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METHYLENEAMINO-DERIVATIVES OF SOME TRANSITION METAL CARBONYLS

by

Christopher Midcalf, B.Sc.

A thesis submitted to the University of Durham
for the degree of Doctor of Philosophy

July 1971

MEMORANDUM

The work described in this thesis was carried out in the University of Durham between October 1968 and July 1971. It has not been submitted for any other degree and is the original work of the author except when acknowledged by reference.

Part of the work in this thesis has formed the subject matter of the following publications:

(i) Unsaturated Organonitrogen Groups in Carbonyl Complexes of Molybdenum, Tungsten and Manganese.
Abstracts of the 4th International Conference on Organometallic Chemistry, Bristol, July 1969, S5.

(ii) Organonitrogen Groups in Metal Carbonyl Complexes. Part I. Diphenylmethyleneamino-derivatives of π-Cyclopentadienylmolybdenum and -tungsten Carbonyl Complexes.
K. Farmery, M. Kilner and C. Midcalf, J.Chem.Soc.A, 1970, 2279.

(iii) Conformational Changes about the Molybdenum-Nitrogen Bond in $[Mo-(\pi-C_5H_5)(CO)_2N:CBu^t_2]$: Infrared and ^1H Nuclear Magnetic Resonance Studies.
M. Kilner and C. Midcalf, J. Chem. Soc.D, 1970, 552.

(iv) Organonitrogen Groups in Metal Carbonyl Complexes. Part II. Di-t-butylmethyleneamino-derivatives of π-Cyclopentadienylmolybdenum and -tungsten Carbonyl Complexes.
M. Kilner and C. Midcalf, J. Chem. Soc.A, 1971, 292.

(v) $[Fe_2(CO)_6I(N:CRR')]$ Complexes with Bridging Atoms of Widely Differing Sizes and Bridging Characteristics.
M. Kilner and C. Midcalf, J. Chem. Soc.D, 1971, in press.

ACKNOWLEDGEMENTS

I should like to express my sincere gratitude to Dr. M. Kilner, under whose supervision this research was carried out, for his continual advice and encouragement.

Thanks are also due to my wife for checking the original manuscript, and Miss B.D. Rothery for the preparation of starting materials.

I am indebted to the Science Research Council for a maintenance grant.

C. Midcalf.
Durham 1971

SUMMARY

The methyleneamino-group has the potential to bond to transition metals in low oxidation states in a variety of ways. New methyleneamino-complexes of molybdenum, tungsten, iron and manganese are described, and the bonding mode investigated using a variety of spectroscopic techniques. The effect of the nature of the substitituents attached to the >C:N unit or the metal system, on the bonding mode of the methyleneamino-groups and the course of the reactions is also described.

$\pi\text{-}C_5H_5M(CO)_3Cl$[I] (M = W) reacted with $Ph_2C{:}NLi$ to give the aza-allyl/allene complex $\pi\text{-}C_5H_5W(CO)_2Ph_2CNCPh_2$ [II], together with LiNCO and LiCl. With $Ph_2C{:}NSiMe_3$, [I] gave $\pi\text{-}C_5H_5W(CO)_2N{:}CPh_2$ [III] which liberated carbon monoxide and dimerised on heating to form $[\pi\text{-}C_5H_5W(CO)N{:}CPh_2]_2$ [IV]. No reaction occurred when the above compounds were reacted with Ph_3P but [III] and [IV] reacted with iodine to produce the green $(\pi\text{-}C_5H_5)_3W_3I_3O_4$.

Sterically bulky Bu^t substituents on the methyleneamino-group were used in an attempt to achieve a linear M-N-C skeleton. $\pi\text{-}C_5H_5M(CO)_2N{:}CBu^t{}_2$ [V] (M = Mo,W) were prepared by the reaction of [I] with $Bu^t{}_2C{:}NLi$ or $Bu^t{}_2C{:}NSiMe_3$, and showed no tendency to form dinuclear or aza-allyl/allene type complexes. Variable temperature spectral changes consistent with rotation of the methyleneamino-ligand about the multiple M-N bond were observed for $\pi\text{-}C_5H_5Mo(CO)_2N{:}CBu^t{}_2$. Reaction of [V] with iodine produced monocarbonyl complexes $\pi\text{-}C_5H_5M(CO)I_2N{:}CBu^t{}_2$ which showed two equivalent Bu^t signals in the ^1H n.m.r. spectra believed to arise from a <u>cis</u> geometrical arrangement of the iodine atoms. In hexane solution no reaction occurred between [V] and Ph_3P, but in monoglyme or CCl_4 the solvent was involved as a reactant, $\pi\text{-}C_5H_5Mo(CO)(PPh_3)_2H$ and $[Ph_3PBu^t][\pi\text{-}C_5H_5MoCl_4]$ respectively being isolated.

Iron complexes were prepared to investigate the effect of the transition metal on the $>$C:N system. With π-$C_5H_5Fe(CO)_2Cl$ [VI], R_2C:NLi (R = Ph, Bu^t) produced only a very unstable complex π-$C_5H_5Fe(CO)N$:$CBu^t{}_2$ and, although spectroscopic evidence existed for the diphenyl complex it could not be isolated even at low temperatures. With R_2C:$NSiMe_3$ (R = Ph, Bu^t), [VI] gave no reaction.

$Fe(CO)_4I_2$ [VII] and R'R"C:NLi (R' = R" = Ph, p-tolyl; R' = Ph, R" = Bu^t) produced the symmetrically bridged $[Fe(CO)_3N$:$CR'R"]_2$ [VIII] and complexes containing bridging methyleneamino- and iodine- ligands, $Fe_2(CO)_6(I)N$:CR'R" [IX]. [IX] reacted further with R'R"C:NLi in a 1:1 molar ratio to form [VIII] in quantitative yields. A Mossbauer study of these compounds was undertaken. [VII] with $Bu^t{}_2C$:NLi gave only $Fe(CO)_5$ in good yield.

In an attempt to incorporate manganese as the transition metal in these complexes, o-metallated ring closure reaction products were obtained.

CONTENTS

CHAPTER 2 Metal Carbonyl Compounds containing Bridging Atoms

CHAPTER 1

INTRODUCTION

1. General Considerations

The ability of carbon monoxide to bond to transition metals in low oxidation states relies on the simultaneous σ-donation of the lone pair of electrons from the weakly donating carbon monoxide and the back donation from non-bonding metal d-orbitals to the antibonding π-orbitals of the carbon monoxide molecule. This 'synergic effect' prevents excessive build up of electron density on the metal and results in a metal-carbon bond order greater than one. Replacement of a carbonyl group by another ligand results in competition between the new and remaining ligands for the bonding potentialities of the metal. Thus the stability to disproportionation of the complex will depend upon the relative σ- and π-bonding capabilities of the ligands concerned.

Replacement of carbon monoxide from a binary metal carbonyl by a stronger Lewis base with a lower π-bonding capacity has the effect of increasing the electronic charge build up on the metal and reducing the competition to dissipate the charge. Consequently the metal-carbon bonds are strengthened. Organic amines, R_3N (including ammonia), are strong Lewis bases having no π-bonding capacity, and their introduction into a carbonyl complex strengthens the metal-carbon bonding to the remaining carbonyl groups, through an increase in $d\pi$- $p\pi^*$ bonding. Successive replacement of carbonyl groups by R_3N groups becomes increasingly difficult, and a stage is reached when the remaining groups are unable to dissipate further charge build up e.g.[1]

$$Cr(CO)_6 + liq.NH_3 \xrightarrow{120^o} Cr(CO)_3(NH_3)_3 + 3CO$$

When the organonitrogen ligand (L) has a π^*electron system available for bonding, the charge build up at the metal is somewhat reduced. Consequently further replacement of CO may occur from an $M(CO)_3L_3$ complex.[2]

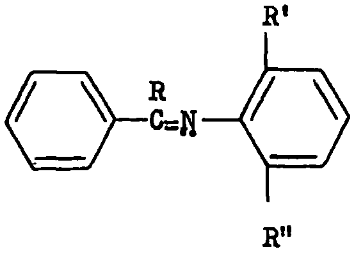
Interest has recently been focused on those complexes which contain a nitrogen atom and which can reduce the electron density on the metal. This has led to the developments in the chemistry of unsaturated organonitrogen ligands in which a 'synergic effect' may also operate.

2. Carbonyl Complexes in Organic Syntheses

The use of transition metal carbonyl and related complexes as homogeneous and heterogeneous catalysts in cyclisation and polymerisation reactions of organic compounds has become widespread.[3] The reactions often occur under mild conditions and polymerisation reactions are usually extremely stereospecific, very slight changes in the metal catalyst causing the formation of different products.

Of particular interest here are the reactions of unsaturated organonitrogen molecules containing carbon-nitrogen and/or nitrogen-nitrogen multiple bonds in the presence of transition metal carbonyl complexes. A review of these reactions has recently appeared.[4] Schiff's bases, azo compounds, oximes, phenylhydrazones, semicarbazones, azines, unsaturated imides, amides and nitriles all react with carbon monoxide in the presence of a metal carbonyl catalyst, usually at fairly high temperature and pressure to yield cyclisation products. Schiff's bases yield only substituted phthalimidines but all other reactions lead to a mixture of products.

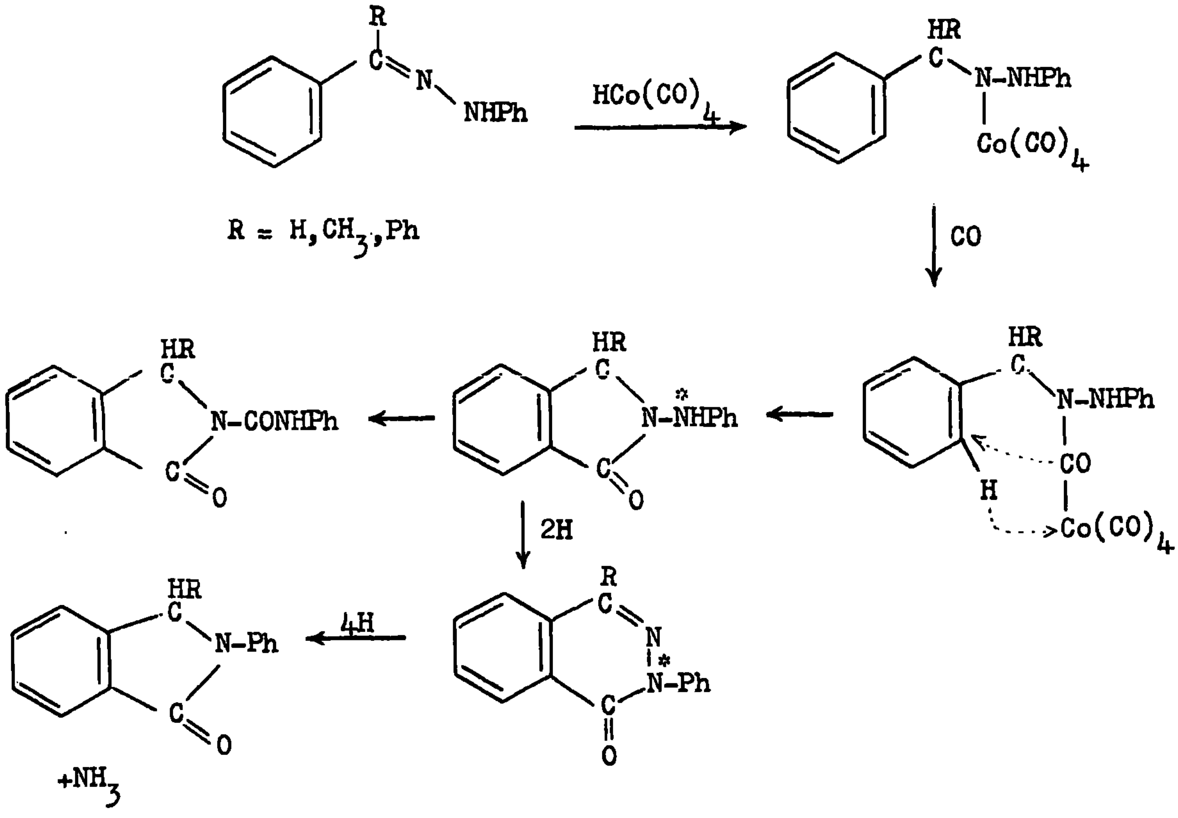
Dicobalt octacarbonyl is by far the most commonly used catalyst in these reactions.[4] Other metal carbonyls have been tried, such as $Fe(CO)_5$, $Ni(CO)_4$ and $Rh_2(CO)_8$ but in general they are less efficient than $Co_2(CO)_8$ or exhibit no catalytic activity at all. Some studies have been undertaken[4] to try to elucidate the mechanism of the catalysed cyclisation of these unsaturated compounds with carbon monoxide. The reaction rates of a series of anils Fig.I.1 in which R, then R' and R" were varied, were observed, and from the observations it was concluded that the metal carbonyl became attached to the



I.1

lone pair of electrons on the nitrogen atom, rather than the π-electrons of the imino group. The ring closure of benzonitrile with carbon monoxide in the presence of hydrogen and deuterium was also studied,[4] and the results support the hypothesis that the true catalyst in ring closure reactions of nitrogen compounds is cobalt hydrocarbonyl and not dicobalt octacarbonyl.

Although Rosenthal and Wender[4] had insufficient experimental evidence to support a rigorous mechanism of ring closure, they suggested the following possible sequence of steps for the cyclisation of aromatic aldehyde and ketone phenylhydrazones (ring closure of these probably parallels that of Schiff's bases and azo compounds):



Recently, a number of complexes of some of these unsaturated nitrogen compounds with iron carbonyls have been isolated,[4,5] and their structures elucidated. These complexes are interesting in themselves, but they may also prove useful in attempts to elucidate the mechanisms of the catalysed cyclisation reactions.

Amines react with cobalt, ruthenium, and manganese carbonyls under forcing conditions to yield formamides and ureas.[4] Low temperature stoichiometric studies have revealed much about the mechanism of these reactions.[2] Hydrazine with carbon monoxide in the presence of iron, cobalt or nickel carbonyls at elevated temperatures and pressures yield semicarbazide and hydrazodicarbonamide. These reactions have also been studied at low temperature.

3. Nitrene Intermediates

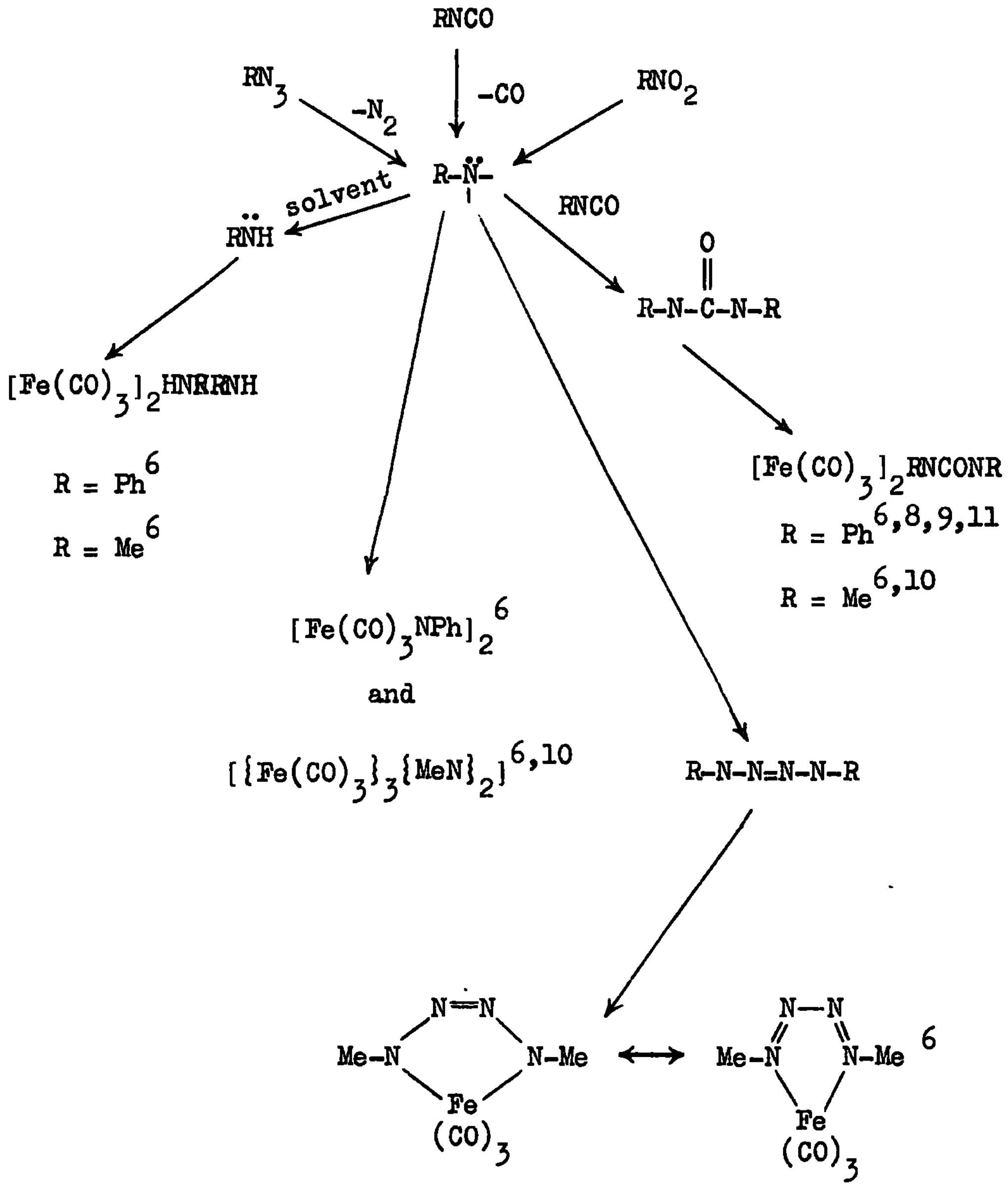
Many reactions of iron carbonyls with azido-,[6,7,8,9] isocyanate[6,10] and nitro[6] compounds are thought to involve the catalytic production of triplet nitrene intermediates. These intermediates may be trapped by the formation of iron carbonyl complexes. The scheme below can account for the formation of some of the products from the various organo-nitrogen molecules shown. (page 5).

4. The methyleneamino-group as a ligand in metal carbonyl systems

There are a number of ways in which the methyleneamino-group may bond to a transition metal and in this respect it is a very versatile ligand.

The neutral ligand, $R_2C{:}NH$, sigma bonds to the metal via the nitrogen lone pair, and as the nitrogen is part of an unsaturated system, back bonding from filled metal d-orbitals to antibonding π-orbitals of the $>C{:}N$ bond is also possible. The most likely geometrical arrangement of the relevant atoms is shown in Fig.I.2(a). (page 9).

As the anionic ligand, $R_2C{:}N^-$, further bonding modes are possible. In one extreme the bonding to the metal will involve an sp^2 hybrid orbital of

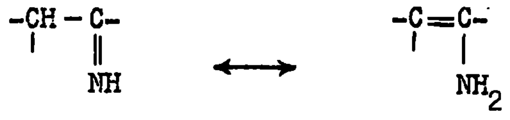

RNCO
-CO
RN3
-N2
RNO2
R-N̈-
solvent
RN̈H
RNCO
R-N-C-N-R
O
[Fe(CO)3]2HNRRNH
R = Ph6
R = Me6
[Fe(CO)3]2RNCONR
R = Ph6,8,9,11
R = Me6,10
[Fe(CO)3NPh]2 6
and
[{Fe(CO)3}3{MeN}2]6,10
R-N-N=N-N-R
N=N
Me-N
N-Me
Fe
(CO)3
N—N
Me-N
N-Me
Fe
(CO)3
6

nitrogen, and the lone pair will occupy a similar hybrid orbital. The lone pair may still contribute to the ligand to metal π-bonding in such an arrangement - Fig.I.2(b). Ebsworth[12] calculated the overlap integrals for nitrogen bonded to silicon and concluded that substantial (p-d) π-bonding from a nitrogen lone pair to vacant silicon d-orbitals is possible in a non-linear system. Similar multiple bonding may occur for non-linear C-N-M skeletons, where M is a transition metal, but there is the added possibility that the lone pair will donate to a second metal atom as shown in Fig.I.3. Thus, in a ligand bridged dinuclear complex, overlap of the d-orbitals of both metal atoms with π^*-orbitals of the $>$C:N bond could occur, resulting in a weakening of the $>$C:N which would be reflected in the vibrational frequency of the bond. In this way the bridging $>$C:N$^{\ominus}$ unit would closely resemble the bridging carbonyl unit with which it is isoelectronic.

Alternatively the C-N-M skeleton may be linear and not bent. The nitrogen atom would be sp hybridised, one hybrid orbital being used to sigma bond to the metal. A pure p-orbital would be used for the $>$C:N π-system, and the lone pair accommodated in a p-orbital lying in the plane of the R_2C:N group. Maximum overlap of the metal d-orbitals with both the lone pair and π^*-orbitals would then be achieved as shown in Fig.I.4. The bonding would then involve electron donation via σ- and pπ-dπ bonding, and back donation via dπ-pπ^* bonding.

Finally there is the added possibility, as with all unsaturated ligands, of lateral co-ordination of the $>$C:N group to form a π-complex analogous to the olefin complexes.

We have tried various synthetic routes to methyleneamino derivatives and in all cases so far, we have avoided the possibility of complications arising from enamine tautomerism by using compounds with no hydrogen atom in the α position to the $>$C:N group



$$-\underset{|}{C}H-\underset{\underset{NH}{\|}}{C}- \longleftrightarrow -\underset{|}{C}=\underset{\underset{NH_2}{|}}{C}-$$

methyleneamine　　enamine

The method of introducing a formal 'anionic' ligand into a metal carbonyl system is generally achieved by use of a metathetical process, and some possible routes are listed below.

1.(a) $M(CO)_nNa + L{-}X \longrightarrow M(CO)_nL + NaX$ (X = halogen etc.)

(b) $M(CO)_nX + L{-}M' \longrightarrow M(CO)_nL + M'X$ (M' = Li,Na)

2. $M(CO)_nX + LM'R_3 \longrightarrow M(CO)_nL + R_3M'X$ (M' = Si,Sn)

3. $M(CO)_nX + LH \xrightarrow{\text{base}} M(CO)_nL$ + salt of HX

4. $M(CO)_nH + LH \longrightarrow M(CO)_nL + H_2$

5. $[M(CO)_n]_2 + L_2 \longrightarrow 2M(CO)_nL$

6. $M(CO)_nR + R'C{:}N \longrightarrow M(CO)_nN{:}CRR'$

Methods 1(b) and 2 have been found to be most satisfactory and are used in the work described later. A common byproduct in both reactions is the dimeric carbonyl. Method 1(a) is not satisfactory and leads largely to the dimeric carbonyl and dimeric ligand (azine) as well as small amounts of $M(CO)_nX$. Method 3 results in formation of complexes with methyleneamine as a neutral ligand without elimination of HX.[13]

$$Mn(CO)_5X + 2Ph_2C{:}NH \longrightarrow Mn(CO)_3(Ph_2C{:}NH)_2X + 2CO$$

Method 4 has not so far been investigated. Method 5 was found to be successful in the preparation of $[Fe(CO)_3N{:}C.(C_6H_4.CH_3)_2]_2$,[14] but with molybdenum and tungsten it led to the recovery of starting materials. Method 6 has been very satisfactory in the preparation of main group methyleneamino derivatives[15] but has not proved successful for the very limited transition metal carbonyl systems studied.

This thesis describes part of a general study of methyleneamino derivatives of molybdenum, tungsten and iron carbonyl compounds. The nature of the bonding between the metal and the methyleneamino-group in the compounds prepared, is of particular interest and in this work we set out to investigate the apparent effect of, (i) the nature of the groups attached to the $>C{:}N$ system and, (ii) the metal system used, on the bonding mode of the methyleneamino ligand. Prior to this work only the molybdenum complexes of the diphenylmethyleneamino-ligand were known[13] (Fig.1.5), and the crystal structure of a doubly bridged methyleneamino-compound $Fe_2(CO)_6((C_7H_7)_2C{:}N)_2$ had been reported.[14]

The synthesis and general features of the chemistry of metal carbonyl compounds containing bridging ligands are relevant to the research in this thesis and are reviewed in the next chapter.

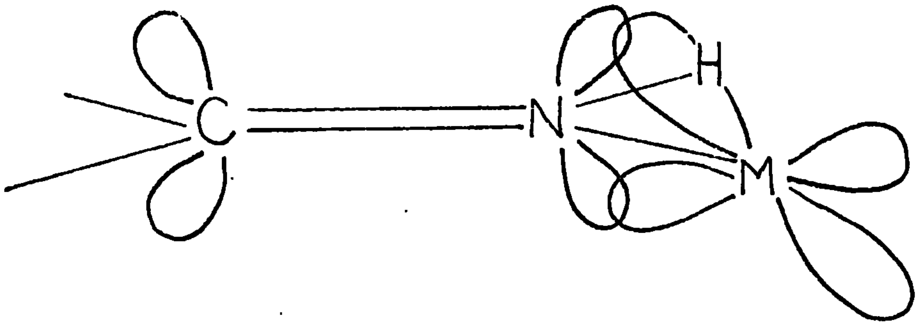


Fig.I.2(a) dπ-π* bonding involving a neutral methyleneamino ligand

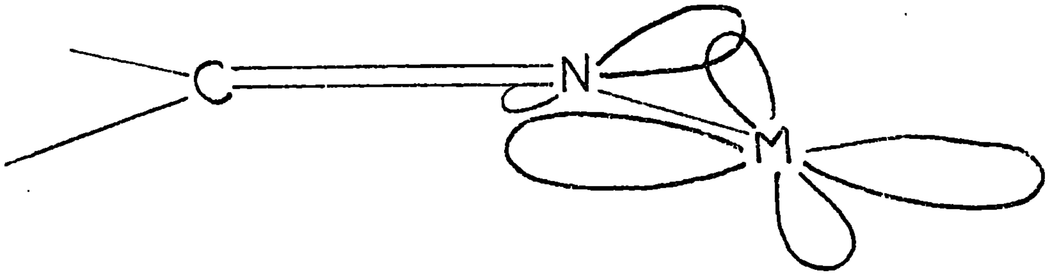


Fig.I.2(b) π-bonding involving a bent C:N-M skeleton

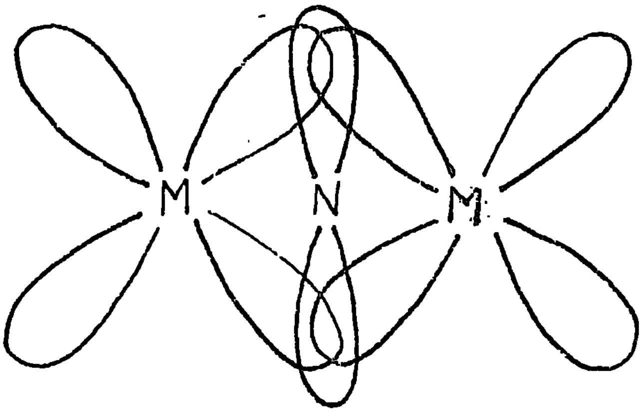


Fig.I.3 π-bonding involving one of the bridging C:N groups

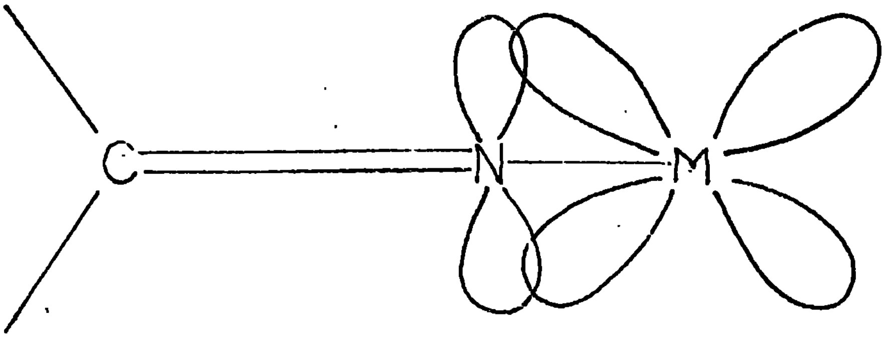


Fig. I.4(a) pπ-dπ bonding involving a linear C:N-M skeleton

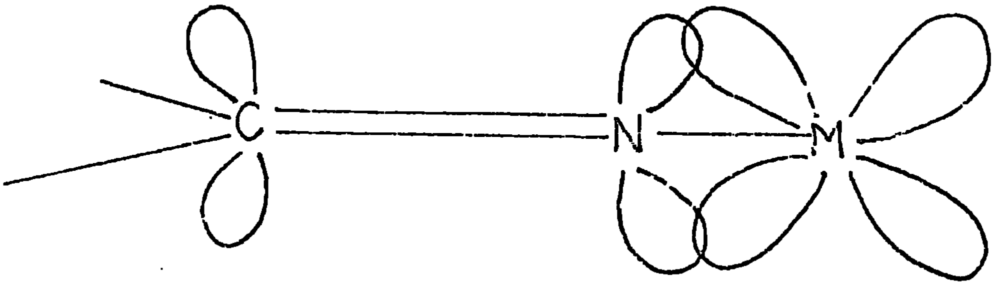


Fig. I.4(b) dπ-π* bonding involving linear C:N-M skeleton

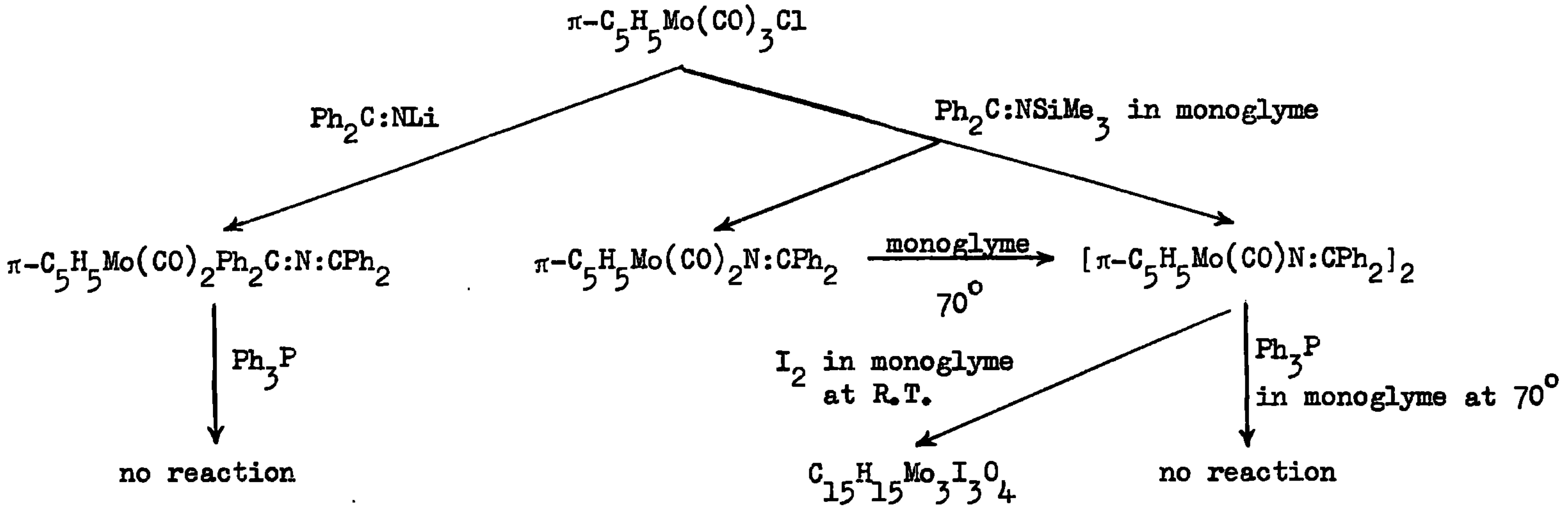


Fig.I.5. Diphenylmethyleneamino Complexes of Molybdenum

CHAPTER II

METAL CARBONYL COMPOUNDS CONTAINING BRIDGING ATOMS

1. Introduction

The chemistry of transition metal carbonyls has been the subject of many thousands of research papers, most of them published during the last decade. This survey is focused upon ligands which bond terminally to, or act as a bridge between, transition metal carbonyl systems. Emphasis has been placed upon ligands containing the following non-metal bridging atoms:

				H
B	C	N	O	F
	Si	P	S	Cl
	Ge	As	Se	Br
		Sb	Te	I

Carbon monoxide is a ligand which has not been included as it is the subject of many of the most recent reviews.[16]

2. Complexes with bridging carbon atoms

Various substituted methinyl tris(tricarbonylcobalt) complexes $[YCCo_3(CO)_9]$[17-23] (Y = H, alkyl, aryl, halogen, COOR, COOH, CH_2CH_2COOH, CH_3, CH:CHCOOH), are known to possess an aliphatic carbon atom triply bridged to three metal atoms. They are prepared by acidification of acetylene complexes $(RC{:}CH)Co_2(CO)_9$ (R = H,[25] n-Pr,[25] CH_3,[17] C_6H_5[17]), or by reaction of trihalogenomethane derivatives $[R'CX_3]$ (R' = CH_3,[18] F,[19] Cl,[19,20] C_6H_5,[19] CO_2CH_3[19,20] or $CO_2C_2H_5$,[20] X = Cl; R' = H[19] or Br,[20] X = Br; R' = H[19] or I,[20] X = I) with $Co_2(CO)_8$ or $[R'CX_3]$ (R' = CH_3, X = Cl) with $Na[Co(CO)_4]$.[26] The reaction of octacarbonyldicobalt with tetrafluoroethylene[22,27] gave complexes $CF_3CCo_3(CO)_9$ and $(CO)_4CoCF_2CF_2Co(CO)_4$. On prolonged heating the latter compound loses carbon monoxide to give $C_2F_4Co_2(CO)_7$. ^{19}F n.m.r. indicates a $CFCF_3$ grouping and a bridged structure similar to that found in $H_2C_4O_2Co_2(CO)_7$.[28] The first stage of the reaction II.1 is reversible and formation of the insertion product is inhibited by a high pressure of carbon monoxide.

$$\begin{tikzcd} CF_2{:}CF_2 + Co_2(CO)_8 \arrow[r, shift left] & (CO)_4Co\cdot CF_2\cdot CF_2\cdot Co(CO)_4 \arrow[l, shift left] \arrow[d] \\ CF_3CCo_3(CO)_9 + FCo(CO)_4 & (CO)_3Co(CF\cdot CF_3)(CO)Co(CO)_3 + CO \arrow[l, "Co_2(CO)_8"'] \end{tikzcd} \qquad (II.1)$$

$CF_3CFCo_2(CO)_7$ can occur in two isomeric forms depending upon the orientation of the CF_3 group. On reaction with $Co_2(CO)_8$, $CF_3CCo_3(CO)_9$ is obtained, which has the carbon triply bridged to three cobalt atoms.[24] A structurally related complex $(CO)_3Co((CF_3)_2C)(CO)Co(CO)_3$, Fig.II.1, is formed by the reaction of octacarbonyldi-cobalt with bis-(trifluoromethyl)diazomethane.[29] Irradiation of $Fe(CO)_5$ or $Co(CO)_3NO$ in the presence of gaseous CF_2Br_2 gave $(CO)_3Fe(CF_2)_2(CO)Fe(CO)_3$[30] Fig.II.2 and $(CO)_3Co(CF_2)_2Co(CO)_3$[30] Fig.II.3 respectively. $(\pi\text{-}C_5H_5)(CO)Fe(CO)(CNC_6H_5)Fe(CO)\pi\text{-}C_5H_5$ Fig.II.4 is formed by the reaction of iodocarbonyl(phenylisocyanide)cyclopentadienyliron[31] and seems to indicate that phenylisocyanide has a greater bridging potential than carbon monoxide. Octacarbonyldi-cobalt with a slight excess of 3,3,3-trifluoropropyne gave a compound which analysed as $Co_2(CO)_6CF_3CCH$ Fig.II.5. Its spectroscopic properties were consistent with a bridging alkyne metal complex.[32,33] Complexes of this type, where the C-C linkage lies above and normal to the Co-Co bond axis, are well known.[34,35]

3. Complexes with bridging silicon atoms

$(C_6H_5)_2SiH_2Re_2(CO)_8$,[36] obtained by irradiation of a benzene solution of $Re_2(CO)_{10}$ and $(C_6H_5)_2SiH_2$ at room temperature, under nitrogen, was shown to have the structure Fig.II.6. A unique pair of hydrogen atoms has been placed in the conspicuously vacant sixth co-ordination site on each rhenium atom. The overall i.r. spectrum resembles $(C_6H_5)_2GeFe_2(CO)_8$.[37] Hydrogen bridges between a main group atom and a transition metal atom have only previously been encountered with boron as in $HMn_3(CO)_{10}(BH_3)_2$,[38] $[(CH_3)_4N][Cr(CO)_4B_3H_8]$,[39]

$[(C_6H_5)_3P]_2CuBH_4$.[40] The Re-Re bond length of 3.121Å in $(C_6H_5)_2SiH_2Re_2(CO)_8$ is slightly longer than the 3.02Å obtained for rhenium carbonyl.[41] Each Si-H functions as a two electron donor to rhenium effectively taking the place of a carbonyl group. The interaction could be described as a three centre two electron bond with the two electrons supplied by the original Si-H bond, or the protonated form of a hypothetical anion Fig.II.7 which is isoelectronic with $Ph_2Ge(Fe(CO)_4)_2$[37] Fig.II.8. In general, silanes give similar products with cobalt carbonyl, to those obtained using germanes e.g. Ph_2SiH_2 and $PhSiH_3$ give $Ph_2SiCo_2(CO)_7$ and $PhSiCo_3(CO)_{11}$ respectively.[42] Attempts to convert $Ph_2SiCo_3(CO)_{11}$ to $Ph_2SiCo_3(CO)_9$ failed and attempts to repeat the preparation of the previously reported $Co_3(CO)_9SiCH{:}CH_2$[43] were unsuccessful.[42]

4. Complexes with bridging germanium atoms

(a) *Group VI metal complexes*. Insertion of $SnCl_2$, GeI_2 and InBr into $[\pi C_5H_5Fe(CO)_2]_2$, $Co_2(CO)_8$[44-47] and $[M_2(CO)_{10}]^{2-}$.[48] (M = Cr,W) give products in which the non-transition metal is bonded to two transition metal atoms, see reaction II.2.

$$Co_2(CO)_8 + GeI_2 \longrightarrow (CO)_4CoGeI_2Co(CO)_4 \qquad \text{II.2}$$

Since this insertion reaction did not occur with $Mn_2(CO)_{10}$ nor $[\pi C_5H_5Mo(CO)_3]_2$[47] it seems likely that the presence of bridging carbonyl groups are essential for the reaction to occur.

