UNSATURATED DITERTIARY ARSINE DERIVATIVES OF SOME METAL CARBONYLS

By

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B.Sc. (Hons.), University of Waterloo, 1970

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY in the Department of CHEMISTRY

We accept this thesis as conforming to the required standard

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Department of CHEMISTRY

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Vancouver 8, Canada

Date Nov 4 1974
The meso and racemic forms of the new ditertiary arsine, cis-2,3-bis(methylphenylarsino)-1,1,1,4,4,4-hexafluorobut-2-ene (L-L)', were prepared by the reaction of hexafluorobutyne-2 with 1,2-dimethyl-1,2-diphenylarsine in hexafluoroacetone. The two diastereomers were isolated and reacted with iron pentacarbonyl affording (L-L)'Fe(CO)₃ and (L-L)'Fe₂(CO)₆. Two of the three possible geometric isomers of the latter were obtained and their properties allowed assignment of the configuration of the starting ligands. Minor amounts of the symmetric and asymmetric forms of Fe₂(CO)₆[As(CH₃)(C₆H₅)]₂ were also obtained through loss of fluorocarbon.

The complexes Fe₂(CO)₆[E(R₁)(R₂)]₂ (E = As, P; R₁ = R₂ = CH₃; R₁ = CH₃, R₂ = C₆H₅) were prepared and studied by ¹H and ¹³C nmr spectroscopy. Variable temperature ¹H nmr studies indicate the hexacarbonyl complexes are fluxional with respect to the [Fe-E]₂ cluster. Activation parameters were calculated for the motion and possible mechanisms are discussed. The ¹³C nmr spectra of the carbonyl groups at 25° and -70° suggest an independent intramolecular scrambling of the carbonyl groups about the iron atom.

Reactions of (L-L)' and the related ditertiary arsine ligand, cis-2,3-bis(dimethylarsino)-1,1,1,4,4,4-hexafluorobut-2-ene (L-L), with the Group VI metal hexacarbonyls gave the chelate complexes (L-L)'M(CO)₄ and (L-L)M(CO)₄. The (L-L)M-(CO)₄ complexes were irradiated with the 450W lamp in the
presence of excess (L-L), giving four different types of complexes: $\text{fac-(L-L)}^b_\text{M(CO)}_3$ and $\text{fac-(L-L)}^b_\text{trans-M(CO)}_3$ (where $b$ and $m$ denote bidentate and monodentate ligand respectively), $\text{cis-(L-L)}_2\text{M(CO)}_2$ and $\text{trans-(L-L)}_2\text{M(CO)}_2$.

The seven-coordinate complexes $(\text{L-L})\text{M(CO)}_3^X_2$ and $(\text{L-L})\text{M(CO)}_3^X_2$ ($\text{M} = \text{Mo, W}$; $X = \text{Br, I}$) were prepared and characterized. $^1\text{H}$ and $^13\text{C}$ nmr spectra at $25^\circ$ and $-70^\circ$ suggest the complexes are nonrigid. Similarly $^1\text{H}$ nmr studies indicate the seven-coordinate $(\text{L-L})\text{LMO(CO)}_2\text{Br}_2$ complexes are also nonrigid at $25^\circ$ and $-70^\circ$. The $(\text{L-L})_2\text{Mo(CO)}_2\text{Br}_2$ complexes ($\text{L}$ is a monodentate phosphite or phosphine) are rigid at $25^\circ$ and nonrigid at higher temperatures. Activation parameters were calculated for the motion of two of the complexes.

Finally, two novel Group VII metal carbonyl complexes of $(\text{L-L})$ of formula $\text{C}_{16}\text{H}_{18}\text{AsF}_3\text{O}_6\text{Mn}_2$ and $\text{C}_{11}\text{H}_8\text{AsF}_6\text{O}_5\text{Re}$ are described. The former contains a fluorinated $\pi$-allyl group bonded to one manganese atom and the latter a $\text{CH}_2\text{O}$ fragment $\sigma$-bonded to rhenium.
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CHAPTER I
INTRODUCTION

This thesis is concerned with the preparation, characterization, and general chemistry of some ditertiary arsine complexes of transition metal carbonyls with the emphasis on complexes of the Group VI metal carbonyls. Thus, the general introductory discussion is restricted to work on related six and seven-coordinate Group VI metal carbonyl complexes.

1. Six-Coordinate Group VI Metal Carbonyl Complexes

A. Preparative Methods

The general preparative methods for metal carbonyl complexes of chromium, molybdenum, and tungsten can be divided into two major routes as follows:

(1.) Direct displacement of carbon monoxide by a donating group—The displacement can be effected by refluxing the metal carbonyl and ligand in an appropriate solvent e.g. equation \([I]^{1}\), heating the reactants in a sealed tube e.g. equation \([II]^{2}\), or by ultraviolet irradiation of the reactants e.g.
equation [III]^3.

\[ \text{Mo(CO)}_6 + f_6\text{fos}^* \xrightarrow{\text{reflux in toluene}} (f_6\text{fos})\text{Mo(CO)}_4 \]  \[ \text{[I]} \]

\[ \text{Mo(CO)}_6 + (C_2H_5)_2\text{PC}_2H_4\text{P(C}_2H_5)_2 \xrightarrow{\text{sealed tube}} (C_2H_5)_2\text{PC}_2H_4\text{P(C}_2H_5)_2\text{Mo(CO)}_4 \]  \[ \text{[II]} \]

\[ \text{Mo(CO)}_6 + \text{NCCH}_3 \xrightarrow{\text{hv}} (\text{NCCH}_3)_2\text{Mo(CO)}_4 \]  \[ \text{[III]} \]

(2.) Displacement of substituent groups from partially substituted complexes by the desired ligand—
This route is useful for the preparation of specific complexes not obtainable through direct carbon monoxide replacement e.g. equations [IV]^2 and [V]^4.

\[ \text{Cr(CO)}_3(\text{mesitylene}) + \text{diphos}^{**} \xrightarrow{\text{sealed tube}} \text{trans-}(\text{diphos})_2\text{Cr(CO)}_2 \]  \[ \text{[IV]} \]

\[ \text{Mo(CO)}_3(\text{toluene}) + \text{piperazine} \rightarrow (\text{piperazine})_3\text{Mo(CO)}_3 + \text{toluene} \]  \[ \text{[V]} \]

Purification of the products is achieved by chromatography, recrystallization, or vacuum sublimation.

Thermal substitution reactions of the Group VI metal carbonyls can generally be carried out between 50 and 150° providing a strong donor ligand is present. However, certain

\[ * \quad f_6\text{fos} = (C_6H_5)_2\text{PC} = \text{CP(C}_6H_5)_2(\text{CF}_2)_3 \]

\[ ** \quad \text{diphos} = (C_6H_5)_2\text{PCH}_2\text{CH}_2\text{P(C}_6H_5)_2 \]
metal carbonyl derivatives (see Chapter IV) do not undergo thermal reaction even at very high temperatures. The maximum temperature which can be used for thermal substitution is limited by the range of stability of starting materials and final products.

In the photochemical reaction of metal carbonyl derivatives it is possible to isolate relatively unstable substitution products (at or below room temperature) not obtainable by the thermal method. Thus, a wide range of new compounds have become accessible by the photochemical procedure.

B. Infrared (ir) Studies

Ir spectroscopy has proven to be a valuable tool in studies of Group VI carbonyl reactions, both in characterizing the complexes and in monitoring the reactions. The number of ir-active carbonyl stretching fundamentals for geometrical isomers of the octahedral derivatives $L_xM(CO)_{6-x}$ can be derived (using group theory) on the basis of the local symmetry of the carbonyl groups undisplaced from the original octahedral array by substituent groups (i.e. only interactions among the carbonyl groups need be considered). This so-called "energy-factoring" approach is possible because the vibrational frequencies of carbonyl groups are so well separated from other vibrational frequencies.

Thus the number and intensity of carbonyl stretching vibrations have been used primarily to differentiate between Group VI metal cis$^{2,6,7}$ and trans$^{2,8}$ dicarbonyl, fac$^{2,7,9,10}$...
and mer$^{7,11}$ tricarbonyl, and cis$^{2,6,7,12}$ and trans$^{7,13,14}$ tetracarbonyl complexes.

The following section is concerned with a description of the widely accepted bonding mechanism in metal carbonyl complexes (which in turn is reflected in the carbonyl ir stretching frequencies). A knowledge of the bonding scheme is essential to understand the reactivity of the metal-carbon bond (in Group VI metal carbonyl complexes) with varying degrees of substitution.

C. Bonding in Metal Carbonyls

Carbon monoxide forms stable complexes with transition metals such as chromium, molybdenum, and tungsten, in which the metal is in a low oxidation state. The stabilization results from the fact that the carbon atom in carbon monoxide possesses vacant $\pi^*$ orbitals in addition to a lone pair.

Bonding is thought to involve the formation of $\sigma$ and $\pi$ bonds. The $\sigma$ bond results from the donation of the lone pair of electrons on the carbon atom to a vacant metal orbital as illustrated in 1. The $\pi$ bond results from back donation of electrons from the filled nonbonding $d$ orbitals on the metal to the low-lying $\pi$ antibonding orbitals of the carbon monoxide as illustrated in 2.*

* The metal-carbonyl bond would be quite weak if the bond is formed merely through donation of the lone pair since the nucleophilicity of carbon monoxide is considered to be quite low.
The two modes of bonding are mutually reinforcing or synergic since the charge removal from the metal through π "back bonding" increases the electron density on carbon, which then strengthens its σ bond formation. This then increases the electron density on the metal and strengthens its π bond formation.

In metal carbonyl complexes two types of "back bonding" mechanisms are possible:

1. dπ-π* "back bonding" and
2. dπ-dπ "back bonding".

Ligands such as carbon monoxide accept charge through dπ-π* "back bonding" since they have low-lying π* orbitals. Other
ligands such as arsines and phosphines accept charge through $d\pi-d\pi$ "back bonding" (illustrated in 2), since the coordinating atom, arsenic or phosphorus, possesses vacant $d$ orbitals. The degree of "back bonding" for these ligands varies as a function of the electronegativities of substituents on the donor atom.

Replacing some of the carbon monoxide groups of the parent carbonyl (e.g. Group VI metal hexacarbonyls) with ligands of lower $\pi$-acceptor ability causes the remaining carbon monoxide groups to accept $d\pi$ electrons from the metal to a greater extent, to prevent accumulation of charge on the metal atom. This produces a decrease in the carbonyl stretching frequency with corresponding increases in metal-carbon stretching frequencies.

As the degree of substitution of carbon monoxide with poorer $\pi$-acceptor ligands increases, the metal-carbon bond strength further increases making the ease of carbon monoxide displacement more difficult. Complete displacement of carbon monoxide from the Group VI metal hexacarbonyls has been achieved with trifluorophosphine,\textsuperscript{15,16} a ligand that is quite similar to carbon monoxide in $\pi$-accepting ability.\textsuperscript{17}

There appears to be differing schools of thought as to whether the change in the carbonyl stretching frequencies for a series of derivatives is a function of the relative $\sigma$ or $\pi$ bonding abilities of the ligands in the complex. Cotton\textsuperscript{18} has proposed that changes in the carbonyl stretching frequencies depend only on the $\pi$-accepting ability of the ligand
while Bigorgne believes the v(CO) changes are affected by the σ-donating ability of the donor atom. This is still a controversial subject; suffice it to say both effects influence the carbonyl stretching frequencies.

An important feature in the determination of stereochemistry and reactivity of metal carbonyl derivatives is the trans effect. Two carbonyl groups trans to each other compete across the metal atom for the same metal π bonding orbitals, whereas a carbonyl group trans to a weaker π-acceptor ligand is primarily responsible for the delocalization of the charge on the metal atom. Thus, in a reaction of a carbonyl derivative and a donor ligand, one of the trans carbonyl groups is the more labile and is usually displaced.

D. Nuclear Magnetic Resonance (nmr) Studies

The characterization of many Group VI metal carbonyl derivatives has been based mainly on $^1$H nmr spectroscopy. In metal complexes containing arsine or phosphine ligands, the protons in the ligands are deshielded and the $^1$H resonance peaks move downfield, providing a criterion of complex formation.

The $^1$H methyl resonance patterns of some tertiary phosphine disubstituted Group VIII metal complexes have been shown to be useful in determining the stereochemistry of the phosphine ligands, cis phosphines giving a well defined 1:1 doublet and trans phosphines a well defined 1:2:1 "triplet". However, Shaw and coworkers have shown, in some tertiary
phosphine disubstituted Group VI metal carbonyls, that the $^1H$ methyl resonance pattern is not generally useful in determining the stereochemistry of these complexes. Intermediate patterns (i.e. a broad resonance flanked by a 1:1 doublet) are observed for complexes in which the phosphine ligands are in \textit{cis} or \textit{trans} positions rather than the well defined doublet or "triplet" patterns.

$^{13}C$ nmr studies have been applied to a variety of Group VI metal carbonyl derivatives. Gansow et al.\textsuperscript{23} studied the $^{13}C$ nmr spectra of a series of monosubstituted LW(CO)$_5$ complexes and found a linear correlation between the carbonyl chemical shifts and the carbonyl stretching force constants. This was taken to suggest that changes in metal-carbon-oxygen $\pi$ bonding exert a dominant influence on $^{13}C$ chemical shifts. Very recently, Bodner and Todd\textsuperscript{24} found a correlation between the $^{13}C$ nmr carbonyl chemical shifts and the carbonyl stretching frequencies for a series of (\textit{$\pi$}-arene) tricarbonylchromium complexes. From the sign of the correlation they postulate that changes in the carbonyl chemical shift with varying substituents on the arene ring can be explained in terms of changes in the extent of metal to carbonyl $\pi$ back donation.

$^{31}P$ nmr studies on phosphine substituted Group VI metal carbonyl derivatives have yielded further information on the bonding and structure in these compounds. Grim et al.\textsuperscript{25} have shown in Group VI metal complexes of the type (L)(L')M(CO)$_4$ (L and L' are a tertiary phosphine and organophosphite or
two different tertiary phosphines) containing phosphorus atoms in cis positions, the $^{31}$P-$^{31}$P spin-coupling constant is considerably smaller than for the corresponding compounds with trans phosphorus atoms. Grim et al.\textsuperscript{26} have also found that in complexes of the type $(R_n^3$-$^3$-P)$^5$W(CO)$_5$ where $R$ is alkyl, n is 0-3, the size of the $^{183}$W-$^{31}$P spin-coupling constant appeared to be a measure of the $\pi$-acceptor ability of the phosphorus compound.

E. Mass Spectrometric Studies

The mass spectra of Group VI metal carbonyl derivatives are routinely used in conjunction with nmr and ir spectra in the elucidation of molecular structure. A typical spectrum usually gives a peak attributed to the parent ion as well as peaks due to the consecutive loss of carbonyl groups. Thus, the number of carbonyl groups present in a metal complex can generally be deduced from its mass spectrum; however, caution must be exercised in the interpretation of the mass spectral data of Group VI carbonyl complexes since the parent ion is not always obtained.

The fragmentation pattern has been used as a tool to differentiate between complexes $^4$ and $^5$,\textsuperscript{27} exhibiting no monomeric ions of the type $[(\text{CO})_n^\text{MP}_2(\text{CH}_3)_4]^+$ or $[(\text{CO})_n^\text{MP}(\text{CH}_3)_2]^+$ ($M=\text{Cr, Mo, W}; n=0-4$).

Apart from its use in structural elucidation, mass spectroscopic studies on Group VI carbonyl complexes have yielded other information. The mass spectra and ionization
potentials of some Group VI $\text{LM(CO)}_5$ complexes, where $L$ represents a series of monodentate ligands, have been reported. Variations in the donor-acceptor ability of the ligands were found to influence molecular ionization potentials and cracking patterns. The molecular ionization potentials were found to depend on the metal and the ligand.

Mass spectrometric studies of the effect of alkyl substituents in benzene rings on the metal-ligand bond strength in a series of substituted dibenzenechromium derivatives, have shown the chromium-ligand bond to be strengthened by increased donor ability of the ring alkyl substituents.

F. Reaction Mechanisms

The Group VI metal hexacarbonyls show no detectable exchange of carbon monoxide in solution at room temperature. However, at elevated temperature in the gas phase exchange occurs and the rate of exchange is independent of carbon monoxide concentration suggesting a dissociative process of the type represented by equation [VI]. Studies conducted
with substituted derivatives of chromium and molybdenum\textsuperscript{30} show that exchange of carbon monoxide is slower with the substituted complexes than with the parent hexacarbonyls. This is in agreement with an increase in the metal-carbon bond strength with increased substitution.

There have been no reports of kinetic studies of substitution of the Group VI metal hexacarbonyls by bidentate ligands. However, some data are available for the substitution of Group VI metal hexacarbonyl derivatives by bidentate ligands.

Connor et al.\textsuperscript{31, 32} have investigated the chelation reactions of some Group VI pentacarbonyl complexes containing potentially bidentate ligands that are monocoordinated. Their kinetic studies suggested the mechanism of chelation is concerted although the chromium reactions appeared to have more dissociative or $S_{N1}$ character in this concerted process.

Basolo et al.\textsuperscript{33} have studied the reaction of diphos with a series of cis- and trans-$L_2\text{Mo(CO)}_4$ complexes where $L$ is a phosphine or phosphite and have found that the rates do not depend on the concentration of diphos. A possible mechanism in accord with their findings can be represented as follows:
Dobson and coworkers have examined bidentate ligand replacement in some disubstituted Group VI metal tetracarbonyl complexes with such bidentate ligands as \((\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{N(CH}_3)_2\), \(\text{CH}_3\text{SCH}_2\text{CH}_2\text{SCH}_3\) and \((\text{C}_6\text{H}_5)_2\text{AsCH}_2\text{As}(\text{C}_6\text{H}_5)_2\). The bidentate ligands were completely displaced in all cases and there was no evidence for the ring-opened complex in which only one end of the ligand was coordinated. Kinetic results suggested ring-opening was rate determining but the ring-opened intermediate rapidly lost the ligand to give the observed product.

Recently, Angelici and Knebel\(^{37}\) have investigated chelate ring-opening reactions of a series of Group VI \((\text{P N})\text{M(CO)}_4\) complexes with carbon monoxide, giving the monocordinated ligand complex \((\text{P N})\text{M(CO)}_5\) (\(\text{P N}\) is a phosphorus-nitrogen donor bidentate ligand). They found the
rates of the reaction to be dependent upon the bulkiness of the groups on the nitrogen donor group of the ligand and the size of the chelate ring. Their kinetic studies provide some evidence that the reaction proceeds via a ring-opened five-coordinate intermediate according to the following mechanism:

\[
\begin{align*}
(CO)_4M\overset{N}{P} & \rightleftharpoons (CO)_4M\overset{P}{N} + CO \rightarrow (CO)_5M\overset{P}{N} \\
\text{[VIII]} 
\end{align*}
\]

The reactions of the Group VI metal hexacarbonyls with tertiary phosphines and phosphites have been extensively studied.\textsuperscript{38-41} It has been found that chromium hexacarbonyl usually favours reactions by a dissociative mechanism (S\textsubscript{N}1) while molybdenum and tungsten hexacarbonyls react via dissociative and associative mechanisms (S\textsubscript{N}1 and S\textsubscript{N}2). Equations [IX] and [X] illustrate the dissociative and associative processes respectively.

\[
\begin{align*}
M(CO)_6 \xrightarrow{-CO \text{ slow}} & M(CO)_5 \xrightarrow{+L \text{ fast}} LM(CO)_5 \\
\text{M} = \text{Cr, Mo, W} \\
\text{M(CO)}_6 + L \xrightarrow{\text{slow}} & LMo(CO)_6 \xrightarrow{-CO \text{ fast}} LM(CO)_5 \\
\text{M} = \text{Mo, W} \\
\text{[IX]} \\
\text{[X]} 
\end{align*}
\]
2. Seven-Coordinate Group VI Metal Carbonyl Complexes

This discussion is concerned with substituted halocarbonyls of molybdenum (II) and tungsten (II).

A. Preparative Methods

There are two principal methods of preparing substituted halocarbonyls of molybdenum (II) and tungsten (II). The first general method developed by Lewis and coworkers\textsuperscript{42-45} can be represented by the general equation \[\text{(XI)}\].

\[
\begin{align*}
\text{M(CO)}_6 & \xrightarrow{2L} \text{L}_2\text{M(CO)}_4 \xrightarrow{X_2} \text{L}_2\text{M(CO)}_3X_2 \\
\text{M} & = \text{Mo, W; } X = \text{Cl, Br, I}
\end{align*}
\]

In the equation \(L\) is a monodentate ligand, but the reaction works equally well if \(L_2\) is bidentate. Nyholm and coworkers\textsuperscript{44,45} have investigated the oxidation reactions of \((L_2)_2\text{M(CO)}_2\) (\(L_2\) is bidentate) and have found that complexes of differing metal oxidation state were formed depending on the halogen.

The second general method of preparation of the title compounds involves preparation of the parent halocarbonyls followed by reaction with the appropriate ligand, as illustrated in equation \[\text{(XII)}\] where \(L\) is a monodentate ligand.

\[
\begin{align*}
\text{M(CO)}_6 & \xrightarrow{X_2} \text{M(CO)}_4X_2 \xrightarrow{2L} \text{L}_2\text{M(CO)}_3X_2 \\
\text{M} & = \text{Mo, W; } X = \text{Cl, Br, I}
\end{align*}
\]

This method developed exclusively by Colton and associates.
involves the preparation of derivatives of monodentate and bidentate ligands.\textsuperscript{51-53} Dicarbonyl derivatives of bidentate ligands\textsuperscript{51-54} represented by the general formula $(\text{ligand})_2M(\text{CO})_2X_2$ ($M = \text{Mo, W}; X = \text{Cl, Br, I}$) have also been prepared by Colton and associates.

B. Conductometric Studies

Molar conductivity studies show that the complexes of the type $(\text{bidentate ligand}) M(\text{CO})_3X_2$ ($M = \text{Mo, W}; X = \text{Cl, Br, I}$) are all nonelectrolytes,\textsuperscript{44,45,51-53} whereas the dicarbonyl complexes can be formulated as either 1:1 electrolytes\textsuperscript{44,45,52} or nonelectrolytes.\textsuperscript{51-54}

C. Crystallographic Studies

For coordination number seven, three basic polyhedral geometries are possible: pentagonal bipyramid, capped octahedron, and capped trigonal prism. Recently X-ray structural determinations have been performed on four substituted Group VI metal halocarbonyl derivatives. These are briefly described below.

The complex bis[bis(diphenylarsino)methane]dibromodicarbonylmolybdenum(II)\textsuperscript{55} is best described as a distorted capped octahedron with a carbonyl group in the unique capping position; one of the arsine ligands is bi- and the other monodentate.

The tungsten atom in ditromotricarbonylbis[bis(diphenylarsino)methane]tungsten(II)\textsuperscript{56} has a distorted capped octahedral
environment, a carbonyl group occupying the unique capping position. Both ligands are monodentate. It is significant that the capped octahedral configuration in this complex and the one described in the preceding paragraph are very similar even though a carbonyl group has been replaced in the tungsten complex by the bulky and less electronegative diphenylarsino group in the molybdenum complex.

In the complex dibromotricarbonyl[1,2-bis(diphenylphosphino)ethane]molybdenum(II)-1-acetone\(^57\) the molybdenum atom has a slightly distorted capped octahedral environment with a carbonyl group again occupying the unique capping position.

The coordination sphere of the molybdenum atom in dicarbonylchlorobis[o-phenylenebis(dimethylarsino)]-molybdenum(II)tri-iodide-bischloroform\(^58\) is a capped trigonal prism, the chlorine atom occupying the capping position. The prism skeleton is illustrated in 6 where As As is the ditertiary arsine ligand.

![Diagram](image)

6 The ligand occupies bites a
It appears that the choice of polyhedron for a given substituted Group VI metal halocarbonyl is dictated by such factors as ligand-ligand repulsions, steric constraints of multidentate ligands, electronic structure of the metal, and crystal packing energies.

D. Ir Studies

In studies have been used to distinguish between the Group VI metal halotricarbonyl and halodicarbonyl complexes;\textsuperscript{44,45,51-54} the former exhibiting three strong carbonyl absorptions and the latter two strong carbonyl absorptions.

Ir studies have been applied to detect carbon monoxide carrying systems\textsuperscript{51,53} represented by the general equation [XIII].

\[
(ligand)_2M(CO)_3X_2 \xrightarrow{40^\circ} \text{CO} \rightleftharpoons (ligand)_2M(CO)_2X_2
\]

M = Mo, W; X = Cl, Br, I

The difference in carbonyl stretching frequencies has been applied to differentiate between an ionic and covalent bromotricarbonyl complex.\textsuperscript{45}

E. Nmr Studies

Nmr studies have been used principally to study the modes of coordination of potentially bidentate ligands in Group VI metal halocarbonyl complexes.\textsuperscript{51-54} In these studies information
is derived from the chemical shift of the methylene protons since the ligands employed are of the type \((C_6H_5)_2E(CH_2)_nE(C_6H_5)_2\) \((E = \text{As}, \text{P}, n = 1; E = \text{P}, n = 2)\); little information can be obtained from the chemical shifts of the phenyl groups.

Equation [XIV] illustrates a unique equilibrium\(^{53}\) that has been studied by nmr as each complex differs in the mode of coordination of the bidentate ligand \(L_2\).

\[
L_2\text{Mo(CO)}_3\text{I}_2 + L_2 \rightleftharpoons (L_2)\text{Mo(CO)}_3\text{I}_2 \rightleftharpoons (L_2)\text{Mo(CO)}_2\text{I}_2 + \text{CO} \tag{XIV}
\]

\(L_2 = (C_6H_5)_2\text{AsCH}_2\text{As}(C_6H_5)_2\)

Variable temperature nmr studies have been particularly useful in demonstrating stereochemical nonrigidity in some Group VI metal halocarbonyl complexes.

A variable temperature nmr study of the dicarbonyl complexes \([(C_6H_5)_2\text{AsCH}_2\text{As}(C_6H_5)_2]_2\text{M(CO)}_2\text{X}_2\) \((M = \text{Mo, W}; X = \text{Cl, Br, I})\) shows that, near room temperature, exchange occurs between the nonequivalent ligand molecules in the manner depicted in [XV]. The exchange ceases at lower temperature. This nmr study represents the first reported example of the nonrigid character of a seven-coordinate Group VI metal halocarbonyl complex.

Very recently, Rix et al.\(^{60}\) reported a variable temperature nmr study of the cationic species \((\text{P}_2\text{P})_2\text{Mo(CO)}_2\text{I} \quad (M = \text{Mo, W}; \text{P}_2\text{P} = (\text{CH}_3)_2\text{PCH}_2\text{CH}_2\text{P(CH}_3)_2)\) further demonstrating the
nonrigid character of seven-coordinate Group VI metal halocarbonyls. The limiting low temperature nmr spectra are consistent with a monocapped trigonal prismatic structure $Z$. The nonrigidity at higher temperatures is explained by a polytopal rearrangement, possibly by rapid migration of iodine over the five faces of the prism.
3. **This Work**

Chapter II of this thesis is devoted entirely to describing the preparation of the ditertiary arsine ligands cis-2,3-bis(methylphenylarsino)-1,1,1,4,4,4-hexafluorobut-2-ene (denoted as (L-L)) and cis-2,3-bis(dimethylarsino)-1,1,1,4,4,4-hexafluorobut-2-ene (denoted as (L-L)) and their transition metal carbonyl complexes. Analytical and spectroscopic data for the ligands and metal complexes are also included.

Chapter III is concerned with a discussion of the two ligands (L-L) and (L-L)' and some of their iron carbonyl complexes.

Chapter IV presents a discussion on some Group VI metal carbonyl complexes of (L-L) and (L-L)'.

Chapter V is concerned with a discussion on some seven-coordinate Group VI metal halocarbonyl derivatives of (L-L) and (L-L)' with the emphasis on the nonrigid character of these complexes.

Chapter VI includes a discussion on some novel manganese and rhenium carbonyl complexes of (L-L). The bridging methylphenylarsenido manganese carbonyl complex is also described.
CHAPTER II
EXPERIMENTAL

This chapter describes the various synthetic procedures used in the preparation of the ditertiary arsine ligands and their transition metal carbonyl complexes. Analytical and spectroscopic data for all new complexes are given in tabular form where applicable.

1. General Techniques and Physical Measurements

Air-sensitive starting materials were handled in a nitrogen atmosphere. All pyrolysis and photochemical (200W) reactions were carried out in sealed evacuated thick-walled Carius tubes. A standard vacuum system was used for the manipulation of volatile reactants.

Infrared (ir) spectra were recorded on a Perkin-Elmer 457 double beam spectrophotometer and calibrated using polystyrene and cyclohexane.

Nuclear magnetic resonance (nmr) spectra were run on Varian T-60, HA-100, XL-100, and CFT-20 spectrometers with chemical shifts given in ppm downfield from internal TMS for $^1H$ and $^{13}C$ spectra, and upfield from internal CFCl$_3$ for
$^{19}$F spectra. Heteronuclear decoupling experiments with noise modulation utilized instrumentation already described in the literature. Temperature studies were carried out on the HA-100 and XL-100 instruments using a Varian V-4343 variable temperature unit which was calibrated against an ethylene glycol standard sample.

Mass spectra were measured with an AEI MS-9 spectrometer with direct introduction of the solid sample.

Melting points were determined in open capillaries using a Gallenkamp melting point apparatus and are uncorrected. Unless otherwise stated all ultraviolet irradiations were performed using a 200W Hanovia 654A-36 lamp situated 20 cm from the reaction tube. The tube was continuously shaken and cooled by an air stream. In some cases irradiations were performed using a 450W Hanovia lamp placed in a water cooled quartz jacket. This was inserted into a larger glass jacket containing the solution to be irradiated. Nitrogen was bubbled through the solution during the course of the reactions.

Microanalyses were performed by P. Borda of this department.
2. **Starting Materials**

The following chemicals were obtained commercially and used without further purification.

