SYNTHETIC AND SPECTROSCOPIC STUDIES OF PENTADIENYL COMPLEXES OF TRANSITION ELEMENTS AND RELATED COMPOUNDS

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SYNTHETIC AND SPECTROSCOPIC STUDIES OF PENTADIENYL COMPLEXES OF TRANSITION ELEMENTS AND RELATED COMPOUNDS.

Mariá de los Angeles Paz Sandoval.

ABSTRACT.

The pentadienyl complexes $\{M(\eta^5\text{-}C_5H_6R)(CO)_3\}$ $\{M{=}Mn,\ R{=}H,\ Me{:}M{=}Re,\ R{=}H\}$ and $\{Mn(\eta^5\text{-}syn\text{-}(1,5\text{-}Ph_2C_5H_5)(CO)_3\}$ have been synthesised from the corresponding metal carbonyl halides $M(CO)_5Br$ $\{M{=}Mn,Re\}$ by reaction with pentadienyltrialkyltin reagents $\{R'_3Sn(C_5H_6R)\}$ $\{R{=}H,\ Me,\ R{=}Me,n\text{-}Bu\}$ and $\{Me_3Sn(1,5\text{-}Ph_2C_5H_5)\}$ respectively.

The organotin intermediates were prepared by reaction of organotin halides with substituted pentadienyl anions.

Treatment of the dimer $\{RuCOCl_2(PMe_2Ph)_2\}_2$ with $(Bu_3SnC_5H_7)$ yields $\{RuCl(CO)(\eta^3\text{-}C_5H_7)(PMe_2Ph)_2\}$.

Attempts to prepare the pentadienyl compounds from pentadienyl anions and different complexes such as $\{RuCl_2(C_6H_6)\}_2$, $\{RhCl(1,5\text{-}C_8H_{12})\}_2$, $Mo(CO)_6$, $\{MoCl(CO)_2(\eta^3\text{-}C_3H_5)\text{-}(MeCN)_2\}$, $\{RuCl_2(1,5\text{-}C_8H_{12})\}_n$ were unsuccessful.

The complexes $\{Mn(\eta^5\text{-}C_5H_7)(CO)_2L\}\{L{=}PPh_3, AsPh_3, P(C_6H_{11})_3, P(OMe)_3, P(OEt)_3, P(OPh)_3, PMe_3, PMe_2Ph\}$ and $\{Mn(\eta^3\text{-}C_5H_7)(CO)_3L\}\{L{=}PBu_3, PMe_3, PMe_2Ph\}$ have been prepared from $\{Mn(\eta^5\text{-}C_5H_7)(CO)_3\}$ using thermal and photolytic methods. The thermal substitution reactions with L show the formation of $\{Mn(\eta^3\text{-}C_5H_7)(CO)_3L\}$ as an intermediate step followed by a decarbonylation, giving the corresponding

$\{Mn(\eta^5-C_5H_7)(CO)_2L\}$.

Only the strongest Lewis bases proved to be useful for obtaining both the η^3- and the η^5-pentadienyl complexes, $\{Mn(\eta^3-C_5H_7)(CO)_3L\}$ and $\{Mn(\eta^5-C_5H_7)(CO)_2L\}$.

The compounds have be characterised by infrared spectroscopy, elemental analysis and ^{1}H-NMR, and some also by mass spectrometry and ^{13}C-NMR.

He(I) and He(II) u.v.-photoelectron spectra for $\{M(\eta^5-C_5H_6R)(CO)_3\}$ $\{M=Mn, R=H, Me: M=Re, R=H\}$are reported.

The protonation of some derivatives $\{Mn(\eta^5-C_5H_7)(CO)_2L\}$ $\{L=P(C_6H_{11})_3,PPh_3,CO\}$ with strong acids was studied but the site for the proton attack was not definitely established.

Photolysis of $\{Mn(\eta^5-C_5H_7)(CO)_3\}$ in hexane under carbon monoxide (1 atm) gives spectroscopic evidence of $\{Mn(\eta^3-C_5H_7)(CO)_4\}$. The preparation of η^3-pentadienyl complexes $\{MoX(CO)_2(\eta^3-C_5H_6Me)(MeCN)_2\}$ $\{X=Cl,Br\}$ by oxidative addition of chloro- and bromo- 2,4-hexadiene to intermediate compounds such as $\{Mo(CO)_3(CH_3CN)_3\}$ are also reported.

^{1}H-NMR shows solvent dependent ionisation of these complexes in solution with liberation and free acetonitrile. The bromo-complex ionises to a less extent than the chloro-complex.

The bidentate ligand 2,2'-bipyridine replaces the two acetonitrile molecules to yield the substitution product $\{MoBr(CO)_2(\eta^3-C_5H_6Me)Bipy\}.\frac{1}{2}MeCN$.

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CHAPTER ONE

THE PENTADIENYL LIGAND IN ORGANOMETALLIC CHEMISTRY

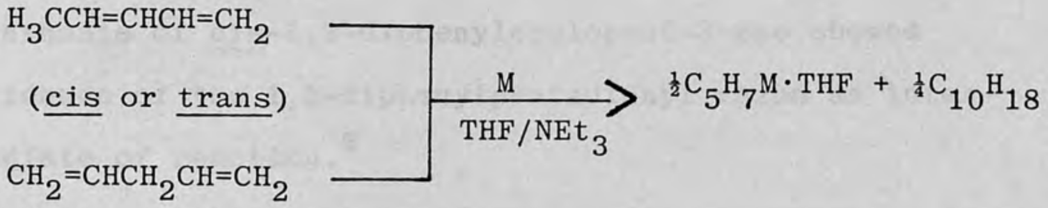
CHAPTER ONE

THE PENTADIENYL LIGAND IN ORGANOMETALLIC CHEMISTRY.

In this chapter we review the syntheses, structural aspects and essential chemical properties of pentadienyl complexes. Firstly, the pentadienyl ligand is discussed, basically as an anionic species formed by the action of alkali metals. Secondly, complexes formed between transition metals and the dienyl ligand are examined, and to some extent compared with the analogous cyclopentadienyl complexes.

1.1. Pentadienyl anions and cations.

Pentadienyl anions have been postulated as intermediates in different organic reactions such as the isomerisation of 1,3- and 1,4-dienes[1] and in nucleophilic substitution of aromatics.[2] Direct metallation of dienes with alkali metals (Li,Na,Rb,Cs) is the commonest procedure used to obtain the pentadienyl anions. A series of acyclic and cyclic dienyl anions have been reported by Nakamura[3] from both conjugated and non-conjugated dienes, who found that all the pentadiene isomers: cis-1,3-pentadiene, trans-1,3-pentadiene and 1,4-pentadiene, gave the identical pentadienyl anion $\{C_5H_7M\cdot THF\}$ and the reduced pentadiene dimers $(C_{10}H_{18})$, in a (2:1) molar ratio, irrespective of the alkali metal used (M=Na,K,Rb or Cs). (SCHEME 1).



SCHEME 1

The advantage of using THF is due to its good solvating properties, through complex formation between the ether and the metal, as mentioned by Bates in the preparation of pentadienyllithiums.[4] The addition of triethylamine inhibits polymerisation of the conjugated dienes in these reactions. The formation of polymer, however, competed with the preparation of lithium derivative using 1,3-pentadiene even in the presence of excess of aliphatic tertiary amines.[3]

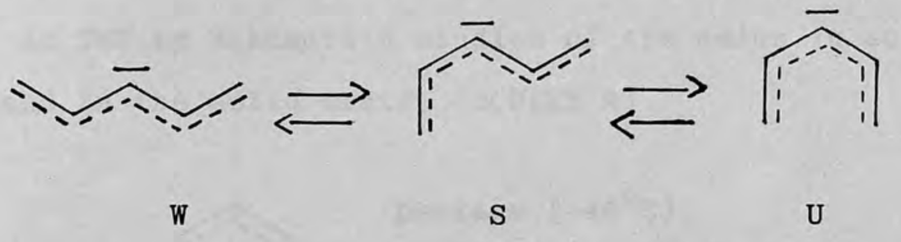
The pentadienyl anions ($C_5H_7M\cdot THF$) were isolated as yellow needles; their solubility in THF decreased in the order Li>Na>K>Rb>Cs with increasing ionic character of the metal-carbon bond.

In a similar manner, hexadienyl anions have been prepared from the metallation of the four isomeric hexadienes (trans, trans- or trans,cis -2,4-hexadiene, trans-1,4-hexadiene, 1,3-hexadiene and 1,5-hexadiene) with potassium giving an orange powder in high yield. The conjugated dienes were more reactive than the non-conjugated ones.

The substituted 1,5-diphenylpentadienyl anion has also been prepared, without isolation, by metallation with lithium and a mixture of isomeric substituted dienes.[5] Synthesis of <u>cis</u>-1,2-diphenylcyclopent-3-ene showed evidence of the 1,5-diphenylpentadienyl anion as intermediate of reaction.[6]

The unstable cyclohexadienyl anion was prepared from the respective cyclohexadiene with potassium amide in liquid ammonia below -20°C; this species decomposed thermally at 0°C giving benzene and cyclohexene.[3]

Pentadienyl anions could exist in three planar conformations, W, sickle (S) and U. An ideal geometry for the pentadienyl ligand seems to be the strain-free

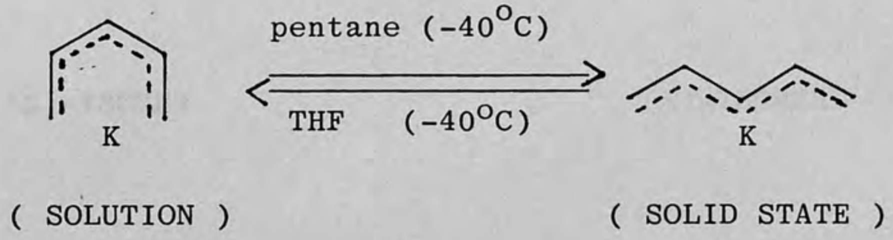


W conformer, which can keep the coplanarity of the carbon backbone in order to spread out, over the entire dienyl system, the electron excess imposed on the organic group. Comparatively, the S conformer is disfavoured to some extent (~ 16 kJ mol^{-1}) and same is observed with the U conformer due to a severe crowding,[7] eclipsing effects and an estimated steric repulsion of the order ≳40 kJ mol^{-1}.

Direct experimental evidence of the anions with different alkali-metals, by ^{1}H-and ^{13}C-NMR spectroscopy and preparation of derivatives from some of these species, has been interpreted to indicate that pentadienyl-[4], hexadienyl-[8] and 3-methylpentadienyllithium[8] in THF, as well as pentadienyl- and hexadienylpotassium in liquid ammonia[8] have preferentially a W-configuration. In contrast, 2-methylpentadienylpotassium and 2,4-dimethylpentadienyllithium or potassium in THF, show a strong preference for the U-shaped structure.[7]

Earlier theoretical calculations on the geometry of open chain pentadienyl anions suggested that the U conformer was favoured over the W or S conformers,[9] but recent studies have indicated that the W-shaped structure is the most stable.[10]

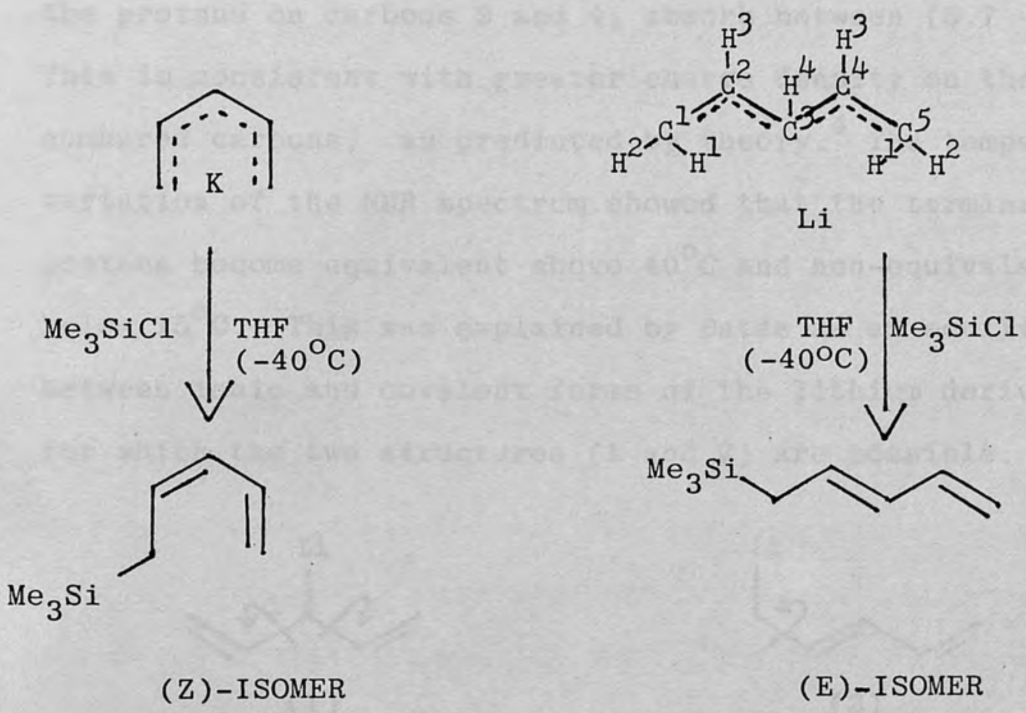
A facile method of control of the preferred geometry has been observed for the pentadienylpotassium complex in THF by Nakamura's studies of the anion in solution and in the solid state. (SCHEME 2).



SCHEME 2

The solid product is obtained quantitatively by addition of an excess of pentane (10 mol per mol of THF) to the THF solution at -40°C. The weakly solvated molecule of solvent (Scheme 1) was easily removed by heating at 80-100°C under vacuum conditions.[3] Treatment with chlorotrimethylsilane at -40°C of the respective anions with U and W conformations, contrast sharply giving regioselectively the (Z)- and (E)- isomers of

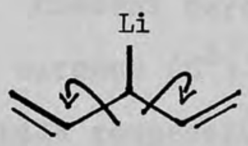
2,4-pentadienyltrimethylsilane respectively.[11] Identical (E)- isomer is obtained from trimethylsilylation of the W-pentadienyllithium.[11,12] (SCHEME 3.).



SCHEME 3

These observations show the influence of the metal and the medium on the conformation of the pentadienyl anions, and according to Nakamura, this fact may be rationalised by regarding the pentadienylpotassium as composed of contact ion pairs, and the pentadienyllithium involving strongly solvated ion pairs.[7,11] The last is supported by unsuccessful attempts to remove the solvent coordinated to the lithium even at 120°C under vacuum.[3]

^{1}H-NMR studies of the pentadienyllithium indicate that the charge is distributed non-uniformly along the chain according to the chemical shifts.[4] (Assignment according to Scheme 3). The protons attached to terminal and central carbons resonate in the range (2.1 - 4.3δ), whereas the protons on carbons 2 and 4, absorb between (5.7 - 6.2δ). This is consistent with greater charge density on the odd-numbered carbons, as predicted by theory.[4] The temperature variation of the NMR spectrum showed that the terminal protons become equivalent above 40°C and non-equivalent below 15°C. This was explained by Bates as an equilibrium between ionic and covalent forms of the lithium derivative, for which the two structures (1 and 2) are possible.



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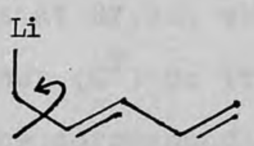

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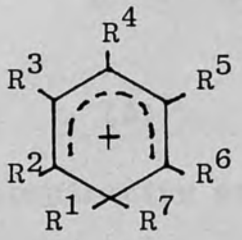
Rotation about the single bond leads to interchange of the positions of the terminal protons. The spectral data show that rotation occurs more readily about inner than outer carbon-carbon bonds. Coupling constants reported for the non-equivalent terminal methylene protons and the proton attached to carbon 2 are 9, 15.3 and 2.7 Hz for <u>cis</u>-, <u>trans</u>- and geminal couplings respectively.[4]

According to the large (H^2,H^3) coupling constants for the <u>cis</u>-oriented hydrogen atom at (C^1) and its vicinal neighbour {$J(H^2,H^3)=9Hz$}, Schlosser suggests that hydrogens should be in opposite directions with respect to the carbon atom plane, and this fact gives the clue for a plausible explanation of the pleated structure of the pentadienyl alkali-metal structures.[13] The metal atom essentially establishes a binding interaction with the electron-rich odd number sites of the pentadienyl ligand, along with a compensating effect by polarization of the even numbered sites in the opposite sense. Considering that, an electrostatic repulsion of the CH bonds it is expected to move towards the electron deficient side and the planar ideal structure is deformed to give a pleated structure.

The ^{13}C-NMR spectrum also confirmed the strain-free W-shaped structure as the major conformer of pentadienyllithium.[8] Central carbon (C^3) resonates at 87.3δ, whereas terminal carbons (C^1) and their neighbour (C^2) do it at 66δ and 144δ respectively (in THF). The corresponding (C,H) coupling constants of the anion are: $J(CH^1)$=146.5Hz, $J(CH^2)$=153.8Hz, $J(CH^3)$=134.2Hz and $J(CH^4)$=141.6Hz.[13]

Contrastingly with the pentadienyllithium and related systems with a W-shaped structure, studies on 2,4-dimethylpentadienyl-lithium and potassium suggest that introduction of two methyl groups at positions 2 and 4 would hardly affect the free energy of the U conformer, being only slightly disfavoured with respect to the S and W conformers.[7] A strong steric strain for the W conformer was observed, being destabilized by ~33 kJ mol^{-1}. Finally, a modest steric strain is expected for the S conformer. Then, the small energy difference between the conformers permits both the lithium and potassium derivatives to adopt the U structure.

Systems containing polyenylic cations have played an important part in the development of organic chemistry. They are found as intermediates in electrophilic additions to unsaturated organic compounds.[14a] Spectroscopic evidence of such cations, as well as isolation of some stable species, as the cyclic (3) and acyclic (4) tetrafluoroborate salts, have been reported.



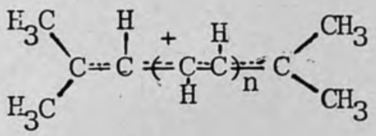
$\{\mathrm{Ph(CH} \overset{---}{-} \mathrm{CH)}_n \overset{---}{-} \mathrm{CHPh}\}^+$

(3) (4)

The cyclic pentadienyl systems contained in a six-membered ring are obtained by protonation of aromatic compounds or by their reaction with alkyl cations. A particularly stable member of this class, the heptamethylcyclohexadienyl cation[15a] (3, R=Me), and also other substituted cations, such as $\{R^1=R^3=R^5=Me,\ R^2=R^4=R^6=H,\ R^7=Et\}$ are formed on treatment of 1,3,5-trimethylbenzene with EtF in presence of BF_3 at -80°C.[14b]

The acyclic species (4, n=4), and also (n=0-3) have been prepared showing that their stability increases with the chain length. Whereas the tetrafluoroborate salt with n=0 is stable only below -40°C, that of the longest polyenylic cation is stable at room temperature.[15a]

Many linear pentadienyl cations have been observed from studies on cyclization reactions, in which the rate of cyclization seems to be controlled to a large extent by steric factors.[16] Among other substituted acyclic dienyl intermediates, Sorensen reported the cations (5, n=0,1) and (6), which are quite stable in strongly acid media.[16,17]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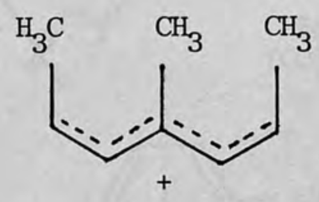
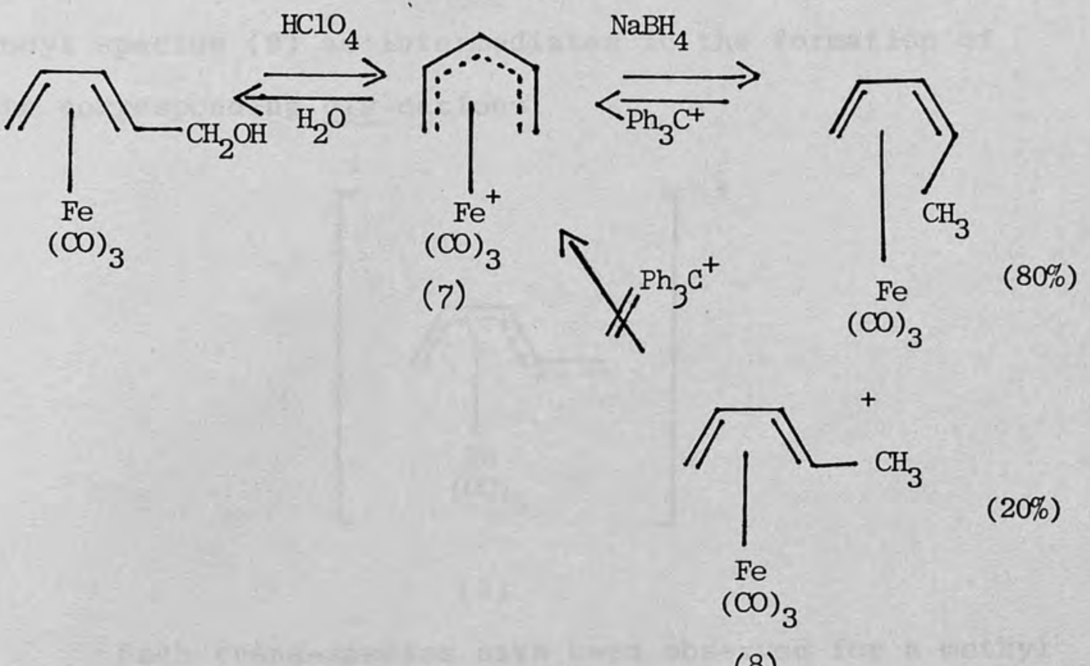

(6)

A comparative study between allyl and pentadienyl cations showed that they are frequently unstable with respect to possible secondary reaction products and pentadienyl species are thermodynamically more stable than those of the allyl intermediates with respect to the precursors.[15b]

A pentadienyl radical has been generated by photolysis of a mixture of 1,4-pentadiene and di-tert-butyl peroxide in hydrocarbon solvents at room temperature and identified by electron paramagnetic resonance spectroscopy.[18]

1.2. Pentadienyl-transition metal complexes.

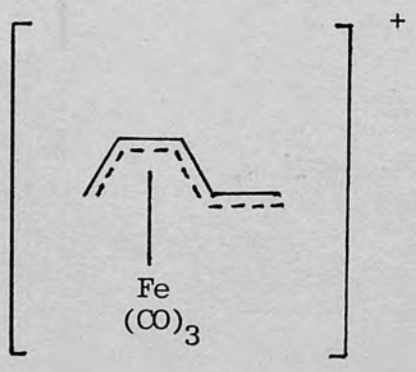
The syntheses of salts of η^5-pentadienylirontricarbonyl cations are the first examples in the chemistry of the acyclic and pentahapto-coordinated ligands. These cationic compounds can be prepared by the protonation of conjugated dien-ols with strong acids such as $HClO_4$, HBF_4 and HPF_6, or by hydride abstraction from a coordinated conjugated diene[19,20] (SCHEME 4).



SCHEME 4

As for the large majority of η^5-pentadienyl complexes known, this cation (7) has a cis-ligand configuration, which was confirmed by the characteristic four widely separated and symmetrical signals in the ^{1}H-NMR spectrum.[20] Attempts to prepare a trans-η^5-pentadienyliron tricarbonyl cation from trans -1,3-$C_5H_8Fe(CO)_3$ (8) by hydride ion abstraction using triphenylmethyl tetrafluoroborate were unsuccessful.[19,20] A similar extraction of a hydride ion is a standard method in the synthesis of the corresponding (η^5-cyclohexadienyl)-[21] and (η^5-cycloheptadienyl)-[22]tricarbonyliron salts, as is discussed later.

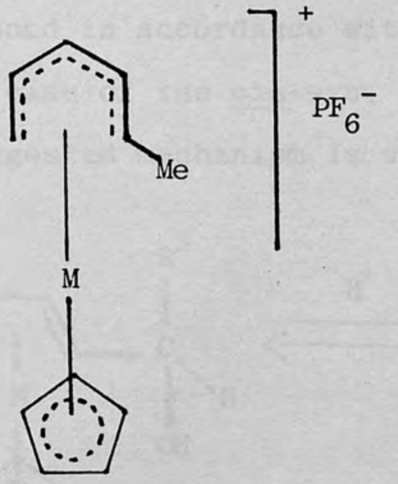
These cationic η^5-pentadienyl complexes have been widely studied, including reactions with nucleophiles,[23] proton abstraction,[24] as well as kinetic studies[25] and spectroscopic characterisations.[26] These two last support also the evidence of the trans-η^5-pentadienyliron tricarbonyl species (9) as intermediates in the formation of the corresponding cis-cations.



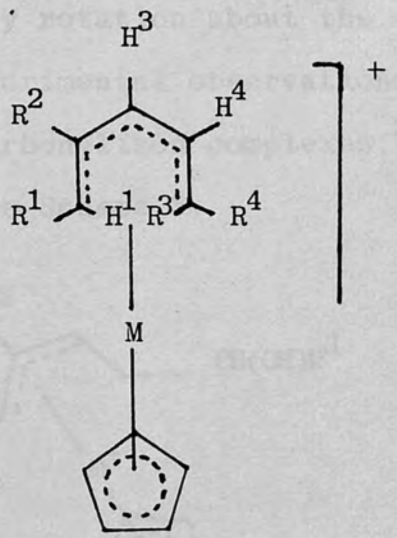
(9)

Such trans-species have been observed for a methyl substituted pentadienyl cation, only at low temperatures by direct NMR studies.[26a]

Powell has carried out studies on pentadienyl complexes with rhodium and iridium metals. Protonation of η^5-cyclopentadienyl-η^4-hexa-2,4-dien-1-ol complexes gave the isolated hexafluorophosphate salts of the cations $\{M(\eta^5\text{-}C_5H_5)(\eta^5\text{-syn-1-}MeC_5H_6)\}^+$ (M=Rh, Ir)[27] (10).



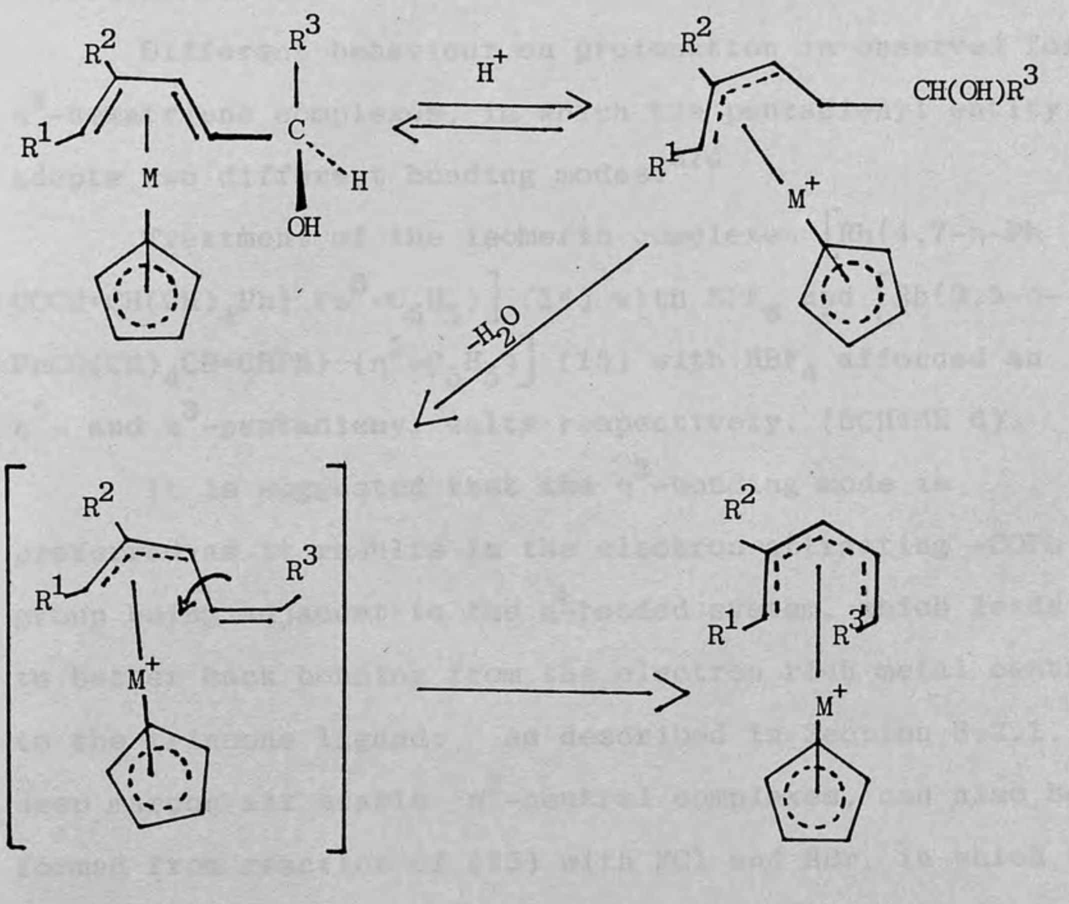
(10)



(11)

Comparison between these complexes and the methylpentadienyltricarbonyliron cation showed that (10) are less susceptible to addition to nucleophiles, whereas the tricarbonyl iron salt is easily hydrolysed.[20b] Positions attacked by nucleophile in the pentadienyl group are also contrasting between them {(10) (central carbon), iron complex (terminal carbons)} and certain cyclic dienyl cations (carbon in 2-position).[27b]

Many substituted pentadienyl rhodium and iridium cations have been similarly prepared $\{M(\eta^5\text{-}R^1CHCR^2CHCHCR^3R^4)\text{-}(\eta^5\text{-}C_5H_5)\}^+$ ($R^1=R^3=Ph$, $R^2=R^4=H$, M=Rh or Ir ; $R^1=Ph$, $R^2=R^3=H$, $R^4=Bu^t$, M=Rh or Ir ; $R^1=R^3=Ph$, $R^2=Me$, M=Rh or Ir ; among others) (11), where the aryl group at R^3 adopts an unsymmetrical structure which suggests a cis-syn, anti configuration.[27c] This structure could be expected from an η^3-pentadienyl intermediate (12) by rotation about the C^3-C^4 bond in accordance with the experimental observations in the case of the cis-syn, syn-tricarbonyliron complexes.[26a] The suggested mechanism is seen in the Scheme 5.



(12) (13)

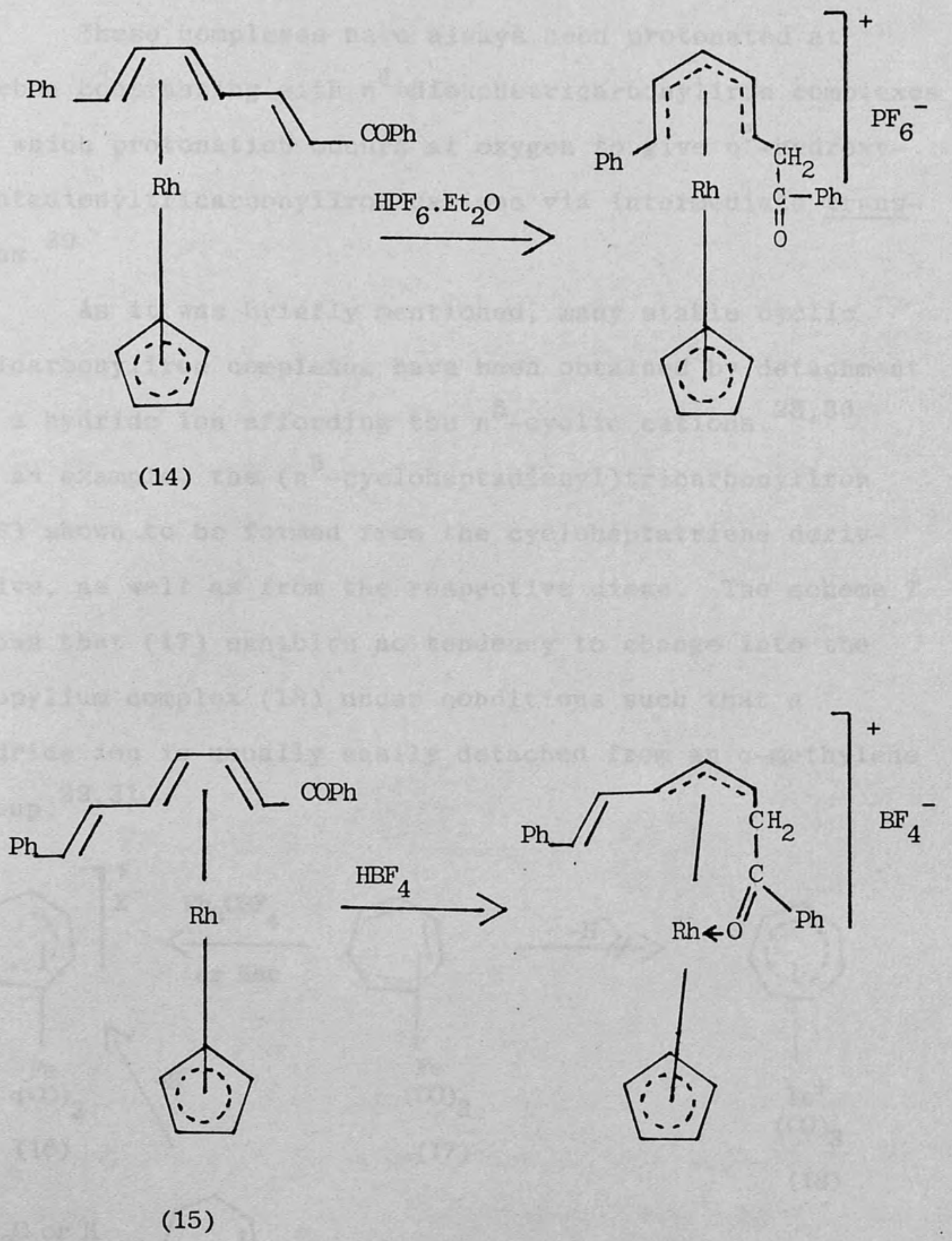
SCHEME 5.

At -30°C spectroscopic evidence of the allylic rhodium protonated product (R^1=R^3=Ph,R^2=H) is observed and on standing at room temperature, water is eliminated, yielding the substituted pentadienyl cation (13). In general, analogous protonated species for iridium complexes did not persist long enough to characterise by ^{1}H-NMR. The intermediate allylic protonated species in the preparation of (11) when R^1=Ph, R^2=R^3=H, R^4=Bu^t and M=Rh is sufficiently stable and it was isolated as the hexafluorophosphate salt.[27c] Again, faster reactions on iridium complexes prevented isolation of the respective allylic cation intermediate.

Different behaviour on protonation is observed for η^4-hexatriene complexes, in which the pentadienyl entity adopts two different bonding modes.[27d]

Treatment of the isomeric complexes $[Rh\{4,7\text{-}\eta\text{-}PhCOCH{=}CH(CH)_4Ph\}(\eta^5\text{-}C_5H_5)]$ (14) with HPF_6 and $[Rh\{2,5\text{-}\eta\text{-}PhCO(CH)_4CH{=}CHPh\}(\eta^5\text{-}C_5H_5)]$ (15) with HBF_4 afforded an η^5- and η^3-pentadienyl salts respectively. (SCHEME 6).

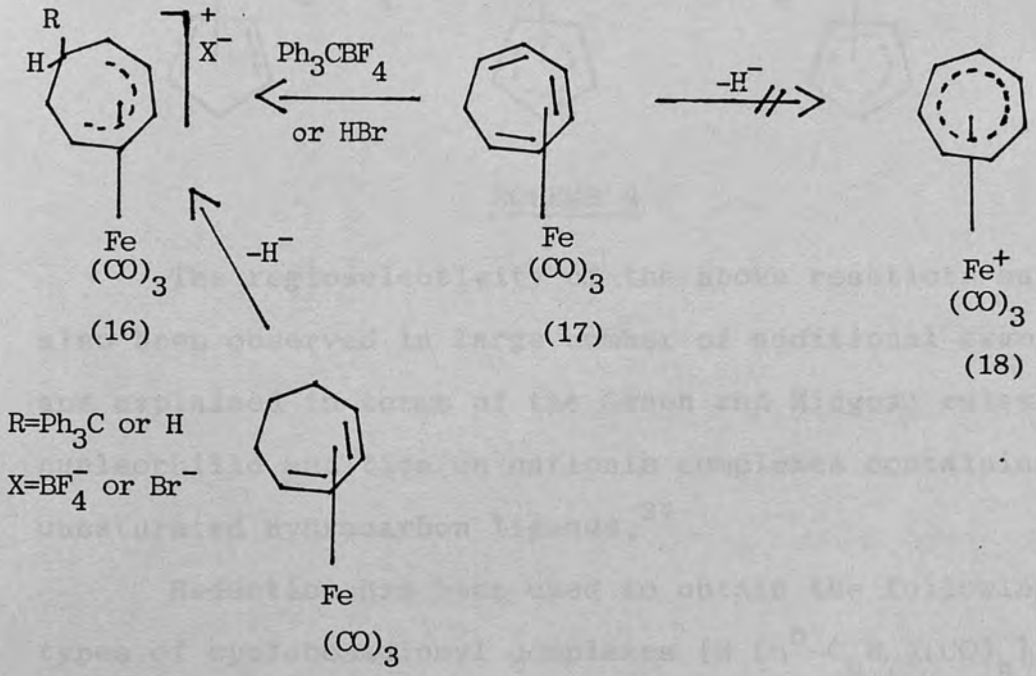
It is suggested that the η^3-bonding mode is preferred as it results in the electron attracting -COPh group being adjacent to the η^4-bonded system, which leads to better back bonding from the electron rich metal centre to the trienone ligand. As described in Section 3.2.1. deep maroon air stable η^3-neutral complexes, can also be formed from reaction of (15) with HCl and HBr, in which the halogen is bonded to the metal and there is no coordination of the acyl oxygen to rhodium atom.


Ph
COPh
Rh
$HPF_6.Et_2O$
Ph
Rh
CH_2
C—Ph
O
+
PF_6^-
(14)
COPh
Ph
Rh
HBF_4
Ph
CH_2
C
Rh←O
Ph
+
BF_4^-
(15)

SCHEME 6

These complexes have always been protonated at carbon contrasting with η^4-dienonetricarbonyliron complexes in which protonation occurs at oxygen to give η^5-hydroxypentadienyltricarbonyliron cations via intermediate <u>trans</u>-ions.[29]

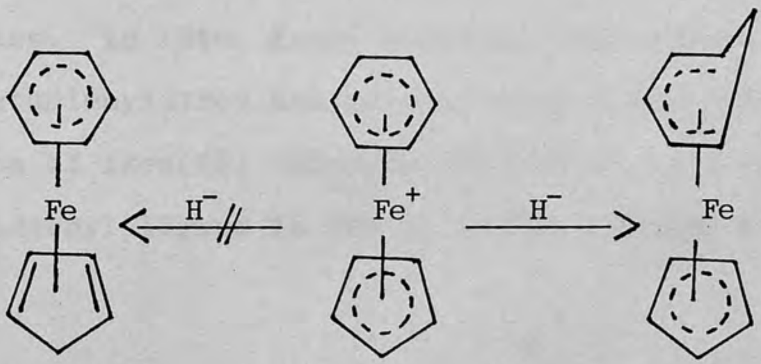
As it was briefly mentioned, many stable cyclic tricarbonyliron complexes have been obtained by detachment of a hydride ion affording the η^5-cyclic cations.[28,30] As an example, the (η^5-cycloheptadienyl)tricarbonyliron (16) shown to be formed from the cycloheptatriene derivative, as well as from the respective diene. The scheme 7 shows that (17) exhibits no tendency to change into the tropylium complex (18) under conditions such that a hydride ion is usually easily detached from an α-methylene group.[22,31]



SCHEME 7.

The stability of these cyclic pentadienyl complexes has been explained in terms of the diminution in electrophilicity under the influence of the tricarbonyl group.[32] Many studies on the tricarbonylcyclohexadienyliron complex have been reported by Pearson.[28]

Studies on the reduction of arene iron cyclopentadienyl salts by hydride reductants[33] and also the addition of other nucleophilic reagents to them have been widely reported.[33d] Pauson and coworkers showed that the six-membered ligand changes, giving only one product (SCHEME 8)



SCHEME 8

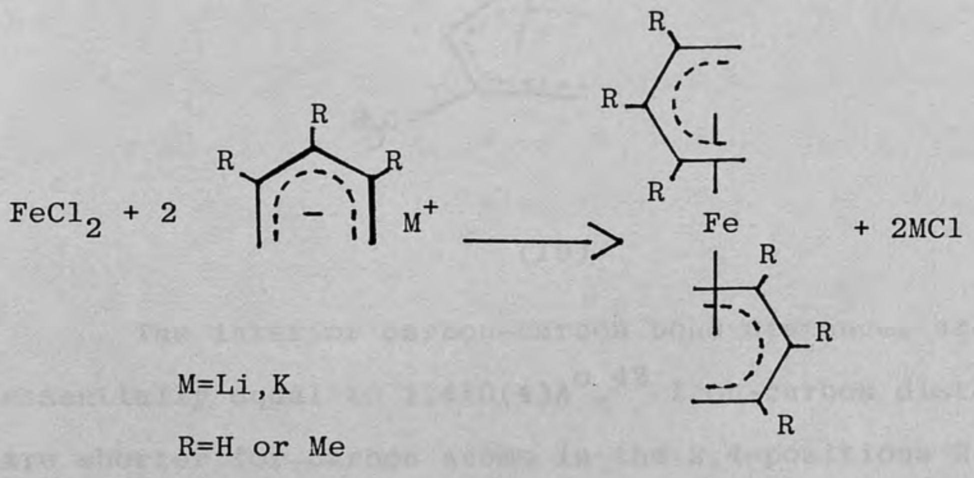
The regioselectivity of the above reactions has also been observed in large number of additional examples and explained in terms of the Green and Mingos rules for nucleophilic addition on cationic complexes containing unsaturated hydrocarbon ligands.[34]

Reduction has been used to obtain the following types of cyclohexadienyl complexes $\{M(\eta^5\text{-}C_6H_7)(CO)_n\}$ $(M=V, n=4)$[35], $(M=Mn, n=3)$[36,37]; $\{M(\eta^5\text{-}C_6H_7)(\eta^6\text{-}C_6H_6)\}(M=Re)$,[21b,38] $(M=Tc)$[39]; $\{Ru(\eta^5\text{-}C_6H_7)_2\}$[21b]; $[Co(\eta^5\text{-}C_6H_7)(\eta^5\text{-}C_5H_5)]PF_6$.[40]

Some of the cyclic polyenyls with an η^5-geometry for manganese and rhenium are dicussed in Section 2.2.1.

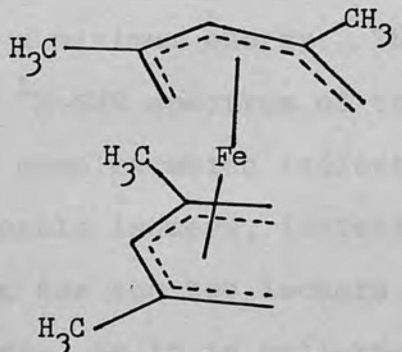
Several substituted biscyclohexadienyliron complexes were reported to be formed by reduction of the respective dibenzeneiron cation with two moles of reductant. These complexes have temperature-dependent ^{1}H-NMR spectra and the plausible structure suggested by these studies was also confirmed by X-ray crystallography.[41]

Direct reaction between alkali- metal pentadienyl derivatives and salts of transition metals has recently been used as a method of general application in the syntheses of sandwich and nonsandwich acyclic pentadienyl complexes. In 1980, Ernst reported the isolation of the bis(pentadienyl)iron and several methyl derivatives, by reaction of iron(II) chloride with an anionic source of a pentadienyl ligand in THF at -78°C. (SCHEME 9).



SCHEME 9.

The parent complex $\{Fe(\eta^5-C_5H_7)_2\}$ readily decomposes to dipentadienyl and ferromagnetic iron byproducts, and thus, complete characterisation has not yet been achieved. This feature contrasts with stable isolated and fully characterised methylated complexes, it being clear that the methyl substituents in the pentadienyl ligand impart a great deal of stability to these complexes.[42] The structure of bis(2,4-dimethylpentadienyl)iron (19) determined by X-ray crystallography shows that this open sandwich complex in the solid state is oriented in a gauche-eclipsed conformation with methyl groups interlocked in the nearly planar pentadienyl ligand.



(19)

The interior carbon-carbon bond distances are essentially equal to 1.410(4)A°.[42] Iron-carbon distances are shorter for carbon atoms in the 2,4-positions 2.071(3)A° than carbons in odd-positions, 2.084(3)A° and {2.092(5)A°, 2.135(4)A°} for central and terminal carbons, respectively. These values have been compared with the slightly shorter iron-carbon distance of 2.033(3)A° found in the cyclic counterpart ferrocene.[43] The distances between the iron atom and the mass centre of the bonded ligand-fragment is shorter in the acyclic complex (1.50A^{o}) than in ferrocene (1.66A^{o}) which is attributed by Ernst to a geometric origin.

The electronic structure of the "open ferrocene" and its methyl derivatives has been investigated by means of semiempirical molecular orbital calculations, as well as by the HeI photoelectron spectra of the bis(2,4-pentadienyl-, 2,3-dimethyl- and 3-methyl-pentadienyl) iron complexes.[44]

A comparative study with ferrocene shows that a significant rotational barrier in the acyclic complexes is predicted, with the _trans_ or eclipsed conformation corresponding to a minimum energy. The prediction was also supported by the ^{1}H-NMR spectrum of the bis(2,3-dimethyl pentadienyl)iron complex which indicates the presence of two nonsuperimposable isomers, instead of the expected identical spectra for the two isomers in case of a low rotational barrier. As it is well-known, energy difference between the eclipsed and staggered forms in ferrocene is less than 4 kJ mol^{-1}.

The electronic structure of these new open ferrocenes indicates that the overall charge distribution in these systems is comparable to the ferrocene case. However, differences are predicted for central carbons in the pentadienyl ligands. Finally, significant differences are also predicted with respect to the ionisation pattern of the iron complexes; a very large degree of metal–ligand coupling is calculated for the open ferrocenes with a bonding interaction of partial δ character, which appears to be the origin of the presence of an eclipsed conformation for these open chain complexes, which is not observed in ferrocene.

In 1982, Ernst reported studies on pentadienyl complexes of other transition metals as vanadium,[45] chromium,[45] titanium,[46] manganese[45] and neodymium,[47] which are discussed below.

The deep green crystalline complexes $\{M(\eta^5\text{-}2,4\text{-}Me_2C_5H_5)_2\}$ (M=V,Cr) have been synthesised by the reactions of VCl_2 or $CrCl_2$ with 2 mol of potassium salt of the 2,4-dimethylpentadienyl anion in THF at $-78^{\circ}C$. Similar products are claimed to be isolated for the 3-methylpentadienyl ligand.

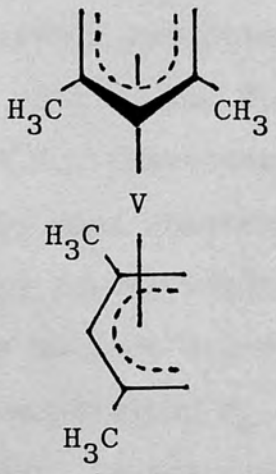
The chromium complex $\{Cr(\eta^5\text{-}2,4\text{-}Me_2C_5H_5)_2\}$ seems to resemble the analogous bis(pentadienyl)chromium[48] and chromocene,[49] according to the presence of two unpaired electrons in each system, and the similar cell volume increase passing from Fe to Cr in $\{M(\eta^5\text{-}2,4\text{-}Me_2C_5H_5)_2\}$ (M=Fe,Cr) (7%) and in the corresponding metallocenes (6.5%).[45] Then, a tentative formulation as open sandwich compounds is proposed for this and other bis(pentadienyl)-chromium compounds.

The unsubstituted complex $\{Cr(C_5H_7)_2\}$ was the first example (1968) of a pentadienyl complex prepared by reaction of a pentadienyl anion with a metal salt:[48]

$$CrCl_2 + 2\ Na\ C_5H_7 \xrightarrow[-30^oC]{THF} Cr(C_5H_7)_2 + 2\ NaCl$$

The product of this reaction was shown to exist as a monomer, thermally stable (m.p.122^oC) and with two unpaired electrons. Its chemical behaviour was compared with the triallyl chromium complex due to extreme sensitivity to air, easy elimination of pentadiene on appropriate treatment with protic solvents and slow reaction with hydrogen giving n-pentane. This bis(pentadienyl)chromium complex in spite of lacking two electrons to reach the stable configuration, does not react at room temperature with the donor ligand PPh_3. It reacts slowly in a hydrocarbon solution with carbon monoxide under pressure and at room temperature, affording a complex assigned as $\{Cr(C_5H_7)_2(CO)\}_2$. No definite structure was established for either complex.

Magnetic susceptibility measurements on the vanadium complex $\{V(\eta^5\text{-}2,4\text{-}Me_2C_5H_5)_2\}$ indicate the presence of only one unpaired electron which contrasts with vanadocene with three unpaired electrons.[45] An X-ray diffraction study claimed an open sandwich structure, which adopts a staggered conformation (20) contrasting with the eclipsed conformation for the bis(pentadienyl)iron systems.



(20)

Ernst claimed that these staggered conformation should be more favourable for metals having low d electron configurations, according to the expected decrease in the relative δ bonding as explained above.[46] A monocarbonyl derivative $\{V(\eta^5\text{-}2,4\text{-}Me_2C_5H_5)_2CO\}$ has also been isolated (ν (CO) 1942 cm^{-1}).[46]

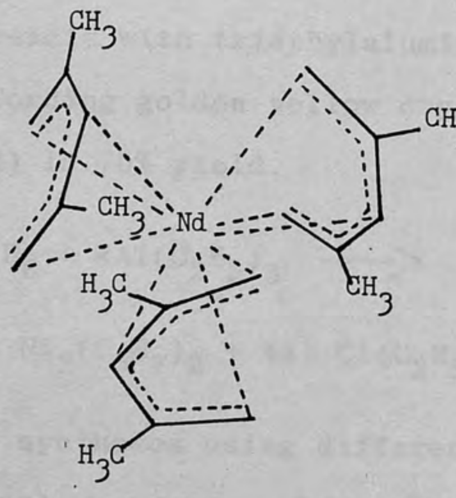
The manganese derivative $\{Mn_3(3\text{-}MeC_5H_6)_4\}$, as described in Section 2.2.1 shows a new facet of behaviour for pentadienyl ligands bonded to transition metals.[45] An ionic constitution is claimed and speculative mechanisms involving initial formation of $\{Mn(3\text{-}MeC_5H_6)_2\}$ are suggested.

The recent isolated "open titanocene" $\{Ti(\eta^5\text{-}2,4\text{-}Me_2C_5H_5)_2\}$ seems to have an interesting structure, the study of which might help in the understanding of the often confusing chemistry of titanocene complexes.[50] It was synthesised by reaction of titanium dichloride, prepared in situ by the magnesium reduction of titanium tetrachloride, with the potassium salt of the 2,4-dimethylpentadienyl anion in THF at -78°C. Characterisation of the pyrophoric deep-green liquid by mass spectrum, infrared, ^{1}H- and ^{13}C-NMR spectroscopy (seven resonances are observed in each spectrum. See Section 2.2.2.3), as well as verification of the absence of coordinated N_2, suggest that the monomeric species is a divalent, 14-electron open sandwich compound. This is contrasting sharply with the feature observed in the corresponding titanocene which has never actually been isolated as a discrete complex.[50] It is suggested that the large size of the pentadienyl ligand is helping in the stabilization of the electron-deficient complex. This argument is also supported by the rapid reaction of $\{Ti(\eta^5\text{-}2,4\text{-}Me_2C_5H_5)_2\}$ in presence of carbon monoxide giving the yellow solid $\{Ti(CO)(\eta^5\text{-}2,4\text{-}Me_2C_5H_5)_2\}$ which is adopting only a 16-electron configuration. The monocarbonyl complex is much less air sensitive, but is thermally less robust. The structure of this adduct differs markedly from the "open titanocene" complex according to ^{1}H- and ^{13}C-NMR spectra (four characteristic resonances. See Section 2.2.2.3). Ernst suggests a near cis-eclipsed conformation, in which the central positions of the ligands are bent toward one another and the CO ligand is bound near the open portions of the pentadienyl ligand.[46]

Coordination of three acyclic pentadienyl ligands to a lanthanide has been observed with neodymium, in which the bonding is essentially ionic.[47] The reaction of anhydrous neodymium trichloride with 3 equivalents of the potassium salt of the 2,4-dimethylpentadienyl anion leads to the formation of a bright green crystalline product which is highly sensitive to air and water.

$$NdCl_3 + 3\,K\,(2,4\text{-}Me_2C_5H_5) \xrightarrow{THF} \{Nd(\eta^5\text{-}2,4\text{-}Me_2C_5H_5)_3\} + 3KCl$$

The structure of this compound in the solid state confirms the apparent pentahapto mode of bonding for the nearly planar ligands to the trivalent Nd ion. The ligands are found fairly symmetrically located around the metal, with an average distance between the metal and the centre of mass (defined by atoms of terminal carbons) of 2.375(5)A° (see Figure 21).



(21)

The neodymium-carbon bond distances for odd-carbon positions are shorter {average of the three pentadienyl groups: Nd-C(3) 2.749(10)A^{o}; Nd-C(1,5) 2.801(9)A^{o}} than that of even-numbered positions {Nd-C(2,4)2.855(8)A^{o}}.[47] A flexible nature of the pentadienyl ligands can be established if we compare this data with the opposite feature observed in the case of bis(pentadienyl)iron, as described above.

The relative ordering of the metal-carbon distances observed supports the presence of a high degree of ionic character in the metal-ligand bond, being in agreement with the localised anionic charge in the odd-carbon positions reported by Bates[4] and described in Section 1.1.

The only example in which an isolated pentadienyl complex is not coordinated in a cis-ligand configuration, is the bis(pentadienyl)dinickel.[51a]

A suspension of anhydrous nickel chloride in 1,4-pentadiene reacts with triethylaluminium at room temperature, affording golden yellow crystals of {$Ni_2(C_5H_7)_2$} (22) in 75% yield.

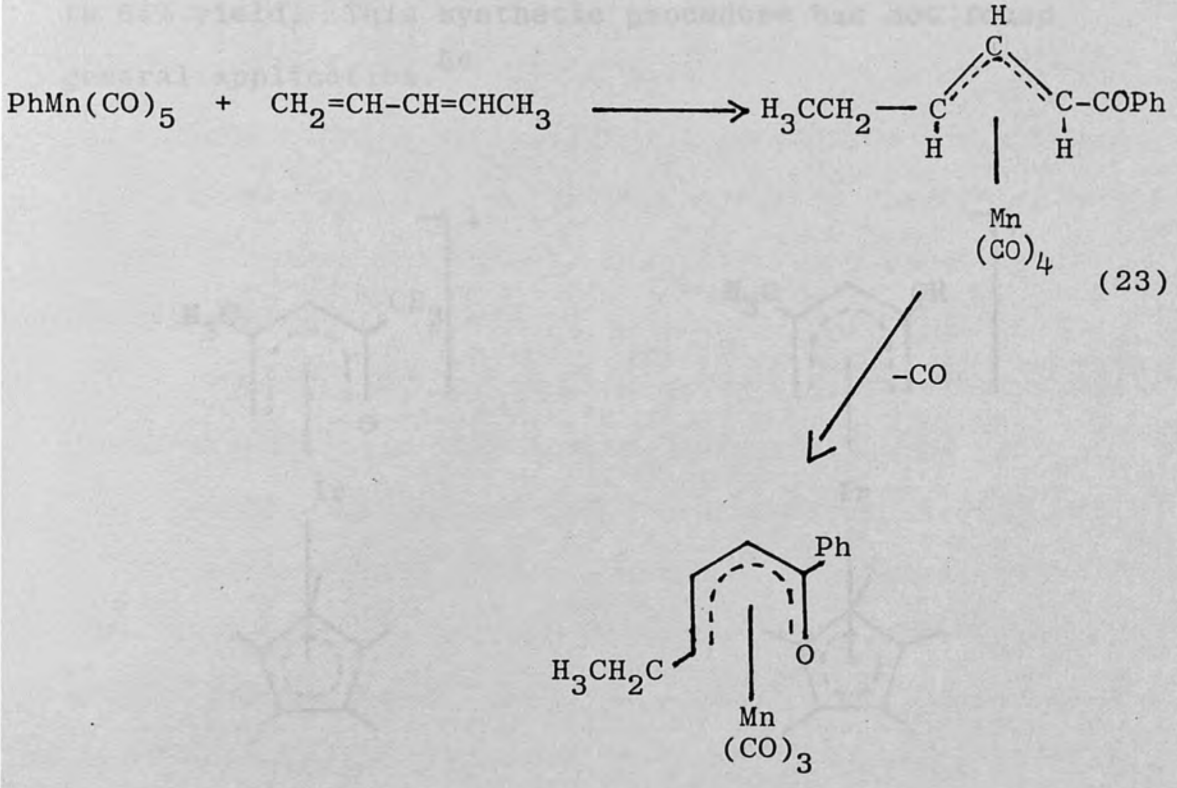
$$2\ NiCl_2 + 5C_5H_8 + 4Al(C_2H_5)_3 \longrightarrow Ni_2(C_5H_7)_2 + 4Al\ Cl(C_2H_5)_2 + 4C_2H_4 + 3C_5H_{10}$$

Attempted syntheses using different solvents (ether, benzene or pentane) were unsuccessful. The pentadienyl ligands are displaced by treatment of the nickel complex with triphenylphosphine.

The crystalline structure showed that the carbon-carbon bond distances between the terminal carbons and their vicinal neighbours are shorter (average 1.40A^{o}), showing more double bond character than the internal carbon-carbon bonds (average 1.44A^{o}).[51b] The distances between metal and carbon are longest at the central carbon (2.24A^{o}) than for the others (average 1.994A^{o}). Metal-metal distance is 2.59A^{o}. According to the data, Krüger suggests that the complex could be formulated as (22). Recent studies on the electronic structure demonstrated that a less efficient metal to ligand charge transfer is present in this complex compared to the bis(η^3-allyl) nickel system.[51c]

(22)

Pentadienyl complexes are formed in several cases by reaction between unsubstituted alkenes and various metal derivatives. Some examples of cyclic η^5-pentadienyl species are given in Section 2.2.1. The same method of preparation is reported for an oxapentadienyl complex (24). Phenyl manganese carbonyl reacts slowly with trans-penta-1,3-diene giving a yellow allylic complex (23) which by decarbonylation at 120^{o}C/0.1 mm Hg afforded the complex η^5-2-phenyl-5-ethyl-1-oxapentadienyltricarbonylmanganese in 73% yield.[52] (SCHEME 10).



(23)

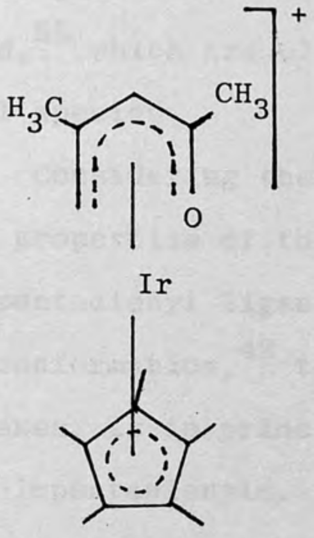
(24)

SCHEME 10.

Similar complexes have also been prepared by other methods. Condensation of two molecules of 1-phenylpropan-2-one with methylpentacarbonylmanganese afforded in 9% yield the complex η^5-2-benzyl-4-methyl-1-oxapentadienyltricarbonylmanganese.[53]

A cationic pentadienyl iridium complex (26) was obtained in 32% yield by heating an acetone solution of $\{Ir(\eta^5\text{-} C_5Me_5)(Me_2CO)_3\}\{PF_6\}_2$. This species (26) is believed to be formed through an oxa-pentadienyl intermediate (25) which was independently prepared from the same starting material and mesityl oxide ($CH_3C(CH_3){=}CHCOCH_3$)

in 64% yield. This synthetic procedure has not found general application.[54]



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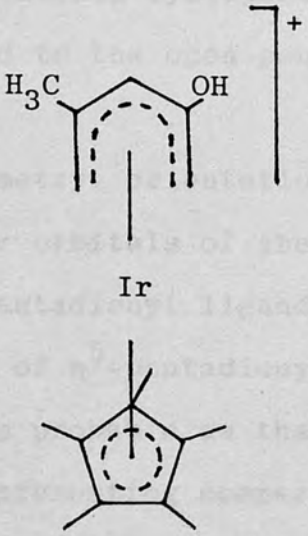


(26)

As far as η^3-pentadienyl complexes are concerned, only a few have been reported and they are included in Section 3.2.1.

Finally, through this work, as described in Chapter 2, it was found that pentadienyltrialkyltin reagents are good intermediates in the syntheses of η^3- and η^5-pentadienyl complexes. The direct reaction between pentadienyl anions and various complexes of Ru, Rh and Mo proved unsuccessful as described in Section 4.1.3. The preparation of η^3- pentadienyl molybdenum complexes by oxidative addition reactions is presented in Section 4.1.2.

It can be concluded from the experimental and theoretical results, that an extensive acyclic pentadienyl chemistry is expected in the organometallic field. Indeed, these considerations seem to be borne out by two of the most common ligands, the acyclic three-membered allyl ligand and the cyclic five-membered cyclopentadienyl ligand,[55] which are closely related to the open pentadienyl species.

Considering the similar symmetry, orientation and nodal properties of the π molecular orbitals of the cyclopentadienyl ligands and the pentadienyl ligand in a U conformation,[42] the existence of η^5-pentadienyl complexes, is in principle quite as probable as that of η^5-cyclopentadienyls. Then, an interesting comparison of the chemical and physical properties of every pair of analogous compounds could emerge, which would be useful in the understanding of their chemistry. Recently, comparative studies have begun through the isolation of many acyclic complexes, as mentioned in this section. A great deal of similarity between cyclic- and acyclic-pentadienyls is shown in Chapters 2 and 3 with some manganese and rhenium complexes. On the other hand, a variety of pentadienyl complexes showing completely new features, such as the stabilization of electron-deficient complexes, flexibility and readily modifiable ligands with different transition metals (Fe,Nd), suggest that this species would exhibit a high chemical versatility. Furthermore, throughout this work interesting new facets for the pentadienyl ligand have been demonstrated. It should be able to coordinate with transition metals in three alternative ways, being a greater advantage compared to the similar η^5-cyclopentadienyl derivatives. Different chemical properties are also observed from the established mechanism of reaction, which shows the participation of the pentadienyl ligand in the substitution reactions of $\{Mn(\eta^5-C_5H_7)(CO)_3\}$ as described in Section 3.2.2.3.

The availability of these new types of ligands allows us to extend the comparative study to the allyl group, expecting higher versatility in the pentadienyl complexes due to delocalisation and chelation effects.[45] In particular, this could be important in catalytic reactions where this acyclic ligand should have the possibility to isomerise to η^3- or η^1- configurations.[42] Apparently, high catalytic activity has already been observed for some of the bis(pentadienyl) complexes, but the results have yet not been published.[45] In this regard, the stability of this ligand could be discussed considering Wilke's study about stability in alkyl, allyl and cyclopentadienyl systems,[56] which is discussed in Section 3.2.1. Ernst suggests that the bis(η^5-pentadienyl)iron complexes should be more stable than the corresponding allyl complexes, according to theoretical calculations and Mössbauer data.[44,45]

The η^3-pentadienyl-ruthenium, manganese and molybdenum complexes isolated during this work can also be compared to some extent with similar allylic complexes, as described in Chapters 2, 3 and 4 respectively.

CHAPTER TWO

η^3- AND η^5-PENTADIENYL COMPLEXES OF MANGANESE, RHENIUM AND RUTHENIUM FROM ORGANOTIN COMPOUNDS

CHAPTER TWO

η^3- AND η^5-PENTADIENYL COMPLEXES OF MANGANESE, RHENIUM AND RUTHENIUM FROM ORGANOTIN COMPOUNDS.

2.1. Organotin reagents as Synthetic Intermediates in Organometallic Chemistry.

2.1.1. Introduction

The organotin compounds have been found useful as synthetic intermediates in chemistry in general and in organometallic chemistry in particular where in most cases the reactions take place under very mild conditions.

Abel[57] has developed a wide variety of these organotin derivatives with oxygen, arsenic, nitrogen,[58] sulphur[59], selenium[60], silicon,[61] among others. They are excellent precursors for novel ligand types in organometallic compounds. In addition to these reactive intermediates, Abel found that unsaturated organic groups on tin can react in a similar manner and behave as useful precursors.[62]

The preparation of vinylic and allylic derivatives of tin was studied a long time ago,[63] and among the methods used previously to prepare them, the reactions of Grignard reagents with tin halides, organotin-lithium or sodium reagents with organic halides and the addition of an organotin hydride to acetylenes or 1,3-dienes are the most important.[64]

Mixed vinyl- or allyl- and alkyl- or aryl-tin compounds are accessible in good yield from the corresponding alkenyl magnesium bromide and the appropriate alkyl- or aryl-tin halide in tetrahydrofuran.

$$R'_n\,Sn\,Y_{4-n} + (4-n)\,\{(olefin)MgX\} \longrightarrow R'_n\,Sn(olefin)_{4-n} + (4-n)MgXY$$

{ where R' = alkyl or aryl group, olefin = vinyl group,[65] Y and X are halogens and n=0,1,2,3 ; if olefin = allyl group[66] n=0,2,3 } .

An alternative route for allylic derivatives of tin using a Wittig reaction was reported by Seyferth.[67] The construction of the allyl substituent from the respective β-trimethylstannyl ethylidene triphenyl phosphorane { $Ph_3P{=}CHCH_2SnMe_3$}, on reaction with aldehydes and ketones, gives the desired allyltin compounds.

$$Ph_3P = CHCH_2SnMe_3 + RCH{=}O \longrightarrow Me_3Sn\,CH_2CH = CHR$$

{where RCH=O is n-heptaldehyde giving 2-nonyltrimethyltin in 69% yield, or if RCH=O is benzaldehyde, then the <u>trans</u>-3-phenylallyltrimethyltin is afforded in 40% yield. }

This reaction has the advantage that open chain compounds with different alkyl or aryl substituents can be synthesised, but only moderate yields are observed.

Recently, the 2,4-pentadienyltrimethylsilane has been obtained independently by Oppolzer[12b] and by Seyferth[12a] by the action of pentadienyllithium[4] on trimethylchlorosilane.

A similar reaction of pentadienyllithium, with trimethyltin chloride, gives the 2,4-pentadienyltrimethyltin, which was also reported by Seyferth[68] in 1981; at this stage we had also independently prepared this derivative and others by a similar method.

This work reports the syntheses of pentadienyl tin reagents which serve as convenient intermediates for the formation of various complexes with η^5- or η^3-pentadienyl ligands.

