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CANADIAN THESES ON MICROFICHE

THÈSES CANADIENNES SUR MICROFICHE

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TITLE OF THESIS/*TITRE DE LA THÈSE* Some ASPECTS OF THE ORGANOMETALLIC CHEMISTRY OF THE GROUP VI TRANSITION METALS

UNIVERSITY/*UNIVERSITÉ* Alberta

DEGREE FOR WHICH THESIS WAS PRESENTED/ *GRADE POUR LEQUEL CETTE THÈSE FUT PRÉSENTÉE* Ph.D.

YEAR THIS DEGREE CONFERRED/*ANNÉE D'OBTENTION DE CE DEGRÉ* 1974

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THE UNIVERSITY OF ALBERTA

SOME ASPECTS OF THE ORGANOMETALLIC CHEMISTRY OF THE GROUP VI TRANSITION METALS

by

EZRA EDDY ISAACS

A THESIS

SUBMITTED TO THE FACULTY OF
GRADUATE STUDIES IN PARTIAL FULFILMENT
OF THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

Department of Chemistry

EDMONTON, ALBERTA

Fall, 1974

THE UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled SOME ASPECTS OF THE ORGANOMETALLIC CHEMISTRY OF GROUP VI TRANSITION METALS submitted by EZRA EDDY ISAACS in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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Robert B Jordan

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External Examiner

DATE ....June 7th....... 1974

ABSTRACT

The reaction of cycloheptatrienyltricarbonyl molybdenum cation with various main group V donor ligands (L) yielded, in general, mono-substituted complexes, $[C_7H_7Mo(CO)_2L]^+$. ^{31}P nmr studies on some related di-tertiary phosphine complexes provided a convenient and unequivocal determination of the stereochemistry.

The reduction of the cation cycloheptatrienyl complexes with sodium borohydride provided a suitable synthetic route to the group V derivatives of cycloheptatrienetricarbonylmolybdenum. The infrared, ^1H and ^{13}C nmr, and mass spectral properties of these complexes were studied. Some main group IV ligands bonded to cycloheptatrienyldicarbonylmolybdenum were also prepared and studied by spectral means.

A number of main group IV - group VI metal pentacarbonyl anionic derivatives have been prepared by the reaction of the chloropentacarbonyl anions with the organolithium compounds of the group IV elements. These compounds have the general formula, $[R_3M'-M(CO)_5]^-$ (where R = Me, Ph or halogen; M' = Si, Ge, Sn or Pb; M = Cr, Mo or W). Approximate carbonyl force constants were calculated from the infrared carbonyl stretching vibrations and these provided some insight into the nature of the metal-metal bonds.

Transition metal nitrosyl derivatives have also been prepared by the reaction of some anionic complexes with nitrosonium hexafluorophosphate. These compounds have the general formula $LM(CO)_4NO$ (where L is a main group IV ligand or a halogen group and M is Mo or W). The carbonyl and nitrosyl force constants were calculated and are discussed in terms of the relative bonding properties of CO and NO ligands.

Finally, the oxidation reaction of some dinuclear metal carbonyls with $AgNO_2$ led to the formation of metal carbonyls containing nitro ligands. Linkage isomerism involving nitro and nitrito species was encountered in solution. The $[(CH_3CN)_3Re(CO)_3]^+$ cation was formed from the oxidation reaction of $[Re_4(CO)_{16}]^{2-}$ in acetonitrile.

ACKNOWLEDGEMENTS

The author wishes to express his appreciation and gratitude to:

Professor W. A. G. Graham for his guidance and help throughout the course of this work.

The members of Professor Graham's research group, past and present, for many suggestions, criticism and assistance.

Darlene Mahlow and Andrea Dunn for microanalyses.

Dr. A. Hogg and his staff for mass spectra.

Dr. T. Nakashima and his staff for ^{31}P and ^{13}C nmr spectra.

Glen Johanson for drafting of Figures.

John Jeffery and Mike Webb for assistance in proofreading.

Lu Ziola for her excellent preparation of the manuscript.

The National Research Council of Canada for a Postgraduate Scholarship, and

The University of Alberta for other financial support.

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CHAPTER I

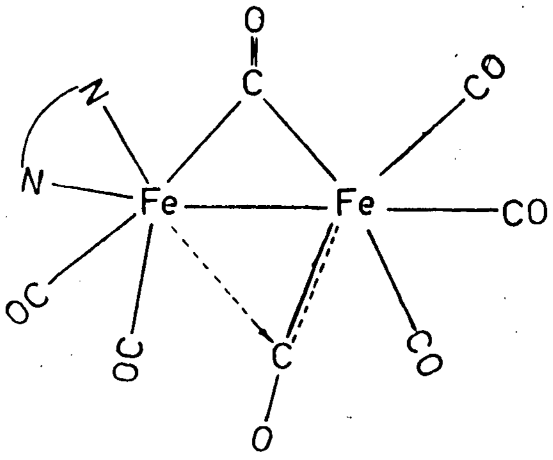
INTRODUCTION

The first portion of this thesis (Chapter II to IV) concerns the preparation of cycloheptatriene and cycloheptatrienyl molybdenum derivatives. The second part deals with the properties and synthesis of main group IV metal-transition metal anionic complexes (Chapter V) and the preparation of main group IV-molybdenum,-tungsten nitrosyl complexes (Chapter VI). The last section (Chapter VII) involves a study on the oxidation of metal carbonyl complexes using silver salts. A review of the literature relevant to each of the fields mentioned above is given as an introduction at the beginning of each chapter. This chapter is intended to serve as a brief general introduction to certain basic concepts in transition metal carbonyl chemistry. The main types of ligands present in the complexes mentioned in the thesis are introduced and the nature of the bonding between these ligands and transition metals are discussed briefly. There are numerous texts[1,2,3] and periodicals[4,5,6] which give a comprehensive introduction to the chemistry of metal carbonyls and their derivatives; what follows owes much to these reviews.

Transition metal carbonyl complexes

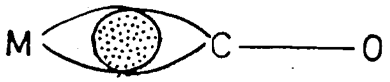
The discovery of $Ni(CO)_4$ by Mond[7] in 1890 led to the development of the chemistry of metal carbonyls and subsequently to derivatives of metal carbonyls. Whereas in the ensuing sixty years progress was only modest, at the present time the study of transition metal complexes containing carbon monoxide groups as ligands has become one of the most active areas for research. This research activity has stemmed mainly from the realization that the metal carbonyls form numerous derivatives, and in part from the amenability of many of the compounds to study by physical methods. A very practical stimulus is provided by the fact that metal carbonyls are also excellent catalysts for certain industrial processes.

A carbonyl ligand is known to bond either in a linear fashion to a single metal atom (terminal carbonyl) or form a bridge between two or more metal atoms (bridging carbonyl). An intermediate situation involving unsymmetrical carbonyl bridges (semibridging carbonyl) has recently been shown to occur.[8] As an example the X-ray structure of a 2,2'-bipyridine derivative of nonacarbonyldiiron, dipy $Fe_2(CO)_7$, which contains all three types of CO groups, is shown in **1**.



1

The molecular orbital description of the M-CO bond is as follows: An overlap of a filled sp hybrid of carbon and a vacant orbital on the metal as shown in 2, is accompanied by dative overlap of a filled $d\pi$ or a hybrid $dp\pi$ metal orbital with an empty antibonding π^* orbital of CO as shown in 3.



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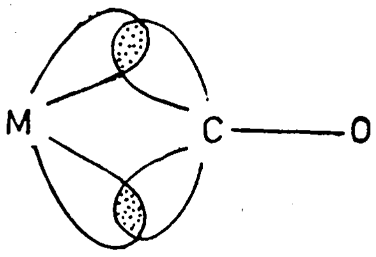


3

The bonding mechanism is synergic, since the π bond removes the excess charge built up on the metal by the

σ-donation and a stronger bond is produced than the sum of the two effects separately.

A significant consequence of the presence of electrons in the π^* orbitals of CO is the reduction of C-O bond order. The infrared (ir) spectra of these systems provide a most convenient and useful estimate of this as demonstrated by the values of the carbonyl stretching frequency [ν(CO)] for the iso-electronic complexes listed below.

$Mn(CO)_6^+$	$Cr(CO)_6$	$V(CO)_6^-$
2090	1981	1859

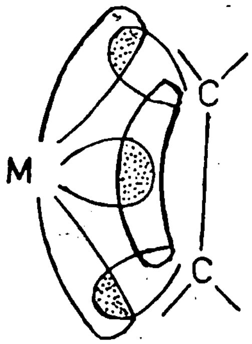
A negative charge, or lower oxidation state of the metal, places a large electron density on the metal, which means more metal to π^* bonding and as a result a decrease in the C-O bond order and lowering of ν(CO). Since the ν(CO) are sensitive to changes in the electron density on the metal they will also depend on the nature of the other ligands attached to the metal.

Effective atomic number rule

The great majority of transition metal carbonyls and their derivatives are diamagnetic, and their stoichiometry is dictated by the very useful effective atomic number (ean) rule. This formalism requires that the ligands contribute electrons such that the metal atom takes up an electronic configuration like the succeeding noble-gas atom. Thus chromium has six valence electrons and requires twelve more to attain a noble gas configuration. A molecule of CO contributes two electrons; it follows that six molecules are needed to give the stable compound $Cr(CO)_6$.

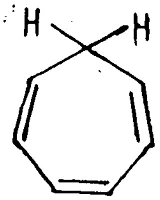
Complexes with unsaturated organic ligands

The investigation of the interaction of olefins with transition metals has proceeded at a rapid pace over the past decade. There are many types of π-complexes including mono- and di-olefin, π-allyl, π-cyclopentadienyl and π-arene complexes. The nature of bonding in all complexes of this type appears to be similar. In the simplest case of the mono-olefin complexes the bonding is believed to consist of two independent components, as shown pictorially in 4; (a) the π-electron density of the olefin overlaps with a σ-type acceptor orbital on the metal atom; and (b) back donation from the metal into the antibonding π* orbital of the ligand.



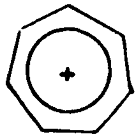
This view is thus similar to the bonding of CO discussed earlier, except that in the case of the olefin the π-electrons themselves provide the primary (dative) σ-bond. Thus in contrast to the carbonyls, where the metal lies in the nodal plane of the π-electrons, bonding in the olefin complexes is at right angles to the nodal plane.

In this work we shall consider the complexes of the following species:



cycloheptatriene

5

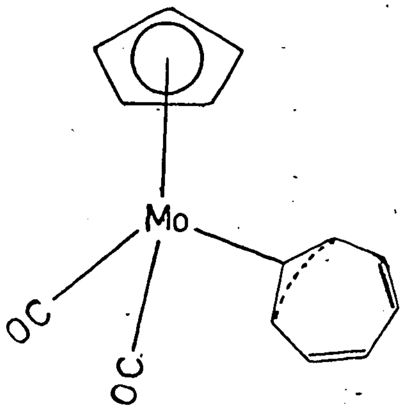


cycloheptatrienyl or
tropylium ion

6

In classifying π-complexes it is convenient to use the number of electrons formally available from the neutral hydrocarbon. In ean formalism each olefinic linkage can be regarded as a two-electron donor, so that cycloheptatriene, C_7H_8, can potentially act as a six-electron ligand. In this category are the $(h^6\text{-}C_7H_8)M(CO)_3$ complexes formed with the group VI metal carbonyls. Each double bond supplies two electrons, so that with the six electrons from the carbonyls the metal attains the rare gas configuration. On the other hand, iron favors a diene rather than a triene and forms the cycloheptatriene complex $(h^4\text{-}C_7H_8)Fe(CO)_3$, where only four of the π-electrons of the triene bond to iron.

Cotton[9] has proposed a convenient notation to specify the number of carbon atoms that are attached to a metal atom by use of a prefix such as tetrahapto-, pentahapto-, hexahapto-, etc., abbreviated as h^4-, h^5-, h^6-, etc. This notation will be used in this work in cases where the number of carbon atoms attached to the metal is less than the maximum of two per olefinic linkage. As an example, in the cyclopentadienyl-(cycloheptatrienyl)dicarbonylmolybdenum complex the cycloheptatrienyl is known to function as a three electron donor as shown in **7**; this is symbolized as $(h^5\text{-}C_5H_5)Mo(CO)_2(h^3\text{-}C_7H_7)$.



7

The tropylium ion[†], $C_7H_7^+$, is an aromatic six

[†] In this thesis tropylium will refer to the unco-ordinated ion and cycloheptatrienyl to the complexes of the latter.

π-electron system, iso-electronic with $C_5H_5^-$ and C_6H_6, and would be expected to form analogous π-complexes with transition metals. Cycloheptatrienyl complexes are prepared indirectly from cycloheptatriene; for example, the latter reacts with $V(CO)_6$ forming cycloheptatrienyltricarbonylvanadium, $(h^7\text{-}C_7H_7)V(CO)_3$.

Complexes with group V ligands

A variety of trivalent phosphorus, arsenic, antimony, and bismuth ligands also form complexes with the transition metals. In addition to being quite strong Lewis bases these donor atoms have empty dπ orbitals and back bonding into these orbitals is possible. The relative importance of these two contributions to the bonding depends markedly on the electronegativity of groups attached to the donor atoms.

Considering that other ligands are generally stronger σ-donors and poorer π-acceptors, the replacement of CO with other ligands decreases the ν(CO) of the remaining carbon monoxide in the substituted product. Based on extensive ir studies, the group V donor atoms can be arranged in the following order of decreasing importance of π-bonding and increasing importance of σ-bonding contribution.[1]

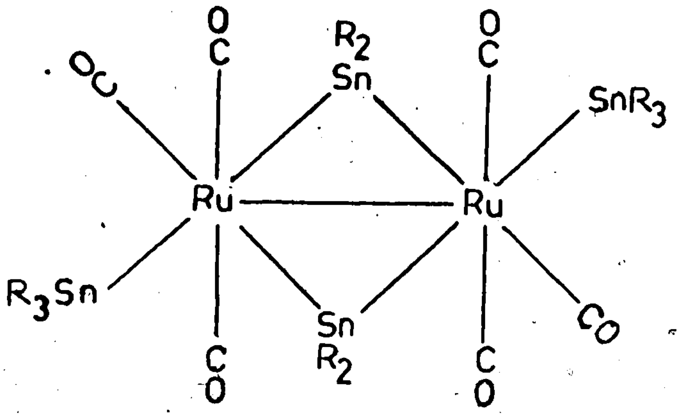
$$PF_3 > PCl_3 \sim AsCl_3 \sim SbCl_3 > P(OR)_3 > PR_3 \sim AsR_3 \sim SbR_3$$

(R = alkyl or aryl)

Complexes with main group IV metals

In the past decade numerous compounds containing the elements silicon, germanium, tin and lead bonded directly to transition metals have been prepared. The metal-metal bonds in these compounds are normally assumed to consist of a σ-bond and a d_π-bond combination analogous to the formal σ-donor and π-acceptor system of the tertiary phosphines and arsines (R_3Ge^- and R_3As are iso-electronic). Attempts to correlate CO stretching frequencies or force constants with σ and π effects of the metal-metal bonds suggest that while π-bonding is present, it is secondary energetically to the σ-bond.[10,11] The π-character appears to be appreciable only when halogen groups are attached to the group IV metals as shown by ^{119}Sn Mössbauer[12] and ^{59}Co NQR[13] studies as well as molecular orbital calculations.[14]

Apart from direct attachment to a single transition metal the group IV elements, like CO, can act as a bridge between two or more metals. As an example of this versatility, the X-ray diffraction structure[15] of the product from the reaction of triorganotin hydrides with $Ru_3(CO)_{12}$ is shown in 8.



8

Metal-nitrosyl complexes

Nitric oxide, NO, like carbon monoxide, forms stable complexes with transition metals but not with the simple acceptor molecules or non-transition metals. However, NO has an additional electron in an antibonding π* orbital which is readily lost (ionization potential 9.5 ev) to give the nitrosonium ion, NO^+, isoelectronic with CO.

Although most terminal metal nitrosyls contain essentially linear M-N-O bond angles, a considerable number occur with bent M-N-O bond angles which are close to 120°. The nitrosyl complexes prepared in this work contain linear M-N-O linkages.

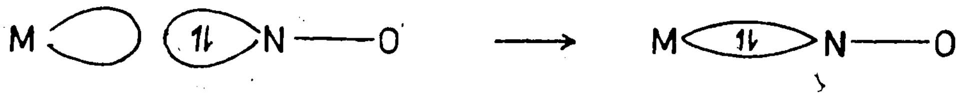
Traditionally terminal NO groups have been regarded as bonding to the metal in one of three ways:

(a) Transfer of an electron from a π^* orbital of NO to the metal followed by an electron-pair donation from NO^+, in a manner analogous to CO. This gives rise to a linear bond with NO contributing three electrons.

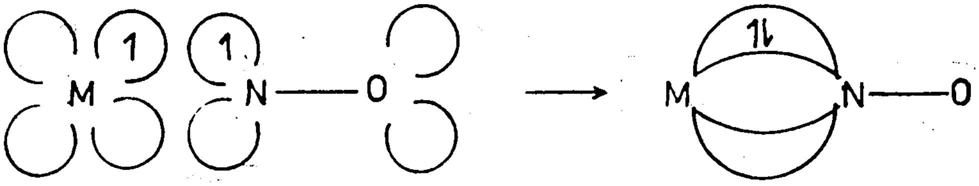
(b) By acceptance of one electron from the metal followed by co-ordination of the nitrosyl anion, NO^-, resulting in a bent bond and a single electron contribution from NO.

(c) By donation of two electrons from the neutral NO, with the unpaired electron remaining in the π^* orbital.

A more convenient description of linear metal-nitrosyl bonding is illustrated in 9 and 10.



9

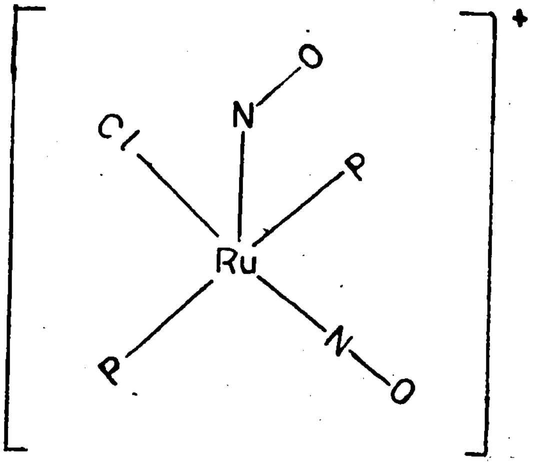


10

According to this description, in linear MNO groups the basic interaction is by donation of a σ pair from N along with a covalent $N\pi^*-d\pi$ bond, often with some additional bonding due to $d\pi \rightarrow N\pi^*$ interaction. The advantage of this scheme is that the occupation of the π^* orbital is either unaffected or increased on co-ordination, so that the nitrosyl stretching frequency in the infrared is expected to be close to or lower than that of free NO (1876 cm^{-1}). In fact most nitrosyl complexes absorb at frequencies lower than this, indicating an increase in electron density in the π^* orbital.

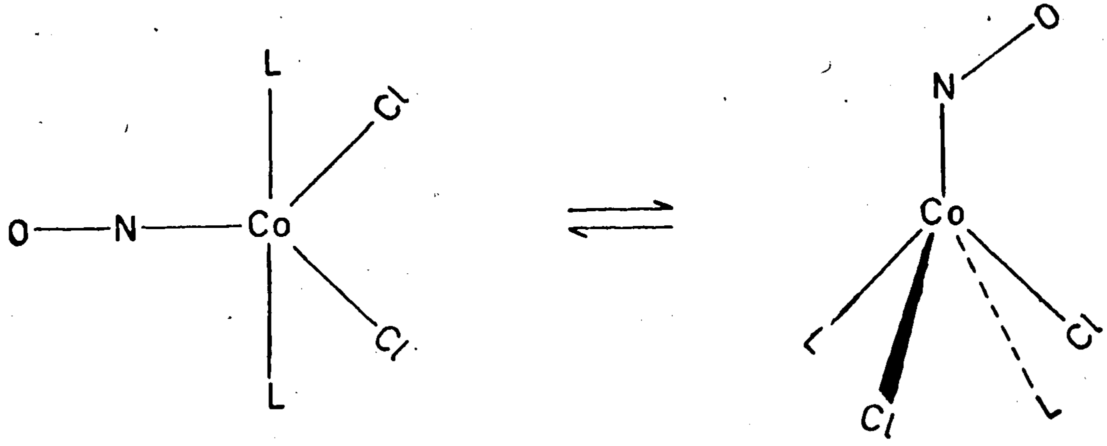
In bent MNO groups the interaction is basically a single covalent bond formed by a σ electron in an sp^2 orbital on nitrogen.[1]

The complex $[Ru(NO)_2(PPh_3)_2Cl]^+$ [16] provides an elegant example of both bent and linear NO groups in the same molecule, 11



11

An example of reversible isomerism between linear (NO^+) and bent (NO^-) forms have been proposed for $Co(NO)L_2Cl_2$,[17] where L is a phosphine ligand, shown in 12.



12

Although it now appears that further studies are warranted to clarify this hypothesis,[18] it has been suggested[6] that systems of this type, where there is a reversible change in the formal oxidation state of the metal, will be useful as catalysts.

CHAPTER II

REACTIONS OF CYCLOHEPTATRIENYLTRICARBONYLMOLYBDENUM HEXAFLUOROPHOSPHATE WITH GROUP V DONOR LIGANDS

INTRODUCTION

In contrast to the numerous accounts of π-cyclopentadienyl metal carbonyl complexes,[19] the chemistry of other π-bonded ring systems has been much less studied. This work was begun in a modest attempt to fill this void and to develop a suitable synthetic route to group V derivatives of $C_7H_8Mo(CO)_3$. The preparation of these derivatives will be described in the succeeding chapter. The present chapter deals with the reactions of $[C_7H_7Mo(CO)_3]^+$ cation with tertiary and ditertiary group V ligands. In Chapter IV the preparation of some main group IV derivatives will be discussed. A brief introduction and a review of relevant work in this field is presented at the beginning of each chapter. The metal carbonyl complexes of cycloheptatriene and cycloheptatrienyl have been extensively reviewed.[20,21,22]

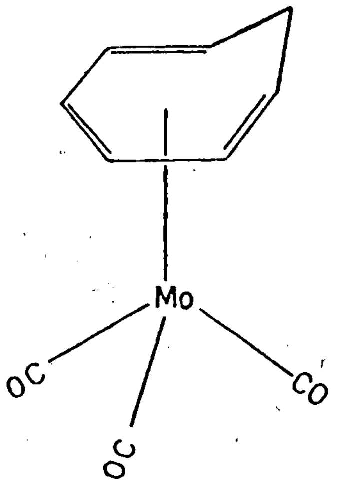
Initial attempts to prepare cycloheptatrienyl complexes from tropylium salts, thereby extending the known aromatic π-complexes of cyclopentadienyl and benzene, failed.[23] It was hoped that successful preparation could be achieved by reacting suitable metal compounds with free C_7H_8. The first reaction of C_7H_8 with a metal carbonyl [$Mo(CO)_6$] led to a cycloheptatriene complex, $C_7H_8Mo(CO)_3$, and not a cycloheptatrienyl complex.[24] Infrared and nmr studies showed the presence of co-ordinated cycloheptatriene.[23,25,26] The six olefinic CH groups were assumed to lie approximately in the same plane forming a delocalized π-electron system, with the methylene group bent away from the metal, 13.

Subsequently it was shown that triphenylmethyl tetrafluoroborate abstracts a hydride ion from $C_7H_8Mo(CO)_3$ to give the cycloheptatrienyl complex salt, $[C_7H_7Mo(CO)_3]^+BF_4^-$.[27]

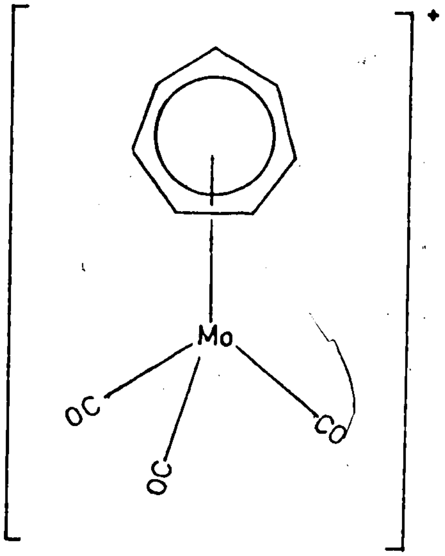
$$C_7H_8Mo(CO)_3 + [Ph_3C]^+BF_4^- \xrightarrow[CH_2Cl_2]{} [C_7H_7Mo(CO)_3]^+BF_4^- + Ph_3CH \qquad \text{II-1}$$

The nmr spectrum shows only one sharp signal confirming the presence of a symmetrical seven-membered ring; and the ir spectrum contains only two carbonyl frequencies pointing to a symmetrical structure for the whole molecule, 14.[27] In $C_7H_8Mo(CO)_3$ three carbonyl bands are observed due to the asymmetry caused by the methylene group.

X-ray analysis has confirmed the proposed structure for both $C_7H_8Mo(CO)_3$ [28] and $[C_7H_7Mo(CO)_3]^+$ [29]. The C-C ring distances found in 13 (1.36 Å and 1.43 Å) are



13



14

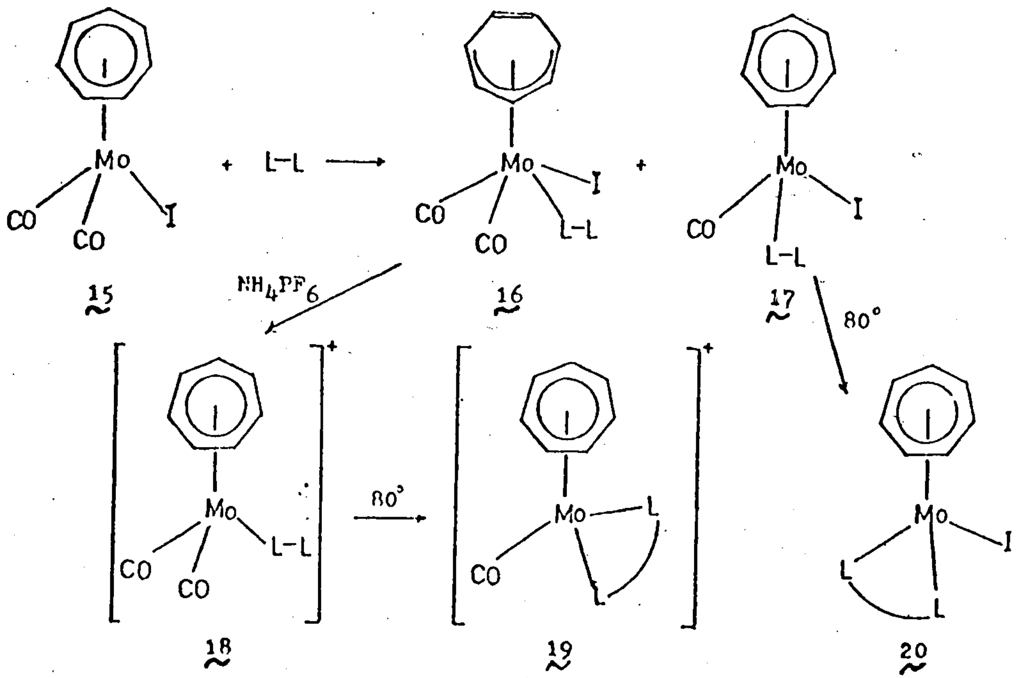
those to be expected for alternate single and double bonds. In 14 the C-C distances are nearly equal averaging 1.400 Å. The average Mo-C (carbonyl) distances are 1.97 Å and 2.032 Å respectively. The latter is the longest found in a Mo(CO)$_3$ complex. This, coupled with the Mo-C (ring) distance of 2.314 Å, one of the shortest found in Mo-arene complexes, has been taken to indicate a stronger than normal interaction between the Mo atom and the C_7H_7 ring.[29] By contrast the short Mo-C (carbonyl) distance in 13, appreciably shorter than 2.08 Å in Mo(CO)$_6$, indicates a relatively weak interaction between the metal and the C_7H_8 ring. The present work will attempt to show that the difference in the chemistry of 13 and 14 is related to their contrasting structural features.

Complexes of the type $C_7H_7Mo(CO)_2X$ (X = Cl, Br, and I) have been prepared by treating 14 with the appropriate halide ion.[30] The reaction of $C_7H_7Mo(CO)_2I$ with group V donor ligands has been investigated. With tertiary phosphines and phosphites, monosubstituted complexes resulted;[31,32]

$$C_7H_7Mo(CO)_2I + PR_3 \xrightarrow[C_6H_6]{} C_7H_7Mo(CO)PR_3I + CO \tag{II-2}$$

where R = OPh, OMe, OEt, Ph and NMe_2.

Reaction with bidentate ligands has led to the formation of five types of product.[33] The overall reaction sequence and types of complexes formed, 15 to 20, are summarized below.



where L-L = $Ph_2PC_2H_4PPh_2$, $Ph_2PCH{=}CHPPh_2$ or $Ph_2AsCH_2AsPh_2$. In the present work complexes of type 18 and 19 will be prepared by an alternate route.

By contrast to the reaction of $C_7H_8Mo(CO)_3$ with Lewis base ligands, which result in the displacement of the C_7H_8 ring (see introduction to chapter III), there are no accounts of similar reactions of $[C_7H_7Mo(CO)_3]^+$. *A priori* this cation may be expected to react with donor ligands in two ways.

Mode 1: $[C_7H_7Mo(CO)_3]^+ + 3L \rightarrow L_3Mo(CO)_3 + C_7H_7^+$ II-3

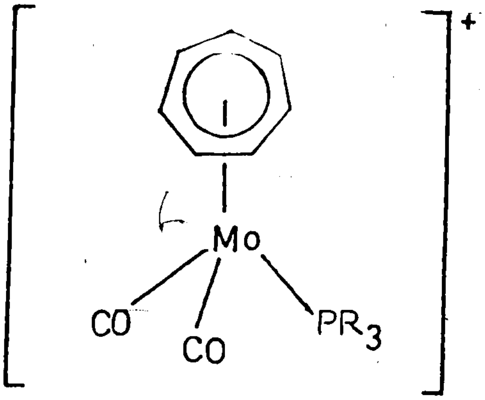
Mode 2: $[C_7H_7Mo(CO)_3]^+ + L \rightarrow [C_7H_7Mo(CO)_2L]^+ + CO$ II-4

It was hoped that these reactions would lead to CO substitution, II-4, and not to ring displacement, II-3. The results of the reactions with mono-tertiary group V ligands will now be described.

RESULTS AND DISCUSSION

1) Reactions with Tertiary Group V Ligands

It was found that $P(OPh)_3$, PPh_3, PPh_2Me, $AsPh_3$ and $SbPh_3$ reacted with $[C_7H_7Mo(CO)_3]^+PF_6^-$ in ethanol at reflux temperature. The carbonyl substituted product, **21**, resulted as the only carbonyl containing product in all cases.

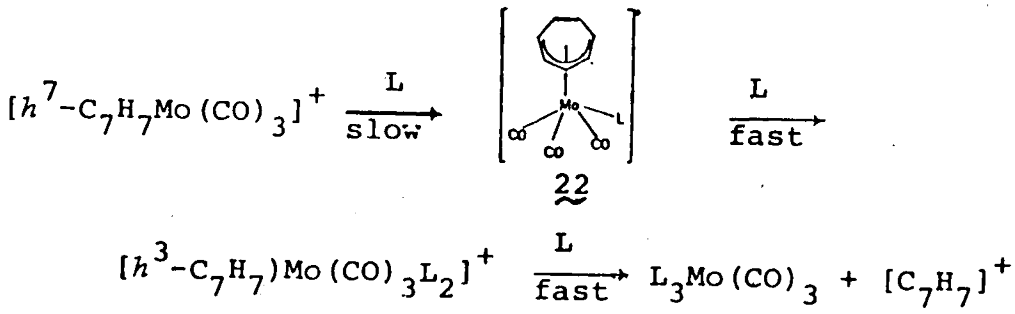


21

With $PPhMe_2$, a small amount of $(CO)_3Mo(PPhMe_2)_3$ was also formed. Reaction with $P(OMe)_3$, $P(OEt)_3$, $P(n\text{-}Bu)_3$ and $P(Et)_3$ resulted largely in ring displacement with formation of the tris-phosphine substituted product.

These results are in marked contrast to the reaction of $C_7H_8Mo(CO)_3$, where displacement of the ring was the only mode of reaction. A comparison of the X-ray structures of $C_7H_8Mo(CO)_3$ and $[C_7H_7Mo(CO)_3]^+$ as noted earlier, revealed a greater degree of metal-ring interaction for C_7H_7 than for C_7H_8. This may reflect the decreased tendency toward ring displacement in the latter complex.

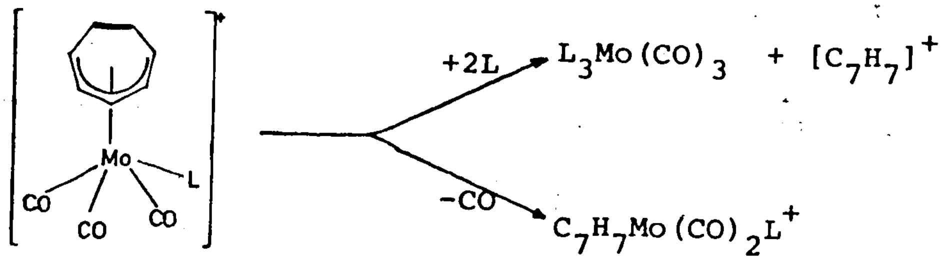
A possible mechanism of the reaction resulting in the displacement of the ring from $[C_7H_7Mo(CO)_3]^+$ may be the same in general detail as that found by Al-Khathumi and Kane-Maguire in a kinetic study using acetonitrile as nucleophile.[34] The reaction is first order in both reactants, and the postulated S_N2 displacement mechanism is shown in II-5.



II-5

This mechanism is very similar to that proposed for reactions of areneMo$(CO)_3$ complexes with phosphines.[35]

Formation of 22 as an intermediate in these reactions offers a qualitative rationalization of the observed variation in our results. Two competitive pathways are envisaged for the fate of 22.



II-6

II-7

22

The less basic and bulkier aryl substituted ligands would tend to favor II-7 while the superior nucleophiles and less sterically hindered alkyl substituted phosphites favor II-6. Moreover in the reaction of $PPhMe_2$ the ratio of products formed could be varied markedly by changing the stoichiometric concentration of the ligand. With a large excess of ligand $(CO)_3Mo(PPhMe_2)_3$ was formed almost exclusively whereas with slow addition of ligand the carbonyl substituted product was predominant.

It must be emphasized that the solvent appears to play a critical role in these reactions. When '98% ethanol' (containing ca. 2% benzene) was used, in some reactions no carbonyl product was obtained and in other cases the yield was considerably curtailed. The presence of ca. 5% water, '95% ethanol', is necessary for most of these reactions. We are unable to rationalize this observation at this time.

The compounds of type $[C_7H_7Mo(CO)_2L]^+ PF_6^-$ range in color from orange to wine-red. They are insoluble in water and hydrocarbon solvents but readily soluble in dichloromethane, acetone, and acetonitrile. In solution these compounds undergo slow decomposition, even under nitrogen, with the liberation of tropylium hexafluorophosphate. Solid samples are air stable for long periods of time. The compounds were characterized by ir, nmr and elemental analysis. Results were consistent with the postulated formulation 21. The ir spectra in the CO region are discussed next.

Infrared spectra

In general the infrared spectrum is the most widely reported feature of metal carbonyl complexes. In addition to providing a means of distinguishing one compound from another, for recognizing structural similarities in groups of compounds, and for deducing molecular symmetry, the infrared aids in understanding of the bonding in carbonyl complexes.

The CO stretching frequencies of metal carbonyl compounds are found between 2150 and 1650 cm^{-1}. They are dependent upon the C-O bond order, which in turn reflects the metal-carbon double bonding, itself dependent upon the nature of the other ligands present. Lewis bases, which are poorer π-acceptors than carbon monoxide, lower the CO frequency when they replace carbonyls. Thus the effect on ν(CO) provides an indication of the π and σ-bonding capabilities of the ligand.

In the present work, for example, the compound $[C_7H_7Mo(CO)_2PPh_3]^+$ shows ν(CO) at 2027 and 1985 cm^{-1} compared to 2082 and 2030 cm^{-1} in the parent tricarbonyl. This shift to lower frequency is observed for all compounds reported in Table I, which lists the infrared spectra. The ir spectra of these complexes are typical

TABLE I

INFRARED CARBONYL AND NMR DATA FOR $[C_7H_7Mo(CO)_3]^+PF_6^-$ DERIVATIVES AND RELATED COMPOUNDS

Compound	Carbonyl Stretching Frequencies (cm^{-1})[a]		NMR Data[b] $\tau(C_7H_7)$	$\tau(CH_2)$	Solvent
$[C_7H_7Mo(CO)_2P(OPh)_3]^+PF_6^-$	2040(10.0)	2000(8.2)	4.52		C
$[C_7H_7Mo(CO)_2PPh_3]^+PF_6^-$	2027(10.0)	1985(8.5)	3.98 d (2.1)		N
$[C_7H_7Mo(CO)_2PPh_2Me]^+PF_6^-$	2023(10.0	1981(8.4)	4.23 d (2.4)		C
$[C_7H_7Mo(CO)_2PPhMe_2]^+PF_6^-$	2020(10.0)	1976(8.0)	4.16 d (2.5)		C
$[C_7H_7Mo(CO)_2AsPh_3]^+PF_6^-$	2031(10.0)	1987(8.4	3.94 s		A
$[C_7H_7Mo(CO)_2SbPh_3]^+PF_6^-$	2027(10.0)	1986(8.3)	3.77 s		A
fac-$(CO)_3Mo(Ph_2PCH_2PPh_2)_2$	1943(10.0) 1938(10.0) 1825(10.0)	1848(9.6,br) 1840(10.0) (nujol)		7.4m, 8.7br	D
mer-$(CO)_3Mo(Ph_2PCH_2PPh_2)_2$	1969(2.2) 1841(6.0,sh) 1959(6.0) 1845(10.0)	1867(10.0) 1858(8.1,sh) (nujol)		6.8m, 8.9br	D
$[C_7H_7Mo(CO)_2Ph_2PCH_2PPh_2]^+PF_6^-$	2025(10.0)	1978(8.2)	4.22 d (2.3)	6.3(9.0,2.0)	N
$[C_7H_7Mo(CO)_2Ph_2PC_2H_4PPh_2]^+PF_6^-$ [d]	2024(10.0)	1978(8.1)			
$[C_7H_7Mo(CO)Ph_2PCH_2PPh_2]^+PF_6^-$	1963 br		4.30 t (2.7)	e	N

TABLE I (continued)

$[C_7H_7Mo(CO)Ph_2PC_2H_4PPh_2]^+PF_6^-$	1958 br		4.40 t (2.3)	7.2 br	N
$[\{C_7H_7Mo(CO)_2\}_2Ph_2PC_2H_4PPh_2]^{2+}(PF_6^-)_2$	2018(10.0)	1937(8.8) (CH_3CN)	4.74 t (1.1)	8.20 br	N
$[C_5H_5Fe(CO)_2Ph_2PCH_2PPh_2]^+PF_6^-$	2055(9.9)	2012(10.0)	4.85 d (1.6)	6.5(11,1.7)	N
$[C_5H_5Fe(CO)_2Ph_2PC_2H_4PPh_2]^+PF_6^-$	2058(10.0)	2010(10.0)	4.86 d (1.6)	7.2 br	N
$[C_5H_5Fe(CO)Ph_2PCH_2PPh_2]^+PF_6^-$	1983		4.92 t (1.4)	f	N
$[C_5H_5Fe(CO)Ph_2PC_2H_4PPh_2]^+PF_6^-$	1981		4.92 t (1.5)	7.5 br	N

[a] Dichloromethane solutions except when noted; Figures in parenthesis are relative band heights measured on a linear transmittance scale; br = broad, sh = shoulder.

[b] Key: br = broad; m = multiplet; s = singlet; d = doublet; t = triplet. J values in parenthesis are in Hz. Phenyl τ values not given.

[c] C = $CDCl_3$; A = Acetone-d_6; D = CD_2Cl_2; N = CD_3CN. TMS as internal standard.

[d] Observed in ir only. Reference 33.

[e] AB pattern with $\nu_A = 4.8$; $\nu_B = 5.6$; $J_{AB} = 16$ Hz; ${}^1J_{P\text{-}CH_2} = 10$ Hz.

[f] AB pattern with $\nu_A = 4.9$; $\nu_B = 5.5$; $J_{AB} = 16$ Hz; ${}^1J_{P\text{-}CH_2} = 12$ Hz.

of compounds of general formula (Ring) $M(CO)_2L$ showing two bands assigned to the symmetric A' (higher frequency) and the anti-symmetric A" modes. The infrared spectrum of $[C_7H_7Mo(CO)_2P(OPh)_3]^+ PF_6^-$ measured in CH_2Cl_2 is shown in Figure 1 as a representative example.

^{1}H nmr spectra

The proton nmr spectra show, in addition to phenyl and/or methyl groups bonded to the ligands, one sharp signal at ca. 4 τ confirming the presence of the symmetrical seven-membered ring. For the phosphine and phosphite complexes, the signal is split into a doublet by coupling to the phosphorus nucleus. The C_7H_7 resonance is shifted to higher field in these complexes as compared to the parent tricarbonyl which shows a signal at 3.38 τ. This represents an increased shielding of the ring protons due to an increase in electron density on the metal which in turn is brought about by a greater σ-donor and a lesser π-acceptor power of the group V ligands compared to CO. Results of the nmr spectra are included in Table I.

Reaction with $PPhMe_2$

The reaction of $[C_7H_7Mo(CO)_3]^+ PF_6^-$ with $PPhMe_2$ affords in addition to $[C_7H_7Mo(CO)_2PPhMe_2]^+ PF_6^-$, a low yield of a white crystalline compound. The latter,

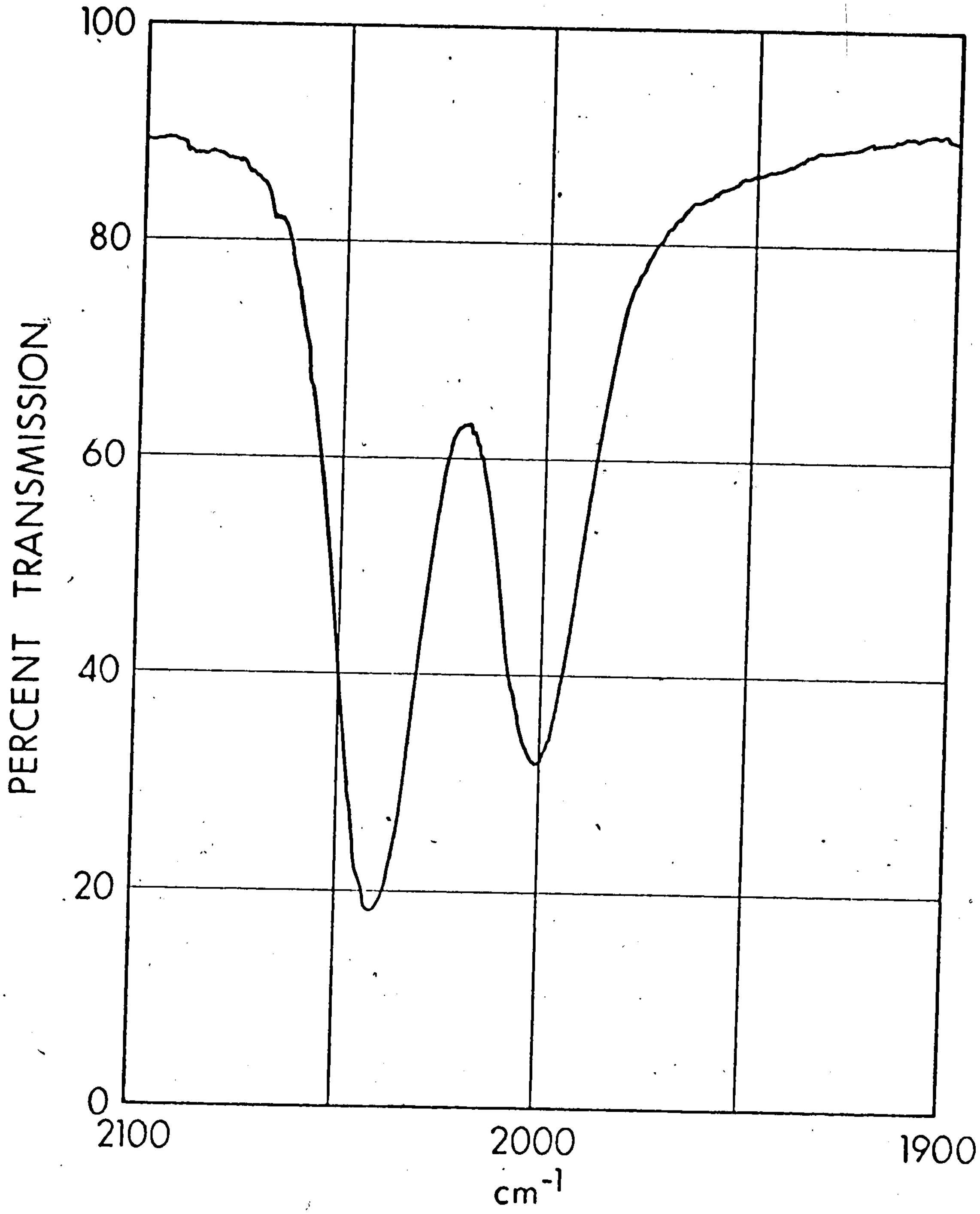
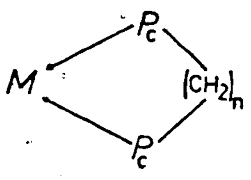


Figure 1. $[C_7H_7Mo(CO)_2P(OPh)_3]^+PF_6^-$ in CH_2Cl_2.

identified as the known *fac*-$(CO)_3Mo(PPhMe_2)_3$,[36] exhibits one intense and one very intense carbonyl ir band at 1934 and 1830 cm^{-1}, indicative of *fac*-stereochemistry (see Figure 5). The ^{1}H nmr in the methyl region, shown in Figure 2, consists of a broad central peak flanked by two side peaks. Analysis of nuclear spin systems of this type has been developed by various researchers.[37] This type of spectrum has been considered as a special case of a "deceptively simple" spectra in an X part of an $AX_6A'X'_6A''X''_6$ nuclear spin system (X = H, A = P).[38]

2) Reactions With Bis Tertiary Phosphine Ligands

The bis tertiary phosphine ligands are known to co-ordinate to transition metals in three ways. They most commonly behave as bidentate chelates, 23, more rarely as bidentate bridging ligands, 24, and in a few cases as monodentate ligands with the possibility of either end being attached to the metal, 25.



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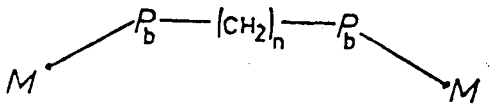

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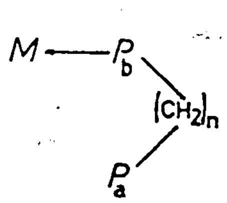

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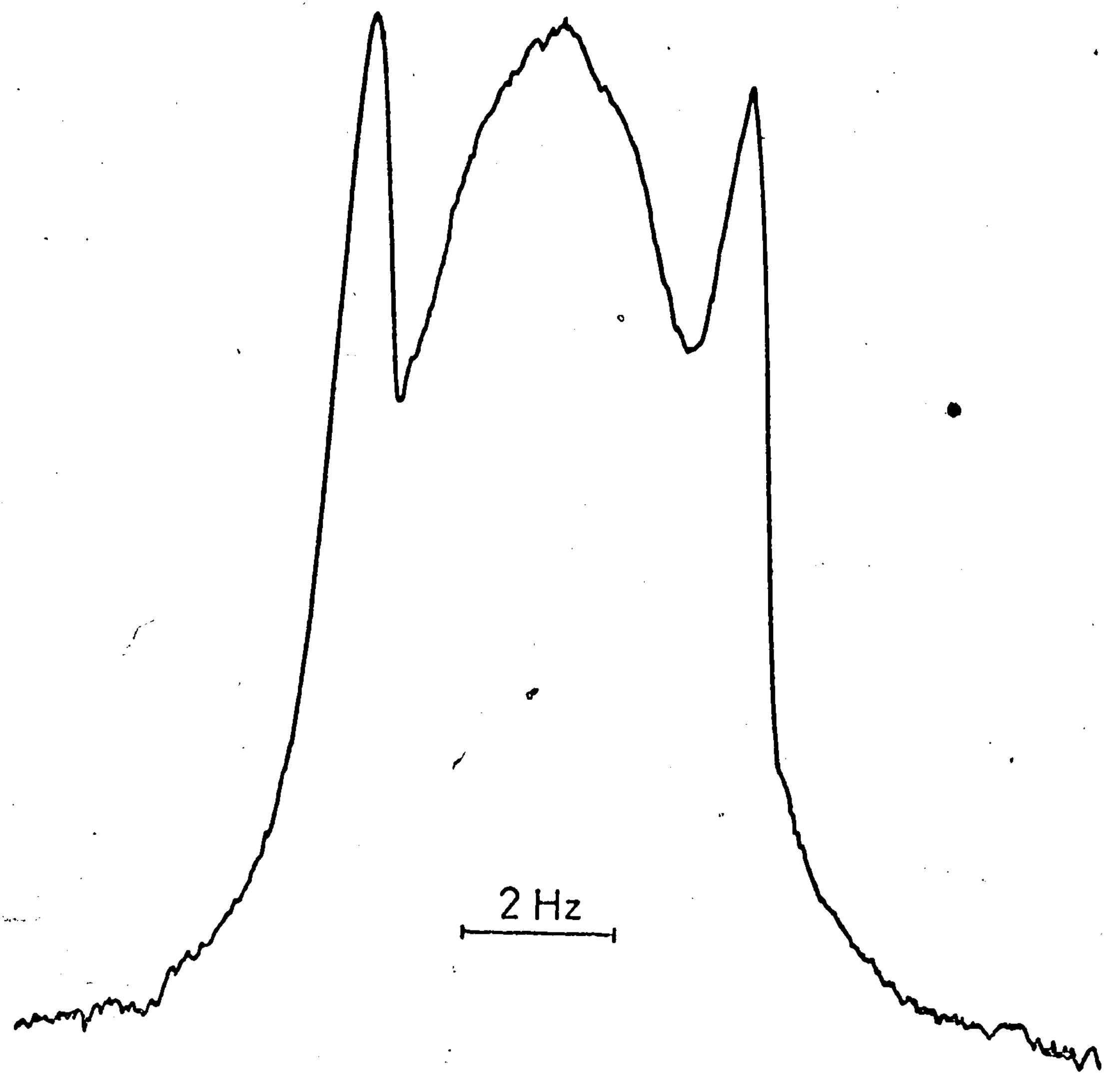


Figure 2. $^1H(CH_3)$ nmr spectrum of *fac*-$(CO)_3Mo(PPhMe_2)_3$ in $CDCl_3$.

In this work bis(diphenylphosphino)methane (dpm) and bis(diphenylphosphino)ethane (dpe) were reacted with $[C_7H_7Mo(CO)_3]^+PF_6^-$, the results of which will now be described.

Reaction with $Ph_2PCH_2PPh_2$ (dpm)

A mixture of dpm and $[C_7H_7Mo(CO)_3]^+PF_6^-$, when gently heated in acetone for a short period of time afforded two compounds which were separated by column chromatography. A yellow compound, whose properties will be described in the next section, was eluted first in CH_2Cl_2. A red ionic compound eluted with CH_2Cl_2-CH_3CN (4:1), was identified as $[C_7H_7Mo(CO)_2dpm]^+PF_6^-$. The ir spectrum showed two carbonyl bands at 2025 and 1978 cm^{-1}.

