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**"The Mechanism of Olefin Exchange at Five-Coordinate Iron
and Six-Coordinate Chromium."**

by

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This thesis is the author's own account of work carried out by the author under the supervision of Dr. J.A.S. Howell. No part of the work incorporated in the thesis has been incorporated in a thesis submitted for a Higher Degree at any University.

To my Family.

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ABSTRACT.

A number of topics related to olefin exchange in five- and six-coordinate transition metal complexes have been investigated. Alkene exchange at $\text{Fe}(\text{CO})_4 \cdot (\eta^2\text{-alkene})$ is found to follow a simple dissociative pathway with competition ratios for the forward and backward reactions indicating that alkenes are poorer nucleophiles than Group V^a ligands and carbon monoxide. The thermal stability of ligand exchange products with cycloalkenes appears to depend on entering group conformation. In contrast alkadiene substitution at $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-enone})$ appears to follow a "ring-opening" pathway with competing associative and dissociative initial steps since the rate of reaction depends on the electronic and steric properties of the entering group. The stereochemistry of the products of the reaction using the asymmetric entering group 7-methylcycloheptatriene suggests no significant stereospecificity for the substitution. Work on alkadiene exchange at the six-coordinate centre in $\text{Cr}(\text{CO})_4 \cdot (\eta^4\text{-alkadiene})$ indicates that the rate is dependent on substrate concentration only. Perfect first-order kinetics are found with the exchange rate influenced by the electronic properties of the leaving group. When using the substrates $\text{Fe}(\text{CO})_4 \cdot (\eta^2\text{-alkene})$ or $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-alkadiene})$ ligand exchange may be accompanied by isomerisation of the free olefin. The isomerisation is interpreted in terms of a π -allylmetalhydride mechanism. In the case of $\text{Fe}(\text{CO})_4 \cdot (\eta^2\text{-alkene})$ the catalytic species seems to be generated through a carbonyl bridged intermediate; the equilibrium free alkene ratios indicate thermodynamic control. Alkadiene isomerisation at iron and ruthenium centres yields conjugated dienes as the primary products; however ratios of the free dienes generated suggest rather different rates of isomerisation and dechelation of the ligands at the two types of metal centre.

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1.1 A HISTORICAL PERSPECTIVE.

The systematic study of transition metal organometallic chemistry is generally accepted to have originated in the early 1950's with the publication of the Dewar-Chatt-Duncanson model for bonding in complexes between transition metals and alkenes. The volume of work published in the field has shown a continuous expansion since that period, with emphasis primarily directed towards the development of synthetic methods of investigating the reactivity of the new class of compounds. Quantitative methods of study, which are needed if an adequate theoretical framework for describing the underlying trends in reactivity is to be established, have received considerably less attention. Indeed in 1967 it was still possible to produce a review article covering all work published in the field of ligand substitution in metal carbonyl complexes, perhaps the most extensively studied group of organometallic complexes¹. Nevertheless, research into mechanistic transition metal organometallic chemistry does offer considerable rewards in determining the factors influencing the reactivity of low valent transition metals, and for this reason an increasing number of workers have taken advantage of the opportunities offered by the growth of this new area of study.

With the advent of systematic organometallic chemistry it has become possible to study the reactions of low valent transition metals in non-polar media^{2,3}, with consequent advantages in terms of mechanistic interpretation. Unlike transition metal coordination complexes, which are generally studied in polar media such as water or methanol, organometallic complexes can be studied under conditions where solvent effects are negligible. Accordingly rather more subtle influences on transition metal

reactivity can be identified when studying organometallic complexes. Indeed a number of recent publications⁴⁻⁶ have attempted to use molecular orbital treatments to describe the change in reactivity of an organic ligand on coordination to a low valent transition metal centre.

This type of approach to transition metal reactivity offers exciting possibilities, particularly in view of the importance of transition metals as catalysts in organic synthesis.

1.2 CLASSIFICATION OF METAL TO LIGAND BOND TYPES IN ORGANOMETALLIC COMPLEXES.

In view of great variety of transition metal organometallic complexes which have been described in the literature it is perhaps appropriate to outline the most commonly encountered forms of metal to ligand bonding. The most convenient model for describing bonding in transition metal complexes is that put forward by Dewar, Chatt and Duncanson to account for the structures of complexes of silver and platinum with alkenes⁷. The synergistic, or "back bonding", model originally proposed has been developed considerably in recent years and now provides a versatile tool for describing the structure of a wide variety of organometallic species⁸. The model envisages two concurrent bonding processes in the formation of a metal to ligand bond :

(a) σ -donation : This process involves donation of electron density from a suitable σ -type orbital of the ligand to a suitably orientated σ -type acceptor orbital of the metal. It should, however, be noted that the donor orbital is only of σ -symmetry and may in fact be of σ^* or π -character. The term " σ -donor" is often used to describe the latter case.

(b) The π -acceptor process : This process involves transfer of electron density from a π -type orbital of the metal to a suitably orientated π -type orbital of the ligand. Again it should be noted that the acceptor orbital is only required to be of π -symmetry and may in fact be of π^* or d^* character.

The bond order of the resulting species is dependent on the relative importance of the two competing processes for each of the ligands concerned; and consequently ligands are often described as " σ -donors" or " π -acceptors" depending upon which of the processes predominates in the particular case. A special term has arisen to describe the type of bond formed between a metal and an unsaturated organic ligand. Since, in this case, both the ligand donor orbital and the ligand acceptor orbital are of π -character the resultant complex is termed a metal π -complex. A typical example of a " σ -donor" ligand is piperidine which bonds to the metal by a σ -bond through the amino group. Since the nitrogen has no available orbitals of π -symmetry to serve as π -acceptors σ -bonding only is observed with this type of ligand⁹. The carbonyl group is a good example of a π -acceptor ligand. In this case the σ -donor orbital of the ligand is a formally antibonding σ^* -molecular orbital, whilst the acceptor orbital is of π^* -character.

An examination of the literature indicates that a wide variety of ligand types have been used in studies of substitution mechanisms operating at metal centres; " σ -donor" and " π -acceptor" ligands are represented in addition to more typical ligands exhibiting both donor and acceptor properties. To date the majority of published kinetic and mechanistic work has been concerned with the study of ligand substitution or ligand isomerisation occurring in mononuclear metal complexes. It is only recently that metal-metal bonded complexes have become the objects of mechanistic

study¹⁰. Complexes of metals in the d^6 , d^8 and d^{10} electron configurations have received most attention in the literature.

When considering the mononuclear metal complexes it is noticeable that species involving organic π -ligands have received relatively little attention. In view of the extensive use of complexes of coordinated organic ligands as intermediates in organic and organometallic synthesis, and of the importance of transition metal catalysts in the manufacture of organic chemicals, detailed work in this area seemed desirable. The work described in this thesis is concerned with the mechanism of π -ligand exchange at five and six-coordinate transition metal centres; rather more information is available for complexes of the four coordinate metals¹¹.

In choosing complexes for kinetic and mechanistic study a number of factors need to be taken into consideration. Perhaps the most important consideration is the need for a substrate whose physical properties are suited to rapid and accurate spectroscopic measurement, thus permitting convenient monitoring of the reaction. Early workers found that metal carbonyl complexes were readily synthesised and could be monitored conveniently by means of infrared spectroscopy. For this reason a large number of publications have been concerned with the mechanisms of substitution of metal carbonyl complexes despite the poor " σ -donor" properties of the carbonyl group which make it a rather atypical ligand. The very strong infrared and ultraviolet absorption of this ligand enable studies to be carried out at metal complex concentrations of the order of 10^{-4} Mol dm^{-3} ; whilst the sensitivity of the infrared spectrum of the carbonyl group to small changes in the electron distribution at the metal centre enable the experienced chemist to follow the course of a reaction in great detail. Infrared intensities may further be used to calculate metal-ligand bond strengths¹² and to obtain information concerning the symmetry

of the substrate and hence its structure. In view of the large amount of information to be gained about the course of a reaction taking place at a metal carbonyl centre employing such simple and inexpensive methods of spectroscopic analysis¹³ the relative paucity of information on other types of metal complex is perhaps not surprising. However with the increasing availability of more sophisticated instrumental techniques such as Fourier Transform nuclear magnetic resonance spectroscopy it is to be hoped that the range of ligand types investigated kinetically will widen rapidly.

1.3 CLASSIFICATION OF LIGAND SUBSTITUTION PATHWAYS.

On the basis of the information currently available it is possible to outline a number of elementary processes which are believed to operate during ligand substitution at a low-valent transition metal centre. The principal processes are given in the following subsections; it should be emphasised at this stage that the term "Nucleophilicity" should be interpreted with caution when applied to organometallic systems since such systems involve ligands with both σ -donor and π -acceptor properties¹⁴. For this reason the Langford and Gray terminology¹⁵ will be used in preference to the more common Ingold classification wherever possible.

1.3.1 The "Dissociative" Pathway.

The "Dissociative" or "d" process is the analogue of the Ingold S_N1 (limiting) mechanism when applied to organometallic systems. The rate determining step of the "d" process is taken to involve complete dissociation of the leaving group to form a coordinatively unsaturated intermediate; the free coordination site is then rapidly attacked by the entering group. For the "d" process to be assigned it is necessary that a stable intermediate be observed, whilst an " I_d " description is to be

FIGURE 1-1

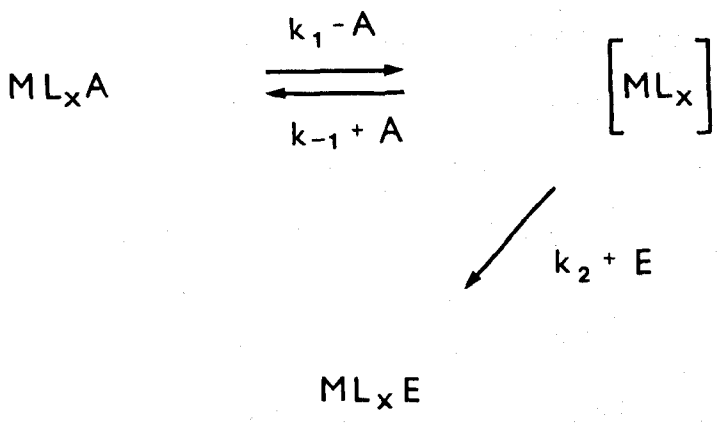
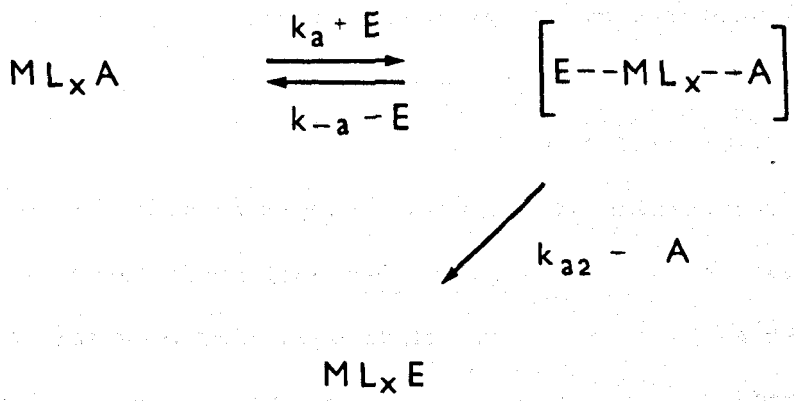


FIGURE 1-2



preferred if an intermediate cannot be directly observed. The "d" process involves a rate determining step in which the metal-ligand bond order decreases and for this reason a reaction proceeding by this pathway would be expected to show a small positive activation entropy accompanied by a high activation enthalpy. A true "d" process should display a negligible solvent effect and should be completely independent of the entering ligand concentration if pseudo-first-order conditions are employed. This is reflected in the applicable rate law, given as equation (1-1).

$$(1-1) \quad \frac{-[dS]}{dt} = k_1[S]$$

FIGURE 1-1 illustrates a typical example of a reaction proceeding by the "d" pathway.

1.3.2 The "Associative" Pathway.

The "Associative" or "a" pathway is the organometallic analogue of the Ingold S_N^2 (limiting) mechanism. The rate determining step is taken to involve the formation of an intermediate in which both entering and leaving groups have formed bonds to the metal centre. As in the case of the "d" mechanism the intermediate must be observed for the pathway to be unambiguously assigned. When considering organometallic substrates it should be remembered that an eighteen electron transition metal complex would form a twenty electron intermediate if substitution were to take place by an "a" pathway. This type of intermediate would be expected to be favoured only for complexes of low initial coordination number or large atomic radius and it is interesting that "a" type kinetic behaviour is often seen to become more important in going down a metal triad where the latter effect would be expected to apply¹⁶. In considering the "a" process it would be expected that rates of reaction would be markedly effected by both entering group and solvent properties, since the intermediate involves

increased bond order¹⁷. The increased bond order would also be expected to be reflected in a large negative activation entropy whilst the absence of bond-breaking should result in a relatively small activation enthalpy.

The strong entering group dependency of the "a" pathway is illustrated by the applicable rate law as given in equation (1-2) :

$$(1-2) \quad \frac{-d[S]}{dt} = k_a [S] [L]$$

FIGURE 1-2 illustrates a typical reaction pathway.

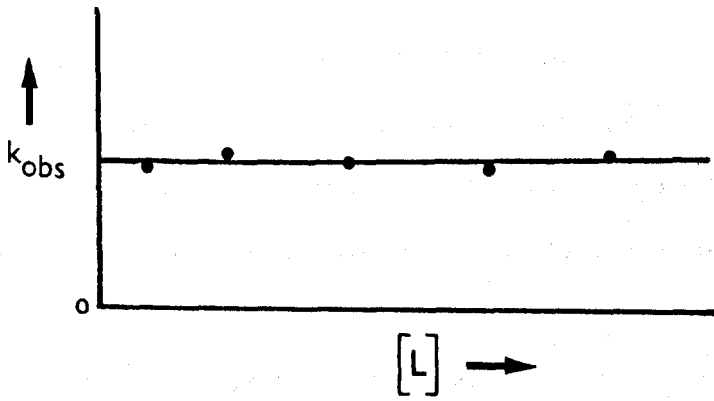
1.3.3 The "Interchange (dissociative)" Pathway.

The "Interchange (dissociative)" or "I_d" pathway resembles the S_N1 (general) mechanism of the Ingold classification and is therefore taken to involve a transition-state in which both entering and leaving groups have formed bonds to the metal centre. For a process to be designated as "I_d" the transition-state must involve more bond-breaking than bond-making character. For this reason the pathway may be seen as a ligand-assisted dissociative mechanism without formation of an observable intermediate. Solvent effects in "I_d" systems should not be large but rates will increase in polar solvents capable of behaving as additional entering groups. Covey and Brown¹⁸ have provided a detailed analysis of the "I_d" pathway which appears to be very common in transition metal substitution reactions. The rate law applicable to "I_d" systems has been demonstrated to vary with the solvent properties¹⁸ but the general form is given in equation (1-3).

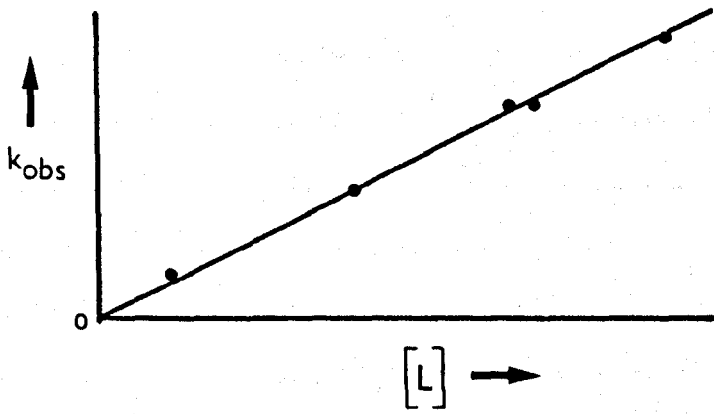
$$(1-3) \quad \frac{-d[S]}{dt} = k_1 [S] + k_a [S] [L]$$

It should be noted that the k_a term in the rate law is much less strongly influenced by entering group properties than the corresponding term in the "a" process rate law, and that the magnitude of the observed k_a value for a

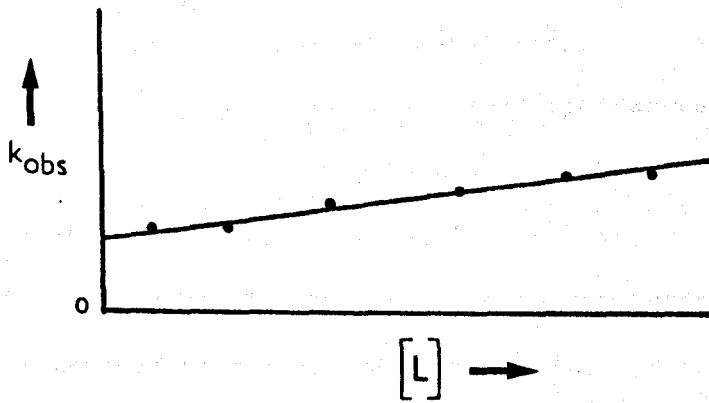
FIGURE 1-3



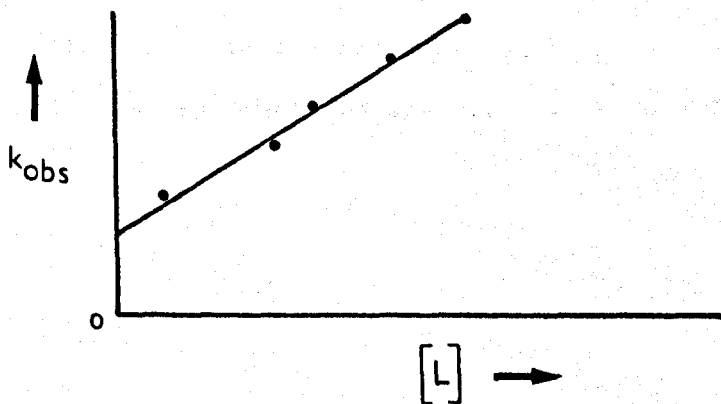
d



a



d



a

given entering group will be seen to diminish with increasing solvent coordinating power. Since " I_d " processes involve transition-states with more bond-breaking than bond-making character Activation Entropies should be close to zero in most cases with Enthalpies resembling those of true "d" processes. The " I_d " process provides perhaps the most plausible explanation of entering group dependent kinetics in systems where expansion of the metal coordination number is unlikely for kinetic or steric reasons.

1.3.4 The "Interchange (associative)" Pathway.

A fourth mechanism commonly invoked to describe organometallic systems is the "Interchange (associative)" or " I_a " pathway. The " I_a " process resembles the S_N2 (general) mechanism of Ingold, involving the formation of a transition-state in which bond-making is more important than bond-breaking. In terms of kinetic behaviour it is very difficult to discriminate between "a" and " I_a " processes, with the latter distinguished only by the absence of an observable intermediate. Solvent and entering group effects should be of much greater magnitude than those observed for " I_d " processes though rate equation (1-3) applies to both " I_d " and " I_a " processes. The " I_a " process may be distinguished from the " I_d " process by the fact that $k_a[L] \gg k_i$ except at low [L], whilst the " I_a " is distinguished from the "a" by the non-zero intercept of a plot of k_{obs} (the pseudo-first-order rate constant) against [L] for the former.

The differences in the forms of the k_{obs} against [L] plots for each of the mechanisms so far outlined are given in FIGURE 1-3.

1.3.5 The "Ring-opening" Mechanism for substitution of Chelating ligands.

When ligand substitution at a low valent transition metal centre involves displacement of a polydentate chelating ligand the observed kinetic behaviour may not resemble that to be expected for any of the mechanisms so far described. It was for this reason that Dobson and coworkers proposed the so-called "Ring-opening" mechanism¹⁹. The mechanism is illustrated in FIGURE 1-4 and provides the general rate law given in (1-4):

$$(1-4) \quad \frac{-d[S]}{dt} = \frac{k_1 \cdot k_2 [S] [L]}{k_{-1} + k_2 [L]}$$

where (L= a mono or bi-dentate entering group).

Detailed consideration of the mechanism indicates that three different types of kinetic behaviour may be displayed by "ring-opening" systems.

(a) If rechelation of the free end of the leaving group, as represented by k_{-1} , is less favoured than displacement by the entering group, $k_2 [L]$, observed kinetic behaviour will follow equation (1-5) :

$$(1-5) \quad \frac{-d[S]}{dt} = k_1 [S] \quad \text{when } k_{-1} \ll k_2 [L]$$

(b) When both entering and leaving groups have similar bonding properties it is likely that rechelation of the leaving group, k_{-1} , will be favoured due to the very high effective leaving group concentration. (see the review by Angelici¹). The applicable rate law then becomes (1-6) :

$$(1-6) \quad \frac{-d[S]}{dt} = \frac{k_1 k_2 [S] [L]}{k_{-1}} \quad \text{when } k_{-1} \gg k_2 [L]$$

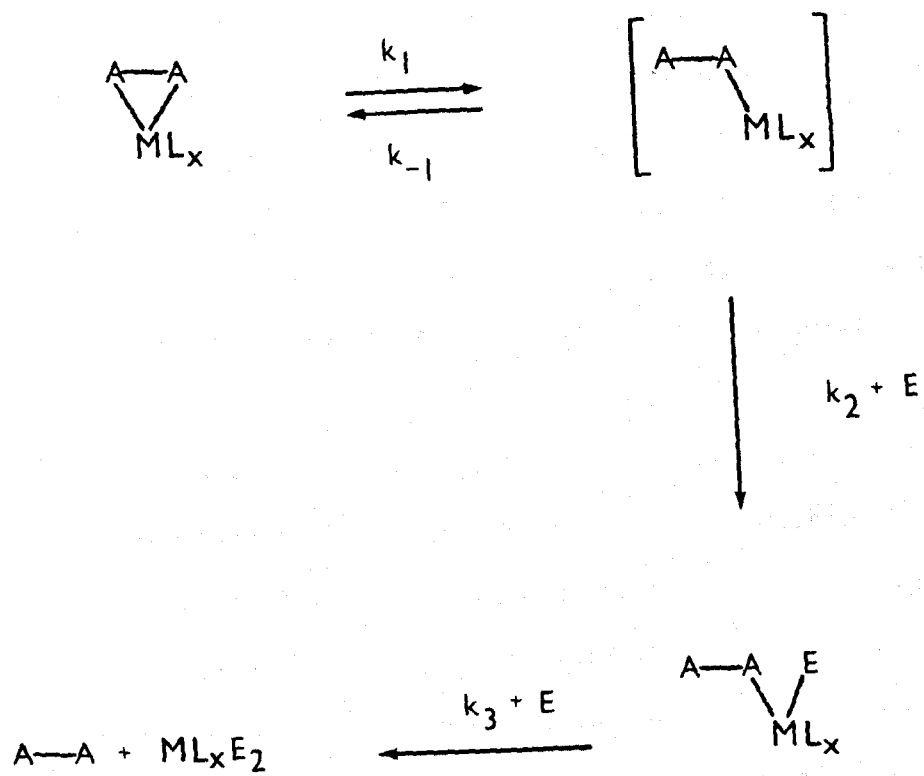


FIGURE 1-4

(c) Under conditions where $k_1 \approx k_2[L]$ for the range of ligand concentrations studied no simplification of the rate law given in (1-4) will be applicable and consequently plots of the pseudo-first-order rate constant (k_{obs}) against $[L]$ will not be linear. Condition (c) is the only case where a "ring-opening" mechanism can be unambiguously invoked from the kinetic evidence. Characteristic plots of k_{obs} against $[L]$ for each of the three conditions are provided in FIGURE 1-5. It will be appreciated from the plots that condition (a) is kinetically indistinguishable from a "d" pathway and that condition (b) from an "a" or "I_a" pathway.

The "ring-opening" pathway is the last of the generally applicable mechanisms which need to be considered in this introductory section; schemes of more specialised application will be outlined at the relevant points in the survey. It should be stressed that the "ring-opening" model put forward in this section covers only the case where the initial "ring-opening" proceeds dissociatively; Dobson's group have also encountered more complicated systems involving a competing associatively activated step.

1.4 FACTORS INFLUENCING THE REACTIVITY OF TRANSITION METAL COMPLEXES.

Before attempting to discuss the implications of the available experimental evidence it is first necessary to outline the factors which are presently believed to influence the reactivity of transition metal complexes. Five different influences on reactivity have been put forward in the literature and these will be discussed in turn in the following sections.

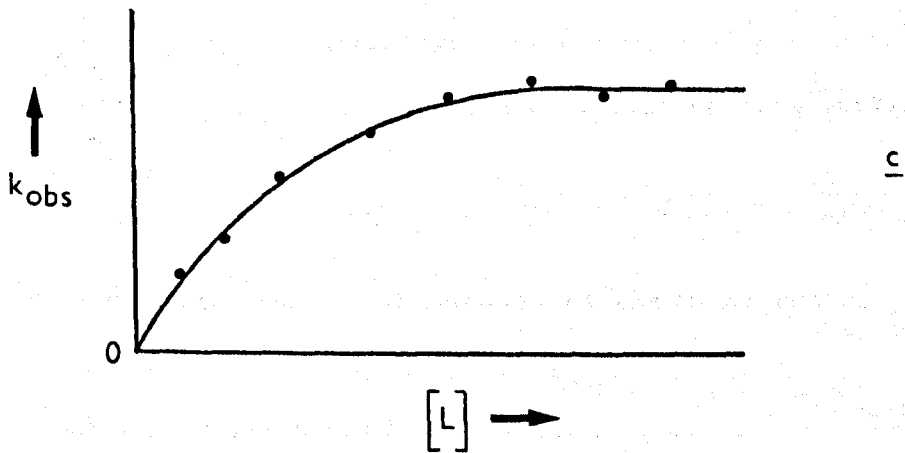
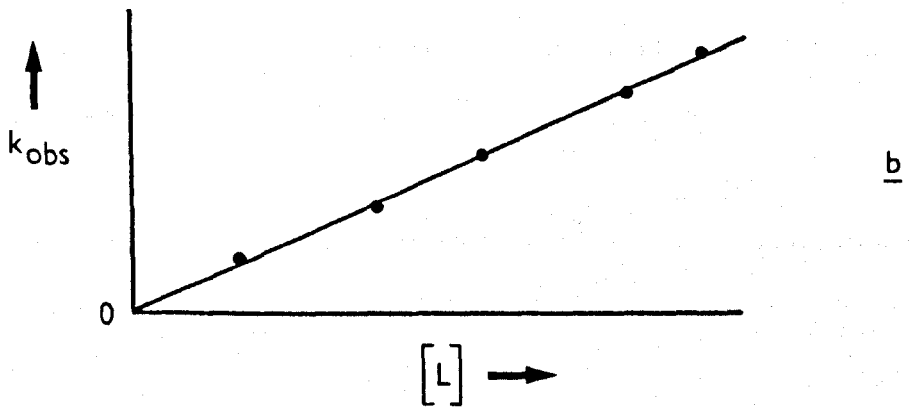
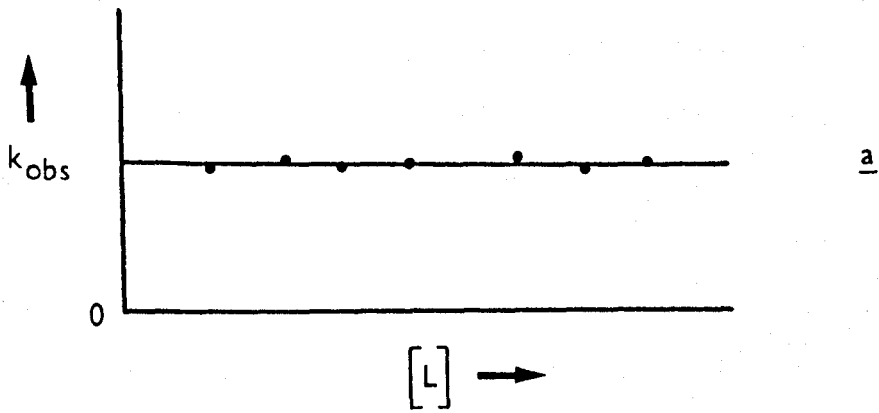


FIGURE 1-5

1.4.1 Effective Atomic Number.

The concept of Effective atomic number, or E.A.N., was proposed by C.A.Tolman specifically to account for marked preference of low valent transition metals for particular electron configurations. The main tenets are laid out in the author's 1972 review article²⁰.

"(a) Diamagnetic organometallic complexes of transition metals may exist in significant concentration at moderate temperatures only if the metal's valence shell contains 16 or 18 electrons. A significant concentration is one that may be detected spectroscopically or kinetically and may be in the gaseous, liquid or solid state.

(b) Organometallic reactions, including catalytic ones, proceed by elementary steps involving only intermediates with 16 or 18 electrons."

Although originally postulated as an empirical rule the E.A.N. concept has been given a theoretical basis following a series of papers by Mingos²¹⁻²³. A topological Huckel model is employed depending on full utilisation of metal valence orbitals.

1.4.2 Coordination Number and Geometry of the Metal centre.

A second factor which has been observed to exert a systematic effect on the reactivity of transition metal complexes is the coordination number of the metal centre. A number of experimental studies have given evidence for subtle electronic and steric effects in examining the behaviour of a series of complexes with similar coordination and geometry but different metal centres. A good example of this approach is provided by a study of the formally four-coordinate series $\text{Ni}(\text{CO})_4$, $\text{Co}(\text{NO})(\text{CO})_3$ and $\text{Fe}(\text{NO})_2(\text{CO})_2$. The

similar structure and properties of these complexes enable comparison of metal reactivities to be carried out. In this case²⁴ increasing the electron density at the metal in passing from Ni to Fe increases the importance of the ligand-dependent component in the rate law derived from kinetic measurements. It is interesting to note that a sophisticated molecular orbital calculation carried out for a similar series of formally four-coordinate complexes produced essentially the same results²⁵. A number of theoretical studies have been produced in an attempt to account for the observed similarities in reactivity of complexes of different transition metals sharing a common coordination number and geometry²⁶⁻³³. The present position is summarised in a review by Mingos³¹, which employs the following rationalisation :

"..the spatial extent, hybridisation, and energies of the valence orbitals of an ML_n fragment are very sensitive to the geometric arrangements of the ligands.."

and in the transition-state the fragments "remember" the position of the low energy orbitals of the parent complex thus effecting product structure.

1.4.3 The Electronic Configuration of the Metal Centre.

Experimental evidence suggests that the strength of a bond formed between a transition metal and a π -acceptor ligand is markedly dependent on the oxidation state of the metal. A further observation is that metal cations form complexes with σ -donor ligands more readily than their isoelectronic neutral analogues. The first attempt to explain these observations employed the Hard and Soft Acid and Base theory of Pearson³⁴. In the Pearson nomenclature metal centres in complexes of low valent transition metals are classified as "soft" acids and as such would be

expected to form strong bonds with "soft" bases such as π -acceptor ligands. An increase in the oxidation state of the metal would be expected to increase the "hard" acid character of the species resulting in increased metal-ligand σ -bonding.

Using molecular orbital arguments it is possible to rationalise the observed trends on the basis of the greater $\pi^* - d\pi$ ligand-metal orbital overlap for metal in a low oxidation state bonding to a π -acceptor ligand, when the π -bonding capability is compared with that of a metal in a higher oxidation state.

The result of the contrasting effects of increased nuclear charge and increasing $d\pi$ electron density are illustrated by the general reactivity order towards π -acceptor ligands in going down a metal triad. The observed order for the reactivity of the Group VI^b metals with π -ligands is $Mo > Cr >> W$. In this case the order reflects the maximum electron polarisability reached at Mo which has a lower effective nuclear charge than W owing to the absence of the lanthanide contraction for the second row transition element. It is significant that thermochemical measurements³⁵ show that the reactivity of the Group VI^b metals towards σ -donor ligands decreases in the order $W >> Mo > Cr$ in line with the decrease in effective nuclear charge.

1.4.4 The Role of Auxiliary Ligands.

The effect of auxiliary ligands in determining the site and rate of bond breaking in substitution reactions has been one of the most intensely studied areas of mechanistic organometallic chemistry since it became apparent that a number of different types of auxiliary ligand will cause labilisation of carbonyl groups towards dissociation¹. Brown and coworkers have carried out extensive investigations of the so-

called "cis-labilisation" effect in the substitution of metal carbonyl complexes^{36,37} but as yet no convincing general model labilisation of leaving groups by auxiliary ligands has been produced. Angelici, in his 1967 review¹, attempted to subdivide ligands into two classes :

(a) Labilising towards carbonyl dissociation;

Halides, chelating nitrogen ligands such as o-phenanthroline, and nitro groups.

(b) Non-labilising towards carbonyl dissociation;

Phosphines, phosphites, isonitriles, arsines, stibines and sulphur ligands.

The reviewer also noted that monodentate amines were readily displaced from aminepentacarbonylmetal complexes.

The two groups fall broadly into the "hard" and "soft" base categories respectively of the H.S.A.B. scheme³⁴. However the detailed behaviour of the metal complexes is difficult to rationalise using either simple H.S.A.B. descriptions or conventional molecular orbital approaches. Recent experimental and theoretical studies have indicated that the orders of reactivity observed reflect a number of factors, which are often subtle. A good example is the labilisation order for complexes of the type $[M(CO)_5X]^{n+}$, where ($M = Cr; n = -1; M = Mn; n = 0; X = Cl, Br, I$). For this series the lability of the carbonyls cis to the halide varies in the order $Cl > Br > I$. Fenske and coworkers³⁸ have explained the observed labilisation order in terms of a "direct-donation" of lone pair electron density from the halogen p_z orbital into the π^* orbitals of the cis-carbonyl ligands. The halogen-carbonyl bond would be expected to be strongest for the iodo complex due to the size and symmetry of the halogen p_z orbitals and the low lability of the complex towards carbonyl

dissociation seems to support this argument. The situation is less clear for labilising ligands with π -acceptor properties as well as a σ -donor capability; the most plausible explanation of the effects of auxiliary ligands on the reactivity of such complexes rests with the ability of the ligands to stabilise the first transition-state of the substitution process. This may be seen as either stabilisation of a coordinatively unsaturated species generated by a dissociative process (typically for complexes with auxiliary ligands which are good π -acceptors); or as a steric rate enhancement due to increased geometrical relaxation energy in the transition-state (where bulky auxiliary ligands are present)³⁷.

More detailed discussion of these effects will be deferred until the appropriate point in the survey of experimental observations.

1.4.5 Entering Group Properties.

The behaviour of a substrate towards a variety of different types of entering group has often been used successfully to provide information about the elementary processes responsible for ligand substitution. It is therefore rather unfortunate that the majority of reported kinetic studies in organometallic chemistry have used a very restricted range of entering groups. Phosphines and phosphites have been the most common entering groups in published work, whilst other trivalent Group V^a ligands have been used extensively. Carbon monoxide has been widely employed as an entering group both in substitution experiments and in carbonyl exchange reactions. Very little information is available for other types of ligand.

Various authors^{1,39} have been tempted to devise tables of entering group "Nucleophilicities". It must be remembered however that several factors are involved in the relative success or failure of a given ligand

as an entering group and, bearing this in mind, the evidence of relevant physical measurements provides a better insight into entering group reactivity. Three useful recent studies of simple, neutral inorganic ligands are available⁴⁰⁻⁴² whilst Tolman⁴³ has provided a simple model for the formation equilibrium constants of a variety of metal-alkene complexes.

Yarbrough and Hall⁴⁰ have carried out a study of a number of complexes of general formula $M(\text{CO})_5 \cdot L$, where ($M = \text{Cr, Mo, W}$; $L = \text{PR}_3, \text{PF}_3, \text{P}(\text{OR})_3, \text{P}(\text{NR}_2)_3, \text{CO}$); using photoelectron spectroscopy. The authors claim that this technique provides direct evidence of the relative σ -donor and π -acceptor properties of the ligands. Results were claimed to be in qualitative agreement with those of Barbeau and Turcotte⁴⁴ based on analysis of carbonyl force constants. A complementary X-Ray crystallographic study by Carty *et al.*⁴¹ suggests that metal-ligand bond order increases with L in the order $\text{PPh}_3 < \text{AsPh}_3 < \text{SbPh}_3 < \text{BiPh}_3$ for complexes of the type $\text{Cr}(\text{CO})_5 \cdot L$, presumably reflecting the increasingly strong s component in the σ -orbital of the Group V^a ligand. Yarbrough and Hall's relative order of σ -donor and π -acceptor abilities is as follows:

σ -donor ability: $\text{PR}_3 > \text{P}(\text{OR})_3 > \text{P}(\text{NR}_2)_3 > \text{PF}_3 = \text{CO}$

π -acceptor ability: $\text{CO} = \text{PF}_3 > \text{P}(\text{OR})_3 > \text{P}(\text{NR}_2)_3 > \text{PR}_3$

The molecular orbital study of Ziegler and Rauk, which was concerned with weakly basic ligands attached to a $[\text{Ni}(\text{CO})_3]$ fragment, suggests that the PF_3 / CO order may be dependent on ligand environment since the following results are claimed:

σ -donor ability: $\text{CS} = \text{CO} > \text{CNCH}_3 > \text{N}_2 = \text{PF}_3$

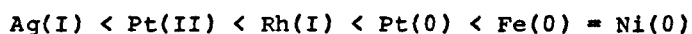
π -acceptor ability: $\text{CNCH}_3 > \text{CS} > \text{CO} > \text{PF}_3 > \text{N}_2$

The reported orders of σ -donor ability are in good agreement with measured ligand "nucleophilicities" for the substitution reactions proceeding by a ligand-dependent pathway, assuming that steric hindrance is disregarded.

The significance of the π -acceptor property order is more difficult to

interpret but does appear to reflect the observed "reservoir" π -density compensation effect for thiocarbonyl and carbonyl complexes⁴⁰. The considerable recent interest in the substitution reactions of complexes of nitrogen donor ligands⁴⁵ with other Group V^a ligands as entering groups would suggest that σ -donor ability determines "nucleophilicity" in ligand-dependent processes but that the stability of the resulting complex is markedly dependent on the π -acceptor properties of the entering group.

Tolman's 1974 study⁴³ of the formation constants for the reactions between tris(tri-*o*-tolylphosphite)Ni(0) and a wide range of alkenes enabled the author to draw up a simple model for the metal-alkene bond strength. The author contended that the rate of dissociation of the metal-ligand bond in nickel-alkene complexes was determined by the degree of back donation from the metal $d\pi$ orbitals, which form the Highest Occupied Molecular Orbital (or H.O.M.O.) set, into the π^* orbitals of the alkene ligand, which form the Lowest Unoccupied Molecular Orbital (or L.U.M.O.) set. The calculated energies of the metal $d\pi$ set were found to increase in the following order:



At nickel the ligand π^* (or L.U.M.O.) set would be expected to lie very close in energy to the metal $d\pi$ (or H.O.M.O.) set, an observation which was supported in the paper by ultraviolet spectroscopic assignments. The author therefore concluded that, in nickel systems, small changes in the energy of the L.U.M.O. set brought about by structural modifications to the alkene ligand would substantially influence the degree of metal-ligand back donation. Evidence for the model was provided by a linear plot of the logarithm of the Equilibrium constant ($\log K$) against the calculated energy of the ligand π^* orbital or L.U.M.O. Tolman's model also provides an interesting explanation for the observed decrease in discrimination of the metal centre towards the structure of the alkene entering group in passing

from Ni(0) to Pt(II) and Ag(I). In the case of the latter elements the H.O.M.O. to L.U.M.O. energy separation should be such that small electronic effects at the alkene should have negligible effect on the metal-ligand bond strength.

1.5 KINETIC AND MECHANISTIC STUDIES OF LIGAND SUBSTITUTION IN SIX-COORDINATE SYSTEMS.

Having outlined the concepts which are needed to describe the structure and reactivity of low valent transition metal complexes according to currently accepted models, it is now important to examine the experimental evidence. The various systems which have been studied in the past are most conveniently classified according to coordination number, since this groups together complexes which display common trends in reactivity. The experimental survey will be largely restricted to low valent mononuclear transition metal complexes which undergo ligand substitution in non-aqueous solvents so that experimental observations may be readily compared and interpreted. For this reason the survey will be concerned primarily with five- and six-coordinate systems, since suitable substrates of other coordination numbers are not common. All experimental measurements have been converted to S.I. units; errors, where quoted, represent one standard deviation of the mean.

1.6 LIGAND SUBSTITUTION PROCESSES AT SIX-COORDINATE TRANSITION METAL CENTRES.

Six-coordinate systems for which kinetic information is available can be described most conveniently using the general formula :

$[ML_{6-m} \cdot A_m]^{n+}$, where L represents the auxiliary ligands and A is the leaving group or groups. For the majority of systems so far studied the

auxiliary ligands (L) are carbon monoxide groups although a few systems have been reported with auxiliary ligands such as PF_3 . For this reason a general symbol for the auxiliary ligands seems appropriate.

1.6.1 Complexes of the General Formula $[\text{ML}_5\text{-A}]^{n+}$.

The most commonly studied six-coordinate systems are those with a single, monodentate leaving group. Since a considerable range of species of this general formula have been investigated this section will be further subdivided to consider related species together. The simplest derivatives of this type, the hexacarbonylmetals, will be considered first.

(i) ($n=0$: $\text{M} = \text{V}, \text{Cr}, \text{Mo}, \text{W}$; $n=1$: $\text{M} = \text{Mn}, \text{Re}$; $\text{L} = \text{CO}$; $\text{A} = \text{CO}$).

The hexacarbonylmetals were the subject of much of the early work in the kinetics of organometallic species and it is for this reason that most of the evidence available was collected in the reviews of Angelici¹ and Werner¹⁴ in the late 1960's. Later experimental and theoretical studies have been concerned with the refinement of mechanistic schemes in the light of observed trends in ligand lability^{37,48}.

Work with hexacarbonylmetals has been hindered by the unusual thermal stability of the complexes towards carbonyl dissociation; indeed the paramagnetic species $\text{V}(\text{CO})_6$, which is reported to be the most thermally labile of the species⁴⁶, undergoes carbon monoxide at 25°C with a half-life of several hours. Of the other hexacarbonylmetals, $\text{Mn}(\text{CO})_6^+$ shows no measurable exchange with isotopically labelled carbon monoxide in acetic acid at 30°C , whilst $\text{Re}(\text{CO})_6^+$ has been shown to be inert to carbonyl exchange at temperatures as high as 60°C ⁴⁷. In contrast to the above species for which little accurate data is available, the reactivity of the Group VI^b hexacarbonylmetals towards ligand substitution has been

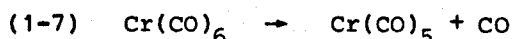
extensively documented and the results suggest that two types of pathway are distinguishable.

Processes exhibiting a ligand-independent rate law.

A number of ligand exchange experiments with Group VI^b hexacarbonylmetals have been shown to follow ligand-independent kinetics consistent with a "d" type pathway. For measurable exchange to occur with these substrates rather high temperatures are required; in the case of $\text{Mo}(\text{CO})_6$ exchange studies require temperatures in the range 100 - 120°C, whilst $\text{W}(\text{CO})_6$ does not undergo exchange below 150°C.

Cetini's group have carried a comparison of ligand exchange in the gas phase and in decalin solution for the substrates $\text{M}(\text{CO})_6$ (M= Cr, Mo, W). The results indicate that the solvent effect on the rate of exchange is negligible⁴⁹. TABLE 1-1 gives the experimental data with the authors' derived activation parameters for the reactions. It is interesting that the enthalpies of activation of the hexacarbonylmetals towards carbonyl dissociation reflect the calculated force constants of the metal-carbonyl bonds⁵⁰.

More recent studies⁵¹ employing flash photolysis methods, indicate that the rate constant for carbonyl recombination according to equation (1-7) is approximately $3 \times 10^6 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$.



This observation reflects a low discrimination of the pentacarbonylmetal intermediate towards the entering group.

Werner⁵² has reported that hexacarbonylmolybdenum is substituted by monodentate amine σ -donor ligands by a ligand-independent rate law to yield aminepentacarbonylmolybdenum and carbon monoxide.

Processes exhibiting a ligand-dependent rate law.

Reactions of hexacarbonylmetals with entering groups of appreciable basicity have generally been found to exhibit a second-order component in the rate law. With neutral Group V^a ligands as entering groups reactions in solvents of low polarity almost invariably display a two term rate law of the form (1-8):

$$(1-8) \quad k_{\text{obs}} = k_1 + k_2[\text{entering group}]$$

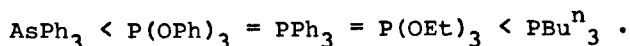
The ligand-dependent term becomes more important with change in the metal centre in the following order: Cr < Mo < W ; suggesting that the effective atomic radius influences the mechanism of substitution.

Angelici and coworkers have published extensively on the kinetics of substitution of the Group VI^b hexacarbonylmetals by trivalent phosphorus and arsenic compounds^{53,54}. The processes studied are given in equation (1-9):



where (M= Cr; L= P Buⁿ₃, PPh₃, P(OPh)₃; M=Mo; L= P Buⁿ₃, PPh₃, P(OPh)₃, AsPh₃, P(OCH₂)₃CR; M=W; L= P Buⁿ₃, PPh₃, P(OEt)₃, P(OCH₂)₃CR).

The experiments were found to require temperatures similar to those used for carbonyl exchange. Using a solvent of low polarity the first-order term in the rate law was found to be identical to that found for ligand exchange (within experimental error) whilst the derived activation parameters were consistent with a dissociative pathway. The second-order term was found to depend on the relative σ -donor abilities of the entering groups and increased in magnitude in the order :



In all cases the second-order rate constant was found to fall within an order of magnitude of the first-order constant, whilst solvent effect work suggested that the second-order term was inhibited by increasing solvent polarity. TABLE 1-2 gives representative rate and activation parameters for the systems with (E= PBu₃ⁿ).

Although activation parameters for systems exhibiting two term rate laws must be treated with caution it appears that the second-order pathway has a substantially lower activation enthalpy than the ligand-independent pathway, but that the increased order of the transition-state produces a markedly less favourable entropy of activation. The low discrimination of the second-order term towards nucleophiles, with the significant negative entropies of activation, would suggest that an "I_d" pathway operates for ligand-dependent substitution in these systems.

More recent work by Dobson⁵⁵ concerned with amine substitution at hexacarbonylmetal centres (M= Cr, Mo, W; L= benzylamine, cyclohexylamine, aniline) suggests that a two term rate law is applicable to these systems as well. This is in marked disagreement with Werner's observations⁵². On the basis of the low discrimination of the intermediate towards the entering group the author postulates competing "d" and "I_d" pathways.

A contrasting ligand-dependent mechanism has been proposed by Asali and Dobson⁵⁶ for the reaction between W(CO)₆ and strongly nucleophilic entering groups of the type [PPN⁺ X⁻] , where (PPN⁺ = bis(triphenylphosphine)iminium⁺ ; X= CN, OCN, SCN). These reactions which yield W(CO)₅.X⁻ (PPN)⁺ and CO, show perfect second-order kinetics in chlorobenzene at 90 - 120°C . The rate law for the substitution process and the strongly negative entropies of activation

suggest that an associative pathway is involved with initial nucleophilic attack at carbonyl carbon.

Substitution of hexacarbonylmetals by chelating ligands.

Little work has been published on the kinetics of substitution of hexacarbonylmetals by polydentate ligands. Werner⁵⁷ and Brown⁵⁸ have both investigated the kinetics of substitution of hexacarbonylmolybdenum by arenes and related carbocyclic ligands. Both groups concluded that a purely dissociative mechanism was involved but it is noticeable that values for the measured dissociative rate constant (k_1) were found to be significantly smaller than those reported for work with carbon monoxide or Group V^a entering groups at the same temperature. The marked discrepancy between values of k_1 for bicyclo[2.2.1]hepta-2,5-diene and cyclohepta-1,3,5-triene entering groups also casts doubt on the simple mechanism put forward.

(ii) ($n = -1$: $M = Cr, Mo, W$; $n = 0$: $M = Mn, Re$; $L = CO$; $A = Cl, Br, I$).

Kinetic studies show that the pentacarbonylmetal halides of the Group VI^b and VII^b elements undergo carbonyl substitution at a substantially greater rate than the analogous hexacarbonylmetals and this observation has resulted in considerable interest amongst theoretical workers attempting to establish the causes of carbonyl labilisation. Halide ligands are unusual in causing *cis*-carbonyl labilisation whilst being very poor π -acceptor ligands; indeed the filled p orbitals of the halide ion would suggest that π -donor properties would be exhibited but with negligible π -acceptor capability³⁸.

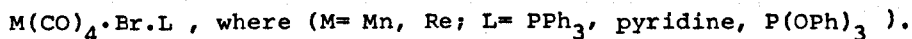
Systems exhibiting a ligand-independent rate law.

The neutral halide complexes of the Group VII^b metals show a rate law which is independent of the nature and concentration of the entering group but is strongly influenced by the nature of the halogen atom.

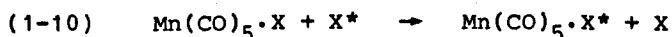
Investigations of the rate of carbonyl exchange for the species of the type $\text{Mn}(\text{CO})_5 \cdot \text{X}$ show the following order of increasing exchange rate:



Isotopic labelling experiments suggest that the postulated five-coordinate intermediate in the exchange process is fluxional during its lifetime since labelled carbon monoxide shows no preferential site of incorporation into the product^{59,60}. Brown and coworkers⁶¹ and Cetini *et al.*⁶² have studied carbonyl exchange for $\text{Re}(\text{CO})_5 \cdot \text{X}$ and have obtained results similar to those found for the manganese analogues; indeed Brown's report includes a direct comparison of the rates of ^{13}C O exchange for the species $\text{M}(\text{CO})_5 \cdot \text{Br}$, where ($\text{M} = \text{Mn}, \text{Re}$), in hexane. Although both processes were observed to be ligand-independent it is notable that the rhenium complex is several orders of magnitude less labile than the manganese analogue. The same trend was noted for species of the type:

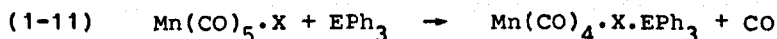


Early work carried out on the systems given in equation (1-10) should be treated with suspicion since a ligand-independent pathway is postulated though the quoted entropies of activation are strongly negative⁶³.



where ($\text{X} = \text{Br}, \text{I}$; $\text{X}^* = \text{labelled halogen}$)

The reactions of the Group VII^b pentacarbonyl halides with Group V^a ligands closely parallel the carbonyl exchange experiments. Angelici and coworkers⁶⁴ have studied the kinetics of ligand substitution for the systems illustrated by (1-11).



where ($\text{E} = \text{P}, \text{As}$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$)

Temperatures of 25 - 45°C were required for substitution to take place with chloroform as the chosen solvent. Activation parameters were determined for systems with AsPh_3 as the entering group; for the case ($\text{X} = \text{Br}$) identical parameters were obtained if the reaction was carried out in nitrobenzene,

thus indicating that solvent participation in the carbonyl dissociation step is negligible.

The most recent work for the analogous rhenium systems is that of Brown and Sane⁶⁵; considerably higher temperatures were required for measurable substitution with these substrates. The temperatures used were 55 - 60°C for (X= Cl) up to 75 - 85°C for (X= I). Despite the lower lability of the rhenium complexes an analogous rate law was found to apply, with the observed carbonyl lability order (X= I < Br < Cl) paralleling that for the manganese systems.

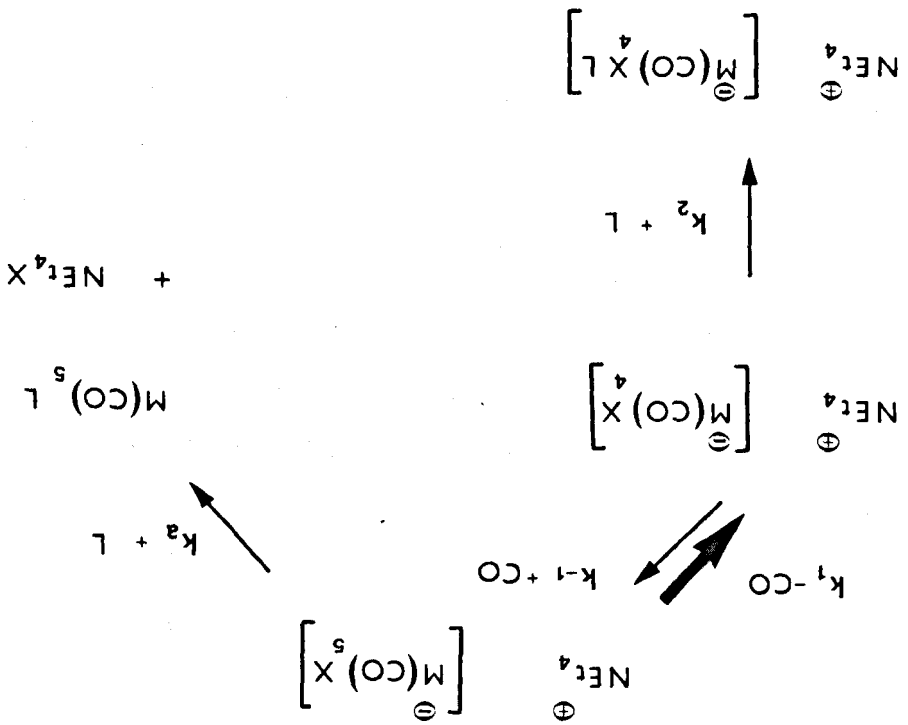
The published activation parameters for ligand substitution by Group V^a entering groups are given in TABLE 1-3 . The data available is fully consistent with a limiting "d" process, whilst the most satisfactory explanation of the observed carbonyl labilisation order is the Fenske Direct Donation model³⁸ outlined earlier. Brown et al. have provided a useful transition-state geometrical argument to account for the labilising properties of halide ligands as a group³⁷.

Systems exhibiting a ligand-dependent term in the rate law.

The anionic Group VI^b pentacarbonylmetal halides have been shown to undergo ligand substitution by a two term rate law involving ligand-dependent and ligand-independent components.

Kinetic measurements on these halide systems have been carried out by Allen and Barrett⁶⁶ employing a variety of Group V^a ligands as entering groups. The reactions, carried out in diglyme, required temperatures in the range 15 - 25°C. The authors observed that the ligand-dependent pathway resulted in a different product to that resulting from the ligand-independent route. The mechanistic scheme illustrated in FIGURE 1-6 is

FIGURE 1-6



claimed to be applicable to the cases:

(M= Cr: X= Cl, Br, I; M= Mo: L= Cl, Br, I; M= W: L= Cl, PPh₃, P(p-chlorophenyl)₃, P(p-fluorophenyl)₃) .

The results for the molybdenum systems give a good illustration of the trends displayed by the Group VI^b pentacarbonylmetal halides in general and relevant kinetic data are presented in TABLE 1-4 . It is notable that the order of carbonyl labilisation for the first-order process parallels that for the manganese and rhenium systems and is the only pathway observed when (X= Cl). For the cases (X= Br, I) a ligand-dependent term becomes significant; this second-order term shows only a relatively small variation with basicity of the entering group. It is perhaps significant that the term increases in importance in the order (M= Cr < Mo = W) as the effective atomic radius of the metal becomes greater. From the evidence presented it is not possible to draw any more definite conclusions as to the second order pathway.

(iii) (n= 0; M= Cr, Mo, W; L=CO; A= NR₃).

The study of the kinetics and mechanism of ligand substitution at aminepentacarbonylmetals has been a very important area in recent times. The evidence to date suggests that a two term rate law of the form:

$$k_{\text{obs}} = k_1 + k_2[\text{entering group}]$$

is generally applicable to this type of system with simple ligand-independent kinetics found only for thermolytic reactions. A substantial body of work has been carried out in elucidating the detailed mechanism of the ligand-dependent pathway for these systems.

Systems for which a ligand-dependent term has not been observed.

A number of simple monodentate amine-pentacarbonylmetal complexes of the Group VI^b elements have been found to undergo thermolysis in solution at ambient temperature to yield the free amine, the hexacarbonylmetal, and metallic decomposition products. Darensbourg, Brown and coworkers have published a number of papers concerned with the thermolysis of this type of complex, with results which are in good general agreement^{67-70, 18}. The earliest report was concerned with the decomposition of $\text{Mo}(\text{CO})_5 \cdot \text{amine}$, where (amine = piperidine, pyridine), in hexane and in carbon disulphide⁶⁷. Activation parameters obtained suggested that the amine-metal bond was approximately 40 kJ mol^{-1} weaker than the mean carbonyl-metal bond strength in hexacarbonylmolybdenum. Subsequent work with ¹³C-labelled species such as $\text{Mo}(\text{CO})_5 \cdot \text{piperidine}$ suggested that the five-coordinate intermediate $[\text{Mo}(\text{CO})_5]$, generated by dissociation of the amine-metal bond, was fluxional over its expected lifetime⁶⁸. A much more comprehensive study by Dennenberg and Darensbourg⁶⁹ provides useful information about the factors contributing to amine-metal bond strength. By comparing the infrared structural data and decomposition kinetics of a number of complexes of the type $\text{Mo}(\text{CO})_5 \cdot (\text{cyclic amine})$ where (M = Cr, Mo), the authors reached the following conclusions:

(a) Saturated amines were found to show σ -donation exclusively; the strength of the metal-ligand bond was a direct reflection of amine basicity.

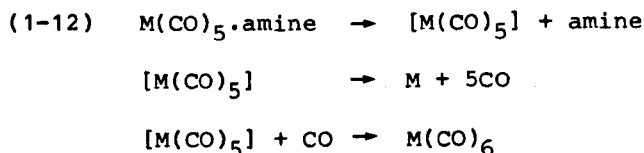
(b) Unsaturated amines, such as pyridine, showed a small π -acceptor component in the metal-ligand bond; rate constants, but not entropies of activation or infrared force constants indicated that a stronger metal-ligand bond was formed with this type of amine. Within the unsaturated

amine complexes bond strength again correlated directly with amine basicity.

(c) The enthalpies of activation for the $M(\text{CO})_5$.amine species were calculated to decrease in the order ($M = \text{Cr} > \text{Mo} = \text{W}$), reflecting the expected maximum in metal-ligand orbital overlap population for the chromium systems. The enthalpies of activation within the chromium series were found to be identical within experimental error indicating that the structure of the amine had little influence on the metal-ligand bond strength. In general, reaction rates seemed to be dependent on the activation entropies, which probably reflected steric control in the transition-state. Measured activation entropies varied from $-4 \text{ J K}^{-1} \text{ mol}^{-1}$ for ($M = \text{Mo}$; amine = piperidine) to $+19 \text{ J K}^{-1} \text{ mol}^{-1}$ for ($M = \text{Cr}$; amine = aniline) with substantially more negative values for the molybdenum systems than their chromium analogues.

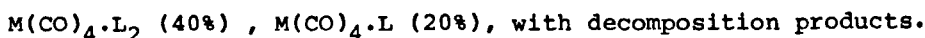
(d) The calculated enthalpies of activation for $M(\text{CO})_5$.amine were found to be consistently $40 - 60 \text{ kJ mol}^{-1}$ lower than those for $M(\text{CO})_6$ suggesting that the reduced π -acceptor properties of amines when compared with carbon monoxide produced weaker metal-ligand bonding.

Covey and Brown, in a later analysis¹⁸, confirmed the general conclusions of Darensbourg et al. with experiments on the thermolysis of $\text{Mo}(\text{CO})_5$.piperidine. However it was noted that the reported rate constants of the prior work⁶⁹ were based on the disappearance of the amine complex and that to adequately represent the stoichiometry of the decomposition process the rate constants should be divided by two according to equation (1-12):



Hyde and Darensbourg have studied the thermal decomposition of the analogous systems of the type: $\text{M(CO)}_4 \cdot \text{amine} \cdot \text{L}$, where (M= Mo; amine= piperidine, pyridine; L= PPh_3).

The products of this reaction were found to be:

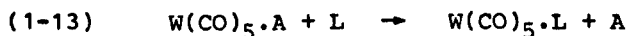


The activation parameters were found to be in accord with those of the aminepentacarbonylmetal analogues.

Darensbourg and Kump⁷⁶ have observed that thermal substitution of monodentate amine complexes by isotopically labelled carbon monoxide proceeds stereospecifically to yield an equatorially substituted *cis*- $\text{Mo(CO)}_4 \cdot \text{amine} \cdot (^{13}\text{CO})$ product from *cis*- $\text{Mo(CO)}_4 \cdot \text{amine}_2$ starting materials. It is claimed that the postulated $[\text{Mo(CO)}_4 \cdot \text{amine}]$ intermediate does not display fluxional properties over its expected lifetime.

Systems exhibiting a ligand-dependent term in the rate law.

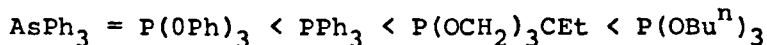
Preliminary studies of the substitution of aminepentacarbonylmetals by strongly basic entering groups were reported in 1968 by two groups^{67,71}. Work by Angelici et al. was concerned with systems of the type illustrated by equation (1-13):



where (A= amine; L= PR_3 , P(OR)_3 , AsR_3).

The amines used in the study showed a wide range of pK_a and the authors reported that the ligand-independent term in the rate law increased with increasing leaving group pK_a , as had been observed for the thermolysis experiments. The ligand-dependent term was found to increase according to

the following entering group series:



Activation parameters for the two pathways were as follows:

$$k_1: \quad \Delta H = 94.1 \text{ kJ mol}^{-1} ; \quad \Delta S = -54.4 \text{ eu.}$$

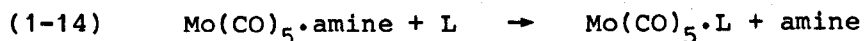
$$k_a: \quad \Delta H = 87.9 \text{ kJ mol}^{-1} ; \quad \Delta S = -46.0 \text{ eu.}$$

Although the relatively low discrimination of the substrate towards the entering ligand is suggestive of an "Interchange" pathway rather than a true associative process the close similarities between the activation parameters for the k_1 and k_2 processes does seem rather surprising. The same authors produced a later paper⁷² which provided "equilibrium constants" for the above reactions. In view of the unusual behaviour claimed for the thermodynamic properties of the complexes and the fact that a later author⁷³ has claimed that the reactions in question are irreversible the results must be treated with suspicion.

The most detailed study which has been published for substitution of monodentate amine complexes of the pentacarbonylmetals is that of Covey and Brown¹⁸. The following aspects of the substitution process were investigated:

- (a) Competition ratios, with recombination constants.
- (b) The dependence of the rate of substitution on the leaving group.
- (c) The activation parameters for the ligand-dependent
and ligand-independent terms in the rate law.
- (d) The solvent dependence of the rate for both the ligand-dependent
and ligand-independent terms in the rate law.
- (e) The dependence of rate on the entering group.

The system studied can be represented by equation (1-14):



where (amine= quinuclidine, piperidine, cyclohexylamine; L= PPh₃, AsPh₃, SbPh₃, P(OPh)₃, P(OMe)₃, P(OCH₂)₃CET, P(p-tolyl)₃).

The authors deduced that the observed rate law in non-polar media (1-13) could be explained in terms of concurrent dissociative and "I_d" pathways. For reactions taking place in the presence of added amine the rate law (1-15) was found to apply.

$$(1-15) \quad \frac{-d[\text{MA}]}{dt} = \frac{(k_1 \cdot k_3 [\text{L}] + k_{a2} \cdot k_a [\text{L}]) [\text{MA}]}{(1 + k_{-2} [\text{A}] \quad k_{-a} + k_{a2})}$$

The observations of the authors concerning the ligand-independent pathway are fully in accord with earlier work. In addition solvent effect data show that the dissociative pathway is independent of the nature of the solvent system unless a highly polar solvent such as 1,4-dioxane or nitromethane is used.

The information to be obtained concerning the ligand-dependent pathway is of more importance in a general context. The authors made the following significant observations:

- (a) The ligand-dependent term in the rate law showed only small variations with entering groups of widely different basicities, suggesting that the transition state had low discrimination towards the entering group.
- (b) The solvent effect measurements indicated that the second-order term was absent in highly polar solvents, suggesting that the the solvent functioned as an additional nucleophile under these conditions.

- (c) The leaving group effects suggested that the steric requirement of the amine exerted a greater influence on the rate than the basicity of the entering group. This observation gained additional support from an analysis of the activation parameters for the substitution process.
- (d) A comparison of the activation parameters for the k_1 process and the k_a process indicated that the transition-state for the second-order pathway was significantly more ordered than that for the first-order process. TABLE 1-5 provides a summary of the activation parameters obtained.

It is interesting that Covey and Brown's activation parameters for the k_1 and k_2 processes differ markedly from those reported by Angelici and coworkers⁷¹. The conclusion which can be drawn from Brown's study is that the sensitivity of the rate to the steric requirement and basicity of the leaving group, coupled with low sensitivity towards the steric and electronic requirements of the entering group reflect a transition-state involving more bond-breaking than bond-making.

Darensbourg's group have published a number of papers on this topic but the most relevant to a general discussion of the reactivity of aminopentacarbonylmetal species are concerned with entering group competition ratios⁷⁰ and reactions involving ligands capable of forming hydrogen bonds^{74,75}. Substitution reactions of amine complexes have now been described in terms of an " I_d " mechanism and accordingly the authors find that a two term rate law applies to systems where the entering group is present in considerable (eightfold or greater) excess⁶⁷. The size of the second order term in the rate law is influenced by the nature of the entering group.

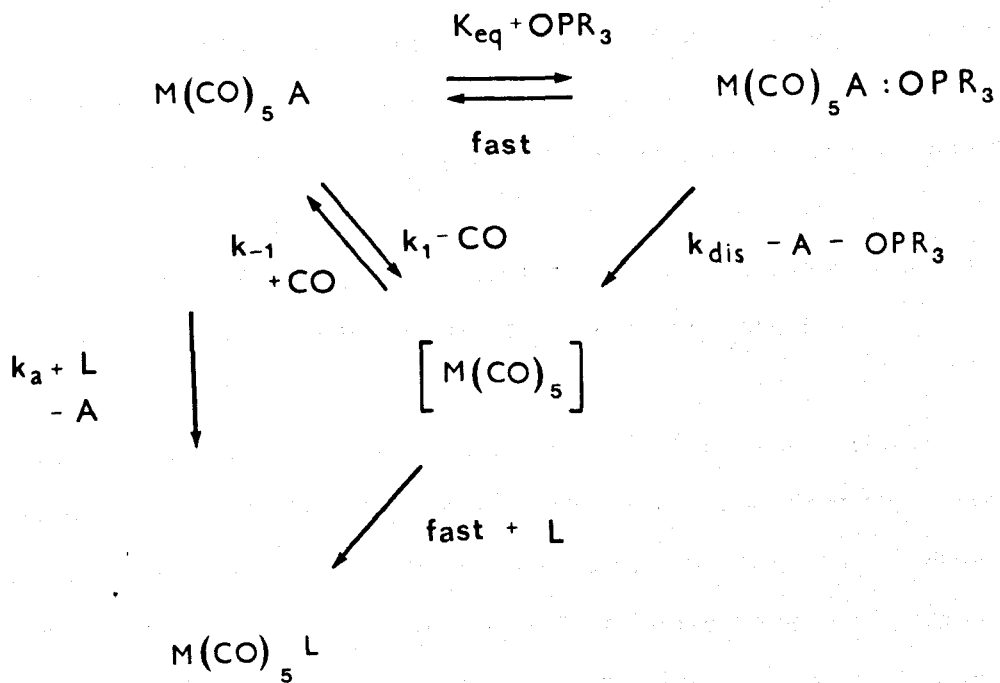


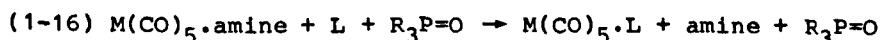
FIGURE 1-7

Hyde and Darensbourg⁷⁰ report competition studies for the reaction between $\text{Mo}(\text{CO})_4 \cdot \text{PPh}_3 \cdot \text{amine}$, where (amine = piperidine, pyridine) and a variety of Lewis bases in hexane in the temperature range 15 - 35°C. By comparison of the results of competition studies at equilibrium and of partial rate constant ratios k_{-1}/k_2 , derived from kinetic measurements, the authors have devised an order of apparent nucleophilicity for the entering groups used. The nucleophilicities are given in increasing order:

CO (0.31) < AsPh_3 (0.47) < PBu^n (0.68) < piperidine (1.0) < SbPh_3 (1.1)
 SbPh_3 (1.1) < PPh_3 (1.5) = pyridine (1.5) < $\text{P}(\text{OCH}_2)_3\text{Cet}$ (2.4)

The values given in parentheses represent relative nucleophilicities based on piperidine = 1.0. The inference which may be drawn from the series is that the intermediate, which is postulated as $[\text{Mo}(\text{CO})_4 \cdot \text{PPh}_3]$, shows a remarkable lack of discrimination towards entering group electronic properties with the result that steric properties are almost of equal significance in determining rate behaviour. The results are fully consistent with the Covey and Brown model for competing "d" and "I_d" pathways in the analogous $\text{Mo}(\text{CO})_5 \cdot \text{amine}$ derivatives.

A more recent paper from the Darensbourg group⁷⁴ casts an interesting light on the reported solvent dependence of the k_1 rate constant in highly polar solvents¹⁸. By a study of the ternary systems given in equation (1-16) the authors found that considerable rate enhancement resulted from adduct formation between the amine ligand of the substrate and the phosphine oxide catalyst.



where (M = Mo; amine = piperidine; L = PPh_3 , PBu^n_3 ; R = Ph, Bu^n , OMe).

The mechanistic scheme illustrated in FIGURE 1-7 provides a plausible explanation of the limiting substitution rate obtained once adduct

formation is complete. Under the conditions employed adduct formation is extremely rapid and once equilibrium is established the normal ligand-dependent pathway (k_a) would be expected to be completely suppressed. The adduct assisted dissociation, labelled k_{diss} , is then postulated to be of considerably higher rate than the conventional "d" pathway. The authors claimed that this type of rate enhancement was general to all bases or solvent systems capable of forming hydrogen bonds to ligated amines, thus providing a convenient explanation for the anomalous rates of substitution of amine complexes in such solvents as dioxane. Darensbourg^{75(a)} reports that hydrogen bonding may also be responsible for the greater lability of the species $Mo(CO)_4 \cdot PPh_3 \cdot piperidine$ towards amine dissociation when compared with its pentacarbonyl analogue $Mo(CO)_5 \cdot piperidine$. In this case it is believed that intramolecular hydrogen bonding, as detected by physical measurements, is the cause of ligand lability. Earlier work by the same author however suggested that the low lability of $Mo(CO)_4 \cdot P(OMe)_3 \cdot piperidine$ relative to the triphenylphosphine complex reflected the stronger intramolecular hydrogen bonding possible with a phosphite as auxiliary ligand^{75(b)}.