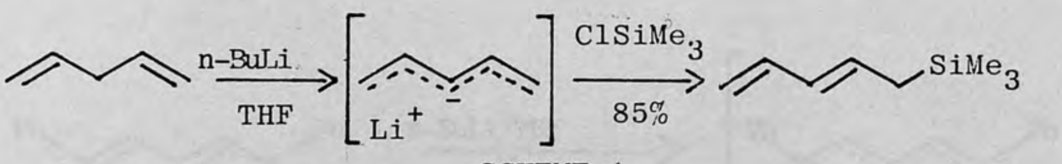
Similar studies using the allylic tin compounds for the preparation of η^3-allyl derivatives of transition metals were reported by Abel and Moorhouse in 1973.[62]

2.1.2. RESULTS AND DISCUSSION.

The compounds $\{R'_3Sn(C_5H_6R)\}$; $\{R=H,Me$; $R'=Me, n\text{-}Bu\}$ and $\{Me_3Sn\ (1,5\text{-}Ph_2C_5H_5)\}$.

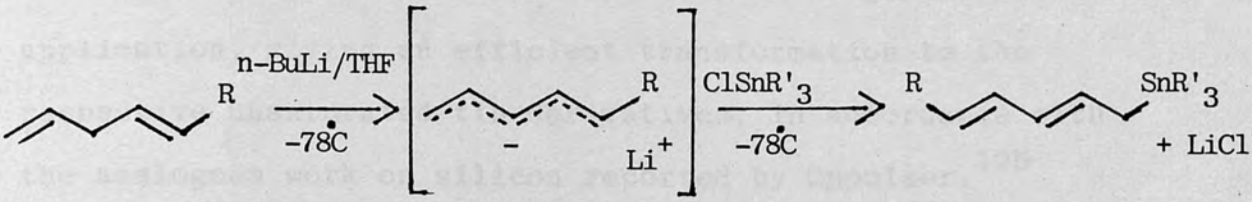
2.1.2.1. Preparation, Properties and Spectrocopic Studies.

Oppolzer, Burford and Marazza[12b] have shown that pentadienyllithium[4] was regioselectively and efficiently transformed to 1-trimethylsilyl-2,4-pentadiene (SCHEME 1).



SCHEME 1

A similar reaction of methyl- (1) and pentadienyllithium (2) prepared from 1,4-hexadiene[8] (3) and 1,4-pentadiene[4] (4) was smoothly and selectively stannylated at carbon (1) by reaction with trialkyltin chloride to furnish the dienes, 2,4-pentadienyltrialkyltin (5 or 6) and 2,4-hexadienyltrialkyltin (7 or 8) in high yield (SCHEME 2).

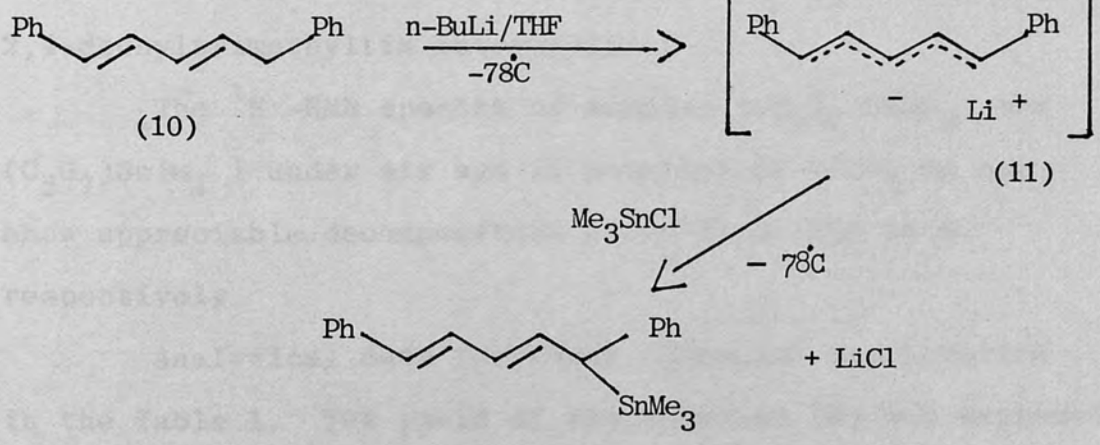


(4 R=H) (2 R=H) (5 R=H.R'=Me)(5 R=H,R'= n-Bu)

(3 R=Me) (1 R=Me) (7 R=R'=Me) (8 R=Me,R'= n-Bu)

SCHEME 2

The 1,5-diphenyl-2,4-pentadienyltrimethyltin (9) derivative was obtained by the corresponding metallation of 1,5-diphenylpenta-1,3-diene (10) to 1,5-diphenylpentadienyllithium[5] (11) and then treated with trimethyl tin chloride (SCHEME 3).



(10) (11) (9)

SCHEME 3

This synthesis method seems to be of general application, giving an efficient transformation to the respective unsaturated tin derivatives, in accordance with the analogous work on silicon reported by Oppolzer.[12b]

The generation of pentadienyl anions from 1,3- and 1,4-dienes in essentially quantitative yield was reported by Bates,[4] who discussed the possible nature and polarity of the carbon-lithium bonds. These bonds are strongly affected by interaction with solvent molecules, and it has been observed that in the absence of THF, there is no reaction. (See Section 1.1.). According to the above findings it is an advantage to use THF as a solvent for the metallation, followed by the addition of the organotin chlorides R'_3SnCl {where R' = Me or n-Bu}.

All the new compounds are colourless or pale yellow liquids slightly air-sensitive, but can be stored for long periods under inert atmosphere. The trimethyltin derivatives proved to be more air-sensitive than the tributyltin analogues, but not as much as the 1,5-diphenylpenta-2,4-dienyltrimethyltin intermediate.

The ^1H -NMR spectra of samples {$(C_5H_7)SnMe_3$} and {$(C_5H_7)SnBu_3$ } under air and in solution of $CDCl_3$ do not show appreciable decomposition after 24 h. and 48 h. respectively.

Analytical data for these compounds are reported in the Table 1. The yield of the compound (9) was extremely low in comparison with the others, because most of the product polymerised under distillation.

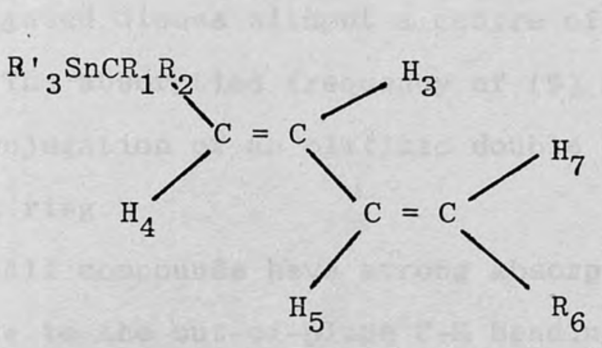
TABLE 1 ANALYTICAL DATA FOR COMPOUNDS OF THE TYPE {$R'_3Sn(C_5H_6R)$} {R=H,Me;R'=Me,n-Bu} AND {Me_3Sn (1,5-$Ph_2C_5H_5$)}.

COMPOUND	R'	ANALYSES (FOUND (CALC.)(%) CARBON	HYDROGEN	YIELD (%)	BOILING POINT (^oC/mm Hg)
CH_2=CHCH=CH$CH_2SnR'_3$	Me	41.57[b]	7.02[b]	82	80-82/28
		(41.61)	(6.98)		
	n-Bu	56.77	9.16	90	102-105/0.1
		(57.17)	(9.60)		
CH_3CH=CHCH=CH$CH_2SnR'_3$	Me	44.17	6.95	85	104-105/28
		(44.14)	(7.40)		
	n-Bu	58.53	10.18	95	120-126/0.2
		(58.25)	(9.78)		
(C_6H_5)CH=CHCH=CHCH(C_6H_5)SnR'_3	Me	62.96	6.62	32[a]	154-166/0.025
		(62.70)	(6.31)		

a) See the text ; b) Reference 68.

These pentadienyl organotin derivatives have been studied by infrared (Table 2) and ^{1}H-NMR spectroscopy with assignments according to (12).

The method of their synthesis gives a mixture of two isomers, the E isomer (12) always being the predominant product.



(12)

TABLE 2 INFRARED DATA[a] FOR COMPOUNDS $\{R'_3Sn(C_5H_6R)\}$ AND $\{Me_3Sn\ (1,5\text{-}Ph_2\text{-}C_5H_5)\}$.

COMPOUND	CHARACTERISTIC CONJUGATED OLEFIN FREQUENCIES[b] (cm^{-1})
5	3080(m), 1770(w), 1630(vs), 1595(vw), 998(vs), 885(vs).
6	3080(m), 1775(w), 1632(vs), 1593(w), 998(vs), 885(vs).
7	3005(w), 1635(w), 1610(m), 980(vs).
8	3005(w), 1645(m), 1615(s), 982(vs).
9	3060(m), 1620(vw), 1597(s), 998(vs).

a) Using neat films; b) See Instrumentation in the Experimental Section 2.1.3.

The spectra of the tin derivaties show very similar and typical olefinic structure according to the literature.[69]

The presence of two C=C stretching bands with different intensities in the range 1650-1590 cm^{-1} can be assigned to the olefinic bond stretching vibrations in conjugated dienes without a centre of symmetry.

The absorption frequency of (9) at 1597 cm^{-1} shows conjugation of an olefinic double bond with an aromatic ring.

All compounds have strong absorption at 998-980 cm^{-1}, due to the out-of-plane C-H bending vibrations, suggesting a trans-disubstituted products(E-geometry) that is consistent with the W-configuration of the pentadienyllithium, as observed by Oppolzer.[12b]

A characteristic absorption for the vinyl groups at 885 cm^{-1} was observed for (5) and (6) exhibiting an overtone near 1770 cm^{-1}.

Olefinic C-H stretching vibrations were found above 3000 cm^{-1}, absorbing vinyl groups in higher frequency than the others.

The ^1H NMR spectra were recorded in deuterated chloroform, using a Bruker 250 MHz instrument at King's College, London. The data are reported in Table 3.

Assignments were made on the basis of published data on dienes[5,70] and vinyltin derivatives.[71]

All the spectra showed that a mixture of the E and Z isomers was present. The major isomer is assigned

TABLE 3.

HYDROGEN-1 N.M.R. SPECTRA OF THE TIN COMPOUNDS $\{R'_3Sn(CR^1R^2CH^3CH^4CH^5R^6CH^7)\}^a$

					CHEMICAL SHIFTS AND COUPLING CONSTANTS[b]							
COMPOUND	R^1	R^2	R^6	R'	R^1	R^2	H^3	H^4	H^5	R^6	H^7	R'
5	H	H	H	Me	1.81(d) J_4=7.5		5.88(m)	5.78(m)	6.28(dt) J_6=10	4.79(dd) J_7=2	4.96(dd) J_5=16.8	0.16(s,9H)
6	H	H	H	n-Bu	1.81(d) J=7.7		5.90(m)	5.70(m)	6.27(dt) J_6=9.8	4.78(dd) J_7=2	4.94(dd) J_5=17	0.89(m,15H) 1.31(m,6H) 1.49(m,6H)
7	H	H	Me	Me	1.77(d) J=8.5			5.6-6.10[c]		1.71(d) J=1.1 6.5	5.43(m) J=1.1 6.7 14.5	0.09(s,9H)
8	H	H	Me	n-Bu	1.79(d) J=8.5			5.6-6.05[c]		1.72(d) J=0.8 6.8	5.41(m) J=0.8 6.8 14.3	0.91(m,15H) 1.31(m,6H) 1.49(m,6H)
9	H	Ph	Ph	Me	3.46(d) J_4=6.5-6.8	7.20(m)	6.26(q) J_4=14.8	5.94(sextet)	6.76(q) J_3=10.5	7.28(m)	6.46(d) J_5=15.5	0.22(s,9H)

a) Assignments according to (12); b) In $CDCl_3$ relative to tetramethylsilane (δ = 0 ppm). 250 MHz. Coupling constants in hertz; c) H^3, H^4, H^5.

the E configuration on account of the similarity of the NMR spectra with that of E-trimethylsilyl-2,4-pentadiene.[12b] The integration of the $SnCH_2$ and SnCH signals showed an E/Z ratio = 4 for $\{R'_3Sn(C_5H_7)\}$ {where R'=Me (5) or R'= n-Bu (6)}and $\{Me_3Sn\ (1,5\text{-}Ph_2\text{-}C_5H_5)\}$ (9) respectively. The close chemical shift of the methyl group in $\{R'_3$ Sn $(C_6H_9)\}$ {where R'=Me (7) or R'=n-Bu (8)} and their respective $SnCH_2$ prevent the measurement of the integration.

The trimethyltin group protons appear as sharp singlets at (0.16δ and 0.09δ) for (5) and (7) respectively. Each of these singlets has a small double satellite signal arising from splitting of the trimethyltin proton peak by the ^{117}Sn and ^{119}Sn isotopes (7.7 and 8.7% abundant, respectively). The same satellite signal was observed to a greater extent in the trimethyltin group protons (0.22δ) of (9).

The spectra of $\{R'_3Sn(C_5H_7)\}$ {R'=Me (5) or R'=n-Bu (6)} are remarkably similar, differing only slightly in chemical shift and by the presence of a R' group.

The tributyltin group protons show three multiplets at 0.89δ (15H), 1.31δ (6H) and 1.49δ (6H). The methylene groups (R^1=R^2=H) occur as doublets at 1.81δ.

The three vinylic protons of the compounds (5) and (6) showed: Doublet of doublets for the proton (R^6) at 4.79δ (5), 4.78δ (6) and with the same splitting pattern the proton (H^7) was found at 4.96δ (5), 4.94δ (6). At lowest field a doublet of triplets at 6.28δ (5),6.27δ (6) assigned to the proton (H^5). The magnitude of the coupling constants in these vinylic systems is basically the same as in 1,4-pentadiene.[72]

The resonances of the protons (H^3) and (H^4) at 5.78δ(5), 5.70δ (6) and at 5.88δ (5), 5.90δ (6) respectively, are assigned on the basis of the double resonance study for the similar silicon compound reported by Oppolzer, et al.[12b] They carried out an irradiation of the methylene group at 1.56 δ (J=7) observing that a doublet of triplets at 5.77δ(J=7,15)collapses to a doublet (J=15).

A different assignment has been reported[68] for the protons (H^4) (6.28δ,doublet of triplets) and (H^5) (6.59δ, doublet of doublet of doublets) in $Me_3Sn(C_5H_7)$ (5), but on account of intensity measurements between the multiplet at 5.78 δ (H^4) and the one reported at 6.59δ, we prefer to assign the spectra as discussed above.

The spectra of $R'_3Sn(C_5H_6R^6)$ $R'=R^6=Me$ (7) or $R'=n\text{-}Bu$, $R^6=Me$ (8) :

The tributyltin group protons of (8) resonate at 0.91 δ (15H), 1.31δ (6H) and 1.49 δ(6H) giving multiplet signals. The methylene protons resonate at 1.77δ(7) and 1.79δ (8) as doublets at slightly higher field than in the spectra of (5) and (6), where (R^6) is a hydrogen.

The presence of the methyl groups at (R^6) [1.71 δ (7), 1.72δ (8)] in these compounds produces a more complex multiplet pattern for most of the hydrogens, making the complete assignment too difficult. A deshielding effect on the corresponding (H^7) protons is observed, giving low field resonances at 5.43 δ (7), 5.41δ (8). Furthermore, the vinylic protons (H^5) are also shielded by the methyl groups, giving an olefinic region in the spectra without a first order splitting pattern as has been found in previous studies on conjugated double bond systems.[72]

The area under the olefinic regions at 5.6-6.1 δ was approximately equivalent to three protons (H^3), (H^4) and (H^5), complicated by the presence of the isomers.

The ^{1}H-NMR spectrum of Me_3Sn (1,5-Ph_2-C_5H_5) was basically assigned by comparison with the similar spectrum of the E isomer of 1,5-diphenyl-1,3-pentadiene.[5] All the resonances were found at low field, compared with the other spectra, as would be expected from the presence of the phenyl groups. The phenyl protons (R^2) and (R^6) resonate at 7.20 δ and 7.28δ respectively and a strongly deshielded doublet at 3.46 δ is observed for the proton (R^1).

The spectrum exhibits a multiplet for the (H^4), (H^3), (H^7) and (H^5) protons, not as complex as the spectra of $R'_3Sn(C_5H_6R^6)$ [where R^6=Me, R'=Me or n-Bu], which are resonating from high to low field showing a sextet for (H^4) at 5.94δ, proton (H^3) as a quartet at 6.28δ, (H^7) as a doublet at 6.46δ and finally the proton (H^5) also as a quartet at 6.76δ. Again in this compound the assignment of (H^4) proton is given on the basis of the double resonance study reported for the respective diene, in which the irradiation of the methylene group at 3.42δ transformed the signal of the (H^4) proton into a doublet at 5.90δ.

In this spectrum the coupling constant $J_{3,4}$ which is required for the assignment of the E-geometry is determined (14.8Hz). This value corresponds well to the mentioned E isomer according to Brenner[5] and characteristic trans coupling constants in unsaturated systems.[70]

2.1.3 · Experimental Section

All preparative work was carried out in an atomosphere of dry oxygen-free nitrogen. Solvents were carefully dried and THF was freshly distilled from sodium benzophenone ketyl under nitrogen. The following compounds were prepared as described previously: 1,4-pentadiene[73] was prepared by Dr.P.Powell from the pyrolysis of 1,5-pentanedioldiacetate.

The 1,4-hexadiene (99% mixture of cis and trans) was purchased from Aldrich Chemical Co. and the 1,5-diphenyl-1,3-pentadiene[74] was prepared by modified literature procedures:

The phosphonium salt $PPh_3{}^+CH_2CH_2PhBr^-$ was prepared by Dr.P.Powell using 2-bromoethylbenzene and triphenylphosphine in the following manner:

70g. (0.27 mol.) of PPh_3 and 44g. (0.24 mol.) of $PhCH_2CH_2Br$ were heated under reflux for 12-16 h. in toluene. The precipitate was filtered, washed and dried under vacuum. The product is hygroscopic and it was stored in a desiccator under phosphorus pentoxide.

A Wittig reaction from cinnamaldehyde PhCH=CHCHO and the respective phosphorus ylide $PhCH_2CH=PPh_3$ afforded the 1,5-diphenyl-1,3-pentadiene in a 53% yield, as is described below.

The salt $PPh_3^+ CH_2CH_2PhBr^-$ (42.21g., 94.35 mmol.) was treated in 350 cm^3 of dry diethyl ether (in a 1 l. flask equipped with a mechanical stirrer, addition funnel and a double surface condenser with nitrogen inlet) with 61 cm^3 of 1.55M n-butyllithium (95 mmol.) in hexane.

The red mixture was stirred for 2 h., cooled to 0^oC and treated with cinnamaldehyde (12.47 g., 94.35 mmol.)

The colour of the mixture changed several times, from red to brown, green, blue and white. This solution was stirred for 1h. and then heated under reflux for 5 h. The mixture was filtered and the yellow filtrate washed several times with 300 cm^3 portions of 0.01 M HCl, and then with 100 cm^3 of saturated brine, dried over anhydrous $MgSO_4$ and concentrated in vacuo, affording 13.5 cm^3 of crude yellow liquid (66% yield).

Distillation of the latter was carried out under reduced pressure ($124-132^oC$)/0.2mmHg. ^1H-NMR showed an impurity in the aliphatic region. A second distillation gave 10.8 cm^3 (53% yield) which was collected at $126-129^oC$/ 0.2 mmHg.

The organotin reagents, trimethyltin chloride and tributyltin chloride were purchased from Aldrich Chemical Co. and Koch-Light Laboratories respectively and they were used without purification.

GENERAL METHOD OF PREPARATION OF THE COMPOUNDS $R'_3Sn(C_5H_6R)$ AND $Me_3Sn(1,5\text{-}Ph_2C_5H_5)$

1.55 M Butyllithium in hexane (61.5 mmol.) was added to a stirred mixture of 3.6M diene in hexane (61 mmol.) and dry THF (100 cm^3) at -70°C. The solution was allowed to warm to 0° over 30 min and then for 1 h at 5 to 10°C. The resulting orange-red mixture* was cooled to -70°C and trialkyltin chloride (61.5 mmol) was added. After complete addition the mixture became colourless and a precipitate started to separate. The reaction mixture was allowed to warm up to room temperature over 40 min and the solvents were removed in vacuo. Hexane (30 cm^3) was added and the precipitate of lithium chloride was filtered off. Distillation of the filtrate afforded the title compound.

INSTRUMENTATION

Unless it is stated otherwise the apparatus and conditions used during the work were as follows:

Infrared spectra were determined on Perkin-Elmer 177 and 257 spectrometers, calibrated with polystyrene film. The intensity of absorptions are described with the letters, vs, s, m, w, br, sh, in brackets immediately after the respective frequencies indicating very strong, strong, medium, weak, broad and shoulder.

Hydrogen-1 and carbon -13 NMR spectra were

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*For 1,5-diphenyl-1,3-pentadiene this mixture was deep blue-purple. A 5% excess of Me_3SnCl was used for this diene.

recorded using a Bruker 250 MHz and 90 MHz instruments respectively at King's College, London. The chemical shifts are expressed in parts per million (ppm) in terms of δ values with tetramethylsilane (TMS) as an internal reference (δ-0 ppm).

Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected.

Elemental analyses were performed by Butterworth Laboratories, Teddington, Middlesex, U.K.

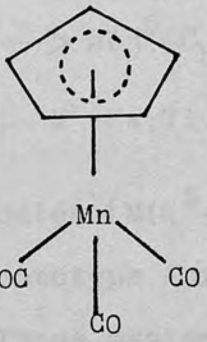
Mass spectra were recorded using a VG ZAB-IF spectrometer, with an ionising energy of 70 eV (EI) at The School of Pharmacy, London.

2.2 η^5-Complexes of Manganese and Rhenium

2.2.1 Introduction

The cyclopentadienyl ring has played an important role in the development of organometallic chemistry since the discovery of the sandwich compound ferrocene, in 1951.

Systems containing only one (η-C_5H_5) ring of the general type M (η-C_5H_5)L_n also represent a major class of transition metal organo derivatives, in which the tricarbonyl(η^5-cyclopentadienyl)manganese (13), was one of the first half sandwich complexes ever prepared.



(13)

It was first obtained by the treatment of manganocene with carbon monoxide, and reported simultaneously by Fischer[75] in 1954 and by Cotton and Wilkinson[76] in 1955. After that, a variety of preparative methods have been given in the patent literature[77] due to the applications in the past of this complex and the methyl derivative {$Mn(\eta^5$-$C_5H_4CH_3)(CO)_3$} as petrol additives and as a catalyst in a number of industrial processes. Generally these methods are based on the treatment of manganese salts with carbon monoxide in the presence of cyclopentadiene and a strong reducing agent.[78] In a similar manner Pruett and Morehouse[79] reported in 1958 how to obtain the analogous tricarbonyl(η^5-cyclopentadienyl)rhenium in 16% yield. The carbonylation of $\{Re(\eta\text{-}C_5H_5)_2H\}$ under different reaction conditions afforded $\{Re(\eta\text{-}C_5H_5)(CO)_2H\}$ at low temperature and $\{Re(\eta\text{-}C_5H_5)(CO)_3\}$ at higher reaction temperature. At the same time Green and Wilkinson[80] isolated the rhenium derivative by refluxing dicyclopentadiene with rhenium carbonyl in an attempt to prepare $\{Re(\eta^1\text{-}C_5H_5)(\eta^5\text{-}C_5H_5)(CO)_2\}$. An improved synthesis was reported by Fischer[81] and Nesmeyanov.[82]

$$M(CO)_5Cl + M'C_5H_5 \longrightarrow M(\eta^5\text{-}C_5H_5)(CO)_3 + M'Cl + 2CO$$

$$M{=}Mn,Re \; ; \; M'{=}Na,Tl.$$

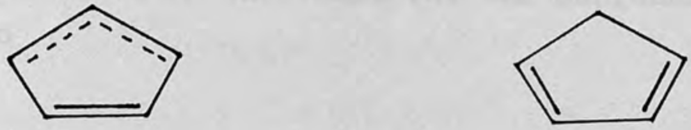
These simple molecules $\{M(\eta^5\text{-}C_5H_5)(CO)_3\}$ $\{M{=}Mn,Re\}$ may be regarded as a prototype for the transition metal carbonyl complexes. These systems possess only low symmetry, but discussions have been greatly simplified by considering that certain portions of the molecule possess high symmetry locally. The cyclopentadienyl-metal fragment transforms according to C_{5v} symmetry and the metal carbonyl fragment according to C_{3v}. The separate analysis of each fragment of the molecule has been proved to be useful for understanding the complete molecule.

Recently, the crystal and molecular structures of these compounds have been investigated, showing that these complexes{$M(\eta\text{-}C_5H_5)(CO)_3$} {M=Mn,Re} are isostructural.[83]

Both {$Mn(\eta^5\text{-}C_5H_5)(CO)_3$} and {$Re(\eta^5\text{-}C_5H_5)(CO)_3$} are cylindrically symmetrical and as expected, the $M(CO)_3$ fragment possesses effective C_{3v} symmetry with a common molecular axis passing through the mid point of the ($\eta\text{-}C_5H_5$)ring, the three carbonyl groups and the metal atom (13). There is an essential difference in the OC-M-CO angle in such systems, for Mn this angle is 92.02(5)°,[83a] which is consistent with the strong donating capacity of the cyclopentadienyl ring in comparison with the rhenium complex with a smaller angle 90.0(2)° [83b], increasing the pyramidality of the $M(CO)_3$ fragment.

However, the cyclopentadienyl metal fragment appears to deviate significantly from a regular pentagon so as to approach planar C_{2v} symmetry. This fact is also confirmed by vibrational spectroscopic studies in the solid state, vapour phase and in solution.[84]

The presumed equivalent C-C bond distances within the cyclopentadienyl ring observed in {$M(\eta\text{-}C_5H_5)(CO)_3$} {M=Mn,Re} showed small but significant deviations. This distortion, according to Butler,[83a] is consistent with a model in which the $(\eta\text{-}C_5H_5) \longrightarrow M$ π donation is fairly large and from this electronic considerations assumed that these complexes are susceptible to Jahn-Teller distortion, which gives rise to two structures of lower symmetry (C_{2v}) one possessing "allylic" (14a) and the other "dienyl" character (14b).



(a) (b)

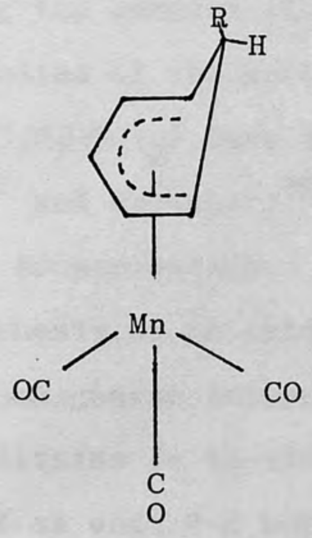
(14)

This result is indicative of some localized carbon-carbon bonding throughout the ring, which in principle should be highly unexpected for a molecule that possesses effective cylindrical symmetry about the metal atom.

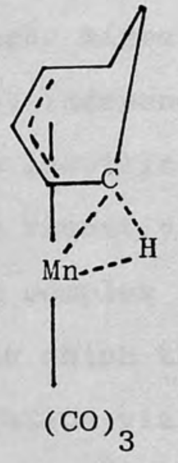
The complexes {M(η-C_5H_5)$(CO)_3$} {M=Mn,Re} are well suited for study due to their availability and reasonable stability, however the manganese complex has been received more attention on account of the lower reactivity of the rhenium complex.

The organic chemistry of these complexes, as well as substitution reactions on them have been widely studied. Some aspects of the substitution reactions are described in Chapter 3.

Several cyclic polyenyls with a pentahapto geometry have been found to form complexes with manganese and rhenium. The reduction of {Mn(η^6-C_6H_6)$(CO)_3$} ClO_4 by lithium aluminium hydride by Wilkinson[36] in 1961 was found to be the best synthetic method for preparing (η^5-cyclohexadienyl)manganese tricarbonyl in 41% yield. (R=H, 15). Attempts to prepare the rhenium analogue by methods based on that used for the manganese compound failed.[85]



(15)



(16)

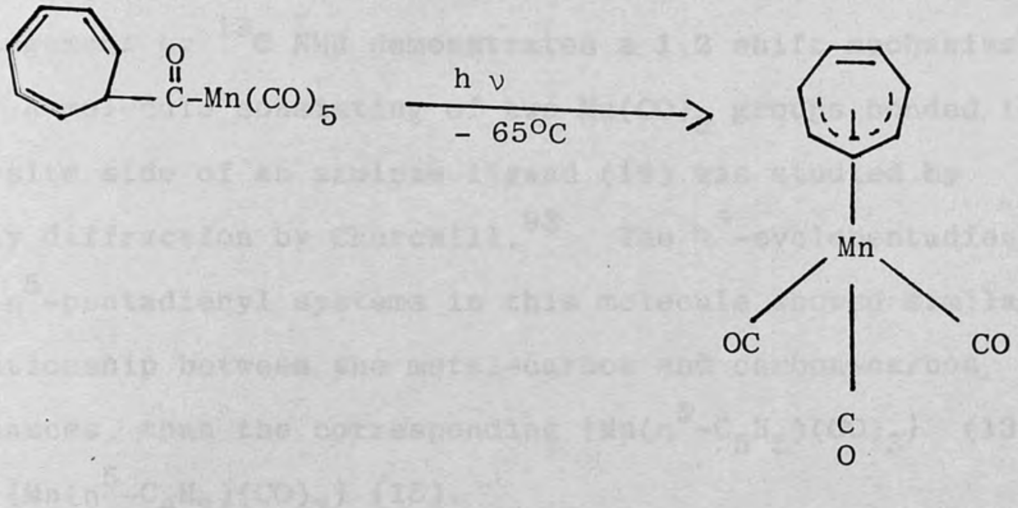
Spectral and X-ray diffraction[37] results suggest that the nucleophilic species (R = H^-, $C_6H_5^-$, CH_3^-) add on the outside of the ligand, and the incoming substituent occupies a syn position. This destroys the coplanarity of the ring, and the cyclohexadienyl ligands assume the form (15), in which the hydrogens situated in the coordinated part exhibit an unsymmetrical distribution of electron density, according to the ^1H NMR spectra.

A comparative study with $\{Mn(\eta^5-C_5H_5)(CO)_3\}$[83a] (13) showed that the carbon-carbon distances around the delocalized system, are rather shorter in the cyclohexadienyl than in the cyclopentadienyl ligand, while the mean metal-carbon distances are longer. This indicates stronger bonding of the metal to the cyclopentadienyl than to the cyclohexadienyl ligand, or else stronger bonding inside the cyclohexadienyl than in the cyclopentadienyl fragment.

Similar stereochemistry and conformation was found studying the complex $\{Re(\eta^5-C_6Me_6H)(CO)_3\}$ [86]

Studies of the mechanism of hydrogen migration in the $\{Mn(\eta^5-C_6H_7)(CO)_3\}$ have been carried out independently by Pauson[87] and Brookhart[88] via deuterium labelling and thermal isomerisation. Further, they recently reported the synthesis of an interesting bridge complex (η^3-cyclohexenyl)manganese tricarbonyl[89] (16) in which the metal centre attains an 18-electron configuration via coordination of an endo C-H bond adjacent to the η^3-allyl unit (called agostic hydrogen) from the reduction of $\{Mn(\eta^5-C_6H_7)(CO)_3\}$ (15) by lithium aluminium hydride.

Other cyclic η^5-pentadienyl species have been synthesised in high yields by treatment of cyclic conjugated dienes with metal carbonyls as $\{M(\eta^5-C_7H_9)(CO)_3\}$ {where M=Mn[90], Re[85] ; C_7H_9 = cycloheptadienyl} and the bright orange cycloheptatrienyl complex $\{Mn(\eta^5-C_7H_7)(CO)_3\}$ (17) from photolysis of (7-cycloheptatrienylacyl) pentacarbonylmanganese[91] (18) at low temperature in 11% yield. {SCHEME (4)}..



(18)

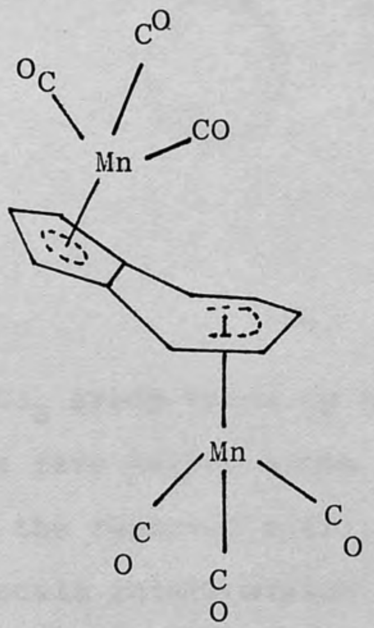
(17)

(SCHEME 4).

All these cyclic η^5-dienyl complexes have shown to be stereochemically non-rigid.[92] Whitesides and Budnik[85] reported the rotation of the coordinated cyclohexadienyl and cycloheptadienyl groups from the neutral complexes {(dienyl) M $(CO)_x$ $(EPTB)_{3-x}$} (where dienyl= cyclopentadienyl, cyclohexadienyl, cycloheptadienyl; M=Mn, Re ; x = 1,2 ; and EPTB = 4-ethyl-1-phospha-2,6,7-trioxabicyclo {2.2.2.} octane) from low temperature ^{31}P NMR studies showing a mixture of [illegible] isomers which are undergoing rapid interconversion at ambient temperature.

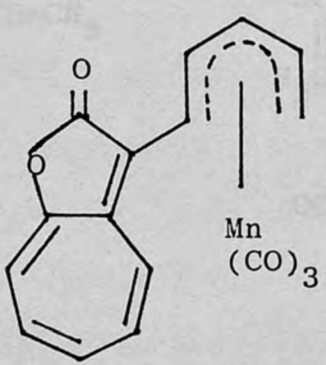
They have also obtained evidence of sequential occupation by the manganese fragment of several eqivalent locations around the cycloheptatrienyl ring in $\{Mn(\eta^5-C_7H_7)(CO)_3\}$ (17) by NMR analysis. A pattern consistent with the η^5-structure was observed at low temperature ^1H NMR and characterisation of the mechanism of the fluxional rearrangement by ^{13}C NMR demonstrates a 1,2 shift mechanism.[91b]

A molecule consisting of two $Mn(CO)_3$ groups bonded to opposite side of an azulene ligand (19) was studied by X-ray diffraction by Churchill.[93] The η^5-cyclopentadienyl and η^5-pentadienyl systems in this molecule showed similar relationship between the metal-carbon and carbon-carbon distances, than the corresponding $\{Mn(\eta^5-C_5H_5)(CO)_3\}$ (13) and $\{Mn(\eta^5-C_6H_7)(CO)_3\}$ (15).



(19)

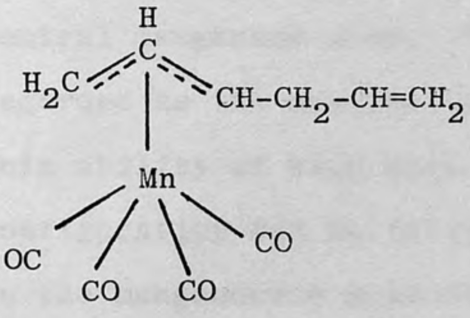
The first recognised example of an open-chain η^5-pentadienyl complex of manganese was reported by Pauson and Mills[94] in 1971. The reaction of tropone (2,4,6-cycloheptatrien-1-one) with decacarbonylmanganese gave a purple crystalline solid whose molecular structure was shown to be the complex (20).



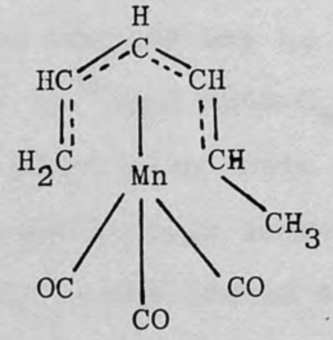
(20)

The $Mn(CO)_3$ group takes up the same orientation with respect to the five carbon atoms of the pentadienyl group as it does in the reported cyclic pentadienyl complexes.[37,93b]

The organotin intermediates 2,5-hexadienyltrimethyltin and 1,5-hexadienyl-3-trimethyltin (obtained by the Grignard reagent of 3-bromohexa-1,5-diene with chlorotrimethyltin) treated with bromopentacarbonylmanganese gave rise to the liquid η^3-allyl tetracarbonyl species (21) which was isolated along with a small amount of decarbonylated pentadienyl product (22) by Abel and Moorhouse.[62a] Further, it was found that the η^3-allyl tetracarbonyl complex could be converted into the η^5-pentadienyl tricarbonyl. These results were rationalised by the uncoordinated olefinic group displacing carbon monoxide followed by an immediate rearrangement by a 1-3 proton shift to form the methyl-pentadienyl complex (22).

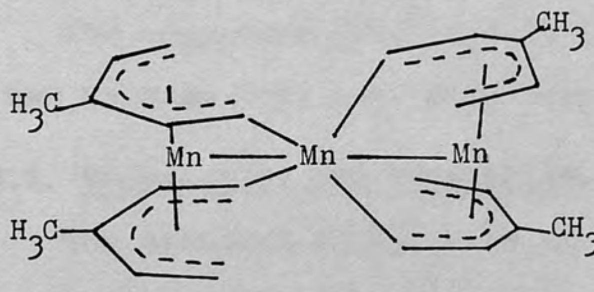


(21)



(22)

Recently, an unexpected and unusual pentadienyl trimetallic complex of formulation $\{Mn_3(3-C_6H_9)_4\}$ {where $(3-C_6H_9)=(3-Me-C_5H_6)\}$ (23) was reported by Ernst et al.[45] in 1982.



(23)

The amber-brown product (23) has been synthesised from $MnCl_2$ with 2 equivalents of 3-methyl-pentadienyl anion.[3] The structural results from an X-ray diffraction study reveals that terminal manganese atoms are coordinated by two 3-methylpentadienyl ligands and to the central manganese atom. Ernst claimed that the terminal fragments $Mn(3\text{-}C_6H_9)_2$ must obtain the noble gas configuration by each abstracting a single electron from the central manganese atom. Then, this complex may be regarded as the associated salt of Mn^{2+} and $Mn(3\text{-}C_6H_9)_2^-$. This ability of high spin Mn^{2+} to adopt such ionic configuration can be related with the similar behaviour in the manganocene molecule[95] which is considered to be mainly ionic; and also could be taken as evidence of the terminal metal and ligand basicities in the system.

This section reports the novel synthesis of η^5-pentadienyl complexes of manganese and rhenium. Complexes with substituted η^5-pentadienyl ligands are also reported for manganese.

2.2.2. Results and Discussion

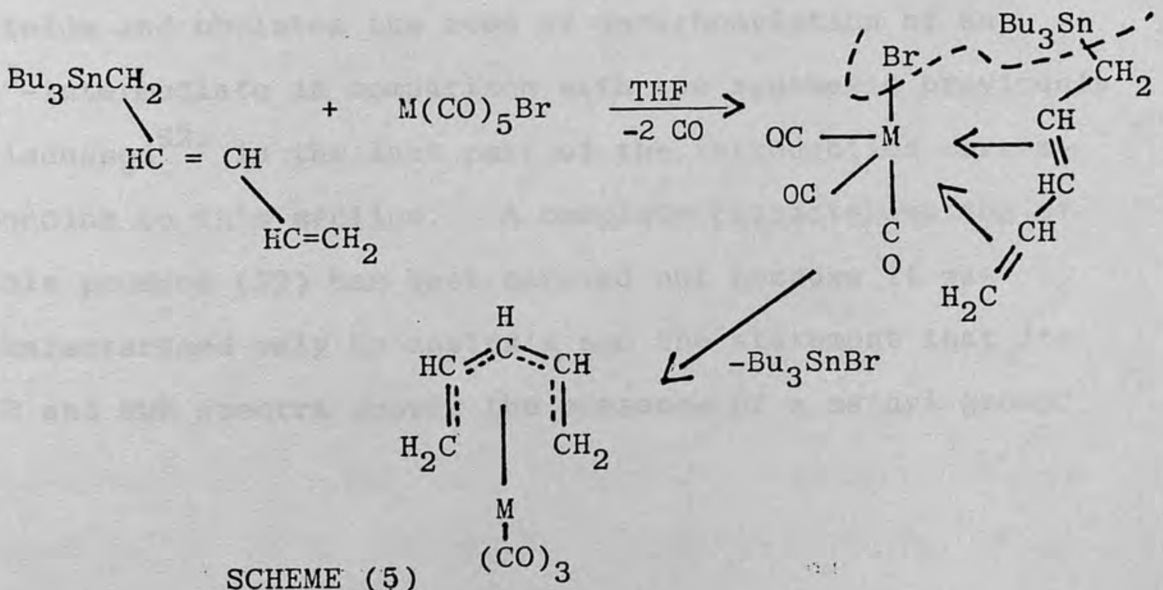
The complexes $\{M(\eta^5\text{-}C_5H_6R)(CO)_3\}$ $\{M=Mn,R=H,Me:M=Re,R=H\}$ and $\{Mn(\eta^5\text{-syn-syn-}1,5\text{-}Ph_2C_5H_5)(CO)_3\}$

2.2.2.1. Preparation and Properties.

The standard preparation of η-enyl metal carbonyl complexes by the organotin method,[62a] where the enyl group is an allyl, cyclopentadienyl or indenyl, can also be applied to the synthesis of η^5-pentadienyltricarbonyl metal complexes.

A series of species of the type $\{M(\eta^5\text{-}C_5H_5R_1R_2)(CO)_3\}\{M=Mn, R_1=R_2=H; R_1=H, R_2=Me; R_1=R_2=Ph: M=Re, R_1=R_2=H\}$ have been synthesised employing pentadienyl tin compounds, some containing methyl or phenyl substituents, by transfer of the pentadienyl group from tin to the transition metals. The η^5-pentadienyltricarbonylmanganese (24) was obtained by the action of 2,4-pentadienyltrimethyltin (5) as well as 2,4-pentadienyltributyltin (6) with bromopentacarbonylmanganese in 52 and 42% yields respectively. A similar trend was observed for the trimethyltin- and tributyltin allyls used by Abel in the synthesis of $\{Mn(\eta^3\text{-}C_3H_5)(CO)_4\}$.[62a] The synthesis of this η^5-pentadienyl complex from the trimethyltin derivative was reported by Seyferth[68] sometime after we obtained it independently.

The reaction could be exemplified below, based on the generalisation of Abel's mechanism for allyl groups[62a] (SCHEME 5).



SCHEME (5)

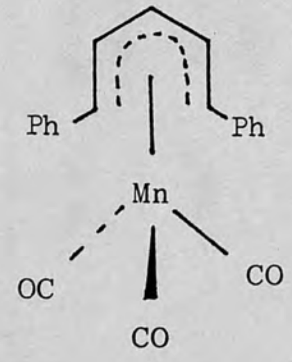
(24)

The initial step involves olefin coordination of the double bonds of pentadienyltrialkyltin along with the carbonyl displacement, followed by intramolecular elimination of the organotin halide.

As it was observed before,[62a] the use of a mixture of isomers in these reactions was unimportant since the final step of organotin halide elimination gave an identical product from the two isomers.

The reaction mixture was monitored by infrared spectroscopy, until it showed complete consumption of the pentacarbonyl halide. The products were isolated by chromatography on alumina and vacuum sublimation. In cases where the by-product trimethyltinbromide was present, separation was effected by water washing, extraction and vacuum sublimation.

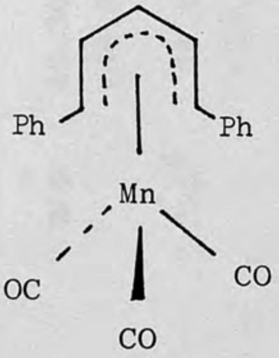
Use of 2,4-hexadienyltrialkyltin (7 or 8) in the synthesis of the methyl substituted η^5-pentadienyl complex $\{Mn(\eta^5\text{-syn-1-}MeC_5H_6)(CO)_3\}$ (22) leads to improved yields and obviates the need of decarbonylation of an η^3-intermediate in comparison with the synthesis previously discussed[62a] in the last part of the introduction corresponding to this section. A complete characterisation of this product (22) has been carried out because it was characterised only by analysis and the statement that its IR and NMR spectra showed the presence of a methyl group.



(25)

All the complexes are slightly air sensitive as solids, in solution they decompose faster. Excepting $\{Mn(\eta^5\text{-syn-syn-1,5-}Ph_2C_5H_5)Mn(CO)_3\}$ (25) they easily sublime under vacuum at ambient temperature (manganese compounds) or at 60°C (rhenium compound). Analytical data are reported in Table (4).

The lower reactivity of the carbonyl derivatives of the heavy 5d transition metal rhenium in comparison with the lighter 3d was observed in the synthesis of the analogous$\{M(\eta^5\text{-}C_5H_7)(CO)_3\}$ {M=Mn, Re }. The synthesis of the rhenium complex affords $\{Re_2(CO)_{10}\}$ {infrared 2070(m), 2014(s), 1976(m) in saturated hydrocarbon[96a] (Found: 2080(m), 2020(s), 1982(m), in THF)and m.p. 177°C (found: 180°C)}as by-product reducing strongly the yield of the pentadienyl complex. It is also observed in the infrared of the reaction mixture of the manganese complex similar bands that may suggest the presence of $Mn_2(CO)_{10}$, but during the time of the reaction these bands are



(25)

All the complexes are slightly air sensitive as solids, in solution they decompose faster. Excepting $\{Mn(\eta^5\text{-syn-syn-1,5-}Ph_2C_5H_5)Mn(CO)_3\}$ (25) they easily sublime under vacuum at ambient temperature (manganese compounds) or at 60°C (rhenium compound). Analytical data are reported in Table (4).

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TABLE 4

ANALYTICAL DATA FOR THE COMPLEXES $\{M(\eta^5\text{-}C_5H_6R)(CO)_3\}$ AND $\{Mn(\eta^5\text{-syn-syn-}1,5\text{-}Ph_2C_5H_5)(CO)_3\}$

COMPLEX	COLOUR	MELTING POINT (°C)	YIELD %	MOLECULAR WEIGHT [c]	ANALYSIS FOUND (CALC) (%)	
					CARBON	HYDROGEN
$\{Mn(\eta^5\text{-}C_5H_7)(CO)_3\}$	Yellow	100-101	42[a]	206	46.30	3.50
					(46.63)	(3.42)
$\{Re(\eta^5\text{-}C_5H_7)(CO)_3\}$	White	70-72	15	338[d]	28.49	1.90
					(28.48)	(2.09)
$\{Mn(\eta^5\text{-syn-}1\text{-}MeC_5H_6)(CO)_3\}$	Yellow	29-30	60	220	49.0[b]	4.20
					(49.1)	(4.10)
$\{Mn(\eta^5\text{-syn-syn-}1,5\text{-}Ph_2C_5H_5)(CO)_3\}$	Pale yellow	151-152	10	358	67.19	4.03
		(decomp.)			(67.05)	(4.22)

a) Same complex from $Me_3Sn(C_5H_7)$ gives 52%; b) Reference 62a; c) Determined from mass spectra;

d) Based on ^{187}Re isotope only.

disappearing along with those of the starting material.

During the preparation of the manganese complexes using the tributyltin derivatives, cream-white solids precipitate in the hydrocarbon solvent or even in small volume of THF. It seems a mixture of products, which are very hygroscopic and decompose at high temperature ($>100^{o}C$) without melting. Also, a pale yellow solid with the same characteristics was isolated from the reaction with $\{Me_3Sn(1,5\text{-}Ph_2C_5H_5)\}$ and $Mn(CO)_5Br$ before the treatment with water (see Experimental section 2.2.3.)

Similarity of the complex $\{M(\eta^5\text{-}C_5H_6R)(CO)_3\}$ $\{M=Mn,R=H,Me:M=Re,R=H\}$ with the cyclic analogues is noteworthy. Therefore, it is interesting to observe the low value reported for the m.p. of the rhenium acyclic complex, which is expected to be higher according to the trend observed in manganese and the respective m.p. of the η^5-cyclopentadienyltricarbonylrhenium complex ($111\text{-}114^{o}C$).[97] The reason for this value may be the presence of solvent in the solid.

The only product known with phenyl groups substituted in a pentadienyl acyclic ligand is the cation $\{Fe(\eta^5\text{-}syn\text{-}syn\text{-}1,5\text{-}Ph_2C_5H_5)(CO)_3\}^+$. The orange solid had been reported in kinetic studies[25b] and in isomerisation studies[98], although detailed characterisation has not been reported.

The probable structure for these complexes will be discussed on the basis of the spectroscopic studies because unfortunately attempts by Dr M.G.B.Drew to determine the crystal and molecular structure of $\{Mn(\eta^5-C_5H_7)(CO)_3\}$ were unsuccessful.

The crystal data obtained were: $C_8H_7MnO_3$, M=206; Orthorhombic, a=22.204(8), b=6.225(4), c=24.63(1)A^o, $\alpha=\beta=\gamma=90^o$, U=3404.4A$^{o\ 3}$, Dm=1.60, Dc=1.59 g cm^{-3}.[99]

1891 independent reflections were measured on a Stoe Stadi-2 diffractometer of which 1146 reflections with $I > 3\,\sigma(I)$ were used in the refinement. Systematic absences were hkl, $h + l = 2n+1$ and hol, $h=2n+1$. There were several possible space groups and all of them were tried without success. The Mn position was obtained, but the remainder of the molecule was disordered and we were unable to establish a suitable model.

The mass spectra of the pentadienyl metal carbonyl complexes showed an easily identified parent molecular ion. The successive fragmentation of CO groups precedes the loss of the pentadienyl ligand, giving:

COMPLEX	IONS			
$\{Mn(\eta^5-C_5H_7)(CO)_3\}$(m/e):	206(14)	178(26)	150(23)	122(100)
$\{Mn(\eta^5-MeC_5H_6)(CO)_3\}$ (m/e):	220(10.4)	192(25)	164(19)	136(63)
$\{Mn(\eta^5-Ph_2C_5H_5)(CO)_3\}$(m/e):	358(< 4)	330(<7)	302(< 7)	274(47)
$\{Re(\eta^5-C_5H_7)(CO)_3\}$ (m/e):	338(64)	310(32)	282(100)	254(64)

(Relative intensity in parenthesis).

The rhenium-containing ions were clearly identified by the isotopic ratio ^{187}Re: ^{185}Re (1:0.59), and the data reported above is based on ^{187}Re isotope only. The pentadienyl rhenium complex presents intense parent molecular ion peaks in the spectrum. This characteristic feature has also been observed in several analogous rhenium complexes and suggests the high stability of the rhenium species towards electron impact.[100]

The spectrum of $\{Mn(\eta^5-Ph_2C_5H_5)(CO)_3\}$ contains many ions associated with ligand fragments, and these are often of high intensity, but they have not been considered in detail. The base peak was found at (m/e): 128 and for the methylpentadienyl derivative at (m/e): 81 $(C_6H_9)^+$.

A similar simple fragmentation is observed for the $\{Mn(\eta^3-C_5H_7)(\eta^2-C_5H_8)(CO)_3\}$ as described in Section 3.2.2.1.

2.2.2.2. Infrared studies.

In this discussion we shall be referring only to the C-O stretching modes of the carbonyl ligands, since it is these that provide the greatest amount of information about molecular structure and bonding. The vibrational spectra outside the CO stretching region are also informative, although interpretation is less easy. Then, the pentadienyl ligand will be considered under some other spectroscopic methods as ^1H-, ^{13}C-NMR and low energy photoelectron spectroscopy.

The spectra of the pentadienyl $M(CO)_3$ complexes, according to the number and pattern of bands, as well as their position, are very close to those resulting from the η^5-dienyl compounds as $\{M(\eta^5-C_5H_5)(CO)_3\}$ {where M=Mn,Re}[101a] (13) and $\{Mn(\eta^5-C_{6+n}H_{7+m})(CO)_3\}$ {where n=m=o (15); n=1, m=2; n=1, m=o (17)}[36,91b], indicating that the orientation of their carbonyls with respect to the metal atom is not greatly altered from that in the corresponding cyclic complexes. Therefore, the $M(CO)_3$ group in the new complexes can be considered as having C_{3v} local symmetry.

The band frequencies of the complexes are listed in the Table 5, also some values of the cyclic compounds are annotated for an easy comparison.

In solution or mull, all the tricarbonyl complexes display two strong ν(CO) bands, the band at higher frequency, assignable to the symmetric stretching mode[101b,96c] (A_1) is very sharp and more intense than that of the lower frequency asymmetric mode (E), which is also intense and broad, showing a splitting for degenerate vibrations due to internal dissymmetry of the ligands.

Raman spectra were obtained for $\{M(\eta^5-C_5H_7)(CO)_3\}$ {where M=Mn, Re }as solid samples in sealed capillary tubes at room temperature, with a Coderg PHO spectrometer using Ar laser (coherent radiation) 19,434 cm^{-1} (see Table 6).

Again, similarity between the analogous acyclic and cyclic complexes was observed. The symmetric mode as noted earlier for the cyclic compounds,[96c] has a smaller intensity than the asymmetric band.

TABLE 5

INFRARED DATA[a] FOR COMPOUNDS $\{M(\eta^5\text{-}C_5H_6R)(CO)_3\}$ AND $\{Mn(\eta^5\text{-}syn\text{-}1,5\text{-}Ph_2C_5H_5)(CO)_3\}$.

COMPOUND	CARBONYL STRETCHING FREQUENCY (cm-1)			
$\{Mn(\eta^5\text{-}C_5H_7)(CO)_3\}$	2020	1957	1937	(nujol)
	2018	1943	1929	($CHCl_3$)
$\{Re(\eta^5\text{-}C_5H_7)(CO)_3\}$	2028	1953	1932	(CCl_4)
	2028	1945	1922	($CHCl_3$)
$\{Mn(\eta^5\text{-}syn\text{-}1\text{-}MeC_5H_6)(CO)_3\}$	2020	1945(br)		($CHCl_3$)
$\{Mn(\eta^5\text{-}syn\text{-}1,5\text{-}Ph_2C_5H_5)(CO)_3\}$	2007	1947	1925	(nujol)
$\{Mn(\eta^5\text{-}C_5H_5)(CO)_3\}$[b]	2028	1945		(C_6H_{12})
$\{Re(\eta^5\text{-}C_5H_5)(CO)_3\}$[c]	2026	1931		(CS_2)
$\{Mn(\eta^5\text{-}C_6H_7)(CO)_3\}$[d]	2020	1942		(CCl_4)
$\{Mn(\eta^5\text{-}C_7H_7)(CO)_3\}$[e]	2025	1951	1930	(CS_2)
$\{Mn(\eta^5\text{-}C_7H_9)(CO)_3\}$[e]	2015	1945	1931	(CCl_4)

a) All bands have very strong intensity; b) Reference 101a, 84b; c) Reference 96c; d) Reference 36; e) Reference 91b.

TABLE 6

RAMAN[a] SPECTRA DATA FOR COMPOUNDS $\{M(\eta^5-C_5H_7)(CO)_3\}$.

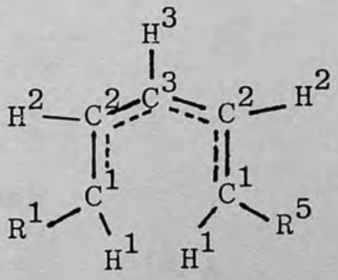
COMPOUND	FREQUENCY (cm^{-1})
$\{Mn(\eta^5-C_5H_7)(CO)_3\}$	2018(m), 1946(s), 1935(s), 1918(vs) 1518(w), 1468(w), 1458(w), 1240(w), 1098(br 1012(m), 1003(m), 978(s), 950(s), 918(s), 902(w), 670(s), 658(w), 640(w), 535(s), 528(s), 500(vs),497(s), 468(s), 385(vs), 355(vs), 318(vs), 305(vs), 162(s).
$\{Re(\eta^5-C_5H_7)(CO)_3\}$	2018(m), 1946(m), 1935(m), 1915(s) 1510(w), 1098(w), 1008(m), 940(s), 530(m), 525(sh), 500(vs), 385(s), 345(s), 310(m), 285(m), 120(s).
$\{Mn(\eta^5-C_5H_5)(CO)_3\}$[b]	2014(m), 1943(ms), 1921(s), 1914(m), 1428(wm),1423(wm),1361(wm), 1219(w,br), 1161(w), 1120(vs), 1108(wm,sh), 1067(ms), 1060(ms), 1014(w), 1006(wm), 933(w, br), 846(wm), 835(wm), 667(wm), 639(vw), 633(vw) 610(wm), 545(m), 539(sh),502(m),489(wm), 387(wm), 370(wm), 359(vvs), 128(ms)120(s), 112(ms), 100(sh), 49(w).
$\{Re(\eta^5-C_5H_5)(CO)_3\}$[c]	2014(s), 1934(vs), 1909(vs), 1419(m), 1348(m), 1225(w),1104(vs), 1060(w), 1059(s), 1028(vw), 1023(vw), 1006(vw), 997(w), 928(w), 913(w),838(w), 825(m), 615(m), 603(m), 597(sh), 510(vs), 504(vs), 380(w), 348(w), 327(vs), 125(w), 113(s), 98(m).

a) Solid spectra; b) Reference 84a; c) Reference 96c.

These carbonyl stretching vibrations are found at 2018 and 1946, 1935 cm^{-1} for the manganese complex, and at 2014 and 1943, 1921 cm^{-1} for the cyclic analogue. According with assignments of the Raman spectra of the rhenium[96c] and manganesecyclopentadienyltricarbonyl[84a] complexes, the stretching M-C modes are observed between 400-500 cm^{-1} as is usual in metal carbonyl spectra. In this region for $Mn(\eta^5-C_5H_7)(CO)_3$ strong bands at 500 and 497 cm^{-1} are observed and the corresponding rhenium shows a very strong band at 500 cm^{-1}. The M-CO bending modes are expected between 500 and 700 cm^{-1}. For the manganese complex these bands are at 670, 640 and 535 cm^{-1}. In the rhenium complex only the medium intensity band at 530 cm^{-1} is observed.

2.2.2.3. <u>^{1}H- and ^{13}C-NMR spectroscopy</u>.

The pentadienyl fragments of the new complexes have been studied by ^{1}H- and ^{13}C-NMR spectroscopy. In both the symmetrical structure of the η^5-pentadienyl ligand (26) was evident. Assignments, relative intensities and coupling constants are related to those previously reported for various allyl (A_2M_2X) and pentadienyl ($A_2M_2X_2X'$) systems.



(26)

^{1}H-NMR data are reported in the Table 7 and assigned according to (26).

The 250 MHz ^{1}H-NMR spectrum for $\{Re(\eta^5-C_5H_7)(CO)_3\}$ (24) can be seen in Figure 1. This typical spectrum of an η^5-pentadienyl group with four widely separated bands of relative areas 1:2:2:2 is clearly in accord with the structure (26). The two pairs of protons in anti (H^1) and syn ($R^1 = R^5 = H$) configuration give rise to the two sets of doublets at 0.40δ and 2.35δ respectively, the syn pair being assigned at lower field from analogy with acyclic complexes[20] under double irradiation experiments and also from the respective studies with the substituted η^5-pentadienyl complexes. A multiplet centred at 4.22δ is associated with the protons (H^2) and a triplet in the lowest field (4.68δ) from the proton (H^3) attached to the central carbon of the η^5-system.

Two isomeric complexes could conceivably exist as stable species, however, only the cis isomer (27) is present, suggesting that the η^5-dienyl ligand in this configuration is the more stable in these new complexes in which the metal atom should be strongly bonded simultaneously to each of the five carbon atoms.

cis-isomer trans-isomer

(27)

TABLE 7

^{1}H-NMR DATA FOR COMPOUNDS $\{M(\eta^5\text{-}R^1CH^1CH^2CH^3CH^2CH^1R^5)(CO)_3\}$.

			Chemical shifts [a]					Coupling constants (Hz)				
COMPOUND	R^1	R^5	R^1	H^1	H^2	H^3	R^5	R^1H^2	H^1H^2	H^2H^3	R^1H^1	R^1H^3
$\{Mn(\eta^5\text{-}C_5H_7)(CO)_3\}$[b]	H	H	2.11(d)	0.11(d)	4.42(m)	4.77(t)	2.11(d)	10.0	11.0	6.25	~ 2.5	~0.9
			2.95(d)[e]	0.61(d)	5.15(m)	5.67(m)	2.95(d)					
$\{Re(\eta^5\text{-}C_5H_7)(CO)_3\}$	H	H	2.35(d)	0.40(d)	4.42(m)	4.68(t)	2.35(d)	10.3	11.3	6.3	~ 2.5	~0.9
$\{Mn(\eta^5\text{-syn-1-}MeC_5H_6(CO)_3\}$[c]	H	CH_3	2.52(d)	0.64(d)	4.92(m)	5.54(t)	1.61(s)	9.4	11.4	6.3	~ 2.7	
				1.61[d]	5.06(m)[d]							
$\{Mn(\eta^5\text{-syn-1,5-}Ph_2C_5H_5)(CO)_3\}$	Ph	Ph	7.08(m)	2.48(d)	5.18(q)	4.93(t)	7.08(m)		11.5	6.5		

a) In C_6D_6 relative to TMS (δ=0). 250MHz ; b) In C_6D_6 relative to TMS (δ=0). 300MHz ;

c) In $CDCl_3$ relative to TMS (δ=0). 250MHZ ; d) See text ; e) Values in the second line in $CDCl_3$ relative to TMS (δ=0) 90MHZ. Reference 68.

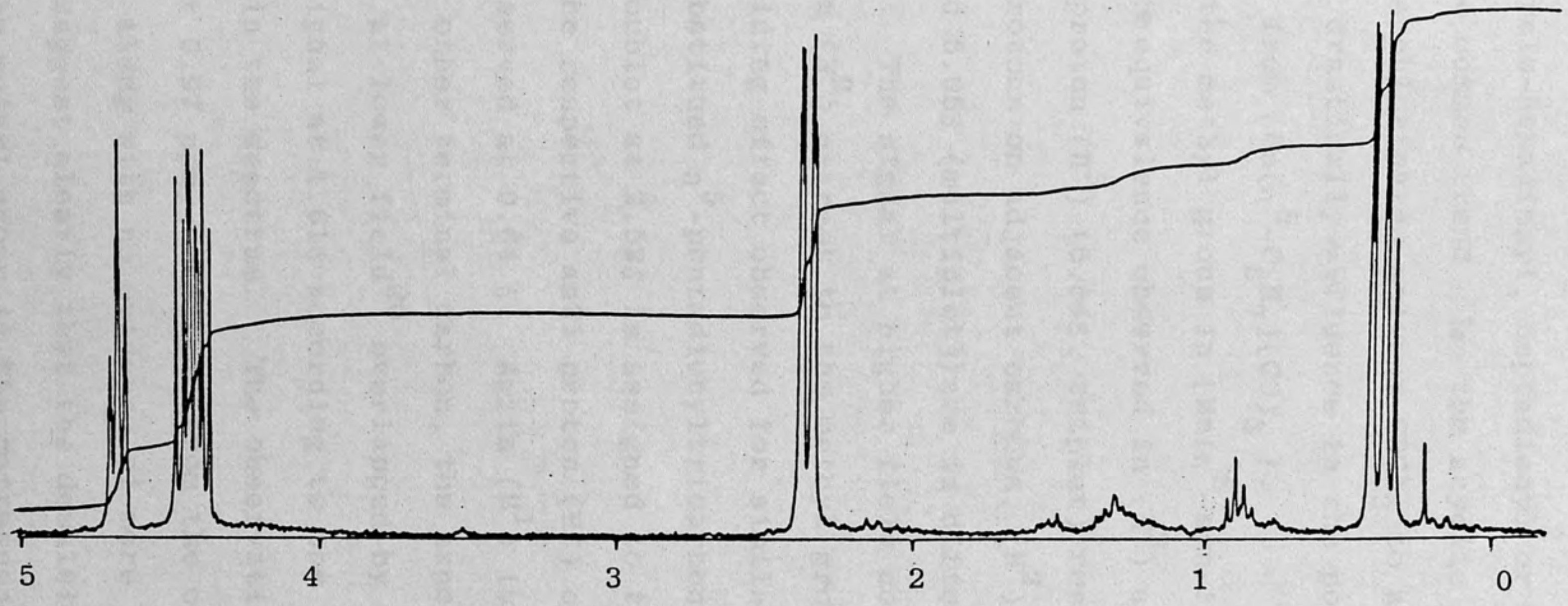


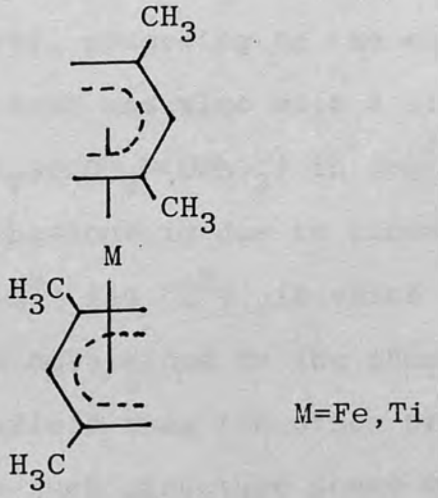
Figure 1. ^{1}H-NMR spectrum of η^{5}-pentadienyltricarbonylrhenium (24) in C_6D_6 at 250 MHz.

The chemical shifts of the dienyl ligand as a part of a cyclic system (η^5-cyclo-hexadienyl, heptadienyl or heptatrienyl) show the same common trend to the acyclic systems.[36,85,90,91]

The change from a chlorinated solvent $CDCl_3$ to an aromatic C_6D_6, showed drastically an influence in the position of the ^{1}H-NMR signals from $\{Mn(\eta^5-C_5H_7)(CO)_3\}$.

The presence of the methyl group in $\{Mn(\eta^5\text{-syn-1-MeC}_5H_6)(CO)_3\}$ (22) breaks up with the equivalence observed in (H^2) and (H^1) (see Table 7). The proton (H^3) (5.54δ, triplet) resonates to low field of the protons on adjacent carbons, (H^2) {4.92δ (multiplet) and 5.06δ (multiplet)} are in different magnetic environments. The signal at higher field could be assigned to the proton (H^2) nearest to the methyl group, according to the shielding effect observed for similar methyl mono- and disubstitued η^5-pentadienyltricarbonyl iron cations.[20] A doublet at 2.52δ is assigned to the syn proton (R^1) and the respective anti proton (H^1) on the same carbon is observed at 0.64 δ. Again (H^1) is not equivalent in the other terminal carbon, the expected resonance is observed at lower field[20] overlapped by the methyl protons (R^5) signal at 1.61δ according to the relative intensities in the spectrum. The observation of this proton (H^1) at 0.97 ppm, downfield from the other proton (H^1) at 0.64δ, along with no evidence of more signals around 2.52δ suggest clearly that the deshielded proton (H^1) next to the methyl group is the corresponding anti proton. The preference of the syn configuration of the methyl group in the pentadienyl ligands has also been observed in the η^5-cyclopentadienyl-η^5-syn-1-methylpentadienylrhodium and iridium cations by Powell.[27a,b]

Recent reports of NMR studies of methyl substituted η^5-pentadienyl complexes by Ernst[46] have shown an interesting feature. The complex $\{Fe(\eta^5\text{-}2,4\text{-}C_7H_{11})_2\}$ {where $(2,4\text{-}C_7H_{11})=2,4\text{-}Me_2C_5H_5\}$ (28) gives the typical four resonances in the ^1H NMR spectrum, consistent with the symmetric structure of the ligands, while seven resonances are observed for $\{Ti\ (2,4\text{-}C_7H_{11})_2\}$. Ernst claimed that it is apparent that the two C_7H_{11} ligands are equivalent but lack the mirror plane of symmetry perpendicular to the idealised ligand plane.



