Neil J. Coville Ph.D. Chemistry

Organomanganese chemistry.

SYNTHESES AND STRUCTURAL STUDIES OF SOME ORGANOMANGANESE(I) COMPLEXES WITH GROUP VA LIGANDS

Neil John Coville

A Thesis Submitted to the Faculty of
Graduate Studies and Research at
McGill University in Partial Fulfillment
of the Requirements for the
Degree of Doctor of Philosophy

From the Inorganic Chemistry Laboratory
under the Supervision of
Dr. I.S. Butler

McGill University,
Montreal, Quebec.

March, 1973

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ABSTRACT

The reactions of $Mn(CO)_5X$ (X = Halogen) with Diphos, Triphos and Tetraphos were studied. Products such as *cis*-$Mn(CO)_2$(Tetraphos)X, *fac*-$Mn(CO)_3$(L)(Diphos)X (L = group VA ligand) and $X(CO)_3Mn$(Triphos)M' (M' = metal centre) have been isolated and characterized.

The single crystal and molecular structures of the two diastereomers α- and β-$Br(CO)_3Mn$(Triphos)$Cr(CO)_5$ were determined by three-dimensional X-ray crystallography. The difference between two structures was found to reside in the orientation of the groups around the central phosphorus atom of the Triphos ligand. This atom has become optically active on being bonded to the manganese atom.

Two new series of complexes $C_5H_5Mn(CO)(CS)(L)$ and $C_5H_5Mn(CS)(L)_2$ (L = group VA ligand) have been characterized by IR, NMR and mass spectrometry. The chemical and physical evidence suggests that the CS ligand is a better π acceptor and/or a better σ donor than the CO ligand.

SYNTHESES ET ETUDES STRUCTURALES
DE QUELQUES COMPLEXES D'ORGANOMANGANESE(I)
AVEC DES LIGANDES DU GROUPE VA

Ph.D. Département de Chimie

Neil John Coville

RESUME

On a étudié les réactions des $Mn(CO)_5X$ (X = halogène) avec le Diphos, le Triphos et le Tétraphos. On a isolé et caractérisé des produits tels que les *cis*-$Mn(CO)_2$(Tétraphos)X, *fac*-$Mn(CO)_3$(L)(Diphos)X (L = ligande du groupe VA) et $X(CO)_3Mn$(Triphos)M' (M' = centre métallique).

Par cristallographie tridimensionnelle aux rayons X on a déterminé les structures monocristalline et moléculaire des deux diastéréoisomères α- et β-$Br(CO)_3Mn$(Triphos)$Cr(CO)_5$. On a trouvé que la différence entre les deux structures réside dans l'orientation des groupements autour de l'atome central de phosphore de la ligande Triphos. Par sa liaison avec l'atome de manganèse cet atome est devenu optiquement actif.

Par spectrométries de masse, IR et RMN on a caractérisé deux nouvelles séries de complexes $C_5H_5Mn(CO)(CS)(L)$ et $C_5H_5Mn(CS)(L)_2$ (L = ligande du groupe VA). Les preuves chimiques et physiques mènent à la conclusion que la ligande CS est un meilleur accepteur d'électrons π et/ou un meilleur donneur d'électrons σ que la ligande CO.

To the Covilles:

Present, Past and Future.

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ACKNOWLEDGEMENTS

The author wishes to express his many thanks to Dr. I.S. Butler for his supervision. His encouragement throughout the years greatly influenced the course of this work.

The initial co-supervision by Dr. M. Onyszchuk is appreciated.

Thanks are extended to Drs. P.H. Bird and M.L. Schneider for introducing the author to the world of crystallography. The use of the crystallographic facilities, provided by Dr. G. Donnay (McGill University) and Dr. P.H. Bird (Sir George Williams University) is acknowledged.

Mr. B. Budd is thanked for the mass spectra.

Appreciation is expressed to Miss D. Pearse for the many hours spent in typing this manuscript.

The author wishes to acknowledge the outside influences; Edie Shtull, Paris Georghiou and Room 335, who also made this work possible.

The author is grateful to the National Research Council and McGill University for scholarships.

LIST OF ABBREVIATIONS

Bu : Butyl
Et : Ethyl
Me : Methyl
Ph : Phenyl
C_5H_5 : Cyclopentadienyl
nor-C_7H_8 : Norbornadiene
THF : Tetrahydrofuran

P : Phosphorus
P-P : Biligate ligand
P-P-P : Triligate ligand
X : Halogen

Diphos* : 1,2-bis(diphenylphosphino)ethane
DP* : *o*-phenylenebis(diphenylphosphine)
DPM* : bis(diphenylphosphino)methane
EP : bis(*o*-diethylphosphinophenyl)phenylphosphine
Hexaphos* : 1,2-bis[bis(2-diphenylphosphinoethyl)phosphino]ethane)
MA* : *o*-phenylenebis(dimethylarsine)
Tetraphos* : hexaphenyl-1,4,7,10-tetraphosphadecane
Tetraphos-Sp* : tetra(diphenylphosphinomethyl)methane
Tetraphos-U* : tris(2-diphenylphosphinoethyl)phosphine
Triphos* : bis(2-diphenylphosphinoethyl)phenylphosphine
Triphos-U* : 1,1,1-tris(diphenylphosphinomethyl)ethane
TP* : bis-(*o*-diphenylphosphinophenyl)phenylphosphine
QP* : tris(*o*-diphenylphosphinophenyl)phosphine

* Schematic representation of this ligand is given on p. 11.

SOURCE OF CHEMICALS

Compound	Source
$Cr(CO)_6$	Strem Chemicals Ltd.
$Mo(CO)_6$	Strem Chemicals Ltd.
$C_5H_5Mn(CO)_3$	Ethyl Corporation
$Ph_3P=O$	Aldrich Chemicals Co. Ltd.
$Ph_3P=S$	Aldrich Chemicals Co. Ltd.
PMe_2Ph	Strem Chemicals Inc.
$P(C_6H_{11})_3$	Strem Chemicals Inc.
Tetraphos	Strem Chemicals Inc.
Triphos	Strem Chemicals Inc.
$Mn_2(CO)_{10}$	Alfa Inorganics
PPh_3	Alfa Inorganics
$AsPh_3$	Aldrich Chemicals Co. Inc.
$SbPh_3$	Aldrich Chemicals Co. Inc.
$P(OPh)_3$	Aldrich Chemicals Co. Inc.
$P(OMe)_3$	Aldrich Chemicals Co. Inc.
$P(OEt)_3$	Aldrich Chemicals Co. Inc.
$P(OCH_2CH=CH_2)_3$	Aldrich Chemicals Co. Inc.
Diphos	Aldrich Chemicals Co. Inc.
$P(OCH_2CH_2Cl)_3$	Aldrich Chemicals Co. Inc.
PCl_2Ph	Aldrich Chemicals Co. Inc.
Carbon disulfide	Fisher Scientific Co.

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FIGURE

Manganese - An Introduction

In 1774, C.W. Scheele recognised that manganese was a unique metal rather than an ore of one of the other known metals. Ores of manganese had been known since antiquity, and the property of pyrolusite (MnO_2) to remove the green colour from glass in the glass-making industry had long been utilized. Interestingly, Pliny, the Latin Scholar, thought that *pyrolusite* was a magnetic oxide of iron and he attributed the fact that it did not attract iron to its sex[1]. Because *pyrolusite* was not attractive it had to be female!

The derivation of the word, "manganese", is uncertain. However, by the Middle Ages the term "magnesia" was applied to the ore *pyrolusite*, and by the middle of the nineteenth century the mineral was designated as "mangan". The word "manganese" came into general use during the same century.

Manganese is found in large quantities in the earth's crust - in fact it is the twelth most abundant element by weight[2]. It occurs predominantly in crystalline rocks and can be dissolved out and deposited as the oxide, hydroxide or carbonate. Among the major ores are the oxides MnO_2 (*pyrolusite*) and $Mn_2O_3.H_2O$ (*manganite*).

The prime importance of manganese is its use as a scavenger and refining agent in the steel industry. The manganese removes oxygen and sulfur which would normally combine with the iron, while excess manganese alloys to the steel. The overall effect is the preparation of a high-strength steel.

Manganese compounds in which the manganese is in a high oxidation state (Mn(IV), Mn(V) etc.) have been used down through the ages in various non-metallurgical processes, e.g., in the glass making and ceramic industries and in the Leclanche type batteries.

The chemistry and industrial applications of manganese in low oxidation states [Mn(0), Mn(1)], e.g., $Mn_2(CO)_{10}$, $K_5[Mn(CN)_6]$ have a much shorter history. Decacarbonyldimanganese(0), $Mn_2(CO)_{10}$, was first detected by mass spectrometry in 1949[3]. Five years later Brimm *et al.*[4] isolated the first manganese carbonyl complexes. Their method of preparation, which involved reduction of a manganese salt or oxide in the presence of carbon monoxide, is still used today. A variety of substituted manganese carbonyl complexes have since been prepared. Since one of these complexes $MeC_5H_4Mn(CO)_3$ has proven to be important as an anti-knock agent in fuels[5], much interest has been generated in this class of compounds.

The work described in this thesis was undertaken to explore two aspects of the chemistry of manganese(I) complexes.

Part A describes the reaction of linear polyphosphine ligands with $Mn(CO)_5X$ (X = halogen). In contrast to metal-polyamine chemistry, the field of metal-polyphosphine chemistry is relatively unexplored but it is gaining impetus as a result of the recent facile syntheses of polyphosphines[6]. Metal-polyphosphine chemistry poses a variety of stereochemical problems and the first five chapters describes an attempt to elucidate a number of these problems by a variety of physical techniques (IR, NMR, X-ray crystallography).

In Part B, the reactions of $C_5H_5Mn(CO)_3$ and $C_5H_5Mn(CO)_2(CS)$ with group VA donors are described. That so few metal thiocarbonyls complexes are known is surprising considering that theoretical calculations[7] predict that they should be more stable than the corresponding metal carbonyl complexes - of which thousands are known. This study was undertaken to determine the cause of this anomalous situation.

PART A

REACTIONS OF $Mn(CO)_5X$ WITH LINEAR POLYPHOSPHINE LIGANDS

CHAPTER I. INTRODUCTION

Since the mid-50's, numerous manganese polyphosphine complexes have been prepared and the chemistry of these complexes is reviewed in Chapter II.

Chapters III - V describe the syntheses and characterization (IR, NMR, UV) of a number of new manganese complexes. Thus, the preparation of a new class of halodicarbonyl complexes, *cis*-$Mn(CO)_2(L)(P\text{-}P)X$ (L = group VA donor) and *cis*-$Mn(CO)_2(P\text{-}P\text{-}P)X$ is given in Chapter III. This is an extension of earlier work in this laboratory in which substitution of three CO groups in $Mn(CO)_5X$ was achieved by tertiary phosphites[8].

In Chapter IV, the preparation and reactions of three *fac*-$Mn(CO)_3$(Triphos)X complexes are presented. Since Triphos is bonded through only two of its three P atoms in these complexes, the unbonded P atom can, and does, undergo typical phosphine type reactions. Single crystal structure determinations of the two hetero-bimetallic complexes $Br(CO)_3Mn$(Triphos) $Cr(CO)_5$, obtained from the reaction of *fac*-$Mn(CO)_3$(Triphos)Br and $Cr(CO)_5THF$, were carried out (Chapter VI). These determinations reveal that in both structures the Triphos is bonded to the manganese atom through two adjacent P atoms. The difference between the two isomeric structures is related to the fact that the central P atom in the bonded Triphos ligand has become optically active. The two complexes are thus diastereomers, differing only in the orientation of the groups bonded to the central P atom.

Chapter V describes the reaction of a linear tetraphosphine ligand with $Mn(CO)_5X$ to give products of the type *fac*-$Mn(CO)_3$(Tetraphos)X and *cis*-$Mn(CO)_2$(Tetraphos)X. The results suggest that the *meso* and *racemic* forms of the optically active ligand can be resolved by these reactions.

CHAPTER II. REACTIONS OF POLYPHOSPHINES WITH MANGANESE CARBONYLS - LITERATURE SURVEY

Of great importance in coordination chemistry is the ability of polydentate ligands to form complexes with metal atoms. By the correct choice of the ligand,complexes with metal atoms in low-spin states can be stabilized. It is found that ligands containing phosphorus as the donor atom cause spin-pairing more readily than the analogous ligands containing nitrogen as the donor atom . Also of importance is the ability of polydentate ligands to stabilize complexes with unusual coordination numbers. The steric requirements of the ligand play an important role in the geometry of the complexes formed[9]. A third feature of polyphosphine ligands is their ability to stabilize metal atoms in low oxidation states. It is to this aspect that most of the following review is directed.

A literature survey of the reaction of metal carbonyls with diphosphines was recently published and included a brief review of manganese carbonyl-diphosphine reactions[10]. However, it is since this review was published that the most exciting advances in the field have been reported. This survey attempts to bring the earlier work up to date, and also to include a complete coverage (up to December, 1972) of the reactions of all other polyphosphine ligands with dimanganese decacarbonyl and its derivatives. No reactions involving direct phosphorus-

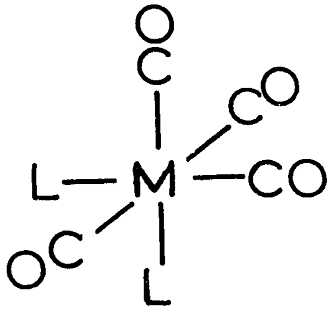
phosphorus bonded polyphosphines are included in this or any subsequent chapters.

Prior to the review, it is necessary to describe the nomenclature that is to be used throughout this thesis.

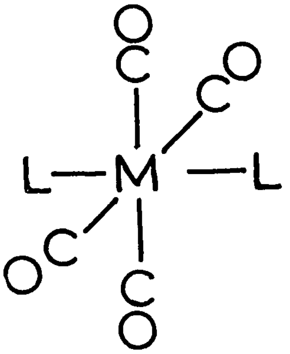
A. NOMENCLATURE

As more and more polyphosphine ligands are prepared, more and more confusion arises over the naming of the resulting complexes formed with these ligands. The recent proposals of King[11] to give a general idea of the coordinating ability of a ligand will be used throughout this work. These can be summarized as follows: 1. monodentate, bidentate, etc., indicate the number of phosphorus atoms that bond to a *single* metal atom in a complex, e.g., Diphos in *fac*-$Mn(CO)_4(Diphos)Br$ is a monodentate ligand. 2 monoligate, biligate, etc., refer to the *total* number of phosphorus atoms that bond to metal atoms in a complex; e.g., in $Br(CO)_4Mn(Diphos)Mn(CO)_4I$, the Diphos is acting as a biligate ligand. 3. monometallic, bimetallic, etc. describe the total number of metal atoms to which the ligand is bonded in a complex; e.g., in $[BrMn(CO)_4]_2(Diphos)$, the term bimetallic would be used. (In this example the ligand is called bimetallic biligate).

The terms *mer* and *fac* will be used to describe the stereochemistry in octahederal complexes, as shown overleaf (Figure II-1).



CIS



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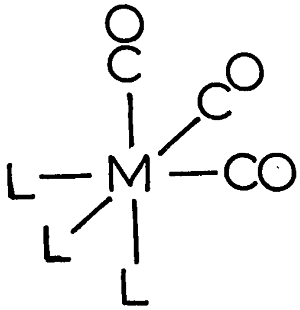
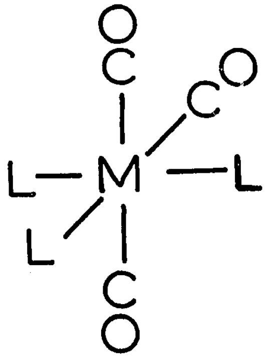
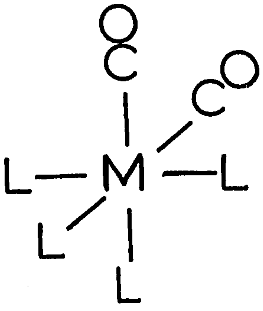


FAC



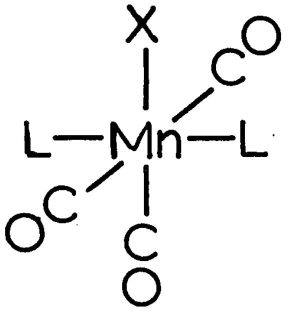
MER



CIS

FIGURE II-1 NOMENCLATURE USED TO DESCRIBE THE GEOMETRY IN OCTAHEDERAL METAL COMPLEXES.

Throughout this thesis complexes of the type *mer*-(*trans*-L_2)Mn(CO)$_3$X will be referred to as *trans*-Mn(CO)$_3L_2$X complexes.



TRANS

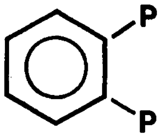
B. PREPARATION OF THE POLYPHOSPHINES

A comprehensive listing of all diphosphines prepared until early 1971 has been reported[10]. This section includes some general details from this review together with a coverage of the more important developments in the preparation of polyphosphines which have occurred in the last two years. The structures of the ligands to be discussed are shown in Figure II-2.

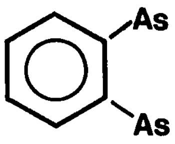
The first polyphosphine was prepared in 1956 by Wymore and Bailar[10], and the first detailed study of the preparation of a variety of diphosphines was reported in 1958[12].

A convenient synthesis of Diphos was developed in 1960 by Chatt and Hart[13] and involved reaction of Ph_2PLi (formed by reaction of PPh_3 and Li in THF) with $ClCH_2CH_2Cl$. This general method has been extended to a number of other PR_2Li (R = alkyl, aryl) intermediates and various halogenated ethylene or ethane compounds[14]. The same method has also been used to prepare triphosphines[13] and a tetraphosphine[15].

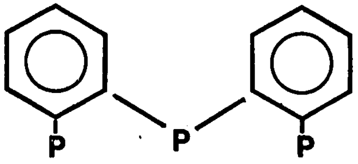
DP :



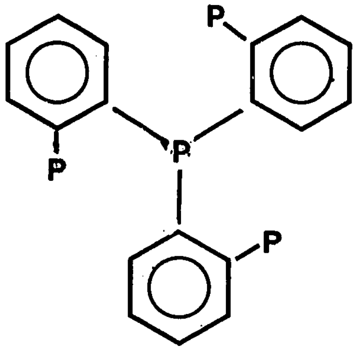
MA :



TP :



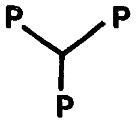
QP :



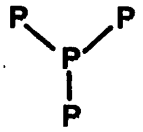
TRIPHOS : P—P—P

TETRAPHOS : P—P—P—P

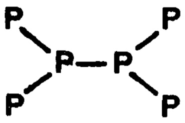
TRIPHOS-U :



TETRAPHOS-U :



HEXAPHOS :



TETRAPHOS-Sp :

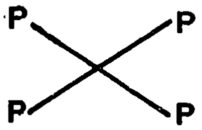


FIGURE II-2 SCHEMATIC REPRESENTATION OF THE MORE IMPORTANT LIGANDS ENCOUNTERED IN THIS THESIS. Full formulae are given

Triphos, the ligand used extensively in this work, was first prepared in low yield by Hewertson and Watson in 1962[16]. Their method involved addition of PPh_2Na to the product obtained by the reaction of $PhP(C_2H_4OEt)_2$ with HBr. Cloyd and Meek[17] were able to synthesize Triphos in much higher yield (∿85%), as shown below.

$$Ph_2PK + (\text{excess})\ ClCH_2CH_2Cl \longrightarrow Ph_2PCH_2CH_2Cl + KCl$$

$$Ph_2PCH_2CH_2Cl + PhPHNa \xrightarrow{\text{liq } NH_3/THF} Ph_2PCH_2CH_2P(H)Ph + NaCl$$

$$Ph_2PCH_2CH_2P(H)Ph \xrightarrow[\text{(b) } Ph_2PCH_2CH_2Cl/THF]{\text{(a) BuLi/hexane}} PhP(CH_2CH_2PPh_2)_2$$

Recently the discovery of the base-catalysed addition of P-H bonds to C-C multiple bonds by King and Kapoor[6] has revolutionized the preparation of polyphosphines. A large number of tertiary polyphosphines have been prepared in high yield by this simple procedure. For example, when $Ph_2PCH{=}CH_2$ and $PPhH_2$ (together with t-BuOK as catalyst) are refluxed in benzene for 24 h , Triphos is obtained in 87% yield. In an extension of this work, King and Cloyd[18] have also prepared primary and secondary polyphosphines. Thus, addition of PPh_2H to $CH_2{=}CHP(O)HPh$ followed by reduction with $LiAlH_4$ gives $Ph_2PCH_2CH_2P(H)Ph$. In a similar manner $H_2PCH_2CH_2P(H)Ph$ and $PhP(CH_2CH_2PH_2)_2$ can also be prepared. It should be noted that these are unsymmetrical polyphosphines, i.e., the various P atoms have different substituents attached to them.

Unsymmetrical polyphosphines, of the type $Ph_2PCH_2CH_2P(Ph)R$ (R = Me, Et, etc.), have also been prepared by addition of PhPRLi to $Ph_2PCH{=}CH_2$ in THF at 0°C[19].

Another variation on this theme has involved the preparation of the ligands $Ph_2PCH_2CH_2OPR_2$ (R = n-Bu, Ph) from Ph_2Li and ethylene oxide[20].

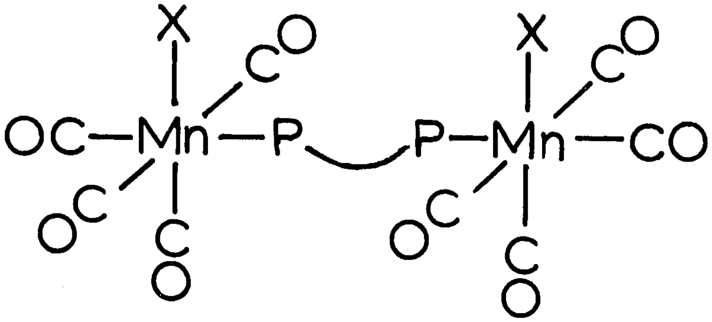
C. LITERATURE SURVEY

a) $Mn_2(CO)_{10}$

The product of the first reaction of $Mn_2(CO)_{10}$ with Diphos was formulated as $Mn_2(CO)_8$(Diphos) but no structural data were given[21]. A more thorough study of this reaction was carried out by Sacco[22]. A variety of products of the type $Mn(CO)_3$(Diphos), Mn(CO)$(Diphos)_2$(both paramagnetic) and $[Mn(CO)_2(Diphos)_2]X$ [X = Cl, Br, BPh_4, $Mn(CO)_5$] was obtained.

Recently, yet another study, repeating much of the work of Sacco has been reported[23]. Thus, reaction of $Mn_2(CO)_{10}$ and Diphos again gave the products $Mn(CO)_3$(Diphos) and Mn(CO)$(Diphos)_2$. However, in the light of the recent work on the reaction of $Mn_2(CO)_{10}$ with PPh_3[24], the formulation of these products must be questioned. Although magnetic studies were carried out by Sacco and paramagnetism was detected, this does not exclude the possibility that the complexes are hydrides such as $HMn(CO)_3$(Diphos)[25] together with a paramagnetic impurity.

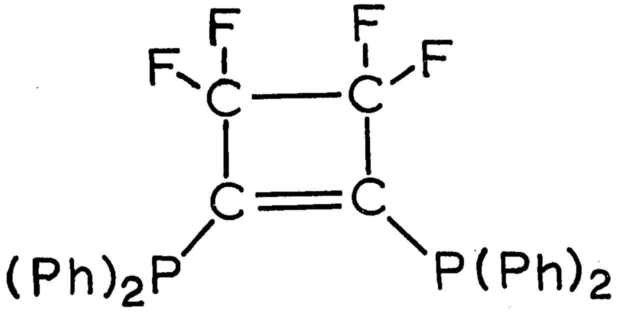
Reaction of $Mn_2(CO)_{10}$ with a stochiometric amount of DPM , $(Ph_2PCH_2PPh_2)$, gives $Mn_2(CO)_8(DPM)$ while reaction with excess diphosphine gives $[Mn(CO)_3(DPM)]_2$[23]. Treatment of $Mn_2(CO)_8(DPM)$ with bromine causes Mn-Mn bond cleavage and affords the phosphine bridged complex $[BrMn(CO)_4]_2(DPM)$. The structure of this complex (X = Br) is shown below (the phenyl and methylene groups have been left out for the sake of clarity).



Metal-metal bond cleavage occurs in the reaction of $Mn_2(CO)_{10}$ with the spirocyclic polyphosphine $(Ph_2PCH_2)_4C$, Tetraphos-Sp, to produce an ionic complex $[Mn(CO)_3(Tetraphos\text{-}Sp)][Mn(CO)_5]$[26].

Recently, Cullen *et al.*[27] have prepared $Mn_2(CO)_8[Ph_2P\overline{C{=}C(PPh_2)CF_2C}F_2]$ in which the diphosphine does not bridge the two metal atoms. This conclusion was drawn from the ^{19}F NMR spectrum - a doublet was observed, whereas a single resonance would be anticipated for a bimetallic ligand.

The ligand used in this study is shown below. It consists of two phosphorus atoms bonded to a four-membered ring system.



b) Mn(CO)$_5$X

fac-Mn(CO)$_3$(Diphos)Br has been prepared in a variety[22] of ways. If the reaction of Mn(CO)$_5$X (X = Br,I) and Diphos is carried out at 150°C in the absence of solvent *fac*-Mn(CO)$_3$(Diphos)Br is obtained[28]; but for X = Cl, the ionic complex [Mn(CO)$_2$(Diphos)$_2$]X is isolated. The reaction of Mn(CO)$_5$X (X = Br, I) with Diphos in MeOH gives the corresponding ionic complexes [Mn(CO)$_2$(Diphos)$_2$]X[29]. On the basis of IR data, the CO groups are thought to be *trans* to each other.

The cationic complex [Mn(CO)$_2$(Diphos)$_2$]$^+$ can be oxidized readily to the green [Mn(CO)$_2$(Diphos)$_2$]$^{2+}$ species[30].

Irradiation of Mn(CO)$_5$Br with $Ph_2P(CH_2)_nPPh_2$ (n = 1,2) yielded the expected disubstituted products[23]. Further irradiation with another mole of diphosphine readily gave the tetrasubstituted complexes $Mn(CO)[Ph_2P(CH_2)_nPPh_2]_2Br$ (n = 1,2). The disubstituted species can be oxidized by $NOPF_6$ to give *fac*-$[Mn(CO)_3(Ph_2P(CH_2)_nPPh_2)Br]PF_6$ (n = 1,2)[31].

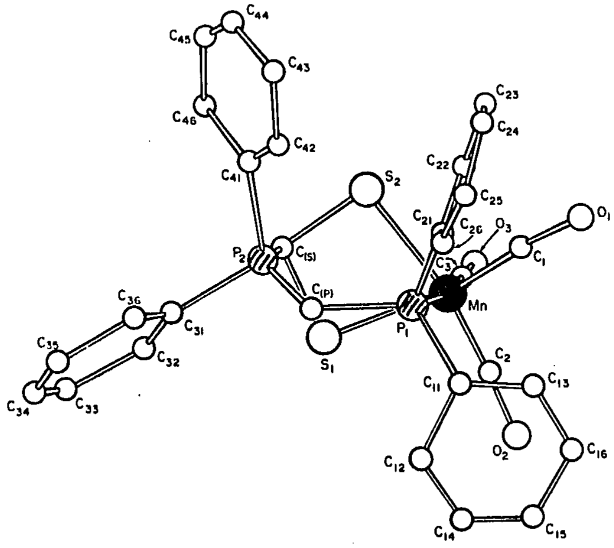
The only other diphosphine that has been reacted with $Mn(CO)_5X$ is DP, which gives *fac*-$Mn(CO)_3(DP)Cl$[32].

Prior to the recent work reported by King *et al.*[33,34,35], the only report of the reaction of polyphosphines larger than diphosphines, with $Mn(CO)_5X$, was that by Chiswell and Venanzi[32]. Use of TP and QP gave products of the type $Mn(CO)(CN)(QP)$, $Mn(CO)_3(TP)Cl$, $[Mn(CO)_3(QP)]X$ (X = Cl, Br) and $[Mn(CO)_2(QP)]X$ (X = Cl, Br, ClO_4).

King has shown that the reaction of $Mn(CO)_5Br$ with polyphosphines can readily give products of the type *cis*-$Mn(CO)_2(P\text{-}P\text{-}P)Br$[33,34], i.e. replacement of three CO groups. One CO group is thought to be *trans* to the Br atom.

c) $RMn(CO)_5$ (R = H, alkyl, aryl)

The identity of the product from the reaction of $HMn(CO)_5$ and Diphos has been confirmed by IR and NMR (1:2:1 triplet at $\tau = 17.8$ for the H atom) to be *fac*-$HMn(CO)_3(Diphos)$[25]. Einstein *et al.*[36] have reacted the complexes *fac*-$HMn(CO)_3(Ph_2P(CH_2)_nPPh_2)$ (n = 1,2) with CS_2 and found that for n = 2 the CS_2 insertion product *fac*-$HC(S)SMn(CO)_3(Diphos)$ is obtained. However, in the case of n = 1, a secondary reaction takes place, the product of which was shown by X-ray crystallography to be *fac*-HC(S)SMn(CO)$_3$(Ph$_2$PCH$_2$PPh$_2$). Both S atoms are attached to the manganese, as shown below.



The most recent study[37] on the reaction of PPh$_2$(CH$_2$)$_n$PPh$_2$ (n = 1,2) with MeMn(CO)$_5$ gave the disubstituted product *fac*-MeMn(CO)$_3$(Ph$_2$P(CH$_2$)$_n$PPh$_2$), as well as the products caused by methyl migration *viz.*, *fac*-MeCOMn(CO)$_3$(Diphos). This study made use of both IR and NMR and has clarified some earlier confusing results on related complexes[38,39], in which the ligands were thought to be arranged around the Mn atom in the *mer* configuration (*vide infra*, p. 21).

The bridging complex *cis*-[MeCOMn(CO)$_4$]$_2$(Diphos) has also been prepared[38], and evidence has been presented for the unstable monometallic complex, *cis*-MeMn(CO)$_4$(Diphos)[39].

The phenyl complex gives only *fac*-PhMn(CO)$_3$(Diphos) and no product obtained by aryl migration[38].

King has carried out some pioneering experiments with polyphosphines to give MeMn(CO)$_2$(P-P-P), MeCOMn(CO)$_2$(P-P-P) and [MeMn(CO)$_2$]$_2$(Hexaphos) [33,34,35].

d) $RC_5H_4Mn(CO)_3$ (R = H, Me)

Reactions of polyphosphine ligands with $RC_5H_4Mn(CO)_3$ (R = H,Me) leads to two types of products: $[RC_5H_4Mn(CO)_2]_2$(P-P) and $RC_5H_4Mn(CO)$(P-P)[40-46]. The product formed is dependent on the type of ligand and/or the reactant ratios of the starting materials. Thus, reactions of $C_5H_5Mn(CO)_3$ with linear polyphosphines $Ph_2P(CH_2)_nPPh_2$ (n = 1-4) leads to the complexes $C_5H_5Mn(CO)(Ph_2P(CH_2)_nPPh_2)$ (n = 1-4) and $[C_5H_5Mn(CO)_2]_2$ $(Ph_2P(CH_2)_nPPh_2)$ (n = 1,2).

Similar reactions with triphosphines lead exclusively to the products $C_5H_5Mn(CO)$(P-P)[34,35]. Although the product from the reaction of $C_5H_5Mn(CO)_3$ and a hexaphosphine has been formulated as $(C_5H_5)_2Mn_2(CO)_3$(P-P-P), it was mentioned that the analysis was more in line with a trimetallic complex[35].

In all cases reported, the reactions of polyphosphines with $C_5H_5Mn(CO)_3$ are in accord with the known chemistry of $C_5H_5Mn(CO)_3$, i.e. CO replacement necessitates UV irradiation. A preliminary report on the reaction of $C_5H_5Mn(CO)(CS)(C_8H_{14})$ with Diphos in n-hexane at 60° mentions that both $[C_5H_5Mn(CO)(CS)]_2$Diphos and $C_5H_5Mn(CS)$Diphos can be prepared[47]. Presumably the latter product is formed by thermal replacement of a CO group.

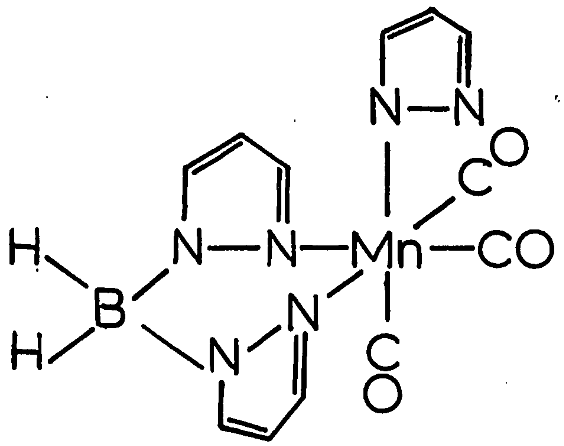
e) Reactions of $[C_5H_5Mn(CO)_2NO]PF_6$

The reactions are similar to those in (d) above in that both bridging and chelate complexes have been prepared[48,49]. However, reactions are carried out thermally.

f) Miscellaneous reactions

i) $Ph_3MMn(CO)_5$ + polyphosphines: The products from the reactions of $Ph_3MMn(CO)_5$ (M = Si, Ge,[50] Sn[51]) with Diphos have been formulated as *mer*-$Ph_3MMn(CO)_3$Diphos. As will be discussed shortly this geometry must be questioned as it was based only on IR evidence. (*vide infra*, p. 29)

ii) The reaction of $Mn(CO)_5Br$ and dihydrobis(pyrazolyato)borate gave the tricarbonyl product shown below[52]. This product reacted readily with group VA donors to give *cis* or *trans*



dicarbonyl products.

iii) R = CF_3COO: When benzene/*n*-hexane solutions of the compound $CF_3COOMn(CO)_5$ and the appropriate ligand are irradiated, the complexes $RMn(CO)(P-P)_2$, *fac*-$RMn(CO)_3(DPM)$ and *fac*-$RMn(CO)_2$(*cis*-$Ph_2PCH=CHPPh_2$) are formed[53].

iv) R = NCS: Diphos reacts with $NCSMn(CO)_5$ to give *fac*-SCNMn $(CO)_3$(Diphos) for which IR evidence suggests that the SCN group is N-bonded[54].

In conclusion, the following two comments can be made. In all cases studied,the diphosphines reacted with manganese carbonyl have been "symmetrical".

Until recently, little work had been reported on polyphosphines, other than diphosphines. Indeed, when the work described in this thesis was initiated, no work had been reported on the reactions of Triphos and Tetraphos with manganese carbonyls.

D. IR SPECTRA OF MANGANESE CARBONYL - POLYPHOSPHINE COMPLEXES [ν(CO)]

In general, IR spectroscopy is the principal technique used by most workers in attempting to determine the bonding characteristics of polyphosphine systems. The IR results reported so far on manganese carbonyl - polyphosphine complexes are presented in Tables II-1a and II-1b. From the results in these Tables, certain conclusions can be drawn and these are indicated below (Table II-2) and in Figure II-3.

However, it must be emphasized that these are only general conclusions, and extreme care must be taken in using only IR data to assign structures. For instance, the solution IR spectra of $MeCOMn(CO)_3(Diphos)$ exhibits two strong peaks in the ν(CO) region[39]. A *mer* configuration was thus suggested. However, later work on band intensity determinations, together with results from an NMR study, indicated that the complex was *fac*-$MeCOMn(CO)_3(Diphos)$[37]. The lower frequency band (CO stretching region) really consisted of two closely overlapping bands.

TABLE II-1a IR SPECTRA OF METAL CARBONYL POLYPHOSPHINE COMPLEXES - ν(CO) REGION

Complex	ν(CO) (cm^{-1})^{a}	Solvent^{b}	Ref.
	Neutral Complexes		
[RMn(CO)$_4$]polyphosphine			
cis-[MeCOMn(CO)$_4$]$_2$(Diphos)	2075(m), 2000(s) 1969(s)	c	38
	2075 2000 1965	cm	39
cis-[BrMn(CO$_4$]$_2$(DPM)	2094(s), 2021(sh), 2012(vs), 1970(s)	cm	23
RMn(CO)$_3$polyphosphine			
fac-HMn(CO)$_3$(Diphos)	1985(s), 1914(sh), 1905(s), 1896(s)	n	25
fac-MeMn(CO)$_3$(Diphos)	1994(s), 1917(m), 1890(m)	cm	37
fac-PhMn(CO)$_3$(Diphos)	1996(s), 1919(s)	cc	38
fac-MeMn(CO)$_3$(DPM)	1997(s), 1918(m), 1893(m)	cm	37
fac-MeMn(CO)$_3$(Triphos)	1999(s), 1921(s), 1865(m)	cy	33
fac-MeMn(CO)$_3$(Tetraphos)	1991(s), 1904(vs), 1860(m,sh)	cm	34
fac-MeCOMn(CO)$_3$(DPM)	1999(s), 1919(br)	cm	37
fac-MeCOMn(CO)$_3$(Diphos)	1999(s), 1916(br)	cm	37
	1996(s), 1914(s)	cm	39
fac-MeCOMn(CO)$_3$(Tetraphos-U)	1995(s), 1911(vs,br)	cm	34
fac-MeCOMn(CO)$_3$(Hexaphos)	1995(s), 1911(vs)	cm	35
fac-CF$_3$COOMn(CO)$_3$(*cis*-DP)^{c}	2026(s), 1968(s), 1925(s)	cm	53
fac-CF$_3$COOMn(CO)$_3$(DPM)	2028(s), 1973(s), 1929(s)	cm	53
fac-SCNMn(CO)$_3$(Diphos)	2033(s), 1965(s), 1930(s)	c	54
fac-HC(S)SMn(CO)$_3$(Diphos)	2017 1962 1928	cs	36
fac-HC(S)SMn(CO)$_3$(DPM)^{d}	2014 1937 1898	cs	36
fac-ClMn(CO)$_3$(DP)·EtOH	2042 1966 1912	n	32
fac-ClMn(CO)$_3$(QP)	2030 1960 1910	n	32
fac-BrMn(CO)$_3$(Diphos)	2020(s), 1958(s), 1918(m)	c	22
	2023(s), 1956(s), 1917(m)	b	23
	2020(s), 1959(s), 1918(m)	c	28
fac-BrMn(CO)$_3$(DPM)	2025(s), 1955(m), 1920(s)	b	23
fac-BrMn(CO)$_3$(QP)	2035 1965 1910	n	32
fac-IMn(CO)$_3$(Diphos)	2020(s), 1958(s), 1920(m)	c	28

TABLE II-1a (continued)

Complex	ν(CO) (cm^{-1})^a	Solvent ^{b}	Ref.
$[Mn(CO)_3(Diphos)]_2$	1992(w), 1899(s), 1859(m)	cm	23
$[Mn(CO)_3(DPM)]_2$	1994(w), 1918(s), 1870(m)	cm	23
$Mn_2(CO)_8(DPM)$	2057(s), 1999(vs), 1977(vs), 1966(sh), 1954(sh), 1924(s)	b	23
$Mn_2(CO)_8[Ph_2P\overline{C=C(PPh_2)CF_2C}F_2]$	2074(m), 2034(s), 2000(s) 1982(vs), 1976(s), 1960(s), 1934(s)	cy	27
Charged Complexes			
$[Mn(CO)_3(TP)]Cl\cdot 2EtOH$	2025 1955 1900	n	32
$[Mn(CO)_3(QP)]Cl\cdot 3EtOH$	2030 1960 1905	n	32
$[Mn(CO)_3(QP)]\ I\cdot 3EtOH$	2040 1975 1925	n	32
$[Mn(CO)_3(Tetraphos\text{-}Sp)]L^e$	2035(s), 1966(s), 1862(s), 1904(s),	cm	26
$[Mn(CO)_3(Tetraphos\text{-}Sp)]BPh_4$	2034(s), 1968(s)	cm	26
trans-$[Mn(CO)_2(Diphos)_2]Cl\cdot 2CHCl_3$	1897	c	29
trans-$[Mn(CO)_2(Diphos)_2]Cl$	1900	c	22
trans-$[Mn(CO)_2(Diphos)_2]Br\cdot 2CHCl_3$	1898	c	29
trans-$[Mn(CO)_2(Diphos)_2]I\cdot EtOH$	1900	c	22
trans-$[Mn(CO)_2(Diphos)_2]BPh_4$	1895	n	22
trans-$[Mn(CO)_2(Diphos)_2]ClO_4$	1897	c	29
trans-$[Mn(CO)_2(Diphos)_2]Mn(CO)_5$	1898, 1892, 1883, 1863, 1854	n	22
$[Mn(CO)_2QP)]Cl$	1985 1865	n	32
$[Mn(CO)_2QP)]I\cdot EtOH$	2000 1880	n	32
$[Mn(CO)_3(Diphos)Br]PF_6$	2106(m) 2068(m) 2030(s)	n	31
$[Mn(CO)_3(DPM)Br]PF_6$	2124(m) 2085(m) 2032(s)	n	31
$[Mn(CO)_2(Diphos)_2](ClO_4)_2$	1975	?	30

TABLE II-1a (continued)

Complex	ν(CO) $(cm^{-1})^a$		Solvent^b	Ref.
$Ph_3SiMn(CO)_3$(Diphos)	1990(m)	1910(vs)	?	50
$Ph_3GeMn(CO)_3$(Diphos)	1993(m)	1915(vs)	?	50
$Ph_3SnMn(CO)_3$(Diphos)				51
$RMn(CO)_2$polyphosphine				
$MeMn(CO)_2$(Tetraphos-U)	1906(s)	1836(s)	cm	34
$MeMn(CO)_2$(Hexaphos)	1915(s)	1841(s)	cm	35
$[MeMn(CO)_2]_2$(Hexaphos)	1997(sh), 1822(sh),	1888(s), 1816(s)	k	35
cis-$BrMn(CO)_2$(Triphos)	1936(s)	1864(s)	cm	33
cis-$BrMn(CO)_2$(Tetraphos)	1933(s)	1862(s)	cm	34
cis-$BrMn(CO)_2$(Tetraphos-U)	1906(s)	1836(s)	cm	34
cis-H_2B-  $_2$-$Mn(CO)_2$(Diphos)	1949(s)	1874(s)	h	52
RMn(CO)polyphosphine				
$CF_3COOMn(CO)(Me_2PCH_2CH_2PMe_2)_2$	1826		cm	53
$BrMn(CO)(Diphos)_2$	1821(br)		b	23
$BrMn(CO)(DPM)_2$	1842(br)		b	23
CNMn(CO)(QP)·EtOH	1833		n	32
Miscellaneous				
$Mn(CO)_3$(Diphos)	2020(s) 1998(s)	1915(s) 1918(br,s)	c b	22 23
$Mn(CO)(Diphos)_2$	1810		c	22
red	1818		b	23
yellow	1822		b	23

TABLE II-1b IR SPECTRA OF CYCLOPENTADIENYL MANGANESE POLYPHOSPHINE COMPLEXES

L-L	ν(CO) (cm^{-1})^a	ν(NO) (cm^{-1})^f	Solvent^b	Ref.
$[C_5H_5Mn(CO)(NO)(L\text{-}L)]^+$				
$Ph_2PCH_2CH_2PPh_2$	2038 2051	1808 1802	k -	49 48
$Ph_2PC{\equiv}CPPh_2$	2041	1797	k	49
trans-$Ph_2PC{=}CPPh_2$	2040	1800	k	49
$[(C_5H_5Mn(CO)(NO)]_2(L\text{-}L)]^{++}$				
$Ph_2PCH_2CH_2PPh_2$	2033 2010	1805 1779	k	49
$Ph_2PC{\equiv}CPPh_2$	2042 2020	1814 1789	k	49
trans-$Ph_2PC{=}CPPh_2$	2043	1803	k	49
$Ph_2PCC{\equiv}CCPPh_2$	2030	1803	k	49
$[C_5H_5Mn(NO)(L\text{-}L)]^+$				
$Ph_2PCH_2CH_2PPh_2$		1753	-	48
cis-$Ph_2PC{=}CPPh_2$		1770	k	49
Tetraphos-U		1742	cm	34
$[(C_5H_5)_2(Mn)_2(CO)(NO)_2(L\text{-}L)]^{++}$				
Triphos	2046	1798 1754	cm	33
Triphos-U	2022	1790 1742	k	49
Tetraphos	2043	1798 1752	cm	34
Hexaphos	2040	1794 1741	cm	35
Miscellaneous				
$C_5H_5Mn(CS)(Diphos)$	ν(CS):	1208	cs	49
$[C_5H_5Mn(CO)(CS)]_2(Diphos)$	ν(CS): ν(CO):	1226 1920	cs cs	49 49

TABLE II-1b (continued)

R	L-L	$\nu(CO)$ $(cm^{-1})^a$		Solvent[b]	Ref.
$[RC_5H_4Mn(CO)_2](L-L)$					
H	$Ph_2PCH_2PPh_2$	1932	1971	ce	40
H	$Ph_2PCH_2CH_2PPh_2$	1929 1934	1863 1862	ce c	40 41,42
Me	$Ph_2PCH_2CH_2PPh_2$	1934	1862	c	41,42
H	$Me_2PCH_2CH_2PMe_2$	1931	1866	ce	40
$RC_5H_4Mn(CO)(L-L)$					
H	$Ph_2PCH_2PPh_2$	1837 1854		cs cs	43 40
H	$Ph_2PCH_2CH_2PPh_2$	1818 1837 1834		c cm cs	41,42 43 40
Me	$Ph_2PCH_2CH_2PPh_2$	1818		c	41,42
Et	$Ph_2PCH_2CH_2PPh_2$	?			44
H	$Ph_2P(CH_2)_3PPh_2$	1822		cm	43
H	$Ph_2P(CH_2)_4PPh_2$	1815		?	45
Me	$Ph_2P(CH_2)_4PPh_2$	1815		?	45
H	$Me_2PCH_2CH_2PMe_2$	1828		cs	40
H	$Ph_2PCH=CHPPh_2$	1840		cm	46
H	$RP(Ph)CH_2CH_2P(Ph)R$[g,h]	1960(m) 1890(m) 1818(vs)		cm	35
H	PR_3[g]	1838		cs	34
H	$R_2PCH_2CH_2PR_2$[g]	1818		cm	34

a) All bands are strong unless otherwise stated. Abbreviations used are: br = broad, m = medium, sh = shoulder, s = strong, vs = very strong.

b) Abbreviations used are: c = $CHCl_3$, cc = CCl_4, ce = $ClCH_2CH_2Cl$, cm = CH_2Cl_2, cy = cyclohexane, cs = CS_2, b = benzene, k = KBr, h = n-hexane, n = nujol.

c) *cis*-DP = *cis*-$Ph_2PCH=CHPPh_2$.

d) The diphosphine is bonded to the metal through only one P atom.

e) L = $Mn(CO)_5$

f) All bands are strong unless otherwise stated.

g) R = $Ph_2PCH_2CH_2$

h) The polyphosphine is thought to be acting as a bimetallic ligand.

TABLE II-2 GENERALIZED IR RESULTS FOR THE MANGANESE CARBONYL-POLYPHOSPHINE COMPLEXES[a]

Complex	No. of ν(CO) bands in the IR spectrum	Strength of bands in order of decreasing frequency[b]
	Neutral Complexes	
cis-$[RMn(CO)_4]_2(P{-}P)$	4	m, w, s, s
fac-$RMn(CO)_3(P{-}P)$	3 (or 2)	s, s, s (or s,vs)
cis-$RMn(CO)_2(P{-}P{-}P)$	2	s, s
$[C_5H_5Mn(CO)_2]_2(P{-}P)$	2	s, s
$C_5H_5Mn(CO)(P{-}P)$	1	s
$RMn(CO)(P{-}P)_2$	1	s
	Cationic Complexes	
$[Mn(CO)_3(P{-}P)]^+$	3	s, s, s
$[Mn(CO)_3(P{-}P{-}P)]^+$	2	s, s
$[Mn(CO)_2(P{-}P{-}P)]^+$	2	s, s
$[C_5H_5Mn(CO)_2NO]^+$	2	s, s
trans-$[Mn(CO)_2(P{-}P)_2]^+$	1	s
$[C_5H_5Mn(CO)(NO)(P{-}P)]^+$	1	s

---

a) For illustrative examples, see Figure II -3

b) M = medium, w = weak, s = strong, vs = very strong.

