A STUDY OF REACTIONS INVOLVING ORGANOMETALLIC FREE RADICAL INTERMEDIATES

BY

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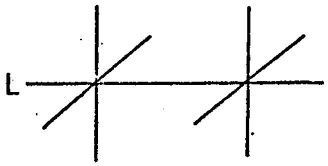
NOTES ON NOMENCLATURE

Structural isomers exist for many of the dimeric and monomeric complexes discussed in this Thesis. These are shown in the figures below, together with the naming conventions which will be used throughout the text. (In all cases the carbonyl groups have been omitted for clarity).



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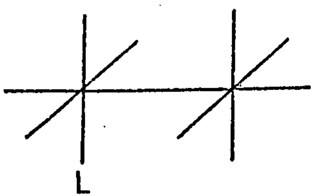

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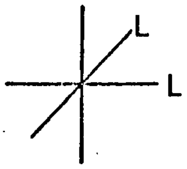

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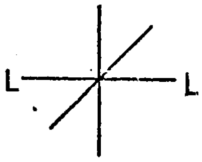

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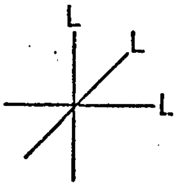

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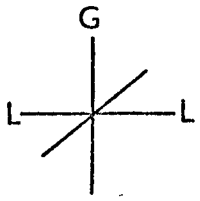

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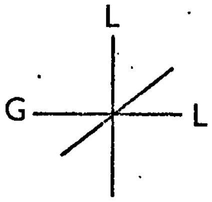
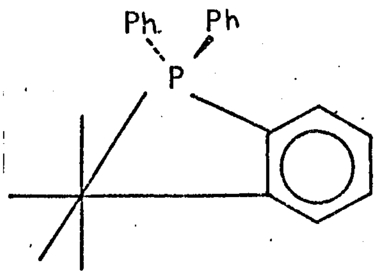


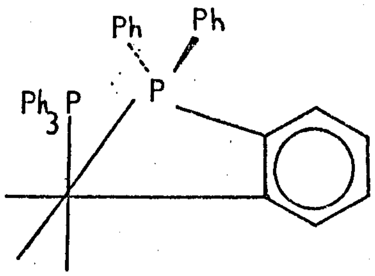
mer-cis

* names apply even if L's are different

Metalated species such as those shown in I and II are designated by $Re(CO)_4(L-H)$ and $Re(CO)_3L(L-H)$ respectively.



I



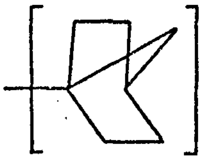
II

For the neutral products formed by the reduction of cyclo-olefin cationic derivatives of the Group VIA and VIII metal carbonyls, endo , III, and exo, IV, isomers are possible:

III

IV

Where formulae are written in the text, the customary abbreviations are used:

cp	η^5-cyclopentadienyl
py	pyridyl
bipy	2.2′-bipyridyl
ν triars	tris-1,1,1-dimethylarsionomethylethane
diphos	1,2-diphenylphosphinoethane
norbornyl	bicyclo(2,2,1)hept-1-yl; 
diars	o-phenylenebisdimethylarsine
CHT	cycloheptarienyl

References are given in parentheses, compounds by Roman numerals, and oxidation states by Roman numerals in parentheses.

SUMMARY

A study of the reaction between decacarbonyldirhenium and triphenylphosphane has been completed. Contrary to previous reports, no paramagnetic complexes could be isolated, although they are implicated in the reaction scheme. The major products of this reaction have been found to be mer-trans-$HRe(CO)_3(PPh_3)_2$ and bis- ax- $Re_2(CO)_8(PPh_3)_2$; and it has been shown that water in the xylene solvent is the source of the hydride ligand in the former.

Preparative thin layer chromatography of the residual reaction mixture resulted in the isolation and identification of a further four components, and based partly upon the nature of these complexes and their reactivities a complete reaction scheme has been constructed. The transient presence of radicals in this sequence has been demonstrated by several independant techniques.

In seeking to stabilise mononuclear rhenium-centred radicals, reactions with organophosphanes and phosphites that are approaching the extremes of the range of electronically transmitted effects, as well as those capable of shielding the metal because of their bulk, have been investigated. These attempts all failed to provide the necessary stabilisation, but experiments with these ligands yielded some novel cyclometalated complexes as opposed to the hydrides isolated with triphenylphosphane. This change is discussed in terms of stereochemistry and the favoured nature of five membered metalation rings. This latter feature has been demonstrated in the present work by proton NMR studies.

The generation of $Re(CO)_5^{\bullet}$ radicals under milder conditions has been achieved by the chemical oxidation of the pentacarbonylrhenium anion. Although this seventeen electron complex could not be isolated, its presence was confirmed by the nature of the isolated reaction products.

The chemical reduction of cations derived from some cyclo-olefin complexes of the Group VIA and Group VIII metal carbonyls has also been used to generate radical intermediates. However, only dimers formed by coupling of these intermediates could be isolated. The site of dimerisation is governed by the nature of the highest occupied molecular orbital in the radical intermediate.

CHAPTER 1

PARAMAGNETIC CARBONYL AND ORGANOMETALLIC COMPLEXES

INTRODUCTION

A study of the growing volume of published organometallic chemistry reveals that much of it overlaps with that of free-radicals (1,2). Not only are numerous stable species paramagnetic, but the transient existance of others is invoked in many reaction mechanisms.

This chapter is intended to serve as an introduction to the literature, and takes the form of a review of the free-radical organometallic chemistry of the elements of groups IVA to VIII; each triad being considered in turn. In this context, organometallic compounds are taken as those having at least one metal-carbon bond, although some closely related complexes in which phosphanes or phosphites are the only ligands are included for completeness.

The chapter is divided into two sections: (I) Organometallic paramagnetic compounds of the transition elements; and (II) Some reactions of organometallic complexes in which free-radicals are involved in the mechanism. Class (I) may be further divided into compounds in which the unpaired electron density is localised principally on the metal, I, or on the ligand, II:

$$\underset{\text{I}}{\dot{M}L} \qquad\qquad\qquad \underset{\text{II}}{M^{1}L\text{--------}\cdot}$$

The former belong to a wider group which encompasses not only organometallics such as $Cr[CH(SiMe_3)_2]_3$ (3) but also inorganics such as $CrCl_3$. Stable paramagnetic compounds of these types are seldom referred to as "radicals" since this term has traditionally had the connotation of species of low kinetic stability. This distinction is clearly recognised here but it is felt more useful to have a complete review than to make what, in some cases, must be arbitary decisions on whether a particular example is worthy of inclusion. The problems associated with attempting to define a set of criteria for conferring "radical" status on paramagnetic complexes are currently the centre of much discussion (3a). It is felt that either the ability of compoundsto dimerise, or a consideration of the directional nature of the orbital in which the odd electron resides may be two possible methods for classifying molecules into "radical" or "non-radical" species.

Although the first direct demonstration of the existance of a transient alkyl free-radical involved an organometallic system of the type given in equation 1 (4) the topic of free-radical chemistry in this field remained largely neglected until the last decade:

$$LM + R^{\bullet} \rightleftharpoons LMR \qquad 1$$

This observation was made by Paneth (4) during the pyrolysis of tetramethyllead and the recombination of methyl radicals with metallic lead, zinc, antimony, bismuth or beryllium. Further comment on main group compounds is outside the scope of this work, but reference is made to several excellent published reviews on this subject (5-8).

In contrast to the present state of affairs in organic chemistry, the chemical properties of odd electron organo-transition metal species are not well known. This is particularly true for the carbonyls, where the vast majority of well characterised compounds are spin paired. Nevertheless, a number of paramagnetic species are stable under ambient conditions, and relevant ligands include CO; R^-; olefin; $(\eta^5\text{-}C_5H_5)^-$ or η-arene. The complexes themselves may be neutral, eg $V(CO)_6$; $Cr(CH_2SiMe_3)_4$; $Cr[CH(SiMe_3)_2]_3$; anionic, eg $Os(CO)_{12}{}^-$; $Cr(CH_2SiMe_3)_4{}^-$; or cationic eg $Cr(\eta^6\text{-}ArH)_2{}^+$. Both electron delocalisation from the metal to the organic ligands and steric effects have been invoked to explain the stability of compounds of this type. The former feature is particularly applicable to π bonding ligands, whereas the stability of metal alkyls is ascribed to steric crowding around the metal, thereby preventing reaction; and to the exclusion of normal decomposition pathways such as β-elimination. (see for example ref 9).

This is the predominant route for destruction of metal-carbon bonds (10) and is illustrated by equation 2.

$$M - CH_2CH_2R \rightleftharpoons MH + CH_2 = CHR \qquad 2$$

This reaction can be inhibited if (a) there is a group of the type $M\text{-}CH_2XHR$ where X is any atom that can form a single, but not a double, bond to carbon, or (b) the β carbon atom in the alkyl chain bears atoms nor group of atoms which cannot be as readily transferred to the metal as hydrogen. A large number of groups fulfil these requirements, eg $(\text{-}CH_2SnR_3)$, $(\text{-}CH_2Mn(CO)_5)$ and (-1-norbornyl).

By analogy with some of the chemistry of carbon compounds one may expect that free-radical organometallic species could be generated by the following methods:

(a) homolysis of an M-C or M-M bond (11)

(b) atom abstraction, as of H from $HRe(CO)_5$ (12) or Cl from $ClRe(CO)_5$

(c) outer sphere electron transfer oxidation of an 18 electron species, as in the reaction of decacarbonyldimanganese with tetracyanoethylene(13) or with NO^+ (14)

(d) electrochemical oxidation or reduction of a stable 18 electron compound, eg oxidation of $Cr(CO)_6$ (15) or $(\eta^5-C_5H_5)Mn(CO)L_2$ (14); and reduction of $M(CO)_6$ (16)

(e) chemical oxidation and reduction of anions and cations eg the oxidation of $(\eta^5-C_5H_5)Cr(CO)_3{}^-$ with tropylium bromide (17) or the reductive dimerisation of $(\eta^5-C_6H_7)Fe(CO)_3{}^+$ by means of a zinc/copper couple (18)

(f) from paramagnetic precursors such as $V(CO)_6$ or compounds of Ti(III); or by reactions which result in oxidation states with electrons in a paramagnetic configuration.

(g) by the co-condensation of metal atoms with carbon monoxide in inert matrices at low temperatures (19)

PART I

Some examples of known paramagnetic species in a particular Group are given in the tables which preface each section of this part of Chapter 1. The designation of oxidation state may in some cases be somewhat formal, and in some instances it may be more appropriate to describe a molecule as being derived from a paramagnetic ligand such as nitroxide.

Group IVA: Titanium, Zirconium, Hafnium

TABLE 1

Paramagnetic species of Group IVA metals

Ion	Compounds	Reference
d^1 Ti (III)	$Ti(\eta^5-C_5H_5)_2(SR)_2$	20
	$(\eta^5-C_5H_5)_2TiR$	21
	$(\eta^5-C_5H_5)_2TiH_2AlH_2$	22
	$(\eta^5-C_5H_5)TiH_2M$ M = Na; Li; MgBr	23
	$(\eta^5-C_5H_5)Ti(\eta^8-C_8H_8)$	24
Zr(III)	$Zr(\eta^5-C_5H_5)_2(PPh_2)_2{}^-$	25

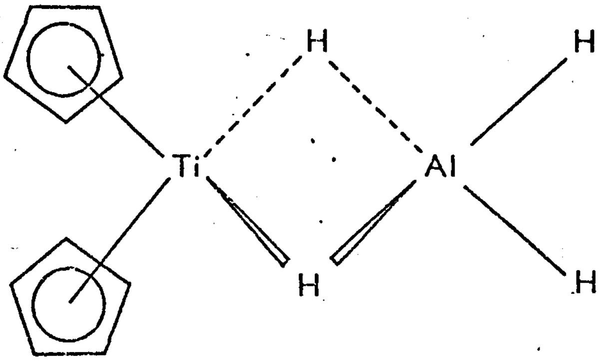
d^1Ti (III)

The complex $(\eta^5\text{-}C_5H_5)TiH_2AlH_2$ has been prepared (22) in solution by reacting $[(\eta^5\text{-}C_5H_5)TiCl]_2$ with $LiAlH_4$ in THF, presumably according to equation 3.

$$[(\eta^5\text{-}C_5H_5)TiCl]_2 + 2LiAlH_4 \longrightarrow 2\ (\eta^5\text{-}C_5H_5)_2TiH_2AlH_2 + 2LiCl \qquad 3$$

The dimeric $[(\eta^5\text{-}C_5H_5)_2TiCl]_2$ was prepared beforehand by the reduction of $(\eta^5\text{-}C_5H_5)_2TiCl_2$ with lithium naphthalenide (Li/Ti = 1) and was identified by its ESR signal. It has also been reported elsewhere (26). The synthesis is similar to that reported by Nöth (27) for the preparation of $(\eta^5\text{-}C_5H_5)_2TiH_2BH_2$ from $(\eta^5\text{-}C_5H_5)_2TiCl_2$ and $NaBH_4$, except for the intermediate preparation of the dimeric Ti(III) species.

The structure of this compound has been given as III.

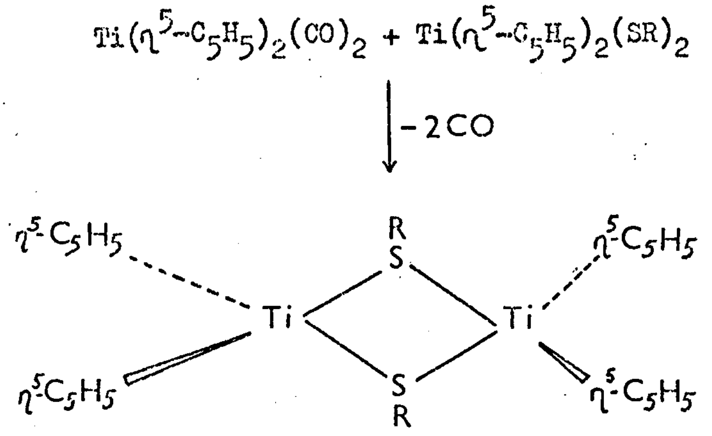


III

This is based upon that found for the corresponding tetra-chloro-compound $(\eta^5\text{-}C_5H_5)_2TiCl_2AlCl_2$ (28), in which both metal atoms are in essentially tetrahedral environments linked by three centre bonds.

The molecule $(\eta^8\text{-}C_8H_8)Ti(\eta^5\text{-}C_5H_5)$ is an extremely air sensitive material which must be handled under vacuum (24,29). Its structure has been elucidated using X-ray techniques (30) and it appears to be a "sandwich type" molecule very similar to $(\eta^5\text{-}C_5H_5)V(\eta^7\text{-}C_7H_7)$ (31). In both of these compounds the unpaired electron is in an a_{1g} orbital, which is essentially d_{z^2} in character. Both rings are planar, and parallel to each other to within ± 1.9°.

Di-μ-alkylthio and di-μ-arylthio-bis[bis (η^5-cyclopentadienyl)] titanium (III) complexes are known (20). These compounds, with the structure IV have been synthesised by reacting $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$ with the appropriate bis(alkylthio)bis(η^5-cyclopentadienyl)titanium (IV) derivative:

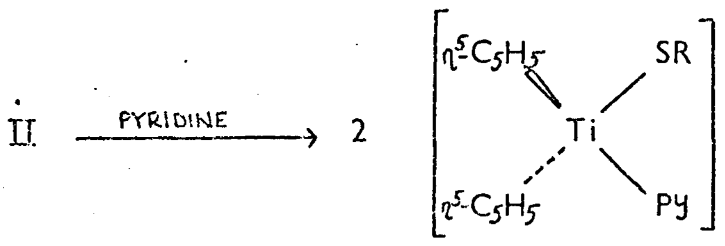


IV

This reaction can be used as a general synthetic route to titanium (III) derivatives of the type $(\eta^5\text{-}C_5H_5)_2Ti(\mu X)_2Ti(\eta^5\text{-}C_5H_5)_2$ where X = halogen (32), O or S. Reaction of titanocene with disulphides is also reported to give similar products (33).

The dimeric compounds IV were prepared by refluxing a toluene solution of the reagents for some thirty minutes. Rapid evolution of carbon monoxide was observed during the crystallisation of the product. The particular complex IV in which R = Ph is also available via the displacement of chloride from $(\eta^5\text{-}C_5H_5)_2Ti(\mu Cl)_2Ti(\eta^5\text{-}C_5H_5)_2$ using Na(SPh) (20).

The bridged dimers are generally insoluble in non-coordinating solvents; but in coordinating media dissolution seems to occur through bridge splitting reactions:



V

It is not possible to isolate products such as V from solution (32); evaporation of the brown pyridine solutions or addition of heptane or toluene always results in the separation of IV.

All of the derivatives of the type IV were found to be paramagnetic (Table 2) but with reduced magnetic moments. These lower values were taken as being a consequence of unpaired spin interaction via the sulphur bridges.

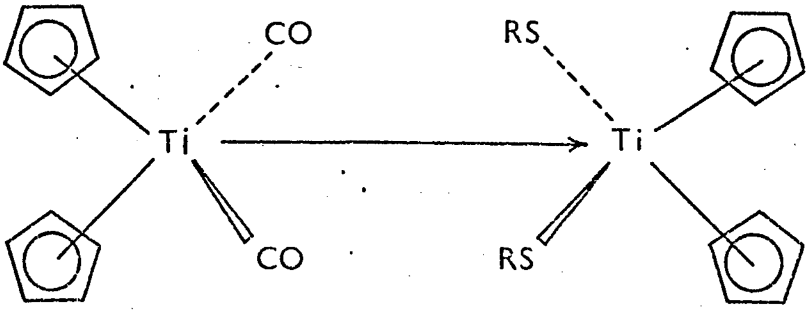
TABLE 2

Magnetic moments of some dimeric Ti (III) species

Complex	μeff/BM*	(T/K)
$(\eta^5\text{-}C_5H_5)_2Ti(\mu SPh)_2Ti(\eta^5\text{-}C_5H_5)_2$	1.43	(291)
$(\eta^5\text{-}C_5H_5)_2Ti(\mu SC_6H_4Me)_2Ti(\eta^5\text{-}C_5H_5)_2$	1.43	(292)
$(\eta^5\text{-}C_5H_5)_2Ti(\mu SEt)_2Ti(\eta^5\text{-}C_5H_5)_2$	1.13	(295)

* 1 BM = $0{,}927 \times 10^{-23}$ Am ^{2}

The preparative route itself deserves some comment. It can be interpreted as the result of an interaction between acidic Ti (IV) and basic Ti(II) species. This acid/base intermediate VI is not isolated, but arises as a consequence of reduced electron density at titanium (II) corresponding to decreased back bonding to CO.

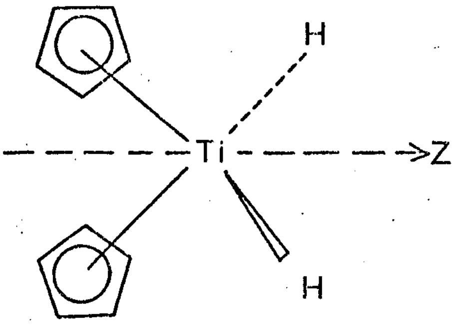


VI

It has been demonstrated that complexes such as IV can absorb carbon monoxide at one atmosphere pressure at room temperature to give $Ti(\eta^5\text{-}C_5H_5)_2(CO)_2$ and $Ti(\eta^5\text{-}C_5H_5)_2(SR)_2$ in quantitative yields. This assymetric splitting (together with supporting mass spectral data) shows that the complexes behave as adducts of the units $Ti(\eta^5\text{-}C_5H_5)_2$ and $Ti(\eta^5\text{-}C_5H_5)_2(SR)_2$.

The ESR spectra of a series of Ti(III) hydrides have been studied (23). These compounds are of the general formula $(\eta^5\text{-}C_5H_5)_2TiH_2M$, where M = Na, Li or MgBr.

An approximate tetrahedral environment is postulated for the titanium atom (34) with the unpaired electron in the $d_z{}^2$ orbital. This is taken to lie along the symmetry axis between the cyclopentadiene rings, bisecting the H-Ti-H angle, as shown in VII.

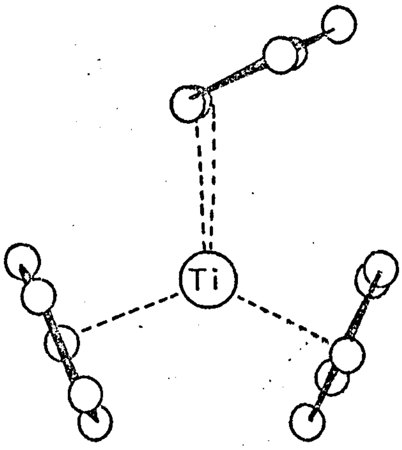


VII

These hydrides may be written as $(\eta^5\text{-}C_5H_5)_2TiH_2^-M^+$ in the case of the ionic sodium and lithium compounds, and $(\eta^5\text{-}C_5H_5)_2TiH_2\cdot MgBr$ for the more covalent species. The metal-hydrogen interaction will become progressively more ionic and less directional in going from Group III to Group I.

While titanium forms stable compounds of composition $(\eta^5\text{-}C_5H_5)_2Ti^{(IV)}R_2$, complexes of the type $(\eta^5C_5H_5)_2Ti^{(III)}R$ (R = alkyl or aryl) are extremely unstable and as yet have not been isolated. In $(\eta^5\text{-}C_5H_5)_2Ti^{(III)}C_3H_5$ and homologues, the allyl group is π bonded to the metal (35). It has been suggested that complexes containing the $(\eta^5\text{-}C_5H_5)_2Ti^{(III)}$ moiety are stable only if two further coordination sites are occupied. Acccordingly, $(\eta^5\text{-}C_5H_5)_2Ti_2Cl_2$, where chlorine forms bridges between the metal atoms, is a stable entity. However, since alkyl and aryl groups are far less effective as bridging ligands, stabilisation of $(\eta^5\text{-}C_5H_5)_2TiR$ by dimerisation is not possible. It is believed that this is the reason why compounds of this latter type have not been prepared.

The structure of the paramagnetic molecule$(C_5H_5)_3Ti$, VIII, first prepared in 1960 (36) has recently been reported (37). In this molecule, two cyclopentadienyl groups from five equivalent M-C bonds, while the third adopts an unusual position in which only two adjacent carbon atoms are at bonded distances from the metal. This latter group acts as a 4 electron ligand, resulting in the complex being overall a 17 electron species. The distortion of the third ring is necessary in order to relieve steric interaction between the ligands.



VIII

Zr(III) and Hf(III)

Little work has been reported on the paramagnetic complexes of these two elements. The reduction of $(\eta^5\text{-}C_5H_5)_2ZrCl_2$ with $NaPPh_2$ is reported to yield a product whose ESR spectrum suggested two equivalent phosphorus atoms. The postulated structure which would give rise to such a pattern is $[(\eta^5\text{-}C_5H_5)_2Zr(PPh_2)_2]^-$ (25).

Group VA: Vanadium, Niobium, Tantalum

TABLE 3

Paramagnetic species of Group VA metals

Ion	Compounds	Reference
d^1 V(IV)	$(\eta^5\text{-}C_5H_5)_2VCl_2$	38
	$(\eta^5\text{-}C_5H_5)_2V(SR)_2$	20
	$(\eta^5\text{-}C_5H_5)_2V(X)_2$	
	X = SCN; OCN; CN	39
	$(\eta^5\text{-}C_5H_5)_2V(C\equiv CC_6H_5)_2$	40
	$V(CH_2Ph)_4$	41
	$V(CH_2SiMe_3)_4$	42, 39
	$V(1\text{-norbornyl})_4$	43
	$V(\eta^8\text{-}C_8H_8)_2$	24
	$V(\eta^3\text{-}C_3H_5)Cl_3$	44
Nb (IV)	$(\eta^5\text{-}C_5H_5)_2NbH_2$	45
	$(\eta^5\text{-}C_5H_5)2NbCl_2$	46
	$(\eta^5\text{-}C_5H_5)_2NbX_2$	
	X = SCN; OCN; CN	39
	$(\eta^5\text{-}C_5H_5)_2NbR_2$	45
Ta (IV)	$(\eta^5\text{-}C_5H_5)_2TaCl_2$	47, 45
	$(\eta^5\text{-}C_5H_5)_2TaR_2$	45
d^2 V(III)	$(\eta^5\text{-}C_5H_5)_2VX$ X = Cl, Ph, SR	20, 1
	$(\eta^5\text{-}C_5H_5)_2V(C\equiv CC_6H_5)$	40
d^3 V(II)	$(\eta^5\text{-}C_5H_5)_2V$	48
d^5 V(0)	$V(CO)_6$	1
	$V(\eta\text{-arene})_2$	49
	$(\eta^5\text{-}C_5H_5)V(\eta^7\text{-}C_7H_7)$	31
Nb (0)	$(\eta^5\text{-}C_5H_5)Nb(\eta^7\text{-}C_7H_7)$	50

d^5 V(0)

In the zero oxidation state, vanadium is paramagnetic, so the hexacarbonyl occupies what may be considered to be an unique position in that this is the only commonly encountered binary carbonyl which has this property. It exists as black crystals, which give yellow-orange solutions. It is easily reduced by sodium to give the hexacarbonyl anion.

It was first reported in 1960 by two groups of workers (51, 52). The preparation was carried out in diglyme solution according to the following scheme:

$$\begin{tikzcd}
VCl_3 + CO + Na \arrow[r, "100^\circ C", "250\ atm"'] & Na(diglyme)_2^+\ V(CO)_6^- \arrow[d, "+H_3PO_4"] \\
V(CO)_6 & HV(CO)_6 \arrow[l]
\end{tikzcd}$$

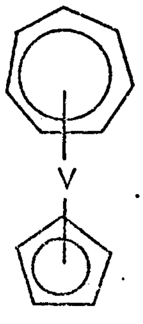
The dimeric $V_2(CO)_{12}$ has been reported (51) as a blue solid. NMR and ESR spectroscopy has confirmed its diamagnetism in both solid in solution. More recent work has shed doubt on this and it is generally accepted that vanadium hexacarbonyl is isomorphous with the monomeric chromium complex, and has a magnetic moment close to that expected for one unpaired electron (experimental value 1.81 BM at 20° in toluene or benzene).

Tertiary phosphines are also well know to stabilise low oxidation states. Thus VCl_3 in THF in the presence of 1,2,bisdimethylphosphinoethane can be reduced by sodium naphthalenide to the deep brown zero-valent complex $V[Me_2P(CH_2)_2PMe_2]_3$ (53).

This particular compound is thermally stable but easily oxidised in air. Its magnetic moment at 2.10 BM suggests the spin paired t_{2g}^5 configuration. The evidence is in favour of the compound being an octahedrally coordinated monomer. Triethyl-, triphenyl- and tri-n-propyl phosphine form red-brown complexes of the type $V(CO)_4L_2$ on treatment with vanadium hexacarbonyl (54). These compounds are monomeric and have magnetic moments of 1.79 BM; and the presence of only one IR band suggests that the phosphine groups substitute in the trans arrangement.

Tricyclohexylphosphine reacts with the hexacarbonyl to form the yellow dimeric complex $[V(CO)_4L_2]_2$. The structure of this molecule is not known but it may contain phosphine bridges in which case each vanadium atom would be two electrons short of the favoured inert gas configuration. Derivatives of phosphine itself are also known.

King and Stone, who first prepared $(\eta^5-C_5H_5)V(\eta^7-C_7H_7)$, IX, in 1959 (55) reported the complex to be paramagnetic with one unpaired electron



IX

The crystal structure was determined by Engebretsan and Rundle (56) who confirmed the π sandwich type structure of the molecule. The perpendicular distance from vanadium to the five membered ring was found to be 1,90 Å, while that to the seven membered ring was 1.50Å. All metal-carbon distances were equal within experimental error. This particular compound (also known by another route (57)) has been studied by ESR and NMR (31). In the solid state, the NMR showed two broad lines: one at -310 ppm (with respect to external water) of line width 15000 Hz for C_7H_7; and one at -130 ± 5 ppm of line width 12000 Hz for C_5H_5.

Sandwich type compounds are also known with condensed arene molecules. Thus the reaction of VCl_3 with lithium naphthalenide (LiNp) in THF ($LiNp/VCl_3 = 3$, corresponding to the stoichiometric amount of reagent for effecting the reduction of V(III) to V(0)) leads to a dark homogenous solution exhibiting an ESR spectrum which suggests that only one ring of each naphtalene molecule is interacting with the metal (49). At higher ratios of LiNp/V, for example if $LiNp/V \geqslant 4$, the ESR signal is practically absent. A reasonable explanation for this observation would be a further electron transfer from naphthalenide anions to the V(0) complex providing a pairing of the so far unpaired electron. In the range $5 \leqslant LiNp/V \geqslant 6$, a new, although relatively weak ESR spectrum is observed which is attributed to V(-III)species.

From these observations it follows that excess LiNp can be used for further reduction, and that no ESR signal for this molecule can be detected for $LiNp/V < 6$ indicates that vanadium cannot be reducedbeyond V(-III).

If the vanadium (III) chloride is reduced with lithium anthracenide, an ESR signal identical to that observed with the naphthalenide anion is found suggesting that a bisarene compound is also formed with anthracene, again making use of only one of the outer rings of each molecule.

Dibenzenevanadium, $(\eta^6-C_6H_6)_2V$, was first prepared by Fischer and Kögler in 1957 (58) as follows:

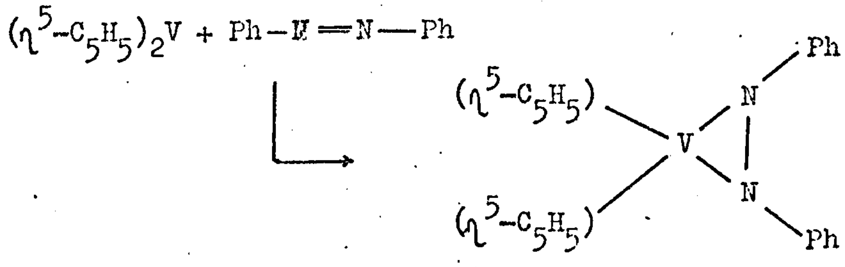
$$VCl_4 + Al + 2C_6H_6 \xrightarrow{AlCl_3} V(C_6H_6)_2\ AlCl_4.$$

The orange paramagnetic reaction product was then hydrolysed to give dibenzenevanadium (0) and a derivative of vanadium (V). The compound forms as red/brown crystals, which, in the absence of air, form stable solutions in the common organic solvents and water. It may be sublimed in high vacuum at 120-125° and it melts at 277-8°C. Its magnetic moment is 1.73 BM and it exists in two crystalline forms depending upon the method of purification (viz sublimation or crystallisation).

d^3 V(II)

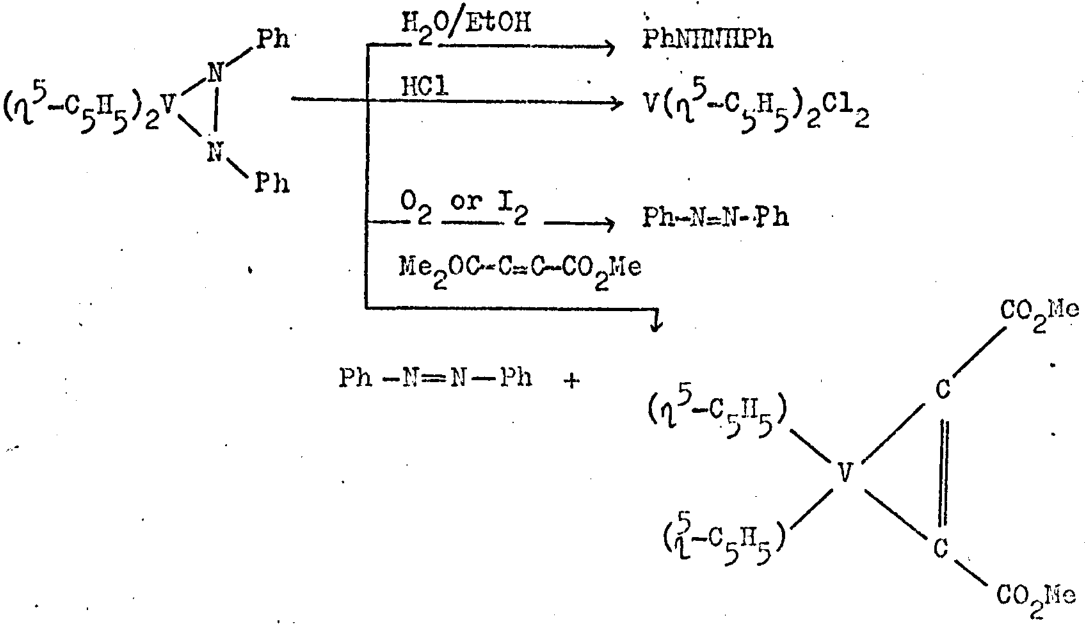
The paramagnetic bis(η^5-cyclopentadienyl)vanadium (II) (Vanadocene) (48) has been prepared by treating vanadium (IV) chloride with excess cyclopentadienylmagnesium bromide or sodium cyclopentadienide with rigorous exclusion of air. If the Grignard reagent is used the resulting mixture of $V(\eta^5-C_5H_5)_2$ and $(\eta^5-C_5H_5)_2Mg$ is sublimed out of the reaction flask, dissolved in ether, and the magnesium compound converted to the insoluble biscyclopentadienylcarboxylato compound with CO_2. The vanadocene is then sublimed out as black crystals in 50% yield. It is reasonably thermally stable, not melting until 167-8°C.

It reacts during one day with azobenzene in toluene at room temperature to give black/maroon crystals of X in 80% yield (59)

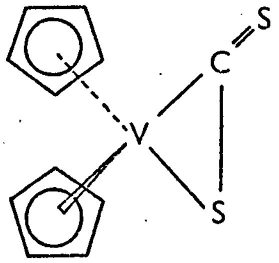


X

Elemental analysis, molecular weight determination and magnetic moment (1.77 BM at 292K) indicate a mononuclear vanadium azobenzene complex. It is thermally stable, soluble in aromatic hydrocarbons, and enters several oxidative hydrolylic and displacement reactions giving products in very high yield (> 80%).



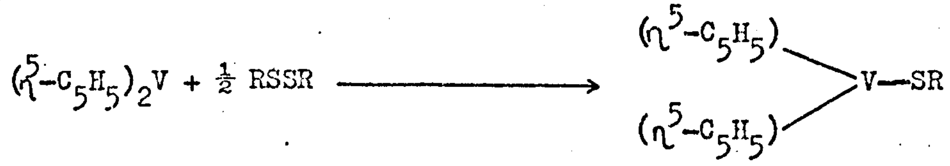
Freshly sublimed vanadocene reacts immediately with carbon disulphide under anaerobic conditions to form a deep green extremely air sensitive material XI (60). Although this complex has not been isolated, preliminary IR and NMR evidence indicate that it should be formulated as π bonded CS_2 complex of vanadium (II)



XI.

d^1 V(IV) and d^2 V(III)

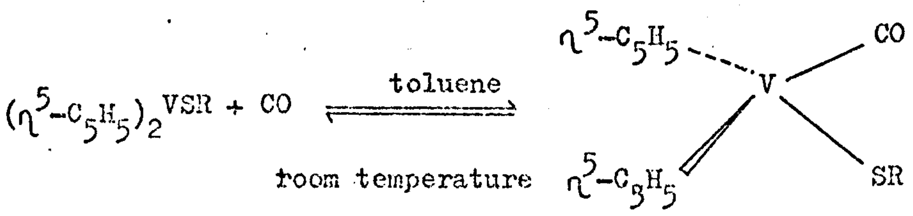
The reaction of alkyl or aryl disulphides with bis(η^5-cyclopentadienyl) vanadium (II) in toluene at room temperature is reported to give, on addition of hexane and cooling, green crystals of $(\eta^5-C_5H_5)_2V(SR)$ (20). These complexes are monomeric in benzene, and magnetic moments confirmed the derivatives to be of high spin vanadium (III) ions.



$$(\eta^5-C_5H_5)_2V + \tfrac{1}{2}\,RSSR \longrightarrow (\eta^5-C_5H_5)_2V{-}SR$$

R = Me, Et, Ph, $PhCH_2$

One of the more interesting properties of the $(\eta^5-C_5H_5)_2V(SR)$ compounds (if R = Me or Ph) is the reversible addition of carbon monoxide in hydrocarbon solvents.



$$(\eta^5-C_5H_5)_2VSR + CO \underset{\text{room temperature}}{\overset{\text{toluene}}{\rightleftharpoons}} (\eta^5-C_5H_5)_2V(CO)(SR)$$

R = Me, νCO = 1940 cm^{-1}
R = Ph, νCO = 1943 cm^{-1}

A similar reaction has recently been observed and quantitatively evaluated for $(\eta^5\text{-}C_5H_5)_2VI$ (61).

It was not possible to say whether the preparation of $(\eta^5\text{-}C_5H_5)_2VSR$ is a one electron oxidative addition, or whether insertion of vanadium into the S–S bond to give $(\eta^5\text{-}C_5H_5)_2V(SR)_2$ is followed by fast redox between V(II) and V(IV) with ligand transfer. However, the possibility that the synthesis of $(\eta^5\text{-}C_5H_5)_2VSR$ results from the instability of $(\eta^5\text{-}C_5H_5)_2V(SR)_2$ has been excluded. In fact, the synthesis of, for example, $(\eta^5\text{-}C_5H_5)_2V(SPh)_2$ can be quite easily realised. Either the displacement of chloride in $(\eta^5\text{-}C_5H_5)_2VCl_2$ by Na(SPh) or further reaction of PhSSPh with $(\eta^5\text{-}C_5H_5)_2VSPh$ gives the same product:

$$(\eta^5\text{-}C_5H_5)_2VCl_2 + 2Na(SPh) \longrightarrow (\eta^5\text{-}C_5H_5)_2V(SPh)_2 + NaCl$$

$$(\eta^5\text{-}C_5H_5)_2V(SPh) + \tfrac{1}{2}\,PhSSPh \longrightarrow (\eta^5\text{-}C_5H_5)_2V(SPh)_2$$

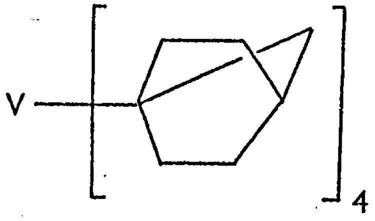
The electronic configuration of the ground state of $(\eta^5\text{-}C_5H_5)_2VCl_2$ has been studied (38) and the unpaired electron density found to be heavily localised on the metal. The compound may be prepared by allowing vanadium (IV) chloride to react with sodium cyclopentadienide in diglyme (62, 63). The corresponding dithiocyanate, dicyanate and dicyanide were then prepared from the dichloride by appropriate reaction with KSCN, KOCN or KCN respectively (64).

Several stable compounds of the type $(\eta^5\text{-}C_5H_5)_2\,V^{(III)}R$ (65) have been isolated, but none of the corresponding bis alkyls of vanadium (IV) have been prepared (66). The instability of the $(\eta^5\text{-}C_5H_5)_2V^{(IV)}R_2$ molecules, in contrast to the titanium and niobium analogues, has been ascribed to steric effects, since the atomic radius of vanadium (1,22Å) is smaller than Ti (1.32Å) or Nb (1.34Å). This hypothesis was tested using the phenylmethynyl group, which possesses the minimum steric interaction in the neighbourhood of the metal, and compounds such as $(\eta^5\text{-}C_5H_5)_2V^{(IV)}(C{\equiv}CC_6H_5)_2$, $(\eta^5\text{-}C_5H_5)_2V^{(III)}(C{\equiv}CC_6H_5)$ have successfully been prepared (67). Dimethyl and diethyl vanadium dichloride have also been reported (68).

Tetrabenzylvanadium, the first example of a vanadium (IV) compound with four V–C σ bonds has recently appeared in the literature (69). It is prepared by the reaction between dibenzylmagnesium and VCl_4 in pentane/ether at $-20^\circ C$. The increased stability of tetrabenzylvandium when compared with alkyl or aryl analogues is in part due to the absence of β-hydrogens which would promote an elimination process (70, 10). A similar stabilisation is noted for $V(CH_2SiMe_3)_4$ (42, 39).

Bridged or fused alicyclic ring systems of appropriate geometry are also rather inert to β-elimination processes, homolysis or nucleophilic displacements of substituents bonded to bridgehead carbon atoms (71, 72, 73).

Thus the bicyclo(2.2.1)hept-1-yl (1-norbornyl complexes) of V(IV), XII, and other metals, are stable molecules



XII

$V(1\text{-norbornyl})_4$ has a magnetic moment of 1.82 BM indicating 1 unpaired electron.

d^1Nb(IV)

The organometallic chemistry of niobium and tantalum is a relatively new field, and fewer such compounds are known of these two elements than for vanadium.

The complex $Cl_2Nb(\eta^5\text{-}C_5H_5)_2$ has been reported (74) and in the temperature range 83-301 K a magnetic moment of 1.63 ± 0.01 BM has been recorded. This value corresponds to one unpaired electron per molecule. The black volatile complex is prepared from sodium cyclopentadienide and niobium (V) chloride in benzene, followed by treatment with HCl:

$$NbCl_5 + 5\ CpNa \longrightarrow Cp_4Nb + 5NaCl + C\dot{p}$$
$$Cp_4Nb + 2HCl \longrightarrow Cp_2NbCl_2 + 2CpH$$

It can also be obtained by successive reactions with isopropylmagnesium bromide and sodium cyclopentadienide:

$$NbCl_5 + iPrMgBr \longrightarrow NbCl_4 + MgBrCl + iP\dot{r}$$
$$NbCl_4 + 2CpNa \longrightarrow Cp_2NbCl_2 + 2NaCl$$

The ESR spectrum of dicyclopentadienylniobium (IV) dihydride, produced in solution by abstraction of a single hydrogen from the diamagnetic trihydride $(\eta^5\text{-}C_5H_5)_2NbH_3$ (75, 76) has recently been recorded (77). The synthesis is performed by photolysing a rigourously degassed solution of the trihydride in benzene and cyclopropane in the presence of tert-butyl peroxide at -80°C in the cavity of an ESR spectrometer (78)

$$(\eta^5\text{-}C_5H_5)_2NbH_3 + t\text{-}BuO^{\bullet} \longrightarrow (\eta^5\text{-}C_5H_5)_2NbH_2 + tBuOH$$

A thermal reaction which produces paramagnetic niobium containing species is observed when isobutylene is mixed with a solution of $(\eta^5\text{-}C_5H_5)_2NbH_3$ in benzene and cyclopropane at room temperature in a sealed tube (77). The same material is also generated by the reaction of $(\eta^5\text{-}C_5H_5)_2NbH_3$ with tert butyl magnesium bromide.

These authors believed this product to be $(\eta^5\text{-}C_5H_5)_2Nb(tBu)H$, and thus investigated the synthesis and stability of the corresponding dialkyl derivatives of dicyclopentadienylniobium dichloride. The preparative route used was:

$$(\eta^5\text{-}C_5H_5)_2NbCl_2 + 2RY \longrightarrow (\eta^5\text{-}C_5H_5)_2NbR_2 + YCl$$

$$Y = Li,\ MgX$$

indeed, adding methyllithium or methyl magnesium bromide to an ethereal solution of $(\eta^5\text{-}C_5H_5)_2NbCl_2$ causes the ESR spectrum to change to one which is unambiguously assigned to $(\eta^5\text{-}C_5H_5)_2Nb(Me)_2$ which can be isolated as dark red crystals.

In contrast to these observations, the addition of ethyl- or tert-butyllithium or a Grignard reagent to a solution of $(\eta^5\text{-}C_5H_5)_2NbCl_2$ readily caused the collapse of the ESR spectrum of the latter without the appearance of a new signal corresponding to that of a dialkylniobium (IV) species. It is concluded that the expected dialkyl complexes are quite unstable as shown previously for similar derivatives of the $(\eta^5\text{-}C_5H_5)_2Ti$ (III) moiety susceptible to decomposition by β -elimination (79, 80).

d^1Ta (IV)

The tantalum analogues of the niobium species described above show similar behaviour but are generally less reactive (77). Thus photolysis of $(\eta^5\text{-}C_5H_5)_2TaH_3$ gave a paramagnetic hydride; and a species $(\pi\ CH_3C_5H_4)_2Ta(Me)_2$ is also known.

$(\eta^5\text{-}C_5H_5)_2TaCl_2$ is paramagnetic and prepared in an identical fashion to the niobium species. Its magnetic moment of 1.59 BM (97-300 K) indicates one unpaired electron per molecule.

Group VIA: Chromium, Molybdeum, Tungsten

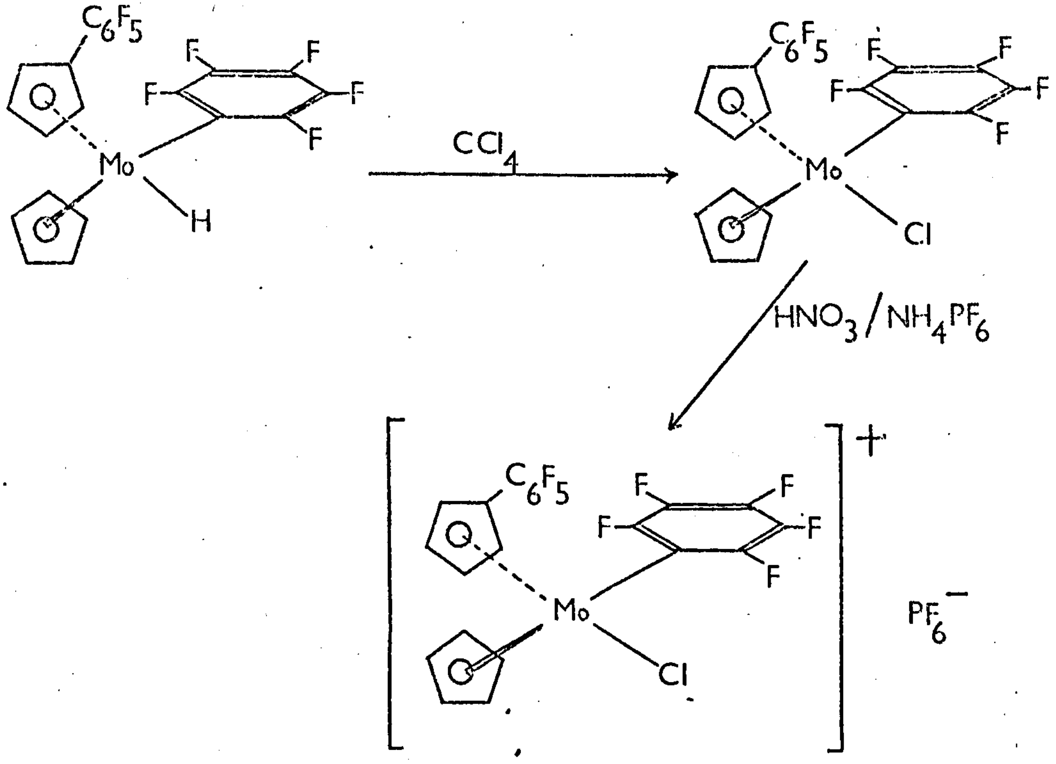
TABLE 4

Paramagnetic species of Group VIA metals

Ion	Compounds		Reference
d^1Mo (V)	$(\eta^5\text{-}C_5H_4C_6H_2)$ $(\eta^5\text{-}C_5H_5)MoCl(C_6F_5{}^+)$		81
d^2W (IV)	$W(C_6F_5)_5$		82
Cr(IV)	Cr(1-norbornyl)$_4$		43
	$Cr(CH_2CMe_2Ph)_4$		83
	$Cr(CH_2CH_2CH_2CH_3)_4$		84
d^3Cr (III)	$Cr(CH_2SiMe_3)_4{}^-$		42
	CrR_3 R = $CH(SiMe_3)_2$		3
	Cr(4 camphyl)$_3$		43
d^5Cr (I)	Cr(ηarene)$_2{}^+$		2
	Cr(bisnaphthalene)$_2{}^+$		49
	$Cr(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6H_6)$		85
	$Cr(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_7H_8)$		86
	$Cr(\eta^5\text{-}C_5H_5)(\eta^8\text{-}C_8H_8)^-$	)	
	$Cr(CH_2Ph)L^+$	)	87
Mo (I)	$Mo(\eta^5\text{-}C_5H_5)(CO)_3(NOAr)$		88
	$Mo(CO)_2(diphos)_2{}^+$		89
W (I)	$W(CO)_2(diphos)_2{}^+$		89
d^7Cr (-I)	$Cr(C_{10}H_8)_2{}^-$		49
d^9Cr (-III)	$Cr(C_{10}H_8)_2{}^{3-}$		49

d^1Mo(V)

Reaction of the hydride complex $(\eta^5\text{-}C_5H_4C_6F_5)$ $(\eta^5\text{-}C_5H_5)MoH(C_6F_5)$ with CCl_4 gives the chloroanalogue (X = Cl). Oxidation of this forms the corresponding d^1 cation which may be isolated as its salt (81):



Similar compounds are known for tungsten (81).

d^2W(IV)

The simple alkyl and aryl derivatives of the heavier transiton metals are, in general, unstable and poorly characterised; for example $LiW(C_6H_5)_5.3Et_2O$ has been isolated from the reaction of tungsten (V) bromide with phenyllithium is a black pyrophoric power (90). However, the preparation of $LiW(C_6F_5)_5.$ $2Et_2O$ has been reported (82) and found to be more amenable to study. When an etheral solution of pentafluorophenyllithium is stirred with tungsten (VI) chloride, the solution assumes a green colouration. Removal of the precipitated lithium chloride followed by crystallisation under an inert atmosphere produced the bright green dietherate in very high yield. Controlled thermal decomposition at 100° gave the orange/red $W(C_6F_5)_5$ as very air sensitive crystals. Their mass spectra have been recorded (82).

d^2Cr(IV)

A similar tetranorbornyl complex to that given for vanadium is known for Cr(IV) (43).

Preliminary X-ray studies and ESR spectra suggest tetrahedral arrangement of norbornyl groups. Ligand interrepulsions would favour this arrangement. Magnetic data suggest a spin free configuration. It is a red/brown material with μeff 2.84 BM (43), stable in air in isooctane solution and in 0. 1 M H_2SO_4 in dioxan.

A reason for the stability of this molecule apart from those mentioned earlier, is apparent from a study of models: it is evident that small molecules cannot pentrate the coordination sphere.

Recently, tetra tert-butyl chromium (IV) has been reported (91) from $CrCl_3.3THF$ and tert-butyllithium in pentane via a disproportionation reaction. It was isolated by sublimation and characterised by esr, UV, visible and IR spectra. Models show that the four tertiary butyl groups fit snugly around the chromium atom making it difficult for them to achieve the correct geometry required in the transition state for β-elimination. The following complexes have been characterised by ESR (91).

$CrMe_4$
Cr(iso propyl)$_4$
Cr(sec-butyl)$_4$
Cr(n-butyl)$_4$
Cr(cyclohexyl)$_4$

The ESR spectra of many other tetralkyl chromium species have been recorded (92).

Tetrabis(2-methyl-2-phenylpropyl)chromium (IV), $Cr(CH_2CMe_2Ph)_4$, was first reported by Mowat and Wilkinson (93) and shows remarkable chemical inertness: in benzene solution it is decomposed by concentrated sulphuric acid at room temperature only after several hours. The molecules form flat purple prisms from pentane at -40°C. The crystal structure has been reported (94) and found to be a slightly distorted tetrahedron with a mean Cr-C distance of 2.05 Å.

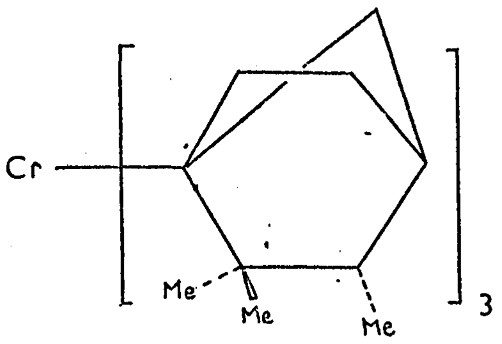
The compound $Cr(CH_2SiMe_3)_4$ is also quite unreactive except towards oxygen. It is unaffected by most solvents by primary aliphatic and aromatic amines, ethylene diamine, alkyl and aryl tertiary phosphines, carbon disulphide, and carbon monoxide at 100°C and 200 psi. Although inert towards water and dilute mineral acids, concentrated hydrochloric and sulphuric acids give green solutions of Cr (III) ions and tetramethylsilane is lost. Other reactions with hydrogen chloride, chlorine or nitric oxide have been described (42).

d^3Cr (III)

Tetrakis(trimethylsilylmethyl) chromate (III) ion has been prepared (42) from a suspension of $CrCl_3.3THF$ and trimethylsilyllithium. The reaction appears qualitative, but attempts to prepare crystalline salts with large cations have not proved successful. The solution may be oxidised in air to $Cr(CH_2SiMe_3)_4$. In THF solution the magnetic moment is 3.7 BM, measured by the Evans' NMR line shift method at 308 K (95), and its geometry is tetrahedral.

Using bulky $(Me_3Si)_2CH^-$ groups, presumed trigonal or distorted trigonal d^3 complexes CrR_3 have been made (96). A typical synthetic procedure involved addition of bis(trimethylsilyl)methyllithium in diethyl ether to chromium (III) chloride at 0°C to give bright green air sensitive crystals of the tris substituted product. The geometry was determined from ESR studies. The chromium atom appears to be very shielded by the ligands, and does not react with carbon dioxide or pyridine. However, with one equivalent of nitric oxide in hexane, a diamagnetic deep red solution is formed, presumed to be $CrR_3 \cdot NO$, ($\nu NO = 1672\ cm^{-1}$). Trityl chloride yielded $Ph_3C\cdot$ (detected by ESR) and a purple solution thought to contain $ClCrR_3$.

If chromium (III) chloride is reacted with 4 camphyllithium, a Cr(III) species XIII results.



XIII

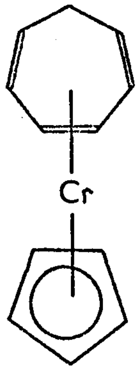
Further groups coming into close approach to the metal to give a a derivative of Cr(IV) are prevented from doing so by the steric interactions of the methyl groups.

The analagous reaction of lithium diethylamide with chromium (III) chloride is reported to give tetrakis(diethylamide)chromium (IV), while the bulkier lithium diisopropylamide gives the corresponding trisamidochromium, (97, 98).

d^5Cr (I)

In contrast to the bisnaphthalene vanadium (0) complex, the isoeletronic Cr(I) species cannot be obtained directly by adding the correct amount of lithium naphthalenide to $CrCl_3$. (Li/Cr = 2) (52). The ESR signal of the Cr(I) species is, however, observed if the $CrCl_3$ solution is added to an excess of naphthalenide anion (Li/Cr > 5), which is then hydrolysed with water and the chromium oxidised with oxygen (often the amount of oxygen present in the water is sufficient).

As ESR study of the mixed sandwich campounds $(\eta^5-C_5H_5)Cr(\eta^6-C_6H_6)$ and $(\eta^5-C_5H_5)Cr(\eta^7-C_7H_7)^+$ has been carried out (85). The paramagnetic complex XIV has been prepared (99).



XIV

It is an air sensitive material and its ESR spectrum has been recorded (86).

The deep green cyclopentadienylchromium tricarbonyl dimer has been prepared (100) from the reaction of $[(\eta^5\text{-}C_5H_5)Cr(CO)_3]^-$ with tropylium bromide. This oxidation evidently proceeds via $(\eta^5\text{-}C_5H_5)Cr(CO)_3$ radicals which then dimerise, since ditropyl is also isolated. It is reported (109) that sublimation of the dimer yields the paramagnetic monomer which has been studied by ESR spectroscopy (101) and for which a distorted structure is recorded. The monomer is obtained as a dark green polycrystalline mass which must be handled under nitrogen.

The proton NMR spectrum of the dimer in toluene-d_8 solvent at 25° consists of one very broad resonance (width at half height of 18Hz) at τ 4.16 (102). However, at higher temperatures the line becomes broader. At -61°, the resonance has narrowed to 1.5 Hz and has shifted to τ 5.90. This behaviour would seem to suggest the appearance at elevated temperatures of some paramagnetic species, and a temperature dependant equilibrium between monomer and dimer has been proposed. In view of the extraordinary length of the Cr-Cr bond (3,28Å) this does not seem unlikely (cf 2.923 Å for Mn-Mn in $Mn_2(CO)_{10}$ (103)).

d^5Mo(I) and W(I)

Irradiation at -30° of the metal-metal bonded dimer $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ yields the paramagnetic monomer which has been spin trapped with ArNO (88). The use of ArNO as a spin trapping agent for metal centred radicals formed by homolysis is widespread, and allows their identification by ESR spectroscopy.

The complex $Mo(CO)_2(diphos)_2$ (89) reacts with iodine in dichloromethane at room temperature to give air stable red/black crystals of $[Mo(CO)_2(diphos)_2]^+I_3$. This is a paramagnetic material (μeff (solid): 1.66 BM at 20°C) and conductivity data in nitrobenzene are consistent with its formulation as a monomeric complex behaving as a uni-valent electrolyte.

The dicarbonyl tungsten complex $W(CO)_2(diphos)_2$ reacts with iodine in the same manner to produce the red $[W(CO)_2(diphos)_2]I_3$, which has similar properties to those observed for the molybdenum species (99). These compounds may be considered as either octahedral tri-iodide derivatives of M(I) or an eight coordinate derivative of M(III) such as $[Mo(CO)_2(diphos)_2I_2]I$. However, the rather low value of the single IR active carbonyl stretching mode (1864 cm^{-1}) is consistent with the M(I) formulation.

d^7, d^9 Cr(-I), Cr(-III)

Further reaction of bisnaphthalene chromium (I) with lithium naphthalenide is reported to generated complexes containing the reduced Cr(-I) and Cr(-III) ions (49).

Group VII A: Manganese, Technetium, Rhenium

TABLE 5

Paramagnetic species of Group VIIA metals

Ion	Compounds	Reference
d^1 Re(VI)	$Re(Me)_6$	104
d^3 Mn(IV)	$Mn(1\text{-norbornyl})_4$	43
d^5 Mn(II)	$Mn(C_5H_4Me)(CO)_2$	105
	$C(OMe)(1\text{-ferrocenyl})^+$	
	$Mn(CO)_2(diphos)_2^{2+}$	106
d^7 Mn(0)	$Mn_2(CO)_{10}^-$	23
	$Mn(CO)_5Br^-$	107
	$Mn(CO)_4(PPh_3)$	108
	$Mn(CO)_5O_2.Mn(CO)_5$	109,110
	$Mn(CO)_4P(NOAr)$	11
	$(P = CO \text{ or } PPhMe_2)$	
Tc (0)	$Tc(CO)x$	111
Re(0)	$Re(CO)_3P_2$	
	$P = PPh_3$	112
		113
	$P = PMePh_2$	114
	$P = PMe_2Ph$	115
	$Re(CO)_5(ArON)$	11

d^1 Re(VI)

The green, crystalline, paramagnetic d^1 hexamethylrhenium (VI) has recently been obtained by reaction of tetramethoxorhenium (VI) with trimethylaluminium (104). In the solid it may be kept indefinately at -20° but decomposes above 10°C to a black residue and methane. It is noted that the crystals should be handled with caution since in one case admission of nitrogen to a sample in vacuo caused a violent detonation. It is very volatile, subliming at -30°C at 10^{-3} mm Hg and extremely air sensitive. In its mass spectrum all ions $ReMe_n^+$ (n = 6-0) were observed at both 70 eV and 16 eV. The ESR spectrum has been recorded (116).

d^3 Mn (IV)

In common with the elements hafnium, zirconium, titanium, vanadium, chromium, iron and cobalt, manganese forms a stable compound of the type MR_4 where R = 1-norbornyl (43). It is a green, crystalline solid with a magnetic moment of 3.78 BM. The mass spectrum showed a molecular ion corresponding to a tetraalkyl complex.

d^5 Mn(II)

The oxidation of a number of derivatives of manganese (I) such as $Mn(CO)_3(py)_2Br$, $Mn(CO)_3(bipy)Br$ and $Mn(CO)_3(triars)ClO_4$ has been shown to lead to complexes of manganese (II) only by complete expulsion of carbon monoxide. This behaviour contrasts with the reaction of bromine with $[Mn(CO)_3(diars)]_2$, which appears to lead to the manganese (II) derivative $Mn(CO)_2(diars)Br_2$ (117). It has recently been reported (118) that the cation $[Mn(CO)_2(diphos)_2]^+$ (119,120) readily loses one electron to form the green paramagnetic di-cation $[Mn(CO)_2(diphos)_2]^{2+}$. The oxidation from Mn(I) to Mn(II) is effected by nitric acid, bromine, antimony pentachloride or potassium permanganate (at pH <6). The di-cation is most conveniently isolated as the perchlorate, which is remarkably stable. However, a suspension in acetone is reduced to the manganese (I) species by sodium borohydride. A <u>trans</u> configuration has been proposed and conductance measurements show the salt to act as a 1:2 electrolyte. A magnetic moment of 1.80BM (independent of temperature) was recorded, suggesting the t_{2g}^5 configuration.

d^7 Mn(0)

Solid state γ irradiation at low temperatures has been used to produce new paramagnetic species from decacarbonyldimanganese and bromopentacarbonylmanganese (I), (23). The ESR spectrum of the product formed on irradiation of pure powdered $Mn_2(CO)_{10}$ at 77K is characteristic of a species containing two magnetically equivalent manganese atoms and one unpaired. This electron is considered to be largely confined to the σ^* antibonding orbital of the Mn-Mn bond. The ESR signal caused by γ irradiation of pure $Mn(CO)_5Br$ is one whose parameters are again close to the spin only value.

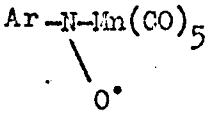
The sublimation of $Mn_2(CO)_{10}$ onto a cold finger has been reported to yield $Mn(CO)_5\cdot$ radicals (121,122). However, it has subsequently been shown (109 that sublimation in the absence of oxygen gives no detectable ESR signal. Admission of a trace of oxygen to the apparatus results in a spectrum similar to that originally assigned to the pentacarbonyl species. This result suggests that the radical is in fact the peroxo species $O_2Mn(CO)_5$, a proposal supported by work using $Co_2(CO)_8$ (109).

Wojicki and Hallock (123) have shown that the 350 nm photolysis of $Mn_2(CO)_{10}$ in THF (the wavelength corresponding to the $\sigma \rightarrow \sigma*$ transition in the metal-metal bond (124))produced an orange paramagnetic complex which on standing at room temperature reverted to the decacarbonyl. Addition of the orange solution to iodine in THF yielded 30-35% of $Mn(CO)_5I$ (124) whereas $Mn_2(CO)_{10}$ and iodine in THF do not react at ambient temperature, proving the presence of radical species.

The 17 electron entity $Mn(CO)_5\cdot$ has been trapped out of the products of UV irradiation of either the decacarbonyl or $RMn(CO)_5$ (R = Me or $PhCH_2$) using nitrosodurene (11).

$$RMn(CO)_5 \xrightarrow[CHCl_3]{h\nu\ -30^{\circ}} R^{\cdot} + {}^{\cdot}Mn(CO)_5$$

Both fragments were trapped to give the nitroxides XV and XVI



XV

XVI

The photolysis products of bis phosphine substituted dimers have also been spin trapped (11). Examples are: ${}^{\cdot}Mn(CO)_4P$ where P = $P(OPh)_3$; PPh_3; $PMePh_2$; PMe_2Ph; PBu_3; $P(C_6H_{11})_3$.

Similar radicals have been trapped from the purely thermal decomposition of $[LMn(CO)_4]_2$ species. The radical $(CH_3)CN(O)Mn(CO)_5$ has been detected in experiments in which $Mn(CO)_5^-$ is oxidised by the tropylium cation (125). It is noteworthy that no paramagnetic species were obtained from $Mn_2(CO)_{10}$ in the dark at 23° due to the greater activation energy needed to cleave the M-M bond in this case. It appears that increasing the σ electron density of these axial ligands (in $Mn_2(CO)_8L_2$) while decreasing their ability to act as π acceptors does weaken the metal-metal bond, and therefore lowers the activation energy for its facture. Further arguments concerning the strength of the M-M bond in various bis axially substituted dimers is present elsewhere (126).

Tc (0)

The study of paramagnetic technetium compounds has been governed by its scarcity, since it was only isolated on the gram scale in 1952.

The compounds $Tc_2(CO)_{10}$ and $ITc(CO)_5$ have been prepared (127) and characterised, but no mention was made of intermediate species or radicals of the type $\cdot Tc(CO)_x$. It has since been shown (128) that the $^{\cdot}Tc(CO)_5$ radical is formed by the β decay of $^{99}Mo(CO)_6$ and that it displays several of the properties which would be expected of it. Its stability in the solid $Mo(CO)_6$ matrix is greater than that of the analogous $Mn(CO)_5$ in $Mn_2(CO)_{10}$ (8 hour compared to 1 hour) (128, 129). It seems to be rapidly destroyed by nitric oxide if present during the early stages of the chemical workup and to be somewhat sensitive to atmospheric oxygen. The $^{\cdot}Tc(CO)_5$ radical reacts slowly with $^{\cdot}Mn(CO)_5$ to produce a species which is likely to be $MnTc(CO)_{10}$ and rapidly with $IMn(CO)_5$ to give $ITc(CO)_5$ (128).

It must be emphasised that the concentration of radioactive technetium compounds produced in the $Mo(CO)_6$ matrix is extremely small; about 10^5 Tc atom/mg of $Mo(CO)_6$. This means that no conventional means of study are applicable. Moreover, it is important to note that reactions involving two Tc atoms are thus not expected, so the reaction:

$$2(^{\cdot}Tc(CO)_5) \longrightarrow Tc_2(CO)_{10}$$

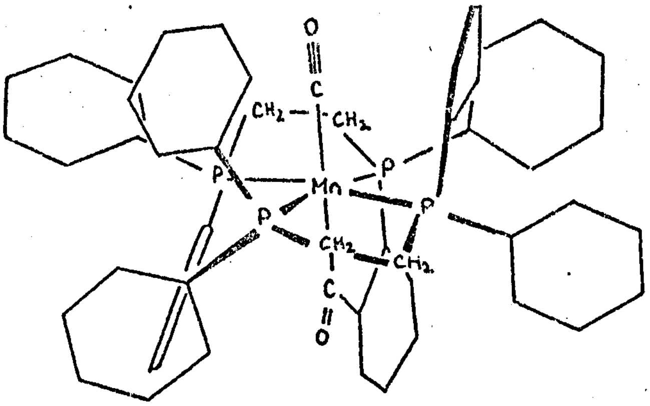
would not be prominent. When still trapped in the $Mo(CO)_6$ lattice, the radical survives heating to 110°.

Re (0)

The reaction between decacarbonyldirhenium and triphenylphosphine in boiling xylene has been reported to yield $Re(CO)_3(PPh_3)_2$ (112, 113) and this has been assigned a trans trigonal bipyramidal structure on the basis of the single peak at 1934 cm^{-1} in its IR spectrum (113). Its magnetic moment is reported as 1.7 BM (113) and it reacts quantitatively with iodine to give the known trans $Re(CO)_3(PPh_3)_2I$ (131).

The monomeric, paramagnetic crystalline compound $Re(CO)(diphos)_2$ has been reported (131) from the reaction of $Re_2(CO)_{10}$ with 1,2-diphosphinoethane followed by treatment of the resulting $Re(CO)_2(diphos)_2$ with excess reagent in a sealed tube in vacuo. Its dipole moment was not recorded due to its low solubility.

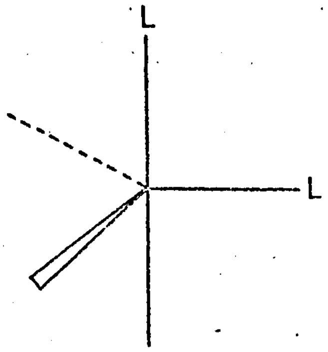
$Re(CO)_3(diphos)$ has also been reported. Two strong IR bands and one weak one agree with a C_s or C_{2v} structure with the carbonyl groups in the trans positions. However, it is noteworthy that the complex initially reported as $Mn(CO)(diphos)_2$ (132) has recently been shown by X-ray crystallography to be the diamagnetic metalated species $Mn(CO)(CO\cdot C_6H_4\cdot P\cdot (Ph).\ CH_2CH_2PPh_2)(diphos)$ (133) which has the structure shown below XVII.



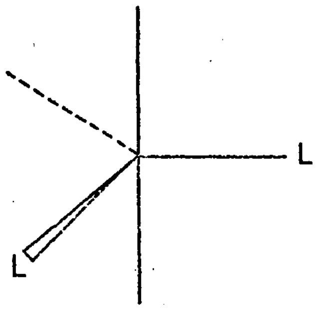
XVII

The paramagnetic complex $Re(CO)_3(PMe_2Ph)_2$ has been isolated in low yield from the photochemical reaction of $Re_2(CO)_{10}$ with two moles of PMe_2Ph (115). The IR spectrum of this molecule is consistent with a structure belonging to the C_s point group.

Three CO stretching bands are reported for this molecule which indicates either trigonal or square pyramidal skeleton. The structure XVIII is reported for $Re(CO)_3(PMe_2Ph)_2$ (115)



XVIII



XIX

XIX would also give three bands, but it is doubtful whether the formal distinction between these two has any real meaning. Pentacoordinated species are known to be fluxional, and so XVIII and XIX are merely representations of extreme cases. $Re(CO)_3(PMePh_2)_2$ has also been reported (114) and this has the structure XVIII but once again the assignment of a particular configuration may be erroneous.

Complexes of the type $[Re(CO)_3L_2]_2$ (L = PPh_3 or $P(OPh)_3$) have been prepared (112). These are stated to be dimeric and diamagnetic in the solid state but monomeric and paramagnetic in solution. $Re(CO)_3(PPh_3)_2$ has also been reported by heating $HRe(CO)_3P_2$ under vacuum (131) and the paramagnetic $Re(CO)_5^{\bullet}$ has been identified by Lappert in the photolysis of the decacarbonyl (88).

The photolylic reaction of $Re_2(CO)_{10}$ and PBu_3 is reported to yield not only $Re_2(CO)_8L_2$ and $Re_2(CO)_9L$, but also $Re(CO)_3L_2$ (134).

Group VIII: Iron, Ruthenium, Osmium

TABLE 6

Paramagnetic species of Group VIII metals

Ion	Compounds	Reference
d^4 Fe(IV)	$Fe(norbornyl)_4$ *	43
d^5 Fe(III)	Ferricenium salts	135
	$Fe(olefin)^{3+}$	136
d^7 (FeI)	$Fe(\eta^5-C_5H_5)(C_5H_4NOBu^t)$	137
	$Fe(\eta^5-C_5H_5)[C_5H_4CO(Ph)]^-$	138
	$Fe(\eta-C_5H_4C_6H_4NO_2)^-$	139
	$Fe(\eta^5-C_5H_5)[C_5H_4CO(COR)]^-$	140
	$Fe(\eta^5-C_5H_5)(CO)_2(NOAr)$	88
d^9 Fe(-I)	$Fe(\eta^4-C_6H_8)(CO)_2(PPh_3)^-$	141
	$Fe(CO)_5^-$	142
Fe(0)/Fe(-I)	$Fe_2(CO)_9^-$ $Fe_3(CO)_{12}^-$	142
	$Fe_3(CO)_{11}P(OPh)_3^-$	
	$RuFe_2(CO)_{12}^-$	
	$Fe_2(CO)_8Pt\ P(OPh)_3\ {}_2^-$	
Ru(0)/Ru(-I)	$Ru_3(CO)_{12}^-$	143
	$Ru_6(CO)_{17}C^-$	142
Os (0)/Os(-I)	$Os_3(CO)_{12}^-$	143
		142

* diamagnetic, included for completeness.

d^4 Fe(IV)

In common with many elements which have already received attention the norbornyl derivative of iron (IV) is also known (43). However, this particular molecule is unique in this series in that the d electrons are spin paired resulting in a diamagnetic configuration.

d^6 Fe(II)

Ferrocene itself is thermally stable and melts without decomposition. It is also inert towards hydrolysis, but is very readily oxidised by iodine in acid solution to give the ferricenium cation $(\eta^5-C_5H_5)_2Fe^+$ (143). This is normally isolated as salts with anions such as BF_4^-. Fritz, Keller and Schwarzhaus (144) have shown that because of too short a spin- lattice relaxation time the ESR spectrum of $Fe(\eta^5-C_5H_5)_2^+$ cannot be observed at 77 K. Ring substitution, however, increases this relaxation period and ESR spectra of several such derivatives of this cation have been recorded (145), (146). Their preparation has been described (147).

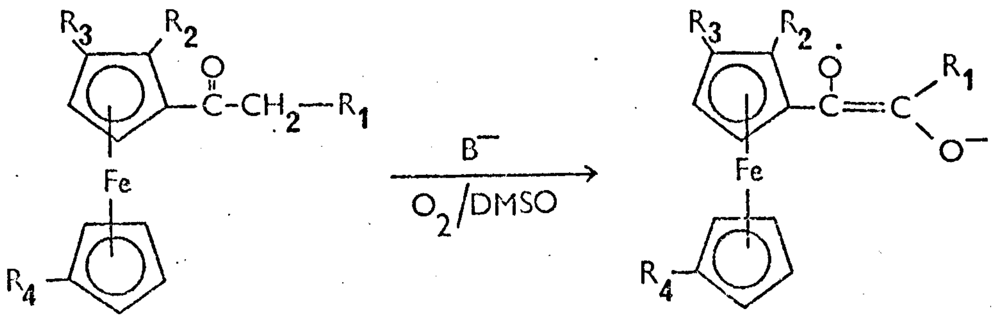
d^7 Fe(I)

The ESR spectra of a number of radical anions derived from substituted ferrocenes have been recorded (138). Compounds studied include benzoylferrocene, *p*-toluoylferrocene, *p*-nitrophenyl ferrocene and *p*-cyanophenylferrocene. These radicals were generated in a modified eletrolytic cell, full details of which are given in the literature (139).

In all cases, the observed spectra were symmetrical with respect to their centre, so it is reasonable to conclude that only one type of radical is formed during the reduction, and that other species, generated through secondary reactions of the radical anion with solvent molecules, are too short lived to build up to a detectable concentration.

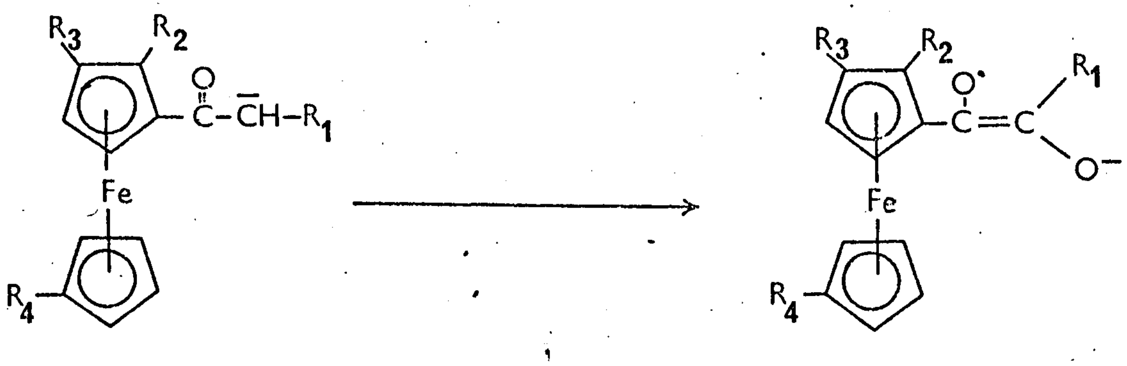
Despite the applications of metallocenes as antioxidants, combustion control additives, photoprotecting UV absorbers and medicinals, areas which clearly involve free radical chemistry, it is not until recently that stable metallocenes have received much attention.

Ferrocenyl ketones, XX, which have an α-methylene group, may be oxidised to the stable paramagnetic semidiones XXI with molecular oxygen in DMSO containing an excess of potassium <u>tert</u>-butoxide (140).



XX XXI

This reaction is quite general, and many semidiones may be prepared in this way (some 23 are given in reference 140). Their ESR spectra indicate a remarkably small amount of electron spin delocalisation into the metallocene ring. The intermediacy of XXII has been postulated, and steric and electronic factors have been found to control the rate of enolate anion formation (140).

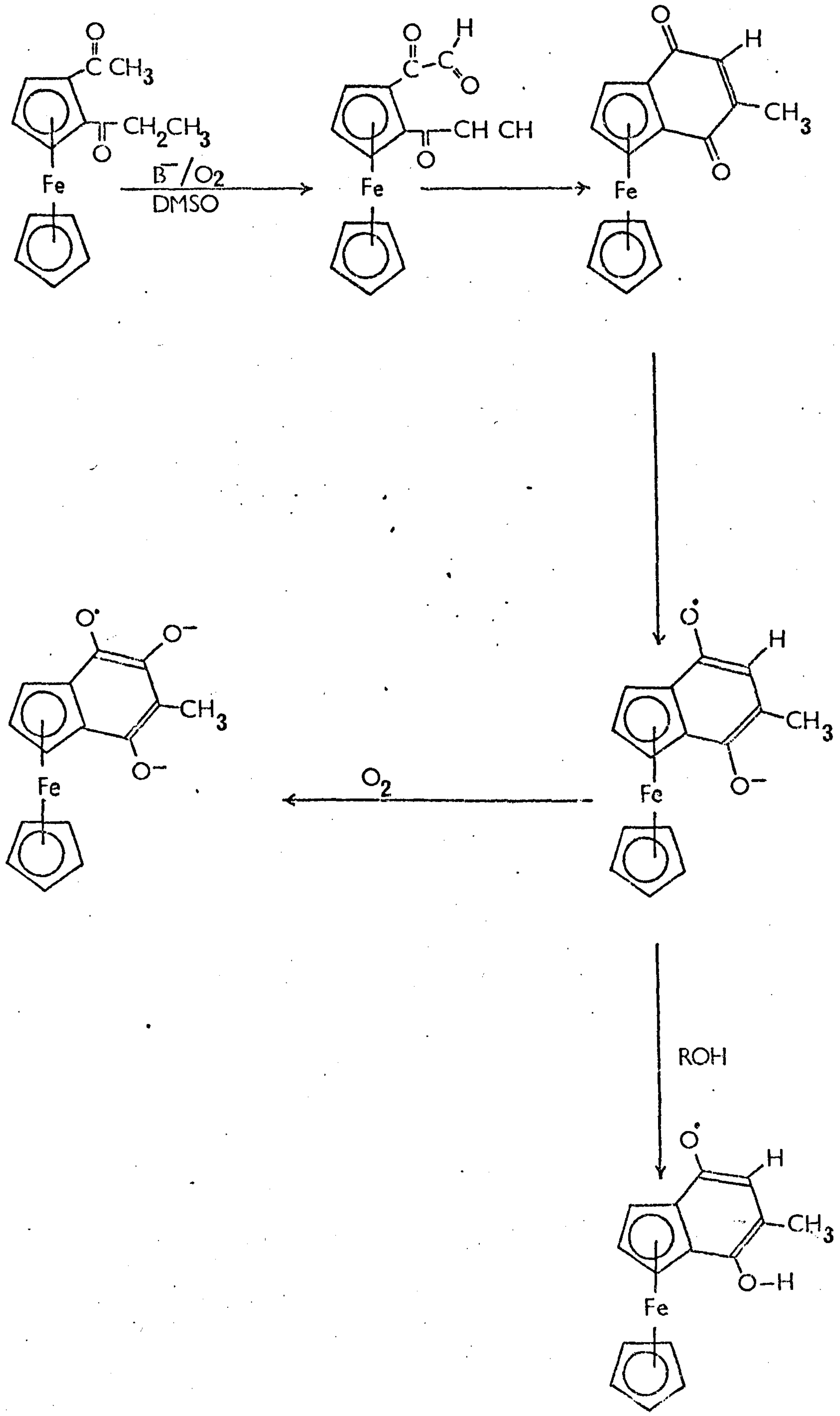


XXII XXI

Using the same reaction conditions, 1,2-ferrocenyl diketones have been observed to condense upon initial oxidation to form the corresponding quinones according to the following scheme (148).

The radical species $(\eta^5\text{-}C_5H_5)Fe(CO)_2$ has been detected by spin trapping techniques (88) from photolysis of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$.

The binuclear $[(\eta^3\text{-}C_3H_5)Fe(CO)_3]_2$ dissociates in solution to give a paramagnetic species (149), and analysis of the ESR signal over the temperature range of +40°C to -90°C establishes that the solution state of the compounds is fully represented as an equilibrium between dimer and monomer. No gas phase data are available, but mass spectral studies show dimer to be present. Solvent effects on the equilibrium were small. The dimer rapidly isomerised 1-hexane to <u>trans</u>-2-hexane at 25°C, and rapidly polymerised allene at 22°C to a solid polymer. It is noteworthy that the substituted compound $(\eta^3\text{-}C_3H_5)Fe(CO)_2PPh_3$ does not dimerise but exists as a paramagnetic monomer (149). This must be a result of the bulkiness of the phosphine ligand, since monomers where PPh_3 was replaced by $P(OPh)_3$; PEt_3 or PMe_3 or PMe_3 all existed in equilibrium with the dimer.


CH3
CH2CH3
Fe
B⁻/O2
DMSO
H
CH CH
Fe
H
CH3
Fe
O·
H
CH3
O⁻
Fe
O2
O·
O⁻
CH3
O⁻
Fe
ROH
O·
H
CH3
O-H
Fe

d^9 Fe(-I), Ru(-I), Os(-I)

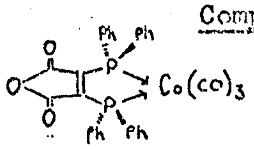
Theoretical studies (150) indicate that metal carbonyls with a metal-metal backbone have empty low-lying molecular orbitals associated with this system; one electron reduction of these compounds is therefore expected to be relatively facile. The addition or removal of an electron from a closed shell configuration of polynuclear metal carbonyls is also known to cause structural distortions (151) and this may prove to be a method for expanding or contracting metal polyhedra in cluster compounds.

In order to test this hypothesis, a number of new radical anions of the type $M(CO)_x^{-\bullet}$, $M_2(CO)_y^{-\bullet}$, $M_3(CO)_{12}^{-\bullet}$ have been characterised (142). Their preparation involves alkali metal and/or electrochemical reduction of the appropriate metal carbonyl compound in dry, oxygen-free ether solvent. A number of substituted metal carbonyl radical anions have previously been studied by the electrochemical method of Dessy et al (152). With most compounds reduction is rapid and reversible. Solutions of the radicals are stable, but attempts to isolate solid salts have so far proved unsuccessful. Quantitative yields of the parent carbonyls are obtained when the solutions are quenched with iodomethane, indicating that no gross structural changes have occured upon reduction. The ESR spectral parameters of the compounds listed have been determined: $Fe(CO)_5^{-\bullet}$; $Fe_2(CO)_9^{-\bullet}$; $Fe_3(CO)_{12}^{-\bullet}$; $Fe_3(CO)_{11}P(OPh)_3^{-\bullet}$; $RuFe_2(CO)_{12}^{-\bullet}$; $Ru_3(CO)_{12}^{-\bullet}$; $Os_3(CO)_{12}^{-}$ and $Ru_6C(CO)_{17}^{-\bullet}$.

The anion $Fe(\eta^4\text{-}C_6H_8)(CO)_2PPh_3^{-}$ has been prepared (141) by irradiating the neutral complex with ^{60}Co γ rays. The irradiation was carried out on the pure solid, or on glassy beads of frozen solutions at liquid nitrogen temperatures. The ESR spectrum was recorded.

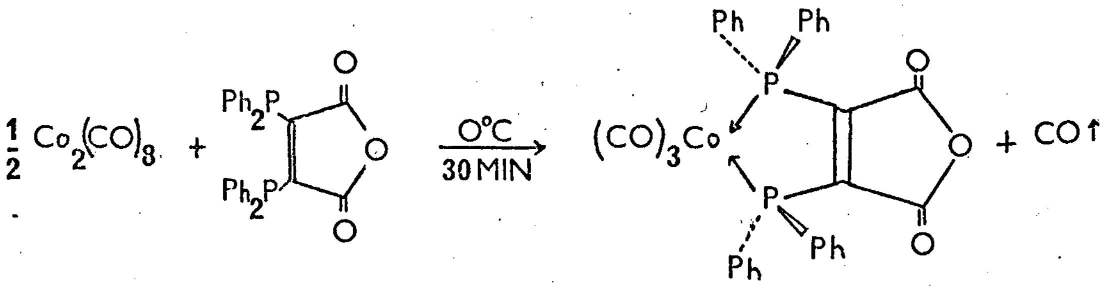
Some paramagnetic complexes of the remaining elements in Group VIII (Cobalt, Iridium, Nickel, and Platinum)

TABLE 7

Ion	Compounds	Reference
d^9 Co(0)		153
Ir(0)/Ir(I)	$Ir_4(CO)_{12}^{-\bullet}$	142
Ni(I)	($M(PR_3)_3$	
	($M(PR_3)_4E^-$	154
Pt(I)	($E = C_2(CN)_4$, $Cl_2(CN)_2^-$	
	benzoquinone or chloranil	
	M = Ni or Pt	

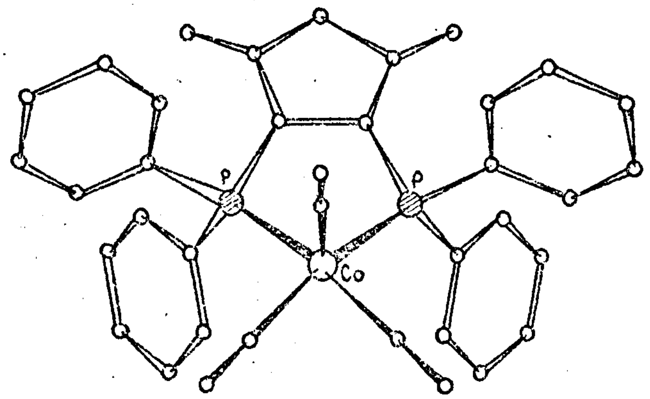
d^9 Co(0)

A new paramagnetic cobalt (0) complex, XXIII, has recently been reported (153) in which five electron pair donors are coordinated to the metal:



XXIII

Compound XXIII crystallises from ether/dichloromethane as dark green column shaped crystals. They are air stable, but decompose slowly in solution. A simple electron count shows the molecule to be a 19 electron species. The higher carbonyl vibration of the CO ligand which corresponds to that of the cationic complex $Co(CO)_3[P(C_6H_5)_3]_2{}^+$ (155), and the lower carbonyl vibration of the anhydride group in XXIII are regarded as indicating that the unpaired electron is heavily delocalised over the phosphine ligand.



Molecular structure of [bis(diphenylphosphino)maleic anhydride)] tricarbonylcobalt(0)

Various phosphine complexes of cobalt have been studied (156, 157). One in particular is formulated as $Co(Ph_2PC_2H_4PPh_2)_2X^+X^-$ which is essentially a square based pyramid of C_{2v} symmetry. It's ESR spectrum suggests that the unpaired electron is in a largely $d_{x^2-y^2}$ orbital.

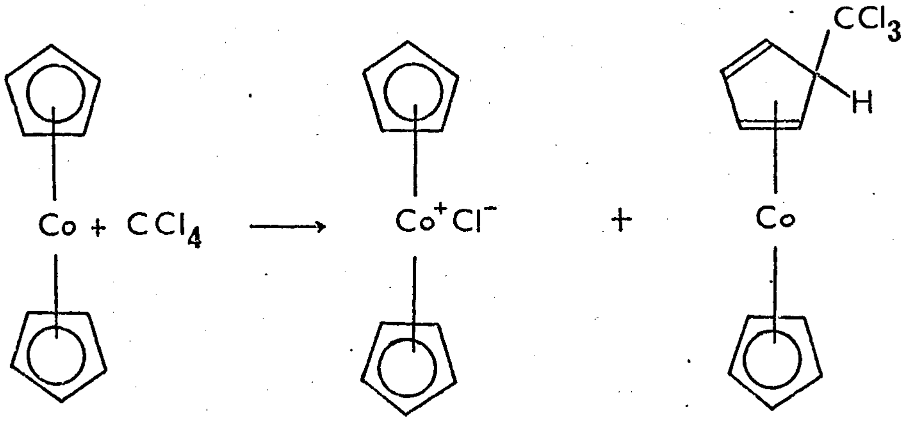
The ESR spectrum of the radical anion $Ir_4(CO)_{12}^{-\bullet}$ has been reported (142). This species is prepared by reduction (either chemical or electrolytic) of the parent carbonyl in thoroughly degassed solvents.