(28)

Moreover, the monocarbonyl adduct $\{Ti(CO)(2,4\text{-}C_7H_{11})_2\}$ obtained from $\{Ti(2,4\text{-}C_7H_{11})_2\}$ treated with carbon monoxide, showed the restoration of the perpendicular mirror plane for the ligand by only four resonances displaying in the ^1H-NMR spectrum.

The proton spectrum of the phenyl substituted complex (25) with four bands of area 10:2:1:2 assigned respectively to the protons (R^1,R^5), (H^2), (H^3) and (H^1) is consistent with the cis, syn, syn pentadienyl structure. All resonances are deshielded by the phenyl groups to lower field in comparison with unsubstituted complexes (24). The terminal protons of the dienyl unit resonate at 2.48δ with a coupling with (H^2) of 11.5 Hz (closely related to other $J_{H^1H^2}$) giving evidence of an anti configuration. The proton (H^3) attached to the central carbon atom of the η^5-system (4.93δ,triplet) resonates to high field of the protons on the adjacent protons (H^2) (5.18δ, quartet). This contrasts with observations on most of the cis-η^5pentadienyl systems which has a characteristic low field value for the position of the proton(H^3). However, according to the equivalence of the protons in the spectrum and also with a similar pattern reported for {Mn(η^5-C_5H_7)$(CO)_2P(OPh)_3$} in Chapter 3, we suggest that this behaviour is due to close chemical shifts of the protons (H^3) and (H^2), in which the latter should be more strongly deshielded by the phenyl groups and resonate at lower field than the other proton.

For steric reasons such structure seems more likely. However, we must be careful using this argument, because there is evidence of cationic complexes {M(η^5-syn,anti-1,5-$Ph_2C_5H_5$)(η^5-C_5H_5)}$^+$(M=Rh, Ir)[27c] with the phenyl groups in unsymmetrical position.

The ^{13}C-NMR spectrum of $\{Mn(\eta^5\text{-syn,syn-1,5-}Ph_2\ C_5H_5)(CO)_3\}$ (25) confirmed the symmetric structure in the pentadienyl ligand and it can be seen in Figure 2. The resonances of carbons are assigned according to(26). The carbonyl resonances could not be easily observed in these complexes, as previously reported in ^{13}C-NMR spectra of transition metal carbonyl complexes of manganese due to coupling with the 5/2 spin ^{55}Mn nucleus undergoing rapid quadruple relaxation.[102] Relaxation agents are not particularly useful for Mn-CO complexes.[102a] According to Bodner, allowing sufficient time for relaxation of the carbonyl resonance between pulses permits to obtain high resolution spectra for the complex $\{Mn(\eta^5\text{-}C_5H_5)(CO)_3\}$ and their respective derivatives $\{Mn(\eta^5\text{-}C_5H_5)(CO)_2L\}$[103]. A broad signal was observed at 221.9 ppm for the tricarbonylpentadienylmanganese.[68] The ^{13}C chemical shift and coupling constants for the pentadienyl portion of this complex have also been reported ($CDCl_3$); δC 57.52(t of d,C^1, J(CH)=161 Hz,J(CH^2)=9 Hz); 83.34 (d of t, C^3, J(CH)=170 Hz, J(CH^2)=11 Hz; 100.14 (d of d, C^2, J(CH)=163 Hz, J(CR^1)=J(CR^5)=J(CH^3)=10Hz). The same pattern is observed in the spectrum of the diphenyl derivative (25) in which the resonances of C^1 (77.7 ppm) and C^3 (82.3 ppm) lie to high field of that of C^2(96.2 ppm). (Phenyl groups attached to C^1 are found at 125.6, 127.2, 129 and 139.5 ppm).(In C_6D_6 relative to TMS (δ=0); 22.63MHz).

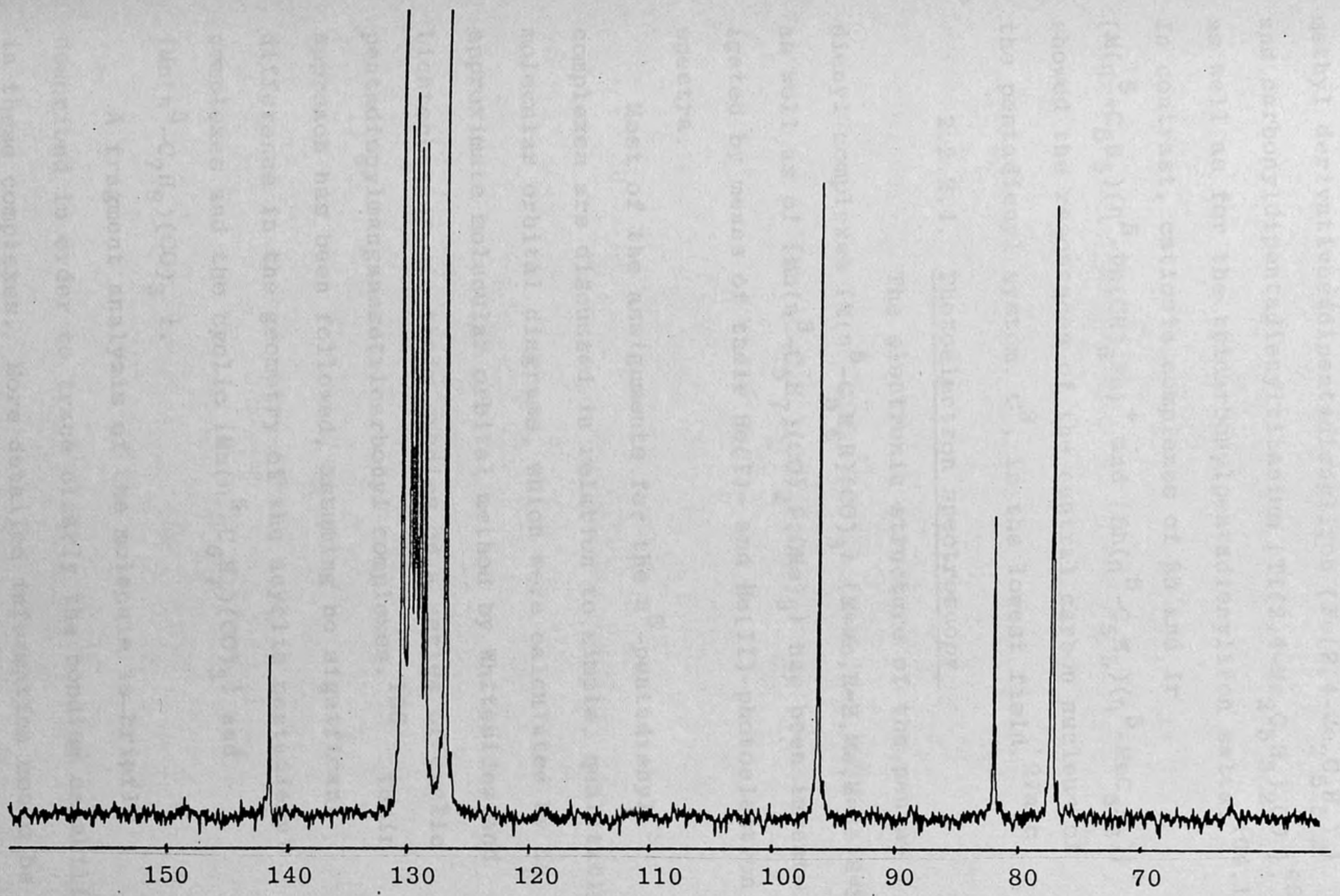


Figure 2. ^{13}C-NMR spectrum of "syn-syn" η^5-1,5-diphenylpentadienyltricarbonyl manganese (39) in C_6D_6 at 22.63MHz.

Similarly, the ^{13}C-NMR spectra of other pentadienyl systems indicate the same order of resonances for the methyl derivatives {dipentadienyliron $\{Fe(2,4\text{-}Me_2C_5H_5)_2\}$ and carbonyldipentadienyltitanium $\{Ti(2,4\text{-}Me_2C_5H_5)_2CO\}$,[46] as well as for the tricarbonylpentadienyliron salts.[104,105] In contrast, cationic complexes of Rh and Ir $\{M(\eta^5\text{-}C_5H_5)(\eta^5\text{-}Ph(CH)_5Ph\}^+$ and $\{Rh(\eta^5\text{-}C_5H_5)(\eta^5\text{-}MeC_5H_6)\}^+$ showed the resonances of the central carbon nucleus of the pentadienyl system, C^3, in the lowest field.[27a,c]

2.2.2.4. Photoelectron spectroscopy

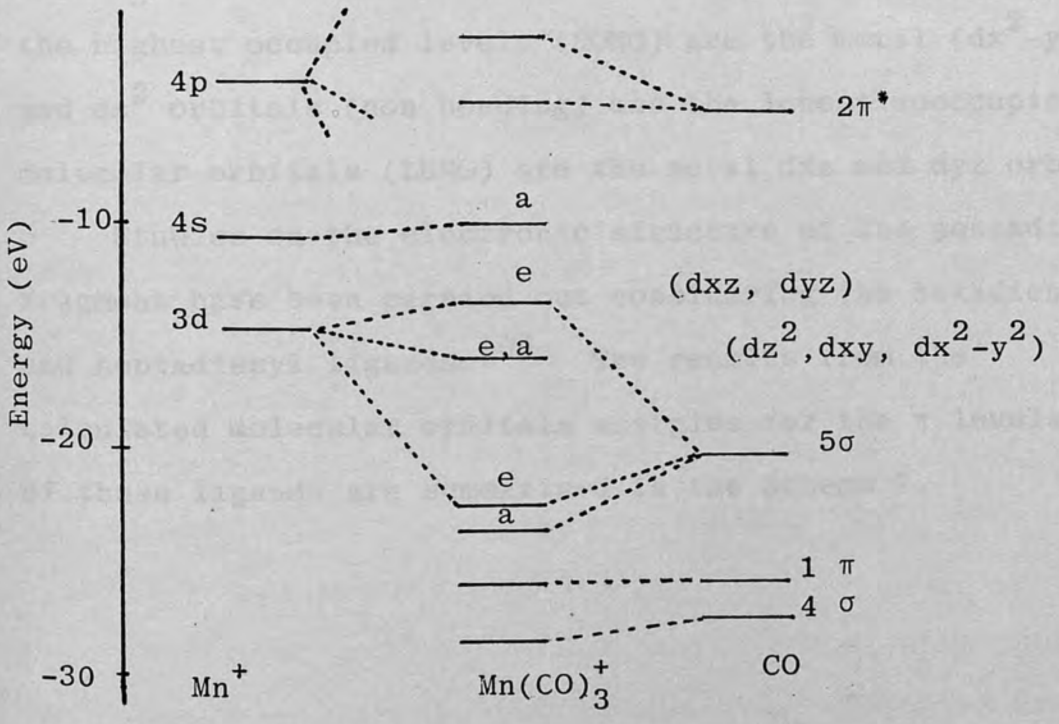
The electronic structure of the pentadienyl complexes $\{M(\eta^5\text{-}C_5H_6R)(CO)_3\}$ $\{M{=}Mn, R{=}H, Me; M{=}Re, R{=}H\}$, as well as of $\{Mn(\eta^5\text{-}C_5H_7)(CO)_2P(OMe)_3\}$ has been investigated by means of their He(I)- and He(II)-photoelectron spectra.

Most of the assignments for the η^5-pentadienyl complexes are discussed in relation to simple, qualitative molecular orbital diagrams, which were calculated by an approximate molecular orbital method by Whitesides and Lichtenberger, in their studies on a series of cyclic pentadienylmanganesetricarbonyl complexes.[106] Their approach has been followed, assuming no significant difference in the geometry of the acyclic pentadienyl complexes and the cyclic $\{Mn(\eta^5\text{-}C_6H_7)(CO)_3\}$ and $\{Mn(\eta^5\text{-}C_7H_9)(CO)_3\}$.

A fragment analysis of the molecule is briefly described in order to trace clearly the bonding capabilities in these complexes. More detailed information could be obtained about the energy ordering, symmetry and extent in space of the valence molecular orbitals of tricoordinate fragment $Mn(CO)_3$, in Hoffmann's studies.[107] The pentadienyl fragment has been analysed by Mingos [108a] and by Hoffmann.[108b]

The geometry of the $Mn(CO)_3$ fragment is idealised to C_{3v} symmetry. Then, for $Mn(CO)_3^+$ the metal dz^2 orbital transforms according to the a_1 representation and the (dx^2-y^2, dxy) and (dxz, dyz) sets of metal orbitals both transform according to the e_2 and e_1 representation respectively.[106]

The carbonyl orbitals are considered in terms of their symmetry combinations and the molecular orbital diagram according to Whitesides[106] is shown in the Scheme 6.



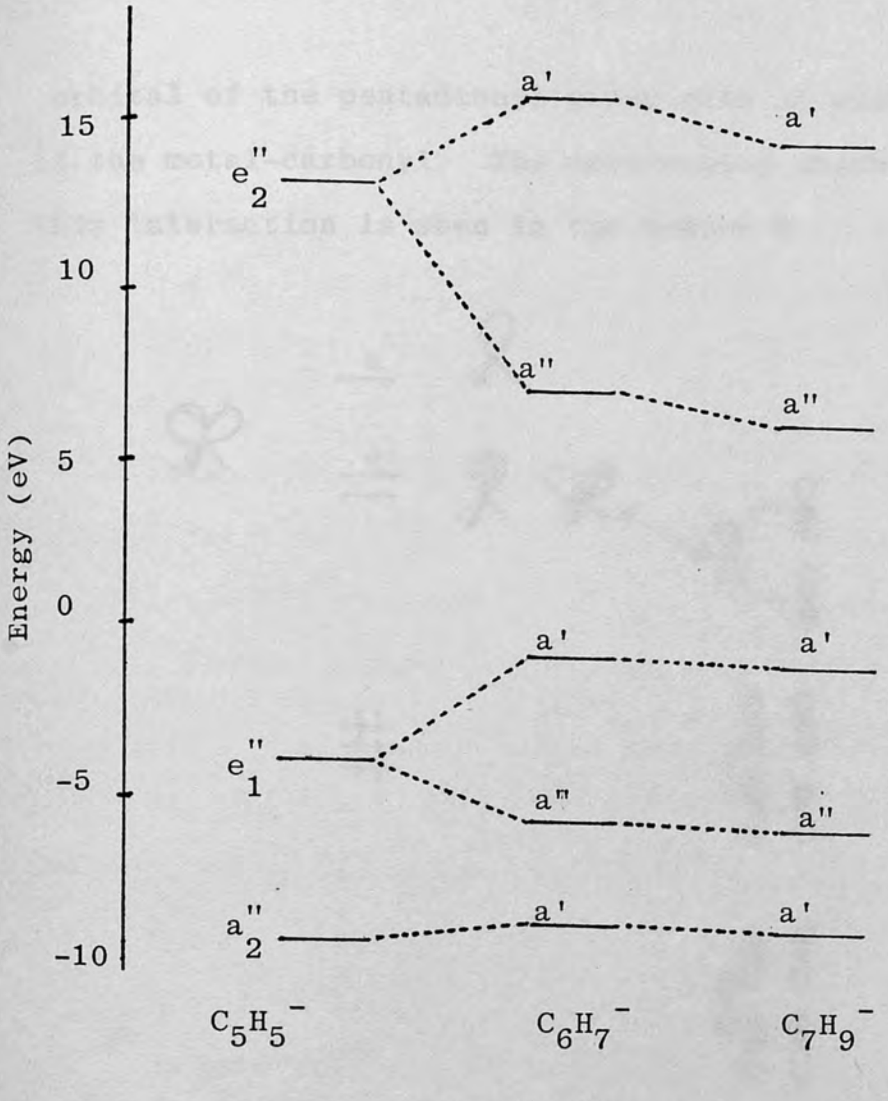
SCHEME 6

Considering the interaction of the carbonyl 5σ with the metal d orbitals, it is seen from the diagram that these σ orbitals interact primarily with the metal (dxz,dyz) orbitals. The bonding combinations represent σdonation from the carbonyl groups to the metal. The antibonding combination is primarily (dxz,dyz) in character. This level is virtual and is of the correct symmetry to act as a π acceptor from the cyclic η^5-pentadienyl ligand.

The π^* orbitals of the carbonyls are available for backbonding from the metal. In this coordinate system the carbonyl π^* orbitals interact primarily with the metal dz^2 and (dx^2-y^2,dxy) orbitals. The levels are split only slightly.

According to the primary metal character of the $Mn(CO)_3$ orbitals, it is observed from the diagram that the highest occupied levels (HOMO) are the metal (dx^2-y^2) and dz^2 orbitals (non bonding) and the lowest unoccupied molecular orbitals (LUMO) are the metal dxz and dyz orbitals.

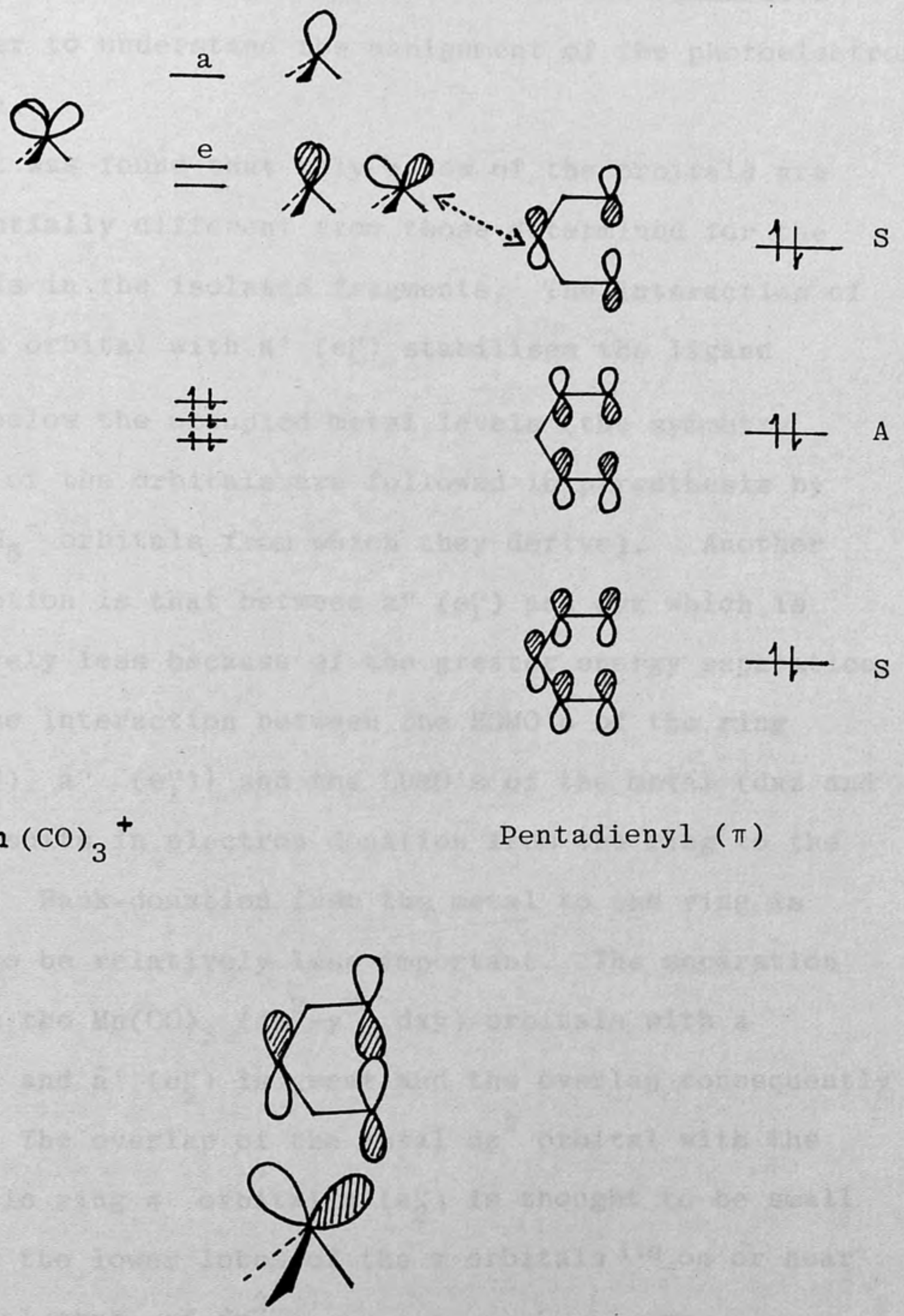
Studies on the electronic structure of the pentadienyl fragment have been carried out considering the hexadienyl and heptadienyl ligands.[106] The results from the calculated molecular orbitals energies for the π levels of these ligands are summarised in the Scheme 7.



SCHEME 7.

The reduction in symmetry for the pentadienyl fragment compared to the cyclopentadienide ion $C_5H_5^-$ belongs to the point group D_{5h}. The five carbons p π orbitals transform as a_2'', e_1'', and e_2'' representations) is produced by increasing the distance between two of the trigonal carbon atoms, causing splitting of the e_1'' and e_2'' levels. The resulting orbitals transform as a' and a''.

An interaction diagram for the formation of a pentadienyl-metal tricarbonyl complex has been formulated by Hoffmann.[108b] It shows that the most important interaction in the complex corresponds to that of nonbonding molecular orbital of the pentadienyl group with an acceptor orbital of the metal-carbonyl. The combination which results from this interaction is seen in the Scheme 8.

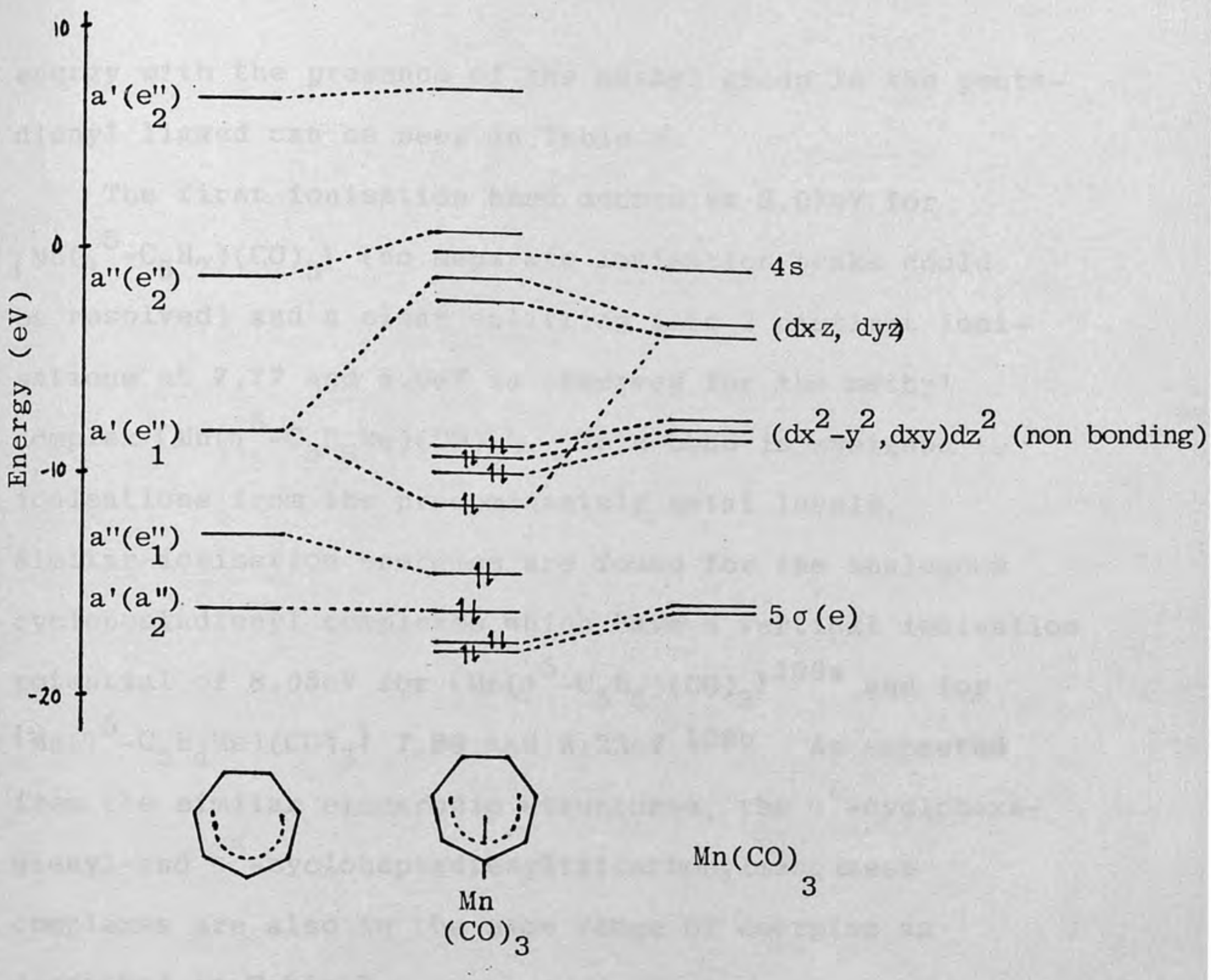


SCHEME 8.

Finally, the molecular orbital diagram of $\{Mn(\eta^5-C_7H_9)(CO)_3\}$ in terms of $C_7H_9^-$ and $Mn(CO)_3^+$ is given in the Scheme 9. Some of the important features described by Whitesides et.al.[106] are also summarised in order to understand the assignment of the photoelectron spectra.

It was found that only a few of the orbitals are substantially different from those determined for the orbitals in the isolated fragments. The interaction of the dxz orbital with a' (e_1'') stabilises the ligand level below the occupied metal levels (the symmetry labels of the orbitals are followed in parenthesis by the $C_5H_5^-$ orbitals from which they derive). Another interaction is that between a" (e_1'') and dyz which is relatively less because of the greater energy separation.

The interaction between the HOMO's of the ring {a' (e_1''), a" (e_1'')} and the LUMO's of the metal (dxz and dyz) results in electron donation from the ring to the metal. Back-donation from the metal to the ring is found to be relatively less important. The separation between the $Mn(CO)_3$ (dx^2-y^2, dxy) orbitals with a a" (e_2'') and a' (e_2'') is great and the overlap consequently small. The overlap of the metal dz^2 orbital with the symmetric ring π orbital a'(a_2'') is thought to be small because the lower lobes of the π orbitals lie on or near the nodal cone of dz^2.



SCHEME 9.

Assignment of Photoelectron Spectra . The He(I) and He(II) photoelectron spectra of $\{M(\eta^5\text{-}C_5H_6R)(CO)_3\}$ { M=Mn,R=H,Me}, $\{Re(\eta^5\text{-}C_5H_7(CO)_3\}$ and $\{Mn(\eta^5\text{-}C_5H_7)(CO)_2P(OMe)_3\}$ were recorder in a Perkin Elmer PES 16/18 spectrometer for an electron binding energy range of 7-17eV.

Because of the size and low symmetry of these molecules, the spectra are quite complex. No vibrational fine structure is observed. Certain features of the spectra are similar and the He(I) and He(II) spectra of $\{Mn(\eta^5\text{-}C_5H_7)(CO)_3\}$ and $\{Mn(\eta^5\text{-}C_5H_6Me)(CO)_3\}$ are presented in Figure 3 and 4.

The general shift of the ionisations to lower binding energy with the presence of the methyl group in the pentadienyl ligand can be seen in Table 8.

The first ionisation band occurs at 8.07eV for {$Mn(\eta^5-C_5H_7)(CO)_3$} (no separate ionisation peaks could be resolved) and a clear splitting into 2 distinct ionisations at 7.77 and 8.0eV is observed for the methyl complex {$Mn(\eta^5-C_5H_6Me)(CO)_3$}. This bond is assigned to ionisations from the predominantely metal levels. Similar ionisation energies are found for the analogous cyclopentadienyl complexes which have a vertical ionisation potential of 8.05eV for {$Mn(\eta^5-C_5H_5)(CO)_3$}[109a] and for {$Mn(\eta^5-C_5H_4Me)(CO)_3$} 7.89 and 8.23eV.[109b] As expected from the similar electronic structures, the η^5-cyclohexadienyl-and η^5-cycloheptadienyltricarbonylmanganese complexes are also in the same range of energies as described in Table 8.

The second ionisation band occurs at 9.02eV and 8.72eV for the pentadienyl and methylpentadienyl complexes respectively. This is associated with the orbital resulting from the bonding interaction between the π_3 ligand orbital $\left[a' (e_1'')\right]$ and the metal dxz orbital, as was predicted from the theoretical analysis.

A marked increase in the intensity of the first ionisation band relative to the second band, when the ionising radiation is changed from He(I) to He(II) also confirms these assignments. Figure 3 illustrates the differences in relative band intensities in the He(I) and He(II) spectra of $\{Mn(\eta^5\text{-}C_5H_7)(CO)_3\}$. The relative area under some bands of the complexes are reported in Table 9.

The third ionisation bands, a little above than 10eV, represent the π_2 ligand orbitals $\{a''\ (e_1'')\}$.

The broad intense bands occurring with ionisation potentials higher than 12eV, have been attributed to the ionisation from the σ-structure of the organic ligand, and from the carbonyl 5σ and 1π orbitals. These bands are common in photoelectron spectra of organometallic compounds and very few deductions have been made from them, due to the large number of overlapping ionisations.[108c]

The methyl derivative displays some additional ionisation structure around 12eV, similar to several cyclopentadienyl methylated complexes of the type $\{Mn(\eta^5\text{-}C_5H_{5-n}Me_n)(CO)_3\}$ (n=0,1,5).[109b] (Figure 4).

The He(I) and He(II) spectra of $\{Re(\eta^5\text{-}C_5H_7)(CO)_3\}$ (Figure 5) have the same general features as the manganese analogue, except for the considerable splitting observed in the lowest energy ionisation band (8.05, 8.36 and 8.67eV). A similar pattern has been observed for the analogous cyclopentadienyl complex $\{Re(\eta^5\text{-}C_5H_5)(CO)_3\}$ (8.05, 8.44 and 8.72 eV),[109] and it is attributed to spin-orbit coupling in the third-row metal. Accordingly the assumption that these ionisations are associated primarily with the metal d electrons is reinforced. Moreover, another additional indication of high metal character in this ionisation is the increased relative intensity of this low energy ionisation band compared to the manganese analogue in the corresponding He(I) spectra. It has been observed that for photoionisation of the metal n d orbitals there is a significant increase in relative band intensity as the principal quantum number, n, increases. This trend is known as the "heavy atom effect".[108c]

The ionisation data and relative intensities of each band for the rhenium complex spectra are reported in Tables 8 and 9.

The second ionisation band at 9.25eV is to some extent overlapped by the ionisations from the d metal orbitals and is assigned in the same way as that of the pentadienylmanganese complexes. Low vertical ionisation potential values are found for these bands in all the η^5-pentadienyl complexes compared with the cyclic analogous complexes, as expected from the splitting of the e_1'' levels in the pentadienyl ligand.

The ionisation at 10.7eV is associated again with the π_2 ligand orbital a" (e_1''). A shoulder at 12.1eV can perhaps be assigned to ionisation from the π_1 orbital. Higher ionisation potentials represent the deeper σ levels.

Considering that no appreciable change is expected for the decrease in symmetry of the dicarbonyl substituted fragment{$Mn(CO)_2P(OMe)_3$} compared to $Mn(CO)_3$ we assigned the He(I) and He(II) photoelectron spectra according to the suitable molecular orbital diagram

TABLE 8

He(I) IONISATION DATA[a] FOR THE COMPLEXES $\{M(\eta^5\text{-}C_5H_6R)(CO)_3\}$

COMPLEX	TYPE OF ORBITAL				
	Nonbonding metal			π ligand	
	Band 1			Band2	Band 3
$\{Mn(\eta^5\text{-}C_5H_7)(CO)_3\}$	8.07			9.02	10.39
$\{Mn(\eta^5\text{-}C_5H_6Me)(CO)_3\}$	7.77	8.0		8.72	10.11
$\{Re(\eta^5\text{-}C_5H_7)(CO)_3\}$	8.05	8.36	8.67	9.25	10.70
$\{Mn(\eta^5\text{-}C_5H_7)(CO)_2P(OMe)_3\}$	7.16	7.59		8.42	9.94
$\{Mn(\eta^5\text{-}(C_6H_7))(CO)_3\}^b$	8.06			8.59	10.25
$\{Mn(\eta^5\text{-}(C_7H_9))(CO)_3\}^b$	7.86	8.10		8.67	9.97

a) Ionisation potentials in eV. b) Reference 106.

TABLE 9

RELATIVE BAND INTENSITIES FOR {$M(\eta^5-C_5H_6R)(CO)_3$}

COMPLEX	BAND	He(I)		He(II)	
		Distribution (%)	Relative area[a]	Distribution (%)	Relative area[a]
{$Mn(\eta^5-C_5H_7)(CO)_3$}	1	48.1	1	54.2	1
	2	25.0	0.52	24.6	0.45
	3	26.9	0.56	21.2	0.39
{$Mn(\eta^5-C_5H_6Me)(CO)_3$}	1	46.2	1	53.3	1
	2	27.4	0.59	22.8	0.43
	3	26.4	0.57	23.9	0.45
{$Re(\eta^5-C_5H_7)(CO)_3$}	1	51.72	1	57.40	1
	2	26.30	0.51	26.62	0.46
	3	21.98	0.43	15.98	0.28
{$Mn(\eta^5-C_5H_7)(CO)_2P(OMe)_3$}	1	34.89	1	45.32	1
	2	25.53	0.73	26.45	0.58
	3	39.57	1.13	28.22	0.62

a) Relative to the lowest ionisation potential.

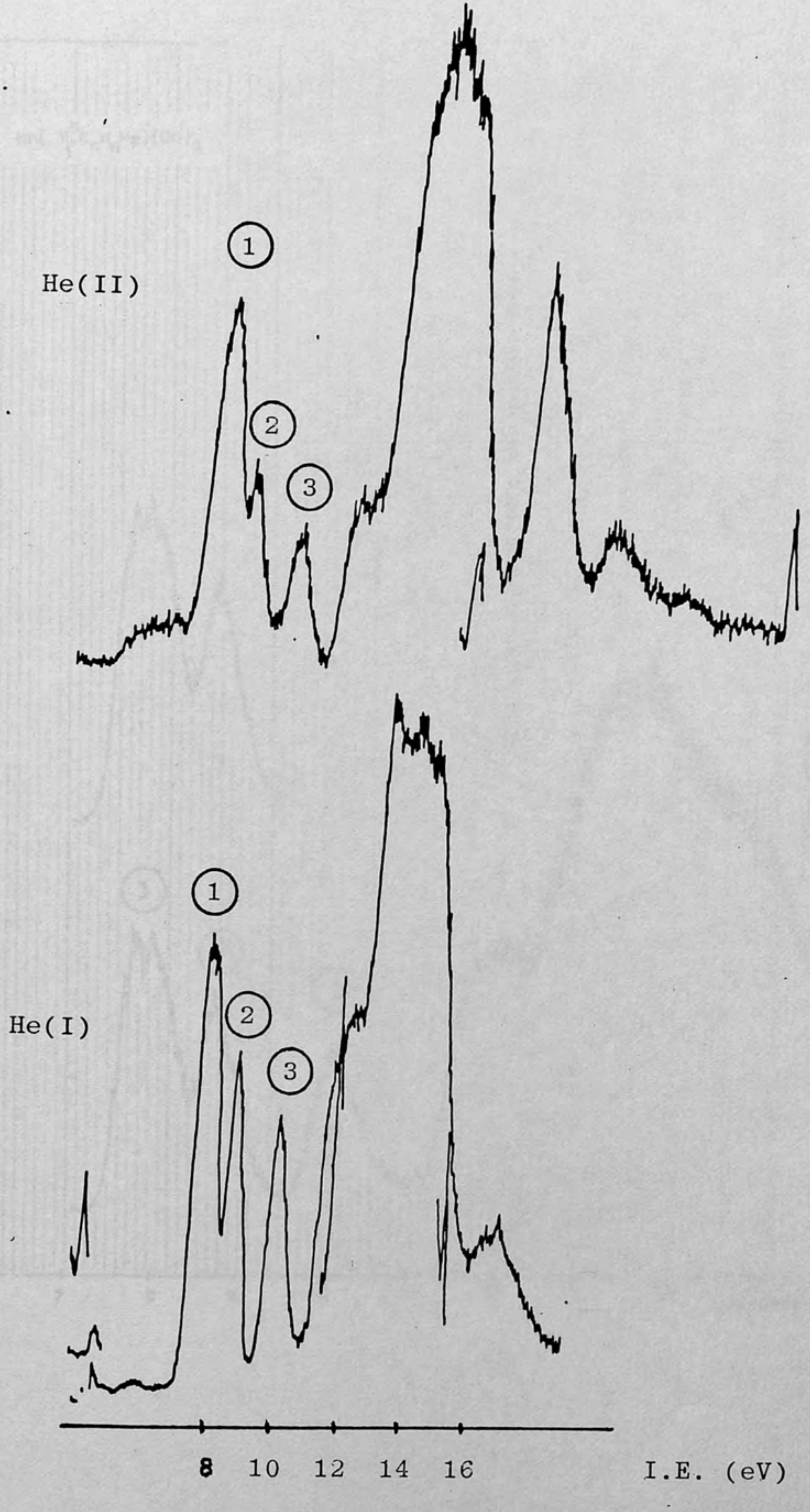


Figure 3. The photoelectron spectra of $\{Mn(\eta^5-C_5H_7)(CO)_3\}$

Figure 4a. He(I) photoelectron spectrum of methylpentadienyltricarbonylmanganese. (22).

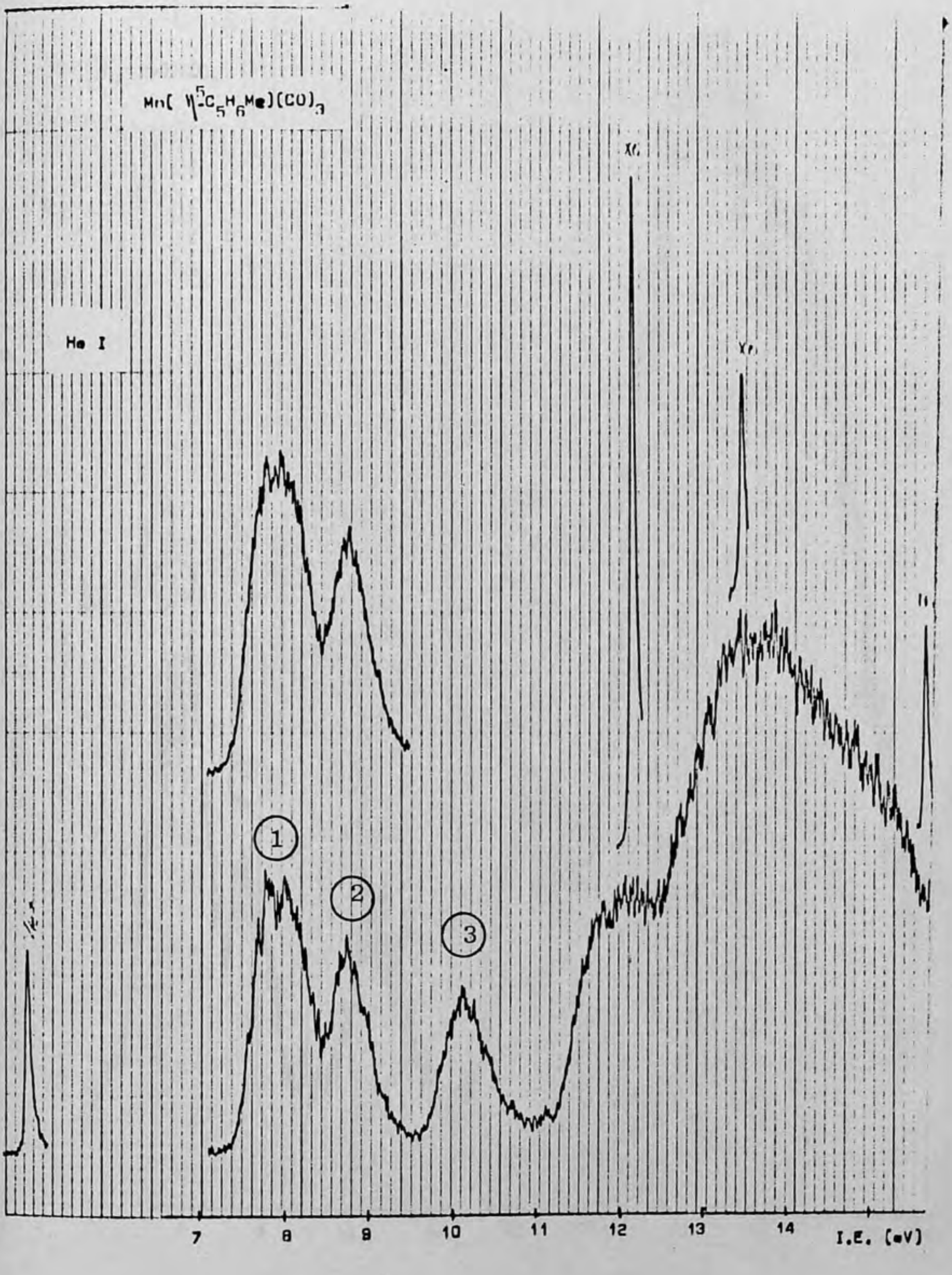


Figure 4b. He(II) photoelectron spectrum of methylpentadienyltricarbonylmanganese (22).

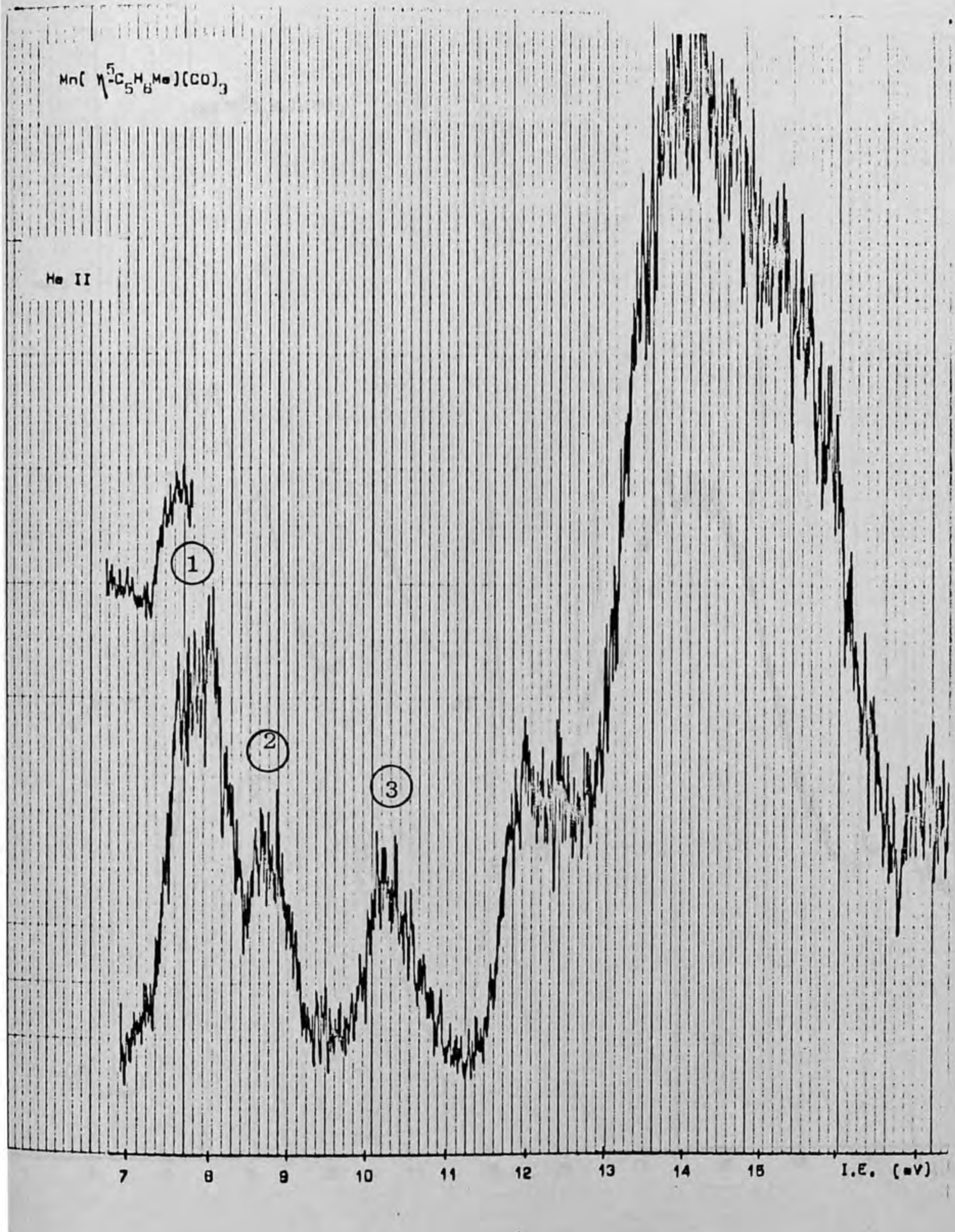


Figure 5a. He(I) photoelectron spectrum of pentadienyltricarbonylrhenium (24).

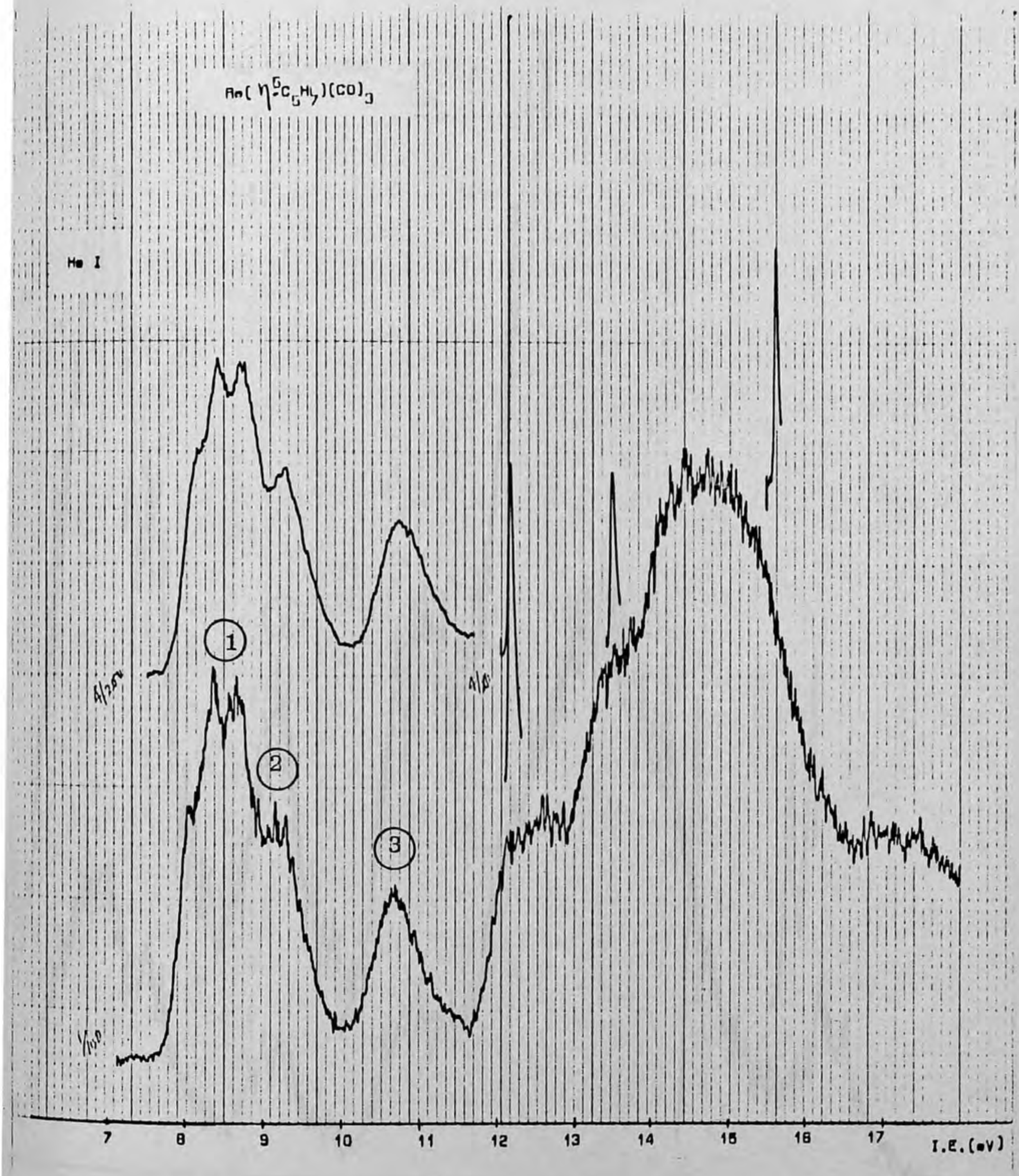
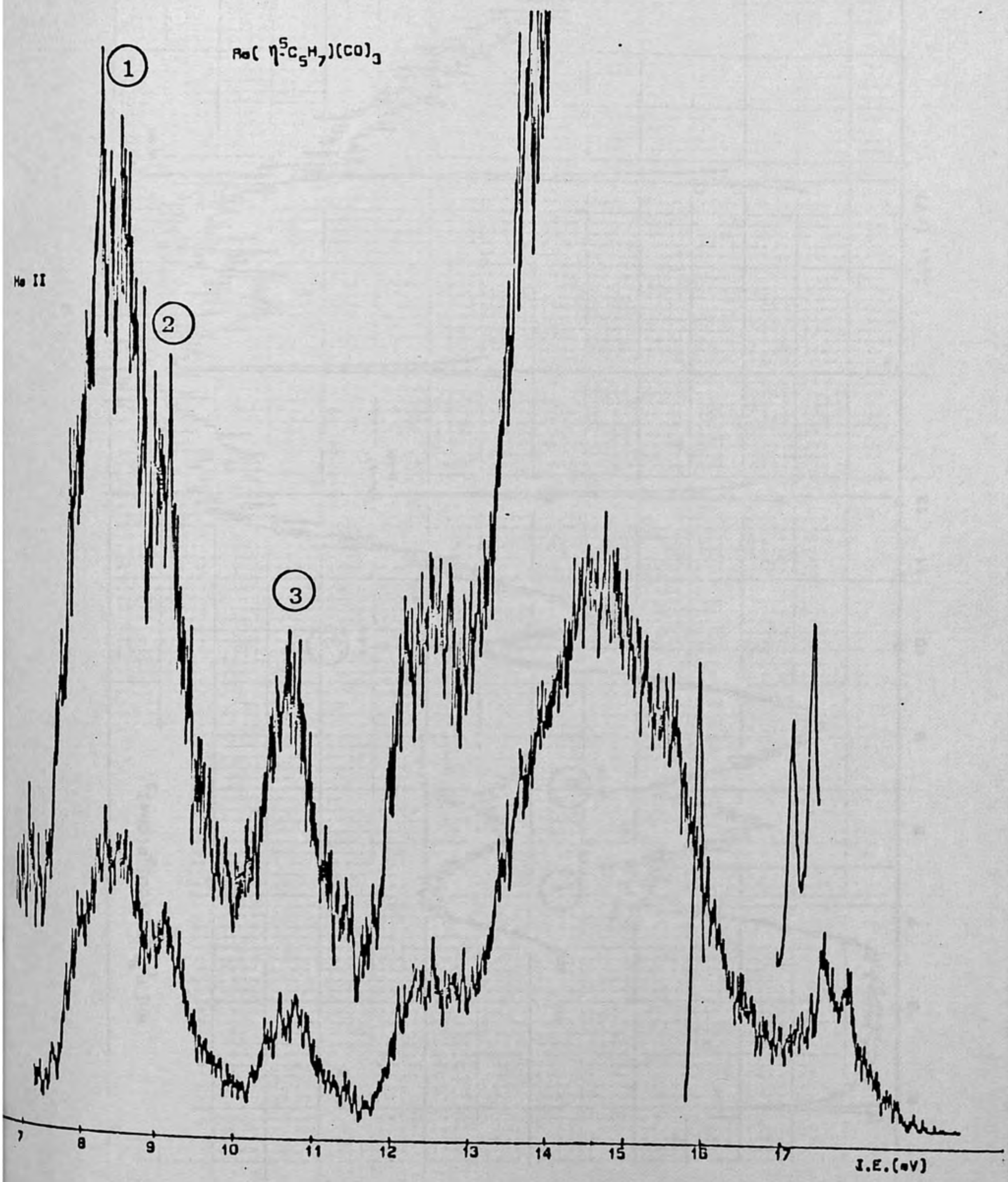


Figure 5b. He(II) photoelectron spectrum of pentadienyltricarbonylrhenium (24).



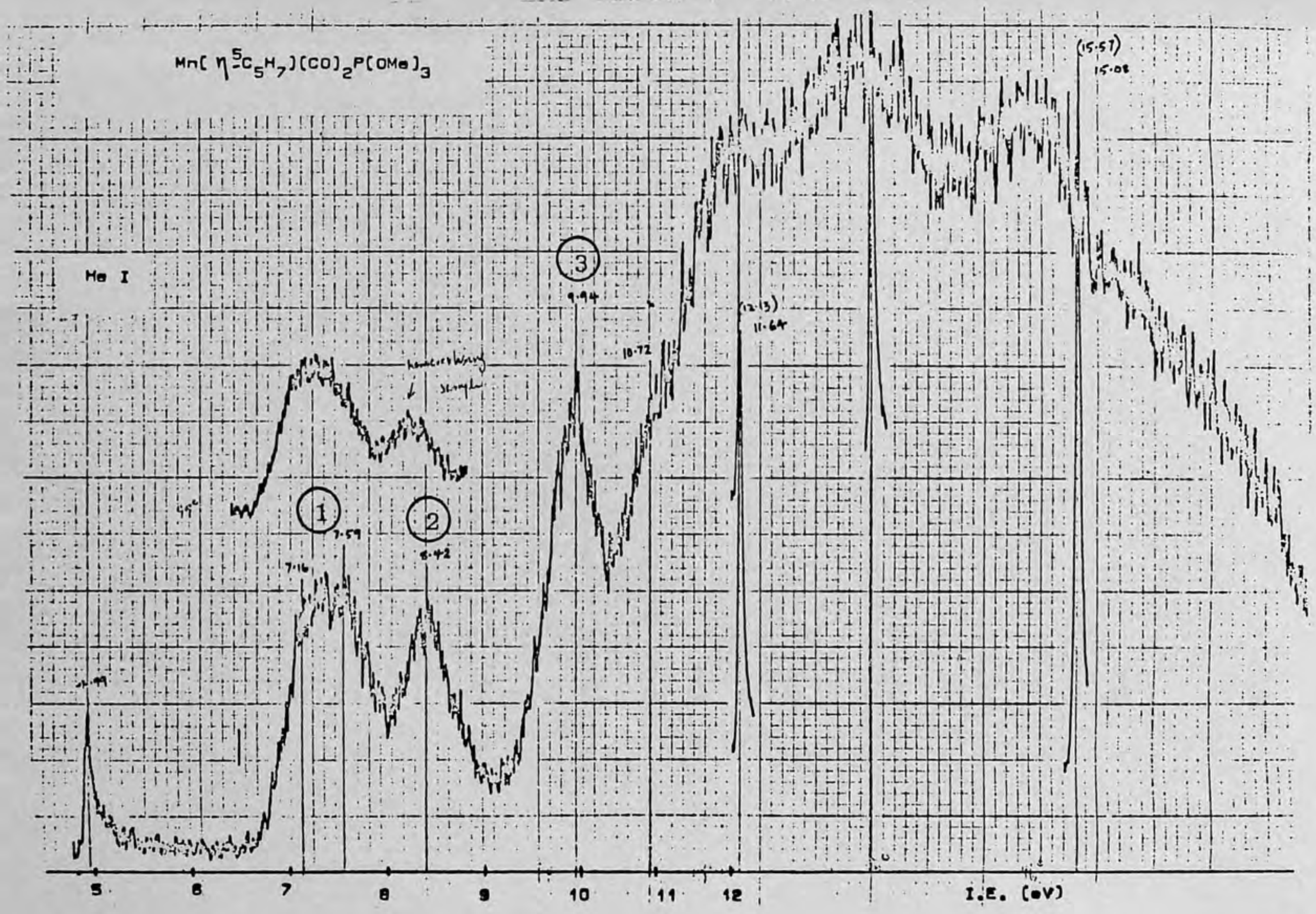


Figure 6a. He(I) photoelectron spectrum of pentadienylcarbonyl(trimethylphosphite)manganese

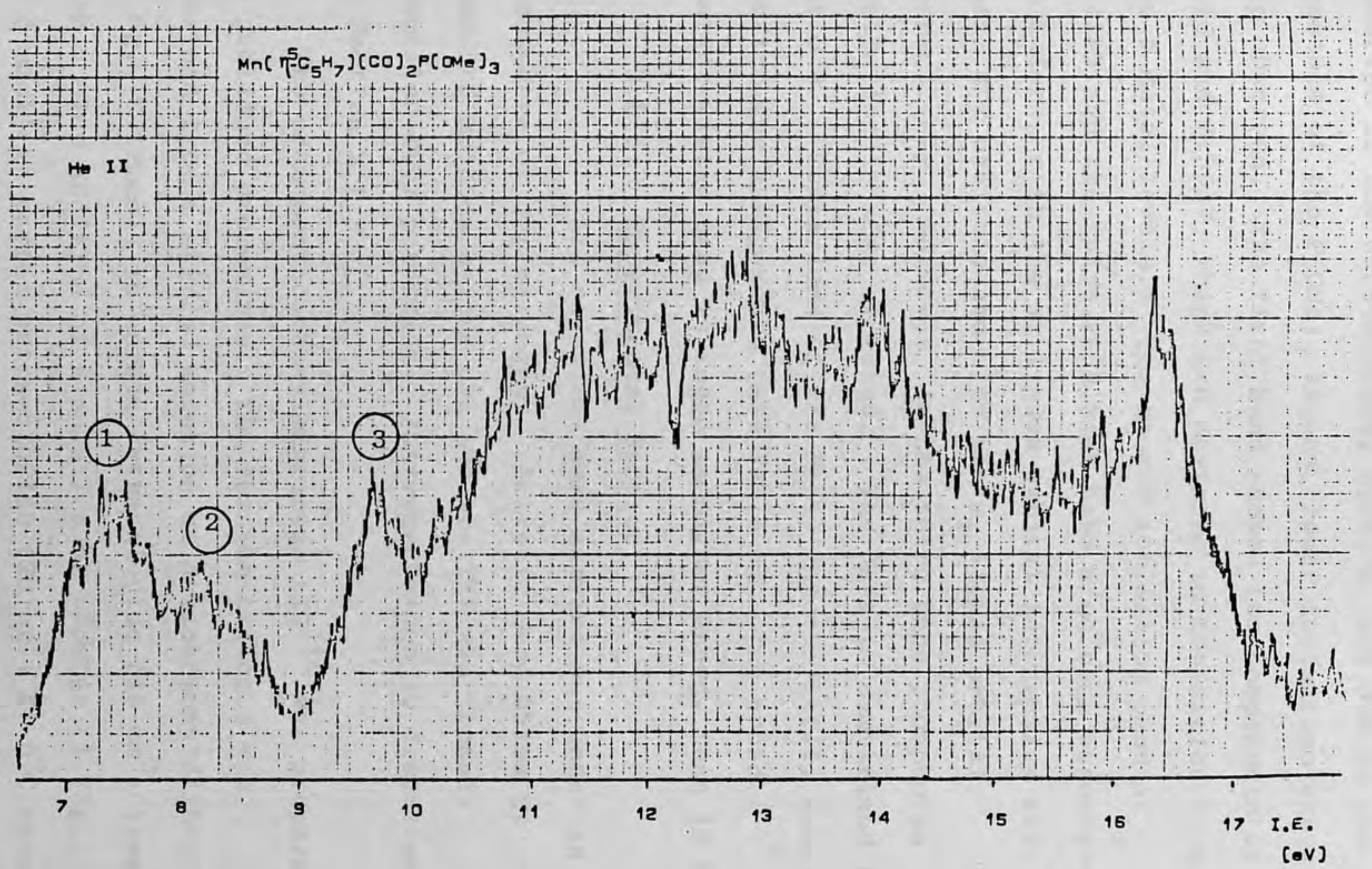


Figure 6b. He(II) photoelectron spectrum of pentadienyldicarbonyl(trimethylphosphite)-manganese.

described in Scheme 9 (Figure 6). A similar pattern is observed in the corresponding spectra, but due to the presence of the $P(OMe)_3$ ligand, lower ionisation energies are observed. The first band showed two components at 7.16 and 7.59eV, which are assigned to ionisation from the d metal levels. The second ionisation band at 8.42eV and the third at 9.94eV have also been associated, as before, with the π_3 ligand orbital interacting with the metal dxz orbitals and with the π_2 ligand orbital, respectively. Moreover, in the third band phosphorus ionisation is also expected. The data is summarised in Table 8. Comparison of the He(I) and the He(II) spectra confirm the assignments (see Table 9). The broad characteristic band is found at higher energy than 10.5eV.

2.2.3. Experimental Section.

All reactions were carried out under an atmosphere of dry nitrogen. Solvents were dried by standard methods before use and the THF was freshly distilled from potassium. Instrumentation is described in Section 2.1.3.

The bromopentacarbonylmanganese (I)[110] was prepared by published procedures. The rhenium analogue was obtained from a stirred solution of decacarbonyldirhenium (5.3g., 8.12mmol) in carbon tetrachloride (45 cm^3) treated with a slow addition of a solution of bromine (1.73g., 10.8 mmol) in carbon tetrachloride (20 cm^3) at 0^oC under nitrogen. The temperature of the reaction mixture was allowed to rise to room temperature and stirring continued for a further 2h. Carbon tetrachloride and excess of bromine were removed under reduced pressure. Recrystallisation was carried out from chloroform/light petroleum 40-60°C) yielding white crystals of bromopentacarbonylrhenium (I) in 83% yield. This preparation was kindly given by Professor E.W.Abel.

The pentadienylorganotin derivatives were prepared as described in the last section 2.1.3.

General method of preparation of the complexes $\{M(\eta^5\text{-}C_5H_6R)(CO)_3\}$ $\{M=Mn, R=H, CH_3 : M=Re, R=H\}$ using the tributyltin derivatives.

The corresponding $MBr(CO)_5$ (14.5mmol) in THF (100 cm^3) was heated under reflux with 2,4-pentadienyltributyltin or 2,4-hexadienyltributyltin (14.5 mmol) until no further change in the infrared spectrum of the mixture was observed (3h. M=Mn, R=H; 3½ h. M=Mn, $R=CH_3$; 9 h. M=Re,R=H). During this time the colour of the solution changed from orange to orange-yellow and from colourless to slight yellow from the manganese and rhenium complexes respectively. The solution was evaporated to small bulk and filtered from a cream-white precipitate. The filtrate was taken up in hexane and chromatographed on alumina using light petroleum (b.p. below 40°C). The first colourless (rhenium) or yellow (manganese) band was collected and the solution evaporated in vacuo to small volume, cooling and filtration afforded the corresponding complex. Purification by sublimation could be carried out at room temperature and 0.1mm Hg (manganese complexes) or at 60°C at 0.03mm Hg (rhenium complex). Physical properties and experimental yields are given in the Table 4 .

General method of preparation of the complexes $\{M(\eta^5\text{-}C_5H_6R)(CO)_3\}$ $\{M=Mn, R=H, CH_3\}$ using the trimethyltin derivatives.

A similar procedure to that above with reflux times of 2½h M=Mn, R=H and 4h. M=Mn, R=CH_3 and the same colour characteristics mentioned before, were observed. The solution was evaporated to small bulk (40 cm^3) and deaerated distilled water (2 x 30 cm^3) was added. A yellow-orange oil separated which was extracted with 50 cm^3 of diethyl ether and dried with anhydrous magnesium sulphate. After filtration and evaporation at reduced pressure a yellow oil is obtained, which can be recrystallised from light petroleum (b.p. below 40°C) on cooling or can be sublimed at room temperature and 0.05 mm Hg. The low melting point methyl complex was also chromatographed on alumina with light petroleum (b.p. below 40°C), because recrystallisation is not easy and an impure product is obtained from sublimation.

Preparation of the complex $\{Mn(\eta^5\text{-}syn\text{-}syn,\text{-}1,5\text{-}Ph_2C_5H_5)(CO)_3\}$

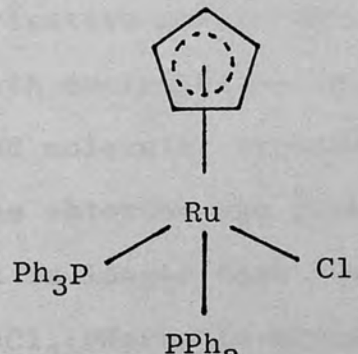
Bromopentacarbonylmanganese (3.18g., 11.57mmol) in THF (100 cm^3) was heated under reflux with $\{Me_3Sn(1,5\text{-}Ph_2C_5H_5)\}$ (4.44g. 11.6 mmol) for 6h. The red solution was evaporated and benzene (30 cm^3) was added. Filtration of a pale yellow solid was carried out and the orange filtrate was taken up in deaerated distilled water ($2 \times 25\ cm^3$), dried with anhydrous magnesium sulphate and then filtered off. The evaporation of the solvent under reduced pressure to small volume gave a pale-orange powder (with a broad $\nu(CO)(1920\text{-}1990\ cm^{-1})$ region in the spectrum) which was filtered and chromatography on alumina with benzene afforded a yellow solution that was evaporated and recrystallised from benzene/hexane giving the crystalline pale yellow title compound.

Several attempted reactions with the organotin reagents with various metal carbonyl halides are described in the experimental section 2.3.3.

2.3. An η^3-pentadienyl complex of ruthenium.

2.3.1. Introduction.

Treatment of $\{RuCl_2(PPh_3)_3\}$ with cyclopentadiene in benzene yields yellow crystals of $\{RuCl(\eta\text{-}C_5H_5)(PPh_3)_2\}$ (29) in 60% yield according to work reported by Gilbert and Wilkinson in 1969.[111]



(29)

Subsequent studies of this complex have been carried out by Bruce and Stone,[112] who showed that it is a rich source of unusual chemistry.

They found that this triphenylphosphine derivative shows two types of reactions:

a) Reactions involving the Ru-Cl bond. Replacement of the Cl atom by anionic reagents as R $\{R=H, Me, C_6F_5, SnCl_3, I\}$ giving $\{Ru\ R\ (\eta-C_5H_5)(PPh_3)_2\}$, and also by neutral ligands with the formation of cations $\{Ru\ L(\eta-C_5H_5)(PPh_3)_2\}^+\{L=CO, MeCN\}$[112,113]

A comparative study of the reactivity of $\{RuCl(\eta-C_5H_5)(PPh_3)_2\}$ and $\{RuCl(CO)_2(\eta-C_5H_5)\}$[114] towards certain nucleophiles was carried out by Haines,[115] with the object of establishing the influence of the CO and PPh_3 ligands in these complexes. $\{RuCl(CO)_2(\eta-C_5H_5)\}$ shows no evidence for dissociation in alcohol, while $\{RuCl(\eta-C_5H_5)(PPh_3)_2\}$ reveals considerable ionic behaviour, whereas the equilibrium:

$$\{RuCl(\eta-C_5H_5)L_2\} + CH_3OH \rightleftharpoons \{Ru(CH_3OH)(\eta-C_5H_5)L_2\}^+ + Cl^-$$

lies far to the left for L=CO and it is considerably more to the right for $L=PPh_3$. Consistent with this, the triphenylphosphine derivative reacts more readily than the carbonyl complex with nucleophiles in alcohol.