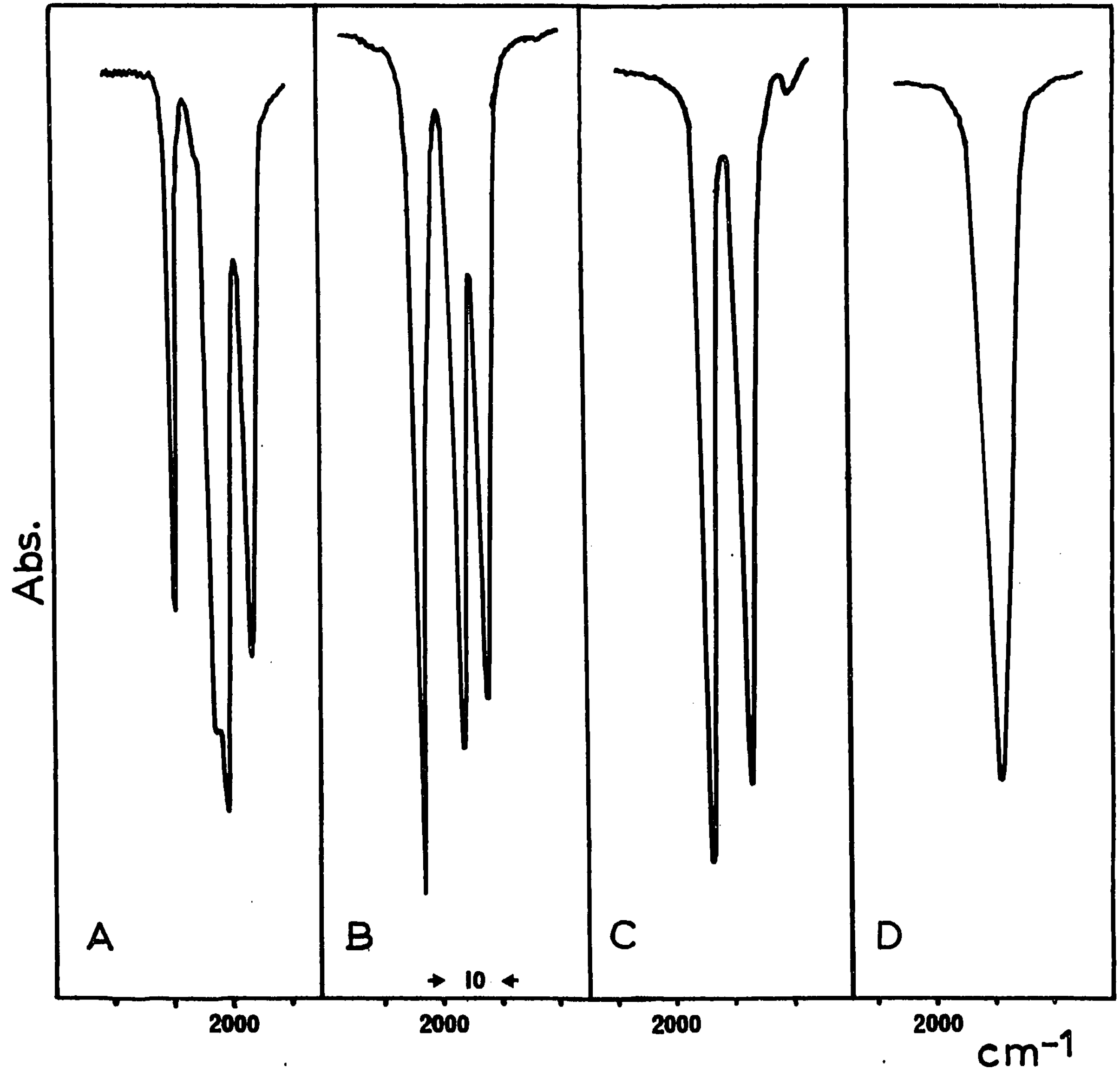


FIGURE II-3 TYPICAL IR SPECTRA [ν(CO)] OF MANGANESE(I) POLYPHOSPHINE COMPLEXES. All spectra were recorded in CH_2Cl_2 solution.

A. $[Mn(CO)_4Br]_2$Diphos

B. *fac*-$Mn(CO)_3$(Triphos)Br

C. *cis*-$Mn(CO)_2$(Triphos)Br

D. Mn(CO)[$P(OEt)_3$](Triphos)Br

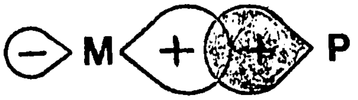
In view of the reasons given above, this author feels that the *trans* structure[50,51] proposed for complexes of the type $Ph_3MMn(CO)_3$(Diphos)(M = Si, Ge, Sn) is probably incorrect and the complexes should be formulated with *fac* configurations. The solution to this problem must await further physical studies such as single crystal X-ray diffraction.

The two complexes, $[Mn(CO)_2(Diphos)_2]^+$ [ν(CO) = 1897 cm^{-1}] and $[Mn(CO)_2(Diphos)_2]^{2+}$ [ν (CO) = 1975 cm^{-1}] readily show the effect of charge on the CO stretching frequency of metal carbonyl complexes.

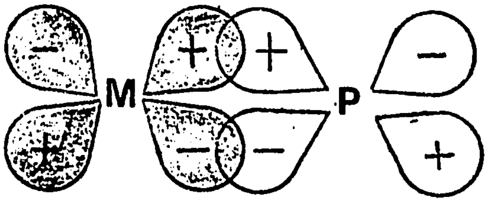
E. BONDING IN METAL POLYPHOSPHINE COMPLEXES

The CO group is believed to bond to metals by a synergic effect[55] involving σ-donation of the lone pair on the C atom to the metal, and π-acceptance of metal d electrons into empty π* orbitals on the CO group. The bonding scheme for metal phosphine (and phosphite) complexes is expected to be similar[56], and is thought to arise from σ-donation of the lone pair on the phosphorus atom (to the metal atom) as well as π-acceptance of the dπ electrons from the metal into the empty dπ orbital (s) on the phosphorus atom. This is shown schematically below.

σ bond formation:



π bond formation:



However, the case for metal-phosphorus bonding is still open to debate[57].

The recent theoretical calculations by Fenske and co-workers[58] on octahederal metal carbonyl systems interprets metal-ligand bonding in terms of Mulliken overlap populations. In this way, they have been able to separate σ and π bonding contributions for a variety of ligands, for instance, Cl, Br, H, CF_3. Unfortunately, to date, no calculations have been performed for phosphines (or phosphites).

Some special bonding properties are associated with metal polyphosphine complexes. Once one P atom of a polyphosphine is bonded to a metal, the other P atoms are held in close proximity to the metal. As a result of this, the metal atom is prone to further substitution reactions by the other P atoms of the polyphosphine, e.g., although *cis*-$Mn(CO)_4(Diphos)Br$ has been detected[39], it has never been isolated, since the reaction always proceeds further to give *fac*-$Mn(CO)_3(Diphos)Br$. On the other hand the equivalent complex, *cis*-$Mn(CO)_4(PEtPh_2)Br$, in which no ring formation can take place has been isolated.

The increase in stability of complexes containing chelate rings over a similar complex with no chelate rings is called the chelate effect and is well known in metal polyamine chemistry[56].

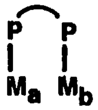
F. ISOMERISM IN THE METAL-LIGAND COMPLEXES

As much of the first part of the thesis relates to the isomerism found on coordination of polyphosphines to metal atoms, it is necessary to determine the total number of isomers possible for certain metal polyphosphine systems.

A paper recently published by King[11] contains a theoretical treatment from which it is possible to determine the number of isomers possible for a general polyphosphine ligand, when bonded to metal atoms. It is felt that this approach is somewhat restrictive. The restriction arises from one of the assumptions made - that the total number of ways in which polyphosphines "can coordinate to one or more metal atoms is $1/2P(P + 1)$ or $\sum_{i=1}^{P} i$, if the differences arising from the nonequivalence of the phosphorus atoms in the polytertiary phosphines are ignored" (P = number of phosphorus atoms in the ligand). It can readily be shown that this is a very severe restriction and, in most of the cases to be encountered in organometallic chemistry, this assumption will not be adhered to.

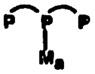
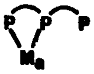
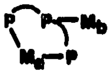
Consider the results obtained (from first principles). The total number of complexes formed on coordination of a metal atom to the two linear polyphosphines Diphos and Triphos used in this study, are listed in Tables II-3 and II-4 respectively, and are for the most general case $M_a \neq M_b \neq M_c$ (M_i = metal atom) and $\angle P\text{-}M_i\text{-}P \neq 180°$. All mirror images are included.

TABLE II-3 BONDING IN METAL DIPHOS COMPLEXES

King nomenclature	Schematic representation
A monometallic monodentate	
B monometallic bidentate	
C bimetallic biligate	

It is apparent that King's nomenclature describes all the possible bonding situations for metal Diphos complexes but only six of the fifteen possibilities (twenty-four, if all mirror images are included) for metal Triphos complexes. His analysis only allows for eight different bonding situations. The additional further bonding situations arise because:

TABLE II-4 BONDING IN METAL TRIPHOS COMPLEXES

King nomenclature		Schematic representation	Number of enantiomers	No. of isomers when M_a = $Mn(CO)_nX^a$
monometallic monodentate	A1		1	1
	A2		1	1
monometallic bidentate	B1		2	4
	B2		1	2
monometallic tridentate	C1		1	2
bimetallic biligate	D1		2	2
	D2		2	2
	D3		2	2
bimetallic triligate	E1		2	4
	E2		1	2
	E3		2	4
	E4		1	2
trimetallic triligate	F1		2	2
	F2		2	2
	F3		2	2

a) The value of n in $Mn(CO)_nX$ will be dependent on the number of CO groups displaced by the Triphos ligand, e.g., if Triphos acts as a monometallic tridentate ligand, three CO groups will be displaced by Triphos and the value of n = 2. In determining the number of isomers that could be formed, only substitution of CO groups *cis* to the halogen was considered. This is in conformity with the known chemistry of these types of complexes.

This column includes both enantiomers and diastereomers.

1) No allowance was made for bonding through non-adjacent P atoms; B2, E2, E4.

2) No allowance was made for the interchange of the different metal atoms; D3, E3, F2, F3.

3) When allowance is made for optical isomers, nine further isomers are possible. This arises from the optical activity induced in the central P atom on being bonded (except in D2) to the metal.

(Note: Unbonded Triphos is optically inactive).

All twenty-four isomers are permissible theoretically but difficulties might be encountered in separating the nine sets of optical isomers. Chemical restrictions could prevent the formation of other isomers.

If $M_a = Mn(CO)_5X$, even more isomers become possible. Thus, placing the restriction that only CO groups *cis* to X may be substituted by the polyphosphine, 10 extra isomers are generated.

When Diphos (or Triphos) replaces only one CO group in $Mn(CO)_5X$, conformational isomers are anticipated. Two examples of this effect are shown overleaf for the complex *cis*-$Mn(CO)_4(Diphos)Br$.

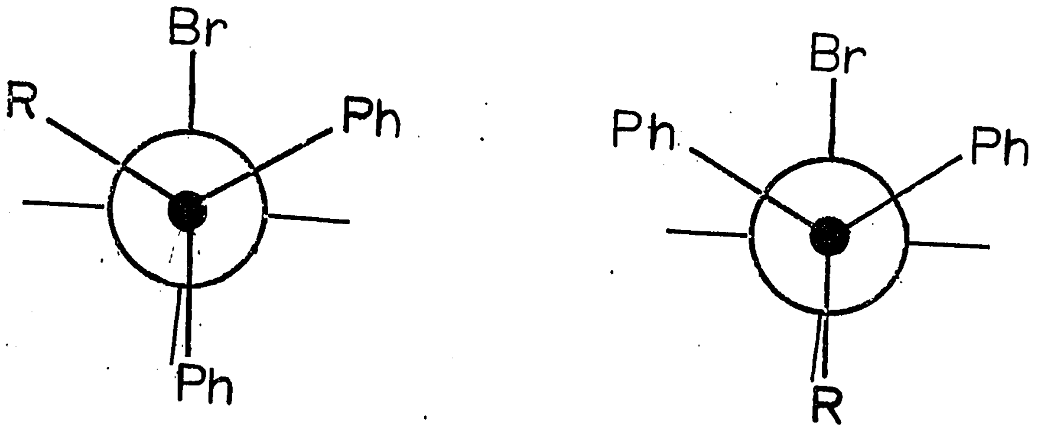
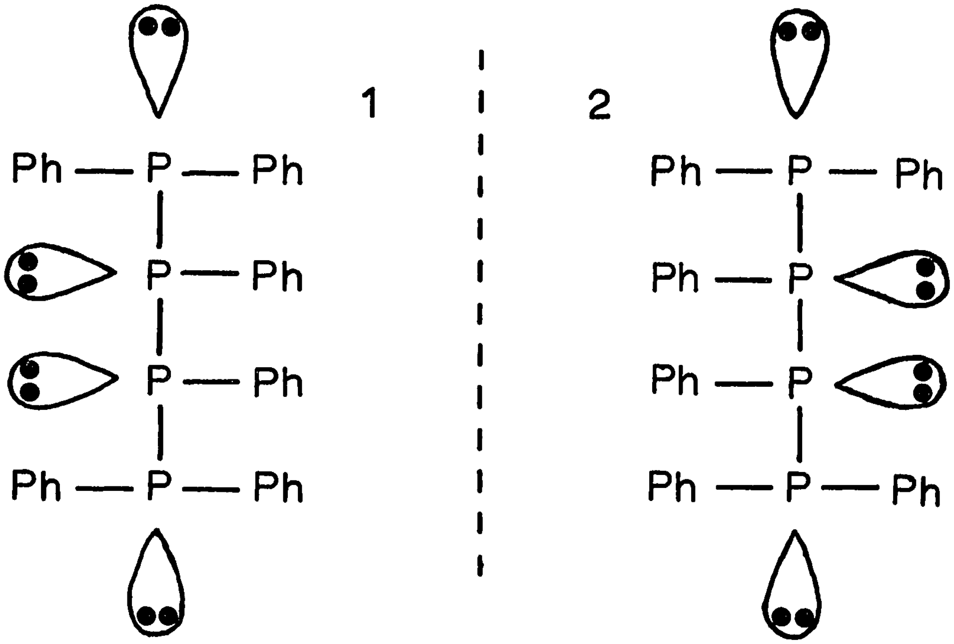


FIGURE II-4 TWO ROTATIONAL CONFORMATIONS OF *cis*-$Mn(CO)_4(Diphos)Br$ The view is along the Mn-P bond; the large open circles being the manganese atoms, the smaller solid ones the phosphorus atoms. All CO groups have been left out and R = $CH_2CH_2PPh_2$.

This effect will not be discussed further.

As can be seen from the preceeding discussion, an analysis of the bonding possibilities for the coordination of $Mn(CO)_5X$ to Triphos requires an analysis from first principles. When a similar analysis for Tetraphos is restricted to monometallic systems, thirty-seven isomers are possible (no restriction placed on the metal). One of the major reasons for the increase in the number of isomers arises because the Tetraphos ligand contains two optically active P atoms. The ligand thus exists in three isomeric forms as shown in Figure II-5. Note that isomers (1) and (2) are superimposable and are thus identical.

meso:



racemic:

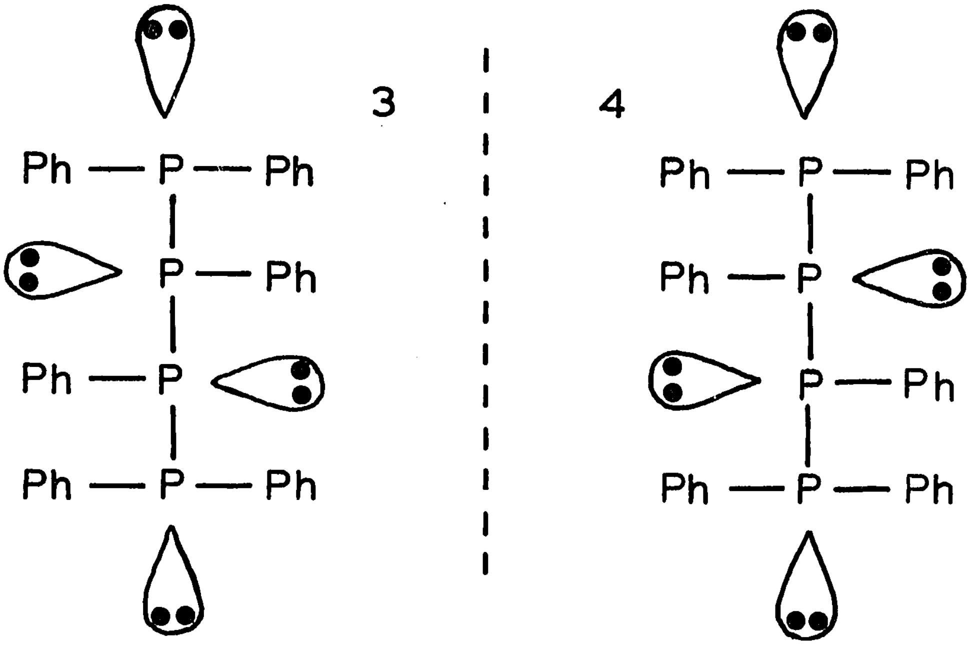


FIGURE II-5 FISCHER PROJECTIONS OF THE OPTICALLY ACTIVE FORMS OF TETRAPHOS. The methylene groups have been omitted for the sake of clarity.

CHAPTER III. HALODICARBONYL COMPLEXES OF MANGANESE(I)*

INTRODUCTION

This chapter provides an extension of work carried out recently in this laboratory on the preparation of halodicarbonyl complexes of manganese(I)[8]. When the present study was originally undertaken, the CO substitution reactions of the halopentacarbonylmanganese(I) complexes, $Mn(CO)_5X$ (X = Cl, Br, I), with a wide variety of ligands, L, could be summarized by the following stepwise reaction sequence:[59]

$$\begin{tikzcd}
Mn(CO)_5X \arrow[r, "L"] & \textit{cis}\text{-}Mn(CO)_4LX \arrow[d, "L"] \\
 & \textit{fac}\text{- and/or }\textit{trans}\text{-}Mn(CO)_3L_2X
\end{tikzcd}$$

Attempts to substitute more than two CO groups by ligands such as triphenylphosphine and pyridine had all failed, even at elevated temperatures. This has been explained on the basis of a π-bonding argument, *viz.*, the first two CO groups are replaced by ligands which are not as good π-acceptors as CO and this leads to a strengthening of the three remaining

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* This work has been published in part[60].

Mn-CO bonds such that no further substitution can take place[56]. This explanation is supported by the fact that phenylisocyanide, a ligand which is considered to be a better π-acceptor than CO, replaces all five CO groups in $Mn(CO)_5Br$[61].

There is also some evidence that suggests that the substitution process is usually arrested at the $Mn(CO)_3L_2X$ stage because of the inability of the manganese atom to accommodate more than two bulky L groups in its coordination sphere. For instance, the *cis*-$Mn(CO)_3L_2Br$ [L = $P(OPh)_3$, $P(O\underline{n}\text{-}Bu)_3$, PCl_2Ph] complexes readily isomerize to the less sterically crowded *trans* isomers[62], while the presence of the larger rhenium atom in the analogous $Re(CO)_3L_2X$ complexes apparently obviates the need for isomerization as only the *cis* isomers (with the exception of L = PPh_3) are formed[63].

On the basis of infrared studies on substituted metal carbonyl complexes, tertiaryphosphites are believed to be as good if not better π-acceptors than CO[64]. Moreover, tertiaryphosphites such as trimethylphosphite, $P(OMe)_3$, triethylphosphite, $P(OEt)_3$, and triallylphosphite, $P(OCH_2CH{=}CH_2)_3$, are not as bulky as any of the ligands that so far have been reacted with the $Mn(CO)_5X$ complexes. In view of this, an investigation of the reactions of this type of tertiaryalkylphosphite with the $Mn(CO)_5X$ complexes was carried out to see whether or not more than two CO groups could be replaced by these ligands. As hoped, it was found that three CO groups could readily be replaced by the phosphites. It was thus decided to also investigate whether three CO groups could be replaced by polyphosphine ligands. In addition, the reactions of dimethylphenylphosphine, PMe_2Ph, and dichlorophenylphosphine, PCl_2Ph, with the $Mn(CO)_5X$ complexes and some of their derivatives were studied.

EXPERIMENTAL

i) Preparation and Purification of Materials*

Chemicals were obtained from the sources given on p.vii. The ligands were used without further purification. Reagent

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* *Thin layer chromotography*: The following procedure was used to prepare the silica gel thin layer chromotography plates used throughout this thesis. Silica gel $HF_{254 + 366}$ (50 g) was shaken in distilled water (115 ml) for two minutes. The mixture was placed in a Desaga applicator and the silica gel spread over four 25 x 25 cm glass plates (thickness 0.75 - 1.0 mm). The plates were then allowed to stand in air for 12 h, after which they were activated in an oven (120°C) for 3 h.

Routine composition and purity checks of the reaction mixtures and their products were also carried out by thin layer chromotography. The pre-coated silica gel plates used for this purpose (Eastman Chromogram Sheet 6060) were purchased from Brinkmann Instruments, Ltd.

The eluent system used to separate and purify the required product(s) was chosen in such a way that the required product had an R_f value of $\sim$0.5 .

Column chromotography: A 15"x3/4" column containing silica gel (Davison commercial grade H) was used in all cases.

grade solvents were dried over calcium hydride and were distilled under nitrogen before use. THF was distilled from sodium/benzophenone while benzene and xylene were distilled from sodium.

The literature methods were used to prepare and purify $Mn(CO)_5X$ (X = Cl, Br[65]; X = I[4]), *fac*-$Mn(CO)_3$(Diphos)Br[28], $Fe(CO)_2(NO)_2$[66] and $C_5H_5Mn(CO)_2C_8H_{14}$[67].

ii) <u>Physical Measurements</u>

The IR spectra were obtained with a Perkin Elmer 337 grating spectrophotometer coupled to a Texas Instruments Servo/Riter model II expanded scale recorder. The spectra were calibrated against the 2143.2 cm^{-1} band of CO and the 1601.4 and 1583.1 cm^{-1} bands of polystyrene; the frequencies are precise to ±1-2 cm^{-1}.

The ^1H NMR spectra (60 MHz) were recorded at approximately 36°C on a Varian Associates T-60 spectrometer. The 100 MHz spectra were recorded on a Varian HA-100 spectrometer. The τ values are relative to tetramethylsilane as an internal standard at τ10 and are precise to ±0.05. The J values are precise to ±0.3 Hz. UV spectra were recorded on a Unicam SP-800 spectrometer (precision ± 2 nm).

Conductivity measurements were carried out on an Industrial Instruments RC 16B2 conductivity bridge for approximately 1 x 10^{-3}M nitromethane solutions at 22°.

The decomposition points were determined in capillaries on a Gallenkamp melting point apparatus and are uncorrected.

The elemental analyses and molecular weight determinations were performed by Schwarzkopf Microanalytical Laboratory Inc., Woodside, New York, U.S.A.

Preparation of the Halodicarbonyl Complexes.

All the reactions described below were performed under an atmosphere of nitrogen. The reactions were monitored by following the changes in the C-O stretching region of the IR spectra of the reaction mixtures, and were terminated when no further changes could be detected. The reaction times, analytical data, and molar conductivities for the halodicarbonyl complexes are given in Table III-1. The C-O stretching frequencies for all the complexes and NMR data for some of the complexes are given in Tables III-2 and III-3, respectively. All the complexes are readily soluble in polar solvents.

$Mn(CO)_2L_3X$ (Method I)

A mixture of the appropriate $Mn(CO)_5X$ complex (2 mmole) and tertiaryalkylphosphite or PMe_2Ph (6-8 mmole) was dissolved in chloroform (50-100 ml) and the solution was maintained at reflux until no further reaction occurred. The solvent volume was then reduced on a rotary evaporator to about 5 ml and *n*-hexane (50 ml) was added. This mixture was reduced in volume to about 5 ml. The precipitate which formed at this point was filtered off and was recrystallized from a chloroform/n-hexane mixture. In a few cases, the reaction products were oils which could not be induced to crystallize. The products were dried *in vacuo* (25°/0.001 mm Hg) for 24 h.

$Mn(CO)_2(Triphos)X$ (Method II)

A xylene solution (20 ml) containing $Mn(CO)_5X$ (1 mmole) and Triphos (1 mmole) was heated at 130° until the reaction was complete. The volume of the reaction mixture was then reduced at 25°/0.1 mmHg to about 5 ml and n-hexane (50 ml) was added. The precipitate which formed was filtered off and was purified by column chromatography on silica using a 1/1 acetone/n-hexane mixture as eluent. The resulting product was recrystallized from a chloroform/n-hexane mixture.

The iodo complex, $Mn(CO)_2(Triphos)I$, was also prepared in about 10% yield from the reaction of $Mn(CO)_5I$ with Triphos in refluxing dichloromethane for 17 days.

$Mn(CO)_2L(Diphos)X$ and $Mn(CO)_2L(Triphos)X$ (Method III)

Method A

A chloroform solution (20 ml) containing $Mn(CO)_2L_3X$ (1 mmole) and Triphos (1-2 mmole) was maintained at reflux until no further reaction took place. On cooling, n-hexane (50 ml) was added to the reaction mixture and the solvent volume was then reduced to about 5 ml. The precipitate which formed was filtered off.

The Triphos complexes were chromatographed on silica columns using 1/2 acetone/benzene mixtures as eluent. After removal of solvent, the required products were obtained by recrystallization from chloroform/n-hexane mixtures.

Method B

A mixture of *fac*-$Mn(CO)_3(Diphos)Br$ (0.5-1 mmole) and excess tertiaryalkylphosphite or PMe_2Ph (2-4 mmole) in xylene (20 ml) was heated at 90-100° until no further reaction occurred. The solvent was removed under reduced pressure (25°/0.1 mmHg) and the resulting residue was crystallized from a chloroform/n-hexane mixture to give the desired product.

In the case of the PMe_2Ph complexes, the residue was dissolved in a minimum of chloroform and then chromatographed on a silica column using a 3/5 acetone/n-hexane mixture as eluent. The products were then purified as above.

Preparation of the Trimethylphosphite Complexes

A dichloromethane solution (25 ml) containing $Mn(CO)_5Br$ (1 mmol) and $P(OMe)_3$ (1 mmol) was refluxed for 2 h. Solvent was then reduced on a rotary evaporator to 5 ml. The resulting oil was eluted on silica gel thin layer plates with 2/1 benzene/n-hexane as eluent. Two products were extracted from the plates. The product with the higher R_f value, *cis*-$Mn(CO)_4[P(OMe)_3]Br$, was an orange oil which could not be induced to crystallize. The other product, *fac*-$Mn(CO)_3[P(OMe)_3]_2Br$, was crystallized from dichloromethane/

TABLE III-1 HALOCARBONYL COMPLEXES OF MANGANESE(I)

COMPLEX	Prep. meth.	Reaction time(h)	Yield (%)	Colour	Decomp. (°C)	Analysis found(calcd.)(%)				Λ_m ($cm^{-1}.\Omega^{-1}.M^{-1}$)
						C	H	P	X	
cis-$\mathrm{Mn(CO)_2[P(OCH_2CH_2Cl)_3]_3Br}$[a]	I	23	70	Orange	Oil	25.1 (24.0)	3.6 (3.6)			3.9
cis-$\mathrm{Mn(CO)_2(Triphos)Cl}$	II	3	25	Lemon-yellow	226-228	62.9 (63.5)	5.0 (4.9)	11.9 (13.6)	7.6 (5.2)	0.37
cis-$\mathrm{Mn(CO)_2(Triphos)Br}$	II	1	50	Yellow	220-222	58.4 (59.6)	4.5 (4.6)	12.8 (12.5)		1.1
cis-$\mathrm{Mn(CO)_2(Triphos)I}$	II	5	40	Orange	224-226	55.4 (56.0)	4.2 (4.3)		15.8 (16.4)	5.6
cis-$\mathrm{Mn(CO)_2[P(OMe)_3](Diphos)Br}$	IIIB	4	32	Yellow	83-88	50.9 (52.2)	4.8 (4.7)			
cis-$\mathrm{Mn(CO)_2[P(OMe)_3](Triphos)Br}$	IIIA	6	40	Yellow	80-85	53.7 (55.1)	4.9 (5.0)	14.5 (14.6)		
cis-$\mathrm{Mn(CO)_2[P(OEt)_3](Triphos)Br\cdot\frac{1}{2}CHCl_3}$	IIIA	8	52	Yellow	52-56	53.9 (53.8)	5.6 (5.1)	13.1 (13.1)		
cis-$\mathrm{Mn(CO)_2[P(OPh)_3](Diphos)Br}$	IIIB	2	24	Yellow	153-157	61.4 (61.4)	4.7 (4.4)	9.9 (10.3)	9.1 (8.9)	3.9
cis-$\mathrm{Mn(CO)_2[P(OCH_2CH_2Cl)_3](Triphos)Br}$	IIIA	8	65	Yellow	58-63	51.7 (50.7)	4.6 (4.6)			
cis-$\mathrm{Mn(CO)_2(PMe_2Ph)(Diphos)Br}$	IIIB	24	30	Yellow	≈ 85	60.3 (59.4)	5.2 (4.9)	12.3 (12.8)		2.5
cis-$\mathrm{Mn(CO)_4[P(OMe)_3]Br}$[a]	-	2	60	Orange	Oil	22.7 (23.1)	2.5 (2.3)			
fac-$\mathrm{Mn(CO)_3[P(OMe)_3]_2Br}$[a]	-	6	55	yellow		23.2 (23.5	3.9 (4.2)			

a) The C and H analyses for these complexes were performed in this laboratory on a Hewlett-Packard Model 185 CHN analyser.

n-hexane as a yellow solid. This second product was also prepared in higher yield by the reaction of $Mn(CO)_5Br$ (1 mmol) and $P(OMe)_3$ (1 mmol) in refluxing dichloromethane (25 ml) for 7 h.

RESULTS AND DISCUSSION

Immediately prior to and shortly after this work was published, a number of papers appeared in the literature reporting results similar to those described below[68,69]. The results from these other research groups will be included in the discussion which follows.

The facile preparative route to the complexes *cis*-$Mn(CO)_2L_3X$ [L = $P(OMe)_3$, $P(OEt)_3$, $P(OCH_2CH{=}CH_2)_3$] was used to re-prepare these complexes for further study[8]. The complex *cis*-$Mn(CO)_2[P(OCH_2CH_2Cl)_3]_3Br$ was also prepared by the same procedure.

The ease with which these dicarbonyl products are formed must be related to the steric rather than the electronic requirements of the manganese atom. This point is emphasized by the fact that the small ligands PMe_2Ph [a very strong σ-donor (base)] and $P(OMe)_3$ (a good π-acceptor) both form dicarbonyl complexes*. The recent preparation of the complexes *cis*-$Mn(CO)_2L_3Br$ (L = $AsMe_2Ph$, PMe_3) containing other *small* ligands confirms this view[69]. This is in contrast to

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* Another preparation of *cis*-$Mn(CO)_2(PMe_2Ph)_3Br$ has been reported[70]. This preparation involves the reaction of $Mn(CO)_2(PMe_2Ph)_3NCO$ with dry HBr gas in carbon tetrachloride solution at 0°.

an earlier report of the preparation of *cis*-$Mn(CO)_2[(P(OMe_3)_3]_3Br$, in which it was suggested that the dicarbonyl was formed because "trimethylphosphite is probably a ligand somewhat unique in behaviour"[68].

The $Mn(CO)_5X$ complexes were also found to react with the potentially tridentate ligand, Triphos, to produce the halodicarbonyl complexes *cis*-$Mn(CO)_2$(Triphos)X. The reactions initially carried out in refluxing chloroform (∿65°) did not go to completion, even after one month. However, in xylene solution at 130° the reactions are complete in less than 5 h.

An attempt to prepare *cis*-$Mn(CO)_2$(Triphos)Br by the method of King *et al.*[33] *viz.*, $Mn(CO)_5Br$ and Triphos in refluxing benzene, gave a mixture of *fac*-$Mn(CO)_3$(Triphos)Br and *cis*-$Mn(CO)_2$(Triphos)Br, even after 96 h.

The IR spectra of the reaction mixtures in the C-O stretching region indicate that, as expected, all the reactions proceed by the stepwise replacement of CO groups. In the case of the reactions with the monodentate ligands, they have all reached the disubstituted stage after 1 h. Slower reactions then transform the disubstituted complexes into trisubstituted ones. On the basis of the IR spectra there is no evidence of any further substitution occurring.

The Triphos reactions are slow enough for the intermediate complexes $Mn(CO)_3$(Triphos)X to be isolated and characterized. The Triphos ligand in these complexes is coordinated to the manganese atom through only two of its three phosphorus atoms. The complexes are similar to those of the potentially tetradentate ligand *tris*[(o-diphenylphosphinophenyl)]phosphine (QP), *cis*-$Mn(CO)_3(QP)X$, in which the QP ligand functions as a bidentate ligand[32]. The preparation and the physical and chemical properties of the "monodentate ligands", *fac*-$Mn(CO)_3(Triphos)X$, are discussed in Chapter IV.

The degree of CO substitution in the $Mn(CO)_5X$ complexes by PhNC is known to be highly solvent dependent[61]. For instance, the bis-, tris-, and tetrakisisocyanide complexes are produced when $Mn(CO)_5Br$ is reacted with PhNC in ethanol, diglyme, and tetrahydrofuran, respectively. Therefore, it seems that the more basic the solvent the higher the degree of CO substitution. Consequently, it was hoped that similar reactions would lead to tetra- or even pentasubstitution. However, reaction of *cis*-$Mn(CO)_2[P(OMe)_3]_3X$ with excess $P(OMe)_3$ in refluxing tetrahydrofuran afforded no new products.

Further substitution, to replace a fourth CO group has been reported, but only by UV irradiation of the dicarbonyl in the presence of excess L[68,69]. The only exception to this is the reaction of $Mn(CO)_2[P(OMe_3]_3Br$ (in which the CO groups are *trans* to each other) with excess $P(OMe)_3$ in *refluxing* petroleum-ether (b.p. 60-80°). This reaction readily gives the the monocarbonyl complex.

The reaction of $P(OMe)_3$ with $Mn(CO)_2[P(OMe)_3]_3Br$ was repeated in this laboratory using a 100 W Hanovia High-Pressure Hg lamp. Under these conditions, the monocarbonyl species was readily prepared [ν(CO) = 1866 in THF]. Irradiation of the THF solution of *cis*-$Mn(CO)_2$(Triphos)Br with L[L = $P(OMe)_3$, $P(OEt)_3$] was then attempted and the reaction monitored by following changes in the IR spectrum. Although solid products were isolated and the CH_2Cl_2 solution IR spectra of the complexes showed only one peak in the ν(CO) region [L = $P(OMe)_3$: 1843; L = $P(OEt)_3$: 1840 cm^{-1}], thin layer chromotography indicated that the products were impure. Attempted purification of the products failed. By comparison with the other reports of similar reactions, the products formed are almost certainly the monocarbonyl complexes Mn(CO)(Triphos)LBr[L = $P(OMe_3)$, $P(OEt_3)$)] in which the CO and the Br are *trans* to each other.

The mixed ligand complexes *cis*-$Mn(CO)_2$L(Diphos)Br [L = $P(OMe)_3$, $P(OPh)_3$, PMe_2Ph, PCl_2Ph] are obtained by reaction of *fac*-$Mn(CO)_3$(Diphos)Br with L in xylene at 90-100°. In the case of PMe_2Ph some replacement of Diphos does take place because *trans*-$Mn(CO)_3(PMe_2Ph)_2Br$ is present in the crude reaction product. Presumably, two PMe_2Ph ligands displace the Diphos ligand to give initially *fac*-$Mn(CO)_3(PMe_2Ph)_2Br$ which, at the temperature of the reaction, readily isomerizes to the *trans* isomer[62]. This suggestion is supported by the fact that the reaction of $Mn(CO)_5Br$ with PMe_2Ph in xylene at 65° yields a complex whose IR spectrum in the C-O stretching region is typical of a *fac*-$Mn(CO)_3L_2X$ species. On raising the temperature to 95°, the spectrum becomes characteristic of a mixture of *trans*-$Mn(CO)_3L_2X$ and *cis*-$Mn(CO)_2L_3X$.

All other attempts to obtain mixed ligand complexes of the type *cis*-$Mn(CO)_2L(Diphos)X$ failed. For instance, similar reactions of *fac*-$Mn(CO)_3(Diphos)Br$ with L = PPh_3, Diphos or CH_3CN (xylene at 90-100°) gave no new products. Since the complexes $MnCO(Ph_2P(CH_2)_nPPh_2)_2Br$ (n = 1,2) have recently been prepared[23], the inability of the diphosphines to replace a third CO is presumably not related to steric effects but is due to the relatively "mild" reaction conditions employed.

The non-ionic formulation of the new halodicarbonyl complexes *cis*-$Mn(CO)_2L_3X$, *cis*-$Mn(CO)_2(Triphos)X$ and *cis*-$Mn(CO)_2L(A\text{-}A)X$ (A-A Diphos or Triphos) is supported by the low molar conductances of representative examples of the complexes in nitromethane solution (Table III-1). All the complexes exhibit two strong IR active C-O stretching frequencies (Table III-2). Because of this, the two CO groups in each complex are assigned *cis* rather than *trans* stereochemistry. [One weak band (symmetric C-O stretching mode) and one strong band (asymmetric C-O stretching mode) would be expected for a *trans* arrangement of the two CO groups.]

TABLE III-2

IR SPECTRA IN THE C-O STRETCHING REGION OF THE NEW HALODICARBONYLMANGANESE(I) COMPLEXES (CH_2Cl_2 SOLUTION)

Complex	ν_{CO} (cm^{-1})[a]			
cis-$Mn(CO)_2[P(OMe)_3]_3Br$[b]		1977	1893	
cis-$Mn(CO)_2[P(OEt)_3]_3Br$[c]		1966	1883	
cis-$Mn(CO)_2[P(OCH_2CH_2Cl)_3]_3Br$		1977	1901	
cis-$Mn(CO)_2[P(OCH_2CH{=}CH_2)_3]_3Br$		1974	1892	
cis-$Mn(CO)_2(PMe_2Ph)_3Br$[c,d]		1926	1848	
cis-$Mn(CO)_2$(Triphos)Cl		1934	1861	
cis-$Mn(CO)_2$(Triphos)Br[e,f]		1935	1865	
cis-$Mn(CO)_2$(Triphos)I[g]		1936	1869	
cis-$Mn(CO)_2[P(OMe)_3]$(Diphos)Cl[h]		1947	1870	
cis-$Mn(CO)_2[P(OMe)_3]$(Diphos)Br		1947	1874	
cis-$Mn(CO)_2[P(OMe)_3]$(Triphos)Br		1945	1871	
cis-$Mn(CO)_2[P(OEt)_3]$(Triphos)Br		1943	1869	
cis-$Mn(CO)_2[P(OCH_2CH_2Cl)_3]$(Triphos)Br		1947	1874	
cis-$Mn(CO)_2[P(OCH_2CH{=}CH_2)_3]$(Diphos)Br[c,h]		1951	1877	
cis-$Mn(CO)_2[P(OCH_2CH{=}CH_2)_3]$(Triphos)Br[c]		1949	1875	
cis-$Mn(CO)_2[P(OPh)_3]$(Diphos)Br		1958	1885	
cis-$Mn(CO)_2[P(OPh)_3]$(diarsine)Br[c,h]		1959	1885	
cis-$Mn(CO)_2[P(OPh)_3]$(Diars)Br[h]		1957	1881	
cis-$Mn(CO)_2(PMe_2Ph)$(Diphos)Br		1934	1860	
cis-$Mn(CO)_2(PCl_2Ph)$(Diphos)Br		1942	1868	
cis-$Mn(CO)_4[P(OMe)_3]Br$	2099	2030	2013vs	1968
fac-$Mn(CO)_3[P(OMe)_3]_2Br$[i]	2042	1976	1931	
trans-$Mn(CO)_3(P(OMe)_3]_2Br$[j,k]	2047w	1972	1932m	

[a] The bands are strong unless otherwise stated.

[b] In $CHCl_3$ solution (ref. 68): 1980s, 1898s.

[c] These complexes were not isolated on a preparative scale. The similarity of their IR spectra to those of authentic halocarbonyl complexes was taken as sufficient proof of their identity.

[d] In C_6H_6 solution (ref. 70): 1912, 1839s.

[e] Data from ref. 33 : 1936s, 1864s.

[f] In far-infrared spectrum (Nujol mull; Perkin Elmer FIS-3 spectrometer): ν_{Mn-Br} = 209 cm^{-1}.

[g] In solid-state Raman spectrum [krypton laser (647.1 nm) excitation; Jarrell-Ash model 25-300 spectrometer]: ν_{Mn-I} = 190 cm^{-1}.

[h] These complexes were prepared by H.K. Spendjian[8].

[i] In s-tetrachloroethane (ref.81): 2040(s), 1978(s), 1929(s).

[j] In $CHCl_3$ solution (ref.68): 2052(w), 1975(s), 1939(m).

[k] Isomerisation of *fac*-$Mn(CO)_3[P(OMe)_3]_2Br$ to *trans*-$Mn(CO)_3[P(OMe)_3]_2Br$ was achieved in refluxing chloroform (4 h).

The structures shown in Figure III-1 for the three different types of halodicarbonyl complex are favoured because of the established geometry of $CH_3Mn(CO)_3[P(OMe)_3]_2$, $CH_3Mn(CO)[P(OMe)_3]_4$[68], and $CH_3COMn(CO)_3[P(OMe)_3]_2$[71] in which the $P(OMe)_3$ ligands are *cis* to the CH_3 and CH_3CO groups. Moreover, a $C^{18}O$ exchange study carried out in this laboratory on *trans*-$Mn(CO)_3[P(OPh)_3]_2Br$ indicates that the two *trans* CO groups are much more labile than the CO group *trans* to Br[8]. This suggests that the latter CO group is the least likely to undergo substitution. Structure A is the same structure that was preferred for $Mn(CO)_2[P(OMe)_3]_3Br$ in the preliminary report of its preparation[68]. Furthermore, it is identical to the structure proposed for the analogous $Re(CO)_2L_3Cl$ [$L = PPh_2H, PPh_2Me, P(OPh)_3$] complexes which are formed in the reaction of $[Re(CO)_6]ClO_4$ and the appropriate ligand, L[63].

Although the complexes *cis*-$Mn(CO)_2$(Triphos)X and

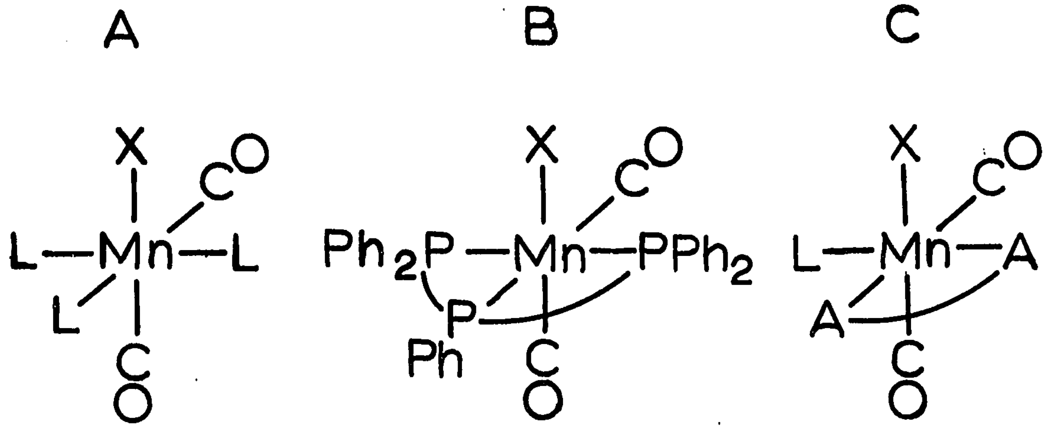


FIGURE III-1 PROPOSED STRUCTURES FOR THE DICARBONYL COMPLEXES. A-A = Diphos or Triphos and L = phosphine or phosphite.

cis-Mn(CO)$_2$(Triphos)LX are expected to exist in a variety of isomeric forms, no separation of these expected isomers was achieved by the techniques employed in this study. This point is discussed further in Chapter IV.

Proton NMR data for representative examples of the halodicarbonyl complexes are given in Table III-3. The observed areas of the signals are in agreement with the proposed assignments in all instances.

An analysis of the NMR data was only attempted for *cis*-Mn(CO)$_2$[P(OMe)$_3$]$_3$Br because the data for the other complexes were of poor quality and/or very complex.

At 60 MHz the NMR spectrum of *cis*-Mn(CO)$_2$[P(OMe)$_3$]$_3$Br exhibits a "1:1:1 triplet" which is resolved into a five line spectrum at 100 MHz (Figure III-2).

The spectra of a series of trimethylphosphite-manganese(I) carbonyl complexes were also recorded (Table III-4) in the hope that information would be obtained which would aid in elucidating the stereochemistry of the dicarbonyl complex.

A similar series of complexes have been prepared for the analogous molybdenum carbonyls. The NMR data[72] together with J_{P-H} values for P(OMe)$_3$, (MeO)$_3$P=O and (MeO)$_3$P=S[73] are listed below (Table III-5).

TABLE III-3

^{1}H NMR DATA FOR SOME OF THE NEW HALODICARBONYLMANGANESE(I) COMPLEXES (IN $CDCl_3$ SOLUTION)

Complex	Group	$\tau^{a,b,c}$		
cis-$Mn(CO)_2[P(OMe)_3]_3Cl$	OCH_3	6.24	T	(10.0)
cis-$Mn(CO)_2[P(OMe)_3]_3Br$	OCH_3	d		
cis-$Mn(CO)_2[P(OCH_2CH_2Cl)_3]_3Br$	OCH_2	5.48	T	(18.0)
	CH_2Cl	6.17	T	(21.0)
cis-$Mn(CO)_2$(Triphos)Br	C_6H_5	2.43 , $\sim$3.0		
	CH_2	7.24	br	
cis-$Mn(CO)_2[P(OMe)_3]$(Diphos)Br	C_6H_5	2.65		
	OCH_3	6.33	D	(10.4)
	CH_2	$\sim$8	br	
cis-$Mn(CO)_2[P(OMe)_3]$(Triphos)Br	C_6H_5	2.50		
	OCH_3	6.31	M	
	CH_2	7.5	br	
cis-$Mn(CO)_2[P(OEt)_3]$(Triphos)Br	C_6H_5	2.68		
	OCH_2	5.99	M	
	CH_2	$\sim$8	br	
	CH_3	8.77	br	
cis-$Mn(CO)_2[P(OCH_2CH_2Cl)_3]$(Triphos)Br	C_6H_5	2.53		
	OCH_2	5.81	M	
	CH_2Cl	6.48	M	
	CH_2	7.94	br	
cis-$Mn(CO)_2(PMe_2Ph)$(Diphos)Br	C_6H_5	2.62		
	CH_3, CH_2	8.37	M	

---

a) D = doublet, T = triplet like, M = complex multiplet, br = broad.

b) Values in parenthesis are the distances between the outer two peaks (Hz).

c) Sample concentration $\sim$0.2 M.

d) Details of this spectrum are given in Table III-4.

TABLE III-4 NMR SPECTRA OF A SERIES OF TRIMETHYLPHOSPHITE MANGANESE CARBONYL COMPLEXES

	$\tau^{a,b}$	N^c
$P(OMe)_3$	6.39 (d)	11.0
cis-$Mn(CO)_4[P(OMe)_3]Br$	6.15 (d)	10.8
fac-$Mn(CO)_3[P(OMe)_3]_2Br$	6.19 (t)	10.1
trans-$Mn(CO)_3[P(OMe)_3]_2Br^d$	6.00 (t)	11.0
cis-$Mn(CO)_2[P(OMe)_3]_3Br$	6.20 (t) 6.22 (d)	10.0 ∿9.5

a) Spectra recorded in $CDCl_3$ relative to TMS (τ = 10.0)

b) Abbreviations used: d = doublet, t = triplet like.

c) N = Separation of the outer two lines in Hz. See text for further details.

d) Ref. 68 τ = 6.19 (t), N = 11 Hz.

TABLE III-5 NMR SPECTRA OF A SERIES OF TRIMETHYLPHOSPHITE MOLYBDENUM CARBONYL COMPLEXES

	$\tau^{a,b}$		N^c	J_{P-P}
$P(OMe)_3{}^d$	6.56	(d)	10.6	
$(MeO)_3P{=}O^d$			10.5	
$(MeO)_3P{=}S^d$			12.9	
$Mo(CO)_5[P(OMe)_3]$	6.35	(d)	11.6	
cis-$Mo(CO)_4[P(OMe)_3]_2$	6.38	(t)	11.6	-40^e
trans-$Mo(CO)_4[P(OMe)_3]_2$	6.38	(t)	11.6	162^e
mer-$Mo(CO)_3[P(OMe)_3]_3$	6.40	(t)	11.1	
	6.46	(d)	10.8	47
fac-$Mo(CO)_3[P(OMe)_3]_3$	6.42	(t)	10.8	

a) Spectra recorded in CCl_4 relative to TMS (τ=10.0).

b) Abbreviations used: d = doublet, t = "1:2:1 triplet"

c) N = separation of the outer two lines in Hz. See text for further details

d) NMR spectrum recorded of neat liquid.

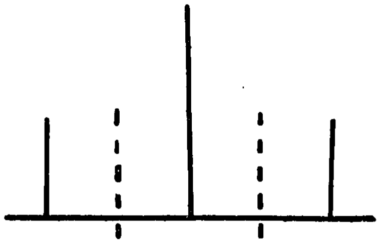
e) Ref. 73

The similarity of the spectra for the molybdenum complexes with those recorded for the manganese complexes is remarkable. The constancy of the N values, ($\sim J_{P-H}$) is to be noted. This suggests that the coupling constant is little affected by the nature of the substituents attached to the metal atom.