Table I

Purchased Chemicals and Suppliers

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Suppliers</th>
</tr>
</thead>
<tbody>
<tr>
<td>deuterochloroform</td>
<td>Merck, Sharp, and Dohme of Canada Ltd.</td>
</tr>
<tr>
<td>$d_2$-methylene chloride</td>
<td>Merck, Sharp, and Dohme of Canada Ltd.</td>
</tr>
<tr>
<td>$d_6$-benzene</td>
<td>Merck, Sharp, and Dohme of Canada Ltd.</td>
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<tr>
<td>dimethylarsinic acid</td>
<td>Fisher Scientific Co.</td>
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<td>molybdenum hexacarbonyl</td>
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</tr>
<tr>
<td>tungsten hexacarbonyl</td>
<td>Strem Chemical Co.</td>
</tr>
<tr>
<td>dimanganese decacarbonyl</td>
<td>Pressure Chemical Co.</td>
</tr>
<tr>
<td>dirhenium decacarbonyl</td>
<td>Strem Chemical Co.</td>
</tr>
<tr>
<td>iron pentacarbonyl</td>
<td>Alfa Inorganics Inc.</td>
</tr>
<tr>
<td>triphenylphosphine</td>
<td>Eastman Organic Chemicals</td>
</tr>
<tr>
<td>dimethylphenylphosphine</td>
<td>Strem Chemical Co.</td>
</tr>
<tr>
<td>methyldiphenylphosphine</td>
<td>Strem Chemical Co.</td>
</tr>
</tbody>
</table>
### Table I (Continued)

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Suppliers</th>
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<tbody>
<tr>
<td>dimethyl phenylphosphonite</td>
<td>Strem Chemical Co.</td>
</tr>
<tr>
<td>trifluorophosphine</td>
<td>Strem Chemical Co.</td>
</tr>
<tr>
<td>trimethylphosphite</td>
<td>Eastman Organic Chemicals</td>
</tr>
<tr>
<td>triethylphosphite</td>
<td>Eastman Organic Chemicals</td>
</tr>
</tbody>
</table>
3. **Preparation of the Diarsines and Diphosphine**

   A. **1,2-Dimethyl-1,2-Diphenyldiarsine**\(^{62,63}\)

   Benzenearsonic acid (100 g, 495 mmol) was dissolved in 240 ml of warm concentrated hydrochloric acid with a trace (0.1 g) of potassium iodide being added. Sulphur dioxide was passed through the solution for 1 h producing crude dichlorophenylarsine (106 g, 96%) as a dense yellow oil.

   The dichloroarsine (106 g, 475 mmol) was slowly added with stirring to a solution of sodium hydroxide (92 g, 2.3 mol) in water (200 ml). A cloudy white solution resulted. This was cooled and placed in a 3-necked flask equipped with condenser, stirring bar, and dropping funnel. Dimethyl sulfate (75 g, 590 mmol) was added, dropwise, with stirring, keeping the temperature between 20 and 30\(^\circ\). After stirring overnight, the temperature was raised to 80\(^\circ\) for 1 h. The precipitated salts were filtered off, the filtrate evaporated to 250 ml and made neutral to litmus paper with sulphuric acid (18N). The solution was treated with absolute ethanol (250 ml) and filtered. The filtrate was made acid to congo red paper with sulphuric acid (18N), the precipitated salts removed, and the residual solution concentrated to 200 ml. After dilution with absolute ethanol (600 ml), the salts which separated were filtered and the ethanol solution evaporated to dryness. The salt fractions were washed out with acetone and then dried in vacuo yielding white crystals of methylphenylarsinic acid (85 g, 90%).
Methylphenylarsinic acid (21.7 g, 109 mmol) with 38.3 g (580 mmol) of aqueous 50% hypophosphorous acid and 290 ml of absolute ethanol were refluxed for 6 h under nitrogen. The system rapidly became murky. Upon cooling, the ethanol was removed from the suspension of white crystals. The solid residues were extracted from the acid layer with 300 ml of degassed petroleum ether (bp 65-110°). The extract was filtered and cooled to -20°, yielding air-sensitive white needles of 1,2-dimethyl-1,2-diphenyldiarsine (10 g, 56%).

The nmr spectrum (CCl₄ solution) showed two singlets at 1.20 (CH₃)(area 6) and 1.30 (CH₃)(area 6), and a multiplet centred at 7.30 (C₆H₅)(area 20).

B. Tetramethyldiarsine

Tetramethyldiarsine was prepared by the reduction of dimethylarsinic acid in 2M hydrochloric acid with hypophosphorous acid; the diarsine was used without further purification.

C. Tetramethyldiphosphine

Tetramethyldiphosphine was obtained via a sulphur exchange between tetramethyldiphosphine disulphide and tributylphosphine.
4. Preparation of the Ligands

A. Cis-2,3-Bis(methylphenylarsino)-1,1,1,4,4,4-
Hexafluorobut-2-ene (L-L)

1,2-dimethyl-1,2-diphenyldiarsine (8 g, 24 mmol), dissolved in 25 ml of petroleum ether (bp 30-60°) and excess hexafluoroacetone (14 g, 84 mmol) were sealed under vacuum in a Pyrex tube and allowed to stand (with occasional shaking) for 4 h at 20°. The tube was then opened and hexafluorobutyne-2 (6 g, 36 mmol) was added. The tube contents were allowed to react at 20° for 5 days with periodic shaking. Excess volatile starting materials and solvent were taken into the vacuum system leaving a viscous yellow liquid (8 g, 67%) to which hexane (50 ml) was added until the solution turned cloudy. Upon cooling in dry ice, white air-stable crystals of the racemic isomer of cis-2,3-bis(methylphenylarsino)-1,1,1,4,4,4-hexafluorobut-2-ene were isolated (mp 79-81°).

The nmr spectra (CCl₄ solution) consisted of a singlet at 1.20 (CH₃), a multiplet centred at 7.40 (C₆H₅), and a singlet at 53.2 (CF₃).

Anal. Calcd. for C₁₈H₁₆F₆As₂: C, 43.6; H, 3.2. Found: C, 43.6; H, 3.1.

The solvent was removed under reduced pressure leaving a yellow air-stable liquid which was warmed to 34° at 0.1 mm to remove a small amount of impurity. The substantially pure meso isomer of cis-2,3-bis(methylphenylarsino)-1,1,1,4,4,4-
hexafluorobut-2-ene remained. It was not possible to distill the product without decomposition.

The nmr spectra (CCl₄ solution) consisted of a broad singlet at 1.50 (CH₃), a multiplet centred at 7.20 (C₆H₅) and a singlet at 53.0 (CF₃). Traces of the trans-adduct (containing the meso and racemic diastereomers) were also present in this fraction, as indicated by the presence of absorptions at 50.0 and 50.8 in the ¹⁹F spectrum.

Anal. Calcd. for C₁₈H₁₆F₆As₂: C, 43.6; H, 3.2. Found: C, 43.5; H, 3.1.

The ir spectrum of both diastereomers showed the following bands (liquid film): 3071(w), 3051(w), 2955(w), 2923(m), 1565(m), 1483(s), 1435(s), 1377(w), 1333(w), 1305(w), 1230(vs,br), 1145(vs,br), 1077(m), 1025(m), 995(m), 855(m), 837(m), 731(s), 689(s), 645(m) cm⁻¹.*

B. Cis-2,3-Bis(dimethylarsino)-1,1,1,4,4,4-Hexa-
fluorobut-2-ene⁶⁷ (L-L)

Tetramethyldiarsine (14 g, 67 mmol) and excess hexa-
fluoroacetone (30 g, 180 mmol) were sealed under vacuum in a Pyrex tube and allowed to stand (with occasional shaking) for 2 h at 20°. The tube was opened and hexafluorobutyne-2 (18 g, 108 mmol) was added. After resealing the tube

* vs = very strong, s = strong, m = medium, w = weak, br = broad
the contents were allowed to react at room temperature for 2 days. Excess volatile starting materials were taken into the vacuum system leaving a yellow liquid.

The nmr spectra (CCl₄ solution) showed a singlet at 1.32 (CH₃) and a singlet at 53.2 (CF₃).

The ir spectrum showed the following bands (liquid film): 2990(w), 2915(w), 1570(w), 1425(m), 1300(w), 1230(vs), 1175(sh,s), 1152(vs), 1135(vs), 897(w), 867(w), 852(w), 652(m) cm⁻¹.
A number of reactions between iron pentacarbonyl and the meso and racemic forms of (L-L)' are given in tabular form in Table II. In all cases the crude reaction mixture was evaporated to dryness and the residue was chromatographed on Florisil (100-200 mesh) using nitrogen saturated solvents as eluents as indicated in Table II.

Analytical and spectroscopic data for the products of all these reactions are listed in Tables III, IV, and V.

The following gives the detailed experimental conditions for a typical reaction between iron pentacarbonyl and (L-L)'.

Iron pentacarbonyl (5 g, 25.5 mmol) and rac-(L-L)' (1 g, 2.0 mmol) in 20 ml of benzene were sealed in an evacuated thick-walled Carius tube, and heated at 150° for 2 days. The final solution (initially yellow) was dark brown-red. The tube was opened and volatile material removed under reduced pressure. The resulting dark oil was dissolved in a minimum of methylene chloride and chromatographed on Florisil. Petroleum ether (bp 30-60°) eluted a brown band which upon solvent removal and recrystallization (from petroleum ether) at dry ice temperature, yielded brown crystals of rac-(L-L)'Fe(CO)₃ (0.19 g, 15%); mp 142-143° (with decomposition).

A 5% diethyl ether, 95% petroleum ether mixture eluted
an orange band which upon solvent removal and recrystallization from the same solvent mixture at dry ice temperature, afforded dark red-brown crystals of rac-(L-L)'Fe₂(CO)₆ (0.55 g, 35%); mp 173-175°.

B. Reactions of (L-L)' with Group VI Metal Hexacarbonyls

All reactions between (L-L)' and M(CO)₆ (M = Cr, Mo, W) were performed at 150° for the time indicated in Table VI.

Analytical, preparative, and spectroscopic data for the diastereomeric (L-L)'M(CO)₄ products are given in Tables VI, VII, and VIII.

The following experimental details are given for a typical reaction between (L-L)' and chromium hexacarbonyl.

The hexacarbonyl (0.2 g, 0.91 mmol) and rac-(L-L)' (0.5 g, 1.0 mmol) in 15 ml of benzene were sealed in an evacuated Carius tube and heated at 150° for 29 h. The final solution (initially pale yellow) was deep amber. After removal of suspended solid material the solvent was evaporated under reduced pressure and the resulting oily residue recrystallized from hexane at 0°, yielding amber crystals of rac-(L-L)'Cr(CO)₄ (0.33 g, 55%); mp 148-149°.
### Table II

Reactions of Iron Pentacarbonyl with (L-L)'

<table>
<thead>
<tr>
<th>No</th>
<th>Fe(CO)$_5$</th>
<th>(L-L)'</th>
<th>Conditions</th>
<th>Products</th>
<th>Yield %</th>
<th>Purification</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5 g</td>
<td>rac 1 g</td>
<td>Uv irradiation in benzene (25 ml) for 3 days</td>
<td>rac-(L-L)'Fe(CO)$_3$</td>
<td>40</td>
<td>C (1)</td>
</tr>
<tr>
<td></td>
<td>25 mmol</td>
<td>2 mmol</td>
<td></td>
<td>rac-(L-L)'Fe$_2$(CO)$_6$</td>
<td>10</td>
<td>C (3)</td>
</tr>
<tr>
<td>2</td>
<td>5 g</td>
<td>rac 1 g</td>
<td>Pyrolysis in benzene (20 ml) at 150° for 2 days</td>
<td>rac-(L-L)'Fe(CO)$_3$</td>
<td>15</td>
<td>C (1)</td>
</tr>
<tr>
<td></td>
<td>25 mmol</td>
<td>2 mmol</td>
<td></td>
<td>rac-(L-L)'Fe$_2$(CO)$_6$</td>
<td>35</td>
<td>C (3)</td>
</tr>
<tr>
<td>3</td>
<td>5 g</td>
<td>rac 1 g</td>
<td>Pyrolysis in benzene (20 ml) at 150° for 3 days</td>
<td>Fe$_2$(CO)$_6$[As(CH$_3$)(C$_6$H$_5$)$_2$]**</td>
<td>10</td>
<td>C (1)</td>
</tr>
<tr>
<td></td>
<td>25 mmol</td>
<td>2 mmol</td>
<td></td>
<td>rac-(L-L)'Fe$_2$(CO)$_6$</td>
<td>15</td>
<td>C (2)</td>
</tr>
<tr>
<td>4</td>
<td>5 g</td>
<td>meso 1 g</td>
<td>Uv irradiation in benzene (25 ml) for 3 days</td>
<td>Fe$_2$(CO)$_6$[As(CH$_3$)(C$_6$H$_5$)$_2$]**</td>
<td>trace</td>
<td>C (1)</td>
</tr>
<tr>
<td></td>
<td>25 mmol</td>
<td>2 mmol</td>
<td></td>
<td>meso-(L-L)'Fe(CO)$_3$</td>
<td>25</td>
<td>C (2)</td>
</tr>
<tr>
<td>5</td>
<td>5 g</td>
<td>meso 1 g</td>
<td>Pyrolysis in benzene (20 ml) at 150° for 2 days</td>
<td>Fe$_2$(CO)$_6$[As(CH$_3$)(C$_6$H$_5$)$_2$]**</td>
<td>10</td>
<td>C (1)</td>
</tr>
<tr>
<td></td>
<td>25 mmol</td>
<td>2 mmol</td>
<td></td>
<td>meso-(L-L)'Fe$_2$(CO)$_6$</td>
<td>15</td>
<td>C (2)</td>
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</table>
### Table II (Continued)

<table>
<thead>
<tr>
<th>No</th>
<th>Fe(CO)$_5$ (L-L)'</th>
<th>Conditions</th>
<th>Products</th>
<th>Yield %</th>
<th>Purification</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>5 g meso 1 g</td>
<td>Pyrolysis in benzene (20 ml) at 150° for 3 days</td>
<td>Fe$_2$(CO)$_6$[As(CH$_3$)(C$_6$H$_5$)]$_2$ (1)</td>
<td>35</td>
<td>C (1)</td>
</tr>
<tr>
<td>25</td>
<td>2 mmol</td>
<td></td>
<td>meso-(L-L)'Fe$_2$(CO)$_6$ (2)</td>
<td>15</td>
<td>C (2)</td>
</tr>
</tbody>
</table>

* C indicates chromatography in Florisil. The arabic numeral indicates the solvent required to elute the product: (1) is 100% petroleum ether (bp 30-60°), (2) is 98% petroleum ether, 2% diethyl ether, (3) is 95% petroleum ether, 5% diethyl ether. In each case after chromatographing, the solvent was removed and resulting solid (or oil) recrystallized at dry ice temperature in the same solvent mixture used for elution.

** This is mainly the symmetric isomer with trace amounts of the asymmetric one.
Table III

Analytical Data for Iron Carbonyl Complexes of (L-L)'

<table>
<thead>
<tr>
<th>Compound</th>
<th>Colour</th>
<th>Mp(°C)</th>
<th>Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Calcd.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe₂(CO)₆[As(CH₃)(C₆H₅)]₂</td>
<td>orange</td>
<td>162-164</td>
<td>39.20</td>
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<tr>
<td>(symmetric)</td>
<td></td>
<td></td>
<td>39.00</td>
</tr>
<tr>
<td>Fe₂(CO)₆[As(CH₃)(C₆H₅)]₂</td>
<td>orange</td>
<td>93-95</td>
<td>39.20</td>
</tr>
<tr>
<td>(asymmetric)</td>
<td></td>
<td></td>
<td>39.49</td>
</tr>
<tr>
<td>rac-(L-L)'Fe(CO)₃</td>
<td>brown</td>
<td>142-143*</td>
<td>39.62</td>
</tr>
<tr>
<td>meso-(L-L)'Fe(CO)₃</td>
<td>brown</td>
<td>117-120*</td>
<td>39.62</td>
</tr>
<tr>
<td>rac-(L-L)'Fe₂(CO)₆</td>
<td>red-brown</td>
<td>173-175*</td>
<td>37.12</td>
</tr>
<tr>
<td>meso-(L-L)'Fe₂(CO)₆</td>
<td>red-brown</td>
<td>144-146</td>
<td>37.12</td>
</tr>
</tbody>
</table>

* With decomposition
Table IV

Ir Spectra (2100-1900 cm\(^{-1}\)) for Iron Carbonyl Complexes of (L-L)'

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\nu(CO)(\text{cm}^{-1})^*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Fe}_2\text{(CO)}_6[\text{As(CH}_3\text{)(C}_6\text{H}_5\text{)}]_2) (symmetric)</td>
<td>2052(s), 2009(vs), 1979(vs), 1965(vs), 1955(m)</td>
</tr>
<tr>
<td>(\text{Fe}_2\text{(CO)}_6[\text{As(CH}_3\text{)(C}_6\text{H}_5\text{)}]_2) (asymmetric)</td>
<td>2052(s), 2007(vs), 1977(vs), 1965(vs), 1955(m)</td>
</tr>
<tr>
<td>rac-(L-L)'Fe(CO)(_3)</td>
<td>2003(vs), 1937(s), 1919(vs)</td>
</tr>
<tr>
<td>meso-(L-L)'Fe(CO)(_3)</td>
<td>2003(vs), 1939(s), 1921(vs)</td>
</tr>
<tr>
<td>rac-(L-L)'Fe(_2\text{(CO)}_6)</td>
<td>2064(m), 2023(s), 1999(m), 1985(m), 1971(w), 1959(w)</td>
</tr>
<tr>
<td>meso-(L-L)'Fe(_2\text{(CO)}_6)</td>
<td>2064(m), 2023(s), 1995(m), 1983(m), 1967(w), 1955(w)</td>
</tr>
</tbody>
</table>

* \(\text{C}_6\text{H}_{12}\) solution
Table V

Nmr Data for Iron Carbonyl Complexes of (L-L)*

<table>
<thead>
<tr>
<th>Compound</th>
<th>$^1$H</th>
<th>$^{19}$F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_2$(CO)$_6$[As(CH$_3$)(C$_6$H$_5$)]$_2$ (symmetric)</td>
<td>Singlet at 1.93 (CH$_3$). Multiplet centred at 6.93 (C$_6$H$_5$)</td>
<td>-</td>
</tr>
<tr>
<td>Fe$_2$(CO)$_6$[As(CH$_3$)(C$_6$H$_5$)]$_2$ (asymmetric)</td>
<td>Singlets at 0.93 and 2.0 (CH$_3$). Multiplets centred at 6.93 and 7.4 (C$_6$H$_5$)</td>
<td>-</td>
</tr>
<tr>
<td>rac-(L-L)'Fe(CO)$_3$</td>
<td>Singlet at 2.27 (CH$_3$). Singlet at 7.50 (C$_6$H$_5$)</td>
<td>Singlet at 51.0 (CF$_3$)</td>
</tr>
<tr>
<td>meso-(L-L)'Fe(CO)$_3$</td>
<td>Singlet at 2.23 (CH$_3$). Singlet at 7.53 (C$_6$H$_5$)</td>
<td>Singlet at 51.8 (CF$_3$)</td>
</tr>
<tr>
<td>rac-(L-L)'Fe$_2$(CO)$_6$</td>
<td>Singlets at 1.22 and 2.57 (CH$_3$). Multiplets centred at 7.0, 7.5, and 7.9 (C$_6$H$_5$)</td>
<td>Quartets centred at 41.0 and 46.8 (CF$_3$) $J$(F,F) = 11.3 Hz</td>
</tr>
<tr>
<td>meso-(L-L)'Fe$_2$(CO)$_6$</td>
<td>Singlet at 2.57 (CH$_3$). Multiplet centred at 7.0 (C$_6$H$_5$)</td>
<td>Singlet at 44.5 (CF$_3$)</td>
</tr>
</tbody>
</table>

* CDC$_3$ solution
### Table VI

Analytical and Preparative Data for Diastereomeric Group VI (L-L) M(CO)$_4$ Complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Colour</th>
<th>Mp(°C)</th>
<th>Reaction Time</th>
<th>Yield</th>
<th>Calcd. C</th>
<th>Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>rac-(L-L) Cr(CO)$_4$</td>
<td>amber</td>
<td>148-149</td>
<td>29</td>
<td>60</td>
<td>40.00</td>
<td>40.12</td>
</tr>
<tr>
<td>meso-(L-L) Cr(CO)$_4$</td>
<td>amber</td>
<td>158-161</td>
<td>25</td>
<td>55</td>
<td>40.00</td>
<td>40.11</td>
</tr>
<tr>
<td>rac-(L-L) Mo(CO)$_4$</td>
<td>yellow</td>
<td>140-143</td>
<td>19</td>
<td>75</td>
<td>37.50</td>
<td>37.21</td>
</tr>
<tr>
<td>meso-(L-L) Mo(CO)$_4$</td>
<td>yellow</td>
<td>164-166*</td>
<td>17</td>
<td>75</td>
<td>37.50</td>
<td>37.49</td>
</tr>
<tr>
<td>rac-(L-L) W(CO)$_4$</td>
<td>yellow</td>
<td>156-158</td>
<td>47</td>
<td>90</td>
<td>33.33</td>
<td>33.45</td>
</tr>
<tr>
<td>meso-(L-L) W(CO)$_4$</td>
<td>yellow</td>
<td>166-169</td>
<td>46</td>
<td>90</td>
<td>33.33</td>
<td>33.05</td>
</tr>
</tbody>
</table>

* With decomposition
Table VII

Ir Spectra (2100-1900 cm\(^{-1}\)) for Diastereomeric Group VI (L-L)\(^\prime\)M(CO)\(_4\) Complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>(v)(CO)(cm(^{-1}))*</th>
</tr>
</thead>
<tbody>
<tr>
<td>rac-(L-L)'Cr(CO)(_4)</td>
<td>2021(m), 1935(s), 1913(vs)</td>
</tr>
<tr>
<td>meso-(L-L)'Cr(CO)(_4)</td>
<td>2021(m), 1937(s), 1911(vs)</td>
</tr>
<tr>
<td>rac-(L-L)'Mo(CO)(_4)</td>
<td>2040(m), 1947(s), 1925(vs)</td>
</tr>
<tr>
<td>meso-(L-L)'Mo(CO)(_4)</td>
<td>2040(m), 1947(s), 1923(vs)</td>
</tr>
<tr>
<td>rac-(L-L)'W(CO)(_4)</td>
<td>2036(m), 1935(s), 1913(vs)</td>
</tr>
<tr>
<td>meso-(L-L)'W(CO)(_4)</td>
<td>2032(m), 1937(s), 1915(vs)</td>
</tr>
</tbody>
</table>

* C\(_6\)H\(_{12}\) solution
### Table VIII

Nmr Data for Diastereomeric Group VI (L-L) \( \text{M(CO)}_4 \) Complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>( l_H^* )</th>
<th>( l_F^* )</th>
</tr>
</thead>
<tbody>
<tr>
<td>rac-(L-L)'Cr(CO)_4</td>
<td>Singlet at 2.15</td>
<td>Singlet at 50.6</td>
</tr>
<tr>
<td></td>
<td>((\text{CH}_3)). Multiplet centred at 7.40 ((\text{C}_6\text{H}_5))</td>
<td>((\text{CF}_3))</td>
</tr>
<tr>
<td>meso-(L-L)'Cr(CO)_4</td>
<td>Singlet at 2.13</td>
<td>Singlet at 51.4</td>
</tr>
<tr>
<td></td>
<td>((\text{CH}_3)). Multiplet centred at 7.40 ((\text{C}_6\text{H}_5))</td>
<td>((\text{CF}_3))</td>
</tr>
<tr>
<td>rac-(L-L)'Mo(CO)_4</td>
<td>Singlet at 2.18</td>
<td>Singlet at 50.8</td>
</tr>
<tr>
<td></td>
<td>((\text{CH}_3)). Multiplet centred at 7.40 ((\text{C}_6\text{H}_5))</td>
<td>((\text{CF}_3))</td>
</tr>
<tr>
<td>meso-(L-L)'Mo(CO)_4</td>
<td>Singlet at 2.15</td>
<td>Singlet at 51.0</td>
</tr>
<tr>
<td></td>
<td>((\text{CH}_3)). Multiplet centred at 7.40 ((\text{C}_6\text{H}_5))</td>
<td>((\text{CF}_3))</td>
</tr>
<tr>
<td>rac-(L-L)'W(CO)_4</td>
<td>Singlet at 2.30</td>
<td>Singlet at 50.3</td>
</tr>
<tr>
<td></td>
<td>((\text{CH}_3)). Multiplet centred at 7.40 ((\text{C}_6\text{H}_5))</td>
<td>((\text{CF}_3))</td>
</tr>
<tr>
<td>meso-(L-L)'W(CO)_4</td>
<td>Singlet at 2.28</td>
<td>Singlet at 50.3</td>
</tr>
<tr>
<td></td>
<td>((\text{CH}_3)). Multiplet centred at 7.43 ((\text{C}_6\text{H}_5))</td>
<td>((\text{CF}_3))</td>
</tr>
</tbody>
</table>

* \( \text{CS}_2 \) solution
C. Preparation of the Diastereomeric (L-L)\(\text{M(CO)}_3X_2\) Complexes (M = Mo, W; X = Br, I)

The (L-L)\(\text{M(CO)}_4\) complexes (M = Mo, W) in degassed methylene chloride (25 ml) were treated slowly with an equimolar amount of the halogen (bromine, iodine) in degassed methylene chloride (25 ml) under nitrogen, at 0°, with efficient stirring to avoid local concentration of the halogen. The solution was then stirred for 3 h at room temperature and filtered. Upon concentration of the methylene chloride at reduced pressure, addition of degassed hexane, and cooling to -20° the crystalline (L-L)\(\text{M(CO)}_3X_2\) complexes separated. They were washed with hexane and dried in vacuo.

Analytical, preparative, and spectroscopic data for the diastereomeric (L-L)\(\text{M(CO)}_3X_2\) complexes are given in Tables IX, X, and XI.

* It was found that a higher yield of the tricarbonyl complexes could be obtained by doing the halogen addition at 0°, then warming the solution to room temperature rather than performing the entire reaction at room temperature. The latter method appeared to give the required complex as well as substantial amounts of other species probably resulting from the replacement of more than one carbonyl group by the halogen.
Table IX

Analytical and Preparative Data for Diastereomeric (L-L)′M(CO)ₓ² Complexes*  
(M = Mo, W; X = Br, I)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Colour</th>
<th>Yield</th>
<th>Calcd.</th>
<th>Analyses</th>
<th>Found</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>%</td>
<td>C</td>
<td>H</td>
<td>X</td>
</tr>
<tr>
<td>rac-(L-L)′Mo(CO)₃I₂</td>
<td>orange</td>
<td>75</td>
<td>27.09</td>
<td>1.72</td>
<td>27.31(I)</td>
</tr>
<tr>
<td>meso-(L-L)′Mo(CO)₃I₂</td>
<td>orange</td>
<td>75</td>
<td>27.09</td>
<td>1.72</td>
<td>27.31(I)</td>
</tr>
<tr>
<td>rac-(L-L)′Mo(CO)₃Br₂</td>
<td>yellow</td>
<td>42</td>
<td>30.14</td>
<td>1.91</td>
<td>19.14(Br)</td>
</tr>
<tr>
<td>meso-(L-L)′Mo(CO)₃Br₂</td>
<td>yellow</td>
<td>45</td>
<td>30.14</td>
<td>1.91</td>
<td>19.14(Br)</td>
</tr>
<tr>
<td>rac-(L-L)′W(CO)₃I₂</td>
<td>orange</td>
<td>65</td>
<td>24.76</td>
<td>1.57</td>
<td>24.95(I)</td>
</tr>
<tr>
<td>meso-(L-L)′W(CO)₃I₂</td>
<td>orange</td>
<td>57</td>
<td>24.76</td>
<td>1.57</td>
<td>24.95(I)</td>
</tr>
<tr>
<td>rac-(L-L)′W(CO)₃Br₂</td>
<td>yellow</td>
<td>60</td>
<td>27.27</td>
<td>1.73</td>
<td>17.31(Br)</td>
</tr>
<tr>
<td>meso-(L-L)′W(CO)₃Br₂</td>
<td>yellow</td>
<td>60</td>
<td>27.27</td>
<td>1.73</td>
<td>17.31(Br)</td>
</tr>
</tbody>
</table>

* All complexes decomposed without melting above 120°.
Table X

Ir Spectra (2100-1900 cm\(^{-1}\)) for Diastereomeric \((L-L)'M(CO)\(_3\)X\(_2\) Complexes (M = Mo, W; X = Br, I)

<table>
<thead>
<tr>
<th>Compound</th>
<th>(v(CO)(\text{cm}^{-1})^*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>rac-(L-L)'Mo(CO)(_3)I(_2)</td>
<td>2056(s), 1989(vs), 1937(s)</td>
</tr>
<tr>
<td>meso-(L-L)'Mo(CO)(_3)I(_2)</td>
<td>2056(s), 1991(vs), 1937(s)</td>
</tr>
<tr>
<td>rac-(L-L)'Mo(CO)(_3)Br(_2)</td>
<td>2076(s), 1989(vs), 1927(s)</td>
</tr>
<tr>
<td>meso-(L-L)'Mo(CO)(_3)Br(_2)</td>
<td>2076(s), 1997(vs), 1933(s)</td>
</tr>
<tr>
<td>rac-(L-L)'W(CO)(_3)I(_2)</td>
<td>2048(s), 1971(vs), 1919(s)</td>
</tr>
<tr>
<td>meso-(L-L)'W(CO)(_3)I(_2)</td>
<td>2048(s), 1977(vs), 1923(s)</td>
</tr>
<tr>
<td>rac-(L-L)'W(CO)(_3)Br(_2)</td>
<td>2068(s), 1974(vs), 1923(s)</td>
</tr>
<tr>
<td>meso-(L-L)'W(CO)(_3)Br(_2)</td>
<td>2068(s), 1971(vs), 1925(s)</td>
</tr>
</tbody>
</table>

* \(\text{CH}_2\text{Cl}_2\) solution
Table XI

Nmr Data for Diastereomeric \((L-L)^\prime M(\text{CO})_3 X_2\) Complexes
\((M = \text{Mo, W}; X = \text{Br, I})\)

<table>
<thead>
<tr>
<th>Compound</th>
<th>(^1 H^*)</th>
<th>(^{19} F^*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>rac-(L-L)'Mo(\text{CO})_3\text{I}_2</td>
<td>Singlet at 2.64 (\text{CH}_3).</td>
<td>Singlet at 50.4</td>
</tr>
<tr>
<td></td>
<td>Singlet at 7.55 ((\text{C}_6\text{H}_5))</td>
<td>((\text{CF}_3))</td>
</tr>
<tr>
<td>meso-(L-L)'Mo(\text{CO})_3\text{I}_2</td>
<td>Singlet at 2.87 ((\text{CH}_3)).</td>
<td>Singlet at 50.8</td>
</tr>
<tr>
<td></td>
<td>Multiplet centred at 7.40 ((\text{C}_6\text{H}_5))</td>
<td>((\text{CF}_3))</td>
</tr>
<tr>
<td>rac-(L-L)'\text{W}(\text{CO})_3\text{I}_2</td>
<td>Singlet at 2.63 ((\text{CH}_3)).</td>
<td>Singlet at 50.8</td>
</tr>
<tr>
<td></td>
<td>Singlet at 7.53 ((\text{C}_6\text{H}_5))</td>
<td>((\text{CF}_3))</td>
</tr>
<tr>
<td>meso-(L-L)'\text{W}(\text{CO})_3\text{I}_2</td>
<td>Singlet at 2.90 ((\text{CH}_3)).</td>
<td>Singlet at 51.2</td>
</tr>
<tr>
<td></td>
<td>Multiplet centred at 7.38 ((\text{C}_6\text{H}_5))</td>
<td>((\text{CF}_3))</td>
</tr>
<tr>
<td>rac-(L-L)'\text{W}(\text{CO})_3\text{Br}_2</td>
<td>Singlet at 2.50 ((\text{CH}_3)).</td>
<td>Singlet at 51.2</td>
</tr>
<tr>
<td></td>
<td>Singlet at 7.58 ((\text{C}_6\text{H}_5))</td>
<td>((\text{CF}_3))</td>
</tr>
<tr>
<td>meso-(L-L)'\text{W}(\text{CO})_3\text{Br}_2</td>
<td>Singlet at 2.70 ((\text{CH}_3)).</td>
<td>Singlet at 51.6</td>
</tr>
<tr>
<td></td>
<td>Multiplet centred at 7.50 ((\text{C}_6\text{H}_5))</td>
<td>((\text{CF}_3))</td>
</tr>
</tbody>
</table>

* CDC\(_3\) solution
6. Reactions of Cis-2,3-Bis(dimethylarsino)-1,1,1,4,4,4-Hexafluorobut-2-ene (L-L) with Transition Metal Carbonyls

A. Reaction of (L-L) with Triiron Dodecacarbonyl

The diteriary arsine (L-L) (1.1 g, 0.30 mmol) and triiron dodecacarbonyl (1.9 g, 0.38 mmol) in acetone solution (20 ml) were irradiated with ultraviolet light for 24 h. The solvent was removed under reduced pressure and chromatography of the solid residue on Florisil gave two bands which were eluted with petroleum ether. The first band off the column gave a red-brown solid identified as (L-L)Fe(CO)$_3$ (1.0 g, 66%). The mass spectrum showed a parent ion followed by loss of three carbonyl groups. The carbonyl ir spectrum ($C_6H_{12}$ solution) consisted of three bands at 2001(s), 1933(s), 1917(vs) cm$^{-1}$.