Transient paramagnetic Nickel complexes have been detected (154) during the exposure of typical diamagnetic d^{10} species of nickel (0) and platinum (0) species to known one-electron acceptors. The rapid reduction of such reagents as tetracyanoethylene (TCNE), dichlorodicyano-pbenzoquinone (DDQ) and chloranil (CH) was readily indicated by the immediate discharge of the colours of the metal (0) compounds in solution and the simultaneous appearance of the ESR spectrum of the corresponding radical anion. Complexes which have been treated in this way are NiR_4, R = PEt_3; PPh_3; $(diphos)_2$; $(PPh_3)_2(diphos)_2$ and $Pt(PEt_3)_3$.

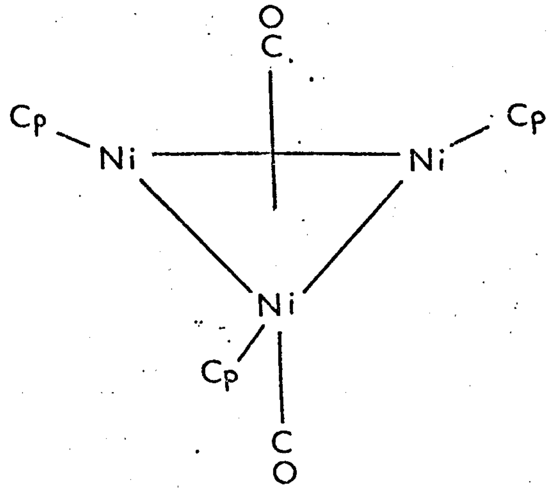
Very little ESR work has been carried out on rhodium complexes; Dessy et al (158) have observed resonances from a species thought to be $(\eta^5\text{-}C_5H_5\ Rh(\eta^2\text{-}C_2H_2)_2\ ^{+}$. In $(\eta^5\text{-}C_5H_5)_2Rh$, Keller and Wawersik (159) have considered the electron to be in the d_z2 orbital, as expected. The only ESR experiment on Ir(II) is that on $(\eta^5\text{-}C_5H_5)_2Ir$ where a small hyperfine coupling is detected (159).

Sublimation of octacarbonyldicobalt on to a cold finger at 77K yields a paramagnetic species identified from its ESR spectrum as the tetracarbonylcobalt radical (160). In the presence of oxygen, the peroxy radical is obtained. The structure of these radicals has been discussed.

Bis(η^5-cyclopentadienyl)cobalt (cobaltocene), the cobalt analogue of ferrocene, can be prepared in a variety of ways, but is most usually obtained from stoichiometric amounts of sodium cyclopentadienide and anhydrous cobalt (II) chloride (161). This reaction is exothermic and the mixture becomes dark purple. After heating at reflux to ensure completeness of reaction the solvent is removed in vacuo and the cobaltocene purified by sublimation at 60°C and 0,1 mm Hg. It forms purple/black air sensitive crystals which melt at 173°C. They are readily oxidised to the more stable cobaltocenium ion $[(\eta^5\text{-}C_5H_5)_2Co]^+$. Having one electron more than ferrocene, cobaltocene is paramagnetic (μeff 1,76 BM at room temperature), and so the ready loss of one electron to attain the more favourable 18 electron configuration is not surprising. Cobaltocene is insoluble in water and liquid ammonia but gives red/purple solutions in organic solvents. One of its more interesting reactions is that with carbon tetrachloride, in which the ionic cobaltocenium chloride is precipitated (162)



The use of ESR spectroscopy has shown (163) that in $(\eta^5\text{-}C_5H_5)_3Ni(CO)_2$, XXIV, the unpaired electron is in the π bonding molecular orbital linking the three nickel atoms.

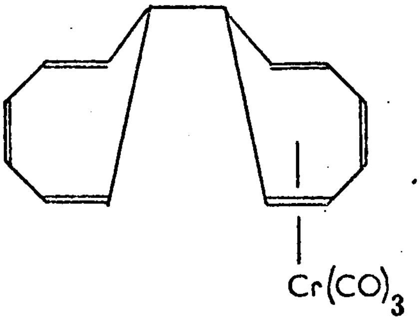


XXIV

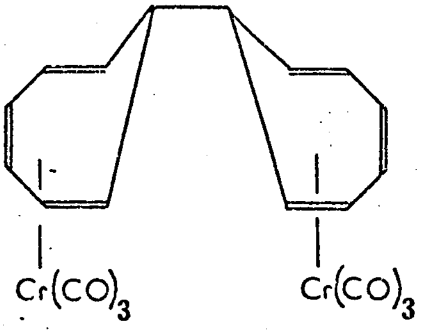
Dessy et al (164) have reported electrolytic reduction of $[(CO)_2NiPPh_2]_2$ and $[(\eta^5\text{-}C_5H_5)_2NiPPh_2]_2$. In each case, one electron only is added.

PART II

Many organometallic reaction mechanisms have now been constructed in which transient paramagnetic species play a vital role. One of the earlier reports of a free-radical reaction is due to Pauson and Munro (165), although the presence of radicals was not definitely confirmed. The reaction they reported was that of $[(\eta^7\text{-}C_7H_7)Cr(CO)_3]^+ClO_4^-$ with cyanide ion, in which the major products were found to be XXV and XXVI

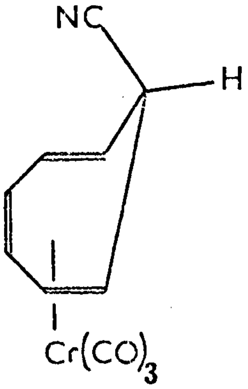


XXV



XXVI

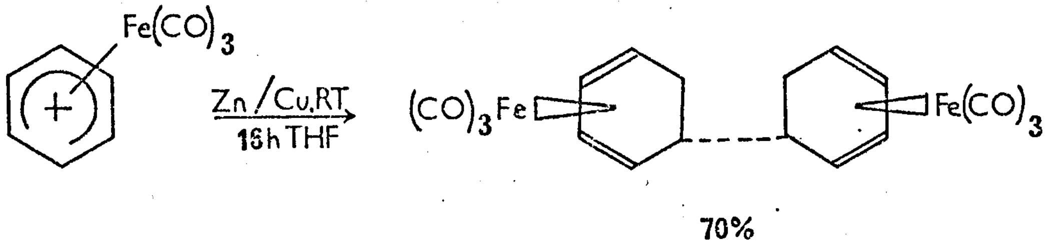
with only minor amounts of the expected cyano complex XXVII.

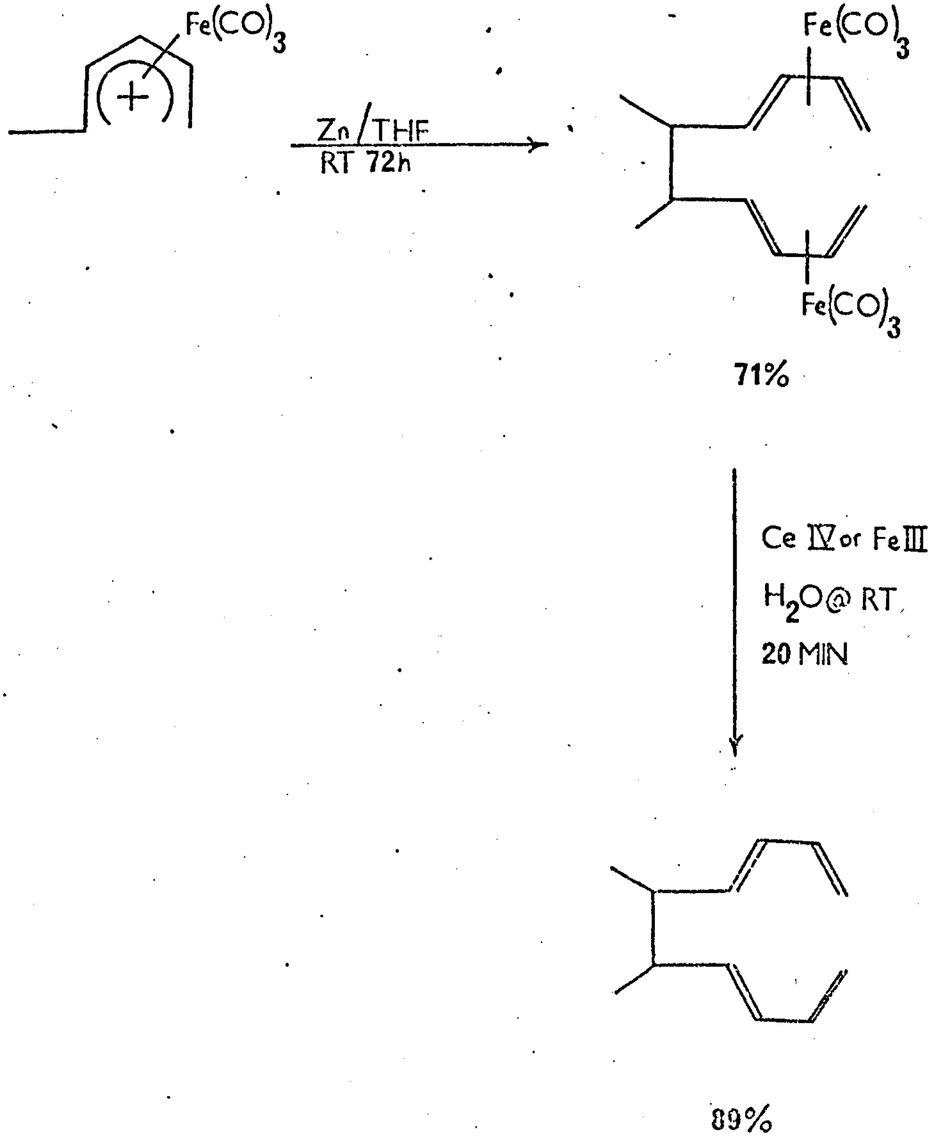


XXVII

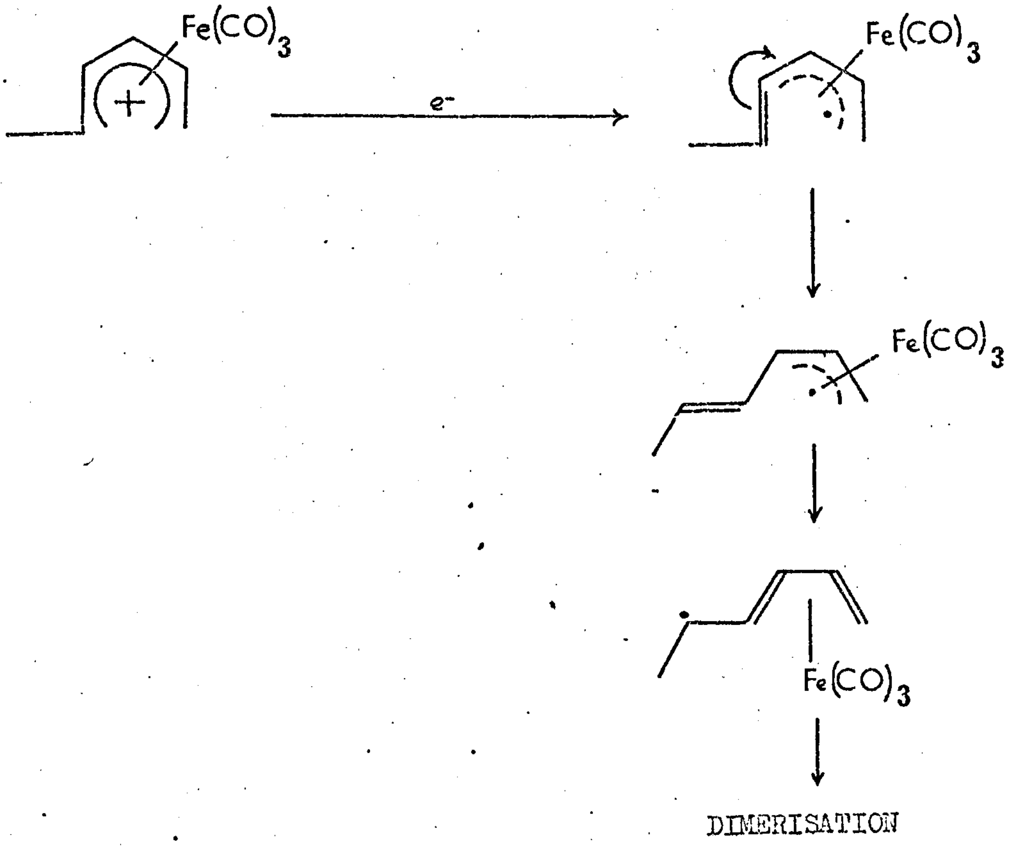
A detailed mechanism for this unusual reaction was not proposed, but the partial removal of chromium was considered significant. In general terms, it appeared that attack by the anion on chromium in the salt lead to cleavage with the formation of a Cr(0) complex which then (like zinc) reduces the salt to the dimeric species XXV by electron transfer. This seems likely to be a radical process. Similar dimers were obtained when the cation was treated with sodium acetate, sodamide, phenyllithium or benzamide.

A parallel reductive dimerisation has also been observed using either zinc (166) or a zinc/copper couple (18), as illustrated in the following scheme:





The mechanism which has been postulated for these reactions is as shown below.



The reaction of decacarbonyl dimanganese with triphenylphosphine has been investigated under a number of conditions (108), and both binuclear and mononuclear products obtained. By carrying out the reaction in an ESR cavity it was verified that paramagnetic species were formed during the reaction, but none were isolable. Basolo and Wawersik (167) have suggested a scheme which explained the paramagnetism but did not include the formation of the isolated trans hydride. The following scheme is more comprehensive, and is due to Miller and Myers (108)

$$Mn_2(CO)_{10} + PPh_3 \longrightarrow Mn_2(CO)_9PPh_3 + CO$$
$$Mn_2(CO)_9PPh_3 + PPh_3 \longrightarrow Mn_2(CO)_8(PPh_3)_2 + CO$$
$$Mn_2(CO)_8(PPh_3)_2 + [H] \longrightarrow PPh_3Mn(CO)_4 + HMn(CO)_4PPh_3$$
$$PPh_3Mn(CO)_4 + [H] \longrightarrow HMn(CO)_4PPh_3$$
$$HMn(CO)_4PPh_3 + PPh_3 \longrightarrow HMn(CO)_3(PPh_3)_2 + CO$$

where [H] denotes hydrogen abstracted from the solvent, and not triphenylphosphine (159a).

Although the substitution of $HRe(CO)_5$ by triphenylphosphane and other related ligands has been reported (169), no kinetic studies have been undertaken until recently. Indeed reproducible results are apparently difficult to obtain. Under the most rigorous attainable conditions of solvent and reagent purity, with the exclusion of light, the thermal reaction at 25°C in hexane under nitrogen of $HRe(CO)_5$ with tributylphosphane exhibited no change even after 60 days (169). Thus the pentacarbonyl hydride appears extraordinarily inert towards substitution via carbon monoxide dissociation or hydride migration pathways, in comparision with the manganese analogue (170). Exposure to light, failure to exhaustively purify the reagents, or other circumstances, caused the reaction to go to completion at widely varying rates to yield $HRe(CO)_4L$ and $HRe(CO)_3L_2$. With triphenylphosphane $HRe(CO)_4PPh_3$ was formed at similarly erratic rates. Exposure to air or hydroquinone in low concentration retarded the reaction.

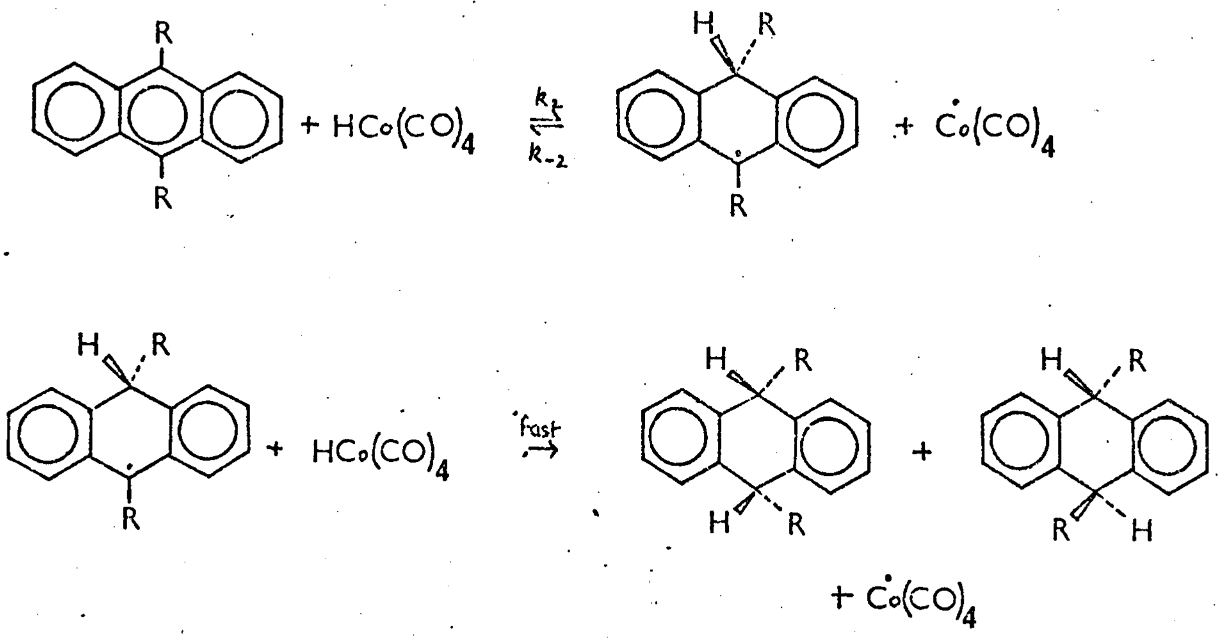
These observations suggested a radical pathway for the reaction, invoking adventitious radicals as initiators (169).

$$\begin{aligned}
R^{\bullet} + HRe(CO)_5 &\longrightarrow RH + {}^{\bullet}Re(CO)_5 \\
{}^{\bullet}Re(CO)_5 + L &\longrightarrow LRe(CO)_4^{\bullet} + CO \\
LRe(CO)_4^{\bullet} + L &\longrightarrow Re(CO)_3L_2^{\bullet} + CO \\
Re(CO)_4L^{\bullet} + HRe(CO)_5 &\longrightarrow Re(CO)_5^{\bullet} + HRe(CO)_4L \\
Re(CO)_3L_2^{\bullet} + HRe(CO)_5 &\longrightarrow Re(CO)_5^{\bullet} + HRe(CO)_3L_2 \\
Re(CO)_{5-n}L_n + Re(CO)_{5-m}L_m &\longrightarrow Re_2(CO)_{10-n-m}L_{n+m}
\end{aligned}$$

Chain termination involving the formation of $RRe(CO)_5$, $Re_2(CO)_9L$ and $Re_2(CO)_8L_2$ (but probably not $Re_2(CO)_6L_4$) are all possible.

A variety of polycyclic aromatic hydrocarbons are homogenenously hydrogenated in a highly selective manner (171) in the presence of $Co_2(CO)_8$ and synthesis gas at elevated temperatures and pressures. The operation of this catalyst, being one of the few known homogenous catalysts for aromatic hydrogenation has special interest. The proposed reaction scheme is given below (172)

$$Co_2(CO)_8 + H_2 \overset{K}{\rightleftharpoons} 2\,HCo(CO)_4$$



$$2\,\dot{C}o(CO)_4 \xrightarrow{fast} Co_2(CO)_8$$

The findings of various experiments using different substrates have been discussed in terms of this mechanism (172).

Recently (173), the hydrogenation of α -methylstyrene by hydridopentacarbonylmanganese (I) has been studied, and a free radical mechanism constructed:

$$C_6H_5C(CH_3) = CH_2 + HMn(CO)_5 \rightleftharpoons \{C_6H_5\dot{C}(CH_3)_2,\ \dot{M}n(CO)_5\}$$

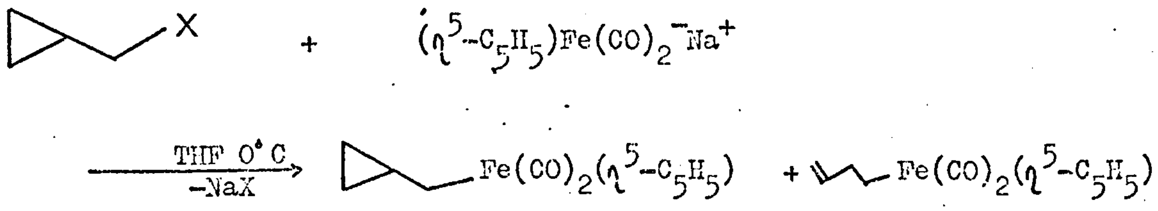
$$\xrightarrow[apart]{diffusion} C_6H_5\dot{C}(CH_3)_2 + \dot{M}n(CO)_5$$

$$C_6H_5\dot{C}\ (CH_3)_2 + HMn(CO)_5 \xrightarrow{fast} C_6H_5CH(CH_3)_2 + \dot{M}n(CO)_5$$

$$2\dot{M}n(CO)_5 \xrightarrow{fast} Mn_2(CO)_{10}$$

The reaction was found to proceed quantitatively as determined by NMR and UV spectroscopy and GLC analysis. Definitive evidence for this route was provided by the observation of CIDNP effects when the reaction was followed at 70°C in the probe of an NMR spectrometer, spectra being taken at 75 second intervals over the 90 minute duration of the reaction. The mechanism is interpreted in the form of the generally accepted "radical pair" route, involving competition between the back reaction of the geminate radicals to give the original reactants, and their separation (cage escape) with ultimate product formation. No evidence was found for the accumulation of detectable quantities of the cage-combination product $C_6H_5(CH_3)_2C{-}Mn(CO)_5$. This compound has not been reported in the literature and is expected to be unstable to decomposition via Mn–C bond homolysis under the conditions of the reaction.

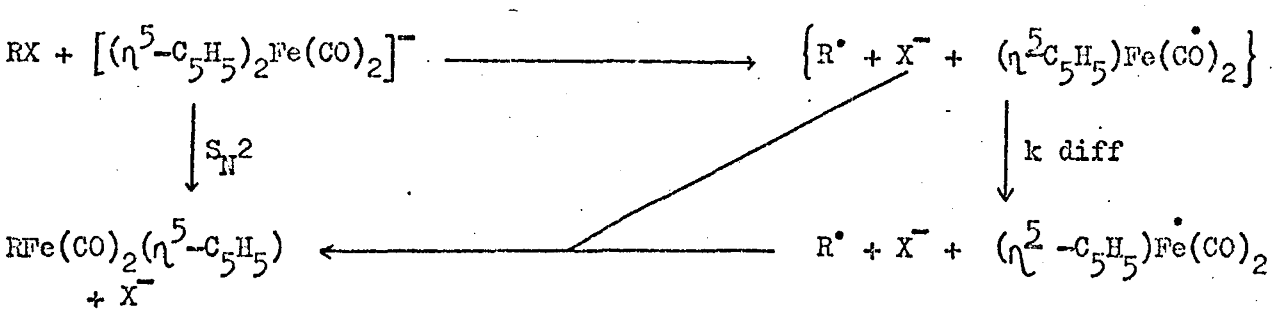
An intense ESR spectrum of isopropyl radicals has been detected by mixing solutions of sodium cyclopentadienyl(dicarbonyl)iron and cyclopropylcarbinyl iodide (174):



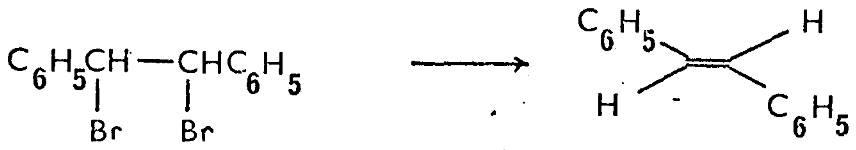
X= I	70%	30%
X= Br	97%	3%

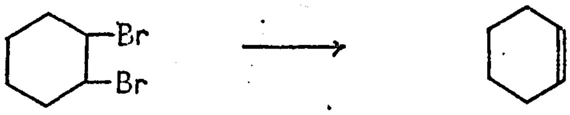
ESR spectra of similar quality of n -butyl, sec-butyl and tert-butyl radicals were recorded in the reaction of the iron anion with the corresponding iodides, and reaction with tropylium tetrafluoro borate gave an intense signal due to the $C_7H_7\cdot$ species.

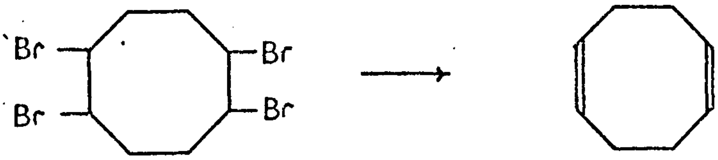
No ESR spectra were observed in any of these reactions which could be attributed to organometallic radicals, presumably because of the combined effects of short lifetimes, low steady state concentrations and the broad line widths expected for such species. The mechanism proposed is as follows:

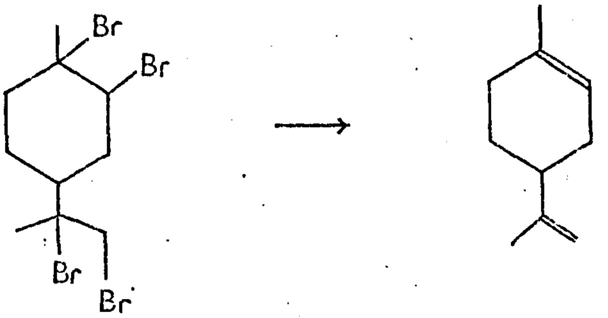


The selective removal of halogen atoms from organic halides using the paramagnetic $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$ has been reported (175). For example, the dimer reacts in a 1:1 ratio with vic-dihaloalkanes in refluxing THF to produce the corresponding alkenes:



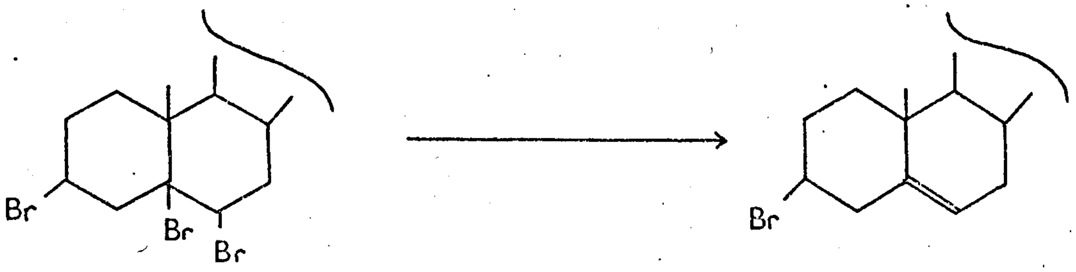






Total dehalogenation occurs in all reactions and the olefins are isolable in yields exceeding 75%. There is no reaction between the dimer and non-vicinal non-benzylic haloalkanes:

$$C_6H_5CHBrCHBr_2 \longrightarrow C_6H_5CH = CHBr \qquad 73\%$$



89%

trans dibromide
of cholesterol bromide

The ordering of reactivity of metal carbonyl radicals generated by the photoinduced cleavage of metal-metal bonds has been reported (176). For example, the order with respect to reaction with 1-iodopentane is found to be $Re(CO)_5 > Mn(CO)_5 > W(CO)_3(\eta^5\text{-}C_5H_5) > Mo(CO)_3(\eta^5\text{-}C_5H_5) > Fe(CO)_2(\eta^5\text{-}C_5H_5) > Co(CO)_4$. It was noted that the ordering of reactivity seemed to correlate with the lability of the metal-metal bonded complexes. For example, $Co(CO)^{\bullet}_4$ is the least reactive and and $Co_2(CO)_8$ has a labile Co-Co bond, whereas $Re(CO)_5$ is the most reactive and $Re_2(CO)_{10}$ has a fairly inert metal-metal bond. This conclusion is clearly a consequence of the greater energy needed to rupture a strong metal-metal interaction.

The photoinitiation of polymerisation and hydrogen abstraction by metal carbonyls has received much attention recently (177). Many transition metal complex/organic halide combinations are photoreactive. Among the carbonyls which have been investigated in detail from this point of view are decacarbonyldimanganese and decacarbonyldirhenium. In systems of this type, the active species produced photochemically enters into a redox reaction with the halide, and as a result the metal atom attains a higher oxidation state while the halide is converted into a free-radical:

$$Mn_2(CO)_{10} \xrightarrow{h\nu} 2Mn(CO)_5^{\bullet}$$
$$Mn(CO)_5 + CCl_4 \longrightarrow ClMn(CO)_5 + \overset{\bullet}{C}Cl_3$$

By replacing the simple halide with a preformed polyhalide, a wide variety of graft, block and network copolymers have been synthesised.

In 1972, it was found (178) that both decacarbonyldimanganese and decacarbonyldirhenium are very active photoinitiators for the polymerisation of liquid tetrafluoroethylene at -92°. The actual initiating species is though to be $(CO)_5MnCF_2\dot{C}F_2$. Other carbonyl complexes such as $Os_3(CO)_{12}$ and $Ru_3(CO)_{12}$ also show photoinitiating properties but are generally less active. The photoreactions of a great many carbonyl species are given in a published review (179).

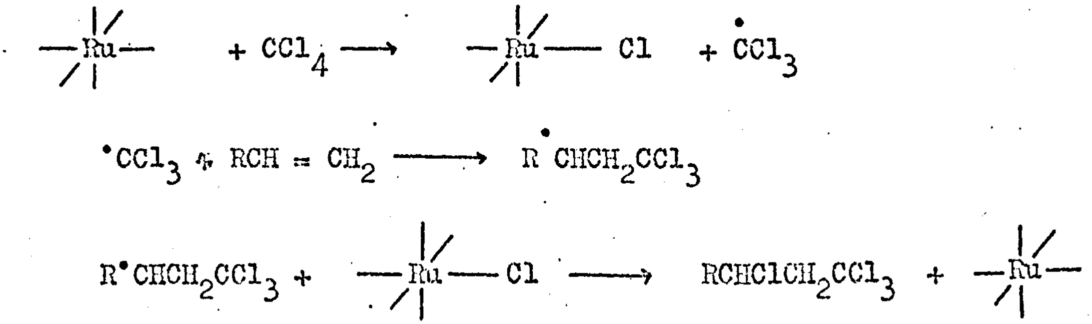
The complex dichlorotris(triphenylphosphane) ruthenium (II) has been used as a catalyst for the addition of CCl_4 to 1-olefins (180). The reaction proceeded smoothly under mild conditions to afford the corresponding 1:1 adducts. The good yields of these products indicated that the catalysed reaction was accompanied by little telomerisation. Some examples of the reactions are give in Table 8.

TABLE 8

Experiments on the addition of CCl_4 and $CHCl_3$ to 1-alkenes (180)

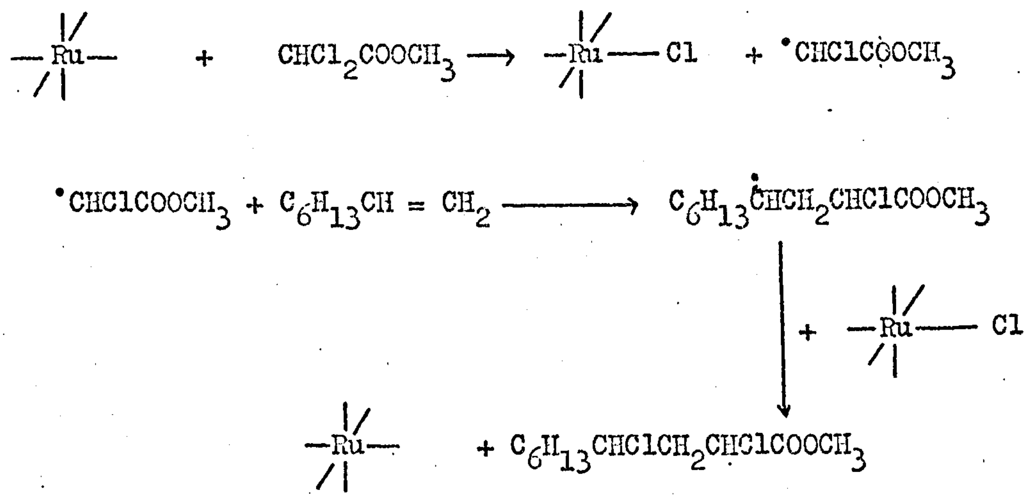
Alkene	Halide	Conditions	Adduct/yield %	
1-octene	CCl_4	80°/4h	$CCl_3CH_2CHClC_6H_{13}$	(97)
1-octene	$CHCl_3$	140°/15h	$CHCl_2CH_2CHClC_6H_{13}$	(67)
1-nonene	CCl_4	80°/4h	$CCl_3CH_2CHClC_7H_{15}$	(95)
1-hexene	CCl_4	80°/4h	$CCl_3CH_2CHClC_4H_9$	(88)

The reaction mechanism was proposed as:



That the reaction was completely inhibited by small concentrations of galvinoxyl was offered as evidence of the presence of radical intermediates.

More recently, the same authors have reported the similar reaction of polychloroacetic acid esters with 1-alkenes (181). For example, methyldichloroacetate with 1-octene at $120^{\circ}C$ for 20h gave methyl-2,4-dichlorodecanoate in 95% yield:



This reaction was found to be equally applicable to easily polymerised alkenes such as styrene, acrylonitrile and methyl methacrylate.

The reaction between low valent metal complexes and an alkyl halide belongs to the class known collectively as oxidative additions, and much controversy has centred on its mechanism. Recent evidence suggests free-radical intermediates in many cases. This type of reaction is of widespread occurence and is important due to its usefulness in synthesis and some catalytic systems. In one of its forms it may be described as:

$$[LM] \quad + \quad A\text{–}B \longrightarrow [LM(A)B]$$

The complex LM may be neutral or positively or negatively charged, and the molecule A–B may be for example, O_2, H_2, RX, R_3SiH or RHgX.

Mechanisms involving free-radicals in this reaction were not proposed until 1972. The addition of an alkyl halide to the d^7 complex $[Co(CN)_5]^{3-}$ results in a one-electron oxidation of the metal and proceeds via homoltlic abstraction of halogen (182, 183). For a methyl or benzyl halide, an organocobalt product is formed:

$$[Co(CN)_5]^{3-} + RX \longrightarrow [Co(X)(CN)_5]^{3-} + R^{\cdot}$$
$$[Co(CN)_5]^{3-} + R^{\cdot} \longrightarrow [Co(R)(CN)_5]^{3-}$$

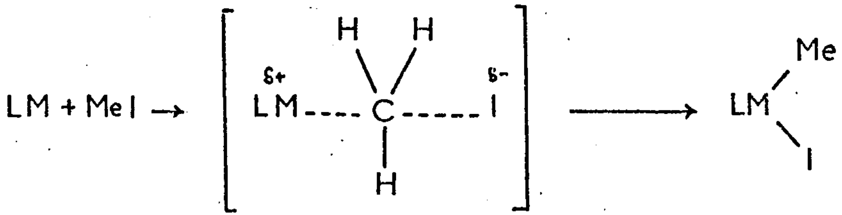
whereas for other halides alkenes may be formed in a competing reaction:

$$[Co(CN)_5]^{3-} + C^{\cdot}{}_2H_5 \longrightarrow [Co(H)(CN)_5]^{3-} + C_2H_4$$

Most of the mechanistic work on oxidative addition to d^8 complexes has been concerned with Ir(I), and in particular with trans $Ir(CO)Cl(PPh_3)_2$:

$$Ir(CO)Cl(PPh_3)_2 + MeI \longrightarrow Ir(CO)(Me)(Cl)(I)(PPh_3)_2$$

An early kinetic study (184) suggested that the Ir(I) complex was acting as a nucleophile in an SN2 reaction:

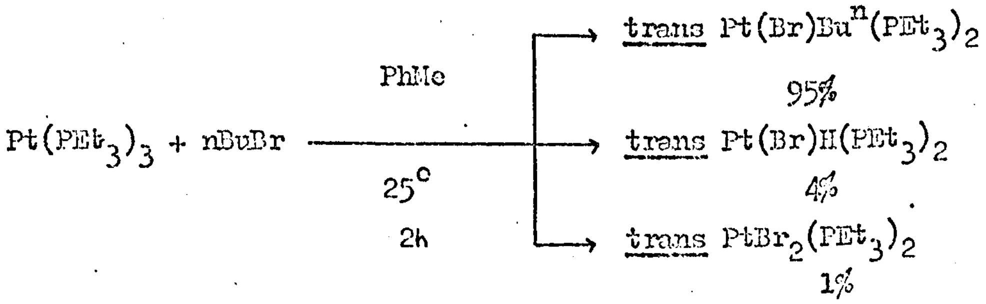


LM = $Ir(CO)Cl(PPh_3)_2$.

After 1972, radical chain processes as a means of explaining the oxidative addition reaction gained support, and such a mechanism was suggested for the addition of $PhCHFCH_2Br$ to <u>trans</u> $Ir(CO)Cl(PMe_3)_2$ to give $IrBr(CO)Cl(CH_2CHFPh)(PMe_3)_2$ (185). The evidence cited for radical intermediates was (i) initiation by O_2 or Bz_2O_2; (ii) retardation by hydroquinone and (iii) a reactivity order in which the rate of addition of halide was increased by its having electronegative substituents. The mechanism proposed is now outlined:

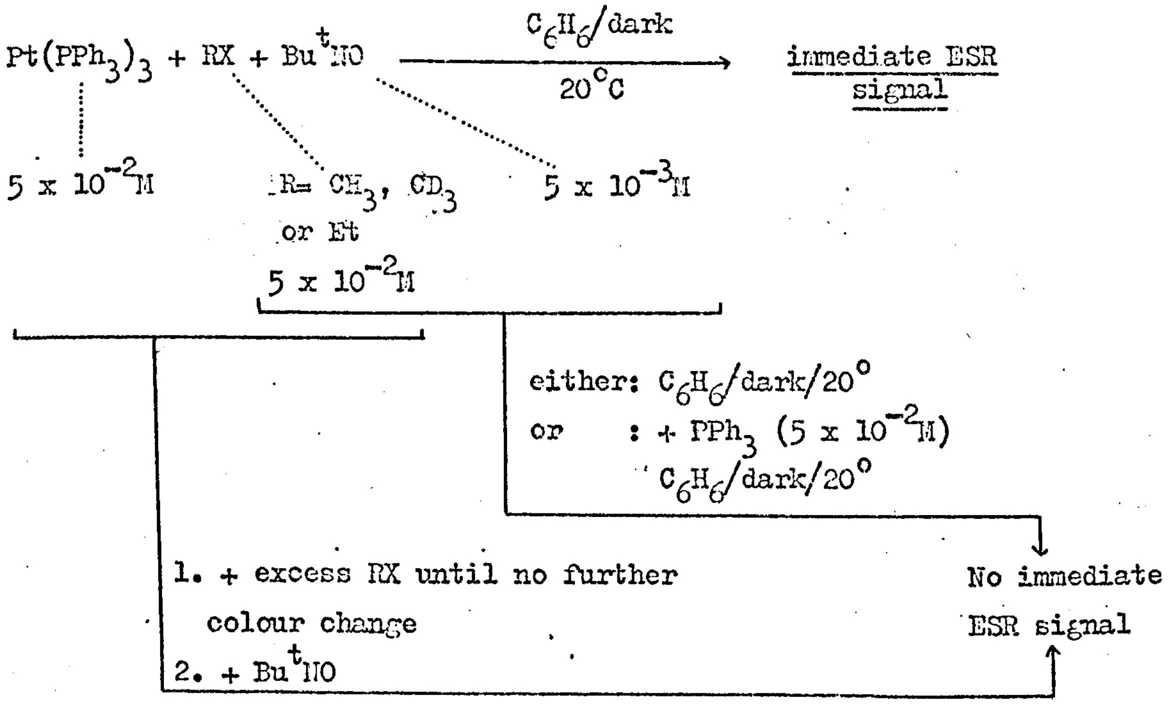
$$Q^{\bullet} + [Ir(I)] \longrightarrow [Ir(II)\text{-}Q]$$
$$[Ir(II)\text{-}Q] + RBr \longrightarrow [BrI(III)\text{-}Q] + R^{\bullet}$$
$$[Ir(I)] + R^{\bullet} \longrightarrow [Ir(II) - R]$$
$$[Ir(II) - R] + RBR \longrightarrow [BrIr(III)\text{-}R] + R^{\bullet}$$

Initiation is believed to be by some unknown radical $Q^{\bullet}$, and the last two equations represent the propagation sequence. Since this mechanism was first proposed, many other such reactions have been explained by invoking free-radical intermediates (see eg 186, 187). The oxidative addition reaction may yields a mixture of several products. For example, $Pt(PEt_3)_3$ and <u>n</u>BuBr in toluene at 25° reacted (186) as follows:



Further reaction afforded the dibromide at the expense of $Pt(Br)Bu^n(PEt_3)_2$ whereas the yield of hydride increased to a maximum and then declined as it reacted with more 1-bromobutane to yield the dibromide.

The use of spin trapping techniques has provided unequivocal proof of the intermediacy of radical species in this type of reaction (188). When the addition of iodomethane, iodomethane d_3, and iodoethane to $Pt(PPh_3)_3$ was carried out in the presence of Bu^tNO, strong signals for the corresponding nitroxide $Bu^t(R)N\dot{O}$ were observed. Control experiments showed that the signals were not derived from either of the reactants nor from either of the products. This is summarised in the scheme below:



The proposed mechanism is non chain (188)

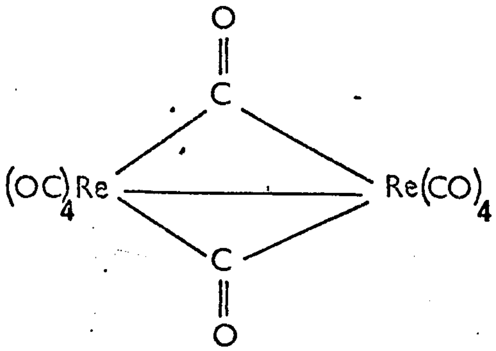
$$Pt(PPh_3)_3 \longrightarrow Pt(PPh_3)_2 + PPh_3$$
$$Pt(PPh_3)_2 + RX \underset{}{\overset{slow}{\rightleftharpoons}} PtX(PPh_3)_2 + R^\bullet$$
$$PtX(PPh_3)_2 + R^\bullet \overset{fast}{\rightleftharpoons} \underline{trans}\ Pt(X)(R)(PPh_3)_2$$

CHAPTER 2

STUDIES ON THE REACTIONS OF DECACARBONYLDIRHENIUM WITH ORGANOPHOSPHANES AND PHOSPHITES

Introduction

Decacarbonyldirhenium was first prepared in 1941 (189) from the reaction between rhenium heptaoxide and carbon monoxide at 200 atmospheres pressure and 200°C for 16 hours. The molecules form colourless monoclinic crystals of typical carbonyl character, and cryoscopic measurements have shown it to be dimeric. It may be purified by sublimation or by crystallisation. Its decomposition to the metal and carbon monoxide only is complete at 400°C. The first proposed structure was one involving carbonyl bridges (189):



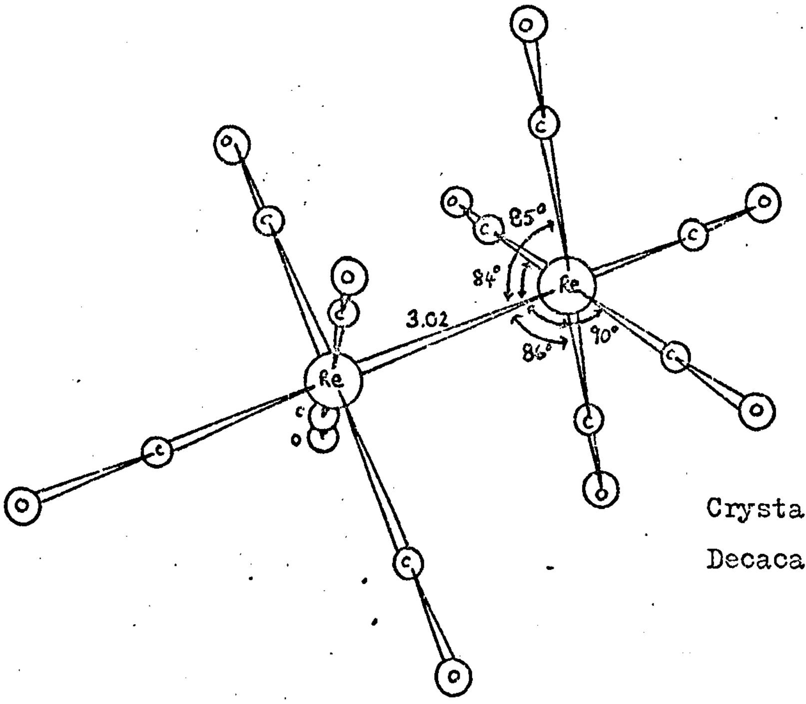
This arrangement would allow each metal atom to attain the favoured inert gas configuration of electrons. On the basis of an infra-red study, this structure was shown to be incorrect (190) since none of the three observed stretching bands lie in the region usually associated with bridging carbonyl groups (1700–1900 cm^{-1}). The actual frequencies are given in Table 9.

TABLE 9

$\nu_{C\equiv O}$/cm^{-1} for $Re_2(CO)_{10}$ in iso-octane at 25°C (191)

2071	(ε 8369 l mol^{-1} cm^{-1})
2015	(42400)
1972	(12300)

The observed diamagnetism and IR spectrum of the complex were originally explained in terms of a pseudo-ring of six carbon monoxide groups situated between the two rhenium atoms, perpendicular to the metal-metal axis and somehow bonded to each metal centre (190). This postulate was short lived however, when it was shown by X-ray diffraction work (192) that the dimeric molecule appeared as two octahedra linked by a rhenium-rhenium bond of length 3.02Å. The dimer persists in solution and the vapour phase.



Crystal structure of Decacarbonyldirhenium

The first report of the reaction between decacarbonyldirhenium and a tertiary phosphane was by Hieber (193) who found that triphenylphosphane and the carbonyl in boiling xylene for 48 hours gave the diamagnetic $[Re(CO)_4PPh_3]_2$. When this was repeated in 1965 by Nyman (113), the major product isolated was the paramagnetic monomer $Re(CO)_3(PPh_3)_2$, which had a magnetic moment of 1.7 BM, and melted with decomposition at 197-9°. This complex was assigned a <u>trans</u>-trigonal bipyramidal structure on the basis of the single peak (at 1934 cm^{-1}) in the carbonyl stretching region of the IR spectrum and its zero dipole moment. When the reaction time was reduced to 10 hours, a product melting at 227-8°C was obtained, and molecular weight determination indicated a dimeric species, presumably that originally reported by Hieber.

This latter compound was also prepared in high yield (70%) by the photochemical reaction of the parent carbonyl with triphenylphosphane in light petroleum (113). Substituted complexes with other phosphane type ligands have been reported from similar reactions. Thus with diethylphenylphosphane in xylene under reflux or photolysis at room temperature the product $[Re(CO)_3(PEt_2Ph)_2]_2$ is obtained (113). This compound is reported to be diamagnetic in the solid state, but paramagnetic in solution, i.e. largely dissociated. Other workers have also studied the reaction of $Re_2(CO)_{10}$ with PPh_3 (112, 194). Jolly and Stone confirmed Hieber's reported preparation of the dimeric $[Re(CO)_4PPh_3]_2$ and verified Nyman's report (113) that longer reaction times lead to a paramagnetic monomer, although their identification was merely by comparison with the published IR spectrum.

A polynuclear carbonyl of rhenium has been reported from the reaction of rhenium heptasulphide and carbon monoxide in the presence of copper powder (195):

$$Re_2S_7 + Cu + CO \xrightarrow[7h]{200^\circ} Re_2(CO)_{10} + [Re(CO)_4]_n$$

The evidence supporting the structure given for the tetracarbonyl species is not conclusive, but a tetrahedron of rhenium atoms is envisaged. However, subsequent studies by Johnson and co-workers showed the tetranuclear product to be $H_4Re_4(CO)_{12}$ (195a). Nevertheless the original report also states that the molecule reacts photochemically with triphenylphosphane and triphenylphosphite to yield complexes of empirical formulae $Re(CO)_3L_2$ (195). Magnetic moments in the solid state indicate that the triphenylphosphane complex is paramagnetic (μeff= 1.1 BM) and that the triphenylphosphite complex is diamagnetic. They may thus be considered as monomeric and dimeric respectively. Both are monomeric in benzene, however, and the dissociation of the triphenylphosphite species has been checked by measuring its magnetic moment in this solvent (195). This monomer was found to have a magnetic moment of 1.0 BM. The complex $Re(CO)_3(PPh_3)_2$ had been previously formulated as a dimer (196).

The preparation of $Re_2(CO)_8(PPh_3)_2$ and $Re_2(CO)_9PPh_3$ has also been reported by Poë's group (197). It was found that the latter complex could not be prepared in a similar fashion to its manganese analogue (167) since the former was found to be the major product even with less than two equivalents of triphenylphosphane. The preparation was effected by reacting $[Re(CO)_4PPh_3]_2$ with carbon monoxide, kinetic studies (198) having shown that this goes to completion at 125° in hydrocarbon solvents and with complex concentrations of the order of 10^{-3} M. With higher concentrations the triphenylphosphane released during the reaction prevents it from proceeding to completion, but separation of mono- and bis- phosphane derivatives is efficient by chromatography. The reaction was carried out by passing a stream of CO gas through a solution of $[Re(CO)_4PPh_3]_2$ in xylene at 130°C for 30 hours. After this time, the solvent was removed under reduced pressure and the product separated by chromatography as described for the manganese species (167).

The redox behaviour of the group VII metal-metal bonded carbonyls has been the subject of some study (199). The electrochemical reduction parameters of $M_2(CO)_{10}$ (M_2 = Mn_2, MnRe or Re_2) were compared with those of the related axially substituted $M_2(CO)_8L_2$ compounds. From the electronic absorption spectra of these complexes, the energies of the $\sigma \rightarrow \sigma^*$ transitions associated with the metal-metal bond were calculated. In $Mn_2(CO)_{10}$ and $MnRe(CO)_{10}$ these energies correlate well with the electrochemical results:

replacement of two axial carbonyl groups by triphenylphosphane weakens the metal-metal interaction. In contrast, the same substitution into $Re_2(CO)_{10}$ appears to lead to an increase in metal-metal bond strength. The energy associated with the $\sigma \rightarrow \sigma^*$ transition has been found to follow this sequence:

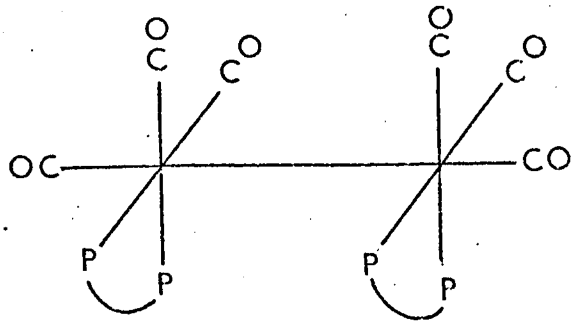
$$Re_2(CO)_8L_2 > Re_2(CO)_{10} > Re_2(CO)_9L$$

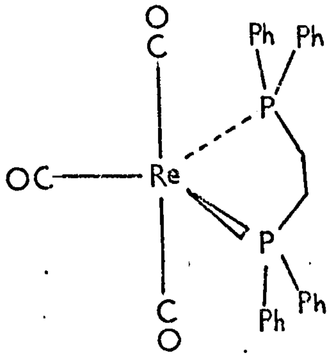
It is noteworthy that the nonacarbonyl dimer has a weaker metal-metal bond than the parent carbonyl.

The preparation of the paramagnetic species $Re(CO)_3(PPh_3)_2$ which first prompted the current work was reported by Freni et al in 1967 (112). The reaction was performed in the following manner: decacarbonyldirhenium (0.33 g) and triphenylphosphane (1.25 g) were heated in boiling xylene (15 ml) under nitrogen for 48 hours. The deep red solution was then concentrated under reduced pressure to dryness. The orange solid residue was dissolved in boiling benzene (10 ml) and on addition of hexane, orange crystals separated (0.7 g; 85%). This product was found to be soluble in benzene, xylene and chloroform, but insoluble in methanol, ethanol and hexane. Its IR spectrum as a nujol mull or in benzene solution showed three absorption bands in the carbonyl stretching region, at 2020, 1920 and 1820 cm^{-1}. A dipole moment of 5.1 D was found and this suggested either a square pyramidal or a trigonal bipyramidal structure. It was found to react with iodine to give trans-$Re(CO)_3(PPh_3)_2I$, which is known by another route (131)

Decacarbonyldirhenium reacts with 1,2-bisdiphenylphosphinoethane(diphos to yield [cis-$Re(CO)_3$(diphos)$]_2$, trans-$Re(CO)_3$(diphos), cis-$Re(CO)_2$(diphos)$_2$ and Re(CO)(diphos)$_2$ (112). In order to isolate well defined products, it was found necessary to operate using solid reagents in vacuo, and to keep the temperature and the reaction time under strict control. In fact, when the reagents were rapidly heated for a short time, two isomeric products, differing in solubility, were formed. Each had empirical formula $Re(CO)_3$(diphos) one was diamagnetic, dimeric and a non-electrolyte; and the other paramagnetic and therefore considered monomeric, although due to its low solubility no molecular weight determination was undertaken.

The diamagnetic compound [cisRe$(CO)_3$(diphos)$]_2$ showed three strong bands in its nujol mull IR spectrum, at 1965, 1905 and 1855 cm^{-1}. This indicated a C_s type structure in which the carbonyl groups are in the cis-position, and hexaco-ordination is achieved through formation of the metal-metal bond. The IR spectrum of the paramagnetic species, where two strong bands appear at 1905, 1855 cm^{-1} and a weak one at 1985 cm^{-1}, suggested a C_{2v} structure, with the carbonyl groups in a trans configuration:





Both of these compounds react with iodine, the first requiring two equivalents although the product is not well defined. The second is oxidised by one equivalent yielding trans $Re(CO)_3(diphos)I$, which exhibits three bands in the IR spectrum; one medium at 2010 and two strong bands at 1900 and 1848 cm^{-1}.

When the reaction between decacarbonyldirhenium and disphos is carried out at higher temperatures, the hexacoordinated compound $Re(CO)_2(diphos)_2$ is formed, which appears to be monomeric and paramagnetic. This 19 electron species is reported to react with acids to give a cationic species together with quantitative evolution of hydrogen (112):

$$Re(CO)_2(diphos)_2 + H^+ \longrightarrow Re(CO)_2(diphos)_2{}^+ + \tfrac{1}{2}H_2$$

The manganese analogue, $Mn(CO)_2(diphos)_2$ is not known (120); in the reaction between $Mn_2(CO)_{10}$ and 1,2-bisdiphenylphosphinoethane an ionic compound is formed, which has been considered to be dicarbonylbis(1,2,-bisdiphenylphosphinoethane)manganese (I) pentacarbonylmanganate(-I).

The oxidation of $Re(CO)_2(diphos)_2$ with iodine takes place in an anomalous way: it reacts with three equivalents of iodine giving $Re(CO)_2(diphos)_2I_3$, which is diamagnetic and a non-electrolyte. Since it is very unlike compounds in which Re(III) has a coordination number of nine, it is suggested that oxidation with iodine gives a Re(I) species in which the diphosphinoethane molecule acts as a unidentate ligand, one of the two phosphorous atoms having been oxidised to P(V).

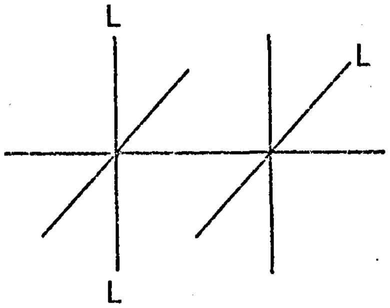
A crystalline compound of formula Re(CO)(diphos)$_2$, monomeric and paramagnetic, is formed during the preparation of Re(CO)$_3$(diphos)$_2$I$_3$, or when this latter complex is treated with excess diphenylphosphinoethane at high temperatures (112). Its dipole moment was not reported due to its low solubility. It was found to react with one equivalent of iodine giving Re(CO)(diphos)$_2$I which has also been reported by another route (131).

The basic dimethylphenylphosphane reacts with decacarbonyldirhenium (115) substituting cis to the Re–Re bond. This is in contrast to reaction with triphenylphosphane in which substitution occurs in the trans position (112, 113, 194, 200). The photochemical reaction with one equivalent of dimethylphenylphosphane per rhenium atom yields [Re(CO)$_4$(PMe$_2$Ph)]$_2$, Re(CO)$_3$(PMe$_2$Ph)$_2$ and Re$_2$(CO)$_7$(PMe$_2$Ph)$_3$. Intermediates such as Re(CO)$_3$(PMe$_2$Ph)$_2$ and [Re(CO)$_3$(PMe$_2$Ph)$_2$]$_2$ were found to react with the chlorinated solvents dichloromethane and chloroform in which the crude material was dissolved and gently warmed to form halocarbonyl-phosphane complexes such as cis and trans Re(CO)$_3$(PMe$_2$Ph)$_2$Cl. These compounds were, however, formed only in very low yields of normally less than 10%. Thermal reactions, tended to give similar products in higher yields although the reaction time was considerably longer. For example, the disubstituted compound [Re(CO)$_4$PMe$_2$Ph]$_2$ was obtained in 46% yield in a thermal reaction, but only in 4.3% yield photochemically. The products of these reactions were readily separated and purified by column chromatography.

The disubstituted products [Re(CO)$_4$PMe$_2$Ph]$_2$ appeared to be dimeric in both solid and solution. The paramagnetic compound Re(CO)$_3$(PMe$_2$Ph)$_2$ shows two strong bands and one medium band in its IR spectrum in the carbonyl region. This is in contrast to Nyman's reported spectrum for the analogous triphenylphosphane complex (113) which exhibited only one band. There appears to be a descrepancy here, since Freni's group (112) claimed three bands for this molecule.

The compound Re$_2$(CO)$_7$(PMe$_2$Ph)$_3$ exhibits six carbonyl type bands in its IR spectrum; four strong, one medium and one weak (115). Reactions carried out on this molecule indicate that two carbonyls trans to one another on one rhenium atom have been substituted, while only one on the other. The authors considered the local symmetry of each half of the molecule in order to explain the observed spectrum.

On the basis of ^{31}P-coupled NMR spectra, the following structure has been given for Re$_2$(CO)$_7$(PMe$_2$Ph)$_3$:



The unusual paramagnetic species $Re(CO)_5(PMe_2Ph)$ has been isolated (115) from the reaction of decacarbonyldirhenium and PMe_2Ph. In this particular molecule there are six donor ligands around a rhenium (0) d^7 atom. It shows two weak bands at high frequency in its IR spectrum, a strong band at 1950 cm^{-1} and a third weak band at 1905 cm^{-1}.

Decacarbonyldirhenium reacts with methyldiphenylphosphane on refluxing for 15 hours in xylene solution to produce the disubstituted dirhenium compound $[Re(CO)_4(PMePh_2)]_2$ in only a moderate yield (114). This compound was isolated and purified chromatographically using alumina, but no other products were separated in any significant amounts (114). On the other hand, the photolytic reaction with one mole of PMe_2Ph per rhenium atom in cyclohexane yielded five main products which were readily separated from unreacted decacarbonyl and isolated by chromatography. The products isolated were $Re_2(CO)_9(PMePh_2)$, $[Re(CO)_4PMePh_2]_2$, two isomers of formula $Re_2(CO)_7(PMePh_2)_3$ and the new cluster compound $Re_4(CO)_{10}(PMePh_2)_6$. When decacarbonylderhenium was reacted (114) photochemically with two moles of $PMePh_2$ per rhenium atom, two unsymmetrical substituted dirhenium complexes were obtained. In addition to these a paramagnetic complex $Re(CO)_3(PMePh_2)_2$ was isolated in low yield. This is extremely soluble in all organic solvents, even petroleum either, and is difficult to purify. The bright yellow oily residue from which the $Re(CO)_3(PMePh_2)_2$ compound could be isolated reacted with HCl gas at $0^{\circ}C$ to yield trans $Re(CO)_3(PMePh_2)_2Cl$.

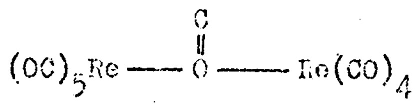
The $Re_2(CO)_8L_2$ complexes are oxidised by halogens or by hydrogen halides to yield both cis- and trans- $Re(CO)_4LX$ species. The stereochemistry of these resulting Re(I) compounds reflect to a certain extent the arrangement of ligands in the original dimer. Thus trans- $Re(CO)_4XPPh_3$ species are obtained from $Re_2(CO)_8(PPh_3)_2$ (112, 194) and cis complexes from $Re_2(CO)_8(PMe_2Ph)_2$ (115) and $Re_2(CO)_8(PMePh_2)_2$ (114).

The substitution reaction of decacarbonyldirhenium with triphenylphosphane has been studied kinetically between 130 and 150° in decalin (200). The kinetic behaviour is generally good, and the reaction shows a strong resemblance to the corresponding manganese system (201). A general reaction scheme is thought to involve the formation at $(OC)_5M{-}\overset{\overset{O}{\|}}{C}{-}M(CO)_5$ species (vide infra)

Samples of reaction mixtures of decacarbonyldirhenium and a large excess of triphenylphosphane showed the growth with time of a strong band at 1960 cm^{-1}. This was considered consistent with the formation of $Re_2(CO)_8(PPh_3)_2$, both the phosphine ligands being in axial positions. Peaks at 2106, 2034 and 1998 cm^{-1} were also observed, and these were assigned to $Re_2(CO)_9PPh_3$ (201). The loss of $Re_2(CO)_{10}$ was monitored by following the decrease of its IR absorption at 2070 cm^{-1}. The reaction was first order in concentration of $Re_2(CO)_{10}$, and good rate plots were obtained for up to 80-90% reaction.

Plots of absorbance against time were made for the growth of absorption maxima at 1998 cm^{-1} $[Re_2(CO)_9PPh_3]$, and 1960 cm^{-1} $[Re_2(CO)_8(PPh_3)_2]$ for a set of reactions at 150°C and various values of $[PPh_3]$. When $[PPh_3]$ was 50 and 10 mM, the plots were essentially identical, the absorbance due to $Re_2(CO)_9PPh_3$ rising to a maximum after about 70 minutes and then showing a steady decline. The absorbance of the bis-phosphine complex rose steadily to reach a maximum after ca 300 minutes. The nonacarbonyl complex is more reactive towards further substitution than the manganese analogue, and at lower concentrations of PPh_3 it appears to comprise about 25 to 30% of the product after 70 minutes.

Most of the kinetic results can be readily explained by the slow formation (governed by a first-order rate constant, k_1) of a reactive intermediate which can then either revert to the original carbonyl by a first order reaction, or react further to form products (k_2). It was established that the reactive intermediate could not be $Re_2(CO)_9$ (and an equivalent of CO) or a pair of independant $Re(CO)_5$ radicals, since if this were so k_{-1} would be a second-order rate constant, which was not the case. The favoured intermediate was envisaged as being the carbonyl bridged species mentioned earlier:



$$(OC)_5Re{-}\overset{\overset{O}{\|}}{C}{-}Re(CO)_4$$

This is formed by a migration of one $Re(CO)_5$ group, leaving the other metal atom co-ordinatively unsaturated and thus readily subject to further attack.

The substitution of a carbonyl ligand by triphenylphosphane was considered to proceed mainly by this mechanism, but an additional path was also available. This was completely suppressed by one atmosphere of carbon monoxide and was therefore, thought to involve easily reversible formation of $Re_2(CO)_9$ + CO by a dissociative path, a mechanism favoured by Basolo and Wawersik (167) for the manganese analogue.

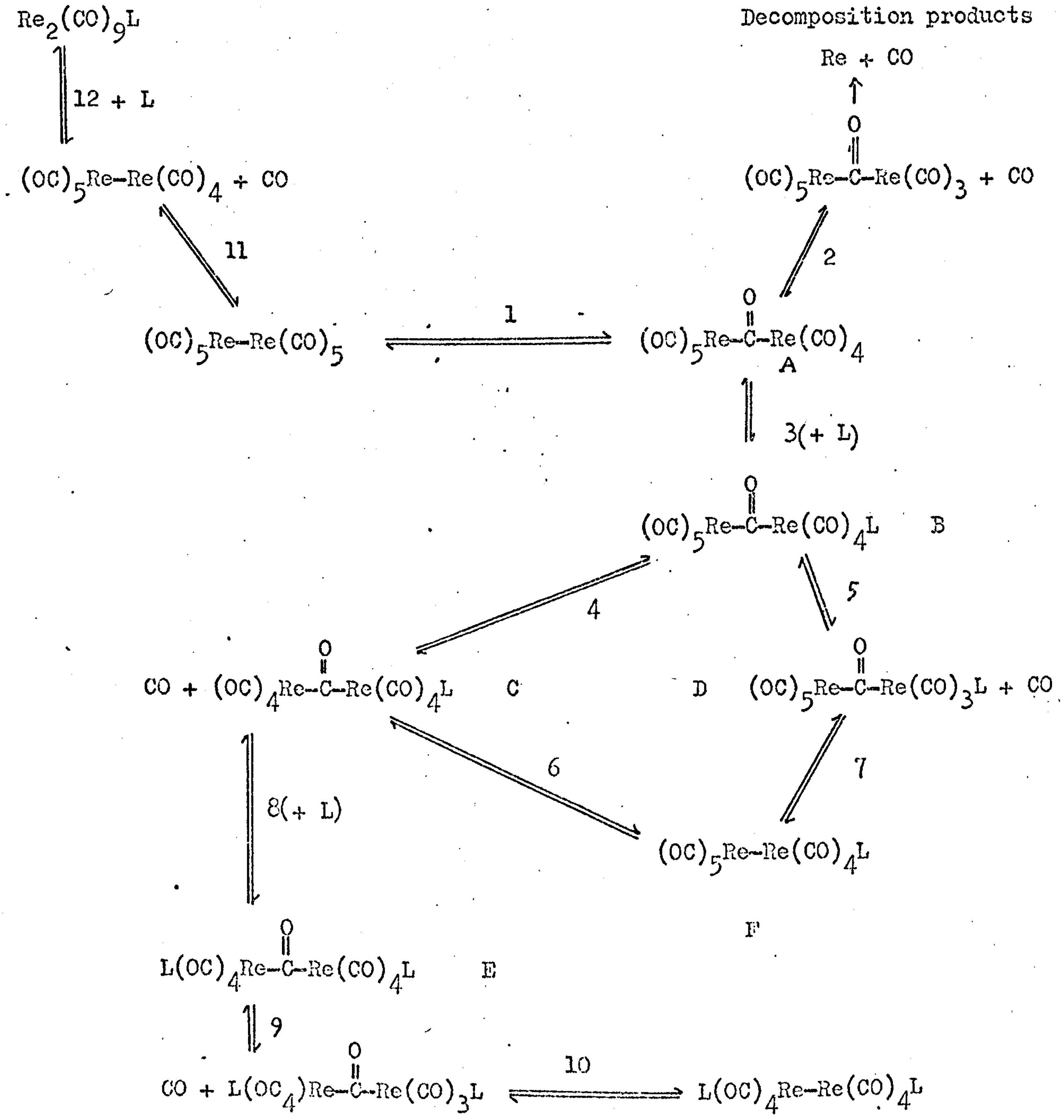
All of these features have been incorporated into a reaction Scheme (1). The substitutions can all proceed by formation of the carbonyl bridged intermediate followed by addition of a reactant molecule at the vacant co-ordination site. Further reaction involves the loss of one CO ligand from B followed by re-formation of the M–M bond. Loss of CO can occur from either metal atom. The intermediate D differs from C in that addition of another phosphane ligand L, to D, apparently cannot occur since no complex $M_2(CO)_8(PPh_3)_2$ is known with both phosphane ligands attached to the same metal atom (no doubt a consequence of steric hinderance). Reaction via D can, therefore, give directly only the mono-phosphane complex. On the other hand, C can undergo either re-formation of the Re–Re bond to form the mono-phosphane complex, or addition of a further phosphane molecule to form E. Subsequent loss of one CO ligand (reaction 9) and re-formation of the M–M bond (reaction 10) leads to the bis-phosphane complex. The choice between reaction 6 and 8 is dependant on the concentration of triphenylphosphane, and endorses what was stated earlier concerning the build up of F.

The retardation by carbon-monoxide of the decompositions of decacarbonyldirhenium is accounted for by the reversibility of reaction 2, and the retardation of the substitutions by the reversibility of 3, 4 and 5.

The occurence of some substitution by a path completely inhibited by 1 atm. of carbon monoxide is account for by reactinns 11 and 12.

SCHEME 1

The general reaction scheme for substitution reactions of $Re_2(CO)_{10}$



A kinetic study of the further reaction of $Re_2(CO)_8(PPh_3)_2$ with PPh_3 has been made (198). The reaction produces a variety of mononuclear species, and the half order kinetics (with respect to $Re_2(CO)_8(PPh_3)_2$) strongly suggest a reversible fission process of the type shown below:

$$Re_2(CO)_8(PPh_3)_2 \rightleftharpoons 2[Re(CO)_4PPh_3]$$
$$Re(CO)_4PPh_3 + PPh_3 \longrightarrow Re(CO)_3(PPh_3)_2$$

The possibility that further substitution into $Re_2(CO)_8(PPh_3)_2$ may occur prior to dissociation was not considered by these workers.

This particular aspect of the triphenylphosphane/decacarbonyldirhenium system is clearly an area of considerable interest. Its complexity makes difficult the assignment of a definitive reaction pathway.

2. RESULTS AND DISCUSSION OF THE REACTION OF $Re_2(CO)_{10}$ WITH PPh_3

2.1.1 Introduction and isolated products

Freni's report of the reaction between decacarbonyldirhenium and triphenylphosphane (112) has been discussed in some detail earlier and the salient features are summarised below:

$$Re_2(CO)_{10} + PPh_3 \xrightarrow[\substack{\text{reflux under}\\ \text{nitrogen, 48h}}]{\text{xylene soln}} Re(CO)_3(PPh_3)_2$$

1 : 5 85% yield; orange crystals

purification procedure:

(i) evaporate to dryness

(ii) dissolve residue in degassed benzene and precipitate with hexane

Following the reported purification procedure in the present study, use of identical conditions resulted in the isolation of either mer-trans-$HRe(CO)_3(PPh_3)_2$, bis-ax-$Re_2(CO)_8(PPh_3)_2$ or a mixture of these two depending on the rate of cooling or the composition of the benzene/hexane mixture. The products precipitated were identified by their very different and characteristic infra-red spectra (figures 4 and 6). The total number of products formed in the reaction are listed in Table 10, major components being underlined.

TABLE 10

Isolated products from the reaction of $Re_2(CO)_{10}$ and PPh_3 in a 1:9 molar ratio

	Mass spectral data *
eq - $Re_2(CO)_9PPh_3$	MS1; M^+884, $M^+-nCO(n = 1-9)$
bis-ax-$Re_2(CO)_8(PPh_3)_2$	M^+1118, $M^+-nCO(n = 1-8)$
cis-$HRe(CO)_4PPh_3$	MS3; M^+560, $M^+-nCO(n = 1-4)$
mer-trans-$HRe(CO)_3(PPh_3)_2$	MS4; M^+794, $M^+-nCO(n = 1-3)$
fac - $HRe(CO)_3(PPh_3)_2$	M^+794, $M^+-nCO(n = 1-3)$
$Re(CO)_3(PPh_3)(C_6H_4PPh_2)$	MS5; M^+792, $M^+-nCO(n = 1-3)$
$H_3Re_3(CO)_{12-n}(PPh_3)_n$	**

* MS numbers refer to the bar diagrams in Appendix 1

** highest mass ion observed was consistent with the formula $H_2Re_3(CO)_7PPh_3^+$

The minor products were isolated by thin layer chromatography. This method was adopted since the corresponding column technique met with little success. In some instances the separation had to be performed in two stages; once to isolate a particular band, and then again using a different eluent system to resolve it into its constituents. In these latter cases, 72 plates were run in order to give sufficient material for the second separation. In instances when the band concerned contained only one component, 36 plates were found to yield satisfactory amounts of product. The appearance of the plate in UV light after elution in a mixture of petrol (bp 80-100°) and ethyl acetate (3:1, V/V) of a sample of reaction product is shown in Figure 1.

Band 4 was further separated by use of a mixture of petrol and ethyl acetate (9.5:0.5 V/V) into the following components: bis- ax-$Re_2(CO)_8(PPh_3)_2$ (identified by mass spectrometry and infra-red spectroscopy), eq-$Re_2(CO)_9PPh_3$ (identified by mass spectrometry and infra-red spectroscopy), $Re(CO)_3(C_6H_4PPh_2)(PPh_3)$ (identified mass spectrometrically) and a very small quantity of either $HRe(CO)_4PPh_3$ or $Re(CO)_4(C_6H_4PPh_2)$. This last compound could not be positively identified because its mass spectrum was of poor quality due to difficulties involved in handling the very small samples of material available. A very small quantity of fac - $HRe(CO)_3(PPh_3)_2$ was also isolated from this band.

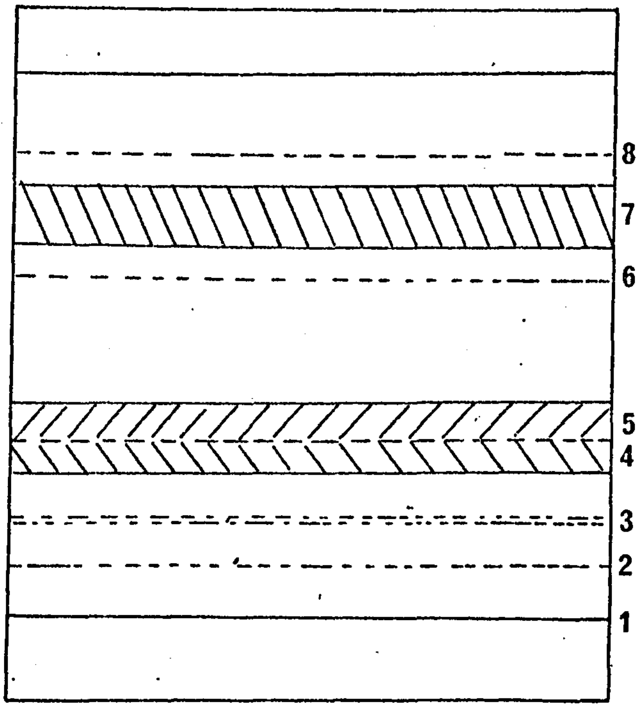


FIGURE 1

Band 3 gave three components when separated by the 9.5:0.5 mixture of petrol and ethyl acetate. These were: a compound whose mass spectrum showed successive losses of 14 a.m.u. which may have been an impurity in the xylene; and a very small quantity of unidentifiable material. A compound giving a cluster of peaks centred at m/e 1015 exhibiting an isotope pattern characteristic of three rhenium atoms (see Appendix 1) and corresponding to a complex of formula $H_2{}^{185}Re_3(CO)_7PPh_3{}^+$ was isolated. This was clearly not the molecular ion and thus a positive identification was not possible. For this reason, the molecule is not placed in the reaction scheme presented in Section 2.1.2. Its formation may be due to reactions between monomeric radical species (see Section 2.2.3).

The same range of products were obtained for a 16 hour reaction in a 1:9 ratio and these conditions were adopted as the "standard reaction" employed in these investigations. It should be noted that in Freni's paper (112) the quantities of reagents quoted represent a molar ratio of reactants of 1:9 and not of 1:5 as reported by these workers.

The isolated species were characterised by spectroscopic methods and by elemental analyses whenever the quantities isolated permitted.

The mass spectra are collected in Appendix 1, but the infra-red specta are presented below.

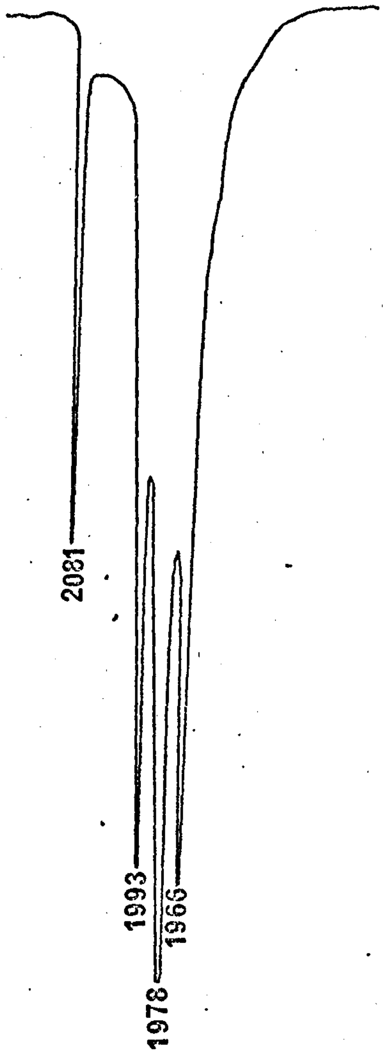


FIGURE 2 cis HRe(CO)$_4$PPh$_3$

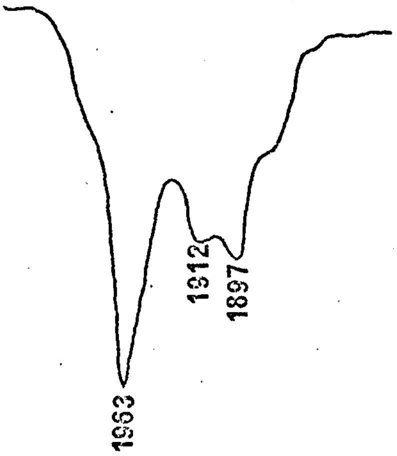


FIGURE 3 eq-Re$_2$(CO)$_9$PPh$_3$

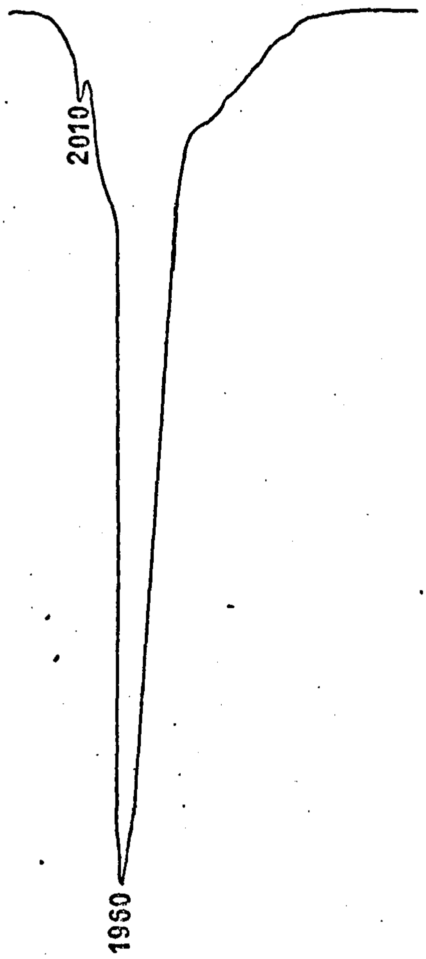


FIGURE 4 bis-ax $-Re_2(CO)_8(PPh_3)_2$

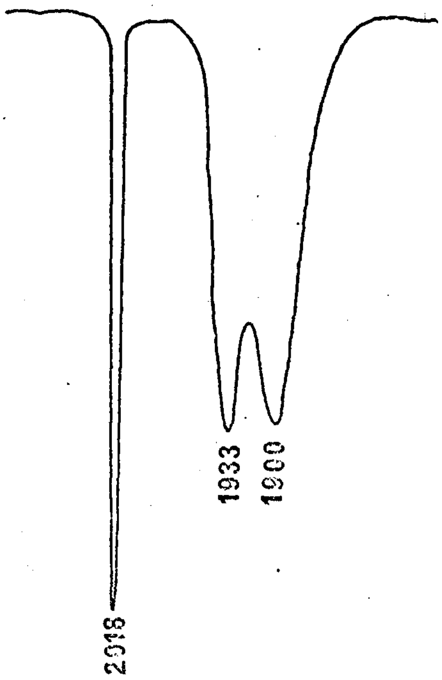


FIGURE 5 $Re(CO)_3(C_6H_4PPh_2)(PPh_3)$

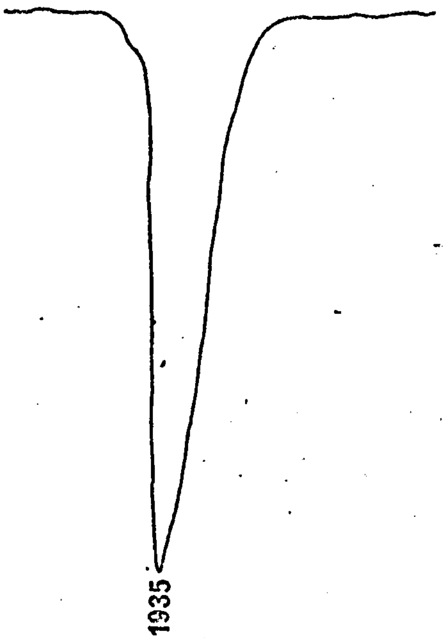


FIGURE 6 mer-trans-$HRe(CO)_3(PPh_3)_2$

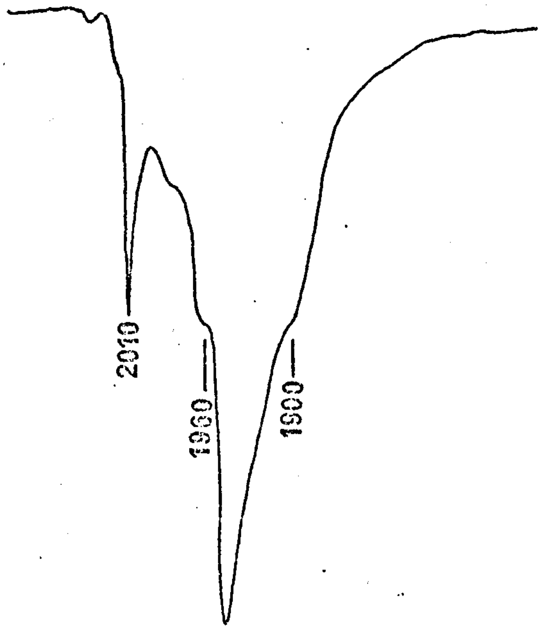
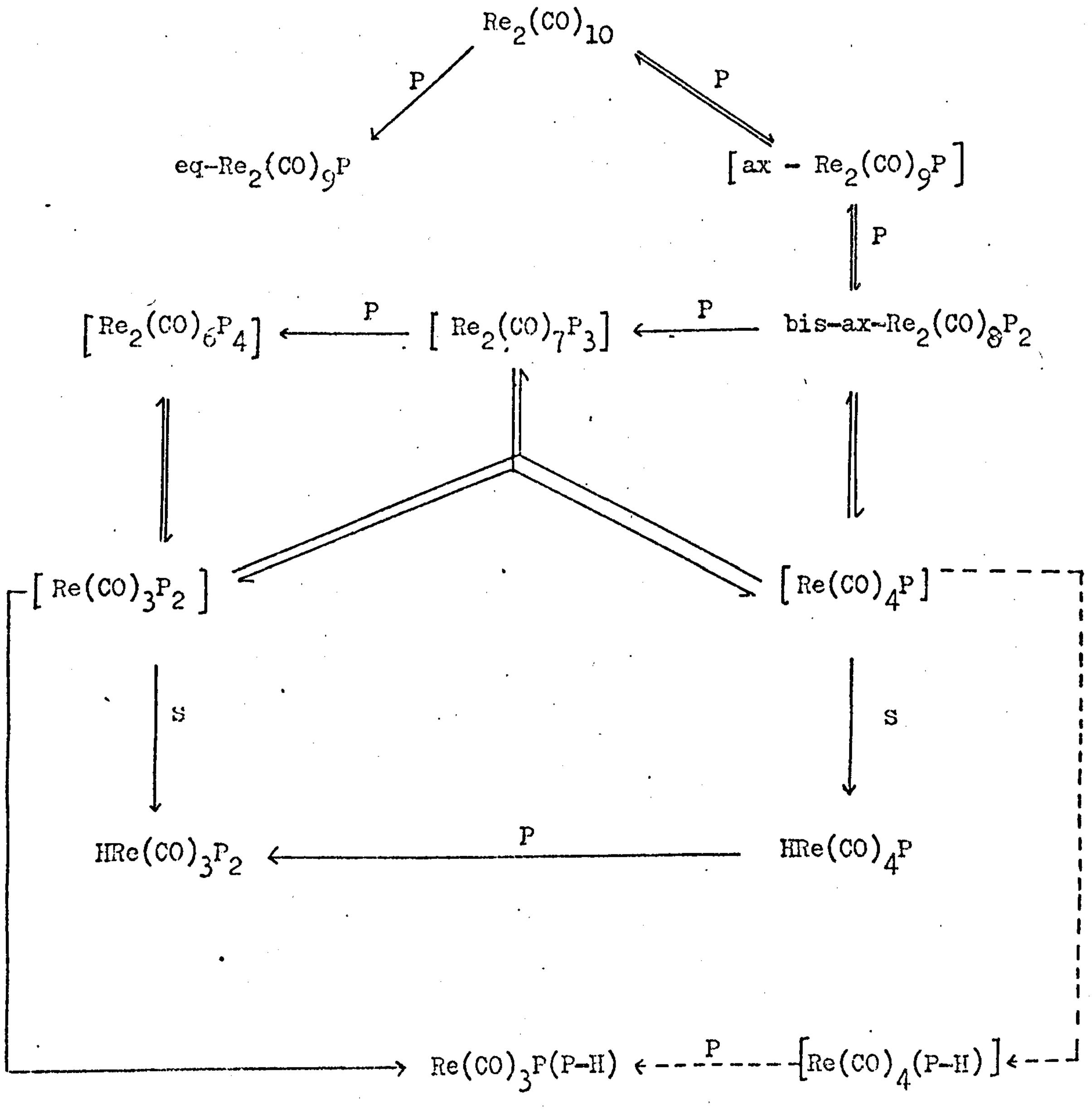


FIGURE 7 fac-$HRe(CO)_3(PPh_3)_2$

2.1.2 Aspects of the reaction and the reaction scheme

On the basis of the nature of the isolated products (and supporting evidence to be presented in the following sections) the scheme below is proposed for this reaction:



P = PPh$_3$

S = water in solvent (Section 2.1.6)

Compounds in square brackets were not isolated

It has been found that the reaction can proceed by either one of two possible routes. The first of these is predominant when the reaction is conducted in daylight, and the second when it is conducted in the dark.

Both pathways have common steps up to the formation of $Re_2(CO)_8(PPh_3)_2$, via a sequential substitution of the two axial positions in the parent carbonyl. Under the influence of light, this dimer dissociates homolytically generating reactive intermediate radicals which achieve stabilisation either by recombination, abstraction of a hydrogen atom from traces of water in the solvent (section 2.1.6), or internal metalation. Further substitution then occurs producing the final bis-substituted hydrido derivative.

In the absence of light this dissociation does not occur, and it has been suggested that phosphane substitution strengthens the metal-metal interaction (199). The energies associated with the $\sigma \rightarrow \sigma^*$ transition of this bond in $Re_2(CO)_{10}$ and $Re_2(CO)_8(PPh_3)_2$ have been determined (202) and are given in Table 11. This increase in metal-metal bond energy presumably excludes dissociation at thermal energies.