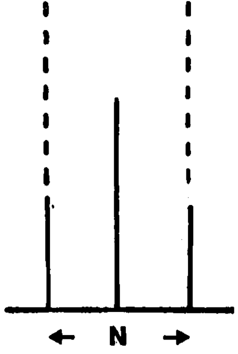
Analysis of the NMR Spectra (Table III-4)

Un-coordinated $P(OMe)_3$ exhibits a doublet for the methyl protons due to coupling of these protons with the ^{31}P nucleus (J_{P-H} = 11.0). As expected, coordination of the phosphite in *cis*-$Mn(CO)_4[P(OMe_3)]Br$ results in only a small change in the coupling constant (J_{P-H} = 10.8 Hz).

At first glance the spectra of the disubstituted complexes (Table III-4) are deceptively simple. It would seem that the 1:2:1 apparent triplet arises from coupling of the methyl protons with both P atoms.



Spectrum expected for an AX_2 spin system (X region).



Spectrum obtained for *fac*- or *trans*-$Mn(CO)_3[P(OMe)_3]_2Br$

However, a closer examination reveals that the spectra are not really 1:2:1 triplets, since the central peak in the triplet is not sharp and the outer peaks of the triplet are much closer together than would be expected for equal coupling of the methyl protons to both P atoms.

To analyse these spectra, it is necessary to treat them in terms of an $A_9XX'A'_9$ spin system (X = phosphorus, A = hydrogen). A total analysis for the more general case $A_nXX'A'_n$ has been given[74,75], in which a number of limiting cases are described. In particular, for the limiting case $J_{X-X} >> |N|$ $(N = J_{A-X} - J_{A-X'})$, a triplet-like X resonance is expected with an intensity ratio of 1:2:1. For $P(OMe)_3$, in $Mn(CO)_3[P(OMe)_3]_2Br$ complexes, $N = J_{P-H} - J_{P-H'} \sim J_{P-H}$ (i.e. $J_{P-H'} \sim 0$) and since $J_{P-P} >> |N| \sim |J_{P-H}|$, J_{P-P} must be large. Thus, the appearance of an apparent triplet in the NMR Spectrum of transition complexes containing $P(OMe)_3$ is interpreted as a sign of strong P-P coupling.*

For *trans*-$Mn(CO)_3[P(OMe_3)]_2Br$ this is not unusual, and a triplet spectrum as well as large J_{P-P} values have been reported for many metals[76] which contain phosphines and phosphites that are *trans* to each other.

For the *cis* complex the situation is not as straightforward. In certain cases [e.g. octahederal complexes of Ir(III)], $J^{cis}_{P-P} \sim 0$[77].

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* An apparent triplet can also be obtained when J_{P-P} is small, provided that J_{P-H} is also small[78].

The spectra of these complexes give doublets which can readily be explained as arising from a special case, $|J_{P-P}| << |J_{P-X} - J_{P-X'}|$, of the spin system $A_nXX'A'_n$. This difference in the NMR spectra of *cis* and *trans* complexes (doublet vs. triplet) has been used in assigning the stereochemistry of many metal complexes.

Recent studies on Group VI metal carbonyls has shown that J^{cis}_{P-P} can be as large as J^{trans}_{P-P}[78]. A triplet spectrum is then expected (and found) for the *cis* complex as well as the *trans* complex.

Very little information is available on manganese complexes[71]. One report mentions that "from preliminary data it appears that the magnitudes of J_{P-P} in *cis* and *trans* complexes of the type $Mn(CO)_3L_2X$ (X = Cl, Br, I) are approximately equal"[78]. However, crude calculations of J_{P-P} for the complexes *cis*- and *trans* - $PhCOMn(CO)_3L_2$ [L = $P(OCH_2)_3CEt_3$] gave values of 5 ± 2 and 70 ± 20 Hz, respectively[79]. This latter result may be due to to some special feature of the constrained phosphite or to an incorrect analysis of the data. Since $N(\sim J_{P-H})$ for *fac*-$Mn(CO)_3[P(OMe)_3]_2Br$ is the same as N for *trans*-$Mn(CO)_3[P(OMe)_3]_2Br$ and since a "1:2:1 triplet" was obtained for the *fac* complex*, a large value for J_{P-P} is anticipated for *cis* phosphites in manganese complexes.

The complex *cis*-$Mn(CO)_2[P(OMe)_3]_3Br$ gives a five-line NMR spectrum which has to analysed as a $[AX_n]_2[BR_n]$ spin system.

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* A 1:2:1 triplet like resonance was also obtained for the complexes $C_5H_5Mn(L)[P(OMe)_3]_2$ (L = CO, CS) (*vide infra*, p. 192).

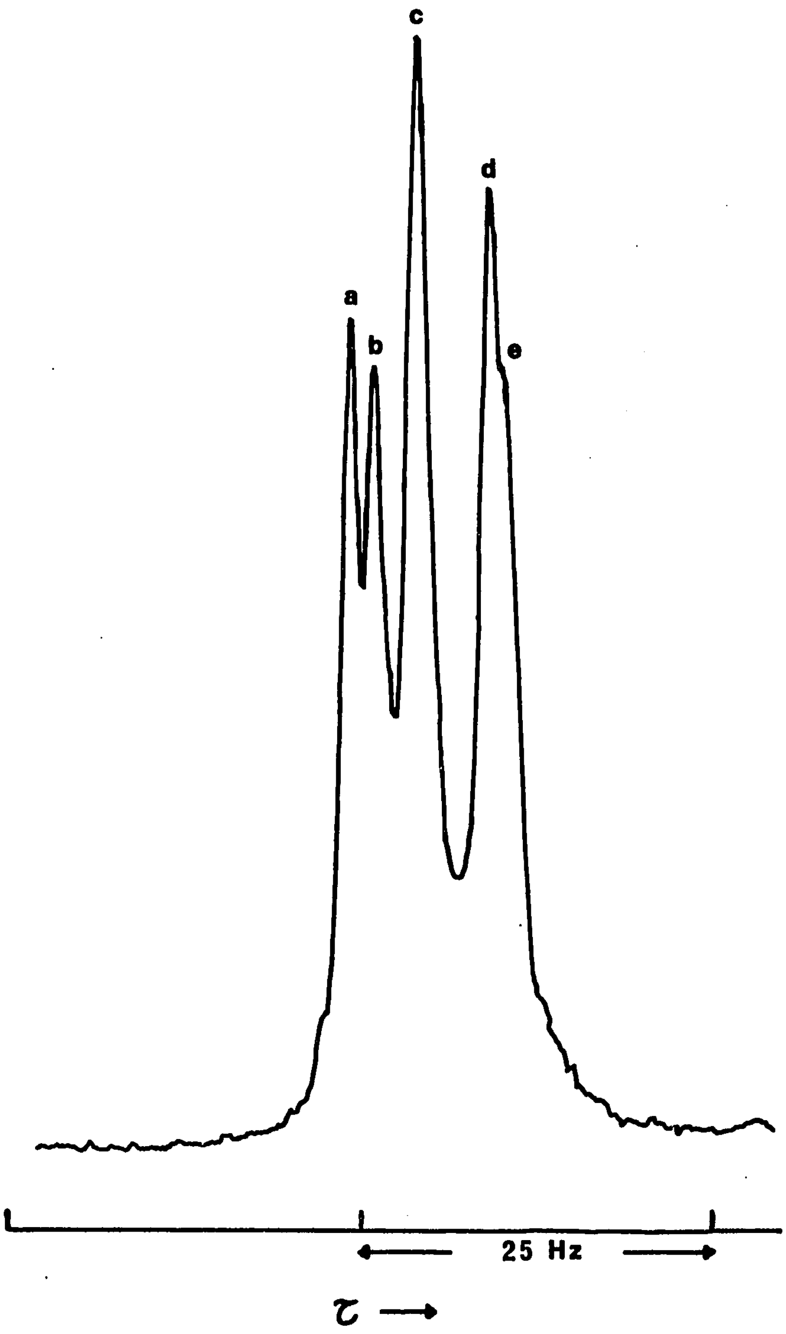

FIGURE III-2 100 MHz NMR SPECTRUM OF *cis*-$Mn(CO)_2[P(OMe)_3]_3Br$

Unfortunately, no analysis of this complicated spin system has been reported. However, spectra for complexes of this type have been reported[80] and in many instances "deceptively simple" spectra have been recorded. In these spectra, the X region shows a "doublet" while the R region shows a "triplet"[76]. The five line spectrum, Figure III-2,can similarly be interpreted as arising from a "triplet" (peaks (a), (c), (d); N = 10.0) and a "doublet" (peaks (b) and (e); N ∿ 9.5).

In summary, the NMR spectra do not distinguish between the *fac*- and *trans*-isomers of $Mn(CO)_3[P(OMe)_3]_2Br$* . Thus, information obtained from these spectra is of little help in interpreting the spectrum of *cis*-$Mn(CO)_2[P(OMe)_3]_3Br$. Even though the dicarbonyl NMR spectrum is consistent with the spectra of other similar complexes, it seems that NMR may be of limited use in determining the stereochemistry of this type of complex.

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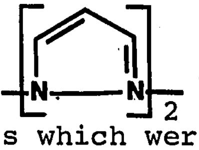
* This point has not been appreciated by some research groups. For instance[52], the appearance of a 1:2:1 triplet in the complex $Mn(CO)_2[P(OMe)_3]_2(Bz)$ ($Bz=H_2B$–



)was interpreted as arising from phosphite ligands which were *trans* to each other, even though other chemical information suggests that the phosphite ligands should be *cis* to each other. The authors assumed that *cis* phosphites would give a doublet resonance for the methoxy protons.

CONCLUSION

This study indicates that the dicarbonyl complexes *cis*-$Mn(CO)_2(P\text{-}P\text{-}P)X$ and *cis*-$Mn(CO)_2(L)(P\text{-}P)X$ (L = group VA donor) can be easily synthesized from $Mn(CO)_5X$ and polyphosphines. Since steric requirements do seem to be important in the formation of these halodicarbonyl complexes, chelate effects could contribute to their formation.

In addition, the reaction of $Mn(CO)_5X$ with $P(OMe)_3$ has been re-investigated and the two isomers, *fac*- and *trans*-$Mn(CO)_3[P(OMe)_3]X$ were isolated. The NMR spectra of these complexes both exhibit 1:2:1 triplets for the methoxy resonance. Thus, NMR alone cannot be used to decide between the two configurations.

CHAPTER IV SYNTHESIS AND REACTIONS OF $Mn(CO)_3(Triphos)X$*

(X = Cl, Br, I)

INTRODUCTION

Reactions involving the use of triphosphine ligands in substitution reactions of metal carbonyls have been limited in the past by the availability of the ligand. Thus, until late 1971, the only ligands studied were Triphos-U e.g., $[(C_5H_5)_2Mn_2(CO)(NO)_2(Triphos\text{-}U)][PF_6]_2$ [83], $(C_5H_5)_2V_2(CO)_5(Triphos\text{-}U)$[84], $M(CO)_3(Triphos\text{-}U)$ for M = Mo, Cr, W[85]; TP e.g., $Mn(CO)_3(TP)Br$[32], $Ru(CO)_2(TP)$[86]; EP e.g., $Mo(CO)_3(EP)$[85]; $PhP(CH_2CH_2CH_2PPh_2)_2$, e.g., $Rh[PhP(CH_2CH_2CH_2PPh_2)_2]Cl\cdot CO$[87] and Triphos e.g., $Mo(CO)_3(Triphos)$[85].

However, the new preparative techniques developed by King and Kapoor[6] last year (*vide supra*, p.12) have resulted in the preparation of triphosphine ligands in high yields by simple techniques. Furthermore, a number of new complexes involving these ligands have now been reported.

In Chapter III, the reaction of the tri-tertiary phosphine $PhP(CH_2CH_2PPh_2)_2$ (Triphos) with the halopentacarbonyl manganese(I) complexes $Mn(CO)_5X$ (X = Cl, Br, I) to form the halodicarbonyl complexes $Mn(CO)_2(Triphos)X$ was discussed.

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* This work has been published in part[82].

It was pointed out that these reactions were slow enough for the intermediate complexes $Mn(CO)_3(Triphos)X$ to be isolated and characterized. The Triphos ligand in these complexes is coordinated to the manganese atom through only two of its three phosphorus atoms.

In this chapter, the experimental details of these reactions are presented. The reactions of these "monodentate phosphine ligands" with various metal carbonyls,to produce a new class of Triphos complexes in which the Triphos ligand acts as a bimetallic triligate ligand, e.g., $Br(CO)_3Mn(Triphos)Cr(CO)_5$, are also given.

The reactions of phosphine oxides [$Ph_3P{=}O$, $(\underline{n}\text{-}Bu)_3P{=}O$] and $Ph_3P{=}S$ with $Mn(CO)_5X$ (X = Br, I) are also described.

EXPERIMENTAL

The ligands were used as purchased, without further purification.

All preparative reactions were carried out under an atmosphere of nitrogen using dry, degassed, reagent-grade solvents. The air-stable reaction products were dried *in vacuo* (25°/0.01 mmHg) for 24 h. Details of the physical techniques used to identify and characterize the new complexes have already been described (*vide supra*, p.39).

Analytical data and CO stretching frequencies for all the new complexes are given in Tables IV-1 and IV-2, respectively.

Preparation of the Triphos Complexes

fac-Mn(CO)$_3$(Triphos)X (X = Cl, Br, I)

A mixture of the appropriate Mn(CO)$_5$X complex (1 mmol) and Triphos (1 mmol) was dissolved in chloroform (25 ml) and the solution was maintained at reflux until the IR spectrum indicated that all of the starting material had reacted (1-6 h). The reaction mixture was then filtered and the solvent volume was reduced to about 5 ml on a rotary evaporator. Addition of *n*-hexane (40 ml) afforded a yellow product which was filtered off and then recrystallized from a chloroform/*n*-hexane mixture.

Thin layer chromatography of the products revealed that they were in fact mixtures of *two* compounds. However, complete separation on a preparative scale was only successful in the case of the iodo complex (chromatography on a silica gel column using a 1/1 acetone/*n*-hexane mixture as eluent). Separation was achieved for the bromo complex on a silica gel preparative thin layer chromatography plate eluted with benzene,but with difficulty.

α-I(CO)$_3$Mn(Triphos)Mn(CO)$_4$I

A dichloromethane solution (15 ml) containing Mn(CO)$_5$I (1 mmol) and Triphos (0.5 mmol) was refluxed for 12 h. At this stage, the relative intensities of the CO stretching absorptions in the IR spectrum of the reaction mixture remained constant. The solution was filtered and then reduced in volume on a rotary evaporator to about 5 ml. Separation of the desired product from the starting materials was accomplished by preparative thin layer chromatography (silica gel plates/ benzene eluent). Three components were isolated - the required product being the second eluted. Purification of the product was achieved by recrystallization from a chloroform/n-hexane mixture.

α- and β-$Br(CO)_3Mn(Triphos)Mn(CO)_4Br$

An equimolar mixture of $Mn(CO)_5Br$ and *fac*-$Mn(CO)_3(Triphos)Br$ in dichloromethane (15 ml) was maintained at reflux until no further changes took place in the IR spectrum (CO stretching region) of the reaction mixture (∿10 h). The solvent was then removed under reduced pressure and the two products were isolated by preparative thin layer chromatography (silica gel plates eluted with benzene). These products were recrystallized from dichloromethene/n-hexane mixtures.

Reaction of $Mn(CO)_5Br$ (1 mmol) with Triphos (0.5 mmol) in refluxing dichloromethane (20 ml) for 12 h also afforded the two desired products. These products were isolated and purified as described above.

α- and β-$Br(CO)_3Mn(Triphos)M(CO)_5$ (M = Cr, Mo)

First, the $M(CO)_5THF$ complexes were prepared *in situ* by irradiation of a tetrahydrofuran (THF) solution (100 ml) of $M(CO)_6$(10 mmol) with a 100 W Hanovia UV lamp for 12 h.

fac-Mn(CO)$_3$(Triphos)Br (0.12 mmol) was then added to the yellow solutions and the mixtures were stirred for 12 h. (M = Cr, at room temperature; M = Mo, at 60°C). After filtration, solvent was removed from the reaction mixtures on a rotary evaporator. Excess metal hexacarbonyl was removed from the crude products by sublimation (40°C/0.01 mmHg). Elution with benzene on silica gel thin layer chromatography plates gave the required products which were then recrystallized from dichloromethane/n-hexane mixtures.

The reaction of *fac*-Mn(CO)$_3$(Triphos)Br with Cr(CO)$_4$(C$_7$H$_8$) in dichloromethane solution also yielded the bimetallic complexes but in very small amounts (<5%). However, reaction of *fac*-Mn(CO)$_3$(Triphos)Br with Cr(CO)$_6$ in chloroform solution at 60°C for 24 h gave no new products.

α- and β-I(CO)$_3$Mn(Triphos)Mo(CO)$_5$

A tetrahydrofuran solution (100 ml) of Mo(CO)$_6$ (10 mmol) was irradiated with a 100 W Hanovia UV lamp for 12 h. *fac*-Mn(CO)$_3$(Triphos)I (0.2 mmol) was added to the resulting solution which contained Mo(CO)$_5$THF. This mixture was stirred for 12 h. at 60°C. Following filtration, the solvent was removed under reduced pressure. Excess Mo(CO)$_6$ was removed from the solid residue by sublimation (40°/0.01 mmHg) . The crude product was chromatographed on a silica gel column using a 1/1 acetone/n-hexane mixture as eluent. Two complexes were separated; the one with the smaller R$_f$ value (β-isomer) was only obtained in milligram quantities and so only its IR spectrum could be recorded. The other complex (α-isomer) was recrystallized from a dichloromethane/n-hexane mixture.

The reaction of *fac*-$Mn(CO)_3(Triphos)I$ with $Cr(CO)_5THF$ was investigated on a spectroscopic scale under the same experimental conditions described above. The two resulting isomers were characterized by their IR spectra in the CO stretching region and their movement on a thin layer plate.

α- and β-$Br(CO)_3Mn(Triphos)Mn(C_5H_5)(CO)_2$

A mixture of $C_5H_5Mn(CO)_2(C_8H_{14})$ (0.3 mmol) and *fac*-$Mn(CO)_3(Triphos)Br$ (0.25 mmol) in chloroform (15 ml) was refluxed for 12 h. The resulting solution was filtered and the solvent was removed under reduced pressure. The crude product remaining was chromatographed on silica gel thin layer plates with benzene as eluent. The two products obtained were recrystallized from dichloromethane/n-hexane mixtures.

fac-$Mn(CO)_3(Triphos{=}o)C\ell \cdot 1/2CHCl_3$

A chloroform solution (25 ml) of $Mn_2(CO)_{10}$ (1 mmol) and Triphos (1 mmol) was refluxed until no further change occurred in the IR spectrum (∿4 days). During this time, much decomposition had occurred. After filtration, the solvent volume was reduced to 5 ml on a rotary evaporator. The solution was then eluted on silica gel thin layer plates using a 1/2 acetone/n-hexane mixture as eluent. The desired product was removed from the plates and then crystallized from a dichloromethane/n-hexane mixture.

fac-$Mn(CO)_3(Triphos{=}O)X$ (X = Br, I)

fac-$Mn(CO)_3(Triphos)X$ (1 mmol) was dissolved in dichloromethane (15 ml) and ozone (1.5 mmol) was bubbled through the solution. The solvent was then removed under reduced pressure and the resulting yellow material was chromatographed on a preparative silica gel thin layer plate with chloroform as eluent. The products obtained were recrystallized from dichloromethane/n-hexane mixtures.

$Br(CO)_2[P(OMe)_3]Mn(Triphos)Cr(CO)_5$

$Cr(CO)_5THF$ was prepared *in situ* by irradiation of $Cr(CO)_6$ (10 mmol) in tetrahydrofuran (100 ml) with a Hanovia 100 W UV lamp for 3 h. The halodicarbonyl complex, $Mn(CO)_2[P(OMe)_3](Triphos)Br$, (0.2 mmol) was added to the solution and the mixture was stirred at room temperature for 12 h. The solvent was then removed under reduced pressure and the crude product was eluted on thin layer chromatography plates with a 1/2 acetone/n-hexane mixture. The two products which separated were recrystallized from a dichloromethane/n-hexane mixture.

Preparation of the Diphos Complexes

Two previously unreported Diphos complexes were prepared for comparative spectral studies.

TABLE IV-1

ANALYTICAL DATA FOR THE NEW MANGANESE(I) COMPLEXES

Complex	Colour	Yield (%)	Decomp (°C)	Analysis found (calcd.) (%)			
				C	H	P	X
fac-Mn(CO)$_3$(Triphos)Cl[a]	yellow	45	97-100	62.7 (62.7)	4.8 (4.7)	13.6 (13.1)	
fac-Mn(CO)$_3$(Triphos)Br[a,b]	yellow	68	127-130	57.9 (59.0)	4.5 (4.4)	12.1 (12.3)	11.0 (10.6)
α-*fac*-Mn(CO)$_3$(Triphos)I	yellow	60	∿85	55.3 (55.5)	4.1 (4.2)	11.5 (11.6)	
β-*fac*-Mn(CO)$_3$(Triphos)I	yellow	10	∿145	55.7 (55.5)	4.1 (4.2)	11.4 (11.6)	
fac-Mn(CO)$_3$(Triphos=O)Cl$\cdot\frac{1}{2}$CHCl$_3$	yellow	20	-	57.3 (56.7)	5.0 (4.3)	11.3 (11.7)	
fac-Mn(CO)$_3$(Triphos=O)Br[c]	yellow	75	∿110	57.4 (57.8)	4.6 (4.3)	11.9 (12.1)	11.5 (10.4)
fac-Mn(CO)$_3$(Triphos=O)I	yellow	75	102-106	54.6 (54.4)	4.3 (4.1)	11.4 (11.4)	15.1 (15.6)
α-Br(CO)$_3$Mn(Triphos)Cr(CO)$_5$	yellow	30	96-100	54.0 (53.4)	3.4 (3.5)	9.8 (9.8)	
β-Br(CO)$_3$Mn(Triphos)Cr(CO)$_5$	orange	30	∿85	53.6 (53.4)	3.5 (3.5)	10.0 (9.8)	
α-Br(CO)$_3$Mn(Triphos)Mo(CO)$_5$	yellow	20	96-100	50.2 (51.0)	4.0 (3.4)	8.8 (9.4)	8.1 (8.1)

Table IV-1 (continued)

β-Br$(CO)_3$Mn(Triphos)Mo$(CO)_5$	yellow	20	94-98	51.0 (51.0)	3.3 (3.4)	8.4 (9.4)	8.6 (8.1)
α-I$(CO)_3$Mn(Triphos)Mo$(CO)_5$	yellow	75	99-105	48.1 (48.7)	3.2 (3.2)	8.7 (9.0)	12.5 (12.3)
α-Br$(CO)_3$(Triphos)Mn$(CO)_4$Br	yellow	25	∿158	49.6 (49.2)	3.7 (3.3)	9.8 (9.3)	15.2 (16.0)
β-Br$(CO)_3$(Triphos)Mn$(CO)_4$Br	yellow	25	∿160	49.4 (49.2)	3.8 (3.3)	9.4 (9.3)	
α-I$(CO)_3$(Triphos)Mn$(CO)_4$I	yellow	35	∿168	45.8 (45.0)	3.5 (3.0)		21.7 (23.2)
α-Br$(CO)_3$(Triphos)Mn$(C_5H_5)(CO)_2$	yellow	30	105-110	57.4 (56.9)	4.9 (4.1)	9.5 (10.0)	
β-Br$(CO)_3$(Triphos)Mn$(C_5H_5)(CO)_2$	yellow	30	∿108	57.6 (56.9)	4.7 (4.1)	9.6 (10.0)	
α-Br$(CO)_2$[P$(OMe)_3$]Mn(Triphos)Cr$(CO)_5^d$	yellow	25	∿95	51.3 (50.8)	4.1 (4.1)		
β-Br$(CO)_2$[P$(OMe)_3$]Mn(Triphos)Cr$(CO)_5^d$	orange	25	∿93	50.8 (50.8)	4.2 (4.1)		
fac-Mn$(CO)_3$(Diphos)Cl	yellow	45	168-172	59.7 (60.8)	4.5 (4.2)		
$[Mn(CO)_4Br]_2$(Diphos)	orange	35	178-184	45.2 (45.8)	2.5 (2.7)		

---

a) Mixture of α- and β-isomers (b) Mn (%): Found (calcd.) 7.53 (7.29) (c) Conductivity in CH_3NO_2 at 21°C (1 x 10^{-3} M): Λ_m = 2.52 $cm^{-1}\Omega^{-1}M^{-1}$ (d) The C and H analyses for these complexes were performed in our laboratory on a Hewlett-Packard Model 185 CHN analyser.

fac-$Mn(CO)_3(Diphos)Cl$

A dichloromethane solution (20 ml) containing $Mn(CO)_5Cl$ (1 mmol) and Diphos (1.2 mmol) was stirred at room temperature for 1 h. The solvent was then removed under reduced pressure and the resulting yellow crystals were washed with n-hexane. Recrystallization from a dichloromethane/n-hexane mixture afforded the pure product.

cis-$[Mn(CO)_4Br]_2(Diphos)$

A mixture of $Mn(CO)_5Br$ (2 mmol) and Diphos (1 mmol) in dichloromethane (20 ml) was refluxed for 1 h. Removal of solvent under reduced pressure afforded the crude product which was then chromatographed on a silica gel column using benzene as eluent. Two products were separated - the one with the smaller R_f value was *fac*-$Mn(CO)_3(Diphos)Br$ (identified by comparison of its IR spectrum with that of an authentic sample), the other was the desired product which was then recrystallized from a chloroform/n-hexane mixture.

RESULTS AND DISCUSSION

The halopentacarbonylmanganese(I) complexes, $Mn(CO)_5X$ (X = Cl, Br, I), react with Triphos in refluxing chloroform solution to produce $Mn(CO)_3(Triphos)X$ in good yield. The potentially tridentate Triphos ligand is believed to be coordinated to the manganese atom in these complexes through only two of its three phosphorus atoms. The appearance of three strong CO stretching absorptions in their IR spectra (Table IV-2) strongly suggests a *fac* stereochemistry for the three CO groups[87].

As expected, monitoring the reactions by IR spectroscopy indicated that they proceed *via* the formation of a tetracarbonyl intermediate. In the case of the iodo complex, it was possible to isolate in milligram amounts a complex of the type $[Mn(CO)_4I]_n$(Triphos) (n = 1 or 2) whose IR spectrum in the CO stretching region corresponded closely to that of $[Mn(CO)_4Br]_2$(Diphos). All attempts to isolate any other reaction intermediates failed. The IR spectra of the final halotricarbonyl products are virtually identical to that of *fac*-$Mn(CO)_3$(Diphos)Cl.

The reactions most probably proceed with initial replacement of one CO group in $Mn(CO)_5X$ by Triphos followed by chelate formation and the expulsion of another CO group*.

---

* The reactions proceed with replacement of a CO group in $Mn(CO)_5X$ by either a terminal or non-terminal P atom of the polyphosphine. Since the substitution reactions of $Mn(CO)_5X$ by phosphines have been shown to proceed by a dissociative mechanism[88], the steric and/or basicity requirements of the respective P atoms are thought to have little effect on the reaction path. However, since there are two terminal P atoms and only one non-terminal P atom in Triphos, the reaction is statistically favoured to proceed *via* initial reaction of a terminal P atom.

Table IV-2 IR SPECTRA IN THE CO STRETCHING REGION OF THE NEW TRIPHOS COMPLEXES (CH$_2$Cl$_2$ SOLUTION)

COMPLEX	ν(CO) (cm^{-1})^a			
fac-Mn(CO)$_3$(Triphos)Cl^b	2024	1955	1911	
α-*fac*-Mn(CO)$_3$(Triphos)Br^{b,c}	2022	1953	1917	
β-*fac*-Mn(CO)$_3$(Triphos)Br^{b,c}	2022	1955	1910	
α-*fac*-Mn(CO)$_3$(Triphos)I	2015	1949	1918	
β-*fac*-Mn(CO)$_3$(Triphos)I	2015	1949	1913	
fac-Mn(CO)$_3$(Triphos=O)Cl^d	2024	1954	1915	
fac-Mn(CO)$_3$(Triphos=O)Br^{d,e}	2022	1953	1917	
fac-Mn(CO)$_3$(Triphos=O)I^d	2018	1952	1915	
α-Br(CO)$_3$Mn(Triphos)Cr(CO)$_5$	2063w	2022m	1981sh	1940vs
β-Br(CO)$_3$Mn(Triphos)Cr(CO)$_5$	2064w 1914sh	2024m	1982sh	1935vs
α-I(CO)$_3$Mn(Triphos)Cr(CO)$_5$	2062w 1923sh	2018m	1980w	1938vs
β-I(CO)$_3$Mn(Triphos)Cr(CO)$_5$	2064w 1917sh	2019m	1978w	1937vs
α-Br(CO)$_3$Mn(Triphos)Mo(CO)$_5$	2073w	2022	1943vs	1924sh
β-Br(CO)$_3$Mn(Triphos)Mo(CO)$_5$	2074w	2024	1945vs	1916sh
α-I(CO)$_3$Mn(Triphos)Mo(CO)$_5$	2083vw 1935sh	2073	2019	1945br
β-I(CO)$_3$Mn(Triphos)Mo(CO)$_5$	2083vw 1919	2073	2017	1948br
α-Br(CO)$_3$Mn(Triphos)Mn(CO)$_4$Br	2091m 1918	2022	2011	1956
β-Br(CO)$_3$Mn(Triphos)Mn(CO)$_4$Br	2091m 1913	2022	2012	1957
α-I(CO)$_3$Mn(Triphos)Mn(CO)$_4$I	2084m 1919m	2019	2004sh	1955
α-Br(CO)$_3$Mn(Triphos)Fe(CO)(NO)$_2$^{f}	2022	2002sh	1954	1918
β-Br(CO)$_3$Mn(Triphos)Fe(CO)(NO)$_2$^{f}	2023	2002sh	1956	1914
α-Br(CO)$_3$Mn(Triphos)Mn(π-C$_5$H$_5$)(CO)$_2$	2022	1952	1923	1859
β-Br(CO)$_3$Mn(Triphos)Mn(π-C$_5$H$_5$)(CO)$_2$	2022 1862	1954	1929	1915
α-Br(CO)$_2$[P(OMe)$_3$]Mn(Triphos)Cr(CO)$_5$	2061w 1873	1979sh	1944sh	1936vs
β-Br(CO)$_2$[P(OMe)$_2$]Mn(Triphos)Cr(CO)$_5$	2062w 1872	1980sh	1944sh	1935vs
[Mn(CO)$_4$I]$_n$(Triphos)^g	2080	2014	1997	1952

Table IV-2 (continued)

[a] The bands are strong in every case except where otherwise stated; s = strong, w = weak, v = very, sh = shoulder, br = broad. Precision: ± 1-2cm^{-1}.

[b] Compare with the spectra of the related *fac*-Mn(CO)$_3$(Diphos)X complexes: X = Cl, 2025s, 1957s, 1915s; X = Br, 2022s, 1956s, 1915s cm^{-1}(CH_2Cl_2 solution).

[c] ^{1}H NMR CH_2Cl_2 solution; TMS as internal standard (τ 10 ppm); Varian Associates A-60 spectrometer for the isomeric mixture: τ 2.75 (complex multiplet), Ph; τ ∿ 7.5 (broad), CH_2.

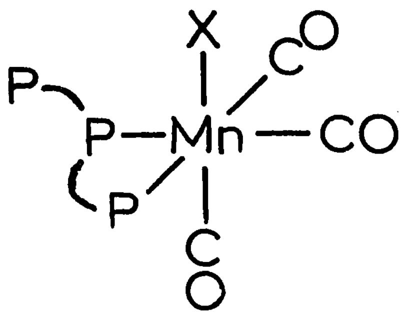
[d] These complexes show a number of peaks in the 1200-400 cm^{-1} region consistent with phosphine oxides (see Table IV-4).

[e] ^{1}H NMR: τ 2.58 (complex multiplet), Ph; τ ∿ 7.5 (broad), CH_2.

[f] ν_{NO}: 1762s, 1716s cm^{-1} (α); 1760s, 1714s cm^{-1} (β).

[g] Compare with the spectrum of $[Mn(CO)_4Br]_2$(Diphos): 2091s, 2018s 2005s, 1960s cm^{-1} (CH_2Cl_2 solution).

Therefore, the most likely structure for *fac*-Mn(CO)$_3$ (Triphos)X is as shown below (the methylene and the phenyl groups of the Triphos ligand have been omitted for the sake of clarity).



Thin layer chromatography of the *fac*-Mn(CO)$_3$(Triphos)X complexes revealed that they were mixtures of two compounds. Although complete separation of the compounds was achieved for the iodo complex, the separations for the chloro and bromo complexes proved difficult. Elemental analyses for the various compounds are in accord with the molecular formula Mn(CO)$_3$ (Triphos)X (Table IV-1). Moreover, the IR spectra (Table IV-2) are almost identical. In view of these results, it is felt that each pair of compounds are in fact isomers of *fac*-Mn(CO)$_3$ (Triphos)X.

In Chapter II, (*vide supra*, p.31) the possible isomers for the general reaction of a metal atom (or atoms) with Triphos were enumerated. When Triphos acts as a monometallic bidentate ligand, and M_a = $Mn(CO)_5X$, six isomers are possible (three sets of mirror images). The isomer, B2, can be ruled out on a number of grounds.

The formation of *fac*-$Mn(CO)_3$(Triphos)X proceeds *via* the formation of the intermediate *cis*-$Mn(CO)_4$(Triphos)X. In the case of the intermediate, in which Triphos is bonded through a terminal P atom, the central P atom of the linear polyphosphine would be held much closer to the manganese atom than the other terminal P atom. Thus, further reaction of the ligand with the manganese atom would favour this central P atom. Furthermore, formation of a five-membered chelate ring in *fac*-$Mn(CO)_3$(Triphos)X should also be preferable compared to the larger eight-membered chelate ring. If the reaction path to the *fac* isomer involves formation of *cis*-$Mn(CO)_4$(Triphos)X in which Triphos is bonded through the central P atom, isomer B2 cannot be formed.

Thus, two isomers (diastereomers) of B1 together with their mirror images are still expected. Molecular models confirm that these two diastereomers are possible for *fac*-$Mn(CO)_3$(Triphos)X and differ only in the orientation of the phenyl group attached to the central phosphorus atom of the Triphos ligand with respect to X. In one case this phenyl group can be regarded as *trans* to X, while in the other it is *cis*. A somewhat related type of isomerism has been described recently for platinum and palladium complexes of $Me(Ph)AsCH_2CH_2As(Ph)Me$[89].

The coordinated Triphos in *fac*-$Mn(CO)_3$(Triphos)X displaces a third CO group to give $Mn(CO)_2$(Triphos)X (Chapter III). Only two isomers are expected (type C1), since the mirror images of the respective diastereomers are superimposable. These isomers are again related to the orientation of the phenyl ring relative to the halogen. Even though the isomeric mixture of *fac*-$Mn(CO)_3$(Triphos)X was used to prepare the dicarbonyl complexes, no separation of the dicarbonyl diastereomers was achieved.

The *fac*-$Mn(CO)_3$(Triphos)X complexes can be regarded as potentially "monodentate phosphine ligands" and should therefore undergo typical substitution reactions with metal carbonyls. Indeed, reaction of the isomeric mixtures of the *fac*-$Mn(CO)_3$(Triphos)X complexes with $Cr(CO)_5THF$, $Mo(CO)_5THF$, $Mn(CO)_5Br$, and $C_5H_5Mn(CO)_2(C_8H_{14})$ gave rise to a new series of bimetallic complexes, *viz.*, $X(CO)_3Mn$(Triphos)$Cr(CO)_5$, $X(CO)_3Mn$(Triphos)$Mo(CO)_5$, $X(CO)_3Mn$(Triphos)$Mn(CO)_4X$, and $X(CO)_3Mn$(Triphos)$Mn(C_5H_5)(CO)_2$ respectively. It should be emphasized here that these reactions were carried out under *mild* conditions so that there was no chance of forming the halodicarbonyl complexes, $Mn(CO)_2$(Triphos)X (*vide supra*, p.46). Other known examples of this type of bimetallic complex are the cobalt-iron complexes, $(NO)(CO)_2Co$(Diphos)$Fe(CO)(NO)_2$[39] and $C_5H_5Fe(CO)_2$(Diphos)$CoCl_2^+$[90].

As anticipated, the new bimetallic complexes are in fact mixtures of two isomers which can readily be separated by thin layer chromatography. The IR spectra in the CO stretching region of each pair of isomers are very similar (Table IV-2) and are essentially superpositions of the spectra of *fac*-$Mn(CO)_3$(Triphos)X and the appropriate metal carbonyl starting material. Again, it is felt that the stereochemistry of the phenyl group on the central phosphorus atom of the Triphos ligand is responsible for the formation of two different isomers. In the case of α- and β-$Br(CO)_3Mn$(Triphos)$Cr(CO)_5$, X-ray diffraction studies have shown this to be true (*vide infra*, Chapter VI). The phenyl group in the α-isomer is *trans* to Br while it is *cis* in the β-isomer.

Since the α-isomer in this case corresponds to the faster moving of the two isomers on a silica gel thin layer plate, it is *assumed* that this is true for all the other bimetallic complexes which were prepared. This is not an unreasonable assumption when one considers that α-*fac*-$Mn(CO)_3$(Triphos)Br reacts with $Cr(CO)_5$THF to produce only α-$BrMn(CO)_3$(Triphos)$Cr(CO)_5$ (identified by its IR spectrum and its thin layer chromatography R_f value). This reaction also suggests that there is no isomerization to the corresponding β-isomer taking place.

Moreover, in both cases, the three CO groups in the $Br(CO)_3Mn$(Triphos) moiety adopt a *facial* stereochemistry, as would be expected if the original $Mn(CO)_3$(Triphos)Br species has the same stereochemistry, as was suggested earlier.

The ultimate stereochemistry of the unique phenyl group when the Triphos ligand is coordinated to the manganese atom in *fac*-$Mn(CO)_3$(Triphos)X appears to play a role in the relative yields of the two isomers of these complexes. For example, reaction of $Mn(CO)_5Br$ with Triphos affords an approximately 50:50 mixture of α- and β-*fac*-$Mn(CO)_3$(Triphos)Br. However, with $Mn(CO)_5I$, an 85:15 mixture of the α- and β-isomers is obtained. Presumably, steric interaction between the bulky iodine and phenyl groups renders formation of the β-isomer less likely.

The reaction of $Mn(CO)_3$(Triphos)Br and $Fe(CO)_2(NO)_2$ was also studied. A 1:1 mixture of the reactants was stirred in CH_2Cl_2 (in the dark) until the IR spectrum remained unchanged. Elution of the crude material in benzene on a silica gel column gave two air sensitive complexes. These complexes were crystallized from CH_2Cl_2/n-hexane. Although the IR spectra are consistent for the bimetallic complexes , $BrMn(CO)_3$(Triphos) $Fe(CO)(NO)_2$, the elemental analyses were poor (most probably the products decomposed before the analyses were completed). The reaction was not investigated further.

The UV spectra of a series of manganese Triphos complexes were recorded (Table IV-3). There is little, if any, significant difference in the spectra of α- or β-*fac*-$Mn(CO)_3$(Triphos)Br or *fac*-$Mn(CO)_3$(Triphos=O)Br. As noted previously[81], an effect due to the variation of the halogen can be detected - for the dicarbonyl complexes the absorption maximum increases in the order I>Br>Cl.

TABLE IV-3

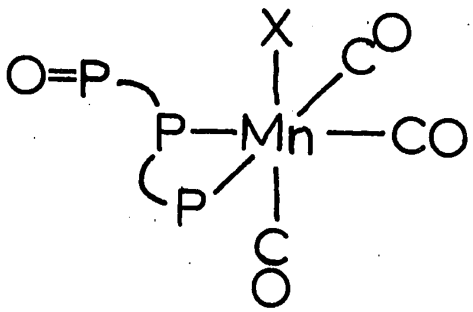
U.V. SPECTRA OF SOME MANGANESE POLYPHOSPHINE COMPLEXES (IN CH_2Cl_2 SOLUTION)

Complex	λ_{max}^{a} (nm)					
fac-$Mn(CO)_3$(Diphos)Cl	383	(1400)				
fac-$Mn(CO)_3$(Diphos)Br	391	(1000)				
α-*fac*-$Mn(CO)_3$(Triphos)Br	390	(1000)				
β-*fac*-$Mn(CO)_3$(Triphos)Br	388	(1100)				
fac-$Mn(CO)_3$(Triphos=O)Br	389	(800)	∿274	sh	∿267	sh
cis-$Mn(CO)_2$(Triphos)Cl	416	(600)	∿355	sh	∿290	sh
cis-$Mn(CO)_2$(Triphos)Br	425	(700)	∿370	sh	∿290	sh
cis-$Mn(CO)_2$(Triphos)I	432	(600)	365	(3700)	292	(9500)

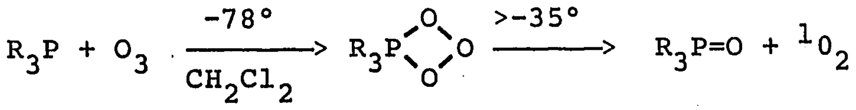
a) Value in brackets is ε_{max} ($l\ mol^{-1}\ cm^{-1}$)

Preparation and Reactions of some Phosphine Oxide Complexes

Reaction of the isomeric mixtures of *fac*-$Mn(CO)_3(Triphos)X$ (X = Br, I) with O_2 (or preferably O_3 because of the cleaner reaction) gave the phosphine oxide complexes *fac*-$Mn(CO)_3(Triphos{=}O)X$. These were characterized by the appearance of new absorptions due to ν(P=O) modes in the 1200-1100 cm^{-1} region).



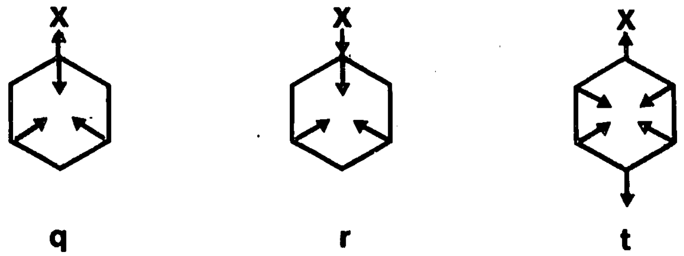
The reaction of phosphines with ozone to give phosphine oxides is well known; the mechanism is shown below:[91]



Presumably, the same mechanism is in operation for the Triphos complexes.

Other characteristic absorptions for the phosphine oxides were detected in the 1200-400 cm^{-1} region of the IR. The spectra of PPh_3 and $Ph_3P{=}O$ (1600-400 cm^{-1} region) have been reported[92] and the major differences in the IR spectra of these complexes have been related to the "X-sensitive" fundamental modes[93], as shown below.

Modes involving P-C stretching:



Modes involving P-C bending:

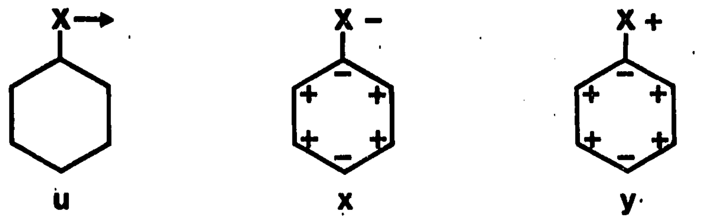


FIGURE IV-1 "X-sensitive" MODES FOR TRIPHENYLPHOSPHINE AND RELATED COMPLEXES. Only the q, r, and y modes were detected in this study.

The spectra for *fac*-$Mn(CO)_3$(Triphos)Br and *fac*-$Mn(CO)_3$(Triphos=O)Br are shown in Figure IV-2. The values for the "X-sensitive" modes (q, r and y) of the complexes α- and β-*fac*-$Mn(CO)_3$(Triphos)X and *fac*-$Mn(CO)_3$(Triphos)X are given in Table IV-4

Apparently, the *facial* stereochemistry of the three CO groups in the original complexes is maintained because there are still three strong CO stretching absorptions observed. The non-ionic formulation of the complexes is supported by the low molar conductance (2.5 $cm^{-1}\ \Omega^{-1}\ M^{-1}$) of the bromo complex in nitromethane solution at 21°C.

Although two diastereomers of the *fac*-$Mn(CO)_3$(Triphos=O)X complexes were expected, only one compound could be separated by thin layer chromatography.

The reaction of $Mn(CO)_5Br$ with *fac*-$Mn(CO)_3$(Triphos)X (at 60° in $CHCl_3$) to give the bimetallic complex was used as a diagnostic test to detect the presence of the un-coordinated P atom. It was anticipated that the corresponding addition of $Mn(CO)_5Br$ to *fac*-$Mn(CO)_3$(Triphos=O)X (at 60° in $CHCl_3$) would give no reaction, since all three P atoms are coordinated and hence unavailable for further reaction. However, the IR spectrum of the $CHCl_3$ solution did show changes over a period of time. Since the changes were unexpected and were unlike the changes recorded for the reaction of *fac*-$Mn(CO)_3$(Triphos)Br with $Mn(CO)_5Br$, an investigation of the reaction of phosphine oxides (and phosphine sulfide) with $Mn(CO)_5X$, (X = Br, I) was undertaken.

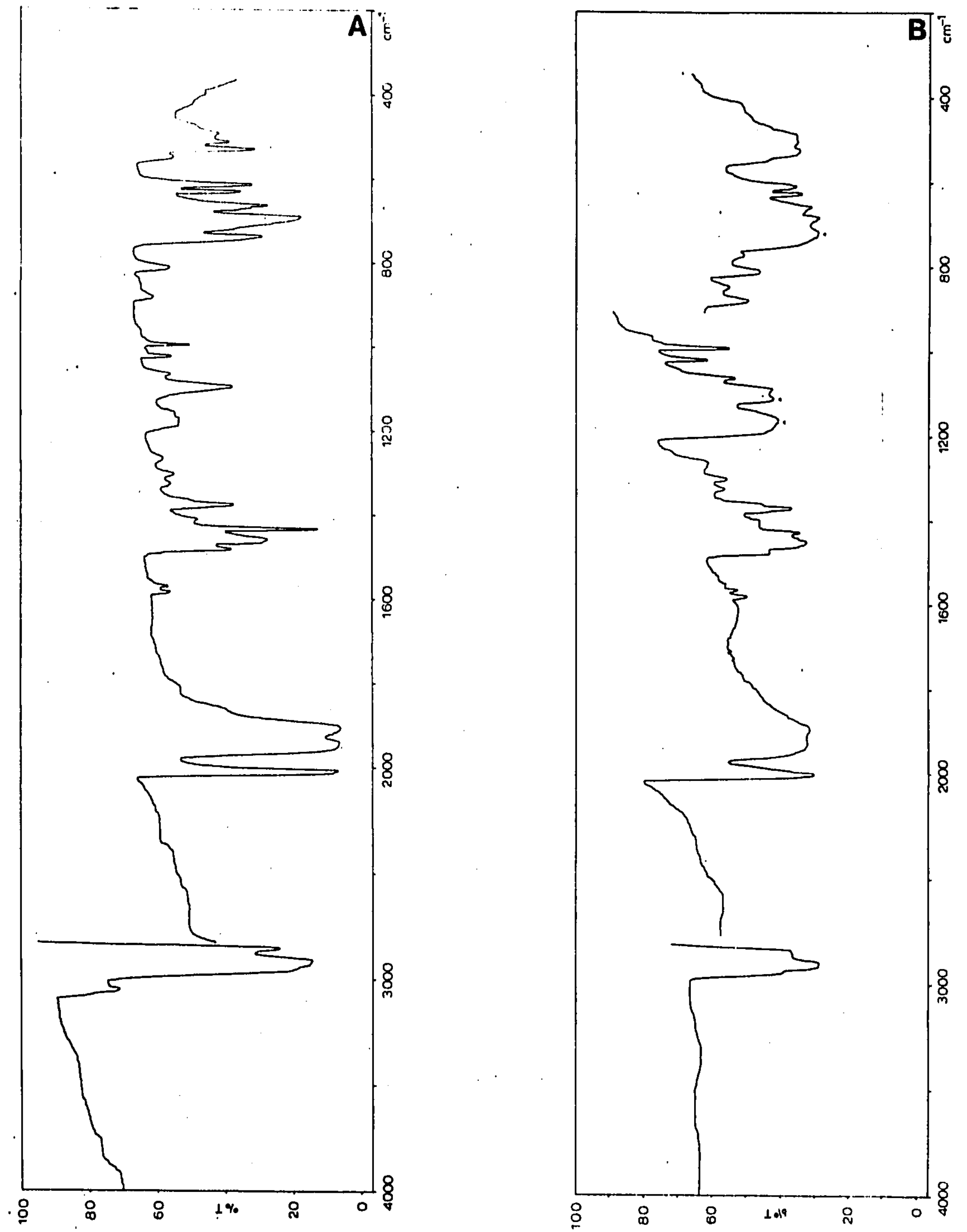


FIGURE IV-2 INFRARED SPECTRA OF (A) *fac*-Mn(CO)$_3$(Triphos)Br (B) *fac*-Mn(CO)$_3$(Triphos=O)Br. The spectra were recorded in nujol.