Anal. Calcd. for $C_{11}H_{12}As_2F_6FeO_3$: C, 25.8; H, 2.3; F, 22.3. Found: C, 25.8; H, 2.3; F, 22.4.

The second band gave a yellow-red solid of (L-L)Fe$_2$(CO)$_6$ (0.1 g, 5%). The mass spectrum showed a parent ion followed by loss of six carbonyl groups. The carbonyl ir spectrum showed the following absorptions: 2062(m), 2024(s), 1996(m) 1986(m), 1968(w), 1956(w) cm$^{-1}$.

Anal. Calcd. for $C_{14}H_{12}As_2F_6Fe_2O_6$: C,25.8; H, 1.8. Found: C, 26.0; H, 1.7.
B. Reaction of (L-L) with Group VI Metal Hexacarbonyls

The following general method was used for the preparation of all new (L-L)M(CO)$_4$ complexes (M = Cr, Mo, W) from the reaction of (L-L) with the Group VI hexacarbonyls.

A benzene solution (15-20 ml) containing a 1:1 mole ratio of ligand to hexacarbonyl was heated at 150° in an evacuated Carius tube for 19-42 h. At the end of the reaction period the solution (initially pale yellow) was dark yellow (except for (L-L)Cr(CO)$_4$ which was amber). The solvent was removed under reduced pressure and the resulting solid residue chromatographed on Florisil. Petroleum ether eluted a yellow band which upon recrystallization from a methylene chloride-hexane mixture afforded the (L-L)M(CO)$_4$ complexes.

Analytical, preparative, and spectroscopic data for the new complexes are listed in Tables XII, XIII, and XIV.

C. Reactions of (L-L)M(CO)$_4$ and M(CO)$_6$ (M = Cr, Mo, W) with Excess (L-L)

A number of reactions between M(CO)$_6$ and the (L-L)M(CO)$_4$ complexes (M = Cr, Mo, W) with (L-L) are given in tabular form in Table XV. All pyrolysis reactions were performed in evacuated Carius tubes; ultraviolet irradiations (200W) were performed in evacuated quartz tubes. In all cases the crude reaction mixture was evaporated to dryness and the residue was chromatographed on Florisil using nitrogen saturated solvents as indicated in Table XV. All complexes were recrystallized
Table XII

Analytical and Preparative Data for Group VI (L-L)M(CO)₄ Complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Colour</th>
<th>Mp(°C)</th>
<th>Reaction Time h</th>
<th>Yield %</th>
<th>Analyses</th>
</tr>
</thead>
<tbody>
<tr>
<td>(L-L)Cr(CO)₄</td>
<td>amber</td>
<td>138-140</td>
<td>27</td>
<td>82</td>
<td>26.87 2.24 26.80 2.30</td>
</tr>
<tr>
<td>(L-L)Mo(CO)₄</td>
<td>yellow</td>
<td>141-143</td>
<td>19</td>
<td>80</td>
<td>24.83 2.07 25.08 2.20</td>
</tr>
<tr>
<td>(L-L)W(CO)₄</td>
<td>yellow</td>
<td>155-157</td>
<td>42</td>
<td>70</td>
<td>21.56 1.80 21.76 1.95</td>
</tr>
</tbody>
</table>
Table XIII
Ir Spectra (2100-1900 cm\(^{-1}\)) for Group VI (L-L)M(CO)\(_4\) Complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\nu(\text{CO})(\text{cm}^{-1})^*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(L-L)Cr(CO)(_4)</td>
<td>2020(m), 1931(s), 1911(vs)</td>
</tr>
<tr>
<td>(L-L)Mo(CO)(_4)</td>
<td>2036(m), 1939(s), 1921(vs)</td>
</tr>
<tr>
<td>(L-L)W(CO)(_4)</td>
<td>2036(m), 1931(s), 1911(vs)</td>
</tr>
</tbody>
</table>

* \(\text{C}_6\text{H}_{12}\) solution

Table XIV
Nmr Data for Group VI (L-L)M(CO)\(_4\) Complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>(1^H^*)</th>
<th>(1^9\text{F}^*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(L-L)Cr(CO)(_4)</td>
<td>Singlet at 1.85 (CH(_3))</td>
<td>Singlet at 50.2 (CF(_3))</td>
</tr>
<tr>
<td>(L-L)Mo(CO)(_4)</td>
<td>Singlet at 1.85 (CH(_3))</td>
<td>Singlet at 50.6 (CF(_3))</td>
</tr>
<tr>
<td>(L-L)W(CO)(_4)</td>
<td>Singlet at 1.97 (CH(_3))</td>
<td>Singlet at 50.6 (CF(_3))</td>
</tr>
</tbody>
</table>

* \(\text{CS}_2\) solution
from a degassed methylene chloride-hexane mixture at -20°.

Analytical and spectroscopic data for the new complexes are listed in Tables XVI, XVII, and XVIII.

D. Preparation of the (L-L)M(CO)$_3X_2$ Complexes (M = Mo, W; X = Br, I)

The new complexes were prepared by slow addition of the halogen (bromine, iodine) in methylene chloride to a vigorously stirred methylene chloride solution of an equimolar amount of (L-L)M(CO)$_4$ (M = Mo, W) under a nitrogen atmosphere. Halogen addition to the (L-L)W(CO)$_4$ species was performed at 0°; after the addition, the ice-water bath was removed and solution stirred for 1 h at room temperature. Iodination of the (L-L)Mo(CO)$_4$ complex was performed entirely at 0° and bromination entirely at dry ice temperature. In all cases the solution was filtered and concentrated. Addition of degassed hexane, and cooling to -20° yielded the crystalline (L-L)M(CO)$_3X_2$ complexes.

Analytical, preparative, and spectroscopic data for the new halogen derivatives are listed in Tables XIX, XX, and XXI.
<table>
<thead>
<tr>
<th>No</th>
<th>Carbonyl</th>
<th>(L-L)</th>
<th>Conditions</th>
<th>Products*</th>
<th>Yield</th>
<th>Purification**</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cr(CO)₆</td>
<td>0.82 g</td>
<td>Pyrolysis in benzene (15 ml) at 195° for 22 h</td>
<td>(L-L)Cr(CO)₄</td>
<td>70%</td>
<td>C (1)</td>
</tr>
<tr>
<td></td>
<td>0.2 g</td>
<td>2.2</td>
<td>mmol</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.90 mmol</td>
<td></td>
<td></td>
<td>(L-L)Cr(CO)₇</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>(L-L)Cr(CO)₄</td>
<td>0.82 g</td>
<td>Pyrolysis in benzene (15 ml) at 190° for 46 h</td>
<td>(L-L)Cr(CO)₄</td>
<td>0.060 g</td>
<td>C (1)</td>
</tr>
<tr>
<td></td>
<td>0.3 g, 0.56 mmol</td>
<td>2.2</td>
<td>mmol</td>
<td>cis-(L-L)₂Cr(CO)₂</td>
<td>trace</td>
<td>C (2)</td>
</tr>
<tr>
<td>3</td>
<td>(L-L)Cr(CO)₄</td>
<td>4.5</td>
<td>Uv irradiation (450W) in benzene (350 ml) for 85 min</td>
<td>(L-L)Cr(CO)₄</td>
<td>trace</td>
<td>C (1)</td>
</tr>
<tr>
<td></td>
<td>1.2 g</td>
<td>12.0</td>
<td>mmol</td>
<td>cis-(L-L)₂Cr(CO)₂</td>
<td>32%</td>
<td>C (2)</td>
</tr>
<tr>
<td></td>
<td>2.2 mmol</td>
<td></td>
<td></td>
<td>fac-(L-L)₁⁶Cr(CO)₃</td>
<td>3%</td>
<td>C (4)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>fac-(L-L)₁⁸Cr(CO)₃</td>
<td>trace</td>
<td>C (3)</td>
</tr>
<tr>
<td>4</td>
<td>(L-L)Cr(CO)₄</td>
<td>2.3</td>
<td>Uv irradiation (450W) in benzene (350 ml) for 20 min</td>
<td>(L-L)Cr(CO)₄</td>
<td>0.030 g</td>
<td>C (1)</td>
</tr>
<tr>
<td></td>
<td>0.6 g, 1.1 mmol</td>
<td>6</td>
<td>mmol</td>
<td>cis-(L-L)₂Cr(CO)₂</td>
<td>26%</td>
<td>C (2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>fac-(L-L)₁⁶Cr(CO)₃</td>
<td>9%</td>
<td>C (4)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>fac-(L-L)₁⁸Cr(CO)₃</td>
<td>trace</td>
<td>C (3)</td>
</tr>
<tr>
<td>No</td>
<td>Carbonyl</td>
<td>(L-L)</td>
<td>Conditions</td>
<td>Products*</td>
<td>Yield</td>
<td>Purification**</td>
</tr>
<tr>
<td>----</td>
<td>----------</td>
<td>-------</td>
<td>------------</td>
<td>-----------</td>
<td>-------</td>
<td>----------------</td>
</tr>
<tr>
<td>5</td>
<td>Mo(CO)$_6$</td>
<td>0.70 g</td>
<td>Pyrolysis in benzene (15 ml) at $175^\circ$ for 23 h</td>
<td>(L-L)Mo(CO)$_4$</td>
<td>46%</td>
<td>C (1)</td>
</tr>
<tr>
<td></td>
<td>0.2 g</td>
<td>1.88</td>
<td></td>
<td>cis-(L-L)$_2$Mo(CO)$_2$</td>
<td>30%</td>
<td>C (2)</td>
</tr>
<tr>
<td></td>
<td>0.76 mmol</td>
<td>mmol</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>(L-L)Mo(CO)$_4$</td>
<td>0.24 g</td>
<td>Pyrolysis in benzene (15 ml) at $175^\circ$ for 20 h</td>
<td>(L-L)Mo(CO)$_4$</td>
<td>trace</td>
<td>C (1)</td>
</tr>
<tr>
<td></td>
<td>0.36 g</td>
<td>0.62</td>
<td></td>
<td>cis-(L-L)$_2$Mo(CO)$_2$</td>
<td>36%</td>
<td>C (2)</td>
</tr>
<tr>
<td></td>
<td>0.62 mmol</td>
<td>mmol</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Mo(CO)$_6$</td>
<td>2.8 g</td>
<td>Uv irradiation (200W) in benzene at $175^\circ$ for 266 h</td>
<td>(L-L)Mo(CO)$_4$</td>
<td>trace</td>
<td>C (1)</td>
</tr>
<tr>
<td></td>
<td>0.4 g</td>
<td>7.60</td>
<td></td>
<td>cis-(L-L)$_2$Mo(CO)$_2$</td>
<td>trace</td>
<td>C (2)</td>
</tr>
<tr>
<td></td>
<td>1.52 mmol</td>
<td>mmol</td>
<td></td>
<td>fac-(L-L)$_2$Mo(CO)$_3$</td>
<td>20%</td>
<td>C (4)</td>
</tr>
<tr>
<td>8</td>
<td>(L-L)Mo(CO)$_4$</td>
<td>3.0 g</td>
<td>Uv irradiation (450W) in benzene at $175^\circ$ for 65 min</td>
<td>cis-(L-L)$_2$Mo(CO)$_2$</td>
<td>26%</td>
<td>C (2)</td>
</tr>
<tr>
<td></td>
<td>1 g</td>
<td>8.0</td>
<td></td>
<td>fac-(L-L)$_2$Mo(CO)$_3$</td>
<td>19%</td>
<td>C (4)</td>
</tr>
<tr>
<td></td>
<td>1.7 mmol</td>
<td>mmol</td>
<td></td>
<td>fac-(L-L)$_2$Mo(CO)$_3$</td>
<td>3%</td>
<td>C (3)</td>
</tr>
<tr>
<td>9</td>
<td>Mo(CO)$_6$</td>
<td>4 g</td>
<td>Uv irradiation (450W) in benzene at $175^\circ$ for 1.5 h</td>
<td>(L-L)Mo(CO)$_4$</td>
<td>trace</td>
<td>C (1)</td>
</tr>
<tr>
<td></td>
<td>0.6 g</td>
<td>10.8</td>
<td></td>
<td>cis-(L-L)$_2$Mo(CO)$_2$</td>
<td>15%</td>
<td>C (2)</td>
</tr>
<tr>
<td></td>
<td>2.3 mmol</td>
<td>mmol</td>
<td></td>
<td>fac-(L-L)$_2$Mo(CO)$_3$</td>
<td>33%</td>
<td>C (4)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>fac-(L-L)$_2$Mo(CO)$_3$</td>
<td>3%</td>
<td>C (3)</td>
</tr>
<tr>
<td>No</td>
<td>Carbonyl</td>
<td>(L-L)</td>
<td>Conditions</td>
<td>Products*</td>
<td>Yield</td>
<td>Purification**</td>
</tr>
<tr>
<td>----</td>
<td>----------</td>
<td>-------</td>
<td>------------------------------------</td>
<td>---------------------</td>
<td>-------</td>
<td>----------------</td>
</tr>
<tr>
<td>10</td>
<td>W(CO)$_6$</td>
<td>1.0 g</td>
<td>Pyrolysis in benzene (10 ml) at 185° for 69 h</td>
<td>(L-L)W(CO)$_4$</td>
<td>70%</td>
<td>C (1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.4 g</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.1 mmol</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>(L-L)W(CO)$_4$</td>
<td>0.12 g</td>
<td>Pyrolysis in benzene (15 ml) at 195° for 66 h</td>
<td>(L-L)W(CO)$_4$</td>
<td>0.1 g</td>
<td>C (1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.2 g</td>
<td></td>
<td>cis-(L-L)$_2$W(CO)$_2$</td>
<td></td>
<td>C (2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.30</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>mmol</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>195° for 66 h</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pyrolysis in benzene (15 ml) at 210° for 48 h</td>
<td>Complete Decomposition</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>(L-L)W(CO)$_4$</td>
<td>1.1 g</td>
<td>Uv irradiation (200W) in benzene (15 ml) for 141 h</td>
<td>(L-L)W(CO)$_4$</td>
<td>0.15 g</td>
<td>C (1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.4 g</td>
<td></td>
<td>fac-(L-L)$_b$(L-L)$_c$W(CO)$_3$</td>
<td>17%</td>
<td>C (4)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>mmol</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(15 ml) for 141 h</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>W(CO)$_6$</td>
<td>2.7 g</td>
<td>Uv irradiation (450W) in benzene (350 ml) for 29 h</td>
<td>(L-L)W(CO)$_4$</td>
<td>9%</td>
<td>C (1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.6 g</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>mmol</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(350 ml) for 29 h</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table XV (Continued)

<table>
<thead>
<tr>
<th>No</th>
<th>Carbonyl</th>
<th>(L-L)</th>
<th>Conditions</th>
<th>Products*</th>
<th>Yield</th>
<th>Purification**</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>(L-L)W(CO)$_4$</td>
<td>2 g</td>
<td>Uv irradiation</td>
<td>(L-L)W(CO)$_4$</td>
<td>trace</td>
<td>C (1)</td>
</tr>
<tr>
<td>1</td>
<td>(L-L)W(CO)$_2$</td>
<td>5.4 g</td>
<td>(450W) in benzene</td>
<td>cis-(L-L)$_2$W(CO)$_2$</td>
<td>10%</td>
<td>C (2)</td>
</tr>
<tr>
<td>1.5 mmol</td>
<td>mmol</td>
<td>(300 ml) for 6.5 h</td>
<td>fac-(L-L)$_2$W(CO)$_3$</td>
<td>13%</td>
<td>C (4)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>fac-(L-L)$_b$(L-L)$_m$W(CO)$_3$</td>
<td>2%</td>
<td>C (3)</td>
</tr>
</tbody>
</table>

* Not including excess ligand which was recovered in each experiment. Refluxing fac-(L-L)$_b$-(L-L)$_c$Mo(CO)$_3$ with a 25 molar excess of (L-L) in benzene for 16 h gave (L-L)$_2$[As(CH$_3$)$_2$]$_2$Mo$_2$(CO)$_4$ which was eluted by a 50% petroleum ether, 50% diethyl ether solution. Irradiation (450W) of cis-(L-L)$_2$Cr(CO)$_2$ for 85 min gave trans-(L-L)$_2$Cr(CO)$_2$ and irradiation (450W) of cis-(L-L)$_2$Mo(CO)$_2$ for 3.5 h gave trans-(L-L)$_2$Mo(CO)$_2$. In each case, the trans-isomer was recrystallized from a methylene chloride-hexane mixture at -20°. cis-(L-L)$_2$W(CO)$_2$ did not isomerize. (L-L)$_b$ denotes bidentate ligand; (L-L)$_c$ denotes monodentate ligand in a cis configuration and (L-L)$_m$ monodentate ligand in a trans configuration.

** C indicates chromatography on Florisil. The arabic numeral indicates the solvent required to elute the product: (1) is 99% petroleum ether (bp 30-60°), 1% diethyl ether, (2) is 98% petroleum ether, 2% diethyl ether, (3) is 95% petroleum ether, 5% diethyl ether, (4) is 90% petroleum ether, 10% diethyl ether.
Table XVI

Analytical Data for (L-L) Derivatives of M(CO)₆ (M = Cr, Mo, W)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Colour</th>
<th>Mp(°C)</th>
<th>Analyses</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Calcd.</td>
<td>Found</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C    H</td>
<td>C    H</td>
<td></td>
</tr>
<tr>
<td>fac-(L-L)₆Cr(CO)₃</td>
<td>pale orange</td>
<td>150-155*</td>
<td>25.91</td>
<td>2.73</td>
<td>25.98</td>
<td>2.91</td>
</tr>
<tr>
<td>fac-(L-L)₆Cr(CO)₃</td>
<td>orange</td>
<td>115-118</td>
<td>25.91</td>
<td>2.73</td>
<td>25.60</td>
<td>2.79</td>
</tr>
<tr>
<td>cis-(L-L)₂Cr(CO)₂</td>
<td>brown-red</td>
<td>168-170</td>
<td>25.35</td>
<td>2.82</td>
<td>25.50</td>
<td>3.00</td>
</tr>
<tr>
<td>trans-(L-L)₂Cr(CO)₂</td>
<td>brown-red</td>
<td>141-143</td>
<td>25.35</td>
<td>2.82</td>
<td>25.21</td>
<td>3.02</td>
</tr>
<tr>
<td>fac-(L-L)₆Mo(CO)₃</td>
<td>yellow</td>
<td>167-170*</td>
<td>24.67</td>
<td>2.60</td>
<td>24.45</td>
<td>2.72</td>
</tr>
<tr>
<td>fac-(L-L)₆Mo(CO)₃</td>
<td>orange</td>
<td>118-120</td>
<td>24.67</td>
<td>2.60</td>
<td>24.66</td>
<td>2.81</td>
</tr>
<tr>
<td>cis-(L-L)₂Mo(CO)₂</td>
<td>orange</td>
<td>160-162</td>
<td>24.11</td>
<td>2.68</td>
<td>24.33</td>
<td>2.76</td>
</tr>
<tr>
<td>trans-(L-L)₂Mo(CO)₂</td>
<td>orange</td>
<td>152-154</td>
<td>24.11</td>
<td>2.68</td>
<td>24.28</td>
<td>2.86</td>
</tr>
<tr>
<td>(L-L)₂[As(CH₃)₂]₂Mo₂(CO)₄</td>
<td>yellow</td>
<td>116-118</td>
<td>22.90</td>
<td>2.86</td>
<td>23.26</td>
<td>3.00</td>
</tr>
<tr>
<td>fac-(L-L)₆W(CO)₃</td>
<td>yellow</td>
<td>168-170*</td>
<td>22.53</td>
<td>2.37</td>
<td>22.30</td>
<td>2.31</td>
</tr>
<tr>
<td>fac-(L-L)₆W(CO)₃</td>
<td>orange</td>
<td>136-137</td>
<td>22.53</td>
<td>2.37</td>
<td>22.43</td>
<td>2.55</td>
</tr>
<tr>
<td>cis-(L-L)₂W(CO)₂</td>
<td>red-orange</td>
<td>177-179</td>
<td>21.95</td>
<td>2.44</td>
<td>21.70</td>
<td>2.61</td>
</tr>
</tbody>
</table>

* Complex melted with decomposition.
Table XVII

Ir Spectra (2000-1800 cm\(^{-1}\)) for (L-L) Derivatives of M(CO)\(_6\) (M = Cr, Mo, W)

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\nu)(CO)(cm(^{-1}))*</th>
</tr>
</thead>
<tbody>
<tr>
<td>fac-(L-L)(_b)(L-L)(_m)Cr(CO)(_3)</td>
<td>1953(vs), 1873(s), 1863(s)</td>
</tr>
<tr>
<td>fac-(L-L)(_b)(L-L)(_t)Cr(CO)(_3)</td>
<td>1953(vs), 1873(s), 1863(s)</td>
</tr>
<tr>
<td>cis-(L-L)(_2)Cr(CO)(_2)</td>
<td>1883(vs), 1829(s)</td>
</tr>
<tr>
<td>trans-(L-L)(_2)Cr(CO)(_2)</td>
<td>1829</td>
</tr>
<tr>
<td>fac-(L-L)(_b)(L-L)(_m)Mo(CO)(_3)</td>
<td>1963(vs), 1885(s), 1873(s)</td>
</tr>
<tr>
<td>fac-(L-L)(_b)(L-L)(_t)Mo(CO)(_3)</td>
<td>1963(vs), 1885(s), 1873(s)</td>
</tr>
<tr>
<td>cis-(L-L)(_2)Mo(CO)(_2)</td>
<td>1899(vs), 1845(s)</td>
</tr>
<tr>
<td>trans-(L-L)(_2)Mo(CO)(_2)</td>
<td>1845</td>
</tr>
<tr>
<td>(L-L)(_2)[As(CH(_3)(_2))(_2)]Mo(_2)(CO)(_4)</td>
<td>1963(s), 1881(s, br)</td>
</tr>
<tr>
<td>fac-(L-L)(_b)(L-L)(_m)W(CO)(_3)</td>
<td>1959(vs), 1879(s), 1867(s)</td>
</tr>
<tr>
<td>fac-(L-L)(_b)(L-L)(_t)W(CO)(_3)</td>
<td>1959(vs), 1879(s), 1867(s)</td>
</tr>
<tr>
<td>cis-(L-L)(_2)W(CO)(_2)</td>
<td>1890(vs), 1839(s)</td>
</tr>
</tbody>
</table>

* \(\text{C}_6\text{H}_{12}\) solution
Table XVIII

Nmr Data for (L-L) Derivatives of M(CO)$_6$ (M = Cr, Mo, W)

<table>
<thead>
<tr>
<th>Compound</th>
<th>$^1$H*</th>
<th>$^{19}$F**</th>
</tr>
</thead>
<tbody>
<tr>
<td>fac-(L-L)$_b$(L-L)$_c$Cr(CO)$_3$</td>
<td>Singlets at 1.33, 1.68, and 1.80 (CH$_3$)</td>
<td>Singlet at 52.0 (CF$_3$). Quartets centred at 53.6 and 54.6 (CF$_3$) $J$(F,F) = 12.0 Hz</td>
</tr>
<tr>
<td>fac-(L-L)$_b$(L-L)$_t$Cr(CO)$_3$</td>
<td>Singlets at 1.31, 1.70, and 1.82 (CH$_3$)</td>
<td>Singlet at 51.6 (CF$_3$). Quartets centred at 50.4 and 52.0 (CF$_3$) $J$(F,F) = 2.2 Hz</td>
</tr>
<tr>
<td>cis-(L-L)$_2$Cr(CO)$_2$</td>
<td>Singlets at 1.30, 1.70, 1.82, and 1.88 (CH$_3$)</td>
<td>Singlet at 50.6 (CF$_3$)</td>
</tr>
<tr>
<td>trans-(L-L)$_2$Cr(CO)$_2$</td>
<td>Singlet at 1.83 (CH$_3$)</td>
<td>Singlet at 49.8 (CF$_3$)</td>
</tr>
<tr>
<td>fac-(L-L)$_b$(L-L)$_c$Mo(CO)$_3$</td>
<td>Singlets at 1.33, 1.70, and 1.82 (CH$_3$)</td>
<td>Singlet at 50.8 (CF$_3$). Quartets centred at 52.9 and 53.0 (CF$_3$) $J$(F,F) = 11.3 Hz</td>
</tr>
<tr>
<td>fac-(L-L)$_b$(L-L)$_t$Mo(CO)$_3$</td>
<td>Singlets at 1.30, 1.68, and 1.80 (CH$_3$)</td>
<td>Singlet at 50.2 (CF$_3$). Quartets centred at 49.2 and 50.3 (CF$_3$) $J$(F,F) = 2.3 Hz</td>
</tr>
</tbody>
</table>
Table XVIII (Continued)

<table>
<thead>
<tr>
<th>Compound</th>
<th>$^{1}H$*</th>
<th>$^{19}F$**</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-$(L-L)<em>{2}Mo(CO)</em>{2}$</td>
<td>Singlets at 1.37, 1.70, 1.83 and 1.90 (CH$_3$)</td>
<td>Singlet at 50.6 (CF$_3$)</td>
</tr>
<tr>
<td>trans-$(L-L)<em>{2}Mo(CO)</em>{2}$</td>
<td>Singlet at 1.87 (CH$_3$)</td>
<td>Singlet at 49.6 (CF$_3$)</td>
</tr>
<tr>
<td>$(L-L)<em>{2}[As(CH</em>{3})<em>{2}]</em>{2}Mo_{2}(CO)_{4}$</td>
<td>Singlets at 1.67 and 1.93 (CH$_3$)</td>
<td>Singlet at 50.8 (CF$_3$)</td>
</tr>
<tr>
<td>fac-$(L-L)^{b}(L-L)^{c}W(CO)_{3}$</td>
<td>Singlets at 1.33, 1.77, 1.83, and 1.93 (CH$_3$)</td>
<td>Singlet at 50.8 (CF$_3$). Quartets centred at 52.7 and 53.0 (CF$_3$) $J(F,F) = 13.5$ Hz</td>
</tr>
<tr>
<td>fac-$(L-L)^{b}(L-L)^{c}W(CO)_{3}$</td>
<td>Singlets at 1.27, 1.72, 1.77, and 1.90 (CH$_3$)</td>
<td>Singlet (br) at 50.8 (CF$_3$). Quartet centred at 49.6 (CF$_3$) $J(F,F) = 2.2$ Hz</td>
</tr>
<tr>
<td>cis-$(L-L)<em>{2}W(CO)</em>{2}$</td>
<td>Singlets at 1.43, 1.80, 1.97, and 2.05 (CH$_3$)</td>
<td>Singlet at 50.2 (CF$_3$)</td>
</tr>
</tbody>
</table>

* CDC$_3$ solution  
** CH$_2$Cl$_2$ solution
Table XIX

Analytical and Preparative Data for \((L-L)M(CO)_{3}X_{2}\) Complexes* (M = Mo, W; X = Br, I)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Colour</th>
<th>Yield %</th>
<th>C</th>
<th>H</th>
<th>X</th>
<th>C</th>
<th>H</th>
<th>X</th>
</tr>
</thead>
<tbody>
<tr>
<td>((L-L)Mo(CO)<em>{3}I</em>{2})</td>
<td>orange</td>
<td>70</td>
<td>16.38</td>
<td>1.49</td>
<td>31.51(I)</td>
<td>16.20</td>
<td>1.61</td>
<td>31.28(I)</td>
</tr>
<tr>
<td>((L-L)Mo(CO)<em>{3}Br</em>{2})</td>
<td>yellow</td>
<td>73</td>
<td>18.54</td>
<td>1.69</td>
<td>22.47(Br)</td>
<td>18.62</td>
<td>1.71</td>
<td>22.35(Br)</td>
</tr>
<tr>
<td>((L-L)W(CO)<em>{3}I</em>{2})</td>
<td>orange</td>
<td>72</td>
<td>14.76</td>
<td>1.35</td>
<td>28.41(I)</td>
<td>14.64</td>
<td>1.21</td>
<td>28.25(I)</td>
</tr>
<tr>
<td>((L-L)W(CO)<em>{3}Br</em>{2})</td>
<td>yellow</td>
<td>50</td>
<td>16.50</td>
<td>1.50</td>
<td>20.00(Br)</td>
<td>16.54</td>
<td>1.53</td>
<td>20.05(Br)</td>
</tr>
</tbody>
</table>

* All complexes decomposed without melting above 120°.
Table XX

Ir Spectra (2100-1900 cm\(^{-1}\)) for \((L-L)M(\text{CO})_3X_2\) Complexes (\(M = \text{Mo, W; X = Br, I}\))

<table>
<thead>
<tr>
<th>Compound</th>
<th>(v(\text{CO})(\text{cm}^{-1})^*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>((L-L)\text{Mo(\text{CO})}_3\text{I}_2)</td>
<td>2056(s), 1985(vs), 1927(s)</td>
</tr>
<tr>
<td>((L-L)\text{Mo(\text{CO})}_3\text{Br}_2)</td>
<td>2076(s), 1993(vs), 1925(s)</td>
</tr>
<tr>
<td>((L-L)\text{W(\text{CO})}_3\text{I}_2)</td>
<td>2052(s), 1971(vs), 1917(s)</td>
</tr>
<tr>
<td>((L-L)\text{W(\text{CO})}_3\text{Br}_2)</td>
<td>2068(s), 1977(vs), 1911(s)</td>
</tr>
</tbody>
</table>

* \(\text{CH}_2\text{Cl}_2\) solution

Table XXI

Nmr Data for \((L-L)M(\text{CO})_3X_2\) Complexes (\(M = \text{Mo, W; X = Br, I}\))

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\text{H}^*)</th>
<th>(\text{F}^*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>((L-L)\text{Mo(\text{CO})}_3\text{I}_2)</td>
<td>Singlet at 2.17 ((\text{CH}_3))</td>
<td>Singlet at 51.1 ((\text{CF}_3))</td>
</tr>
<tr>
<td>((L-L)\text{Mo(\text{CO})}_3\text{Br}_2)</td>
<td>Singlet at 2.05 ((\text{CH}_3))</td>
<td>Singlet at 52.6 ((\text{CF}_3))</td>
</tr>
<tr>
<td>((L-L)\text{W(\text{CO})}_3\text{I}_2)</td>
<td>Singlet at 2.23 ((\text{CH}_3))</td>
<td>Singlet at 52.4 ((\text{CF}_3))</td>
</tr>
<tr>
<td>((L-L)\text{W(\text{CO})}_3\text{Br}_2)</td>
<td>Singlet at 2.10 ((\text{CH}_3))</td>
<td>Singlet at 53.2 ((\text{CF}_3))</td>
</tr>
</tbody>
</table>

* \(\text{CDCl}_3\) solution
E. Preparation of the \((L-L)L\text{Mo(CO)}_2\text{Br}_2\) Complexes
\((L = \text{a Monodentate Ligand})\)

The following general procedure represents the method used to synthesize the \((L-L)L\text{Mo(CO)}_2\text{Br}_2\) complexes.