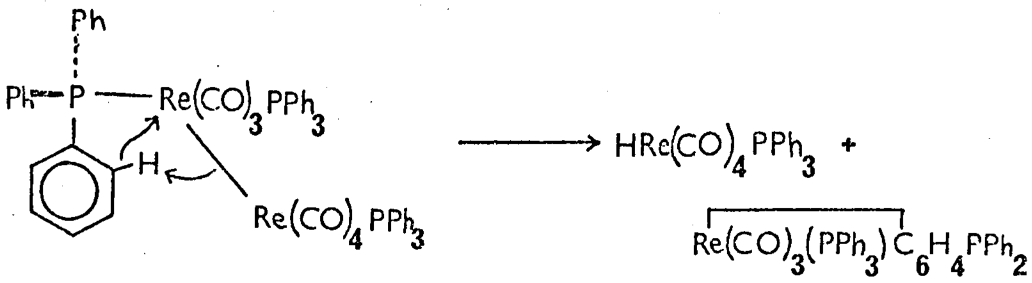
TABLE 11

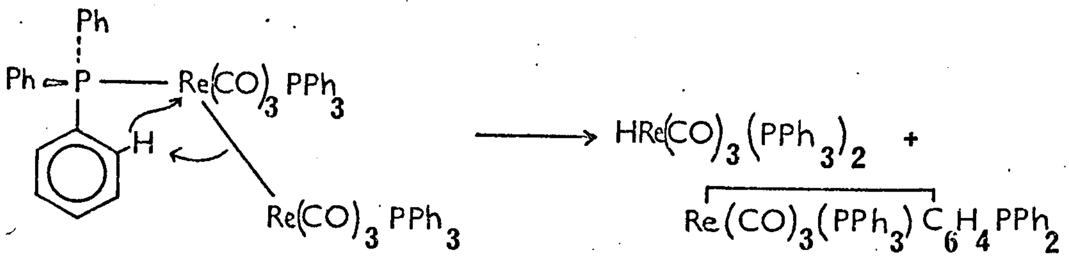
Energies of $\sigma \rightarrow \sigma^*$ transitions calculated from UV data

Complex	Energy/kJ mol^{-1}
$Re_2(CO)_{10}$	386
$Re_2(CO)_8(PPh_3)_2$	398

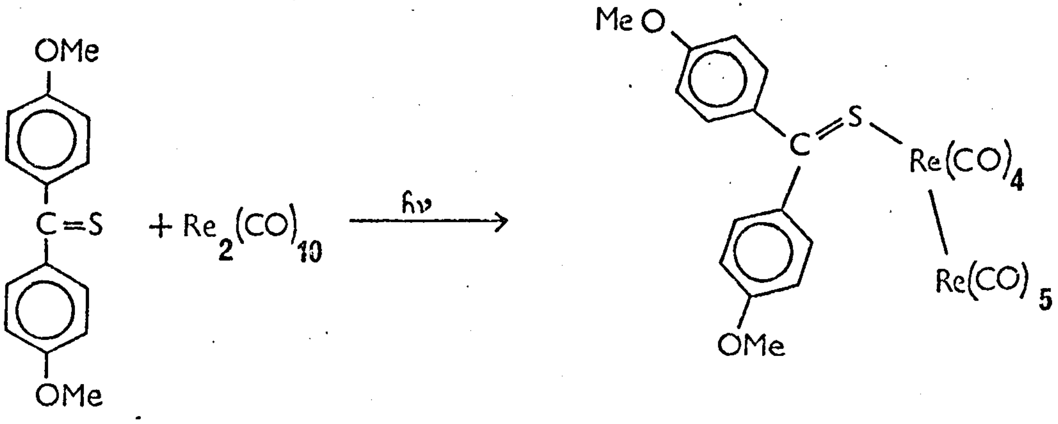
It is therefore proposed that radicals are generated via thermal decomposition of polysubstituted dimers as indicated in the scheme. The fact that virtually no tetra-carbonyl hydride is detected in reactions carried out in the dark suggests that the tri-phosphane substituted dimer is short lived, and further reaction occurs to give $Re_2(CO)_6(PPh_3)_4$ which then readily dissociates as shown.

The ortho-metalated species is included as being formed via $Re(CO)_3(PPh_3)_2$ but the possibility exists that it may also arise upon dissociation of dimeric species with attendant elemination of $HRe(CO)_4PPh_3$ or $HRe(CO)_3(PPh_3)_2$:



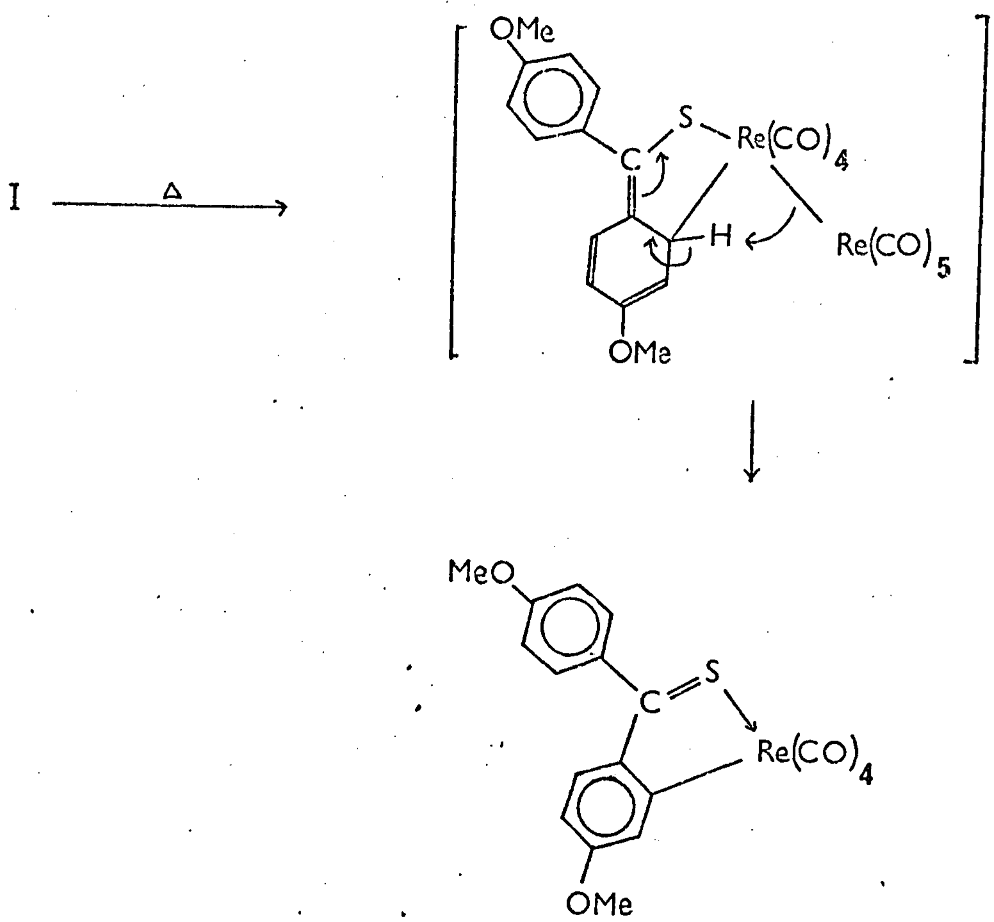


This mechanism was suggested by Alper's study of the reaction of decacarbonyldirhenium with thiobenzophenones (203), in which the photochemical reaction between the carbonyl and 4,4′-dimethoxythiobenzophenone was found to give the axially mono-substituted derivative I, in 95% yield as a purple oil:



I

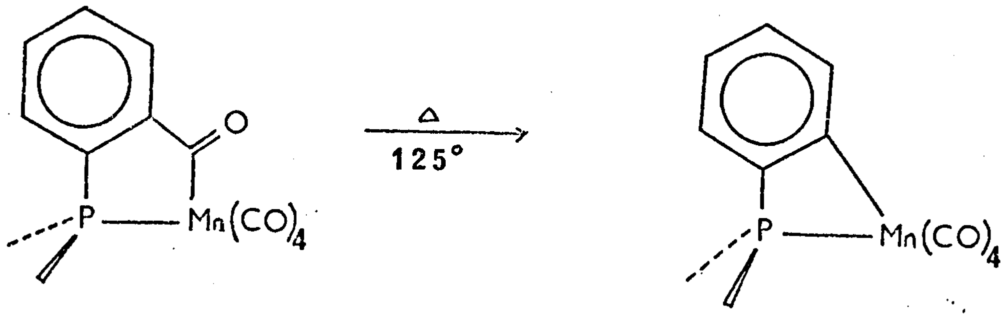
Pyrolysis of I gave the monomeric metalated species as orange crystals in 54% yield after 6 days in boiling toluene:



However, the only evidence advanced in support of this mechanism is the fact that some $Re_2(CO)_{10}$ was found in the pyrolysis products. This is cited as being derived by decomposition of the pentacarbonyl hydride, although it could equally well arise via recombination of $Re(CO)_5\cdot$ radicals produced by homolysis of I.

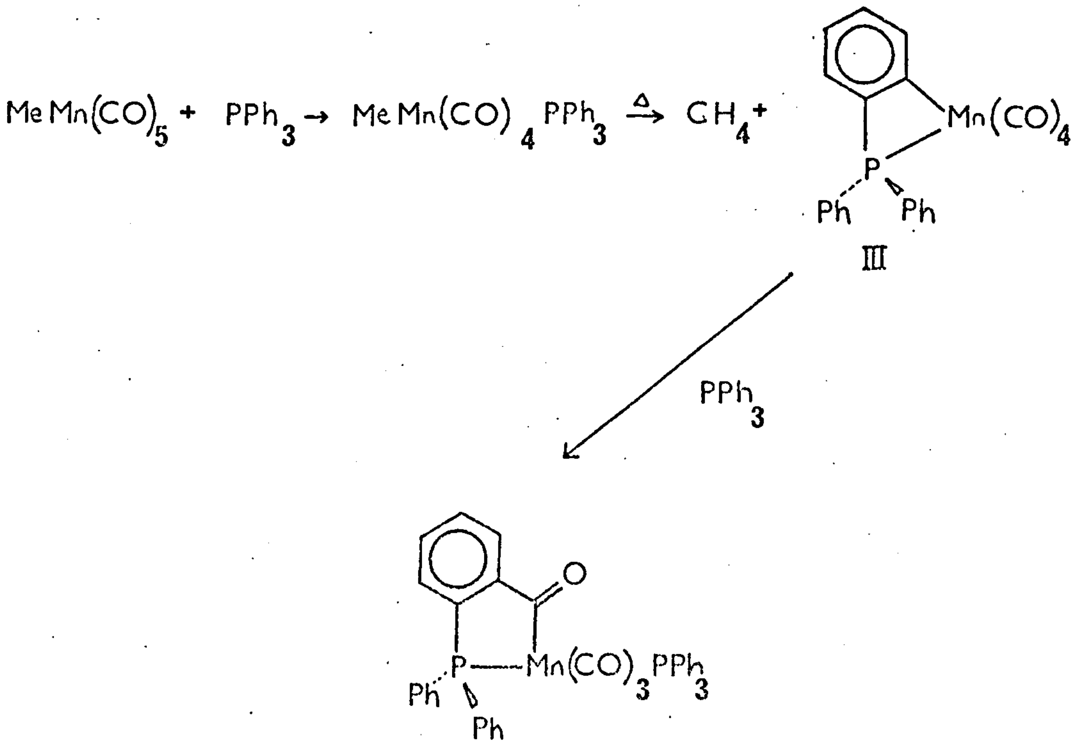
The metalated complex isolated in this work with triphenylphosphane was only found in very low yields. This is presumably a consequence of the fact that its formation necessitates the construction of a strained four membered ring.

The more favoured nature of five membered metalation rings is well known (204, 205) and can be illustrated by the facile metalation of $PtX_2[P(OR)_3]_2$ (R = o-tolyl) via a methyl group rather than a site on an aromatic residue (206). A further example of the enhanced stability of five membered metalates over four membered systems is the observation that only 10% of decarbonylated material III is found even when II is heated in octane at 125° for 1.5 hours (207):



II III

The formation of $Re(CO)_3(C_6H_4PPh_2)(PPh_3)$ is not thought to proceed by substitution of a carbonyl ligand in $Re(CO)_4(C_6H_4PPh_2)$ by PPh_3 as indicated by the broken line in the scheme, since this reaction with the analogous manganese system is reported to give the acyl compound IV (207). As no compounds were isolated in the present work which exhibited organo-type carbonyl bands in their infra-red spectra, this route does not appear to be relevant to the present study.



IV

This acyl insertion reaction also serves as another illustration of the facile formation of five membered rings. A thermal reaction of $HRe(CO)_3(PPh_3)_2$ in boiling xylene to give the metalated complex and hydrogen, paralleling the evolution of methane indicated above, was shown not to occur, the bis phosphane hydride being extremely stable under these conditions.

No reaction occurred between decacarbonyldirhenium and triphenylphosphane if it was performed in a solution contained in sealed evacuated vessel. This observation was interpreted in terms of a ligand dissociative mechanism which is inhibited as soon as the concentration of carbon monoxide builds up to a significant level:

$$\begin{tikzcd}
Re_2(CO)_{10} + PPh_3 \arrow[r, shift left] & Re_2(CO)_9PPh_3 + CO \arrow[l, shift left] \arrow[d, shift left, "PPh_3"] \\
& Re_2(CO)_8(PPh_3)_2 + CO \arrow[u, shift left]
\end{tikzcd}$$

Some confirmation of this was obtained from the fact that when the contents of the Schlenk tube were transferred to a vented flask and heated under a stream of nitrogen the reaction proceeded in the normal manner. Separate experiments in both the presence and absence of PPh_3 at lower temperatures have shown that the reaction proceeds in the same way in the former, but no $HRe(CO)_5$ was detected spectroscopically in the latter, although the experiments were conducted below the decomposition point of this compound. This would seem to indicate that homolytic fission of the parent carbonyl is not an important process, and that phosphane substitution precedes radical formation. Thus the left hand sequence in the scheme below is considered the more important:

$$\begin{tikzcd}
Re_2(CO)_9PPh_3 \arrow[d] & Re_2(CO)_{10} \arrow[l] \arrow[r] & 2Re(CO)_5^{\bullet} \arrow[d] \\
Re_2(CO)_8(PPh_3)_2 \arrow[d] & & Re(CO)_4PPh_3^{\bullet} \arrow[d] \\
\text{dissociation} & & HRe(CO)_4PPh_3
\end{tikzcd}$$

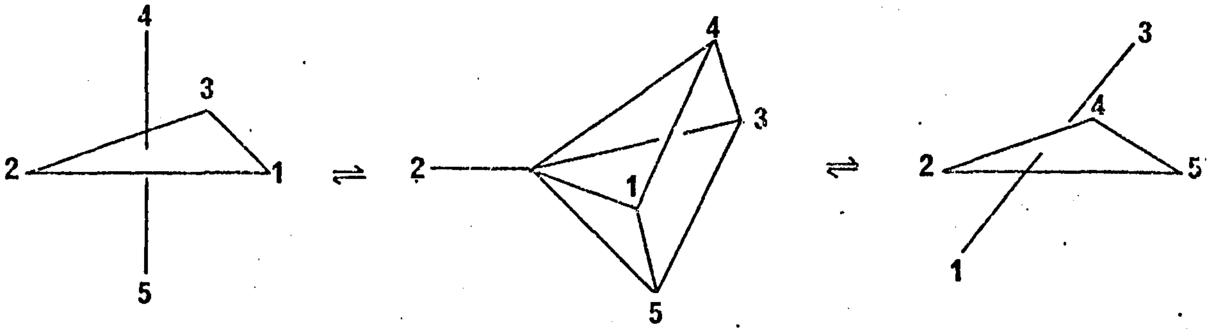
Some confirmatory evidence for the early substitution steps in the reaction scheme is provided by the following observations. Reactions starting with ax-$Re_2(CO)_9PPh_3$ or bis-ax-$Re_2(CO)_8(PPh_3)_2$ generated the same product distribution as those originating from the parent decacarbonyl. A xylene solution of bis-ax-$Re_2(CO)_8(PPh_3)_2$ in the absence of any added reagents at room temperature in daylight slowly afforded the cis-tetracarbonyl hydride (identified by the comparison with an authentic sample). In boiling xylene solution, with the total exclusion of light and in the absence of added triphenylphosphane, the bis axially substituted dimer underwent total thermal decomposition to a brown solid which was devoid of carbonyl bands in its infra-red spectrum and was considered to contain some rhenium metal. This result endorses the scheme, since in the dark $HRe(CO)_3(PPh_3)_2$ is still generated. Added triphenylphosphane saves the octacarbonyl derivative from decomposition by further substitution leading to radicals and hydrides as indicated. This is consistent with a report in the literature (198) which examined the substitution reactions of the octacarbonyl complex. A xylene solution of this dimer in daylight under reflux gave a spectrum corresponding to the axial nonacarbonyl (198), and this was initially against expectations since the tetracarbonyl hydride was expected. This observation suggests that the decomposition via $Re_2(CO)_9PPh_3$ and the formation of $HRe(CO)_4PPh_3$ are competing reactions, the latter being normally favoured by the large excess of triphenylphosphane present:

$$\begin{tikzcd}
Re_2(CO)_9PPh_3 + PPh_3 \arrow[r, shift left] & Re_2(CO)_8(PPh_3)_2 + CO \arrow[l, shift left] \arrow[d, shift left] \\
& [{}^{\bullet}Re(CO)_4PPh_3] \arrow[u, shift left] \arrow[d] \\
HRe(CO)_3(PPh_3)_2 & HRe(CO)_4PPh_3 \arrow[l, "PPh_3"']
\end{tikzcd}$$

To summarise, in the absence of added triphenylphosphane, the equilibrium lies to the left hand side, but addition of this reagent forces the reaction to proceed. Consequently, an excess of carbon monoxide will suppress the forward reaction. This has been demonstrated by the reaction of the octacarbonyl with carbon monoxide (Section 2.1.9).

The isolation of the isomeric pair of tricarbonylhydrides suggests that rearrangement of these complexes is possible, or more likely that their radical precursors are fluxional.

Barriers to rearrangement vary widely depending on coordination number and the size of the ligands, and non-rigidity is a common feature of five-coordinate structures (208). A mechanism for isomerisation in these systems has been proposed by Berry (209):



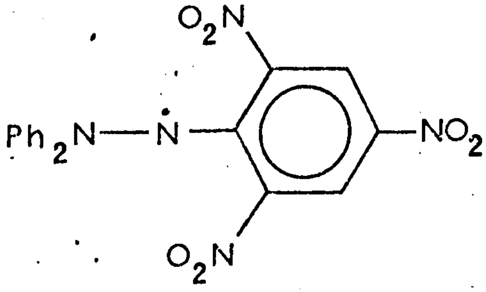
The simplicity and high symmetry of this process make it attractive, and demonstrates how a pair of axial ligands may be exchanged with a pair of equatorial groups, passing through a square pyramidal intermediate. Support for this route has been obtained by a ^{31}P NMR study of $(Me)_2NPF_4$ (210). At -100° the spectrum consists of the triplet of triplets expected for a static trigonal bipyramidal structure having the $(Me)_2N$ group in an equatorial position. As the temperature is raised pseudo rotation becomes rapid on the NMR time scale and the pattern of peaks changes to a 1:4:6:4:1 quintet resulting from coupling of ^{31}P nucleus to four equivalent fluorine nuclei.

2.1.3 The evidence for radical intermediates

The evidence supporting the inclusion of free radicals in the reaction scheme is given below:

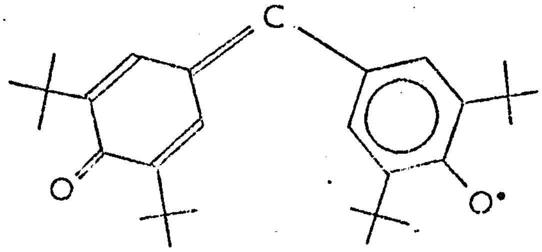
(i) The rate of the reaction is slowed considerably by the admission of oxygen and for this reason the normal reaction is performed in a nitrogen atmosphere. This partial inhibition by oxygen of reactions involving free radicals is well known. For example, salts of methacrylic acid have been subjected to high frequency discharge in hydrogen, and the decay of radical concentration in the presence of oxygen monitored by ESR spectrometry (211). The generation of peroxo species was verified by liberation of iodine from acidic potasium iodide solution. It was concluded that the oxygen caused a decline in radical concentration by an interaction of the previously unpaired electron spins. No evidence for an oxidative chain reaction was observed.

Others have reported similar findings. For example, the interaction of oxygen with α,α' -diphenyl-β- picrylhydrazyl, V, in benzene has been investigated by studying ESR spectra (212). The spectrum of the radical in this solvent showed five bands, and interaction with oxygen caused a significant broadening. Over a period of 80 days the interaction lead to a decrease in the intensity of the lines as the radicals were transformed into peroxo species.



V

(ii) The free radical trapping agent Galvinoxyl, VI, was decolourised when added to the reaction mixture. This test was compared with controls prepared at the same time in an identical manner containing only PPh_3 or $Re_2(CO)_{10}$



VI

A xylene solution of bis-ax-$Re_2(CO)_8(PPh_3)_2$ in the presence of VI was left under nitrogen at room temperature in daylight. This was to demonstrate the inclusion of radical intermediates formed by photolytic dissociation of the dimer. The red colouration discharged slowly, but more readily than a blank prepared at the same time. No tetra-carbonyl hydride was detected in this instance, and these observations indicate the reasonably facile photolytic dissociation of bis-ax-$Re_2(CO)_8(PPh_3)_2$.

(iii) An aliquot of fresh reaction mixture initiated the polymerisation of a 1:1 molar mixture of styrene and methylmethacrylate and of methyl methacrylate alone, reactions known to proceed via radical processes (213). Control experiments were also run for comparison.

(iv) The ESR spectrum of the mixture formed by the reaction of bis-ax-$Re_2(CO)_8(PPh_3)_2$ with PPh_3 has been reported in the literature (198). A rather broad signal was recorded and fine structure was not clearly defined due to an unfavourable signal/noise ratio. However, five of the six bands expected for one electron coupled to a nucleus of spin 5/2 were discernable, and this supports the inclusion of mononuclear rhenium (o) species.

(v) The reaction was performed in carbon tetrachloride with a view to producing the known chloro-compounds via the radical intermediates. However, triphenylphosphane reacts with the solvent according to the equation below (214) and thus this test was inconclusive.

$$PPh_3 + CCl_4 \longrightarrow Ph_3P^+ - CCl_2 \xrightarrow{O_2/H_2O} Ph_3PO + COCl_2$$

2.1.4 The determination of product distribution

In order to establish a complete study of the reaction between $Re_2(CO)_{10}$ and PPh_3 it was felt necessary to obtain information concerning the quantities of each product generated in this system.

The fact that such a wide range are isolated meant that the determination of the yields of individual components was very difficult, since separation by preparative thin layer chromatography does not provide reliable quantitative results. Indeed, it was found that recovery from the plates was of the order of only 40-50%. For example, the following results were obtained from a standard reaction when 0,707 g of reaction product were applied to the plates.

TLC band number	Yield (mg)
8, $Re_2(CO)_{10}$	4.0
7, PPh_3	191.5
6, $HRe(CO)_4PPh_3$	2.1
5, $HRe(CO)_3(PPh_3)_2$	45.0
4, mixture	45.4
3, mixture	15.3
unseparated material	68.5
	371.8 = 52.8% recovery

Prolonged washing of the silica containing each band in chloroform or other solvents (eg benzene or ethyl acetate) did not elute any further material. It was this inadequacywhich lead to the evolution of a spectrophotometric method of determining the yields of the two major components of the reaction mixture (i.e. mer-trans-$HRe(CO)_3(PPh_3)_2$ and bis-ax-$Re_2(CO)_8(PPh_3)_2$). These two complexes were often precipitated together in the work up procedure, and their separation by column chromatography was not at all satisfactory. The UV method allowed the calculation of the proportion of each compound in the precipitate. Figures 8 and 9 show that the UV spectra of the two complexes have very different profiles: that of the dimer being dominated by a very strong band at 299 nm attributed to the $\sigma \rightarrow \sigma^*$ transition in the M-M band (191), and that of the hydride consisting of an absorbance at 227 nm due to the aromatic residues in the phosphane ligand. This means that the absorbance of each at 350 nm is significantly different, and this fact was exploited in the analytical procedure.

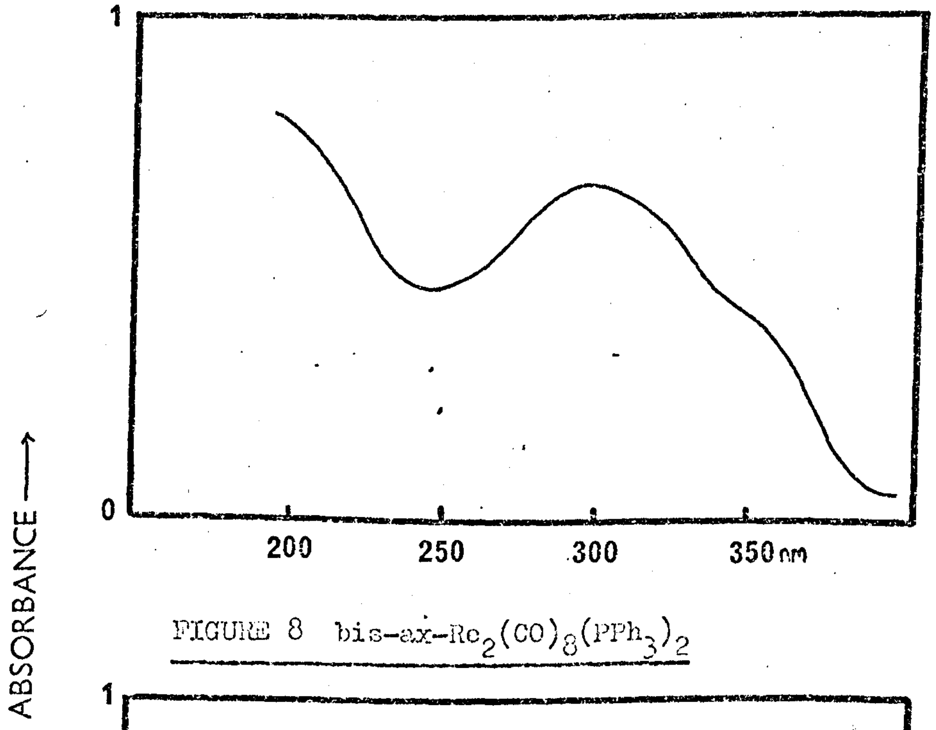


FIGURE 8 bis-ax-$Re_2(CO)_8(PPh_3)_2$

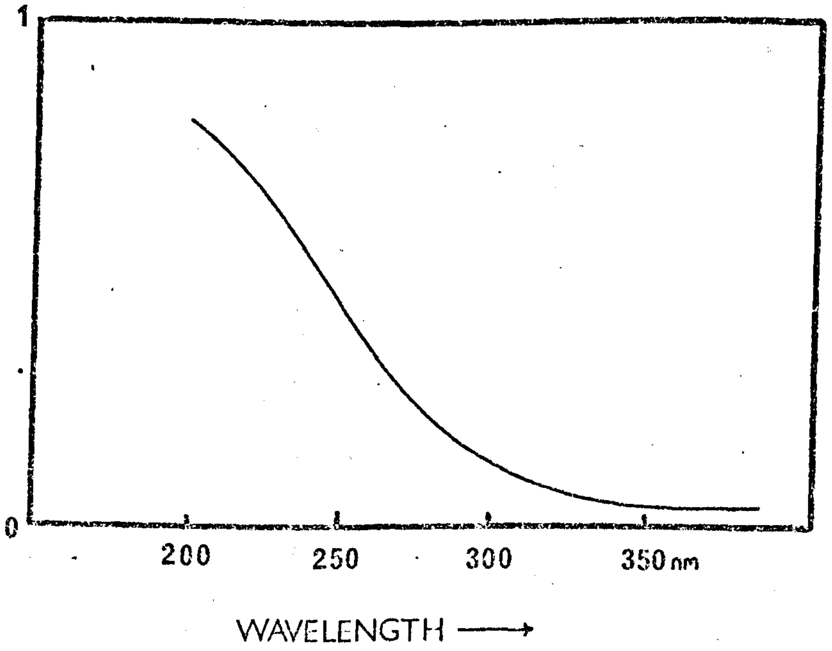


FIGURE 9 mer-trans-$HRe(CO)_3(PPh_3)$

solvent: CH_3CN

pathlength: 10 mm

The determination was performed in the following way: The UV spectrumof the mixture was recorded, and the knowledge of the extinction coefficient at 350 nm for the pure dimer, the path length, the concentration of mixture in solution and its absorbance at 350 nm enable the concentration of pure dimer to be calculated by application of the appropriate equation. The results are given in Table 12.

TABLE 12

Yields of Products Based on UV Analysis*

Exp No	Yield of $HRe(CO)_3(PPh_3)_2$/g	Yield of $Re_2(CO)_8(PPh_3)_2$/g	% of the Re in the system contained in these cpds
1	0,2422		35.5
2	0,2147		31.5
3	0,2756		40.4
4		0.318	46.4
5	0,2372	0.1608	58.3
6	0,3443	0.1479	68.7
7	0,3700	0.0214	57.3
8	0,1972	0.0534	36.6
9	0,2778	0.0136	42.5

*from a "standard reaction"

NOTE: Results 5-9 were determined spectroscopically
In experiments 1-4 only one product was precipitated

The results of experiments 5-9 show a variation which is partly a reflection of the limitations of this method, which are listed below.

1. The monomeric hydride has a small but finite absorbance at 350 nm.
2. Not all of the dimer and hydride are precipitated as discovered during preparative tlc work up of the reaction mixture remaining after removal of these two compounds.

3. The ratio determined in the precipitate may not be the same as the ratio in the reaction mixture since the two complexes may precipitate at different rates.
4. Slight variations may have occurred concerning the concentration of water in the solvent affecting the yield of hydride (Section 2.1.6). Drying the solvent consistently to the same degree is difficult.

The results of this exercise showed that on average the complexes mer-trans-$HRe(CO)_3(PPh_3)_2$ and bis-ax-$Re_2(CO)_8(PPh_3)_2$ contained some 50% of the rhenium present, the other components isolated accounting for an estimated 20%. This latter figure was arrived at from preparative tlc results so its precision may not be very high.

2.1.5 The attempted preparation of $Re_2(CO)_6(PPh_3)_4$

This dimeric complex occupies an important position in the reaction scheme, so attempts to synthesise it were considered necessary to verify its proposed intermediacy.

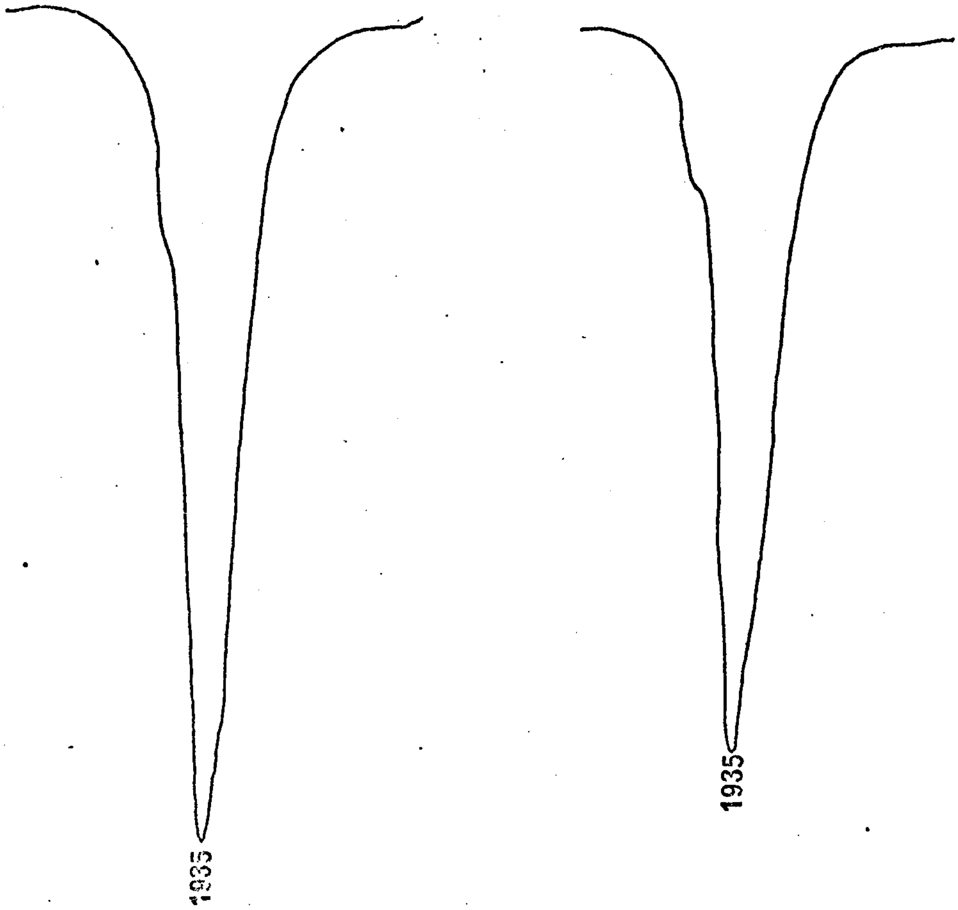
Two reports concerning its preparation have appeared in the literature (112, 215).

The first of these involved the thermal reaction between $Re_2(CO)_{10}$ and five mole equivalents of PPh_3 in a fashion very similar to that detailed for the preparation of $Re(CO)_3(PPh_3)_2$ (112). When this was repeated the product isolated had the same IR spectrum as reported for the hexacarbonyl dimer (one strong band at 1930 cm^{-1} in benzene solution) but was found mass-spectrometrically to be $HRe(CO)_3(PPh_3)_2$.

The second report described the solid state reaction between $HRe(CO)_3(PPh_3)_2$ and PPh_3 in a sealed evacuated tube, but when this was repeated no reaction at all was detected. It is interesting to note that Freni and co-workers assign identical IR spectra to both the dimeric species and the tri-carbonyl hydride (215).

2.1.6 The source of hydrogen in the hydrido complexes

It has been observed (216) that when triruthenium dodecacarbonyl was heated under reflux in *n*-nonane, small amounts of the tetranuclear hydrides $\alpha - Ru_4(CO)_{13}H_2$ and $\alpha - Ru_4(CO)_{12}H_4$ (217, 218) were obtained. It was initially thought that the formation of these hydrido clusters indicated possible activation of the alkanes by a simple and direct method in a process of hydrogen abstraction. Following Ugo and Bonati's work with deuterated triphenylphosphane (159a) which confirmed that this molecules is not involved in hydride formation, a similar reaction with the xylene was originally postulated in the reaction of $Re_2(CO)_{10}$ with PPh_3. More recently (219) the source of hydrogen atoms in the tetranuclear ruthenium hydrides was found to be not the alkane solvent but traces of water. In this present study, some experiments have been performed in which either a small volume of water or D_2O was added to the reaction medium prior to commencement of reflux. Adhering to the normal work-up procedure, the major monomeric product in each case was isolated. Both had identical infra-red spectra in the carbonyl region (Figure 10) but only one (from the water reaction) showed a high field triplet in the ^1H NMR spectrum for the Re-H proton coupled to two equivalent phosphorus muclei, (Figure 11).



mer-trans-$HRe(CO)_3(PPh_3)_2$ mer-trans-$DRe(CO)_3(PPh_3)_2$

FIGURE 10

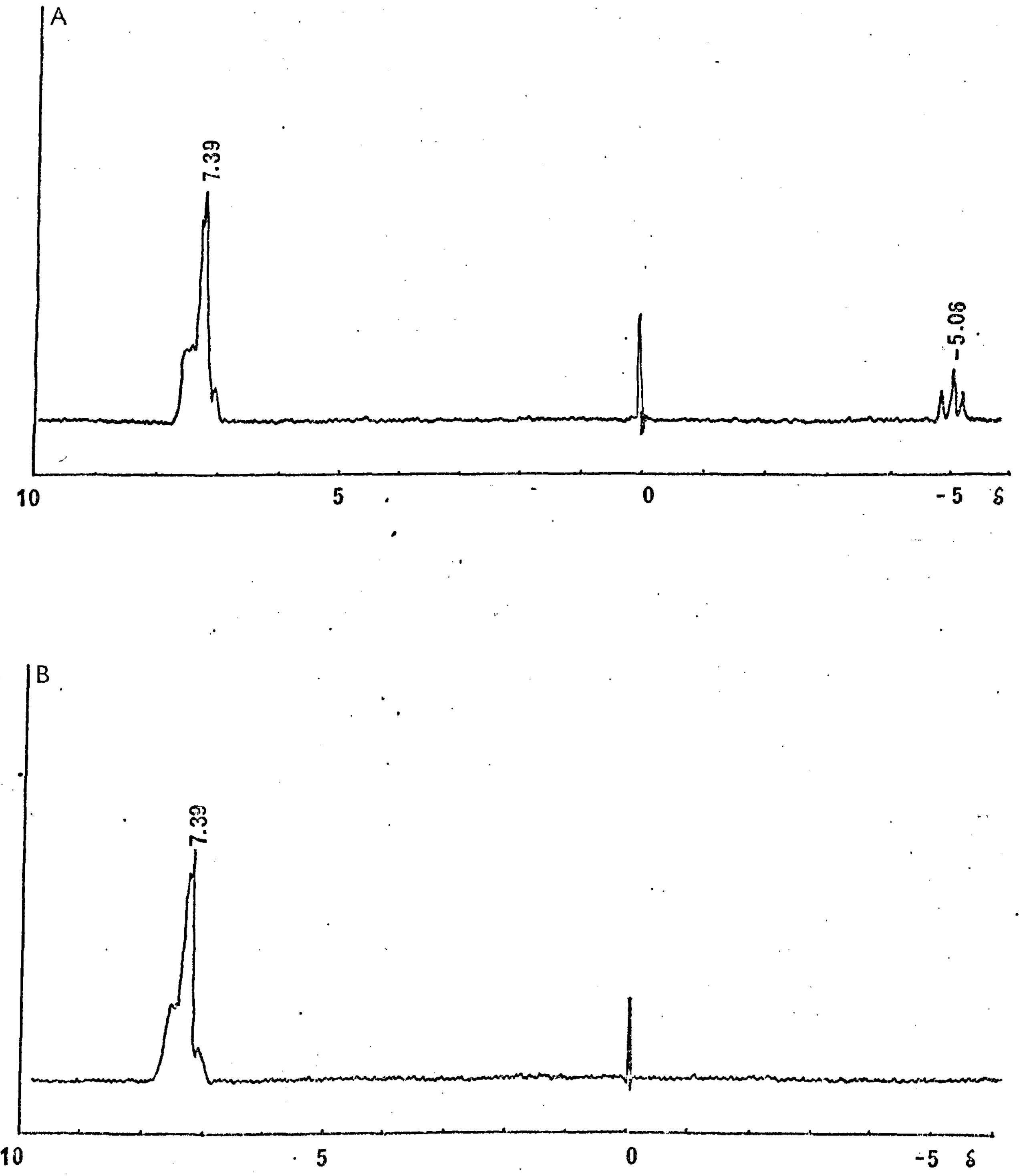


FIGURE 11

A mer-trans-HRe(CO)$_3$(PPh$_3$)$_2$

B mer-trans-DRe(CO)$_3$(PPh$_3$)$_2$

solvent: CDCl$_3$
temperature: 35°

The possibility that the observed difference in the ^{1}H NMR spectra may have been due to an alkane activation reaction giving $HRe(CO)_3(PPh_3)_2$ followed by a deuterium exchange in the latter experiment with added D_2O was considered. If this were happening, then water could not be taken as the source of hydrogen atoms in the hydride complexes.

Although K_a data are not available for $HRe(CO)_3(PPh_3)_2$ the unsubstituted hydride is reported to be only very weakly acidic in water (220). Phosphane substitution is likely to make the proton even less labile, by comparison with the observed effects in the analogous cobalt complex.

TABLE 13 (220)

K_a values for transition metal hydrides

Complex	K_a	Solvent
$HCo(CO)_4$	2	H_2O
"	same as HCl	CH_3OH
$HCo(CO)_4PPh_3$	1.13×10^{-5}	H_2O
$HMn(CO)_5$	0.8×10^{-7}	H_2O
$HRe(CO)_5$	"v. weakly acid"	H_2O

Such an exchange reaction was shown not to occur by the experiment which attempted to effect this reaction by treating $HRe(CO)_3(PPh_3)_2$ with boiling xylene/D_2O for the same length of time as the original reactions were run. When the solvent was removed and the ^{1}H NMR spectrum of the solid residue recorded, the high field triplet was still observed.

It thus appears that water is responsible for generation of the hydrido complexes, being small enough to come into contact with the metal atom in the radical species, thereby allowing reaction.

The variation of yields seen in Table 10 may thus be a result, not only of the factors mentioned in Section 2.1.4, but also of the amount of water present in the solvent. Two consecutive reactions in the same solvent (distilled from the first flask into the second under nitrogen) still resulted in the formation of hydrides, since the amount of water needed to produce these complexes is very small ($< 0{,}01\%$). The fate of the $OH^{\bullet}$ moiety is uncertain; no simple rhenium containing molecules with this group were identified in the products. It is unlikely that an analogous $HORe(CO)_3(PPh_3)_2$ species would be formed because of the very low concentrations of free $OH^{\bullet}$ and $\cdot Re(CO)_3(PPh_3)_2$ radicals available at any one time. It is suggested that either they react with the wall of the flask;

dimerise to give H_2O_2 which under the reaction conditions dissociates to give oxygen and water (which re-enters the cycle); or form other hydroxy species. The oxygen may be scavanged by the triphenylphosphane, since $O = PPh_3$ has been positively identified in the reaction products. The triphenylphosphane itself was found to be free of this contaminant. Even the most rigorous drying of the xylene, and distillation under nitrogen from lithium aluminium hydride immediately prior to use, still resulted in hydride formation.

Having established the source of hydrogen atoms, a reaction between decacarbonyldirhenium and triphenylphosphane in xylene with a large excess of added water was run. It was thought that this would lead to an increased yield of hydride, but in practice this was not observed. Reaction with water occurs late in the sequence of events, and the yield of hydrido species may be governed by the proportion of parent carbonyl which decomposes before the first substitution. A very large excess of water (1:1 v/v with xylene) failed togive any reaction since the boiling point of this mixed solvent was too low, and it was also unable to maintain the reagents in solution.

2.1.7 The preparation of cis-$HRe(CO)_4PPh_3$ and its reaction with PPh_3

This particular step in the reaction sequence was verified by preparing the cis-tetracarbonyl hydrido species according to the literature method (168) and then reacting it with triphenylphosphane under standard reaction conditions. The reaction proceeded smoothly to give mer-trans-$HRe(CO)_3(PPh_3)_2$, the isomer predicted from purely steric considerations. These apparently over-ride the trans labilisation effect of the hydride ion (221) which would tend to give the mer-cis configuration. This substitution was quite slow under these conditions needing 24 hours to go to completion, and this would seem to endorse the intermediacy of $Re(CO)_3(PPh_3)_2$ radicals, since even after 16 hours reaction time in the standard experiment little tetracarbonyl hydride is detected.

An attempted synthesis based on the reduction of bis-ax-$Re_2(CO)_8(PPh_3)_2$ followed by acidification failed. This problem has been experienced by others (222) and is believed to be a consequence of the strengthening of the Re-Re bond caused by substitution (199).

2.1.8 The reaction of $Re_2(CO)_{10}$ with PPh_3 in different mole ratios

The "standard" reaction between decacarbonyldirhenium and triphenylphosphane employed a molar ratio of 1:9 for these reagents. When the reaction was performed using a 1:1 ratio, the major product isolated was quite different. A solid, crystalline material was obtained which had the infra-red spectrum shown below (figure 12)

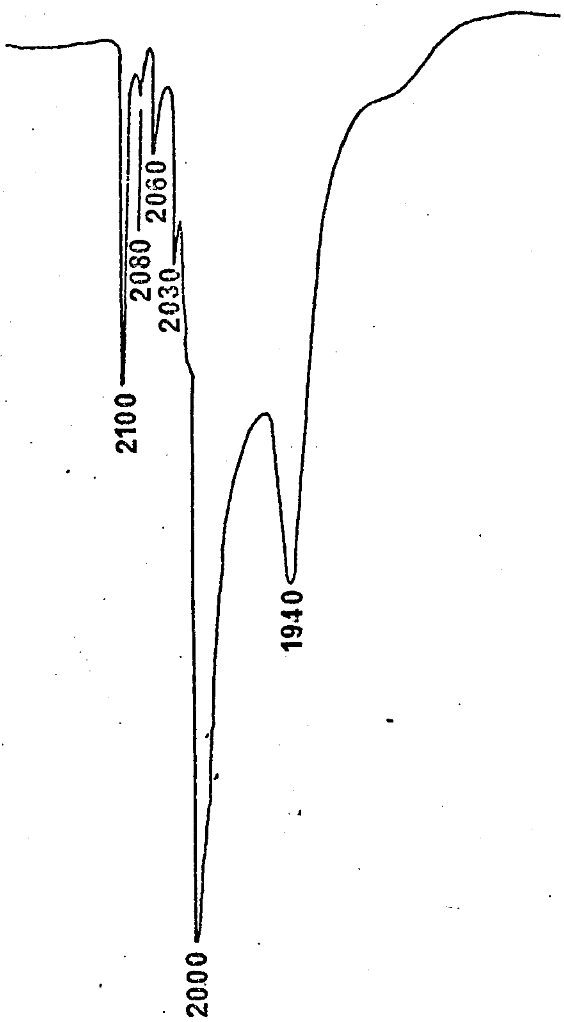


FIGURE 12

Mass spectral data gave a molecular ion at m/e 884 showing a two rhenium isotope pattern, and nine losses of carbon monoxide were observed. This compound was thus formulated as ax-$Re_2(CO)_9PPh_3$, and that it was isolated from a reaction which used a low concentration of PPh_3 endorses Poe's report of this reaction in which the same nonacarbonyl derivative was obtained (200) and its UV spectrum compared favourably with the literature example (198). Increasing the ratio of reagents even slightly away from 1:1 leads to the normal range of products. It is noteworthy that the dimeric nonacarbonyl species obtained from the standard reaction is the equatorial isomer. This is clearly a less reactive molecule since it persists to the conclusion of the reaction.

2.1.9 The reaction of bis-as-$Re_2(CO)_8(PPh_3)_2$ with carbon monoxide

This reaction was performed to verify the stereochemistry of the isolated nonacarbonyl dimers. In the octacarbonylderivative, it is known that the two phosphane groups occupy the axial positions. Replacement by CO of one of these must therefore give the axial isomer of the nonacarbonyl The reaction was carried out by passing a steady stream of carbon monoxide through a boiling solution of bis-ax-$Re_2(CO)_8(PPh_3)_2$ in xylene. The reaction proceeded smoothly to completion to give a product whose infra-red spectrum was identical to that recorded for the nona-carbonyl complex from the 1:1 reaction. This also confirmed the equatorial position of the PPh_3 ligand in the $Re_2(CO)_9PPh_3$ compound isolated from the standard 1:9 reaction.

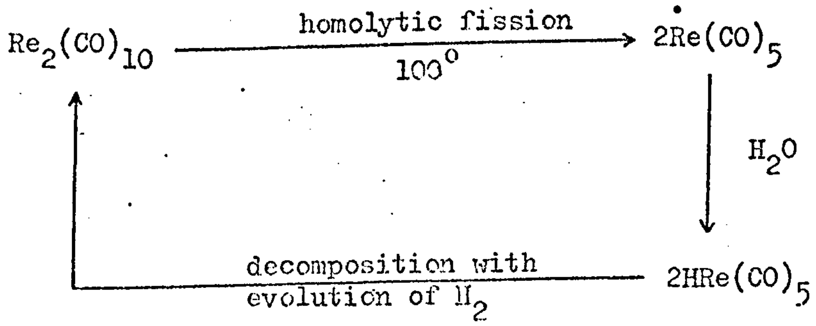
2.2 MISCELLANEOUS REACTIONS RELATING TO THIS STUDY

2.2.1 The reaction of $Re_2(CO)_{10}$ with water

The importance of hydrogen as a potentially non-polluting fuel is well known and many industrial processes consume large quantities of hydrogen as their basic feedstock. With the increasing demandfor this raw material, and the predictable shortage of hydrocarbons which will arise it is clear that new, non-fossil sources should be investigated. One of the more active areas of research is in the production of hydrogen from water using chemical cycles, which should involve as few steps as possible and regenerate the active agents. For example (223):

$$\begin{array}{ll}
2H_2O + 2Cs \longrightarrow 2CsOH + H_2 & 100^\circ \\
2CsOH + {}^3/2\ O_2 \longrightarrow H_2O + 2CsO_2 & 500^\circ \\
2CsO_2 \longrightarrow Cs_2O + {}^3/2\ O_2 & 700^\circ \\
Cs_2O \longrightarrow 2Cs + \tfrac{1}{2}O_2 & 1200^\circ
\end{array}$$

The discovery that water may react with organorhenium radicals prompted a series of experiments investigating the possible catalytic use of decacarbonyldirhenium for generating hydrogen from water. Decomposition of this dimer probably occurs via a homolytic fission reaction, by analogy with the reported decompositions of $Mn_2(CO)_{10}$ and $MnRe(CO)_{10}$ (224), and the basic concept behind this experiments is given below:



The last step in this cycle has been reported by Heiber (225). If $Re_2(CO)_{10}$ is heated under nitrogen in xylene solution at reflux (135°) decomposition occurs to a grey residue, presumably containing some rhenium metal. This decomposition was found to be completely inhibited if the reaction was performed under carbon monoxide at one atmosphere pressure. This was compared to a control run at the same time under nitrogen, and no change was noted even at the end of the 5 hour experiment.

It would seem that one of two things may be occuring. Either the radicals formed by homolytic fission are stabilised with respect to decomposition by the carbon monoxide, and so recombine in an equilibrium process:

$$Re_2(CO)_{10} \rightleftharpoons 2\dot{R}e(CO)_5$$

or the radicals are reacting with water, and then decomposing with evolution of hydrogen, since the pentacarbonyl hydride is unstable at reaction temperature (225). A similar inhibition was noted in a sealed evacuated tube experiment, but in this case some decomposition must occur in order to generate the carbon monoxide which prohibits further reaction.

The hydrogen generation experiments employing the rhenium cycle mentioned earlier were performed in a stainless steel autoclave at 150°C under a carbon monoxide pressure of 10 atmospheres. A typical charge was decacarbonyldirhenium (0,33g); degassed xylene (25 ml) and D_2O (100 μl). D_2O was used in order to have a definite peak in the mass spectrum of the effluent gas of the desired product, to determine if the reaction had been successful. Had ordinary water been used then the peak at m/e2 (H_2^+) could have arisen from fragmentation of the xylene. The experimental arrangement is drawn in Figure 13.

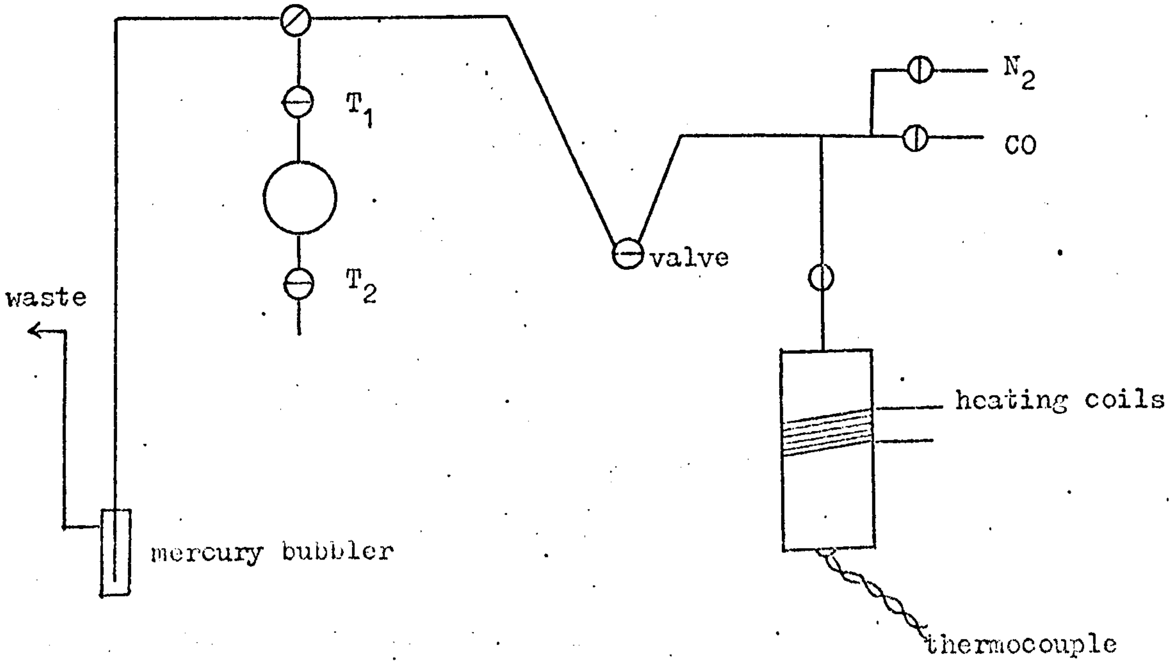
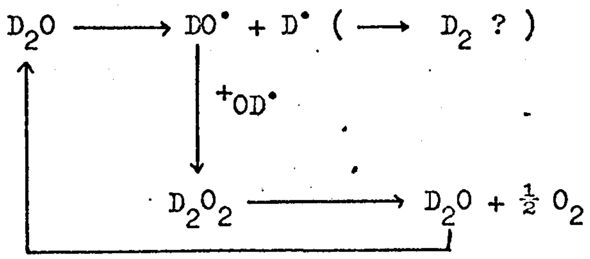


FIGURE 13

After the alloted reaction time the valve was opened and the gases vented through the bubbler. Once the line between the valve and the gas exit had been flushed, T_1 was opened and a sample of gas collected. T_1 was then closed, the bulb removed and then attached to the inlet of a mass spectrometer, for gas analysis. When the spectrum was recorded some D_2 and HD were seen, indicating some measure of success. A peak at m/e 32 (more intense than that in the blank) was also found. This could in part be due to dissolved oxygen in the solvent (which is difficult to remove even by using numerous freeze/pump/thaw cycles), or by oxygen formed in the autoclave:



The intensities of the peaks at m/e 28 and 32 were in the ratio 5:1, suggesting the presence of air (4:1) with some carbon monoxide making it up to the observed values. Calculations showed less than a 2% conversion of D_2O to D_2 over the 48 hour duration of the experiment. The possibility also exists that the deuterium may have arisen by a decacarbonyldirhenium catalysed water gas shift reaction:

$$CO + D_2O \longrightarrow D_2 + CO_2$$

The homogenuous catalyst $Ru_3(CO)_{12}$ has been shown to be active in this conversion (226).

The reason for such a low conversion may lie in the fact that two $HRe(CO)_5$ molecules did not have the chance to collide and react, the reported decomposition below being for pure hydride not a solution (225):

$$2HRe(CO)_5 \longrightarrow H_2 + Re_2(CO)_{10}$$

A further cause of the failure of this experiment may be the fact that it was performed in a closed vessel under pressure suppressing the release of hydrogen gas. However, if the reaction with water was still occuring then peaks in the infra-red spectrum of the reaction mixture due to $DRe(CO)_5$ would have been observed, but this was not the case. It therefore, seems most likely that the predominant reaction is recombination of the $Re(CO)_5$ radicals promoted by the atmosphere of carbon monoxide (preventing their decomposition).

Having established that under these conditions very little reaction with water was detected, the following question was raised: In a standard reaction, was the reaction drawn below occuring?

$$\begin{tikzcd}
Re_2(CO)_8(PPh_3)_2 + H_2O \arrow[r] & 2HRe(CO)_4(PPh_3) \arrow[d, "A"] \\
{} \arrow[u] & Re_2(CO)_8(PPh_3)_2 + H_2\uparrow \arrow[l, dash]
\end{tikzcd}$$

Step A is analogous to the pentacarbonylhydride reaction described above. To answer this question, a normal reaction was run and the gas above it was analysed by mass spectrometry. A typical charge was $Re_2(CO)_{10}$ (0.33 g), PPh_3 (1.25 g), xylene (15 ml) and D_2O (300 μl), and the reaction was performed in a flask fitted with a condenser and mercury manometer, and a sampling device as depicted in Figure 14.

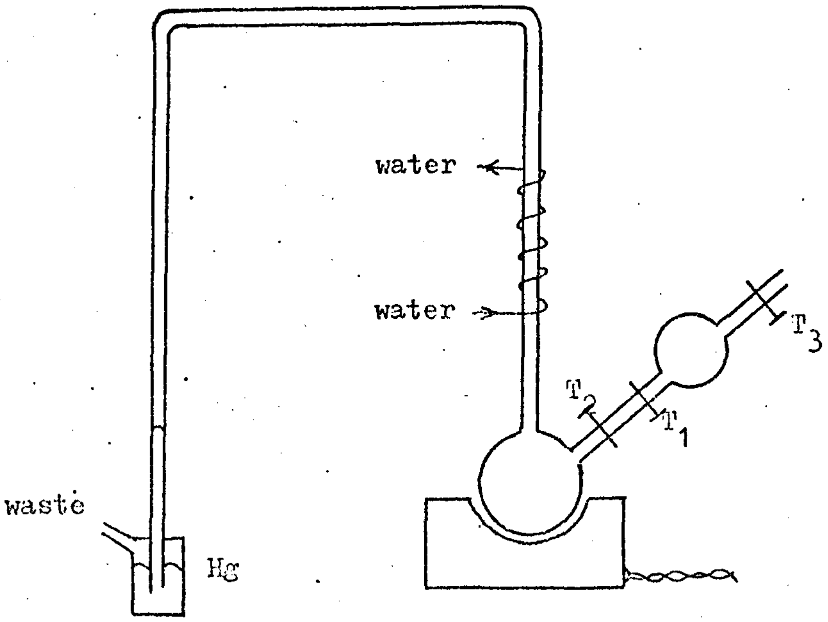


FIGURE 14

Gas samples were withdrawn by using an evacuated bulb as before: with T_3 and T_1 closed, T_2 was opened. T_1 was then opened slightly to withdraw a sample of gas for analysis, and then T_2 was closed. Throughout the experiment, evolution of gas was witnessed by a small movement in the mercury level. The whole apparatus was flushed with nitrogen prior to commencement of the run. When the gas was examined, no D_2 was detected, so it can be tentatively assumed that the above reaction does not take place. The infra-red spectrum of the reaction mixture confirmed that reaction had taken place to give the normal products.

An analogous reaction has been reported in the literature (227).

$$\begin{tikzcd} \underset{\text{VII}}{Ir_2(PF_3)_8} \arrow[r, "H_2O"] & \underset{\text{VIII}}{HIr(PF_3)_4} \arrow[l, dash, bend left=60, "h\nu + H_2\uparrow"] \end{tikzcd}$$

The diamagnetic dimer VII has a metal-metal bond between the two trigonal bipyramidal halves of the molecule, and an infra-red study has revealed that even the slightest trace of water causes decomposition as shown, apparently at ambient temperatures. The dimer can be regenerated by photolysis of an ethereal solution of VIII.

2.2.2 The attempted reduction of fac-$Re(CO)_3(PPh_3)_2Cl$

The radical species generated under the rather forcing conditions of the decacarbonyldirhenium-triphenylphosphane reaction could not be isolated, so an effort was made to investigate their synthesis using milder reactions.

Collman et al (228) have reported a successful reduction of chloro $\alpha, \beta, \gamma, \delta$ -tetraphenylporphinatoiron (III) to $\alpha, \beta, \gamma, \delta$ -tetraphenylporphinatoiron (II) using bis(2,4-pentanedionato)chromium (II) as a halogen abstracting agent. It was believed that this may provide a route for the production of $Re(CO)_3(PPh_3)_2$ by a similar reduction of $Re(CO)_3(PPh_3)_2Cl$. The proposed outline of the reaction was:

$$\begin{tikzcd} Re_2(CO)_{10} \arrow[r, "CCl_4/Cl_2", "0^{\circ}"'] & Re(CO)_5Cl \arrow[d, "2PPh_3 \text{ in EtOH}"] \\ & \text{fac-}Re(CO)_3(PPh_3)_2Cl \arrow[d, "{[Cr(II)(acac)_2]_2}"] \\ & Re(CO)_3(PPh_3)_2 \end{tikzcd}$$

However, examination of the final product after treatment with the chromium complex revealed that no reaction had taken place. This presumably reflects both the increased Re(I)-Cl bond strength compared to that of Fe(III)-Cl, and the enhanced stability of Re(I) with respect to Re(0) compared to Fe(III) with respect to Fe(II)

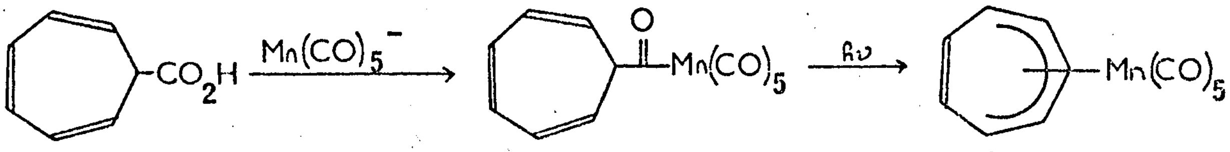
2.2.3 Oxidation reactions of $Na^+Re(CO)_5^-$

The oxidation of the pentacarbonylrhenium anion as another possible method of synthesising radicals under mild conditions was investigated. The general reaction is given below:

$$Na^+Re(CO)_5^- + R^+X^- \longrightarrow Re(CO)_5^{\bullet} + R^{\bullet} + NaX$$

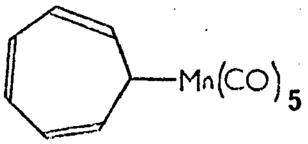
Initially, allyl bromide was used as the oxidising agent, but a complex reaction mixture resulted which was believed to contain allyl derivatives of the pentacarbonylrhenium moiety. This complication has been noted by others(229).

When the oxidant was changed to tropylium hexafluorophosphate, the reaction proceeded more smoothly, and although the paramagnetic intermediates were not isolable, their transient existence was inferred by the nature of the reaction products. That tropylium ion was found more effective in oxidation is possibly a consequence of the inability of a tropyl radical to react with the organometallic moiety, since no such σ bonded compounds are known. The orange air stable complex IX has been prepared according to the scheme below (230);



IX

but no decarbonylation to X has been detected



X

Thus, when a solution containing the pentacarbonylrhenium anion was treated with an excess of tropylium hexafluorophosphate, decacarbonyldirhenium was obtained as one of the products. After extraction of this material into hexane, the residue was examined by infra-red spectroscopy, and two strong bands were observed (Figure 15):

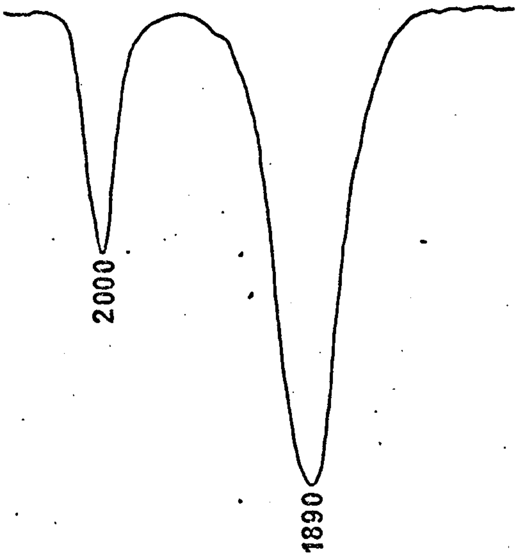


FIGURE 15

The mass spectrum of the product was consistent with the structure $H_3Re_3(CO)_{12}$, which has previously been reported by Kaesz (231). However, the infra-red spectrum was totally different from that of the literature example (Figure 16)

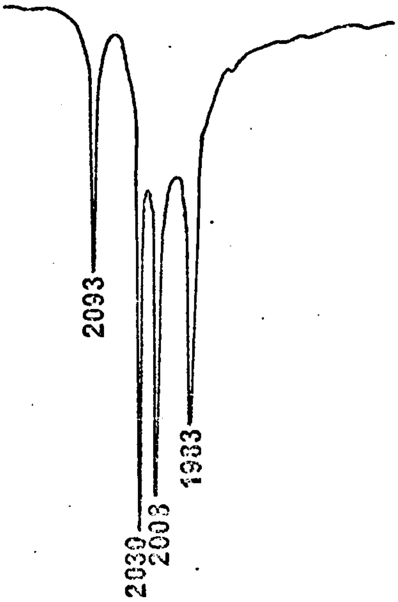
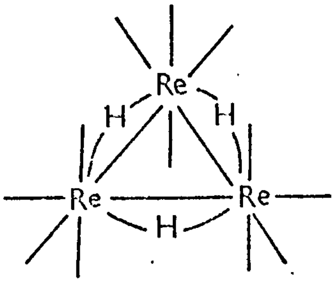


FIGURE 16

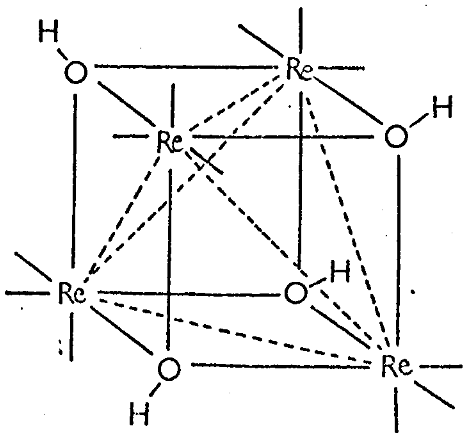
It was noted that a considerable residue of non-volatile material was left on the mass spectrometer probe, and it was concluded that it was this material whose infra-red spectrum was recorded, and that the spectrum of the trinuclear hydride was hidden beneath it. This assumption was verified by preparing the complex $H_3Re_3(CO)_{12}$ by the published method (231) and recording its mass spectrum (MS11). This was found to be identical to that obtained for the hexane insoluble product from the oxidation reaction.

The infra-red spectrum of the pentacarbonyl anion prior to oxidation showed no evidence of $Re_2(CO)_{10}$, and thus the decacarbonyl found in the reaction is a genuine product, and is not present by being "carried through". This was verified against a "blank" reaction employing identical conditions but in which no tropylium hexafluorophosphate was used. In this case only a minimal amount of $Re_2(CO)_{10}$ was isolated. It is interesting to note that no $HRe(CO)_5$ was detected in any of these reactions, which may have been expected from reactions of the pentacarbonyl radical with water. This may be due to the fact that dimerisation is more favourable at room temperature or that $HRe(CO)_5$ is susceptible to attack by $Re(CO)_5^\bullet$ species. The cluster compounds are presumably generated by some form of CO elimination reaction, although the precise manner in which this happens could not be determined.

The position and number of the bands in the infra-red spectrum of the non-volatile material which was obscuring those of the trihydrido complex suggested that this former product was the tetranuclear hydroxy compound XII.



XI



XII

This has been reported as being produced, together with XI, in a photochemical reaction of $Re_2(CO)_{10}$ with water (232). Under the reaction conditions, XI was transformed into XII, so that this latter was obtained exclusively if irradiation was continued for a sufficient time. The hydroxo compound is colourless, air stable, and its simple two band infra-red spectrum suggests a highly symmetrical structure (ν c≡o $/\text{cm}^{-1}$ 2021(s) and 1919 (vs) in THF).

In its ^1H NMR spectrum (diamagnetic) just one broad singlet at δ 7.5 in acetone-d_6 is observed (corresponding to the hydroxy protons) and this slowly disappears in deuterated water. It was found to be insufficiently volatile for mass spectroscopic study. All of these characteristics strongly suggest that the unidentified compound from the chemical oxidation is in fact this tetranuclear species XII. This was reinforced by rhenium analysis on the residue remaining after prolonged soxhlet extraction to remove $Re_2(CO)_{10}$ and XI.

According to studies of the photolysis of $Re_2(CO)_{10}$ in CCl_4 (233) the initial step of the photoreaction appears to be homolysis to give $Re(CO)_5$ radicals. It is thought that these then react with water in some manner (with attendant loss of CO) to give the polynuclear carbonylrhenium complexes.

In conclusion, chemical oxidation of $Re(CO)_5^-$ ions appears to give radical species. The products are identical to those formed by $Re(CO)_5^\bullet$ species known to be generated by the homolysis of $Re_2(CO)_{10}$. The polynuclear species in Table 10 may have been formed by a similar combination reaction of $Re(CO)_4P^\bullet$ intermediates.

2.3 Some Conclusions and Comments

It appears that the $Re_2(CO)_{10}$-PPh_3 reaction has a basic similarity to that of the analogous manganese system (108) in that reactive metal centre radicals are generated but cannot be isolated.

The complex "$Re(CO)_3(PPh_3)_2$" reported by Nyman (113) is now believed to have been mischaracterised and to be in fact mer-trans-$HRe(CO)_3(PPh_3)_2$, presumably contaminated with some paramagnetic impurity in this earlier work. The second form of "$Re(CO)_3(PPh_3)_2$" reported by Freni (112) has not been confirmed, as nothing with an analogous infra-red spectrum has been detected or isolated. Furthermore, it is clear that the compound reported as $Re_2(CO)_6(PPh_3)_4$ (112, 215) is alos mer-trans-$HRe(CO)_3(PPh_3)_4$

2.4 EXPERIMENTAL

Virtually all of the compounds prepared in this work were thermally stable and sufficiently volatile to make them amenable to mass spectroscopic study. Indeed, this technique above all others was most used to determine the stoichiometry of isolated products.

UV spectra were recorded on a Unicam SP800 spectrophotometer using matched 10 mm cells.

Infra-red spectra were obtained using either a Perkin Elmer 257 or 457 spectrophotometer calibrated with polystyrene or the integral wavenumber marker on the latter instrument. Samples were run normally as chloroform solutions in 0.1 mm NaCl cells unless otherwise stated.

^{1}H NMR spectra were taken on a Perkin Elmer R32 instrument operating at 90 MHz and 35°C, employing an FT attachment whenever only small samples were available or difficulty with effecting solution was experienced. Resonance positions are quoted on the δ scale.

Mass spectra were run using an AEI MS9 instrument operating at 70 eV with a probe temperature of 100-150°C. MS numbers refer to the bar diagrams of the mass spectrum which appear in appendix 1. Gas analyses were performed using a VG-micromass 6 spectrometer.

Preparative thin layer chromatography plates were prepared by coating degreased 20 x 20 cm glass plates with a 0.3 mm layer of Merck silica gel (type PF_{254}) and developed with the appropriate solvent, compositions of which are given in Table 14.

TABLE 14

TLC MIXTURES

No	Composition (by volume)
1	80/100 Petrol 3: ethyl acetate 1
2	80/100 Petrol 9.5: ethyl acetate 0.5

The plates were washed with methanol prior to use.

Decacarbonyldirhenium (Strem Chemicals) and triphenylphosphane (BDH Ltd) were used as received. Other solid reagents were purified as considered necessary by standard methods. Solvents were dried, distilled and degassed by at least three freeze/pump/thaw cycles prior to use. Reactions were performed under an atmosphere of dry carbon dioxide-and oxygen-free nitrogen. Melting points were determined in open capillaries and are uncorrected. Laser Raman Spectra were recorded for solid samples using a Jeol JRS-S1 instrument. Carbon, hydrogen, phosphorus and halogen microanalyses were by Butterworths, Teddington, Middlesex.

Manipulations and transfer of air sensitive solutions were facilitated by the use of the coupled vacuum/nitrogen line sketched in Figure 17.

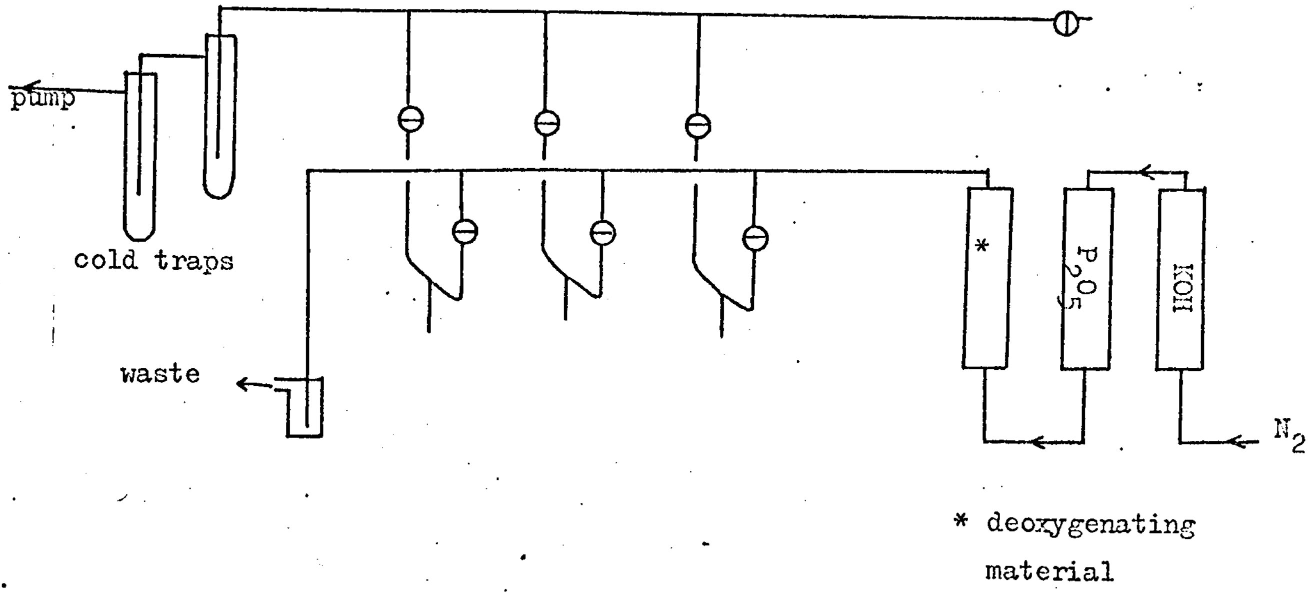


FIGURE 17

This enabled the reaction apparatus to be evacuated or pressurised without exposure to the air. Transference of solutions using hyperdermic tubing and "suba-seal" caps was effected by applying slight vacuum to the receiving flask. The mercury manometer was incorporated as a safety device should the nitrogen line be accidentally opened to the vacuum line.

Preparative reactions were normally run without precautions against daylight.

Preparation of mer-trans-$HRe(CO)_3(PPh_3)_2$ and $Re(CO)_3(PPh_3)(C_6H_4PPh_2)$ by reaction of $Re_2(CO)_{10}$ with PPh_3

Decacarbonyldirhenium (0.33 g; 5.07 x 10^{-4} mole) and triphenylphosphane (1.25 g; 4.77 x 10^{-3} mole, mole ratio 1:9) were dissolved in xylene (15 ml) and heated under reflux for 48 hours. After this time the solvent was removed in vacuo to give an orange residue. This was dissolved in boiling benzene (10 ml) and cooled to 60°. Hexane was then added to just induce crystallisation, and the mixture was then cooled in ice. The cream powder was collected, dried in vacuo, and crystallised from benzene/hexane to give white flakes, 0.2422 g (45.31% based on $HRe(CO)_3(PPh_3)_2$), mp 210d; ν C≡O (benzene and chloroform) 1935(s) cm^{-1} (Figure 6); found C 59.09, H3.86, $C_{39}H_{31}O_3P_2Re$ requires C 58.93, H3.80%; MS4, M^+ 794, M^+-nCO (n = 1-3); ^1H NMR -5.06 (triplet, J_{P-H} 18 Hz). Raman spectrum, 2020 (s), 1920(s), 1780 (s) cm^{-1} compared favourably with literature values (168). The orange filtrate was concentrated to an oily residue. This was extracted with hexane (2 x 10 ml) and the then solid residue crystallised from diethyl ether to give colourless lozenge shaped crystals, 29 mg (5,1% based on $Re(CO)_3(C_6H_4PPh_2)(PPh_3)$) mp 203°; ν C≡O 2018 (s), 1933 (m), 1900 (m) cm^{-1}; MS5, M^+ 792, M^+- n CO (n = 1-3)

Preparation of bis-ax-$Re_2(CO)_8(PPh_3)_2$ by the reaction of $Re_2(CO)_{10}$ with PPh_3

A solution of $Re_2(CO)_{10}$ (1.0 g; 1.5×10^{-3} mole) and PPh_3 (3.75 g, 0.0143 mole; mole ratio 1:9) in xylene (45 ml) was heated under reflux for 16 hours. After this time, the solvent was removed in vacuo, the residue dissolved in hot benzene and precipitation induced by addition of hexane. The white powder was crystallised from benzene/hexane to give white plates 0.318 g (20% based on $Re_2(CO)_8(PPh_3)_2$) mp 239-41°; ν C≡O, 2010 (w), 1960 (vs) cm^{-1}; found C47.75, H2.70 $C_{44}H_{30}O_8P_2Re_2$ requires C47.20, H2.68%. ^1H NMR 2.60 (mult) UV (CH_3CN) λ max 300 nm (ε 31863), 330 (inf) (17647).

The isolation and identification of products from a "standard reaction"

A mixture of $Re_2(CO)_{10}$ (0.33 g, 5.07×10^{-4} mole) and PPh_3 (1.25 g, 4.77×10^{-3} mole; mole ratio 1:9) in xylene (15 ml) was heated under reflux for 16 hours. The solvent was removed in vacuo and the residue taken up in a little chloroform and applied to 36 prep tlc plats and eluted in mixture 1, to give a plate whose appearance is depicted in Figure 1. The bands were scraped off the plate and the silica washed using chloroform. Filtration and concentration of the filtrate afforded the product. Infra-red spectroscopy of each fraction was used initially to provide a guide as to its nature. Band 8 gave a spectrum consistent with it being $Re_2(CO)_{10}$ and this was verified mass spectrometrically.

Band 7 was unreacted PPh_3.

Band 6 gave four peaks in the terminal carbonyl stretching region at 1966 (s), 1978 (vs) 1993 (s) and 2081 (m) cm^{-1} identical in fact to those reported for cis-$HRe(CO)_4PPh_3$ (168); MS3, M^+ 600, M^+-nCO (n = 1-4).

Band 5 was mer- trans-$HRe(CO)_3(PPh_3)_2$.

Bands 3 and 4 gave complex infra-red spectra, and were concluded to contain several compounds which had to be resolved using a different eluent system.

Band 2 was identified by mass spectroscopy and the comparison with an authentic sample to be triphenylphosphane oxide.

Band 1, which did not move from the baseline, did not exhibit any carbonyl bands and was considered to be composed of metal containing decomposition products and perhaps some polymeric material.

Separation of the components of bands 3 and 4 was effected using mixture 2. The first was resolved into three bands and each of these was removed from the plates and isolated in the usual manner. One of these gave an inconclusive mass spectrum due to the paucity of the sample. Another gave a spectrum which showed successive losses of 14 a.m.u. which suggested that this was possibly some organic impurity in the xylene (losing CH_2 groups). The third fraction was the polynuclear species mentioned earlier, and the highest mass ion observed was clearly not the molecular ion. There was insufficient material to record its infra-red spectrum and thus positive identification of this particular compound was not possible.

Band 4 was also separated using mixture 2, and in this case five components were eluted, four of which were positively identified. These were: eq-$Re_2(CO)_9PPh_3$ (MS1), bis-ax-$Re_2(CO)_8(PPh_3)_2$ (identified by infra-red spectroscopy), and $Re(CO)_3(PPh_3)(PPh_2C_6H_4)$ (identified by mass spectrometry). The fourth could have been either an isomer of $HRe(CO)_4PPh_3$ or $Re(CO)_4(PPh_2C_6H_4)$, but the mass spectral data was not of sufficient quality to confirm the formula. Fac-$HRe(CO)_3(PPh_3)_2$ was also isolated.

The preparation of cis-$HRe(CO)_4PPh_3$ (168) and its reaction with PPh_3 under standard conditions

Sodium amalgam was prepared under nitrogen using clean sodium (0.25 g) and mercury (27 g). A solution of $Re_2(CO)_{10}$ (2.5 g, 3.85×10^{-3} mole) in THF (35 ml) was added carefully with stirring. The solution became clear orange (due in part to the formation of yellow $Re(CO)_5^-$ ions and red polynuclear anions (234)). The reaction was left at ambient temperature for 4 hours to ensure completion. After this time, the spent amalgam was run off and the THF solution concentrated slightly. This was then acidified with syrupy phosphoric acid (20 ml; 90%) and the hydride isolated by vacuum distillation into a trap of liquid nitrogen temperature. The infra-red spectrum of the clear distillate (2015 (s) 2006 (s) cm^{-1}, see Appendix 2) confirmed the presence of the pentacarbonyl hydride by comparison with the literature values (235). The total distillate was then allowed to react with excess PPh_3 in benzene (60 ml) at room temperature for 3 hours. The mixture was then concentrated in vacuo to give a mixture of cis-$HRe(CO)_4PPh_3$ (identified by infra-red spectroscopy) and PPh_3. These were separated by preparative thin layer chromatography in mixture 1 to give cis-$HRe(CO)_4PPh_3$ as white air stable crystals, ν C≡O, 2081 (m), 1993 (s), 1978 (vs), 1966 (s) cm^{-1}; found C 47.88, H3.06 $C_{22}H_{16}O_4PRe$ requires C 47.14, H2.85%.

This sample of cis-$HRe(CO)_4PPh_3$ was then allowed to react with PPh_3 in boiling xylene in the normal fashion, and the reaction followed by infra-red spectroscopy. After 24 hours, none of the original hydride was detected, and one new band had appeared at 1935 cm^{-1}. This very characteristic spectrum with a broad shaped peak (Figure 6) was attributed to mer-trans-$HRe(CO)_3(PPh_3)_2$, the expected product. Since this reaction was performed using an unknown quantity of $HRe(CO)_5$ (due to its air sensitivity making manipulation difficult) no yield data are available, but it is obvious from the infra-red spectra that the reaction goes to completion.

The preparation of $Re(CO)_3(PPh_3)_2Cl$ and its reaction with $(Cr(II)(acac)_2)_2$

1. Preparation of $Re(CO)_5Cl$

A solution of $Re_2(CO)_{10}$ (2.0 g 3 m mol) in CCl_4 (100 ml) was cooled in ice for at least one hour with stirring. When thoroughly chilled, a gentle stream of chlorine was passed through the solution for 30 minutes. A fine white powder formed. This was filtered and extracted with chloroform. The suspension obtained was filtered, and the filtrate concentrated to give pale yellow crystals 0.562 g (26% based on $Re(CO)_5Cl$) mp > 250°; ν C≡O; 2046 (s), 1992 (s) cm^{-1}.

2. Preparation of $Re(CO)_3(PPh_3)_2Cl$.

$Re(CO)_5Cl$ (0.2 g; 5.5 x 10^{-4} mole) and PPh_3 (0.29 g 0.0011 mole, mole ratio 1:2) were dissolved in absolute ethanol (50 ml) and heated at reflux under nitrogen for 2 hours. After this time the reaction vessel was cooled in ice to give white crystals, 0.399 g (86.9% based on $Re(CO)_3(PPh_3)_2Cl$) mp > 250°; ν C≡O; 2034 (vs), 1958 (s), 1905 (s) cm^{-1}.

3. Preparation of bis(2,4-pentanedionato)chromium (II) (236) and its reaction with $Re(CO)_3(PPh_3)_2Cl$.

$CrCl_3.6H_2O$ (0.319 g, 0.0011 mole) was reduced using zinc (0.85 g, 0.013 g at) in C.HCl (1 ml) and water (15 ml) to give a sky blue solution of Cr(II) ions. This was filtered onto a slurry of sodium acetate (anhydrous, 1.375 g, 0.016 mole) in water (15 ml). The mixture immediately became dark blood red. After standing for 15 minutes at room temperature, the precipitated chromium (II) acetate was filtered, and treated with 2,4-pentanedione (0.5 ml: 0.486 g, 0.0041 mole) in water (10 ml). The resulting red-brown air sensitive solid was then filtered, and pumped dry. It was then treated with benzene (10 ml) and a solution of $Re(CO)_3(PPh_3)_2Cl$ (0.39 g, 4.7 x 10^{-4} mole) in benzene (5 ml) added. The reaction was warmed briefly and then left at toom temperature for 5 hours. An aliquot was removed and it was found to be unaffected by air. Hexane was then added to induce precipitation and the flask left in the icebox overnight. A crop of white crystals were filtered off, dried in vacuo, and examined by infra-red spectroscopy in benzene solution. This indicated that no reaction had taken place and this was verified by comparison of spectra obtained from an authentic sample of starting material, and by microanalysis; found C 56.47, H 3.78, Cl 4.41, $C_{39}H_{30}ClO_3P_2Re$ requires C 56.44, H 3.65, Cl 4.27%.

The polymerisation of methylmethacrylate at room temperature

This was one of the tests used to confirm the presence of radicals in the reaction scheme. Thus $Re_2(CO)_{10}$ (0.33 g; 5.07×10^{-4} mole) and PPh_3 (1,25 g, 4.77×10^{-3} mole; mole ratio 1:9) in xylene (15 ml) was heated under reflux for 2 hours. After this time an aliquot (1 ml) was taken and added to destablised methylmethacrylate. After some days, this material has polymerised convincingly into a solid residue, whereas a control reaction run concurrently was still a mobile liquid. A similar preparative route was employed for the copolymerisation of styrene and methylmethacrylate.

The reaction between $Re_2(CO)_{10}$ and PPh_3 in a 1:1 mole ratio

$Re_2(CO)_{10}$ (0.325 g; 5×10^{-4} mole) and PPh_3 (0.131 g, 5×10^{-4} mole) were dissolved in xylene (15 ml) and heated under reflux for 19 hours. Examination of the reaction mixture by tlc showed a cleaner reaction mixture than the usual 1:9 mole ratio experiment, and no formation of $HRe(CO)_3(PPh_3)_2$. The solvent was removed in vacuo, and the residue applied to preparative tlc plates and eluted in mixture 1. The major band was collected in the usual manner to give off-white crystals, 0.150 g (33.7% based on $Re_2(CO)_9PPh_3$, $\nu C\equiv 0$ 2100 (s); 2080 (w); 2060 (w) 2030 (w) 2000 (vs) 1940 (vs) cm^{-1}. found: C 36.67, H 1.7%, MS2 M^+ 884, M^+-nCO(n = 1-9). $C_{27}H_{15}O_9PRe_2$ requires C 36.67, H 1.7%.

The reaction of bis-ax-$Re_2(CO)_8(PPh_3)_2$ with CO (ref 198)

Bis-ax-$Re_2(CO)_8(PPh_3)_2$ (0.143 g; 1.3×10^{-4} mole) was dissolved in xylene (65 ml) and heated under reflux while a steady stream of CO gas was passed through it. After 16 hours, the solvent was removed and the residue examined by infra-red spectroscopy. This showed a very strong band at 2000 cm^{-1} and a weaker one at 1940 cm^{-1}; confirming the axial stereochemistry of the nonacarbonylderivative produced in the 1:1 mole ratio reaction.

The solid phase reaction between $HRe(CO)_3(PPh_3)_2$ and PPh_3

This reaction has been reported (215) to yield $Re_2(CO)_6(PPh_3)_4$. Thus a mixture of $HRe(CO)_3(PPh_3)_2$ (0.3 g, 3.8×10^{-4} mole) and PPh_3 (0.3 g, 1.1×10^{-3} mole) were heated in a sealed evacuated tube at 230° for 3 hours, during which time the melt became a tan colour. Following the reported work-up procedure, the tube was allowed to cool to room temperature and then opened. Benzene (10 ml) was then added, giving a clear orange solution. This was filtered to remove a little insoluble material, and absolute ethanol (10 ml) was added to the filtrate. On cooling, a cream powder was precipitated. This was isolated, and crystallised from benzene/hexane to give white flakes (55 mg), melting point and mixed melting point demonstrated these to be $HRe(CO)_3(PPh_3)_2$. No reaction had therefore occured.

Preparation of tropylium hexafluorophosphate

A solution of triphenylmethyl hexafluorophosphate (3.0 g, 0.0077 mole) in methylene chloride (40 ml) was treated with a solution of cyclohepta-1,3,5-triene (1.0g, 0.0011 mole) in methylene chloride (10 ml) with stirring at room temperature. A buff precipitate formed immediately but the reaction was left for 30 minutes to ensure completeness. The product was then isolated by filtration and dried in vacuo to give a tan powder 1.50 g (82.5% based on $C_7H_7{}^+PF_6{}^-$) IR (KBr disc) 3020 (w), 1480 (s), 850 (vs, PF_6 moiety) cm^{-1}. The product appeared slightly deliquescent so was stored in a dessicator over lithium aluminium hydride.

