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STUDIES OF SOME ORGANONITROGEN

DERIVATIVES OF CHROMIUM AND IRON

by

Richard James Eales, B.Sc.

A thesis submitted to the University of
Durham for the degree of Master of Science

April 1977

MEMORANDUM

The work described in this thesis was carried out in the University of Durham between October 1974 and September 1975. It has not been submitted for any other degree and is the original work of the author except where acknowledged by reference.

ACKNOWLEDGEMENTS

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

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

R. J. Eales

1977

ABSTRACT

The thesis describes synthetic and structural studies of ketimino - and amidino - complexes of chromium, and comparisons of their properties with the analagous molybdenum and tungsten derivatives. Studies of an amidino - complex of iron are also described.

The reaction of $h^5-C_5H_5Cr(CO)_3Br$ with R_2CNLi ($R = Ph, p\text{-tolyl}, t\text{-butyl}$) produced green complexes $h^5-C_5H_5Cr(CO)_2(N:CR_2)$. Substitution of carbonyl groups in the latter could not be achieved with triphenylphosphine under a variety of conditions. The spectral properties of the complexes are discussed and compared with the corresponding molybdenum and tungsten systems.

Reaction of $Fe(CO)_4I_2$ with $(p\text{-tolyl})NLi.CMe:N(p\text{-tolyl})$ produced an unidentified yellow powder. Subsequent reaction of this powder with alumina produced the orange air-sensitive complex $Fe(CO)_4\{(p\text{-tolyl})NH.CMe:N(p\text{-tolyl})\}$. This complex gave no reaction with N-bromosuccinimide. Spectral data for the complex is given and discussed.

Exploratory investigations of the reaction between $h^5-C_5H_5Cr(CO)_3Br$ and $RNLi.CR':NR$ ($R = p\text{-tolyl}, R' = Me; R = Me, R' = Ph$) gave evidence for the formation of a cyclopentadienyl chromium dicarbonyl amidino complex but its instability prevented its isolation. An investigation of the reaction between Ph_2CNLi and $h^5-C_5H_5Cr(CO)_3HgBr$ is also described. A small quantity of $h^5-C_5H_5Cr(CO)_2(N:CPh_2)$ was detected.

NOTES ON NOMENCLATURE

The Chemical Society have requested the name 'methylenamine' be used for the (unknown) compound $\text{CH}_2:\text{NH}$ and that derivatives be named accordingly. Hence compounds containing the units $\text{R}_2\text{C}:\text{N}-$ are known as di-alkyl or di-aryl methylenamino derivatives depending on the nature of the group R.

In this thesis, however, the older, but rather clearer term, 'ketimino' will also be used for this group, partly for the sake of brevity and partly because such terminology clearly distinguishes 'imino' from 'amino' derivatives.

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CHAPTER 1

INTRODUCTION

1. General Considerations

The scope and extent of transition metal carbonyl chemistry has increased dramatically over the past decade, resulting in, amongst other things, improved industrial processes and a better understanding of some naturally occurring reactions. The stability of many organometallic complexes can be traced back to the so-called "synergic" effect, operative in the bonding of metals with carbonyl and π -bonded organo - groups, and which refers to the simultaneous σ -donation of the lone pair, or π -electrons, from, for example, the carbon of a carbonyl group or π -bond of the ethylene molecule respectively, together with back donation from non-bonding d -orbitals to antibonding π -orbitals of the ligand. Each process has the effect of mutually increasing the other and for carbonyls results in a metal-carbon bond order of greater than one and also a stronger bond than would be possible by combining the separate effects of σ - and π -bonding. Such a synergic effect prevents excessive charge build-up on the metal and thus allows the carbonyl group to stabilise the metal in low oxidation states. Replacement of a carbonyl group by another ligand will result in competition for metal electron density between the new and remaining ligands and the outcome 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 and ammonia are strong Lewis bases having no π -bonding capacity, and consequently their introduction into a carbonyl complex strengthens

the metal-carbon bonding to the remaining carbonyl groups via increased $d_{\pi} \rightarrow \pi^*$ 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



Thus further substitution past the $M(\text{CO})_3L_3$ stage is not possible in this case. However, if the ligand L has π -acceptor properties (e.g. NO, CN^- , C_2H_4), the charge build-up at the metal is somewhat reduced. Consequently it may be possible to effect further replacement of CO from the $M(\text{CO})_3L_3$ complex.