By contrast with the substitution reactions of monodentate amine complexes, which undergo substitution with dissociation of the amine, a number of complexes of bidentate chelating nitrogen ligands have been observed to undergo substitution with loss of carbon monoxide. Angelici and Graham⁷⁷ carried out the first detailed studies of systems involving bidentate chelating ligands. Their work, which was concerned with systems of the type given in equation (1-17), established that a two term rate law was applicable to this form of ligand substitution process. The authors noted that nitrogen donor ligands labilised the cis carbonyls appreciably relative to the most labile carbonyls of the hexacarbonylmetal parent species.



where (M= Cr, Mo, W; L= P(OEt)₃, P(OCH₂)₃CMe, PO₃C₆H₉; N-N= o-phenanthroline, 2,2'-dipyridyl, 1,2-diamino-2-methylpropane) The ligand-dependent pathway was considerably more important for molybdenum and tungsten than for chromium whilst ligand-dependent dechelation of the nitrogen ligands occurred in competition with carbonyl dissociation for the systems: (M= Mo, W; N-N= 2,2'-dipyridyl, 1,2-diamino-2-methylpropane) .

Two further general points could be deduced from the experimental evidence. Firstly the ligand-independent rate constant was found to increase with increasing basicity of the chelating diamine, and secondly the ligand-dependent term was found to show only limited discrimination towards the nature of the entering phosphite ligand. Activation parameters were derived from the kinetic data suggested that the transition-state for the ligand-dependent pathway was of considerably higher order than the ground state. The results obtained in this study have however been disputed by Dobson et al.⁷⁸ in view of the apparent "ligand-dependency" of the k₁ partial rate constant in the substitution of the species W(CO)₄·(N-N) and in view of the negative entropies of activation quoted for what is presumably a dissociative process. A study of the systems described by equation (1-18) led the author to reach the following conclusions concerning the substitution process:

- (a) For (N-N)= 2,2'-bipyridyl the reaction appeared to reach equilibrium once one-half of the substrate had undergone ligand substitution.
- (b) Three distinct mechanisms could be distinguished for the ligand substitution process in view of the observed deviations from

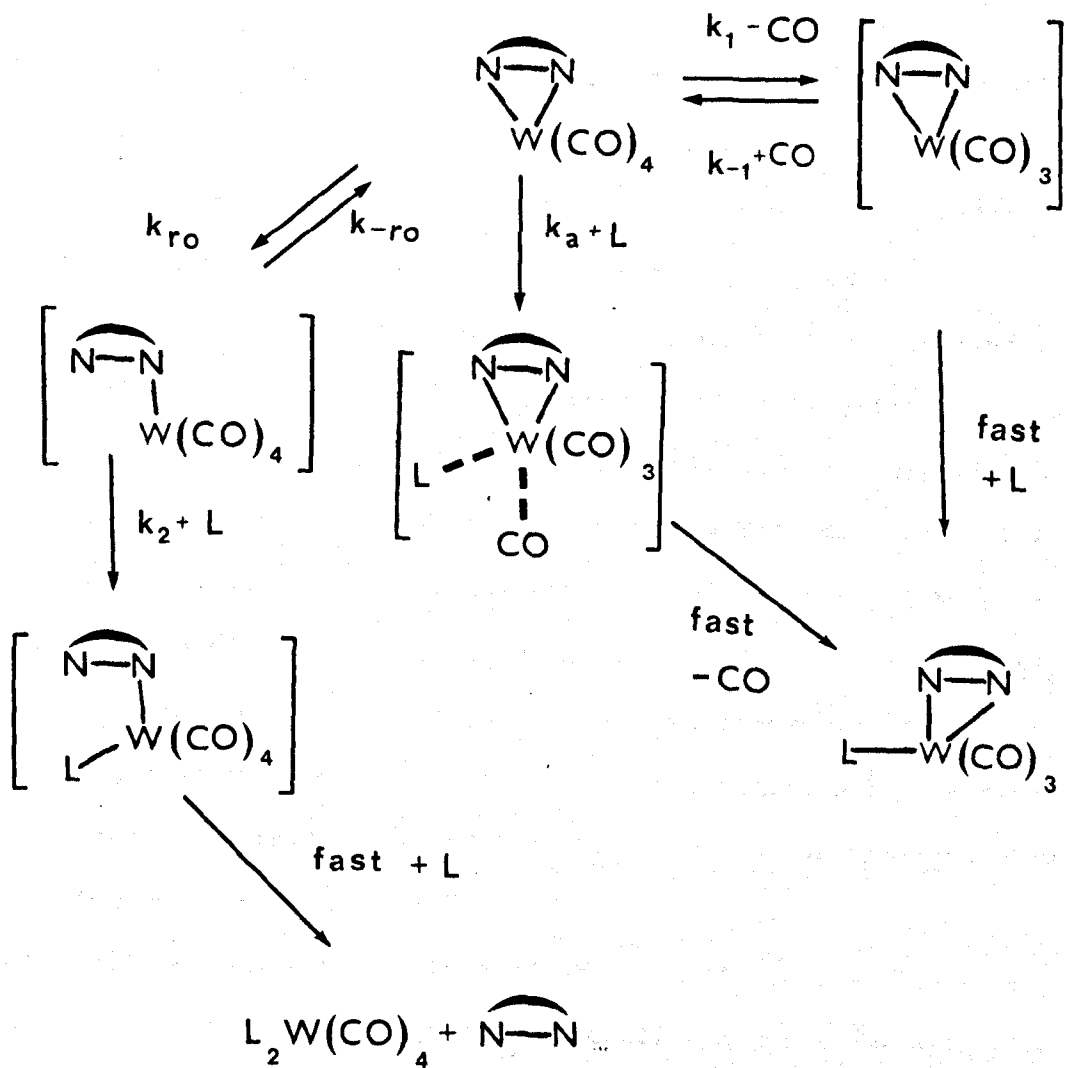
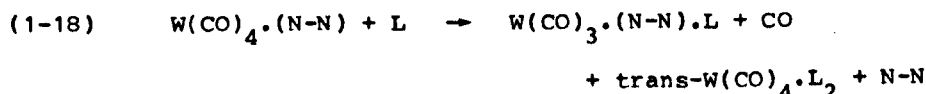


FIGURE 1-8

linearity of plots of k_{obs} against $[L]$ when the entering ligand was present at very high concentrations.



where ($L = \text{P(OEt)}_3, \text{P(OCH}_2)_3\text{CMe}$; $\text{N-N} = 2,2'$ -bipyridyl, o -phenanthroline)

The distinct pathways were designated as follows:

- (i) A ligand-independent dissociative pathway resulting in the dissociation of a metal - carbon bond; this process was observed for both ($\text{N-N} = 2,2'$ -bipyridyl) and ($\text{N-N} = o$ -phenanthroline) and was assumed to be the k_1 pathway of the Angelici rate law.
- (ii) A ligand-dependent pathway resulting in ligand assisted carbonyl dissociation; this process, observed with both nitrogen ligands, was assumed to correspond to the k_a term of Angelici.
- (iii) A ligand-dependent pathway characterised by "ring-opening" of the chelated nitrogen ligand as part of a stepwise dechelation process; this pathway, resulting in substitution of the diamine ligand to yield a $\text{trans-W(CO)}_4 \cdot \text{L}_2$ product, was observed only for the nitrogen donor ligand $2,2'$ -bipyridyl.

The overall results were interpreted in terms of the reaction scheme of FIGURE 1-8. The "ring-opening" pathway (iii) was put forward to account for the curvature of pseudo-first-order plots of k_{obs} against $[L]$ in the case of $2,2'$ -bipyridyl leaving groups with strongly nucleophilic entering groups. No products of the type $\text{W(CO)}_4 \cdot \text{L}_2$ were observed and the authors rationalised this in terms of the rigidity of the amine leaving group which was seen to prevent the rotation needed for a stepwise dechelation process. It may also be pointed out however that another research group⁸³ have observed that there is measurable $d\pi$ - $p\pi$ overlap in the metal-amine bond of $\text{W(CO)}_4(o\text{-phenanthroline})$ which suggests a greater synergistic effect for this system. Activation parameters have been supplied for the substitution of $\text{W(CO)}_4(2,2'\text{-bipyridyl})$ by $\text{P(OCH}_2)_3\text{CMe}$ and are as follows:

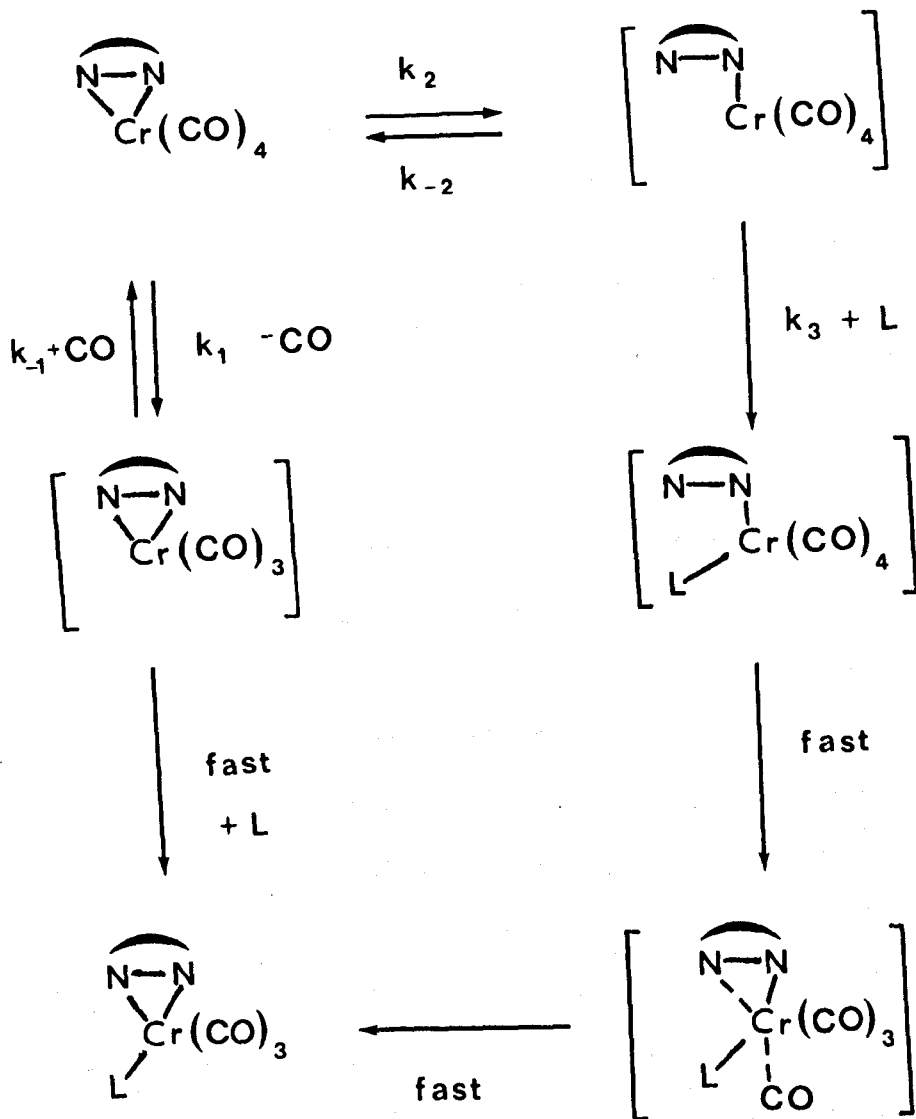


FIGURE 1-9

$$k_1: \quad \Delta H = 141.8 (2.5) \text{ kJ mol}^{-1}; \quad \Delta S = 52.2 (4.2) \text{ eu.}$$

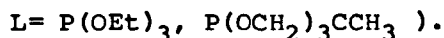
$$k_a: \quad \Delta H = 93.3 (1.7) \text{ kJ mol}^{-1}; \quad \Delta S = -55.2 (2.9) \text{ eu.}$$

The values obtained appear to be in good agreement with the proposed mechanism.

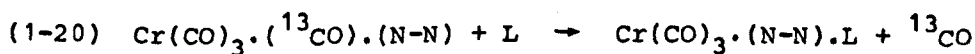
Dobson et al.⁷⁹ have carried out a reinvestigation of the kinetics of ligand substitution at bidentate nitrogen donor complexes of chromium using the systems given in equation (1-19):



where (N-N= o-phenanthroline, 2,2'-bipyridyl;



Ligand-dependent behaviour can be observed for these systems only at low concentrations of the entering group. Since there is no evidence for a product resulting from amine displacement the authors account for the observed behaviour in terms of competing dissociative and "ring-opening" pathways, using the mechanistic scheme illustrated in FIGURE 1-9. It should be pointed out that a seven-coordinate, twenty electron transition-state for the "ring-opening" pathway does not seem likely for a chromium system. A more plausible explanation would involve a simple dissociative process which, at non-limiting ligand concentration, involved competition between the forward and back reactions; i.e. $k_2[\text{L}] = k_{-1}$. A subsequent report from the same group⁸⁰ describing work on the systems illustrated in equation (1-20) has confirmed that carbonyl substitution occurs stereospecifically to yield a product in which an apical carbonyl has been displaced.



where (N-N= o-phenanthroline, 2,2'-bipyridyl; L= PPh₃).

Cohen and Brown⁸¹ have studied the kinetics of ^{13}CO exchange with a number of complexes of the type $\text{Cr}(\text{CO})_4 \cdot (\text{chelate})$. For the cases (chelate = o-phenanthroline, 2,2'-bipyridyl) the labelling experiments have indicated that a "d" process involving rate-determining loss of a carbonyl ligand was in best agreement with experiment. The postulated intermediate $[\text{Cr}(\text{CO})_3 \cdot (\text{chelate})]$ was expected to be partially fluxional over its lifetime on the basis of the ^{13}CO distribution found for different sites in the product. The authors discounted a "ring-opening" mechanism on the isotopic evidence since the 1:2 ratio of trans:cis isomers of the product to be expected for such a pathway was not found. For similar reasons the authors discounted arguments for a completely non-fluxional intermediate.

The most recent report of the kinetics of substitution of bidentate nitrogen complexes of the Group VI^b metals has been that of Rousche and Dobson⁸². From a study of the reaction between allyl bromide and $\text{Mo}(\text{CO})_4 \cdot (\text{o-phenanthroline})$ to yield the products $\text{Mo}(\text{CO})_2 \cdot \text{Br} \cdot (\eta^3\text{-allyl})$ and carbon monoxide the rate law of equation (1-21) was deduced:

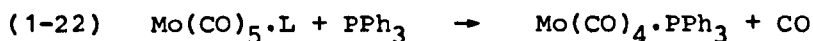
$$(1-21) \quad \frac{-d[S]}{dt} = k_1[S] + k_a[S][L]$$

The k_1 pathway, proceeding by rate-determining loss of a carbonyl group, is found to predominate in dichloromethane; whilst in tetrahydrofuran the ligand-dependent pathway (k_a) becomes significant. Pseudo-first-order plots of k_{obs} against entering group concentration are found to be linear with non-zero intercepts and for this reason the authors favour the idea of competing "d" and solvent assisted " I_d " pathways for the molybdenum systems.

(iv) (n=0: M= Cr, Mo, W; n=1: M= Mn, Re; L= CO;

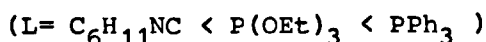
A= PR₃, AsPh₃, SbPh₃) .

There is a marked contrast between the kinetic and thermodynamic behaviour of nitrogen donor complexes and those of other Group V^a ligands. Werner described some early studies of the kinetics of substitution of N donor complexes in his 1968 review article¹⁴. For systems of the type given in equation (1-22) the reviewer reported that a ligand-independent rate law was found at 0°C in decane.



where (L= PPh₃, P(OEt)₃, C₆H₁₁NC) .

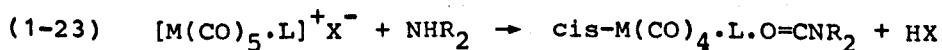
The reactivity of the substrates increased in the order



with the phosphorus ligands appearing to be only weakly labilising towards carbonyl dissociation when compared with hexacarbonylmolybdenum. Later studies of the thermal substitution of complexes containing monodentate Group V^a ligands other than nitrogen donors have not been abundant, although a number of physical measurements have been made for this type of system⁴⁰⁻⁴². The following evidence can be cited however:

(a) Qualitative studies by Darensbourg et al.⁸⁴

suggest that cationic complexes of manganese and rhenium may undergo carbonyl insertion rather than substitution when reacted with amines. The systems studied may be represented by equation (1-23):



where (L= PR₃, P(OR)₃; X= Cl, Br, I) .

(b) A study of the intermediate formed by amine dissociation from the

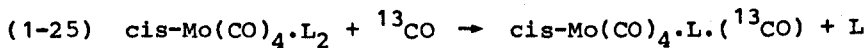
complex $\text{cis-W}(\text{CO})_4\cdot\text{PPh}_3\cdot(\text{piperidine})$ using ^{13}C and PPh_3 entering groups suggests that the five-coordinate intermediate generated is fluxional⁸⁵. The postulated structure of the intermediate is $[\text{W}(\text{CO})_4\cdot\text{PPh}_3]$, which closely resembles likely intermediates formed by carbonyl dissociation from pentacarbonylmetal derivatives such as $\text{W}(\text{CO})_5\cdot\text{PPh}_3$.

(c) Dobson⁸⁶ has carried out an investigation of the kinetics of substitution of the arsenic donor ligand in $\text{W}(\text{CO})_5\cdot\text{PPh}_3$ using the entering group *o*-phenanthroline in mesitylene solvent; a two term rate law was obtained with author proposing competing "d" and "I_d" pathways. An unusual aspect of the results reported is the very similar values of the activation parameters for the two pathways. Dobson cites earlier results obtained by Graziani for substitution of $\text{W}(\text{CO})_5\cdot(\text{aniline})$ by stibines to show that such similar activation parameters are not unknown for transition metal systems. The authors' quoted activation parameters are given by equation (1-24):

$$(1-24) \Delta H_{k_1} = 124.7 (3.3) \text{ kJ mol}^{-1} ; \Delta H_{k_2} = 114.6 (3.3) \text{ kJ mol}^{-1} \\ \Delta S_{k_1} = -20.1 (8.4) \text{ eu} ; \quad \Delta S_{k_2} = -15.9 (8.8) \text{ eu}.$$

(d) Darensbourg^{87,88} has published a series of papers on the substitution and isomerisation of species such as $\text{M}(\text{CO})_4\cdot\text{L}_2$. For the case ($\text{M} = \text{Mo}$; $\text{L} = \text{PBu}_3^n, \text{PEt}_3$) cis - trans isomerisation of the complex was found to occur without measurable dissociation of the carbonyl ligands⁸⁷; whilst the enthalpy of activation for the isomerisation was calculated to be: more than 20 kJ mol^{-1} less than that for ($\text{M} = \text{Mo}$; $\text{L} = \text{PPh}_3$) analogues which have been shown to

isomerise by a pathway involving carbonyl dissociation⁸⁸. In a subsequent paper the authors also give details of phosphine substitution by isotopically labelled carbon monoxide; the systems investigated are summarised in equation (1-25):



where (L = PR₃, P(OR)₃) .

The authors favour a simple dissociative pathway with the rate of ligand dissociation becoming greater as the steric requirement of the leaving group is increased.

Considerably more information is available concerning carbonyl substitution processes for complexes containing bidentate phosphorus and arsenic donor ligands; systems displaying ligand-independent and ligand-dependent kinetics have been described enabling useful comparisons to be made.

Rather surprisingly ligand-independent kinetics are the rule for bidentate phosphorus systems, behaviour which is in marked contrast with that of bidentate arsine and mixed chelate systems⁸⁹ .

Dobson and coworkers have made extensive studies of bidentate phosphorus complexes which undergo carbonyl substitution by pseudo-first-order kinetics⁹⁰⁻⁹², the earliest report⁹⁰, which describes the substitution of Mo(CO)₄·[1,2-bis(diphenylphosphino)ethane] by a variety of phosphines, indicates that dissociation of a metal-carbonyl bond was the rate-determining step. This unusual behaviour towards strongly nucleophilic entering groups was postulated as evidence of steric hindrance due to the bulky diphosphine which prevented formation of a transition-state of expanded coordination number. Later studies employing the same substrate and its analogue fac-Mo(CO)₃·[1,2-bis(diphenylphosphino)ethane]·(¹³CO) confirmed that the ligand-independent pathway proceeded by way of cis-carbonyl bond dissociation to yield a partially fluxional intermediate of

structure $[\text{Mo}(\text{CO})_3(\text{P-P})]$.

Cohen and Brown^{81(a)} have studied the carbonyl exchange reactions of $\text{Cr}(\text{CO})_4(\text{P-P})$ where (P-P= diphos, 1,3-bis(diphenylphosphino)propane) in decalin at 90 - 110°C . Difficulties were encountered due to decomposition of the product thermally under the reaction conditions but it was concluded that for both systems a simple dissociative pathway operated with no evidence for an accessible "ring-opening" pathway.

Jernigan⁹³ has rationalised the observed trends in carbonyl dissociation for complexes involving chelating Group V^a ligands in terms of the Fenske "direct donation" model. Analysis of carbonyl vibrational spectra according to this model led the author to conclude that the π -acceptor component in the metal-ligand bond increased in the order $\text{N} < \text{As} = \text{P}$ for bidentate chelating ligands. The analysis was taken to indicate that axial carbonyl labilisation increases with increasing bidentate ligand π -acceptor ability.

(v) ($n=0$; $M= \text{Cr}, \text{W}$; $L= \text{CO}$, o-phenanthroline; $A= \text{CS}$) .

Work on ligand substitution processes involving six-coordinate thiocarbonyl complexes has been carried out almost exclusively by Angelici and coworkers⁹⁵; and despite the difficulties of purification and characterisation of the species used in kinetic studies the authors have managed to reach a number of conclusions likely mechanisms for substitution. All species so far investigated involve a ligand-dependent term in the rate law for substitution.

Systems exhibiting a ligand-dependent term in the rate law.

Investigations of the systems illustrated in equation (1-26) have been essentially qualitative in nature although rather more information is available for the tungsten complex⁹⁶.



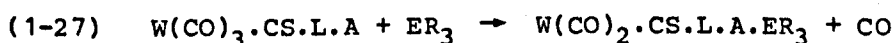
where (M= Cr, W; L= PPh₃) .

The kinetic data are suggestive of competing ligand-dependent and ligand-independent pathways; behaviour which is analogous to that of the parent hexacarbonylmetal complexes. The thiocarbonyl complexes are however considerably more labile towards carbonyl substitution than the hexacarbonyls, with substitution claimed to occur exclusively trans to the thiocarbonyl ligand. The quoted activation parameters are consistent with competing dissociative and interchange (dissociative) pathways:

$$k_1: \quad \Delta H = 131.8 (4.2) \text{ kJ mol}^{-1}; \quad \Delta S = 13.0 (12.6) \text{ eu.}$$

$$k_a: \quad \Delta H = 100.4 (4.2) \text{ kJ mol}^{-1}; \quad \Delta S = -50.2 (12.6) \text{ eu.}$$

Later reports^{97,98} have dealt with more detailed studies for the systems given in equation (1-27):



where (L= CO; A= PR₃; or L=A= o-phenanthroline; E= P)

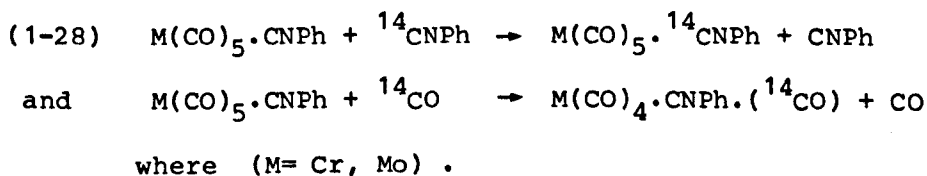
For both chelating and monodentate auxiliary ligands the kinetic behaviour of the thiocarbonyl complexes parallels that of the analogous all-carbonyl complexes, but with significantly greater carbonyl lability due to the thiocarbonyl substituent. Theoretical and spectroscopic studies on the bonding of the thiocarbonyl complexes suggest that, like the carbonyl group, the thiocarbonyl ligand may influence the reactivity of the auxiliary ligands by contributing a "reservoir" of π -density to the metal centre⁹⁹. It is noticeable that nucleophilic attack at the carbon of the thiocarbonyl group occurs more readily than at carbonyl carbon; Angelici's group have documented generation of thiocarbamide complexes by nucleophilic

attack on thiocarbonyl carbon by amines¹⁰⁰.

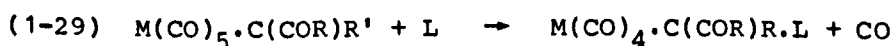
(vi) (n=0; M= Cr, Mo; L= CO; A= CNR; n=0; M= Cr, Mo, W; L= CO; A= carbene; n=0; M= W; L= CO; A= acetone; n=0; M= Mn, Re; L= CO; A= SnR₃, GeR₃; n=0; M= Re; L= CO; A= NCO).

This rather diverse group of compounds have been found to show simple, ligand-independent kinetics. Since no single class of these compounds has been the subject of recent study it seems appropriate to deal with all of the systems under a single heading.

Data on the substitution mechanisms of isonitrilepentacarbonylmetals has been provided by Cetini and Gambino¹⁰¹. By carrying out separate isonitrile and carbon monoxide exchange experiments using the systems given in (1-28) the authors claimed to find that both exchanges occurred by dissociative mechanisms; but whereas isonitrile exchange was immeasurably fast at 5°C, carbon monoxide exchange was too slow for accurate measurement in refluxing toluene. It is very difficult to provide a plausible explanation of the reported kinetic behaviour.



Other early work reported to establish a ligand-independent rate law was that of Werner on metal-carbene complexes¹⁰². The reactions studied are indicated in equation (1-29):



where (M= Cr, Mo, W; R= CH₃; R'= CH₃, Ph; L= PR₃) .

Carbon monoxide exchange experiments were also carried out for the case (M= Cr) . Activation parameters were calculated for the system: (M= Cr; R= CH₃; R'= CH₃; L= PBuⁿ₃) in octane yielding the following values: $\Delta H =$

FIGURE 1-10

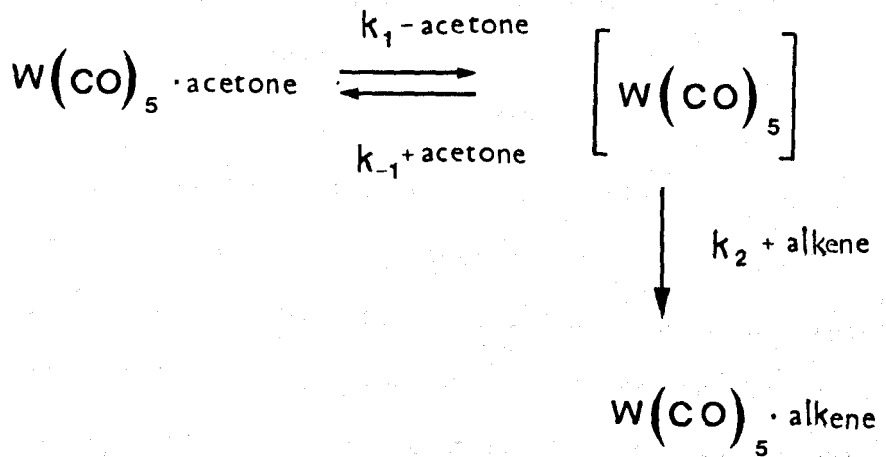
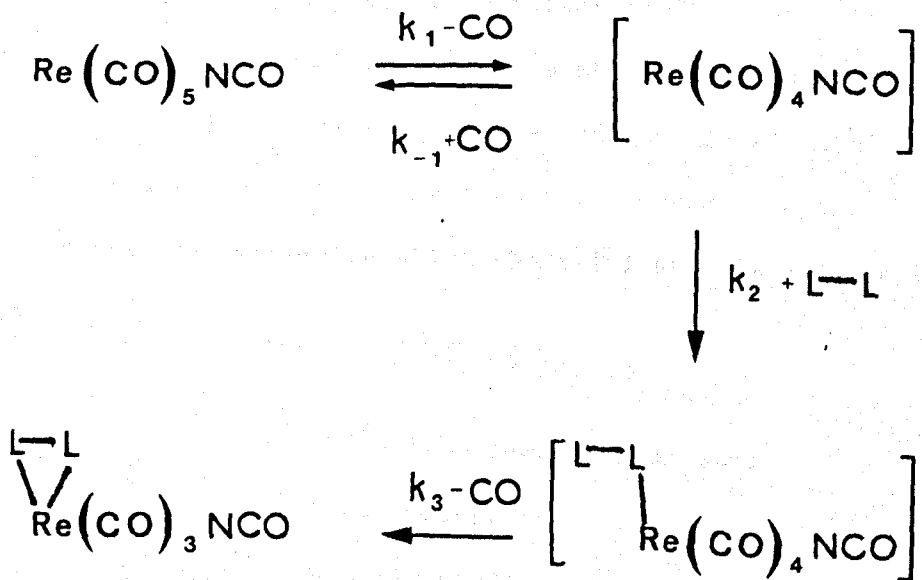


FIGURE 1-11



108.8 kJ mol⁻¹ ; $\Delta S = 40.2$ eu. In view of these parameters and the similarities of the pseudo-first-order rate constants obtained for these systems with a wide variety of entering groups it seems that the mechanism approaches S_N1 (limiting) . Recent spectroscopic evidence¹⁰³ supports the view that the carbene ligand labilises the carbonyl dissociation by virtue of its strong σ -donor characteristics.

Wrighton has studied the kinetics and mechanism of acetone substitution for the substrate W(CO)₅.(acetone) with alkenes as the entering groups¹⁰⁴. Although the rate of ligand substitution for this substrate is not dependent on entering group concentration beyond a limiting condition, it is interesting that the limiting substitution rate varies significantly with the nature of the entering group. This observation is not easy to rationalise if a simple dissociative mechanism is invoked; the author was unable to account for the observed behaviour. Activation parameters were calculated for the dissociative process using several different entering groups and competition studies also carried out in attempt to determine the metal-acetone bond strength. Both methods indicated that the bond is very weak (of the order of 28 kJ mol⁻¹). As will be seen from FIGURE 1-10 the overall reaction scheme proposed by the author is a dissociative pathway in which the k₂[L] step is assumed to be rate-determining.

Dobson et al. have reported experiments to measure the reactivity of species of the type Mn(CO)₅.EPh₃ , where (E= Sn, Ge) , with mono- and bidentate Group V^a ligands¹⁰⁵. Kinetic studies were found to be feasible at 50 - 60°C in decalin producing results consistent with a simple dissociative mechanism. Activation parameters supplied by the authors are compatible with a carbonyl dissociation and suggest that the Group IV^a ligands are not significantly labilising towards carbonyl dissociation.

$$(E = Sn) \quad \Delta H = 173.2 \text{ kJ mol}^{-1}, \quad \Delta S = 61.9 \text{ eu.}$$

$$(E = Ge) \quad \Delta H = 164.8 \text{ kJ mol}^{-1}, \quad \Delta S = 67.4 \text{ eu.}$$

Another report of a simple dissociative process for a Group VII^b metal carbonyl species was provided by Angelici and Faber¹⁰⁶ with a description of the kinetics of substitution of

isocyanatopentacarbonylrhenium by chelating nitrogen and phosphorus ligands. The postulated mechanistic scheme is illustrated by FIGURE 1-11 .

Activation parameters supplied are consistent with the proposed mechanism:

$$(\Delta H = 98.3 (7.1) \text{ kJ mol}^{-1}, \quad \Delta S = 7.5 (18.4) \text{ eu.}) .$$

It is interesting that although the k_2 and k_3 steps are too fast to be measured for (L-L= 2,2'-dipyridyl, o-phenanthroline) an intermediate of type (A) is observed spectroscopically when the bidentate phosphine 1,2-bis(diphenylphosphino)ethane is the auxiliary ligand. This perhaps reflects the relative labilising effects of chelating nitrogen and phosphorus ligands.

To this point the survey has been concerned with the kinetic behaviour of hexacoordinate systems undergoing substitution by either ligand dissociation or by expansion of coordination caused by entering group attack at the metal centre. There are, however, two further types of ligand substitution pathway accessible to hexacoordinate systems and these will be outlined in the following sections.

(vi) (n=0; M= Mn, Re; L= CO; A= H) .

The hydridopentacarbonylmetals of the Group VII^b elements are perhaps the least well understood of the readily available six-coordinate systems. It has been known for some time^{1,14} that the hydridometal complexes of this type display anomalously high substitutional reactivity, but it is only relatively recently that the reasons for this behaviour have

become clearer. Hydridopentacarbonylrhenium is considerably more inert towards phosphine substitution than its manganese analogue providing that it is in the dark and in the pure state. Indeed it is reported that no significant substitution will take place under these conditions over a period of sixty days at ambient temperature¹⁰⁷. By contrast early reports suggested that $\text{Mn}(\text{CO})_5\text{H}$ was capable of exchanging all five carbonyl groups with isotopically labelled carbon monoxide at -21°C ¹⁰⁸. Whereas $\text{Mn}(\text{CO})_5\text{H}$ appears to react by a ligand-dependent mechanism in polar solvents, the ligand exchange processes of $\text{Re}(\text{CO})_5\text{H}$, once initiated, proceed by a ligand-dependent pathway.

T.L. Brown and coworkers have published a series of papers documenting the reactivity of the complexes in the pure state^{109,110}. Reactions have been carried out in polar and non-polar media with a variety of entering groups including carbon monoxide. The behaviour of the pure species has been compared with that of systems containing free radical impurities or under photochemical irradiation. The authors have concluded that early work in this field is unreliable due to the use of starting materials of unsatisfactory purities under conditions conducive to free radical initiation. Brown's group suggest that the following inferences can be drawn from their experimental observations:

- (a) In the absence of free radical initiators or of photochemical excitation $\text{Mn}(\text{CO})_5\text{H}$ reacts by a hydride migration pathway similar to that proposed by Basolo and Pearson¹¹¹ and yielding a product of the type $\text{Mn}(\text{CO})_4\text{H.L}$. The rate of substitution is ligand-dependent but only slightly effected by the nature of the entering group in the order:

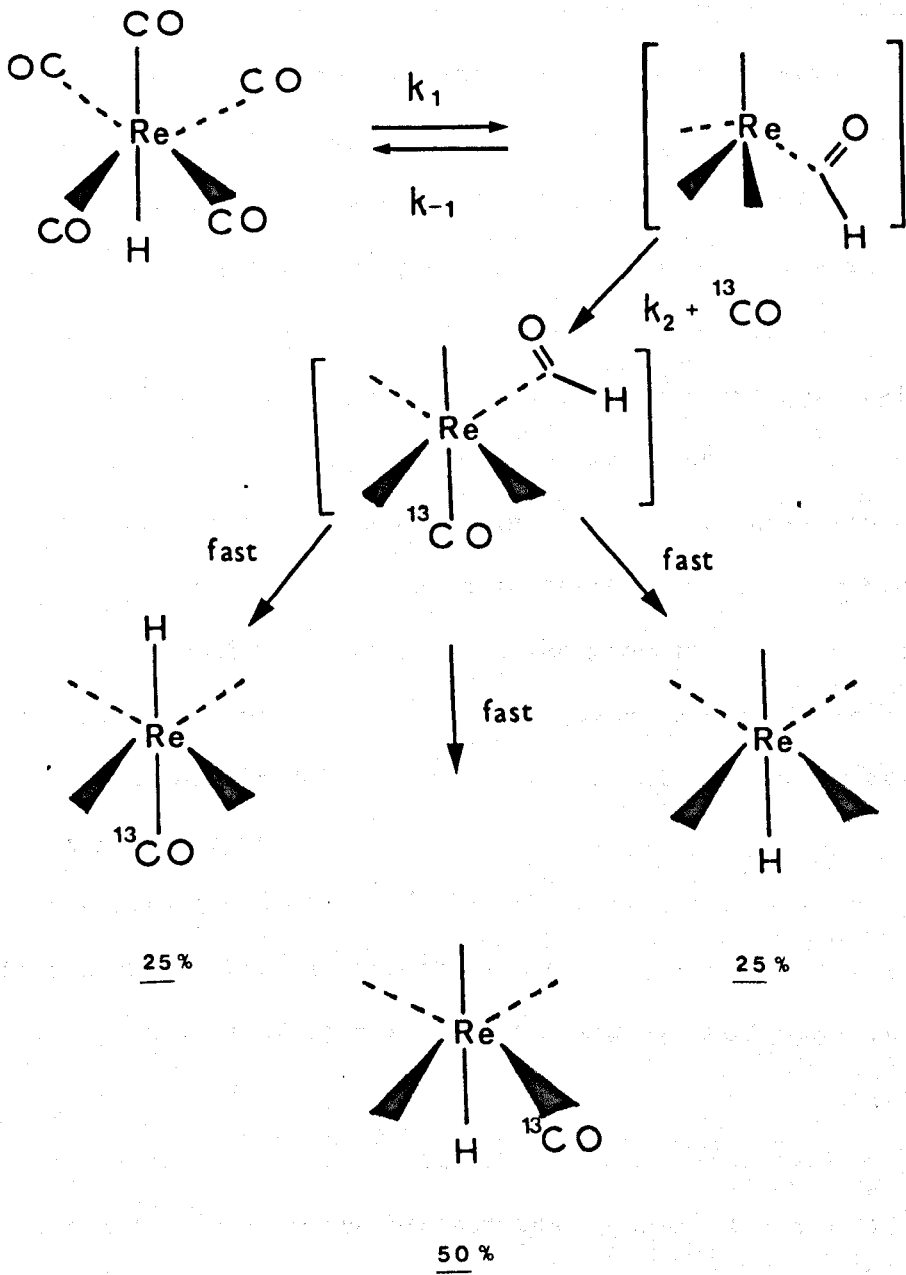


FIGURE 1-12

($L = CO = AsPh_3 < PPh_3 < P Bu^n_3$) .

Solvent effects on the rate are small whilst no evidence for simple carbonyl dissociation has been obtained. However the rates of axial and equatorial ^{13}CO exchange are comparable with those for $Mn(CO)_5 \cdot CH_3$, a species which is known to undergo substitution by an alkyl migration step.

(b) In the presence of free radical initiators both $Mn(CO)_5 \cdot H$ and $Re(CO)_5 \cdot H$ react rapidly by a radical chain mechanism involving a preliminary hydrogen abstraction step followed by rapid dissociation of the seventeen electron pentacarbonylmetal radical generated to yield the tetracarbonylmetal and carbon monoxide. The tetracarbonylmetal species is then seen as the site of incoming ligand attack. The chain terminating step is hydride capture. FIGURE 1-12 illustrates the proposed reaction scheme. It should be noted that the scheme given in the figure represents a non-fluxional model but the experimental evidence does not rule out a partially fluxional intermediate.

(c) Photoexcitation studies¹⁰⁹ have shown that triphenylphosphine is a considerably better entering group for these substrates than tributylphosphine. This may reflect the ease of photolysis of PPh_3 to yield diphenylphosphine and phenyl radicals which serve as initiators for the reaction.

(d) Brown cites evidence to explain the apparent inaccessibility of the hydride migration pathway for the rhenium complex. The molecular orbital arguments of Pearson¹¹² for a transition-state of reduced bond order in hydride transfer mechanisms is coupled with spectroscopic¹¹³ and thermochemical¹¹⁴ measurements in

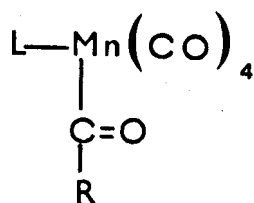
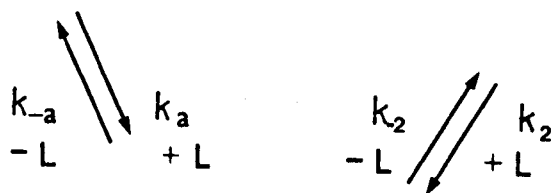
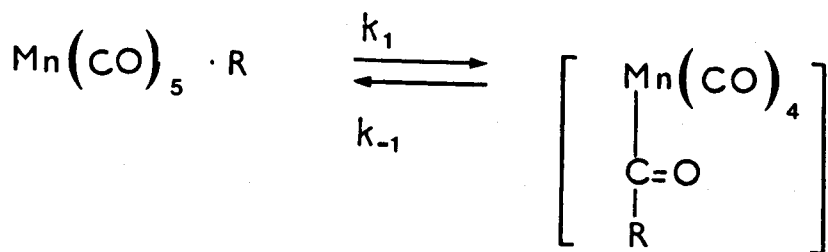


FIGURE 1-13

an attempt to assign the relative inertness of the rhenium complex to the greater strength of the metal-hydride bond.

Evidence points to the unusual mechanisms described above also being applicable to the isoelectronic species $[\text{Fe}(\text{CO})_5\text{H}]^+$. Studies by Noack et al.¹¹⁵ suggest that earlier work was carried out using impure materials resulting in rate measurements influenced by a radical chain process. The ^{13}C studies carried out by Noack are broadly compatible with a hydride migration pathway being operative for iron systems in the absence of free radical initiators.

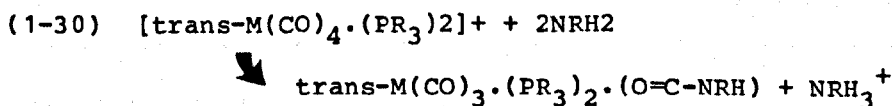
(vii) ($n=0$: $\text{M} = \text{Mn}, \text{Re}$; $\text{L} = \text{CO}$; $\text{A} = \text{CO}$, R ; $\text{M} = \text{W}$; $\text{L} = \text{CO}$; $\text{A} = \text{CS}$) .

The second group of complexes displaying anomalous mechanisms of ligand substitution are those undergoing carbonyl insertion. Early work has been covered by an excellent review from Wojcicki¹¹⁶, whilst more recent work has been carried by Angelici's group using carbamoyl and thiocarbamoyl metal complexes. The most comprehensive studies of a ligand migration pathway are those of Green¹¹⁷, of Calderazzo et al.¹¹⁸ and of Basolo and coworkers¹¹⁹ for the substitution reactions of alkylpentacarbonylmetals. The following model for alkyl migration reactions alkylpentacarbonylmetals. The currently accepted model for alkyl migration reactions is illustrated in FIGURE 1-13. It will be noted that competing k_1 and k_a pathways are proposed, with the k_1 pathway involving ligand migration to form an acyltetracarbonylmetal intermediate. The k_a pathway involves a concerted ligand-dependent ligand substitution whilst the k_1 process is essentially ligand-independent once the condition $k_{-1} \ll k_2[\text{L}]$ is satisfied.

Solvent effect experiments¹¹⁷ indicate that the k_1 pathway involves considerable solvent stabilisation in the transition-state and this is reflected in the unusually low entropies of activation for the pathway

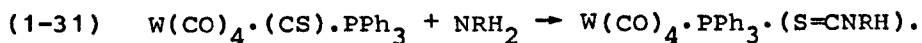
($\Delta S = -60$ to -80 eu.) . Variation of the alkyl group at the metal centre results in substantial changes in the measured rate¹¹⁸, which appear to reflect the electron donor capability of the ligand in the order (R= benzyl = CF_3 < Ph = Me < propyl < ethyl) . Entering group effects are rather more subtle but it appears that the ligand-dependent pathway involves low discrimination towards the entering group in the transition-state. The lower reactivity of the rhenium systems towards ligand migration has been explained in terms of the greater strength of the metal-alkyl bond in these systems as shown by thermochemical measurements¹¹⁴ .

The recent work of Angelici et al.¹²⁰ on the kinetics and position of equilibrium for formation of carbamoyl and thiocarbamoyl complexes of the Group VII^b metal carbonyls, has provided a further insight into entering group at carbonyl carbon in metal complexes. For the systems represented by equation (1-30) a base catalysed attack by amine has been proposed to explain the observed rate law.



where (M= Mn: $\text{PR}_3 = \text{PPh}_3, \text{PPhMe}_2, \text{PPh}_2\text{Me}$; M= Re: $\text{PR}_3 = \text{PPh}_3$)

A concerted attack at carbonyl carbon is considered to provide the best explanation of the rate-law: $k_{\text{obs}} = k_a [\text{NRH}_2]^2$. It is significant that the larger rhenium centre reacts twenty to thirty times as fast as the manganese species. No marked difference in the rate is obtained by varying the phosphine ligands present at the metal centre but a small decrease in the rate is observed with increasing steric hindrance for the amine entering groups. Calculated equilibrium constants are also found to reflect the effect of amine steric hindrance on the rate of substitution. Work with an analogous tungsten complex¹⁰⁰ has indicated that a similar mechanism is applicable.



Although an identical rate law is applicable to both carbonyl and thiocarbonyl systems it appears that the thiocarbonyl carbon is rather more susceptible to nucleophilic attack than carbonyl carbon. The rate-determining step in these systems is found to be base catalysed but acid inhibited, whilst the *cis*-isomer of $W(CO)_4 \cdot (CS) \cdot PPh_3$ is two orders of magnitude more reactive towards insertion than the *trans*-isomer. The activation parameters quoted by the authors reflect a highly ordered transition-state resulting from bond-making rather than bond-breaking.

$$\Delta H = 29.3 (4.2) \text{ kJ mol}^{-1}; \quad \Delta S = -163.2 (12.6) \text{ eu.}$$

A recent communication by Brown¹²¹ reaches the conclusion that this type of base catalysed nucleophilic attack at carbonyl carbon may be of more general significance than has previously been realised.

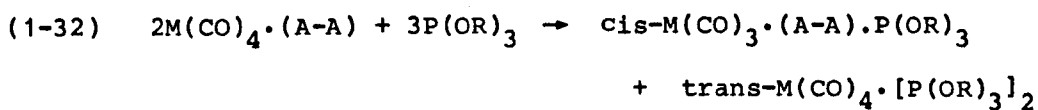
1.6.2 COMPLEXES OF THE GENERAL FORMULA $[ML_4 \cdot (A-A)]$.

The mechanisms of substitution of bidentate chelating ligands at a six-coordinate metal centre have been the subject of a number of studies in recent years. Evidence presently available suggests that systems involving chelating ligands generally display more complicated rate laws than systems involving monodentate ligand substitution.

(i) ($n=0$: $M = Cr, Mo, W$; $L = CO$; $A-A = 2,2'$ -bipyridyl, *o*-phenanthroline, pyridylphosphine, tetramethylenediamine, tetramethyldiaminopropane).

The substitution reactions of complexes containing bidentate chelating ligands bonding to the metal centre through nitrogen have been the subject of extensive investigation since the early reports of Angelici and Graham¹²³⁻¹²⁶ in the mid-1960's. The first studies were concerned with a comparison of the reactivity of complexes of the type $M(CO)_4 \cdot (2,2'$ -

dipyridyl) and $M(\text{CO})_4 \cdot (\text{o-phenanthroline})$, where ($M = \text{Cr, Mo, W}$). When the chromium systems were reacted with phosphite entering groups no bidentate ligand displacement was observed and the sole product was $\text{cis-Cr}(\text{CO})_3 \cdot (\text{A-A}) \cdot \text{P}(\text{OR})_3$. The rate law showed no dependence on entering group concentration but both entropies of activation and rates of substitution seemed to vary with the nature of the entering group. The authors were unable to provide a plausible explanation of the behaviour observed¹²². For the analogous molybdenum and tungsten systems the reaction scheme of equation (1-32) is found to apply:

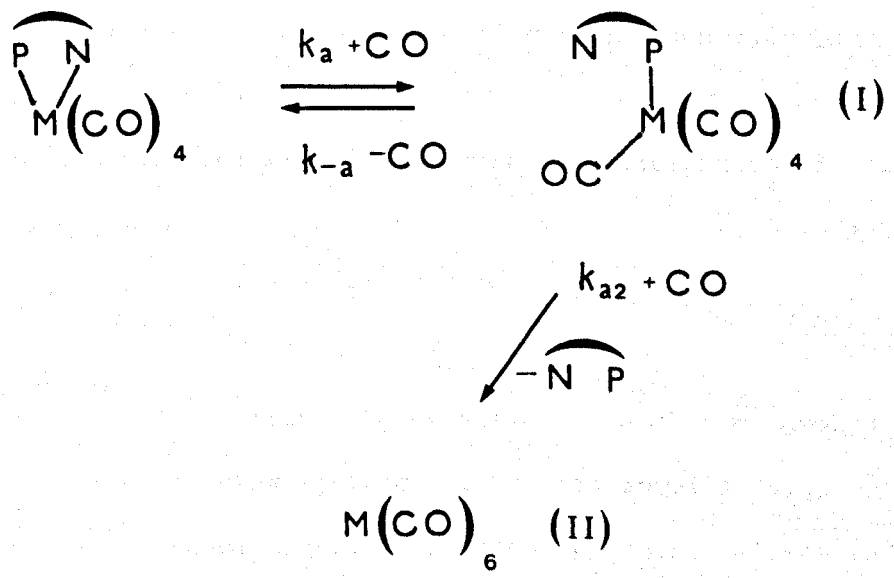
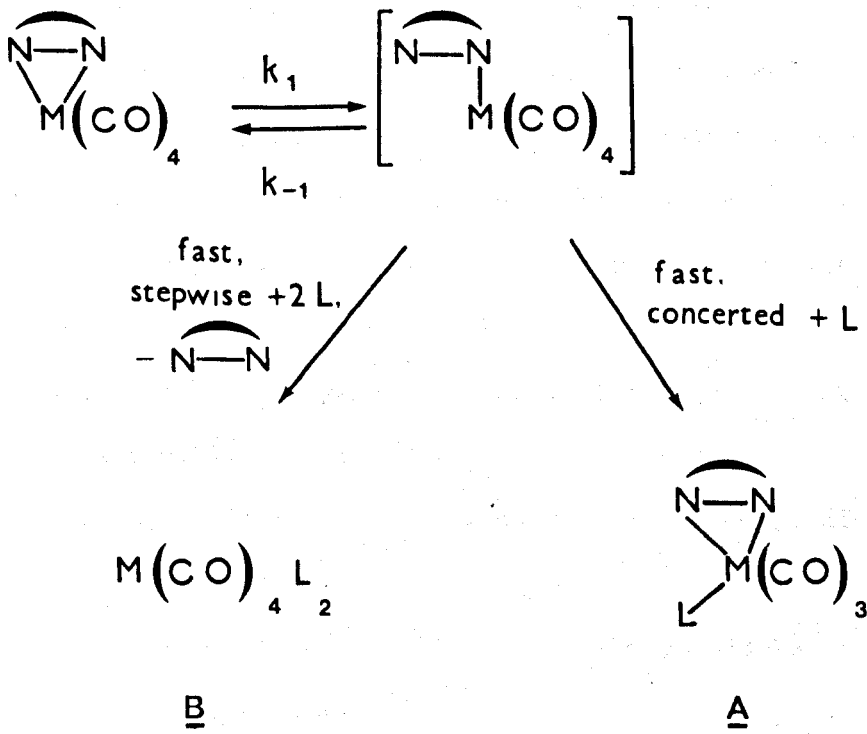


A small amount of a trisubstituted product, $M(\text{CO})_3 \cdot [\text{P}(\text{OR})_3]_3$, was also isolated. The authors postulated concurrent "d" and "a" processes to account for the kinetics of carbonyl substitution, which had the rate law: $k_{\text{obs}} = k_1 + k_a[\text{L}]$, whilst the chelating ligand substitution was thought to follow an additional "a" pathway; for this process a dissociative "ring-opening" pathway was put forward as a plausible alternative. Solvent effect measurements revealed that the solvent played a minor role in determining reaction rate¹²³. The k_1 or dissociative rate constant again showed a dependence on the nature but not the concentration of the entering group. The authors found that an associative mechanism provided a more plausible explanation for the ligand-dependent kinetic behaviour on the grounds that the second-order component in the rate law was far more important for the large molybdenum and tungsten centres than for the chromium centre. Further evidence for the nature of the second-order term was provided by a comparative study of the systems:

($M = \text{Cr, Mo, W}$; $\text{A-A} = 1,2\text{-diamino-2-methylpropane, o-phenanthroline}$)

with monodentate phosphine and phosphite entering groups^{124, 125}. Both chelating ligands displayed a ligand-independent term in the rate law, and for ($M = \text{Cr}$) this was the only accessible pathway. The dissociative pathway

FIGURE 1-14



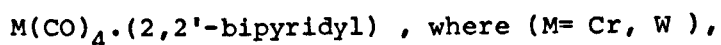
was found to result exclusively in carbonyl displacement to yield $M(CO)_3 \cdot (A-A)_2 \cdot L$. When tungsten and molybdenum systems were used a ligand-dependent term was also found. The type of product generated from this second pathway was found to depend on the nature of chelating nitrogen ligand of the substrate. The relatively flexible diaminopropane ligand was found to be readily displaced to yield a $cis-M(CO)_4 \cdot L_2$ product whilst the rigid o-phenanthroline group did not undergo dechelation and the second-order term resulted in carbonyl dissociation. From these last observations the authors were able to draw the following conclusions:

Three separate pathways are available for ligand substitution with nitrogen chelating ligands :-

- (a) A simple dissociative pathway resulting in carbonyl displacement *cis* to the chelating ligand.
- (b) An associative pathway resulting in carbonyl displacement via a fluxional intermediate.
- (c) A "ring-opening" pathway with a dissociative initial step which permits flexible chelating ligands such as diaminopropanes and bipyridyls to partially dechelate to form a coordinatively unsaturated intermediate. The intermediate can then undergo ring reclosure with carbonyl displacement or can completely dechelate the nitrogen ligand to result in substitution of the bidentate by two monodentate entering groups. The proposed scheme for (c) is given in FIGURE 1-14.

As a result of Angelici's observations a number of groups have made subsequent studies investigating the importance of a "ring-opening" pathway for displacement of bidentate nitrogen chelating ligands.

Dobson et al.^{78,79} have reinvestigated the systems:



with phosphites and explained the dependency of the apparently ligand-independent rate constant k_1 on the nature of the entering group using an extension of pathway (c). For the tungsten system three competing pathways (dissociative, associative, and dissociative "ring-opening") are seen as the basis of the observed kinetic behaviour. As was mentioned earlier Cohen and Brown⁸¹ dispute the accessibility of a "ring-opening" pathway for the chromium systems with carbon monoxide entering groups.

Studies of the kinetic behaviour of complexes containing mixed bidentate chelating ligands have provided further insight into substitution mechanisms in these systems¹²⁶⁻¹²⁸. Second-order kinetic behaviour typical of a "ring-opening" pathway was observed for a series of substitution reactions of the type illustrated in FIGURE 1-15. In all cases studied the nitrogen end of the chelating ligand was displaced before the phosphine grouping and it was generally possible to stop the reaction to isolate intermediate (A) of FIGURE 1-15. Rates of displacement were found to depend on the steric hindrance at the nitrogen centre and on the size of the metal-chelate ring. However in all cases displacement was found to be much slower for derivatives of type $M(CO)_4 \cdot A \cdot A'$, where (A = monodentate amine and A' = monodentate phosphine). Experimental evidence indicated that five membered metal-chelate rings were less reactive towards chelate substitution than their six membered analogues. Evidence for a "ring-opening" pathway was provided by kinetic studies of pyridylphosphine complexes under strongly acid conditions. Under these conditions it would be expected that, following displacement of the nitrogen end of the chelating ligand, protonation of the amine would occur preventing rechelation. As a result there should be no competition between rechelation (ring-reclosure) and dechelation (displacement of the phosphorus end of the

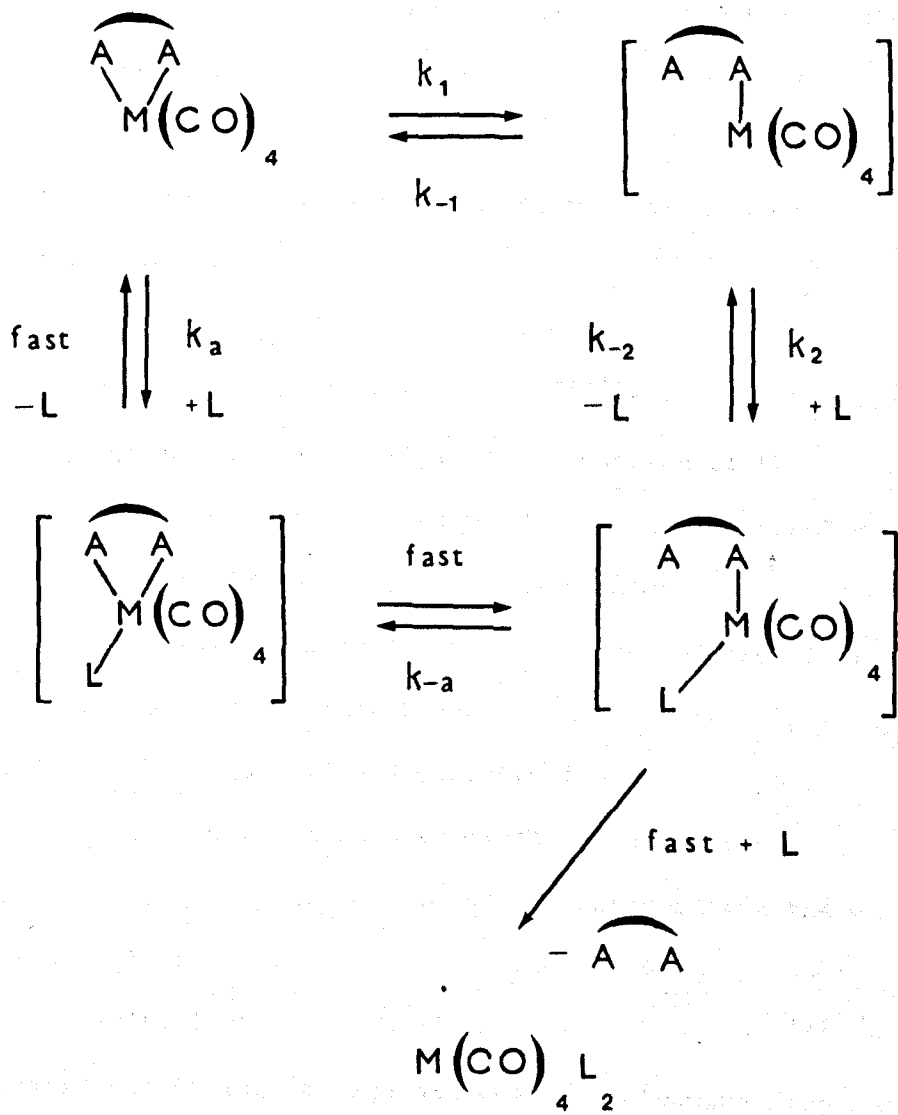


FIGURE 1-16

ligand and replacement by a second entering group). Consequently the rate of substitution should be independent of incoming ligand concentration. This type of behaviour was observed once a limiting concentration of the protonating acid had been reached¹²⁸. Work with the tridentate ligand ($\text{Ph}_2\text{PCH}_2\text{CH}_2\text{N}(\text{Et})\text{CH}_2\text{CH}_2\text{PPh}_2$) established that a similar stepwise dechelation pathway was applicable to this system^{126, 127} and involved initial nitrogen-metal bond dissociation with entering group attack cis to both of the phosphine sites.

Studies by Dobson's group^{85, 129-131} for the substitution kinetics of diaminopropane and diaminoethylene derivatives of the Group VI^b carbonyls illustrate further aspects of the "ring-opening" mechanism. This group find that the "ring-opening" pathway is common to all of the systems studied; no true dissociative pathway is observed but, in the case of the larger molybdenum and tungsten centres, an associative pathway may also be accessible for bidentate ligand substitution. The proposed mechanism is given in FIGURE 1-16. The authors distinguish between a simple dissociative "ring-opening" mechanism (as observed for the chromium systems in their view) and a mechanism involving competing dissociative and associative initial steps in the "ring-opening" process¹³¹. Angelici's observation that chelating ligands capable of forming five membered rings on coordination to a metal were less labile than corresponding ligands forming six membered rings was confirmed by the Dobson group. The relative labilities have been rationalised¹³⁰ in terms of increased strain energies for the six membered metal-chelate rings promoting ligand dissociation and, perhaps of more importance, making ring reclosure less likely for the five-coordinate intermediate generated by the initial dissociation step.

(ii) ($n=0$; $M = \text{Cr, Mo, W}$; $L = \text{CO, X}$; $A-A = \text{diphosphine, diarsine}$) .

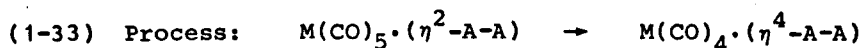
Conclusive studies of the kinetics and mechanism of bidentate phosphorus and arsenic ligands from six-coordinate metal complexes are less abundant than for the analogous nitrogen systems and in view of recent studies on the reactivity of other bidentate systems it may well be that these systems merit further work¹³².

The available studies can be subdivided into two categories: those involving dechelation of a bidentate ligand at a metal centre; and those concerned with chelation of a potentially bidentate ligand bound in monodentate fashion to a metal centre.

(a) Dobson and Rettenmaier have carried out kinetic experiments for ligand substitution at the non-rigid bidentate phosphine complex $\text{Mo}(\text{CO})_4 \cdot (1,2\text{-diphosphinoethane})$, which would be expected to undergo phosphine displacement by a "ring-opening" mechanism by analogy with the related diamine systems⁹⁴. The authors claim that three parallel pathways are operative, with carbonyl displacement to yield $\text{Mo}(\text{CO})_3 \cdot (\text{P-P}) \cdot \text{L}$ occurring by both "d" and "a" mechanisms when the entering group is a monodentate phosphine. A product of structure $\text{Mo}(\text{CO})_3 \cdot \text{L}_3$ is accounted for in terms of a dissociative "ring-opening" mechanism. The kinetics of bidentate ligand substitution with tributylphosphine entering groups are strongly suggestive of a "ring-opening" pathway with an associative initial step whilst those for triethylphosphite and triphenylphosphite suggest competing dissociative and associative initial steps since in these cases plots of k_{obs} against $[\text{L}]$ show marked curvature. The authors' conclusions, which are based on activation parameters, seem rather ambitious in view of the complicated rate law obtaining.

The reactions of phosphites with $\text{Cr}(\text{CO})_4 \cdot [1,2\text{-bis}(\text{diphenylarsino})\text{ethane}]$ were also studied by the same group¹³³. In this case no carbonyl displacement was observed with the products ascribed solely to displacement of the chelating arsenic ligand. Ligand-dependent kinetics were observed with the dependence of rate on entering ligand concentration diminishing at higher ligand concentrations as is typical of a process occurring by a dissociative "ring-opening" pathway. This type of pathway seems the most plausible for a ligand-dependent process involving a bulky but flexible leaving group.

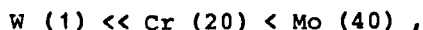
Connor and coworkers have carried out a number of experiments into the chelation of ditertiary phosphines bound to a metal centre in monodentate fashion¹³⁴⁻¹³⁶. Since the reactions were intramolecular the mechanistic information obtained did not include any ligand-dependency terms but was restricted to steric and basicity effects of the potential chelate on the rate of the chelation process. The following order of chelating rates was found:



where (M = Cr, Mo, W) .

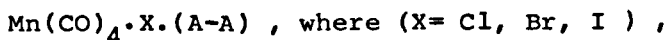
Order: (A-A = bis(dimethylphosphino)ethane = bis(dimethylarsino)ethane > bis(diphenylphosphino)ethane > bis(dicyclohexylphosphino)ethane)

It appears that steric hindrance effects the rate to a far greater degree than basicity of the chelating ligand. For the same chelating ligand the rate of chelation increases in the order:



where relative rates are given in parentheses. Another factor contributing to the chelation rate would appear to be the size of the metal-chelate ring to be formed. The smallest ring, the three membered ring, would be expected to form most rapidly on the grounds of the "high local concentration" effect¹ and this seems to be the case with the kinetic effect outweighing

the opposing ring strain effect which would be expected to reach a minimum for five membered rings. It is interesting that the isoelectronic manganese complexes of structure:



display rates of chelation which are several orders of magnitude more rapid than those for the chromium species.

When considering the authors' detailed arguments it must be noted that a great deal of emphasis is placed on the interpretation of trends in calculated activation parameters. These parameters seem to be of dubious significance however in view of the reported temperature control ($\pm 1^\circ\text{C}$) which would mean that the uncertainties in the quoted values were unrealistically small.

(iii) ($n=0$; $\text{M} = \text{Cr, Mo, W}$; $\text{L} = \text{CO}$; $\text{A-A} = \text{dithia-alkane}$).

The displacement of bidentate sulphur ligands at six-coordinate metal centres has been investigated in some detail by Dobson and coworkers. Early reports indicated that a "ring-opening" mechanism was the most plausible explanation of ligand substitution in these systems^{130, 137, 138}. For all the systems studied (dithia-alkane = dithiahexane, dithiaoctane, dithianonane; $\text{M} = \text{Cr, Mo, W}$) the displacement of the sulphur ligand is the only process observed.

Kinetic experiments for the displacement of dithiahexane by phosphines and phosphites were found to exhibit ligand-dependence for both chromium and molybdenum systems suggesting that a stepwise, dissociative "ring-opening" pathway was the principal accessible route to substitution. A concurrent associatively initiated pathway was proposed in the case of the less sterically hindered molybdenum complex¹³⁷. The results published

in following papers^{130, 138} have been reassessed in the light of a recent reinvestigations^{139, 140}. The latter papers were concerned with tungsten systems and no new or revised information for the chromium or molybdenum species has been published. For the chromium and molybdenum centres with dithia-octane and dithianonane as leaving groups the mechanisms postulated are essentially simple dissociative "ring-opening" processes with "nucleophilicities" of the entering groups reflecting the competition ratios for the free site of the coordinatively unsaturated intermediate between rechelation and dechelation. The ligand-dependent term in the derived rate law becomes less significant for the more sterically demanding dithia-alkanes.

The more recent reinvestigations of the kinetics of substitution of dithia-octane and dithianonane by monodentate entering groups at a tungsten centre are more useful in understanding the complexity of the rate behaviour for bidentate sulphur systems. The authors' present thinking can be encompassed in terms of the reaction scheme given in FIGURE 1-17. It will be noted that this scheme is essentially an expanded form of the mechanism proposed for bidentate nitrogen ligand displacement, cf. FIGURE 1-16, with the important difference that a new term, k_3 , enters into the rate law. The term was found necessary in view of the isolation of an intermediate of type (A) for the system $W(CO)_4 \cdot (\text{dithianonane})$ with the entering group $[P(\text{OCH}_3)_2\text{CMe}]$. The intermediate was found to undergo sulphur ligand dechelation by an ligand-independent pathway and presumably represents a purely dissociative step. Since appreciable concentrations of the intermediate are formed during the displacement reactions the derived rate law becomes appreciably more complicated than for the nitrogen donor systems. For this reason little definite information concerning ligand or substrate contributions to the rate of substitution can be deduced from the rate data. However it does appear that the pathway dependent on k_a is

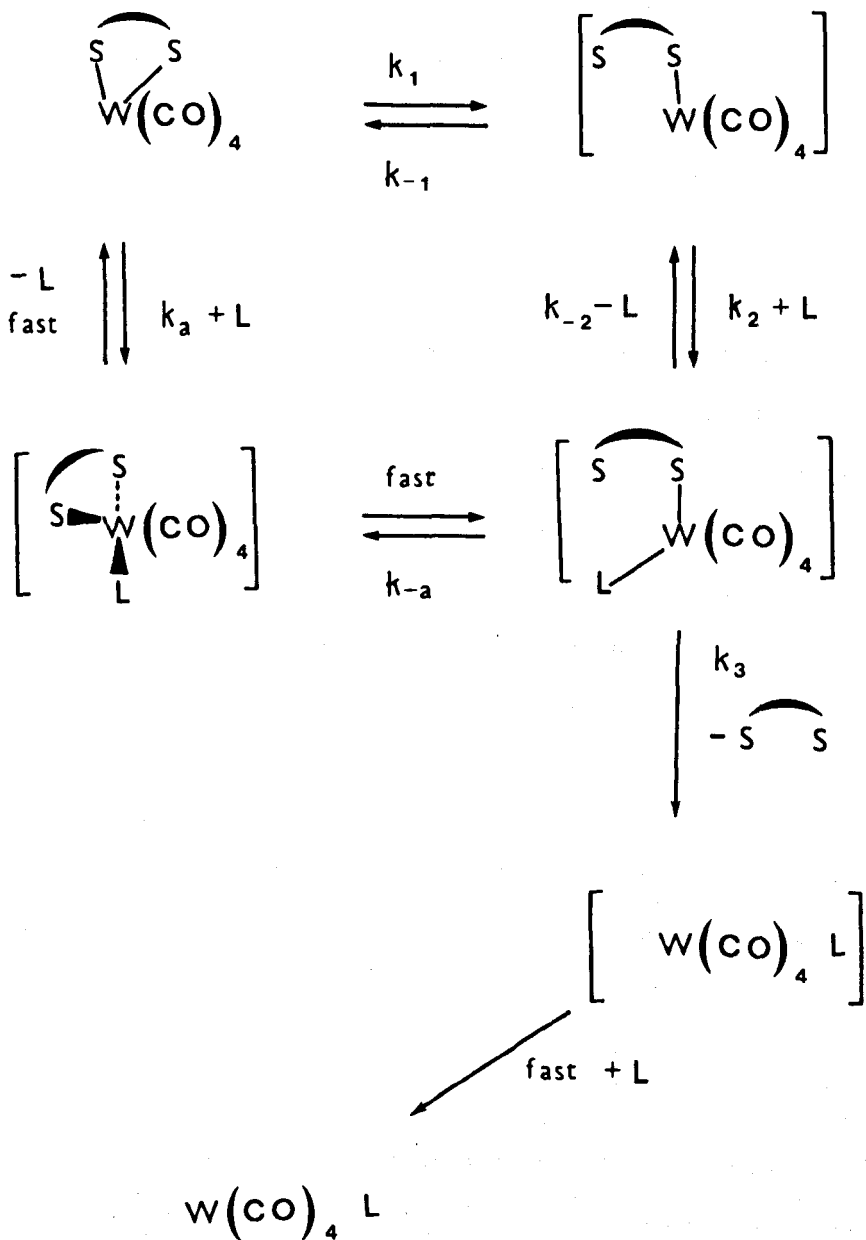


FIGURE 1-17

of negligible importance for dithiaoctane leaving group systems¹³⁹ but it is significant for complexes of dithianonane¹⁴⁰ and dithiahexane¹⁴¹.