The dicarbonyl complexes were prepared by the addition of \(L\) to an equimolar amount of \((L-L)\text{Mo(CO)}_3\text{Br}_2\) in methylene chloride (5 ml) at room temperature under a nitrogen atmosphere. The orange solution was filtered and concentrated under a reduced pressure. Addition of degassed hexane, and cooling to -20\(^{\circ}\) afforded the crystalline \((L-L)L\text{Mo(CO)}_2\text{Br}_2\) complexes.

Analytical, preparative, and spectroscopic data for the new "mixed" seven-coordinate species are listed in Tables XXII, XXIII, and XXIV.

F. Preparation of the \((L-L)L_2\text{Mo(CO)}\text{Br}_2\) Complexes*

All reactions between excess \(L\) and \((L-L)\text{Mo(CO)}_3\text{Br}_2\) were carried out in refluxing benzene (for the time indicated in Table XXV) under a nitrogen atmosphere, except for \((L-L)_2\text{Mo(CO)}\text{Br}_2\) which was synthesized by warming a benzene solution (50\(^{\circ}\)) of \((L-L)^b(L-L)^m\text{Mo(CO)}_2\text{Br}_2\) for 30 min.

Analytical, preparative, and spectroscopic data for the new \((L-L)L_2\text{Mo(CO)}\text{Br}_2\) complexes are given in Tables XXV, XXVI, and XXVII.

Attempts to produce other complexes of the type

* In the general formula \(L\) is a monodentate ligand; however, the formula also applies to complexes where \(L_2\) is bidentate.
Table XXII

Analytical and Preparative Data for (L-L)LMo(CO)₂Br₂ Complexes*

<table>
<thead>
<tr>
<th>Compound</th>
<th>Colour</th>
<th>Yield %</th>
<th>C</th>
<th>H</th>
<th>Br</th>
<th>C</th>
<th>H</th>
<th>Br</th>
</tr>
</thead>
<tbody>
<tr>
<td>(L-L)₄(L-L)₄Mo(CO)₂Br₂**</td>
<td>pale yellow</td>
<td>60</td>
<td>20.46</td>
<td>2.27</td>
<td>15.15</td>
<td>20.50</td>
<td>2.40</td>
<td>14.87</td>
</tr>
<tr>
<td>(L-L)(C₅H₅N)Mo(CO)₂Br₂***</td>
<td>yellow</td>
<td>60</td>
<td>23.59</td>
<td>2.23</td>
<td>15.15</td>
<td>20.50</td>
<td>2.40</td>
<td>14.87</td>
</tr>
<tr>
<td>(L-L)[P(OCH₂CH₃)₃]Mo(CO)₂Br₂</td>
<td>yellow</td>
<td>59</td>
<td>22.59</td>
<td>3.18</td>
<td>18.82</td>
<td>22.76</td>
<td>3.40</td>
<td>19.10</td>
</tr>
<tr>
<td>(L-L)[P(C₆H₅)₃]Mo(CO)₂Br₂</td>
<td>orange</td>
<td>65</td>
<td>35.52</td>
<td>2.85</td>
<td>16.91</td>
<td>35.35</td>
<td>2.73</td>
<td>16.70</td>
</tr>
<tr>
<td>(L-L)[P(CH₃)(C₆H₅)₂]Mo(CO)₂Br₂</td>
<td>yellow</td>
<td>54</td>
<td>31.22</td>
<td>2.83</td>
<td>18.09</td>
<td>31.40</td>
<td>3.06</td>
<td>17.87</td>
</tr>
<tr>
<td>(L-L)[P(CH₃)₂(C₆H₅)]Mo(CO)₂Br₂</td>
<td>yellow</td>
<td>58</td>
<td>26.28</td>
<td>2.80</td>
<td>19.46</td>
<td>26.34</td>
<td>2.88</td>
<td>19.14</td>
</tr>
<tr>
<td>(L-L)[P(OCH₃)₃]Mo(CO)₂Br₂</td>
<td>yellow</td>
<td>59</td>
<td>19.31</td>
<td>2.60</td>
<td>19.80</td>
<td>19.21</td>
<td>2.70</td>
<td>19.60</td>
</tr>
<tr>
<td>(L-L)[P(OCH₃)₂(C₆H₅)]Mo(CO)₂Br₂</td>
<td>yellow</td>
<td>56</td>
<td>25.29</td>
<td>2.69</td>
<td>18.74</td>
<td>25.44</td>
<td>2.70</td>
<td>18.46</td>
</tr>
</tbody>
</table>

* All complexes decomposed without melting above 120°.

** (L-L)₄ designates (CH₃)₂As(CF₃)C = C(CF₃)As(CH₃)₂ acting as a bidentate ligand and (L-L)₄ the same ligand acting in a monodentate manner.

*** Analysis for %N gave 1.82 (Calcd. 1.83%).
Table XXIII

Ir Spectra (2000-1800 cm\(^{-1}\)) for (L-L)\(\text{LMo(CO)}_2\text{Br}_2\) Complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\nu(\text{CO})(\text{cm}^{-1})^*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{L-L})^b(\text{L-L})^\text{m}\text{Mo(CO)}_2\text{Br}_2)</td>
<td>1981(vs), 1913(s)</td>
</tr>
<tr>
<td>((\text{L-L})(\text{C}_5\text{H}_5\text{N})\text{Mo(CO)}_2\text{Br}_2)</td>
<td>1957(vs), 1883(s)</td>
</tr>
<tr>
<td>((\text{L-L})[\text{P(OCH}_2\text{CH}_3)_3]\text{Mo(CO)}_2\text{Br}_2)</td>
<td>1959(vs), 1879(s)</td>
</tr>
<tr>
<td>((\text{L-L})[\text{P(C}_6\text{H}_5)_3]\text{Mo(CO)}_2\text{Br}_2)</td>
<td>1951(vs), 1869(s)</td>
</tr>
<tr>
<td>((\text{L-L})[\text{P(CH}_3\text{)}_3\text{C}_6\text{H}_5)_2]\text{Mo(CO)}_2\text{Br}_2)</td>
<td>1951(vs), 1869(s)</td>
</tr>
<tr>
<td>((\text{L-L})[\text{P(CH}_3\text{)}_2\text{C}_6\text{H}_5)_2]\text{Mo(CO)}_2\text{Br}_2)</td>
<td>1951(vs), 1867(s)</td>
</tr>
<tr>
<td>((\text{L-L})[\text{P(OCH}_3\text{)}_3\text{C}_6\text{H}_5)_2]\text{Mo(CO)}_2\text{Br}_2)</td>
<td>1965(vs), 1883(s)</td>
</tr>
<tr>
<td>((\text{L-L})[\text{P(OCH}_3\text{)}_2\text{C}_6\text{H}_5)_2]\text{Mo(CO)}_2\text{Br}_2)</td>
<td>1957(vs), 1875(s)</td>
</tr>
</tbody>
</table>

* \(\text{CH}_2\text{Cl}_2\) solution
Table XXIV

Nmr Data for (L-L)Mo(CO)_{2} Complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \text{^1}H^* )</th>
<th>( \text{^19}F^{**} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>((L-L)^b(L-L)^m\text{Mo(CO)}_2\text{Br}_2)</td>
<td>Singlets at 2.47 and 2.25 (As-CH\textsubscript{3})</td>
<td>Singlet at 51.2 (CF\textsubscript{3})</td>
</tr>
<tr>
<td>((L-L)(C_5H_5N)\text{Mo(CO)}_2\text{Br}_2)</td>
<td>Singlet at 2.08 (As-CH\textsubscript{3}). Multiplets centred at 7.47, 7.82, and 9.02 (C\textsubscript{5}H\textsubscript{5}N)</td>
<td>Singlet at 51.2 (CF\textsubscript{3})</td>
</tr>
<tr>
<td>((L-L)[P(OCH}_2\textsubscript{CH}_3]_3\text{Mo(CO)}_2\text{Br}_2)</td>
<td>Singlet at 1.98 (As-CH\textsubscript{3}). Triplet centred at 1.33 (P-OCH\textsubscript{2}CH\textsubscript{3}) J(H,H) = 7.0 Hz. Pentet centred at 4.25 (P-OCH\textsubscript{2}CH\textsubscript{3}) J(H,H) = 7.0 Hz J(H,P) = 7.0 Hz</td>
<td>Singlet at 51.6 (CF\textsubscript{3})</td>
</tr>
<tr>
<td>((L-L)[P(C}_6H_5]_3\text{Mo(CO)}_2\text{Br}_2)</td>
<td>Singlet at 1.87 (As-CH\textsubscript{3}). Multiplets centred at 7.40 and 7.83 (P-C\textsubscript{6}H\textsubscript{5})</td>
<td>Singlet at 51.4 (CF\textsubscript{3})</td>
</tr>
<tr>
<td>((L-L)[P(CH}_3)(C}_6H_5]_2\text{Mo(CO)}_2\text{Br}_2)</td>
<td>Singlet at 1.70 (As-CH\textsubscript{3}). Doublet centred at 2.48 (P-CH\textsubscript{3}) J(H,P) = 10.0 Hz.</td>
<td>Singlet at 51.4 (CF\textsubscript{3})</td>
</tr>
<tr>
<td>Compound</td>
<td>$^1H^*$</td>
<td>$^{19}F^*$</td>
</tr>
<tr>
<td>----------</td>
<td>---------</td>
<td>----------</td>
</tr>
<tr>
<td>$(L-L)[P(CH_3)_2(C_6H_5)]Mo(CO)_2Br_2$</td>
<td>Multiplets centred at 7.50 and 7.80 (P-C_6H_5)</td>
<td>Singlet at $51.4$ (CF_3)</td>
</tr>
<tr>
<td>$(L-L)[P(OCH_3)_2(C_6H_5)]Mo(CO)_2Br_2$</td>
<td>Singlet at 1.83 (As-CH_3). Doublet centred at 2.12 (P-CH_3) $J(H,P) = 11.0$ Hz. Multiplets centred at 7.43 and 7.80 (P-C_6H_5)</td>
<td>Singlet at $51.2$ (CF_3)</td>
</tr>
<tr>
<td>$(L-L)[P(OCH_3)_2(C_6H_5)]Mo(CO)_2Br_2$</td>
<td>Singlet at 1.85 (As-CH_3). Doublet centred at 3.80 (P-OCH_3) $J(H,P) = 11.2$ Hz</td>
<td>Singlet at $51.6$ (CF_3)</td>
</tr>
</tbody>
</table>

* CDCl$_3$ solution

** CH$_2$Cl$_2$ solution
(L-L)L₂Mo(CO)Br₂ failed for ligands such as triphenylphosphine, pyridine, trichlorophosphine, trifluorophosphine, methyl-diphenylphosphine, methyl diphenylphosphinite, bis(diphenyl-phosphino)methane, and bis(diphenylphosphino)ethane.

The following experimental details are given for a typical reaction between (L-L)Mo(CO)₃Br₂ and excess trimethylphosphite.

(L-L)Mo(CO)₃Br₂ (0.30 g, 0.41 mmol) and trimethylphosphite (0.120 g, 0.96 mmol) in dry, degassed benzene (15 ml) were refluxed under nitrogen for 75 min. The ir spectrum of the solution indicated complete reaction of (L-L)Mo(CO)₃Br₂. The deep red-orange solution (initially orange) was filtered and the benzene removed under reduced pressure. Recrystallization of the red oil from a degassed methylene chloride-hexane mixture at -20° afforded orange plates of (L-L)[P(OCH₃)₃]₂Mo(CO)Br₂ (0.24 g, 63%); mp 150° (decomposes).
Table XXV

Analytical and Preparative Data for (L-L)\textsubscript{2}Mo(CO)Br\textsubscript{2} Complexes *

<table>
<thead>
<tr>
<th>Compound</th>
<th>Reaction time h</th>
<th>Yield %</th>
<th>Calcd. C</th>
<th>Calcd. H</th>
<th>Calcd. Br</th>
<th>Found C</th>
<th>Found H</th>
<th>Found Br</th>
</tr>
</thead>
<tbody>
<tr>
<td>(L-L)\textsubscript{2}Mo(CO)Br\textsubscript{2}</td>
<td>0.5</td>
<td>60</td>
<td>19.84</td>
<td>2.34</td>
<td>15.56</td>
<td>19.87</td>
<td>2.56</td>
<td>15.28</td>
</tr>
<tr>
<td>(L-L)[P(OCH\textsubscript{2}CH\textsubscript{2})\textsubscript{3}]\textsubscript{2}Mo(CO)Br\textsubscript{2}</td>
<td>14</td>
<td>72</td>
<td>25.51</td>
<td>4.25</td>
<td>16.19</td>
<td>25.48</td>
<td>4.10</td>
<td>15.86</td>
</tr>
<tr>
<td>(L-L)[P(OCH\textsubscript{3})\textsubscript{3}]\textsubscript{2}Mo(CO)Br\textsubscript{2}</td>
<td>1.25</td>
<td>63</td>
<td>19.91</td>
<td>3.32</td>
<td>17.55</td>
<td>19.93</td>
<td>3.61</td>
<td>17.70</td>
</tr>
<tr>
<td>(L-L)[P(OCH\textsubscript{3})\textsubscript{2}(C\textsubscript{6}H\textsubscript{5})]\textsubscript{2}Mo(CO)Br\textsubscript{2}</td>
<td>24</td>
<td>60</td>
<td>30.12</td>
<td>3.41</td>
<td>16.06</td>
<td>30.23</td>
<td>3.50</td>
<td>15.80</td>
</tr>
<tr>
<td>(L-L)[P(CH\textsubscript{3})\textsubscript{2}(C\textsubscript{6}H\textsubscript{5})]\textsubscript{2}Mo(CO)Br\textsubscript{2}</td>
<td>24</td>
<td>51</td>
<td>32.19</td>
<td>3.65</td>
<td>17.15</td>
<td>32.47</td>
<td>3.76</td>
<td>17.00</td>
</tr>
</tbody>
</table>

* All complexes decomposed without melting above 120°. (L-L)\textsubscript{2}Mo(CO)Br\textsubscript{2} was brown and all other complexes were orange.
Table XXVI

Ir Spectra (1900-1700 cm$^{-1}$) for (L-L)$_2$Mo(CO)Br$_2$ Complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>$v$(CO)(cm$^{-1}$)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>(L-L)$_2$Mo(CO)Br$_2$</td>
<td>1829</td>
</tr>
<tr>
<td>(L-L)[P(OCH$_2$CH$_3$)$_3$]$_2$Mo(CO)Br$_2$</td>
<td>1841</td>
</tr>
<tr>
<td>(L-L)[P(OCH$_3$)$_3$]$_2$Mo(CO)Br$_2$</td>
<td>1843</td>
</tr>
<tr>
<td>(L-L)[P(OCH$_3$)$_3$(C$_6$H$_5$)]$_2$Mo(CO)Br$_2$</td>
<td>1829</td>
</tr>
<tr>
<td>(L-L)[P(CH$_3$)$_3$(C$_6$H$_5$)]$_2$Mo(CO)Br$_2$</td>
<td>1792</td>
</tr>
</tbody>
</table>

* CH$_2$Cl$_2$ solution
### Table XXVII

<table>
<thead>
<tr>
<th>Compound</th>
<th>1\textsubscript{H}*</th>
<th>19\textsubscript{F}**</th>
</tr>
</thead>
<tbody>
<tr>
<td>(L-L)\textsubscript{2}Mo(CO)Br\textsubscript{2}</td>
<td>Singlet at 1.98 (As-CH\textsubscript{3})</td>
<td>Singlet at 50.8 (CF\textsubscript{3})</td>
</tr>
<tr>
<td>(L-L)[P(OCH\textsubscript{2}CH\textsubscript{3})\textsubscript{3}]\textsubscript{2}Mo(CO)Br\textsubscript{2}</td>
<td>Singlets at 2.07 and 1.50 (As-CH\textsubscript{3}). Triplet centred at 1.28 (P-OCH\textsubscript{2}CH\textsubscript{3}). Multiplet centred at 4.25 (P-OCH\textsubscript{2}CH\textsubscript{3}) (see Chapter V for coupling constants)</td>
<td>Singlet at 52.4 (CF\textsubscript{3})</td>
</tr>
<tr>
<td>(L-L)[P(OCH\textsubscript{3})\textsubscript{3}]\textsubscript{2}Mo(CO)Br\textsubscript{2}</td>
<td>Singlets at 2.08 and 1.50 (As-CH\textsubscript{3}). Intermediate pattern centred at 3.90 (P-OCH\textsubscript{3})</td>
<td>Singlet at 52.2 (CF\textsubscript{3})</td>
</tr>
<tr>
<td>(L-L)[P(OCH\textsubscript{3})\textsubscript{2}(C\textsubscript{6}H\textsubscript{5})\textsubscript{2}]\textsubscript{2}Mo(CO)Br\textsubscript{2}</td>
<td>Singlets at 1.88 and 1.53 (As-CH\textsubscript{3}). Intermediate pattern centred at 3.44 (P-OCH\textsubscript{3})</td>
<td>Singlet at 52.4 (CF\textsubscript{3})</td>
</tr>
</tbody>
</table>

J(H,P) + J'(H,P') = 10.0 Hz and 3.59 (P-OCH\textsubscript{3}) | J(H,P) + J'(H,P') = 10.0 Hz. Multiplets centred at 7.37 and 7.70 (P-C\textsubscript{6}H\textsubscript{5}) |
<table>
<thead>
<tr>
<th>Compound</th>
<th>$^{1}H^*$</th>
<th>$^{19}F^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(L-L)[P(CH\textsubscript{3})\textsubscript{2}(C\textsubscript{6}H\textsubscript{5})\textsubscript{2}]Mo(CO)Br\textsubscript{2}</td>
<td>Quartets centred at 2.32 (As-CH\textsubscript{3}) (J(H,F) = 2.5) Hz and 0.907 (As-CH\textsubscript{3}) (J(H,F) = 2.0) Hz. Singlet at 1.00 (As-CH\textsubscript{3}). Doublets centred at 2.07 (P-CH\textsubscript{3}) (J(H,P) = 9.75) Hz, 1.85 (P-CH\textsubscript{3}) (J(H,P) = 8.25) Hz, 1.27 (P-CH\textsubscript{3}) (J(H,P) = 7.75) Hz, and 0.912 (P-CH\textsubscript{3}) (J(H,P) = 8.75) Hz. Multiplets centred at 7.12 and 7.85 (P-C\textsubscript{6}H\textsubscript{5})</td>
<td>Quartets centred at 51.4 and 53.2 (CF\textsubscript{3}) (J(F,F) = 15.0) Hz</td>
</tr>
</tbody>
</table>

* Spectra of all complexes obtained from CDCl\textsubscript{3} solution except for the spectrum of (L-L)[P(CH\textsubscript{3})\textsubscript{2}(C\textsubscript{6}H\textsubscript{5})\textsubscript{2}]Mo(CO)Br\textsubscript{2} which was obtained from C\textsubscript{6}D\textsubscript{6} solution. Intermediate pattern refers to a broad central resonance lying between a 1:1 doublet. | \(|J(H,P) + J'(H,P')|= the separation of the 1:1 doublet. |

** CH\textsubscript{2}Cl\textsubscript{2} solution
G. Reaction of (L-L) with Dimanganese Decacarbonyl
And Dirhenium Decacarbonyl

A number of different reactions (photolytic and thermal) between (L-L) and Group VII metal carbonyls were attempted. It was found that the reaction of (L-L) with dimanganese decacarbonyl gave a different product from that formed in the reaction of (L-L) with dirhenium decacarbonyl.

i. Reaction of (L-L) with Dimanganese Decacarbonyl

Dimanganese decacarbonyl (0.6 g, 1.6 mmol) and (L-L) (2.2 g, 5.95 mmol) in 15 ml of degassed toluene were refluxed under an atmosphere of nitrogen for 100 min. The reaction was monitored by observing the disappearance of the dimanganese decacarbonyl. The final solution was dark brown-red (initially yellow). The toluene was removed under reduced pressure and the brown tarry oil chromatographed on Florisil under nitrogen. A 0-2% diethyl ether, 100-98% petroleum ether mixture eluted a yellow band which afforded yellow crystals. Recrystallization from a methylene chloride-hexane mixture at -20° gave yellow crystals of formula $\text{C}_{16}\text{H}_{18}\text{AsF}_{3}\text{O}_{6}\text{Mn}_{2}$ (0.1 g, 9%); mp 190° (decomposes); sublimes at 105° (0.1 mm).

The mass spectrum gave a parent ion peak followed by a peak due to the loss of three carbonyl and a peak due to the loss of six carbonyl groups.

The ir spectrum in the carbonyl region ($\text{C}_{6}\text{H}_{12}$ solution) showed the following absorptions: 2036(m), 2009(vs), 1977(m), 1949(s), 1941(w), 1933(m) cm$^{-1}$. Carbon-fluorine bands
(CCl₄ solution) were seen at 1277(sh), 1269(s), 1195(s), 1131(s), 1093(s) cm⁻¹.

The ¹H nmr spectrum (C₆H₆ solution) showed singlets at 1.357, 1.302, 1.252, 1.112 (CH₃) and doublets centred at 1.272 (CH₃) J(H,F) = 2.0 Hz and 1.047 (CH₃) J(H,F) = 6.0 Hz. The ¹⁹F nmr spectrum (CH₂Cl₂ solution) consisted of a C-CF₃ doublet centred at 42.5 J(CF₃,F) = 26 Hz, a broad C-F doublet centred at 60.86 J(F,F) = 121 Hz, and another C-F doublet of quartets centred at 67.78 J(H,F) = 121 Hz, J(CF₃,F) = 26 Hz.

Anal. Calcd. for C₁₆H₁₈AsF₆O₆Mn₂: C, 26.09; H, 2.44; Mn, 14.95; mol wt 736. Found: C, 26.10; H, 2.65; Mn, 15.10; mol wt 736 (mass spec).

The identical complex was also obtained using the following reaction conditions in which a three to four molar excess of ligand was employed: (1) refluxing in benzene for 22 h (8%) (2) pyrolysis in benzene at 110° for 3.5 h in a thick-walled Carius tube (23%) (3) ultraviolet irradiation (200W) in benzene for 73 h (2%). Ultraviolet irradiation using the 450W lamp produced no complex as complete decomposition occurred.

ii. Reaction of (L-L) with Dirhenium Decacarbonyl

Dirhenium decacarbonyl (1g, 1.5 mmol) and (L-L) (1.7g, 4.5 mmol) in 375 ml of degassed benzene were irradiated with the 450W lamp for 85 min. The reaction was monitored by observing the disappearance of the dirhenium decacarbonyl. The final solution was dark orange (initially colourless). The benzene was removed under reduced pressure and the red oil
chromatographed on Florisil under nitrogen. Petroleum ether eluted a pale yellow band of unreacted ligand (0.5 g). A 2-10% diethyl ether, 98-90% petroleum ether mixture eluted an orange band which afforded oily orange crystals. Recrystallization from a methylene chloride-hexane mixture at -20° gave dark orange air-stable crystals of formula \( \text{C}_{11} \text{H}_8 \text{AsF}_6 \text{O}_5 \text{Re} \) (0.4 g, 22%); mp 151-152° (sealed evacuated capillary).

The mass spectrum showed peaks due to the parent ion followed by loss of four carbonyl groups.

The ir spectrum (\( \text{CsH}_{12} \) solution) gave carbonyl frequencies at 2100(m), 2021(s), 1995(s,br), 1981(vs) cm\(^{-1} \).

The \( ^1 \text{H} \) nmr spectrum (CDCl\(_3 \) solution) showed a singlet at 2.13 (shoulder on the low field side at 100 MHz). The \( ^{19} \text{F} \) nmr spectrum (CH\(_2\)Cl\(_2 \) solution) consisted of quartets centred at 53.2 and 59.1 (CF\(_3 \)) \( J(F,F) = 12.4 \text{ Hz} \).

Anal. Calcd. for \( \text{C}_{11} \text{H}_8 \text{AsF}_6 \text{O}_5 \text{Re} \): C, 22.18; H, 1.34; F, 19.12; mol wt 596. Found: C, 22.02; H, 1.10; F, 18.90; mol wt (mass spec) 596.

Reaction between dirhenium decacarbonyl and excess (L-L) in refluxing toluene or xylene resulted in complete decomposition as no stable complexes were isolated.
7. Reactions of Tetramethyldiarsine with Iron Pentacarbonyl and Dimanganese Decacarbonyl

A. Tetramethyldiarsine and Iron Pentacarbonyl

Tetramethyldiarsine and excess iron pentacarbonyl in benzene were heated at 150° for 19 h in a sealed evacuated Carius tube. Chromatography on Florisil using benzene as the eluting solvent and recrystallization from a benzene-heptane mixture at -20° gave dark red-orange crystals of Fe₂(CO)₆-[As(CH₃)₂]₂.

The ¹H nmr spectrum, ir spectrum, and mp were identical with those of authentic Fe₂(CO)₆[As(CH₃)₂]₂.⁶⁸

B. Tetramethyldiarsine and Dimanganese Decacarbonyl

An equimolar amount of dimanganese decacarbonyl and tetramethyldiarsine in toluene (30 ml) were refluxed for 20 h under an atmosphere of nitrogen. Chromatography on Florisil using petroleum ether and recrystallization from a methylene chloride-hexane mixture afforded yellow crystals of Mn₂(CO)₈[As(CH₃)₂]₂.

Spectroscopic properties were in agreement with those of authentic Mn₂(CO)₈[As(CH₃)₂]₂.⁶⁹
8. Reaction of Tetramethyldiphosphine with Iron Pentacarbonyl

Tetramethyldiphosphine and excess iron pentacarbonyl in benzene were heated at 140° for 24 h in a sealed evacuated Carius tube. Chromatography on Florisil using petroleum ether and recrystallization from a methylene chloride-hexane mixture afforded orange crystals of Fe$_2$(CO)$_6$[P(CH$_3$)$_2$]$_2$ whose $^1$H nmr spectrum, ir spectrum, and mp were in agreement with the literature values.

9. Reactions of 1,2-Dimethyl-1,2-Diphenyldiarsine with Iron Pentacarbonyl and Dimanganese Decacarbonyl

A. 1,2-Dimethyl-1,2-Diphenyldiarsine and Iron Pentacarbonyl

Iron pentacarbonyl (4 g, 20 mmol) and 1,2-dimethyl-1,2-diphenyldiarsine (2 g, 6 mmol) in benzene (25 ml) were heated at 150° for 3 days in a sealed evacuated Carius tube. The final solution was dark brown. The benzene and excess iron pentacarbonyl were removed under reduced pressure and the residual orange solid chromatographed on Florisil under nitrogen. Petroleum ether eluted a yellow band which after solvent removal and recrystallization from petroleum ether at -20° gave orange crystals of asymmetric Fe$_2$(CO)$_6$[As(CH$_3$)-(C$_6$H$_5$)]$_2$ (0.2 g, 5%); mp 93-96°.

A second orange band eluted by a 5% diethyl ether, 95% petroleum ether mixture gave after recrystallization from
the same solvent mixture at -20°, orange crystals of symmetric
\( \text{Fe}_2(\text{CO})_6[\text{As}(\text{CH}_3)(\text{C}_6\text{H}_5)]_2 \) (1.2 g, 33%); mp 162-164°.

Analytical and spectroscopic data for both isomers were
previously given in Tables III, IV, and V.