TABLE IV-4 "X-sensitive" MODES OF THE MANGANESE POLYPHOSPHINE AND MANGANESE POLYPHOSPHINE-OXIDE COMPLEXES

Complex	ν(P=O)	Mode (in Figure IV-1)		
		q	r	y
PPh_3[a]	-	1089(m)	692(vs)	512(s) 497(s) 489(s)
$Ph_3P{=}O$[a]	1193	1122(vs)	721(vs)	542(vs)
fac-Mn(CO)$_3$(Triphos)Br	-	1094(m)	691(vs)	529(s) 512(m) 493(m)
α-*fac*-Mn(CO)$_3$(Triphos)Br	-	1098(m)	691(vs)	?
β-*fac*-Mn(CO)$_3$(Triphos)Br	-	1096(m)	691(s)	?
fac-Mn(CO)$_3$(Triphos=O)Br	1168(s,br)	1120(s) 1095(m)	720(vs) 690(vs)	530(s) 510(s,br)
α-*fac*-Mn(CO)$_3$(Triphos)I	-	1097(m)	694(s)	534(s) 518(m)
β-*fac*-Mn(CO)$_3$(Triphos)I	-	1096(s)	694(vs)	530(s) 515(s) 498(sh)
fac-Mn(CO)$_3$(Triphos=O)I	1175(s,br)	1120(s)	728(br,s) 692(s)	538(s) 515(s) 495(sh)
fac-Mn(CO)$_3$(Tetraphos)Br	-	1094(s)	691(vs)	528(s) 510(m) 493(m)
fac-Mn(CO)$_3$(Tetraphos=O$_n$)Br	1187(s)	1117(m) 1096(m)	723(s) 692(vs)	532(m) 514(m) 496(m)
cis-Mn(CO)$_2$(Tetraphos)Br	-	1096(s)	710(sh)	541(w) 526(sh) 515(m) 486(br)
cis-Mn(CO)$_2$(Tetraphos=O)Br	1193(s)	1119(m) 1098(s)	723(s)	543(sh) 537(s) 515(s) 492(m)
cis-Mn(CO)$_2$(Tetraphos)I	-	1095(s)	693(s)	?
cis-Mn(CO)$_2$(Tetraphos=O)I	1185(s)	1119(s) 1098(s)	721(s)	535(m) 513(m)
cis-Mn(CO)$_2$[P(OMe)$_3$] (Triphos)	-	1096(w)	720(w) 696(s)	520(s)
cis-Mn(CO)$_2$[P(OMe)$_2$] (Triphos=O)Br	1180(vs)	1121(s) 1095(m)	723(sh) 695(s)	539(m) 512(m)

a) Data taken from Ref. 92

Attempts to isolate the reaction products of these reactions by thin layer chromotography met with limited success. The IR data, together with other relevant data for the "purified" complexes are given in Table IV-5.

TABLE IV-5 REACTIONS OF $Mn(CO)_5X$ WITH PHOSPHINE OXIDES $R_3P{=}O$, (R=Ph, n-Bu) AND A PHOSPHINE SULFIDE ($Ph_3P{=}S$)

Reactants	Solvent[a]	Temp.		ν(CO) IR in CH_2Cl_2[b]		
$Mn(CO)_5Br + Ph_3P{=}O$[c]	$CHCl_3$	60°	A[e]:	2036	1944	
			B:	2088 (w)	2019	1979 (w) 1930
$Mn(CO)_5Br + Ph_3P{=}O$[d]	benzene	60°		2046 (m)	2015 (s)	1982 (w)
$Mn(CO)_5Br + (n\text{-}Bu)_3P{=}O$	$CHCl_3$	60°	A:	2049 (vw)	2027	2004 (w) 1928 (vs)
			B:	2088 (w)	2020	1980 (w) 1926 (vs)
$Mn(CO)_5Br + Ph_3P{=}S$	$CHCl_3$	40°		2047 (vw)	2017	1930
$Mn(CO)_5I + Ph_3P{=}O$[f]	$CHCl_3$	60°	A:	2074 (w)	2003	1978 (w) 1935
			B:	2088 (w)	2034	2009 1976

a) reaction time = 72 h. b) all peaks are strong unless stated; w = weak, m = medium, vs = very strong. c) reaction in the absence of light. d) reaction time = 36 h. e) product A has the larger R_f value on a thin layer plate product B, the smaller R_f value. f) IR record in $CHCl_3$.

In chloroform, a slow reaction took place in which the final product(s) showed two strong absorptions in the $\nu(CO)$ region of the IR. As higher yields of products were obtained when the reaction was performed in the absence of light, it is assumed that the reaction is light sensitive.

Reaction of $Ph_3P=O$ with $Mn(CO)_5Br$ gave $Mn_2(CO)_{10}$. The identity of this product was confirmed by its IR spectrum[94] and R_f value on a thin layer plate.

One of the products from the reaction of $Mn(CO)_5I$ and $Ph_3P=O$ was identified as $[Mn(CO)_4I]_2$*. At room temperature in chloroform this dimer is readily converted to the monomer $Mn(CO)_5I$. A similar reaction occurred for the dimer $[Mn(CO)_4Br]_2$** in either benzene or chloroform. The conversion to the monomer took less than 30 minutes.

Recently, Bamford *et al.*[94] reported their studies of the reaction of $Mn(CO)_5X$ (X = Cl, Br) with weak donors and showed that products of the type $Mn(CO)_3Y_2X$ (Y = weak donor) could be formed. Their conclusions were drawn from UV data. Thus, the reaction of $Ph_3P=O$ (a weak donor) with $Mn(CO)_5Br$ to displace CO groups would not be unprecedented.

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* The dimer, $[Mn(CO)_4I]_2$, prepared independently, gave an identical IR spectrum[65].

** This complex was prepared according to the literature method[65].

Analysis of one of the products (A) from the reaction of $Mn(CO)_5Br$ and $Ph_3P=O$ is given below. Apart from bromine, these values are close to those expected for $Mn(CO)_3$ $(Ph_3P=O)_2Br$. The elemental analysis as well as the conductivity (for molecular weight = 775, $\Lambda_m = 2.3\ cm^{-1}\ \Omega^{-1}\ M^{-1}$) thus favour a complex in which the phosphine oxide forms a covalent complex in which two CO groups are displaced from $Mn(CO)_5Br$. The IR data (two strong bands) could possibly indicate a *mer* configuration in which the bromine is *cis* to both $Ph_3P=O$ groups. At this stage, no further conclusions can be drawn about the composition of the products formed in the above reactions. Similarly, the reaction of $Mn(CO)_5Br$ with *fac*-$Mn(CO)_3$(Triphos = O) is presumed to involve displacement of the CO group(s) in $Mn(CO)_5Br$ by the Triphos P=O group but the composition of the final product formed is unknown.

TABLE IV-6 ELEMENTAL ANALYSIS FOR THE PRODUCT (A) FROM THE REACTION OF $Mn(CO)_5Br$ and $Ph_3P=O$

	Calcd. (%)		Found (%)
	$Mn(CO)_3(Ph_3P=O)_2Br$	$Mn(CO)_2(Ph_3P=O)_3Br$	
C	60.4	65.6	62.2
H	3.9	4.4	4.3
P	8.0	9.1	7.8
Br	10.3	7.8	6.0 (± 0.5)

Miscellaneous Reactions

Preliminary reactions with Triphos and $Mn_2(CO)_{10}$ were attempted in chloroform and xylene. The reaction in refluxing chloroform solution yielded one major product, $Mn(CO)_3(Triphos{=}O)Cl\cdot\frac{1}{2}CHCl_3$. Other products were obtained in low yield e.g., $Mn(CO)_2(Triphos)Cl$ which was identified by its IR spectrum. In the absence of light, no reaction took place. The reaction is thought to proceed by a free radical mechanism in which the solvent is the source of the Cl^- ion.

The reaction in xylene (90°) gave a large number of reaction products but all in low yield, as detected by thin layer chromotography. The IR spectra of the products were recorded but no work-up of products was attempted.

In Chapter III, the synthesis of $Mn(CO)_2(Triphos)LX$ (L = tertiary phosphite; X = Cl, Br) was reported. The Triphos ligand in these "mixed ligand" complexes is acting as a bidentate ligand. Consequently, these complexes should also exist in a number of diastereomeric forms. However, thin layer chromatography using various solvents as eluents showed the presence of only one compound. Nevertheless, reaction of $Mn(CO)_2[P(OMe)_3](Triphos)Br$ with $Cr(CO)_5THF$ yielded a mixture of products which could be separated. Since the $P(OMe)_3$ group can be either *cis* or *trans* to the central phosphorus atom of the Triphos ligand, four different diastereomers (together with their four mirror images) are theoretically possible. However, isolation of only two of these expected products, *viz.*, α- and β-$Br(CO)_2[P(OMe)_3]Mn(Triphos)Cr(CO)_5$ (the α-isomer having the larger R_f value in 1/2 acetone/n-hexane) was achieved. In this case both the IR spectra and the decomposition points are virtually identical. Again, the IR spectra are essentially superpositions of the spectra of the two starting materials. It is thought that the difference between these two isomers is related to the difference in orientation of the phenyl ring on the central P atom. Thus, each complex which was isolated could consist of a mixture of the two diastereomers, as shown below.

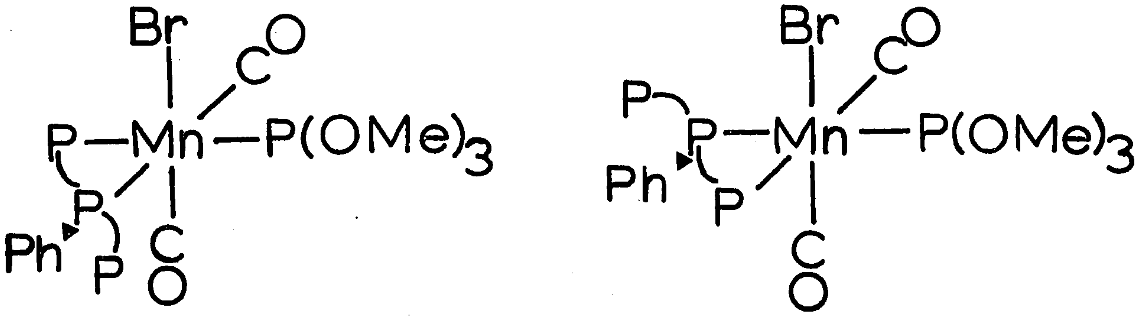

FIGURE IV-3 TWO DIASTEREOMERS OF α-*fac*-$Mn(CO)_2[P(OMe)_3](Triphos)Br$

CONCLUSION

It is apparent that the chemistry of poly-tertiary phosphines such as Triphos is far more complex than was heretofore realized. Not only are the expected substitution products formed with metal carbonyls but in many cases the existence of diastereomers can be demonstrated. Moreover, these diastereomers arise because of the different stereochemical coordination abilities of particular phosphorus atoms.

CHAPTER V REACTION OF TETRAPHOS WITH $Mn(CO)_5X$ (X = Br, I)

INTRODUCTION

In the previous Chapter, the reaction of $Mn(CO)_5X$ (X = Br, I) and Triphos led to the formation of two diastereomers, α- and β-*fac*-$Mn(CO)_3$(Triphos)X. These arose because the central P atom of the ligand became optically active *on bonding* to the manganese atom. A natural extension of this work was to attempt a series of reactions in which the polyphosphine was optically active *before* coordination. The "simplest" phosphine which would meet this requirement and differ as little as possible from Triphos is the linear tetraphosphine ligand, $[Ph_2PCH_2CH_2P^*(Ph)CH_2]_2$ (Tetraphos). In fact, to date, only four tetraphosphines are known: $P(C_6H_4\underline{o}\text{-}PPh_2)_3$ (QP)[32], $(Ph_2PCH_2CH_2)_3P$ (Tetraphos-U)[6], $(Ph_2PCH_2)_4C$ (Tetraphos-Sp)[15] and Tetraphos[6]. Very little work has been reported on the general reactions of these ligands with metal complexes; even less for the reactions with metal carbonyls[26,32,34,86,96-99].

It is assumed that the preparation of Tetraphos by the base-catalysed addition of $Ph_2PCH{=}CH_2$ to $Ph(H)PCH_2CH_2P(H)Ph$[6] (prepared by the cleavage of Diphos with sodium in liquid ammonia) does not give a stereospecific isomer, but rather a mixture of the *meso* and *racemic* isomers (Figure II-5).

A recent communication[100] reported that the diastereomers of an analogous linear tetra-arsine $Me_2As(CH_2)_3As(Ph)CH_2CH_2As(Ph)(CH_2)_3AsMe_2$ can be resolved by reaction with a cobalt salt*. It was thus of interest to determine whether the diastereomers of Tetraphos could be similarly resolved with a metal centre.

As can be appreciated, going from the potentially triligate Triphos ligand to the tetraligate Tetraphos ligand greatly increases the number of possible metal phosphine isomers.

Since chemical restrictions should impose limitations on the total number of isomers which can be formed and thus reduce the complexity of the problem, it was thought that a study of the reaction of $Mn(CO)_5X$ with Tetraphos would provide further confirmation of the arguments presented for the reaction of Triphos and $Mn(CO)_5X$ (X = Br, I).

This Chapter describes the reaction of $Mn(CO)_5X$ (X = Br, I) with Tetraphos to form complexes in which the polyphosphine acts as a monometallic-bidentate, monometallic-tridentate, bimetallic-tridentate and bimetallic-tetradentate ligand.

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[*] See Ref. 101 for the resolution of bidentate arsine ligands by similar techniques.

EXPERIMENTAL

The Tetraphos ligand was used as purchased without further purification. (*nor*-C_7H_8)Mo(CO)$_4$ was prepared by the literature method[102].

All reactions were carried out under an atmosphere of nitrogen. The physical methods of product purification and structure elucidation have been described previously (*vide supra*, p.39 and p.63)

Reaction of Mn(CO)$_5$Br and Tetraphos

A chloroform solution (20 ml) containing Mn(CO)$_5$Br (0.3 mmol) and Tetraphos (0.33 mmol) was refluxed with stirring, until the IR spectrum showed no changes (∿ 30 minutes). The solvent was removed under reduced pressure and the crude product was eluted with benzene on silica gel thin layer plates. Three major products were isolated. The first two of these were the αα isomer (largest R_f value) and αβ isomer of *fac*-Mn(CO)$_3$(Tetraphos)Br. The third product, with the smallest R_f value, was the bimetallic complex [Mn(CO)$_3$Br]$_2$(Tetraphos). This bimetallic complex could be prepared in higher yield with little monometallic product formation, if the above reaction was repeated using a 2/1 Mn(CO)$_5$Br/Tetraphos ratio. The products were crystallized from chloroform/n-hexane mixtures.

Mn(CO)$_2$(Tetraphos)X (X = Br, I)

A xylene solution (40 ml) containing Mn(CO)$_5$X (1 mmol) and

Tetraphos (1 mmol) was stirred at 60° for 1 h. and then at 130° until the IR spectrum remained constant. (∿ 10 h.). Solvent was removed under reduced pressure and the crude product was eluted on silica gel thin layer plates with a 1/1 acetone/n-hexane mixture. The product was crystallized from a chloroform/n-hexane mixture.

cis-$Mn(CO)_2$(Tetraphos=O)X (X = Br, I)

cis-$Mn(CO)_2$(Tetraphos)X (0.1 mmol) was dissolved in dichloromethane (20 ml) and ozone (0.13 mmol) bubbled through the resultant solution. The solvent was then removed under reduced pressure and the crude product was eluted on silica gel thin layer plates with a 2/1 acetone/n-hexane mixture. Crystallization from dichloromethane/n-hexane gave the required product.

$[Br(CO)_3Mn(Tetraphos)]_2Mo(CO)_4 \cdot CHCl_3$

A xylene solution (15 ml) containing (*nor*-C_7H_8)$Mo(CO)_4$ (0.12 mmol) and *fac*-$Mn(CO)_3$(Tetraphos)Br (0.1 mmol) (mixture of αα and αβ isomers) was stirred for 6 h. at 60°. After the solvent had been removed under reduced pressure, the product was crystallized from a chloroform/n-hexane mixture to give the required complex in high yield. Only one isomer was detected.

TABLE V-1 ANALYTICAL DATA FOR THE NEW TETRAPHOS COMPLEXES

Complex	Colour	Yield(%)	Decomp. (°C)	Analysis found (calcd.) (%)			
				C	H	P	Br
αα-*fac*-$Mn(CO)_3$(Tetraphos)Br	yellow	10	∿63	59.4 (60.8)	4.4 (4.8)	11.9 (13.9)	
αβ-*fac*-$Mn(CO)_3$(Tetraphos)Br	yellow	20	∿66	60.5 (60.8)	5.0 (4.8)	13.4 (13.9)	
$[Mn(CO)_3Br]_2$(Tetraphos)^a	yellow	45	∿165	52.5 (52.0)	4.0 (3.8)	11.2 (11.2)	14.5 (14.4)
$[Br(CO)_3Mn$(Tetraphos)$]_2Mo(CO)_4 \cdot CHCl_3{}^b$	yellow	70	∿135	53.9 (54.2)	4.2 (4.0)	11.4 (11.8)	
cis-$Mn(CO)_2$(Tetraphos)Br	bright yellow	40	∿115	61.4 (61.3)	5.0 (4.9)	13.6 (14.4)	8.2 (9.7)
cis-$Mn(CO)_2$(Tetraphos)I^c	bright yellow	40	98-102	59.4 (58.2)	5.1 (4.7)		
cis-$Mn(CO)_2$(Tetraphos=O)Br	yellow	60	∿130	60.6 (60.2)	5.3 (4.8)	14.5 (14.1)	8.2 (9.1)
cis-$Mn(CO)_2$(Tetraphos=O)I^c	yellow	60	∿115	57.8 (57.2)	4.9 (4.6)		
$Br(CO)_2Mn$(Tetraphos)$Mn(C_5H_5)(CO)_2$	orange	50	∿93	60.3 (59.0)	5.2 (4.6)	11.6 (11.9)	

a) Mol. wt.: Found (calcd.) 1307 (1108) (b) Mol. wt.: Found (calcd.) 1620 (1987) in $CHCl_3$ (c) The C and H analyses for these complexes were performed in this laboratory on a Hewlett-Packard Model 185 CHN analyser.

$Br(CO)_2Mn(Tetraphos)Mn(C_5H_5)(CO)_2$

A chloroform solution (20 ml) containing $C_5H_5Mn(CO)_2(C_8H_{14})$ (0.13 mmol) and $Mn(CO)_2(Tetraphos)Br$ (0.1 mmol) was refluxed for 24 h. Solvent was then removed under reduced pressure and the resulting mixture was eluted on silica gel thin layer plates with a 1/1 acetone/n-hexane mixture. The desired product was obtained in high yield and crystallized from a chloroform/n-hexane mixture.

RESULTS AND DISCUSSION

Changes in the IR spectrum [ν(CO) region] were readily detected when $Mn(CO)_5Br$ and Tetraphos were refluxed together in chloroform. After 1 h the spectrum remained constant. The three strong bands which had developed were indicative of a *facial* configuration, typical of *fac*-$Mn(CO)_3L_2X$ complexes. Thin layer chromotography revealed that the reaction mixture contained at least three new products.

The three major products were separated by preparative thin layer chromotography. Elemental analyses, the presence of three strong CO absorptions in the IR and chemical reactions (see later) showed that the two complexes with the larger R_f values are of the type *fac*-$Mn(CO)_3(Tetraphos)Br$*. The third

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* The complex with the largest R_f value will be called the αα isomer to distinguish it from the other isomer, to be called the αβ isomer. The reason for this nomenclature will become clear as the text proceeds.

TABLE V-2 IR SPECTRA IN THE C-O STRETCHING REGION OF THE NEW TETRAPHOS COMPLEXES (CH_2Cl_2 SOLUTION)

Complex	$\nu(CO)^a$ (cm^{-1})		
αα-*fac*-$Mn(CO)_3$(Tetraphos)Br	2021	1953	1915
αβ-*fac*-$Mn(CO)_3$(Tetraphos)Br	2021	1954	1913
$[Mn(CO)_3Br]_2$(Tetraphos)	2024	1954	1913
$[Br(CO)_3Mn(Tetraphos)]_2Mo(CO)_4$	2023	1953(m)	1908(br) 1881(sh)
cis-$Mn(CO)_2$(Tetraphos)Br^b		1932	1864
cis-$Mn(CO)_2$(Tetraphos)I		1935	1868
cis-$Mn(CO)_2$(Tetraphos=O)Br		1932	1864
cis-$Mn(CO)_2$(Tetraphos=O)I		1935	1869
$Br(CO)_3Mn(Tetraphos)Mn(C_5H_5)(CO)_2{}^c$		1930	1860
αα-$Br(CO)_3Mn(Tetraphos)Mn(CO)_4Br^d$	2092(m) 1958	2024 1917	2009(sh)
αβ-$Br(CO)_3Mn(Tetraphos)Mn(CO)_4Br^d$	2091(m) 1958	2024 1918	2009(sh)

a) All bands strong unless otherwise stated; m = medium, br = broad vs = very strong, sh = shoulder.

b) Ref. 34: ν(CO) = 1933, 1862 in CH_2Cl_2.

c) IR recorded in CS_2 showed no band splitting ν(CO)= 1931, 1863 The IR ν(CO) of $C_5H_5Mn(CO)_2(PPh_3)$: 1931, 1860 cm^{-1} in CH_2Cl_2.

d) IR recorded in $CHCl_3$

product, with the smallest R_f value, is the bimetallic complex $[Mn(CO)_3Br]_2$(Tetraphos).

A consideration of the complex *fac*-$Mn(CO)_3$(Tetraphos)Br suggests that seven diastereomers, in which adjacent P atoms bond to the metal, are possible. The likelihood of isomer formation, in which the polyphosphine bonds to the manganese through non-adjacent P atoms seems doubtful, particularly in light of the crystal structure determinations for the Triphos complexes (Chapter VI). The seven diastereomers are shown in Figure V-1.

In all seven of these isomers, there are two P atoms which are available for undergoing typical "phosphine type" reactions. Consequently, "phosphine type" reactions were undertaken to show that this was indeed the case.

Reaction of the isomeric mixture of αα- and αβ-*fac*-$Mn(CO)_3$(Tetraphos)Br with (*nor*-C_7H_8)$Mo(CO)_4$ gave a single product, which from IR data was suggestive of $[Br(CO)_3Mn(\text{Tetraphos})]_n$ $[Mo(CO)_4]$, (n = 1,2). No IR evidence was observed for the species $[Br(CO)_3Mn(\text{Tetraphos})][Mo(CO)_5]_n$ (n = 1,2). Analytical data, together with a molecular weight determination, are more consistent with the product for which n = 2*, as shown overleaf (Figure V-2).

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* The complex $Br(CO)_3Mn(\text{Tetraphos})Mo(CO)_4$ (i.e. n = 1) has a molecular weight of 1098 (Found: 1620).

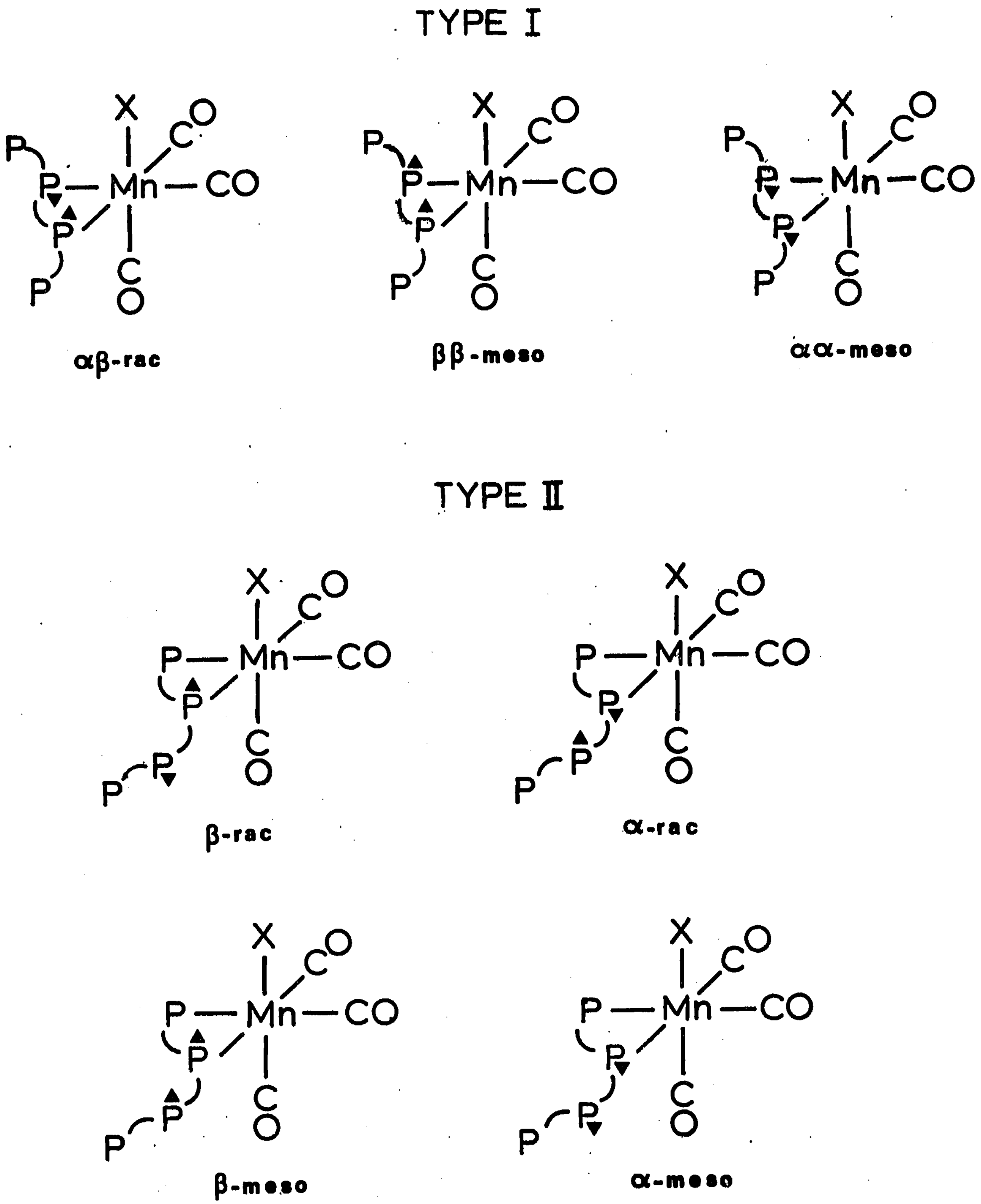


FIGURE V-1 DIASTEREOMERS OF *fac*-Mn(CO)$_3$(Tetraphos)X (X = Br) All methylene and phenyl groups have been omitted for the sake of clarity. ▲ represents the orientation of a phenyl ring pointing in the same direction as the halogen (β-isomer); ▼ in the opposite direction. Note that αβ-*rac* and βα-*rac* are enantiomers.

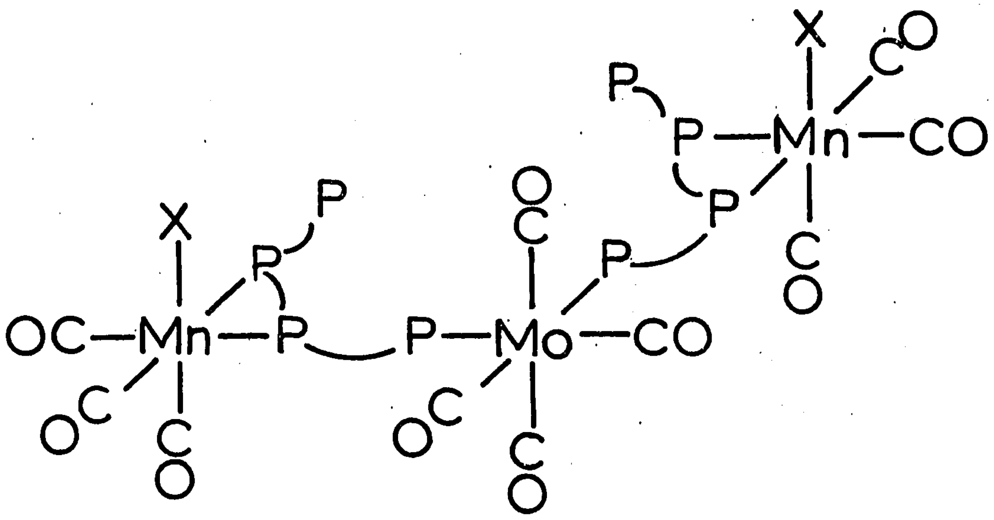
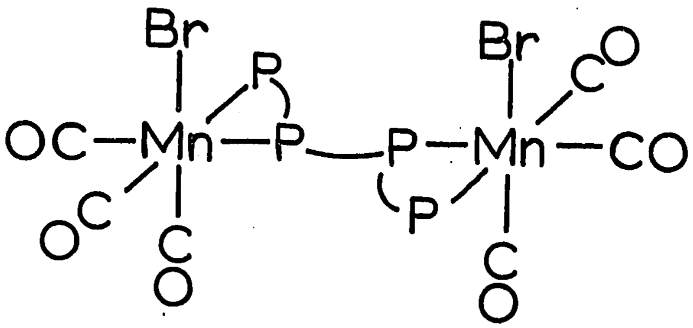


FIGURE V-2 STRUCTURE OF $[X(CO)_3Mn(Tetraphos)]_2Mo(CO)_4$ (X = Br) All phenyl and methyl groups have been omitted for the sake of clarity.

The above results suggest that isomers αα- and αβ-*fac*-$Mn(CO)_3$(Tetraphos)Br are of Type I rather than Type II. Unexpectedly, only one isomer of the trimetallic complex was obtained, even though the starting material consisted of an isomeric mixture. This no doubt is related to the methods of isomer detection rather than to the non-existence of the isomers.

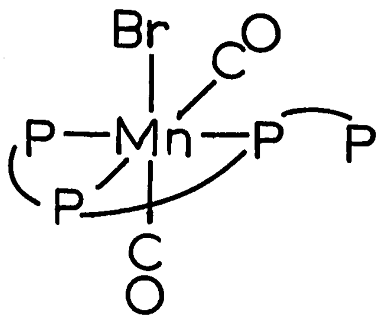
Further evidence which suggests that the isomers are of Type I comes from the small scale reactions of the separate isomers, αα-*fac*-$Mn(CO)_3$(Tetraphos)Br (∿ 5 mg) and αβ-*fac*-$Mn(CO)_3$(Tetraphos)Br (∿ 5 mg) with $Mn(CO)_5Br$ (∿ 5 mg). The IR[ν(CO)] was followed during the course of the reaction and in both cases the final spectrum was consistent with a product of the type $Br(CO)_3Mn$(Tetraphos)$Mn(CO)_4Br$ and not the symmetrical bridging complex $[Mn(CO)_3Br]_2$(Tetraphos). Type II tricarbonyl complexes should undergo reactions in which two CO groups are readily displaced from $Mn(CO)_5Br$.

The third complex obtained from the the reaction of $Mn(CO)_5Br$ and Tetraphos (smallest R_f value) could be obtained in much higher yield by using a 2:1 ratio of the reactants $Mn(CO)_5Br$: Tetraphos. The product was confirmed as $[Mn(CO)_3Br]_2$(Tetraphos).



The IR spectrum (three strong absorptions in the ν(CO) region), its lack of reactivity towards (*nor*-C_7H_8)Mo$(CO)_4$ and Mn$(CO)_5$Br, elemental analyses and a molecular weight determination all suggest this formulation. This bimetallic complex is almost certainly of Type II (Figure V-1) in which the "dangling" P atoms are now coordinated to the second manganese atom. Moreover, molecular models indicate that reactions of the Type I isomers to give this bimetallic complex is highly unlikely.

If the reaction of Mn$(CO)_5$Br and Tetraphos is allowed to continue for longer periods of time or, preferably, if the reaction is carried out in xylene at 130°, the dicarbonyl complex *cis*-Mn$(CO)_2$(Tetraphos)Br is obtained. This complex has been reported previously^{34}. A similar reaction with Mn$(CO)_5$I gave the analogous monometallic complex.
The complexes are thought to be similar to the corresponding Triphos complexes in which one CO group is *trans* to the Br atom, as shown below.



The dicarbonyl Tetraphos complexes should still contain one "dangling" P atom. This was confirmed by reaction of the dicarbonyl with ozone to give $Mn(CO)_2$ (Tetraphos=O)X (X = Br, I).

The new phosphine oxide complexes exhibit two strong bands in the $\nu(CO)$ stretching region, suggesting that the stereochemistry is unaffected by the ozone reactions. The presence of the phosphine oxide was indicated by a strong absorption in the IR at $\sim$1180 cm^{-1} [$\nu(P{=}O)$] and other characteristic absorptions in the 1600-400 cm^{-1} region as discussed earlier (*vide supra*, p.81). These are listed in Table IV-4. These phosphine oxide complexes were also obtained from the reaction of $Mn(CO)_5X$ and Tetraphos but in low yield, presumably as a result of air oxidation.

As found previously, reaction of $Mn(CO)_5Br$ with the coordinated phosphine oxide [in *cis*-$Mn(CO)_2$(Tetraphos=O)Br] gave an unusual reaction as detected by IR spectroscopy, but the composition of the final product is unknown.

The presence of one un-coordinated P atom in *cis*-$Mn(CO)_2$(Tetraphos)Br was also confirmed by its reaction with $C_5H_5Mn(CO)_2(C_8H_{14})$. Only one product was obtained. Its IR spectrum showed only two strong CO bands, presumably due to the superposition of the two sets of bands for both metal carbonyl moeities.

A variety of other complexes were also obtained from the reaction of $Mn(CO)_5Br$ and Tetraphos but in very low yield. From their position on thin layer plates and their IR spectra the products are most probably of the type $Mn(CO)_3(Tetraphos{=}O_n)Br$ $(n = 1,2)$ i.e. products of the type shown in Figure V-1 with either one or two of the "dangling" P atoms oxidized to a phosphine oxide.

From the above studies, some comments can be made about the reaction mechanisms of $Mn(CO)_5Br$ with Tetraphos. Use was also made of earlier conclusions drawn from the reaction of $Mn(CO)_5X$ with Triphos:

i) Adjacent P atoms coordinate to the manganese atom in preference to coordination through non-adjacent P atoms.
ii) Using 1:1 molar ratios of reactants, only monometallic complexes of the type *fac*-$Mn(CO)_3(Triphos)X$ are formed.
iii) Formation of *cis*-$Mn(CO)_2(Triphos)X$ from *fac*-$Mn(CO)_3(Triphos)X$ requires a temperature of ∿100°C.

Initially, the reaction of $Mn(CO)_5Br$ and Tetraphos gives products of the type $Mn(CO)_4(Tetraphos)Br$, as evidenced by the rapid formation of two new peaks in the IR spectrum at 2090 and 2007 cm^{-1}. The Tetraphos ligand in these complexes bonds through, either one of the terminal P atoms (A), or one of the central P atoms (B) (Figure V-3). Statistically, both products should be formed with equal probability*.

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* Presumably, the *meso* and *racemic* forms of the ligand will affect the course of the reaction differently, and hence the nature of the final product composition. This effect will be ignored in the present discussion.

If the reaction occurs initially by coordination through a terminal P atom (A), further reaction of the ligand can occur through a central P atom to give a bidentate product (Figure V-3, path a). This product then reacts with $Mn(CO)_5Br$ to give eventually the dimer $[Mn(CO)_3Br]_2$(Tetraphos), (path b). The reaction could also proceed by coordination of the other terminal P atom (path c) to give a dimeric product, as shown in Figure V-3. This reaction then proceeds further to give the bimetallic complex by chelate formation (path d).

The other reaction path starts from the product $Mn(CO)_4$(Tetraphos)Br in which the Tetraphos is bonded to the manganese atom through a central P atom of the ligand (B). If the second P atom which bonds to the metal atom is the adjacent terminal P atom, a metal chelate is formed (Figure V-3, path e). This product can then react with $Mn(CO)_5Br$ to give eventually $[Mn(CO)_3Br]_2$(Tetraphos), (path b). Reaction though the other terminal P atom is also shown in Figure V-3, and once again the final product is almost certainly the dimer (paths f and g). The remaining possibility, reaction through the other central P atom, gives *fac*-$Mn(CO)_3$(Tetraphos)Br (path h). This product does not react further, either with itself or with more $Mn(CO)_5Br$. This reaction scheme rationalizes the presence of both the

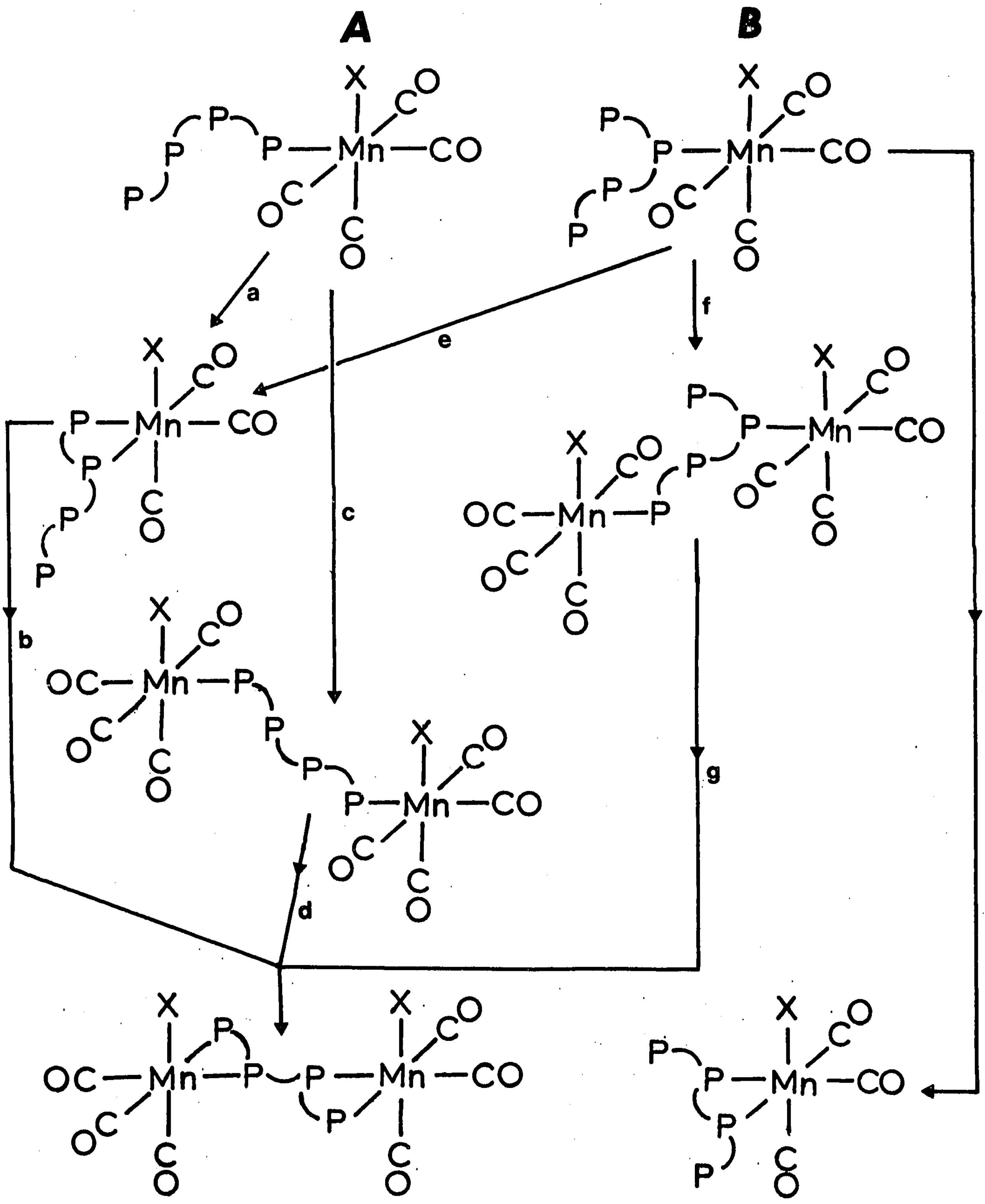

FIGURE V-3 REACTION OF Mn(CO)$_5$X (X = Br) with TETRAPHOS.

dimer, $[Mn(CO)_3Br]_2$(Tetraphos), and the Type-I *fac*-$Mn(CO)_3$(Tetraphos)Br isomer (Figure V-1).

Tetraphos is an optically active ligand. Hence it was hoped that separation of the *meso* and *racemic* isomers might be possible when the ligand was reacted with $Mn(CO)_5Br$. In general, this was not achieved. The only separation of isomers achieved in this work was with the Type I isomers. From the previous work reported on the reaction of Triphos (Chapter IV), the product with the largest R_f value, the α isomer, had the phenyl ring on the central P atom *trans* to the Br atom. A similar isomer ordering (for R_f values) is thought to be the case for the Tetraphos complexes *viz.* αα > αβ(βα) > ββ. Although three isomers are expected, only two were isolated. It is thought that the ββ-isomer is the isomer which did not form because of the greater steric interaction of two phenyl rings with the bromine atom. Similar reasoning was used earlier to explain the isomer product ratio for the reaction of $Mn(CO)_5I$ and Triphos. Thus, it is tentatively suggested that resolution of the diastereomers of the optically active ligand has been achieved, with the αα isomer containing the *meso* ligand, and the αβ isomer the *racemic* ligand.

CONCLUSION

Very little work of any description has been reported on the reaction of linear tetraphosphine ligands with metal complexes. Moreover, reports to date have made no mention of the existence of enantiomers and diastereomers of the linear tetraphosphine ligand. The results obtained in this study indicate that a wide variety of products can be obtained on reaction of Tetraphos with $Mn(CO)_5X$. Further studies, especially X-ray diffraction or ^{31}P NMR studies will, however, be needed to provide further confirmation of the stereochemistry of the complexes prepared in this work.

CHAPTER VI THE CRYSTAL AND MOLECULAR STRUCTURES OF TWO ISOMERIC TRITERTIARY PHOSPHINE COMPLEXES OF MANGANESE(I) AND CHROMIUM(O)*

INTRODUCTION

As a result of the technical advances in both the computing field and the manufacture of fully automated X-ray diffractometers, X-ray crystallography is becoming an increasingly important field in all branches of chemistry. It has the advantage over other physical methods of structure determination, of providing specific information on the exact coordination of all atoms in a complex. It is thus of great importance in determining, among other features, the stereochemistry of novel complexes[103,104]. As mentioned in Chapter IV, Triphos reacts with $Mn(CO)_5X$ to give two complexes of *fac*-$Mn(CO)_3$(Triphos)X. Further chemical information added weight to the argument that these two complexes were diastereomers. Since four diastereomers are possible (*vide supra*,p.33) it was of interest to determine by X-ray crystallography which diastereomers had been prepared and to correlate the structures of the complexes with their R_f values (on silica gel thin layer plates).

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* This has been published in part[105].

Unfortunately, the two isomers of *fac*-Mn(CO)$_3$(Triphos)X are difficult to separate in high yield. Moreover, they are oxidized slowly to *fac*-Mn(CO)$_3$(Triphos=O)X on standing in air and the un-coordinated P atoms can react with the manganese atoms to give *cis*-Mn(CO)$_2$(Triphos)X. Therefore, it was decided to determine the crystal structures of two separable bimetallic complexes of the type *fac*-X(CO)$_3$Mn(Triphos)M. Since the complexes with X = Br and M = Cr(CO)$_5$ were prepared in good yield and because the crystals do not decompose on standing in air (even over a period of three weeks), crystals of the two isomers of Br(CO)$_3$Mn(Triphos)Cr(CO)$_5$ were used for the structural determinations.

EXPERIMENTAL

The Br(CO)$_3$Mn(Triphos)Cr(CO)$_5$ complexes were prepared as reported previously (Chapter IV). Crystallization of the α-isomer* from CH$_2$Cl$_2$/n-hexane solution afforded yellow needles which were dried *in vacuo* (25°C/0.01 mmHg).

The β-isomer crystallizes from CH$_2$Cl$_2$/n-hexane solution in the form of orange plates. Attempted drying of these crystals under reduced pressure caused them to become opaque; consequently the crystals used in the X-ray study were dried under a stream of nitrogen.

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* The α-isomer is the one which has the larger R_f value on a silica gel thin layer chromotography plate after elution with benzene.

Crystallographic Data: α-Isomer

The space group of a crystal was determined from Weissenberg *h0l*, *h1l* and precession *hk0*, *0kl* zones as Pbcn (no. 60) with unit cell parameters *a* = 21.260(6), *b* = 14.451(3), *c* = 28.338(9) Å^3 and *V* = 8710 Å^3. The density, determined by flotation in ZnI_2 solution was $\rho_{obs} = 1.44(1)$ g cm^{-3} (for *Z* = 8, $\rho_{calc} = 1.44$ g cm^{-3}).

Unit cell and intensity data for the crystal structure were collected on the McGill University Picker FACS-I diffractometer using graphite monochromated Cu-K_α radiation ($\lambda = 1.5419$ Å). Accurate values for 2θ, ω,χ and ϕ were obtained for ten Bragg reflections by an automatic centering process. Refined unit cell constants and the orientation matrix were fitted to these values by a least squares process[106a].

A new crystal was mounted and used for data collection in which a θ-2θ scanning process was employed. An asymmetric set of 3789 diffraction intensities to $2\theta_{max} = 90°$ was collected. Instrumental and crystal instabilities were checked by remeasuring three standards every 50 reflections. The intensity of these reflections fell by 36% during data collection. The data were corrected for decomposition by locally written computer programs but no absorption correction was applied ($\mu = 7.30$ cm^{-1}).

Data reduction, as well as structure solution and refinement, were performed with the aid of the "X-RAY 70" program package[106b] adapted for use on the McGill University IBM 360/75 computer. Scattering factors for the atoms were taken from Cromer[107]. Anomalous dispersion corrections ($\Delta f'$ and $\Delta f''$) were made for the six heavy atoms (Mn, Br, Cr, 3P)[108]. All data with $I < 2\sigma(I)$ were rejected and the remaining data (1324 reflections) were corrected for Lorentz and polarization effects [$1/(Lp) = \sin 2\theta_s(\cos^2 2\theta_m + 1)/(\cos^2 2\theta_m + \cos^2 2\theta_s)$, where $2\theta_s$ and $2\theta_m$ are the diffraction angles at the sample crystal and monochromator respectively].

Structure Solution and Refinement: α-Isomer

Three-dimensional Patterson and sharpened Patterson maps did not prove helpful in the structure determination, owing to severe overlap of peaks. Therefore direct methods were employed and the six heavy atoms were located on the E-map computed after phasing 380 reflections[109]. The remaining non-hydrogen atoms were found from successive difference Fourier maps.

Least-squares refinement using isotropic temperature and positional parameters gave R = 15.4% ($R = [\Sigma(||F_o|-|F_c||)/\Sigma|F_o|]$). Three reflections were considered extinct (1 0 4, 1 0 6, 3 0 4) and were thus rejected. Anisotropic thermal parameters for the six heavy atoms were then included and block diagonal least-squares refinement gave R = 9.9%. The weighting scheme $W = (F_o/A)^2$ for $F_o \leqslant A$ and $W = (A/F_o)^2$ for $F_o > A$ (A = 120), was employed during the latter cycles of refinement (Table VI-1). A final difference Fourier map showed no peak higher than 0.9 e/A^3. Final atomic parameters are given in Table VI-2.

Crystallography Data: β-Isomer

A preliminary photographic survey of Weissenberg h0l, and precession 0kl, hk0, hkl zones gave two possible space groups, Cc (no.9) and C2/c (no.15), consistent with the observed systematic absences of X-ray diffractions. The refined unit cell parameters, a = 24.41(3), b = 10.76(1), c = 17.42(2) Å, β = 89.11(3)°, and V = 4575 Å^3, were obtained after transferring the crystal to the diffractometer.

The density of the complex, found by flotation in ZnI_2 solution, was ρ_{obs} = 1.50(1) g cm^{-3} [for Z = 4, ρ_{calc} = 1.50 g cm^{-3} for the monosolvate, $Br(CO)_3Mn(Triphos)Cr(CO)_5 \cdot CH_2Cl_2$]. In C_2/c, with Z = 4, the molecules lie on special positions. As the molecule has no symmetry, this space group was ruled out. Successful structure solution confirmed Cc as the appropriate space group.

Data were collected on the Sir George Williams University Picker FACS-I fully automated diffractometer, using monochromatic Mo-K_α radiation (λ = 0.71069 Å).*

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* A more detailed description of the experimental procedure is given in Ref. 110.

