obtained from Aldrich Chemical Co., Milwaukee, Wisc., and was used without further purification. Analyzed Reagent, 1,2-dichloroethane, was purchased from J. T. Baker Chemical Co., Phillipsburg, N.J., was fractionally distilled over phosphorus pentoxide and under nitrogen,

and was used within 2-3 days. Germanium tetraiodide (99.999%) was obtained from Alpha Inorganics, Danvers, Mass., and was further purified by the method of Foster and Williston (116). The substrate, (o-phen)Mo(CO)$_4$, was prepared by the method of Angelici and Graham (28). The preparation of the substrate and product identification were carried out under an atmosphere of purified nitrogen. Since germanium tetraiodide is highly hygroscopic, it was kept in a vacuum desiccator placed in a glove bag which had been flushed and filled with purified nitrogen. The handling of this ligand, therefore, was carried out in the nitrogen-filled glove bag.

Infrared spectra were recorded on a Perkin-Elmer Model 621 grating spectrophotometer, and were calibrated against a water vapor band at 1869.4 cm^{-1} (65). Ultraviolet-visible spectra were monitored on a Cary Model 14 spectrophotometer. The kinetic measurements were carried out employing an Aminco-Morrow stopped-flow spectrophotometer coupled with an external Sargent Model MR recorder. Kinetic data were analyzed by a least-squares program on an IBM 360 Model 50 computer at the NTSU Computing Center.

Determination of Reaction Rates

Employing a technique similar to the one described in Chapter II, the optimum wavelength was determined to be 500 nm for monitoring the progress of this reaction. Since the rate of this reaction is very fast, it was impossible to use

conventional techniques described in the previous chapter. Thus, an Aminco-Morrow stopped-flow spectrophotometer was employed. These rates, however, were too slow to be measured on the oscilloscope. To avoid this problem, a Sargent Model MR recorder was coupled with the stopped-flow instrument. The stopped-flow spectrophotometer, which is easily capable of measuring the rates of the reactions having half-lives in the order of msec (when the scope is used), is described in detail by Jernigan (117) and will be briefly discussed here.

For each kinetic run, two 10 ml volumetric flasks, which were dried in the oven for several hours at 120°C and cooled in a desiccator, were purged with purified nitrogen. One flask was charged with a small amount of the substrate, (2 mg) and the other flask was charged with a calculated amount of ligand (enough for pseudo first-order conditions). Both flasks were placed in a constant-temperature water bath (described in Chapter II), and gradually filled to the mark by the solvent. After allowing time for thermal equilibrium, two Hamilton gas-tight syringes equipped with Luer-lok tips and needles were filled with the substrate and the ligand solutions, respectively. By using the three-way values V_1 and V_2 on the appropriate settings, the corresponding "drive syringes" were filled (See Fig. 18). These syringes are surrounded by a block through which water from a constant-temperature bath circulates. After filling the drive syringes, 20 minutes were
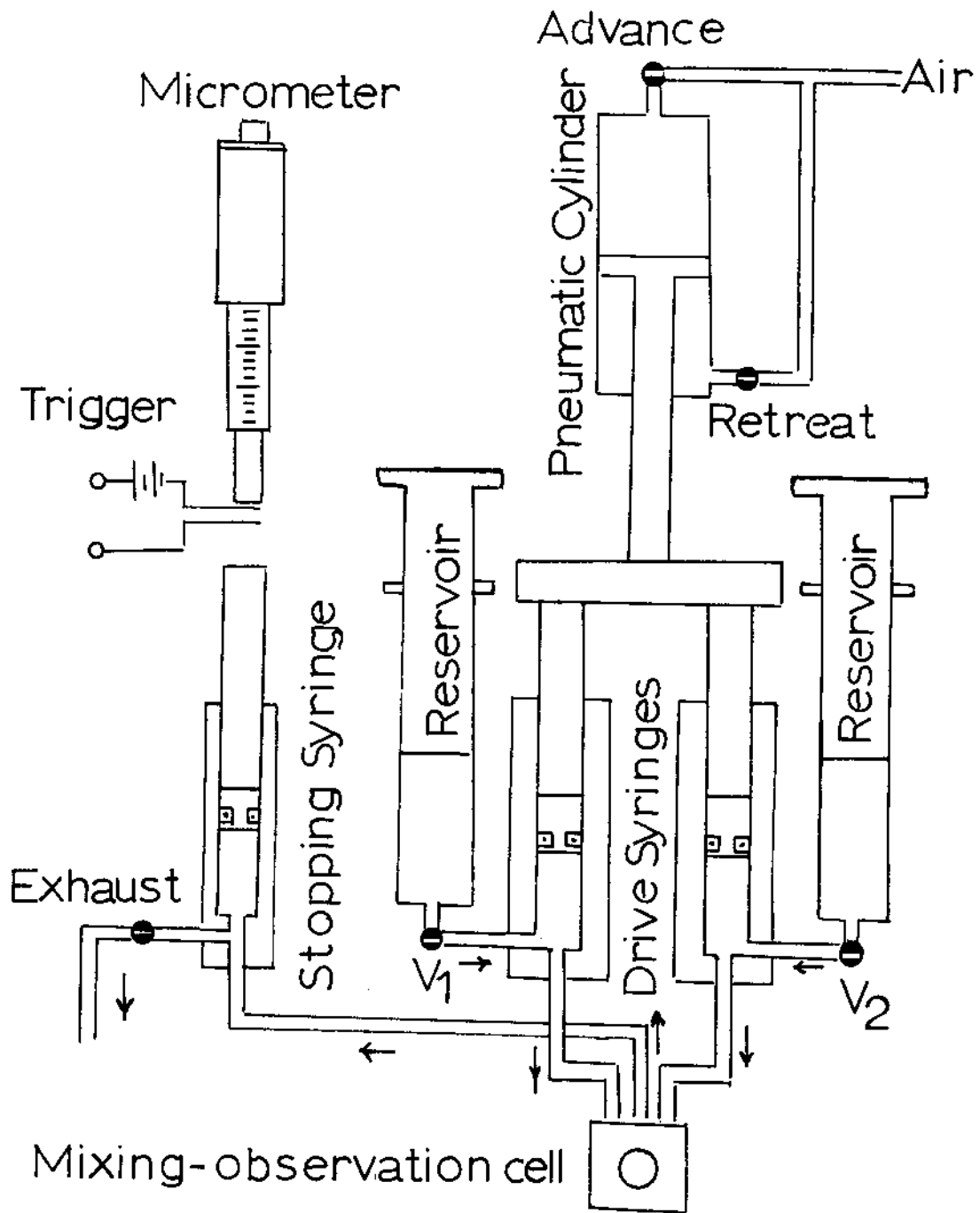
Fig. 12—Schematic diagram of stopped-flow instrument