B. 1,2-Dimethyl-1,2-Diphenyldiarsine and Dimanganese
Decacarbonyl

Dimanganese decacarbonyl (1.3 g, 3.3 mmol) and 1,2-
dimethyl-1,2-diphenyldiarsine (1.1 g, 3.3 mmol) in toluene
(30 ml) were refluxed for 20 h under a nitrogen atmosphere.
The final solution was dark brown-red. The toluene was
removed under reduced pressure and the oily solid chromatographed
on Florisil under nitrogen. Petroleum ether eluted a yellow
band containing 0.1 g of unreacted dimanganese decacarbonyl.
A 1% diethyl ether, 99% petroleum ether mixture eluted two
yellow bands. The first band off the column gave a yellow
solid which was recrystallized from a methylene chloride-hexane
mixture at -20° and identified as \( \text{Mn}_2(\text{CO})_8[\text{As}(\text{CH}_3)(\text{C}_6\text{H}_5)]_2 \)
(isomer A) (0.55 g, 27%) mp 158-160° (sealed evacuated
capillary).

The mass spectrum showed a peak due to the parent ion
followed by the loss of eight carbonyl groups.

The ir spectrum (\( \text{C}_6\text{H}_{12} \) solution) showed carbonyl
frequencies at 2048(s), 1995(s), 1985(vs), 1961(vs) cm\(^{-1}\).

The \( ^1\text{H} \) nmr spectrum (\( \text{CDCl}_3 \) solution) gave an arsenic
methyl singlet at 1.92 and arsenic phenyl multiplets centred
at 7.42 and 7.68.
Anal. Calcd. for C\textsubscript{22}H\textsubscript{16}As\textsubscript{2}O\textsubscript{8}Mn\textsubscript{2}: C, 39.52; H, 2.40; mol wt 668. Found: C, 39.55; H, 2.61; mol wt (mass spec) 668.

The second band gave a yellow solid which was identified as Mn\textsubscript{2}(CO)\textsubscript{8}[As(CH\textsubscript{3})(C\textsubscript{6}H\textsubscript{5})]\textsubscript{2} (isomer B) (0.55 g, 27%); mp 199-201\textdegree (sealed evacuated capillary).

The mass spectrum showed a parent ion followed by loss of eight carbonyl groups.

The ir spectrum (C\textsubscript{6}H\textsubscript{12} solution) gave carbonyl frequencies at 2048(s), 1985(vs), 1961(vs) cm\textsuperscript{-1}.

The \textsuperscript{1}H nmr spectrum (CDC\textsubscript{13} solution) consisted of an arsenic methyl singlet at 1.83 and arsenic phenyl multiplets centred at 7.45 and 7.75.

Anal. Calcd. for C\textsubscript{22}H\textsubscript{16}As\textsubscript{2}O\textsubscript{8}Mn\textsubscript{2}: C, 39.52; H, 2.40; mol wt 668. Found: C, 39.70; H, 2.60; mol wt (mass spec) 668.
CHAPTER III
RESULTS AND DISCUSSION

This chapter is divided into five major sections. The first section is concerned with the preparation and characterization of the two ligands employed in this study. A short discussion on the stereomutation of arsenic and phosphorus is given in the second section. Section 3 is concerned with the preparation and characterization of some iron carbonyl complexes. In section 4 the nonrigidity of the Fe₂(CO)₆[E(R₁)(R₂)]₂ complexes (E = As, R₁ = R₂ = CH₃; R₁ = CH₂, R₂ = C₆H₅; E = P, R₁ = R₂ = CH₃) is discussed. Section 5 is concerned with a description of the method used in the computation of activation parameters for the nonrigid complexes.

1. **The Ligands**

Hexafluoroacetone and tetramethyl-diarsine react at 20° to give a compound containing two sets of inequivalent methyl groups and equivalent trifluoromethyl groups as shown by nmr spectroscopy. This compound (R = CH₃) dissociates to some extent at 20° as indicated in [XVI].
(R)(CH₃)AsAs(CH₃)(R) + (CF₃)₂CO ⇌ (CH₃)₂(R)₂As₂·(CF₃)₂CO

[XVI]

The complex is assigned structure 8a or 8b in which one arsenic atom, acting as a donor, is four-coordinate and the other, acting as an acceptor, is five-coordinate (R = CH₃) (if the lone pair is thought of occupying one site).

When tetramethyldiarsine reacts with hexafluorobutyne-2 at 20⁰, facile quantitative addition across the triple bond occurs with the formation of an approximate 1:1 mixture of the cis- and trans-isomers of 2,3-bis(dimethylarsino)-1,1,1,4,4,4-hexafluorobut-2-ene 2 (R = CH₃) and 10 (R = CH₃). However,

CH₃ As-As + CF₃C≡CCF₃ → C≡C + (CH₃)RAs
R   R

2

[XVII]
when excess hexafluoroacetone is used as solvent and if the diarsine is first allowed to mix with the solvent before the acetylene is added, the product is exclusively the cis-adduct. The stereospecificity is thought to be due to the initial formation of a complex such as 8a, 8b (R = CH₃) which allows attack of the acetylene on only one side of the arsenic-arsonic bond. Other workers have evidence for the existence of similar adducts.

The related 1,2-dimethyl-1,2-diphenyldiarsine reacts similarly with hexafluoroacetone and hexafluorobutyne although no nmr parameters were obtained for the hexafluoroacetone adduct. Figure 1(a) shows the $^{19}\text{F nmr}$ spectrum of the reaction product obtained in the absence of hexafluoroacetone. Figure 1(b) shows the spectrum of the product obtained when hexafluoroacetone is present. The two low field peaks in the spectra can be assigned to the meso and racemic forms of the trans-adduct 10 (R = C₆H₅) and the two high field peaks to the meso 11 and racemic 12 forms of the cis-adduct 9 (R = C₆H₅). The effect of the hexafluoroacetone is to change the ratio from

\[
\text{meso } 11 \quad \text{racemic } 12
\]
Figure 1. The $^{19}$F nmr spectrum of the products of equation [XVII] ($R = C_6H_5$) (a) in the absence of hexafluoroacetone and (b) in the presence of hexafluoroacetone.
55% trans: 45% cis in its absence to 12% trans: 88% cis in its presence, presumably due to the formation of a similar adduct $8a, 8b$ ($R = C_6H_5$).

The meso- and racemic isomers of the cis-adduct can be separated by virtue of their different solubility in hexane. One isomer which is obtained as a pure solid and identified as the racemic isomer $12$ (see section 3 of this chapter) is responsible for the $^{19}F$ singlet at 53.2 and the $^1H$ singlet at 1.20. The other isomer, obtained as an oil and identified as the meso isomer $11$ can be obtained free of the racemic form but it is usually contaminated with traces of the two forms of the trans-adduct $10$ ($R = C_6H_5$). Its $^{19}F$ spectrum is thus comprised of singlets at 50.0, 50.8 (trans-adduct), and 53.0 (cis-adduct), while the $^1H$ nmr spectrum shows a broad peak at 1.50.

The cis-diastereomers $11$ and $12$, once separated, are stable. The cis configuration allows them to act as monometallic bidentate (chelating) ligands or as bimetallic tridentate ligands since the double bond can also act as a coordination site. Examples of both types of behaviour will be presented in the following sections of this chapter and the following chapters.

Identification of complexes formed from the reactions of $\underline{2}$ ($R = CH_3$ or $C_6H_5$) with various metal carbonyls are based, to a large extent, on the nmr spectra of the products. Simple chelate complexes formed by replacing two carbonyl groups of the metal carbonyl by the ligand show arsenic methyl signals
shifted downfield from the free ligand value. This deshielding effect arises because the arsenic lone pairs are no longer available for shielding of the methyl groups since they are involved in coordination to the metal. Similar deshielding effects are observed for the trifluoromethyl groups. A further deshielding of trifluoromethyl groups occurs in complexes utilizing the double bond as an additional coordination site.

The carbon-fluorine stretching region in the ir (1300-1000 cm\(^{-1}\)) for complexes possessing normal chelate structures are nearly identical with those of the free ligand. Any loss of symmetry would have resulted in obvious changes in band number and distribution. Complexes containing fragmented ligand show a drastic change in the carbon-fluorine stretching region.

2. **The Stereomutation of Arsenic and Phosphorus**

A. General Discussion

The pyramidal inversion of configuration about a central atom, such as arsenic or phosphorus, surrounded by three substituents and a lone pair is illustrated in [XVIII].

\[
\begin{align*}
E &= \text{As or P}
\end{align*}
\]
Arsenic and phosphorus are well known to have high barriers to inversion, these barriers being influenced by such factors as steric and conjugation \((p-d)_{\pi}\) conjugation) effects.

As the steric requirement of a substituent increases the pyramidal ground state is destabilized relative to the less crowded transition state, with a resultant decrease in the barrier to inversion. The difference in steric requirements of a methyl group and a t-butyl group is reflected in the different inversion rates for a methyl substituted and t-butyl substituted phosphetane, the rate being much slower for the methyl derivative. The effect of steric requirements on the inversion rate is also reflected by the behaviour of the two ligands ethylene-1,2-bis(n-butylphenylarsine) and ethylene-1,2-bis(methylphenylarsine), rapid inversion occurring in the n-butyl derivative and no inversion occurring in the methyl derivative.

During the inversion process, the hybridization of the bonding orbitals at the arsenic or phosphorus atom is regarded as changing from \(sp^3\) to \(sp^2\), and that of the lone pair of electrons from \(sp^3\) to \(p\). Thus \(\pi\) delocalization of the lone pair favours the rehybridization process and lowers the barrier to inversion. In phosphines the effect of aryl substitution is to lower the barrier by \(2-3\) kcal mol\(^{-1}\). The lowering of inversion barriers in the diarsine and diphosphine systems is thought to be due to delocalization of the lone pair electrons into empty d orbitals by \((p-d)_{\pi}\) conjugation. In the transition state to inversion the lone pair of electrons offers the best
geometry for overlap to empty 3d orbitals on an adjacent phosphorus or arsenic atom.

Nmr experiments performed on 1,2-dimethyl-1,2-diphenyldiarsine and 1,2-dimethyl-1,2-diphenyldiphosphine give barriers to inversion of 27 and 26 kcal mol$^{-1}$ respectively. The collapse of the two methyl peaks in the $^1$H nmr spectrum over a high temperature range is thought to be due to the stereomutation of the arsenic and phosphorus atoms causing rapid interconversion of the two diastereomeric forms. Equation [XIX] illustrates the interconversion of the meso and racemic forms for 1,2-dimethyl-1,2-diphenyldiarsine.

$$\begin{align*}
\text{meso} & \quad \text{inversion} \quad \longrightarrow \quad \text{meso} \\
\text{meso} & \quad \text{rotation} \quad \longrightarrow \quad \text{racemic}
\end{align*}$$

[XIX]

B. Separation and Identification of the Stereoisomers of Ditertiary Arsines

The identification of the geometrical isomers of ditertiary arsines involves the formation of the metal complexes which may be separated by column chromatography followed by resolution of the racemic modification by fractional crystallization.

Some ligands such as ethylene-1,2-bis(n-butylphenylarsine) are actually stabilized by complex formation. Once the ligands
are set free, the two diastereomeric forms rapidly interconvert by pyramidal inversion about the arsenic atom, whereas other ligands do not interconvert in the free form.

The ditertiary arsine \( \mathcal{Z} (R = \text{C}_6\text{H}_5) \) can be separated into the \textit{meso} and racemic forms by fractional crystallization without any apparent interconversion of the two forms; the two isomers are stable to heat at \( 150^\circ \). Once separated, they are reacted with various metal carbonyls giving diastereomeric derivatives. In particular, reaction with iron pentacarbonyl affords a complex \( \text{Fe}_2(\text{CO})_6 \) as one of the reaction products. The properties of the geometric isomers of \( \text{Fe}_2(\text{CO})_6 \) allow assignment of the configuration of the starting ligands.

3. \textbf{Iron Carbonyl Complexes of (L-L) and (L-L)'}

The reaction of iron pentacarbonyl or triiron dodecacarbonyl with \textit{cis}-2,3-bis(dimethylarsino)-1,1,1,4,4,4-hexafluorobut-2-ene (L-L) and \textit{cis}-2,3-bis(methylphenylarsino)-1,1,1,4,4,4-hexafluorobut-2-ene (L-L)' affords two major carbonyl derivatives; \( (\text{L-L})\text{Fe}(\text{CO})_3 \), \( (\text{L-L})'\text{Fe}(\text{CO})_3 \) and \( (\text{L-L})\text{Fe}_2(\text{CO})_6 \), \( (\text{L-L})'\text{Fe}_2(\text{CO})_6 \).

A. \( (\text{L-L})\text{Fe}(\text{CO})_3 \) and \( (\text{L-L})'\text{Fe}(\text{CO})_3 \)

The tricarbonyl complexes are best prepared by ultraviolet irradiation. When heated at \( 150^\circ \) with iron pentacarbonyl the corresponding \( (\text{L-L})\text{Fe}_2(\text{CO})_6 \) and \( (\text{L-L})'\text{Fe}_2(\text{CO})_6 \) derivatives are produced. Prolonged heating of iron pentacarbonyl and
(L-L) or (L-L)', (3 days) drastically lowers the yield of the 
(L-L)Fe(CO)₃ or (L-L)'Fe(CO)₃ complexes. Thus they seem to be 
the intermediates in the thermal production of (L-L)Fe₂(CO)₆ 
and (L-L)'Fe₂(CO)₆. This conversion process has also been 
observer for a variety of other ligands.³

Mass spectra (which show peaks corresponding to the parent 
ion (ligand)Fe(CO)₃⁺ and stepwise loss of three carbonyl groups) 
and the analytical data suggest the formula (ligand)Fe(CO)₃.

The ¹H nmr spectra of these tricarbonyl species indicate 
that both arsenic atoms are coordinated symmetrically since 
only one lower field arsenic methyl singlet is observed. In the 
¹⁹F spectra the presence of only one trifluoromethyl singlet 
also indicates a symmetrical structure. The ir spectra in the 
carbonyl region show three terminal carbonyl bands indicative 
of either an equatorial-equatorial substituted trigonal 
bipyramid (Cᵥ²)³⁴ or an equatorial-axial substituted trigonal 
bipyramid * (Cᵥ)³⁴. The axial-equatorial substituted species, 
if rigid in solution, would give two arsenic methyl absorptions 
in the ¹H nmr spectrum whereas the equatorial-equatorial 
substituted species would only give one arsenic methyl signal.

* Other structures consistent with the ir spectrum are: (1) 
an axial-equatorial substituted square pyramid (Cᵥ);³⁴ (2) 
an equatorial-equatorial substituted square pyramid (Cᵥ).³⁴ 
In view of the fact that five-coordinate transition metal d⁸ 
compounds generally adopt trigonal-bipyramidal configurations³⁵ 
and since iron pentacarbonyl itself has the same con-
figuration,³⁶ the trigonal bipyramidal structures are more 
favoured.
However, the latter would require the ligand to subtend an angle of ca. 120° at the iron atom and angles of ca. 90° have usually been found in chelate complexes\textsuperscript{87-89} corresponding to ligand substitution at an axial and equatorial position. In the solid, the ligands are probably coordinated at an axial and equatorial position as is reported for (diars)Fe(CO)\textsubscript{3},\textsuperscript{90} diars = \(\text{C}_6\text{H}_4[\text{As(CH}_\text{3})_2]\). In solution, the tricarbonyl complexes, like other (ligand)Fe(CO)\textsubscript{3} and (ligand)Ru(CO)\textsubscript{3} complexes are probably undergoing positional exchange,\textsuperscript{93} whereby axial and equatorial substituents are exchanging as depicted in [XX]. Recently Odom\textsuperscript{94} and coworkers provided further evidence for the nonrigidity of these five-coordinate complexes utilizing \(^{13}\text{C}\) nmr spectroscopy. The \(^{13}\text{C}\) nmr spectrum of the carbonyl groups in tricarbonyl-1,2-bis(dimethylphosphino-ethane)iron(0) exhibits only one peak at 25° and -80°, and is consistent with the molecule having a nonrigid structure on the nmr time scale due to rapid intramolecular exchange.

The spectroscopic results for the diastereomeric (L-L)'Fe(CO)\textsubscript{3} complexes do not allow a decision to be made regarding the
structure of the initial ligand (L-L)', i.e., whether it is racemic or meso, since the complexes are too symmetrical; one having methyl groups cis with respect to the chelate ring (the meso complex) and the other trans (the racemic complex).

B. (L-L)Fe₂(CO)₆ and (L-L)'Fe₂(CO)₆

The dinuclear complexes are best prepared by heating the iron carbonyl with either (L-L) or (L-L)' at 150°C. (L-L)Fe₂(CO)₆ crystallizes as a yellow-red solid whereas the diastereomeric (L-L)'Fe(CO)₆ complexes crystallize as dark red-brown solids. All complexes are soluble in polar organic solvents (such as diethyl ether, chloroform, and acetone), but only slightly soluble in the nonpolar solvents (such as cyclohexane and petroleum ether). They can be heated at 150°C for 6 days without any noticeable decomposition occurring.

The mass spectra (which show peaks corresponding to the parent ion and a stepwise loss of six carbonyl groups) and the analytical data suggest the formula (ligand)Fe₂(CO)₆. The ir spectra in the carbonyl region are very similar to those reported for other (ligand)Fe₂(CO)₆ complexes whose structures are well established. The crystal structure of (ffars)Fe₂(CO)₆ is shown in Figure 2. The molecule consists of two inequivalent iron atoms Fe⁹ and Fe¹. Fe⁹ is approximately octahedrally coordinated to three carbonyl groups, two arsenic atoms, and Fe¹; Fe¹ is coordinated to the C=C bond of the cyclobutene ring, three carbonyl groups, and Fe⁹ (acting as a donor). Thus the coordination around Fe¹ can be regarded
Figure 2. Crystal structure of (ffars)Fe₂(CO)₆.
as either a distorted trigonal bipyramid (with the \( \text{C}=\text{C} \) bond occupying one site) or a distorted octahedron (with the two carbon atoms occupying two sites). Since the \((\text{L-L})\text{Fe}_2(\text{CO})_6\) and \((\text{L-L})'\text{Fe}_2(\text{CO})_6\) complexes resemble the reported \((\text{ligand})\text{Fe}_2(\text{CO})_6\) complexes in nearly every respect, it is reasonable to propose an analogous structure \[13\] \((R = \text{CH}_3 \text{ or } \text{C}_6\text{H}_5)\).

\[\begin{align*}
\text{Fe} & \quad \text{CO}_3 \quad \text{Fe} \\
\text{(CH}_3\text{)R} & \quad \text{C} \quad \text{As} \quad \text{CF}_3 \\
\text{As} & \quad \text{C} \quad \text{CF}_3 \\
\text{(CH}_3\text{)R} &
\end{align*}\]

If it is assumed that no interconversion of the \textit{meso} and racemic forms of \((\text{L-L})'\) occurs during the reaction with iron pentacarbonyl (this assumption seems justified since no interconversion is observed in other metal carbonyl reactions with \((\text{L-L})'\); see Chapter IV), the racemic isomer should give one \((\text{L-L})'\text{Fe}_2(\text{CO})_6\) complex \[14\] and the \textit{meso} could give two \((\text{L-L})'\text{Fe}_2(\text{CO})_6\) isomers \[15\] and \[16\]. The crystalline ligand affords a \(\text{Fe}_2(\text{CO})_6\) complex whose nmr spectrum shows two arsenic methyl and two trifluoromethyl absorptions (the trifluoromethyl groups are deshielded with respect to the free ligand value due to coordination of the \(\text{C}=\text{C}\) moiety to an iron

\* For \(R = \text{C}_6\text{H}_5\) this diagram is not intended to represent a specific diastereomer.
atom). The two trifluoromethyl groups belong to the same molecule since there is spin-spin coupling between them ($J(F,F) = 11.3 \text{ Hz}$). Such a spectrum would be expected only for 14 and thus the solid starting ligand is the racemic form of (L-L)' . The nmr spectrum of the Fe$_2$(CO)$_6$ complex obtained from the oily ligand shows only one type of arsenic methyl group to be present and only one trifluoromethyl group. Such a spectrum would be possible for either 15 or 16, but not from a mixture of both. Thus the oily ligand is the meso form of (L-L)' and gives the same product, probably 15, on heating and ultraviolet irradiation. The reason for preferring 15 is that phenyl-phenyl repulsions appear to be less than methyl-methyl in this sort of system (see section 4 of this chapter).
C. \( \text{Fe}_2(\text{CO})_6[\text{As(CH}_3\text{)}(\text{C}_6\text{H}_5)]_2 \)

Prolonged thermal reaction of \((\text{L-L})'\) with iron pentacarbonyl (3 days) also yields, in addition to the \( \text{Fe}_2(\text{CO})_6 \) complexes, a compound having the empirical formula \( \text{Fe}(\text{CO})_3\text{As(CH}_3\text{)}(\text{C}_6\text{H}_5) \). This proved to be identical with the product obtained by heating iron pentacarbonyl with 1,2-dimethyl-1,2-diphenyldiarsine: lower yields are obtained on irradiation. The meso ligand is a better source of the fluorocarbon-eliminated product. In fact the yield is almost that which is obtained by treating iron pentacarbonyl with the diarsine under identical conditions. The \((\text{L-L})'\) \( \text{Fe}_2(\text{CO})_6 \) complexes are stable by themselves in benzene solution for at least 5 days \((150^\circ)\) so they are not the unique source of the arsenido bridged complexes. The reaction mixture is very complex and it is difficult enough to establish when the fluorocarbon is lost, let alone rationalize the differences in behaviour between the two ligands. There is spectroscopic evidence for the existence of tetrakis(trifluoromethyl)cyclopentadienoneiron tricarbonyl in solution. This would be formed by reaction of the free acetylene with iron pentacarbonyl.98

The reaction of 1,2-dimethyl-1,2-diphenyldiarsine with iron pentacarbonyl gives two isomeric products which can be easily separated by careful chromatography by virtue of their differing solubilities. The major product is assigned structure 17 \((E = \text{As})\). The nmr spectrum shows only one type of arsenic methyl; hence the structure is symmetrical \((C_{2v})\). The lower
volatility and solubility of this isomer, compared with the other isomer, are also in accord with this formulation. The carbonyl ir frequencies are very similar to the phosphorus analogue\(^9\) which, in the solid state, has the two phenyl groups axial as in \(\text{17 (E = P)}\)\(^{100}\) and it is thus reasonable to believe that the arsenic analogue would be iso-structural.

The minor product of the reaction of the diarsine with iron pentacarbonyl is an isomer of \(\text{17 (E = As)}\) which has the asymmetric structure \(\text{18}\) since the \(^1\)H nmr spectrum shows two distinct singlets in the arsenic methyl region. One of these resonances is at relatively high field (0.93) and this can be assigned to the methyl group which is adjacent to the phenyl group on the other arsenic atom (the shift to high field is
due to through-space shielding of the methyl group by the phenyl group). The ir spectra of 17 (E = As) and 18 in the ν(CO) region are identical as is the case for the two phosphorus analogues.99

4. Stereochemical Nonrigidity of the Fe₂(CO)₆[E(R₁)(R₂)]₂ Complexes (E = As, R₁ = R₂ = CH₃, R₁ = CH₃, R₂ = C₆H₅; E = P, R₁ = R₂ = CH₃)

A recent structural determination of the symmetric analogue of Fe₂(CO)₆[P(CH₃)(C₆H₅)]₂ has shown it to have a folded structure consisting of two octahedrally coordinated iron atoms (assuming a "bent" iron-iron bond) with bridging phosphido groups as in 17 (E = P): the two phenyl groups are axial. It is likely that the Fe₂(CO)₆[P(CH₃)]₂ and Fe₂(CO)₆-[As(CH₃)]₂ complexes possess similar skeletons as depicted in 19a and 19b respectively. As stated in section 3.C, 17 (E = As) and 18 are probably the structures of the symmetrical and asymmetrical isomers of Fe₂(CO)₆[As(CH₃)(C₆H₅)]₂. A third isomer of this complex 19c was not formed presumably because of repulsion between the two axial methyl groups.
When a benzene solution of 18 (the asymmetric form) is heated at 150°, 17 (E = As) (the symmetric form) is produced and an equilibrium is established after 15 h with the ratio of 17 (E = As) to 18 being 6:1. The same equilibrium is attained after 90 h at 150° starting with the symmetric isomer. This process [XXI] of necessity involves bond breaking.

\[
\begin{align*}
\text{C}_6\text{H}_5 & \quad \text{CH}_3 \\
\text{As} & \quad \text{As} \\
\text{Fe} & \quad \text{Fe(CO)}_3
\end{align*}
\]

[XXI]

At temperatures below 120° the nmr spectrum of the symmetric isomer is independent of temperature. However the asymmetric isomer has a temperature dependent \(^1\)H nmr spectrum and this is shown in Figure 3. As the temperature is increased the two initially sharp singlets broaden, collapse, and coalesce into a single line which sharpens as the temperature is further increased. This indicates that at the higher temperature all the methyl groups are equivalent on the nmr time scale and suggests that the molecule is fluxional in the manner indicated in [XXII] \((E = As, R_1 = R_4 = \text{CH}_3, R_2 = R_3 = \text{C}_6\text{H}_5)\). The two methyl resonances of the dimethylarsino compound 19b behave in the same manner when the sample is heated suggesting that
Figure 3. Variable temperature $^1$H nmr spectra in benzene in the arsenic methyl region of the asymmetric isomer of Fe$_2$(CO)$_6$[As(CH$_3$)(C$_6$H$_5$)]$_2$. 
the molecule is fluxional in the manner indicated in [XXII]

(E = As, R₁ = R₂ = R₃ = R₄ = CH₃). The temperature dependence
of the ¹H nmr spectrum of this compound is shown in Figure 4.
Thermodynamic parameters were calculated for the motion using
the procedure of Gutowsky and Holm¹⁰¹ (see section 5 of this
chapter for an outline of the method). The parameters are
listed in Table XXVIII which also contains the values obtained
for the dimethylphosphino analogue ¹⁹a initially studied by
Dessy and coworkers.¹⁰²

Table XXVIII

Thermodynamic Parameters for Bridging Phosphido and Arsenido
Diiron Hexacarbonyl Complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>ΔHᵣ (kcal mol⁻¹)</th>
<th>ΔSᵣ (eu)</th>
<th>Tₐ (°K)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₂(CO)₆[As(CH₃)₂]₂</td>
<td>16.1±0.6</td>
<td>-3.7±1.5</td>
<td>347±2</td>
</tr>
<tr>
<td>Fe₂(CO)₆[P(CH₃)₂]₂</td>
<td>15.0±0.6</td>
<td>-6.6±1.2</td>
<td>347±3</td>
</tr>
<tr>
<td>Fe₂(CO)₆[As(CH₃)(C₆H₅)]₂</td>
<td>17.4±0.9</td>
<td>-3.8±1.5</td>
<td>373±4</td>
</tr>
</tbody>
</table>

* Coalescence temperature.
** Values from reference 102.
Figure 4. Variable temperature $^1$H nmr spectra in benzene of Fe$_2$(CO)$_6$[As(CH$_3$)$_2$]$_2$. 
The phosphorus decoupled spectrum was used in the variable temperature study of $\text{Fe}_2(\text{CO})_6[\text{P(CH}_3)_2]_2$ and the temperature dependent behaviour of the resulting two singlets (otherwise two virtually coupled triplets) is very similar to the arsenic analogues. No explanation can be given for the discrepancy in the values but those values determined during the present investigation make a consistent set and are in agreement with the values obtained from a study of the motion of a related complex $\text{CO}_2(\text{CO})_6[\text{Ge(CH}_3)_2]_2$.\textsuperscript{103}

The motion of the bridging arsenido and phosphido species is characterized by a high activation enthalpy and a small negative activation entropy suggesting the intermediate or transition state of the "butterfly" motion is of comparable entropy to the static forms. In order to account for the high temperature nmr results various mechanisms can be postulated for the motion: one could involve dissociation to an intermediate such as $(\text{CO})_3(R_1R_2E)\text{Fe-Fe}(\text{ER}_3R_4)(\text{CO})_3$ and others could involve no bond breaking. The dissociative mechanism seems unlikely since an intermediate such as that indicated above could allow rotation about the Fe-E and Fe-Fe bonds. Consequently in the case of the bridging methylphenylarsenido compounds $\text{17}$ (E = As) and $\text{18}$, interconversion of the symmetric and asymmetric isomers would occur. However this interconversion only happens at much higher temperatures ($150^\circ$) no conversion occurring at $100^\circ$. Another fact which seems to eliminate a dissociative mechanism is that the bridging dimethylphosphido derivative remains virtually
coupled over the entire temperature range. A doublet might be expected in the high temperature region for the phosphorus methyl groups if bond dissociation occurred. The other type of mechanism to account for the motion and which appears more likely is a nondissociative mechanism. Two likely intermediates have been suggested by other workers\textsuperscript{102,103} and have the $C_{2h}$ and $D_{2h}$ skeletons shown in 20 and 21 respectively. Neither of these intermediates has been detected by nmr spectroscopy since they are very short-lived. Dessy and coworkers\textsuperscript{102} suggest the "butterfly" motion proceeds through the highly symmetrical $D_{2h}$ intermediate 21 because of the large negative entropy value they find. But this value now appears to be incorrect (Table XXVIII) and there is no means of deciding in favour of either 20 or 21 or any other intermediate on the basis of the data at hand. This has been pointed out by Klemperer\textsuperscript{104} in an analysis based on topological representations.