TABLE VI-1 WEIGHTING SCHEME USED IN THE FINAL CYCLES OF STRUCTURE REFINEMENT (α-ISOMER)

WEIGHTING SCHEME

$$F_{obs} \leqslant A \quad ; \quad w=(F_{obs}/A)^2$$

$$F_{obs} > A \quad ; \quad w=(A/F_{obs})^2$$

$$(A = 120)$$

F_{obs} (range)	no. of planes (N)	$(\sum w\Delta^2)/N$
0 — 45	217	11·4
45 - 50	157	19·7
50 - 57	170	11·5
57 - 68	207	8·1
68 - 90	192	6·6
90 - 130	185	7·8
130 ——	193	8·6

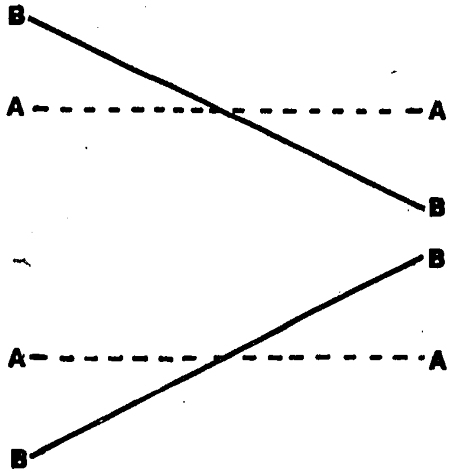
Refined cell constants and the orientation matrix were obtained as described earlier, but in this case, twelve reflections centered at both positive and negative 2θ values were used, after averaging.

Intensities in the range 2° < 2θ < 45° were collected by a θ-2θ scanning procedure. Instrumental and crystal instabilities were checked by monitoring three standards every 50 reflections. The intensity of the three standard reflections decreased by 2% during data collection; they were used to scale the observed data.

Of the 3265 reflections collected, 2277 reflections [$\underline{I} > 3\sigma(\underline{I})$] were corrected for Lorentz and polarization effects, using locally written programs for the Sir George Williams University CDC 6400 computer. No absorption correction was made ($\mu = 11.8\ cm^{-1}$).

Structure Solution and Refinement: β-Isomer

Inspection of the sharpened three-dimensional Patterson synthesis suggested several possibilities for the positions of the heavy atoms (Br, Mn, Cr). These possibilities were tested in trial structure factor calculations; a Fourier synthesis based on the best of these gave the positions of the three phosphorus atoms. Subsequent syntheses yielded the positions of the remaining atoms. Owing to computer memory restrictions, least - squares refinement of positional and isotropic thermal parameters necessitated dividing the parameters into two matrices. The discrepancy index, $\underline{R} = [\Sigma(||\underline{Fo}|-|\underline{Fc}||)/\Sigma|\underline{Fo}|]$, at this stage dropped to 9.6%. Since the non-centrosymmetric space group Cc specifies an absolute configuration for the molecule, least-squares refinement was also carried out on the inverse structure and gave a final R = 9.9%. The significance of the difference between the two R values was supported by application of the Hamilton R test[111]. The λ isomer[112], with the lower R value was thus chosen as the correct isomer. A further four cycles of refinement including anisotropic temperature refinement on atoms other than carbon, hydrogen and oxygen gave a final R value of 8.7% and $\underline{R}w$ of



(a) δ-conformation

(b) λ-conformation

The figure shows pairs of nonorthogonal skew lines in projection upon a plane parallel to both lines. The line BB is above the plane of the paper, line AA below the plane. (a) Defines a right-handed helix. (b) Defines a left-handed helix.

TABLE VI-2

FINAL PARAMETERS

POSITIONS AND ISOTROPIC THERMAL PARAMETERS[a] WITH E.s.d.'s[b]

	α-Isomer				β-Isomer			
Atom	x	y	z	B	x	y	z	B
Br	0.2582 (2)	0.1075 (3)	-0.0373 (2)	c	0.5000	0.3009 (2)	0.5000	c
Mn	0.3647 (4)	0.1589 (4)	-0.0680 (2)	c	0.56250 (15)	0.1147 (3)	0.5151 (2)	c
Cr	0.3882 (3)	-0.0173 (5)	0.1684 (3)	c	0.75173 (16)	0.0338 (3)	0.8289 (2)	c
P1	0.3097 (5)	0.2823 (7)	-0.1009 (4)	c	0.5113 (3)	0.0518 (6)	0.6249 (4)	c
P2	0.3762 (5)	0.2569 (7)	-0.0046 (4)	c	0.6095 (2)	0.2390 (5)	0.6029 (4)	c
P3	0.3423 (5)	0.1205 (7)	0.1350 (4)	c	0.7656 (2)	0.1931 (6)	0.7361 (3)	c
O1	0.344 (1)	0.048 (2)	-0.152 (1)	10.3 (8)	0.4973 (6)	-0.0352 (15)	0.4085 (9)	4.7 (4)
O2	0.488 (1)	0.209 (2)	-0.100 (1)	10.8 (9)	0.6413 (6)	-0.0855 (14)	0.5334 (8)	4.9 (4)
O3	0.416 (1)	-0.001 (2)	-0.017 (1)	11.7 (9)	0.6217 (6)	0.2097 (15)	0.377 (1)	5.8 (4)
O4	0.334 (2)	-0.120 (2)	0.087 (1)	14.6 (11)	0.7787 (6)	0.2128 (17)	0.957 (1)	6.5 (4)
O5	0.506 (1)	0.023 (2)	0.118 (1)	10.5 (8)	0.8711 (7)	-0.0341 (16)	0.815 (1)	6.5 (5)
O6	0.453 (2)	-0.186 (2)	0.209 (1)	13.9 (11)	0.7377 (7)	-0.1612 (16)	0.948 (1)	6.5 (5)
O7	0.431 (1)	0.075 (2)	0.254 (2)	10.6 (9)	0.7156 (7)	-0.1569 (17)	0.716 (1)	7.6 (5)
O8	0.276 (2)	-0.061 (2)	0.229 (1)	15.3 (12)	0.6344 (7)	0.1137 (14)	0.849 (1)	5.5 (4)
C1	0.354 (2)	0.095 (3)	-0.116 (1)	9 (1)	0.5211 (9)	0.022 (2)	0.446 (1)	4.8 (6)
C2	0.433 (2)	-0.088 (3)	-0.088 (1)	10 (1)	0.6077 (8)	-0.008 (2)	0.525 (1)	2.9 (5)
C3	0.395 (2)	0.068 (3)	-0.038 (2)	11 (1)	0.6015 (9)	0.175 (2)	0.429 (1)	4.0 (6)
C4	0.360 (2)	-0.081 (3)	0.120 (2)	12 (2)	0.7712 (10)	0.145 (3)	0.907 (2)	6.6 (8)
C5	0.456 (2)	0.002 (3)	0.137 (1)	9 (1)	0.8240 (10)	-0.006 (2)	0.818 (1)	5.0 (6)
C6	0.428 (2)	-0.128 (4)	0.195 (2)	15 (2)	0.7440 (10)	-0.082 (2)	0.900 (2)	5.9 (7)

C7	0.410 (2)	0.034 (3)	0.222 (1)	8 (1)	0.7287 (10)	-0.082 (3)	0.761 (2)	6.1 (7)
C8	0.317 (3)	-0.046 (4)	0.205 (2)	15 (2)	0.6787 (9)	0.080 (2)	0.838 (1)	4.0 (5)
C9	0.286 (1)	0.353 (2)	-0.050 (1)	5.0 (9)	0.5442 (8)	0.120 (2)	0.708 (1)	3.6 (5)
C10	0.336 (2)	0.372 (2)	-0.019 (1)	6 (1)	0.5653 (7)	0.257 (2)	0.687 (1)	2.4 (4)
C11	0.338 (2)	0.232 (2)	0.051 (1)	5.5 (9)	0.6736 (8)	0.165 (2)	0.640 (1)	2.8 (5)
C12	0.359 (2)	0.135 (2)	0.073 (1)	5.1 (8)	0.7005 (8)	0.259 (2)	0.696 (1)	2.9 (5)
C13	0.357 (2)	0.360 (2)	-0.139 (1)	5.7 (9)	0.5067 (8)	-0.114 (2)	0.649 (1)	3.3 (5)
C14	0.396 (2)	0.322 (3)	-0.172 (1)	8 (1)	0.4967 (9)	-0.200 (2)	0.593 (1)	4.1 (5)
C15	0.430 (2)	0.381 (3)	-0.205 (1)	8 (1)	0.4884 (9)	-0.328 (2)	0.612 (1)	4.9 (6)
C16	0.420 (2)	0.477 (3)	-0.202 (1)	10 (1)	0.4876 (9)	-0.361 (2)	0.688 (2)	5.6 (6)
C17	0.384 (2)	0.513 (3)	-0.168 (2)	13 (1)	0.4949 (10)	-0.276 (2)	0.745 (2)	6.1 (7)
C18	0.345 (2)	0.457 (3)	-0.134 (2)	10 (1)	0.5065 (10)	-0.144 (2)	0.726 (2)	5.9 (7)
C19	0.238 (2)	0.268 (2)	-0.138 (1)	5.8 (9)	0.4395 (7)	0.101 (2)	0.628 (1)	2.5 (4)
C20	0.184 (2)	0.303 (3)	-0.123 (2)	10 (1)	0.4055 (9)	0.064 (2)	0.565 (1)	4.0 (5)
C21	0.129 (2)	0.296 (3)	-0.156 (2)	10 (1)	0.3508 (10)	0.098 (2)	0.567 (2)	5.2 (6)
C22	0.141 (2)	0.257 (3)	-0.200 (1)	9 (1)	0.3265 (9)	0.166 (2)	0.627 (2)	4.9 (6)
C23	0.194 (2)	0.216 (3)	-0.215 (2)	10 (1)	0.4198 (9)	0.172 (2)	0.687 (1)	4.0 (5)
C24	0.248 (2)	0.223 (3)	-0.182 (1)	8 (1)	0.3617 (11)	0.198 (2)	0.686 (2)	6.9 (7)
C25	0.453 (2)	0.290 (3)	0.014 (1)	8 (1)	0.6312 (7)	0.392 (2)	0.578 (1)	2.4 (4)
C26	0.504 (2)	0.230 (3)	0.011 (2)	10 (1)	0.6725 (8)	0.409 (2)	0.522 (1)	3.8 (5)
C27	0.569 (2)	0.254 (3)	0.029 (2)	12 (2)	0.6945 (9)	0.531 (2)	0.508 (1)	4.7 (6)

C28	0.575 (2)	0.342 (4)	0.047 (2)	14 (2)	0.6774 (9)	0.632 (2)	0.555 (1)	4.6 (6)
C29	0.529 (2)	0.396 (3)	0.054 (2)	12 (2)	0.6364 (10)	0.617 (2)	0.608 (1)	5.2 (1)
C30	0.463 (2)	0.375 (3)	0.040 (2)	11 (1)	0.6123 (9)	0.500 (2)	0.624 (1)	4.9 (6)
C31	0.254 (2)	0.130 (2)	0.140 (1)	6.0 (9)	0.8098 (8)	0.155 (2)	0.644 (1)	3.0 (5)
C32	0.231 (2)	0.150 (2)	0.183 (1)	7 (1)	0.8232 (9)	0.034 (2)	0.627 (1)	4.5 (6)
C33	0.165 (2)	0.156 (3)	0.192 (1)	9 (1)	0.8560 (10)	0.012 (3)	0.561 (2)	6.4 (7)
C34	0.135 (2)	0.148 (3)	0.151 (1)	8 (1)	0.8705 (9)	0.109 (3)	0.517 (1)	5.2 (6)
C35	0.150 (2)	0.122 (3)	0.106 (1)	9 (1)	0.8552 (11)	0.222 (3)	0.538 (2)	6.5 (7)
C36	0.222 (2)	0.115 (3)	0.098 (1)	7 (1)	0.8231 (9)	0.262 (2)	0.605 (1)	3.9 (5)
C37	0.367 (2)	0.235 (3)	0.156 (1)	8 (1)	0.7981 (8)	0.334 (2)	0.776 (1)	2.9 (5)
C38	0.433 (2)	0.240 (3)	0.166 (1)	8 (1)	0.8537 (11)	0.319 (3)	0.793 (2)	6.7 (7)
C39	0.464 (2)	0.326 (3)	0.176 (1)	9 (1)	0.8787 (12)	0.421 (3)	0.836 (2)	8.2 (9)
C40	0.426 (2)	0.403 (3)	0.181 (1)	8 (1)	0.8497 (11)	0.520 (3)	0.854 (2)	5.7 (6)
C41	0.361 (2)	0.400 (3)	0.174 (1)	7 (1)	0.7931 (11)	0.534 (3)	0.836 (2)	7.6 (8)
C42	0.331 (2)	0.316 (2)	0.163 (1)	7 (1)	0.7677 (9)	0.432 (2)	0.799 (1)	4.7 (6)
Cℓ1					0.6084 (4)	0.4768 (9)	0.8405 (5)	c
Cℓ2					0.5029 (4)	0.3640 (11)	0.8757 (5)	c
C43					0.5577 (17)	0.406 (4)	0.906 (1)	c

a Isotropic Thermal Parameters in Å^2

b Esd's are shown in parantheses. These are right justified to the least significant digit in the preceeding number.

c Atoms refined anisotropically.

ANISOTROPIC THERMAL PARAMETERS[a] (x 10^4)

	α-Isomer						β-Isomer					
	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br	47 (2)	66 (2)	28 (1)	-11 (2)	0 (1)	-1 (2)	20.0 (6)	103 (3)	44 (1)	8 (1)	0.4 (7)	14 (2)
Mn	35 (2)	67 (4)	22 (1)	6 (3)	2 (1)	1 (2)	12.8 (7)	76 (4)	23 (1)	0 (2)	-1.4 (8)	0 (2)
Cr	47 (2)	82 (5)	28 (2)	1 (3)	-4 (2)	7 (2)	14.3 (8)	98 (5)	21 (2)	-6 (1)	-1.1 (9)	9 (3)
P1	39 (4)	44 (6)	21 (2)	3 (4)	3 (2)	-3 (3)	17.6 (13)	103 (8)	32 (3)	-8 (3)	0.3 (15)	0 (4)
P2	26 (2)	73 (7)	24 (2)	-3 (4)	3 (2)	-2 (3)	16.8 (13)	93 (8)	28 (3)	-2 (3)	-1.1 (14)	4 (4)
P3	40 (4)	50 (7)	29 (2)	-8 (4)	0 (2)	2 (3)	18.7 (15)	93 (8)	32 (3)	-4 (3)	-0.6 (16)	-2 (4)
Cl1							40 (2)	193 (13)	46 (4)	-26 (5)	6 (3)	-41 (6)
Cl2							29 (2)	319 (19)	53 (5)	-31 (6)	4 (3)	-44 (8)
C43							82 (14)	360 (70)	15 (12)	90 (27)	-2.5 (11)	-25 (25)

[a] of the form $\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})]$

6.7% ($R_w = [\Sigma w(F_o - F_c)^2/\Sigma F_o^2]$, where $w = [\sigma(F_o)]^{-2}$. The "goodness of fit" parameter, defined by $[\Sigma w(F_o-F_c)^2/(n-m)]^{1/2}$ where n and m are numbers of observations and variables, respectively, was 2.010.

The final atomic parameters are given in Table VI-2.

RESULTS

The molecular structures of the two isomers are shown in Figures VI-1 and VI-2. The packing diagram for the β-isomer is given in Figure VI-3. Tables VI-3 and VI-4 list bond lengths and bond angles, respectively. The average bond lengths and angles for the ten phenyl rings are collected together in Table VI-5, while the least-squares planes through these ten rings are given in Table VI-6. The least-squares planes for the coordination around the manganese and chromium atoms are shown in Table VI-7. The structure factor tables are given in Tables VI-8a and VI-8b for the α and β isomers respectively. No inter-molecular contacts less than 3°A were found.

DISCUSSION

The overall geometry of both isomers consists of two metal atoms linked together by the Triphos ligand. The coordination around the Mn atom in both structures is essentially octahedral with the three CO groups *cis* to each other (*facial*

TABLE VI-3

PRINCIPAL INTERMOLECULAR BOND DISTANCES (°A)[a]

	α-Isomer	β-Isomer
Br-Mn	2.537 (8)	2.534 (4)
Mn-P1	2.328 (12)	2.369 (7)
Mn-P2	2.301 (13)	2.346 (7)
Mn-C1	1.65 (4)	1.86 (2)
Mn-C2	1.61 (4)	1.73 (2)
Mn-C3	1.70 (5)	1.87 (2)
C1-O1	1.26 (5)	1.08 (3)
C2-O2	1.26 (5)	1.19 (3)
C3-O3	1.22 (5)	1.10 (3)
Cr-P3	2.41 (1)	2.376 (7)
Cr-C4	1.77 (5)	1.88 (3)
Cr-C5	1.71 (4)	1.82 (2)
Cr-C6	1.96 (5)	1.77 (3)
Cr-C7	1.75 (4)	1.81 (3)
Cr-C8	1.88 (5)	1.86 (3)
C4-O4	1.23 (6)	1.16 (3)
C5-O5	1.24 (5)	1.19 (3)
C6-O6	1.07 (6)	1.20 (3)
C7-O7	1.18 (5)	1.18 (3)
C8-O8	1.12 (6)	1.16 (3)
P1-C9	1.83 (3)	1.83 (2)
P1-C13	1.86 (3)	1.84 (2)
P1-C19	1.87 (4)	1.83 (2)
P2-C10	1.91 (3)	1.82 (2)
P2-C11	1.82 (3)	1.89 (2)
P2-C25	1.78 (4)	1.78 (2)
P3-C12	1.82 (3)	1.88 (2)
P3-C31	1.89 (4)	1.96 (2)
P3-C37	1.83 (4)	1.85 (2)
C9-C10	1.43 (4)	1.60 (3)
C11-C12	1.59 (4)	1.56 (3)
Cℓ1-C43		1.84 (4)
Cℓ2-C43		1.52 (4)

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[a] The Esd's shown in parantheses are right adjusted.

TABLE VI-4

PRINCIPAL BOND ANGLES (DEG)

	α-Isomer	β-Isomer
Br-Mn-P1	85.0 (3)	89.9 (2)
Br-Mn-P2	90.4 (3)	85.3 (2)
Br-Mn-C1	90 (1)	91.5 (8)
Br-Mn-C2	178 (2)	177.4 (7)
Br-Mn-C3	87 (2)	86.6 (7)
P1-Mn-P2	83.9 (4)	83.9 (3)
P1-Mn-C1	92 (2)	94.4 (8)
P1-Mn-C2	96 (2)	91.6 (7)
P1-Mn-C3	171 (2)	176.2 (7)
P2-Mn-C1	176 (2)	176.3 (8)
P2-Mn-C2	92 (2)	92.7 (7)
P2-Mn-C3	93 (2)	94.2 (7)
C1-Mn-C2	89 (2)	91 (1)
C1-Mn-C3	91 (2)	87 (1)
C2-Mn-C3	92 (2)	92 (1)
Mn-C1-O1	177 (3)	178 (2)
Mn-C2-O2	175 (4)	176 (2)
Mn-C3-O3	177 (4)	176 (2)
P3-Cr-C4	89 (2)	89.9 (9)
P3-Cr-C5	90 (1)	88.2 (8)
P3-Cr-C6	179 (2)	177.3 (9)
P3-Cr-C7	96 (1)	95.5 (9)
P3-Cr-C8	94 (2)	89.5 (7)
C4-Cr-C5	87 (2)	88 (1)
C4-Cr-C6	92 (2)	88 (1)
C4-Cr-C7	172 (2)	174 (1)
C4-Cr-C8	93 (2)	91 (1)
C5-Cr-C6	89 (2)	90 (1)
C5-Cr-C7	99 (2)	95 (1)
C5-Cr-C8	176 (2)	178 (1)
C6-Cr-C7	84 (2)	87 (1)

TABLE VI-4 (continued)

C6-Cr-C8	87	(2)	92	(1)
C7-Cr-C8	80	(2)	86	(1)
Mn-P1-C9	105	(1)	107.2	(7)
Mn-P1-C13	114	(1)	119.7	(7)
Mn-P1-C19	123	(1)	116.1	(7)
C9-P1-C13	106	(2)	103.4	(9)
C9-P1-C19	106	(2)	106.5	(10)
C13-P1-C19	101	(2)	102.6	(9)
Mn-P2-C25	119	(1)	122.5	(7)
C10-P2-C11	99	(2)	104.4	(9)
C10-P2-C25	104	(2)	105.1	(9)
C11-P2-C25	102	(2)	103.2	(9)
Mn-P2-C10	109	(1)	107.5	(6)
Mn-P2-C11	121	(1)	113.7	(7)
C12-P3-C31	105	(1)	103.8	(9)
C12-P3-C37	99	(2)	101.5	(9)
Cr-P3-C12	113	(1)	114.1	(7)
Cr-P3-C31	116	(1)	118.5	(7)
Cr-P3-C37	120	(1)	112.7	(7)
C31-P3-C37	101	(2)	104.3	(9)
Cr-C4-O4	172	(4)	174	(2)
Cr-C5-O5	172	(4)	176	(2)
Cr-C6-O6	175	(5)	179	(2)
Cr-C7-O7	170	(3)	178	(2)
Cr-C8-O8	175	(5)	174	(2)
Cℓ1-C43-Cℓ2			119	(2)

TABLE VI-5 AVERAGE VALUES FOR BOND DISTANCES AND ANGLES OF THE 10 PHENYL RINGS IN THE ∝- AND β-ISOMERS

	Distance (Å)		Angle (deg)	
	∝	β	∝	β
Ring 1 (C13-C18)	1.41	1.41	120	120
Ring 2 (C19-C24)	1.43	1.40	120	120
Ring 3 (C25-C30)	1.43	1.43	120	120
Ring 4 (C31-C36)	1.40	1.38	119	120
Ring 5 (C37-C42)	1.43	1.40	119	120

TABLE VI-6 EQUATIONS OF THE BEST LEAST-SQUARES PLANES OF THE TEN PHENYL RINGS IN THE α AND β ISOMERS

Ring (1)[a]	A	B	C	D	χ^2 [b]	σ [b]
C13, C14, C15, C16, C17, C18	0.7646	0.0540	0.6422	3.5525	1.71	0.024
C13(0.003), C14(0.008), C15(0.003), C16(-0.028), C17(0.038), C18(-0.024)						
Ring (2)						
C19, C20, C21, C22, C23, C24	0.2621	0.8789	-0.3992	6.2666	2.36	0.028
C19(0.017), C20(-0.005), C21(-0.026), C22(0.044), C23(-0.030), C24(-0.001)						
Ring (3)						
C25, C26, C27, C28, C29, C30	-0.2001	-0.4092	0.8902	-3.2348	5.10	0.047
C25(-0.064), C26(0.022), C27(0.035), C28(-0.052), C29(0.006), C30(0.052)						
Ring (4)						
C31, C32, C33, C34, C35, C36	0.0561	0.9768	-0.2066	1.3130	2.67	0.028
C31(0.010), C32(-0.001), C33(-0.027), C34(0.046), C35(-0.030), C36(0.002)						
Ring (5)						
C37, C38, C39, C40, C41, C42	-0.1311	-0.1995	0.9711	2.6294	2.21	0.026
C37(0.034), C38(0.040), C39(-0.021), C40(-0.005), C41(0.108), C42(0.008)						

TABLE VI-6 (continued)

Ring (6)						
C13, C14, C15, C16, C17, C18	0.2111	0.8485	-0.4852	-2.0697	1.63	0.018
C13(-0.019), C14(0.000), C15(0.009), C16(0.002), C17(-0.020), C18(0.029)						
Ring (7)						
C19, C20, C21, C22, C23, C24	0.9818	-0.1816	-0.0549	11.9104	1.38	0.018
C19(0.010), C20(-0.023), C21(0.015), C22(0.007), C23(-0.021), C24(0.012)						
Ring (8)						
C25, C26, C27, C28, C29, C30	0.7127	-0.1908	0.6750	17.0927	1.75	0.021
C25(0.002), C26(0.012), C27(-0.027), C28(0.030), C29(-0.018), C30(0.002)						
Ring (9)						
C31, C32, C33, C34, C35, C36	0.8418	0.0942	0.5315	22.9124	0.13	0.006
C31(-0.002), C32(-0.006), C33(0.008), C34(-0.003), C35(-0.005), C36(0.007)						
Ring (10)						
C37, C38, C39, C40, C41, C42	-0.2298	-0.4380	0.8702	5.6974	1.09	0.019
C37(-0.016), C38(-0.007), C39(0.018), C40(-0.006), C41(-0.018), C42(0.029)						

Equations of best least-squares planes in the form Ax+By+Cz=D where x, y, z are co-ordinates in Å with deviations (Å) of atoms from the plane given in brackets.

a. α-isomer: rings 1-5
   β-isomer: rings 6-10

b. X^2 is defined by $\Sigma d_i^2/\sigma_i^2$ where d_i is the deviation of the atom from the plane and σ_i is the atom's positional standard deviation

TABLE VI-7 EQUATIONS OF THE BEST LEAST-SQUARES PLANES AROUND THE MANGANESE AND CHROMIUM ATOMS FOR BOTH THE α AND β ISOMERS[a]

	A	B	C	D	χ^2	σ
PLANE (1)						
Br, Mn, P2, C1, C2	0.4331	-0.7501	0.5000	0.6532	10.8	0.045
Br(0.030), Mn(0.019), P2(-0.039), C1(0.056), C2(0.046)						
PLANE (2)						
Br, Mn, P1, C2, C3	0.1445	0.5504	0.8223	0.8103	8.30	0.042
Br(-0.032), Mn(-0.012), P1(0.036), C2(-0.043), C3(0.051)						
PLANE (3)						
Mn, P1, P2, C1, C3	0.8770	0.3116	-0.3658	8.1657	31.42	0.080
Mn(0.054), P1(-0.075), P2(0.052), C1(0.067), C3(-0.098)						
PLANE (4)						
Cr, C4, C5, C7, C8	-0.4139	0.8478	-0.3315	-5.2635	2.17	0.030
Cr(0.054), C4(-0.016), C5(-0.013), C7(-0.016), C8(0.010)						
PLANE (5)						
Cr, P3, C4, C6, C7	0.8680	0.2219	-0.4442	4.9548	13.61	0.068
Cr(0.032), P3(0.049), C4(-0.072), C6(0.065), C7(0.074)						
PLANE (6)						
Cr, P3, C5, C6, C8	0.3662	0.5434	0.7554	6.4947	0.11	0.007
Cr(-0.003), P3(0.006), C5(-0.006), C6(0.007), C8(-0.005)						

TABLE VI-7 (continued)

PLANE (7)						
Br, Mn, P2, C1, C2	0.5636	0.3444	-0.75	1.5068	0.00	0.030
Br(0.025), Mn(0.000), P2(-0.027), C1(-0.033), C2(0.035)						
PLANE (8)						
Br, Mn, P1, C2, C3	0.5937	0.5486	0.5881	14.2213	0.00	0.016
Br(0.009), Mn(-0.028), P1(0.003), C2(0.012), C3(0.004)						
PLANE (9)						
Mn, P1, P2, C1, C3	0.6511	-0.7496	0.1191	9.1275	4.83	0.027
Mn(0.048), P1(-0.011), P2(-0.010), C1(-0.013), C3(-0.014)						
PLANE (10)						
Cr, C4, C5, C7, C8	-0.1095	-0.6928	0.7128	8.0233	11.76	0.062
Cr(-0.020), C4(0.065), C5(-0.055), C7(0.067), C8(-0.057)						
PLANE (11)						
Cr, P3, C4, C6, C7	0.9497	-0.2848	-0.130	15.6537	4.60	0.036
Cr(0.008), P3(0.028), C4(-0.039), C6(0.041), C7(-0.038)						
PLANE (12)						
Cr, P3, C5, C6, C8	0.2410	0.6535	0.7175	15.0942	1.14	0.017
Cr(-0.020), P3(0.016), C5(-0.009), C6(0.020), C8(-0.007)						

a) The equations of the planes, as well as χ and σ are defined in Table VI-6 configuration). The coordination around the Cr atom is also octahedral.

The β-isomer crystallizes as the mono-CH_2Cl_2-solvate, $Br(CO)_3Mn(Triphos)Cr(CO)_5 \cdot CH_2Cl_2$. Structures containing CH_2Cl_2 have been previously reported (e.g., $[(PPh_3)_2Rh(CO)_2] \cdot 2CH_2Cl_2$[113]) in which the possibility of bonding between one of the Cl atoms of the CH_2Cl_2 molecule and a carbonyl group seemed probable. For the β-isomer, no contacts less than 3.5 Å were found between either Cl atom and a CO group. The shortest distance between Br and a hydrogen atom in a computed position on methylene chloride (2.88 Å) is only slightly less than the sum of the Van der Waals radii (3.15 Å).

In the α-isomer, the plane around the Mn atom, defined by P1-P2-C3-C1, is almost co-planar with the P3-C7-C6-C4 plane around Cr and this no doubt arises from packing effects. In the β-isomer these planes are not co-planar.

In both structures, the Triphos ligand is linked to the Mn atom through two adjacent P atoms with the remaining P atom bonding to Cr. The difference between the two isomers is found to reside on P2 only. This difference can be more readily seen if one considers the position of the phenyl ring (C25-C30) and the Br atom relative to the Mn-P1-C9-C10-P2 plane, as shown in Figure VI-4 . In the α-isomer the Br atom is *trans* to the phenyl ring while in the β-isomer it lies *cis* to the phenyl ring.

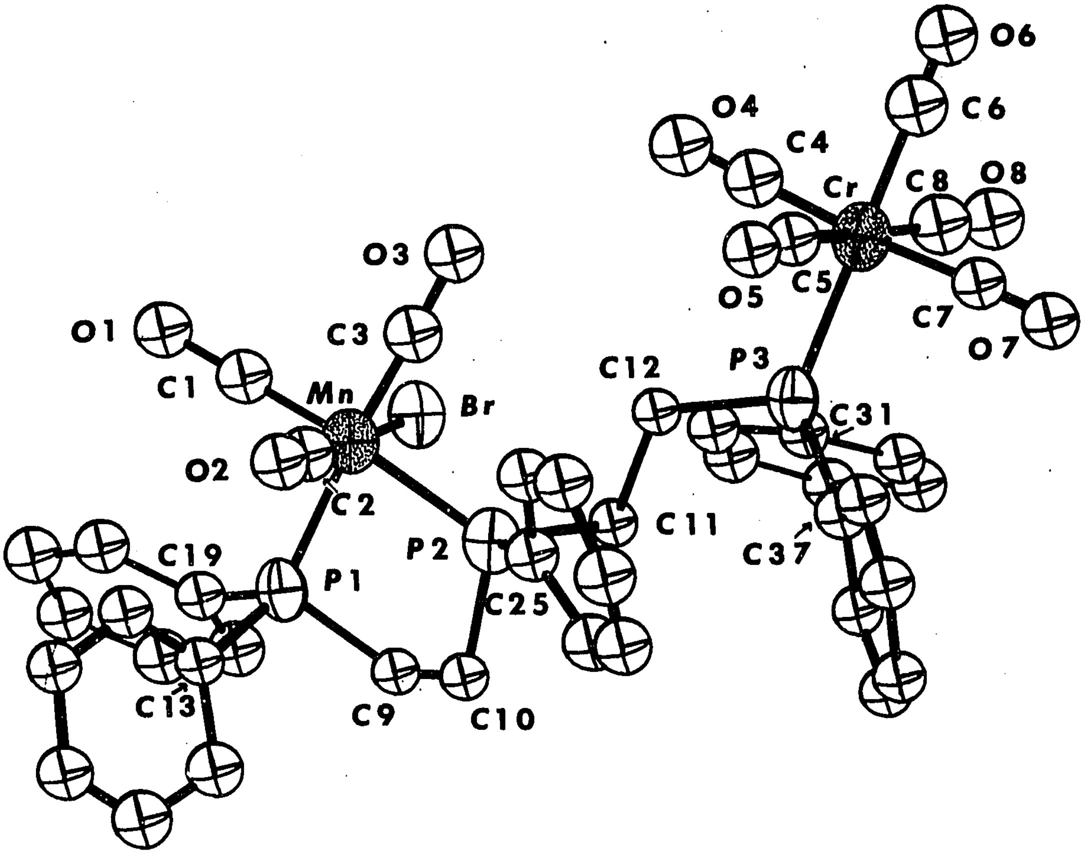

FIGURE VI-1. MOLECULAR STRUCTURE OF THE α-ISOMER PROJECTED APPROXIMATELY DOWN [010].

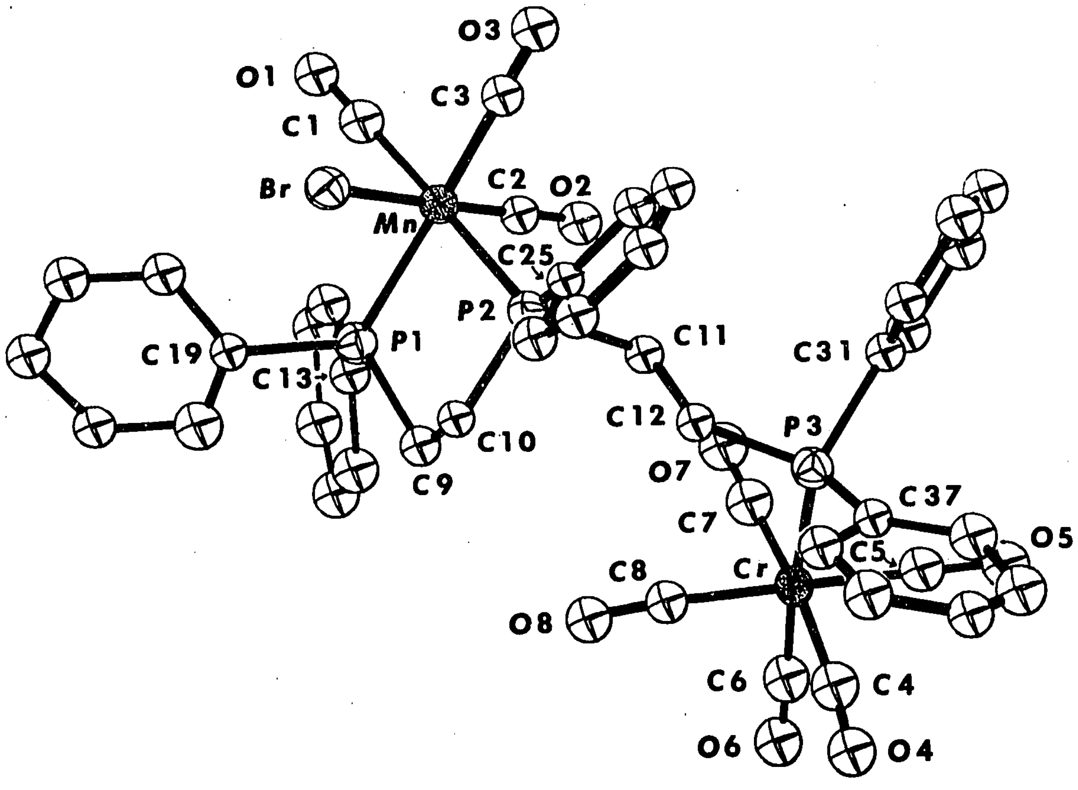

FIGURE VI-2. MOLECULAR STRUCTURE OF THE β-ISOMER PROJECTED DOWN [010].

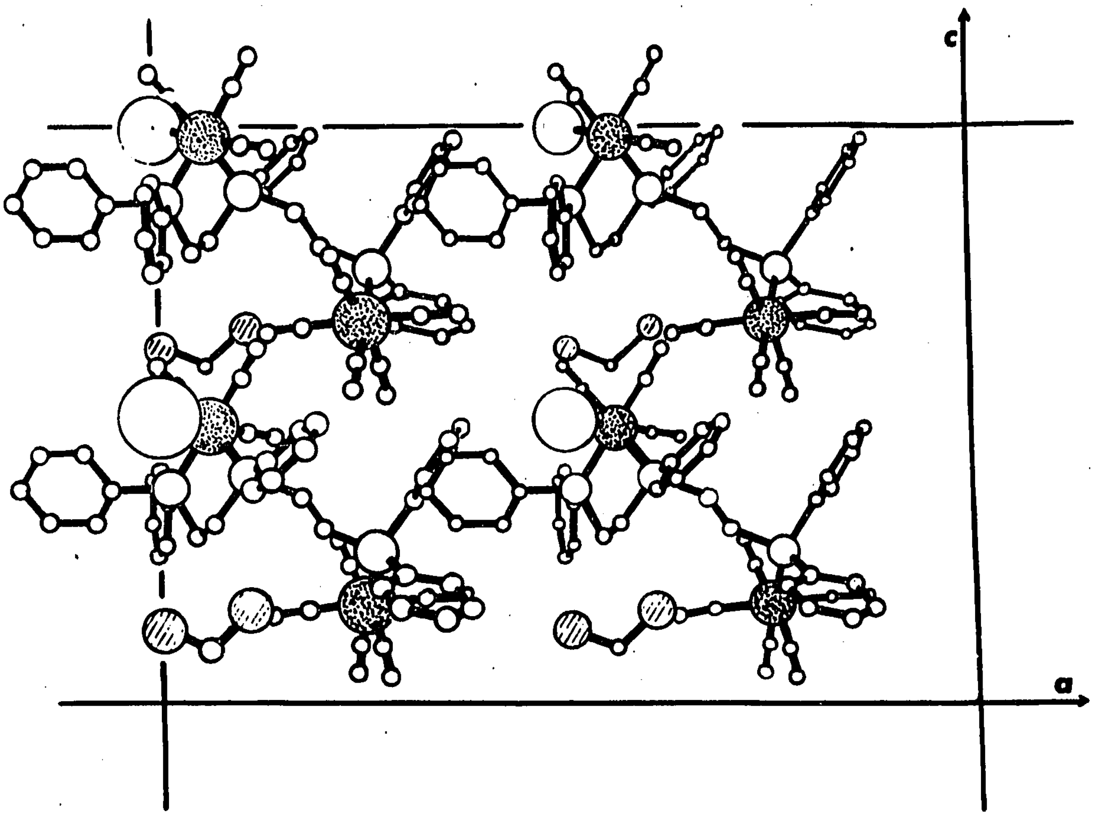

FIGURE VI-3. PROJECTION OF THE CONTENTS OF THE UNIT CELL ON [010] FOR THE β-ISOMER.

Reactions involving the substitution of CO groups in $Mn(CO)_5X$ (X = Cl, Br, I) by tertiary phosphines and phosphites (L), to give products of the type *mer*- and *fac*- $Mn(CO)_3L_2X$ have been well documented[114]. The reactions are known to proceed by sequential substitution of the CO groups and the intermediate product, $Mn(CO)_4LX$, can in most cases be readily isolated. Further reaction of this product, $Mn(CO)_4LX$, with a different phosphine or phosphite (L') should give products of the type *mer*- and *fac*- $Mn(CO)_3LL'X$, but as yet no known products of this type have been isolated*.

Since reaction of $Mn(CO)_5X$ with Triphos led to the formation of the disubstituted complexes *fac*-$Mn(CO)_3(Triphos)X$ in which only two of the three phosphorus atoms are bonded to manganese, and since these atoms are not equivalent i.e. the phosphorus atoms are bonded to *different* groups, the complex formed is of the type $Mn(CO)_3LL'X, L \neq L'$.

Such isomerism is well documented in the case of the reactions of ethylenediamine and its derivatives with Co(III) and Cu(II) salts[116]. Recently, the reaction of metal complexes with bridging arsine ligands have also been shown to produce isomers of this type[89,101]. Reaction of the tertiary diphosphine $PPh(Me)CH_2CH_2P(Me)Ph$ (*meso* or *racemic* form) with $RuCl_3$ also yields similar complexes[117].

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* A kinetic study of the reaction of $Mn(CO)_4LX$, L = phosphine, with $P(OBu^{\underline{n}})_3$ has been reported, but no products were isolated[115].

The conformation of the five-membered ring (Mn-P1-C9-C10-P2) would be expected to be influenced by the groups attached to the P atoms. An attempt was thus made to try and determine the factors responsible for the observed conformations.

An analysis of the chelate rings involving substituted ethylenediamine has shown that a series of energetically equivalent "minimum energy" conformations can exist[112]. These depend on, among other factors, the relative positions of the groups attached to the N atoms. This analysis has been extended to phosphine-type ligands[118]. The results show that in all cases (using symmetrical bridging phosphine ligands), the conformation of the ring is largely determined by steric interaction of the phenyl rings on the phosphine phosphorus atoms. However, in the present work, this does not seem to be the only factor responsible for the conformational changes.

Using the P-Mn-P plane as reference plane[119], a comparison of the angles between the normal to this plane and the substituent attached to the P atoms, for both the α- and β-isomers, is shown in Figure VI-4. The α-isomer can have either ring conformation depending on which enantiomer is chosen. Consider the λ-conformation, as shown in Figure VI-4a; C9 and C10 are on opposite sides of, though not equidistant from, the P-Mn-P plane. Since the phenyl ring (C19-C24) is much bulkier than the methylene group (C11), it will move as far away as possible from the large Br atom. It does this by "buckling" the chelate

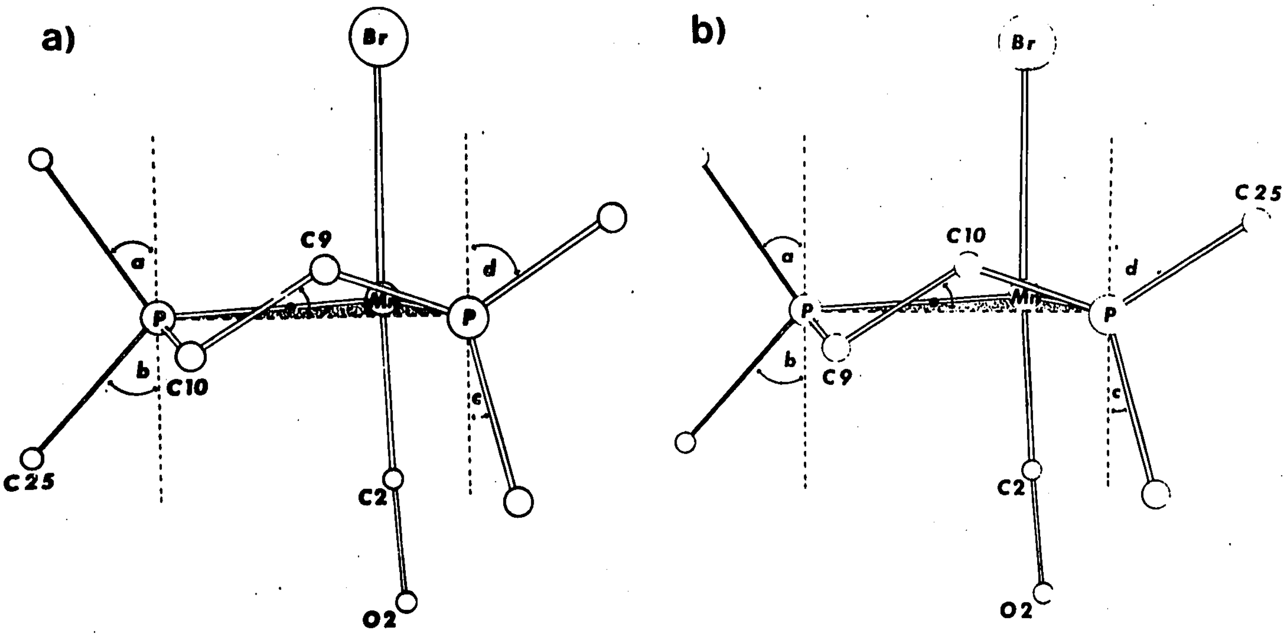

FIGURE VI-4. PROJECTION OF THE MOLECULE SHOWING THE CONFORMATION OF THE CHELATE RING. (a) α-ISOMER (b) β-ISOMER.

Angle*	α-isomer	β-isomer
a	41°	34°
b	38°	44°
c	25°	24°
d	59°	58°
e**	28°	31°

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* This is the angle between the normal to the plane and the bond joining P with a carbon atom.

** e is the angle between the P-Mn-P plane and the bond joining C9-C10.

ring, thus giving rise to the conformation observed. Although the C2-02 group remains normal (within experimental error) to the P-Mn-P plane, the Br-Mn-P1 angle is less than 90°. The non-bonded interaction is thus relieved by distortion of the groups attached to the phosphorous atoms with concomitant distortion of the chelate ring.

In the β-isomer, which has the λ conformation, atoms C9 and C10 are on opposite sides of, though not equidistant from the P-Mn-P plane (Figure VI-4b). The phenyl ring (C25-C30) tends to move as far away from the Br atom as possible, "buckling" the ring in the opposite direction, with the methylene group (C11) moving in towards C2-02. The phenyl ring (C19-C24) on P1 is blocked from moving further away from the Br atom by interaction of ring C13-C18 with C2-02. The C2-02 group remains normal to the P-Mn-P plane but in this isomer the Br-Mn-P2 angle is reduced to less than 90°. The steric interaction is again relieved by the distortion of the chelate ring and by the groups attached to the P atoms.

The structures of numerous tertiary phosphine and phosphite derivatives containing manganese carbonyl and chromium carbonyl moieties have been reported[120-132]. The present results for the various metal carbonyl bond lengths correlate well with those obtained previously*.

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* The following discussion will be confined to the more accurately determined β-isomer, unless otherwise stated.

The Mn-C bond length with CO groups *trans* to the tertiary phosphines (1.86, 1.87) are longer than the Mn-C bond length for the CO *trans* to Br (1.73Å). A related, but opposite effect, should be observable[56] in the corresponding CO bond lengths. Although the trend in the CO bond lengths is in the right direction, the effect is small.

Mention of the structure determination of $Mn(CO)_5Br$ has been made[133], but as yet no results have been published. Mn-Br bond lengths have been reported for the complexes *fac*-$Mn(CO)_3(CNCH_3)_2Br$ (2.537(2)Å)[134] and *cis*-$Mn(CO)_4(C{=}C{=}PPh_3)Br$ (2.507(8)Å)[135], and are similar to the values found in this work (2.534(4)Å) (α-isomer = 2.537(8)Å). The Mn-Br bond length reported for the Br bridged complex, $[Mn(CO)_4Br]_2$, is 2.526(5)Å[136].

Bond length data are available for the Cr-P bond in $Cr(CO)_5PPh_3$ (2.442(1)Å) and $Cr(CO)_5P(OPh_3)$ (2.309(1)Å)[122]. If the phosphine ligand attached to Cr in the β-isomer is regarded as a $PEtPh_2$ type ligand, comparisons with these other Cr-P bond lengths can be made. The Cr-P bond length for the β-isomer would thus be expected to have a value intermediate between that for the Cr-phosphite bond (in which the π-acceptor property of the ligand predominates in bond formation) and that for the Cr-phosphine bond (in which σ-donating effects predominate). Indeed, the value obtained (2.376(7)Å) lies between these two values.

According to current σ-π bonding theory, as the CO groups in $Cr(CO)_6$ are replaced by phosphines, the remaining CO groups become more strongly bound to the Cr atom. So, replacement of two CO's is more difficult to achieve than replacement of one CO group. Since structural parameters for $Cr(CO)_4$Diphos[131] and $Cr(CO)_3(PNP)$[121] ($PNP=[PPh_2CH_2CH_2]_2NEt$) are available, it is possible to draw some tentative conclusions concerning the effect of the substitution of more than one CO group in a metal carbonyl by the same ligand *viz.*, $PEtPh_2$. The average Cr-C bond length (*trans* to phosphine), for instance, in $Cr(CO)_4$ Diphos (1.83 (1)Å) is apparently slightly *longer* than the equivalent bond length in the β-isomer (1.77(3)Å) being considered here, contrary to what is expected. This result must be due to some special effect of the chelate ring which causes a bond strengthening in the Cr-C bonds, strongly suggesting that CO substitution reactions of metal carbonyls containing chelating phosphines (e.g., Diphos) will depend on both steric and *electronic* effects.

TABLE VI-8a FINAL MEASURED AND CALCULATED STRUCTURE FACTORS
(α ISOMER)

[illegible]

TABLE VI-8a (continued)

TABLE VI-8a (continued)

[illegible]

TABLE VI-8b FINAL MEASURED AND CALCULATED STRUCTURE FACTORS

(β ISOMER)

[illegible]

PART B

REACTION OF $C_5H_5Mn(CO)_3$ AND $C_5H_5Mn(CO)_2(CS)$ GROUP VA DONORS

CHAPTER VII. INTRODUCTION

In 1966, Baird and Wilkinson[137] prepared the first transition metal thiocarbonyl complex. Soon afterwards, Richards[7] predicted that, on the basis of molecular orbital calculations, metal thiocarbonyl complexes should be more stable than the corresponding metal carbonyl complexes. To date, however, thousands of metal carbonyl complexes are known, but only a handful of metal thiocarbonyl complexes have been reported[47].

Recently, the first manganese thiocarbonyl complex $C_5H_5Mn(CO)_2(CS)$ was prepared in our laboratory by a very simple procedure[138]. Consequently, since a great deal of information is available on $C_5H_5Mn(CO)_3$ and its derivatives, $C_5H_5Mn(CO)_2(CS)$ provides an ideal starting point for comparing the characteristics of the CS and CO ligands in related complexes.

Chapter VII contains a general survey of the reactions of $C_5H_5Mn(CO)_3$ and its derivatives with a variety of ligands. It was hoped that when analogous reactions with $C_5H_5Mn(CO)_2(CS)$ were undertaken, they would provide valuable information on the nature of the manganese thiocarbonyl bond. Two comparative studies of the reactions of $C_5H_5Mn(CO)_3$ and $C_5H_5Mn(CO)_2(CS)$ were undertaken.