allowed to obtain thermal equilibrium. Two equal volumes of the reactants were then forced through the 10 mm mixing-observation cell by means of a pneumatically driven block which advances both drive pistons simultaneously. The flow continues until it fills the mixing-observation cell and the "stopping syringe" which, when it stops, activates the trigger to send a signal which is the transmittance change as a function of time across the oscilloscope (a signal which can be stored). The signal may also be sent to the recorder, which can record the change in the transmittance of the solution vs. time. The cell temperature was monitored employing an iron-constant thermocouple attached directly to the cell window. Data were taken from traces of per cent transmittance vs. time and their corresponding absorbance values were calculated. Since it was impossible to obtain the true A_∞ value for each run, the Guggenheim method (118) was employed. Plots of $A_t - A_{t + \delta t}$, where δt is a constant interval at least twice as long as the half-life, were linear to two or more half-lives. A semi-logarithmic least-squares program was employed to fit the data to Guggenheim's method. which computed the corresponding k_{obsd} value for each run. Finally, a linear least-squares program was employed to fit k_{obsd} vs. [L] data, which calculated the k_2 value. This program was designed to reject the points which deviated from the mean by more than two standard deviations. Limits of errors given in parenthesis are one standard deviation.

Identification of the Reaction Product: Two equal

volumes (25 ml each) of a 10^{-3} M solution of (o-phen)Mo(CO)$_4$

and a 10^{-2} M solution of GeI$_4$ in 1,2-dichloroethane, were

mixed in a larger volumetric flask under nitrogen and placed

in a constant-temperature water bath, set at 25.0°C. Samples

were withdrawn periodically and analyzed on a Perkin-Elmer

Model 621 spectrophotometer. After an hour, the solvent was

removed under vacuum and a saturated solution of the product

in dichloromethane was prepared. The infrared spectrum of

this solution was identical with the one obtained by Kummer

and Graham(109) for a solution of (dipy)Mo(CO)$_3$(GeI$_3$)(I) in

dichloromethane. Since the latter product is a capped tri-

goanl prismatic isomer (115), the former product, most

probably, has an identical configuration (because 2,2'-dipyridyl

is similar to o-phenanthroline except with one less phenyl ring).

Results and Discussion: The computer calculated k$_{obsd}$

values for the reaction of (o-phen)Mo(CO)$_4$ with GeI$_4$ at 25°C,

are given in Table VII. As Fig. 19 shows, the plot of k$_{obsd}$

vs. [L] is linear and has a zero intercept within experimental

error.

The results obtained for similar kinetic studies carried

out for the reactions of (dipy)W(CO)$_4$ with some tin-containing

oxidizing agents (119) forming products, which are exclusively

capped octahedral, showed that plots of k$_{obsd}$ vs. [L]^2 were

linear passing through the origin for the reactions monitored

at 25°C. At higher temperatures (95°C and over), however,

TABLE VII

PSEUDO FIRST-ORDER RATE CONSTANTS (K_{OBSD})