Prolonged refluxing of reactants resulted in the formation of the chelated complex $[C_7H_7Mo(CO)dpm]^+$ with only one ir carbonyl absorption at 1963 cm^{-1}.

The CO substitution reactions are envisaged to involve two steps:

$$[C_7H_7Mo(CO)_3]^+ + dpm \xrightarrow{\text{fast}} [C_7H_7Mo(CO)_2dpm]^+ + CO \qquad \text{II-8}$$

$$[C_7H_7Mo(CO)_2dpm]^+ \xrightarrow{\text{slow}} [C_7H_7Mo(CO)dpm]^+ + CO \qquad \text{II-9}$$

The isolation of $[C_7H_7Mo(CO)_2dpm]^+$ can thus be attributed to the relative slowness of II-9 under mild conditions.

It is noteworthy that the barrier to chelation is reasonably large, as exemplified by a kinetic study on the rate of the chelation reaction shown in II-10;

$$dpmM(CO)_5 \longrightarrow dpmM(CO)_4 + CO \qquad \text{II-10}$$

where M = Cr, Mo, W, the enthalpy of activation is of the order of 33 kcal mole^{-1}.[39]

The $^1H(C_7H_7)$ and proton decoupled ^{31}P nmr of both cycloheptatrienyl complexes formed with dpm are shown in Figures 3 and 4. The ^1H nmr shows a doublet for the monodentate complex, $[C_7H_7Mo(CO)_2dpm]^+$, arising from the coupling of the ring protons to the co-ordinated phosphorus nucleus. The ^{31}P spectrum shows two phosphorus signals (AB pattern) and demonstrates conclusively that the potentially bidentate ligand is co-ordinated to the metal through only one of its phosphorus atoms, and that rapid exchange between the two phosphorus atoms does not take place. The chelated complex, $[C_7H_7Mo(CO)dpm]^+$, shows a 1:2:1 triplet in the ^1H nmr spectrum consistent with the splitting of the ring protons by the two complexed phosphorus nuclei. The chemical equivalence of the latter is manifested in a single ^{31}P resonance.

On the basis of the nmr spectra the dpm derivatives were formulated as shown, 26 and 27.

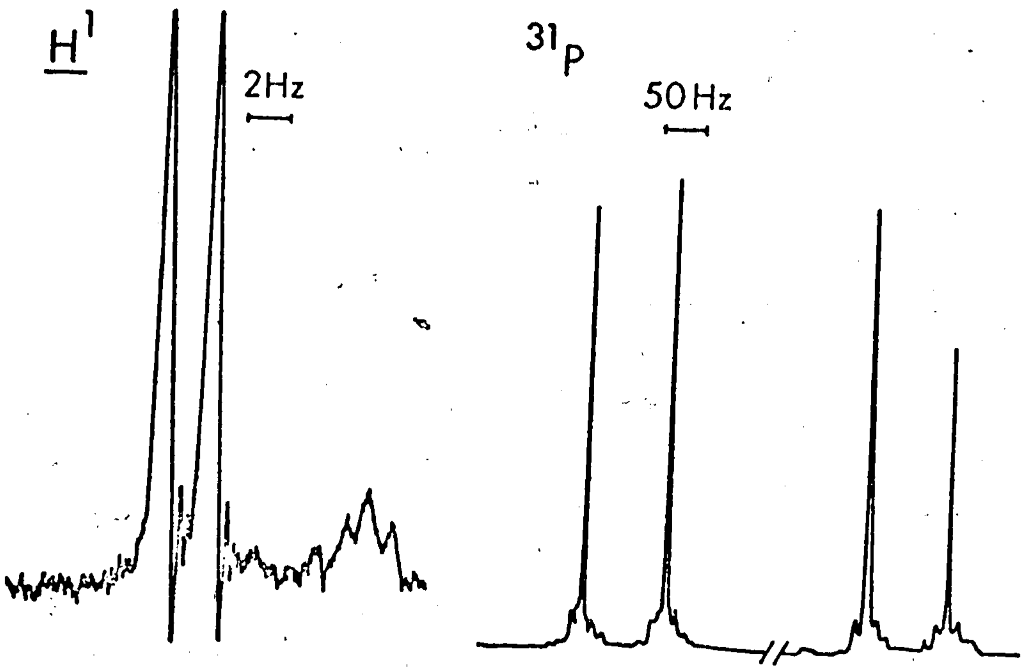


Figure 3. $^1H(C_7H_7)$ and ^{31}P nmr spectra of $[C_7H_7Mo(CO)_2dpm]^+PF_6^-$.

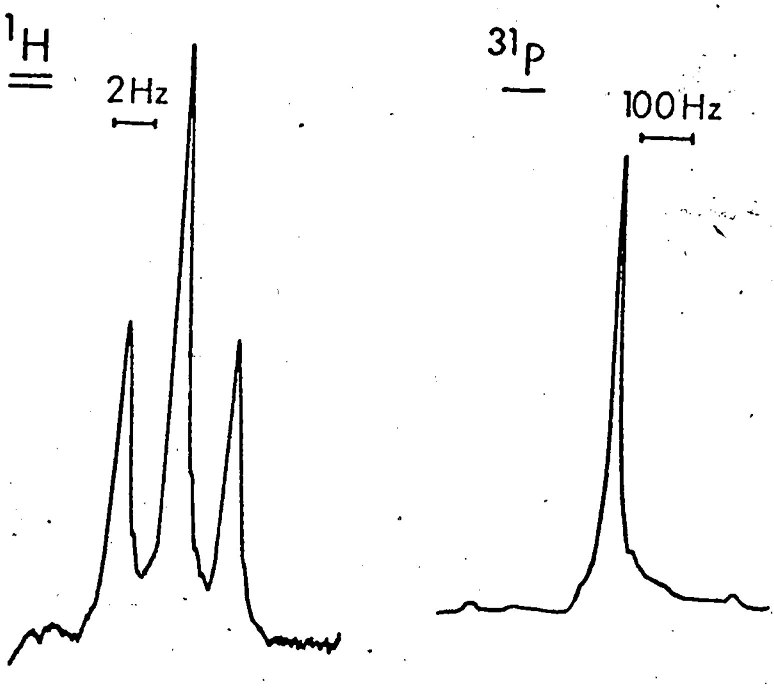
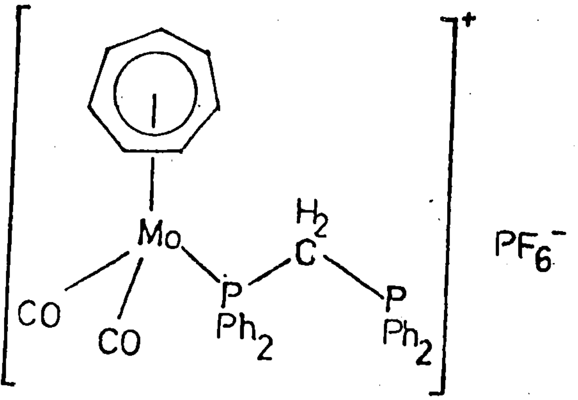


Figure 4. $^1H(C_7H_7)$ and ^{31}P nmr spectra of $[C_7H_7Mo(CO)dpm]^+PF_6^-$.



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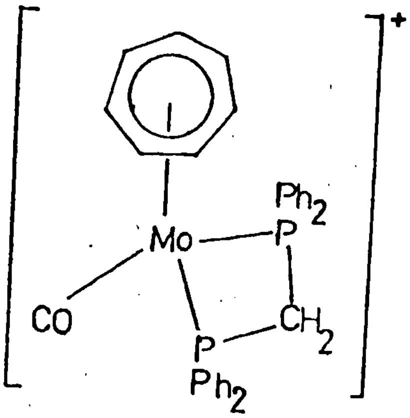
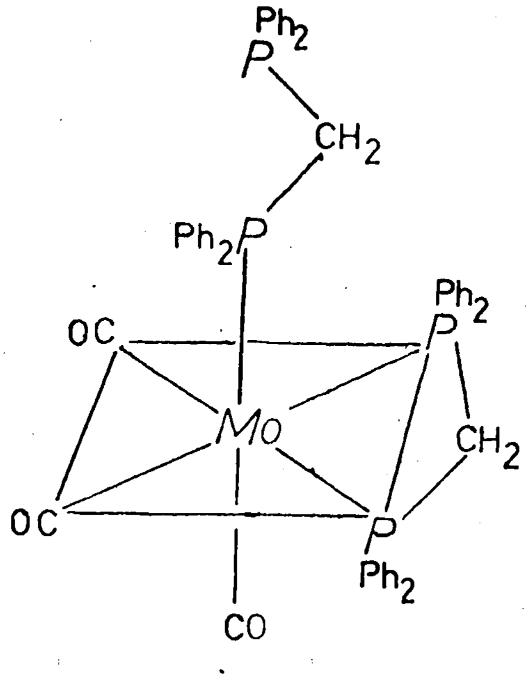


27

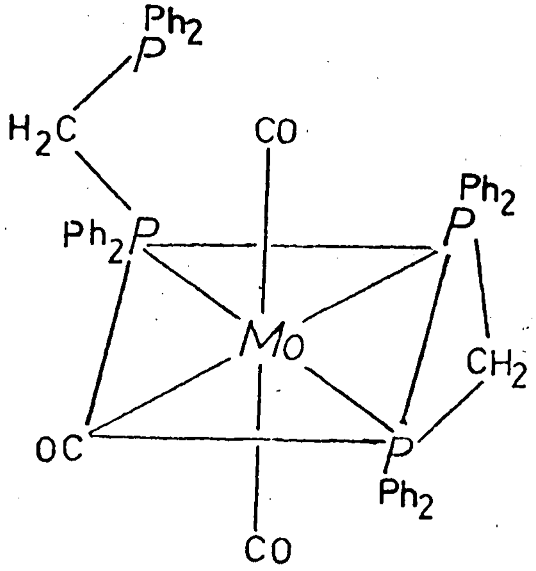
Fac- and *mer*-isomerism

The nature of the additional yellow compound formed in the reaction of dpm with $[C_7H_7Mo(CO)_3]^+PF_6^-$ was at first uncertain. It showed ν(CO) at 1968, 1943, 1868, and 1845 cm^{-1} in CH_2Cl_2. The relative intensities of the bands varied between successive recrystallizations, indicating the possible presence of isomers. Indeed, evidence which will be presented led us to formulate these as mixtures of facial (*fac*) and meridonal (*mer*) isomers of $(CO)_3Mo(dpm)_2$ as shown in 28 and 29, respectively.

When this yellow compound was refluxed overnight in benzene, a yellow solid was isolated. Its ir showed ν(CO) at 1969(w), 1867 (vs), and 1841 (m,sh), the relative intensities suggesting the *mer* configuration.[40]



28 (*fac*)



29 (*mer*)

No change was observed when the compound was refluxed in acetonitrile or ethanol.

We found that by reacting dpm with $C_7H_8Mo(CO)_3$ in benzene, a yellow compound having identical physical properties as the above *mer* isomer could be prepared. Moreover the identical reaction performed in dichloromethane afforded an off-white compound; the relative intensity of the ir bands at 1958(vs), 1845 (vs,br) are reminiscent of *fac* stereochemistry.[41]

In this way it was possible to obtain the one isomer free of the other. The infrared spectra of the *fac* and *mer* isomers are shown in Figures 5 and 6.

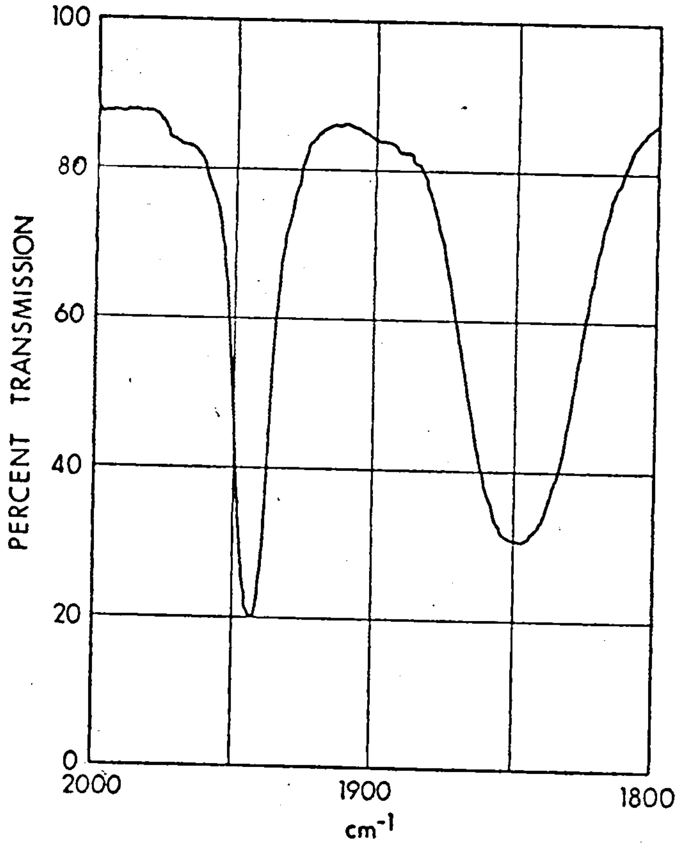


Figure 5. *fac*-$(CO)_3Mo(dpm)_2$ in CH_2Cl_2.

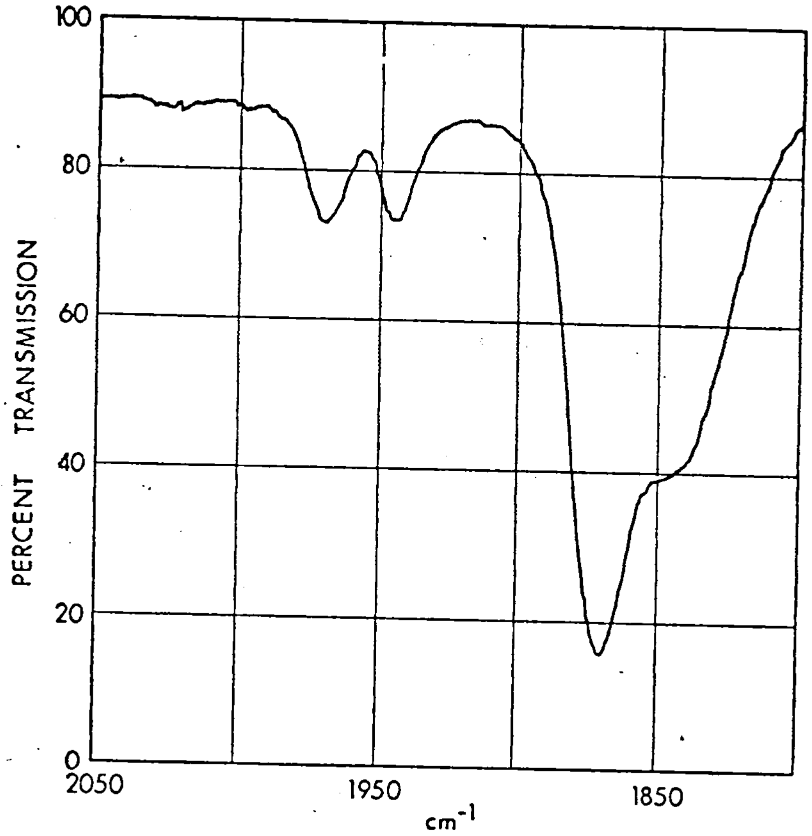


Figure 6. *mer*-$(CO)_3Mo(dpm)_2$ in CH_2Cl_2.

More direct evidence for the stereochemistry of these isomers was provided by their ^{31}P nmr spectra. The ^{31}P nmr of *fac*-$(CO)_3Mo(dpm)_2$, shown in Figure 7, demonstrated conclusively the presence of both chelating and non-chelating ligands in the same molecule. It consists of three types of phosphorus atoms, in the ratio of 1:2:1. The doublet of triplets at lowest field is assigned to P_b, the phosphorus atom of the monodentate dpm co-ordinated to the metal. It is split into a doublet by the uncomplexed P_a ($|^2J_{ab}|$ = 34.2 Hz.) which in turn is split into triplets by coupling to the two chemically equivalent atoms, P_c, of the chelate ($|^2J_{bc}|$ = 24.4 Hz.). The high field doublet which has a chemical shift very similar to that of pure dpm is therefore assigned to the free phosphorus atom, P_a, in the complex. The lower field doublet corresponds to the chemically equivalent P_c atoms of the chelate. The shift downward from that of pure dpm has been described as the chelation shift.[39]

By contrast, the ^{31}P nmr of the *mer* isomer, shown in Figure 8, shows four signals and demonstrates the stereochemical difference with the *fac* isomer. All four phosphorus atoms are unique, the P atoms of the chelate are no longer equivalent, P_c having P_b and P_d cis to it and P_d having P_c and P_b trans. The lower field triplet is assignable to P_c having similar coupling to the two P atoms in cis positions. The higher field

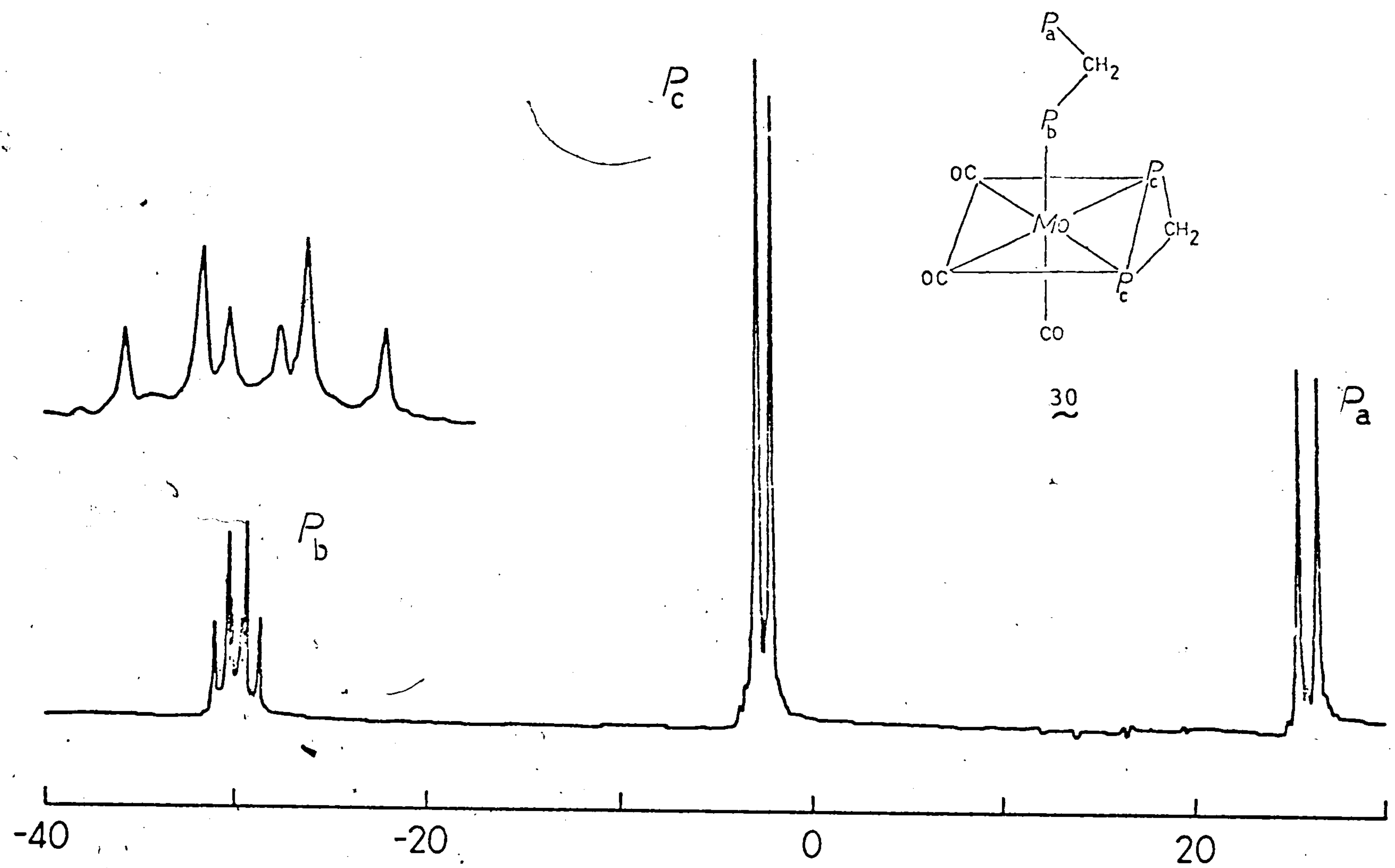
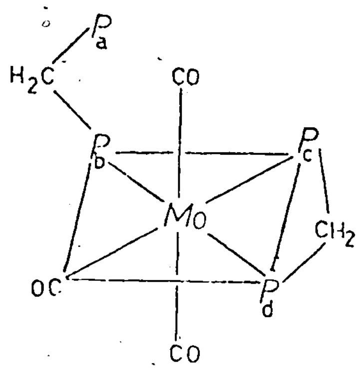


Figure 7. ^{31}P nmr spectrum of *fac*-(CO)$_3$Mo(dpm) in CD_2Cl_2. Chemical shift relative to 85% H_3PO_4 in PPM.



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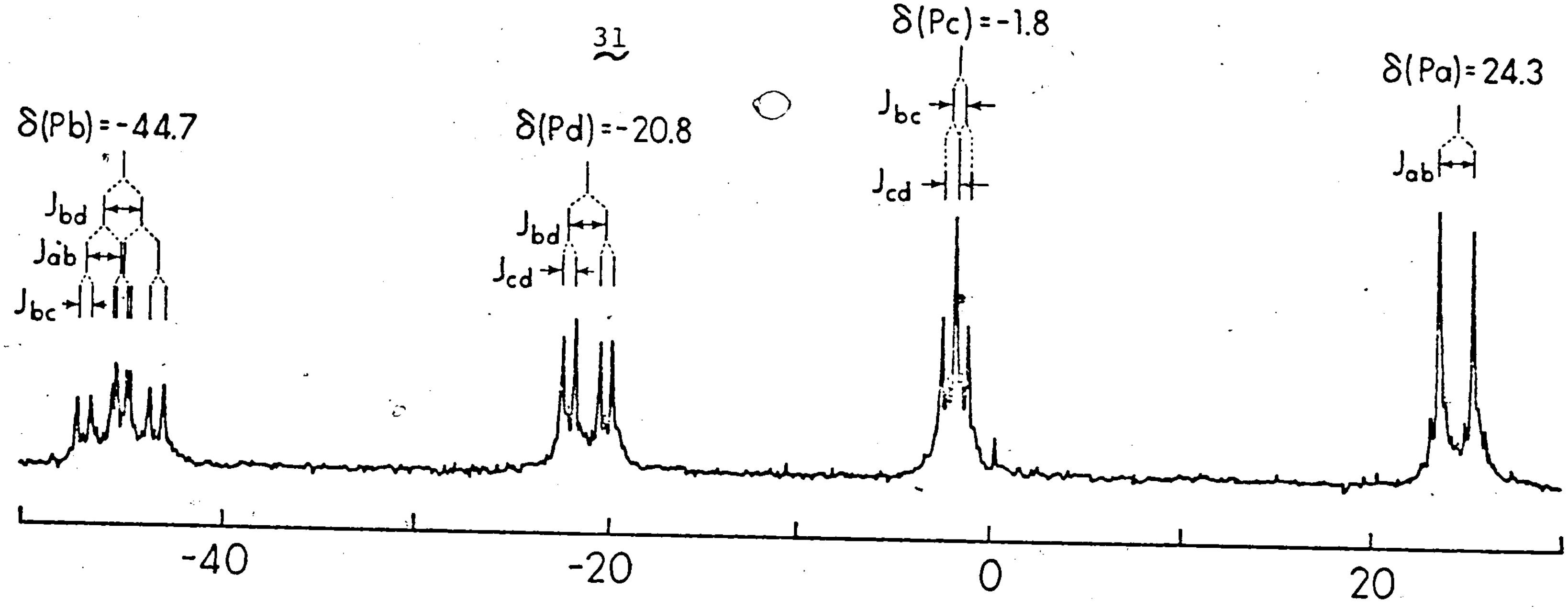


Figure 8. ^{31}P nmr spectrum of *mer*-$(CO)_3Mo(dpm)$ in CD_2Cl_2. Chemical shift relative to 85% H_3PO_4 in PPM.

quartet results from cis and trans coupling and is assigned to P_d. P_b is now coupled to three chemically inequivalent P atoms giving rise to the doublet of quartets at lower field.

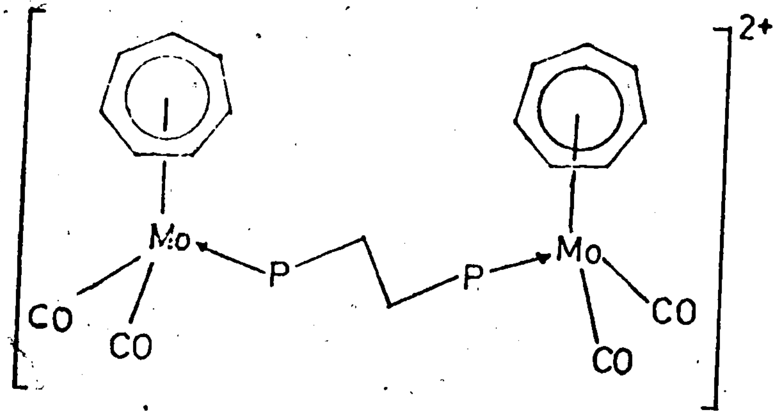
There are many examples of *fac* and *mer* isomerism,[36,40,41] however little is known about the mechanism of isomerization. This is the first example of isomerization involving potentially bidentate ligands.

It may be noteworthy here that bis(diphenylarsino) methane, $Ph_2AsCH_2AsPh_2$ reacts with $C_7H_8Mo(CO)_3$ in benzene to give $(CO)_3Mo(Ph_2AsCH_2AsPh_2)_3$ of *fac* stereochemistry.[42] And with dpe in benzene, $C_7H_8Mo(CO)_3$ was reported to give the binuclear species $Mo_2(CO)_6(dpe)_2$.[43,44,45] Our attempts to obtain the ^{31}P nmr spectrum of the latter were not successful due to solubility limitations.

Reaction of $Ph_2PCH_2CH_2PPh_2$(dpe)

Two products were isolated from the reaction of (dpe) with $[C_7H_7Mo(CO)_3]^+$. The first was identified as the chelating complex $[C_7H_7Mo(CO)dpe]^+$. Its ir and nmr compared well with the same compound prepared by Houk et al.[33] Attempts to isolate a monodentate complex of dpe were not successful, although ir evidence for its formation during the reaction was obtained.

The additional compound formed was insoluble in dichloromethane and could thus be separated from the above. Its infrared showed two ν(CO) bands in acetonitrile and its ^1H nmr (C_7H_7) in CD_3CN showed a single triplet due to C_7H_7 ($^3J_{P-H}$ = 1.1 Hz.). The ^{31}P nmr showed a single resonance having a chemical shift indicative of a bridging dpe group (see next section). This data favors a binuclear structure where dpe is bridging two $C_7H_7Mo(CO)_2$ moieties as shown in 32.



32

In accordance with the ean rule a dipositive species is predicted. The measured molar conductivity in nitromethane gave a value of 172.7 $ohm^{-1}cm^2mole^{-1}$. For 1:2 electrolytes, in nitromethane, values claimed cover the range 115 - 250 $ohm^{-1}cm^2mole^{-1}$, an average value being 168 $ohm^{-1}cm^2mole^{-1}$.[46] The conductivity of some compounds reported in this chapter are tabulated in Table III. The values obtained for the mononuclear species are close to 88.5 $ohm^{-1}cm^2mole^{-1}$, the average value reported for 1:1 electrolyte complexes.[46]

Other reported dpe bridge complexes containing a π-ring, $[C_5H_5Fe(CO)I]_2$-μ-dpe[47] and $[C_5H_5Fe(CO)]_2$-μ-dpe,[48] also showed one signal for the C_5H_5 groups, although no coupling was observed to the phosphorus nuclei of the dpe. The coupling constant of 1.1 Hz. we observe for 30, is substantially decreased in comparison to a value of 2.7 Hz. in the chelated complex $[C_7H_7Mo(CO)dpe]^+$. A corresponding decrease in going from $[C_5H_5Fe(CO)dpe]^+$ ($^3J_{P-H}$ = 1.6 Hz.) to the bridged systems would result in a coupling constant too small to be observed.

Reactions of $[C_5H_5Fe(CO)_2CH_3CN]^+PF_6^-$

It seemed desirable to extend the study of systems in which a potentially bidentate ligand acts also as a monodentate ligand. To this end we prepared $[C_5H_5Fe(CO)_2CH_3CN]^+PF_6^-$ by the literature method,[49] and reacted it with both dpm and dpe. We found that reaction in toluene at 110° afforded the chelated complexes

$$[C_5H_5Fe(CO)_2CH_3CN]^+ + Ph_2P(CH_2)_nPPh_2 \xrightarrow{110°} [C_5H_5Fe(CO)Ph_2P(CH_2)_nPPh_2]^+ + CH_3CN + CO \qquad \text{II-11}$$

where n = 1 or 2. Both complexes have been prepared by other synthetic routes.[50,51] Reaction in ethanol at

78° resulted in the exclusive formation of the monodentate complexes

$$[C_5H_5Fe(CO)_2CH_3CN]^+PF_6^- + Ph_2P-(CH_2)_n-PPh_2 \xrightarrow{78°}$$

$$[C_5H_5Fe(CO)_2Ph_2P-(CH_2)_n-PPh_2]^+PF_6^- + CH_3CN \qquad \text{II-12}$$

where n = 1 or 2. While this work was in progress Meyer and co-workers[52] reported the preparation of the above by an alternate route

$$[C_5H_5Fe(CO)_2 \cdot OC(CH_3)_2]^+ClO_4^- + Ph_2P(CH_2)_nPPh_2 \xrightarrow[25°]{C_6H_6}$$

$$[C_5H_5Fe(CO)_2PhP-(CH_2)_n-PPh_2]^+ClO_4^- + (CH_3)_2CO \qquad \text{II-13}$$

where n = 1 or 2. Our method is advantageous, affording a higher overall yield and the handling of perchlorate salts is avoided.

The ^{31}P nmr of these complexes has been measured and included in Table II, which lists the results of all ^{31}P nmr measurements. A discussion of these results follows.

<u>^{31}P nmr spectra</u>

^{31}P nmr spectroscopy was used to distinguish the form of complexation in the ditertiary compounds prepared in this chapter. The large variation in chemical shift (δ) is diagnostic of the mode of bonding.

The spectra of the complexes containing dpm as the monodentate ligand (25) demonstrated conclusively the presence of the complexed and uncomplexed phosphorus atom. The resonance of the unco-ordinated end remained essentially unshifted from that of the free ligand. The complexed end showed a lower field resonance. This shift on co-ordination, which is defined as $\Delta_{coord} = \delta_{coordinated} - \delta_{free\ ligand}$, is of the order of -50 ppm for Mo and -80 ppm for Fe complexes.

An anomalous behavior was observed in the spectrum of the dpe complex, $[C_5H_5Fe(CO)_2dpe]^+$. While the lower field signal due to the co-ordinated phosphorus showed the expected doublet with $\Delta_{coord} = -74.7$ ppm, only a broad signal was observed for the free end of the ligand. The spectrum did not change down to a temperature of -40°.

The chemical shift of the chelated bidentate complexes, which is defined as $\Delta_{chel} = \delta_{chelate} - \delta_{free\ ligand}$, is heavily dependent on the number of $-CH_2-$ groups separating the two phosphorus atoms. A shift to *higher* field is observed for the chelated complexes containing dpm as ligands, in comparison to the monodentate complexes, i.e. $\Delta_{coord} > \Delta_{chelation}$. For example, $\delta = -28.3$ ppm for $[C_7H_7Mo(CO)dpm]^+$ and $\delta = -12.8$ ppm for $[C_5H_5Fe(CO)dpm]^+$, a shift to higher field by ca. 27 ppm and more dramatically 60 ppm respectively.

A shift to *lower* field is observed for the complexes containing dpe as ligands, i.e. $\Delta_{chel} > \Delta_{coord}$. For example, δ = -81.1 ppm for $[C_7H_7Mo(CO)dpe]^+$ and δ = -105.2 ppm for $[CpFe(CO)dpe]^+$, this represents a shift to lower field by ca. 28 and 23 ppm respectively. This parallels the result of other ^{31}P nmr studies[39,53] where a large *lower* field shift was observed in going from complexes of the type $LM(CO)_5$ to the chelated $LM(CO)_4$, where M = Cr, Mo or W and L = $Me_2PC_2H_4PMe_2$,[39] $Ph_2PC_2H_4PPhMe$,[53] or $Ph_2PC_2H_4PPh(i\text{-}pr)$.[53] These authors have pointed out that the dramatic influence of chelation upon ^{31}P shift is evident from a comparison of, for example, the complexes $Me_3PCr(CO)_5$ and cis-$(Me_3P)_2Cr(CO)_4$ in which the shifts remain almost identical at -6.5 and -6.7 ppm respectively.

It is generally agreed that three factors determine the ^{31}P chemical shifts; these are, briefly, the following:[39,55]

a) Electronegativity differences among the substituents on phosphorus,

b) The occupancy of p and d orbitals (by p_π-d_π or d_π-d_π bonding) on phosphorus,

c) Changes in the bond angles at phosphorus

From the above, Connor et al[39] attributed their observed chelation shift to lower field, to the constraints in the chelate ring which leads to a change in the bond angle on phosphorus. Our results which show a shift to both higher and lower field substantiate this conclusion.

In summary, the dpm chelates form a four-membered ring with a consequent decrease in the bond angle at phosphorus which results in a chelation shift to higher field. The dpe chelates form a five-membered ring and a greater bond angle at phosphorus causing a shift to lower field.

In the case of the bidentate ligand bridging two metals, the co-ordination shifts are in the small range normally expected for ordinary monodentate ligands. In monodentate complexes there are two types of phosphorus atoms whereas in the bidentate bridging ligand only one signal is observed and thus unequivocal assignment can be made. The observed co-ordination shift for **30** is reminiscent of those reported for complexes $(CO)_5MP\sim PM(CO)_5$.[53]

The spectra of the *fac*- and *mer*-$(CO)_3Mo(dpm)_2$ have been discussed earlier and provide an elegant example where ^{31}P nmr affords a rapid, convenient and unequivocal determination of the stereochemistry.

TABLE II

PHOSPHORUS-31 CHEMICAL SHIFT DATA FOR THE DI-TERTIARY PHOSPHINE COMPLEXES[a]

Compound	$\delta(P_a)$[b]	$\delta(P_b)$[b]	$\delta(P_c)$[b]	Δ_{coord}[c]	Δ_{chel}[d]	$\lvert J_{P-P}\rvert$[e]	Solvent[f]
$Ph_2PCH_2PPh_2$	21.4/ 21.7	-	-	-	-		D/N
$[C_7H_7Mo(CO)_2Ph_2PCH_2PPh_2]^+PF_6^-$	24.9	-33.6		-55.0		97.7(J_{ab})	D
$[C_5H_5Fe(CO)_2Ph_2PCH_2PPh_2]^+PF_6^-$	24.6	-60.3		-82.0		90.0(J_{ab})	N
$[C_7H_7Mo(CO)Ph_2PCH_2PPh_2]^+PF_6^-$			- 6.9		-28.3		D
$[C_5H_5Fe(CO)Ph_2PCH_2PPh_2]^+PF_6^-$			8.9		-12.8		N
fac-$(CO)_3Mo(Ph_2PCH_2PPh_2)_2$	25.2	-30.0	- 3.0	-51.4	-18.4	34.2(J_{ab})	D
						24.4(J_{bc})	
mer-$(CO)_3Mo(Ph_2PCH_2PPh_2)_2$	24.3	-44.7	- 1.8	-66.1	-23.2	64.4(J_{ab})	D
			-20.8(P_d)		-45.7	25.6(J_{bc})	
						72.4(J_{bd})	
						24.4(J_{cd})	
$Ph_2PC_2H_4PPh_2$	12.9						D

TABLE II (continued)

Compound	$\delta(P_a)^b$	$\delta(P_b)^b$	$\delta(P_c)^b$	$\Delta_{coord}{}^c$	$\Delta_{chel}{}^d$	$\lvert J_{P-P}\rvert^e$	Solvent^f
$[C_5H_5Fe(CO)_2Ph_2PC_2H_4PPh_2]^+PF_6^-$	-11 ^{g}	-61.8	-	-74.7		38.0(J_{ab})	D
$[C_7H_7Mo(CO)Ph_2PC_2H_4PPh_2]^+PF_6^-$			-68.3		-81.1		D
$[C_5H_5Fe(CO)Ph_2PC_2H_4PPh_2]^+PF_6^-$			-92.3		-105.2		D
$[\{C_7H_7Mo(CO)_2\}_2Ph_2PC_2H_4PPh_2]^{2+}(PF_6^-)_2$		-35.7		-48.0			N

---

[a] Values given in ppm relative to 85% H_3PO_4. PF_6^- resonance not included. Positive shifts taken as upfield from 85% H_3PO_4. Spectra measured with P_4O_6 as external standard; 85% H_3PO_4 taken as 112.5 ppm upfield from P_4O_6.

[b] Assignment follows 23, 24, 25, 30, and 31.

[c] Co-ordination shift defined as $\delta_{coordinated} - \delta_{free\ ligand}$.

[d] Chelation shift defined as $\delta_{chelated} - \delta_{free\ ligand}$.

[e] $|^2J_{PP}|$ or $|^3J_{PP}|$ in Hz are given in parenthesis, $J_{ab} = J_{P_a-P_b}$; $J_{bc} = J_{P_b-P_c}$; $J_{bd} = J_{P_b-P_d}$.

[f] $D = CD_2Cl_2$; $N = CD_3CN$

[g] Observed as a very broad resonance (see text).

EXPERIMENTAL

Melting points were determined using a microscope equipped with a Kofler hot stage. Microanalyses were performed at the microanalytical laboratory of this department by Mrs. Darlene Mahlow and Mrs. Andrea Dunn. Results are given in Table III.

The conductivity measurements were made on a 10^{-3} M nitromethane solution using a Philips conductivity bridge, model PR 9500, and a cell with platinum electrodes. The specific conductivity for nitromethane was 4.2×10^{-7} ohm^{-1} and the cell constant was 1.4 cm. Results are included in Table III.

Infrared spectra in the carbonyl stretching region were measured using a Perkin-Elmer model 337 spectrometer equipped with expanded scale readout accessory and a Hewlett Packard 7127A recorder. The expanded spectrum obtained on the recorder was calibrated by introducing a carbon monoxide gas cell during a continuous run. Spectra were then measured by use of a calibration chart "Circos", which was conceived by Dr. R. K. Pomeroy and drafted by Mr. G. R. Johanson. The spectra were obtained in dichloromethane solution using 0.5 mm NaCl cells. Carbonyl stretching frequencies are given in Table I.

The proton nuclear magnetic resonance spectra were

TABLE III

ANALYTICAL DATA, COLORS, MELTING POINTS, YIELDS AND CONDUCTIVITY FOR THE GROUP V DERIVATIVES OF $[C_7H_7Mo(CO)_3]^+PF_6^-$ AND RELATED COMPOUNDS

Compound	% Yield[a]	Color	M.P. (°C)	Molar Cond.[b]	Calcd. %		Found %	
					C	H	C	H
$[C_7H_7Mo(CO)_2P(OPh)_3]^+PF_6^-$	45	orange	131		46.44	3.19	46.42	3.22
$[C_7H_7Mo(CO)_2PPh_3]^+PF_6^-$	77	orange-red	~206 dec.	76.9	49.86	3.41	49.76	3.20
$[C_7H_7Mo(CO)_2PPh_2Me]^+AsF_6^-$	44	wine	~185 dec.		41.80	3.19	41.79	3.27
$[C_7H_7Mo(CO)_2PPhMe_2]^+PF_6^-$	30	red-brown	~170 dec.	63.2	38.80	3.42	38.41	3.19
$[C_7H_7Mo(CO)_2AsPh_3]^+PF_6^-$	67	red	218-219 dec.	80.0	46.71	3.19	46.55	3.13
$[C_7H_7Mo(CO)_2SbPh_3]^+PF_6^-$	41	red	209-211 dec.	80.7	43.76	2.99	43.65	2.89
fac-$(CO)_3Mo[Ph_2PCH_2PPh_2]_2$[c]	86	cream	178-180		67.10	4.67	66.88	4.45
mer-$(CO)_3Mo(Ph_2PCH_2PPh_2)_2$[c]	91	yellow	184-186	4.5	67.10	4.67	66.70	4.70
$[C_7H_7Mo(CO)_2Ph_2PCH_2PPh_2]^+PF_6^-$	30	red	242-245	87.9	52.87	3.78	52.50	3.60
$[C_7H_7Mo(CO)Ph_2PCH_2PPh_2]^+PF_6^-$	43	red-brown	231-233		53.24	3.93	53.03	3.88
$[C_7H_7Mo(CO)Ph_2PC_2H_4PPh_2]^+PF_6^-$	40	red-brown	228-231	71.4	53.84	4.12	53.73	4.60
$[(C_7H_7Mo(CO)_2)_2Ph_2PC_2H_4PPh_2]^{2+}(PF_6)_2^-$	16	orange-red	~ 220 dec.	172.7	44.[illegible]9	3.26	44.94	3.30
$[C_5H_5Fe(CO)_2Ph_2PCH_2PPh_2]^+PF_6^-$	79	yellow	200-205		54.41	3.85	53.84	3.97
$[C_5H_5Fe(CO)_2Ph_2PC_2H_4PPh_2]^+PF_6^-$	71	pale yellow	198-199		55.00	4.05	54.18	4.15
$[C_5H_5Fe(CO)Ph_2PCH_2PPh_2]^+PF_6^-$	88	orange-yellow			54.70	3.98	54.71	4.09
$[C_5H_5Fe(CO)Ph_2PC_2H_4PPh_2]^+PF_6^-$	58	yellow	191-194		55.51	4.22	55.06	4.32

TABLE III (continued)

[a] The yields varied between successive runs; the values given are not necessarily the highest.

[b] Conductance ($cm^2ohm^{-1}mole^{-1}$) of ca. 10^{-3} M solutions in nitromethane at 25°.

[c] A mixture of *fac* and *mer* isomers obtained by the reaction of dpm and $[C_7H_7Mo(CO)_3]^+$. *Anal.* of mixture, Found: C, 67.11; H, 5.14.

measured on Varian A56/60 and A56/60a instruments using tetramethylsilane as an internal standard. All the compounds described in this chapter gave sharp nmr resonances with expected chemical shifts and are thus presumed to be diamagnetic. Results are included in Table I.

The proton decoupled phosphorus-31 nmr spectra were measured on a Bruker HFX-90 operating at 36.4 MHz and a deuterium lock using P_4O_6 in a sealed capillary as an external standard. The values in Table II are given relative to 85% H_3PO_4 which was taken at 112.5 ppm upfield from P_4O_6.

Reactions were performed under a nitrogen atmosphere. Work up procedures were generally performed in air; however, nitrogen was bubbled through the solutions before storing in the refrigerator. Chromatographic separations were done using Florisil (100 - 200 mesh) obtained from the J. T. Baker Co. and Fisher Scientific Co.

Cycloheptatrienetricarbonylmolybdenum and cycloheptatrienyltricarbonylmolybdenum hexafluorophosphate were prepared by established methods.[56] Group V ligands were obtained from Strem Chemical Co. Triphenylphosphine, -arsine, and -stibine were recrystallized from *n*-pentane before use.

n-Octane purchased from the Phillips Petroleum Co. was used in the preparation of $C_7H_8Mo(CO)_3$. Reactions were carried out in 95% ethanol and reagent acetone. Dichloromethane was dried over P_2O_5. Skelly 'B' refers to petroleum ether 60 - 80° fraction.

The basic synthetic procedure involved stirring equimolar amounts of $[C_7H_7Mo(CO)_3]^+PF_6^-$ (hereafter will be denoted by **14**) and ligand at reflux temperatures. Filtration of the solution resulted in solid residues which were purified by recrystallization from dichloromethane-ethanol mixtures. In some instances column chromatography was used for further purification and/or separation.

Preparation of π-cycloheptatrienyldicarbonyl(triphenylphosphine)-molybdenum hexafluorophosphate, $[(\pi\text{-}C_7H_7)Mo(CO)_2PPh_3]^+PF_6^-$

Triphenylphosphine (2.7 g, 10.7 mmol) and **14** (4.2 g, 10.1 mmol) in 120 ml of ethanol were heated at refluxing temperatures for 60 minutes. The red reaction mixture was allowed to cool to room temperature, affording a massive precipitate. This was filtered, washed with ethanol and air dried to give 5.1 g (78% yield) of product. The red solid was used as obtained for further reaction. The analytical sample was recrystallized from dichloromethane-ethanol.

The PPh_2Me, $AsPh_3$ and $SbPh_3$ derivatives were prepared similarly.

Preparation of π-cycloheptatrienyldicarbonyl(triphenylphosphite)-molybdenum hexafluorophosphate,

$[\pi\text{-}C_7H_7Mo(CO)_2P(OPh)_3]^+PF_6^-$

Triphenylphosphite (3.3 g, 10.7 mmol) and **14** (4.2 g, 10.1 mmol) in 60 ml of ethanol were heated at refluxing temperature for 0.5 hr. Some $Mo(CO)_6$ was formed and sublimed onto the water-cooled condenser. The orange-red reaction mixture was filtered while hot and the solution was cooled overnight at -20°. The orange solid formed was filtered and washed with ether. Recrystallization from dichloromethane-ether afforded 3.2 g (45% yield) of product.

Preparation of π-cycloheptatrienyldicarbonyl(phenyldimethylphosphine) molybdenum hexafluorophosphate,

$[(\pi\text{-}C_7H_7)Mo(CO)_2PPhMe_2]^+PF_6^-$

To a suspension of **14** (6.0 g, 14.4 mmol) in 60 ml of ethanol at reflux temperature, phenyldimethylphosphine in 20 ml of ethanol was added through a dropping funnel over the course of 1.5 hr. The reaction was monitored by the dissolution of the orange starting material and addition was stopped when the solution became clear. The hot solution was filtered and cooled to 0°. The brown precipitate was filtered, washed with ether, dried, and purified by chromatography over an alumina column. It eluted as a red band with dichloromethane.

The product was recrystallized from dichloromethane-ethanol yielding 2.4 g (30% yield) of $[C_7H_7Mo(CO)_2-PPhMe_2]^+PF_6^-$.

To the filtrate from the reaction mixture was added 30 ml of ether. On cooling overnight .4 g of white crystals were obtained. This compound was characterized as the known *fac*-$(CO)_3Mo(PPhMe_2)_3$ (see text). A large excess of ligand resulted in a greater yield of this substance.

Preparation of π-cycloheptatrienyldicarbonyl{bis(diphenylphosphino)methane}molybdenum hexafluorophosphate, $[\pi\text{-}C_7H_7Mo(CO)_2Ph_2PCH_2PPh_2]^+PF_6^-$

Bis(diphenylphosphino)methane (1.8 g, 4.8 mmol) and 14 (2.0 g, 4.8 mmol) were stirred at 50-55° in 100 ml acetone for 0.5 hr. The ir spectrum showed that some starting material was still present, and thus an additional .5 g of ligand was added. After a further 15 min, the solvent was removed on a rotary evaporator using water aspiration. The resulting oil was chromatographed over a Florisil column (2.5 x 20 cm). Dichloromethane eluted a yellow band of $(CO)_3Mo(Ph_2PCH_2PPh_2)_2$, which was recrystallized from dichloromethane-ethanol to yield .5 g of pale yellow crystals. A second red band consisting of $[C_7H_7Mo(CO)_2Ph_2PCH_2PPh_2]^+PF_6^-$ was eluted with dichloromethane-acetonitrile (4:1) and was recrystallized from dichloromethane to give 1.1 g (30% yield) of red crystals.

Use of a twofold excess of ligand, under otherwise identical reaction conditions and purification procedures, resulted in 1.6 g (35% yield) of $(CO)_3Mo(Ph_2PCH_2PPh_2)_2$ as the major product.

Preparation of *fac*-tricarbonyl[bi{bis(diphenylphosphino) methane}]-molybdenum, *fac*-$(CO)_3Mo(Ph_2PCH_2PPh_2)_2$

Bis(diphenylphosphino)methane (2.2 g, 5.7 mmol) and $C_7H_8Mo(CO)_3$ (0.5 g, 1.8 mmol) were stirred in 50 ml dichloromethane at room temperature for 1 hr. After turning pale yellow, the solution was filtered and 50 ml of ether added. On cooling overnight off-white crystals resulted. The sample was recrystallized once more from dichloromethane-ether to yield 1.5 g (86% yield) of the *fac* isomer.

Preparation of *mer*-tricarbonyl[bi{bis(diphenylphosphino) methane}]-molybdenum, *mer*-$(CO)_3Mo(Ph_2PCH_2PPh_2)_2$

Bis(diphenylphosphino)methane (2.2 g, 5.7 mmol) and $C_7H_8Mo(CO)_3$ (0.5 g, 5.7 mmol) were stirred in benzene (30 ml) for 15 min; the solution turned yellow. The benzene was removed using water aspiration vacuum. Recrystallization from dichloromethane and ether afforded 1.6 g (91% yield) yellow crystals of the *mer* isomer.

Preparation of π-cycloheptatrienylcarbonyl{bis(diphenylphosphino)-methane}molybdenum hexafluorophosphate, $[\pi\text{-}C_7H_7Mo(CO)Ph_2PCH_2PPh_2]^+PF_6^-$

Bis(diphenylphosphino)methane (1.6 g, 4.2 mmol) was added to a 100 ml hot ethanol solution of 14 (2.0 g, 4.8 mmol) and the mixture refluxed for [illegible].5 hr. The red reaction mixture was allowed to cool to room temperature and the precipitated solid was filtered and washed with ethanol and dichloromethane. Recrystallization from acetonitrile-ether afforded needle-like red crystals; 1.9 g, 43% yield.

Preparation of π-cycloheptatrienylcarbonyl{bis(diphenylphosphino)ethane}molybdenum hexafluorophosphate, $[\pi\text{-}C_7H_7Mo(CO)Ph_2PC_2H_4PPh_2]^+PF_6^-$ and bis(π-cycloheptatrienyldicarbonylmolybdenum)-μ-bis(diphenylphosphino)ethane hexafluorophosphate, $[(\pi\text{-}C_7H_7Mo(CO)_2)_2\text{-}\mu\text{-}Ph_2PC_2H_4\text{-}PPh_2]^{2+}(PF_6^-)_2$

Bis(diphenylphosphino)ethane (1.5 g, 3.8 mmol) and 14 (1.5 g, 3.6 mmol) in 70 ml ethanol were refluxed for 3 hr. The brown reaction mixture was filtered and the brown solid residue washed with 25 ml hot ethanol and the washings added to the filtrate. The residue was then washed with several portions of dichloromethane and recrystallized from acetonitrile-ether affording orange-red crystals of $[(C_7H_7Mo(CO)_2)_2\text{-}\mu\text{-}Ph_2PC_2H_4PPh_2]^{2+}(PF_6^-)_2$.

The filtrate was allowed to cool at -20° overnight affording a brown solid. This was filtered, washed with cold ethanol and ether and recrystallized from dichloromethane-ether to give the red-brown $[C_7H_7Mo(CO)Ph_2PC_2H_4PPh_2]^+PF_6^-$; 1.1 g, 40% yield.