2. Organonitrogen derivatives

The importance of organonitrogen groups in transition metal chemistry, particularly in the field of homogeneous catalysis where organonitrogen-metal intermediates are postulated,²⁻³ has long been recognised. More recently, interest has been focused on the versatility of the bonding in unsaturated organonitrogen groups, especially those containing carbon-nitrogen and nitrogen-nitrogen multiple bonded systems, the reactions of which, in the presence of transition metal carbonyl complexes, have recently been reviewed.²

3. 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 is a very versatile ligand.

The neutral ligand, $R_2C:NH$, as in complexes of the type, $[Mn(CO)_3 (Ph_2C:NH)_2 Br]$,⁴ σ -bonds to the metal via the nitrogen lone-pair and thus acts as a 2-electron donor. Backbonding is also possible from filled metal d-orbitals into π^* -orbitals on the ligand. The MNC system will necessarily be bent, due to sp^2 hybridisation at nitrogen (fig. 1.1.)

As the anionic ligand, $R_2C:N^-$, there is the possibility of donation of 1 or 3 electrons, depending on the involvement of the nitrogen lone pair in the bonding. For maximum orbital overlap it is thought that the MNC skeleton should be linear. In this situation nitrogen would be sp hybridised and the lone pair in a pure p orbital (of the correct symmetry to overlap with metal d-orbitals); bonding would then involve electron donation via σ - and $p_\pi \rightarrow d_\pi$ bonding and back donation via $d_\pi \rightarrow p_{\pi^*}$ bonding (figs. 1.2 and 1.3).

If the MNC skeleton were bent then σ -donation and $d_\pi \rightarrow p_{\pi^*}$ back donation would still be possible, but the lone pair would now occupy an orbital which in the limit would approximate to sp^2 (fig. 1.4). Although Ebsworth⁵ has calculated overlap integrals for nitrogen bonded to silicon and concluded that substantial $p_\pi \rightarrow d_\pi$ bonding from a nitrogen lone pair to vacant silicon d-orbitals is possible in a non-linear system, it is not expected to be as extensive as in a linear system. There is also the increased possibility in non-linear systems that the lone pair will donate to a second metal atom forming nitrogen-bridged dinuclear species (fig. 1.5).