FOR THE REACTION OF $(O-PHEN)Mo(CO)_4$

WITH GeI_4 IN 1,2-DICHLOROETHANE AT 25.0°C

10^2 LIGAND CONC. M	10^3 k_{obsd} sec^{-1}
0.629	0.985(11)
0.724	0.804(13)
0.809	0.874(11)
0.889	1.16(1)
1.13	1.40(1)
1.18	1.26(2)
1.53	1.69(3)
1.62	1.83(4)
2.18	2.43(2)
2.54	2.94(6)
2.69	3.30(6)
3.34	3.88(4)
3.70	4.17(11)

$$k_2 = (1.13 \pm 0.03) \times 10^{-1} \text{ M}^{-1} \text{ sec}^{-1}$$
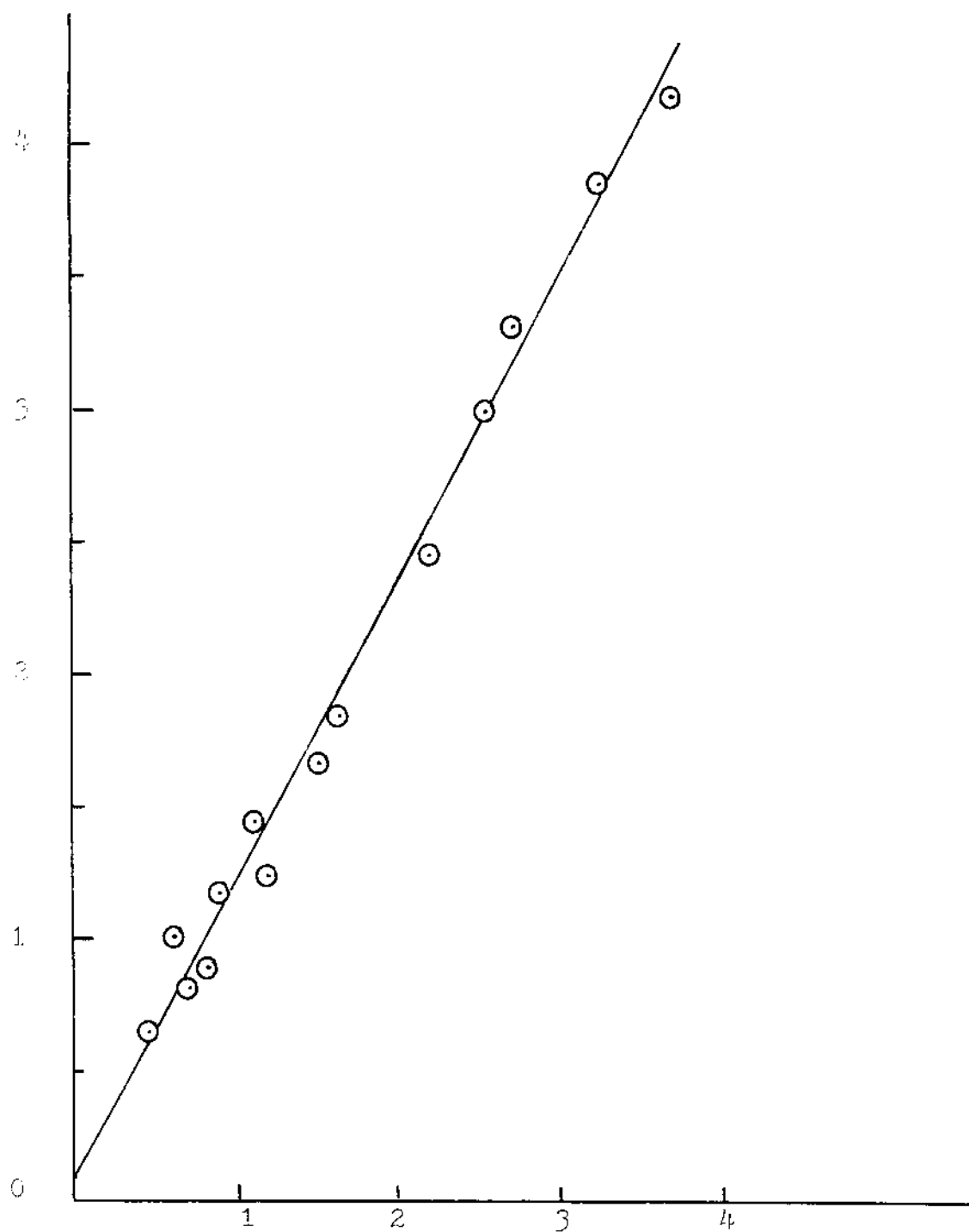
Fig. 19--Plot of k_{obsd} vs. [L] for the reaction of (o-phen)-Mo(CO)$_4$ with GeI$_4$ in 1,2-dichloroethane at 25°C (Ordinate = k_{obsd} x 10^3 sec^{-1}, Abscissa = [L] x 10^2 in moles/l).

these plots were linear with a finite intercept which increased with increasing temperature. The following rate law, therefore, is consistent with the observed behavior:

$$- d[S]/dt = k_1[S] + k_3[S][TX]^2 \qquad \text{(III-2)}$$

(where $S = (dipy)W(CO)_4$ and $TX = R_nSnCl_{4-n}$)

The first-order term, which is only observed at the elevated temperatures, represents the dissociation of a carbon monoxide molecule in a rate-determing step to form a five-coorddinate activated complex, or intermediate, $[(dipy)W(CO)_3]$, which rapidly reacts with one molecule of $(C_6H_5)_2SnCl_2$, followed by some other rapid step(s) to form the final product.