Connor and coworkers have investigated the rates of chelation for systems involving potentially bidentate phosphorus ligands. The complexes studied were of the type $\text{Mo}(\text{CO})_5 \cdot (\text{S-S})$, where $(\text{S-S} = \text{RSCH}_2\text{CH}_2\text{SR}; \text{R} = \text{para-substituted phenyl group})$, and both steric and electronic effects on the chelation rate were measured¹⁴². The studies revealed that electronic effects, as displayed by a Hammett plot of aryl substituent effect against chelation rate, were of greater importance than steric considerations. The authors concluded that the experimental evidence supported an increased degree of order in the transition-state when compared to bidentate phosphorus systems, which were found to undergo sterically accelerated loss of a carbonyl as would be expected for a transition-state with more bond-breaking than bond-making character. Connor's results are thus found to be in qualitative agreement with those of Dobson.

(iv) ($n=0$: $\text{M} = \text{Cr}, \text{Mo}, \text{W}$; $\text{L} = \text{CO}$; $\text{A-A} = \text{alkadiene}$) .

Kinetic data for alkadiene substitution in six-coordinate systems is very limited in scope, with the main emphasis on the reactions of the thermally inert bicyclo[2.2.1]hepta-2,5-diene (norbornadiene) and cycloocta-1,5-diene non-conjugated diene systems.

The reactions of $\text{Mo}(\text{CO})_4 \cdot (\text{cycloocta-1,5-diene})$ with Group V^{a} ligands have been studied by Zingales et al.^{143, 144} in non-polar solvents between 25 and 45°C. Products of the form $\text{Mo}(\text{CO})_4 \cdot (\text{PR}_3)_2$ are generated by way of a two term rate law which has the general form:

$$(1-34) \quad k_{\text{obs}} = k_1 + k_a [L] .$$

The authors note that the k_1 rate constant is not truly ligand-independent since it is found to vary with the nature but not the concentration of the entering group. There is only a limited degree of discrimination towards the entering group for the second-order term with bidentate entering groups generally producing higher rates of substitution than monodentate ligands of similar electronic structure. This type of behaviour would seem to be best accommodated by a stepwise dechelation mechanism such as a dissociative "ring-opening".

More recent work concerned with the displacement of norbornadiene from $\text{Mo}(\text{CO})_4 \cdot (\text{norbornadiene})$ also suggests this type of pathway. Harrill and Kaesz¹⁴⁵ report that norbornadiene is completely displaced by isotopically labelled carbon monoxide within three days at ambient temperature if this substrate is used. Although no kinetic or mechanistic work was included in this study it appears that the dechelation of the diene proceeded through a fluxional intermediate since the labelled carbon monoxide was "scrambled" throughout the $\text{Mo}(\text{CO})_6$ generated. Darensbourg et al.¹⁴⁶ have examined the rate of axial-equatorial carbon monoxide exchange in $\text{Mo}(\text{CO})_4 \cdot (\text{norbornadiene})$ and concluded that the process occurs by an intramolecular pathway involving dissociative "ring-opening" followed by Berry pseudorotation of the five-coordinate intermediate. The activation parameters are consistent with an initial dechelation step since they are very similar to those for substitution of norbornadiene by Group V^a ligands in $\text{W}(\text{CO})_4 \cdot (\text{norbornadiene})$ ¹⁴⁷.

Schroeder and Wrighton¹⁴⁸ have published preliminary results for the mechanism of hydrogenation of conjugated alkadienes in the presence of a six-coordinate transition metal catalyst. Using the catalyst $\text{Cr}(\text{CO})_3 \cdot (\text{acetonitrile})_3$ the authors discovered that the stereochemistry of

the alkadiene exerted a considerable influence on the rate of hydrogenation. The assumption was made that an intermediate of the form $\text{Cr}(\text{CO})_3 \cdot \text{H} \cdot (\text{alkadiene})$ was involved in the catalytic process and that the steric effect of the alkadiene on the rate reflected the ease with which it was able to adopt the preferred s-cis geometry for formation of the intermediate.

1.6.3 COMPLEXES OF THE GENERAL FORMULA $[\text{ML}_3 \cdot (\text{A-A-A})]$.

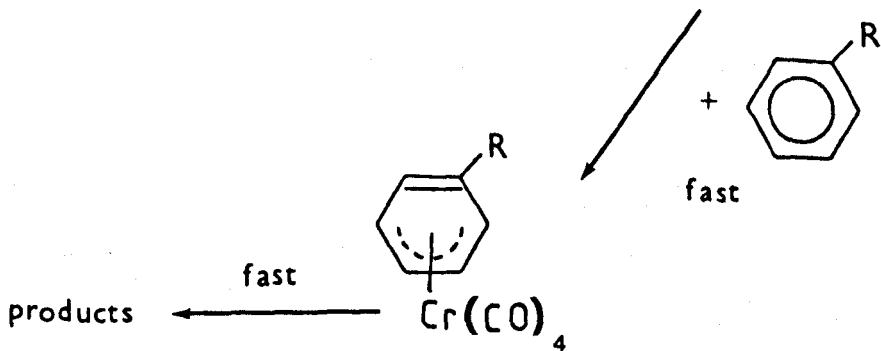
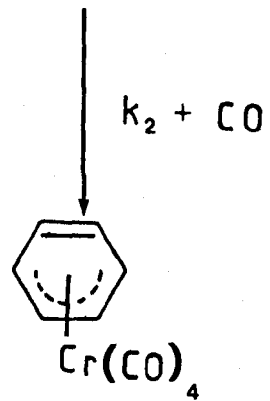
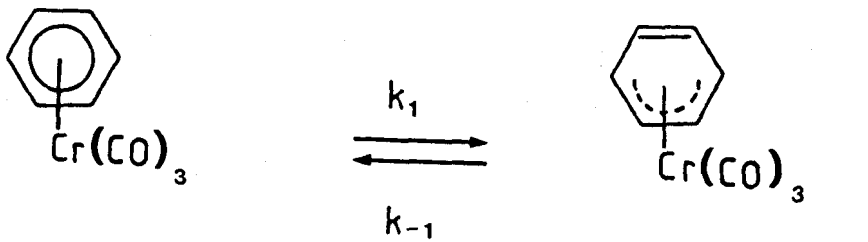
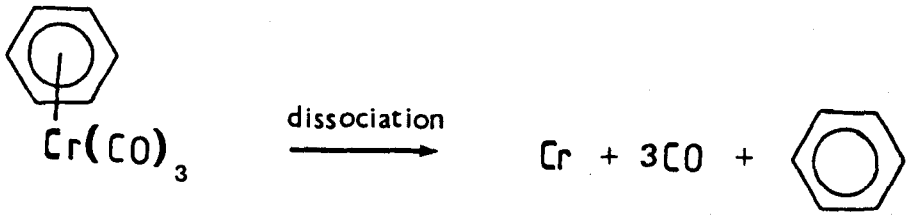
The final important group of six-coordinate systems for which kinetic investigations have been reported involve a tridentate leaving group. In contrast to the other systems discussed the leaving groups studied for this category of complex are almost exclusively organic π -ligands and for this reason tridentate systems provide a useful insight into the catalytic activity of low valent transition metals.

(i) ($n=0$: $\text{M} = \text{Cr}, \text{Mo}, \text{W}$; $\text{L} = \text{CO}$; $\text{A-A-A} = \text{arene}, \text{alkatriene}$) .

Evidence for the mechanism of arene substitution in arenetricarbonylmetal complexes is conflicting: it is particularly noticeable that experiments carried out in solvents of very low polarity disagree markedly with similar experiments carried out in solvents capable of coordinating with the substrate.

The earliest kinetic work carried out on arene systems was that of Strohmeier et al.¹⁴⁹ concerned with arene exchange at $\text{Cr}(\text{CO})_3 \cdot (\text{arene})$ and with the substitution of an alkatriene complex, $\text{Cr}(\text{CO})_3 \cdot (\text{cyclohepta-1,3,5-triene})$ with arenes. The authors claimed that the rate law for the exchange reactions in alkane solvents using temperatures between 90 and 200°C was as follows:

FIGURE 1-18



$$(1-35) \quad \frac{-d[S]}{dt} = k_1[S]^2 + k_a[S][L]$$

The second-order dependence on substrate concentration is not easy to understand since this type of behaviour is not found when the reactions are carried out in solvents of higher polarity¹⁵⁰. The most plausible explanation has been provided by Pauson and his coworkers¹⁵¹ in a useful review of arenetricarbonylmetal chemistry. It is envisioned that one molecule of substrate participates in the reaction by evolving carbon monoxide which is then trapped by a second substrate molecule to yield an intermediate of structure $\text{Cr}(\text{CO})_4 \cdot (\eta^4\text{-arene})$. The proposed sequence of events is given in FIGURE 1-18.

Recent studies of arene exchange for chromium systems¹⁵⁰⁻¹⁵² have been carried out in more polar solvents such as cyclohexanone or tetrahydrofuran. In general milder reaction conditions have been necessary with substitution proceeding in temperature range 25 - 100°C. The reactions have been found to be essentially independent of the entering group but strongly dependent on the electronic and steric characteristics of the leaving group. Entropies of activation, where measured, are suggestive of a strong solvent participation in the transition-state. Since the entering group is a poor nucleophile when ligand exchange is studied the solvent participation should perhaps be interpreted as evidence of an "I_d" mechanism on the basis of the activation entropy data ($\Delta S = -40$ to -80 eu.). The unusual behaviour observed by Strohmeier would, according to this model, be best seen as a consequence of the low coordinating power of the solvents chosen.

Studies of the substitution of arenetricarbonylmetals by Group V^a ligands to yield $\text{M}(\text{CO})_3 \cdot (\text{ER}_3)_3$ and the free arene have provided rather more consistent results. Two groups have published kinetic data for this type of

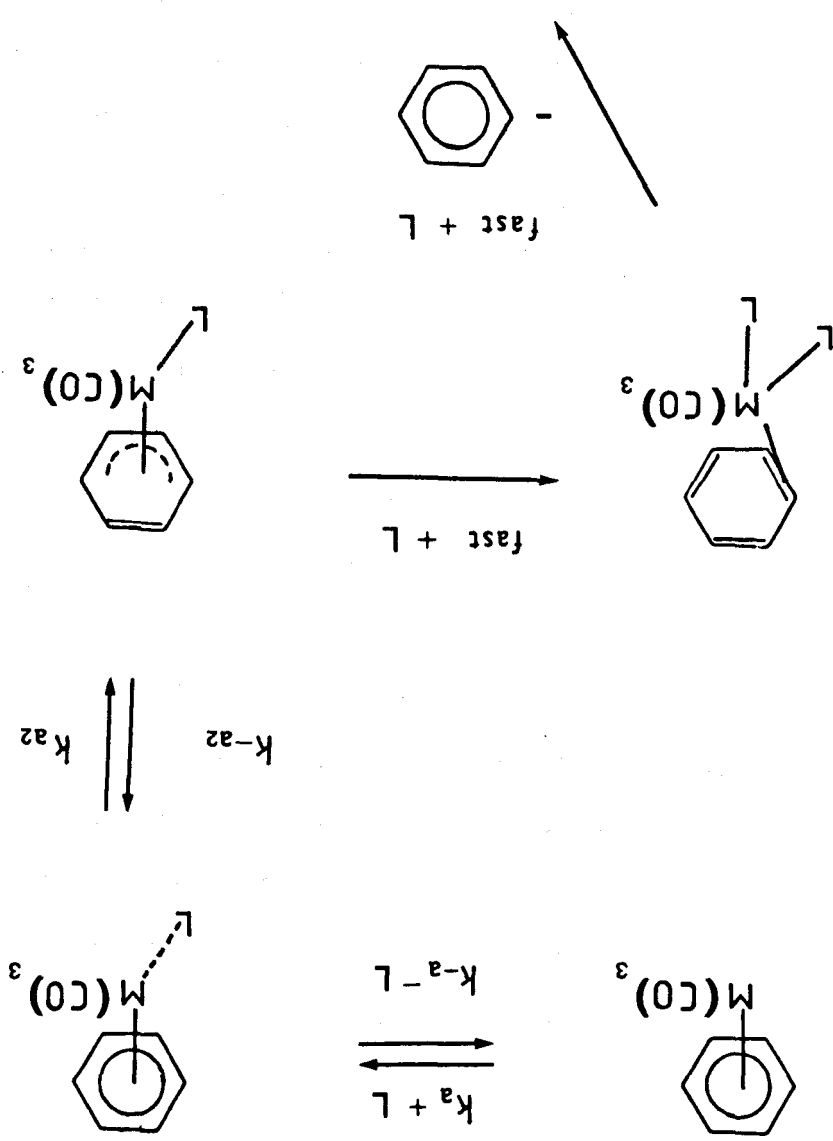
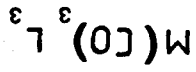


FIGURE 1-19

reaction¹⁵³⁻¹⁵⁷ and in both cases a completely second-order process has been found, with the applicable rate law given in equation (1-36) :

$$(1-36) \quad \frac{-d[S]}{dt} = k_a [S][L]$$

Combining the experimental results it is possible to say that second-order kinetics are obeyed exactly for a wide range of substrate and entering group concentrations whilst solvent effects are found to be negligible. Rates of substitution are strongly influenced by the steric characteristics of the entering group to produce an order of apparent "nucleophilicities" which is only slightly effected by the electronic properties of the ligand. Pidcock et al.¹⁵⁶ pointed out that phosphate esters and polar aprotic solvents catalyse the substitution process but were unable to advance a convincing explanation of this behaviour. The lability of the chelating arene appears to decrease with increasing electron donor ability of the aromatic ring, a finding which is in agreement with the linear free energy relationships reported by Strohmeler and coworkers^{149, 157}. Large negative entropies of activation combined with enthalpies of activation which are considerably smaller than the metal-ligand bond dissociation energy support a rate-determining step involving entering group assisted metal-arene bond cleavage. The activation parameters are suggestive of a transition-state in which bond-making approaches the importance of bond-breaking¹⁵⁵. No kinetic evidence is available as to the pathway followed by the reaction subsequent to the initial associative rate-determining step but a rapid stepwise dechelation mechanism such as that illustrated in FIGURE 1-19 might be expected by analogy with the dechelation mechanisms favoured by other metal-bound π -donor ligands.

Pidcock and coworkers¹⁵⁴ report that a similar mechanism is applicable to alkatriene substitution in $M(\text{CO})_3 \cdot (\eta^6\text{-cyclohepta-1,3,5-triene})$, where ($M = \text{Cr}, \text{Mo}$). The authors found that the triene leaving group was considerably labile towards substitution by phosphites than an arene leaving group. No plausible explanation of this behaviour was advanced.

Two other groups have studied the reactivity towards substitution of triene ligands occupying three coordination sites at a Group VI^b metal centre; in both cases the measurements involved triene displacement by isotopically labelled carbon monoxide. Harrill and Kaesz¹⁴⁵ found that cycloocta-1,3,5-triene was displaced from $\text{Mo}(\text{CO})_3 \cdot (\eta^6\text{-cycloocta-1,3,5-triene})$ by ^{13}CO at ambient temperature to yield hexacarbonylmolybdenum in which the labelled entering group was "scrambled" throughout all the sites in the molecule. From this evidence it was concluded that the substitution process involved at least one fluxional intermediate. The more recent observations of Darensbourg's group^{158, 159} confirm this conclusion and suggest that dechelation proceeds by a second-order "ring-opening" mechanism. Following isolation of the postulated intermediate $[\text{Mo}(\text{CO})_3 \cdot (\eta^4\text{-triene}) \cdot (^{13}\text{CO})]$ it was discovered that the isotopically labelled carbon monoxide was present exclusively in the axial position. Reaction of the intermediate with phosphite entering groups resulted in $\text{Mo}(\text{CO})_3 \cdot (^{13}\text{CO}) \cdot [\text{P}(\text{OR})_3]_2$ showing retention of configuration. On the basis of these additional experiments the authors proposed that the statistical distribution of labelled carbon monoxide in the product of the carbonyl substitution reaction must be assigned to a fluxional $[\text{Mo}(\text{CO})_5]$ intermediate, since replacement of one of the carbonyls of this species by a ligand displaying a site preference results in retention of configuration in the product.

(ii) ($n=0$; $M=Cr$; $L=CO$; $A-A-A=$ hexa-alkylborazole) .

Perhaps the most interesting study of the kinetics of substitution of a complex with a tridentate leaving group is that by Werner, Connor et al. on the displacement of hexa-alkylborazoles from six-coordinate chromium centres¹⁶⁰. The behaviour of this type of pseudo-aromatic ligand seems to offer scope for significant investigation in the future. For those systems so far studied simple second-order kinetics have been followed. Using phosphites as entering groups products of the structure $Cr(CO)_3 \cdot [P(OR)_3]_3$ are generated with the rate of substitution of the hexa-alkylborazole strongly dependent on the steric requirements of the leaving group. On the basis of the decrease in substitution rate with increasing bulkiness of the leaving group and on the large negative entropies of activation the authors propose a stepwise dechelation mechanism with a rate-determining step of the " I_a " type. Thus the borazoles display a very similar mechanism of substitution to arenes.

The final point to be established was that the strength of the metal-borazole bond, as measured thermochemically, was not reflected in the measured Gibbs free energy of activation for the substitution process, supporting the common observation that ground-state properties do not have a decisive influence on the substitutional reactivity of transition metal complexes.

1.7 LIGAND SUBSTITUTION PROCESSES AT FIVE-COORDINATE TRANSITION METAL CENTRES.

Reaction sequences involving ligand substitution steps are of fundamental importance in considering the use of five-coordinate organotransition metal complexes in synthetic chemistry. For this reason it is surprising that kinetic and mechanistic studies of ligand substitution

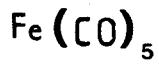
in such complexes have been very limited in the past. At present, kinetic information is largely restricted to systems with monodentate leaving groups, with the polydentate leaving group systems most common in synthetic applications represented by a rather small number of studies of metal-alkadiene complexes.

Following the model employed in the classification of the six-coordinate kinetic studies, based on the number of coordination sites occupied by the leaving group, five-coordinate systems with monodentate leaving groups will be described first.

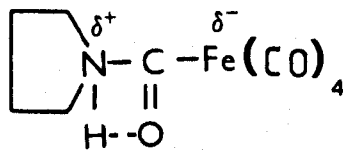
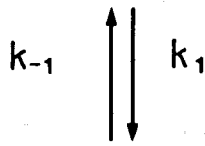
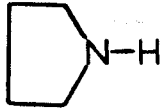
1.7.1 COMPLEXES OF THE GENERAL FORMULA $[ML_4 \cdot A]$.

(i) ($n=0$; $M=V, Mn, Fe$; $L=CO, \eta^5$ -cyclopentadienyl, NO ; $A=CO$).

A number of kinetic studies of ligand substitution have been published for five-coordinate complexes with structures analogous to pentacarbonyliron. Kinetic measurements for pentacarbonyliron itself have been hampered by the practical difficulties of obtaining this highly toxic substrate in a state sufficiently pure to avoid catalysis of carbonyl dissociation caused by the presence of decomposition products of the complex^{1, 161}. In consequence very few reliable measurements have been reported in the literature. Siefert and Angelici¹⁶² have concluded that, in the pure state, pentacarbonyliron does not undergo measurable thermal substitution of the carbonyl ligands at temperatures below 90°C. At higher temperatures it is difficult to carry out accurate kinetic studies due to the rapid decomposition of the substrate. However Frankel and coworkers¹⁶³ have reported that pentacarbonyliron becomes an effective catalyst for the hydrogenation of alkenes at 140°C. The authors postulate that the catalytically active species is tetracarbonyliron, with the rather extreme reaction conditions reflecting the strength of the metal-carbonyl bond



+



hydrolysis

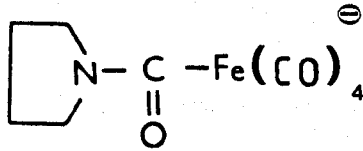


FIGURE 1-20

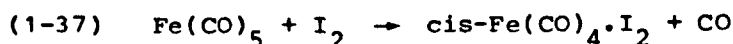
which must dissociate to generate the catalytic species. These observations, which are indicative of the inertness of pentacarbonyliron towards substitution by a simple dissociative pathway, contrast strongly with the evidence that rapid carbonyl substitution will take place at relatively low temperatures in the presence of amines or amine oxides. In this context two studies are of interest: those of Edgell and Bulkin¹⁶⁴ and of Schvo and coworkers¹⁶⁵.

The former work indicated that pentacarbonyliron will react with saturated cyclic amines such as pyrrolidine or piperidine at moderate temperatures to form a product attributed to nucleophilic attack at carbonyl carbon. The infrared, nuclear magnetic resonance, and conductimetric evidence supported the mechanism given in FIGURE 1-20.

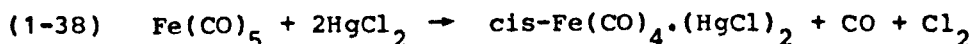
In the recent report¹⁶⁵ Schvo et al. have noted that pentacarbonyliron reacts very rapidly with alkadienes at 0°C in the presence of amine oxides to yield products of the structure $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-diene})$. The yield for the reaction is surprisingly good. For the reaction to proceed in the absence of the amine oxide temperatures in excess of 120°C are needed. In view of the absence of marked solvent effects it seems that the catalytic effect of the amine or amine oxide reflects a rapid pre-equilibrium to form a hydrogen bonded pentacarbonyliron-N donor adduct which then undergoes rate determining ligand dissociation. In this regard it is useful to compare the reported behaviour with that of analogous six-coordinate systems⁷⁴.

Further ligand assisted substitution reactions of pentacarbonyliron have been reported by Dobson. The reactions, which fall into the category of oxidative eliminations, involve the entering groups iodine¹⁶⁶ and mercuric iodide¹⁶¹. The reaction with iodine proceeds

according to equation (1-37) and is extremely rapid requiring stopped-flow kinetic techniques at 25°C .



After an initial induction period during which second-order kinetics were operative the reaction was found to follow a two term rate law. In the absence of photochemical excitation the substitution was postulated to follow the mechanism given in FIGURE 1-21. The importance of the ligand-independent term in the rate law operative after the induction period would support initial formation of a 1:1 adduct via nucleophilic attack at carbonyl carbon. When mercuric chloride is used as the entering group temperatures in the range 25 - 45°C are required for measurable reaction and therefore conventional infrared kinetic monitoring techniques are adequate. A consecutive reaction pathway is found, with an intermediate of structure $\text{Fe}(\text{CO})_4 \cdot (\text{HgCl})_2$ isolatable from the mixture. The generation of this first intermediate is believed to follow equation (1-38) with third-order kinetic behaviour.



The activation parameters for this step are:

$$\Delta H = 48.5 (3.3) \text{ kJ mol}^{-1} ; \quad \Delta S = -124.3 (5.9) \text{ eu.}$$

The subsequent step, which follows second-order kinetics, results in the formation of $\text{cis-Fe}(\text{CO})_4 \cdot (\text{HgCl} \cdot \text{HgCl}_2)_2$. The activation parameters in this case are claimed to be:

$$\Delta H = 8.4 (0.1) \text{ kJ mol}^{-1} ; \quad \Delta S = -257.3 (4.2) \text{ eu.}$$

The authors suggest that the mechanism illustrated in FIGURE 1-21 for the reaction with iodine also applies to mercuric chloride entering group. However the following important difference results in the apparent dissimilarity of the kinetic behaviours: $k_a \gg k_1$ when HgCl_2 is used as the entering group. The authors claim that this reflects the thermodynamically favourable loss of COCl_2 in the rate-determining step in this case. However it must be stressed that no evidence for generation of COCl_2 at any stage

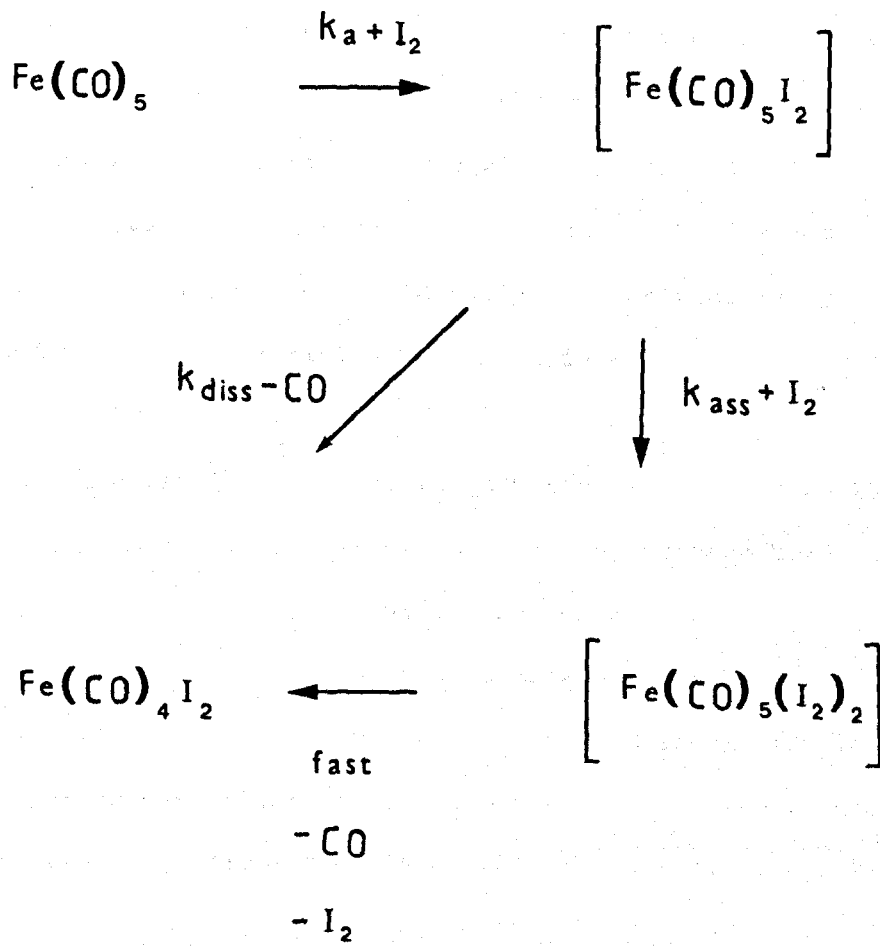


FIGURE 1-21

of the reaction could be given.

It seems from the above that carbonyl dissociation from pentacarbonyliron is thermodynamically unfavourable in the absence of a suitable catalyst ($\Delta H > 190 \text{ kJ mol}^{-1}$ ¹⁶²) and that no lower energy pathway exists for entering group attack at the metal centre; for this reason ligand assisted substitution occurs via nucleophilic attack at carbonyl carbon. However several species belonging to the "pseudo-pentacarbonyliron" series do show considerably greater reactivity than the iron complex and trends in reactivity have been investigated.

Faber and Angelici ¹⁶⁷ have carried out kinetic studies on the substitution of a carbonyl ligand at cyclopentadienyltetracarbonylvandium by phosphines and phosphites. Steric hindrance due to the bulky cyclopentadienyl ligand would be expected to prevent substitution in this system proceeding via an associative intermediate and indeed simple dissociative kinetics were observed. The substitution process required temperatures in the range 110 - 130°C and yielded the following activation parameters:

$$\Delta H = 230.5 (5.0) \text{ kJ mol}^{-1} ; \quad \Delta S = 150.6 (11.7) \text{ eu.}$$

Basolo et al. have investigated the kinetics of substitution of nitrosyltetracarbonylmanganese by Group V^a ligands to yield products with the structure $\text{Mn}(\text{CO})_3 \cdot (\text{NO}) \cdot \text{L}$, where (L = PPh_3 , PBu_3^{n} , P(OPh)_3). Simple second-order kinetics are reported ¹⁶⁸, whilst the substrate shows considerable discrimination towards the entering group. The following order of nucleophilicities was compiled:

(L = PBu_3^n (40) > PPh_3 (1) > P(OPh)_3 (0.1) > AsPh_3 (0.02)).

The values given in parentheses are the relative reactivities. Activation parameters supplied for reactions in xylene at 50°C were as follows:

$$\Delta H = 79.5 (4.2) \text{ kJ mol}^{-1}; \quad \Delta S = -46.0 (12.6) \text{ eu.}$$

An associative pathway of the "a" or "I_a" type seems to provide the best explanation of the observed behaviour. In contrast, when measurements are made for the substitution of a carbonyl ligand in the species generated by the previous reaction, more complicated rate behaviour is reported. When the substrate has the structure $\text{Mn(CO)}_3 \cdot (\text{NO}) \cdot \text{L}$ and (L = PPh_3 , P(OPh)_3) ligand-independent kinetics are observed, but for the case (L = PBu_3^n) a two term rate law seems to apply. Temperatures of the order of 120°C are required for measurable reaction. The authors suggest that steric retardation due to the presence of bulky phosphorus ligands causes suppression of the ligand-dependent pathway in the cases:

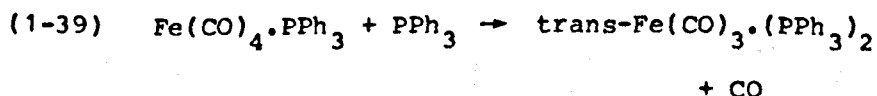
(L = PPh_3 , P(OPh)_3).

(ii) (n=0,1; M = Fe, Ru, Mn; L = CO, PR_3 , NO, C(OEt)R; A = CO, PR_3 ;

n=0: M = Os, Ir; L = CO, H, PR_3 ; A = PR_3 ; n=1: M = Co, Rh;

L = PR_3 , AsR_3 , RNC; A = PR_3 , AsR_3 , RNC).

A number of research groups have investigated the kinetics of ligand substitution in five-coordinate complexes containing monodentate phosphorus and arsenic ligands. The simplest system, that involving $\text{Fe(CO)}_4 \cdot \text{PR}_3$, was examined by Siefert and Angelici¹⁶². The authors found that ligand-independent kinetics were observed for the reaction given by equation (1-39) in decalin between 160 and 180°C.



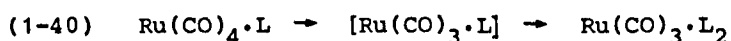
A dissociative mechanism is postulated with the following activation parameters:

$$\Delta H = 177.8 (5.0) \text{ kJ mol}^{-1} ; \quad \Delta S = 77.0 (11.7) \text{ eu.}$$

The very high enthalpy of activation is consistent with the inert behaviour of the parent complex pentacarbonyliron towards ligand substitution by attack at the metal centre, and provides additional evidence for the inaccessibility of an associative pathway in sterically hindered five-coordinate systems. Johnson and Lewis¹⁷⁰ have found that the analogous ruthenium system also shows first-order kinetics consistent with a dissociative pathway; a reversible carbonyl dissociation step is proposed followed by irreversible capture of the coordinatively unsaturated intermediate by the entering group. Activation parameters are as follows:

$$\Delta H = 125.9 (1.3) \text{ kJ mol}^{-1} ; \quad \Delta S = 72.4 (3.3) \text{ eu.}$$

Competition studies carried out under a carbon monoxide atmosphere yielded values of the nucleophilicity ratio k_2/k_{-1} following the scheme of equation (1-40):



A ratio of 0.3 was obtained for ($\text{L} = \text{PPh}_3$) whilst for the case ($\text{L} = \text{PBu}_3^n$) the value of this term was 0.2¹⁷¹. The influence of leaving group size on dissociation rate is illustrated by the observed rates:



In an isolated study Darensbourg and Conder¹⁷⁶ have investigated the mechanism of phosphorus ligand exchange for complexes of the structure $\text{Fe}(\text{CO})_3 \cdot [\text{C}(\text{OEt})\text{R}] \cdot \text{PR}'_3$. Ligand-independent kinetics are claimed with the rate of dissociation of the phosphorus leaving group dependent on the electron withdrawing properties of the carbene auxiliary ligand. The rate of dissociation is greater for ($\text{R} = \text{C}_6\text{H}_5$) than for ($\text{R} = \text{Me}$). Competition studies both with added leaving group, and with mixtures of phosphorus ligands as entering groups, suggest that the four-coordinate intermediate $[\text{Fe}(\text{CO})_3 \cdot [\text{C}(\text{OEt})\text{R}]]$ is only slightly discriminating towards the entering group.

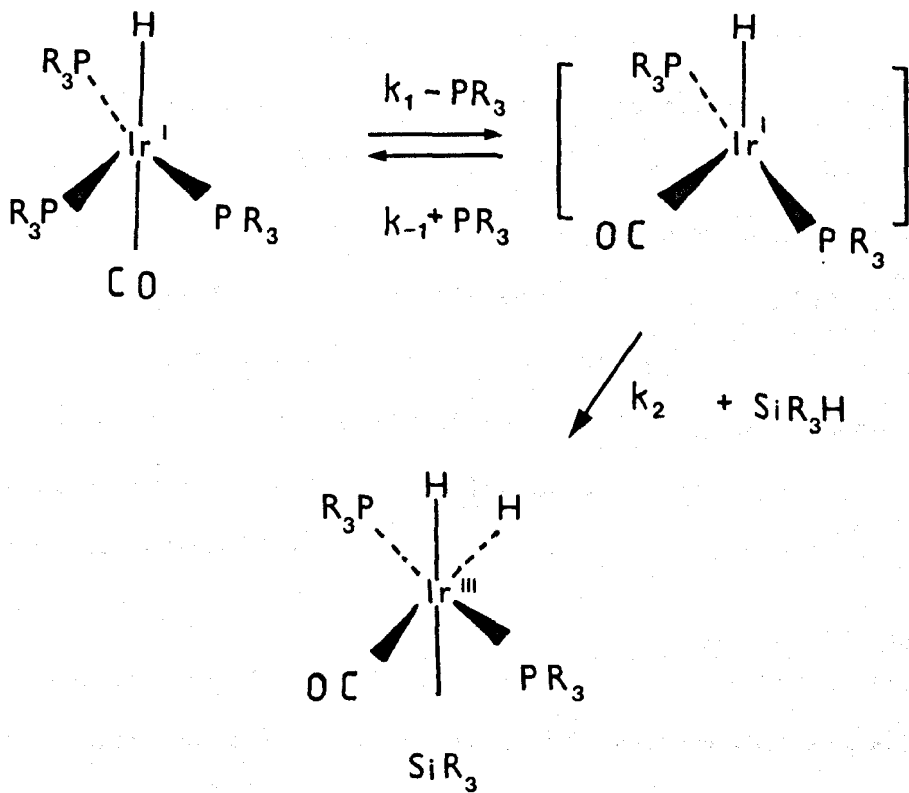


FIGURE 1-22

A few studies of phosphine substitution in five-coordinate systems are also available. For simple systems of the general formula ML_5^+ , where ($M = Co, Rh$; $L = Bu^tNC, PR_3, AsR_3$), ligand exchange has been monitored by means of nuclear magnetic resonance techniques. Muetterties has reported very rapid exchange of isonitrile ligands in $Co(Bu^tNC)_5^+$ at $90^\circ C$ ¹⁷². A dissociative pathway is proposed, resulting in both intermolecular and intramolecular ligand exchange. The ligand exchange rate is approximately $10 s^{-1}$ at $90^\circ C$, which is in marked contrast to the rates of exchange reported for the Group V^a ligands of CoL_5^+ when ($L = PR_3, AsR_3$). The authors state that for these leaving groups the rate of exchange is considerably smaller, but no details are provided. Similar studies¹⁷³ using the substrate $Rh[P(OMe)_3]_5^+$ indicate that the phosphite ligands exchange rapidly in solution in acetonitrile even at $25^\circ C$. The authors postulate a dissociative mechanism with the following activation parameters:

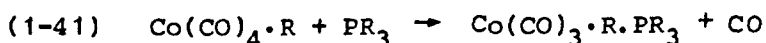
$$\Delta H = 66.5 \text{ kJ mol}^{-1}; \quad \Delta S = 25.9 \text{ eu.}$$

Phosphine dissociation has also been postulated as the rate-determining step in the oxidative addition reactions of the complexes $Ir(CO).(H).(PPh_3)_3$ ¹⁷⁴ and $Os(CO)_3.(PPh_3)_2$ ¹⁷⁵. Using the calculated activation parameters: $\Delta H = 96.2 \text{ kJ mol}^{-1}$, $\Delta S = 62.8 \text{ eu}$, the authors suggested the mechanistic scheme given in FIGURE 1-22 to account for the behaviour observed for the iridium system.

(iii) ($n=0$: $M = Co$; $L = CO, SiCl_3, GeCl_3, SnCl_3, SnCl_3, SnR_3, R, RCO$;
 $A = CO$; $n=0$: $M = Mo, W$; $L = CO, \eta^5\text{-cyclopentadienyl, H}$; $A = CO$).

The most active area of current research into mechanism for five-coordinate organometallic systems relates to the substitution processes of complexes between cobalt or chromium group metals and monodentate Group IV^a ligands. The first reports for the cobalt complexes were produced by Heck¹⁷⁷ in the early 1960's, and were concerned with

systems such as those described by equation (1-41):



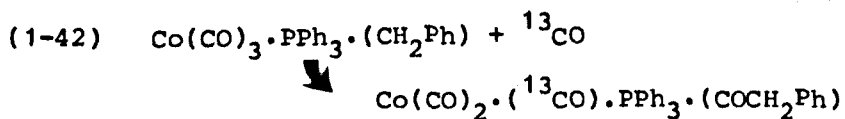
where (R= HCO, CH₃CO).

The work indicated that formyltetracarbonylcobalt was 10⁵ times more reactive towards phosphines than its acetyl analogue. For (R= CH₃CO) ligand-independent kinetics were found in a variety of solvents with the highest rates obtained in solvents with the greatest coordinating power. In toluene between 0 and 25°C the following activation parameters were obtained:

$$\Delta H = 90.8 \text{ kJ mol}^{-1} ; \quad \Delta S = 19.7 \text{ eu.}$$

The formyl complex was found to react too fast for accurate kinetic study even at -70°C . The results given are consistent with a dissociative pathway although it is difficult to rationalise the extreme change in reaction rate in going from a formyl auxiliary ligand to an acetyl ligand. In a later study¹⁷⁸ Breitschaft and Basolo have shown that acetyltetracarbonylcobalt also follows ligand-independent kinetics for carbonyl exchange at 0°C in dibutylether.

In contrast Bor et al.¹⁷⁹ have presented convincing evidence that benzyltriphenylphosphinetricarbonylcobalt reacts with isotopically labelled carbon monoxide at 10°C by a ligand migration pathway (1-42):



The incorporation of only unlabelled carbon monoxide into the acyl carbonyl group of the product is very strong evidence for initial intramolecular carbonyl insertion.

A carbonyl insertion process does not seem to be accessible for triaryl- and trialkyl-tin complexes of tetracarbonylcobalt since both carbonyl exchange¹⁷⁸ and phosphine substitution¹⁸⁰ reactions result in

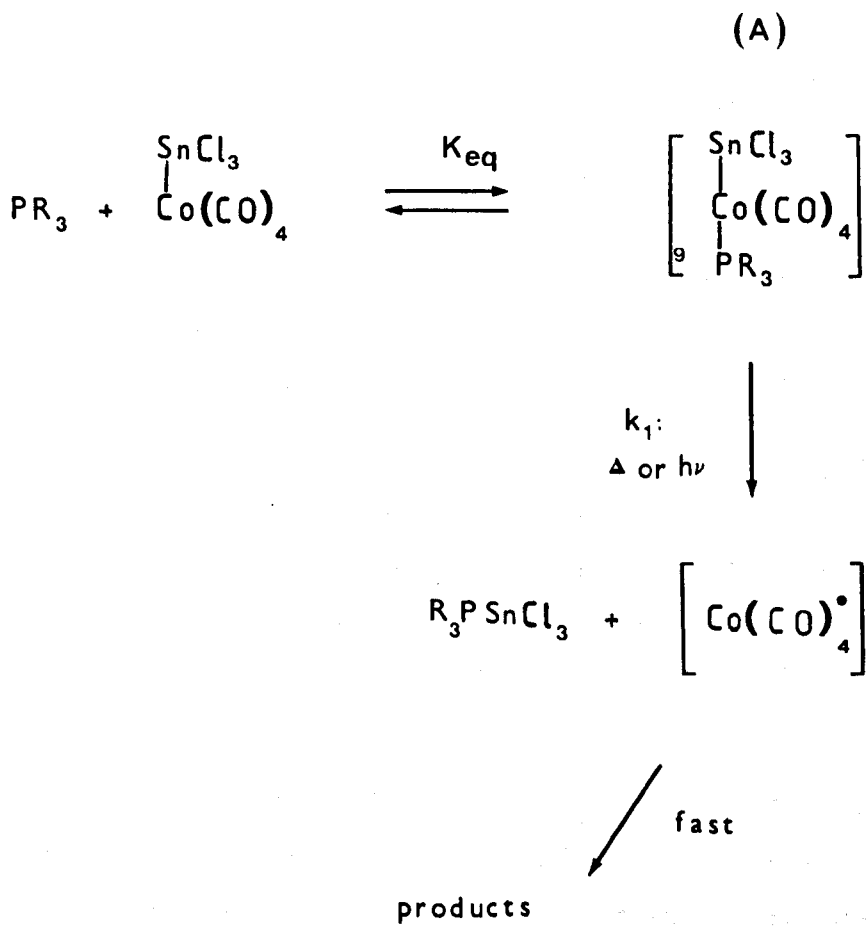
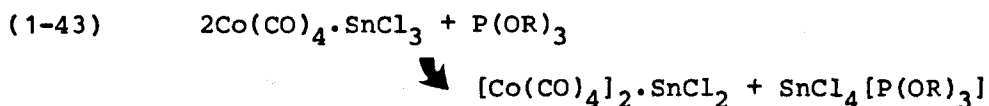


FIGURE 1-23

products of the form $\text{Co}(\text{CO})_3 \cdot \text{SnR}_3 \cdot \text{L}$ by ligand-independent processes. It may however be significant that carbonyl exchange takes place readily in dibutylether at 20°C but that much higher temperatures are required for phosphine substitution.

Ogino and Brown¹⁸¹ have carried out studies for the reaction between trichloro-tetracarbonylcobalt and phosphites which proceeds according to equation (1-43):



Second-order kinetic behaviour is observed. A more precise study by the same group¹⁸² has revealed the substitution of $\text{Co}(\text{CO})_4 \cdot \text{SnCl}_3$ by Group V^a ligands follows a "three-halves" order rate law, in the absence of light and free radical inhibitors. A radical chain pathway has been proposed with the rate-determining step generating two free radicals by homolysis of the intermediate (A) of FIGURE 1-23; the intermediate is explained in terms of a fast pre-equilibrium step.

The kinetics of substitution of the isoelectronic molybdenum and tungsten species have also been investigated. Green et al.¹⁶⁹ reported that complexes of the general formula $\text{M}(\text{CO})_3 \cdot (\text{H}) \cdot (\eta^5\text{-Cp})$, where (Cp= cyclopentadienyl ; M= Mo, W) , reacted with triphenylphosphine by a second-order kinetic process to yield a mixture of cis and trans hydridocyclopentadienylphosphinedicarbonylmetal complexes. For the tungsten complex in benzene at 70°C no kinetic isotope effect was observed when hydride was replaced by deuteride; the reaction was found to proceed at a slightly greater rate in benzene than in acetonitrile. From this evidence the authors discounted a ligand-migration pathway and concluded that an "I_a" or "a" process was responsible for the observed kinetic behaviour. In marked contrast Hoffmann and Brown, in a reinvestigation¹⁸³, noted that

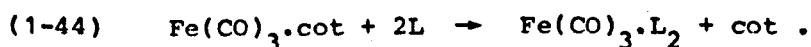
the substitution reaction proceeded thermally in the dark at nonreproducible rates to yield the products described in the earlier work. Reaction rates were found to be strongly dependent on the nature of the entering group, but were also greatly affected by the presence of free radical inhibitors. The authors concluded that a radical chain pathway provided a satisfactory explanation of the experimental results.

1.7.2 COMPLEXES OF THE GENERAL FORMULA $ML_3 \cdot (A-A)$.

($n=0$: $M = Fe, Ru$; $L = CO$; $A-A = \text{alkadiene, polyene}$).

The use of five-coordinate complexes of the iron group metals as hydrogenation and isomerisation catalysts for simple unsaturated organic compounds has prompted a number of research groups to investigate the kinetics of ligand substitution for complexes in which iron or ruthenium is bonded to a simple organic π -ligand. Information is restricted at present to a small number of the more labile systems, notably those with strained cycloalkadiene π -ligands.

Kinetic studies are available for the substitution of seven and eight membered cycloalkadiene ligands in cycloalkadienetricarbonyliron systems by Group V^a entering groups. The earliest report¹⁸⁴ involved displacement of the η^4 -cycloocta-1,3,5,7-tetraene (cot) ligand from $Fe(CO)_3 \cdot cot$ by tertiary and ditertiary phosphines according to equation (1-44):



Second-order kinetics were found for the substitution process when carried out in decalin or methylcyclohexane. The activation parameters for the substitution were found to depend on the nature of the entering group; when tributylphosphine was used as the entering group the following values were obtained:

$$\Delta H = 47.7 \text{ kJ mol}^{-1} ; \quad \Delta S = -159.8 \text{ eu.}$$

whilst with the bidentate phosphine 1,2-bis(diphenylphosphino)ethane the values were:

$$\Delta H = 59.8 \text{ kJ mol}^{-1}, \quad \Delta S = -126.8 \text{ eu.}$$

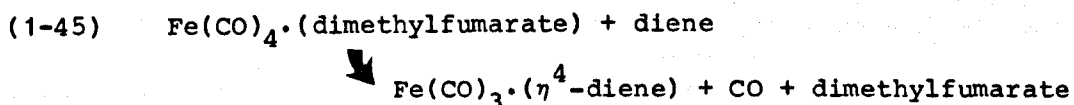
These observations were taken by the authors as evidence for a mechanism involving a transition-state of greater order than the substrate.

Accordingly the most likely pathways were stipulated as "a" or "I_a".

Johnson and Lewis¹⁸⁵⁻¹⁸⁷ have investigated the kinetics of thermal substitution of a series of complexes of the iron group metals with carbocyclic ligands capable of occupying more than one coordination site. The published results suggest that substitution of the carbocyclic ligand is only a significant process at accessible temperatures for complexes containing strained seven and eight membered carbocyclic ligands. When complexes containing planar six and seven membered carbocycles are studied carbonyl substitution is found to be the preferred pathway, yielding species of formula: $M(\text{CO})_2 \cdot (\text{A-A}) \cdot \text{L}$ and $M(\text{CO}) \cdot (\text{A-A}) \cdot \text{L}_2$. A summary of the experimental findings is given in TABLE 1-8. Several useful insights into the bonding of metal complexes can be obtained from the experimental measurements. It is significant that the planar coordinated

π -donor ligand cyclohexa-1,3-diene undergoes carbonyl dissociation exclusively and that the postulated dissociative process yields activation parameters which are very similar to those for carbonyl dissociation in the complex triphenylphosphinetetracarbonyliron¹⁶². Evidently therefore the planar diene does not behave as a labilising ligand towards carbonyl dissociation. This behaviour is in marked contrast to the σ, π -allyl ligand cycloocta-1-3,6-diene, which causes considerable labilisation of carbonyl ligands in $\text{Fe}(\text{CO})_3 \cdot (1-3,6\text{-cod})$. The implication seems to be that the rate of carbonyl dissociation in such π -complexes is dependent on the π -acceptor properties of the non-carbonyl ligands. In considering the

dienetricarbonylmetal complexes it is apparent that planar dienes form much stronger bonds to the metal centre than the carbonyl auxiliary ligands with substitution of the carbocycle only accessible for very strained ring systems. The small negative entropies of activation for the second-order process which results in the substitution of the bidentate organic ligand suggest a stepwise dechelation, or dissociative "ring-opening", pathway proceeding by way of an intermediate such as $[\text{FeL}(\eta^2\text{-diene})\cdot\text{L}]$ ¹⁸³. Cais and coworkers¹⁸⁸ have studied diene exchange in $\text{Fe}(\text{CO})_3\cdot(\text{diene})$ complexes and also chelation of dienes initially bound to the metal centre in dihapto fashion in an attempt to clarify the mechanism of metal carbonyl catalysed hydrogenation of alkenes. The diene chelation proceeds according to equation (1-45) at 110°C in toluene.



First-order kinetics are observed with the activation parameters:

$$\Delta H = 140.6 \text{ kJ mol}^{-1} ; \quad \Delta S = 63.6 \text{ eu.}$$

The authors postulated a rate-determining step involving dissociation of dimethylfumarate to yield a tetracarbonyliron intermediate. More extreme conditions were required for diene exchange; second-order kinetics were observed for diene exchange at $\text{Fe}(\text{CO})_3\cdot(\eta^4\text{-dimethylmuconate})$ in tetralin at 260°C. Accurate measurement was hampered by difficulties with precise temperature control. On the basis of the experimental evidence Cais et al. proposed a mechanism involving stepwise dechelation of the diene leaving group. However it did not prove possible to distinguish between initial concerted dissociation of one η -centre by a ligand assisted pathway or a simple stepwise dissociative pathway as proposed by Johnson and Lewis.

1.8 CONCLUDING REMARKS.

The preceding sections have given a broad outline of currently accepted views of the reactivity of mononuclear five- and six-coordinate organotransitionmetal complexes towards ligand substitution. No attempt has been made to discuss the rather more specialised topic of ligand substitution in polynuclear complexes since a number of useful articles on this subject are available^{16, 189-191}. In considering the reactivity of five-coordinate complexes emphasis has been placed on complexes of the zerovalent metals although some recent work is available on related five-coordinate coordination complexes¹⁹². The kinetics and mechanism of ligand substitution in low valent four-coordinate species are rather less easily defined than those for complexes of higher coordination number. A very large body of review literature is available for the substitution reactions of square planar complexes of Pd(II) and Pt(II) in aqueous media¹⁹³ but only in relatively recent times have reliable studies carried out in non-aqueous solvents become available¹⁹⁴⁻¹⁹⁶. Substitution pathways of the "a" type are the most commonly observed for this class of complex. Information on the kinetics of substitution of formally zerovalent four-coordinate complexes is rather more restricted; the mechanism of substitution of tetracarbonylnickel and related isoelectronic species has been studied in detail¹⁹⁷ but little reliable kinetic information is available¹⁹⁸ for substitution in zerovalent complexes of palladium and platinum despite the current interest in complexes of this type¹¹.

It is notable that in recent years studies of the mechanisms of substitution of five- and six-coordinate species have become considerably more detailed and thorough in approach and in consequence derived rate equations have tended towards increasing complexity. In particular the increased accuracy of the models available for describing the behaviour of

systems involving chelating ligands has given useful insights into the likely mechanisms of transition metal catalysed reactions of coordinated organic substrates. With the recognition of two entirely new pathways to account for second-order kinetic behaviour in organometallic systems, namely the "ring-opening" and "radical chain" pathways, and the detection of concurrent, parallel reaction pathways, it is likely that much early work will have to be reevaluated. As improved synthetic techniques make accessible an increasingly wide range of labile systems of possible application to kinetic studies, a more general model for the reactivity of low valent transition metals should emerge.

TABLE 1-1.

<u>Substrate</u>	<u>Entering</u> <u>Group</u>	<u>T/°C</u>	<u>k_{obs}</u> <u>/s⁻¹</u>	<u>Δ_H^a</u> <u>/kJ mol⁻¹</u>	<u>Δ_H^b</u> <u>/kJ mol⁻¹</u>	<u>Δ_S^a</u> <u>/eu.</u>
Cr(CO) ₆	¹⁴ CO	130	0.99	161.9	163.2	77.4
Mo(CO) ₆	¹⁴ CO	115	0.75	126.4	132.2	-1.7
W(CO) ₆	¹⁴ CO	150	0.08	166.5	169.9	46.0

Footnotes.

^a Gas phase reaction.

^b Reaction carried out in decalin solution.

TABLE 1-2.

<u>Substrate</u>	<u>Entering</u> <u>Group</u>	<u>k₁/k₂</u> <u>ratio</u>	<u>Δ_H^{k1}</u> <u>/kJ mol⁻¹</u>	<u>Δ_H^{k1}</u> <u>/eu.</u>	<u>Δ_H^{ka}</u> <u>/kJ mol⁻¹</u>	<u>Δ_S^{ka}</u> <u>/eu.</u>
Cr(CO) ₆	PBu ⁿ ₃	1.7	168.2	94.6	106.7	-61.1
Mo(CO) ₆	PBu ⁿ ₃	0.1	132.6	28.0	90.8	-62.3
W(CO) ₆	PBu ⁿ ₃	0.15	166.9	57.7	122.2	-28.9

TABLE 1-3.

<u>Substrate</u>	<u>Entering</u> <u>Group</u>	ΔH k1 <u>/kJ mol⁻¹</u>	ΔS k1 <u>/eu.</u>
ClMn(CO) ₅	AsPh ₃	112.5	65.7
BrMn(CO) ₅	AsPh ₃	122.2	79.1
I.Mn(CO) ₅	AsPh ₃	132.2	86.2
ClRe(CO) ₅	PPh ₃	114.2
BrRe(CO) ₅	PPh ₃	123.0
I.Re(CO) ₅	PPh ₃	133.1

TABLE 1-4.

<u>Substrate</u>	<u>Entering</u> <u>Group</u>	<u>T/°C</u>	$10^4 k_1$ <u>/s⁻¹</u>	$10^4 k_a$ <u>/s⁻¹</u>	<u>Products</u>
Mo(CO) ₅ Cl ⁻	PPh ₃	19.6	>10	(B) only.
Mo(CO) ₅ Br ⁻	PPh ₃	19.6	1.3	4.1	(A) + (B).
Mo(CO) ₅ I ⁻	PPh ₃	29.8	1.1	1.8	(A) + (B)
Mo(CO) ₅ I ⁻	PBu ⁿ ₃	29.8	1.1	2.8	(A) + (B)
Mo(CO) ₅ I ⁻	PBu ⁿ ₃	29.8	1.1	3.6	(A) + (B)

TABLE 1-5.

<u>Substrate</u>	<u>Δ_H^{k1}</u>	<u>Δ_S^{k1}</u>	<u>Δ_H^{Id}</u>	<u>Δ_S^{Id}</u>
	<u>/kJ mol⁻¹</u>	<u>/eu.</u>	<u>/kJ mol⁻¹</u>	<u>/eu.</u>
Mo(CO) ₅ .Quinuclidine	112.5	23.0	55.2	-159.0
Mo(CO) ₅ .Piperidine	107.9	11.7	69.0	-84.1
Mo(CO) ₅ .Cyclohexylamine	102.5	9.2	66.5	-77.8

TABLE 1-6.

<u>System</u>	<u>Substrate</u>	<u>Entering Group</u>	<u>Product</u>
I	$\text{Fe}(\text{CO})_3 \cdot (1,3\text{-chd})$	PPh_3	$\text{Fe}(\text{CO})_2 \cdot \text{PPh}_3 \cdot (1,3\text{-chd})$
II	$\text{Fe}(\text{CO}) \cdot (1,3\text{-chd})$ $\cdot (1,4\text{-chpd})$	PPh_3	$\text{Fe}(\text{CO}) \cdot (\text{PPh}_3)_2 \cdot (1,3\text{-chd})$
III	$\text{Fe}(\text{CO})_3 \cdot (1,3,5\text{-chpt})$	PPh_3	$\text{Fe}(\text{CO})_2 \cdot \text{PPh}_3 \cdot (1,3,5\text{-chpt})$
IV	$\text{Fe}(\text{CO})_3 \cdot (1,3\text{-cod})$	PPh_3	$\text{Fe}(\text{CO})_3 \cdot (\text{PPh}_3)_2$
V	$\text{Fe}(\text{CO})_3 \cdot (1\text{-}3,6\text{-cod})$	PPh_3	$\text{Fe}(\text{CO})_2 \cdot (\text{PPh}_3)_2 \cdot (1\text{-}3,6\text{-cod})$
VI	$\text{Fe}(\text{CO})_3 \cdot (1\text{-}3,6\text{-cod})$	$\text{P}(\text{OEt})_3$	$\text{Fe}(\text{CO})_2 \cdot [\text{P}(\text{OEt})_3]_3$
VII	$\text{Ru}(\text{CO})_3 \cdot (1\text{-}3,6\text{-cod})$	PPh_3	$\text{Ru}(\text{CO})_2 \cdot (\text{PPh}_3)_2 \cdot (1\text{-}3,6\text{-cod})$

Footnotes:

Abbreviations employed: $1,3\text{-chd} = \eta^4\text{-cyclohexa-1,3-diene}$
 $1,4\text{-chpd} = \eta^4\text{-cyclohepta-1,4-diene}$
 $1,3,5\text{-chpt} = \eta^4\text{-cyclohepta-1,3,5-triene}$
 $1,3\text{-cod} = \eta^4\text{-cycloocta-1,3-diene}$
 $1\text{-}3,6\text{-cod} = \eta^3\text{-cycloocta-1-}3,6\text{-diene.}$

TABLE 1-7.

<u>System</u>	<u>T/°C</u>	<u>Rate law</u>	<u>ΔH</u> <u>/kJ mol⁻¹</u>	<u>ΔS</u> <u>/eu.</u>
I	160-180 ^a	$k_{\text{obs}} = k_1$	176.1 (3.3) ^c	69.0 (7.5) ^c
II	30-50 ^b	$k_{\text{obs}} = k_1 + k_a [\text{L}]$	185.4 (2.9) ^d	-12.6 (8.4) ^d
III	154 ^a	$k_{\text{obs}} = k_1 + k_a [\text{L}]$
IV	50-80 ^b	$k_{\text{obs}} = k_a [\text{L}]$	87.0 (0.8) ^d	-33.5 (2.5) ^d
V	40-70 ^b	$k_{\text{obs}} = k_1$	122.2 (0.8) ^c	63.6 (2.1) ^c
VI	40-70 ^b	$k_{\text{obs}} = k_1 + k_a [\text{L}]$	57.3 (2.1) ^d	-113.0 (6.7) ^d
VII	20-45 ^b	$k_{\text{obs}} = k_1$	110.9 (0.4) ^c	57.7 (2.1) ^c

Footnotes:

- a Reaction carried out in solution in decalin.
- b Reaction carried out in heptane.
- c Activation parameters given refer to the ligand-independent pathway.
- d Activation parameters refer to the ligand-dependent pathway.

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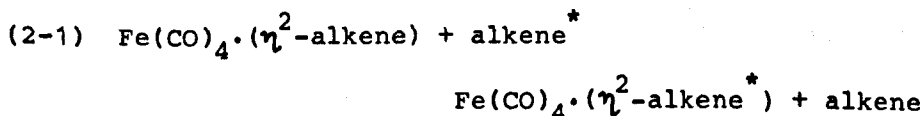
CHAPTER TWO: THE KINETICS AND MECHANISM OF ALKENE EXCHANGE AT

FIVE-COORDINATE IRON.

2.1 INTRODUCTION.

It is rather surprising that although a large number of kinetic studies of ligand substitution in organometallic systems have been described, systems involving carbon monoxide exchange are the only exchange reactions well represented in the literature. Amongst a group of exchange reactions of synthetic and industrial importance which do not appear to have been adequately investigated is the class of η -ligand exchange processes, which are believed to be involved in many transition metal catalysed reactions.

The work described in this chapter was designed to clarify the mechanism of monodentate η -ligand exchange in five-coordinate transition metal systems, whilst succeeding chapters detail work on bidentate η -ligand exchange in five- and six-coordinate systems. Since alkenes are representative monodentate η -ligands and form complexes which have been shown to undergo ligand substitution at accessible temperatures¹⁻⁶, it was decided to use readily synthesised species of the type $\text{Fe}(\text{CO})_4 \cdot (\eta^2\text{-alkene})$ as substrates in the exchange studies. It was found that alkene exchange with this type of substrate resulted in a clean but reversible reaction with the stoichiometry given by equation (2-1):



A further advantage of the chosen substrates was that the results of substitution reactions using Group V^a ligands as entering groups were available⁴ thus allowing comparison of substrate reactivity towards entering groups of widely differing steric and electronic properties. The

model obtained from comparison of these low temperature studies could then be examined against evidence obtained from work carried out at high temperatures and pressures using $\text{Fe}(\text{CO})_4 \cdot (\eta^2\text{-alkene})$ complexes as hydrogenation catalysts.

2.2 RESULTS AND DISCUSSION.

The alkene exchange reactions of two different substrates, $\text{Fe}(\text{CO})_4 \cdot (\eta^2\text{-styrene})$ and $\text{Fe}(\text{CO})_4 \cdot (\eta^2\text{-methylacrylate})$, were studied with a number of different entering groups. The substrates have been prepared and characterised by previous workers^{7,8} as have the products of π -ligand exchange reactions with acyclic alkenes. Species of the type $\text{Fe}(\text{CO})_4 \cdot (\eta^2\text{-cycloalkene})$, the products of ligand exchange with cycloalkene entering groups, are thermally unstable oils, which it did not prove possible to characterise fully. Only one similar species has been reported in the literature⁹. All reactions for which kinetic data are supplied produce a quantitative yield of the π -ligand exchange product when a large excess of the entering group is used although with cycloheptene entering group thermal decomposition of the substrate $\text{Fe}(\text{CO})_4 \cdot (\eta^2\text{-styrene})$ to yield dodecacarbonyltriiron is a significant side-reaction with substrate to entering group concentrations of less than 1:80. Ligand exchange reactions for which kinetic data are given were carried out in 100-120° petroleum ether using infrared monitoring techniques as described in Appendix A; the infrared carbonyl absorption bands of the complexes used for the studies are given in the experimental section. Despite the use of a solvent which interacts only weakly with the infrared carbonyl stretching absorptions of the metal carbonyls involved in the study overlap of substrate and product absorptions was generally observed, particularly for the lower frequency bands. The apparent overlap of the spectra was not found to effect the rate measurements, which showed good pseudo-first-order behaviour both for

substrate disappearance and for product appearance; and for this reason deconvolution of the spectra was not deemed necessary.

TABLE 2-1 gives the results of preliminary ligand exchange experiments which were carried out at 60°C. The preliminary studies provide several interesting insights into the mechanism of ligand exchange in monodentate five-coordinate systems. Firstly it is apparent that the substrates undergo slow thermolysis to yield $\text{Fe}_3(\text{CO})_{12}$ and other decomposition products if the reaction is carried out in the absence of a suitable entering group. In the case of the substrate styrenetetra carbonyliron the thermolysis was studied by a variety of physical techniques including infrared and nuclear magnetic resonance spectroscopy and gas-liquid chromatography. The reaction was found to proceed by a rate-determining step involving loss of the coordinated alkene, presumably to yield a tetracarbonyliron intermediate. The coordinatively unsaturated intermediate would then be expected to polymerise rapidly to yield $\text{Fe}_3(\text{CO})_{12}$. It was noted that extended reaction times resulted in a further thermolysis, that of $\text{Fe}_3(\text{CO})_{12}$ to yield pentacarbonyliron and associated decomposition products. The rate of the thermolysis of the $\text{Fe}(\text{CO})_4 \cdot (\eta^2\text{-styrene})$ complex to yield $\text{Fe}_3(\text{CO})_{12}$ was found to be at least an order of magnitude smaller than that for η^1 -ligand exchange, whilst the thermolysis was inhibited entirely by the presence of a large excess of entering group.

A second point arising was that the ligand exchange system $\text{Fe}(\text{CO})_4 \cdot (\eta^2\text{-styrene})$ - methylacrylate is potentially reversible as has been previously reported¹. The reaction $\text{Fe}(\text{CO})_4 \cdot (\eta^2\text{-methylacrylate})$ - styrene does not go to completion but does produce an appreciable yield of the styrene exchange product. In this context it is noteworthy that the reaction between $\text{Fe}(\text{CO})_4 \cdot (\eta^2\text{-styrene})$ and acrylonitrile produces an

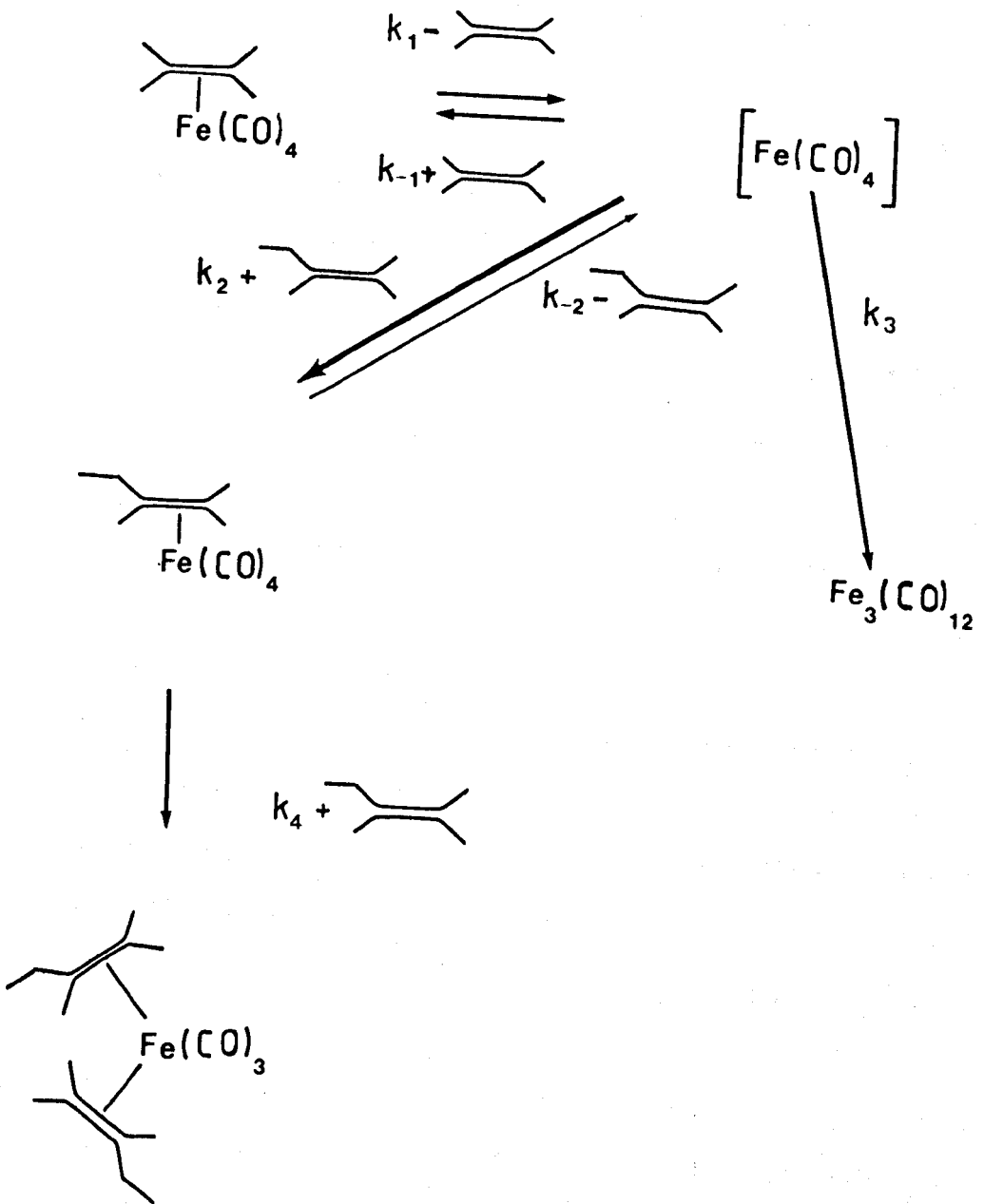


FIGURE 2-1

infrared spectrum indicative of more than one product of π -ligand exchange. This finding is consistent with the evidence of synthetic studies^{10(a)} since acrylonitrile is capable of coordinating to a metal either as a π -donor through the carbon-carbon double bond or through a σ -bond via the nitrogen of the nitrile substituent. The reported spectrum of the π -bonded species exhibits a characteristic axial carbonyl vibration at 2063cm^{-1} in hexane^{10(a)} whilst the σ -bonded species has a vibration at 2031cm^{-1} . An alternative structure for the second product species in the ligand exchange studies is $\text{Fe}(\text{CO})_3 \cdot (\text{alkene})_2$ ^{10(b)}, for which the reported axial carbonyl stretching frequency is approximately 2024cm^{-1} , also in good agreement with that found in the present study. In view of the absence a second metal carbonyl product for the other systems studied the former explanation of the experimental observations seems the more plausible.

On the basis of the preliminary studies the reaction scheme illustrated in FIGURE 2-1 can be derived for alkene exchange at $\text{Fe}(\text{CO})_4 \cdot (\eta^2\text{-alkene})$. The proposed mechanism involves rate-determining loss of alkene to yield tetracarbonyliron as the reactive intermediate, and is exactly analogous to the mechanism proposed for alkene substitution at $\text{Fe}(\text{CO})_4 \cdot (\eta^2\text{-alkene})$ with Group V^a ligands as entering groups¹⁻⁵.