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

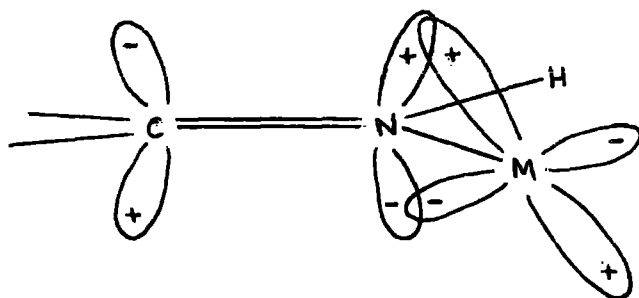


Fig 1.1 $d_{\pi}-\pi^*$ bonding involving a neutral methyleneamino ligand

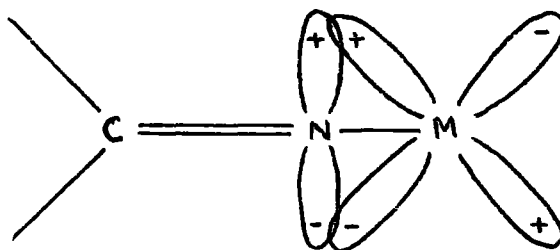


Fig 1.2 $p_{\pi}-d_{\pi}$ bonding involving a linear C = N - M skeleton

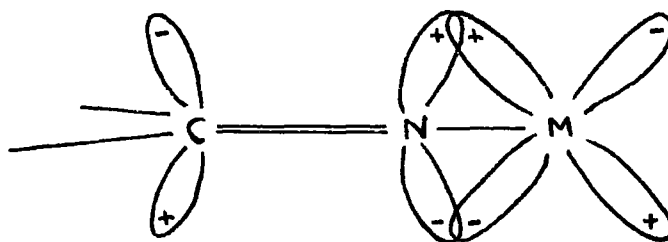


Fig 1.3 $d_{\pi}-\pi^*$ bonding involving a linear C = N-M skeleton

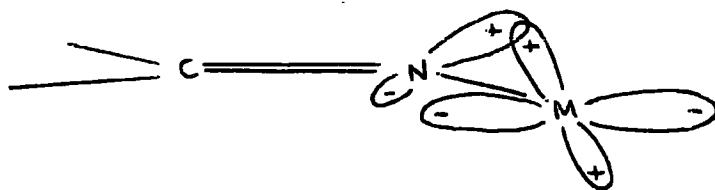


Fig 1.4

π -bonding involving a bent C = N-M skeleton.

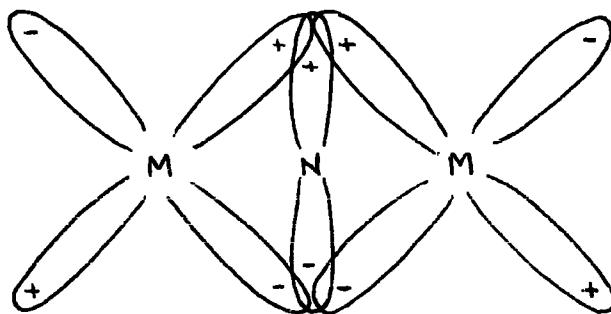


Fig 1.5

π -bonding involving one of the bridging
C:N groups

π -complex analogous to olefin complexes.

Studies carried out so far on ketimino-derivatives of molybdenum and tungsten suggest that in mononuclear complexes the ligand assumes a near linear MNC skeleton⁶. A crystal structure of the complex $h^5-C_5H_5Mo(CO)_2NCBu_2^t$ shows a small deviation from linearity of 8° , thought to be due to crystal packing. The short MO-N bond length of $1.87\overset{\circ}{\text{A}}$ indicates considerable multiple bonding between the metal and nitrogen.

A number of ketimino complexes of molybdenum, tungsten and iron have been prepared and investigated.⁶⁻¹⁴ $h^5C_5H_5M(CO)_3Cl$ (M = Mo, W) reacts with Bu_2^tCNLi , $Bu_2^tCNSiMe_3$, $Ph_2CNSiMe_3$ and (p-tolyl)₂ CNLi to give the corresponding ketimine complexes $h^5-C_5H_5M(CO)_2(N:CR_2)$ (R = Bu^t , Ph, p-tolyl). Some dinuclear complexes containing bridging ketimino-groups have also been prepared. Examples are $[h^5-C_5H_5M(CO)(N:CPh_2)]_2$ (M = Mo, W), $[Fe(CO)_3N:CPh_2]_2$ and $Fe_2(CO)_6(I)(N:CPh_2)$.

However, ketimino complexes are not the sole products obtained in reactions of $R_2C:N$ - systems with transition metal derivatives. With $h^5-C_5H_5M(CO)_3Cl$ (M = Mo, W), under certain conditions, 2-aza-allyl complexes, of formula $h^5-C_5H_5M(CO)_2(R_2CNCR_2)$ (M = Mo, W) are formed⁷; 11-13, 15-17 The aza-allyl group acts as a 3-electron ligand and is formed by "condensation" of two $R_2C=N$ - units, the extra nitrogen atom appearing as cyanate ion together with the carbonyl group lost.