The first of these studies is presented in Chapter IX. The reaction of $C_5H_5Mn(CO)_3$ with group VA donors, L, has been studied by a number of research groups and the physical properties of the products $C_5H_5Mn(CO)_2L$ and $C_5H_5Mn(CO)L_2$ are well documented. Reactions of L with $C_5H_5Mn(CO)_2(CS)$ reveal that substitution of the CO groups takes place and that products of the type $C_5H_5Mn(CO)(CS)L$ and $C_5H_5Mn(CS)L_2$ are readily prepared. These new products were characterized by their IR, NMR and mass spectra.

Chapter X describes the second of the comparative studies. In this study, the reaction of linear polyphosphines (Triphos and Diphos) with $C_5H_5Mn(CO)_3$ and $C_5H_5Mn(CO)_2(CS)$ gave both chelate and bimetallic complexes. It was anticipated that the reaction of Triphos with $C_5H_5Mn(CO)_3$ and $C_5H_5Mn(CO)_2(CS)$ would lead to the formation of diastereomers, similar to those reported in Chapter IV. Indeed, the results indicate that $C_5H_5Mn(CO)(Triphos)$ and $C_5H_5Mn(CS)(Triphos)$ exist as a mixture of complexes. The physical properties of all the new complexes are reported.

CHAPTER VIII A BRIEF SURVEY OF THE CO SUBSTITUTION REACTIONS OF $C_5H_5Mn(CO)_3$

A. INTRODUCTION

This survey covers the CO substitution reactions of $C_5H_5Mn(CO)_3$ and its derivatives, and is considered to be complete until December, 1972. The results obtained from the physical methods of structure elucidation, as well as kinetic results, are also included in this review.

This topic has been dealt with in part in a number of previous reviews[5a] - the latest one being in 1969[139] - but it is felt that a complete review has not been published since 1964[140].

B. REVIEW

a) Substitution Reactions of $C_5H_5Mn(CO)_3$ and its Derivatives

Substitution of the CO groups in $C_5H_5Mn(CO)_3$ by monodentate ligands under thermal conditions can only be achieved at high temperatures and even then extensive decomposition occurs[42], for example,

$$C_5H_5Mn(CO)_3 + PPh_3 \xrightarrow[\text{no solvent}]{220°C} C_5H_5Mn(CO)_2(PPh_3) \text{ (∿15\% yield)}.$$

However, the UV irradiation of a solution of $C_5H_5Mn(CO)_3$ and a variety of ligands, L, readily affords the dicarbonyl products, $C_5H_5Mn(CO)_2L$, in high yield. The reactions proceed *via* formation of $C_5H_5Mn(CO)_2$. This intermediate has been detected recently by IR spectroscopy, after photolysis of $C_5H_5Mn(CO)_3$ at 80°K in a 1/3 nujol/methylcyclohexane matrix[141]. The $C_5H_5Mn(CO)_2$ intermediate then reacts with L to give $C_5H_5Mn(CO)_2L$. When the reaction is performed in coordinating solvents such as THF, the $C_5H_5Mn(CO)_2THF$ complex can be detected[140]. This THF complex is unstable and the THF can readily be displaced by other ligands. The existence of the $C_5H_5Mn(CO)(THF)_2$ complex has also been demonstrated at low temperatures[142].

Whereas a great variety of monosubstituted products have been prepared, the same is not true of di- and trisubstituted products. In general, these complexes tend to be unstable[143].

The products from the reaction of a wide range of ligands L, with $C_5H_5Mn(CO)_3$ are presented in Table VIII-1.

Reaction of $C_5H_5Mn(CO)_3$ with MX_4 (M = Si, Ge, Sn; X = Cl) to give products of the type $[C_5H_5Mn(CO)_2MX_3]^-$ has been reported[144-146]. Addition of $HSiPh_3$ to $C_5H_5Mn(CO)_3$ leads to the formation of a seven coordinate complex, $C_5H_5Mn(CO)_2(H)SiPh_3$ [145,147]. An X-ray structure determination of the analogous complex, $C_5H_5Mn(CO)_2(H)SiCl_3$, revealed that the H atom is bonded to both the manganese and the silicon atom[148].

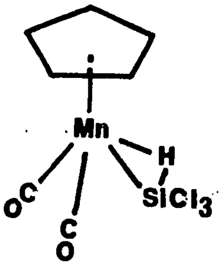


TABLE VIII-1 PRODUCTS OBTAINED FROM THE CO SUBSTITUTION REACTIONS OF $C_5H_5Mn(CO)_3$

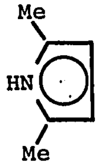
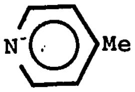
Donor [a]	IR-ν(CO) cm^{-1} [b]	NMR [c]	Identification	Ref.
	$C_5H_5Mn(CO)_2L$			
Nitrogen				
N_2	1980, 1923 h	5.16 da	MS, Anal.	157,158
N_2H_4			Anal.	159
$N_2C_5H_8$	1947, 1883 h	5.30 da	Anal.	164
$HN[CH_2]_2NH$			Stability Det., Anal.	161,165
$N[CH_2]_3N$			Stability Det., Anal.	161,165
$C_6H_{12}N_4$			Stability Det., Anal.	161,165
NEt_3			Stability Det. Anal, SS	161,166
$N(\underline{n}\text{-}Pr)_3$			Anal., Stability Det.	161
$N(\underline{n}\text{-}Hexyl)_3$			Anal., Stability Det.	161
Me_2NH	1932, 1859 cy	5.78 b	Anal., Stability Det. M.S.	67,161, 255a
HNC_5H_{10}			Stability Det. SS, Anal., NQR	161,167 168
NC_5H_5	1934, 1866 cy	5.67 b	Stability Det. Anal., NQR	67,161 166,168 169.
$NH_2C_6H_5$			Anal.	167
NH_3			Stability Det., Anal.	161
$HN(CH_2)_4$	1930 - b		Stability Det.	161
NMe_3			Anal., Stability Det.	161
			Anal., Stability Det.	161
			Anal., Stability Det.	161
Nitrile				
MeCN	1933, 1859 h	5.59 da	Stability Det., Anal. SS, UV, IR, NQR	161,166 168,170- 173
HCN	1919, 1859 k	5.83 db	MS, IR, ^{14}N NMR, Anal.	174,175
DCN	1919, 1859 k		MS, Anal., IR	174

TABLE VIII-1 (continued)

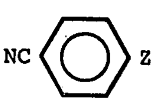
Donor^{a}	IR-ν(CO) cm^{-1} ^{b}		NMR^{c}		Identification	Ref.
$C_6H_{11}CN$	1957, 1905	cy	5.57	b	^{14}N NMR , M.S. (I.P=7.12)	.67,167 175,255a
PhCN					Anal.	168,171
$PhCH_2CN$	1929, 1862	b	5.55	da	UV, IR, Anal.	172,173
C_6F_5CN	1939, 1886	b	5.36	da	^{14}N NMR, UV, IR, Anal.	172,173 175
trans-NCC=CCN	1939, 1887	b	5.39	da	UV, IR, Anal.	172,173 176
trans PhNC=CCN	1934, 1873	b	5.47	da	UV, IR, Anal.	172,173 176
						
Z = NO_2	1934, 1877	b	5.36	da	UV, IR, Anal.	172,173
CF_3	1934, 1876	b	5.37	da	UV, IR, Anal.	172,173
CN	1936, 1877	b	5.38	da	UV, IR, Anal.	172,173
COOEt	1932, 1875	b	5.39	da	UV, IR, Anal.	172,173
H	1935, 1871	b	5.43	da	UV, IR, Anal.	172,173
Me	1933, 1869	b	5.45	da	UV, IR, Anal.	172,173
OMe	1932, 1867	b	5.45	da	UV, IR, Anal.	172,173
Phosphorus						
PH_3	1958, 1899	h	6.30 (2.8)	db	MS(I.P.=7.28), Anal.	177,178
PH_2Ph	1940, 1873	cy	5.88 (2.8)	db	MS(I.P.=7.28), Anal.	150,151 179
PF_3	1996, 1938	h	5.02	-	MS(I.P.=8.24), Anal. ^{19}F NMR	142,179- 182 151
PCl_3	1994, 1944	h			MS(I.P.=8.12)	177,179 181-182
PBr_3	1994, 1945	h			MS(I.P.=8.01),	177,179
PF_2Ph	1976, 1916	cc			Anal.	179
PCl_2Ph	1973, 1916	cc			Anal.	179,182
$PCl_2C_5H_4Mn(CO)_3$	-	-			Anal.	183
PBr_2Ph	1973, 1918	cc			Anal.	179
PI_2Ph	1973, 1918	cc			Anal.	179
PFClPh	1972, 1915	cc			Anal.	179
$PClPh_2$	1956, -	cs			Anal.	182
$PFPh(NEt_2)$	1950, 1887	cc			Anal.	179

TABLE VIII-1 (continued)

Donor ^{a}	IR-ν(CO) cm^{-1} ^{b}		NMR ^{c}	Identification	Ref.
$PClPh(NEt_2)$	1946, 1884	cc			179
$PBrPh(NEt_2)$	1945, 1884	cc			179
$PIPh(NEt_2)$	1948, 1888	cc			179
PMe_3	1939, 1876	cy		NQR, Anal.	168,181 182
PEt_3	1931, -	cs		Anal.	182
P(i-Pr)$_3$	1932, 1870	h	5.69(d)^{d}cs	IR, NQR, MS(I,P.=7.40) protonation, Anal.	43, 44 168,181, 182,255a
P(n-Bu)$_3$	1935, 1872	cy	5.74(d)^{d}cs	IR, NQR, Anal.	44,168 181,182
$P(C_6H_{11})_3$	1931, 1869	cy	5.72(d)^{d}cs	protonation, Anal.	43,44, 181,182
P(s-Bu)$_3$	1930, -	cs		Anal.	182
PPh_3	1944, 1883	h	5.78(d)^{d}b	X-ray MW,MS(I,P.=6.93), NQR, IR, conductivity, protonation, Anal., dipole moment.	41-44, 143,155, 167,168, 177,181, 182,184-186
P(o-$CH_3C_6H_4$)	1937, -	cs		Anal.	44,182
P(p-$CH_3C_6H_4$)	1936, 1868	cs	5.94(d)^{d}cs	Anal., protonation	43,182
$P(CH_2Ph)_3$	1929, 1865	cs	6.32(d)^{d}cs	Anal., Protonation	43, 44, 182
PMe_2Ph	1932, 1867	cs	5.82 cs (2.0)	MS(I.P.=8.32), Anal.	40,147, 182
P(n-Bu)$_2$Ph	1930, -	cs		Anal.	182
$PMePh_2$	1935, 1872	cs	5.91 b (1.9)	Anal.	40,147 182
P(n-Bu)Ph_2	1930, -	cs		Anal.	182
P(NEt)$_2$Ph	1933, 1865	cc		Anal.	179
$P(CMe_3)_3$	1920, 1891	p		UV, ^{31}P NMR, H NMR, Anal.	187
$P(SiMe_3)_3$	1923, 1859	p		UV, ^{31}P NMR, H NMR, Anal.	187
$P(GeMe_3)_3$	1923, 1852	p		UV, ^{31}P NMR, H NMR, Anal.	187
$P(SnMe_3)_3$	1919, 1852	p		UV, ^{31}P NMR, H NMR, Anal.	187
$P(OMe)_3$	1954, 1891	cy		Anal.	181,182
$P(OEt)_3$	1949, 1886	cy		Anal.	182,188
P(Oi-Pr)$_3$	1947, 1881	h		Anal. MS(I.P.=7.17)	177,182
P(On-Bu)$_3$	1948, 1886	cy			182,188
$P(OCH_2CH_2Cl)_3$	1952, -	cs			182
$P(OPh)_3$	1970, 1909	cy	6.20(d)^{d}cs	NQR, IR, MS(I.P.=7.40) protonation, Anal.	181 43,44 168,177 182,188
P(p-$OC_6H_4CH_3$)$_3$	1963, -	cs	5.86(d)^{d}cs	Anal.	44,182

TABLE VIII-1 (continued)

Donor ^{a}	IR-ν(CO) cm^{-1} ^{b}		NMR ^{c}	Identification	Ref.
$P(\underline{o}-OC_6H_4CH_3)_3$	1965, -	cs		Anal.	182
$P(\underline{o}-OC_6H_4C_6H_5)_3$	1965, -	cs		Anal.	182
$P[(C_5H_4)Fe(C_5H_5)]_3$	1938, 1874		5.23(d) (1.3)	Anal.	189,190
Arsenic					
AsH_3			5.46 dc	MS(I.P.=7.16), Anal.	191
AsF_3	2006, 1953	h	4.90 dc	MS(I.P.=8.34), Anal.	149,180
$AsPh_3$	1934, 1862	c	5.72 b	MW, IR, NQR, Anal. conductivity, dipole moment, protonation	41, 44, 143,155, 168
$AsF_2(OEt)_2$					149
$AsF(OEt)_2$					149
$As(GeMe_3)_3$				Anal.	192
$As(SnMe_3)_3$				Anal.	192
$As(OMe)_3$	1969, 1907	cy		Anal.	188
$As(OEt)_3$	1962, 1904	cy		Anal.	188
$As(O-\underline{n}Bu)_3$	1962, 1905	cy		Anal.	188
$As(OPh)_3$	1978, 1932	cy		Anal., NQR	168,188
Antimony					
SbF_3				MS	180
$SbPh_3$	1917, 1857	n	5.64 b	IR, NQR, protonation, NMR, Anal. dipole moment	43,44 143,167 168,155
$Sb(OEt)_3$	1947, 1881	n		Anal.	188
$Sb(O\underline{n}-Bu)_3$	1943, 1879	cy		Anal.	188
$Sb(OPh)_3$	1964, 1908	cy		Anal.	188
Bismuth					
$BiPh_3$	1900, 1860	n	5.64 b	Dipole moment, Anal.	143

TABLE VIII-1 (continued)

Donor[a]	IR-ν(CO) cm^{-1} [b]	NMR[c]	Identification	Ref.
Oxygen				
Et_2O			Stability Det.	161
Me_2CO			Stability Det, SS	166
$\mathrm{Me\overline{CHCH_2O}}$			Stability Det, SS	161,196
Me(Et)CO			SS	196
CH_3CHO			SS	196
$O(CH_2CH_2)_2O$			Stability Det.	161
THF	2020, 1965, cs		Stability Det, SS	161,166 196,67
Sulfur				
SH_2	1938, - b			194,195
SMe_2	1951, 1887 1944, 1880 h	5.59 cs	IR, NMR, Raman, MS, Anal.	197
SEt_2	1951, 1887 1942, 1878 h	5.67 cs	IR, NMR, Raman, MS, Anal.	194, 195,197
$S(\underline{n}Pr)_2$	1949, 1885 1941, 1887 h	5.59 cs	IR, NMR, Raman, MS, Anal.	197
$S(\underline{n}Bu)_2$	1949, 1885 1941, 1877 h	5.60 cs	IR, NMR, Raman, MS, Anal.	197
$S(Ph)_2$	1938, - b			194,195
$S(CH_2Ph)_2$	1948, 1886 1939, 1875 h	5.89 cs	IR, NMR, Raman, MS, Anal.	197
$S(CH_2)_4$	1953, 1889 1942, 1878 h	5.60 cs	IR, NMR, Raman, MS, Anal.	194, 195,197
SO_2	2028, 1969 -			167,194, 195
SF_4			MS	180
$SOMe_2$	1949, 1894 b		Anal.,MS (I.P.=7.12)	167,193 194,195 255a
$SO(CH_2)_4$	1949 - b			194,195
$SOPh_2$	1953 - b			194,195
$SO(OCH_2)_2$	1976, 1919 b	5.83 b		167,194 195
$C_5H_5Fe(CO)_2SMe$	1947, 1858 cy	5.83 b	Anal.	228
$C_5H_5Mo(CO)_3SMe$	1932, 1878 cy	5.72 5.88 b	Anal.	228
$C_5H_5W(CO)_3SMe$	1948, 1854 cy	5.70 b	Anal.	228
$SMeSnMe_2$	1938, 1863 cy	5.75 b	Anal.	228

TABLE VIII-1 (continued)

Donor[a]	IR-ν(CO) cm^{-1} [b]		NMR[c]		Identification	Ref.
Carbon						
(i) Olefin						
C_2H_4	1976 1916	cy	6.02	b	IR, Anal.	67,170, 198
C_5H_8	1969, 1905	cy	5.97	b	MS(I.P.=7.29), NQR, IR, Anal.	67,198
C_7H_{12}	1967, 1905	cy	5.93	b	NQR, IR, Anal, MS Dipole moment	67,198 255a
C_8H_{14}	1967, 1905	cy	5.90	b	NQR, IR, Anal, MS Dipole moment	67,198 255a
C_9H_{16}	1969, 1905	cy	5.87	b	IR, Anal.	67
C_9H_8	1960, 1904	b	5.30	da	IR, Anal.	199
$C_{12}H_8$	1969, 1916	b	5.20	da	IR, Anal.	199
C_7H_{10}	1972, 1912	cy	5,93	b	IR, Anal., NQR	67,198, 200
C_7H_8	1972, 1912	cy	5.90	b	IR, Anal., NQR , MS X-ray, NMR	67,200 210,226
$C_{10}H_{14}$	1970, 1908	cy	5.95	b	IR, Anal.	67,199 200
$C_{10}H_{12}$	1972, 1912	cy	5.95	b	IR, Anal.	67,199
$C_9H_8O_3$	1968, 1899	mc	5.22	da	IR, Anal., NQR	198,200
C_4H_6	1976, 1916	h			IR, Anal., MS	170,255a
C_6H_8	1976, 1916	cy	5.93	b	IR, Anal., SS	166,201
C_5H_{10}	1978, 1920	h				198
C_3H_6	1978, 1920	mc				198
C_5H_6O	1973, 1914	b	5.14	da	IR, Anal.	199,200
$C_3H_2O_3$	2001, 1942	b	5.09	da	IR, Anal., MS	199,200 255a
$C_4H_2O_3$	2016, 1957	b	4.78	da	IR, Anal., MS	199,200 225
CH_2=CHCN	1996, 1940	h	5.10	da	IR	176
CH_3HC=CHCN			5.17 5.19	da		170,176
NCHC=CHCN			5.84	da		176
$(NC)_2C=C(CN)_2$			4.48	da		176,202
$(OMe)_2C=C(OMe)_2$	1984, 1925	cy	5.72	db	Anal.	203
$C_6F_4C_6H_6$			5.46	-	Anal., MS, IR	204
$C_6F_4C_6H_8$					IR	204
$C_8H_8O_3$					NQR	168

TABLE VIII-1 (continued)

Donor[a]	IR-ν(CO) cm^{-1} [b]		NMR[c]		Identification	Ref.
(ii) Acetylene						
$PhC\equiv CH$					IR	205
$EtO_2CC\equiv CCO_2Et$					IR	205
$PhC\equiv CPH$					IR,SS	205,166 206
$CF_3C\equiv CCF_3$	2033, 1969	cc	5.72	db		207
(iii) Miscellaneous						
CS	2006, 1954	cs	5.18	cs	IR, NMR, MS,	208,138
C(OMe)Me	1962, 1899 1976, 1915	h	5.63	b	Anal.,IR	47 162,163
C(OMe)Ph	1954, 1890	h	5.80	b	Anal.,IR	162,163
			$[C_5H_5Mn(CO)_2]_2(L-L)^e$			
Me_2PPMe_2	1929, 1866	ce	5.49	c	Anal.	40
Ph_2PPPh_2	1937, 1874	ce	5.77	c	Anal.	40
AM	1934, 1862	c			MW, Anal. Conductivity	41,42
$Ph_2As(CH_2)_2AsPh_2$	1925, 1835	-			Anal.,Conductivity	45
$Me_2AsAsMe_2$	1930, 1867	ce	5.52	c	Anal.	40
C_4H_8	1961, 1896	a			Anal., NMR	170
C_6H_8	1972, 1912	cy	5.97	b	Anal., NMR	67,201
C_8H_{12}	1961, 1894	cs	5.87	b	Anal., NMR	67
C_7H_8	1980, 1921	cy	5.84	b	Anal., NMR	67
$HN[CH_2]NH$					Anal.	165
$N[CH_2]_3N$					Anal.	165
trans-NH=NH	1915, 1880	b	5.18	da	Anal.	160

TABLE VIII-1 (continued)

Donor^a	IR-ν(CO) cm^{-1} ^{b}	NMR^c	Identification	Ref.
	$C_5H_5Mn(CO)_2L^-$			
C(O)Ph	1877, 1792	5.68 cm	Anal., X-ray	162,209
$SnCl_3$	1926 1863 cm		Anal., Conductivity	144
$GeCl_3$	1924 1858 cm		Anal., Conductivity	144
$SiCl_3$	{2026(m) 1907(s)cm {1969(m) 1839(s)		Anal., Conductivity	146
CN	1905 1828 k	5.78 db		174
	$C_5H_5Mn(CO)_2LL'$			
$SnCl_3$,$SiCl_3$	2022 1981 cm		Anal.,	146
$SiCl_3$,H	2028(vs), 1972 h	4.89 an	Anal., X-ray, IR	145,148
$SiCl_3$,D	2026(vs), 1973 cc		IR	145
$SiPh_3$,H	1986, 1929 hp		IR	147
$SiPh_3$,D	1985, 1928 hp		IR	147
	$C_5H_5Mn(CO)L_2$			
PF_3	1953 k		^{19}F NMR	142
PF_2NMe_2	1920 cy	5.58 dc	Anal.	211
$PF_2NC_5H_{10}$	1915 cy	5.67 dc (t)(2)	^{19}F NMR, Anal.	211
$PMePh_2$	1835 cs	5.96 b (t)(1.7)	Anal.	40
PPh_3	1836 n	5.88 b	Dipole moment, X-ray Anal.	{67,143, {212
$AsPh_3$	1836 n	5.85 b	Dipole moment, Anal.	143
$SbPh_3$	1825 n	5.85 b	Dipole moment, Anal.	143
CS	1991 cs	5.18 cs	MS, IR, Raman, Anal.	{47,138b {208
$OSMe_2$			Anal.	193
C_4H_6	1932 h	6.o3 b	Anal.	67,170 213

Table VIII-1 (continued)

Donor[a]	IR-ν(CO) cm^{-1} [b]	NMR[c]	Identification	Ref.
CS,C_8H_{14}	1951 cs		Anal., IR, MS.	47,138a
CS,PPh_3	1925 cs		Anal., IR	47,138a
		$C_5H_5MnL_3$		
PF_3		5.17(t) (2.3)	Anal., ^{19}F NMR, IR, MS	142
CS			IR	138a
PhCN			IR, Anal.	214
C_6H_6				215,216
C_5C_5				216
CS,CS,C_8H_{14}			IR	138a
		$RC_5H_4Mn(CO)_2L$		
R Donor[a]				
Nitrogen				
Me NC_5H_{11}			Anal.	217
Me NC_5H_5			Anal.	169
Phosphorus				
Me PH_3	1953 1888 c	5.82(2.8)db	Anal.	150
Me PH_2Ph	1940 1873 c	5.88(2.8)db	Anal.	150,152
Me $PHPh_2$				152
Me $PMePh_2$				152
Me PPh_3	1934 1862 c		Anal., Conductivity MW, IR, NMR	41,42 44,218
Me $P(CMe_3)_3$	1921 1892 p		NMR, Anal.	187
Me $P(GeMe_3)_3$	1920 1855 p		NMR, Anal.	187
Me $P(SnMe_3)_3$	1918 1850 p		NMR, Anal.	187
CH_2Ph PPh_3			Anal., NMR	44
Et PPh_3			Anal., NMR	44
Et $P(C_6H_{11})_3$			Anal., NMR	44
Et $P(CH_2Ph)_3$			Anal., NMR	44
CH_3CO PPh_3			Anal., NMR	140
Z PPh_3	(Z = SMe, Cl, Br, I, COMe, COOH, $COOCH_3$;		preparation reported)	184

TABLE VIII-1 (continued)

R	Donor[a]	IR-ν(CO) cm^{-1} [b]			NMR[c]	Identification	Ref.
Arsenic							
Me	$AsPh_3$	1934	1862	c		Anal., IR, MW Conductivity	41,42
Me	$As(CMe_3)_3$					Anal.	192
Me	$As(GeMe_3)_3$					Anal.	192
Me	$As(SiMe_3)_3$					Anal.	192
Me	$As(SnMe_3)_3$					Anal.	192
Et	$AsPh_3$					Anal., NMR	44
CH_2Ph	$AsPh_3$					Anal., NMR	44
Antimony							
Me	$SbPh_3$	1929	1869	cs		IR	218
Sulfur							
Me	$SOMe_2$					MS (I.P.=7.19)	140,255b
Me	SO_2						140
Me	$SOPh_2$					MS (I.P.=6.76)	140,255b
Me	$S(CH_2)_4$					MS (I.P.=6.45)	195,255b
Me	SPh_2					MS (I.P.=6.27)	255b
Me	$S(OCH_2)_4$					MS (I.P.=6.79)	255b
Me	$S(OCH_2)_2$					MS (I.P.=7.38)	255b
Carbon							
Me	PhC≡CPh					IR	267
Me	CS	2009	1959	cs			47
Me	$C(OMe)C_5H_4FeC_5H_5$					IR	219
$[(RC_5H_4)Mn(CO)_2]_2(L-L)$							
Me	AM	1934	1862	c		X-ray, Anal., MW, Conductivity	41,42, 227
Me	$Ph_2As(CH_2)_4AsPh_2$	1910	1815	-			45

TABLE VIII-1 (continued)

R	Donor[a]	IR-ν(CO) cm^{-1} [b]	NMR[c]	Identification	Ref.
		$RC_5H_4Mn(CO)_2L^-$			
Me	$SiCl_3$	2026 (m) 1969(m) 1907 (s) 1839(s)	cm	Anal., IR.	146
Me	$GeCl_3$	1922 1855	cm	Conductivity Anal.	144
Me	$SnCl_3$	1924 1859	cm	Conductivity,Anal.	144
		$RC_5H_4Mn(CO)_2LL'$			
Me	$SiCl_3$ $SnCl_2Ph$	2000 1957	cm	Anal.	146
Me	$SiCl_3$ $SnClPh_2$	1990 (m) 1939	cm	Anal.	146
Me	H $SiPh_3$	1983(vs) 1926	h	Anal.	145
Me	$SnCl_2$ [f] $SiCl_3$	2018 1978	cm	Anal.	146
		$(\underline{Ring})Mn(CO)_2L$			
$\underline{HEt_4C_5}$					
PPh_3		1859 1924	cs	Protonation, Anal. NMR	43
$\underline{Et_5C_5}$					
PPh_3		1919 1865	cs	Protonation, Anal. NMR	43
$\underline{Me_5C_5}$					220
PPh_3					
$\underline{NC_4H_4}$					
PPh_3		1940 1870	n	NMR, Anal.	221
$AsPh_3$		1941 1870	n	NMR, Anal	221
$SbPh_3$		1941 1871	n	NMR, Anal.	221

TABLE VIII-1 (continued)

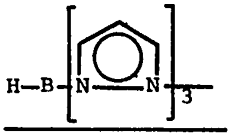
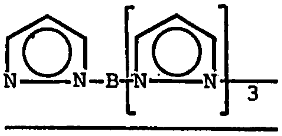
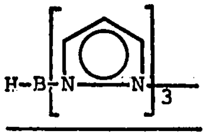
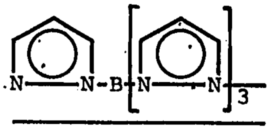
Donor[a]	IR-ν(CO) cm^{-1} [b]			NMR[c]	Identification	Ref.
						
PMe_3	1927	1840	cy		Anal.	181
$P(OMe)_3$	1949	1869	cy		Anal.	181
$P(OPh)_3$	1961	1883	cy		Anal.	181
P(n-Bu)$_3$	1903	1820	th		Anal.	181
PF_3	1988	1925	cy		Anal.	181
						
PF_3	2000	1940	cy			181
PCl_3	1998	1937	cy			181
$P(OPh)_3$	1974	1901	cy		Anal.	181
$P(OMe)_3$	1961	1887	cy		Anal.	181
PPh_3	1945	1870	cy		Anal.	181
PMe_3	1941	1865	cy		Anal.	181
P(n-Bu)$_3$	1937	1861	cy		Anal.	181
P(i-Pr)$_3$	1937	1861	cy		Anal.	181
$P(C_6H_{11})_3$	1935	1859	cy		Anal.	181
Cs[π-(3)-1,2-$B_9H_{11}C_2$]						
PPh_3	1918	1845	cc		Anal.	222
[π-(2)-1,7-$B_9H_{10}CPCH_3$]						
PPh_3	1972	1918	cc		Anal.	222
Toluene						
$CONHC_6H_{11}$	1968 (vs)	1912	cm			223
p-Xylene						
$CONHC_6H_{11}$	1964 (vs)	1905	cm			223

TABLE VIII-1 (continued)

Donor[a]	IR-ν(CO) cm^{-1} [b]		NMR[c]	Identification	Ref.
Mesitylene					
$CONHC_6H_{11}$	1957(vs)	1902	cm	Anal., NMR	223
$CONH_2$	1965	1910	cm		223
NCO	1997	1951	cm		223
$CONHNH_2$	1964	1906	cm		223
CN	2000	1954	cm	NMR, Anal.	224
Durene					
$CONHC_6H_{11}$	1951(vs)	1893	cm		223
$C_6(CH_3)_6$					
$CONHC_6H_{11}$	1943(vs)	1882	cm	Anal., MS, NMR	223
$CONH_2$	1939	1875	cm		223
$CONHNH_2$	1948	1888	cm		223
NCO	1982	1927	cm		223

(Ring)Mn(CO)L_2

				
PF_3	1958	cy		181
$P(OMe)_3$	1871	cy	Anal.	181
$P(OPh)_3$	1895	cs	Anal.	181
				
PF_3	1948	cy		181

Note: A patent[262] has appeared listing a wide range of complexes of the type $RR'C_5H_5Mn(CO)LL'$, R,R' = H, alkyl group; L = CO, group VA donor; L' = group VA donor.

TABLE VIII-1 (continued)

a) Abbreviations used:

i) Solvents; k = KBr; n = nujol; cc = CCl_4; mc = methylcyclohexane; cm = CH_2Cl_2; cy = cyclohexane; b = benzene; c = $CHCl_3$; p = pentane a = acetone; th = THF; ce = dichloroethane; an = acetonitrile; h = hexane; hp = heptane; dc = $CDCl_3$; db = C_6D_6; da = $(CD)_3CO$

ii) IR bands; w = weak; m = medium; vs = very strong

iii) NMR: d = doublet; t = triplet. The value in brackets following the C_5H_5 resonance is J_{P-H}.

iv) Identification: Anal. = Elemental analyses; MS = Mass spectrum; IP = Ionization potential; SS = Solvent study; MW = Molecular weight determination.

b) All bands strong unless otherwise stated

c) All values relative to TMS (τ = 10) unless otherwise stated.

d) τ values relative to hexamethyldisilane

e) For L-L = polyphosphine, see Tables II-1a and II-1b.

f) $SnCl_2$ acts as a bridging ligand.

A recent trend in the chemistry of $C_5H_5Mn(CO)_2L$ (L = phosphine) compounds has been the preparation of a new class of phosphine complexes of $C_5H_5Mn(CO)_2L'$, L' = phosphine, formed by conversion of L into L' <u>while attached to the metal</u>[149-152] e.g.,

$$C_5H_5Mn(CO)_2(PPhCl_2) \xrightarrow{NaBH_4} C_5H_5Mn(CO)_2(PPhH_2)$$

$$C_5H_5Mn(CO)_2(PPh_2H) \xrightarrow{MeLi} C_5H_5Mn(CO)_2(PPh_2Me)$$

Protonation studies of $C_5H_5Mn(CO)_3$ and its derivatives have been investigated[43,153-156]. The ease of protonation of the metal depends on the nature of the ring substituents and the solvent media and, in products of the type $C_5H_5Mn(CO)_2(L)$ (L = group VA donor), on the nature of L. Any effect which causes an increase of negative charge at the metal atom results in an increase in the protonation of the complex.

The first dinitrogen complex of manganese was prepared recently[157,158].

$$C_5H_5Mn(CO)_2(THF) + N_2 \longrightarrow C_5H_5Mn(CO)_2(N_2) + THF$$

The intermediates in the reduction of nitrogen to ammonia (NH_2NH_2[159], *trans*-NH=NH[160]), as well as NH_3[161], have also been complexed to manganese.

Carbene complexes of manganese are also known[162,163,219]. The preparation of $C_5H_5Mn(CO)_2[C(OMe)Ph]$ is shown below:

$$C_5H_5Mn(CO)_3 + LiPh \longrightarrow Li[C_5H_5Mn(CO)_2(COPh)]$$

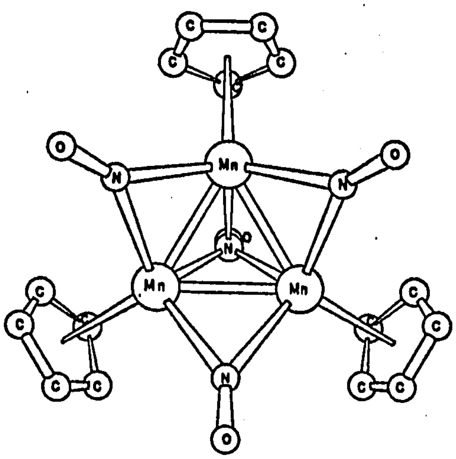
$$Li[C_5H_5Mn(CO)_2(COPh)] + MeI \longrightarrow C_5H_5Mn(CO)_2[C(OMe)Ph] + LiI$$

b) $[C_5H_5Mn(CO)_2(NO)]^+$ and its Derivatives

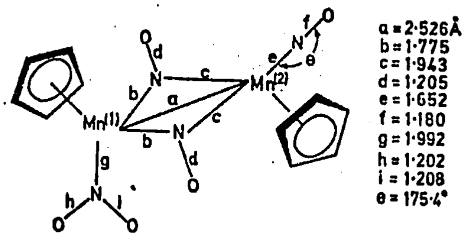
The reactions of $[C_5H_5Mn(CO)_2(NO)]^+$ with polyphosphines have been discussed earlier. (*vide supra*, p.19)

The parent nitrosyl complex was first prepared as the chloroplatinate salt, $[C_5H_5Mn(CO)_2(NO)]_2PtCl_6$, in 1955[229]. Reaction of $(C_5H_5)_2Mn$ and NO gave the product $(C_5H_5)_3Mn_2(NO)_3$ in which the cyclopentadienyl rings are thought to be in non-identical environments[230] because two resonances were detected in the C_5H_5 region of its NMR spectrum.

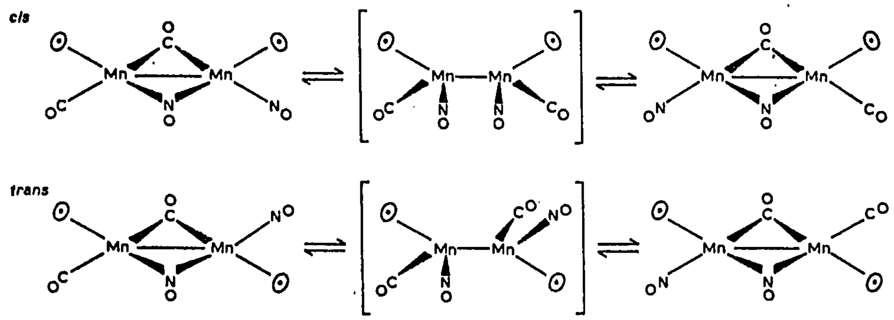
King and Bisnette[231] were able to prepare the complex $[C_5H_5Mn(CO)_2(NO)]PF_6$ in good yield by the reaction of $C_5H_5Mn(CO)_3$ with $HCl/NaNO_2$. Sodium borohydride ($NaBH_4$) reduction of the product gave $[C_5H_5Mn(CO)(NO)_2]$. Irradiation of this complex readily afforded black crystals of the trimer $(C_5H_5)_3Mn_3(NO)_4$ in which all the cyclopentadiene rings are equivalent[232]. This product can also be prepared by maintaining $[(C_5H_5)Mn(CO)(NO)]_2$ in refluxing benzene for 6 h[211].



A by-product of the above reaction has been recently shown, by X-ray crystallography, to be $(C_5H_5)_2Mn_2(NO)_3(NO_2)$[233].



The initial report that $[(C_5H_5)Mn(CO)(NO)]_2$ was weakly paramagnetic has not been confirmed[234]. Low temperature NMR studies indicate that the complex undergoes a dynamic equilibrium in solution, as shown below:



Recently, a rapid high yield preparation of $[C_5H_5Mn(CO)_2NO]^+$ from $C_5H_5Mn(CO)_3$ and $NOPF_6$ has been reported[235].

Substitution of the CO groups in $[C_5H_5Mn(CO)_2NO]PF_6$ has been explored by three different research groups.

(1) King *et al.*

Reactions with a variety of mono-, di- and triphosphines have resulted in the synthesis of a large number of products in which one or two CO groups have been replaced[33-35,49]. On the other hand, reaction with a series of substituted fluro-phosphines did not give the expected products, e.g., reaction with Et_2NPF_2 in methyl alcohol gave the known complex, $[C_5H_5Mn(CO)(NO)P(OMe)_3]^+$ [211].

The neutral complex $C_5H_5Mn(CO)(NO)(COOMe)$ was obtained from the reaction of $[C_5H_5Mn(CO)_2NO]^+$ with Na/MeOH[236]. Further reaction with the Grignard reagent, MeMgX, resulted in the formation of $C_5H_5Mn(CO)(NO)(COMe)$.

(2) Brunner, Schindler *et al.*

Initially, Brunner, Schindler *et al.* prepared a series of monosubstituted complexes[237,238] $[C_5H_5Mn(CO)(NO)(L)]^+$, similar to those prepared by King *et al.* Reaction of these complexes with Na/MeOH gave the optically active complexes $C_5H_5Mn(COOMe)(NO)(L)$[48,239] (e.g., L = PPh_3, Diphos, NC_5H_5). Reaction with the ℓ-mentholate group, $OC_{10}H_{19}$, resulted in the resolution of the enantiomers of $C_5H_5Mn(COOC_{10}H_{19})(NO)(PPh_3)$. Acid hydrolysis of these complexes gave the enantiomers $[C_5H_5Mn(CO)(NO)(PPh_3)]^+$. The rate of isomerization of these optically active manganese complexes was studied[240-242], and the rate was found to be identical to that of the rate of reaction:

$[C_5H_5Mn(CO)(NO)(PPh_3)]^+ + P(C_6D_5)_3 \rightleftharpoons (C_5H_5Mn(CO)(NO)[P(C_6D_5)_3])^+ + PPh_3$

The rate determining step is the change in configuration at the asymmetric centre and thus is a consequence of the dissociation of the PPh_3 from the manganese atom. The reaction was found to be first order.

(3) McCleverty *et al.*

A wide range of substituted products in which either one or two CO groups in $[C_5H_5Mn(CO)_2(NO)]^+$ have been replaced by group VA[243] or S donors[244-247] have been prepared. The reversible oxidation and/or reduction of most of these new complexes have been studied. The results indicate that the $[(C_5H_5)Mn(CO)]$ moiety is responsible for the redox behaviour; a plot of ν(NO) versus $E_{1/2}$ shows a linear relationship[247].

c) IR, NMR and Mass Spectra.

In general, most of the complexes discussed have been characterized by at least one of these three methods. The IR spectra [ν(CO) region] readily reveals the extent of substitution in these types of complexes. Thus, two strong bands imply a monosubstituted product of the type $C_5H_5Mn(CO)_2(L)$ while one strong band is indicative of a product of the type $C_5H_5Mn(CO)(L)_2$. The position of the bands appear to be dependent on the substituent, L[248].

The IR spectra of $C_5H_5Mn(CO)_3$ and some of its derivatives have been studied exhaustively in the 4000-200 cm^{-1} region[218,250-253] and the regions of ν(M-C) and δ(M-C-O) absorptions have been determined[10]. The spectra of the thiocarbonyl complexes $C_5H_5Mn(CO)_2(CS)$ and $C_5H_5Mn(CO)(CS)_2$ have also been reported[208].

The NMR spectra of metal complexes containing a cyclopentadienyl ring usually display a singlet resonance due to the ring protons. However, when the metal is also bonded to P donors, the NMR spectra can be used to give information about the number of these donors that are attached to the metal. Thus, for $C_5H_5Mn(CO)_{3-n}(L)_n$ (L = phosphine or phosphite, n = 1,2), the C_5H_5 resonance splits into a doublet (n = 1) or a triplet (n = 2) due to the coupling of the cyclopentadiene hydrogens with the P atom(s) of the ligands.

The position of the C_5H_5 resonance is inversely proportional to the position of $\nu(CO)$ absorption in the IR[44,139,200,249]. King[249] has shown that, in general, an empirical relationship exists which relates the CO force constant and the C_5H_5 NMR resonance.

$$\tau(C_5H_5) = 13.203 - 0.499k_{CO}$$

The mass spectra of $C_5H_5Mn(CO)_3$[254] and a number of its derivatives [$C_5H_5Mn(CO)_2(olefin)$[255], $C_5H_5Mn(CO)_2(L)$ (L = group VA donor)[177,180,255] and $C_5H_5MnC_6H_6$[215]] have been reported. In the above carbonyl complexes, both CO groups are lost similtaneously. However, for the thiocarbonyl complexes[47], $C_5H_5Mn(CO)(CS)(L)$ (L = CO, CS, C_8H_{14}), major fragments involving loss of only one CO group were found. The mass spectra of many other complexes are scattered throughout the literature and are usually reported together with the preparation of the complex(es).

d) Kinetics

To date, the kinetics and mechanisms of the CO substitution reactions of $C_5H_5Mn(CO)_3$ and its derivatives have been restricted to four studies. Angelici and Loewen[198] have investigated the reaction, $C_5H_5Mn(CO)_2(olefin) + L \longrightarrow C_5H_5Mn(CO)_2(L) + olefin$ in cyclohexane (50-95°) for a variety of olefins and monodentate group VA donor ligands, L. The reaction proceeds by an S_N1 dissociative mechanism. This involves slow loss of the olefin in the rate-determining step to form the intermediate $C_5H_5Mn(CO)_2$, followed by rapid entry of L.

A similar study[256] has been carried out for $C_5H_5Mn(CO)(CS)$ (*cis*-cyclooctene):

$$C_5H_5Mn(CO)(CS)(C_8H_{14}) + PPh_3 \longrightarrow C_5H_5Mn(CO)(CS)(PPh_3) + C_8H_{14}$$

The reaction again proceeds *via* an S_N1 mechanism. However, the reaction rates for the thiocarbonyl complex are approximately four times as fast as those for the dicarbonyl complex.

The kinetics of the reaction

$$C_5H_5Mn(CO)_2(H)(SiPh_3) + PPh_3 \longrightarrow C_5H_5Mn(CO)_2(PPh_3) + HSiPh_3$$

have been studied for a number of different solvent systems[147]. The initial process, loss of $HSiPh_3$ to give $C_5H_5Mn(CO)_2$, is thought to be the rate-determining step.

Sawai and Butler[257] have studied the reaction

$C_5H_5Mn(CO)_2(SR_2) + L \longrightarrow C_5H_5Mn(CO)_2(L) + SR_2$ (R = alkyl, aryl; L = phosphine, phosphite). As in the previous studies, the results indicate an S_N1 dissociative mechanism involving loss of SR_2 as the rate-determining step.

e) X-Ray Crystallography

A limited number of crystal structures have been reported for the cyclopentadienyl complexes. The major bond distances and angles for these structures are given in Table VIII-2.

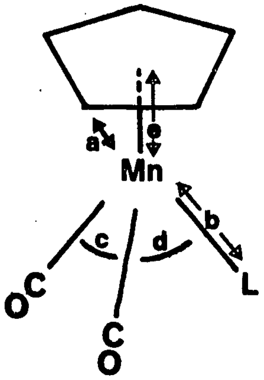


FIGURE VIII-1 STRUCTURE OF $C_5H_5Mn(CO)_2(L)$.

From the data, it seems that <C-Mn-C ∿90°, and so the manganese atom can be considered to be at the centre of an octahedron, even though only four ligands are attached to the metal atom. In the case of $C_5H_5Mn(CO)(PPh_3)_2$, <P-Mn-P = 104° but this is thought to arise from steric interactions between the phenyl rings on the two P atoms.

The structures containing cyclopentadienyl rings and nitrosyl groups have already been mentioned. Diagrams of these two structures are given on pp. 165,166.

TABLE VIII-2 MAJOR BOND DISTANCES AND ANGLES FOR THE KNOWN CYCLOPENTADIENYL-MANGANESE CARBONYL COMPLEXES

	Distances* (Å)				Angles* (Deg)		Ref.
Complex	Mn-C(O)	C-O	Mn-C(ring) (a)	Mn-L(b)	<C-Mn-C(c)	<C-Mn-L(d)	
$C_5H_5Mn(CO)_3$	1.797(20)	1.134(30)	2.151(25)	-	91	-	258
$C_5H_5Mn(CO)_2(PPh_3)$	1.753(9) 1.773(12)	1.163(12) 1.159(14)	2.16(2)	2.237(4)	92	92.7	186
$C_5H_5Mn(CO)(PPh_3)_2$**	1.728(15)	1.197(19)	2.15(2)	2.232(6) 2.245(5)	-	89.7 92.0	212
$C_5H_5Mn(CO)_2(\mathit{nor}\text{-}C_7H_8)$	1.794(7)	1.154	1.805(9)***	2.051(11)	91.9(4)	122.6(4)	210
$[C_5H_5Mn(CO)_2(COPh)]^-$	1.77(3)	1.14	2.17(4)	1.96(2)	89.7(1.4)	85.3(1.2) 90.4(1.2)	209
$[MeC_5H_4Mn(CO)_2]_2(AM)$	1.77(3)		2.15	2.37(5)	94		258
$C_5H_5Mn(CO)_2(H)SiPh_3$							148

* See Figure VIII-1

** <P-Mn-P = 104.2°

*** refers to the distance (e) as shown in Figure VIII-1.

f) Miscellaneous

^{55}Mn NQR data have been reported for a series of $C_5H_5Mn(CO)_2(L)$[168] (L = group VA donor, mono-olefin) complexes. An attempt has been made to correlate the intensities of the ν(CO) absorption with the ^{55}Mn NQR data.

CHAPTER IX SUBSTITUTION REACTIONS OF $C_5H_5Mn(CO)_2(CS)$ WITH GROUP VA DONORS

INTRODUCTION

The first manganese thiocarbonyl, $C_5H_5Mn(CO)_2(CS)$, was recently prepared in this laboratory[138]. The CS ligand, generated from CS_2, is thought to be analogous to the CO group. Confirmation of this is provided by crystal structure determinations of the two metal thiocarbonyl complexes $Rh(CS)Cl(PPh_3)_2$ [260] and $Ir(CO)_2(CS)(PPh_3)_2PF_6\cdot Me_2CO$[261]. In both cases, bonding occurs through the C atom. The metal-C(S) bond is linear and is shorter than the metal-C(O) bond in the related metal carbonyl complexes.

In keeping with the theoretical prediction of Richards[7], metal thiocarbonyl complexes are expected to be more stable than the corresponding metal carbonyl complexes. However, chemical evidence on the greater stability of the metal-C(S) bond relative to the metal-C(O) bond has not been forthcoming. A recent review of metal thiocarbonyl complexes[47] reveals that fewer than forty of these complexes have been detected (even fewer have been isolated).

Many reactions of $C_5H_5Mn(CO)_3$ and group VA ligands have been reported (Chapter VIII) and the physical properties of these complexes (IR, NMR, mass spectra) have been collected in Table VIII-1. An analogous study of the reactions of group VA donors with $C_5H_5Mn(CO)_2(CS)$ was thus undertaken. An earlier study of the reaction of $C_5H_5Mn(CO)_2(CS)$ with C_8H_{14} and $C^{18}O$ has shown that the CO is preferentially replaced by the new ligands[138]. It was hoped that a preferential replacement of the CO group by group VA donors, L, would also occur in these dicarbonyl complexes to give products of the type $C_5H_5Mn(CO)(CS)(L)$ and $C_5H_5Mn(CS)(L)_2$. The results of this study are described below.

EXPERIMENTAL

$C_5H_5Mn(CO)_2(CS)$ was prepared as reported previously[138]. All ligands were used as purchased. The reactions were performed routinely under a nitrogen atmosphere.

Physical measurements were recorded as carried out previously (*vide supra*, p.39).

The mass spectra were recorded in the temperature range 80-165° on an AEI model MS902 spectrometer at 70 eV.

Photochemical reactions were carried out in a pyrex vessel (∿150 ml capacity) fitted with a water-cooled pyrex finger*. The UV source (Hanovia 100 W high-pressure mercury lamp) was placed inside this finger.

Preparation of $C_5H_5Mn(CO)(CS)(L)$ complexes (L = PPh_3, $AsPh_3$, $SbPh_3$, $P(C_6H_{11})_3$, PMe_2Ph, $P(OR)_3$ with R = Me, Et, Ph and CH_2CH_2Cl)

$C_5H_5Mn(CO)_2(CS)$ (1 mmol) was dissolved in freshly distilled terahydrofuran (THF) (100 ml) and the irradiation vessel was

---

* An illustration of this apparatus is given in Ref. 140.

immersed in an ice bath. The solution was then irradiated for appropriate lengths of time; the irradiation was continued until no further reaction occurred, as evidenced by changes in the IR spectrum [ν(CO)].Extensive decomposition occurred during the irradiation process.