The yield of the binuclear complex can be improved by addition of less than stoichiometric amount of ligand. For example, $Ph_2PC_2H_4PPh_2$ (1.0 g, 2.5 mmol) and 14 (1.5 g, 3.6 mmol) reacted as described above to yield 0.7 g (16% yield) of $[(C_7H_7Mo(CO)_2)_2\text{-}\mu\text{-}Ph_2PC_2H_4PPh_2]^{2+}(PF_6^-)_2$.

Preparation of π-cyclopentadienyldicarbonyl{bis(diphenylphosphino)ethane}iron hexafluorophosphate, $[\pi\text{-}C_5H_5Fe(CO)_2Ph_2PC_2H_4PPh_2]^+PF_6^-$

A solution of bis(diphenylphosphino)ethane (1.2 g, 3.0 mmol) and $[C_5H_5Fe(CO)_2CH_3CN]^+PF_6^-$ (1.0 g, 2.8 mmol) in 120 ml ethanol was refluxed overnight. The solution was filtered while hot and allowed to cool to room temperature; brown-yellow crystals separated out. These were washed liberally with benzene and ether and recrystallized from dichloromethane and skelly B to give 1.4 g (71% yield) of yellow needles.

Preparation of π-cyclopentadienyldicarbonyl{bis(diphenylphosphino)methane}iron hexafluorophosphate, $[\pi\text{-}C_5H_5Fe(CO)_2Ph_2PCH_2PPh_2]^+PF_6^-$

A solution of bis(diphenylphosphino)methane (1.2 g, 3.1 mmol) and $[\pi\text{-}C_5H_5Fe(CO)_2CH_3CN]^+PF_6^-$ (1.0 g, 2.8 mmol) in 120 ml ethanol were refluxed for 5 hr. The solvent was removed on a rotary evaporator using water aspiration, the residue chromatographed on florisil with dichloromethane as solvent and eluent. Recrystallization from dichloromethane and skelly B afforded the analytical sample, 1.4 g, 72% yield.

CHAPTER III

GROUP V DERIVATIVES OF CYCLOHEPTATRIENETRICARBONYLMOLYBDENUM

INTRODUCTION

In the introductory remarks made in Chapter II, we have seen that the earliest π-complexes of C_7H_8 and C_7H_7 were those formed with the group VI metal carbonyls. It is not surprising that the chemical behavior of these complexes has been studied in great detail.

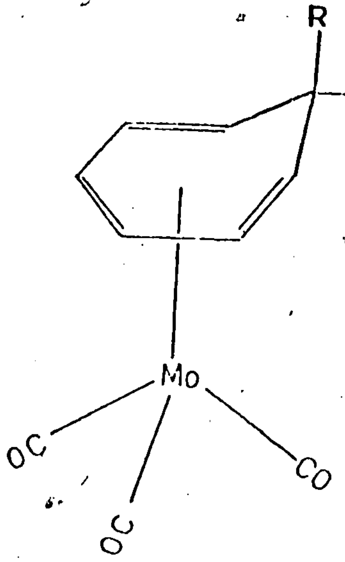
The reactions of the cations $[C_7H_7M(CO)_3]^+$ (M = Cr or Mo) with nucleophilic reagents, can proceed by four different routes:

(a) Ring substitution takes place with various anions giving rise to 7-substituted cycloheptatriene complexes[57,27]

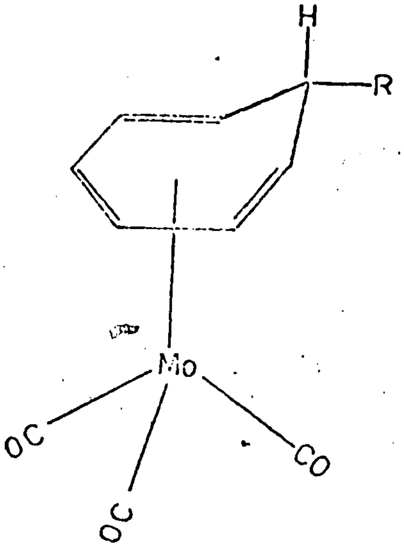
$$[C_7H_7M(CO)_3]^+ + R^- \longrightarrow (C_7H_7R)M(CO)_3 \qquad \text{III-1}$$

where M = Cr, R = H, OMe, HS, or $C_5H_4Bu^t$; M = Mo, R = H. The net effect of this mode of attack views the positive charge as residing on the ring.

When R is not equal to H, *exo* and/or *endo* isomers are possible as shown in **33** and **34** respectively. X-ray[58] and nmr[59] studies have identified the *exo* isomer as being formed in all the cases studied.



33 (*exo*)



34 (*endo*)

(b) A second mode of attack assumes that sufficient of the positive charge is located at the metal for anionic attack at this point,

$$[C_7H_7Mo(CO)_3]^+ + X^- \longrightarrow C_7H_7Mo(CO)_2X + CO \qquad \text{III-2}$$

Only the halogen ions (X = Cl, Br or I) have been found to react in this way.[30]

(c) When the chromium cation is reacted with basic substances, such as potassium cyanide, sodium amide, phenyllithium and sodium acetate, the so-called *abnormal* reaction occurs. The main products are the dicycloheptatriene complexes $C_{14}H_{14}Cr(CO)_3$ and $C_{14}H_{14}\{Cr(CO)_3\}_2$.[57]

(d) With sodium cyclopentadienide or sodium diethyl malonate a contraction of the ring takes place and the seven-membered cycloheptatrienyl ring is converted into a six-membered benzene ring.[57]

$$[C_7H_7M(CO)_3]^+ + C_5H_5^- \longrightarrow C_6H_6M(CO)_3 + C_6H_6 \qquad \text{III-3}$$

Attempts to prepare derivatives of $C_7H_8Mo(CO)_3$ have not met with much success. Thus Friedel-Crafts substitution reactions on the seven-membered ring were unsuccessful.[23] Attempts to replace one of the carbonyl groups by other ligands also failed; instead the cycloheptatriene ring is easily displaced by a large variety of Lewis base ligands (L) such as amines, phosphines, arsines, stibines and sulphides with formation of $L_3Mo(CO)_3$.[23,60,61] This facile displacement of the ring has made $C_7H_8Mo(CO)_3$ a most useful intermediate in the preparation of numerous tris-substituted complexes. However, this has meant that carbonyl substituted derivatives of $C_7H_8Mo(CO)_3$ could not be prepared directly. An exception is a derivative of 9-phenyl-9-phosphobicyclo [4.2.1]nonatriene formed from the following reaction.[61]

$$C_8H_8PC_6H_5 + C_7H_8Mo(CO)_3 \xrightarrow{110°}$$

$$C_7H_8Mo(CO)_2(C_8H_8PC_6H_5) + (C_8H_8PC_6H_5)_2Mo(CO)_4 \qquad \text{III-4}$$

The relatively poor yield of 3% indicates the low tendency of this type of reaction to take place.

In contrast, the cycloheptatriene ring in the chromium complex, $C_7H_8Cr(CO)_3$, is not readily displaced, as evidenced by the formation of triphenylphosphine and -phosphite derivatives under photochemical conditions.[62]

$$C_7H_8Cr(CO)_3 + L \xrightarrow[\text{THF, 46 hr}]{h\nu,\ -78°} C_7H_8Cr(CO)_2L + CO \qquad \text{III-5}$$

The present chapter describes the synthesis of cycloheptatriene molybdenum derivatives of the group V elements by reduction of the cationic complexes prepared in chapter II.

RESULTS AND DISCUSSION

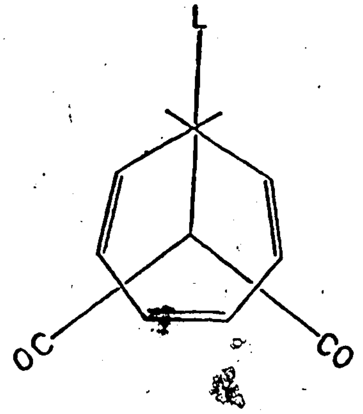
The addition of sodium borohydride to the cycloheptatrienyl complexes containing tertiary Group V ligands, afforded the corresponding cycloheptatriene derivatives

$$[C_7H_7Mo(CO)_2L]^+PF_6^- + NaBH_4 \longrightarrow$$

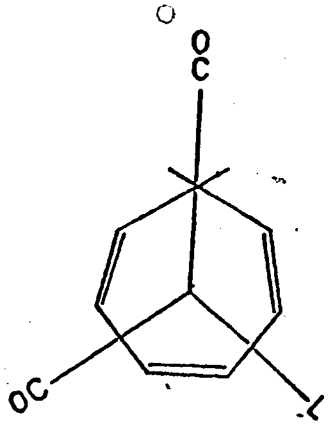
$$C_7H_8Mo(CO)_2L + NaPF_6 + \text{'}BH_3\text{'} \qquad \text{III-6}$$

where L = $P(OPh)_3$, PPh_3, PPh_2Me, $PPhMe_2$, $AsPh_3$, and $SbPh_3$. The reactions were carried out using either a two layer benzene-water system, or more conveniently using tetrahydrofuran (THF) as solvent.

In theory, two conformational isomers are possible; a symmetric conformation having C_s symmetry with a reflection plane bisecting the cycloheptatriene and he CO groups, 35, and two enantiomeric conformations having C_1 symmetry, 36. Results of temperature depen-



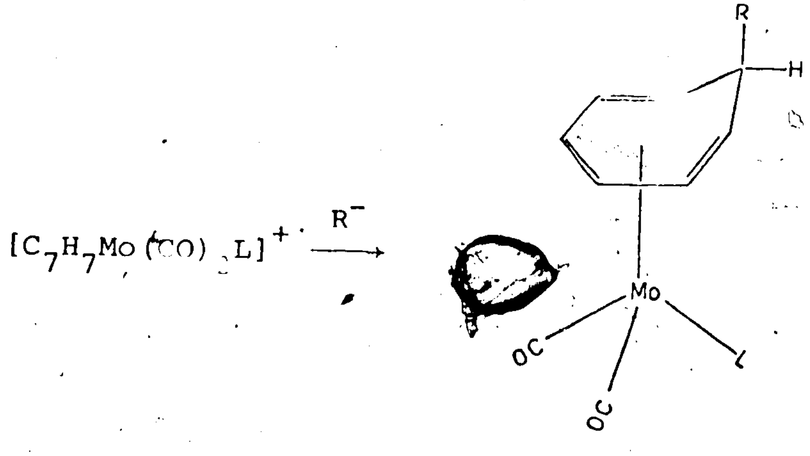
35 (C_s)



36 (C_1)

dent ^{13}C nmr spectra, which will be presented later, favor the existence of only a single conformer, 35.

Addition of alkyllithium reagents to some $[C_7H_7Mo(CO)_2L]^+$ complexes in THF or ether resulted in the formation of alkyl-substituted complexes:



37

III-7

where R = Me, L = $P(OPh)_3$, PPh_3 and PPh_2Me; R = Bu^t, L = PPh_3.

Again, although two isomers are possible, only the *exo*-isomer, shown in 37, is thought to be formed. Similar additions to cationic complexes have been studied in the $[C_6H_6Mn(CO)_3]^+$,[63] $[C_5H_5Fe(CO)_3]^+$,[64] and $[C_7H_7Cr(CO)_3]^+$ [57] series. All additions have been shown to occur from the less sterically hindered *exo* side. The most convincing evidence, which includes nmr[59] and mass spectral[65] studies as well as an X-ray examination of 7-phenylcycloheptatrienetricarbonylchromium, has been accumulated for the chromium series.

When $[C_7H_7Mo(CO)_3]^+$ was treated with methyllithium complete decomposition resulted. The latter is evidently much less stable than its phosphine substituted derivatives. Likewise, Pauson[57] had noted the instability of $[C_7H_7Mo(CO)_3]^+$ to nucleophilic attack in comparison to the chromium analogue.

The $C_7H_8Mo(CO)_2$-PPh_3 and -$AsPh_3$ complexes failed to react with additional PPh_3 and $AsPh_3$ even in refluxing benzene. As noted earlier $C_7H_8Mo(CO)_3$ reacts with donor molecules at room temperature. No doubt, the bulky phenyl substituted ligands diminish the availability of sites for further attack on the metal.

The cycloheptatriene compounds prepared, form red crystals which are air stable for long periods. The stability of these derivatives is in marked contrast to that reported for $C_7H_8Cr(CO)_2$-$P(OPh)_3$ and -PPh_3.[62] The derivatives prepared in the present work are sufficiently soluble in hydrocarbon solvents for infrared measurements. In donor solvents such as acetonitrile, and acetone they begin to oxidize after a few hours. The compounds were characterized by thei [illegible] mr and mass spectra and by elemental analysis. [illegible] ctroscopic properties are discussed next.

Infrared spectra

The ir spectra show, with one notable exception, the expected two bands in the carbonyl region. The spectra of the triphenylphosphite derivatives, $C_7H_8Mo(CO)_2P(OPh)_3$ and $(C_7H_7Me)Mo(CO)_2P(OPh)_3$, are anomalous in showing more carbonyl stretching bands than there are CO groups in the molecule. The typical spectra, shown in Figures 9 and 10, are to be contrasted with the complex spectra displayed by the $P(OPh)_3$ derivatives, Figures 11 and 12. The observed carbonyl stretching bands are listed in Table IV.

The $P(OPh)_3$ derivatives show at least three terminal stretching bands, a symmetrical high frequency band and a lower frequency band split into two peaks and a shoulder (see arrow). Repeated recrystallization and chromatography did not change these spectra. A complete elemental analysis of $C_7H_8Mo(CO)_2P(OPh)_3$ ruled out the possibility of a different molecular formu Molecular weight and exact mass spectral measurements established these derivatives to be monomeric. Moreover, the ^1H and ^{13}C nmr spectra displayed no unusual features.

It is generally accepted that the appearance of 'extra' carbonyl stretching bands is due to the presence of isomeric forms, and considerable interest in their detection has developed in recent years. Optical isomerism such as in $C_5H_5Mo(CO)_2Y$ (Y^- = pyrrolcarbaldehyde(2)methylbenzylamine ion)[66] and cis-trans isomerism observed in $C_5H_5Mo(CO)_2P(OPh)_3(Me)$[67] can be immediately excluded in this case. The only other type of isomeri

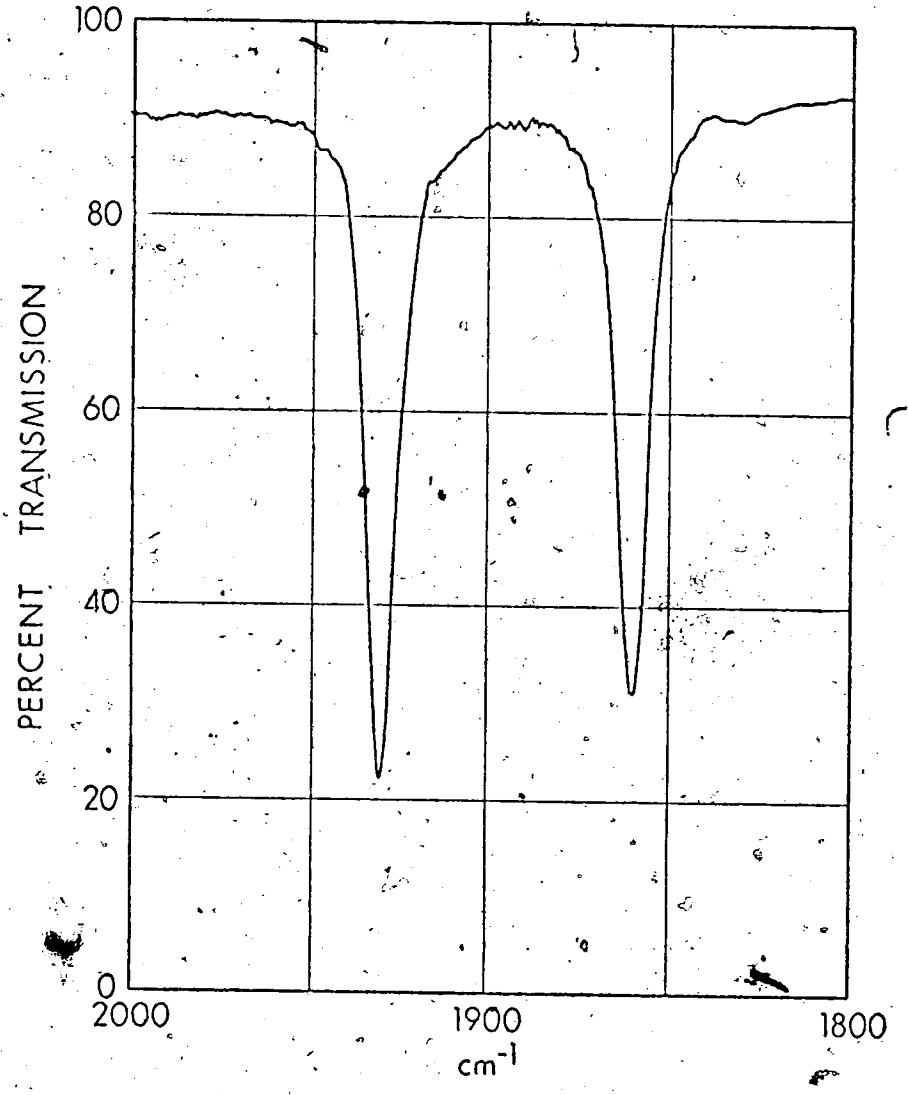


Figure 9. $C_7H_8Mo(CO)_2SbPh_3$ in *n*-hexane.

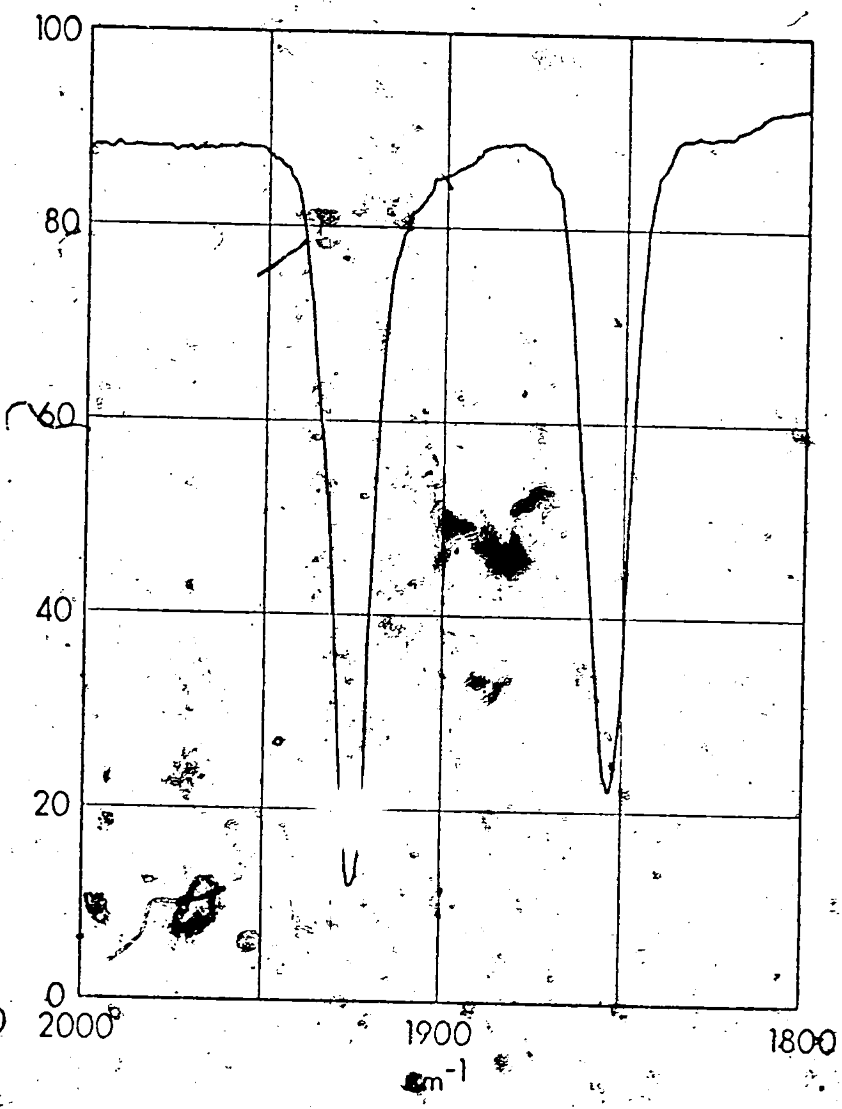


Figure 10. $(C_7H_7Me)Mo(CO)_2PPh_2Me$ in *n*-hexane.

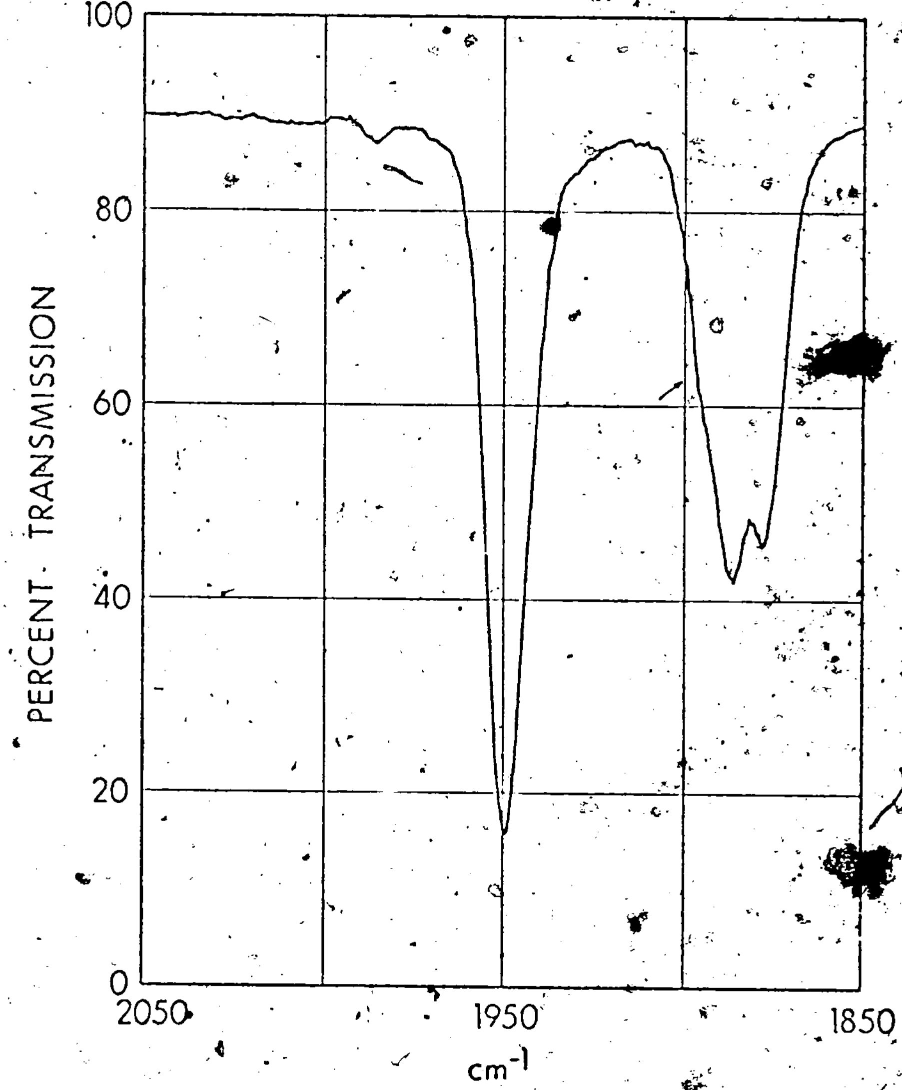


Figure 11. $C_7H_8Mo(CO)_2P(OPh)_3$ in *n*-hexane.

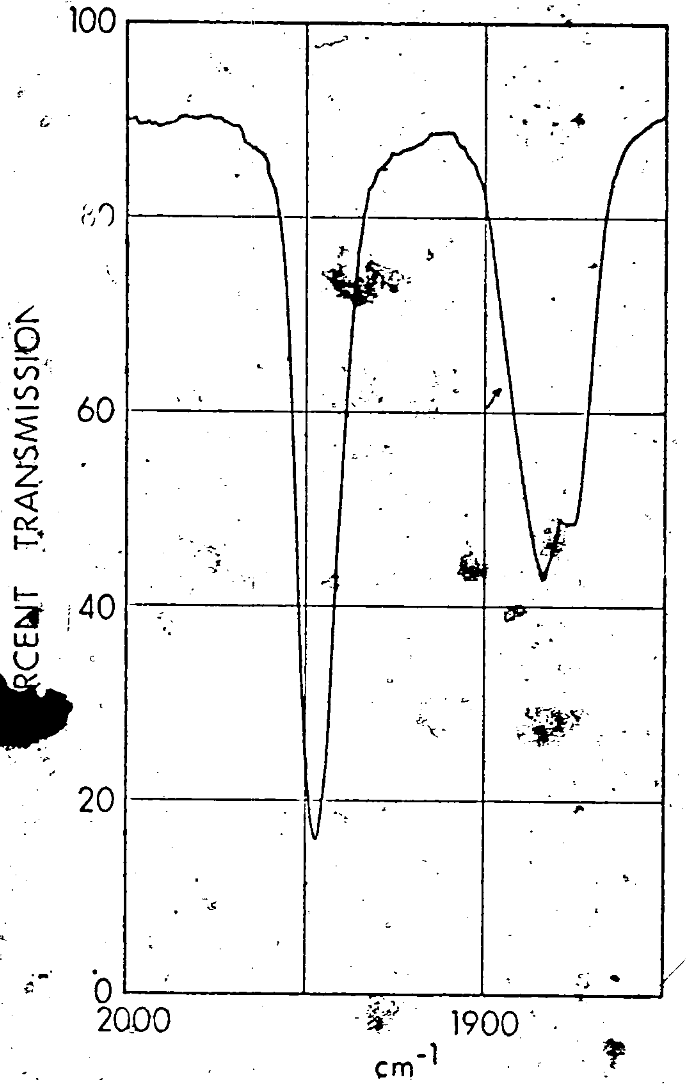


Figure 12. $(C_7H_7Me)Mo(CO)_2P(OPh)_3$ in *n*-hexane.

TABLE IV

INFRARED AND APPROXIMATE FORCE CONSTANT DATA FOR THE GROUP V DERIVATIVES OF CYCLOHEPTATRIENETRICARBONYLMOLYBDENUM

Compound	Carbonyl Stretching Frequencies (cm^{-1})[a]		Force Constants[d] k_1	k_i
$C_7H_8Mo(CO)_3$	1997(10.0) 1908(7.7)	1933(7.7)[b]	15.32;15.26	.48;.23
$C_7H_8Mo(CO)_2P(OPh)_3$	1948.5(10.0) 1885(6.6)	1892(4.3,sh) 1876(6.1)	14.81[e]	.53
$(C_7H_7Me)Mo(CO)_2P(OPh)_3$	1947.5(10.0) 1885(7.9)	1894(5.5) 1876(7.1,sh)	14.83[e]	.48
$C_7H_8Mo(CO)_2PPh_3$	1931(10.0)	1857(8.5)	14.49	.57
$(C_7H_7Me)Mo(CO)_2PPh_3$	1905(10.0)	1826(8.0)[c]		
$(C_7H_7Bu^t)Mo(CO)_2PPh_3$	1932(10.0)	1855(8.4)	14.49	.59
$C_7H_8Mo(CO)_2PPh_2Me$	1926(10.0)	1854(8.4)	14.43	.55
$(C_7H_7Me)Mo(CO)_2PPh_2Me$	1926(10.0)	1854(8.4)	14.43	.55
$C_7H_8Mo(CO)_2PPhMe_2$	1925.5(10.0)	1851(8.3)	14.41	.57[c]
$C_7H_8Mo(CO)_2AsPh_3$	1931(10.0)	1858(8.1)	14.50	.56
$C_7H_8Mo(CO)_2SbPh_3$	1932.5(10.0)	1862(8.5)	14.54	.54

TABLE IV (continued)

[a]Measured in *n*-hexane; figures in parenthesis are relative band intensities.

[b]Bands due to mono-^{13}CO molecule at 1985 and 1880 cm^{-1} were used in the force constant calculations.

[c]Measured in CH_2Cl_2.

[d]Force constants in mdyn/Å.

[e]The average value of the bands at 1885 and 1876 cm^{-1} were used in calculations.

reported in organometallic chemistry, conformational isomerism, falls into two classes:

(a) Isomerism due to restricted rotation about a metal-ligand bond as in $C_5H_5Fe(CO)_2SiCl_2Me$ [68] and $C_5H_5Mn(CO)_2SR_2$ [69] (R = alkyl group); the isomeric forms differ in orientation of groups on the ligand relative to the ring and the carbonyls.

(b) Isomerism due to restricted rotation within the ligand itself such as in phosphite complexes of the type $C_6H_6Cr(CO)_2P(OPh)_3$ [70] and $C_7H_7Mo(CO)P(OPh)_3(I)$.[32]

Conformational isomerism of the latter type seems a reasonable explanation for the multiplicity of ν(CO) bands in the ir spectra of the phosphite derivatives. In general the effect of conformational isomerism causes the splitting or asymmetry of both ir active modes. Thus the observed spectra are *not typical*, showing splitting of only the asymmetric lower frequency mode. To our knowledge only in one other system $(C_3H_4X)Co(CO)_2L$[71] (X = H, Me, Cl and L = $P(OPh)_3$, $P(OMe)_3$, PPh_3), do the ir spectra show the same features observed in the present work. The reason for the differences are not understood and this emphasizes the need to further investigate the nature of this isomerism.

The ir spectra when measured in dichloromethane and other polar solvents are shifted to lower frequency in comparison to the spectra measured in hydrocarbon solvents. For example, $C_7H_8Mo(CO)_2PPh_3$ shows carbonyl bands at 1931 and 1857 cm^{-1} in *n*-hexane and in dichloromethane at 1909 and 1826 cm^{-1}. Although shifts of this type are not uncommon in metal carbonyl complexes, the ones observed here are larger than in most systems.

Force constants

The force constants for $C_7H_8Mo(CO)_2L$, derived for the C_s isomer 35, consist of one CO stretching constant (k_1) and one CO interaction constant (k_i). The two observed ir bands, which are assigned to the symmetric A' and asymmetric A" normal modes are sufficient to calculate the force constants in this system. The values for the force constants are included in Table IV; those of the parent $C_7H_8Mo(CO)_3$ require further comment. In this system there are two CO stretching constants and two interaction constants. Along with the three bands from the all-^{12}CO molecule, the two bands from the mono-^{13}CO molecule are well resolved and were used in the calculation. The all-^{12}CO bands at 1997 and 1933 cm^{-1} were assigned to the symmetric A' and asymmetric A" stretch of the two equivalent CO groups in the molecule, while the band at 1908 cm^{-1} to the A' mode of the unique CO group. The two ^{13}CO bands at 1985 and 1878 cm^{-1} were assigned to A (C_1) and A' (C_s) corresponding to substitution of one of the equivalent CO and the unique CO groups respectively.

The "weighted average force constant" for $C_7H_8Mo(CO)_3$ has been calculated by Mann[illegible] and is considerably different from the values calculated in this work. The former was based on ir spectra measured in CH_2Cl_2, which, as has already been mentioned, causes a substantial decrease in ν(CO). The above observed all-^{12}CO bands in *n*-hexane should be compared with bands at 1985, 1918, and 1880 cm^{-1} in CH_2Cl_2. This shift results in abnormally low values for the force constants.

It is generally assumed that the variation in the CO force constants arise predominately from the variation in the extent of π-bonding.[10,73,74] Substituting a CO by a poorer π-acceptor and/or better σ-donor reduces the value of the force constants. This is reflected in the ca. .7 mdyn/A decrease in value of the principle force constant in the $C_7H_8Mo(CO)_2L$ derivatives as compared to the parent tricarbonyl. The relatively low value of ca. 14.5 mdyn/A observed for these derivatives, points to a healthy degree of π-bonding between the metal and the carbonyls.

The variations in the force constants between the various donor ligands are very small; and due to the approximation inherent in the calculation no meaningful conclusions can be drawn.

^1H nmr spectra

The ^1H nmr spectra of $C_7H_8M(CO)_3$ (M = Cr, Mo and W) and the cycloheptatriene-substituted analogues have been assigned.[35,59] They are characterized by three types of olefinic signals shifted to higher field from the parent hydrocarbon and, in the case of the unsubstituted derivatives, signals due to the methylene protons which have become non-equivalent on co-ordination.

The ^1H nmr spectra of the $C_7H_8Mo(CO)_2L$ derivatives were measured and are similar to that of $C_7H_8Mo(CO)_3$. The signals in the dicarbonyl derivatives are all shifted to higher field. For example, the nmr spectrum of $C_7H_8Mo(CO)_2P(OPh)_3$ in CD_2Cl_2 showed broad cycloheptatriene proton peaks centred at 4.6, 5.6, 7.2, and 7.5 τ having relative area 2:2:2:2 in good agreement with the spectrum of $C_7H_8Mo(CO)_3$ (multiplets centred at 4.0, 5.1, 6.4, and 7.2 τ). The shift to higher field in the ring protons has also been observed in $C_7H_8Cr(CO)_2L$ (L = $P(OPh)_3$ and PPh_3) in comparison with the corresponding tricarbonyl compound.[62] The upfield shift is consistent with an increased electron density on the cycloheptatriene ring as a result of substitution of donor Group V ligands for CO.

Nmr spectroscopy has also been used to distinguish between *exo* and *endo* isomers in substituted cycloheptatriene derivatives of chromium.[59] It was found that *exo* alkyl groups were shifted to higher field and *endo* to lower field by comparison with the unco-ordinated parent hydrocarbon. In the present work the methyl resonance of $(C_7H_7Me)Mo(CO)_2L$ (L = $P(OPh)_3$ and PPh_2Me) occurred at 9.9 τ, shifted to higher field from 9.06 τ in C_7H_7Me and are indicative of the *exo* geometry.

The results of the nmr spectra are listed in Table V. The spectrum of $(C_7H_7Me)Mo(CO)_2PPh_2Me$ is shown in Figure 13 along with the conventional assignment in 38. Not all compounds exhibited such well defined spectra and in many the ring peaks were broad.

^{13}C nmr spectra

The use of carbon-13 nmr spectroscopy in organometallic chemistry is increasing rapidly and is fast becoming a powerful tool for deducing structures in solution.[75]

The ^{13}C nmr spectrum of $C_7H_8Mo(CO)_3$ has recently been assigned by Mann;[72] it showed only one type of carbonyl group at room temperature. Two ^{13}C (carbonyl) signals are expected due to the asymmetry caused by the methylene group. Indeed at -50°, Kreiter and Lang[76] observed two ^{13}C (carbonyl) signals in the ratio of 1:2. On warming to ambient temperatures the two signals coalesced due to an averaging process on the nmr time scale.

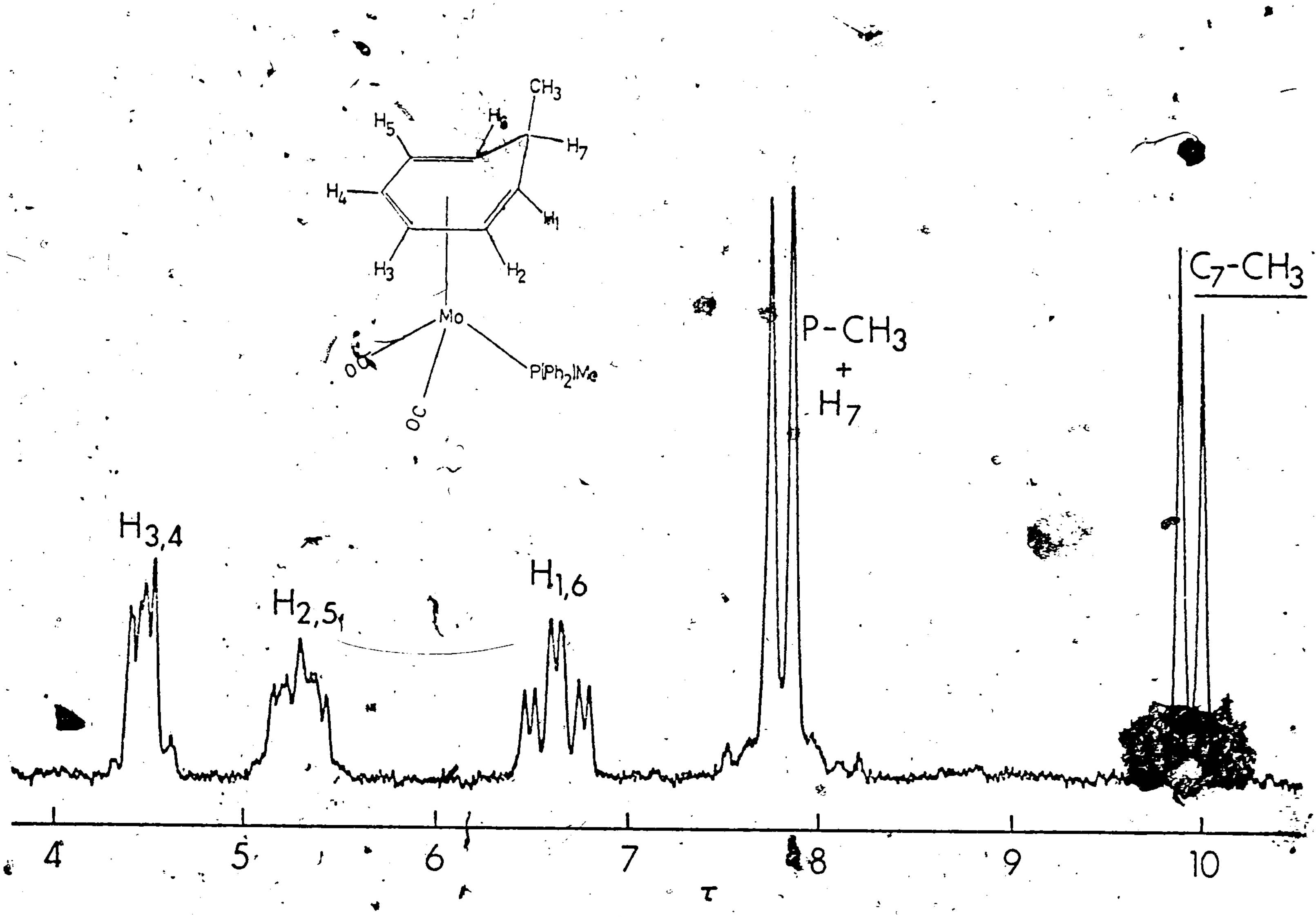


Figure 13. ^{1}H nmr spectrum of $(C_7H_7Me)Mo(CO)_2PPh_2Me$ in CD_2Cl_2. Chemical shift relative to TMS (not shown).

TABLE V.[illegible]

^1H NMR SPECTRA FOR THE GROUP V DERIVATIVES OF CYCLOHEPTATRIENETRICARBONYLMOLYBDENUM[a]

Compound	Chemical Shift (τ-value)[b]					Solvent[c]
	H_3+H_4	H_2+H_5	H_1+H_6	H_7	Other	
$C_7H_8Mo(CO)_3$	4.0 dd	5.1 q	6.4 dt	~7.2 c		C
$C_7H_8Mo(CO)_2P(OPh)_3$	4.7 t	5.6 m,br	7.2 m	~7.5 c		D
$(C_7H_7Me)Mo(CO)_2P(OPh)_3\cdot CH_2Cl_2$	~4.6	5.5 cm	6.8 dt	~7.2 qu	$C_7-CH_3=9.92(6.5)$ $\cdot CH_2Cl_2 = 4.6$	D
$C_7H_8Mo(CO)_2PPh_3$	4.4 dd	5.2 br	7.0 br	~7.7 c		C
$(C_7HBu^t)Mo(CO)_2PPh_3$	4.7 dd	5.3 br	6.8 dt	~9.1 c	$C_7-\overset{\mid}{\underset{\mid}{C}}-CH_3=9.75$	D
$C_7H_8Mo(CO)_2PPh_2Me$	4.3 br	5.3 br	7.0 br	~7.7 br	$P-CH_3 = 7.82(7.0)$	C
$(C_7H_7Me)Mo(CO)_2PPh_2Me$	4.5 dd	5.3 q	6.7 dt	~7.8	$P-CH_3 = 7.81(7.0)$ $C_7-CH_3 = 9.92(6.8)$	D
$C_7H_8Mo(CO)_2PPhMe_2$	4.4 dd	5.2 br	7.0 m	~7.7	$P-CH_3 = 8.00(7.5)$	C
$C_7H_8Mo(CO)_2AsPh_3$	4.4 br	5.3 br	7.0 m	~8.0 m		C
$C_7H_8Mo(CO)_2SbPh_3$	4.2 dt	5.3 br	6.7 m	~8.1 m		C

Table V (continued)

[a]Assignment according to 38.

[b]Relative to TMS. P-C_6H_5 τ values not given. Figures in parenthesis are J values in Hz. Key: br = broad, m = multiplet, c = complex, dd = 'double doublet', t = triplet, dt = 'double triplet', q = 'quintet', [illegible] = 'quartet'.

[c]C = $CDCl_3$, D = CD_2Cl_2.

The Fourier transform proton decoupled ^{13}C nmr spectra of some $C_7H_8Mo(CO)_2L$ (L = $P(OPh)_3$, PPh_3, PPh_2Me, $PPhMe_2$) derivatives were measured at various temperatures in acetone-d_6 and CD_2Cl_2. The results a[illegible]sted in Table VI. The spectrum of $C_7H_8Mo(CO)_2PPh_3$ and its assignment based on that of C_7H_8 [77] and $C_7H_8Mo(CO)_3$ [76,72] is shown in Figure 14 and 39.

The $^{13}C(C_7H_8)$ chemical shifts are in good agreement with those reported for $C_7H_8Mo(CO)_3$, remaining sharp at all the measured temperatures. No coupling between the ring carbon and the phosphorus nuclei was observed. This parallels the result in complexes of the type $C_5H_5W(CO)_2PR_3(X)$[78] (R = Me, Ph, OMe, and X = I, $SnMe_3$) and in $C_5H_5Fe(CO)_2PPh_3$ [79] where $^2J_{P-C}$ is also zero. The reason for this phenomenon is not well understood and conflicting views exist on its implication.[78,80]

The possibility of C_s and C_1 conformational isomers 35 and 36, has been mentioned earlier. For [illegible] both CO groups are equivalent and a single ^{13}C (carbonyl) signal is expected. For 36, two signals are expected and moreover C_2 and C_5, C_3 and C_4, C_1 and C_6 (see 39) are no longer chemically equivalent.

Only one ^{13}C (carbonyl) signal, split by the phosphorus nucleus with $^2J_{P-CO}$ ranging between 10 and 17 Hz, was observed down to the lowest temperature obtainable (-70° in the most favorable case). Above 20° the signal

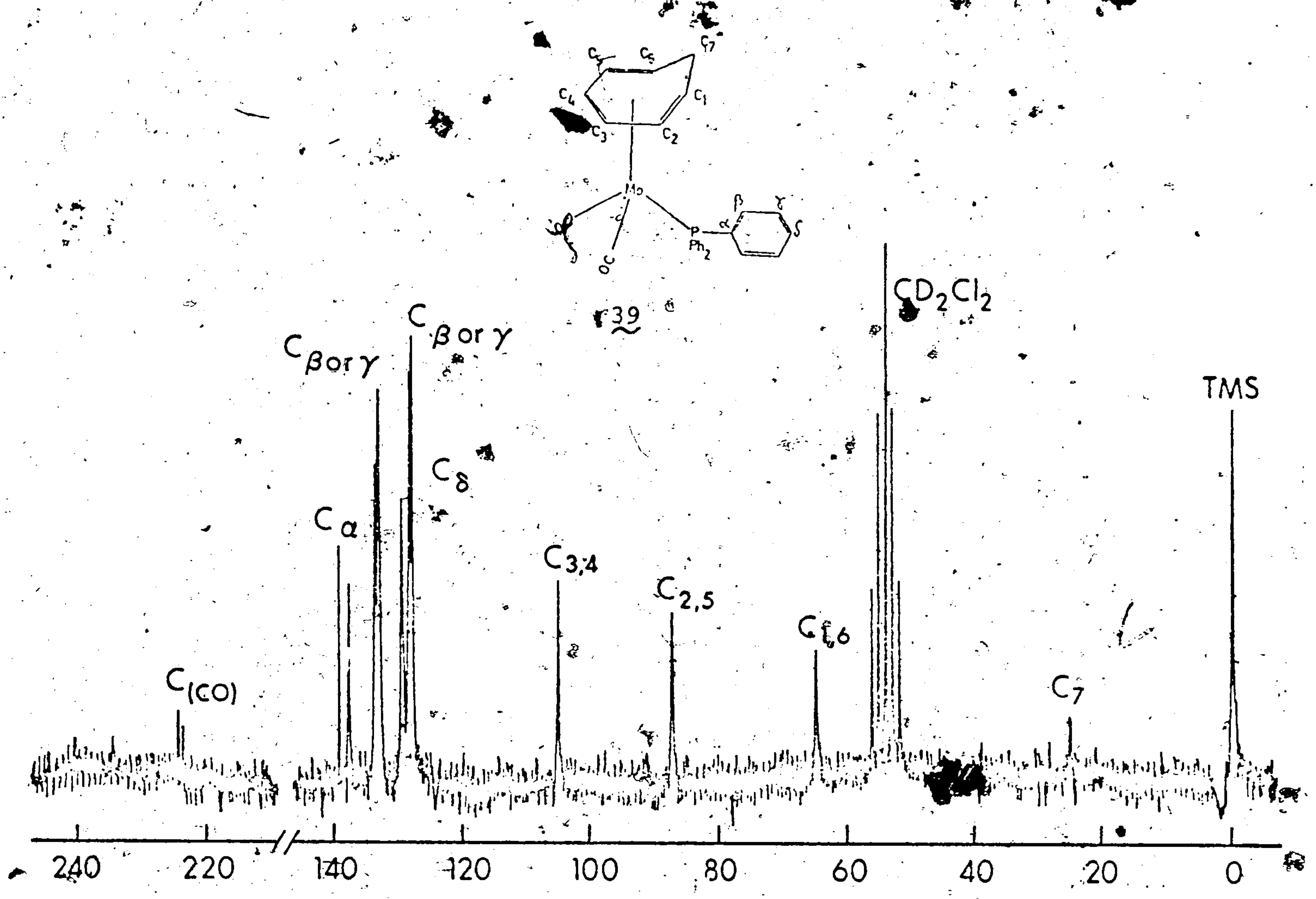


Figure 14. The ^{13}C nmr spectrum of $C_7H_8Mo(CO)_2PPh_3$ in CD_2Cl_2. Chemical shift relative to TMS in PPM.

TABLE VI

^{13}C-NMR DATA FOR $C_7H_8Mo(CO)_2L$ (L = CO, $P(OC_6H_5)_3$, $P(C_6H_5)_3$, $P(C_6H_5)_2CH_3$, $P(C_6H_5(CH_3)_2)$[a]

Compound	$\delta(C_{3,4})$	$\delta(C_{2,5})$	$\delta(C_{1,6})$	$\delta(C_7)$	$\delta(CO)$	T(K)	$\delta(C_q)$	$\delta(C_\beta)$ or	$\delta(C_\gamma)$	$\delta(C_\delta)$	$\delta(CH_3)$
$C_7H_8Mo(CO)_3$ [b]	104.00	98.82	61.88	27.47	220.79[e]	300					
$C_7H_8Mo(CO)_2P(OPh)_3$ [c]	101.90	94.89	58.15	27.19		273	152.22(4)	121.81(4)	129.80	124.67	
	102.98	92.46	61.01	26.60	213.47(17)	203	151.62(4)	121.70	129.85		
$C_7H_8Mo(CO)_2PPh_3$ [c]	105.37	87.46	65.00	25.53	224.14(11)	228	139.37(38)	128.62(17)	133.70	129.78	
$C_7H_8Mo(CO)_2PPh_2Me$ [b]	105.41	88.58	62.04	27.62	224.78(10)	203	140.91(36)	129.05(11)	132.40(11)	120.26	21.86(24)
	104.6	89.5	61.6	27.2	224.45(10)	300	141.9(35)	129.8	132.4	129.0	21.6(25)
$C_7H_8Mo(CO)_2PPhMe_2$ [b]	104.97	88.20	61.63	26.83	224.25(12)	233	f	f	f	f	21.27(28)

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[a] Chemical shifts in ppm relative to TMS. J_{P-C} values in brackets (Hz).

[b] Acetone-d_6; $^{13}C(CO)$ = 207.69.

[c] CD_2Cl_2.

[e] Reference 76; 217.93 and 229.17 PPM (2:1) at 222°K.

[f] not measured.

was lost due to an increase in noise. Only four signals due to the ring were observed at all temperatures.

An activation energy of ca. 11 kcal was estimated for the averaging process involving $C_7H_8Mo(CO)_3$.[76] The effect of substituting a phosphine ligand for CO would be to increase the barrier for interconversion, regardless of whether the mechanism involved rotation of the carbonyls or the ring or both. It seems unlikely that the single carbonyl signal is an averaged one, and argues in favor of the existence of the C_s isomer alone.

In connection with the above, attempts to measure the low temperature ^1H nmr spectrum of $(C_7H_7Bu^t)Mo(CO)_2PPh_3$ and $(C_7H_7Me)Mo(CO)_2L$ (L = $P(OPh)_3$ and PPh_2Me) in CD_2Cl_2 were not successful because of the tendency of the solutions of these compounds to become very viscous at about -20°. The ^1H (Me) signals in these compounds remain sharp up to a temperature of 100° in toluene-d_8.

Mass spectra

Mass spectroscopy, together with nmr and ir spectroscopy, is nowadays one of the most important standard methods of investigation in organometallic chemistry.[81] Mass spectral data of numerous compounds have been reported in the literature; most have dealt with parent ion identification for the purpose of characterization of new compounds, a few have dealt with a detailed analysis of the fragmentation patterns as an aid in establishing molecular geometries.[82,83] For example, it has been shown that *exo* or *endo* stereochemistry of ring substituents in cycloheptatriene and cyclopentadiene metal complexes can be distinguished conclusively by examination of the mode of decomposition in the mass spectra.[65,84]

In the present work, mass spectra were employed mainly as an aid in characterization of new compounds. This involved the identification of observed ions from the mass numbers. Molybdenum contains a mixture of isotopes and in combination with the mainly monoisotopic elements such as carbon, phosphorus and arsenic or the bi-isotopic antimony characteristic patterns are formed which are diagnostic of the presence of the metal in a given ion. The interpretation of the mass spectra was facilitated by calculation of theoretical peak masses and isotopic combination patterns (for a comparison of observed and calculated patterns see chapters IV and VI). Some isotopic patterns were complicated by the loss of hydrogen fragments. The relative ratio of the ions forming the 'complex' isotopic patterns were estimated by comparison of the observed and theoretical isotopic patterns.

The important fragments in the mass spectra of $C_7H_8Mo(CO)_2L$ (L = CO, $P(OPh)_3$, PPh_3, $PPhMe_2$, and $AsPh_3$),

$(C_7H_7Me)Mo(CO)_2PPh_2Me$ and $(C_7H_7Bu^t)Mo(CO)_2PPh_3$ are listed in Table VII as representative of the spectra obtained. All compounds showed similar features in their fragmentation patterns.