Chapter 3 of this thesis describes the preparation and properties of some new ketimino complexes of chromium. The work was carried out in order to extend the ketimine work previously done for molybdenum and tungsten to the corresponding

chromium system and to compare the properties and structures of any new complexes obtained. As a comparison to the $\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{CO})_3\text{-Br/R}_2\text{CNLi}$ system, the reaction of $\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{CO})_3\text{HgBr}$ with Ph_2CNLi was also investigated. This work is described in appendix 2.

4. The amidino group as a ligand in transition metal systems

The amidino group R^1NCRNR^1 , behaves as a 3-electron-donor to a transition metal and is isoelectronic with both the allyl and the carboxylato-groups. It may fulfil its 3-electron-donor role by bonding through either (i) one nitrogen atom or (ii) more than one skeletal atom. The latter is preferred for the complexes $[\eta^5\text{C}_5\text{H}_5\text{M}(\text{CO})_2(\text{RNC}(\text{Ph})\text{NR})]$ ($\text{M} = \text{Mo}, \text{W}; \text{R} = \text{Ph}, \text{p-tolyl}$) so far prepared¹⁹ for two reasons. In the first place, complexes of the type $[\eta^5\text{-C}_5\text{H}_5\text{M}(\text{CO})_2\text{NR}^1\text{R}^1]$ ($\text{M} = \text{Mo}, \text{W}$) are not known and attempts to prepare them have failed.²³ Secondly, the amidino complexes $[\eta^5\text{C}_5\text{H}_5\text{M}(\text{CO})_2(\text{R}^1\text{NCRNR}^1)]$ ($\text{M} = \text{Mo}, \text{W}$) are found to have carbonyl stretching frequencies at positions close to those found for the corresponding 2-aza-allyl complexes, $[\eta^5\text{-C}_5\text{H}_5\text{M}(\text{CO})_2(\text{R}_2\text{CNCR}_2)]$ ($\text{M} = \text{Mo}, \text{W}$),¹¹ and at lower frequencies than those for the corresponding methylenamino complexes, $[\eta^5\text{-C}_5\text{H}_5\text{M}(\text{CO})_2(\text{N:CR}_2)]$ ($\text{M} = \text{Mo}, \text{W}$),¹⁰ indicative of the greater degree of electron donation expected from a bidentate ligand.

For the amidino group, a number of modes of bidentate attachment are feasible (fig. 1.6). Structure (A) has a completely delocalised, pseudo- π -allyl arrangement, (B) has localised σ, π -bonding in which a M-N σ -bond is supported by olefinic-type bonding through the $\text{C} = \text{N}$ double bond, (C) has the chelate ring completed by lone-pair donation from the second nitrogen atom, and (D) has a σ, σ -