(b) *Group VII metal complexes*. $Ph_2Ge(Mn(CO)_5)_2$ and $[Ph_2GeMn(CO)_5]_2$ were obtained by adding Ph_2GeBr_2 to a solution of $Na[Mn(CO)_5]$.[49] Germanium tetrachloride and $Co_2(CO)_8$ at 20°C in tetrahydrofuran (T.H.F.) gave the bridged $GeCl_2(Co(CO)_4)_2$ complex.[50] $((CH_3)_2Ge)_2Co_2(CO)_6$[51] was one of several products isolated from the reaction between $(CH_3)_2GeH_2$ and $Co_2(CO)_8$ in toluene at -78°C. The proton magnetic resonance spectrum showed two non-equivalent methyl signals at low temperature, and a singlet at room temperature. The structure proposed is analogous to $Co_2(CO)_8$ and the methyl groups on a given germanium atom lie in different environments Fig.II.9.

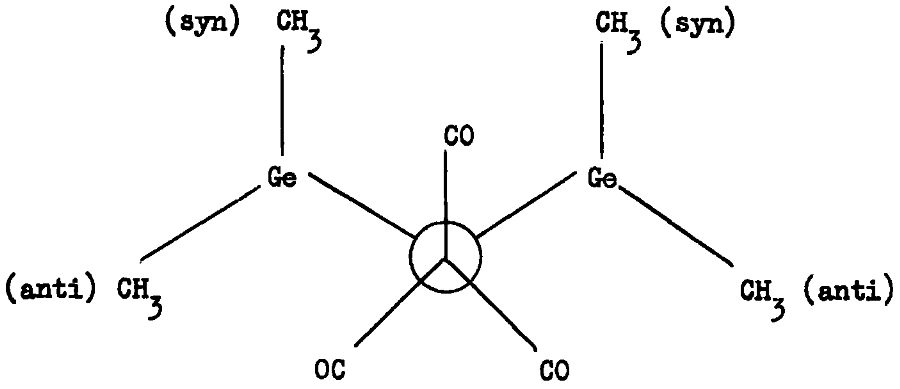


Fig.II.9

A non-bridging carbene type intermediate is proposed to account for the rapid interchange of syn and anti methyl groups at room temperature.[51] The X-ray structure of $PhGeCo_3(CO)_{11}$[42] shows germanium bridging three cobalt atoms Fig.II.10. The molecule can be regarded as a derivative of octacarbonyldicobalt in which a bridging carbonyl group has been replaced by a $PhGeCo(CO)_4$ moiety, whilst $Ph_2GeCo_2(CO)_7$ may be considered to be derived by replacement of one carbonyl with the Ph_2Ge group.[52,53] On heating a solution of $C_6H_5GeCo_3(CO)_{11}$ in hexane to the refluxing temperature it is transformed to $PhGeCo_3(CO)_9$ by loss of carbon monoxide. The formulation resembles that of $PhCCo_3(CO)_9$[19] and a similar structure has been proposed.[24] Treatment of $PhGeCo_3(CO)_{11}$ with carbon monoxide under pressure gave $PhGe(Co(CO)_4)_3$, which was not isolated, but was shown by i.r. spectroscopy to be analogous to $PhSn(Co(CO)_4)_3$.[54] The crystal structure of $Co_4(CO)_{12}Sb_4$[55] revealed a cubane type structure with four $Co(CO)_3$ fragments interconnected by triply bridging antimony atoms.

(c) Group VIII metal complexes. The crystal structures of $(GeMe_2)_3Fe_2(CO)_6$,[37] $(GePh_2)_2Fe_2(CO)_7$,[56] and $Fe_2(CO)_9$[57] show a marked similarity. The two $Fe(CO)_3$ units in each case are bridged by three ligands. The complexes in Table II.1 are in order of decreasing steric requirements of the bridging ligands, and it shows the effect of the bridging ligands on the bond lengths and angles. Vigorous reaction conditions are needed to obtain $[(CO)_4FeGeX_2]_2$ from the reaction of iron pentacarbonyl and the germanium tetrahalides.[58] Me_2GeH_2, in excess, reacts with $Fe_3(CO)_{12}$ at 65°C to give $Me_6Ge_3Fe_2(CO)_6$ and $(Fe(CO)_4)_2GePh_2$.[37]

Table II.1

	Fe-Fe (dist.A°)	Fe-Ge (dist.A°)	Fe-Ge-Fe (angle °)	Fe-bridging-CO (dist.A°)
$(GeMe_2)_3Fe_2(CO)_6$	2.75	2.39	66.8	-
$(GePh_2)_2Fe_2(CO)_7$	2.66	2.42	70.0	2.03
$Fe_2(CO)_9$	2.46			1.80

5. Complexes with bridging nitrogen atoms

The di-μ-amido-hexacarbonyldi-iron[5] originally thought to be di-μ-imido-hexacarbonyldi-iron[59] was prepared by the reaction of tetracarbonylferrate(II) anion with nitrite ion or hydroxylamine. The X-ray crystal structure (Fig. II.11) showed each iron atom co-ordinated to two nitrogen atoms and three carbonyl groups at the corners of a distorted square pyramid. The di-μ-amido complex $[H_2NFe(CO)_3]_2$ is electronically equivalent and structurally similar to $[C_2H_5SFe(CO)_3]_2$,[60] $[C_6H_5CSFe(CO)_3]_2$,[61] and $[CH_3SFe_2(CO)_6]_2S$.[62] The bridging angles subtended at the iron atoms in $[C_2H_5SFe(CO)_3]_2$[60] are not appreciably changed when the two bridging RS ligands are replaced by the two sterically uninhibited NH_2 ligands. Direct evidence for the strength of the Fe-Fe bond is given by its unusually short distance 2.402Å at least 0.1Å smaller than the analogous S and P bridged complexes shown in Table II.2. A structure (Fig. II.12) was proposed for $Fe_2(CO)_6(C_4H_8N_2)$,[63] prepared by the reaction between 2-(methylazo)propane and enneacarbonyldi-iron in benzene at ambient temperatures, in which the inert gas configuration could only be achieved by bridging nitrogen atoms and an Fe-Fe bond. Binuclear complexes of the type $(\pi\text{-}C_5H_5Co)_2(t\text{-}C_4H_9N)_2CO$ are obtained when π-cyclopentadienyldicarbonyl-cobalt is reacted with the sulphur diimide $(t\text{-}C_4H_9N)_2S$.[67] This polynuclear cobalt compound has an extremely short Co-Co distance of 2.367Å [24,68] and its precursor is postulated as the nitrene complex $Co(\pi\text{-}C_5H_5)(CO)(t\text{-}C_4H_9N)$. The phenylisocyanate[8] and dodecacarbonyltri-iron reaction forms a similar complex to which the term ureylene complex was applied.[9] It was found to have structure Fig.II.13 with a carbonyl group bridging the two PhN bridging units, and a different structure from that first postulated by Manuel.[7,69] Derivatives of thionitrosoalkane or benzene are obtained as orange diamagnetic crystalline solids (Eqn.II.3)[70], by reacting $(RN)_2S$ or RNSO with iron carbonyls.

$$Fe(CO)_5 + (t\text{-}C_4H_9N)_2S \xrightarrow[h\nu]{\text{hexane}} Fe_2(CO)_6(t\text{-}C_4H_9NS) \qquad \text{II.3}$$

With $(C_6H_5N)_2S$ and iron pentacarbonyl or enneacarbonyldi-iron the only product isolated from the reaction was azobenzene. However the following reaction (Eqn.II.4) produced an orange diamagnetic complex in very low yield.

$$Fe_2(CO)_9 + C_6H_5NSO \xrightarrow{\text{benzene}} Fe_2(CO)_6(C_6H_5NS) \qquad \text{II.4}$$

Table II.2

Comparison of mean geometrical parameters of $[H_2NFe(CO)_3]_2$ with those of structurally and electronically related Fe-S, Co-P dimeric systems.[a,b]

	$[H_2NFe(CO)_3]_2$	$[C_2H_5SFe(CO)_3]_2$ 60	$[C_6H_5CSFe(CO)_3]_2$ 61	$[CH_3SFe_2(CO)_6]_2S$ 62	$[SFe(CO)_3]_2$ 64	$[(C_6H_5)_2PCoC_5H_5]_2$ 65
M-M	2.40(0.6)	2.54(1)	2.51(0.5)	2.54(0.5)	2.55(0.2)	2.56(1)
M-X	1.98(1)	2.26(0.7)	2.26(0.3)	2.27(0.4)	2.23(0.2)	2.16(0.4)
X-X	2.50(3)	2.93(1)	2.88(0.7)	2.81(0.6) 2.82(0.7)	2.01(0.5)	2.88(2)
$\frac{1}{2}$M-M	1.20	1.27	1.26	1.27	1.28	1.28
((M-X)-Xrad)[c]	1.28	1.22	1.22	1.23	1.19	1.06
M-X-M	74.4(5)	68.3(3)	67.4(1)	68.8(1)	69.9(1)	72.5(5)
X-M-X	77.8(6)	81.0(3)	78.7(1)	77.1(1)	53.5(1)	83.7(5)
d	101.9(8)	95.2(5)	91.8(5)	88.0(3) 88.5(3)	79.8(5)	105.1(4)

Bond distances in Å, Bond Angles in degrees

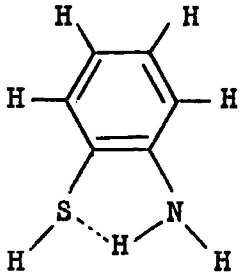
a. M = metal atom, X = bridging atom

b. The values in parentheses are mean values.

c. X rad = Pauling's estimated single covalent radii for atoms.
N, 0.70Å; S, 1.04Å; P, 1.10Å.[66]

d. Dihedral angles between two XMX planes

For the two iron atoms to attain the inert gas configuration the structure proposed (Fig.II.14) on the basis of spectroscopic data implies that lone pairs on the N and S atoms participate in co-ordination. This is the first known example of an alkyl or aryl thionitroso complex. A phenylnitroso complex $[Fe(CO)_3(C_6H_5NO)]_2$ was reported as the product from the reaction of iron pentacarbonyl and nitrobenzene[71] but the stereochemistry of this product is different from that of the thionitroso complex. The reaction (Eqn.II.5) between o-aminobenzenethiol and iron pentacarbonyl[72] formed a complex having both



$$+ Fe(CO)_5 \longrightarrow Fe_2(CO)_6C_6H_4SNH \qquad \text{II.5}$$

bridging RS and RNH groups. On the basis of spectroscopy a structure (Fig.II.15) was proposed analogous to that of the complex (Fig.II.16) obtained from a similar reaction with toluenedithiol.[73] A similar structure to Fig.II.15 was proposed for the trace amounts of material formed from the reaction of 2-aminoethanethiolhydrochloride and dodecacarbonyltri-iron.[72] Azobenzene[74] and azomethane[75] with enneacarbonyldi-iron yield the binuclear complexes $R_2N_2Fe_2(CO)_6$ ($R = C_6H_5, CH_3$). The crystal structure of the azobenzene compound shows the azo link to be ruptured and the complex ligand to be present with an o-semidine skeleton.[76,77] It was proposed[75] that the methyl compound maintains the N-N bond to give a structure (Fig.II.17) analogous to the sulphur bridged dimer $[SFe(CO)_3]_2$.[64] The structure[78] was found to be the first of a series of binuclear complexes bridged by a R-N-N-R unit containing a short N-N distance of 1.366Å and a very acute NFeN bond angle of 42.7°. The iron-iron distance of 2.496Å is the longest reported for a nitrogen bridged Fe-Fe compound. An X-ray structure[79] confirms the proposed structure[6] (Fig.II.18) for $(CH_3N)_2Fe_3(CO)_9$, which is one of several products obtained from the reaction of methylazide, or nitromethane with enneacarbonyldi-iron. The structure is analogous to $S_2Fe_3(CO)_9$,[80] and the molecular structure is closely related to that of $[(C_6H_5)_2CNN]_2Fe_3(CO)_9$.[81] The structures are formally related to binuclear nitrogen bridged iron carbonyls e.g. the structure of the μ_3-methylimido complex (Fig.II.18) may be formally derived from that of the dimethylureylene bridged compound $[(CH_3N)_2CO]Fe_2(CO)_6$[10] by replacement of the bridging carbonyl group by a third $Fe(CO)_3$ moiety and the formation of an additional metal-metal bond. In $(CH_3N)_2Fe_3(CO)_9$ the tetrahedral bridging nitrogen atoms have a fairly short Fe-N distance of 1·928Å compared with 1·95Å for $(C_6H_5CNN)_2Fe_3(CO)_9$, and 1·94Å for the trigonal doubly bridging nitrogen atoms in $[(p\text{-}CH_3C_6H_4)_2CNFe(CO)_3]_2$.[14] Bonds from iron to doubly bridging nitrogen atoms are usually longer (Table II.3). The methylimido groups in $(CH_3N)_2Fe_3(CO)_9$ are analogous to triply bridging chalcogen atoms in $Se_2Fe_3(CO)_9$ and $S_2Fe_3(CO)_9$.[82] The SR and the NR group function effectively as four electron donors. The shortening of the mean Fe-N distance is similar to the mean contraction in Fe-S distance from 2·259Å in $[C_2H_5SFe(CO)_3]$ to 2·229Å in $S_2Fe_3(CO)_9$. $[(CH_3N)_2CO]Fe_2(CO)_6$, the principal product of the reaction of enneacarbonyldi-iron with methylazide,[6] was shown by X-ray crystallography[10] to have a structure consisting of two $Fe(CO)_3$ groups symmetrically linked through the nitrogen atoms of a dimethylureylene group. The structure of the phenyl analogue is considered to be similar (Fig.II.13, R = CH_3).[9,11]

Recently, binuclear metal complexes with substituted ureylene groups have been formed from a variety of nitrogen containing materials including, azides,[6] isocyanates,[7,8,9] nitromethane,[6] and di-t-butylsulphurdiimide,[67] and in at least one case[67] a substituted urea was detected in the reaction mixture. The formation of the bridged dimers from a variety of starting materials, supports the suggestion[6] that all reactions proceed through nitrene type intermediates. Further it is likely that one or more of the compounds $[RNFe(CO)_3]_2$, $[RNHFe(CO)_3]_2$ or $R_2N_4Fe(CO)_3$, all isolated from the same reaction in which the ureylene bridged dimer is formed,[6] may be its precursors under appropriate conditions. The remarkable cationic bridged azido species Fig.II.19, formed from the reaction of iron pentacarbonyl and chloro- or bromo-azides, has the highest reported paramagnetism (μ = 5·29 B.M.) for a metal carbonyl compound.[83] The structure of benzo[c]cinnolinebis(tricarbonyliron) (Fig.II.20) proposed by Bennett[84] and confirmed by X-ray analysis[85] was prepared from the reaction of benzo[c]cinnoline with iron pentacarbonyl, and also obtained as a minor product from the reaction of 2,2'-diazidobiphenyl with enneacarbonyldi-iron.[86] In Table II.3 the bond lengths and angles of compounds containing the $Fe(CO)_3$ group doubly bridged by tetravalent nitrogen atoms are compared. It can be seen that the iron-iron distances in these compounds fall into two groups depending on the presence or absence of the N-N bond. In $C_{12}H_8N_2Fe_2(CO)_6$ and $[CH_3NFe(CO)_3]_2$, each containing a N-N bond, the Fe-Fe distances are longer by ~0·1Å and the Fe-N distances are shorter by comparable amounts than would be expected for corresponding values for the other compounds. It appears likely that the differences are stereochemical consequences of the presence of a N-N bond, and in general a correlation exists[61,78] in both the N and S bridged systems in which a lengthening of the M-M bond is associated with a shortening in the metal bridging atom distance. A structural parameter of some interest is the dihedral angle between the two Fe-N-N planes (Table II.3). The value for a given Fe-Fe and Fe-N distance depends on the N-N distance, asymptotically approaching a lower limit equal to the Fe-N-Fe angle as the N-N distance becomes small. The X-ray crystal structure of the orange complex $C_{36}H_{28}N_2O_6Fe_2$,[14] formed by the reaction of 4,4'-dimethylbenzophenoneazine with iron pentacarbonyl, shows two $Fe(CO)_3$ units bridged by two 4,4'-dimethylbenzophenoniminato groups (Fig.II.21). The average Fe-N distance (Table II.3) of 1·94Å is shorter than in any previously reported structure not containing a N-N bond. The nitrogen is considered to be sp^2 hybridised in the present structure whereas in the other compounds with Fe-N distances of 1·97-2·00Å the hybridisation would be sp^3. In all cases the nitrogen can be regarded as a three electron donor to the metal. The reaction of $Fe_2(CO)_9$ with 3,5,7-triphenyl-4H-1,2-diazepine[87] leads to cleavage of a N-N bond and formation of a nitrogen bridged dimer which has been shown by X-ray crystallography to be a bicyclo[5,1,1]-derivative (Fig.II.22). The two $Fe(CO)_3$ units have been inserted into a seven membered heterocyclic ring, and it is the first example of an eight membered unsaturated metallocyclic ring system. This compound is unusual in that a Mossbauer spectrum indicates nonequivalent iron atoms and ^1H n.m.r. spectrum shows a peak due to an isolated CH_2 group. On symmetry grounds there is no apparent explanation for these results. The molecular parameters in Table II.3 show a difference in Fe-N bond distance, and this is explained as a steric effect resulting from the location of the two phenyl groups on the same side of the molecule.

6. Complexes with bridging phosphorus atoms

(a) Vanadium. Vanadiumhexacarbonyl reacts with PH_3, $C_6H_5PH_2$, and $(C_6H_5)_2PH$[88] to give compounds of the type $V(CO)_4L_2$ which were isolated only for $L = C_6H_5PH_2$ and $(C_6H_5)_2PH$. In the presence of a solvent the reaction proceeds rapidly with loss of hydrogen and a phosphine ligand to form $[V(R_2P)(CO)_4]_2$ ($R = H$ and C_6H_5), which can not be prepared photochemically.[89] Tetraphenylbiphosphine and biarsine react with vanadium carbonyl and the carbonyl nitrosyl[90] according to equation II.6 and II.7

$$V(CO)_6 + Ph_4E_2 \longrightarrow [(CO)_4V(EPh_2)]_2 \quad (E = P \text{ or } As) \qquad II.6$$

$$V(CO)_5NO + Ph_4P_2 \longrightarrow [(CO)_3(NO)VPPh_2]_2 \qquad II.7$$

Table II.3

Comparison of molecular parameters of binuclear nitrogen bridged iron carbonyls

Compound	Fe-Fe	Fe-N	N-N	Fe-N-Fe	N-Fe-N	b	Ref.
$(HNC_6H_4NC_6H_5)Fe_2(CO)_6$	2·372(2)	2·00(1)	2·38	72·5(4)	72·9(4)	95·4	29
$[(CH_3C_6H_4)_2CNNH]_2Fe_2(CO)_6$	2·40	2·00	c	c	c	c	38
$[(C_6H_5N)_2CO]Fe_2(CO)_6$	2·409	2·00(1)	2·15	74·5(3)	65·0(3)	92·4	37,19
$[H_2NFe(CO)_3]_2$	2·402(6)	1·98(2)	2·50(3)	74·4(7)	77·8(8)	101·9(8)	2
$[(CH_3N)_2CO]Fe_2(CO)_6$	2·391(7)	1·97(1)	2·10(2)	75·0(7)	64·8(7)	92·2(8)	35
$[(CH_3N)Fe(CO)_3]_2$	2·496(3)	1·878(4)	1·366(8)	83·4(2)	42·7(2)	91·1(2)	30
$[(C_{12}H_8N_2)Fe_2(CO)_6]$	2·508(4)	1·914(6)	1·399(8)	81·9(2)	42·9(2)	89·5(2)	42
$[(C_7H_7CN)_2Fe_2(CO)_6]$	2·403	1·94	c	c	c	c	43
$[PhC(CH_2PhCN)_2Fe_2(CO)_6]$	2·393	1·920 1·965	2·248	c	c	98·1	44

The bond lengths are in Å and the angles in degrees.[a]

a) Where more than one value reported for a distance or angle an average value is tabulated

b) Dihedral angle between two Fe-N-N planes

c) Not available

d) The values in parenthesis are mean values.

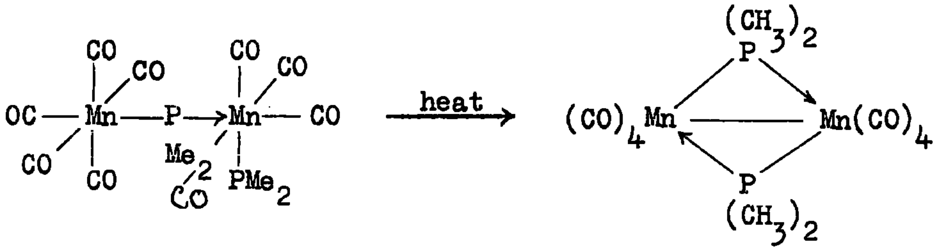
(b) Group VI metal complexes. From the reactions of E_2R_4 (E = P,As; R = Me,Ph)[91,92] with the group VI hexacarbonyls two types of binuclear complexes were identified. In general the biphosphine and biarsine ligands react in hydrocarbon solvents to give binuclear complexes of the uncleaved ligand (Fig.II.23)[92,93,94] which undergo further reaction[91,92] with the formation of the doubly bridged complex (Fig.II.24). Two compounds are produced from the reaction between equal molar quantities of $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ and $P_2(CH_3)_4$. One was identified as $[\pi\text{-}C_5H_5Mo(CO)_2P(CH_3)_2]_2$ and the other was found to be a singly bridged phosphine hydride species identical to the product from the reaction of $Na[C_5H_5Mo(CO)_3]_2$ and $(CH_3)_2PCl$.[95] The source of hydridic hydrogen in these products is unknown. $(C_6H_5)_4P_2$ with $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ in boiling toluene gave a dark green polynuclear compound $[\pi C_5H_5Mo(P(C_6H_5)_2)_2(CO)]_3$ of unknown structure.[95] Two structures (Fig.II.25 and II.26) were proposed on the basis of a single absorption in the infrared spectrum at 1852 cm^{-1}. Tetrakis(trifluoromethyl)diarsine reacts with $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ to give the mononuclear $\pi\text{-}C_5H_5MoAs(CF_3)_2(CO)_3$ complex, and on irradiation this dimerises with loss of carbon monoxide to give $[\pi\text{-}C_5H_5MoAs(CF_3)_2(CO)_2]_2$.[96] Under similar conditions tetramethyldiarsine reacts to give the arsenic bridged complex $[\pi\text{-}C_5H_5MoAs(CH_3)_2(CO)_2]_2$.[95,97] The stability of the mononuclear $\pi\text{-}C_5H_5MoAs(CF_3)_2(CO)_3$ species is probably due to the weakening of the electron donating power of the arsenic atom by the strongly electronegative trifluoromethyl groups. The mononuclear species are analogous to the halogeno- and organo-derivatives $\pi\text{-}C_5H_5Mo(CO)_3X$ (X = halogen, alkyl, aryl).[98] Investigations involving the reaction of bispentafluorophenylphosphorus and arsenic chloride with the metal anion $[\pi\text{-}C_5H_5Mo(CO)_3]^-$ produced air stable monomers $(C_6F_5)_2EMo(CO)_3\pi\text{-}C_5H_5$,[99] and attempts to form the dinuclear complexes in refluxing toluene, failed. However on irradiation high yields of polymeric complexes of empirical formula, $[(C_6F_5)_2EMo(CO)_2\pi\text{-}C_5H_5]_n$ were obtained.[99] A benzene solution of di-μ-dimethylphosphidobis(tetracarbonylmolybdenum) reacts further with mono and bidentate phosphines to form substituted derivatives.[100] In the case of PR_3 (R = Et,Ph) further replacement of carbonyl groups occur (Eqn.II.8). For R = C_2H_5 the crystal structure[101] shows that the phosphines

$$(CO)_4Mo(P(CH_3)_2)_2Mo(CO)_4 + PR_3 \longrightarrow R_3P(CO)_3Mo(P(CH_3)_2)_2Mo(CO)_3PR_3 \qquad II.8$$

$$R = C_6H_5,\ C_2H_5$$

have replaced carbonyl groups trans to the M-M bond, indicating that one carbonyl group on each metal atom must be unique.

(c) Group VII metal complexes. $[Mn(P(C_6H_5)_2)(CO)_4]_2$ and $[MnAs(CH_3)_2(CO)_4]_2$ were obtained from manganese carbonyl and the corresponding biphosphine or biarsine or from $NaMn(CO)_5$ and the monochloroarsine.[102] $[MnAs(C_6H_5)_2(CO)_4]_2$ was obtained from $Mn_2(CO)_{10}$ and triphenylarsine in xylene.[103] The phosphine analogue could not be prepared by this method. Dimethylchlorophosphine reacts with $NaMn(CO)_5$ at room temperature to give $Mn_2(P(CH_3)_2)_2(CO)_9$ which loses a further mole of carbon monoxide on heating to give $[MnP(CH_3)_2(CO)_4]_2$[104] e.g.



Reactions of diphenylchlorophosphine and $NaMn(CO)_5$,[105] or $Mn_2(CO)_{10}$[102] and $P_2(C_6H_5)_4$ in boiling toluene produce the hydride $(CO)_4Mn(H)P(C_6H_5)_2Mn(CO)_4$ in low yield, as well as the expected diphosphine bridged compound $[MnP(C_6H_5)_2(CO)_4]_2$ in 40-46% yields. It was originally suggested[106] that $Mn_2IP(CF_3)_2(CO)_8$ formed by the reaction Eqn.II.9 had a structure with a terminal iodine and a Mn-Mn bond.

$$Mn_2(CO)_{10} + 2(CF_3)_2PI \longrightarrow Mn_2I(P(CF_3)_2)(CO)_8 \qquad II.9$$

Sodium borohydride reduction of the iodine complex, formed a compound $Mn_2H(P(CF_3)_2)(CO)_8$ closely related to $Mn_2(H)(PPh_2)(CO)_8$. It seems most likely that $Mn_2I(P(CF_3)_2)(CO)_8$ also has a structure containing phosphorus and iodine as bridging atoms and is analogous to $[Mn(PR_2)(CO)_4]_2$.[104] $(CF_3)_2EX$ (E = P, X = Cl,Br,I,SCF_3,$SeCF_3$; E = As, X = I) undergo cleavage reactions with $Mn_2(CO)_{10}$[106,107,108] under autoclave conditions to give compounds of the type $(CO)_4MnE(CF_3)_2(X)Mn(CO)_4$. PF_3I and $Mn_2(CO)_{10}$ under similar conditions gave a diamagnetic compound separated by fractional sublimation and found to have the structure[109] shown in Fig.II.27. In benzene Ph_4P_2 and $Mn(CO)_5X$ (X = Cl,Br,I) at 35-40° gave $X(CO)_4Mn(Ph_2PPh_2)$ but the reactants in a 2:1 molar ratio at 80° for several hours gave $X(CO)_3Mn(Ph_2PPh_2)Mn(CO)_3X$.[90] Under milder conditions trimethylsilyldiphenylphosphine, $(CH_3)_3SiP(C_6H_5)_2$, and pentacarbonyl halides of manganese and rhenium gave the expected bridged dimers $[M(CO)_4P(C_6H_5)_2]_2$ (Equation II.10).

$$2M(CO)_5Br + 2Me_3SiP(C_6H_5)_2 \longrightarrow [M(CO)_4P(C_6H_5)_2]_2 + 2(CH_3)_3SiBr + CO$$

$$M = Mn, Re \qquad II.10$$

Under more vigorous conditions for prolonged periods a tricarbonyl species $[M(CO)_3P(C_6H_5)_2]_3$ was isolated and structure (Fig.II.28) proposed.[110] Whilst this structure is consistent with the evidence obtained, there is a striking similarity in infrared absorptions in the carbonyl region to the sulphur bridged tetramers.[111] π-Cyclopentadienyltricarbonyl-manganese was found to be remarkably inert to thermal replacement of carbonyl groups by neutral ligands,[93] although substitution readily occurs on irradiating with ultraviolet light.[112] Its reactions with biphosphines and biarsines follow this general behaviour and on irradiating, stable mono-substituted complexes are obtained (Fig.II.29).

Attempts to convert them into bridged complexes by further irradiation were unsuccessful.[93]

(d) Group VIII metal complexes. Two types of compound are again isolated from these reactions, depending on reaction conditions, phosphido- or arsenido-bridged complexes forming under more severe conditions and diphosphine and diarsine bridged complexes under milder conditions. $[Fe(CO)_3P(CH_3)_2]_2$ may be prepared in 84% yield at 180° in a sealed tube,[92] or in boiling cyclohexane[91] or xylene.[92] In reactions involving the diarsines the As-As bond cleaves more readily than does the P-P bond in the corresponding diphosphine and thus reaction times tend to be shorter, and yields higher for the arsenic bridged complexes.[91,92,97] Various methods of preparation (Eqn.II.11, II.12, II.13, and II.14) are shown.

$$Fe_3(CO)_{12} + P_2(CH_3)_4 \longrightarrow Fe_2(CO)_8P_2(CH_3)_4 \qquad \text{II.11}$$

$$As_2(CH_3)_4 \not\longrightarrow \qquad \text{II.12}$$

$$Fe(CO)_5 + E_2R_4 \longrightarrow [Fe(ER_2)(CO)_3]_2 \qquad \text{II.13}$$

$E = P; R = CH_3, C_2H_5, C_6H_5$
$E = As; R = CH_3$

$$[\pi\text{-}C_5H_5Fe(CO)_2]_2 + E_2R_4 \longrightarrow [\pi\text{-}C_5H_5Fe(ER_2)(CO)_2]_2 \qquad \text{II.14}$$

$E = P; R = CH_3, C_6H_5$
$E = As; R = CH_3$

From reaction II.14 in boiling toluene (when $E = P$; $R = C_6H_5$ or CH_3) a hydride complex $(\pi\text{-}C_5H_5)_2Fe_2(H)(PR_2)(CO)_2$ was isolated,[97] for which a structure analogous to the Mn and Mo compounds was proposed.[113] Diphosphines and diarsines are reported to react with $\pi\text{-}C_5H_5Fe(CO)_2Br$ in boiling toluene, to form a singly bridged ionic species (Fig.II.30) which was isolated from aqueous solution as the crystalline perchlorate or tetraphenylborate salt.[114] The compounds $[FeE(CH_3)_2(CO)_3]_2$ can absorb one molecule of bromine or iodine to give the crystalline compounds $[FeX(E(CH_3)_2)(CO)_3]_2$ (E = P,As; X = Br,I)[91] in which the M-M bond is cleaved by the halogen. The reaction of iron pentacarbonyl with $(CF_3)_2PI$,[106,115] or $(CF_3)_2AsI$,[115] produce analogous compounds $[FeI(P(CF_3)_2)(CO)_3]_2$ and $[FeI(As(CF_3)_2)(CO)_3]_2$, whereas $(CF_3)_2PCl$ gave only the unsubstituted dimer $[Fe(P(CF_3)_2)(CO)_3]_2$.[115] Halogens X_2 (X = Cl,Br,I) in carbon tetrachloride react with $[Fe(CO)_3P(CF_3)_2]_2$ to cleave the Fe-Fe bond and give near quantitative yields of $[Fe(CO)_3(PR_2)X]_2$ shown to exist as a mixture of isomers.[116] U.v. irradiation of $\pi\text{-}C_5H_5Fe(CO)_2I$ in benzene in the presence of $Me_2PCH_2CH_2PMe_2$ gave green $[\pi\text{-}C_5H_5Fe(CO)I]Me_2PCH_2CH_2PMe_2[\pi\text{-}C_5H_5Fe(CO)I]$; the chloride and bromide gave the mono-substituted derivatives.[117] An alternative route to the bridged complexes when the chlorophosphines or arsines are readily available[97] is shown in Eqn.II.15.

$$2Na[\pi\text{-}C_5H_5Fe(CO)_2] + 2(CH_3)_2AsCl \longrightarrow [\pi\text{-}C_5H_5Fe[As(CH_3)_2](CO)]_2 + 2NaCl + 2CO \qquad \text{II.15}$$

Treatment of $(C_6F_5)_2ECl$ (E = P or As) with the anion $[\pi\text{-}C_5H_5Fe(CO)_2]^-$ affords the mononuclear complexes $[(C_6F_5)_2EFe(CO)_2\pi\text{-}C_5H_5]$. The arsenic complex can also be prepared by the reaction of $[(C_6F_5)_2As]_2$ with $[\pi\text{-}C_5H_5Fe(CO)_2]_2$. Attempts to react $(C_6F_5)_2PLi$ with $\pi\text{-}C_5H_5Fe(CO)_2Cl$ failed.[99] U.v. irradiation of the mononuclear arsenic complexes gave polymers $[(C_6F_5)_2AsFe(CO)\pi\text{-}C_5H_5]_n$ of unknown molecular weight. Reaction of $(C_6F_5)_4E_2$ or $(C_6F_5)_2PH$ with $Fe_3(CO)_{12}$ gave the bridged binuclear complexes $[(C_6F_5)_2EFe(CO)_3]_2$ (E = P,As), whereas dodecacarbonyltri-ruthenium reacts with $(C_6F_5)_4E_2$ to give $[(C_6F_5)_2ERu(CO)_3]_2$ (E = P,As). $(CO)_4FePPh_2PPh_2Fe(CO)_4$ was prepared thermally and by u.v. irradiation of iron pentacarbonyl and tetraphenyldiphosphine.[118] Irradiation of $[Fe(CO)_3PMe_2]_2$ in the presence of phosphines (PPh_3, PEt_3, $Ph_2P(CH_2)_2PPh_2$) causes the replacement of one carbonyl group per metal atom.[100,119] The only reported bridged ruthenium carbonyl compound

$Ru_2(CO)_6(P(CH_3)_2)_2$ was prepared by reacting $Ru_3(CO)_{12}$ with Me_4P_2 in benzene at 80-90°.[120] The mixed phosphorus and sulphur bridged complex obtained by the reaction shown in (Eqn.II.16) was found to be a useful polymerisation catalyst in the preparation of urethanes.[121,122]

$$Fe(CO)_5 + PhSPPh_2 \longrightarrow Fe(CO)_3(Ph_2P)(PhS)Fe(CO)_3 \qquad II.16$$

The reaction scheme shown in (Eqn.II.17) was used to synthesise mixed metal carbonyls with phosphido bridges and metal-metal bonds.[123]

$$(CO)_4FePPh_2H + \pi\text{-}C_3H_5M(CO)_n \longrightarrow (CO)_4Fe(PPh_2)M(CO)_n \qquad II.17$$
$$(M = Co,\ n = 3;\ M = Mn,\ n = 4)$$

The closest analogies to these compounds are those which contain a single phosphorus group bridging two homonuclear metal atoms and containing a hydrido bridge.[95,97,102,105,113,124]

$Co_2(CO)_8$ reacts with $P_2(CH_3)_4$ in boiling benzene to give the polynuclear complex $Co_3(P(CH_3)_2)_2(CO)_7$ and with $P_2(C_6H_5)_4$ in cold toluene to give $(Co(PPh_2)_2(CO)_3)_n$.[102] The latter complex can be prepared from diphenylchlorophosphine with either $Na[Co(CO)_4]$ or $Na[Co(CO)_3P(OC_6H_5)_3]$, and although the product is soluble in most organic solvents it is apparently polymeric.[102,125] No definite compound has been isolated from the reaction of cobalt carbonyl and $As_2(CH_3)_4$.[93,102] π-Cyclopentadienyldicarbonyl-cobalt and R_4P_2 ($R = CH_3$,Ph) after eighteen hours under forcing conditions gave a black crystalline compound[93] (Fig.II.31). When $Co(NO)(CO)_3$ is reacted with Ph_4P_2, a red diphosphine complex is formed first, which after several days heating in p-xylene gave the dark brown complex $[Co(CO)(NO)(Ph_2P)]_2$.[90] In general, metal carbonyls $M(CO)_n$ (M = Cr,Mo,W,Fe) react with tetramethyl diphosphine[91,92,126] to give two series of products (Fig.II.23 and II.24). With tetraphenyldiphosphine however a compound $[(CO)_3MP(Ph_2)P(Ph_2)M(CO)_3]$, of type (Fig.II.23) has been isolated only when M = Ni.[127] A similar product

$[(CO)_3Ni(CF_3)_2P(CF_3)_2PNi(CO)_3]$ was also obtained from the reaction between $P_2(CF_3)_4$ and nickel tetracarbonyl at room temperature.