A parent peak was observed for all compounds, the relative intensity of which decreased markedly from that of $C_7H_8Mo(CO)_3$. The ion corresponding to a loss of one CO was also of very low intensity by comparison to the parent tricarbonyl. This is consistent with the results for $C_5H_5Mn(CO)_2L$[85] and $C_7H_8Cr(CO)_2L$[62] ($L = PPh_3, P(OPh)_3$). It has been suggested that the presence of the L group weakens the M-CO bonds.[62]

The loss of the last CO was accompanied by the elimination of H_2. In most cases the loss of 58 mass units ($2CO + H_2$) from the parent ion corresponded to the most intense peak containing the molybdenum ion and in some cases to the base peak. It appears that there is a general tendency for π-bonded cyclic hydrocarbons to eliminate H_2. In both the mass spectra of $(h^4\text{-}C_6H_8)Fe(CO)_3$[86] and $C_7H_8W(CO)_3$,[83] the tendency for the carbonyl-free ions $C_6H_8Fe^+$ and $C_7H_8W^+$ to undergo dehydrogenation producing $C_6H_6Fe^+$ and $C_7H_6W^+$ has been noted. It is likely that the elimination of H_2 is facilitated in particular if it involves the formation of a 6-π-electron system. A likely, but nevertheless speculative, species that may be formed with a loss of

TABLE VII

RELATIVE INTENSITIES OF IMPORTANT FRAGMENTS IN THE MASS SPECTRA OF $C_7H_8Cr(CO)_2L$ [L = CO, $P(OC_6H_5)_3$, $P(C_6H_5)_3$, $P(C_6H_5)(CH_3)_2$, $As(C_6H_5)_3$] AND $(C_7H_7Bu^t)Mo(CO)_2P(C_6H_5)_3$ AND $(C_7H_7Me)Mo(CO)_2P(C_6H_5)_2CH_3$

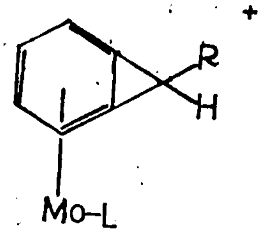
	$C_7H_8Mo(CO)_2L$				
Fragment	L = CO	L = $P(OPh)_3$	L = PPh_3	L = $PPhMe_2$	L = $AsPh_3$
$C_7H_8Mo(CO)_2L^+$	40	14	5	23	2
$C_7H_8Mo(CO)L^+$	18	7	2	7	.5
$C_7H_8MoL^+$	15		3	7	5
$C_7H_6MoL^+$		68	35	100	2
$C_7H_4MoL^+$			3		
$C_7H_8Mo^+$	100	3			8
$C_7H_6Mo^+$	45				
$C_7H_8^+$	24	3	1	22	12
$C_7H_7^+$	39	24	5	43	29
$C_7H_6^+$		67	11	2	
L^+		45	100	21	35
$(L-Ph)^+$			12		100
$(L-OPh)^+$		100			
$(L-Me)^+$				16	

TABLE VII (continued)

$(C_7H_7Bu^t)Mo(CO)_2PPh_3$		$(C_7H_7Me)Mo(CO)_2PPh_2Me$	
Fragment	Rel. int.	Fragment	Rel. int.
$(C_7H_7Bu^t)Mo(CO)_2PPh_3^+$	6	$(C_7H_7Me)Mo(CO)_2PPh_2Me^+$	16
$(C_7H_7Bu^t)Mo(CO)PPh_3^+$	~ 0	$(C_7H_7Me)Mo(CO)PPh_2Me^+$	5
$(C_7H_7Bu^t)MoPPh_3^+$	~ 0	$(C_7H_7Me)MoPPh_2Me^+$	4
$C_7H_7Mo(CO)_2PPh_3^+$	22	$(C_7H_5Me)MoPPh_2Me^+$	100
$(C_7H_5Bu^t)MoPPh_3^+$	20		
$C_7H_7Mo(CO)PPh_3^+$	8		
$C_7H_7MoPPh_3^+$	100	$C_7H_8^+$	~ 0
$C_7H_7^+$	55	$C_7H_7^+$	37
		$C_7H_6^+$	~ 0
PPh_3^+	65	PPh_2Me^+	48
$P(C_6H_4)_2^+$	30	PPh_2^+	19

H_2 is shown in 40.

$$(C_7H_7R)Mo(CO)_2L^+ \xrightarrow{-2CO} (C_7H_7R)MoL^+ \xrightarrow{-H2}$$



40

It is interesting to note that the methyl substituted compounds (R = Me, L = P(OPh)$_3$, PPh$_2$Me) showed no CH_3 loss. In contrast $(C_7H_7Bu^t)Mo(CO)_2PPh_3$ showed prominent peaks due to loss of C_4H_9 and the base peak in the spectrum corresponded to $C_7H_7MoPPh_3^+$. Simultaneous loss of 58(H_2 + 2CO) and 57(C_4H_9) units was also observed.

The ions $C_7H_8Mo^+$ and Mo–L$^+$ were either not observed or of weak intensity. By contrast $C_7H_8Mo^+$ forms the base peak in the spectrum of $C_7H_8Mo(CO)_3$. Also, Cr–L$^+$ is prominent in the spectra of $C_7H_8Cr(CO)_2L$ (L = P(OPh)$_3$ and PPh$_3$).[62]

Free cycloheptatriene loses an H atom on electron impact to form the very stable tropylium ion, $C_7H_7^+$, whereas this tendency is not shown by the π-bonded C_7H_8; peaks corresponding to both $C_7H_8^+$ and $C_7H_7^+$ as well as $C_7H_6^+$ are observed.

In connection with the complex ir spectra displayed by the triphenylphosphite derivatives, the exact mass of the parent ion in the mass spectrum of $(C_7H_7Me)Mo(CO)_2P(OPh)_3$ was measured at 570.0495. The calculated value, using the ^{98}Mo isotope, is 570.0490.

EXPERIMENTAL

Melting points, microanalyses, infrared and proton nmr spectra were obtained as previously described. Melting points and microanalytical results are given in Table VII; infrared carbonyl stretching bands are tabulated in Table IV; the ^{1}H nmr results are summarized in Table V.

Energy factored force field vibrational analyses were carried out using the MOLVIBS program written by Dr. R. S. Gay.[87] The program, based on the work of Schactschneider and Snyder[88] refines force constants and calculates frequencies for a group of isotopically substituted molecules, given an input set of frequencies. Results are included in Table IV.

Carbon-13 nmr spectra were recorded on a Bruker HFX-10 operating at 22.6 MHz and a Varian HLFT operating at 22.15 MHz and using the pulse Fourier transform technique. The number of scans was usually 4k and the spectra were proton decoupled. Results are given in Table VI.

Mass spectra were obtained by electron impact (70 eV), with direct probe, using Associated Electronics Industries MS-2 or MS-9 instruments. Mass spectra were interpreted with the aid of a computer program which calculated exact masses and isotopic combination patterns.

TABLE VIII

ANALYTICAL DATA, COLORS, MELTING POINTS, AND YIELDS FOR THE GROUP V DERIVATIVES OF CYCLOHEPTATRIENETRICARBONYLMOLYBDENUM

Compound	% Yield	Color	M.P. (°C)	Calcd. % C	Calcd. % H	Found % C	Found % H
$C_7H_8Mo(CO)_2P(OPh)_3$[a]	71	orange-red	190	58.50	4.18	58.91	3.63
$(C_7H_7Me)Mo(CO)_2P(OPh)_3 \cdot CH_2Cl_2$	82	red	72-73	53.31	4.16	53.13	3.95
$C_7H_8Mo(CO)_2PPh_3$	70	red	177-178	64.04	4.58	64.59	4.96
$(C_7H_7Me)Mo(CO)_2PPh_3$	85	brown-red	175-178	64.62	4.84	63.62	4.38
$(C_7H_7Bu^t)Mo(CO)_2PPh_3$	48	orange-red	155-157	66.19	5.55	66.06	5.42
$C_7H_8Mo(CO)_2PPh_2Me$	65	deep red	116-120	59.60	4.55	58.79	4.86
$(C_7H_7Me)Mo(CO)_2PPh_2Me$	68	red	120	60.27	5.06	59.58	5.21
$C_7H_8Mo(CO)_2PPhMe_2$	64	red-orange	117	53.42	4.90	53.04	4.79
$C_7H_8Mo(CO)_2AsPh_3$	72	orange	~172 dec.	58.93	4.21	58.40	4.10
$C_7H_8Mo(CO)_2SbPh_3$	74	deep red	150-151 dec.	54.31	3.88	54.21	3.81

[a] Calcd: Mo = 17.30; O = 14.43; P = 5.59; Mol. Wt. = 554.
Found: Mo = 17.58; O = 14.34; P = 5.48; Mol. Wt. = 562. (Alfred Bernhardt, Micro-Analytisches Laboratorium, West Germany).

This program, based on the algorithm described by Carrick and Glocking,[89] was written in this department by Drs. E. H. Brooks and R. S. Gay.

A least squares computer program, developed by Dr. A. S. Foust in this department, fits the computed patterns with observed peak heights and calculates the ratio of the species which give rise to the observed isotopic pattern.

The important fragments observed in the mass spectra are summarized in Table VII.

Sodium borohydride was purchased from the American Drug and Chemical Co. and Fisher Scientific Co. Alkyllithium reagents were purchased from the Ventron Corp.; Florisil (Fisher 100-200 mesh) was used in chromatography columns.

Two methods were found convenient for the reduction of the cycloheptatrienyl salts (prepared in chapter II) to the neutral cycloheptatriene derivatives. The first, using sodium borohydride in a heterogeneous water-benzene mixture, is a modification of the method used by Pauson[57] for the conversion of $[C_7H_7Cr(CO)_3]^+ClO_4^-$ to $C_7H_8Cr(CO)_3$. The second utilizes THF or ether as solvent and either sodium borohydride or alkyllithium reagents as nucleophiles to give cycloheptatriene and alkyl substituted cycloheptatriene derivatives.

Preparation of π-cycloheptatrienedicarbonyl(triphenylphosphine)molybdenum, π-$C_7H_8Mo(CO)_2PPh_3$.

Method A

The compound $[C_7H_7Mo(CO)_2PPh_3]^+PF_6^-$ (2.2 g, 3.4 mmol) was placed in a benzene-water (300-100 ml) mixture, containing a few drops of acetone to allow better mixing between the phases. Excess sodium borohydride (5 - 8 g) was added in small portions and the mixture was stirred vigorously for three hours. The benzene layer acquired a deep red coloration as the product was formed. The reaction mixture was then transferred to a seperatory funnel and the water layer discarded. The benzene layer was washed with several portions of water and then placed over anhydrous magnesium sulphate to dry overnight. The solution was filtered and the solvent removed on a rotary evaporator using water aspiration. Recrystallization from dichloromethane-pentane afforded 1.1 g (63% yield) of the red crystals.

The $P(OPh)_3$, PPh_2Me, $PPhMe_2$ derivatives were prepared similarly with the exception that they were recrystallized from hot skelly 'B'.

Method B

To a magnetically stirred THF solution of $[C_7H_7Mo(CO)_2PPh_3]^+PF_6^-$ (1.1 g, 1.7 mmol) excess sodium borohydride was added in small portions over a period of 1 hr. The solution was filtered and the solvent removed on a rotary evaporator. Chromatography on Florisil, using dichloromethane as solvent and eluent, was followed by recrystallization from dichloromethane-heptane to give .6 g (70% yield) of product.

The $AsPh_3$ and $SbPh_3$ derivatives were prepared similarly with the exception that they were recrystallized from hot skelly 'B'.

Preparation of π-7-methylcycloheptatrienedicarbonyl-(triphenylphosphite)molybdenum, $(\pi\text{-}C_7H_7Me)Mo(CO)_2P(OPh)_3$

To a suspension of $[C_7H_7Mo(CO)_2P(OPh)_3]^+PF_6^-$ (0.75 g, 1.1 mmol) in 60 ml of ether, 1.5 M methyllithium in ether (0.9 ml, 1.3 mmol) was added. After stirring for one hour the deep-red reaction mixture was filtered and the ether solvent removed on a rotary evaporator. The product was extracted with 50 ml hot skelly 'B' and crystallized on cooling to -20°. Recrystallization from dichloromethane afforded red plate like crystals; 0.5 g, 82% yield.

Preparation of π-7-methylcycloheptatrienedicarbonyl-(diphenylmethylphosphine)molybdenum, $(\pi\text{-}C_7H_7Me)Mo(CO)_2PPh_2Me$

To a solution of $[C_7H_7Mo(CO)_2PPh_2Me]^+PF_6^-$ (1.7 g, 2.9 mmol) in 20 ml tetrahydrofuran, 2 ml of 1.5 M methyllithium in ether was added slowly and the solution stirred for 1 hr. The solvent was removed under reduced pressure and the residue extracted with dichloromethane and filtered.

The solution was concentrated and chromatographed on Florisil, eluting as a single red band in dichloromethane. Recrystallization from hot skelly 'B' afforded 6.9 g (68% yield) of product.

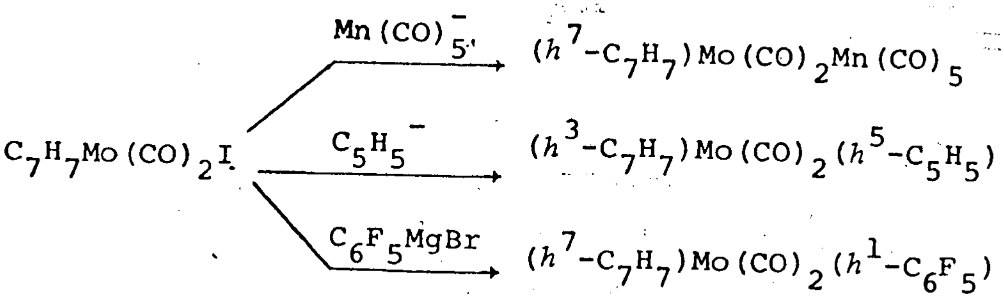
The compounds (π-$C_7H_7Bu^t$)$Mo(CO)_2PPh_3$ and (π-C_7H_7Me)$Mo(CO)_2PPh_3$ were prepared similarly. The latter was only slightly soluble in dichloromethane and was purified by washing with dichloromethane and THF.

CHAPTER IV

CYCLOHEPTATRIENYLDICARBONYLMOLYBDENUM DERIVATIVES OF THE GROUP IV ELEMENTS

INTRODUCTION

Cycloheptatrienyliododicarbonylmolybdenum reacts with anions such as $Mn(CO)_5^-$,[90] $C_5H_5^-$,[90] and C_6F_5MgBr[91] with the displacement of the iodo group



IV-1

IV-2

IV-3

The X-ray structure of $C_7H_7Mo(CO)_2C_6F_5$ has been determined[92] and is remarkably similar to that of the $[C_7H_7Mo(CO)_3]^+$ cation.

The above compounds together with the phosphite and phosphine substituted compounds, discussed in the introduction to Chapter II, are the only reported derivatives of $C_7H_7Mo(CO)_2I$. No previous attempt has been made to prepare derivatives of the group IV elements. It was with this end in view that the preparation of some cycloheptatrienyldicarbonylmolybdenum derivatives of the group IV elements was undertaken.

RESULTS AND DISCUSSION

Synthetic procedures

Trichlorotin and trichlorogermanium derivatives were prepared by the direct reaction of cycloheptatrienylchlorodicarbonylmolybdenum with $SnCl_2$ or $HGeCl_3$ in dichloromethane solvent:

$$C_7H_7Mo(CO)_2Cl + SnCl_2 \xrightarrow{40°} C_7H_7Mo(CO)_2SnCl_3 \qquad IV\text{-}4$$

$$C_7H_7Mo(CO)_2Cl + HGeCl_3 \xrightarrow{25°} C_7H_7Mo(CO)_2GeCl_3 + HCl \qquad IV\text{-}5$$

Reactions of tin(II) and germanium(II) halides with a variety of transition metal halides, classified as insertion reactions, have been widely investigated and often provide convenient synthesis of compounds containing a transition metal bound to a main group IV element.[93,94] In many chemical reactions $HGeCl_3$ is considered to be a source of $GeCl_2$.

The mechanism of these reactions is not entirely clear but it has been suggested, for $C_5H_5Fe(CO)_2SnCl_3$, that initially $SnCl_2$ is co-ordinatively bonded to the transition metal, and that intramolecular migration of the halogen from the transition metal to tin occurs.[95]

Trichlorosilane reacted with $C_7H_7Mo(CO)_2Cl$ only in the presence of triethylamine using acetonitrile as solvent

$$C_7H_7Mo(CO)_2Cl + HSiCl_3 + Et_3N \xrightarrow{25°} C_7H_7Mo(CO)_2SiCl_3 + Et_3NH^+Cl^- \qquad IV-6$$

Benkeser et. al.[96] in a study of $HSiCl_3$-amine system in acetonitrile have shown that the trichlorosilyl anion, $SiCl_3^-$, is present, and that the following equilibrium lies far to the right:

$$(n\text{-}Pr)_3N + HSiCl_3 \rightleftarrows (n\text{-}Pr)_3NH^+ + SiCl_3^- \qquad IV-7$$

This anion is no doubt the reactive species in the formation of the trichlorosilyl derivative.

A trifluorogermanium derivative was prepared by fluorination of the trichlorogermanium compound as shown:

$$C_7H_7Mo(CO)_2GeCl_3 + 3AgBF_4 \longrightarrow C_7H_7Mo(CO)_2GeF_3 + 3AgCl + 3BF_3 \qquad IV-8$$

The use of silver tetrafluoroborate for the synthesis of fluoro-group IV metal organotransition metal compounds was first described by Marks and Seyam.[97]

The anion, $[C_7H_7Mo(CO)_2]^-$, was prepared by the reduction of $C_7H_7Mo(CO)_2Cl$ using sodium amalgam. A solution of $C_7H_7Mo(CO)_2Cl$ in THF was stirred with excess sodium amalgam for about 1 hr. At the end of this period the solution had lost its original green color and became brown. The progress of the reaction was followed by the ir spectrum; the bands at 2023 and 1975 cm^{-1} due to the starting material disappeared and new bands at 1926 and 1857 cm^{-1} emerged.

It was hoped that additional group IV derivatives could be prepared by treatment of this anion with a stoichiometric amount of organometallic [illegible]es. Only triphenylchloro-germane and -tin reacted [illegible] this way:

$$Na^+[C_7H_7Mo(CO)_2]^- + Ph_3M'Cl \xrightarrow[THF]{} C_7H_7Mo(CO)_2M'Ph_3 \qquad \text{IV-9}$$

The progress of the reaction could again be followed by the ir spectra, and solutions were stirred until the bands due to the anion had disappeared.

Triphenylchlorosilane and trimethylchlorotin did not react even after prolonged stirring at reflux. The failure of the $[C_7H_7Mo(CO)_2]^-$ anion to react has not been confined to this study. King and Bisnette[89] noted that the sodium amalgam reduction of $C_7H_7Mo(CO)_2I$ followed by methyl iodide treatment failed to give the desired $C_7H_7Mo(CO)_2CH_3$. Nor is this anion unique in its lack of reactivity. Thus $[C_3F_7Fe(CO)_4]^-$ fails to react even with Ph_3SnCl.[98]

Sasse and Ziegler[99] have recently reported the formation of $C_7H_7Mo(CO)_2$-$SnPh_2Cl$ and -$SnPhCl_2$ from the reverse salt reaction of $C_7H_7Mo(CO)_2Br$ and $LiSnPh_3$. No preparative detail for this peculiar reaction has been given, although the structures have been determined.

In addition, the authors refer to the preparation of Ph_3Sn, Cl_3Sn and Br_3Sn derivatives in a forthcoming publication.

Physical and spectroscopic properties

The six derivatives prepared in this chapter range in color from brown to red. They are insoluble in hydrocarbon solvents, ether and only slightly soluble in benzene. With one exception, the compounds are very soluble in dichloromethane, acetonitrile, and acetone. The trichlorotin derivative is only sparingly soluble in these solvents. In general, the compounds can be handled in air for short periods, but are gradually oxidized on long exposure.

All compounds were characterized by their ir, nmr and mass spectra. The ir spectra showed the expected two bands in the carbonyl region and the ^1H nmr spectra confirmed the presence of the cycloheptatrienyl group.

The molecular formulae of the group IV compounds was confirmed by their mass spectra. The molecular ions were observed for all compounds in their electron impact (ei) mass spectra except for the trichlorotin derivative, whose molecular ion was observed only in the methane chemical ionization (ci) spectrum. The ei spectrum for the $SnCl_3$ derivative did not show a parent peak but peaks due to loss of the two carbonyls, chlorine, dichlorotin, and tropilium from the parent were observed in low abundance.

Extraneous peaks, identified by computer fitting of the observed patterns, due to $C_{15}H_{14}O_2Cl_3Mo_2^+$ (m/e 525) and $C_{14}H_{14}Cl_3Mo_2^+$ (m/e 481) were observed in the ei mass spectra of both the trichloro-germanium and -tin but not for trichlorosilicon. The pattern centred at m/e 481 was also observed in the mass spectrum of $C_7H_7Mo(CO)_2Cl$. It is not clear if the extraneous peaks are due to the presence of an impurity in the starting material or formed in the mass spectrum.

The results of the ei mass spectra are summarized in Table IX which lists the main fragments. The ions in the mass spectrum were readily identified by comparison of the calculated and observed patterns. They are shown in Figure 15 for some of the complexes.

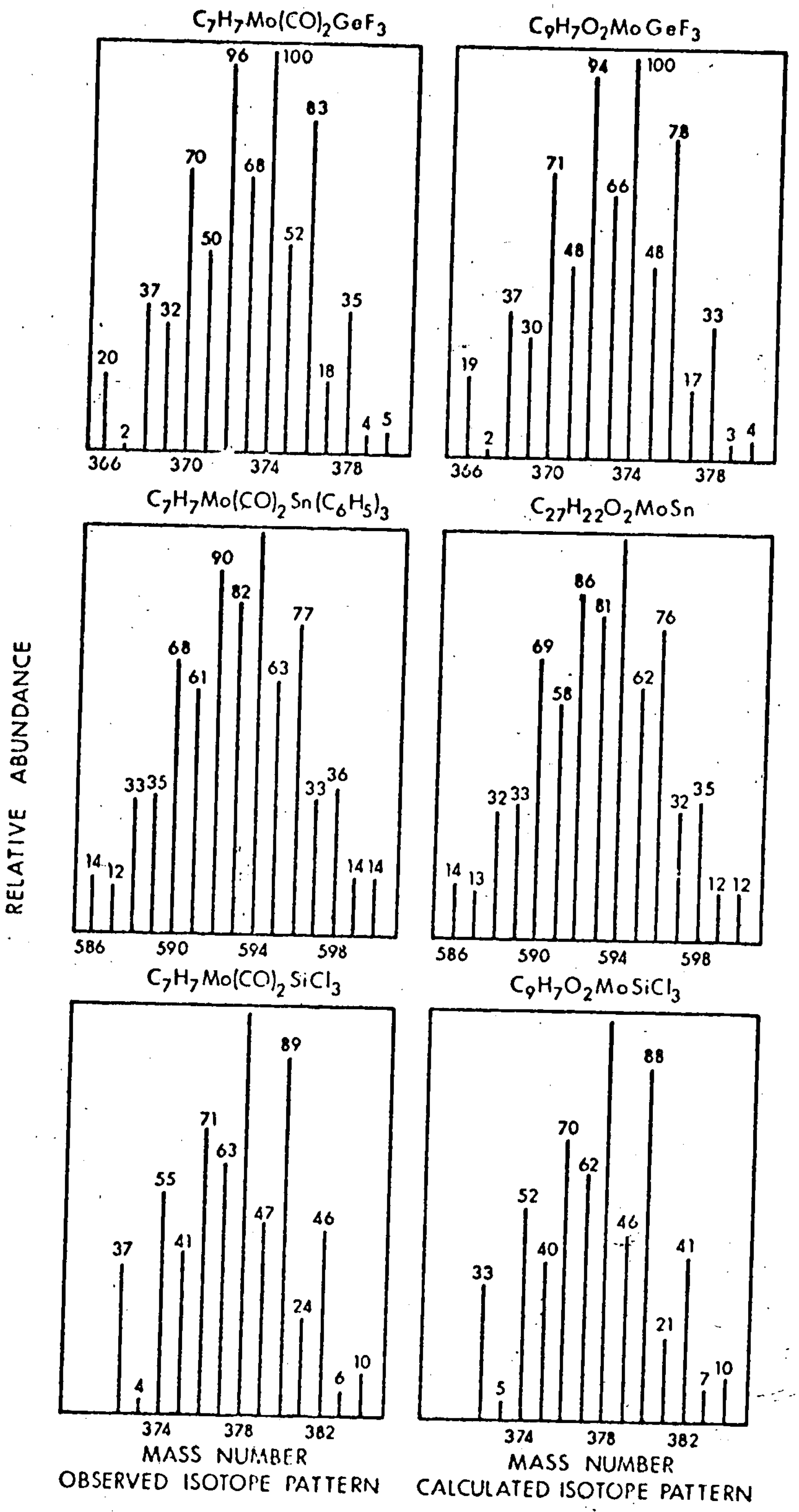


Figure 15. Calculated and observed mass spectral isotope patterns.

TABLE IX

RELATIVE INTENSITIES OF IMPORTANT FRAGMENTS IN THE MASS SPECTRA OF $C_7H_7Mo(CO)_2M'X_3$ ($M'X_3$ = $SiCl_3$, $GeCl_3$, GeF_3, $SnCl_{\beta}$, $Ge(C_6H_5)_3$ and $Sn(C_6H_5)_3$

Fragment	$M'X_3=SiCl_3$ Rel. Int.	$M'X_3=GeCl_3$ Rel. Int.	$M'X_3=GeF_3$ Rel. Int.	$M'X_3=SnCl_3$ Rel. Int.	$M'X_3=GePh_3$ Rel. Int.	$M'X_3=SnPh_3$ Rel. Int.
$C_7H_7Mo(CO)_2M'X_3^+$	2.2	1.6	8.5	~0	3.5	7.8
$C_7H_7Mo(CO)M'X_3^+$	1.4	0.6	~0	.1	8.5	2.7
$C_7H_7MoM'X_3^+$	3.3	2.2	2.7	.3	54.0	21.5
$C_7H_7Mo(CO)_2M'X_2^+$	1.3	3.9	1.5	-	-	3.0
$C_7H_7Mo(CO)_2M'X^+$	1.6	-	-	.4	-	-
$C_7H_7MoM'X_2^+$	-	-	.3	-	6.5	20.0
$C_7H_7Mo(CO)X^+$	-	7.4	5.6	3.5	-	-
$C_7H_7MoX^+$	24.5	100	-	94.0	100.0	50.0
$C_5H_5MoX^+$	8.0	18.7	32.6	20.0	-	-
$Mo(CO)_2M'X_3^+$	-	0.6	-	-	-	-
$Mo(CO)_2M'X_2^+$	-	1.4	-	2.4	-	-
$MoM'X_2^+$	-	-	100.0	-	-	-

TABLE IX (continued)

Fragment	$M'X_3=SiCl_3$ Rel. Int.	$M'X_3=GeCl_3$ Rel. Int.	$M'X_3=GeF_3$ Rel. Int.	$M'X_3=SnCl_3$ Rel. Int.	$M'X_3=GePh_3$ Rel. Int.	$M'X_3=SnPh_3$ Rel. Int.
$M'X_3^+$	–	–	–	–	70.0	100
$M'X_2^+$	–	24.8	–	15.3	16.0	37.5
$M'X^+$	–	32.0	–	20.0	36.0	38.5
$C_7H_7^+$	100	72.2	33.6	100.0	26.0	2.0

EXPERIMENTAL

Melting points, microanalyses, infrared and proton nmr spectra were obtained as previously described. Melting points and microanalytical results are given in Table X; infrared carbonyl bands and the ^1H nmr results are summarized in Table XI.

Electron impact mass spectra were measured and interpreted as previously described. The chemical ionization mass spectrum of $C_7H_7Mo(CO)_2SnCl_3$ was recorded on an AEI MS-12 instrument equipped with a dual ei/ci source.

Reaction work-up procedures were performed under a nitrogen atmosphere by use of Schlenk apparatus.

Aluminum oxide purchased from Baker Chemical Co. was used for column chromatography. All other reagents were obtained from commercial sources and were used without further purification.

Dichloromethane was distilled from P_2O_5 and tetrahydrofuran from CaH_2 prior to use. In every other case reagent grade solvents were used.

Attempts at preparing $C_7H_7Mo(CO)_2Cl$ by analogy to the preparation of $C_7H_7Mo(CO)_2I$ failed. It was discovered that only in the presence of small amount of water does the reaction proceed to give the desired product. Thus treatment of $[C_7H_7Mo(CO)_3]^+PF_6^-$ with sodium chloride or tetraethylammonium chloride in reagent acetone failed,

TABLE X

ANALYTICAL DATA, COLORS, MELTING POINTS AND YIELDS FOR THE GROUP IV DERIVATIVES

Compound	% Yield	Color	M.P. (°C)	Calcd. %			Found %		
				C	H	Cl	C	H	Cl
$C_7H_7Mo(CO)_2Cl$	82	green	150-160 dec.	38.88	2.53	12.73	38.57	3.07	13.38
$C_7H_7Mo(CO)_2SiCl_3$	35	red-brown	160 dec.	28.63	1.87	28.17	29.10	2.60	28.56
$C_7H_7Mo(CO)_2GeCl_3$	72	red	166-170	25.61	1.67	25.20	25.69	1.95	25.64
$C_7H_7Mo(CO)_2GeF_3$	75	pink	~200 dec.	29.08	1.90	-	28.94	1.73	-
$C_7H_7Mo(CO)_2SnCl_3$	68	red-brown	182-184 dec.	23.09	1.51	22.72	23.06	1.56	22.69
$C_7H_7Mo(CO)_2GePh_3$	32	deep red	202-205	59.29	4.05	-	59.19	4.20	-
$C_7H_7Mo(CO)_2SnPh_3$	30	red	211-214	54.68	3.74	-	54.50	3.99	-

TABLE XI

INFRARED CARBONYL AND ^{1}H NMR DATA FOR THE GROUP IV DERIVATIVES

Compound	Carbonyl Stretching Frequencies (cm^{-1})^a		Chemical Shifts $\tau_{C_7H_7}$ ^{b}
$C_7H_7Mo(CO)_2Cl$	2023(10.0)	1975(7.7)	4.52
$C_7H_7Mo(CO)_2SiCl_3$	2011(10.0)	1963(7.7)	4.48
$C_7H_7Mo(CO)_2GeCl_3$	2027(10.0)	1985(7.9)	4.42
$C_7H_7Mo(CO)_2GeF_3$	2028(10.0)	1984(8.0)	4.00^d
$C_7H_7Mo(CO)_2SnCl_3$	2026(10.0)	1983(7.0)	4.62^c
$C_7H_7Mo(CO)_2GePh_3$	1980(10.0)	1923(8.3)	4.89^{e,f}
$C_7H_7Mo(CO)_2SnPh_3$	1973(10.0)	1919(9.1)	4.65^e

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[a] Dichloromethane solutions; figures in parenthesis are relative band heights.

[b] Chloroform-d$_1$ solutions relative to TMS as internal standard, except as noted.

[c] Pyridine-d$_5$.

[d] ^{19}F nmr, singlet -4586 Hz from CFCl$_3$.

[e] Phenyl region complex multiplet.

[f] $J(^{117,119}Sn-C_7H_7)$ = 5Hz.

whereas tetraphenylarsonium chloride, which contains water of hydration, reacted to give the chloride. The preparation of $C_7H_7Mo(CO)_2Cl$ from sodium chloride is included in the synthetic descriptions which follow.

Preparation of π-cycloheptatrienyl(chloro)dicarbonylmolybdenum, π-$C_7H_7Mo(CO)_2Cl$.

The compound $[C_7H_7Mo(CO)_3]^+PF_6^-$ (4.2 g, 10.1 mmol) was stirred with a large excess of sodium chloride in 100 ml of reagent acetone containing 5 ml of water. The solution turned deep green immediately with vigorous gas evolution. The reaction mixture was stirred for at least 4 hr to insure complete reaction. The solvent was then removed on a water aspirator vacuum. A black residue remained, which was washed with water to remove sodium hexafluorophosphate and air dried. The residue was extracted with dichloromethane, filtered and the solvent removed on a water aspirator vacuum. Deep green crystals remain, and these were washed on a filter with ether and pentane and sucked dry to give 2.3 g (82% yield).

Preparation of π-cycloheptatrienyl(trichlorosilicon)-dicarbonylmolybdenum, π-$C_7H_7Mo(CO)_2SiCl_3$.

To a solution containing $C_7H_7Mo(CO)_2Cl$ (1.2 g, 4.3 mmol) and $HSiCl_3$ (2.5 g, 18.5 mmol) in 30 ml acetonitrile at room temperature triethylamine (3.0 g, 29.7

mmol) was added dropwise. The initial green color of the solution turned red after a few minutes and stirring was continued for 1 hr. The solution was filtered through Celite, degassed just prior to use, and the solvent was removed under reduced pressure. After pumping in vacuum for 24 hr the residue was extracted with 20 ml dichloromethane, filtered and *n*-heptane was added dropwise until the solution became cloudy. This was cooled at -78° affording red-brown crystals; 0.5 g, 35% yield. The crystals darkened on exposure to air and/or light.

Preparation of π-cycloheptatrienyl(trichlorogermanium)-dicarbonylmolybdenum, π-$C_7H_7Mo(CO)_2GeCl_3$.

Trichlorogermane (1.8 g, 10.0 mmol) was added to a magnetically stirred dichloromethane solution of $C_7H_7Mo(CO)_2Cl$ (2.0 g, 7.2 mmol). The solution turned deep red immediately and a red precipitate formed. After stirring for 20 min the reaction mixture was filtered, the precipitate washed with ether and sucked dry. The filtrate was cooled at -20° overnight, affording more of the red crystalline product. The two batches of product were combined and recrystallized from dichloromethane to give 2.2 g (72% yield).

Preparation of π-cycloheptatrienyl(trifluorogermanium)-dicarbonylmolybdenum, π-$C_7H_7Mo(CO)_2GeF_3$.

Solid silver tetrafluoroborate (2.3 g, 12.0 mmol) was added to a 25 ml acetonitrile solution of $C_7H_7Mo(CO)_2GeCl_3$ (1.5 g, 3.6 mmol). A white precipitate of AgCl immediately formed, no visible color change took place. After stirring for a short period, 15 ml of ether was added, the reaction mixture filtered and concentrated under reduced pressure. Addition of more ether precipitated an orange-red solid which was recrystallized from dichloromethane-ether to yield 1.0 g (75% yield) of the analytical sample.

Preparation of π-cycloheptatrienyl(trichlorotin)dicarbonylmolybdenum, π-$C_7H_7Mo(CO)_2SnCl_3$.

Anhydrous $SnCl_2$ (2.3 g, 12.0 mmol) and $C_7H_7Mo(CO)_2Cl$ (2.8 g, 10.0 mmol) were refluxed in dichloromethane for 12 hr. The reaction mixture turned brown and a brown precipitate was formed. This was filtered, washed with dichloromethane and sucked dry. Recrystallization from hot acetonitrile gave red-brown plate-like crystals of product; 3.2 g, 68% yield.

Preparation of π-cycloheptatrienyl(triphenyltin)dicarbonylmolybdenum, π-$C_7H_7Mo(CO)_2SnPh_3$.

The reaction was conducted in a 250 ml three-necked flask with a stopcock fused to the bottom. After filling with nitrogen, the flask was charged with 10 ml of mercury and 1.0 g of sodium metal was added in small portions with stirring. After all the sodium had reacted, $C_7H_7Mo(CO)_2Cl$ (2.0 g, 7.2 mmol) and 100 ml of tetrahydrofuran were added. The progress of the reaction was followed by ir spectroscopy, and the disappearance of the bands at 2023 and 1974 cm^{-1} and emergence of bands at 1926 and 1857 cm^{-1}. When the formation of the anion was complete, excess amalgam was removed through the stopcock at the bottom. Then, Ph_3SnCl (2.6 g, 7.7 mmol) in 50 ml tetrahydrofuran was added and the mixture stirred overnight. The solution was then filtered through celite and the solvent removed under reduced pressure leaving a muddy brown solid. This was extracted with dichloromethane, filtered, concentrated and chromatographed on alumina, eluting as a single red band. Recrystallization from dichloromethane-skelly 'B' afforded 1.3 g (30% yield).

The Ph_3Ge analogue was prepared in the same manner.

CHAPTER V

MAIN GROUP IV ANIONIC CARBONYL COMPLEXES OF CHROMIUM, MOLYBDENUM, TUNGSTEN, AND IRON

INTRODUCTION

The formation of metal-metal bonds between the group IV elements and transition metals has been a subject of widespread interest as evidenced by the numerous reviews in this field.[94,100,101]

Several synthetic routes have been developed for the synthesis of these compounds and are briefly outlined below.

a) Halide displacement by metal carbonyl anions

This method has been applied extensively where metal carbonyl anions are easily prepared.

$$Na^+[C_5H_5Fe(CO)_2]^- + Me_3SiCl \rightarrow C_5H_5Fe(CO)_2SiMe_3 + NaCl \quad ^{102} \qquad V\text{-}1$$

$$2Na^+[Re(CO)_5]^- + Ph_2SnCl_2 \rightarrow Ph_2Sn[Re(CO)_5]_2 + 2NaCl \quad ^{103} \qquad V\text{-}2$$

$$Na_2^+[Fe(CO)_4]^{2-} + 2Me_3GeCl \rightarrow (Me_3Ge)_2Fe(CO)_4 + 2NaCl \quad ^{104} \qquad V\text{-}3$$

b) Insertion reactions

As discussed in Chapter IV these reactions involve the halides of the group IV elements in the divalent state. Illustrations are given below.

$Mn_2(CO)_{10} + SnCl_2 \rightarrow Cl_2Sn[Mn(CO)_5]_2$ [105] V-4

$HPt(Et_3P)_2Cl + SnCl_2 \rightarrow Cl_3SnHPt(Et_3P)_2$ [106] V-5

c) Oxidative-addition reactions

The reaction involves addition of a group IV molecule to an electronically unsaturated transition metal with subsequent increase in its oxidation number and coordination number by two.

$Ir(CO)(Ph_3P)_2Cl + HSiCl_3 \rightleftarrows Cl_3SiHIr(CO)(PPh_3)_2Cl$ [107]

V-6

d) Oxidative-elimination reactions

The result is similar to that of (c), except that a neutral ligand, such as CO, is ejected in the process.

$C_5H_5Mn(CO)_3 + HSiPh_3 \rightarrow C_5H_5Mn(CO)_2HSiPh_3 + CO$ [108] V-7

$Re_2(CO)_{10} + HSiCl_3 \rightarrow Cl_3SiHRe_2(CO)_9 + CO$ [109] V-8

$Fe(CO)_5 + Sn_2Me_6 \rightarrow (Me_3Sn)_2Fe(CO)_4 + CO$ [110] V-9

e) Other elimination reactions

This refers to the reactions where a group IV metal-transition metal bond is formed with the displacement of a neutral molecule(s).

$Co_2(CO)_8 + 2HSiR_3 \rightarrow 2R_3SiCo(CO)_4 + \underline{H_2}$ 111 V-10

$C_5H_5W(CO)_3H + Me_3SiNMe_2 \rightarrow C_5H_5W(CO)_3SiMe_3 + \underline{Me_2NH}$ 112 V-11

$C_5H_5Mo(CO)_3Cl + (Et_3Ge)_2Hg \rightarrow C_5H_5Mo(CO)_3GeEt_3 + \underline{Hg} + Et_3GeCl$ 113 V-12

f) Reactions of group IV anions

This reaction has been used as the reverse salt elimination [i.e. complementary to (a)] or in displacement of CO by the group IV anion.

$Fe(CO)_5 + LiSiPh_3 \rightarrow Li^+[Ph_3SiFe(CO)_4]^- + CO$ 114 V-13

$(C_5H_5)_2ZrCl_2 + LiSiPh_3 \rightarrow (C_5H_5)_2Zr(SiPh_3)Cl + LiCl$ 115 V-14

$Ph_3PAuCl + LiGePh_3 \rightarrow Ph_3GeAuPPh_3 + LiCl$ 116 V-15

The last two examples resemble somewhat the type of reaction to be discussed in this work.

Recently there has been a renewed interest in the anionic carbonyl complexes of the group VI transition metals.[117-121] The first compounds in this category, the pentacarbonyl halides, were prepared by the reaction of the hexacarbonyls with tetra-alkyl ammonium halide.[122]

$M(CO)_6 + R_4NX \rightarrow [R_4N]^+[M(CO)_5X]^- + CO$ V-16

where X = Cl, Br, I; M = Cr, Mo, W, and R = alkyl group. The isolation of the anions $Cr(CO)_5F^-$ and $W(CO)_5F^-$ has only recently been described.[118]

Other anionic bases such as pseudohalides,[123] alkylacetylides,[124] difluorothiophosphate,[125] trichlorostannate(II),[126] and cyanotrihydroborate[119] are known to react with the group VI carbonyls under thermal or photolytic conditions to give anionic complexes.

More recently an alternative preparative route to certain $[M(CO)_5X]^-$ anions has been developed which utilizes the reaction of the bimetallic anions $[M_2(CO)_{10}]^{2-}$ with mercury(II) and silver(I) derivatives as illustrated in V-17 to V-19:

$$[W_2(CO)_{10}]^{2-} + Hg(CN)_2 \rightarrow 2[W(CO)_5CN]^- + Hg \quad ^{127} \qquad \text{V-17}$$

$$[Cr_2(CO)_{10}]^{2-} + 2AgO_2CR \rightarrow 2[Cr(CO)_5O_2CR]^- + 2Ag \quad ^{128} \qquad \text{V-18}$$

$$[Mo_2(CO)_{10}]^{2-} + Hg(SCF_3)_2 \rightarrow 2[Mo(CO)_5SCF_3]^- + Hg \quad ^{117} \qquad \text{V-19}$$

The only reported anionic complexes of the group VI metals containing a main group IV element are those derived from SnX_3^- (X = Cl, Br, I) and $GeCl_3^-$.[121,126,129] This coupled with a general lack of a group IV-transition metal anionic complex, particularly with alkyl- or aryl-substituents, led us to investigate the synthesis and properties of this class of complexes. This chapter describes the result of these efforts.

RESULTS AND DISCUSSION

Synthesis of Cr, Mo and W derivatives

Ruff[126] found that the photolytic reactions of $GeCl_3^-$ and $SnCl_3^-$ with group VI hexacarbonyls proceed with the displacement of CO:

$$M(CO)_6 + Ph_4AsM'Cl_3 \xrightarrow[CH_2Cl_2]{h\nu} Ph_4As^+[Cl_3M'-M(CO)_5]^- + CO \qquad \text{V-20}$$

where M = Cr, Mo or W, and M' = Sn or Ge.

We found that an alternative and perhaps more convenient route to the group IV metal halide derivatives was by an insertion reaction of $SnCl_2$, $SnBr_2$, and $HGeCl_3$ into the halogen-metal bond of the halopentacarbonyl anions of the group VI metals.

$$[M(CO)_5Cl]^- + SnCl_2(HGeCl_3) \xrightarrow[CH_2Cl_2]{40°} [Cl_3M'-M(CO)_5]^- \qquad \text{V-21}$$

$$[W(CO)_5Br]^- + SnBr_2 \xrightarrow[CH_2Cl_2]{40°} [Br_3SnW(CO)_5]^- \qquad \text{V-22}$$

where M = Cr, Mo, W and M' = Sn, Ge. Reaction was complete within a few minutes as the initial yellow color of the solution disappeared and high yields of products were obtained.

Recently Uhlig and co-workers have intimated that the $[Cl_3SnM(CO)_5]^-$ anions were formed by the same reaction as above; no detail has been given.[129]

The additional anionic complexes of the group VI metals were prepared by the reaction of the organolithium compounds of the group IV elements and the chloropentacarbonyl anions.

$$[M(CO)_5Cl]^- + LiM'R_3 \xrightarrow[THF]{} [R_3M'-M(CO)_5]^- + LiCl \qquad V\text{-}23$$

where M = Cr, Mo, W, and R_3M' = Ph_3Si, $MePh_2Si$, Ph_3Ge, Ph_3Sn, Me_3Sn, Ph_3Pb.

The organolithium compounds triphenylsilyllithium, diphenylmethylsilyllithium, triphenylgermyllithium, triphenyltinlithium and triphenylleadlithium were prepared by the reaction of the various chlorides with lithium in THF. The direct method of preparing triphenylsilyllithium from chlorotriphenylsilane and lithium was first reported by Gilman et. al.[130] This reaction was subsequently applied to other elements of group IV.[131] Hexaphenyldigermane and hexamethylditin have been cleaved by lithium in THF to yield triphenylgermyllithium and trimethyltinlithium. The cleavage of $Ph_3M'-M'Ph_3$ (M = Si, Ge, Sn, or Pb) by lithium in THF has also been well established.[131]

The above organolithium compounds prepared *in situ* were added to THF solutions of the halopentacarbonyl anions. The progress of the reaction was monitored by the disappearance of the A_1^2 carbonyl band (see section on ir spectra) of the starting material in the ir spectrum. In this manner an excess of organolithium compound could be avoided. Reaction took place within a few minutes leading smoothly to the formation of the tetraethylammonium salt of the monosubstituted anions, $Et_4N^+[R_3M'-M(CO)_5]^-$.

To our knowledge this is the first application of the reverse salt elimination reaction involving anionic complexes. At first glance it appears that an attack by, for example, triphenylsilyl ion, Ph_3Si^-, on $[M(CO)_5Cl]^-$ would be unfavorable from an electrostatic point of view. However, not only does the reaction take place, it also proceeds readily and under relatively mild conditions. Considering that the central metal atom of the halopentacarbonyl anions is in a formal oxidation state of zero, substitution of the halo group by another anionic base becomes possible without alteration of the formal charge on the central metal atom. It must also be considered that, for example, Ph_3Si^- ion is not only isoelectronic with the commonly used complexing ligand, Ph_3P, but it also contains free 3d orbitals on Si which can be used for back-bonding with the metal. Furthermore, owing to its negative charge it should be a stronger σ-donor than the phosphine ligand.

Synthesis of Fe derivatives

It seemed useful to extend the reaction of the organolithium group IV compounds to other simple halogenocarbonyl anions. Abel et. al.[132] reported in low yield the preparation of $Et_4N^+[Fe(CO)_4I]^-$ by the following two methods:

$$Fe_3(CO)_{12} + 3Et_4NI \xrightarrow[\text{diglyme}]{60°} 3Et_4N^+[Fe(CO)_4I]^- \qquad \text{V-24}$$

$$Fe(CO)_5 + Et_4NI \xrightarrow[\text{diglyme}]{90°} Et_4N^+[Fe(CO)_4I]^- \qquad \text{V-25}$$

In this laboratory[133] attempts to prepare this compound by the above method afforded a compound which was identified as $Et_4N^+[HFe_3(CO)_{11}]^-$ by comparison of its ir with that of an authentic sample. The ir spectrum and color of the latter was consistent with the reported "$[Fe(CO)_4I]^-$". The formation of the trinuclear anion is not surprising since the above reactions (V-24 and V-25) are somewhat reminiscent of the method of preparation of $[HFe_3(CO)_{11}]^-$ from $Fe(CO)_5$ with a tertiary amine in water.[134,135]

$$3Fe(CO)_5 + R_3N + 2H_2O \rightarrow R_3NH^+[HFe_3(CO)_{11}]^- + 2CO_2 + 2CO + H_2 \qquad \text{V-26}$$

Not unrelated is the base reaction of THF with $Ph_3SiHFe(CO)_4$ to give the trinuclear anion.[136] Moreover, our attempts to obtain $Et_4N^+[Fe(CO)_4Cl]^-$ from Et_4NCl and $Fe(CO)_5$ under photolytic conditions in CH_2Cl_2, consistently yielded $Et_4N^+[HFe_3(CO)_{11}]^-$. Prior to our identification of the product in these reactions, we found that it reacted with $LiSiPh_3$ in THF to give the known $[Ph_3SiFe(CO)_4]^-$ ion.[114,137] This reaction led to the preparation of some anionic derivatives of iron containing group IV elements.

$Et_3NH^+[HFe_3(CO)_{11}]^-$ prepared by the literature method[135] was converted into the Et_4N^+ salt by reaction with Et_4NCl in CH_2Cl_2. The reactions of $Et_4N^+[HFe_3(CO)_{11}]^-$ with $LiSiPh_3$, $LiGePh_3$, and $LiSnPh_3$ were examined in THF and found to yield the mononuclear anions, $[R_3M'Fe(CO)_4]^-$:

$$[HFe_3(CO)_{11}]^- + LiM'R_3 \xrightarrow[THF]{} [R_3M'\text{-}Fe(CO)_4]^- + \ldots \qquad \text{V-27}$$

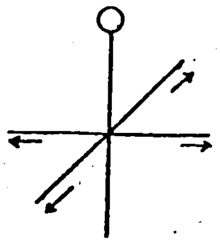
where M' = Si, Ge, and Sn. The reaction again proceeds smoothly under mild conditions with no ir evidence for the formation of other carbonyl species. While the mechanism of the above reaction remains unclear we presume that it may involve attack by the organolithium compound on the unique iron atom containing the four carbonyl groups (see structure by Dahl and Blount[138]) with the ensuing cleavage of the Fe-Fe bonds.

Properties

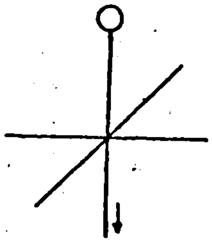
The anionic metal carbonyl derivatives prepared in this work all form colorless crystals. In a few cases they appeared pale yellow due to adsorbed impurities; the yellow color was removed by shaking the crystals in a mixture of water-methanol (1:1). These compounds are readily soluble in polar solvents such as dichloromethane, acetone, and tetrahydrofuran but not in ether or in hydrocarbon solvents. They are all air stable in the solid state for long periods. On dissolving in organic solvents all compounds decompose at varying rates. Most are stable for long periods (days) in solution, however $Et_4N^+[Cl_3SnW(CO)_5]^-$ was found to decompose in THF after a few minutes.

Infrared spectra

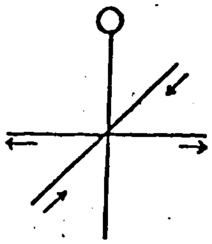
The carbonyl stretching modes of several octahedral pentacarbonyl molecules have been assigned,[11,73,139-142] and may be classified as belonging to the $2A_1 + B_1 + E$ representations in the C_{4V} point group. The $2A_1$ and E vibrations are ir-active while the B_1 is ir-forbidden. The symmetry co-ordinates are conveniently given in terms of the internal bond-stretching vibrations of the molecule as illustrated below.



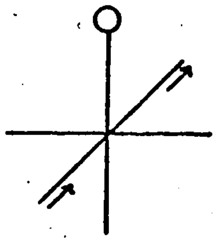
A_1^2



A_1^1



B_1



E

The ir spectra of the Cr, Mo and W pentacarbonyl derivatives prepared in this work were assigned using these well established methods. The results are given in Table XII.

The spectrum of a typical molecule, $Et_4N^+[Ph_3GeMo(CO)_5]^-$, measured in THF is shown in Figure 16. The strong band at 1908 cm^{-1} is due to the E mode, the two A_1 bands are at 2034 cm^{-1} and at 1878 cm^{-1} (on the low energy side of the E band). In addition the B_1 band at 1946 cm^{-1} shows some absorption. Reasons for the activation of the ir-forbidden B_1 mode have been advanced.[141,143] The lower trace shows the spectrum of a more concentrated solution, which allows the B_1 mode to be measured more accurately and the A' of the C_s radial mono-^{13}CO substituted species is seen as a shoulder at 2027 cm^{-1} to the A_1^2 band (see arrow). On standing for a short period in THF solution, the growth of an additional broad band at ca. 1960 cm^{-1} is also observed. This band remains relatively weak even after refluxing in THF overnight and may be attributed to $Mo(CO)_5THF$ [144] species present in the following equilibrium:

$$[R_3M'-M(CO)_5]^- + THF \rightleftharpoons R_3M'^- + M(CO)_5THF \qquad V-28$$

The heterolytic cleavage of transition metal-main group metal covalent bonds by tertiary amines,[145] acetonitrile[146] and dimethylformamide[147] have been observed.