In order to gain additional information concerning the mechanism of π -ligand exchange in this type of system detailed kinetic studies were carried out for reactions IIa, IIc and IIId. The results of pseudo-first-order kinetic experiments for these systems are given in TABLE 2-2 with plots of the observed rate constant (k_{obs}) against entering group concentration ($[L]$) for each system given in FIGURES 2-2, 2-3 and 2-4. Only reactions producing quantitative yields of the expected $\text{Fe}(\text{CO})_4 \cdot (\eta^2\text{-alkene})$ product, i.e. $k_3 = 0$, are listed. The data for the systems with methylacrylate and cis-cyclooctene as entering groups can be treated

System \square^a

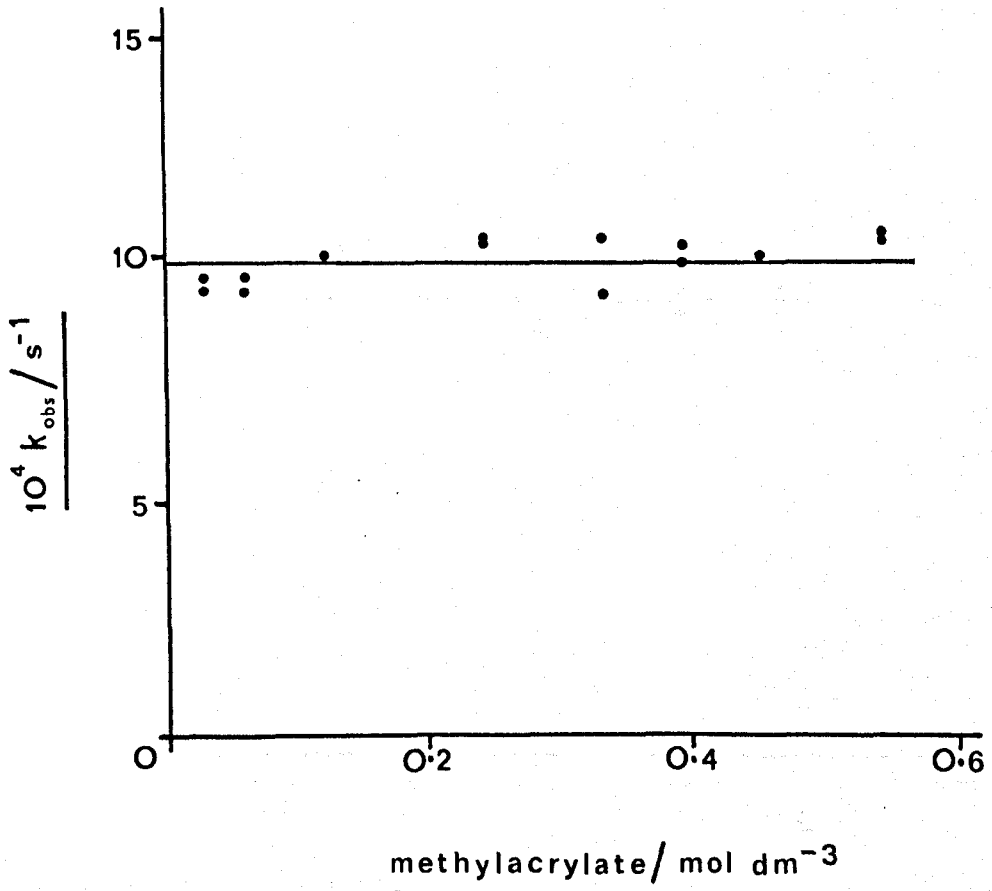


FIGURE 2-2

System \square^c

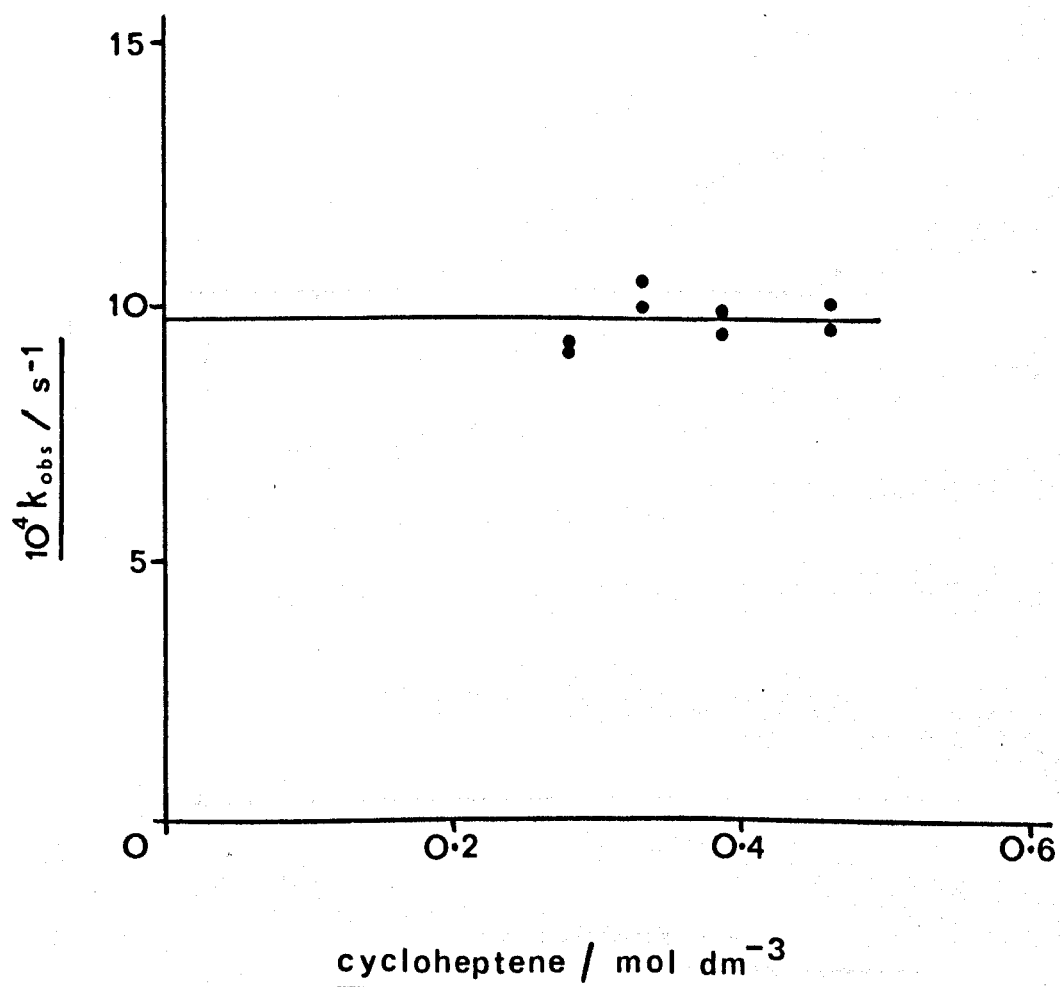


FIGURE 2-3

System Π^d

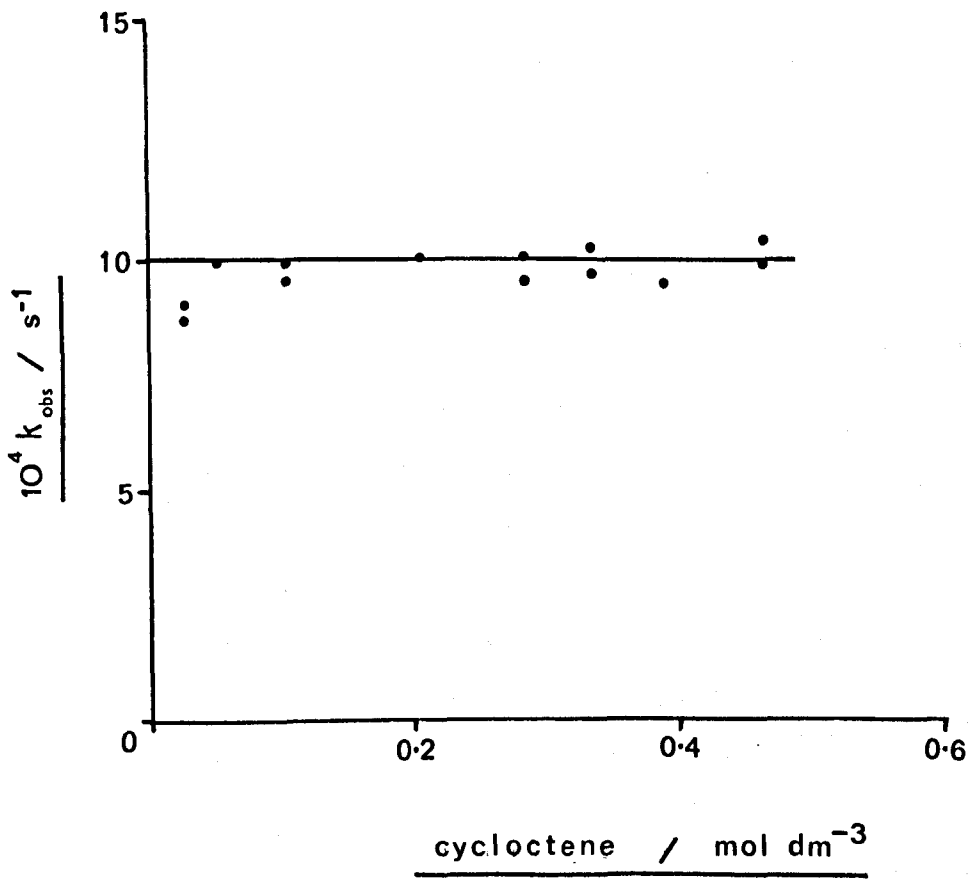


FIGURE 2-4

mechanistically as irreversible under the conditions employed but it appears that with the entering group cycloheptene this assumption cannot be made. At substrate to ligand ratios of less than 1:80 this system shows good pseudo-first-order kinetic behaviour with respect to substrate disappearance but not with respect to product appearance. The evidence suggests that under these conditions exchange is not quantitative, perhaps indicating that the partial rate constants k_{-1} and k_3 are sufficiently large to prevent complete ligand exchange.

If the data obtained from experiments resulting in quantitative ligand exchange is treated according to the model given in FIGURE 2-1 the applicable rate law is represented in equation (2-2):

$$(2-2) \quad \frac{-d[SA]}{dt} = \frac{k_1 k_2 [SA] [L]}{k_{-1} [A] + k_2 [L]}$$

where (SA= substrate, A= leaving group and L= entering group.)

Equation (2-2) reduces to the simplified form (2-3) when pseudo-first-order reaction conditions are used:

$$(2-3) \quad k_{obs} = \frac{k_1 k_2 [L]}{k_{-1} [A] + k_2 [L]}$$

Under these conditions it can be seen that once $k_2 [L] \gg k_{-1} [A]$ the applicable rate expression should reduce to the (2-4) with a limiting exchange rate at high entering group concentrations:

$$(2-4) \quad k_{obs} = k_1$$

Therefore, if the model is consistent with the experimental findings, the value of k_{obs} obtained at high [L] should reflect k_1 , the rate-determining loss of alkene from the substrate. Examination of the data presented in TABLE 2-2 reveals that this is indeed the case. Since all three systems investigated employ the substrate $Fe(CO)_4 \cdot (\eta^2\text{-styrene})$ the k_1 term in each case reflects the dissociation of a metal-styrene bond, a process which should be independent of the nature and concentration of the entering

Mass Effect Data.

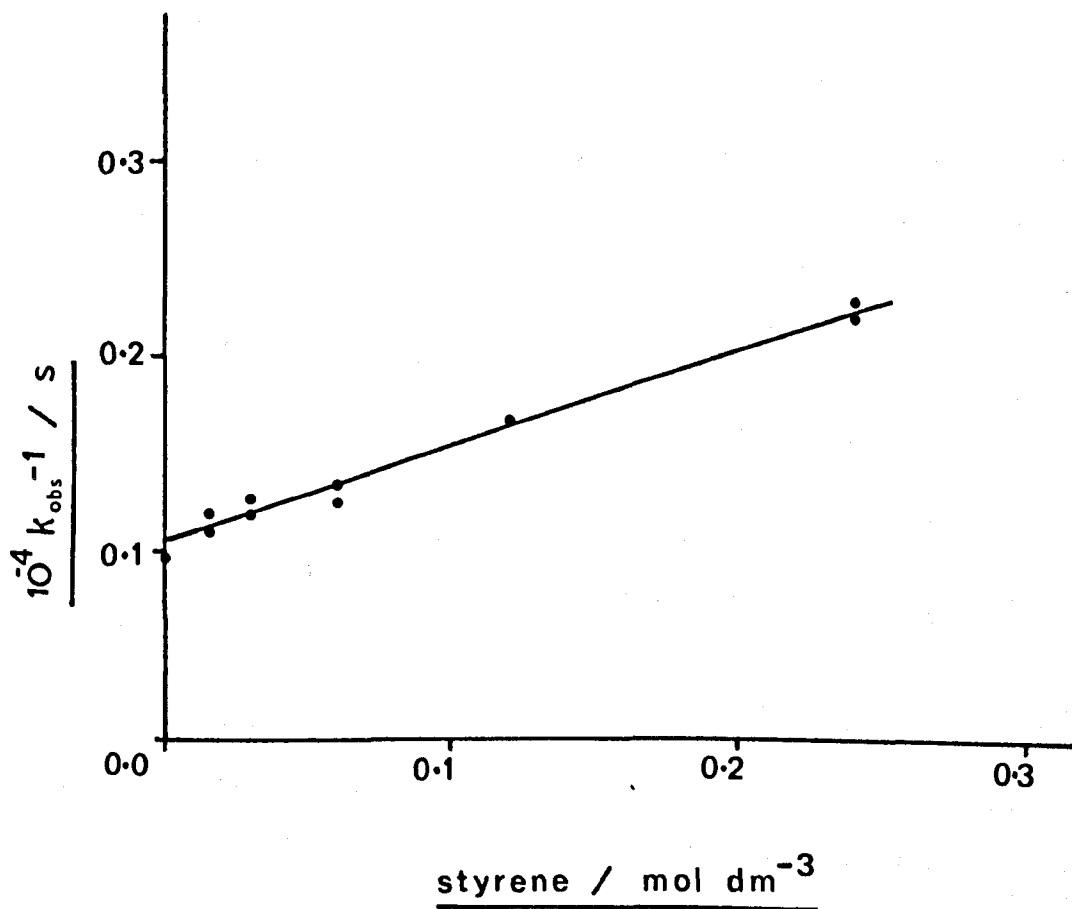


FIGURE 2-5

group. This being the case the value of k_1 obtained for each of the systems should be identical and this is found to be so, within experimental error.

A further test of the proposed mechanism is provided by investigation of the kinetics of ligand exchange carried out under pseudo-first-order conditions but in the presence of added leaving group. Rearranging equation (2-3) reveals that a plot of the reciprocal of the observed rate constant against concentration of added leaving group should be linear for a series of experiments carried out at constant entering group concentration. Equation (2-5) indicates that a plot of this type would have a slope reflecting the k_{-1}/k_2 ratio with an intercept which was the reciprocal of k_1 .

$$(2-5) \quad \frac{1}{k_{obs}} = \frac{k_{-1}[A]}{k_1 k_2 [L]} + \frac{1}{k_1}$$

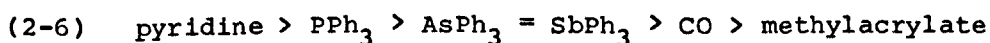
A series of experiments to test this relationship was carried using the system $\text{Fe}(\text{CO})_4(\eta^2\text{-styrene})$ - methylacrylate - styrene and the results are given in TABLE 2-3. An examination of FIGURE 2-5 shows clearly that model is in accord with the experimental data. The value of k_1 obtained from the intercept of the plot is in good agreement with that obtained by direct methods following equation (2-4), whilst the value of the k_{-1}/k_2 ratio is 1.06 ± 0.06 . Since k_2 reflects the rate of formation of the metal-entering group bond, and k_{-1} measures the recoordination of the leaving group, it would appear that both entering group and leaving group have similar reactivity towards the coordinatively unsaturated intermediate. A competition ratio close to unity does not seem unreasonable in this case, as both ligands have very similar structures in that they are alkenes with electron-withdrawing substituents.

It is instructive to compare the results of the present study using alkene entering groups with work carried out with rather more nucleophilic entering groups. Cardaci and his coworkers have carried out a detailed study of the substitution of alkenes at $\text{Fe}(\text{CO})_4 \cdot (\eta^2\text{-alkene})$ by Group V^a ligands, and by carbon monoxide¹⁻⁵. The mechanism postulated for these systems is exactly analogous to that given in FIGURE 2-1 for alkene exchange. With the more nucleophilic Group V^a ligands the substrate polymerisation term k_3 was found to be of negligible importance, whilst a product of form $\text{Fe}(\text{CO})_3 \cdot \text{L}_2$, presumably generated by further substitution of the product of the alkene substitution pathway, as represented by k_4 in FIGURE 2-1, was found to be present in significant concentration. Additional information concerning the mechanism was provided by studies of the solvent dependency of the observed rate³ and of the effect of substituents at the leaving group in determining lability⁴. The finding that:

- (a) there was no significant solvent effect on substitution rate;
- (b) the rate of substitution decreased when electron-withdrawing substituents were present at the leaving group;

were consistent with a dissociative mechanism. From data on the temperature dependence of the partial rate constant k_1 it is possible to compare the alkene-metal bond dissociation rate in the presence of a strong nucleophile with that found with alkenes as entering groups. An extrapolation of the data for the system $\text{Fe}(\text{CO})_4 \cdot (\eta^2\text{-styrene})$ - triphenylphosphine in hexane provides a value for k_1 of $10.4 \times 10^{-4} \text{ s}^{-1}$ at 60°C , in good agreement with the values obtained in the present work for reactions carried out in a solvent of similar properties. Perhaps the most interesting additional information is provided by an examination of the k_2/k_{-1} ratios obtained by Cardaci's group for a series of different entering groups with the substrate $\text{Fe}(\text{CO})_4 \cdot (\eta^2\text{-styrene})$. The values published are referenced to 50°C ; however competition ratios of this type would not be expected to show

appreciable temperature dependence and for this reason it should be possible to combine the results of the earlier work¹ with those obtained in the present study to produce an order of entering group nucleophilicity. The resultant list is given by (2-6):



It is interesting that the order of the k_2/k_{-1} values suggests that carbon monoxide is a better nucleophile towards tetracarbonyliron than the electron deficient alkene methylacrylate since a similar order appears to hold for the analogous chromium species¹⁶. The implication of this observation would appear to be that the π -acceptor ability of the entering group is of greater importance in determining the bond strength of the complex in this case than the electron donor characteristics (carbon monoxide is a notoriously poor donor ligand but a very good π -acceptor species, whilst the reverse is generally true of alkene ligands).

High temperature studies by Cais and coworkers⁶ have shown that complexes of the type $\text{Fe}(\text{CO})_4 \cdot (\eta^2\text{-alkene})$ are effective hydrogenation catalysts for alkenes. Results suggest that the catalytic species is generated by rate-determining loss of an alkene ligand to yield a coordinatively unsaturated intermediate. The favoured intermediate is believed to be tetracarbonyliron and the implication is that substitution in alkenetetracarbonyliron complexes occurs almost exclusively by a dissociative mechanism, regardless of the reaction conditions. Since species such as alkadienetricarbonyliron and heterodienetricarbonyliron have been shown to undergo ligand substitution by ligand-dependent kinetics^{6, 15} the ligand independent kinetics of the tetracarbonyl systems requires some explanation.

The most likely reason for the differences in kinetic behaviour for complexes containing monodentate π -ligands and those containing bidentate π -ligands lies with the structures of the two types of complex. Structural studies have revealed that species of the type $\text{Fe}(\text{CO})_4 \cdot (\eta^2\text{-alkene})$ adopt a trigonal bipyramidal configuration in the solid state and in solution^{11,12}, with the alkene occupying an equatorial site. In contrast structural information for the species of the type $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-diene})$ suggest a distorted square pyramidal structure with the diene occupying two basal sites^{13,14}. From this evidence it is plausible to suggest that the differences in behaviour are of steric origin since the trigonal bipyramidal structure of the tetracarbonyl complexes does not possess a suitable site for the coordination of a sixth ligand as would be required for an associative term in the rate law. On the other hand an exchange process taking place at a complex with a square pyramidal structure may readily coordinate a sixth ligand to generate an octahedral intermediate with the additional ligand occupying an apical site.

It is considerably more difficult to provide an adequate explanation for the trends in entering group reactivity observed in the present study. A comparison of the relative reactivities of the acyclic entering groups methylacrylate and acrylonitrile is inconclusive. Both alkenes are electron deficient and form well defined π -complexes with five-coordinate iron; however, in the present work, the exchange reaction with acrylonitrile appears to generate more than one product with the result that detailed comparison of the two entering groups is not possible. The competition studies between styrene, methylacrylate and their respective complexes do suggest that electronic and steric effects are not marked for acyclic entering groups since the k_2/k_{-1} ratios obtained are close to unity, though it must be added that the slightly greater nucleophilicity of methylacrylate than styrene is reflected in TABLE 2-1 where it is shown

that the reaction $\text{Fe}(\text{CO})_4 \cdot (\eta^2\text{-methylacrylate})$ - styrene does not go to completion.

When considering the trends in reactivity for the cycloalkene entering groups structural correlations are not easily discerned. Cyclohexene, cycloheptene and cyclooctene would be expected to have very similar electronic configurations whilst the observed order of reactivity towards tetracarbonyliron (2-7) correlates with increasing rather than decreasing ring size.

(2-7) cyclooctene > cycloheptene >> cyclohexene

Since conventional arguments would predict that the least sterically demanding of the cycloalkenes should be the best entering group, if other effects were not significant, a more subtle influence on reactivity must be found. Ring strain energy and ring conformation seem to provide a suitable explanation of the observed behaviour. Following Benson¹⁷ the measured ring strain enthalpy for cycloalkenes increases in the order given by (2-8):

(2-8) cyclohexene (5.8) << cycloheptene (23) < cyclooctene (25) ;

where the numbers in parentheses represent strain enthalpies in kJ mol^{-1} .

The ring strain entropies are also observed to increase in the same order, giving rise to the idea that the driving force of the exchange reactions is related to the ring conformation of the entering group. In this regard molecular orbital calculations on the free cycloalkenes provide interesting information^{18, 19}. Each of the cycloalkenes used in the kinetic studies had the cis-configuration at the double bond. Molecular orbital calculations indicate that cyclohexene occurs almost exclusively in the chair conformation which would be expected to be less favourable towards metal coordination than the boat form in which metal-methylene interactions would be minimised. Since the boat form of the free ligand is less thermodynamically favourable than the chair form by 23.5 kJ mol^{-1} metal-ligand coordination for this alkene would not be expected to be a

thermodynamically favoured process. However when the more strained systems cycloheptene and cyclooctene are considered a rather different picture emerges. Calculations on cycloheptene suggest that the chair conformation is favoured over the twist-boat form (not accessible to cyclohexene) by 2.2 kJ mol⁻¹ and over the boat form by 14.5 kJ mol⁻¹ 18. In the case of cis-cyclooctene the authors concluded that the molecule was flexible with no obvious preferred conformations although barriers to rotation were of the order of 20 kJ mol⁻¹. From these results it seems that exchange will proceed at a measurable rate only if twist-boat or boat conformations of the cyclic entering group are readily accessible. This finding is in agreement with the results of work carried out on trans-cyclooctene and its metal complexes^{9,19}.

2.3 EXPERIMENTAL SECTION.

(i) Preparation of starting materials and characterisation of products.

The alkenetetracarbonyliron complexes Fe(CO)₄·(η²-styrene) and Fe(CO)₄·(η²-methylacrylate) were prepared by literature methods^{7,8}. Fe(CO)₄·(η²-styrene) was purified by recrystallisation from pentane at -70°C to give yellow crystals with an infrared spectrum (ν-CO str. = 2085, 2013, 2006 and 1982 cm⁻¹; 100-120° petroleum ether) consistent with that reported in the literature. Fe(CO)₄·(η²-methylacrylate) was purified by sublimation at 0.1mm Hg / 70°C to give yellow crystals with an infrared spectrum (ν-CO str. = 2101, 2033, 2019 and 1996 cm⁻¹; 100-120° petroleum ether) in agreement with literature values.

In order to confirm the structure of the products of the reactions between $\text{Fe}(\text{CO})_4 \cdot (\eta^2\text{-styrene})$ and cycloalkenes as $\text{Fe}(\text{CO})_4 \cdot (\eta^2\text{-cycloalkene})$ the ligand exchange reactions were carried out on a preparative scale and an attempt was made to characterise the products. All synthetic procedures were carried out under a dinitrogen atmosphere.

(a) $\text{Fe}(\text{CO})_4 \cdot (\eta^2\text{-cis-cyclooctene})$.

1.2g (4.4 mmol) of $\text{Fe}(\text{CO})_4 \cdot (\eta^2\text{-styrene})$ in 100cm^3 of dry degassed 40-60° pet.ether was refluxed for 3 hours with 2cm^3 (15.3 mmol) of cis-cyclooctene. After filtration and removal of volatiles by rotary evaporation the product was dissolved in 40-60° pet.ether and filtered through a 10cm column of Activity 1 alumina to remove $\text{Fe}_3(\text{CO})_{12}$. Evaporation of the solvent followed by molecular distillation gave the product as a yellow oil. It was noted that the product underwent steady thermal decomposition at room temperature to yield $\text{Fe}_3(\text{CO})_{12}$ and free cis-cyclooctene though the thermolysis was inhibited by the presence of excess free ligand. The failure to obtain an accurate microanalysis for the product was probably due to this rapid thermolysis. Analysis (Found: C=50.4%, H=4.83%; Calculated: C=51.8%, H=5.00%). The infrared spectrum of the product ($\nu\text{-CO str.} = 2072, 2002, 1994$ and 1972 cm^{-1} ; 100-120° pet.ether) was found to be very similar to that of the species $\text{Fe}(\text{CO})_4 \cdot (\eta^2\text{-trans-cyclooctene})$ characterised by other workers⁹.

(b) $\text{Fe}(\text{CO})_4 \cdot (\eta^2\text{-cycloheptene})$.

The method used in preparation (a) was used for the entering group cycloheptene in an attempt to prepare $\text{Fe}(\text{CO})_4 \cdot (\eta^2\text{-cycloheptene})$. However this species was found to undergo rapid thermolysis to yield $\text{Fe}_3(\text{CO})_{12}$ and the free cycloalkene in the absence of excess free ligand and consequently attempts at purification of the product resulted only in decomposition. The infrared spectrum of the product before attempted purification ($\nu\text{-CO str.}$

= 2074, 2000, 1995 and 1975 cm^{-1} ; 100-120° pet. ether) was consistent with the structure assigned.

The free organic ligands styrene, methylacrylate, acrylonitrile, cyclohexene, cycloheptene and cis-cyclooctene were obtained from commercial sources and were further purified before use in the kinetic experiments by distillation under a dinitrogen atmosphere.

Petroleum ether (100-120°; analytical grade), used as a solvent in the kinetic studies was purified by distillation under a dinitrogen atmosphere and was consequently degassed and stored under dinitrogen prior to use.

The exchange reaction between $\text{Fe}(\text{CO})_4 \cdot (\eta^2\text{-styrene})$ and acrylonitrile in 100-120° pet. ether was found to result in the formation of more than one product. Two species ($\nu\text{-CO str.} = 2105, 2050 \text{ and } 2028 \text{ cm}^{-1}$, and 2060 cm^{-1} ; respectively) were observed and assigned to $\text{Fe}(\text{CO})_4 \cdot (\eta^2\text{-acrylonitrile})$ and to $\text{Fe}(\text{CO})_4 \cdot (\sigma\text{-N-acrylonitrile})$ on the basis of the infrared data^{10(a)}.

(ii) Experimental conditions used for the kinetic experiments.

All kinetic experiments were carried out under an atmosphere of dinitrogen using sealed vessels immersed in a constant temperature bath controlled to within 0.02°C. Experiments were carried out in duplicate. Aliquots of the reaction mixture were taken at regular intervals using a syringe, with at least ten absorbance-time pairs taken for each of the kinetic experiments. Infrared spectra were recorded on a Perkin-Elmer 257 spectrophotometer fitted with 1mm NaCl cells, with all measurements

referenced to a solvent-ligand blank of the appropriate concentration. Details of the method of analysis of the kinetic data are given in the appropriate sections of Appendix A.

TABLE 2-1Preliminary π -ligand Exchange Reactions of
 $\text{Fe}(\text{CO})_4 \cdot (\eta^2\text{-alkene})$ substrates.

<u>Reaction Number</u>	<u>Leaving Group</u>	<u>Entering Group</u>	<u>Result</u>
I	methylacrylate	styrene or cyclooctene	20% π -ligand exchange only with extensive substrate decomposition.
IIa	styrene	methylacrylate	complete π -ligand exchange.
IIb	styrene	cyclohexene	no π -ligand exchange and complete substrate decomposition.
IIc	styrene	cycloheptene	complete π -ligand exchange.
IId	styrene	cyclooctene	complete π -ligand exchange.
IIe	styrene	acrylonitrile	slow ligand exchange with some substrate decomposition. More than one exchange product formed.
III	styrene	(thermolysis)	slow decomposition to yield $\text{Fe}(\text{CO})_5$, $\text{Fe}_3(\text{CO})_{12}$ and styrene.

TABLE 2-2.

Rate constants for Reactions of $\text{Fe}(\text{CO})_4 \cdot (\eta^2\text{-styrene})$.

<u>Entering Group</u>	<u>Concentration</u> <u>/mol dm⁻³</u>	<u>10⁴ k_{obs}</u> <u>/s</u>
methylacrylate T/K = 333.2	0.030	9.67 , 9.82 ^a
	0.060	9.98 , 9.67
	0.120	10.38 , 10.38
	0.240	10.66 , 10.65
	0.330	10.74 , 9.54
	0.390	10.54 , 10.28
	0.450	10.33 , 10.31
	0.540	10.82 , 10.90
$k_1 = 10.22 \pm 0.31 \times 10^4 \text{ s}^{-1}$		
cycloheptene T/K = 333.2	0.282	9.45 , 9.34
	0.333	10.25 , 10.66
	0.387	10.02 , 9.64
	0.462	9.74 , 10.17
$k_1 = 10.01 \pm 0.88 \times 10^4 \text{ s}^{-1}$		
cyclooctene T/K = 333.2	0.026	9.02 , 8.72
	0.051	9.90 , 9.92
	0.102	9.85 , 9.56
	0.204	10.01 , 9.99
	0.282	9.45 , 10.01
	0.333	9.66 , 10.20
	0.387	9.41 , 9.42
0.462	10.33 , 9.84	
$k_1 = 9.98 \pm 0.36 \times 10^4 \text{ s}^{-1}$		

Footnote.

^a All kinetic experiments were carried out in duplicate in 100-120° petroleum ether.

TABLE 2-3.

Rate data for Mass Effect Experiments of $\text{Fe}(\text{CO})_4 \cdot (\eta^2\text{-styrene})$
with Methylacrylate Entering Group^a.

<u>Leaving Group</u>	<u>Concentration</u> /mol dm ⁻³	<u>$10^4 k_{\text{obs}}$</u> /s ⁻¹
styrene T/K = 333.2	0.000	10.65 , 10.66 ^b
	0.015	8.25 , 9.08
	0.030	8.25 , 7.82
	0.060	7.98 , 7.39
	0.120	5.98 , 5.93
	0.240	4.39 , 4.57

Footnotes.

^a Reactions carried out in 100-120° petroleum ether using the entering group methylacrylate at a concentration of 0.240 mol dm⁻³. A plot of k_{obs}^{-1} versus [styrene] has a correlation coefficient for a linear fit of better than 0.992 (1.00 = perfect linear relationship).

^b Where two values are given for k_{obs} at a single concentration duplicate experiments were carried out.

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CHAPTER THREE: THE KINETICS AND MECHANISM OF DIENE AND POLYENE

EXCHANGE AT FIVE-COORDINATE IRON.

3.1 INTRODUCTION .

Complexes in which a diene or polyene functions as a four electron π -ligand towards a zerovalent metal centre are of considerable importance in synthetic organometallic chemistry. The exchange reactions of diene-like ligands are especially important since this class of reaction has been found to provide a useful route to a number of otherwise inaccessible organic and organometallic species. It is therefore unfortunate that little evidence is available concerning the mechanism of this type of exchange process, particularly for iron and chromium species similar to those used as catalysts or synthetic intermediates.

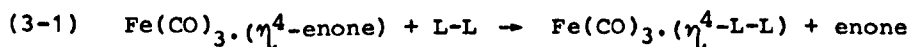
The majority of the work published on alkadiene exchange for iron systems has been carried out by two groups; Lewis and coworkers¹, and Cais and Maoz². Results suggest that the substitution of tetrahapto-alkadiene ligands does not occur at a measurable rate at temperatures low enough for thermal decomposition of the substrate to be insignificant. In marked contrast the structurally similar tetrahapto-heterodiene complexes of iron, where (heteroatom = O, N), have been found to undergo π -ligand substitution under comparatively mild reaction conditions. Brookhart et al., in a series of recent publications³⁻⁵, have reported that α, β -unsaturated ketone complexes of tricarbonyliron have potential synthetic utility since the results of exchange reactions with tautomeric polyene mixtures reveal a marked selectivity of the tricarbonyliron moiety towards the stereochemistry of the trapped polyene. The authors have also reported preliminary kinetic studies for the substitution of the heterodiene by a cyclohexa-1,3-diene ligand to yield $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-cyclohexa-1,3-diene})$. The

reaction is reported to be first-order in both substrate and entering group, with a dissociative mechanism finding favour with the authors.

No other comparable study is available for exchange reactions involving diene-like ligands but it is notable that the detailed studies of Cardaci et al.⁶⁻⁹ for the substitution of $\text{Fe}(\text{CO})_3(\eta^4\text{-enone})$ complexes by Group Va ligands indicate that competing associative and dissociative pathways are operative. In view of the apparently contradictory evidence for the mechanism of substitution in $\text{Fe}(\text{CO})_3(\eta^4\text{-enone})$ complexes a detailed study of exchange reactions with alkadiene and polyene entering groups was undertaken; the results are discussed in the following sections.

3.2 RESULTS AND DISCUSSION.

In view of the limited amount of work previously reported on the displacement of diene-like ligands from five-coordinate iron centres by potentially bidentate entering groups a series of complementary kinetic and stereochemical experiments were carried out. The results were found to provide some insight into the mechanism of substitution for this type of process. The stoichiometry of the reactions studied kinetically is given by equation (3-1) :



A number of different enone leaving groups were employed with entering groups investigated including both conjugated and non-conjugated alkadienes, and diphosphines. Under the conditions described all kinetic systems were found to give quantitative yields, whilst product decomposition was not significant over the time-scale of the experiments.

Diene exchange reactions at five-coordinate iron have been shown to exhibit a first-order dependence on both substrate and entering group concentrations⁴; however practical difficulties in obtaining reliable kinetic measurements for systems with high substrate concentrations limit useful experiments to systems which are pseudo-first-order with respect to entering group. Despite this limitation the effect of a number of factors on the observed rate can be investigated. Perhaps the most significant effects would be expected to be those due to the structure and properties of the entering and leaving groups and these experiments will be described first.

3.2.1 The Effect of Variation of the Entering Group.

Two distinct types of entering group were employed for this series of experiments. The ligands used may be broadly classified as :

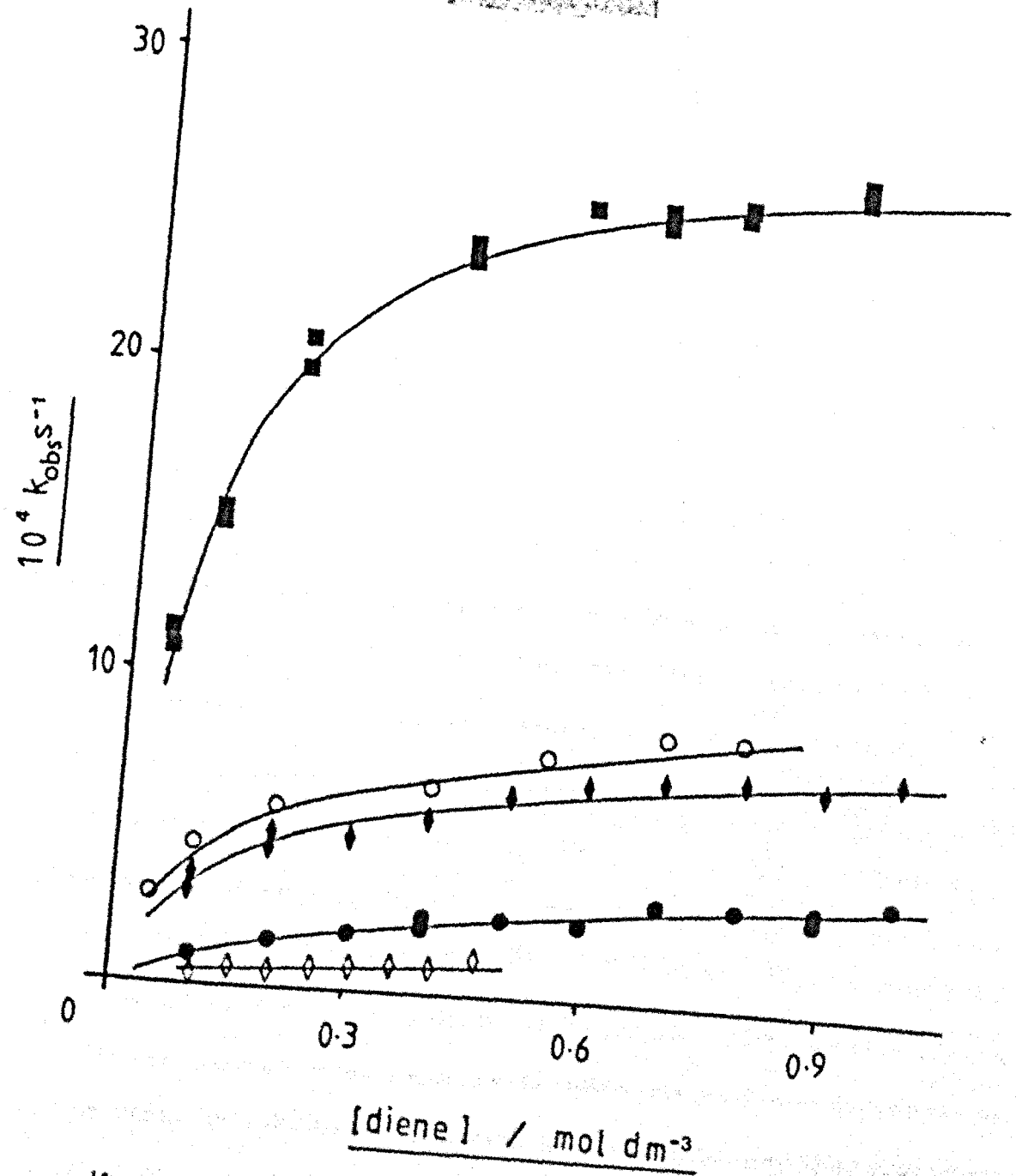
- (a) Diene-like entering groups;
- (b) Bidentate phosphine entering groups.

For all experiments described the substrate used was $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-bda})$, where (bda= benzalacetone [4-phenylbut-3-en-2-one]).

(a) Systems with diene-like entering groups.

Pseudo-first-order kinetic experiments were carried out in toluene at 70°C and involved displacement of the enone ligand of $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-bda})$ by a variety of conjugated cyclic and acyclic hydrocarbons capable of bidentate coordination to the metal centre. Satisfactory kinetic behaviour was obtained with the following entering groups: cyclohexa-1,3-diene, cyclohepta-1,3-diene, cyclohepta-1,3,5-triene, cycloocta-1,3,5,7-tetraene and 1,4-diphenylbuta-1,3-diene. The tetrahaptodienetricarbonyliron products formed by the diene exchange reactions with these entering groups have, in each case, been synthesised

FIGURE 3-1



Key:

- 1,3-chd
- 1,3,5-chpt
- ♣ 1,3-chpd
- 1,3,5,7-cot
- ◇ 1,3-but

by an alternative route and satisfactorily characterised. Full details are given in the experimental section. A number of other entering groups were investigated and found to be unsuitable for kinetic studies for a variety of reasons. Ligand exchange with the entering group cycloocta-1,3-diene was found to proceed too slowly at 70°C for accurate kinetic measurement. In the case of the non-conjugated eight membered carbocyclic entering group cycloocta-1,5-diene simple ligand exchange did not occur and in addition to the expected:

$\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-cycloocta-1,5-diene})$ product a second species identified as $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-cycloocta-1,3-diene})$ was isolated from the reaction mixture. When the entering group cycloocta-1,4-diene was used the sole product of the ligand substitution was $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-cycloocta-1,3-diene})$. Since thermal isomerisation of the 1,4- and 1,5-isomers of cyclooctadiene to yield the 1,3-isomer takes place only at elevated temperatures in the absence of a catalyst the ligand isomerisation for the non-conjugated dienes during the exchange reactions suggested a metal-assisted isomerisation pathway. This topic is discussed further in Chapter Five. The rigid non-conjugated diene norbornadiene (bicyclo[2.2.1]hepta-2,5-diene), which cannot readily isomerise to a conjugated species on coordination, was found to yield only small amounts of the expected exchange product $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-norbornadiene})$ whilst extensive substrate decomposition was observed.

Kinetic data for the systems found to give quantitative yields of the $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-diene})$ products to be expected for simple diene exchange are given in TABLE 3-1. Plots of k_{obs} (the observed rate constant) against entering group concentration for these systems are provided in FIGURE 3-1. It should be noted that the low solubility of the entering group 1,4-diphenylbuta-1,3-diene in toluene limited kinetic experiments to a maximum ligand : complex ratio of 95 : 1. From an analysis of the plots of k_{obs} against entering group concentration it is apparent that the systems

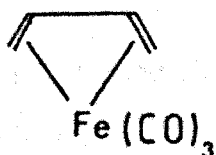
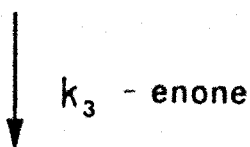
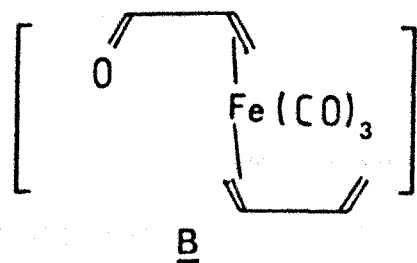
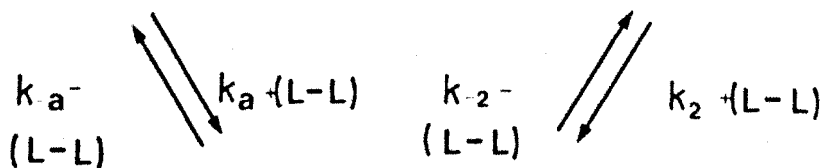
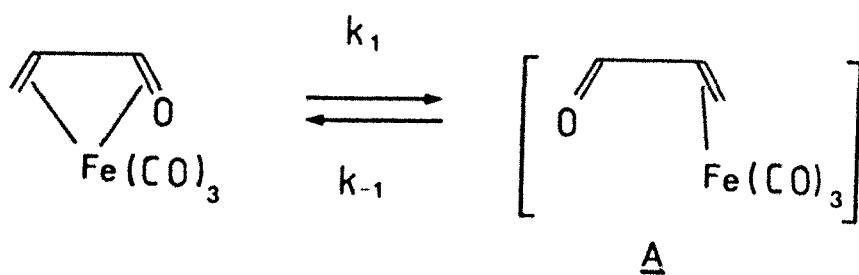


FIGURE 3-2

investigated cannot be adequately described by either a simple associative or simple dissociative mechanism. The mechanism which appears to give the best description of the observed kinetic behaviour is illustrated in FIGURE 3-2. The mechanism proposed is of the "ring-opening" type and involves competing associative, k_a , and dissociative, k_1 , initial steps resulting in a common intermediate in which both entering and leaving groups are bound to the metal centre in dihapto fashion. The intermediate then rearranges in the k_3 step to yield the tetrahapto-diene product species and the free enone leaving group. It is significant that all steps, with the exception of k_3 , are potentially reversible. Application of the steady-state approximation to intermediates A and B of the mechanistic scheme yields a rate equation of the form given by equation (3-2) :

$$(3-2) \quad \frac{-d[S]}{dt} = \left\{ \frac{[S] (k_a [L] + k_\beta [L])}{(k_\gamma + k_\delta [L])} \right\}$$

Equation (3-3) will then describe the system if pseudo-first-order conditions are maintained:

$$(3-3) \quad k_{obs} = \frac{k_\beta [L]}{k_\gamma + k_\delta [L]} + k_a [L]$$

$$\text{where } k_a = \frac{k_3 k_a}{k_{-a} + k_3}$$

$$k_\beta = \frac{k_3 (k_1 k_2 k_{-a} + k_1 k_2 k_3 - k_a k_{-2} k_{-1})}{(k_{-a} + k_3)}$$

$$k_\gamma = k_{-a} k_{-1} + k_{-2} k_{-1} + k_3 k_1$$

$$\text{and } k_\delta = k_{-a} k_2 + k_3 k_2$$

The full derivation of this rate law is to be found in Appendix B.

A similar type of complex "ring-opening" mechanism has been postulated by Dobson and coworkers¹⁰⁻¹² to describe the displacement of bidentate chelating ligands from Group VI^b metal centres. However the systems studied by Dobson's group differed significantly in behaviour from

those presently described since the simplifying assumption $k_1 \gg k_a$ could be made, producing the modified rate expression given by equation (3-4) :

$$(3-4) \quad k_{\text{obs}} = \frac{k_1 k_2 k_3 [L]}{(k_{-1} k_{-2} + k_{-1} k_3 + k_2 k_3 [L])}$$

Cardaci et al.⁶⁻⁹ have put forward a second simplified "ring-opening" scheme of this type to account for the kinetics of the reaction between $\text{Fe}(\text{CO})_3(\eta^4\text{-bda})$ and monodentate Group Va entering groups. In the case of these systems stable intermediates of type B (FIGURE 3-2) have been isolated^{6,7}. For these iron systems the reasonable assumption $k_{-a} = k_{-2} = 0$ may be made since the entering groups are considerably more nucleophilic than the leaving group. The rate law then simplifies to the form given by equation (3-5) :

$$(3-5) \quad k_{\text{obs}} = \frac{k_1 k_2 [L]}{k_{-1} + k_2 [L]} + k_a [L]$$

since the k_3 term will drop out of the equation under these circumstances.

Preliminary analysis revealed that no such simplifications of rate law (3-3) could be readily justified for the systems presently under consideration, since entering and leaving groups would be expected to show comparable nucleophilicity. Accordingly the kinetic results were fitted to the expanded rate equation using a non-linear least-squares analysis described in section A.3 of Appendix A. Input of the data as k_{obs} against [L] pairs produced estimates of the following combinations of partial rate constants : k_a , k_β / k_δ , and k_γ / k_δ . Values of the computed partial rate constants for each of the systems studied are to be found in TABLE 3-2. Values for the standard deviation of the fit of the experimental points to the theoretical "best-fit" curve are provided as are the values for the standard deviation of the differences between values of k_{obs} obtained from duplicate kinetic experiments. Since the latter reflect experimental reproducibility a comparison of the two standard deviations

provides an indication of the compatibility of the rate law chosen with the experimental data. As there are no large discrepancies between the standard deviations for any of the systems employed it appears that the model proposed is consistent with the experimental evidence. FIGURE 3-1 gives a graphical representation of the fit of the postulated model to the data, with full lines indicating the position of the computed curve of "best-fit" for each data set. It is noticeable that when cyclohepta-1,3,5-triene is used as entering group the accuracy and reproducibility of the experimental data is not reflected by the standard deviations of the derived partial rate constants. It appears that reliable estimates of the partial rate constants could only be obtained for this system if additional k_{obs} against [L] measurements were to be possible at concentrations greater than 1.0 mol dm^{-3} in the entering ligand. Since practical difficulties due to substrate decomposition and changing solution properties were encountered with very concentrated solutions of this type no kinetic measurements could be made in this region during the present study.

The complexity of rate law (3-3) makes precise conclusions concerning trends in entering group kinetic behaviour difficult, but a number of general arguments may be advanced. The difference in kinetic behaviour between the exchange reactions of $\text{Fe}(\text{CO})_4(\eta^2\text{-alkene})$ species and those of $\text{Fe}(\text{CO})_3(\eta^4\text{-enone})$ appear to reflect the differences in geometry of the two types of complex, as reflected by both solid state and solution measurements¹³⁻¹⁶. The site of alkene attachment in the former complexes is in the equatorial plane of a trigonal-bipyramidal structure. This would be expected to preclude mechanisms of exchange involving expansion of coordination due to marked steric hindrance, and probably accounts for the observed dissociative rate-determining step observed for this type of substrate. In the case of metal-enone complexes a more open square-pyramidal structure has been reported in which the enone occupies two basal

sites. This structure might be expected to allow expansion of coordination to yield an octahedral transition-state due to capture of the entering group to fill the free second apical position. A low energy " I_d " or " I_a " pathway is well established for Group VI^b metal complexes which would be expected to be more greatly sterically hindered than the five-coordinate iron complex used in the present study. It is believed that such associatively activated "ring-opening" pathways proceed through a transition-state in which bond-breaking is more important than bond-making, and should consequently be favoured by entering groups capable of functioning as good π -acceptors for excess metal $d\pi$ electron density.

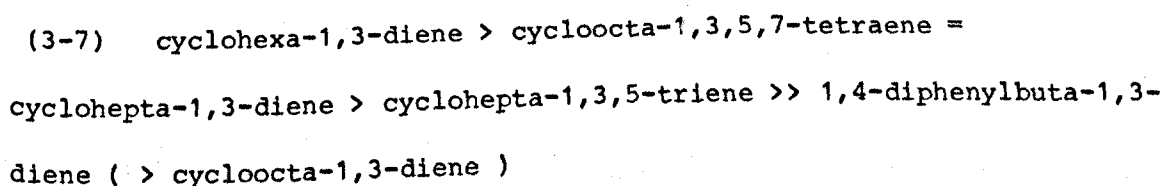
The effect of entering group structure on reactivity can be assessed in terms of the trends in k_a , k_β / k_δ and k_γ / k_δ for the systems studied. There is found to be little variation in the values of constants k_a and k_γ / k_δ with change in the entering group, if experimental uncertainty is taken into account. On the other hand the value of k_{obs} seems to be strongly correlated with the k_β / k_δ term, and this does show marked variation with entering group change. Since k_β / k_δ represents a very complicated expression, as indicated by the footnotes to equation (3-3), trends can only be described in qualitative terms. The full form of the expression is given by equation (3-6) :

$$(3-6) \quad \frac{k_\beta}{k_\delta} = \frac{k_3 (k_1 k_2 k_{-a} + k_1 k_2 k_3 - k_a k_{-2} k_{-1})}{(k_{-a} + k_3) (k_{-a} k_2 + k_3 k_2)}$$

indicating a significant dependence on k_3 and on the constants attributable to reversible dissociative "ring-opening". Four possible entering group contributions to k_β / k_δ need to be considered when examining the observed trends:-

- (a) Steric hindrance to initial dihapto coordination of the entering group.
- (b) Steric hindrance to the subsequent rearrangement of the diene to allow tetrahapto coordination (k_3) .
- (c) The degree of angular distortion required to convert the dihapto coordinated diene to a planar configuration suited to tetrahapto coordination (k_3) .
- (d) The amount of strain energy released by the alkadiene on coordination due to partial rehybridisation.

In analysing the importance of each of these factors the observed order of decreasing k_β / k_δ ratios must be considered and this is given by equation (3-7) :



(a) The importance of the contribution due to factor (a) would be expected to reflect a balance between the conformation and ring size of the cyclic alkadienes used. The additional steric hindrance to initial coordination caused by the presence of non-bonding methylene groups should also be taken into consideration. This initial steric contribution appears to account satisfactorily for the high k_β / k_δ ratio observed for the large ring system cyclooctatetraene since the absence of hindrance due to methylene groups would be expected to influence reactivity. It is, however, difficult to explain the relative k_β / k_δ ratios of cyclohepta-1,3-diene and cyclohepta-1,3,5-triene on this basis. Both of these ring systems are puckered and consequently it would be expected that the triene, which has two less methylene groups, would have the greater k_β / k_δ ratio, if factor (a) was of overriding importance. The small ratio found for 1,4-

diphenylbuta-1,3-diene may be explained in terms of the steric hindrance caused by the aromatic rings if this model is invoked.

(b) Factor (b) would not be expected to exert a significant effect for the cyclic entering groups but might seriously effect the rate of chelation of the acyclic 1,4-diphenylbuta-1,3-diene entering group. This species is reported to have *s-trans* geometry in the free state¹⁷ and accordingly severe steric hindrance due to the aromatic ring substituents should effect the chelation rates for this ligand. Direct steric hindrance due to the phenyl groups would be anticipated to effect the rate of dihapto coordination for the butadiene ligand but should be less severe than that generated during final tetrahapto coordination since a conversion to the less favourable *s-cis* geometry would be required at this stage.

(c) The degree of angular distortion needed for tetrahapto coordination of the ligand has been put forward as a significant factor by Brookhart et al. The present studies do not reveal any clear link between the postulated torsion angle of the diene as indicated by electron diffraction studies¹⁸⁻²² and the ratio of k_{β} / k_{δ} . (3-8) gives the anticipated order of reactivity based solely on necessary torsion angles. The values in parentheses give the torsion angles in degrees.

(3-8) cyclohepta-1,3-diene (0) > cyclohexa-1,3-diene (18) >>
cyclohepta-1,3,5-triene (40) > cycloocta-1,3,5,7-tetraene (43)

A comparison of lists (3-7) and (3-8) shows little similarity. It is interesting that if factor (c) is decisive in determining k_{β} / k_{δ} , cycloocta-1,3-diene, torsion angle 38° , would be expected to be more reactive towards $\text{Fe}(\text{CO})_3(\eta^4\text{-enone})$ than either cyclohepta-1,3,5-triene or cycloocta-1,3,5,7-tetraene.

(d) Molecular relaxation would be anticipated to influence both the rate of dihapto and tetrahapto coordination of the entering group. The degree of molecular relaxation to be expected is perhaps best measured in terms of strain energies obtained from thermochemical studies of the entering groups and their alkane and alkene analogues. The partial rehybridisation of an alkene on coordination to a metal centre has been reported to result in an increase in the measured carbon-carbon bond length²³; it might therefore be expected that a tetrahapto coordinated alkadiene would resemble the corresponding free alkene more closely than the free alkadiene. From the tables prepared by Benson²⁴ it is possible to estimate the amount of relaxation energy to be gained by the rehybridisation of a cyclopolyene on tetrahapto coordination. The values predicted are given in list (3-9) in units of kJ mol^{-1} .

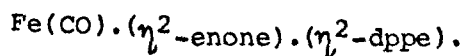
(3-9) cycloocta-1,3,5,7-tetraene (30) > cyclohexa-1,3-diene (14) > cyclohepta-1,3-diene (5) > cyclohepta-1,3,5-triene (-8).

The values available, although unfortunately not complete, do seem to provide an explanation for the unexpected difference in reactivity between cyclohepta-1,3-diene and cyclohepta-1,3,5-triene. The considerable relaxation energy available to cycloocta-1,3,5,7-tetraene on coordination offers some explanation for the unexpectedly high k_B/k_C ratio found for this entering group.

Overall it appears that contribution (a) is most important in determining the reactivity of cyclic entering groups with a significant effect due to contribution (d). Factors (a) and (b) are the critical contributors to the reactivity of the acyclic entering group 1,4-diphenyl-1,3-butadiene. Factor (c) does not appear to play a significant role in determining entering group reactivity.

(ii) Systems with bidentate phosphine entering groups.

A limited series of experiments was carried out using a bidentate phosphine as the entering group. The ligand employed was 1,2-bis[diphenylphosphino]ethane (or dppe). Two substrates were employed for these studies; both were of the type $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-enone})$, where (enone = benzalacetone or chalcone [1,3-diphenylprop-2-en-1-one]). To obtain the best balance of solubility of the crystalline entering group and rate of reaction it was found to be necessary to carry out experiments in toluene at 34°C. Under these conditions the solubility of dppe precludes infrared monitoring of substitution reactions with $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-enone})$ substrates at ligand : substrate ratios of greater than 25:1. Since the half-life of the pseudo-first-order reaction under these conditions is less than three minutes accurate kinetic measurements are not possible using conventional monitoring techniques. However initial rate studies at ligand : substrate ratios varying from 8:1 to 25:1 did indicate that the reaction rate was more strongly influenced by ligand concentration than the systems which used dienes as entering groups. The most important observation made for the substitution reactions with dppe as entering group was that an intermediate of type B (FIGURE 3-2) could be observed by infrared techniques during the course of the reaction. When reactions were carried out with either of the enone complexes as substrates an equilibrium concentration of a species displaying characteristic $\nu\text{-CO}$ str. at 2036 cm^{-1} was rapidly established. The band remained constant in intensity until the late stages of the reaction, disappearing only after the last of the substrate had been exhausted. The product of the reaction was the known species $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-dppe})$ ⁴³. The spectroscopic characteristics of the intermediate are very similar to those reported for the known species $\text{Fe}(\text{CO})_3 \cdot (\eta^2\text{-enone}) \cdot \text{SbPh}_3$ and $\text{Fe}(\text{CO})_3 \cdot (\eta^2\text{-enone}) \cdot (\eta^2\text{-diazalkane})$ ^{6,7} which have been successfully isolated, and this would suggest that the intermediate has the structure



Details of the initial rate measurements for the systems $\text{Fe}(\text{CO})_3(\eta^4\text{-enone}) - \text{dppe}$ are given in TABLE 3-3.

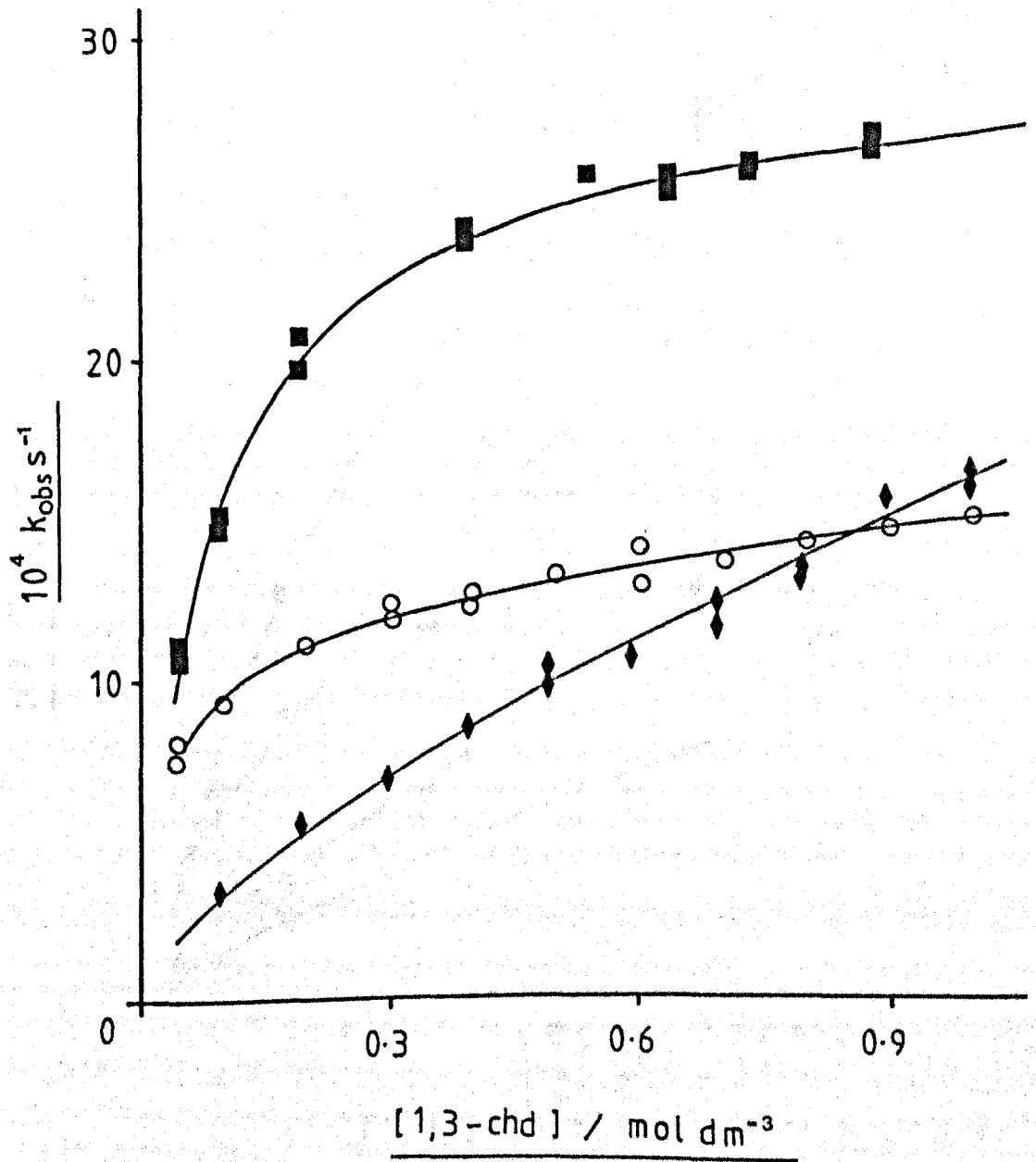
3.2.2 The Effect of Variation of the Leaving Group.

In order to study the effects of variation of the leaving group on the rate of ligand exchange in $\text{Fe}(\text{CO})_3(\eta^4\text{-enone}) - \text{alkadiene}$ systems a total of five different enone complexes were employed as substrates. Experiments were carried out using two different alkadiene entering groups to assess differences due to a sterically demanding entering group (cyclohepta-1,3,5-triene) and a less hindered entering group (cyclohexa-1,3-diene). Reactions were monitored in toluene solution with a temperature of 70°C used for experiments with cyclohexa-1,3-diene as entering group and 90°C for the less reactive cyclohepta-1,3,5-triene. The results of pseudo-first-order kinetic experiments using the entering group cyclohexa-1,3-diene are given in TABLE 3-4 with those for cyclohepta-1,3,5-triene in TABLE 3-5. The enone leaving groups employed in these studies were as follows:

(3-10)

<u>Abbreviation</u>	<u>Trivial Name</u>	<u>Systematic Name</u>
Bda	Benzalacetone	4-phenylbut-3-en-2-one
Cin	Cinnamaldehyde	3-phenylprop-2-enal
Cha	Chalcone	1,3-diphenylprop-2-en-1-one
Dyp	Dypphone	1,3-diphenyl-2-methylprop-2-en-1-one

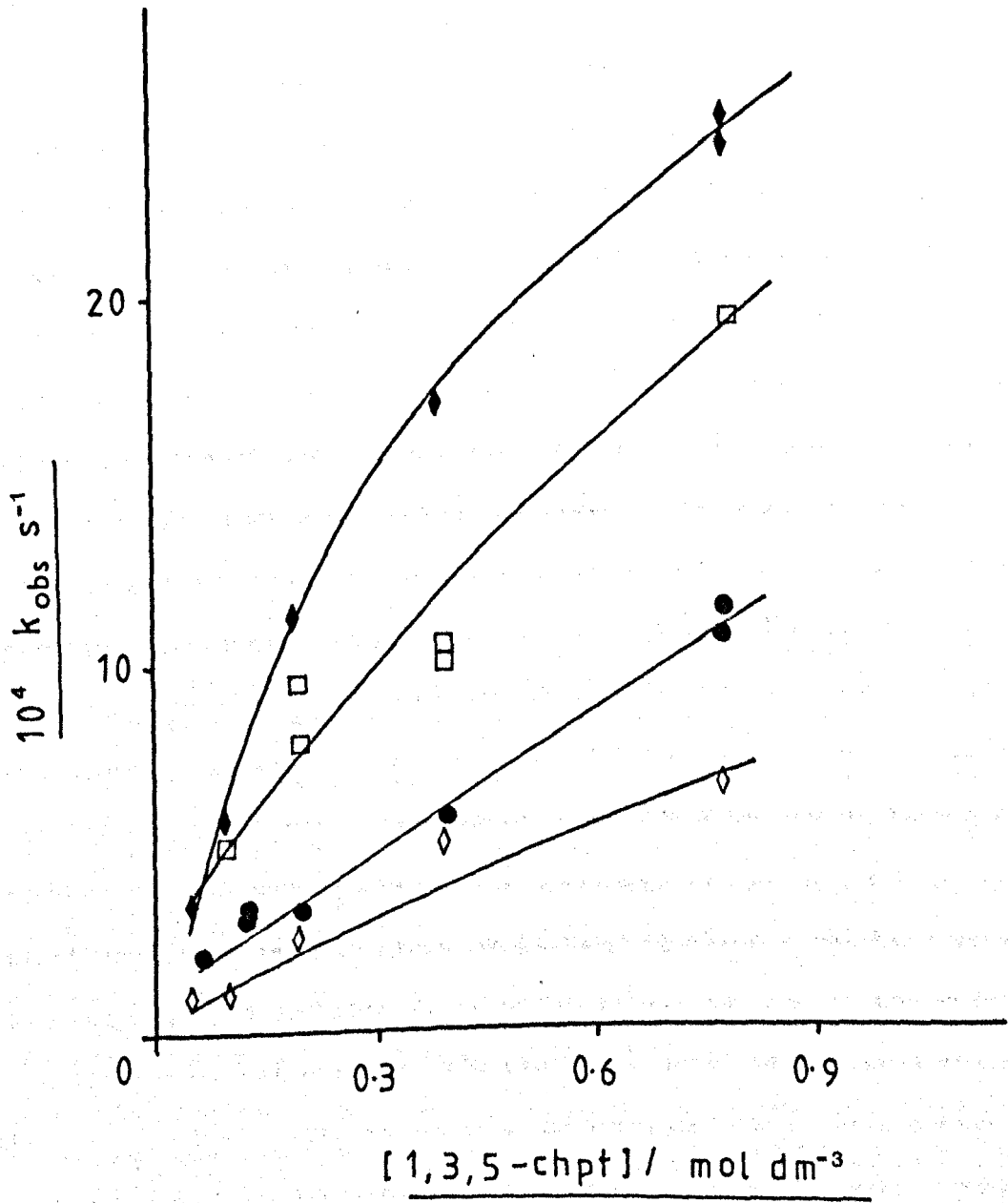
FIGURE 3-3



Key:

- bda
- cin
- ◆ cha

FIGURE 3-4



Key:

- ◆ bda
- cin
- dyp
- ◇ cha

Reactions carried out using the substrate $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-Dbch})$, where (Dbch = 2,6-dibenzalcylohexan-1-one), were found to proceed at rates too small for accurate kinetic measurement, a result which suggested that free rotation of the carbonyl group of the enone is necessary for ligand substitution to proceed readily.

For systems giving satisfactory kinetic behaviour results were treated according to the rate law given in equation (3-3). Using the techniques previously described estimates of the partial rate constants k_α , k_β / k_δ and k_γ / k_δ with their standard deviations were obtained and are given in TABLE 3-6 for reactions using the entering group cyclohexa-1,3-diene and in TABLE 3-7 for cyclohepta-1,3,5-triene. The corresponding plots of k_{obs} against entering ligand concentration are given in FIGURE 3-3 and FIGURE 3-4. Experiments carried out using the triene entering group were limited to a smaller set of ligand concentrations than those for the diene and for the experiments involving variation of entering group. The effects of this restriction are most noticeable in the case of the reactions in which benzalacetone was used as the leaving group. Despite a very small scatter of the experimental points as indicated by the standard deviation of the differences between k_{obs} values for duplicate reactions (d_{re}), the partial rate constants obtained by fitting equation (3-3) have very large estimated standard deviations. It seems likely in view of the results of the analogous experiments at 70°C that this particular system could only be fitted to the model with any degree of precision if it were possible to use extremely high ligand : substrate ratios.

Analysis of the results of the leaving group experiments must again be possible only in qualitative terms due to the complexity of the applicable rate law. If experiments with the two different entering groups are considered separately it is apparent that there is no major

change in the k_γ / k_δ expression with variation of the leaving group. In considering experiments carried out with cyclohexa-1,3-diene as entering group it is immediately apparent that the values of the expressions k_α and k_β / k_δ show marked variation with the nature of the leaving group. k_α was found to decrease sharply in the order: chalcone > cinnamaldehyde > benzalacetone, whilst the k_β / k_δ value was found to increase sharply in the same order. Since the entering group used for this study is sterically undemanding the order observed presumably reflects subtle effects of the enone electronic structure on a number of different steps in the mechanism. It is perhaps of relevance that cinnamaldehyde, the least sterically hindered leaving group, reacts at approximately the same overall rate as chalcone which is the most hindered of the leaving groups employed with this entering group. Benzalacetone, which has an electron donating methyl group α to the ketonic carbonyl group, is found to react at a considerably greater overall rate than the other leaving groups, which do not possess an electron donor group in this position.

Results with the more sterically hindered entering group cyclohepta-1,3,5-triene must be treated with rather more suspicion for the reasons outlined earlier. This is particularly true in the case of the benzalacetone leaving group due to the precision of the derived partial rate constant expressions. With this leaving group it may be said that k_β / k_δ has a larger magnitude than k_α . However analysis of the results with other leaving groups does indicate that the behaviour of systems with a sterically hindered entering group is significantly different from that observed with entering groups such as cyclohexa-1,3-diene. k_α is found to decrease in the order cinnamaldehyde > dypnone = chalcone; but unlike the reactions carried out with sterically undemanding entering groups k_β / k_δ is found to decrease in the same order. The overall rate of reaction with the least sterically hindered leaving groups, benzalacetone and

cinnamaldehyde, is considerably greater than that with dypnone and chalcone and would support the view that the rate of reaction with cyclohepta-1,3,5-triene as entering group is predominantly sterically controlled. The fact that systems with benzalacetone as leaving group react slightly faster than the less sterically hindered cinnamaldehyde and that dypnone is a slightly better leaving group than chalcone may indicate that electronic factors are also significant. In each case the better leaving group is the more hindered enone but possesses a methyl group α to one of the sites of metal-ligand π -bonding, with resultant electron donation into the π -system.