Reaction of $Re(CO)_5{}^-Na^+$ with tropylium hexafluorophosphate

Sodium amalgam was produced under nitrogen from clean sodium (0.05g, 0.0022 g atom) and mercury (6 g). To this was added a solution of $Re_2(CO)_{10}$ (0.137 g, 2.11×10^{-4} mole) in THF (10 ml). After 4 hours stirring at room temperature, the yellow solution was siphoned off and treated with tropylium hexafluorophosphate (0,1g; 4.3×10^{-4} mole) in THF (20 ml). The reaction was left at room temperature for 2 hours, and then concentrated to dryness. The yellow residue was extracted with hot n-hexane (5 x 20 ml) the extracts were combined and concentrated to dryness to give an off white powder, 81 mg (59% based on $Re_2(CO)_{10}$); ν C≡O, 2070 (s), 2010 (vs), 1965 (s) cm^{-1} $M^+ = 650$, $M^+ - nCO$ (n = 1-10).

The hexane insoluble residue was pumped for 2 hours at room temperature, to give a buff solid 80 mg, mp > 200°, ν C≡O 2000 (m), 1890 (s,br), ν O-H, 3500 (w) cm^{-1}; MS11 M^+ 894, $M^+ - n$ CO (n = 1-12)($H_3Re_3(CO)_{12}$).As described in Section 2.2.3, it was found that the major product whose infra-red bands were observed was $[(HO)Re(CO)_3]_4$.

It was found that both $Re_2(CO)_{10}$ and $H_3Re_3(CO)_{12}$ could be removed from the tetranuclear complex by prolonged extraction in a soxhlet apparatus using n-hexane. The residue in the thimble showed no other products in its tlc after 4 hours extraction. The residue was then analysed for rhenium by Headridge's method (237). Found Re 61.6%, $C_{12}H_4O_{16}Re_4$ requires 64.6%. The slightest trace of $Re_2(CO)_{10}$ in the sample would account for the error in the microanalysis.

A control experiment performed in an identical manner to that just described but without the addition of tropylium ion resulted in the isolation of 5 mg of $Re_2(CO)_{10}$, clearly indicating that it is a genuine reaction product, and that reduction of this complex by sodium amalgam is very efficient.

The construction of a calibration graph for rhenium analysis

Standard solutions of ammonium perrhenate in the molarity range 5×10^{-4} to 1×10^{-4} were prepared in water, and the absorbance of each at 228 nm determined. From these data a graph of absorbance vs concentration was plotted allowing the determination of rhenium in an unknown. The analysis of an unknown is carried out by first digesting a known weight with hot perchloric acid to oxidise the rhenium to rhenium (VII), then making the solution up to a known volume with water and measuring its absorbance at 228 nm. Consultation of the calibration curve then allows calculation of percentage rhenium. The UV spectra and calibration curve are given in Figures 18 and 19.

Preparation of $H_3Re_3(CO)_{12}$ (231)

$Re_2(CO)_{10}$ (1.0 g, 1.6 x 10^{-3} mole) was treated with $NaBH_4$ (2.8 g; 0.074 mole) in THF (40 ml) under nitrogen at reflux temperature for 20 hours. The supernatant liquid was transferred through hyperdermic tubing into a second flask and the red solution concentrated to dryness to give a solid cake. This was then treated with syrupy phosphoric acid (6 ml; degassed by passing nitrogen through for 2 hours, in freshly distilled and degassed cyclohexane) and heated under reflux for 5 hours. After this time, the mixture was subjected to liquid/liquid extraction with cyclohexane. The extracts were then dried ($CaCl_2$) and concentrated to dryness. The residue was extracted with hexane (to remove unreacted $Re_2(CO)_{10}$) to leave a buff solid which gave white flakes from cyclohexane, 95 mg (11% based on $H_3Re_3(CO)_{12}$) mp 225 d; ν C≡O, 2093 (m), 2030 (vs), 2008 (s) 1983 (m) cm^{-1}, found C 16.33, H 0.41, $C_{12}H_4O_{12}Re_3$ requires C 16.05, H 0.34%. MS11, M^+ 894, M^+-nCO (n = 1-12).

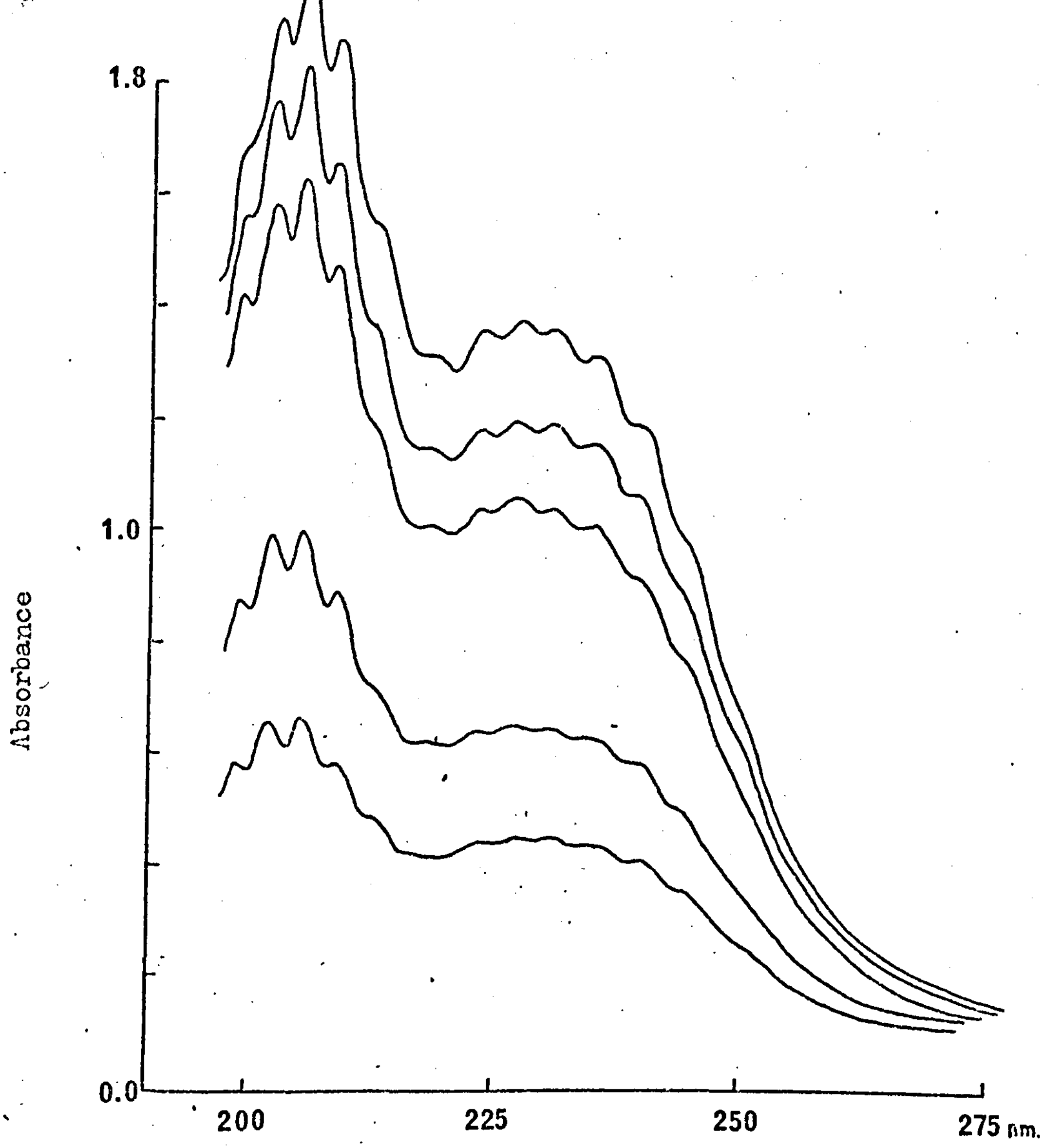


FIGURE 18

UV. spectra of ReO_4^- ion at various concentrations

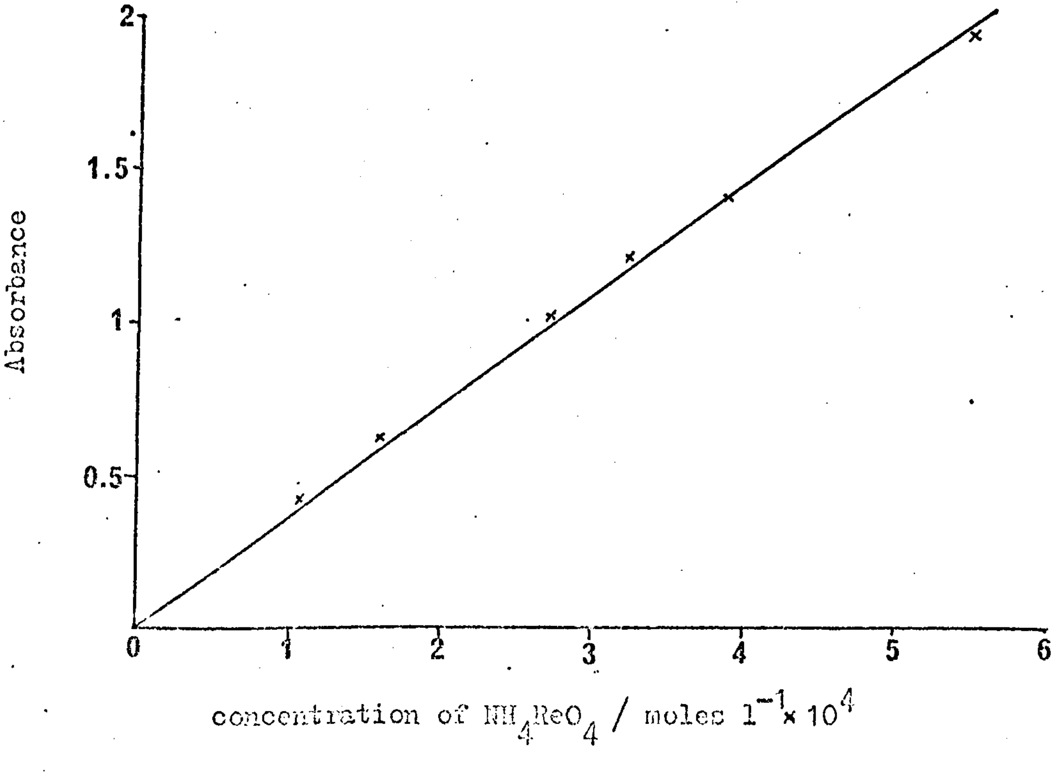
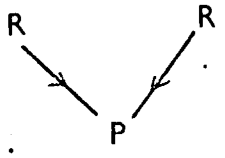


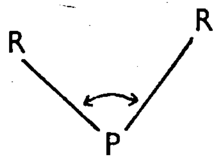
FIGURE 19

3 THE REACTIONS OF $Re_2(CO)_{10}$ WITH OTHER PHOSPHANES AND PHOSPHITES

3.1.1 Introduction

The experiments of Section 2 of this Chapter lead to the conclusion that 17 electron species exist as transient intermediates in the reaction between $Re_2(CO)_{10}$ and PPh_3, but that their isolation was not possible. In seeking to stabilise these mono-nuclear rhenium centred radicals, the reactions of $Re_2(CO)_{10}$ with a range of organophosphanes and phosphites that are approaching the extremes of the range of electronically transmitted and steric effects have been investigated. It is important to realise the stereochemistry of phosphorus containing ligands may have significant electronic consequences and vice versa. For example, increasing the angles between substituents will decrease the percentage of s character in the phosphorus lone pair orbital and changing the electronegativity of atoms can affect bond distances. Thus electronic and steric effects are intimately related, and difficult to separate in a pure way. Their different modes of action are sketched below:





The values of these parameters for a wide range of phosphanes and phosphites have been determined by Tolman (238). The magnitude of the electronic factor is based upon the position of one of the carbonyl stretching bands in the infra-red spectrum of $Ni(CO)_3L$, electron withdrawing groups causing a shift to higher wavenumber. This particular nickel complex is chosen since its preparation is easily carried out at room temperature, and its infra-red bands are sharp and can be measured to ± 0.1 cm^{-1}. The magnitude of the shifts are given in Table 15.

TABLE 15. (238)

Electronic parameters for some phosphanes and phosphites

	ν C≡O /cm^{-1}	$\Delta\nu$
$Ni(CO)_4$	2066.8	0
$Ni(CO)_3L$: L = $P(p\text{-}tol)_3$	2066.7	−0.1
L = $P(o\text{-}tol)_3$	2066.6	−0.2
L = $P(C_6H_{11})_3$	2056.4	−10.4
L = PPh_3	2068.9	+ 2.1
L = PH_3	2083.2	+16.4
L = $P(O\text{-}o\text{-}tol)_3$	2084.1	+17.3
L = $P(OPh)_3$	2085.3	+18.5
L = $P(O\text{-}pClC_6H_4)_3$	2089.3	+22.5

The measurement of the size of a number of phosphane and related compounds has also been carried out on a standardised basis (238), using the concept of ligand cone angles. This is defined as the angle subtended by a surface which just contains all three groups on the phosphorus atom, while maintaining three fold symmetry. This is depicted in Figure 20 which shows the relevant angle θ .

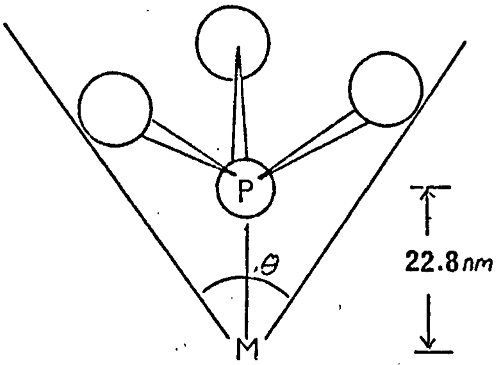


FIGURE 20

The distance of 22.8 nm was chosen since this represents the distance between phosphorus and nickel centres in trans-bis(phenylethynyl)bis(triethylphosphane)nickel II (239). Values of θ for the ligands used in this work are given in Table 16.

TABLE 16

Ligand cone angles (238)

Ligand	θ /degrees
PH_3	87 ± 2
$P(OPh)_3$	121 ± 10
$P(O\text{-}pClC_6H_4)_3$	121 ± 10
PPh_3	145 ± 2
P(p-tolyl)$_3$	145 ± 3
P(O-o-tolyl)$_3$	165 ± 10
$P(C_6H_{11})_3$	179 ± 10
P(o-tolyl)$_3$	194 ± 6

It was believed that electron releasing phosphanes would make the radicals more "18-electron like" and therefore more stable, while the size of the ligand would protect them from further attack. Electron withdrawing substituents would tend to make the metal more "16-electron like" and therefore possibly susceptible to some interesting oxidative addition type reactions.

However, in all the experiments performed, the desired stabilisation was not achieved, but a range of novel metalated species have been prepared. The formation of these is discussed with reference to the ring size of the metalated product, and bulkiness of the ligand.

3.1.2 The reaction between $Re_2(CO)_{10}$ and triphenylphosphite

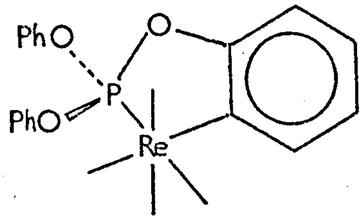
Triphenylphosphite was the first compound to receive attention in this part of the work since it would provide information concerning the importance of electron withdrawal on the stability of radicals produced in this type of reaction. The experiments were performed under identical conditions with identical molar ratios to those used for PPh_3, and the products isolated are given in Table 17.

TABLE 17

Products isolated from the reaction of $Re_2(CO)_{10}$ with $P(OPh)_3$

Product	Identification
ax-$Re_2(CO)_9L$	mass spectrometry
bis-ax-$Re_2(CO)_8L_2$	MW; analysis; IR; ^{31}PNMR, UV
mer-$Re(CO)_3L(L-H)$	mass spectrometry
fac-$Re(CO)_3L(L-H)$	IR; MS; analysis
minor product	inconclusive

The minor product, although it could not be positively identified, was shown not to be $HRe(CO)_4L$ by comparison of its infra-red spectrum with the literature example (168). The important point of note in these isolated compounds, is the exclusive formation of metalated species rather than hydrides. This can be rationalised by invoking enhanced stability for the radicals by removal of unpaired electron density from the metal, so that they are not so susceptible to solvent attack. Their lifetimes would therefore, be sufficient to allow the aromatic nucleus to adopt the correct geometry for ring closure thereby generating the metalated complex. Two possible stereochemistries are available for the isolated nonacarbonyl derivative, but since no infra-red data are available an assignment cannot be made. It may have been the equatorial isomer (by analogy with the complex isolated from the standard triphenylphosphane system) or some axially substituted material which had not yet undergone further reaction. The metalated species identified only by mass spectrometry is assumed to have mer-configuration since this is the only available alternative to the fac-arrangement. It was considered to have the former stereochemistry since it had very different thin layer chromatography characteristics from its mer isomer. The formation of these cyclic species is presumably enhanced by the production of a sterically favoured five membered ring, XIII, which has been discussed earlier (Section 2.1.2)



XIII

It must be borne in mind that the above results do not allow complete exclusion of the alternative mechanism in which the metalated species is formed by elimination of $HRe(CO)_5$ or one of its derivatives as discussed for the triphenylphosphane reaction (Section 2.1.2). It is reported (168) that $HRe(CO)_4P(OPh)_3$ is a thermally sensitive material, decomposing at 135° to a yellow gum. Dissociation of $Re_2(CO)_7L_3$ may thus give $Re(CO)_3L(L-H)$ but the coproduct, $HRe(CO)_4L$, decomposes before it is able to react with more phosphite to give the apparently stable $HRe(CO)_3P(OPh)_{3\ 2}$ (168). It would perhaps be for this reason that no hydrides have been detected.

The infra-red spectra of the two major products are shown in Figures 21 and 22. The position of the main absorbance band in the spectrum of $Re_2(CO)_8[P(OPh)_3]_2$ has moved to a higher wavenumber (1984 cm^{-1}). This is because the former ligand is a better π acceptor and a poorer σ donor than PPh_3. This results in decreased electron density at the metal, and so back donation into the CO antibonding orbitals is decreased. This causes the bond order between carbon and oxygen to increase and consequently it absorbs radiation of higher energy. The solution infra-red spectrum of the dimer (and all other bis axially substituted complexes prepared in this work) exhibits one very strong and one weak band in the carbonyl stretching region indicative of D_{4d} symmetry (240). This spectral pattern is well established, having been observed previously for all the known phosphane substituted $Mn_2(CO)_8L_2$ species (241), and the validity of the stereochemical assignment has been demonstrated by X-ray crystal data of bis-ax-$Mn_2(CO)_8(PEt_3)_2$ (242) and $Mn_2(CO)_8(PMePh_2)_2$ (243).

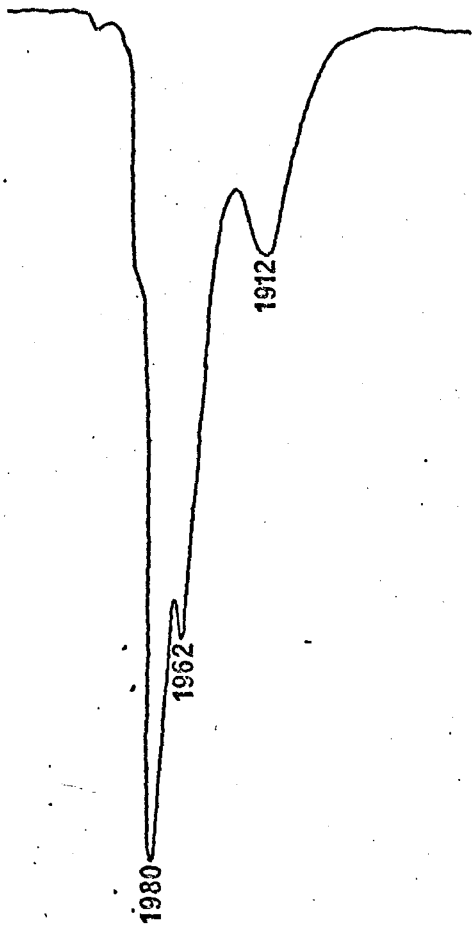


FIGURE 21

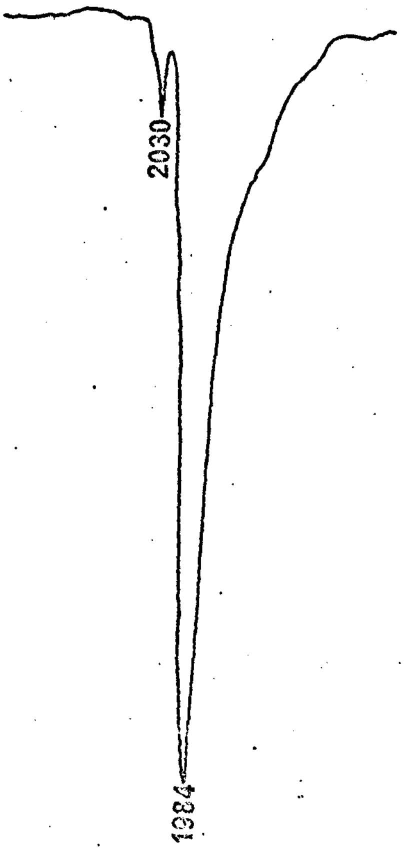


FIGURE 22

Despite an intensive search, no evidence was found for the formation of the intermediate metalated species $Re(CO)_4(L-H)$. It is suggested that $Re(CO)_3L(L-H)$ is formed by phosphite substitution into $Re_2(CO)_8[P(OPh)_3]_2$ followed by facile dissociation of the more highly substituted dimer to give the metalated species directly, rather than by substitution into $Re(CO)_4(L-H)$. Some evidence supporting this suggestion is gained from the fact that phosphites tend to replace more CO groups than PPh_3, since the former are better π acceptors. The smaller size of the triphenylphosphite group (Table 16) may also help in this respect.

A report in the literature (195) discusses the homolytic dissociation of bis-ax-$Re_2(CO)_8[P(OPh)_3]_2$ in benzene solution, and this was investigated by molecular weight determination in this medium. The value measured clearly demonstrated that the dimeric molecule persists in solution.

3.1.3 The reaction of $Re_2(CO)_{10}$ with tri(o-tolyl)phosphite

Six membered rings are of such widespread occurence in chemistry that it was initially believed that this would be the most favourable arrangement in metalation reactions. In order to investigate this a reaction with tri(o-tolyl)phosphite was studied since such a hexacyclic configuration would be possible if bonding to the metal were via the methyl group on the aromatic residue. Thus, a 1:9 molar ratio mixture of $Re_2(CO)_{10}$ and tri(o-tolyl)phosphite was heated under reflux in xylene solution for 15 hours. After removal of the solvent in vacuo, the oily residue was separated by preparative thin layer chromatography and the sole major band collected. Its infra-red spectrum (Figure 23.) strongly suggested the bis-ax-$Re_2(CO)_8L_2$ species, and this was confirmed by microanalysis.

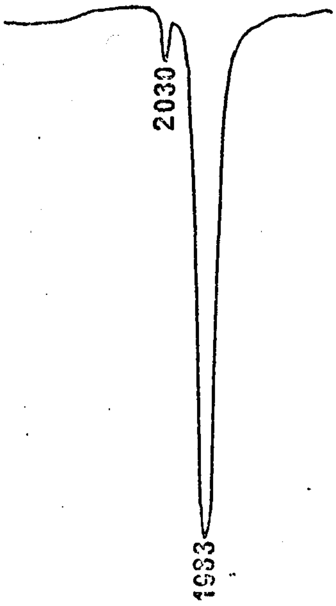


FIGURE 23

When the same reaction was run for 52 hours, a different unique major band was seen on the plates. This was isolated in the usual fashion to give a monomeric species of molecular weight 972 (mass spectroscopically). A signal due to a proton bonded to rhenium could not be detected in its ^{1}H NMR spectrum showing that the compound was not a hydride. The spectrum demonstrated two multiplets of peaks as shown in figure 25. Integration suggested a metalated complex with bonding through a site on a phenyl ring rather than through a methyl group, demonstrating the favoured nature of the five membered ring. Only two losses of carbon monoxide were seen from the molecular ion, but infra-red date (Figure 24) and microanalysis confirmed that this particular compound was fac-$Re(CO)_3L(L-H)$

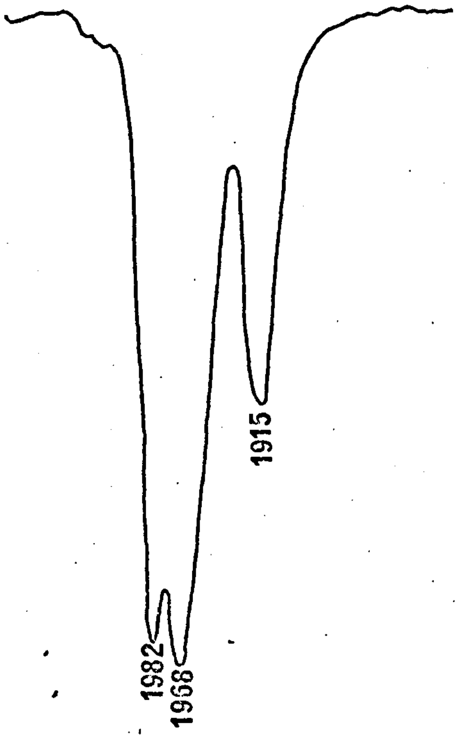


FIGURE 24

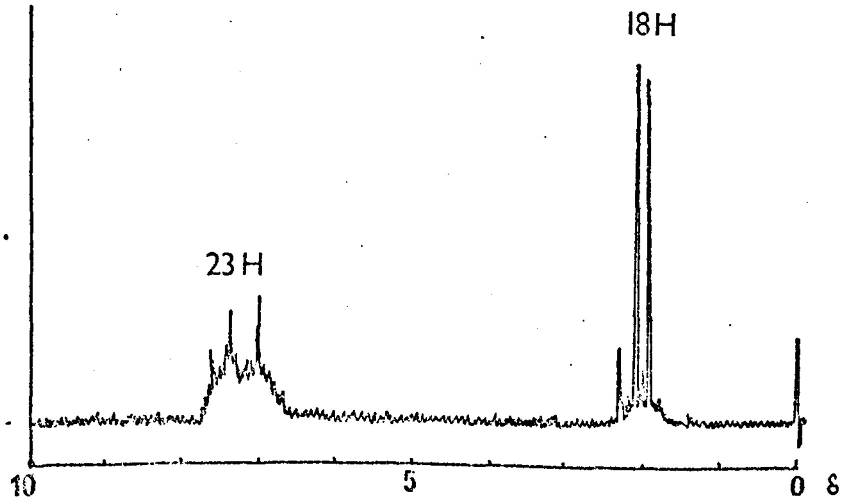


FIGURE 25

In similarity to the triphenylphosphite reaction, no evidence was found for formation of $Re(CO)_4(L-H)$ despite careful work up procedures and careful monitoring of the reaction by infra-red spectroscopy with time. Presumably one further substitution into $Re_2(CO)_8L_2$ is possible and this must occur in one of the eight equatorial positions. It is thought that this dimer then dissociates in a similar manner to that described in the literature (203) to give $Re(CO)_3L(L-H)$ and $HRe(CO)_4L$, the latter decomposing under the prevailing conditions. A final possibility is that substitution proceeds to give $Re_2(CO)_6L_4$ which then dissociates to give a pair of $Re(CO)_3L_2$ radicals which then metalate with attendant evolution of a molecule of hydrogen. The successful design of specific experiments to confirm which mechanism is actually occuring has not been achieved.

3.1.4 The reaction of $Re_2(CO)_{10}$ with tri(p-chlorophenyl)phosphite

From Table 15 it can be seen that inclusion of a chlorine atom into the aromatic residues of $P(OPh)_3$ further increases the electron withdrawing nature of the ligand. With this in mind, this reaction was performed with a view to isolating a "16 electron like" species. However, reactions using this ligand gave complex mixtures. A dimeric bis axially substituted dimer was isolated, but with difficulty. It was identified by microanalysis, and by comparison of its UV and infra-red spectra with those of authenticated dimers. Figure 26 shows its infra-red spectrum.

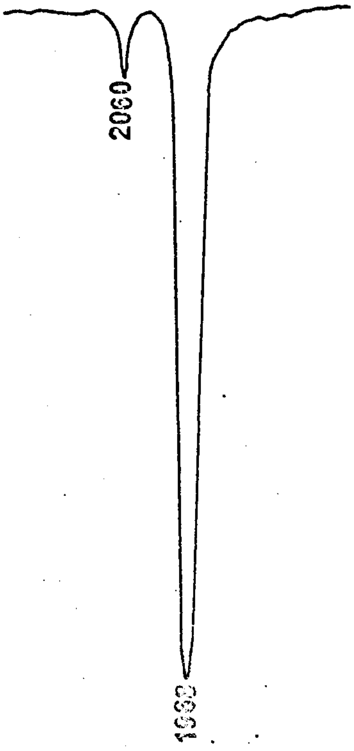


FIGURE 26

No other products were found even after a reaction time of 100 hours.

3.1.5 The reaction of $Re_2(CO)_{10}$ with tri(o-tolyl)phosphane

In order to investigate the role of cone angle on metalation reactions, experiments were conducted using tri(o-tolyl)phosphane. The large size of this ligand was also considered as a potential menas of protecting the radical complexes from further attack. Thus, a 1:9 molar ratio reaction was run in xylene solution under reflux for 23 hours. Removal of solvent and application of the solid residue to preparative thin layer chromatography plates revealed one band only. This was isolated in the usual fashion and identified by mass spectrometry, infra-red spectroscopy, microanalysis and PMR spectrometry to be $Re(CO)_4(L\text{-}H)$. The infra-red and PMR spectra are given in Figures 27 and 28. Integration of the latter demonstrated that metalation had occured via the methyl group, thereby generating the favoured five membered ring. The free ligand has a sharp singlet for the methyl protons and if bonding were via the ring then this signal may be expected to persist in the spectrum of the product. As can be seen, the pattern changes slightly.

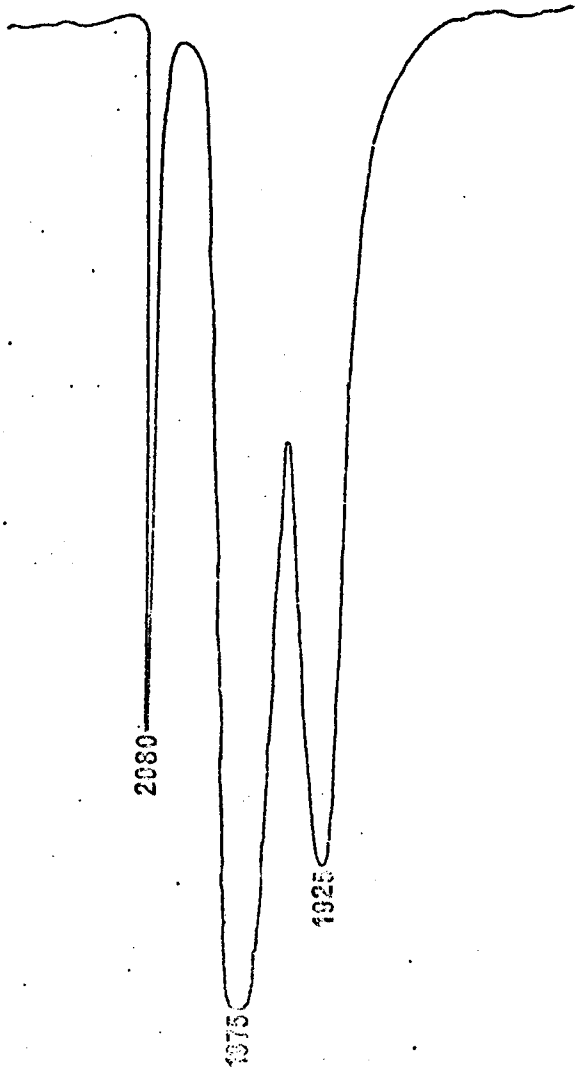


FIGURE 27

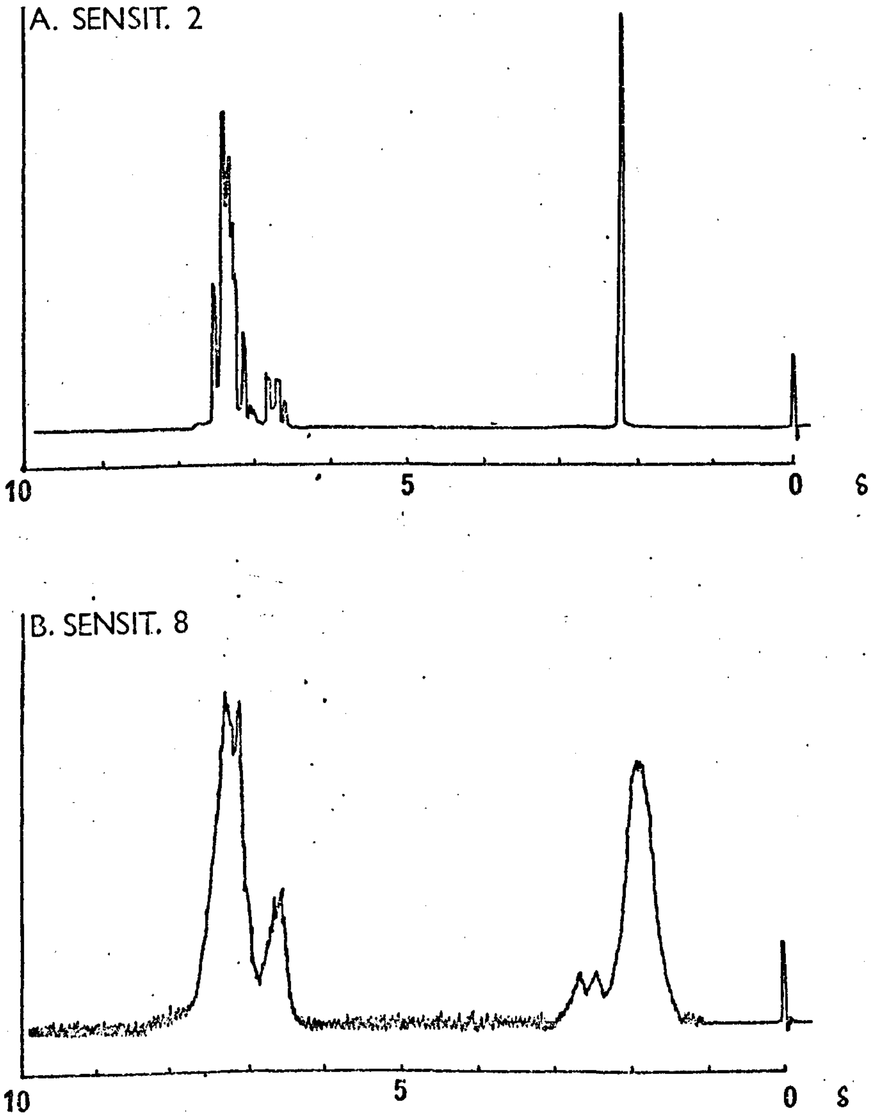


FIGURE 28

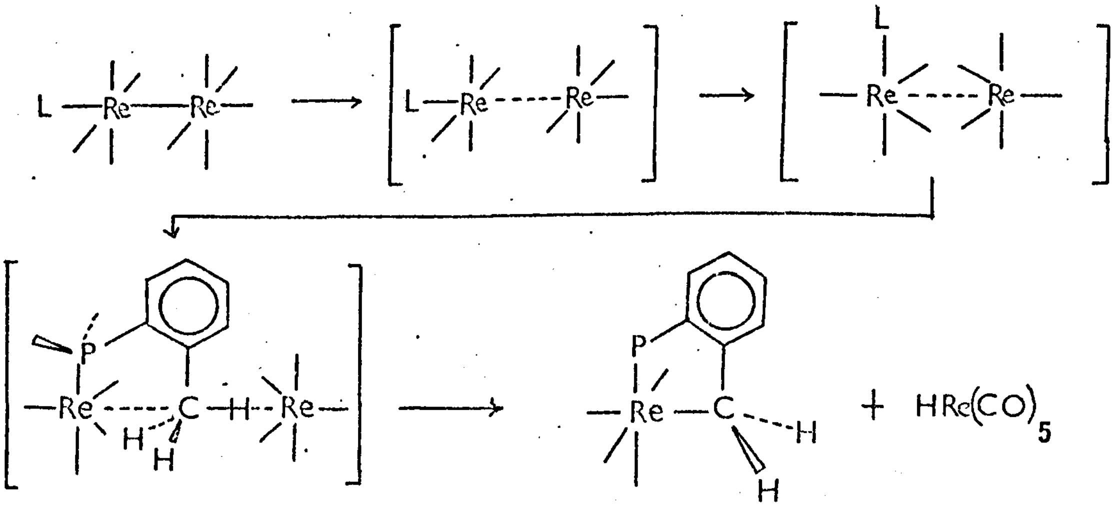
A tri(o-tolyl)phosphane

B $\overline{\mathrm{Re(CO)_3\ P(oC_6H_4CH_3)_2(C_6H_4}}\mathrm{CH_2)}$

The two signals in the aliphatic region in the PMR spectrum of the product arise from metalation causing the three methyl groups to be split into a group of two and a methylene unit. The two methylenic protons couple to each other to give a pair of doublets, but the outer two peaks are lost in the baseline noise. The same metalated species was obtained from reactions in the dark, or when using different mole ratios of reactants. In a 1:1 ratio reaction, the product was expected to be ax $Re_2(CO)_9L$ by analogy with the triphenylphosphane reaction. However, even in this instance, the metalated product was isolated. The gross cone angle of this ligand (194 ± 6^{o}) (238) and the fact that no dimeric species were obtained suggested the following mechanism:

$$\begin{tikzcd}
Re_2(CO)_{10} + L \arrow[r] & axRe_2(CO)_9L + CO\uparrow \arrow[d] \\
 & HRe(CO)_5 + Re(CO)_4(L\text{-}H)
\end{tikzcd}$$

Axial substitution of one carbon monoxide molecule occurs, but then the extreme size of the phosphane ligand forces the equatorial carbonyls adjacent to it towards those on the second rhenium atom. The metal-metal bond then ruptures to relieve the strain, giving the radicals $Re(CO)_5^{\bullet}$ and $Re(CO)_4L^{\bullet}$. Generation of the final metalated complex is then thought to proceed via formation of $HRe(CO)_5$:



Examination of models shows that the methyl group is in just the correct position to interact with the rhenium atom, as indicated, without straining any bonds or causing the ligands to adopt unfavourable configurations.

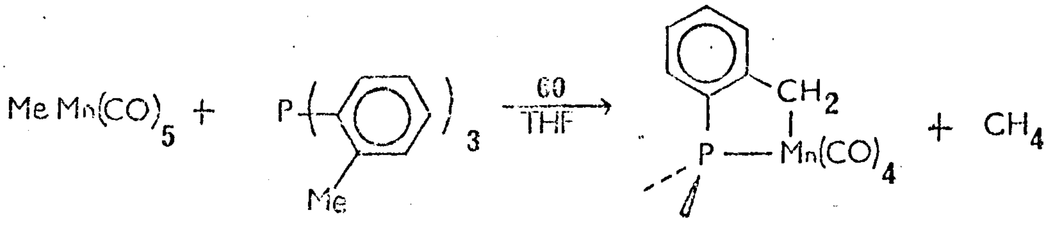
This reaction was performed at 125° in an NMR tube in order to determine if $HRe(CO)_5$ could be detected, as this would verify the scheme. However, since the tube needed to be sealed, no reaction was detected, presumably due to inhibition caused by the carbon monoxide released during the early stages of the reaction. This conclusion was endorsed when the contents of the tube were transferred to a vented flask and heated in the usual way. The reaction then proceeded normally to give the metalated species, identified by its infra-red spectrum.

The reaction was also run in a vented flask at 95°. This is below the decomposition point of the pentacarbonylhydride complex and it was hoped that sufficient quantities of this material would accumulate to allow its detection by infra-red spectroscopy. However, no reaction was noted even after 17 days.

Verification of this proposed scheme is therefore difficult, but it seems reasonable in view of the fact that the same product is obtained from reactions using any ratio of reagents, in daylight or in the dark.

In the light of experiments detailed earlier (Section 2.1.6) in which water was shown to be the source of hydrogen atoms in the hydrido complexes isolated, the possibility that the preparation of metalated complexes with this ligand was due to the solvent being particularly dry was considered. This question was answered by running the experiment in the presence of added water (0.6% v/v with xylene). In solvent of this composition, the sole product was again the metalated complex, demonstrating the facility of this reaction over hydride formation, and also the fact that after dissociation of the dimer the two radicals do not diffuse apart.

This direct formation of a metalated species with this ligand has been noted in the literature (207). Whereas $MeMn(CO)_5$ reacts with PPh_3 to give $MeMn(CO)_4PPh_3$ which is metalated only at the temperature of boiling toluene, the reaction of $MeMn(CO)_5$ with tri(o-tolyl)phosphane proceeds under much milder condiations directly to the ring closed compound:



3.1.6 The reaction of $Re_2(CO)_{10}$ with tri(p-tolyl)phosphane

This reaction was investigated in order to study the role of electronic effects in metalation mechanisms. Tri(p-tolyl)phosphane has the same magnitude of electronic parameter as tri(o-tolyl)phosphane, but a much small cone angle, and can only metalate via a four membered ring.

When a standard 1:9 ratio reaction was carried out the principal products isolated were bis-ax-$Re_2(CO)_8L_2$ and mer-trans-$HRe(CO)_3L_2$, L=P(p-tolyl)$_3$, paralleling those obtained for triphenylphosphane itself.

It is thus apparant that steric effects are far more important than electronic effects in determing whether metalation will occur or not.

3.1.7 The reaction of $Re_2(CO)_{10}$ with tri(cyclohexyl)phosphane

Reactions with this particular ligand were performed since the alkyl group is electron donating (see Table 15) and it was believed that this would make the central metal more "18-electron like" and therefore perhaps allow its isolation. The fairly large size of the ligand may also offer some protection against subsequent reactions.

The investigation was prompted by an unpublished report (244) concerning the photochemical reaction of $Mn_2(CO)_{10}$ with tri-n-butylphosphane which produced a green solution exhibiting an ESR signal which decayed with time but could be regenerated on further photolysis. (When this was repeated in this work (Section 3.1.9), however, hydrido type compounds, not radicals, were isolated).

From a standard 1:9 molar ratio reaction of $Re_2(CO)_{10}$ with tri(cyclohexyl)phosphane, the major products isolated were bis-ax-$Re_2(CO)_8L_2$ and mer-trans-$HRe(CO)_3L_2$. The infra-red spectra of both of these compounds (Figures 29 and 30) fitted into the pattern associated with each type of molecule.

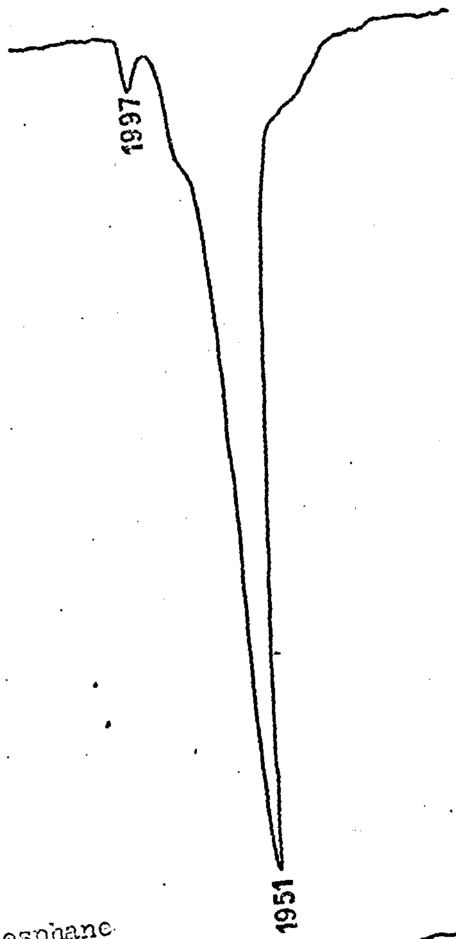


FIGURE 29

bis-ax-(Re$_2$(CO)$_8$L$_2$

L = tri(cyclohexyl)phosphane

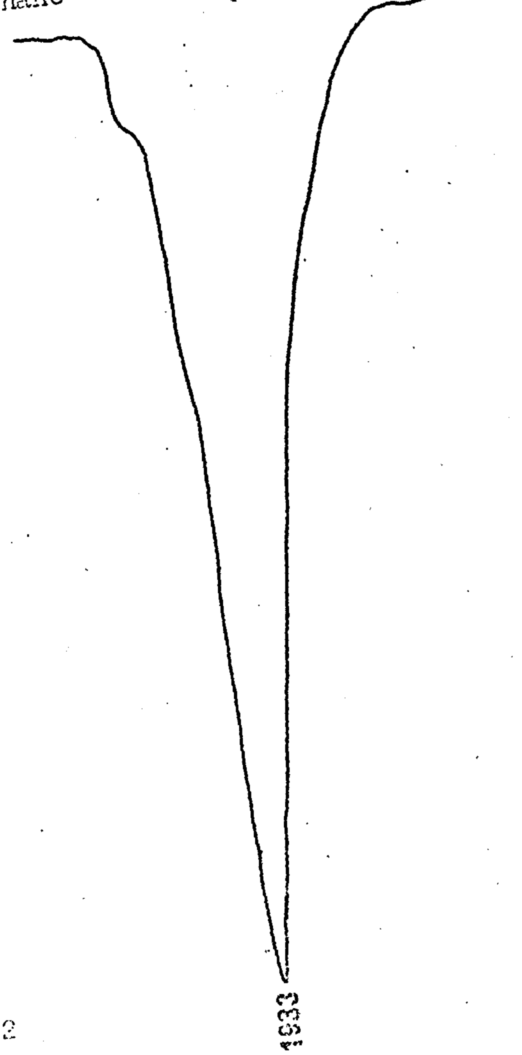
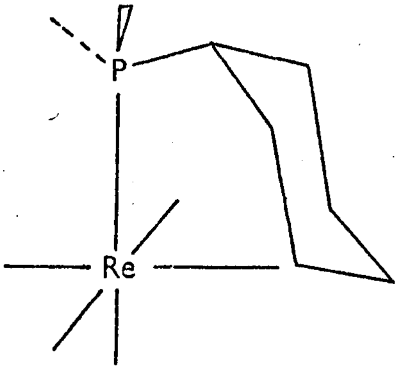


FIGURE 30

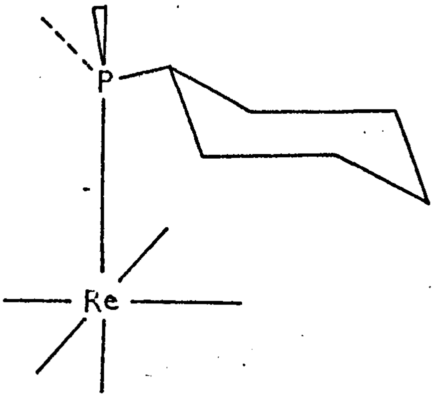
mer-trans-HRe(CO)$_3$L$_2$

L = tri(cyclohexyl)phosphane

The fact that no metalated species were observed in this reaction with a ligand of appreciable cone angle (179± 10°) appears surprising on first sight. Although a five membered ring is theoretically possible (via the γ carbon atom) it would appear that the flexible cyclohexane ring never attains the correct conformation for metalation to occur. This is demonstrated pictorally below:



XIV

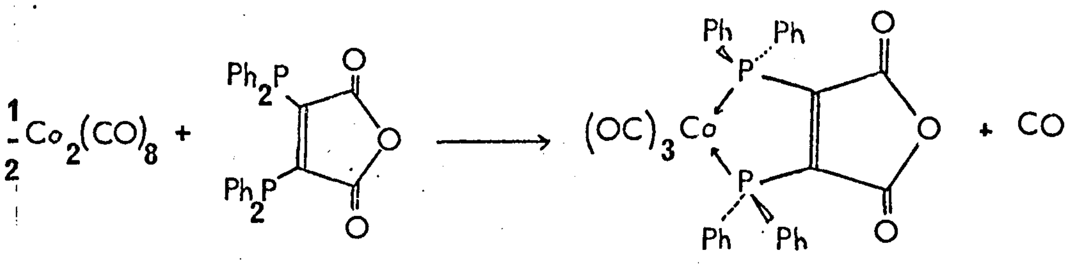


XV

Metalation can only occur if the ring adopts the position depicted in XIV. This is a high energy state due to steric crowding, and the ring normally relaxes to the position shown in XV. This relieves the interactions between the hydrogen atoms at the γ position and the carbon monoxide groups on the metal. In such a position, metalation is obviously impossible As this phosphane has a large cone angle, these results indicate that metalation does not arise simply as a result of gross steric effects, but also requires of the ligand the ability to bring the potential metalation site close to the metal. In rigid systems such as tri(p-tolyl)phosphane this configuration is easily achieved, but with flexible ligands, metalation is by no means a definitely predictable reaction. The cone angle seems of little importance in terms of ability of ligands to undergo this reaction, but possibly plays a vital role in determining the mechanism by which these molecules are formed. It does become a significant consideration when deciding on the number of ligands which can be accommodated around a single rhenium atom in an octahedral environment.

3.1.8 The reaction of $Re_2(CO)_{10}$ with bis(diphenylphosphino)maleic anhydride

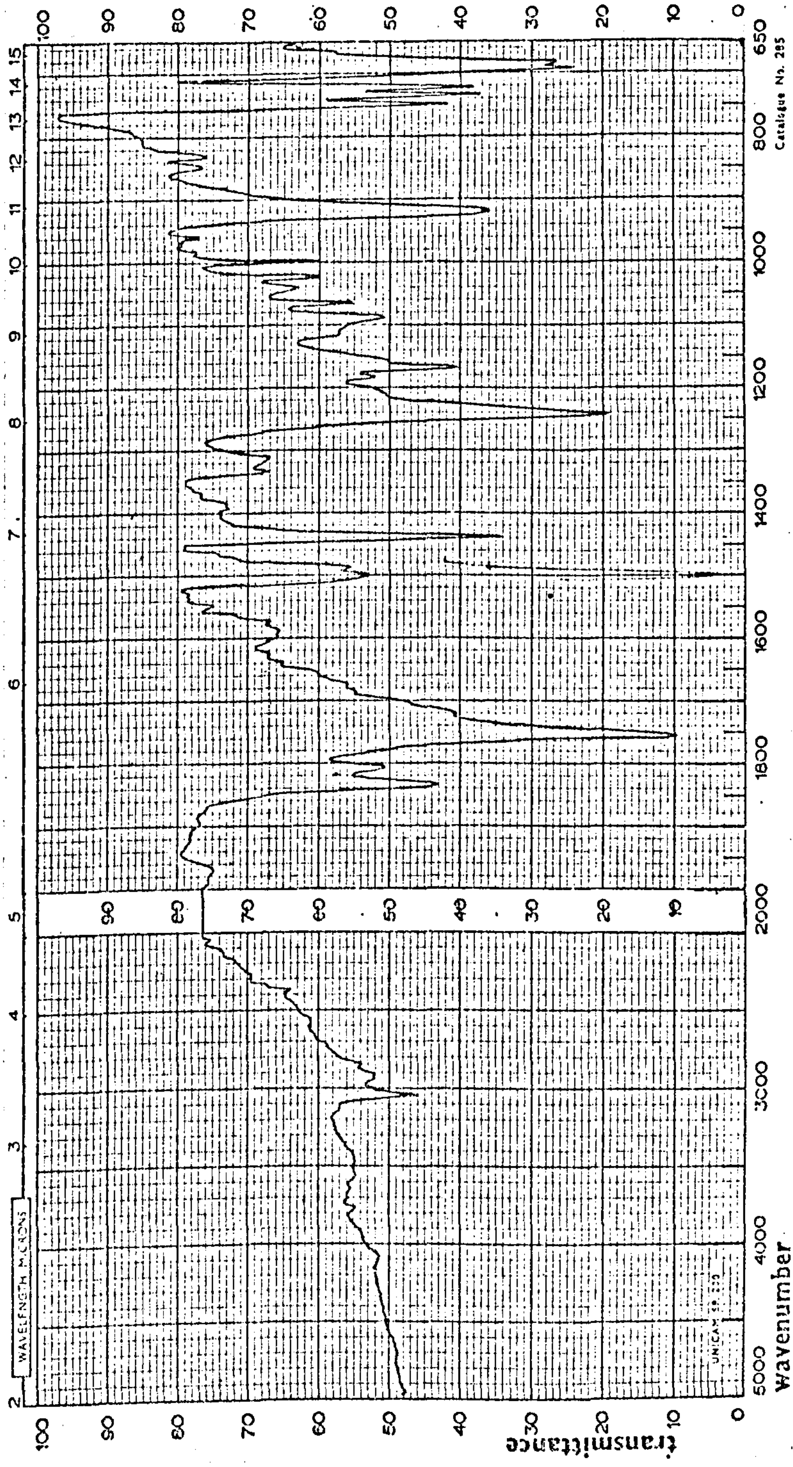
A report has appeared in the literature describing the preparation of the stable 19-electron cobalt complex XVI



XVII

XVI

Stabilisation is achieved by delocalisation of the unpaired electron over the phosphane ligand XVII, thereby making XVI more "18-electron like". The reaction between this ligand and decacarbnnyldirhenium was investigated as part of the general search for stable organorhenium radicals. XVII was prepared according to the published method (245) and fully characterised. Its IR spectrum (figure 31) was identical to that reported in the literature (245).


transmittance
0
10
20
30
40
50
60
70
80
90
100
Wavenumber
5000
4000
3000
2000
1800
1600
1400
1200
1000
800
650
WAVELENGTH MICRONS
2
3
4
5
6
7
8
9
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15
UNICAM SP 200
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FIGURE 31

The first reaction between $Re_2(CO)_{10}$ and XVII was performed using a 1:1 ratio of reagents in xylene solution under reflux in a nitrogen atmosphere. Shortly after heating had begun, a dark red spot XVIII was detected on tlc. No $Re_2(CO)_{10}$ was found after 2$\frac{1}{2}$ hours and the reaction was halted after this time. The appearance of the tlc plate (developed in mixture 1) after this time is shown in Figure 32.

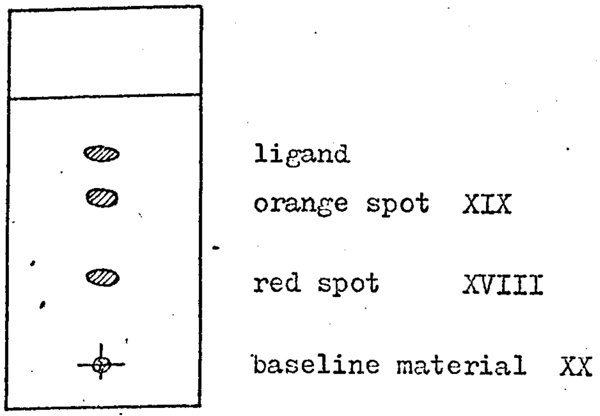


FIGURE 32

The red band XVIII was isolated by column chromatography on silica as a dark red solid. Its infra-red spectrum (Figure 33) was very similar indeed to that recorded for ax-$Re_2(CO)_9PPh_3$ (Figure 12) so it was postulated that XVIII was the analogous nona-carbonyl derivative. That it is formed first in the reaction tends to support this view. Its microanalytical data showed it to exist as a solvate, but a particular formula bearing n molecules of solvent could not be proposed since the petroleum ether solvent contained a range of hydrocarbons. The faster moving orange spot XIX was also isolated by preparative tlc. Its infra-red spectrum (Figure 34) strongly resembled others found for the bis-axially substituted dimers. The nature of the base-line material XX was not known at this stage.

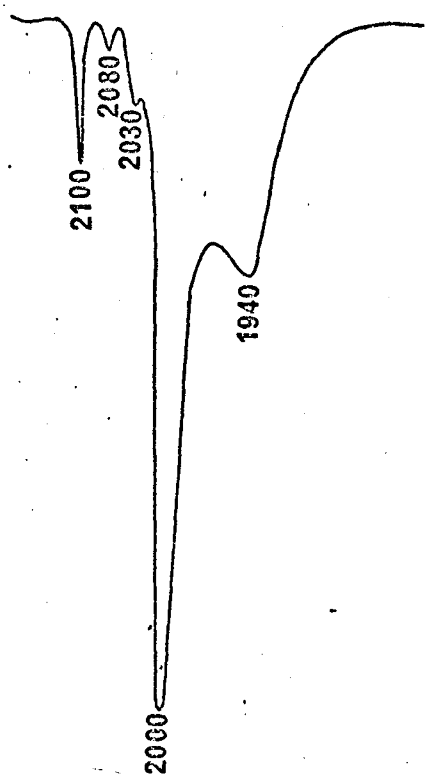


FIGURE 33

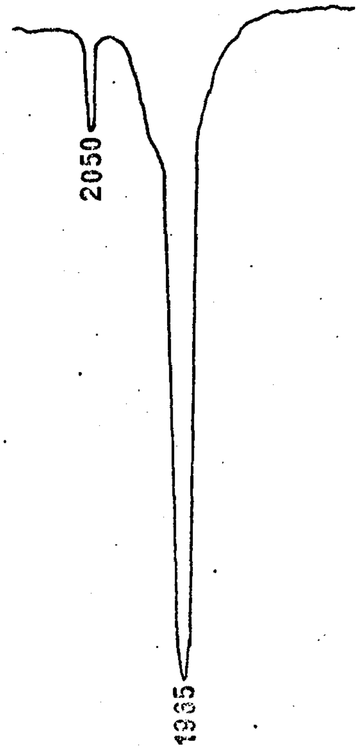


FIGURE 34

The ^{1}H NMR spectrum of XVIII revealed a trace of petrol adhering to the material, but no proton bonded to rhenium could be detected, endorsing the earlier assignment based on infra-red data. The microanalysis was slightly outside the normally acceptable range for organometallic species due to the solvent which could not be removed despite prolonged pumping.

From the experience gained from previous experiments on the substitution reactions with organophosphanes and phosphites the structural assignments of XVIII and XIX were considered quite valid. No other products were isolable from this particular reaction, nor from others employing a 1:4 ratio of carbonyl/ligand. Presumably decomposition takes place after the second substitution to give molecules devoid of CO ligands.

The production of the two characteristic dimeric species was always accompanied by the precipitation of a powder which varied in colour from dull orange to buff. This material did not move on tlc when eluted with mixture 1. The very first reaction carried out between XVII and $Re_2(CO)_{10}$ lead to the separation of a pale yellow powder which gave the solution infra-red spectrum depicted in Figure 35. This was devoid of all organic type carbonyl bands which might have been expected had the product contained only phosphane ligand molecules.

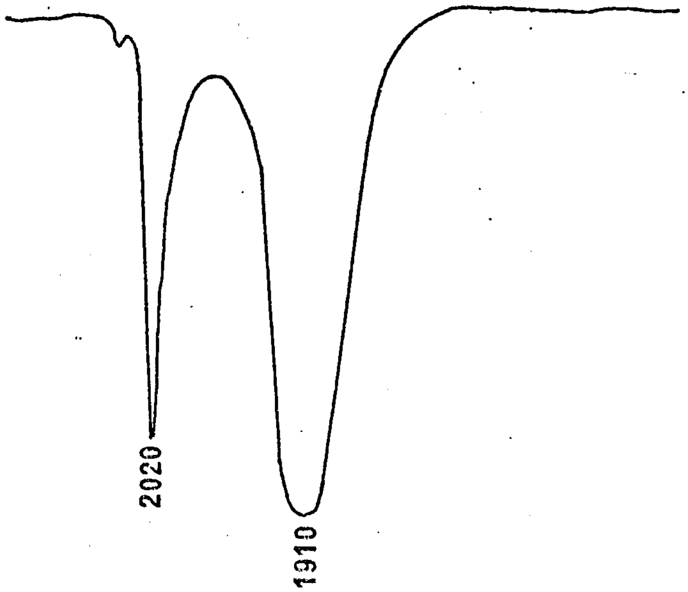
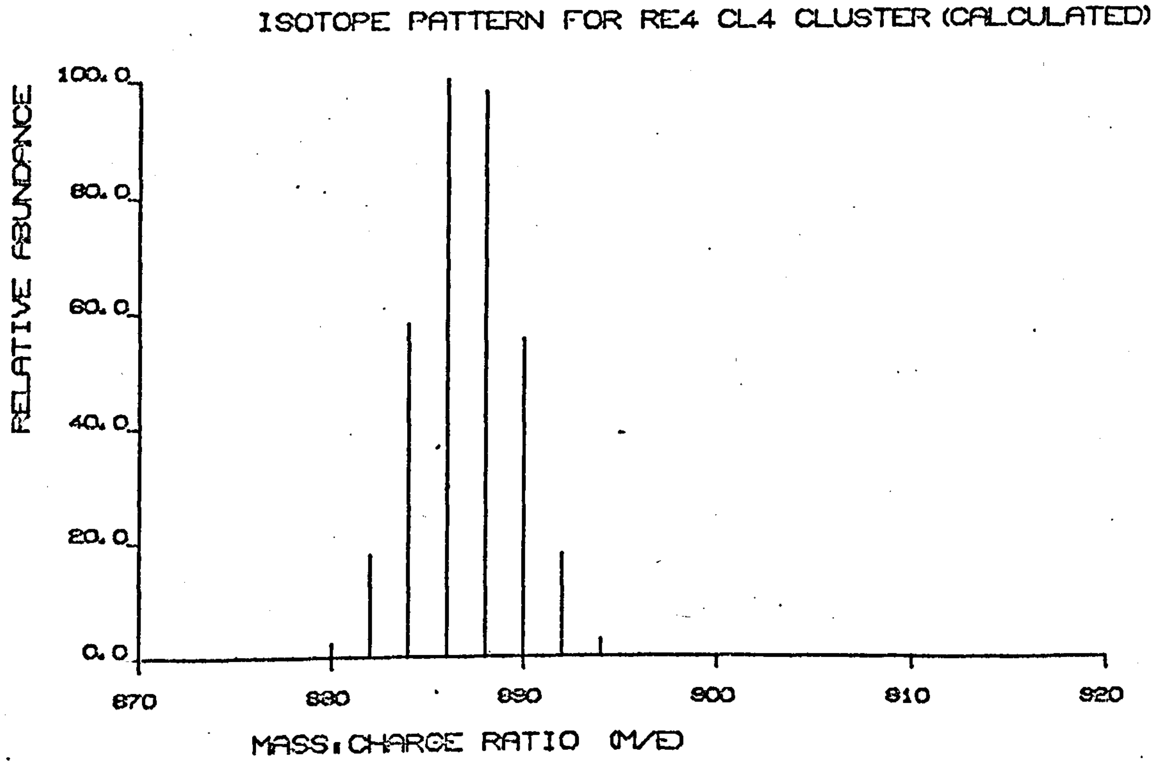
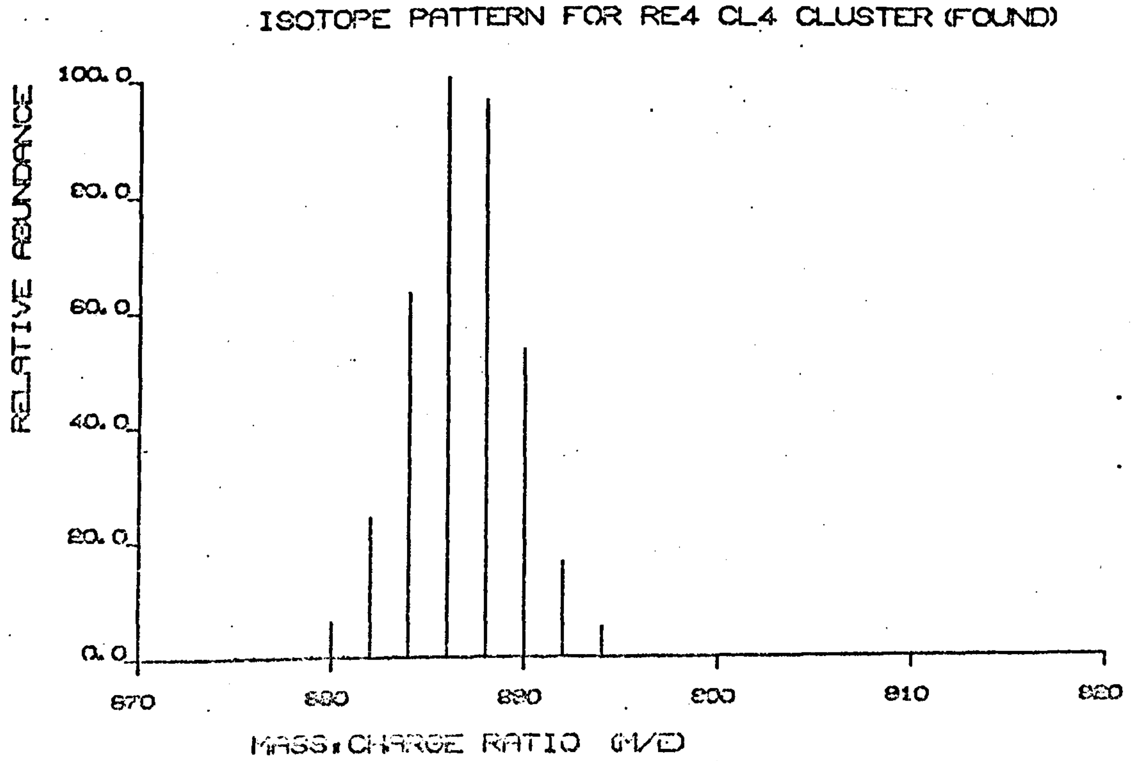


FIGURE 35

The mass spectrum of this material (MS12) suggested the formula $Re_4Cl_4(CO)_{12}$, by comparison with earlier work (246). The isotope pattern for the molecular ion cluster matched that calculated for Re_4Cl_4 (Figure 36) endorsing the structural assignment.





Microanalysis confirmed the presence of chlorine, but because the sample could not be completely freed from the petrol used in the preparation, the results were inconclusive. Nevertheless, the similarity in mass spectra and infra-red spectra seem to strongly indicate the identity of this sample.

The mechanism by which a tetranuclear cluster compound could be formed by such a reaction could not be elucidated, but the presence of chlorine atoms strongly suggest that the sample of XVII was not entirely free from the dichloromaleic anhydride used in its synthesis. This was verified by a reaction of $Re_2(CO)_{10}$ with dichloromaleic anhydride whichyielded a light brown solid whose infra-red spectrum (Figure 37) was extremely similar to that recorded for the product obtained in the previous reaction.

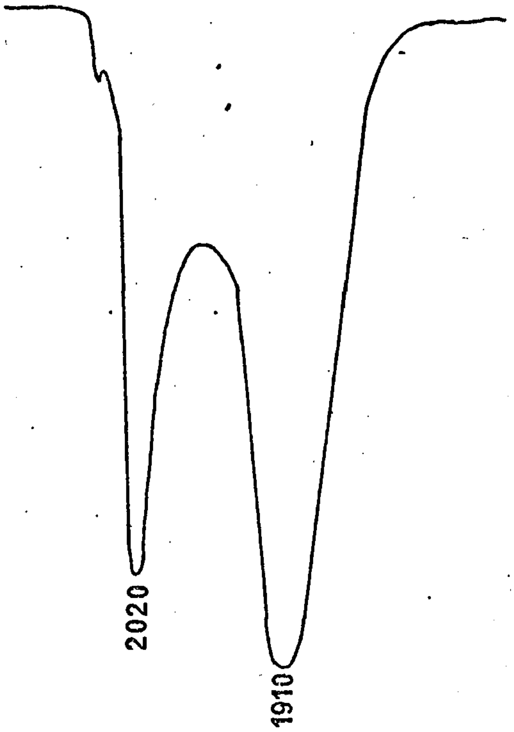


FIGURE 37

This unusual reaction prompted further study, since its presence raised some uncertainties concerning reaction of $Re_2(CO)_{10}$ with XVII.

A reaction of $Re_2(CO)_{10}$ with maleic anhydride was performed in the belief that, by analogy with the dichloromaleic anhydride example, a tetranuclear hydrido cluster would result. Indeed, when this reaction was performed in a 1:5 mole ratio of carbonyl to anhydride in xylene under reflux, an appreciable quantity of a red powder was precipitated. The infra-red spectrum of this (Figure 38) was very similar indeed to that recorded for the other precipitates obtained in this type of experiment, and also to that obtained for the tetranuclear hydroxy compound XII (Figure 15).

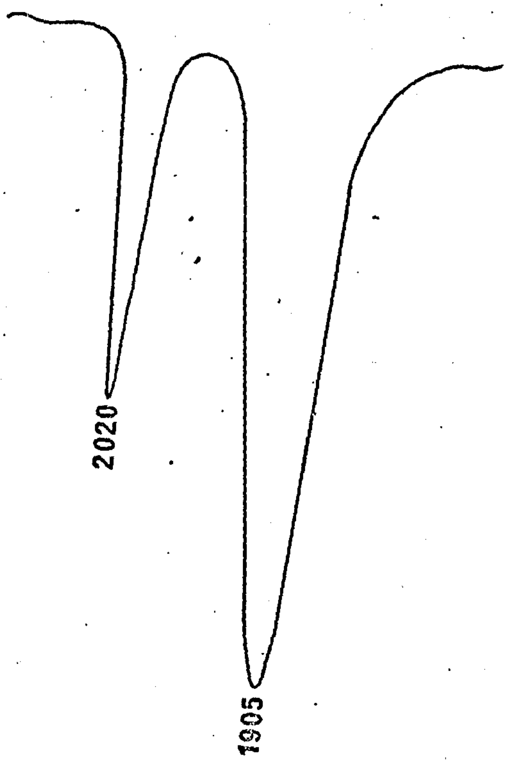


FIGURE 38

No signals were detected in the ^1H NMR spectrum from $10 \rightarrow -20\delta$ and the mass spectrum was inconclusive. It is tentatively proposed that the compound isolated in the reaction with maleic anhydride is a polynuclear hydroxy compound, formed by reaction with traces of free acid in the former. A report has appeared in the literature describing the compound $H_4Re_4(CO)_{12}$ (247) as a dark red powder, but the precipitates in this work did not have the same infra-red spectrum as that quoted for this tetranuclear hydride. The rhenium content was analysed and found to be 67.5%. However, the value required for $H_4Re_4(CO)_{12}$ is 68.6% and for the analogous hydroxy compound 64.68%, so this was not helpful. Products showing identical infra-red spectra to that of the red powder from the maleic anhydride/$Re_2(CO)_{10}$ system were obtained from reactions of the carbonyl with succinic anhydride, succinic acid and siccinimide. An unequivocal structural assignment to these compounds could thus not be made. They have very limited solubility in a range of solvents, and are non-volatile, properties which largely preclude spectral characterisation. Very weak bands in the OH stretching region were seen in the KBr disc spectra of the precipitates, which would seem to partially endorse their assignment as polynuclear hydroxy compounds.

3.1.9 Miscellaneous Reactions

3.1.9.1 The photochemical reaction of $Mn_2(CO)_{10}$ with tri-n-butylphosphane

A communciation by Brown (244) had indicated that if a hexane solution of decacarbonyldimanganese and tri-n-butylphosphane is irradiated by UV light, a green solution is obtained which exhibits an ESR spectrum which disappears with time, but which can be regenerated by further irradiation. When this experiment was repeated in this study, no green colour was observed, but a buff solid began to precipitate. This was isolated by first concentrating the reaction mixture to dryness and then separating the major component by chromatography. The infra-red spectrum exhibited by the major product (Figure 39) was very similar to that reported for mer-trans-$HMn(CO)_3(PMePh)_2$ (240).

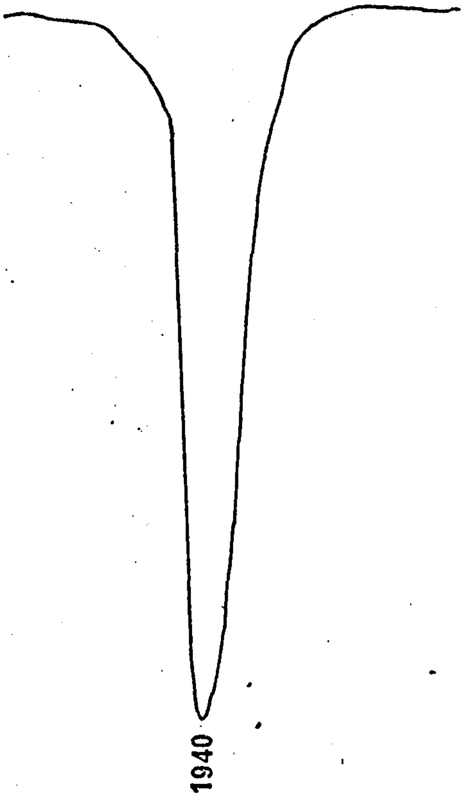


FIGURE 39

A second band was isolated by tlc showed this to be a mixture of the hydrido complex and one other product. The infra-red spectrum of this mixture gave two strong bands in the carbonyl stretching region; one due to the hydride, and the other, at 1950 cm^{-1}, which was assigned to bis-ax-$Mn_2(CO)_8(PBu_3)_2$ by comparison with $Mn_2(CO)_8(PMe_2Ph)_2$ (240).

It was thus concluded that this experiment gave products analogous to the thermal reaction of $Re_2(CO)_{10}$ with PPh_3. These were obtained despite the most careful drying of solvents.

3.1.9.2 Infra-red data on the reactions of $Re_2(CO)_{10}$ with PPh_3 and $P(OPh)_3$

The reactions of $Re_2(CO)_{10}$ and PPh_3 or $P(OPh)_3$ were monitored by the following decline in intensity of the band at 2070 cm^{-1} with time. The reactions were carried out in daylight, using identical conditions and ratio of reagents. It was found that the phosphite (being a poorer σ donor) reacted less rapidly with $Re_2(CO)_{10}$ than PPh_3. This observation may account for the considerable build up of $Re_2(CO)_9L$ found when the decacarbonyl is reacted with bis(diphenylphosphino)maleic anhydride, a molecule is known to be very electron withdrawing.

The graphs of absorbance against time are given in Figure 40 .

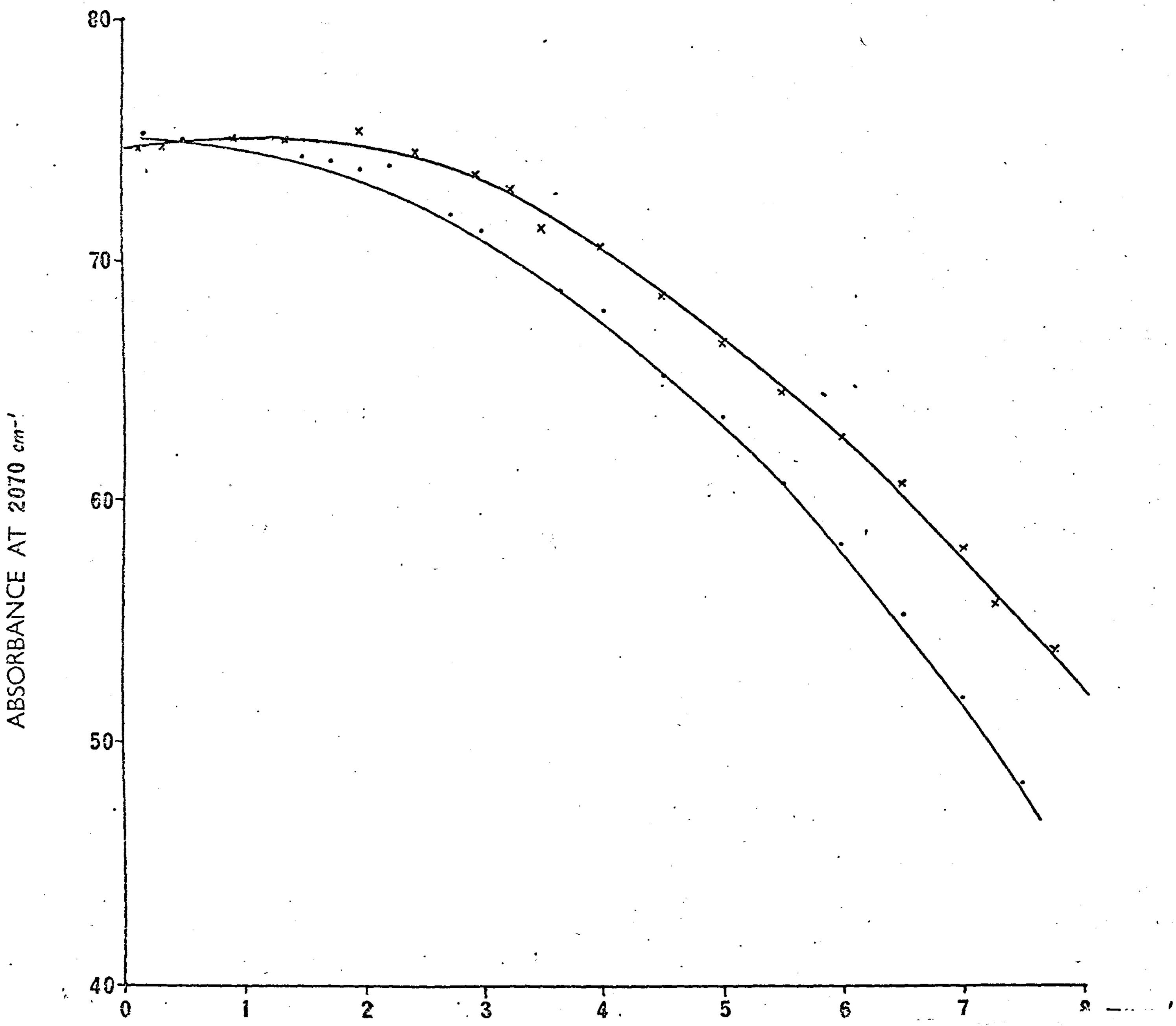


FIGURE 40

3.2 SOME CONCLUSIONS AND COMMENTS

The reactions of decacarbonyldirhenium with various phosphanes and phosphites have generated metalated species whenever transition state geometries which can lead to five membered rings are attainable. Reactions with tri(o-tolyl)phosphane and tri(p-tolyl)phosphane, which possess identical electronic parameters, have shown that this is not a very important consideration in deciding whether a metalation reaction will occur or not. In the reaction with tri(cyclohexyl)phosphane, the products isolated parallel those of the triphenylphosphane reaction. This is because the stereochemistry of the transition state is extremely specific, and hydride formation is more facile.

The over-riding factor which enables certain ligands to undergo metalation reactions is the ability to bring the metalation site close to the metal centre.

3.3 EXPERIMENTAL

The details given in Section 2.4 apply here, in particular the fact that all preparations were carried out under nitrogen. Yields of products are given, but it must be borne in mind that separations by preparative thin layer chromatography are not likely to give reproducible results due to differences in operating conditions. Phosphanes and phosphites were purified by standard techniques as appropriate.

The reaction of $Re_2(CO)_{10}$ with $P(OPh)_3$

$Re_2(CO)_{10}$ (0.66 g, 0.00101 mole) and $P(OPh)_3$ (2.4 ml, 2.842 g, 0.0091 mole) were heated together in xylene (25 ml) under reflux for 17½ hours. After this time, the solvent was removed in vacuo and the oily residue extracted with n-hexane. Concentration of the extracts gave white crystals, 172 mg (15% based on bis-ax-$Re_2(CO)_8[P(OPh)_3]_2$); mp 157-8°, ν C≡O 2030 (w), 1984 (vs) cm^{-1}; found C 43.60, H 2.50, P 5.41; $C_{44}H_{30}O_{14}P_2Re_2$ requires C 43.50, H 2.49, P 5.09%; ^{31}PNMR ($CDCl_3$) - 117.9 ppm (s) (wrt external H_3PO_4) (compatible with the bis-axial assignment).

The hexane insoluble material was separated by preparative thin layer chromatography (using mixture 1) into three components. The first gave a further crop of bis-as-$Re_2(CO)_8[P(OPh)_3]_2$. The second gave a colourless solid, mp 130-1°; ν C≡O 1980 (vs), 1962 (s), 1912 (w) cm^{-1}; found C 49.41, H 3.21, P 5.95, $C_{39}H_{29}O_9P_2Re$ $[Re(CO)_3L(L-H),\ L = P(OPh)_3]$ requires C 52.70, H 3.26, P 6.98%; MS8, M^+ 880, $M^+-n(CO)$ (n = 1-3) showed contamination with some dimer; UV (CH_3CN), λmax 316 nm (ε 14661), 280 (15000), 275 inf (12410). The last band gave a mixture shown mass spectrometrically to be $Re(CO)_3L(L-H)$ and $Re_2(CO)_9L$.

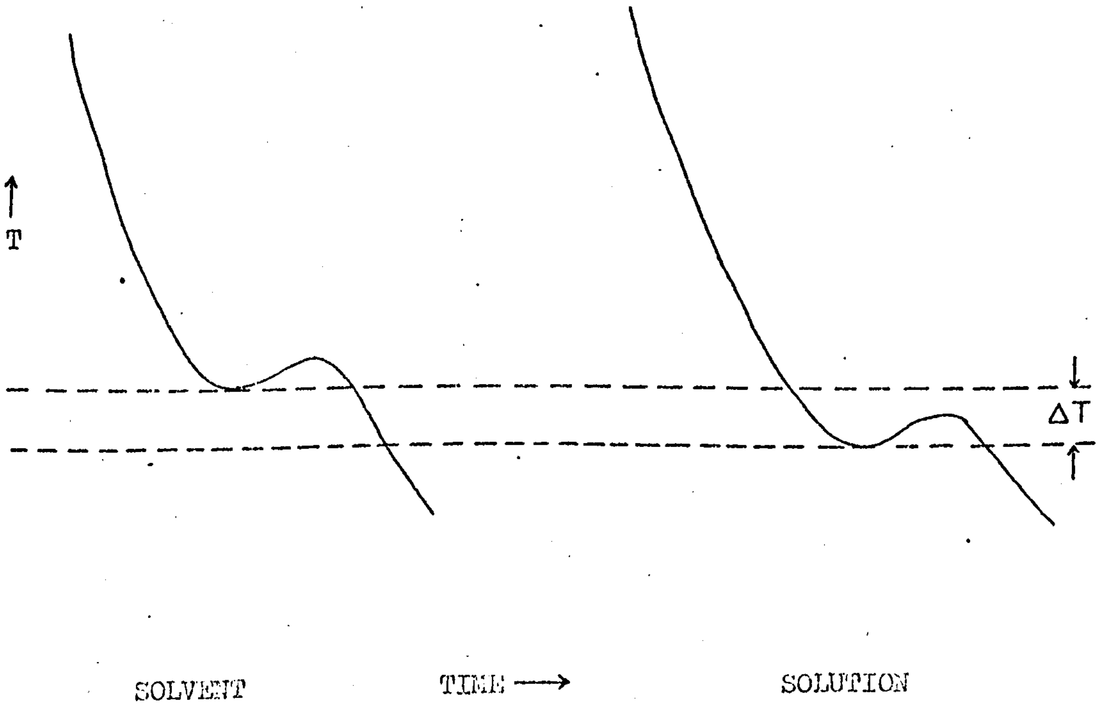
A report has appeared (195) claiming that the bis-axially substituted dimer $Re_2(CO)_8[P(OPh)_3]_2$ dissociates in benzene solution, and the magnetic moment of the monomer has been measured. To verify this, the molecular weight of the dimer in this solvent was measured.

An experiment was designed employing a thermocouple and a servoscribe recorder to enable small depressions of the freezing point of a benzene solution to be measured. The fomula below was used to calculate the molecular weight of the solute:

$$MW = \frac{K \times 1000 \times W_2}{T \times W_1}$$

where W_2 = mass of solute
W_1 = mass of solvent
and T = depression of freezing point observed

The value of the constant K was determined using solutes of known molecular weight and found to be 26.37 for this particular apparatus. The depression of freezing point was read directly from the servoscribe print out:



Using this system, employing an IMS/"drikold" slush bath as coolant, a molecular weight of 1364 in solution was found for $Re_2(CO)_8[P(OPh)_3]_2$ against the calculated value of 1214 thereby confirming its dimeric nature. However, this technique was not widely use in this study, primarily because appreciable amounts of solute were needed to ensure a meaningful depression of freezing point.

The reaction between $Re_2(CO)_{10}$ and tri(o-tolyl)phosphite

A mixture of $Re_2(CO)_{10}$ (0.33 g, 5.07×10^{-4} mole) and tri(o-tolyl) phosphite (1.61 g, 0.0046 mole) was heated in xylene (15 ml) under reflux for 16 hours. After this time the solvent was removed in vacuo to give a solid in an oily residue of unreacted phosphite. The infra-red spectrum of this mixture gave one very strong band in the region associated with the bis axially substituted dimers. The residue was separated using preparative thins layer chromatography and the two most intense bands isolated. One of these major components was unreacted phosphite and the other a white solid which gave white needles form hexane, 245 mg (37.8% based on bis-ax-$Re_2(CO)_8L_2$); mp 197-9°; ν C≡O, 2030 (w), 1983 (vs) cm^{-1}; found C 46.82, H 3.26, P 4.80, $C_{50}H_{42}O_{14}P_2Re_2$ requires C 46.22, H 3.23, P 4.77%; UV (CH_3CN) λ_{MAX} 317 nm (ε 14823), 288 (15341), 275 (inf) (13200).

When the reaction was allowed to proceed for 52½ hours a different major product was isolated by preparative thin layer chromatography, as off white crystals, 150 mg (16% based on $Re(CO)_3L(L-H)$) mp 109-11°; ν C≡O, 1982 (s), 1968 (vs), 1915(m) cm^{-1}; found C 57.99, H 4.70, P 6.69, $C_{45}H_{41}O_9P_2Re$ requires C 55.55, 4.21, P 6.37%; MS9, M^+ 972 M^+-n(CO) (n = 1,2;3rd loss not detected, slight contamination by $Re_2(CO)_8L_2$); ^1H NMR ($CDCl_3$) no signals below 0δ (ie no Re-H function); 7.01 (mult, 23H), 2.03 (mult, 18 H).

The reaction of $Re_2(CO)_{10}$ with tri(o-tolyl)phosphane

$Re_2(CO)_{10}$ (0.33 g, 5.07×10^{-4} mole) and tri(o-tolyl)phosphane (1.45 g, 0.0047 mole) were heated together in xylene (15 ml) under reflux for 23½ hours. The solvent was then removed in vacuo to give a crystalline solid. This was taken up in a little chloroform and separated by preparative thin layer chromatography using mixture 1 as eluent. The major band was isolated (faint traces of two others were seen but were not further investigated) to give white crystals 125 mg (41% based on $Re(CO)_4(L-H)$); mp 174-5°; ν C≡O, 2080 (s), 1975 (vs), 1925 (s) cm^{-1}; found C 50.14, H 3.38, P 5.48, $C_{25}H_{19}O_4PRe$ requires C 50.00, H 3.33, P 5.16%; MS10, M^+ 600, M^+-nCO (n = 1-4); ^1H NMR ($CDCl_3$) 7.10 (mult, 12H), 2.42 (mult, 8H). A similar product was obtained in a 1:1 ratio reaction, or in reactions performed in light or darkness, in yields of the same order.

The reaction of $Re_2(CO)_{10}$ with tri(p-tolyl)phosphane

A solution of $Re_2(CO)_{10}$ (0.33 g, 5.07×10^{-4} mole) and tri(p-tolyl)phosphane (1.45 g, 0.0047 mole) in xylene (15 ml) was heated under reflux for 16 hours. After this time, the xylene was removed in vacuo and the residue taken up in hot benzene. Addition of n-hexane and cooling induced the precipitation of a cream coloured powder which was thought to be a mixture of $HRe(CO)_3L_2$ and $Re_2(CO)_8L_2$ by comparison of its infra-red spectrum with that recorded for the mixed precipitates often obtained in the $Re_2(CO)_{10}$ /PPh_3 reaction. The two components were separated using preparative thin layer chromatography (with mixture 1 as eluent). One band gave a product whose infra-red spectrum (ν C≡O, 1935 (s, br) cm^{-1}) was identical in position and shape to that recorded for mer-trans-$HRe(CO)_3(PPh_3)$ MS7, M^+ 878, M^+-nCO (n = 1-3).

The other band gave an infra-red spectrum consisting of one very strong band at 1958 cm^{-1} and one weaker one at 2000 cm^{-1} which suggested that this product was the bis axially substituted dimer. Peaks in the mass spectrum of this compound centred around m/e 1161 were seen (calculated value for $Re_2(CO)_8L_2$ 1202) but excessive baseline noise made accurate counting impossible. Nevertheless, the strong resemblance of its infra-red spectrum to others shown positively to be dimers, and the isolation of mer-trans-$HRe(CO)_3L_2$, suggests that the assignment made is valid.