7. Complexes containing bridging oxygen atoms

Treatment of the hexacarbonyls of chromium, molybdenum and tungsten with aqueous or alcoholic hydroxide ion at elevated temperatures led to a variety of anionic derivatives[128] with hydroxide, water and even alcohol substituents. The product obtained from chromium hexacarbonyl and an ethanolic base was found to be the anion $[(CO)_3Cr(OH)_3Cr(CO)_3H]^{2-}$ formed in accordance with the following equation II.18.[129]

$$2Cr(CO)_6 + 10(OH)^- + H_2O \longrightarrow [(CO)_3Cr(OH)_3Cr(CO)_3H]^{2-} + 2H_2 + 2CO_3^{2-} + 4HCO_2^- \qquad \text{II.18}$$

One possible structure, Fig.II.32, contains two bridging hydroxide ions and one bridging water molecule. The analogous reaction when performed with molybdenum hexacarbonyl, (Eqn.II.19) gave $[(CO)_3Mo(OH)_3Mo(CO)_3]^{3-}$.[129]

$$2Mo(CO)_6 + 9(OH)^- \longrightarrow [(CO)_3Mo(OH)_3Mo(CO)_3]^{3-} + 6HCO_2^- \qquad \text{II.19}$$

Acidification of this anion with hydrochloric acid yields the free acid, $Mo_2(CO)_6(OH)_3H_3$ as bright yellow crystals. On treatment with Ph_3P, Ph_3As and dimethylsulphoxide, $Mo_2(CO)_6(OH)_3H_3$ reacts to form compounds of the type $L_3Mo(CO)_3$[129] at room temperature. Possible structures suggested for $[Mo_2(CO)_6(OH)_3]^{3-}$ and $Mo_2(CO)_6(OH)_3H_3$ are shown in Fig.II.33 and Fig.II.34. The reaction between the hydroxide ion and tungsten hexacarbonyl is even more complex. At 80-100°, in methanol solution, the anions $[W_2(CO)_6(OH)_2(CH_3OH)_2]^{2-}$ and $[W_2(CO)_6(OH)_2(CH_3OH)_2]^{4-}$ are formed, whereas at 130° the trinuclear anion $[W_3(CO)_9(OH)(OCH_3)(CH_3OH)]^{3-}$ is formed.[130] Treatment of $[W_2(CO)_6(OH)_2CH_3OH]^{4-}$ with HCl yields both the following derivatives, $W_3(CO)_9(OH)_2(H_2O)H_4$ and $W_2(CO)_6(OH)_3H_3$.[131] In 1956 Hieber and Schuster[132] reported that $Re_2(CO)_{10}$ and

$Re(CO)_5Cl$ react with 2N KOH in methanol solution after 6/8 hr. at 100° in accordance with equations II.20 and 21. The complex (Fig.II.35) is formulated as containing O and OH bridges.

$$Re_2(CO)_{10} + 3KOH + H_2O \longrightarrow Re_2(CO)_8O_2HK + K_2CO_3 + 2H_2 + CO \qquad II.20$$

$$2Re(CO)_5Cl + 3KOH \longrightarrow Re_2(CO)_8O_2HK + 2KCl + 2CO + H_2O \qquad II.21$$

The structure of $[Mo(OH)(CO)_2(NO)]_4 4(OPPh_3)$ has recently been described, and formulated as a four-fold triphenylphosphine adduct of tetrakis-[μ_3-hydroxodicarbonylnitrosylmolybdenum(o)].[133] The parent diamagnetic compound having CO in place of NO (i.e.) $[HMo(OH)(CO)_3]_4.4(OPPh_3)$, has also been obtained.[133a] The crystal structure of the salts $K_3[M_2(OH)_3(CO)_6]$ (M = Mo,W), which are the alkaline hydrolysis products of $M(CO)_6$,[129,130] showed the two metals to be symmetrically bridged by hydroxo bridges and the six carbonyl groups to be terminally bound to the metal. The reaction of OsO_4 in methanol under a carbon monoxide atmosphere at various pressures and temperatures gives essentially $Os_3(CO)_{12}$. However, small amounts, $Os_3(CO)_{10}XY$ (X = H, Y = H, OH, OMe; X = Y = OMe) were isolated from the reaction mixture by chromatography.[134] The structure of these compounds (X = Y = H, OMe) has been established[135] and they contain a cyclic structure similar to the parent carbonyl $Os_3(CO)_{12}$[136] with the X and Y groups bridging two osmium atoms.

8. Complexes containing bridging sulphur atoms

(i) Derivatives of sulphides

Cyclopentadienylironcarbonylsulphide $[\pi-C_5H_5Fe(CO)_2]_2S_3$ has been isolated[137] along with other products, e.g. $[\pi-C_5H_5FeS]_4$,[138] from the reaction of cyclohexene sulphide with $[\pi-C_5H_5Fe(CO)_2]_2$. The two ternary sulphides $[Fe(CO)_3]_3S_2$ and $[Fe(CO)_3]_2S_2$ are well characterised and can be prepared by various methods (Table II.4). A structure similar to that of $Co_2(CO)_8$ was proposed[142] and confirmed by X-ray diffraction for $[Fe(CO)_3]_2S_2$.[64] The air

Table II.4

Reactants		Conditions	Products	Ref.
Iron Compound	Sulphur Compd.			
Iron powder	H_2S, Sulphur	under CO pressure	$Fe(CO)_5$ + $[Fe(CO)_3]_3S_2$	139,140
$Fe_2(CO)_9$	SO_2		$[Fe(CO)_3]_3S_2$	141
Aqueous alkaline carbonyl ferrate solution	sulphite ions	acidification	$[Fe(CO)_3]_3S_2$	140
Tetracarbonyl ferrate soln.	polysulphides	oxidation reaction	sulphur + $[Fe(CO)_3]_3S_2$ + $[Fe(CO)_3]_2S_2$	140
Tetracarbonyl ferrate	sulphoxylic acid		$[Fe(CO)_3]_2S_2$	59

sensitive triiron compound is isomorphous[143] with the selenium analogue $[Fe(CO)_3]_3Se_2$. A low yield of $CH_2S_2Fe_3(CO)_{10}$ was reported[144] from the reaction of dodecacarbonyltri-iron with 2-mercaptobenzothiazole or parathioformaldehyde, but this was later shown to be $[Fe(CO)_3]_3S_2$.[145] Episulphides with $Fe_3(CO)_{12}$ gave a product claimed to be a new isomer of this sulphide,[146] but X-ray analysis showed it to be a mixture of di- and tri-iron compounds in an ordered array in the crystal.[80] Repetition of this experiment with cyclohexene sulphide gave mainly the triiron compound with $[Fe(CO)_3]_2S_2$ in trace amounts. A tetrairon carbonyl sulphide, $[Fe(CO)_3]_4S_2$ and a sulphide-mercaptide, $[Fe(CO)_3]_3S(SC_6H_5)_2$ were said to be the products in the reaction of $Fe_3(CO)_{12}$

with benzyl thiocyanate.[147,148] Iron tricarbonyl sulphide, $[Fe(CO)_3]_2S_2$, reacts with triphenylphosphine at room temperature to form symmetrical disubstitution products, $[Ph_3PFe(CO)_2]_2S_2$,[149,150] and with $Co_2(CO)_8$ to form a mixed metal sulphide, $Co_2Fe(CO)_9S$, together with traces of other cobalt carbonyl sulphides. The latter are also formed when thiophen, sulphur, or ethanethiol react, under hydroformylation conditions with a mixture of iron and cobalt carbonyls,[151] or cobalt octacarbonyl alone.[152] $Co_2Fe(CO)_9S$ probably has a structure analogous to $[Co(CO)_3]_3S$ (Fig.II.36).

Cobalt octacarbonyl reacts with sulphur in an atmosphere of carbon monoxide to yield a mixture of cobalt carbonyl sulphides, mainly $[Co(CO)_3]_3S$[153,154] and $[Co_2(CO)_5S]_n$,[154,155,156,157] with some $Co_3(CO)_7S_2$.[154] The latter two complexes are also formed as by-products in many reactions of cobalt carbonyl sulphur compounds.[158] The structures are shown in Fig.II.37 and 38. $[Co(CO)]_3S$ is also obtained from $[(Co_2(CO)_5S)]_n$ and carbon monoxide under pressure at elevated temperatures, or from cobalt sulphide and cobalt octacarbonyl, or by acidification of the product of the reaction of tetracarbonylcobaltate salts with sulphite ions.[153,154] Treatment of cobalt octacarbonyl solutions with hydrogen sulphide gives cobalt sulphide as well as carbonyl sulphides,[158] (Eqn.II.22).

$$Co_2(CO)_8 + H_2S \longrightarrow CoS + [Co_2(CO)_5S]_n + [Co(CO)_3]_3S \qquad II.22$$

Sulphide-mercaptides, $Co_3(CO)_6S(SR)$[158] and $Co_6(CO)_{11}S(SR)_4$,[159] have also been reported as being formed by the above reaction (II.22). An X-ray structure analysis of $[SCo_3(CO)_7]_2S_2$ shows the first case of a disulphide group symmetrically co-ordinated to four transition metal atoms, essentially two $SCo_3(CO)_7$ moeties linked by a disulphide bridge.[160]

(ii) Derivatives of sulphur dioxide

Strohmeier[161] was unable to prepare a substitution product from the reaction of iron pentacarbonyl and sulphur dioxide under u.v. light. However

Braye and Hubel[162] found that enneacarbonyldi-iron reacts with sulphur dioxide, in the absence of ultra-violet light, to give μ-S-sulphonato-octacarbonyldi-iron, whose structure (Fig.II.39) has been confirmed by X-ray analysis.[163] Under the same conditions $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ does not react, but under more extreme conditions two isomers are obtained with the following formula $\pi\text{-}C_5H_5Fe(CO)_2.\pi\text{-}C_5H_5.Fe(SO_2)_3Fe.\pi\text{-}C_5H_5.\pi\text{-}C_5H_5Fe(CO)_2$.[164]

(iii) Derivatives of mono-thiols

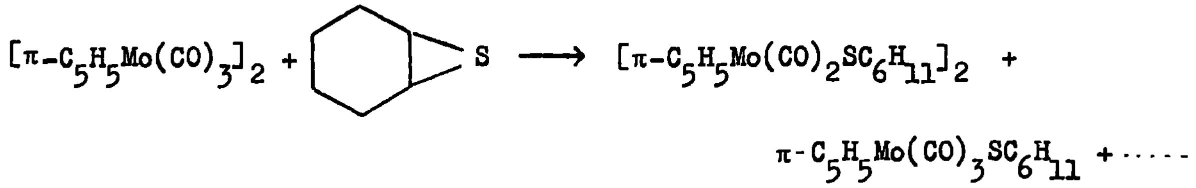
(a) Group VI metal derivatives. $\pi\text{-}C_5H_5M(CO)_3H$ is reported to react with dimethyldisulphide to give $[\pi\text{-}C_5H_5M(CO)_2SMe]_2$ (M = Mo,W)[165] but formulation of the tungsten product, as a dimer, from this reaction is in doubt, since alternative routes to the mercapto-tungsten complexes have led to the isolation of monomeric compounds[166] (Eqn. II.23 and II.24).

$$\pi\text{-}C_5H_5W(CO)_3Cl + NaSR \longrightarrow \pi\text{-}C_5H_5W(CO)_3SR \qquad \text{II.23}$$

$$\pi\text{-}C_5H_5W(CO)_3Cl + RSH \longrightarrow \pi\text{-}C_5H_5W(CO)_3SR \qquad \text{II.24}$$

$$(R = Me,Ph)$$

Photochemical conversion of the monomers to the dimer $[\pi\text{-}C_5H_5W(CO)_2SR]_2$ could be effected in solution. Both the tungsten and molybdenum dimers $[\pi\text{-}C_5H_5M(CO)_2SR]_2$ are obtained as a mixture of products when R = Me, but only as a single species when R = Ph. Cyclohexylthio complexes have been obtained from $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ using cyclohexene sulphide and the monomeric complex also isolated, was found to be unstable[167] (Eqn.II.25).



II.25

A stable monomeric molybdenum derivative has been obtained by the following metathetical reaction[168] (Eqn.II.26).

$$\pi\text{-}C_3H_5Mbipy(CO)_2Cl + TlSC_6F_5 \longrightarrow \pi\text{-}C_3H_5Mbipy(CO)_2SC_6F_5 \qquad II.26$$

$$(M = Mo, W)$$

The dinuclear π-allylmolybdenum complex (Fig.II.40) was obtained by the treatment of its tris-μ-chloro analogue with sodium phenyl mercaptide.[169] Another somewhat uncertain derivative "$PhSMo(CO)_2py$", has been reported from the reaction of thiophenol with tris(pyridine)molybdenum tricarbonyl.[144]

The alkylthio bridged anionic metal carbonyl derivatives, $M_2(CO)_{10}SR^-$,[170] are reported as the only product of reaction II.27, even in the presence of a large excess of R'_3SnSR. No evidence was found for the mononuclear derivative $M(CO)_5SR^-$.

$$2M(CO)_5Cl^- + R'_3SnSR \longrightarrow M_2(CO)_{10}SR^- + R'SnCl + Cl^- \qquad II.27$$

$$R = CH_3,\ CH_2C_6H_5,\ C_6H_5,\ R' = CH_3 \text{ or } C_4H_9,\ M = Cr, Mo, W$$

(b) Group VII metal derivatives. Manganese,[171] technetium,[172] and rhenium[132] pentacarbonyl chlorides are reported to react when heated with thiophenol to yield dimeric tetracarbonyl derivatives. Several alkyl and aryl analogues of the manganese compound were prepared by the reaction of the carbonyl hydride with dialkyl[165] and aryl[173,174] disulphides. The mass spectra of some of these manganese and rhenium dimers show that they can exist as trimers and tetramers in the vapour state.[175] By using an electron withdrawing group viz. pentafluorophenyl or trifluoromethyl on the sulphur atom, the monomeric compounds $M(CO)_5SC_6F_5$ (M = Mn,Re) and $CF_3SRe(CO)_5$ can be isolated, but these rapidly lose carbon monoxide and dimerise. However in the presence of a substituent chelating ligand, quite stable monomers can be obtained.[174,176]

Phosphine substituted derivatives of the tetracarbonyl dimers can be obtained by treatment of the phosphine substituted carbonyl halides with alkylthio derivatives of tin[176] (Eqn.II.28 and 29).

$$Ph_3PM(CO)_4Br + Me_3SnSR \longrightarrow [Ph_3PM(CO)_3SR]_2 + CO \qquad II.28$$

$$(Ph_3P)_2M(CO)_3Cl + Me_3SnSR \longrightarrow [Ph_3PM(CO)_3SR]_2 + Ph_3P \qquad II.29$$

The reactions of alkylthio derivatives of tin and silicon with manganese and rhenium pentacarbonyl halides, result in high yields of oligomeric tricarbonyl derivatives.[177,178,179] The manganese compounds have also been obtained, but only in low yields, by irradiating manganese carbonyl/mercaptan solutions,[180] treatment of $Mn_2(CO)_{10}$ with alkylthiocyanates,[181] or prolonged refluxing of the carbonyl bromide with mercaptan in an inert solvent.[174,180]

Extension of the last reaction to rhenium has led to the isolation of $[Re(CO)_3SR]_n$ in good yields.[173,174] The isolation of $[Re(CO)_4SR]_2$ compounds from the same reaction under milder conditions, suggests that the tricarbonyls arise from the pyrolysis of the tetracarbonyls, and this has been demonstrated with the corresponding alkylseleno derivatives.[176,182] However prolonged refluxing of $Re(CO)_5Cl$ with pentafluorothiophenol, produces only the tetracarbonyl derivative.[174] This is quite compatible with the fact that $[Mn(CO)_3SC_6F_5]_n$, prepared via the organotin thiolate route, proves to be quite unstable (Eqn.II.30).

$$Mn(CO)_5Br + Me_3SnSC_6F_5 \longrightarrow [Mn(CO)_3SC_6F_5]_n \longrightarrow Mn_2(CO)_{10} + Mn(SC_6F_5)_2 \qquad II.30$$

Although the alkylthio tricarbonyls of manganese and rhenium were originally formulated as trimers (Fig.II.41) on the basis of molecular weight data in benzene,[173,174,178,179] mass spectral studies indicate that the manganese compound is a tetramer in the vapour phase.[175,183] However both the tetramer and trimer of $Re(CO)_3SPh$ have been detected in the mass spectrum.[175]

The variation in solution molecular weights may be due to a breakdown of the molecules in certain solvents. Braterman[184] confirmed the existence of the tetramers $[Mn(CO)_3SR]_4$, (R = Et, p-tolyl, Ph), in solution by infrared spectroscopic measurements.

(c) Group VIII metal derivatives. The first known metal carbonyl mercaptide was prepared in 1928 by passing carbon monoxide into an alkaline suspension of ferrous hydroxide and ethane thiol.[185] Soon afterwards, the same compound was obtained by irradiating iron pentacarbonyl in the presence of ethanethiol[186] (Eqn. II.31).

$$Fe(CO)_5 + EtSH \xrightarrow{h\nu} [Fe(CO)_3SEt]_2 \qquad II.31$$

Alkyl- and aryl-thioiron tricarbonyls have subsequently been prepared in a number of ways by heating dodecacarbonyltri-iron with mercaptans,[144,187,188,189] dialkylsulphide,[144] dialkyl disulphide,[144,189,190,191,192] alkyl thiocyanate[147] or pentafluorophenylsulphide,[193] or from a carbonyl ferrate and mercaptan[144] (Table II.5). Excess disulphide is normally used but yields can be increased by using stoichiometric amounts.[194] Iron pentacarbonyl does not readily undergo these reactions except with dithiols, but in an autoclave under CO pressure it reacts to give good yields.[195]

$[Fe(CO)_3SPh]_2$ was originally formulated as monomeric,[144,187] but was subsequently shown to be a dimer[188] which possibly dissociates in solution.[142] X-ray study of the ethyl compound showed the alkyl groups to be in an anti-conformation.[60] The methyl compound is obtained in two isomeric forms, with 'syn' and 'anti' alkyl groups;[147,190,195] facile inversion of the pure isomers occurs to give an equilibrium mixture.[196] Both the t-butyl[192] and pentafluorophenyl[197] compounds can be obtained only as isomers with non equivalent organic groups, presumably due to steric hindrance. Controlled dimerisation of π-$C_5H_5Fe(CO)_2SPh$ gives two isomers, the most stable being the

Table II.5

Reactants		Conditions	Products	Ref.
Iron Carbonyl Compound	Organo Sulphur Compound			
$Fe(CO)_5$	EtSH	u.v.	$[Fe(CO)_3SEt]_2$	220
$Fe(CO)_5$	R_2S_2 or R_2S	Heat under CO pressure	$[Fe(CO)_3SR]_2$	220
$Fe(CO)_5$	R_2S_2	Autogenious pressure (140°)	$[Fe(CO)_2(SR)]_n$ mainly	220
$Fe_3(CO)_{12}$	RSH, R_2S_2, R_2S	Heat alone or in solvent	$[Fe(CO)_3SR]_2$	220
$Fe_3(CO)_{12}$	RSCN	Heat in benzene	$[Fe(CO)_3SR]_2 + [Fe(CO)_3]_3(SR)_2S$ + other polymers	220
$[\pi\text{-}C_5H_5Fe(CO)_2]_2$	R_2S_2	Reflux in pentane or irradiation in benzene	$[\pi\text{-}C_5H_5Fe(CO)SR]_2$	221
$[\pi\text{-}C_5H_5Fe(CO)_2]_2$	R_2S_2	u.v. room temp.	$\pi\text{-}C_5H_5Fe(CO)_2SR$	221
$[\pi\text{-}C_5H_5Fe(CO)_2]_2$	C_6F_5SH	Heat	$\pi\text{-}C_5H_5Fe(CO)_2SC_6F_5$	197
$\pi\text{-}C_5H_5Fe(CO)_2H$	R_2S_2	Room temperature	$\pi\text{-}C_5H_5Fe(CO)_2SR$	221
$\pi\text{-}C_5H_5Fe(CO)_2Br$	NaSEt	Ether, r.t.	$\pi\text{-}C_5H_5Fe(CO)_2SEt$	219

contd./

<u>Table II.5 contd.</u>

Reactants		Conditions	Products	Ref.
Iron Carbonyl Compound	Organo Sulphur Compound			
π-$C_5H_5Fe(CO)_2SR$	-	Heat or u.v.	$[\pi$-$C_5H_5Fe(CO)SR]_2$	219
$C_3F_7Fe(CO)_4I$	$AgSCF_3$	r.t. benzene solution	$[C_3F_7Fe(CO)_3SCF_3]_2$	73
π-$C_5H_5Fe(CO)_2S.CS.SR$	-	Heat	$[\pi$-$C_5H_5Fe(CO)SR]_2$	222
$Fe(CO)_4I_2$	iso-PrSH	Heat	$[Fe(CO)_3S$-iso-$Pr]_2$ + $Fe_2(CO)_5(S$-isoPr$)_3I$	223

cis isomer.[198] Alkylthioiron tricarbonyls have also been obtained by the cleavage of vinyl groups from μ-alkylthio-μ-vinyldiiron hexacarbonyls with trifluoroacetic acid.[189] The alkylthio-iron tricarbonyls react with tertiary phosphines and arsines and stibines in organic solvents to give asymmetric monosubstituted compounds $LFe_2(CO)_5(SR)_2$, whilst use of the molten ligand results in symmetrical disubstitution.[150] Both monomeric and dimeric complexes are amongst the products when $MeSC_2H_4Fe(CO)_2\pi\text{-}C_5H_5$ is irradiated,[199,224] but from $CH_3SC_3H_6Fe(CO)_2\pi\text{-}C_5H_5$[224] the monomer alone is obtained. The latter is remarkably stable and unlike the manganese and rhenium monomers, only evolves carbon monoxide to give a dimer, above 70°. The pentafluorophenyl monomer, prepared thermally, is so stable that it will not dimerise up to the decomposition temperature.[197] Displacement of one carbonyl group can however be effected by a donor ligand like trimethylphosphite. The Lewis base properties of the co-ordinated sulphur atom in $\pi\text{-}C_5H_5Fe(CO)_2SCH_3$, allow it to be used to form an adduct with methyl iodide,[192,199] or mercuric chloride,[192] similar to those formed by dialkylsulphides.

Electrochemical studies provide evidence for the existence of the species $[\pi\text{-}C_5H_5Fe(CO)_2SMe]^+$, $[\pi\text{-}C_5H_5Fe(CO)_2SMe]^{2-}$, $[\pi\text{-}C_5H_5Fe(CO)SMe]_2^{2+}$, $[\pi\text{-}C_5H_5Fe(CO)SMe]_2^{2-}$ and $[\pi\text{-}C_5H_5Fe(CO)SMe]_2^{+}$.[200] The last complex has been isolated as the $[SbF_6]^-$ salt by reaction of the neutral species with silver hexafluoroantimonate.[201] A mass spectral study of the dimer molecule shows fragmentation to occur by the initial loss of the carbonyl groups to form the $[\pi\text{-}C_5H_5FeSCH_3]_2^+$ cation.[202]

Cobalt octacarbonyl was originally reported to react with mercaptans at 0° to yield derivatives of empirical formula $Co(CO)_3SR$, which were assigned dimeric formulations when R = Et and monomeric formulations when R = Ph.[187] o-Phenanthroline was said to substitute the ethyl compound to give $LCo(CO)_2SEt$ but subsequent workers have been unable to repeat these results,[158] and find the following complex behaviour. Cobalt octacarbonyl reacts with ethane thiol or diethyl disulphide to yield $Co_4(CO)_5(SEt)_7$. Progressive treatment of cobalt octacarbonyl with small amounts of thiol gives a different mercaptide, $Co_4(CO)_7(SEt)_3$ along with the sulphides $[Co(CO)_3]_3S$ and $[Co_2(CO)_5S]_n$, whilst stepwise use of the disulphide gives both the polynuclear mercaptides together with $Co_3(CO)_6S.SEt$. The benzyl analogue of the latter complex is formed by treatment of $Co_2(CO)_8$ or $[Co(CO)_3]_3S$ with benzyl mercaptan, but addition of more cobalt octacarbonyl gives mainly the sulphide.

Tetracobalt dodecacarbonyl and ethanethiol give a mixture of the mercaptide complexes, $Co_4(CO)_5(SEt)_7$ and $Co_4(CO)_7(SEt)_3$. The latter complex may be converted to the former by treatment with more ethanethiol. Aqueous alkaline cobalt(II) solutions in the presence of ethanethiol absorb carbon monoxide to give mainly $Co_4(CO)_5(SEt)_7$[158] but methanolic solutions give only small amounts of this product and mainly a new mercaptide complex $Co_4(CO)_4(SEt)_8$, only identifiable as a trace product in the aqueous system.[203] On thermolysis, $Co_4(CO)_4(SEt)_8$ gives the heptamercapto-compound along with cobaltic mercaptide. Both mercapto-compounds are formed when thiol saturated carbon monoxide is passed through a hexane solution of cobalt stearate. $Co_4(CO)_7(SEt)_3$ has now been shown by X-ray diffraction to be really another sulphide-mercaptide $Co_6(CO)_{11}S(SEt)_4$,[204] and $Co_4(CO)_5(SEt)_7$ has been shown to be $Co_3(CO)_4(SEt)_5$.[205] $Co_5(CO)_{10}(SEt)_5$, is also prepared from cobalt octacarbonyl and ethane thiol, and its X-ray crystal structure has been reported.[206]

In view of the wide range of complexes formed with cobalt carbonyls it is not surprising that ethane thiol and diethyldisulphide inhibit hydroformylation reactions.[207,208,209,210]

(d) The Noble metal derivatives. Carbonyl mercaptides of these metals are so far restricted to complexes of ruthenium, rhodium and iridium. Rhodium carbonyl chloride reacts with mercaptans to give mercapto-bridged complexes[197,211] (Eqn.II.32), but unlike the chloride, the complex will not add dienes.[212]

$$[Rh(CO)_2Cl]_2 + RSH \longrightarrow [Rh(CO)_2SR]_2 \qquad II.32$$

The mercapto bridges can be broken by treatment with phosphine ligands.[197,211]

The corresponding halogeno-complexes of iridium e.g. $(Ph_3P)_2Ir(CO)Cl$ will add mercaptans and sulphenyl chlorides to give mercapto derivatives.[213,214] A trimeric ruthenium complex $[Ru(CO)_2(SPh)_2]_3$ has been obtained by carbonylation of an alcoholic solution of ruthenium trichloride, and treatment with thiophenol.[215] The product obtained similarly with o-aminothio-phenol viz. $Ru(CO)_2(SC_6H_4NH_2)_2$ may well be monomeric with two chelating ligands.[216] In contrast, treatment of triruthenium dodecacarbonyl with thiols (including thiophenol) has given $[Ru(CO)_3SR]_2$ and polymeric $[Ru(CO)_2(SR)_2]_n$[217] analogous to iron compounds. Other workers report that ruthenium and osmium carbonyls react with thiols, RSH, (R = Et, Bu, Ph) to produce trinuclear hydrido carbonyl complexes $HM_3(CO)_{10}SR$.[218]

9. Complexes containing bridging selenium and tellurium atoms

Both bis and tris tricarbonyl iron diselenides are known. The latter, first made by the action of carbon monoxide under pressure on an iron/selenium mixture,[139,140] but by analogy with the routes to sulphur derivatives, they have also been obtained by the action of selenite on an aqueous alkaline carbonyl ferrate solution.[140] Only the latter method is applicable to the telluride $[Fe(CO)_3]_3Te_2$. $[Fe(CO)_3]_2Se_2$ is obtained on acidification of an alkaline solution of tetracarbonylferrate and sodium sulphide-polyselenide; physical measurements suggest a similar structure to that of the sulphur analogue.[142] The tellurium analogue is unknown.

X-ray study of $[Fe(CO)_3]_3Se_2$ shows its configuration to be roughly square pyramidal, with Se and Fe atoms at alternate corners of the basal plane, and an apical iron atom[82] (Fig.II.42). It may be regarded as arising from insertion of a $Fe(CO)_3$ moiety into a M-M bond of $[Fe(CO)_3]_2S_2$.

The only known carbonyl selenide or telluride of cobalt was obtained from the reaction of cobalt octacarbonyl with diphenyltelluride[225] (Eqn.II.33).

$$Co_2(CO)_8 + TePh_2 \longrightarrow [Co_2(CO)_5Te]_n \qquad II.33$$

Irradiation of $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ with Ph_2Te_2 at 25° gives $\pi\text{-}C_5H_5Mo(CO)_3TePh$ which decomposes with loss of CO to give $[\pi\text{-}C_5H_5Mo(CO)_2TePh]_2$.[226]

10. Complexes containing bridging hydrogen atoms

Beginning with the isolation of iron carbonyl hydride in 1931,[227] the chemistry of the hydridocarbonyls has been extensively studied, and several reviews of the work have appeared.[16] The three types of complexes known in which the hydrogen atoms act as bridging ligands are (i) complexes in which hydrogen is the only bridging atom e.g. $[(CO)_5MHM'(CO)_5]^-$ (M = M' = Cr, M = Cr, M' = W) (ii) complexes in which the hydrogen atom is part of a double bridge e.g. $\pi\text{-}C_5H_5(CO)_2Mo(H)(P(Me)_2)Mo(CO)_2\pi\text{-}C_5H_5$, and (iii) complexes in which the hydrogen is part of a multiple bridge e.g. $[HFe_2(CO)_8]^-$.

(a) Group VI metal derivatives. The major products from the reaction of the group VI metal hexacarbonyls with sodium borohydride in T.H.F. (Eqn.II.34) are the anionic complexes $[(CO)_5MHM'(CO)_5]^-$ (M = M' = Cr, M = Cr, M' = W),[228]

$$M(CO)_6 + NaBH_4 \longrightarrow Na[M_2H(CO)_{10}] + 2CO + BH_3 \qquad II.34$$

identical with $[M_2H(CO)_{10}]^-$ complexes prepared by Behrens either by hydrolysis of $[M_2(CO)_{10}]^{2-}$ [229,230] or by oxidation of $[M(CO)_5]^{2-}$ with aqueous ammonia solution.[229,231] A linear Cr-H-Cr bond is consistent with the spectroscopic and diffraction data for the anion $[HCr_2(CO)_{10}]^-$.[232,233] An X-ray study failed to locate the hydrogen atom but showed the Cr-H-Cr distance to be 3.41Å, the two halves of the ion being related by a centre of symmetry. The metal-hydrogen-metal bond may be described in terms of a delocalized three centre two electron bond. In this manner both chromium atoms have a closed shell electronic configuration and the bonding is reminiscent of that in the B-H-B bridge bonds of the boron hydrides. This is illustrated by the characteristics of several mixed hydrides e.g. $HMn_3(CO)_{10}(BH_3)_2$,[234] the first known polyborane transition metal carbonyl complex, obtained as a by-product in the synthesis of $[HMn(CO)_4]_3$.[235] This compound, $HMn_3(CO)_{10}(BH_3)_2$, has a Mn-Mn distance of 2.845Å which is shorter than the 2.923Å found in $Mn_2(CO)_{10}$.[236] In $[Cr(CO)_4B_3H_8]^-$ the chromium atom is in an octahedral environment bonded to the B_3H_8 moiety by two cis-Cr-H-B linkages.[237]

The compound π-$C_5H_5(CO)_2Mo(H)(PMe_2)Mo(CO)_2\pi$-$C_5H_5$[95] is an example of a compound in which hydrogen is part of a double bridge. The unique hydrogen was not detected by X-ray diffraction measurements.[113] The stereochemical environment at each molybdenum atom is identical; however only three of the four basal co-ordination positions are occupied by ligands located by X-rays. The hydrogen atom is thought to occupy the fourth position, thus occupying a co-ordination site of both metal atoms. The Mo-Mo distance of 3.26Å compares well with 3.22Å found in $[\pi$-$C_5H_5Mo(CO)_3]_2$.[238] The average Mo-P distance 2.42Å is relatively short and indicative of significant π-bonding. The Mo-P-Mo angle is 85°. A Mo-H distance of 1.8Å in π-$C_5H_5(CO)_2Mo(H)(PMe_2)Mo(CO)_2\pi$-$C_5H_5$[113] is very similar to the observed Cr-H distance of 1.7Å found in $[Cr_2H(CO)_{10}]^-$[232] and the Mn-H distance of 1.65Å in $Mn_3H(B_2H_6)(CO)_{10}$.[234] It would be of interest to attempt to remove the proton from these compounds without further degradation, perhaps by using a Lewis acid to form a mono-bridged complex, which may be stabilized by a M-M bond. The cationic bridged hydrides, $[(\pi$-$C_5H_5M(CO)_3)_2H]^+$ (M = Mo,W) and $[(\pi$-$C_5H_5Fe(CO)_2)_2H]^+$ are obtained on acidification of the parent dimers.[239]

(b) Group VII metal derivatives. The structure of $(CO)_4MnH(PPh_2)Mn(CO)_4$[105,12 revealed that the hydrogen was symmetrically bridged between the metal atoms. The Mn-P distance of 2.28Å is comparable with the terminal Mn-P distance of

2.27Å in $Mn(NO)(CO)_2P(C_6H_5)_3$,[240] perhaps indicating that the bond distance is not significantly changed when it bridges. However, if one considers the tetrahedral radius of phosphorus as 1.10Å[66] and estimates the Mn single bond radius to be either 1.39Å[241] or 1.46Å[113] then one would conclude that significant Mn-P multiple bonding must be taking place.

In $HRe_2Mn(CO)_{14}$[242] on the basis of comparisons of M-M bond lengths it is assumed that the hydrogen atom is located between the two rhenium atoms. Assuming a linear symmetrical Re-H-Re bond, the Re-H distance 1.696Å is very close to 1.68Å found in K_2ReH_9 by neutron diffraction.[243] As in the ion $[HCr_2(CO)_{10}]^-$ the $(CO)_4ReHRe(CO)_5$ portion of the molecule has an eclipsed configuration of carbonyl groups and in the $(CO)_4Re\text{-}Mn(CO)_5$ portion they are staggered.

Through reduction and simultaneous carbon monoxide cleavage from $Re_2(CO)_{10}$ a number of polynuclear carbonyl anions and hydrides have been isolated containing the rhenium tetracarbonyl groups e.g. $[H_2Re_3(CO)_{12}]^-$,[244] $H_3Re_3(CO)_{12}$,[245] $HRe_3(CO)_{14}$.[246] A new species containing a rhenium tricarbonyl species $[H_6Re_4(CO)_{12}]^{2-}$ was isolated from the reaction of $Re_2(CO)_{10}$ and sodium borohydride by adding tetraphenyl arsenium chloride.[247] The crystal structure indicates six hydrogen atoms in the anion, detected also by ^1H n.m.r., associated with the six edges of a tetrahedral metal cluster. The average Re-Re distance of 3.160Å is closer to the hydrogen bridged Re-Re distance of 3.177Å in $[H_2Re_3(CO)_{12}]^-$,[244] than to the non hydrogen bridged Re-Re distance of 2.987Å in $[Re_4(CO)_{16}]^{2-}$ [248] or 3.02Å in $Re_2(CO)_{10}$.[249]

(c) <u>Group VIII metal derivatives</u>. The structure of the anion $[HFe_3(CO)_{11}]^-$ is closely related to that of $Fe_3(CO)_{12}$ and can be regarded as $Fe_3(CO)_{12}$ in which the bridging carbonyl group is replaced by H^-.[250] The compound originally formulated $HFe_3(CO)_{11}NMe_2$[251] has been shown, by accurate mass measurements and Mossbauer spectroscopy, to be $HFe_3(CO)_{10}CNMe_2$.[252] A structure similar to $Fe_3(CO)_{12}$ in which the two bridging carbonyl groups have been replaced by bridging hydrogen and $CNMe_2$ groups has been suggested. Hydrogen is also part of a multiple bridged system in the anion $[HFe_2(CO)_8]^-$. The structure was elucidated by infrared and Mossbauer spectroscopy,[253] and was found to be similar to $Fe_2(CO)_9$ in which a bridging carbonyl has been replaced by the hydride.

Many polynuclear hydrido-carbonyls of iron and cobalt sub-groups have been characterised, but as yet their structures are formulated with uncertainty. It was suggested,[254] on the basis of infrared and mass-spectroscopic data, that the hydrides $HMCo_3(CO)_{12}$ (M = Fe or Ru) have structures similar to those of $M_4(CO)_{12}$ (M = Co,Rh), with the hydrogen atom located inside the metal cluster. Since the hydrides $H_2Ru_4(CO)_{13}$, α-$H_4Ru_4(CO)_{12}$, β-$H_4Ru_4(CO)_{12}$ are isoelectronic with $Rh_4(CO)_{12}$ and the hydride $H_2Fe_4(CO)_{13}$ is isoelectronic with $Co_4(CO)_{12}$, it is reasonable to assume that the metal atoms in these hydrides have a tetrahedral arrangement. On the basis of infrared and ^1H n.m.r. data the structure of $H_2Ru_4(CO)_{13}$ may be similar to that of the anion $[Fe_4(CO)_{13}]^{2-}$ but with two Ru-H-Ru bridges.[255] Similar bridge bonding probably occurs in the α and β forms of $H_4Ru_4(CO)_{12}$.[255]

Mass spectral, infrared and ^1H n.m.r. studies[218,256] suggest that the hydrides $Os_3(CO)_{10}(H)(X)$ (X = H,OH,OMe) and $HRu_3(CO)_{10}(SR)$ are structurally similar to $Fe_3(CO)_{12}$ with H and X, and H and SR groups, respectively, replacing the two bridging carbonyl groups. Such a structure has recently been confirmed for $Os_3(CO)_{10}(OMe)_2$ and $H_2Os_3(CO)_{10}$.[135] The complex $HOs_3(CO)_{10}(SPh)$ dissolves in sulphuric acid to form cationic hydrido-species $[H_2Os_3(CO)_{10}SPh]^+$ in α- and β-forms.[257] $H_2Ru_6(CO)_{18}$ is isolated[258] from the reduction of $Ru_3(CO)_{12}$ with mononuclear carbonyl anions $[Mn(CO)_5]^-$ or $[\pi$-$C_5H_5Fe(CO)_2]^-$ in T.H.F. solution. The molecule is isoelectronic with known species $Ru_6(CO)_{16}$,[259] and $Ru_6C(CO)_{17}$.[260] The hydrogens were found to occupy triply bridging positions on two opposite faces of the metal octahedron, each Ru having three terminal carbonyl groups.