The crystal and molecular structure shows that the distance between the chlorine and ruthenium atoms is $2.453(2)A^o$,[116] that is longer than found in $\{RuCl_2(PPh_3)_3\}$ $\{2.387(7)A^o,\}$[117] $\{RuCl_2(PMePh_2)(\eta\text{-arene})\}$ $\{2.41-2.415A^o\}$[118]; but similar to those found in $\{RuCl_2(dmppe)_2\}$ $\{2.438A^o\}$

(dmppe=$PhMeP(CH_2)_2PMePh$).[119] This is consistent with the tendency to lose chloride ion.

b) Reactions involving ligand displacement: Replacement of one of the phosphine ligands by L', to give {$RuCl(\eta\text{-}C_5H_5)$ L L'} {where L=PPh_3, L'=CO, PMe_2Ph, PMe_3}[112, 116], or in some cases the replacement of both phosphine ligands by L' {where L'=PMe_3,[116] $P(OPh)_3$[120]}, yielding {$RuCl(\eta\text{-}C_5H_5)L'_2$}.

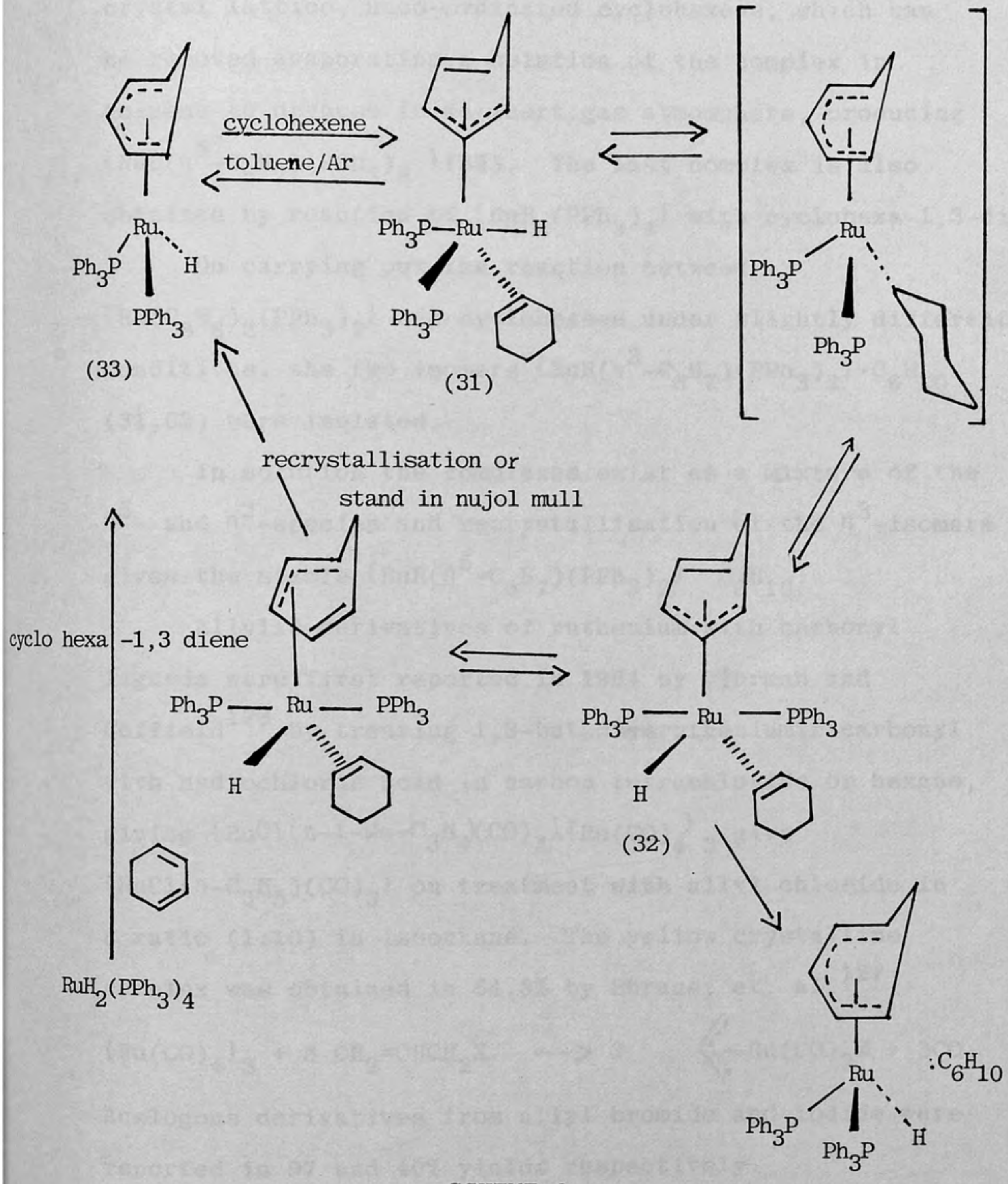
Evidence of the lability of one PPh_3 ligand is the high relative abundance of the ion $\{Ru(\eta\text{-}C_5H_5)(PPh_3)\}^+$ in the mass spectra of {Ru $X(\eta\text{-}C_5H_5)(PPh_3)_2$} complexes; according to Bruce's studies this is often the most abundant metal-containing ion.[116] These studies on ligand substitution revealed that the triphenylphosphine in compounds of the type {$RuCl(\eta\text{-}C_5H_5)(PPh_3)_2$} is labile and readily removed and this has led to the synthesis of a number of novel derivatives.

Similar ruthenium complexes containing different phosphines such as PPh_2Me, $P(OMe)_3$ and $AsPh_3$ were obtained by reacting compounds related to {$RuCl_2(PPh_3)_3$} and cyclopentadiene.[112] Owing to the smaller size of the PMe_3 ligand {$RuCl(\eta\text{-}C_5H_5)(PMe_3)_2$} is highly reactive towards unsaturated molecules, affording cationic complexes {Ru L $(\eta\text{-}C_5H_5)(PMe_3)_2$} PF_6 {L=olefin, allene, diene, alkyne, CS_2} in reactions carried out in the presence of NH_4PF_6.[121,122]

η^5-Cyclohexadienyl complexes of ruthenium are well-known and may be formed by nucleophilic attack of hydride on coordinated η-benzene complexes such as $\{Ru(\eta^6-C_6H_6)_2\}^{2+}$ 21b and $\{Ru(\eta^6-C_6H_6)(PR_3)(N\text{-}N)\}^{2+}$ 123,124 giving $\{Ru(\eta^5-C_6H_7)_2\}$ and the cationic complexes $\{Ru(\eta^5-C_6H_7)(PR_3)(N\text{-}N)\}PF_6$ $\{PR_3=PMe_2Ph, PMePh_2; (N\text{-}N)=$ 2,2'-bipyridyl, 1,10-phenanthroline$\}$.

An interesting reaction has also been reported in 1978 by Chaudret and Wilkinson,[125] between the styrene complex $\{Ru(C_8H_8)_2(PPh_3)_2\}$ and cyclohexene, giving several products that proved to be: $\{RuH(\eta^5-C_6H_7)(PPh_3)_2\}.C_6H_{10}$ (30) and the two isomers of $\{RuH(\eta^3-C_6H_7)(PPh_3)_2\}.C_6H_{10}$ (31,32). (SCHEME 9).

These hydrido species are formed by reactions invoving hydride transfer from cyclohexene to ruthenium.


cyclohexene
toluene/Ar
Ph$_3$P
Ru
H
PPh$_3$
(33)
Ph$_3$P—Ru—H
Ph$_3$P
(31)
Ru
Ph$_3$P
Ph$_3$P
recrystallisation or
stand in nujol mull
cyclo hexa -1,3 diene
Ph$_3$P—Ru—PPh$_3$
H
Ph$_3$P—Ru—PPh$_3$
H
(32)
RuH$_2$(PPh$_3$)$_4$
Ru
:C$_6$H$_{10}$
Ph$_3$P
Ph$_3$P
H
(30)

SCHEME 9

The most stable compound isolated was the η^5-cyclohexadienyl species (30) that contains in the crystal lattice, unco-ordinated cyclohexene, which can be removed evaporating a solution of the complex in toluene to dryness in an inert gas atmosphere, producing $\{RuH(\eta^5-C_6H_7)(PPh_3)_2\}$(33). The last complex is also obtained by reaction of $\{RuH_2(PPh_3)_4\}$ with cyclohexa-1,3-diene.

On carrying out the reaction between $\{Ru(C_8H_8)_2(PPh_3)_2\}$ and cyclohexene under slightly different conditions, the two isomers $\{RuH(\eta^3-C_6H_7)(PPh_3)_2\}\cdot C_6H_{10}$ (31,32) were isolated.

In solution the complexes exist as a mixture of the η^5- and η^3-species and recrystallisation of the η^3-isomers gives the stable $\{RuH(\eta^5-C_6H_7)(PPh_3)_2\}\cdot C_6H_{10}$.

Allylic derivatives of ruthenium with carbonyl ligands were first reported in 1964 by Ihrman and Coffield[126] by treating 1,3-butadienerutheniumtricarbonyl with hydrochloric acid in carbon tetrachloride or hexane, giving $\{RuCl(\eta-1-Me-C_3H_4)(CO)_3\}$.$\{Ru(CO)_4\}_3$ gave $\{RuCl(\eta-C_3H_5)(CO)_3\}$ on treatment with allyl chloride in a ratio (1:10) in isooctane. The yellow crystalline complex was obtained in 64.5% by Sbrana, et. al.[127]

Analogous derivatives from allyl bromide and iodide were reported in 97 and 40% yields respectively.

The (η-allyl) tricarbonylchlororuthenium(II) is an effective catalyst for homogeneous oligomerisation and isomerisation of olefins.[128] Reaction with unsaturated substrates can be explained, as occurring through a η-σ perturbation of the η-allyl group and formation of highly reactive σ-allyl species which may undergo insertion reactions of the substrate coordinated to the metal.

The analogous bromo allylic complex is a good precursor to other allylic complexes, reacting with organotin compounds such as allyl-, cyclopentadienyl- and indenyltrimethyltin in refluxing THF to afford the corresponding η-enyl metal carbonyl derivatives.[62a] (SCHEME 10).

Starting Material	Organotin compound	Product	Yield
$\{RuBr(\eta\text{-}C_3H_5)(CO)_3\}$	$Me_3SnC_3H_5$	$\{Ru(\eta\text{-}C_3H_5)_2(CO)_2\}$	83%
	$Me_3SnC_5H_5$	$\{Ru(\eta\text{-}C_3H_5)(\eta\text{-}C_5H_5)(CO)\}$	36%
		$\{Ru(\eta\text{-}C_3H_5)_2(CO)_2\}$	20%
		$\{RuBr(\eta\text{-}C_5H_5)(CO)_2\}$	10%
		$\{Ru(\eta\text{-}C_5H_5)(CO)_2\}_2$	3%
		$\{Ru(\eta\text{-}C_5H_5)(CO)_2SnMe_3\}$	2%
	$Me_3SnC_9H_7$	$\{Ru(\eta\text{-}C_3H_5)(\eta\text{-}C_9H_7)(CO)\}$	77%

SCHEME 10

Reaction with cyclopentadienyl trimethyltin reagent produced a mixture of five products (Scheme 10), in which the yield of $\{Ru(\eta\text{-}C_3H_5)(\eta\text{-}C_5H_5)(CO)\}$ is substantially reduced, mainly by the competitive formation of the bisallyl derivative.

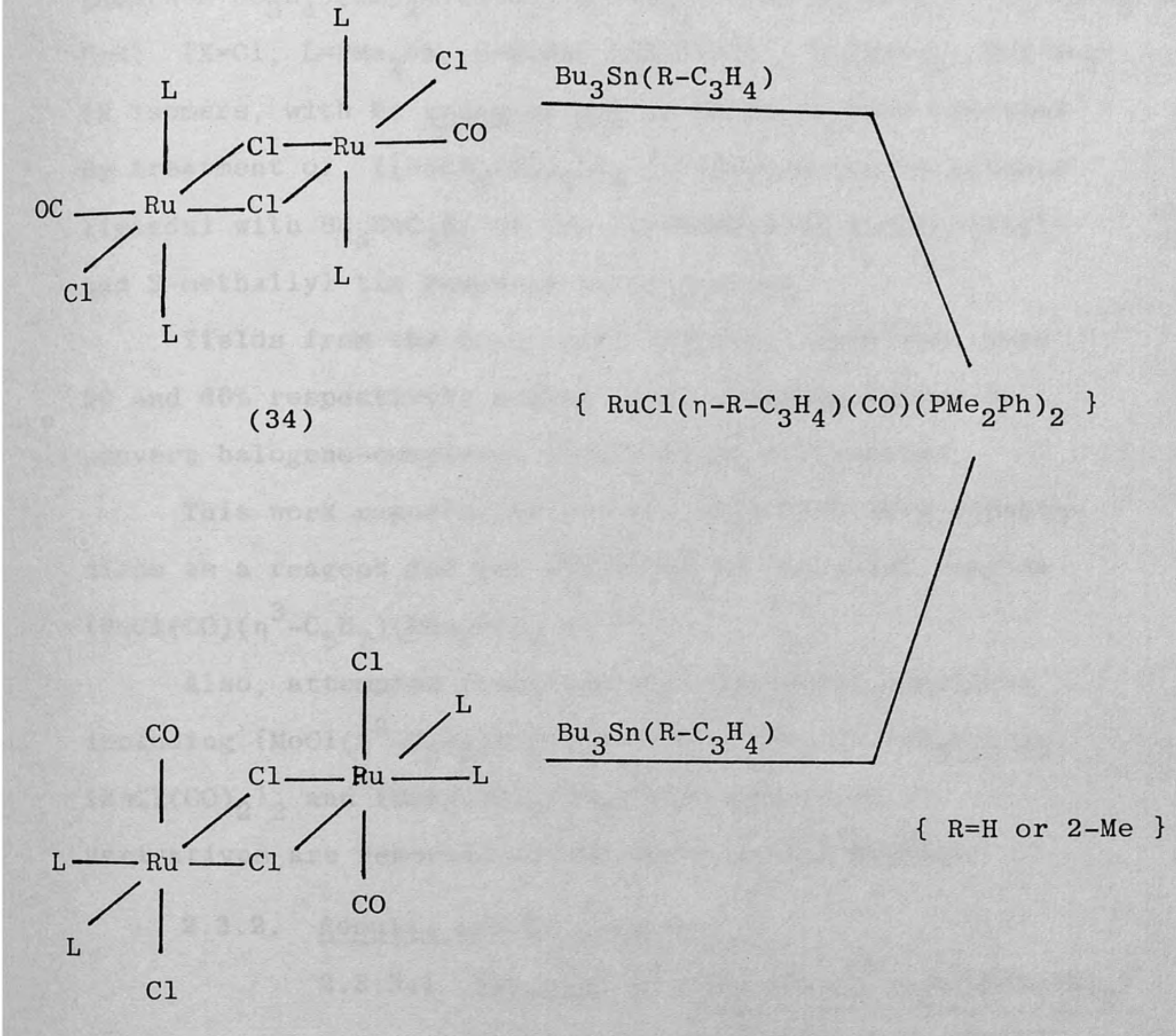
The use of allyltrimethyltin reagent has been shown to be a better synthetic method for the bis-allyl ruthenium complex, than reaction of the same starting material with sodium amalgam in THF followed by allyl bromide which gave a 40% yield.[129]

Organotin reagents reacting with other ruthenium complexes such as $\{RuCl_2(CO)_3\}_2$ and $\{RuBr(\eta\text{-}C_5H_5)(CO)_2\}$ gave mixtures of products and very low yields of the respective allyl- and cyclopentadienyl derivatives.

However, under phase transfer catalysis treatment of $\{Ru(Br)(\eta\text{-}C_5H_5)(CO)_2\}$ with allyl bromide or 2-methallyl chloride afford very high yields of the complexes $\{Ru(\eta\text{-}R\text{-}C_3H_4)(\eta\text{-}C_5H_5)(CO)\}$ {R=H or 2-Me} respectively according to a recent report by Gibson,et.al.[130]

Considering the reactivity and catalytic properties of $\{RuX(\eta\text{-}C_3H_5)(CO)_3\}$ {X=Cl,Br}, Mawby et.al.[131] investigated the influence of stronger donor ligands instead of some carbonyl groups.

The preparation of $\{RuCl(\eta\text{-}R\text{-}C_3H_4)(CO)L_2\}$ $\{L=PMe_2Ph$, R=H or 2-Me} was achieved by reacting either of two isomers of $\{[RuCl_2(CO)(PMe_2Ph)_2]_2\}$ (34,35) with organotin allyls in chloroform (SCHEME 11).



(34)

(35)

(L = PMe_2Ph)

SCHEME 11.

Similarly, the dicarbonyl complexes $\{RuX(\eta\text{-}R\ \text{-}C_3H_4)(CO)_2L\}\{X{=}Cl;\ L{=}PMe_2Ph,\ PMePh_2, PPh_3, AsPh_3, AsMe_2Ph;\ R{=}H\}$ $\{X{=}Cl;\ L{=}PMe_2Ph,\ R{=}2\text{-}Me\}$ and $\{X{=}Cl;\ L{=}PMePh_2;\ R{=}1\text{-}Me;$ (2 isomers, with Me *trans* or *cis* to $PMePh_2$)} were obtained by treatment of $\{[RuCl_2(CO)_2L]_2\}$ {L=phosphorus or arsenic ligands} with $Bu_3SnC_3H_5$ or the corresponding 1-methyallyl- and 2-methallyl tin reagents in propanone.

Yields from the mono- and dicarbonyl complexes were 50 and 60% respectively giving an alternative method to convert halogeno-complexes into η-allyl derivatives.

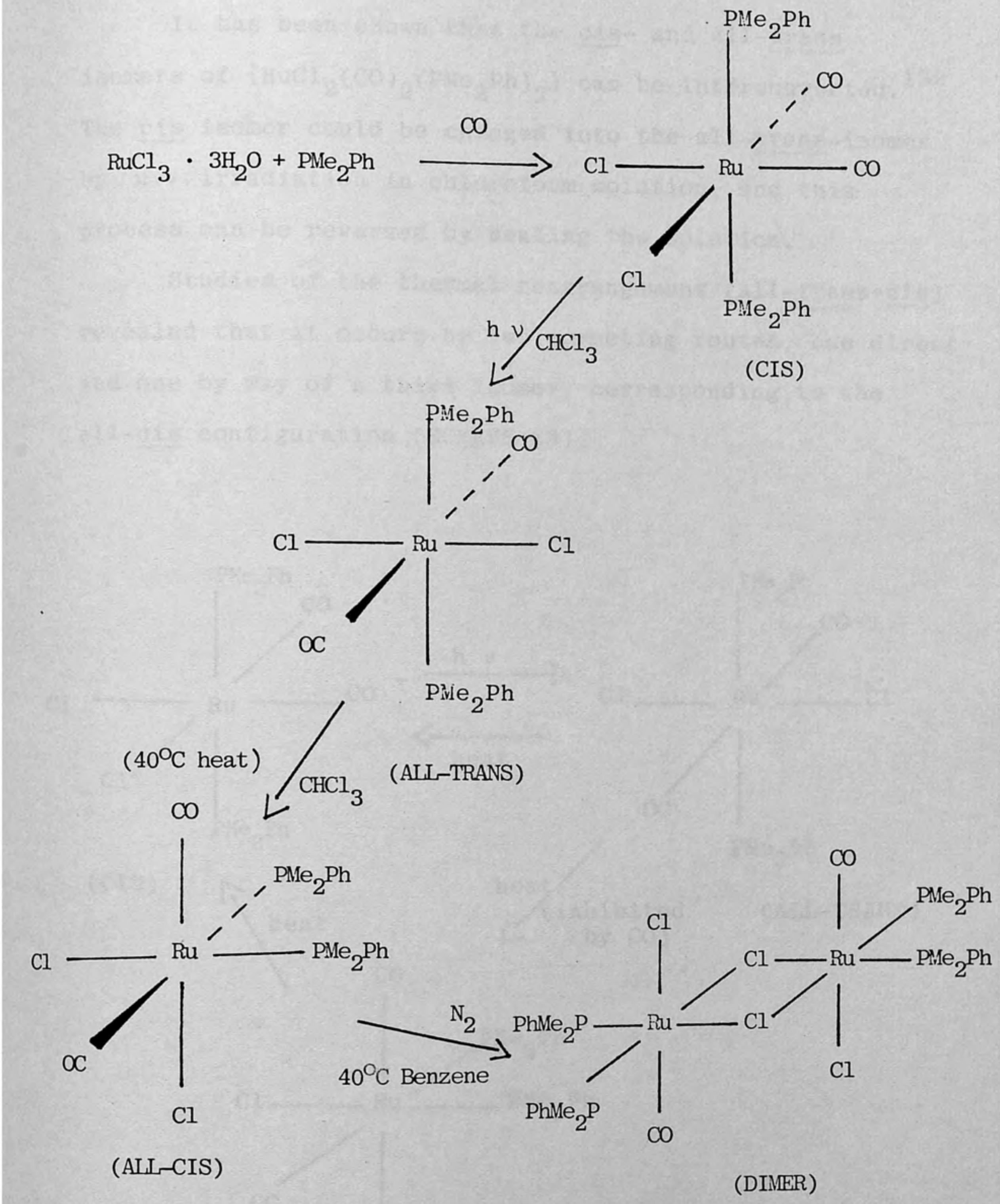
This work reports the use of 1-tributyltin-2,4-pentadiene as a reagent for the synthesis of the novel complex $\{RuCl(CO)(\eta^3\text{-}C_5H_7)(PMe_2Ph)_2\}$.

Also, attempted reactions with different complexes including $\{MoCl(\eta^3\text{-}C_3H_5)(CO)_2(MeCN)_2\}$, $\{RhCl(1,5\text{-}C_8H_{12})\}_2$, $\{RhCl(CO)_2\}_2$ and $\{MnBr(CO)_4PPh_3\}$ with organotin derivatives are reported in the experimental section.

2.3.2. Results and Discussion

2.3.2.1. The complex $\{RuCl(CO)(\eta^3\text{-}C_5H_7)(PMe_2Ph)_2\}$ Preparation properties and spectroscopic studies.

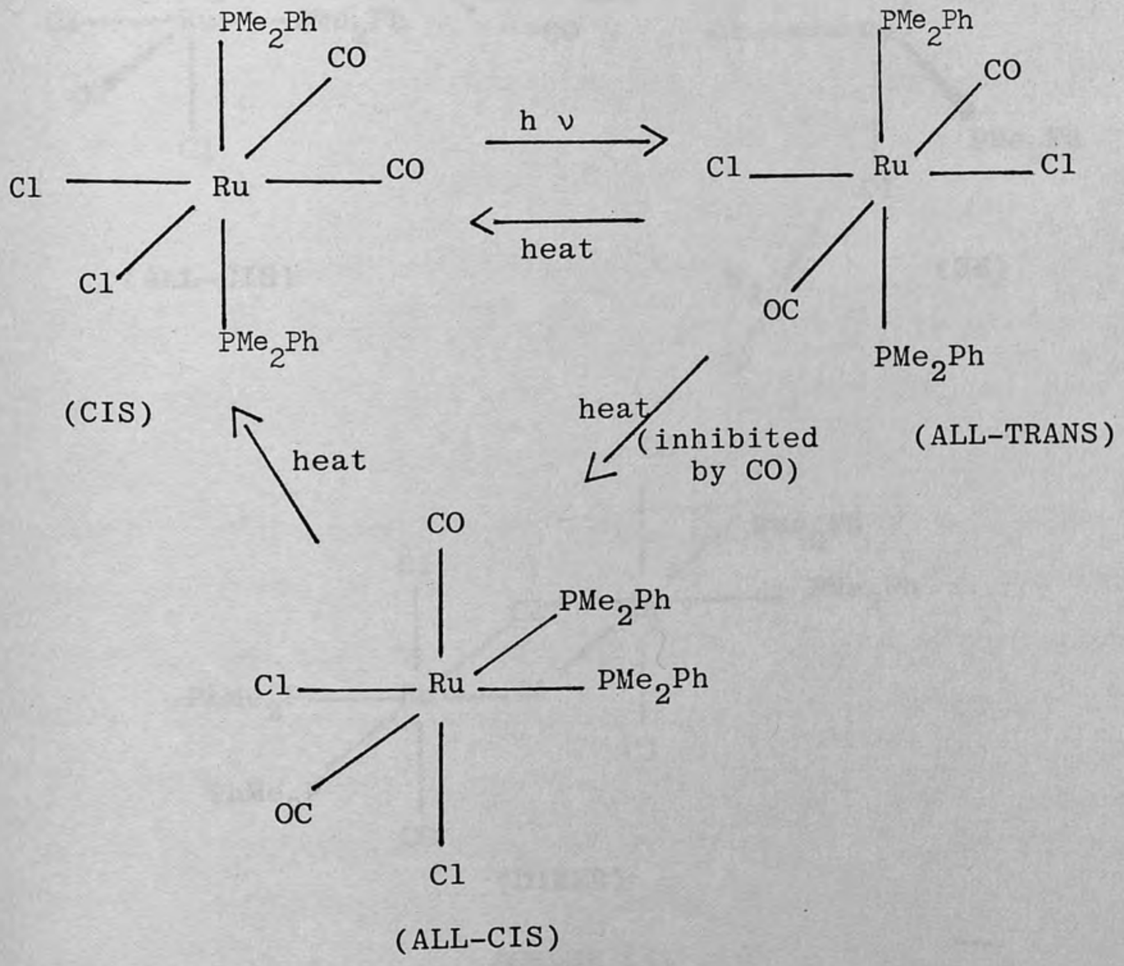
Based on Mawby's observations[131] that both *trans*- and all-*cis*- $\{RuCl_2(CO)_2(PMe_2Ph)_2\}$ complexes are not the best starting materials for the synthesis of η-allyl complexes of ruthenium(II) due to the side formation of a *cis*-unreactive isomer as a major product, the dimeric complex $\{[RuCl_2(CO)(PMe_2Ph)_2]_2\}$ was prepared by a sequence of four steps (SCHEME 12).


RuCl3 · 3H2O + PMe2Ph
CO
PMe2Ph
CO
Cl
Ru
CO
Cl
PMe2Ph
(CIS)
h ν
CHCl3
PMe2Ph
CO
Cl
Ru
Cl
OC
PMe2Ph
(ALL-TRANS)
(40°C heat)
CHCl3
CO
PMe2Ph
Cl
Ru
PMe2Ph
OC
Cl
(ALL-CIS)
N2
40°C Benzene
CO
PMe2Ph
Cl
Cl
Ru
PMe2Ph
PhMe2P
Ru
Cl
PhMe2P
CO
Cl
(DIMER)

SCHEME 12

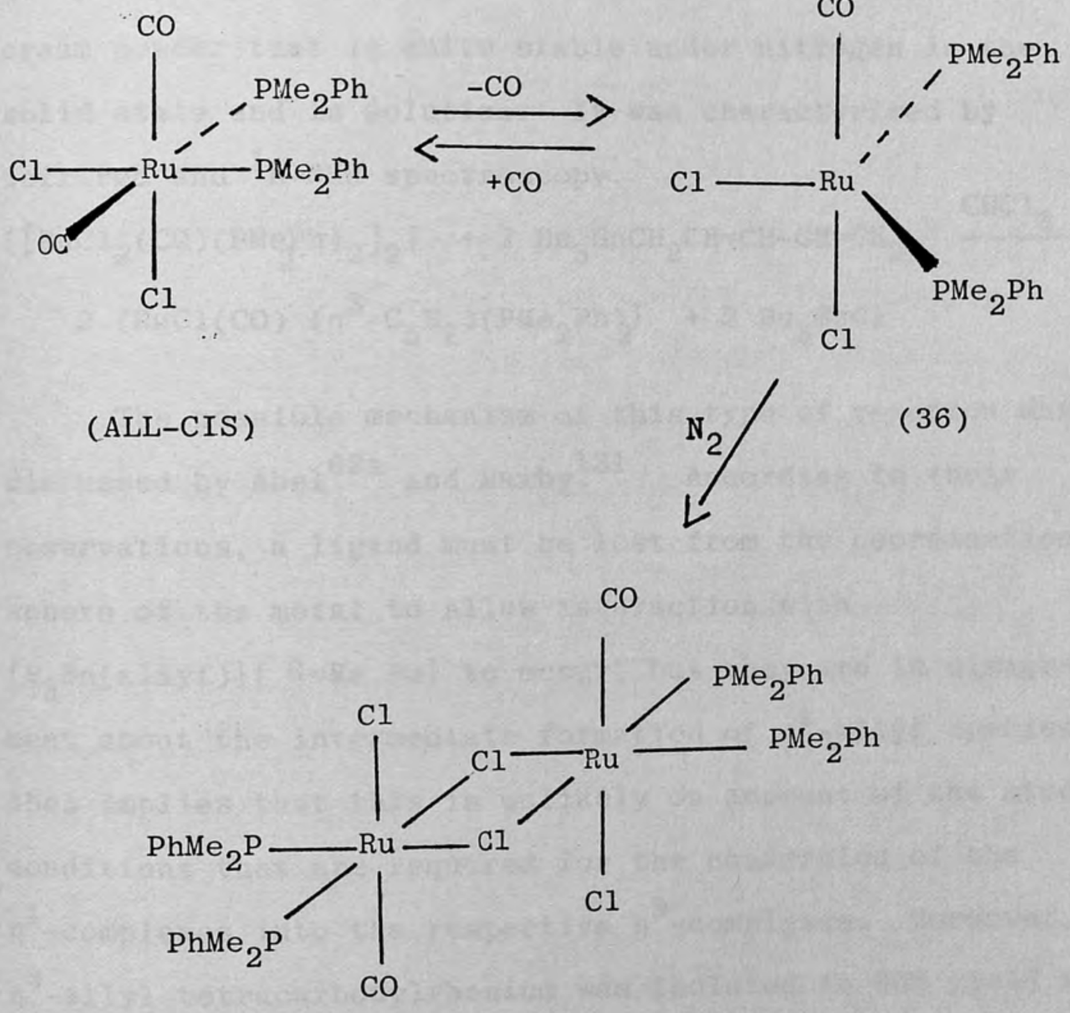
It has been shown that the *cis*- and all-*trans* isomers of $\{RuCl_2(CO)_2(PMe_2Ph)_2\}$ can be interconverted.[132] The *cis* isomer could be changed into the all-*trans*-isomer by u.v. irradiation in chloroform solution, and this process can be reversed by heating the solution.

Studies of the thermal rearrangement (all-*trans*→*cis*) revealed that it occurs by two competing routes, one direct and one by way of a third isomer, corresponding to the all-*cis* configuration (SCHEME 13).



SCHEME 13

Then, in order to avoid the competition in the reaction from the cis-isomer, the dimeric species $\{RuCl_2(CO)(PMe_2Ph)_2\}_2$ can be formed from the all-<u>cis</u>-isomer (all-<u>trans</u>-isomer converts into the dimer in very small quantities) by loss of CO, with a chlorine ligand on each molecule acting as a nucleophile, attacking the other molecule in the kinetically preferred direction <u>trans</u> to a PMe_2Ph ligand. (SCHEME 14).



(ALL-CIS)

(36)

(DIMER)

SCHEME 14.

The stereochemistry of the dimer is that to be expected from the combination of two five coordinated molecules of $\{RuCl_2(CO)(PMe_2Ph)_2\}$(36). Treatment of the dimer with CO yields the all-<u>cis</u>-isomer and the process can be reversed almost quantitatively by passing nitrogen through a benzene solution.

In this work a solution of the dimer was stirred with the 1-tributyltin-2,4-pentadiene at 40°C for 2h. and the product purified by chromatography giving a pale cream powder that is quite stable under nitrogen in the solid state and in solution. It was characterised by infrared and ^1H-NMR spectroscopy.

$$\{[RuCl_2(CO)(PMe_2Ph)_2]_2\} + 2\ Bu_3SnCH_2CH{=}CH{-}CH{=}CH_2 \xrightarrow{CHCl_3}$$

$$2\ \{RuCl(CO)(\eta^3\text{-}C_5H_7)(PMe_2Ph)_2\} + 2\ Bu_3SnCl$$

The possible mechanism of this type of reaction was discussed by Abel[62a] and Mawby.[131] According to their observations, a ligand must be lost from the coordination sphere of the metal to allow interaction with $\{R_3Sn(allyl)\}$$\{R{=}Me,Bu\}$ to occur, but they are in disagreement about the intermediate formation of η^1-allyl species. Abel implies that this is unlikely on account of the strong conditions that are required for the conversion of the η^1-complexes into the respective η^3-complexes. Moreover, η^3-allyl tetracarbonylrhenium was isolated in 80% yield via the organotin method. It was first reported that the η^3-allyl compound is not formed from the η^1-allylpentacarbonylrhenium[133] either by heat or irradiation, but later work showed that this conversion does occur on photolysis.[134]

Furthermore, a continuously monitored reaction did not show traces of η^1-species by infrared spectroscopy.

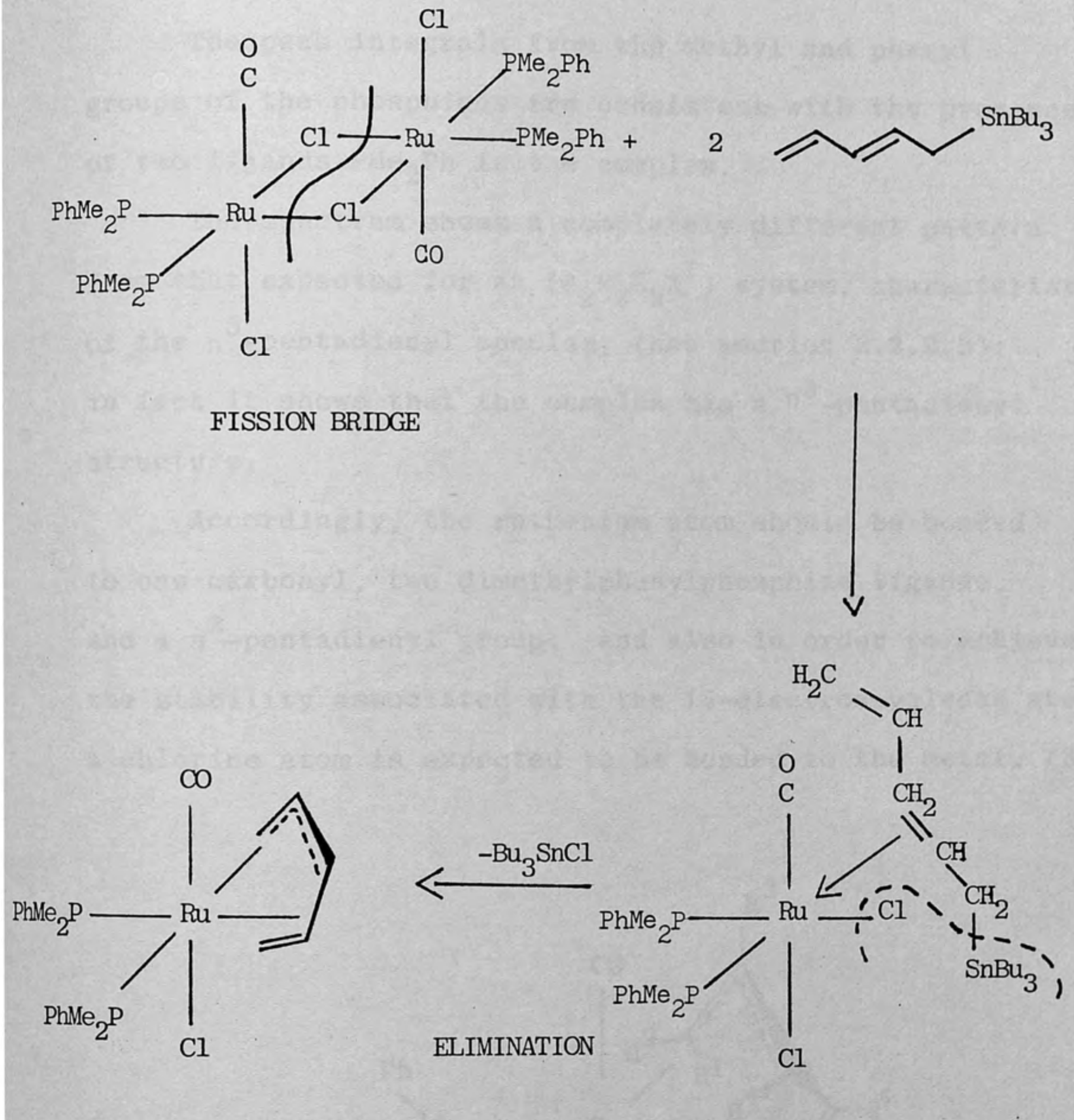
Mawby, working with dimeric isomers (34,35) found that they react giving the same complex as a final product, and since both isomers do not interconvert under the reaction conditions used, it seems that rearrangement must occur after the exchange of the halogen and allyl ligands. An intermediate formation of the five-coordinated η^1-allyl complex was proposed and supported by the extremely rapid rearrangement of these species. However, there is no spectrocopic evidence for the presence of such intermediates.

In this work, the reaction was continuously monitored by infrared spectroscopy and there was no evidence of intermediate species in the reaction mixture. Furthermore, as only one isomer of the dimeric ruthenium complex was used it was not possible to compare and discuss Mawby's view.

In agreement with our experimental observations, the mechanism should involve a fission of the chlorine bridges (which are more labile being trans to the dimethylphenylphosphine substituents than the chlorine trans to carbon monoxide),[135] followed by intramolecular elimination of tributyltin chloride. (SCHEME 15).

There is no evidence of carbonyl displacement during the reaction, infrared spectra shows a strong stretching band at 1932 cm^{-1} ($CHCl_3$), that could be compared with $\{RuCl(CO)(PMe_2Ph)_2(\eta^3-C_3H_5)\}$ $\{1940 cm^{-1} (CHCl_3)\}$.[131]

The replacement of the remaining carbonyl group probably requires strong conditions.


Cl
O
C
PMe$_2$Ph
Cl
Ru
PMe$_2$Ph
+
2
SnBu$_3$
PhMe$_2$P
Ru
Cl
CO
PhMe$_2$P
Cl
FISSION BRIDGE
H$_2$C
CH
O
C
CH$_2$
CO
CH
-Bu$_3$SnCl
CH$_2$
PhMe$_2$P
Ru
PhMe$_2$P
Ru
Cl
SnBu$_3$
PhMe$_2$P
PhMe$_2$P
PhMe$_2$P
Cl
ELIMINATION
Cl
OLEFIN COORDINATION

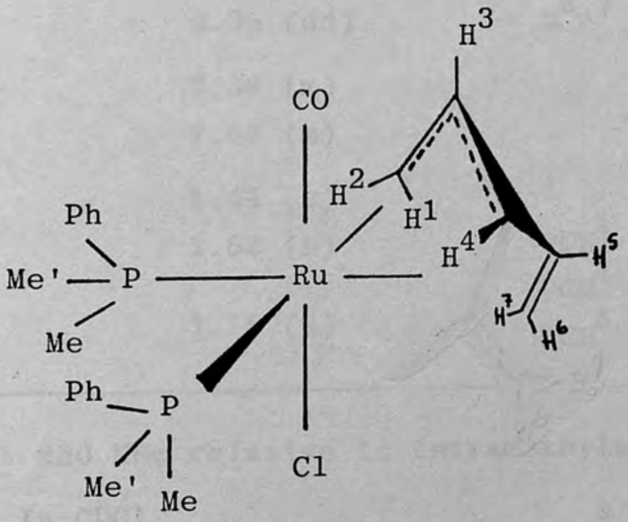
SCHEME 15

The ^{1}H NMR spectrum is reported in Table 10 and assigned according to the structure (37).

The peak integrals from the methyl and phenyl groups of the phosphines are consistent with the presence of two ligands PMe_2Ph in the complex.

The spectrum shows a completely different pattern from that expected for an ($A_2M_2X_2X^1$) system, characteristic of the η^5-pentadienyl species, (see section 2.2.2.3); in fact it shows that the complex has a η^3-pentadienyl structure.

Accordingly, the ruthenium atom should be bonded to one carbonyl, two dimethylphenylphosphine ligands, and a η^3-pentadienyl group; and also in order to achieve the stability associated with the 18-electron valence shell a chlorine atom is expected to be bonded to the metal. (37)



(37)

The ^1H NMR spectrum was measured in $CDCl_3$ at room temperature and at 40° giving exactly the same result. Assignments were made on the basis of published data on vinyl[70] and allyl groups,[131] and also by comparison with the analogous structures of the manganese and molybdenum complexes (see next chapters).

TABLE 10

Hydrogen-1 NMR DATA[a]

	Chemical Shifts	Coupling Constants (Hz)
H^1	2.24 (dt)	
H^2	2.83 (d)	$H^{1,3} = 12.2$
H^3	4.83 (td)	$H^{2,3} = 7.80$
H^4	3.67 (t)	$H^{3,4} = \sim 11$
H^5	6.07 (dt)	$H^{5,6} = 10.3$
H^6	4.96 (dd)	$H^{5,7} = 17.0$
H^7	5.20 (dd)	$H^{6,7} = 1.80$
Ph	7.36 (m)	
	7.47 (m)	
Me	1.44 (s)	
	1.58 (s)	$PCH^1 = 5.8$
Me'	1.75 (s)	$PCH^4 \simeq 5.8$ $PCH^5 \simeq 1.5$ $PCH^6 = PCH^7 \simeq 0.8-1$

a) Measured at 250 MHz relative to tetramethylsilane, $\delta = 0$ ppm. In $CDCl_3$.

The spectrum shows strong proton-phosphorus coupling (Figure 7), and for that reason a phosphorus-decoupled spectrum was also obtained (Figure 8), in order to establish the proton-proton coupling constants and the respective multiplicity in each signal.

The phosphorus-decoupled spectrum shows:

Seven widely separated bands with the same relative area for the respective hydrogens of the η^3-pentadienyl ligand.

The proton (H^3) attached to the central carbon atom of the η^3-system (4.83 δ, multiplet) resonates to low field of the protons on adjacent carbon atoms.

Resonances centred at 2.24 δ and 2.85 δ are from the anti-proton (H^1)(doublet of triplets) and the syn-proton (H^2) (doublet) respectively. These assignments are confirmed from the coupling constants with (H^3) {$J(H^1,H^3)$= 12.2 Hz, $J(H^2,H^3)$= 7.8 Hz} and also by the characteristics of the proton-phosphorus coupling that will be discussed below.

The proton (H^4) (3.67 δ ,triplet) resonates to low field of the anti- and syn- protons, and to high field than the proton (H^3), in contrast with observations on the tricarbonylphosphine-η^3-pentadienyl manganese systems in which the resonances of (H^4) is at low field than (H^3). The corresponding coupling constant (~ 11Hz) between these protons (H^3) and (H^4) suggest a trans arrangement.

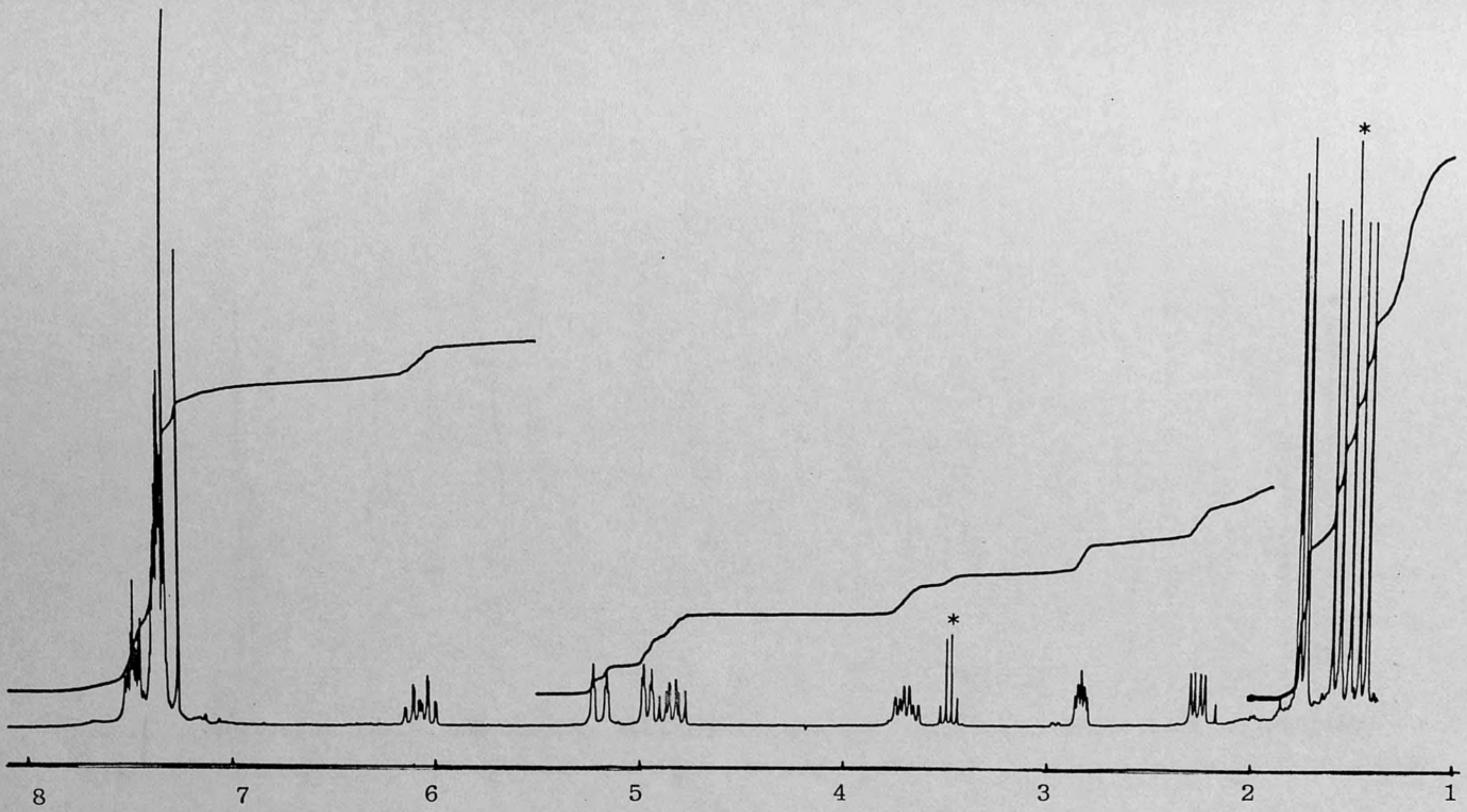


Figure 7. ^{1}H-NMR spectrum of carbonylchlorobis(dimethylphenylphosphine)(η^3-pentadienyl) ruthenium in C^DCl_3 at 250 MHz. (* impurity).

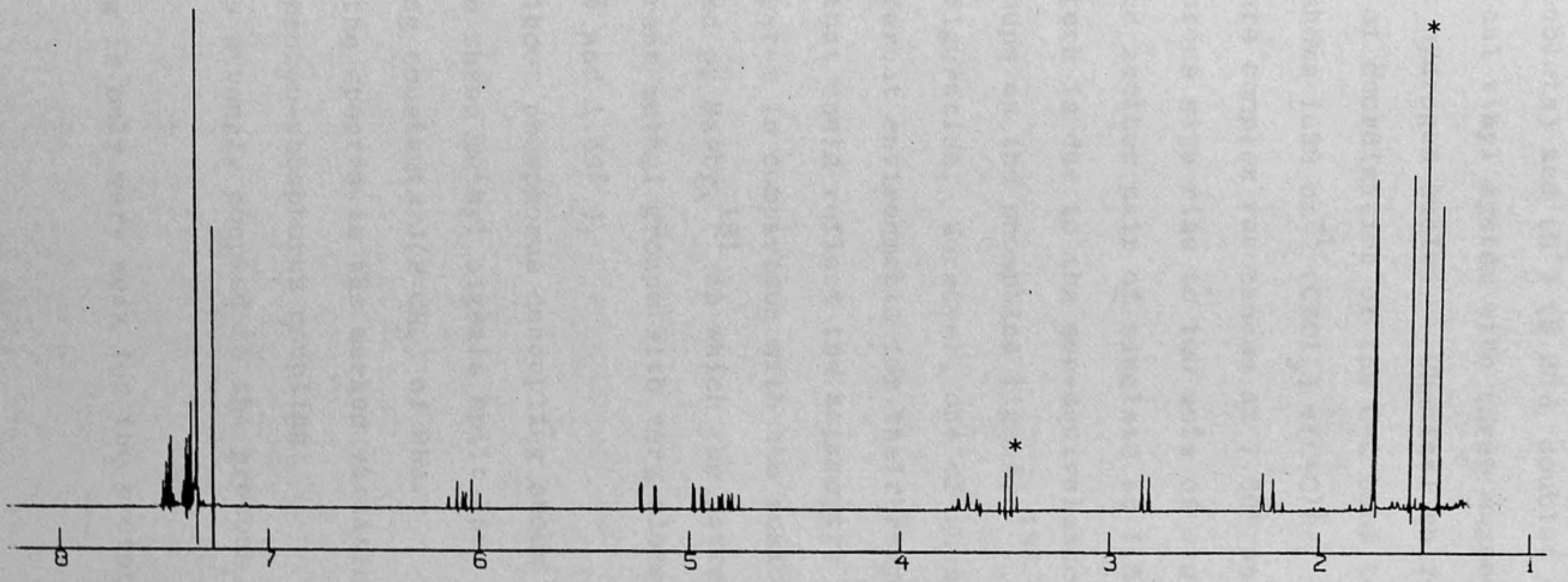


Figure 8. ^{1}H-NMR spectrum of RuCl(CO)(η^3-C_5H_7)(PMe_2Ph)$_2$ (37) with ^{31}P decoupling.
(*impurity)

The protons (H^5) (6.07δ, doublet of triplets), (H^6) (4.96δ, doublet of doublets) and (H^7) (5.20 δ, doublet of doublets) show a typical vinyl system with three magnetically non-equivalent hydrogen nuclei. Chemical shifts do not show evidence of coordination of the C=C bond to ruthenium {Infrared shows 1620 cm^{-1} ($CHCl_3$) ν(C=C)}.

Phenyl protons are complex resonances at 7.36δ and 7.47 δ, and methyl protons give rise to two sets of signals, a singlet at 1.75 δ and another pair of singlets at 1.58δ and 1.44δ. This pattern is due to the non-equivalence of the two methyl groups on the phosphine ligand,[136] suggesting a <u>cis</u> configuration. Moreover, one of these groups must have different environments for their respective methyl protons, that could reflect the asymme try of the η^3-pentadienyl system in comparison with the analogous allyl complex reported by Mawby,[131] in which the pattern shows only two different methyl groups with very close chemical shift (1.58δ and 1.59δ).

The spectrum without phosphorus decoupling shows the occurrence of the three methyl signals split into doublets with coupling constants $J(P\text{-}CH_3)$ of 9Hz.

One feature of the spectra is the marked variation in the range of the proton-phosphorus coupling:

a) Phosphorus is strongly coupled to the protons (H^1), (H^2) and (H^4).

b) Same coupling is only very weak for the protons (H^5),(H^6) and (H^7).

c) No coupling between phosphorus and the proton (H^3) was observed.

This should be useful in the elucidation of the possible stereochemistry of the complex.

The anti-proton (H^1) is strongly coupled to one of the phosphorus nuclei which should be <u>trans</u> to the carbon atom bearing the proton concerned according to the characteristic value of the splitting 5.8Hz, giving a quartet of triplets. Coupling with the cis-phosphorus nucleus is too weak to measure accurately.

The pattern of resonances for the syn-proton (H^2) is a complex multiplet with significant coupling to both phosphorus nuclei. Quite similar observations in this respect were found for the complexes $\{RuCl(\eta\text{-}C_3H_5)(CO)(PMe_2Ph)_2\}$ and $\{RuCl(\eta\text{-}C_3H_5)(CO)_2(PMe_2Ph)\}$[131]. The resonance of (H^4) appears as a pair of overlapping triplets with a splitting of 5.8Hz, similar to H^1, suggesting that the proton (H^4) is also coupled to a <u>trans</u>-phosphorus nucleus.

The absence of phosphorus coupling to the proton (H^3) suggests that the most probable position of the central atom of the η^3-pentadienyl system would be remote from the phosphine ligands, as is shown in (37). This feature also supports the assignment of the chemical shift.

Weak couplings from one of the phosphorus nuclei (of the order of 1-1.5Hz) are observed for the protons attached to the carbon-carbon double bond suggesting that the vinyl hydrogens are not in such direct interaction with the phosphorus as the rest of the hydrogens in the system. The proton (H^5) appears as a pair of overlapping doublets of triplets and (H^6) and (H^7) as doublets of doublets.

Similarities between the infrared and ^1H NMR spectra of this complex and those reported by Mawby, along with the X-ray studies on the $\{RuCl(\eta-C_3H_5)(CO)_2(PMe_2Ph)\}$, establish that the complex should possess the structure (37). The orientation of the pentadienyl ligand is considered following the same arguments as applied to the allyl complex. The rotation through 180° about an axis through the metal and the centre of the ligand would result in the central carbon atom of the η^3-system being forced away from the metal by the bulky chlorine atom, thereby weakening the bonding to ruthenium.

Conversion of this η^3-pentadienyl ruthenium complex into the η^5- complex could probably be promoted by removal of the chlorine ligand by reagents as $AgBF_4$ which should afford the cationic complex $\{Ru(CO)(\eta^5-C_5H_7)(PMe_2Ph)_2\}\ BF_4$.

Also, it could be interesting to carry out the displacement of the remaining carbonyl group (probably not very easy) by photolytic methods which may give the complex $\{RuCl(\eta^5-C_5H_7)(PMe_2Ph)_2\}$, that should be a versatile synthetic intermediate for new pentadienyl systems, analogous to the well-known compounds $\{RuCl(\eta^5-C_5H_5)L_2\}$ {where L=PPh_3,PMe_3}.

2.3.3. Experimental Section

All reactions were carried out under an atmosphere of dry nitrogen. Chloroform was reagent grade and was used directly. Instrumentation is described in Section 2.1.3.

The complex cis-{$RuCl_2(CO)_2(PMe_2Ph)_2$} was prepared by the method of Shaw and Jenkins[135] and then converted to the dimeric isomer {$[RuCl_2(CO)(PMe_2Ph)_2]_2$} (SCHEME 12) as reported by Mawby et al.[132]

i) Preparation of the complex {$RuCl(\eta^3$-$C_5H_7)(CO)(PMe_2Ph)_2$}

A solution of the isomer (35) (0.36g., 0.38mmol) in $CHCl_3$ (90cm^3) was stirred with {$(C_5H_7)SnBu_3$} (0.41g., 1.14mmol) at 40°C for 3½h.

The pale yellow solution was evaporated and the residue purified by chromatography on alumina, using $CHCl_3$ as an eluant. A yellow oil was obtained, which was crystallised from light petroleum (40-60°C), then filtered, washed with the same solvent and dried in vacuo. The product was obtained as a pale cream powder (0.16g., 41%). It had a m.p. 127°C (decomp.). Analysis. Calcd.for $C_{22}H_{29}P_2OClRu$: C,52.02; H,5.76. Found: C, 51.52; H,5.90.

ii) Attempted reactions with organotin reagents and various complexes.

Similar reactions to the above with various complexes proved unsuccessful or gave low yields from a mixture of products.

a) the reaction of {$MoCl(\eta^3$-$C_3H_5)(CO)_2(MeCN)_2$}[137] with {$(C_5H_7)SnR_3$} {where R=Me, n-Bu}.

A mixture of the molybdenum complex (2.37g., 7.6mmol) and {$C_5H_7SnMe_3$ }(1.76g., 7.6mmol) was heated under refluxing THF. The orange solution became dark brown. A couple of new carbonyl bands appeared after 2 h. (2010(vw), 1940(s), 1900(sh), 1845(s) cm^{-1}). {Starting material 1951, 1855 ν(CO); and 2312, 2286 cm^{-1} νCN).}[137]

Treatment of the solution was carried out in two different ways:

1) Removing Me_3SnCl by chromatography.- Evaporation of the solvent gave a brown-orange oil that chromatographed on alumina with diethyl ether gave a yellow eluate. After evaporation a very small amount of a yellow solid showed only one broad carbonyl band at ~1920 cm^{-1}.

2) Removing Me_3SnCl with water.- Product of reaction was treated with H_2O, extracted with diethyl ether, dried with $MgSO_4$ and evaporated giving an orange oil. Attempted purification using chromatography failed from decomposition of the sample. {It showed a sharp peak at 1984 cm^{-1} from $Mo(CO)_6$}.

Another attempt was carried out with the same complex and (C_5H_7)$SnMe_3$ in the same ratio (1:1) with THF at room temperature showing after 3 days an extra strong carbonyl band at 1980 cm^{-1} from $Mo(CO)_6$. Product could not be purified by chromatography due to decomposition.

The unsuccessful attempt to synthesize {$Mo(CO)_2(\eta^3-C_3H_5)(\eta^5-C_5H_7)$} was in contrast with the good yields and fast reactions of {$MoCl(\eta-C_3H_5)(CO)_2(MeCN)_2$}

with cyclopentadienyl- and indenyltrimethyltin compounds.[62a]

b) The reaction of $\{RhCl(CO)_2\}_2$[138] with $\{(C_6H_9)SnBu_3\}$.

A solution of the dimer (0.71 mmol) in diethyl ether (50 cm^3) at -78^oC was stirred and treated with $\{(C_6H_9)SnBu_3\}$ (1.42 mmol) giving a dark orange solution. The reaction mixture was allowed to warm up to -20^oC over 30 min., the dark red solution was evaporated giving a dark-brown product that was taken up in light petroleum (40-60°C). The insoluble fraction showed two stretching frequencies of CO at 1980 and ~1830 cm^{-1}, the lowest frequency suggests a bridging CO ligand. The formation of a cluster carbonyl is quite likely according with the infrared and the slight solubility of the product in organic solvents. The soluble product was chromatographed on alumina with the same solvent and a pink band was collected in very low yield showing no carbonyl groups.

c) The reaction of $\{RhCl(1,5-C_8H_{12})\}_2$[139] with $\{(C_5H_7)SnBu_3\}$

A mixture of $\{RhCl(1,5-C_8H_{12})\}_2$ (0.63g., 1.28mmol) and $\{(C_5H_7)SnBu_3\}$ (0.92g., 2.56mmol) was stirred at room temprature in THF for 5h. The immediate addition of the tin reagent changed the yellow solution into a brown-yellow colour, together with a black product of decomposition.

The brown oil obtained on evaporation was chromatographed on alumina with light petroleum/ether. The first yellow band was starting material. A very small amount of a yellow oil was collected from a second fraction, which would not sublime even at 85°C/0.1mm Hg when most of the product had been decomposed.

The same reaction was carried out at a higher temperature. Above 50°C the solution darkened completely. Reflux for 4 h. followed by evaporation of THF, and addition of light petroleum (< 40°C) gave a solution with a black solid. Filtration and then chromatography afforded an orange oil. The ^{1}H NMR spectra indicated the absence of the pentadienyl resonances.

d) The reaction of $\{MnBr(CO)_4PPh_3\}$ [140] with $\{(C_5H_7)SnBu_3\}$.

A mixture of $\{MnBr(CO)_4PPh_3\}$ (3.2mmol) and $\{(C_5H_7)SnBu_3\}$ (3.2mmol) was heated under refluxing THF (50 cm^3) for 10h. A partial removal of the solvent gave a white precipitate (Product 1). Complete evaporation followed by addition of light-petroleum (40-60°C) gave another yellow precipitate (Product 2). The solids were filtered off and washed with the same solvent. Several recrystallisations from dichloromethane/hexane were carried out for the separation of these products. (Product 1 is more soluble in CH_2Cl_2 than product 2).

The dry yellow solid weighed 0.73g. (m.p.228°C, with decomposition). NMR studies showed the presence of butyl and phenyl groups in the complex. The infrared spectrum had 2 peaks in the CO stretching region at 2100(w), 1958(vs) ($CHCl_3$) and with a nujol mull the spectra showed split bands due to the low solubility of the sample with the mulling agent {2050(m) doublet, 1962(sh), 1950(vs), 1925(s)}.

The product soluble in light petroleum (40-60°C) was chromatographed on alumina giving 3 fractions with different eluents: the first very small fraction of an oily $\{Mn(\eta^5-C_5H_7)(CO)_3\}$ (Product 3) was eluated with light petroleum. The second fraction gave a yellow oil (Product 4) with several carbonyl bands in the spectra [light petroleum/ether (12:1)]. The third with the same mixture of solvents but (2:1) afforded the golden yellow crystals of $\{Mn(\eta^5-C_5H_7)(CO)_2(PPh_3)\}$ (Product 5) in 13% yield (0.18g.). This product was recrystallised twice. Analytical data, spectroscopic studies and a better synthetic method for obtaining the product 5 is reported in Chapter 3.

CHAPTER THREE

SUBSTITUTION REACTIONS OF η^5-PENTADIENYLTRICARBONYLMANGANESE

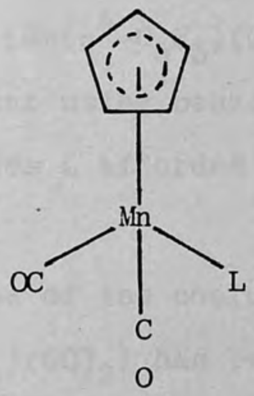
CHAPTER THREE

SUBSTITUTION REACTIONS OF η^5-PENTADIENYLTRICARBONYLMANGANESE

3.1. η^5-Pentadienyldicarbonylmanganese complexes.

3.1.1. Introduction

The effect of ligand substitution has been studied in the greatest detail for η^5-pentadienyltricarbonmanganese. Many different monosubstituted $\{Mn(\eta^5\text{-}C_5H_5)(CO)_2L\}$ (1) have been prepared.[141]



(1)

The interest in these complexes is generally on the ligand L, normally a soft nucleophile, which can be captured by the fragment $\{Mn(\eta^5\text{-}C_5H_5)(CO)_2\}$. This half-sandwich molecular fragment having only 16 valence electrons has an exceptional affinity for two electron ligands such as many conventional Lewis bases or pairs of one-electron ligands such as alkyl or acyl groups.

The complex $\{Mn(\eta^5\text{-}C_5H_5)(CO)_3\}$ is quite inert to thermal substitution and the majority of syntheses producing $\{Mn(\eta^5\text{-}C_5H_5)(CO)_2L\}$ complexes have been carried out using photochemical procedures.[142] The photo-excitation of the tricarbonyl complex shows that the dissociative loss of one carbon monoxide is quite efficient.[143]

$$\{Mn(\eta^5\text{-}C_5H_5)(CO)_3\} \xrightarrow[L]{h\nu} \{Mn(\eta^5\text{-}C_5H_5)(CO)_2L\} + CO$$

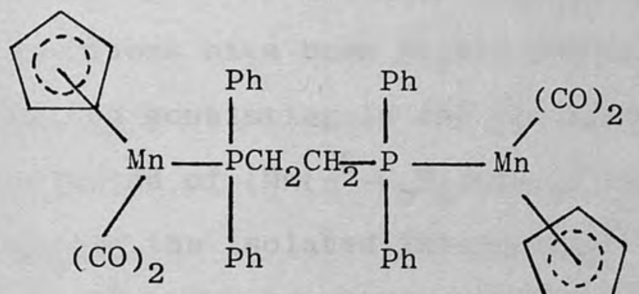
Comparatively, a few complexes are obtained by further loss of CO from $\{Mn(\eta^5\text{-}C_5H_5)(CO)_2L\}$ by stronger π-acceptor ligands such as triphenylphosphine,[144] trimethylphosphite,[145] 1,3-butadiene,[146] 1,2-bisdiphenylphosphinoethane (Diphos),[147,148] among others, giving the monocarbonyl complexes $\{Mn(\eta^5\text{-}C_5H_5)(CO)L_2\}$. A complete carbonyl displacement using benzene[143] and some cyclic trienes[149] as ligands L afforded the less stable products $\{Mn(\eta^5\text{-}C_5H_5)L_3\}$.

The formation of the coordinatively unsaturated species $\{Mn(\eta^5\text{-}C_5H_5)(CO)_2\}$ has been detected after photolysis of the tricarbonyl complex by matrix isolation studies.[150] This species has only a limited life time and warming led to regeneration of the parent tricarbonyl complex. In the synthetic work the use of coordinating solvents is common in order to provide temporary stabilization of this fragment. Tetrahydrofuran is the solvent most commonly employed,[141,151] giving on photolysis of $\{Mn(\eta^5\text{-}C_5H_5)(CO)_3\}$ the labile and not isolable red complex $\{Mn(\eta^5\text{-}C_5H_5)(CO)_2(THF)\}$. Subsequently, the solvent can be displaced by addition of different ligands L without irradiation, affording the products $\{Mn(\eta^5\text{-}C_5H_5)(CO)_2L\}$(1).

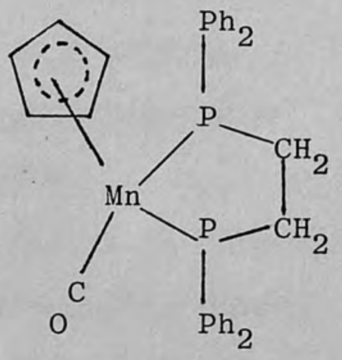
This indirect method of synthesis often provides very pure products in high yield.[142,152] An alternative route for the synthesis of (1) is the direct irradiation of {$Mn(\eta^5-C_5H_5)(CO)_3$} in the presence of a photostable ligand L in hydrocarbon solvents. Commonly, this method has the disadvantage of giving rise to side-reactions, and occurrence of extensive decomposition during the irradiation process.[153]

Strohmeier and Müller[153] reported that the tertiary phosphine and phosphite Lewis bases PR_3 [where R=Me, n-Bu and $(C_6H_{11})_3$] and $P(OR)_3$ [(where R=Me, Et and Ph)] react readily with {$Mn(\eta^5-C_5H_5)(CO)_3$} in benzene or via the labile complex {$Mn(\eta^5-C_5H_5)(CO)_2(THF)$} giving the corresponding complexes {$Mn(\eta^5-C_5H_5)(CO)_2L$}. The phosphine derivatives are yellow solids and the phosphite complexes are pale yellow liquids, except for the triphenylphosphite derivative which is a solid. The last has also been obtained in a slightly better yield (45%) by a long period of irradiation of the tricarbonyl complex and excess of ligand in toluene.[154] {$Mn(\eta^5-C_5H_5)(CO)_2PPh_3$} was similarly obtained in 52% yield. This triphenylphosphine complex was also synthesised from a thermal reaction at 250°C by Nyholm and Stiddard.[147b] Attempts to prepare the triphenylarsine analogue by the same method failed. Irradiation for 20 h. in a cyclohexane solution however gave bright yellow crystals of {$Mn(\eta^5-C_5H_5)(CO)_2AsPh_3$}.

The bidentate ligand $Ph_2PCH_2CH_2PPh_2$(Diphos) reacts on irradiation with the tricarbonyl complex in cyclohexane giving a yellow complex in which the ligand behaves as a bridging group, with the phosphorus atoms coordinated independently to two manganese atoms (2). Prolonged irradiation of the same reactants in benzene produces the disubstituted orange complex reported above $\{Mn(\eta^5\text{-}C_5H_5)(CO)Diphos\}$[148] (3) in 34% yield.