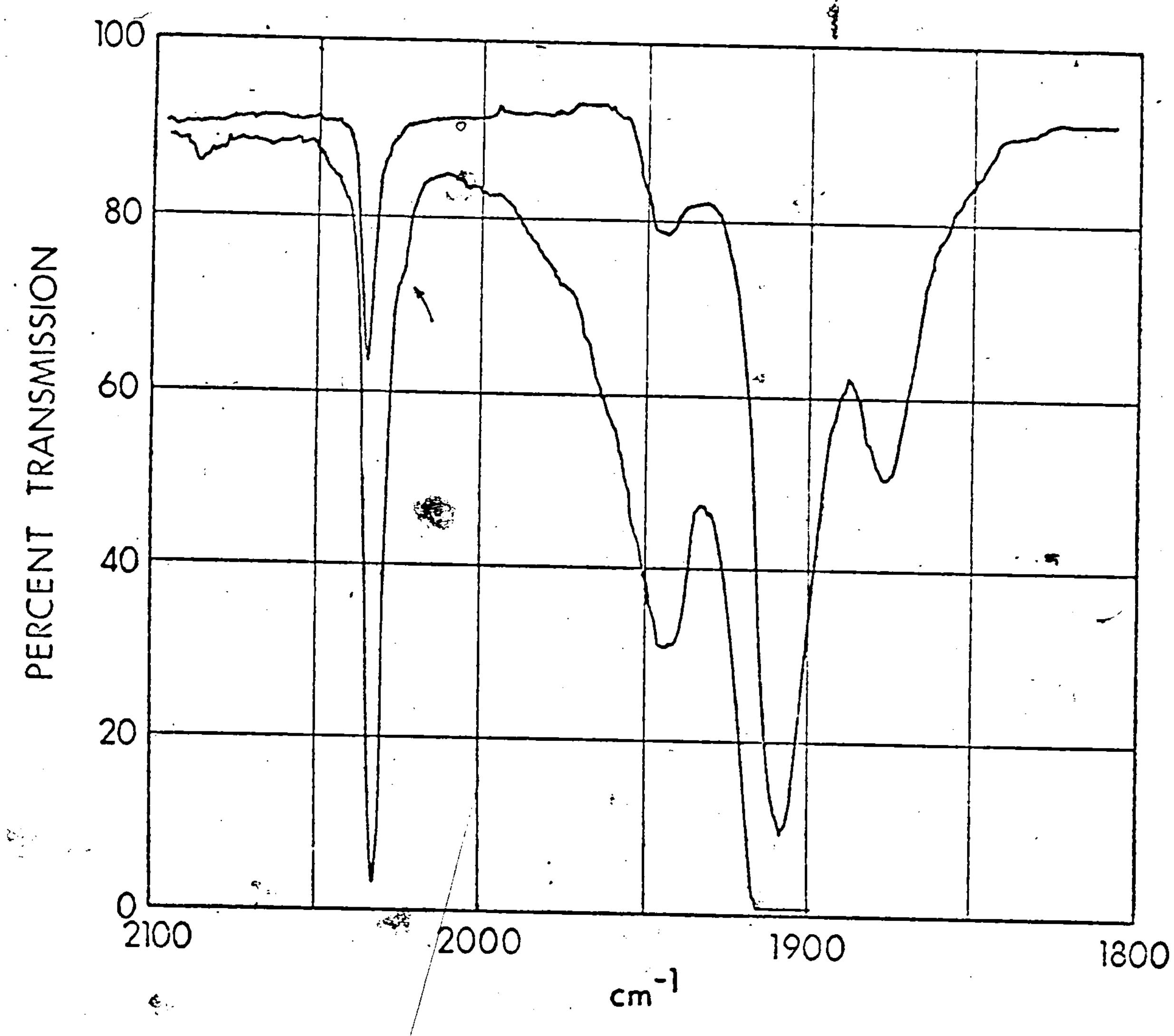


Figure 16. $Et_4N^+[Ph_3GeMo(CO)_5]^-$ in THF.

TABLE XII

CARBONYL STRETCHING FREQUENCIES, ASSIGNMENTS, AND NMR DATA[b-d,f-h] FOR THE ANIONIC COMPLEXES CONTAINING GROUP IV LIGANDS

Compound	Frequencies (cm^{-1})[a] all-^{12}CO molecule				radial-^{13}CO
	A_1^2	A_1^1	B_1	E	A '
$Et_4N^+[Ph_3SiCr(CO)_5]^-$	2014.5	1877	1928	1894	2006
$Et_4N^+[MePh_2SiCr(CO)_5]^-$ [b]	2010.5	1872	1922	1888	2004
$Et_4N^+[Cl_3GeCr(CO)_5]^-$	2059	1930	(1966)	1945	2052
$Et_4N^+[Ph_3GeCr(CO)_5]^-$	2017.5	1872.5	1934	1898	2010
$Et_4N^+[Cl_3SnCr(CO)_5]^-$	2056	(1927)	(1960)	1942	2049
$Et_4N^+[Ph_3SnCr(CO)_5]^-$	2014.5	1877	1930.5	1897	2008
$Et_4N^+[Me_3SnCr(CO)_5]^-$ [c]	2002.5	1867	1913	1844	1995
$Et_4N^+[Ph_3PbCr(CO)_5]^-$	2020	1879	1940	1907	2012
$Et_4N^+[Ph_3SiMo(CO)_5]^-$	2031	1880	1943	1904.5	2023
$Et_4N^+[MePh_2SiMo(CO)_5]^-$ [d]	2026	1876	1936	1899	2019
$Et_4N^+[Cl_3GeMo(CO)_5]^-$	2069	1925		1947	2060

TABLE XII (continued)

Compound	A_1^2	A_1^1	B_1	E	A '
$Et_4N^+[Ph_3GeMo(CO)_5]^-$	2034	1878	1946	1908	2027
$Et_4N^+[Cl_3SnMo(CO)_5]^-$[e]	2068			1938	2060
$Et_4N^+[Ph_3SnMo(CO)_5]^-$	2033	1884	1946	1910	2026
$Et_4N^+[Me_3SnMo(CO)_5]^-$	2021	1871	1930	1896	2015
$Et_4N^+[Ph_3PbMo(CO)_5]^-$	2039	1883.5	1954	1918	2032
$Et_4N^+[Ph_3SiW(CO)_5]^-$	2030.5	1875	1936	1899	2022.5
$Et_4N^+[MePh_2SiW(CO)_5]^-$[g]	2026	1871	1928	1894	2019
$Et_4N^+[Cl_3GeW(CO)_5]^-$	2066.5	1919	(1966)	1938	2059
$Et_4N^+[Ph_3GeW(CO)_5]^-$	2033.5	1873	1939	1902	2027
$Et_4N^+[Br_3SnW(CO)_5]^-$	2065	1915	(1958)	1940.5	2058
$Et_4N^+[Cl_3SnW(CO)_5]^-$	2069	1929	(1985)	1942	2062
$Et_4N^+[Cl_2PhSnW(CO)_5]^-$	2058	1915	(1970)	1930	2051
$Et_4N^+[ClPh_2SnW(CO)_5]^-$	2045	1897		1916	2039
$Et_4N^+[Ph_3SnW(CO)_5]^-$	2032	1878	1939	1903	2024.5
$Et_4N^+[Me_3SnW(CO)_5]^-$[h]	2020.5	1868	1924	1891	2013

TABLE XII (continued)

Compound	A_1^2	A_1^1	B_1	E	A '
$Et_4N^+[Ph_3PbW(CO)_5]^-$	2037.5	1879	1947	1909.5	2031
$Et_4N^+[Ph_3SiFe(CO)_4]^-$	1994	1907		1881,1869 sh	
$Et_4N^+[Ph_3GeFe(CO)_4]^-$	1994	1906		1887,1873 sh	
$Et_4N^+[Ph_3SnFe(CO)_4]^-$	1991.5	1905		1983,1869 sh	
	3A' + A" (C_s)				
$Ph_3GeHFe(CO)_4$ [i]	2096.5	2036	2027	2022	

---

[a] All frequencies measured in THF unless otherwise noted. Bands in parenthesis were too broad to measure accurately.

[b] $\tau(Si-CH_3)$ = 9.25; acetone-d_6 with acetone-d_5 internal standard.

[c] $\tau(Sn-CH_3)$ = 9.96; $J_{(Sn-CH_3)}$ = 37 Hz (^{117}Sn and ^{119}Sn coupling not resolved); acetone-d_6.

[d] $\tau(Si-CH_3)$ = 9.28; $J_{(^{29}Si-CH_3)}$ = 5.2 Hz; CD_3CN with CD_2HCN internal standard.

[e] Ir measured in CH_2Cl_2; compound unstable in THF.

[f] $\tau(Sn-CH_3)$ = 10.0; $J_{(Sn-CH_3)}$ = 33 Hz; acetone-d_6.

[g] $\tau(Si-CH_3)$ = 9.12; $J_{(^{29}Si-CH_3)}$ = 5.4 Hz; CD_3CN.

TABLE XII (continued)

[h] $\tau(\mathrm{Sn\text{-}CH_3}) = 9.90$; $J_{(^{117}\mathrm{Sn\text{-}CH_3})} = 37.0$ Hz, $J_{(^{119}\mathrm{Sn\text{-}CH_3})} = 35.5$ Hz; $\mathrm{CD_3CN}$.

[i] Ir measured in *n*-hexane.

Ruff[126] measured the spectra of the $[Cl_3M'M(CO)_5]^-$ derivatives in CH_2Cl_2 and noted that the A_1^1 and E mode are accidentally degenerate. The spectrum of $Et_4N^+[Cl_3SnW(CO)_5]^-$ measured in CH_2Cl_2 is shown in Figure 17, to be contrasted with the spectrum measured in THF, Figure 18. While there are no significant differences in the frequencies measured in the two solvents, it is apparent that the spectrum in THF is much less broad and allows the separation of the A_1^1 and E modes to be clearly resolved. As another example to illustrate this difference, the spectra of $Et_4N^+[Ph_3SiMo(CO)_5]^-$ measured in CH_2Cl_2 and THF are shown in Figures 19 and 20 respectively. Some reference spectra (Figures 28 - 39) are presented at the end of the chapter.

The strong lower frequency shift of $\nu(CO)$ in these complexes in relation to the [illegible]o-steric $(CO)_5MPPh_3$[139,141,148] (M = Cr, Mo, W) and the iso-electronic $R_3M'M(CO)_5$ (M' = Si, Ge, Sn, Pb; M = Mn and Re)[11,142] complexes is in agreement with the ionic character of the new compounds, which leads to a high negative charge on the metal, and hence to considerable M→CO backbonding.

Ideally, the iron tetracarbonyl anions are assumed to have a trigonal bipyramidal structure.[137,149] For C_{3V} symmetry, three ir active modes $2A_1 + E$ are expected and correspond to the vibrational forms as illustrated below:

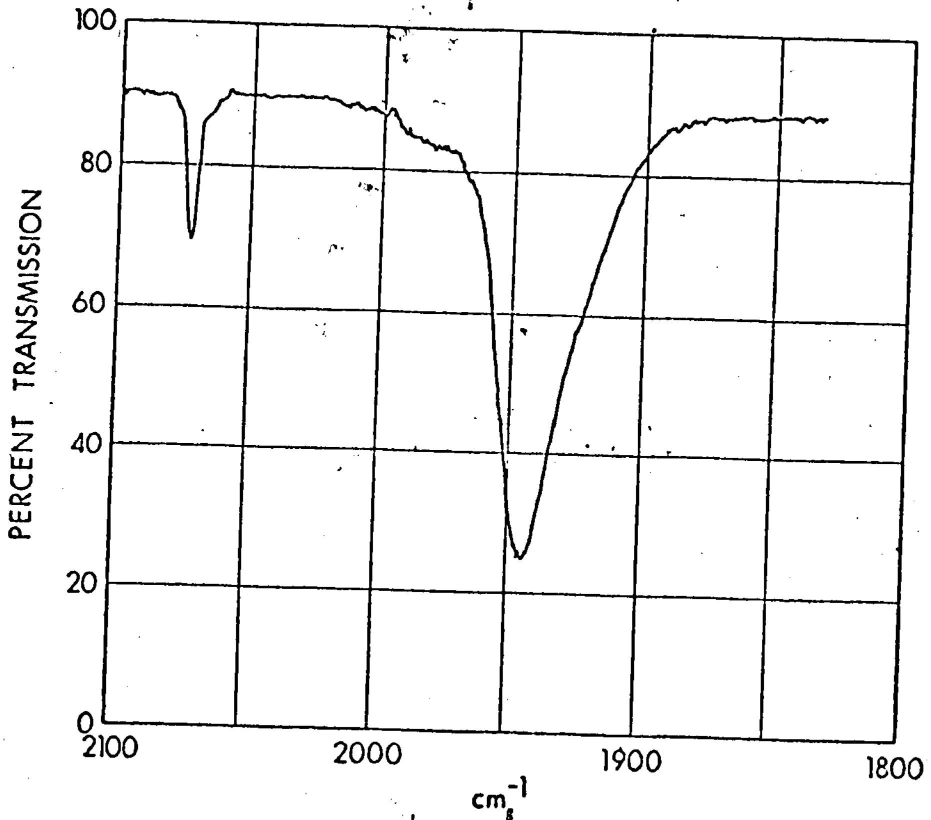


Figure 17. $Et_4N^+[Cl_3SnW(CO)_5]^-$ in CH_2Cl_2.

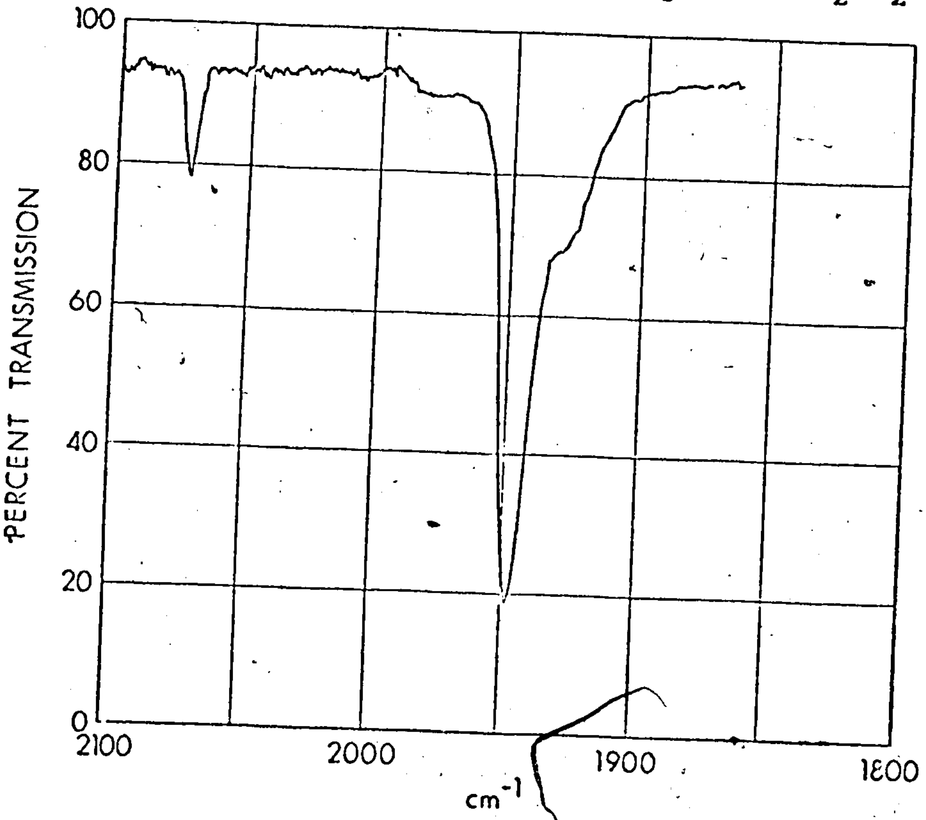


Figure 18. $Et_4N^+[Cl_3SnW(CO)_5]^-$ in THF.

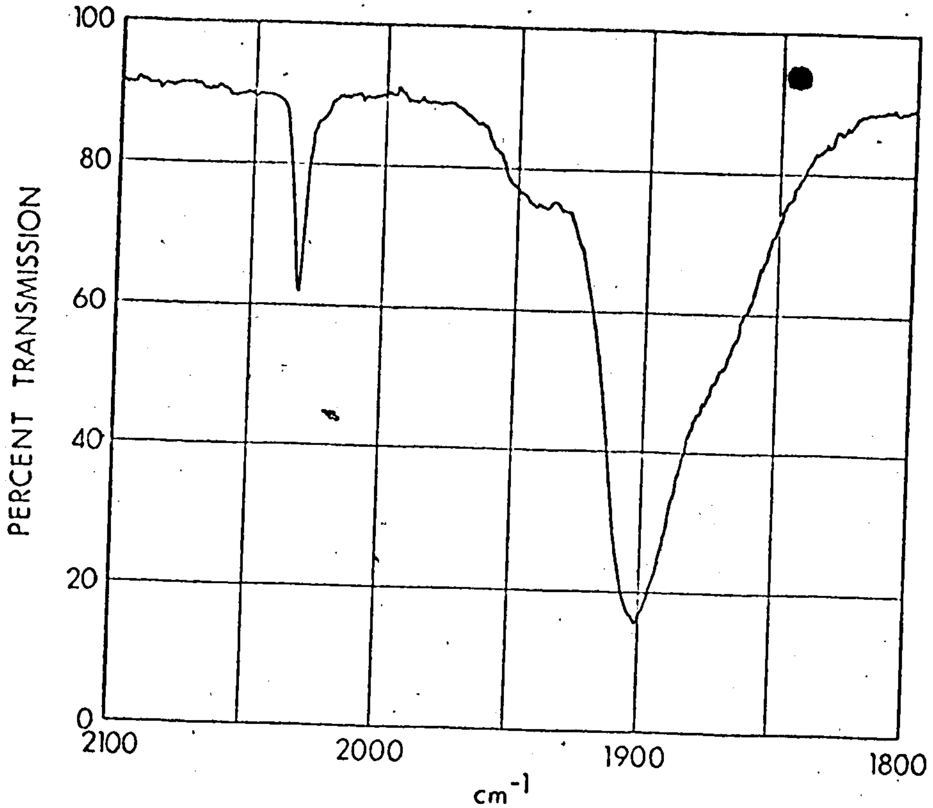


Figure 19. $Et_4N^+[Ph_3SiMo(CO)_5]^-$ in CH_2Cl_2.

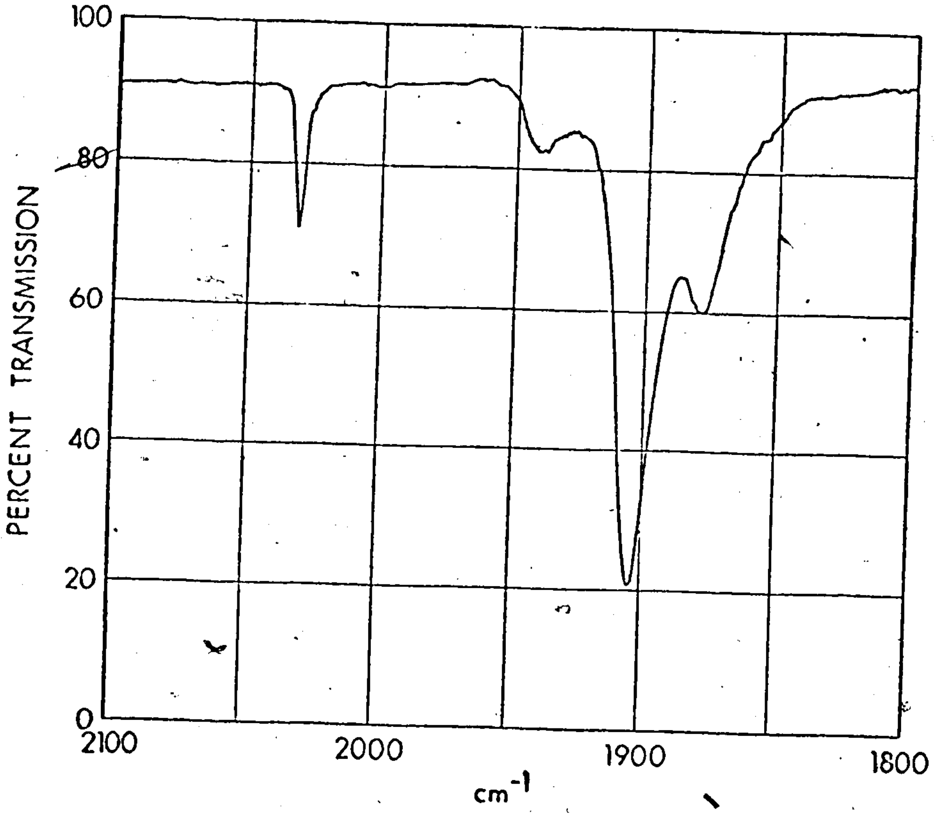
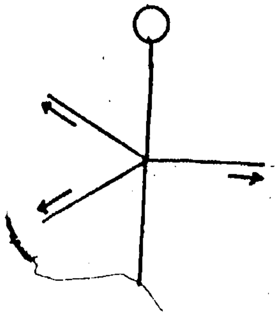
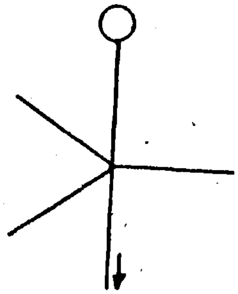


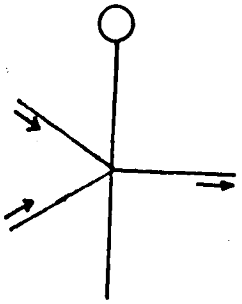
Figure 20. $Et_4N^+[Ph_3SiMo(CO)_5]^-$ in THF.



A_1^2



A_1^1



E

The spectrum of $Et_4N^+[Ph_3GeFe(CO)_4]^-$ measured in THF is shown in Figure 21. The most intense, low frequency band which is assigned to the E mode is split somewhat and a shoulder on the low energy side is apparent. This splitting of the E mode, also observed in $Et_3NH^+[Ph_3SiFe(CO)_4]^-$ by Jetz and Graham[137] was attributed to a lowering of the symmetry caused by ion pairing. Ion pairing has also been used to interpret the splitting of the carbonyl bands in $Na^+[Co(CO)_4]^-$ [150] and $Na_2^+[Cr_2(CO)_{10}]^{2-}$.[151] It has been perceived that ion pairing which occurs in salts dissolved in solvents of low dielectric constants, such as THF, is not observed in solvents of high dielectric constants, such as dimethylsulfoxide.[151] Indeed the spectrum of $Et_4N^+[Ph_3GeFe(CO)_4]^-$ measured in DMSO, shown in Figure

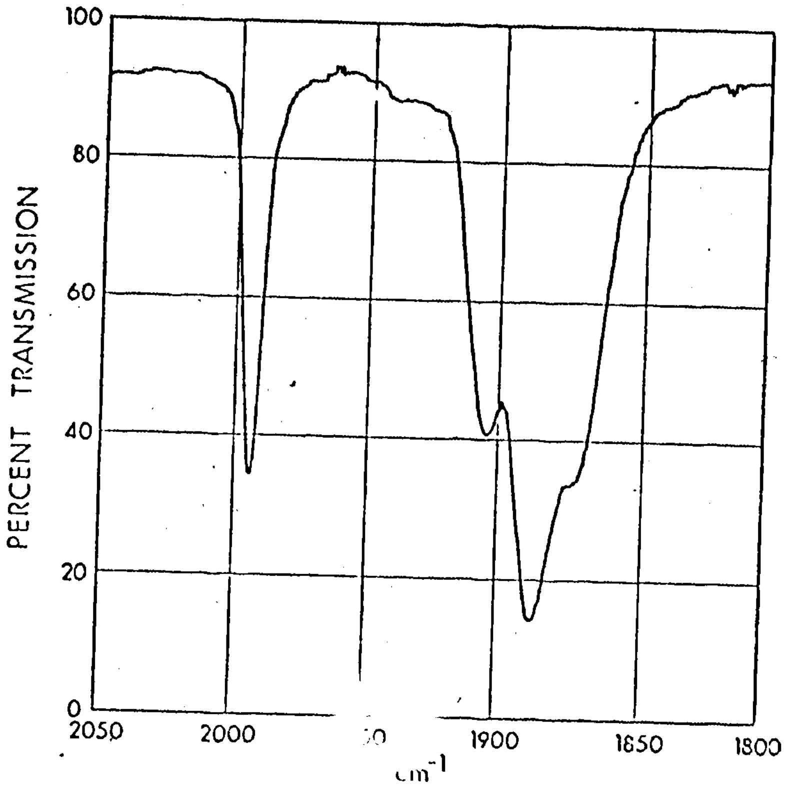
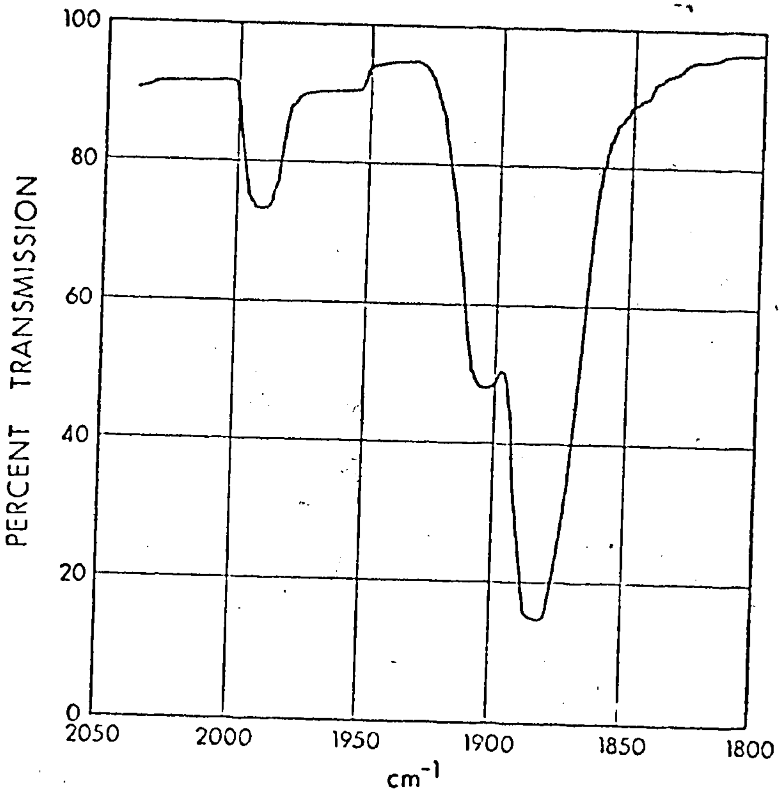


Figure 21. $Et_4N^+[Ph_3GeFe(CO)_4]^-$ in THF.

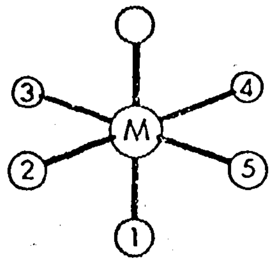


~~Figure~~ 22. $Et_4N^+[Ph_3GeFe(CO)_4]^-$ in DMSO.

22, confirms this view. In Figure 21, the A_1^2 mode is assigned to the band at 1994 cm^{-1}, the band at 1906 cm^{-1} on the high energy side of the E band is assigned to the A_1^1 mode.

Force constants

The idealized geometry and definition of force constants in $M(CO)_5X$ derivatives are shown in Figure 23.



$XM(CO)_5$

CO stretching: k_1, k_2

CO interaction: k_{12}, k_{23}, k_{24}

Cotton-Kraihanzel approximation:

$$k_{12} = k_{23} = 1/2\ k_{24} = k_i$$

Figure 23.

Since there are five force constants, five $\nu(CO)$ are required to evaluate them using the energy factored force field (efff) approximation.[87] The assumption provided by the Cotton-Kraihanzel (CK) method,[73] as summarized in Figure 23, reduces the number of required bands to three.

As seen from the ir spectra in the last section, five frequencies can be obtained, namely the $2A_1$, B_1, and E of the all-^{12}CO molecule and the A' of the axial monosubstituted molecule. However in some spectra, particularly of the trihalo-tin and -germanium substituted derivatives, the B_1 mode was too broad to measure accurately and the A^1 was not clearly resolved from that of the A_1^2. Thus Table XIII, which lists the force constants evaluated using the efff method, includes only the values where accurate measurement could be obtained.

Force constants were also evaluated by the CK method using the $2A_1$ and E band positions. Results are listed in Table XIV. The position of the B_1 mode was calculated using the obtained force constants and provides a check on the observed B_1.

Comparison of Tables XIII and XIV shows that the values of k_2 are insensitive to their method of calculation. On the other hand values of k_1 are slightly larger in the efff method, in some cases by as much as .3 mdyn/Å. It is difficult to ascertain the reasons for this difference or to attribute this difference to the additional approximation of the CK method, since there is no real check on the calculated efff force constants.

A comparison of the force constants obtained in

TABLE XIII

ENERGY FACTORED CARBONYL FORCE CONSTANTS FOR SOME GROUP VI ~~METAL~~ PENTACARBONYL ANIONS [a]

Compound	k_1 [b]	k_2	k_{12}	k_{23}	k_{24}
$Et_4N^+[Ph_3SiCr(CO)_5]^-$	14.46	15.04	.33	.29	.55
$Et_4N^+[MePh_2SiCr(CO)_5]^-$	14.64	14.89	.45	.23	.50
$Et_4N^+[Ph_3GeCr(CO)_5]^-$	14.34	15.10	.35	.27	.53
$Et_4N^+[Ph_3SnCr(CO)_5]^-$	14.70	15.01	.45	.22	.48
$Et_4N^+[Me_3SnCr(CO)_5]^-$	14.30	14.86	.32	.30	.52
$Et_4N^+[Ph_3PbCr(CO)_5]^-$	14.33	15.24	.20	.30	.56
$Et_4N^+[Ph_3SiMo(CO)_5]^-$	14.43	15.26	.29	.31	.61
$Et_4N^+[Ph_2MeSiMo(CO)_5]^-$	14.63	15.10	.45	.26	.54
$Et_4N^+[Ph_3GeMo(CO)_5]^-$	14.68	15.24	.47	.24	.54
$Et_4N^+[Ph_3SnMo(CO)_5]^-$	14.75	15.26	.45	.25	.53
$Et_4N^+[Me_3SnMo(CO)_5]^-$	14.82	14.97	.45	.19	.54
$Et_4N^+[Ph_3PbMo(CO)_5]^-$	14.75	15.38	.46	.24	.52
$Et_4N^+[Ph_3SiW(CO)_5]^-$	14.52	15.15	.42	.30	.58

TABLE XIII (continued)

Compound	k_1	k_2	k_{12}	k_{23}	k_{24}
$Et_4N^+[MePh_2SiW(CO)_5]^-$	14.60	15.02	.48	.28	.54
$Et_4N^+[Cl_3GeW(CO)_5]^-$	15.21	15.71	.42	.32	.54
$Et_4N^+[Ph_3GeW(CO)_5]^-$	14.72	15.12	.44	.24	.51
$Et_4N^+[Br_3SnW(CO)_5]^-$	15.31	15.66	.49	.31	.45
$Et_4N^+[Cl_3SnW(CO)_5]^-$	15.45	15.81	.44	.24	.58
$Et_4N^+[Cl_2PhSnW(CO)_5]^-$	15.24	15.61	.48	.25	.57
$Et_4N^+[Ph_3SnW(CO)_5]^-$	14.56	15.20	.41	.29	.57
$Et_4N^+[Me_3SnW(CO)_5]^-$	14.40	15.00	.40	.31	.56
$Et_4N^+[Ph_3PbW(CO)_5]^-$	14.86	15.23	.54	.21	.50

---

[a] Values in mdyn/Å.

[b] Force constant designation as in Figure 23.

TABLE XIV

COTTON-KRAIHANZEL CARBONYL FORCE CONSTANTS FOR SOME GROUP VI METAL PENTACARBONYL ANIONS[a]

Compound	k_1	k_2	k_i
$Et_4N^+[Ph_3SiCr(CO)_5]^-$	14.39	15.06	.29
$Et_4N^+[MePh_2SiCr(CO)_5]^-$	14.32	14.98	.29
$Et_4N^+[Cl_3GeCr(CO)_5]^-$	15.16	15.79	.28
$Et_4N^+[Ph_3GeCr(CO)_5]^-$	14.31	15.12	.29
$Et_4N^+[Cl_3SnCr(CO)_5]^-$	15.20	15.84	.28
$Et_4N^+[Ph_3SnCr(CO)_5]^-$	14.39	15.10	.28
$Et_4N^+[Me_3SnCr(CO)_5]^-$	14.24	14.90	.28
$Et_4N^+[Ph_3PbCr(CO)_5]^-$	14.40	15.23	.27
$Et_4N^+[Ph_3SiMo(CO)_5]^-$	14.42	15.26	.31
$Et_4N^+[MePh_2SiMo(CO)_5]^-$	14.38	15.18	.31
$Et_4N^+[Cl_3GeMo(CO)_5]^-$	15.13	15.91	.30
$Et_4N^+[Ph_3GeMo(CO)_5]^-$	14.40	15.31	.31
$Et_4N^+[Cl_3SnMo(CO)_5]^-$[b]	15.38	15.80	.31
$Et_4N^+[Ph_3SnMo(CO)_5]^-$	14.50	15.33	.30
$Et_4N^+[Me_3SnMo(CO)_5]^-$	14.30	15.12	.30
$Et_4N^+[Ph_3PbMo(CO)_5]^-$	14.48	15.45	.30
$Et_4N^+[Ph_3SiW(CO)_5]^-$	14.37	15.20	.32
$Et_4N^+[MePh_2SiW(CO)_5]^-$	14.71	15.45	.31
$Et_4N^+[Cl_3GeW(CO)_5]^-$	15.05	15.80	.32
$Et_4N^+[Ph_3GeW(CO)_5]^-$	14.40	15.25	.32
$Et_4N^+[Br_3SnW(CO)_5]^-$	14.98	15.82	.31

TABLE XIV (continued)

Compound	k_1	k_2	k_i
$Et_4N^+[Cl_3SnW(CO)_5]^-$	15.21	15.85	.31
$Et_4N^+[Cl_2PhSnW(CO)_5]^-$	14.99	15.67	.31
$Et_4N^+[ClPh_2SnW(CO)_5]^-$	14.71	15.45	.31
$Et_4N^+[Ph_3SnW(CO)_5]^-$	14.41	15.25	.32
$Et_4N^+[Me_3SnW(CO)_5]^-$	14.26	15.06	.31
$Et_4N^+[Ph_3PbW(CO)_5]^-$	14.42	15.35	.31

---

[a] Evaluated from A_1 and E band positions of All-^{12}CO molecules. Values in mdyn/Å.

[b] Based on ir spectrum in CH_2Cl_2; the A_1^1 and E bands are unresolved.

this study with those obtained for group V ligands of the same metal, for example $Ph_3PW(CO)_5$ [148] (k_1 = 15.52, k_2 = 15.88 mdyn/Å) and $[Ph_3SiW(CO)_5]^-$ (k_1 = 14.52, k_2 = 15.15 mdyn/Å) shows a greatly increased σ-donor and decreased π-acceptor strength for the group IV ligands containing phenyl substituents. On the other hand the trihalo group IV derivatives, for example $[Cl_3SnW(CO)_5]^-$ (k_1 = 15.45 and k_2 = 15.85 mdyn/Å), appear to be quite similar to Ph_3P in π-bonding ability. Although the actual numerical values of the force constants are not entirely reliable, due to the approximation in the force field and the comparison of force constants obtained from spectra measured in different solvents, they should offer a good basis for comparing general trends.

A comparison of the force constants with those of the isoelectronic manganese[11,87] and rhenium[11] complexes, for example $Ph_3SiRe(CO)_5$ (k_1 = 16.57, k_2 = 16.85 mdyn/Å), shows the expected decrease in the force constants. In most cases the decrease in k_1 is significantly greater than in k_2. This reflects the greater importance of metal to CO π-bonding in the anionic system, as evidenced by lower force constants. Since k_1 feels the π-effect to a greater extent than k_2,[10] the difference between k_1 and k_2 is expected to be greater for the group VI anionic complexes.

Graham Parameters

Graham[10] has proposed a semi-quantitative method to distinguish between π-withdrawal and σ-withdrawal effects by a ligand L in an $LM(CO)_5$ molecule. The overall changes in force constants resulting from a change of L were expressed as $\Delta k_1 = \Delta\sigma + 2\Delta\pi$ and $\Delta k_2 = \Delta\sigma + \Delta\pi$. The relative σ-donor and π-acceptor components of L were evaluated by computing the $\Delta\sigma$ and $\Delta\pi$ parameters relative to one compound which was selected as a standard.

The CK method, which is used in this analysis, has been both criticized[152,153] and defended.[154] Hall and Fenske[155] have pointed out that since the potential due to the ligand affects the metal orbital levels in an essentially isotropic fashion, the weakness of the Graham analysis is that the isotropic and σ-donor effects are automatically lumped together.

While the absolute values of the Graham parameters are not significant, this method is serviceable in that it provides a qualitative and simplified picture for a very complicated bonding situation. It thus appeared a useful method for comparing general bonding trends of the group IV ligands with other ligands bonded to the same metal.

Table XV lists the CK force constants and the derived σ and π values for the pentacarbonylmolybdenum complexes prepared in this work, together with some

TABLE XV

GRAHAM σ- AND π-BONDING PARAMETERS FOR SOME PENTACARBONYL MOLYBDENUM COMPLEXES[a]

L in LMo(CO)$_5$	Force constants[b] (mdyn/Å) k_1	k_2	σ mdyn/Å	π mdyn/Å
$SnMe_3^-$	14.30	15.12	-0.64	-0.08
$SiPh_2Me^-$	14.38	15.18	-0.60	-0.06
$SiPh_3^-$	14.42	15.26	-0.48	-0.10
$SnPh_3^-$	14.50	15.33	-0.42	-0.09
$GePh_3^-$	14.40	15.31	-0.36	-0.17
$PbPh_3^-$	14.48	15.45	-0.16	-0.23
PPh_3 [c]	15.49	15.96	-0.15	0.27
$P(OPh)_3$ [c]	15.93	16.19	-0.13	0.48
CO [c]	16.52	16.52	-0.06	0.74
Cyclohexylamine [c]	15.10	15.84	0	0
$GeCl_3^-$	15.13	15.91	0.11	-0.04
CH_3CN [c]	15.14	16.04	0.36	-0.16

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[a] Listed in order of decreasing σ-donation. Reference compound is cyclohexylamine.

[b] Cotton-Kraihanzel.

[c] Data from Reference 10.

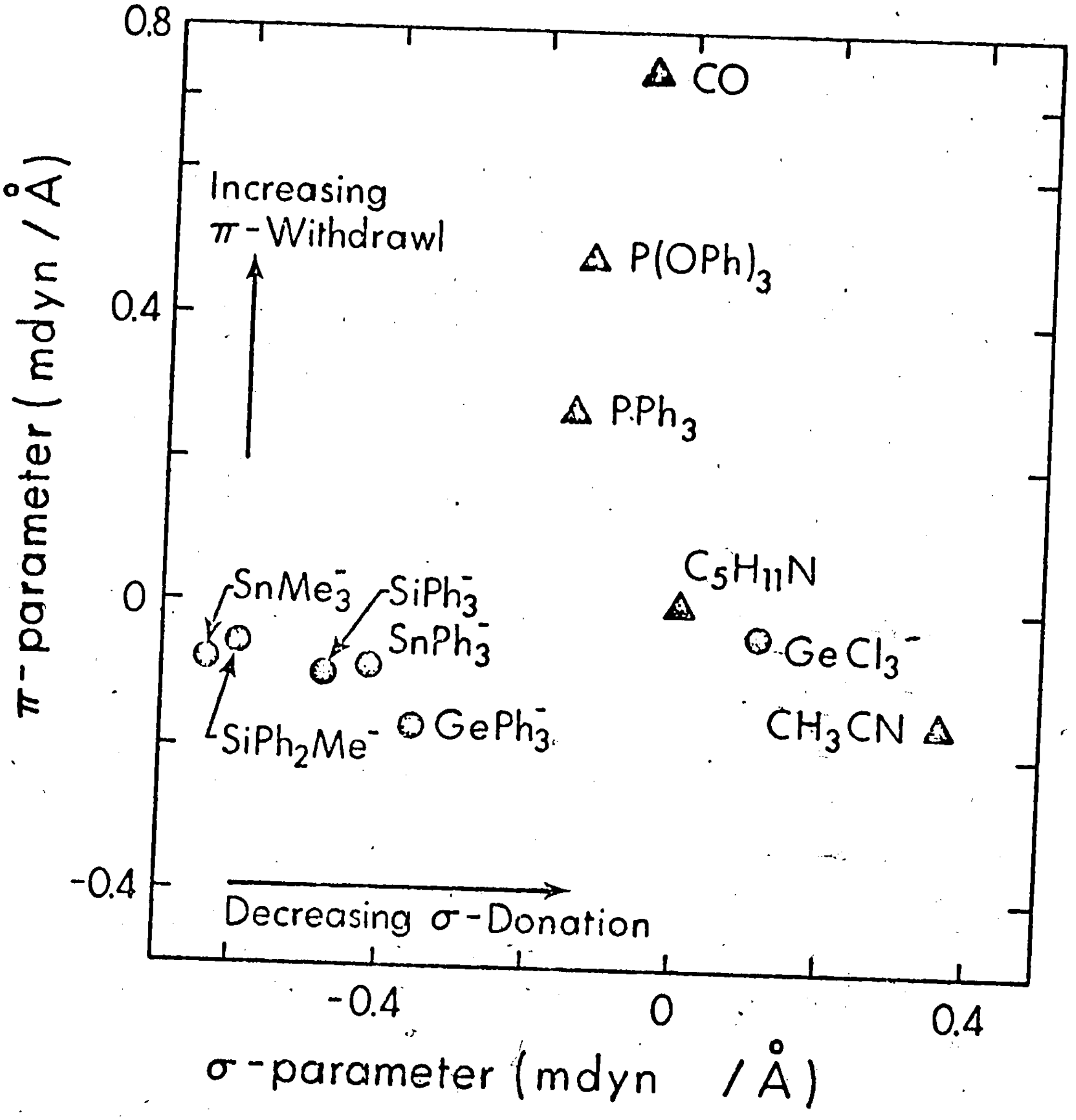


Figure 24. Relative σ and π parameters for pentacarbonylmolybdenum derivatives. Points are labeled L in $LMo(CO)_5$. Triangles denote data taken directly from the work of Graham.[10]

comparative complexes from the data of Graham.[10] A graphical representation is given in Figure 24.

It is immediately apparent that the aryl- and alkyl-substituted group IV ligands have a high σ-donor property consistent with the generally accepted qualitative views. The model further indicates essentially no π-bonding to the metal for all the group IV ligands. The higher force constants for $GeCl_3^-$ are reflected in its very poor σ-donor ability as compared to Ph_3P and not necessarily in an improved π-acceptor capability.

Nmr Spectra

The nmr spectra, measured in acetone-d_6 or CD_3CN, provided further evidence for the ionic constitution of the compounds proposed in this chapter. The presence of the tetraethylammonium cation was a characteristic feature showing a triplet at ca. 8.6 τ and a quartet at ca. 6.4 τ as expected for the ethyl derivatives. The peaks of the triplet are split equally into three by coupling with the nitrogen atom. The phenyl substituents on the group VI metal appeared as a complex multiplet at 2.2 - 2.8 τ. Only values for the methyl resonance in the $MePh_2Si$ and Me_3Sn derivatives are included in footnotes to Table XII.

Chemical Reactions

In the anionic compounds containing group IV-transition metal bonds, four sites are subject to attack by electrophilic, nucleophilic, or neutral chemical reagents.

(a) Substituent-group IV metal linkage

Mixed halogen-phenyl derivatives could be obtained by the so-called redistribution reaction.[156] For example $Et_4N^+[ClPh_2SnW(CO)_5]^-$ and $Et_4N^+[Cl_2PhSnW(CO)_5]^-$ were obtained by heating of a 2:1 and 1:2 molar ratio of $Et_4N^+[Ph_3SnW(CO)_5]^-$ and $Et_4N^+[Cl_3SnW(CO)_5]^-$ at 150° in the absence of solvent. The reaction was conveniently monitored by removing samples at various intervals and observing the disappearance of the bands at 2034 and 2070 cm^{-1}, due to the A_1^2 modes of the starting materials and the appearance of the product A_1^2 mode in the ir spectrum. This is illustrated in Figure 25 and Figure 26 which shows the changes in the ir spectrum (A_1^2 modes) during the formation of $ClPh_2Sn$ (A_1^2 at 2058 cm^{-1}) and Cl_2PhSn (A_1^2 at 2046 cm^{-1}) derivatives respectively.

(b) Cleavage of the metal-metal bond

When a solution of HCl in ether was added to some anionic derivatives of tungsten in THF, the cleavage

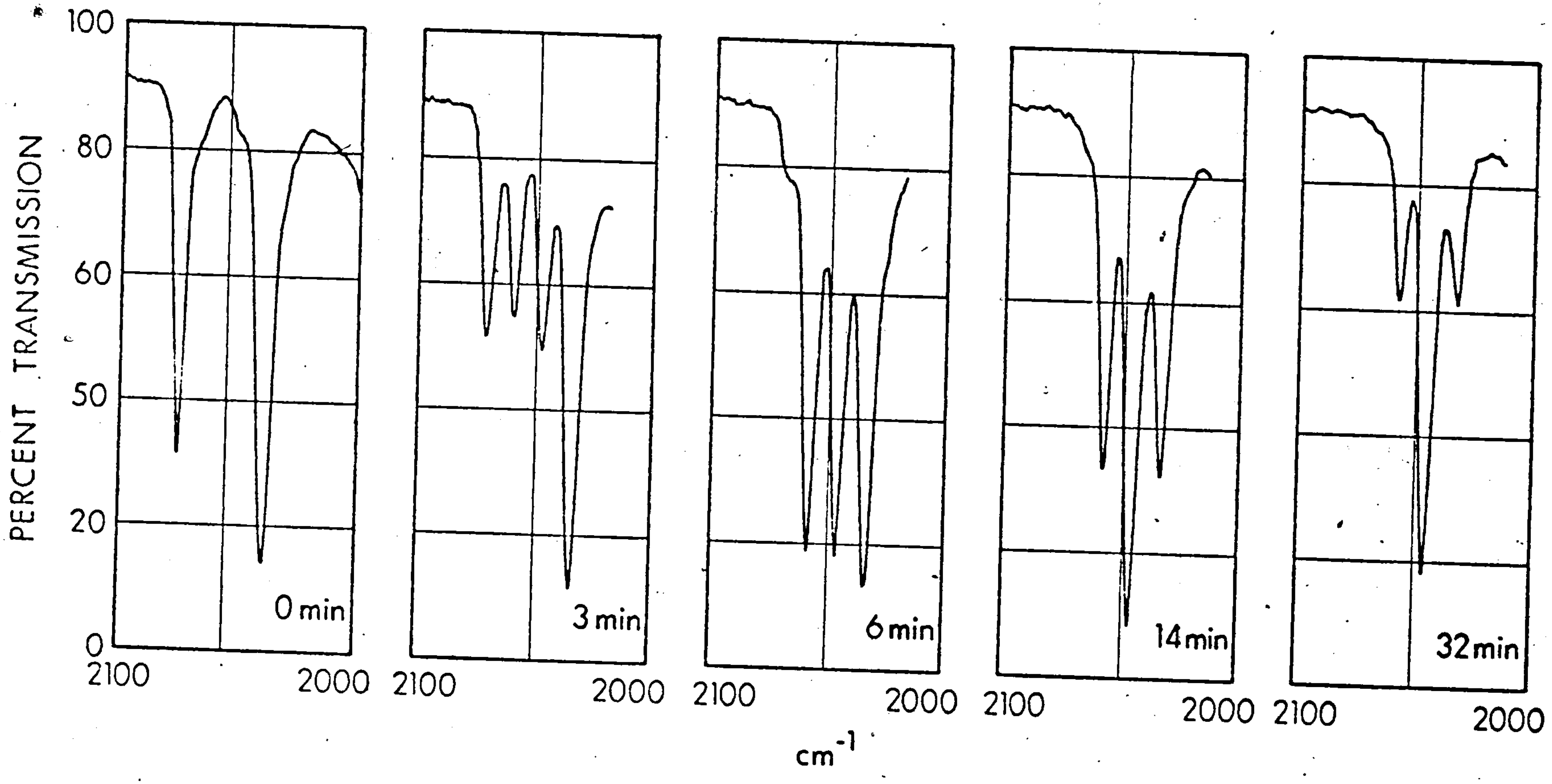


Figure 25. The infrared spectral (A_1^2 mode) changes with lapse of time in the reaction of $[Cl_3SnW(CO)_5]^-$ and $[Ph_3SnW(CO)_5]^-$ (1:2).

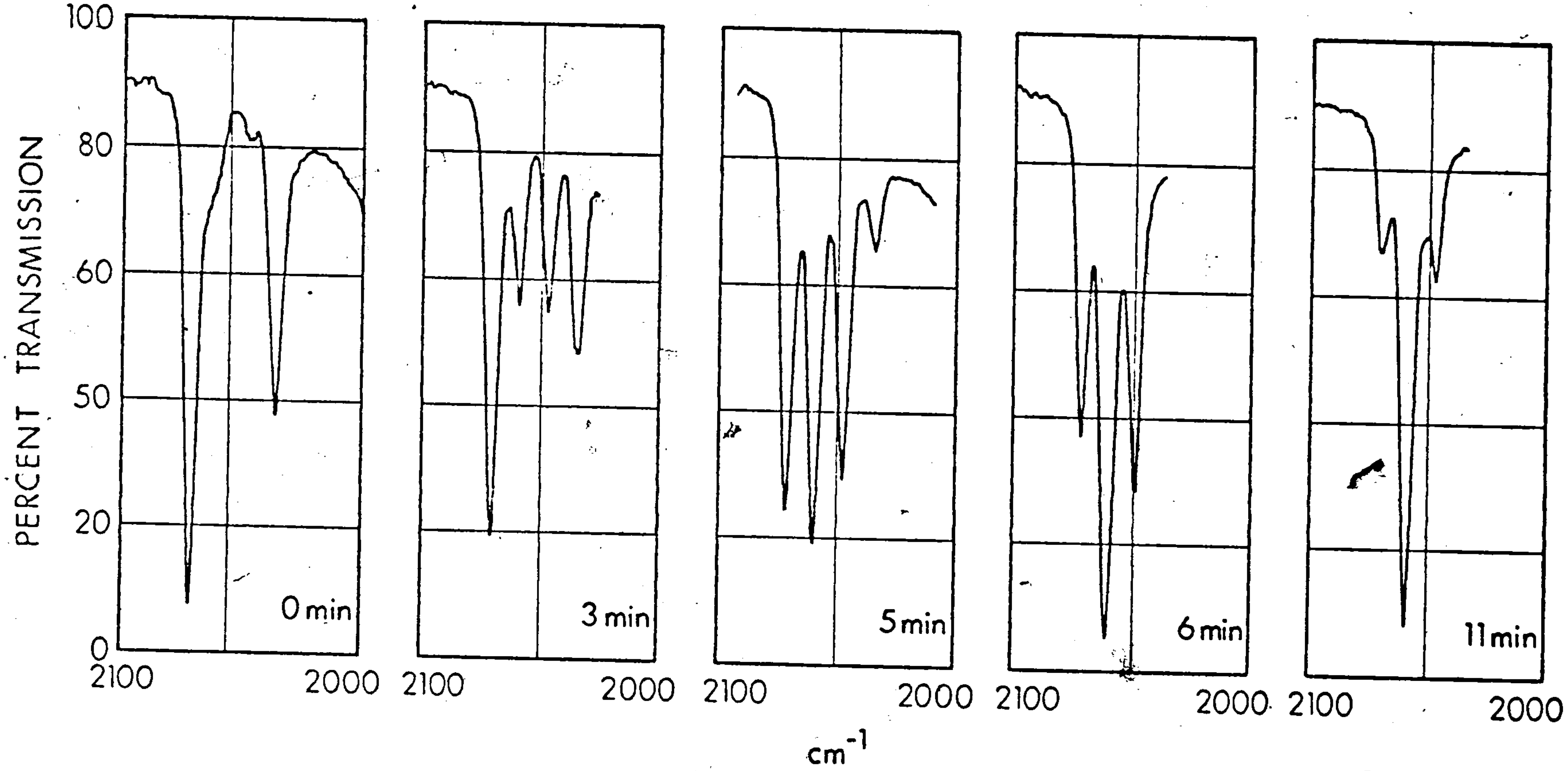


Figure 26. The infrared spectral (A_1^2 mode) changes with lapse of time in the reaction of $[Cl_3SnW(CO)_5]^-$ and $[Ph_3SnW(CO)_5]^-$ (2:1).

of the metal-metal bond resulted.

$$Et_4N^+[R_3M'W(CO)_5]^- + HCl \rightarrow Et_4N^+[W(CO)_5Cl]^- + HM'R_3 \qquad V\text{-}29$$

where M' = Si, Ge and Sn. The formation of $[W(CO)_5Cl]^-$ was identified by a comparison of its ir spectrum to that of an authentic sample.