In an attempt to gain more information concerning the motion of these fluxional molecules, the $^{13}C$ nmr spectrum of 19a and 19b was determined. Chemical shifts and coupling
constants are listed in Table XXIX.*

In agreement with the $^1$H nmr spectrum, the $^{13}$C nmr spectrum of the arsenic compound $^{19b}$ consists of two singlets for the dimethylarsino groups; however, only one singlet is observed for the carbonyl groups at $25^\circ$ and $-70^\circ$. Similarly the spectrum of the phosphorus compound $^{19a}$ at $25^\circ$ consists of two "triplets" for the dimethylphosphino groups and one "triplet" for the carbonyl groups which remains as one "triplet" at $-70^\circ$. The single resonance associated with the carbonyl groups indicates that a carbonyl scrambling process is taking place which is still fast at $-70^\circ$ on an nmr time scale and which takes place via an intramolecular pathway since $^{13}$C-$^{31}$P coupling is maintained. Rapid interchange of the carbonyl groups has also been observed in such molecules as (polyolefin)-$\text{Fe}_2(\text{CO})_6$, $^{108}$($\text{C}_8\text{H}_8)$Fe(\text{CO})$_3$, $^{109}$Rh$(\text{CO})_12$, $^{110}$ and RhCo$_3$(\text{CO})$_12$. $^{111}$

Note that the $^{13}$C spectra are obtained from CDCl$_3$ solutions containing a trace amount of Cr(acac)$_3$[tris(acetylacetonato) chromium(III)] using a Fourier transform technique. Long pauses between successive pulses in the Fourier transform technique are required since carbonyl carbons have long spin-lattice relaxation times. However, the addition of a paramagnetic compound reduces the length of $T_1$ so that a shorter accumulation time (machine time) is required. $^{105}$ An effective paramagnetic reagent that has been employed in the studies of organometallic molecules is Cr(acac)$_3$. $^{106,107}$ When Cr(acac)$_3$ is used in our work, a two-fold increase in intensity of the carbonyl peak of $^{19b}$ resulted which is equivalent to a twenty-fold decrease in the time needed to obtain the spectrum.
### Table XXIX

**$^{13}$C Nmr Data**

<table>
<thead>
<tr>
<th>Compound</th>
<th>$^{13}$C*</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Fe}_2(\text{CO})_6[\text{As(CH}_3]_2\text{]}_2$</td>
<td>Singlet at 212.8 (CO). Singlets at 16.7 and 13.5 (CH$_3$)</td>
</tr>
</tbody>
</table>
| $\text{Fe}_2(\text{CO})_6[\text{P(CH}_3\text{]}_2\text{]}_2$ | "Triplet" centred at 213.0 (CO)  
$|J(C,P) + J'(C,P')| = 10.0 \text{ Hz.}$  
"Triplets" centred at 23.4  
$|J(C,P) + J'(C,P')| = 40.0 \text{ Hz.}$  
and 17.4 $|J(C,P) + J'(C,P')| = 20.0 \text{ Hz (CH}_3\text{)}$ |

* Spectra from CDCl$_3$ solutions (with $^1$H decoupling) in the presence of a trace amount of Cr(acac)$_3$. The $|J(C,P) + J'(C,P')|$ refers to the separation of the two outer peaks of the "triplet".

Another possibility to account for the single carbonyl resonance at room temperature is that the equatorial and axial carbonyl carbons have the same chemical shift and $^{13}$C-$^{31}$P coupling constant. In view of the great sensitivity of $^{13}$C chemical shifts with respect to their environment, as demonstrated, for example, by the observation that the cis and trans chemical shifts of the carbonyl carbons in $[(\text{C}_6\text{H}_5)_3\text{P}]\text{Cr(CO)}_5^{24}$ differ by 4.8 ppm, it is unlikely that accidental superposition of chemical shifts and $^{13}$C-$^{31}$P coupling constants are responsible for the single carbonyl "triplet".
It is apparent that the "butterfly" motion of the \([\text{Fe-E}]_2\) skeleton and the scrambling of the carbonyl groups are independent processes. Thus it seems fruitless to attempt to explain the butterfly motion in terms of the properties of intermediates\(^{103}\) such as 20 and 21.

5. **A Description of the Method Used in the Calculation of Thermodynamic Parameters for Nonrigid Molecules**

Gutowsky and Holm\(^{101}\) have developed mathematical expressions that can be applied to the nmr method for processes that interchange protons between two sites. When the temperature dependence of an exchange process is being studied, the separation of the two lines under conditions where the exchange process is slow (at lower temperatures) is first determined. Then as the sample is heated, the two lines begin to come closer and closer together and \(\tau\) can be calculated at each temperature where

\[
\tau = \frac{\tau_A \tau_B}{(\tau_A + \tau_B)} \quad (\tau_A \text{ and } \tau_B \text{ are the average lifetimes of the protons at each different site A and B})
\]

using expression [XXIII]:

\[
\frac{\tau}{2}(\delta\omega^2 - \delta\omega_e^2) = 2 \text{ if } \tau\delta\omega > \sqrt{2}
\]

[XXIII]

\(\delta\omega\) is the separation of the two peaks in radians sec\(^{-1}\) assuming no interchange and \(\delta\omega_e\) is the experimentally measured peak separation (radians sec\(^{-1}\)) at each different temperature. This simplified equation can only be used when the width of the signals is small in comparison with the separation of the two
signals; otherwise a more detailed expression must be used. Table XXX lists the data used in the calculation of thermodynamic parameters for the asymmetric isomer of \(\text{Fe}_2(\text{CO})_6^-[\text{As(CH}_3\text{)(C}_6\text{H}_5])_2\). The data of Table XXX are plotted in Figure 5.

Table XXX

<table>
<thead>
<tr>
<th>(T(\degree\text{K}))</th>
<th>(\frac{1}{T} \times 10^3 (\degree\text{K}^{-1}))</th>
<th>(\delta\omega_e (\text{rad sec}^{-1}))</th>
<th>(\frac{1}{\tau\delta\omega} (\text{rad}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>345</td>
<td>2.90</td>
<td>568.3</td>
<td>0.07</td>
</tr>
<tr>
<td>350</td>
<td>2.86</td>
<td>565.2</td>
<td>0.11</td>
</tr>
<tr>
<td>355</td>
<td>2.82</td>
<td>555.8</td>
<td>0.16</td>
</tr>
<tr>
<td>360.5</td>
<td>2.77</td>
<td>540.1</td>
<td>0.22</td>
</tr>
<tr>
<td>362.5</td>
<td>2.76</td>
<td>533.8</td>
<td>0.26</td>
</tr>
<tr>
<td>365</td>
<td>2.74</td>
<td>515.0</td>
<td>0.31</td>
</tr>
</tbody>
</table>

as \(\log_{10} \left(\frac{1}{\tau\delta\omega}\right)\) versus \(\frac{1}{T}\). Using equation [XXIV], the slope and intercept of the graph then give the activation energy \(E_a\) and the frequency factor \(v_0\) respectively.

\[
\log_{10}(\frac{1}{\tau\delta\omega}) = \log_{10}(2v_0/\delta\omega) - \frac{E_a}{2.3RT} \quad [\text{XXIV}]
\]

The frequency factor is related to \(\Delta S^\dagger\) through expression [XXV] where the symbols have their usual significance.

\[
v_0 = \frac{e k_b T e^\Delta S^\dagger}{h} \quad [\text{XXV}]
\]
Figure 5. Temperature dependence of $1/\tau_{\delta\omega}$ for the asymmetric isomer of Fe$_2$(CO)$_6$[As(CH$_3$)(C$_6$H$_5$)]$_2$.
(Semilog plot)
CHAPTER IV
RESULTS AND DISCUSSION

This chapter is concerned with the preparation, characterization, and general chemistry of some Group VI metal carbonyl complexes of cis-2,3-bis(dimethylarsino)-1,1,1,4,4,4-hexafluorobut-2-ene (L-L) and cis-2,3-bis(methylphenylarsino)-1,1,1,4,4,4-hexafluorobut-2-ene (L-L'). Section 1 discusses some tetracarbonyl complexes; section 2, some tricarbonyl complexes; and section 3, some dicarbonyl complexes. Section 4 summarizes the preceding three sections.

1. (L-L)M(CO)$_4$ and (L-L')M(CO)$_4$ Complexes (M = Cr, Mo, W)

A. Preparation

Reaction of the Group VI metal hexacarbonyls with an equimolar amount of either (L-L) or (L-L)' (150°, benzene) for 1-2 days in a sealed evacuated Carius tube, yields in the usual manner,$^2$,$^6$,$^{115}$ the disubstituted chelate complexes (L-L)M(CO)$_4$ and (L-L')M(CO)$_4$:
\[
\begin{align*}
M(CO)_6 + (L-L) & \xrightarrow{150^\circ \text{ benzene}} (L-L)M(CO)_4 + 2CO \\
(L-L)' & \xrightarrow{\text{benzene}} (L-L)'M(CO)_4 + 2CO
\end{align*}
\]

M = Cr, Mo, W

[XXVI]

The complexes are yellow (except for the chromium derivative which is amber), air-stable, crystalline solids moderately soluble in nonpolar organic solvents and very soluble in polar organic solvents.

B. Spectroscopic Results

The mass spectra of the chelate complexes show a peak due to the parent ion \((\text{ligand})M(CO)_4^+\) as well as peaks due to the stepwise loss of four carbonyl groups.

The \(^1\text{H}\) and \(^{19}\text{F}\) nmr spectra show one arsenic methyl singlet and one trifluoromethyl singlet. This suggests that either the five-membered ring (determined by the metal, two arsenic, and two carbon atoms of the ligand) is planar in solution as in 22 (i.e. a symmetric structure), or the ring is involved in a conformational change that is rapid, on an nmr time scale, at room temperature in the manner indicated in [XXVII].
The chemical shift of the arsenic methyl groups of the meso- and racemic-(L-L)M(CO)_4 complexes differs by only ca. 0.02 ppm; however, the diastereomeric (L-L)M(CO)_4 complexes are considerably shifted to lower field (ca. 0.3 ppm) in comparison with the (L-L)M(CO)_4 complexes. The deshielding of the methyl groups in the free ligands as well as their chelate complexes can be attributed to the replacement of a methyl group on an arsenic atom by the more electronegative phenyl group.

The nmr results for the Group VI diastereomeric (L-L)M(CO)_4 complexes do not allow a decision to be made regarding the initial configuration of the ligand (L-L)' since the complexes are too symmetrical; the meso complex having methyl groups cis with respect to the chelate ring and the racemic complex having methyl groups trans with respect to the chelate ring.

The tetracarbonyl chelate complexes exhibit C_{2v} local symmetry of the carbonyl groups for which four ir-active carbonyl stretching modes are expected (2A_1 + B_1 + B_2) as shown in Figure 6. The intensity of the highest frequency
As–As = (L–L) or (L–L)'

Figure 6. The normal carbonyl vibrational modes for the Group VI (L–L)M(CO)₄ and (L–L)'M(CO)₄ complexes.
mode $A_1(1)$ is enhanced in the spectra of these complexes possibly because of coupling with the $A_1(2)$ mode or because of distortion of the molecule from ideal $C_{2v}$ symmetry. The tetracarbonyl complexes usually show the expected four bands,\textsuperscript{2,6,7} although accidental superposition of two of the lower frequency bands can occur.\textsuperscript{117} A similar superposition is observed in the spectra of the $(L-L)M(CO)_4$ and $(L-L)'M(CO)_4$ complexes.

A comparison of the carbonyl stretching frequencies of the $(L-L)M(CO)_4$ complexes with those Group VI chelate complexes of the related less electronegative ditertiary arsine ligand cis-1,2-bis(dimethylarsino)ethylene (cis-edas) is given in Table XXXI. The frequencies of the complexes of $(L-L)$ are somewhat higher than those of their cis-edas counterparts. This trend is consistent with the expected greater amount of metal-arsenic double bonding in the complexes of $(L-L)$. The more electronegative trifluoromethyl groups in $(L-L)$ increase the amount of $\pi$ donation from the metal to the arsenic ligand relative to cis-edas. This leads to a decrease in $\pi$ "back bonding" between the metal and carbonyl groups with subsequent
Ir Spectra (2100-1800 cm\(^{-1}\)) for Some Group VI Chelate Complexes

<table>
<thead>
<tr>
<th>Chelate Complex</th>
<th>(v(\text{CO})(\text{cm}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(L-L)Cr(CO)(_4)(^*)</td>
<td>2020, 1931, 1911</td>
</tr>
<tr>
<td>(\text{cis-edas})Cr(CO)(_4)(\text{**})</td>
<td>2010, 1935, 1900, 1880</td>
</tr>
<tr>
<td>(L-L)Mo(CO)(_4)(^*)</td>
<td>2036, 1939, 1921</td>
</tr>
<tr>
<td>(\text{cis-edas})Mo(CO)(_4)(\text{**})</td>
<td>2020, 1905, 1890, 1870</td>
</tr>
<tr>
<td>(L-L)W(CO)(_4)(^*)</td>
<td>2036, 1931, 1911</td>
</tr>
<tr>
<td>(\text{cis-edas})W(CO)(_4)(\text{**})</td>
<td>2009, 1903, 1873, 1852</td>
</tr>
</tbody>
</table>

\(^*\) This work, \(\text{C}_6\text{H}_{12}\) solvent.

\(^{**}\) Reference 118, KBr disk.

strengthening of the carbon-oxygen bond and higher carbonyl stretching frequencies.

Further evidence that the complexes possess a normal chelate structure is obtained from the carbon-fluorine stretching region in the ir. In this region (1300-1000 cm\(^{-1}\)) the spectra of the metal complexes are nearly identical with those of the free ligands; any loss of symmetry would have resulted in changes in the number and intensity of the bands.

C. Possible Mechanism of Formation

The ditertiary arsine ligands, (L-L) and (L-L)', probably react with the Group VI metal hexacarbonyls in the manner
indicated in equations [XXVIII] and [XXIX].

\[
M(\text{CO})_6 + \text{As-As} \rightarrow (\text{As-As})M(\text{CO})_5 + \text{CO} \quad [\text{XXVIII}]
\]

\[
(\text{As-As})M(\text{CO})_5 \rightarrow (\text{As-As})M(\text{CO})_4 + \text{CO} \quad [\text{XXIX}]
\]

\[M = \text{Cr, Mo, W}; \text{As-As} = (L-L) \text{ or } (L-L)'\]

The first step involves the formation of a pentacarbonyl complex in which one arsenic atom of the bidentate ligand is coordinated and the second step involves the coordination of the other arsenic atom with simultaneous loss of carbon monoxide. The chromium reactions probably occur via a dissociative process \(S_{N1}\) while the molybdenum and tungsten reactions occur via an associative process \(S_{N2}\) or a combination of the two processes.\(^{31,32,38-41}\)

Carbonyl bands attributed to the pentacarbonyl intermediates are seen in the ir spectra of the reaction mixtures; however, the \(M(\text{CO})_5\) species have not been isolated. Ward\(^{115}\) has isolated pentacarbonyl intermediates of the type shown in [XXVIII] from reactions of the Group VI metal hexacarbonyls and related ditertiary arsine ligands.
2. \( \text{Fac-(L-L)}^b(L-L)_c^M(CO)_3 \) and \( \text{Fac-(L-L)}^b(L-L)_t^mM(CO)_3 \) Complexes

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

A. Preparation

The tricarbonyl complexes are best prepared by photolysing a benzene solution of the parent hexacarbonyl or tetracarbonyl derivative and excess \((L-L)\) (pyrolysis at temperatures of 150-200\(^\circ\) apparently does not yield the tricarbonyl derivative):

\[
\begin{align*}
M(CO)_6 \text{ or } (L-L)M(CO)_4 & \quad + \quad \text{excess } (L-L) \\
& \quad \xrightarrow{hv \text{ benzene}} \quad (L-L)^b(L-L)_{c}^mM(CO)_3 \\
& \quad \quad + \quad (L-L)^b(L-L)_{t}^mM(CO)_3
\end{align*}
\]

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

The photolysis reaction is performed using a 200W and 450W lamp (for the molybdenum and tungsten derivatives only; the chromium reaction is performed using the 450W lamp). The 450W reaction gives the tricarbonyl derivative in a much shorter time than does the 200W reaction. For example, the photolysis (200W) of a benzene solution of molybdenum hexacarbonyl and excess \((L-L)\) affords, after 266 h, a 20% yield of the molybdenum tricarbonyl derivative, whereas performing the same photolysis using a 450W lamp gives, after 1.5 h a 36% yield of the same product. The shorter reaction time with the 450W lamp can be

* \((L-L)^b\) denotes bidentate ligand and \((L-L)^m_c\) the ligand in a cis configuration acting in a monodentate manner and \((L-L)^m_t\) the ligand in a trans configuration acting in a monodentate manner.
attributed to: (1) increase in the flux and (2) greater efficiency of the reaction apparatus - the carbon monoxide that is evolved is constantly removed from the reaction solution by the nitrogen and the lamp is situated very close to the solution (30 mm) which completely surrounds the quartz jacket containing the lamp.

Hitherto no tricarbonyl complex containing two bidentate ligands has been reported from the reaction of a Group VI metal hexacarbonyl with an excess amount of a potentially bidentate ligand. However, the literature relating to complexes of the type \((L_2)(L)M(CO)_3\) (\(M = \text{Cr, Mo, W} \); \(L_2\) is a bidentate ligand and \(L\) is a monodentate ligand) has been well documented.\(^{11,119,120}\)

**B. Characterization**

Two isomeric tricarbonyl derivatives are obtained from the 450W photochemical reaction and one tricarbonyl derivative from the 200W reaction. Analytical data suggest the formula \((L-L)_2M(CO)_3\). Therefore, from a consideration of the "effective atomic number" rule (which most organometallic molecules obey), the coordination sphere about the metal atom consists of three carbon monoxide groups, one bidentate, and one monodentate ligand \((L-L)\).

The ir spectra of the two isomers are identical in the carbonyl region; hence, the configuration of the carbonyl groups is probably the same in both isomers. However, for molecules of the type \((L-L)^b(L-L)^mM(CO)_3\) two basic configurations are possible: one having all carbonyl groups cis to each other and
designated as the fac isomer 24, and the other having two carbonyl groups trans to each other and designated as the mer isomer 25.

The fac isomer 24 exhibits $C_{3v}$ local symmetry of the carbonyl groups and two ir-active bands are expected. However, Dobson and Houk\textsuperscript{119} found that in complexes of the type fac-M(CO)$_2$X$_2$Y (where $X_2$ is a bidentate ligand and Y is a monodentate ligand) where the net charge-releasing ability of the ligands is expected to be in the order $X_2 > Y$, the lowest frequency mode is split into two components ($C_s$ symmetry). The more dissimilar the bonding properties of $X_2$ and Y the greater the splitting of the mode. These three vibrational stretching modes, indicated in Figure 7, involve a change in dipole moment and are expected to result in strong absorptions.

The mer isomer 25 exhibits $C_{2v}$ local symmetry of the carbonyl groups for which three ir-active carbonyl stretching modes are also expected. The normal vibrational modes are shown in Figure 7. Modes A and C involve a change in dipole moment of the molecule and are expected to result in strong absorptions;
Mer:

\[ \text{As-As} = (L-L) \]

Fac:

\[ \text{As-As} = (L-L) \]

Figure 7. The normal carbonyl vibrational modes for Group VI mer and fac isomers of \((L-L)^b-(L-L)^mM(CO)_3\).
however, mode B does not involve a change in dipole moment and this vibration should result in a weak absorption.

Indeed, reported fac-11,119-122 and mer-11,121,122 M(CO)₃X₂Y complexes do show the distinctive carbonyl patterns described above.

Both isomers of (L-L)ₐ(L-L)ₐM(CO)₃ show three strong bands in the ν(CO) region indicative of a fac configuration. A sample spectrum in the ν(CO) region of one of the two isomers is shown in Figure 8. The lowest frequency band of the tricarbonyl derivatives is split into a doublet, the separation being ca. 10-12 cm⁻¹. The splitting is in agreement with the findings of Dobson et al.¹¹⁹ since the bidentate ligand has a larger net charge-releasing ability than the monodentate ligand.

The production of isomers possessing a fac configuration is not unreasonable because a carbonyl group trans to another carbonyl group in (L-L)M(CO)₄ is more labile than a carbonyl trans to an arsenic atom and is more likely to be displaced by (L-L). Dobson and Houk¹¹ have found that the geometry of the tricarbonyl product seems to also depend on the steric requirements of both the incoming ligand and the chelate.

The basic difference in the nmr spectra of the two isomeric fac-(L-L)ₐ(L-L)ₐM(CO)₃ complexes is the magnitude of the ¹⁹F-¹⁹F coupling constant. This and other data previously discussed suggest the two isomers differ in the configuration of the monodentate ligand since the bidentate ligand in each isomer must possess a cis configuration to form a chelate complex.
Figure 8. The carbonyl ir spectrum in cyclohexane of an isomer of \((L-L)^b(L-L)^m\text{Mo(CO)}_3\).
The major chromium and molybdenum tricarbonyl product shows three arsenic methyl singlets (relative area 1:2:1 in order of increasing field) and the tungsten complex four equal area arsenic methyl singlets in the $^1$H nmr spectra. It appears that there is an accidental superposition of two absorptions in the chromium and molybdenum spectra. Their $^{19}$F nmr spectra all consist of a trifluoromethyl singlet (relative area 2) followed, at slightly higher field, by two trifluoromethyl quartets (each of relative area 1; $J(\text{F}, \text{F}) = 12.0 \text{ Hz}$ for chromium, $11.3 \text{ Hz}$ for molybdenum, and $13.5 \text{ Hz}$ for tungsten). The magnitude of the $^{19}\text{F}-^{19}\text{F}$ coupling constants suggests the two trifluoromethyl groups are $\text{cis}^{123,124}$ to each other in the monodentate ligand. Hence the major derivative is designated as fac-$(\text{L-L})^b(\text{L-L})^c\text{M(CO)}_3$.

The minor tricarbonyl product is assigned the fac structure in which the two trifluoromethyl groups in the monodentate ligand are $\text{trans}$ to each other. The $^1$H nmr spectrum should consist of four equal area arsenic methyl singlets. This is observed for the tungsten derivative but the chromium and molybdenum derivatives show three arsenic methyl singlets (relative area 1:2:1 in order of increasing field) presumably due to an accidental superposition of two absorptions. The corresponding $^{19}\text{F}$ spectra should consist of a trifluoromethyl singlet (relative area 2) for the fluorine atoms of the bidentate ligand and two trifluoromethyl quartets (each of relative area 1) for the fluorine atoms of the monodentate ligand. The chromium and molybdenum derivatives exhibit a quartet (relative
area 1; \( J(F,F) = 2.2 \text{ Hz for chromium and } 2.3 \text{ Hz for molybdenum} \) followed by a higher field singlet (relative area 2) and another quartet (relative area 1; same coupling constants as the lower field quartet). However, the tungsten derivative shows a quartet (relative area 1; \( J(F,F) = 2.2 \text{ Hz} \)) followed, at slightly higher field, by a broad singlet (relative area 3). The singlet contains absorptions due to the chelate ring trifluoromethyl groups and one trifluoromethyl group of the monodentate ligand. The smaller \( J(F,F) \) observed in these complexes is in agreement with the assignment of a trans configuration in the monodentate ligand. Hence the minor product is designated as \( \text{fac-} (L-L)^b(L-L)^{t}M(CO)^3 \).

The source of the trans ligand in \( \text{fac-} (L-L)^b(L-L)^{t}M(CO)^3 \) is an isomerization of \( (L-L) \) that occurs in the 450W photochemical reaction such that the cis and trans forms of the ligand are in equilibrium, with the ratio of cis to trans being 9:1 as shown by \( ^{19}\text{F nmr spectroscopy} \). No apparent ligand isomerization occurs in the 200W reaction.

The 200W reaction yields the \( \text{fac-} (L-L)^b(L-L)^cM(CO)^3 \) complexes whose spectroscopic properties are identical with the cis isomer (i.e. monodentate ligand in a cis configuration) obtained from the 450W reaction.

The \( ^{19}\text{F nmr data of } (L-L)^b(L-L)^{t}M(CO)^3 \) and \( (L-L)^b(L-L)^cM(CO)^3 \) also support the assignment of a fac configuration since the two trifluoromethyl groups of the chelating ligand are chemically equivalent. If the complexes adopted a mer configuration the two trifluoromethyl groups would be chemically inequivalent and
two additional quartets for the fluorine atoms of the bidentate ligand should appear.

It is not possible to determine whether the five-membered chelate ring in the two isomeric tricarbonyl complexes is planar in solution or undergoing conformational changes that are rapid on an nmr time scale at room temperature, similar to that discussed for the tetracarbonyl complexes in the preceding section.

C. Chemical Properties

Fac-(L-L)$_b$M(CO)$_3$$_c$ crystallize as yellow needles (except for fac-(L-L)$_b$M(CO)$_3$$_c$Cr(CO)$_3$ which gives pale orange needles) and fac-(L-L)$_b$M(CO)$_3$$_t$ crystallize as large orange plates. The lower solubility of fac-(L-L)$_b$M(CO)$_3$$_c$ compared with fac-(L-L)$_b$M(CO)$_3$$_t$ allows a facile separation of the two isomers by column chromatography.

The tricarbonyl complexes are unstable in nondegassed solvents but indefinitely stable in the solid state. A nondegassed deuterochloroform solution of either fac-(L-L)$_b$-(L-L)$_c$Mo(CO)$_3$ or fac-(L-L)$_b$-(L-L)$_t$Mo(CO)$_3$ produces a brown precipitate of unknown composition and the (L-L)Mo(CO)$_4$ complex after ca. 15 min. Decomposition is slower in benzene. The stability of the complexes, which decreases in the order tungsten > molybdenum >> chromium, is considerably enhanced in nitrogen saturated solvents.

The monodentate ligand in the two isomeric tricarbonyl derivatives is easily displaced by carbon monoxide, resulting
in the formation of the tetracarbonyl complexes, according to the general equation [XXXI].

$$\text{fac-}(L-L)(L-L)M(CO)_3 + CO \rightarrow (L-L)M(CO)_4 + (L-L)$$

[XXXI]

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

Irradiation of the $\text{fac-}(L-L)^b(L-L)^cM(CO)_3$ complexes gives the corresponding tetrasubstituted dicarbonyl derivatives (see following section), suggesting the tricarbonyl species are intermediates in the photochemical production of the dicarbonyl derivatives.

Refluxing a benzene solution of either tricarbonyl isomer results in the formation of $(L-L)M(CO)_4$ ($M = \text{Mo, W}$) which appears to attain an equilibrium concentration as judged by the ir spectra of the reaction mixture. When the tricarbonyl species is refluxed in the presence of excess ligand, ca. ten molar, no $(L-L)M(CO)_4$ forms. Possibly, at this temperature the tricarbonyl complex exists in an equilibrium with uncomplexed ligand as shown in equation [XXXII]. Decomposition by the evolution of carbon monoxide can give $(L-L)M(CO)_4$.

$$\text{fac-}(L-L)(L-L)M(CO)_3 \overset{80^\circ}{\rightarrow} (L-L)M(CO)_3 + (L-L)$$

[XXXII]

$$M = \text{Mo, W}$$

However, refluxing a benzene solution of either of the fac molybdenum isomers with a very large excess of the ligand, ca. twenty-five molar, slowly gives a new product of empirical formula $(L-L)[\text{As(CH}_3)_2]\text{Mo(CO)}_2$. Nmr, ir, and mass spectroscopic
data are consistent with a dimeric structure 26 in which the two metal centres are linked by a metal-metal bond and two bridging dimethylarsenido groups.

![Structure diagram](image)

26 As-As = (L-L); R = CH₃

The trans carbonyl complex 26 possesses $C_{2h}$ symmetry for which three ir-active carbonyl bands are expected. The ir spectrum in the carbonyl region shows two bands, the low frequency band being broad possibly due to an accidental superposition of two absorptions.

The $^1$H nmr spectrum shows a singlet for the arsenic methyl groups of the bidentate ligand and a singlet at slightly higher field for the bridging dimethylarsenido groups. The $^{19}$F spectrum shows one trifluoromethyl singlet.

The geometry of the four-membered [Mo₂As₂] ring, with the metal-metal bond in the plane of the ring, appears similar to that of Mo₂(CO)₈[As(CH₃)₂]₂.⁶⁸

A possible source of the bridging arsenido groups in 26 is tetramethyldiarsine formed from the decomposition of (L-L). Similar decomposition of the related (L-L)' ligand in a thermal
reaction giving 1,2-dimethyl-1,2-diphenyldiarsine, has been suggested to account for the formation of a dimeric iron complex with bridging methylphenylarsenido groups (see Chapter III; section 4.C).

Refluxing a benzene solution of \( \text{fac-}(L-L)^b(L-L)^m \text{Mo(CO)}_3 \) with a good \( \pi \)-acceptor ligand such as diphenylacetylene, gives \((L-L)\text{Mo(CO)}_4\) and \(\text{cis-}(L-L)^2\text{Mo(CO)}_2\) (discussed in section 3 of this chapter). Note, that merely refluxing a benzene solution of \( \text{fac-}(L-L)^b(L-L)^m \text{Mo(CO)}_3 \) does not give \(\text{cis-}(L-L)^2\text{Mo(CO)}_2\).

A possible mechanism to account for its formation based on an initial ligand dissociation (\(S_{N1}\)) is outlined in \([\text{XXXIII}]\)–\([\text{XXXVII}]\).

Coordination of the acetylene followed by elimination of a carbonyl group from the acetylene complex, (where a carbonyl group would be more labile than in \( \text{fac-}(L-L)^b(L-L)^m \text{Mo(CO)}_3 \)), and attack by the more nucleophilic ligand \((L-L)\) gives \(\text{cis-}(L-L)^2\text{Mo(CO)}_2\).

\[
\begin{align*}
\text{fac-}(L-L)^b(L-L)^m \text{Mo(CO)}_3 & \xrightarrow{\text{slow}} (L-L)^b \text{Mo(CO)}_3 + (L-L) & [\text{XXXIII}] \\
(L-L)^b \text{Mo(CO)}_3 + \text{acetylene} & \xrightarrow{\text{—}} (L-L)^b \text{Mo(CO)}_3(\text{acetylene}) & [\text{XXXIV}] \\
(L-L)^b \text{Mo(CO)}_3(\text{acetylene}) & \xrightarrow{\text{—}} (L-L)^b \text{Mo(CO)}_2(\text{acetylene}) & [\text{XXXV}] \\
& + \text{CO} \\
(L-L)^b \text{Mo(CO)}_2(\text{acetylene}) & + (L-L) & [\text{XXXVI}]
\end{align*}
\]
(L-L)\textsubscript{b}(L-L)\textsubscript{c}Mo(CO)\textsubscript{2}(acetylene) \rightarrow \textit{cis-}(L-L)\textsubscript{2}Mo(CO)\textsubscript{2} + \text{acetylene} [\text{XXXVII}]

Another possible mechanism based on the initial formation of a complex between fac-(L-L)\textsubscript{b}(L-L)\textsubscript{c}Mo(CO)\textsubscript{3} and the acetylene (S\textsubscript{N}2), followed by elimination of carbon monoxide and coordination of the free arsenic atom of the monodentate ligand with concomitant loss of the acetylene, is outlined in [XXXVIII]-[XL].

fac-(L-L)\textsubscript{b}(L-L)\textsubscript{c}Mo(CO)\textsubscript{3} + \text{acetylene} \xrightleftharpoons{\text{slow}} [\text{XXXVIII}]

(L-L)\textsubscript{b}(L-L)\textsubscript{c}Mo(CO)\textsubscript{3}(acetylene)

(L-L)\textsubscript{b}(L-L)\textsubscript{c}Mo(CO)\textsubscript{3}(acetylene) \xrightleftharpoons{} [\text{XXXIX}]

(L-L)\textsubscript{b}(L-L)\textsubscript{c}Mo(CO)\textsubscript{2}(acetylene) + CO

(L-L)\textsubscript{b}(L-L)\textsubscript{c}Mo(CO)\textsubscript{2}(acetylene) \rightarrow \textit{cis-}(L-L)\textsubscript{2}Mo(CO)\textsubscript{2} + \text{acetylene} [\text{XL}]

In either case, the formation of an acetylene complex facilitates the loss of a carbonyl group. There is no spectroscopic evidence (ir) for the existence of any of the postulated intermediates.