This third-order term is consistent with the reversible formation of a 1:1 "adduct", I_1, followed by the formation of a 1:2 "adduct", I_2, which in some fast step(s) forms the final product. An overall mechanism consistent with such rate behavior is shown in Fig. 20. Assuming steady-state approximation on the intermediate, I_1, one can derive the following rate law (as shown in Appendix V):

$$- \frac{d[S]}{dt} = \frac{k_4k_6[S][L]^2 + k_5k_7[S] + k_6k_7[S][L]}{k_5 + k_6[L]} \qquad \text{(III-3)}$$

Under pseudo first-order reactions conditions, Eqn. III-3 can be written as $- d[S]/dt = k_{obsd}[S]$, where the k_{obsd} term, after some manipulation, can be expressed as below:
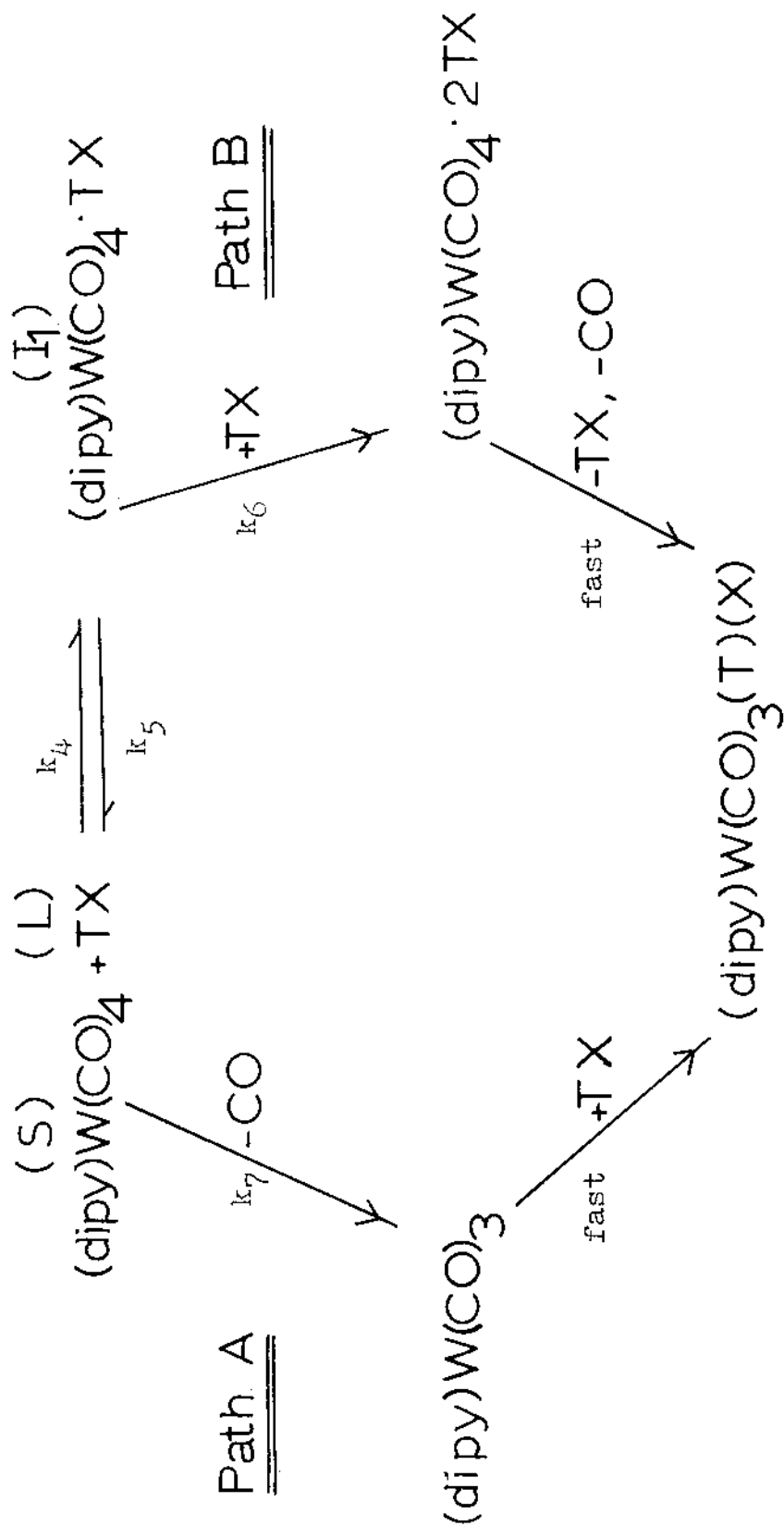
Fig. 20--The overall mechanism for oxidative elimination reactions

$$k_{obsd} = k_7 + \frac{k_4 k_6 [L]^2}{k_5 + k_6 [L]} \tag{III-4}$$

This equation indicates that, if the reaction is carried out at high enough temperature (where path A can compete with path B), plots of k_{obsd} vs. $[L]^2$ should be linear with an intercept of k_7, provided that $k_5 >> k_6 [L]$. Indeed, this is the case for the reaction of $(dipy)W(CO)_4$ with $(C_6H_5)_2SnCl_2$, which is carried out at temperatures above 90°C.