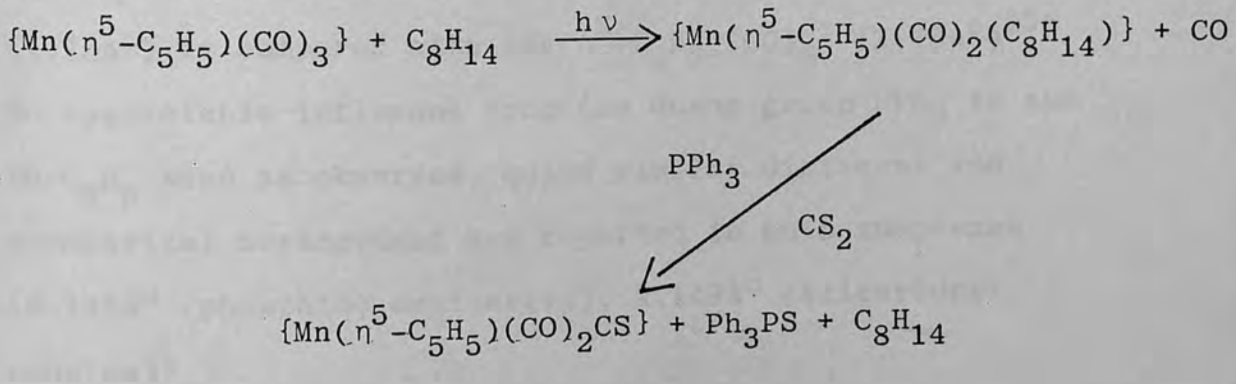
(2)



(3)

The yellow complex $\{Mn(\eta^5\text{-}C_5H_5)(CO)_2PMe_2Ph\}$ was obtained from the irradiation of the tricarbonyl complex with a stoichiometric amount of PMe_2Ph in methylcyclohexane in 52% yield.[148]

Butler et.al., have been studying the metal thiocarbonyl complexes. They carried out a comparative work in order to ascertain whether the CS complexes are more stable than the CO analogues, in agreement with molecular orbital calculations which predict that CS should be a better σ-donor and a better π-acceptor than CO.[145b] In order to achieve this, the attack of different Lewis bases on {$Mn(\eta^5-C_5H_5)(CO)_2(CS)$} was carried out. The reactions proceed by successive substitution of the CO groups, giving first monocarbonyl complexes {$Mn(\eta^5-C_5H_5)(CO)(CS)L$} {L=$PPh_3$,$AsPh_3$,$P(C_6H_{11})_3$$PMe_2Ph$, among others} and then {$Mn(\eta^5-C_5H_5)(CS)L_2$}{L=PPh_3,$P(OPh)_3$,$P(OMe)_3$, $P(OEt)_3$ and $P(OCH_2CH_2Cl)_3$}.[145a] Efficient synthesis of the starting material {$Mn(\eta^5-C_5H_5)(CO)_2(CS)$} used in these reactions have been highly developed.[155] An indirect method consisting in the irradiation of a n-hexane solution of {$Mn(\eta^5-C_5H_5)(CO)_3$} with cis-cyclooctene giving the isolated intermediate complex {$Mn(\eta^5-C_5H_5)(CO)_2(C_8H_{14})$}which under reflux in carbon disulphide in the presence of PPh_3 affords the bright yellow solid {$Mn(\eta^5-C_5H_5)(CO)_2CS$} in 85% yield.[155] (SCHEME 1). An alternative synthesis from {$Mn(\eta^5-C_5H_5)(CO)_2PPh_3$} in CS_2 gives the product in approximately 30% yield.[156]



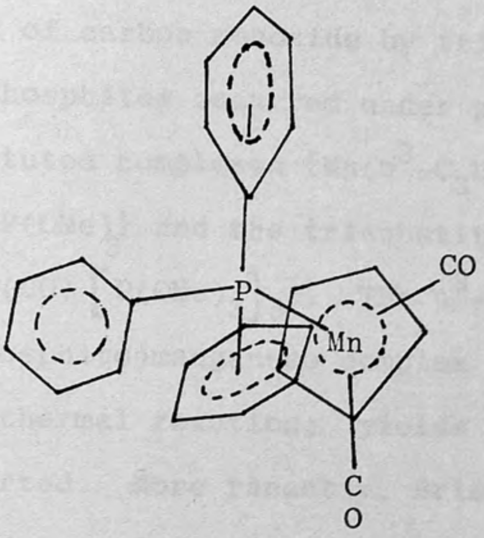
$$\{Mn(\eta^5-C_5H_5)(CO)_3\} + C_8H_{14} \xrightarrow{h\nu} \{Mn(\eta^5-C_5H_5)(CO)_2(C_8H_{14})\} + CO$$

$$\xrightarrow[CS_2]{PPh_3} \{Mn(\eta^5-C_5H_5)(CO)_2CS\} + Ph_3PS + C_8H_{14}$$

SCHEME 1.

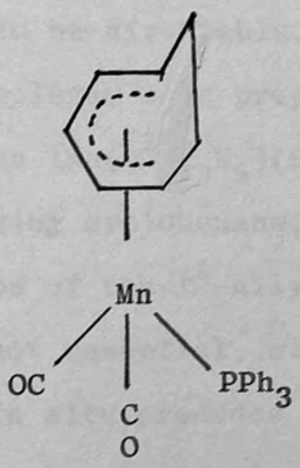
The basicity of the metal in tricarbonylcyclopentadienylmanganese and several dicarbonylphosphine complexes {$Mn(\eta^5-C_5H_5)(CO)_2L$ }{ $L=PPh_3$, $P(C_6H_{11})_3$, $P(CH_2Ph)_3$,$P(i-C_3H_7)_3$} and monocarbonyldiphosphine complexes {$Mn(\eta^5- C_5H_5)(CO)L_2$} {$L_2=Ph_2PCH_2CH_2PPh_2$,$Ph_2$ $P(CH_2)_3PPh_2$or $L=PPh_3$}have been studied by Setkina, Kursanov and Ginzburg,[157] who found that protonation becomes easier with the substitution of carbonyl groups for phosphine ligands by increasing the basicity on the manganese atom,[157a] and the tertiary phosphines in turn are found to be stronger donors if the phosphorus contain an alkyl groups such as C_6H_{11}, $i-C_3H_7$ and CH_2Ph compared with phenyl groups.[157b] Addition of excess of trifluoroacetic acid to solutions of the cyclopentadienylcarbonylphosphine complexes in dichloromethane give rise to the Mn-H proton NMR signal in the high field region (δ = -4 to -6 ppm)[157c] confirming the site of the proton attack.

The crystal and molecular structure of {$Mn(\eta^5-C_5H_5)(CO)_2PPh_3$} (4) was determined and compared with the tricarbonyl analogue.[158] The substituted molecule shows a stronger Mn-CO bond, the shorter distance (1.75A°) is compared with {$Mn(\eta^5-C_5H_5)(CO)_3$} (1.78A°)[83a] No appreciable influence from the donor group PPh_3 in the $Mn-C_5H_5$ bond is observed, quite similar distances and geometrical arrangement are reported in both complexes {2.145A° (phosphine derivative), 2.149A° (tricarbonyl complex)}.



(4)

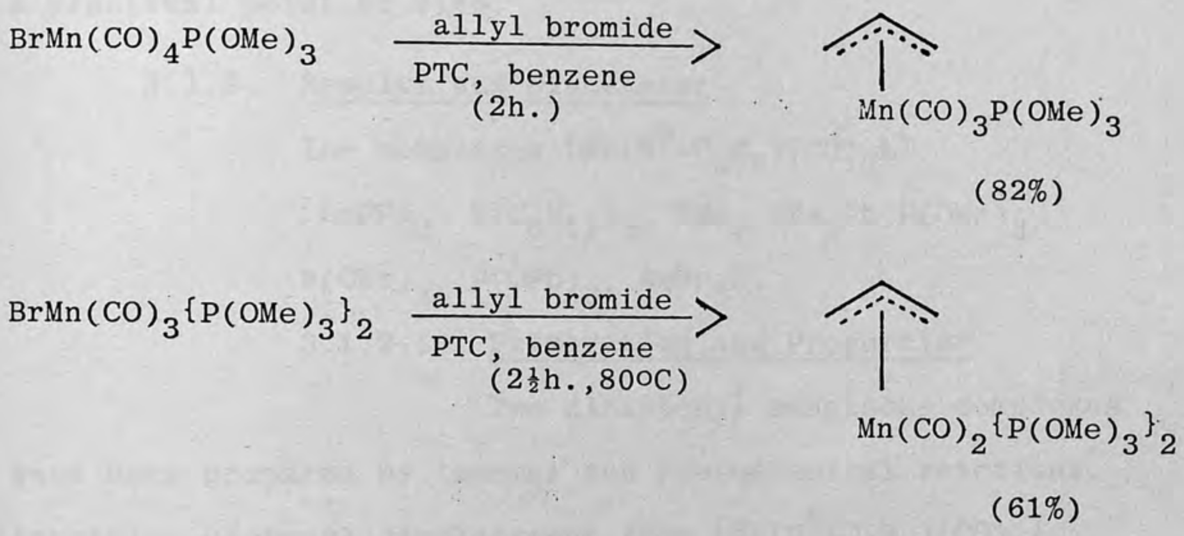
An example of dienyl systems, is the triphenylphosphine derivative obtained from the smooth replacement of one carbonyl group of tricarbonylcycloheptadienylmanganese under irradiation in benzene (5).[159]



(5)

In the matter of acyclic complexes, Stuhl and Muetterties[160] have studied the catalytic activity of some derivatives of tetracarbonylallylmanganese. Partial substitution of carbon monoxide by trialkylphosphines or trialkylphosphites occurred under photolysis giving the disubstituted complexes $\{Mn(\eta^3-C_3H_5)(CO)_2L_2\}$$\{L=PEt_3, P(O-i-C_3H_7)_3, P(OMe)_3\}$ and the trisubstituted $\{Mn(\eta^3-C_3H_5)(CO)\left[P(OMe)_3\right]_3\}$. The η^3-allyldicarbonylbis-(trimethylphosphite)manganese complex have also been isolated by thermal reaction; yields from both methods are not reported. More recently, Brisdon, et. al.[161] have reported a series of allylmanganese tricarbonyl and dicarbonyl complexes by the same process. They prepared the complexes $\{Mn(\eta^3-C_3H_5)(CO)_3L\}$ $\{M=Mn, L=PPh_3, P(C_6H_{11})_3, PBu^n_3, PMePh_2, AsPh_3\ ;\ M=Re, L=PPh_3\}$ and $\{Mn(\eta^3-C_3H_5)(CO)_2L_2\}$ $\{M=Mn, L=PMePh_2, P(OMe)_3, P(OEt)_3; M=Re, L=PPh_3\}$ from $\{M(\eta^3-C_3H_5)(CO)_4\}$ using thermal or photolytic methods. The yellow manganese complexes are markedly susceptible to air oxidation in contrast with the rhenium complexes that appear to be air-stable. In a number of cases the manganese complexes were prepared by direct thermal reaction between $\{Mn(\eta^1-C_3H_5)(CO)_5\}$ and phosphorus donor ligands in refluxing cyclohexane, showing that separate decarbonylation of the η^1-allyl complex to $\{Mn(\eta^3-C_3H_5)(CO)_4\}$ is not essential, since presumably ready decarbonylation in situ precedes the carbonyl substitution steps in such reactions.

The monosubstituted $P(OMe)_3$ derivative was detected by infrared spectroscopy, but it could not be isolated by these synthetic methods. Gibson, et al.,[162] reported a general synthetic route to η^3-allyl-transition metal complexes by phase transfer catalysis (PTC), including the syntheses of $\{Mn(\eta^3-C_3H_5)(CO)_3P(OMe)_3\}$ and $[Mn(\eta^3-C_3H_5)(CO)_2\{P(OMe)_3\}_2]$. In these reactions phase-transferred OH^- acts on a metal carbonyl halide in the presence of an allylic halide. (SCHEME 2).



SCHEME 2.

$BrMn(CO)_3\{P(OMe)_3\}_2$ is much less reactive than the monosubstituted complex.

In this work an initial study of the chemistry of $\{Mn(\eta^5-C_5H_7)(CO)_3\}$ has been made. Monosubstituted phosphine, phosphite and arsine derivatives have been isolated. Such complexes should allow detailed physical and chemical properties for open-ligand systems, which will provide a great deal of information and comparison between these new complexes and analogues prepared with allyl and cyclopentadienyl ligands could be established. Moreover, new facets of the chemistry of these pentadienyl complexes have been observed and reported here, such as the potential for exhibiting a higher degree of chemical versatility than the η^5- and η^3-bonding patterns. Also a different mechanism of reaction contrasting with the corresponding one for cyclopentadienyl derivatives is discussed. It is anticipated that the chemistry of the pentadienyl ligand would likewise prove interesting from a theoretical and a practical point of view.

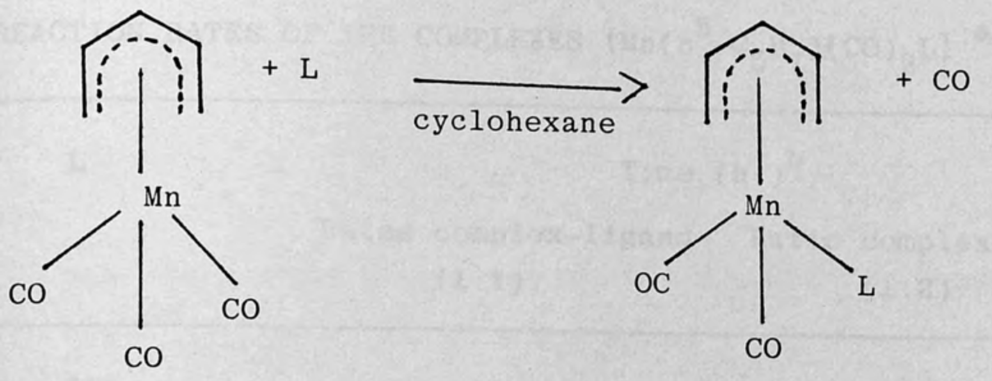
3.1.2. Results and Discussion

The complexes $\{Mn(\eta^5-C_5H_7)(CO)_2L\}$ $\{L=PPh_3, P(C_6H_{11})_3, PMe_3, PMe_2Ph, P(OMe)_3, P(OEt)_3, P(OPh)_3, AsPh_3\}$.

3.1.2.1. Preparation and Properties

The dicarbonyl manganese complexes have been prepared by thermal and photochemical reactions, involving carbonyl displacement from $\{Mn(\eta^5-C_5H_7)(CO)_3\}$ as the starting material. These complexes are yellow crystalline materials or yellow liquids, which are slightly air sensitive, but they can be stored long periods under nitrogen at ambient temperature.

The thermal reaction between $\{Mn(\eta^5-C_5H_7)(CO)_3\}$ and phosphorus donor ligands in refluxing cyclohexane affords the substituted complexes $\{Mn(\eta^5-C_5H_7)(CO)_2L\}$ $\{L=PPh_3, P(C_6H_{11})_3, PMe_3, PMe_2Ph, P(OMe)_3, P(OEt)_3, P(OPh)_3\}$ (SCHEME 3). Triphenylarsine, however, does not react under these conditions.



SCHEME 3.

The products were isolated by chromatography on a florisil column or directly by treatment and recrystallisation with different solvents.

When a stoichiometric ratio was used in the syntheses of these complexes, the reaction rates increase depending on the nature of the entering ligand as: $PMe_2Ph \approx PMe_3$ > $P(OPh)_3$ > PPh_3 > $P(C_6H_{11})_3$ > $P(OMe)_3 \approx P(OEt)_3$. (See Table 1).

TABLE 1

REACTION RATES OF THE COMPLEXES $\{Mn(\eta^5-C_5H_7)(CO)_2L\}$ [a]

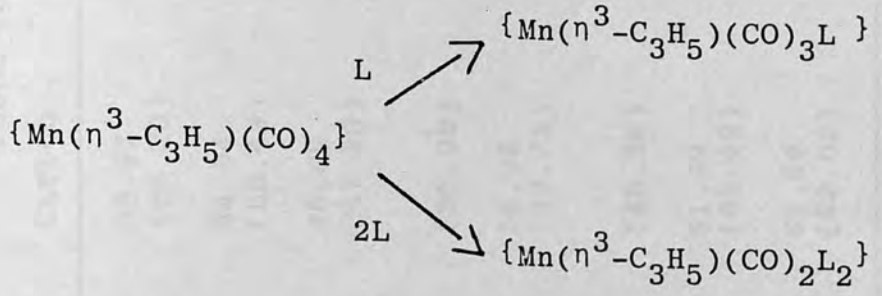
L	Time (h.)[b] Rates complex-ligand (1:1)	Ratio complex-ligand (1:2)
PPh_3	11	-
$P(C_6H_{11})_3$	13	-
PMe_3	4	-
PMe_2Ph	4	-
$P(OMe)_3$	20	7
$P(OEt)_3$	19	7
$P(OPh)_3$	8	3

a) Reactions under refluxing cyclohexane;

b) See Experimental Section 3.1.3.

Dependence of the reaction rate with the concentration of the ligand was observed for phosphites which are faster when they are in excess (ratio 1:2). Usually, pure complexes were not obtained from reaction mixtures with an excess of ligand.

A comparison between the reaction rates of similar L derivatives of the allyl complexes:[161]



and the analogous dicarbonylpentadienylmanganese complexes and bearing in mind the inertness of $\{Mn(\eta^5-C_5H_5)(CO)_3\}$ to thermal substitution,[141,163] leads to the conclusion that the ease of replacement of carbonyl groups by phosphines and phosphites decreases in the order: allyl > pentadienyl > cyclopentadienyl. The analytical data for the pentadienyl complexes are reported in Table 2.

The complex $\{Mn(\eta^5-C_5H_7)(CO)_2PPh_3\}$ has also been isolated from the reaction of $\{MnBr(CO)_4PPh_3\}$ with $\{C_5H_7SnBu_3\}$ but in lower yield (13%), due to formation of several side-products (See Experimental Section 2.3.3.).

Regardless of the stoichiometric ratio used in the syntheses of the dicarbonyl phosphite derivatives $P(OMe)_3$ and $P(OEt)_3$, as well as for the PMe_2Ph derivative, the infrared spectra from the reaction mixture (cyclohexane) exhibit four, not two, CO stretching frequencies, presumably indicating the presence of a mixture of two dicarbonyl products, the η^5-pentadienyl complex $\{Mn(\eta^5-C_5H_7)(CO)_2L\}$ and the η^3-pentadienyl complex $\{Mn(\eta^3-C_5H_7)(CO)_2L_2\}$ $\{L=P(OMe)_3, P(OEt)_3, PMe_2Ph\}$. Also the presence of isomers of the η^5-pentadienyl complex

TABLE 2

ANALYTICAL DATA FOR THE COMPLEXES $\{Mn(\eta^5-C_5H_7)(CO)_2L\}$

COMPLEX	COLOUR	MELTING POINT (^{o}C)	YIELD[a] (%)	MOLECULAR WEIGHT [f]	ANALYSIS Found (Calc.) (%)	
					Carbon	Hydrogen
$\{Mn(\eta^5-C_5H_7)(CO)_2PPh_3\}$	Golden yellow	146-147 (decomp.)	44	440	68.97 (68.20)	5.08 (5.04)
$\{Mn(\eta^5-C_5H_7)(CO)_2P(C_6H_{11})_3\}$	Lemon yellow	173-175 (decomp.)	39	458	64.64 (65.49)	8.50 (8.79)
$\{Mn(\eta^5-C_5H_7)(CO)_2PMe_3\}$	Yellow	88.5-89.5	26[b]	254	46.69 (47.26)	6.41 (6.36)
$\{Mn(\eta^5-C_5H_7)(CO)_2PMe_2Ph\}$	Yellow	Liquid[c]	~10		(56.98)	(5.74)
$\{Mn(\eta^5-C_5H_7)(CO)_2P(OMe)_3\}$	Pale yellow	81-83	51	302	38.98 (39.75)	5.48 (5.34)
$\{Mn(\eta^5-C_5H_7)(CO)_2P(OEt)_3\}$	Pale yellow	Liquid[d]	~20	344	(45.36)	(6.44)
$\{Mn(\eta^5-C_5H_7)(CO)_2P(OPh)_3\}$	Pale yellow	55-57	40	488	61.62 (61.49)	4.54 (4.54)
$\{Mn(\eta^5-C_5H_7)(CO)_2AsPh_3\}$	Golden yellow	128-129 (decomp.)	39[e]	484	61.69 (62.00)	4.88 (4.58)

a) By thermal reactions ; b) 8% by photochemical reaction ; c) At -20^{o}C is a lemon yellow solid; d) Very pale yellow crystals melts at ~18^{o}C ; e) By photochemical reaction ; f) These values were determined from the mass spectra.

has been considered as another possibility. After isolation of the product some changes are observed in the corresponding spectra and these are discussed in Section 3.1.2.2.

The stronger donor ligands PMe_3, PBu^n_3 and PMe_2Ph have also given the respective η^3-pentadienyl tricarbonyl complexes which are described in the Section 3.2.

Attempts to prepare the complex $\{Mn(\eta^5-C_5H_7)(CO)_2PBu^n_3\}$ by thermal reaction were carried out, although pure product has not been isolated because of separation problems. Infrared evidence from the ν(CO) region after 1½ h. refluxing clearly indicates that a mixture of products is present, probably $\{Mn(\eta^3-C_5H_7)(CO)_3PBu^n_3\}$ {1998, 1927 and 1912 cm^{-1} (cyclohexane)} and $\{Mn(\eta^5-C_5H_7)(CO)_2PBu^n_3\}$ {1946 and 1882 cm^{-1}}(cyclohexane) by comparison with the isolated product $\{Mn(\eta^3-C_5H_7)(CO)_3PBu^n_3\}$ (in Section 3.2.2.2.) and with similar infrared patterns from other dicarbonyl complexes reported in this work (Literature values reported for $\{Mn(\eta^5-C_5H_5)(CO)_2PBu^n_3\}$ are 1935 and 1872 cm^{-1} in cyclohexane solution).[164] The mixture of reaction was chromatographed but the product decomposed. Evaporation of the yellow eluate showed by infrared spectroscopy a single and very strong carbonyl band at 1948 cm^{-1} (nujol) or 1942 cm^{-1} ($CHCl_3$). This product could suggest the monocarbonyl complex which could not be observed before in the infrared spectrum of the reaction mixture due to overlapping with the asymmetric band of the dicarbonyl complex (1946 cm^{-1}

in cyclohexane). Brisdon, et al., also found evidence of mixtures from {$Mn(\eta^3-C_3H_5)(CO)_{4-x}(PBu^n_3)_x$} (x=1-3) under longer reaction times during the synthesis of the complex {$Mn(\eta^3-C_3H_5)(CO)_3PBu^n_3$}.[161]

Similar separation problems were observed for the η^5-PMe_2Ph derivative. However, in this case very pale lemon yellow crstals were isolated at -20°C in very small yield, but enough to characterise the product by infrared and ^1H-NMR spectroscopy. This oily product at room temperature is much more air sensitive than the other complexes.

Reaction between {$Mn(\eta^5-C_5H_7)(CO)_3$} and $AsPh_3$, pyridine and $Ph_2PCH_2CH_2PPh_2$ in refluxing cyclohexane, after 46 h., 10 h. and 26 h. respectively showed the infrared spectra of starting material. The same reaction with $AsPh_3$ (ratio complex-ligand 1:2) exposed to ultraviolet light with a low-pressure mercury arc lamp (6w) was also unsuccessful, but after 3 h. or irradiation with a medium-pressure mercury lamp (125w) using a soda glass filter (λ > 325nm), the reaction was complete and the yellow crystalline product easily isolated. The bidentate ligand $Ph_2PCH_2CH_2PPh_2$ was not tested under irradiation but it may be possible to obtain the corresponding derivative by this method in a similar manner to that reported for the cyclopentadienyl complex.[147b]

The use of the nitrogen donor ligand pyridine under 30 h. of irradiation did not lead to substituted pentadienyl complexes. No more attempts using nitrogen ligands were carried out in view of previous unsuccessful results for the allylic complexes.[161]

The complexes $\{Mn(\eta^5-C_5H_7)(CO)_2L\}$ $\{L=PMe_3,PMe_2Ph,P(OEt)_3\}$ can also be prepared photolytically, but the yields are poorer than those attained in thermal reaction. It was observed that mixtures of products are always present, suggesting that longer times of irradiation should be tested in order to increase yields. However, we must be careful because it has been observed here and in the synthesis of some allyl derivatives[161] that prolonged photolysis leads to lower yield of the desired complex.

Other analogous reactions have also been studied by photochemical process with $\{Mn(\eta^5-C_5H_7)(CO)_3\}$ and excess of cis-cyclooctene (C_8H_{14}), dimethyl maleate (MeCOOCH=CHCOOMe) or tetrahydrofuran (THF), but these attempts were unsuccessful. Particularly interesting is the contrast observed in the reaction with THF. The well-known red solution of the intermediate $\{Mn(\eta^5-C_5H_5)(CO)_2(THF)\}$ (1930 and 1845 cm^{-1})[141] can be completely formed after 5 h. of irradiation with a 100W UV lamp at 366 nm.[165] For $\{Mn(\eta^5-C_5H_7)(CO)_3\}$ and THF under the same conditions no evidence of reaction is observed in the infrared spectrum even after prolonged irradiation (20 h.) According with the higher lability shown by the pentadienyl complex $\{Mn(\eta^5-C_5H_7)(CO)_3\}$, it seems that the expected THF substituted species is not formed because of the absence of a similar reactive fragment {$Mn(\eta^5-C_5H_7)(CO)_2$ }. This fact has been confirmed by the isolation of some intermediates during the ligand replacement reactions, which suggest an associative interchange mechanism instead of the dissociative mechanism observed for the cyclopentadienyl substituted complex. A detailed discussion will be given in the Section 3.2.2.1 and 3.2.2.3.

The mass spectra of the dicarbonyl pentadienyl complexes have also been obtained in order to confirm the molecular weight of the synthesised complexes.

The metal-containing ions, as well as L^+ and $C_5H_7{}^+$ observed, are listed in Table 3. Each spectrum contains many ions associated with ligand fragments which are or not attached to the metal. These fragment ions are often of high intensity, but have not been considered in detail.

The parent molecular ion always showed a low relative intensity but was observed in every case except { $Mn(\eta^5-C_5H_7)(CO)_2AsPh_3$ } . These complexes undergo their primary fragmentation by sequential loss of both carbonyl groups. In fact, there is evidence of the fragment ions $\{C_5H_7Mn(CO)L\}^+$, ($L=P(OEt)_3$, $P(OMe)_3$, $P(OPh)_3$, PMe_3, $AsPh_3$) but they are present in very low abundance (< 5%). For these manganese dicarbonyl complexes there is no evidence of the fragment ions $\{C_5H_7Mn(CO)_{2-x}\}^+$ (x=0,1), showing that the followed fragmentation pattern is different to that of the tricarbonyl-(η^3-pentadienyl) species (Section 3.2.2.1.).

TABLE 3

MASS SPECTRA FOR THE COMPLEXES $\{Mn(\eta^5-C_5H_7)(CO)_2L\}$ [a,b]

ION				L			
	$P(OMe)_3$	$P(OEt)_3$	$P(OPh)_3$	PMe_3	$P(C_6H_{11})_3$	PPh_3	$AsPh_3$
$\{C_5H_7Mn(CO)_2L\}^+$	302 (4.5)	344 (7.5)	488 (<1)	254 (8.5)	458 (<5)	440(<1)	
$\{C_5H_7Mn(CO)\ L\}^+$	274 (<1)	316 (1.7)		226 (5.5)			456(<5)
$\{C_5H_7MnL\}^+$	246 (100)	288 (100)	432 (100)	198 (80)	402 (5)	384 (3)	428(< 5)
$\{Mn\ L\}^+$	179(62.5)	221(85.7)	365 (10)	131 (35)	335 (7)	317 (<1)	361(<5)
$\{C_5H_7Mn\}^+$	122 (42)	122(28.6)	122 (7.6)	122 (98)	122 (7)	122 (<1)	122(<5)
$\{L\}^+$	124(12.5)	166 (8.3)	310 (7.4)	76 (17)	280(23)	262 (100)	306(28)
$\{C_5H_7\}^+$	67(20.8)	67(21.4)	67 (6.6)	67 (20)	67(16.6)	67(8)	67(10)
Mn^+	55(42.5)	55(57)	55(28.5)	55(100)	55(64)	55(5)	55(10)
Other				85 (60) 83 (90)	118(100)		152(100)

a) Samples were introduced in $CHCl_3$ solution at temperatures of 120°C $\{PMe_3, P(OMe)_3, P(OEt)_3\}$, 160°C $\{L= AsPh_3\}$, 185°C $\{L=P(OPh)_3, PPh_3, P(C_6H_{11})_3\}$; b) Relative intensities in parenthesis.

So loss of the ligand L prior to carbonyl cleavage, being a competitive process between these two groups, is not favoured.

The pentadienyl ligand was not lost until all the carbonyls were not dissociated. This is confirmed by the absence of the ion $\{Mn(CO)_nL\}^+$ (n=1,2).

For the phosphite derivatives it is clear that the loss of both carbonyl groups is a favoured process, since $\{C_5H_7Mn\ L\}^+$ are the most abundant metal- containing ions in each of the three spectra. A different feature was observed for the phosphine derivatives which showed low abundance for these fragment ions. The most intense ions for the phosphine complexes arise from different fragment ions, as observed in the Table 3.

Ligand fragmentation whilst still attached to the metal is a favoured process for these dicarbonyl complexes, particularly for the phosphite derivatives. Some examples are ions not listed in Table 3, such as $\{MnO{=}P(OR)_2\}^+$ (R=Me,Et,Ph), $\{MnHOPOR\}^+$ (R=Me,Et); $\{MnP(OPh)_2\}^+$, which are at least in moderate intensity.

3.1.2.2. Infrared Studies

The infrared data of the new monosubstituted complexes in the carbonyl stretching region are presented in Table 4. As expected, because of the lowering of symmetry of the molecule $\{Mn(\eta^5\text{-}C_5H_7)(CO)_2L\}$ from the substitution of one carbonyl in the C_{3v} $Mn(CO)_3$ group, the spectra exhibit two bands for $\nu(CO)$ attributed to the symmetric mode A' and the antisymmetric mode A"

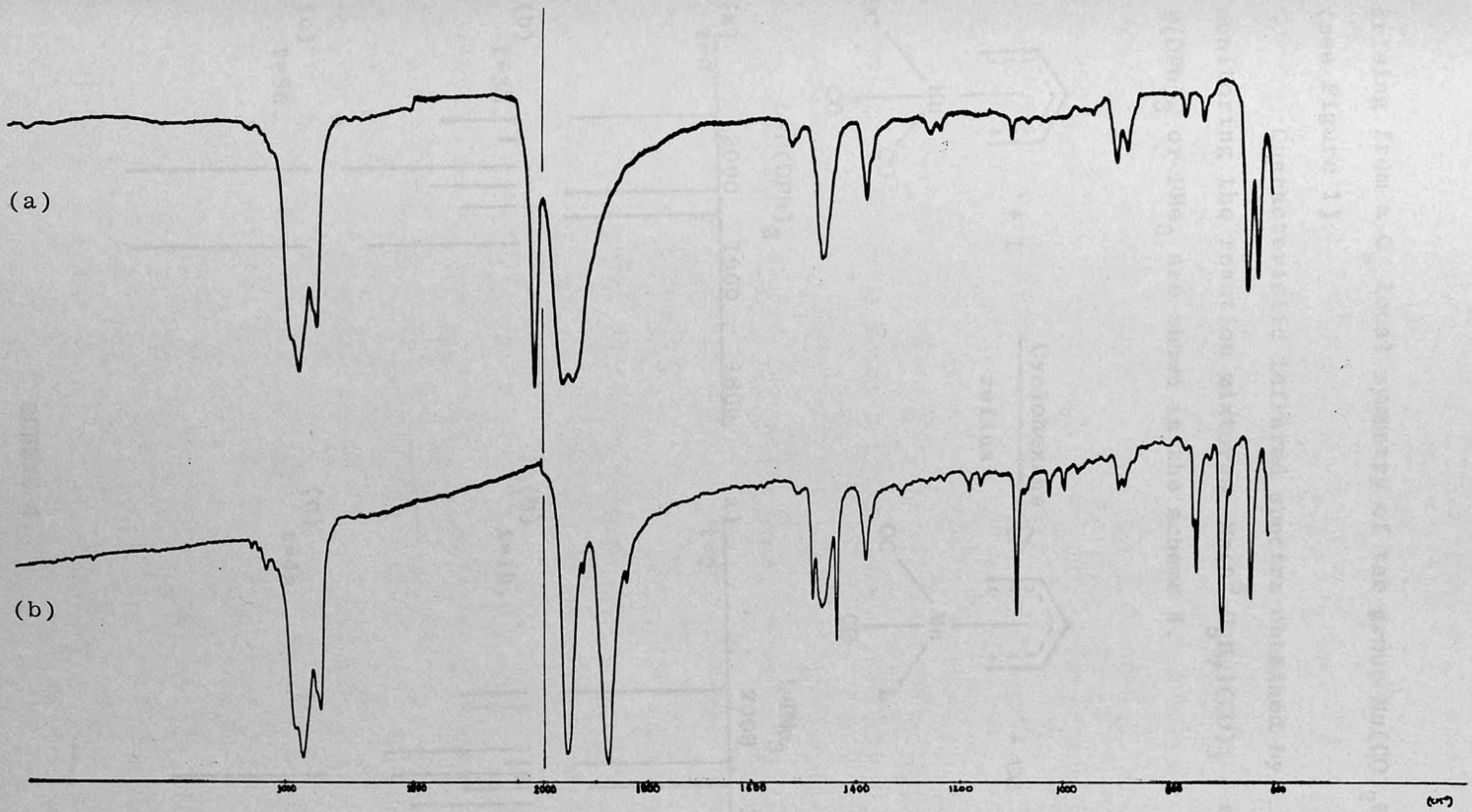
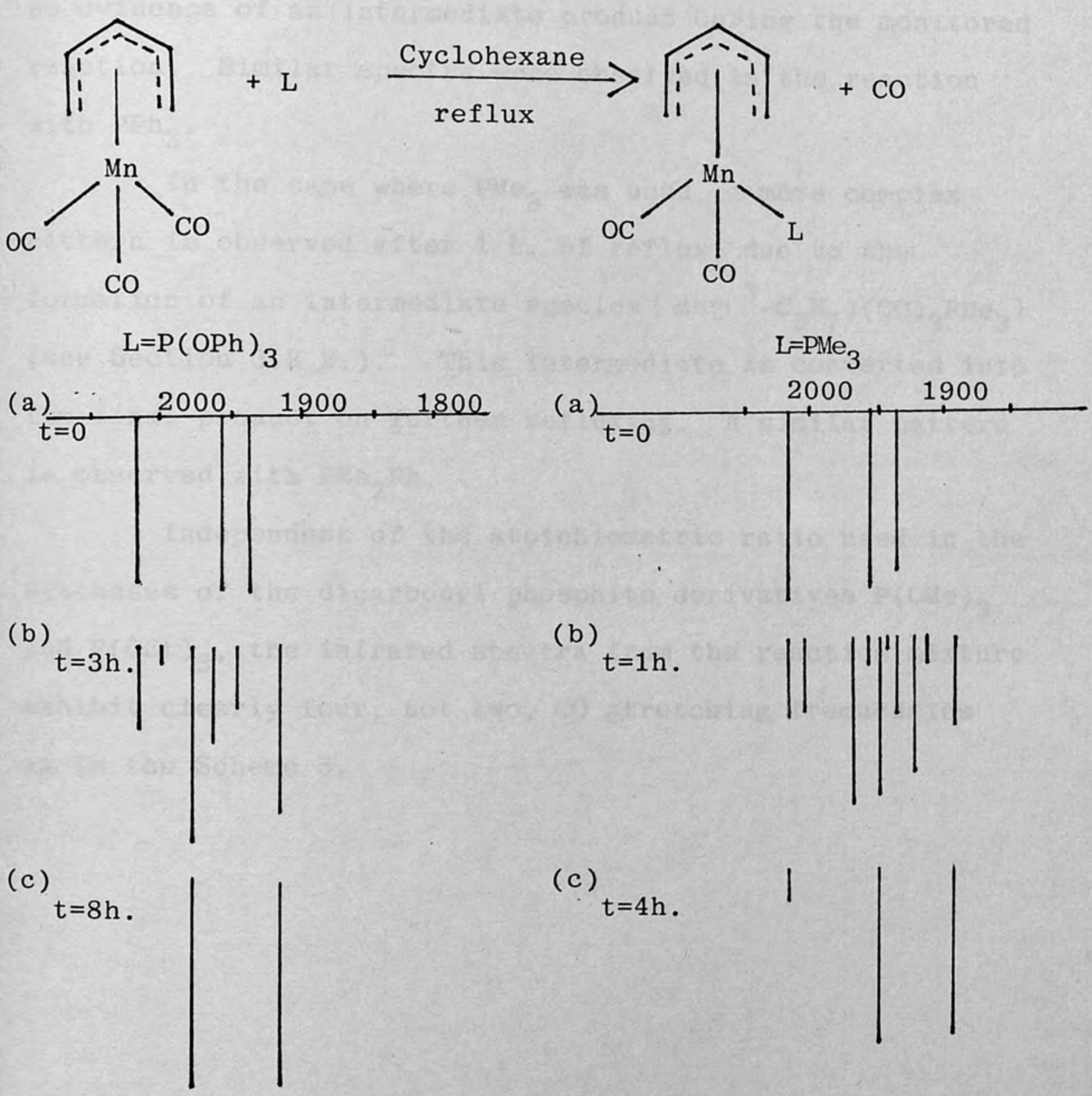


Figure 1. Infrared spectra of a) pentadienyltricarbonylmanganese and
b) pentadienyldicarbonyl(triphenylphosphine)manganese.

arising from a C_s local symmetry of the group $Mn(CO)_2L$ (see Figure 1).

Characteristic infrared spectra obtained by monitoring the reaction mixtures $Mn(\eta^5-C_5H_7)(CO)_3$ and $P(OPh)_3$ or PMe_3 are shown in the scheme 4.

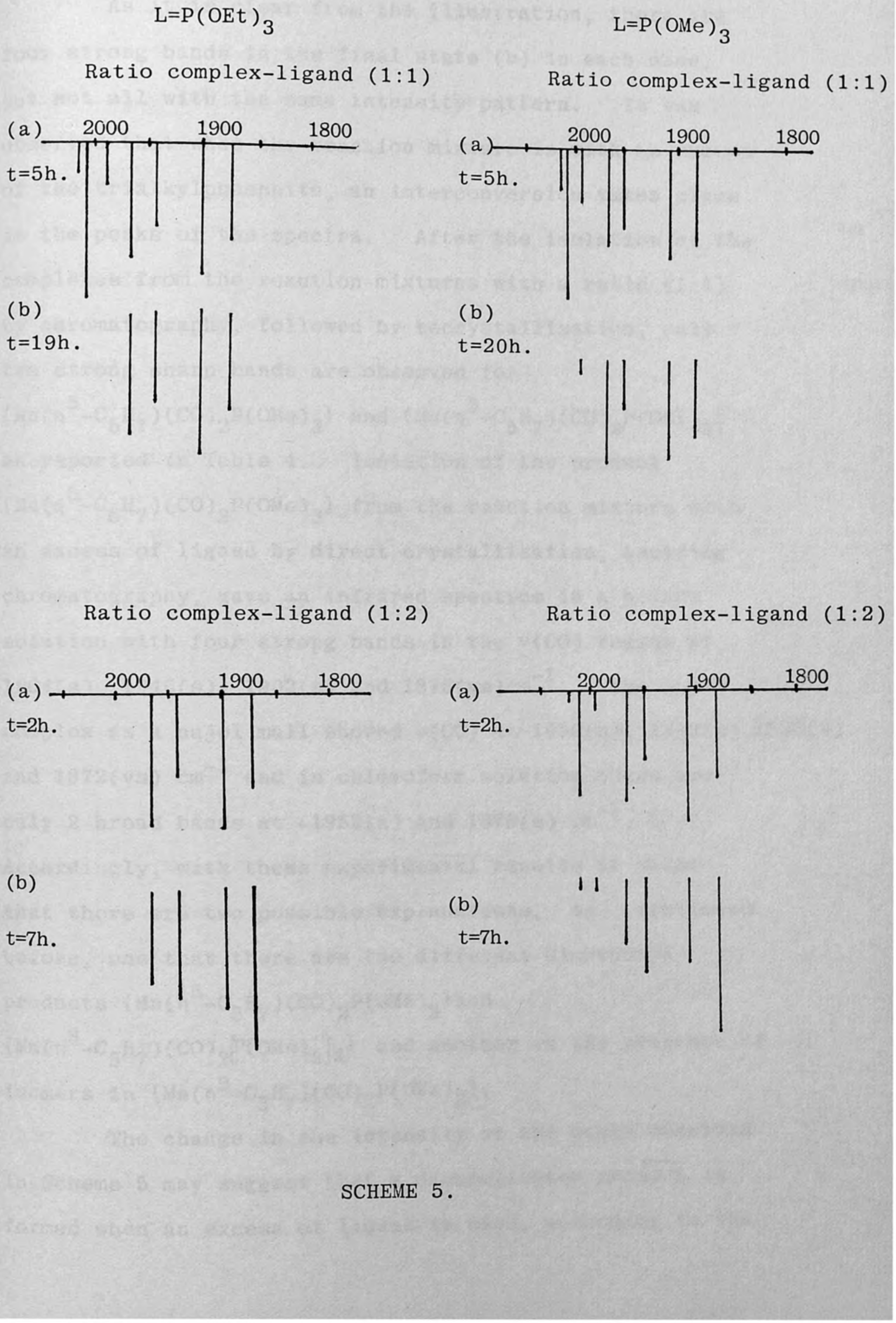


SCHEME 4.

The starting material $\{Mn(\eta^5-C_5H_7)(CO)_3\}$ [(a) time=o] as described before in Section(2.2.2.2), showed a split band at lower frequency and this is the reason for "3" bands in the figure 1. Reaction with $P(OPh)_3$ showed immediately the appearance of new peaks, with a complete consumption of the starting material after 8 h. There is no evidence of an intermediate product during the monitored reaction. Similar spectra were observed in the reaction with PPh_3.

In the case where PMe_3 was used, a more complex pattern is observed after 1 h. of reflux, due to the formation of an intermediate species $\{Mn(\eta^3-C_5H_7)(CO)_3PMe_3\}$ (see Section 3.2.2.). This intermediate is converted into the final product on further refluxing. A similar pattern is observed with PMe_2Ph.

Independent of the stoichiometric ratio used in the syntheses of the dicarbonyl phosphite derivatives $P(OMe)_3$ and $P(OEt)_3$, the infrared spectra from the reaction mixture exhibit clearly four, not two, CO stretching frequencies as in the Scheme 5.


L=P(OEt)$_3$
Ratio complex-ligand (1:1)
(a)
t=5h.
2000
1900
1800
(b)
t=19h.
L=P(OMe)$_3$
Ratio complex-ligand (1:1)
(a)
t=5h.
2000
1900
1800
(b)
t=20h.
Ratio complex-ligand (1:2)
(a)
t=2h.
2000
1900
1800
(b)
t=7h.
Ratio complex-ligand (1:2)
(a)
t=2h.
2000
1900
1800
(b)
t=7h.

SCHEME 5.

As it is clear from the illustration, there are four strong bands in the final state (b) in each case, but not all with the same intensity pattern. It was observed that when the reaction mixture is with an excess of the trialkylphosphite, an interconversion takes place in the peaks of the spectra. After the isolation of the complexes from the reaction mixtures with a ratio (1:1) by chromatography, followed by recrystallisation, only two strong sharp bands are observed for $\{Mn(\eta^5-C_5H_7)(CO)_2P(OMe)_3\}$ and $\{Mn(\eta^5-C_5H_7)(CO)_2P(OEt)_3\}$ as reported in Table 4. Isolation of the product $\{Mn(\eta^5-C_5H_7)(CO)_2P(OMe)_3\}$ from the reaction mixture with an excess of ligand by direct crystallisation, avoiding chromatography, gave an infrared spectrum in a hexane solution with four strong bands in the ν(CO) region at 1964(s), 1946(s), 1902(s) and 1876(vs)cm^{-1}. The same complex as a nujol mull showed ν(CO) at 1959(s), 1942(s),1897(s) and 1872(vs) cm^{-1} and in chloroform solution there are only 2 broad bands at ~1952(s) and 1878(s) cm^{-1}. Accordingly, with these experimental results it seems that there are two possible explanations, as mentioned before, one that there are two different dicarbonyl products $\{Mn(\eta^5-C_5H_7)(CO)_2P(OMe)_3\}$and $\{Mn(\eta^3-C_5H_7)(CO)_2[P(OMe)_3]_2\}$ and another is the presence of isomers in $\{Mn(\eta^5-C_5H_7)(CO)_2P(OMe)_3\}$.

The change in the intensity of the peaks observed in Scheme 5 may suggest that a disubstituted product is formed when an excess of ligand is used, according to the large peaks observed at low frequency. The spectra could be compared to with those of the isolated samples $\{Mn(\eta^5-C_5H_7)(CO)_2P(OMe)_3\}$ $\{\nu(CO)(nujol)$ 1959(s), 1897(s) $cm^{-1}\}$ and $\{Mn(\eta^3-C_3H_5)(CO)_2[P(OMe)_3]_2\}\{$ $\nu(CO)(pentane)$ 1943(s), 1872(vs) $cm^{-1}\}$.[161]

After sublimiation at 45-50°C/0.01 mm Hg of the solid sample, synthesised with an excess of ligand, a marked change is observed in the infrared spectrum showing basically two strong sharp bands with weak shoulders in the top ($\nu(CO)$ 1959, 1940(sh), 1897 and ~1875(sh) cm^{-1} in nujol) corresponding to the volatile complex $\{Mn(\eta^5-C_5H_7)(CO)_2P(OMe)_3\}$.

The ^1H-NMR spectrum of the sample prepared in ratio (1:2) showed in deuterated acetone the presence of an η^5- and an η^3-pentadienyl species, as described in Section 3.1.2.3. In spite of the fact that four peaks are observed in the $\nu(CO)$ region when a reaction mixture in a stoicheiometric ratio is used, ^1H-NMR spectroscopy showed only the presence of an η^5-pentadienyl ligand, whether chromatography is carried out or not.

The suggested presence of isomers is based on similar infrared observations for the methyl-cyclopentadienyl complexes $\{Mn(\eta^5-C_5H_4Me)(CO)_2P(OMe)_3\}$(1955,1949, 1895 and 1887 cm^{-1} in CS_2 solution) and $\{Mn(\eta^5-C_5H_4Me)(CO)_2P(OPh)_3\}$ (1964(sh), 1960, 1905(sh) and 1901 cm^{-1} in CS_2 solution),[166] which were prepared by irradiation of $\{Mn(\eta^5-C_5H_4Me)(CO)_3\}$ in the presence of an excess of the corresponding ligand. The complex $\{Mn(\eta^5-C_5H_4Me)(CO)_2P(OMe)_3\}$ is reported to be an unstable liquid which did not give a satisfactory analysis. ^1H-NMR studies are not reported. According to the above we are more in favour of the first explanation, the lack of isolation of the suggested dicarbonyl disubstituted complex however, prevents a definite conclusion.

The reaction mixture with $\{Mn(\eta^5-C_5H_7)(CO)_3\}$ and PMe_2Ph, after 4 h. of irradiation and consumption of the intermediate species, gave rise to 4 peaks, instead of 2 in the infrared spectra with cyclohexane, but the product $\{Mn(\eta^5-C_5H_7)(CO)_2PMe_2Ph\}$ after chromatography showed only the characteristic 2 strong peaks.

A decrease in the frequency of the two carbonyl bands from the $\{Mn(\eta^5-C_5H_7)(CO)_2L\}$ systems compared with $\{Mn(\eta^5-C_5H_7)(CO)_3\}$ (2020, 1957 and 1937 cm^{-1} in nujol) is thought to result from an increase in the electron density on the metal by the replacement of CO by L which is a stronger electron donor. It is evident from the Table 4 in the first instance, that the amount of electron density on the manganese atom increases in the order $P(OPh)_3 < P(OMe)_3 \sim P(OEt)_3 < PPh_3 < PMe_3 \sim PMe_2Ph < P(C_6H_{11})_3 < AsPh_3$. There is a general agreement on the observed trend in carbonyl stretching frequencies with the donor strength or acceptor ability for the phosphorus ligands between the series of the isoelectronic complexes $\{Mn(\eta^5-C_5H_5)(CO)_2L\}$ and $\{Mn(\eta^5-C_5H_7)(CO)_2L\}$. The triphenylarsine derivative

TABLE 4

FREQUENCIES OF CO STRETCHING MODES (cm^{-1}) FOR COMPLEXES OF FORMULA $\{Mn(\eta^5-C_5H_7)(CO)_2L\}$ [a] AND RELATED CYCLIC COMPLEXES $\{Mn(\eta^5-C_5H_5)(CO)_2L\}$

$\{Mn(\eta^5-C_5H_7)(CO)_2L\}$	ν(CO)		$\{Mn(\eta^5-C_5H_5)(CO)_2L\}$	ν(CO)
	nujol	$CHCl_3$		cyclohexane
PPh_3	1953,1923(sh),1878,1838(sh)	1943,1874	PPh_3	1945,1884 [e]
$P(C_6H_{11})_3$	1939,1927(sh),1877,1858(sh)		$P(C_6H_{11})_3$	1931,1869 [e]
PMe_3	1948,1881	1938,1866	PMe_3	1939,1876 [e]
PMe_2PH	1944,1878		PMe_2Ph	1932,1867 [f]
$P(OMe)_3$	1959,1897	1955,1887 [c]	$P(OMe)_3$	1954,1891 [d]
$P(OEt)_3$	1958,1896	1952,1882 [c]	$P(OEt)_3$	1949,1886 [d]
$P(OPh)_3$	g	1967,1903	$P(OPh)_3$	1970,1909 [d]
$AsPh_3$	1933,1859	1940,1873	$AsPh_3$	1935,1872 [h]

a) All bands have strong intensity; b) cyclohexane solution. See the text; c) Broad peaks ; d) Ref.165 ; e) Ref.164 ; f) Ref.148 in CS_2 solution ; g) Intermediate solubility in the mull giving broad signal ; h) Ref.159 in CS_2 solution.

{$Mn(\eta^5-C_5H_7)(CO)_2AsPh_3$} showed the lowest CO stretching frequency values (in a nujol mull) in the pentadienyl series. However, an appreciable shift is observed for this complex, and also for the PPh_3 derivative when the intensities are determined in solution ($CHCl_3$) giving close values, and producing doubt about the relative donor strength of this $AsPh_3$ complex. For the cyclic complexes {$Mn(\eta^5-C_5H_5)(CO)_2L$} {L=PPh_3 or $AsPh_3$} have been reported very similar frequencies in CS_2 solution (L=PPh_3, 1934, 1874 cm^{-1} and L=$AsPh_3$, 1935, 1872 cm^{-1}) by Brill,[159] and by others (L=PPh_3, 1937, 1875 cm^{-1} and L=$AsPh_3$, 1936, 1874 cm^{-1}).[157a] Studying the influence of P, As and Sb in these cyclic compounds, Barbeau reports that the electron density on the manganese atom decreases in the order $SbPh_3 > AsPh_3 > PPh_3$.[167]

Matrix Isolation Studies

Photochemistry of {$Mn(\eta^5-C_5H_7)(CO)_3$} in frozen gas matrices at 20 K has been studied by Perutz and Powell.[168]

The photolysis of the complex was carried out under inert (argon) and reactive matrices (N_2,CO). The infrared spectroscopy shows evidence for the formation of the tetracarbonyl species {$Mn(\eta^3-C_5H_7)(CO)_4$}. The results for the photolysis of {$Mn(\eta^5-C_5H_7)(CO)_3$} in argon and nitrogen matrices is still under analysis.

The infrared spectrum from the parent complex {$Mn(\eta^5-C_5H_7)(CO)_3$} in a CO matrix showed strong bands in the $\nu(CO)$ region at 2027, 1959 and 1942 cm^{-1}. A period of u.v. photolysis (3 min.) with the filtered medium pressure arc lamp using a {$CoSO_4/NiSO_4$} filter produced the spectrum in the ν(CO) region: 2072, 1997, 1980 and 1965 cm^{-1} (new peaks) along with starting material. With 6 min.of irradiation a photostationary state is observed and after 20 min. no more change was detected. Further irradiation was carried out with a soda glass ($\lambda > 325$nm) filter for 3 h., showing only the final product {$Mn(\eta^3-C_5H_7)(CO)_4$}{ν(CO) 2075(m), 1997(s), 1979(s), 1964(vs), 1932(vvw)}.[169] The reaction in solution of the pentadienyltricarbonylmanganese with carbon monoxide (1 atm) also gave evidence of the same carbonyl stretching bands and is described in Section 3.2.2.2.

Infrared spectra from an experiment with {$Mn(\eta^5-C_5H_7)(CO)_3$} in argon matrix showed before irradiation (with $CoSO_4/NiSO_4$ filter) ν(CO) at 2031, 1964 and 1945 cm^{-1} and after 12 min of irradiation a new band appears at 1959 cm^{-1}.

The corresponding ν(CO) bands for the manganese complex in N_2 matrix are 2030, 1964 and 1944 cm^{-1}. Irradiation of the matrix with a Hg/soda glass filter (λ >325nm) for 18 min showed small peaks. After 20 min. more the new peaks were at ν(N≡N) 2185, ν(CO) 1987, 1959 and 1935 cm^{-1}. The relative intensities of these new terminal carbonyl bands remained constant. Then, removal of the filter and irradiation of the matrix at lower wavelengths (Hg/pyrex λ >290nm) showed after 20 min. bands at ν(N≡N) 2180, ν(CO)2035, 2000, 1948 and 1929 cm^{-1}.

Comparison of these frequencies with the corresponding values for {$Mn(\eta^5-C_5H_5)(CO)_2N_2$} {$\nu$(N≡N)2175.3, ν(CO)1978.7, 1927 [170]} suggest that the dicarbonyl product is not the expected product, which is in agreement with the primary process during the reaction of these pentadienyl complex, as described in Section 3.2.2.1 and 3.2.2.3.

Protonation Studies.

Protonation of the pentadienyltricarbonylmanganese and the phosphine derivatives {$Mn(\eta^5-C_5H_7)(CO)_2L$ } {$L=PPh_3,P(C_6H_{11})_3$}, as well as {$Mn(\eta^3-C_5H_7)(CO)_3PMe_3$} (Section 3.2.2.2) with the weak coordinating acid CF_3COOH, have been carried out using infrared and ^{1}H-NMR spectroscopy.

^{1}H-NMR studies (250MHz) showed no evidence of the formation of a Mn-H bond. No resonance was observed in the high field region (δ=0 - 14 ppm), when a deuterated dichloromethane solution of {$Mn(\eta^5-C_5H_7)(CO)_2\ P(C_6H_{11})_3$ } in the presence of trifluoroacetic acid was studied. Also, only poor information could be obtained from the rest of the spectrum due to broad signals at -15°C and at room temperature.

The infrared spectra of the mentioned compounds in a mixture of trifluoroacetic acid and dichloromethane (1/4) always showed bands shifted to high frequency compared with the corresponding ν(CO) of starting materials; this could suggest that protonation of the complexes had occurred due to a decrease in the electron density on the metal atom, reflected by the CO stretching frequency.

Moreover, a change in the symmetry of the fragment $\{Mn-(CO)_n\}$ seems to occur because the number of bands observed changes. Spectroscopic data are reported in Table 5.

TABLE 5

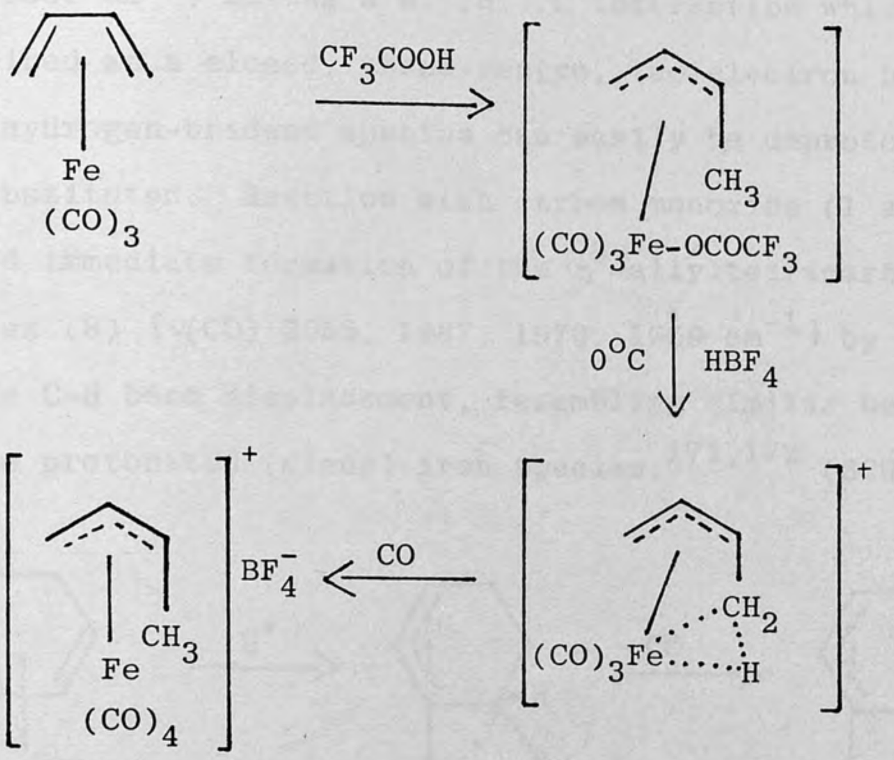
INFRARED CARBONYL STRETCHING FREQUENCIES FOR COMPLEXES STUDIED.

Complex	Ratio ($CF_3COOH:CH_2Cl_2$)	$\nu(CO)$ cm^{-1}
$\{Mn(\eta^5-C_5H_7)(CO)_3\}$	(1:4)	2100(m),2038(vs), 2005(s),1975(s).
	(4:1)	2100(m),2038(vs). 2005(s),1975(s).
$\{Mn(\eta^5-C_5H_7)(CO)_2PPh_3\}$	(1:4)	2085(m),2005(vs), ~1965(br).
	(4:1)	2090(m),2005(vs) ~1970(br)
$\{Mn(\eta^5-C_5H_7)(CO)_2P(C_6H_{11})_3\}$	(1:4)	2078(m), 2003(vs), 1957(s)
$\{Mn(\eta^3-C_5H_7(CO)_3PMe_3\}$	(1:4)	2085(m),2005(vs), 1962(s).

Addition of the acid at room temperature to the yellow CH_2Cl_2 solution of $\{Mn(\eta^5-C_5H_7)(CO)_3\}$ leads a stronger yellow solution, which after 30 minutes showed the unchanged spectrum, with the ν(CO) given in Table 5. Before this time a mixture with starting material is observed. The phosphine dicarbonyl derivatives in CH_2Cl_2 solution gives after treatment, at room temperature, of one drop of acid a red-brown solution, which after immediate addition of more acid turns yellow. The product from $\{Mn(\eta^5-C_5H_7)(CO)_3\}$ gives four bands, and those from the dicarbonyl complexes three. This feature contrasts with the protonation characteristics observed for the analogous cyclopentadienyl complexes $\{Mn(\eta^5-C_5H_5)(CO)_2L\}$ $\{L=CO,PPh_3,P(C_6H_{11})_3\}$ reported by Ginzburg et al.[157] As described in Section 3.1.1., an increase of negative charge at the metal atom by replacement of phosphine ligand of a CO group stimulates the protonation. Thus, $\{Mn(\eta^5-C_5H_5)(CO)_2P(C_6H_{11})_3\}$ was entirely protonated in pure CF_3COOH, whereas $\{Mn(\eta^5-C_5H_5)(CO)_2PPh_3\}$ and $\{Mn(\eta^5-C_5H_5)(CO)_3\}$ were partially and non-protonated respectively, under the same conditions. The protonated species $\{Mn(\eta^5-C_5H_5)(CO)_2P(C_6H_{11})_3\}$ showed two carbonyl stretching bands at 2001 and 2041 cm^{-1}.[157a] The above experimental results suggest that the acyclic ligands,in these analogous complexes, are more easily attacked in an acidic medium; resembling in principle, the behaviour of acyclic diene complexes under protonation reactions. However, based only on the information obtained by infrared spectroscopy it is not possible to establish definitely the site for the proton attack and further studies are obviously necessary in order to understand the exact nature of these complicated reactions.

On the basis of the infrared results and several investigations of the behaviour of tricarbonyldiene iron complex and tricarbonylcyclohexadiene manganese anion, we could suggest the following analysis:

Proton addition to pentadienyltricarbonylmanganese complex showed four carbonyl stretching bands (see Table 5) which is not in agreement with tricarbonyl species. This pattern would suggest a possible tetracarbonyl species formed with an extra carbonyl arising from partial decomposition of the starting material. Earlier work on the protonation of diene iron tricarbonyl complexes with poorly coordinating acids, gave species formulated as η^3-allyltetracarbonyl cations[171] which are formed by capture of CO from an intermediate bridge species.[172] (SCHEME 6).



SCHEME 6

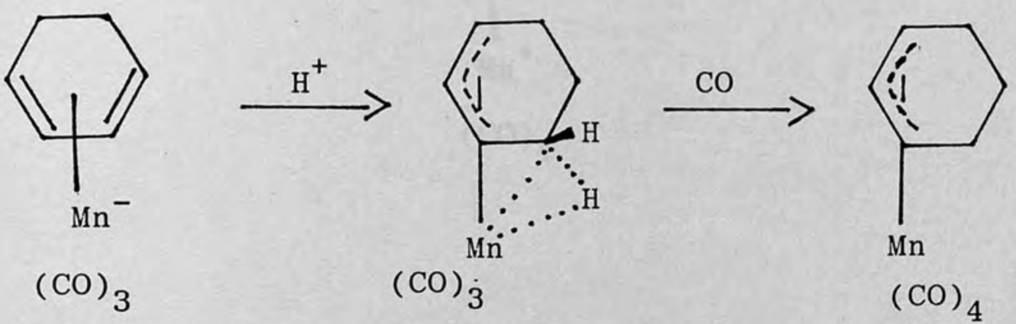
The infrared spectrum of the isolated salt $\{Fe(\eta^3\text{-1-syn-}MeC_3H_4)(CO)_4\}BF_4$ in nitromethane exhibits $\nu(CO)$ at 2145, 2100, 2088 and 2080 cm^{-1}.[171a]

Other tetracarbonyl neutral complexes reported are given in order to compare, $\{Cr(\eta^4\text{-}C_5H_8)(CO)_4\}$ $\{\nu(CO)$ 2030, 1964, 1938, 1923 $cm^{-1}\}$[173]; $\{Mo(\eta^2\text{-}C_4H_6)_2(CO)_4\}$ $\{\nu(CO)$ 1965 $cm^{-1}\}$[174];

$\{Fe(\eta^2\text{-}C_4H_6)(CO)_4\}$ $\{\nu(CO)$ 2082,2003,1980 $cm^{-1}\}$[175]

Studies on tricarbonylmanganese complexes by Brookhart,[89b,176] have shown that protonation of (η^4-cyclohexadiene) manganese tricarbonyl anion (6) $\{\nu(CO)$ 1930, 1840 and 1789 cm^{-1} (K or Na salts)$\}$yields neutral

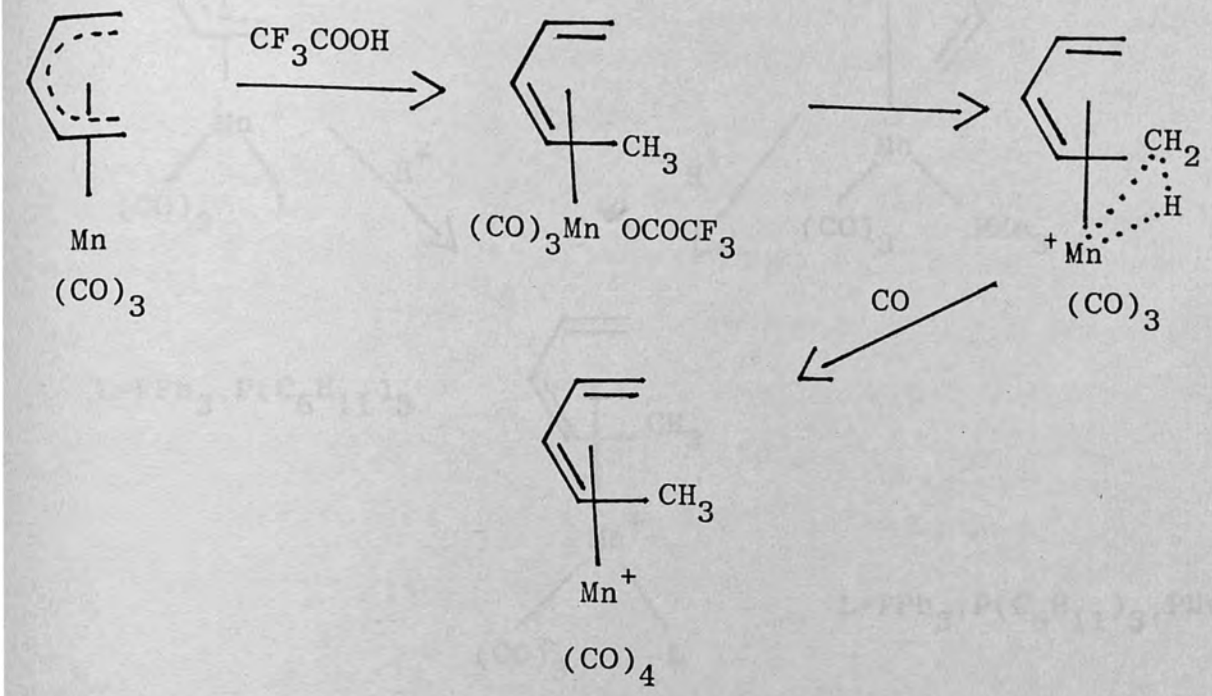
(η^3-cyclohexenyl)manganesetricarbonyl (7) (ν(CO) 2020, 1945,1937 cm^{-1}) having a M...H...C interaction which is described as a closed, three-centre, two-electron bond.[176a] This hydrogen-bridged species can easily be deprotonated or substituted. Reaction with carbon monoxide (1 atm) showed immediate formation of the η^3-allyltetracarbonyl complex (8) {ν(CO) 2055, 1987, 1970, 1959 cm^{-1}} by simple C-H bond displacement, resembling similar behaviour of the protonated (diene) iron species.[171,172] (SCHEME 7).