Unlike the molybdenum and tungsten derivatives, a refluxing benzene solution of fac-(L-L)\textsubscript{b}(L-L)\textsubscript{c}Cr(CO)\textsubscript{3} shows carbonyl absorptions in the ir characteristic of the tetracarbonyl and dicarbonyl complexes. However, it does not appear that
the complexes attain an equilibrium concentration. In the presence of a very large ligand excess the ir shows a pattern similar to that seen for the molybdenum reaction, suggesting the presence of \((L-L)_2[As(CH_3)_2]_2Cr_2(CO)_4\). However this product was not isolated.

3. **Cis-\((L-L)_2M(CO)_2\)** (\(M = Cr, Mo, W\)) and **Trans-\((L-L)_2M(CO)_2\)** Complexes (\(M = Cr, Mo\))

**A. Preparation**

The **cis** dicarbonyl complexes are best prepared by irradiating (450W) a benzene solution of the tetracarbonyl complex and excess ligand (\(L-L\));

\[(L-L)M(CO)_4 + \text{excess } (L-L) \xrightarrow{hv} \text{cis-}(L-L)_2M(CO)_2 + 2CO\]

\(M = Cr, Mo, W\)

Heating the reactants at 175° yields the molybdenum dicarbonyl complex: trace amounts of the chromium and tungsten derivatives are obtained at higher temperatures (190-210°) after prolonged heating and occasional removal of the accumulated carbon monoxide.

Further irradiation (450W) of **cis-\((L-L)_2M(CO)_2\)** (\(M = Cr, Mo\)) gives the isomeric **trans-\((L-L)_2M(CO)_2\)** derivative:

\[\text{cis-}(L-L)_2M(CO)_2 \xrightarrow{hv} \text{trans-}(L-L)_2M(CO)_2\]

\(M = Cr, Mo\)
Other related ditertiary arsine and ditertiary phosphine Group VI metal cis dicarbonyl complexes have been prepared by heating the corresponding tetracarbonyl derivative with the ligand at temperatures > 200 °C.2,6

There does not appear to be any report of the existence of ditertiary arsine trans dicarbonyl complexes. However, trans-(diphos)₂M(CO)₂ complexes (M = Cr, Mo; diphos = (C₆H₅)_2 PCH₂CH₂P(C₆H₅)₂) have been described.²⁸

The cationic species [(diphos)₂M(CO)₂]⁺,⁺² (M = Cr, Mo, W) are prepared by chemical oxidation of the corresponding neutral complexes.⁴²,¹²⁵-¹²⁷ In some cases retention of isomerism is observed and in others trans to cis or cis to trans rearrangements occur.

B. Characterization

The cis complexes have a configuration 2⁷ with the two carbonyl groups in relative cis positions (C₂ symmetry) for which two ir-active carbonyl bands are expected and observed. The spectra are consistent with other characterized Group VI metal cis dicarbonyl complexes.²,⁶,⁷ A sample spectrum in the ν(CO) region of cis-(L-L)₂Mo(CO)₂ appears in Figure 9(a). The

\[
\text{cis-M(CO)₂}
\]

₂⁷ M = Cr, Mo, W; As-As = (L-L)
Figure 9. The carbonyl IR spectra in cyclohexane of $\text{cis-}(\text{L-L})_2\text{Mo}($CO$)_2$ (A) and $\text{trans-}(\text{L-L})_2\text{Mo}($CO$)_2$ (B).
carbonyl frequencies of cis-(L-L)₂M(CO)_₂ are lowered considerably with respect to (L-L)M(CO)_₄. It is apparent that the two remaining carbonyl groups are able to share a much greater proportion of the available metal d-electrons; the resulting strong bonding to the metal explains their resistance to further substitution.

The carbonyl stretching frequencies of cis-(L-L)₂M(CO)_₂ and other cis dicarbonyl complexes are listed in Table XXXII. The higher carbonyl frequencies of the (L-L) derivatives are compatible with the expected greater amount of metal-arsenic double bonding due to the presence of the electronegative trifluoromethyl groups.

The ^1H nmr spectra of the tetrasubstituted complexes show four arsenic methyl singlets of equal area in accordance with the cis dicarbonyl structure. The ^19F nmr spectra show a trifluoromethyl singlet rather than two quartets as is expected, presumably due to the fact that the trifluoromethyl groups are insensitive to the different methyl environments about each arsenic atom.

The trans complexes have a configuration 28 with the two carbonyl groups in relative trans positions.

M = Cr, Mo; As-As = (L-L)
Table XXXII
Ir Spectra (1900-1700 cm\(^{-1}\)) for Some Group VI Cis Dicarbonyl Complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>(v(\text{CO})(\text{cm}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>((L-L)_2\text{Cr(CO)}_2)*</td>
<td>1883, 1829</td>
</tr>
<tr>
<td>((\text{diphos})_2\text{Cr(CO)}_2)**</td>
<td>1848, 1708</td>
</tr>
<tr>
<td>((\text{diars})_2\text{Cr(CO)}_2)**</td>
<td>1845, 1771</td>
</tr>
<tr>
<td>((L-L)_2\text{Mo(CO)}_2)*</td>
<td>1899, 1845</td>
</tr>
<tr>
<td>((\text{diphos})_2\text{Mo(CO)}_2)**</td>
<td>1852, 1786</td>
</tr>
<tr>
<td>((\text{diars})_2\text{Mo(CO)}_2)**</td>
<td>1859, 1786</td>
</tr>
<tr>
<td>((L-L)_2\text{W(CO)}_2)*</td>
<td>1890, 1839</td>
</tr>
<tr>
<td>((\text{diphos})_2\text{W(CO)}_2)**</td>
<td>1847, 1782</td>
</tr>
<tr>
<td>((\text{diars})_2\text{W(CO)}_2)**</td>
<td>1850, 1774</td>
</tr>
</tbody>
</table>

* This work, \(C_6\text{H}_{12}\) solvent.
** Data taken from reference 2, \(\text{CHCl}_3\) solvent; diphos = \((C_6\text{H}_5)_2\text{P(\text{CH}_2)_2P(C_6\text{H}_5)_2}\).
*** Data taken from reference 6, \(\text{CHCl}_3\) solvent; diars = \(\text{o-C}_6\text{H}_4[\text{As(\text{CH}_3)_2}_2]\).

These complexes possess \(C_{2h}\) symmetry for which two carbonyl stretching vibrations (\(A_g + B_{3g}\)) are expected, one (\(B_{3g}\)) being ir-active. The ir spectra of the trans derivatives show the expected one carbonyl band. A sample spectrum of trans-\((L-L)_2\text{Mo(CO)}_2\) is seen in Figure 9(b).

The \(^1\text{H}\) nmr and \(^{19}\text{F}\) nmr spectra of both trans complexes.
show one arsenic methyl and one trifluoromethyl singlet.

C. Trans to Cis Isomerization

The cis complexes are thermodynamically more stable than the isomeric trans complexes. Complete trans to cis isomerization occurs for the molybdenum derivative upon refluxing in benzene for 44 h and the chromium derivative upon refluxing for 1.5 h:

\[
\text{trans-}(\text{L-L})_2\text{M(CO)}_2 \xrightarrow{\text{heat}} \text{cis-}(\text{L-L})_2\text{M(CO)}_2
\]

\[\text{[XLIII]}\]

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

Presumably methyl-methyl interactions are greatest in the trans derivative, these interactions being greater for chromium due to its smaller atomic size.

Trans to cis isomerization is also found when the molybdenum and chromium derivatives are chromatographed on Florisil. The trans chromium derivative even isomerizes in the solid state.

The trans-(diphos)\(_2\)M(CO)\(_2\) complexes (M = Cr, Mo) are known to undergo facile isomerization in solution giving the cis isomer. Bond et al. have recently shown that cyclic voltammetry is an extremely useful technique for studying isomerism of the [(diphos)\(_2\)M(CO)\(_2\)]\(^{0,+1,+2}\) complexes (M = Cr, Mo, W).

The cis-trans isomerization processes of necessity involve bond breaking. Perhaps, a five-coordinate intermediate is involved, as indicated in [XLIV].
4. Summary

Pyrolysis ($150^\circ$) of $M(CO)_6$ ($M = Cr, Mo, W$) and $(L-L)$ or $(L-L)'$ in benzene affords the tetracarbonyl chelate complexes $(L-L)M(CO)_4$ and $(L-L)'M(CO)_4$ ($M = Cr, Mo, W$). Ultraviolet irradiation (450W) of the Group VI $(L-L)M(CO)_4$ derivatives and excess $(L-L)$ in benzene yields $\text{fac-}(L-L)_b^c(L-L)_c^mM(CO)_3$, $\text{fac-}(L-L)_b^c(L-L)_t^mM(CO)_3$ (where one ligand functions in a bidentate manner and another, in either a cis or trans configuration, functions in a monodentate manner), and $\text{cis-}(L-L)_2^cM(CO)_2$ ($M = Cr, Mo, W$). Prolonged irradiation of $\text{cis-}(L-L)_2^cM(CO)_2$ yields $\text{trans-}(L-L)_2^cM(CO)_2$ ($M = Cr, Mo$) which can be thermally reconverted into the cis form.

All reactions were monitored by observing the characteristic carbonyl bands of the substituted products. Figure 10 shows a typical spectrum of a reaction mixture where all bands can be assigned. Further characterization of the complexes, once isolated, was aided by nmr spectroscopy.
Figure 10. The carbonyl ir spectrum in cyclohexane of a mixture of (L-L)W(CO)$_4$ (A), $\text{fac-}(L-L)^b$-(L-L)$_c^m$W(CO)$_3$ (B), and $\text{cis-}(L-L)_2$W(CO)$_2$ (C).
CHAPTER V
RESULTS AND DISCUSSION

This chapter examines some seven-coordinate Group VI metal halocarbonyl complexes of cis-2,3-bis(dimethylarsino)-1,1,1,4,4,4-hexafluorobut-2-ene (L-L) and cis-2,3-bis(methylphenylarsino)-1,1,1,4,4,4-hexafluorobut-2-ene (L-L)', with the emphasis on the stereochemical nonrigidity of these complexes as revealed by nmr studies of the $^1$H, $^{13}$C, $^{19}$F, and $^{31}$P nuclei. Section 1 concerns some halotricarbonyl complexes; section 2, some bromodicarbonyl complexes; and section 3, some bromomonocarbonyl complexes. Section 4 summarizes aspects of the preceding three sections.

1. \((L-L)M(CO)\text{X}_2\) and \((L-L)'M(CO)\text{X}_2\) Complexes (\(M = Mo, W; X = Br, I\))

A. Preparation and Chemical Properties

The general method of preparation of the halogen derivatives \((L-L)M(CO)\text{X}_2\) and \((L-L)'M(CO)\text{X}_2\) can be represented as follows:
\[
\begin{align*}
(L-L)M(CO)_4 + X_2 & \rightarrow (L-L)M(CO)_3X_2 + CO \\
(L-L)'M(CO)_4 & \rightarrow (L-L)'M(CO)_3X_2 + CO
\end{align*}
\]

\[\text{[XLV]}\]

\(M = \text{Mo, W}; \ X = \text{Br, I}\)

Slow dropwise addition of a solution of the halogen to a vigorously stirred methylene chloride solution of the metal complex is essential in order to prevent local accumulation of the halogen. The conditions for the production of the halotricarbonyl complexes are found to depend on the metal, ligand, and halogen (see Chapter II; sections 5.C and 6.D).

In general the preparation of the \((L-L)M(CO)_3X_2\) complexes requires lower temperatures than does the \((L-L)'M(CO)_3X_2\) complexes. Possibly this reflects a greater stability of the \((L-L)'\) species, since the replacement of two methyl groups in \((L-L)\) by two phenyl groups in \((L-L)'\) results in reduced methyl-halogen interactions.

The halogen complexes are crystalline orange or yellow nonionic \(^*\) solids considerably more soluble in polar solvents than in nonpolar ones. They appear to decolourize in the solid state after a few months and are quite unstable in oxygenated solvents. The stability of these complexes \(^**\) which is enhanced

\(^*\) For example, \((L-L)\text{Mo(CO)}_3\text{I}_2\) has a molar conductivity of 0.9 ohm\(^{-1}\) cm\(^2\) in nitrobenzene; 1:1 electrolytes show conductivities of 20-30 ohm\(^{-1}\) cm\(^2\) in the same solvent. \(^4^4\)

\(^**\) Refluxing a sample of \((L-L)\text{Mo(CO)}_3\text{Br}_2\) in methylene chloride under a nitrogen atmosphere for 6 h results in complete decomposition; similar results are observed after stirring a solution at room temperature for 39 h.
in nitrogen saturated solvents, decreases in the order tungsten >> molybdenum; iodine >> bromine.

B. Characterization

The crystal structure of \((L\text{-}L)\text{W(CO)}_3\text{I}_2\), which is very similar to that of \((\text{C}_6\text{H}_5)_2\text{P(CH}_2\text{)}_2\text{P(C}_6\text{H}_5)_2\text{Mo(CO)}_3\text{Br}_2\), is shown in Figure 11. The tungsten atom is seven-coordinate with a distorted capped octahedral environment*, the capping group being a carbonyl. The capped face consists of the two remaining carbonyl groups and one of the arsenic atoms from the bidentate ligand, while the uncapped face consists of the two iodine atoms and the remaining arsenic atom. The capping group exhibits close nonbonded contacts with the other three atoms in the capped face.

The angle subtended at the tungsten atom by the bidentate ligand is \(75.9^\circ\) which is considerably decreased from the angles subtended by similar chelating ligands in octahedral complexes.\(^{87-89}\)

The two tungsten-arsenic bonds are significantly shorter than a normal tungsten-arsenic single bond by ca. \(0.19\ \text{Å}\). This shortening is thought to be due to some metal-arsenic double bond character caused by \(d\sigma-d\pi\) back donation from the tungsten atom. There is also a significant difference between the two metal-arsenic bond lengths, the metal-arsenic bond \(\text{trans}\) to an iodine atom being shorter than the metal-arsenic bond \(\text{trans}\) to a carbonyl group. Since an iodine is expected to be a

* The choice of the capped octahedron appears to describe the observed geometry more exactly.
Figure 11. Crystal structure of (L-L)W(CO)₃I₂.
weaker $d\pi$-acceptor than a carbonyl group, there is a greater amount of back donation to the arsenic atom trans to the halogen. In fact, it appears as though the halogen has no apparent $\pi$-acceptor properties, the tungsten-iodine bond length being essentially the sum of their single bond radii.

The nmr spectra of the tungsten complex are not in accordance with its X-ray crystal structure. The $^{1}H$ nmr spectrum at room temperature and $-70^\circ$ exhibits one arsenic methyl singlet characteristic of chelating (L-L) and the $^{19}F$ nmr spectrum one trifluoromethyl singlet. The $^{13}C$ nmr spectrum at room temperature consists of one singlet for the dimethylarsino groups ($^{1}H$ decoupled), one quartet for the trifluoromethyl groups ($J(C,F) = 285$ Hz), a broad absorption for the olefinic carbons (due to long range coupling to the fluorine atoms), and one singlet for the carbonyl groups.

No static polyhedron can exist that is in agreement with all the nmr data. Thus the $^{1}H$, $^{19}F$, and $^{13}C$ nmr data suggest that in solution the molecule has a nonrigid structure at room temperature on an nmr time scale; the $^{1}H$ and $^{19}F$ nmr spectra are consistent with the molecule having this nonrigid structure down to $-70^\circ$. Rapid exchange of the three carbonyl groups could possibly explain the appearance of one carbonyl absorption in the $^{13}C$ nmr spectrum; however, this would not explain the $^{1}H$ and $^{19}F$ nmr spectra since the two arsenic atoms would still be in an asymmetric environment. A more likely mechanism to explain the nonrigidity, consistent with all the nmr data, is a drastic rearrangement process involving rapid
scrambling of the carbonyl groups and iodine atoms, and simultaneous migration of the capping group over the faces of the \( \text{[As}_2\text{C}_2\text{I}_2] \) octahedron. This process can proceed via an intramolecular rearrangement or a carbonyl dissociative process forming a six-coordinate intermediate.

The solid-state structure may correspond to the low temperature form of the molecule but this limit was not reached at -70°.

The \( ^1\text{H} \) and \( ^{19}\text{F} \) nmr spectra of the other halotricarbonyl derivatives are very similar to that of \((\text{L-L})\text{W(CO)}_3\text{I}_2\) suggesting they also are nonrigid in solution in the manner discussed above.

Note that in the \( \text{meso-} (\text{L-L})' \text{M(CO)}_3\text{X}_2 \) complexes a multiplet is observed in the \( ^1\text{H} \) nmr spectra in deuterochloroform for the phenyl protons whereas in the \( \text{rac-} (\text{L-L})' \text{M(CO)}_3\text{X}_2 \) complexes a singlet is seen for the phenyl protons. Presumably the singlet is due to an accidental superposition of peaks since the racemic isomers exhibit a multiplet for the phenyl protons in deuterobenzene.

A feature of the \( ^1\text{H} \) nmr spectra of the \( (\text{L-L})\text{M(CO)}_3\text{X}_2 \) complexes is that for a given metal, as \( \text{X} \) changes from \( \text{Br} \) to \( \text{I} \), the arsenic methyl absorption moves downfield. This trend is also observed for a given metal and ligand configuration in the diastereomeric \( (\text{L-L})' \text{M(CO)}_3\text{X}_2 \) complexes. A further unique feature of the diastereomeric complexes is that for a given metal and halogen, the arsenic methyl signal in \( \text{rac-} (\text{L-L})' - \text{M(CO)}_3\text{X}_2 \) is considerably more shielded than in \( \text{meso-} (\text{L-L})' - \text{M(CO)}_3\text{X}_2 \).
M(CO)\textsubscript{3}X\textsubscript{2}. This could reflect a difference in the relative conformations of the five-membered chelate ring in the two types of diastereomeric complexes.

The ir spectra of the tricarbonyl complexes in the carbonyl region, which consist of three bands, are similar to other seven-coordinate Group VI metal tricarbonyl derivatives (Table XXXIII).

Table XXXIII

<table>
<thead>
<tr>
<th>Compound</th>
<th>(v(\text{CO})(\text{cm}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{L-L})\text{Mo(CO)}\textsubscript{3}I\textsubscript{2})*</td>
<td>2056, 1985, 1927</td>
</tr>
<tr>
<td>((\text{dam})\text{Mo(CO)}\textsubscript{3}I\textsubscript{2})**</td>
<td>2040, 1975, 1920</td>
</tr>
<tr>
<td>((\text{diphos})\text{Mo(CO)}\textsubscript{3}I\textsubscript{2})**</td>
<td>2036, 1986, 1925</td>
</tr>
<tr>
<td>((\text{diars})\text{Mo(CO)}\textsubscript{3}I\textsubscript{2})**</td>
<td>2053, 1982, 1925</td>
</tr>
<tr>
<td>((\text{L-L})\text{W(CO)}\textsubscript{3}Br\textsubscript{2})*</td>
<td>2068, 1977, 1911</td>
</tr>
<tr>
<td>((\text{diphos})\text{W(CO)}\textsubscript{3}Br\textsubscript{2})**</td>
<td>2050, 1965, 1910</td>
</tr>
</tbody>
</table>

* This work, \(\text{C}_\text{6}H\textsubscript{12}\) solvent.

** Data taken from reference 53, KBr disk; \(\text{dam} = (\text{C}_\text{6}H\textsubscript{5})\textsubscript{2}-\text{AsCH}_2\text{As(}\text{C}_\text{6}H\textsubscript{5}\text{)}\textsubscript{2}\).

*** Data taken from reference 52, KBr disk; \(\text{diphos} = (\text{C}_\text{6}H\textsubscript{5})\textsubscript{2}\text{P(}\text{CH}_2\text{)}\textsubscript{2}\text{P(}\text{C}_\text{6}H\textsubscript{5}\text{)}\textsubscript{2}\).

**** Data taken from reference 44, nujol mull; \(\text{diars} = \text{o-C}_\text{6}H\textsubscript{4}[\text{As(CH}_3\text{)}\textsubscript{2}]\textsubscript{2}\).
2. (L-L)LMo(CO)$_2$Br$_2$ Complexes (L = a Monodentate Ligand)

A. Preparation and Chemical Properties

The addition of a methylene chloride solution of L to a methylene chloride solution of (L-L)Mo(CO)$_3$Br$_2$ under a nitrogen atmosphere, results in the facile replacement of a carbonyl group by L giving (L-L)LMo(CO)$_2$Br$_2$:

(L-L)Mo(CO)$_3$Br$_2$ + L $\xrightarrow{25^\circ}$ (L-L)LMo(CO)$_2$Br$_2$ + CO

The dicarbonyl complexes are seven-coordinate yellow (except for (L-L)[P(C$_6$H$_5$)$_3$]Mo(CO)$_2$Br$_2$ which is orange) crystalline solids considerably more stable and more soluble than the parent (L-L)Mo(CO)$_3$Br$_2$ complex. These complexes do not melt but only decompose on heating in an open capillary tube.

B. Spectroscopic Results

For the (L-L)LMo(CO)$_2$Br$_2$ complexes in which L is a monodentate tertiary phosphine or phosphite, the $^1$H nmr spectra show an arsenic methyl singlet in the region associated with chelating (L-L) and absorptions due to substituents on the phosphine or phosphite. The $^{19}$F nmr spectra exhibit a trifluoromethyl singlet for (L-L). The complex (L-L)[P(OCH$_3$)$_3$]Mo(CO)$_2$Br$_2$ shows one arsenic methyl singlet in the $^1$H nmr spectrum at 25$^\circ$ and -80$^\circ$. Thus, the nmr spectra of the dicarbonyl complexes (L-L)LMo(CO)$_2$Br$_2$ in the (L-L) region
are very similar to those of the \((L-L)M(CO)\_3X\_2\) complexes suggesting they too are nonrigid in solution.

If the dicarbonyl complexes adopt an asymmetric octahedral configuration (similar to \((L-L)W(CO)\_3I\_2\) with \(L\) replacing a carbonyl group), the \(^1H\) nmr spectra could be accounted for by a scrambling process of \(L\), the carbonyl groups, and bromine atoms as well as a simultaneous rapid migration of the capping group over faces of the octahedron.

Equilibration of the arsenic methyl groups by rapid migration of the capping group over faces of the octahedron would dictate a static octahedral configuration \(^{29}\) (it suggests carbonyl groups are \textit{cis}) with \(L\) in the capping position.

Connor et al.\(^ {60}\) have recently reported a fluxional seven-coordinate molybdenum and tungsten iododicarbonyl complex. They explain the fluxionalism by a polytopal rearrangement, possibly by rapid migration of the iodine over the faces of a static trigonal prism.

\[
\begin{align*}
\text{Br} & \quad \text{CO} \\
\text{As} & \quad \text{Mo} \\
\text{As} & \quad \text{CO} \\
\text{Br} &
\end{align*}
\]

\(^{29}\) \text{As-As} = (L-L)
The \((L-L)^b(L-L)^m\)Mo\((CO)_2\)Br\(_2\) complex (where \((L-L)^b\) denotes bidentate ligand and \((L-L)^m\) monodentate ligand) provides an interesting example where the nmr data suggest three different types of processes are occurring in solution. The \(^1H\) nmr spectrum shows two equal area arsenic methyl singlets, while the \(^{19}F\) nmr spectrum exhibits one trifluoromethyl singlet. If scrambling between the carbonyls, bromine atoms, and \((L-L)^m\) and rapid migration of the capping group over the octahedral faces are occurring, the resultant \(^1H\) nmr spectrum should give an arsenic methyl singlet (relative area 2) for the bidentate ligand and two arsenic methyl singlets (each of relative area 1) for the monodentate ligand; one of the singlets for \((L-L)^m\) would also have a chemical shift characteristic of a uncoordinated arsenic atom. The \(^{19}F\) spectrum should give a trifluoromethyl singlet for the fluorine atoms of the bidentate ligand (relative area 2) and two trifluoromethyl quartets (each of relative area 1) for the monodentate ligand with a characteristic coupling constant for cis trifluoromethyl groups.\(^{123,124}\) It appears that in addition to a scrambling and migration process, exchange is also occurring between the coordinated and uncoordinated arsenic atoms of the monodentate ligand thereby equilibrating the methyl groups of this ligand. Scrambling and ligand exchange appear to be fast on an nmr time scale at -80\(^0\).

An exchange process between the chelated and monodentate ligands would probably result in the appearance of a single arsenic methyl absorption. Colton et al.\(^{59}\) have reported
a variable temperature $^1$H nmr study of the seven-coordinate complexes $[(C_6H_5)_2AsCH_2As(C_6H_5)_2]_2M(CO)_2X_2$ ($M = Mo, W; X = Cl, Br, I$), containing one chelated and one monodentate ditertiary arsine ligand. Their study shows that, near room temperature, exchange occurs between the nonequivalent ligands, resulting in the appearance of one methylene absorption, and at lower temperatures this exchange ceases, resulting in the appearance of two different methylene absorptions. They suggested the transition state for the exchange process has configuration 30.

The ir pattern in the carbonyl region of all the (L-L)LMo-(CO)$_2$Br$_2$ complexes is very similar suggesting the carbonyl groups have identical relative configurations. The presence of two strong carbonyl absorptions indicates the carbonyl groups possibly possess a cis orientation.

The carbonyl frequencies vary as a function of the π-acceptor ability of L, the better the π-acceptor the higher the carbonyl frequency. Thus the phosphite complexes give higher carbonyl frequencies than the phosphine complexes.
3. (L-L)L₂Mo(CO)Br₂ Complexes

A. Preparation and Chemical Properties

The seven-coordinate monocarbonyl complexes are prepared by refluxing the parent (L-L)Mo(CO)₃Br₂ species in benzene with an excess amount of the monodentate ligand L.

(L-L)Mo(CO)₃Br₂ + excess L \xrightarrow{80^\circ \text{ benzene}} (L-L)L₂Mo(CO)Br₂ + 2CO [XLVII]

(L-L)₂Mo(CO)Br₂ is prepared by warming the (L-L)ᵇ(L-L)ᵐ-Mo(CO)₂Br₂ complex in benzene to 50⁰:

(L-L)ᵇ(L-L)ᵐMo(CO)₂Br₂ \xrightarrow{50^\circ \text{ benzene}} (L-L)₂Mo(CO)Br₂ + CO [XLVIII]

The bromomonocarbonyl complexes are orange (except for (L-L)₂Mo(CO)Br₂ which is brown) crystalline solids, stable in the solid-state but unstable in nondegassed solvents, giving the corresponding (L-L)LMo(CO)₂Br₂ complex as one of the decomposition products. The complexes show a great tendency to crystallize as methylene chloride adducts, but the solvent of crystallization is readily removed in vacuo. They, like the (L-L)M(CO)₃X₂ and (L-L)LMo(CO)₂Br₂ derivatives, do not melt on heating.

All the (L-L)L₂Mo(CO)Br₂ complexes containing monodentate phosphines or phosphites are carbon monoxide carriers:

(L-L)L₂Mo(CO)Br₂ \xrightarrow{80^\circ} (L-L)LMo(CO)₂Br₂ + L [XLIX]
The (L-L)\(_2\)Mo(CO)Br\(_2\) complex does not appear to react with carbon monoxide at room temperature.

B. Stereochemical Nonrigidity

The nmr results of the (L-L)L\(_2\)Mo(CO)Br\(_2\) complexes (L is monodentate) indicate the species are rigid at room temperature and are nonrigid at higher temperatures on an nmr time scale. This is in contrast to the (L-L)M(CO)\(_3\)X\(_2\) and (L-L)LMo(CO)\(_2\)Br\(_2\) derivatives which appear to be nonrigid at room temperature.

The (L-L)[P(OCH\(_3\))\(_3\)]\(_2\)Mo(CO)Br\(_2\) and (L-L)[P(OCH\(_3\))\(_2\)(C\(_6\)H\(_5\))]\(_2\)Mo(CO)Br\(_2\) complexes are examples of H\(_n\)PP'H\(_n\)' spin systems. The theory of nuclear spin systems of the type H\(_n\)PP'H\(_n\)' has been developed by Harris\(^{130,131}\) who has shown that a simple 1:2:1 "triplet" resonance will be observed for H\(_n\) when \(|J(P,P')|\gg |J(H,P) + J'(H,P')|\) (i.e. when \(^{31}\)P-\(^{31}\)P coupling is strong). When \(^{31}\)P-\(^{31}\)P coupling is small a 1:1 doublet should be observed. However, when \(^{31}\)P-\(^{31}\)P coupling is intermediate several methyl absorption resonances are expected and appear as an unresolved, broad resonance lying between a 1:1 doublet of separation \(|J(H,P) + J'(H,P')|\).\(^{130,131}\) The two monocarbonyl complexes exhibit the latter type of resonance pattern for the methyl and methoxy groups. Henceforth this type of resonance absorption is referred to as an intermediate pattern.

The \(^1\)H nmr spectrum of (L-L)[P(OCH\(_3\))\(_3\)]\(_2\)Mo(CO)Br\(_2\) at room temperature consists of two equal area arsenic methyl singlets
and a phosphite methyl intermediate pattern; the $^{19}$F nmr spectrum shows a trifluoromethyl singlet. When phosphorus is decoupled the phosphite methyl proton absorbance appears as a single sharp line indicating all six methyl groups are equivalent. These spectra can be interpreted in terms of a seven-coordinate capped octahedral structure (P = P(OCH$_3$)$_3$) with a carbonyl group in the capping position above the $[P_2Br]$ face.

The arsenic methyl groups on one side of the [As$_2P_2$] plane experience a different environment from those on the other side.