The ligand (1-2 mmol) was then added to the THF solution and the solution was stirred at 35-40° for 12 h*. After filtration of the decomposition products, the solvent was removed from the filtrate under reduced pressure. The crude product was then eluted on thin layer plates (silica gel) and the new products were isolated in 30-60% yield. The eluent systems used are listed in Table IX-1.

The solid products were crystallized from CH_2Cl_2/n-hexane solutions. All products (including any oils) were dried *in vacuo* (25°/0.001 mmHg) for 24 h.

Preparation of $C_5H_5Mn(CS)(L)_2$ Complexes (L = PPh_3 and $P(OR)_3$, R = Me, Et, Ph and CH_2CH_2Cl).

$C_5H_5Mn(CO)_2(CS)$ (1 mmol), and excess of the appropriate ligand (2-5 mmol), were dissolved in freshly distilled benzene (100 ml) and the solution was irradiated until the IR spectrum remained constant (2-4 h). The solution was then filtered and the solvent was removed under reduced pressure. Elution

---

* An alternative method of preparation involved irradiation of a solution of $C_5H_5Mn(CO)_2(CS)$ (1 mmol) and L(L = PPh_3, $AsPh_3$, $SbPh_3$) (1 mmol) in benzene (100 ml).

TABLE IX-1 ANALYTICAL DATA FOR THE NEW COMPLEXES

Complex	Eluent[a] mixture		Colour	Decomp. (°C)	Analysis found (calcd.) (%)				Molecular[b] weight
					C	H	P	S	
$C_5H_5Mn(CO)(CS)[P(C_6H_{11})_3]$[c]	10/2	h/a	yellow	∿180	64.1 (63.5)	8.4 (8.1)			472
$C_5H_5Mn(CO)(CS)(PMe_2Ph)$[c]	1/1	h/b	yellow	oil	53.6 (54.6)	4.5 (4.9)			330
$C_5H_5Mn(CO)(CS)(PPh_3)$	4/1	h/a	orange	∿110	66.0 (66.1)	4.5 (4.4)		6.3 (7.0)	
$C_5H_5Mn(CO)(CS)(AsPh_3)$	4/1	h/a	yellow	175-180	59.8 (60.3)	3.9 (4.1)		7.5 (6.4)	
$C_5H_5Mn(CO)(CS)(SbPh_3)$[d]	2/1	h/a	orange	140-145	55.3 (55.1)	3.9 (3.7)		6.1 (5.9)	544
$C_5H_5Mn(CO)(CS)[P(OEt_3]$[c]	3/1	h/a	yellow	oil	44.2 (43.6)	5.9 (5.6)			
$C_5H_5Mn(CO)(CS)[P(OMe)_3]$[c]	3/1	h/a	yellow	oil	38.5 (38.0)	4.4 (4.5)			
$C_5H_5Mn(CO)(CS)[P(OCH_2CH_2Cl)_3]$[c]	3/2	h/b	yellow	oil	34.0 (33.8)	4.0 (3.7)			460
$C_5H_5Mn(CO)(CS)[P(OPh)_3]$[c]	3/1	h/a	yellow	100-106	60.1 (59.8)	4.1 (4.0)			502
$C_5H_5Mn(CS)(PPh_3)_2$	10/3	h/a	red	∿135	72.6 (73.2)	5.5 (5.1)			
$C_5H_5Mn(CS)[P(OEt)_3]_2$[c]	-	-	yellow	oil	42.9 (43.6)	7.3 (7.1)			496

TABLE IX-1 (continued)

$C_5H_5Mn(CS)[P(OMe)_3]_2$	4/1	h/a	yellow	∿180	35.1 (35.0)	5.6 (5.6)	14.6 (15.0)	8.3 (7.8)	
$C_5H_5Mn(CS)[P(OCH_2CH_2Cl)_3]_2$[e]	2/1	h/a	yellow	70-75	31.0 (30.3)	4.3 (4.6)	8.7 (8.8)		460
$C_5H_5Mn(CS)[P(OPh)_3]_2$	h		yellow	108-112	64.9 (64.3)	4.7 (4.5)	7.8 (7.9)	3.9 (4.1)	
$C_5H_5Mn(CO)[P(OMe)_3]_2$	3/2	h/b	yellow	100-103	36.6 (36.4)	6.0 (5.9)	16.0 (15.6)		396

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a) Abbreviations used: h = n-hexane; b = benzene; a = acetone

b) These values were determined from the mass spectrum. Values quoted are for the ^{121}Sb, ^{32}S and ^{35}Cl isotopes. All values agree with the theoretical values.

c) The C and H analyses for these complexes were performed in our laboratory on a Hewlett-Packard 185 CHN analyser.

d) Sb(%); Found (calcd.) 21.6 (22.3)

e) Cl(%); Found (calcd.) 30.4 (30.3)

of the material on thin layer plates (silica gel) afforded three products; $C_5H_5Mn(CO)_2(CS)$ (<5%), $C_5H_5Mn(CO)(CS)(L)$ (5-10%) and $C_5H_5Mn(CS)(L)_2$ (>80%). These could readily be separated. The eluent systems used are given in Table IX-1.

The solid products were crystallized from CH_2Cl_2/n-hexane. The oil, $C_5H_5Mn(CS)[P(OEt)_3]_2$, was sublimed at 80° (0.001 mm Hg). All the products were dried *in vacuo* (25°/0.001 mm Hg) for 24 h (yields 30-60%).

Preparation of $C_5H_5Mn(CO)[P(OMe)_3]_2$

$C_5H_5Mn(CO)_3$ (1 mmol) and $P(OMe)_3$ (5-10 mmol) were irradiated for two hours in benzene (100 ml). Little decomposition occurred. The solution was filtered and the solvent was removed under reduced pressure. Elution of the crude material on silica gel thin layer plates with a 2/3 benzene/n-hexane mixture afforded the yellow product as the major component. This was crystallized from CH_2Cl_2/n-hexane solution and then dried *in vacuo* (25°/0.001 mm Hg) for 24 h (yield 60%).

RESULTS AND DISCUSSION

Irradiation of $C_5H_5Mn(CO)_2(CS)$ in THF yielded a red solution containing an unstable intermediate, presumed to be $C_5H_5Mn(CO)(CS)(THF)$ [$\nu(CO) = 1912\ cm^{-1}$]. Extensive decomposition occurred on irradiation, as evidenced by the formation of a heavy brown precipitate. Addition of the ligand (L) to this irradiated solution resulted in displacement of the THF to give almost exclusively a product of the type $C_5H_5Mn(CO)(CS)(L)$. A small quantity of $C_5H_5Mn(CO)_2(L)$ was also formed (identified by the IR and mass spectra). This dicarbonyl "impurity" could not be separated from the thiocarbonyl product by thin layer chromatography. Since the starting material contained no $C_5H_5Mn(CO)_3$, a small amount of CS must be removed in the irradiation process [yielding $C_5H_5Mn(CO)_2(THF)$]. However, as a result of the weaker bond strength of the Mn-CO bond, relative to the Mn-CS bond, the predominant reaction is removal of the carbonyl group.

The thiocarbonyl complex, $C_5H_5Mn(CO)(CS)(PPh_3)$, has been prepared previously by the reaction of $C_5H_5Mn(CO)(CS)(C_8H_{14})$ and PPh_3[138]. This indirect method of preparation gives a very low yield of product [∿15% based on $C_5H_5Mn(CO)_2(CS)$].

Irradiation of $C_5H_5Mn(CO)_2(CS)$ and excess ligand (L), in benzene, readily gave the disubstituted products $C_5H_5Mn(CS)(L)_2$ in good yield. IR and mass spectral results indicate that minute amounts (∿1%) of $C_5H_5Mn(CO)(L)_2$ were also present as by-products in the reactions.

Although no quantitative measurements were made, the disubstituted products seem to be more air- and light-stable than the related $C_5H_5Mn(CO)(CS)(L)$ complexes. This is in contrast to the known stabilities of $C_5H_5Mn(CO)_2(PPh_3)$ and $C_5H_5Mn(CO)(PPh_3)_2$[143]. This stability must be associated with the greater bonding ability of the CS ligand. Normally, replacement of CO groups in metal carbonyls by phosphines results in the remaining CO groups being more firmly bonded to the metal atom. However, the presence of the CS ligand results in Mn-CO *bond weakening*.

There is only one previous report in the literature[262] (a patent) of the synthesis of $C_5H_5Mn(CO)(L)_2$ (L = phosphite) complexes which included little detail of the physical properties of the complexes. Very few $C_5H_5Mn(CO)(L)_2$ complexes are known even for L = phosphine, so it was considered of interest to re-investigate the direct reaction of $C_5H_5Mn(CO)_3$ with group VA donors.

Two preliminary reactions were thus undertaken to prepare the phosphite complexes $C_5H_5Mn(CO)[P(OMe)_3]_2$ and $C_5H_5Mn(CO)[P(OPh)_3]_2$. The tricarbonyl starting material, together with a five-ten fold excess of phosphite were irradiated in benzene. Whereas the $P(OMe)_3$ complex was readily obtained, and is air-stable, the $P(OPh)_3$ complex is air-sensitive and only its IR spectrum [ν(CO)] was recorded. Since the corresponding thiocarbonyl complex $C_5H_5Mn(CS)[P(OPh)_3]_2$ is air-stable, electronic and not steric factors must be responsible for the instability of the carbonyl complex. Further work will be required before more conclusive evidence can be given for the dominance of electronic effects over steric effects.

IR Spectra

The IR spectra of the new thiocarbonyl complexes in the carbonyl and thiocarbonyl stretching region are reported in Table IX-2. As expected, one ν(CO) absorption (1920-1955 cm^{-1}) and one ν(CS) absorption (1225-1255 cm^{-1}) were observed for the $C_5H_5Mn(CO)(CS)(L)$ complexes. A comparison with data for the $C_5H_5Mn(CO)_2(L)$ complexes shows that the high frequency (A_1) mode in the dicarbonyl follows the same trend as the CO stretching mode for the thiocarbonyl complexes. The constant difference of ∿12 cm^{-1} implies that the ligand (L) has a very similar effect on both the CO and CS ligands.

The IR spectra of the $C_5H_5Mn(CS)(L)_2$ complexes were also recorded in the ν(CS) region (1190-1225 cm^{-1}). These complexes absorb at lower frequencies than the $C_5H_5Mn(CO)(CS)(L)$ complexes. The lower thiocarbonyl stretching frequencies for the former can be taken to imply that the C-S bond has become weaker with concomitant strengthening of the Mn-C(S) bond. The difference between the two series of thiocarbonyls, $C_5H_5Mn(CO)(CS)(L)$ and $C_5H_5Mn(CS)(L)_2$, is replacement of a CO group by L. A similar bond weakening/bond strengthening effect for C-O/Mn-C(O) was found on replacement of CO by L in the analogous $C_5H_5Mn(CO)_2L$ complexes. Once again, the CO and CS ligands are seen to behave in a similar manner.

A serious drawback to the above discussion is that, whereas the carbonyl stretching region is well removed from the other bending and stretching modes within the molecules, this is not true for the thiocarbonyl stretching modes. Consequently, the

TABLE IX-2 IR SPECTRA OF THE NEW COMPLEXES

Complex	CS_2 Solution (cm^{-1})				*n*-Hexane Solution (cm^{-1})	
	ν(CS)[a]	ν(CO)	ν(CO)[b]	ΔCO[c]	ν(CS)	ν(CO)
$C_5H_5Mn(CO)(CS)[P(C_6H_{11})_3]$	1222	1914			1230	1923
$C_5H_5Mn(CO)(CS)(PMe_2Ph)$	1228	1920	1932[d]	-12	1234	1928
$C_5H_5Mn(CO)(CS)(PPh_3)$[e]	1231	1925	1940[f] 1937[g]	-14	1236	1938,1929
$C_5H_5Mn(CO)(CS)(AsPh_3)$	1231	1926	1936[g]	-10	-	1937,1930
$C_5H_5Mn(CO)(CS)(SbPh_3)$	1230	1925	1935[g]	-10	1237	1932
$C_5H_5Mn(CO)(CS)[P(OEt)_3]$	1236	1933	1945[f]	-12	1243	1950sh,1939
$C_5H_5Mn(CO)(CS)[P(OMe)_3]$	1239	1936	1949[f]	-13	1245	1952,1943
$C_5H_5Mn(CO)(CS)[P(OCH_2CH_2Cl)_3]$	1240	1939	1952[f]	-13	1247	1946,1940sh
$C_5H_5Mn(CO)(CS)[P(OPh)_3]$	1254	1951	1965[f] 1963[g]	-13	-	1961,1954
$C_5H_5Mn(CS)[PMe_2Ph]_2$[h]	1195					
$C_5H_5Mn(CS)[PPh_3]_2$	1193					
$C_5H_5Mn(CS)[P(OEt)_3]_2$	1214					

TABLE IX-2 (continued)

$C_5H_5Mn(CS)[P(OMe)_3]_2$	1218	
$C_5H_5Mn(CS)[P(OCH_2CH_2Cl)_3]_2$	1223	
$C_5H_5Mn(CS)[P(OPh)_3]_2$	1219	
$C_5H_5Mn(CO)[P(OMe)_3]_2$		1865
$C_5H_5Mn(CO)[P(OPh)_3]_2$		1892

---

a) All bands are strong.
b) This column lists the $A_1 \nu(CO)$ stretching mode for the corresponding $C_5H_5Mn(CO)_2(L)$ complexes.
c) $\Delta_{CO} = \nu(CO)(\text{thiocarbonyl}) - \nu(CO)(\text{dicarbonyl})$.
d) Ref. 40
e) Ref. 138
f) Ref. 182
g) Ref. 43
h) No attempt was made to isolate this product.

CS band positions almost certainly are affected by coupling with other low frequency modes.

n-Hexane solution spectra of the $C_5H_5Mn(CO)(CS)(L)$ complexes were also recorded. As reported previously[138], in this solvent, two absorptions were found in the carbonyl region for $C_5H_5Mn(CO)(CS)(PPh_3)$. In this study a similar effect was found for the monothiocarbonyl complexes when L = $AsPh_3$, $P(OEt)_3$, $P(OMe)_3$, $P(OCH_2CH_2Cl)_3$ and $P(OPh)_3$ but not for L = PMe_2Ph, $P(C_6H_{11})_3$ and $SbPh_3$. The reason for this effect is not known, but it is presumably related to the existence of different conformers in solution [263]. Steric effects are thought not to be responsible because absorptions were found for both $P(OMe)_3$ (a relatively small ligand) and PPh_3 (a relatively bulky ligand).

No splitting of the thiocarbonyl stretching modes was detected in n-hexane.

NMR Spectra

The NMR spectra of all the complexes in CS_2 solution were recorded (Table IX-3). The splitting of the C_5H_5 resonance, due to coupling with the ^{31}P atoms, was used as a diagnostic tool for determining the nature of the new products. The mono-substituted products $C_5H_5Mn(CO)(CS)(L)$, (L = phosphine or phosphite), display doublets while the di-substituted products give triplets for the C_5H_5 resonance. A number of these spectra are shown in Figure IX-1.

The position of the C_5H_5 resonance provides a means of

TABLE IX-3 NMR SPECTRA OF THE NEW COMPLEXES [a]

Complex	C_5H_5	Other
$C_5H_5Mn(CO)(CS)[P(C_6H_{11})_3]$	5.49, doublet (1.2)	v. complex at ∿8.5, C_6H_{11}
$C_5H_5Mn(CO)(CS)(PMe_2Ph)$	5.73 doublet (1.6)	2.70, complex, Ph; 8.21, 8.30, doublets (9.0), CH_3
$C_5H_5Mn(CO)(CS)(PPh_3)$	5.75 doublet (1.6)	2.73, complex, Ph.
$C_5H_5Mn(CO)(CS)(AsPh_3)$	5.65	2.70 complex, Ph
$C_5H_5Mn(CO)(CS)(SbPh_3)$	5.50	2.68 complex, Ph
$C_5H_5Mn(CO)(CS)[P(OEt)_3]$	5.53 doublet (1.7)	6.08 multiplet, CH_2; 8.79 triplet (6.9), CH_3
$C_5H_5Mn(CO)(CS)[P(OMe)_3]$	5.48 doublet (1.8)	6.40 doublet (11.5), CH_3
$C_5H_5Mn(CO)(CS)[P(OCH_2CH_2Cl)_3]$	5.40 doublet (1.6)	5.79 quartet, OCH_2; 6.40, triplet (5.6), CH_2Cl
$C_5H_5Mn(CO)(CS)[P(OPh)_3]$	6.09 doublet (1.7)	6.09 complex, Ph
$C_5H_5Mn(CS)[PPh_3]_2$	6.23 triplet (1.8)	2.62, 2.88 complex, Ph
$C_5H_5Mn(CS)[P(OEt)_3]_2$	5.81 triplet (1.9)	6.10 multiplet, CH_2; 8.81, triplet (7.0), CH_3
$C_5H_5Mn(CS)[P(OMe)_3]_2$	5.63 triplet (1.7)	6.45 triplet (11.2)[b], CH_3
$C_5H_5Mn(CS)[P(OCH_2CH_2Cl)_3]_2$	5.55 triplet (1.8)	5.80 multiplet OCH_2; 6.36, triplet (5.4), CH_2Cl

TABLE IX-3 (continued)

$C_5H_5Mn(CS)[P(OPh)_3]_2$	6.41	triplet (1.9)	2.92	complex Ph
$C_5H_5Mn(CO)[P(OMe)_3]_2$	5.97	triplet (1.8)	6.60	triplet (11.2)[b], CH_3

---

a) τ values listed, with coupling constant (J_{P-H} Hz) given in brackets following the multiplicity. The spectra were recorded for ∿0.5M solutions in CS_2.

b) Value in brackets is the separation for the outer two peaks in the apparent triplet.

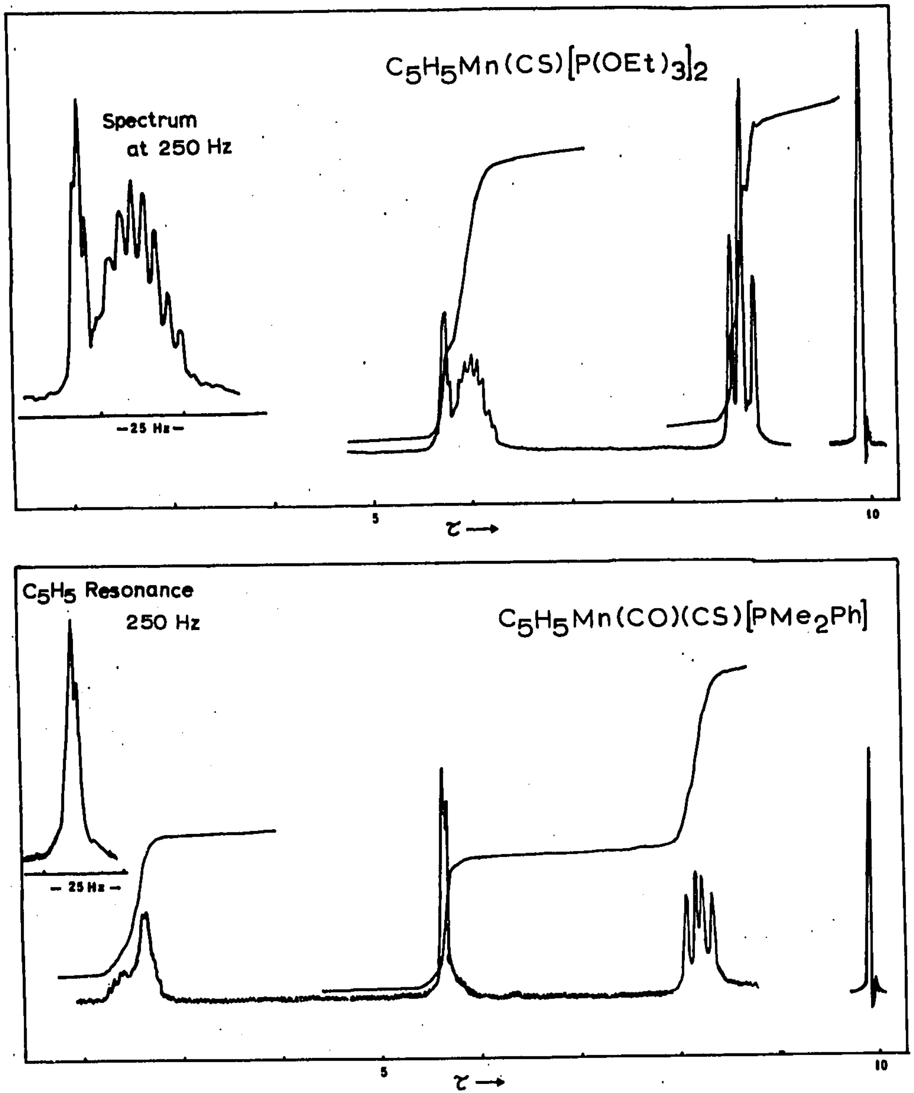


FIGURE IX-1 NMR SPECTRA OF THE NEW COMPLEXES

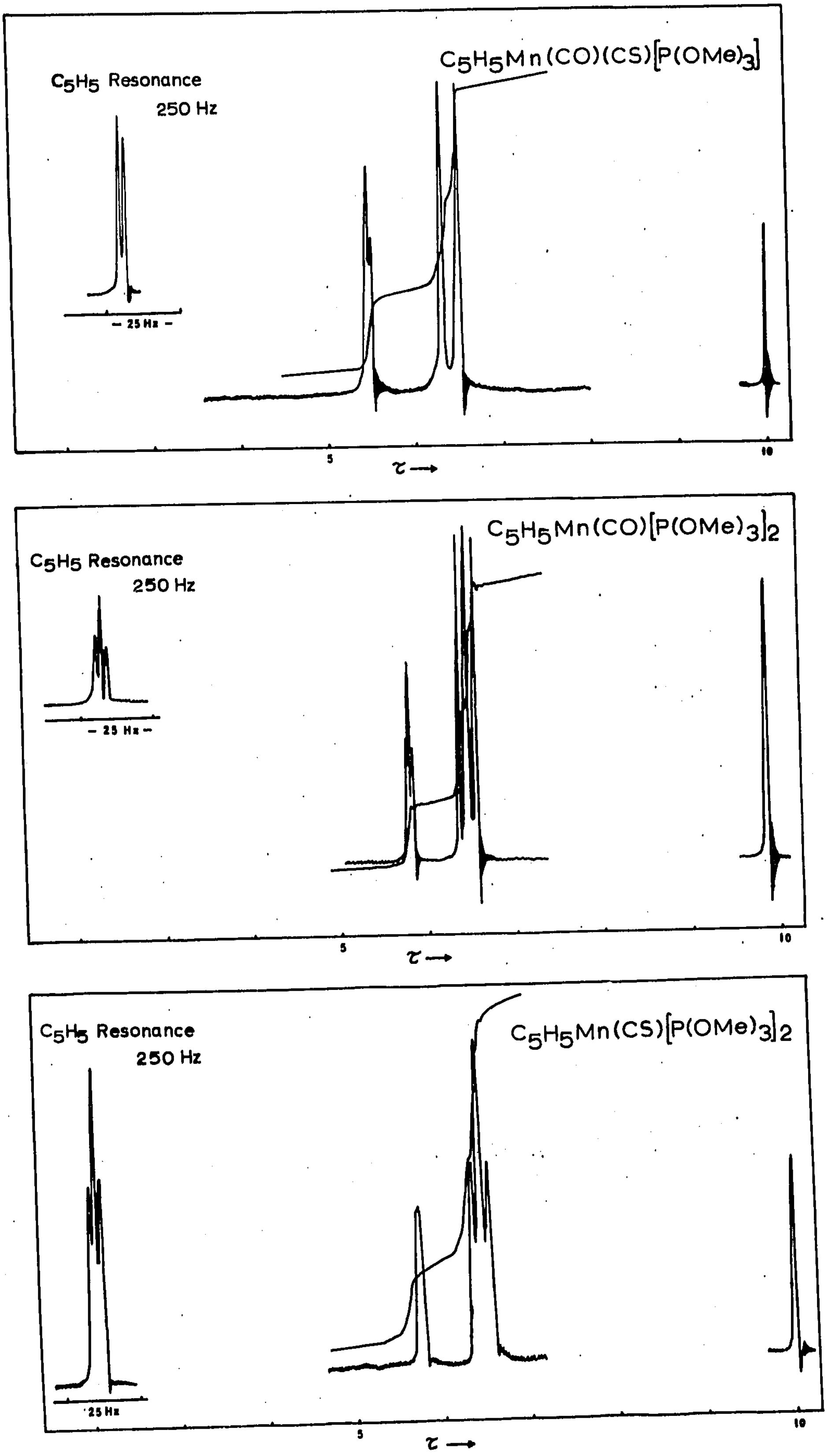


FIGURE IX (continued)

determining the amount of charge on the manganese atom. Increased charge on the metal increases the electron density on the C_5H_5 ring. The C_5H_5 protons thus become more shielded and the τ value increases. A comparison of the τ values for $C_5H_5Mn(CO)(L)_2$, $C_5H_5Mn(CS)(L)_2$, $C_5H_5Mn(CO)_2(L)$[44] and $C_5H_5Mn(CO)(CS)(L)$ indicates that in complexes containing the CS ligand there is less charge on the metal than in complexes containing the CO ligand. This implies that the CS ligand is a better π acceptor and/or better σ donor than the CO ligand.

It has been noted previously that for moieties of the type "$C_5H_5M(CO)$", $\nu(CO)$ decreases as τC_5H_5 increases[249]. Plots of k_{CO} and k_{CS} against τC_5H_5 are shown in Figures IX-2a and IX-2b. In general, the results do show the expected correlations in both cases. However, complexes containing the $P(OPh)_3$ ligand are distinctly anomalous. A similar anomaly has been found by other workers[44] for $C_5H_5Mn(CO)_2[P(OPh)_3]$ when compared to other dicarbonyl complexes. In this instance, the large shift in the C_5H_5 resonance [relative to $C_5H_5Mn(CO)_3$] was attributed to the electron donating properties of the donor group as well as to an increase in the magnetic anisotropy of the "$Mn(CO)_2(L)$" moeity. This second factor was also used to explain the anomalous behaviour of $C_5H_5Mn(CO)_2[P(CH_2Ph)_3]$ (▲ in Figure IX-2a).

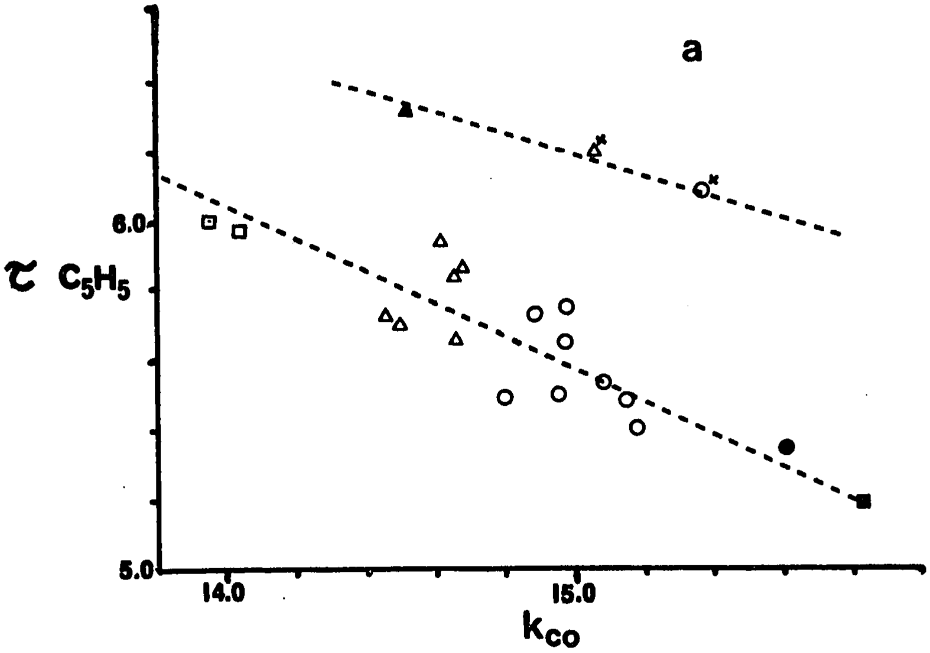


FIGURE IX-2a PLOT OF k_{CO} AGAINST τC_5H_5 FOR THE NEW COMPLEXES.

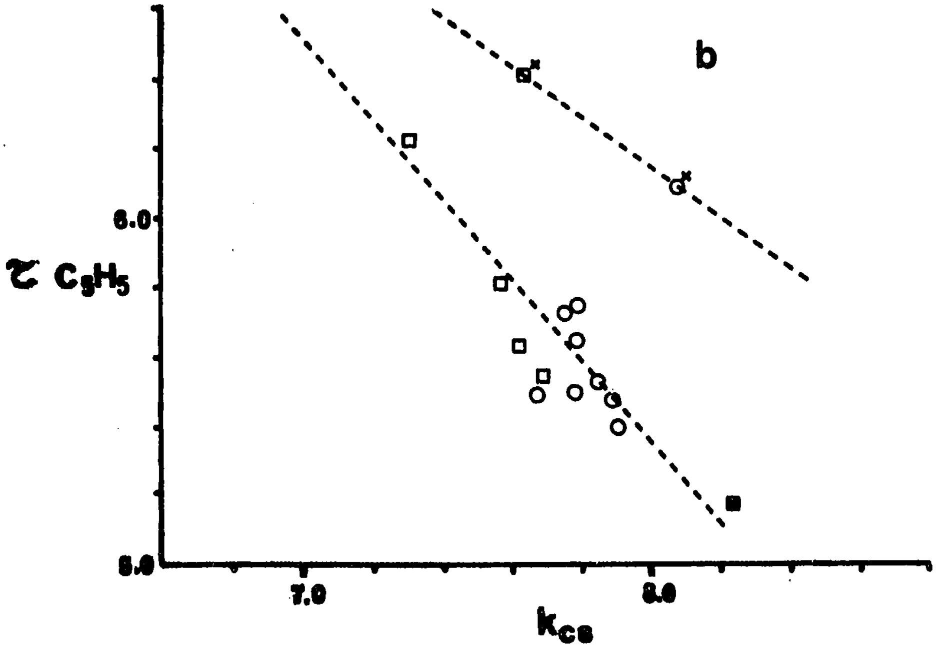


FIGURE IX-2b PLOT OF k_{CS} AGAINST τC_5H_5 FOR THE NEW COMPLEXES
For both Figures: ○ $C_5H_5Mn(CO)(CS)(L)$; □ $C_5H_5Mn(R)(L)_2$ (R = CO or CS); △ $C_5H_5Mn(CO)_2(L)$, data taken from Refs. 43,44; ● $C_5H_5Mn(CO)_3$; ■ $C_5H_5Mn(CO)_2(CS)$, Ref. 47; × $P(OPh)_3$ complexes. All IR and NMR spectra were recorded in CS_2 solution.

The ligand resonances for the complexed ligands are complicated, and in general, could not be analysed. This complexity arises from the coupling of the protons to the ^{31}P atom(s) and to proton-proton coupling within the ligands themselves.

The methoxy resonances in $C_5H_5Mn(CS)[P(OMe)_3]_2$ and $C_5H_5Mn(CO)[P(OMe)_3]_2$ appear as "triplet-like" resonances. At first glance, this would seem to be a case of the protons being coupled equally to both P atoms. However, comparison with the J_{P-H} value for the mono-substituted complex, $C_5H_5Mn(CO)(CS)[P(OMe)_3]$, $J_{P-H} = 11.5$, would imply that the coupling constant has been halved in the di-substituted complexes. But, it is apparent from the spectra (Figure IX-1) that the resonances are not true 1:2:1 triplets. Earlier, all the results of X-ray determinations of $C_5H_5Mn(CO)_2(L)$ complexes were collected together in Table VIII-2 (*vide supra*, p.172). The important feature arising from these data is that the manganese atom can be regarded as being at the centre of an octahedron. This implies that the two $P(OMe)_3$ groups are thus 90° apart and consequently *cis* to each other.

The most likely explanation is that the spectra must be analysed as a special case of the $X_9AA'X'_9$ system in which J_{P-P} is large, (*vide supra*, p.57). Then, J_{P-H} is approximately equal to the distance between the outer two peaks (∿11 Hz) and so is similar to the coupling constant for the mono-substituted complex. It can be inferred from this analysis that a large value for J_{P-P} is again anticipated for *cis* phosphites in manganese complexes as discussed earlier, for *fac*-$Mn(CO)_3[P(OMe)_3]_2Br$, (*vide supra*, p.56).

The methyl resonance for the PMe_2Ph ligand in $C_5H_5Mn(CO)(CS)(PMe_2Ph)$ occurs as two doublets (Figure IX-1). This situation has been described before[264], and arises from the *gem*-methyl groups of the ligand becoming magnetically non-equivalent when bonded to an optically active metal centre. In this work, the two doublets have tentatively been assigned as arising from the first and third and the second and fourth peaks in the 1:1:1:1 "quartet". This assignment was based on the similarity of J_{P-H} for the methyl resonance in $C_5H_5Mn(CO)_2(PMe_2Ph)$ (8.4 Hz)[40] and J_{P-H} value found for this complex (9.0 Hz). The alternative choice of peaks gives J_{P-H} = 5.8 Hz.

Mass Spectra

The mass spectra of a number of the new complexes were recorded and are shown in Figure IX-3. The parent ions of these complexes are reported in Table IX-1. The major fragment ions of these complexes observed in the mass spectra together with their relative abundances are listed in Tables XI-4 to XI-9. Relative intensities of the peaks were estimated by measuring their heights on the chart paper. The base peak in all cases was $C_5H_5Mn^+$ (m/e 120) and the intensity of this peak was arbitarily set to 100.0. The m/e values reported here are for ^{32}S and ^{121}Sb. Since the naturally occurring isotopic composition for

FIGURE IX-3 MASS SPECTRA OF SOME CYCLOPENTADIENYL MANGANESE COMPLEXES

EXPERIMENTAL CONDITIONS

Electron energy : 70 ev

Accelerator voltage: 6 kv

Resolution : 1000

Inlet temperature : A) $C_5H_5Mn(CS)[P(OEt)_3]_2$ 80°C

B) $C_5H_5Mn(CS)[P(OMe)_3]_2$ 150°C

C) $C_5H_5Mn(CO)[P(OMe)_3]_2$ 95°C

D) $C_5H_5Mn(CO)(CS)[P(OPh)_3]$ 165°C

E) $C_5H_5Mn(CO)(CS)[P(C_6H_{11})_3]$ 150°C

F) $C_5H_5Mn(CO)(CS)(PMe_2Ph)$ 150°C

G) $C_5H_5Mn(CO)(CS)(SbPh_3)$ 145°C

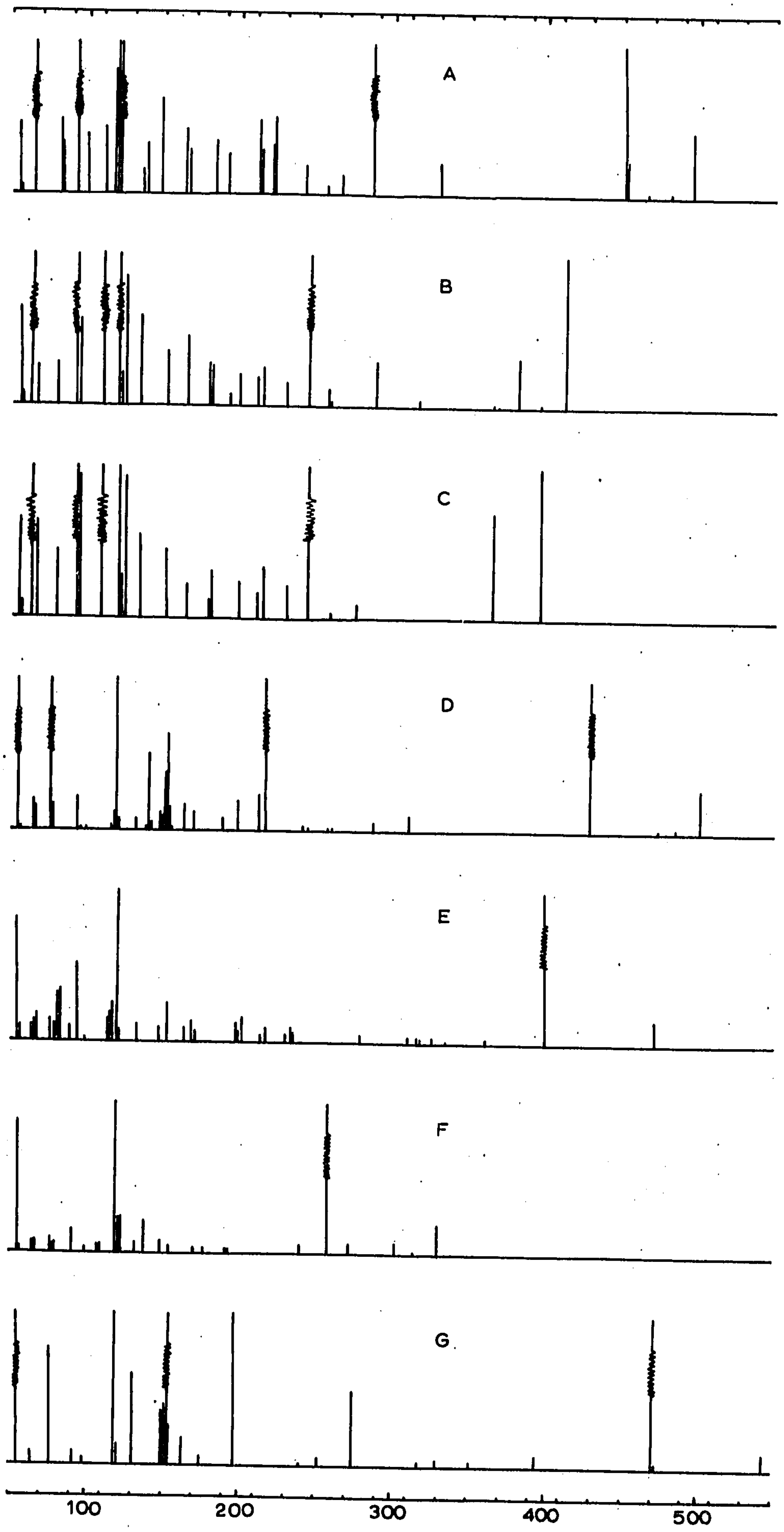

A
B
C
D
E
F
G
100
200
300
400
500

TABLE IX-4 MASS SPECTRUM OF $C_5H_5Mn(CS)[P(OEt)_3]_2$

m/e	Ion	Relative abundance	
		Complex	Ligand [a]
496	$C_5H_5Mn(CS)[P(OEt)_3]_2^+$	43	
481	$C_5H_5Mn(CS)[P(OEt)_3][P(OEt)_2OCH_2]^+$	2.9	
467	$C_5H_5Mn(CS)[P(OEt)_3][P(OEt)_2O]^+$	2.9	
452	$C_5H_5Mn[P(OEt)_3]_2^+$	24	
451	$C_5H_5Mn(CS)[P(OEt)_3][P(OEt)_2]^+$	100	
330	$C_5H_5Mn(CS)[P(OEt)_3]^+$	21	
286	$C_5H_5MnP(OEt)_3^+$	>1000	
266	?	13	
257	?	5.7	
242	?	18.6	
222	$MnP(OEt)_3H^+$	51	
221	$MnP(OEt)_3^+$	33	
213	$C_5H_5MnP(OEt)OH^+$	30	
212	$C_5H_5MnP(OEt)O^+$	50	
192	?	26	
184	?	36	
166	$P(OEt)_3^+$	29	36
164	$C_5H_5MnCS^+$	43	
148	$MnP(OEt)OH^+$	63	
139	$HP(OEt)_2OH^+$	33	52
136	?	16	
121	$P(OEt)_2^+$, $C_5H_5MnH^+$	171	37
120	$C_5H_5Mn^+$	100	
118	$MnPO_2^+$	82	
111	$HP(OEt)(OH)_2^+$	43	76
99	$Mn(CS)^+$	39	
93	$P(OEt)OH^+$	214	46
83	$HP(OH)_3^+$	33	76
82	$P(OH)_3^+$	48	94
65	$P(OH)_2^+$, $C_5H_5^+$	314	100
56	MnH^+	4.6	
55	Mn^+	46	

TABLE IX-5 MASS SPECTRUM OF $C_5H_5Mn(L)[P(OMe)_3]_2$ (L = CO, CS)

		Rel. Abund.	
m/e	Ion	L=CO	CS
412	$C_5H_5Mn(CS)[P(OMe)_3]_2^+$	-	98
396	$C_5H_5Mn(CO)[P(OMe)_3]_2^+$	100	2
381	$C_5H_5Mn(CS)[P(OMe)_3][P(OMe)_2]^+$	-	43
368	$C_5H_5Mn[P(OMe)_3]_2^+$	0.3	1.4
365	$C_5H_5Mn(CO)[P(OMe)_3][P(OMe)_2]^+$	68.8	1.3
316	$Mn(CS)[P(OMe)_3][P(OMe)_2]^+$	-	5
288	$C_5H_5Mn(CS)[P(OMe)_3]^+$	-	30
275	$C_5H_5Mn[P(OMe)_2][P(OMe)]^+$	8.8	1.1
258	$C_5H_5Mn[P(OMe)_2][PCH_2]^+$	2.5	4.1
257	$C_5H_5Mn(CS)[P(OMe)_2]^+$	-	11
244	$C_5H_5Mn[P(OMe)_3]^+$, $C_5H_5Mn[P(OMe)\ ][P(OMe)]^+$	>700	>200
229	$C_5H_5MnP(OMe)_2O^+$	21	16
214	$C_5H_5MnP(OMe)_2H^+$	34	25
210	$MnP(OMe)_3P^+$	16	9
198	$C_5H_5MnP(OMe)O^+$	23	21
192	$Mn(CS)[P(OMe)_2]^+$	-	7.4
180	$C_5H_5MnP(OCH)^+$	31	27
179	$MnP(OMe)_3^+$	13	28
164	$MnP(OMe)_2O^+$, $C_5H_5Mn(CS)^+$	22	46
151	$C_5H_5MnP^+$	45	35
134	$MnP(OMe)OH^+$	56	59
124	$P(OMe)_3^+$	94	85
121	$C_5H_5MnH^+$	28	22
120	$C_5H_5Mn^+$	100	100
109	$P(OMe)_2O^+$	131	102
99	$MnCS^+$	-	1
94	$P(OMe)_2H^+$	94	57
93	$P(OMe)_2^+$	606	>200
79	$P(OMe)OH^+$	45	28
66	$C_5H_6^+$	63	26
63	$P(OMe)H^+$	175	124
56	MnH^+	10	9
55	Mn^+	65	65

TABLE IX-6 MASS SPECTRUM OF $C_5H_5Mn(CO)(L)[P(OPh)_3]$ (L = CO, CS)

m/e	Ion	Relative abundance		
		L = CS	L = CO[a]	Ligand[b]
502	$C_5H_5Mn(CO)(CS)[P(OPh)_3]^+$	27.3		
486	$C_5H_5Mn(CO)_2[P(OPh)_3]^+$	1.3	57.9	
474	$C_5H_5Mn(CS)[P(OPh)_3]^+$	1.3	-	
430	$C_5H_5MnP(OPh)_3^+$	>300	550	
310	$P(OPh)_3^+$	9.6		15
287	?	5.3		
260	$C_5H_5MnP(OPh)O^+$	2		
257	?	2		
244	$C_5H_5MnP(OPh)^+$	1.6	6.5	
241	?	2.3		
217	$P(OPh)_2^+$	>300	418	55
213	$C_5H_5Mn(OPh)^+$	23	28	
199	$C_{12}H_8PO^+$	20	26	4
189	$C_5H_5POC_6H_5^+$	8	18	
170	$C_6H_5OC_6H_5^+$	11.6	17	3
164	$C_5H_5MnCS^+$	17		
155	?	2		
154	$C_6H_5C_6H_5^+$	15		
153	$C_6H_5C_6H_4^+$	63.3	82.2	15
152	$C_6H_5C_6H_3^+$	37	38.5	0.8
151	C_5H_5MnP	8	13	
148	?	12	13	
142	?	4.3		
141	$P(OPh)OH^+$	50		
140	$P(OPh)O^+$	2.6		
139	?	2		
132	$MnC_6H_5^+$	7		
121	$C_5H_5MnH^+$	7		
120	$C_5H_5Mn^+$	100	100	
118	$MnPO_2^+$	12.6	13	
116	?	3		

TABLE IX-6 (continued)

m/e	Ion	Relative abundance L = CS	 L = CO[a]	 Ligand[b]
99	$MnCS^+$	1.3		
96	$PC_5H_5^+$		2.8	
95	$PC_5H_4^+$		5.5	
94	$C_6H_5OH^+$	22		100
78	$C_6H_6^+$	17		
77	$C_6H_5^+$	>300		48
66	$C_5H_6^+$	17		23
65	$C_5H_5^+$	20		23
56	MnH^+	2	1.7	
55	Mn^+	103	132	

a) Data taken from Ref. 177

b) Data taken from Ref. 266

TABLE IX -7 MASS SPECTRUM OF $C_5H_5Mn(CO)(CS)[P(C_6H_{11})_3]$

m/e	Ion	Rel. abund.	m/e	Ion	Rel. abund.
472	$C_5H_5Mn(CO)(CS)[P(C_6H_{11})_3]^+$	16	164	$C_5H_5Mn(CS)^+$	9.3
456	$C_5H_5Mn(CO)_2[P(C_6H_{11})_3]^+$	1.1	153	?	26
444	$C_5H_5Mn(CS)[P(C_6H_{11})_3]^+$	0.6	148	?	9.6
400	$C_5H_5Mn[P(C_6H_{11})_3]^+$	200	133	?	12
361	?	2.6	121	$C_5H_5MnH^+$	7.4
335	$MnP(C_6H_{11})_3^+$	1.5	120	$C_5H_5Mn^+$	100
326	?	3.3	117	?	26
318	$C_5H_5MnP(C_6H_{11})_2H^+$	3.0	116	$P(C_6H_{11})H_2^+$	10
316	$C_5H_5MnP(C_6H_{11})(C_6H_{10})^+$	3.7	115	$P(C_6H_{11})H^+$	15
310	?	3.3	99	$MnCS^+$	2.2
279	$P(C_6H_{11})_2(C_6H_{10})^+$	5.6	94	$C_7H_{10}^+$	52
235	$C_5H_5MnP(C_6H_{11})H^+$	6.7	89	$C_7H_5^+$	11
234	$C_5H_5MnP(C_6H_{11})^+$	10	83	$C_6H_{11}^+$	35
230	?	5.9	81	$C_6H_9^+$	32
217	?	10	79	$C_6H_7^+$	11
214	?	4.8	77	$C_6H_5^+$	15
202	$C_5H_5MnC_6H_{10}^+$	17	67	$C_5H_7^+$	18
199	$P(C_6H_{11})_2H_2^+$	6.7	66	$C_5H_6^+$	15
198	$P(C_6H_{11})_2H^+$	13	65	$C_5H_5^+$	11
171	$MnP(C_6H_{11})H_2^+$	7.8	56	MnH^+	11
169	$MnP(C_6H_{11})^+$	14	55	Mn^+	81

TABLE IX-8 MASS SPECTRUM OF $C_5H_5Mn(CO)(CS)(PMe_2Ph)$

m/e	Ion	Rel. abund.	m/e	Ion	Rel. abund.
330	$C_5H_5Mn(CO)(CS)(PMe_2Ph)^+$	19.6	123	$PMePh^+$	24
314	$C_5H_5Mn(CO)_2(PMe_2Ph)^+$	1.2	121	$C_5H_5MnH^+$	24
302	$C_5H_5Mn(CS)(PMe_2Ph)^+$	8.0	120	$C_5H_5Mn^+$	100
272	$C_5H_5Mn(CS)(PPh)^+$	6.4	109	$PPhH^+$	6
258	$C_5H_5MnPMe_2Ph^+$	168	107	?	4.8
243	$C_5H_5MnPMePh^+$	5.6	99	$MnCS^+$	2.4
193	$MnPMe_2Ph^+$	2.8	91	$C_7H_7^+$	14.8
192	$MnPMePhCH_2^+$	2.8	79	$C_6H_7^+$	6.8
177	$MnPPhCH_2^+$	2.8	78	$C_6H_6^+$	6.0
170	$C_6H_5OC_6H_5^+$	2.8	77	$C_6H_5^+$	9.6
164	$C_5H_5MnCS^+$	2.4	66	$C_5H_6^+$	8.0
154	$C_6H_5C_6H_5^+$	3.5	70	$C_5H_{10}^+$	6.4
149	$MnC_6H_5OH^+$	8.0	65	$C_5H_5^+$	7.6
138	PMe_2Ph^+	20.8	56	MnH^+	4.0
132	$MnC_6H_5^+$	6.8	55	Mn^+	88

TABLE IX-9 MASS SPECTRUM OF $C_5H_5Mn(CO)(CS)(SbPh_3)$

m/e	Ion	Rel. Abund.	m/e	Ion	Rel. abund.
544	$C_5H_5Mn(CO)(CS)(SbPh_3)^+$	11	164	$C_5H_5MnCS^+$ (?)	17.4
528	$C_5H_5Mn(CO)_2(SbPh_3)^+$	< 0.1	155	?	26.4
473	$C_5H_5MnSbPh_3H^+$	4.4	154	$C_6H_5C_6H_5^+$	187
472	$C_5H_5MnSbPh_3^+$	132	153	$C_6H_5C_6H_4^+$	41.8
395	$C_5H_5MnSbPh_2^+$	8.8	152	$C_6H_5C_6H_3^+$	35.2
352	$SbPh_3^+$	3.6	132	$MnC_6H_5^+$	59.4
330	$MnSbPh_2^+$	3.6	121	$C_5H_5MnH^+$, Sb^+	14
318	$C_5H_5MnSbPh^+$	3.2	120	$C_5H_5Mn^+$	100
275	$SbPh_2^+$	50	99	$MnCS^+$	3.5
253	$MnSbPh^+$	5.1	93	$C_6H_5O^+$	9
241	$C_5H_5MnSb^+$	2.2	77	$C_6H_5^+$	77
198	$SbPh^+$	100	65	$C_5H_5^+$	6.6
176	$MnSb^+$	4.4	55	Mn^+	220

S and Sb are ^{32}S: 95.0, ^{33}S: 0.75 and ^{34}S: 4.2%, ^{121}Sb: 57.25 and ^{123}Sb: 42.75%, the peak ratio of (m + 2)/m for any ion (m) containing either (or both) of these atoms was used to identify particular ions.