(6) (7) (8)

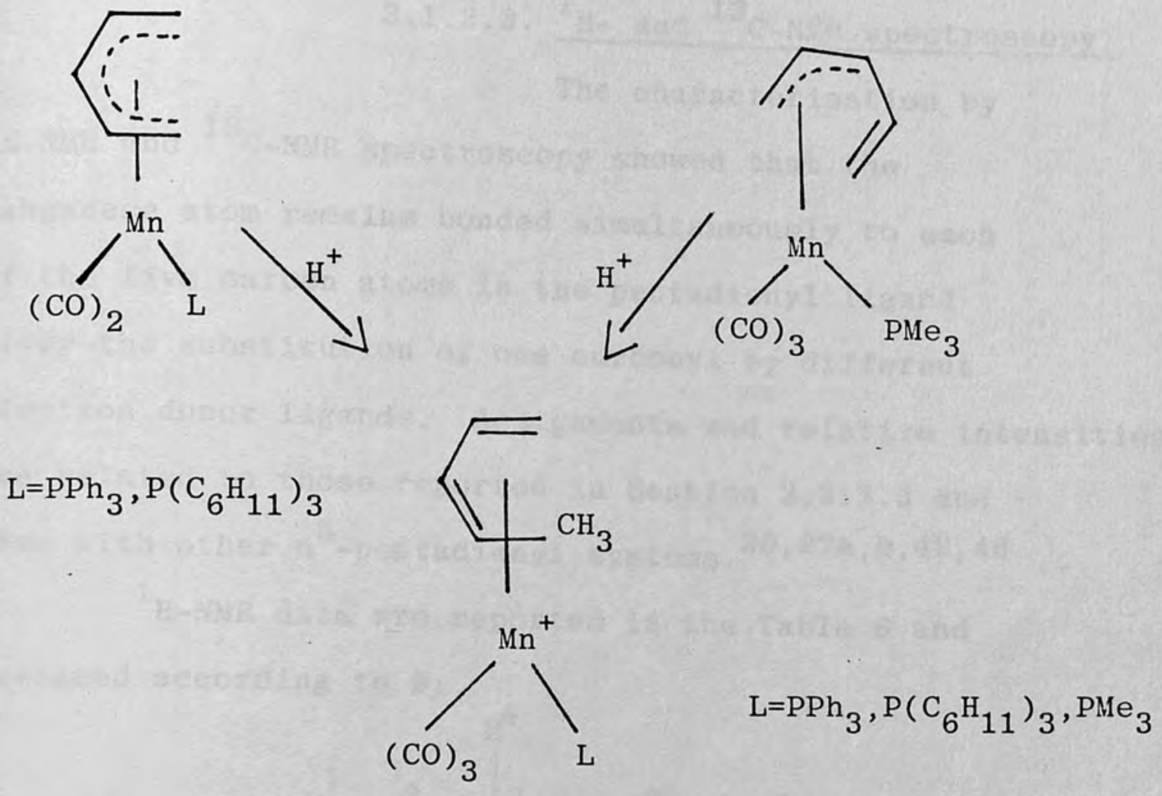
SCHEME 7

Accordingly, we suggest a similar feature as a probable explanation of the spectrum observed for the pentadienyltricarbonylmanganese complex (SCHEME 8).



SCHEME 8

In a similar manner, the phosphine derivatives could be explained, due to the presence of more than two carbonyl stretching bands in the spectra. Moreover, it is interesting to observe the identical infrared pattern obtained from the protonation of the dicarbonyl complexes $\{Mn(\eta^5\text{-}C_5H_7)(CO)_2L\}$ $\{L{=}PPh_3,P(C_6H_{11})_3\}$ and the corresponding to $\{Mn(\eta^3\text{-}C_5H_7)(CO)_3PMe_3\}$ which could also support the capture of the CO group from the dicarbonyl species in order to obtain 18-electron configuration. (SCHEME 9).



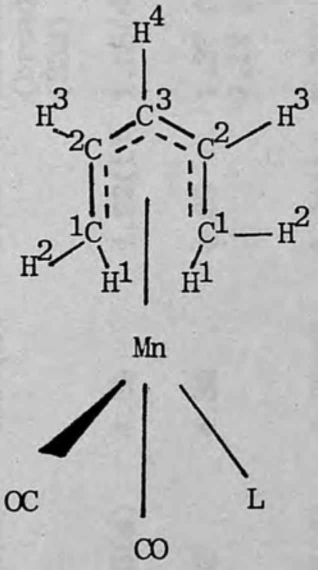
SCHEME 9

Elimination of the acyclic ligand is reported for the allylmanganese complex $\{Mn(\eta^3-C_3H_5)(CO)_2[P(OR)_3]_2\}$ ($R=i-C_3H_7$) by treatment with CF_3SO_3H or CH_3SO_3H giving the neutral complexes $\{Mn(CO)_2[P(OCHMe_2)_3]_2(CF_3SO_3)\}$ {ν(CO) 1980, 1965 cm^{-1} (hexane)} and the methanesulfonate derivative {ν(CO) 1960, 1885 cm^{-1}(nujol)},respectively. Protonation of the same allyl complex with CF_3SO_3H in the presence of norboradiene afforded the cationic complex $[Mn(CO)_2(diene)\{P(OR)_3\}_2]\ CF_3SO_3$ ($R=i-C_3H_7$), {ν(CO) 2020, 1955 cm^{-1} (KBr)}[160].

3.1.2.3. ^{1}H- and ^{13}C-NMR spectroscopy

The characterisation by ^{1}H-NMR and ^{13}C-NMR spectroscopy showed that the manganese atom remains bonded simultaneously to each of the five carbon atoms in the pentadienyl ligand after the substitution of one carbonyl by different electron donor ligands. Assignments and relative intensities are related to those reported in Section 2.2.2.3 and also with other η^5-pentadienyl systems.[20,27a,b,42,46]

^{1}H-NMR data are reported in the Table 6 and assigned according to 9.



(9)

The 250 MHz ^{1}H-NMR spectrum for $\{Mn(\eta^5\text{-}C_5H_7)(CO)_2PPh_3\}$ is shown in Figure (2). Four resonances are observed consistent with a symmetrical structure of the η^5-pentadienyl ligand in the dicarbonyl complexes (9). This pattern is similar to that shown by the tricarbonyl complex $\{Mn(\eta^5\text{-}C_5H_7)(CO)_3\}$ in $CDCl_3$[68] but with all resonances to

TABLE 6

^{1}H-NMR DATA FOR COMPLEXES $\{Mn(\eta^5-CH^1H^2CH^3CH^4CH^3CH^2H^1)(CO)_2L\}$

COMPLEX	CHEMICAL SHIFTS ^{a,c}					COUPLING CONSTANTS (Hz)			
	H^1	H^2	H^3	H^4	L	H^1H^3	H^2H^3	H^3H^4	OTHER
$\{Mn(\eta^5-C_5H_7)(CO)_2PPh_3\}$	0.24(d)	2.08(d)	4.70(m)	5.38(t)	7.35and 7.52 (m) (15H)	11.3	10	6.15	$J(PH^1)=2.5$; $J(PH^3)=2$
$\{Mn(\eta^5-C_5H_7)(CO)_2P(C_6H_{11})_3\}^b$	0.18(d)	2.28(d)	4.94(m)	5.52	1.24and 1.86 (broad,m) (33H)	11.2	9.7		$J(H^3)=6.2$; $J(PH^3)=3$
$\{Mn(\eta^5-C_5H_7)(CO)_2PMe_3\}$	−0.12	2.05(d)	4.69	4.92(t)	1.05(d)(9H)				$J(H^4)=6.7$; $J(PH^4)\sim1$
$\{Mn(\eta^5-C_5H_7)(CO)_2PMe_2Ph\}^b$	0.29	2.02	4.56	4.85	1.37 (6H) 7.12 (5H)				
$\{Mn(\eta^5-C_5H_7)(CO)_2P(OMe)_3\}$	0.26(d)	2.45(d)	4.75(m)	5.04(t)	3.32(d) (9H)	11.5	9.8	6.25	$J(PH^1)=2.2$; $J(PH^3)J(PH^4)\sim1$
$\{Mn(\eta^5C_5H_7)(CO)_2P(OEt)_3\}^d$	0.31(dd)	2.52(dd)	4.79(td)	5.10(t)	3.85(m)(6H) 1.06(m)(9H)	11.3	9.75	6.25	$J(H^1H^4)\sim0.9$; $J(PH^1)=3$; $J(PH^2)\sim1$;$J(H^1H^2)=2$; $J(PH^3)=2.4$; $J(PH^4)=1.25$.
$(Mn(\eta^5-C_5H_7)(CO)_2P(OPh)_3\}$	0.18(d)	2.31(d)	4.63(t)	4.42(m)	7.09(m)(15H)	11.2	9.8	6.5	$J(PH^1)=2.6$; $J(PH^3)=3$
$[Mn(\eta^5-C_5H_7)(CO)_2AsPh_3\}$	0.05(d)	2.13(d)	4.64	5.31(m)	7.03(m)(9H) 7.56(m)(6H)	~11.5			$J(H^2)\sim10$; $J(H^3)\sim6$

a) In C_6D_6 relative to TMS (δ = 0), 250MHz ; b) In $CDCl_3$ relative to TMS (δ = 0), 250MHz ;

c) Broad signals if multiplicity is not indicated ; d) Assignment based on ^{31}P decoupling.

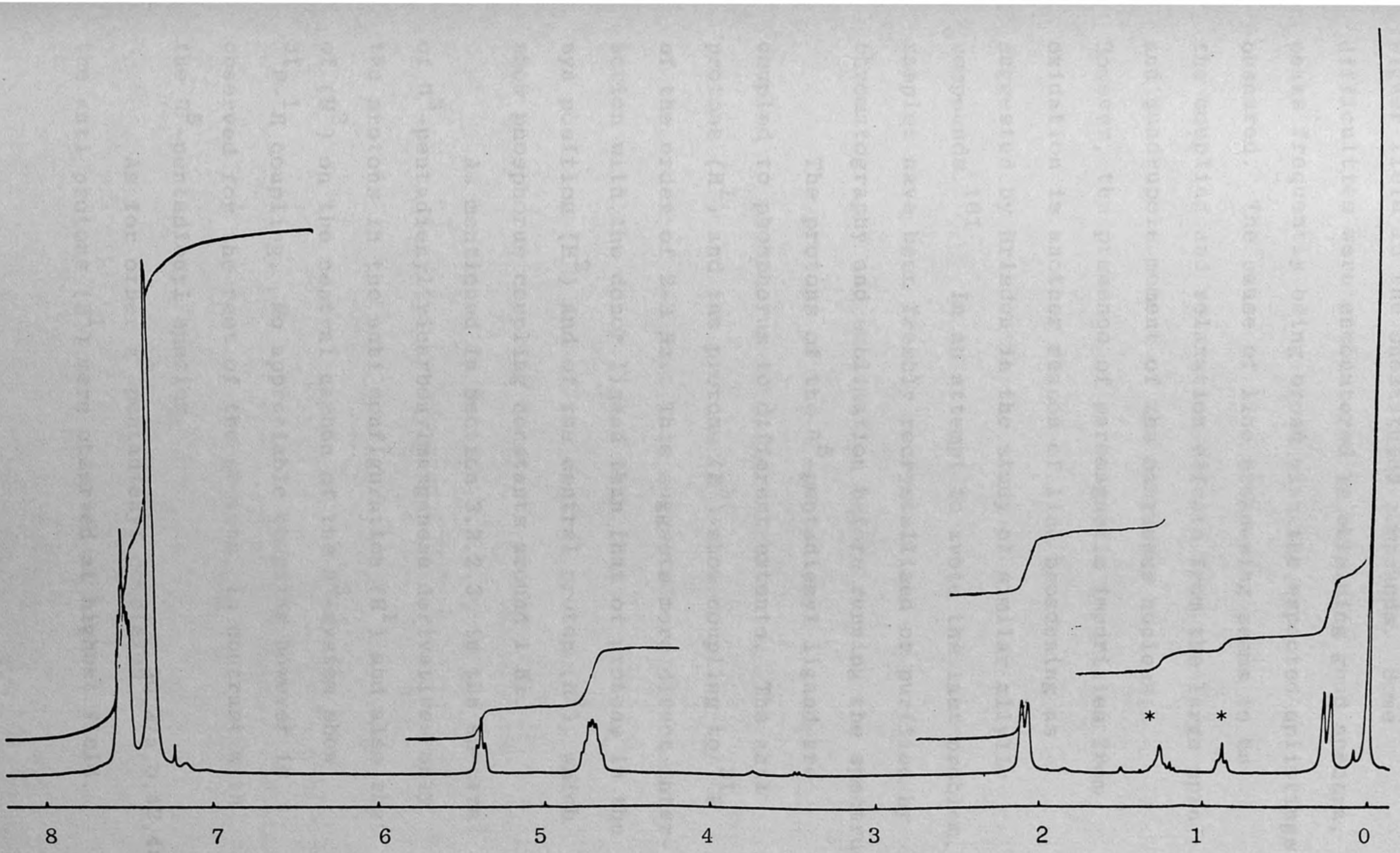


Figure 2. ^{1}H-NMR spectrum of η^5-pentadienyldicarbonyl(triphenylphosphine)manganese (9) in C_6D_6 at 250 MHz. (* impurity).

higher field in the substituted compounds. Some difficulties were encountered in obtaining good spectra, peaks frequently being broad with the expected splittings obscured. The cause of line broadening seems to be the coupling and relaxation effects from the large spin and quadrupole moment of the manganese nucleus. However, the presence of paramagnetic impurities from oxidation is another reason of line broadening as suggested by Brisdon in the study of similar allylic compounds.[161] In an attempt to avoid the last problem, samples have been freshly recrystallised or purified by chromatography and sublimation before running the spectrum.

The protons of the η^5-pentadienyl ligand are coupled to phosphorus to different extents. The anti protons (H^1) and the protons (H^3) show coupling to ^{31}P of the order of 2-3 Hz. This suggests more direct interaction with the donor ligand than that of protons in the syn position (H^2) and of the central proton (H^4), which show phosphorus coupling constants around 1 Hz.

As mentioned in Section 3.2.2.3, in the spectra of η^3-pentadienyltricarbonylmanganese derivatives only the protons in the anti configuration (H^1) and also that of (H^3) on the central carbon of the η^3-system show ^{31}P-^1H coupling. No appreciable coupling however is observed for the rest of the protons, in contrast with the η^5-pentadienyl species.

As for other η^5-pentadienyl complexes,[20,27a,b,42,46] the anti protons (H^1) were observed at highest field.

The more weakly phosphorus coupled syn protons (H^2) resonate in the range of 2 - 2.55δ. The resonances for (H^3)(multiplet) and (H^4)(triplet) protons are widely separated at lower field from the two pairs of protons (H^1) and (H^2). The proton (H^4) attached to the central carbon atom in these η^5-complexes resonates at lowest field, except in the case of $\{Mn(\eta^5-C_5H_7)(CO)_2P(OPh)_3\}$ in which this proton is observed at higher field than the (H^3) protons, as mentioned in Section 2.2.2.3. The strong phosphorus coupling with these protons (H^3) suggest that the triphenylphosphite ligand is interacting with them. Then, it is expected that the deshielding effect observed for (H^3), is due to the influence of the aromatic groups of the ligand $P(OPh)_3$. Similar shift was also detected in the presence of the phenyl group of the disubstituted pentadienyl ligand in the complex $\{Mn(\eta^5$-syn,syn-1,5-$Ph_2C_5H_5)(CO)_3\}$.

Long range couplings $J(H^1H^4)$ and $J(H^2H^4) \sim$ 0.9Hz were observed in the phosphorus-decoupled spectrum of $\{Mn(\eta^5-C_5H_7)(CO)_2P(OEt)_3\}$.

Values for the vicinal proton coupling constants were of similar magnitude to those of tricarbonyl complexes (Section 2.2.2.3.); with the trans-coupling (11.2-11.5Hz) larger than for the cis-couplings (9.7-10 Hz). A similar feature is observed in the ^{1}H-NMR spectra of the η^3-allyl complexes $\{Mn(\eta^3-C_3H_5)(CO)_3L\}$ $\{L=PPh_3, AsPh_3, P(C_6H_{11})_3\}$ and $\{Mn(\eta^3-C_3H_5)(CO)_2L_2\}\{L=P(OMe)_3, P(OEt)_3\}$ [161] (J=12 and 7Hz respectively).

In the phosphite series the resonances are observed at increasingly higher field with the phenyl, methyl and ethyl derivatives respectively.

Solvent shift effects were observed in {$Mn(\eta^5-C_5H_7)(CO)_2L$} {$L=P(OMe)_3$ and $P(OPh)_3$} with chloroform and benzene deuterated solvents, all the signals being shifted to low field with chloroform {$\Delta\delta=0.05 - 0.43$ [$P(OMe)_3$] and $0.04 - 0.16$ [$P(OPh)_3$]}.

The product obtained after direct crystallisation from a reaction mixture with {$Mn(\eta^5-C_5H_7)(CO)_3$} and an excess of ligand $P(OMe)_3$ showed a ^1H-NMR spectrum, in deuterated acetone, with a mixture of η^5- and η^3-pentadienyl species. The typical four resonances with an intensity ratio 2:2:2:1 from the η^5-pentadienyl ligand are found at 0.32δ (H^1) as doublet of triplets due to ^{31}P coupling. The doublet at 2.43δ is assigned to the syn protons (H^2), and the multiplet at 5.0δ and the triplet at 5.61δ arise from the protons (H^3) and the proton (H^4) respectively. Coupling constants found are $J(H^1H^3)=11.6Hz$, $J(H^2H^3)=9.8Hz$, $J(H^3H^4)=6.3Hz$. The phosphorus coupling pattern was the same as described before for other η^5-pentadienyldicarbonyl complexes, with $J(PH^1) \sim 2.1Hz$, $J(PH^3)=2.2Hz$ and $J(PH^4) \sim 1Hz$. Two doublets from the methoxy protons at 3.62δ and 3.70δ coupled with ^{31}P nuclei (10.5Hz) suggest non-equivalent systems as expected from the mixture of products. The assignment attributed to the η^3-pentadienyl species is based on the analogous characteristic pattern observed for purified η^3-complexes (Section 3.2.2.3). The vinylic region of the ligand can be clearly assigned {see (23) in Section 3.2.2.3.} with resonances at 6.16δ (dt), 4.65δ(dd) and 4.92δ (dd) corresponding to protons (H^5), (H^6) and (H^7) respectively. However, the rest of the ligand is not definitely assigned because of partial overlapping of one of the signals (4.68δ) and also the observed shifted values for corresponding resonances {4.68δ(1H), (3.03δ,(1H), J=7.3,10.6Hz) and (2.88δ, (2H), J=7.3Hz) }.

The ^{13}C-NMR spectra of some of the substituted dicarbonylpentadienylmanganese complexes $\{Mn(\eta^5-C_5H_7)(CO)_2L\}$ have been determined and are summarised in Table 7. The ^{1}H- decoupled ^{13}C-NMR of the complex $\{Mn(\eta^5-C_5H_7)(CO)_2P(OPh)_3\}$ is presented as an example of these well resolved spectra in Figure 3. Assignments are according to (9).

The ^{13}C-NMR spectra recorded with proton-noise decoupling consist of three separated resonances from the carbon skeleton of the pentadienyl ligand confirming their symmetric structure. The chemical shifts of the (C^2) resonances were found at lowest field, followed by the resonances of the central carbon atom (C^3) and the terminal carbons (C^1) which resonate at highest field. Off resonance decoupling provided evidence of the number of hydrogen atoms attached to each carbon atom. A pair of doublets resonate at the chemical shift corresponding

TABLE 7

^{13}C-NMR data for the complexes {Mn(η^5-C_5H_7)(CO)$_2$L}

	CHEMICAL SHIFTS[a]			
L	C^1	C^2	C^3	L
CO[b]	57.52	100.14	83.34	221.90 (broad)
PMe_3	55.08	99.37	87.77	20.2 226.4 (broad CO)
PMe_2Ph	56.11	99.32	87.98	19.39,129.20[d]
$P(C_6H_{11})_3$	55.32	96.80	87.02	26.8,28.3,30.3, 38.0
$P(OMe)_3$[c]	56.13	98.60	88.30	51.59
$P(OPh)_3$[c]	56.41	97.99	88.70	120.94,124.35, 129.59,151.66
$AsPh_3$	54.90	97.71	88.86	128.84,129.58, 133.12,138.11

a) In C_6D_6 relative to TMS (δ=0). 22.63 MHz;

b) Reference 68 ($CDCl_3$) ;

c) In $CDCl_3$ relative to TMS (δ=0).22.63MHz;

d) Ph overlapped with C_6D_6

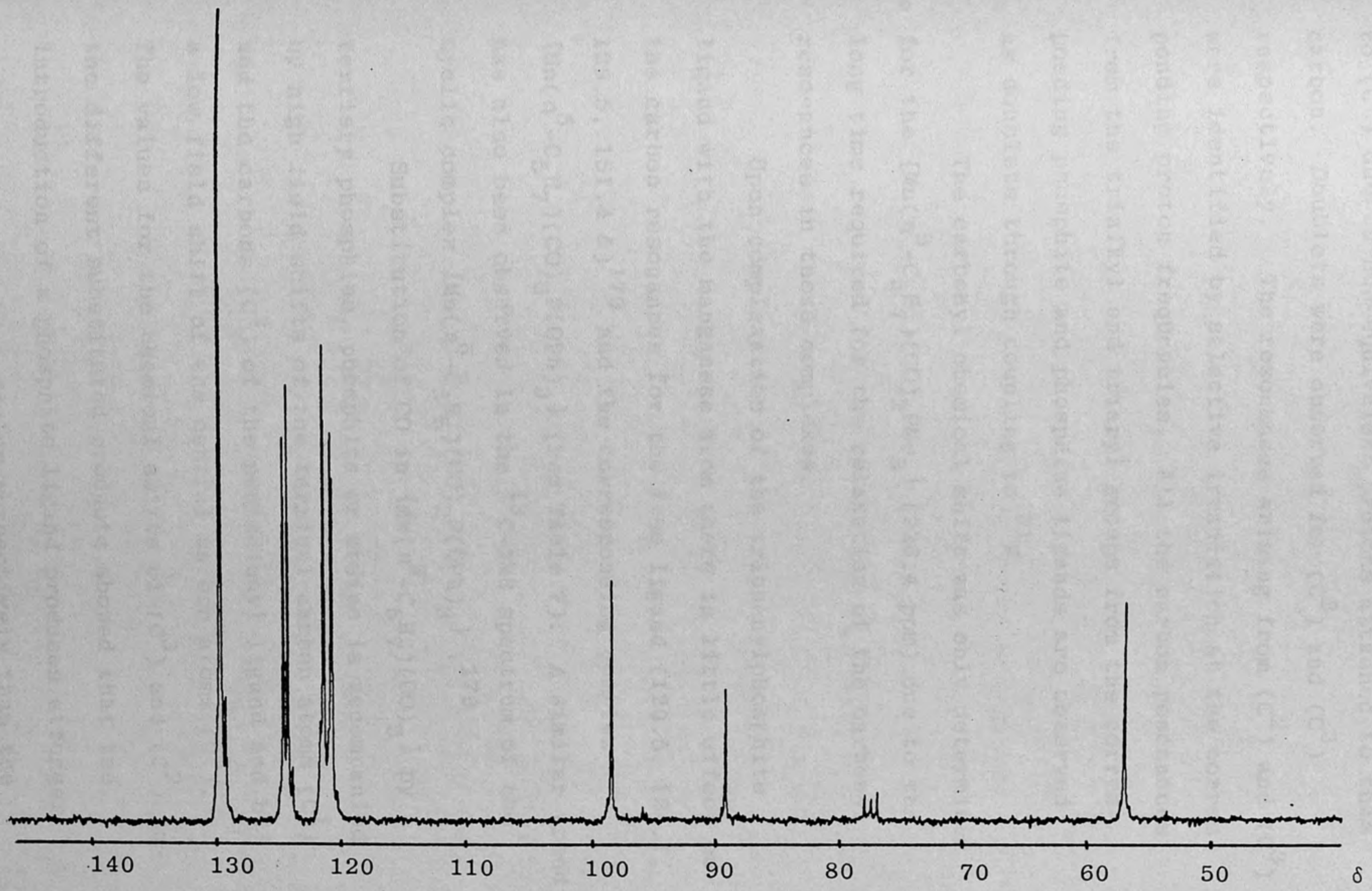


Figure 3. ^{13}C-NMR spectrum of η^5-pentadienyldicarbonyl(triphenylphosphite)manganese in $CDCl_3$ at 22.63 MHz.

to (C^1) due to non-equivalent protons attached to this carbon. Doublets were observed for (C^2) and (C^3) respectively. The resonances arising from (C^2) and (C^3) were identified by selective irradiation at the corresponding proton frequencies. All the carbon resonances from the trialkyl and triaryl groups from the corresponding phosphite and phosphine ligands are observed as doublets through coupling to ^{31}P.

The carbonyl chemical shift was only determined for the $\{Mn(\eta^5-C_5H_7)(CO)_2PMe_3\}$ (226.4 ppm) due to the long time required for the relaxation of the carbonyl resonances in these complexes.

Upon complexation of the triphenylphosphite ligand with the manganese atom there is little effect on the carbon resonances for the free ligand (120.5, 124.1, 129.5, 151.4 δ)[179] and the corresponding complex $\{Mn(\eta^5-C_5H_7)(CO)_2P(OPh)_3\}$ (see Table 7). A similar trend has also been observed in the ^{13}C-NMR spectrum of the cyclic complex $\{Mn(\eta^5-C_5H_5)(CO)_2P(OPh)_3\}$.[179]

Substitution of CO in $\{Mn(\eta^5-C_5H_7)(CO)_3\}$ by a tertiary phosphine, phosphite or arsine is accompanied by high field shifts of the terminal carbon atoms (C^1) and the carbons (C^2) of the pentadienyl ligand and by a low field shift of the central carbon atoms (C^3). The values for the chemical shifts of (C^3) and (C^2) in the different substituted products showed that the introduction of a phosphite ligand produces stronger shift to low and high fields respectively than the phosphines. The terminal carbons (C^1) showed stronger shielding effect by the presence of the phosphines than that of the phosphites.

The ^{13}C-NMR spectra of methylated pentadienyl complexes such as $\{Fe(\eta^5\text{-}2,4\text{-}Me_2C_5H_5)_2\}$ and $\{Ti(CO)(\eta^5\text{-}2,4\text{-}Me_2C_5H_5)_2\}$ have shown similar carbon resonances in the acyclic ligand. The resonances for the iron compound appear at 99.7δ(C^2), 93.9δ(C^3), 51.1δ(C^1) and 26.8δ(Me) in C_6D_6, and for the titanium compound appear at 123.5δ(C^2), 116.6δ(C^3), 72.5δ(C^1) and 29.9δ(Me) in C_6D_6.[46] Only minor changes in the spectra of the pentadienyl ligands occur compared to the cyclic cationic complex $\{Fe(\eta^5\text{-}C_6H_7)(CO)_3\}^+$ 64.5δ(C^1), 89.9δ(C^3), 103.2δ (C^2) and 24.7δ(CH_2) in CF_3CO_2H},[105] probably indicating that the major contributors to the chemical shift are not greatly determined by the cyclic or acyclic nature of the ligand.

3.1.3. Experimental Section

All thermal reactions were carried out under an atmosphere of dry nitrogen using dried and degassed solvents. Conventional Schlenk techniques were used. Cyclohexane was freshly distilled from CaH_2. Chromatography was carried out on a Florisil column (30 x 2 cm). Except where stated otherwise, the boiling range of the light petroleum used was 40-60°C.

The solid ligands PPh_3, $P(OPh)_3$, $AsPh_3$ were used as received and $P(C_6H_{11})_3$ was recrystallised from acetone and it was stored under nitrogen. Liquid phosphines and phosphites were freshly distilled under vacuum before use, except PMe_3 (Strem Chemicals) that was used as obtained. The phosphites $P(OMe)_3$ and $P(OEt)_3$ (Aldrich) were dried by storage over sodium and distilled. The $\{Mn(\eta^5-C_5H_7)(CO)_3\}$ was prepared as described in Experimental Section 2.2.3 from $C_5H_7SnBu_3$ and $Mn(CO)_5Br$.

Photochemical reactions were carried out in a conventional reaction vessel fitted with a quartz water-cooled immersion well, a reflux condenser and a cannula for admission of dry nitrogen. The irradiation source was a 125W medium-pressure mercury arc lamp (λ =365-366 nm, and also in u.v. 265, 297, 303, 313 and 334 nm and visible 404-408, 436, 546, 577-579 nm).

Instrumentation is described in Section 2.1.3.

General Method for the Preparation of the Complexes $\{Mn(\eta^5-C_5H_7)(CO)_2L\}$ via Thermal Reactions.

The complexes were prepared using a procedure similar to that of Brisdon, et al.[161]

A mixture of $\{Mn(\eta^5-C_5H_7)(CO)_3\}$ (2.43 mmol) and the respective phosphine or phosphite (2.43 mmol) was heated in refluxing cyclohexane (30 cm^3), until infrared monitoring of the reaction mixture showed complete consumption of the starting material and no further change in the spectrum was observed. The reaction times are given in Table 1. Evaporation of the solvent at reduced pressure gave a yellow solid or a yellow oil. Further purification was effected as follows:

Dicarbonyl-η^5-pentadienyl(triphenylphosphine)manganese.- The yellow residue was dissolved in light petroleum-diethyl ether (12:1), the solution was filtered and slow evaporation afforded golden yellow crystals, which were filtered and recrystallised from light petroleum-diethyl ether (6:1).

Dicarbonyl-η^5-pentadienyl(tricyclohexylphosphine)manganese.- The pale yellow solid was dissolved in dichloromethane and the solution filtered. Hexane was added and the solution slowly evaporated giving a lemon yellow precipitate which was collected and dried under vacuum.

Dicarbonyl-η^5-pentadienyl(triphenylphosphite)manganese.- A yellow oil was dissolved in the minimum volume of light petroleum-diethyl ether (12:1). Chromatography using the same mixed solvent for elution followed by removal of the solvent gave pale yellow crystals.

Dicarbonyl-η^5-pentadienyl(dimethylphenylphosphine)manganese. - A similar procedure to that above for the $P(OPh)_3$ complex gave a yellow oil from the first light-yellow band collected from chromatography. A very small amount of pale lemon yellow crystals at -20°C was obtained from the oil by recrystallisation three times from hexane at -78°C, and kept at -20°C. Analysis is not reported because of solvent contamination in the sample observed by ^{1}H-NMR.

The same reaction was carried out changing only the time of reflux. After 6 h. the infrared spectrum showed an identical pattern as for the 4 h. reaction. However, after chromatography only one product was obtained. It was a solid with a strong yellow colour and high melting point (160-172°C) with decomposition above 115^{o}C. The carbonyl region in the spectrum showed a wide band (1980-1888 cm^{-1}) with several terminal peaks at 1980, 1965, 1952, 1933, 1903 and 1888 cm^{-1}.

Dicarbonyl-η^5-pentadienyl(trimethylphosphine)manganese. - A yellow oil was dissolved in hexane. The product was precipitated and filtered at -50^{o}C. Two recrystallisations of the solid were carried out, firstly, with a small amount of CH_2Cl_2 and hexane and then with hexane at -20^{o}C, giving a yellow powder that easily sublimed at room temperature and 0.05 mmHg. The first fraction sublimed was contaminated with starting material. A sample sublimed at 25^{o}C and 0.05 mmHg in a temperature gradient afforded yellow crystals.

Dicarbonyl-η^5-pentadienyl(trimethylphosphite)manganese. - a) The yellow oil was dissolved in light petroleum - diethyl ether (12:1), filtered and reduced to a small volume. The solution was cooled in ice giving a pale yellow precipitate, which was filtered, washed with hexane and dried. A wide melting point (71-81^{o}C) was observed, presumably for the presence of a mixture of products (See Section 3.1.2.2.).

b) The yellow oil was chromatographed using the mixed solvent light petroleum - diethyl ether (12:1). Removal of the solvent, filtration of the solid and finally sublimation at 40^{o}C and 0.05 mmHg afforded the very pale yellow product, with a sharp melting point (81-83^{o}C).

Dicarbonyl-η^5-pentadienyl(triethylphosphite)manganese. - A similar procedure as that above gave a yellow-orange oil after double chromatography. The addition of hexane and then cooling the solution with liquid nitrogen and filtering the solid at -78°C four times, gave a very pale yellow product which melted at ~ 18°C.

Method for the Preparation of the Complexes {Mn(η^5-C_5H_7)(CO)$_2$L} via Photochemical Reactions.

Dicarbonyl-η^5-pentadienyl(triphenylarsine)manganese. - A mixture of {Mn(η^5-C_5H_7)(CO)$_3$} (0.5 g., 2.43mmol) and $AsPh_3$ (1.49 g., 4.86mmol) dissolved in cyclohexane (75 cm^3) was photolysed at room temperature for 3 h. using the method described above. Infrared evidence indicated complete consumption of the tricarbonyl complex after this time, showing only two strong νCO bands from the dicarbonyl complex. The solution was filtered and evaporated giving an orange oil which was dissolved in light petroleum - diethyl ether (1:2). This solution was filtered again and reduced in volume giving a yellow precipitate. The solid was recrystallised from a benzene-light petroleum mixture to give golden yellow crystals.

Dicarbonyl-η^5-pentadienyl(trimethylphosphine)manganese. - A mixture of {Mn(η^5-C_5H_7)(CO)$_3$} (0.53 g., 2.57mmol) and PMe_3 (0.2 g., 2.57mmol) dissolved in cyclohexane (75 cm^3), was photolysed using a soda glass filter (λ >325nm) for 7½ h. The irradiation solution was kept in an ice bath during the first 2½ h. An infrared spectrum of the mixture showed several bands corresponding to unchanged starting material, η^3-pentadienyltricarbonylmanganese derivative (described in Section 3.2.2.), the expected product and also two sharp bands more at the lowest frequency {1867 and 1848 cm^{-1} (cyclohexane)}. However, no prolonged photolysis was carried out because every time the intensity of the carbonyl bands at 1867 and 1848 cm^{-1} was increasing without appreciable change observed in the peaks of the dicarbonyl product. Further purification was effected by evaporation of the cyclohexane after filtration of a pyrophoric beige solid. The yellow oil was dissolved in hexane and chromatographed on a Florisil column using light petroleum. Only one yellow band was observed and collected but after evaporation of the solvent, the infrared spectrum of the oil showed no successful separation of the dicarbonyl complex from the tricarbonyls. The oil was kept at -78°C giving crystals which were filtered and recrystallised twice from hexane at -78°C. The solid can be sublimed at 25°C/0.05mmHg yielding the title complex (8%).

<u>Dicarbonyl-η^5-pentadienyl(dimethylphenylphosphine)manganese</u>. - A mixture of {$Mn(\eta^5-C_5H_7)(CO)_3$} (0.5 g., 2.43mmol) and PMe_2Ph (0.34 g., 2.43mmol) dissolved in cyclohexane (75 cm^3) was photolysed at 0°C using a soda glass filter ($\lambda > 325$nm) for 9¼ h. A very similar spectrum as for PMe_3 derivative was found, with the respective mixture of η^3- and η^5-pentadienyl complexes and a very strong peak at 1840 cm^{-1} with a shoulder at 1860 cm^{-1}. After 4¼ h. of irradiation,

infrared evidence indicated the presence of η^3- and η^5-pentadienyl in similar intensity and the very strong peak at 1840 cm^{-1} and the shoulder growing quickly. Contrasting with the above, after the 9¼ h. of irradiation the bands corresponding to the dicarbonyl complex had almost gone, the other bands remaining. The orange solution was evaporated giving a yellow-orange oil, treated with light petroleum -diethyl ether (12:1), filtered and evaporated again. Distillation of the sample at 55-65°C/0.05mmHg gave a few drops which were dissolved in hexane and kept at -20°C giving the dicarbonyl complex in very small yield.

Attempted Photochemical Reactions with $\{Mn(\eta^5-C_5H_7)(CO)_3\}$ and various Ligands.

Attempted isolation of $\{Mn(\eta^5-C_5H_7)(CO)_2P(OEt)_3\}$. - A stoichiometric mixture of $\{Mn(\eta^5-C_5H_7)(CO)_3\}$ and $P(OEt)_3$ (2.69mmol) in cyclohexane (75 cm^3) was irradiated using a soda glass filter for 22 h. After this time, the infrared spectrum showed only 2 strong bands in the carbonyl stretching region at 1938 (small shoulder at 1905 cm^{-1}) and 1867 cm^{-1} in cyclohexane. Filtration and evaporation of the solution gave a yellow oil. Distillation at 40-60°C and 0.03mmHg was unsuccessful and chromatography with light petroleum - diethyl ether gave one pale yellow band. Evaporation of the solvent afforded a quite air sensitive oil which after several recrystallisations from hexane at -78°C showed a broad carbonyl band with peaks at 1998, 1923, 1907 and 1858 cm^{-1} (neat film), that suggest as possible mixture of products: $\{Mn(\eta^3-C_5H_7)(CO)_3P(OEt)_3\}$ and the title product. No further purification could be done with this mixture.

The reaction of $\{Mn(\eta^5-C_5H_7)(CO)_3\}$ with THF. - The complex $\{Mn(\eta^5-C_5H_7)(CO)_3\}$ (0.53 g., 2.57mmol) in THF (75 cm^3) was irradiated at 0°C, with and without soda glass filter during 4 h. and 10 h. respectively, giving slightly orange-yellow solutions, but infrared spectra indicated no evidence of reaction. The spectrum of the solution irradiated 19 h. showed apart from starting material a very strong peak at 1713 cm^{-1} which in principle, (even though it is at too low frequency) could suggest the possible formation of some complex with bridging carbonyls.[177] Addition of PPh_3 to this solution caused immediate and complete disappearance of the strong band at low frequency. After refluxing this solution for 16 h. no appreciable change was observed in the monitored infrared spectra but the formation of $\{Mn(\eta^5-C_5H_7)(CO)_2PPh_3\}$ was not complete.

The oily product from evaporation gave many different bands on chromatography using Florisil and light petroleum - diethyl ether (10:1). Only two fractions gave isolated products: the second band salmon pink was collected giving after recrystallisation from hexane, very pale yellow crystals which melted at 78-79°C. Characterisation by ^{1}H-NMR showed no evidence of the pentadienyl ligand and the infrared spectrum in the ν(CO) region showed bands at 1992(s), 1918(br), 1900(sh), 1858(sh) in $CHCl_3$. From the third yellow band collected, $\{Mn(\eta^5-C_5H_7)(CO)_2PPh_3\}$ was isolated in low yield.

The reaction of $\{Mn(\eta^5-C_5H_7)(CO)_3\}$ with pyridine. -

a) A mixture of $\{Mn(\eta^5-C_5H_7)(CO)_3\}$ (0.53 g., 2.57mmol) and pyridine (0.2 g., 2.57mmol) disssolved in THF (75 cm^3) was photolysed at room temperature for 7 h. with a soda glass filter and 3 h. more without it. After this time, no evidence of the dicarbonyl product expected from the substitution of pyridine was observed. When irradiation was stopped the infrared spectra showed basically four bands at 2000(s), 1970 {br,1950(sh) }, 1920(s), 1870(vvw) cm^{-1}. The solution was filtered and evaporated giving an orange oil. Distillation at 48°C and 0.03mmHg gave a yellow oil which crystallised on storage at 0°C. Recrystallisation from hexane, followed by sublimation (40°/0.05mmHg) afforded yellow crystals with m.p. 66-67°C. Spectrocopic studies and chemical analysis showed no evidence of the pyridine ligand in the complex. Instead of the dicarbonyl complex expected, analysis of the data suggests the formation of a novel η^3-pentadienyl complex $\{Mn(\eta^3-C_5H_7)(\eta^2-C_5H_8)(CO)_3\}$ that is discussed in Section 3.2.2.

b) The same mixture as above dissolved in cyclohexane (75 cm^3) was photolysed at room temperature for 30 h. showing a complicated infrared absorption pattern. A complete disappearance of starting material was observed, however, possible bands for the expected product $\{Mn(\eta^5-C_5H_7)(CO)_2py\}$ were not observable [1933 and 1865 cm^1 in isooctane for the cyclopentadienyl derivative $\{Mn(\eta^5-C_5H_5)(CO)_2py\}$]178 the substitution by pyridine failed by thermal and photolytical methods.

<u>The reaction of $\{Mn(\eta^5-C_5H_7)(CO)_3\}$ with maleic acid dimethyl ester (MeOOCCH=CHCOOMe)</u>.-

A pale yellow solution of $\{Mn(\eta^5-C_5H_7)(CO)_3\}$ (0.99 g., 2.38mmol) and a ten fold excess of dimethylmaleate (3.46 g.) in THF (75 cm^3) was photolysed at room temperature for 9 h. giving a golden-brown solution. The infrared spectrum showed a single broad peak at 1972 cm^{-1}. Evaporation of the mixture of reaction gave a dark yellow solid and a brown-orange oil. The crude reaction product was sublimed at room temperature and 0.05mmHg removed the excess of ester. The infrared spectra of both solid and oil showed the absence of C≡O groups.

<u>The reaction of $\{Mn(\eta^5-C_5H_7)(CO)_3\}$ with *cis*-cyclooctene.</u> -

The complex $\{Mn(\eta^5-C_5H_7)(CO)_3\}$ (1.83 g., 8.9mmol) was dissolved in hexane (200 cm^3) with an excess of *cis*-cyclooctene (89mmol). After irradiation at 0°C for 10 h. there was no noticeable change in the infrared spectrum [CO stretching region (2080-1920 cm^{-1})]. Evaporation of the sample gave a yellow oil which was sublimed at room temperature and 0.05mmHg removing the remaining starting material. The oily residue sublimed very slowly at 60°C/0.05mmHg, giving a spectrum with very broad carbonyl band at 2000-1910 cm^{-1}. We have not been able to obtain a crystalline product from this mixture after treatment with hexane and cooling the solution at low temperature.

Attempted isolation of $\{Mn(\eta^5-C_5H_7)(CO)_2NO\}BF_4$. - The complex $\{Mn(\eta^5-C_5H_7)(CO)_3\}$ (0.43 g., 2.1mmol) was dissolved in SO_2 (20 cm^3) at -40°C with rapid stirring, then addition of $NOBF_4$ (0.36 g., 3.1mmol) was made into the yellow solution. Immediately after addition the solution turned deep red with some precipitate. Stirring was continued for 20 minutes. The solvent was removed by evaporation leaving a red solid. Addition of dry CH_3NO_2 (15 cm^3) gave a deep orange solution and small amount of precipitate which was filtered off giving a brown sticky solid. Addition of diethyl ether in excess into the solution, gave a fine yellow-beige powder, filtered and dried under vacuum. This product decomposed without melting. The infrared spectrum showed both carbonyl and (B-F) groups while NO was absent. The high frequency of the $\nu(CO)$ bands at ~2110, 2070 and ~2030 cm^{-1} in nujol, would suggest the oxidation of the product giving the tetrafluoroborate salt $\{Mn(\eta^5-C_5H_7)(CO)_3\}^+BF_4^-$. Similar reaction was carried out using CH_3NO_2 instead of SO_2 but was also unsuccessful.

Attempted protonation of $\{Mn(\eta^5-C_5H_7)(CO)_2P(C_6H_{11})_3\}$ with hexafluorophosphoric and diethyl etherate $HPF_6.(C_2H_5)O$. - A small sample of the manganese derivative (0.04 g., 0.09mmol) was dissolved in dry diethyl ether (25 cm^3), cooled to

$-50^{o}C$ and then the slow addition of HPF_6 (0.05 cm^3) was carried out. At $-35^{o}C$ the acid in contact with the product gave a strong yellow solution. The reaction mixture was allowed to warm up to room temperature over 75 min. A sticky oil and a yellow solid were separated. The solvent was decanted and the sample dissolved in CH_2Cl_2 (10 cm^3). Addition of diethyl ether afforded a white precipitate (without evidence of carbonyl bands in the infrared spectrum). The yellow solution was therefore evaporated.

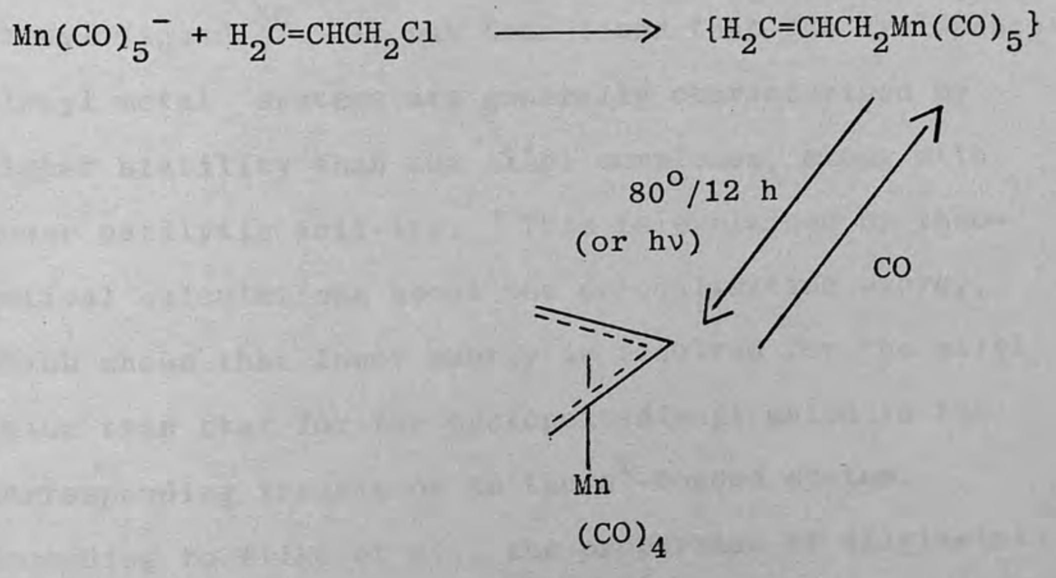
The infrared spectrum of a neat film of the yellow oil showed bands in the carbonyl stretching region at 2075(m), 1997(s), 1942(s), ~1928(sh) and 1878(w) cm^{-1} and PF_6 at 905(m) and 845 cm^{-1}. For comparison the infrared spectrum of starting material showed bands at 1939(s), 1927(sh), 1877(s) and 1858(sh) in nujol which suggests that protonation was incomplete.

Protonation studies of the similar cyclic complex $\{Mn(\eta^5-C_5H_5)(CO)_2P(C_6H_{11})_3\}$ in CH_2Cl_2: CF_3COOH (4:1) showed two pairs of bands at 2035, 1991 and 1920, 1851 cm^{-1} for the protonated and non-protonated forms respectively.[157a] However, we have not been successful in isolating the expected cation.

3.2. η^3-Pentadienyltricarbonylmanganese complexes.

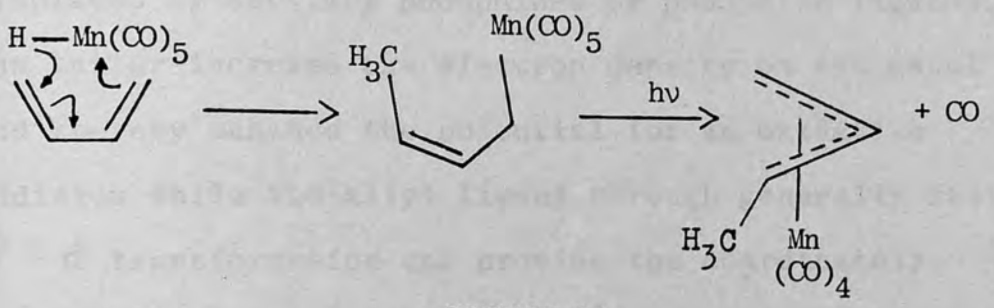
3.2.1. Introduction.

The chemistry of the η^3-allyl complexes has been substantially extended since Heck and Breslow in 1960, showed that the allyl group in{$Co(\eta^3-C_3H_5)(CO)_3$} is bonded as a symmetrical system to the metal atom.[180] Further confirmation of this η^3-allyl structure was obtained from ^{1}H-NMR spectroscopy by McClellan,et al.,[181] along with several allylmanganese complexes, such as {$Mn(\eta^1-C_3H_4R)(CO)_5$} and {$Mn(\eta^3-C_3H_4R)(CO)_4$}{R=H,Me,Cl}. The two synthetic methods used for these manganese complexes are now considered standard methods for preparing allyl complexes: a) Allyl chloride and lithium or sodium pentacarbonylmanganate react at room temperature to give the distillable yellow liquid {$Mn(\eta^1-C_3H_5)(CO)_5$} in 71% yield, which decomposed to {$Mn(\eta^3-C_3H_5)(CO)_4$} by heating to 80°C, affording the pale yellow crystals in 88% yield.[181,182a] (SCHEME 10).



SCHEME 10.

b) The addition of pentacarbonylhydridomanganese to conjugated dienes, such as 1,3-butadiene gives the substituted η^1-allyl complexes, which can be converted into the η^3-allyl by heating or, often more cleanly, by photolysis.[181,183] (SCHEME 11).



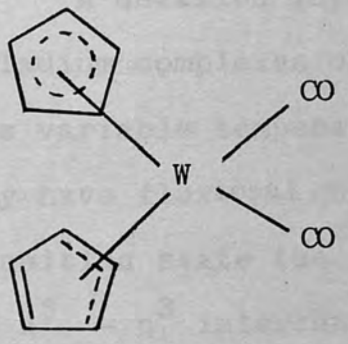
SCHEME 11

The reaction of $\{Mn(\eta^3-C_3H_5)(CO)_4\}$ with carbon monoxide (see Scheme 10) involves the partial displacement of the η^3-allyl ligand from the metal, being a reversible $\eta^3 \leftrightarrows \eta^1$ reaction.[182b] The versatile hapticity of the ligand is often important in catalytic processes and it has been discussed and compared to the cyclopentadienyl ligand.[56] It has been found that the cyclopentadienyl metal systems are generally characterised by higher stability than the allyl complexes, along with lower catalytic activity. This is explained by theoretical calculations about the delocalisation energy, which shows that lower energy is required for the allyl anion than that for the cyclopentadienyl anion in the corresponding transition to the η^1-bonded system. According to Wilke et al., the properties of allylmetal complexes evidently lie between those of stable cyclopentadienyl metal compounds and those of unstable alkyl metal compounds.[56]

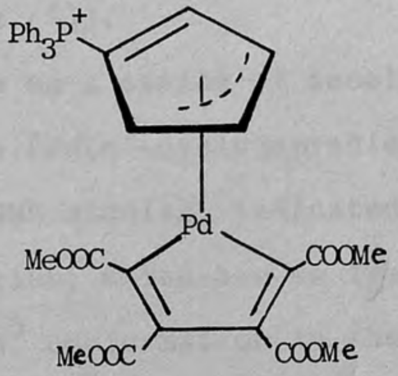
The resistance of η^3-allylic group in $\{Mn(\eta^3-C_3H_5)(CO)_4\}$ to displacement by other ligands is observed when the carbonyl group is preferentially displaced by tertiary phosphines or phosphite ligands.[160,161] The latter increase the electron density on the metal atom and thereby enhance the potential for an oxidative addition while the allyl ligand through generally facile $\eta^3 \rightarrow \eta^1$ transformation can provide the coordinately unsaturated intermediate. The dicarbonyl complexes $\{Mn(\eta^3-C_3H_5)(CO)_2(PR_3)_2\}$ (R=Et,OMe, OPr^i) have been reported as the first examples of manganese coordination catalyst precursors in hydrogenation of alkenes and alkynes, which involve a Mn(I)-Mn(III) couple.[160] The preparation of these complexes as well as the tricarbonyl derivatives $\{Mn(\eta^3-C_3H_5)(CO)_3L\}$ $\{L=PPh_3, P(C_6H_{11})_3, PBu^n_3, PMePh_2, AsPh_3\}$[161] have been described in Section 3.1.1. The $\{Mn(\eta^3-C_3H_5)(CO)_3PPh_3\}$ has also been isolated in 90% yield from a phase-transfer catalysed reaction between $\{MnBr(CO)_4PPh_3\}$ and C_3H_5Br in refluxing CH_2Cl_2 for 1 h.[184]

Certain classes of organometallic compounds containing the cyclopentadienyl ligand show bonding variations with possible η^1-η^3- or η^5-coordination. Such bonding involves dynamic processes which can be regarded as $\eta^5 \rightarrow \eta^1$ or $\eta^5 \rightarrow \eta^3$ rearrangements.

Some monohaptocyclopentadienyl complexes as $\{(\eta^1\text{-}C_5H_5)(\eta^5\text{-}C_5H_5)M(CO)_2\}$ {M=Fe,Ru} and $\{(\eta^1\text{-}C_5H_5)(\eta^5\text{-}C_5H_5)Cr(NO)_2\}$ among others, have been the object of much study;[185] nuclear magnetic resonance studies providing significant support for the identification of reversible $\eta^5 \rightarrow \eta^1 \rightarrow \eta^5$ rearrangements. These observations contrast with the lack of evidence reported for an $\eta^5 \rightarrow \eta^3$ rearrangement in the cyclopentadienyl group,[186] even though complexes containing an η^3-cyclopentadienyl ligand, are known. Crystallographic studies of the complexes $\{W(CO)_2(\eta^3\text{-}C_5H_5)(\eta^5\text{-}C_5H_5)\}$[187] (10) and $\{[PdC_4(CO_2Me)_4]\text{-}(\eta^3\text{-}PPh_3C_5H_4)\}$[188] (11) have shown that the respective structures contain a trihaptocyclopentadienyl ligand.



(10)

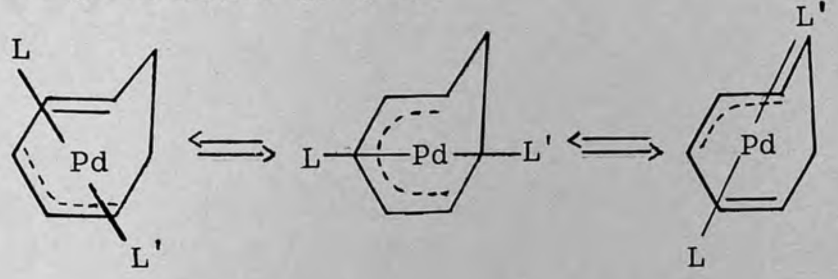


(11)

The tungsten complex was prepared from the reduction of $\{WCl_2(\eta^5-C_5H_5)_2\}$ under higher carbon monoxide pressures (140 atm), in the absence of hydrogen, in 20% yield.[189] Also this dark blue complex can be prepared at atmospheric CO pressure by a reaction sequence in which $\{WCl_2(\eta^5-C_5H_5)_2\}$ is treated with one equivalent of $AlCl_3$ under carbon monoxide in a chlorobenzene suspension isolating the complex $\{WCl(CO)(\eta^5-C_5H_5)_2(AlCl_4)\}$ which treated with sodium amalgam in a toluene suspension under CO at atmospheric pressure afforded the light sensitive dicarbonyl complex $\{W(CO)_2(\eta^3-C_5H_5)(\eta^5-C_5H_5)\}$ in30-40% yield.[190]

Treatment of the oligomeric tetrakis(methoxycarbonyl) palladiacyclopentadiene with triphenylphosphonium cyclopentadienylide in dry acetone afforded the monomeric palladiacyclopentadiene complex (11).

A detailed investigation on a series of isoelectronic palladium complexes of the type $\{Pd(\eta^3\text{-cycloheptadienyl})L_2\}^+$ from variable temperature ^{13}C-NMR studies, indicated that they have fluxional characteristics, which has as its transition state the in-plane η^5 conformation in the $\eta^3 - \eta^5 - \eta^3$ interchange (12).[191]

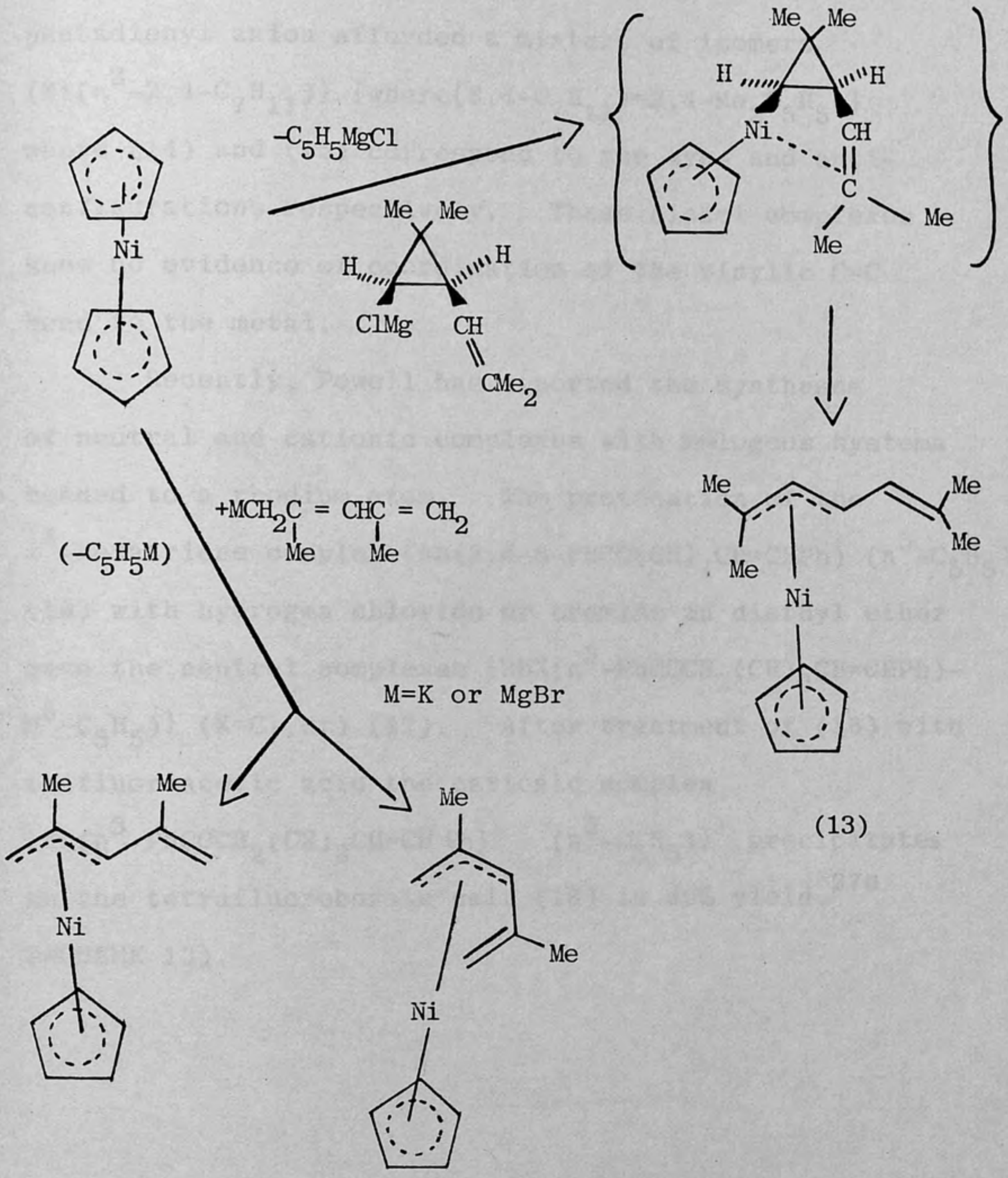


(12)

Extended Hückel molecular orbital calculations on the model compound $\{Pt(\eta-C_6H_7)(PH_3)_2\}^+$ have demonstrated that the η^3-geometry is the preferred ground state structure than the η^5-geometry. However, since the difference in energy is small it is expected to lead a low energy fluxional process for these species, being consistent with the results reported for the related cyclic palladium complexes (12) which take up a η^3-16-electron ground state structure rather than a η^5-18-electron structure.[191]

More versatile systems are expected with the acyclic η^3-pentadienyl ligand which should be more well-disposed to isomerize to η^5- or η^1-bonded configurations. A few complexes of this kind have been reported in the literature for different transition metals.

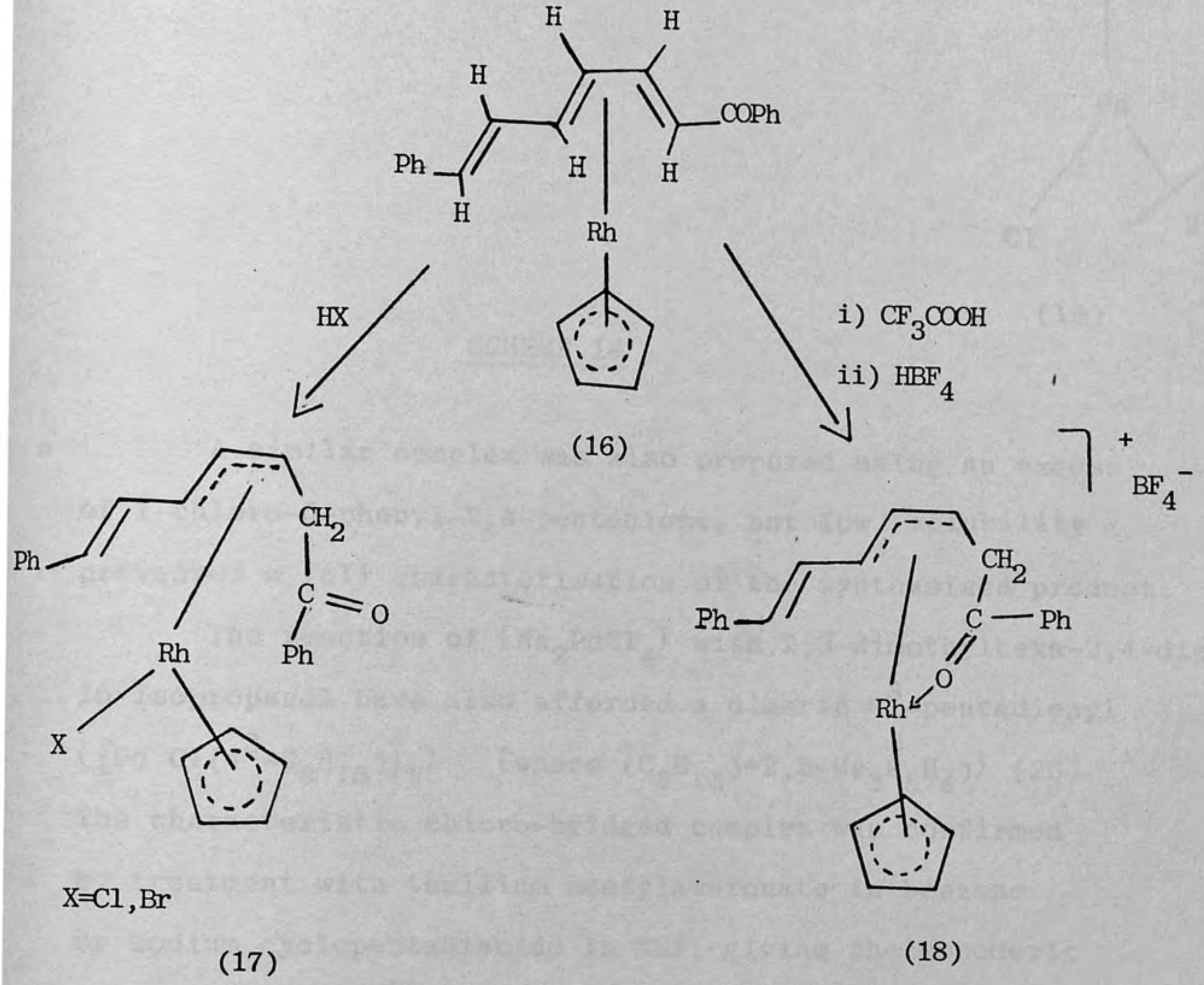
The reaction between the easily oxidised nickelocene and vinylcyclopropylmagnesium gave a vinylcyclopropylnickel intermediate which is readily converted into the η^3-pentadienyl complex $\{Ni(\eta^5-C_5H_5)(\eta^3-1,5-C_9H_{15})\}$ {where $(1,5-C_9H_{15})=(1,5-Me_4C_5H_3)$ }[192] (13).


$-C_5H_5MgCl$
Me
Me
H
H
ClMg
CH
CMe_2
Ni
Me
Me
H
H
Ni
CH
C
Me
Me
(13)
$(-C_5H_5M)$
$+MCH_2C = CHC = CH_2$
Me
Me
M=K or MgBr
Me
Me
Ni
(14)
Me
Me
Ni
(15)

SCHEME 12

The same metallocene treated with the 2,4-dimethylpentadienyl anion afforded a mixture of isomers $\{Ni(\eta^3\text{-}2,4\text{-}C_7H_{11})\}$ $\{where(2,4\text{-}C_7H_{11})=2,4\text{-}Me_2C_5H_5\}$ where (14) and (15) correspond to the syn- and anti-configurations respectively. These nickel complexes show no evidence of coordination of the vinylic C=C bond to the metal.

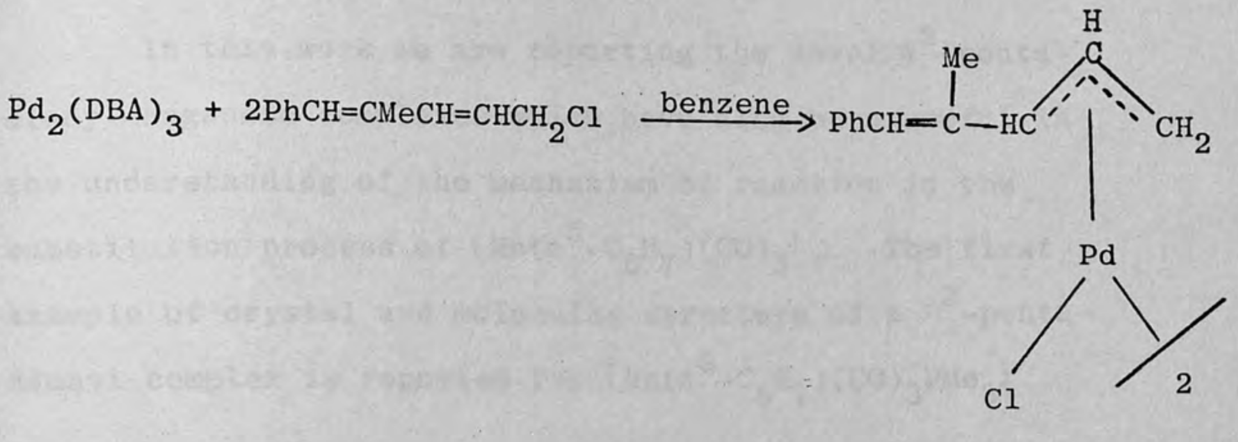
Recently, Powell has reported the syntheses of neutral and cationic complexes with analogous systems bonded to a rhodium atom. The protonation of the η^4-hexatriene complex $\{Rh(2,5\text{-}\eta\text{-}PhCO(CH)_4CH{=}CHPh)\ (\eta^5\text{-}C_5H_5)\}$ (16) with hydrogen chloride or bromide in diethyl ether gave the neutral complexes $\{RhX(\eta^3\text{-}PhCOCH_2(CH)_3CH{=}CHPh)\text{-}(\eta^5\text{-}C_5H_5)\}$ (X=Cl,Br) (17). After treatment of (16) with trifluoroacetic acid the cationic complex $\{Rh(\eta^3\text{-}PhCOCH_2(CH)_3CH{=}CH\ Ph)\ \ (\eta^5\text{-}C_5H_5)\}^+$ precipitates as the tetrafluoroborate salt (18) in 80% yield.[27d] (SCHEME 13).



SCHEME 13

It is observed for (18) that the acyl group is coordinated to the metal preserving the 18 electron configuration of the metal atom.