The chloropentacarbonyl anion was also formed by reaction with Ph_3PAuCl.

$$Et_4N^+[Ph_3GeW(CO)_5]^- + Ph_3PAuCl \xrightarrow[THF]{} Et_4N^+[W(CO)_5Cl]^- + Ph_3GeAuPPh_3 \qquad V\text{-}30$$

Treatment of $Et_4N^+[Cl_3SnW(CO)_5]^-$ with $AgBF_4$ did not result in the fluorination reaction[97] but in the cleavage of the metal-metal bond with formation of $CH_3CNW(CO)_5$. The latter was identified by its ir and mass spectra.

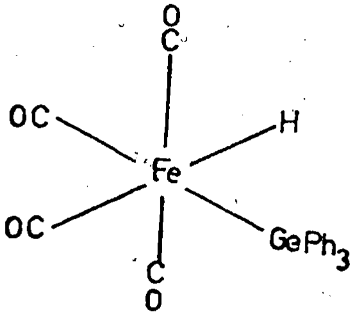
Attempts at protonation of $Et_4N^+[Ph_3SnW(CO)_5]^-$ and $Et_4N^+[Cl_3GeMo(CO)_5]^-$ using 85% H_3PO_4 in a water-pentane slurry failed, resulting in the cleavage of the metal-metal bond as evidenced by the formation of $W(CO)_6$.

(c) Protonation of the metal - the preparation of $Ph_3GeHFe(CO)_4$.

Treatment of $Et_4N^+[Ph_3GeFe(CO)_4]^-$ with HCl in ether surprisingly did not result in the cleavage of the Ge-Fe bond but in protonation of the metal giving $Ph_3GeHFe(CO)_4$.

An attempt to prepare this compound from $Fe(CO)_5$ and $HGePh_3$ by ultraviolet irradiation was not successful.[157]

The compound is a white crystalline solid which is extremely air-sensitive at room temperature; solutions deteriorate quickly even under nitrogen. Its ir spectrum, Figure 27, showed four carbonyl bands characteristic of a cis-octahedral geometry, 41. The relative intensities and position of the bands are almost identical to that of $Ph_3SiHFe(CO)_4$.[108]



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The band at 2000.5 cm^{-1} is due to $Fe(CO)_5$. The presence of a signal at 19.35 τ in the nmr spectrum, measured in toluene-d_8, confirmed the presence of the metal-hydride

The mass spectrum measured at 80° showed a parent at m/e 474 with fragments corresponding to consecutive loss of carbonyl groups from the parent ion. Fragments which had lost a phenyl group were also observed in low abundance.

A mass spectrum run at 135° showed in low abundance some extraneous peaks above the parent ion. The highest

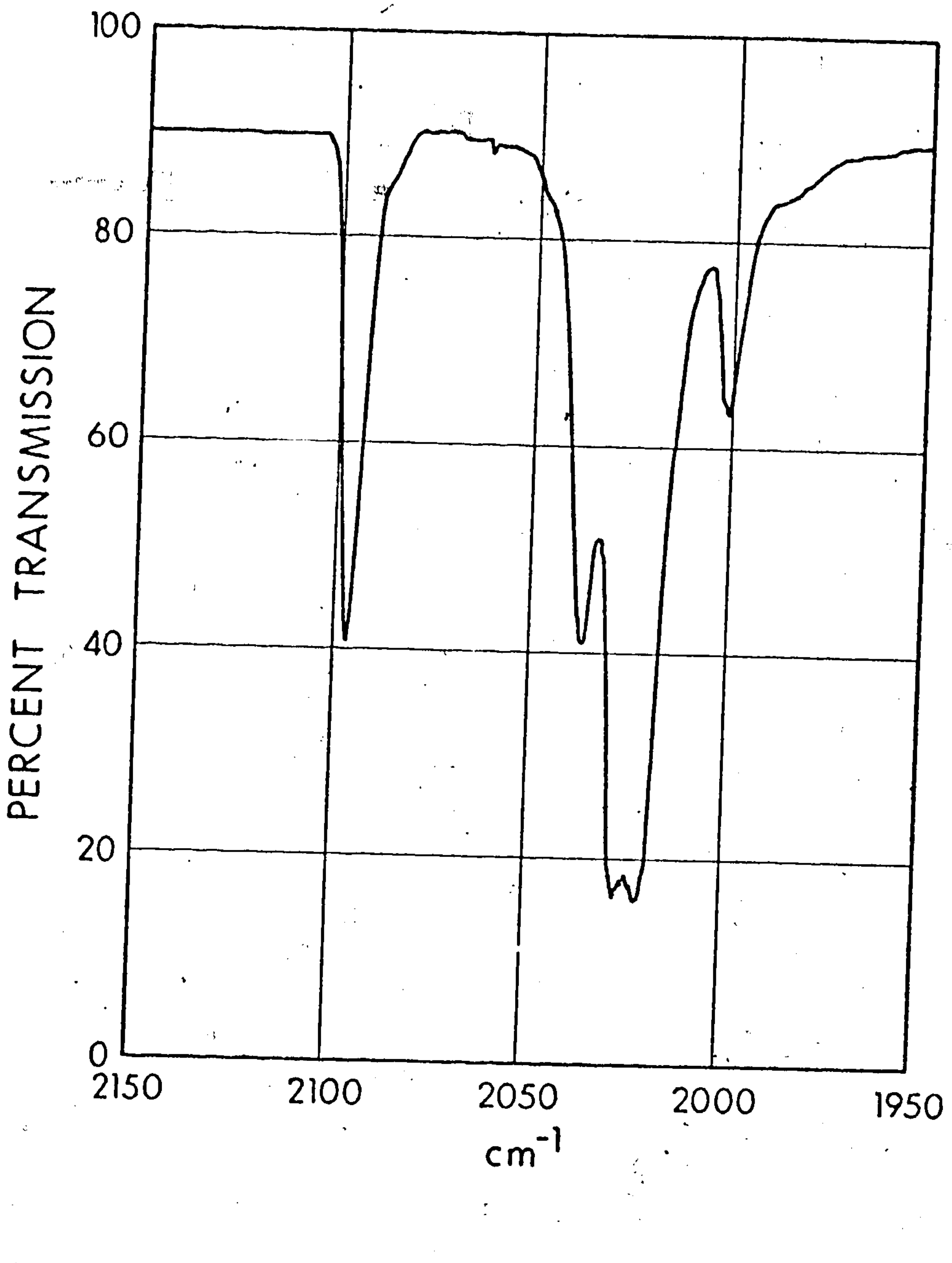


Figure 27. $Ph_3GeHFe(CO)_4$ in *n*-hexane.

peak at m/e 811 corresponds to $Ph_5Ge_2Fe(CO)_6^+$, and this showed loss of six consecutive carbonyls. The presence of a dinuclear species was also featured in the mass spectrum of the triphenylsilyl analog run at 105°; a parent peak was not observed.[158]

Addition of Et_4NCl to a CH_2Cl_2 solution of $Ph_3GeHFe(CO)_4$ generates the anion and provides the following equilibrium expression

$$HCl + Et_4N^+[Ph_3GeFe(CO)_4]^- \rightleftarrows Ph_3GeHFe(CO)_4 + Et_4NCl$$

(d) Carbonyl substitution

The group VI anions containing phenyl substituted group VI elements proved to be extremely resistant to the displacement of a carbonyl group by PPh_3. For example, there was no appreciable reaction when $Et_4N^+[Ph_3SnW(CO)_5]^-$ was heated with excess PPh_3 at 210° in the absence of solvent for 48 hr. This is in marked contrast to $Ph_4As^+[Cl_3GeMo(CO)_5]^-$ which reacted with Ph_3P at ambient temperatures.[126]

$Et_4N^+[Ph_3SnMo(CO)_5]^-$ proved to be more amenable to substitution by Ph_3P using photolytic conditions. The product obtained after 6 hr of irradiation in CH_2Cl_2 showed ν(CO) bands at 2021 (ms), 1920 (sh), 1902 (vs) and 1887 (m) cm^{-1}. A good analysis could not be obtained for this compound.

The reaction of the group VI anions with the nitrosonium ion NO^+ gave products resulting from the displacement of CO by the nitrosyl group. The results of these reactions are the subject matter of the succeeding Chapter.

The infrared spectra presented in the following pages were measured in THF.

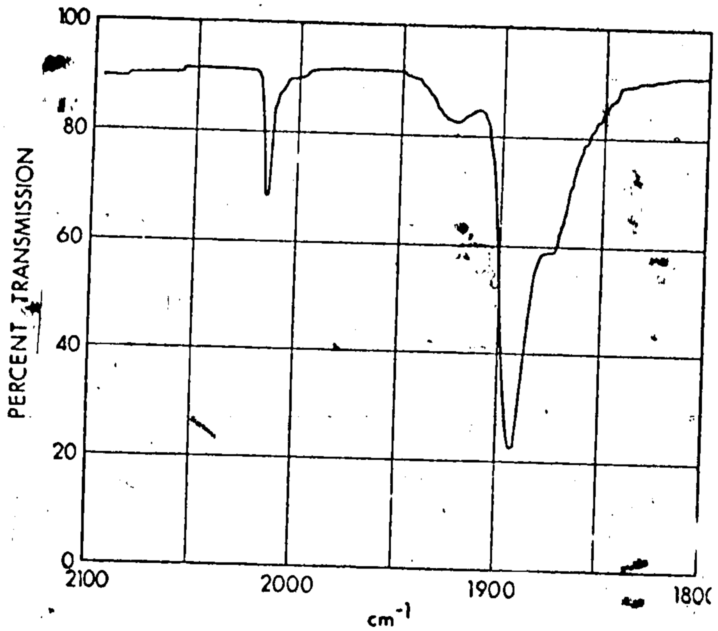


Figure 28. $Et_4N^+[Ph_3SiCr(CO)_5]^-$.

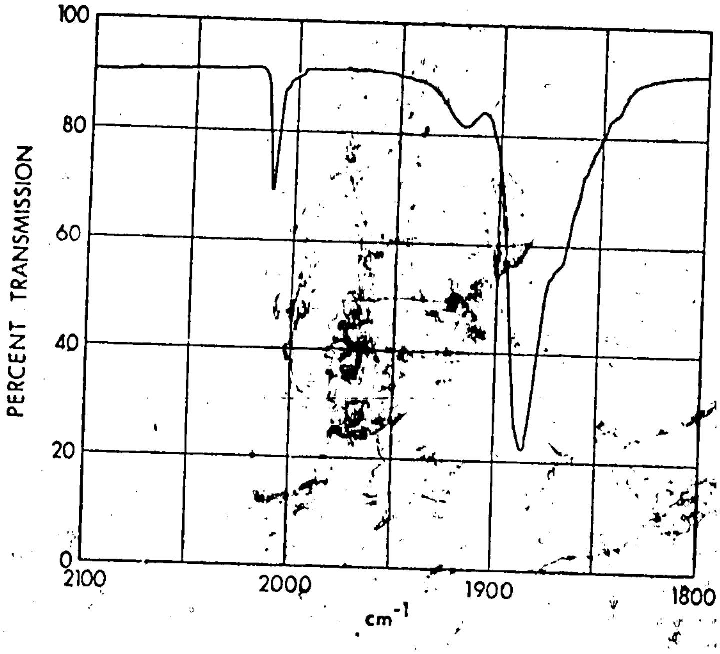


Figure 29. $Et_4N^+[MePh_2SiCr(CO)_5]^-$

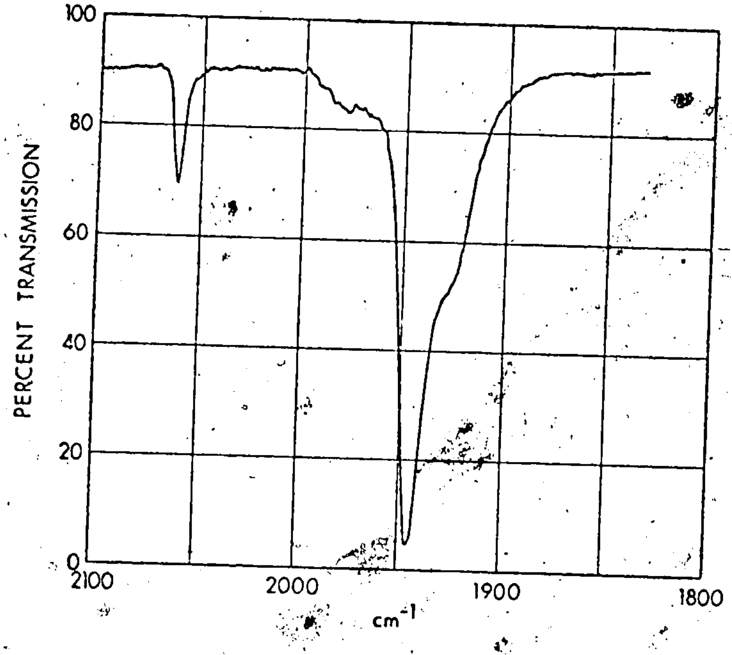


Figure 30. $Et_4N^+[Cl_3GeCr(CO)_5]^-$.

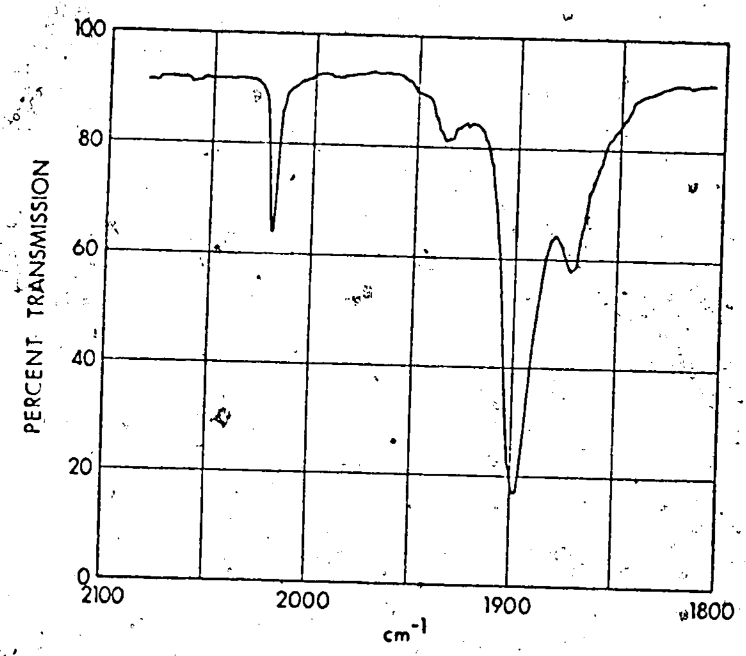


Figure 31. $Et_4N^+[Ph_3GeCr(CO)_5]^-$.

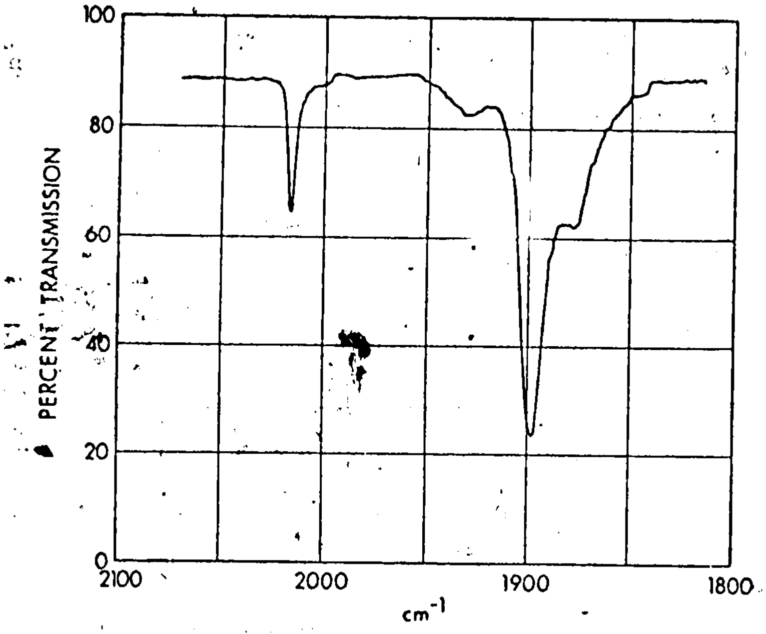


Figure 32. $Et_4N^+[Ph_3SnCr(CO)_5]^-$.

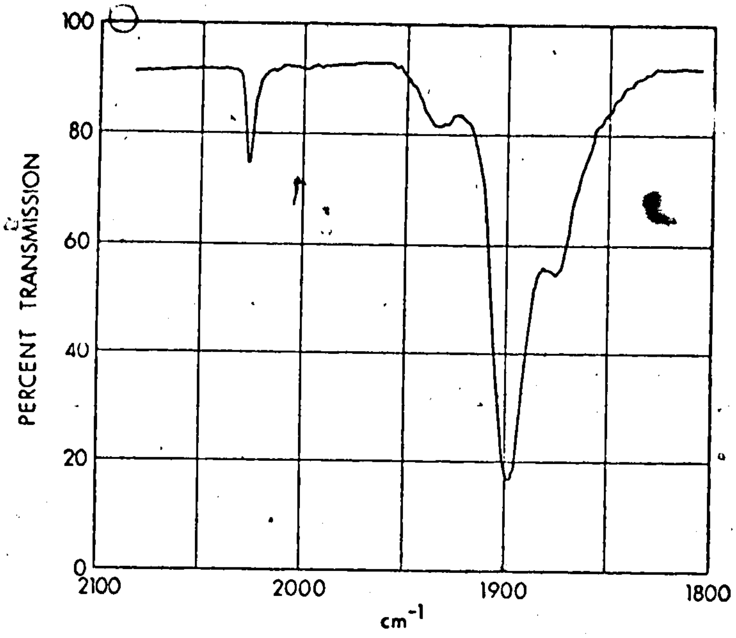


Figure 33. $Et_4N^+[MePh_2SiMo(CO)_5]^-$.

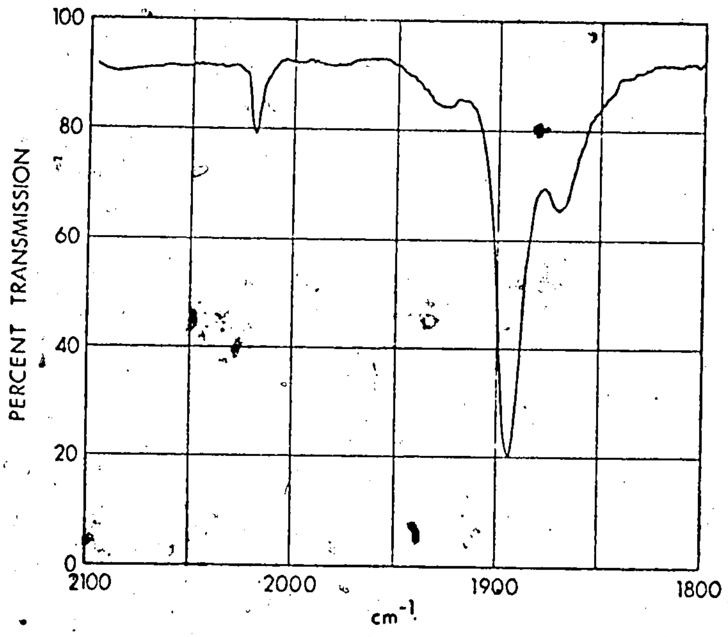


Figure 34. $Et_4N^+[Me_3SnMo(CO)_5]^-$.

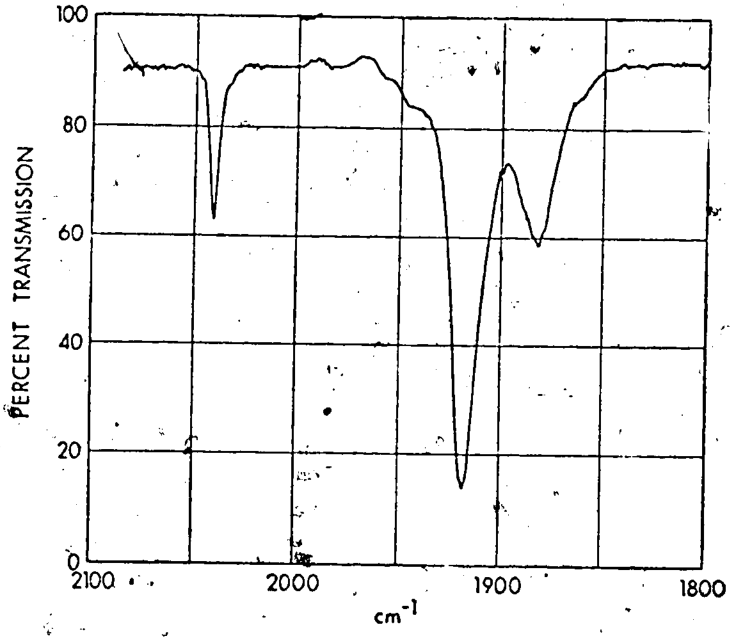


Figure 35. $Et_4N^+[Ph_3PbMo(CO)_5]^-$.

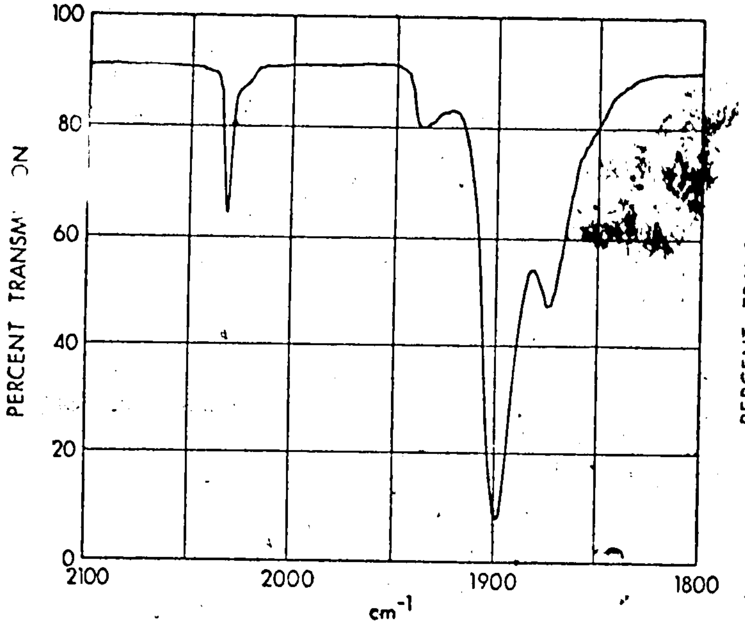


Figure 36. $Et_4N^+[Ph_3SiW(CO)_5]^-$.

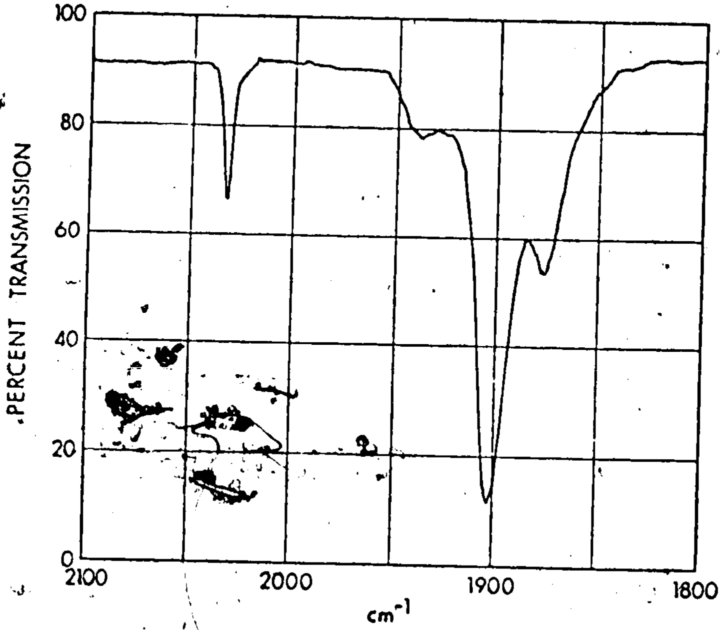


Figure 37. $Et_4N^+[Ph_3SnW(CO)_5]^-$.

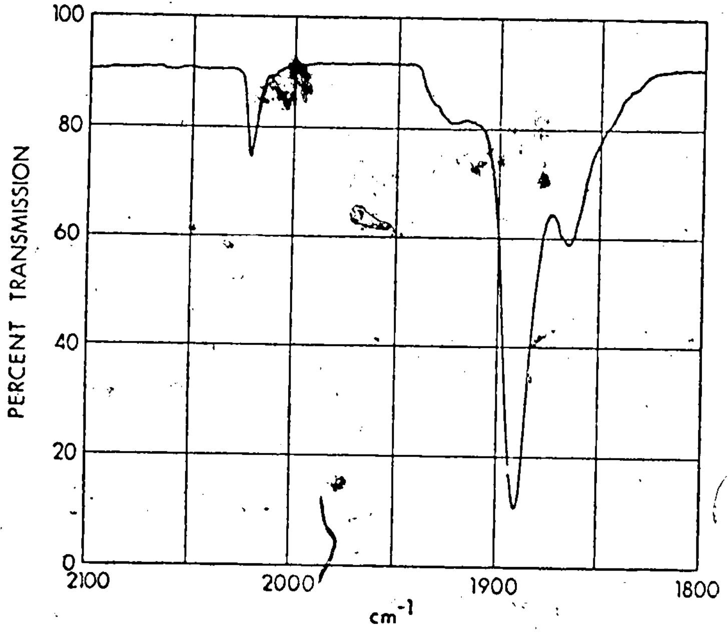


Figure 38. $Et_4N^+[Me_3SnW(CO)_5]^-$.

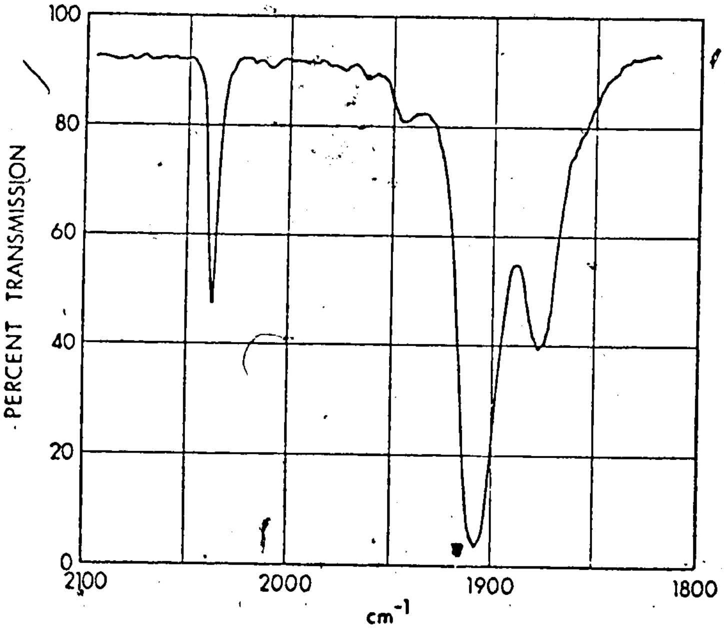


Figure 39. $Et_4N^+[Ph_3PbW(CO)_5]^-$.

EXPERIMENTAL

Melting points and microanalyses (Table XVI), nmr and mass spectra were measured as previously described.

Unless specified otherwise, infrared spectra were measured in tetrahydrofuran, which was dried and distilled from potassium and benzophenone. Solid samples of the group VI anions were pumped in high vacuum for Ca. 3 hr at 60° to remove traces of hexacarbonyls. Solutions were made up under nitrogen just prior to each run. Results of the ir spectra are given in Table XII.

The energy factored force field vibrational analysis was carried out as previously described. The program VALUE[87] was used to calculate force constants under the Cotton-Kraihanzel approximation. Approximate force constants are listed in Tables XIII and XIV.

Tetrahydrofuran used in the chemical reactions was dried over calcium hydride, dichloromethane over P_2O_5, pentane over calcium hydride. In every other case reagent solvents were used. All solvents were purged with nitrogen before use.

The group VI hexacarbonyls and iron pentacarbonyl were purchased from Strem Chemical Inc., Danvers, Mass. Lithium wire (1/8", .01% Na and/or 1/8", 1% Na) was obtained from Alfa Inorganics, Beverly, Mass. Anhydrous

TABLE XVI

ANALYTICAL DATA, MELTING POINTS AND YIELDS FOR THE GROUP IV ANIONIC COMPLEXES

Compound	% Yield	M.P. (°C)	Calcd. % C	H	N	Cl	Found % C	H	N	Cl
$Et_4N^+[Ph_3SiCr(CO)_5]^-$	82	181-185	64.05	6.07	2.41	-	63.59	5.90	2.41	-
$Et_4N^+[MePh_2SiCr(CO)_5]^-$	91	139-141	60.00	6.40	2.70	-	59.92	6.33	2.93	-
$Et_4N^+[Cl_3GeCr(CO)_5]^-$	78	185-187	31.15	4.02	2.79	21.29	30.87	4.12	2.86	21.72
$Et_4N^+[Ph_3GeCr(CO)_5]^-$	59	175-177 dec.	59.46	5.63	2.24	-	58.99	5.65	2.42	-
$Et_4N^+[Cl_3SnCr(CO)_5]^-$	96	135-138 dec.	28.53	3.68	2.56	19.43	28.37	3.82	2.64	19.56
$Et_4N^+[Ph_3SnCr(CO)_5]^-$	75	164-166 dec.	55.41	5.25	2.10	-	55.10	5.25	2.10	-
$Et_4N^+[Me_3SnCr(CO)_5]^-$	64	~160 dec.	39.53	6.01	2.88	-	39.68	5.95	3.39	-
$Et_4N^+[Ph_3PbCr(CO)_5]^-$	45	87-93	48.94	4.64	1.84	-	47.97	4.75	1.95	-
$Et_4N^+[Ph_3SiMo(CO)_5]^-$	73	150-154	59.51	5.64	2.24	-	58.80	5.71	2.25	-
$Et_4N^+[MePh_2SiMo(CO)_5]^-$	71	130-131	55.41	5.90	2.48	-	54.77	5.80	2.49	-
$Et_4N^+[Cl_3GeMo(CO)_5]^-$	74	~180 dec.	28.64	3.70	2.57	19.51	28.54	3.88	2.61	19.68
$Et_4N^+[Ph_3GeMo(CO)_5]^-$	57	150-153	55.56	5.26	2.09	-	54.79	5.44	2.04	-
$Et_4N^+[Cl_3SnMo(CO)_5]^-$	38	82-85	26.41	3.41	2.37	17.99	26.43	3.76	2.61	18.98
$Et_4N^+[Ph_3SnMo(CO)_5]^-$	58	139	51.98	4.92	1.96	-	51.62	5.06	2.18	-
$Et_4N^+[Me_3SnMo(CO)_5]^-$	58	>220°	36.26	5.51	2.64	-	35.52	5.54	3.39	-
$Et_4N^+[Ph_3PbMo(CO)_5]^-$	43	129-131	46.27	4.38	1.74	-	45.81	4.33	1.92	-
$Et_4N^+[Ph_3SiW(CO)_5]^-$	85	165	52.18	4.94	1.96	-	51.70	5.00	1.86	-
$Et_4N^+[MePh_2SiW(CO)_5]^-$	91	132-135 dec.	47.93	5.10	2.15	-	47.28	5.14	2.25	-
$Et_4N^+[Cl_3GeW(CO)_5]^-$	100	174 dec.	24.66	3.18	2.21	16.70	24.74	3.29	2.18	17.37
$Et_4N^+[Ph_3GeW(CO)_5]^-$	55	163-165	49.12	4.65	1.85	-	49.05	4.42	1.95	-

TABLE XVI (continued)

Compound	% Yield	M.P. (°C)	Calcd. %				Found %			
			C	H	N	Cl	C	H	N	Cl
$Et_4N^+[Br_3SnW(CO)_5]^-$	42	138-140	19.22	2.48	1.72	29.50(Br)	19.38	2.39	1.68	29.32(Br)
$Et_4N^+[Cl_3SnW(CO)_5]^-$	90	130 dec.	22.99	2.97	2.06	15.66	22.99	2.97	2.37	14.39
$Et_4N^+[Cl_2PhSnW(CO)_5]^-$	88	95-96	31.66	3.50	1.94	9.84	31.59	4.01	2.06	10.83
$Et_4N^+[ClPh_2SnW(CO)_5]^-$	61	100-104	39.38	3.97	1.84	4.65	38.84	4.10	1.53	5.14
$Et_4N^+[Ph_3SnW(CO)_5]^-$	72	142 dec.	46.30	4.37	1.74	-	46.51	4.45	2.31	-
$Et_4N^+[Me_3SnW(CO)_5]^-$	87	181	31.10	4.73	2.27	-	30.86	4.70	3.13	-
$Et_4N^+[Ph_3PbW(CO)_5]^-$	59	140-144 dec.	41.71	3.95	1.57	-	41.25	3.94	1.45	-
$Et_4N^+[Ph_3SiFe(CO)_4]^-$	82	205-209 dec.	64.63	6.33	2.51	-	65.70	6.64	2.36	-
$Et_4N^+[Ph_3GeFe(CO)_4]^-$	86	196-200	59.85	5.86	2.53	-	59.25	6.12	2.63	-
$Et_4N^+[Ph_3SnFe(CO)_4]^-$	75	158-160 dec.	55.59	5.44	2.16	-	55.29	5.57	2.40	-
$Ph_3GeFe(CO)_4H$	59	-	55.93	3.41	-	-	55.80	4.06	-	-

tetraethylammonium chloride was purchased from Aldrich Chemical Co., Milwaukee, Wis. Group IV reagents were obtained from Pierce Chemical Co., Rockford, Ill.

The $Et_4N^+[M(CO)_5X]^-$ (M = Cr, Mo or W; X = Cl or Br) compounds were prepared by the literature method[122] and were recrystallized before use.

Preparation of tetraethylammonium (triphenylsilicon)-pentacarbonylchromium, $Et_4N^+[Ph_3SiCr(CO)_5]^-$

About 6 cm of lithium wire was wrapped in a piece of polyethylene, pounded with a hammer, cut into small pieces and dropped into ca. 25 ml THF solution containing Ph_3SiCl (3.5 g, 11.9 mmol). The solution was magnetically stirred for 3-4 hours by which time it had become deep red. It was then transferred by means of a 50 ml syringe, taking care to leave any excess lithium behind, and added slowly to a solution of $Et_4N^+[Cr(CO)_5Cl]^-$ (3.3 g, 9.2 mmol) in 50 ml THF. The reaction mixture was stirred at room temperature for 1 hr and then the solvent removed under reduced pressure. The sticky solid residue was extracted with ca. 120 ml dichloromethane, filtered through celite and ether was added to precipitate a white solid. The analytical sample was recrystallized twice from dichloromethane-ether to give 4.4 g (82% yield) of flaky white crystals.

Preparation of tetraethylammonium (trichlorogermanium)-pentacarbonylchromium, $Et_4N^+[Cl_3GeCr(CO)_5]^-$

1.5 mls of $HGeCl_3$ (2.7 g, 15.0 mmol) was added to a magnetically stirred solution of $Et_4N^+[Cr(CO)_5Cl]^-$ (3.0 g, 8.4 mmol) in 80 ml dichloromethane. The solution was heated to reflux for 15 min and then filtered through Celite. Addition of ether precipitated a pale yellow compound which was collected and shaken up with a methanol-water (1:1) solution to remove yellow adsorbed impurities. This was filtered, dried, and recrystallized from dichloromethane-ether to give 3.3 g (78% yield) of white crystals.

Preparation of tetraethylammonium (trichlorotin)pentacarbonylmolybdenum, $Et_4N^+[Cl_3SnMo(CO)_5]^-$

Dichlorotin (2.0 g, 10.6 mmol) and $Et_4N^+[Mo(CO)_5Cl]^-$ (3.0 g, 7.5 mmol) were refluxed in 80 ml dichloromethane for 1 hr. The yellow solution became pale orange and was filtered through Celite. Addition of ether precipitated an oil; the solvents were decanted and the oil washed with ether and *n*-pentane. This was then extracted with 60 ml dichloromethane, 40 ml ether was added and the solution was filtered leaving behind an orange solid residue. An additional 20 ml of ether was added to the colorless solution and it was left to cool overnight at 0° affording the white crystalline product; 1.7 g (38% yield).

Preparation of tetraethylammonium (trimethyltin)pentacarbonylmolybdenum, $Et_4N^+[Me_3SnMo(CO)_5]^-$

To a solution of Sn_2Me_6 (1.8 g, 8.6 mmol) in ca. 25 ml THF, lithium clippings were added and the solution stirred for 1 hr. The deep red solution was added to a solution containing $Et_4N^+[Mo(CO)_5Cl]^-$ (3.1 g, 7.7 mmol) in ca. 100 ml of THF and the reaction mixture stirred for 1 hr. The solvent was removed and the solid residue extracted with dichloromethane and filtered through a 10 cm column packed with aluminium oxide. Addition of ether precipitated an oil which gave a pale yellow solid by pumping overnight in high vacuum. Careful recrystallization from dichloromethane-ether-pentane twice afforded the analytical sample; 2.4 g (58% yield).

Preparation of tetraethylammonium (triphenyllead)pentacarbonylmolybdenum, $Et_4N^+[Ph_3PbMo(CO)_5]^-$

To a solution containing Ph_3PbCl (5.0 g, 10.6 mmol) in Ca. 25 ml THF was added lithium clippings. The reaction was slightly exothermic, the mixture turning black after ca. 3 hr stirring. The organolithium solution was then added to a solution of $Et_4N^+[Mo(CO)_5Cl]^-$ (3.6 g, 9.0 mmol) in 100 ml THF and the reaction mixture was stirred for an additional 0.5 hr. The solvent was removed under reduced pressure, the solid residue extracted with dichloromethane and filtered through Celite. The solution was concentrated and ether was added in ca. 5 ml portions until the solution became cloudy. On cooling overnight, white crystals were formed which were filtered and collected affording 3.1 g (43% yield). The sample was sufficiently pure for further reaction, however, the analytical sample was recrystallized twice from dichloromethane-ether.

Preparation of tetraethylammonium (triphenylgermanium)-pentacarbonyltungsten, $Et_4N^+[Ph_3GeW(CO)_5]^-$

Hexaphenyldigermanium (3.5 g, 6.5 mmol) or alternatively Ph_3GeCl (3.2 g, 10.6 mmol) in 20 ml THF was treated with lithium wire. The reaction was slightly exothermic and a milky precipitate appeared. The disappearance of the white precipitate was followed by color changes from deep yellow through dark green to a deep red color over a period of 4 to 6 hr (3 hr for Ph_3GeCl). This was added slowly to a 100 ml THF solution of $Et_4N^+[W(CO)_5Cl]^-$ (4.5 g, 9.3 mmol) and stirred for 0.5 hr. The solvent was removed under reduced pressure. The residue was extracted with dichloromethane, filtered through Celite and the solution concentrated by passing nitrogen. On cooling at 0° overnight fluffy white crystals were formed; 4.5 g, 55% yield.

Preparation of tetraethylammonium (diphenylchlorotin)-pentacarbonyltungsten, $Et_4N^+[ClPh_2SnW(CO)_5]^-$

A mixture of $Et_4N^+[Ph_3SnW(CO)_5]^-$ (2.38 g, 2.96 mmol) and $Et_4N^+[Cl_3SnW(CO)_5]^-$ (1.00 g, 1.47 mmol) was heated at 150° in the absence of solvent. The progress of the reaction was followed by the removal of samples at short intervals and recording the ir spectra in dichloromethane (see text). After 1 hr the mixture was cooled to room temperature and the crude product extracted with dichloromethane. The solvent was removed and the ensuing oil solidified on pumping overnight at 60°. Three recrystallizations from dichloromethane-ether afforded the analytical sample; 2.0 g, 88% yield. Trace amounts of starting materials were difficult to eliminate.

The $PhSnCl_2$ analogue was prepared in a similar fashion using the reverse mole ratios of starting materials.

Preparation of tetraethylammonium hydridoundecacarbonyltriferrate, $Et_4N^+[HFe_3(CO)_{11}]^-$

A mixture of $Et_3NH^+HFe_3(CO)_{11}^-$ (22 g, 38.0 mmol) and Et_4NCl (8 g, 49.3 mmol) were stirred for 0.5 hr in dichloromethane. The solvent was removed on a rotary evaporator (water aspiration). The deep red crystalline compound was washed with several portions of water and pumped dry overnight. Samples for further reaction were recrystallized from methanol prior to use.

Preparation of tetraethylammonium (triphenyltin)tetracarbonyliron, $Et_4N^+[Ph_3SnFe(CO)_4]^-$

A solution containing Sn_2Ph_6 (8 g, 11.5 mmol) in 50 ml THF was treated with cut-up pieces of lithium wire and the reaction mixture stirred for ca. 3 hr. The resulting $LiSnPh_3$ solution was added to 100 ml THF solution of $Et_4N^+[HFe_3(CO)_{11}]^-$ (10.0 g, 16.6 mmol). Initially 20 ml of the organolithium compound was added and the progress of the reaction monitored by the ir spectra. Additional 5 ml portions were added until the bands due to starting material had disappeared. The THF solvent was removed in vacuo and the solid residue washed with several portions of water until the washings became free of a red coloration. The brown residue was dried by pumping overnight, then dissolved in a minimum of THF and filtered through a column packed [illegible] a layer of aluminum oxide (5 cm) and Celite (5 cm [illegible]ion of ether precipitated a cream colored crude [illegible]uct; 8 g, 75% yield. The analytical sample was recrystallized from THF-ether to give white crystals.

Preparation of triphenylgermanium(hydrido)tetracarbonyliron

An HCl solution was prepared by passing HCl gas through ether for ca. 30 min; and its molarity was calculated by titrating 10 ml aliquots placed in water, with a standard NaOH solution. The above solution (1.5 ml, 4.0 mmol) was added to a solution containing $Et_4N^+[Ph_3GeFe(CO)_4]^-$ (2.0 g, 3.6 mmol) in 25 ml THF cooled to 0°. The solution was then stirred under closed vacuum for 20 min, a white precipitate was formed. The THF was removed while maintaining the reaction at 0° and iso-pentane was distilled into the reaction mixture. The nearly colorless extract was filtered and the iso-pentane removed in vacuo, affording 1.0 g (59% yield) of the crude product. The analytical sample was prepared from a second preparation, by coolin [illegible] iso-pentane solution at -78°.

Apart from being air-sensitive the compound appears to be thermally unstable and solutions at room temperature deteriorate very quickly.

CHAPTER VI

NITROSYL DERIVATIVES OF MAIN GROUP IV-MOLYBDENUM AND -TUNGSTEN CARBONYLS

INTRODUCTION

Developments in transition metal nitrosyl chemistry have been reviewed by Johnson and McCleverty,[159] Griffith,[160] and more recently by Connelly.[6]

In the past, organometallic nitrosyls have been prepared by treatment of metal carbonyls or their derivatives with nitric oxide, nitrite ion, nitrosyl halides or N-nitroso-N-methyl-p-toluenesulfonamide (DIAZALD). The use of nitrosonium salts such as $NOBF_4$ and $NOPF_6$ has come into prominence in the last three years. A representative list of reactions involving the use of the nitrosonium ion (NO^+) as a nitrosylating agent is given below.

$$C_5H_5Re(CO)_3 + NOHSO_4 \xrightarrow[CH_2Cl_2]{40°} [C_5H_5Re(CO)_2NO]^+HSO_4^- \quad {}^{161} \qquad \text{VI-1}$$

$$IrCl(CO)(PPh_3)_2 + NOBF_4 \xrightarrow[C_6H_6/CH_3OH]{25°} [IrCl(CO)(NO)(PPh_3)_2]^+BF_4^- \quad {}^{162} \qquad \text{VI-2}$$

$$(C_6H_5Me)Cr(CO)_3 + NOPF_6 \xrightarrow{CH_3CN} [Cr(NO)_2(CH_3CN)_4]^{2+}(PF_6^-)_2 \quad {}^{163} \qquad \text{VI-3}$$

$M(CO)_6 + NOPF_6 \xrightarrow[CH_3CN]{} [M(NO)_2(CH_3CN)_4]^{2+}(PF_6^-)_2$ 164 VI-4

(M = Cr, Mo, or W)

$Fe(CO)_3(PPh_3)_2 + NOPF_6 \xrightarrow[CH_3CN]{} [Fe(CO)_2NO(PPh_3)_2]^+PF_6^-$ 165 VI-5

$Ru_3(CO)_9(PPh_3\text{[illegible]} + NOPF_6 \xrightarrow[CH_3OH]{} [Ru(CO)_2NO(PPh_3)_2]^+PF_6^-$ 165 VI-6

$C_5H_5M(CO)PPh_3 + NOPF_6 \xrightarrow[CH_3OH/C_7H_8]{} [C_5H_5M(NO)PPh_3]^+PF_6^-$ 166 VI-7

(M = Co, Rh, or Ir)

$Ni(CO)_2(PPh_3)_2 + NOPF_6 \xrightarrow[CH_3OH/C_7H_8]{} [\text{[illegible]}(NO)(PPh_3)_3]^+PF_6^-$ 167 VI-8

$M(CO)_4(dpe) + NOP\text{[illegible]} \xrightarrow[CH_3OH/C_7H_8]{} [M(CO)_3(NO)\text{[illegible]}]^+PF_6^-$ 167,168 VI-9

(M = Mo or W)

$Et_4N^+[W(CO)_5X]^- + NOHSO_4 \xrightarrow[CH_2Cl_2]{} W(CO)_4(NO)X$ 169 VI-10

(X = Cl, Br, or I)

$Mn(CO)\{P(OMe)_3\}_4Br + NOPF_6 \xrightarrow[CH_3CN]{}$

$[Mn(CO)(NO)\{P(OMe)_3\}_4]^{2+}(PF_6^-)_2$ 170 VI-11

$(C_6Me_{6-n}H_n)Cr(CO)_2L + NOPF_6 \xrightarrow[CH_3OH/C_7H_8]{}$

(n = 0-3,
L = CO or PPh$_3$)

$[(C_6Me_{6-n}H_n)Cr(CO)(NO)L]^+PF_6^-$ 171 VI-12

$R_4C_4Fe(CO)_3 + NOPF_6 \xrightarrow[CH_3CN]{} [R_4C_4Fe(CO)_2NO]^+PF_6^-$ 172 VI-13

R = H, Me or Ph)

With the exception of VI-10, all of the above reactions involve the formation of cationic nitrosyl complexes from the neutral metal carbonyls. The reaction of NO^+ with some metal carbonyl anions has been investigated by Okamoto,[164] who found that weak nucleophiles such as $[Co(CO)_4]^-$ produced the neutral nitrosyl, $Co(CO)_3NO$. Strong nucleophiles, $[C_5H_5Fe(CO)_2]^-$ and $[Re(CO)_5]^-$ were oxidized to their respective dimers. Anions of intermediate nucleophilic strength, $[C_5H_5Mo(CO)_3]^-$ and $[Mn(CO)_5]^-$ produced both their respective dimers and nitrosyl derivatives, $C_5H_5Mo(CO)_2NO$ and $Mn(CO)_4NO$.

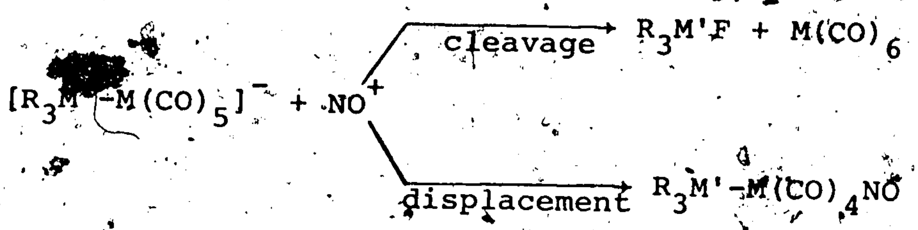
In addition to its ability to act as a reagent in the preparation of nitrosyls by replacement of CO groups, NO^+ has been utilized as a single electron oxidizing agent. In poorly co-ordinating solvents such as dichloromethane, single electron oxidation takes place without solvent inclusion into the metal co-ordination sphere,[170-173,174] whereas in acetonitrile solution oxidized products containing CH_3CN bonded to the metal atom are formed.[163,164,166]

The present chapter describes the products obtained by the interaction of NO^+ with some of the anionic complexes prepared in chapter V.

RESULTS AND DISCUSSION

In the treatment of the $[R_3M'-M(CO)_5]^-$ salts, prepared in chapter V, with the nitrosonium cation, there are two potential points of chemical reaction, the metal-metal or metal-carbonyl linkages. The former represents NO^+ as a one electron oxidant and will depend on the strength of the metal-metal bond. The latter involves the displacement of CO by the e[illegible]philic NO^+ and, as suggested by Okamoto,[164] may depend on the nucleophilic properties of the anions.

All reactions were performed in dichloromethane, often at -78°. The course of the reactions and the products isolated can be summarized by the two competitive processes shown below:



$$[R_3M'-M(CO)_5]^- + NO^+ \xrightarrow{\text{cleavage}} R_3M'F + M(CO)_6 \qquad \text{VI-14}$$

$$[R_3M'-M(CO)_5]^- + NO^+ \xrightarrow{\text{displacement}} R_3M'-M(CO)_4NO \qquad \text{VI-15}$$

The source of fluorine in VI-14 is assumed to be the PF_6^- counterion. Nitrosyl substituted products were characterized where M = Mo, R_3M' = $GePh_3$, $SnPh_3$, $SnMe_3$, and $PbPh_3$; M = W, R_3M' = $SiPh_3$, $SiPh_2Me$, $GePh_3$, $SnPh_3$, $SnMe_3$, and $PbPh_3$. A binuclear species, $Me_2Sn[W(CO)_4NO]_2$ was also isolated and will be discussed separately.

The yield in these reactions was reduced by the formation of relatively large amounts of hexacarbonyls (pathway VI-14) and decreased in going from tungsten to molybdenum. In the chromium series no evidence for the formation of any nitrosyl product was detected. A comparison of the yields offers a crude view of the oxidative stability of the metal-metal bonds. Thus it appears that the Ge-Mo and Ge-W bonds are the most stable. The Si-Mo linkage is easily cleaved, as evidenced by the failure to isolate a nitrosyl containing species, whereas the Si-W bond is dramatically less sensitive to oxidation as evidenced by the relatively high yield of $Ph_3SiW(CO)_4NO$.