$^{31}$ (P = P(OCH$_3$)$_3$) has a temperature dependent $^1$H nmr spectrum shown in Figure 12. As the temperature is increased the two initially sharp arsenic methyl singlets broaden, collapse, and coalesce into a single line which sharpens as the temperature is further increased. This indicates that at the higher temperatures all the arsenic methyl groups are equivalent on an nmr time scale and suggests that the molecule
Figure 12. Variable temperature $^1$H nmr spectra in benzene in the arsenic methyl region of (L-L)[P(OCH$_3$)$_3$]$_2$-Mo(CO)Br$_2$. 
An intramolecular polytopal rearrangement from a capped octahedral geometry through a pentagonal bipyramid intermediate to another capped octahedral geometry, possibly by rapid migration of the carbonyl group over the two \([P_2Br]\) faces, would lead to an averaging of the two types of arsenic methyl environments. Rather than restricting the migration to the two faces as shown in \([L]\), migration of the carbonyl group over all the faces would also lead to an averaging process.

A polytopal rearrangement process as depicted in \([L]\) \((P = P(OCH_3)_3)\) but involving a phosphite dissociation forming a six-coordinate intermediate can be eliminated by the fact that the phosphite methyl groups remain virtually coupled over the entire temperature range. If bond dissociation occurred a doublet might be expected for the phosphite methyl groups.

The room temperature nmr spectra of \((L-L)[P(OCH_3)_2(C_6H_5)]_2^-\)
Mo(CO)Br$_2$ indicate the molecule has configuration 31 ($P = P(OC\text{H}_3)_2(C_6\text{H}_5)$). Thus, the $^1$H nmr spectrum shows two equal area arsenic methyl singlets followed, at lower field, by two methoxy methyl intermediate patterns and phosphorus phenyl multiplets. The intermediate patterns collapse to two sharp singlets with phosphorus decoupling. The $^{19}$F nmr spectrum consists of a trifluoromethyl singlet. Since the $^{31}$P nmr spectrum indicates the two phosphorus nuclei are chemically equivalent, the two intermediate patterns are assigned to the diastereotropic methoxy methyl groups on each phosphorus atom. The intermediate patterns result from virtually coupled spin systems.

Similarly the (L-L)[P(OC\text{H}_3)_2(C_6\text{H}_5)]$_2$Mo(CO)Br$_2$ complex has a temperature dependent $^1$H nmr spectrum indicating it is fluxional. The two arsenic methyl singlets broaden, collapse, and coalesce as the temperature is increased. However, there is no equilibration of the two diastereotropic methoxy methyl resonances. Figure 13 shows the two intermediate patterns for the methyl groups, with and without phosphorus decoupling, at room temperature and the temperature corresponding to coalescence of the arsenic methyl absorptions.

The high temperature spectra appear to be best accounted for by a process \([L (P = P(OC\text{H}_3)_2(C_6\text{H}_5))]\) which would lead to an equilibration of the arsenic methyl resonances but not the diastereotropic methoxy methyl resonances.

Thermodynamic parameters were calculated for the fluxional motion using the method of Gutowsky and Holm.
Figure 13. Variable temperature $^1$H nmr spectra in benzene in the methoxy methyl region of $(L-L)[P(OCH_3)_2(C_6H_5)]_2$Mo(CO)Br$_2$. A and D are the phosphorus decoupled spectra. B and C are the normal spectra.
The parameters for this complex and \( (L-L)\left[P(OCH_2CH_3)_3\right]_2Mo(CO)Br_2 \) are listed below in Table XXXIV.

### Table XXXIV

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \Delta H^\dagger ) (kcal mol(^{-1}))</th>
<th>( \Delta S^\dagger ) (eu)</th>
<th>( T_c (^\circ K) )*</th>
</tr>
</thead>
<tbody>
<tr>
<td>( (L-L)\left[P(OCH_2CH_3)_2(C_6H_5)\right]_2Mo(CO)Br_2 )</td>
<td>6.7 ± 0.6</td>
<td>-29 ± 2</td>
<td>368 ± 3</td>
</tr>
<tr>
<td>( (L-L)\left[P(OCH_2CH_3)_3\right]_2Mo(CO)Br_2 )</td>
<td>4.9 ± 0.6</td>
<td>-35 ± 2</td>
<td>368 ± 3</td>
</tr>
</tbody>
</table>

* \( T_c \) = coalescence temperature of the arsenic methyl resonances.

\( (L-L)\left[P(OCH_3)_2(C_6H_5)\right]_2Mo(CO)Br_2 \) is characterized by a low activation enthalpy and a very large negative activation entropy suggesting the intermediate or transition state of the fluxional motion is of considerable less entropy than the static forms. Process [L], involving the formation of a pentagonal bipyramid as the intermediate is in accord with the entropy value of Table XXXIV, since this symmetrical intermediate should have a smaller entropy than either of the static forms. Thus the capped octahedral ground state configuration is destabilized relative to the less crowded transition state, resulting in a low barrier for the motion.

The thermodynamic parameters do not favour a polytopal rearrangement process with dissociation giving a six-coordinate intermediate. Dissociation of the phosponite can also be
eliminated by the fact that the methoxy methyl groups remain virtually coupled over the entire high temperature range. Dissociation of one end of the chelate ligand (L-L) to form a six-coordinate intermediate followed by recombination would probably require a much higher barrier than is observed. For example, Meaker et al.\textsuperscript{133} report an activation energy of 12.8 kcal mol\textsuperscript{-1} for an exchange process involving dissociation of one end of a ditertiary alkylphosphine ligand in a seven-coordinate tantalum carbonyl complex. They note that a polytopal rearrangement could occur but would possibly have a much lower barrier than observed.

The nmr spectra of (L-L)[P(OCH\textsubscript{2}CH\textsubscript{3})\textsubscript{3}]\textsubscript{2}Mo(CO)Br\textsubscript{2} at room temperature differ from those of the other monocarbonyl complexes suggesting it has a different relative configuration. The \textsuperscript{1}H nmr spectrum exhibits two equal area arsenic methyl singlets, an apparent triplet for the methyl protons of the ethoxy group, and a multiplet structure for the methylene protons of the ethoxy group due to coupling to the methyl protons and phosphorus atom; the \textsuperscript{19}F nmr spectrum consists of a trifluoromethyl singlet.

A more detailed examination of the \textsuperscript{1}H nmr spectrum of the phosphite group shows, that with proton decoupling, the methylene absorption collapses to two doublets with \textsuperscript{1}H-\textsuperscript{31}P coupling constants of 6.0 and 4.0 Hz. It is not possible to say whether the two different sets of methylene protons are further coupled across the molybdenum centre to the other
phosphorus atom. With broad band phosphorus decoupling, the methylene multiplet collapses to two equal area quartets \((J(H,H) = 7.0 \text{ Hz})\). The decoupling experiments indicate there are two chemically inequivalent sets of methylene protons. In accordance with these observations the \(^{31}\text{P}\) nmr spectrum indicates the two phosphorus atoms are in an asymmetric environment. There appears to be an accidental superposition of two absorptions in the methyl resonance since one triplet is seen; furthermore, the methyl protons do not appear to be coupled to the phosphorus atom.

These spectra can be interpreted in terms of a seven-coordinate capped octahedral structure \(^{32}\) \((P = P(\text{OCH}_2\text{CH}_3)_3)\) with the phosphite groups in a \textit{trans} position. A carbonyl group occupies the capping position above the \([\text{PBr}_2]\) face. There is a different environment on each side of the \([\text{As}_2\text{Br}_2]\) plane, so that arsenic methyl groups on one side of the plane have a different chemical shift from those on the other side; similarly the two phosphite groups are in an asymmetric environment.

\[\text{As-As} = (L-L)\]
$^{32} (P = P(OCH_2CH_3)_3)$ has a temperature dependent $^1H$ nmr spectrum indicating it also is fluxional. As the temperature is increased the two arsenic methyl singlets broaden, collapse, and coalesce in a manner analogous to $^{31} (P = P(OCH_3)_3$, or $P(OCH_3)_2(C_6H_5)$). Similarly the two methylene quartets (phosphorus decoupled) collapse into one quartet at the temperature corresponding to coalescence of the arsenic methyl singlets. Since the chemical shift difference between the two methylene quartets is so small (1.5 Hz) the collapse may be a temperature effect rather than indicating an equilibration of the methylene groups.

The high temperature spectra can be satisfactorily explained by an intramolecular polytopic rearrangement process $^{[LI]}$ ($P = P(OCH_2CH_3)_3$) which leads to an averaging of the two types of arsenic methyl and ethoxy methylene environments.

Thermodynamic parameters were calculated (Table XXXIV) for the motion and are very similar to those of $^{31} (P = P(OCH_3)_2(C_6H_5)$.
suggesting the two complexes behave in an analogous manner at high temperatures.

The nmr spectra of \((\text{L-L})[\text{P(CH}_3)_2(\text{C}_6\text{H}_5)]_2\text{Mo(CO)Br}_2\) differ considerably from the other seven-coordinate monocarbonyl complexes. At room temperature the \(^1\text{H}\) nmr spectrum in the \((\text{L-L})\) region consists of an arsenic methyl quartet (relative area 1; \((J(H,F) = 2.5 \text{ Hz})\), followed at higher field by an arsenic methyl singlet (relative area 2) and an arsenic methyl quartet (relative area 1; \((J(H,F) = 2.0 \text{ Hz})\). The 1:2:1 arsenic methyl ratio is presumably due to an accidental superposition of peaks in benzene since four equal area absorptions appear in deuterochloroform. The phosphine ligand exhibits four phosphine methyl doublets (each of relative area 1) arising from \(^1\text{H}-^3\text{P}\) coupling and two phosphine phenyl multiplets (each of relative area 1.7). With broad band phosphorus decoupling, the phosphine methyl doublets collapse to four singlets. The room temperature \(^1\text{H}\) nmr spectrum of this complex with and without phosphorus decoupling is shown in Figure 14.

The \(^19\text{F}\) nmr spectrum gives two equal area trifluoromethyl quartets \((J(F,F) = 15.0 \text{ Hz})\); the \(^19\text{F}-^19\text{F}\) coupling constant indicates the trifluoromethyl groups are \text{cis}.\(^{123,124}\) The \(^3\text{P}\) nmr spectrum at room temperature suggests the two phosphorus atoms are in an asymmetric environment.

Possible configurations for \((\text{L-L})[\text{P(CH}_3)_2(\text{C}_6\text{H}_5)]_2\text{Mo(CO)Br}_2\) consistent with the room temperature nmr spectra are shown in 23 and 24 \((P = \text{P(CH}_3)_2(\text{C}_6\text{H}_5))\). In either configuration the capping carbonyl group is above the \([\text{AsPBr}]\) face such that
Figure 14. Variable temperature $^1$H nmr spectra (methyl region) in benzene of (L-L)[P(CH$_3$)$_2$(C$_6$H$_5$)$_2$]$_2$Mo(CO)Br$_2$. A is the normal spectrum and B, C, D, E are the phosphorus decoupled spectra.
the two arsenic atoms are in an asymmetric environment and all four arsenic methyl groups are inequivalent. Similarly the two different phosphorus atoms produce two different pairs of diastereotropic$^{132}$ phosphine methyl groups.

(L-L)[P(CH$_3$)$_2$(C$_6$H$_5$)$_2$Mo(CO)Br$_2$] has a temperature dependent $^1$H and $^{19}$F nmr spectrum. The variable temperature $^1$H nmr spectrum is shown in Figure 14. It was not possible to obtain a limiting high temperature spectrum; thus the spectrum is not as defined at high temperatures as those of the other monocarbonyl complexes. As the temperature is increased it appears that there is broadening of the arsenic methyl and phosphine methyl resonances. Since the two types of methyl resonances are not as well separated as in the phosphite and phosphonite complexes, overlap of the resonances can occur. The broad resonance observed at high temperatures possibly is due to arsenic and phosphine methyl absorptions.

At high temperatures there is no equilibration of the two phosphorus atoms. However, as the temperature is increased
the two trifluoromethyl quartets broaden, collapse and coalesce into a single broad peak which sharpens as the temperature is further increased, indicating the trifluoromethyl groups are equivalent on an nmr time scale at high temperatures.

Invoking a polytopal rearrangement process at high temperatures involving carbonyl migration over faces of the octahedron such as to equilibrate the trifluoromethyl groups but not the phosphorus atoms, suggests the complex has configuration \( \text{3} \) \( \text{4} \) \( (P = P(CH_3)_2(C_6H_5)) \). Rapid migration of a carbonyl over the \([\text{AsPBr}], [\text{PBr}_2],\) and \([\text{AsPBr}]\) faces, illustrated in [LII], would equilibrate the trifluoromethyl groups but not the phosphorus atoms. A limiting fast exchange high temperature \(^1\text{H} \) nmr spectrum for this type of process should consist of two arsenic methyl resonances and four phosphine methyl resonances.

\[ \text{As-As} = (\text{L-L}) \]

A similar type of motion for \( \text{3} \) \( \text{3} \) \( (P = P(CH_3)_2(C_6H_5)) \) would equilibrate the trifluoromethyl groups and the phosphorus atoms.
Had it been possible to calculate thermodynamic parameters for \( \mathcal{H} (P = P(CH_3)_2(C_6H_5)) \), they may have yielded further information concerning the fluxional motion.

The \( ^1H \) nmr spectrum of \((L-L)_2Mo(CO)Br_2\) at 25° and -70° exhibits one arsenic methyl singlet in the region associated with coordinated arsenic; the \( ^{19}F \) nmr spectrum at 25° consists of a trifluoromethyl singlet.

No static polyhedron can be drawn to account for the nmr data, suggesting the complex is fluxional in solution at 25° and -70°. Since a limiting slow exchange low temperature spectrum was not obtained, it is only possible to speculate on possible mechanisms to account for the motion. One such process, similar to that postulated for the other seven-coordinate monocarbonyl complexes, is a polytopal rearrangement by rapid migration of a carbonyl group over the faces of an \([As_4Br_2]\) octahedron. This process would dictate the complex having a relative configuration 35 (omitting the capping carbonyl). Rapid migration of a carbonyl over the faces of an octahedron in which the two bromine atoms are cis to each other as in 36, would not lead to an averaging of the arsenic methyl groups, since As(1) will always be different from As(2).

\[
\begin{align*}
35 & \quad \text{As-As} = (L-L) \\
36 & \quad \text{As(1)-As(2)} = (L-L)
\end{align*}
\]
C. \textit{Ir Spectra}

Each of the \((L-L)L_2\text{Mo(CO)Br}_2\) complexes shows one carbonyl band in the ir spectrum. The carbonyl frequency of \((L-L)L_2\text{Mo(CO)Br}_2\) \((1843-1792 \text{ cm}^{-1})\) is considerably lowered compared with \((L-L)L\text{Mo(CO)}_2\text{Br}_2\) \((1981-1867 \text{ cm}^{-1})\) and \((L-L)\text{Mo(CO)}_3\text{Br}_2\) \((2076-1925 \text{ cm}^{-1})\), reflecting the fact that the remaining carbonyl group is able to share a much greater proportion of the available metal d-electrons. From a consideration of the carbonyl frequency of the \((L-L)L_2\text{Mo(CO)Br}_2\) complexes, the \(\pi\)-acceptor properties of \(L\) decrease in the order trimethylphosphite \(\approx\) triethylphosphite \(>\) dimethyl phenylphosphonite \(>\) dimethylphenylphosphine.

4. \textit{Summary}

Halogen oxidation of \((L-L)\text{M(CO)}_4\) and \((L-L)'\text{M(CO)}_4\) \((M = \text{Mo, W})\) yields the seven-coordinate complexes \((L-L)\text{M(CO)}_3\text{X}_2\) and \((L-L)'\text{M(CO)}_3\text{X}_2\) \((M = \text{Mo, W}; X = \text{Br, I})\) which appear to be nonelectrolytes. Nmr spectra suggest the complexes are stereochemically nonrigid at room temperature.

Facile replacement of a carbonyl group in \((L-L)\text{Mo(CO)}_3\text{Br}_2\) by a monodentate ligand \(L\) yields \((L-L)L\text{Mo(CO)}_2\text{Br}_2\) which appear to be best described as seven-coordinate molecules also nonrigid at room temperature.

Heating the \((L-L)\text{Mo(CO)}_3\text{Br}_2\) complex with excess \(L\) \((L\) is a phosphine, phosphite, or phosphonite) gives \((L-L)L_2\text{Mo(CO)Br}_2\); heating \((L-L)^b(L-L)\text{Mo(CO)}_2\text{Br}_2\) gives \((L-L)_2\text{Mo(CO)Br}_2\).
The complexes are seven-coordinate, the former being rigid at room temperature and nonrigid at higher temperatures, while the latter appears to be nonrigid at room temperature and -70°.

The nmr spectra at room temperature for the monocarbonyl complexes containing phosphorus ligands can be satisfactorily interpreted in terms of a static seven-coordinate capped octahedral structure with a carbonyl group in the capping position; at higher temperatures the spectra are consistent with a polytopal rearrangement by rapid migration of the carbonyl group over octahedral faces.

The different relative configurations postulated for the monocarbonyl complexes are probably dictated largely by steric interactions such as that experienced between a capping group and other groups in the capped face.

In conclusion, this work represents some of the first reported examples of nonrigidity in seven-coordinate Group VI halocarbonyl complexes where hitherto only two reports have appeared; however, there have been a few reports of this phenomena being observed in other seven-coordinate complexes.
CHAPTER VI
RESULTS AND DISCUSSION

In section 1 two novel compounds obtained from the reaction of (L-L) with dimanganese decacarbonyl and dirhenium decacarbonyl are examined. In section 2 the $\text{Mn}_2(\text{CO})_8[\text{As}((\text{CH}_3)(\text{C}_6\text{H}_5))]_2$ complexes are discussed.

1. Reactions of (L-L) with Dimanganese Decacarbonyl and Dirhenium Decacarbonyl

Although the reactions of fluorocarbon-bridged ditertiary arsines with metal carbonyl species usually afford complexes in which the ligand remains intact, some interesting cleavage reactions have recently been discovered. For example, the ligand $f_4fars, (\text{CH}_3)_2\text{AsC} = \text{CAs}((\text{CH}_3)_2\text{CF}_2\text{CF}_2$, when treated with triiron dodecacarbonyl, $\text{dimanganese}$ or $\text{dirhenium decacarbonyl}$, forms complexes in which one arsenic-carbon bond of the ligand has been replaced by a metal-carbon bond; the displaced dimethylarsino group appearing elsewhere in the resulting product. However, unusual ligand reactions are not confined to fluorocarbon-bridged donors (e.g. references 142-145).
The reaction of \( (L-L) \) with dimanganese decacarbonyl and dirhenium decacarbonyl gives a different product for each metal carbonyl species in which ligand cleavage has occurred.

A. \( (L-L) \) and Dimanganese Decacarbonyl

Pyrolysis of \( (L-L) \) and dimanganese decacarbonyl in benzene at \( 110^\circ \) in a sealed evacuated Carius tube gives a yellow air-stable compound of formula \( C_{16}H_{18}As_{3}F_{0}O_{6}Mn_{2} \) as determined by microanalysis and mass spectrometry. The identical complex is obtained upon refluxing the above reactants in benzene or toluene or photolysing the reactants \( (200W) \); however, the yields are considerably decreased from that of the pyrolysis reaction.

An X-ray structural determination of the complex\(^{146,147}\) indicated the presence of a novel fluorine substituted \( \pi \)-allyl fragment. A view of the molecule showing all atoms except the methyl groups is given in Figure 15. The coordination around Mn(1) is closely octahedral, having three arsenic atoms (\( \text{cis} \) to each other) and three carbonyl carbon atoms within its inner coordination sphere. The coordination around Mn(2) is distorted octahedral and includes a bridging arsenic atom, three carbonyl carbon atoms, and three allyl carbon atoms C(11), C(12), and C(16). The allyl carbon atoms occupy two adjacent sites and form part of an asymmetrically substituted \( \pi \)-allyl system which is linked to Mn(1) via two manganese-arsenic bonds. A further link between the two manganese atoms is provided by the
bridging dimethylarsenido group.

The carbon-carbon distances \( (C(11) - C(12) = 1.39 \pm 0.03 \text{ Å}, \)
\( C(11) - C(16) = 1.38 \pm 0.03 \text{ Å}) \) of the \( \pi \)-allyl group fall in the
range of carbon-carbon distances previously reported.\(^{148,149}\) The angle subtended at the central carbon atom \( (C(12) - C(11) - C(16) = 122 \pm 2^\circ) \) has the expected value.

Although the literature is well documented on hydrocarbon
\( \pi \)-allyl derivatives of transition metals, e.g., \( \pi-C_3H_5Co(CO)_2,^{150}\)
\( \pi-C_3H_5Mn(CO)_4,^{151} \) \( \pi-C_3H_5PdBr)_2,^{152} \) \( \pi-C_3H_5NiBr)_2,^{153} \) this
study appears to be the first reported example of a fluorinated
\( \pi \)-allyl transition metal derivative. However, the existence
of a long-lived fluorinated allyl cation has been reported in
a communication by Chambers et al.\(^{154}\)

In accord with the X-ray crystal structure of the manganese
complex, the \( ^1H \) nmr spectrum shows six inequivalent arsenic
methyl resonances. Four resonances appear as singlets and two
appear as doublets due to \( ^1H - ^19F \) coupling. Since two different
fluorine decoupling frequencies are required to collapse the
doublets to single sharp lines, each of the two arsenic methyl
groups are coupled to a different fluorine atom (either F(4)
or F(5)). Possibly, coupling involves the methyl groups on
As(2) rather than As(3) as the coupling is transmitted through
one less bond. The \( ^19F \) nmr spectrum consists of a trifluoro-
methyl doublet \( (J(CF_3,F) = 26 \text{ Hz}) \) followed at higher field
by a broad carbon-fluorine doublet \( (J(F,F) = 121 \text{ Hz}) \) and
another carbon-fluorine doublet of quartets \( (J(F,F) = 121 \text{ Hz}, \)
\( J(CF_3,F) = 26 \text{ Hz}) \). The trifluoromethyl group appears to be
coupled to either F(4) or F(5). The large geminal $^{19}\text{F}-^{19}\text{F}$ coupling constant is in accord with other reported geminal fluorine coupling constants.$^{154-156}$ The chemical shifts of the two fluorine atoms (60.86 and 67.78) are at higher field than the trifluoromethyl group (42.5) due to shielding by the allyl linkage.

The ir spectrum indicates six terminal carbonyl groups, consistent with the $C_s$ symmetry of the complex.

The $\pi$-allyl manganese complex is the result of a ligand rearrangement reaction as a carbon-fluorine bond has been cleaved giving the allyl fragment. The complex also contains a bridging dimethylarsenido group, presumably resulting from the cleavage of an arsenic-carbon bond in the ligand (L-L). Stone et al. have reported the preparation of fluorocarbon complexes obtained by nucleophilic displacement of a fluoride ion from hexafluorobutyne-2,$^{156}$ fluoro-olefins,$^{157}$ or polyfluoroaromatic compounds,$^{158}$ by carbonylmanganese anions.

B. (L-L) and Dirhenium Decacarbonyl

Reaction of (L-L) with dirhenium decacarbonyl on ultraviolet irradiation (450W, benzene solution) affords an orange air-stable solid of formula $C_{11}H_8AsF_6O_5Re$ (22%) as determined by microanalysis and mass spectrometry. Thermal reaction of the carbonyl and ligand does not appear to yield any stable complex.

The ir spectrum of the rhenium complex in the terminal carbonyl region consists of four bands, indicating a Re(CO)$_4$
fragment (mass spectrum shows the loss of four carbonyl groups). The C=C frequency is increased to 1608 cm\(^{-1}\), compared with 1569 cm\(^{-1}\) found in the free ligand.

The \(^{19}\)F nmr spectrum consists of two trifluoromethyl quartets (\(J(F,F) = 12.4\) Hz), the \(^{19}\)F–\(^{19}\)F coupling constant being indicative of cis trifluoromethyl groups.\(^{123,124}\)

The \(^1\)H nmr spectrum consists of a singlet with a shoulder (fluorine decoupled) on the low field side at 100 MHz.

These data best fit the structures \(37a\) or \(37b\). Addition of the shift reagent, tris(2,2-dimethyl-6,6,7,7,8,8,8-heptfluoro-3,5-octanedionato)europium(III) (commonly referred to as Eu(FOD)\(_3\)), to a solution of the rhenium complex, separated the methylene resonance from the dimethylarsino signal, confirming its presence.

![Structures 37a and 37b](image)

The effect of adding the shift reagent is shown in Figure 16. The separation and shift of the two peaks also confirm the presence of the oxygen atom since it is our experience that terminal carbonyl groups do not interact with shift reagents.
Figure 16. The $^1$H nmr spectrum of the rhenium complex (a) in the absence of Eu(FOD)$_3$ and (b) in the presence of Eu(FOD)$_3$. 
Under high resolution, the low field $^{19}$F quartet is split further because of coupling to the dimethylarsino group$^{159}$ but the high field quartet shows no triplet structure expected for $37b$. Thus $37a$ is preferred.

The origin of the methylene group in the rhenium tetracarbonyl complex is unknown but it does not come from the solvent as the identical product was produced using benzene-$d_6$ as solvent.

Although paramagnetic lanthanide complexes have found a wide application in organic nmr studies (e.g. references 160-163), there do not appear to be any reports concerning the use of a lanthanide shift complex in elucidating an organometallic structure. A preliminary account has appeared showing the effect of added shift reagent on some iron complexes; however, the different proton signals were resolvable in the absence of the lanthanide reagent.$^{164}$

2. Reaction of 1,2-Dimethyl-1,2-Diphenyldiarsine with Dimanganese Decacarbonyl

The diarsine reacts with dimanganese decacarbonyl in refluxing toluene with cleavage of the arsenic-arsenic bond, giving two isomers of formula $\text{Mn}_2(\text{CO})_8[\text{As}(\text{CH}_3)(\text{C}_6\text{H}_5)]_2$ as determined by microanalysis and mass spectrometry. It should be noted that iron pentacarbonyl reacts with the same diarsine with cleavage of the arsenic-arsenic bond, resulting in the formation of two isomeric $\text{Fe}_2(\text{CO})_6[\text{As}(\text{CH}_3)(\text{C}_6\text{H}_5)]_2$ complexes (see Chapter III; section 3.C).
Spectroscopic properties of the two manganese isomers are similar to other reported Mn$_2$(CO)$_8$[E(R)$_2$]$_2$ complexes (E = As or P; R = CH$_3$ or C$_6$H$_5$)$^{69}$ indicating they possess a similar skeleton$^{38}$ with bridging methylphenylarsenido groups.

The two isomers differ in the configuration about the arsenic atom, one having two methyl and two phenyl groups opposite each other (symmetric) and one having a methyl and phenyl group opposite each other (asymmetric). However, the spectroscopic properties do not allow a decision to be made regarding the configuration of the two isomers.

Both species exhibit an arsenic methyl singlet in the $^1$H nmr spectrum. The ir spectrum in the carbonyl region of isomer A (which eluted faster) consists of four bands as expected for a cis M(CO)$_4$L$_2$ complex;$^{12}$ isomer B exhibits three carbonyl bands, presumably due to an accidental superposition of two
absorptions. The spectra of other known \( \text{Mn}_2(\text{CO})_8[\text{E}(\text{R})_2]_2 \)
complexes (\( \text{E} = \text{As} \) or \( \text{P} \); \( \text{R} = \text{CH}_3 \) or \( \text{C}_6\text{H}_5 \)) also show only three
of the expected four bands, (Table XXXV).

### Table XXXV

Ir Spectra (2100-1900 cm\(^{-1}\)) for Some Manganese Complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>( v(\text{CO})(\text{cm}^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Mn}_2(\text{CO})_8[\text{As}(\text{CH}_3)(\text{C}_6\text{H}_5)]_2 ) * A</td>
<td>2048, 1995, 1985, 1961</td>
</tr>
<tr>
<td>( \text{Mn}_2(\text{CO})_8[\text{As}(\text{CH}_3)(\text{C}_6\text{H}_5)]_2 ) * B</td>
<td>2048, 1985, 1961</td>
</tr>
<tr>
<td>( \text{Mn}_2(\text{CO})_8[\text{As}(\text{CH}_3)_2]_2 ) **</td>
<td>2039, 1975, 1952</td>
</tr>
<tr>
<td>( \text{Mn}_2(\text{CO})_8[\text{As}(\text{C}_6\text{H}_5)_2]_2 ) **</td>
<td>2050, 1987, 1955</td>
</tr>
<tr>
<td>( \text{Mn}_2(\text{CO})_8[\text{P}(\text{CH}_3)_2]_2 ) **</td>
<td>2044, 1978, 1955</td>
</tr>
<tr>
<td>( \text{Mn}_2(\text{CO})_8[\text{P}(\text{C}_6\text{H}_5)_2]_2 ) **</td>
<td>2053, 1992, 1957</td>
</tr>
</tbody>
</table>

\* This work, \( \text{C}_6\text{H}_{12} \) solvent; A and B are the isomers.

\*\* Data taken from reference 69, \( \text{ClCH}_2\text{CH}_2\text{Cl} \) solvent.
SUGGESTIONS FOR FUTURE INVESTIGATIONS

The reaction of fac-(L-L)_b(L-L)_mMo(CO)_3 with strong π acceptor ligands warrants further study. By varying the acceptor property of the added ligand, it should be possible to spectroscopically identify a complex between it and the tricarbonyl species. The ultimate fate of the added ligand should also be determined since the reaction has possible catalytic utility.

An attempt to determine the mechanism of trans to cis isomerization in the chromium and molybdenum dicarbonyl complexes could be made by performing the isomerization in the presence of carbon monoxide.

Further studies of the reaction of (L-L)Mo(CO)_3Br_2 with ditertiary phosphine ligands to produce complexes of the type (L-L)(ditertiary phosphine)Mo(CO)_2Br_2 could lead to further information concerning the nonrigidity of the dicarbonyl complexes, e.g. by examining the ^31P nmr spectrum of the product. It would also be interesting to obtain a crystal structure of at least one of the seven-coordinate monocarbonyl complexes. A high temperature ^31P nmr spectrum of the (L-L)[P(OCH_2CH_3)_3]_2 Mo(CO)Br_2 complex could be performed in an attempt to provide more information on the rearrangement mechanism of these seven-coordinate complexes.


64. V. Auger, Compt. Rend., 142, 1151 (1906).
72. E.W. Abel, Private communication to W.R. Cullen.
100. L.F. Dahl and J.J. Huntsman. Submitted for publication and quoted in ref. 99.


136. Experimental results of this work.


147. F.W.B. Einstein and J.S. Field. Submitted for publication.