3.2.3 The Effect of Addition of Excess Leaving Group on Reaction Rate.

Mass effect experiments were carried out for the system $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-Bda})$ - cyclohepta-1,3,5-triene. The reactions were carried out in toluene at 90°C under pseudo-first-order conditions in which the entering group : substrate ratio was a constant 97:1. Results corresponding to a typical set of experiments are given in TABLE 3-8. Analysis of the kinetic data reveals a linear dependence of the observed rate constant on the concentration of added leaving group and an example plot is given in FIGURE 3-5 for the data provided in TABLE 3-8. The behaviour observed is fully consistent with the mechanism previously postulated since competition would be expected between the added enone ligand and the alkadiene entering group in the steps represented by k_2 and k_a in the reaction scheme of FIGURE 3-2. It is also possible that the steps of the reaction pathway represented by the k_3 term in the rate law may proceed through a coordinatively unsaturated intermediate which would also be liable to competition with excess leaving group. Qualitative studies, carried out using infrared spectroscopy and thin layer chromatography, have shown that enone exchange occurs between $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-enone})$ and any of the free

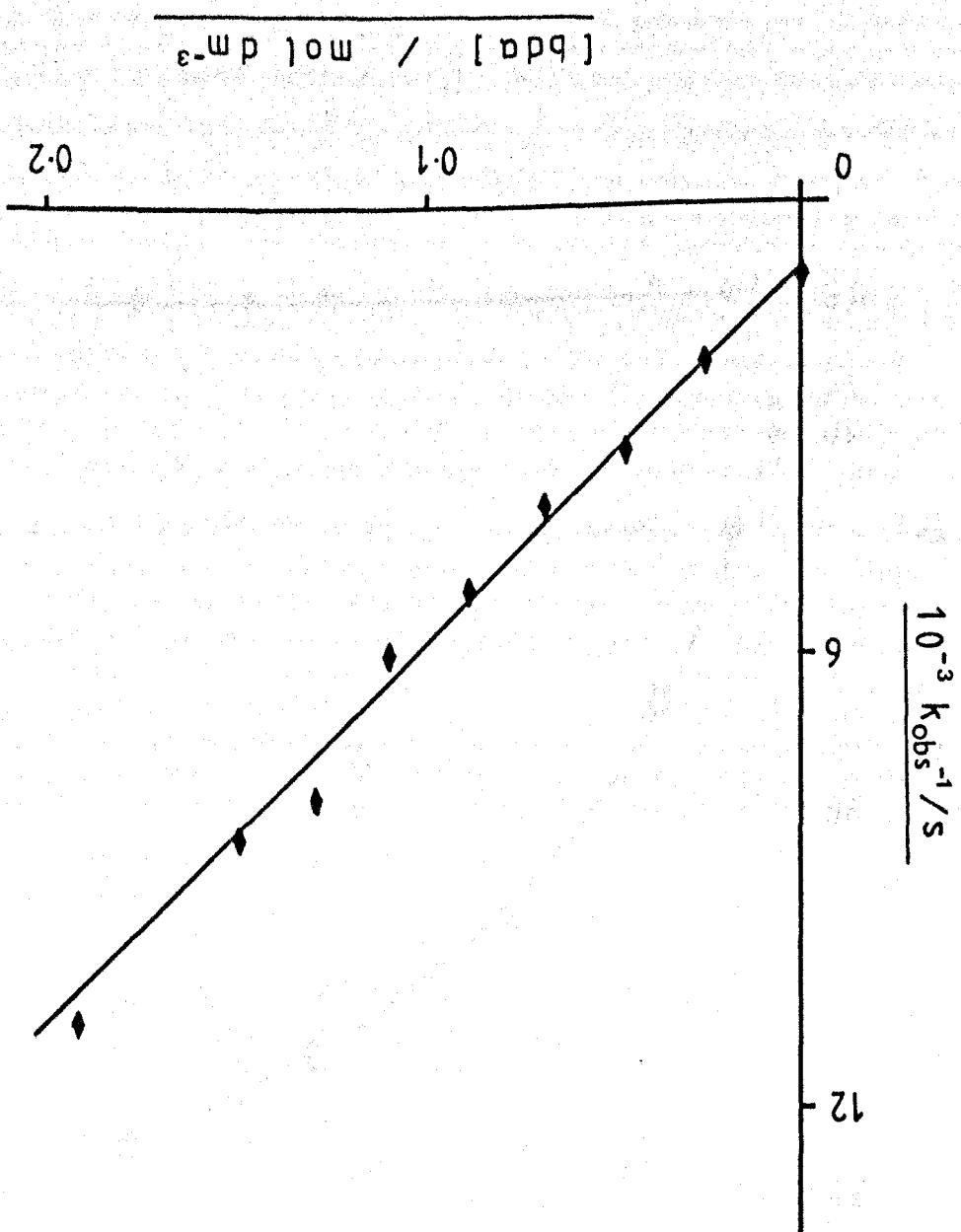
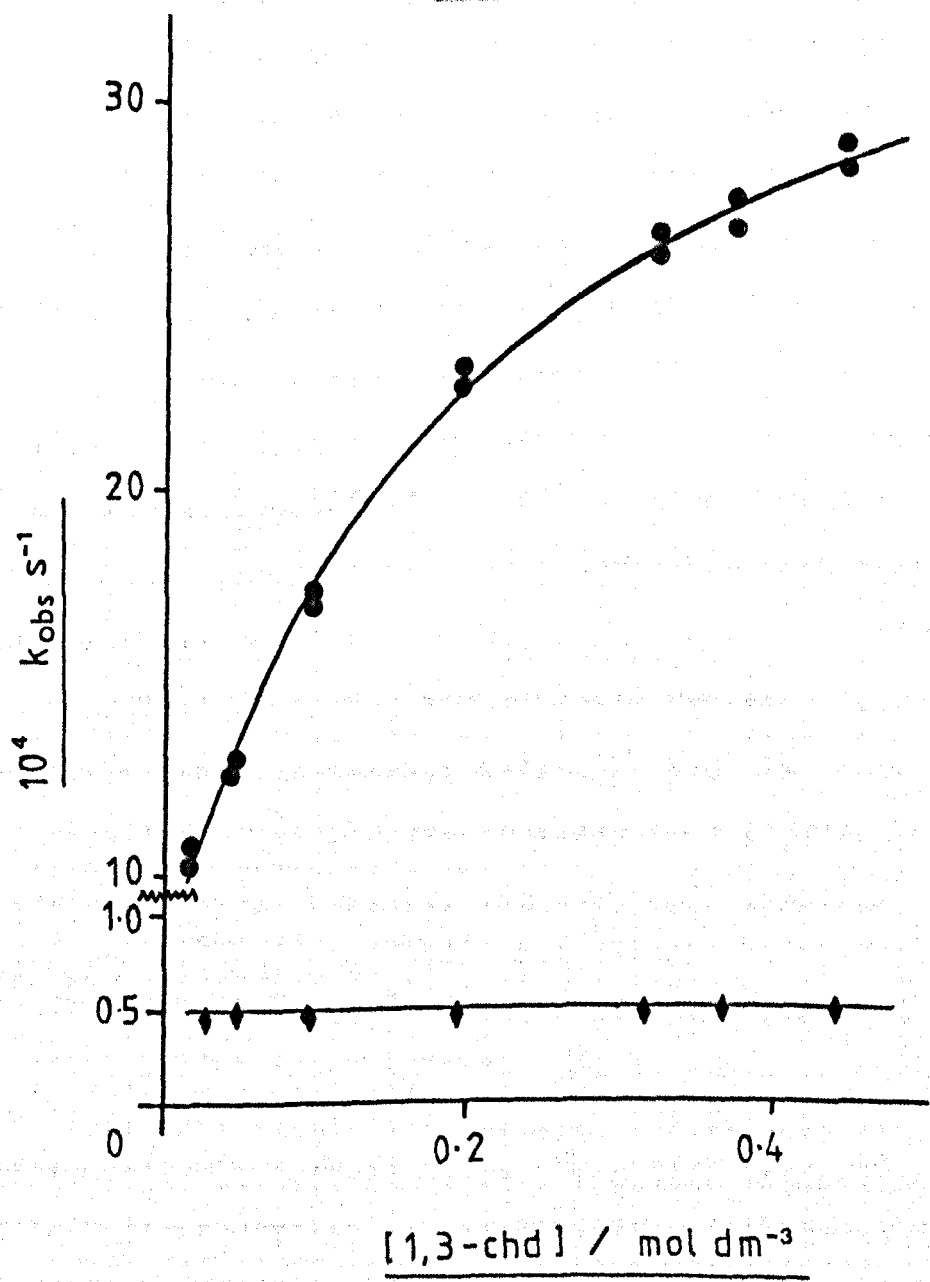


FIGURE 3-5

FIGURE 3-6



Key:

- L = CO
- ◆ L = PPh₃

enones used in the leaving group studies.

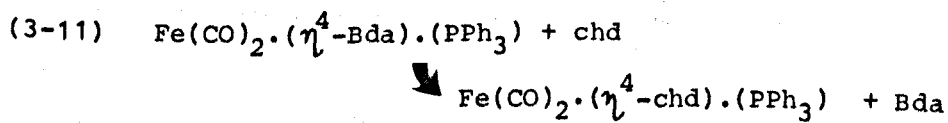
3.2.4 The Effects of Solvent Change and of Variation of the Auxiliary Ligand on Reaction Rate.

In an attempt to discover the effect on observed rate caused by variation of the auxiliary ligand, substrates of the general formula $\text{Fe}(\text{CO})_2 \cdot (\eta^4\text{-Bda}) \cdot \text{L}$ where ($\text{L} = \text{CO}, \text{PPh}_3$), were reacted with cyclohexa-1,3-diene. Due to the low solubility of the phosphine-bearing complex in organic solvents experiments were carried out in 100-120° pet. ether at 70.2°C. Using this solvent the infrared $\nu\text{-CO}$ str. vibrations of the substrates are sufficiently sharp and intense for reactions to be monitored at a concentration of $0.00245 \text{ mol dm}^{-3}$. If toluene is used as the infrared solvent, as in the other kinetic experiments described, a concentration of substrate of $0.0049 \text{ mol dm}^{-3}$ is required for full scale deflection using the Perkin-Elmer 257 spectrophotometer with 1mm cells. The rate data obtained for the diene exchange using the two substrates is listed in TABLE 3-9 and the derived partial rate constants given by TABLE 3-10. A graphical representation of the fit of the rate law to the experimental data for the complexes is given by FIGURE 3-6.

In analysing the results of the kinetic experiments it is first necessary to consider the effects of solvent change on the system $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-Bda})$ - cyclohexa-1,3-diene. The overall rate of reaction, as given by the limiting value of k_{obs} , appears to be only slightly solvent dependent in changing from toluene to a pet. ether medium. A comparison of the estimated partial rate constants in the new medium shows that there are however significant differences. Although k_β / k_ζ shows no change within error k_γ / k_ζ diminishes appreciably in the new solvent, whilst k_α shows a marked increase. Since the k_α term has a strong correlation with the

k_a / k_{-a} elements in the mechanistic scheme this solvent effect is not unexpected. For a "ring-opening" pathway with competing initial steps the associative "ring-opening" pathway would be expected to be promoted by those solvents such as aliphatic hydrocarbons which cannot function as an additional nucleophile in the substitution process.

The rate behaviour of the phosphine substituted enone complex differs greatly from all of the other bidentate ligand substitution systems so far discussed and in fact resembles more closely the monodentate ligand exchange systems described in Chapter Two. The product of the reaction has an identical infrared spectrum to the known complex $\text{Fe}(\text{CO})_2 \cdot (\eta^4\text{-chd}) \cdot (\text{PPh}_3)$ ²⁵, where (chd= cyclohexa-1,3-diene). This suggests that the reaction studied has the stoichiometry given in equation (3-11) :



However application of rate law (3-3) indicates that both the k_α and k_γ / k_δ terms are of negligible importance in the ligand exchange process, with $k_{\text{obs}} = k_\beta / k_\delta$ as is typical of a simple "ring-opening" pathway with a dissociative rate-determining step. Since the observed rate of reaction for the phosphine substituted complex is more than an order of magnitude smaller than that for $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-Bda})$ under the same conditions it is likely that steric hindrance due to the bulky triphenylphosphine ligand effectively precludes associatively initiated "ring-opening". The observed behaviour can thus be best described in terms of a modified form of equation (3-3) in which $k_a = k_{-a} = k_{-2} = 0$.

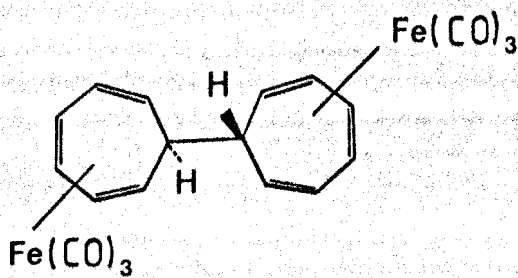
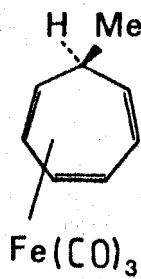
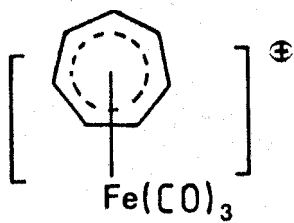
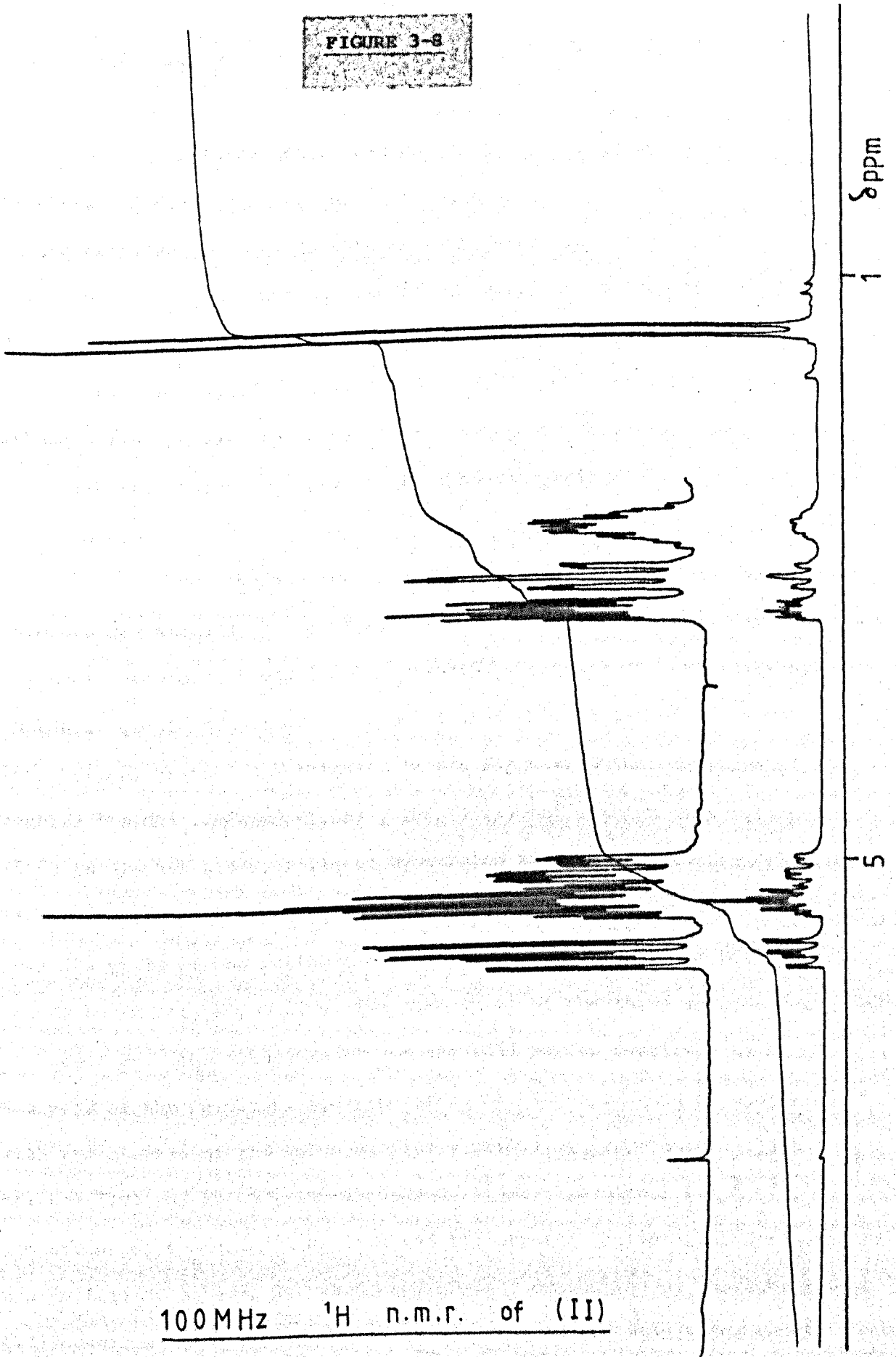


FIGURE 3-7

FIGURE 3-8



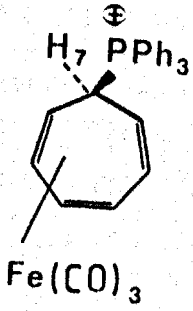
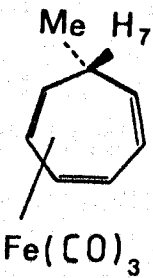
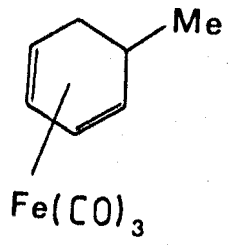
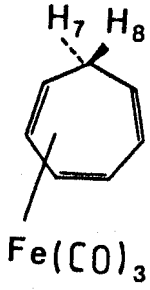
100 MHz ¹H n.m.r. of (II)

3.2.5 The stereochemistry of the Ligand Exchange Process.

A final consideration in attempting to establish the mechanism of diene exchange at five-coordinate iron is the stereochemistry of the exchange process. To determine the stereochemistry of the process a series of experiments was carried out in which the substrate $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-Bda})$ was allowed to react with an asymmetric entering group, the polyene 7-methylcyclohepta-1,3,5-triene. The products of the exchange process were subsequently analysed by means of proton magnetic resonance spectroscopy to establish the stereochemistry of the product species.

To obtain accurate structural assignments from the proton magnetic resonance spectrum of the product mixture resulting from the exchange reactions it was first necessary to prepare stereospecifically an authentic sample of either the exo- or endo- methyl isomer of $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-7-methylcyclohepta-1,3,5-triene})$. It was discovered that reaction of the complex $[\text{Fe}(\text{CO})_3 \cdot (\eta^5\text{-tropylium})^+] (\text{PF}_6^-)$ (I) and lithium dimethylcuprate at -50°C in diethyl ether, followed by warming to room temperature, resulted in a 10% yield of the 7-exomethylcycloheptatriene complex (II) in addition to a 17% yield of the $\text{Fe}_2(\text{CO})_6 \cdot (7,7'\text{-bicycloheptatrienyl})$ derivative (III), formed by reductive coupling. The structures of the three species are given in FIGURE 3-7. The structure of species (II) may be confirmed by an analysis of the ^1H n.m.r. spectrum given in FIGURE 3-8 and by comparison with the spectra of the known species : $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-cyclohepta-1,3,5-triene})$ (IV) and $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-5-methylcyclohexa-1,3-diene})$ (V) ^{38,44}. Comparison of the spectra of (II) and (IV) reveal characteristic resonances due to (II) at δ 5.73, 5.09 and 2.09. Proton decoupling of the spectrum of (II) confirms the structure since irradiation of the signal due to H^2 reduces the H^3 multiplet to a doublet; irradiation of the signals due to the central diene protons H^4 and H^5 reduces the outer diene resonances H^3

FIGURE 3-9



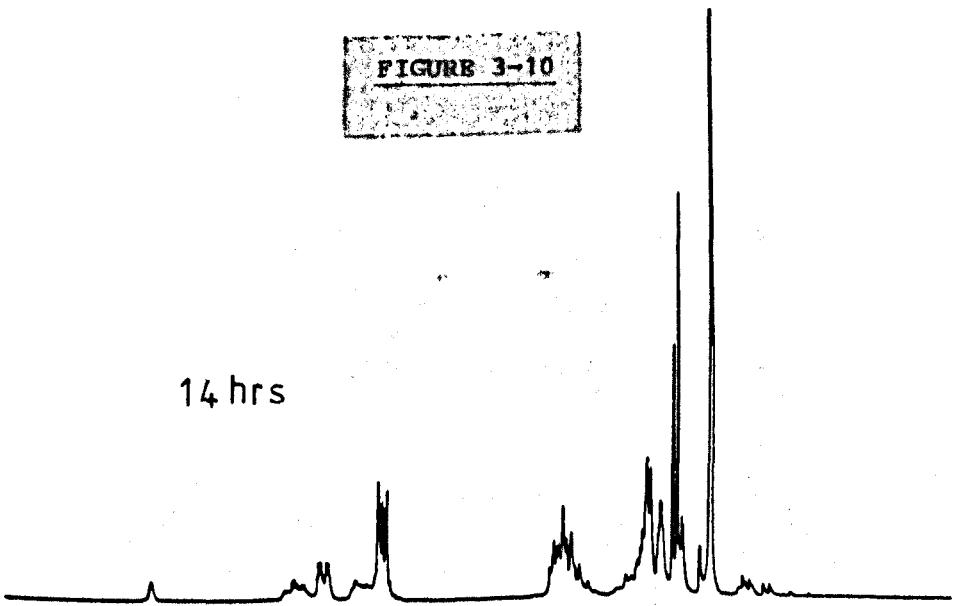
and H⁶ to doublets; whilst irradiation of the signal due to H⁷ reduces H¹ to a doublet and the resonance due to the methyl substituent to a singlet. The chemical shift and coupling constant (J= 7.1 Hz) of the uncoupled methyl signal are consistent with those due to the methyl signal in complex (V) and provide further support for the assignment⁴⁴. Full details of the assignments for species (II) to (V) are given in the experimental section.

An attempt to generate the 7-endomethyl analogue (VI) by the reaction of $[\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-C}_7\text{H}_7\text{PPh}_3^+)] (\text{PF}_6^-)$ (VII) with lithium dimethylcuprate under the conditions used for the synthesis of (II) was unsuccessful. The only iron carbonyl derivative isolated from the reaction mixture was found to be (IV) suggesting that hydrolysis of the ylide intermediate had taken place rather than the endo-methylation anticipated.

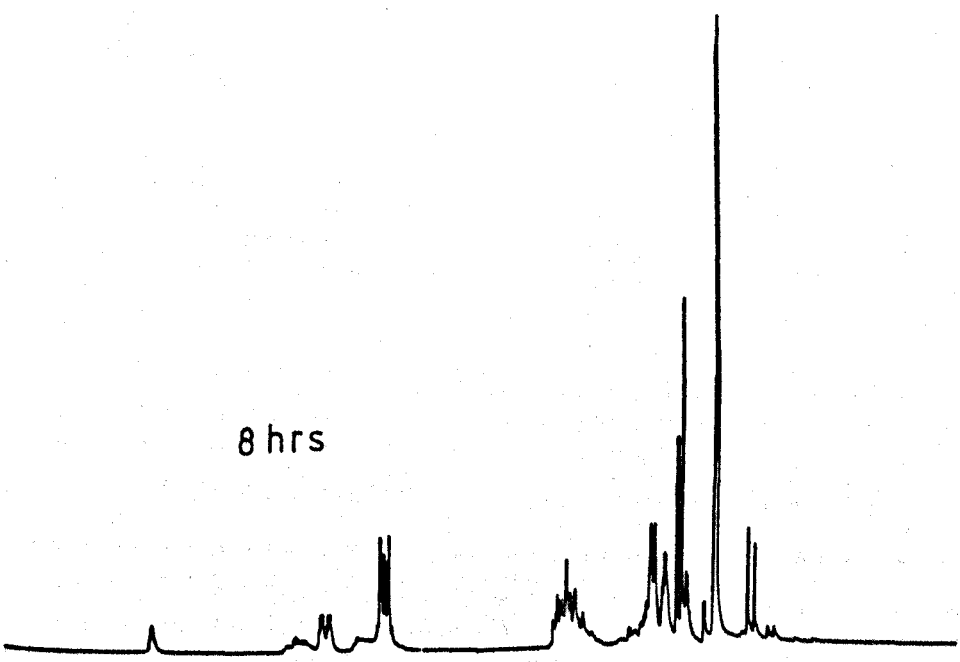
Since it is well established that 7-alkyl derivatives of free cyclohepta-1,3,5-triene undergo thermal isomerisation at 170 to 200°C to yield a mixture of the 1-, 2- and 3-alkyl substituted isomers metal-assisted isomerisation of the ligand would seem likely at lower temperatures. For this reason the thermal isomerisation of (II) was studied in d⁶-benzene at 70°C, under conditions similar to those used for the exchange reactions. It has been proposed that isomerisation of the free ligand proceeds by a mechanism involving transannular 1,5-hydride shifts^{26,27} since the 1-isomer does not occur initially, but becomes the dominant component in the reaction mixture after 12 hours at 170°C. Evidence provided by analysis of the ¹H n.m.r. spectra of a solution of (II) in d⁶-benzene after various periods of heating indicated that metal-assisted isomerisation does indeed take place, but follows a different mechanism to that for the free ligand. Spectra corresponding to the reaction mixture after 3, 8 and 14 hours are illustrated in FIGURE 3-10. Examination of the spectrum taken after 14 hours indicates that

FIGURE 3-10

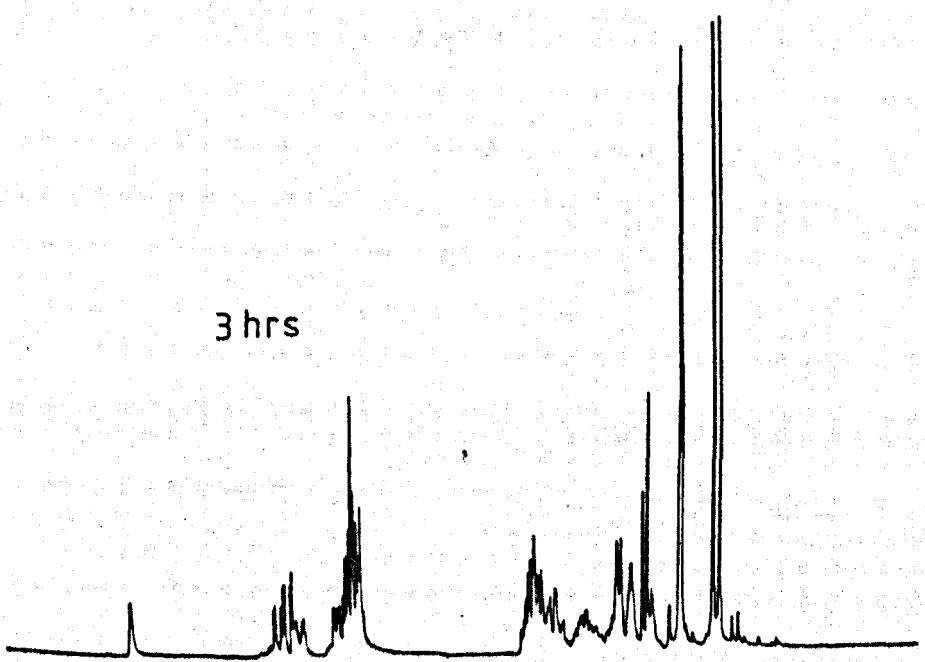
14 hrs



8 hrs



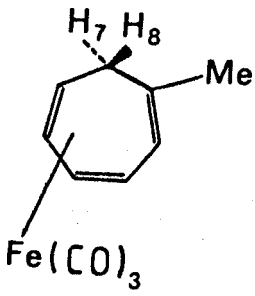
3 hrs



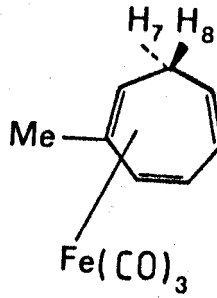
Thermal isomerisation of (II)

5 1 δ ppm

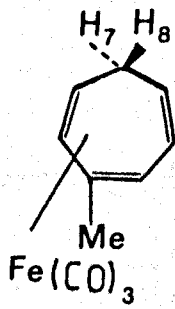
FIGURE 3-11



VIII

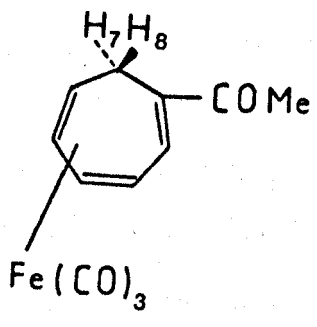


IX

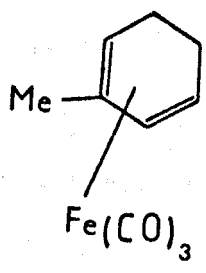


X

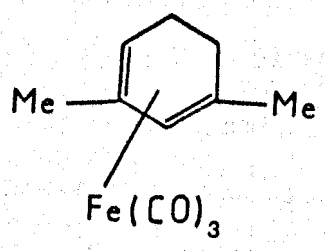
FIGURE 3-12



XI



XII



XIII

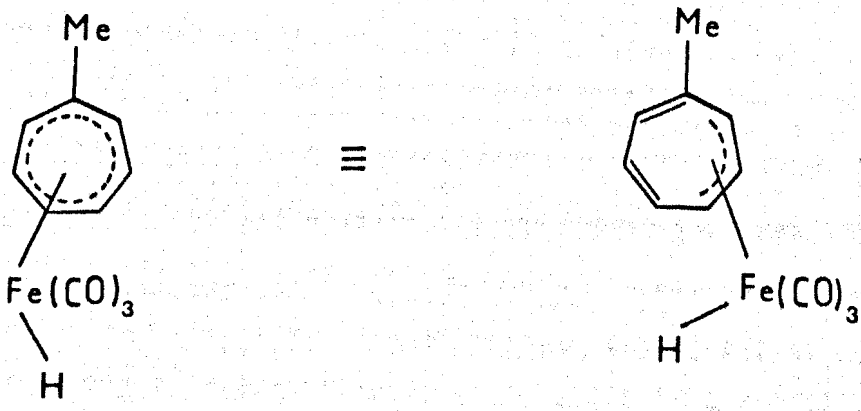
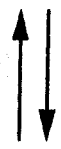
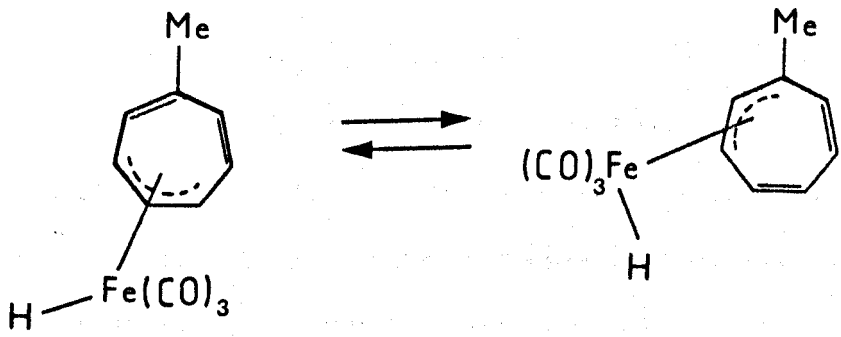
isomerisation is complete; all resonances due to (II) have disappeared from the spectrum, whilst three new methyl resonances can be observed at δ 1.40 (quartet; $J= 1.1$ Hz) and δ 1.63 and 1.68 (singlets). The methyl resonances have an integration ratio of 5.5 : 1.5 : 1. Assignment of the spectrum indicates that the major isomer present is the 1-methyl derivative (VIII) with the other new resonances attributable to structures (IX) and (X), the 2- and 3-methylcycloheptatriene derivatives. Analysis of the spectrum is simplified by reference to the spectra of suitable model species. The proton spectrum of the known species $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-1-acetylcycloheptatriene})$ (XI), given in the experimental section, shows a very similar pattern to that of (VIII) with the coupling constant for the H^2 doublet almost identical ((VIII); $J= 8$ Hz; (XI); $J= 8.0$ Hz). An important difference between the two spectra is the unique H^2 resonance of (VIII) at δ 5.43; this doublet is reduced to a singlet by irradiation of the resonances due to H^3 and H^6 at δ 2.82. The acetylcycloheptatriene complex shows equivalent coupling constants for both H^2 and H^3 . The methyl resonance of (VIII) is observed as a quartet suggesting coupling to both H^7 and H^8 . The proton resonances at δ 1.63 and 1.68 cannot be assigned to (VIII) and probably indicate the presence of the two species (IX) and (X). Decoupling of the spectrum by irradiation in the region of the spectrum corresponding to the outer diene protons of (IX) and (X) reduces the δ 5.74 multiplet to a second order doublet suggesting a coupling between H^1 and H^2 whilst that at δ 4.96 reduces to a doublet of triplets suggesting an $\text{H}^1\text{-H}^2$ coupling superimposed on couplings between H^1 and H^7 and H^1 and H^8 . The chemical shift of the methyl singlets is consistent with the presence of both (IX) and (X) since the signals can be compared with those of the model compounds $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-2-methylcyclohexa-1,3-diene})$ (XII) and $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-1,3-dimethylcyclohexa-1,3-diene})$ (XIII). The extensive overlap of the resonances due to (VIII), (IX) and (X) prevents more detailed assignments for the latter compounds; it is however notable that in CDCl_3 solvent the

methyl signal of (XII) is found at δ 2.07, whilst that of the 3-methyl substituent of (XIII) is found at δ 2.05 and those assigned to (IX) and (X) fall at δ 2.08 and 2.14. Full details of the ^1H n.m.r. spectra of (VIII) to (XIII) are to be found in the experimental section.

The fact that (VIII), (IX) and (X) were each observed in the early stages of the isomerisation of the 7-exomethyl isomer (II) and that the relative proportions of the three isomerisation products remained constant during the course of the reaction suggests that isomerisation of the coordinated ligand proceeds by a different pathway to that proposed for isomerisation of the free ligand. The low temperature needed for isomerisation suggests that the process is metal-promoted since isomerisation of (II) is complete within 16 hours at 70°C, whilst isomerisation of the 7-methylcycloheptatriene free ligand in the absence of catalyst takes 7 hours at 170°C. The type of behaviour observed during the isomerisation of (II) is typical of a number of isomerisation processes found to take place at zerovalent iron centres³⁰ and suggests that isomerisation proceeds by way of a fluxional π -allyl metal hydride intermediate through a series of 1,3-hydride shifts. FIGURE 3-13 illustrates the structure of the likely intermediate. The mechanism postulated accounts both for the low energy pathway available for the metal-assisted isomerisation process and for the observed thermodynamic ratio of isomerisation products formed even in the early stages of the reaction.

An interesting point which arises from this mechanism is that the initial hydride transfer step would not be accessible for the 7-endomethyl isomer (VI), since the proton of the methylenic carbon would be shielded from the metal by the alkatriene ring system. Accordingly the rate of isomerisation of (VI) under the conditions used for the exchange reaction would be expected to be negligible, since reactivity should

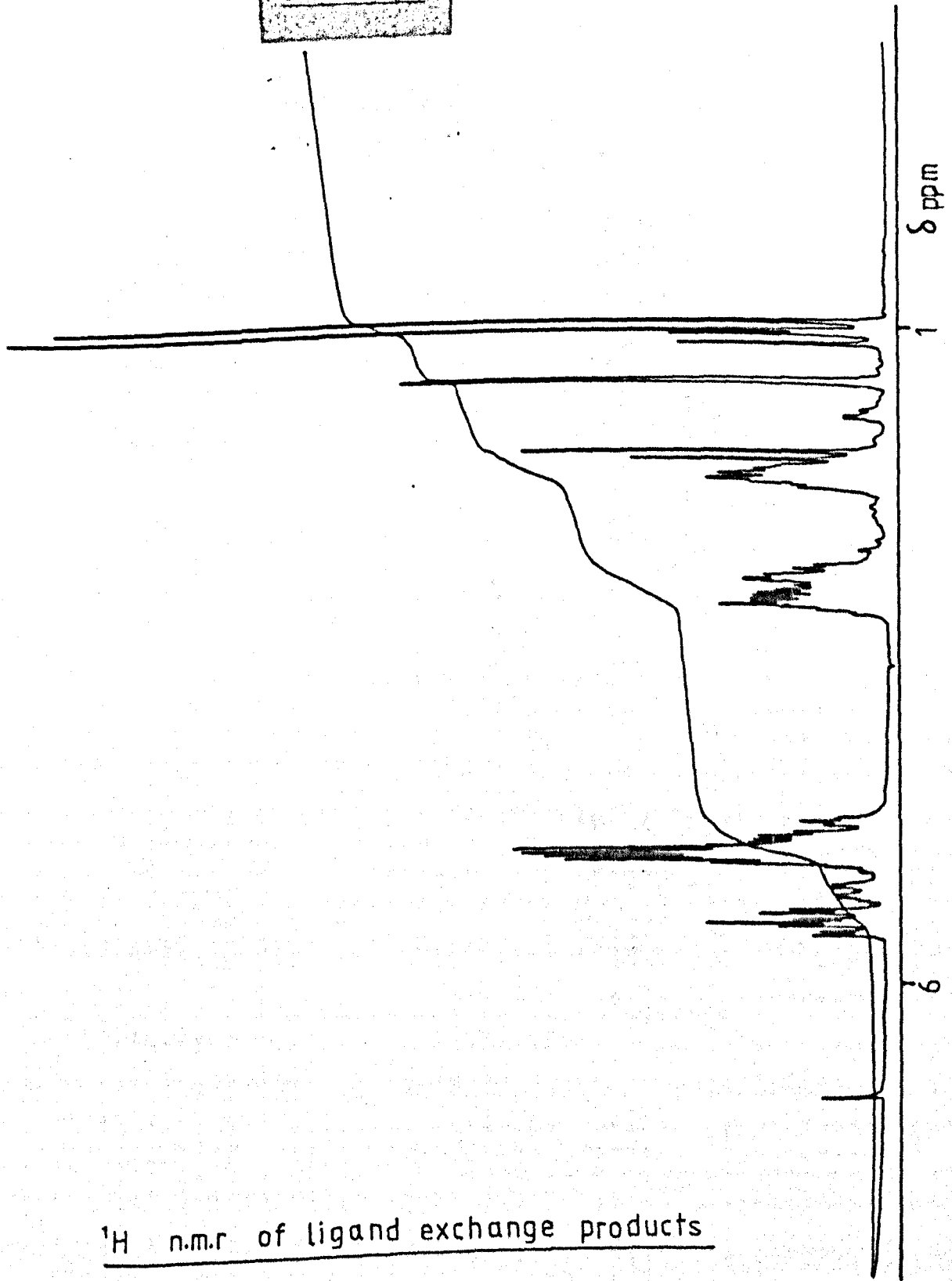
FIGURE 3-13



resemble that of the free ligand which does not undergo isomerisation at this temperature. It is noteworthy that the complex $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-7-exodeuteriocycloheptatriene})$ undergoes deuterium scrambling when heated to 73°C . This reaction, which has a half-life of approximately 7 hours, results in deuterium incorporation into each of the sites H^1 to H^6 ³⁸.

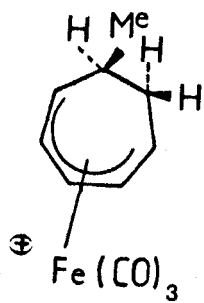
The reaction between $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-Bda})$ and 7-methylcycloheptatriene was carried out in benzene at 70°C . Reaction was found to be complete after 6 hours with the infrared vibrations corresponding to the enone complex completely absent. The products of the exchange reaction were then filtered, the solvent was removed by rotary evaporation and the resulting oil taken up in CDCl_3 . The ^1H n.m.r. spectrum of the product mixture is given in FIGURE 3-14 and indicates considerable isomerisation of the coordinated cycloheptatriene derivative under the reaction conditions. Assignment of the methyl resonances of the product reveals that the doublet at δ 1.17 is due to species (II), whilst the signals at δ 1.53, 2.08 and 2.14 may be assigned to (VIII), and to (IX) and (X) by analogy with the spectra obtained during thermal isomerisation of (II). Evaporation of the solvent and analysis of the spectrum in d^6 -benzene confirms the assignment. Several new resonances may be observed in the spectrum which may be assigned to the 7-endomethyl isomer (VI) by analogy with the known exo- and endo-substituted isomers of $\text{Cr}(\text{CO})_3 \cdot (\eta^6\text{-cycloheptatriene})$ ³¹. Of particular interest are the methyl doublet at δ 1.00 and the resonance due to H^7 which is found at δ 2.21. The corresponding resonances of (II) occur at δ 1.17 and 2.67 with the large change in the chemical shift of H^7 suggesting shielding of this proton by the triene η -system in the endomethyl complex. For the analogous chromium complexes H^7 is found at δ 3.0 for the 7-exo-substituted species and at

FIGURE 3-14

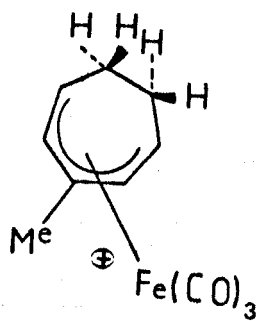


^1H n.m.r. of ligand exchange products

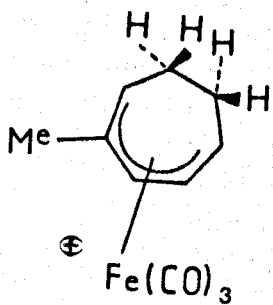
FIGURE 3-15



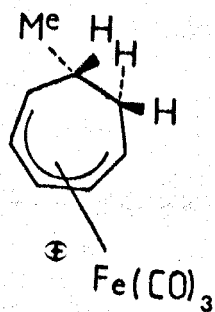
XIV



XV

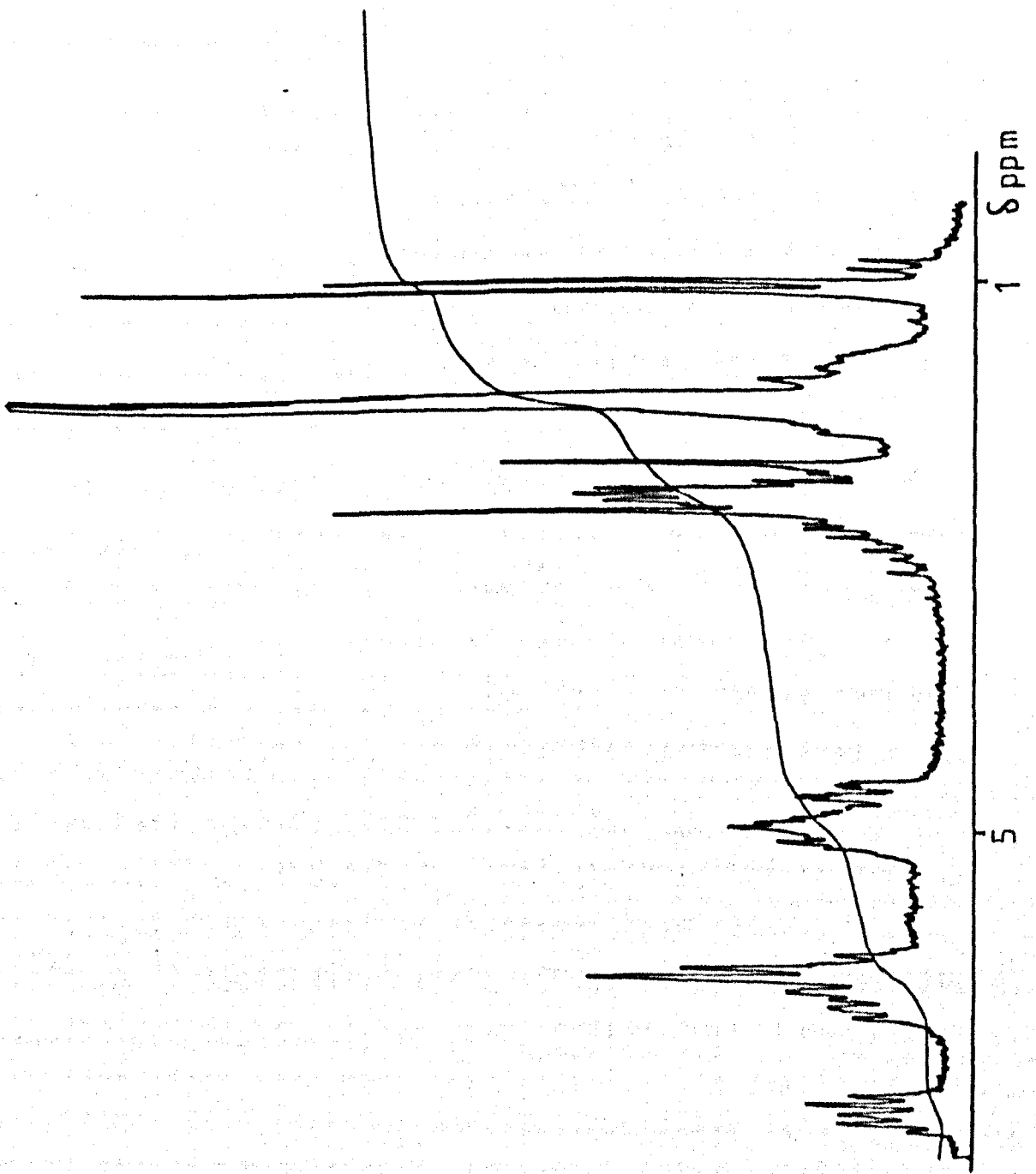


XVI



XVII

FIGURE 3-16



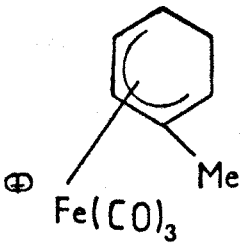
^1H n.m.r. of protonation products

δ 1.5 for the 7-endo-substituted derivatives³¹.

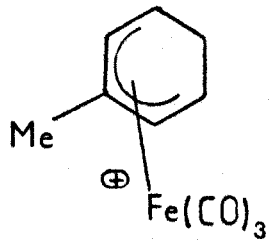
Further confirmation of the spectroscopic structural assignments was provided by protonation of the product mixture from the exchange reaction. If it is assumed that protonation occurs exclusively at the uncoordinated double bond, with exo-attack³⁸, protonation of (II) would be expected to generate species (XIV), whilst protonation of (IX) and (X) would be expected to generate (XV) and (XVI) respectively. Protonation of both (VI) and (VIII) would be expected to generate (XVII). The structures of the protonated species are to be found in FIGURE 3-15. The ¹H n.m.r. spectrum of the product mixture of the exchange reaction following protonation is illustrated by FIGURE 3-16 and is seen to show four distinct methyl resonances at δ 1.02 (doublet; J= 7.6 Hz), δ 1.17 (doublet; J=7.6 Hz), δ 2.44 (singlet) and δ 2.78 (singlet). These resonances may be assigned to species (XIV), (XVII), (XVI) and (XV) respectively. The chemical shifts of the methyl resonances assigned to (XV) and (XVI) may be compared usefully with those of species (XVIII) and (XIX) for which the assignments are known. The resonances assigned to the dienyl protons; δ 5.04 (H1), δ 6.20 (H2) and δ 7.15 (H3) correspond with those of the known species (XX) which occur at δ 4.98, δ 6.02 and δ 7.17 respectively. Structures of the species (XVIII) to (XX) are given in FIGURE 3-17 with full spectral assignments for (XVIII) and (IX) in the experimental section.

Having established the stereochemistry of the products of the ligand exchange reaction it is now possible to deduce the degree of stereospecificity of the exchange. Integration of the ¹H n.m.r. spectrum of the product mixture in the methyl region indicates that the 7-endomethyl species (VI) accounts for approximately 50% of the observed methyl resonances. Since the remaining methyl resonances may be assigned to

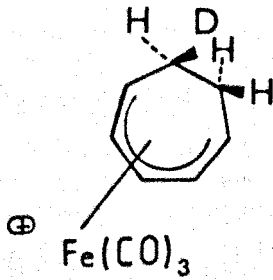
FIGURE 3-17



XVIII



XIX

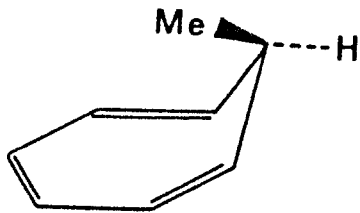


XX

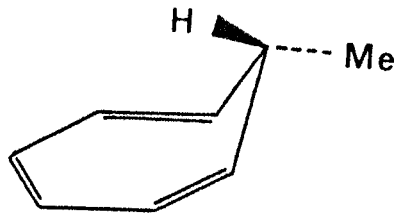
structures (II), (XIII), (IX) and (X) it appears that ligand exchange is essentially quantitative, resulting in a 1:1 mixture of the 7-exomethyl and 7-endomethyl species (II) and (VI). Species (XIII), (IX) and (X) are then generated by isomerisation of (II) under the reaction conditions. It must therefore be concluded that ligand exchange using this particular system shows negligible stereospecificity towards the entering group. In view of the reported selectivity of the $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-enone})$ substrate towards tautomeric polyene mixtures³⁻⁵ and of the large steric influence on rate for η -ligand exchange as reported earlier in this chapter this finding is rather surprising. The present results may indeed be a reflection of the likely conformation of free 7-methylcycloheptatriene in that the isomer (a) (FIGURE 3-18) responsible for the 7-endomethyl product (VI) would be expected to have the methyl to methylene carbon bond in the ring plane. The conformational isomer (b) responsible for the formation of the 7-exomethyl product (II) would be expected to have one face of the triene system shielded by the methyl group. Thus the observed 1:1 product ratio may be seen as a balance of two effects; the lower steric hindrance to trapping of the iron carbonyl moiety for isomer (a); and the reduced metal to ligand steric interactions found in the product formed by isomer (b). It might therefore be expected that work with a bulkier trapping agent would lead to increased stereospecificity since the size of the steric interactions in the product would be of increased importance in this case, with the ratio of the sites of initial attack presumably little changed.

Reaction of 7-methylcycloheptatriene with $\text{Fe}_2(\text{CO})_9$ does indeed result stereospecifically in the formation of the exomethyl species (XXI) whose structure is given in FIGURE 3-19. Assignment of the ^1H n.m.r. spectrum can be made by reference to the known species (XXII), also prepared during the course of the present work. The chemical shift of the H^4 resonance of (XXI) is consistent with increased shielding in this

FIGURE 3-18

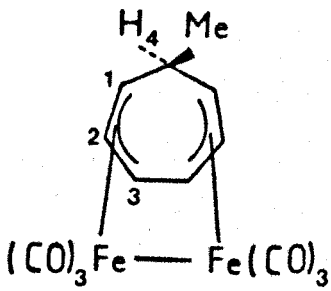


a

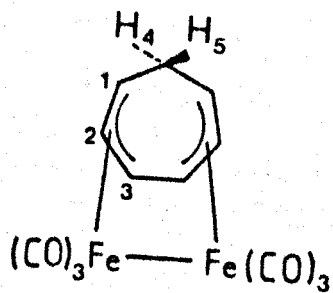


b

FIGURE 3-19



XXI



XXII

species relative to (XXII) rather than increased deshielding of the exo-hydrogen H^5 of species (XXII).

3.3 EXPERIMENTAL.

3.3.1 Kinetic Experiments.

(i) Preparation of Starting Materials and Product Characterisation.

The $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-enone})$ complexes used in the kinetic studies have all been previously prepared and characterised. Literature methods were used to synthesise $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-benzalacetone})$ ³², $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-cinnamaldehyde})$ ³³, $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-chalcone})$ ³², $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-dypnone})$ ³² and $\text{Fe}(\text{CO})_2 \cdot (\eta^4\text{-benzalacetone}) \cdot (\text{PPh}_3)$ ²⁵. The species were found to give satisfactory infrared and ¹H n.m.r. spectra. $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-2,6-dibenzalicyclohexan-1-one})$ was prepared according to the general method given in reference³². All substrates were purified by recrystallisation from 40-60° pet. ether prior to use and were stored under a dinitrogen atmosphere at 0°C.

All alkadienes used in the kinetic experiments were commercial materials, with the exception of cyclohepta-1,3-diene which was synthesised according to the method given in reference³⁴. Alkadienes, with the exception of 1,4-diphenylbuta-1,3-diene, a crystalline solid, were purified by distillation under a dinitrogen atmosphere immediately prior to use in kinetic reactions.

Enones, used in the mass effect experiments, were commercial materials, with the exception of dypnone which was prepared by the method of reference³⁵, and were purified prior to use by distillation or recrystallisation as appropriate.

The $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-diene})$ products of the kinetic exchange reactions have all been previously characterised³⁶⁻⁴² and it was therefore possible to check the identity of the products by comparison with infrared data published in the literature.

1,2-bis(diphenylphosphino)ethane was obtained commercially and used without further purification. The identity of the product of the kinetic substitution reactions, $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-dppe})$, where (dppe = 1,2-bis(diphenylphosphino)ethane), was established by comparison of the spectrum with that of authentic sample prepared according to reference⁴³.

Petroleum ether (100-120°; Analytical Grade) and toluene (Analytical Grade), used as solvents in the kinetic experiments, were purified by distillation under a dinitrogen atmosphere prior to use and were then degassed and stored under dinitrogen.

(ii) Experimental Conditions.

All kinetic experiments were carried out under an atmosphere of dinitrogen using sealed vessels immersed in a constant temperature bath controlled to within 0.02°C. Unless specified to the contrary in the appropriate table, experiments were carried out in duplicate, to enable experimental reproducibility to be assessed. Aliquots of the reaction mixture were taken at regular intervals using a syringe, with at least ten absorbance-time pairs taken during each of the kinetic experiments. Infrared spectra were recorded on a Perkin-Elmer 257 spectrophotometer fitted with 1mm NaCl cells, with all measurements referenced to a solvent-ligand blank of the appropriate concentration. Details of the method of analysis of the kinetic data are given in the appropriate sections of Appendix A.

Experiments carried out using the entering group dppe were found to proceed at a rate too large for accurate analysis at 34°C in toluene. The values given for dppe experiments (TABLE 3-3) were obtained following the same methodology used for the diene exchange experiments but only three to four absorbance-time pairs could be obtained during the course of the reaction and the values of k_{obs} quoted must be regarded as approximations.

3.3.2 Stereochemical Experiments.

(i) Preparation and Characterisation of the Products of Ligand Exchange and Isomerisation Reactions.

7-methylcyclohepta-1,3,5-triene was prepared by the literature method²⁷, whilst all other organic ligands employed were obtained commercially. Reactions described were carried out under an atmosphere of dinitrogen using the appropriate degassed solvents.

1. The reaction between $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-Bda})$ and 7-methylcycloheptatriene.

1.0g of $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-Bda})$ and 2.1g of 7-Mechpt (7-Mechpt = 7-methylcycloheptatriene) were stirred in 50cm³ of benzene at 70°C for 6 hours. The solvent was then removed by rotary evaporation and the residue chromatographed on neutral alumina (Activity III) using 40-60° pet. ether as eluant. The broad yellow band eluted was dried under oil pump vacuum to remove excess 7-Mechpt and the residue then purified by molecular distillation onto a cooled probe at 50°C / 0.01mm Hg. The product was an orange oil (500mg; 50% yield).

I.R. spectrum (hexane) ν -CO str. = 2050, 1989, 1979 cm^{-1} .

Analysis: calculated C= 53.6% H= 4.07% ;

found C= 52.9% H= 3.90% .

Details of the ^1H n.m.r. spectrum and assignments are given in section (ii).

Mass spectrum: No parent ion but $(\text{M}^+ - \text{CO})$, $(\text{M}^+ - 2\text{CO})$

and $(\text{M}^+ - 3\text{CO})$ clearly observed.

2. Protonation of the product mixture obtained from the ligand exchange reactions.

The product mixture was dissolved in 20cm^3 of degassed diethyl ether and 75% aqueous HPF_6 added dropwise until precipitation had ceased. The solution was stored overnight at 0°C and then filtered to yield a pale yellow solid. A quantitative yield was obtained.

I.R. spectrum (dichloromethane) : ν -CO str. = 2166 (s), 2055 (b) cm^{-1} .

Analysis: calculated C= 33.7% , H= 2.81% ;

found C= 34.5% , H= 2.67% .

3. Preparation of $\text{Fe}_2(\text{CO})_6 \cdot (\eta^4\text{-7-methylcycloheptatriene})$.

5.2g of $\text{Fe}_2(\text{CO})_9$ and 2.1g of 7-methylcycloheptatriene were allowed to react in degassed diethyl ether for 36 hours under an atmosphere of dinitrogen. After filtration and removal of volatiles by rotary evaporation the residue was pumped to dryness at 0.01mm Hg for 3 hours. The residue was chromatographed on Activity III alumina using 40-60° pet. ether eluant. A bright orange band was collected and was found to yield an oily solid. Crystallisation from 40-60° pet. ether yielded the desired product as red crystals (500mg; 9% yield).

I.R. spectrum (hexane) : ν -CO str. = 2055, 2009,
1991, 1973, 1959 cm^{-1} .

Analysis: calculated C= 43.5% , H= 2.59% ;
found C= 43.0% , H= 2.58% .

Mass spectrum: peaks at (M^+) and ($M^+ - n\text{CO}$) ($n=1$ to 6) observed.

4. Preparation of $\text{Fe}_2(\text{CO})_6 \cdot (\eta^4\text{-cycloheptatriene})$.

5.0g of $\text{Fe}_2(\text{CO})_9$ and 7.0g of freshly distilled cycloheptatriene were refluxed in degassed diethyl ether for 1 hour under a dinitrogen atmosphere. After filtration and evaporation of volatiles the residue was pumped in vacuo for 3 hours. Following chromatography on Activity III alumina using 40-60° pet. ether eluant the product was collected as a bright orange band yielding an oily red solid. Crystallisation from 40-60° pet. ether gave orange crystals (1.0g; 15% yield).

I.R. spectrum (hexane) : ν -CO str. = 2055, 2010,
1993, 1975, 1959 cm^{-1} .

This in good agreement with literature values.

Mass spectrum: peaks at (M^+) and ($M^+ - n\text{CO}$) ($n=1$ to 6) observed.

5. Preparation of $\text{Fe}(\text{CO})_3 \cdot (\eta^6\text{-7-exomethylcycloheptatriene})$.

3.24g of copper(I) iodide was suspended in 40 cm^3 of dry diethyl ether and cooled to -10°C. 26 cm^3 of a 1.5 molar solution of LiMe.LiBr in dry diethyl ether were added to give a cloudy yellow solution of lithium dimethylcuprate, which was then cooled to -70°C. 5.0g of $[\text{Fe}(\text{CO})_3 \cdot (\text{C}_7\text{H}_7)^+] (\text{PF}_6^-)$ was added and the solution became light brown-black in colour. The solution was then poured into 100 cm^3 of a 5% solution of aqueous hydrochloric acid. Following separation of the ether layer, the aqueous layer was extracted twice with 25 cm^3 portions of diethyl ether and the combined ether extracts were then dried over anhydrous magnesium

sulphate. The residue was then purified by preparative thin layer chromatography on silica plates using 40-60° pet. ether as eluant.

Two yellow bands developed on the plates; the faster moving band yielded a yellow oil (300mg; 10% yield) which was further purified by molecular distillation onto a cooled probe at 50°C / 0.01mm Hg. Infrared spectroscopy and microanalysis when combined with the ^1H n.m.r. spectrum given in the following section confirmed that this was the desired product.

I.R. spectrum (hexane) : ν -CO str. = 2050, 1989, 1979 cm^{-1} .

Analysis: calculated C= 53.6% , H= 4.07% ;

found C= 53.0% , H= 4.00% .

The slower moving of the two yellow bands was also collected and found to yield a viscous yellow oil (500mg; 17% yield) which crystallised on cooling to 0°C. The structure of this material was confirmed by infrared spectroscopy, mass spectroscopy and nuclear magnetic resonance as $\text{Fe}_2(\text{CO})_6 \cdot (7,7'\text{-bicycloheptatrienyl})$.

I.R. spectrum (hexane) : ν -CO str. = 2049, 1987, 1979 cm^{-1} .

Mass spectrum: No parent ion but peaks due to $(\text{M}^+ - n\text{CO})$ (n=1 to 6) clearly visible.

6. Thermal isomerisation of $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-7-exomethylcycloheptatriene})$.

0.080g of $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-7-exomethylcycloheptatriene})$ was dissolved in d^6 -benzene. The solution was thoroughly degassed and then transferred to an n.m.r. tube under a dinitrogen atmosphere. The isomerisation of the substrate was observed by ^1H n.m.r. spectroscopy over a 16 hour period at 70°C. Assignment of the n.m.r. spectrum at the end of the reaction revealed that the isomerisation resulted in complete disappearance of the 7-exomethyl isomer with a yield of 70% of the 1-methyl isomer and 30% of combined 2- and 3-methyl derivatives.

7. Attempted synthesis of $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-7-endomethylcycloheptatriene})$.

1.4g of copper(I) iodide was suspended in 25cm^3 of dry diethyl ether. 9.5cm^3 of 1.5M LiMe.LiBr in diethyl ether was added to the solution at -10°C and the resultant lithium dimethylcuprate solution cooled to -70°C . 4.7g of $\text{Fe}(\text{CO})_3 \cdot (\text{C}_7\text{H}_7 \cdot \text{PPh}_3^+)(\text{PF}_6^-)$ was then added to the solution to yield a red suspension. The mixture was allowed to warm to room temperature and then poured into 100cm^3 of a solution of 5% aqueous hydrochloric acid. After separation of the ether layer the aqueous layer was extracted twice with 25cm^3 portions of diethyl ether. The ether fractions were combined, washed with distilled water and dried over anhydrous magnesium sulphate. Following removal of the solvent by rotary evaporation the residue was purified by preparative thin layer chromatography on silica plates using $40\text{-}60^\circ$ pet. ether as eluant. A single fast moving yellow band was obtained and purified by molecular distillation. Following infrared and ^1H n.m.r. spectroscopic analysis of the orange oil obtained this product was identified as the known species $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-cycloheptatriene})$ ^{37,38}.

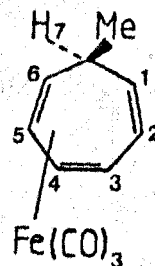
I.R. spectrum (hexane) : $\nu\text{-CO str.} = 2049, 1987, 1979 \text{ cm}^{-1}$.

(ii) Tables of ^1H n.m.r. spectral data .

All n.m.r. experiments were carried out using a JEOL FX100 spectrometer with variable temperature probe; data given correspond to the 100 MHz ^1H spectrum of the species described.

Reference Chemical Shift(δ) Structure

	Me	1.17 (doublet; J= 7.1 Hz)
	1	5.09 (m)
This work	2	5.73 (m)
	3	2.99 (m)
	4,5	5.34 (m)
	6	3.25 (m)
	7	2.67 (m)

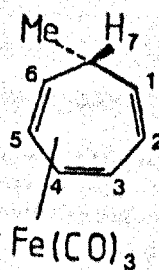


(CDCl₃)

	Me	1.00 (doublet; J= 7.1 Hz)
	1	5.00 (m)
This work	2	5.59 (m)
	3	2.64 (m)
	4,5	4.75 (m)
	6	2.87 (m)
	7	2.34 (m)

(C₆D₆)

	Me	1.00 (doublet; J= 7.4 Hz)
	1,4,5	5.25 (m)
This work	2	5.79 (m)
	3	3.29 (m)
	6	3.08 (m)
	7	2.21 (m)



(CDCl₃)

Chemical shifts for the protons of this species are approximate due to partial overlap with the spectra of the 1-, 2-, and 3-methyl isomers.

	Me	1.40 (quartet; $J = 1.1$ Hz)	
	2	5.43 (doublet; $J = 8.0$ Hz)	
This work	3,6	2.82 (m)	
	4,5	4.70 (m)	
	7,8	1.85 (m)	

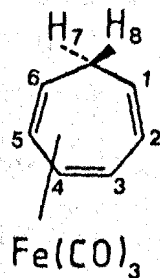
Chemical shifts for the protons of this species are approximate due to partial overlap with the spectra of the 2-, 3-, and 7-methyl isomers.

	Me	1.68 , 1.63 (singlet)	
This work	1	4.96 (m)	
	2	5.74 (m)	

The low intensity of these two spectra relative to the 7-methyl isomers and the 1-methyl isomer prevented definite assignment of the proton spectra.

Resonances other than those given were lost under the more intense proton resonances of the other species.

(38)	1	5.03 (m)
	2	5.68 (m)
	3	2.72 (m)
	4,5	4.65 (m)
	6	2.89 (m)
	7	2.12 (m)
	8	1.89 (m)

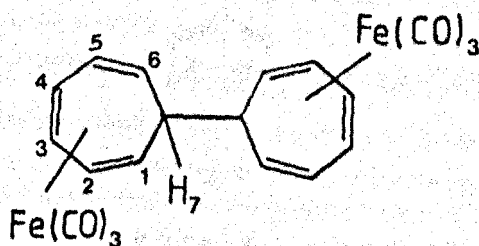


(C_6D_6)

This work	1,4,5	5.28 (m)
	2	5.82 (m)
	3	3.37 (m)
	6	3.08 (m)
	7,8	2.35 (m)

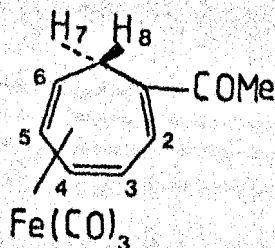
(CDCl_3)

This work	1	4.86 (m)
	2	5.85 (m)
	3,6,7	2.94 (m)
	4,5	5.42 (m)



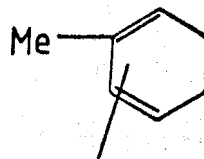
(CDCl_3)

(28)	Me	2.04 (singlet)
	2	6.94 (doublet; $J = 8.0$ Hz)
	3	3.02 (triplet; $J = 8.0$ Hz)
	4,5	5.35 (m)
	6	3.46 (m)
	7,8	2.45 (m)



(CS_2)

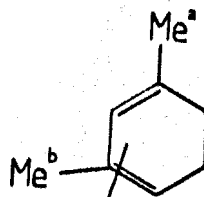
(29) Me 2.07



$\text{Fe}(\text{CO})_3$

(CDCl_3)

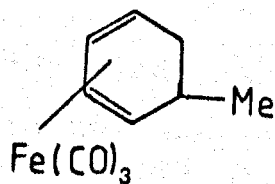
(29) Me^a 1.59
Me^b 2.05



$\text{Fe}(\text{CO})_3$

(CDCl_3)

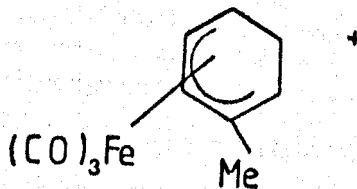
(44) Me 0.92 (doublet; $J = 7.0$ Hz)



$\text{Fe}(\text{CO})_3$

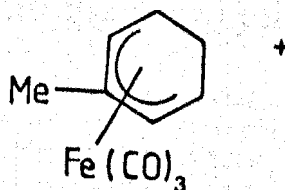
(CDCl_3)

(29) Me 2.29



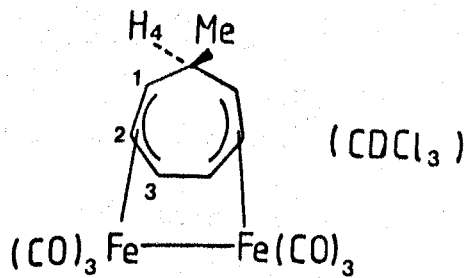
(CF_3COOH)

(29) Me 2.88



(CF_3COOH)

	Me	1.05 (doublet; J= 6.7 Hz)
	1	2.69 (m)
This work	2	4.21 (m)
	3	5.10 (m)
	4	2.41 (m)



	1	2.74 (m)	
	2	4.25 (m)	
(45)	3	5.12 (m)	
&	4	3.00 (doublet; J= 18 Hz)	
this work	5	2.16 (doublet; J= 18 Hz)	

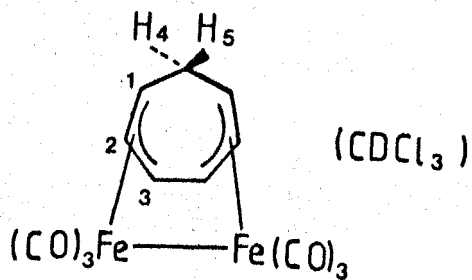


TABLE 3-1.

Rate constants for Reactions of $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-bda})^a$.

<u>Entering Group</u>	<u>Concentration</u> <u>/mol dm⁻³</u>	<u>10⁴k_{obs}</u> <u>/s⁻¹</u>
cyclohexa-1,3-diene T/K = 343.2	0.049	10.86 , 11.18 ^b
	0.098	14.84 , 15.15
	0.196	20.71 , 19.65
	0.392	23.63 , 24.03
	0.539	25.53 , 25.49
	0.637	25.04 , 25.55
	0.735	25.92 , 25.65
0.882	26.40 , 26.86	
cyclohepta-1,3-diene T/K = 343.2	0.049	2.30 , 1.79 ^b
	0.099	3.49 , 3.12
	0.198	4.37 , 4.98
	0.297	5.23 , 4.79
	0.396	5.59 , 5.97
	0.495	6.40 , 6.56
	0.594	6.87 , 6.99
	0.693	7.13 , 7.33
	0.792	7.30 , 7.39
	0.891	7.31 , 7.48
0.990	7.72 , 7.69	
cyclohepta-1,3,5-triene T/K = 343.2	0.099	0.75 , 0.89 ^b
	0.197	1.42 , 1.40
	0.296	1.73 , 1.86
	0.394	2.12 , 2.42
	0.493	2.56 , 2.35
	0.591	2.59 , 2.49
	0.690	3.02 , 3.20
	0.789	3.20 , 3.09
	0.887	3.30 , 3.05
	0.986	3.64 , 3.58
cycloocta-1,3,5,7-tetraene T/K = 343.2	0.049	2.72
	0.098	4.48
	0.196	5.77
	0.392	6.62
	0.539	7.78
	0.686	8.59
	0.784	8.61
1,4-diphenylbuta-1,3-diene T/K = 343.2	0.103	0.38 , 0.42 ^b
	0.154	0.53 , 0.52
	0.206	0.48 , 0.47
	0.257	0.60 , 0.57
	0.308	0.63 , 0.64
	0.359	0.79 , 0.74
	0.411	0.79 , 0.73
0.463	0.89 , 0.84	

Footnotes.

- a Reactions carried out in toluene solution.
b Where two values are given for k_{Obs} at a single concentration duplicate experiments were carried out.

TABLE 3-2.

Derived Rate Constants for Reactions of $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-bda})$.

Entering Group	$10^4 k_\alpha$ / a	$10^4 k_\beta / k_\delta$ / s ⁻¹	$10^4 k_\gamma / k_\delta$ / b	$10^4 \sigma_{\text{fit}}$ / s ⁻¹	$10^4 \sigma_{\text{re}}$ / s ⁻¹
1,3-chd	0.4 ± 1.2	28.6 ± 1.1	0.82 ± 0.07	0.45	0.29
1,3-chpd	1.4 ± 0.6	7.1 ± 0.7	1.3 ± 0.2	0.28	0.19
1,3,5-chpt	0.8 ± 0.8	3.6 ± 1.5	3.9 ± 1.7	0.13	0.09
1,3,5,7-cot	2.5 ± 1.4	7.2 ± 1.1	0.8 ± 0.2	0.29
1,3-but	1.3 ± 0.1	0.3 ± 0.1	0.05	0.02

Footnotes

a Units are $\text{dm}^{-3} \text{mol}^{-1} \text{s}^{-1}$.

b Units are mol dm^{-3} .

σ_{fit} Gives an estimate of the fit of the experimental data to the theoretical model.

σ_{re} Gives an estimate of experimental reproducibility.

Abbreviations:

1,3-chd = cyclohexa-1,3-diene ;

1,3-chpd = cyclohepta-1,3-diene ;

1,3,5-chpt = cyclohepta-1,3,5-triene ;

1,3,5,7-cot = cycloocta-1,3,5,7-tetraene ;

1,3-but = 1,4-diphenylbuta-1,3-diene.

TABLE 3-3.Rate data for Reactions of $\text{Fe}(\text{CO})_5 \cdot (\eta^4\text{-enone})$ with dppe^a .