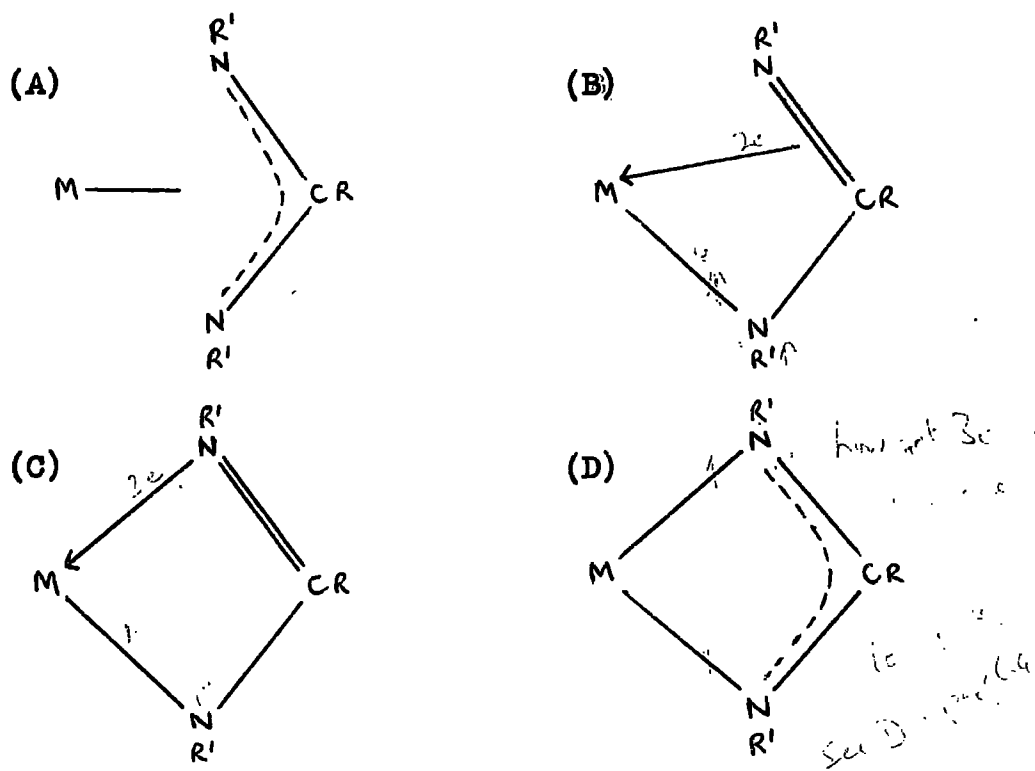


Fig 1.6 Possible modes of bidentate attachment of the amidino group

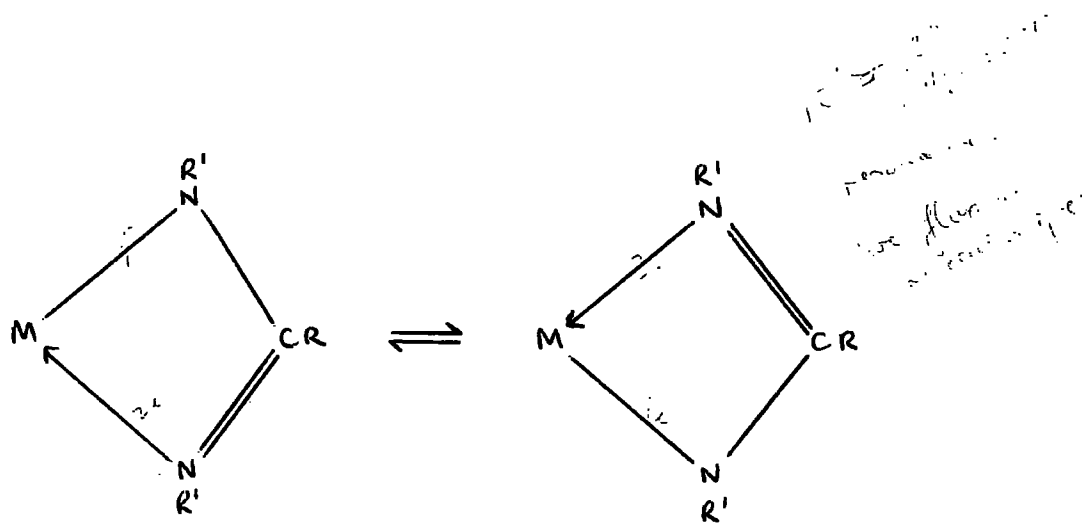


Fig 1.7 Equilibrium between structures of type (C)

attached delocalised group with the metal lying in the NCN plane. There is also the further possibility of a rapid equilibrium between structures of type (C) as shown in fig. 1.7. For the complexes, $[\eta^5\text{C}_5\text{H}_5\text{M}(\text{CO})_2(\text{R}^1\text{NCRNR}^1)]$ ($\text{M} = \text{Mo}, \text{W}$), the choice of any specific mode is rendered difficult by the equivocal nature of the spectroscopic data. In the light of findings with other 3-atom 3-electron-donor ligands,²⁴ structure (D) appears to be the most likely and makes the ligand strictly comparable with bidentate carboxylate, carbonate groups, etc.