An oxidative addition reaction with the binuclear palladium complex $\{Pd_2(DBA)_3\}$ {DBA=dibenzylideneacetone (PhHC=CHCOCH=CHPh)}and the allylic halide ($PhCH=CMeCH=CHCH_2Cl$) was carried out at room temperature, giving the dimeric η^3- pentadienyl complex (19) in 76% yield.[193] (SCHEME 14)

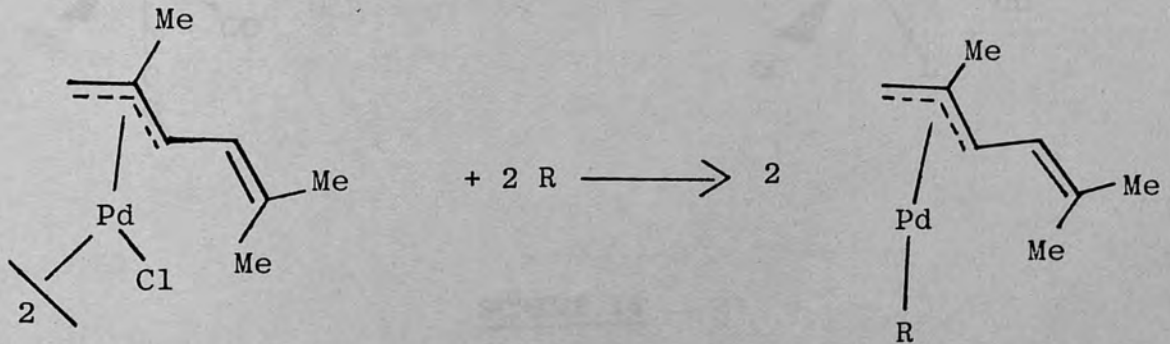


(19)

SCHEME 14

A similar complex was also prepared using an excess of 1-chloro-5-phenyl-2,4-pentadiene, but low solubility prevented a full characterisation of the synthesised product.

The reaction of $\{Na_2PdCl_4\}$ with 2,5-dimethylhexa-2,4-diene in isopropanol have also afforded a dimeric η^3-pentadienyl $\{[Pd\ Cl(\eta^3\text{-}C_8H_{13})]_2\}$ $\{$where (C_8H_{13})=2,5-$Me_3C_5H_4)\}$ (20). The characteristic chloro-bridged complex was confirmed by treatment with thallium acetylacetonate in benzene or sodium cyclopentadienide in THF, giving the monomeric derivatives $\{Pd(\eta^3\text{-}C_8H_{13})R\}$ $\{$R=MeCOCHCOMe(acac) or $(\eta^5\text{-}C_5H_5)\}$ (21) (SCHEME 15).



(20)

(21)

SCHEME 15

In this work we are reporting the novel η^3-pentadienylmanganese complexes which have also been useful in the understanding of the mechanism of reaction in the substitution process of $\{Mn(\eta^5-C_5H_7)(CO)_3\}$. The first example of crystal and molecular structure of a η^3-pentadienyl complex is reported for $\{Mn(\eta^3-C_5H_7)(CO)_3PMe_3\}$.

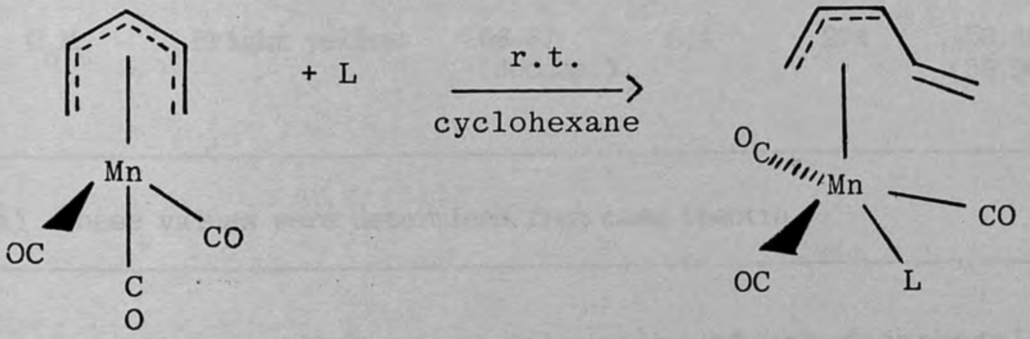
3.2.2. Results and Discussion

The complexes $\{Mn(\eta^3-C_5H_7)(CO)_3L\}\{L=PMe_2Ph, PMe_3, PBu^n_3\}$

3.2.2.1. Preparation and properties.

The tricarbonylmanganese complexes have been prepared by reaction between $\{Mn(\eta^5-C_5H_7)(CO)_3\}$ and the phosphorus donor ligand at room temperature. (SCHEME 16).

Analytical data are reported in Table 8.



SCHEME 16

The pale yellow crystalline complexes were isolated by treatment and recrystallisation with different solvents, as reported in the experimental section 3.2.3; they proved to be more easily handled than the corresponding η^5-pentadienyl analogues. They can also be stored long periods under nitrogen at room temperature.

TABLE 8

ANALYTICAL DATA FOR THE COMPLEXES $\{Mn(\eta^3-C_5H_7)(CO)_3L\}$

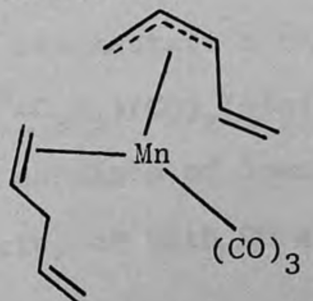
L	COLOUR	MELTING POINT (°C)	YIELD (%)	MOLECULAR WEIGHT [a]	ANALYSIS FOUND (CALC.) Carbon	Hydrogen
PMe_2Ph	Lemon yellow	78-79	46	344	56.04 (55.83)	5.58 (5.27)
PMe_3	Lemon yellow	74-75	66	282	46.79 (46.82)	5.86 (5.72)
PBu^n_3	Pale yellow	42-43	31	408	58.51 (58.82)	8.26 (8.39)
C_5H_8	Bright yellow	66-67 (decomp.)	6.4	274	56.40 (56.90)	5.72 (5.52)

a) These values were determined from mass spectra.

Oily residues after filtration of the dicarbonyl complex $\{Mn(\eta^5-C_5H_7)(CO)_2PPh_3\}$ (Section 3.1.2.1) showed spectroscopic evidence of the $\{Mn(\eta^3-C_5H_7)(CO)_3PPh_3\}$ {2000(s), 1938(s), 1909(s) cm^{-1}} which can be compared with the allyl complex $\{Mn(\eta^3-C_3H_5)(CO)_3PPh_3\}$ {2000(s), 1930(s), 1908(vs) cm^{-1} (in pentane) }.[161]

The reaction of {$Mn(\eta^5-C_5H_7)(CO)_3$} with carbon monoxide (1 atm)under irradiation was monitored by infrared spectroscopy showing evidence of the tetracarbonyl species {$Mn(\eta^3-C_5H_7)(CO)_4$} which is discussed in the infrared studies of Section 3.1.2.2. and 3.2.2.2. The evidence of these intermediate species {$Mn(\eta^3-C_5H_7)(CO)_3L$} {L=PMe_2Ph, PMe_3, PBu^n_3, CO} supports the mechanism of reaction, described in Section 3.2.2.3. on the basis of NMR studies. The rearrangement observed in the pentadienyl ligand $\eta^5 \rightarrow \eta^3 \rightarrow \eta^5$ by the introduction of an electron donor and displacement of a carbon monoxide respectively, suggest that the acyclic ligand is more labile compared to the cyclopentadienyl which does not show changes in the coordination mode. Then, a more versatile chemistry for the acyclic complexes is expected, as far as the pentadienyl fragment is concerned.

The complex {$Mn(\eta^3-C_5H_7)(\eta^2-C_5H_8)(CO)_3$} (22) was obtained from the irradiation of {$Mn(\eta^5-C_5H_7)(CO)_3$} in THF solution at room temperature, during the unsuccessful pyridine substitution reaction described in Section 3.1.3. The bright yellow crystals sublime readily at about 40°C in vacuum and are not very air sensitive. Analytical data are reported in Table 8.



(22)

The mass spectra of the tricarbonyl complexes with phosphorus donor ligands {$Mn(\eta^3-C_5H_7)(CO)_3L$} {$L=PMe_2Ph, PMe_3, PBu^n_3$} show the familiar stepwise loss of carbonyl groups.[194] In addition, however, the phosphine ligand is lost as observed from the fragments {$C_5H_7Mn(CO)_n$}$^+$ (n=1,2,3). All the ion fragments involving CO groups have low relative intensity. (See Table 9). No fragmentation of the organic ligand is observed until all carbonyl groups have been lost. During further decomposition of the ion {C_5H_7MnL}$^+$ the ligand L can either be split off as a unit or still coordinated to the Mn atom. The most intense peaks were {C_5H_7MnL}$^+$, { C_5H_7Mn}$^+$, {MnL}$^+$, {C_5H_7}$^+$, Mn^+ and the free ligand ion L^+.

The spectrum of {$Mn(\eta^3-C_5H_7)(\eta^2-C_5H_8)(CO)_3$} is markedly different, showing the simple pattern observed for the tricarbonylpentadienyl complexes {$M(\eta^5-C_5H_6R)(CO)_3$} {M=Mn, R=H,Me; M=Re R=H } described in Section 2.2.2.1. This complex undergoes primary fragmentation by loss of the three carbonyl groups; the {C_5H_7MnL}$^+$ fragment then loses the ligand L to give the {C_5H_7Mn}$^+$ ion, which has the highest intensity. To a lesser extent, the fragment ion containing the metal and the olefin {MnL}$^+$ is also observed.

The mode of fragmentation contrasts with the pattern observed for {$Mn(\eta^5-C_5H_5)(CO)_2(olefin)$} in which the first decomposition step consists of loss of the olefin or simultaneous splitting of both CO groups giving the ions

TABLE 9

MASS SPECTRA FOR THE COMPLEXES $\{Mn(\eta^3-C_5H_7)(CO)_3L\}^{a,b}$

ION	L			
	PMe_3	PMe_2Ph	Pbu^n_3	C_5H_8 c
$\{C_5H_7Mn(CO)_3L\}^+$	282 (<2)	344(~1)	408(4)	274(<1)
$\{C_5H_7Mn(CO)_2L\}^+$	254 (<2)	316(~1)	380(<1)	246(<1)
$\{C_5H_7Mn(CO)L\}^+$	226(<1)			218(6)
$\{C_5H_7Mn(CO)_3\}^+$	206(<2)	206(3)	206(6)	-
$\{C_5H_7MnL\}^+$	198(27.7)	260(33)	324(16.4)	190(22.2)
$\{C_5H_7Mn(CO)_2\}^+$	178(7.7)	178(3)	178(18)	-
$\{C_5H_7Mn(CO)\}^+$	150(9.2)	150(5)	150(16.4)	-
$\{MnL\}^+$	131(13.8)	193(15)	257(5)	123(6.7)
$\{L\}^+$	76(12.3)	138(100)	202(18)	68(11)
$\{C_5H_7Mn\}^+$	122(58.5)	122(35)	122(48)	122(100)
$\{C_5H_7\}^+$	67(3)	67(13.3)	67(22)	67(33)
$\{Mn\}^+$	55(90)	55(42)	55(64.4)	55(50)
OTHER	132(13)	108(12)	173(42.5) 146(13.7)	260(<1)
	120(60)	91(35)	131(19) 118(23.3)	149(<1)
	85(30.8)	78(12)	104(30.8)	135(<1)
	71(53.8)		76(100)	79(5.5)
	57(100)		62(59)	58(80)

a) Relative intensities in parenthesis ;

b) Samples were introduced in $CHCl_3$ at temperatures of 170°C $\{L=PMe_2Ph,\ PBu^n_3\}$, 220°C $\{L=PMe_3\}$; c) Acetone, 140°C

$\{C_5H_5Mn(CO)_2L\}^+$, $\{C_5H_5Mn(CO)_2\}^+$, $\{C_5H_5Mn(CO)\}^+$ and $\{C_5H_5Mn\text{olefin}\}^+$.[195]

Crystal structure of $\{Mn(\eta^3\text{-}C_5H_7)(CO)_3PMe_3\}$.[99]- The structure consists of discrete units of $\{Mn(\eta^3\text{-}C_5H_7)(CO)_3PMe_3\}$ as shown in Figures 4 and 5. Figure 4 also gives the atomic numbering scheme. The structure has C_s symmetry within the experimental error, and the metal atom bonded to mutually trans phosphorus atom and a carbonyl group, two mutually cis carbonyl groups and a pentadienyl ligand. The metal atom can be regarded as having slightly distorted octahedral coordination, if the η^3-pentadienyl ligand is considered to span two coordination positions on the manganese atom. This geometry however is considerably more distorted than that observed in the similar allyl complex $\{Mn(\eta^3\text{-}C_3H_5)(CO)_2\ P(OMe)_3\}$.[161]

The trihapto pentadienyl fragment bonded to the metal is not symmetrical according to the manganese-carbon pentadienyl distances {Mn-C(13) 2.217(13) Mn-C(12) 2.116(10) and Mn-C(11) 2.349(12)}A^{o}. The first two values, for the terminal and central carbons of the η^3-pentadienyl fragment are quite similar to distances found in symmetric allyl systems, such as $\{Mn(\eta^3\text{-}C_3H_5)(CO)_2[P(OMe)_3]_2\}$ which have the respective distances Mn-C 2.223(17) or 2.229(13) and 2.114(15)A^{o} respectively.[161] It is the distance between Mn-C(11) which suggests the lack of symmetry according to the long value observed 2.349(12) A^{o}.

The C(11)-Mn-C(13) and C(11)-C(12)-C(13) angles of 71.5(5) and 128.1(10) exceed the typical values of many η^3-allyl complexes[161,204] which is reasonable from the presence of rather long bonds within the pentadienyl ligand {C(13)-C(12) 1.440(20)},{C(12)-C(11) 1.527(19)}. The last bond distance {C(12)-C(11)} is considerably longer than {C(12)-C(13)}, confirming the asymmetry in the η^3-pentadienyl system. Carbon-carbon bond lengths for {C(11)-C(14) 1.438(19)} and {C(14)-C(15) 1.398(19)} lie between single (1.54 A^o) and double bond (1.34 A^o) values. The olefinic segment is not coordinatively bonded to the manganese atom.

Some examples of η^3-cyclopentadienyl systems are reported for W and Pd complexes, as described in Section 3.2.1., but there are no other acyclic η^3-pentadienyl structures reported in the literature..

The Mn- carbonyl bond lengths {Mn-C(1) 1.783(11), Mn-C(2) 1.812(12 and Mn-C(3) 1.909 (14)A^o} are as commonly observed, and the respective angles from the metal-carbonyl groups are close to 180^o for the <u>cis</u> carbonyl-manganese bond and smaller angle was found for Mn-C(1)-O(1) 173.9(11).

The <u>cis</u> carbonyl groups to the metal show angles of C(3)-Mn-C(11) $164.6(4)^o$ and C(2)-Mn-C(13) $163.2(5)^o$. The <u>trans</u> C(1)-carbonyl to the metal and the phosphorus atom is $170.6(3)^o$.

Mean distances and angles of the trimethylphosphine ligand are (P-C) 1.864 A^o and (Mn-P-C) 114.8^o respectively.

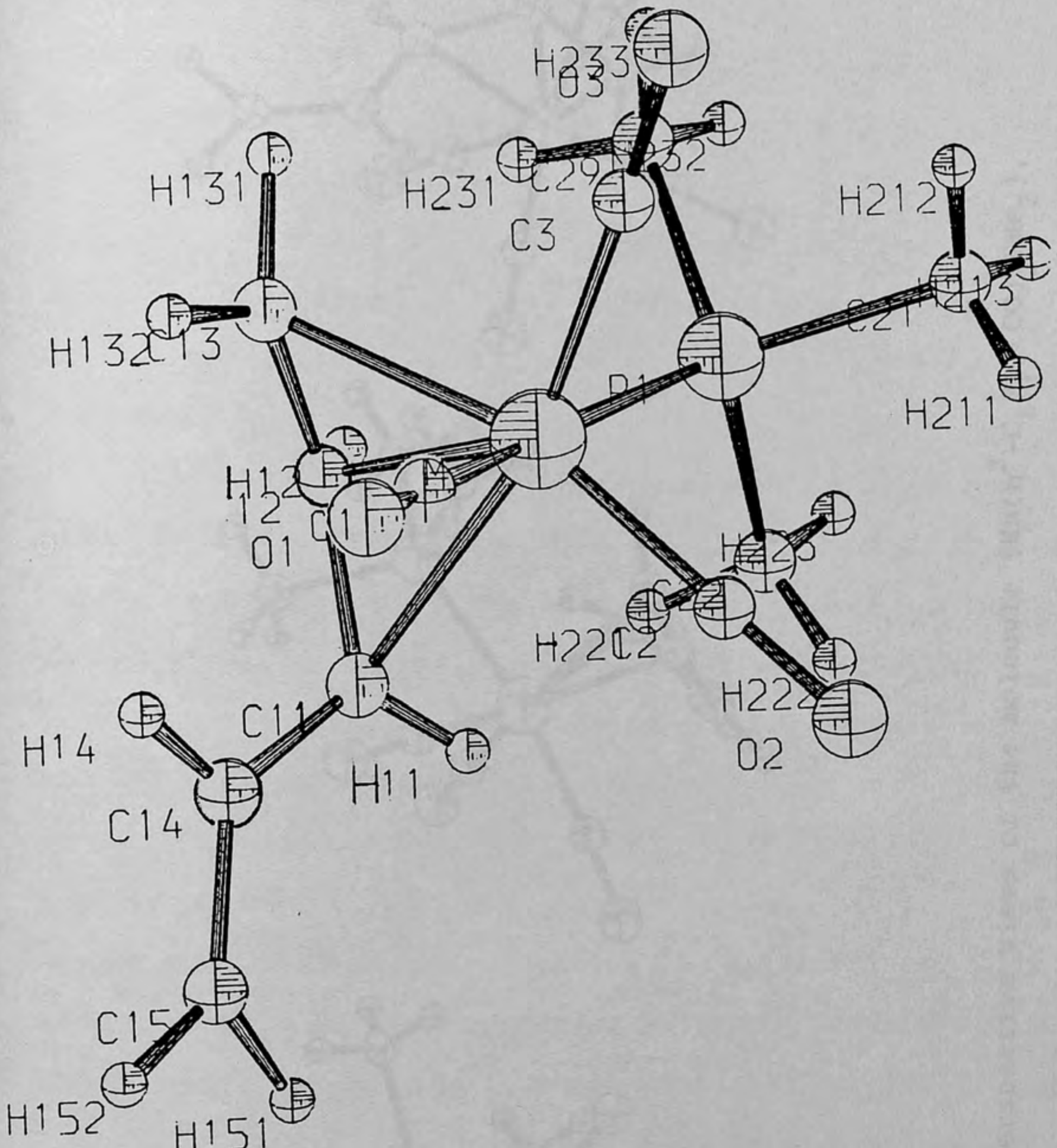


Figure 4. Structure of $\{Mn(\eta^3-C_5H_7)(CO)_3PMe_3\}$ showing the atom-numbering scheme.

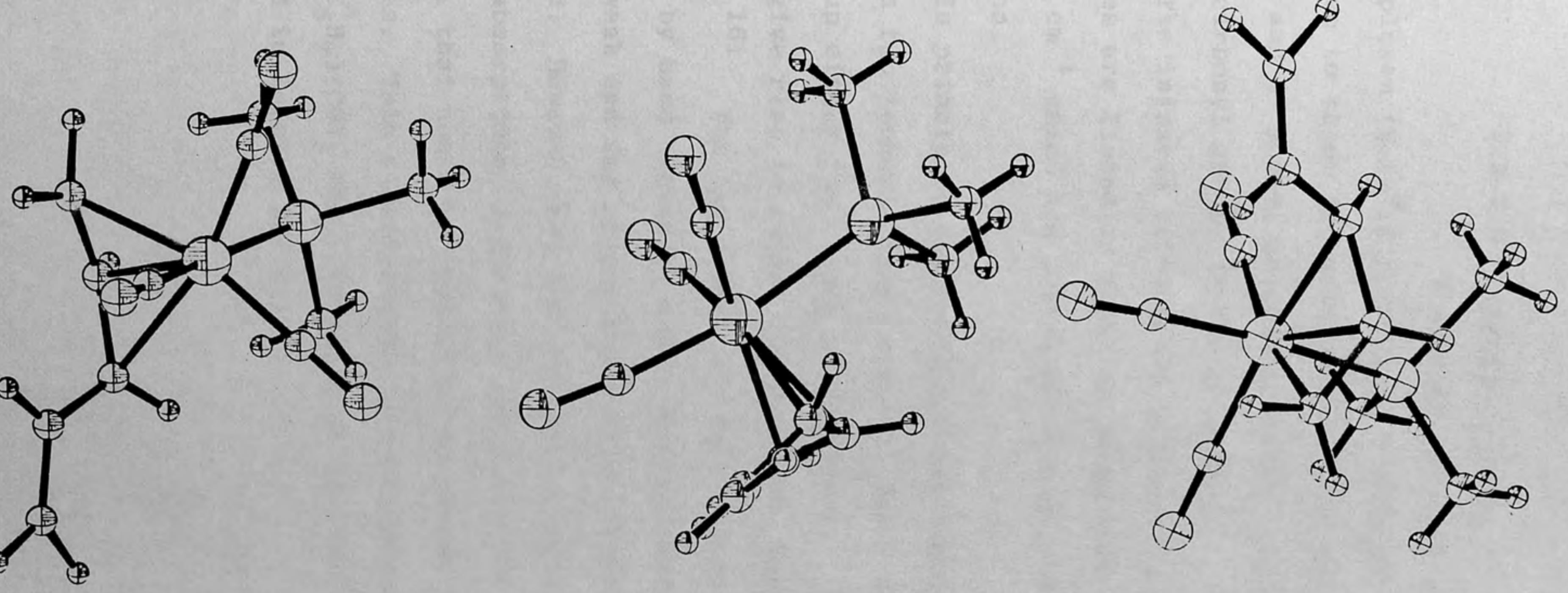


Figure 5. Perspective views of the molecule $\{Mn(\eta^3-C_5H_7)(CO)_3PMe_3\}$.

3.2.2.2. Infrared studies

The metal carbonyl fragments in the complexes {$Mn(\eta^3-C_5H_7)(CO)_3L$} {L=PMe_2Ph, PMe_3,PBu^n_3} give rise to three infrared active ν(CO) bands attributed to 2 A' and A" modes, according to the C_S local symmetry of the carbonyl groups in the molecule.

The infrared ν(CO) bands frequencies of the complexes are listed in Table 10 along with weak bands at 1612 cm^{-1} which are characteristic of the C=C stretching vibration.

In principle, these tricarbonyl complexes could exist in two isomeric forms with the three carbonyl ligands taking up either fac or mer arrangements. Both isomers should give rise to three ν(CO)bands as described by Brisdon.[161] The fac isomer may be distinguished from the mer by band intensity measurements, three strong bands or one weak and two strong bands respectively being expected. However, all the complexes display three strong absorptions, indicating the isolation of fac isomers, that could be considered as pseudo six-coordinate complexes. This consideration is confirmed for the complex {$Mn(\eta^3-C_5H_7)(CO)_3$ PMe_3} by means of its crystal structure reported in Section 3.2.2.1.

TABLE 10

FREQUENCIES OF CO STRETCHING MODES FOR COMPLEXES $\{Mn(\eta^3-C_5H_7)(CO)_3L\}$

COMPLEX	$\nu(CO)^a$	$\nu(C=C)^b$ (cm^{-1})
$\{Mn(\eta^3-C_5H_7)(CO)_3PMe_2Ph\}$	2000, 1935, 1903	1612
$\{Mn(\eta^3-C_5H_7)(CO)_3PMe_3\}$	2000, 1937, 1905	1612
$\{Mn(\eta^3-C_5H_7)(CO)_3PBu^n_3\}$	1997, 1923,1897	1612

a) In nujol mull. All bands have strong intensity;

b) Weak intensity bands.

The infrared spectra of these η^3-pentadienyltricarbonyl complexes show very similar $\nu(CO)$ band patterns as reported for analogous allyl complexes $\{Mn(\eta^3-C_3H_5)(CO)_3L\}$,[161,162] for example $\{Mn(\eta^3-C_3H_5)(CO)_3PBu_3\}$ {1997(s), 1921(s), 1898(s)(liquid film)}.[161]

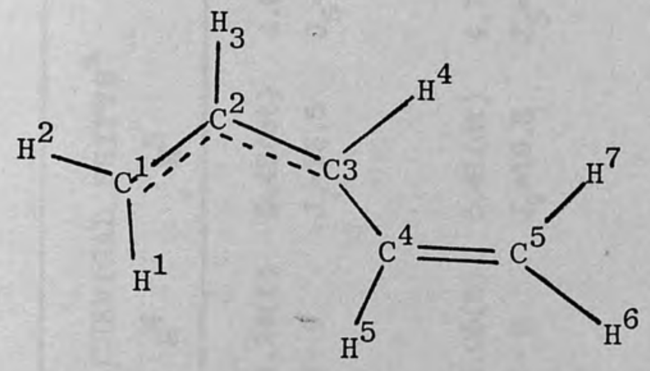
With the isolation of these stable intermediate η^3-pentadienyl species, we then sought to obtain evidence for the formation of the tetracarbonyl complex. Photolysis of $\{Mn(\eta^5-C_5H_7)(CO)_3\}$ in hexane under carbon monoxide (1 atm) was monitored by infrared spectroscopy for 31 h. (no attempt of prolonged time of reaction was carried out due to slow change observed in the infrared spectra). After this time several bands were observed in the $\nu(CO)$

region {2070(m), 2047(m), 2025(s), 2012(s), 1998(s), 1985(m), 1980(s), 1964(s), 1959(s), 1945(s) cm^{-1}}. A comparative study based on the spectrocopic evidence of {$Mn(\eta^3-C_5H_7)(CO)_4$} obtained by Perutz and Powell[168] under matrix isolation studies of {$Mn(\eta^5-C_5H_7)(CO)_3$} in a CO matrix at 20 K [2027, 1959, and 1942 cm^{-1} (starting material); 2072, 1997, 1980 and 1965 cm^{-1} (η^3-tetracarbonyl species)] suggest that one could reasonably expect to isolate the tetracarbonyl product {2070(m), 1998(s), 1980 (s), and 1964(s) cm^{-1}} under high strong carbon monoxide pressure. The frequency of bands at 2047(m), 2012(s), and 1985(m) in comparison with {$Mn(\eta^1-C_3H_5)(CO)_5$} {2108(m), 2046(vw), 2014(vs), 1993(s), 1926(vvw)} would suggest the possible formation of the monohapto system {$Mn(\eta^1-C_5H_7)(CO)_5$} which could be confirmed by CO matrix isolation on the η^3-pentadienyltricarbonyl complexes.

The presumed complex {$Mn(\eta^2-C_5H_8)(\eta^3-C_5H_7)(CO)_3$} showed very strong carbon stretching peaks in the infrared spectrum at 2008, 1928 cm^{-1} (nujol) and 2000, 1922 cm^{-1} ($CHCl_3$). The corresponding low frequency band is more wide than that found at higher frequency.

3.2.2.3. ^1H- and ^{13}C spectroscopy

Nuclear magnetic resonance techniques showed the unsymmetrical pentadienyl fragments in the complexes {$Mn(\eta^3-C_5H_7)(CO)_3L$} {$L=PMe_2Ph, PMe_3, PBu_3$} confirming the 18 electron configuration of these tricarbonyl systems. Assignments, relative intensities and coupling constants are related to those previously reported for various allyl systems and published data on vinyl groups. The ^{1}H-NMR data are reported in Table 11 according to 23.



(23)

The 250 MHz ^{1}H-NMR spectrum for {$Mn(\eta^3-C_5H_7)(CO)_3PMe_3$} can be seen in Figure 6.

The ^{1}H-NMR spectra of these manganese complexes, as for the ruthenium analogue {$RuCl(CO)(\eta^3-C_5H_7)(PMe_2Ph)_2$} show different chemical shifts for each proton, contrasting with the four pattern shift of the symmetric η^5-pentadienyl systems reported before.

Better quality spectra than for the monosubstituted η^5-pentadienyl complexes were always observed. The proton (H^1) for the PBu_3 derivative is at the highest field, but not shielded as much as the η^5-anti-protons which are close to $\delta=0$. This is in agreement with typical spectra of

TABLE 11

^{1}H-NMR DATA FOR COMPLEXES { $Mn(\eta^3-CH^1H^2CH^3CH^4CH^5CH^6H^7)(CO)_3L$ }

COMPLEX	CHEMICAL SHIFTS^a							
	H^1	H^2	H^3	H^4	H^5	H^6	H^7	L
{$Mn(\eta^3-C_5H_7)(CO)_3PBu_3$ }	2.37(dt)	2.48(d)	3.63(m)	4.24(t)	5.48(dt)	4.84(dd)	5.22(dd)	0.84 and
	J_3=12.8	J_3=7.8		J~ 9	J_7=16.5	J_5=10	J_6=2	1.22(broad m, 27H).
	$J(PH^1)$=2.75		$J(PH^3)$~12.5					
{$Mn(\eta^3-C_5H_7)(CO)_3PMe_3$}	2.24(m)	2.30(m)	3.27(m)	4.05(t)	5.41(dt)	4.78(dd)	5.15(dd)	0.48(d)
			J=7.5,12.8	J~ 9	J_7=16.8	J_5=10	J_6=2	$J(PCH_3)$=9.8
			$J(PH^3)$~12.8					
{$Mn(\eta^3-C_5H_7)(CO)_3PMe_2Ph$}^{b}	2.26(m)^c		3.44(m)	3.77(t)	5.19(dt)	4.64(dd)	4.95(dd)	1.49(d)(3H)
								1.57(d)(3H)
			J=7.5	J~8.6	J_7= 16.7	J_5=10	J_6=2	7.44(s,br)(6H)
			$J(PH^3)$~13					$J(PCH_3)$=9

a) In C_6D_6 relative to TMS (δ =0). 250MHz; b) In $CDCl_3$ relative to TMS (δ =0). 250MHz; c) see text.

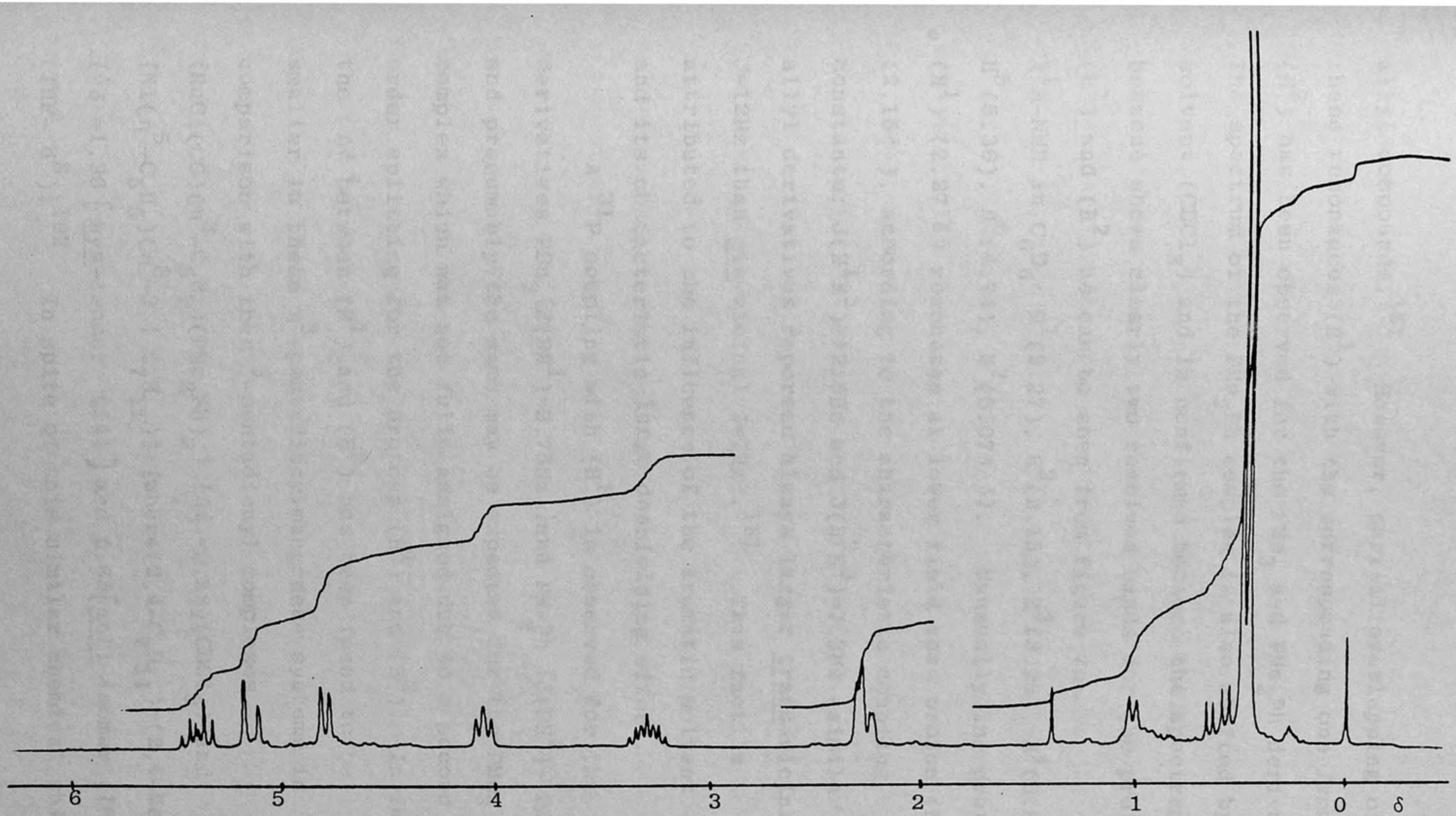


Figure 6. ^{1}H-NMR spectrum of $\{Mn(\eta^3-C_5H_7)(CO)_3PMe_3\}$ in C_6D_6 at 250 MHz.

allyl compounds.[161] However, partial overlapping of these resonances (H^1) with the corresponding one from (H^2) has been observed for the PMe_3 and PMe_2Ph derivatives. The spectrum of the PMe_2Ph complex is also shifted by the solvent ($CDCl_3$) and is confirmed because the spectrum in benzene shows clearly two resolved bands for the protons (H^1) and (H^2) as can be seen from Figure 7e . {^{1}H-NMR in C_6D_6: H^1(2.27), H^2(2.15), H^3(3.25), H^4(3.83), H^5(5.36), H^6(4.74), H^7(5.07) δ}. Unusually the proton (H^1) (2.27 δ) resonates at lower field than proton (H^2) (2.15δ), according to the characteristic coupling constants: $J(H^1H^3)$=12.5Hz and $J(H^2H^3)$=7.3Hz (similar allyl derivatives reported always larger *trans*-vicinal J=12Hz than *cis*-vicinal J=7Hz).[161] This fact is attributed to the influence of the aromatic solvent and its characteristic large deshielding effect.

A ^{31}P coupling with (H^1) is observed for the derivatives PBu_3{$J(PH^1)$=2.75Hz }and PMe_2Ph {$J(PH^1)$~ 2.5Hz} and presumably the same may be expected for the PMe_3 complex which was not fully assigned due to a second order splitting for the protons (H^1) and (H^2). In fact, the Δδ between (H^1) and (H^2) has been found to be smaller in these η^3-pentadienylmanganese systems in comparison with the η^3-pentadienyl complexes {$RuCl(CO)(\eta^3-C_5H_7)(PMe_2Ph)_2$} {Δδ =0.59)($CDCl_3$) and {$Ni(\eta^5-C_5H_5)(\eta^3-2,4-C_7H_{11})$} {where($2,4-C_7H_{11}$)=($2,4-Me_2C_5H_5$)} {Δδ =1.36 [*syn*-isomer (14)] and 0.85[*anti*-isomer (15)] (THF- d^8)}.[192] In spite of this similar chemical shift for the protons (H^1) and (H^2), characteristic values of the coupling constants of allyl complexes[161] have been found: $J(H^1H^3) \sim 12.8$Hz and $J(H^2H^3) \sim 7.5$Hz.

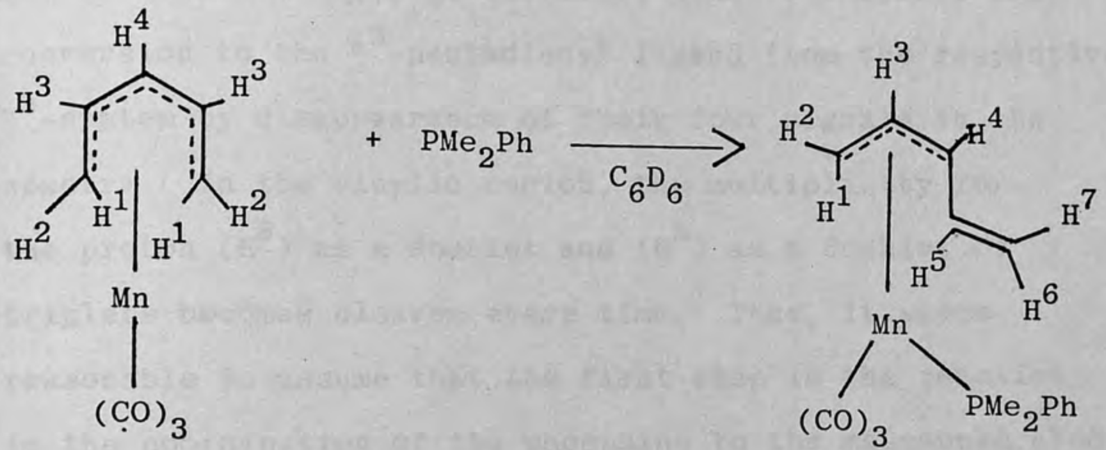
The protons (H^4) (3.77-4.24δ) resonate to low field of the protons (H^3). This assignment was confirmed by double resonance experiments on $\{Mn(\eta^3\text{-}C_5H_7)(CO)_3PMe_3\}$ and generalized for the other complexes due to similar multiplicity and coupling constant values. Irradiation at 4.05δ, shows that a doublet of triplets at 5.41δ collapse to a doublet of doublets, modifying the multiplet at 3.27δ, and leaving unaffected the resonances at 2.24δ and 2.30δ. The assignment of the proton (H^3) was also confirmed when a triplet at 4.05δ collapsed to a doublet by irradiation at 3.27δ. These assignments for the protons (H^3) and (H^4) contrast with observations on the η^3-pentadienylruthenium complex described in Section 2.3.2.1., in which the resonance of (H^3) lies to low field of that of (H^4), suggesting a different orientation in the η^3-pentadienyl group in the molecule, in which the proton (H^3) for the manganese complexes should interact more directly with the phosphorus atom, as observed from the solid state structure (Section 3.2.2.1.).

The η^3-pentadienyl ligand in these complexes, in contrast with the η^5-pentadienyldicarbonylmanganese complexes and the η^3-pentadienylcarbonylruthenium complex, showed ^{31}P coupling only with (H^1) and (H^3).

There is no evidence of coordination of the carbon-carbon double bond in the η^3-pentadienyl fragment to the manganese atom according to the downfield shift observed for these vinylic systems (H^5)(5.19-5.48δ), H^6(4.64-4.8δ) and H^7 (4.95-5.22δ) and the coupling constants of a trans $J(H^5H^7)$= 16.7Hz, cis $J(H^5H^6)$=10Hz and geminal arrangements $J(H^6H^7)$=2Hz. This is also confirmed by infrared studies {1612 cm^{-1} ν(C=C). Section 3.2.2.2.} and from the solid-state structure from {$Mn(\eta^3-C_5H_7)(CO)_3PMe_3$} (Figure 4).

The pattern of shifts described for these η^3-pentadienylmanganese complexes allows comparison between the different phosphine ligands substituted in {$Mn(\eta^3-C_5H_7)(CO)_3$ L} {L=PMe_2Ph, PMe_3, PBu_3}. The deshielding of the protons in the molecule increases in the order $PMe_2Ph < PMe_3 < PBu_3$ according to the spectra recorded in C_6D_6. In principle, we could suggest that the donor capacity would be proportional to upfield shifts, however, this is not conclusive because there is a very little difference in the chemical shift of this series of phosphorus (Δδ =0.08 $PMe_2Ph-PMe_3$) and (Δδ =0.15 PMe_3-PBu_3). It is too risky to affirm this, without more studies that could provide more information about this trend. (See also discussion and infrared studies in Section 3.2.2.2.).

The mechanism of reaction for these complexes was studied by ^{1}H-NMR spectroscopy. The starting material {$Mn(\eta^5-C_5H_7)(CO)_3$} (0.02 g., 0.097mmol) was dissolved in deuterated benzene (0.5 cm^3) and filtered into a NMR tube, and then addition of PMe_2Ph (0.015 g., 0.11mmol) was carried out at low temperature. The spectra at room temperature can be seen in Figure 7. Assignments are according to Scheme 17.



SCHEME 17.

The first spectrum (a) at initial time (t=0) indicates an immediate formation of the vinylic system from a broad signal observed at 5 - 5.8δ and there is also slight evidence of the different electronic environment of the protons (H^1), (H^3) and (H^4). The protons corresponding to starting material resonate at 4.74δ (H^4), 4.40δ (H^3), 2.09δ$(H^2)$and 0.09δ (H^1). (250MHz).

After 30 min., the spectrum (b) (t=30min) confirm clearly that the symmetric η^5-pentadienyl structure is broken by the presence of several resonances which suggest the new chemical environment of the pentadienyl ligand. Different chemical shifts are observed at 2.27δ, 3.25δ and 3.83δ for protons (H^1), (H^3) and (H^4) respectively. The signals for (H^2) and (H^6) are also growing overlapped with the protons of the starting material (H^2) and (H^4). The last is responsible for the collapse of the triplet observed at t=0.

The next NMR spectra at different times, (c) (t=60 min.); (d) (t=90 min.); (e) (t=135 min.) tend to indicate the conversion to the η^3-pentadienyl ligand from the respective η^5-system by disappearance of their four signals in the spectra. In the vinylic region, the multiplicity for the proton (H^6) as a doublet and (H^5) as a doublet of triplets becomes clearer every time. Thus, it seems reasonable to assume that the first step in the reaction is the coordination of the phosphine to the manganese atom with an immediate rearrangement of the pentadienyl ligand from η^5- to η^3- fashion in order to maintain the stable 18 electron configuration. This interaction can be described as a kind of associative interchange mechanism as mentioned earlier in which an interchange of ligands between the inner and next-nearest coordination spheres is expected,[196] instead of a transient intermediate with a high coordination number which has not been observed.

The product isolated from the irradiation of $\{Mn(\eta^5\text{-}C_5H_7)(CO)_3\}$ in THF in the presence of pyridine, showed a complex ^{1}H-NMR spectrum. According to analytical data it seems to be $\{Mn(\eta^3\text{-}C_5H_7)(\eta^2\text{-}C_5H_8)(CO)_3\}$ (22), which is expected to have a characteristic diolefin pattern spectrum, along with the η^3-pentadienyl protons.

The number of protons determined by integration are in agreement with the proposed complex, as well as the range

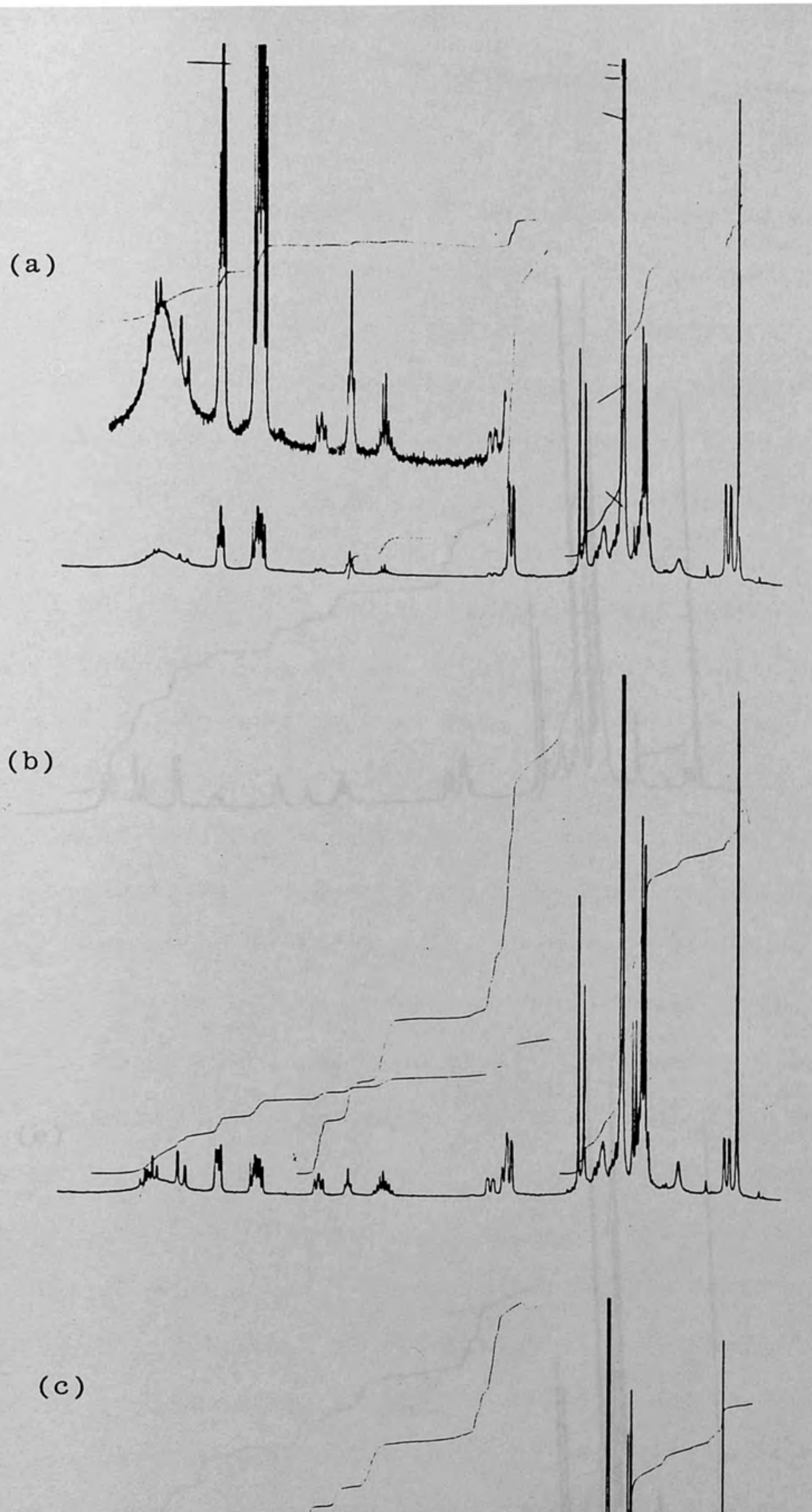
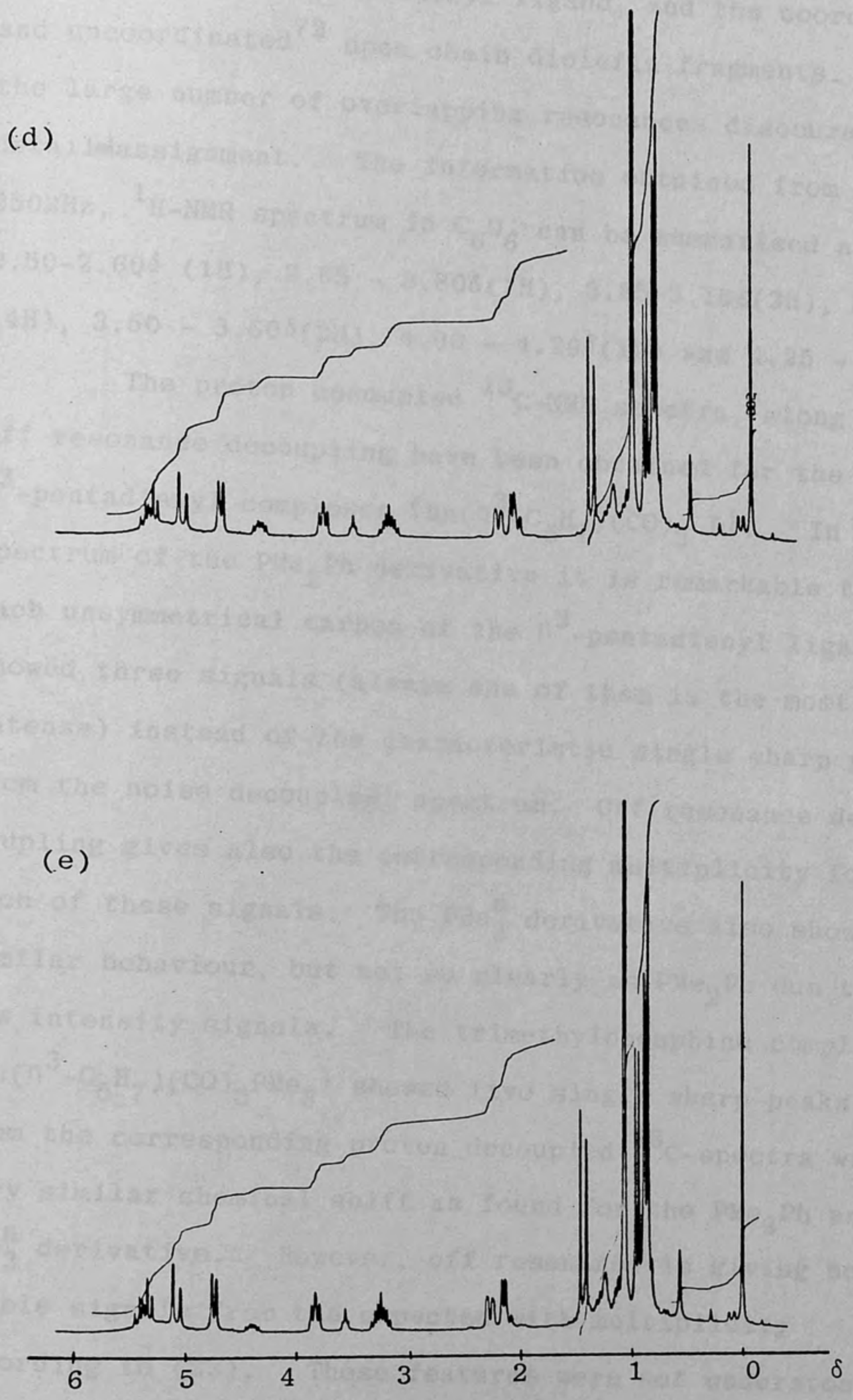


Figure 7. ^{1}H-NMR spectra of the reaction of $\{C_5H_7Mn(CO)_3\}$ with PMe_2Ph in C_6D_6 at 250 MHz. (a) Initial time, t=0; (b) t=30 min ; (c) t=60 min.



<u>Figure 7.</u> ^{1}H-NMR spectra of the reaction of $\{C_5H_7Mn(CO)_3\}$ with PMe_2Ph in C_6D_6 at 250MHz. (d) t=90 min ; (e) t=135 min.

of chemical shifts expected, if we are considering the presence of an η^3-pentadienyl ligand, and the coordinated[196] and uncoordinated[72] open chain diolefin fragments. However, the large number of overlapping resonances discouraged any detailed assignment. The information obtained from the 250MHz, ^{1}H-NMR spectrum in C_6D_6 can be summarised as follows: 2.50-2.60δ (1H), 2.65 - 2.80δ(1H), 2.85-3.10δ(2H), 3.20-3.40δ (4H), 3.50 - 3.60δ(2H), 4.00 - 4.20δ(1H) and 4.25 - 4.70δ(4H).

The proton decoupled ^{13}C-NMR spectra, along with off resonance decoupling have been obtained for the η^3-pentadienyl complexes $\{Mn(\eta^3-C_5H_7)(CO)_3\ L\}$. In the spectrum of the PMe_2Ph derivative it is remarkable that each unsymmetrical carbon of the η^3-pentadienyl ligand showed three signals (always one of them is the most intense) instead of the characteristic single sharp peak from the noise decoupled spectrum. Off resonance decoupling gives also the corresponding multiplicity for each of these signals. The PBu^n_3 derivative also shows similar behaviour, but not so clearly as PMe_2Ph due to low intensity signals. The trimethylphosphine complex $\{Mn(\eta^3-C_5H_7)(CO)_3PMe_3\}$ showed five single sharp peaks from the corresponding proton decoupled ^{13}C-spectra with very similar chemical shift as found for the PMe_2Ph and PBu^n_3 derivative. However, off resonance is giving now, double signals from the expected with multiplicity according to (23). These features were not understood, and the study of the spectra will be confined to analysing

TABLE 12

^{13}C-NMR DATA FOR THE COMPLEXES {$Mn(\eta^3-C_5H_7)(CO)_3L$ }

COMPLEX	CHEMICAL SHIFTS ^{a,c}					
	C^1	C^2	C^3	C^4	C^5	L
{$Mn(\eta^3-C_5H_7)(CO)_3PMe_3$ }	40.5	92.1	65.5	140.0	109.6	14.7(m)
{$Mn(\eta^3-C_5H_7)(CO)_3PMe_2Ph$}^{b}	46.23	100.32	(69.73)	140.45	117.74	129(m)
	39.99	(93.77)	68.44	(137.96)	(111.42)	126.43
	(34.97)	89.47	57.75	136.02	108.33	15.98(m)
{$Mn(\eta^3-C_5H_7)(CO)_3PBu^n_3$ }	(38.6)	94.6	(70.3)	141.6	112.2	26.16
	35.2	94.2	65.8	141.0	(108.5)	25.65
		(90.1)	64.9	(139.0)		24.67
						13.80

a) In C_6D_6 relative to TMS (δ=0). 100 MHz. b) In $CDCl_3$ relative to TMS (δ=0) 100 MHz.

c) Value in parentheses denotes high intensity signal.

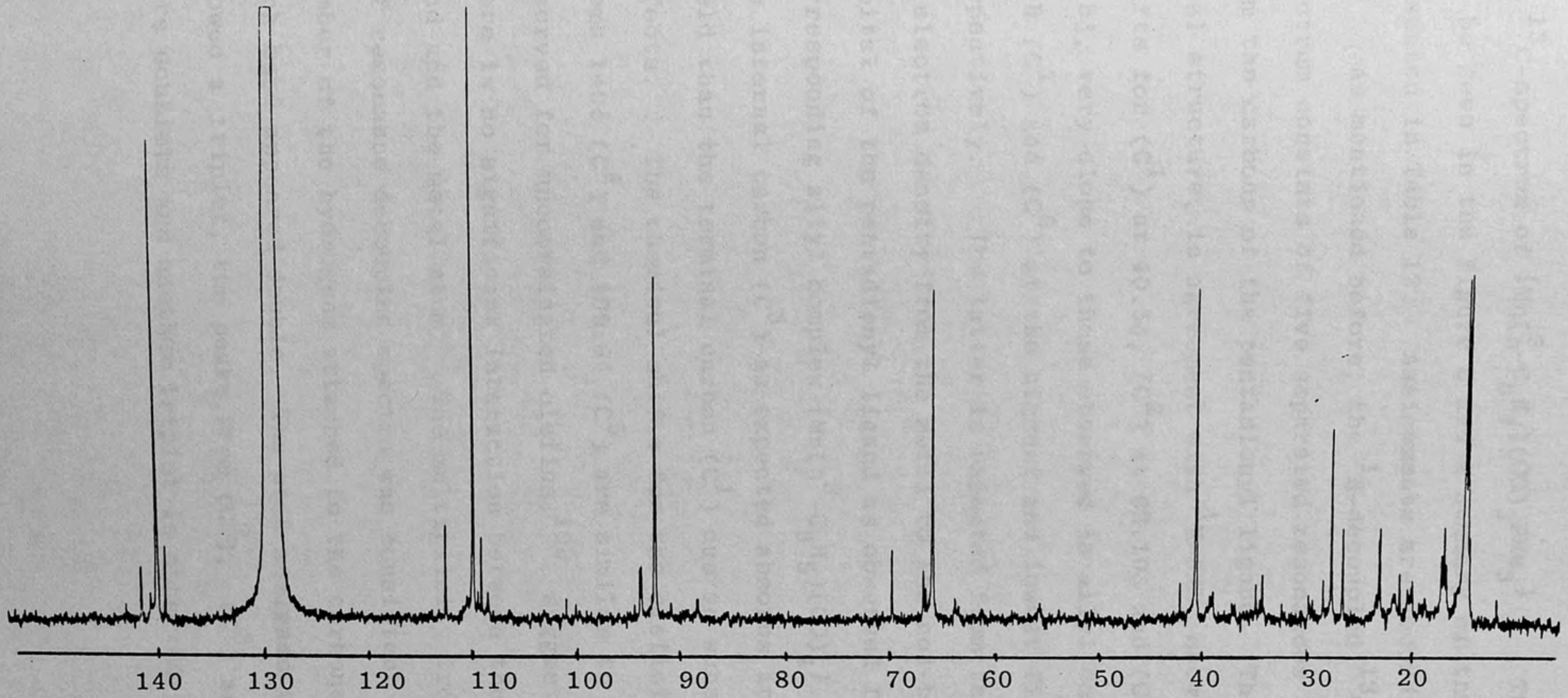


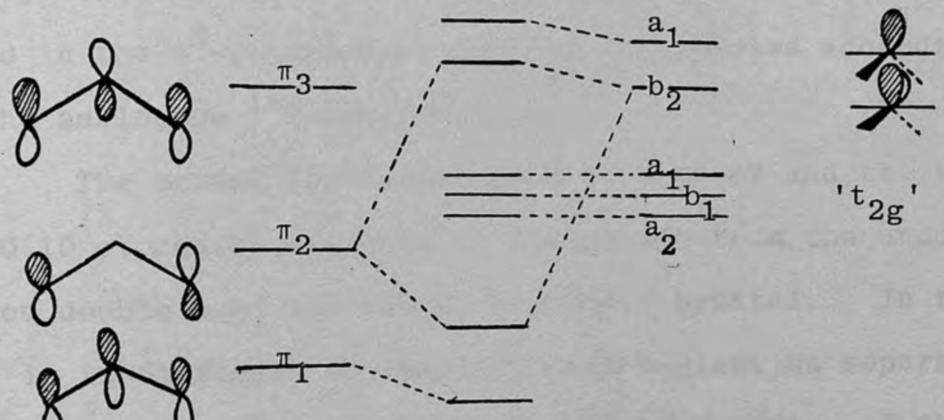
Figure 8. ^{13}C-NMR spectrum of η^3-pentadienyltricarbonyl(trimethylphosphine)manganese (Figure 4) in C_6D_6 at 100 MHz.

the ^{13}C-spectrum of $\{Mn(\eta^3-C_5H_7)(CO)_3PMe_3\}$. The spectrum can be seen in the Figure 8 and a summary of the data is presented in Table 12. Assignments are according to (23).

As mentioned before, the ^{1}H-decoupled ^{13}C-NMR spectrum consists of five separated resonances arising from the carbons of the pentadienyl ligand. The unsymmetrical structure, in agreement with ^{1}H-NMR, showed chemical shifts for (C^1) at 40.5δ, (C^2) at 92.10δ and (C^3) at 65.5δ, very close to those observed in allyl complexes,[197] with (C^1) and (C^2) at the highest and lowest fields, respectively. The latter is expected from the donation of electron density from the metal to the non-bonding π orbital of the pentadienyl ligand as observed for the corresponding allyl complex $\{Mn(\eta^3-C_3H_5)(CO)_4\}$.[199] The internal carbon (C^3) as expected absorbs at lower field than the terminal carbon (C^1) due to substituent effects. The chemical shifts for the olefinic carbon atoms 140δ (C^4) and 109.6δ (C^5) are similar to those observed for uncoordinated olefins,[198] suggesting that there is no significant interaction between the double bond and the metal atom. The multiplicity from the off resonance decoupled spectra was consistent with the number of the hydrogens attached to the carbons, although each band appeared double. The peak assigned to (C^1) showed a triplet, the peaks from (C^2), (C^3) and (C^4) were doublets and another triplet is observed for (C^5)

3.2.2.4. Photoelectron spectroscopy.

The He(I) and He(II) photoelectron spectra of the complex $\{Mn(\eta^3-C_5H_7)(CO)_3PMe_3\}$ are presented in Figure 9. To a first approximation the bonding in this complex can be considered as comprising a $[Mn(allyl)(CO)_3L]$ system and a free C=C unit. (See Figure 4). Using the treatment of Elian and Hoffmann,[107a] one can qualitatively compare the energy levels of a C_{2v} octahedral fragment $M(CO)_4$ with $M(CO)_3L$. The fragment interaction diagram between the $Mn(CO)_4$ and an allyl fragment[200a] is presented in the Scheme 18 and it is used in the assignment of some of the bands for the spectrum of $\{Mn(\eta^3-C_5H_7)(CO)_3PMe_3\}$.



SCHEME 18

The first ionisation band could be resolved in three ionisation peaks at 7.18(shoulder), 7.50 and 7.86 eV. The components at 7.18 and 7.50 eV (1a) are assigned to ionisation of the "t2g" type electrons involved in the backbonding to the carbonyl ligands. Comparison of the He(I) and He(II) spectra (Figures 9a and 9b) confirm that this assignment is primarily confined to the transition metal. (See Table 13). The next ionisation at 7.86 eV (1b) is assigned to the perturbed π_2 orbitals on the delocalised region of the η^3-pentadienyl ligand considered as an allyl. It is observed for the complex $\{Mn(\eta^3-C_3H_5)(CO)_4\}$ that the π_2 orbital of the allyl fragment is receiving the donation of the electron density from the metal, being a strong directional interaction, as detected from the lowest field in which the central (C^2)carbon (which contains a nodal plane)resonates in the ^{13}C-NMR spectrum.[199] A similar trend in the η^3-pentadienyl complex is expected according to the analogous ^{13}C-NMR spectrum.

The second ionisation band at 9.59 eV and the third at 10.10 eV can be assigned to ionisation from the uncomplexed double bond and the π_1 molecular orbital. In this case it is difficult to identify each ionisation separately. Some interaction between the delocalised fragment of the η^3-pentadienyl system is expected with the uncomplexed π bond of the C=C unit, which suggests that the ionisation from this molecular orbital will be at lower energy than that corresponding to a free ligand (C_2H_4, I.E. 10.51 eV).[200b] On the other hand, comparison between the He(I) photoelectron spectrum of $\{Mn(\eta^3-C_3H_5)(CO)_4\}$ [201] and the corresponding spectrum of the η^3-pentadienyl complex suggest that in principle we may assign the band at 10.10 eV to ionisation from the π_1 molecular orbital from the delocalised pentadienyl fragment, according to the similar separation (2.24 eV) observed between π_1 with respect to π_2, in this system and the allyl (2.10 eV). The second band showed a small separation (1.73 eV).

TABLE 13

AREAS UNDER SOME $\{Mn(\eta^3-C_5H_7)(CO)_3PMe_3\}$BANDS

BANDS	1		2	3	4
	a	b			
I.E.(eV)	(7.17,7.50)	(7.86)	(9.59)	(10.10)	(10.82)
He(I) % distribution	29.65	27.58	12.09	16.72	13.96
Area relative to 1a	1	0.93	0.41	0.56	0.47
He(II)% distribution	36.25	29.48	10.49	14.78	9.00
Area relative to 1a	1	0.81	0.29	0.41	0.25

Finally, it is clear that the fourth ionisation band at 10.82 eV decreases in intensity relative to the first ionisation band in the He(II) photoelectron spectrum (see Table 13), which suggests that this band can be assigned to the phosphorus ionisation.

The broad intense band from 11 to 16 eV, as described in Section 2.2.2.4, results from the overlap of CO 5σ and other σ-bonding orbitals from the ligand and the large number of closely spaced orbitals in this region makes meaningful interpretation difficult.

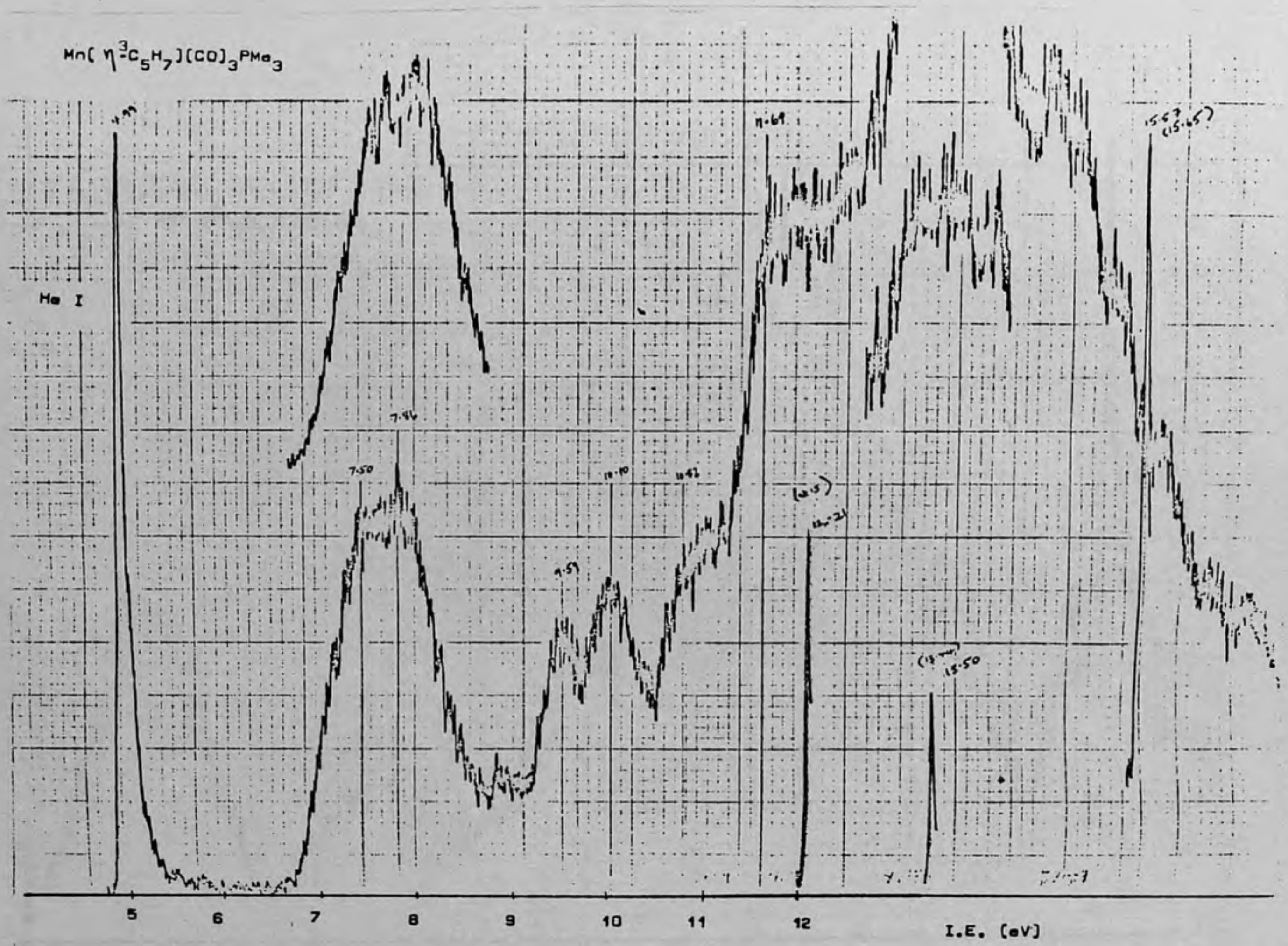


Figure 9a He(I) photoelectron spectrum of η^3-pentadienyltricarbonyl-(trimethylphosphine)maganese.