<u>Enone</u>	<u>Phosphine Concentration</u> <u>/mol dm⁻³</u>	<u>10⁴ k_{obs}</u> <u>/s⁻¹</u>
benzalacetone T/K = 307.2	0.039	11.37
	0.049	13.22
	0.074	15.76
	0.123	21.92
chalcone T/K = 307.2	0.039	6.78
	0.049	8.49
	0.074	9.77
	0.123	12.79

Footnote.^a Reactions carried out in toluene solution.

TABLE 3-4.

Rate constants for Reactions of $\text{Fe}(\text{CO})_2(\eta^4\text{-enone})$
with cyclohexa-1,3-diene^a.

<u>Leaving Group</u>	<u>Ligand Concentration</u> <u>/mol dm⁻³</u>	<u>10⁴ k_{obs}</u> <u>/s⁻¹</u>
benzalacetone T/K = 343.2	0.049	10.86 , 11.18 ^b
	0.098	14.84 , 15.15
	0.196	20.71 , 19.65
	0.392	23.63 , 24.03
	0.539	25.53 , 25.49
	0.637	25.04 , 25.55
	0.735	25.92 , 25.65
	0.882	26.40 , 26.86
cinnamaldehyde T/K = 343.2	0.050	7.73 , 8.05 ^b
	0.100	9.29 , 9.24
	0.200	11.16 , 11.11
	0.301	11.84 , 12.33
	0.401	12.35 , 12.58
	0.501	12.78 , 13.08
	0.601	13.96 , 12.60
	0.702	13.40 , 13.73
	0.802	13.95 , 14.19
	0.902	14.36 , 14.68
1.002	14.78 , 15.18	
chalcone T/K = 343.2	0.099	3.29 , 3.45 ^b
	0.198	5.55 , 5.39
	0.298	6.88 , 6.96
	0.397	8.48 , 8.41
	0.496	10.22 , 9.77
	0.595	10.59 , 10.55
	0.694	12.34 , 11.50
	0.800	12.97 , 13.39
0.900	15.50 , 15.48	
1.000	15.89 , 16.39	

Footnotes.

^a Reactions carried out in toluene solution.

^b Where two values are given for k_{obs} at a single concentration duplicate experiments were carried out.

TABLE 3-5.

Rate constants for Reactions of $\text{Fe}(\text{CO})_2(\eta^4\text{-enone})$
with cyclohepta-1,3,5-triene^a.

<u>Leaving Group</u>	<u>Ligand Concentration</u> <u>/mol dm⁻³</u>	<u>10⁴ k_{obs}</u> <u>/s⁻¹</u>
benzalacetone T/K = 363.0	0.049	3.75 , 3.64 ^b
	0.098	5.27 , 5.91
	0.196	11.00 , 11.36
	0.392	16.77 , 17.03
	0.784	23.70 , 24.30
cinnamaldehyde T/K = 363.2	0.049	3.81 , 3.94 ^b
	0.098	5.80 , 5.42
	0.196	7.88 , 9.66
	0.392	10.32 , 9.93
	0.784	18.86 , 18.85
chalcone T/K = 363.2	0.049	0.77 , 1.04 ^b
	0.098	1.15 , 1.22
	0.196	2.52 , 2.62
	0.392	4.97 , 5.50
	0.784	6.49 , 6.74
dypnone T/K = 363.0	0.061	2.59 , 2.56 ^b
	0.123	3.50 , 3.21
	0.196	3.32 , 3.39
	0.392	5.76 , 5.76
	0.784	11.12 , 10.56

Footnotes.

- ^a Reactions carried out in toluene solution.
^b Where two values are given for k_{obs} at a single concentration duplicate experiments were carried out.

TABLE 3-6.

Derived Rate Constants for Reactions of $\text{Fe}(\text{CO})_3 \cdot (\text{^4-enone})$
with cyclohexa-1,3-diene.

<u>Leaving Group</u>	$10^4 k_\alpha$ / a	$10^4 k_{\beta} / k_\delta$ /s ⁻¹	$10^4 k_\gamma / k_\delta$ / b	$10^4 \sigma_{\text{fit}}$ /s ⁻¹	$10^4 \sigma_{\text{re}}$ /s ⁻¹
bda	0.4 ± 1.2	28.6 ± 1.1	0.82 ± 0.07	0.45	0.29
cin	3.4 ± 0.3	11.8 ± 0.2	0.29 ± 0.02	0.24	0.36
cha	12.5 ± 0.7	4.7 ± 0.7	0.92 ± 0.32	0.29	0.27

Footnotes

a Units are $\text{dm}^{-3} \text{mol}^{-1} \text{s}^{-1}$.

b Units are mol dm^{-3} .

σ_{fit} Gives an estimate of the fit of the experimental data to the theoretical model.

σ_{re} Gives an estimate of experimental reproducibility.

Abbreviations:

bda = benzalacetone ;

cin = cinnamaldehyde ;

cha = chalcone.

TABLE 3-7.

Derived Rate Constants for Reactions of $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-enone})$
with cyclohepta-1,3,5-triene.

Leaving Group	$10^4 k_\alpha$ / a	$10^4 k_\beta / k_\delta$ /s ⁻¹	$10^4 k_\gamma / k_\delta$ / b	$10^4 \sigma_{\text{fit}}$ /s ⁻¹	$10^4 \sigma_{\text{re}}$ /s ⁻¹
bda	4.9 ± 9.5	31.9 ± 17.8	0.45 ± 0.31	0.58	0.22
cin	15.9 ± 3.4	5.1 ± 1.8	0.30 ± 0.28	0.78	0.72
cha	6.7 ± 1.4	1.8 ± 1.0	1.4 ± 1.0	0.39	0.45
dyp	10.4 ± 0.8	1.8 ± 0.1	0.37	0.23

Footnotes

a Units are $\text{dm}^{-3} \text{mol}^{-1} \text{s}^{-1}$.

b Units are mol dm^{-3} .

σ_{fit} Gives an estimate of the fit of the experimental data to the theoretical model.

σ_{re} Gives an estimate of experimental reproducibility.

Abbreviations:

bda = benzalacetone ;

cin = cinnamaldehyde ;

cha = chalcone ;

dyp = dypnone.

TABLE 3-8.Rate data for Mass Effect Experiments with $\text{Fe}(\text{CO})_5$ (η^4 -enone)

<u>Leaving Group</u>	<u>Concentration</u> <u>/mol dm⁻³</u>	<u>10⁴</u> <u>s⁻¹ k_{obs}</u>
	0.000	9.67
benzalacetone	0.027	4.35
	0.048	2.99
T/K = 363.2	0.069	2.52
	0.089	1.98
	0.110	1.69
	0.130	1.28
	0.151	1.19
	0.192	0.93

Footnote.

^a Reactions carried out in toluene solution using the entering group cyclohepta-1,3,5-triene at a concentration of 0.475 mol dm⁻³. A plot of k_{obs}⁻¹ versus [benzalacetone] has a correlation coefficient for a linear fit of better than 0.995 (1.00 = perfect linear relationship).

TABLE 3-9.

Rate data for Reactions of $\text{Fe}(\text{CO})_2 \cdot (\eta^4\text{-bda}) \cdot (\text{L})$
with cyclohexa-1,3-diene^a.

<u>Auxiliary Group (L)</u>	<u>Ligand Concentration</u> <u>/mol dm⁻³</u>	<u>10⁴ k_{obs}</u> <u>/s⁻¹</u>
carbon monoxide T/K = 343.4	0.025	10.54 , 11.00 ^b
	0.049	13.02 , 12.67
	0.098	17.40 , 17.68
	0.196	23.18 , 22.57
	0.270	25.20 , 26.40
	0.319	26.56 , 25.96
	0.368	26.64 , 27.52
	0.441	28.17 , 28.73
triphenylphosphine T/K = 343.4	0.025	0.47 , 0.49 ^b
	0.049	0.58 , 0.50
	0.098	0.45 , 0.46
	0.196	0.50 , 0.50
	0.270	0.50 , 0.52
	0.319	0.51 , 0.55
	0.368	0.51 , 0.51
	0.441	0.52 , 0.55

Footnotes.

- ^a Reactions carried out in 100-120° petroleum ether.
^b Where two values are given for k_{obs} at a single concentration duplicate experiments were carried out.

TABLE 3-10.

Derived Rate Constants for Reactions of $\text{Fe}(\text{CO})_2 \cdot (\text{}^4\text{-bda}) \cdot (\text{L})$
with cyclohexa-1,3-diene.

<u>Auxiliary Ligand</u>	$10^4 k_\alpha$ / a	$10^4 k_\beta / k_\delta$ / s ⁻¹	$10^4 k_\gamma / k_\delta$ / b	$10^4 \sigma_{\text{fit}}$ / s ⁻¹	$10^4 \sigma_{\text{re}}$ / s ⁻¹
CO	18.5 ± 4.6	22.8 ± 2.2	0.04 ± 0.01	0.81	0.30
PPh ₃	1.4 ± 0.6	7.1 ± 0.7	1.3 ± 0.2	0.28	0.19

Footnotes

a Units are $\text{dm}^{-3} \text{mol}^{-1} \text{s}^{-1}$.

b Units are mol dm^{-3} .

σ_{fit} Gives an estimate of the fit of the experimental data to the theoretical model.

σ_{re} Gives an estimate of experimental reproducibility.

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CHAPTER FOUR : THE KINETICS AND MECHANISM OF ALKADIENE EXCHANGE AT
SIX-COORDINATE CHROMIUM.

4.1 INTRODUCTION.

The substitution reactions of six-coordinate metal carbonyl derivatives have been an area of intensive study in recent years. The kinetics of substitution of species of the type $M(CO)_5 \cdot L$ and $M(CO)_4 \cdot (L-L)$ have been the subject of a number of careful studies, with the mechanism of substitution well established in several cases, notably those systems with bidentate nitrogen or sulphur donors as leaving groups¹⁻⁴. An important class of reactions for which the mechanism is not established involve the substitution of monodentate and bidentate organic π -donor ligands at zerovalent metal centres. Kinetic information for the substitution reactions of $Mo(CO)_4 \cdot (\eta^4\text{-alkadiene})$, where (alkadiene = norbornadiene (bicyclo[2.2.1]hepta-2,5-diene), cycloocta-1,5-diene), has been reported but ligand exchange was not considered^{5,6}. The reactions described used monodentate Group V^a ligands as entering groups with the kinetic behaviour observed typical of the two term rate law often found for six-coordinate systems with highly nucleophilic entering groups. The rate law has the form given by equation (4-1) :

$$(4-1) \quad k_{obs} = k_1 + k_a [L] .$$

The investigations reported were not sufficiently detailed to establish whether the behaviour described by (4-1) was representative of a particular type of "ring-opening" pathway. Work on alkatriene and arene substitution by Group V^a monodentate ligands using substrates of the type $M(CO)_3 \cdot (\eta^6\text{-arene})$ has demonstrated that complete displacement of the hexahapto arene or alkatriene occurs according to equation (4-2) :

temperatures^{11(b)}. In marked contrast to the above the complexes $\text{Cr}(\text{CO})_4 \cdot (\eta^4\text{-alkadiene})$, where (alkadiene = trans,trans-hexa-2,4-diene or buta-1,3-diene), have been found to exchange rapidly with non-conjugated diene entering groups at ambient temperature. Kinetic measurements were found to be possible for these two substrates using the non-conjugated alkadienes norbornadiene and cycloocta-1,5-diene as entering groups. The products of ligand exchange were thus the known species $\text{Cr}(\text{CO})_4 \cdot (\eta^4\text{-norbornadiene})$ and $\text{Cr}(\text{CO})_4 \cdot (\eta^4\text{-cycloocta-1,5-diene})$ and this enabled product yield and identity to be confirmed by comparison with the infrared spectra of authentic samples^{12,13}. So that the results of the present study could be compared with those of reactions with non-conjugated alkadienes as leaving groups^{5,6}, and with other more well established kinetic systems with bidentate leaving groups^{1-4,14}, a second set of kinetic experiments was carried out with more nucleophilic monodentate phosphite entering groups. The products of this type of substitution reaction are species of the type $\text{Cr}(\text{CO})_4 \cdot (\text{L})_2$ which exhibit geometric isomerism and consequently it was possible to consider the stereochemistry of the substitution process by comparison of the spectra of the product species with those of bis(phosphite) complexes of known geometry¹⁵⁻¹⁷.

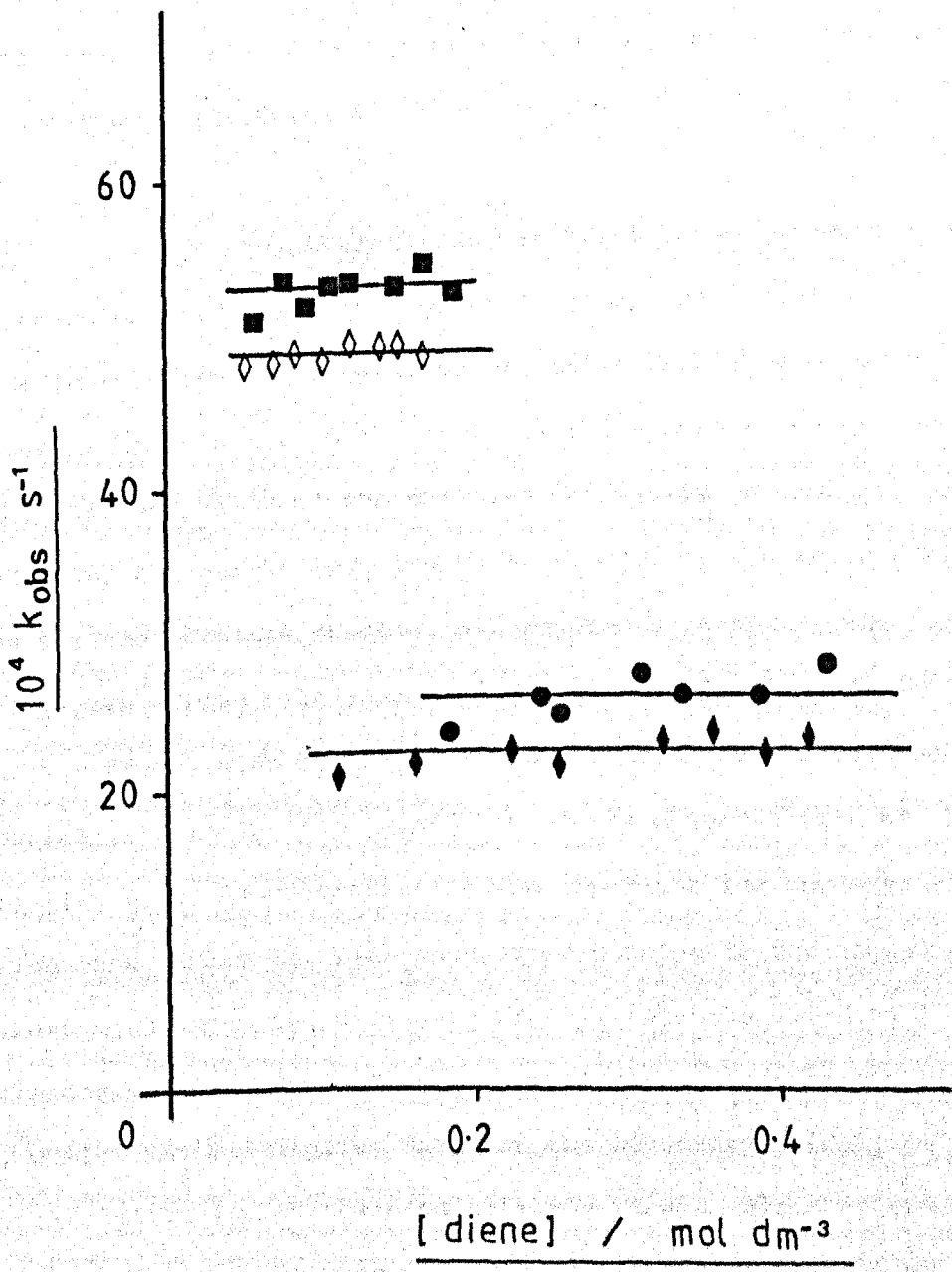
4.2.1 Alkadiene Exchange Reactions.

Alkadiene exchange reactions were carried out in hexane at 26.5°C employing pseudo-first-order conditions in which the entering group was present in a greater than ten-fold excess relative to the substrate. Kinetic experiments were carried out using an apparatus described in the experimental section; the treatment of kinetic data is described in Appendix A. Satisfactory pseudo-first-order plots could be obtained from an analysis of the change in infrared spectrum with time. Both substrate disappearance and product appearance could be monitored and were found to

give values of k_{obs} (the observed rate constant) which were identical within experimental error. Measurements quoted in the tables refer to the rates of disappearance of the 1943 and 1932 cm^{-1} stretching vibrations of the carbonyl groups of $\text{Cr}(\text{CO})_4 \cdot (\eta^4\text{-buta-1,3-diene})$ and those at 1937 and 1920 cm^{-1} for the substrate $\text{Cr}(\text{CO})_4 \cdot (\eta^4\text{-trans,trans-hexa-2,4-diene})$ since product-ligand spectral overlap was minimised in this region of the spectrum. The small amount of overlap found in this region had no measurable effect on the linearity of the pseudo-first-order plots obtained.

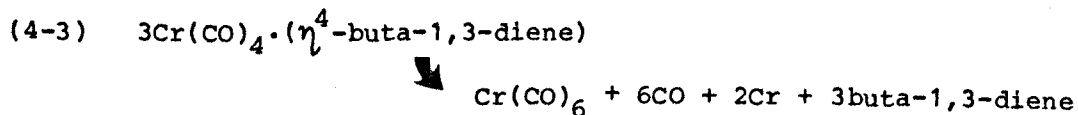
Preliminary experiments with the substrate $\text{Cr}(\text{CO})_4 \cdot (\eta^4\text{-buta-1,3-diene})$ revealed that a thermolytic process was competitive with ligand exchange at low concentrations of the entering ligand. No competing thermolysis was observed with the substrate $\text{Cr}(\text{CO})_4 \cdot (\eta^4\text{-trans,trans-hexa-2,4-diene})$ over the time-scale of the kinetic experiments. Since the thermolysis is the only process observed when the butadiene complex is heated in the absence of a suitable entering group this was studied kinetically. The thermolysis was found to proceed at a reproducible rate of $12.8 \times 10^{-4} \text{ s}^{-1}$ in the absence of a suitable entering group, with hexacarbonylchromium as the sole product containing carbonyl groups active in the infrared region. In marked contrast to the thermolysis of non-conjugated alkadiene complexes, which proceed at non-reproducible rates and produce varying yields of hexacarbonylchromium, the conjugated species was found to give a yield of exactly one mole of hexacarbonylchromium for each three moles of substrate consumed. No attempt was made to identify other products of the thermolysis owing to the very low concentration of the substrate solution available. However, since no crystalline chromium oxide residues were observed at the end of the reaction, the most likely products would be carbon monoxide, buta-1,3-diene and free chromium metal. The probable stoichiometry of the thermolysis is given by equation (4-3) :

FIGURE 4-1



Key:

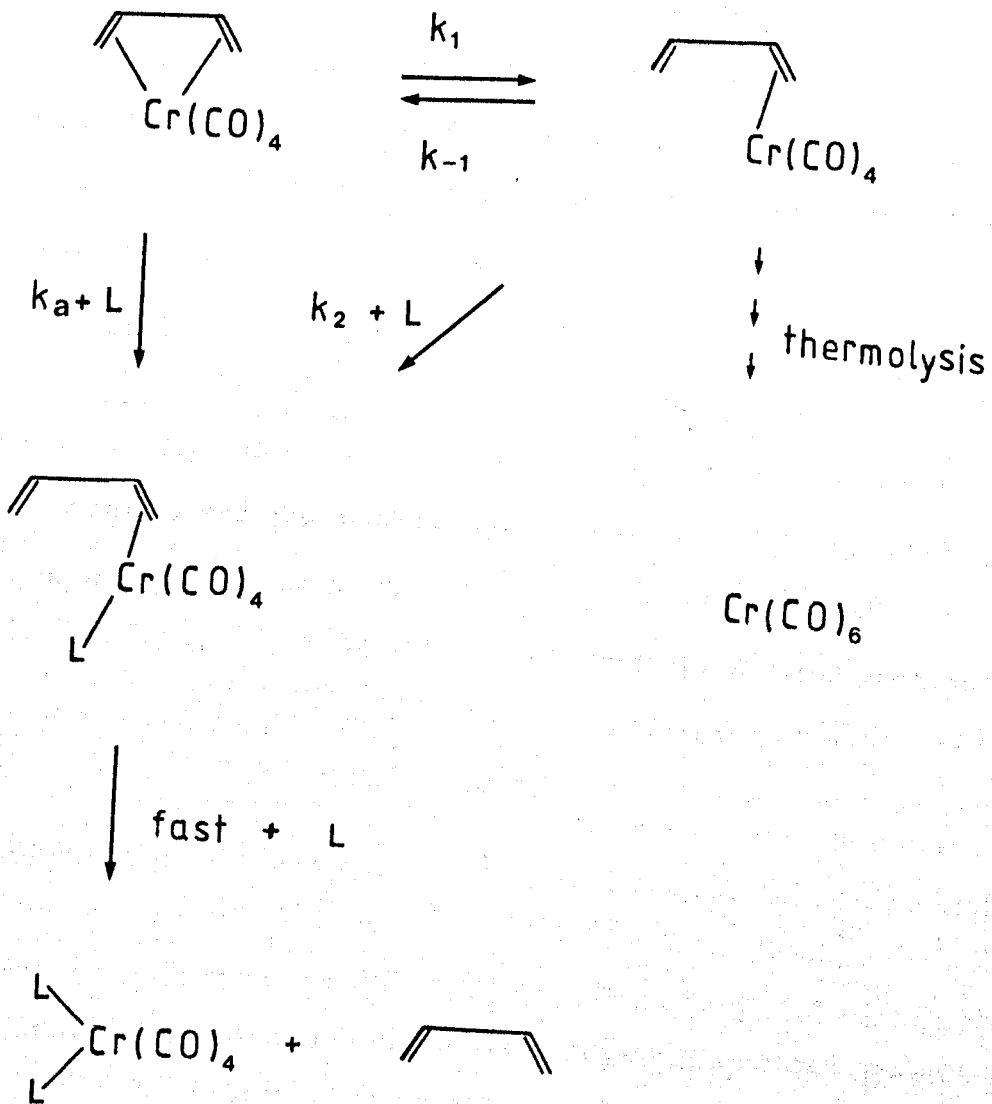
- ◆ 1,3-but + 2,5-nbd
- 1,3-but + 1,5-cod
- ◇ 2,4-hex + 1,5-cod
- 2,4-hex + 2,5-nbd



It is noteworthy that the rate of thermolysis was found to increase if the reaction was carried out in daylight, an observation in keeping with the photoinduced hydrogenation of alkenes by this substrate, which is postulated to proceed by way of a coordinatively unsaturated intermediate of the type : $[\text{Cr}(\text{CO})_3 \cdot (\text{H}) \cdot (\eta^2\text{-alkadiene})]$ ^{9, 18}.

The thermolysis was found to be competitive with ligand exchange only at the lowest entering group concentrations used with the butadiene-bearing substrate; quantitative yields were found for all other concentrations used. Only reactions which were found to result in quantitative yields of the expected $\text{Cr}(\text{CO})_4 \cdot (\eta^4\text{-alkadiene})$ product, as indicated by Beer-Lambert law measurements, were used in deriving the rate-law for the exchange process. All reactions involving the substrate $\text{Cr}(\text{CO})_4 \cdot (\eta^4\text{-trans,trans-hexa-2,4-diene})$ were found to result in quantitative yields of the expected products, and in consequence it was possible to examine the dependence of the observed rate of exchange on entering group concentration in the important low concentration region using this substrate. Rate data corresponding to the ligand exchange reactions between the substrate $\text{Cr}(\text{CO})_4 \cdot (\eta^4\text{-buta-1,3-diene})$ and the entering groups norbornadiene and cycloocta-1,5-diene are given in TABLE 4-1, whilst TABLE 4-2 gives data for the substrate $\text{Cr}(\text{CO})_4 \cdot (\eta^4\text{-trans,trans-hexa-2,4-diene})$ with the same entering groups. Plots of the observed rate constant against entering ligand concentration for the four kinetic systems are provided in FIGURE 4-1 and indicate clearly that the observed reaction rate is a linear function of ligand concentration over the entire concentration range studied in each case. Since there is no observable curvature of the rate plots at low entering ligand concentrations for the reactions which produce quantitative yields the applicable rate law will

FIGURE 4-2



have the form given by equation (4-4) :

$$(4-4) \quad \frac{-d[S]}{dt} = k_1[S] + k_a[S][L]$$

k_1 is a ligand-independent term, estimated from the intercept of the linear plot with the y-axis of the graph, whilst k_a , the ligand-dependent term corresponds to the slope of the plot. This type of kinetic behaviour is well known for the substitution reactions of six-coordinate transition metal complexes¹ and may be interpreted in terms of the mechanism illustrated in Figure 4-2. Application of the steady-state hypothesis to intermediates A and B of FIGURE 4-2 yields the expanded rate law given in equation (4-5) :

$$(4-5) \quad \frac{-d[S]}{dt} = \frac{k_1 k_2 [S][L] + k_a [S][L]}{k_{-1} + k_2 [L]}$$

Under the conditions where $k_2 [L] \gg k_{-1}$, rate law (4-5) reduces to the form given in (4-4). For the systems used in the present study these conditions would be expected to hold true even at the lowest entering group concentrations employed since the metal-conjugated diene bond has been shown to be considerably weaker than the corresponding bond between a chromium and a non-conjugated diene¹⁰.

Values of k_1 and k_a derived using equation (4-4) were calculated by means of a weighted linear least-squares analysis given in Appendix A and the values obtained are presented in TABLE 4-3 with standard deviations reflecting the fit of the model to the experimental data. It will be seen that in all cases k_1 has a considerably greater magnitude than k_a ; indeed, in view of the large experimental uncertainty in k_a the value of this constant does not differ significantly from zero. On the basis of the limited information available it appears that the much higher reactivity of the complex $\text{Cr}(\text{CO})_4 \cdot (\eta^4\text{-trans,trans-hexa-2,4-diene})$ towards ligand exchange can be accounted for in terms of the electron donor ability

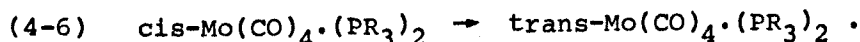
of the alkadienes which is influenced by the substituents at the ligand π -centres. This type of behaviour is analogous to the electronic contribution to the metal-alkene bond cleavage in complexes of the type $\text{Fe}(\text{CO})_4 \cdot (\eta^2\text{-CH}_2\text{CHX})$ ¹⁹. Steric acceleration is not a likely cause of ligand lability for these systems since the ability of the alkadiene to adopt an *s-cis* geometry is well known and would prevent metal-methyl interactions in the resultant complex.

The influence of the entering group on the ligand exchange process is difficult to discern since the rate-determining step of the reaction appears to involve a simple bond dissociation. It is noteworthy, however, that the observed values of k_1 show no marked variation with a change in entering group for either substrate. This is in marked contrast to another study of a six-coordinate system involving alkenes as entering groups where it was observed that the k_1 constants showed significant variation with entering group geometry suggesting a form of steric control on the overall reaction rate²⁰.

4.2.2 Phosphite Substitution Reactions.

The isomerisation of bis(phosphite) complexes of six-coordinate transition metals has been studied extensively in recent years. The thermal isomerisation of species of the type $\text{M}(\text{CO})_4 \cdot (\text{PR}_3)_2$ has been the subject of a number of reports²¹⁻²³. Separation of the *cis*- and *trans*-isomers of these complexes has proved possible in several different cases and the *cis*-isomer of $\text{Cr}(\text{CO})_4 \cdot [\text{P}(\text{OCH})_3(\text{CH}_2)_3]_2$ has been reported to undergo thermal isomerisation to yield the *trans*-isomer under mild conditions²¹. The most recent reports of the kinetics of isomerisation of related species indicate that for the process represented by equation (4-6) intramolecular isomerisation occurs when the phosphine ligands are tributylphosphines

whilst with the bulkier ligand triphenylphosphine metal-ligand bond dissociation is required for isomerisation to take place.



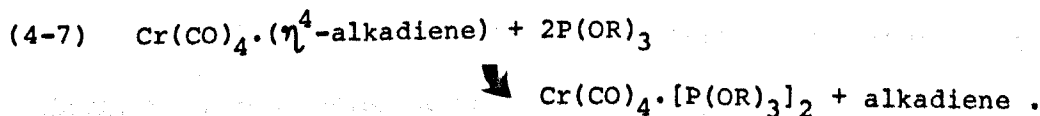
With the former ligand no incorporation of isotopically labelled carbon monoxide is observed during isomerisation which proceeds with :

$$\Delta H = 102.5 (6.7) \text{ kJ mol}^{-1};$$

whilst with the more sterically hindered phosphine triphenylphosphine the reported value is :

$$\Delta H = 125 (10) \text{ kJ mol}^{-1}.$$

In view of these observations it was interesting to find that reactions of the type given in equation (4-7) yielded a mixture of the cis- and trans-isomers of $\text{Cr(CO)}_4 \cdot [\text{P(OR)}_3]_2$.



where $\text{P(OR)}_3 = \text{P(OMe)}_3$ or P(OPh)_3).

In the case of the bis(trimethylphosphite) complex both the cis- and the trans-isomers have previously been characterised and the infrared spectrum of the products of the substitution reaction could therefore be compared with literature values¹⁶ :

Observed ν -CO str. (reaction mixture) = 2026(w), 1942(w),
(hexane) 1937(w), 1917(s) cm^{-1} .

Reported ν -CO str. (cis-isomer) = 2026, 1947, 1939, 1921 cm^{-1} .
(hexadecane) (trans-isomer) = 1914(vs) cm^{-1} .

The substitution reactions reported in the present study were carried out at 26.5°C and this may explain the curious spectrum of the product mixture for ligand substitution with the entering group triphenylphosphite :

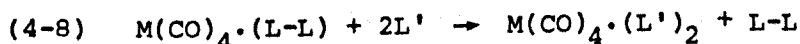
Observed ν -CO str. (reaction mixture) = 2036(m), 1957(m),
 (heptane) 1941(sh), 1930(s) cm^{-1} .

Only the trans-isomer of $\text{Cr}(\text{CO})_4 \cdot [\text{P}(\text{OPh})_3]_2$ has been reported in the literature and this species has only a single strong vibration at 1930 cm^{-1} in the solvent tetrachloromethane¹⁷. However the literature synthesis used rather more vigorous conditions than used for the present study and under the reported conditions the initially formed cis-isomer would be expected to undergo thermal isomerisation to the trans-isomer by analogy with the similar molybdenum complexes. For this reason the infrared stretching vibrations seen for the reaction mixture in the present study can be assigned to the previously unreported species cis- $\text{Cr}(\text{CO})_4 \cdot [\text{P}(\text{OPh})_3]_2$ in view of the similarities with the spectrum of cis- $\text{Cr}(\text{CO})_4 \cdot [\text{P}(\text{OMe})_3]_2$.

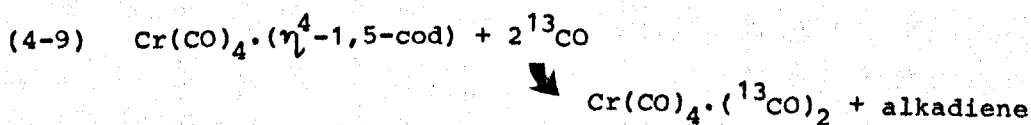
The relative intensities of the carbonyl stretching vibrations of the products of the two substitution reactions suggest that, in both cases, the trans-isomer predominates in the product mixture, but in the case of the triphenylphosphite entering group systems the proportion of the cis-isomer in the product is greater than for the less sterically hindered triphenylphosphite ligand.

Though these findings are in accord with the differing mechanisms of isomerisation for the two phosphites put forward by Darensbourg et al.^{22,23} the results can equally well be explained in terms of a mechanism involving a fluxional intermediate. In this regard it is perhaps interesting to note that the reaction of $\text{Mo}(\text{CO})_4 \cdot (\eta^4\text{-}1,5\text{-cod})$ where (1,5-cod = cycloocta-1,5-diene), with a variety of Group V^a ligands as entering groups results exclusively in products of the structure cis- $\text{Mo}(\text{CO})_4 \cdot (\text{L})_2$ for reactions carried out at $30 - 40^\circ\text{C}$ in a variety of solvents^{5,6}. It is known²⁴ that $\text{Cr}(\text{CO})_4 \cdot (\eta^4\text{-}1,3\text{-diene})$ exhibits stereochemical non-rigidity on the n.m.r. time-scale whilst the complex

$\text{Cr}(\text{CO})_4 \cdot (\eta^4\text{-cycloocta-1,5-diene})$ does not rearrange at readily accessible temperatures. When considering the possibility of cis-trans isomerisation during the substitution process the evidence of a number of relevant studies is available. An increasing number of reactions are known which have the stoichiometry given in equation (4-8) whilst generating a mixture of cis- and trans- $\text{M}(\text{CO})_4 \cdot (\text{L})_2$ products.



Several examples of systems displaying spectroscopic or kinetic evidence of fluxional intermediates have been reported in the literature^{2,3,25}. Perhaps the most compelling evidence concerns those reactions for which a constant ratio of the stereochemical isomers of the product is established at an early stage in a kinetically measured substitution reaction and maintained throughout the remainder of the reaction. Studies of a reaction of this type have resulted in Dobson and coworkers postulating a five-coordinate intermediate of the type $[\text{M}(\text{CO})_4 \cdot (\text{L}')]_2$, possessing fluxional properties, as the species responsible for the isomerisation^{2,3,25}. Cohen and Brown²⁶ have reached similar conclusions in considering the stereochemistry of the alkadiene substitution reactions of the species $\text{Cr}(\text{CO})_4 \cdot (\eta^4\text{-1,5-cod})$ by isotopically labelled carbon monoxide. These reactions proceed according to equation (4-9) :



Taking into consideration the very mild conditions used in the present study it is tempting to favour a model involving a fluxional five-coordinate intermediate to account for the observed behaviour. Thermal isomerisation subsequent to product formation does not seem likely under these conditions whilst isomerisation of a seven-coordinate intermediate of the form $\text{Cr}(\text{CO})_4 \cdot (\eta^4\text{-alkadiene}) \cdot [\text{P}(\text{OR})_3]$ or of the possible alternative five-coordinate intermediate $\text{Cr}(\text{CO})_4 \cdot [\text{P}(\text{OR})_3]$ generated at a later stage in

the substitution process would accord with observations of fluxional intermediates in related systems^{2,3}.

A study of the kinetics of ligand substitution under pseudo-first-order conditions using the leaving group buta-1,3-diene with the entering groups P(OMe)_3 and P(OPh)_3 was undertaken. Following the substitution reaction by infrared spectroscopy, as used for the ligand exchange reactions, showed that a rate law of the type (4-4) was applicable to the entering group P(OMe)_3 whilst extensive overlap of the reagent and product carbonyl absorptions prevented accurate determination of the rate of substitution when P(OPh)_3 was employed as the entering group. Rate data corresponding to the ligand substitution reactions with P(OMe)_3 as entering group are given in TABLE 4-3. An examination of the derived plot of k_{obs} against entering ligand concentration confirms that rate law (4-4) is applicable to this system, indicating that in this case also $k_2[\text{L}] \gg k_{-1}$ for all concentrations of the entering group. Values of the k_1 and k_a partial rate constants derived according to this rate law are to be found in TABLE 4-4. It can be seen that the k_1 constant obtained from this reaction is identical to that obtained for the alkadiene exchange reactions with buta-1,3-diene as leaving group; this would be expected for a wholly dissociative pathway. On the other hand the k_a constant is at least two orders of magnitude greater than that observed for alkadiene exchange. This almost certainly indicates the greater "nucleophilicity" of the phosphite ligand and suggests that the ligand-dependent pathway involves a transition-state with rather more bond-making character than observed for the ligand-dependent pathway in the analogous five-coordinate systems described in the previous chapter. Qualitative work with the entering group P(OPh)_3 suggests that the $k_a > k_1$ for this system with k_a falling in the range $40-80 \times 10^{-4} \text{ s}^{-1} \text{ dm}^3 \text{ mol}^{-1}$ whilst k_1 is of comparable magnitude to that observed for the other systems with the butadiene leaving group. This being the case, it

appears that the k_a constant does not represent a true "a" pathway since in square-planar d^{10} systems exhibiting true "a" kinetics, observed k_a values show a range of 10^6 in going from the most highly nucleophilic entering groups to the least nucleophilic. Since the observed spread of k_a 's is of the order of 10^2 to 10^3 in going from $P(OMe)_3$ to the alkadiene entering groups it would appear that the kinetic behaviour may be described in terms of an " I_a " or " I_d " mechanism. Ligand-dependent pathways of this type are not uncommon in d^6 six-coordinate systems and are generally ascribed to an " I_d " pathway¹. The present results are not conclusive in this regard since the solvent dependency of the rate has not been investigated but the rather large span of observed k_a values seems to suggest that bond-making is of considerable importance in the rate-determining step and accordingly an " I_a " mechanism cannot be discounted.

4.3 EXPERIMENTAL SECTION.

4.3.1 Preparation of Materials.

The substrates $Cr(CO)_4 \cdot (\eta^4\text{-buta-1,3-diene})$ and $Cr(CO)_4 \cdot (\eta^4\text{-trans,trans-hexa-2,4-diene})$ were prepared and purified according to the method of Koerner von Gustorf et al.⁹. Following purification the substrates were dissolved in degassed heptane at $-40^\circ C$ to produce solutions of a concentration of $0.00075 \text{ mol dm}^{-3}$ suitable for the kinetic experiments. The solutions were stored under an atmosphere of dinitrogen in a cryogenic bath at $-20^\circ C$. The infrared spectra of the substrates:

$Cr(CO)_4 \cdot (\eta^4\text{-buta-1,3-diene}) \nu\text{-CO str.} = 2035(m), 1979(m),$
 (heptane) 1948(s), 1935(s) cm^{-1} .

$\text{Cr}(\text{CO})_4 \cdot (\eta^4\text{-hexa-2,4-diene}) \nu\text{-CO str.} = 2034(\text{m}), 1959(\text{m}),$
 (heptane) 1943(s), 1929(s) cm^{-1} .

were consistent with literature values. The substrates are extremely air-sensitive and consequently the concentrations of the stock solutions of the substrates were checked by Beer-Lambert law measurements prior to each set of kinetic experiments in order to establish the exact concentration of the solution used.

$\text{Cr}(\text{CO})_4 \cdot (\eta^4\text{-cycloocta-1,5-diene})$ and $\text{Cr}(\text{CO})_4 \cdot (\eta^4\text{-norbornadiene})$ were prepared by literature methods^{12,13}. The infrared spectra of the authentic samples were used for comparison with the products of the ligand exchange experiments:

$\text{Cr}(\text{CO})_4 \cdot (\eta^4\text{-cycloocta-1,5-diene}) \nu\text{-CO str.} = 2032(\text{m}), 1952(\text{w}),$
 (heptane) 1938(s), 1910(s) cm^{-1} .

$\text{Cr}(\text{CO})_4 \cdot (\eta^4\text{-norbornadiene}) \nu\text{-CO str.} = 2029(\text{m}), 1957(\text{m}),$
 (heptane) 1945(s), 1915(s) cm^{-1} .

Cycloocta-1,5-diene, norbornadiene and the phosphites trimethylphosphite and triphenylphosphite were commercial products which were distilled under reduced pressure and stored under dinitrogen prior to use in the kinetic experiments. Heptane (Analar grade) was degassed and purged with dry dinitrogen before use. Infrared spectra were measured using 1mm cells on a Perkin-Elmer 257 spectrophotometer using an solvent-ligand blank of the appropriate concentration as the reference.

4.3.2 Kinetic Experiments.

All kinetic experiments described in the text were carried out in solution in heptane in sealed vessels in a constant temperature bath thermostatted to 26.5°C with control to 0.1°C. Reactions were carried out under a dinitrogen atmosphere in the absence of light. Aliquots of the substrate stock solutions were transferred from the cryogenic apparatus at -20°C into the reaction vessels by means of Schlenk tube techniques. Dinitrogen was then admitted to the reaction vessels at atmospheric pressure with the temperature maintained at 0°C. The appropriate quantity of the entering ligand was then added to the solution at 0°C by a syringe. After rapid mixing of the solution the reaction vessel was transferred to the thermostatted constant temperature bath. Rapid sampling of the solutions was carried out by flushing the sample, which was now stored under a slight over-pressure of dinitrogen, from the vessel into the infrared cell through a small bore plastic tube fitted with a tap. In this procedure allowance was made for the dead volume of the tubing to ensure that the spectrum of the freshly sampled reaction mixture was obtained. Reactions were followed to completion, yielding an average of ten absorbance against time pairs, when points due to reaction before thermal equilibrium had been reached were excluded. The measurements were processed by the method given in Appendix A and the derived plots of k_{obs} against entering ligand concentration fitted to rate law (4-4) by means of an unweighted linear least-squares computer program given in section A-4.

TABLE 4-1.

Rate constants for Reactions of $\text{Cr}(\text{CO})_4 \cdot (\eta^4\text{-buta-1,3-diene})^a$
with alkadienes.

<u>Entering Group</u>	Concentration /mol dm ⁻³	10 ⁴ k _{obs} /s ⁻¹
cycloocta-1,5-diene T/K = 299.7	0.1863	23.76
	0.2459	25.75
	0.2563	24.51
	0.3106	26.94
	0.3428	25.89
	0.3870	25.92
	0.4318	26.86
norborna-2,5-diene T/K = 299.7	0.1125	20.98
	0.1632	21.63
	0.2250	22.75
	0.2563	21.58
	0.3250	22.99
	0.3541	23.59
	0.3875	22.04
	0.4213	23.31

Footnote.

^a Reactions carried out in heptane solution.

TABLE 4-2.

Rate constants for Reactions of
Cr(CO)₄·(η⁴-t,t-hexa-2,4-diene)^a with alkadienes.

<u>Entering Group</u>	<u>Concentration</u> /mol dm ⁻³	<u>10⁴ k_{obs}</u> /s ⁻¹
cycloocta-1,5-diene T/K = 299.7	0.0510	48.07
	0.0680	47.71
	0.0850	48.79
	0.1021	48.01
	0.1191	49.26
	0.1361	48.98
	0.1531	49.03
	0.1701	48.54
norborna-2,5-diene T/K = 299.7	0.0561	50.70
	0.0748	53.65
	0.0935	51.70
	0.1122	53.07
	0.1309	52.96
	0.1496	52.48
	0.1683	54.26
	0.1870	52.33

Footnote.

^a Reactions carried out in heptane solution.

TABLE 4-3.

Derived Rate Constants for Reactions of $\text{Cr}(\text{CO})_4 \cdot (\eta^4\text{-alkadiene})$.

<u>Leaving Group</u>	<u>Entering Group</u>	$10^4 k_1$ <u>/s⁻¹</u>	$10^4 k_a$ <u>dm⁻³ mol⁻¹</u>	10^4 <u>/s⁻¹</u>
1,3-but	1,5-cod	22.4 1.2	10.6 3.8	0.08
1,3-but	2,5-nbd	20.6 0.7	6.3 2.3	0.07
1,3-but	P(OMe) ₃	19.0 2.6	375.7 29.7	3.42
2,4-hex	1,5-cod	47.6 5.1	8.2 4.4	0.48
2,4-hex	2,5-nbd	51.4 1.2	10.6 8.9	1.06

Footnotes

Gives an estimate of the fit of the experimental data to the theoretical model.

Abbreviations:

1,3-but = buta-1,3-diene ;
 2,4-hex = t,t-hexa-2,4-diene ;
 1,5-cod = cycloocta-1,5-diene ;
 2,5-nbd = norborna-2,5-diene.

TABLE 4-4.

Rate constants for Reactions of
Cr(CO)₄·(η⁴-t,t-hexa-2,4-diene)^a with trimethylphosphite.

<u>Entering Group</u>	<u>Concentration</u> /mol dm ⁻³	<u>10⁴ k_{obs}</u> /s ⁻¹
	0.0144	26.54
trimethylphosphite	0.0288	30.53
	0.0576	38.53
T/K = 299.7	0.0721	45.19
	0.0865	53.81
	0.0883	53.79
	0.1009	49.99
	0.1135	61.19
	0.1441	77.07

Footnote.

^a Reactions carried out in heptane solution.

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CHAPTER FIVE: THERMAL ISOMERISATION OF ALKENES AND ALKADIENES

INDUCED BY METAL CARBONYLS AND THEIR DERIVATIVES.

5.1 ALKADIENE ISOMERISATION REACTIONS.

5.1.1 Introduction.

Potentially one of the most important uses of the d^8 metal carbonyls and their derivatives lies in the catalysis of organic reactions. It has been known for some years^{1,2} that the thermal isomerisation of a number of alkenes and related compounds takes place under less rigorous conditions in the presence of a transition metal carbonyl catalyst. This being the case it would seem that a detailed knowledge of the mechanism of transition metal assisted isomerisation reactions would be of value in the design of organic syntheses involving unsaturated hydrocarbons. It is for this reason that a number of investigations of transition metal carbonyl catalysed alkene isomerisation reactions have been published in recent times³⁻¹⁵. The available evidence suggests that metal assisted isomerisation proceeds through a series of 1,3-hydride shifts, whilst in the absence of catalyst the isomerisation proceeds through 1,5-hydride shifts. Currently the most widely accepted model for transition metal catalysed isomerisation involves formation of a η -allyl metal hydride intermediate as the catalytically active species. The η -allyl metal hydride mechanism, illustrated in FIGURE 5-1, was originally proposed by Manuel¹ and by Pettit² and has been the subject of a number of reviews, notably³ and¹³. Experimental evidence for the mechanism has been largely inferential, since it has not proved possible to isolate intermediates A, B or C during the isomerisation of acyclic alkenes by iron carbonyls and their derivatives^{3-9,15}. When work is carried out on metal assisted isomerisation of cyclic alkenes and alkadienes, systems for which species

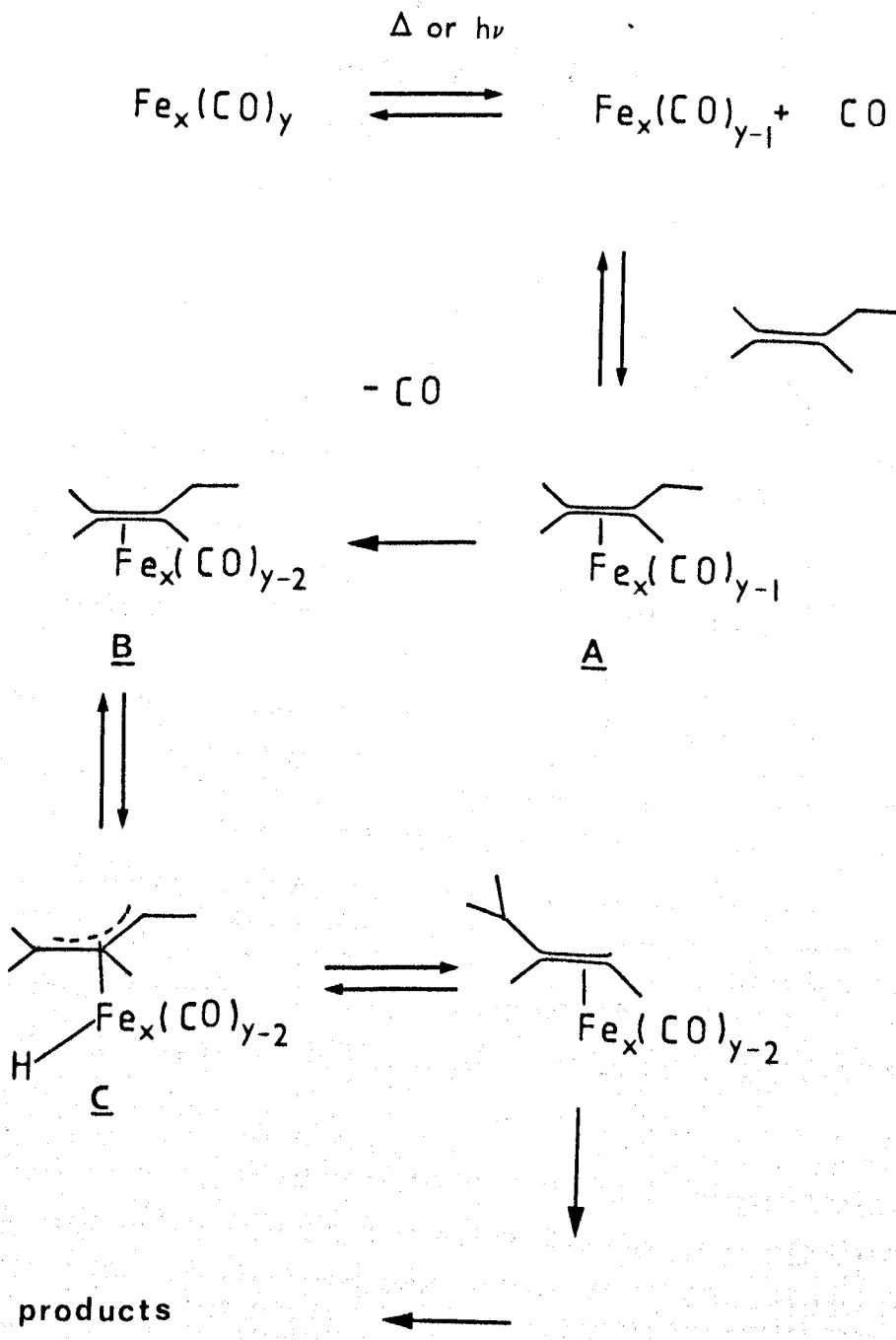


FIGURE 5-1

FIGURE 5-2

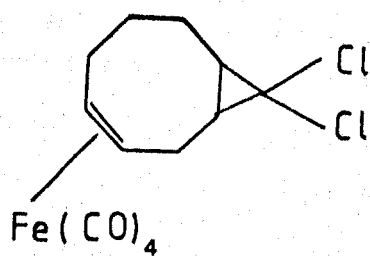
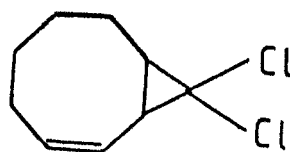
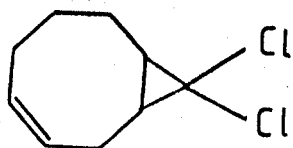
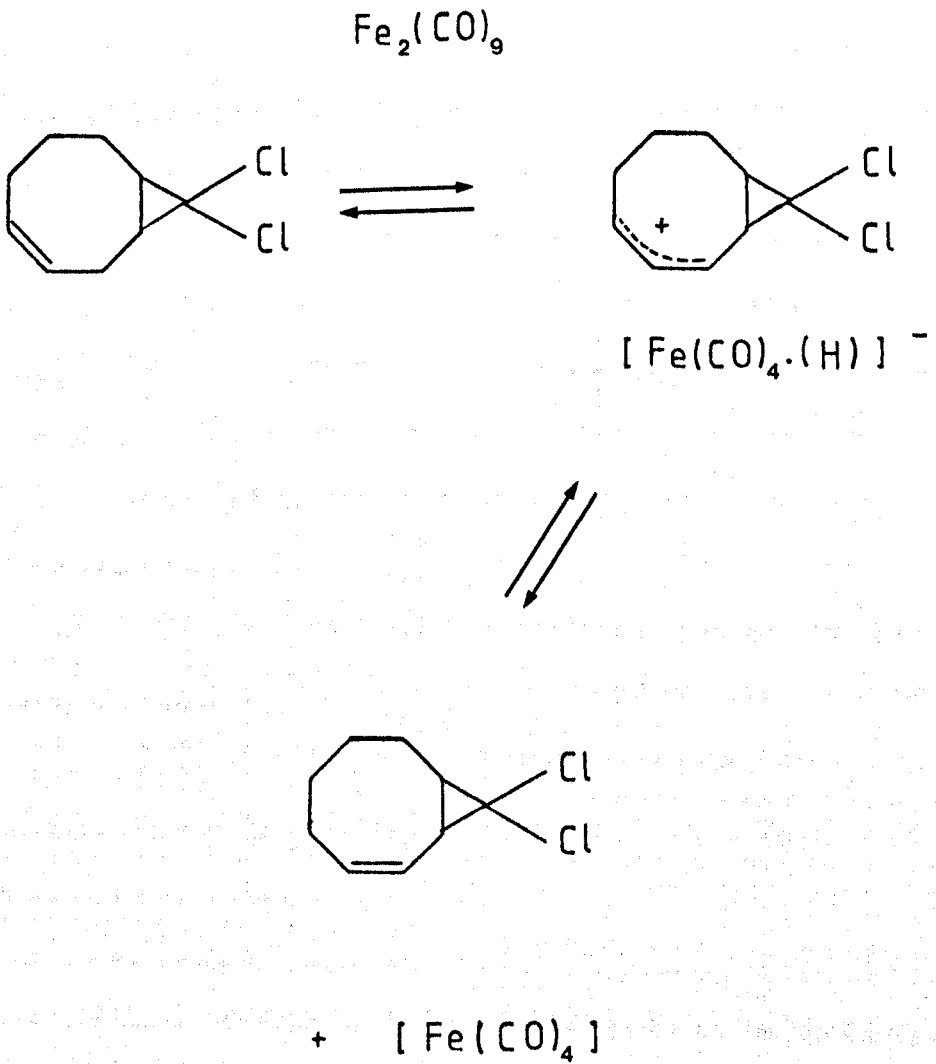


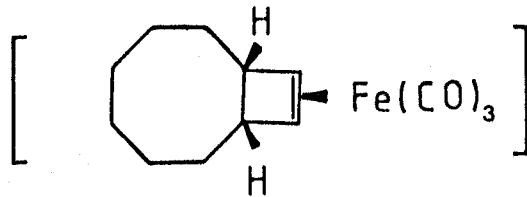
FIGURE 5-3



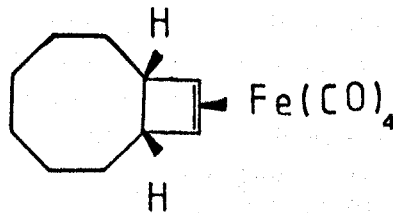
such as A (FIGURE 5-1) may be independently synthesised, the results are not wholly consistent with the simple η -allyl hydride model.

A careful study by Barborak and coworkers has revealed that the catalytic isomerisation of 9,9-dichlorobicyclo[6.1.0]non-3-ene (I) by $\text{Fe}_2(\text{CO})_9$ to yield the corresponding non-2-ene isomer (II) does not proceed by way of the tetracarbonyliron complex of (I) as would be predicted if the model given by FIGURE 5-1 was followed. Under conditions found to produce isomerisation of (I) to yield (II) the tetracarbonyliron complex of (I), (III) was found to decompose slowly to yield (I) almost exclusively. It would therefore seem rather unlikely that (III) is formed as an intermediate in the isomerisation of free (I). Since ligand isomerisation is accompanied by extensive formation of $\text{Fe}_3(\text{CO})_{12}$ the authors suggest that complexation of (I) by the tetracarbonyliron moiety is not required for isomerisation to take place, but that an ion pair is formed with an allyl cation and a tetracarbonyliron hydride anion; which may undergo polymerisation to yield the dodecacarbonyltriiron species. The mechanism is illustrated by FIGURE 5-3. A more recent study by the same group¹⁵ has indicated that isomerisation of the bicyclic hydrocarbon cis-bicyclo[6.2.0]dec-9-ene by $\text{Fe}_2(\text{CO})_9$ in refluxing hexane results in multipositional isomerisation of the alkene. The authors consider that the findings can be accounted for in terms of a η -allyltricarboxymetal hydride intermediate. If this is indeed the case it seems that an $[\text{Fe}(\text{CO})_3 \cdot (\eta^2\text{-alkene})]$ intermediate such as (IV) must be generated directly from $\text{Fe}_2(\text{CO})_9$ and the alkene since the alternative alkenetetracarbonyliron intermediate (V) would not be expected to isomerise under the conditions by analogy with species (III).

FIGURE 5-4



(IV)



(V)

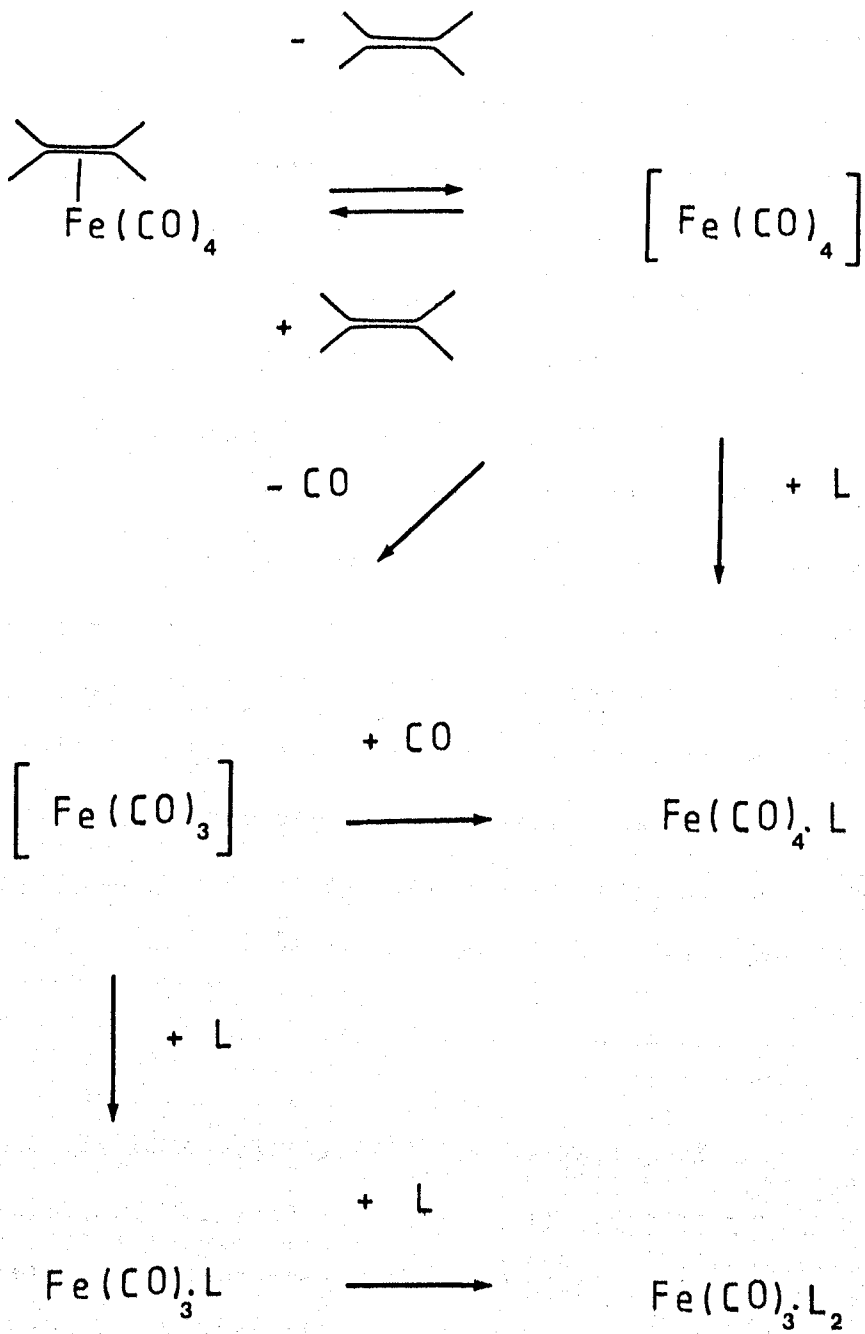
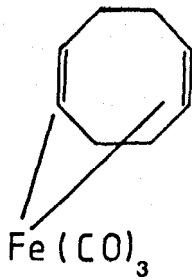


FIGURE 5-5

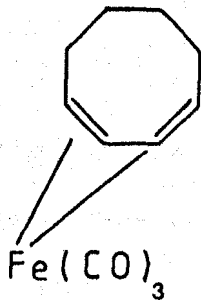
A number of other groups have put forward evidence for the generation of the species $[\text{Fe}(\text{CO})_3]$ by thermal or photolytic dissociation of $\text{Fe}(\text{CO})_5$ and $\text{Fe}_2(\text{CO})_9$. Wrighton et al. have found that the species $\text{Fe}(\text{CO})_3 \cdot (\eta^2\text{-alkene})$ is a primary photoproduct of the reaction between $\text{Fe}(\text{CO})_5$ and alkenes¹⁰; whilst Gibson and coworkers have concluded that $[\text{Fe}(\text{CO})_3]$ is generated in both thermal and photochemical reactions between $\text{Fe}(\text{CO})_5$ and alkadienes⁷. Perhaps the most convincing experimental evidence for the generation of $[\text{Fe}(\text{CO})_3]$ is the kinetic work of Cardaci on substitution reactions between $\text{Fe}(\text{CO})_4 \cdot (\eta^2\text{-alkene})$ and Group V^a ligands³². The author discovered that the reaction resulted in the formation of two products : $\text{Fe}(\text{CO})_4 \cdot \text{L}$ and $\text{Fe}(\text{CO})_3 \cdot \text{L}_2$, where (L = Group V^a ligand). Since it is known that species of the type $\text{Fe}(\text{CO})_4 \cdot \text{L}$ do not undergo further substitution to yield $\text{Fe}(\text{CO})_3 \cdot \text{L}_2$ under the conditions used in Cardaci's experiments³¹ it seems that an $[\text{Fe}(\text{CO})_3]$ intermediate must be implicated. The scheme postulated for the substitution process is given by FIGURE 5-5. It is interesting that $[\text{Fe}(\text{CO})_3]$ has been detected in low yield as a product of the photolysis of pentacarbonyliron in low temperature matrices¹⁶.

In view of the possible intermediacy of alkenetricarbonylmetal species in the alkene isomerisation process, work with suitable alkadienetricarbonylmetal species seemed likely to provide further information on the isomerisation mechanism. A study of the literature indicated that cycloocta-1,5-diene undergoes isomerisation to yield cycloocta-1,3-diene when heated at 145°C in the presence of $\text{Fe}(\text{CO})_5$ ^{2(b)} and that the complexes $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-cycloocta-1,5-diene})$ and $\text{Fe}(\text{PR}_3)_3 \cdot (\eta^4\text{-cycloocta-1,5-diene})$ are thermally isomerised to the corresponding cycloocta-1,3-diene complexes under rather milder conditions^{19,34}. Consequently the reactivity of cycloocta-1,3-diene, cycloocta-1,4-diene and cycloocta-1,5-diene were investigated with iron and ruthenium carbonyls as

FIGURE 5-6



(VI)



(VII)

the potential isomerisation catalysts.

5.1.2 RESULTS AND DISCUSSION.

In Chapter Three of this thesis it was stated that ligand exchange reaction between $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-benzalacetone})$ and cycloocta-1,5-diene resulted in a mixture of $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-cycloocta-1,5-diene})$ and its isomerisation product $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-cycloocta-1,3-diene})$ if the system was studied at 90°C in toluene. Ligand exchange between cycloocta-1,3-diene and $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-benzalacetone})$ was not found to go to completion under the above conditions but no isomerisation of the complexed ligand was observed in this case.

Preliminary studies of the thermal behaviour of the complexes $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-cycloocta-1,5-diene})$ (VI) and $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-cycloocta-1,3-diene})$ (VII), synthesised according to references¹⁷ and¹⁸ revealed that the former underwent smooth isomerisation to yield (VII) without appreciable decomposition whilst the latter decomposed very slowly to yield a mixture of iron carbonyls and free cycloocta-1,3-diene. In view of the results obtained for Group VI^b metal carbonyls^{12,20} where isomerisation results in formation of the 1,5-isomer exclusively by way of a metal catalysed ligand isomerisation a series of experiments was initiated to determine the factors influencing isomerisation in d^8 metal catalysed systems.

In designing a suitable set of experiments account had to be taken of the wide range of metal carbonyls and their derivatives which have been implicated in the catalysis of alkene isomerisation³⁻¹⁸. The preliminary experiments revealed that the following carbonyl complexes were present in the reaction mixture at some stage during the isomerisation of cycloocta-

1,5-diene :

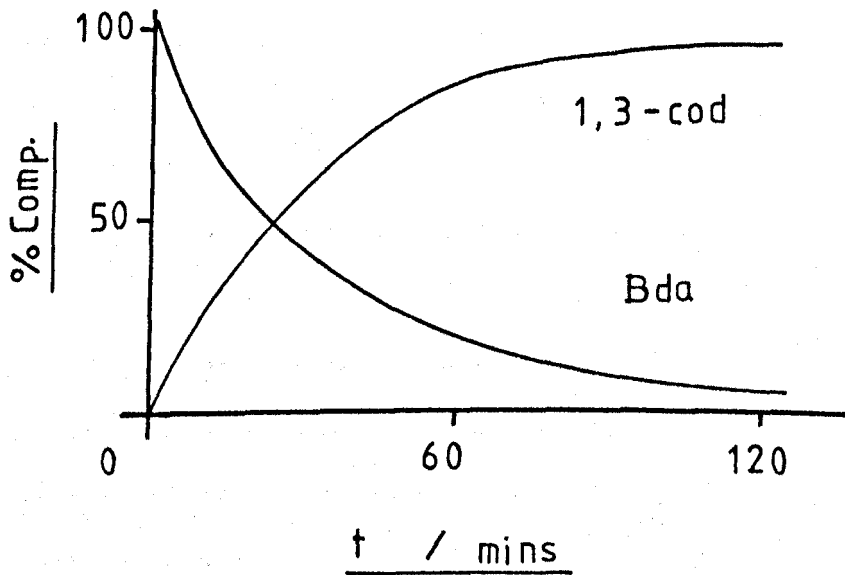
- (i) $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-benzalacetone})$
- (ii) $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-cycloocta-1,5-diene})$
- (iii) $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-cycloocta-1,3-diene})$
- (iv) $\text{Fe}(\text{CO})_5$.

Analysis of reaction mixtures by gas-liquid chromatography (g.l.c.) revealed that cycloocta-1,5-diene and cycloocta-1,3-diene were the only free dienes present at detectable concentration during the course of the isomerisation.

A further consideration was the possibility of the existence in the reaction mixture of free or complexed cycloocta-1,4-diene at some stage of the isomerisation process. Although the preliminary work provided no direct evidence of either species in the reaction mixture at any stage, both of the possible methods of isomerisation, 1,2- and 1,3-hydride shifts, would involve at least transient existence of the free or complexed 1,4-alkadiene.

In view of the need to investigate the role of each of these species in the isomerisation process four different carbonyl species were investigated with each of the cyclooctadiene isomers : the species employed are those given in (5-7). Additional experiments were carried out using the well known metal carbonyl catalysts $\text{M}_3(\text{CO})_{12}$ ($\text{M} = \text{Fe}, \text{Ru}$), whilst the results of the catalytic systems involving the substrate cycloocta-1,4-diene were compared with those for cyclohexa-1,4-diene.

Complex composition



Ligand composition

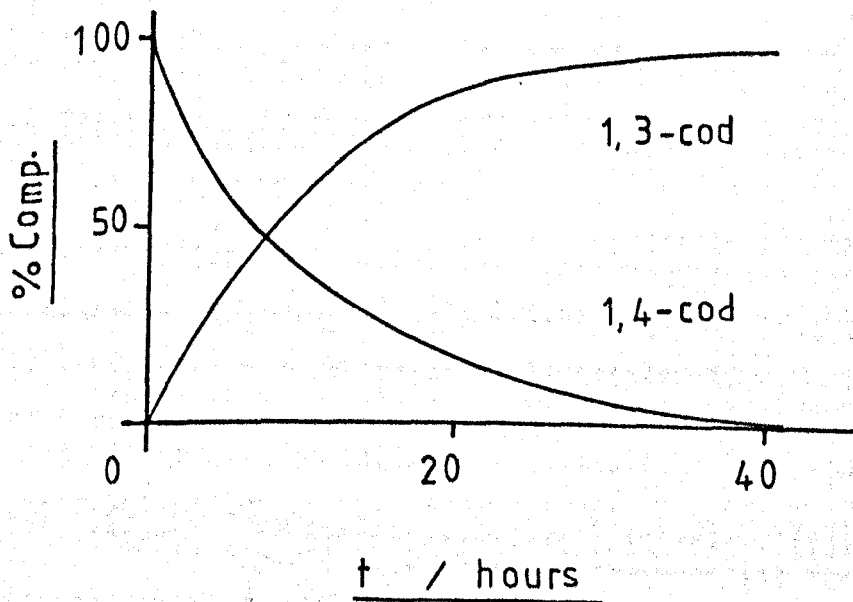


FIGURE 5-7

5.1.3 Ligand Exchange Systems involving the Leaving

Group Benzalacetone.

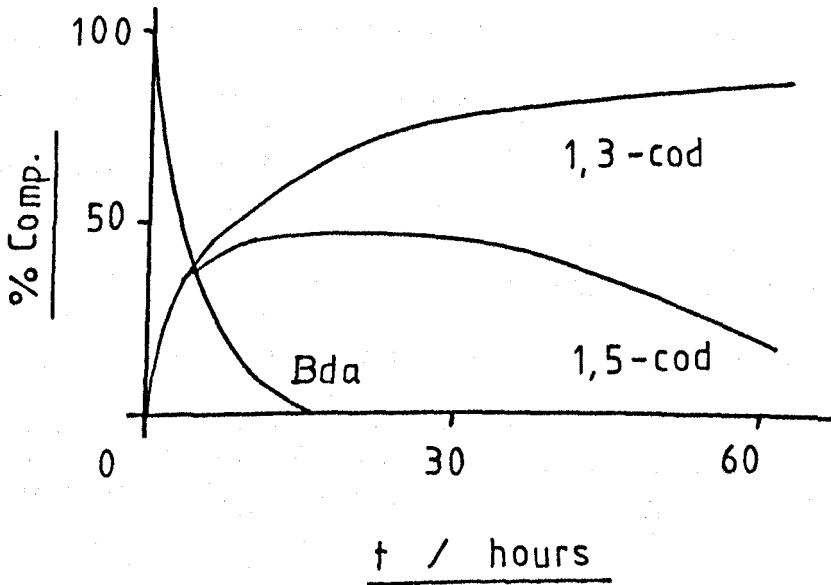
(i) Cycloocta-1,3-diene entering group.