Proposed fragmentation schemes are presented in Figures IX-4 to IX-7. In order to facilitate the assignments of metastable ions , a simple computer program was used. This program utilizes the major m/e values and calculates all the possible combinations according to the equation $m^* = m_2^2/m_1$.

The mass spectra of a number of cyclopentadienyl manganese carbonyl complexes of the type $C_5H_5Mn(CO)_2(L)$ (L = sulfide, olefin or group VA donor[255]) have been reported and the fragmentation patterns have been discussed. The fragmentation process occurs initially by simultaneous loss of *both* CO groups. Thereafter, three pathways are possible: (1) loss of C_5H_5; (2) fragmentation of the bonded ligand, L; (3) loss of L. The mass spectra of three thiocarbonyl complexes, $C_5H_5Mn(CO)_2(CS)$, $C_5H_5Mn(CO)(CS)_2$ and $C_5H_5Mn(CO)(CS)(C_8H_{14})$ have also been reported[138] and the fragmentation patterns are similar to those for the carbonyl complexes above. The major difference being the large number of CS-containing ions (relative to the corresponding CO-containing ions) that are formed.

The mass spectra of the cyclopentadienyl complexes reported in this study agree well with the earlier findings. In most cases, low intensity parent peaks due to the "impurity" ions

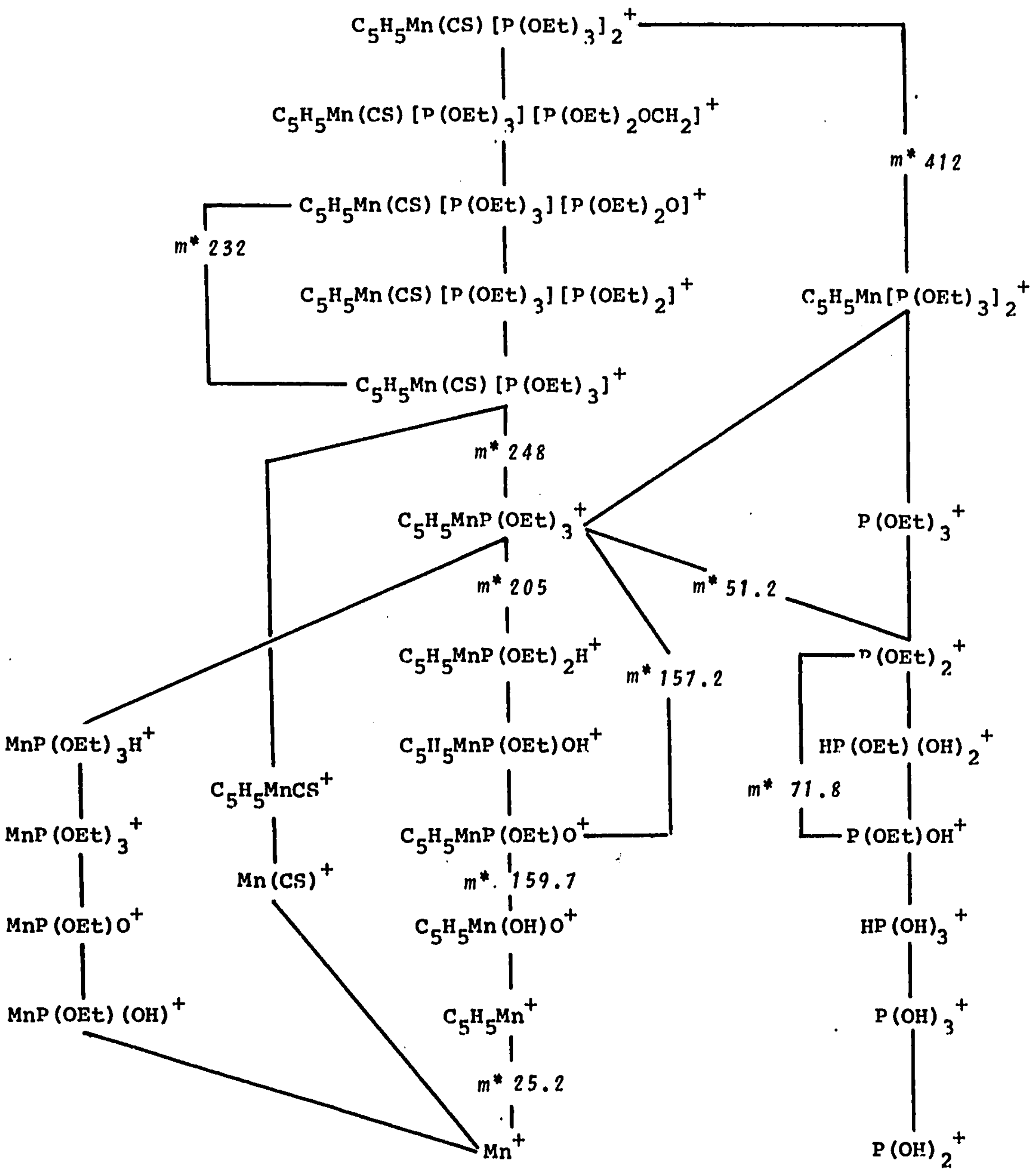


TABLE IX-4 FRAGMENTATION SCHEME FOR $C_5H_5Mn(CS)[P(OEt)_3]_2$.

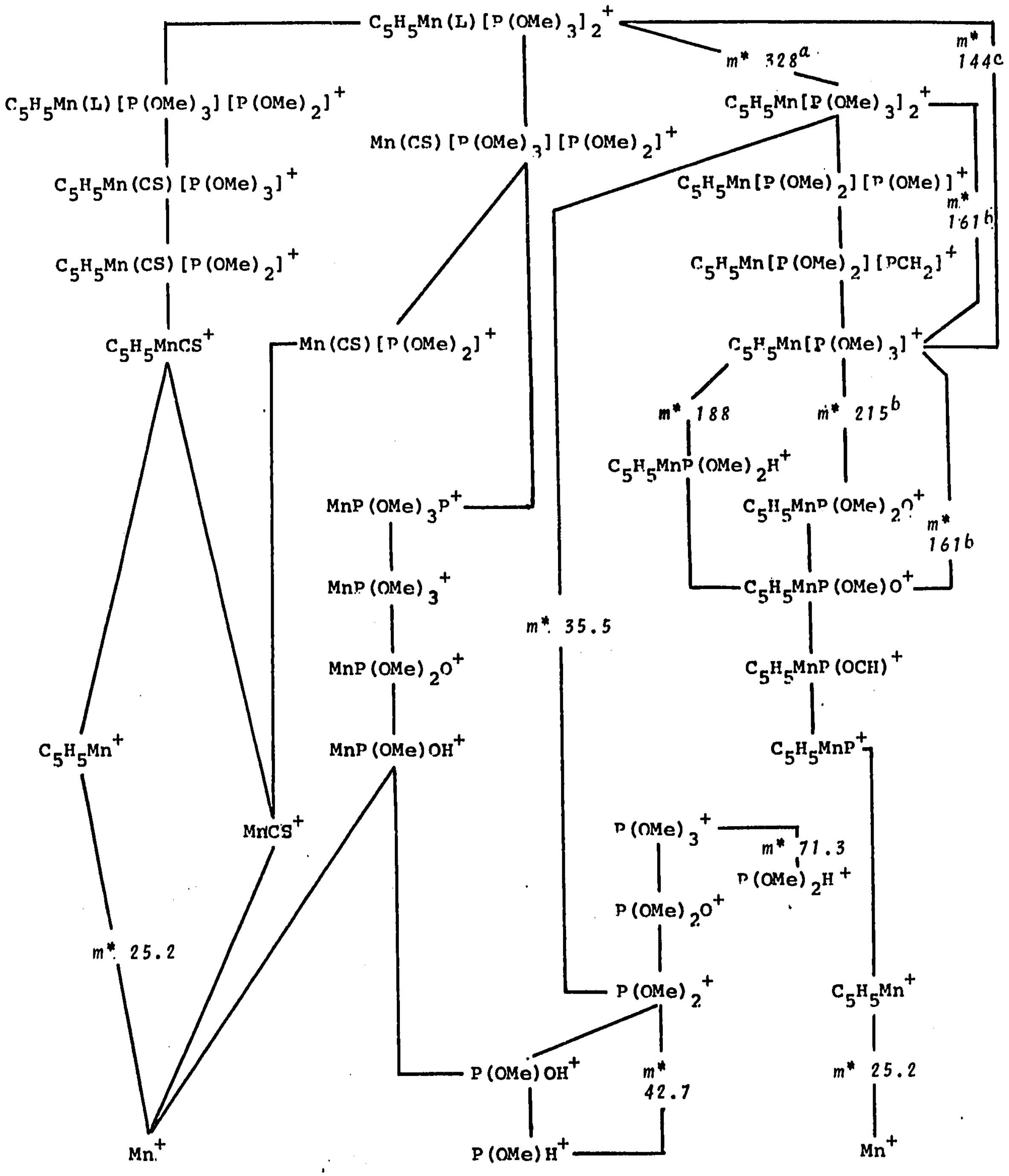


TABLE IX-5 FRAGMENTATION SCHEME FOR $C_5H_5Mn(L)[P(OMe)_3]_2$ (L = CO, CS).

a) This value is for L = CS. For L =CO, m^* = 341.

b) This value is for L = CO.

c) This ialue is for L = CS.

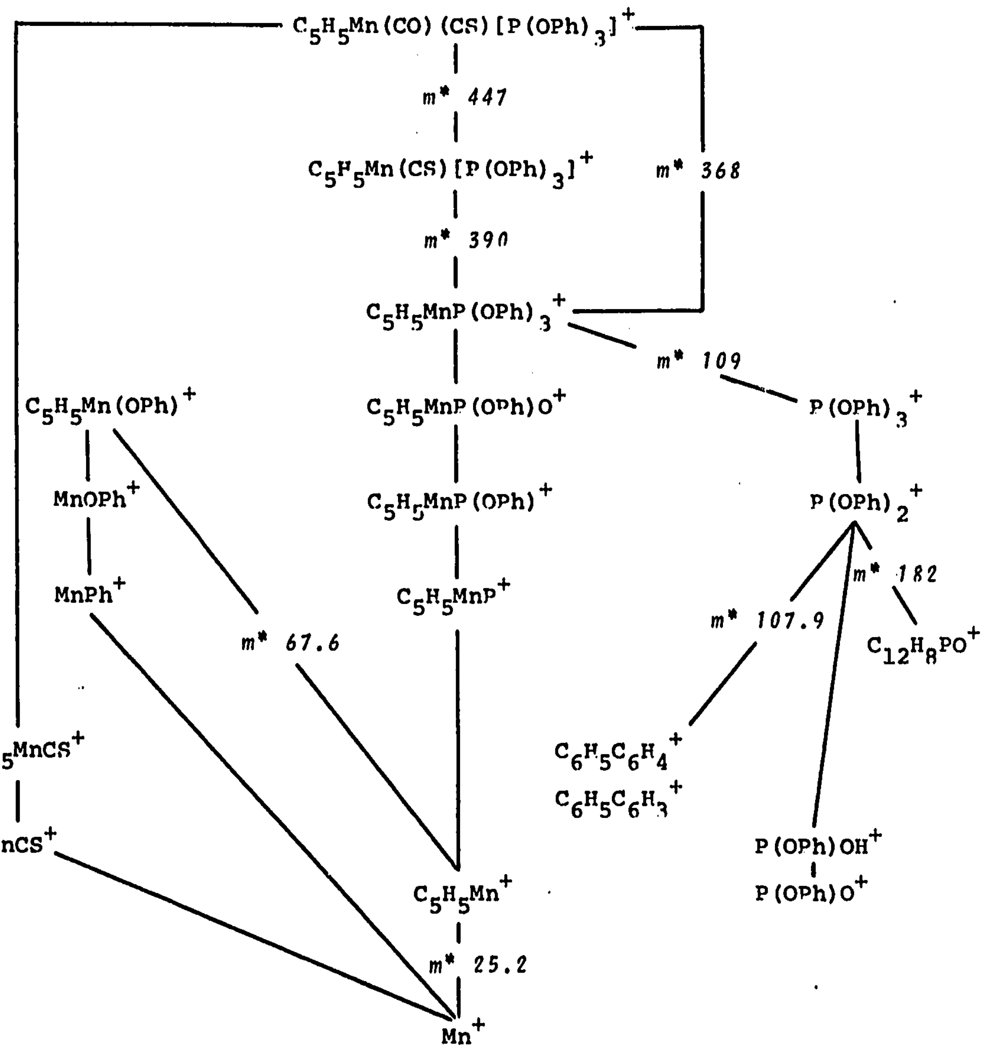


TABLE IX-6 FRAGMENTATION SCHEME FOR $C_5H_5Mn(CO)(CS)[P(OPh)_3]$.
Ions such as $C_5H_5POPh^+$, $C_6H_5OC_6H_5^+$ etc. were also detected. These ions are presumably formed by recombination in the mass spectrometer.

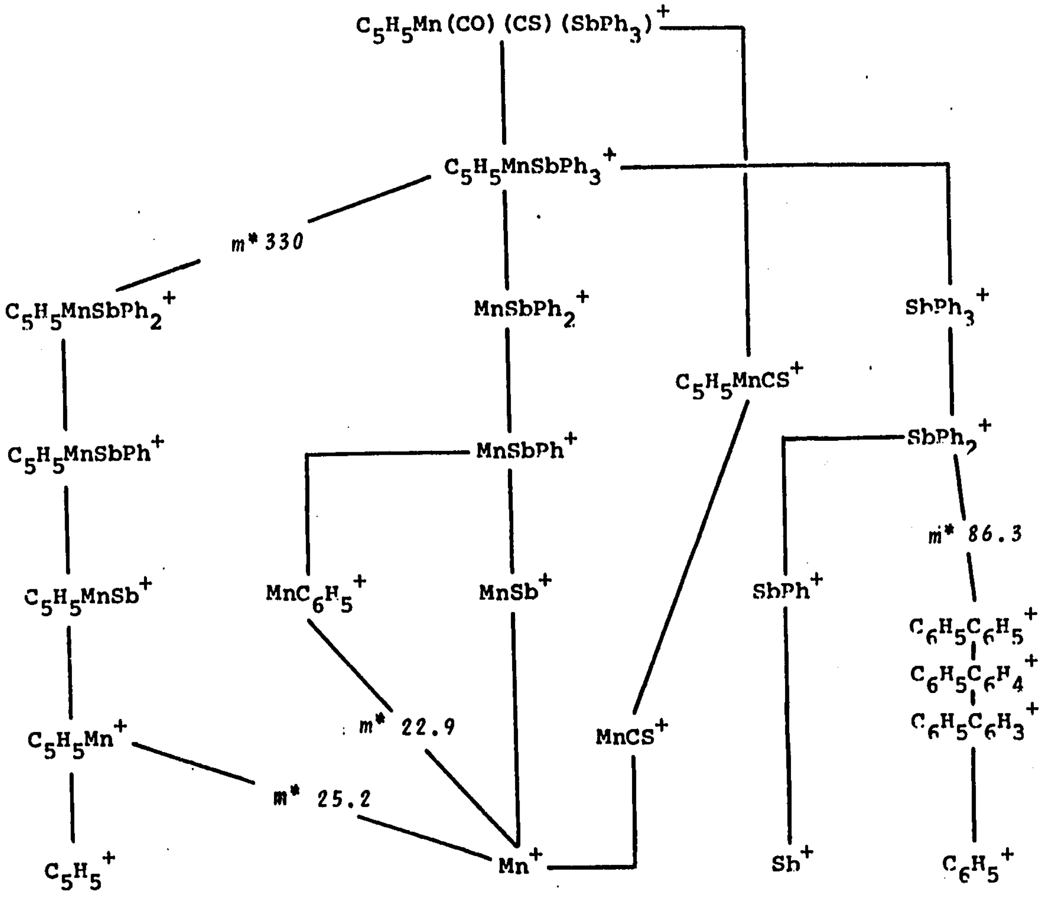
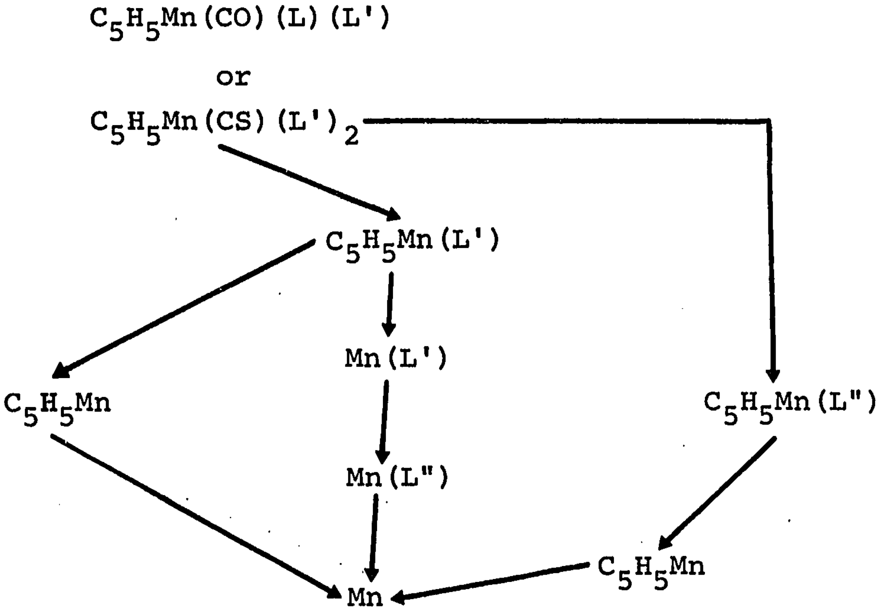


TABLE IX-7 FRAGMENTATION SCHEME FOR $C_5H_5Mn(CO)(CS)(SbPh_3)$.

$C_5H_5Mn(CO)(L)_2$ or $C_5H_5Mn(CO)_2(L)$ (L = group VA donor) could be detected.

For all the complexes, the following fragmentation pathways were in operation:



L = CS, group VA donor

L'= group VA donor

L"= fragment of the group VA donor

Fragments due to the breakdown of the free ligand could readily be detected, although in some instances [for e.g. L' = $P(OPh)_3$, $P(C_6H_{11})_3$] many of the fragmentation ions could not be identified.

Some special features of the spectra require further comment. The $C_5H_5Mn(CS)(L)_2$ and $C_5H_5Mn(CO)(L)_2$ spectra are the first recorded in which only *one* CO (or CS group) and group VA donors are attached to a "C_5H_5Mn" moeity. The most important feature of these spectra is the unexpected simultaneous loss of two ligands to give $C_5H_5Mn(L)^+$. It has been suggested previously that as the metal-C(O) bond in $C_5H_5Mn(CO)_2(L)$ complexes become stronger, the difference in the amount of energy required to remove successive CO groups decreases[265]. In this way, simultaneous loss of two CO groups was readily explained. If this explanation is correct, it suggests that the Mn-CO (or Mn-CS) and Mn-L bonds are of approximately equal strength in these complexes. However, it seems more likely that this phenomenon must rather be attributed to the stability of the $C_5H_5Mn(L)^+$ ion which is one of the major peaks found in all the mass spectra of complexes of this type.

A comparison of the spectra $C_5H_5Mn(L)[P(OMe)_3]_2$ (L = CO, CS) reveals that the major difference is the formation of a greater number of ions containing the Mn-CS group (relative to the Mn-CO group). This adds further confirmation to the proposal that the metal-CS bond is stronger than the metal-CO bond. A comparison of the spectrum of $C_5H_5Mn(CO)(CS)[P(OPh)_3]$ with the reported spectrum of $C_5H_5Mn(CO)_2[P(OPh_3)]$[177] gives similar results.

CONCLUSION

The chemical reactivity, NMR, IR and mass spectra all indicate that the Mn-CS bonds are stronger than the Mn-CO bonds in the complexes which were prepared in this study. Furthermore, the NMR results indicate that the CS ligand is a better π acceptor and/or σ donor than the CO ligand. The results thus confirm the theoretical predictions. This suggests that the lack of CS-containing complexes is a preparative problem and not necessarily a problem of complex stability. The major difficulty seems to be the generation of the CS ligand.

CHAPTER X REACTIONS OF $C_5H_5Mn(CO)_3$ AND $C_5H_5Mn(CO)_2(CS)$ WITH DIPHOS AND TRIPHOS

INTRODUCTION

As discussed earlier (Chapter IV), Triphos can coordinate to metals in a variety of ways: *via* one, two or three of its phosphorus atoms. Moreover, if Triphos coordinates to a manganese atom which is in an octahederal environment, as in *fac*-$Mn(CO)_3$(Triphos)Br, the central phosphorus atom of the coordinated ligand becomes optically active and two diastereomers (α and β) can be isolated.

The reactions of $C_5H_5Mn(CO)_3$ with a number of polyphosphine ligands to give products of the type $C_5H_5Mn(CO)(P-P)$ and $[C_5H_5Mn(CO)_2]_2(P-P)$ were reviewed in Chapter II. Surprisingly, the reaction with Triphos has not been investigated. Consequently, the present study was undertaken to determine whether diastereomers could be detected for $C_5H_5Mn(CO)$(Triphos) The manganese atom in this complex is expected to be in an octahederal environment (*vide supra*, p. 171) Concurrently, it was decided to continue the comparative studies of $C_5H_5Mn(CO)_2(CS)$ and $C_5H_5Mn(CO)_3$ by investigating the reaction of $C_5H_5Mn(CO)_2(CS)$ with Triphos. The reactions of $C_5H_5Mn(CO)_2(CS)$ and $C_5H_5Mn(CO)_3$ with Diphos were also studied.

EXPERIMENTAL

$C_5H_5Mn(CO)_2(CS)$ was prepared as reported previously[138]. $Cr(CO)_5THF$ was prepared *in situ* as described in Chapter IV. All reactions were performed routinely under a nitrogen atmosphere. A 100 W Hanovia high pressure mercury lamp was used for the UV irradiations.

All physical measurements were carried out as reported earlier (*vide supra*, p. 40).

Preparation of $C_5H_5Mn(CS)$(Diphos)

$C_5H_5Mn(CO)_2(CS)$ (1 mmol) and Diphos (1.1 mmol) were dissolved in freshly distilled THF (100 ml) and the solution was irradiated until no further reaction occurred (∿12 h.). Solvent was then removed under reduced pressure, and the product was purified by elution of the crude material on silica gel thin layer plates with a 3/2 benzene/n-hexane solution. The required product was crystallized from a CH_2Cl_2/n-hexane mixture and was dried *in vacuo* (25°/0.01 mmHg) for 24 h (yield 60%).

Preparation of $C_5H_5Mn(CO)$(Diphos)

This was prepared and purified as above but in lower yield (∿40%). Difficulty was experienced in extracting the desired product from the thin layer plates.

Reaction of $C_5H_5Mn(CO)_2(CS)$ and Triphos

$C_5H_5Mn(CO)_2(CS)$ (1.5 mmol) and Triphos (1.5 mmol) were dissolved in freshly distilled benzene (150 ml) and the solution was irradiated for ∿5h. The solvent volume was then reduced to ∿5 ml on a water aspirator and the crude product was precipitated by addition of n-hexane (25 ml). Elution of this material on silica gel thin layer plates with a 13/7 benzene/n-hexane solution afforded three complexes in low yield (∿ 5%). In order of decreasing R_f value, these were γ-$C_5H_5Mn(CS)$(Triphos), ϕ-$C_5H_5Mn(CS)$(Triphos) and $C_5H_5Mn(CS)$(Triphos=O). The complexes were crystallized from CH_2Cl_2/n-hexane mixtures and were dried *in vacuo* (25°/0.01 mmHg) for 24 h.

Reaction of $C_5H_5Mn(CO)_3$ with Triphos

$C_5H_5Mn(CO)_3$ (1.5 mmol) and Triphos (1.5 mmol) were dissolved in freshly distilled benzene (150 ml) and the solution was irradiated for ∿6 h. The solvent was then reduced to ∿5 ml on a water aspirator and the crude product was precipitated by addition of n-hexane (25 ml). Elution of this material on silica gel thin layer plates with a 1/1 acetone/n-hexane mixture afforded two complexes. The complex with the largest R_f value consisted of two compounds, γ-$C_5H_5Mn(CO)$(Triphos) and ϕ-$C_5H_5Mn(CO)$(Triphos), which could be separated in very low yield on silica gel thin layer plates following elution with a 1/5 benzene/n-hexane mixture. From its IR spectrum, the third complex is most probably $C_5H_5Mn(CO)(Triphos{=}O)$.

The three products were crystallized from CH_2Cl_2/n-hexane mixtures and were dried *in vacuo* (25°/0.01 mmHg) for 24 h.

Reaction of $C_5H_5Mn(CS)(Triphos)$ with $C_5H_5Mn(CO)_3$

$C_5H_5Mn(CO)_2(CS)$ (0.5 mmol) and Triphos (0.5 mmol) were dissolved in freshly distilled benzene (150 ml) and the solution was irradiated for 3 h. $C_5H_5Mn(CO)_3$ (1.0 mmol) was then added and the solution was irradiated for a further 10 h. Following solvent removal under reduced pressure, the crude material was eluted on silica gel thin layer plates with a 5/7 acetone/n-hexane mixture. One major fraction was separated. Subsequent elution of the first fraction with a 1/1 acetone/n-hexane mixture afforded two products analyzing as $C_5H_5(CS)Mn(Triphos)Mn(CO)_2C_5H_5$. The two new complexes were crystallized from CH_2Cl_2/n-hexane mixtures and were then dried *in vacuo* (25°/0.01 mmHg) for 24 h.

Reaction of $C_5H_5Mn(CO)(Triphos)$ with $C_5H_5Mn(CO)_3$

$C_5H_5Mn(CO)_3$ (1 mmol) and Triphos (1 mmol) were dissolved in freshly distilled benzene (150 ml) and the solution was irradiated for 8 h. After a further addition of $C_5H_5Mn(CO)_3$ (1.5 mmol), the irradiation was continued for an additional 12 h. The solvent was then removed under reduced pressure and the crude material was eluted on silica gel thin layer plates with 1/1 acetone/n-hexane mixtures. Two isomers of $C_5H_5(CO)Mn(Triphos)Mn(CO)_2C_5H_5$ were isolated. These two complexes were crystallized from CH_2Cl_2/n-hexane and were dried *in vacuo* (25°/0.01 mmHg) for 24 h.

Reactions of $C_5H_5Mn(CS)(Triphos)$ with $Cr(CO)_5THF$

$C_5H_5Mn(CS)(Triphos)$ was added to a THF solution (100 ml) of $Cr(CO)_5THF$ [freshly prepared from $Cr(CO)_6$(1 mmol)] and the solution was stirred at room temperature for 12 h. Following solvent removal under reduced pressure, the excess $Cr(CO)_6$ was sublimed off (60°/0.01 mmHg). The crude product remaining was eluted on silica gel thin layer plates with a 3/5 benzene/n-hexane solution. Two products were isolated from the plates. These were crystallized from CH_2Cl_2/n-hexane and were dried *in vacuo* (25°/0.01 mmHg) for 24 h.

Reaction of $C_5H_5Mn(CO)(Triphos)$ with $Cr(CO)_5THF$

$C_5H_5Mn(CO)(Triphos)$(0.2 mmol) was added to a THF solution (100 ml) of freshly prepared $Cr(CO)_5THF$ [from $Cr(CO)_6$(1 mmol)] and the solution was stirred at room temperature for 20 h. The solvent was evaporated off under reduced pressure and the excess $Cr(CO)_6$ was removed by vacuum sublimation (60°/0.01 mmHg). The crude product was then eluted on silica gel thin layer plates with a 3/5 acetone/n-hexane mixture, and one major fraction was isolated. Elution of this product on silica gel

TABLE X-1 ANALYTICAL DATA FOR THE MANGANESE(I) COMPLEXES

Complex	Colour[a]	Decomp. (°C)	Analysis Found (Calcd.) (%) C	H	P
C_5H_5Mn(CS)(Diphos)	o	$\sim$140	67.8 (68.3)	5.8 (5.2)	11.2 (15.0)
γ-C_5H_5Mn(CO)(Triphos)	y	$\sim$55	68.3 (70.4)	6.3 (5.6)	
ϕ-C_5H_5Mn(CO)(Triphos)	o	$\sim$55	69.5 (70.4)	6.1 (5.6)	
γ-C_5H_5Mn(CS)(Triphos)	o	$\sim$75	68.0 (68.8)	6.3 (5.5)	13.6 (13.3)
ϕ-C_5H_5Mn(CS)(Triphos)	y	73-77	68.6 (68.8)	6.0 (5.5)	13.1 (13.3)
γ-C_5H_5(CO)Mn(Triphos)Mn(CO)$_2C_5H_5$	y	81-84	66.4 (65.7)	5.8 (5.0)	
ϕ-C_5H_5(CO)Mn(Triphos)Mn(CO)$_2C_5H_5$	y	93-96	66.4 (65.7)	5.6 (5.0)	
γ-C_5H_5(CS)Mn(Triphos)Mn(CO)$_2C_5H_5$	y	97-100	65.2 (64.5)	5.5 (5.0)	
ϕ-C_5H_5(CS)Mn(Triphos)Mn(CO)$_2C_5H_5$	y	97-100	65.4 (64.5)	5.6 (5.0)	
γ-C_5H_5(CO)Mn(Triphos)Cr(CO)$_5$	y	54-56	61.0 (61.8)	4.6 (4.4)	9.7 (10.6)
ϕ-C_5H_5(CO)Mn(Triphos)Cr(CO)$_5$	y	54-56	61.2 (61.8)	4.7 (4.4)	
γ-C_5H_5(CS)Mn(Triphos)Cr(CO)$_5$	y	83-86	59.9 (60.9)	4.5 (4.3)	10.4 (10.4)
ϕ-C_5H_5(CS)Mn(Triphos)Cr(CO)$_5$	y	83-86	60.9 (60.9)	4.8 (4.3)	9.2 (10.4)
C_5H_5Mn(CS)(Triphos=O)	y	108-113	66.9 (62.7)	5.8 (5.4)	13.4 (13.0)

a) y = yellow, o = orange (b) Mol. Wt: Found(calcd.) 562 (634) thin layer plates with a 1/1 benzene/n-hexane mixture afforded two fractions in very poor yield. These two complexes were crystallized from CH_2Cl/n-hexane solution and these were dried *in vacuo* (25°/0.01 mmHg) for 24 h.

Preparation of $C_5H_5Mn(CS)(Triphos{=}O)$

The isomeric mixture of $C_5H_5Mn(CS)(Triphos)$ (0.1 mmol) was dissolved in CH_2Cl_2 (20 ml) and ozone (0.12 mmol) was bubbled through the solution. Solvent was then removed under reduced pressure and the crude material was eluted on silica gel thin layer plates with a 1/1 acetone/n-hexane solution. One major component was obtained which was crystallized from a CH_2Cl_2/n-hexane mixture and dried *in vacuo* (25°/0.01 mmHg) for 24 h.

RESULTS AND DISCUSSION

Addition of Diphos to $C_5H_5Mn(CO)_3$ or $C_5H_5Mn(CO)_2(CS)$ in a 1:1 mole ratio results in the formation of $C_5H_5Mn(CO)(Diphos)$ or $C_5H_5Mn(CS)(Diphos)$. The reactions almost certainly proceed by initial replacement of one CO group to give either $C_5H_5Mn(CO)_2(Diphos)$ or $C_5H_5Mn(CO)(CS)(Diphos)$. No attempt was made to isolate these intermediates. The preparation of $C_5H_5Mn(CO)(Diphos)$ has been previously reported[40] and it was prepared in this study solely for comparative spectral purposes. This complex is readily characterized by the presence of one strong IR-active CO stretching absorption. The thiocarbonyl complex, $C_5H_5Mn(CS)(Diphos)$ has also been described previously. It was prepared from the reaction of $C_5H_5Mn(CO)(CS)(C_8H_{14})$ with Diphos[47]. This product is also characterized by its IR spectrum *viz.*, one strong band in the thiocarbonyl stretching region.

UV irradiation of a benzene solution of Triphos and $C_5H_5Mn(CO)_2(CS)$ was continued until all the $\nu(CO)$ bands in the IR spectrum had disappeared. Thin layer chromotography revealed that the reaction mixture contained three major components. These could be separated by preparative thin layer chromotography, but with great loss of material as a result of the products "sticking" to the plates*. All three products showed one strong $\nu(CS)$ absorption in the IR, similar to that for $C_5H_5Mn(CS)(Diphos)$ ($\sim$1200 cm^{-1}). Elemental analyses of these two products with the larger R_f values are consistent with their being isomers of $C_5H_5Mn(CS)(Triphos)$. This result would imply that the Triphos ligand is bonded to the manganese atoms in these complexes through two of its P atoms. Such a situation is thought to occur through adjacent P atoms. This would then give rise to two diastereomers.

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*This "sticking" presumably arises from decomposition of the complexes on the thin layer plates and presented a major problem in the isolation of *all* the products prepared in this study.

The difference between these diastereomers would then be related to the orientation of the groups on the central P atom, as shown in Figure X-1.

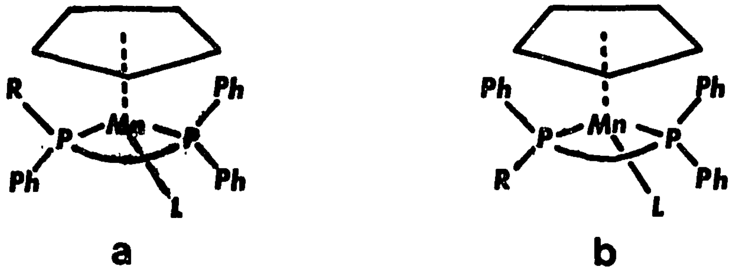

FIGURE X-1 TWO DIASTEREOMERS OF $C_5H_5Mn(L)$(Triphos). In the above figures L = CO or CS and R = $Ph_2PCH_2CH_2$. Figure (a) represents the γ isomer and (b) represents the ϕ isomer.

For convenience, the two diastereomers will be referred to as the γ and ϕ isomers respectively. By analogy with the previous study on the reactions of $Mn(CO)_5X$ with Triphos, the isomer with the larger R_f value (γ) will be assumed to have the phenyl ring pointing away from the cyclopentadienyl ring.

The third product isolated from the reaction mixture (smallest R_f value) was not obtained in a pure form. However, comparative IR evidence [ν(CS) = 1203 cm^{-1}] and thin layer

TABLE X-2 IR SPECTRA IN THE CO STRETCHING REGION FOR THE MANGANESE(I) COMPLEXES (CS_2 SOLUTION)

Complex		ν(CO)[a]	cm^{-1}
$C_5H_5Mn(CO)(Diphos)$[b]		1845	
$C_5H_5Mn(CS)(Diphos)$[c]		1206	
γ-$C_5H_5Mn(CO)(Triphos)$		1839	
ϕ-$C_5H_5Mn(CO)(Triphos)$		1841	
γ-$C_5H_5Mn(CS)(Triphos)$		1203	
ϕ-$C_5H_5Mn(CS)(Triphos)$		1206	
γ-$C_5H_5(CO)Mn(Triphos)Mn(CO)_2C_5H_5$	1929	1865	1834 (m)
ϕ-$C_5H_5(CO)Mn(Triphos)Mn(CO)_2C_5H_5$	1929	1864	1845 (sh)
γ-$C_5H_5(CS)Mn(Triphos)Mn(CO)_2C_5H_5$	1930	1865	1204 (m)
ϕ-$C_5H_5(CS)Mn(Triphos)Mn(CO)_2C_5H_5$	1931	1867	1208 (m)
γ-$C_5H_5(CO)Mn(Triphos)Cr(CO)_5$	2061 (m)	1980 (w) 1933	1942 (sh) 1838
ϕ-$C_5H_5(CO)Mn(Triphos)Cr(CO)_5$	2061 (m)	1979 (w) 1933	1942 (sh) 1845
γ-$C_5H_5(CS)Mn(Triphos)Cr(CO)_5$	2061 (m)	1979 (w) 1932	1943 (sh) 1205 (m)
ϕ-$C_5H_5(CS)Mn(Triphos)Cr(CO)_5$	2061 (m)	1981 (w) 1933	1943 (sh) 1209 (m)
$C_5H_5Mn(CS)(Triphos{=}O)$[d]	1203		

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a) All bands strong unless otherwise stated.

b) Ref. 43: 1837 cm^{-1} (CS_2).

c) Ref. 47: 1208 cm^{-1} (CS_2).

d) q "X-sensitive" mode: 1131 cm^{-1} (nujol).

comparative studies with the known sample suggested that this complex should be formulated as $C_5H_5Mn(CS)(Triphos{=}O)$.

The reaction of $C_5H_5Mn(CO)_3$ with Triphos also yielded three products. Elemental analyses and IR data (one strong band in the CO stretching region) for the two complexes with the larger R_f values suggested that these were the two diastereomers, γ- and ϕ-$C_5H_5Mn(CO)(Triphos)$. The third product is thought to be $C_5H_5Mn(CO)(Triphos{=}O)$.

The complexes $C_5H_5Mn(CS)(Triphos)$ and $C_5H_5Mn(CO)(Triphos)$ contain "dangling" P atoms. Reactions were thus undertaken to show the presence of the un-coordinated P atoms, e.g., with $Cr(CO)_5(THF)$ and $C_5H_5Mn(CO)_3$. Two bimetallic complexes were obtained in every case. For instance, the reaction of $C_5H_5Mn(CS)(Triphos)$ with $Cr(CO)_5THF$ yields two isomers of $C_5H_5(CS)Mn(Triphos)Cr(CO)_5$. These isomers most probably correspond to the γ- and ϕ-$C_5H_5Mn(CS)(Triphos)$ isomers in which the "dangling" P atoms are now coordinated to the $Cr(CO)_5$ group. Unfortunately, even these bimetallic complexes were obtained in low yield.

The relative stability towards oxidation of the complexes containing either a thiocarbonyl or carbonyl group was readily shown by ozonolysis of $C_5H_5Mn(CS)(Triphos)$ and $C_5H_5Mn(CO)(Triphos)$. Whereas, ozonolysis of the thiocarbonyl complex yielded $C_5H_5Mn(CS)(Triphos{=}O)$, a similar reaction with the carbonyl analogue caused product decomposition. Since the P=O stretching mode occurs at about the same frequency as the CS stretching mode, the q mode (*vide supra*, p. 82) provided IR spectral evidence for the presence of the P=O group. Diastereomers of $C_5H_5Mn(CS)(Triphos{=}O)$ are expected but no separation of the isomers was achieved.

All Mn-C(O) and Mn-C(S) stretching modes were found in the expected regions of the IR spectrum. These are listed in Table X-2.

The frequency ranges for the δ(Mn-C-O) and δ(Mn-C-S) modes for the complexes $C_8H_5Mn(CO)_{3-n}(CS)_n$ (n = 0-2) have been determined as 645-473 cm^{-1} and 625-448 cm^{-1} respectively[208]. The associated values for these modes in selected examples of the complexes prepared in this study are shown in Table X-3. The observed values provide definitive evidence for the assignments proposed earlier.

In most instances, insufficient amounts of the new complexes were isolated and so only a limited number of NMR spectra were recorded (Table X-4). Moreover, the products are not particularly soluble in carbon disulfide which was the solvent used for the NMR spectra described in Chapter IX.

CONCLUSION

This study provided further information on the nature of the CS ligand and the Mn-C(S) bond. Thus, reaction of $C_5H_5Mn(CO)_2(CS)$ with the polyphosphines resulted in displacement

TABLE X-3 IR-ACTIVE δ(Mn-C-O) AND δ(Mn-C-S) MODES FOR THE NEW DIPHOS AND TRIPHOS COMPLEXES

Complex[a,b]				
		δ(M-C-O)		
$C_5H_5Mn(CO)_2(PPh_3)$[c]	662(vs)	621(vs)	599(vs)	
$C_5H_5Mn(CO)(CS)_2$[d]	625(m)	590(s)	570(s) 479(m)	499(m) 488(vw)
$C_5H_5Mn(CO)(Diphos)$[e]	616(m)	594(s)	586(m)	
γ-$C_5H_5Mn(CO)(Triphos)$	620(m)	592(s)		
ϕ-$C_5H_5Mn(CO)(Triphos)$	622(m)	595(s)		
		δ(M-C-S)		
$C_5H_5Mn(CS)(Diphos)$	555(m)	543(s)		
γ-$C_5H_5Mn(CS)(Triphos)$	552(m)	532(s)		
ϕ-$C_5H_5Mn(CS)(Triphos)$	550(m)	530(s)		

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a) IR recorded in nujol on a PE 521 spectrophotometer ($\pm$ 2 cm^{-1})

b) Abbreviations used m = medium, v = very, s = strong, w = weak.

c) Data taken from Ref. 250.

d) Data taken from Ref. 208

e) Ref. 250; 616 ms, 594(vs), 586(vs).

TABLE X-4 NMR DATA FOR SOME OF THE NEW MANGANESE(I) COMPLEXES

Complex[a,b]	C_5H_5			Other
$C_5H_5Mn(CO)(Diphos)$	6.00	(Triplet)	(1.5)[c]	Ph: 2.74 (Complex)
				CH_2: 7.5 (Broad)
$C_5H_5Mn(CS)(Diphos)$	5.85	(Triplet)	(1.5)[c]	Ph: 2.30,2.76,2.95 (Complex)
				CH_2: 7.4,7.6 (Broad)
$C_5H_5Mn(CO)(Triphos)$	5.90	(Complex)		Ph: 2.52 (Complex)
				CH_2: 8.0,8.2 (Broad)
$C_5H_5Mn(CS)(Triphos)$	5.78	(Complex)		Ph: 2.37,2.68,2.83 (Complex)
	5.84			CH_2: 8.20 (Broad)

a) All spectra were recorded in CS_2 relative to TMS (τ=10).

b) Spectra of saturated solutions were recorded.

c) J_{P-H}.

of the CO groups in preference to the CS group. This is in accordance with the results obtained in Chapter IX. Spectral information was also obtained on the location of the δ(Mn-C-S) mode.

The presence of diastereomers for both the thiocarbonyl [C_5H_5Mn(CS)(Triphos)] and the carbonyl complex [C_5H_5Mn(CO)(Triphos)] was demonstrated. This effect is again thought to be due to the optical activity induced upon coordination of the Triphos ligand to the manganese atom.

Unfortunately, the major problem of complex separation restricted further studies on the new complexes.

CONTRIBUTIONS TO KNOWLEDGE

Part A

1) A new series of halodicarbonyl manganese(I) complexes, $Mn(CO)_2(P-P-P)X$ and $Mn(CO)_2(L)(P-P)X$ ($X = Cl, Br, I$), have been prepared and characterized.

2) The NMR spectra of *trans*- and *fac*-$Mn(CO)_3[P(OMe)_3]_2Br$ and $C_5H_5Mn(L)[P(OMe)_3]_2$ ($L = CO, CS$) have been recorded. The results indicate that the stereochemistry of manganese(I) trimethylphosphite complexes cannot be assigned by NMR spectroscopy alone.

3a) The diastereomers α- and β-*fac*-$Mn(CO)_3(Triphos)X$ ($X = Cl, Br, I$) have been synthesized and separated.

b) Reaction of the un-coordinated P atom in the above diastereomers with other metal centers led to the formation of a new series of bimetallic complexes. All the bimetallic complexes exist as diastereomeric pairs.

c) The single crystal and molecular structures of the diastereomers, α- and β-$Br(CO)_3Mn(Triphos)Cr(CO)_5$, have been determined by three-dimensional X-ray crystallography.

d) The difference between the two structures resides in the orientation of the groups around the central P atom of the Triphos ligand. This P atom has become optically active on being bonded to the manganese atom.

4a) The reaction of $Mn(CO)_5X$ ($X = Br, I$) with Tetraphos has been studied. Several complexes such as $Mn(CO)_2(Tetraphos)Br$ and

$Mn(CO)_3$(Tetraphos)Br were isolated.

b) Evidence has been presented for the separation of the *meso* and *racemic* forms of the optically active ligand.

Part B

1) A new series of complexes, $C_5H_5Mn(CO)(CS)(L)$ and $C_5H_5Mn(CS)(L)_2$ (L = group VA donor ligand), have been prepared and characterized by IR, NMR and mass spectrometry. Chemical and physical evidence suggested that the CS ligand is a better π acceptor and/or a better σ donor than the CO ligand. This is in agreement with prior theoretical predictions.

2) The reaction of $C_5H_5Mn(CO)_2(CS)$ and $C_5H_5Mn(CO)_3$ with Diphos and Triphos has been investigated. All the new products were characterized by IR and NMR spectroscopy. The complexes $C_5H_5Mn(L)$(Triphos) (L = CO,CS) exist as a mixture of isomers, γ- and ϕ-$C_5H_5Mn(L)$(Triphos). The isomerism is again thought to arise from the optical activity induced in the central P atom on coordination to the manganese atom.

SUGGESTIONS FOR FUTURE WORK

1) The complex *fac*-$\mathrm{Mn(CO)_3(Triphos)X}$ provides a convenient starting point for determination of the reaction kinetics and mechanisms of chelate formation:

$$fac\text{-}\mathrm{Mn(CO)_3(Triphos)X} \longrightarrow cis\text{-}\mathrm{Mn(CO)_2(Triphos)X}\ .$$

Comparison with non-chelating ligands could be made.

2) The crystal structures determined, suggest that Diphos, in *fac*-$\mathrm{Mn(CO)_3(Diphos)X}$, might cause Mn-C(O) bond weakening relative to *fac*-$\mathrm{Mn(CO)_3(L)_2X}$ (L = phosphine, e.g., $\mathrm{PEtPh_2}$). The kinetics and mechanisms of the reactions

$$fac\text{-}\mathrm{Mn(CO)_3(Diphos)X} + \mathrm{L'} \longrightarrow cis\text{-}\mathrm{Mn(CO)_2(L')(Diphos)X} + \mathrm{CO}$$

and $fac\text{-}\mathrm{Mn(CO)_3(L)_2X} + \mathrm{L'} \longrightarrow cis\text{-}\mathrm{Mn(CO)_2(L)_2(L')X} + \mathrm{CO}$

where L and L' are group VA donors, would provide chemical confirmation of this effect.

3) Separation of the isomers of *fac*-$\mathrm{Mn(CO)_3(Triphos{=}O)}$ might be achieved by reaction with a metal centre which would coordinate to the P=O group (e.g., with $\mathrm{CuCl_2}$).

4) The reaction of Tetraphos with $\mathrm{Mn(CO)_5X}$ proved to be extremely complex. A simplifying feature would be to separate the *meso* and *racemic* forms of the ligand before the reaction with the metal carbonyl. This would confirm or disprove some of the conclusions put forward in this work.

5) A literature survey of the CO substitution reactions of $\mathrm{C_5H_5Mn(CO)_3}$ has been given in this thesis, and a few comparative

substitution reactions with $C_5H_5Mn(CO)_2(CS)$ were initiated. There is still much work to be done in order to obtain a better understanding of the CS ligand and the Mn-CS bond. Possible studies would include the reactions of $C_5H_5Mn(CO)_2(CS)$ with N_2, S donors, polyamines etc.

6) Since few X-ray structures of metal-thiocarbonyl complexes are known, an X-ray structure determination of one of the manganese thiocarbonyl complexes could be attempted.

7) Unexpectedly, the NMR spectra of manganese complexes containing *cis* $P(OMe)_3$ groups gave 1:2:1 triplets for the methoxy resonances. An NMR study of the type $Mn(CO)_3(L)_2X$ ($L = PMe_3$, PMe_2Ph, etc.) would show if this was a general effect or restricted to $P(OMe)_3$ and cyclic phosphites.

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