11. Complexes containing bridging halogen atoms

(a) Group VI metal derivatives. Complexes of the type $M(CO)_4L$ ($M = Mo,W$; L = 2,2-bipyridyl[261,262] or 1,10-phenanthroline[262]) react with iodine in a 1:1 molar ratio at room temperature to give dimeric complexes $[M(CO)_3LI_2]_2$; but in a 2:1 ratio at 150° to give $[M(CO)_2LI]_2$. These compounds, in which the metal atoms are in a formal +1 oxidation state, are linked by two iodine bridges. The anions $[M(CO)_5X]^-$ ($M = Cr,Mo,W$; $X = Cl,Br,I$), react with group VI hexacarbonyls under photolytic conditions to form the dinuclear anions $[M_2(CO)_{10}X]^-$ or $[MM'(CO)_{10}X]^-$. It is assumed that the halogen, bridged between the two group VI metal anions, might formally be considered to be related to the hydride,bridging dinuclear anions, $[M_2(CO)_{10}H]^-$.[263] Two modes of bonding are possible for the halide ions due to the availability of four electron pairs. In the first case two electron pairs are considered as being involved in the M-X-M system and in the second, one electron pair in an 'electron deficient' bond. The former could lead to a bent M-X-M system[264] and the latter to a linear M-X-M bond.[265] The only neutral halides are $Cr_2I(CO)_{10}$.[266,267]

No halogen bridged compounds of the type $[\pi\text{-}C_5H_5M(CO)_2X]_2$ have been reported, yet these type are the most characteristic when X = mercaptide, dialkylphosphide or arsenide. This shows the close correspondence between the latter groups and their greater tendency to bridge than the halides.

(b) Group VII metal derivatives. Kinetic studies of CO exchange[268] and CO substitution[269] reactions of the halides of Mn and Re[270] are consistent in all cases with a dissociative rate-determining step at or just above room temperature. The highly reactive intermediate $[M(CO)_4X]$ then reacts rapidly with any Lewis base present to form the mono-substituted carbonyl halides, but in the absence of a neutral ligand, dimerisation to $[M(CO)_4X]_2$ occurs through formation of halogen bridges. All the dinuclear tetracarbonyl halides of this group have been prepared by heating solutions of the pentacarbonyl halides.[271,272,273] Carbon monoxide under pressure regenerates the pentacarbonyl halides.[271,273]

Compounds containing bridging $(CF_3)_2As$ and $(CF_3)_2P$ groups and compounds containing these and halogen bridges are known.[106,108]

(c) Group VIII metal derivatives. Fairly stable substitution products are formed by halogens and ligands which donate via S, Se, Te, P, As, Sb.[274] The polymeric, presumably halogen bridged, dicarbonyl halides $[M(CO)_2X_2]_n$ have been reported for M = Fe,[275,276], Os;[277] Ru.[278] Osmium differs from the other two metals by forming a more extensive series of halides with a lower carbon monoxide content than the parent species, $M(CO)_4X_2$. $Os(CO)_4X_2$ is unstable at 100°C with respect to $Os(CO)_3X_2$[279] which at 300°C loses CO to give $[Os(CO)_2X_2]_n$. Neutral ligands break the halogen bridges and displace CO,[279] the products $Os(CO)_2L_2X_2$ being the same as those prepared by the action of the ligands on the polymeric dicarbonyls[280,281] or on $M(CO)_4X_2$, although in the latter case both mono-and di-substituted compounds are observed.[282]

Oxidation of triruthenium dodecacarbonyl with halogens[283] leads to the isolation of four classes of ruthenium carbonyl halides $Ru(CO)_4X_2$, $Ru_3(CO)_{12}X_6$, $Ru_2(CO)_6X_4$ and $Ru(CO)_2X_2$. The trimeric $Ru_3(CO)_{12}X_6$ was the first example of a new class of carbonyl halide, and the simplicity of its infrared spectrum suggests a high symmetry and the absence of bridging carbonyl groups. In this compound Ru exceeds the effective atomic number of Xenon by four electrons. The binuclear compounds $Ru_2(CO)_6X_4$ are obtained by carbon monoxide loss when $Ru_3(CO)_{12}X_6$[284] compounds are extracted into polar or hot non-polar solvents, but are prepared more directly by the reactions of halogens with $Ru_3(CO)_{12}$. Together with the osmium bridged analogues they were formulated as halogen bridged binuclear compounds, which was confirmed by X-ray crystallographic studies.[285] $Ru(CO)_2X_2$, prepared by Colton, and $Ru_2(CO)_6X_4$ showed marked similarity in their infrared spectra and were subsequently thought to be the same compound.[286] $Ru(CO)_2X_2$ complexes[287] are highly insoluble polymeric compounds with halogen bridged structures in contrast to some previous suggestions.[288] Infrared spectra indicate carbonyl groups in cis-arrangements giving a non-linear form of chain structure.[289] The preparation of polymeric compounds by reaction of ruthenium trihalides with carbon monoxide at high temperatures[286,290] was examined. Although $Ru(CO)_2X_2$ (X = Cl,Br,I) were readily prepared by this method considerable amounts of $Ru_3(CO)_{12}X_6$ were also obtained. Carbon monoxide is evolved from $(Ph_3P)Ru(CO)_3Cl_2$ on heating to form halogen bridged dimers $[(Ph_3P)Ru(CO)_2X_2]_2$ (X = Cl,Br,I) analogous to $Ru_2(CO)_6X_4$.

Apart from the unstable brown polymer $[CoI_2(CO)]_n$ prepared by reaction of CoI_2 with carbon monoxide under pressure,[291] no lower carbonyl halides of cobalt are known. The range of carbonyl halides and related complexes of rhodium is extensive,[3] based on either octahedral or square planar co-ordination, the latter bring readily involved in oxidation reactions. $[Rh(CO)_2Cl]_2$ readily undergoes bridge splitting reactions.[292] Iridium also forms numerous halocarbon complexes, which then undergo further reactions.[293] Acyl chlorides RCOCl react with $[IrCl(CO)(C_8H_{14})_2]_2$ to give the bridged chloro-complexes $[IrCl_2R(CO)_2]_2$ (R = Me,Et,Pr^i,Ph).[294] The highly asymmetric chlorine bridging system in the crystal structure of $[IrCl_2Me(CO)_2]_2$ is consistent with the known trans bond weakening effect of a methyl group.[295]

On adding nickel carbonyl to a methanolic solution of triphenylcyclopropenylbromide a red air stable complex $[Ni(CO)Br(C_6H_5)_3C_3]_2$ was isolated, and a structure similar to that of tetramethylcyclobutadienenickel dichloride was proposed.[296]

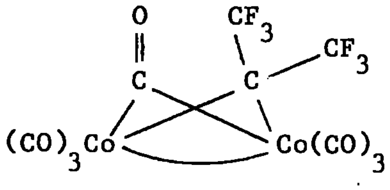


Fig.II.1

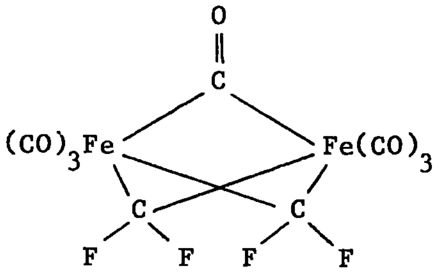
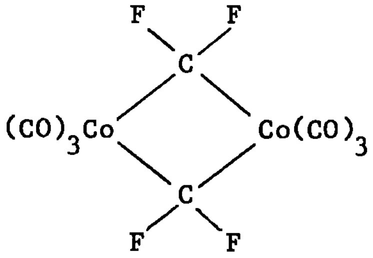


Fig.II.2



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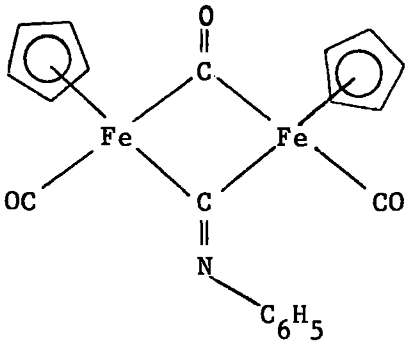
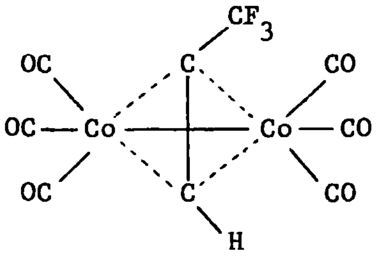


Fig.II.4



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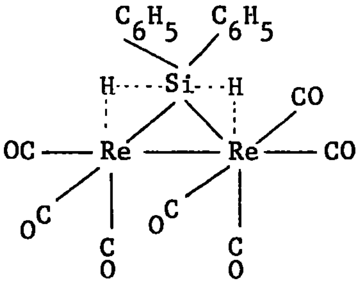

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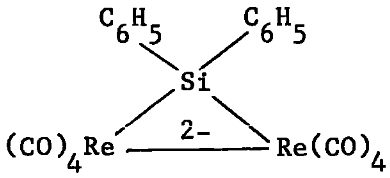
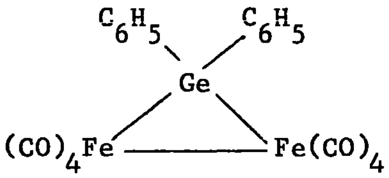


Fig.II.7



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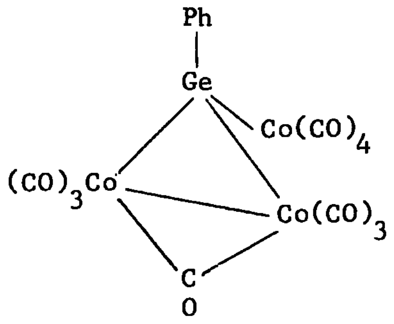

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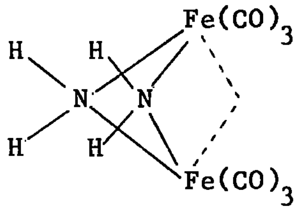


Fig.II.11

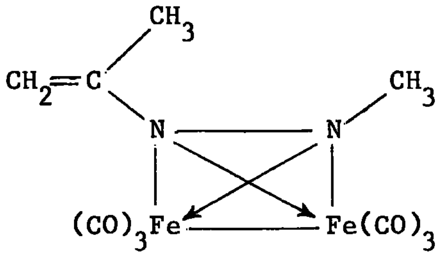
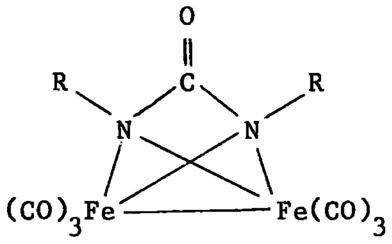
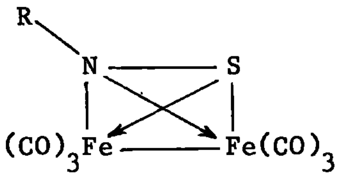


Fig.II.12



(R = Ph,Me)

Fig.II.13



(R = t-C_4H_9,C_6H_5)

Fig.II.14

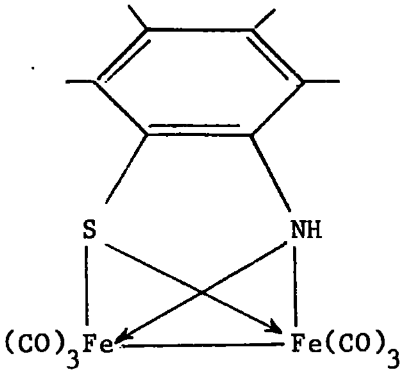


Fig.II.15

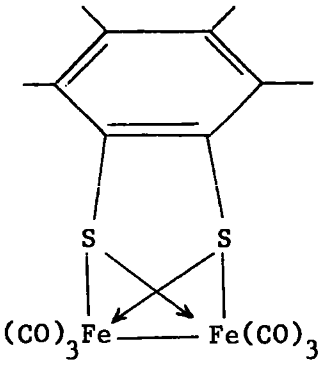


Fig.II.16

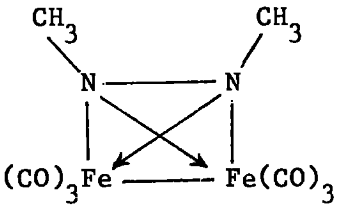


Fig.II.17

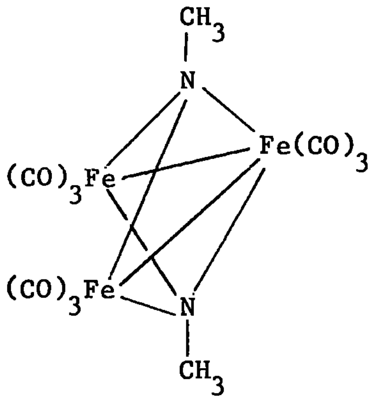


Fig.II.18

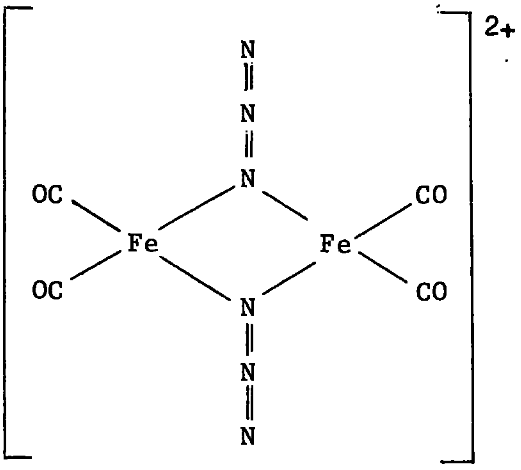


Fig.II.19

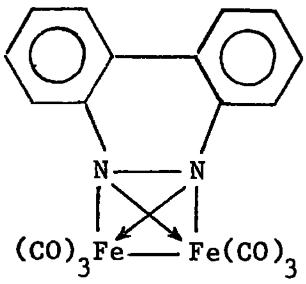
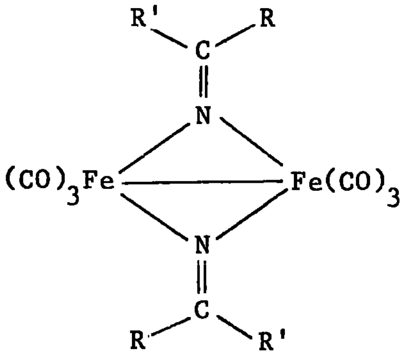


Fig.II.20



(R = R' = C_7H_7,C_6H_5; R = C_6H_5, R' = t-C_4H_9)

Fig.II.21

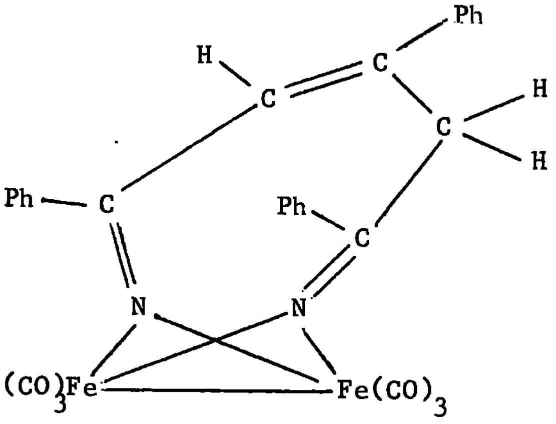
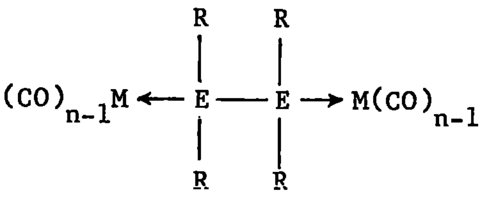
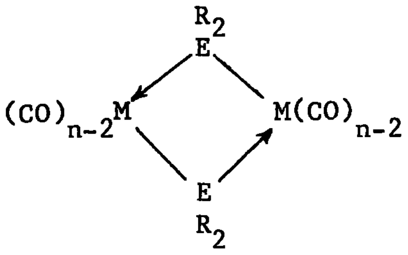


Fig.II.22



(M = Cr,Mo,W; n = 5, R = CH_3, E = P or As)

Fig.II.23



(M = Cr,Mo,W; n = 5,
R = CH_3, E = P or As)

Fig.II.24

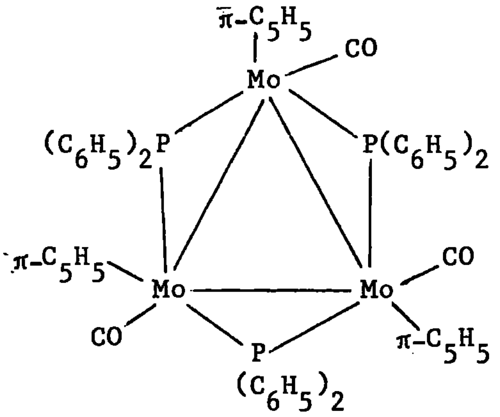


Fig.II.25

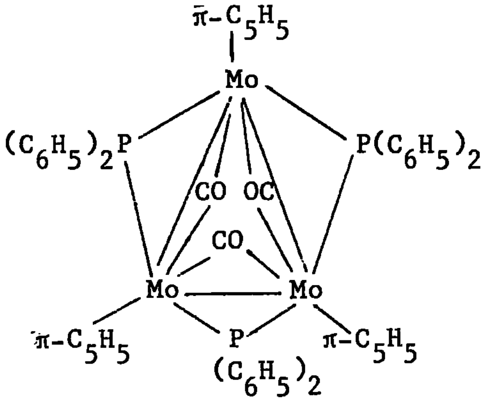


Fig.II.26

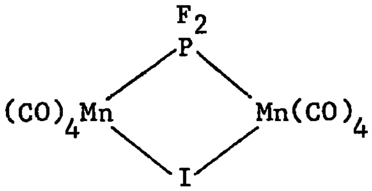


Fig.II.27

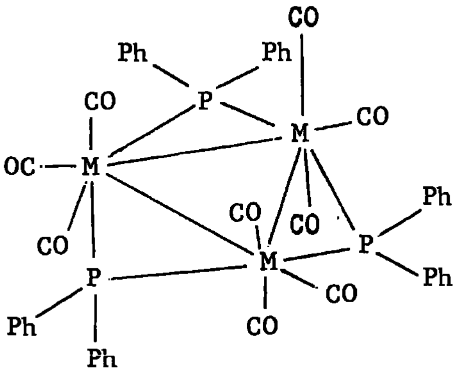
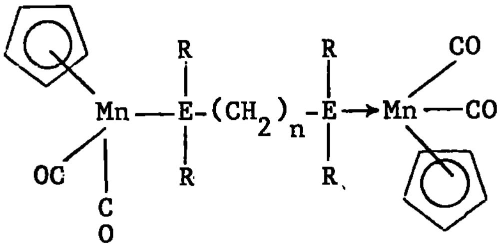


Fig.II.28



E = P; R = CH_3, C_6H_5
E = As; R = CH_3
n = 0,1,2

Fig.II.29

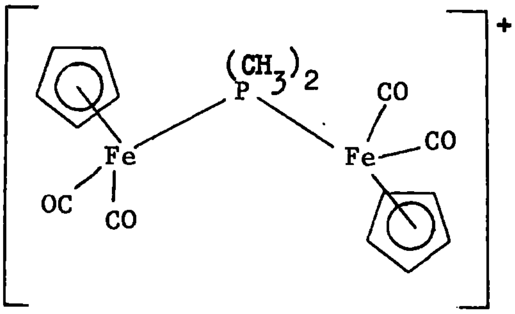


Fig.II.30

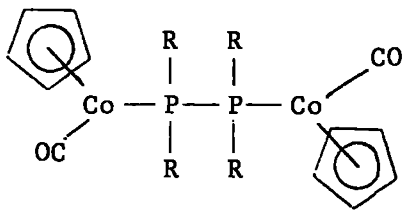


Fig.II.31

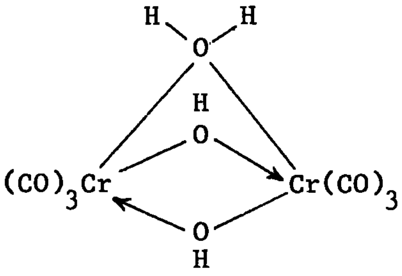


Fig.II.32

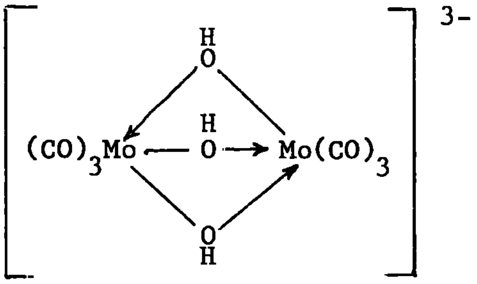


Fig.II.33

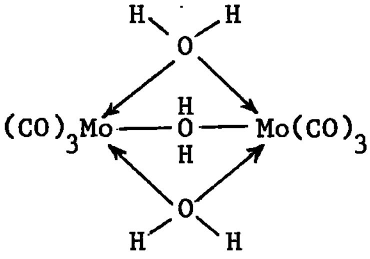


Fig.II.34

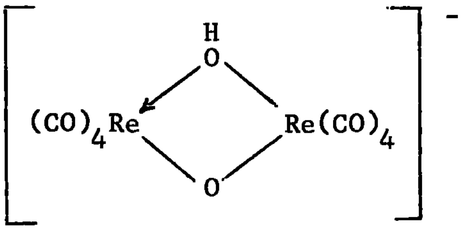


Fig.II.35

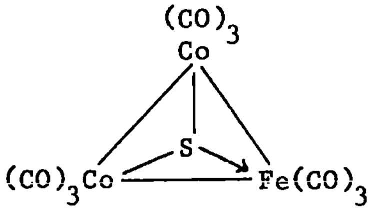


Fig.II.36

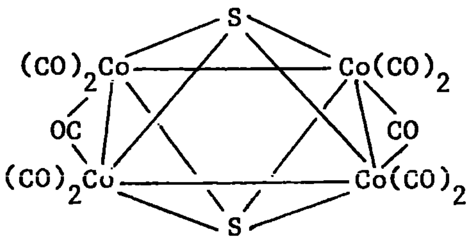


Fig.II.37

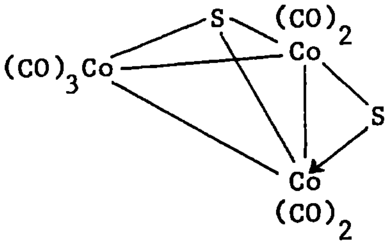


Fig.II.38

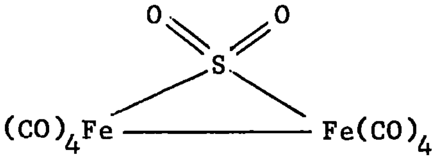


Fig.II.39

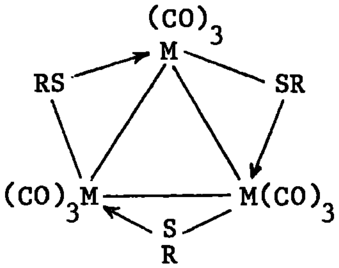


Fig.II.41

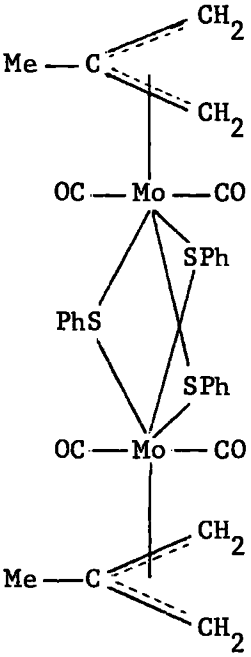


Fig.II.40

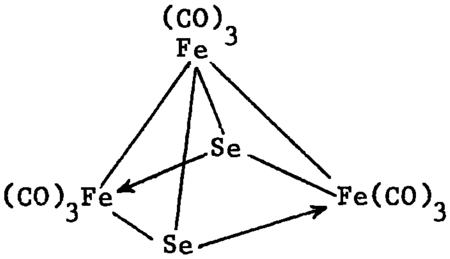


Fig.II.42

CHAPTER III

SYNTHESIS OF DIPHENYL- AND DI-t-BUTYL-METHYLENEAMINO COMPLEXES OF MOLYBDENUM AND TUNGSTEN

In this chapter the synthesis of new diphenyl- and di-t-butylmethyleneamino complexes of molybdenum and tungsten are described. By varying the groups attached to the $>$C:N system we hoped to gain more information on the mode of bonding of the methyleneamino ligand to the metal. t-Butyl groups were introduced into the ligand principally to investigate the effect of sterically bulky groups on the linearity of the M-N-C bonding in the complexes.

A. Experimental

1. Reaction of π-$C_5H_5W(CO)_3Cl$ with $Ph_2C{:}NSiMe_3$

π-$C_5H_5W(CO)_3Cl$ (2.2 g., 6.0 mmole) and the methyleneamino-silane were heated for 4 hr. at 100° in a sealed evacuated tube. The red-orange mixture changed to a deep olive-green colour and gas was evolved. The volatile products were shown by i.r. spectroscopy and v.p.c. to be carbon monoxide and chlorotrimethylsilane. The solid product was extracted with toluene (20 ml.) and the deep green solution was separated from a black-green oily decomposition product by filtration. Addition of hexane (50 ml.) precipitated a non-carbonyl containing decomposition product; when further hexane (30 ml.) was added, and the mixture cooled to -20°, green-black dichroic crystals were obtained, which were recrystallised from toluene-hexane mixtures. Yield 0.3 g. (10%).

Properties: The brown-green dichroic semi-crystalline solid melted at 110-112° in a sealed tube. It was relatively stable in air for short periods, but in solution rapid decomposition occurs. The crystals were very sparingly soluble in hydrocarbon solvents and only sparingly soluble in chloroform and monoglyme forming green-yellow solutions.

Analysis: Found, C,49.21; H,3.14; N,2.92; CO,10.5; $C_{20}H_{15}NO_2W$ requires C,49.4; H,3.24; N,2.9; CO,11.5%.

Infrared spectra (Nujol): The solid gave a yellow-green mull.

ν(CO), 1942s, 1873s, cm^{-1}, ν(CN), 1587m, cm^{-1}.

The full spectrum is: 1942s, 1873s, 1587m, 1470m, 1449m, 1333m, 1299m, 1183m, 1163m, 1070s, 1030m, 1008s, 1018sh, 990m, 970w, 980sh, 934m, 917m, 900m, 855vs, 845m, 840sh, 813vs, 757w, 755s, 751s, 699vs, 689vs, 654s, 637s, 623m, 615m, 593m, 519vs, 505vs, 486vs, 463vs, 453sh. cm^{-1}

<u>^{1}H n.m.r. spectrum</u> ($CDCl_3$): signals at 2.63(2)τ and 4.02(1)τ due to Ph and π-C_5H_5 protons respectively.

<u>Mass Spectrum</u> (direct insertion probe at low source temperature):
For the parent ion $[\pi\text{-}C_5H_5W(CO)_2N{:}CPh_2]^+$ (m/e 485), the isotopic distribution pattern corresponded to that computed for $C_{20}H_{15}NO_2W$. The major peaks in the spectrum are listed in Table III.1 below. Other major peaks corresponding to the organic fragments $[Ph_2CNH]^+$ m/e 181; $[Ph_2CN]^+$ m/e 180; $[PhCN]^+$ m/e 103; $[Ph]^+$ m/e 77; were observed.

<u>Table III.1</u>

<u>Mass spectral data for π-$C_5H_5W(CO)_2N{:}CPh_2$</u>

Ion	m/e	m*	Fragment lost
$[\pi\text{-}C_5H_5W(CO)_2N{:}CPh_2]^+$	485		
		430	CO
$[\pi\text{-}C_5H_5W(CO)N{:}CPh_2]^+$	457		
		403	CO
$[\pi\text{-}C_5H_5WN{:}CPh_2]^+$	429		
		248	PhCN
$[\pi\text{-}C_5H_5WPh]^+$	326		
$[\pi\text{-}C_5H_5WN{:}CPh_2]^{2+}$	214.5		

2. The action of heat on π-$C_5H_5W(CO)_2N:CPh_2$ in monoglyme solution

The green-black complex (0.48 g., 1.0 mmole), obtained from the reaction of π-$C_5H_5W(CO)_3Cl$ with diphenylmethyleneaminotrimethylsilane, was dissolved in monoglyme (30 ml.) and heated at 65° for 1 hr. The olive green colour of the original solution changed to deep orange-brown. After 1 hr. the solvent was removed in vacuo and the oily residue was extracted with ether (30 ml.). Hexane (10 ml.) was added to the solution which was then cooled to -20° to give a brown-orange solid; this was recrystallised from ether-hexane mixtures. Yield 0.1 g. (22%).

Properties: The brown-orange dichroic solid which mulled pink-orange, was stable in air for a few hours but rapidly decomposed in solution to give a brown-green non-carbonyl product. It was very sparingly soluble in hydrocarbon solvents and only sparingly soluble in ethers, $CHCl_3$ and hot monoglyme. On heating the solid, darkening in colour occurred at 200°, before decomposition at 290-300°.

Analysis: Found, C,49.9; H,3.3; N,3.15; CO,6.5; $C_{38}H_{30}N_2O_2W_2$ requires C,49.9; H,3.3; N,3.05; CO,6.1%.

Infrared spectrum (Nujol): The compound gave a pink-orange mull. ν(CO), 1936s, 1847s, cm^{-1}. No absorption could be assigned to ν(CN). The full spectrum is: 1936vs, 1847vs, 1600w, 1449m, 1370m, 1256m, 1235m, 1156m, 1099w, 1072w, 1031m, 1010m, 935w, 820m, 787m, 763w, 741m, 730m, 670s,br, 570w, 476w,br cm^{-1}.

^1H n.m.r. spectrum ($CDCl_3$): signals at 2.63(2)τ and 4.64(1)τ due to Ph and π-C_5H_5 protons respectively.

Mass spectrum (direct insertion probe at source temperature): The parent ion $[(\pi\text{-}C_5H_5)_2W_2(CO)_2(N:CPh_2)_2]^+$ (m/e 914) had an isotopic distribution pattern corresponding with that computed for $C_{38}H_{30}N_2O_2W_2$. The major peaks in the spectrum are listed in Table III.2 below.

Table III.2

Mass spectral data for $[\pi\text{-}C_5H_5W(CO)N{:}CPh_2]_2$

Ion	m/e	m*	Fragment lost
$[(\pi\text{-}C_5H_5)_2W_2(CO)_2(N{:}CPh_2)_2]^+$	914		
		859	CO
$[(\pi\text{-}C_5H_5)_2W_2(CO)(N{:}CPh_2)_2]^+$	886		
		828	CO
$[(\pi\text{-}C_5H_5)_2W_2(N{:}CPh_2)_2]^+$	858		
		663	PhCN
$[(\pi\text{-}C_5H_5)_2W_2Ph(N{:}CPh_2)]^+$	755		
		562	PhCN
$[(\pi\text{-}C_5H_5)_2W_2Ph_2]^+$	652		
		504	C_6H_6
$[\pi\text{-}C_5H_5W_2C_{11}H_9]^+$	574		
$[\pi\text{-}C_5H_5W_2Ph_2H]^+$	588		
$[(\pi\text{-}C_5H_5)_2W_2(N{:}CPh_2)_2]^{2+}$	429		
$[(\pi\text{-}C_5H_5)_2W_2(Ph)(N{:}CPh_2)]^{2+}$	377.5		
$[(\pi\text{-}C_5H_5)_2W_2Ph_2]^{2+}$	326		
$[\pi\text{-}C_5H_5W_2C_{11}H_9]^{2+}$	287		

3. Reaction of $[\pi\text{-}C_5H_5W(CO)N{:}CPh_2]_2$ with triphenylphosphine

Using the reactants on a 5 mmole scale, no reaction was detected in refluxing monoglyme during 24hr. $[\pi\text{-}C_5H_5W(CO)N{:}CPh_2]_2$ was recovered unchanged even after 100 hr.

4. Reaction of $\pi\text{-}C_5H_5Mo(CO)_3Cl$ with Bu^t_2CNLi

A solution of $Bu^t_2C{:}NLi$ (21 mmole) in a hexane-ether mixture (50 ml.) was added to a frozen solution of $\pi\text{-}C_5H_5Mo(CO)_3Cl$ (5.88 g., 21 mmole) in ether (200 ml.) at -196°. The mixture when slowly warmed and kept at room temperature for 1 hr. became deep blue, slowly evolved gas, and deposited a fine white powder. After being separated by filtration, the residue (0.8 g.) was shown by i.r. spectroscopy and elemental tests to consist of lithium chloride, $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ and a green, non-carbonyl, oily decomposition product. The solvent was removed from the filtrate (20°, 10^{-1}mm.Hg), and the oily blue solid was extracted with hexane (2 x 200 ml.) from $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ (0.3 g.). On reducing the combined extracts to small bulk, followed by cooling (-20°), royal blue crystals separated, which were recrystallised from hexane. Yield 4.0 g. (53%).

Properties: At ambient temperatures in the solid state, the complex was thermally stable for many weeks, but in solution, especially in air, decomposition to a green non-carbonyl material occurred more rapidly. The complex was moderately soluble in most organic solvents but was insoluble in water. It dissolved readily in concentrated sulphuric acid and glacial acetic acid with little apparent decomposition to form green-yellow and blue solutions respectively which retained their colours for several days. No solid product could be isolated from the sulphuric acid solution.

Analysis: Found, C,53.7; H,6.4; N,3.9; $C_{16}H_{23}MoNO_2$ requires C,53.8; H,6.4; N,3.9%.

Infrared spectrum: The stretching frequencies ν(CN) and ν(CO) observed for the solid and solution in hexane are given in Table III.3. The solid (KBr disc) showed two strong ν(CO) absorptions in the carbonyl region and extra bands were observed in the Nujol spectrum due to a solution of the complex in Nujol. Variable temperature studies on the hexane and Nujol solutions were carried out and reversible changes observed.

Table III.3

Infrared Spectroscopic Data for π-$C_5H_5Mo(CO)_2N{:}CBu^t_2$

Phase	Temp. (°C)	ν(CO) (cm^{-1})	ν(C:N) (cm^{-1})
KBr	0° and 27°	1946s, 1848s	1621m-w
Hexane solution	25°	1967s, 1883s	1616m-w
	-40°	1938s, 1847s	
Nujol mull-solution	0°	1968s, 1884s	1618m-w
	27°	1949s, 1851s	

The full spectrum (KBr disc) is: 3125w, 2963m, 2924m,sh, 2874m,sh, 1946s, 1848s, 1621m-w, 1364m, 1227m,sh, 1205m, 1036w, 1001m, 981m, 848m, 813m,sh, 800s, 741m, 684w, 565w,br, 540m,br, 503m,br, 488m,br, 464m,br cm^{-1}.

Molecular weight: 354 and 352 by cryoscopy in benzene (Th. 357).

Conductivity: non-electrolyte in nitrobenzene.

Electronic Spectrum: ν(max) 246 (37 x 10^4), 291sh (6.9 x 10^3), 351sh (5.1 x 10^3), 558 (210), 657 mμ (280) in methylcyclohexane at 25°, 0° and -11°. (Molar extinction coefficients are given in parentheses).

^{1}H n.m.r. spectrum: the solutions show a number of signals which varied in intensity and position, with changes in temperature. The τ values for the signals observed are given in Table III.4.

Mass spectrum: (direct insertion probe at source temperature): For the parent ion $[\pi\text{-}C_5H_5Mo(CO)_2N{:}CBu^t_2]^+$ (m/e 357) the isotopic distribution corresponded to that computed for $C_{16}H_{23}MoNO_2$. The major peaks in the spectrum are listed in Table III.5.

Table III.4

Variable temperature ^1H n.m.r. spectral data for π-$C_5H_5Mo(CO)_2N{:}CBu^t_2$

Solvent	Temp.(^oC)	$\tau(\pi\text{-}C_5H_5)$	$\tau(Bu^t)$
$CH_3C_6H_5$	25	4.65(5)	8.93(18)
	-60	4.88(5)	8.98(18)
$CD_3C_6D_{11}$	25	4.35(5)	8.82(18)
	-20	4.32(5)	8.83(18)

Table III.5

Mass spectral data for π-$C_5H_5Mo(CO)_2N{:}CBu^t_2$

Ion	m/e	m*	Fragment lost
$[\pi\text{-}C_5H_5Mo(CO)_2N{:}CBu^t_2]^+$	357		
		303	CO
$[\pi\text{-}C_5H_5Mo(CO)N{:}CBu^t_2]^+$	329		
		275	CO
$[\pi\text{-}C_5H_5MoN{:}CBu^t_2]^+$	301		
		198	Bu^t
$[\pi\text{-}C_5H_5MoN{:}CBu^t]^+$	244		
		158	Bu^tCN
$[\pi\text{-}C_5H_5MoBu^t]^+$	218		
		119	Bu^t
$[\pi\text{-}C_5H_5Mo]^+$	161		
		106	Bu^tCN
$[\pi\text{-}C_5H_5Mo]^+$	161		

5. Reaction of π-$C_5H_5W(CO)_3Cl$ with $Bu^t{}_2C:NLi$

π-$C_5H_5W(CO)_2N:CBu^t{}_2$ was prepared on a 10 mmolar scale as deep blue crystals (19.8%) by the method described above.

Properties. The deep blue crystals were stable in air for short periods but formation of a brown coating was observed on prolonged exposure (one day). All common organic solvents readily dissolved the crystals to form deep blue solutions which were very air sensitive turning green-brown after only a few minutes exposure. The crystals melted in a sealed tube 120-121° (decomposition), sublimed (100°, 10^{-3}mm.Hg).

Analysis. Found, C,43.0; H,5.16; N,3.14; $C_{16}H_{23}NO_2W$ requires C,43.1; H,5.17; N,3.15%.

Infrared spectrum: The stretching frequencies ν(CN) and ν(CO) observed for the solid and solution in methylcyclohexane are given in Table III.6.

Table III.6

Infrared spectroscopic data for π-$C_5H_5W(CO)_2N:CBu^t{}_2$

Form	Temp.(°C)	ν(CO) (cm^{-1})	ν(C:N) (cm^{-1})
KBr	25	1934s, 1834s	1620m-w
Nujol	25	1946sh,1862sh 1929s, 1833s	1620m-w
Methylcyclohexane	25 -3 -40	1954s, 1867s	1621w

The full spectrum (KBr disc) is: 3125w, 2976m, 2924m,sh, 2874m,sh, 1934s, 1834s, 1620m-w, 1481w, 1389w, 1366w, 1258w, 1229w, 1209w, 1047w, 1036w, 1008w, 980w, 854w, 820m,sh, 810s, 752w, 685w, 520w,br, 502w,br, 491w,br, 472m,br cm^{-1}.