In the case of the reaction of $(dipy)W(CO)_4$ with both $C_6H_5SnCl_3$ and $n-C_4H_9SnCl_3$ (which occur at 25°C), plots of k_{obsd} vs. $[L]^2$ are linear, and pass through the origin. This is because for these two reactions path A is not significant.

On the other hand, as was mentioned above, a plot of k_{obsd} vs. $[L]$ for the reaction of $(o-phen)Mo(CO)_4$ with GeI_4 is linear with a zero intercept (passing through the origin) within the experimental error. One might think that this is a limiting case of the above mechanism. That is, since this reaction is carried out at 25°C, path A is not operative, which simplifies the k_{obsd} term as below:

$$k_{obsd} = \frac{k_4 k_6 [L]^2}{k_5 + k_6 [L]} \tag{III-5}$$

This equation can further be simplified as $k_{obsd} = k_4 [L]$, provided that $k_6 [L] >> k_5$. A closer look at this condition shows that at some point or another, where the ligand concentration

is very small, k_5 should become significant relative to $k_6[L]$. The data, however, provides no indication that at low $[GeI_4]$ (even as low as 4×10^{-3} M) this is the case.

The observed kinetic results, therefore, favor a mechanism in which a single "adduct" is formed in the rate-determining step as shown in Fig. 21.

To summarize, one can say that the observed rate behavior for the reaction of germanium tetraiodide with $(o\text{-phen})Mo(CO)_4$ is consistent with an S_N2 type mechanism. While the reactions of $(dipy)W(CO)_4$ with tin-containing oxidizing agents obey path B or both paths shown in Fig. 20.

It is not presently possible to conclude if the observed differences on the rate law are the result of: (a) contrasting stereochemistry of the reaction products; (b) the identity of the transition metal atom; (c) the identity of the Group IV-A, M', in the oxidant; or (d) the substituent on M'. To arrive at more conclusive results, studies of systems which yield mixtures of both isomers as reaction products should be undertaken, a task which requires the use of more specialized kinetic techniques.

$(O-Phen)Mo(CO)_4 + GI_4$
(S)

$\xrightarrow{k_2}$

$(O-Phen)Mo(CO)_4 \cdot GeI_4$
(I)

fast

$(O-Phen)Mo(CO)_3(GeI_3)(I)$
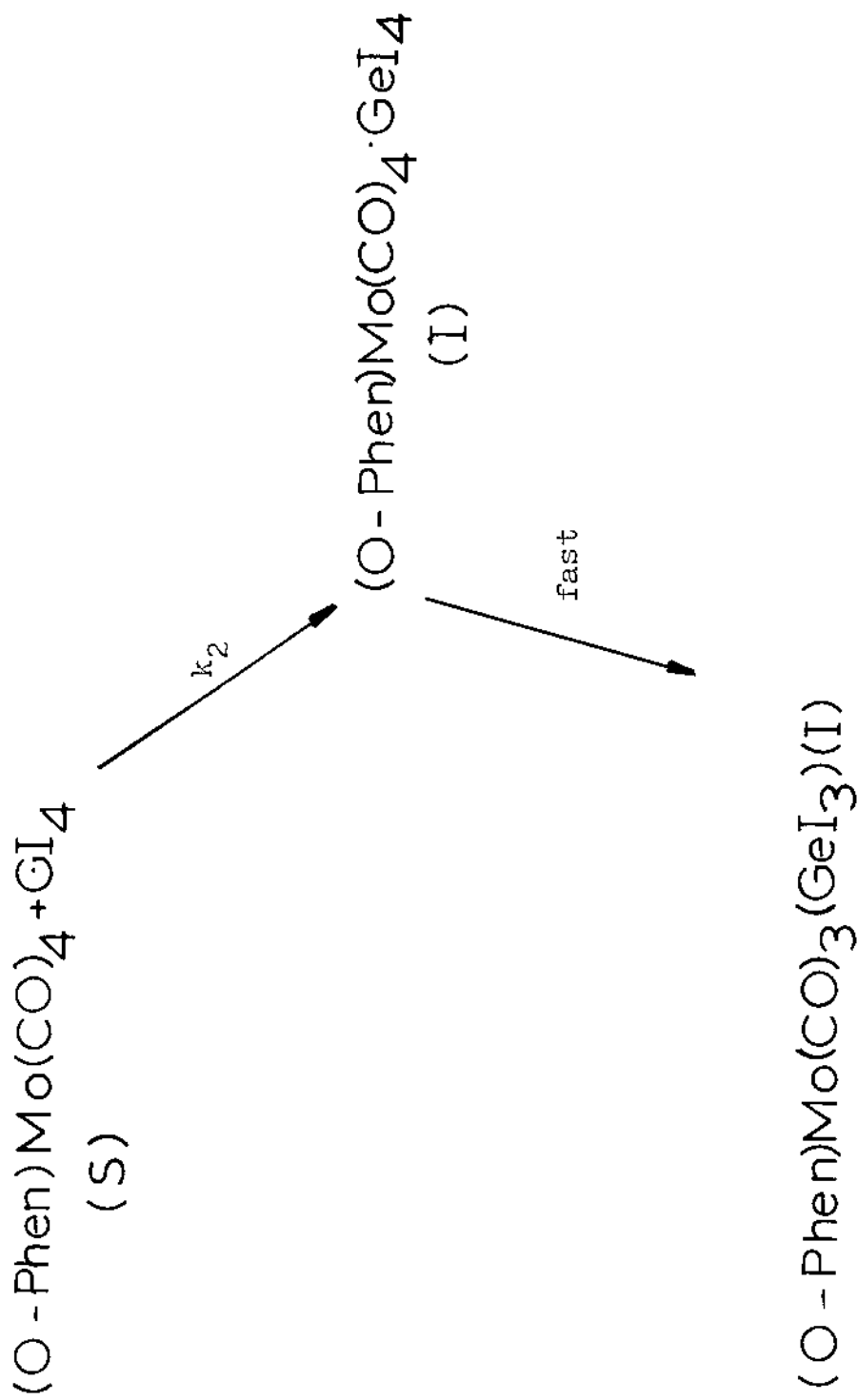
Fig. 21--Modified oxidative elimination mechanism