The reaction of $Re_2(CO)_{10}$ with tri(cyclohexyl)phosphane

A mixture of $Re_2(CO)_{10}$ (0.33 g, 5.07×10^{-4} mole) and tri(cyclohexyl)phosphane (0.987 g, 0.0035 mole) in xylene (15 ml) was heated under reflux for 20 hours. The solvent was then removed in vacuo and the residue taken up in xylene and precipitation induced with methylated spirits. This was repeated several times to give white crystals, 80 mg (14% based on bis-ax-$Re_2(CO)_8L_2$) mp 248°d; ν C≡O, 1997 (vw), 1951 (vs) cm^{-1}; found C 44.34, H 5.52, P 5.10, $C_{44}H_{66}O_8P_2Re_2$ requires C 45.68, H 5.71, P 5.35%. UV (CH_3CN) λ_{INF} 295 nm (ε 3976), 247 (inf) (9764).

When the reaction was run for 24 hours, a new band (at 1933 cm^{-1}) had appeared in the infra-red spectrum of the reaction mixture. This corresponded to the development of a new spot on the tlc plate of the reaction, and this was isolated by preparative thin layer chromatography to give cream crystals, ν C≡O 1933 (s, br) cm^{-1} MS6, M^+ 830, M^+-nCO (n=1-3), ($HRe(CO)_3[P(C_6H_{11})_3]_2$).

The reaction of $Re_2(CO)_{10}$ with tri(p-chlorophenyl)phosphite

$Re_2(CO)_{10}$ (0.33 g, 5.07×10^{-4} mole) was treated with tri(p-chlorophenyl)phosphite (1.86 g 0.0044 mole) in xylene (15 ml) and the solution heated under reflux for 16 hours. Tlc showed (and infra-red spectroscopy confirmed) that very little decacarbonyl remained after this time. One major spot was visible on the plates and this was isolated in the usual manner, to give white crystals, 110 mg (16% based on bis-ax-$Re_2(CO)_8L_2$) mp 150°; ν C≡O, 2060 (w), 1968 (vs) cm^{-1}; found C 40.71, H 1.94, Cl 14.41, P 4.29, $C_{44}H_{24}Cl_6O_{14}P_2Re_2$ requires C 37.12, H 1.68, Cl 14.94, P 4.49%. The UV spectrum had an identical profile to those recorded for the other dimers, although extinction coefficients are not available.

The preparation of bis(diphenylphosphino)maleic anhydride (XVII)

All manipulations were performed under nitrogen.

The maleic anhydride derivative was prepared according to the literature report (245). Thus diphenylchlorophosphane (13 g, 0.0843 mole) in freshly distilled di-n-butyl ether (freed of peroxides by the standard procedure (248)) was treated with sodium wire (5 g; 0,22 g atom) and heated under reflux with stirring for 4 hours. After this time the reaction mixture had attained an intense yellow colour due to the precipitated salt $Na^+PPh_2^-$. It was allowed to cool to room temperature and then treated with trimethylchlorosilane (9.15 g; 0.084 mole) and warmed gently for 1½ hours. The yellow colour discharged quite rapidly, to give a clear supernatant over the precipitate of NaCl. This, and unreacted sodium, was removed by filtration. The filtrate was then treated with dichloromaleic anhydride in di-n-butyl ether and on cooling, a yellow powder precipitated. This was collected by filtration, and appeared air stable. The crude product was crystallised from 80-100 petrol to give golden yellow needles, 2.64 g (13.4%) mp 147-8°; infra-red spectrum has been given previously (Figure 31); UV (CH_3CN)λ_{MAX} 372 nm (ε1311.9), 260 (inf) (9037.9); M^+ 466; ^{1}H NMR ($CDCl_3$) 7.32 (mult) found C 72.73, H 4.49, P 12.99, $C_{28}H_{20}O_3P_2$ requires C 72.10, H 4.29, P 13.30%

The reaction of $Re_2(CO)_{10}$ with bis(diphenylphosphino) maleic anhydride, XVII

A xylene solution of $Re_2(CO)_{10}$ (0.33 g, 5.07×10^{-4} mole) and XVII (0.23 g, 4.93×10^{-4} mole) was heated under reflux for 2½ hours. Examination of the tlc plate of the reaction mixture showed only two products (Figure 30). The slower moving of these two was isolated by chromatography on a silica column (23 x 2.5 cm) using mixture 1 as eluent. A red solid was isolated which had very similar bands in the carbonyl region to those recorded for the ax-$Re_2(CO)_9PPh_3$ complex (Figure 12); the infrared spectrum has been shown previously (Figure 33). The faster running orange band was collected and yielded a very small quantity of orange solid, ν C≡O 2050 (vw), 1965 (vs) cm^{-1} suggesting the bis-axially substituted octacarbonyl derivative; found C 49.94, H 3.05, $C_{64}H_{40}O_{14}P_4Re_2$ requires C 50.32, H 2.62%.

Precipitation of a yellow powder (mp 90-1°) also occured if reactions were run for longer periods with the view to increasing the yields of the characterised products. No organic type carbonyl bands were seen in the infra-red spectra of these precipitates (ν C≡O, ($CHCl_3$) 2020 (m), 1910 (m, br) cm^{-1}; MS 12 M^+ 1216 M^+-12 CO). These data appeared very similar to those for an authentic sample of $Re_4(CO)_{12}Cl_4$. Microanalysis endorsed this conclusion, and confirmed the presence of chlorine. However, as the sample was isolated as a petrol solvate a particular formula could not be deduced from the microanalytical figures.

The reaction of $Re_2(CO)_{10}$ with maleic anhydride

A solution of $Re_2(CO)_{10}$ (0.33 g, 5.07×10^{-4} mole) and maleic anhydride (0.25 g, 0.0025 mole) in xylene (15 ml) was heated under reflux for 2 hours. After this time a copious red-brown precipitate had appeared. Heating was continued for a further 4 hours, and then the reaction was halted. The precipitate was collected by filtration and dried *in vacuo* to give a red powder 140 mg; ν C≡O (Me_2CO) 2015 (m), 1900 (vs, br) cm^{-1}. Similar products were obtained with succinic anhydride or succinimide.

4 CONCLUSIONS

The reaction between decacarbonyl dirhenium and triphenylphosphane appears to follow a similar course to that of the manganese system in that free radicals are implicated in the Reaction Scheme but cannot be isolated. The compounds $Re(CO)_3(PPh_3)_2$ and $Re_2(CO)_6(PPh_3)_4$ could not be prepared by the literature methods (112, 215) and it is believed that the form of "$Re(CO)_3(PPh_3)_2$" reported by Nyman (113) was incorrectly assigned. When Nyman's experiment was repeated, the main product isolated exhibited the same infra-red spectrum, but was shown by mass spectrometry and ^1H NMR spectroscopy to be the corresponding hydrido complex.

Traces of water in the reaction medium have been shown to be responsible for the formation of the compounds, and this has been endorsed by experiments in which D_2O was added to the xylene solvent prior to reflux.

Experiments with other tertiary phosphanes and phosphites have yielded results which fit into the rationalisation proposed for the reaction of $Re_2(CO)_{10}$ with PPh_3. The most significant of these is the exclusive production of metalated species. These are generated whenever a favoured five membered ring, including the central metal atom, can be formed. Phosphanes which may potentially possess such features may nevertheless give hydrido species, since the required transition state stereochemistry for metalation is a high energy state, and only one of a number of favourable orientations available to the ligand. This has been demonstrated in reactions using tri-(cyclohexyl)phosphane.

A reaction of decacarbonyldirhenium with bis(diphenylphosphino) maleic anhydride produced an unexpected polynuclear complex, a reaction which could be repeated as easily using maleic anhydride itself. Despite some considerable effort, the mechanism by which these complexes are formed could not be elucidated.

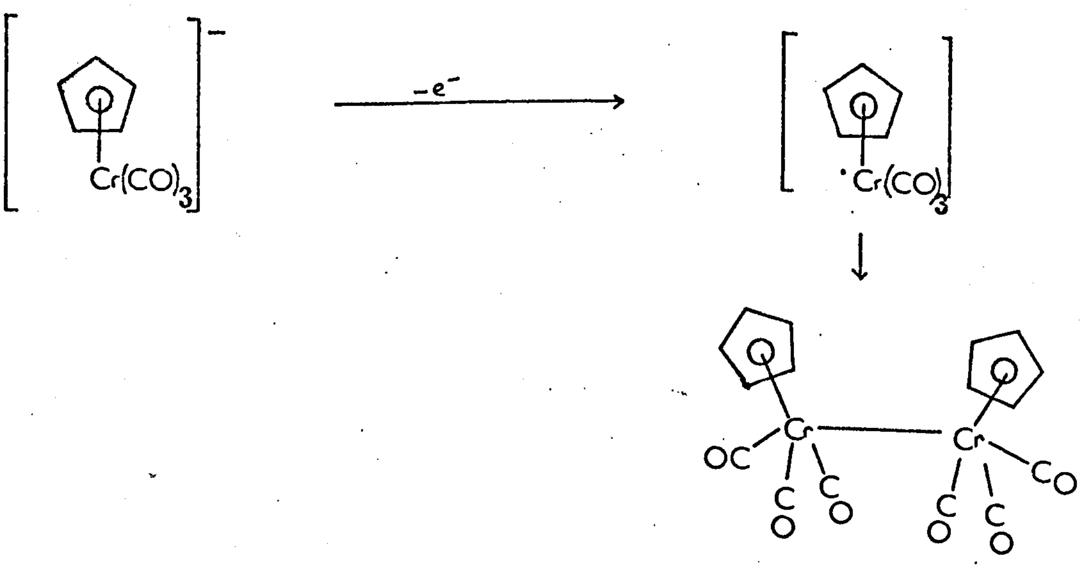
The radical $Re(CO)_5^{\bullet}$ has been generated by the chemical oxidation of the pentacarbonylrhenium anion, but it was not isolable. Its existance was demonstrated by the nature of the reaction products, which parallel those of this radical when produced by photolytically induced homolytic fission of $Re_2(CO)_{10}$.

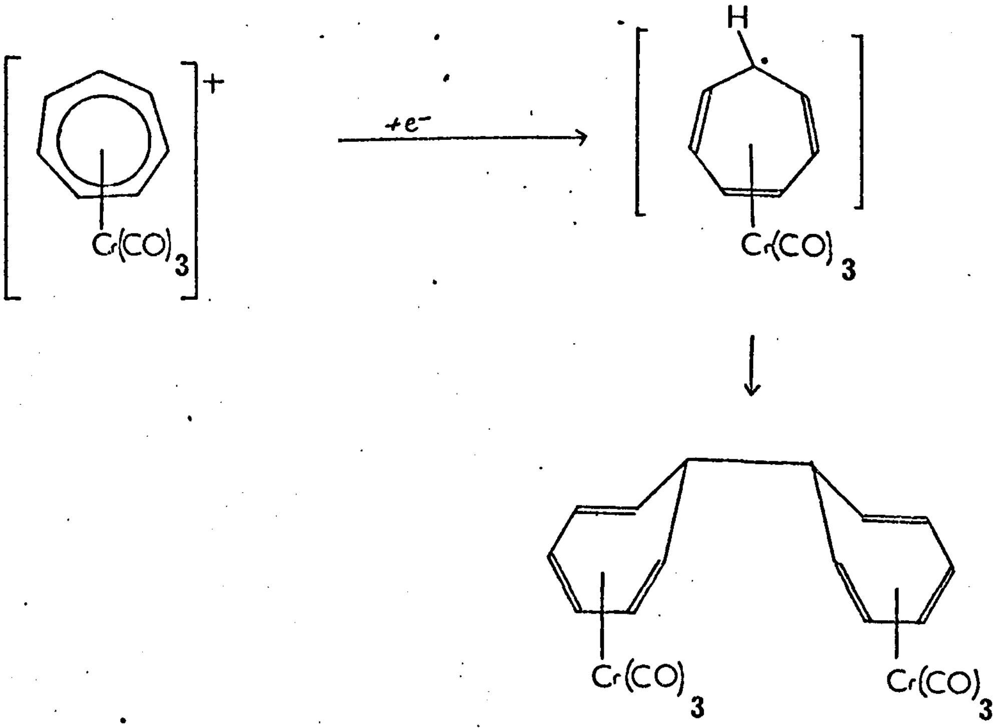
CHAPTER 3

STUDIES ON THE CHEMICAL REDUCTION AND OXIDATION OF SOME CYCLO-OLEFIN METAL CARBONYL COMPLEXES

1. INTRODUCTION

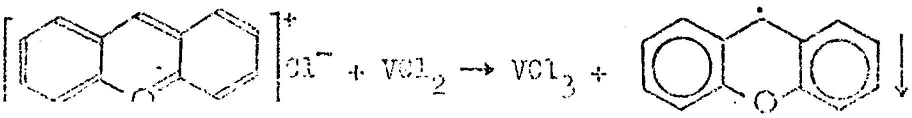
The oxidation and reduction of organometallic anions and cations are two potential methods of generating odd-electron species and it was for this reason that these reactions were investigated. If the reasonable assumption is made that most of the substrates comply with the inert gas formalism, then oxidation will generate a seventeen electron molecule, and reduction one containing nineteen valence electrons. If the dimerisation of the radicals produced is a facile reaction, then the structure of the product will reflect the site of maximum unpaired electron density in the monomer. Thus, in the reduction of $(\eta^7-C_7H_7)Cr(CO)_3{}^+$ by zinc dust (165) a ligand bridged dimer is obtained, suggesting that the lowest unoccupied molecular orbital, (LUMO), of the cation is essentially ligand based. On the other hand, the oxidation of $(\eta^5-C_5H_5)Cr(CO)_3{}^-$ (100) leads to a dimeric species containing a metal-metal bond, resulting from the fact that the highest occupied molecular orbital (HOMO), of the anion is largely metallic in character. These reactions are illustrated below:





This introduction is concerned primarily with those reactions of organometallic cations and anions that generate radical species which then achieve stability by dimerisation (thereby adhering to the definition of "radical" quoted in Chapter 1). However, a brief coverage of the reduction of organic cations is presented first.

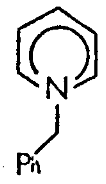
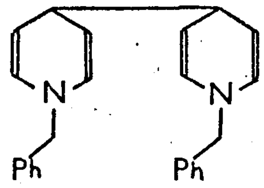
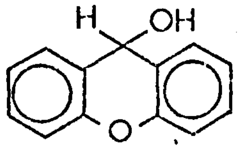
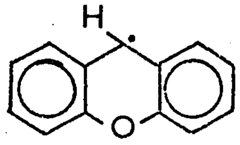
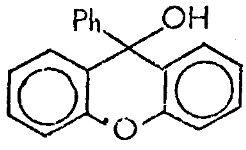
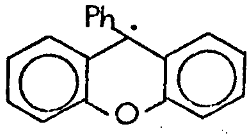
The first report of a reduction of a cation to a radical is by Conant and co-workers (249) who effected this type of reaction between I and cold vanadium (II) chloride solution:



The solid precipitate could be isolated and was found to be stable in air for a number of hours. When it was dissolved in chloroform, however, the colour discharged rapidly and bixanthyl was recovered. These workers found that under strictly anaerobic conditions a maximum of one mole equivalent of vanadium (II) ions was needed to effect the reduction. Further work from this group (250) resulted in similar findings (Table 18); dimeric species being isolated if their radical precursors were too reactive to exist as discrete entities.

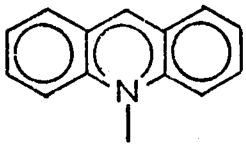
TABLE 18 (250)

Reduction of organic cations

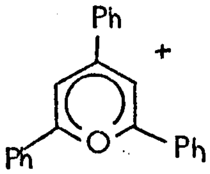
Substrate	Reductant	Product
	VCl_2	
	VCl_2	
	VCl_2	

This subject has been the topic of a more recent study by Bowie and Feldman (251). It has been reported that in aqueous solution, tropylium cation is reduced quantitatively to ditropyl by chromium (II) ion (252), and Okamoto and co-workers have studied this reaction in detail (253). This latter group employed aqueous hydrochloric acid as solvent, and demonstrated that chloride ion acts as a bridging unit in the electron transfer, and that the rate of reduction by chromous ion increases towards a maximum with increasing chloride ion concentration. They also concluded that in the absence of a bridging anion, a water molecule in the co-ordination sphere of the chromium ion acts as the agency for the electron transfer (254).

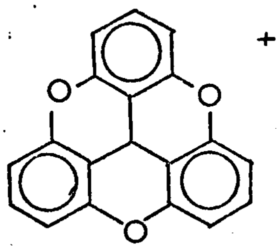
The kinetics of the reduction of a number of organic cations (II-VII) by chromium (II) have been investigated (251)



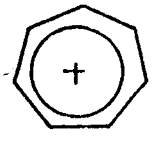
II



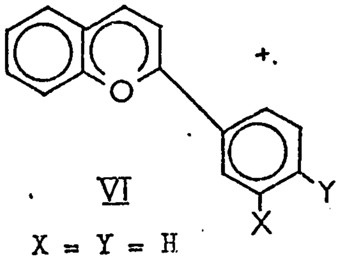
III



IV



V

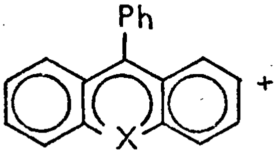


VI

$X = Y = H$

$X = H \quad Y = OCH_3$

$X = OCH_3 \quad Y = H$



VII

$X = O$

$X = S$

When aqueous acidic solutions of these cations were treated with chromium (II) chloride, the expected dimeric species were obtained in very high yields. The stoichiometry of the reaction was determined by allowing an excess of chromium (II) to react with the salt and titrating the surplus chromium ions. It was again found that one mole of each organic cation is fully reduced by one mole of chromium (II) ion.

The simplest scheme which accounts for the formation of free radicals and dimeric products is the electron transfer reaction. (eqn 1) and the radical association (eqn 2):

$$R^+ + Cr^{2+} \rightleftharpoons R^{\cdot} + Cr^{3+} \qquad 1$$

$$2R^{\cdot} \rightleftharpoons R_2 \qquad 2$$

However, an alternative mechanism has been suggested by Kochi and Davis (255) who studied the chromium (II) reduction of benzyl halides, and found that in aprotic media the only reaction product was dibenzyl. The reaction intermediate, detected spectroscopically, was found to be the organochromium ion $(PhCH_2)Cr^{2+}$ (λ max 360 mμ, (255)) which has been reported elsewhere (256). In the reactions described by Bowie and Feldman, dimers could thus arise by a similar mechanism:

$$\begin{array}{llll} R^+ + Cr^{2+} & \longrightarrow & R^\bullet + Cr^{3+} & \text{slow} \\ R^\bullet + Cr^{2+} & \longrightarrow & RCr^{2+} & \text{fast} \\ RCr^{2+} + R^+ & \longrightarrow & RR + Cr^{3+} & \text{fast} \end{array}$$

This route was considered inadmissable, however, since in protic solvents the organochromium ion is reported to react to give hydrido species (255):

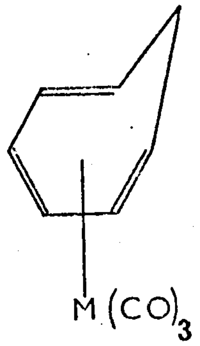
$$RCr^{2+} + H^+ \longrightarrow RH + Cr^{3+} \qquad \text{fast}$$

and as Bowie and Feldman found no hydrides in their experiments, the mechanism outlined in equations 1 and 2 was favourd.

The reaction between cyclohepta-1,3,5-triene and chromium or molybdenum hexacarbonyl was first reported in 1958 (257), when it was noted that the hydrocarbon ligand remains intact:

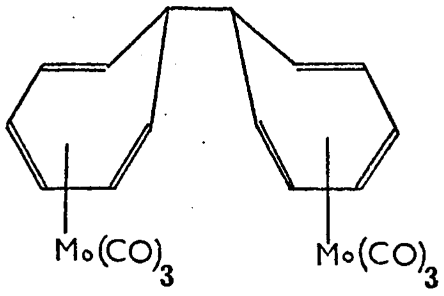
$$C_7H_8 + M(CO)_6 \xrightarrow{\Delta R} (\eta^6\text{-}C_7H_8)M(CO)_3 + 3CO$$

VIII



VIII

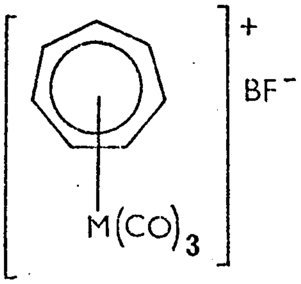
A reaction between dicycloheptatriene and molybdenum hexacarbonyl for a limited time formed the monomolybdenum tricarbonyl complex in which a metallic residue was attached to one ring only. A longer reaction time produced the complex IX with two metal carbonyl residues:



IX

In this early paper, attempts to prepare compounds with the tropylium cation bound to the metal atom proved abortive.

The first successful synthesis of $(\eta^7\text{-}C_7H_7)Mo(CO)_3{}^+$ was reported by Dauben and Honnen in 1958 (258). Their preparation employed a general synthetic route to tropylium ions (259) involving hydride ion abstraction by triphenylmethyl carbonium ions. Thus, equivalent quantities of VIII and triphenylmethyl fluoroborate in methylene chloride reacted immediately to give a crystalline precipitate of $(\eta^7\text{-}C_7H_7)Mo(CO)_3{}^+BF_4{}^-$, X, M = Mo



X

Some aspects of the chemistry of these particular types of cationic complexes have been pursued further by Pauson and Munro (165). These workers studied the interactions of the cation with nucleophiles, reactions which may be expected to belong to either one of the following types:

Mode 1: $(\eta^7\text{-}C_7H_7)Cr(CO)_3{}^+ + X^- \longrightarrow (\eta^6\text{-}C_7H_7X)Cr(CO)_3$

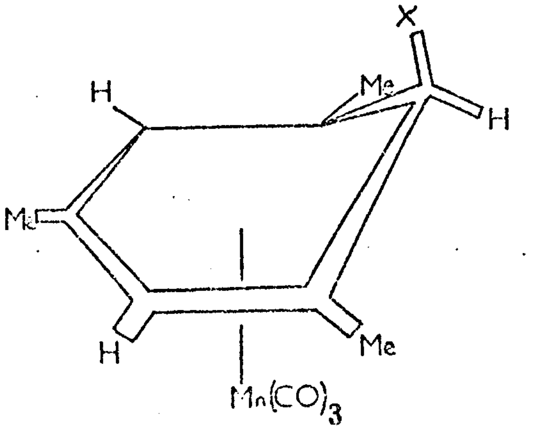
Mode 2: $(\eta^7\text{-}C_7H_7)Cr(CO)_3{}^+ + X^- \longrightarrow (\eta^7\text{-}C_7H_7)Cr(CO)_2X + CO$

Mode 1 assumes that the positive charge resides largely on the seven membered ring and that anions add to this as they do free tropylium ions. This is not an unreasonable suggestion, since an electron count shows that the ring must be a six electron donor if the metal is to remain in the zero oxidation state (d^6). This was the mode of reaction most frequently encountered by Pauson and Munro (165), using a wide range of nucleophiles such as SH^-; $^-CMe(CO_2Et)_2$; Bu^{t-}; $^-C\equiv CPh$; ^-OMe; $^-CH(CO_2Et)_2$ (165, 260).

The related complexes, $(\eta^7\text{-}C_7H_7)M(CO)_3{}^+$ (M = Mo, W) react with halide and pseudohalide ions to give products of the type $(\eta^7\text{-}C_7H_7)M(CO)_2X$ (M = Mo, X = NCO, NCS, N_3; M = W, X = Cl, Br, NCO, N_3) (263). A reaction initially believed to proceed by mode 2 is the interaction of cyanide ion with $(\eta^6\text{-}C_6H_6)Mn(CO)_3{}^+$(261);

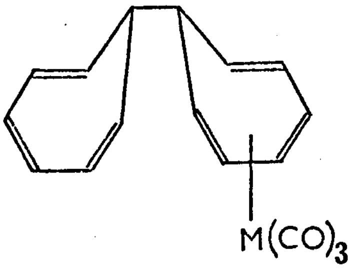
$$(\eta^6\text{-}C_6H_6)Mn(CO)_3{}^+ + CN^- \longrightarrow (\eta^6\text{-}C_6H_6)Mn(CO)_2CN + CO$$

Subsequent re-examination, however, has revealed that the reaction proceeds in two stages, viz ring addition in the usual exo-position, followed by facile rearrangement (262). The intermediate XI has been isolated, mesitylene being substituted for benzene to facilitate study of these molecules by ^1H NMR spectroscopy. This molecule may then be converted to the bis-carbonyl complex by heating in solution (262).

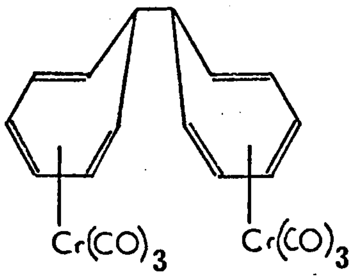


XI

Besides establishing that tropylium metal carbonyl cations may react in the expected way with nucleophiles, Munro and Pauson (165) also observed unusual products in the reactions of the cation with cyanide ion. Although the expected ring bonded cyano derivative was isolated in low yield, the two main products had compositions corresponding to the mono- and the bis-tricarbonylchromium derivatives of bi(cycloheptatriene), (XII, M = Cr, and XIII):



XII



XIII

The structure of the latter was confirmed by its formation upon reduction of the cation by zinc metal. To test whether the alkalinity of the cyanide solutions accounted for the formation of the dimeric products, the salt was treated with sodium hydrogen carbonate. In this case, XII (M = Cr) and XIII were again obtained, and subsequent investigations revealed that dimeric products could be isolated by reacting the cation X (M = Cr) with a variety of reagents. These experiements are summarised in Table 19.

TABLE 19 (165)

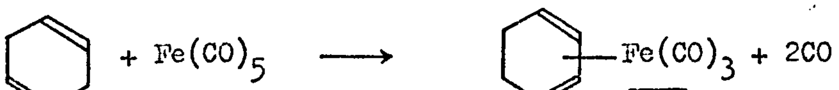
Reagent	Solvent	Reaction time/h*	XII, M=Cr	XIII
$NaHCO_3$(XS)	H_2O	0.25	21%	41%
NaOAc (1≡)	MeOH	1 (reflux)	29%	41%
$NaNH_2$ (2≡)	THF	16	10%	54%
PhLi (1.5≡)	Et_2O	16	12%	33%
$PhCONH_2$ (1≡)	H_2O	6(80°)	23%	45%
HCl (Xs; 2N)	H_2O	1 (reflux)	15%	49%

* at ambient temperature unless stated otherwise.

No mechanism was proposed for these reactions, but some type of electron transfer route was envisaged. Similar reductive couplings have been reported elsewhere (263); thus the reaction of $(\eta^7\text{-}C_7H_7)W(CO)_3{}^+$

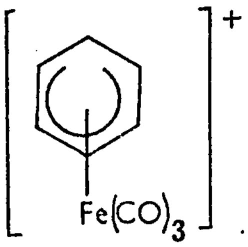
with KOCN gave not only the monomeric $(\eta^7\text{-}C_7H_7)W(NCO)(CO)_2$, but also the dimeric derivative XII (M = W).

Cyclohexa-1,4-diene reacts with pentacarbonyliron to give tricarbonylcyclohexa-1,3-dieneiron, XIV (264):

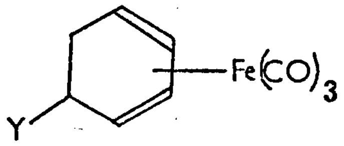


XIV

The dienyl cation, XV, can be prepared by the reaction of the diene complex with triphenylmethyl fluoroborate (265), and gives products of the type XVI with the nucleophiles OMe^- and CN^-.



XV

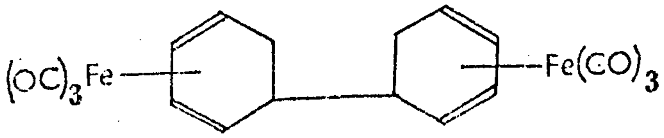


Y= OMe; CN

XVI

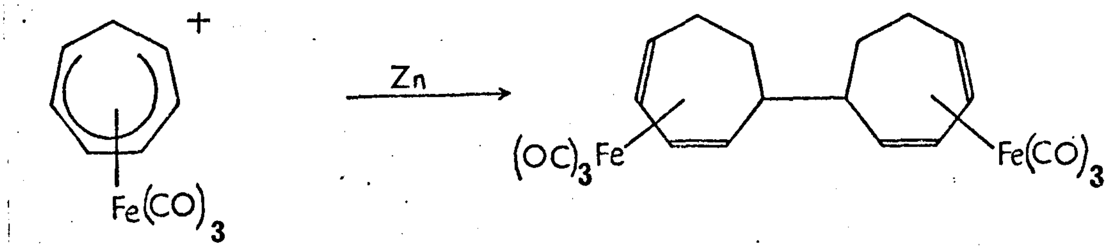
Lewis et al (265) have demonstrated that the cation XV can react with a wide range of other nucleophiles such as water (in the presence of sodium hydrogen carbonate); pyrollidine; methyllithium or acetylacetone, to yield XVI, Y = OH, NC_4H_8, Me or $CHAc_2$.

The reaction with methylmagnesium iodide is of particular interest as far as radical type reactions are involved, since instead of giving XVI, Y = Me, the dimeric complex XVII was obtained:



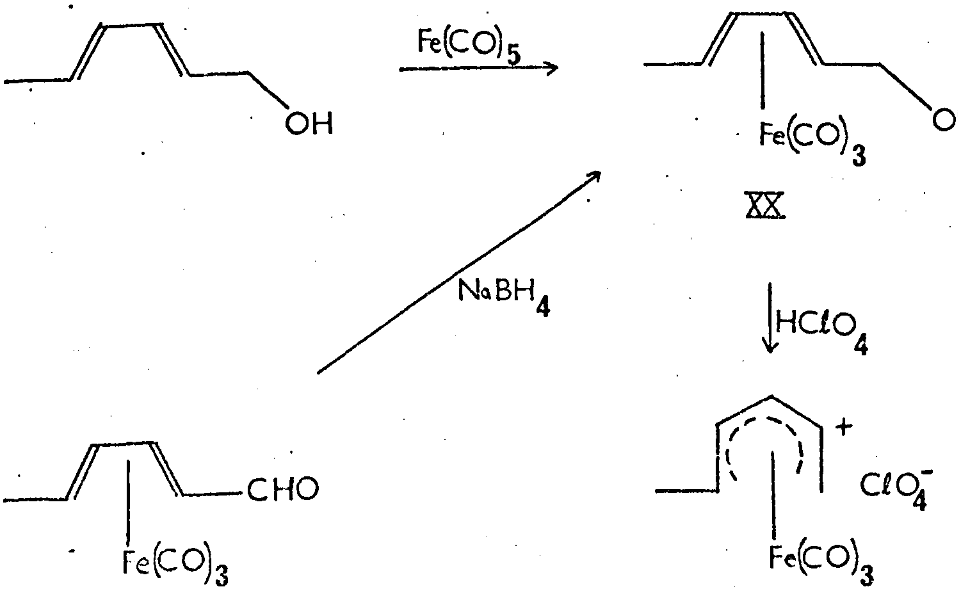
XVII

This is analogous to the cyclcheptadiene complex which has been reported by Pauson (266);



This latter compound has also been prepared by treating the cation with sodium hydroxide (166).

The reduction of syn-1-methylpentadienyl tricarbonyliron cation, XVIII, has been studied (166) and its preparation is outlined below.



XX

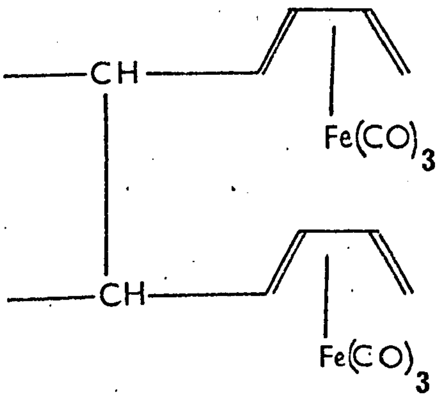
XIX

XVIII

Treatment of the alcohol complex XX with perchloric acid affords syn-η^5-1-methylpentadienyltricarbonyliron perchlorate (XVIII) in quantitative yields. Other salts such as the tetrafluoroborate and hexafluorophosphate are also readily available from the reaction of XX with the appropriate acid.

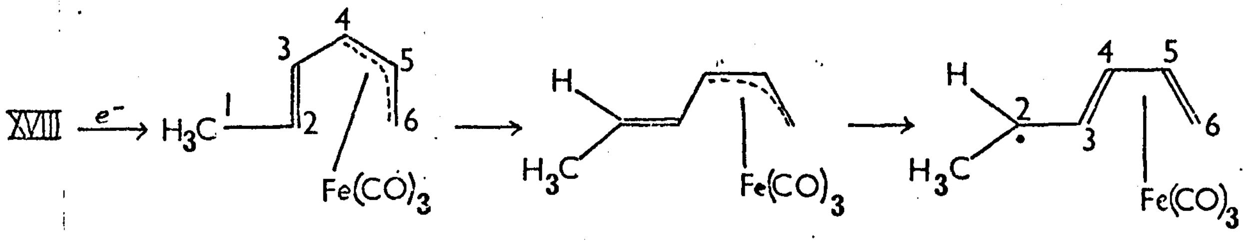
By analogy with the related cyclopentadienyltricarbonyliron cation (166a), the five sp^2 hybridised carbon atoms of the dienyl ligand in XVIII are assigned the completely cissoid configuration shown.

The reduction of this particular cation by zinc metal is a particularly interesting reaction. The crude product is found to contain two isomers in equivalent amounts, and these have been shown to be diastereoisomers of 5,6-dimethyl-1,3,7,9-decatetraenehexacarbonyldiiron:



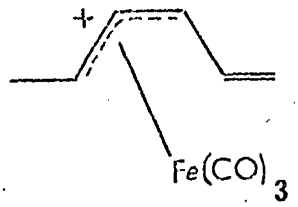
Although a quantitative separation has not been achieved, some 80% of the reaction mixture was accounted for in the terms of the isolated isomers, and the infra-red spectrum of the remaining material suggested that it consisted largely of these two compounds.

The two isomers, A and B, gave identical infra-red and ^1H NMR spectra, but had melting points differing by 20°C, and are presumed to arise through the dimerisation of 1-methylpentadienyliron tricarbonyl free-radicals. The preponderant formation of only two isomers is noteworthy, for literally scores of different compounds could conceivably arise through the random coupling of the various free-radicals which can be written following addition of an electron to the cation XVIII. It would appear that the reaction proceeds almost exclusively through dimerisation of XXIII, which could be reasonably produced in the following manner:

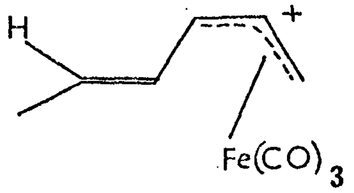


XXI XXII XXIII

In the intermediate XXI, the double bond is not expected to be coordinated to the iron atom, since if it were the inert gas rule would be violated. Free rotation about the 3,4 single bond to giveXXII and hence XXIII is therefore possible. A similar path leading to a structure having the unpaired electron on the terminal methylene carbon would be less likely due to steric consideration. The inductive effect of the methyl group may also be an unfavourable factor in a structure such as XXIV since it would lead to a decrease in bonding via back donation from iron to the allyl system when compared to XXII:

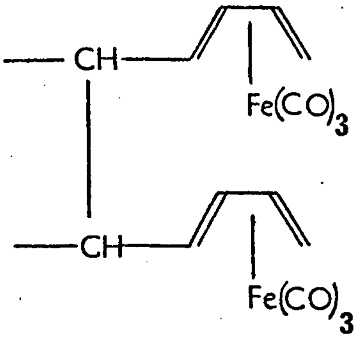


XXIV



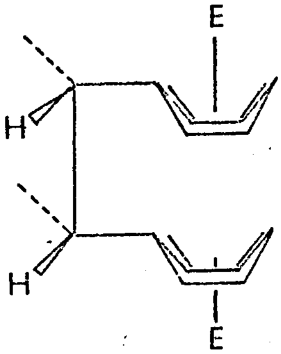
XXII

This mechanism would serve to explain the observed skeletal structures of the two dimeric complexes. However, the radical species XXIII together with its enantiomer, may hypothetically couple to give rise to six different dimeric products of the type XXV, two meso and four racemic:

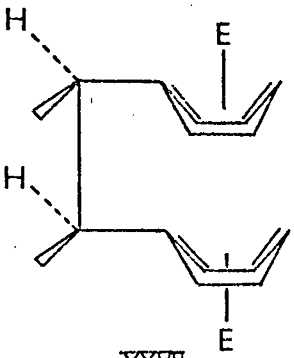


XXV

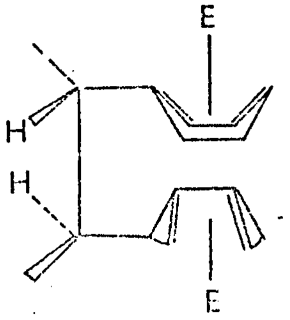
If, however, the reasonable assumption is made that the methyl group and the dieneirontricarbonyl group are fixed trans about the C_2–C_3 bond. in XXIII (and in its enantiomer), and furthermore that the radicals combine with the bulky metallic moieties opposed to each other, then only two dimeric products will be formed. Not only does this then account for the observed number of isomers, but it also allows a prediction to be made as to the stereochemistry of A and B. Thus, the meso structure XXVI will be favoured over XXVII. Similarly the racemate will have structure XXVIII:



XXVI



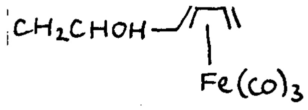
XXVII



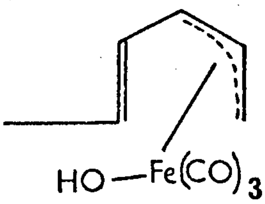
XXVIII

E = Fe(CO)$_3$

A curious reaction ensues upon treatment of the cation XXVIII with potassium hydroxide. When conducted in a MeOH/Me$_2$CO mixture, the reaction yields, as the major organometallic product, the same mixture as produced when XXVIII is treated with zinc dust. Lesser amounts of iron hydroxide and XXIX are formed.



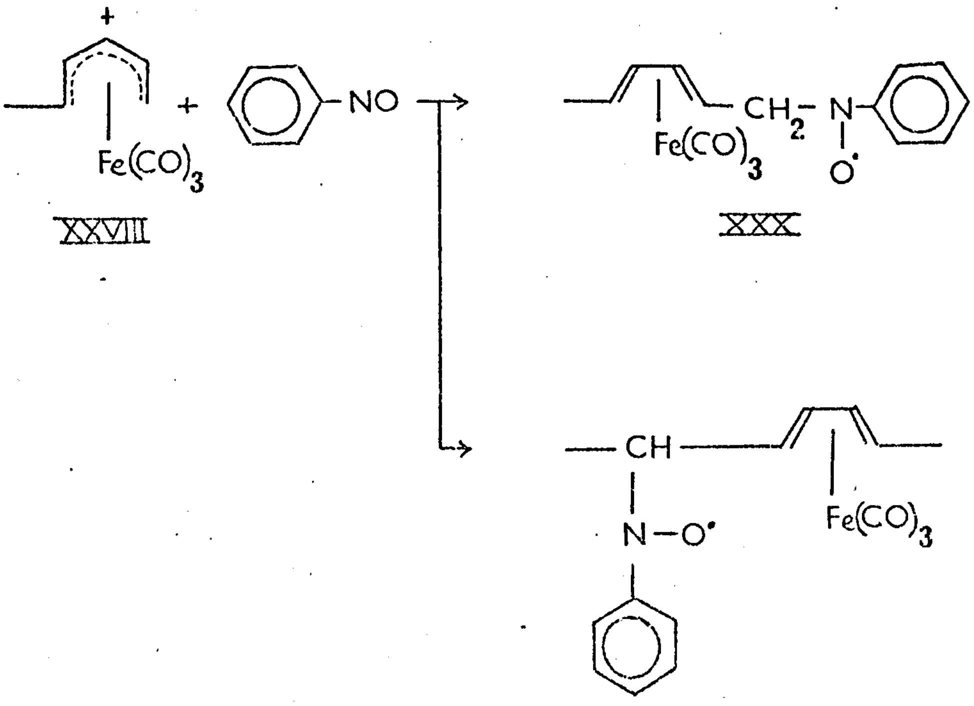
XXIX



XXIXa

The dimeric material accounts for 30% of the cation employed, but when the reaction is conducted in water, the alcohol XXIX is the only product the dimers being present only in traces. One reasonable explanation for the formation of these dimeric complexes would involve attack of hydroxide ion at the iron atom of XXVIII thereby producing the neutral species XXIXa. This then decomposes generating iron oxides, but in this process electrons are transferred to further molecules of XXVIII thereby producing radicals which dimerise in the manner described earlier.

The reaction between dienylirontricarbonyl cations and nitroso-derivatives is resported to give nitroxide radicals which have been detected and characterised by ESR spectroscopy (266a):



XXVIII

XXX

XXXI

However, because the spectra were poorly resolved, no data were available for distinguishing between the two possible nitroxide radicals XXX and XXXI.

An early report of an oxidation reaction generating radical species is given below (257):

$$Na^+Mn^-(CO)_5 + C_7H_7Br \longrightarrow C_{14}H_{14} + NaBr + Mn_2(CO)_{10}$$

The reaction is quantitative and pointed to a usefule route to dimeric molecules.

Cyclopentadienylcarbonyl complexes of a number of transition metals reported during recent years have been shown to undergo a variety of reactions. Two methods have been reported for the preparation of $[(\eta^5\text{-}C_5H_5)Cr(CO)_3]_2$: partial oxidation of the hydride $HCr(CO)_3(\eta^5\text{-}C_5H_5)$ (267), and the reaction of bis(cyclopentadienyl)chromium with carbon monoxide (268). Both of these, however, suffer from the disadvantage that they require the handling of pyrophoric intermediates, and, furthermore, the latter method results in very low yields.

A more convenient method has thus been devised (100):

$$2C_5H_6 + 2Na \longrightarrow 2Na^+ + 2C_5H_5^- + H_2$$

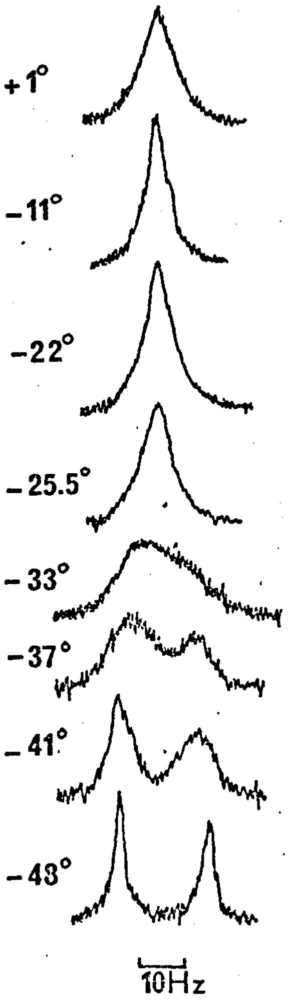
$$NaCp + Cr(CO)_6 \xrightarrow[\Delta]{\text{diglyme}} 3CO + (\eta^5\text{-}C_5H_5)Cr(CO)_3^-\ Na^+$$

$$\xrightarrow{+\ C_7H_7Br} [(\eta^5\text{-}C_5H_5)Cr(CO)_3]_2 + C_{14}H_{14} + Na\ Br$$

This is an analogous reaction to the oxidative coupling of the manganese anion mentioned earlier. The oxidation is effected by tropylium bromide, and that ditropyl is produced endorses the view that the reaction proceeds by a radical process.

Some unusual magnetic resonance properties of the dimer have been reported (102). The proton NMR spectrum of $[(\eta^5\text{-}C_5H_5)Cr(CO)_3]_2$ in toluene-d_8 solvent at 25° consists of one very broad resonance ($\nu_{\frac{1}{2}}$ = 18 Hz) at τ 4.16. At higher temperatures this line becomes broader, but at -61°, the resonance has narrowed to a width at half height of 1.5 Hz, and has shifted to τ 5.90. In a mixed solvent, acetone d_6-toluene d_8 in a 1:1 ratio at -61° the spectrum consists of two narrow lines at τ 5.36 and 5.55. As shown below, as the temperature rises, these two signals broaden and finally coalesce. The singlet then sharpens until -11°

after which it tends to broaden again.



The broadening is reversible and cannot therefore, be attributed to the appearance of paramagnetic decomposition products. It is most likely that increasing temperatures generate small concentrations of some paramagnetic species in equilibrium with the dimer. This has been explained by a simple dissociative mechanism:

$$[(\eta^5\text{-}C_5H_5)Cr(CO)_3]_2 \longrightarrow 2\ (\eta^5\text{-}C_5H_5)Cr(CO)_3^{\cdot}$$

In view of the extraordinary length of the Cr-Cr band (3.28Å (275)), this does not seem unreasonable.

2. CATION REDUCTION REACTIONS

2.1 Results and Discussion

2.1.1 The preparation of the complexes $(\eta^7-C_7H_7)M(CO)_3{}^+PF_6^-$ (M = Cr, Mo or W)and their reduction by Cr(II) ion

2.1.2 The stereochemistry of the reduction products.

2.1.3 The reduction of $(\eta^5-C_6H_7)Fe(CO)_3{}^+PF_6^-$

2.2. Experimental

2.3 Spectra

2.1.1 The preparation of the complexes $(\eta^7\text{-}C_7H_7)M(CO)_3{}^+PF_6{}^-$ (M = Cr, Mo or W) and their reduction by Cr(II) ion

Although the substitution of three carbonyl ligands in the parent hexacarbonyl by the hydrocarbon can be effected directly (257) the reaction was found to be accompanied by considerable decomposition, and in the tungsten case virtually impossible (269). It was thus found more productive to perform the synthesis via the acetonitrile complexes, $(CH_3CN)_3M(CO)_3$ (270). These compounds are obtained in better than 90% yield by prolonged heating of the carbonyl in acetonitrile under reflux (270). Since acetonitrile, like diglyme, is a ligand which has very little $p\pi - d\pi$ bonding ability, it is readily displaced by various olefins, and thus provides an easy method for synthesis of the olefin derivatives.

The three complexes $(\eta^6\text{-}C_7H_8)M(CO)_3$ are all air stable, red crystalline materials exhibiting infra-red spectra characteristic of a <u>fac</u> arrangement of carbonyl ligands in an octahedral environment, (Figures 41, 42, 43).

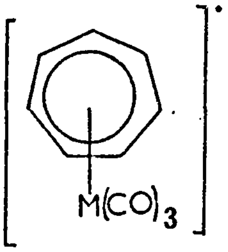
The ^1H NMR spectrum of cyclohepta-1,3,5-triene is shown in Figure 44. The high field triplet is assigned to the methylene group which is oscillating too rapidly on the NMR time scale at 35° to display two discrete signals. Co-ordination to the metal effectively blocks this movement, and so the spectra of the olefin derivatives consist of four resonances as shown in Figures 45, 46 and 47.

The yellow air sensitive material $(CH_3CN)W(CO)_5$ was isolated from the reaction mixture during the preparation of $(\eta^6\text{-}C_7H_8)W(CO)_3$. Its infra-red spectrum (Figure 48) showed the two strong bands associated with a monosubstituted hexacarbonyl species. Tungsten hexacarbonyl itself is known to be rather inert (269) so substitution of one carbonyl group may be expected to give a derivative with similar stability. Further substitution results in a molecule which can undergo facile reaction with the hydrocarbon, and for this reason no bis- or tris-acetonitrile species were isolated.

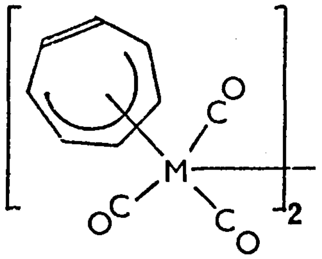
The conversion to salt is easily achieved by reaction of $(\eta^6\text{-}C_7H_8)M(CO)_3$ (M = Cr, Mo or W) with triphenylmethylhexafluorophosphate (259).

The ^1H NMR spectra for the chromium and molybdenum salts have been recorded (Figures 49 and 50). Both showed a singlet resonance in the aromatic region, confirming the planar, symmetrical nature of the seven membered ring.

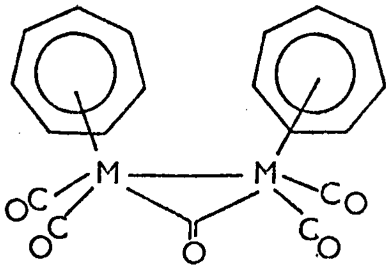
Chromium (II) was chosen as the reductant in these investigations as it can only provide one electron in its oxidation to the more stable chromium (III) species. When the salts are reduced, several products can be envisaged, depending upon the site of maximum unpaired electron density. These could be (i) a radical-like monomer, XXXII; (ii) a dimeric species such as XXXIII; (iii) a dimer XXXIV with a bridging carbonyl group, or (iv) a ligand bridged dimer XXXV:



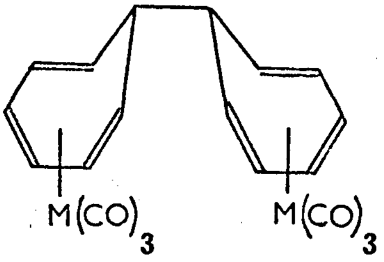
XXXII



XXXIII



XXXIV



XXXV

In the case of the three dimers the metals obey the inert gas rule.

When the sky blue solution of chromium (II) ions was run into solutions of the cycloheptatrienyl cations, a green colouration was obtained immediately. That this was due to the oxidation from Cr(II) to Cr(III) and not just the effect of mixing the blue and yellow solutions was verified by UV spectroscopy in the following manner. A very dilute solution of Cr(II) was prepared and its UV spectrum recorded. After addition to a solution containing an excess of the organometallic cation, the spectrum was recorded again, and comparison of the two provided evidence for the oxidation to Cr(III), since the two chromium ions exhibit different spectral characteristics (Figures 54, 55, and 56).

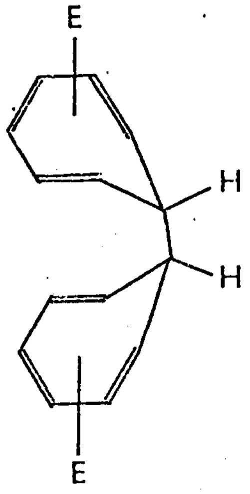
Considerable difficulty was experienced in preparing the tungsten cycloheptatrienyl tricarbonyl derivative meaning that only small quantities of the salt were available for reduction. Nevertheless, the reaction with Cr(II) ion generated a product which could be extracted from the aqueous reaction medium into diethyl ether to give a red solution. No solid product was isolated, but it is tentatively assumed that the tungsten complex behaves in a similar manner to its chromium and molybdenum congeners.

The products of the reduction of the chromium and molybdenum cations were found to be dimeric with the structure XXXV, and their stereochemistry is discussed in Section 2.1.2. These findings confirm the view that the unpaired electron is sited primarily on the olefinic ring. It is unlikely that $(\eta^6\text{-}C_7H_8)M(CO)_3$ would be generated by a reaction of this radical with water, since the tropyl radical in aqueous solution is known to give exclusively ditropyl (252). If the maximum unpaired elctron density were on the metal, a hydrido species of the type $(\eta^7\text{-}C_7H_7)MH(CO)_3$ could be envisaged as a possible reaction product.

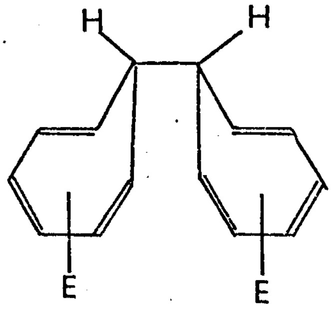
2.1.2 The stereochemistry of the reduction products

The infra-red spectra of the chromium and molybdenum dimers are shown in Figures 57 and 58. Both exhibit the pattern typical of a fac arrangement of carbonyl ligands in an octahedral complex, and no bands due to bridging carbonyl groups were detected. However, as a means of distinguishing structural isomers this particular spectroscopic technique is not very useful.

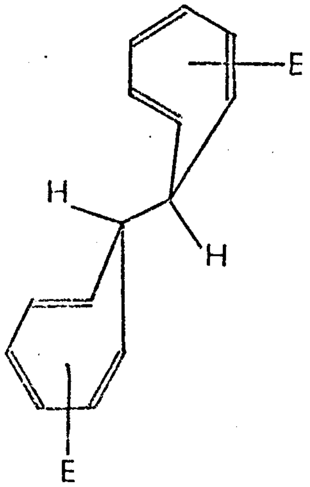
Structural isomers can arise by combination of two radicals of a different configuration, and the conceivable products are given below:



exo-exo



endo-endo



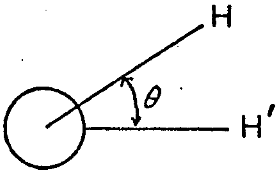
exo-endo

E = $M(CO)_3$

These structures are based upon the reasonable assumption that the radicals will combine with the bulky metal tricarbonyl groups distant from each other, resulting in their being on the opposite side of the rings to the bridge in the dimer.

Stereochemical studies of a wide range of organic molecules have been executed with the aid of proton magnetic resonance spectroscopy. Such studies are almost invariably based upon the relationship between bond angles (or more accurately dihedral angles between hydrogen atoms on adjacent carbon atoms) and vicinal coupling constants.

Vicinal coupling is defined as the interaction between nuclei bound to contiguous atoms, i.e. a coupling across three bonds. A number of factors have been found to affect the magnitude of vicinal couplings, the most important of these being the angle subtended by the two C–H bands when viewed along the C–C axis (θ, the dihedral angle):



Karplus (271) has predicted an empirical relation between the dihedral angle and the vicinal coupling constant J (H-C-C-H^1) which is generally expressed in the forms:

$$J = \begin{cases} 8.5 \cos^2 \theta - 0.28 & 0^\circ \leq \theta \leq 90^\circ \\ 9.5 \cos^2 \theta - 0.28 & 90^\circ \leq \theta \leq 180^\circ \end{cases}$$

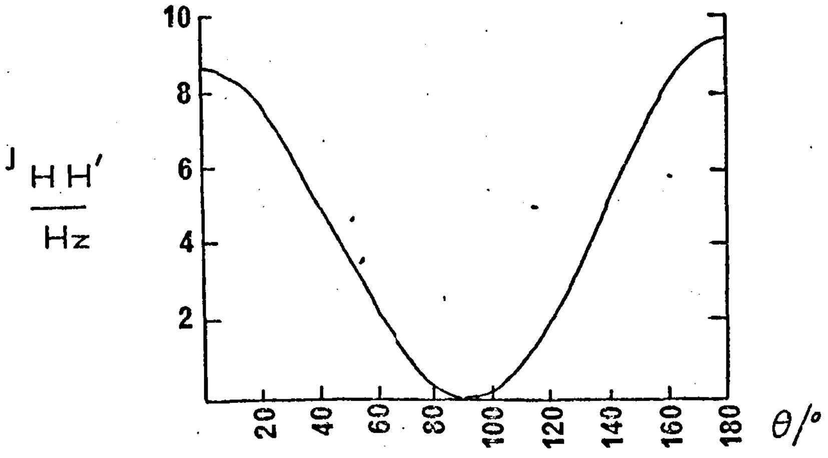
Other factors may also affect the value of the vicinal coupling constants, but their magnitude is such that they are regarded merely as "perturbations" of the Karplus equation. These pertubations may be due to:

(i) electronegativity of substituents

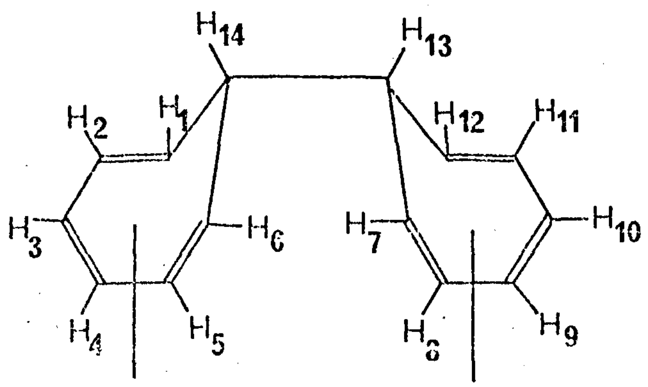
(ii) the orientation of substituents

(iii) hybridisation of the carbon atoms
(iv) bond lenths
(v) bond angles

The graph below is derived from the Karplus equation and demonstrates that J will be largest when the vicinal protons are trans-coplanar, slightly smaller when they are cis-coplanar, and zero when they are at right angles.



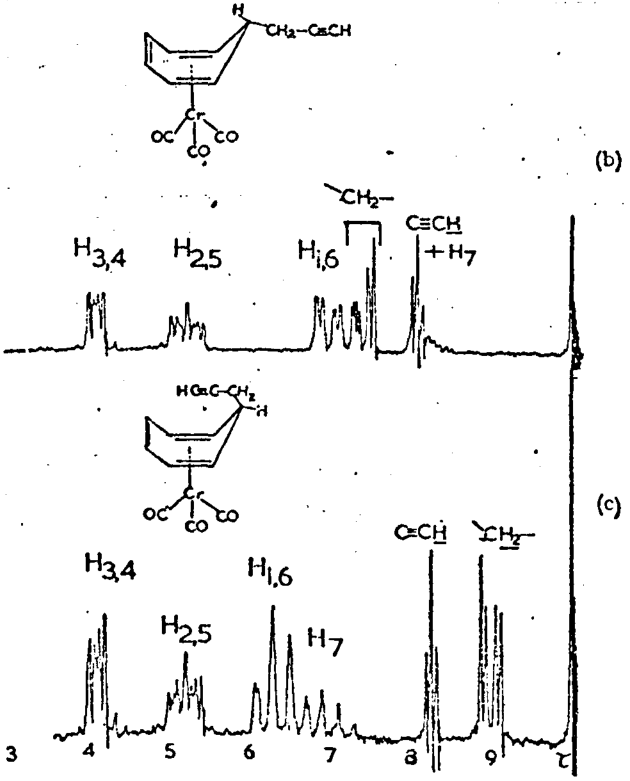
It was originally believed that a study of the proton NMR spectra of the dimers would yield information concerning the stereochemistry of these complexes by measurement of coupling constants for the multiplet derived from the bridgehead protons and application of the Karplus equation. However, as can be seen from Figures 59 and 60 the signals consisted of complex multiplets, so structural information could not be obtained in this manner. The spectra obtained can be rationalised by considering the structure XXXVI:



XXXVI

The protons H_{13} and H_{14} are in a fixed position with respect to H_7H_{12} and H_1H_6, so the triplet derived by coupling of $H_{13}(H_{14})$ with $H_{16}(H_{7\ 12})$ will have a unique coupling constant. The dihedral angle between H_{13} and H_{14}, however, is changing continually due to rotation about the bridging bond, so the coupling constant of the signal of H_{14} coupled to H_{13} will be of variable magnitude. These factors together result in the multiplet detected for the bridghead protons.

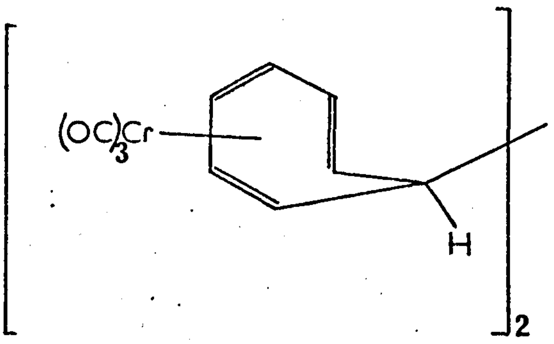
Pauson has reported the ^1H NMR spectra for both endo- and exo- isomers of tricarbonyl-7-propargylcyclohepta-1,3,5-trienechromium (272), and these are reproduced below.



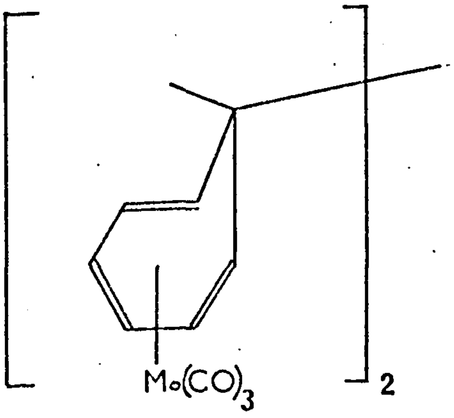
N.m.r. spectra of (a) the 7-proparylcycloheptatriene (Id), and of its two tricarbonylchromium derivatives [(b) *endo*-complex; (c) *exo*-complex]

It can be seen that the signals due to H_1 and H_6 of each isomer differ in shape and position, and a consideration of these provided information concerning the stereochemistry of the dimers.

In the complex $[(\eta^6-C_7H_7)Cr(CO)_3]_2$, the signal due to the protons H_1 and H_6 appears as a triplet and in a similar position to the equivalent protons in the exo- isomer discussed by Pauson (272). Furthermore, the resonances of protons H_3 and H_4, and H_2 and H_5 also compare favourably with the published data for the exo- complex. These likenesses would seem to indicate that the chromium dimer at least has the exo-exo configuration:



The ^{1}H NMR spectrum of $[(\eta^6\text{-}C_7H_7)Mo(CO)_3]_2$ (Figure 60), however, is too poorly resolved to allow similar comparisons to be made, If a structural assignment can be made at all, it would appear that this dimer exists as the endo-endo isomer, although reasons for this variation from the chromium analogue are not apparent.



The mass spectra of exo- and endo-7,7^1-bis(1,3,5-cycloheptatrienyl)-tricarbonylchromium have been recorded (273), and are shown in the figure below:

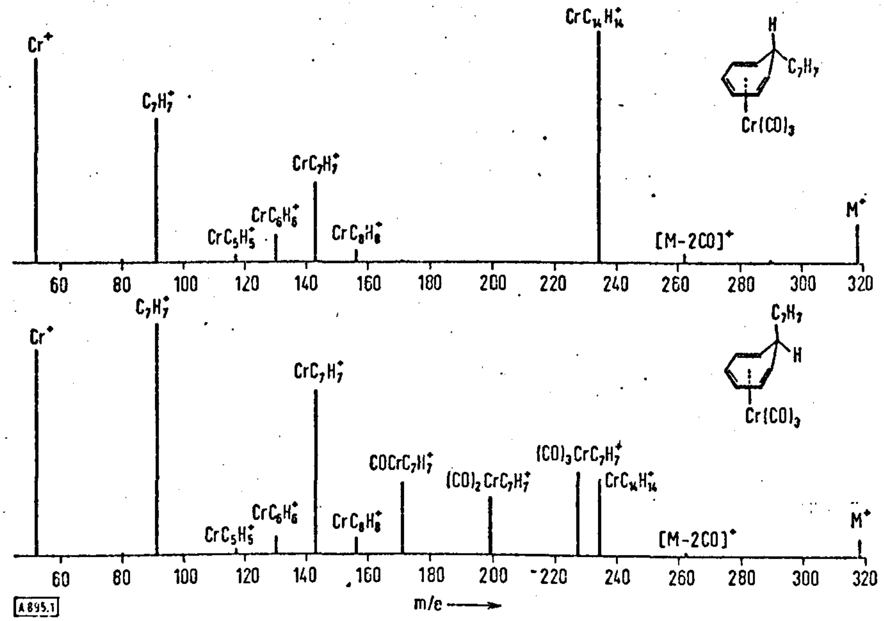
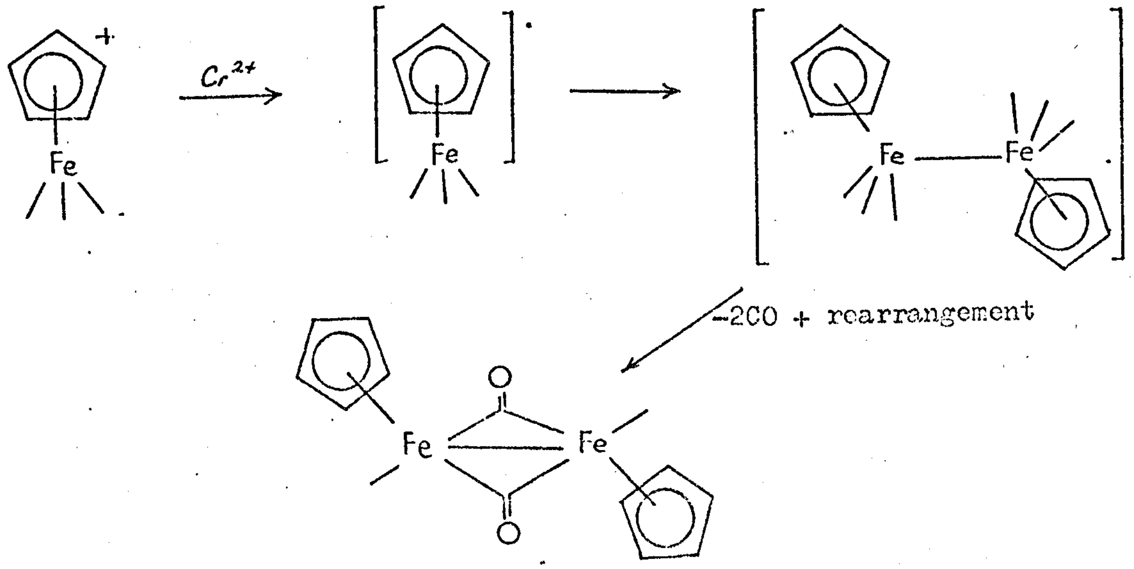


Fig. 1. Mass spectra of *exo*- and *endo*-7,7′-bi(1,3,5-cycloheptatrienyl)tricarbonylchromium (50 eV; the spectra are normalized with respect to the isotope distribution of the ions).

It appears that loss of an endo substituent only occurs after complete decarbonylation. However, since the mass spectra of both the chromium and molybdenum dimers (MS 16 and 17) had characteristics of both isomers it was not possible to use this technique to elucidate the structure of the dimers. Others have found mass spectrometry to be an inappropriate means for distinguishing between stereoisomers in this series (273a).

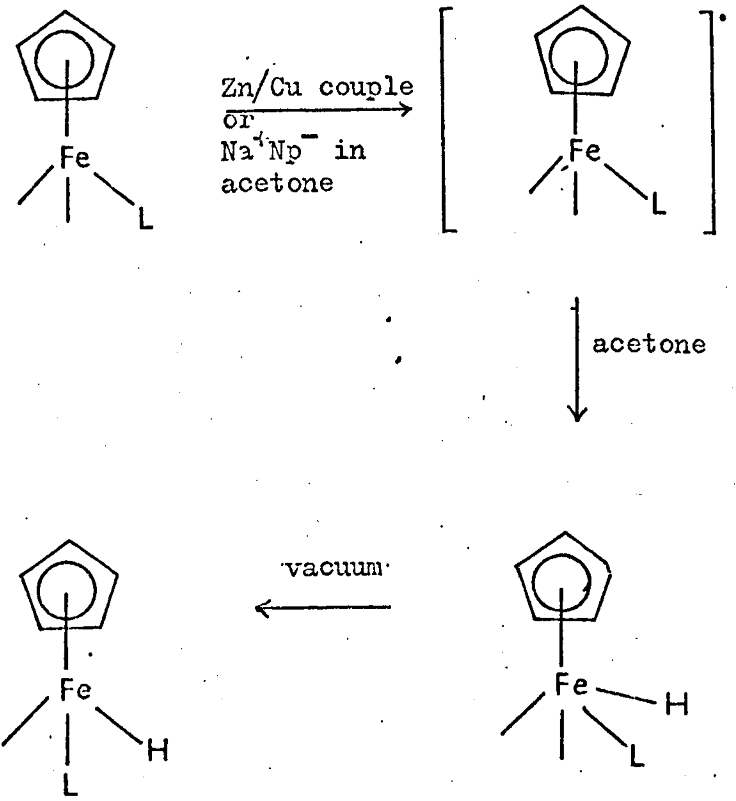
2.1.3 The reduction of $(\eta^5\text{-}C_6H_7)Fe(CO)_3{}^+PF_6^-$

The reduction of $(\eta^5\text{-}C_5H_5)Fe(CO)_3{}^+$ by chromium (II) ions proceeds according to the following scheme (274):



Carbonyl groups ommited for clarity

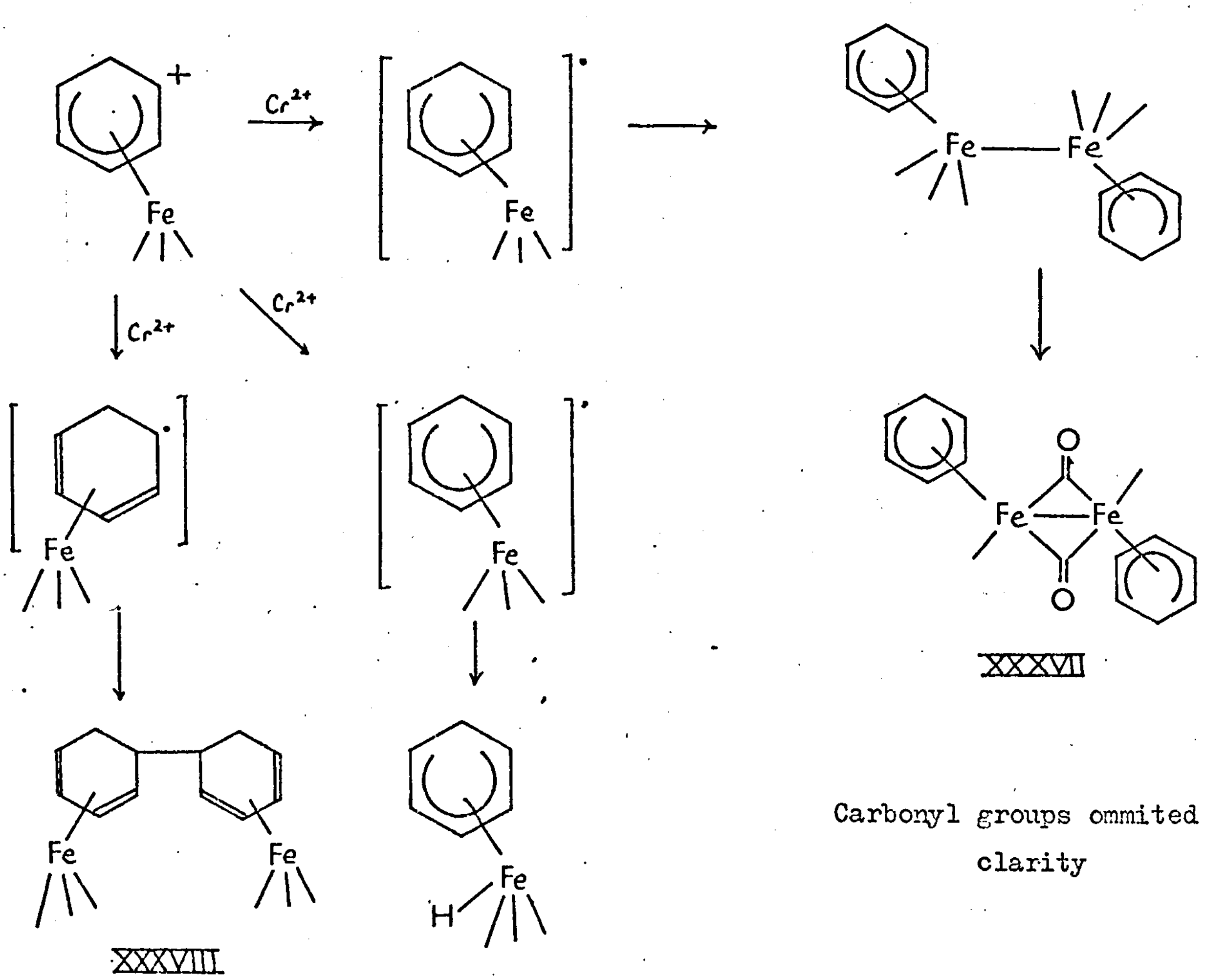
The isolated product has two bridging carbonyl groups, although there is no reason, on the basis of the inert gas rule, why the intermediate species with two terminal carbonyls per iron atom should not be stable. Further work from this laboratory has shown, however, that reduction of $(\eta^5\text{-}C_5H_5)Fe(CO)_2L^+$ ($L = P(OPh)_3$) does not lead to a dimeric compound but to a hydrido complex according to the scheme below:



Carbonyl groups ommited for clarity $L = P(OPh)_3$

The nineteen electron intermediate is not stable, and apparently undergoes an alkane activation reaction with the acetone solvent to give the more stable 20 electron hydride. Attempts to remove the solvent from this complex by pumping always lead to the eighteen electron compound by loss of a carbonyl ligand.

The reduction of $(\eta^5\text{-}C_6H_7)Fe(CO)_3{}^+PF_6{}^-$ therefore has a direct analogy in these reactions. The product of its reduction could thus be either a ligand bridged dimer, a metal-metal bonded dimer XXXVII or a hydrido complex formed according to the following scheme:



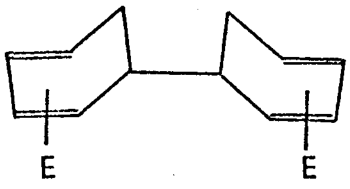
XXXVIII

XXXVII

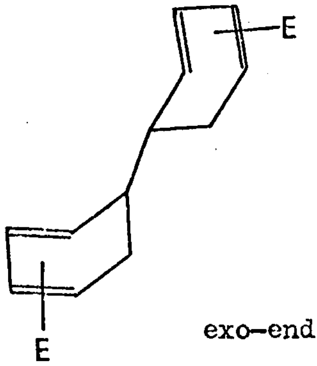
Carbonyl groups ommited for clarity

In the event, the isolated product was found to be the ligand bridged dimer (XXXVIII) similar to those obtained for the chromium and molybdenum compounds, indicating that in $(\eta^5-C_6H_7)Fe(CO)_3{}^+$ the LUMO is ligand based. Reduction therefore occurs at this site rather than at the metal atom. In $(\eta^5-C_5H_5)Fe(CO)_3{}^+$ the reverse appears to be true since the dimeric product contains a metal-metal bond.

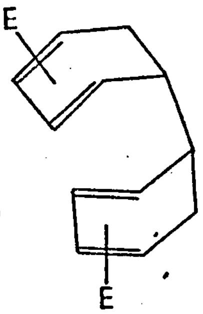
X-ray crystallographic studies on bis(1,3-cyclohexadiene)-monocarbonyliron (275) have shown that the bonding of the olefin ligand to the iron atom stabilises a non-planar conformation of the six membered ring. The molecule can thus be regarded as a substituted butadiene complex of iron. It would not seem unreasonable to assume that a similar bi-planar geometry exists in the dimer, and this would give three stereoisomers analogous to the cycloheptatrienyl chromium and molybdenum complexes:



endo–endo



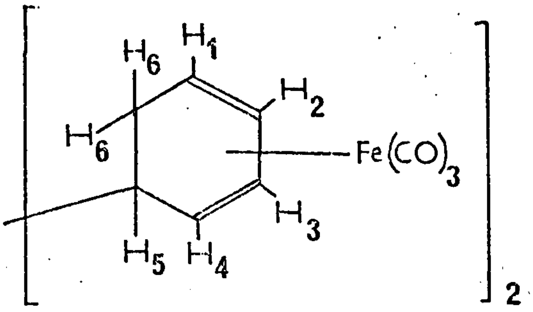
exo–endo



exo–exo

E = Fe(CO)$_3$

The ^1H NMR spectra of exo and endo-sbustituted derivatives of cyclohexadienyliron tricarbonyl have been reported (276), but as can be seen from Figure 61, the spectrum of the dimer was poorly resolved so a definite assignment of stereochemistry could not be made. The ^1H NMR spectrum for the 5-5′ dimer, XXXIX, has been reported, however, and the quoted resonance positions (265) agree well with those found in this work.



XXXIX

	$H^{1,4}$	$H^{2,3}$	H^5	H^6	
literature:	2.92	5.18	1.10	1.82	δ
found:	2.95	5.21	1.10	1.72	δ

FIGURE 61

The reduction of $(\eta^5-C_6H_7)Fe(CO)_3^+$ by chromium (II) ion thus parallels that of $(\eta^6-C_7H_8)Fe(CO)_3^+$ by zinc discussed earlier (266).

2.2. Experimental

Details of the instrumentation used in this section are the same as those given in Chapter 2. The Group VI metal hexacarbonyls (Strem Chemicals) were used as received, as was the cyclohepta-1,3,5-triene (Koch-Light Ltd). Acetonitrile was "Spectrosol Grade" (Hopkins and Williams) and was dried (Linde 4A molecular sieves) and distilled before use. Other solid reagents and solvents were purified by standard techniques. Triphenylmethylhexafluorophosphate (Fluorochem Ltd) was used as received. All preparations and handling of intermediates were carried out under nitrogen, although the final products were air stable. Infra-red spectra were recorded for chloroform solutions using 0.1 mm NaCl cells unless otherwise states. Quoted ^1H NMR resonance positions are on the δ scale.

Preparation of $(\eta^6\text{-}C_7H_8)Cr(CO)_3$

A solution of hexacarbonylchromium (4.7g, 0.0213 mole) in acetonitrile (150 ml) was thoroughly degassed and then heated under reflux for 24 hours. The solvent was then removed in vacuo to give an extremely air sensitive yellow solid residue. This was then treated with cyclohepta-1,3,5-triene (9.84 g, 11.09 ml, 0.107 mole) in hexane (100 ml) and the mixture heated under reflux for 2 hours. After this time, the solvent was removed and the residue recrystallised from petrol (bp 80-100) to give red needles, 1.71 g (35.6% based on $(\eta^6\text{-}C_7H_8)Cr(CO)_3$); mp 131-2°; ν C≡O, 1977 (s), 1910 (m), 1880 (m) cm^{-1}; found C 51.65, H 3.69, $C_{10}H_8CrO_3$ requires C 52.86 H 3.08%; MS 13, M^+ 228, M^+-nCO (n = 1-3); ^1H NMR ($CDCl_3$) 6.05 (br, 2H), 4.81 (br, 2H), 3.35 (br, 2H), 3.00 (br, 1H), 1.75 (br, 1H).

Preparation of $(\eta^7\text{-}C_7H_7)Cr(CO)_3{}^+PF_6^-$

A solution of $(\eta^6\text{-}C_7H_8)Cr(CO)_3$ (1.50 g, 6.5×10^{-3} mole) in methylene chloride (100 ml) was treated with triphenymethyl hexafluorophosphate (4.0 g, 0.011 mole) in methylene chloride (20 ml). The mixture was heated under reflux for 10 minutes and allowed to cool to room temperature. The precipitated salt collected byfiltration and dried in vacuo to give a buff powder, 1.70 g (69.9% based on $(\eta^7\text{-}C_7H_7)Cr(CO)_3{}^+PF_6^-$); ν C≡O (acetone) 2060 (vs), 2030 (vs) cm^{-1}; ^1H NMR (Acetone-d_6) 6.89 (singlet)

The reduction of $(\eta^7\text{-}C_7H_7)Cr(CO)_3{}^+PF_6^-$ by Cr(II)

A sky blue solution of Cr(II) ions was prepared by reducing $CrCl_3.6H_2O$ (3.57 g; 0.014 mole) with zinc (6.06 g: 0.091 g atom) and concentrated hydrochloric acid (8 ml) in water(10 ml). This was then added to a solution of the salt (0.5, 1.34×10^{-3} mole) in water/THF

(1:1 v/v, 20 ml), and the mixture left at room temperature for 30 minutes. After this time, the precipitate was isolated from the green super-natant liquid, and dried in vacuo to give a red powder, 118 mg (38.7% based on $(\eta^6\text{-}C_7H_7)Cr(CO)_{3\ 2}$); mp > 250; ν C≡O; 1982 (vs), 1924 (m), 1894 (m) cm^{-1}; MS 16 M^+ 454, $M^+\text{-}nCO$(n = 1–6); ^1H NMR ($CDCl_3$), 5.95 (mult, 1H), 4.77 (mult, 2H), 3.27(mult, 2H) 1.23 (mult, 1H); found C52.88 H 3.02, $C_{20}H_{14}Cr_2O_6$ requires C 52.86, H 3.08%

Preparation of $(\eta^6\text{-}C_7H_8)Mo(CO)_3$

A solution of hexacarbonylmolybdenum (5.26 g, 0.0213 mole) in acetonitrile(150 ml) was thoroughly degassed and then heated under reflux for 24 hours. The solvent was then removed in vacuo and the bright yellow solid residue treated with cyclohepta-1,3,5-triene(0.79 g; 0.106 mole) in hexane (100 ml) and heated under reflux for 2 hours. The deep red solution was filtered and the filtrate concentrated. The concentrate was then applied to a silica column (30 x 3 cm) and eluted with an equivolume mixture of petrol (bp 80–100) and toluene. The fast running red band was collected to give a dark red solid, 850 mg (16.9% based on $(\eta^6\text{-}C_7H_8)Mo(CO)_3$). A small sample was recrystallised from n-pentane to give red needles mp 97–8°; ν C≡O 1981 (vs), 1914 (s), 1880 (s) cm^{-1}; MS 14, M^+ 274, $M^+\text{-}nCO$ (n = 1–3); ^1H NMR ($CDCl_3$) 6.10 (mult, 2H), 4.95 (mult 2H), 3.69 (mult 2H) 3.10 (mult, 1H), 2.60 (mult, 1H).

Preparation of $(\eta^7\text{-}C_7H_7)Mo(CO)_3{}^+PF_6^-$

A solution of $(\eta^6\text{-}C_7H_8)Mo(CO)_3$ (800 mg; 3.1×10^{-3} mole) in methylene chloride (100 ml) was treated with triphenylmethylhexafluorophosphate (3.0 g; 0.0083 mole) in methylene chloride (20 ml), and the mixture heated under reflux for 20 minutes. The precipitate was collected and dried in vacuo at room temperature to give a rust coloured powder, 0.750 g(50.1% based on $(\eta^7\text{-}C_7H_7)Mo(CO)_3{}^+PF_6^-$); νC≡O (acetone), 2070 (s), 2015 (s) cm^{-1}; ^1H NMR 6.57 (singlet).

The reduction of $(\eta^7\text{-}C_7H_7)Mo(CO)_3{}^+PF_6^-$ by Cr(II)

A solution of chromium (II) ions was produced by reducing $CrCl_3.6H_2O$ (2.25 g, 0.0084 mole) with zinc (3.8 g, 0.057 g atom) and concentrated hydrochloric acid (7 ml) in water (10 ml). This was then added to a solution of $(\eta^7\text{-}C_7H_7)Mo(CO)_3{}^+PF_6^-$ (440 mg; 0.0016 mole) in THF/water (1:1 v/v; 20 ml) and an immediate green colour resulted. After 35 minutes at room temperature, the precipitate was filtered to give a red powder, 150 mg (52.4% based on $(\eta^7\text{-}C_7H_7)Mo(CO)_{3\ 2}$). A small sample was recrystallised from chloroform to give small red needles, mp > 250°; ν C≡O 1990 (vs), 1930 (s), 1888 (s) cm^{-1}; found C 44.18, H 2.71, $C_{20}H_{14}Mo_2O_6$ requires C 44.29, H 2.58%; ^1H NMR (DMSO d_6) 6.75 (mult, 2H), 6.31 (mult, 2H)

5.20 (mult, 2H), 1.88 (mult, 1H); MS 17, M^+ 546, M^+-nCO (n = 1-6).

Preparation of $(\eta^6\text{-}C_7H_8)W(CO)_3$

A solution of hexacarbonyltungsten (1.05g; 3.1×10^{-3} mole) in methylene chloride (50 ml) was thoroughly degassed and heated under reflux for 40 hours. The solvent was then removed, the yellow solid residue treated with cyclohepta-1,3,5-triene (2 ml; 1.775 g, 0.019 mole) in n-hexane (50 ml) and then heated under reflux for 16 hours. After this time the solution was filtered hot and the filtrate concentrated to small volume. This was then applied to a silica column (35 x 3 cm) and eluted with mixture 1.

The first yellow band gave unreacted cyclohepta-1,3,5-triene, identified by comparison of its infra-red spectrum with that of an authentic sample.

The second, dark red, band gave red needles, 63 mg (7% based on $(\eta^6\text{-}C_7H_8)W(CO)_3$) mp 115-6 d; ν C≡O, 1990 (vs), 1918 (s), 1880 (s); found C 33.31, H 2.14, $C_{10}H_8O_3W$ requires C 33.33, H 2.22%; ^1H NMR ($CDCl_3$), 6.01 (mult, 2H), 4.76 (mult, 2H), 3.52 (mult, 2H), 3.18 (mult, 1H) 1.25 (mult, 1H). MS 15, M^+ 360, M^+-nCO (n = 1-3).

The last, yellow, band, gave a yellow solid, 47 mg (3% based on $W(CO)_5CH_3CN$). This was further purified by sublimation in vacuo at 110° to yield yellow plates, 15 mg, mp 67-8d; ν C≡O (n-hexane), 1945 (vs), 1929 (m) cm^{-1}, MS 18, M^+365, M^+-5CO. This material is unstable in air over a period of 48 hours.

Preparation of $(\eta^7\text{-}C_7H_7)W(CO)_3{}^+PF_6{}^-$

This reaction was performed only on a qualitative basis. Thus, a solution of $(\eta^6\text{-}C_7H_8)W(CO)_3$ in methylene chloride (50 ml) was treated with triphenylmethylhexafluorophosphate in methylene chloride (20 ml) and the mixture left at room temperature for 35 minutes. The precipitated orange powder was collected and dried in vacuo. ν C≡O (acetone), 2070 (vs), 2000 (vs) cm^{-1}.

The reduction of $(\eta^7\text{-}C_7H_7)W(CO)_3{}^+$ PF_6 by Cr(II)

A solution of chromium (II) ions was produced by reducing $CrCl_3.6H_2O$ (0.5 g; 0.0018 mole) with zinc (0.85 g; 0.013 g atom) and concentrated hydrochloric acid (5 ml) in water (5 ml). This was added to a solution of $(\eta^7\text{-}C_7H_7)W(CO)_3{}^+PF_6{}^-$ (220 mg; 0.00043 mole) in H_2O/THF (1:1 v/v; 10 ml) to give a clear green solution. No precipitation occured but a red colouration was imparted to diethylether when this was used to extract the aqueous medium, indicating that some reaction had occured. Attempts to isolate the product failed.

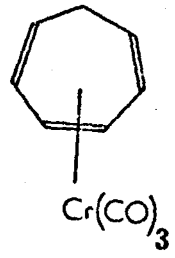
The reduction of $(\eta^5\text{-}C_6H_7)Fe(CO)_3{}^+ PF_6{}^-$ by Cr(II)

A solution of $(\eta^5\text{-}C_6H_7)Fe(CO)_3{}^+PF_6{}^-$ (1.0 g; 0.00274 mole) in water (20 ml) was treated with a solution of chromium (II) ions produced by Zn/HCl reduction of $CrCl_3.6H_2O$ (4.5 g, 0.016 mole). The resulting mixture was warmed gently for 30 minutes and then filtered to remove particles of zinc. The filtrate was extracted with diethylether (3 x 25 ml), the extracts combined, dried ($CaCl_2$) and concentrated to dryness. The yellow gum was then applied in toluene solution to a silica column (20 x 2.5 cm) and eluted in a mixture of toluene and petrol (bp 80–100) (1:1 v/v ratio). The fast running yellow band was collected and the gum which was isolated slowly solidified to give yellow plates, 100 mg (16.6% based on $(\eta^4\text{-}C_6H_7)Fe(CO)_3)_2$), ν C≡O 2030 (vs), 1970 (vs, br) cm^{-1} MS 19, M^+ 438, M^+-nCO (n = 1–6); ^1H NMR ($CDCl_3$) 5.21 (mult), 2.95 (mult), 1.10 (mult), 1.72 (mult).