Ligand exchange experiments with ligand : complex ratios of 150:1 were carried out in toluene at 90-100°C and in heptane at 95°C. In both cases ligand exchange was found to be slow relative to that observed with the other cycloalkadiene entering groups described in Chapter Three. At 90°C in toluene the apparent pseudo-first-order rate constants for the exchange varied between $1.5 \times 10^{-4} \text{ s}^{-1}$ for ligand : complex ratios of 10:1 to $5 \times 10^{-4} \text{ s}^{-1}$ for a ratio of 120:1. At the lower concentrations of the entering group decomposition of the carbonyls was not marked, with $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-cycloocta-1,3-diene})$ as the sole product of the exchange. Decomposition of the carbonyl complexes was markedly faster in heptane solution than in toluene. At the higher ligand concentrations rate plots for the exchange process showed pronounced curvature, whilst decomposition of the product to yield pentacarbonyliron was observed on continued heating. In an attempt to discover the reason for the curvature of the rate plots competition studies using the complexes $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-benzalacetone})$ and $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-cycloocta-1,3-diene})$ with the entering groups listed in TABLE 5-1 were carried out in toluene at 60°C. The clear implication is that the exchange reaction does not show pseudo-first-order rate behaviour due to competition between the leaving group and the entering group for the coordinatively unsaturated intermediate generated by the exchange.

(ii) Cycloocta-1,4-diene entering group.

With the non-conjugated diene entering group, cycloocta-1,4-diene, the exchange reaction with $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-benzalacetone})$ was found to proceed rapidly in heptane at 95°C. Using a ligand : complex ratio of 240:1 exchange was complete after two hours with negligible decomposition of the

Complex composition



Ligand composition

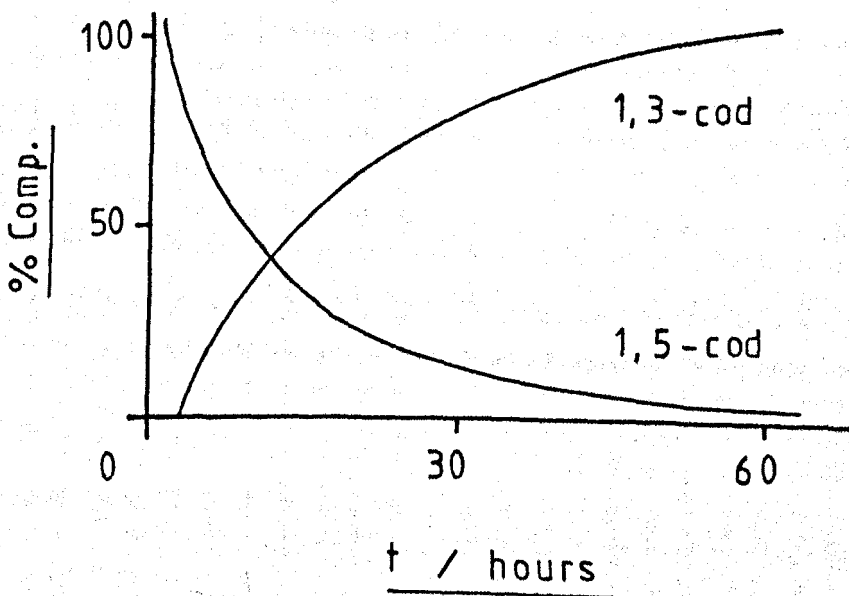


FIGURE 5-8

carbonyl species. The sole complex generated by ligand exchange was $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-cycloocta-1,3-diene})$. A g.l.c. analysis of the free ligand revealed that the 1,3-diene isomer began to appear after two hours and increased steadily in concentration with continued heating. No 1,5-diene was observed at any stage. Prolonged heating of the solution generated increasing amounts of pentacarbonyliron with accompanying decreases in the concentration of the 1,3-diene complex. FIGURE 5-7 illustrates the changes in concentration of the various complexes and free ligands with time.

It is noteworthy that ligand exchange using free 1,4-diene as entering group resulted in rapid and quantitative generation of the complexed 1,3-isomer under conditions where exchange with the free 1,3-diene is slow.

(iii) Cycloocta-1,5-diene entering group.

Exchange reactions with the entering group cycloocta-1,5-diene were carried out in toluene at 100°C and in heptane at 95°C. In all cases isomerisation of the free ligand to yield the 1,3-isomer was observed following initial displacement of the enone to yield a mixture of cycloocta-1,3-diene and cycloocta-1,5-diene tricarbonyl iron complexes. When the exchange reaction was carried out in heptane solution using a ligand to complex ratio of 40:1 the product mixture was found to contain equal concentrations of the complexed 1,3- and 1,5-isomers of cyclooctadiene. Disappearance of the last of the benzalacetone complex was accompanied by a decrease in the proportion of the complexed 1,5-isomer. Analysis of the free ligand revealed a smooth but slow isomerisation of the 1,5-isomer to yield the 1,3-isomer, whilst no evidence for free 1,4-isomer could be obtained. Decomposition of metal carbonyl species was most marked using this solvent. A graphical illustration of the progress of the isomerisation is given by FIGURE 5-8.

In contrast reactions carried out in toluene using ligand to complex ratios of 180:1, 200:1 and 240:1 gave remarkably uniform results with little decomposition over the period of initial ligand exchange. In all cases the disappearance of the $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-benzalacetone})$ complex was accompanied by appearance of a quantitative yield of the ligand exchange product, a 1:1 mixture of the complexed 1,3- and 1,5-isomers. Complete exchange was found to take place over 2 to 4 hours, depending on the initial entering ligand concentration. The initial ligand exchange process was followed by slow isomerisation of the complexed cycloocta-1,5-diene to yield complexed cycloocta-1,3-diene. The isomerisation was accompanied by slow decomposition of the 1,3-diene complex to yield $\text{Fe}(\text{CO})_5$. The first appearance of free cycloocta-1,3-diene in the reaction mixture was found to coincide with the end of the initial ligand exchange. Isomerisation of the free ligand then proceeded smoothly to yield 45% of the 1,5-isomer and 55% of the 1,3-isomer after 60 hours. After 120 hours the proportions of the free ligands in the mixture were 1,5-isomer 5% and 1,3-isomer 95%. No evidence was found for either complexed or free cycloocta-1,4-diene.

(iv) Cyclohexa-1,4-diene entering group.

The reaction between $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-benzalacetone})$ and cyclohexa-1,4-diene was studied in toluene at 90°C and in heptane at 95°C. Ligand exchange was found to be very slow taking 150 hours to go to completion in toluene using an entering ligand : complex ratio of 90:1 and 50 hours in heptane at a ligand : complex ratio of 240:1. The reactions in heptane were found to be very air sensitive, an observation in accord with previous reports^{2(b)} whilst the sole product of the ligand exchange was found to be $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-cyclohexa-1,3-diene})$. No isomerisation of the free cyclohexa-1,4-diene ligand was observed, and no evidence for an intermediate of

structure $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-cyclohexa-1,4-diene})$ appeared in the infrared spectrum.

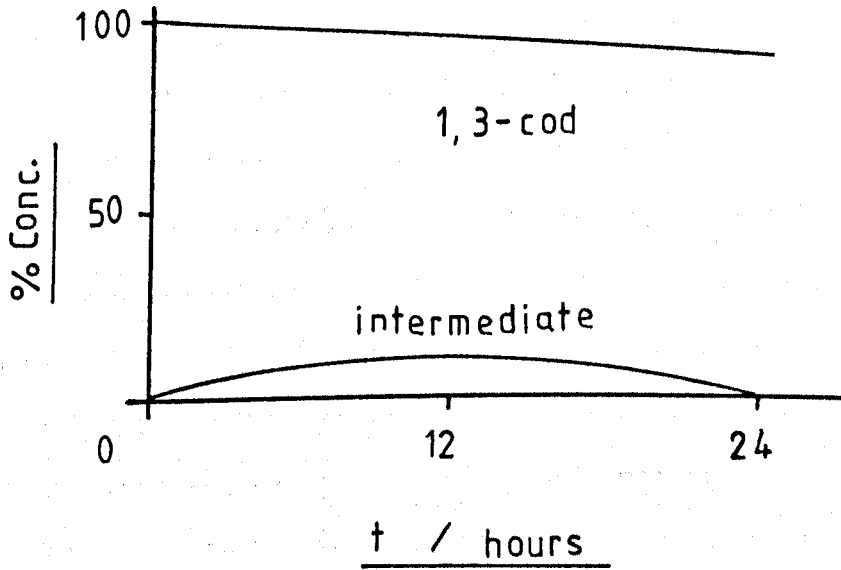
5.1.4 Ligand Exchange Systems involving the Leaving Group Cycloocta-1,3-diene.

(i) Cycloocta-1,3-diene entering group.

The system $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-cycloocta-1,3-diene})$ - cycloocta-1,3-diene was studied in toluene at 100°C and in heptane at 95°C . Using ligand : complex ratios of between 90:1 and 240:1 no evidence of free ligand isomerisation was found, whilst the only carbonyl species observed were $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-cycloocta-1,3-diene})$ and its thermolysis product $\text{Fe}(\text{CO})_5$.

In order to investigate the mechanism of generation of $\text{Fe}(\text{CO})_5$ from $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-cycloocta-1,3-diene})$ the alkadiene complex was thermolysed in heptane. The complex concentration used was $0.245 \text{ mol dm}^{-3}$, significantly more concentrated than that used for the exchange reactions, so that the course of the thermolysis could be followed by n.m.r. spectroscopy. After 6-10 hours of heating the solution took on a deep green colouration suggestive of the formation of $\text{Fe}_3(\text{CO})_{12}$, though the infrared spectrum was inconclusive since the bridging carbonyl stretching vibrations of the cluster carbonyl could not be definitely assigned. The final solution obtained after 50 hours of heating was a deep orange colour with an infrared spectrum characteristic of pentacarbonyliron. A Beer-Lambert law analysis of the thermolysis of an $0.005 \text{ mol dm}^{-3}$ solution of $\text{Fe}_3(\text{CO})_{12}$ under identical conditions was found to yield two moles of $\text{Fe}(\text{CO})_5$ from each mole of $\text{Fe}_3(\text{CO})_{12}$ used in a smooth reaction which had reached completion after 30 minutes.

Complex composition



Ligand composition

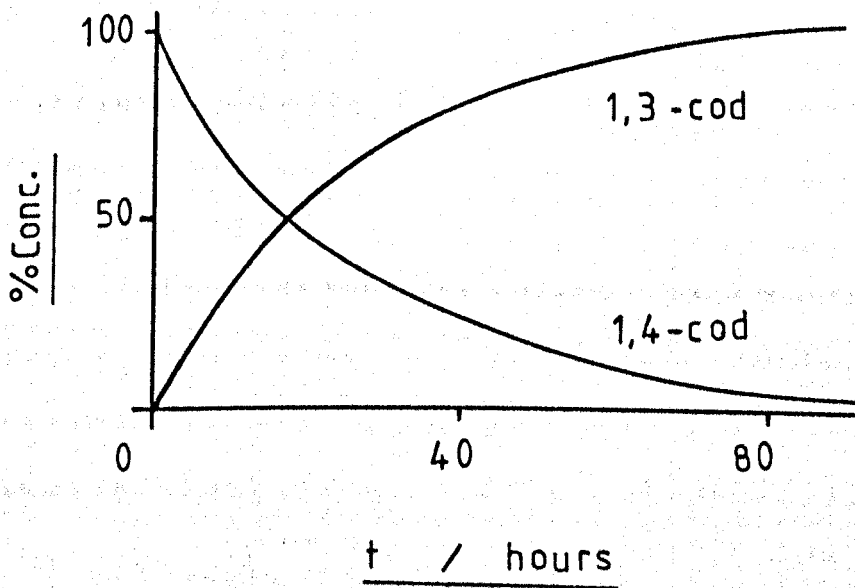


FIGURE 5-9

(ii) Cycloocta-1,4-diene entering group.

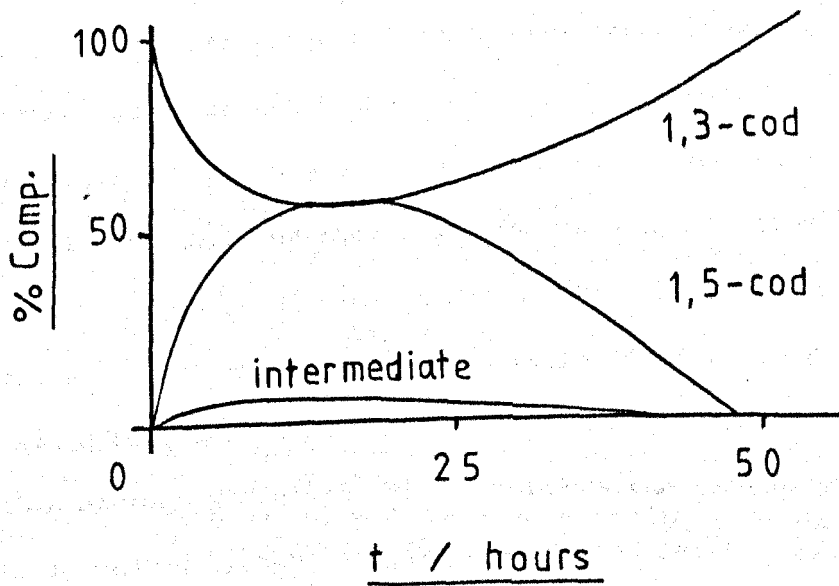
This system was studied in heptane at 95°C with ligand : complex ratios of 40:1 and 240:1. Analysis of the infrared spectrum of the reaction mixture revealed that the principal metal carbonyl species present during the reaction was $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-cycloocta-1,3-diene})$ though a small band with a carbonyl stretching vibration at 2021 cm^{-1} was seen between t_{20} and t_{1540} , reaching a maximum intensity after 270 minutes. This absorption was found to decrease in importance as the concentration of the $\text{Fe}(\text{CO})_5$ generated by thermolysis increased. By analogy with the known species $\text{Fe}(\text{CO})_3 \cdot (\eta^2\text{-benzalacetone}) \cdot (\text{SbPh}_3)^{37}$ the intermediate seems likely to be a bis(η^2 -diene)tricarbonyliron species. After 80 hours the proportions of $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-cycloocta-1,3-diene})$ and $\text{Fe}(\text{CO})_5$ were equal whilst the free cycloocta-1,4-diene ligand had undergone complete isomerisation to the corresponding 1,3-diene free ligand. There was no evidence of the 1,5-isomer in the product mixture. FIGURE 5-9 illustrates the course of the isomerisation.

(iii) Cycloocta-1,5-diene entering group.

Reactions were carried out in toluene at 100°C and heptane at 95°C with results dependent on the degree to which air was excluded from the system.

For the toluene reactions a ligand : complex ratio of 240:1 was used. Under conditions where air was rigorously excluded infrared spectra of the initial period of the reaction showed equal concentrations of the complexes $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-cycloocta-1,5-diene})$ and $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-cycloocta-1,3-diene})$. After 2 hours the concentration of the 1,3-diene complex was found to increase slowly relative to the 1,5-diene complex, which had disappeared entirely after 50 hours. No $\text{Fe}(\text{CO})_5$ was generated during the period of the reaction which resulted in complete isomerisation of the 1,5-diene free

Complex composition



Ligand composition

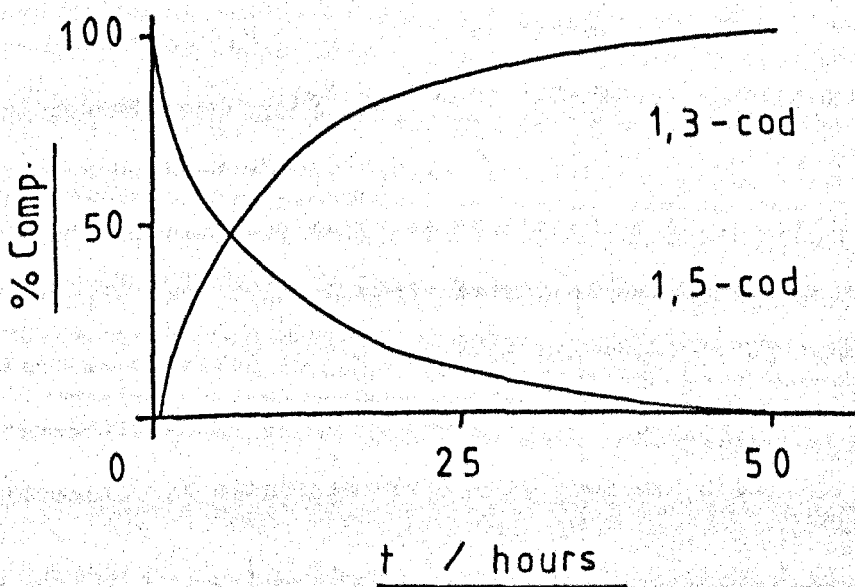


FIGURE 5-10

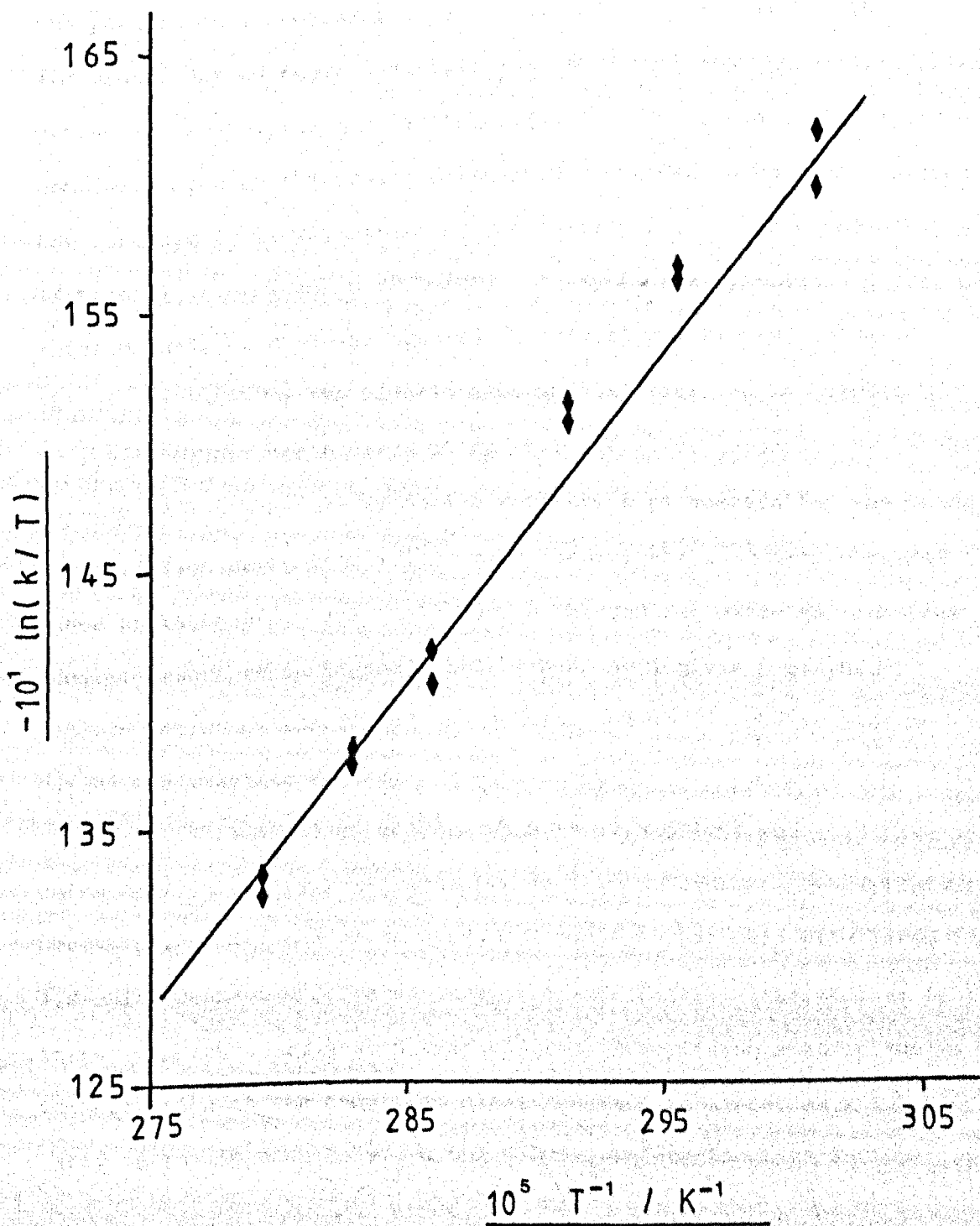
ligand to yield the 1,3-diene within a 60 hour period.

Following the reaction in heptane at 95°C using an entering group to complex ratio of 40:1 complete isomerisation of the 1,5-diene free ligand had occurred after 45 hours at which point the complexed 1,3-isomer and its thermolysis product $\text{Fe}(\text{CO})_5$ were the only metal carbonyl species remaining. Owing to the higher resolution of the infrared spectra in heptane than toluene a small absorption with a maximum at 2021 cm^{-1} could be seen in the early period of the reaction in addition to the bands assigned to $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-cycloocta-1,3-diene})$ and $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-cycloocta-1,5-diene})$. This species attained an absorbance of 0.55 after 6 hours of reaction before decreasing as the proportion of free 1,3-isomer in the reaction mixture increased. After 20 hours the unidentified band became partially masked by the increasing amount of $\text{Fe}(\text{CO})_5$ generated by thermolysis of $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-cycloocta-1,3-diene})$ but could still be observed as a "shoulder" until isomerisation of the free ligand was complete. The course of the isomerisation is illustrated by FIGURE 5-10.

(iv) Cyclohexa-1,4-diene entering group.

The system $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-cycloocta-1,3-diene})$ -cyclohexa-1,4-diene was studied in heptane at 95°C. Ligand : complex ratios of 40:1 and 260:1 were used with the reaction mixtures monitored by a combination of infrared spectroscopy and g.l.c. A small amount of decomposition of the 1,3-diene complex was observed in the infrared spectrum but no isomerisation of free cyclohexa-1,4-diene could be observed from g.l.c. traces. No evidence of the formation of complexed cyclohexadienes was obtained.

FIGURE 5-11



5.1.5. Ligand Exchange Systems involving the Leaving

Group Cycloocta-1,5-diene.

Preliminary experiments using cycloocta-1,5-diene as the leaving group in ligand exchange reactions revealed that, in the absence of free 1,5-isomer, the complex underwent rapid thermal isomerisation to yield $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-cycloocta-1,3-diene})$. The experimental systems then followed the pattern of isomerisation reactions catalysed by $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-cycloocta-1,3-diene})$. The evidence available suggested that the thermal isomerisation proceeded smoothly to give a clean, quantitative yield of the 1,3-diene complex. Based on this information it was decided to undertake a study of the kinetics of isomerisation of complexed 1,5-diene. Accordingly the rate of thermal isomerisation of $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-cycloocta-1,5-diene})$ to $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-cycloocta-1,3-diene})$ was studied in toluene solution by infrared techniques used for the kinetic experiments described in Chapter Three. From rate measurements taken at several different temperatures in the range 60-90°C it was possible to derive activation parameters for the isomerisation using Transition State Theory: the rate data obtained is given in TABLE 5-2. Data analysis was carried out using the computer program described in Appendix A-3. FIGURE 5-11 gives a graphical representation of the fit of the data to the model. The activation parameters calculated were:

$$\Delta H = 112.9 (3.9) \text{ kJ mol}^{-1}, \quad \Delta S = 7.3 (11.6) \text{ eu.}$$

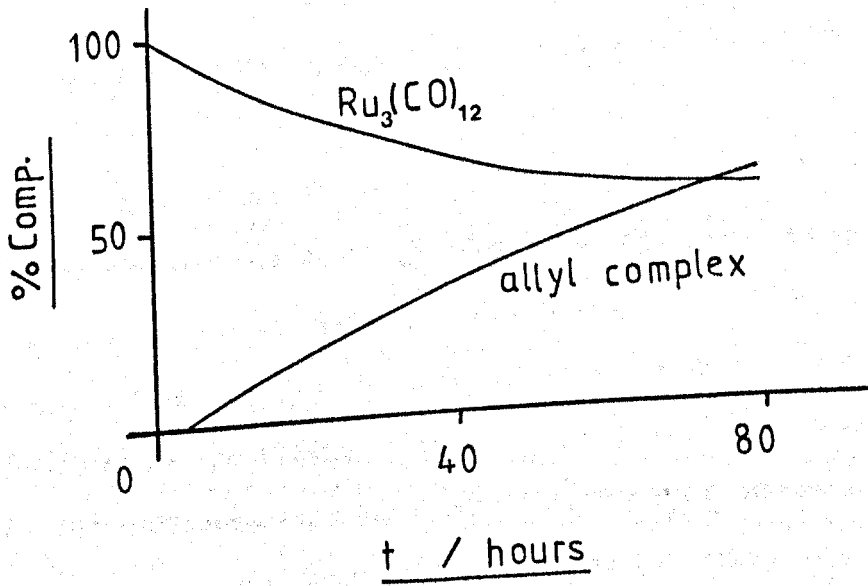
which fall in the typical range for an intramolecular 1,3-hydride shift mechanism, whilst the calculated ΔH would be exceptionally large for a 1,2-shift mechanism³. The absence of any detectable intermediate in the infrared spectrum suggested that the rate-determining step in the isomerisation of the complexed diene resulted in a species which underwent rapid reorganisation to yield the $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-cycloocta-1,3-diene})$ product.

5.1.6 Systems involving Pentacarbonyliron as the Catalyst Precursor.

In view of the known catalytic activity of solutions of pentacarbonyliron towards alkene isomerisation^{2,10} attempts were made to discover whether this complex acted as an isomerisation catalyst under the conditions used for the present diene isomerisation reactions. Since it is known³¹ that the reactivity of $\text{Fe}(\text{CO})_5$ towards substitution is strongly dependent on the purity of the carbonyl, experiments were carried out using fresh samples of the complex dissolved in rigorously degassed solvents.

Pentacarbonyliron was not found to be catalytically active towards the thermal isomerisation of cycloocta-1,5-diene under the conditions used for the other isomerisation reactions, whilst cycloocta-1,4-diene was isomerised only very slowly in refluxing toluene. In attempts to discover the reactivity of the carbonyl complex towards diene isomerisation, a series of experiments was carried out in decalin solvent at temperatures between 125 - 150°C. Using this solvent the cycloocta-1,4-diene ligand was found to undergo smooth isomerisation to cycloocta-1,3-diene at 135°C over a period of 20 hours. Results with the cycloocta-1,5-diene free ligand were less consistent with isomerisation rates appearing to depend strongly on the purity of the reagents used. However the onset of isomerisation required temperatures in excess of 140°C with measurable rates only found at 145°C for pure reagents. The present results are consistent with those of Tayim et al. for systems involving cycloocta-1,4-diene¹², and in outline with those of Pettit and coworkers for the isomerisation of cycloocta-1,5-diene^{2(b)}. The elevated temperatures necessary for isomerisation using pentacarbonyliron as a catalyst precursor seem to indicate that thermal dissociation of the substrate takes place to yield $[\text{Fe}(\text{CO})_4]$ and possibly $[\text{Fe}(\text{CO})_3]$, which then react with the cyclooctadienes. At the temperatures used in references² and¹² it would

Complex composition



Ligand composition

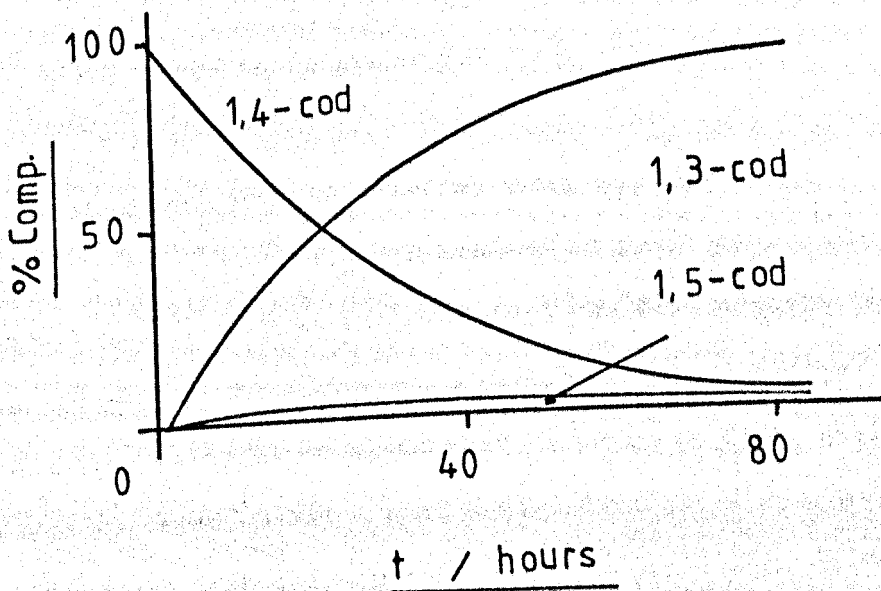


FIGURE 5-12

seem that $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-cycloocta-1,3-diene})$ was generated in a metal-assisted isomerisation and that this complex then decomposed under the rather extreme reaction conditions to regenerate $\text{Fe}(\text{CO})_5$ and the free cycloocta-1,3-diene ligand.

5.1.7 Systems involving $\text{M}_3(\text{CO})_{12}$ as a Catalyst Precursor.

A considerable body of evidence has accumulated to suggest that species of the formula $\text{M}_3(\text{CO})_{12}$, where (M= Fe, Ru), serve as effective catalyst precursors in alkene isomerisation³⁻⁶. In view of the probable generation of $\text{Fe}_3(\text{CO})_{12}$ under the conditions used for the isomerisation experiments the reactivity of $\text{Fe}_3(\text{CO})_{12}$ and $\text{Ru}_3(\text{CO})_{12}$ towards cycloocta-1,5-diene and cycloocta-1,4-diene were investigated. Systems involving $\text{Fe}_3(\text{CO})_{12}$ as catalyst precursor were found to result simply in carbonyl decomposition at 95 - 100°C in toluene and heptane. The only products observed were $\text{Fe}(\text{CO})_5$ and the un-isomerised diene ligand.

In contrast $\text{Ru}_3(\text{CO})_{12}$ was found to behave as a very effective catalyst for diene isomerisation at 95°C in heptane.

(i) Cycloocta-1,4-diene entering group systems.

When $\text{Ru}_3(\text{CO})_{12}$ was allowed to react with cycloocta-1,4-diene using a ligand : complex ratio of 40:1 the free organic ligand was found to isomerise to a mixture of cycloocta-1,3-diene and cycloocta-1,5-diene with the reaction going to completion in 75 hours at 95°C. Analysis of the infrared spectrum revealed that a second carbonyl species had appeared after 2 hours, gradually increasing in importance to reach the same proportion as $\text{Ru}_3(\text{CO})_{12}$ after 70 hours. No marked degree of decomposition of the carbonyl species was noted during the course of the reaction. Free cycloocta-1,3-diene began to occur in the reaction mixture after 4 hours in

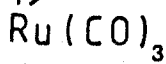
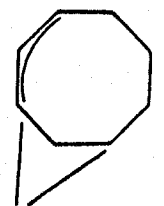


FIGURE 5-13

conjunction with a trace of free cycloocta-1,5-diene. The proportion of free cycloocta-1,3-diene in the mixture increased steadily until the completion of isomerisation at 70 hours, whilst the concentration of the 1,5-isomer showed no appreciable increase following its initial appearance. FIGURE 5-12 illustrates the changes in concentration of the species in the reaction mixture with time. The intermediate observed had the following infrared spectrum :

ν -CO str. = 2069(w), 1991(s), 1983(s) cm^{-1} ; heptane .

This compares with the reported spectrum :

ν -CO str. = 2067(w), 1990(s) cm^{-1} , cyclohexane¹⁸,

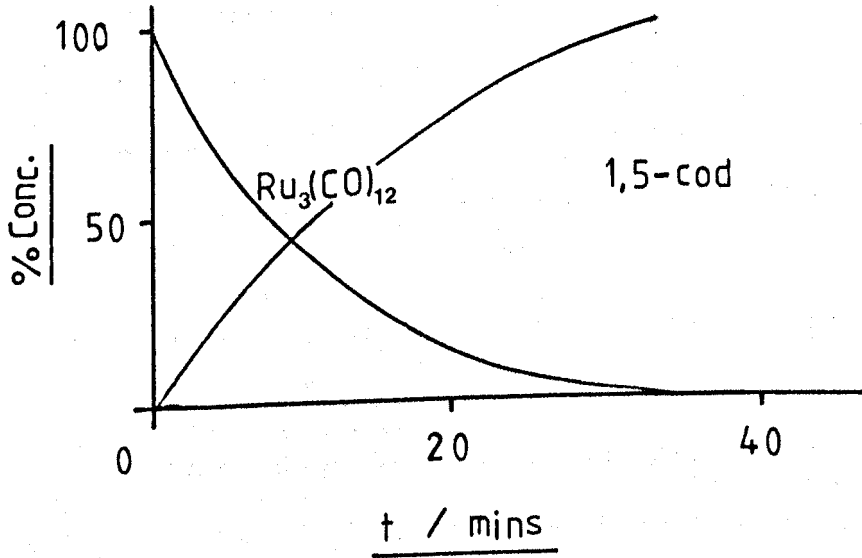
corresponding to the σ, π -allyl complex illustrated in FIGURE 5-13. This species has been reported as the catalytically active species in the isomerisation of cycloocta-1,5-diene using the complex $\text{Ru}(\text{CO})_3 \cdot (\eta^4\text{-cycloocta-1,5-diene})$ as the catalyst precursor¹⁸.

It is notable that all attempts to synthesise the species $\text{Ru}(\text{CO})_3 \cdot (\eta^4\text{-cycloocta-1,3-diene})$ have been unsuccessful.

(ii) Cycloocta-1,5-diene entering group systems.

Reaction between $\text{Ru}_3(\text{CO})_{12}$ and cycloocta-1,5-diene at a ligand : complex ratio of 40:1 in heptane at 95°C was found to result in isomerisation of the free ligand to yield cycloocta-1,3-diene as the sole product at the completion of reaction. Analysis of the infrared spectrum of the reaction mixture revealed that $\text{Ru}_3(\text{CO})_{12}$ underwent rapid reaction with cycloocta-1,5-diene to produce a quantitative yield of the known species $\text{Ru}(\text{CO})_3 \cdot (\eta^4\text{-cycloocta-1,5-diene})$ within 30 minutes of the start of reaction. The 1,5-diene species was the only identifiable carbonyl species present in the reaction mixture during the course of free ligand isomerisation. Isomerisation of the free 1,5-isomer was monitored by g.l.c. and was found to proceed in the manner described by Lewis *et al.*¹⁸ . Free

Complex composition



Ligand composition

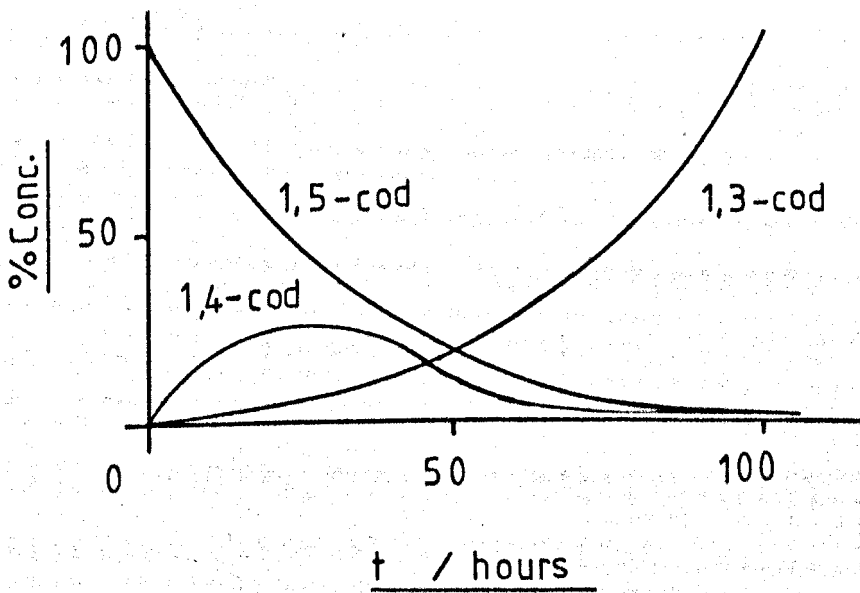


FIGURE 5-14

1,4-isomer accompanied by a trace of the 1,3-isomer was first noted in the reaction mixture after 30 minutes and increased steadily relative to the 1,5-isomer from this point onwards. As the isomerisation proceeded the proportion of the 1,3-diene relative to the 1,4- and 1,5-species also increased. After 20 hours the relative proportions of 1,3-diene : 1,4-diene : 1,5-diene were approximately 40:35:25 with little evidence of decomposition of metal carbonyl species. The isomerisation was found to reach completion after 50 hours with 1,3-diene as the sole free organic product. The course of the isomerisation is illustrated by FIGURE 5-14.

5.1.8 Mechanistic Implications of the Experimental Observations.

It is clear from a cursory examination of the experimental results that ruthenium catalysed alkadiene isomerisation proceeds by a different mechanism to that catalysed by iron complexes. The results of experiments in which the free ligand cyclohexa-1,4-diene is used suggests important differences in ligand reactivity between cyclohexadienes and cyclooctadienes. For this reason the results are best examined in three separate categories.

(a) Iron catalysed alkadiene isomerisation.

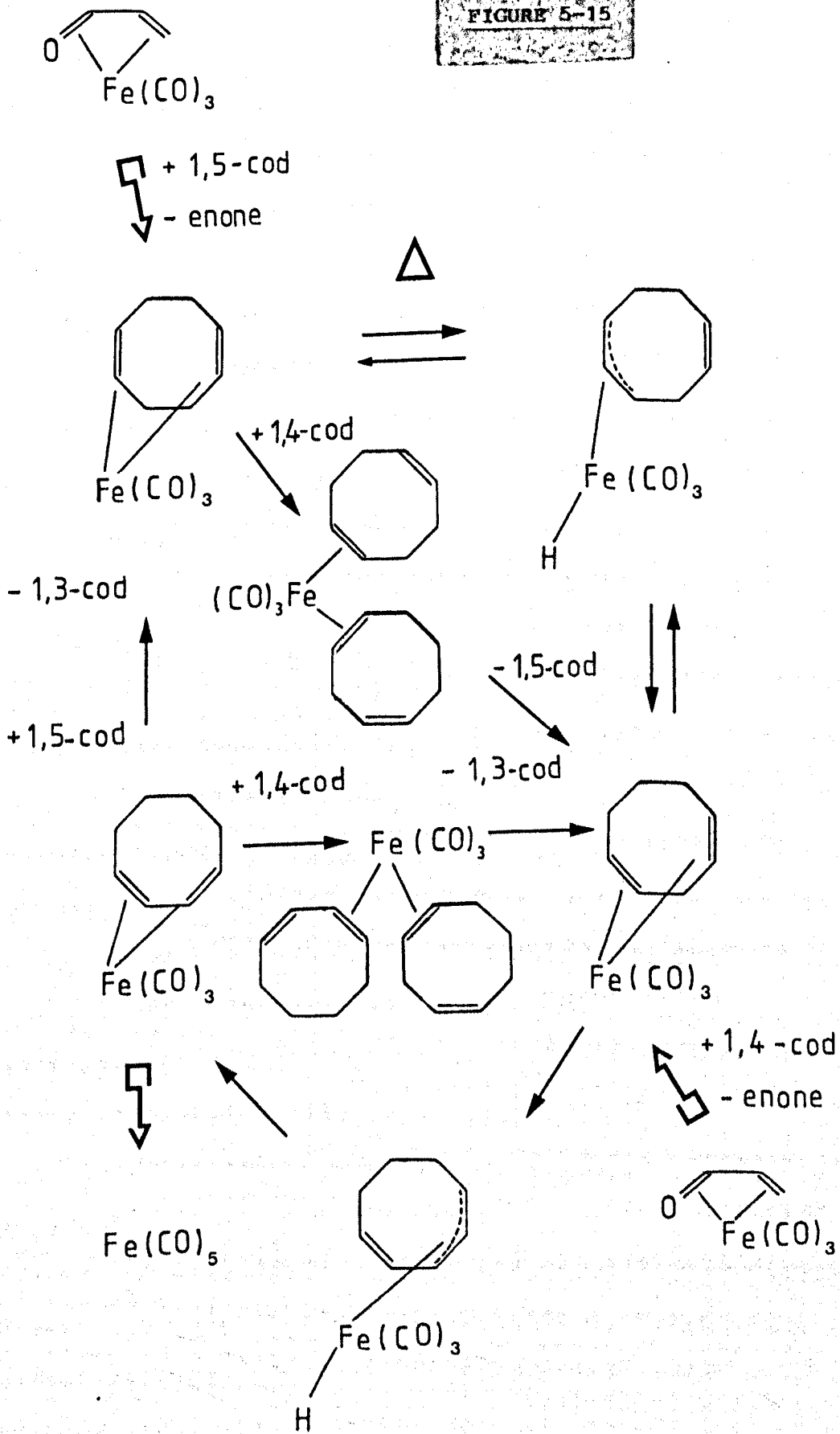
Three other research groups^{2, 12, 22} have studied the isomerisation of cyclooctadienes by iron carbonyls with results which are broadly consistent with those presented here. The following observations may be made :

(i) Free cycloocta-1,5-diene is isomerised to free cycloocta-1,3-diene in the presence of a number of iron carbonyls and their derivatives. Isomerisation catalysed by pentacarbonyliron occurs only under rather extreme conditions²² if pure samples of the carbonyl are used. In this context it should be noted that in the present work isomerisation of free

cycloocta-1,5-diene by $\text{Fe}(\text{CO})_5$ in the absence of solvent was found to proceed at an appreciable rate above 140°C , conditions much more vigorous than those reported by Pettit and coworkers^{2(b)}. Rather less extreme conditions were required for isomerisation of free cycloocta-1,4-diene by pentacarbonyliron, a finding in keeping with the results of Tayim *et al.*¹². However the conditions needed suggest that carbonyl dissociation to yield tetracarbonyliron is necessary for catalytic systems involving pentacarbonyliron.

(ii) Less vigorous conditions were needed for thermal isomerisation using species such as $\text{Fe}(\text{CO})_3 \cdot \text{L}_2$ as catalyst precursors. The experimental evidence suggests that systems involving $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-benzalacetone})$, $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-cycloocta-1,3-diene})$ and $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-cycloocta-1,5-diene})$ as catalyst precursors involve a common mechanism. It may be tentatively suggested that isomerisations proceeding with cycloocta-1,4-diene substrates also follow this mechanism since a long lived intermediate which showed an infrared carbonyl stretching vibration at 2021 cm^{-1} in heptane was observed during the course of the kinetic experiments: this species has been assigned the structure $\text{Fe}(\text{CO})_3 \cdot (\eta^2\text{-diene})_2$. The thermal isomerisation experiments carried out with the complex $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-cycloocta-1,5-diene})$ revealed that isomerisation to the complexed 1,3-diene isomer occurs readily under the conditions used for the free ligand isomerisation reaction. However, although the activation parameters were suggestive of the intramolecular 1,3-hydride shift mechanism to be expected for a metal assisted isomerisation, the 1,3-diene complex generated did not appear to be labile with respect to ligand displacement in the absence of suitable entering group. A comparison of experiments carried out in the presence of free cycloocta-1,5-diene indicated that $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-cycloocta-1,3-diene})$ undergoes exchange with the 1,5-diene free ligand under the conditions used for the free ligand isomerisation. The reaction between the benzalacetone complex and free cycloocta-1,5-diene would, on the other hand, be expected

FIGURE 5-15

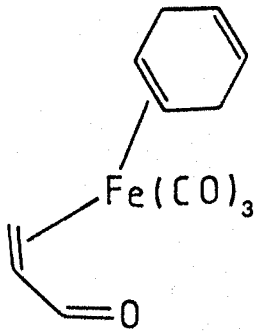


to generate only the complex $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-cycloocta-1,5-diene})$ in the initial steps. Since in practice equal proportions of the 1,3- and 1,5-diene complexes from from the start of the reaction it seems that the rate of ligand exchange is slow relative to the rate of intramolecular isomerisation. A further observation would appear to be that cycloocta-1,5-diene is a better entering group than cycloocta-1,3-diene in this type of system since rates of ligand exchange with the benzalacetone complex are markedly greater with the 1,5-isomer as the entering group than with the 1,3-isomer. Since free ligand isomerisation occurs for all systems at a period before the first appearance of thermolytically generated pentacarbonyliron it seems that the known isomerisation catalyst $\text{Fe}_3(\text{CO})_{12}$ ³⁻⁶ does not play a significant part in the isomerisation processes currently under consideration. In view of the absence of definite evidence for the nature of the intermediates in the isomerisation process the reaction scheme illustrated in FIGURE 5-15 is postulated to account for the experimental evidence found during the isomerisation of free cycloocta-1,4-diene or free cycloocta-1,5-diene by tricarbonylmetal species. The available evidence would suggest that the rate of isomerisation of coordinated cycloocta-1,4-diene to cycloocta-1,3-diene is fast relative to the rate-determining step in the intramolecular isomerisation of $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-cycloocta-1,5-diene})$ to yield $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-cycloocta-1,3-diene})$ which presumably also proceeds by way of coordinated 1,4-diene. Indeed the absence of experimental evidence for the generation of free 1,4-diene during the isomerisation of free cycloocta-1,5-diene suggests that coordinated 1,4-diene undergoes isomerisation at a rate which is several orders of magnitude greater than the rate of ligand dechelation. The relatively low concentration attained by the intermediate whose infrared spectrum includes $\nu\text{-CO str.} = 2021 \text{ cm}^{-1}$ in the isomerisation of free cycloocta-1,4-diene would tend to support this argument. The activation parameters for thermal isomerisation of the complex $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-cycloocta-}$

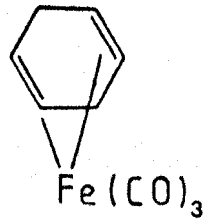
1,5-diene) in toluene support the view that an intramolecular 1,3-hydride shift mechanism operates and, since the ΔS for the process approaches zero a non-dissociative η -allyl metal hydride mechanism gives the best explanation of the high value of ΔH ; owing to the necessity for the rearrangement of the ligand η -bond framework and for the intramolecular transfer of hydride from the ligand to the metal.

Both cycloocta-1,5-diene and cycloocta-1,4-diene isomerisation result exclusively in free cycloocta-1,3-diene when iron carbonyl species are used as the isomerisation catalysts. This presumably reflects the thermodynamic stabilities of the respective cyclooctadienetricarbonyliron species as postulated by the molecular orbital arguments of Hoffmann *et al.*²³. That the results of isomerisation are not a reflection of the thermodynamic stabilities of the free alkadienes is indicated by the fact that, in the presence of hexacarbonylmolybdenum, both cycloocta-1,3-diene and cycloocta-1,4-diene are isomerised to yield cycloocta-1,5-diene as the sole free diene product¹². The results of metal catalysed isomerisation reactions seem therefore to reflect the bonding capabilities of the free dienes with the metal carbonyl species used as catalysts.

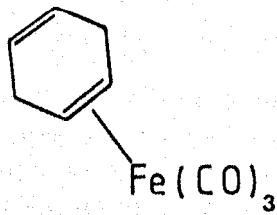
(iii) Further evidence is provided by the results of the cyclohexa-1,4-diene isomerisation reactions. The experiments described in the present work indicate that, under conditions where ligand exchange occurs, iron carbonyls form 1,3-diene complexes with cyclohexadienes. Using the catalyst precursor $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-benzalacetone})$ the complex $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-cyclohexa-1,3-diene})$ is generated as the sole product of ligand exchange with cyclohexa-1,4-diene, although no free 1,3-diene is observed. Using the species $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-cycloocta-1,3-diene})$ as the potential isomerisation catalyst no ligand exchange is observed, with cycloocta-1,3-diene remaining the only coordinated diene in the reaction mixture. No isomerisation of free cyclohexa-1,4-diene is observed. Since isomerisation of the



(VIII)



(IX)



(X)

FIGURE 5-16

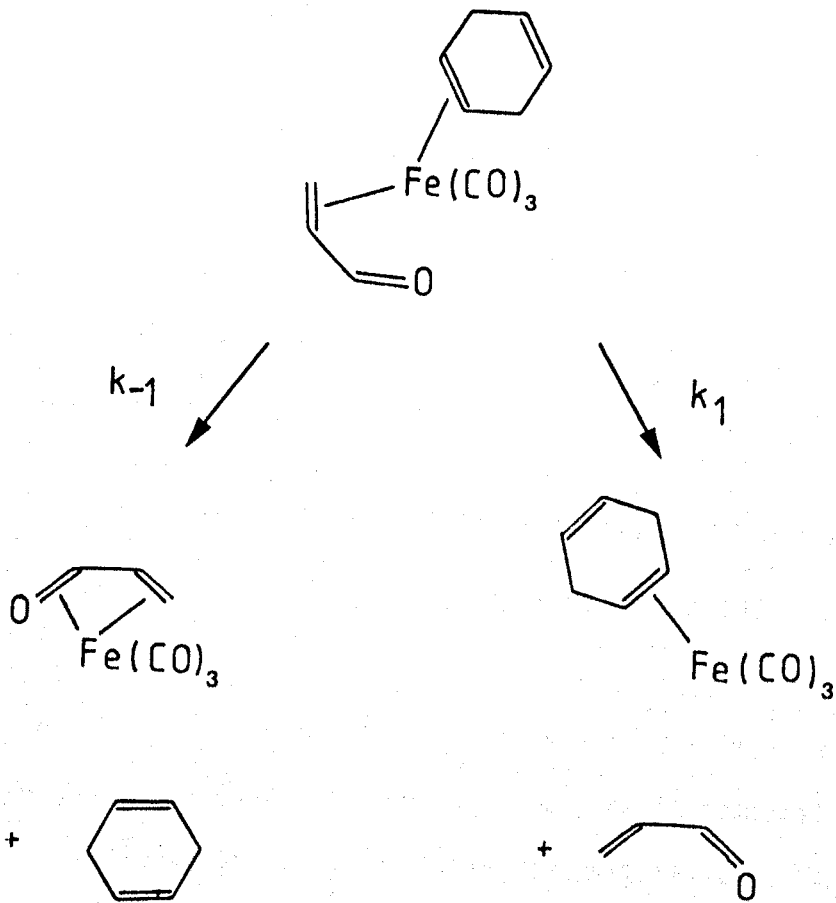


FIGURE 5-17

coordinated diene only occurs when the more kinetically labile leaving group benzalacetone is used it is apparent that the initial step in the mechanism must involve ligand exchange to form an intermediate such as (VIII) or (IX) of FIGURE 5-16. Subsequent metal-carbon bond dissociation to yield a coordinatively unsaturated intermediate such (X) would then follow as has postulated for the isomerisation of analogous 1,4-diene complexes^{9,34}. On the basis of the mechanism found for alkadiene exchange reactions with tetrahapto-heterodiene complexes the initial formation of intermediate (VIII) seems the more likely with the rate of appearance of the product $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-cyclohexa-1,3-diene})$ then reflecting the competing processes illustrated in FIGURE 5-17. The experimental observations suggest that chelation of the free double bond of (X) must be slow relative to the rate of isomerisation since the species $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-cyclohexa-1,4-diene})$ is not observed. The absence of free cyclohexa-1,3-diene in the reaction mixture indicates that cyclohexa-1,4-diene cannot undergo isomerisation in the dihapto form at intermediate (VIII) since k_{-1} would generate free 1,3-diene in this case. The complexed 1,3-diene species generated by the isomerisation does not undergo exchange at temperatures below 150°C²⁴ and for this reason free cyclohexa-1,3-diene in the reaction mixture would result exclusively from decomposition of the product carbonyl complex, effectively ruling out observation of the isomerised free diene by g.l.c. techniques as employed in the present study.

(iv) Accordingly it may be postulated that iron catalysed isomerisation of non-conjugated cyclic dienes to yield the corresponding conjugated diene will take place only if the following conditions can be met :

- (a) A kinetically labile catalyst precursor is used.
- (b) The diene substrate must be capable of forming an $\text{Fe}(\text{CO})_3 \cdot (\eta^3\text{-allyl}) \cdot (\text{H})$ intermediate under the reaction conditions.
- (c) The $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-conjugated diene})$ complex resulting from isomerisation of the coordinated ligand must undergo ready dechelation to yield the free alkadiene.

A η -allyl metal hydride mechanism with the rate of isomerisation of the complexed diene greater than the rate of dechelation of the diene is in accordance with these findings^{3,8}.

(b) Ruthenium catalysed alkadiene isomerisation.

Catalytic isomerisation of alkenes and cycloalkenes using $\text{Ru}_3(\text{CO})_{12}$ as catalyst precursor has been studied by a number of different workers^{4,11,35,36} and a variety of metal-alkene complexes isolated from the reaction mixtures used. Work with alkadiene substrates indicates that hydridotriruthenium carbonyl complexes of the organic ligands are formed most readily under the isomerisation conditions but that smaller proportions of hydridodiruthenium carbonyl complexes and tetrahaptodirutheniumtricarboxyls are also generated^{35,36}. In view of the large number of metal η -complexes implicated in alkene and alkadiene isomerisation by ruthenium carbonyls it is rather difficult to draw definite conclusions concerning the mechanism of isomerisation. In this regard perhaps the most illuminating work has been carried out by Valle and coworkers⁴ on the isomerisation of pentenes by $\text{Ru}_3(\text{CO})_{12}$. In this study the authors isolated six different ruthenium cluster complexes from the reaction mixtures; the organic ligand showed dihapto and trihapto (η -allyl) coordination whilst all structures involved bridging hydride ligands. The authors concluded that equilibrium isomer concentrations of the organic ligands, when associated with the low concentrations of the

metal cluster complexes were not consistent with any of the isolated complexes acting as an isomerisation catalyst. The increased rates of isomerisation obtained by addition of polar substances to the reaction mixtures, and the inhibition of isomerisation by high pressures of carbon monoxide led the authors to postulate a dissociative pathway generating a π -allyl metal hydride catalytic species. Lewis et al. have also postulated a π -allyl metal hydride catalytic species for the isomerisation of cycloocta-1,5-diene by $\text{Ru}(\text{CO})_3 \cdot (\eta^4\text{-cycloocta-1,5-diene})$ ³⁴.

It was for this reason that the isomerisation of 1,4- and 1,5-isomers of cyclooctadiene in the presence of $\text{Ru}_3(\text{CO})_{12}$ was studied with a view to discovering whether a mechanism analogous to that found for the iron systems was applicable to ruthenium systems.

(i) Isomerisation of cycloocta-1,5-diene by $\text{Ru}_3(\text{CO})_{12}$ at 100°C was found to proceed at a rate comparable to that observed for the iron systems. The equilibrium isomer ratio was found to be as follows:

cycloocta-1,3-diene : cycloocta-1,4-diene : cycloocta-1,5-diene .

(95)

(2)

(3)

The most striking difference between the results of the iron and ruthenium catalysed reactions was the observation of free cycloocta-1,4-diene during the pre-equilibrium period. The free 1,4-diene was found to be the predominant isomerisation product during the early stages of the reaction with the appearance of substantial amounts of the 1,3-isomer only after disappearance of the majority of the free 1,5-diene. The free ligand concentrations during the course of the isomerisation are illustrated in FIGURE 5-14. It is interesting that a similar pattern of isomerisation was obtained by Lewis et al. for isomerisation of cycloocta-1,5-diene catalysed by $\text{Ru}(\text{CO})_3 \cdot (\eta^4\text{-cycloocta-1,5-diene})$ ¹⁸. The mechanistic implications of the observations are that isomerisation proceeds through consecutive 1,3-

FIGURE 5-18

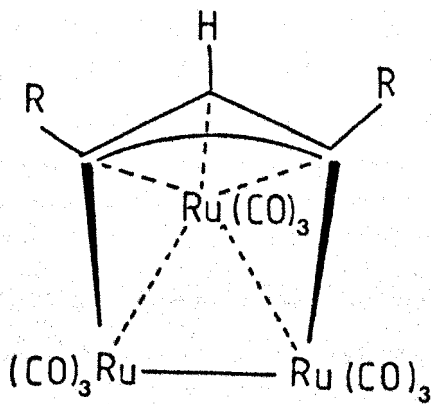
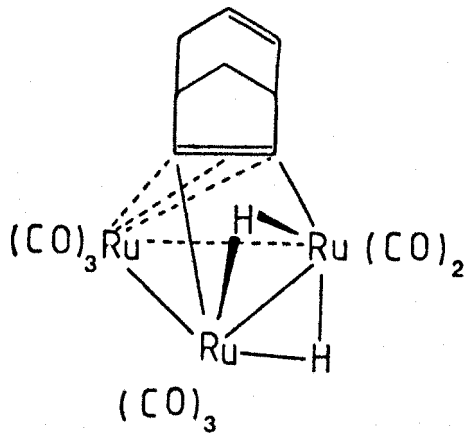
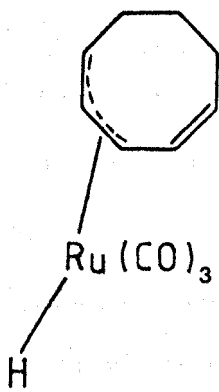
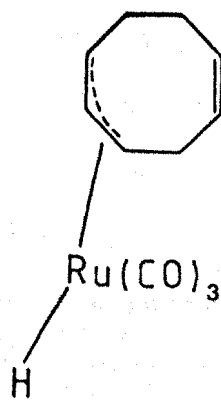


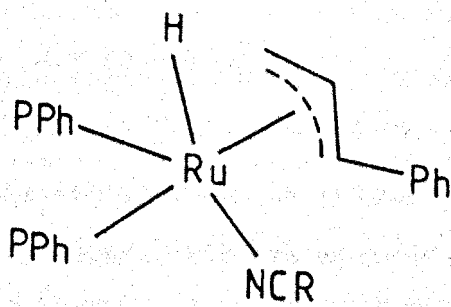
FIGURE 5-19



(XI)



(XII)



(XIII)

hydride shifts to yield both cycloocta-1,4-diene and cycloocta-1,3-diene. If a π -allyl metal hydride mechanism is to be postulated by analogy with the iron systems it seems clear that the rate of dechelation of the coordinated ligand in this case must be of the same order of magnitude as that of ligand isomerisation since free 1,4-diene is observed during the course of the reaction. The differing stabilities of ruthenium and iron alkadiene complexes supports this postulate and is illustrated by the observation that $\text{Ru}(\text{CO})_3 \cdot (\eta^4\text{-cycloocta-1,5-diene})$ is generated during the early stages of the isomerisation process. This species remains the only metal carbonyl derivative detectable by infrared spectroscopy until isomerisation of the free 1,5-diene is complete at which point $\text{Ru}(\text{CO})_3 \cdot (4\text{-}6\eta^3, 1\text{-cyclooctenediyl})$ ¹⁸ becomes the dominant metal complex. Generation of the σ, π -allyl complex at this stage of the reaction presumably reflects a thermal isomerisation of the 1,5-diene complex in the absence of excess free 1,5-diene. This behaviour is in contrast with that of the analogous iron systems for which isomerisation of the complexed 1,5-diene results in the formation of the 1,3-diene complex. It is perhaps significant that independent attempts to synthesise $\text{Ru}(\text{CO})_3 \cdot (\eta^4\text{-cycloocta-1,3-diene})$ have been unsuccessful¹⁸.

(ii) Isomerisation of cycloocta-1,4-diene by $\text{Ru}_3(\text{CO})_{12}$ under similar conditions to those of (i) resulted in steady isomerisation of the free 1,4-diene to yield the 1,3-diene with traces of the 1,5-diene. The equilibrium concentrations of the free dienes were found to be very similar to those found for (i) : these results are consistent with a common π -allyl metal hydride mechanism. A major difference between the two isomerisation systems is that only two metal carbonyl species were observed during the course of the isomerisation: $\text{Ru}(\text{CO})_3 \cdot (4\text{-}6\eta^3, 1\text{-cyclooctenediyl})$ and $\text{Ru}_3(\text{CO})_{12}$. Since the σ, π -allyl species was seen to increase steadily in concentration during the isomerisation of the free 1,4-diene it seems likely that this species is generated by a reversible step from a common intermediate

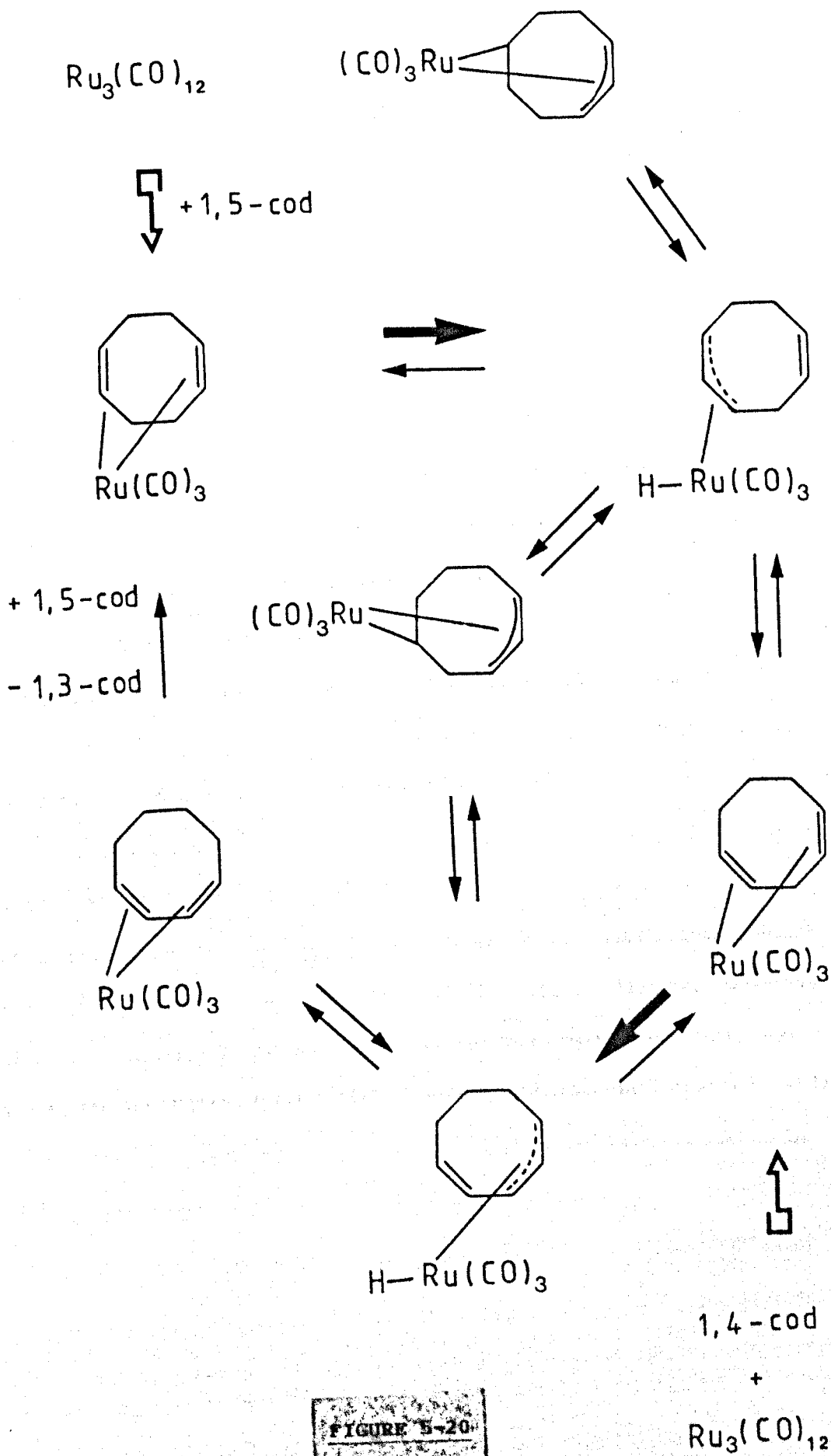


FIGURE 5-20

accessible from both the 1,5-diene and 1,4-diene complexes.

Drawing together the evidence it appears that the most plausible explanation of the experimental observations involves a common η -allyl metal hydride mechanism. Species such as the σ, η -allyl complex illustrated in FIGURE 5-13 and the cluster carbonyl species of references³⁵ and³⁶, illustrated in FIGURE 5-18, whilst present in detectable concentrations in diene isomerisation systems, do not appear to be primary catalytic species. Rates of isomerisation, equilibrium isomer concentrations and the concentrations of metal carbonyl species during the course of the isomerisation would suggest that the primary catalytic species has not been isolated^{35,36}. In view of the observation that $\text{Ru}(\text{CO})_3 \cdot (\eta^4\text{-cycloocta-1,5-diene})$ also acts as a catalyst precursor in the isomerisation of dienes it is attractive to suggest that isomerisation proceeds through simple η -allyl metal hydride species such as (XI) and (XII) (FIGURE 5-19). Such a species would be analogous to that postulated for the iron carbonyl systems and of similar structure to the known catalytic species (XIII), illustrated in FIGURE 5-19 (14). If (XI) and (XII) are accepted as the catalytic species a plausible mechanistic scheme is given by FIGURE 5-20, which resembles that found for the analogous iron systems. It must be emphasised that the above scheme is merely a plausible principal route for diene isomerisation and that in view of the number of carbonyl species isolated from ruthenium catalysed systems other catalytic species may also be involved in the isomerisation process.

5.2 ALKENE ISOMERISATION REACTIONS.

5.2.1 Introduction.

In view of the interesting information obtained for the alkadiene systems a further study was carried out to provide a comparison with the better investigated alkene isomerisation systems^{1,3-6,9-13}. For this purpose it was found convenient to investigate the mechanism of isomerisation of hex-1-ene by two different types of iron carbonyl catalyst precursors.

5.2.2 Systems using Pentacarbonyliron as Catalyst Precursor.

Attempts to catalyse the isomerisation of hex-1-ene using pentacarbonyliron in heptane at 70°C were found to result only in slow decomposition of the carbonyl species, with no alkene isomerisation. Ready isomerisation of hex-1-ene only occurred at 140°C in decalin over a period of several hours. No evidence for formation of a catalytic carbonyl species could be found from the infrared spectrum of the reaction mixture under these conditions. As has been reported previously²⁵ the isomerisation produced a thermodynamic ratio of free linear hexenes:

hex-1-ene (5) : cis-hex-2-ene (25) : trans-hex-3-ene (75)

at equilibrium.

5.2.3 Systems using $\text{Fe}(\text{CO})_4 \cdot (\eta^2\text{-alkene})$ as Catalyst Precursor.

Catalysis of hexene isomerisation by the species $\text{Fe}(\text{CO})_4 \cdot (\eta^2\text{-styrene})$ was found to proceed rapidly in heptane at 70°C resulting in an equilibrium mixture of linear alkenes with the same proportions as were found using $\text{Fe}(\text{CO})_5$ as isomerisation catalyst. Isomerisation of the alkene

free ligand took approximately 2 hours at 70°C according to g.l.c. analysis of the reaction mixture. A study of the infrared spectrum revealed that absorptions due to the styrene complex disappeared within ten minutes to yield a complicated spectrum with a number of broad carbonyl stretching vibrations close to 2020 cm^{-1} , the region of the spectrum characteristic of species of the structure $\text{Fe}(\text{CO})_3 \cdot (\eta^2\text{-alkene})_2$ and of $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-non-conjugated diene})$. No definite evidence for $\text{Fe}(\text{CO})_4 \cdot (\eta^2\text{-hexene})$ was seen in the infrared spectrum of the reaction mixture.

The implication of the above results is that displacement of the styrene leaving group occurs rapidly under the reaction conditions to yield $[\text{Fe}(\text{CO})_4]$ or a polymeric carbonyl species such as $[\text{Fe}_2(\text{CO})_7]$ or $\text{Fe}_3(\text{CO})_{12}$ ^{7,13}. Capture of the free alkene by the coordinatively unsaturated iron carbonyl species then results in isomerisation. In view of the complexity of the infrared spectrum of the reaction mixture it is difficult to draw definite conclusions about the structure of the catalytic intermediate but by analogy with other carbonyl catalysed systems the following observations may be made.

(i) Observations with a number of $\text{Fe}(\text{CO})_4 \cdot (\eta^2\text{-alkene})$ substrates have failed to show evidence that the alkene moieties undergo ready isomerisation under the reaction conditions used for the present work. Where measurable rates of isomerisation are not comparable with the rate of decomplexation of the coordinated ligand in the systems presently under consideration^{3,8}.