APPENDIX I

DERIVATION OF THE RATE LAW FOR THE SIMPLE
RING-OPENING MECHANISM

A close look at the first step of the proposed mechanism shown on Fig. 7 indicates that one can write the following two equations:

$$\frac{-d[S]}{dt} = k_5[S] - k_{-5}[I_1] \tag{1}$$

and

$$\frac{d[I_1]}{dt} = k_5[S] - k_{-5}[I_1] - k_6[I_1][L] \tag{2}$$

Since it is desired to obtain a rate law which does not include $[I_1]$, one can solve the second differential equation which is not an easy task. To avoid such a complicated mathematical calculation, as is done most often, a steady-state approximation for the intermediate, I_1, can be assumed. This is based on the assumption that the concentration of this intermediate, which is very small, remains constant during the course of the reaction. Therefore, $\frac{d[I_1]}{dt} = 0$, which can be substituted in Eqn. 2 and $[I_1]$ can be determined.

$$[I_1] = \frac{k_5[S]}{k_{-5} + k_6[L]} \tag{3}$$

$[I_1]$ can then be substituted in Eqn. 1 to obtain the following relationship.

$$\frac{-d[S]}{dt} = \frac{k_5 k_6 \ [S][L]}{k_{-5} + k_6 [L]} \tag{4}$$

which represents the rate law for such a mechanism.

APPENDIX II

DERIVATION OF THE RATE LAW FOR THE MODIFIED

RING-OPENING MECHANISM

Assuming steady-state approximation for the intermediate I_1 (see Fig. 16), one can write:

$$\frac{d[I_1]}{dt} = k_1[S] - k_{-1}[I_1] - k_2[I_1][L] = 0 \qquad (1)$$

which can be solved for $[I_1]$.

$$[I_1] = \frac{k_1[S]}{k_{-1} + k_2[L]} \qquad (2)$$

A similar treatment for the intermediate I_2, yields,

$$\frac{d[I_2]}{dt} = k_2[I_1][L] - k_3[I_2] - k_4[I_2] = 0 \qquad (3)$$

Therefore

$$[I_2] = \frac{k_2[I_1][L]}{k_3 + k_4} \qquad (4)$$

The $[I_1]$ term in Eqn. 4 can be substituted by Eqn. 2, to obtain the following:

$$[I_2] = \frac{k_1k_2[S][L]}{(k_3 + k_4)(k_{-1} + k_2[L])} \qquad (5)$$

One can also assume steady-state approximation for the intermediate I_3,

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$$\frac{d[I_3]}{dt} = k_4[I_2] - k_5[I_3] = 0 \tag{6}$$

which can be solved for $[I_3]$.

$$[I_3] = \frac{k_4}{k_5}[I_2] \tag{7}$$

The value of $[I_2]$ from Eqn. 5 can be substituted in Eqn. 7.

$$[I_3] = \frac{k_1 k_2 k_4 [S][L]}{k_5 (k_3 + k_4)(k_{-1} + k_2[L])} \tag{8}$$

Now that $[I_1]$ and $[I_3]$ terms are calculated, they can be substituted in Eqn. 9 to obtain the overall rate law as shown in Eqn. 10.

$$\frac{-d[S]}{dt} = k_1[S] - k_{-1}[I_1] - k_5[I_3] \tag{9}$$

$$\frac{-d[S]}{dt} = \frac{k_1 k_2 k_3 [S][L]}{(k_3 + k_4)(k_{-1} + k_2[L])} \tag{10}$$

Under "flooding" condition, Eqn. 10 can be simplified as:

$$\frac{-d[S]}{dt} = k_{obsd}[S]$$

where

$$k_{obsd} = \frac{k_1 k_2 k_3 [L]}{(k_3 + k_4)(k_{-1} + k_2[L])} \tag{11}$$

Eqn. 11 can then be rearranged to obtain Eqn. 12.

$$\frac{1}{k_{obsd}} = \frac{k_{-1}(k_3 + k_4)}{k_1 k_2 k_3 [L]} + \frac{k_3 + k_4}{k_1 k_3} \tag{12}$$

According to this equation, plots of $1/k_{obsd}$ vs. $1/[L]$ for various phosphorus ligands should be linear with the slopes and intercepts given below.

$$\text{slope} = \frac{k_{-1}(k_3 + k_4)}{k_1 k_2 k_3} \tag{13}$$

$$\text{intercept} = \frac{k_3 + k_4}{k_1 k_3} \tag{14}$$

One can divide intercept by slope to obtain the following relationship.

$$\frac{\text{intercept}}{\text{slope}} = \frac{k_2}{k_{-1}} \tag{15}$$

Having the values of slope and intercept for each system, the competition ratio of k_2/k_{-1} can be calculated.