^{1}H n.m.r. spectrum (toluene): a number of signals which varied in position with change in temperature were observed (Table III.7).

Table III.7

^{1}H n.m.r. spectral data for π-$C_5H_5W(CO)_2N{:}CBu^t_2$

Solvent	Temp.(°C)	$\tau(\pi\text{-}C_5H_5)$	$\tau(Bu^t)$
$C_6H_5CH_3$	25	4.55(5)	8.88(18)
	-80	5.02(5)	9.03(18)
$C_6D_{11}CD_3$	25	4.35(5)	8.92(18)

Mass Spectrum (direct insertion probe at source temperature): For the parent ion $[\pi\text{-}C_5H_5W(CO)_2N{:}CBu^t_2]^+$ (m/e 445) the isotopic distribution pattern corresponded to that computed for $C_{16}H_{23}NO_2W$. The major peaks in the spectrum are listed in Table III.8 below.

Table III.8

Mass spectral data for π-$C_5H_5W(CO)_2N{:}CBu^t_2$

Ion	m/e	m^*	Fragment lost
$[\pi\text{-}C_5H_5W(CO)_2N{:}CBu^t_2]^+$	445		
$[\pi\text{-}C_5H_5W(CO)N{:}CBu^t_2]^+$	417	391	CO
$[\pi\text{-}C_5H_5WN{:}CBu^t_2]^+$	389	363	CO
$[\pi\text{-}C_5H_5WN{:}CBu^t]^+$	332	283	Bu^t
$[\pi\text{-}C_5H_5WBu^t]^+$	306	241	Bu^tCN
$[\pi\text{-}C_5H_5W]^+$	249		

6. Reaction of π-$C_5H_5Mo(CO)_3Cl$ with $Bu^t{}_2C{:}NSiMe_3$

A mixture of π-$C_5H_5Mo(CO)_3Cl$ (1.2 g., 5mmole) and $Bu^t{}_2C{:}NSiMe_3$ (1.06 g., 5mmole) dissolved in monoglyme (30 ml.) was heated to reflux and after 3½ hr. the resulting deep brown solution was evaporated to dryness (25°, 0.1 mm.Hg). Extraction of the residue with hexane (30 ml.) produced a blue solution, which after filtration, concentration (25°, 0.1 mm.Hg), and cooling, gave blue crystals of π-$C_5H_5Mo(CO)_2N{:}CBu^t{}_2$ (0.36 g., 30%).

Analysis: Found, C,53.6; H,6.25; N,3.8; $C_{16}H_{23}MoNO_2$ requires C,53.8; H,6.4; N,3.9%.

The red-purple residue, after recrystallisation from chloroform solution, was identified by spectroscopy and elemental analysis as $[\pi$-$C_5H_5Mo(CO)_3]_2$ (0.31 g., 26%).

Analysis: Found, C,39.0; H,2.15; $C_{16}H_{10}Mo_2O_6$ requires C,39.1; H,2.0%.

7. Reaction of π-$C_5H_5W(CO)_3Cl$ with $Bu^t{}_2C{:}NSiMe_3$

The reaction, performed as described above, with the same molar quantities, gave blue crystals identified by i.r. spectroscopy as π-$C_5H_5W(CO)_2N{:}CBu^t{}_2$ (0.18 g., 8%).

Analysis: Found, C,43.0; H,5.15; N,3.90; $C_{16}H_{23}NO_2W$ requires C,43.1; H,5.15; N,3.15%.

The dinuclear complex $[\pi$-$C_5H_5W(CO)_3]_2$ was isolated as the major product (0.72 g., 84%).

Analysis: Found, C,28.8; H,1.5; $C_{16}H_{10}O_6W_2$ requires C,28.8; H,1.5%.

8. Action of Heat on π-$C_5H_5Mo(CO)_2N{:}CBu^t{}_2$

Attempted sublimation: On attempting to purify the complex by sublimation (85-90°, 10^{-3}mm.Hg), the sublimed material was found to be contaminated with a white wax. Attempts to isolate the material in a pure form in reasonable quantity for conventional identification were unsuccessful but it was identified by mass spectroscopy as the azine, $Bu^t{}_2CNNCBu^t{}_2$; m/e 280,

$[Bu^t_2CNNCBu^t_2]^+$; m/e 223, $[Bu^tCNNCBu^t_2]^+$; m/e 197, $[Bu^t_2CNBu^t]^+$; m/e 140, $[Bu^t_2CN]^+$; m/e 83, $[Bu^tCN]^+$.

9. Action of heat on π-$C_5H_5Mo(CO)_2N{:}CBu^t_2$

Attempts to form dinuclear complexes: The complex remained unchanged except for a small amount of decomposition, when (a) the solid was heated in a sealed tube *in vacuo* at 120° for 6 hr.; (b) solutions in hexane or diglyme were heated under reflux for 3-4 days; (c) solutions in hexane or ether were irradiated for ca. 1 hr. with a 500 watt Hg lamp.

10. Reaction of π-$C_5H_5Mo(CO)_2N{:}CBu^t_2$ with carbon monoxide

No reaction was detected by i.r. spectroscopy between the complex in hexane solution and carbon monoxide (ca. 1 atmos. pressure) at room temperature or under reflux during 2 hr.

11. Reaction of π-$C_5H_5Mo(CO)_2N{:}CBu^t_2$ with pyridine

Pyridine (0.1 g., 1 mmole) was added to a solution of π-$C_5H_5Mo(CO)_2N{:}CBu^t_2$ (0.12 g., 0.33 mmole) in hexane (10 ml.) and the mixture heated under reflux. No reaction was detected by i.r. spectroscopy after 6 hr.

12. Reaction of π-$C_5H_5Mo(CO)_2N{:}CBu^t_2$ with carbon disulphide

A blue solution was formed on adding carbon disulphide to the complex. No reaction was detected by i.r. spectroscopy after 12 hr. and the complex was recovered unchanged.

13. Reaction of π-$C_5H_5Mo(CO)_2N{:}CBu^t_2$ with sulphur dioxide

Dry sulphur dioxide was condensed onto π-$C_5H_5Mo(CO)_2N{:}CBu^t_2$ (0.12 g., 0.33 mmole) at -196° and on warming, produced a muddy brown solution. A low-temperature i.r. spectroscopic study of the brown solution of the complex in a hexane-sulphur dioxide mixture, showed no change in the $\nu(CO)$ and $\nu(C{:}N)$ regions, and on removal of the solvent from both the sulphur dioxide solution and the hexane-SO_2 solution, the original blue complex was recovered unchanged.

B. Discussion

1. The dicarbonyl complex π-$C_5H_5W(CO)_2N{:}CPh_2$

Diphenylmethyleneaminotrimethylsilane reacts with π-$C_5H_5M(CO)_3X$ (M = Mo or W; X = Cl, Br, I) to form products of two types, π-$C_5H_5M(CO)_2N{:}CPh_2$ and $[\pi$-$C_5H_5M(CO)N{:}CPh_2]_2$. For molybdenum the reaction normally proceeds through to the dinuclear complex, and careful control of the conditions of the reaction are necessary to enable the mononuclear complex to be isolated. The latter can be converted into the dinuclear complex by heat in the solid state or solution. In contrast to molybdenum, the dinuclear tungsten complex was shown by i.r. spectroscopy to lose carbon monoxide more readily than the mononuclear complex, although formed from the latter by heat. In general, therefore, the mononuclear complexes have been studied using the tungsten complex, and the dinuclear using the molybdenum complex.[13]

The introduction of a methyleneamino group into the π-cyclopentadienyl tungsten carbonyl complex results in the loss of one molecule of carbon monoxide. In the mononuclear complex the methyleneamino group may act either as a three-electron donor and conserve the noble gas configuration of the metal, or act as a one-electron donor in which case the noble gas configuration is broken. I.r. spectroscopy and experimental work with the neutral donor molecule, triphenylphosphine, leads us to believe that the group is behaving as a three-electron donor to a single metal.

Infrared spectroscopic data for π-$C_5H_5W(CO)_2N{:}CPh_2$ is shown in Table III.9. Two strong absorptions in the carbonyl stretching region were observed at relatively low frequencies compared with the starting materials. Loss of carbon monoxide and the consequent increase in π-bonding between the metal and remaining carbonyl groups are unlikely to account alone for the significant changes in stretching frequencies observed when one anionic group is replaced by a similar bonding group. Indeed the positions of absorption are entirely

Table III.9

Infrared absorptions $\nu(CO)$ and $\nu(CN)$ (cm^{-1}) for methyleneamino complexes of Molybdenum and Tungsten

Compound	$\nu(CO)$ (KBr)	$\nu(CO)$ (Nujol)	$\nu(C{:}N)$ (Nujol)
$Ph_2C{:}NH$			1603
$\pi\text{-}C_5H_5Mo(CO)_2NCPh_2$		1920s, 1856s	1534m
$\pi\text{-}C_5H_5W(CO)_2NCPh_2$		1942s, 1873s	1587m
$PhBu^tC{:}NH$			1618
$\pi\text{-}C_5H_5Mo(CO)_2NCPhBu^t$	1942s,1855s,1825w	1965sh,1940s 1881sh,1846s 1821w	1636m-s
$\pi\text{-}C_5H_5W(CO)_2NCPhBu^t$	1931s,1836s,1810w	1951sh,1929s 1869sh,1835s 1808w	1634m-s
$Bu^t_2C{:}NH$			1610
$\pi\text{-}C_5H_5Mo(CO)_2NCBu^t_2$	1946s,1848s	1968s,1949s 1884s,1851s	1618m-w
$\pi\text{-}C_5H_5W(CO)_2NCBu^t_2$	1934s,1834s	1946sh,1929s 1866sh,1833s	1620m-w

consistent with the methyleneamino-group acting as a three-electron donor.[297] The $\nu(C{:}N)$ absorption for the complex occurs at low frequency compared with free diphenylmethyleneamino and its lithio-derivative. Conclusions concerning the extent of π-bonding between nitrogen and the transition metal cannot be made at this stage on the basis of the $\nu(C{:}N)$ frequency.

It is however relevant that multiple bonding involving the nitrogen lone-pair to carbon, boron, and beryllium results in a significant increase in the corresponding frequencies,[298] in the opposite direction to that observed for transition-metal complexes. The high frequency absorptions are thought to be diagnostic of a linear skeleton,[298] which allows maximum overlap of nitrogen 2p-orbitals with vacant orbitals of the co-ordinating group. Such a criterion is not possible for the transition-metal systems studied, although a linear structure also allows maximum overlap with the nitrogen p-orbital, as well as overlap with the π^*-orbitals (Fig.I.4). This latter interaction appears to be the main factor in the differing behaviour of methyleneamino-derivatives of main group and transition elements, and the lowering of the ν(C:N) frequency for the latter is believed to be due to this $d\pi$-π^* back donation. The involvement of the nitrogen lone-pair in the bonding to the metal is indicated by the ν(CO) frequency, and Ebsworth[12] has shown that considerable π-bonding is still possible for systems (particularly of silicon) with a bent skeleton when the lone-pair is in a hybrid orbital (Fig.I.2b). Since this type of π-bonding tends to raise th ν(C:N) frequency, there may be a correlation between ν(C:N) and the availability of the lone-pair to bridge to a second metal. The greater ease of dimerisation for the molybdenum complex is in keeping with its low ν(C:N) frequency.

In the ^{1}H n.m.r. spectra the signals arising from the phenyl protons are broad and unresolved, but occur at typical τ values for this group. For the molybdenum complex two cyclopentadienyl signals are observed[13] in contrast to the single signal for the tungsten complex. The reason for the two signals is not fully understood at this stage and studies are continuing to resolve this problem.

2. The dinuclear complex $[\pi\text{-}C_5H_5W(CO)N:CPh_2]_2$

Loss of carbon monoxide from the mononuclear complexes and dimerisation occurred with heat, both in the solid state and in solution, the products being air-sensitive solids having limited solubility in polar organic solvents. They are both reasonably thermally stable, darkening 200° before melting with decomposition at about 300°. The i.r. spectra in the ν(CO) frequency region, recorded in Table III.9, consist, for the molybdenum complex of a single strong absorption with a weak shoulder to low frequencies,[13] and for the tungsten complex, of two strong absorptions. Both spectra are consistent with dinuclear complexes containing two carbonyl groups, the former with the carbonyl groups in the trans-position and the latter with the carbonyl groups in the cis-position. No absorption can be assigned to $\nu(C{:}N)$, and although a weak band occurs at 1600 cm^{-1}, it is thought to arise from phenyl groups, by comparison with spectra of other diphenylmethyleneamino-derivatives. Unlike derivatives with methyleneamino-groups attached to main group elements for which strong absorptions due to CN stretching vibrations are commonly observed,[299] derivatives of the transition metals are characterised by weak absorptions which are difficult to differentiate from other absorptions in this region.

The ^1H n.m.r. spectrum in deuteriochloroform solution consists of a sharp singlet at 4.64τ (relative intensity 1), which clearly originates from the π-C_5H_5 group[300] and a multiplet centred at 2.63τ (relative intensity 2) originating from the $:CPh_2$ unit.[299] The nuclear complexity of the complex was investigated by mass spectroscopy. The parent ion corresponded to $[\{\pi\text{-}C_5H_5W(CO)N{:}CPh_2\}_2]^+$ and all the ions in the expected breakdown were observed, Table III.2. The isotopic distribution patterns corresponding to the major ions consisted of the basic M_2 pattern,[301] adjusted for the appropriate number of carbon atoms. The primary breakdown path proved by the occurrence of metastable peaks, was by successive loss of two carbonyl groups followed by two phenyl cyanide molecules. The isotopic distribution patterns for most of the ions except M^+ and $(M\text{-}CO)^+$, including the doubly charged ions, are more complex than calculated, and extend to lower mass than expected. This is believed to be a consequence of a secondary breakdown of ions by loss of $H\cdot$ or H_2 and occurs commonly for species with organo-groups in close proximity. The extent of the envelope of peaks, based upon the most intense peak 652 for the tungsten complex, indicates that up to four hydrogen atoms are additionally lost. But the simpler ions at m/e 574 and 588, which correspond to $[\pi\text{-}C_5H_5W_2(Ph)C_5H_4]^+$ or $[(\pi\text{-}C_5H_5)_2W_2C_6H_4]^+$ and $[\pi\text{-}C_5H_5W_2Ph_2H]^+$ respectively, show the normal W_2 isotope pattern after correction for ^{13}C. No mononuclear metal species were detected in the spectrum. Indeed the persistence of dinulcear species is in common with other polynuclear metal carbonyl complexes, where it is found that the metal cluster does not fragment until all the attached groups have been lost.[302] The organic ion of highest mass observed, corresponds to $[Ph_2C{:}N]^+$ and verifies the presence of this group in the complex. Doubly charged ions were observed Table III.2, but their relative intensities were much lower than those of singly charged ions.

π-Cyclopentadienyl-molybdenum and -tungsten complexes normally obey the noble gas rule, and dinuclear complexes either involve a metal-metal bond alone, e.g. $[\pi\text{-}C_5H_5Mo(CO)_3]_2$[238] or a bridging group e.g. $[\pi\text{-}C_5H_5Mo(CO)_2SR]_2$.[165,166] The dinuclear methyleneamino complexes differ from the latter in having only one carbonyl group per metal atom, and this implies either that the molecules are electron deficient or that the metal-metal interactions are equivalent to a double bond. The failure of the complexes to undergo additional reactions with triphenylphosphine even during 48 hr. refluxing in diglyme, and the very ready oxidation by iodine, are suggestive of strong metal-metal interactions. The two most likely structures, Fig.III.1 and Fig.III.2 differ only in the bonding mode of the methyleneamino group. In Fig.III.1 ten electrons are involved in the bridging unit, implying considerable interaction between the metal and nitrogen, and the metal atoms themselves. In structure Fig.III.2, the two $\pi\text{-}C_5H_5M(CO)N{:}CPh_2$ units are held together by a multiple metal-metal bond involving four electrons. Multiple metal-metal bonding has been demonstrated in the complexes $[Mo(CO)_2Ar]_2$ (Ar = C_9H_9[303] or Me_5C_5[304]) in which the two halves of the molecule are bonded solely through a triple metal-metal bond. On the basis of the available data, it is not possible to assign structures Fig.III.1 or Fig.III.2 to the complexes, but for each structure <u>cis</u>- and <u>trans</u>-isomers are possible.

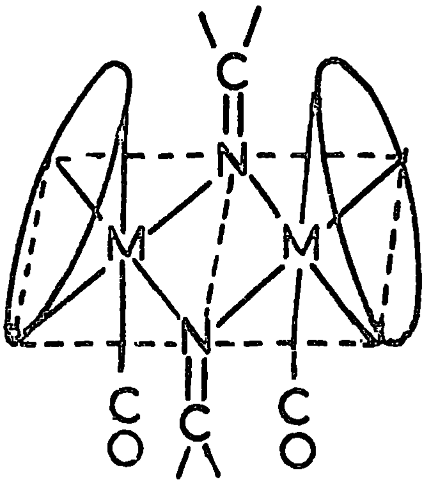


Fig.III.1(a).(cis)

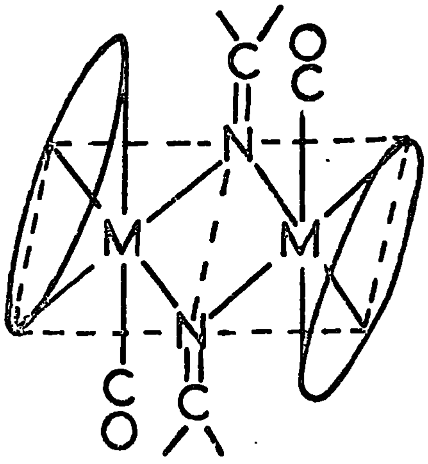


Fig.III.1(b).(trans).

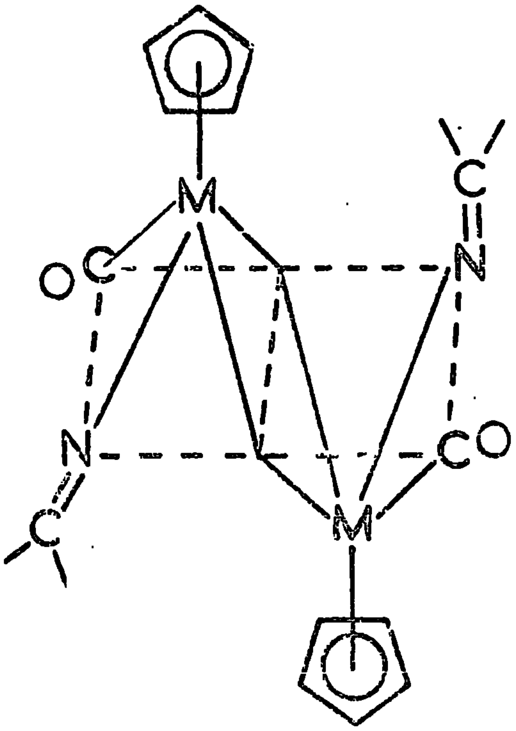


Fig.III.2(a).(a trans-isomer).

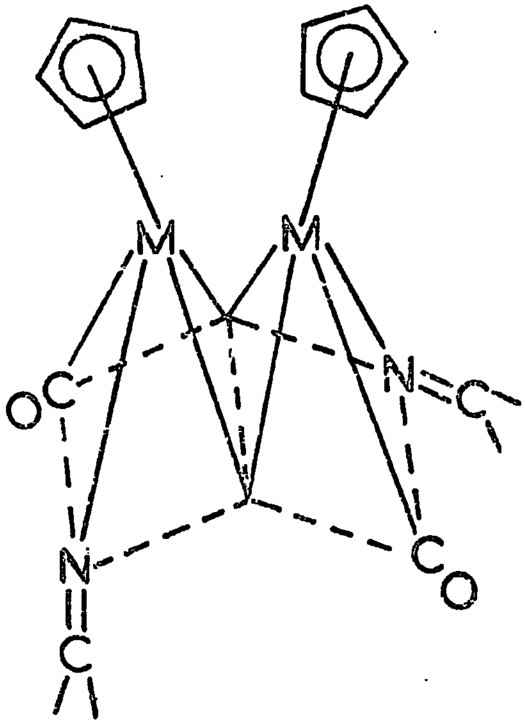


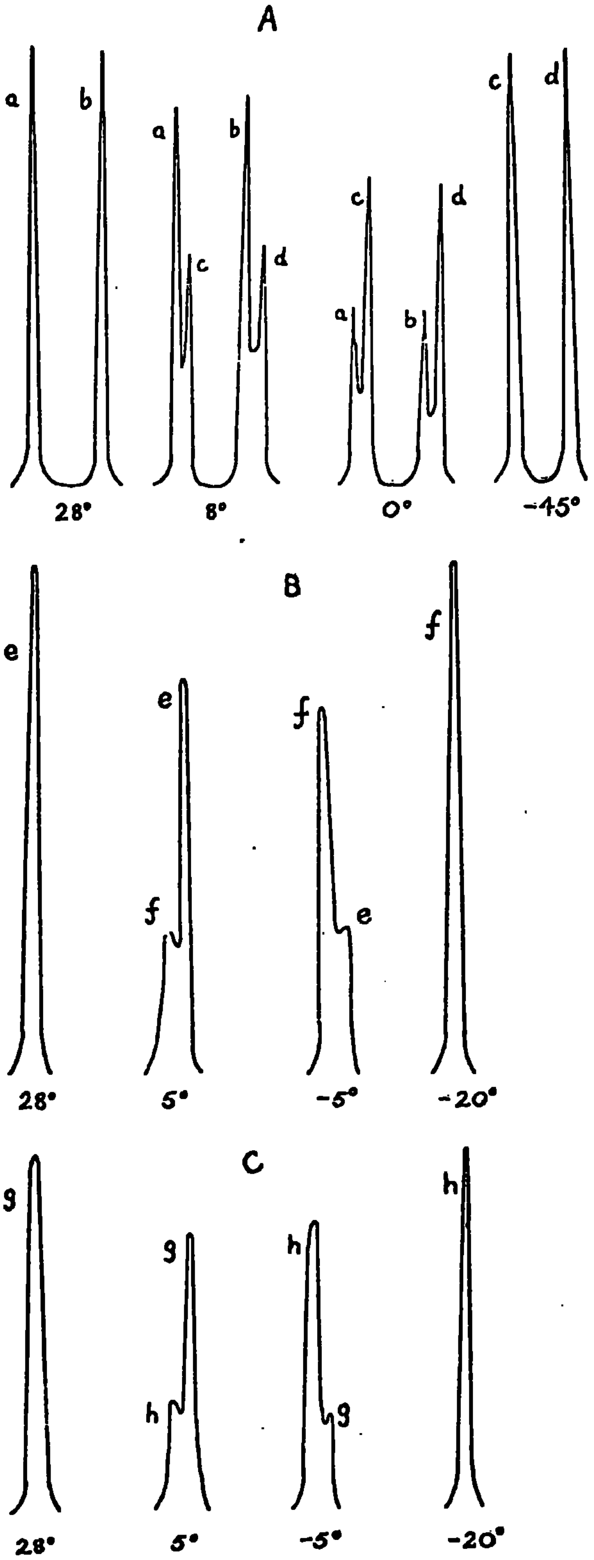
Fig.III. 2(b).(a cis-isomer).

The i.r. spectra in the ν(CO) frequency region may indicate that the molybdenum complex is a cis-isomer and the tungsten complex a trans-isomer.

3. Di-t-butylmethyleneamino complexes π-$C_5H_5M(CO)_2N{:}CBu^t_2$ (M = Mo,W)

Di-t-butylmethyleneamino-groups were introduced into the π-cyclopentadienyl-molybdenum and -tungsten carbonyl complexes using either lithio- or trimethylsilyl-derivatives with the appropriate carbonyl halide. The former method gave moderate yields under controlled conditions, and was preferred to the more vigorous reaction conditions required using $Bu^t_2C{:}NSiMe_3$ which led to the extensive formation of $[\pi\text{-}C_5H_5M(CO)_3]_2$. The products closely resembled the products obtained from the reaction of the carbonyl halide with $PhBu^tC{:}NLi$ and $PhBu^tC{:}NSiMe_3$,[305] and were in contrast to those obtained using $Ph_2C{:}NLi$. No evidence was found for complexes containing a 2-aza-allyl group.[306] Also the dicarbonyl complexes showed no tendency to lose carbon monoxide on heating to form dinuclear complexes.[301] In many respects there was a close similarity between the di-t-butyl and phenyl-t-butyl-methyleneamino derivatives which was reflected in many of their properties.[305] The blue complexes π-$C_5H_5M(CO)_2N{:}CBu^t_2$ (M = Mo and W), which had characteristic camphor-like odours, readily sublimed (85-90° Mo, 100° W; 10^{-3} mm.Hg), but sublimates were often contaminated with a white waxy solid, identified by mass spectroscopy as the azine $Bu^t_2CNNCBu^t_2$ (m/e 280). The tungsten complex, although less air stable than the molybdenum complex, which was unchanged over several weeks, could be handled in the atmosphere for short periods without detectable decomposition, but in solution both complexes decomposed rapidly in air to green, non-carbonyl oils. The complexes, non-electrolytes in nitrobenzene solution, gave freezing point depressions in benzene appropriate for mononuclear formulations.

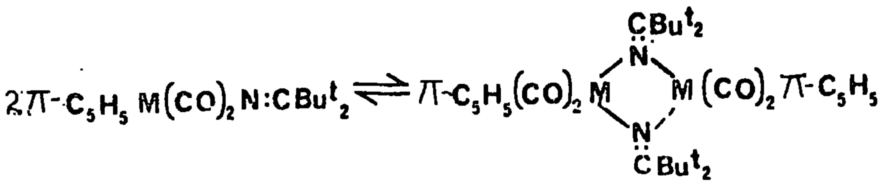
In the carbonyl stretching region of the i.r. spectrum, two strong absorptions occurred for solutions of each complex at ambient temperature but on cooling solutions of the molybdenum complex, the two original absorptions were replaced slowly by two new, lower frequency absorptions Fig.III.3A. At -45°



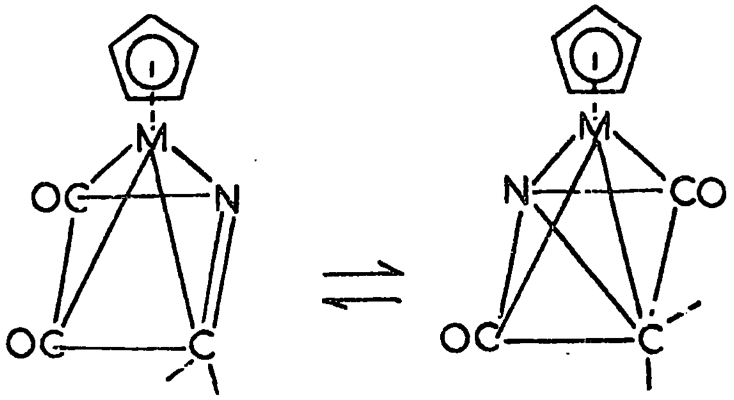
<u>Fig.III.3.</u> Spectra of π-$C_5H_5Mo(CO)_2N{:}CBu^t_2$ at various temperatures. (A) I.r. spectrum in hexane; (B) ^1H n.m.r. spectrum arising from Bu^t groups (τ, e 8.82, f 8.83) in $C_6D_{11}CD_3$; (C) ^1H n.m.r. spectrum arising from the π-C_5H_5 group. (τ, g 4.35, h 4.32) in $C_6D_{11}CD_3$.

only the new absorptions were present, but on warming the change was reversed completely. Changes with temperature occurred also in the ^1H n.m.r. spectrum for both π-C_5H_5 and Bu^t proton signals Table III.4 and Fig.III.3B and C. On cooling a perdeuteriomethylcyclohexane solution of the molybdenum complex, signals at 4.35(5)τ and 8.82(18)τ respectively became weaker in intensity, and new signals appeared at 4.32τ and 8.83τ. The original signals were progressively replaced by the new signals, so that at -20° only the latter were detected. The changes were reversible. Similar changes could not be detected in toluene solution; only two signals were detected over the temperature range +80° to -60°, but the position of the signal did shift slowly with change in temperature Table III.4. In the electronic spectrum no changes were detected on cooling solutions of the molybdenum complex to 0° and -11°. In the mass spectra, parent peaks were observed at masses appropriate for mononuclear species Table III.5 and 8 and isotopic distribution patterns corresponded to those of one metal atom adjusted for the presence of a $C_{16}H_{23}NO_2$ unit. No peaks arising from M_2 species were detected.

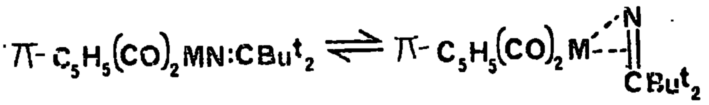
No corresponding changes occurred in the i.r. spectrum of the tungsten complex on cooling solutions from ambient temperatures, but small changes in the position of ^1H n.m.r. signals were detected Table III.7. Two signals were observed at all temperatures, but on cooling from 80° to -80° the π-C_5H_5 signals shifted 0.5 and the Bu^t signal 0.15 p.p.m. to higher field. In contrast to the molybdenum complex in perdeuteromethylcyclohexane no additional signals were detected. Spectral changes in solution with change in temperature may result from structural changes of the following type: (i) a monomer dimer equilibrium (III.1); (ii) geometrical isomerism based upon nine-co-ordination of the metal[307] and a bidentate methyleneamino-group bonding through both nitrogen and carbon (III.2); (iii) linkage isomerism (III.3); (iv) conformational changes about a bent M-N-C skeleton (III.4); (v) rotational changes about the metal-nitrogen bond (III.5). Structural changes (III.1-4) are eliminated on the basis of



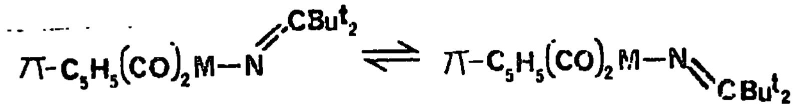
(III.1)



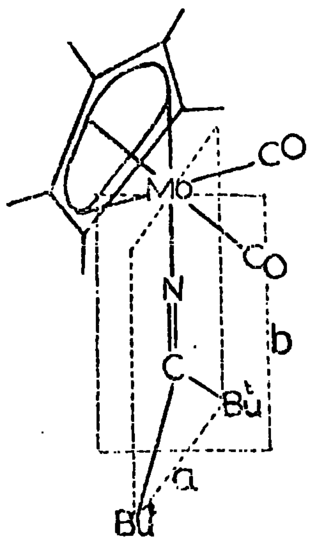
(III.2)



(III.3)



(III.4)

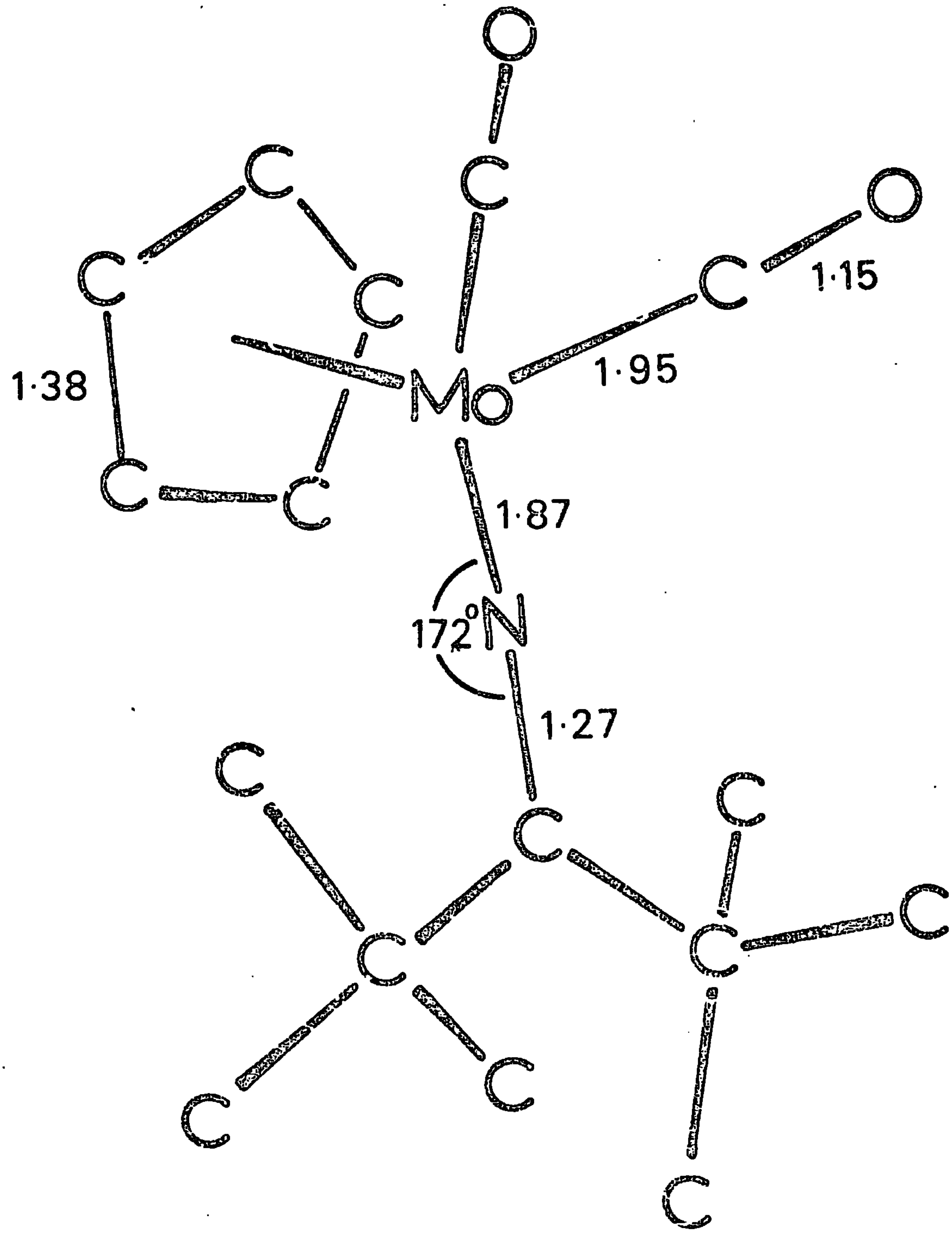


(III.5)

molecular-weight measurements in freezing benzene, ^{1}H n.m.r. spectra, ν(C:N), the absence of change in the electronic absorption spectrum and the steric effects of the Bu^t groups. The structural changes detected are, however, consistent with rotational changes about the metal-nitrogen bond of a complex, having structure (III.5). An approximately linear M-N-C skeleton is indicated by the single ^{1}H n.m.r. signal observed at -60° and confirmed by X-ray structural data on the molybdenum complex Fig.III.4.[308]

Much discussion has occurred on whether nitrogen ligands in complexes of the type π-$C_5H_5M(CO)_2X$ (where X = $RC_6H_4N{:}N$-,[309,310] PhN:N-,[310,311] anthraquinone-N:N-,[310] $Me_3SiCH_2N{:}N$-[312]) act as one- or three-electron donor groups. We believe that the methyleneamino-group acts as a three-electron donor to molybdenum and tungsten on the basis of (i) the effective atomic number rule and the presence of only two carbonyl groups; (ii) the relatively low carbonyl-stretching frequencies; and (iii) the failure of the complex to add a further neutral donor molecule such as pyridine, triphenylphosphine, or carbon monoxide, even under forcing conditions. The short molybdenum-nitrogen bond distance of 1.87Å[308] compared to the average distance of 2.32Å in $Mo(CO)_3[H_2N(CH_2)_2NH(CH_2)_2NH_2]$[313] indicates considerable multiple bonding between the metal and nitrogen, which is believed to involve extensively the p-orbital of nitrogen.

The accumulated spectral data are consistent with only small changes in structure, and are in accordance with conformational changes about a metal-nitrogen bond. The solid state form is thought, on the basis of i.r. data to be the same conformer as the low temperature form and a recent X-ray structural determination[308] has shown this to be the staggered form III.5(a). Staggered conformers have also been detected for π-$C_5H_5Fe(CO)_2SiMeCl_2$,[314] $Mn(CO)_5COCR_3$,[315] and carbene complexes $M(CO)_5CXR$ (M = Cr,W; X = OR', NHR').[316-318] Rotation about the Mo-N bond to form the next sterically favourable form, the staggered conformer III.5(b), appears, on the basis of models, to involve going



<u>Fig.III.4</u> Crystal structure of π-$C_5H_5Mo(CO)_2N:CBu^t_2$

through the most sterically unfavourable eclipsed form. Thus, on rotation the highest energy barrier is possibly overcome, and the higher temperature form may either be the staggered conformer III.5(b) or some other rotamer. Rotation about the multiple metal-nitrogen bond is theoretically possible, in the same way as postulated for the carbene group, because of the π-cylindrical symmetry of the metal orbitals.[319] The methyleneamino- and carbene groups each have a vacant p-orbital for π-bonding on the donating atoms, if carbon of the carbene donates two electrons,[316] and nitrogen of the methyleneamino-group three electrons to the metal. Thus, the methyleneamino- and carbene-groups in this sense are related in the same way as carbonyl and nitrosyl groups.

The absence of changes in the i.r. spectrum of the tungsten complex or the phenyl-t-butyl[305] or di-p-tolyl[320] complexes with change in temperature (+60 to -60°) and the shift in ^{1}H n.m.r. signals to higher field in the π-$C_5H_5W(CO)_2N{:}C$-Bu^t_2 complex, suggests that if similar conformational changes occur to those of the molybdenum complex, the rotational process may be much more rapid and may require a significantly lower energy. This may arise because of the slightly different sizes of the metals, which for tungsten will reduce the steric interactions between the t-butyl groups and the remainder of the complex, particularly the π-cyclopentadienyl group. Interconversion of tungsten conformers appears to be rapid at the temperatures of the measurements, and a time average signal is observed. However at the lower temperatures the signal moves to higher field, and then possibly denotes a greater contribution from conformer III.5(a).