2.4 SPECTRA

The spectra referred to in the earlier part of this section of Chapter 2 are presented below:

Figure No.	Illustration	
41	$(\eta^6\text{-}C_7H_8)Cr(CO)_3$	IR
42	$(\eta^6\text{-}C_7H_8)Mo(CO)_3$	IR
43	$(\eta^6\text{-}C_7H_8)W(CO)_3$	IR
44	C_7H_8	NMR
45	$(\eta^6\text{-}C_7H_8)Cr(CO)_3$	NMR
46	$(\eta^6\text{-}C_7H_8)Mo(CO)_3$	NMR
47	$(\eta^6\text{-}C_7H_8)W(CO)_3$	NMR
48	$MeCNW(CO)_5$	IR
49	$(\eta^7\text{-}C_7H_7)Cr(CO)_3{}^+PF_6{}^-$	NMR
50	$(\eta^7\text{-}C_7H_7)Mo(CO)_3{}^+PF_6{}^-$	NMR
51	$(\eta^7\text{-}C_7H_7)Cr(CO)_3{}^+PF_6{}^-$	IR
52	$(\eta^7\text{-}C_7H_7)Mo(CO)_3{}^+PF_6{}^-$	IR
53	$(\eta^7\text{-}C_7H_7)W(CO)_3{}^+PF_6{}^-$	IR
54	$Cr^{2+}aq$	UV
55	$Cr^{3+}aq$	UV
56	Cr^{2+}/Cr^{3+} aq	UV
57	$[(\eta^6\text{-}C_7H_7)Cr(CO)_3]_2$	IR
58	$[(\eta^6\text{-}C_7H_7)Mo(CO)_3]_2$	IR
59	$[(\eta^6\text{-}C_7H_7)Cr(CO)_3]_2$	NMR
60	$[(\eta^6\text{-}C_7H_7)Mo(CO)_3]_2$	NMR
61	$[(\eta^4\text{-}C_6H_7)Fe(CO)_3]_2$	NMR
62	$[(\eta^4\text{-}C_6H_7)Fe(CO)_3]_2$	IR



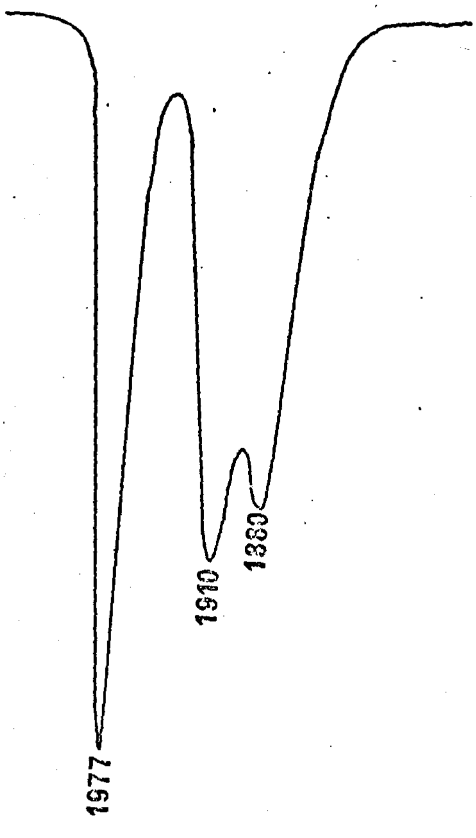
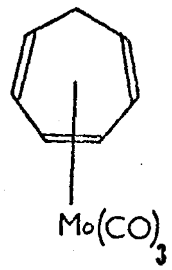


FIGURE 41

solvent: $CHCl_3$



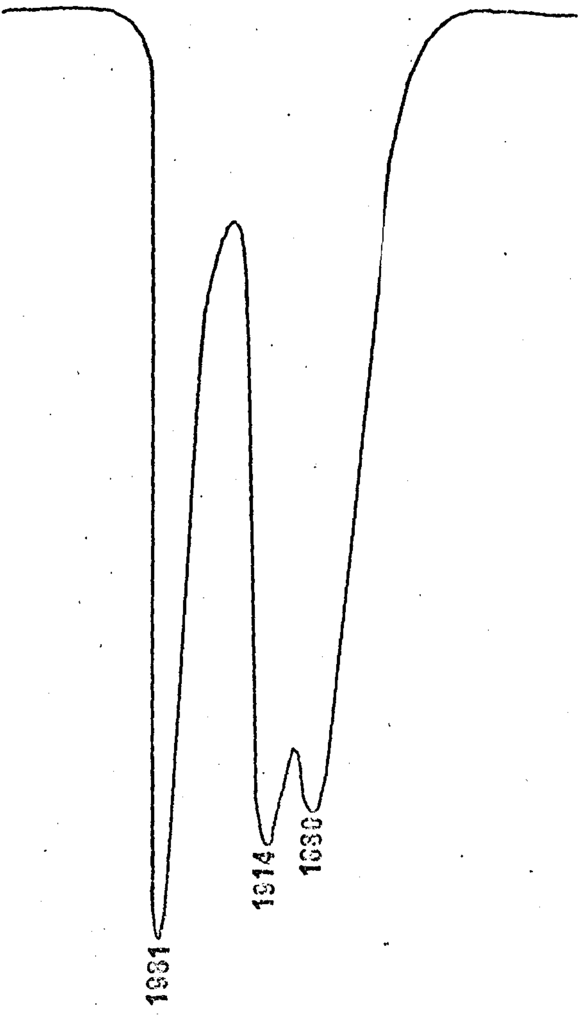
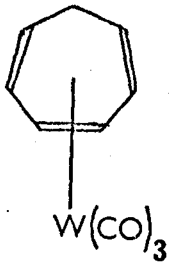


FIGURE 42

solvent: $CHCl_3$



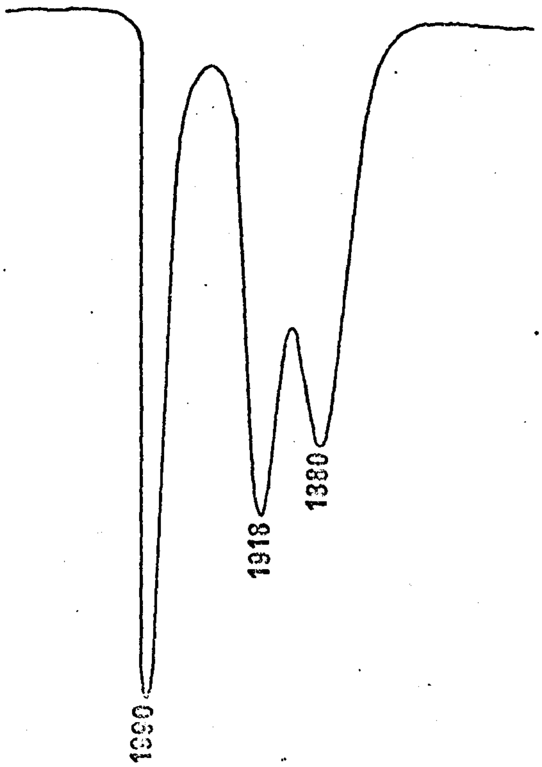


FIGURE 43

solvent: $CHCl_3$

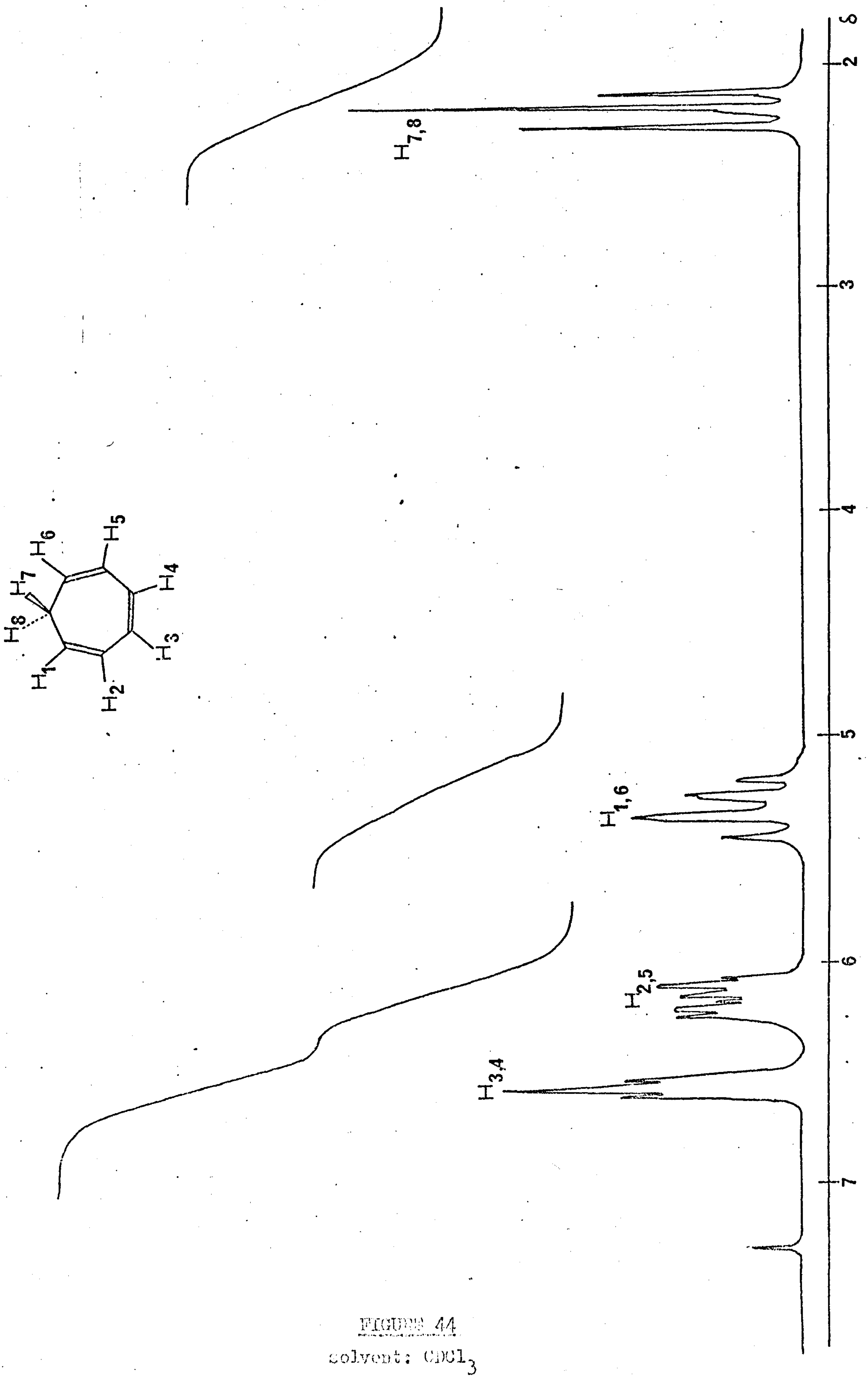


FIGURE 44
solvent: $CDCl_3$

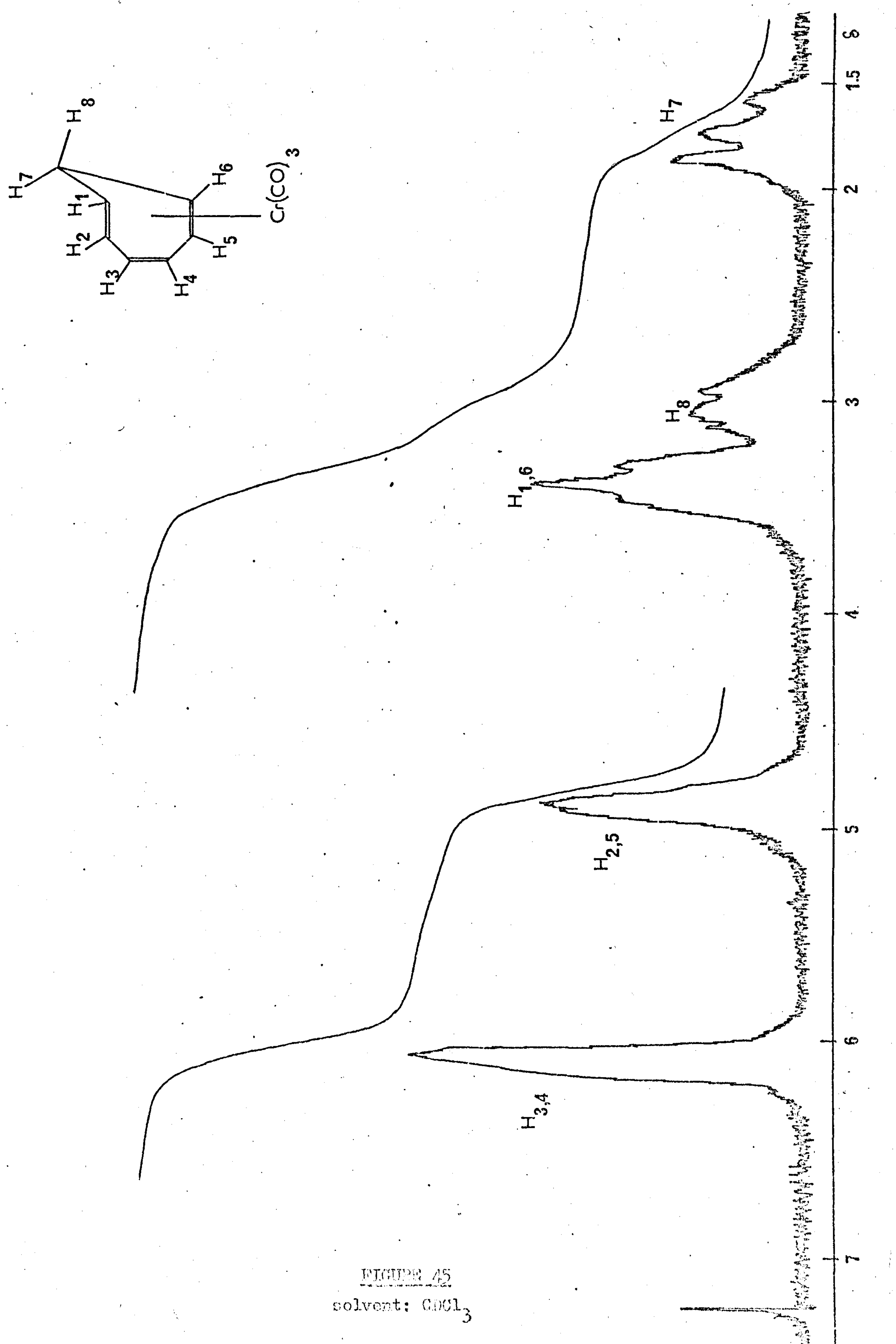


FIGURE 45

solvent: CDCl$_3$

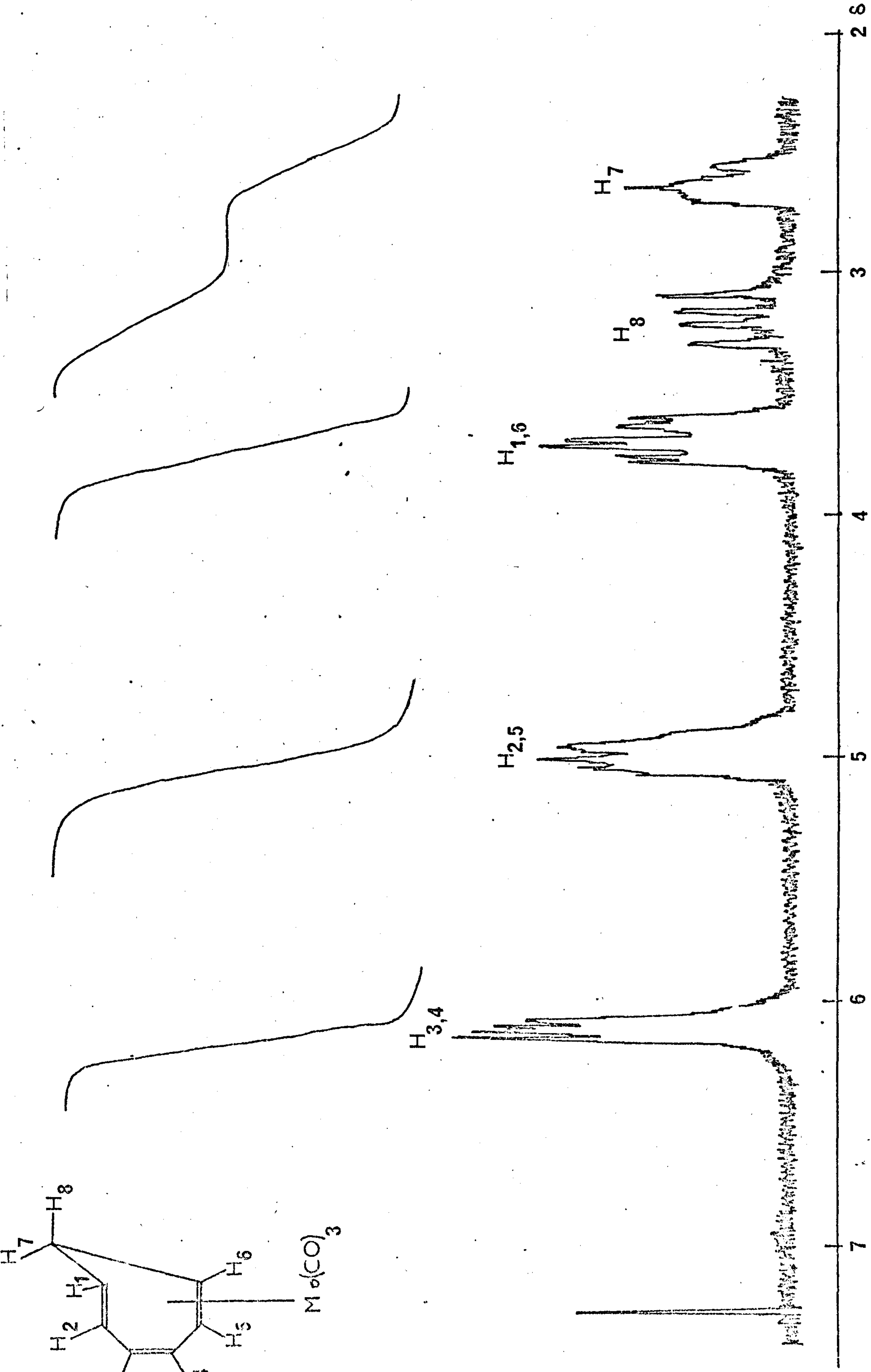


FIGURE 46

solvent: $CDCl_3$

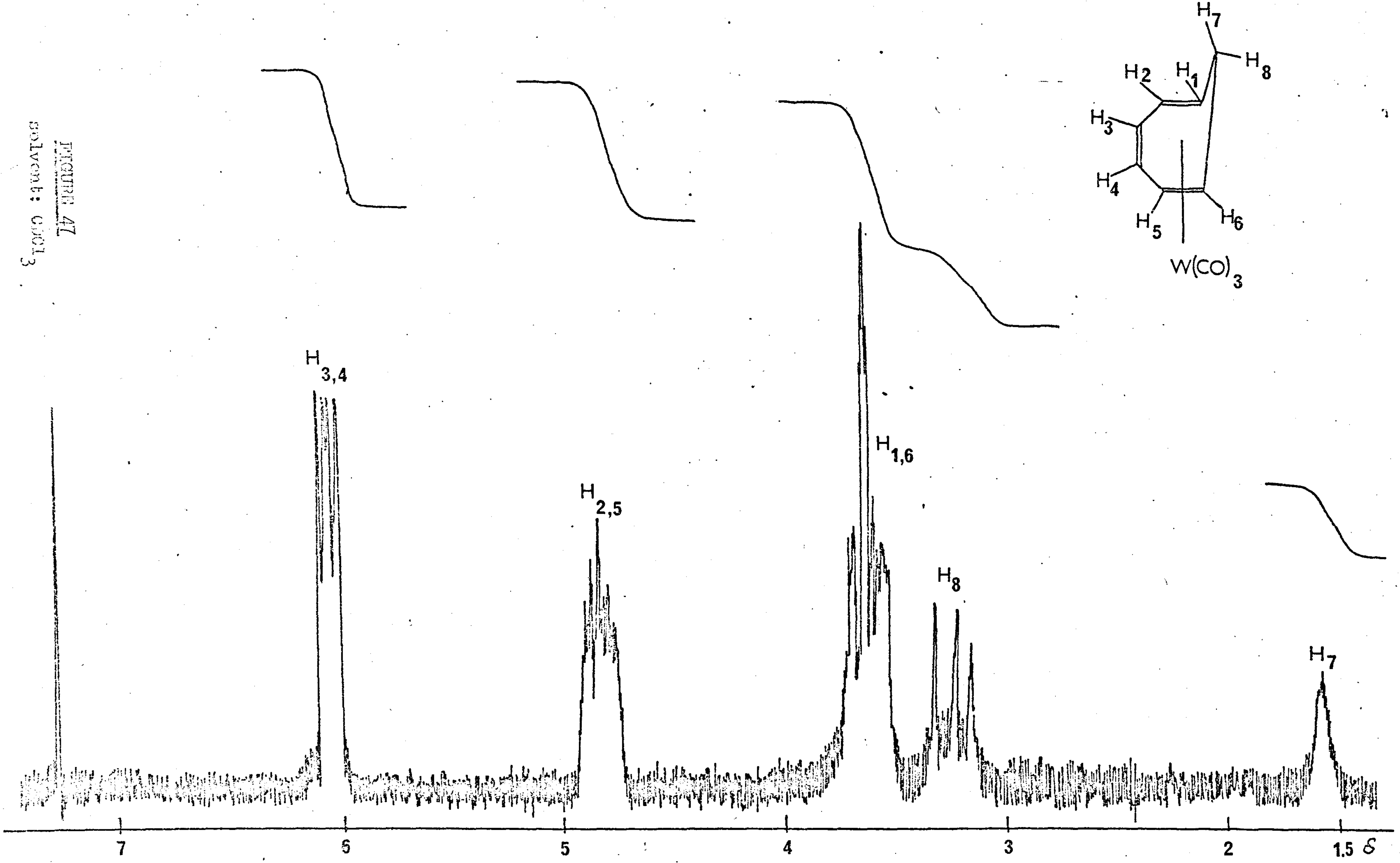


FIGURE 47
solvent: CDCl$_3$

$(CH_3CN)W(CO)_5$

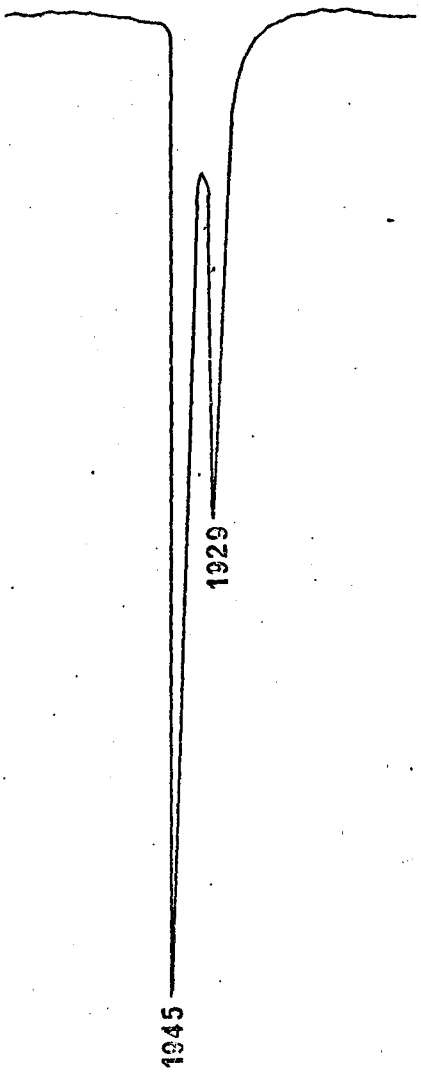


FIGURE 48
solvent: $CHCl_3$

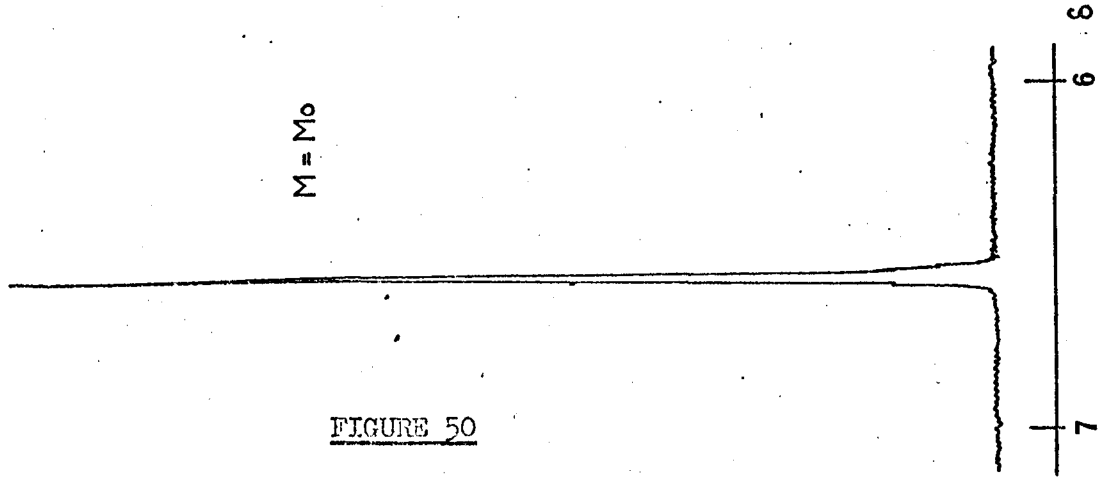
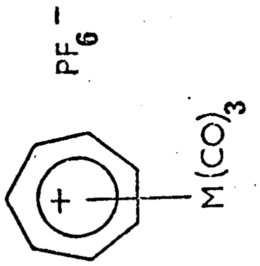


FIGURE 50



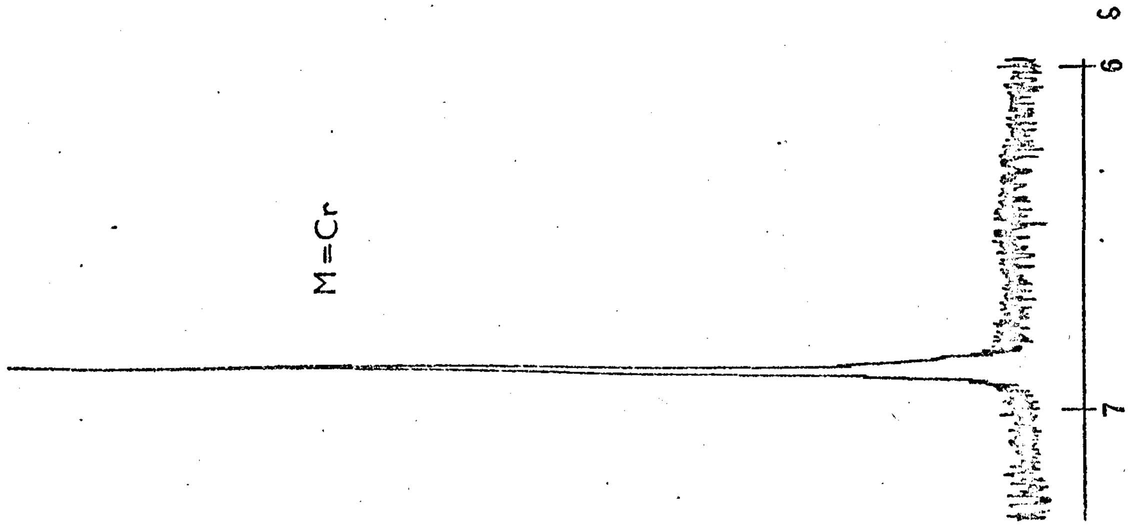


FIGURE 49

solvent: $(CD_3)_2CO$

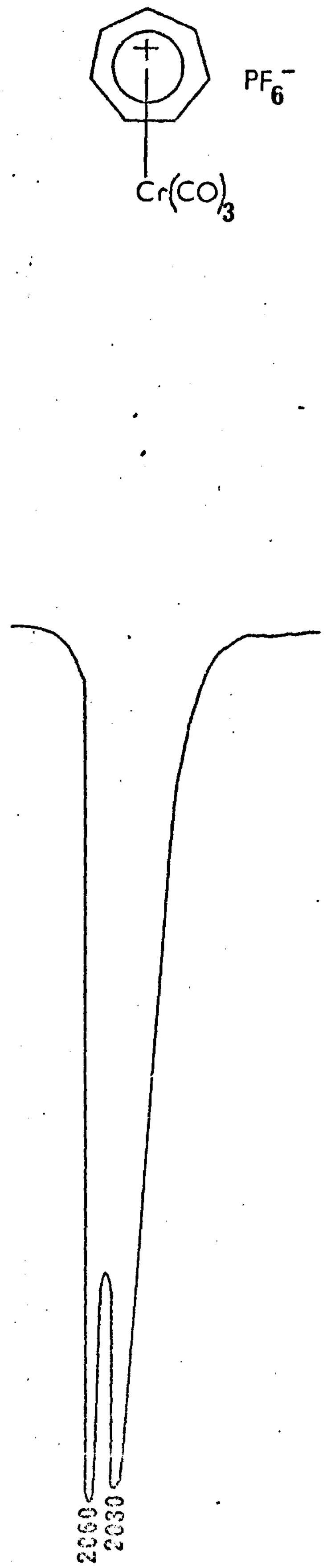


FIGURE 51

solvent: $(CH_3)_2CO$

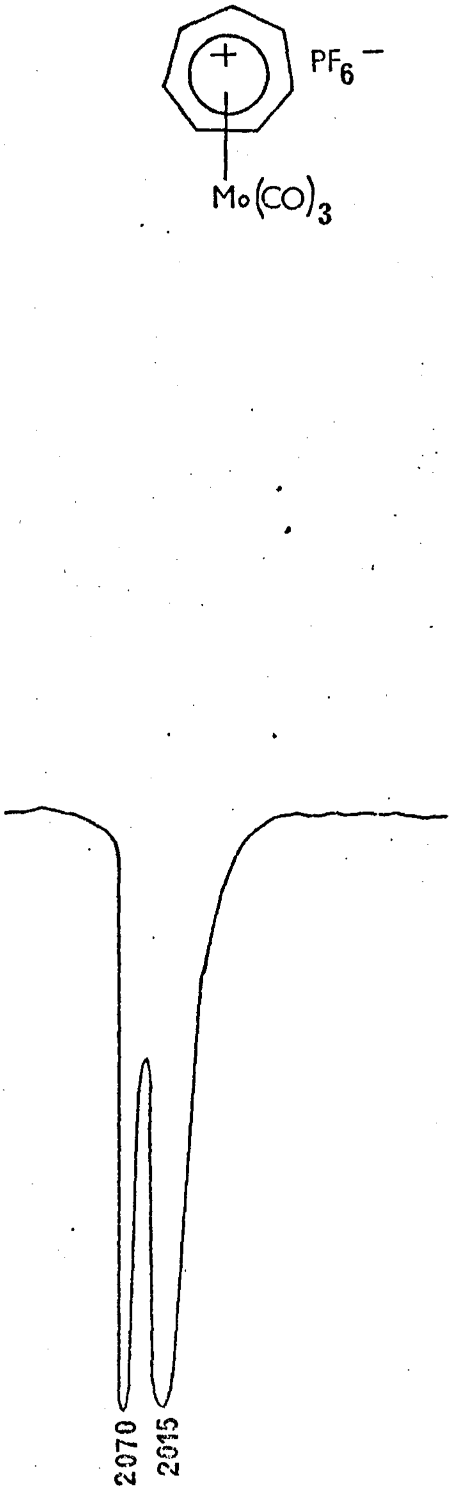
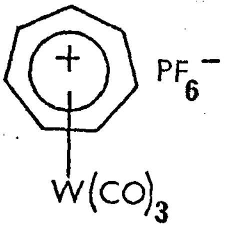


FIGURE 52

Solvent: $(CH_3)_2CO$



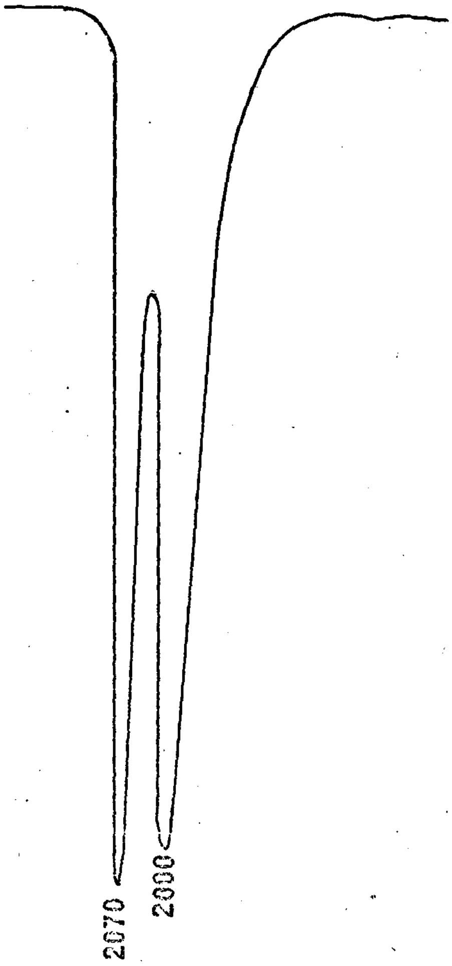


FIGURE 53

solvent: $(CH_3)_2CO$

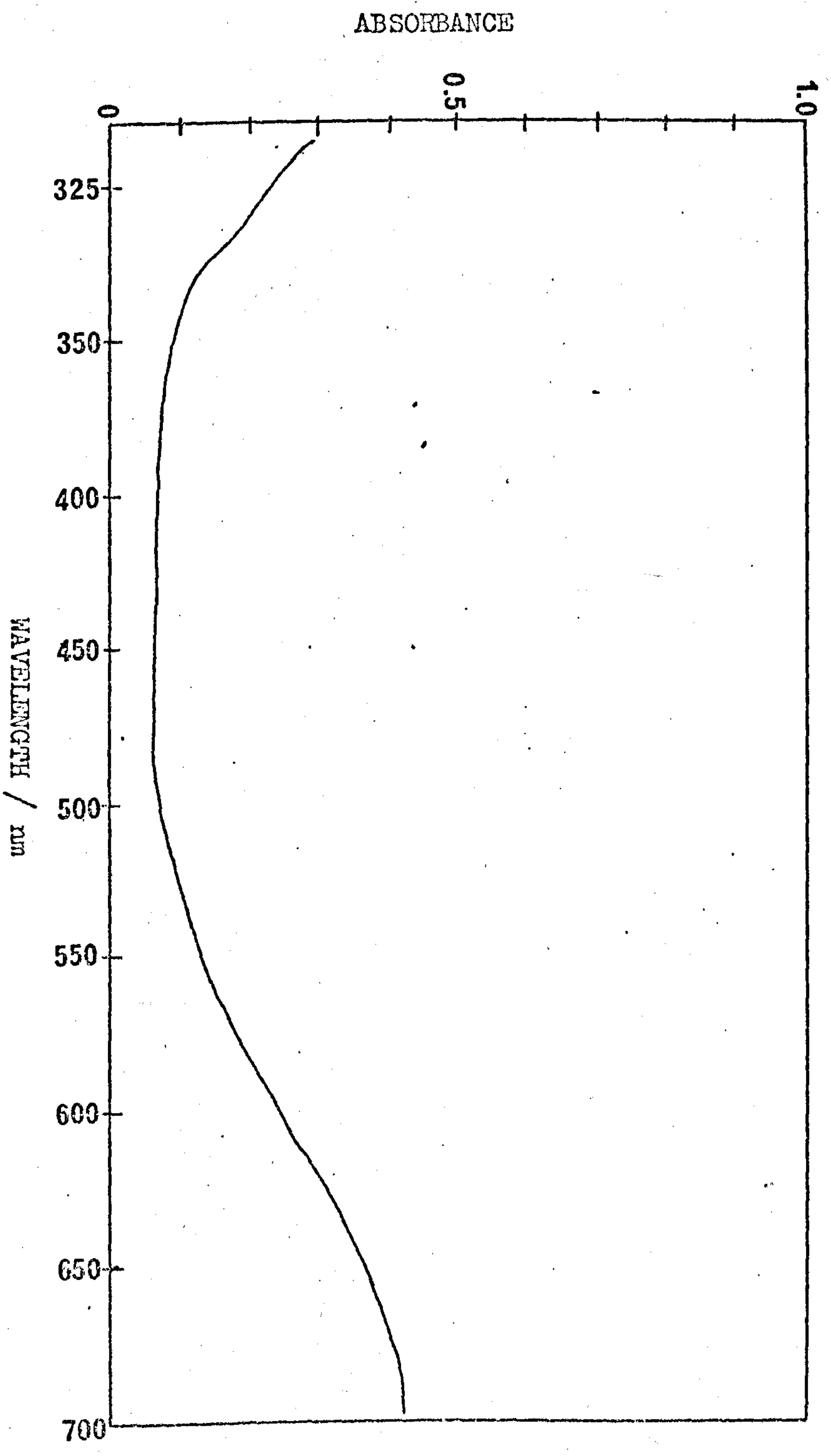


FIGURE 54, $Cr^{2+}aq$

solvent: H_2O

path length: 10 mm

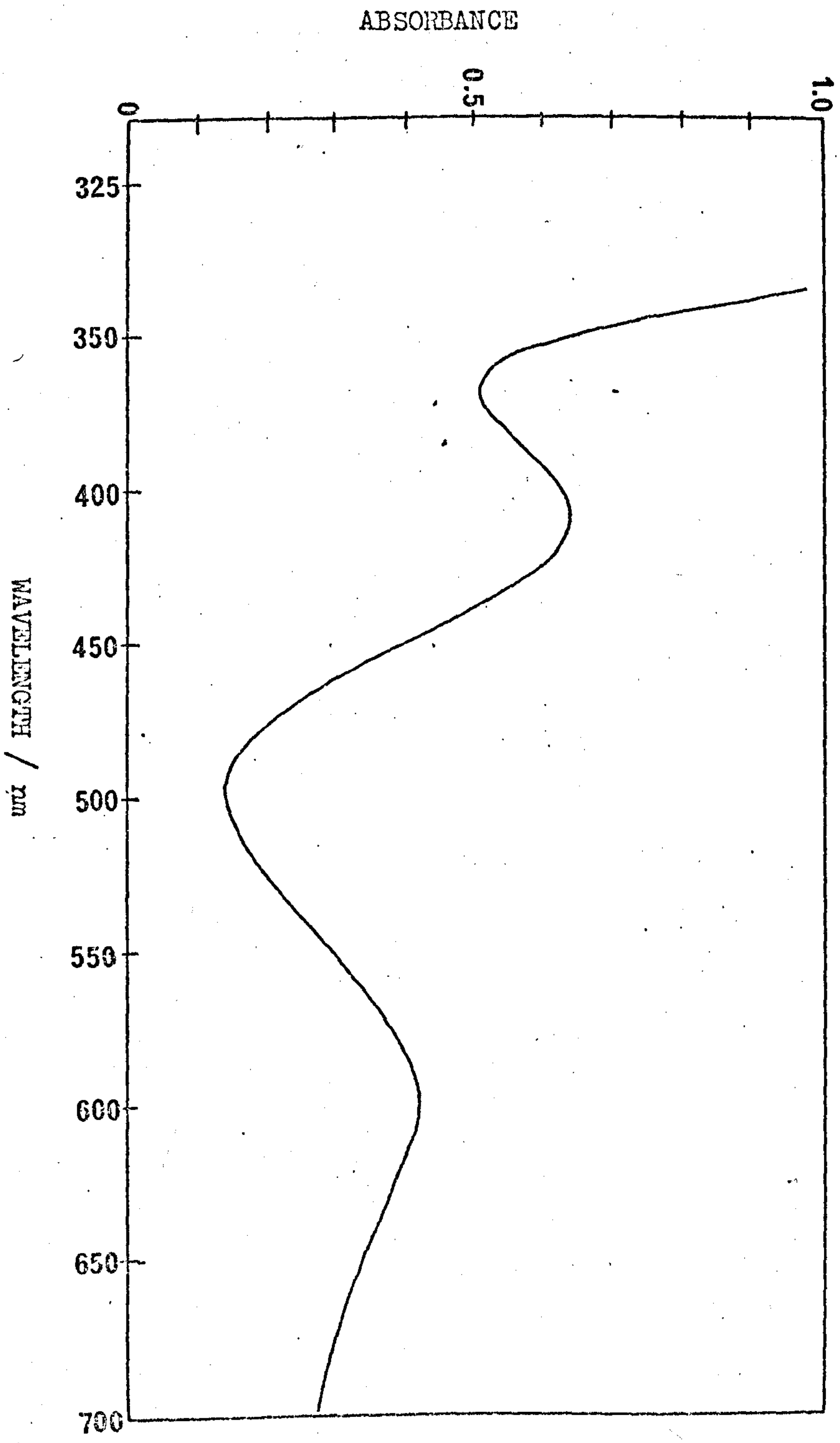


FIGURE 55, $Cr^{3+}aq$

solvent: H_2O

path length: 10 mm

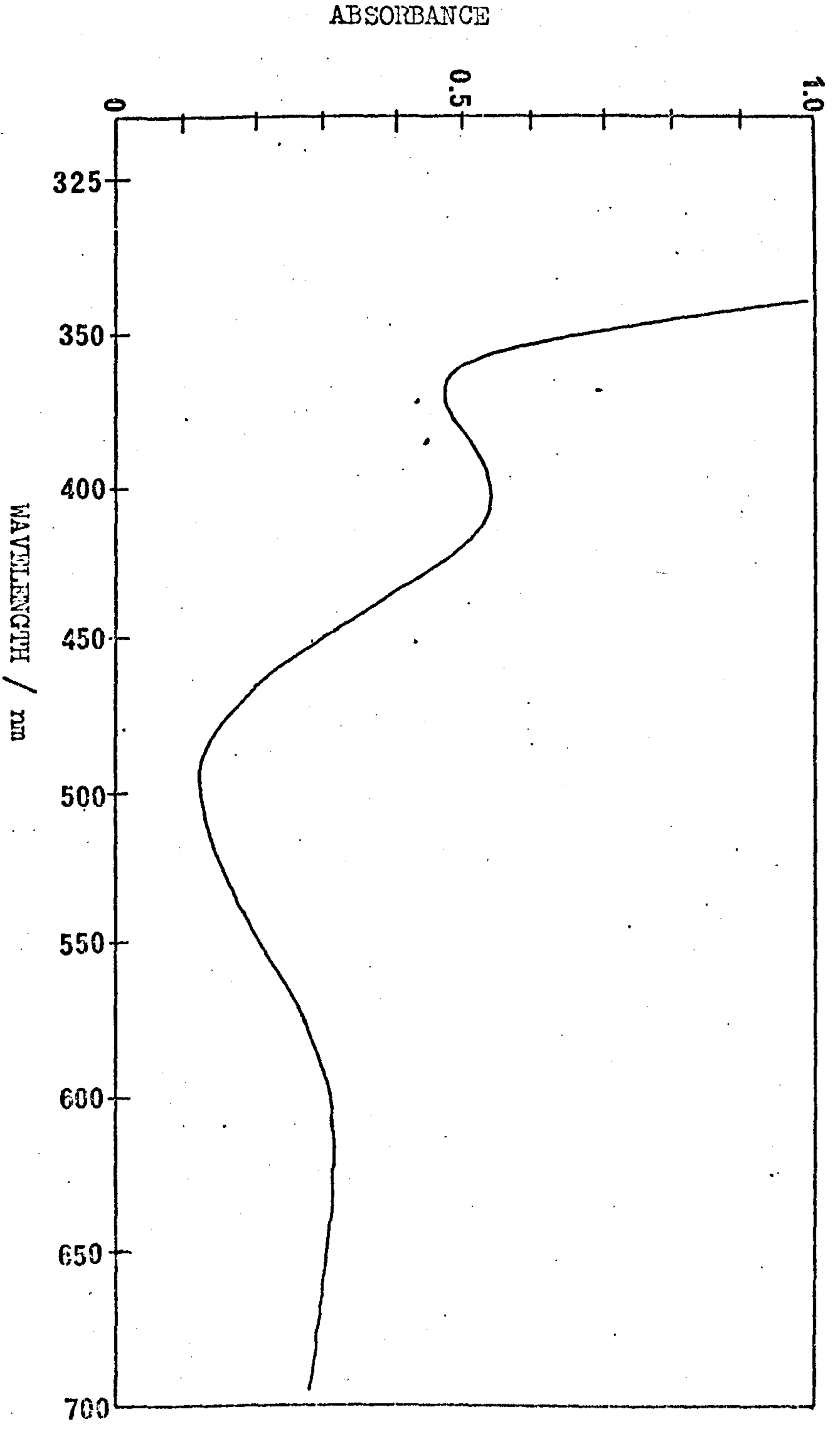
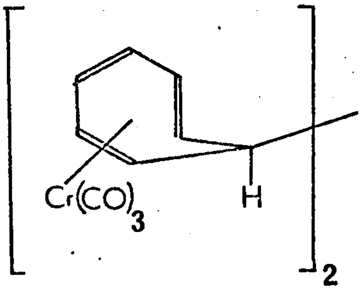


FIGURE 52

Cr^{2+} solution after treatment with $(\eta^7\text{-}C_7H_7)Cr(CO)_3{}^+PF_6^-$

solvent: H_2O

path length: 10 mm



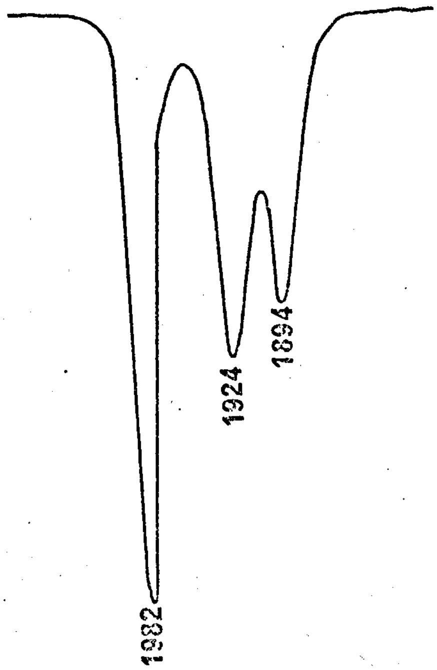
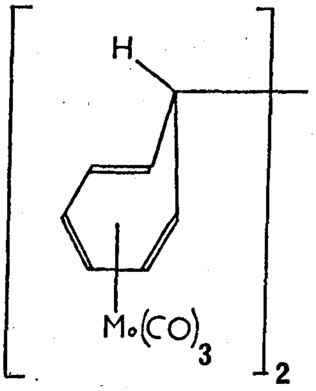


FIGURE 57

solvent: $CHCl_3$



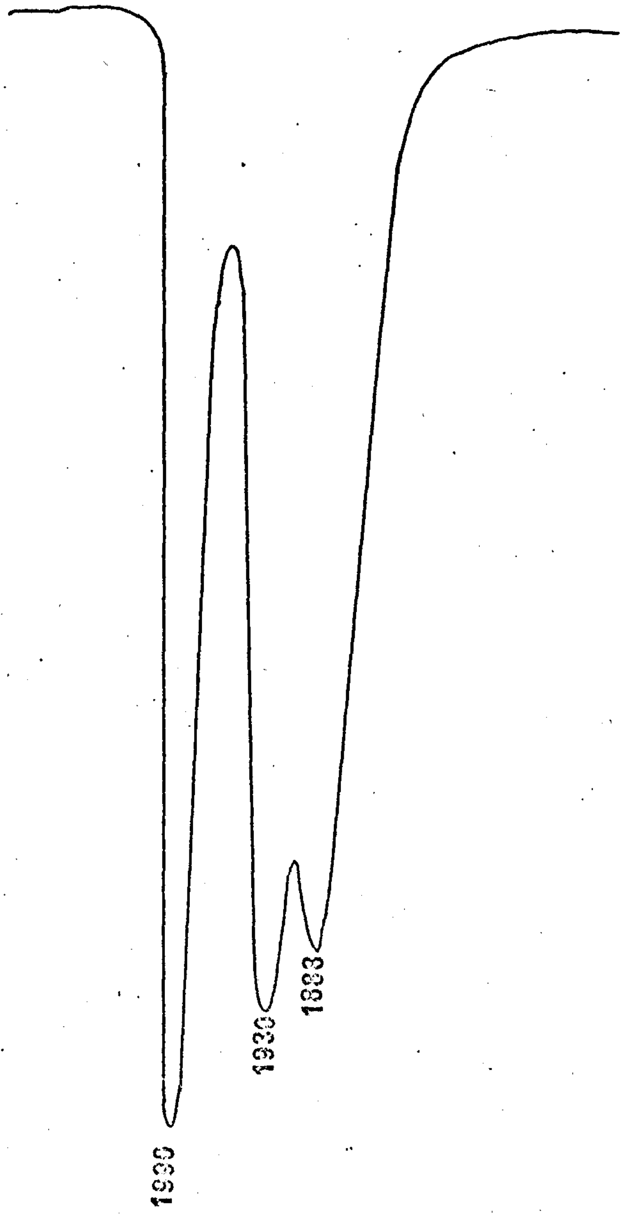


FIGURE 58

solvent: $CHCl_3$

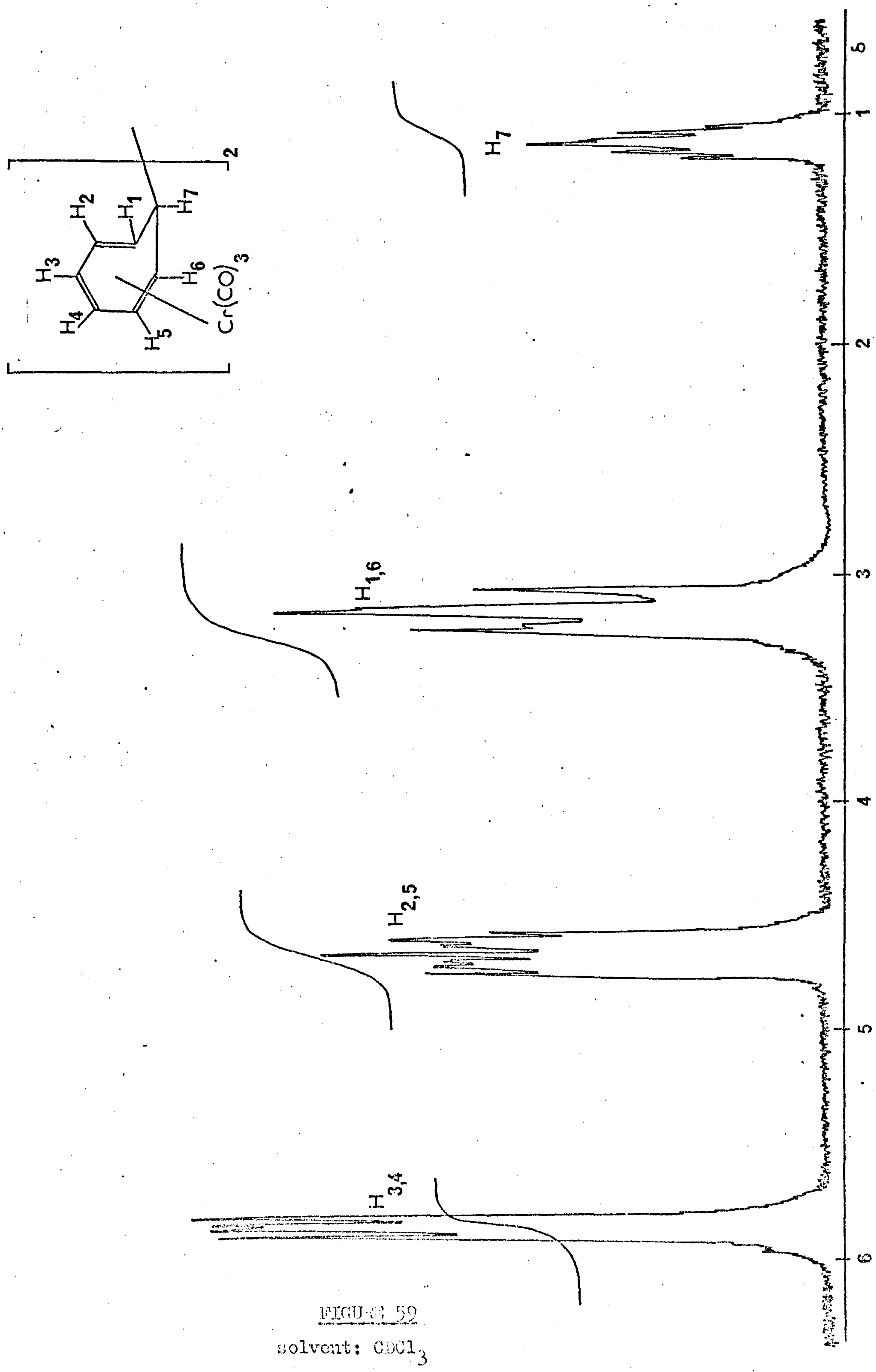


FIGURE 59

solvent: $CDCl_3$

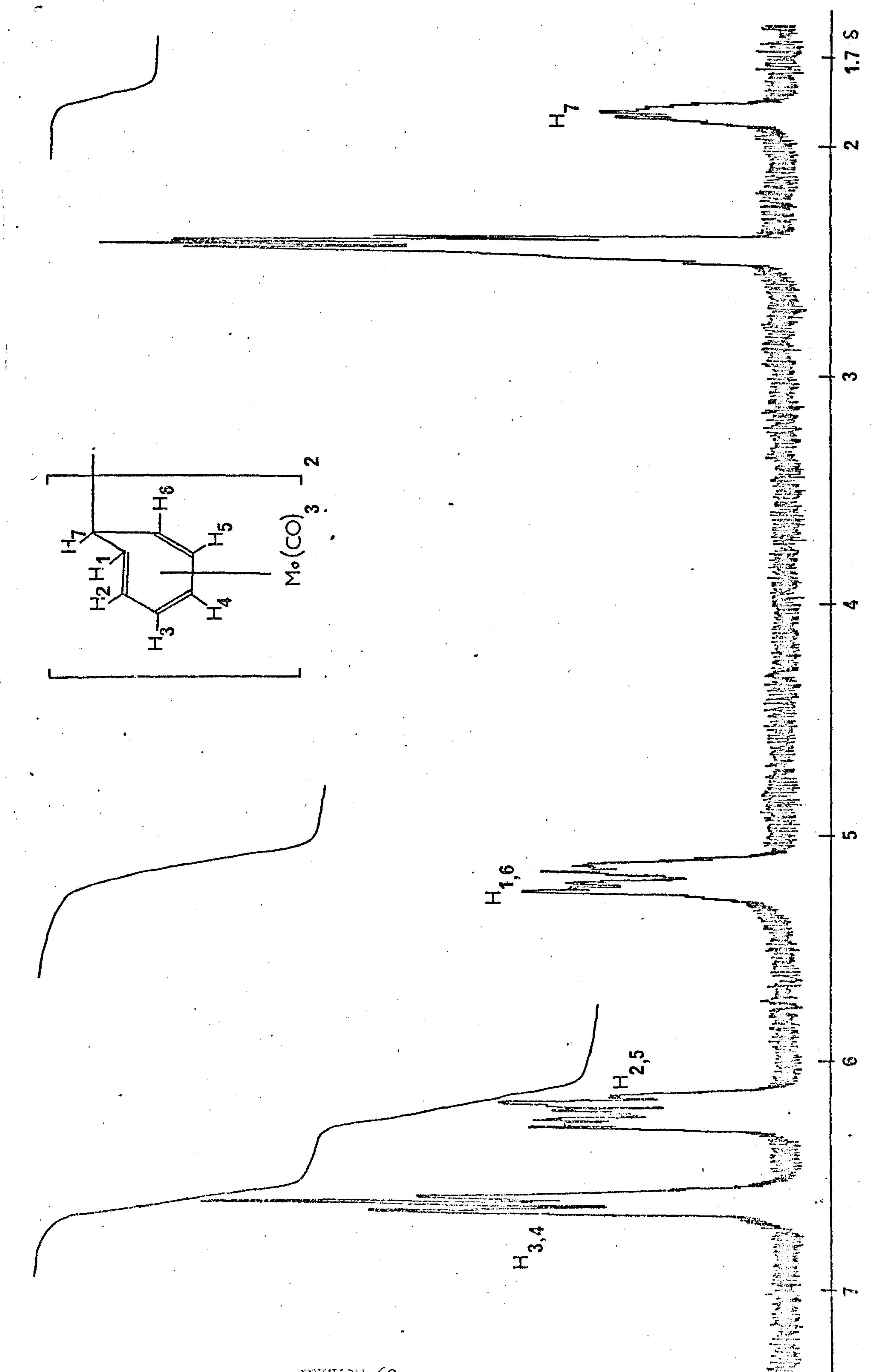


FIGURE 60

solvent: DMSO-d_6

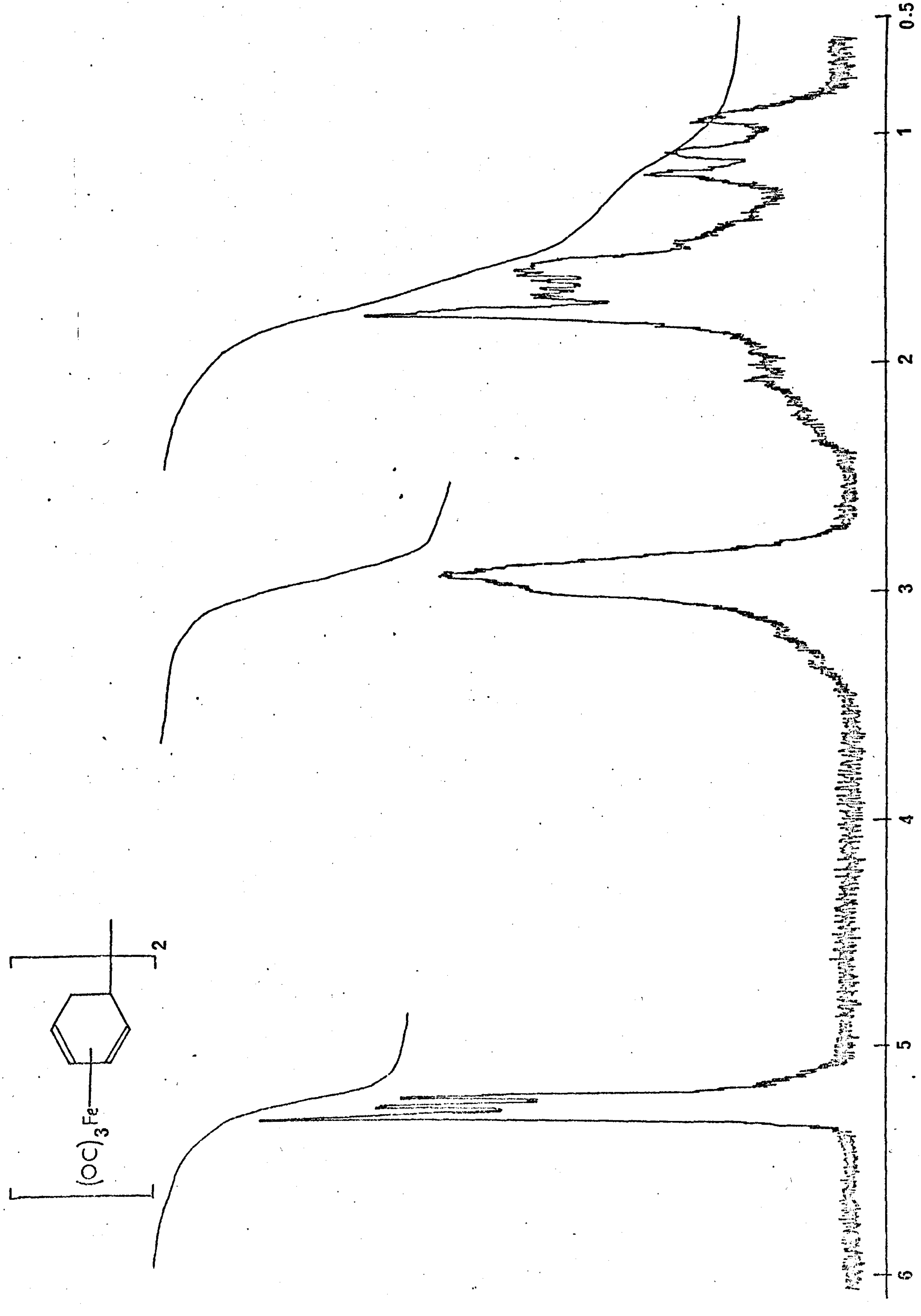
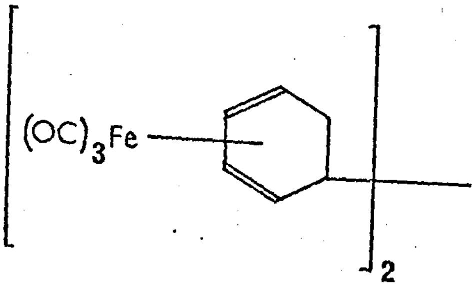


FIGURE 61
solvent: CDCl$_3$



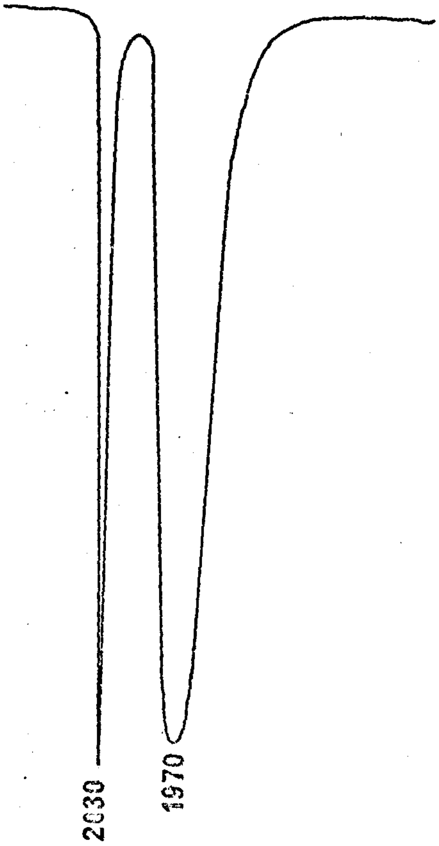


FIGURE 62

solvent: $CHCl_3$

3. ANION OXIDATION REACTIONS

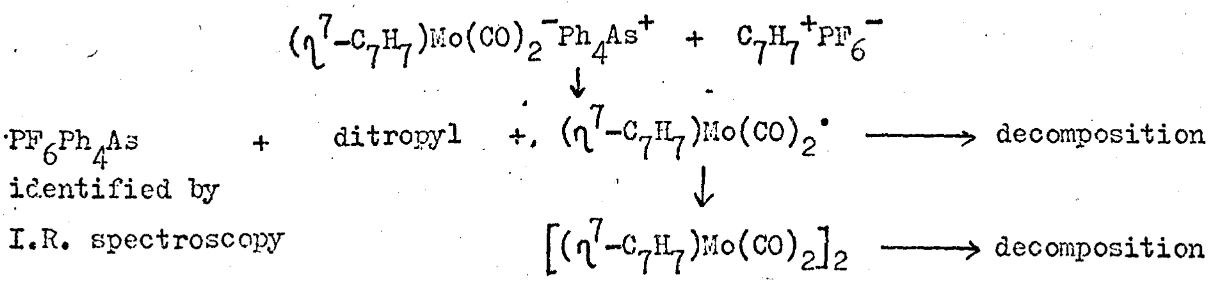
3.1 Results and Discussion

3.2 Experimental

3.1 Results and Discussion

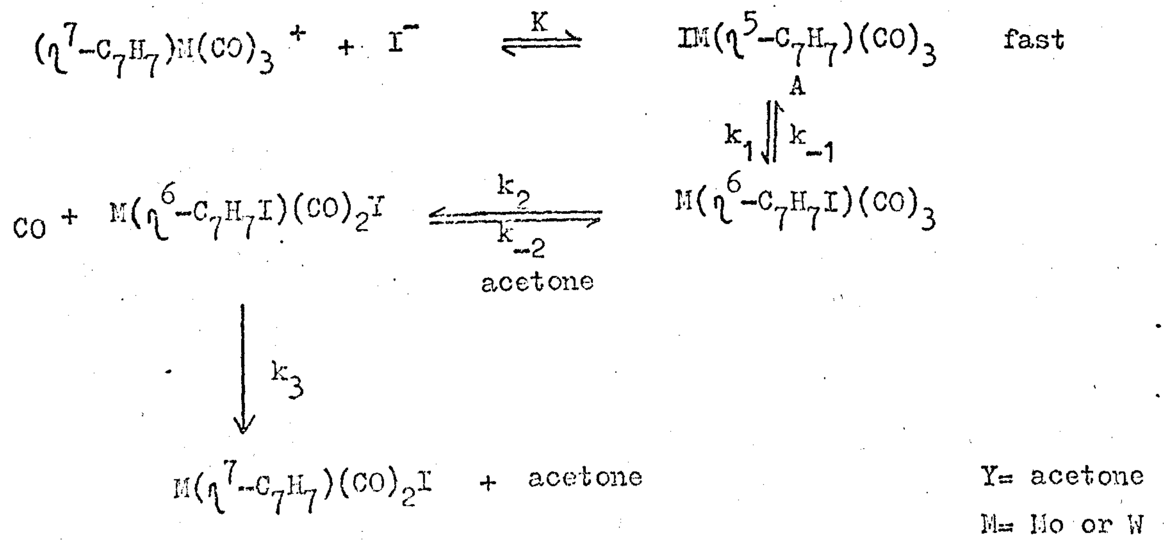
A report has appeared in the literature (102) discussing the dissociation of $[(\eta^5\text{-}C_5H_5)Cr(CO)_3]_2$ in solution into radical species. The preparative route to the dimer involved oxidation of the anion $(\eta^5\text{-}C_5H_5)Cr(CO)_3^-$ with tropylium ion to give the metal-metal bonded dimer and ditropyl.

The oxidation of $(\eta^7\text{-}C_7H_7)Mo(CO)_2^-$ was thus investigated to determine whether an analogous dimeric species could be prepared, and if this were possible, to study its dissociation and the reactivity of the radicals so produced. In the event, the oxidation failed to give a stable product which could be characterised. The probable reaction scheme is given below:

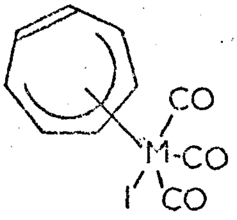


The precursor was prepared by treating a solution of $(\eta^7\text{-}C_7H_7)Mo(CO)_3^+PF_6^-$ with NaI to give $(\eta^7\text{-}C_7H_7)Mo(CO)_2I$ in better than 90% yield. The iodide was then reduced with sodium amalgam (277) to give $(\eta^7\text{-}C_7H_7)Mo(CO)_2^-Na^+$ and the anion subsequently isolated as the tetraphenylarsonium salt.

The kinetics of the reaction of the cation with iodide ion has recently been investigated (278), and the following mechanism proposed:



The structure of intermediate A has been given as :



A

3.2 Experimental

The preparation of $(\eta^7\text{-}C_7H_7)Mo(CO)_2I$, its reduction with Na/Hg and subsequent oxidation with tropylium ion

A solution of $(\eta^7\text{-}C_7H_7)Mo(CO)_3{}^+PF_6^-$ (270 mg, 6.5×10^{-4} mole) in acetone (15 ml) was treated with NaI (0.10 g, 6.6×10^{-4} mole) under N_2. The reaction mixture became dark green with gas evolution. After stirring at room temperature for 3 hours, the solvent was removed to give a black-green solid, 220 mg (92.8% based on $(\eta^7\text{-}C_7H_7)Mo(CO)_2I$), ν $C\equiv O$ 2020 (vs), 1969 (s, br) cm^{-1} (lit (277) $(\eta^7\text{-}C_7H_7)Mo(CO)_2Cl$ 2023 (vs), 1975 (s) cm^{-1}).

This solid was then treated with sodium amalgam (1.4 g, 1%), and infra-red spectroscopy confirmed that all the starting material had been consumed within 10 minutes. After 1 hour the solution was siphoned off the excess amalgam and concentrated to a red solid. This was extracted into water and transferred to an aqueous solution of tetraphenylarsonium chloride. An immediate buff coloured precipitate formed which was isolated by filtration, and dried in vacuo 0.178 g (46.6% based on $(\eta^7\text{-}C_7H_7)Mo(CO)_2{}^-Ph_4As^+$; ν $C\equiv O$ (KBr disc), 1930 (vs), 1860 (s) cm^{-1}. A sample of $(\eta^7\text{-}C_7H_7)Mo(CO)_2{}^-Ph_4As^+$ (0.1 g; 1.61×10^{-4} mole) in methanol (10 ml) was treated with tropylium hexafluorophosphate (0.038 g; 1.6×10^{-4} mole). An immediate white precipitate formed which was collected and dried to give 75 mg (87.6% based on $Ph_4As^+PF_6^-$); ν (KBr disc) 810 (s, P-Fstr), 1490 (s) cm^{-1}. The filtrate was concentrated to a red solid (70 mg), devoid of any type of carbonyl ligands as demonstrated by infra-red spectroscopy.

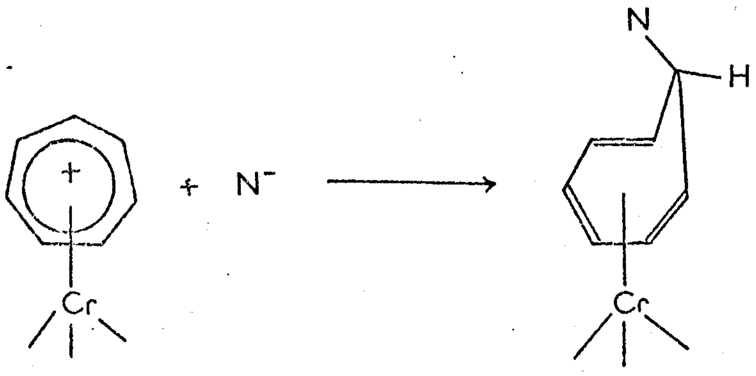
4 CONCLUSIONS AND COMMENTS

The chemical reduction of cations derived from olefin complexes of the Groups VIA and VIII metal carbonyls has been found to yield ligand bridged dimers of the first-formed radicals, but the stereochemistry of these complexes could not be conclusively deduced. The oxidation of an anionic species has led to an extremely air sensitive product which could not be isolated nor characterised.

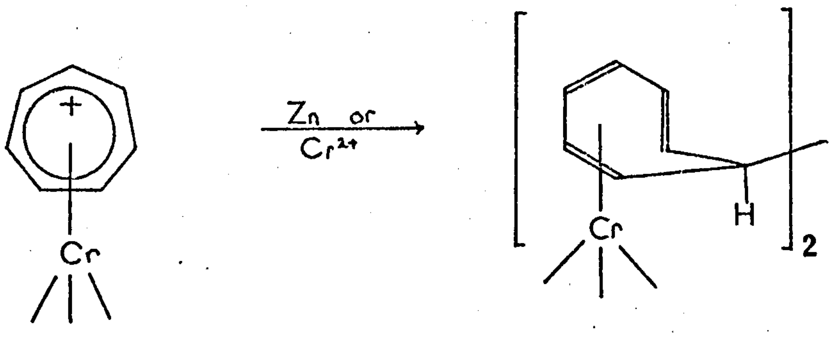
The different products obtained by reactions of various nucleophiles with $(\eta^7\text{-}C_7H_7)M(CO)_3{}^+$ (M = Cr, Mo, W) is of some relevance to this study. Thus reaction with, for example, methoxide ion generates a ring substituted derivative, but reactions with halide and pseudohalide ions give products in which the planar cycloheptatrienyl ring persists and a carbonyl ligand is displaced. At first sight, these alternative modes of attack might suggest that one-electron reduction should occur at either the metal or the seven-membered ring, whereas the products isolated suggest the latter to be the case. It is noteworthy that a recent study of reaction of $(\eta^7\text{-}C_7H_7)M(CO)_3{}^+$ (M = Mo, W) with iodide ions indicates that even in these cases, initial nucleophilic attack occurs at the ring and that the metal-iodo complex is formed subsequently from the intermediate $(\eta^6\text{-}C_7H_7I)M(CO)_3$.

It therefore, appears that one electron reduction reactions of organometallic cations parallel the reactions of these complexes with nucleophiles. Thus, the salient feature of such reactions is the nature of the LUMO in the cationic substrate, those of $(\eta^7\text{-}C_7H_7)M(CO)_3$ (M = Cr, Mo, W) and $(\eta^5\text{-}C_6H_7)Fe(CO)_3$ being principally ligand based, whereas those of $(\eta^5\text{-}C_5H_5)Fe(CO)_2L$ (L = CO, $P(OPh)_3$) are principally of metallic character. This is summarised in the following examples:

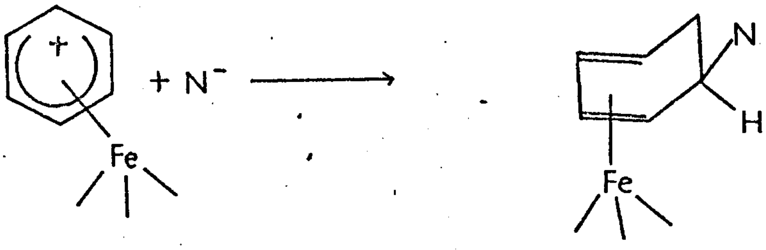
(carbonyl groups ommited for clarity)



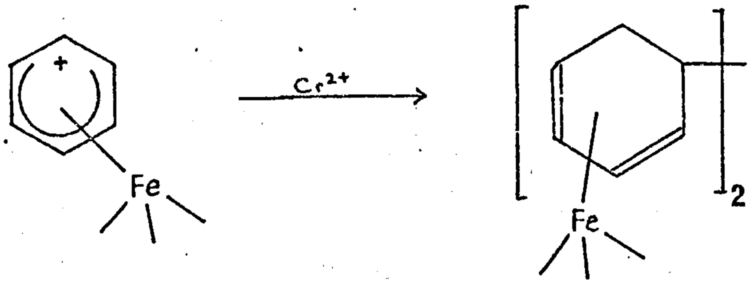
N.= SH; $CMe(CO_2Et)_2$
OMe. ref 165



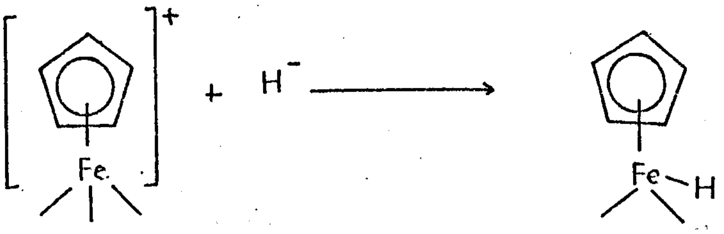
ref 165,
this work



N = OMe;CN;
OH. ref 265



this work



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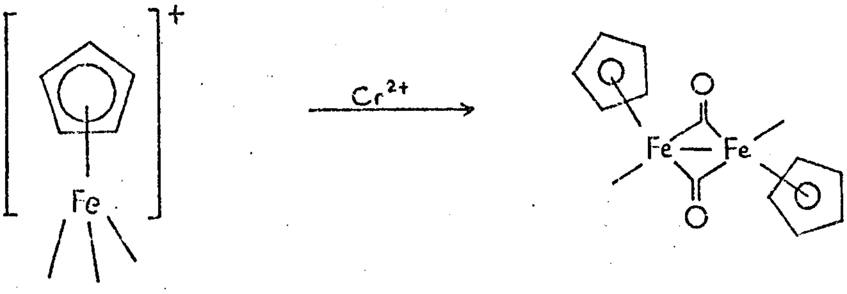


ref 274

APPENDIX 1

The Mass Spectra of the Compounds Discussed in Chapters 2 and 3

Mass spectrometry is becoming increasingly important in the characterisation of new compounds. In this respect the complexes prepared in Chapters 2 and 3 were found to be good subjects for this type of study, being both volatile and thermally stable. Part 1 of this Appendix covers those compounds discussed in Chapter 2 and Part 2 those in Chapter 3. Isotope patterns for the various clusters of metal atoms are also presented, and in many cases the molecular ion, and ions formed by subsequent loss of carbonyl ligands, were seen to have this arrangement. Mass spectrometry provided a convenient and positive method of analysis, which when considered together with infra-red spectroscopy served to completely characterise the material.

PART 1

No report has appeared in the literature discussing the mass spectra of phosphane or phosphite derivatives of decacarbonyldirhenium, although that of the decacarbonyl and the pentacarbonylhydride are known (280). In the latter, it was found that competitive loss of carbon monoxide molecules and the terminal hydride ligand occurs, and this can lead to confusion over the exact determination of fragmentation pathways since the metal is polyisotopic. In complexes containing bridging hydride units, loss of $H^{\bullet}$ does not occur until several carbonyl moieties have been lost.

The mass spectra of both the equatorial and the axial isomers of $Re_2(CO)_9(PPh_3)$ are given in Figures 1 and 2. The greater abundance of molecular ions for the axial isomer is taken to be a consequence of reduced steric strain experienced by the metal-metal bond in this configuration. Substitution into the equatorial site would force the equatorial carbonyl ligands on the second metal atom away from their preferred position so this dimer would be more likely to decompose before detection. Thus, all of the ions from the equatorial complex are reduced in intensity.

The spectra of the three bis-substituted hydrides (mer-trans $HRe(CO)_3L_2$, L = PPh_3, $P(C_6H_{11})_3$ and $P(o\text{-tolyl})_3$; Figures 4, 6 and 7) showed a trend of molecular ion abundance paralleling the variation of the electronic parameters for these ligands (238). The origin and measurement of this parameter has been discussed earlier (Section 3.1.1).

Relative abundance of M^+ in $HRe(CO)_3L_2$	L	ν/cm^{-1} (238)
92.16	$P(C_6H_{11})_3$	2056.4
58.82	$P(o\text{-}tol)_3$	2066.7
11.11	PPh_3	2068.9

This sequence has been rationalised in the following way. During the interaction of the bombarding electron and the molecule, bonding orbitals have been found to be most readily excited and to therefore, preferentially emit an electron (281). In the mononuclear hydrides, the electron is thus lost from a back-bonding π type orbital. Electron-releasing ligands will to a certain extent serve to make up this electron-deficiency, and therefore, help..to stabilise the ion with respect to fragmentation. Molęcular ions for hydrides which possess such groups will therefore be in greater abundance than those that do not.

In the case of the metalated complexes fac-$Re(CO)_3L(L\text{-}H)$, L = PPh_3; $P(OPh)_3$; P(O-otolyl); Figures 5, 8 and 9) a different feature has been invoked to rationalise the abundances of the molecular ions observed in the spectra of the three complexes. The Table below presents the salient data;

Abundance of M^+ in $Re(CO)_3L(L\text{-}H)$	L	ν/cm^{-1} (238)
23.34	PPh_3	2068.9
56.45	$P(O\text{-}o\text{-}tol)_3$	2084.1
12.90	$P(OPh)_3$	2085.3

The tri(o-tolyl)phosphite and tri(phenyl) phosphite complexes are directly comparable since the metalation ring in each contains the same number of atoms. Between these two a similar trend to that noted for the hydrido complexes is found: as the value of the electronic parameter increases, that is, as the ligands become poorer σ donors, so the abundance of the molecular ion declines. The triphenylphosphane complex appears out of sequence, but this is assumed to be a consequence of the strained nature of the metalated ring, causing more facile fragmentation of the molecule, resulting in a reduced molecular ion abundance.

Part 1.1

Mass Spectra of Compounds discussed in Chapter 2

The molecular weights of the fragments observed in the mass spectra are based on the isotope ^{185}Re. The spectra presented are listed below:

Spectrum number	Complex
1	eq-$Re_2(CO)_9PPh_3$
2	ax-$Re_2(CO)_9PPh_3$
3	cis-$HRe(CO)_4PPh_3$
4	mer-trans-$HRe(CO)_3(PPh_3)_2$
5	fac-$Re(CO)_3L(L{-}H)$, L = PPh_3
6	mer-trans-$HRe(CO)_3\ P(C_6H_{11})_{3\ 2}$
7	mer-trans-$HRe(CO)_3L_2$, L = tri(p-tolyl)phosphane
8	fac-$Re(CO)_3L(L{-}H)$, L = $P(OPh)_3$
9	fac-$Re(CO)_3L(L{-}H)$, L = tri(o-tolyl)phosphite
10	$Re(CO)_4(L{-}H)$, L = tri(o-tolyl)-phosphane
11	$H_3Re_3(CO)_{12}$
12	$Re_4Cl_4(CO)_{12}$

ISOTOPE PATTERNS

The isotope patterns were calculated by substituting the natural abundances of ^{185}Re (37.07%) and ^{187}Re(62.93%) into the formula $(a + b)^n$ where n is the number of metal atoms being considered.