APPENDIX III

DERIVATION OF THE RATE LAW FOR THE MODIFIED RING-OPENING MECHANISM WITH A NON-STEADY-STATE APPROXIMATION FOR THE INTERMEDIATE I_2

Assuming steady-state approximation for the intermediate I_1 (see Fig. 16), one obtains:

$$\frac{d[I_1]}{dt} = k_1[S] - k_{-1}[I_1] - k_2[I_1][L] = 0 \qquad (1)$$

which can be solved for I_1.

$$[I_1] = \frac{k_1[S]}{k_{-1} + k_2[L]} \qquad (2)$$

The rate of appearance of intermediate I_2 can be expressed as:

$$\frac{d[I_2]}{dt} = k_2[I_1][L] - (k_3 + k_4)[I_2] \qquad (3)$$

This equation can be solved for $[I_2]$.

$$[I_2] = \frac{k_2[I_1][L] - d[I_2]/dt}{k_3 + k_4} \qquad (4)$$

Upon the substitution of $[I_1]$ from Eqn. 2 into Eqn. 4, one can get:

$$[I_2] = \frac{k_1 k_2[S][L] - (k_{-1} + k_2[L])d[I_2]/dt}{(k_3 + k_4)(k_{-1} + k_2[L])} \qquad (5)$$

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Now let's assume steady-state approximation for the intermediate I_3,

$$\frac{d[I_3]}{dt} = k_4[I_2] - k_5[I_3] = 0 \qquad (6)$$

which can be solved for $[I_3]$.

$$[I_3] = \frac{k_4}{k_5}[I_2] \qquad (7)$$

The value of $[I_2]$ from Eqn. 5 can be substituted in Eqn. 7.

$$[I_3] = \frac{k_1k_2k_4[S][L] - k_4(k_{-1} + k_2[L])d[I_2]/dt}{k_5(k_3 + k_4)(k_{-1} + k_2[L])} \qquad (8)$$

Finally, $[I_1]$ and $[I_3]$ can be substituted in Eqn. 9 to obtain Eqn. 10.

$$\frac{-d[S]}{dt} = k_1[S] - k_{-1}[I_1] - k_5[I_3] \qquad (9)$$

$$\frac{-d[S]}{dt} = \frac{k_1k_2k_3[S][L] + k_4(k_{-1} + k_2[L])d[I_2]/dt}{(k_3 + k_4)(k_{-1} + k_2[L])} \qquad (10)$$

Eqn. 10 represents the overall rate law based on the assumption of non-steady-state behavior for the intermediate I_2.

APPENDIX IV

PROOF FOR THE LINEARITY OF $\ln (A_t - A_\infty)$ VS. t PLOTS

WHEN TWO PRODUCTS ARE PRESENT IN A CONSTANT RATIO

Let us assume that in a reaction two products are formed in a constant ratio of α. Furthermore, let us assume that only A and B absorb light at a given wavelength.

$$
\begin{array}{c}
\text{D does not absorb} \\
A \nearrow \\
\text{absorbs} \searrow \\
\text{B absorbs}
\end{array}
\qquad (1)
$$
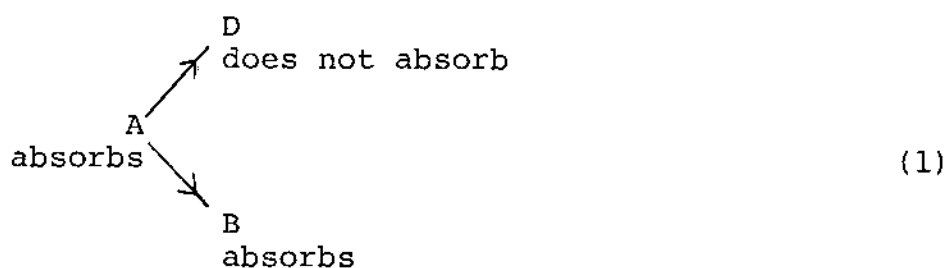
One can then write

$$
P_t = \overline{P}_A [A]_t + \overline{P}_B [B]_t + C \qquad (2)
$$

where P_t is the total absorbance at time t, $\overline{P}_A$ and $\overline{P}_B$ are molar absorptivities of A and B, respectively, while $[A]_t$ and $[B]_t$ represent the concentrations of A and B at a given time t, respectively, and c is a constant.