The ν(CN) stretching frequencies remain little changed from those of the free methyleneamine (1610 cm^{-1}). Bonding to carbon, boron, beryllium, aluminium, and silicon results in a significant increase in the corresponding frequency, and is believed to be indicative of linear skeletons in $R_2C{:}N{:}X$ systems where X = $\overset{+}{C}R_2$, BR'_2, BeR', $Al(NCR_2)_2$ and $SiMe_3$.[15,298,321] As the co-ordinating element becomes heavier, $\Delta\nu$, the difference between ν(CN) for the complex and ν(CN) for the free methyleneamine, becomes less,[15] and the small changes for transition-metal derivatives are in keeping with this trend. Thus, the overall process of σ, dπ-pπ, and dπ-pπ^* bonding leaves the ν(CN) little changed from that of the methyleneamine. The first two types of interaction produce electron donation to, and the last, produces electron withdrawal from the metal. The process of σ and lone-pair donation causes ν(CN) to move to higher energy,[15] and since ν(CN) for transition-metal derivatives remains little changed, dπ-π^* bonding may effectively balance the donation process.

CHAPTER IV

REACTIONS OF METHYLENEAMINO-DERIVATIVES OF π-CYCLOPENTADIENYL-MOLYBDENUM AND -TUNGSTEN CARBONYLS

This chapter describes the reactions of the methyleneamino-derivatives of molybdenum and tungsten with triphenylphosphine and iodine. The aim of these experiments was to effect carbonyl substitution or oxidation of the parent methyleneamino-compounds and to investigate the effect of the new ligands on the $>$C:N system.

A. Experimental

1. Reaction of π-$C_5H_5W(CO)_2N:CPh_2$ with triphenylphosphine

No reaction was detected in refluxing-monoglyme during 24 hr.

2. Reaction of π-$C_5H_5Mo(CO)_2N:CBu^t{}_2$ with triphenylphosphine

(i) In hexane. No reaction was detected by i.r. spectroscopy between π-$C_5H_5Mo(CO)_2N:CBu^t{}_2$ (0.36 g., 1 mmole) and triphenylphosphine (0.26 g., 1 mmole) in refluxing hexane solution (20 ml.) during 96 hr. The reactants were recovered unchanged.

(ii) In monoglyme. π-$C_5H_5Mo(CO)_2N:CBu^t{}_2$ (0.36 g., 1 mmole) and triphenylphosphine (0.53 g., 2 mmole) were heated in boiling monoglyme (30 ml.). Gas was evolved and the solution slowly became red-brown. After 6 hr. the reaction mixture was filtered from non-carbonyl decomposition material, and the filtrate reduced to small bulk (20°, 0.1 mm.Hg). Addition of hexane (10 ml.) produced small red-orange crystals of π-$C_5H_5Mo(CO)(Ph_3P)_2H$ in very small yield (1%).

Properties: The red-orange solid (m. 150-3° (decomp.)) was quite air stable; a sample exposed to air for a few days showed virtually no change in its i.r. spectrum. The solid was insoluble in hexane, benzene and toluene and moderately soluble in ether and chloroform.

Analysis: Found, C,68.5; H,5.15; $C_{42}H_{36}MoOP_2$ requires C,70.4; H,5.05%.

Infrared spectrum (Nujol): The solid gave a yellow mull. ν(CO), 1802s cm^{-1}.

The full Nujol spectrum is: 1997w, 1802s, 1618w, 1183w, 1160w, 1089m, 1099sh, 1070w, 1029w, 1010w, 807m, 794, 740m, 752sh, 748sh, 719w,br, 703sh, 693s, 683sh, 625w,br, 610w,br, 570m,br, 535m,br, 518s,br, 509m,br, 495m,br, and 475w,br cm^{-1}.

^{1}H n.m.r. spectrum ($CDCl_3$): showed a sharp singlet at 4.57(1)τ due to the π-C_5H_5 protons, and a multiplet centred at 2.60(6)τ arising from the phenyl groups of Ph_3P.

Mass spectrum (direct insertion probe at source temperature): The major peaks in the spectrum are listed in Table IV.1, and the precise mass measurements in Table IV2.

3. Reaction of π-$C_5H_5Mo(CO)_2N{:}CBu^t_2$ with triphenylphosphine

The complex π-$C_5H_5Mo(CO)_2N{:}CBu^t_2$ (0.24 g., 0.7 mmole) and triphenylphosphine (0.352 g., 1.3 mmole) were heated in carbon tetrachloride solution (50 ml.) under reflux for 10 min. to give a brown-red precipitate. The solid was filtered off, washed with hexane, and dried in vacuo to give brown-yellow microcrystals of $[PPh_3Bu^t][\pi\text{-}C_5H_5MoCl_4]$. Yield 0.34 g. (77.2%).

Properties: The complex was air, moisture, and thermally stable at ambient temperatures. It was soluble in acetone and chloroform and insoluble in ethers, paraffins, benzene, toluene and water, and melted with decomposition in a sealed tube at 104-5°.

Analysis: Found, C,51.5; H,4.65; $C_{25}H_{29}Cl_4MoP$ requires C,51.8; H,4.65%.

Infrared spectrum (Nujol): ν(max), 1686m, 1587m, 1572m,sh, 1244m,br, 1168m, 1110s, 1053m, 999m, 978m, 944m, 906m, 800w,br, 752m,br, 725s,br, 692s,br, 616w,br, 583w,br, 541s,br, and 521s,br cm^{-1}.

^{1}H n.m.r. spectrum ($CDCl_3$): very weak broad peaks were observed at 2.44τ and 8.84τ due to the phenyl groups and Bu^t respectively.

Mass spectrum: No spectrum could be obtained.

Conductivity: Measurements were made in nitromethane and acetone, at room temperature, and infinite dilution, the results obtained are tabulated in Table IV.3.

Table IV.1

Mass spectral data for π-$C_5H_5Mo(CO)(PPh_3)_2H$

Ion	m/e	m*	Fragment lost
$[\pi\text{-}C_5H_5Mo(CO)(Ph_3P)_2H]^+$	714		
		659	CO
$[\pi\text{-}C_5H_5Mo(Ph_3P)_2H]^+$	686		
		261	Ph_3PH
$[\pi\text{-}C_5H_5Mo(Ph_3P)]^+$	423		
		281	C_6H_6
$[\pi\text{-}C_5H_5Mo(PC_{12}H_9)]^+$	345		
		133	Ph_2PH
$[\pi\text{-}C_5H_5Mo(C_6H_4)]^+$	237		
		262	Ph_3P
$[\pi\text{-}C_5H_5Mo(Ph_3P)H]^+$	424		
		539	C_6H_6
$[\pi\text{-}C_5H_5Mo(Ph_3P)(PC_{12}H_9)H]^+$	608		
		411	PC_6H_5
$[\pi\text{-}C_5H_5Mo(Ph_3P)Ph]^+$	500		

Table IV.2.

Precise mass measurements for π-$C_5H_5Mo(CO)(Ph_3P)_2H$

Measured mass	Possible formula	Calculated mass*	Error (p.p.m.)
713.1304	π-$C_5H_5{}^{95}Mo(CO)(Ph_3P)_2H$	713.1304	0.00
	π-$C_5H_5{}^{96}Mo(CO)(Ph_3P)_2$	713.1225	11.1
714.1290	π-$C_5H_5{}^{96}Mo(CO)(Ph_3P)_2H$	714.1303	1.8
	π-$C_5H_5{}^{97}Mo(CO)(Ph_3P)_2$	714.1236	9.0
715.1310	π-$C_5H_5{}^{97}Mo(CO)(Ph_3P)_2H$	715.1314	0.55
	π-$C_5H_5{}^{98}Mo(CO)(Ph_3P)_2$	715.1227	11.6
716.1296	π-$C_5H_5{}^{98}Mo(CO)(Ph_3P)_2H$	716.1306	1.4
	π-$C_5H_5Mo(CO)(Ph_3P)_2$	716.1256	5.6
717.1330	π-$C_5H_5Mo(CO)(Ph_3P)_2H$	717.1334	0.55
	π-$C_5H_5{}^{100}Mo(CO)(Ph_3P)_2$	717.1249	11.3
718.1316	π-$C_5H_5{}^{100}Mo(CO)(Ph_3P)_2H$	718.1327	1.5
	π-$C_5H_5Mo(CO)(PPh_3)_2$	718.1274	5.8

* Atomic mass of Mo isotopes: 91.906290, 93.904740, 94.90572, 95.904550, 96.905750, 97.905510, and 99.907570.

Table IV.3

Conductivity measurements for $[PPh_3Bu^t][\pi\text{-}C_5H_5MoCl_4]$

Solvent	Concentration (M)	ΔM (ohm^{-1}cm^{2}mole^{-1})
Nitromethane	9.70×10^{-6}	90.29
Acetone	7.46×10^{-6}	165.29

4. Reaction of $\pi\text{-}C_5H_5Mo(CO)I_2N{:}CBu^t{}_2$ with triphenylphosphine

The complex $\pi\text{-}C_5H_5Mo(CO)I_2N{:}CBu^t{}_2$ (0.58 g., 1 mmole) and triphenylphosphine (0.52 g., 2 mmole) were heated together in monoglyme under reflux. After 30 min., when the solution had changed colour from green-yellow to red-brown, it was evaporated to dryness (20°, 10^{-1} mm.Hg) and the residue was washed with light petroleum (3 x 20 ml.). Recrystallisation of the product from acetone yielded red-brown micro-crystals of $[PPh_3Bu^t][\pi\text{-}C_5H_5Mo(PPh_3)I_2]$ (0.32 g., 32%).

Properties: The complex was air, moisture and thermally stable at ambient temperatures. It was soluble in acetone and chloroform and insoluble in ethers and hydrocarbon solvents. On heating in a sealed tube it melted with decomposition at 98-99°.

Analysis: Found, C,54.0; H,4.4; $C_{45}H_{44}I_2MoP_2$ requires C,54.0; H,4.4%.

Infrared spectrum (Nujol): ν(max), 1587w, 1550w, 1156m, 1112s, 1089m, 1070m, 1026mw, 990mw, 962m, 896m, 760m, 745m, 719s, 688m,br, 614w, 555br,sh, 539m,br, 509m,br, 499m,br, and 483m,br cm^{-1}.

Conductivity: Measurements were made in nitromethane and acetone, at room temperature, and infinite dilution; the results obtained are tabulated in Table IV.4.

Mass Spectrum: No spectrum could be obtained even at extreme source temperatures.

Table IV.4.

Conductivity measurements for $[PPh_3Bu^t][\pi\text{-}C_5H_5Mo(PPh_3)I_2]$

Solvent	Concentration (M)	Λm ($ohm^{-1}cm^2mole^{-1}$)
Nitromethane	7.63×10^{-6}	86.92
Acetone	5.98×10^{-6}	151.98

^1H n.m.r. spectrum ($CDCl_3$): very weak broad peaks were observed at 2.48τ and 8.89τ due to the phenyl groups and Bu^t groups respectively.

5. Reaction of $\pi\text{-}C_5H_5W(CO)_2N{:}CPh_2$ with iodine

Addition of a solution of iodine (0.13 g., 1.0 mmole) in monoglyme (10 ml.) to $\pi\text{-}C_5H_5W(CO)_2N{:}CPh_2$ (0.24 g., 0.5 mmole) also in monoglyme (20 ml.) at room temperature caused gas evolution and a darkening of the solution. After 1 hr. the solvent was removed in vacuo, and the residue was extracted with chloroform (20 ml.). Hexane (30 ml.) was added to the solution which was then cooled to -20° to give emerald green crystals in low yield.

Properties: The emerald green crystalline solid is waxy in appearance, and gives a bright purple powder on grinding. It is relatively stable in air and decomposes without melting ca. 320°. The crystals are insoluble in hexane and hydrocarbon solvents and moderately soluble in chloroform and ethers.

Analysis: Found, C,14.95; H,1.30; $C_{15}H_{15}I_3O_4W_3$ requires C,15.10; H,1.25%.

Infrared spectrum (Nujol): ν(max), 3077w, 1408m, 1333w, 1253m, 1075m, 1029m, 1015m, 981s, 892m, 862m, 847m, 794m cm^{-1}.

Mass Spectrum (direct insertion probe at source temperature): The parent ion $[(\pi\text{-}C_5H_5)_3W_3I_3O_4]^+$ (m/e 1192) was observed together with the other ions listed in Table IV.5. The isotopic distribution pattern corresponding to the parent ion was consistent with the basic W_3 pattern, adjusted for the presence of fifteen carbon atoms. Other isotopic patterns observed were consistent with those of W_2 and W adjusted for the appropriate carbon content.

Table IV.5

Mass spectral data for $(\pi\text{-}C_5H_5)_3W_3I_3O_4$

Ion	m/e	Ion	m/e
$[(\pi\text{-}C_5H_5)_3W_3I_3O_4]^+$	1192	$[\pi\text{-}C_5H_5WIO]^+$	392
$[(\pi\text{-}C_5H_5)_2W_2I_2O_3]^+$	800	$[\pi\text{-}C_5H_5WI]^+$	376
$[(\pi\text{-}C_5H_5)_2W_2IO_3]^+$	673	$[(\pi\text{-}C_5H_5)_2W]^+$	314
$[(\pi\text{-}C_5H_5)_3W_2]^+$	563	$[\pi\text{-}C_5H_5WO_2]^+$	281
$[\pi\text{-}C_5H_5WI_2O]^+$	519	$[\pi\text{-}C_5H_5WO]^+$	265
$[(\pi\text{-}C_5H_5)_2WI]^+$	441	$[\pi\text{-}C_5H_5W]^+$	249
$[\pi\text{-}C_5H_5WIO_2]^+$	408		

.6. Reaction of $[\pi\text{-}C_5H_5W(CO)N{:}CPh_2]_2$ with iodine

The reaction of $[\pi\text{-}C_5H_5W(CO)N{:}CPh_2]_2$ (0.23 g., 0.25 mmole) and iodine (0.032 g., 0.25 mmole) in monoglyme (30 ml.) proceeds as described above. The product was obtained in very small yield as emerald green crystals. Analysis: Found, C,15.0; H,1.30; $C_{15}H_{15}I_3O_4W_3$ requires C,15.1; H,1.25%.

7. Reaction of $\pi\text{-}C_5H_5Mo(CO)_2N{:}CBu^t_2$ with iodine

Iodine (0.25 g., 2 mmole) in hexane (40 ml.) was added dropwise to a blue solution of $\pi\text{-}C_5H_5Mo(CO)_2N{:}CBu^t_2$ (0.36 g., 1 mmole) in hexane (10 ml.). Green microcrystalline needles of the product separated and slow evolution of gas occurred. The product was separated from the faintly green solution, washed with hexane, dried, and characterised as $\pi\text{-}C_5H_5Mo(CO)I_2N{:}CBu^t_2$. Yield 80%. Properties: The green-brown microcrystalline solid appeared to be quite air sensitive. The solid was insoluble in hexane but very soluble in chloroform.

On heating in a sealed tube it decomposed without melting at 210-212°.

Analysis: Found, C,30.90; H,3.90; N,2.40; I,43.80; $C_{15}H_{23}I_2MoNO$ requires C,30.90; H,3.95; N,2.40; I,43.60%.

Infrared spectrum (Nujol): The solid gave a yellow green mull. ν(CO), 2027s, cm^{-1} (Nujol), 2035 cm^{-1} ($CHCl_3$); ν (CN), 1639w,br, cm^{-1} (Nujol).

The full Nujol mull spectrum is: 2027s, 1693m-w,br, 1408, 1258vw, 1258vw, 1208s, 1220sh, 1064m, 1036m, 1010m, 971ms, 935w, 885m, 834s, 848sh, 855sh, 735w, 719w, 694m, 588m, 575m, 513s,br, 470s,br, 446s,br, and 429m,br cm^{-1}.

Conductivity: non-electrolyte in nitrobenzene.

Molecular weight: (586) cryoscopically in benzene. (Th.583).

^{1}H n.m.r. spectrum ($CDCl_3$): showed signals at 4.33(5), 8.58(9), 8.87(9)τ due to π-C_5H_5 and Bu^t protons respectively.

Mass spectrum (direct insertion probe at source temperature): The parent ion $[\pi\text{-}C_5H_5Mo(CO)I_2N{:}CBu^t{}_2]^+$ (m/e 583) was not observed even with a cool source temperature. The ion of highest mass (m/e 555) corresponded to $[\pi\text{-}C_5H_5MoI_2N{:}CBu^t{}_2]^+$ with the isotopic distribution pattern appropriate for $C_{14}H_{23}I_2MoN$. The major peaks observed in the spectrum are listed in Table IV.6.

8. Reaction of π-$C_5H_5W(CO)_2N{:}CBu^t{}_2$ with iodine

Iodine (0.25 g., 2 mmole) and π-$C_5H_5W(CO)_2N{:}CBu^t{}_2$ (0.45 g., 1 mmole) when reacted as above gave green crystals of π-$C_5H_5W(CO)I_2N{:}CBu^t{}_2$ in 60% yield.

Properties: The olive green microcrystalline solid was stable in air for short periods. On prolonged exposure (one day) the solid obtained a brown coating and decomposition occurred. The solid was insoluble in hexane but very soluble in chloroform. On heating in a sealed tube the complex did not melt but darkened slowly at 140° before decomposing at 220°.

Analysis: Found, C,26.7; H,3.40; N,2.05; I,37.8; $C_{15}H_{23}I_2WNO$ requires C,26.8; H,3.45; N,2.10; I,37.8%.

Infrared spectrum: The solid gave a yellow-green mull with Nujol. ν(CO), 200s, 1978sh cm^{-1} (Nujol), 2014s cm^{-1} ($CHCl_3$); ν(CN), 1640w,br cm^{-1} (Nujol).

Table IV.6

Mass spectral data for π-$C_5H_5Mo(CO)I_2N{:}CBu^t_2$

Ion	m/e	m*	Fragment lost
$[\pi\text{-}C_5H_5MoI_2N{:}CBu^t_2]^+$	555		
		447	Bu^t
$[\pi\text{-}C_5H_5MoI_2N{:}CBu^t_2]^+$	498		
		346	Bu^tCN
$[\pi\text{-}C_5H_5MoI_2]^+$	415		
		276	I
$[\pi\text{-}C_5H_5MoIN{:}CBu^t]^+$	371		
		224	Bu^tCN
$[\pi\text{-}C_5H_5MoI]^+$	288		
		90	I
$[\pi\text{-}C_5H_5Mo]^+$	161		
		200	I
$[\pi\text{-}C_5H_5MoI]^+$	288		

The full Nujol spectrum is: 3086m, 3067m,sh, 1488s, 1408m, 1366s, 1261m, 1230m, 1215m, 1099m,br, 1064w, 1042w, 1018w, 1010w, 990w, 981m, 935m, 877w,br, 862w, 855w, 841m,sh, 834s, 827w, 807w,br, 699w, 592w, 575m,br, 524m,br, and 481m,br cm^{-1}.

^1H n.m.r. spectrum ($CDCl_3$): signals at 4.23(5), 8.60(9) and 8.82(9)τ were observed due to π-C_5H_5 and Bu^t protons.

Mass spectrum (direct insertion probe at source temperature): No parent ion could be detected, the highest mass peak corresponding to the $(P\text{-}CO)^+$ ion. The isotopic distribution pattern was appropriate for $C_{14}H_{23}I_2WN$. The major peaks in the spectrum are listed in Table IV.7.

Table IV.7

Mass spectral data for π-$C_5H_5W(CO)I_2N:CBu^t{}_2$

Ion	m/e	m*	Fragment lost
$[\pi\text{-}C_5H_5WI_2N:CBu^t{}_2]^+$	643		
		534	Bu^t
$[\pi\text{-}C_5H_5WI_2N:CBu^t]^+$	586		
		432	Bu^tCN
$[\pi\text{-}C_5H_5WI_2]^+$	503		
		360	I
		281	I
$[\pi\text{-}C_5H_5WI(N:CBu^t)]^+$	459		
		308	Bu^tCN
$[\pi\text{-}C_5H_5WI]^+$	376		
		165	I
$[\pi\text{-}C_5H_5W]^+$	249		

B. Discussion

1. The phosphine complexes

Substitution of triphenylphosphine for carbon monoxide could not be achieved for diphenyl-, di-p-tolyl-, nor di-t-butyl-methyleneamino derivatives, but for the mixed phenyl-t-butyl molybdenum complex substitution occurred under relatively mild conditions to produce the complex π-$C_5H_5Mo(CO)(Ph_3P)N{:}CPhBu^t$.[305] The corresponding tungsten complex failed to react.[305] With the di-t-butyl-methyleneamino-derivative of molybdenum no reaction occurred in refluxing hexane solution during several days, thus suggesting co-ordinative saturation of the metal, but in carbon tetrachloride and monoglyme reactions did occur which involved the solvent as a reactant. $[Ph_3PBu^t][\pi\text{-}C_5H_5MoCl_4]$ and π-$C_5H_5Mo(CO)(PPh_3)_2H$ respectively were isolated in small quantities. Formulation of the former as an ionic complex was confirmed by i.r. spectroscopy and by electrical conductivity measurements in acetone solution which indicated a 1:1 electrolyte at infinite dilution. Absorptions at 1110s, 944m, 906m, 725sbr, cm^{-1} indicated the presence of the phosphonium cation.[322,323] Formation of the triphenylphosphine-monoglyme reaction product as π-$C_5H_5Mo(CO)(PPh_3)_2H$ was made on the basis of precise mass measurements on six isotopic components arising for the parent ion. The computed masses for this molecule and for π-$C_5H_5Mo(CO)(PPh_3)_2$ are compared with the experimentally determined masses in Table IV.2 and shown to correspond with the hydride to within ± 2 p.p.m. Since the computed masses for the non-hydrido complex differ from the experimentally determined masses, to an extent (av. 9 p.p.m.) outside the estimated limits of accuracy of the measurements the latter formulation was eliminated. The presence of hydrogen was not detected by other spectroscopic and chemical tests. No absorption could be assigned to the $\nu(M\text{-}H)$ in the i.r. spectrum, nor could we detect a signal in the ^1H n.m.r. at $\tau > 10$. Unlike many metal hydrides[324] the complex dissolved in carbon tetrachloride without change. The ^1H n.m.r. signals associated with the π-C_5H_5 and Ph protons did however indicate that the complex was diamagnetic.

2. Iodine complexes $(\pi\text{-}C_5H_5)_3W_3I_3O_4$

Iodine reacts with $\pi\text{-}C_5H_5W(CO)_2N{:}CPh_2$ and $[\pi\text{-}C_5H_5W(CO)N{:}CPh_2]_2$ in monoglyme at room temperature, with loss of all the carbonyl and methyleneamino-groups. Emerald green crystals of $(\pi\text{-}C_5H_5)_3W_3I_3O_4$, which produce purple mulls in Nujol, were isolated in small yield. In the i.r. spectrum, absorptions typical of $\pi\text{-}C_5H_5$ groups were observed, together with a very strong band at 981 cm^{-1} assigned to $\nu(W{:}O)$,[325] and a medium intensity absorption at 794 cm^{-1} assigned to a ν(W-O-W) vibration.[326] In the mass spectrum Table IV.5, the isotopic distribution pattern corresponding to the parent ion was consistent with the basic W_3 isotope pattern adjusted for the presence of 15 carbon atoms; other isotopic patterns were consistent with those of W_2 and W units adjusted for appropriate carbon content. On the basis of these arguments, and the known tendency of halogen ions in polynuclear metal systems to bridge,[327] structure Fig.IV.1 is tentatively assigned to the complex.

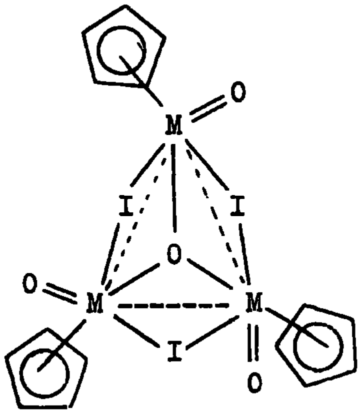


Fig.IV.1

A similar complex $(\pi\text{-}C_5H_5)_3Mo_3I_3O_4$ was obtained from the reaction of $[\pi\text{-}C_5H_5Mo(CO)N{:}CPh_2]_2$ with iodine.[13]

3. The iodine complexes π-$C_5H_5M(CO)I_2N:CBu^t{}_2$ (M = Mo,W)

Iodine displaces one carbonyl group in the complexes π-$C_5H_5M(CO)_2N:CBu^t{}_2$, (M = Mo,W) producing the complexes π-$C_5H_5M(CO)I_2N:CBu^t{}_2$, and similar products are obtained from the mixed arylalkylmethyleneamino complexes.[305] No parent ions were detected in the mass spectra; the peak of highest mass corresponded to $[P-CO]^+$ even at low source temperature (Table IV.6). Co-ordination of the electronegative halogens effectively decreases the electron density on the metal which will favour an increase in σ and dπ-pπ donation but a reduction of dπ-π* bonding to both carbonyl and methyleneamino-groups. Thus ν(CO) and ν(CN) consequently increase compared with the original derivatives (Table III.9). Introduction of electronegative groups into the complex is unlikely to alter the bonding mode of the methyleneamino-group. Indeed the effect of the iodines will be to increase dπ-pπ bonding between nitrogen and the metal, which is most effective when the M-N-C skeleton is linear. Thus, the two sharp signals observed in the ^1H n.m.r. spectrum for the t-butyl groups are thought to arise not from conformations about the metal nitrogen axis, but from different environments of the two t-butyl groups in a nine co-ordinate structure. A cis geometrical arrangement of iodine atoms may give rise to two Bu^t signals in the ^1H n.m.r. spectrum, if the methyleneamino-group is linearly bound, as illustrated in Fig.IV.2. Other geometrical arrangements require either a bent

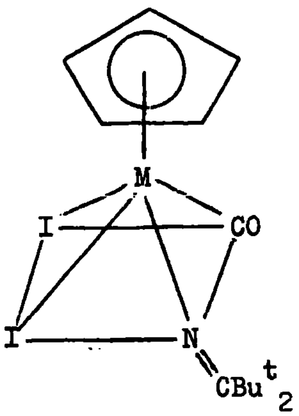


Fig.IV.2

M-N-C skeleton or a particular alignment of the plane of the methyleneamino-group to give rise to two signals.

Addition of triphenylphosphine to the molybdenum iodine complex, or replacement of carbon monoxide could not be achieved in hexane during several days under reflux, but in boiling monoglyme a red-orange crystalline, air- and moisture-stable product was obtained. I.r. spectroscopy indicated the loss of carbon monoxide and methyleneamino-groups, but the presence of Bu^t groups was shown by ^1H n.m.r. spectroscopy. Electrical conductivity measurements in nitrobenzene showed the complex to be a 1:1 electrolyte, and on the basis of analytical and spectroscopic data the complex is formulated as $[Ph_3PBu^t][\pi-C_5H_5Mo(PPh_3)I_2]$. I.r. absorptions at 1112s, 962m, 896m, and 719s are consistent with the presence of a phosphonium cation.[322,323] Here as in the preparation of the $[Ph_3PBu^t][\pi-C_5H_5MoCl_4]$ complex the t-butyl group has migrated from the methyleneamino group to the triphenylphosphine to result in the formation of the phosphonium cation.

CHAPTER V

SYNTHESIS OF AN AZA-ALLYL/ALLENE COMPLEX OF TUNGSTEN

This chapter describes the synthesis, properties and reactions of an aza-allyl/allene complex π-$C_5H_5W(CO)_2Ph_2CNCPh_2$, obtained by the reaction of $Ph_2C{:}NLi$ with π-$C_5H_5W(CO)_3Cl$. The mode of bonding between the Ph_2CNCPh_2 group and the transition metal in this compound is of paramount interest and is discussed in terms of the spectral and analytical data obtained.

A. Experimental

1. Reaction of π-$C_5H_5W(CO)_3Cl$ with $Ph_2C{:}NLi$

A solution of diphenylmethyleneaminolithium was prepared by the addition of n-butyl-lithium (10 mmole) in hexane (15 ml.) to diphenylmethyleneamine (1.81 g., 10 mmole) in diethyl ether (40 ml.) at -196°, and allowing the mixture to warm slowly to room temperature. After 2 hr. the solution was added to a frozen solution of π-$C_5H_5W(CO)_3Cl$ (1.84 g., 5 mmole) in ether (20 ml.). After 2 hr. at room temperature slow evolution of carbon monoxide occurred, accompanied by precipitation of a white powder, and a change of colour of the solution from red-orange to deep purple. The filtered reaction mixture was evaporated to dryness after 12 hr. (20°, in vacuo) and the residue was extracted with chloroform (100 ml.). Filtration yielded a purple solution and a grey white solid which contained lithium chloride and lithium cyanate. Hexane (30 ml.) was added to the solution which was then cooled to -20° to give waxy, golden-brown crystals; these were recrystallised from hexane-chloroform; Yield of recrystallised product 2.1 g. (58%).

Properties: Even after several recrystallisation the microcrystalline solid has a waxy appearance. It is stable in air for long periods but does lose CO after several months to leave a brown residue. Dilute solutions in chloroform although extremely intense in colour when first prepared, rapidly lose their colour to leave a clear solution and a non-carbonyl brown residue. It is unaffected by concentrated boiling alkalis but dissolves in conc. H_2SO_4 to give an orange solution which starts to evolve CO after a few minutes. It is almost insoluble in hexane, benzene and toluene but is soluble in chloroform and ethers but only to a small extent. Its solutions, although weak, are intensely purple, even when extremely dilute although the solid itself never appears this colour. It melts with decomposition in a sealed tube at 210-213°.

Analysis: Found, C,60.4; H,3.90; N,2.05; CO, 8.6; $C_{33}H_{25}NO_2W$ requires C,60.8; H,3.85; N,2.15; CO,8.5%.

Infrared spectroscopic data: The solid gave a purple mull with Nujol. ν(CO), 1918s, 1835s cm^{-1} (Nujol), 1933s, 1835s cm^{-1} ($CHCl_3$). There were no absorptions assignable to ν(CN) or ν(NH). The full Nujol mull spectrum is: 1918s, 1835s, 1585m, 1567w,sh, 1529w,br, 1220w, 1205w, 1176w, 1155m, 1071m, 1059w,sh, 1053m, 1031w, 1024w, 1001w, 971w, 943w, 917w, 893w, 848w, 840w, 826w, 813m, 794w, 755m, 769m, 758m, 725m, 709m, 699m, 693m, 687m, 666w, 628m, 624m, 620w,sh, 607w, 598m, 561m,br, 543m,br, 514m,br, 488m,br, 480m,br, 466w,br cm^{-1}.

^{1}H n.m.r. spectrum ($CDCl_3$): The spectrum was relatively weak due to the low solubility of the compound, but showed a broad signal at 2.75(4)τ and a sharp singlet at 5.23(1)τ due to Ph and π-C_5H_5 protons respectively.

Molecular weight: Due to the instability of the compound in solution no readings were obtained cryoscopically or osmometrically.

Conductivity: non-electrolyte in nitrobenzene.

Mass spectrum (direct insertion probe at source temperature): For the parent ion $[\pi\text{-}C_5H_5W(CO)_2Ph_2CNCPh_2]^+$ (m/e 651) the isotopic distribution pattern corresponded with that computed for $C_{33}H_{25}NO_2W$. The major peaks in the spectrum are listed in Table V.1. Other major peaks corresponding to the organic fragments $[Ph_2CNCPh_2]^+$ m/e 346; $[PhCNCPh_2]^+$ m/e 269; $[Ph_2CN]^+$ m/e 180; were observed. The results of precise mass measurements made on the compound are listed in Table V.II.

2. The reaction of π-$C_5H_5W(CO)_2Ph_2CNCPh_2$ with Ph_3P

With the reactants in a 1:1 molar ratio no reaction occurred in either refluxing chloroform or refluxing toluene during 48 hr. and most of the reactants were recovered unchanged.

Table V.I.

Mass spectral data for $\pi\text{-}C_5H_5W(CO)_2Ph_2CNCPh_2$

Ion	m/e	m*	Fragment lost
$[\pi\text{-}C_5H_5W(CO)_2Ph_2CNCPh_2]^+$	651		
		596	CO
$[\pi\text{-}C_5H_5W(CO)Ph_2CNCPh_2]^+$	623		
		568	CO
$[\pi\text{-}C_5H_5WPh_2CNCPh_2]^+$	595		
		407	PhCN
$[\pi\text{-}C_5H_5WCPh_3]^+$	492		
$[\pi\text{-}C_5H_5WCPh(C_6H_4)_2]^+$	490		
$[\pi\text{-}C_5H_5W(C_6H_4)]^+$	325		
$[\pi\text{-}C_5H_5WCPh(C_6H_4)]^+$	414		
$[\pi\text{-}C_5H_5WPh_4C_2N]^{2+}$	297.5		

Table V.II.

Precise Mass measurements for $\pi\text{-}C_5H_5W(CO)_2Ph_2CNCPh_2$

Measured Mass	Possible formula	Calculated Mass	Error (p.p.m.)
649.143067	$C_{33}H_{25}NO_2{}^{182}W$	649.134158	1.5
650.079680	$C_{22}H_{25}NO_2{}^{183}W$	650.135639	9.0
651.143978	$C_{22}H_{25}NO_2{}^{184}W$	651.136321	1.5
653.144275	$C_{33}H_{25}NO_2{}^{186}W$	653.14577	1.0

B. Discussion

1. The aza-allyl/allene complex π-$C_5H_5W(CO)_2Ph_2CNCPh_2$

Diphenylmethyleneaminolithium and π-$C_5H_5W(CO)_3Cl$ in a 2:1 molar ratio react, in ether solution, at room temperature to produce π-$C_5H_5W(CO)_2Ph_2CNCPh_2$. A similar reaction with molybdenum carbonyl chloride produced π-$C_5H_5Mo(CO)_2Ph_2CNCPh_2$.[328] Other products of the reaction are lithium chloride and cyanate. The presence of the cyanate ion was detected by chemical tests and i.r. spectroscopy. The complex is stable in air for several months, at room temperature, and is unreactive to neutral ligands such as phosphines in refluxing chloroform or toluene. In polar solvents the complex produces intense purple solutions, even when dilute, although the solid is brown. Spectroscopic and analytical data confirm the formulation given. In the mass spectrum the largest organic fragment at m/e 346 has a breakdown pattern appropriate for $[Ph_2CNCPh_2]^+$, and the ^1H n.m.r. spectra indicate that the Ph_2CNCPh_2 group has equivalent phenyl groups in the complex. The ligand may be acting as a three electron donor in three ways (i) as an aziridino group,[328] (ii) as an aza-allylic group, (iii) as an aza-allene group. Complexes containing the aziridino group π-bonded to a transition metal (Fig.V.1) have not previously been reported although the group is well known attached to main group elements.[329] The absence of an infrared absorption band in the region 850-900 cm^{-1}, which has been used as diagnostic of the aziridine ring system[330] led us to believe that Fig.V.1 is not the mode of bonding.

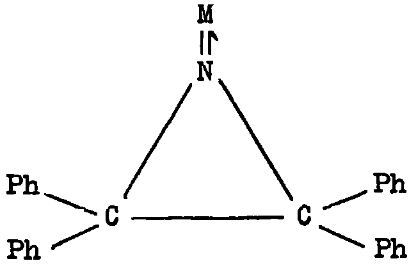


Fig.V.1.

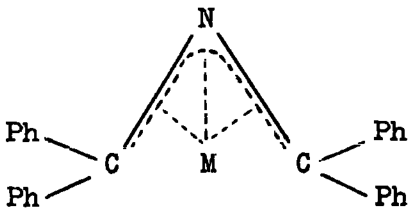


Fig.V.2.

The compound containing the ligand as a 2-aza-allyl group, would be analogous to the well known π-$C_5H_5Mo(CO)_2\pi$-C_3H_5 compound.[331] However the effect of the nitrogen lone-pair (replacing the C-H unit in the allyl group) on the bonding characteristics of the ligand needs to be considered. The infrared carbonyl absorption bands of the π-$C_5H_5Mo(CO)_2\pi$-C_3H_5 complex occur some 40-50 cm^{-1} higher in frequency than the corresponding 2-aza-allyl complex, perhaps indicating the increased donating power of the aza-ligand. The bonding in the 2-aza-allyl complex may be directly analogous to the bonding of the isoelectronic π-allyl group. In both cases the empty metal σ- and π-orbitals have the correct symmetry for overlap. In one form the ligand may be sp^2 hybridized at nitrogen and give a bonding situation directly comparable to the π-allyl group. The lone pair of electrons on the nitrogen will not be involved to any great extent in the bonding to the metal. In the other form sp hybridization at nitrogen will produce a linear C-N-C system with the lone pair in a p-orbital on nitrogen which creates an even more favourable bonding situation for strong bonding with the nitrogen lone pair as well as the aza-allyl π-orbitals.

Further structural data on the nature of the attachment of the R_2CNCR_2 group to the metal was needed, but the diphenyl compounds were unsuitable both for an ^1H n.m.r. spectral study and, as powders, unsuitable for an X-ray crystallographic study. Consequently an attempt was made to introduce different alkyl or aryl groups onto the ligand to facilitate further spectral studies. Work involving the di-t-butyl and phenyl-t-butylmethyleneamino derivatives failed to produce compounds analogous to π-$C_5H_5W(CO)_2Ph_2CNCPh_2$ but the reaction between di-p-tolylmethyleneaminolithium and the tricarbonyl halide produced, amongst other products,[320] the π-$C_5H_5M(CO)_2$p-tolyl$_2$CNCp-tolyl$_2$ complex.[320] The blue crystalline material was isolated in two forms in the solid state, whereas in solution i.r. spectroscopy showed only one species.