A number of amidino derivatives of transition metals have so far been prepared,¹⁸⁻²² The amidino group, like the allyl and carboxylate groups, is also capable of bridging two metal atoms. Examples of complexes of this type are $[\eta^5\text{-C}_5\text{H}_5\text{M}(\text{PhNC}(\text{Ph})\text{NPh})]_n$,¹⁹ $[\text{Mo}_2(\text{PhNC}(\text{Ph})\text{NPh})_4]$,²¹ and $[\text{Re}_2(\text{PhNC}(\text{Ph})\text{NPh})_2\text{Cl}_4]$.²²

Chapter 4 and Appendix 1 of this thesis describe the preparation and properties and the attempted preparations of some new amidino complexes of iron and chromium. The work was carried out in order to extend the amidine work previously done for molybdenum, tungsten and manganese to chromium and iron and to compare the properties and structures of any new complexes obtained. In addition, a comparison with the corresponding chromium- and iron-ketimine systems also proved to be useful.

The synthesis and general features of the chemistry of cyclopentadienyl chromium carbonyl compounds are also relevant to this research and are reviewed in Chapter 2.

CHAPTER 2

A SURVEY OF CYCLOPENTADIENYL

CHROMIUM CARBONYL COMPLEXES

In this chapter, the preparation, reactions and properties of cyclopentadienyl chromium carbonyl compounds are reviewed. The purpose of this review is to place the work done on ketimino complexes of this type, described in chapter 3, in perspective with studies made on other cyclopentadienyl chromium carbonyl compounds. Throughout this review, $\eta^5\text{-C}_5\text{H}_5$ (i.e. when the ligand is bonded to the metal via all of the ring carbons) has been abbreviated to Cp.

A. Introduction

The chemistry of transition metal carbonyls has been the subject of many thousands of research papers, most of them published during the last twenty years. The first cyclopentadienyl chromium carbonyl compounds, obtained by reacting Cp_2Cr with carbon monoxide under pressure, were prepared by Fischer and Hafner in 1955.²⁵

The vast majority of cyclopentadienyl chromium carbonyl compounds so far prepared obey the inert gas rule and so are diamagnetic. An exception is $\text{CpCr}(\text{CO})_3$ ²⁶ which has one unpaired electron and is paramagnetic. To obey the inert gas rule, a monocarbonyl species ($n = 1$ in $\text{CpCr}(\text{CO})_n\text{L}$) would require ligand (s) L to donate 5 electrons, a dicarbonyl species ($n = 2$) would require L to donate 3 electrons and a tricarbonyl species ($n = 3$) would require L to donate 1 electron. The only known tetracarbonyl species is the cation $\text{CpCr}(\text{CO})_4^+$ ^{27,28}

B. Syntheses and Reactions

1. Routes into cyclopentadienyl chromium carbonyl chemistry

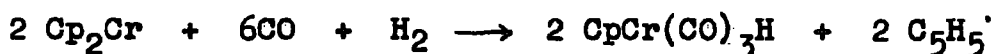
Cyclopentadienyl chromium carbonyl compounds are most conveniently prepared starting from either Cp_2Cr or $\text{Cr}(\text{CO})_6$.

(a) from chromocene

Chromocene reacts with carbon monoxide under pressure at 150-170° to give bluish-green $[\text{CpCr}(\text{CO})_3]_2$ ²⁵,



If hydrogen is included in the reaction mixture, yellow $\text{CpCr}(\text{CO})_3\text{H}$ (m.pt. 57-58°) is obtained,