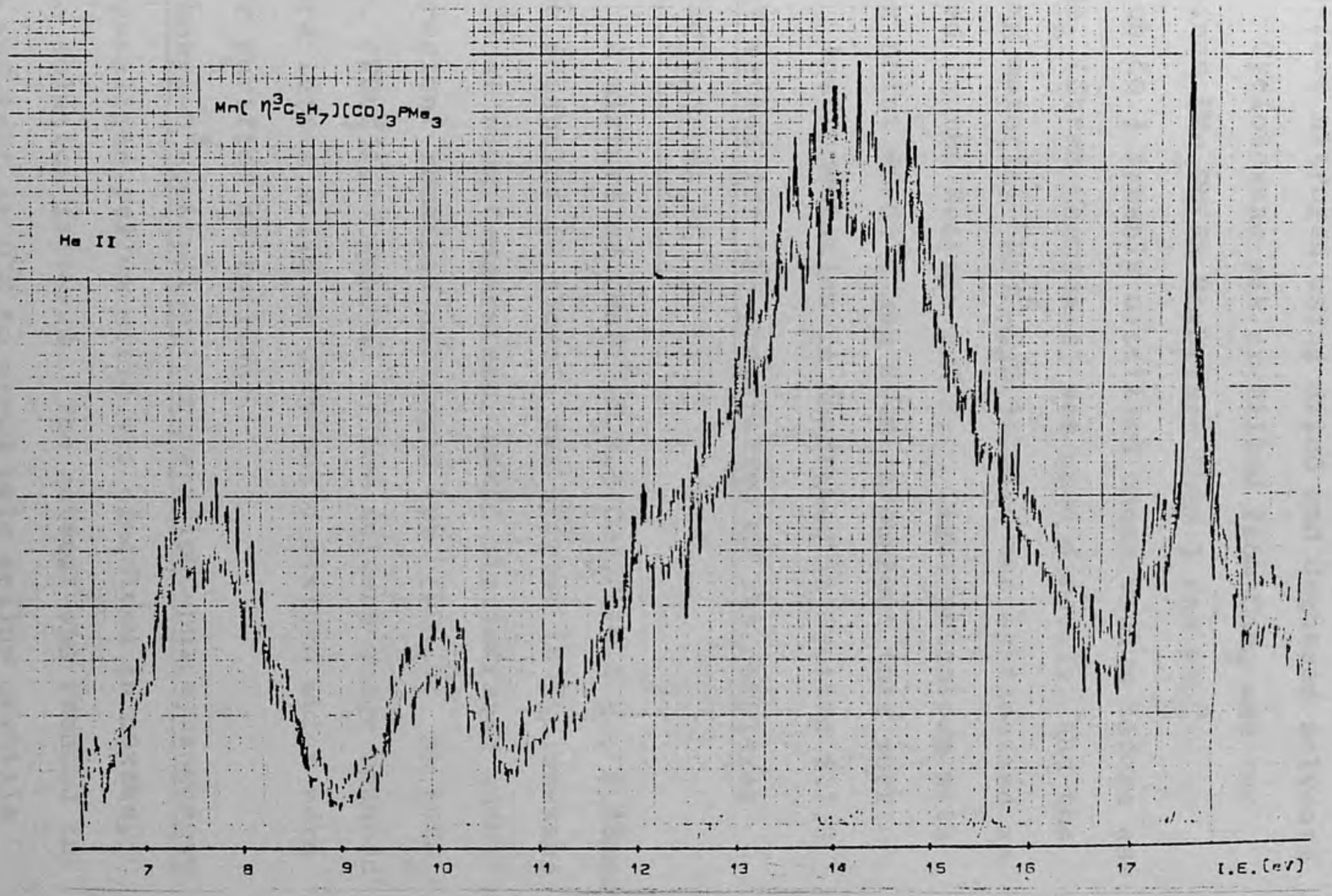


Figure 9b. He(II) photoelectron spectrum of η^3-pentadienyltricarbonyl(trimethylphosphine)manganese.

3.2.3. Experimental Section

All reactions were carried out with conventional Schlenk techniques under an atmosphere of oxygen-free nitrogen using dried and degassed solvents.

Cyclohexane was distilled from CaH_2 and the phosphines PMe_2Ph(Ex-Maybridge Chem.) and PBu^n_3 (Aldrich Co.) freshly distilled under vacuum before use. The PMe_3 (Strem Chemicals) was used directly, and the starting material $\{Mn(\eta^5-C_5H_7)(CO)_3\}$ was synthesised as reported in the Section 2.2.3. Light petroleum with boiling point 60-80°C was used throughout this work.

Instrumentation is described in Section 2.1.3.

General method for the preparation of the complexes $\{Mn(\eta^3-C_5H_7)(CO)_3\}L$.

A mixture of $\{Mn(\eta^5-C_5H_7)(CO)_3\}$ (0.5 g., 2.43mmol) and the phosphine (2.43mmol) was stirred in cyclohexane (40 cm^3) at room temperature, until its infrared spectrum $\{\nu(CO)$region$\}$ remained unchanged $\{$2h. (PMe_3); 3h.(PMe_2Ph) and 3h. (PBu^n_3)$\}$. Removal of the solvent under reduced pressure left a solid or oily-solid mixture which were further purified as follows:

Tricarbonyl-η^3-pentadienyl(trimethylphosphine)manganese. - The crystalline yellow solid was dissolved in hexane, and the solution filtered. The solvent was reduced in volume and kept at 0°C to yield pale yellow crystals which were filtered and dried in vacuum. The solid was recrystallised from a CH_2Cl_2-hexane mixture. A further purification by sublimation at 35°C and 0.03 mmHg was finally carried out. Single crystals were obtained for the X-ray determination, sealing a long ampoule (20 cm) with the sample (100 mg.) under vacuum at 0.01mmHg and 35°C, maintaining a slow gradient of temperature in the system, using a copper tube of similar diameter outside the ampoule.

Tricarbonyl-η^3-pentadienyl(dimethylphenylphosphine)(manganese). - The orange-red residue remaining after the initial solvent removal was dissolved in light petroleum and diethyl ether (12:1). Following similar work-up procedures with cooling the solution at -60°C and recrystallisation from the same solvent mixture, gave lemon yellow crystals in 46% yield. (All physical properties are described in Section 3.2.2.1.).

Tricarbonyl-η^3-pentadienyl(tri-n-butylphosphine)manganese. - The yellow oil-solid mixture was dissolved in light petroleum and filtered. The volume of the filtrate was reduced and kept at -78°C. The solid product was filtered at -40°C and dried under vacuum. Recrystallisation from hexane at -78°C afforded very pale yellow crystals with a low melting point (42-43°C).

Tricarbonyl-η^3-pentadienyl(η^2-pentadiene)manganese. - The preparation of this complex, during the attempt to prepared a pyridine derivative is described in Section 3.1.3.

Reaction of $\{Mn(\eta^5-C_5H_7)(CO)_3\}$ with carbon monoxide. - $\{Mn(\eta^5-C_5H_7)(CO)_3\}$ (0.47 g., 2.28mmol) dissolved in hexane (75 cm^3) was irradiated with a 125 watt u.v. lamp and a soda glass filter (λ >325nm) for 4 h. passing carbon monoxide through the solution (1 atm.), while the system was kept at -78°C. At this temperature some products crystallise in the tube from which CO is passing, then temperature of the solution was changed to -10°C for 15 h. and finally 12 h. at room temperature without soda glass filter. (Infrared is discussed in Section 3.2.2.2.).

Crystal Data -

$C_{11}H_{16}MnO_3P$, M=282.16, monoclinic, a=7.66(1), b=13.757(8), c= 7.535(9) A°, β =113.0(1)°, U = 730.9 A^{o3}, D_c=1.33 $g.cm^{-3}$, z = 2, space group $P2_1$ from systematic absences 0k0 with k=2 n+1.

A sample of $\{Mn(\eta^3-C_5H_7)(CO)_3PMe_3\}$ was sublimed as described before. A crystal with approximate size 0.2 x 0.5 x 0.5mm was set up to rotate around on a Stoe Stadi-2 diffractometer. 1327 reflections with maximum 2 θ of 50° (with Mo-K_α radiation, λ=0.7107 A°) were collected via variable width ω scan. Background counts were 20s and the scan rate of 0.033° s^{-1} was applied to a width of (1.5 + sin μ/taw θ). 1041 reflections with I > 3σ (I) were used in the subsequent refinement. Absorption and extinction corrections were not applied.

Structure Determination. - The position of the Mn atom was obtained from the Patterson function. All non-hydrogen atoms were positioned by Fourier methods. Hydrogen atoms were placed in trigonal or tetrahedral positions. Those bonded to the same atom were given a common thermal parameter. Methyl hydrogen atoms were included as rigid groups. The hydrogen atoms on C(13) and C(15) were also refined as rigid trigonal groups.

The structure was refined by full-matrix least squares with a weighting scheme $W=1/(\sigma^2(I) + 0.003\ F^2)$. The final R value was 0.066 with $R_w=0.065$. Calculations were carried out using SHELX-76 [202] at the University of Manchester Computer Centre. Atomic scattering factors and dispersion corrections were taken from International Tables.[203] Atomic parameters are given in Table (14). Molecular dimensions are given in Table (15). Thermal parameters in Table (16) and hydrogen atom positions in Table (17).

TABLE 14

ATOMIC COORDINATES (x 10^4) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

ATOM	X	Y	Z	
MN(1)	1118(2)	0(0)	2067(2)	78(2)
P(1)	1870(5)	967(2)	4707(4)	81(3)
C(1)	650(20)	-595(9)	-176(16)	102(15)
O(1)	409(22)	-898(8)	-1646(14)	153(17)
C(2)	-597(16)	938(9)	856(14)	80(12)
O(2)	-1731(16)	1568(7)	7(16)	121(13)
C(3)	3421(19)	486(9)	1989(16)	107(14)
O(3)	4888(15)	764(9)	1962(17)	149(14)
C(11)	-1216(18)	-974(9)	2475(18)	104(13)
C(12)	838(20)	-1107(8)	3887(16)	109(13)
C(13)	2453(22)	-1379(9)	3469(23)	135(17)
C(14)	-2171(20)	-1651(9)	950(19)	114(15)
C(15)	-4140(23)	-1745(11)	40(23)	119(19)
C(21)	2541(30)	2215(10)	4369(23)	137(22)
C(22)	-154(23)	1156(10)	5554(20)	124(17)
C(29)	3990(23)	604(13)	6824(18)	95(20)

TABLE 15

MOLECULAR DIMENSIONS

DISTANCES (A°) ANGLES(°) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

MN(1) - P(1)	2.273(3)
MN(1) - C(1)	1.783(11)
MN(1) - C(2)	1.812(12)
MN(1) - C(3)	1.909(14)
MN(1) - C(11)	2.349(12)
MN(1) - C(12)	2.116(10)
MN(1) - C(13)	2.217(13)
P(1) - C(21)	1.838(14)
P(1) - C(22)	1.910(14)
P(1) - C(29)	1.846(12)
C(1) - O(1)	1.129(15)
C(2) - O(2)	1.218(15)
C(3) - O(3)	1.195(17)
C(11) - C(12)	1.527(19)
C(11) - C(14)	1.438(19)
C(12) - C(13)	1.440(20)
C(14) - C(15)	1.398(19)
P(1) - MN(1) - C(1)	170.6(3)
P(1) - MN(1) - C(2)	84.8(3)
C(1) - MN(1) - C(2)	90.7(5)
P(1) - MN(1) - C(3)	84.3(3)
C(1) - MN(1) - C(3)	88.7(5)
C(2) - MN(1) - C(3)	103.4(5)

TABLE 15 (contd)

P(1)	-	MN(1)	-	C(11)	99.5(3)
C(1)	-	MN(1)	-	C(11)	88.9(4)
C(2)	-	MN(1)	-	C(11)	91.9(4)
C(3)	-	MN(1)	-	C(11)	164.6(4)
P(1)	-	MN(1)	-	C(12)	84.8(3)
C(1)	-	MN(1)	-	C(12)	104.5(4)
C(2)	-	MN(1)	-	C(12)	127.0(5)
C(3)	-	MN(1)	-	C(12)¬	
C(11)	-	MN(1)	-	C(12)	39.6(5)
P(1)	-	MN(1)	-	C(13)	99.9(4)
C(1)	-	MN(1)	-	C(13)	86.8(6)
C(2)	-	MN(1)	-	C(13)	163.2(5)
C(3)	-	MN(1)	-	C(13)	93.1(5)
C(11)	-	MN(1)	-	C(13)	71.5(5)
C(12)	-	MN(1)	-	C(13)	38.7(5)
MN(1)	-	P(1)	-	C(21)	114.5(4)
MN(1)	-	P(1)	-	C(22)	114.2(4)
C(21)	-	P(1)	-	C(22)	103.1(7)
MN(1)	-	P(1)	-	C(29)	115.7(5)
C(21)	-	P(1)	-	C(29)	100.0(8)
C(22)	-	P(1)	-	C(29)	107.7(8)
MN(1)	-	C(1)	-	O(1)	173.9(11)
MN(1)	-	C(2)	-	O(2)	178.4(10)
MN(1)	-	C(3)	-	O(3)	178.0(11)
MN(1)	-	C(11)	-	C(12)	62.0(5)
MN(1)	-	C(11)	-	C(14)	116.1(8)
C(12)	-	C(11)	-	C(14)	122.9(11)
MN(1)	-	C(12)	-	C(11)	78.4(6)
MN(1)	-	C(12)	-	C(13)	74.4(7)
C(11)	-	C(12)	-	C(13)	128.1(10)
MN(1)	-	C(13)	-	C(12)	66.8(6)
C(11)	-	C(14)	-	C(15)	124.5(12)

TABLE 16

ANISOTROPIC AND ISOTROPIC THERMAL PARAMETERS

ANISOTROPIC IN THE FORM EXP $\{-2\pi^2$ (U 11 (A STAR H)^2 + ... U23 (B STAR) (C STAR) K L + ...)$\}$.

ISOTROPIC EXP$\{-8\pi^2 U (\sin\theta/\lambda)^2\}$.

(ALL VALUES X 1000)

ATOM	U11(OR U)	U22	U33	U23	U13	U12
MN(1)	85(1)	37(1)	54(1)	0(1)	29(1)	-1(1)
P(1)	95(2)	44(1)	56(1)	-4(1)	25(1)	-3(1)
C(1)	127(10)	60(7)	57(6)	-2(5)	47(6)	-18(6)
O(1)	227(13)	90(7)	67(5)	-21(5)	78(7)	-41(8)
C(2)	87(7)	60(6)	55(5)	1(5)	20(5)	-11(6)
O(2)	112(6)	72(6)	91(6)	29(5)	4(5)	15(5)
C(3)	104(8)	58(6)	72(7)	-3(5)	42(6)	8(6)
O(3)	107(6)	87(7)	132(8)	0(6)	73(6)	-5(5)
C(11)	108(8)	40(5)	79(6)	0(5)	48(6)	-3(5)
C(12)	128(10)	48(5)	54(5)	10(4)	46(6)	0(6)
C(13)	116(9)	50(6)	114(10)	5(6)	53(8)	14(6)
C(14)	117(9)	49(6)	79(7)	8(5)	48(7)	-3(6)
C(15)	117(10)	69(8)	100(9)	1(7)	36(8)	-9(7)
C(21)	189(16)	59(8)	96(9)	-25(7)	71(10)	-37(9)
C(22)	135(11)	63(8)	84(8)	-15(6)	60(8)	-3(7)
C(29)	120(12)	110(12)	54(6)	-1(7)	-18(8)	-5(9)

TABLE 17

ATOMIC COORDINATES (x 10^4) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES.

ATOM	X	Y	Z
H(11)	-1891	-419	2613
H(12)	1083	-997	5208
H(131)	4071	-1312	4599
H(132)	2425	-1874	2198
H(14)	-1413	-2063	529
H(151)	-5300	-1158	55
H(152)	-5007	-2292	-1242
H(211)	1519	2491	3314
H(212)	3657	2225	4105
H(213)	2747	2580	5503
H(221)	-591	553	5839
H(222)	-1162	1474	4550
H(223)	277	1554	6673
H(231)	3867	-46	7187
H(232)	4298	1018	7914
H(233)	4969	635	6348

CHAPTER FOUR

η^3-PENTADIENYL COMPLEXES OF MOLYBDENUM

CHAPTER FOUR

4.1. η^3-Pentadienyl complexes of molybdenum.

4.1.1. Introduction.

The zerovalent molybdenum and tungsten complexes $\{M(CO)_3(MeCN)_3\}$ [205] have been shown readily to undergo oxidative addition reactions with allylic halides to give the η^3- allyl complexes $\{MX(\eta^3\text{-allyl})(CO)_2(MeCN)_2\}$ { M=Mo,W ; X=Cl,Br}; allyl=C_3H_5, C_3H_4Me, C_3H_4Cl, C_3Ph_3, C_6H_9}. The reaction occurs rapidly with evolution of carbon monoxide and displacement of acetonitrile often giving quantitative yields, with a variety of allylic halides.[206]

The acetonitrile intermediate complex $\{W(CO)_3(MeCN)_3\}$ is particularly interesting, since direct interaction between $\{W(CO)_6\}$ and allylic halides using acetonitrile as a solvent does not afford the mentioned complexes.[206]

Many molybdenum complexes, however, have also been isolated from molybdenum hexacarbonyl reacting with allylic compounds in the presence of donor ligands, by Tom Dieck and Friedel[137] (see Scheme 1). They formulated a two step reaction, with the initial substitution of the CO groups by the neutral donor groups, followed by the oxidative addition of the allylic halides to the intermediate complex. As an example:

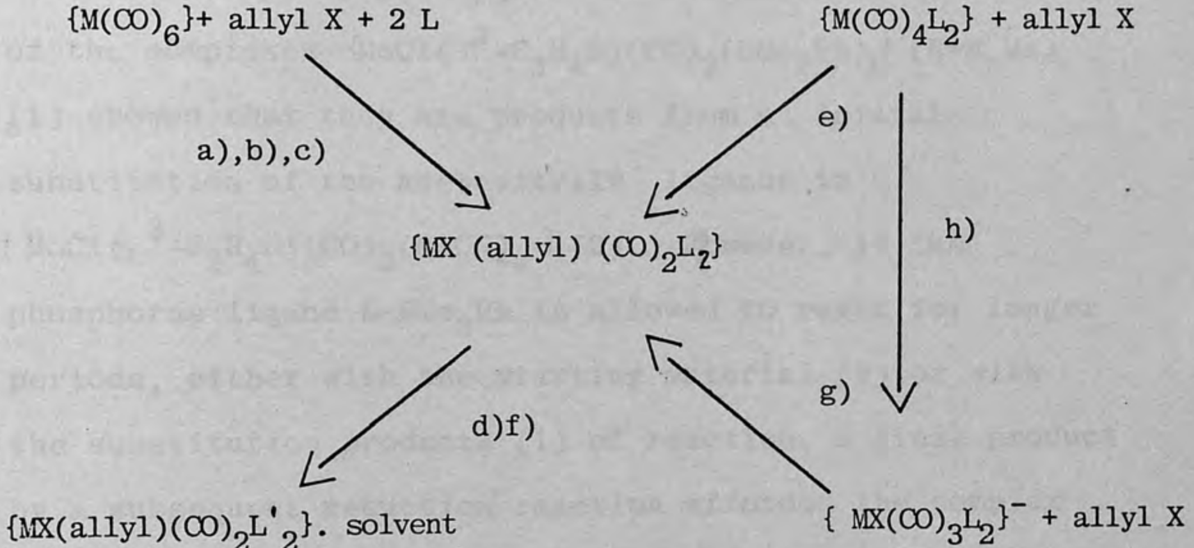
1) $Mo(CO)_6 + 3(MeCN) \longrightarrow Mo(CO)_3(MeCN)_3 + 3CO$

2) $\{Mo(CO)_3(MeCN)_3\} + C_3H_5X \longrightarrow \{MoX(\eta^3\text{-}C_3H_5)(CO)_2(MeCN)_2\}$

X=halides.

A variety of ligands readily displace the labile acetonitrile ligands in the complexes$\{MoX(\eta^3\text{-allyl})(CO)_2(MeCN)_2\}$. Therefore these species are frequently used as starting materials.[207,208,209]

Some studies which involve synthesis and reactions of η^3-allylic complexes are summarised in Scheme 1.



SCHEME 1

a) M=Mo, allyl=C_3H_5, X=Cl,Br,I, L=MeCN, Ref.137;

b) M=Mo, allyl X=C_3H_5Br, L=pyridine(py), Ref.137;

c) M=Mo, allyl X=C_3Ph_3Br, L=MeCN, Ref.210;

d) M=Mo,allyl X=C_3Ph_3Br, L'_2=2,2'-bipyridine(Bipy), 1,10-phenanthroline(phen), 2,2'-dipyridylamine(dpa), solvent= MeCN. Ref.210 ;

e)M=Mo, allyl=C_3H_5,X=Cl,Br,I, L_2=Bipy, phen , Ref.211;

f) M=Mo,allyl X=MeC_3H_4Cl, $L'=PMe_2Ph,PMePh_2$, $L'_2=Ph_2PCH_2CH_2PPh_2$ (diphos), unsolvated, Ref.207;

g) M=W,allyl X=C_3H_5Br,L_2=bipy, Ref.212;

h) M=Mo, W,L_2=Bipy, phen, Ref.213.

Allylic halides oxidise the compounds $\{W(CO)_4L\}$ (L=Bipy or phen) less readily than their molybdenum analogues {SCHEME 1, (e)}, and an alternative, reaction of allyl halides with the trisubstituted derivatives $\{W(CO)_3L(py)\}$ (L = Bipy or phen) in boiling THF, led to the isolation of the tungsten complexes $\{WX(\eta^3\text{-}C_3H_5)(CO)_2L_2\}$ $\{X=Cl,Br,I,\ L_2=\text{Bipy or phen}\}$.[211]

Studies by Mawby on the mechanism of reaction of the complexes $\{MoCl(\eta^3\text{-}C_3H_4R)(CO)_2(PMe_2Ph)_2\}$ (R=H,Me) (1) showed that they are products from an initial substitution of the acetonitrile ligands in $\{MoCl(\eta^3\text{-}C_3H_4R)(CO)_2(MeCN)_2\}$ (2). However, if the phosphorus ligand L=PMe_2Ph is allowed to react for longer periods, either with the starting material (2) or with the substitution products (1) of reaction, a final product by a subsequent reduction reaction afforded the complex $\{Mo(CO)_2(PMe_2Ph)_4\}$. It is suggested that the reduction involves initial nucleophilic attack on the allyl ligand. In the case of the reaction of (2 R=H) with PMe_2Ph, the other product of reaction $\{C_3H_5PMe_2Ph\}Cl$ was also isolated and identified.[207] (SCHEME 2).

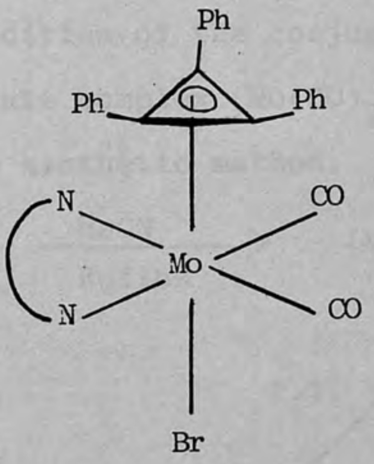
$$\{MoCl(\eta^3\text{-}C_3H_5)(CO)_2(MeCN)_2\} + 2PMe_2Ph \longrightarrow \{MoCl(\eta^3\text{-}C_3H_5)(CO)_2(PMe_2Ph)_2\}$$

$$\{MoCl(\eta^3\text{-}C_3H_5)(CO)_2(PMe_2Ph)_2\} \xrightarrow{3PMe_2Ph} \{C_3H_5PMe_2Ph\}^+Cl^- + \{Mo(CO)_2(PMe_2Ph)_4\}$$

SCHEME 2

Ditertiary phosphines and arsines, such as diphos {Scheme 1(f)}, $Ph_2PCH_2PPh_2$ (dpm), $Ph_2AsCH_2CH_2AsPh_2$ (dae) and $PH_2AsCH_2AsPh_2$(dam) showed the same feature reacting with (2 R=H). In contrast tertiary phosphines PR_3 (R=Ph,n-Bu) react under mild conditions with $\{MoX(\eta^3-C_3H_5)(CO)_2(MeCN)_2\}$ (where X=Cl,Br) to form molybdenum(0)derivatives $\{Mo(CO)_2(PR_3)_2(MeCN)_2\}$ and $\{Mo(CO)_2(PR_3)_3(MeCN)\}$.[209,214,215]

The crystal and molecular structure of the cyclopropenyl complex $\{MoBr(CO)_2(\eta^3-C_3Ph_3)(bipy)\}$. MeCN shows that the Mo atom in a distorted octahedral environment, with the mutually cis carbonyl groups and the Bipy ligand occupying a equatorial plane (3).



(3)

In trans positions are a bromine atom and an η^3-cyclopropenyl group. There is also a solvent molecule in the asymmetric unit, but there is no close contact between it and other molecules.[210]

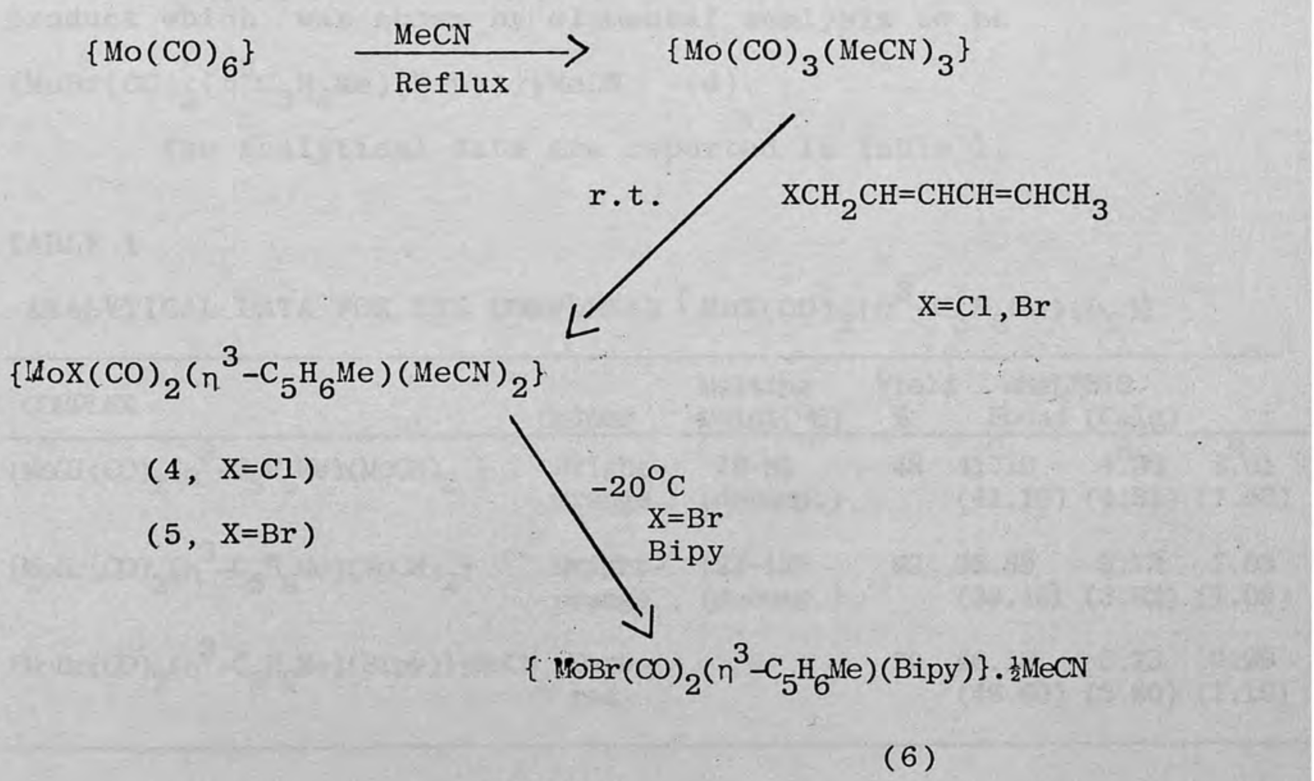
This work reports the use of 1-chloro- and 1-bromohexa-2,4-dienes as reagents for the synthesis of the novel η^3-pentadienyl complexes {MoX(CO)$_2$(η^3-C$_5$H$_6$Me)(MeCN)$_2$} (X = Cl, Br) ; and the readily displacement of the acetonitrile ligands by the bidentate 2,2'-bipyridine, giving the substituted complex {MoBr(CO)$_2$(η^3-C$_5$H$_6$Me)(Bipy)}.½MeCN.

4.1.2. Results and Discussion

The complexes {MoX(CO)$_2$(η^3-C$_5$H$_6$ Me) (MeCN)$_2$} and {MoBr(CO)$_2$(η^3-C$_5$H$_6$Me)(Bipy)} ½MeCN.

4.1.2.1. Preparation, properties and spectroscopic studies.

The η^3-pentadienyl molybdenum complexes were isolated by the route shown in the SCHEME 3. The oxidative addition of the conjugated halohexadienes to the intermediate complex {Mo(CO)$_3$(MeCN)$_3$} proved to be an accessible synthetic method.



SCHEME 3

In contrast, direct treatment of the halohexadienes with molybdenum hexacarbonyl complex, or $\{Mo(CO)_4(Bipy)\}$ gave only products of decomposition and insoluble impure solids respectively. Unfortunately, the low solubility of the latter solids in suitable solvents precluded a thorough investigation of the possible products.

The complexes (4,5) crystallise as bright-orange crystals after slow evaporation of the solvent under a stream of nitrogen. They are quite air-sensitive in solution and also they readily decompose as solids under air. The 1-chloro-2,4-hexadiene yielded the corresponding chloro-complex rather more slowly than the bromo analogue.

The orange solution of $\{MoBr(CO)_2(\eta^3\text{-}C_5H_6Me)(MeCN)_2\}$ in acetonitrile was treated with 2,2'-pyridine, as described in the SCHEME 3, giving a dark-red microcrystalline product which was shown by elemental analysis to be $\{MoBr(CO)_2(\eta^3\text{-}C_5H_6Me)(Bipy)\}\frac{1}{2}MeCN$. (6).

The analytical data are reported in Table 1.

TABLE 1

ANALYTICAL DATA FOR THE COMPLEXES $\{MoX(CO)_2(\eta^3\text{-}C_5H_6Me)(L_2)\}$

COMPLEX	Colour	Melting Point(^oC)	Yield %	ANALYSIS Found (Calc)		
				C	H	N
$\{MoCl(CO)_2(\eta^3\text{-}C_5H_6Me)(MeCN)_2\}$	Bright-orange	79-81 (decomp.)	48	41.10 (41.10)	4.30 (4.31)	8.01 (7.98)
$\{MoBr(CO)_2(\eta^3\text{-}C_5H_6Me)(MeCN)_2\}$	Bright-orange	123-125 (decomp.)	62	35.88 (36.48)	3.73 (3.83)	7.03 (7.09)
$\{MoBr(CO)_2(\eta^3\text{-}C_5H_6Me)(Bipy)\}\frac{1}{2}MeCN$	Dark-red	-	70	46.18 (46.60)	3.73 (3.80)	7.29 (7.15)

The complex $\{MoBr(CO)_2(\eta^3-C_5H_6Me)(MeCN)_2\}$ in the solvents MeOH and Me_2CO at -35°C, was treated with trimethylphosphite in a similar manner to the allylic complexes $\{MoX(CO)_2(\eta^3-C_3H_4R)[P(OMe)_3]_2\}$[208,216] (X=halide, R=H,Me). However, no isolated product could be obtained from the oily residues after evaporation of the solvent.

Attempts to prepare analogous η^3-pentadienyltungsten complexes as (4) and (5) by treating the $\{W(CO)_3(MeCN)_3\}$ with 1-chloro- and 1-bromo-2,4-hexadiene were unsuccessful. The final products of reaction showed the presence of the starting material $\{W(CO)_6\}$. This reverse has also been noted during studies on disproportionation reactions of the tungsten hexacarbonyl-acetonitrile derivatives.[217, 218]

The reaction mixture involving $\{W(CO)_3(MeCN)_3\}$ and 1-chloro-2,4-hexadiene shows the formation of several by-products.

The infrared spectra of the complexes $\{MoX(CO)_2(\eta^3-C_6H_9)L_2\}$ in the CO stretching region contain two strong bands of approximately equal intensity, indicating a cis arrangement of the carbonyl ligands.

The assignment is based on previous studies of similar allyl compexes (including in Table 2 for comparison). Crystal structure determinations on several allyl compounds of the type under investigation have shown very similar stereochemistries.[210, 219] The ligand arrangement is basically octahedral, with the cis-carbonyl groups and the donor atoms of the bidentate ligand approximately co-planar, while the allyl group is trans to the

TABLE 2

SELECTED INFRARED DATA[a] FOR THE COMPLEXES $\{MoX(CO)_2(\eta^3-C_5H_6Me)L_2\}$

COMPLEX	ν(CO)[b]		ν(C=C)	ν(CN)	
$\{MoCl(CO)_2(\eta^3-C_5H_6Me)(MeCN)_2\}$	1927	1845	1645	2325(w)	2295(s)
$\{MoBr(CO)_2(\eta^3-C_5H_6Me)(MeCN)_2\}$	1922	1840	1645	2315(w)	2285(s)
$\{MoBr(CO)_2(\eta^3-C_5H_6Me)(Bipy)\}\frac{1}{2}MeCN$	1924	1861	c		
$\{MoCl(CO)_2(\eta^3-C_3H_5)MeCN)_2$ [d]	1951	1855		2312	2286
$\{MoBr(CO)_2(\eta^3-C_3H_5)(MeCN)_2\}$[d]	1953	1852		2315	2285
$\{MoBr(CO)_2(\eta^3-C_3Ph_3)(Bipy)\}\frac{1}{2}MeCN$ [e]	1936	1868			
$\{MoBr(CO)_2(\eta^3-C_6H_9)(Bipy)\}$ [f]	1920	1838			
$\{MoBr(CO)_2(\eta^3-C_3H_5)(Bipy)\}$	1927	1845 [g]			
	1938	1845 [d]			

(a) Recorded as nujol mulls (cm^{-1}); (b) All bands have strong intensity; (c) Bipy overlap; (d) Reference 137; (e) Ref.210; (f) Ref.213; (g) Ref.211.

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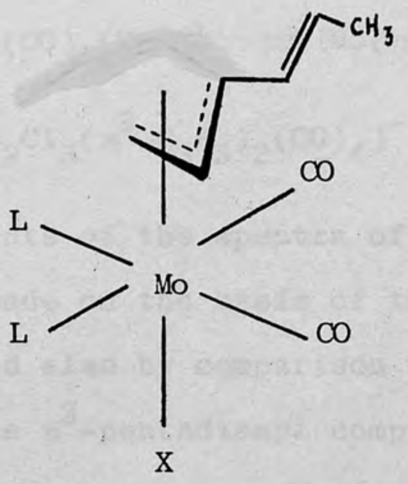
unidentate ligand. According to the similarities in the spectra of all these closely related complexes with the dicarbonyl pentadienyl derivatives, it seems that, in principle, it is reasonable to propose the same pseudo-octahedral structure of local C_s symmetry for the new complexes.

The corresponding bromo (5, L=MeCN) and chloro complex (4, L=MeCN) dissolved in CD_3CN, has been shown by ^1H-NMR studies to ionise with the liberation of free acetonitrile.



(4) L=MeCN,X=Cl
(5) L=MeCN,X=Br
(6) L_2=Bipy,X=Br

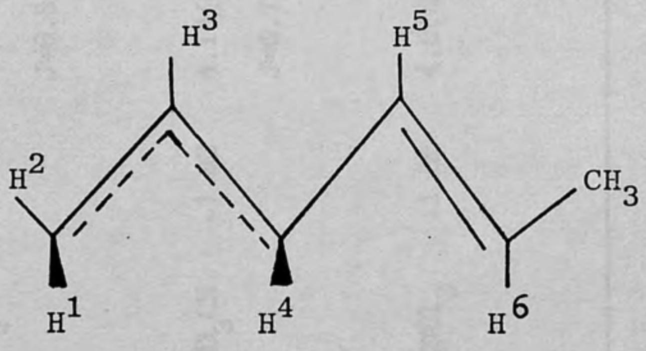
A similar effect has been observed for the allyl complexes {MoX(η^3-C_3H_5)$(CO)_2$$(MeCN)_2$}(X=Cl,Br).[220] The ^{1}H-NMR revealed three allyl containing species with chemical shifts characteristic of anionic, cationic and neutral complexes. Confirmation that ionic species were formed in solution was obtained from conductivity measurements. The assignment of the allyl protons in the spectrum of {MoCl(η^3-C_3H_5)$(CO)_2$$(MeCN)_2$} was based on comparison with the chemical shifts and coupling constants of the allyl protons in analytically pure samples of Ph_4As{Mo_2Cl_3(η^3-C_3H_5)$_2$$(CO)_4$} and {Mo($\eta^3$-$C_3H_5$)$(CO)_2$$(MeCN)_3$}$PF_6$[220b]

An equilibrium involving the liberation of free acetonitrile, is described in the reversible formation of these ionic species:[220b]

$$3\{MoCl(\eta^3\text{-}C_3H_5)(CO)_2(MeCN)_2\} \rightleftarrows \{Mo(\eta^3\text{-}C_3H_5)(CO)_2(MeCN)_3\}^+ + \{Mo_2Cl_3(\eta^3\text{-}C_3H_5)_2(CO)_4\}^- + 3MeCN$$

Assignments of the spectra of the η^3-pentadienyl complexes were made on the basis of these studies on the allyl systems and also by comparison with analogous structures of the η^3-pentadienyl complexes reported in previous chapters.

The ^{1}H-NMR data are reported in Table 3 according to 7. The solubility of $\{MoBr(CO)_2(\eta^3\text{-}C_5H_6Me)Bipy\}.\frac{1}{2}MeCN$ prevents the ^{1}H-NMR studies.



(7)

TABLE 3

^{1}H-NMR DATA FOR THE COMPLEXES $\{MoX(CO)_2(CH^1H^2CH^3CH^4CH^5CH^6Me)\ L_2\}^a$

COMPLEX	SOLVENT	CHEMICAL SHIFTS (δ)						
		H^1H^2 [b]	H^3	H^4	H^5	H^6	CH_3	L
$\{MoCl(CO)_2(\eta^3\text{-}C_5H_6Me)(MeCN)_2\}$	CD_3CN	~1.82	4.07(dt)	2.27(t)	6.12(m)	5.84(dq)	1.78(d)	1.96(m)
			J=6.8,9.0	J ~10	J_4=10	J_5=15	J_6=6.8	2.56(s) [c]
							J=1.6	
$\{MoBr(CO)_2(\eta^3\text{-}C_5H_6Me)(MeCN)_2\}$	CD_3CN	~1.83	4.14(dt)	2.35(t)	6.10(m)	5.88)dq)	1.76(d)	1.99(m)
			J=6.7,9.2	J ~10.5		J_5=14.8	J_6=6.5	2.55(s,br) [c]
							J=1.5	
$\{MoCl(CO)_2(\eta^3\text{-}C_5H_6Me)(MeCN)_2\}$	$CDCl_3$	~1.80	4.0(dt)	2.49	6.30(d)	5.79(dq)	1.80(d)	2.04(s,br)
					J=10.5,1.7	J_5=15	J_6=6.5	2.49(s,br) [c]
							J=1.5	

a) For numbering see (7). Measured at 250MHz relative to tetramethylsilane. δ=0 ppm. Coupling constants in Hz;

b) See text; c) Cationic species.

The ^{1}H-NMR spectrum of $\{MoX(CO)_2(\eta^3-C_5H_6Me)(MeCN)_2\}$ (X=Cl,Br) in deuterated acetonitrile solution at room temperature showed, as mentioned before, the presence of free acetonitrile, (~1.97δ) along with a broad singlet at ~2.55δ which resembled the cationic MeCN signal observed in the allylic complexes.[220b] However, the spectra show barely detectable signals which could be assigned to ionic pentadienyl species. The neutral species (4) and (5) exhibit very similar resonances and as an example, the spectrum of the chloro complex can be seen in Figure 1. Two close resonances at the lowest field 6.12δ and 5.84δ are attributable to the trans protons (H^5) and (H^6) respectively. $\{J(H^5,H^6)=15Hz\}$. The terminal methyl protons resonate at 1.78δ as a doublet, with a characteristic vicinal coupling of 6.8Hz.[72] As for other η^3-pentadienyl complexes, (Section 2.3.2.1. and 3.2.2.3.) a triplet at 2.27δ is assigned to the proton (H^4) for which an anti configuration is suggested according to the magnitude of the coupling constant $J(H^3H^4)$ ~ 9Hz. The proton (H^3) (4.07δ, doublet of triplets) resonates to low field of (H^4), as observed in the ruthenium complex (Section 2.3.2.1.). The coupling constant values of 6.8 and 9Hz are in agreement with those with cis- trans- vicinal protons $J(H^2H^3)$ and $J(H^1H^3)$ in similar systems.[220,224] The corresponding anti and syn protons (H^1) and (H^2) however, are not observed directly, presumably by overlapping with the methyl signals at 1.78δ according to the intensity measurements.

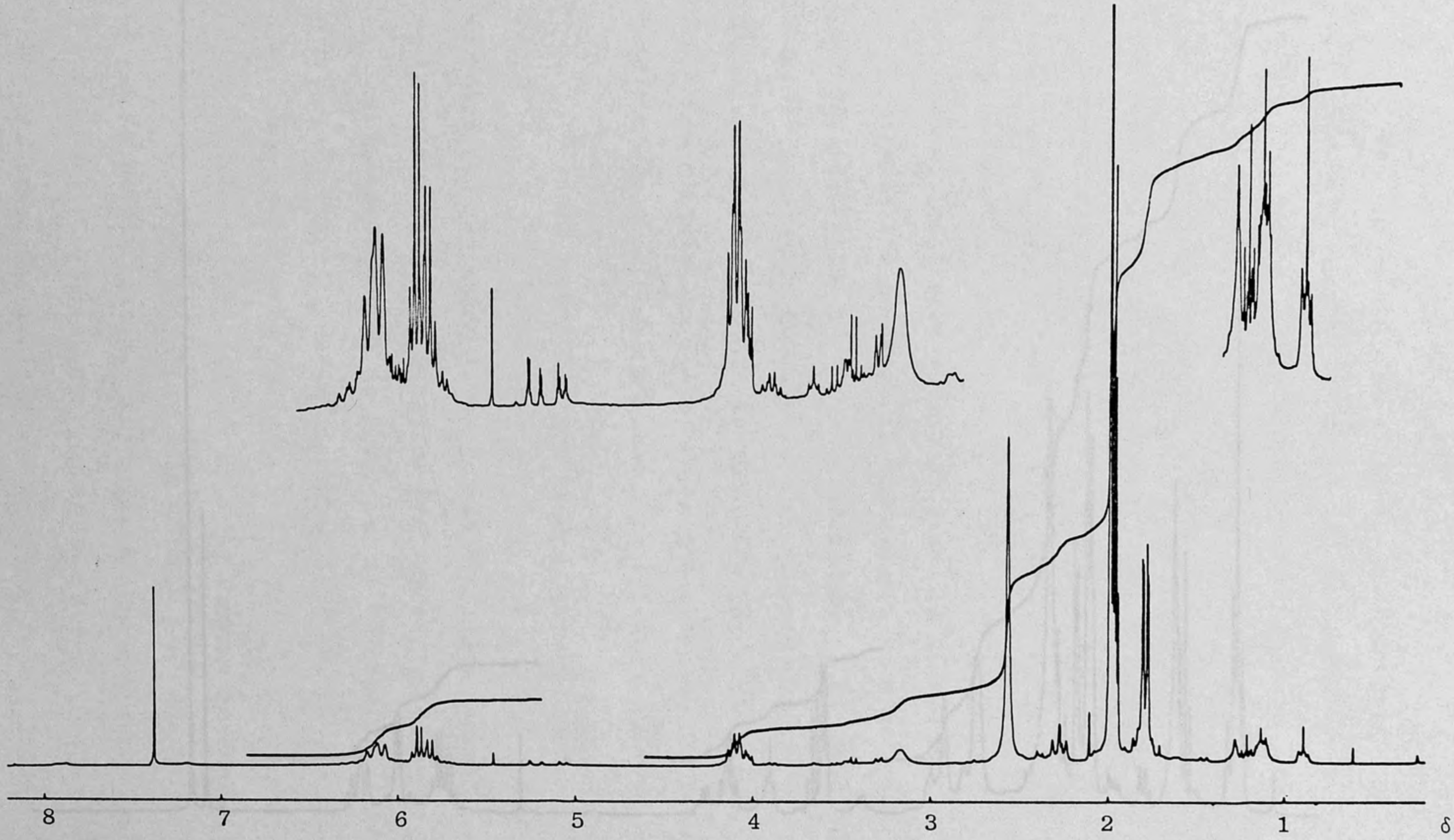


Figure 1. ^{1}H-NMR spectrum of $\{MoCl(CO)_2(\eta^3-C_5H_6Me)(MeCN)_2\}$ (4) in CD_3CN at 250 MHz.

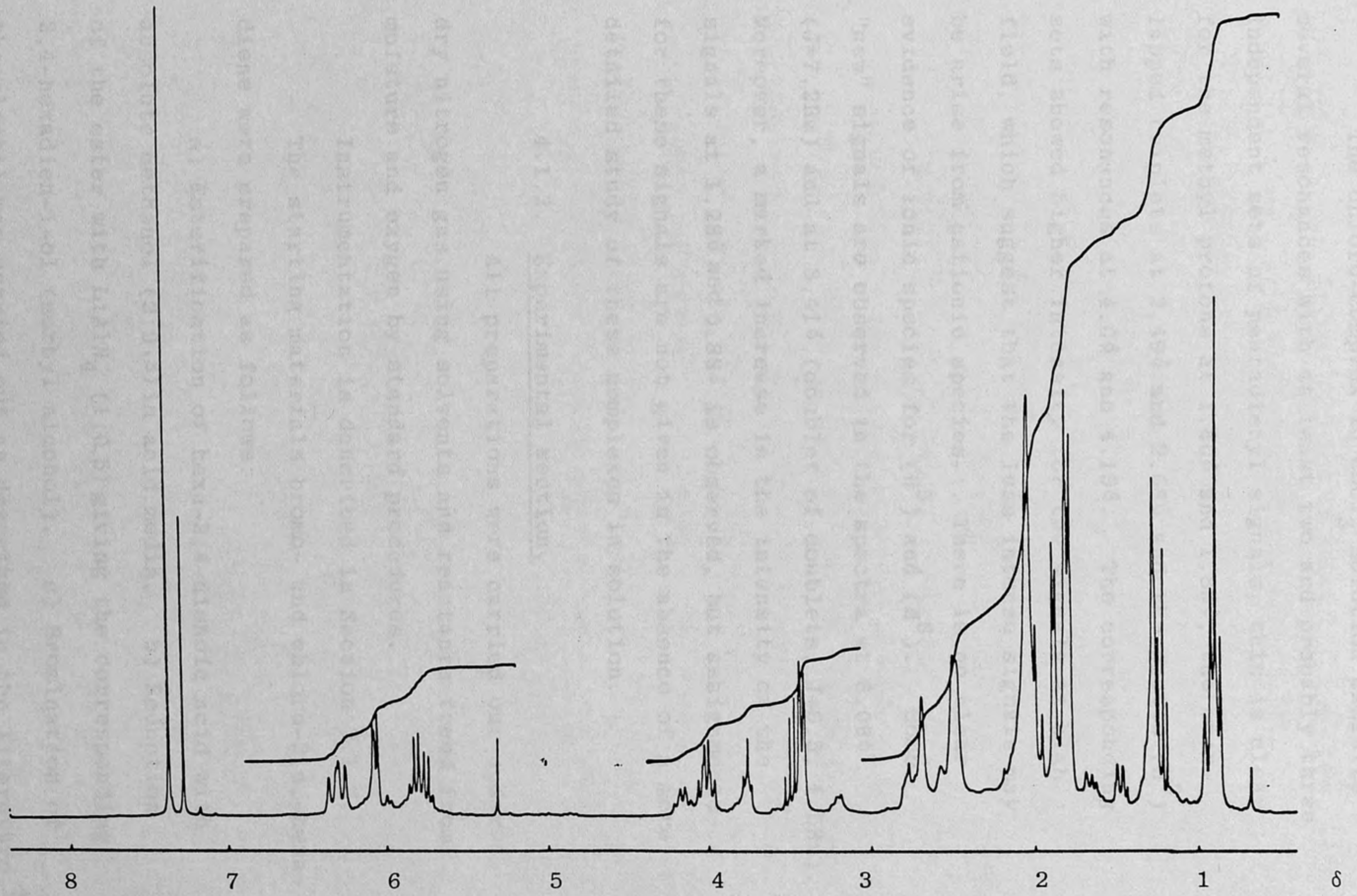


Figure 2. ^{1}H-NMR spectrum of $\{MoCl(CO)_2(\eta^3\text{-}C_5H_6Me)(MeCN)_2\}$ (4) in $CDCl_3$ at 250 MHz.

The chloro-complex in $CDCl_3$ solution exhibits several resonances with at least two and probably three independent sets of pentadienyl signals, this is clear for the methyl protons at 1.80δ and 1.88δ, the overlapped triplets at 2.49δ and 2.68δ and the proton (H^3) with resonances at 4.0δ and 4.15δ. The corresponding sets showed higher intensity for the signals at high field, which suggest that the less intense signals may be arise from cationic species. There is no clear evidence of ionic species for (H^5) and (H^6). Some "new" signals are observed in the spectra at 6.06δ (J=7.2Hz) and at 3.41δ (doublet of doublets, J=6.5, 1.5Hz). Moreover, a marked increase in the intensity of the signals at 1.28δ ~~and~~ 0.88δ is observed, but assignments for these signals are not given in the absence of a more detailed study of these complexes in solution.

4.1.3. Experimental section.

All preparations were carried out under dry nitrogen gas using solvents and reactants freed from moisture and oxygen by standard procedures.

Instrumentation is described in Section 2.1.3.

The starting materials bromo- and chloro-2,4,-hexadiene were prepared as follows:

a) Esterification of hexa-2,4-dienoic acid with absolute methanol (2:9.3) in acid media. b) Reduction of the ester with $LiAlH_4$ (1:0.5) giving the corresponding 2,4-hexadien-1-ol (sorbyl alcohol). c) Bromination of the alcohol was carried out as described in the literature,[221] and collected by distillation at 62-72°C/14mmHg, and the chlorination of the alcohol (0.26 mol) in diethyl ether (100 cm^3) with concentrated HCl (100 cm^3).

A mixture of isomers was obtained from distillation at 68-76°C/50 mmHg.

$\{Mo(CO)_6\}$ and 2,2'-bipyridine were used as received. The phosphite $P(OMe)_3$ was previously treated as described in Section 3.1.3.

i) Preparation of the complexes $\{MoX(CO)_2(\eta^3-C_5H_6Me)(MeCN)_2\}$

$\{Mo(CO)_6\}$ (2.38 g., 9mmol) was heated under reflux with MeCN(100 cm^3) for 4 h. as reported by Brisdon.[210] The yellow-brown solution was stirred and treated with the corresponding 1-bromo- or 1-chloro-2,4-hexadiene (9mmol) at room temperature, giving an orange solution which was then evaporated to small bulk under a slow stream of nitrogen. On standing for several days at 0°C, the product precipitated as bright orange crystals. The chlorine derivative yielded the product rather more slowly, and the solution was cooled to -23°C. The products were recrystallised from MeCN and the crystals washed with hexane and dried under vacuum.

ii) Preparation of the complex $\{MoBr(CO)_2(\eta^3-C_5H_6Me)(Bipy)\}\frac{1}{2}MeCN$

$\{MoBr(CO)_2(\eta^3-C_5H_6Me)(MeCN)_2\}$ (0.33 g., 0.84mmol) in acetonitrile (45 cm^3) gave an orange solution, which was filtered and cooled to -20°C. Addition of bipyridine (0.131 g., 0.84mmol) in MeCN(5 cm^3) gave immediately a red solution. After stirring for 15 min. the temperature was increased to 0°C. Some red-black impure solid precipitated. Recrystallisation with acetonitrile was carried out, reducing volume of the solvent with a slow stream of nitrogen, affording a dark-red microcrystalline product.

iii) Attempted reactions with tungsten instead of molybdenum were unsuccessful.

a) The reaction of $W(CO)_3(MeCN)_3$ with $XCH_2CH{=}CHCH{=}CHCH_3$ (X=Cl,Br).

$\{W(CO)_6\}$ (2.5 g., 7.1mmol) was heated under reflux with acetonitrile(75cm^3) for 40h. giving the intermediate species $\{W(CO)_3(MeCN)_3\}$.[205] Addition of the bromo- and chloro-2,4-hexadiene to the stirred acetonitrile complex was carried out at room temperature. After the addition, the yellow solution changed to orange-yellow and then to olive green. This colour change is faster for the bromo derivative than for the 1-chloro-2,4-hexadiene.

The filtration and slow evaporation of the solvent under a stream of nitrogen for the bromine reaction gave 0.44 g., of starting material $\{W(CO)_6\}\{\nu(CO)$: 1980(vs)$\}$ and a green solution $\{\nu(CO)$ 1975(s), 1935(s) 1895(w)$\}$ from which no crystals could be obtained.

The chloro derivative showed a complex mixture of subproducts along with $\{W(CO)_6\}$. Neither of these reactions showed spectroscopic evidence of the analogous dicarbonyl complexes, which have been isolated with molybdenum.

b) The reaction of {$MoBr(CO)_2(\eta^3$-$C_5H_6Me)(MeCN)_2$} with $P(OMe)_3$.

A solution of the molybdenum complex (0.79 g., 2mmol) in acetone (20 cm^3) was treated with freshly distilled $P(OMe)_3$(0.5 g., 4mmol) at room temperature. After 1 h. sitrring, the solvent was evaporated to low bulk in vacuo. After 3 days at -20°C, no precipitate was observed. Then solvent was completely removed, and the residue evacuated for 3 h. Approximately 4 cm^3 of acetone were added at -20°C and the mixture stored at -20°C, without success.

The same reaction was carried out with the addition of $P(OMe)_3$ at -35°C, increasing slowly the temperature and reducing the volume of solvent under a stream of nitrogen, being again unsuccessful. The same result was obtained using dry methanol instead of acetone.

iv) Attempted reactions with 1-bromo-2,4-hexadiene and various complexes.

a) The reaction of {$Mo(CO)_6$} with 1-bromo-2,4-hexadiene.

A mixture of the carbonyl molybdenum (2.64 g., 10mmol) and the diene (2.42 g., 15mmol) were heated under refluxing MeCN(50 cm^3) for 9 h. The formation of dark yellow solution showed that the product decomposed every time. After 7 h. of reflux monitoring the reaction by infrared spectroscopy showed the consumption of starting material. The final solution showed several ν(CO) bands at 1938, 1915, 1845 and 1790 cm^{-1}. Filtration was carried out and evaporation of the solvent gave a dark yellow oil, which could not be purified. Attempts to prepare the corresponding salt using MeCN(20 cm^3) and KPF_6 (0.88 g., 4.8mmol) also proved unsuccessful.

b) The reaction of $\{Mo(CO)_4Bipy\}$[222] with 1-bromo-2,4-hexadiene.

A mixture of the molybdenum complex (2.5 g., 6.87mmol) and an excess of the diene (5.5 g., 34.3mmol) was heated under refluxing THF (100 cm^3) with vigorous stirring for 2¼ h. The pink product, which separated was filtered off from the cold solution, washed with light petroleum and dried in vacuo (3.24 g.). The final product did not give evidence of carbonyl groups according to the infrared spectrum. It seems that the pink solid must have a high molecular weight.

The same reaction was carried out with a stoichiometric ratio (1:1) and also (1:2), the former giving a purple, slightly impure solid { ν(CO) 1955(m), 1898(s), 1855(s), 1830(s) cm^{-1}(nujol) } and the latter it seems a mixture from the pink and purple solids{ ν(CO) 1955(m), 1898(s), 1850(s), 1828(s) cm^{-1}(nujol) }. Attempts to purify these complexes by recrystallisation were thwarted by the very low solubilities in organic solvents. Spectroscopic infrared data on the solids proved inconclusive.

v) Attempts to prepare pentadienyl compounds from pentadienyl anion with various complexes.

a) The reaction of $\{MoCl(\eta^3-C_3H_5)(CO)_2(MeCN)_2\}$[137] with pentadienyllithium.

Pentadienyllithium has been prepared from metallation of 1,4-pentadiene as described in Experimental Section 2.1.3. The orange-red mixture (3.49mmol) at 0°C was slowly added to a stirred solution of the molybdenum complex (1.08 g., 3.49mmol) in THF (15 cm^3) at -60°C. The yellow solution changed to dark yellow during the addition. After 1 h. stirring, the temperature was allowed to rise slowly to room temperature. Evaporation of the solvent was carried out. Hexane was added and the resultant yellow solution was filtered. The filtrate was evaporated in vacuo to leave a yellow oil, which was sublimed at 20°C/0.06mmHg, giving an air sensitive lemon yellow solid. The infrared spectrum had two peaks in the ν(CO) at {1958(vs), 1895(sh), 1878(vs) cm^{-1} (CCl_4)} and {$Mo(\eta^3-C_3H_5)(CO)_2(\eta^5-C_5H_5)$} shows ν(CO) at 1961(vs), 1886(sh), 1871(vs) cm^{-1} (CCl_4) .[223] The low yield prevented ^{1}H-NMR studies. Carbon analysis was high (54.81%) considering the possible formation of {$Mo(\eta^3-C_3H_5)(CO)_2(\eta^5-C_5H_7)$} . ($C_{10}H_{12}O_2Mo$) requires C,46.17%; H,4.65%.

b) The reaction of {$Mo(CO)_6$} with C_5H_7Li

{$Mo(CO)_6$} (3.9 g., 14.7mmol) was added to the resulting red-orange mixture of pentadienyllithium (14.7mmol) at 0°C. (See above). The mixture was stirred overnight at room temperature. The presence of starting material suggests that the reaction proceeds slowly, and gentle reflux was carried out for 3 h., extensive decomposition had occurred. The mixture was cooled to room temperature and an unidentified carbonyl containing compound {ν(CO) (nujol) 2040(w), 1985(vs), ~1930(br), ~1890(br) cm^{-1}} along with some starting material {ν(CO) 1980(vs)} was obtained. The possible formation of a carbene complex was in mind according to previous studies by Fischer on $Mo(CO)_6$ reacting with LiR giving $\{Mo(CO)_5\ COR\}^{-}Li^{+}$ products, such as $R=C_6H_5$ with {ν(CO) 2049(s), 1965(vs), 1938(vs), 1898(vs), 1880(vs) cm^{-1}}.[225]

The yellow dark filtrate was treated with MeI (17.4mmol) and stirred for 2 h. Solvent was removed under reduced pressure and a dark black product was obtained. The work was stopped at this point.

c) The reaction of $\{RhCl(1,5-C_8H_{12})\}_2$ [139] with C_5H_7Li.

On slow addition of pentadienyllithium (7.42mmol) (as described above) to an orange solution of the rhodium complex (1.83 g., 3.7mmol) in THF (15 cm^3) at -60°C the colour darkened. After gently refluxing for 1 h., cooling and filtration a mixture of products was obtained, which appeared to contain some unreacted starting material. Evaporation of solvent from the filtrate left a red-black oil. Extraction of this oil with CH_2Cl_2 and filtration through silica were carried out. Addition of hexane to the red-dark solution and slow evaporation gave an impure orange product. Sublimation at 50°C/o.o5mmHg afforded a few yellow crystals with melting point 95-98°C. The

^{1}H-NMR spectrum indicated strong resonances near 1 δ, but no evidence of the pentadienyl ligand.

d) The reaction of $\{RuCl_2(1,5\text{-}C_8H_{12})\}_n^{226}$ with C_5H_7Li

The ruthenium complex (2 g., 7.2mmol) in THF (25 cm^3) was treated as described in V a) with pentadienyllithium (15.84mmol). The dark-orange solution was stirred overnight at room temperature. After solvent evaporation, a brown oil was obtained and it was extracted with hexane giving a yellow solution and a large amount of brown polymeric solid. Attempts to recrystallise some product from the yellow filtrate fraction were unsuccessful.

e) The reaction of $\{RuCl_2(\eta^6\text{-}C_6H_6)\}_2^{227}$ with $(1,5\text{-}Ph_2C_5H_5)Li$

Addition of the ruthenium complex (0.9 g., 1.8mmol) to the blue-purple pentadienyl anion (3.6mmol) in THF, changed the last colour to a brown solution. The reaction mixture was stirred for 3 h. at room temperature, followed by evaporation of the solvent. The product was extracted in CH_2Cl_2 and filtered, giving a polymeric brown material, in a similar manner than reaction with $\{RuCl_2(1,5\text{-}C_8H_{12})\}_n$ {v d) }. A red oil was obtained from the evaporation of the filtrate. Addition of diethyl ether to the red oil precipitated a small amount of brown solid which was filtered off. The solution was treated at -20°C with $HPF_6(Et_2O)$ affording a brown-yellow precipitate. Recrystallisation from CH_3NO_2 and diethyl ether gave a small quantity of orange-red product. The ^{1}H-NMR studies were inconclusive.

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DIENE AND DIENYL COMPLEXES OF TRANSITION ELEMENTS

IV*. η^5-PENTADIENYLTRICARBONYLRHENIUM

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Summary

η^5-Pentadienyltricarbonylrhenium has been prepared by reacting 2,4-pentadienyltributyltin with bromopentacarbonylrhenium in refluxing tetrahydrofuran.

The recent report by Seyferth, Goldman and Pornet [2] of the synthesis of η^5-pentadienyltricarbonylmanganese prompts us to describe our results on the rhenium analogue (I). We had also independently prepared the manganese derivative by a similar method to that used by Seyferth, prior to the appearance of his paper. We find good agreement between our characterising data and his observations.

2,4-Pentadienyltributyltin, prepared by the reaction between pentadienyllithium and tributyltin chloride reacts with bromopentacarbonylrhenium in refluxing tetrahydrofuran according to the equation

$$Bu_3SnCH_2CH{=}CHCH{=}CH_2 + BrRe(CO)_5 \xrightarrow[\substack{\text{reflux} \\ \text{9 h}}]{\text{THF}} \underset{\text{(I)}}{(C_5H_7)Re(CO)_3} + Bu_3SnBr$$

The product I was isolated from the reaction mixture by chromatography on alumina followed by vacuum sublimation. It is a white crystalline material which, like its manganese analogue, decomposes slowly in air. The ^{1}H NMR spectrum (in C_6D_6) (250 MHz) is consistent with a symmetrical structure for the η^5pentadienyl ligand.

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* For part III, see ref. 1.

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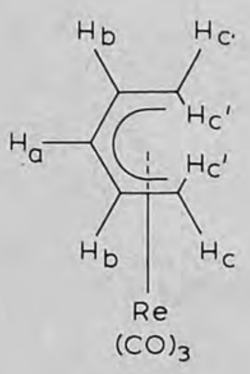

(I)

^{1}H NMR: δ 0.40 [d, $H_{c'}$, $J(H_bH_{c'})$ = 11.3 Hz]; 2.35 [d, H_c, $J(H_bH_c)$ = 10.3 Hz]; 4.42 [m, H_b]; 4.68 ppm [t, H_a, $J(H_aH_b)$ = 6.3 Hz]. Each resonance possesses fine structure indicating coupling constants $J(H_cH_{c'}) \sim 2.5$ Hz, and long range couplings $J(H_aH_c)$ and $J(H_aH_{c'}) \sim 0.9$ Hz.

Experimental

All operations were conducted under dry nitrogen. Solvents were dried by standard methods before use.

Preparation of 2,4-pentadienyltributyltin

To a solution of pentadienyllithium [3] (74 mmol) in tetrahydrofuran (125 cm^3) tributyltin chloride (24.1 g, 74 mmol) was added with stirring at —70°C. The reaction mixture was allowed to warm up to room temperature over 40 min and the solvents were removed in vacuo. Hexane (30 cm^3) was added and the precipitate of lithium chloride was filtered off. Distillation of the filtrate afforded the title compound (24.6 g, 94%) b.p. 102—105°C at 0.1 mm Hg. Anal. Found: C, 56.77; H, 9.16. Calcd. for $C_{17}H_{34}Sn$: C, 57.17; H, 9.60%.

The ^{1}H NMR spectrum (250 MHz in $CDCl_3$) showed the presence of two isomers, in the approximate ratio 4 : 1. The major isomer is assigned the *E* configuration on account of the similarity of its NMR spectrum with that of *E*-1-trimethylsilyl-2,4-pentadiene [3].

^{1}H NMR (*E* isomer): δ 0.89 (m, 15H), 1.31 (m, 6H), 1.49 (m, 6H), 1.81 (d, *J* 7.7 Hz, 2H), 4.78 (dd, *J* 9.8, 2.0 Hz, 1H) 4.94 (dd, *J* 16.8, 2.0 Hz, 1H), 5.70 (m, 1H), 5.90 (m, 1H), 6.27 ppm (dt, *J* 17.0, 9.6 Hz, 1H). The minor isomer showed resonances at 1.91 (d, *J* 7.7 Hz), 4.95 (dd, *J* 9.8, 2.2 Hz) 5.06 (dd, *J* 16.9, 2.2 Hz), 6.61 ppm (dt, *J* 16.9, 10.1 Hz). We prefer to assign a multiplet at δ 5.70 ppm to the *E* isomer rather than the one at δ 6.61 ppm on the basis of intensity measurements. (Compare Seyferth's assignments for 2,4-pentadienyltrimethyltin) [2].)

Preparation of η^5-pentadienyltricarbonylrhenium, I

Bromopentacarbonylrhenium [4] (5.9 g 14.5 mmol) in tetrahydrofuran (150 cm^3) was heated under reflux with 2,4-pentadienyltributyltin (5.2 g, 14.5 mmol) until no further change in the infrared spectrum of the mixture was observed (9 h). The pale yellow solution was evaporated to small bulk and filtered from a white precipitate. The filtrate was taken up in hexane and chromatographed on alumina using petroleum ether (b.p. below 40°C). The first colourless band afforded white crystals (1.23 g) which were purified by sublimation at 60°C and 0.3 mm Hg to give 0.73 g (15%) of the title compound, m.p. 70—72°C.

Anal. Found: C, 28.49; H, 1.90. Calcd. for $C_8H_7O_3Re$: C, 28.48; H, 2.09%. Mass spectrum, *m/e*: 338 (M^+); 310 ($M^+ - CO$); 282 ($M^+ - 2\ CO$); 254 ($M^+ - 3\ CO$).

Raman spectrum (solid): 2018m, 1946m, 1935m, 1915s, 1510w, 1098w, 1008m, 940s, 530m, 525(sh). 500vs, 385s, 345s, 310m, 285m, 120s cm^{-1}.

IR spectrum (in $CHCl_3$) (νCO): 2030vs, 2018(sh), 1945vs, 1922vs cm^{-1}.

Raman spectrum (solid) $[Mn(\eta^5\text{-}C_5H_7)(CO)_3]$: 2018m, 1946s, 1935s, 1918vs, 1915w, 1518w, 1468w, 1458w, 1240w, 1098(br), 1012m, 1003m, 978s, 950s, 918s, 902w, 670s, 658w, 640w, 535s, 528s, 500vs, 497s, 468s, 385vs, 355vs, 318vs, 305vs, 162s cm^{-1}.

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