The crystal structure of one of the crystalline forms of π-$C_5H_5Mo(CO)_2$-p-tolyl$_2$CNCp-tolyl$_2$ is shown in Fig.V.3,[308] in which the bonding of the

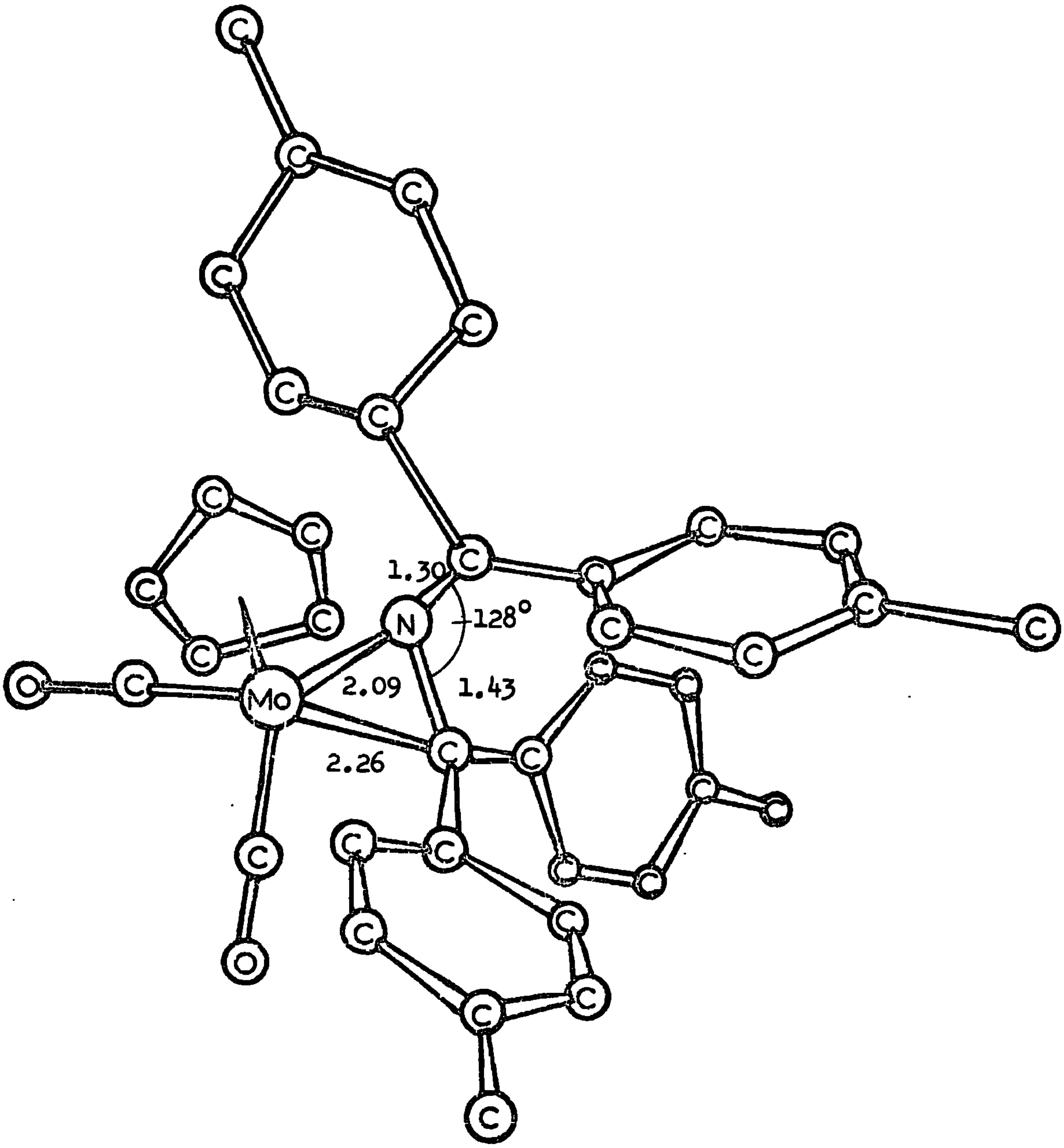


Fig.V.3. Crystal structure of π-$C_5H_5Mo(CO)_2$p-$tolyl_2$CNCp-$tolyl_2$

p-tolyl$_2$CNCp-tolyl$_2$ ligand to the metal involves formation of a three membered ring. The planes of the two p-tolyl$_2$C- groups are mutually perpendicular, and the aza-ligand bonds to the metal as an aza-allene group. If we consider the aza-allene group p-tolyl$_2$CNCp-tolyl$_2$ with a positive charge localized on the nitrogen atom and isoelectronic with the allenes, the bonding can be explained in terms of the ligand acting as a two electron donor to the negative metal. This donation occurs by the transfer of electron density from the π-system of one of the C:N systems to the metal, leading to a reduction in the bond order and lengthening of the C-N distance. Donation from the filled metal d-orbitals to the available π*-antibonding orbitals is expected to be strong on account of the strong electron acceptor nature of the ligand. This will lead to an increase in the antibonding character of the C-N bond, reflected in further weakening and subsequent bond lengthening. The electron density in the π-system of the C-N bond is almost balanced by the increased electron density in the π*-antibonding orbital, due to a large synergic effect since the overall effect is to reduce the original order of the C:N bond to approximately that of a single bond. As a consequence the nitrogen in the ligand takes on more p character and rehybridizes towards sp^2 at nitrogen, causing the CR$_2$ substituent group to bend away from the metal as illustrated in Fig.V.3. Much interest is placed on the crystal structure of the second crystalline form which is considered to have a different structure, which may be related to that of the common species in solution which is thought to involve a σ- and π-type of bonding, Fig.V.4.

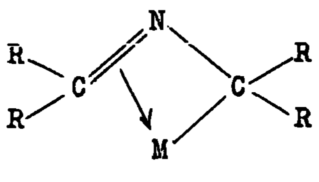


Fig.V.4

Variable temperature ^{1}H n.m.r. studies have indicated that the bonding of the ligand p-tolyl$_2$CNCp-tolyl$_2$ in π-$C_5H_5Mo(CO)_2$p-tolyl$_2$CNCp-tolyl$_2$ is affected by temperature and that small structural changes occur. Work in this area is in progress at the present time.[320]

From the work done on the Ph_2CNCPh_2 and p-tolyl$_2$CNCp-tolyl$_2$ ligands it would appear that there are two main factors which may influence the formation and stability of the R_2CNCR_2 group, (i) the ability of the group R to extend the delocalised π-system and (ii) the bulkiness of the R group.

Complexes containing the $Bu^t{}_2CNCBu^t{}_2$ or $PhBu^tCNCBu^tPh$ groups have not been prepared. In the case of $PhBu^tCNCBu^tPh$ extensive delocalisation of the electron density over the π-system by the Ph groups may not be sufficient or alternatively the steric effect of the bulky Bu^t group may prevent the group from forming at the metal centre. However models suggest that steric hindrance would not preclude the existence of the $PhBu^tCNCBu^tPh$ group. The bulky Bu^t groups may hinder the close approach of the preformed ligand to the metal and prevent strong bonding taking place, or if the ligand is actually formed at the metal centre then the bulky groups or the absence of groups which can delocalise electron density, prevent this from occurring.

How the ligand is initially formed with loss of nitrogen as the cyanate ion is not understood but there has been some speculation that it could involve nucleophilic attack by nitrogen, from a free ligand in solution, at the carbon of a co-ordinated ligand and lead to subsequent transfer of the CR_2 group to the second methyleneamino group.

Much speculation still remains about the bonding mode of this R_2CNCR_2 ligand to transition metals, and further work in this area is being carried out by colleagues.

CHAPTER VI

SYNTHESIS AND REACTIONS OF SOME METHYLENEAMINO-DERIVATIVES OF IRON CARBONYLS

This chapter describes the synthesis and reactions of some iron-methyleneamino-derivatives, with an aim to investigate further the mode of bonding of the methyleneamino group when the metal attached to the nitrogen of the >C:N system is changed.

A. Experimental

1. Reaction of π-$C_5H_5Fe(CO)_2Cl$ with $Ph_2C:NLi$

A solution of $Ph_2C:NLi$ (2 mmole) in a hexane-ether mixture (20 ml.) was added to a frozen solution of π-$C_5H_5Fe(CO)_2Cl$ (0.42 g., 2 mmole) in ether (20 ml.) at -196°. The mixture when slowly warmed to room temperature became dark in colour and slowly evolved gas. The solution was reduced in bulk and chromatographed on alumina (neutral). Elution with petroleum ether/ether mixture (4:1) gave π-$C_5H_5Fe(CO)_2Cl$ and $[\pi$-$C_5H_5Fe(CO)_2]_2$ both identified by infrared spectroscopy. I.r. spectroscopy indicated the presence of a monocarbonyl species [ν(CO) 1946 cm^{-1}] present in small quantity. Attempts to isolate this by low temperature recrystallisation and chromatography failed.

2. Reaction of π-$C_5H_5Fe(CO)_2Cl$ with $Ph_2C:NSiMe_3$

Diphenylmethyleneaminotrimethylsilane (10 mmole) was added to a solution of π-$C_5H_5Fe(CO)_2Cl$ (1.84 g., 10 mmole) in monoglyme (30 ml.). After 48 hr. at the reflux temperature, i.r. spectroscopy showed that nearly all the π-$C_5H_5Fe(CO)_2Cl$ had been consumed and a large amount of $[\pi$-$C_5H_5Fe(CO)_2]_2$ had been formed. The solution was reduced in bulk and some yellow crystals were filtered from the reaction solution. After washing, drying and recrystallisation from n-propanol, the crystals were shown to be $Ph_2CNNCPh_2$ by their melting point and i.r. spectroscopy. The solvent was then removed from the filtrate (20°, 10^{-1}mm.Hg), the residue extracted with ether and the extracts chromatographed on alumina (neutral). Elution with petroleum ether/ether (4:1) gave $\pi\text{-}C_5H_5Fe(CO)_2Cl$ and $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ both identified by infrared spectroscopy and analysis.

3. Reaction of $\pi\text{-}C_5H_5Fe(CO)_2Cl$ with $Bu^t{}_2C{:}NLi$

A solution of di-t-butylmethyleneaminolithium (2 mmole) was prepared by addition of t-butyllithium (2 mmole) in hexane solvent, to t-butylcyanide (2 mmole) in ether (10 ml.) at -196°, and allowing the mixture to warm to room temperature slowly. After 1 hr. the solution was added to a frozen solution of $\pi\text{-}C_5H_5Fe(CO)_2Cl$ (0.42 g., 2 mmole) in ether (100 ml.), excluding air and light. The mixture when slowly warmed and kept at room temperature for ½ hr. became deep blue, slowly evolved gas, and deposited a fine white powder. After being removed by filtration the residue was shown by i.r. spectroscopy and elemental tests to consist of lithium chloride, $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ and a non-carbonyl oily decomposition product. The solvent was then removed from the filtrate (20°, 10^{-1} mm.Hg), and the oily blue residue extracted with hexane (2 x 50 ml.). The hexane was then removed (20°, 10^{-1} mm.Hg) to leave an oil. This was vacuum distilled into a cooled receiver at (20°, 10^{-3}mm.Hg). Yield 0.32 g. (55%).

Properties: The compound was a blue, air and light sensitive oil, soluble in most organic solvents to form intense blue solutions in the absence of oxygen. It decomposed slowly at room temperature by loss of carbon monoxide to leave a black-red oil which could not be characterised.

Analysis: Found, C,62.08; H,8.10; N,4.79; CO,9.56; $C_{15}FeH_{23}NO$ requires C,62.28; H,7.96; N,4.84; CO,9.68%.

Infrared spectrum: The oil gave an intense blue mull with Nujol. ν(CO), 1947s, cm^{-1} (Nujol), 1953s, cm^{-1} ($CHCl_3$); ν(CN), 1610w,mbr cm^{-1} (Nujol), 1612w,mbr cm^{-1} ($CHCl_3$). The Nujol mull spectrum is: 1266m, 1235w,sh, 1214m, 1112m, 1037m, 1010m, 980m, 935w, 894w, 877w, 848w, 833m, 813s, 758m, 725m, 688m, 666w, 580m,br, 558m,br, 534s,br, 497m,br cm^{-1}.

Molecular weight: 295 cryoscopically in benzene (Th.289).

^{1}H n.m.r. spectrum: in perdeuteriomethylcyclohexane solution showed sharp signals at 5.61(5)τ and 8.94(18)τ due to π-C_5H_5 and Bu^t protons respectively. A variable temperature study between ± 40°C showed no changes in the spectrum. Mass spectrum (direct insertion probe at source temperature): For the parent ion [π-C_5H_5Fe(CO)N:$CBu^t{}_2$]$^+$ (m/e 289) the isotopic distribution pattern corresponded to that computed for $C_{15}FeH_{23}NO$. The major peaks in the spectrum are listed in Table VI.1.

Table VI.1

Mass spectral data for π-C_5H_5Fe(CO)N:$CBu^t{}_2$

Ion	m/e	m*	Fragment lost
[π-C_5H_5Fe(CO)N:$CBu^t{}_2$]$^+$	289		
		235	CO
[π-C_5H_5FeN:$CBu^t{}_2$]$^+$	261		
		159	Bu^t
[π-C_5H_5FeN:CBu^t]$^+$	204		
		72	Bu^tCN
[π-C_5H_5Fe]$^+$	121		
		121	Bu^tCN
[π-C_5H_5FeBu^t]$^+$	178		
		83	Bu^t
[π-C_5H_5Fe]$^+$	121		

4. Reaction of π-$C_5H_5Fe(CO)N{:}CBu^t{}_2$ with triphenylphosphine

Triphenylphosphine (0.524 g., 2 mmole) in hexane (100 ml.) was added to π-$C_5H_5Fe(CO)N{:}CBu^t{}_2$ (0.58 g., 2 mmole) and excluding air and light, the reaction was refluxed for two days. No reaction could be detected by i.r. spectroscopy and most of the starting materials were recovered unchanged.

5. Reaction of π-$C_5H_5Fe(CO)N{:}CBu^t{}_2$ with iodine

Iodine (0.25 g., 1 mmole) in hexane (200 ml.) was slowly added to π-$C_5H_5Fe(CO)N{:}CBu^t{}_2$ (0.58 g., 2 mmole) in hexane (100 ml.), excluding air and light. This resulted in rapid decomposition of the carbonyl compound to leave a black oil. The oil could not be obtained pure for further study.

6. Reaction of π-$C_5H_5Fe(CO)_2Cl$ with $Bu^t{}_2C{:}NSiMe_3$

The complex π-$C_5H_5Fe(CO)_2Cl$ (1.84 g., 10 mmole) and $Bu^t{}_2C{:}NSiMe_3$ (10 mmole) were refluxed for 48 hr. in monoglyme (100 ml.). No evolution of gas was observed, and the carbonyl chloride was slowly converted to $[\pi$-$C_5H_5Fe(CO)_2]_2$, this being the only product detected by i.r. spectroscopy. The solution was evaporated to dryness (20°, 10^{-1}mm.Hg), the residue extracted with ether and the extracts chromatographed on alumina (neutral). Elution with petroleum ether/ether (4:1) mixture gave only π-$C_5H_5Fe(CO)_2Cl$ and $[\pi$-$C_5H_5Fe(CO)_2]_2$ identified by i.r. spectroscopy and analysis.

7. Reaction of $Fe(CO)_4I_2$ with $Ph_2C{:}NLi$

A solution of $Ph_2C{:}NLi$ (5 mmole) in diethyl ether (10 ml.) was added to a cooled solution of $Fe(CO)_4I_2$ (2.11 g., 5 mmole) also in diethyl ether (100 ml.). On warming slowly to room temperature and stirring for 1 hr. the slow evolution of carbon monoxide ceased and the solution darkened in colour. The ether was then removed under vacuo (20°, 10^{-1}mm.Hg), and the residue extracted with n-hexane (3 x 20 ml.). The n-hexane was then removed from the extracts (20°, 10^{-1}mm.Hg) and the residue dissolved in the minimum quantity of warm cyclohexane. This solution was reduced in bulk and chromatographed on a 3'0" x 3" Silicar column, using cyclohexane as eluent. Two fractions were separated, the first a deep red colour and the second yellow-orange. The solvent was removed (20°, 10^{-1}mm.Hg) from both fractions, the residues dissolved in hot n-hexane and the solutions left to produce crystals at -20°C.

(a) The first deep red crystals of $Fe_2(CO)_6(N:CPh_2)I$ 0.6 g. (4%) were recrystallised as deep red plates from hot n-hexane.

Properties: The deep red plate like crystals were air and moisture stable for several weeks, both solid and in solution. They melted in a sealed tube with decomposition at 138-139°C to form a red oil, and were soluble in all common organic solvents.

Analysis: Found, C,38.83; H,1.66; N,2.35; I,21.3; $Fe_2C_{19}O_6IH_{10}N$ requires C,38.84; H,1.70; N,2.38; I,21.63%.

Infrared spectrum: The solid gave a deep red mull with Nujol. ν(CO), 2075m, 2040s, 2000s, 1988s, 1976s, 1948vvw cm^{-1} (Nujol); 2083m, 2050s, 2016s, 2006s, 1982vvw cm^{-1} (cyclohexane). No absorption could be assigned to ν(CN). The full Nujol spectrum is: 2075m, 2040s, 2000s, 1988s, 1976s, 1948vvw, 1603vw, 1593vw, 1314vwbr, 1288vwbr, 1265w, 1188w, 1160w, 1074w, 1034w, 1003w, 988vw, 975vw, 947vw, 840vw, 790w,sh, 781s, 743s, 725w,sh, 704s, 700s,sh, 682m, 673wsh, 632s, 623s,sh, 620s, 582s, 567s, 538vw, 519m, 500vw, 480w, 465w, 436w cm^{-1}

^1H n.m.r. spectrum (CS_2): showed a broad signal centred on 2.68τ due to the Ph protons.

Mass spectrum (direct insertion probe at source temperature): The parent ion $[Fe_2(CO)_6(N:CPh_2)(I)]^+$ was observed at m/e 587, the isotopic distribution pattern corresponding to that computed for $Fe_2C_{19}O_6IH_{10}N$. The major peaks in the spectrum are listed in Table VI.2.

(b) The second orange fraction produced deep orange needle like crystals of $[Fe(CO)_3N:CPh_2]_2$ 1.3 g. (8%), which were recrystallised from hot n-hexane.

Table VI.2

Mass spectral data for $Fe_2(CO)_6(N{:}CPh_2)I$

Ion	m/e	m*	Fragment lost
$[Fe_2(CO)_6(N{:}CPh_2)I]^+$	587		
		532	CO
$[Fe_2(CO)_5(N{:}CPh_2)I]^+$	559		
		504	CO
$[Fe_2(CO)_4(N{:}CPh_2)I]^+$	531		
		476	CO
$[Fe_2(CO)_3(N{:}CPh_2)I]^+$	503		
		449	CO
$[Fe_2(CO)_2(N{:}CPh_2)I]^+$	475		
		421	CO
$[Fe_2(CO)(N{:}CPh_2)I]^+$	447		
		393	CO
$[Fe_2(N{:}CPh_2)I]^+$	419		
		238	PhCN
$[Fe_2(Ph)I]^+$	316		

Properties: The orange crystals were air stable even on prolonged exposure, and were soluble in all common organic solvents to form air stable yellow-orange solutions. On heating in a sealed tube they melted with decomposition at 136-8°C.

Analysis: Found, C,60.08; H,3.10; N,4.36; $C_{32}H_{20}Fe_2N_2O_6$ requires C,60.00; H,3.13; N,4.38%.

Infrared spectrum: The solid gave a deep yellow mull with Nujol. ν(CO), 2071m, 2034s, 1985s, 1974s, 1968sh, 1961s, 1935vvw, cm^{-1} (Nujol), 2074s, 2041s, 1994s, 1979vvw cm^{-1} (cyclohexane). No absorption could be assigned to ν(CN). The full Nujol spectrum is: 2071m, 2034s, 1985s, 1974s, 1968sh, 1961s, 1935vvw, 1621vw, 1602vw, 1583vw, 1315vw, 1288vw, 1262vw, 1185vw, 1162w, 1078w, 1030w, 1004vw, 976vw, 771m, 740m, 709sh, 702s, 693sh, 638m, 625m, 618sh, 590m, 573m, 525w, cm^{-1}.

Molecular weight: 635 by cryoscopy in benzene, 635 by osmometry in benzene (Th.640).

^{1}H n.m.r. spectrum (CS_2): showed a medium broad signal centred at 2.8 τ due to the Ph protons.

Mass spectrum (direct insertion probe at source temperature): The parent ion $[Fe_2(CO)_6(N{:}CPh_2)_2]^+$ was observed at m/e 640, the isotopic distribution pattern corresponded to that computed for $C_{32}H_{20}Fe_2N_2O_6$. The major peaks in the spectrum are listed in Table VI.3.

8. Reaction of $Fe(CO)_4I_2$ with p-tolyl$_2$CNLi

A solution of p-tolyl$_2$C:NLi (5 mmole) in diethyl ether (10 ml.) was added to a cooled solution of $Fe(CO)_4I_2$ (2.11 g., 5 mmole) in diethyl ether (100 ml.), and the reaction was carried out as described above.

(a) The first deep red fraction produced $Fe_2(CO)_6$(N:Cp-tolyl$_2$)I as a deep red oil, Yield (3%).

Properties: The deep red waxy oil was air and moisture stable, and soluble without decomposition in most common organic solvents.

Analysis: Found, C,40.91; H,2.23; N,2.19; I,20.51; $Fe_2C_{21}H_{14}NIO_6$ requires C,40.97; H,2.27; N,2.27; I,20.65%.

Infrared spectrum: The solid gave a deep red mull with Nujol. ν(CO), 2079m, 2048s, 2013s, 2000s, 1984s, cm^{-1} (Nujol), 2084m, 2053s, 2018s, 2008s, 1980vw cm^{-1} (cyclohexane). No absorption could be assigned to ν(CN). The full

Table VI.3

Mass spectral data for $[Fe(CO)_3N{:}CPh_2]_2$

Ion	m/e	m*	Fragment lost
$[Fe_2(CO)_6(N{:}CPh_2)_2]^+$	640		
		585	CO
$[Fe_2(CO)_5(N{:}CPh_2)_2]^+$	612		
		557	CO
$[Fe_2(CO)_4(N{:}CPh_2)_2]^+$	584		
		529	CO
$[Fe_2(CO)_3(N{:}CPh_2)_2]^+$	556		
		501	CO
$[Fe_2(CO)_2(N{:}CPh_2)_2]^+$	528		
		473	CO
$[Fe_2(CO)(N{:}CPh_2)_2]^+$	500		
		445	CO
$[Fe_2(N{:}CPh_2)_2]^+$	472		
		288	PhCN
$[Fe_2(N{:}CPh_2)Ph]^+$	369		
		192	PhCN
$[Fe_2Ph_2]^+$	266		
$[Fe_2(N{:}CPh_2)_2]^{2+}$	236		

Nujol spectrum is: 2079m, 2048s, 2013s, 2000s, 1984s, 1618wsh, 1605wbr, 1315w, 1292w, 1265m, 1238vw, 1214w, 1190w, 1184w, 1160vw, 1100m,br, 1044w,br, 1023m, 966w, 840w, 820m,sh, 803m, 744m, 728w, 706w, 682w, 648m, 640w,sh, 621m, 595m, 580m, 564m, 518w, 508w, 482w, 472vw, cm^{-1}.

^1H n.m.r. spectrum (CS_2): showed sharp signals at 2.87(4)τ and 7.63(3)τ due to the C_6H_4 and CH_3 protons of the p-tolyl group respectively.

Mass spectrum (direct insertion probe at source temperature): For the parent ion $[Fe_2(CO)_6(N{:}Cp\text{-}tolyl_2)I]^+$ (m/e 615), the isotopic distribution pattern corresponded with that computed for $Fe_2C_{21}H_{14}NIO_6$. The major peaks in the spectrum are listed in Table VI.4.

(b) The second orange fraction produced orange needle-like crystals of $[Fe(CO)_3N{:}Cp\text{-}tolyl_2]_2$ 0.28 g. (8%), which were recrystallised from hot n-hexane.

Properties: The orange needle-like crystals were quite air stable and soluble in common organic solvents to form air stable solutions. On heating in a sealed tube the crystals decomposed without melting at 157°C.

Analysis: Found, C,61.81; H,3.90; N,4.02; $Fe_2C_{36}H_{28}N_2O_6$ requires C,62.07; H,4.02; N,4.02%.

Infrared spectrum: The crystals gave a 'canary' yellow mull with Nujol. ν(CO), 2070m, 2030s, 1992s, 1984s, 1977s, 1962vw cm^{-1} (Nujol), 2071m, 2038s, 1992s, 1976vvw cm^{-1} (cyclohexane). No absorption could be assigned to ν(CN).

The full Nujol spectrum is: 2070m, 2030s, 1992s, 1984s, 1977s, 1962vw, 1628w, 1612w, 1575vw, 1315w, 1291w, 1266w, 1240w, 1214w, 1190w, 1182w, 1162w, 1120w, 1044wbr, 1025w, 838m, 820m, 785w, 740m, 728wsh, 700w, 688w, 665m, 634m, 628m, 619wsh, 590m, 579m, 522w, 493wsh, 482m, cm^{-1}.

Molecular weight: 681, 677, 680 by cryoscopy in benzene (Th.696).

^1H n.m.r. spectrum (CS_2): showed two sharp signals at 2.95(4)τ and 7.66(3)τ due to the C_6H_4 and CH_3 protons of the p-tolyl group respectively.

Mass spectrum (direct insertion probe at source temperature): For the parent ion $[Fe_2(CO)_6(N{:}Cp\text{-}tolyl_2)_2]^+$ (m/e 696), the isotopic distribution pattern

Table VI.4

Mass spectral data for $Fe_2(CO)_6(N{:}Cp\text{-}tolyl_2)I$

Ion	m/e	m*	Fragment lost
$[Fe_2(CO)_6(N{:}Cp\text{-}tolyl_2)I]^+$	615		
		560	CO
$[Fe_2(CO)_5(N{:}Cp\text{-}tolyl_2)I]^+$	587		
		532	CO
$[Fe_2(CO)_4(N{:}Cp\text{-}tolyl_2)I]^+$	559		
		504	CO
$[Fe_2(CO)_3(N{:}Cp\text{-}tolyl_2)I]^+$	531		
		476	CO
$[Fe_2(CO)_2(N{:}Cp\text{-}tolyl_2)I]^+$	503		
		448	CO
$[Fe_2(CO)(N{:}Cp\text{-}tolyl_2)I]^+$	475		
		419	CO
$[Fe_2(N{:}Cp\text{-}tolyl_2)I]^+$	447		
		243	p-tolylCN
$[Fe_2(p\text{-}tolyl)I]^+$	330		

corresponded with that computed for $Fe_2C_{36}H_{28}N_2O_6$. The major peaks in the spectrum are listed in Table VI.5.

Table VI.5

Mass spectral data for $[Fe(CO)_3N{:}Cp\text{-}tolyl_2]_2$

Ion	m/e	m*	Fragment lost
$[Fe_2(CO)_6(N{:}Cp\text{-}tolyl_2)_2]^+$	696		
		641	CO
$[Fe_2(CO)_5(N{:}Cp\text{-}tolyl_2)_2]^+$	668		
		613	CO
$[Fe_2(CO)_4(N{:}Cp\text{-}tolyl_2)_2]^+$	640		
		585	CO
$[Fe_2(CO)_3(N{:}Cp\text{-}tolyl_2)_2]^+$	612		
		557	CO
$[Fe_2(CO)_2(N{:}Cp\text{-}tolyl_2)_2]^+$	584		
		529	CO
$[Fe_2(CO)(N{:}Cp\text{-}tolyl_2)_2]^+$	556		
		502	CO
$[Fe_2(N{:}Cp\text{-}tolyl_2)_2]^+$	528		
		320	p-tolylCN
$[Fe_2(N{:}Cp\text{-}tolyl_2)(p\text{-}tolyl)]^+$	411		
		208	p-tolylCN
$[Fe_2(p\text{-}tolyl)_2]^+$	294		
$[Fe_2(N{:}Cp\text{-}tolyl_2)_2]^{2+}$	264		

9. Reaction of $Fe(CO)_4I_2$ with $PhBu^tCNLi$

A solution of $PhBu^tC{:}NLi$ (5 mmole) in diethyl ether (10 ml.) was added to a cooled solution of $Fe(CO)_4I_2$ (2.11 g., 5 mmole) in diethyl ether (100 ml.), and the reaction carried out as described above.

(a) The first deep red fraction produced $Fe_2(CO)_6(N{:}CPhBu^t)I$ as a deep red oil. Yield (~4%).

Properties: The deep red waxy oil was air and moisture stable and soluble in common organic solvents without decomposition.

Analysis: Found, C,35.96; H,2.40; N,2.40; I,22.25; $C_{17}H_{14}NIO_6Fe_2$ requires C,35.97; H,2.47; N,2.47; I,22.40%.

Infrared spectrum: The oil gave a deep red mull with Nujol. ν(CO), 2081m, 2044s, 2009s, 1987s, 1980s, 1963vw cm^{-1} (Nujol), 2082m, 2048s, 2014s, 2008s, 1995vw cm^{-1} (cyclohexane). No absorption can be assigned to ν(CN). The full Nujol spectrum is: 2081s, 2044s, 2009s, 1987s, 1980s, 1963vw, 1615vw, 1600vw, 1580vw, 1264w, 1214w, 1203w, 1156vw, 1100wbr, 1075w, 1030wbr, 1002vw, 968vw, 828w, 805w, 785w, 739wsh, 723m, 711m, 703msh, 658m, 623m, 592msh, 588m,sh, 566m, 518w, 470w cm^{-1}.

^1H n.m.r. spectrum (CS_2): shows two signals at 2.70(5)τ and 8.78(9)τ due to the Ph and Bu^t protons respectively.

Mass spectrum (direct insertion probe at source temperature): For the parent ion $[Fe_2(CO)_6(N{:}CPhBu^t)I]^+$ (m/e 567) the isotopic distribution pattern corresponded with that computed for $C_{17}H_{14}NIO_6Fe_2$. The major peaks in the spectrum are listed in Table VI.6.

(b) The second orange fraction produced orange needle-like crystals of $[Fe(CO)_3N{:}CPhBu^t]_2$ 0.3 g. (9.0%) which were recrystallised from n-hexane.

Properties: The air and moisture stable crystalline solid produced a canary yellow mull with Nujol. It decomposed without melting at 160°C, and was soluble in all common organic solvents.

Analysis: Found, C,56.10; H,4.69; N,4.77; $Fe_2C_{28}H_{28}N_2O_6$ requires C,56.0; H,4.66; N,4.66%.

Table VI.6

Mass spectral data for $Fe_2(CO)_6(N:CPhBu^t)I$

Ion	m/e	m^*	Fragment lost
$[Fe_2(CO)_6(N:CPhBu^t)I]^+$	567		
		512	CO
$[Fe_2(CO)_5(N:CPhBu^t)I]^+$	539		
		484	CO
$[Fe_2(CO)_4(N:CPhBu^t)I]^+$	511		
		456	CO
$[Fe_2(CO)_3(N:CPhBu^t)I]^+$	483		
		428	CO
$[Fe_2(CO)_2(N:CPhBu^t)I]^+$	455		
		400	CO
$[Fe_2(CO)(N:CPhBu^t)I]^+$	427		
		372	CO
$[Fe_2(N:CPhBu^t)I]^+$	399		
		250	Bu^tCN
$[Fe_2(Ph)I]^+$	316		
$[Fe_2(N:CPhBu^t)I]^+$	399		
		-	Bu^t
$[Fe_2(N:CPh)I]^+$	342		

Infrared spectrum: ν(CO), 2064m, 2028s, 1991s, 1984s, 1959s cm^{-1} (Nujol), 2073m, 2036s, 1994s, 1987s, 1971m cm^{-1} (cyclohexane). No absorption could be assigned to ν(CN). The full Nujol spectrum is: 2064m, 2028s, 1991s, 1984s, 1959s, 1623vw, 1604vw, 1580vw, 1264vw, 1215w, 1203w, 1183vw, 1076w, 1048vw, 1021vw, 1003vw, 968vw, 929vw, 906vw, 850vw, 839w, 788w, 782wsh, 724msh, 718msh, 713m, 709msh, 700msh, 699w, 669vw, 630m, 623msh, 608w, 596m, 578m, 524w, 490vw, cm^{-1}.

Molecular weight: 595 cryoscopically in benzene (Th.600).

^{1}H n.m.r. spectrum (CS_2): showed two sharp signals at 2.80(5)τ and 8.84(9)τ due to Ph and Bu^t protons respectively.

Mass spectrum (direct insertion probe at source temperature): For the parent ion $[Fe_2(CO)_6(N{:}CPhBu^t)_2]^+$ (m/e 600) the isotopic distribution pattern corresponded to that computed for $Fe_2C_{28}H_{28}N_2O_6$. The major peaks in the spectrum are listed in Table VI.7.

10. Reaction of $Fe(CO)_4I_2$ with $Bu^t_2C{:}NLi$

A solution of $Bu^t_2C{:}NLi$ (5 mmole) in diethyl ether (10 ml.) was added to a cooled solution of $Fe(CO)_4I_2$ (2.11 g., 5 mmole) in diethyl ether (100 ml.) The mixture when slowly warmed and kept at room temperature for 1 hr. darkened in colour with considerable gas evolution. The i.r. spectrum of the solution showed almost total consumption of starting materials. The only product obtained from this reaction, by distillation, was iron pentacarbonyl which was identified by i.r. spectroscopy, mass spectroscopy and analysis. Yield 30-40%.

11. Reaction between $Fe_2(CO)_6(N{:}CPh_2)I$ and $Ph_2C{:}NLi$

Diphenylmethyleneaminolithium (0.5 mmole) in ether (5 ml.) was added to a cooled solution of $Fe_2(CO)_6(N{:}CPh_2)I$ (0.29 g., 0.5 mmole) in hexane (5 ml.). The mixture when slowly warmed, and kept at room temperature for ½ hr., darkened slightly. I.r. spectroscopy showed the reaction to be complete. The solvent was removed from the reaction mixture (20°, 10^{-1}mm.Hg) and the waxy residue was extracted with hot hexane (2 x 2 ml.). On cooling this solution, orange-yellow needle-like crystals of $[Fe(CO)_3N{:}CPh_2]_2$ were obtained. Yield 0.3g. (94%).

Table VI.7.

Mass spectral data for $[Fe(CO)_3N:CPhBu^t]_2$

Ion	m/e	m*	Fragment lost
$[Fe_2(CO)_6(N:CPhBu^t)_2]^+$	600		
		545	CO
$[Fe_2(CO)_5(N:CPhBu^t)_2]^+$	572		
		517	CO
$[Fe_2(CO)_4(N:CPhBu^t)_2]^+$	544		
		489	CO
$[Fe_2(CO)_3(N:CPhBu^t)_2]^+$	516		
		462	CO
$[Fe_2(CO)_2(N:CPhBu^t)_2]^+$	488		
		434	CO
$[Fe_2(CO)(N:CPhBu^t)_2]^+$	460		
		405	CO
$[Fe_2(N:CPhBu^t)_2]^+$	432		
		281	Bu^tCN
$[Fe_2(N:CPhBu^t)(Ph)]^+$	348		
		202	Bu^tCN
$[Fe_2Ph_2]^+$	265		
$[Fe_2(N:CPhBu^t)(Ph)]^+$	348		
		-	Bu^t
$[Fe_2(N:CPh)(Ph)]^+$	291		
$[Fe_2(N:CPhBu^t)_2]^{2+}$	216		

B. Discussion

1. The monocarbonyl complex π-$C_5H_5Fe(CO)N{:}CBu^t_2$

The reaction of π-$C_5H_5Fe(CO)_2Cl$ with $Bu^t_2C{:}NLi$ produced a complex of the type π-$C_5H_5Fe(CO)N{:}CBu^t_2$ as an air and light sensitive blue oil, which decomposed slowly under an atmosphere of nitrogen at room temperature. In contrast, the reactions of the dicarbonyl chloride with $Ph_2C{:}NSiMe_3$ and $Bu^t_2C{:}NSiMe_3$ under refluxing conditions in monoglyme for several hours produced only the parent carbonyl dimer in high yield, though for the diphenyl compound some azine $Ph_2CNNCPh_2$ was isolated. In the reaction of diphenylmethyleneaminolithium, an i.r. absorption band at 1946 cm^{-1}, indicated that a monocarbonyl species was present in solution at low temperatures, but this complex was very unstable since attempts to isolate it at low temperatures failed. No evidence was found in this work for the formation of complexes containing the 2-aza-allyl/allene ligand (R_2CNCR_2), and the monocarbonyl species obtained showed no tendency on heating to form dinuclear complexes, sublimation of the complex occurring under these conditions.

In many respects there is a close resemblance between the properties of the iron system and the molybdenum and tungsten systems studied. In both systems the diphenylmethyleneamino complex would appear to be the most unstable of the complexes containing the terminally bound $R_2C{:}N$-ligand, and in the iron system it is apparently even more unstable than in the group VI metal compounds, in that it decomposes before it can be isolated, even at low temperatures. The air stable crystalline di-t-butylmethyleneamino derivatives of molybdenum and tungsten, have the same blue colour and camphor-like odour as the iron compound π-$C_5H_5Fe(CO)N{:}CBu^t_2$. However the iron compound is an oil which decomposes in air or light with loss of carbon monoxide.

This complex was formulated as π-$C_5H_5Fe(CO)N{:}CBu^t_2$ on the basis of considerable evidence. Analysis confirmed the empirical formula,

$C_{15}FeH_{23}NO$, and cryoscopic determination of the molecular weight indicated a mononuclear species. The presence of a single strong absorption in the carbonyl region of the infrared spectrum at relatively low frequencies indicated a monocarbonyl complex in which the methyleneamino ligand acts as a three electron donor to the metal. The ν(CN) absorption was observed as a medium broad absorption which occurred at the same energy as the free methyleneamine. This is comparable with the values shown in Table III.9 observed for the complexes π-$C_5H_5M(CO)_2N{:}CBu^t_2$ (M = Mo,W) in which the ν(CN) was at a slightly higher energy than that observed for the free ligand. This may indicate that the formation of the σ- and dπ-pπ N ⟶ M bonding which results in electron donation to the metal is effectively balanced by the back donation via dπ-pπ^* bonding.