Isotope pattern for one rhenium atom

m/e	RI
185	58.9
187	100.0

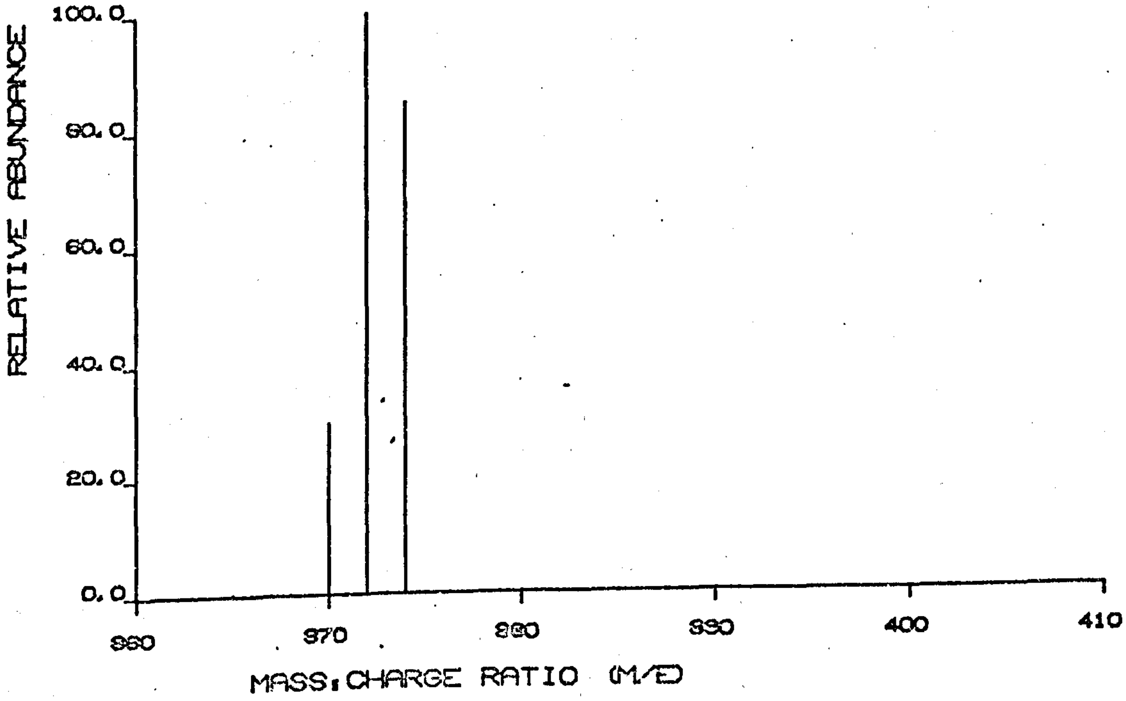
Isotope pattern for two rhenium atoms

m/e	RI
370	29.5
372	100.0
374	84.9

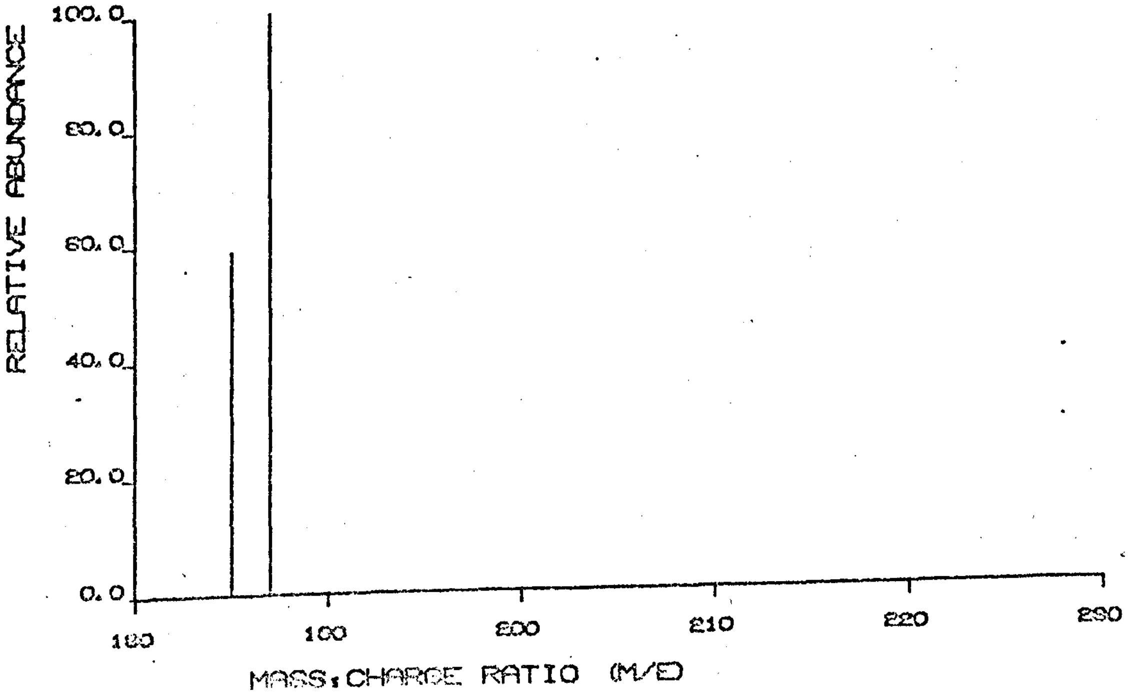
Isotope pattern for three rhenium atoms

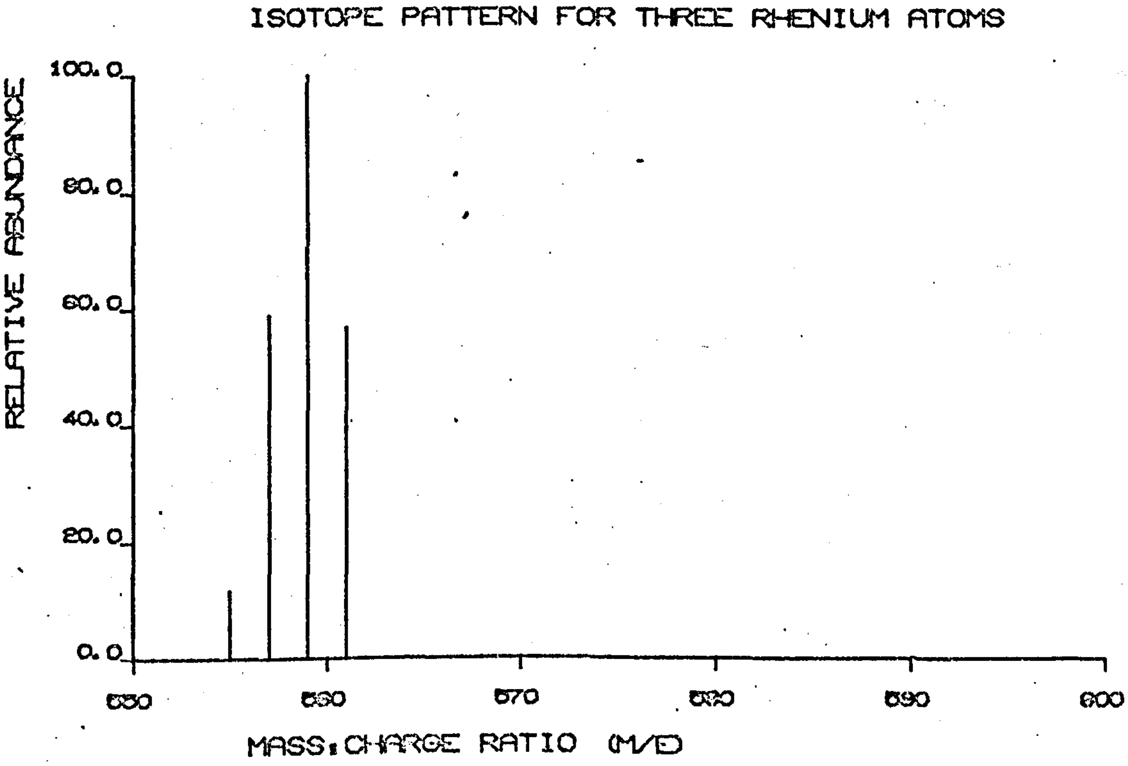
m/e	RI
555	11.5
557	58.9
559	100.0
561	56.6

ISOTOPE PATTERN FOR TWO RHENIUM ATOMS



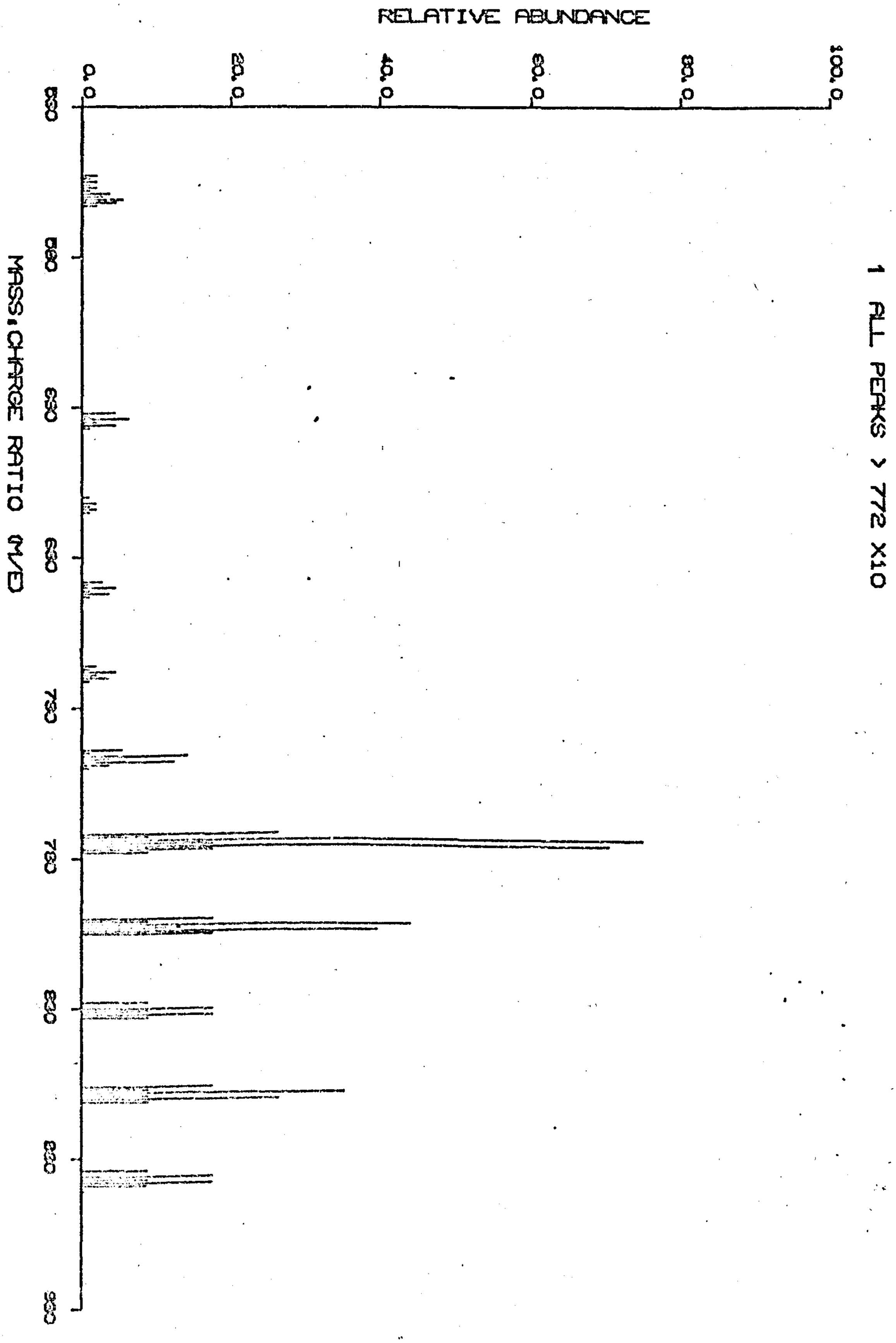
ISOTOPE PATTERN FOR ONE RHENIUM ATOM



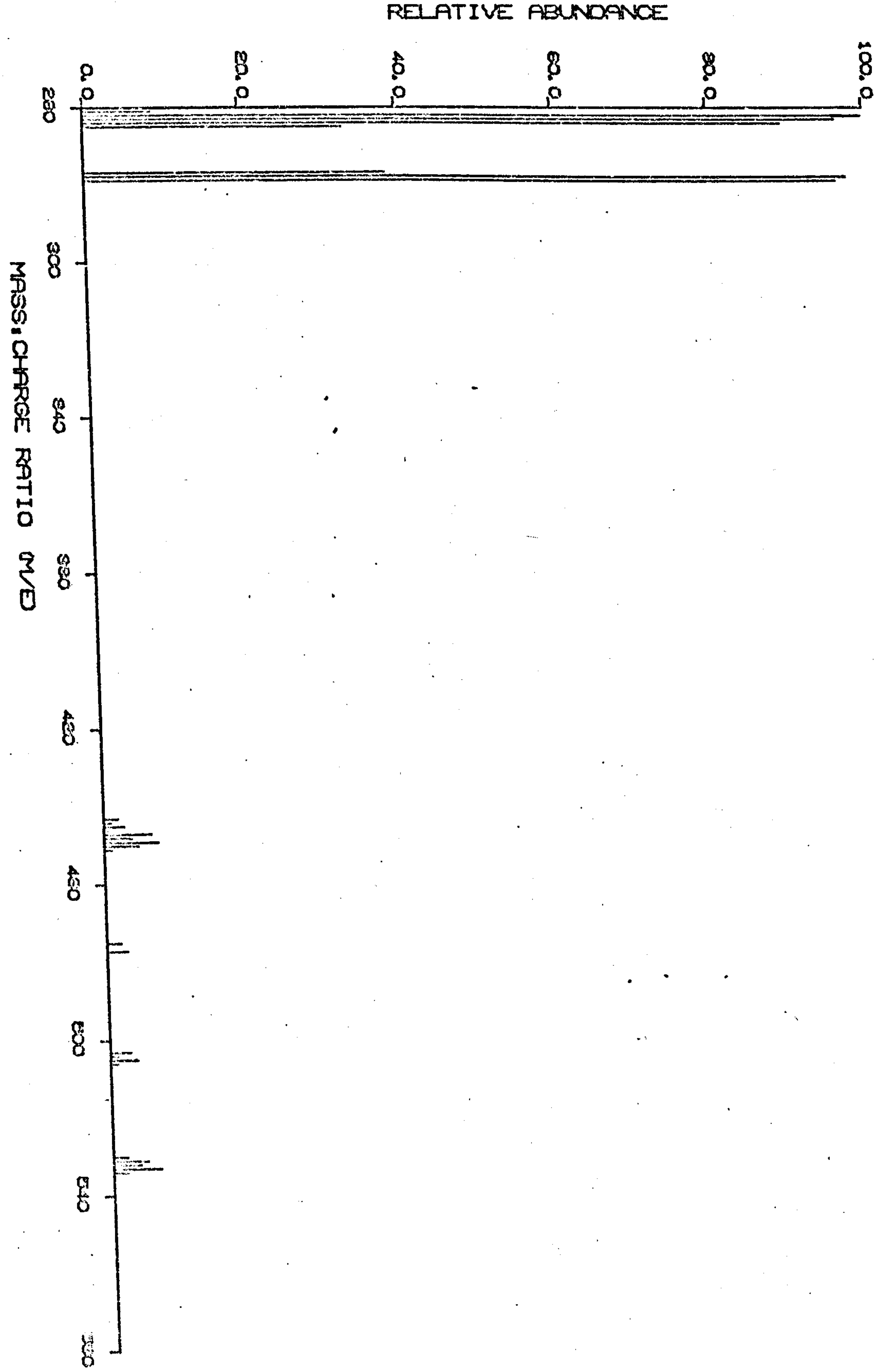

ISOTOPE PATTERN FOR THREE RHENIUM ATOMS

SPECTRUM 1 eq $Re_2(CO)_9(PPh_3)$

m/e	RI	Assignment
884	0.87	$Re_2(CO)_9(PPh_3)^+$
856	1.75	$Re_2(CO)_8(PPh_3)^+$
828	0.87	$Re_2(CO)_7(PPh_3)^+$
800	1.75	$Re_2(CO)_6(PPh_3)^+$
772	2.63	$Re_2(CO)_5(PPh_3)^+$
744	5.26	$Re_2(CO)_4(PPh_3)^+$
716	1.75	$Re_2(CO)_3(PPh_3)^+$
688	2.63	$Re_2(CO)_2(PPh_3)^+$
660	0.88	$Re_2(CO)(PPh_3^+$
632	4.39	$Re_2(PPh_3)^+$
447	6.14	$Re(PPh_3)^+$
262	100.00	PPh_3^+
559	3.51	$Re(CO)_4(PPh_3)^+$
531	4.39	$Re(CO)_3(PPh_3)^+$
503	2.63	$Re(CO)_2(PPh_3)^+$
475	1.75	$Re(CO)(PPh_3)^+$
447	6.14	$Re(PPh_3)^+$
262	100.00	PPh_3^+
325	v.wk	$Re(CO)_5^+$ further fragment ions from this species were not detected


1 ALL PEAKS > 772 X10
RELATIVE ABUNDANCE
0.0
20.0
40.0
60.0
80.0
100.0
530
580
630
680
730
780
830
880
930
MASS:CHARGE RATIO (M/E)

1.8


RELATIVE ABUNDANCE
0.0
20.0
40.0
60.0
80.0
100.0
260
300
340
380
420
460
500
540
580
MASS:CHARGE RATIO (M/E)

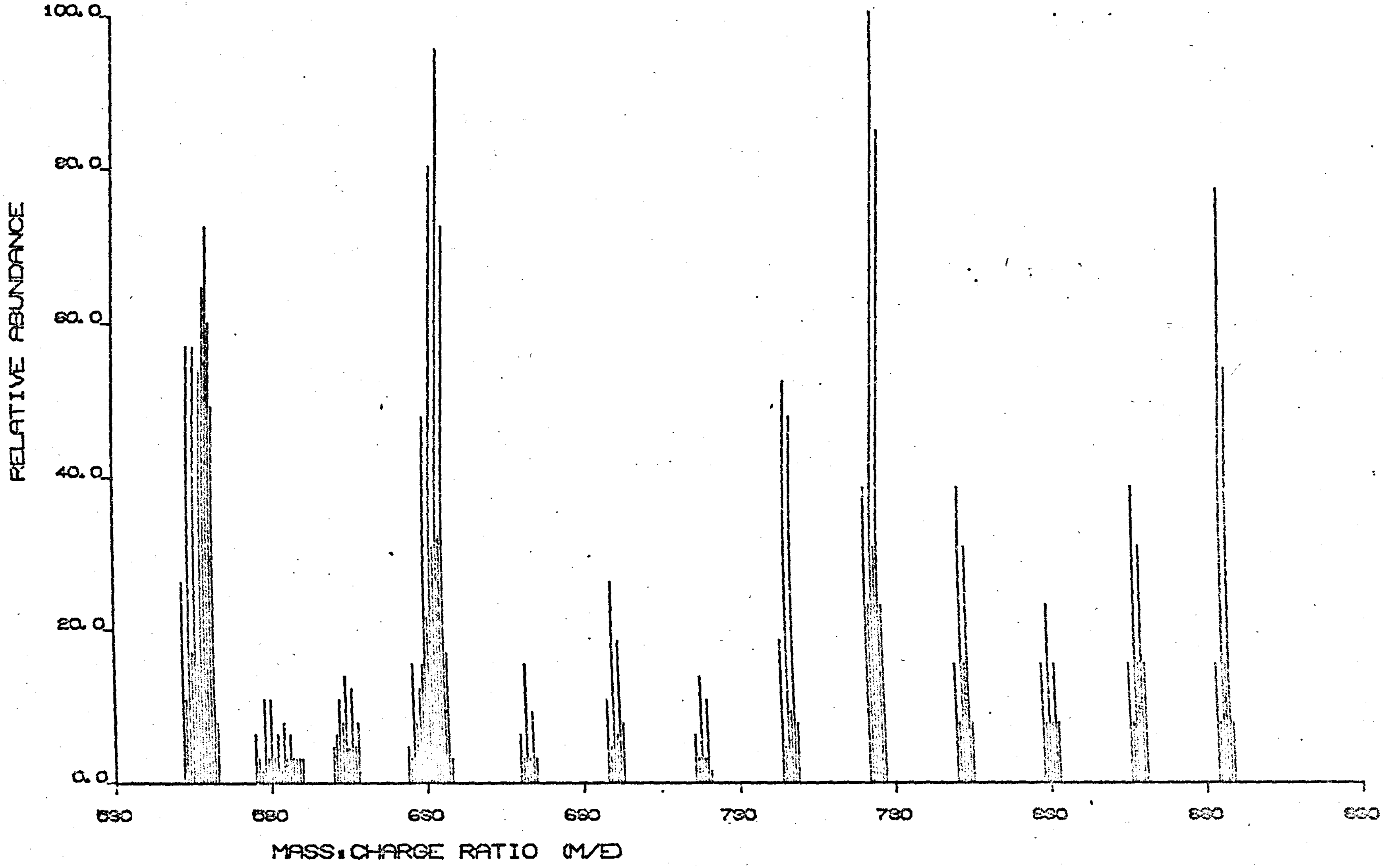
1

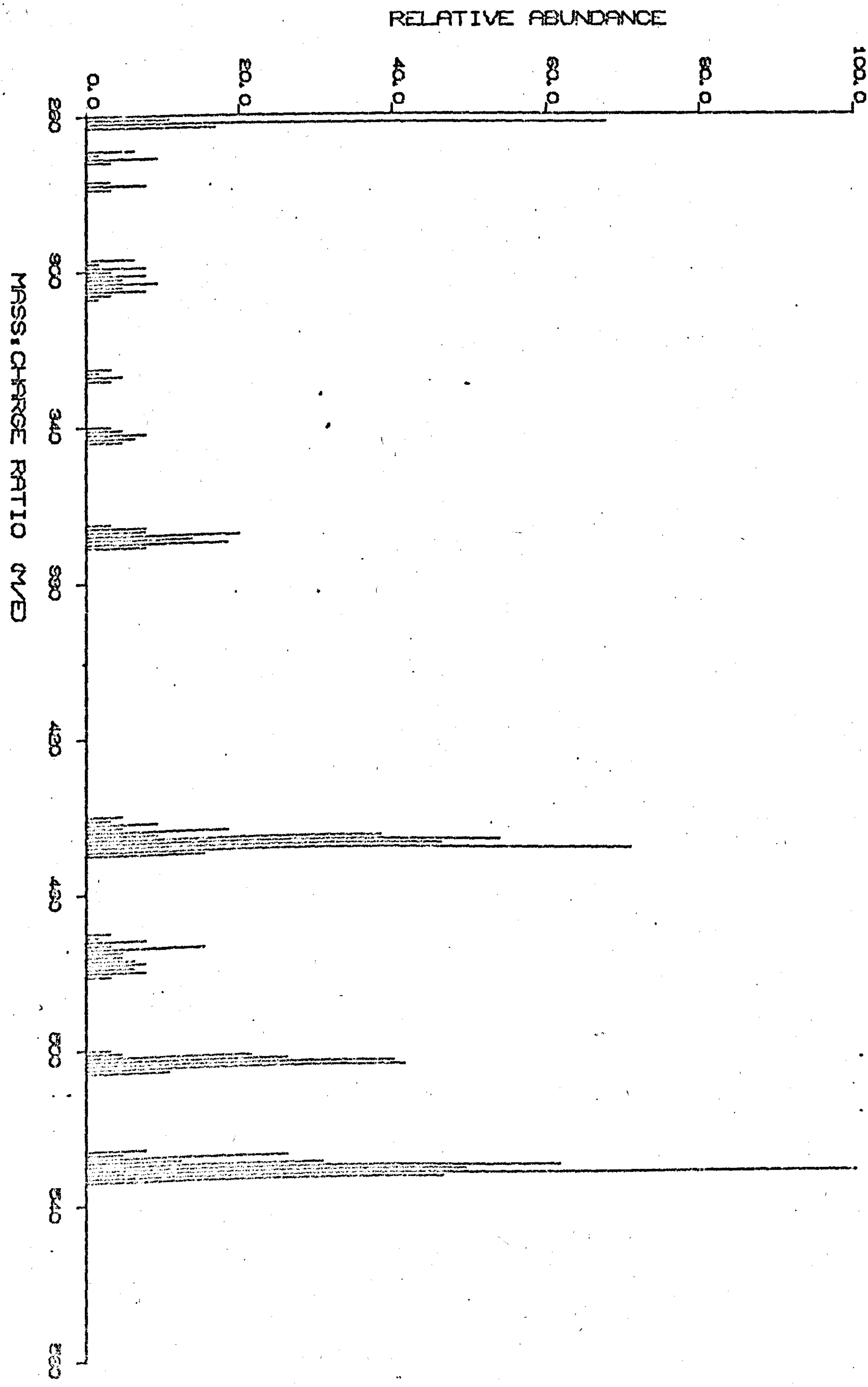
SPECTRUM 2 ax-$Re_2(CO)_9(PPh_3)$

m/e	RI	Assignment
884	15.38	$Re_2(CO)_9(PPh_3)^+$
856	15.38	$Re_2(CO)_9(PPh_3)^+$
828	15.38	$Re_2(CO)_7(PPh_3)^+$
800	15.38	$Re_2(CO)_6(PPh_3)^+$
772	38.46	$Re_2(CO)_5(PPh_3)^+$
744	18.46	$Re_2(CO)_4(PPh_3)^+$
716	6.15	$Re_2(CO)_3(PPh_3)^+$
588	10.77	$Re_2(CO)_2(PPh_3)^+$
660	6.15	$Re_2(CO)(PPh_3)^+$
632	80.00	$Re_2(PPh_3)^+$
447	53.85	$Re(PPh_3)^+$
262	67.69	PPh_3^+
559	54.62	$Re(CO)_4(PPh_3)^+$
531	61.54	$Re(CO)_3(PPh_3)^+$
503	26.15	$Re(CO)_2(PPh_3)^+$
475	4.62	$Re(CO)(PPh_3)^+$
447	53.85	$Re(PPh_3)^+$
262	67.69	PPh_3^+
365	3.08	$Re(CO)_5^+$
297	6.15	$Re(CO)_4^+$
269	6.15	$Re(CO)_3^+$

further losses in this sequence not detectable

2


RELATIVE ABUNDANCE
100.0
80.0
60.0
40.0
20.0
0.0
530
580
630
680
730
780
830
880
930
MASS:CHARGE RATIO (M/E)


RELATIVE ABUNDANCE
0.0
20.0
40.0
60.0
80.0
100.0
MASS:CHARGE RATIO (M/E)
260
300
340
380
420
460
500
540
580

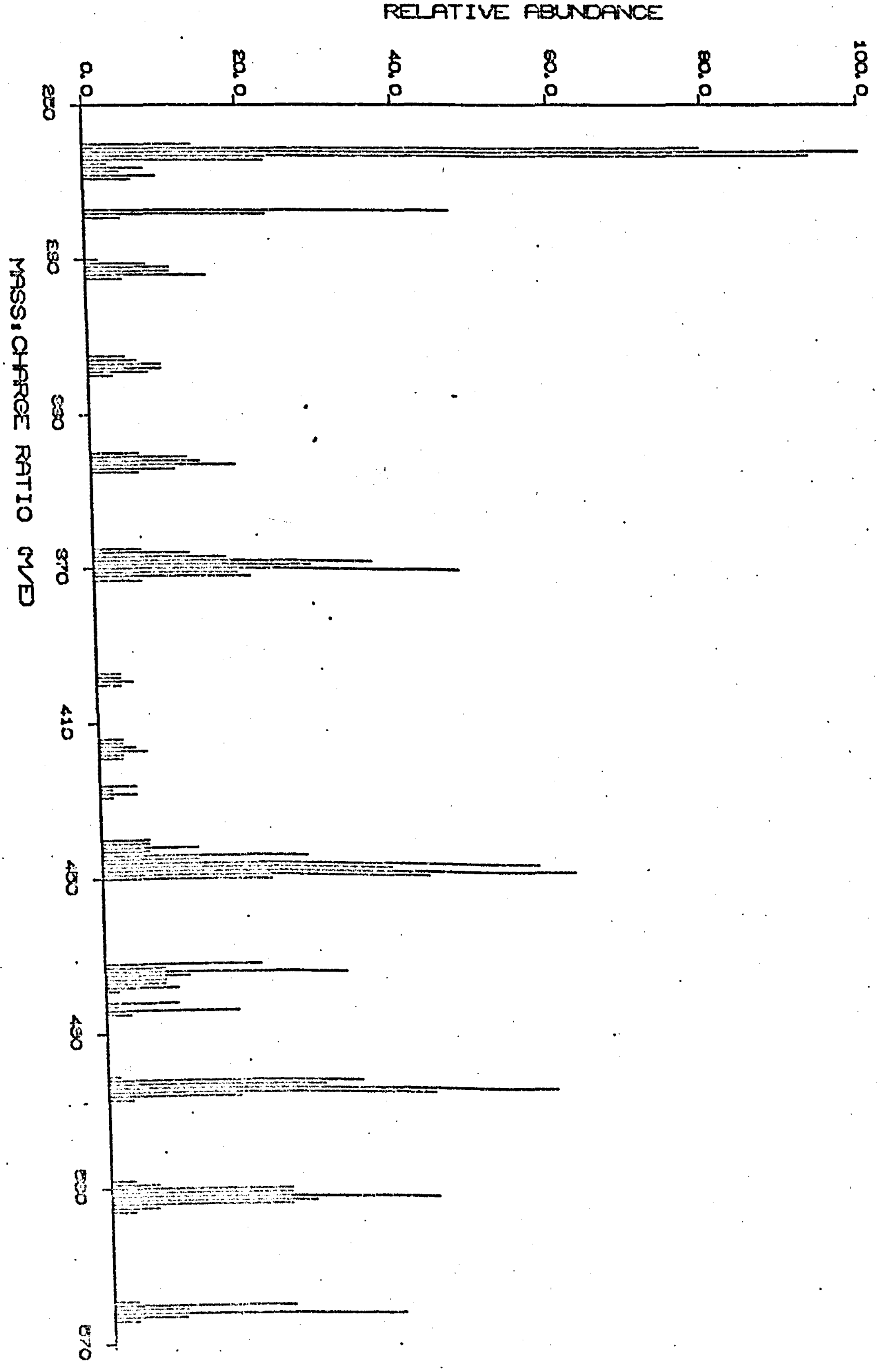
2

SPECTRUM 3 cis-$HRe(CO)_4PPh_3$

m/e	RI	Assignment
560	23.44	$HRe(CO)_4PPh_3^+$
532	42.19	$HRe(CO)_3PPh_3^+$
504	57.81	$HRe(CO)_2PPh_3^+$
476	7.81	$HRe(CO)PPh_3^+$
448	60.94	$HRePPh_3^+$
447	37.50	$RePPh_3^+$
262	100.00	PPh_3^+
483	1.56	$HRe(CO)_4PPh_2^+$
445	12.50	$HRe(CO)_3PPh_2^+$
427	1.56	$HRe(CO)_2PPh_2^+$
399	4.69	$HRe(CO)PPh_2^+$
371	18.75	$HRePPh_2^+$
370	46.88	$RePPh_2^+$
293	10.94	$RePPh^+$

further peaks in this pathway negligible in RI

559	3.13	$Re(CO)_4PPh_3^+$
531	23.44	$Re(CO)_3PPh_3^+$
503	32.81	$Re(CO)_2PPh_3^+$
475	31.25	$Re(CO)PPh_3^+$
447	56.25	$RePPh_3^+$
262	100.00	PPh_3^+


RELATIVE ABUNDANCE
0.0
20.0
40.0
60.0
80.0
100.0
MASS:CHARGE RATIO M/E
250
290
330
370
410
450
490
530
570

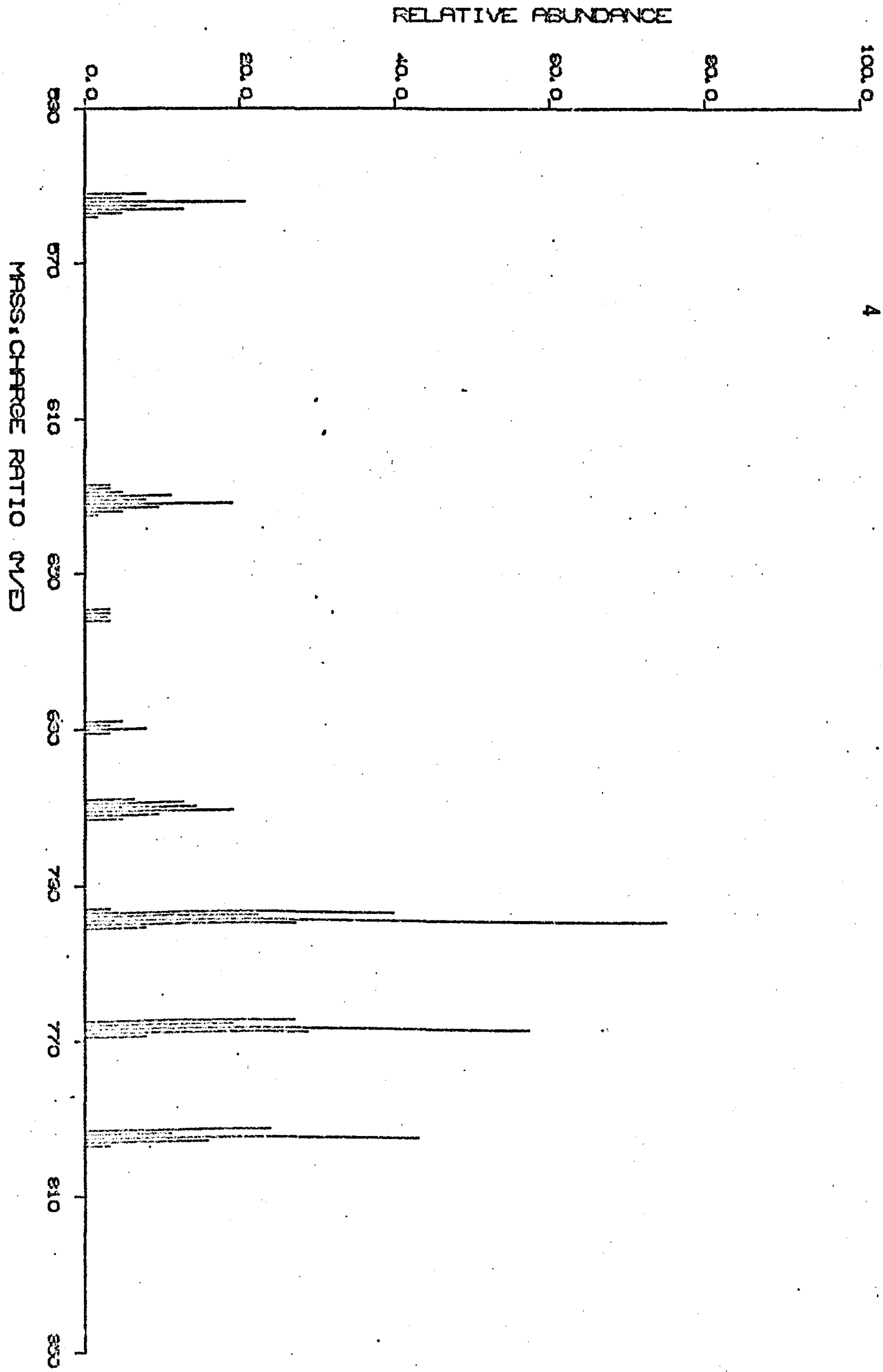
3

SPECTRUM 4 mer-trans$HRe(CO)_3(PPh_3)_2$

m/e	RI	Assignment
794	11.11	$HRe(CO)_3(PPh_3)_2^+$
766	19.05	$HRe(CO)_2(PPh_3)_2^+$
738	22.22	$HRe(CO)(PPh_3)_2^+$
710	14.29	$HRe(PPh_3)_2^+$
448	19.05	$HRePPh_3^+$
447	15.87	$RePPh_3^+$
262	100.00	PPh_3^+
793	23.81	$Re(CO)_3(PPh_3)_2^+$
765	26.98	$Re(CO)_2(PPh_3)_2^+$
737	39.68	$Re(CO)(PPh_3)_2^+$
709	12.70	$Re(PPh_3)_2^+$
447	15.87	$RePPh_3^+$
262	100.00	PPh_3^+

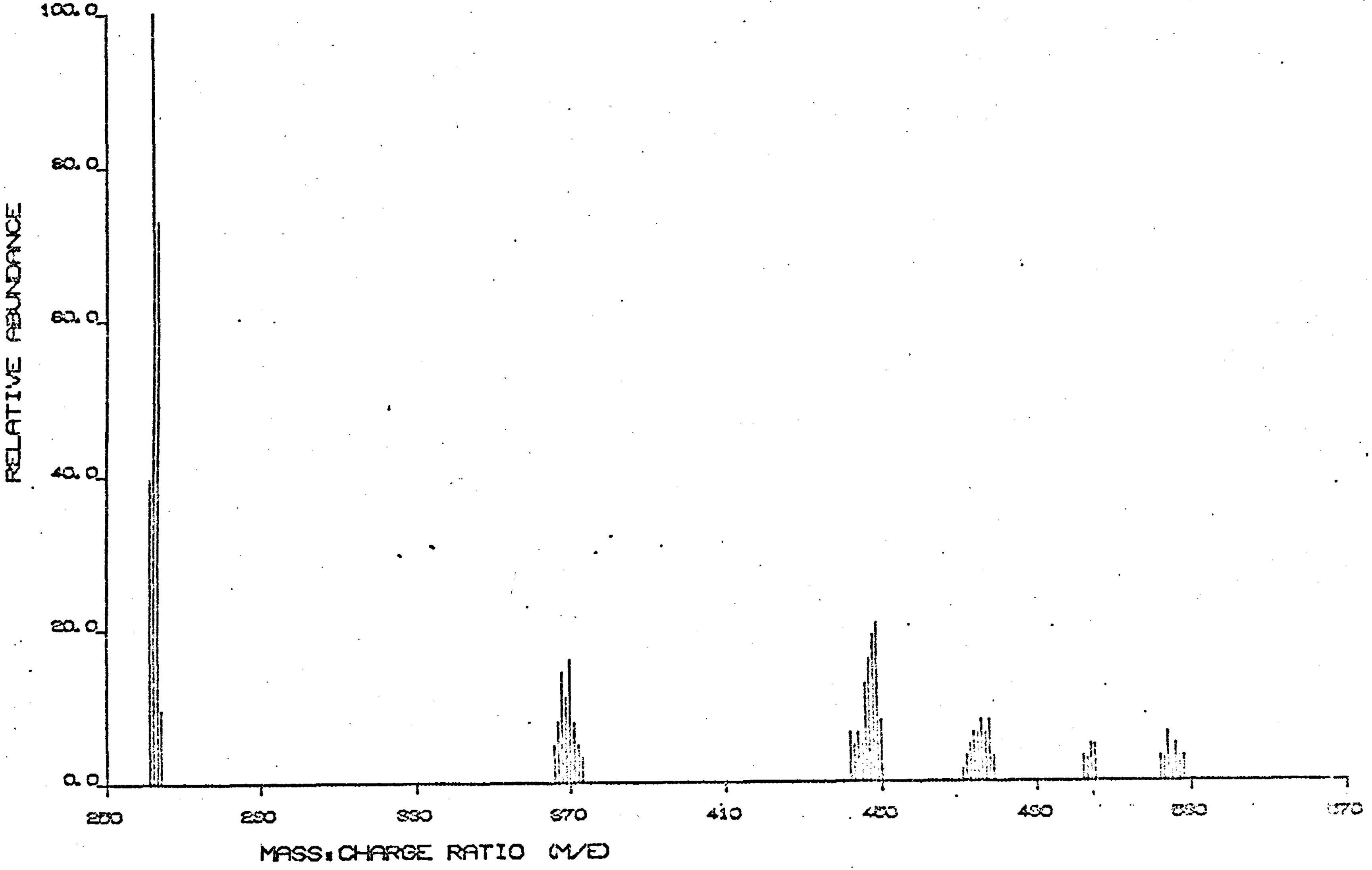
Metastable ions observed:-

794 ⟶ 766	M*	738.9
766 ⟶ 765	M*	764.01
738 ⟶ 737	M*	763.00
710 ⟶ 709	M*	708.00
793 ⟶ 765	M*	737.9
737 ⟶ 709	M*	682.06


RELATIVE ABUNDANCE
0.0
20.0
40.0
60.0
80.0
100.0
MASS:CHARGE RATIO (M/E)
530
570
610
650
690
730
770
810
850

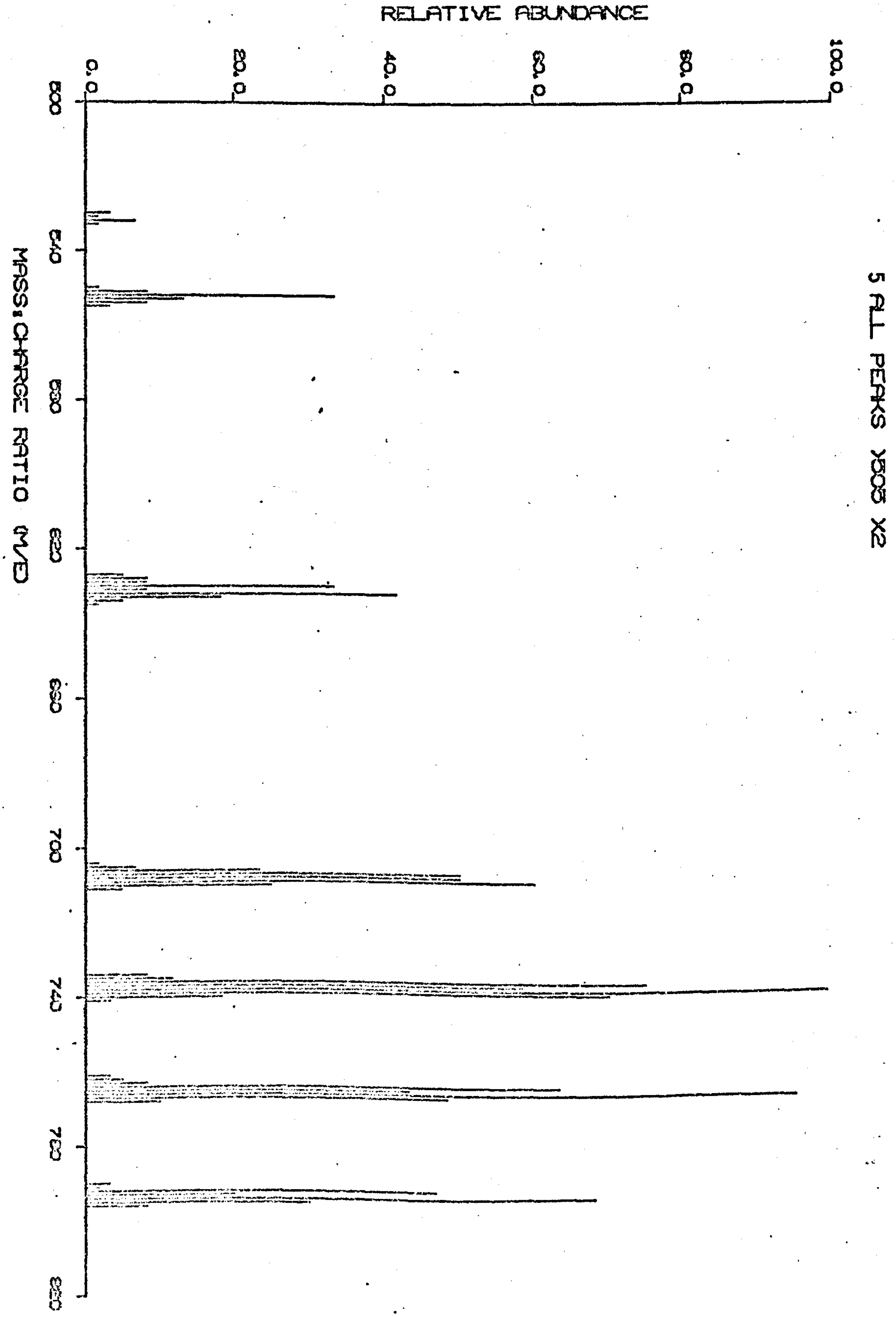
4

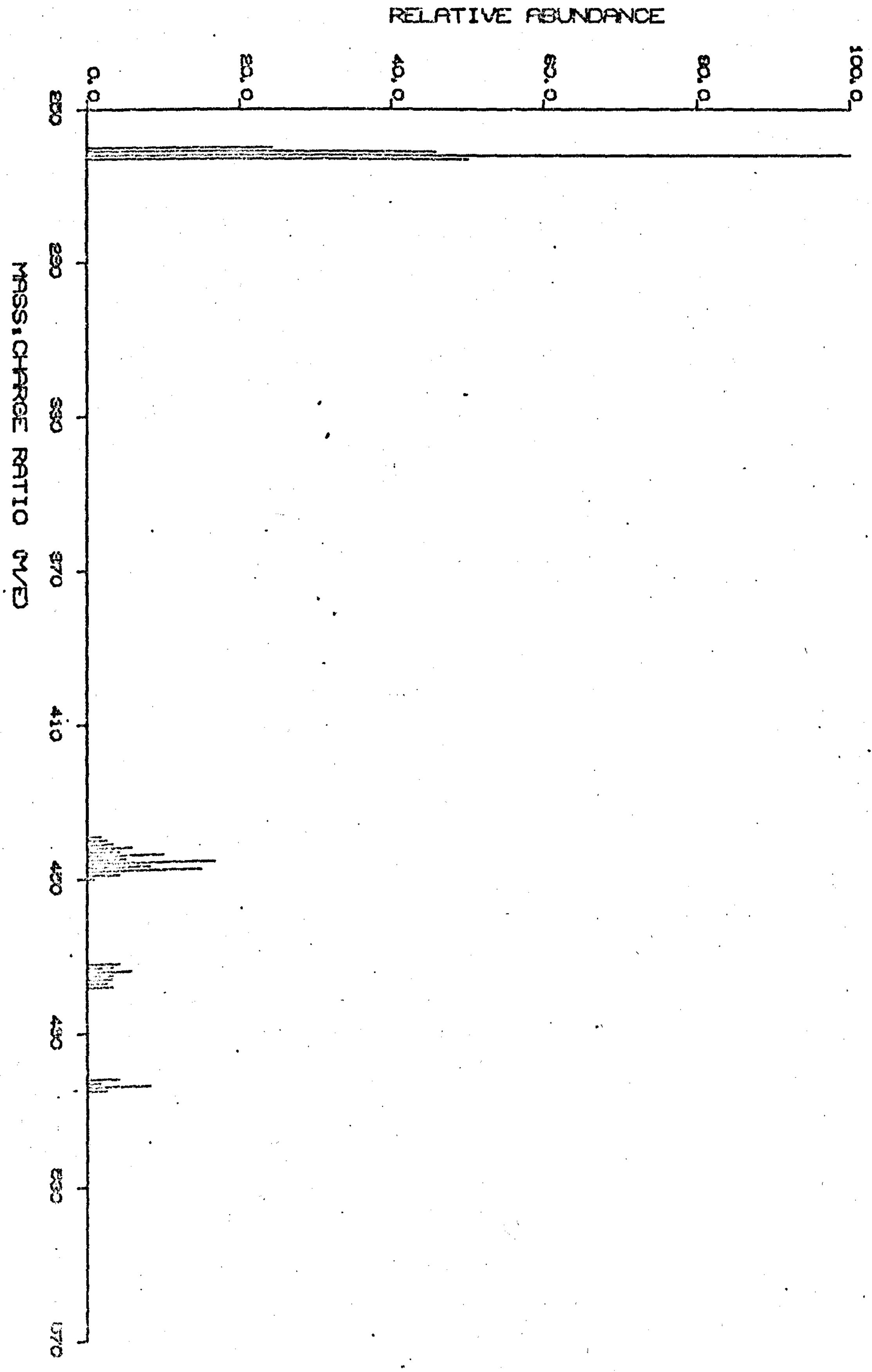
4


RELATIVE ABUNDANCE
100.0
80.0
60.0
40.0
20.0
0.0
250
290
330
370
410
450
490
530
570
MASS:CHARGE RATIO (M/E)

SPECTRUM 5 $Re(CO)_3P(P-H)$ $P = PPh_3$

m/e	RI	Assignment
792	23.34	$Re(CO)_3P(P-H)^+$
764	31.75	$Re(CO)_2P(P-H)^+$
736	37.50	$Re(CO)P(P-H)^+$
708	25.00	$ReP(P-H)^+$
446	16.67	$Re(P-H)^+$
261	45.83	$(P-H)^+$
530	0.88	$Re(CO)_3(P-H)^+$
502	4.17	$Re(CO)_2(P-H)^+$
474	5.83	$Re(CO)(P-H)^+$
446	16.67	$Re(P-H)^+$
261	45.83	$(P-H)^+$
447	8.33	$RePPh_3^+$
262	100.00	PPh_3^+


5 ALL PEAKS >505 X2
RELATIVE ABUNDANCE
0.0
20.0
40.0
60.0
80.0
100.0
500
540
580
620
660
700
740
780
820
MASS:CHARGE RATIO (M/E)


RELATIVE ABUNDANCE
0.0
20.0
40.0
60.0
80.0
100.0
250
290
330
370
410
450
490
530
570
MASS:CHARGE RATIO (M/E)

5

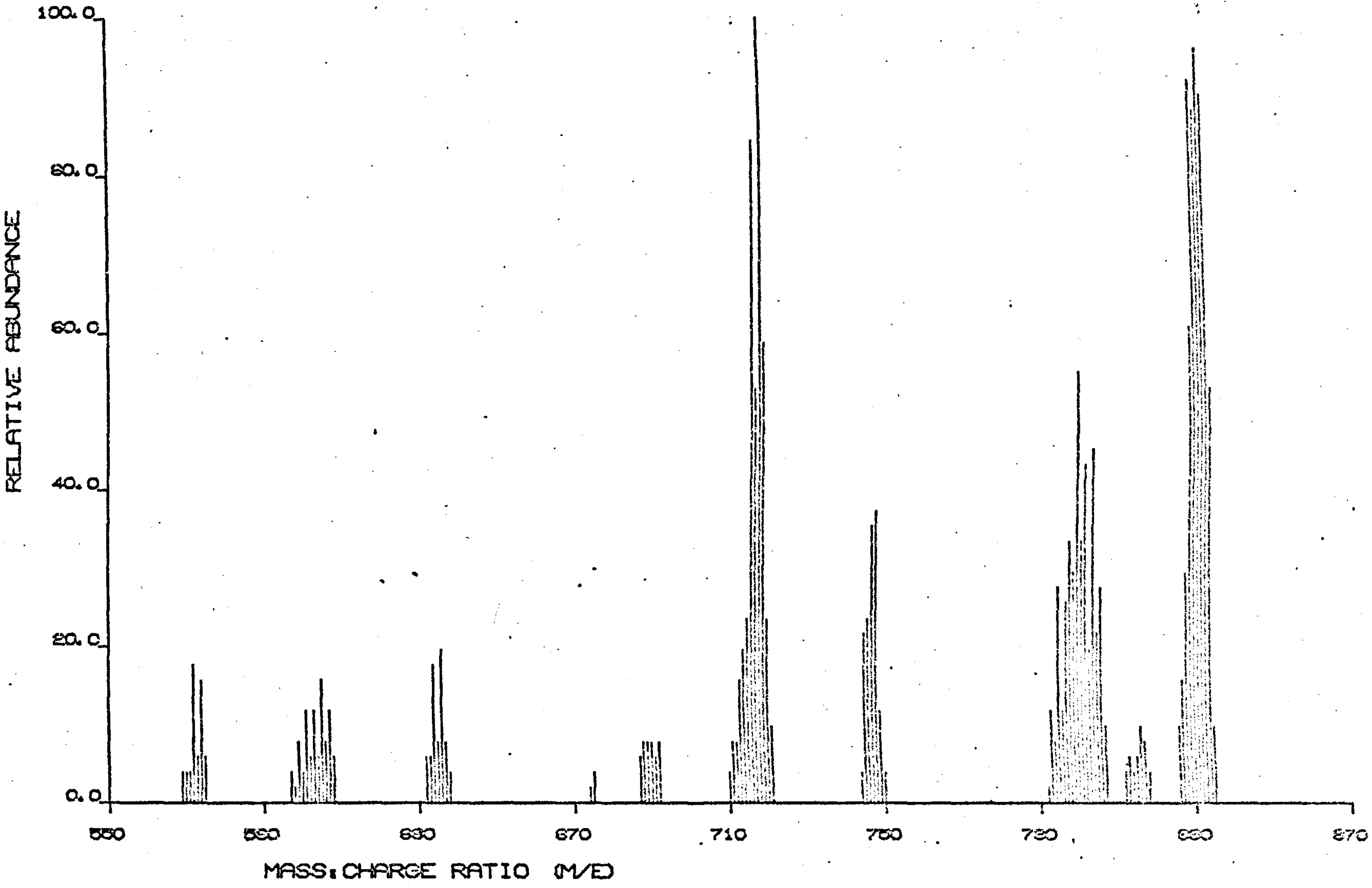
SPECTRUM 6 $HRe(CO)_3P_2$ $P = P(C_6H_{11})_3$

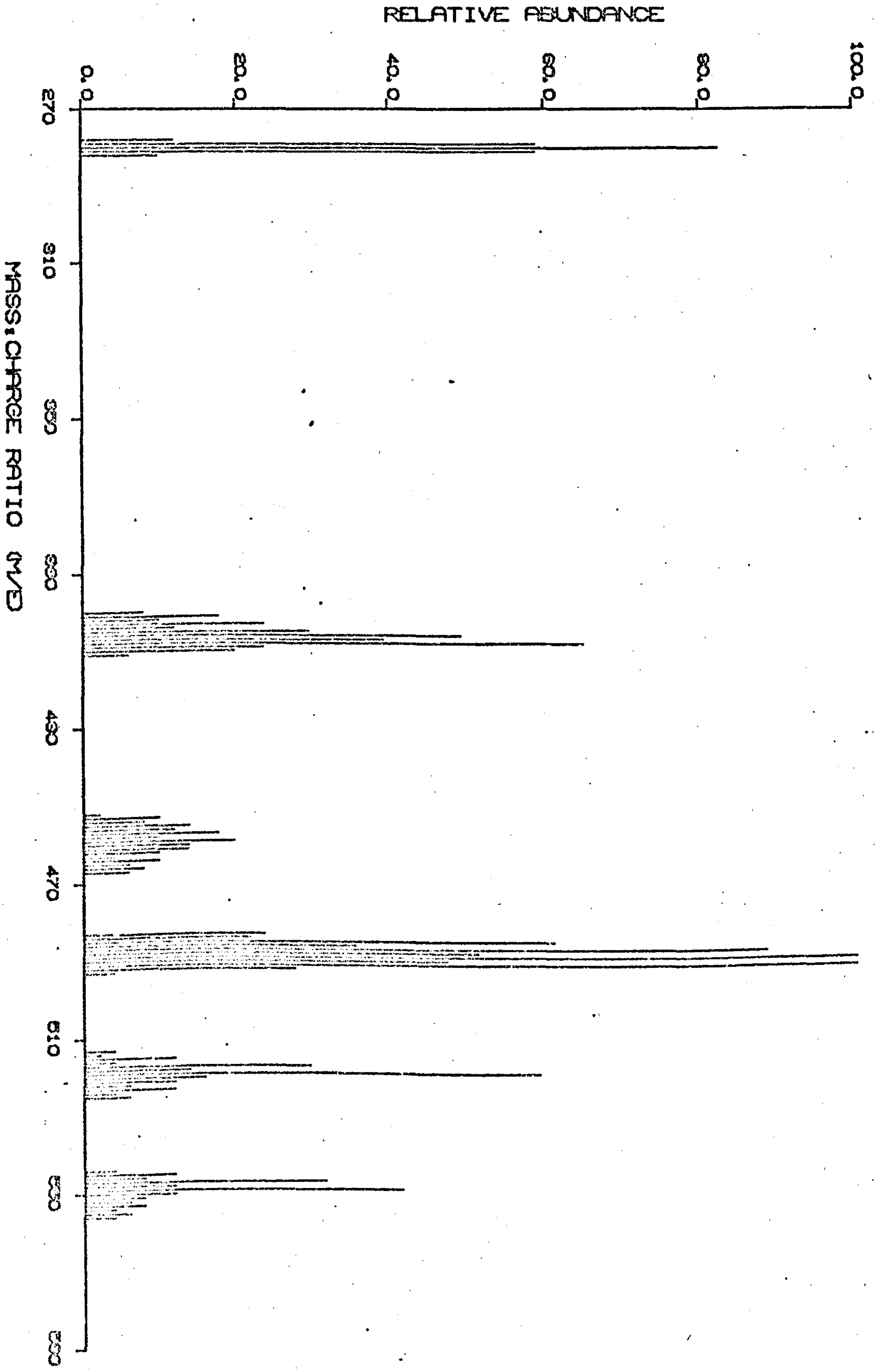
m/e	RI	Assignment
830	92.16	$HRe(CO)_3P_2^+$
802	43.14	$HRe(CO)_2P_2^+$
774	1	$HRe(CO)P_2^+$
746	23.53	$HReP_2^+$
466	7.84	$HReP^+$
465	5.88	ReP^+
280	82.35	P^+
801	33.33	$Re(CO)_2P_2^+$
773	1	$Re(CO)P_2^+$
745	21.57	ReP_2^+
465	5.88	ReP^+
280	82.35	P^+
747	35.29	$HRe(CO)_3P^+$
719	58.82	$HRe(CO)_2P^+$
691	5.88	$HRe(CO)P^+$
663	1	$HReP^+$

The major decomposition pathway can be traced by use of metastable peak analysis:

830 - 802	M*	774.9
802-774	M*	746.9
774-746	M*	719.01
746-466	M*	291.09

6

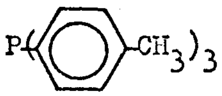

RELATIVE ABUNDANCE
100.0
80.0
60.0
40.0
20.0
0.0
550
590
630
670
710
750
790
830
870
MASS:CHARGE RATIO (M/E)


RELATIVE ABUNDANCE
0.0
20.0
40.0
60.0
80.0
100.0
270
310
350
390
430
470
510
550
590
MASS:CHARGE RATIO (M/E)

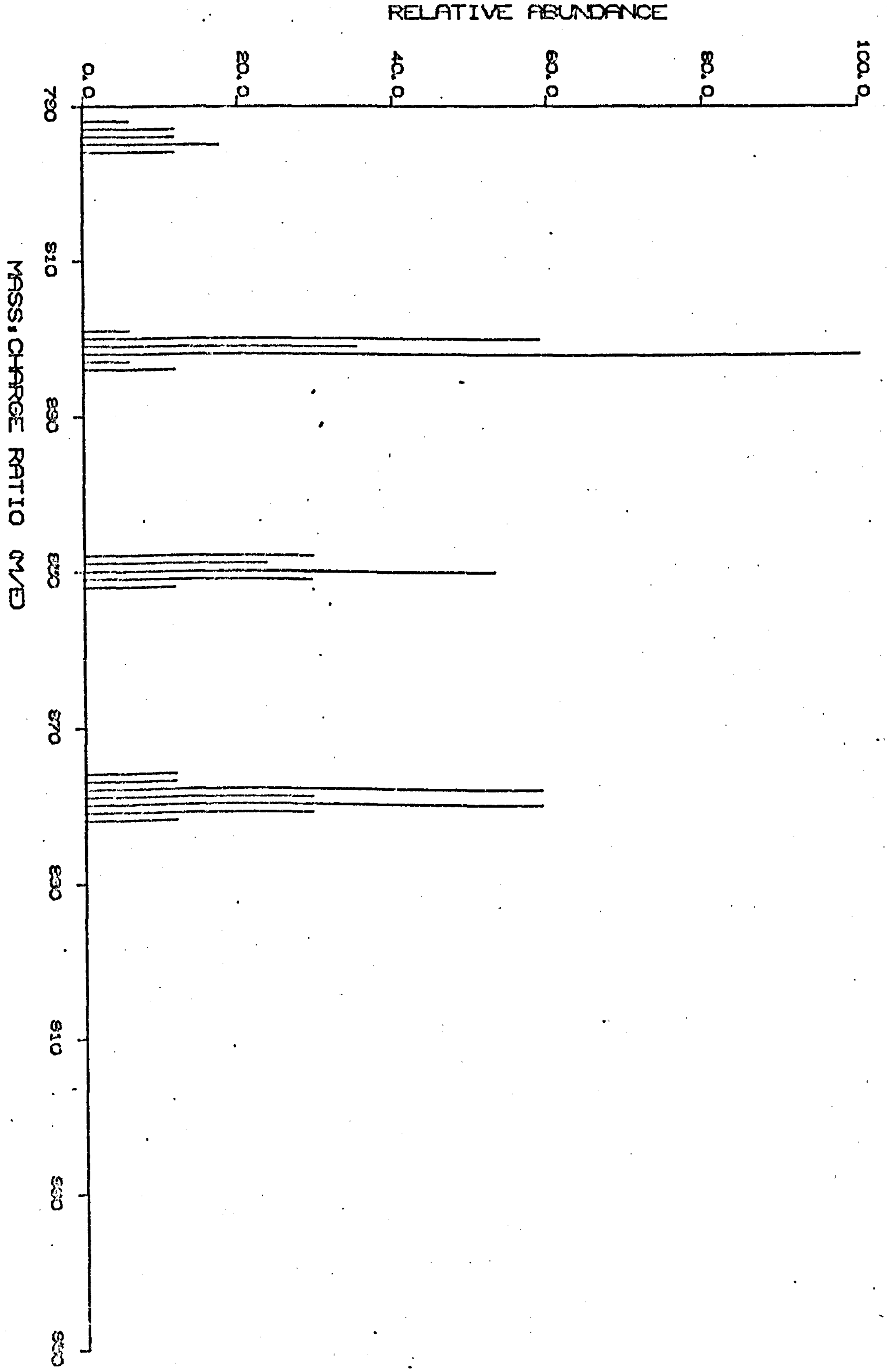
6

SPECTRUM 7

mer-trans $HRe(CO)_3P_2$ P =



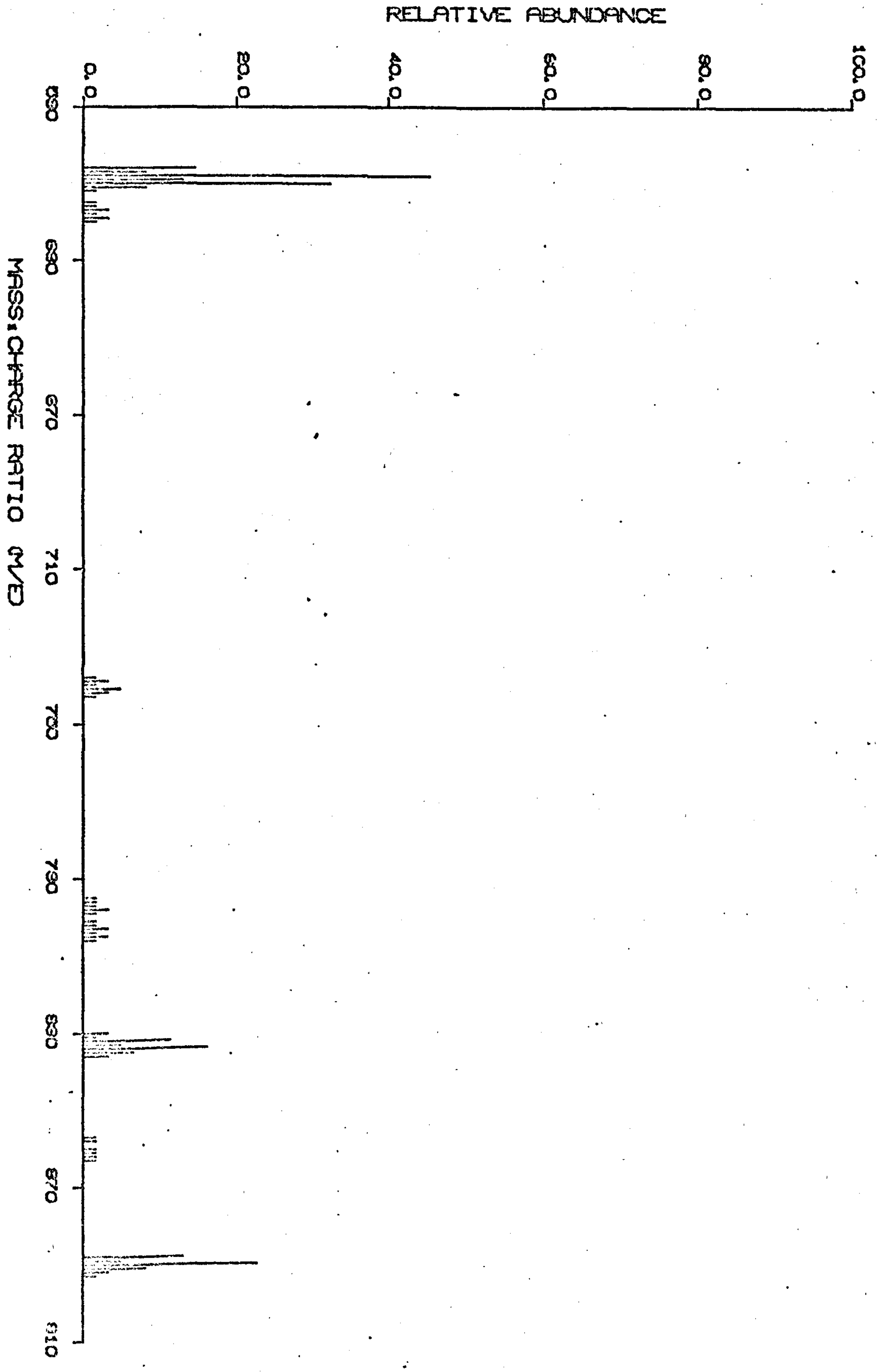
m/e	RI	Assignment
878	58.82	$HRe(CO)_3P_2^+$
876	11.76	$Re(CO)_3P(P-H)^+$
850	52.94	$HRe(CO)_2P_2^+$
848	29.41	$Re(CO)_2P(P-H)^+$
822	100.00	$HRe(CO)P_2^+$
820	58.82	$Re(CO)P.(P-H)^+$
794	11.76	$HReP_2^+$
792	5.88	$ReP(P-H)^+$


RELATIVE ABUNDANCE
0.0
20.0
40.0
60.0
80.0
100.0
790
810
830
850
870
890
910
930
950
MASS:CHARGE RATIO (M/E)

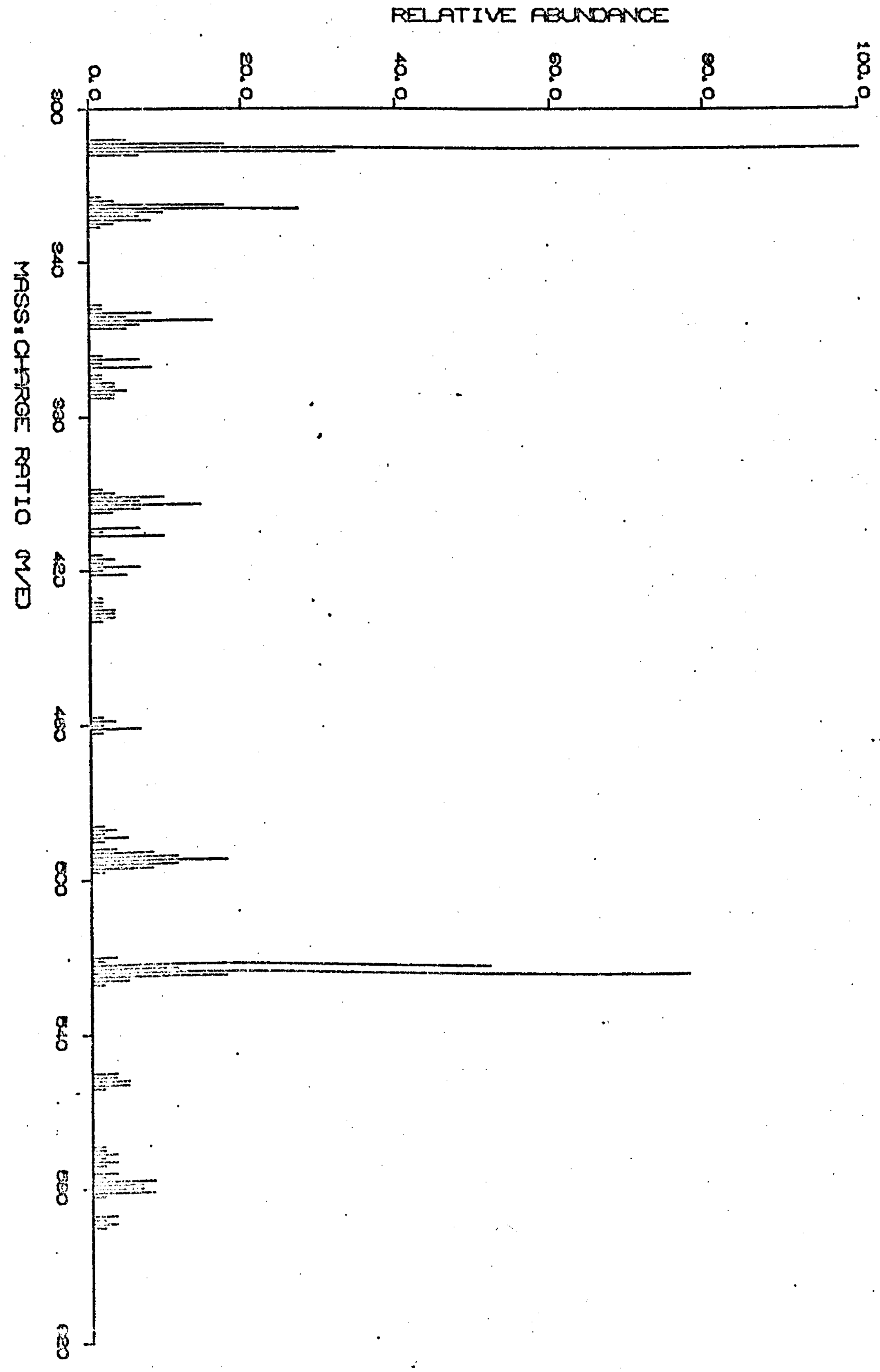
7

SPECTRUM 8 $Re(CO)_3P(P{-}H)$ $P = P(OPh)_3$

m/e	RI	Assignment
888	12.90	$Re(CO)_3P(P{-}H)^+$
860	1.61	$Re(CO)_2P(P{-}H)^+$
832	11.29	$Re(CO)P(P{-}H)^+$
804	1.61	$ReP(P{-}H)^+$
495	17.74	ReP^+
310	100.00	P^+
578	8.06	$Re(CO)_3(P{-}H)^+$
550	3.23	$Re(CO)_2(P{-}H)^+$
522	51.61	$Re(CO)(P{-}H)^+$
494	11.29	$Re(P{-}H)^+$
309	17.74	$P{-}H^+$


RELATIVE ABUNDANCE
0.0
20.0
40.0
60.0
80.0
100.0
590
630
670
710
750
790
830
870
910
MASS:CHARGE RATIO (M/E)

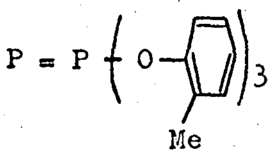
8


RELATIVE ABUNDANCE
0.0
20.0
40.0
60.0
80.0
100.0
MASS:CHARGE RATIO (M/E)
300
340
380
420
460
500
540
580
620

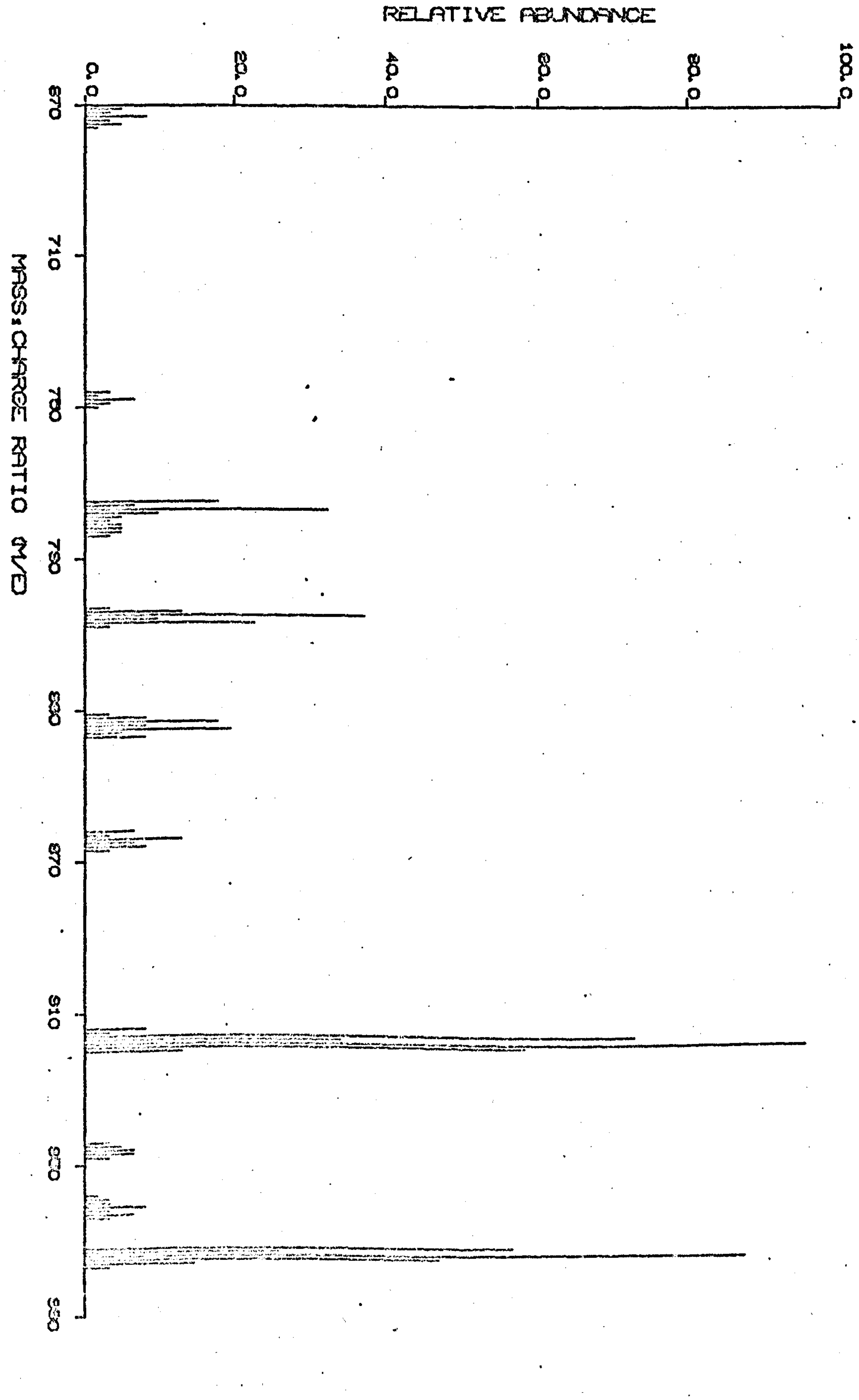
8

SPECTRUM 9

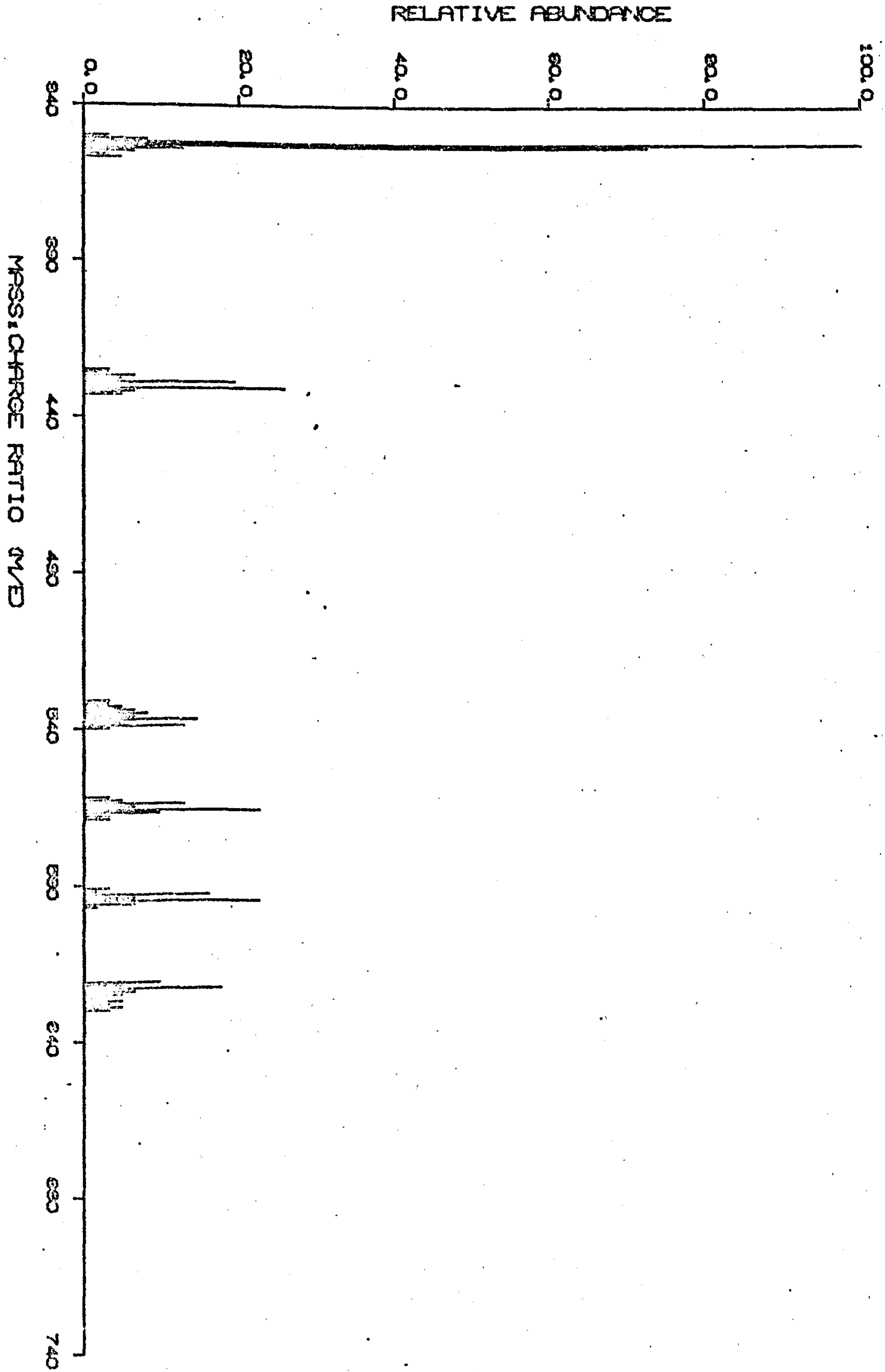
$Re(CO)_3P(P-H)$



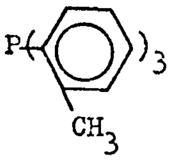
M/e	RI	Assignment
972	56.45	$Re(CO)_3P(P-H)^+$
944	3.23	$Re(CO)_2P(P-H)^+$
916	72.58	$Re(CO)P(P-H)^+$
888	1	$ReP(P-H)^+$
536	6.45	$Re(P-H)^+$
351	8.06	$(P-H)^+$
621	10.21	$Re(CO)_3P^+$
593	16.13	$Re(CO)_2P^+$
565	6.45	$Re(CO)P^+$
537	14.52	ReP^+
352	100.00	P^+

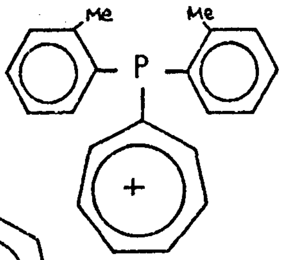
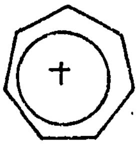

RELATIVE ABUNDANCE
0.0
20.0
40.0
60.0
80.0
100.0
MASS:CHARGE RATIO (M/E)
670
710
750
790
830
870
910
950
990

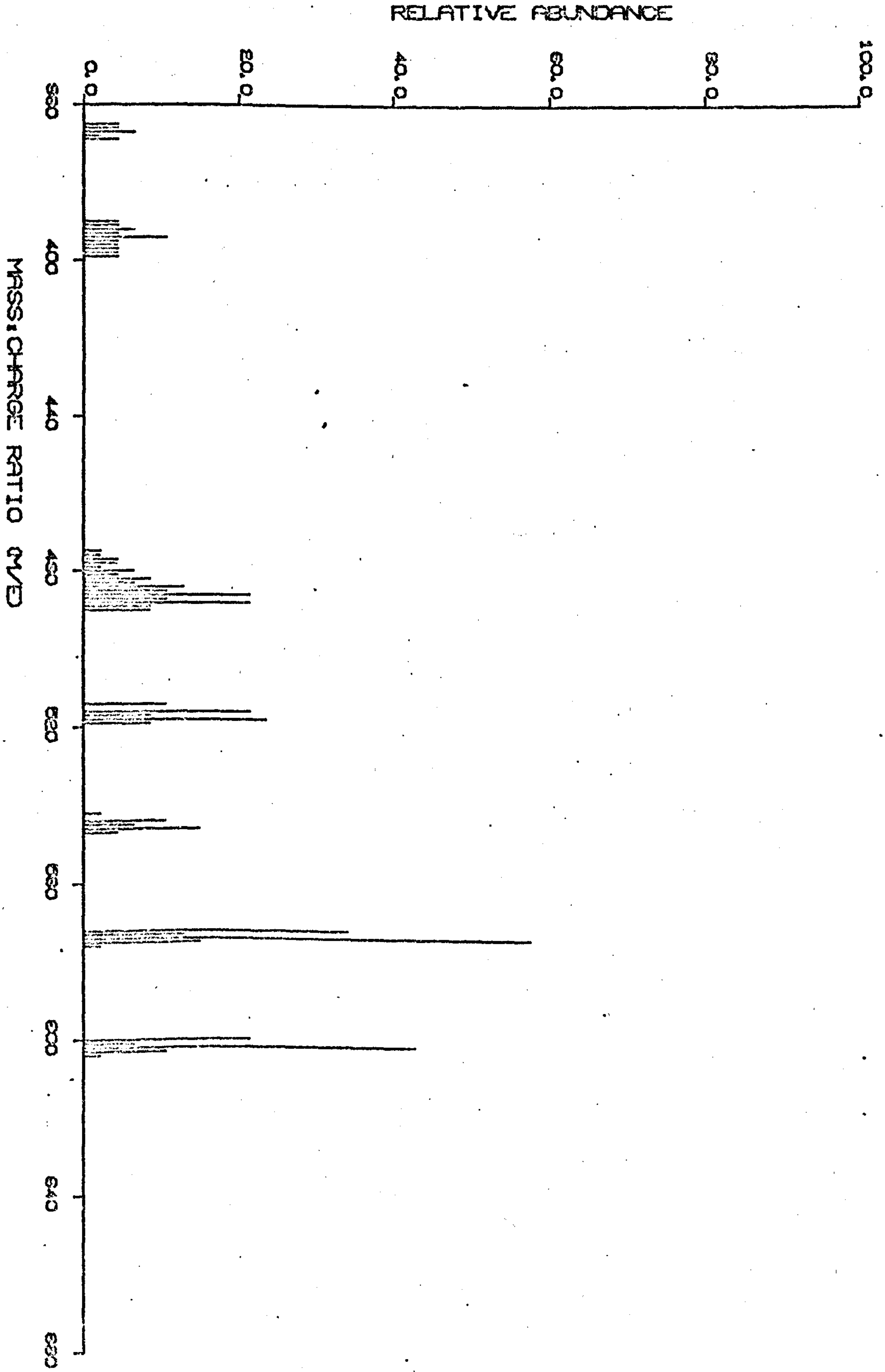
9


RELATIVE ABUNDANCE
0.0
20.0
40.0
60.0
80.0
100.0
340
390
440
490
540
590
640
690
740
MASS:CHARGE RATIO (M/E)

9

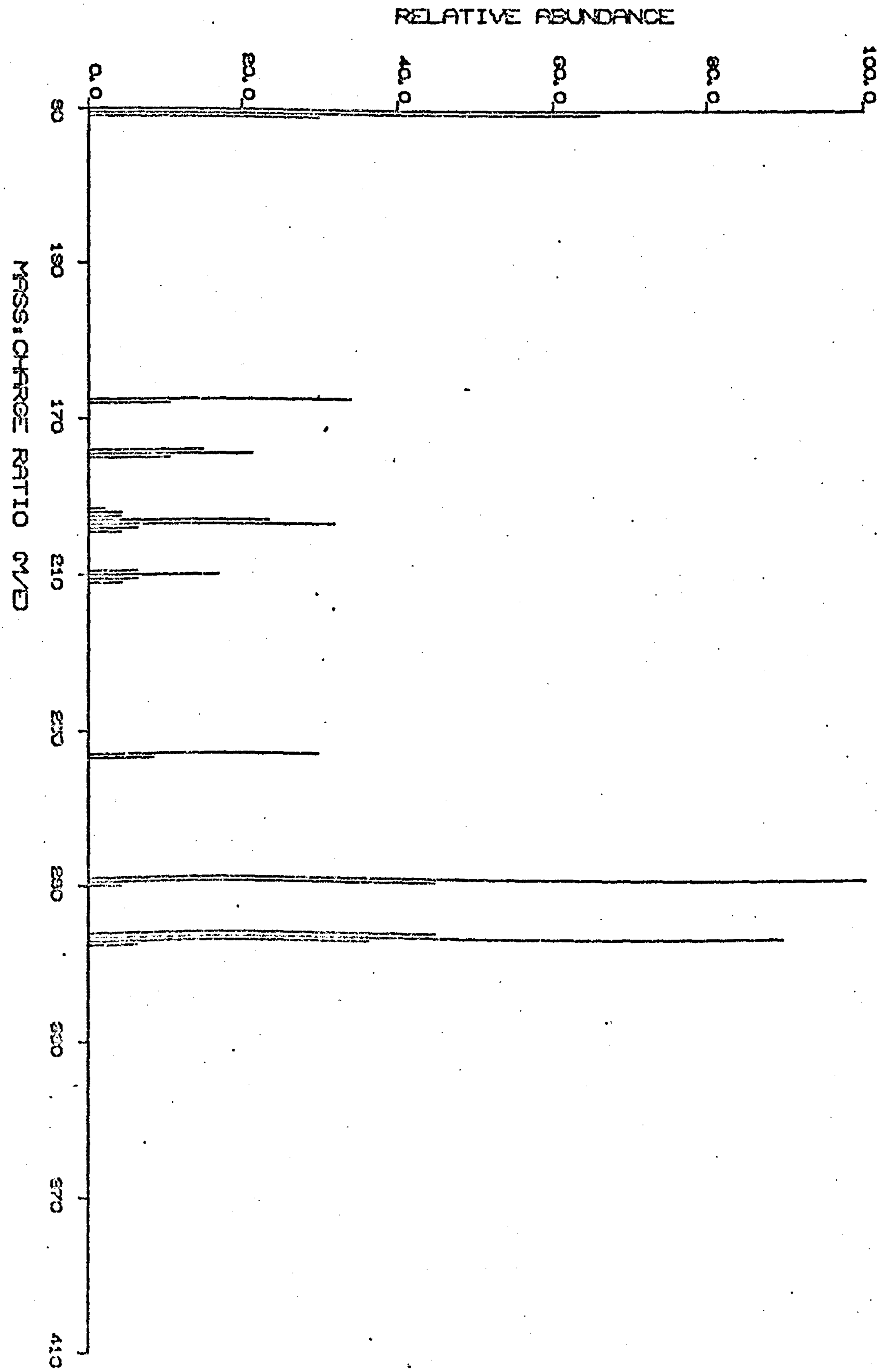
SPECTRUM 10 $Re(CO)_4(P{-}H)$ P = 

m/e	RI	Assignment
600	21.28	$Re(CO)_4(P{-}H)^+$
572	34.04	$Re(CO)_3(P{-}H)^+$
544	10.64	$Re(CO)_2(P{-}H)^+$
516	21.28	$Re(CO)(P{-}H)^+$
488	21.28	$Re(P{-}H)^+$
303	89.36	
91	65.96	


RELATIVE ABUNDANCE
0.0
20.0
40.0
60.0
80.0
100.0
360
400
440
480
520
560
600
640
680
MASS:CHARGE RATIO (M/E)

10

10.

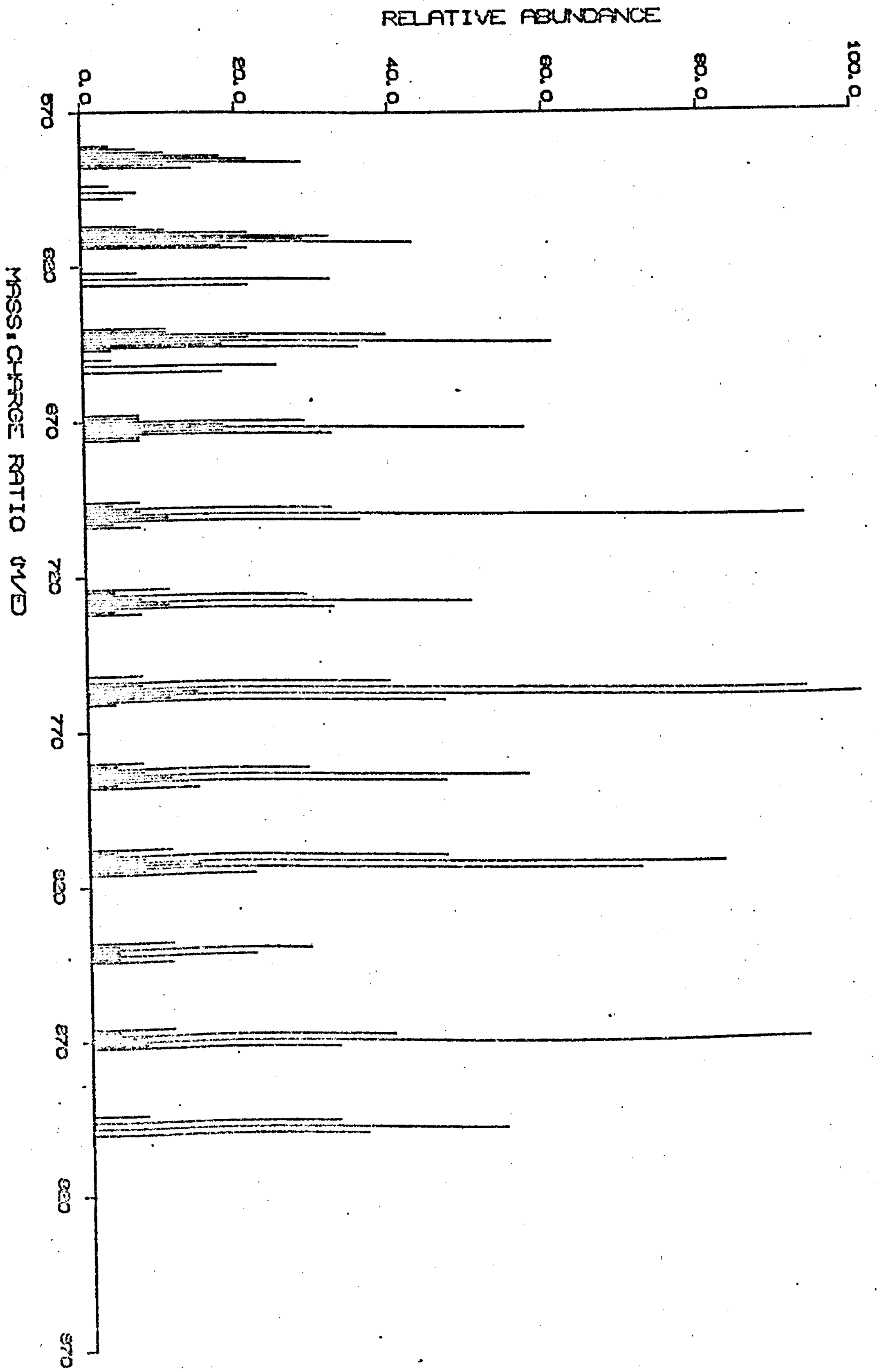

RELATIVE ABUNDANCE
0.0
20.0
40.0
60.0
80.0
100.0
MASS:CHARGE RATIO M/E
90
130
170
210
250
290
330
370
410

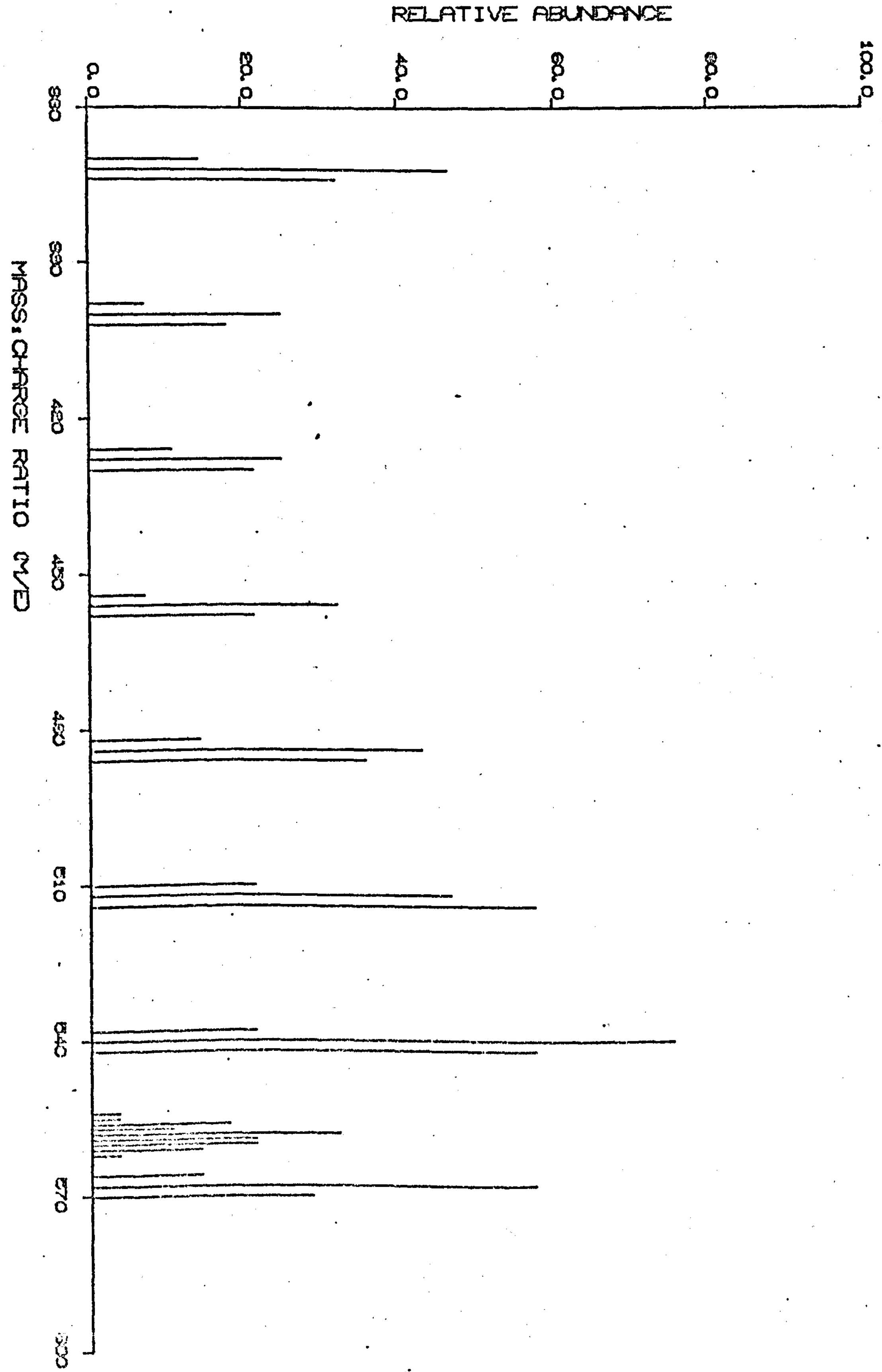
SPECTRUM 11 $H_3Re_3(CO)_{12}$

m/e	RI	Assignment
894	7.14	$H_3Re_3(CO)_{12}^+$
866	10.71	$H_3Re_3(CO)_{11}^+$
838	10.71	$H_3Re_3(CO)_{10}^+$
810	46.43	$H_3Re_3(CO)_9^+$
782	28.57	$H_3Re_3(CO)_8^+$
754	39.29	$H_3Re_3(CO)_7^+$
726	28.57	$H_3Re_3(CO)_6^+$
698	32.14	$H_3Re_3(CO)_5^+$
670	28.57	$H_3Re_3(CO)_4^+$
642	39.29	$H_3Re_3(CO)_3^+$
614	21.43	$H_3Re_3(CO)_2^+$
586	28.57	$H_3Re_3CO^+$
558	32.14	$H_3Re_3^+$
808	10.71	$HRe_3(CO)_9^+$
780	7.14	$HRe_3(CO)_8^+$
752	7.14	$HRe_3(CO)_7^+$
724	10.71	$HRe_3(CO)_6^+$
696	7.14	$HRe_3(CO)_5^+$
668	7.14	$HRe_3(CO)_4^+$
640	10.71	$HRe_3(CO)_3^+$
639	1	$Re_3(CO)_3^+$
611	28.57	$Re_3(CO)_2^+$
583	10.71	$Re_3(CO)^+$
555	3.57	Re_3^+

peaks are also seen in this spectrum due to carbonyl losses from $Re_2(CO)_{10}$ (M^+ 650), which may have been present as a trace impurity.