At t = 0 Eqn. 2 can be simplified as in Eqn. 3.

$$
P_o = \overline{P}_A [A]_o + C \qquad (3)
$$

At infinite time, $\underline{i.e.}$, when all of the starting molecules have reacted, Eqn. 2 takes the following form.

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$$P_\infty = \overline{P}_B [B]_\infty + C \tag{4}$$

Furthermore, at infinite time the sum of molar concentrations of B and D should be equal to $[A]_0$.

$$[B]_\infty + [D]_\infty = [A]_0 \tag{5}$$

Since $[B]/[D]$ ratio is assumed to be constant at all times (except zero time), one can write the following relationships.

$$\frac{[B]_t}{[D]_t} = \alpha \tag{6}$$

$$\frac{[B]_\infty}{[D]_\infty} = \alpha \tag{7}$$

$[D]_\infty$ can be determined from Eqn. 7 as $[D]_\infty = [B]_\infty/\alpha$ and by substitution into Eqn. 5 yields,

$$[B]_\infty + \frac{[B]_\infty}{\alpha} = [A]_0$$

or

$$[B]_\infty = \frac{[A]_0}{1 + 1/\alpha} \tag{8}$$

Eqn. 8 can then be substituted into Eqn. 4.

$$P_\infty = \overline{P}_B \frac{[A]_0}{1 + 1/\alpha} + C \tag{9}$$

One can now subtract Eqn. 9 from Eqn. 2 to obtain,

$$P_t - P_\infty = \overline{P}_A [A]_t + \overline{P}_B [B]_t - \overline{P}_B \frac{[A]_0}{1 + 1/\alpha} \tag{10}$$

Also at a given time, t, the following relationship holds.

$$[B]_t + [D]_t = [A]_o - [A]_t \qquad (11)$$

$[D]_t$ can be determined from Eqn. 6 as $[D]_t = [B]_t/\alpha$ and substitution into Eqn. 11 gives,

$$[B]_t + \frac{[B]_t}{\alpha} = [A]_o - [A]_t$$

or

$$[B]_t = \frac{[A]_o - [A]_t}{1 + 1/\alpha} \qquad (12)$$

This value of $[B]_t$ can be substituted in Eqn. 10 to give,

$$P_t - P_\infty = \bar{P}_A[A]_t + \bar{P}_B(\frac{[A]_o - [A]_t}{1 + 1/\alpha}) - P_B\frac{[A]_o}{1 + 1/\alpha}$$

or

$$P_t - P_\infty = [A]_t(\bar{P}_A - \frac{\bar{P}_B}{1 + 1/\alpha}) \qquad (13)$$

Substracting Eqn. 9 from Eqn. 3 yields,

$$P_o - P_\infty = \bar{P}_A[A]_o + C - (\bar{P}_B\frac{[A]_o}{1 + 1/\alpha} + C)$$

or

$$P_o - P_\infty = [A]_o(\bar{P}_A - \frac{\bar{P}_B}{1 + 1/\alpha}) \qquad (14)$$

One can now divide Eqn. 13 by Eqn. 14, giving:

$$\frac{P_t - P_\infty}{P_o - P_\infty} = \frac{[A]_t}{[A]_o} \qquad (15)$$

It is also known that for a first-order rate law the following equation is true.

$$\ln\frac{[A]_t}{[A]_o} = -kt \tag{16}$$

The $[A]_t/[A]_o$ term in Eqn. 16 can be substituted by its equivalent from Eqn. 15, to give,

$$\ln\frac{(P_t - P_\infty)}{(P_o - P_\infty)} = -kt \tag{17}$$

or

$$\ln(P_t - P_\infty) = \ln(P_o - P_\infty) - kt \tag{18}$$

This means that if the two products are formed in a constant ratio and only two colored species are present, plots of $\ln(P_t - P_\infty)$ vs. t must be linear.

APPENDIX V

DERIVATION OF THE RATE LAW FOR THE OXIDATIVE

ELIMINATION MECHANISM

Assuming steady-state approximation for the intermediate I_1 (See Fig. 20), one obtains:

$$\frac{d[I_1]}{dt} = k_4[S][L] - k_5[I_1][L] - k_6[I_1][L] = 0 \qquad (1)$$

or

$$[I_1] = \frac{k_4[S][L]}{k_5 + k_6[L]} \qquad (2)$$

The rate of disappearance of the substrate can be expressed as Eqn. 3.

$$-\frac{d[S]}{dt} = k_4[S][L] - k_5[I_1] + k_7[S] \qquad (3)$$

Upon the substitution of $[I_1]$ from Eqn. 2 into Eqn. 3, one can write:

$$-\frac{d[S]}{dt} = k_4[S][L] - \frac{k_4 k_5[S][L]}{k_5 + k_6[L]} + k_7[S] \qquad (4)$$

Eqn. 4 can then be simplified to obtain Eqn. 5.

$$-\frac{d[S]}{dt} = \frac{k_4 k_6[S][L]^2 + k_5 k_6[S] + k_6 k_7[S][L]}{k_5 + k_6[L]} \qquad (5)$$

Eqn. 5 represents the rate law for the overall oxidative elimination mechanism shown on Fig. 20.

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