The mass spectrum of the complex confirmed the mononuclear formulation and the presence of one carbonyl group per molecule. The parent ion was observed with isotopic distribution patterns corresponding to those computed for $C_{15}FeH_{23}NO$. The presence of metastable peaks confirmed the initial loss of carbon monoxide followed by losses of $[Bu^t]^+$ or $[Bu^tCN]^+$ ions. The expected organic ions resulting from fragmentation of the methyleneaminogroup were also observed.

The ^1H n.m.r. spectrum of the complex showed single sharp signals at 8.94τ and 5.61τ for Bu^t and π-C_5H_5 protons in positions typical of these groups.[301,332] The variable temperature study between ± 40°C showed no changes in the position of the signals except small movements due to a temperature effect. The crystal structure of π-$C_5H_5Mo(CO)_2N{:}CBu^t_2$[308] showed the presence of an almost linear M-C-N skeleton and the various spectral changes observed for this complex have been interpreted in terms of conformational changes about this linear unit. No crystal structure is available for the π-$C_5H_5Fe(CO)N{:}CBu^t_2$ complex so the question of the bonding mode of the methyleneamino group to the metal remains open to speculation, as the data on the complex could be interpreted in terms of either a linear or a bent skeleton. The structure adopted will undoubtedly be a compromise between achieving the strongest bonding between the metal and nitrogen (i.e. linear skeleton) and relieving steric interactions between bulky groups (i.e. bent skeleton). Rotation of the methyleneamino group is theoretically possible because of the π-cylindrical symmetry of the metal orbitals, but it is not observed by ^1H n.m.r. spectral measurements for the complex. The barrier to rotation may be low, as for π-$C_5H_5W(CO)_2N{:}CBu^t{}_2$, and may be undetectable under the conditions used. Thus any spectral changes which are likely to result from conformational changes may only be detectable at much lower temperatures than possible in this work.

We believe that the methyleneamino group acts as a three electron donor to iron on the basis of (i) the effective atomic number rule and the presence of only one carbonyl group; (ii) the relatively low carbonyl-stretching frequency; and (iii) the failure of the complex to add a further neutral donor molecule such as triphenylphosphine, even under forcing conditions. In contrast to the complexes π-$C_5H_5M(CO)I_2N{:}CR'R''$ and $(\pi$-$C_5H_5)_3M_3I_3O_4$ (M = Mo,W; R' = R" = Bu^t; R' = Ph, R" = Bu^t) obtained by the reaction of the group VI methyleneamino complexes with iodine, the iron complex π-$C_5H_5Fe(CO)N{:}CBu^t{}_2$ undergoes rapid decomposition to produce an inseparable oil mixture of non-carbonyl compounds.

2. The dinuclear complexes $[Fe(CO)_3N{:}CR'R'']_2$ (R' = R" = Ph, p-tolyl; R' = Ph, R" = Bu^t)

Nitrogen bridged binuclear derivatives of metal carbonyls and in particular those of iron are well known and studies have revealed that their structures correspond to at least three different types (i) those containing the nitrogen atom bridging the two metal atoms[5] (ii) those containing the nitrogen atom bridging the two metal atoms and joined by a N-N bond,[85] and (iii) those containing the nitrogen atom bridging the two metal atoms and themselves being connected by a N-CO-N bridge.[10] X-ray crystallographic studies on some of these complexes have provided us with some new insight into factors which determine the stereochemistry of the bridged complex.[5,10,85] The recent availability of a number of these complexes, which are electronically equivalent and contain different bridging groups, has afforded a good opportunity to study the trends in a series of similar compounds and relate these trands to the properties of the bridging ligands. In the $[Fe(CO)_3N:CR'R'']_2$ complexes we have extended the study to include nitrogen ligands attached to unsaturated systems which have the ability to reduce the electron density at the metal atom by a 'synergic effect'.

The reaction of $Fe(CO)_4I_2$ with R'R"C:NLi produced complexes of the type $[Fe(CO)_3N:CR'R'']_2$ with small amounts of $Fe_2(CO)_6(N:CR'R'')I$ (R' = R" = Ph, p-tolyl; R' = Ph, R" = Bu^t), which were separated by chromatography on a long silicar column using cyclohexane as the eluting agent. The $[Fe(CO)_3N:CR'R'']_2$ complexes were all quite air stable yellow-orange crystalline compounds. When Bu^t_2C:NLi was used as the reactant the only product obtained was iron pentacarbonyl.

For the $[Fe(CO)_3N:CR'R'']_2$ compounds in solution, the presence of three carbonyl absorptions in the carbonyl region of the infrared spectrum at relatively low frequency (Table VI.8) is consistent with a hexacarbonyl dinuclear complex in which the two methyleneamino groups are acting as three electron bridging ligands. The infrared absorptions in the carbonyl region, of the sulphur and phosphorus bridged binuclear complexes $[Fe(CO)_3SPh]_2$[189] and $[Fe(CO)_3PPh_2]_2$,[91] occurred at some 5-20 cm^{-1} to lower frequency than those observed for the $[Fe(CO)_3N:CR'R'']_2$ complexes and this may indicate that the methyleneamino ligand is more efficient at reducing the electron density at the metal atom by a 'synergic effect' than are the SPh or PPh_2 bridging groups. The presence of a very weak absorption listed in most of the spectra in Table VI.8 is probably due to satellite $^{13}C\nu(CO)$ absorptions.[333] For the $[Fe(CO)_3N:CR'R'']_2$ complexes no absorption could be assigned to $\nu(CN)$ in the 1500-1900 cm^{-1} region of the spectra. This is somewhat unexpected as strong $\nu(CN)$ absorptions do occur when a methyleneamino ligand bridges main group metals.[15] Compared to the infrared spectra of the $[Fe(CO)_3N:CR_2]_2$ complexes, $[Fe(CO)_3N:CPhBu^t]_2$ shows two extra ν(CO) absorptions in the carbonyl region of the spectrum. This may be due to a lowering of symmetry of the complex on introducing sterically bulky Bu^t groups into the bridging methyleneamino group.

Table VI.8

Infrared spectral data for $[Fe(CO)_3N:CR'R'']_2$

(R' = R'' = Ph, p-tolyl; R' = Ph, R'' = Bu^t)

Compound	State	ν(CO) cm^{-1}
$[Fe(CO)_3N:CPh_2]_2$	Nujol	2071m, 2034s, 1985s, 1974s, 1968sh, 1961s, 1935vvw.
	Cyclohexane	2074m, 2041s, 1994s, 1979vvw
$[Fe(CO)_3N:Cp\text{-}tolyl_2]_2$	Nujol	2070m, 2030s, 1992s, 1984s, 1977s, 1962vvw.
	Cyclohexane	2071m, 2038s, 1992s, 1976vvw
$[Fe(CO)_3N:CPhBu^t]_2$	Nujol	2064m, 2028s, 1991s, 1984s, 1959s.
	Cyclohexane	2073m, 2036s, 1994s, 1987s, 1971m.

The mass spectra of these complexes confirm the molecular formulation and the presence of six carbonyl groups. The spectra of the complexes showed the presence of metal containing ionic species of identical types, as well as the expected organic ions resulting from fragmentation of the methyleneamino groups. No mononuclear metal species were detected in the spectra, which is indicative of bridging groups binding the metal atoms.[302] All the spectra showed strong peaks to support the presence of doubly charged ions $[Fe_2(N:CR'R'')_2]^{2+}$. It is interesting to note that when R' = Bu^t and R'' = Ph, the predominant loss from the $[Fe_2(N:CPhBu^t)_2]^+$ ion is by two successive $[Bu^tC:N]^+$ ions, previously observed in the fragmentation patterns of π-$C_5H_5M(CO)_2N:CPhBu^t$ (M = Mo,W). This must indicate that the Ph group is the more strongly bound to the $>C:N$ system, as would be expected due to its ability to extend the π-delocalised system.

The ^1H n.m.r. spectra of the complexes (Table VI.9) showed peaks corresponding to the R' and R" groups in positions typical of such groups.

The crystal structure of $[Fe(CO)_3N:Cp\text{-tolyl}_2]_2$ prepared by the reaction between $Fe(CO)_5$ and 4,4'-dimethylbenzophenoneazine has been reported,[14] but no other data is recorded in the literature for this complex. It was found to have properties characteristic of the nitrogen bridged iron carbonyl complexes i.e. short Fe-Fe and Fe-N distances and small N-Fe-N and Fe-N-Fe bond angles (Chapter II, Table II.3).

The Mossbauer spectral data for the compounds $[Fe(CO)_3N:CR'R'']_2$ are tabulated in Table VI.10. The low isomer shift values (δ) for all the compounds of the type $[Fe(CO)_3N:CR'R'']_2$ reflect the high s electron density at the metal nucleus.[334] Since the methyleneamino ligands are strong Lewis bases,[335] they donate electrons into hybrid orbitals on the iron atom that will have some 4s character. This strong 'forward co-ordination' thereby increases the s electron density at the nucleus. The filled metal orbitals of appropriate symmetry will tend to form π-bonds with empty orbitals on the ligand to increase the stability of the system (synergic interaction). This "back donation", which involves 3d orbitals lessens the shielding of the s electrons in the iron, so the s electron density increases in this case as well. Both these factors will lead to a negative isomer shift and hence the small values observed. From studies involving a variety of Lewis bases with varying degrees of back co-ordination it has been shown that Lewis basicity is the most dominant feature in the control of isomer shift.[336]

Mossbauer studies on the $Fe_2(CO)_6(N:CPhH)(NHPh)$ complex, previously thought

Table VI.9

^1H n.m.r. spectral data for $[Fe(CO)_3N:CR'R'']_2$ and $Fe_2(CO)_6(N:CR'R'')I$

(R' = R'' = Ph, p-tolyl; R' = Ph, R'' = Bu^t)

Compound	π-C_6H_5 protons τ	$CH_3C_6H_4$ protons τ		C_4H_9 protons τ
		C_6H_4	CH_3	
$[Fe(CO)_3N:CPh_2]_2$	2.8m-br,s,			
$Fe_2(CO)_6(N:CPh_2)I$	2.68m-br,s			
$[Fe(CO)_3N:Cp\text{-}tolyl_2]_2$		2.95sh,s,(4)	7.66sh,s,(3)	
$Fe_2(CO)_6(N:Cp\text{-}tolyl_2)I$		2.87m-sh,s(4)	7.63m,s,(3)	
$[Fe(CO)_3N:CPhBu^t]_2$	2.80br,s(5)			8.84sh,s,(9)
$Fe_2(CO)_6(N:CPhBu^t)I$	2.70br,s,(5)			8.78sh,s,(9)

Table VI.10

Mossbauer spectral data for $[Fe(CO)_3N:CR'R'']_2$ (R' = R" = Ph, p-tolyl; R' = Ph, R" = Bu^t) and $Fe_2(CO)_6(N:CPh_2)I$

Compound	Chemical isomer shift $\delta/(mm.sec^{-1})$	Quadrupole Splitting $\Delta/(mm.sec^{-1})$	Average half-width $(mm.sec^{-1})$	State	Temperature (^{o}K)
$[Fe(CO)_3N:CPh_2]_2$	0.03	0.87	0.23	solid	77
$[Fe(CO)_3N:Cp\text{-}tolyl_2]_2$	0.01	0.85	0.19	solid	77
$[Fe(CO)_3N:CPhBu^t]_2$	0.05	0.87	0.24	solid	77
$Fe_2(CO)_6(N:CPh_2)I$	0.16	1.70	0.25	solid	77

to have the structure Fig.VI.1, have shown that, to account for the sharp

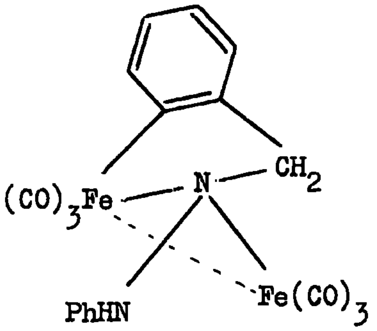


Fig.VI.1

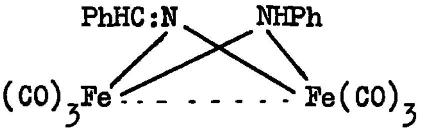


Fig.VI.2

doublet observed in the spectrum, a new structure, Fig.VI.2, must be proposed, in which the N-N bond of the organonitrogen ligand has been ruptured.[337] The chemical isomer shift (δ) of 0.03 mm. sec^{-1} and the quadrupole splitting (Δ) of 0.87 $mm.sec^{-1}$ of this complex, $Fe_2(CO)_6(N:CPhH)(NPhH)$, which contains a methyleneamino group bridging two iron atoms, are consistent with the values obtained for the $[Fe(CO)_3N:CR'R'']_2$ complexes.

These results indicate that the methyleneamino ligand forms strong σ-bonds, increasing the s electron density at the metal and so decreasing the isomer shift. A bent M-M bond is required in the structure of the bridged complexes not only to account for their diamagnetism, but also to complete the slightly distorted octahedral environment of the iron atoms implied by the observed low quadrupole splitting (Δ).

One interesting feature of this series of reactions is the fact that we were unable to prepare the di-t-butylmethyleneamino bridged complex $[Fe(CO)_3N:CBu^t{}_2]_2$. Steric effects may be responsible, the bulky Bu^t group hindering the approach of the ligand to the metal to prevent strong bonding taking place.

From the evidence obtained we predict that the methyleneamino ligand acts as a bridging ligand between two metal atoms, the bridging group donating a total of three electrons. The structure would allow dxy and dyz orbitals of one iron atom to overlap with equivalent orbitals of the other metal atom. The Fe-Fe bonding molecular orbital thus formed would have π-symmetry and would be bent towards the nitrogen, thus being able to overlap with $>C:N$ π* orbitals in the formation of a stabilising extended π-system as in Fig.I.3.

3. The heterobridged dinuclear complexes $Fe_2(CO)_6(N:CR'R'')I$ (R' = R'' = Ph, p-tolyl; R' = Ph, R'' = Bu^t

Bridging groups in metal carbonyl complexes are well established and may involve a range of elements including H, C, O, N, halogens, P, As, S etc., all of which are surveyed in Chapter II. Two metals may be bridged by one atom e.g. $[(CO)_5CrHCr(CO)_5]^-$ [232,233] or by two or more identical or different atoms e.g. $[Fe(CO)_3NH_2]_2$ [5] and $[Fe_2(CO)_8H]^-$, [253] which may be unsymmetrically placed between the metals as in $(\pi\text{-}C_5H_5)_2Ti(EPh_2)_2Mo(CO)_4$ (E = O,S,Se)[338] and $\pi\text{-}C_5H_5Ti(NMe_2)_3Mo(CO)_3$.[339] In addition the bridging unit may be strengthened by a metal-metal bond as for $[Fe(CO)_3SEt]_2$.[60]

In this series of reactions we have synthesised the first known hetero-bridged iron carbonyl nitrogen complexes. These complexes were obtained in small yield as deep red crystals (R' = R'' = Ph) or deep red oils (R' = R'' = p-tolyl; R' = Ph, R'' = Bu^t), from the reaction of $Fe(CO)_4I_2$ with R'R''C:NLi.

The complexes were formulated as $Fe_2(CO)_6(N:CR'R'')I$ on the basis of the following evidence. Analysis confirms the empirical formula and molecular weight measurements indicate the presence of a dinuclear complex. In the infrared spectra of the complexes shown in Table VI.11 the replacement of a bridging methyleneamino group by the electronegative iodine atom effectively reduces the electron density at the metal, which is reflected in the absorption frequency of the carbonyl groups. On the basis of the infrared spectra it was not possible to assign planar or puckered Fe_2NI bridging units. Compared with the symmetrically bridged methyleneamino complexes, the presence of the bridging iodine causes an additional ν(CO) band to appear and the ν(CO) frequencies to shift to higher energies in keeping with the lowering of the symmetry and the presence of a poorer three electron donor.

Table VI.11

Infrared spectroscopic data for $Fe_2(CO)_6(N{:}CR'R'')I$ ($R' = R'' = Ph, p\text{-tolyl}$; $R' = Ph, R'' = Bu^t$)

Compound	State	$\nu(CO)cm^{-1}$
$Fe_2(CO)_6(N{:}CPh_2)I$	Nujol	2075m, 2040s, 2000s, 1988s, 1976s, 1948vvw.
	Cyclohexane	2083m, 2050s, 2016s, 2006s, 1982vvw.
$Fe_2(CO)_6(N{:}Cp\text{-tolyl}_2)I$	Nujol	2079m, 2048s, 2013s, 2000s, 1984s.
	Cyclohexane	2084m, 2053s, 2018s, 2008s, 1980vw.
$Fe_2(CO)_6(N{:}CPhBu^t)I$	Nujol	2081m, 2044s, 2009s, 1987s, 1980s, 1963vw.
	Cyclohexane	2082m, 2048s, 2014s, 2008s, 1995vw.

The mass spectra of the $Fe_2(CO)_6(N{:}CR'R'')I$ complexes confirm the molecular formulation and the presence of the six carbonyl groups. The spectra of the complexes showed very similar fragmentation patterns and metal containing ionic species of identical types were found as well as the expected organic ions resulting from the fragmentation of the methyleneamino groups. The persistence of the complex to fragment without loss of iodine and without formation of mononuclear metal species is in keeping with other polynuclear carbonyl complexes, where it is found that the metal cluster does not fragment until all the attached groups have been lost.[302] Again an interesting feature of the $Fe_2(CO)_6(N{:}CPhBu^t)I$ complex is that it fragments with loss of the $[Bu^tCN]^+$ ion rather than the $[PhCN]^+$ ion, from $[Fe_2(N{:}CPhBu^t)I]^+$.

The ^1H n.m.r. spectra of the compounds (Table VI.9) showed peaks corresponding to the R' and R" groups in positions typical of those groups, and the relatively sharp signals obtained are diagnostic of a diamagnetic compound.

The Mossbauer spectral data for the $Fe_2(CO)_6(N{:}CPh_2)I$ complex is listed in Table VI.10. The decrease in σ-donation from the bridging atom when nitrogen is replaced by iodine, and the decrease in π-bonding to the metal compared with the methyleneamino group are consistent with the larger isomer shift value for $Fe_2(CO)_6(N{:}CPh_2)I$ (0.16 $mm.sec^{-1}$) compared with the value for $[Fe(CO)_3N{:}CPh_2]_2$ (0.03$mm.sec^{-1}$). The differences in quadrupole splitting 1.70 and 0.87 $mm.sec^{-1}$ respectively reflect the expected significant distortion of the structure of the homo-bridged complex[14] to an extent much larger than would be expected in the direct replacement of one bridging methyleneamino group by iodine. The quadrupole splitting of 1.70 $mm.sec^{-1}$ may reflect a tendency towards five co-ordination which could occur through a lengthening of the metal-metal distance and a tendency towards planarity of the Fe_2NI ring.

The nature of the M_2X_2 bridging unit is dependent on the co-ordination of the metal, the size of the bridging atom X and their repulsion across the ring and the presence or absence of the metal-metal bond.[340] Organonitrogen groups bridge between metals so that the M-N-M and N-M-N angles are small and in complexes having metal-metal bonds the dihedral angles are also comparatively small (Table II.3). In $[Fe(CO)_3NH_2]_2$ for example the angles are 74, 78 and 78° respectively.[5] In contrast, the bridging iodine complex $[Fe(NO)_2I]_2$ is planar although the M-I-M angle is approximately the same (73°).[340] Although $[Fe(CO)_3NH_2]_2$ and $[Fe(NO)_2I]_2$ are formally related, in that both complexes have bridging groups, satisfy the noble gas rule, are diamagnetic, have a M-M bond, and comparable Fe-X-Fe angles, they differ in the nature of the metal-metal bond. The iron atoms in the nitrogen bridged complexes are approximately octahedral, the vacant position being occupied by the bent metal-metal bond, whereas in the iodine bridged complex the metal-metal interaction is across the planar Fe_2I_2 ring, conferring five fold co-ordination on each iron atom. The long Fe-Fe distance of 3.05Å in $[Fe(NO)_2I]_2$ is thought to arise from the larger bridging groups.

On considering the $Fe_2(CO)_6(N:CR'R'')I$ complexes, we have seen that nitrogen bridged complexes are characterised by short M-M bond distances and small bond angles whereas the iodine bridged complexes prefer long M-M distances. The two types of bridging atoms are therefore apparently opposed in $Fe_2(CO)_6(N:CR'R'')I$ and the change in replacing one methyleneamino group in $[Fe(CO)_3N:CR'R'']_2$ by iodine results in a lengthening of the M-M bond distance. Thus the stereochemistry at iron changes from pseudooctahedral towards five co-ordination.

Various mixed bridging ligand metal carbonyl complexes have been reported (see Chapter II), but these complexes $Fe_2(CO)_6(N:CR'R'')I$ (R' = R'' = Ph, p-tolyl; R' = Ph, R'' = Bu^t) are novel in containing bridging ligands of such widely differing size and bridging characteristics, as nitrogen and iodine.

On reacting $Fe_2(CO)_6(N:CPh_2)I$ with $Ph_2C:NLi$ in a 1:1 molar ratio, rapid reaction takes place to give the doubly bridged $[Fe(CO)_3N:CPh_2]_2$ complex in good yield. It appears that in this compound ($Fe_2(CO)_6(N:CPh_2)I$) we have a good precursor for the preparation and study of mixed ligand bridged complexes containing nitrogen. An X-ray crystallographic structure determination of this complex ($Fe_2(CO)_6(N:CPh_2)I$) is in progress and more information on the bonding will be revealed by this study.

CHAPTER VII

SYNTHESIS OF SOME o-METALLATED PRODUCTS OF MANGANESE CARBONYL

This chapter describes the syntheses of the ortho-metallated products obtained when $Mn_2(CO)_{10}$ was reacted with $Ph_2C{:}NR$ (R = Ph,Me).

A. Experimental

1. Reaction of $Mn_2(CO)_{10}$ with $Ph_2C{:}NPh$

$Mn_2(CO)_{10}$ (1.95 g., 5 mmole) and $Ph_2C{:}NPh$ (2.5 g., 10 mmole) were refluxed for 96 hr. in petroleum ether (100/120°) (60 ml.). The yellow solution was then reduced in bulk (20°, 10^{-1}mm.Hg) and cooled to -20° to produce yellow crystals. These were purified by chromatography on silicar, eluting with petroleum ether (80/100°). Three fractions were isolated, two of which were found to be $Mn_2(CO)_{10}$ and Ph_2CNCPh_2, identified by analysis and spectroscopy. The other fraction gave $Mn(CO)_4PhN{:}CPh.C_6H_4$. Yield 1.87 g. (44%).

Properties: The mustard yellow crystalline solid appeared to be air and moisture stable and soluble in most common organic solvents. It melted with decomposition in a sealed tube at 117-118°.

Analysis: Found, C,65.2; H,3.41; N,3.39; CO,25.56; $C_{23}H_{14}MnNO_4$ requires C,65.25; H,3.31; N,3.31; CO,26.47%.

Infrared spectrum: ν(CO), 2079m, 2000s, 1980s, 1949s, 1931m,sh cm^{-1} (Nujol) 2070m, 1986s, 1946s, cm^{-1} (cyclohexane); ν(CN) 1545w,br, cm^{-1} (Nujol). The full Nujol spectrum is: 3030m, 1596m, 1587m, 1571s, 1545w,br, 1471m, 1342s, 1259m, 1222w, 1179w, 1171wsh, 1174m, 1076m, 1044w, 1028w, 1014m, 1001m, 990wsh, 988m, 962m, 926w, 909w, 848w, 826w, 800msh, 794ms, 764m, 741s, 730s, 702s,sh, 697s, 671s, 646s,sh, 639s, 621w, 608m, 573mw, 546mbr, 459mbr, 435mbr, 405wbr cm^{-1}.

Molecular weight: 445, 468 by osmometry in benzene (Th.423).

^{1}H n.m.r. spectrum (CS_2): showed a very complex spectrum in the Ph region.

Mass spectrum (direct insertion probe at source temperature): The parent ion $[Mn(CO)_4PhN{:}CPh.C_6H_4]^+$ was observed at (m/e 423). The major peaks in the spectrum are listed in Table VII.1.

Organic fragments observed $[C_6H_4.PhC{:}NPh]^+$ (m/e 256) and $[PhC{:}NPh]^+$ (m/e 179).

Table VII.1

Mass spectral data for $Mn(CO)_4PhN:CPh.C_6H_4$

Ion	m/e	m*	Fragment lost
$[Mn(CO)_4PhN:CPh.C_6H_4]^+$	423		
			CO
$[Mn(CO)_3PhN:CPh.C_6H_4]^+$	395		
		340	CO
$[Mn(CO)_2PhN:CPh.C_6H_4]^+$	367		
		313	CO
$[Mn(CO)PhN:CPh.C_6H_4]^+$	339		
		287	CO
$[MnPhN:CPh.C_6H_4]^+$	311		
		140	PhCN
$[Mn.Ph.C_6H_4]^+$	208		
			Ph or C_6H_4
$[MnC_6H_4]^+$ or $[MnPh]^+$	131 or 132		
$[MnPhN:CPh.C_6H_4]^+$	311		
		55	PhC:NPh
$[Mn.C_6H_4]^+$	131		

2. Reaction of $Mn_2(CO)_{10}$ and Ph_2CNMe

$Mn_2(CO)_{10}$ (1.95 g., 5 mmole) and Ph_2CNMe (10 mmole) were refluxed for 96 hrs. in petroleum ether (100/120°) (60 ml.). The reaction was carried out as described above except that the product $Mn(CO)_4MeN{:}CPh.C_6H_4$ was distilled into a cooled receiver at (20°, 10^{-3}mm.Hg). Yield 1.24 g. (34.4%).

Properties: The dense yellow oil sublimed under high vacuum at room temperature, it appeared to be air stable for short periods of exposure, and was soluble in all the common organic solvents.

Analysis: Found, C,59.8; H,3.28; N,3.79; CO,30.15; $C_{18}H_{12}MnNO_4$ requires C,59.8; H,3.32; N,3.87; CO,31.0%.

Infrared spectrum: ν(CO), 2079s, 1992s, 1972s, 1931s cm^{-1} (Nujol), 2080m, 1986s, 1939s cm^{-1} (cyclohexane); ν(CN), 1580m cm^{-1} (Nujol).

The full Nujol spectrum is: 2079s, 1992s, 1972s, 1931s, 1690w, 1549m, 1498m, 1445s, 1438s,sh, 1409w, 1341s, 1319m, 1292m, 1260m, 1181w, 1163m, 1118w, 1081m, 1049m, 1021s, 1003s, 945m, 911w, 794m, 771m, 738s, 708s, 678s, 637s, 620m, 574mw, 543mbr, 458mbr, 404wbr cm^{-1}.

Molecular weight: 354 by osmometry in benzene (Th. 361).

^{1}H n.m.r. spectrum (CS_2): showed very complex signals in the Ph region and a singlet at 6.8τ assigned to $N\text{-}CH_3$ protons.

Mass spectrum (direct insertion probe at source temperature): The parent ion $[Mn(CO)_4MeN{:}CPh.C_6H_4]^+$ was observed at (m/e 361). The other major peaks in the spectrum are listed in Table VII.2.

Table VII.2.

Mass spectral data for $Mn(CO)_4MeN{:}CPh.C_6H_4$

Ion	m/e	m*	Fragment lost
$[Mn(CO)_4MeN{:}CPh.C_6H_4]^+$	361		
			CO
$[Mn(CO)_3MeN{:}CPh.C_6H_4]^+$	333		
		278	CO
$[Mn(CO)_2MeN{:}CPh.C_6H_4]^+$	305		
		251	CO
$[Mn(CO)MeN{:}CPh.C_6H_4]^+$	277		
		224	CO
$[MnMeN{:}CPh.C_6H_4]^+$	249		
		70	PhC:NMe
$[MnC_6H_4]^+$	131		

3. The reaction of $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ and $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ with $Ph_2C{:}NR$ (R = Ph or CH_3)

Carbonyl (A)	R (B)	Quantities		Solvent	Temp. °C	Time	Remarks
		(A)	(B)				
$[\pi\text{-}C_5H_5Fe(CO)_2]_2$	Ph	1.77 g. (5 mmole)	2.57 g. (10 mmole)	100/120 Pet. Ether	Reflux	90 hr.	No reaction-starting material obtained 96%
"	Me	"	1.95 g. (10 mmole)	"	"	96 hr.	No reaction-starting material obtained 87%
$[\pi\text{-}C_5H_5Mo(CO)_3]_2$	Ph	2.45 g. (5 mmole)	2.57 g. (10 mmole)	"	"	90 hr.	No reaction-starting material obtained 88%
"	Me	"	1.95 g. (10 mmole)	"	"	90 hr.	No reaction-starting materials obtained 90%

B. Discussion

The $Mn(CO)_4RN:CPh.C_6H_4$ complexes (R = Ph,Me)

Many transition metal compounds react with organonitrogen systems of the type PhX:NY (X = RC, N and Y = alkyl, aryl, OH etc.) with orthometallation of the benzene ring occurring e.g. p-azotoluene and p-azoanisole both react with iron carbonyl to form the complex shown in Fig.VII.1 (R = $CH_3C_6H_4$, R' = CH_3; R = $CH_3OC_6H_4$, R' = OCH_3).[74,341]

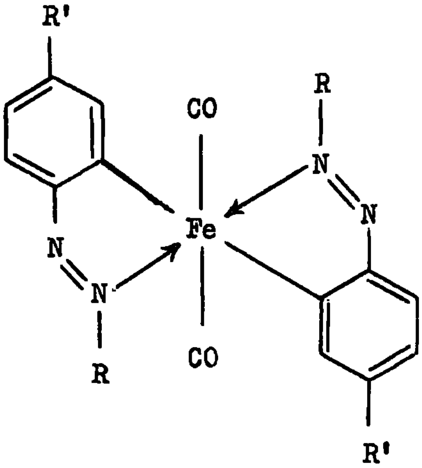
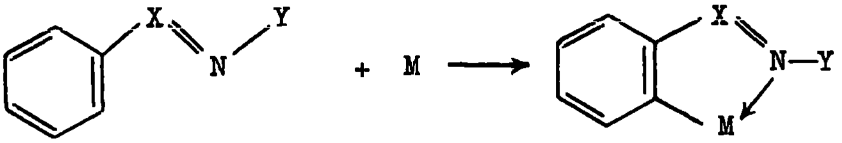


Fig.VII.1

Derivatives of the type shown in Fig.VII.2 are believed to be important intermediates in the carbonylation and ring closure reactions of Schiff's bases under high pressures of carbon monoxide and in the presence of carbonylation catalysts such as $Co_2(CO)_8$. (Eqn.VII.1).



VII.1

Fig.VII.2

Rosenthal and Wender have written a comprehensive review of the carbonylation of organonitrogen molecules using metal carbonyl catalysts[4] and Parshall has reviewed the subject of intramolecular aromatic substitution in transition metal complexes including organonitrogen derivatives.[342]

In this work ortho-metallation reactions occurred when the ligands Ph_2C:NPh and Ph_2C:NMe were reacted with $Mn_2(CO)_{10}$.

The complexes $Mn(CO)_4$RN:CPh.C_6H_4 were obtained as yellow crystals (R = Ph) or a deep yellow oil (R = Me) from the reaction of $Mn_2(CO)_{10}$ with Ph_2C:NR. In contrast, the reaction between Ph_2C:NR and $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ or $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ under the same reaction conditions led to an 85-90% recovery of starting materials and some 10-15% decomposition.

Analysis confirmed the empirical formula $Mn(CO)_4$RN:CPhC_6H_4 and molecular weight measurements indicated a mononuclear species. The infrared spectrum showed four strong absorptions in the carbonyl region at relatively low frequencies and in similar positions to the related $Mn(CO)_4C_{12}H_9N_2$ complex.[343]

The mass spectrum of the complex confirmed the mononuclear formulation and the presence of four carbonyl groups per molecule. The strong parent ion $[Mn(CO)_4RN{:}CPhC_6H_4]^+$ was observed in both cases (R = Ph and Me) and the breakdown of the parent ion was substantiated by metastable peaks.

The ^1H n.m.r. spectrum was obtained for both the complexes in carbon disulphide solution, but the complexity and weak signals in the Ph region made it impossible to interpret even when run at the maximum resolving power of the instrument. For detailed ^1H n.m.r. study it may be necessary to incorporate other groups than phenyl into the ligand. However in some complexes prepared by the reaction of azobenzene with metal carbonyls[343] it has been possible to assign the peaks in the phenyl region of the spectra, and it was found that the signal due to the proton on the carbon atom <u>ortho</u> to the carbon-metal σ bond occurred at lowest field.

The facile ortho-metallation reactions of appropriately substituted benzenes have been reported in the reactions of phenylacetylenes,[344] phenylphosphines,[345] phenylphosphites,[346] and azobenzenes[343] and it seems possible that this type of reaction occurs far more commonly than is at present recognised. In the reactions of azobenzene and related compounds, the formation of carbon-metal bonds has been described as electrophilic metallation of the benzene ring, and compared to mercuration reactions. In the present instances however, it is difficult to consider the electron rich low valent transition metal complex as an electrophile. Alternatively the reaction may involve the initial displacement of carbon monoxide and the co-ordination of the nitrogen to the metal. Reduced back bonding ability in the ligand would then increase the electron density on the metal and cause it to act as a nucleophile. The metal would then act as a template and insert into the sterically favoured ortho carbon-hydrogen bond. The metal hydride which could form would be expected to be unstable and eliminate hydrogen. A similar intramolecular elimination of methane from $(Ph_3P)_3RhCH_3$ results in the formation of the ortho-metallated complex $(Ph_3P)_2RhC_6H_4.PPh_2$.[347]

APPENDICES

Appendix 1

Experimental Details and Starting Materials

Most of the reactions described were carried out in an atmosphere of pure, dry nitrogen either in two-necked flasks or in double Schlenk tubes. Air sensitive materials were handled in a Glove Box, or if in solution were transferred from one vessel to another by syringe against a counter current of nitrogen.

Nitrogen Supply

"White Spot" nitrogen direct from the cylinder was dried by passage through a trap maintained at -196°C and delivered to a multiple outlet system. A constant pressure of nitrogen was maintained in the system by connecting one outlet to an oil bubbler.

Glove Box

The nitrogen atmosphere in the Glove Box was purified by continuously recycling it through a trap at -196°C, through two furnaces at 400°C containing copper wire and back to the box via a second trap at -196°C. Bench nitrogen was used, after passage through this system, to flush out the transfer tube. All external tubing was of copper or glass, and the gloves were made of "Butasol" rubber. An oxygen level of less than 50 p.p.m. was maintained by this system.

Solvents

Hydrocarbon solvents and diethyl ether were dried over extruded sodium, monoglyme and tetrahydrofuran distilled from lithium aluminium hydride, and chloroform freshly distilled from phosphoric oxide. Nitrobenzene and nitromethane for electrical conductivity measurements were dried over magnesium sulphate and phosphoric oxide respectively, before being fractionated in vacuo through a 3 ft. column of glass helices.

Starting Materials

The transition metal carbonyl derivatives used as starting materials are readily available by methods described in the literature e.g. $[\pi\text{-}C_5H_5M(CO)_3]_2$,[348] $\pi\text{-}C_5H_5M(CO)_3Cl$[349] (M = Mo,W), $[\pi\text{-}C_5H_5Fe(CO)_2]_2$,[350] $\pi\text{-}C_5H_5Fe(CO)_2Cl$,[351] $Fe(CO)_4I_2$.[352] $Mn_2(CO)_{10}$ was supplied by the Ethyl Corporation.

The imines $Ph_2C{:}NLi$,[353] $Ph_2C{:}NSiMe_3$,[354] $Bu^t{}_2C{:}NLi$,[355] $Bu^t{}_2C{:}NSiMe_3$,[15] $PhBu^tC{:}NLi$,[305] p-tolyl$_2$C:NLi,[356] $Ph_2C{:}NPh$[357] and $Ph_2C{:}NMe$,[358] were all prepared by standard routes.

Triphenylphosphine was recrystallised from hexane before use and iodine purified by sublimation in vacuo.

Appendix 2

Instrumentation

Infrared Spectra

Infrared spectra in the range 2.5-25 microns were recorded on a Grubb-Parsons Spectromaster.

Spectra of solid samples were recorded in the form of Nujol mulls between KBr plates, the samples being made up in the Glove Box.

Liquid samples (generally solutions) were inserted into a solution cell (thickness 0.1 mm) by syringe and gas phase samples were recorded using a 10 cm. cell. Both cells had KBr windows.

Nuclear Magnetic Resonance Spectra

Nuclear magnetic resonance spectra were recorded on a Perkin-Elmer R10 or Varian A56/60 spectrometer, operating at 60 MHz. Tetramethylsilane (T.M.S.) was used as an internal reference. The sample tubes were filled by syringe against a counter current of nitrogen, and were sealed under nitrogen.

Mass Spectra

Mass spectra were recorded on an A.E.I. MS9 mass spectrometer at 70 eV and an accelerating potential of 8kV, with a source temperature between 60 and 300°C, and electromagnetic scanning. Compounds were introduced by direct insertion into the ion source.

Isotope distribution patterns were computed with a programme kindly supplied to us by Dr. E.H. Brooks.

U.V. and Visible spectra

U.V. and visible spectra were recorded with an Optical spectrophotometer.

Mossbauer Spectra

Mossbauer spectra were recorded at P.C.M.U., A.E.R.E, Harwell. The samples were run in the solid state at -196°C.

Molecular Weights

Molecular weights were determined cryoscopically in benzene and osmometrically using a "Mecrolab Osmometer" in benzene solutions using either analytical grade biphenyl or $Cl.C_6H_3(NO)_2$ as standard solute.

Appendix 3

Analytical Methods

Carbon, Hydrogen and Nitrogen

Carbon, hydrogen and nitrogen were determined using a Perkin-Elmer 240 Elemental Analyser.

Halogens

Halogens were determined by fusion of the complex with potassium, followed by volumetric determination of the halide ions.

Carbon Monoxide

Carbon monoxide was analysed volumetrically on a vacuum line equipped with a mercury filled gas-burette. The compound was decomposed using a mixture of pyridine and iodine, the mixture being heated to 100°C to ensure complete liberation of carbon monoxide. The gasses were then pumped through a trap at -196° into the gas-burette using a Toppler pump.

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