The compounds $R_3M'F$ (R_3M' = $SiPh_3$, $SiPh_2Me$, $GePh_3$ and $SnPh_3$) were isolated and identified mass spectrometrically. The ^1H nmr spectrum of $MePh_2SiF$ displayed a doublet in the methyl region (J_{Me-F} = 7 Hz) and the ^{19}F nmr a quartet with an identical coupling constant.

The $[W(CO)_5X]^-$ salts (X = Cl, Br and I) were also treated with $NOPF_6$ resulting in the formation of the pale yellow compounds, $W(CO)_4(NO)X$. The preparation of the identical derivatives has been reported by Barraclough et. al.[169] since the commencement of this work. We found that the reaction could be conveniently carried out using acetonitrile as solvent and an excess of $NOPF_6$. The excess NO^+ reacted with any $W(CO)_6$

formed in the known fashion, VI-4.[163,164,175] The reaction was followed by ir and $NOPF_6$ was added in small batches until the band due to $W(CO)_6$ gradually diminished. In this way the tedious separation of the nitrosyl halide complexes from $W(CO)_6$ was avoided. The excess NO^+ did not appear to substantially decrease the amount of product formed.

When treated with NO^+, $[X_3SnW(CO)_5]^-$ (X = Cl and Br) reacted with the elision of the SnX_2 group and formation of the nitrosyl halides, $W(CO)_4(NO)X$. In fact for X = Cl, a better yield of the chloronitrosyl complex was obtained in VI-16 than from the direct reaction of the pentacarbonyl ch[illegible]

$$[Cl_3SnW(CO)_5]^- + NO^+ \xrightarrow[CH_2Cl_2]{} W(CO)_4(NO)Cl + SnCl_2 + CO \qquad \text{VI-16}$$

The reaction of NO^+ with the binuclear anionic complexes, $Et_4N^+[MnW(CO)_{10}]^-$ [176] and $[Et_4N^+]_2[W_2(CO)_{10}]^{2-}$ [177] was also investigated. The former reacted, in both CH_2Cl_2 and CH_3CN solvents, with the cleavage of the Mn-W bond; $W(CO)_6$ and $[CH_3CNMn(CO)_5]^+$ [163] were the only carbonyl species identified. The $[W_2(CO)_{10}]^{2-}$ anion reacted in CH_2Cl_2 forming mainly $W(CO)_6$ but also the known $HW_2(CO)_9NO$.[178] This was identified by its ir spectrum and an exact mass measurement of the parent ion in the mass spectrum (calcd. = 650.8620; found = 650.8656).

The nitrosyl complexes prepared formed pale yellow to red-orange crystals which are air stable, deteriorating only after long exposure. They are soluble in common organic solvents such as *n*-pentane, benzene, and dichloromethane, although solutions decompose after a few hours in the presence of air. When irradiated with ultraviolet light, an *n*-hexane solution of $Ph_3SiW(CO)_4NO$ completely decomposed to a non-carbonyl product after 8 hr.

The formation of $Me_2Sn[W(CO)_4NO]_2$

In the reaction of $[Me_3SnW(CO)_5]^-$, the $Me_3SnW(CO)_4NO$ and $W(CO)_6$ formed were sublimed in vacuo at room temperature leaving behind an orange material. This was purified by recrystallization from *n*-pentane and identified as the dinuclear species, $Me_2Sn[W(CO)_4NO]_2$. In the mass spectrum the measured mass of the parent ion, 799.8052, agrees well with the computed mass, 799.8062.

The infrared spectrum is presented in Figure 40. A total of six carbonyl bands can be distinguished if a poorly resolved shoulder is included. The appearance of six bands may be attributed to the coupling of the two $W(CO)_4NO$ groups across the tin atom, as has been observed in other iso-structural systems.[179,180] The bands at 1719 and 1711 cm^{-1} are due to the nitrosyl groups. Two possible geometries for the molecule are

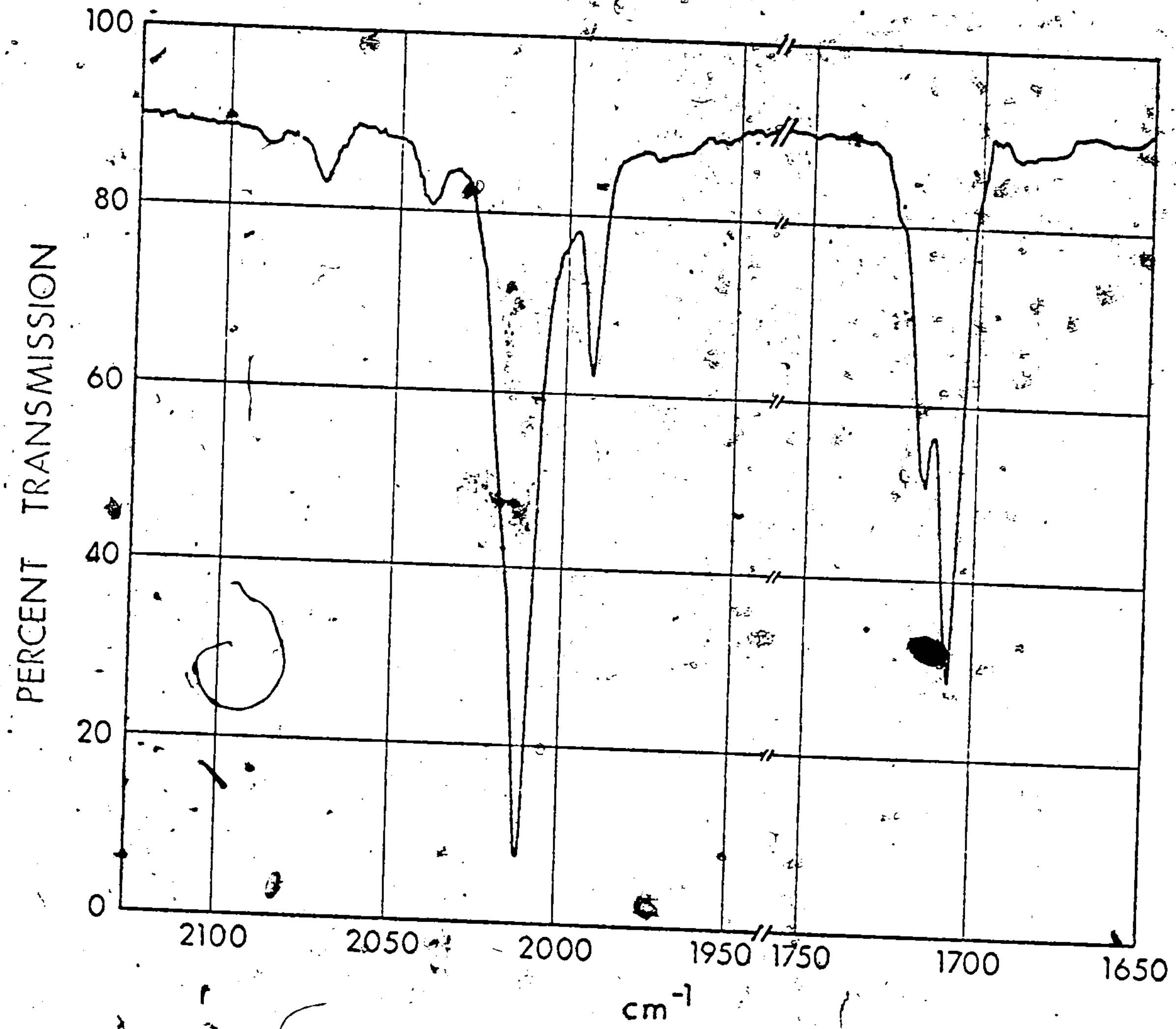
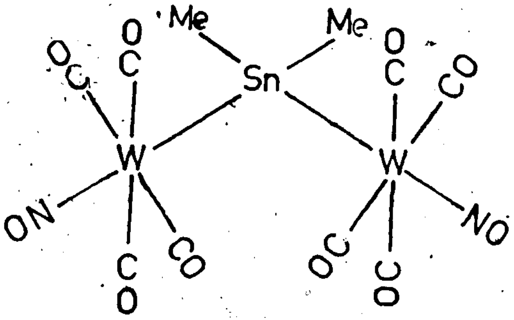
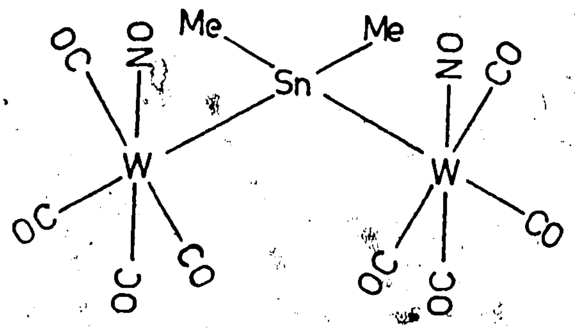


Figure 40. $Me_2Sn[W(CO)_4NO]_2$ in *n*-hexane.

shown in 42 and 43, with either axial or equatorial nitrosyl groups respectively.



42



43

Ideally, in both cases the over-all molecular symmetry is C_{2v}, whence group theory predicts seven ir-active bands ($3A_1 + 3B_1 + B_2$). This is the minimum number of bands predicted, the maximum being eight. Fewer bands are observed than the minimum predicted, which is not surprising, as one band may be weak or accidentally degenerate. Clearly the number of ir bands cannot be used to distinguish possible geometries, and a decision on the basis of relative intensity of the bands is hazardous. On the basis that the monomeric complexes have the group IV ligand trans to the nitrosyl group (see next section), 42 is more likely.

The ^1H nmr spectrum is odd in that *no* coupling which could be attributed to $Sn-CH_3$ was observed (see

Tables XII and XVII for typical values of J(Sn-CH_3)). Instead the methyl resonance at 9.9 τ (C_6D_6) was flanked by two satellites separated by 7.5 Hz. One would normally associate this value (7.5 Hz) at the natural abundance of the satellites (Ca. 5%) with a methyl group on Si. The presence of Si (the glass reaction vessel being the presumed source) can be excluded on the basis of the mass spectrum, run on the same sample used for the nmr experiment, showing no peaks which could be attributed to a Si containing fragment. The measured exact mass of the parent ion (799.8052) makes a species such as $Me_2SiSnW_2(CO)_7NO^+$ (calculated mass of parent ion, 799.8242) unlikely. Moreover, nmr spectra in solvents such as $CDCl_3$, CCl_4, CH_2Cl_2 and C_6D_{12} (taking care to exclude TMS in all cases), on samples of the compound from different preparative runs, consistently gave the same result. We are unable to provide an explanation for this apparent contradiction at this time.

Infrared spectra

The monomeric nitrosyl compounds prepared could exist as *cis* or *trans* isomers. The results of the infrared spectra (Table XVII) are indicative of a *trans* geometry (C_{4v} symmetry), with a planar carbonyl configuration about the metal.

The symmetry co-ordinates for *trans*-$M(CO)_4XY$

TABLE XVII

CARBONYL AND NITROSYL STRETCHING FREQUENCIES, ASSIGNMENT AND NMR DATA[a-d] FOR THE NITROSYL COMPLEXES

Compound	Carbonyl stretching frequencies (cm^{-1})					Nitrosyl Stretching Frequencies (cm^{-1})
	all ^{12}CO (C_{4v})			mono-^{13}CO (C_s)		
	A_1	B_1	E	A'(A_1)	A'(E)	
$Ph_3GeMo(CO)_4NO$	2105	2046.5	2027.5	2097	1998	1722
$Ph_3SnMo(CO)_4NO$	2100.5	2040	2025	2092	1991	1725.5
$Me_3SnMo(CO)_4NO^a$	2091	-	2013	2082	1979	1718.5
$Ph_3PbMo(CO)_4NO$	2103	2045.5	2030.5	2095	1997	1727
$W(CO)_4(NO)Cl$	-	-	2051	-	2017	1703
$W(CO)_4(NO)Br$	2136	-	2048.5	-	2016	1707
$W(CO)_4(NO)I$	2131.5	-	2046.5	-	2013.5	1711
$Ph_3SiW(CO)_4NO$	2102.5	2034.5	2015	2095	1985	1715.5
$Ph_2MeSiW(CO)_4NO^b$	2098	2029.5	2009	-	1974	1713.5
$Ph_3GeW(CO)_4NO$	2104	2038	2019	2097	1985	1717.5
$Ph_3SnW(CO)_4NO$	2099.5	2034	2015	(2091)	1987.5	1720

TABLE XVII (continued)

Compound	Carbonyl stretching frequencies (cm^{-1}) all ^{12}CO (C_{4v}) A_1	 B_1	 E	 mono-^{13}CO (C_s) $A'(A_1)$	 $A'(E)$	Nitrosyl Stretching Frequencies (cm^{-1})
$Me_3SnW(CO)_4NO^c$	2089	-	2004.5	2082	1973	1715.5
$Ph_3PbW(CO)_4NO$	2100.5	2035.5	20[illegible]	2093	1986	1721
	← ν(CO) $3A_1 + 3B_1 + B_2$ (C_{2v}) →					← ν(NO) →
$Me_2Sn[W(CO)_4NO]_2$ ^{d}	2089(.3)	2073(.9)	20[illegible]([illegible].2)	2018 sh(4.9)		1719,1711
	2012(10)		1991.5(2.3)			

---

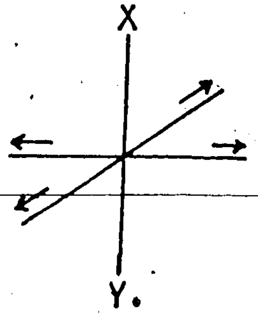
[a] τ_{Sn-CH_3} = 9.8; $J(Sn-CH_3) \approx 40$ Hz; CCl_4 with TMS as external standard.

[b] τ_{Si-CH_3} = 9.15; CCl_4 with TMS as internal standard.

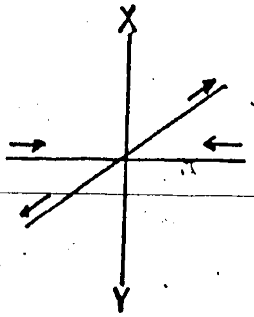
[c] τ_{Sn-CH_3} = 9.73; $J(^{117}Sn-CH_3)$ = 45.3 Hz, $J(^{119}Sn-CH_3)$ = 47.7; $CDCl_3$ relative to acetone at 7.95 τ.

[d] τ_{Sn-CH_3} = 9.86; $J \approx 7.5$ Hz (see text); in C_6D_6 relative to C_6H_6 at 2.73 τ.

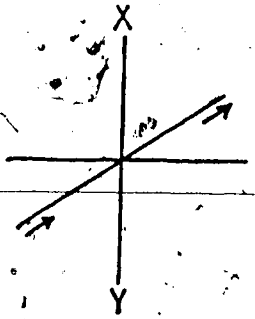
molecules are shown below.



A_1



B_1



E

Group theory predicts two ir active CO stretches $(A_1 + E)$.

The infrared spectrum of a typical molecule, $Ph_3SiW(CO)_4NO$, measured in *n*-hexane is shown in Figure 41. Intensity arguments such as those first put forward by Orgel,[181] allow the assignment of the most intense carbonyl band at 2015 cm^{-1} to the E mode. The very weak band at highest frequency (~ 2100 cm^{-1}) is assigned to the A_1 mode. The weak absorption at 2034 cm^{-1} is attributed to the ir-inactive B_1 mode, which has gained some intensity in the ir due to deviation from true C_{4v} symmetry. The band at 1718 cm^{-1} is due to the nitrosyl group.

The lower trace shows the spectrum of a concentrated solution, which allows the A_1 band to be measured more accurately at 2102.5 cm^{-1}. The weak band at 2095 cm^{-1} on the low energy side of the A_1 band may be attributed to the $A'(A_1)$ of the mono-isotopic species

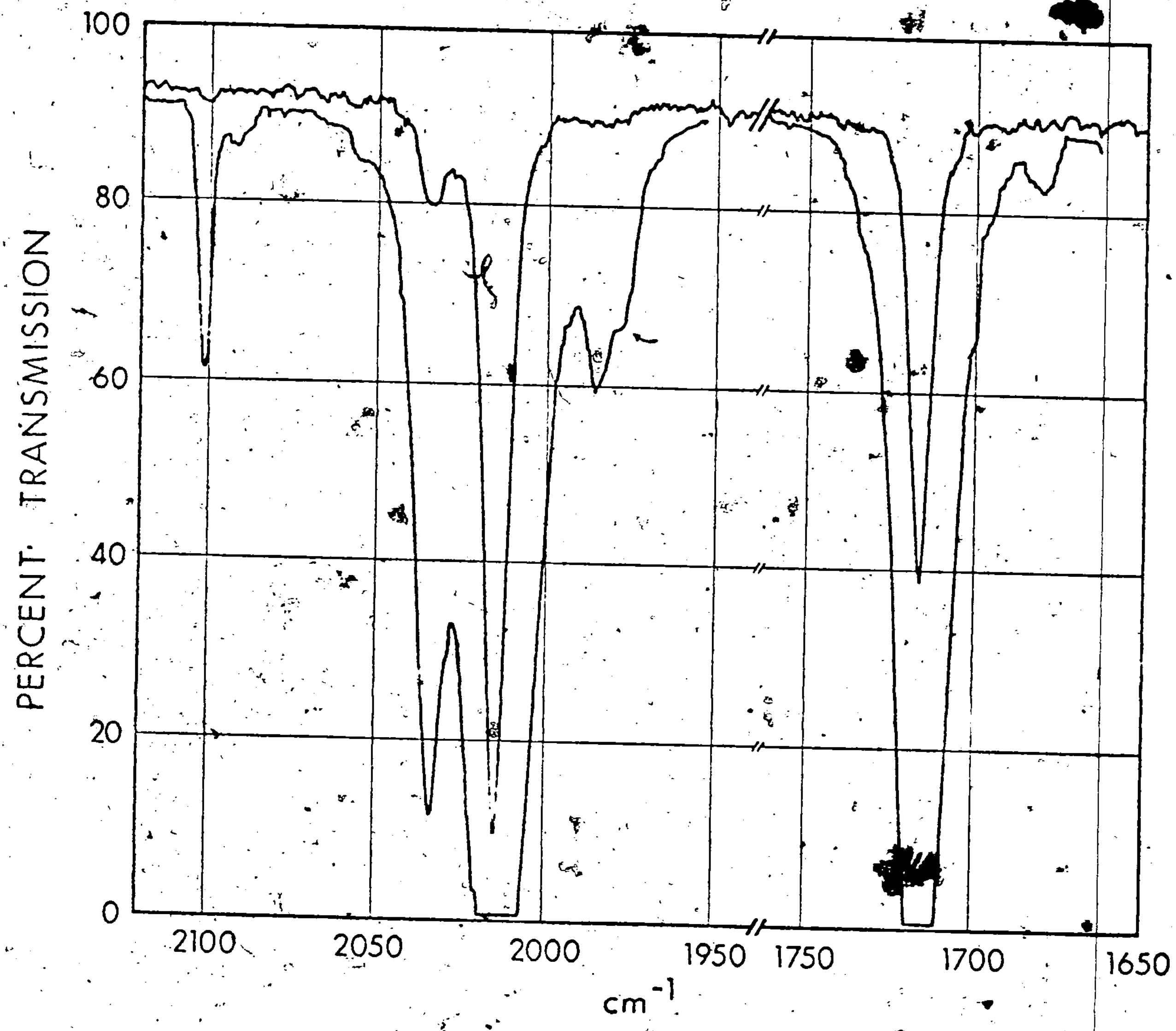


Figure 41. $Ph_3SiW(CO)_4NO$ in *n*-hexane.

W $^{12}CO)_3(^{13}CO)(NO)SiPh_3$ (isotope shift 7.5 cm^{-1}). The absorption at 1985 cm^{-1}, on the low energy side of the E mode, is due to the A'(E) of the mono-^{13}CO species (isotopic shift 30 cm^{-1}). The shoulder to the latter at 1983 cm^{-1} (see arrow) is due to trace amounts of $W(CO)_6$ still present even after pumping in high vacuum for 5 days.

The infrared spectrum of $W(CO)_4(NO)Br$ together with the solid state Raman spectrum are shown in Figure 42. In the ir spectrum the E mode is at 2048.5; the A_1 mode is barely visible even in the concentrated lower trace spectrum. The band at 2016 cm^{-1} is ascribed to the A'(E) mode of the mono-^{13}CO and the ir inactive B_1 mode is not discernible. The Raman spectrum confirms these assignments; the three strong carbonyl modes, at 2140, 2083 and 2066 cm^{-1} are ascribed to the A_1, B_1 and E Raman active modes respectively. The weak band at 2039 cm^{-1} is due to the ^{13}CO frequency of the E mode as noted above. The two additional weak bands in the concentrated trace are presumed to be due to some impurity. The splitting of the nitrosyl band is attributed to a solid state effect. The Raman spectra of the halide derivatives have been reported by Barraclough et. al.[169] and are similar to the above.

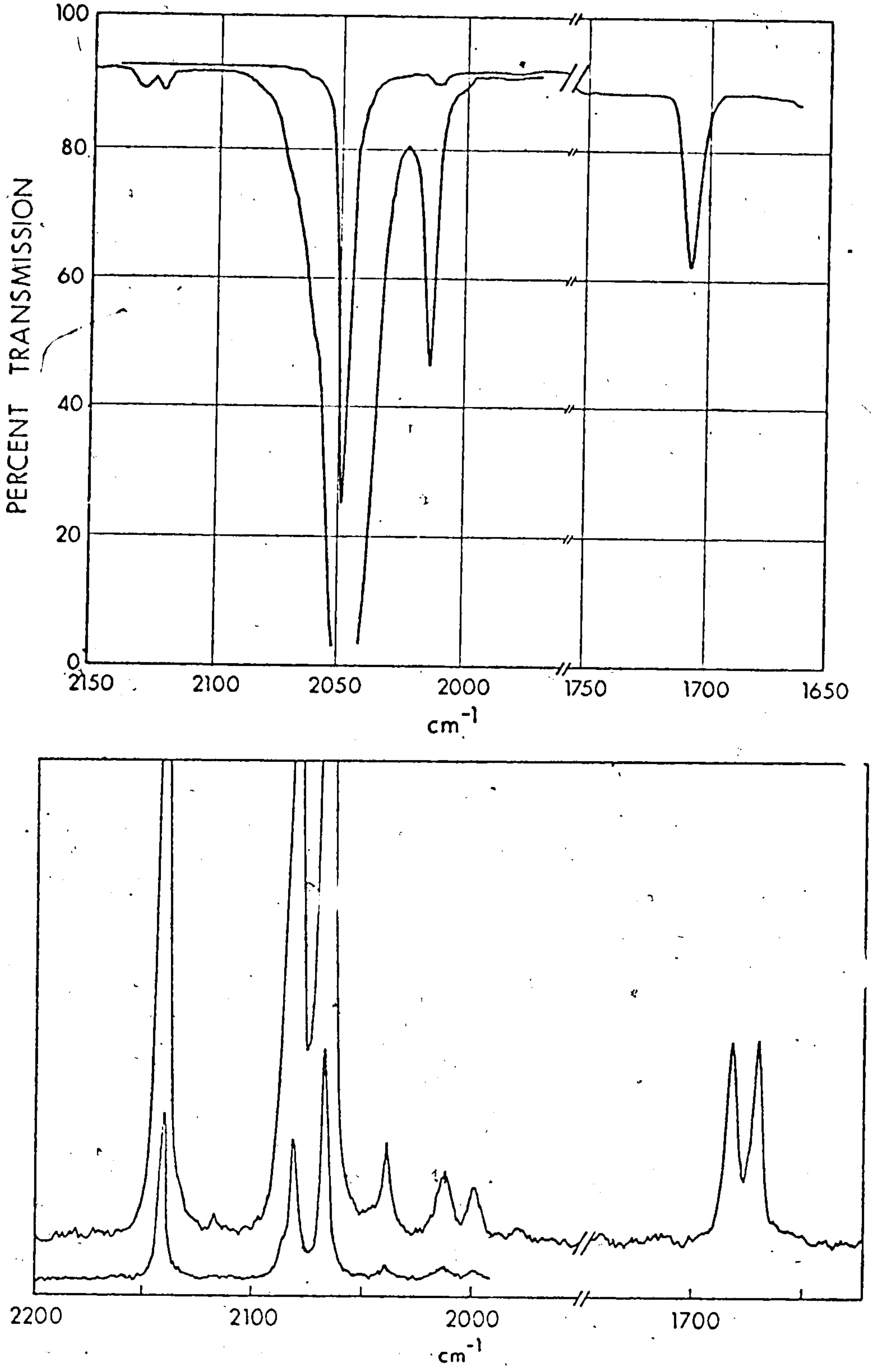
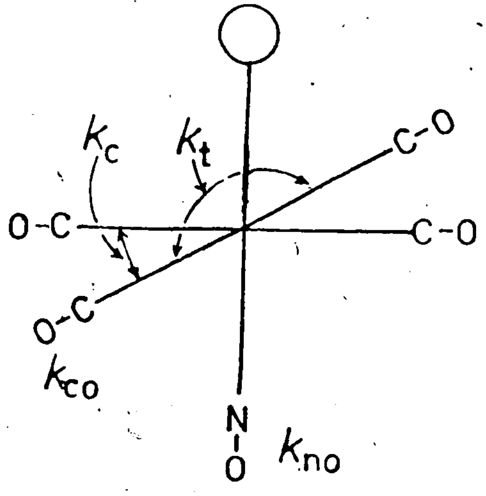


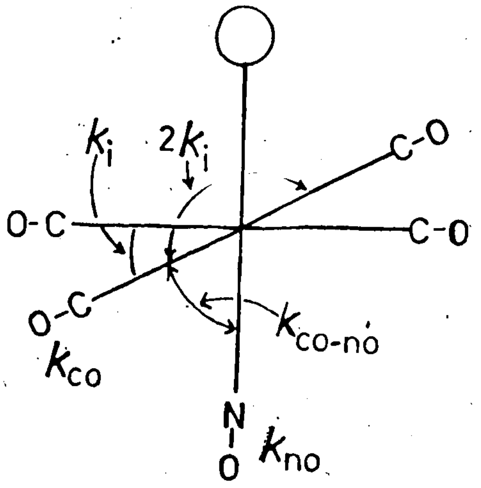
Figure 42, The ir (top) and raman (bottom) spectra of $W(CO)_4(NO)Br$; measured in *n*-hexane and in the solid state respectively.

Force constants

Non-rigorous force constants were calculated using two models; these are defined together with their respective force fields, in 44 and 45.



44



45

In previous force constant calculations involving carbonyl-nitrosyl complexes, the interaction terms between C-O and N-O were assumed to be the same as CO-CO,[182] inferred indirectly,[183] or disregarded on the assumption that they were small.[184]

Model 44 assumes no interaction between the C-O and N-O vibrators and the complete set of carbonyl force constants consists of one CO stretching constant (k_{CO}) and two CO interaction constants (k_c and k_t). At least four and in some cases five input carbonyl frequencies were utilized in the calculation. Since only three frequencies are needed, a check for the closeness of the fit was obtained. The nitrosyl force constants (k_{NO}) were calculated separately using the single nitrosyl band. The results of the calculation are given in Table XVIII.

It seemed useful to compare the force constants obtained as described above to those using model 45, which allowed for interaction between the C-O and N-O vibrators. This model gives rise to an additional interaction constant (k_{CO-NO}) and in this calculation the Cotton-Kraihanzel force field ($k_i = k_c = 1/2\ k_t$) was included. The nitrosyl frequency was incorporated in the input and the reduced mass of the N-O was included in the G matrix. Results are listed in Table XIX.

A comparison of the data from the two models reveals that the CO force constants calculated by both methods are essentially identical. In contrast the nitrosyl force constant k_{NO} is ca. 0.5 mdyn/Å greater when the interaction terms are included. In terms of the principal carbonyl force constants the results indicate that to a good approximation, the interaction between the C-O and N-O vibrators can be ignored. The CO-NO interaction constants k_{CO-NO} are unusually large, the significance of which is not apparent. The assumption of previous workers that k_{CO-NO} was equal to[182] or much smaller than[184] k_{CO-CO} is not substantiated in this study.

TABLE XVIII

ENERGY FACTORED CARBONYL AND NITROSYL FORCE CONSTANTS FOR SOME NITROSYL COMPLEXES [a]

Compound	k_{CO}	k_{NO}	k_c	k_t
$Ph_3GeMo(CO)_4NO$	16.99	13.04	.24	.41
$Ph_3SnMo(CO)_4NO$	16.94	13.09	.25	.38
$Me_3SnMo(CO)_4NO$	16.74	12.99	.27	.37
$Ph_3PbMo(CO)_4NO$	17.02	13.12	.24	.36
$W(CO)_4(NO)I$	17.36	12.88	.27	.44
$Ph_3SiW(CO)_4NO$	16.85	12.94	.28	.44
$Ph_2MeSiW(CO)_4NO$	16.74	12.91	.29	.46
$Ph_3GeW(CO)_4NO$	16.89	12.97	.28	.44
$Ph_3SnW(CO)_4NO$	16.91	13.01	.19	.51
$Me_3SnW(CO)_4NO$	16.68	12.94	.25	.45
$Ph_3PbW(CO)_4NO$	16.88	13.03	.27	.40

---

[a] Calculated assuming no interaction between C-O and N-O vibrators (model 44); no restraints on the force field.

TABLE XIX

COTTON-KRAIHANZEL CARBONYL AND NITROSYL FORCE CONSTANTS FOR SOME NITROSYL COMPLEXES[a]

Compound	k_{CO}	k_{NO}	k_{CO-NO}	k_i
$Ph_3GeMo(CO)_4NO$	16.92	13.44	.75	.15
$Ph_3SnMo(CO)_4NO$	16.81	13.64	.85	.12
$Me_3SnMo(CO)_4NO$	16.57	13.70	.95	.10
$Ph_3PbMo(CO)_4NO$	16.90	13.62	.82	.12
$W(CO)$[illegible]$(NO)I$	17.22	13.43	.91	.15
$Ph_3SiW(CO)_4NO$	16.72	13.50	.87	.15
$Ph_2MeSiW(CO)_4NO$	16.63	13.40	.82	.17
$Ph_3GeW(CO)_4NO$	16.77	13.49	.84	.16
$Ph_3SnW(CO)_4NO$	16.72	13.56	.85	.15
$Me_3SnW(CO)_4NO$	16.61	13.20	.60	.19
$Ph_3PbW(CO)_4NO$	16.73	13.64	.90	.13

---

[a] Calculated by allowing for interaction between C-O and N-O vibrators (model 45); Cotton-Kraihanzel force field.

Table XX below compares the CO force constants obtained for the tungsten series to the radial CO force constants of the iso-electronic $LRe(CO)_5$ system. It is remarkable that for each particular L group the k_{CO} values are essentially identical.

TABLE XX

A COMPARISON OF RADIAL CARBONYL FORCE CONSTANTS (MDYN/Å) IN $LW(CO)_4NO$ and $LRe(CO)_5$ SYSTEMS

	$LRe(CO)_5$		$LW(CO)_4NO$	
L	k_2[a]	k_2[c]	k_{CO}[d]	k_{CO}[e]
I	17.39[b]		17.36	17.22
$SiPh_3$	16.83	16.88	16.85	16.72
$GePh_3$	16.86	16.91	16.89	16.77
$SnPh_3$	16.82	16.86	16.91	16.72
$SnMe_3$	16.67	16.72	16.68	16.61
$PbPh_3$	16.86	16.90	16.88	16.73

[a] Values from Reference 11 using refined Cotton-Kraihanzel force field.

[b] Reference 140; no restraints on force field.

[c] Values from Reference 142; Cotton-Kraihanzel force field.

[d] Values obtained using Model 44; no restraints on force field.

[e] Values obtained using Model 45; Cotton-Kraihanzel force field.

A possible interpretation of this result follows.

The two systems are iso-electronic but Re (Atomic Number 75) has an additional proton compared to W (Atomic Number 74). Likewise, NO^+ and CO are iso-electronic, differing only in that NO^+ possesses an additional proton. One may view the process of going from a Re-CO to W-NO as involving the removal of a proton from Re and transferring it to the carbon atom of CO. There are two possible consequences of this action:

(a) The lower nuclear charge, due to the removal of a proton from Re to form W, would lead to a destabilization of the metal levels, increased back-donation to the radial carbonyls, and hence to a *lower* k_{CO}.

(b) Placement of the proton on the CO to form NO^+ results in lower π^* levels for this ligand, hence more back-bonding by the metal to NO^+, and a *higher* k_{CO}.

Since the k_{CO} values remain the same, the two effects roughly cancel and the greater electron accepting power of NO^+ compensates for the difference in nuclear potential. This discussion assumes that changes in the σ-framework are negligible.

The excellent correspondence in the values of the two iso-electronic series substantiates the view of the linear nitric oxide as formally NO^+ [185] and indicates that NO^+ is a better π-acceptor than CO.

Mass spectra

Mass spectrometry was again used as a major means of determining the exact molecular formulae as was described in chapter III. The calculated and observed molecular ion isotope patterns of $Ph_3SnMo(CO)_4NO$, $Ph_3SiW(CO)_4NO$ and $Me_2Sn[W(CO)_4NO]_2$ are shown in Figure 43 as representative examples. Since there are only a few mass spectral investigations involving nitrosyl compounds,[186-188] it seemed useful to present in some detail the fragmentation patterns of a few typical compounds, Tables XXI to XXIII.

The mass spectrum of $Ph_3GeW(CO)_4NO$ (Table XXI) was relatively simple. Stepwise loss of CO groups from the parent ion occurred; simultaneous loss of the NO group became prominent only after the loss of three CO groups. Loss of phenyl groups from the parent did not take place and the carbonyl-free ion Ph_3GeW^+ (m/e 487) gave rise to the remaining fragmentation process. In the spectra of other aryl substituted group IV complexes the ions $Ph_2M'M(CO)_m(NO)_n^+$ (M' = Sn, Pb; M = Mo, W; m = 0-2, n = 0,1) were observed in low abundance.

The mass spectrum of $Me_3SnMo(CO)_4NO$ (Table XXII)

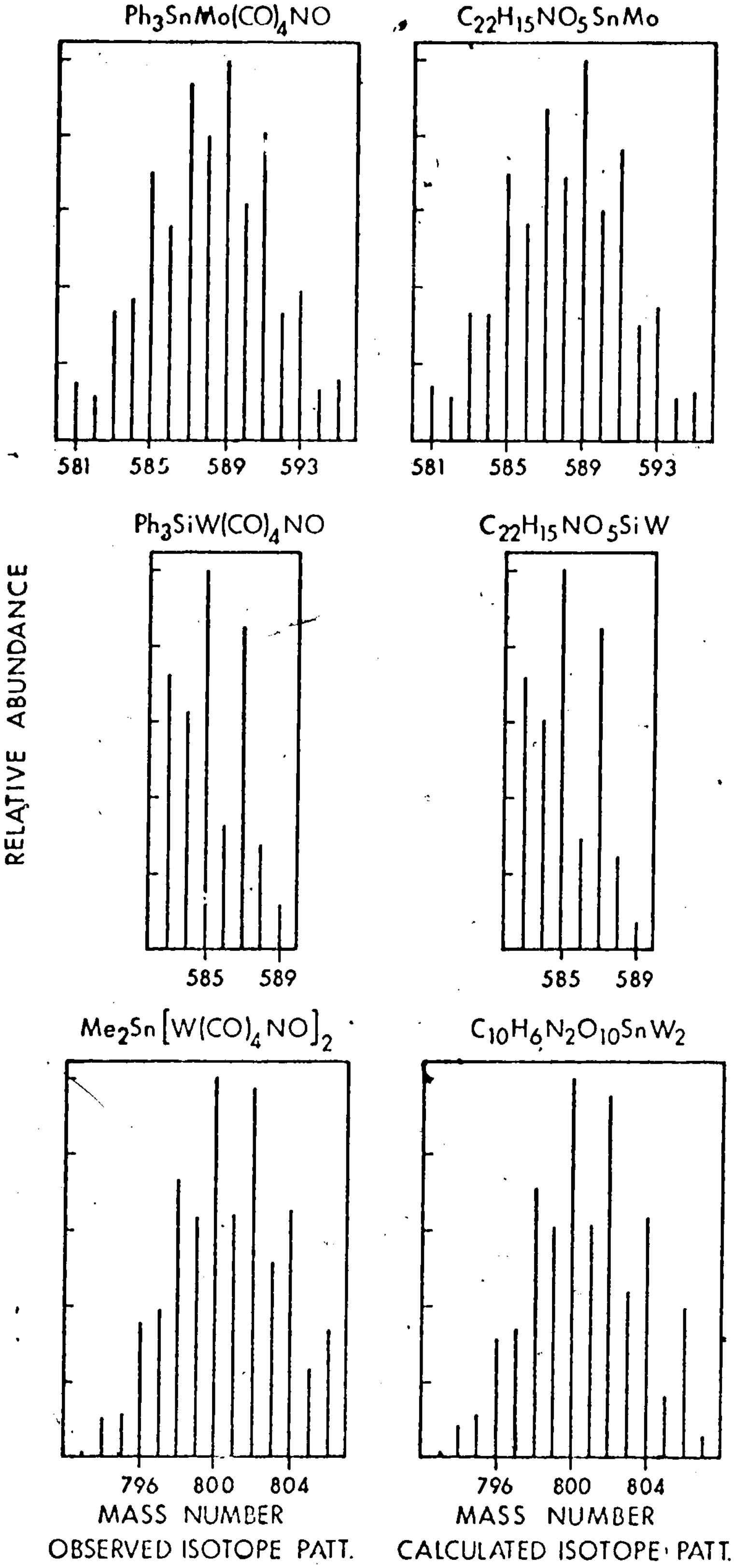


Figure 43. Calculated and observed mass spectral isotope pattern.

TABLE XXI

MASS SPECTRUM OF $Ph_3GeW(CO)_4NO$ [a]

m/e[b]	Ion	Relative Abundance	m/e[b]	Ion	Relative Abundance
629	$Ph_3GeW(CO)_4NO^+$	7	383	$(C_4H_3)PhGeW^+$	6
601	$Ph_3GeW(CO)_3NO^+$	23	333	$PhGeW^+$	3
573	$Ph_3GeW(CO)_2NO^+$	1	305	Ph_3Ge^+	100
545[c]	$Ph_3GeW(CO)NO^+$	22	263	Ph_2GeCl^+	5
517[d]	$Ph_3GeW(NO)^+$	5	228	Ph_2Ge^+	13
487	Ph_3GeW^+	14	151	$PhGe^+$	18
457	$(PhGeW(CO)_4C^+)$	2			
429	$(PhGeW(CO)_3C^+)$	3			
409	$(C_6H_4)PhGeW^+$	20			

---

[a] Measured at 80°, 70 ev.

[b] m/e values for ^{74}Ge-, ^{184}W-, $^{256}(Ge-W)$-containing fragments.

[c] Some contribution from $Ph_3GeW(CO)_2^+$, m/e 543.

[d] Substantial contribution from $Ph_3GeW(CO)^+$, m/e 515.

TABLE XXII

MASS SPECTRUM OF $Me_3SnMo(CO)_4NO$ [a]

m/e[b]	Ion	Relative Abundance	m/e[b]	Ion	Relative Abundance
403	$Me_3SnMo(CO)_4NO^+$	15	259	$MeSnMo(CO)^+$	38
388	$Me_2SnMo(CO)_4NO^+$	30	240[g]		50
375	$Me_3SnMo(CO)_3NO^+$	10	228[g]	($SnMoC^+$)	100
360	$Me_2SnMo(CO)_3NO^+$	21	212[h]		48
345[c]	$MeSnMo(CO)_3NO^+$	10	184	Me_3SnF	43
332	$Me_2SnMo(CO)_2NO^+$	25	165	Me_3Sn^+	29
317	$MeSnMo(CO)_2NO^+$	11	150	Me_2Sn^+	33
302[d]	$Me_2SnMo(CO)_2^+$	17	135	$MeSn^+$	56
291	$Me_2SnMo(NO)^+$	7	120	Sn^+	43
287[e]	$MeSnMo(CO)_2^+$	18			
274[f]	$Me_2SnMo(CO)^+$	19			

---

[a] Measured at 25°, 70 ev.

[b] m/e values for ^{120}Sn-, ^{98}Mo- and $^{216}(Sn\text{-}Mo)$-containing fragments.

[c] Contribution from $Me_3SnMo(CO)_2NO^+$, m/e 347.

[d] Contribution from $Me_2SnMo(CO)NO^+$, m/e 304.

[e] Contribution from $Me_3SnMo(CO)^+$, m/e 289.

[f] Contribution from $Me_2SnMo(NO)^+$ at m/e 276.

[g] Complex pattern due to overlap of fragments.

[h] Presumed impurity having Sn pattern and contribution from $SnMo^+$, m/e 216.

TABLE XXIII

MASS SPECTRUM OF $Me_2Sn[W(CO)_4NO]_2$[a]

m/e[b]	Ion	Relative Abundance
800	$Me_2SnW_2(CO)_8(NO)_2^+$	8
785	$MeSnW_2(CO)_8(NO)_2^+$	6
772	$Me_2SnW_2(CO)_7(NO)_2^+$	9
757	$MeSnW_2(CO)_7(NO)_2^+$	4
744	$Me_2SnW_2(CO)_6(NO)_2^+$	2
729	$MeSnW_2(CO)_6(NO)_2^+$	3
716	$Me_2SnW_2(CO)_5(NO)_2^+$	2
701	$MeSnW_2(CO)_5(NO)_2^+$	6
688[c]	$Me_2SnW_2(CO)_4(NO)_2^+$	4
673	$MeSnW_2(CO)_4(NO)_2^+$	4
658	$Me_2SnW_2(CO)_4NO^+$	7
645	$MeSnW_2(CO)_3(NO)_2^+$	4
630	$Me_2SnW_2(CO)_3NO^+$	4
617	$MeSnW_2(CO)_2(NO)_2^+$	5
602	$Me_2SnW_2(CO)_2NO^+$	6
574	$Me_2SnW_2(CO)NO^+$	15
559	$MeSnW_2(CO)NO^+$	60
544	$Me_2SnW_2(CO)^+$	38
516	$Me_2SnW_2^+$	25
486	SnW_2^+	14
474	$Me_2SnW(CO)_4NO^+$	100
459	$MeSnW(CO)_4NO^+$	2

TABLE XXIII (continued)

m/e[b]	Ion	Relative Abundance
446	$Me_2SnW(CO)_3NO^+$	24
431	$MeSnW(CO)_3NO^+$	6
418	$Me_2SnW(CO)_2NO^+$	23
402	$[Me_2SnW(CO)(NO)C]^+$	15
380	$Me_2SnW(CO)_2^+$	15
368	W_2^+	12
332	Me_2SnW^+ or $SnW(NO)^+$	6
165	Me_3Sn^+	8
135	$MeSn^+$	15
120	Sn^+	55

---

[a] Measured at 100°, 70 ev.

[b] m/e values for ^{120}Sn-, ^{184}W-, $^{370}W_2$-, and $^{586}(W_2-Sn)$-containing fragments. Additional unidentified isotopic pattern at m/e = 586, 530, 500, 347.

[c] Substantial contribution from $Me_2SnW_2(CO)_5NO^+$, m/e 686.

was complicated by pathways which involved loss of one or two methyl groups. Before losing its first CO group the molecular ion loses a Me unit giving the abundant $Me_2SnMo(CO)_4NO^+$ (m/e 388). The latter loses an Me group after losing its first CO giving the ion $MeSnMo(CO)_3NO^+$ (m/e 345). The Me_3Sn-, Me_2Sn- and $MeSn-Mo(CO)_nNO^+$ species proceed with the loss of CO and/or NO groups to give three modes of fragmentation.

The mass spectrum of $Me_2Sn[W(CO)_4NO]_2$ (Table XXIII) showed two modes of fragmentation corresponding to loss of CO and/or NO groups from the parent ion (m/e 800) and from $MeSnW_2(CO)_8(NO)_2^+$ (P-Me). The base peak in the spectrum (m/e 474) corresponds to loss of $W(CO)_4NO$ fragment from the parent and gives rise to the $Me_2SnW(CO)_4NO^+$ ion. The fragmentation pattern of the latter is reminiscent of the same species formed in the mononuclear compound as discussed above.

The mass spectra of the halo derivatives are essentially similar to that of $W(CO)_4(NO)Br$ discussed by Barraclough et. al.,[169] with the exception that dinuclear species were not observed in the present work.

EXPERIMENTAL

Microanalyses were performed by the microanalytical laboratory of this department and by Alfred Bernhardt Microanalytische Laboratorium, West Germany. Analytical data, melting points, and yields are given in Table XXIV.

Infrared spectra were measured using *n*-hexane (Phillips Petroleum Co.) which was distilled from sodium wire under nitrogen before use. The relatively non-volatile solid samples were pumped at ca. 50° under vacuum to remove traces of hexacarbonyls just prior to dissolution. The spectra were measured and the carbonyl bands calibrated as previously described. The nitrosyl bands were calibrated with the polystyrene band at 1583.1 cm^{-1}. Table XVII lists the infrared results.

The Raman spectrum of $W(CO)_4(NO)Br$ was measured on a CARSON Spex 1401 Double Spectrometer, with an Ar-Kr Laser source using the blue exciting line.

Force constant analyses were carried out as previously described, using two different models (see text). Force constants are listed in Tables XVIII and XIX.

Reactions were carried out using dichloromethane solvent, which was distilled from P_2O_5 prior to use. Reagent acetonitrile was used in some reactions. *n*-Pentane used in the extractions was also reagent grade.

TABLE XXIV

ANALYTICAL DATA, COLORS, YIELDS AND MELTING POINTS FOR THE NITROSYL COMPOUNDS

Compound	Color	MP (°C)	Yield (%)	Calcd. % C	Calcd. % H	Calcd. % N	Calcd. % Other	Found % C	Found % H	Found % N	Found % Other
$Ph_3GeMo(CO)_4NO$	orange	>70 dec.	33	48.76	2.79	2.58		48.45	2.91	2.50	
$Ph_3SnMo(CO)_4NO$	yellow-orange	112-114	12	45.93	2.57	2.38		45.43	2.71	2.45	
$Me_3SnMo(CO)_4NO$	orange	62-65	9	20.93	2.26	3.49		20.01	2.47	4.28	
$W(CO)_4(NO)Cl$	pale yellow	>90 dec.	14	13.30	0.0	3.88	Cl, 9.81	13.38	0.0	4.09	Cl, 9.45
$W(CO)_4(NO)Br$	pale yellow	>100 dec.	24	11.84	0.0	3.45	Br, 19.69, O, 19.71 W, 45.30	11.82	0.15	3.44	Br, 19.49 O, 19.34 W, 45.17
$W(CO)_4(NO)I$	pale yellow	>100 dec.	22	10.61	0.0	3.09	I, 28.03 O, 17.67 W, 40.60	10.86	0.12	3.33	I, 29.88 O, 14.46 W, 42.36
$Ph_3SiW(CO)_4NO$	orange	127	25	45.15	2.58	2.39		45.08	2.56	2.12	
$Ph_2MeSiW(CO)_4NO$	orange	69	10	39.02	2.50	2.68		39.21	2.75	2.63	
$Ph_3GeW(CO)_4NO$	yellow-orange	143-146	54	41.96	2.40	2.22	O, 12.70 W, 29.19 Ge, 11.53	42.05	2.48	2.34	O, 12.59 W, 29.01 Ge, 11.49
$Ph_3SnW(CO)_4NO$	orange	118-120	20	39.09	2.24	2.07		39.53	2.31	2.59	
$Me_3SnW(CO)_4NO$	yellow-orange	67	10	17.17	1.85	2.86		16.98	1.87	2.98	
$Me_2Sn[W(CO)_4NO]_2$	red	111-112	8	15.00	0.75	3.50		15.39	1.16	3.77	
$Ph_3PbW(CO)_4NO$	orange	>100 dec.	7	34.57	1.98	1.83	Pb, 27.10	34.40	2.09	1.84	Pb, 27.39

The nitrosonium hexafluorophosphate was purchased from the Ozark-Mahoning Co. and was used without further purification.

Preparation of triphenylgermaniumtetracarbonyl(nitrosyl)-molybdenum, $Ph_3GeMo(CO)_4NO$

A Schlenk tube containing a mixture of $Et_4N^+[Ph_3GeMo(CO)_5]^-$ (1.5 g, 2.2 mmol) and $NOPF_6$ (0.5 g, 2.8 mmol) was evacuated and ca. 30 ml of dichloromethane was distilled into the vessel at -78°. After the reaction mixture was warmed to -10° (salt-ice bath) and stirred for 2.5 hr, the solution had turned red-brown. The solvent was removed under reduced pressure. The residue was extracted with five 50-ml portions of *n*-pentane or until the extracts were colorless. The solvent was removed using water aspiration. A water cooled probe was fitted into the flask and the $W(CO)_6$ and Ph_3GeF, formed as by-products in the reaction, were sublimed in high vacuum at 25-40° over a period of 2-3 days. The sublimation residue was then recrystallized from *n*-pentane affording orange crystals of the analytical sample; 0.4 g, 33% yield.

The $Ph_3SnMo(CO)_4NO$, $Ph_3GeW(CO)_4NO$, and $Ph_3SnW(CO)_4NO$ complexes were prepared in an analogous manner.

Preparation of iodotetracarbonyl(nitrosyl)tungsten, $W(CO)_4(NO)I$

To a solution of $Et_4N^+[W(CO)_5I]^-$ (2.0 g, 3.4 mmol) in 10 ml acetonitrile was added dropwise a solution of $NOPF_6$ (ca. 2 M) in the same solvent. The addition was continued until the ir bands due to $W(CO)_6$ had diminished considerably. The solvent was removed in vacuo and the product extracted with a total of 300 ml *n*-pentane. The yellow solution was filtered and concentrated to ca. 50 ml. On cooling at -78° yellow crystals were formed; these were filtered and sublimed at room temperature to give 0.35 g (22% yield) of the product.

The $W(CO)_4(NO)Br$ complex was prepared in an analogous fashion with the exception that the product was extracted with 1:1 dichloromethane-ether solution.

Preparation of chlorotetracarbonyl(nitrosyl)tungsten, $W(CO)_4(NO)Cl$

To a 40 ml dichloromethane solution of $Et_4N^+[Cl_3SnW(CO)_5]^-$ (1.4 g, 2.1 mmol) solid $NOPF_6$ (0.5 g, 2.8 mmol) was added slowly at room temperature and the solution stirred for 15 min. After removing the solvent in vacuo, the residue was extracted with 300 ml *n*-pentane, and after filtering, the solvent was removed on a rotary evaporator. The solid was transferred to a sublimer and the $W(CO)_6$ formed in the reaction was sublimed at room temperature and 0.25 torr. After removal of the $W(CO)_6$ from the sublimation probe, the product was sublimed at 60° and 0.1 g (14% yield) of pale yellow crystals were obtained.

Preparation of triphenylsilyltetracarbonyl(nitrosyl)tungsten, $Ph_3SiW(CO)_4NO$

To a solution of $Et_4N^+[Ph_3SiW(CO)_5]^-$ (3.0 g, 4.2 mmol) in 50 ml of dichloromethane, 0.5 g of $NOPF_6$ was added and the solution stirred at room temperature. The progress of the reaction was followed by the disappearance of starting material bands in the ir spectrum. An additional 0.5 g of $NOPF_6$ was added after 0.5 hr and stirring continued for 1.5 hr. Ether (20 ml) was added, the solution was filtered and the solvents were removed in vacuo. The residue was extracted with 4 x 50 ml portions of *n*-pentane, filtered and the yellow *n*-pentane solution concentrated to ca. 50 ml. On cooling to 0° crystals were formed and these were transferred into a sublimer. The Ph_3SiF and $W(CO)_6$ formed in the reaction were sublimed at 0.05 torr. The orange solid left behind was recrystallized from *n*-pentane affording 0.6 g (25% yield) of product.