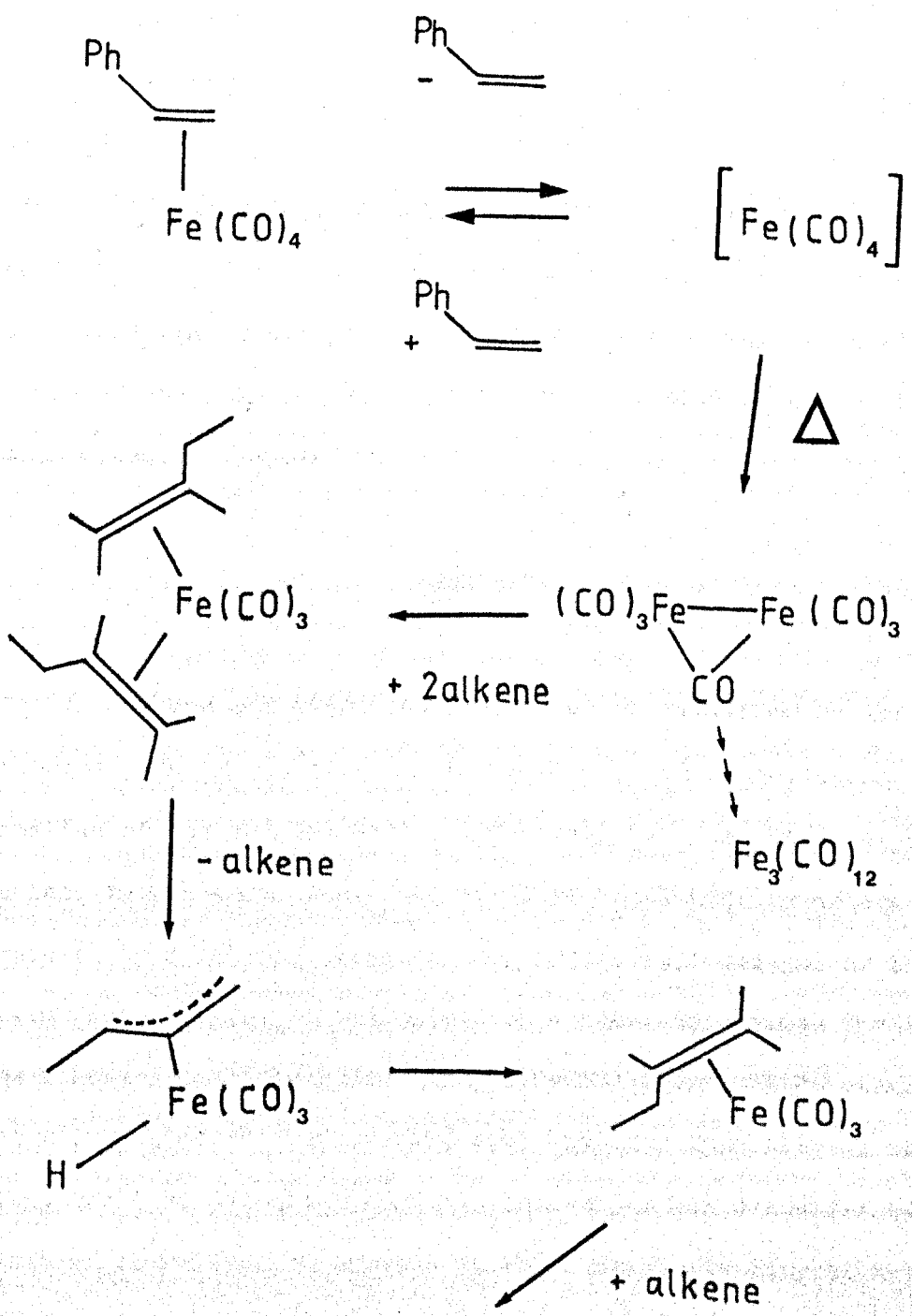
(ii) The rate of isomerisation in the present study is too large to be consistent with an isomerisation catalyst generated by dissociation of a further carbon monoxide dissociation from $[\text{Fe}(\text{CO})_4]$ under the reaction conditions. Although a catalytically active species of the type

$[\text{Fe}(\text{CO})_3 \cdot (\eta^2\text{-alkene})_2]$ would be an attractive model in view of the likelihood that this species would be kinetically labile⁷ and would have an infrared spectrum in accord with that observed experimentally²⁶, it does not seem probable that such a species can be generated from $[\text{Fe}(\text{CO})_4]$ by simple dissociation of carbon monoxide.

(iii) It is well known that tetracarbonyliron polymerises to form $\text{Fe}_3(\text{CO})_{12}$ under the conditions obtaining in the isomerisation reactions. Dodecacarbonyltriiron is a well known isomerisation catalyst for alkenes³⁻⁶ but it seems unlikely that this species is an active isomerisation catalyst for the systems presently under consideration since this would involve a trimolecular reaction to form the catalytic species from the $[\text{Fe}(\text{CO})_4]$. However recent work by Clark³ suggests that a species with bridging carbonyl groups is implicated as the isomerisation catalyst and for this reason the species $[\text{Fe}_2(\text{CO})_7]$ is postulated as the principal catalytic species for the present systems. This species offers the advantages of being a catalyst which is readily generated from $[\text{Fe}(\text{CO})_4]$ whilst also serving as a suitable precursor for the $\text{Fe}_3(\text{CO})_{12}$ side product of the isomerisation reaction. The complexity of the infrared spectrum would be explained by this model which would also provide a convenient route to $\text{Fe}(\text{CO})_3 \cdot (\eta^2\text{-alkene})_2$. A bis(alkene) complex of this type would be expected to generate a η -allyl metal hydride such as (V) under the conditions used in the isomerisation reactions. The lability of the bis(alkene) complex should also ensure rapid isomerisation consistent with the experimental observations.

(iv) The postulated reaction sequence is therefore illustrated by FIGURE 5-21. The mechanism as proposed is necessarily speculative but can offer a number of useful explanations for the experimentally observed features of the isomerisation process. The rate-determining formation of $\text{Fe}(\text{CO})_3 \cdot (\eta^2\text{-alkene})_2$ by thermolysis of $[\text{Fe}_2(\text{CO})_7]$ accords well with the mechanism applicable to the diene isomerisation since the intermediate resembles a

FIGURE 5-21



further isomerisation

non-conjugated diene in properties. Species of the type $\text{Fe}(\text{CO})_3 \cdot (\eta^2\text{-alkene})_2$ have also been shown to be kinetically labile²⁶ and this observation accords well with the higher rate of alkene isomerisation than alkadiene isomerisation. It should also be noted that all species involved in the scheme of FIGURE 5-21 would reasonably be expected to exist under the reaction conditions. Direct formation of a π -allyl metal hydride from $[\text{Fe}(\text{CO})_4]$ and the alkene by way of carbon monoxide producing an $[\text{Fe}(\text{CO})_3 \cdot (\eta^2\text{-alkene})]$ intermediate is not supported by the experimental evidence; and the alternative, carbon monoxide dissociation from $\text{Fe}(\text{CO})_4 \cdot (\eta^2\text{-alkene})$ to yield $[\text{Fe}(\text{CO})_3 \cdot (\eta^2\text{-alkene})]$ is highly unlikely in view of the relative nucleophilicities of alkenes and carbon monoxide as demonstrated in Chapter Two.

5.3 SUMMARY.

Alkene and alkadiene isomerisation catalysed by iron and ruthenium carbonyl species are found to proceed by mechanisms involving the formation of the species $\text{M}(\text{CO})_3 \cdot (\eta^3\text{-allyl}) \cdot (\text{H})$ as the catalytically active species. In the former case the π -allyl metal hydride intermediate is generated by a rate-determining step involving formation of the intermediate $[\text{Fe}(\text{CO})_3 \cdot (\eta^2\text{-alkene})]$ by a reaction between $[\text{Fe}_2(\text{CO})_7]$ and the free alkene, possibly by way of an $[\text{Fe}(\text{CO})_3]$ transition state. In the latter case the rate-determining step involves formation of an $[\text{Fe}(\text{CO})_3 \cdot (\eta^2\text{-alkadiene})]$ by dechelation of the tetrahapto bound alkadiene. The rate and extent of isomerisation depends on the kinetic lability of the intermediate and of the rate of ligand exchange of the product of the isomerisation process.

5.4 EXPERIMENTAL.

5.4.1 Preparation of starting materials and identification of products.

Cycloocta-1,4-diene, $\text{Fe}_3(\text{CO})_{12}$, $\text{Ru}_3(\text{CO})_{12}$, $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-benzalacetone})$, $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-cycloocta-1,3-diene})$, $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-cycloocta-1,5-diene})$ and $\text{Fe}(\text{CO})_4 \cdot (\eta^2\text{-styrene})$ were prepared according to literature methods^{18,27-30} and found to give satisfactory infrared and ^1H n.m.r. spectra. Details of the infrared spectra of the complexes are given in TABLE 5-3. The entering groups cycloocta-1,3-diene, cycloocta-1,5-diene, cyclohexa-1,4-diene and the hexenes hex-1-ene, hex-2-ene and hex-3-ene were commercial materials and were distilled under dinitrogen before use. Pentacarbonyliron (Fluka A.G.) was filtered before use and stored under dinitrogen. Heptane (Analytical Grade), toluene and decalin were commercial materials and prior to use as solvents in the isomerisation reactions these materials were dried and distilled under dinitrogen.

5.4.2 Isomerisation reactions.

All isomerisation reactions were carried out under an atmosphere of dinitrogen using sealed vessels immersed in a constant temperature bath controlled to within 0.02°C . Infrared spectra of aliquots of the reaction mixture were taken at intervals following the procedure in Chapter Three. Infrared spectra were recorded on a Perkin-Elmer 257 spectrophotometer using 1mm NaCl cells. Gas chromatographic analysis of the free organic ligands was carried out on a Pye-Unicam 104 gas-liquid chromatograph fitted with a nineteen foot column of OV101 (3%) using a flame ionisation detector. For g.l.c. analysis of reaction mixtures involving the cyclooctadiene substrates considerable dilution of the samples was required

before resolution of the isomers was possible.

Unless stated the concentration of the metal carbonyl species used was $5 \times 10^{-3} \text{ mol dm}^{-3}$ for reactions in toluene and $2.5 \times 10^{-3} \text{ mol dm}^{-3}$ for reactions in the other solvents.

TABLE 5-1.

Data for Ligand Exchange Reactions of $\text{Fe}(\text{CO})_3 \cdot (\eta^4\text{-diene})$
substrates carried out in toluene at 60°C .

<u>Leaving Group</u>	<u>Entering Group</u>	<u>Ligand:Complex</u>	<u>$10^4 k_{\text{obs}}$ /s⁻¹</u>
benzalacetone	cycloocta-1,3-diene	10:1	0.15
benzalacetone	cycloocta-1,3-diene	60:1	0.50
cycloocta-1,3-diene	benzalacetone	10:1	0.45

TABLE 5-2.

Absolute Rate theory data for the Isomerisation of
Fe(CO)₃·(η⁴-1,5-cod) to Fe(CO)₃·(η⁴-1,3-cod).

<u>T</u> <u>/K</u>	<u>T⁻¹</u> <u>/K⁻¹</u>	<u>10⁴ k_{obs}</u> <u>/s⁻¹</u>	<u>10⁻² ln(k_{obs}/T)</u>
333.2	0.3001	0.32 , 0.39 ^a	-0.162 , -0.160 ^a
338.2	0.2957	0.55 , 0.57	-0.156 , -0.156
343.2	0.2914	0.93 , 1.02	-0.151 , -0.150
349.2	0.2861	2.53 , 2.81	-0.141 , -0.140
353.2	0.2831	3.37 , 3.57	-0.139 , -0.138
357.7	0.2796	6.52 , 6.24	-0.132 , -0.133
363.2	0.2753	9.74 , 9.68	-0.128 , -0.128

Footnotes.

A linear least squares analysis of this data gave a correlation coefficient of 0.993. The calculated activation parameters were as follows:

$$\Delta H = 112.9 \pm 3.9 \text{ kJ mol}^{-1} ; \quad \Delta S = 7.3 \pm 11.6 \text{ kJ mol}^{-1}.$$

- ^a All kinetic measurements were carried out in toluene solution with the substrate at a concentration of 0.0049 mol dm⁻³. Experiments were performed in duplicate so that reproducibility could be assessed.

TABLE 5-3.

Infrared Stretching Vibrations of Potential Catalytic Species.

<u>Species</u>	<u>v-CO str.</u> <u>/cm⁻¹</u>	<u>Reference</u>
Fe ₃ (CO) ₁₂	2047s , 2022m , 1840vw .a	This work
Ru ₃ (CO) ₁₂	2062s , 2029m , 2009w .a	This work
Fe(CO) ₃ ·(1,3-cod)	2042s , 1977s , 1974s .a	This work
	2043s , 1974s , 1971s .b	(18)
Fe(CO) ₃ ·(1,5-cod)	2027s , 1963sb , 1954sb .a	This work
	2027s , 1961sb , 1951sb .b	(18)
Ru(CO) ₃ ·(1,5-cod)	2045s , 1984sh , 1969sb .a	This work
	2043s , 1982sh , 1966sb .b	(18)
Ru(CO) ₃ ·(1,4,6-cod)	2069m , 1991s , 1983s .a	This work
	2067s , 1999sb .b	(18)
Ru ₃ (CO) ₉ ·(H)·(C ₃ H ₉)	2094m , 2066s , 2042vs; 2025s , 2020sh , 2005m ; 1998m , 1984w .c	(35)
Ru ₂ (CO) ₆ ·(C ₆ H ₈)	2081m , 2050s , 2009s ; 1995m , 1984m .c	(35)

Footnotes.Abbreviations.

s= strong; vs= very strong; sb= strong, broad;
m= medium; sh= shoulder; w= weak; vw= very weak.

1,3-cod= η^4 -cycloocta-1,3-diene;

1,5-cod= η^4 -cycloocta-1,5-diene;

1,4,6-cod= $4-6\eta^3$, 1d-cyclooctenediyl.

^a spectrum taken in heptane solution.

^b spectrum taken in cyclohexane solution.

^c spectrum taken in tetrachloromethane solution.

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APPENDIX A: TREATMENT OF KINETIC DATA.

A.1 Preliminary Processing.

All kinetic experiments described in the text were monitored by means of infrared spectroscopy. The reactions studied were carried out in solution with the entering ligand always present in at least ten-fold excess relative to the initial substrate concentration so that pseudo-first-order conditions were maintained. Observations were recorded in percentage transmittance units and rate constants calculated both for the disappearance of suitable carbonyl stretching absorption bands of the substrate and for the appearance of the corresponding bands of the product. For all systems described in the text the rate constants calculated from substrate disappearance were found to be consistent with those calculated for product appearance.

To calculate rate constants from the raw experimental data it was necessary to convert readings recorded in percentage transmittance units (%T), which are not linear with respect to concentration of the observed species, to absorbance units, which show a linear dependence on concentration. Linear concentration dependence of measured absorbance values was independently checked for each of the systems used for kinetic study, with the Beer-Lambert law found to hold exactly in each case. Transmittance readings were converted to absorbance units by means of the standard conversion formula for quantitative infrared spectroscopy¹, as given in equation (A-1):

$$(A-1) \quad A_t = \ln(\%T_2/\%T_1) .$$

In the above equation A_t represents the absorbance at time t whilst $\%T_1$ is the measured transmittance value for the selected carbonyl stretching vibration at that time; $\%T_2$ is the transmittance of an arbitrary baseline in

the infrared spectrum at the corresponding time. Rate constants for substrate disappearance and for product appearance can now be calculated. Under pseudo-first-order conditions the observed rate constant (k_{obs}) for substrate disappearance is found from the slope of a plot of $\ln A$ against time, since the rate equation has the general form (A-2):

$$(A-2) \quad y = (k_{\text{obs}} \cdot \text{time}) + \text{constant} .$$

FIGURE A-1 gives a listing of a computer program used to convert experimental percentage transmittance versus time data to absorbance units and to calculate the observed rate constant according to equation (A-2). An unweighted linear least-squares analysis is used and provides an estimate of random measurement errors on the observed rate constant as a standard deviation about the mean value. A correlation coefficient, which gives a measure of the distribution of the experimental points about the line of best fit, is also supplied by the program.

The conventional method of calculating observed rate constants for product appearance depends on measurement of an accurate value for the absorbance of the product at infinite time. Assuming pseudo-first-order conditions apply a plot of $\ln(A_t - A_\infty)$ against time (t) should then be linear with a slope of k_{obs} . However, when studying air-sensitive species, practical difficulties often make it very difficult to obtain a reliable estimate of A_∞ by direct measurement. A more satisfactory technique involves a non-linear least-squares analysis of the absorbance - time data to provide an estimate of A_∞ by iterative solution. Once this has been achieved, a value of k_{obs} can be obtained by substitution of the calculated A_∞ into the linear least-squares equation. A program used to carry out this procedure is illustrated in FIGURE A-2. It should be noted that in this case standard deviations are calculated using $(N-3)$ degrees of freedom, where N is the number of experimental data pairs, rather than the $(N-2)$ degrees of freedom applicable to the linear least-squares fit used

for substrate disappearance. Accordingly quoted standard deviations for non-linear least-squares analyses are generally greater than those for equivalent linear least-squares solutions.

A.2 Analysis of Rate Data for Alkene Exchange at Five-coordinate Iron.

The full rate law applicable to the alkene exchange reactions treated in Chapter Two has the form given in equation (A-3) :

$$(A-3) \quad \frac{-d[SA]}{dt} = \frac{k_1 k_2 [SA] [L]}{k_{-1} [S] + k_2 [L]}$$

where (SA= substrate, S= leaving group, L= entering group.)

Under the pseudo-first-order conditions used for the rate experiments the measured rate constant (k_{obs}) is represented by the simplified expression:

$$(A-4) \quad k_{obs} = \frac{k_1 k_2 [L]}{k_{-1} [S] + k_2 [L]}$$

It is now possible to derive k_{-1}/k_2 and k_1 from the simplified expression by using a linear least-squares analysis of the appropriate region of the k_{obs} versus [L] plot. (For a discussion of the application of least-squares techniques to chemical data see reference (2)). When the entering group is present in very high concentrations relative to the substrate $k_2 [L] \gg k_{-1} [S]$ and a linear plot is obtained with an intercept of k_1 and a slope of zero. k_1 can therefore be calculated from a least-squares analysis of the linear portion of the k_{obs} versus [L] plots, with the analysis optionally weighted using the reciprocal of the standard deviation on each of the individual k_{obs} values. The program is illustrated in FIGURE A-3 carries out the weighted least-squares calculation by minimising the sum of the squares of the residuals, Q , which can be represented by equation (A-5):

$$(A-5) \quad Q = \sum_{i=1}^n \sigma^{-1} [y_i - \text{intercept} - (\text{slope} \cdot x_i)]^2 .$$

A value for k_1 is returned with a standard deviation in k_1 , a correlation coefficient, and an overall standard deviation, defined according to equation (A-6):

$$(A-6) \quad \text{ovsd} = \sqrt{\frac{Q}{(N-2)}}$$

where (Q = minimised sum of the squares of the residuals and N = number of experimental data point pairs.) The program then provides a graphical representation of the fit of the data to the theoretical model. By rearranging equation (A-4) it is possible to solve for k_{-1}/k_2 :

$$(A-7) \quad \frac{1}{k_{\text{obs}}} = \frac{k_{-1}[S]}{k_1 k_2 [L]} + \frac{1}{k_1} .$$

Accordingly if a series of experiments is carried out with the entering group concentration held constant and the leaving group concentration is varied a plot of $1/k_{\text{obs}}$ versus $[S]$ will give a slope of $k_{-1}/k_1 k_2$ and an intercept of $1/k_1$. The standard deviation in k_1 can then be calculated from the standard deviation in the intercept according to equation (A-8):

$$(A-8) \quad \sigma_{k_1} = \sigma_{\text{intercept}} \cdot k_1^2$$

whilst the standard deviation in the competition ratio k_{-1}/k_2 can be estimated according to equation (A-9):

$$(A-9) \quad \sigma_{k_{-1}/k_2} = (\sigma_{\text{slope}} \cdot k_1) + (\sigma_{\text{intercept}} \cdot \text{slope} \cdot k_1^2) .$$

The calculations above were carried out automatically within a modified linear least-squares computer program.

A.3 Analysis of Rate Data for Alkadiene Exchange at Six-coordinate Chromium.

The full rate law postulated for these systems has the form:

$$(A-10) \quad \frac{-d[SA]}{dt} = \frac{k_1 k_2 [SA] [L]}{k_{-1} [S] + k_2 [L]} + k_a [SA] [L]$$

Under the pseudo-first-order conditions employed, with [L] present in high concentration the observed rate can be represented according to equation (A-11) :

$$(A-11) \quad k_{obs} = k_1 + k_a [L].$$

Accordingly a simple linear least-squares analysis of k_{obs} against [L] should give a slope of k_a with an intercept of k_1 . The weighted linear least-squares program given in FIGURE A-3 was therefore used for the chromium systems without further modification.

A.4 Analysis of Rate Data for Polyene Exchange at Five-coordinate Iron.

As has been explained in Chapter Three the full form of the rate law postulated for this type of system is very complicated. However, if the exchange process is studied under pseudo-first-order conditions and appropriate substitutions are made, the simplified equation (A-12) may be applied :

$$(A-12) \quad k_{obs} = k_\alpha [L] + \frac{k_\beta [L]}{k_\gamma + k_\delta [L]}$$

The full expressions corresponding to the partial rate constants k_α , k_β , k_γ and k_δ are supplied in the text to Chapter Three and are derived in Appendix B.

The simplified rate equation may now be solved for k_{α} , k_{β} / k_{ξ} and k_{γ} / k_{ξ} by means of a suitable non-linear least-squares analysis. The algorithm devised for this purpose is given in FIGURE A-4 with $k_{one} = k_{\alpha}$, $k_{two} = k_{\beta} / k_{\xi}$ and $k_{three} = k_{\gamma} / k_{\xi}$. Since equation (A-12) cannot be rearranged to give a quadratic equation the most convenient method of solution involves expanding the equation by a Taylor series to give a matrix of linear equations. The sum of the squares of the residuals can then be minimised by an iterative correction procedure until convergence is obtained. For the program to operate successfully it is necessary to supply initial estimates for k_{one} and k_{two} , and these may be obtained as the intercept and slope respectively of the apparently linear portion of the plot of k_{obs} versus [L] at high concentrations of the entering group. The calculation may be weighted to take account of the standard deviations in the measured values of k_{obs} as has been described for the earlier rate analyses. The overall procedure can be summarised as follows :

The sum of the squares of the residuals (Q) is calculated according to equation (A-13) :

$$(A-13) \quad Q = \sum_{i=1}^n [y_i - k_{one} \cdot x_i - k_{two} \cdot x_i / k_{three} + x_i]^2$$

The value of Q is then minimised by iterative corrections to k_{one} , k_{two} and k_{three} supplied from a vector of correction coefficients until successive values of Q indicate convergence. At this point values of the partial rate constants are returned with their standard deviations calculated for (N-3) degrees of freedom and with an overall standard deviation for the fit of the solution to the data. A graphical representation of the distribution of the experimental points about the best-fit curve is also generated.

A.5 Calculation of Activation Parameters.

A linear least squares analysis of $\ln(k_{\text{obs}}/T)$ versus $1/T$ data can be used to generate values of the activation parameters ΔH and ΔS according to Absolute Rate theory. A modification of program A-3 was used for this purpose and given a data input of $T / ^\circ\text{C}$ and $k_{\text{obs}} / \text{s}^{-1}$ values of the activation parameters with standard deviations were obtained. The method used produces a slope of $\Delta H/R$ and an intercept of $(23.76 \times \Delta S)/R$.

A.6 Subroutines called by the Applications programs.

A number of general purpose subroutines are called by the programs given in FIGURES A-2 to A-4. Since the subroutine library includes the routines used for linear least squares calculation and also the interactive data handling subprograms a listing of the relevant subroutines is provided in FIGURE A-5.


 FIGURE A-1

```

0010 REM Linear least squares program to calculate the value
0020 REM of the Observed Rate Constant from Infrared data
0030 REM supplied as % Transmittance against Time (minutes).
0040 DIM X(100),Y(100),Z(100)
0050 % "How many pairs of points are there in the data set :";
0060 INPUT N
0061 %
0062 % "Now type in the %Transmittance of the selected band at :";
0063 % " a) before reaction and b) infinite time."
0064 % "i.e. %T base(start),%T band(start),%T base(inf.),%T band(inf.)"
0065 % "What are the values ";
0066 INPUT G1,G2,G3,G4
0067 G1=LOG(G1/G2)
0068 G3=LOG(G3/G4)
0069 G1=G1-G3
0070 X1=0 :X2=0 :Z1=0
0080 Y1=0 :Y2=0
0090 %
0100 % TAB(6);"Observation No. ";TAB(23);"Time(mins.)";TAB(38);"%T (baseline)";
0110 % TAB(54);"%T (band)"
0120 FOR I=1 TO N : % TAB(10);I," :";
0130 INPUT X(I),Y3,Y4 :Y3=LOG(Y3/Y4)
135 Y3=Y3-G3
0140 X(I)=X(I)*60 :Y(I)=LOG(G1/Y3)
0150 X1=X(I)+X1 : Y1=Y(I)+Y1
0160 Z1=Y(I)*X(I)+Z1
0170 X2=X(I)*X(I)+X2 :Y2=Y(I)*Y(I)+Y2
0180 NEXT I
0190 D=N*X2-X1*X1
0200 REM M is the slope ; C is the intercept;
0210 REM M1 & C1 are the corresponding standard deviations ;
0220 REM E1 is the overall standard deviation ; whilst
0230 REM R is the correlation coefficient.
0240 M=(N*Z1-X1*Y1)/D
0250 C=(X2*Y1-X1*Z1)/D
0260 E1=0 :E2=0
0270 M1=0 :C1=0
0280 FOR I=1 TO N
0290 E2=E2+((Y(I)-C-M*X(I))2)
0300 Z(I)=X(I)*M+C :REM Z holds the calculated values of Y
0310 NEXT I
0320 E2=E2/(N-2) :E1=SQR(E2)
0330 M1=SQR(N*E2/D) :C1=SQR((E2/N)*(1+((X1*X1)/D)))
0340 R=SQR((M*M*(X2-X1*X1/N))/(Y2-Y1*Y1/N))
0350%
0360%
0370 % TAB(10);"The Observed Rate Constant is :";-M*10000;" x 10-4 s-1"
0380 % TAB(10);"with a standard deviation of :";M1*10000;" x 10-4 s-1"
0390%
0400 % TAB(10);"Estimated correlation coefficient is :";R;" "
0410 % : % TAB(10);"Do you want a full list of calculated properties :-"
0420 % TAB(15);"if so type 1 otherwise 0 :";
0430 INPUT A2
0440 IF A2=0 GOTO 490
0450 % :% TAB(4);"Observation Time/ s Log A Calculated Diff."
0460 FOR I=1 TO N
0470 % USING "11#,3S,6#.#,4S,2#.4#,4S,2#.4#,4S,2#.4#",I,X(I),Y(I),Z(I),Y(I)-Z(I)
0480 NEXT I
0490%
0500 % TAB(15);"To continue with a new set of data type 1 otherwise 0 :";

```

```
0510 INPUT A1
0520 % : %
0530 IF A1=1 THEN 50
0540 END
0045 % : %
```


 FIGURE A-2

```

0010REM NON-LINEAR LEAST SQUARES RATE CALCULATION
0020 DIM P(30),B(30),G(30),T(30),H(30),D(3),F(3,3),Y(3,1),S(3,3)
0030DIM C(3,1),A$50
0040FILES #1, '.AINF'
0050% "Experiment Title :";
0060INPUT A$
0070B$=" "
0080% #1,B$
0090% #1,B$
0100% #1,A$
0110% #1,B$
0120% "Number of Data points =";
0130 INPUT N
0140% "Type in TIME (MINS), %T base , %T band"
0150 FOR M=1 TO N
0160%
0170 PRINT M; "=";
0180INPUT H(M),B(M),G(M)
0190 LET T(M)=H(M)*60
0200P(M)=LOG(B(M)/G(M))
0210% "Absorbance =",P(M)
0220 NEXT M
0230 LET P0=P(1)
0240 LET K=2/T(N)
0250 LET P1=1.25*P(N)-0.25*P0
0260 LET Z=1
0270 PRINT "CYCLE", "RATE CONST(SEC(-1))", "RESID.SUM"
0280 FOR M=1 TO 3
0290 FOR I=1 TO 3
0300 LET F(M,I)=0
0310 NEXT I
0320 LET Y(M,1)=0
0330 NEXT M
0340 FOR M=1 TO N
0350 LET A=EXP(-K*T(M))
0360 LET D(1)=T(M)*(P1-P0)*A
0370 LET D(2)=1-A
0380 LET D(3)=A
0390 LET E=P(M)-(P1*(1-A)+P0*A)
0400 FOR I=1 TO 3
0410 LET Y(I,1)=E*D(I)+Y(I,1)
0420 LET T1=E^2+T1
0430 FOR J=1 TO 3
0440 LET F(J,I)=D(I)*D(J)+F(J,I)
0450 NEXT J
0460 NEXT I
0470 NEXT M
0480 MAT S=INV(F)
0490 MAT C=S*Y
0500 PRINT
0510 LET K=K+C(1,1)
0520 LET P1=P1+C(2,1)
0530 LET P0=P0+C(3,1)
0540 PRINT Z,K, T1
0550 IF Z=1 THEN 570
0560IF ABS(T1-U)<=1E-4 THEN 610
0570 LET U=T1
0580 LET T1=0
0590 LET Z=Z+1
0600 GOTO 280

```



```
0610 PRINT
0620 PRINT"POINT", "TIME", "VALUE OBS", "VALUE CAL", "DIFF"
0630 LET Q=0
0640 FOR M=1 TO N
0650 LET A=EXP(-K*T(M))
0660 LET V=P1*(1-A)+P0*A
0670 LET D1=P(M)-V
0680 PRINT
0690 PRINT M, T(M), P(M), V, D1
0700 LET Q=D1^2+Q
0710 NEXT M
0720 PRINT
0730% #1, B$
0740 LET D2=SQR(Q/(N-3))
0750 PRINT"STD. DEV. OBS. ="; D2
0760% #1, "STD. DEV. OBS. ="; D2
0770
0780 PRINT"CALC. INF. VALUE="; P1
0790% #1, "CALC. INF. VALUE -"; P1
0800 LET D3=SQR(S(1,1)*Q/(N-3))
0810% "K OBS =", K; "STD. DEV. =", D3
0820% #1, "K OBS =", K; "STD. DEV. =", D3
0830 END
```

FIGURE A-3

```

C Program to calculate the k1 and ka partial rate
C constants for a process having the rate law :
C   k obs = k1 + ka [L]
C A linear regression analysis is used operating on
C an input of k obs vs [L]. The data may be unweighted
C or given a weighting of the reciprocal of the
C standard deviation in k obs.
  DIMENSION X(100),Y(100),W(100),YCALC(100),XOR(100),WOR(100),
  1 YOR(100),RES(100),Y1(2),X1(2),HED(10),SHED(10),XL(8),YL(7),
  2 AFILE(4),BFILE(4)
  COMMON/COSIZE/IPP,ISP,XS,YS
  DATA XL/4HLIGA,4HND C,4HONCE,4HNTRA,4HTION,4H (MO,4HL DM,4H-3) /
  DATA YL/4HOBSE,4HRVED,4H RAT,4HE CO,4HNSTA,4HNT (,4HS-1)/
  IPP=0
  ISP=0
  CALL CONECT("&PFILE/L/ADD",5)
C Input of Data, Headings, Plot type and weighting to be used.
  WRITE(4,*)
  WRITE(4,*)
  WRITE(4,*) "   Data input section"
  WRITE(4,*) "   -----"
  WRITE(4,*)
  WRITE(4,*)
  WRITE(4,*) "Program to fit experimental data to a "
  WRITE(4,*) "rate law of the form :"
  WRITE(4,*) "   k obs = k1 + ka [L]"
  WRITE(4,*) "A linear regression analysis is used."
75  CONTINUE
  IDIR=2
  WRITE(4,*)
  WRITE(4,*) "Type in the main heading (40 characters max.)"
  WRITE(4,*) "followed by a sub-heading (40 characters max.)."
  WRITE(4,*) "The headings should be supplied on separate lines."
  READ(3,19) (HED(I),I=1,10)
19  FORMAT(10A4)
  READ(3,19) (SHED(I),I=1,10)
  WRITE(4,*)
  WRITE(4,*) "What type of plot do you require :-"
  WRITE(4,*) "   Type 1 for a coloured plot"
  WRITE(4,*) " or       2 or black and white."
  READ(3,*) IS
  IF(IS.EQ.2) GO TO 4
  IS1=124
  IS2=121
  GO TO 5
4   IS1=1
   IS2=1
5   CONTINUE
  WRITE(4,*)
  WRITE(4,*) "Do you want an analysis which is weighted :-"
  WRITE(4,*) "   Type 0 for an unweighted analysis"
  WRITE(4,*) " or       1 for an analysis using a weighting of"
  WRITE(4,*) "the reciprocal of the std. devn. in k obs."
  READ(3,*) NW
C Linear regression analysis of the experimental data.

```

C The program will convert the supplied values internally.

```

298 CONTINUE
   WRITE(4,*)
   WRITE(4,*) "Is the data in a file ?"
   WRITE(4,*) " If so type 1"
   WRITE(4,*) "otherwise      2"
   READ(3,*) IFILE
   IF(IFILE.EQ.2) GO TO 66
197 CONTINUE
   WRITE(4,*)
   WRITE(4,*) "Now type in name of the data file"
   WRITE(4,*) "This should not be more than 16"
   WRITE(4,*) "characters long including the full stop"
   WRITE(4,*) "or & sign."
   READ(3,17) (AFILE(I),I=1,4)
   CALL CONECT(0,3)
   CALL CONECT(AFILE,3)
17  FORMAT(4A4)
66  CONTINUE
   IF(NW.EQ.1) GO TO 1
   WRITE(4,*)
   IF(IFILE.EQ.1) GO TO 67
   WRITE(4,*) "Now type in the experimental data as pairs"
   WRITE(4,*) "of points. Each set of [Ligand] and k obs "
   WRITE(4,*) " should be on a new line, with the values"
   WRITE(4,*) "separated by a space."
   WRITE(4,*) "Data should be input as [Ligand] x 100"
   WRITE(4,*) "and k obs x 104."
   WRITE(4,*) "The data should be preceded by the number of"
   WRITE(4,*) "points, supplied on a separate line."
67  CONTINUE
   CALL REDIN(XOR,YOR,WOR,W,N,-1,IFILE)
   CALL CONECT(0,3)
   CALL CONECT(' ',3)
   IF(N.NE.0) GO TO 607
   WRITE(4,*)
   WRITE(4,*) " There is no file with the name :"
   WRITE(4,17) (AFILE(I),I=1,4)
   WRITE(4,*) "in your directory."
   GO TO 197
607 CONTINUE
   CALL VALIN(XOR,YOR,WOR,W,N,-1,IFILE)
   IF(IFILE.EQ.4) GO TO 298
   DO 12 I=1,N
   X(I)=XOR(I)
   Y(I)=YOR(I)
   WOR(I)=1.0
   W(I)=WOR(I)
12  CONTINUE
   GO TO 2
1   CONTINUE
   IF(IFILE.EQ.1) GO TO 68
   WRITE(4,*)
   WRITE(4,*) "Now type in the experimental data as"
   WRITE(4,*) " [Ligand] <space> k obs <space> std. devn ."
   WRITE(4,*) "Each group should be on a new line."
   WRITE(4,*) "Data should be entered as [Ligand] x 100"

```

```

WRITE(4,*) "and k obs and std. devn. (k obs) x 104."
WRITE(4,*) "The data should be preceded by the number of"
WRITE(4,*) "points, supplied on a separate line."
68 CONTINUE
WB=0.0
WZ=0.0
CALL REDIN(XOR,YOR,WOR,W,N,0,IFILE)
CALL CONECT(0,3)
CALL CONECT('*',3)
IF(N.NE.0) GO TO 608
WRITE(4,*)
WRITE(4,*) "There is no file with the name :"
WRITE(4,17) (AFILE(I),I=1,4)
WRITE(4,*) "in your directory."
GO TO 197
608 CONTINUE
CALL VALIN(XOR,YOR,WOR,W,N,0,IFILE)
IF(IFILE.EQ.4) GO TO 298
DO 16 I=1,N
X(I)=XOR(I)
Y(I)=YOR(I)
W(I)=1.0/WOR(I)
16 WZ=WZ+W(I)
WB=WZ/N
DO 20 I=1,N
20 W(I)=W(I)/WB
2 CONTINUE
C Call to the linear regression subroutine.
CALL LLS (W,X,Y,N,A1,AZ,SA1,SAZ,STD,COR)
DO 30 I=1,N
YCALC(I)=X(I)*A1+AZ
30 RES(I)=Y(I)-YCALC(I)
72 CONTINUE
IDIR=IDIR-1
WRITE(4,*)
WRITE(4,*) " Results of the Analysis"
WRITE(4,*) " -----"
WRITE(4,*)
WRITE(4,*) "The experimental system studied was :"
WRITE(4,19) (HED(I),I=1,10)
WRITE(4,19) (SHED(I),I=1,10)
WRITE(4,*)
IF(NW.EQ.0) GO TO 55
WRITE(4,*)
WRITE(4,*) "A weighted analysis was requested :"
WRITE(4,*)
WRITE(4,*) "Tabulated Results :"
WRITE(4,*) "-----"
WRITE(4,*)
WRITE(4,*) "Data supplied (with calculated weighting factors) :"
WRITE(4,*)
WRITE(4,79)
WRITE(4,89) (I,XOR(I),YOR(I),WOR(I),W(I),I=1,N)
WRITE(4,92)
WRITE(4,91)
WRITE(4,99) (I,X(I),Y(I),YCALC(I),RES(I),I=1,N)
WRITE(4,*)

```

```

GO TO 56
55 CONTINUE
WRITE(4,*) "An unweighted analysis was requested : "
WRITE(4,*)
WRITE(4,*) "Tabulated Results : "
WRITE(4,*) "-----"
WRITE(4,*)
WRITE(4,91)
WRITE(4,99) (I,X(I),Y(I),YCALC(I),RES(I),I=1,N)
56 CONTINUE
IF(IDIR.EQ.0) GO TO 70
X1(1)=XMINF(X,N)
X1(2)=XMAXF(X,N)
Y1(1)=AMIN1(XMINF(Y,N),XMINF(YCALC,N))
Y1(2)=AMAX1(XMAXF(Y,N),XMAXF(YCALC,N))
195 CONTINUE
CALL DEVBEG
CALL EASIER(2,X1,Y1,-1,0,-4,IS2)
CALL EASIER(N,X,Y,1,1,2,IS2)
CALL EASIER(N,X,YCALC,0,0,2,IS1)
CALL EASILB(IS2,10,HED,10,SHED,8,XL,7,YL)
CALL DEVEND
IF(IPP.EQ.2) GO TO 194
70 CONTINUE
WRITE(4,45) N,COR
WRITE(4,49) A1,SA1
WRITE(4,59) AZ,SAZ
WRITE(4,69) STD
WRITE(4,*)
IF(IDIR.EQ.0) GO TO 71
WRITE(4,*) "Is the analysis satisfactory ?"
WRITE(4,*) " If so type 1"
WRITE(4,*) "or if not type 2 to modify the data"
WRITE(4,*) "and rerun."
READ(3,*) IANAL
IF(IANAL.EQ.1) GO TO 606
IDIR=2
IF(NW.EQ.1) GO TO 608
GO TO 607
606 CONTINUE
IPP=2
GO TO 195
194 CONTINUE
IPP=0
WRITE(4,*)
WRITE(4,*) "Do you want the results saved in a file ?"
WRITE(4,*) " If so type 1"
WRITE(4,*) "otherwise 2"
READ(3,*) IDIR
IF(IDIR.EQ.2) GO TO 71
WRITE(4,*)
WRITE(4,*) "Now specify a file to which the results"
WRITE(4,*) "are to be sent."
WRITE(4,*) "If a suitable file to take the results does"
WRITE(4,*) "not already exist type in a valid filename"
WRITE(4,*) "followed by /NEW e.g. .OUTFILE/NEW ."
WRITE(4,*) "To add the results to a pre-existing file type"

```

```

WRITE(4,*) "the filename followed by /ADD e.g. &DAT/ADD ."
CALL CONECT(0,4)
READ(3,17) (BFILE(I),I=1,4)
CALL CONECT(BFILE,4)
GO TO 72
71 CONTINUE
IF(IDIR.EQ.0) CALL CONECT(0,4)
IF(IDIR.EQ.0) CALL CONECT('* ',4)
WRITE(4,*)
WRITE(4,*) "Is another calculation required :"
WRITE(4,*) "  Type 1 to continue"
WRITE(4,*) " or    2 to finish."
READ(3,*) ICON
IF(ICON.EQ.1) GO TO 75
WRITE(4,*)
WRITE(4,*) "If you would like the results sent to the"
WRITE(4,*) "graph plotter type POOL.FILEPLOT when the"
WRITE(4,*) "READY prompt appears."
WRITE(4,*) "      To rerun this program just type"
WRITE(4,*) "the instruction KCLGRUN ."
WRITE(4,*)
WRITE(4,*)
45 FORMAT(" ", "There were ", I3, " data points :",
1 /, "The correlation coefficient for the analysis is :", G11.4)
49  FORMAT("The calculated ka is :", G11.4, " x 10-4 ",
1 "Mol dm-3 s-1", /, "with a std. devn. of :", G11.4,
2 " x 10-4 Mol dm-3 s-1 .")
59  FORMAT("The calculated k1 is :", G11.4, " x 10-4 s-1 ",
1 /, "with a std. devn. of :", G11.4,
2 " x 10-4 s-1")
69  FORMAT("The overall std. devn. is :", G11.4)
79  FORMAT("Point", 2X, "[Ligand]", 4X, "k obs", 5X, "Std. devn.", 7X,
1 "Weight calculated", /)
89  FORMAT(I3, 3X, 2G11.4, 3X, G11.4, 5X, G11.4)
91  FORMAT("Point", 2X, "[Ligand]", 6X, "k obs", 5X, "k calc.", 5X,
1 "Residual", /)
92  FORMAT(/, "Calculated data and results.", /)
99  FORMAT(I3, 3X, G13.6, 3G11.4)
      STOP
      END

```

FIGURE A-4

```

C Program to fit experimental kinetic data to
C a model of the type :
C   k obs = k1[L] + k2[L]/(k3+[L])
C An iterative procedure is used based on a
C Taylor series differential correction to
C supplied estimates of k1 , k2 and k3.
  DOUBLE PRECISION X(50),Y(50),W(50),YCALC(50),
  1 RES(50),C1,C2,C3,SC1,SC2,SC3,STD,WB,WZ,
  2 WOR(50),XOR(50),YOR(50)
  DIMENSION HED(10),SHED(10),XL(9),YL(9),X1(50),Y1(50),
  1 U(200),V(200),Y2(2),X2(2),AFILE(4),BFILE(4)
  COMMON/COSIZE/IPP,ISP,XS,YS
  DATA XL/4HLIGA,4HND C,4HONCE,4HNTRA,4HTION,4H - M,4HOL D,
14HM-3 ,4H /
  DATA YL/4HOBSE,4HRVED,4H RAT,4HE CO,4HNSTA,4HNT -,4H S-1,
14H ,4H /
  IPP=0
  ISP=0
  CALL CONECT("&PFILE/L/ADD",5)
  WRITE(4,*)
  WRITE(4,*)
  WRITE(4,*) "   Data input section"
  WRITE(4,*) "   -----"
  WRITE(4,*)
  WRITE(4,*)
  WRITE(4,*) "This is a program to fit experimental data"
  WRITE(4,*) "to a model of the type :"
  WRITE(4,*) "   k obs = k1[L] + k2[L]/(k3+[L])"
  WRITE(4,*) "Initial estimates of k1 , k2 and k3 are"
  WRITE(4,*) "needed for the calculation which uses a"
  WRITE(4,*) "Taylor series differential correction approach."
  WRITE(4,*)
75 CONTINUE
  IDIR=2
  WRITE(4,*) "Type in the main heading (40 characters max.)"
  WRITE(4,*) "followed by a sub-heading (40 characters max.)."
  WRITE(4,*) "The headings should be supplied on separate lines."
  READ (3,19) HED
  READ(3,19) SHED
  WRITE(4,*)
  WRITE(4,*) "What type of plot is required ?"
  WRITE(4,*) "   Type 1 for a coloured plot"
  WRITE(4,*) "   or   2 for black and white."
  READ(3,*) ICOL
  IF(ICOL.EQ.2) GO TO 42
  IS1=124
  IS2=121
  GO TO 43
42 CONTINUE
  IS1=1
  IS2=1
43 CONTINUE
19  FORMAT(10A4)
  WRITE(4,*)
  WRITE(4,*) "What are the estimates of k1 , k2 and k3 ?"

```

```

WRITE(4,*) "Input the values on a single line, separated"
WRITE(4,*) "by a space."
  READ(3,*) C1,C2,C3
WRITE(4,*)
WRITE(4,*) "Is the calculation to be weighted using the"
WRITE(4,*) "reciprocals of the experimental std. devn.s ?"
WRITE(4,*) "For a weighted analysis type 1"
WRITE(4,*) " otherwise type 2."
  READ(3,*) NW
298 CONTINUE
  WRITE(4,*)
  WRITE(4,*) "Is the data in a file ?"
  WRITE(4,*) " If so type 1"
  WRITE(4,*) "otherwise 2."
  READ(3,*) IFILE
  IF(IFILE.EQ.2) GO TO 66
197 CONTINUE
  WRITE(4,*)
  WRITE(4,*) "Now type in the name of the data file"
  WRITE(4,*) "This should not be more than 16"
  WRITE(4,*) "characters long including the full stop"
  WRITE(4,*) "or & sign."
  READ(3,17) (AFILE(I),I=1,4)
17 FORMAT(4A4)
  CALL CONECT(0,3)
  CALL CONECT(AFILE,3)
66 CONTINUE
  IF(NW.EQ.1) GO TO 1
  IF(IFILE.EQ.1) GO TO 67
  WRITE(4,*)
  WRITE(4,*) "Now type in the experimental data as pairs"
  WRITE(4,*) "of points. Each pair of [L] and k obs values"
  WRITE(4,*) "should be on a separate line, with the data"
  WRITE(4,*) "separated by a space. Data should be entered"
  WRITE(4,*) "as k obs x 104 and [L] x 100."
  WRITE(4,*) "The data should be preceded by the number of"
  WRITE(4,*) "points, supplied on a separate line."
67 CONTINUE
  CALL REDIN(XOR,YOR,X,Y,N,-1,IFILE)
  CALL CONECT(0,3)
  CALL CONECT('*',3)
  IF(N.NE.0) GO TO 607
  WRITE(4,*)
  WRITE(4,*) "There is no file with the name :"
  WRITE(4,17) (AFILE(I),I=1,4)
  WRITE(4,*) "in your directory."
  GO TO 197
607 CONTINUE
  CALL VALIN(XOR,YOR,X,Y,N,-1,IFILE)
  IF(IFILE.EQ.4) GO TO 298
  DO 12 I=1,N
  WOR(I)=1.0D0
  X(I)=XOR(I)
  Y(I)=YOR(I)
  W(I)=WOR(I)
12 CONTINUE
  WRITE(4,*)

```



```

GO TO 2
1 CONTINUE
IF(IFILE.EQ.1) GO TO 68
WRITE(4,*) "Now type in the experimental data as follows :"
```

WRITE(4,*) "[L] <space> k obs <space> std. devn. in k obs"

WRITE(4,*) "Each group should be on a separate line."

WRITE(4,*) " The data should be entered as [L] x 10⁰,"

WRITE(4,*) "and k obs and std. devn. (k obs) x 10⁴."

WRITE(4,*) "The data should be preceded by the number of"

WRITE(4,*) "points, supplied on a separate line."

```

68 CONTINUE
WB=0.0D0
WZ=0.0D0
CALL REDIN(XOR,YOR,WOR,W,N,0,IFILE)
CALL CONECT(0,3)
CALL CONECT('* ',3)
IF(N.NE.0) GO TO 608
WRITE(4,*)
WRITE(4,*) "There is no file with the name :"
```

WRITE(4,17) (AFILE(I),I=1,4)

WRITE(4,*) "in your directory."

GO TO 197

```

608 CONTINUE
CALL VALIN(XOR,YOR,WOR,W,N,0,IFILE)
IF(IFILE.EQ.4) GO TO 298
DO 16 I=1,N
X(I)=XOR(I)
Y(I)=YOR(I)
W(I)=WOR(I)
W(I)=1.0D0/W(I)
WZ=WZ+W(I)
16 CONTINUE
WB=WZ/N
DO 20 I=1,N
W(I)=W(I)/WB
20 CONTINUE
WRITE(4,*)
2 CONTINUE
WRITE(4,*)
```

C This section of the program calls the calculation subroutine.

CALL QLS(W,X,Y,N,C1,SC1,C2,SC2,C3,SC3,STD,ITR)

C The coefficients returned by QLS are now used to generate

C values of Y calc. and the Residuals.

```

DO 30 I=1,N
YCALC(I)=X(I)*C1+X(I)*C2/(X(I)+C3)
30 RES(I)=Y(I)-YCALC(I)
```

C This section of the program generates the output.

C Subroutine KCALC is used to find the position of the

C calculated line for the EASY plotting routines.

```

DO 40 I=1,N
X1(I)=X(I)
Y1(I)=Y(I)
40 CONTINUE
R1=C1
R2=C2
R3=C3
STA=XMINF(X1,N)
```

```

FIN=XMAXF(X1,N)
CALL KCALC(STA,FIN,R1,R2,R3,U,V)
IN=200
X2(1)=AMIN1(XMINF(X1,N),XMINF(U,IN))
X2(2)=AMAX1(XMAXF(X1,N),XMAXF(U,IN))
Y2(1)=AMIN1(XMINF(Y1,N),XMINF(V,IN))
Y2(2)=AMAX1(XMAXF(Y1,N),XMAXF(V,IN))
72 CONTINUE
IDIR=IDIR-1
WRITE(4,*)
WRITE(4,*) "      Results of the Analysis"
WRITE(4,*) "      -----"
WRITE(4,*)
WRITE(4,*) "The experimental system studied was :"
WRITE(4,19) (HED(I),I=1,10)
WRITE(4,19) (SHED(I),I=1,10)
WRITE(4,*)
IF(NW.EQ.1) GO TO 55
WRITE(4,*) "An unweighted analysis was requested :"
WRITE(4,*)
GO TO 56
55 CONTINUE
WRITE(4,*) "A weighted analysis was requested :"
WRITE(4,*)
56 CONTINUE
WRITE(4,*) "Tabulated Results :"
WRITE(4,*) "-----"
WRITE(4,*)
IF(NW.EQ.1) GO TO 76
WRITE(4,29)
WRITE(4,39) (I,XOR(I),YOR(I),YCALC(I),RES(I),I=1,N)
WRITE(4,*)
GO TO 77
76 CONTINUE
WRITE(4,*) "Experimental data and calculated weights :"
WRITE(4,*)
WRITE(4,78)
WRITE(4,39) (I,XOR(I),YOR(I),WOR(I),W(I),I=1,N)
WRITE(4,*)
WRITE(4,*) "Calculated data and results :"
WRITE(4,*)
WRITE(4,29)
WRITE(4,39) (I,X(I),Y(I),YCALC(I),RES(I),I=1,N)
WRITE(4,*)
77 CONTINUE
IF(IDIR.EQ.0) GO TO 70
194 CONTINUE
CALL DEVBEG
CALL EASIER(2,X2,Y2,-1,0,-4,IS2)
CALL EASIER(N,X1,Y1,1,1,2,IS2)
CALL EASIER(200,U,V,0,0,2,IS1)
CALL EASILB(IS2,10,HED,10,SHED,9,XL,9,YL)
CALL DEVEND
IF(IPP.EQ.2) GO TO 195
70 CONTINUE
WRITE(4,*)
WRITE(4,49) N, ITR

```

```

WRITE(4,59) C1,SC1
WRITE(4,69) C2,SC2
WRITE(4,79) C3,SC3
WRITE(4,89) STD
WRITE(4,*)
IF(IDIR.EQ.0) GO TO 71
WRITE(4,*) "Is the analysis satisfactory ?"
WRITE(4,*) " If so type 1"
WRITE(4,*) "or if not type 2 to modify the data"
WRITE(4,*) "and rerun."
READ(3,*) IANAL
IF(IANAL.EQ.1) GO TO 606
IDIR=2
IF(NW.EQ.1) GO TO 608
GO TO 607
606 CONTINUE
IPP=2
GO TO 194
195 CONTINUE
IPP=0
WRITE(4,*)
WRITE(4,*) "Do you want the results saved in a file ?"
WRITE(4,*) " If so type 1"
WRITE(4,*) "otherwise 2."
READ(3,*) IDIR
IF(IDIR.EQ.2) GO TO 71
WRITE(4,*)
WRITE(4,*) "Now specify a file to which the results"
WRITE(4,*) "are to be sent."
WRITE(4,*) "If a suitable file to take the results does"
WRITE(4,*) "not already exist type in a valid filename"
WRITE(4,*) "followed by /NEW e.g. .OUTFILE/NEW ."
WRITE(4,*) "To add the results to a pre-existing file type"
WRITE(4,*) "the filename followed by /ADD e.g. &DAT/ADD ."
CALL CONECT(0,4)
READ(3,17) (BFILE(I),I=1,4)
CALL CONECT(BFILE,4)
GO TO 72
71 CONTINUE
IF(IDIR.EQ.0) CALL CONECT(0,4)
IF(IDIR.EQ.0) CALL CONECT(' ',4)
WRITE(4,*)
WRITE(4,*)
WRITE(4,*) "Is another calculation required ?"
WRITE(4,*) " Type 1 to continue"
WRITE(4,*) " or 2 to finish."
READ(3,*) ICON
IF(ICON.EQ.1) GO TO 75
WRITE(4,*)
WRITE(4,*) "If you would like the results sent to the"
WRITE(4,*) "graph plotter type POOL.FILEPLOT when the"
WRITE(4,*) "READY prompt appears."
WRITE(4,*) " To rerun this program just type"
WRITE(4,*) "the instruction KCLGRUN ."
WRITE(4,*)
WRITE(4,*)
STOP

```

```

61 FORMAT(3(3X,D11.4))
62 FORMAT(2(3X,D11.4))
29 FORMAT("Point",5X,"[Ligand]",7X,"k obs",9X,"k calc",
1 9X,"Residual",/,)
39 FORMAT(I3,3X,4D14.4)
49 FORMAT("There were ",I3," experimental data points ;",
1 /,"requiring ",I3," iterations for satisfactory fitting.",
2 /)
59 FORMAT("The calculated coefficients were as follows :",
1 /," k1 had a value of ",G11.4," Mol dm-3 s-1",
2 " x 10-4 with a std. devn. of ",G11.4)
69 FORMAT(/," k2 had a value of ",G11.4," x 10-4",
1 " s-1 with a std. devn. of ",G11.4)
79 FORMAT(/," k3 had a value of ",G11.4," Mol dm-3 s-1",
1 " with a std. devn. of ",G11.4,/)
89 FORMAT(/,"The Overall Geviation of the fit was ",D11.4,
1 " x 10-4 s-1")
78 FORMAT("Point",5X,"[Ligand]",7X,"k obs",8X,"Std. devn.",
1 4X,"Weighting",/)
END
SUBROUTINE QLS(W,X,Y,N,C1,SC1,C2,SC2,C3,SC3,STD,ITR)
C Subroutine to convert input data to a linear least squares form
C by Taylor series expansion. Differential correction is then
C carried out for the supplied k1 , k2 and k3 rate constants.
DOUBLE PRECISION A(3,3),B(3),D(3),R(3),W(N),X(N),Y(N),
1L(3),Q,QP1,VSUM,C1,C2,C3,SC1,SC2,SC3,STD
ITR=0
1 ITR=ITR+1
VSUM=0.0D0
DO 12 I=1,3
B(I)=0.0D0
D(I)=0.0D0
R(I)=0.0D0
DO 12 J=1,3
A(I,J)=0.0D0
12 CONTINUE
DO 16 I=1,N
L(1)=X(I)
L(2)=X(I)/(C3+X(I))
L(3)=-C2*X(I)/((C3+X(I))**2)
Q=Y(I)-C1*X(I)-C2*X(I)/(C3+X(I))
VSUM=VSUM+W(I)*Q*Q
DO 16 J=1,3
D(J)=D(J)+Q*L(J)*W(I)
B(J)=D(J)
DO 16 K=1,3
A(K,J)=A(K,J)+L(J)*L(K)*W(I)
16 CONTINUE
CALL MINT(A,B)
R(1)=D(1)*A(1,1)+D(2)*A(2,1)+D(3)*A(3,1)
R(2)=D(1)*A(1,2)+D(2)*A(2,2)+D(3)*A(3,2)
R(3)=D(1)*A(1,3)+D(2)*A(2,3)+D(3)*A(3,3)
C1=C1+R(1)
C2=C2+R(2)
C3=C3+R(3)
IF(ITR.EQ.1) GO TO 17
IF(DABS(VSUM-QP1).LE.1.0D-4) GO TO 18

```

```

17 QP1=VSUM
   GO TO 1
18 CONTINUE
   STD=VSUM/(N-3)
   SC1=DSQRT(STD*A(1,1))
   SC2=DSQRT(STD*A(2,2))
   SC3=DSQRT(STD*A(3,3))
   STD=DSQRT(STD)
   RETURN
   END
   SUBROUTINE MINT(A,B)

```

C Subroutine to carry out a pivotted matrix inversion
C on supplied data.

```

   DOUBLE PRECISION A(3,3),B(3),DET,PIVMAX,PIVEL,
   1SAVE
   DIMENSION ISWTCH(3),JROW(3),JCOL(3)
   DET=1.0D0
   DO 10 J=1,3
10  ISWTCH(J)=0
   DO 70 I=1,3
   PIVMAX=0.0D0
   DO 30 J=1,3
   IF(ISWTCH(J)) 15,15,30
15  DO 20 K=1,3
   IF(ISWTCH(K)) 16,16,20
16  IF(DABS(PIVMAX)-DABS(A(J,K))) 17,20,20
17  IROW=J
   ICOL=K
   PIVMAX=A(J,K)
20  CONTINUE
30  CONTINUE
   ISWTCH(ICOL)=1
   IF(IROW-ICOL) 35,45,35
35  DET=-DET
   DO 40 L=1,3
   SAVE=A(IROW,L)
   A(IROW,L)=A(ICOL,L)
40  A(ICOL,L)=SAVE
   SAVE=B(IROW)
   B(IROW)=B(ICOL)
   B(ICOL)=SAVE
45  JROW(I)=IROW
   JCOL(I)=ICOL
   PIVEL=A(ICOL,ICOL)
   DET=DET*PIVEL
   A(ICOL,ICOL)=1.0D0
   DO 50 L=1,3
50  A(ICOL,L)=A(ICOL,L)/PIVEL
   B(ICOL)=B(ICOL)/PIVEL
   DO 70 J=1,3
   IF(J-ICOL) 55,70,55
55  PIVMAX=A(J,ICOL)
   A(J,ICOL)=0.0D0
   DO 60 L=1,3
60  A(J,L)=A(J,L)-A(ICOL,L)*PIVMAX
   B(J)=B(J)-B(ICOL)*PIVMAX
70  CONTINUE

```

```
RETURN
END
SUBROUTINE KCALC(STA,FIN,C1,C2,C3,U,V)
C This subroutine calculates the interpolated points
C needed to plot a smooth curve for the theoretical
C best fit when the plotter is called.
  DIMENSION U(200),V(200)
  DIFF=FIN-STA
  STEP=DIFF/190.0
  STA=STA-STEP*4.0
  U(1)=STA
  DO 10 I=2,200
  U(I)=U(I-1)+STEP
10 CONTINUE
  DO 20 I=1,200
  V(I)=C1*U(I)+C2*U(I)/(C3+U(I))
20 CONTINUE
  RETURN
  END
```

FIGURE A-5Library Subroutines.

```

SUBROUTINE LLS (W,X,Y,N,A1,AZ,SA1,SAZ,STD,COR)
C Subroutine to carry out a weighted linear regression
C analysis on data for which weighting factors have
C been pre-calculated. For reliable results the weights
C should be normalised.
  DIMENSION W(N),X(N),Y(N)
  WW=0.0
  WX=0.0
  WY=0.0
  WXY=0.0
  WXX=0.0
  WYY=0.0
  DO 10 I=1,N
  AW=W(I)
  AX=X(I)
  AY=Y(I)
  WW=WW+AW
  WX=WX+AW*AX
  WY=WY+AW*AY
  WXY=WXY+AW*AX*AY
  WXX=WXX+AW*AX*AX
10  WYY=WYY+AW*AY*AY
  DENOM=WW*WXX-WX*WX
  A1=(WW*WXY-WX*WY)/DENOM
  AZ=(WXX*WY-WX*WXY)/DENOM
  VSUM=0.0
  DO 20 I=1,N
20  VSUM=VSUM+W(I)*((Y(I)-AZ-A1*X(I))**2)
  SS=VSUM/(N-2)
  STD=SQRT(SS)
  SA1=SQRT(SS*WW/DENOM)
  SAZ=SQRT((SS/WW)*(1.0+((WX*WX)/DENOM)))
  COR = SQRT((A1*A1*(WXX-WX*WX/WW))/(WYY-WY*WY/WW))
  IF(COR.GT.1.00000) COR=1.00000
  RETURN
  END

FUNCTION XMINF(X,N)
C This function finds the minimum value in the
C user supplied list.
  DIMENSION X(N)
  XMINF=X(1)
  DO 10 I=1,N
10  XMINF=AMIN1(XMINF,X(I))
  RETURN
  END

FUNCTION XMAXF(X,N)
C This function finds the maximum value in the
C user supplied list.
  DIMENSION X(N)
  XMAXF=X(1)
  DO 10 I=1,N
10  XMAXF=AMAX1(XMAXF,X(I))
  RETURN

```

```

END
SUBROUTINE REDIN(X,Y,Z,W,N,IAR,IFILE)
C Subroutine to read in data in free format.
DIMENSION X(100),Y(100),Z(100),W(100)
IF(IFILE.EQ.2) GO TO 10
IFSUM=0
IFP1=0
IF(IAR) 12,13,14
12 CONTINUE
IFP1=IFSUM+1
READ(3,*,END=15) X(IFP1),Y(IFP1)
IFSUM=IFSUM+1
GO TO 12
13 CONTINUE
IFP1=IFSUM+1
READ(3,*,END=15) X(IFP1),Y(IFP1),Z(IFP1)
IFSUM=IFSUM+1
GO TO 13
14 CONTINUE
IFP1=IFSUM+1
READ(3,*,END=15) X(IFP1),Y(IFP1),Z(IFP1),W(IFP1)
IFSUM=IFSUM+1
GO TO 14
15 CONTINUE
N=IFSUM
RETURN
10 CONTINUE
WRITE(4,*)
WRITE(4,*) "How many data points are there in the set ?"
READ(3,*) N
WRITE(4,*)
WRITE(4,*) "Now type in the data :"
IF(IAR) 22,23,24
22 CONTINUE
READ(3,*) (X(I),Y(I),I=1,N)
RETURN
23 CONTINUE
READ(3,*) (X(I),Y(I),Z(I),I=1,N)
RETURN
24 CONTINUE
READ(3,*) (X(I),Y(I),Z(I),W(I),I=1,N)
RETURN
END
SUBROUTINE VALIN(X,Y,Z,W,N,IAR,IFILE)
C Subroutine to validate data input .
DIMENSION X(100),Y(100),Z(100),W(100),MSUB(25)
31 CONTINUE
WRITE(4,*)
WRITE(4,*) "          Validation of input data"
WRITE(4,*) "          -----"
WRITE(4,*)
WRITE(4,*) "          The data has been sorted according to"
WRITE(4,*) "          increasing X coordinate value."
WRITE(4,*)
DO 55 I=1,N-1
DO 55 J=I+1,N
IF(X(J).GE.X(I)) GO TO 55

```



```

XCH=X(I)
XHC=X(J)
YCH=Y(I)
YHC=Y(J)
ZCH=Z(I)
ZHC=Z(J)
WCH=W(I)
WHC=W(J)
X(I)=XHC
X(J)=XCH
Y(I)=YHC
Y(J)=YCH
Z(I)=ZHC
Z(J)=ZCH
W(I)=WHC
W(J)=WCH
55 CONTINUE
   IF(IAR) 32,33,34
32 CONTINUE
   WRITE(4,61) (I,X(I),Y(I),I=1,N)
   GO TO 35
33 CONTINUE
   WRITE(4,161) (I,X(I),Y(I),Z(I),I=1,N)
   GO TO 35
34 CONTINUE
   WRITE(4,261) (I,X(I),Y(I),Z(I),W(I),I=1,N)
35 CONTINUE
61  FORMAT(3X,I3,3X,2G14.6)
161 FORMAT(3X,I3,3X,3G14.6)
261 FORMAT(3X,I3,3X,4G14.6)
   WRITE(4,*)
   WRITE(4,*) "Is the data satisfactory ?"
   WRITE(4,*) "  To continue type 1"
   WRITE(4,*) "otherwise type 2 to correct"
   WRITE(4,*) "data or choose another data source."
   READ(3,*) IDAT
   IF(IDAT.EQ.1) GO TO 43
   WRITE(4,*)
   WRITE(4,*) " Type 0 to have another look at the data ;"
   WRITE(4,*) "      1 to correct existing data ;"
   WRITE(4,*) "      2 to add new data to the set;"
   WRITE(4,*) "      3 to remove selected data from the set ;"
   WRITE(4,*) " or      4 to reselect the method of data input:"
   WRITE(4,*) "      i.e. select another data file or transfer to"
   WRITE(4,*) "      input from a terminal."
   READ(3,*) IED
   IF(IED.EQ.0) GO TO 31
   IF(IED.EQ.1) GO TO 44
   IF(IED.EQ.2) GO TO 42
   IF(IED.EQ.3) GO TO 45
   GO TO 101
42 CONTINUE
   WRITE(4,*)
   WRITE(4,*) "How many points do you wish to add ?"
   READ(3,*) NAD
   N1=N+NAD
   WRITE(4,*)

```

```

WRITE(4,*) "Now type in the additional data,"
WRITE(4,*) "with the values for each new point on"
WRITE(4,*) "on a separate line."
IF(IAR) 36,37,38
36 CONTINUE
READ(3,*) (X(I),Y(I),I=N+1,N1)
GO TO 39
37 CONTINUE
READ(3,*) (X(I),Y(I),Z(I),I=N+1,N1)
GO TO 39
38 CONTINUE
READ(3,*) (X(I),Y(I),Z(I),W(I),I=N+1,N1)
39 CONTINUE
N=N1
GO TO 31
45 CONTINUE
WRITE(4,*)
WRITE(4,*) "How many points do you wish to remove ?"
READ(3,*) NSUB
N=N-NSUB
WRITE(4,*)
WRITE(4,*) "Now list the points to be removed,"
WRITE(4,*) "on a single line, separated by commas."
READ(3,*) (MSUB(I),I=1,NSUB)
DO 75 I=1,NSUB
JSUB=MSUB(I)
X(JSUB)=98.765
75 CONTINUE
NCT=0
DO 85 I=1,N+NSUB
XC=X(I)-98.765
IF(ABS(XC).LE.0.001) GO TO 85
NCT=NCT+1
X(NCT)=X(I)
Y(NCT)=Y(I)
Z(NCT)=Z(I)
W(NCT)=W(I)
85 CONTINUE
GO TO 31
44 CONTINUE
WRITE(4,*)
WRITE(4,*) "How many many points need correcting ?"
READ(3,*) NDT
WRITE(4,*)
WRITE(4,*) "Now list the points to be corrected,"
WRITE(4,*) "on a single line, separated by commas."
READ(3,*) (MSUB(I),I=1,NDT)
DO 98 I=1,NDT
IDT=MSUB(I)
WRITE(4,*)
WRITE(4,*) " The current values for point",IDT," are :"
IF(IAR) 92,93,94
92 CONTINUE
WRITE(4,61) IDT,X(IDT),Y(IDT)
GO TO 95
93 CONTINUE
WRITE(4,161) IDT,X(IDT),Y(IDT),Z(IDT)

```

```

GO TO 95
94 WRITE(4,261) IDT,X(IDT),Y(IDT),Z(IDT),W(IDT)
95 CONTINUE
WRITE(4,*)
WRITE(4,*) "Now type in the correct values."
IF(IAR) 62,63,64
62 CONTINUE
READ(3,*) X(IDT),Y(IDT)
GO TO 65
63 CONTINUE
READ(3,*) X(IDT),Y(IDT),Z(IDT)
GO TO 65
64 CONTINUE
READ(3,*) X(IDT),Y(IDT),Z(IDT),W(IDT)
65 CONTINUE
98 CONTINUE
GO TO 31
101 CONTINUE
IFILE=4
43 RETURN
END

```

```

SUBROUTINE SDN(N,X,XM,SDX)

```

C Subroutine to find the mean and standard deviation
C of a list of supplied numbers.

```

DIMENSION X(100)
XM=0.0
SDX=0.0
X1=0.0
X2=0.0
DO 15 I=1,N
X1=X1+X(I)
X2=X2+X(I)*X(I)
15 CONTINUE
XM=X1/N
SDX=X2-(X1*X1/N)
SDX=SDX/(N-1)
SDX=SQRT(SDX)
RETURN
END

```

References for Appendix A.

1. J.H.van der Maas, "Basic Infrared Spectroscopy", Heyden and Sadtler, London, 1967.
2. T.L.Isenhour and P.C.Jurs, "Introduction to Computer Programming for Chemists : Fortran", 2nd ed., Allyn and Bacon, Boston, 1979.

APPENDIX B: DERIVATION OF THE RATE LAW FOR DIENE EXCHANGE.

The rate law used to describe the diene exchange reactions covered in Chapter Three can be derived in terms of the substrate (S), entering group (L), and intermediates (A) and (B) of FIGURE 3-2. The derivation is as follows:

$$\frac{d[A]}{dt} = \frac{k_1[S] + k_{-2}[B]}{k_{-1} + k_2[L]}$$

$$\frac{d[B]}{dt} = \frac{k_a[S][L] + k_2[A][L]}{k_{-a} + k_{-2} + k_3}$$

This may be rearranged to give the following:

$$\frac{d[B]}{dt} = [S][L] \left\{ \frac{(k_1k_2 + k_{-1}k_a) + k_ak_2[L]}{(k_{-a}k_{-1} + k_{-2}k_{-1} + k_3k_{-1}) + [L]y} \right\}$$

$$\text{where } y = (k_{-a}k_2 + k_3k_2)$$

The equation now has the general form:

$$\frac{d[B]}{dt} = [S][L] \left\{ \frac{w + x[L]}{u + z[L]} \right\}$$

Rearranging:

$$\frac{d[B]}{dt} = [S][L] \left\{ \frac{x + \frac{wz - xu}{z + z(u + z[L])}}{z + z(u + z[L])} \right\}$$

Substituting the partial rate constants into the expression:

$$\frac{d[B]}{dt} = \left\{ \frac{[S][L]}{k_{-a} + k_3} \right\} \frac{\left\{ (k_1 k_2 k_{-a} + k_1 k_2 k_3 - k_a k_{-2} k_{-1}) \right\}}{\left\{ (k_{-a} k_{-1} + k_{-2} k_{-1} + k_3 k_{-1}) + (k_{-a} k_2 + k_3 k_2) [L] \right\}} + k_a$$

Using this expression it is now possible to determine $d[S]/dt$ and the equation has the form:

$$\frac{d[S]}{dt} = \left\{ k_\alpha [L] + \frac{k_\beta [L]}{k_\gamma + k_\delta [L]} \right\} [S]$$

k_α , k_β , k_γ , and k_δ are composite terms corresponding to the following groupings of partial rate constants:

$$k_\alpha = \frac{k_3 k_a}{k_{-a} + k_3}$$

$$k_\beta = \frac{k_3 (k_1 k_2 k_{-a} + k_1 k_2 k_3 - k_a k_{-2} k_{-1})}{\{ k_{-a} + k_3 \}}$$

$$k_\gamma = k_{-a} k_{-1} + k_{-2} k_{-1} + k_3 k_{-1}$$

$$k_\delta = k_{-a} k_2 + k_3 k_2$$

The expression will be seen to be identical to that quoted in Chapter Three.