11

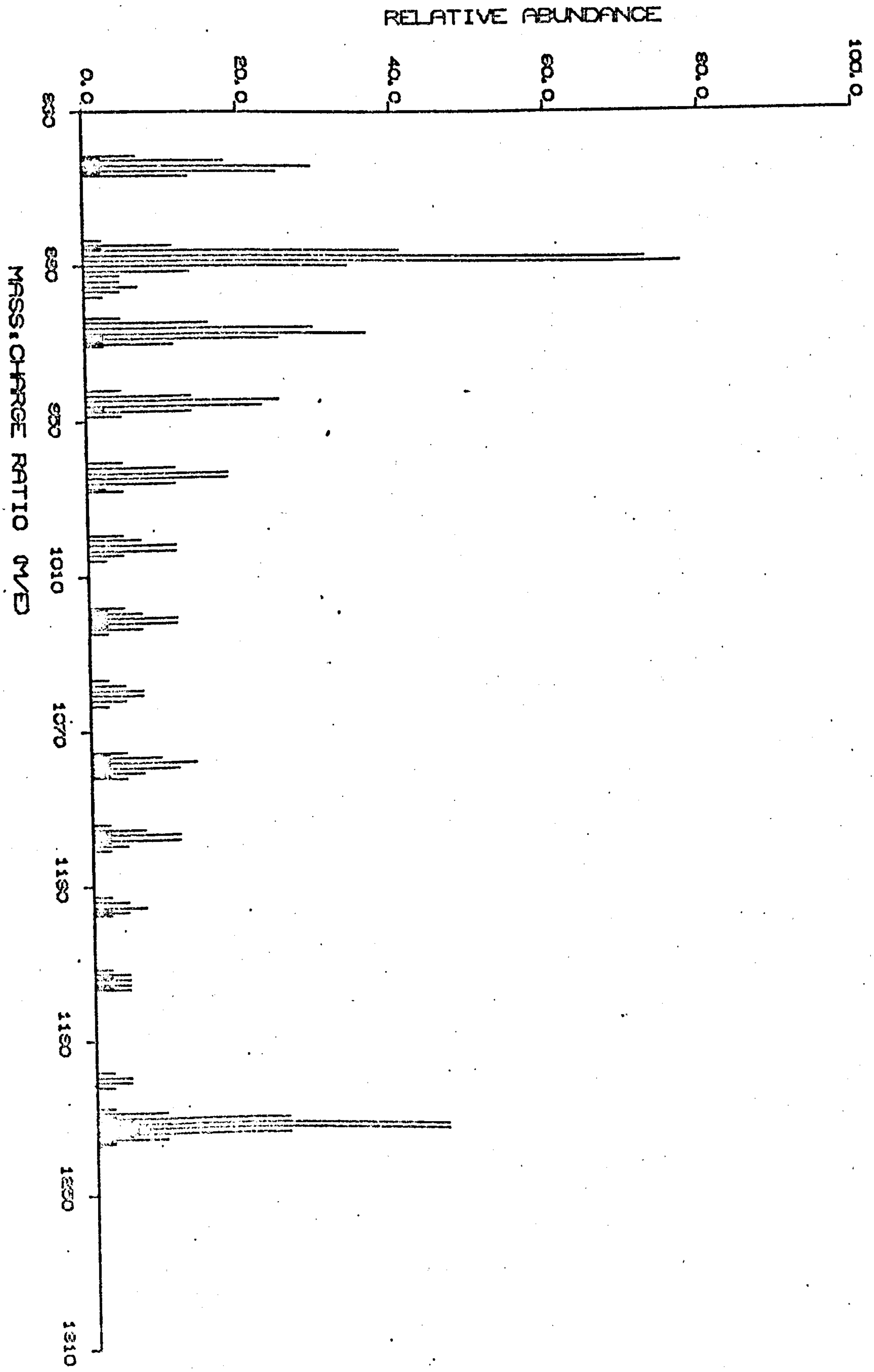

RELATIVE ABUNDANCE
0.0
20.0
40.0
60.0
80.0
100.0
MASS:CHARGE RATIO (M/E)
570
620
670
720
770
820
870
920
970


RELATIVE ABUNDANCE
0.0
20.0
40.0
60.0
80.0
100.0
MASS:CHARGE RATIO (M/E)
360
390
420
450
480
510
540
570
600

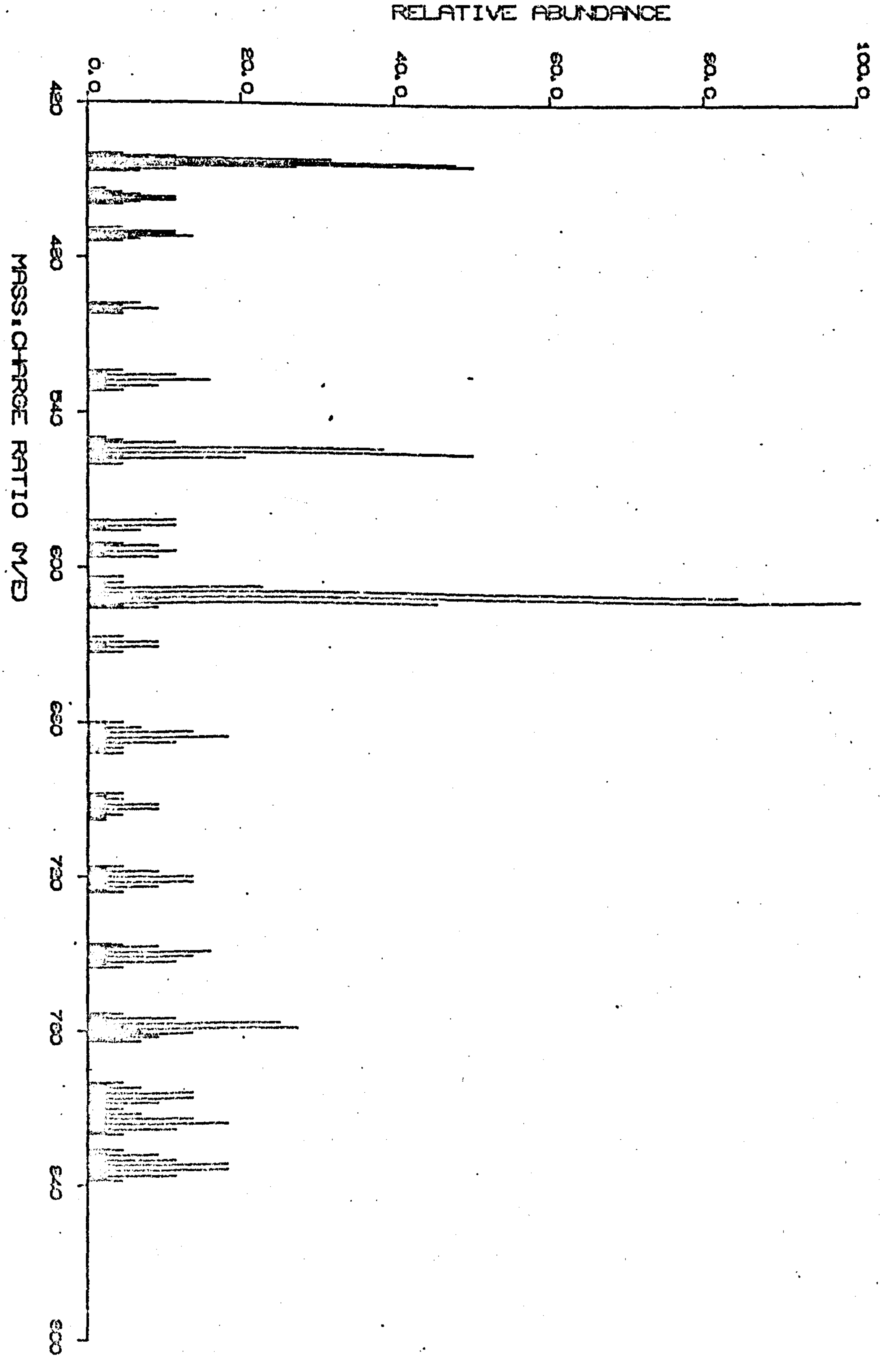
11

SPECTRUM 12 $Re_4(CO)_{12}Cl_4$

m/e	RI	Assignment
1216	2.27	$Re_4Cl_4(CO)_{12}^+$
1188	Not observed	
1160	2.27	$Re_4Cl_4(CO)_{10}^+$
1132	2.27	$Re_4Cl_4(CO)_9^+$
1104	4.55	$Re_4Cl_4(CO)_8^+$
1076	4.55	$Re_4Cl_4(CO)_7^+$
1048	2.27	$Re_4Cl_4(CO)_6^+$
1020	4.55	$Re_4Cl_4(CO)_5^+$
992	4.45	$Re_4Cl_4(CO)_4^+$
964	4.55	$Re_4Cl_4(CO)_3^+$
936	4.55	$Re_4Cl_4(CO)_2^+$
908	4.55	$Re_4Cl_4(CO)^+$
880	2.27	$Re_4Cl_4^+$
826	4.55	$Re_3Cl_3(CO)_6^+$
814	13.64	$Re_3Cl(CO)_8^+$
800	4.55	$Re_3Cl_3(CO)_5^+$
688	4.55	$Re_3Cl_3(CO)_2^+$


RELATIVE ABUNDANCE
0.0
20.0
40.0
60.0
80.0
100.0
MASS:CHARGE RATIO (M/E)
830
890
950
1010
1070
1130
1190
1250
1310

12


RELATIVE ABUNDANCE
0.0
20.0
40.0
60.0
80.0
100.0
MASS:CHARGE RATIO (M/E)
420
480
540
600
660
720
780
840
900

12

PART 2

The mass spectra of compounds discussed in Chapter 3

The nonomeric and dimeric complexes discussed in Chapter 3 all gave straightforward mass spectra. The expected isotope patterns for the metal clusters were observed for the molecular and daughter ions, and m/e values are calculated using the isotopes ^{52}Cr, ^{98}Mo, ^{184}W and ^{56}Fe.

The spectra of the complexes $(\eta^6\text{-}C_7H_8)M(CO)_3$ (M = Cr, Mo or W) are presented in Figures 13-15. The spectrum of the chromium complex is simple showing successive losses of carbon monoxide, followed by loss of cycloheptatriene to give Cr^+ as the base peak. In both the molybdenum and tungsten compounds, however, the bonds between the metal and the hydrocarbon ligand are stronger, so peaks due to metal containing ions derived from $C_7H_8Mo^+$ are seen.

In the dimeric species, several modes of fragmentation are possible; loss of six carbonyl ligands; dissociation to give $(\eta^7\text{-}C_7H_7)M(CO)_3{}^+$ and finally loss of $M(CO)_3$ from the molecular ion. In both the chromium and molybdenum complexes, ions representing all three pathways were detected. The base peak in both spectra was due to the tropylium ion. The very low abundance of ions in the sequence $M^+\text{-}nCO$ (n = 1-6) is presumably a consequence of the facility of the loss of this particular moiety.

Part 2.1

The mass spectra of the olefinic derivatives

The spectra presented in this section are listed below:

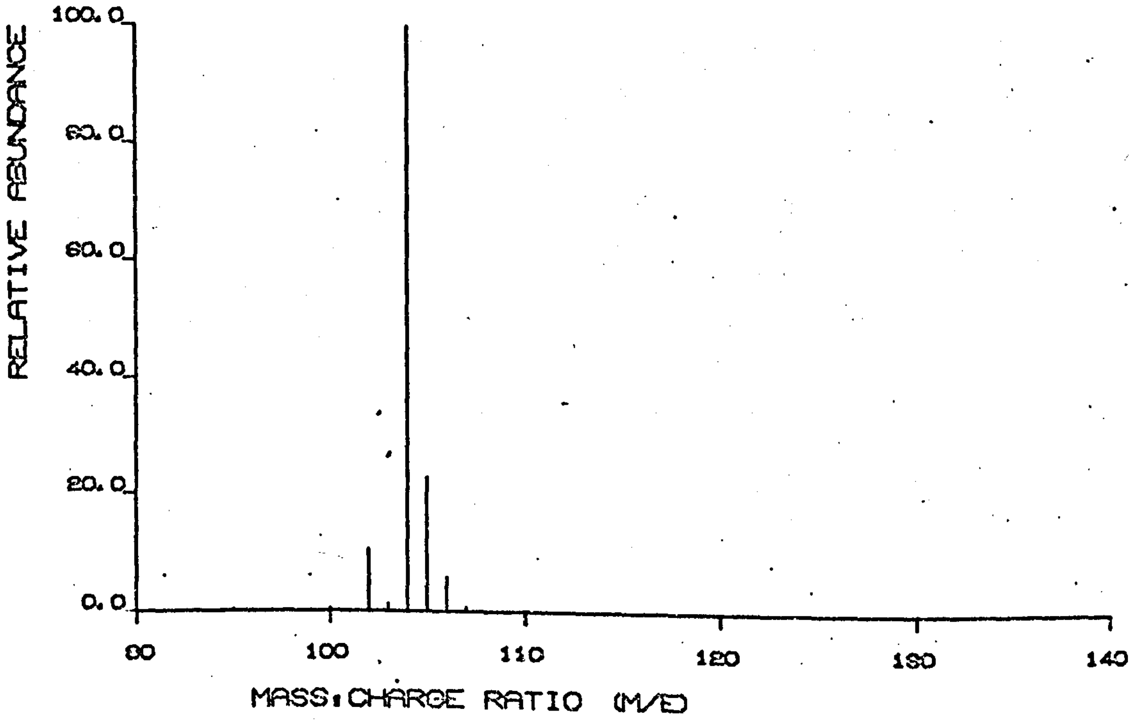
Spectrum number	Complex
13	$(\eta^6\text{-}C_7H_8)Cr(CO)_3$
14	$(\eta^6\text{-}C_7H_8)Mo(CO)_3$
15	$(\eta^6\text{-}C_7H_8)W(CO)_3$
16	$[(\eta^6\text{-}C_7H_7)Cr(CO)_3]_2$
17	$[(\eta^6\text{-}C_7H_7Mo(CO)_3]_2$
18	$(MeCN)W(CO)_5$
19	$[(\eta^4\text{-}C_6H_7)Fe(CO)_3]_2$

ISOTOPE PATTERNS

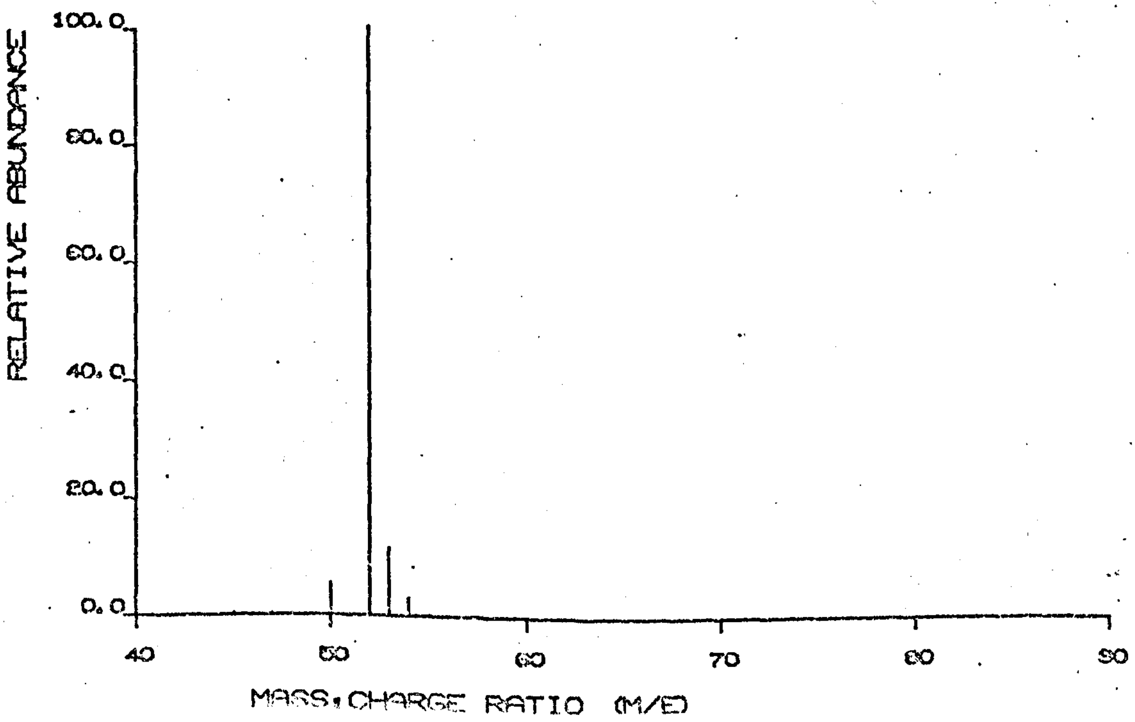
Cluster	m/e	RI
Cr_1	50	5.15
	52	100.00
	53	11.40
	54	2.84
Cr_2	100	0.26
	102	10.26
	103	1.10
	104	100.00
	105	22.73
	106	5.73
	107	0.65
Mo_1	92	66.61
	94	38.02
	95	66.11
	96	69.51
	97	39.78
	98	100.00
	100	40.71
Mo_2	184	15.69
	186	17.92
	187	31.14
	188	37.86
	189	36.55
	190	100.00
	191	66.35
	192	81.80
	193	66.35
	194	65.75
	195	65.75
	196	20.04
	197	28.14
	198	28.81
	200	5.87

Cluster	m/e	RI
W_1	180	0.46
	182	86.19
	183	47.00
	184	100.00
	186	92.72
W_2	364	28.58
	365	31.16
	366	74.83
	367	36.16
	368	100.00
	369	33.54
	370	71.34
	372	33.09
Fe_1	54	6.35
	56	100.00
	57	2.39
	58	0.36
Fe_2	108	0.40
	110	12.69
	111	0.30
	112	100.00
	113	4.78
	114	0.77

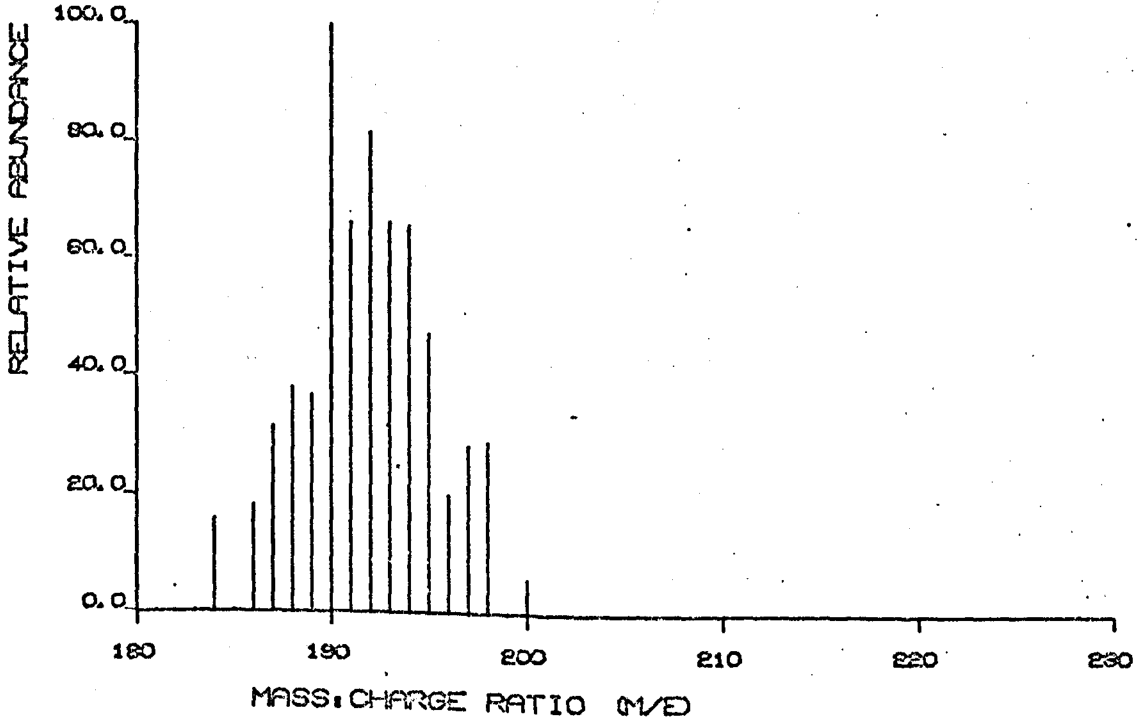
ISOTOPE PATTERN FOR TWO CHROMIUM ATOMS



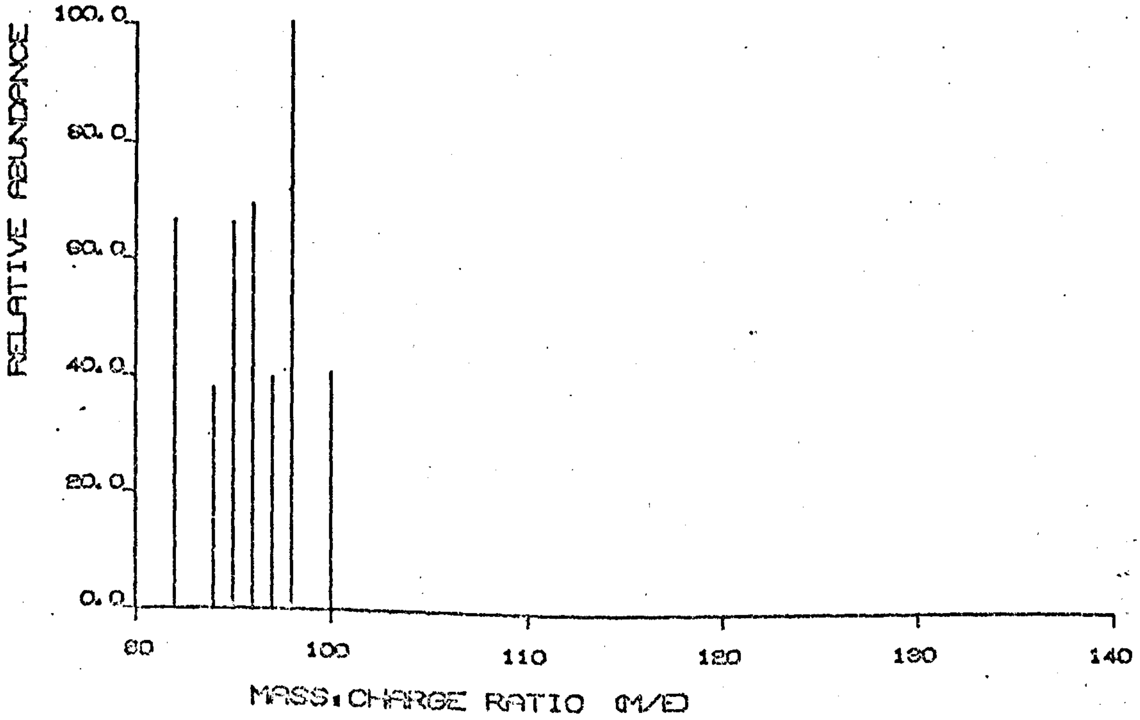
ISOTOPE PATTERN FOR ONE CHROMIUM ATOM



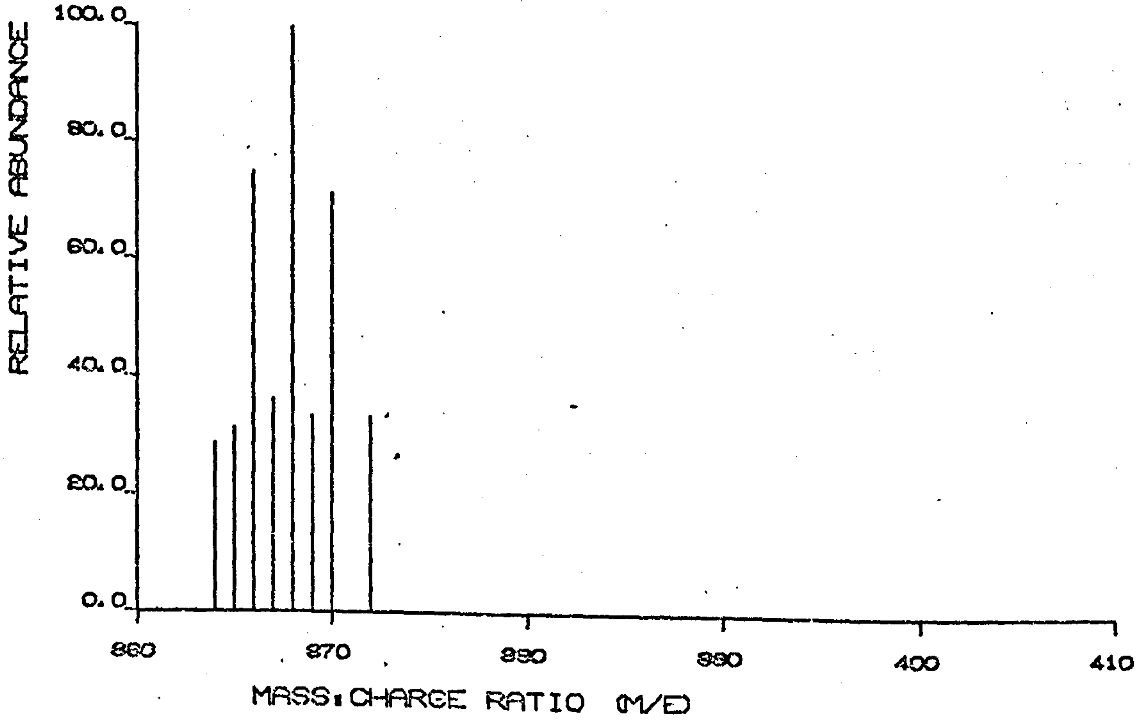
ISOTOPE PATTERN FOR TWO MOLYBDENUM ATOMS



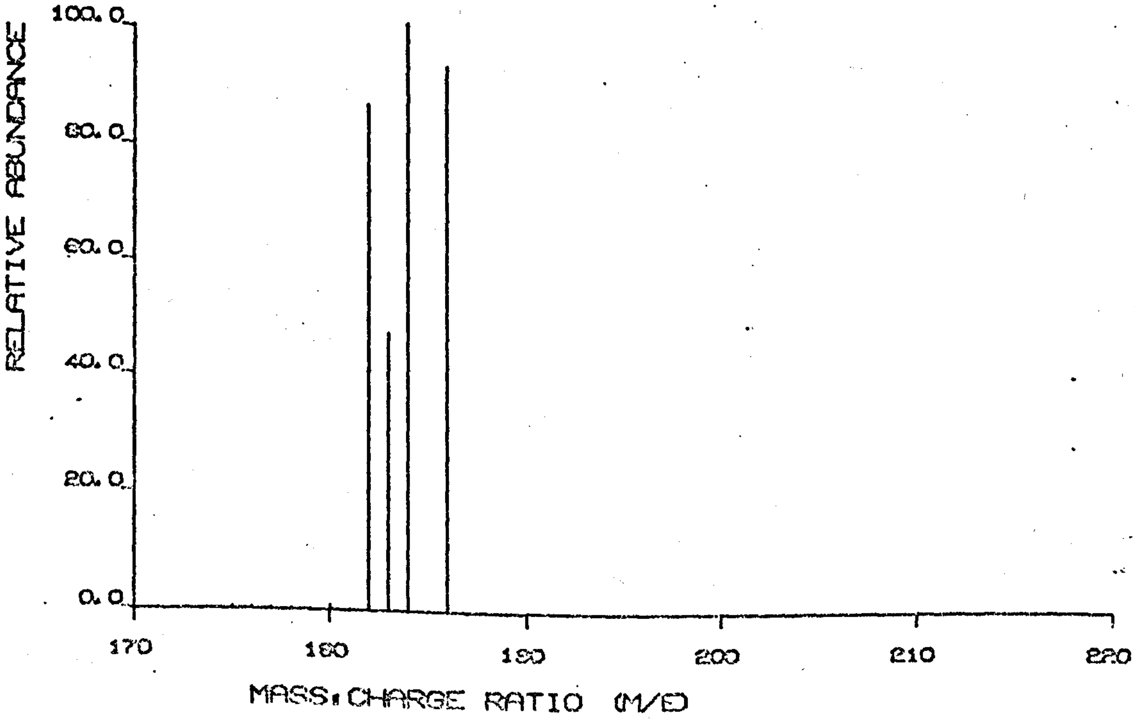
ISOTOPE PATTERN FOR ONE MOLYBDENUM ATOM



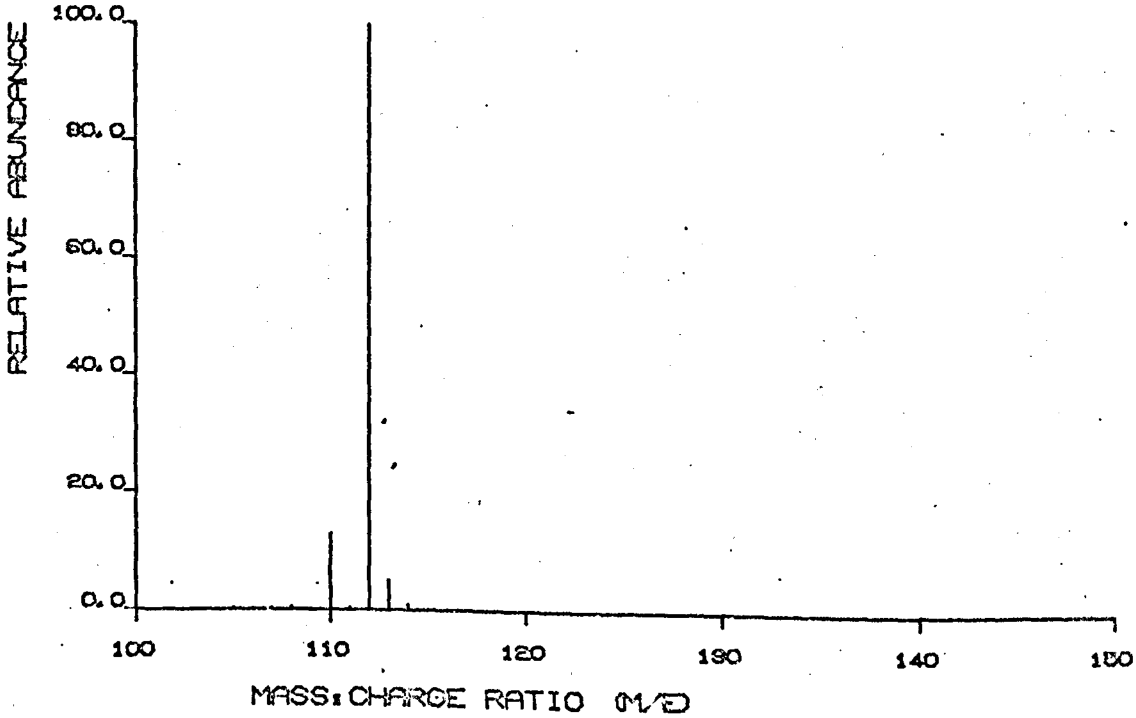
ISOTOPE PATTERN FOR TWO TUNGSTEN ATOMS



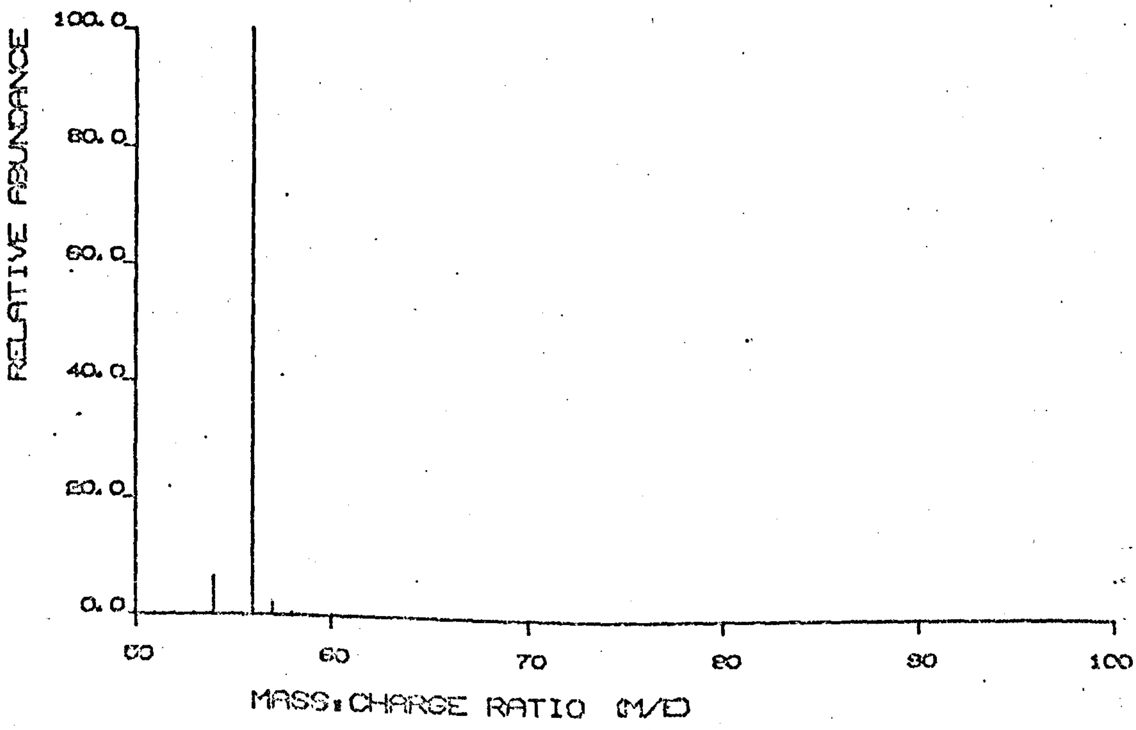
ISOTOPE PATTERN FOR ONE TUNGSTEN ATOM



ISOTOPE PATTERN FOR TWO IRON ATOMS



ISOTOPE PATTERN FOR ONE IRON ATOM

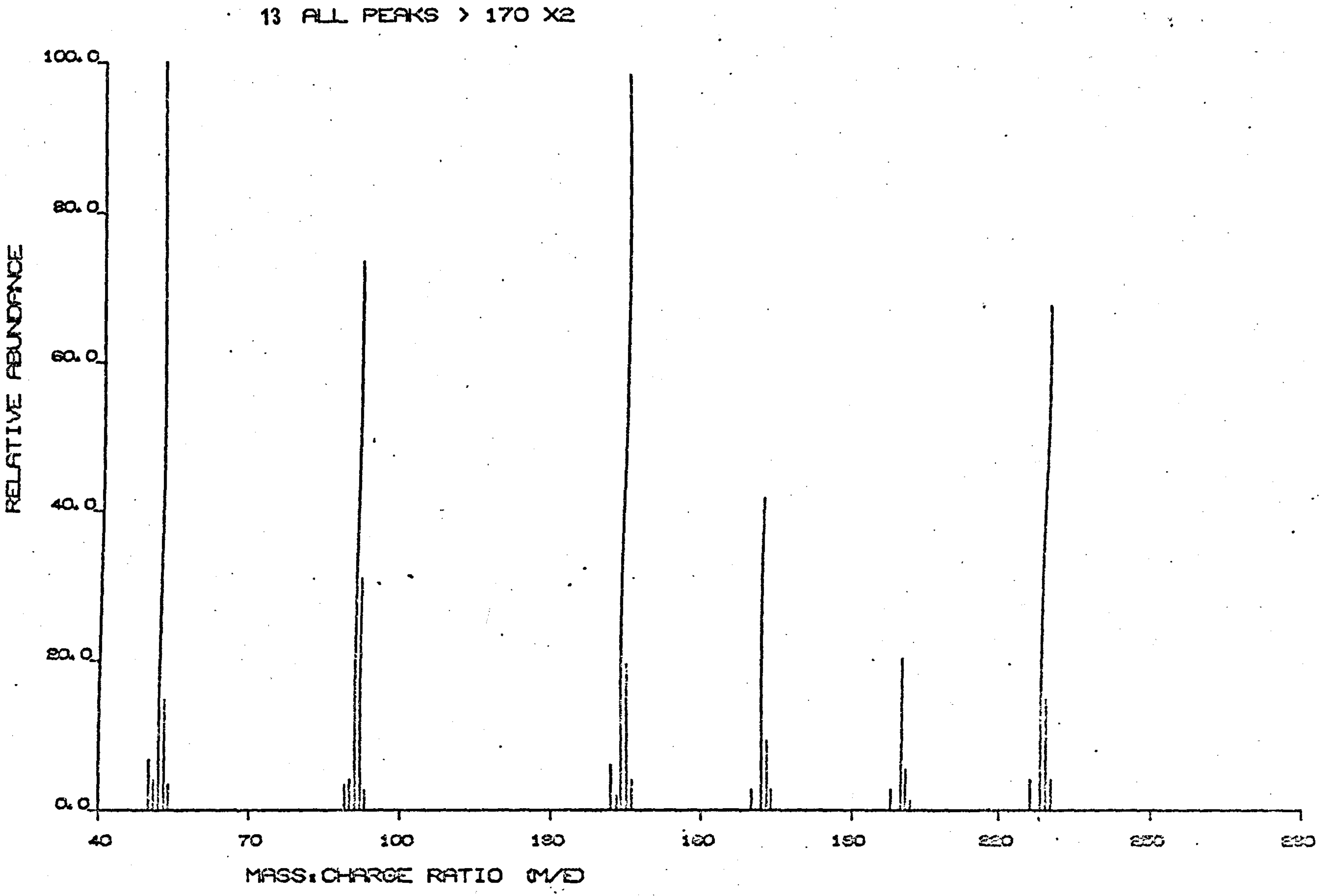


SPECTRUM 13 $(\eta^6\text{-}C_7H_8)Cr(CO)_3$

m/e	RI	Assignment
228	33.56	$C_7H_8Cr(CO)_3^+$
200	10.07	$C_7H_8Cr(CO)_2^+$
172	20.81	$C_7H_8Cr(CO)^+$
144	97.99	$C_7H_8Cr^+$
92	30.87	$C_7H_8^+$
91	73.15	$C_7H_7^+$
52	100.00	Cr^+

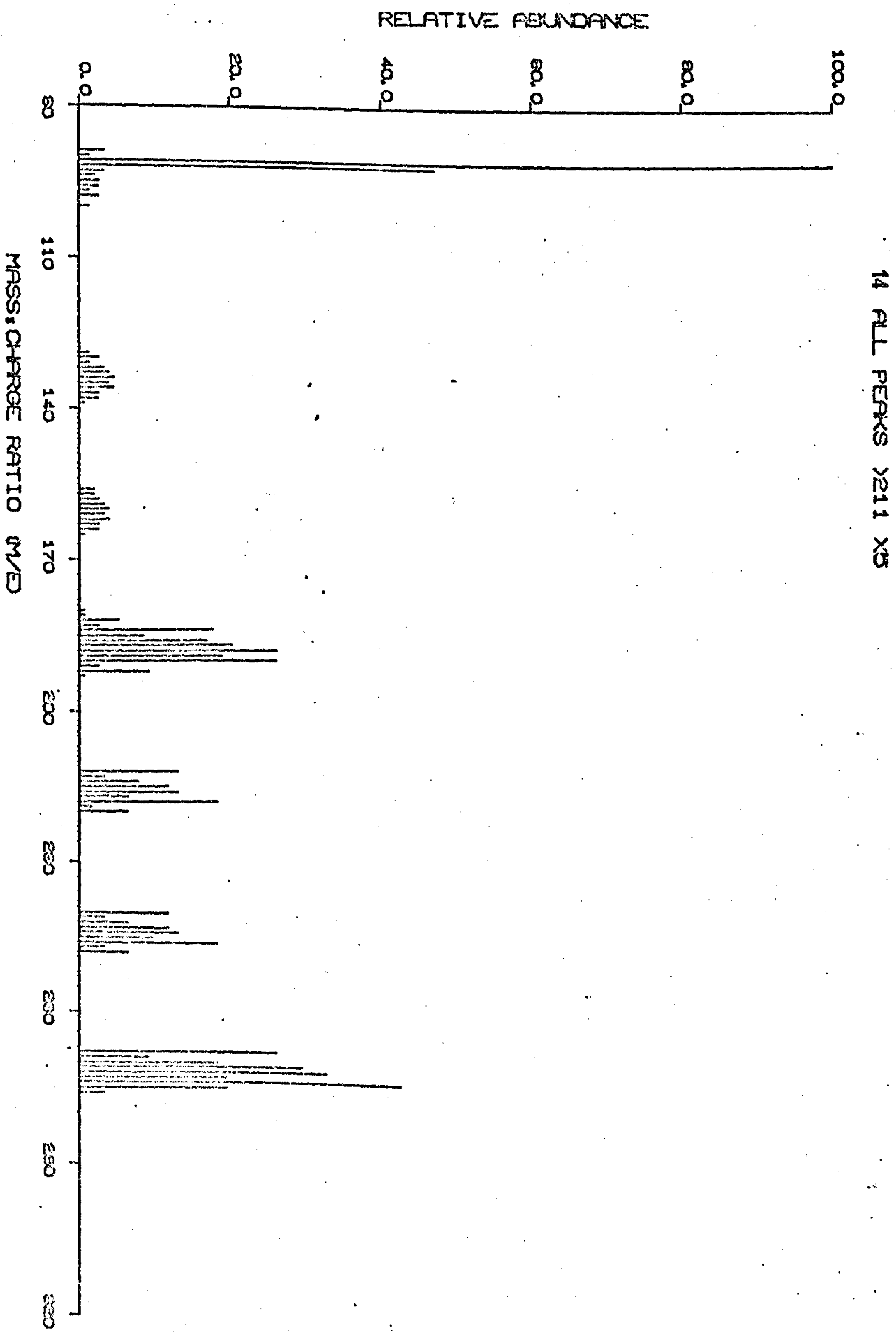
metastable transitions detected:

228 ⟶ 200	M*	175.43
172 ⟶ 144	M*	120.56


13 ALL PEAKS > 170 X2
RELATIVE ABUNDANCE
100.0
80.0
60.0
40.0
20.0
0.0
40
70
100
130
160
190
220
250
280
MASS:CHARGE RATIO (M/E)

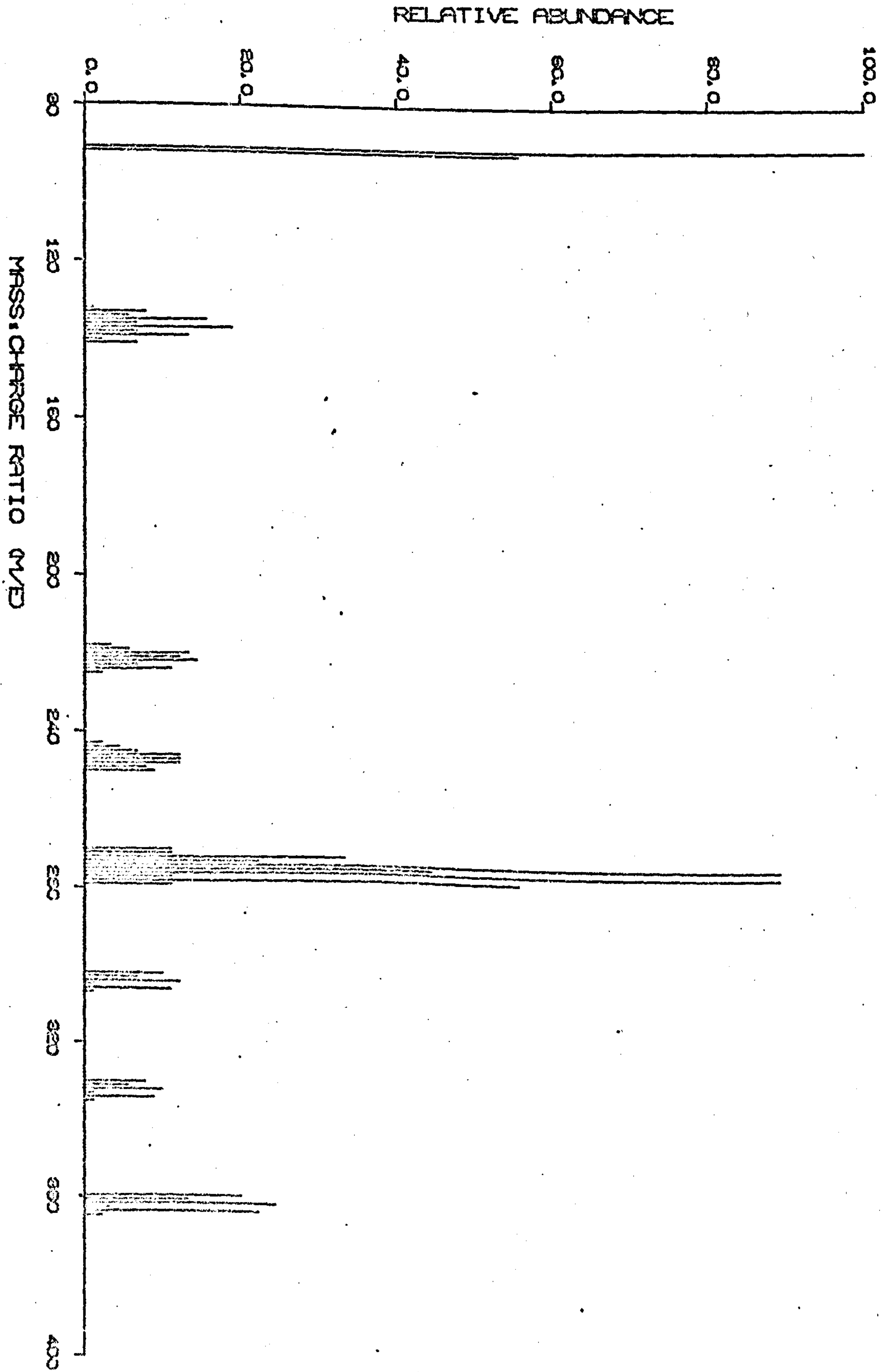
SPECTRUM 14 $(\eta^6\text{-}C_7H_8)Mo(CO)_3$

m/e	RI	Assignment
274	8.52	$C_7H_8Mo(CO)_3^+$
246	3.67	$C_7H_8Mo(CO)_2^+$
218	3.67	$C_7H_8Mo(CO)^+$
190	26.19	$C_7H_8Mo^+$
92	47.15	$C_7H_8^+$
91	100.00	$C_7H_7^+$
164	2.62	$C_5H_6Mo^+$
137	2.62	$C_7H_8Mo(CO)_3^{++}$


14 ALL PEAKS >211 X5
RELATIVE ABUNDANCE
0.0
20.0
40.0
60.0
80.0
100.0
80
110
140
170
200
230
260
290
320
MASS:CHARGE RATIO (M/E)

SPECTRUM 15 $(\eta^6\text{-}C_7H_8)W(CO)_3$

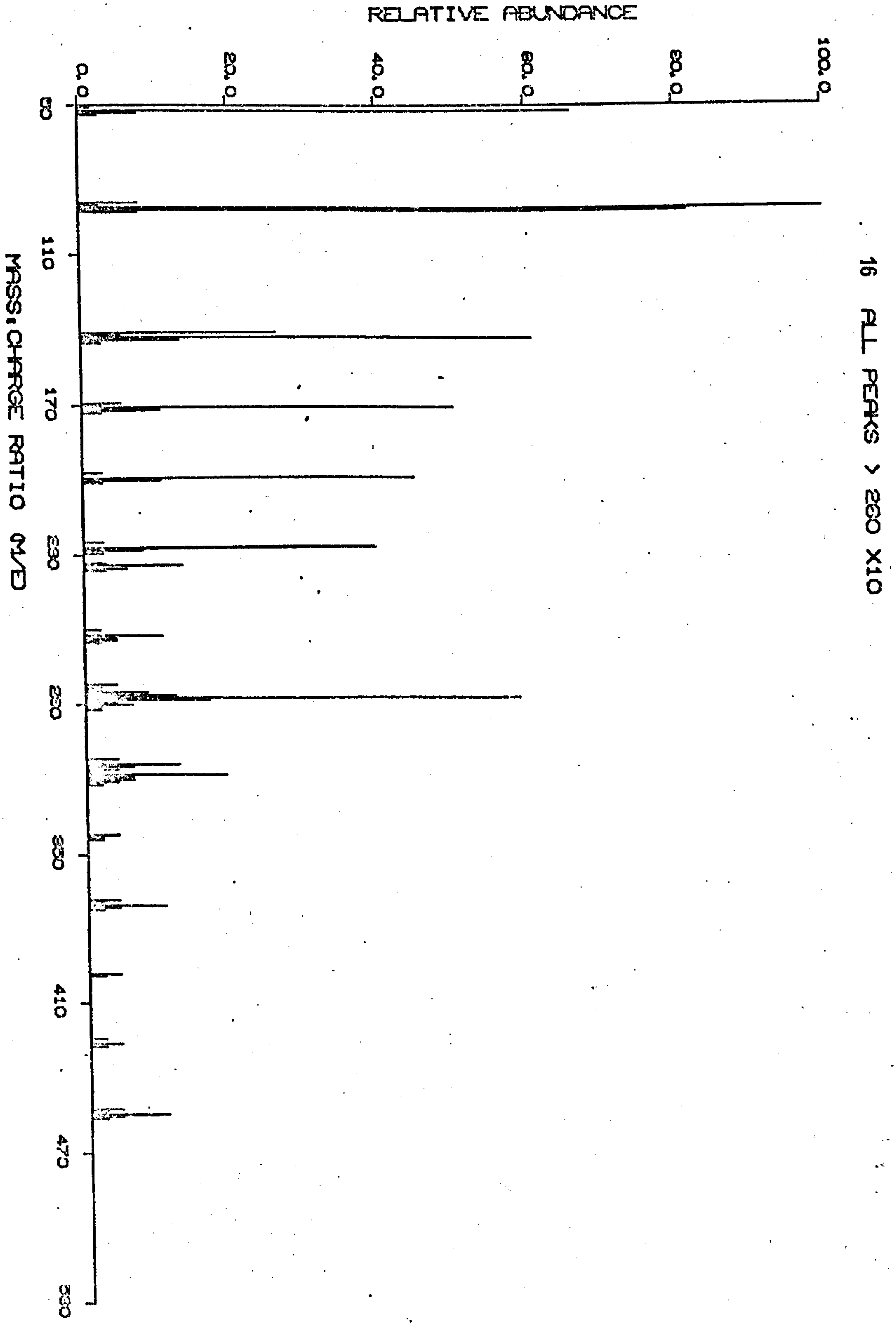
m/e	RI	Assignment
360	20.00	$C_7H_8W(CO)_3^+$
332	10.00	$C_7H_8W(CO)_2^+$
304	12.22	$C_7H_8W(CO)^+$
276	88.89	$C_7H_8W^+$
248	12.22	$C_5H_4W^+$
222	14.44	$C_3H_2W^+$
137	18.89	$C_7H_8W^{++}$
92	55.56	$C_7H_8^+$
91	100.00	$C_7H_7^+$


RELATIVE ABUNDANCE
0.0
20.0
40.0
60.0
80.0
100.0
80
120
160
200
240
280
320
360
400
MASS:CHARGE RATIO (M/E)

15

SPECTRUM 16 $[(\eta^6\text{-}C_7H_7)Cr(CO)_3]_2$

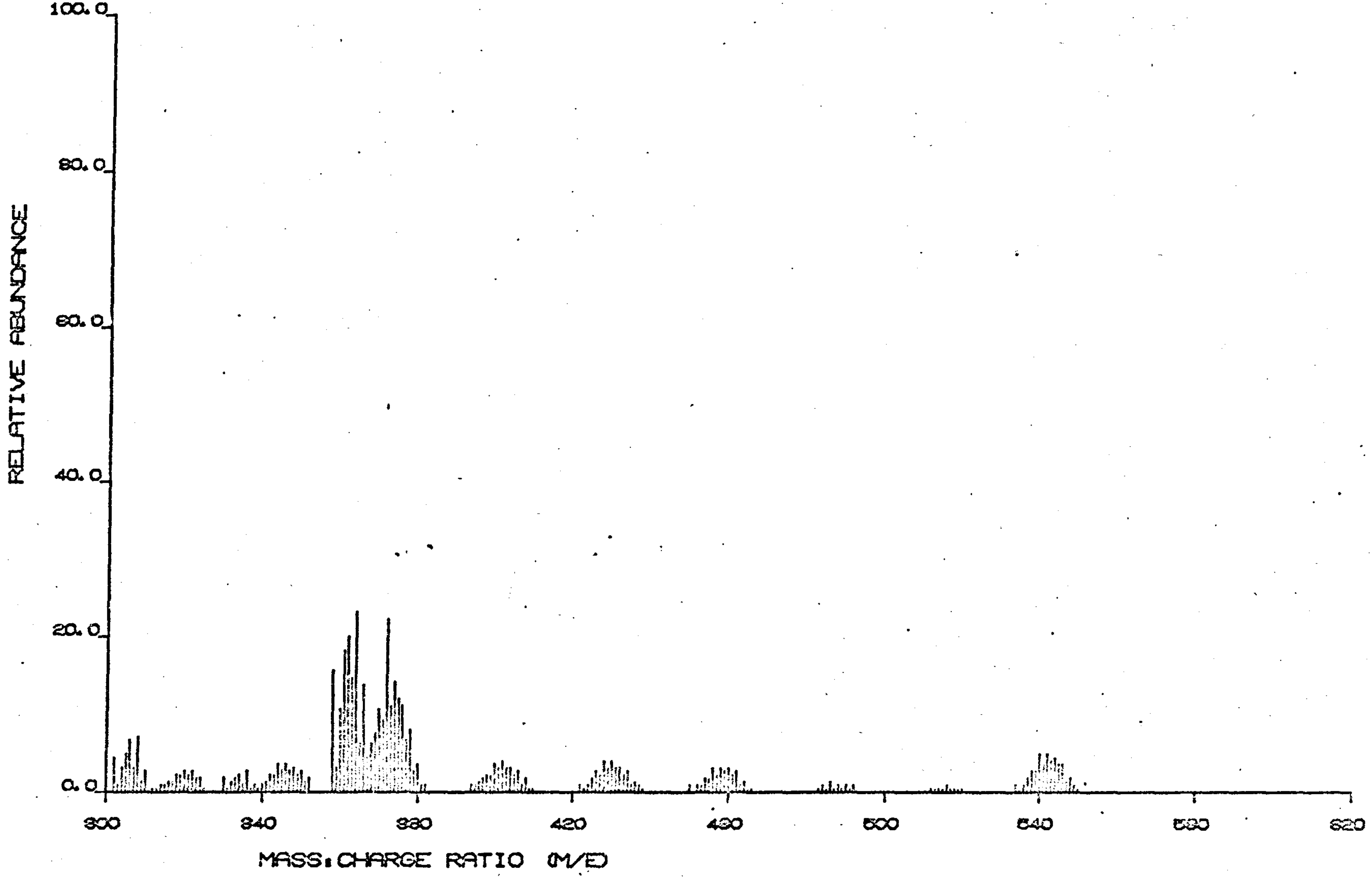
m/e	RI	Assignment
454	1.04	$C_{14}H_{14}Cr_2(CO)_6^+$
426	0.42	$C_{14}H_{14}Cr_2(CO)_5^+$
398	0.42	$C_{14}H_{14}Cr_2(CO)_4^+$
370	1.04	$C_{14}H_{14}Cr_2(CO)_3^+$
342	0.42	$C_{14}H_{14}Cr_2(CO)_2^+$
314	1.25	$C_{14}H_{14}Cr_2(CO)^+$
286	1.21	$C_{14}H_{14}Cr_2^+$
234	13.20	$C_{14}H_{14}Cr^+$
182	1	$C_{14}H_{14}^+$
91	100.00	$C_7H_7^+$
318	1.88	$C_{14}H_{14}Cr(CO)_3^+$
290	6.30	$C_{14}H_{14}Cr(CO)_2^+$
262	1.04	$C_{14}H_{14}Cr(CO)^+$
234	13.20	$C_{14}H_{14}Cr^+$
227	39.4	$C_7H_7Cr(CO)_3^+$
199	44.7	$C_7H_7Cr(CO)_2^+$
171	50.00	$C_7H_7Cr(CO)^+$
143	60.5	$C_7H_7Cr^+$
52	66.10	Cr^+


16 ALL PEAKS > 260 X10
RELATIVE ABUNDANCE
0.0
20.0
40.0
60.0
80.0
100.0
MASS:CHARGE RATIO (M/E)
50
110
170
230
290
350
410
470
530

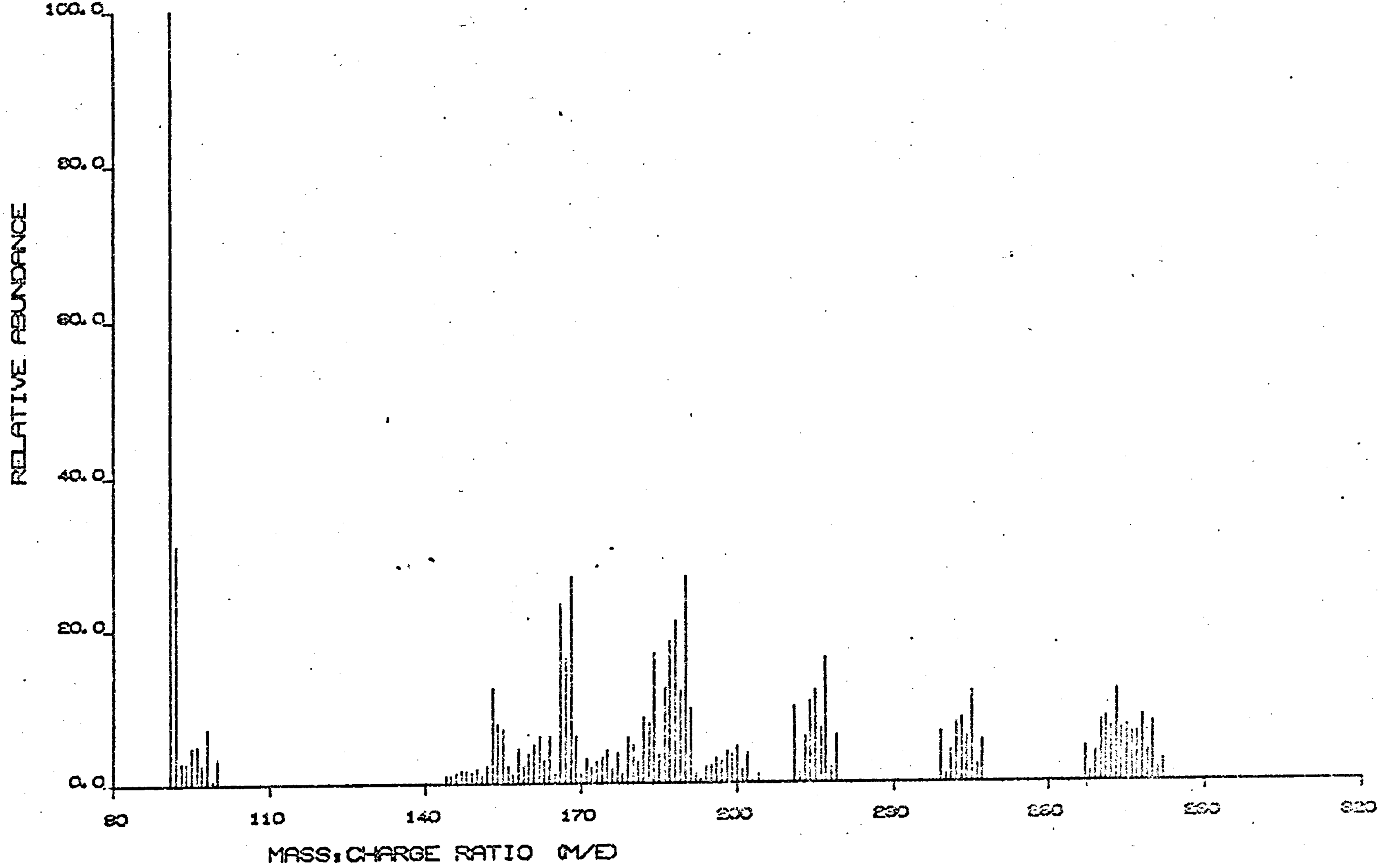
SPECTRUM 17 $[(\eta^6\text{-}C_7H_7)Mo(CO)_3]_2$

m/e	RI	Assignment
546	0.356	$C_{14}H_{14}Mo_2(CO)_6^+$
518	0.044	$C_{14}H_{14}Mo_2(CO)_5^+$
490	0.089	$C_{14}H_{14}Mo_2(CO)_4^+$
462	0.267	$C_{14}H_{14}Mo_2(CO)_3^+$
434	0.267	$C_{14}H_{14}Mo_2(CO)_2^+$
406	0.267	$C_{14}H_{14}Mo_2(CO)^+$
378	0.80	$C_{14}H_{14}Mo_2^+$
364	2.311	$C_{14}H_{14}Mo(CO)_3^+$
336	0.267	$C_{14}H_{14}Mo(CO)_2^+$
308	0.711	$C_{14}H_{14}Mo(CO)^+$
280	7.56	$C_{14}H_{14}Mo^+$
182	8.44	$C_{14}H_{14}^+$
91	100.00	$C_7H_7^+$
98	7.11	Mo^+
273	11.78	$C_7H_7Mo(CO)_3^+$
245	11.56	$C_7H_7Mo(CO)_2^+$
217	16.00	$C_7H_7Mo(CO)^+$
189	11.78	$C_7H_7Mo^+$
191	100.00	$C_7H_7^+$

17 ALL PEAKS > 300 X10



17

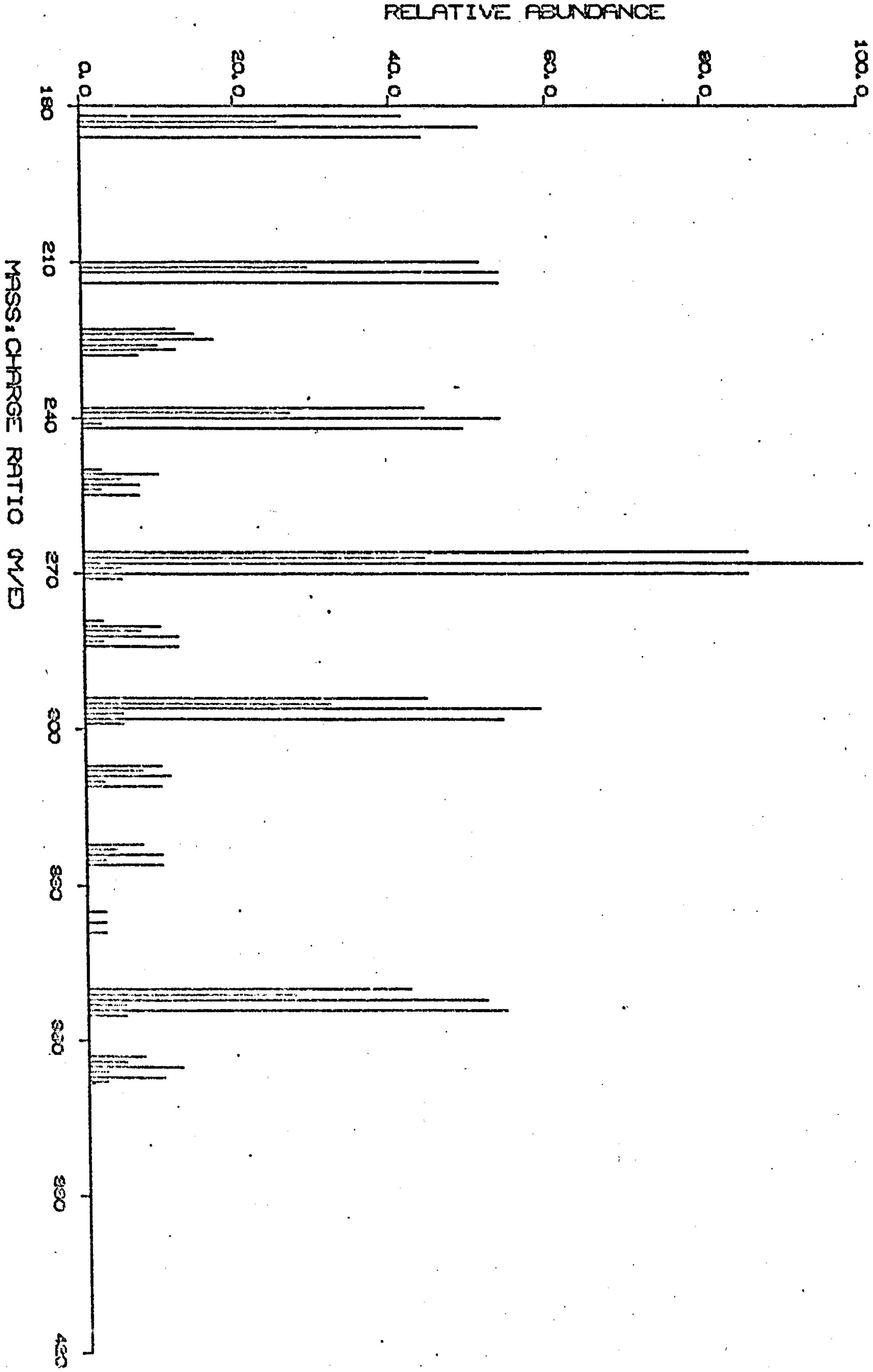

RELATIVE ABUNDANCE
100.0
80.0
60.0
40.0
20.0
0.0
80
110
140
170
200
230
260
290
320
MASS:CHARGE RATIO (M/E)

SPECTRUM 18 $(MeCN)W(CO)_5$

m/e	RI	Assignment
365	12.2	$(MeCN)W(CO)_5^+$
337	2.44	$(MeCN)W(CO)_4^+$
309	10.98	$(MeCN)W(CO)_3^+$
281	7.32	$(MeCN)W(CO)_2^+$
253	7.32	$(MeCN)W(CO)^+$
225	17.07	$(MeCN)W^+$
184	51.22	W^+

Sample contaninated with $W(CO)_6$:

m/e	RI	Assignment
352	51.22	$W(CO)_6^+$
324	9.76	$W(CO)_5^+$
296	58.54	$W(CO)_4^+$
268	100.00	$W(CO)_3^+$
240	53.66	$W(CO)_2^+$
212	53.66	$W(CO)^+$
184	51.22	W^+


RELATIVE ABUNDANCE
0.0
20.0
40.0
60.0
80.0
100.0
MASS:CHARGE RATIO (M/E)
180
210
240
270
300
330
360
390
420

18

SPECTRUM 19 $[(\eta^4\text{-}C_6H_7)Fe(CO)_3]_2$

m/e	RI	Assignment
438	10.31	$C_{12}H_{14}Fe_2(CO)_6^+$
410	21.62	$C_{12}H_{14}Fe_2(CO)_5^+$
382	18.92	$C_{12}H_{14}Fe_2(CO)_4^+$
354	10.81	$C_{12}H_{14}Fe_2(CO)_3^+$
326	16.22	$C_{12}H_{14}Fe_2(CO)_2^+$
298	13.51	$C_{12}H_{14}Fe_2(CO)^+$
270	48.65	$C_{12}H_{14}Fe_2^+$
214	29.78	$C_{12}H_{14}Fe^+$
212	21.62	$C_{12}H_{12}Fe^+$
156	29.73	$C_{12}H_{12}^+$
154	51.35	$C_{12}H_{10}^+$
77	51.35	$C_6H_5^+$
56	100.00	Fe^+

metastable transitions observed:

$438 \longrightarrow 410$ M* 383.8

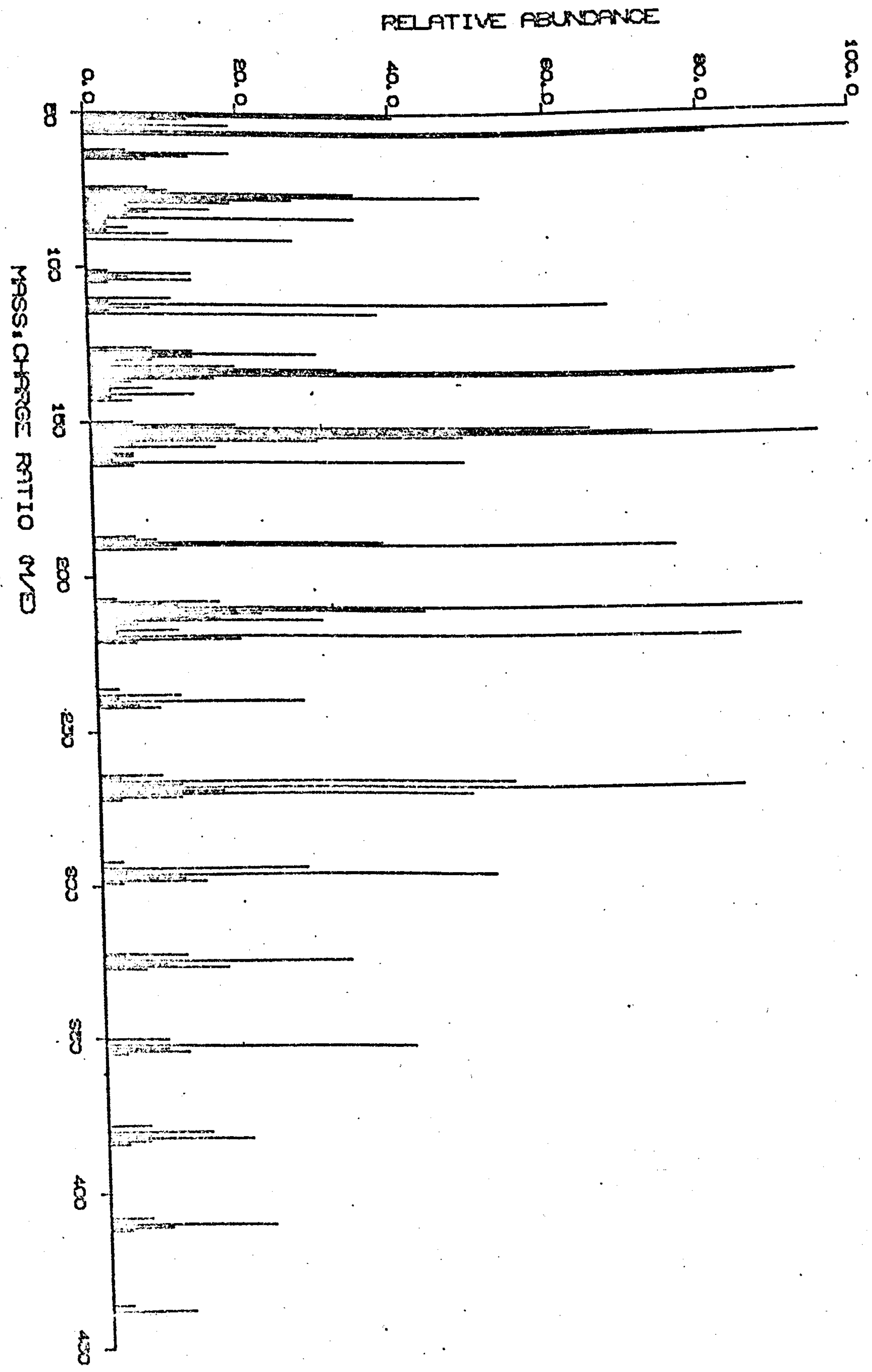
$410 \longrightarrow 382$ M* 355.9

$382 \longrightarrow 354$ M* 328.05

$354 \longrightarrow 326$ M* 300.21

$326 \longrightarrow 298$ M* 272.4

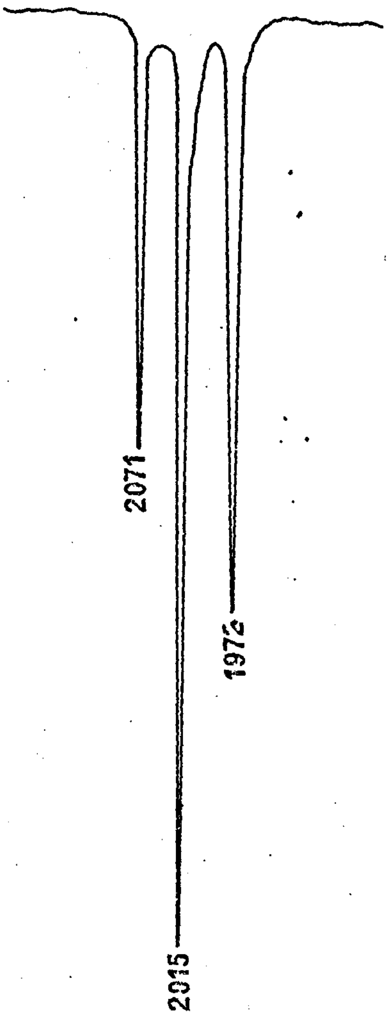
$298 \longrightarrow 270$ M* 244.6


RELATIVE ABUNDANCE
0.0
20.0
40.0
60.0
80.0
100.0
MASS:CHARGE RATIO (M/E)
50
100
150
200
250
300
350
400
450

APPENDIX 2

MISCELLANEOUS SPECTRA

Spectrum No.	Illustration	
63	$Re_2(CO)_{10}$	IR
64	$HRe(CO)_5$	IR



$Re_2(CO)_{10}$

FIGURE 63
solvent: cyclohexane

$HRe(CO)_5$

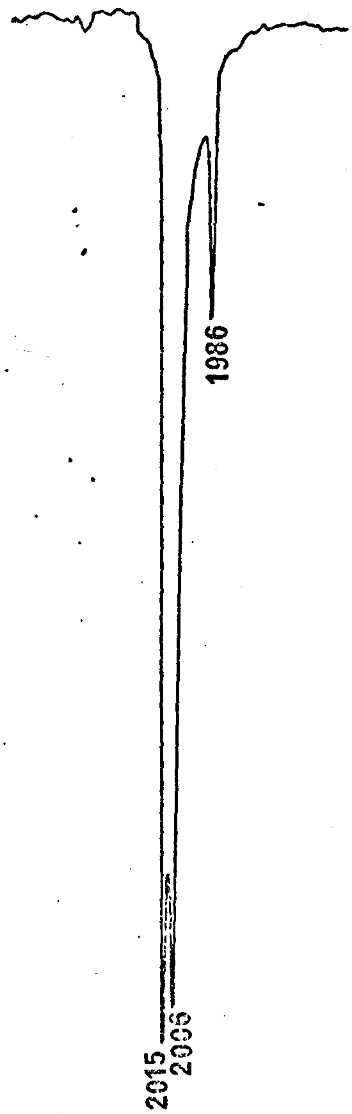


FIGURE 64

solvent: cyclohexane

APPENDIX 3

COURSES ATTENDED DURING THE PERIOD OF THIS STUDY IN FULFILMENT OF CNAA REGULATIONS

Nuclear Magnetic Resonance Spectroscopy	12 lectures
Mass Spectrometry	6 lectures
Thermo-Gravimetric Analysis - Kingston	1 day 1976
Patents in the Chemical Industry - Kingston	1 day 1976
Advances in Catalysis by Transition Metals - Kingston	1 day 1977
Chemical Aspects of Electron Spin Resonance University College, Cardiff	11-14 April 1978

During the period of this study I have attended some 30 colloquia on various chemical topics given by internal and external speakers at Kingston. I have delivered two colloquia at Kingston Polytechnic, and one at the South East England Postgraduates Meeting at Cambridge (10-11 March 1977)

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PUBLICATIONS

Some aspects of the work on the reactions of decacarbonyldirhenium with organo-phosphanes and phosphites have been published as notes in Inorganic and Nuclear Chemistry Letters. Reprints of these are bound herein.

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FREE RADICAL INTERMEDIATES IN THE REACTION OF DECACARBONYLDIRHENIUM AND TRIPHENYLPHOSPHANE

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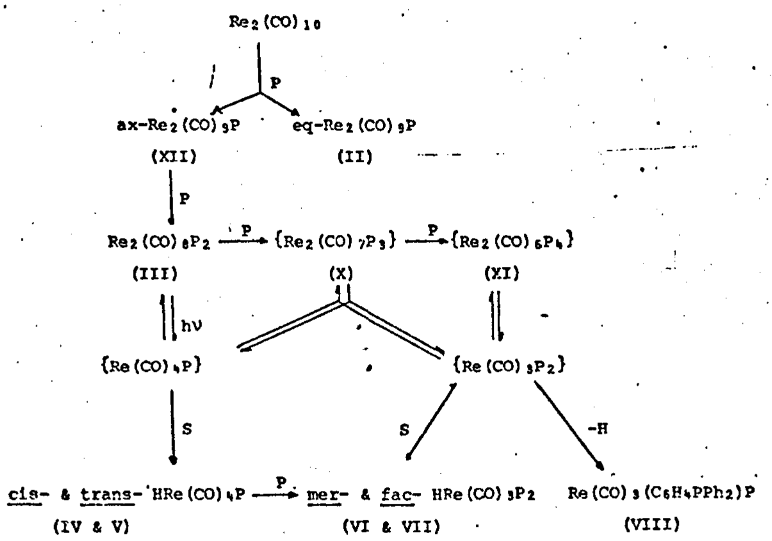
There has recently been much interest in the production and identification of metal-centred free radicals (1). Stable 17-electron transition metal species have been reported by a number of workers, however, some of these have subsequently been shown to be diamagnetic complexes (2,3). Our interest in such compounds, as reactive intermediates, has led us to reinvestigate the preparation of $\{Re(CO)_3(PPh_3)_2\}$(I) (4,5).

We have repeated the reaction reported to yield (I), which involves heating $Re_2(CO)_{10}$ and PPh_3 (1:5 mole ratio) in refluxing xylene for 48 h. in daylight. In our hands the reaction follows a different course. Following the reported work-up procedure, we isolated either 1,2-$Re_2(CO)_8(PPh_3)_2$ (III) or mer-$HRe(CO)_3(PPh_3)_2$ (VI) or a mixture of these two depending on the composition of the benzene/petroleum spirit solvent system and the rate of cooling. T.l.c. examination of the liquor after crystallisation showed the presence of a range of other products and preparative t.l.c. of this mixture yielded the complexes shown in the scheme (except complex XII; vide infra). These were identified by standard spectroscopic and analytical techniques. On the basis of the isolated products and the following observations, we suggest that the reaction follows the scheme shown below. Some of these observations implicate free radical intermediates in the reaction sequence.



P = PPh_3 S = solvent

Compounds in { } brackets were not isolated

Direct evidence for the presence of free radicals comes from inhibition of the reaction by oxygen and the trapping agent, galvinoxyl, the ability of the reaction mixture to initiate polymerisation of a 1:1 mixture of methyl methacrylate and styrene, a reaction known to proceed by a free radical mechanism (6) and the e.s.r studies of Poë *et al.*(7). Separate experiments in both the presence and absence of PPh_3 at lower temperatures have shown the reaction proceeds in the same manner in the former, however, no $HRe(CO)_5$ is observed in the latter although the experiments were conducted below the decomposition point of this compound. This indicates that homolytic fission of the parent carbonyl is not an important process in this reaction and that phosphine substitution precedes radical formation. We suggest that the hydrides are formed by reaction of the unstable radicals with the solvent as demonstrated by Ugo and Bonati (8) and experiments performed in xylene, heptane and benzene under identical conditions implicate aliphatic rather than aromatic hydrogen atoms in hydride formation.

Although VI and VII may be formed by substitution into IV and V (we have found that the separate reaction of IV with PPh_3 gives VI), the intermediacy of the $Re(CO)_3(PPh_3)_2\cdot$ radical provides the most viable route to VIII. However, we cannot totally exclude formation of VIII by elimination of a metal hydrido-complex from either of the proposed intermediates X and XI (9). We invoke these highly substituted dimers and their thermal degradation to I, as reaction of $Re_2(CO)_{10}$ and PPh_3 in the dark yields all products except IV and V. Reactions carried out at room temperature with u.v. irradiation or, more slowly, in daylight, yield the full range of products. This suggests that scission of III is a purely photo-induced process and formation of I does not proceed by substitution of $Re(CO)_4PPh_3\cdot$. Attempts to isolate X and XI have not been successful and we believe the previous reports of XI (5, 10) to be in error, the compound reported, in fact, being VI. Reaction of $Re_2(CO)_{10}$ and PPh_3 in an equimolar ratio yielded the axial isomer, XII, as the main product, however, only the previously unreported equatorial isomer, II, is isolated from the 1:5 mole ratio reaction. This probably reflects a lower reactivity for II compared with XII, by virtue of cis-labilisation and steric effects (11). Complex XII, isolated from the 1:1 reaction and prepared by the alternative route of Fawcett et al (12), underwent very rapid reaction with PPh_3, yielding the full range of products except XII. The reactivity of III with PPh_3 was also examined independently and fits into the scheme.

A polynuclear complex was also isolated from the 1:5 reaction in quantities sufficient only for mass spectral analysis. The highest ion observed corresponds to $H_2Re_3(CO)_7(PPh_3)^+$ and as this is clearly not the molecular ion, we are unable to completely characterise this product and have, therefore, not attempted to place it in the scheme.

This study, therefore, shows a parallel to that observed for the reaction of $Mn_2(CO)_{10}$ and PPh_3, in that reactive metal-centred radicals are generated but cannot be isolated. A kinetic study of certain aspects of this reaction (7) are broadly in agreement with our findings. However, we suggest that the main product observed in that study and reported by Nyman (4) is VI rather than I. We are unable to confirm the isomeric form of I reported elsewhere (5), as we have found nothing with an analogous infrared spectrum to that observed earlier.

We are investigating other possible routes to stable metal-centred free radicals.

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THE REACTIONS OF DECACARBONYLDIRHENIUM WITH SOME ORGANO-PHOSPHANES AND PHOSPHITES

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We recently reported a detailed study of the reaction between $Re_2(CO)_{10}$ and PPh_3 (1), in which we were unable to isolate the metal-centred free radical, $Re(CO)_3(PPh_3)_2\cdot$, although evidence was presented for its existence as a reactive intermediate. In an attempt to stabilize radicals of this type we have studied the reaction of $Re_2(CO)_{10}$ with a range of organo-phosphanes and phosphites.

To date there are no completely characterised stable mononuclear 17-electron complexes in the group VIIb triad, however, there is irrefutable evidence that the complex, $Co(CO)_3L$ (L = bis(diphenylphosphino)maleic anhydride) is a stable 19-electron monomer (2). In this case, it is likely that the electron-withdrawing nature of the anhydride group lowers the unpaired electron density at the metal atom, thereby making the metal more "18-electron-like". In our previous study of the $Re_2(CO)_{10}$-PPh_3 system, metal centred radicals were observed to undergo rapid hydrogen abstraction reactions, thereby yielding 18-electron metal hydrides. In seeking to stabilise mononuclear rhenium-centred radicals, we investigated reactions with organo-phosphanes and phosphites that are approaching the extremes of the range of electronically transmitted effects, as well as those capable of shielding the metal atom because of their bulk (3).

In reactions involving triphenylphosphite (I), tri-o-tolylphosphite (II) and tri-p-chlorophenylphosphite (III) (L), the product isolated in each case, after a thermal reaction of 16 to 20h. in refluxing xylene, was 1,2-diaxial-$Re_2(CO)_8L_2$. In the case of I, a small amount of axial-

$Re_2(CO)_9L$, as well as the metalated species $Re(CO)_3L(L\text{-}H)$, was also isolated from the reaction. A similar metalated species was formed by II after ca. 50h. reaction time, however no products other than the dimer were isolated with III even after a 100h. reaction period. In none of these reactions were any hydridometal complexes formed, in complete contrast to the reaction with PPh_3. It might therefore be inferred that electron-withdrawing phosphite ligands stabilise radicals of the type $Re(CO)_4L\cdot$ or $Re(CO)_3L_2\cdot$ with respect to hydride formation by lowering the unpaired electron density at the metal atom, but that the increase in their life-times is only sufficient for them to achieve the correct geometry for ring closure to yield the metalated complex. However, there will be an increased propensity toward metalation in the case of these phosphites, due to formation of the sterically favoured five-membered ring (4). N.m.r. evidence indicates that metalation occurs at the aromatic ring rather than the methyl group in the case of II. Despite an extensive search, we could find no evidence for the formation of expected intermediate metalated species, $Re(CO)_4(L\text{-}H)$ (L = I, II). It is, therefore, suggested that $Re(CO)_3L(L\text{-}H)$ is formed by phosphite substitution into $Re_2(CO)_8L_2$, followed by facile dissociation of the more highly substituted dimeric product to yield $Re(CO)_3L_2\cdot$, which then undergoes ring closure rather than by direct dissociation of $Re_2(CO)_8L_2$, ring closure of the radical so produced, followed by phosphite substitution into the complex $Re(CO)_4(L\text{-}H)$. This is in agreement with our findings for the reaction of $Re_2(CO)_{10}$ and PPh_3 (1).

In order to investigate the importance of metalation reactions for phosphane ligands, the reaction with tri(o-tolyl)phosphane (IV) was studied. Although the metalated compound $Re(CO)_3L(L\text{-}H)$ (L = PPh_3) is only a minor product of the reaction with PPh_3 (1), IV yields exclusively $Re(CO)_4(L\text{-}H)$. N.m.r. evidence indicates metalation at a methyl group rather than an aromatic ring, as has been observed previously with a related ligand (5). That $Re(CO)_3L(L\text{-}H)$ is not observed is presumably due to the extreme bulk of IV (3). For comparison, tri-(p-tolyl)phosphane (V) reacts with $Re_2(CO)_{10}$ under identical conditions to yield $Re_2(CO)_8L_2$ and mer-$HRe(CO)_3L_2$ (L = V) as the principal products. It is worthy of note that V has a much smaller cone angle than IV and is incapable of forming a five-membered metalated ring. That we have been unable to identify any other product in the thermal reactions of IV and $Re_2(CO)_{10}$ in either daylight or the dark, must cast some doubt on the formation of $Re(CO)_4(L\text{-}H)$ via dissociation of $Re_2(CO)_8L_2$. The alternative mechanism, suggested by Alper (6), of $HRe(CO)_5$ elimination from a very labile dimer, $Re_2(CO)_9L$, may operate in this case, especially in view of the extreme bulk of the ligand (cone angle of IV = 194°, c.f. PPh_3 and V both have the value of 145°).

Finally, while ligands such as I and II, may act as a good means of lowering the electron density at the metal atom in radical species such as $Re(CO)_3L_2\cdot$, this would make these complexes more "16-electron-like" and therefore more likely to undergo oxidative addition reactions. The metalation reactions observed may be classified as a type of oxidative addition. In seeking stability for these radicals we have studied the reaction of $Re_2(CO)_{10}$ and tri(cyclohexyl)phosphane (VI). This ligand should increase the electron density at the metal (3), thus making it more "18-electron like", its relatively large cone angle (170°) should protect the metal from hydrogen abstraction reactions and its steric requirements for metalation are extremely specific and therefore make such internal reactions unlikely. However, thermal reaction of $Re_2(CO)_{10}$ and VI (L) yield $Re_2(CO)_8L_2$ and <u>mer</u>-$HRe(CO)_3L_2$ as the main reaction products. We, therefore, do not believe it likely that stable 17-electron species of the type discussed above will be isolated.

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