Preparation of diphenylmethylsilicontetracarbonyl-(nitrosyl)tungsten, $MePh_2SiW(CO)_4NO$

Dichloromethane was vacuum distilled into a Schlenk tube containing $Et_4N^+[MePh_2SiW(CO)_5]^-$ (2.5 g, 3.8 mmol) and $NOPF_6$ (0.7 g, 4.0 mmol). The solution was stirred at -78° for 7 hr under closed vacuum and then warmed to room temperature before removal of the solvent. The residue was extracted with 150 ml *n*-pentane, filtered and the solvent removed leaving behind a red oil. An orange oily solid, which was identified as $MePh_2SiF$, sublimed onto a dry-ice-acetone probe under vacuum. The residue was pumped for 2 days at room temperature to remove $W(CO)_6$ and residual $MePh_2SiF$. Crystallization of the solid from *n*-pentane afforded orange crystals of $MePh_2SiW(CO)_4NO$; 0.4 g, 20% yield.

The preparation of the complexes $MePh_2SiMo(CO)_4NO$ and $Ph_3SiMo(CO)_4NO$ was attempted in a similar manner but only $Mo(CO)_6$ was isolated.

Preparation of trimethyltintetracarbonyl(nitrosyl)-tungsten, $Me_3SnW(CO)_4NO$ and dimethyltin bis{tetracarbonyl-(nitrosyl)tungsten}, $Me_2Sn[W(CO)_4NO]_2$

Dichloromethane (30 ml) was distilled into a reaction vessel containing $Et_4N^+[Me_3SnW(CO)_5]^-$ (2.0 g, 3.2 mmol) and $NOPF_6$ (0.7 g, 4.0 mmol) cooled to -78°. The mixture was kept at this temperature for three days.

The solvent was removed by vacuum distillation into a trap cooled to -196°. The residue was extracted with several portions of *n*-pentane, filtered and the solvent removed by *water aspiration* vacuum. The residue was charged into a sublimer and the volatile $Me_3SnW(CO)_4NO$ was sublimed onto a water-cooled probe together with some $W(CO)_6$. The product was washed off the probe by squirting with ca. 10 ml of *n*-hexane, leaving most of the $W(CO)_6$ behind. This was then chromatographed on a Florisil column eluting as a red band with *n*-hexane. Cooling at -20° overnight afforded orange crystals of $Me_3SnW(CO)_4NO$; 0.16 g, 10% yield.

The unsublimed material left behind was pumped until the ir spectrum showed only traces of $Me_3SnW(CO)_4NO$ and $W(CO)_6$. Recrystallization from *n*-pentane afforded red crystals of the binuclear species, $Me_2Sn[W(CO)_4NO]_2$; 0.1 g, 7.7% yield.

The $Me_3SnMo(CO)_4NO$ complex was prepared using similar conditions as above. There was no evidence for the formation of a binuclear species in this reaction.

Preparation of triphenylleadtetracarbonyl(nitrosyl)-tungsten, $Ph_3PbW(CO)_4NO$

A dichloromethane solution of $Et_4N^+[Ph_3PbW(CO)_5]^-$ (4.0 g, 4.5 mmol) and $NOPF_6$ (1.0 g, 5.7 mmol) were stirred at -78° for 9 hr. The solvent was removed under reduced pressure with the reaction vessel maintained at -78°. The residue was extracted with 6 x 30 ml portions of *n*-pentane, filtered and the solvent removed. The large amounts of $W(CO)_6$ and other by-products formed in the reaction were sublimed. Red crystals were obtained by crystallization from *n*-pentane; 0.2 g, 7% yield.

The $Ph_3PbMo(CO)_4NO$ complex was prepared under similar conditions. Because of the low yield a sufficient sample for analysis was not obtained and the compound was characterized only mass spectrometrically.

CHAPTER VII

OXIDATION REACTIONS USING SILVER SALTS

In this chapter, two independent investigations involving the oxidation of transition metal compounds are discussed. The first part deals with the reactions of silver nitrite ($AgNO_2$) with some metal-metal bonded dinuclear metal carbonyls. In the second section the oxidation reaction of $(Bu_4N^+)_2[Re_4(CO)_{16}]^{2-}$ will be described.

1) Some Reactions of Silver Nitrite

INTRODUCTION

As was mentioned in chapter VI, the nitrite ion has been used extensively in the preparation of nitrosyl complexes. Heiber and Beutner[189] hypothesized that the formation of $[Fe(CO)_3NO]^-$ proceeded via a nitrite intermediate in two steps:

$$Fe(CO)_5 + NO_2^- \xrightarrow[CH_3OH]{35°} [Fe(CO)_4NO_2]^- + CO \qquad \text{VII-1}$$

$$[Fe(CO)_4NO_2]^- \longrightarrow [Fe(CO)_3NO]^- + CO_2 \qquad \text{VII-2}$$

The reaction of $M(CO)_2L_2Cl_2$ ($M = Ru, Os$; $L = PPh_3$) with sodium nitrite has been reported to initially form a dinitrite complex, $M(CO)_2L_2(NO_2)_2$ which undergoes oxygen transfer to give the dinitrosyl compound,

$M(NO)_2L_2$.[190]

The reaction of $M_2(CO)_{10}$ (M = Mn, Re) with N_2O_4 yields mainly the nitrato complex $M(CO)_5NO_3$.[191-193] The formation of a nitrite intermediate, which reacts with excess N_2O_4 to form the nitrato complex has been inferred by ir spectroscopy.[192]

There are numerous studies dealing with metal-nitrite compounds[194,195] and recent interest has been directed at the conversion of nitrosyl compounds to metal-nitro groups.[196-199] Metal carbonyl complexes containing nitrite ligands are rare.

Our interest in nitrosyl chemistry and in reactions where there is a competition between cleavage of metal-metal and metal-carbonyl bonds, led us to investigate the reactions of silver nitrite with some dinuclear metal carbonyls.

RESULTS AND DISCUSSION

The outcome of the reactions between the dinuclear complexes, $[C_5H_5Mo(CO)_3]_2$, $[C_5H_5Fe(CO)_2]_2$, $[C_5H_5Ru(CO)_2]_2$ and $(Et_4N^+)_2[W_2(CO)_{10}]^{2-}$ with $AgNO_2$ are outlined in VII-3 to VII-5.

$$[C_5H_5Mo(CO)_3]_2 + AgNO_2 \xrightarrow[CH_2Cl_2]{} C_5H_5Mo(CO)_2NO + CO_2 + Ag \qquad \text{VII-3}$$

$$[C_5H_5M(CO)_2]_2 + AgNO_2 \xrightarrow[CH_3CN]{} C_5H_5M(CO)_2NO_2 + Ag \qquad \text{VII-4}$$

(M = Fe, Ru)

$$(Et_4N^+)_2[W_2(CO)_{10}]^{2-} + AgNO_2 \xrightarrow{CH_2Cl_2} 2Et_4N^+[W(CO)_5NO_2]^- + Ag \qquad \text{VII-5}$$

All reactions proceeded initially with the oxidative cleavage of the metal-metal bond by Ag^+.

In VII-3, there was no evidence for the formation of a nitrite species even as an intermediate; the known nitrosyl complex,[200] $C_5H_5Mo(CO)_2NO$, was identified by its ir and mass spectra.

The Fe and Ru dimers in VII-4, reacted to form the nitrite complexes. Infrared data can be used to distinguish between *nitro* (N-bonded, M-NO_2) and *nitrito* (O-bonded, M-ONO) isomers.[201] The $C_5H_5M(CO)_2NO_2$ (M = Fe, Ru) compounds showed four ir absorption bands $\{\nu_{as}(NO_2)$, $\nu_s(NO_2)$, $\delta(ONO)$, and $\rho_w(NO_2)\}$ characteristic of the *nitro* group,[197,201-203] suggesting that these compounds exist as nitro isomers. The metal-nitrogen stretch [ν(M-N)] has also been assigned. Results are listed in Table XXV together with the ν(CO) values. The $\nu_{as}(NO_2)$ and $\nu_s(NO_2)$ bands (1381, 1307 cm^{-1}) measured in CH_2Br_2 and the ν(CO) bands (2064, 2019 cm^{-1}) measured in CH_2Cl_2 of $C_5H_5Fe(CO)_2NO_2$ are shown in Figure 44. The spectrum in the NO_2 region is that of a solution roughly twice as concentrated as that in the CO region. The ν(CO) bands in the nitro derivative are higher than in $C_5H_5Fe(CO)_2Cl$[204] (2058, 2012 cm^{-1}) and comparable

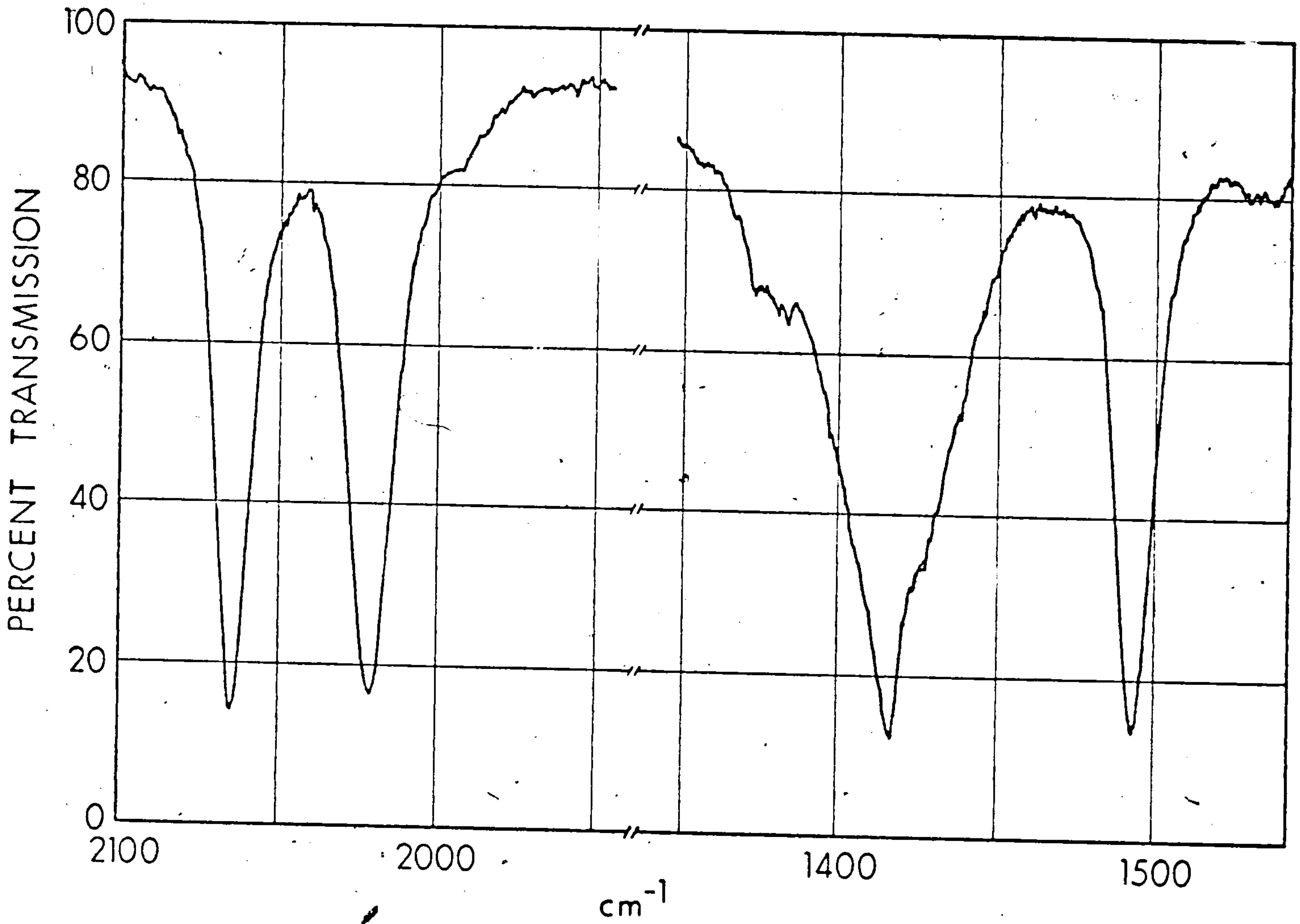


Figure 44. Infrared spectrum of $C_5H_5Fe(CO)_2NO_2$ in ν(CO) and ν(NO_2) regions.

TABLE XXV

CHARACTERISTIC FREQUENCIES IN THE INFRARED SPECTRA (CM^{-1}) OF SOME NITRO COMPLEXES

	$\nu(CO)$	$\nu_{as}(NO_2)^a$	$\nu_s(NO_2)^a$	$\delta(ONO)^a$	$\delta_w(NO_2)^a$	$\nu(M-N)^a$
$C_5H_5Fe(CO)_2NO_2$	2064, 2019 (CH_2Cl_2)	1372	1308	815	620	305
$C_5H_5Ru(CO)_2NO_2$	2066, 2016 (CS_2)	1379	1312	815	610	298
$Et_4N^+[W(CO)_5NO_2]^-$	2069, 2020, 1882 (THF)	1295	1225	805	605	370
	$(2060, 1915, 1862)^b$					

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[a] Obtained in KBr and CSI discs.

[b] Bands assigned to *nitrito* isomer (see text).

to $C_5H_5Fe(CO)_2CN$ [204] (2062 and 2019 cm^{-1}).

In the mass spectrum of $C_5H_5Fe(CO)_2NO_2$, a parent peak was not observed, but a peak due to $C_5H_5Fe(CO)(NO)^+$ ($P-CO_2$) was very prominent. The Ru analogue showed a weak parent ion as well as prominent peaks due to loss of CO_2 and NO_2 units.

The reaction of $[C_5H_5Fe(CO)_2]_2$ with $AgNO_2$ was also performed in CH_2Cl_2 solvent and followed by the ir spectrum in the carbonyl region. After .5 hr ν(CO) bands due to starting materials disappeared and four new bands at 2064, 2049, 2019 and 2011 cm^{-1} emerged. The pair of bands at 2049 and 2011 cm^{-1} gradually disappeared. These are thought to be due to the *nitrito* isomer which slowly rearranges to give the more stable *nitro* isomer (ν(CO) 2064 and 2019 cm^{-1}). It is noteworthy that when NO gas was bubbled through a CH_2Cl_2 solution of the *nitro* derivative, the ν(CO) bands associated with the *nitrito* species emerged gradually until an equilibrium was established. Attempts to isolate the *nitrito* isomer free of the nitro were not successful.

The reaction of $[W_2(CO)_{10}]^{2-}$ with numerous silver salts, AgX, has proved a useful route to many anions of the type $[W(CO)_5X]^-$.[127,128] This reaction pathway has been adopted in VII-5 to prepare an anionic nitrite complex, $Et_4N^+[W(CO)_5NO_2]^-$.

The solution ir spectrum in the ν(CO) region measured in THF is shown in Figure 45. It is apparent that the spectrum is complex and that there is a doubling of the number of bands expected for C_{4v} symmetry. Indeed, two sets of typically C_{4v} ($2A_1 + E$) bands are discernible. Spectra measured in other solvents also exhibited this phenomenon and Figure 46 compares the high frequency bands in THF, CH_2Cl_2, CH_3CN, and DMSO. In solvents other than THF, the lower portion of the spectrum was too broad to clearly observe the two sets of bands. In contrast the solid state spectrum measured in Nujol exhibited only a single sharp high frequency band at 2063 cm^{-1}. Moreover only one crystalline form could be distinguished when crystals were examined under the microscope. The compound exhibited a sharp melting point.

The evidence above suggests that the 'complex' ir spectra are attributable to solution effects. Formation of contact ion pairs can be immediately dismissed since the complex spectra persist even in a solvent of high dielectric constant such as DMSO.[150,151] Isomerization in solution seems likely and a rapid equilibrium between two isomeric forms, such as *nitro* and *nitrito* linkage isomers, is envisaged. The influence of solvent on the ratio of the two high frequency ir bands (Figure 46) provides good evidence for the existence of an equilibrium between two species.

The ir spectrum measured as a CsI disc is consistent

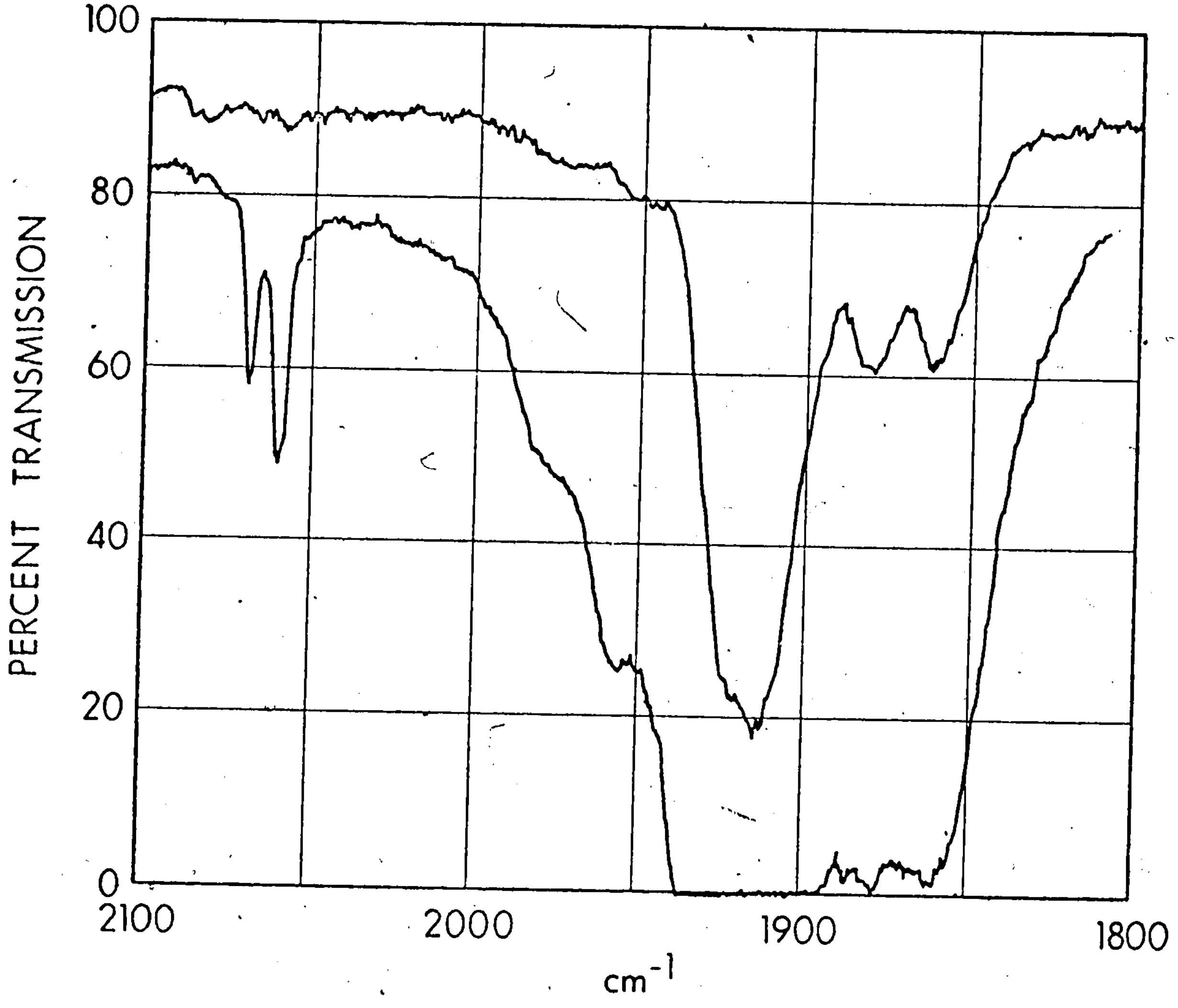


Figure 45. $Et_4N^+[W(CO)_5NO_2]$ in THF.

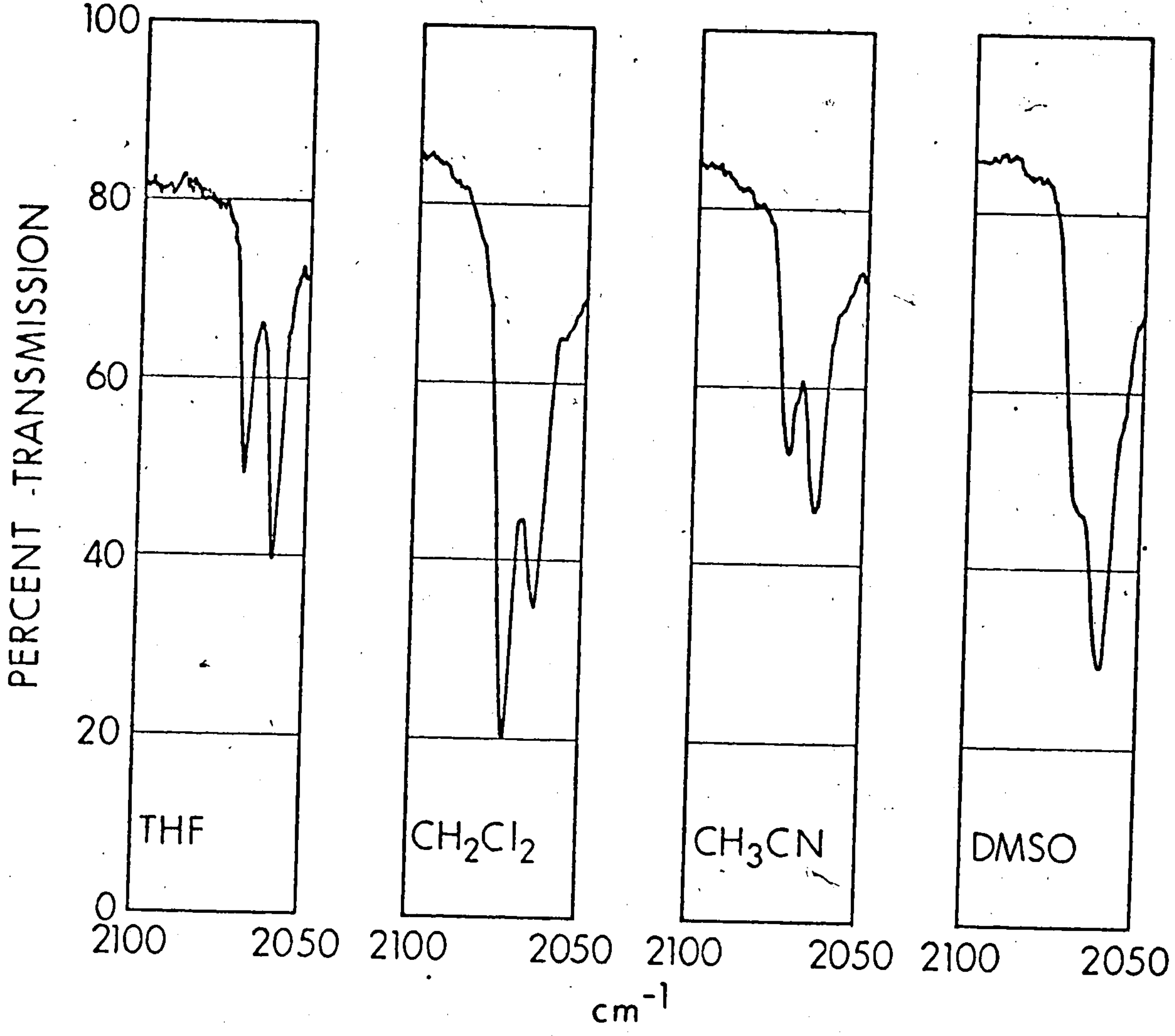


Figure 46. Infrared spectrum (A_1^2 mode) of $Et_4N^+[W(CO)_5NO_2]^-$ in various solvents.

with the presence of only the nitro group in the solid state. The $\nu_{as}(NO_2)$ and $\nu_s(NO_2)$ modes assigned at 1295 and 1225 cm^{-1} (Table XXV) are surprisingly lower than those of free NO_2^- at 1335 and 1250 cm^{-1}.

The two sets of ir bands in THF (Figure 45) at 2069, 1925 and 1883 cm^{-1} and 2060, 1915 and 1863 cm^{-1} are tentatively assigned to the *nitro* and *nitrito* isomers of $[W(CO)_4NO_2]^-$ respectively. The only basis for this assignment is that the bands due to the *nitro* isomer are higher than those of the *nitrito* isomer in $C_5H_5Fe(CO)_2NO_2$.

When the compounds $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$ and $Ph_3SnRe(CO)_5$ were treated with $AgNO_2$, no reaction took place.

The decomposition of $C_5H_5Fe(CO)_2NO_2$

At slightly above room temperature, solutions of $C_5H_5Fe(CO)_2NO_2$ were observed (ir and nmr) to gradually decompose with the formation of $[C_5H_5Fe(CO)_2]_2$ and $C_5H_5Fe(CO)(NO)$. The latter, a noxious smelling and air sensitive liquid, was identified by its ir spectrum (Figure 47).

In the nmr spectrum measured in $CDCl_3$, the C_5H_5 resonance of $C_5H_5Fe(CO)_2NO_2$ at 4.9 τ diminished with time and peaks at 5.1 τ and 5.2 τ emerged. The latter is due to $[C_5H_5Fe(CO)_2]_2$ as evidenced by comparison with the spectrum of an authentic sample. The rate of disappearance

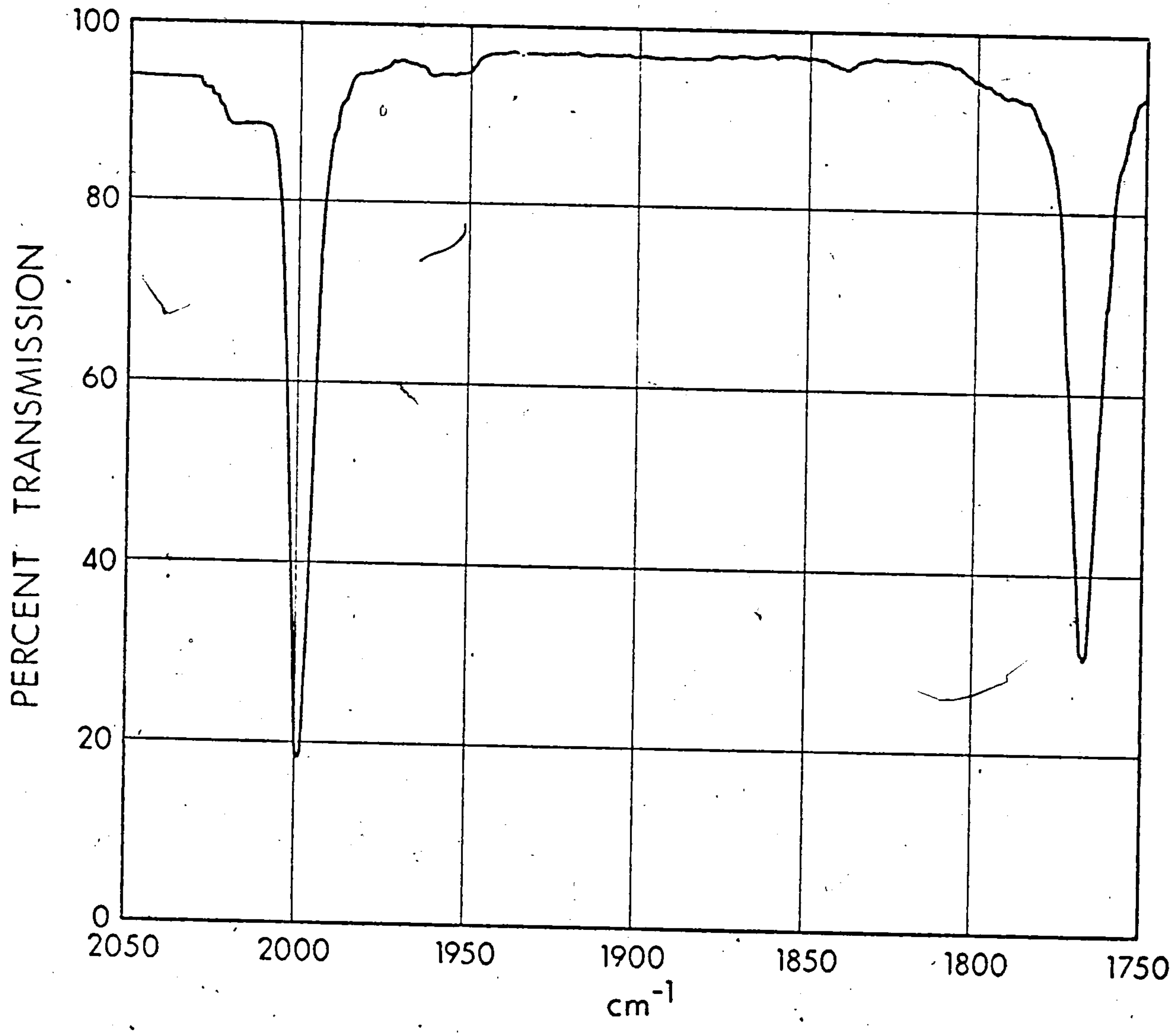


Figure 47. $C_5H_5Fe(CO)(NO)$ in *n*-pentane: ν(CO) at 1999 cm^{-1}; ν(NO) at 1769 cm^{-1}.

of the resonance due to $C_5H_5Fe(CO)_2NO_2$ could be measured by integration. A plot of ln (area) vs time gave a straight line indicating first-order kinetics (or pseudo-first order, if solvent molecules are involved). Runs at four different temperatures (calibrated with methanol) were performed and values for the rate constant (k_{obs}) were obtained from the slope of the ln(disappearance τ_{C5H5}) vs time plots, using a least-squares method. The k_{obs} values are listed together with the activation parameters ($\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$) in Table XXVI. The computer program ACTIVE, written in this Department, was used to evaluate $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ from the Wynne-Jones and Eyring equation.

It must be emphasized that this is not a rigorous kinetic study and that the data must be treated with caution. Nevertheless, it is an attempt to gain insight into the mechanism of the decomposition process. The relatively high positive $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values are consistent with a dissociative mechanism which presumably involves M-CO and/or M-NO_2 bond rupture. A competition between two processes is envisaged:

$$C_5H_5Fe(CO)_2NO_2 \xrightarrow{k_1} C_5H_5Fe(CO)(NO) + CO_2 \qquad \text{VII-6}$$

$$C_5H_5Fe(CO)_2NO_2 \xrightarrow[k_2]{} [C_5H_5Fe(CO)_2]_2 + N_2O_4 \qquad \text{VII-7}$$

It is likely that k_1 and k_2 are of the same order of

TABLE XXVI

RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE DECOMPOSITION REACTION OF $C_5H_5Fe(CO)_2NO_2$

Temp. (°C)	k_{obs} (sec^{-1})
30.5	1.47×10^{-4}
36.8	3.48×10^{-4}
41.5	8.94×10^{-4}
47.0	2.25×10^{-3}

Activation Parameters: $\Delta H^{\ddagger}$ +31.76 (± 1.95) Kcal $mole^{-1}$

$\Delta S^{\ddagger}$ +28.32 (± 6.25) Cal $deg^{-1} mole^{-1}$

magnitude.

It is noteworthy that the Ru analogue was stable in solution up to a temperature of 80°.

EXPERIMENTAL

Preparation of π-cyclopentadienyldicarbonyl(nitrosyl)-molybdenum, π-$C_5H_5Mo(CO)_2NO$.

To a dichloromethane solution containing $[C_5H_5Mo(CO)_3]_2$ (1.0 g, 2.0 mmol) excess $AgNO_2$ was added in small amounts over a period of 4 to 5 days, and the solution was stirred in the absence of light. The reaction mixture was filtered through Celite and the solvent removed in a water aspiration vacuum. The residue was charged into a sublimer and the orange product sublimed at room temperature and .01 torr; .3 g, 30% yield. Anal. calcd. for $C_7H_5NO_3Mo$: C, 34.31; H, 2.06; N, 5.72. Found: C, 34.80; H, 2.30; N, 5.26.

When a larger scale reaction was performed the yield decreased substantially.

Preparation of π-cyclopentadienyl(nitro)dicarbonyliron, π-$C_5H_5Fe(CO)_2NO_2$

To a solution of $[C_5H_5Fe(CO)_2]_2$ (1.0 g, 2.8 mmol) in 30 ml acetonitrile was added excess $AgNO_2$ and the reaction stirred for .5 hr. The reaction mixture was then filtered through degassed Celite and the solvent removed *in vacuo*. The residue was extracted with ca. 15 ml dichloromethane and filtered through an "E" porosity sinter (to remove finely divided particles of Ag), giving a yellow-orange solution. *n*-Pentane was added dropwise until the solution became cloudy; cooling at -78° afforded a brown solid. This sample was re-crystallized once more affording 0.3 g (26% yield) of product. Anal. calcd. for $C_7H_5NO_4Fe$: C, 37.70; H, 2.26; N, 6.28. Found: C, 36.97; H, 1.96; N, 6.10.

This compound forms yellow crystals when pure which can be handled briefly in air but decompose on long exposure. The compound is soluble in organic solvents such as dichloromethane, benzene and carbon disulphide but only sparingly soluble in hydrocarbon solvents. Solutions are stable under nitrogen below room temperature for long periods. A dichloromethane solution when kept in air decomposes completely after 0.5 hr.

Preparation of π-cyclopentadienylcarbonyl(nitrosyl)iron, π-C_5H_5Fe(CO)(NO)

A sample of $C_5H_5Fe(CO)_2NO_2$ was dissolved in chloroform and heated to 45° for 20 min. With the reaction mixture cooled below 0°, the solvent was removed *in vacuo*. A small amount of a brown liquid was distilled from the residue to a Schlenk tube kept at -78°. The identity of this air-sensitive liquid was inferred from its ir spectrum which showed ν(CO) at 1999 cm^{-1} and ν(NO) at 1769 cm^{-1}. The compound was typically contaminated by traces of $[C_5H_5Fe(CO)_2]_2$ and ferrocene. Because of difficulty in handling, the compound was not analyzed.

Preparation of π-cyclopentadienyl(nitro)dicarbonylruthenium, π-$C_5H_5Ru(CO)_2NO_2$

A solution containing $[C_5H_5Ru(CO)_2]_2$ (1.2 g, 2.7 mmol) and $AgNO_2$ (1.5 g, 9.7 mmol) in acetonitrile (50 ml) was stirred overnight. The solution was filtered through degassed Celite and the solvent removed *in vacuo*. The residue was extracted with 60 ml dichloromethane, filtered and 25 ml *n*-heptane added. Some solvent was removed slowly on a rotary evaporator (water aspiration) precipitating a brown solid. This was recrystallized from dichloromethane-heptane to give 1.0 g (69% yield) of product. Anal. calcd. for $C_7H_5NO_4Ru$: C, 31.35; H, 1.88; N, 5.22. Found: C, 31.71; H, 1.86; N, 4.59. M.P. 130-132.

The compound forms brown-yellow crystals which are air stable for long periods. Solutions in polar solvents are air stable for brief periods and stable for long periods under nitrogen. A dichloromethane solution was refluxed for 2 days under nitrogen, without visible decomposition.

Preparation of tetraethylammonium pentacarbonyl(nitro)-tungsten, $Et_4N^+[W(CO)_5NO_2]^-$

The dinuclear anion $(Et_4N^+)_2[W_2(CO)_{10}]^{2-}$ was prepared by the method of Hayter,[205] with the modification that the reaction was carried out in a quartz vessel using an external UV source (Hanovia utility lamp No. 616A) and 4 days of irradiation. Anal. calcd: C, 34.33; H, 4.44; N, 3.08. Found: C, 34.49; H, 4.50; N, 3.15. Attempts to prepare this anion as the more stable bis(triphenylphosphine)iminium (PPN) salt[206] were unsuccessful, affording instead the hydride, $PPN^+[HW_2(CO)_{10}]^-$.

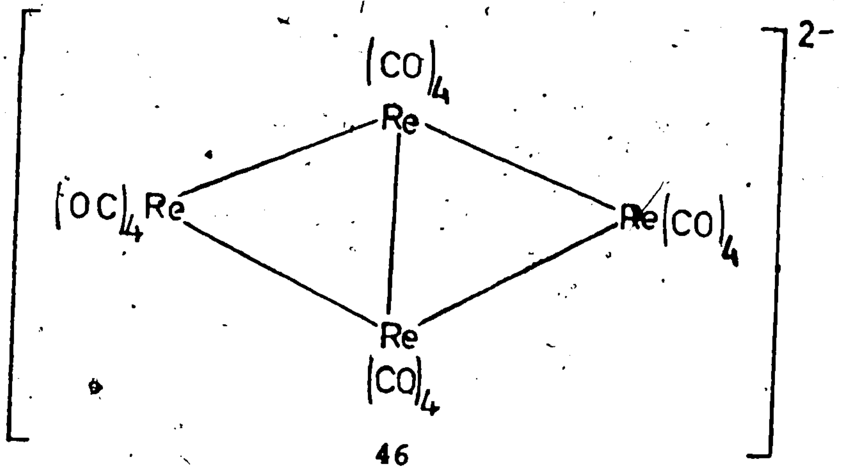
To a solution containing $(Et_4N^+)_2[W_2(CO)_{10}]^{2-}$ (1.0 g, 1.1 mmol) in 40 ml dichloromethane was added excess $AgNO_2$ (.6 g, 3.9 mmol), the mixture then being stirred for 20 min. To the yellow solution obtained by filtration through degassed Celite, 80 ml of ether was added precipitating a yellow-green solid. The crude material was redissolved in 20 ml dichloromethane, 5 ml ether was added and the solution filtered through an "E" porosity sintered glass funnel. An additional 5 ml of ether was added and the solution, when cooled to -78°, afforded yellow crystals. The recrystallization procedure was repeated twice yielding .5 g (45% yield) of product. Anal. calcd. for $C_{13}H_{20}N_2O_7W$: C, 31.22; H, 4.03; N, 5.60. Found: C, 31.66; H, 4.21; N, 6.53. M.P. 86-89°.

A conductivity measurement performed on a 1.4×10^{-3} M nitromethane solution gave a value of 75.9 $ohm^{-1}cm^{2}mole^{-1}$ which did not change on standing up to 24 hr.

2) The Formation of $[(CH_3CN)_3Re(CO)_3]^+$ from the Oxidation Reaction of $[Re_4(CO)_{16}]^{2-}$

INTRODUCTION

The structure of the anionic cluster, $[Re_4(CO)_{16}]^{2-}$ has been shown to consist of two fused, approximately equilateral triangles, with the four Re atoms in the plane, 46.[207]



46

A study of this anion was initiated in an attempt to determine the structural changes which may take place on oxidation.

RESULTS AND DISCUSSION

The reaction of $(Bu_4N^+)_2[Re_4(CO)_{16}]^{2-}$ with $AgBF_4$ in acetonitrile resulted in the isolation of a mononuclear cationic species, $[(CH_3CN)_3Re(CO)_3]^+BF_4^-$:

$$(Bu_4N^+)_2[Re_4(CO)_{16}]^{2-} + 6AgBF_4 \xrightarrow[CH_3CN]{}$$

$$2Bu_4NBF_4 + 6Ag + 4CO + 4[(CH_3CN)_3Re(CO)_3]^+BF_4^- \qquad \text{VII-8}$$

The ir spectrum in CH_2Cl_2, Figure 48, is indicative of *fac* stereochemistry. In addition, the solid state ir spectrum as a KBr disc showed weak bands at 2315 and 2290 cm^{-1} due to the co-ordinated acetonitrile ligands.

The $[(CH_3CN)_3Re(CO)_3]^+$ cation is both iso-electronic and iso-steric with $(CH_3CN)_3W(CO)_3$. Recently, Reimann and Singleton[208] have developed a convenient route to the synthesis of the tris-acetonitrile derivatives of both Mn and Re from the reaction of $M(CO)_5Br$ (M = Mn, Re) and $AgBF_4$ in refluxing acetonitrile.

The X-ray crystallographic structure of $[(CH_3CN)_3Re(CO)_3]^+BF_4^-$ has been determined in this department by Dr. L. Chan and is shown in Figure 49. Table XXVII lists the intramolecular bond lengths and bond angles.

A number of structures containing acetonitrile bonded to main group elements have been determined[209-211]

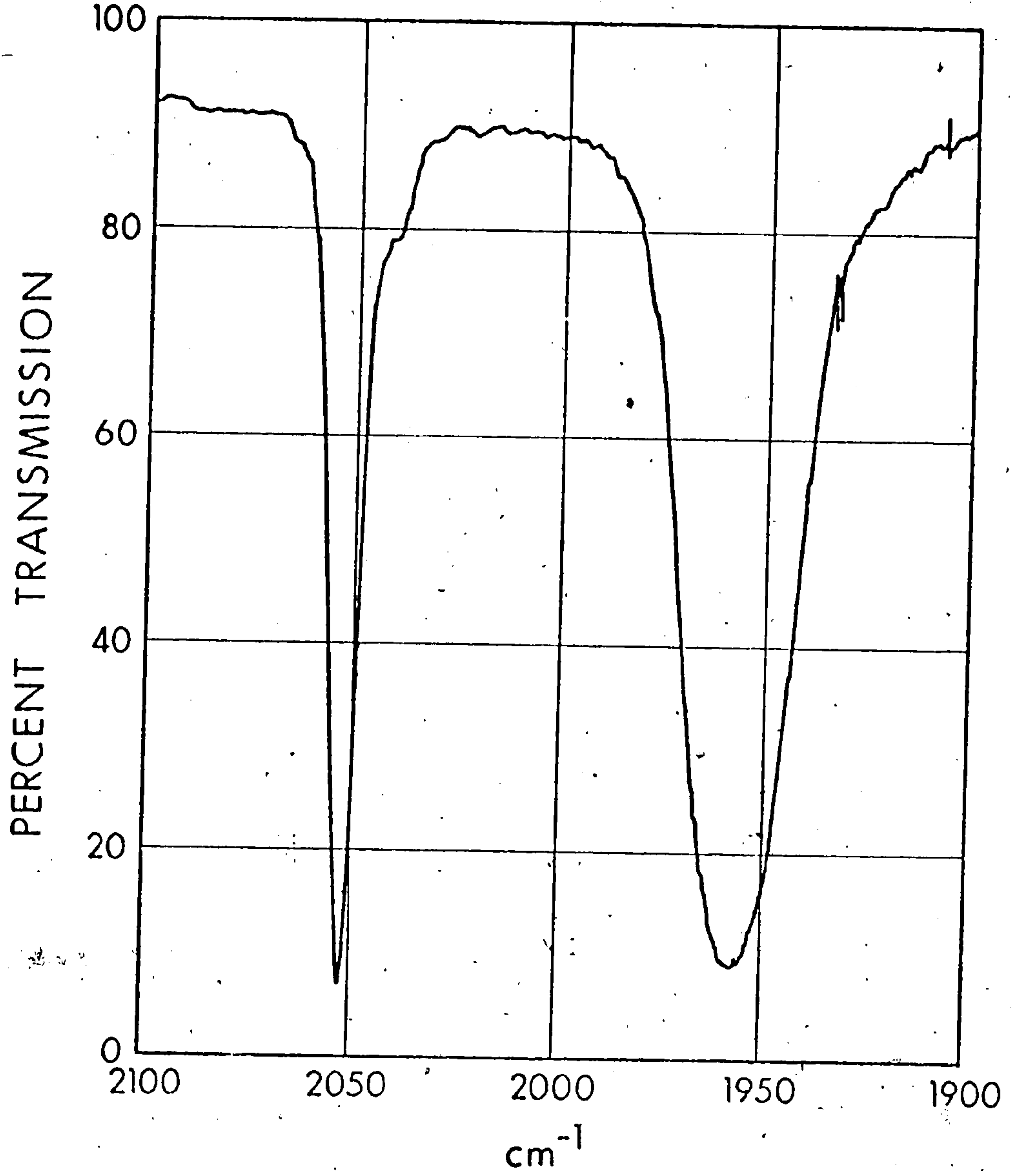


Figure 48. $[(CH_3CN)_3Re(CO)_3]^+BF_4^-$ in CH_2Cl_2.

and there are no marked changes in the ligand geometry. Thus the average C≡N and C-C distances of 1.14 and 1.46 Å are to be compared with 1.13 and 1.44 Å in $CH_3CN \cdot BF_3$ [209] and 1.10 and 1.44 Å in $(CH_3CN)_2 \cdot SnCl_4$.[211]

The average Re-CO distance of 1.91 Å is comparable to other mean terminal Re-CO values; for example, 1.95 Å in $Ph_2SiH_2Re_2(CO)_8$, [212] 1.91 Å in $[Re_4(CO)_{16}]^{2-}$, [207] and 1.85 Å in $(C_5H_5)_2Re_2(CO)_5$. [213]

The electrochemical oxidation of $[Re_4(CO)_{16}]^{2-}$ was also investigated with acetonitrile as solvent and $NaClO_4$ as supporting electrolyte. A current (4.5 V, D.C.) was passed, by means of platinum electrodes, through a cell consisting of two compartments which were separated by a sinter of "E" porosity. The red solution at the anode became colorless after a few hours and a cream colored solid was isolated from this solution. The ir spectrum exhibited ν(CO) bands which were identical to those of $[(CH_3CN)_3Re(CO)_3]^+$. Presumably the ClO_4^- salt of the latter was formed in the electrochemical reaction.

In summary, the chemical and electrochemical oxidation of $[Re_4(CO)_{16}]^{2-}$ under the conditions studied, resulted in the fragmentation of the Re-Re bonds and formation of an oxidized product with the inclusion of solvent molecules.

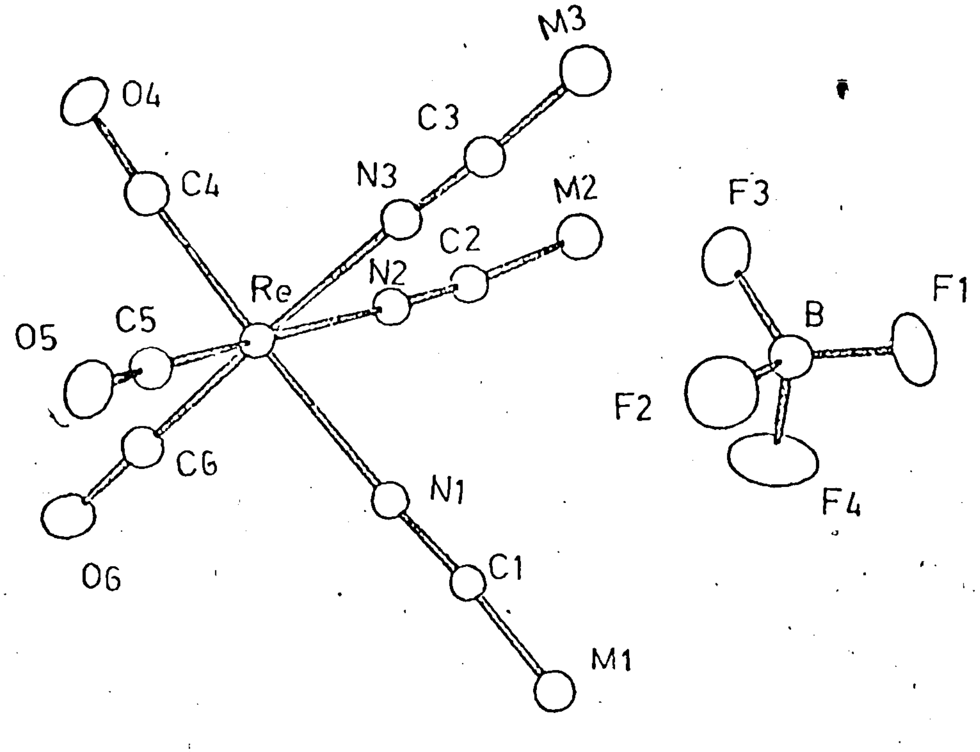


Figure 49. Molecular structure of $[(CH_3CN)_3Re(CO)_3]^+BF_4^-$.

TABLE XXVII

INTRAMOLECULAR DISTANCE AND ANGLES FOR $[(CH_3CN)_3Re(CO)_3]^+BF_4^-$

Distance	Å	Angle	Degrees
Re-N(1)	2.13(2)	Re-N(1)-C(1)	176.2(15)
Re-N(2)	2.13(2)	Re-N(2)-C(2)	173.4(16)
Re-N(3)	2.12(2)	Re-N(3)-C(3)	174.5(18)
Re-C(4)	1.93(2)	Re-C(4)-O(4)	177.5(20)
Re-C(5)	1.92(2)	Re-C(5)-O(5)	177.8(19)
Re-C(6)	1.87(2)	Re-C(6)-O(6)	178.1(20)
		N(1)-C(1)-N(1)	176.5(19)
N(1)-C(1)	1.17(2)	N(1)-Re-N(2)	84.8(6)
C(1)-M(1)	1.46(2)	N(1)-Re-N(3)	85.0(6)
N(2)-C(2)	1.13(2)	N(1)-Re-C(4)	177.2(8)
C(2)-M(2)	1.50(3)	N(1)-Re-C(5)	93.4(7)
N(3)-C(3)	1.13(2)	N(1)-Re-C(6)	93.7(8)
C(3)-M(3)	1.42(3)	N(2)-C(2)-M(2)	174.8(22)
C(4)-O(4)	1.13(2)	N(2)-Re-N(3)	81.9(6)
C(5)-O(5)	1.16(2)	N(2)-Re-C(4)	94.8(8)
C(6)-O(6)	1.18(2)	N(2)-Re-C(5)	175.4(8)
		N(2)-Re-C(6)	95.2(8)
B-F(1)	1.27(3)	N(3)-C(3)-M(3)	178.1(24)
B-F(2)	1.35(3)	N(3)-Re-C(4)	92.2(8)
B-F(3)	1.32(3)	N(3)-Re-C(5)	93.8(7)
B-F(4)	1.28(3)	N(3)-Re-C(6)	176.9(8)
		C(4)-Re-C(5)	86.8(9)
		C(4)-Re-C(6)	89.0(9)
		C(5)-Re-C(6)	89.1(9)
		F(1)-B-F(2)	110.1(28)
		F(1)-B-F(3)	112.2(23)
		F(1)-B-F(4)	105.2(31)
		F(2)-B-F(3)	119.4(38)
		F(2)-B-F(4)	99.0(3.3)
		F(3)-B-F(4)	108.7(27)

EXPERIMENTAL

Preparation of tris(acetonitrile)tricarbonylrhenium-tetrafluoroborate, $[(CH_3CN)_3Re(CO)_3]^+BF_4^-$

To a 10 ml acetonitrile solution of $(Bu_4N^+)_2$-$[Re_4(CO)_{16}]^{2-}$ (.25 g, .15 mmol), $AgBF_4$ (.8 g, 5.1 mmol) was added and the mixture stirred for 24 hr. The initial red color was lost as the solution became colorless with the deposition of Ag metal. The solution was filtered through Celite and the solvent removed in vacuo. The brown residue was washed with several portions of water and then dried by pumping overnight. Two recrystallizations from dichloromethane-heptane afforded .2 g (58% yield) of product. Anal. calcd. for $C_9H_9N_3O_3ReBF_4$: C, 22.50; H, 1.89; N, 8.75. Found: C, 22.56; H, 2.14; N, 8.49. M.P. 171-173°.

The conductivity measurement performed on a 3.5 x 10^{-3} M nitromethane solution gave a value of 104.5 $ohm^{-1}cm^2mole^{-1}$.

The crystals for the X-ray determination were obtained by slow recrystallization from acetone-ethanol.

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