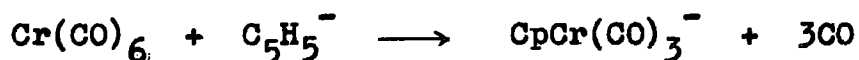


The dimer, $[\text{CpCr}(\text{CO})_3]_2$ absorbs hydrogen under pressure to give $\text{CpCr}(\text{CO})_3\text{H}$.²⁹ $[\text{CpCr}(\text{CO})_3]_2$ can be converted to the anion, $\text{CpCr}(\text{CO})_3^-$, by reaction with Na/naphthalene in THF.³⁰ Sublimation of $[\text{CpCr}(\text{CO})_3]_2$ under high vacuum at 80°K gives the yellow-green paramagnetic complex $\text{CpCr}(\text{CO})_3$,²⁶ while refluxing in toluene results in the loss of carbon monoxide to give $[\text{CpCr}(\text{CO})_2]_2$.³¹ $[\text{CpCr}(\text{CO})_3]_2$ is useful as a catalyst in the selective hydrogenation of conjugated polyenes,³² in which $\text{CpCr}(\text{CO})_3\text{H}$ is an intermediate. It reacts with Cp_2M (M = Ti, V, Cr, Co, Ni) in benzene at room temperature to give $[\text{Cp}_2\text{M}][\text{CpCr}(\text{CO})_3]$ ³³ which also has considerable catalytic activity.

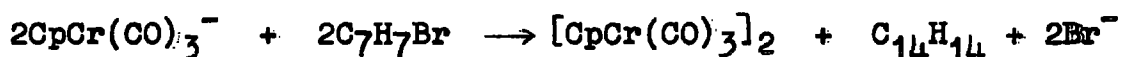
The acidic hydride, $\text{CpCr}(\text{CO})_3\text{H}$, reacts with aqueous alkali to yield the yellow anion $\text{CpCr}(\text{CO})_3^-$.²⁵ It is very air-sensitive and readily converted to the dimer, $[\text{CpCr}(\text{CO})_3]_2$, by the action of heat³⁴ or air³⁵. $\text{CpCr}(\text{CO})_3\text{H}$ reacts with $\text{BF}_3 \cdot \text{Me}_2\text{O}$ in benzene at 70° and under a pressure of carbon monoxide to give the yellow salt, $[\text{CpCr}(\text{CO})_4]^+ [\text{BF}_4]^-$.²⁷ The latter is insoluble in most organic solvents, and decomposes in methanol or water.

(b) from chromium hexacarbonyl

Chromium hexacarbonyl reacts with the alkali-metal cyclopentadienides, C_5H_5M ($M = Li, Na, K$), in DMF at 130° to give the anion, $CpCr(CO)_3^-$.^{34,36,37.}



$CpCr(CO)_3H$ may be prepared from the anion by acidification with glacial acetic acid.³⁴ It is purified by vacuum sublimation. The dimer, $[CpCr(CO)_3]_2$, can be obtained by reaction with tropylium bromide,³⁶



The crude product is purified by precipitation with methanol/water, washing with pentane and sublimation. The deep green crystals, so obtained, are sparingly soluble in organic solvents to give yellow or green solutions, depending on the concentration. Solutions of the anion, $CpCr(CO)_3^-$, may be precipitated as purple-brown $[Cp_2Co]^+ [CpCr(CO)_3]^-$,²⁵ green $[Cr(C_6H_6)_2]^+ [CpCr(CO)_3]^-$ or yellow $[CpCr(CO)_3]_2Hg$.^{25,36} $[Cr(C_6H_6)_2]^+ [CpCr(CO)_3]^-$ is paramagnetic with 1 unpaired electron. The paramagnetism is due to Cr(I) in the cation.

(c) other routes

$(MeCN)_3Cr(CO)_3$ reacts with $Me_3MC_5H_5$ ($M = Ge, Sn$) in refluxing THF under a carbon monoxide atmosphere to give $Cp(CO)_3CrMMe_3$.^{39,69} If C_5H_6 is used instead of $Me_3MC_5H_5$, $CpCr(CO)_3H$ is formed.

A summary of some of the more important reactions of cyclopentadienyl chromium carbonyl complexes is given in figure 2.1.

2. Complexes with chromium-carbon σ -bonds

The only known chromium complex of the general formula

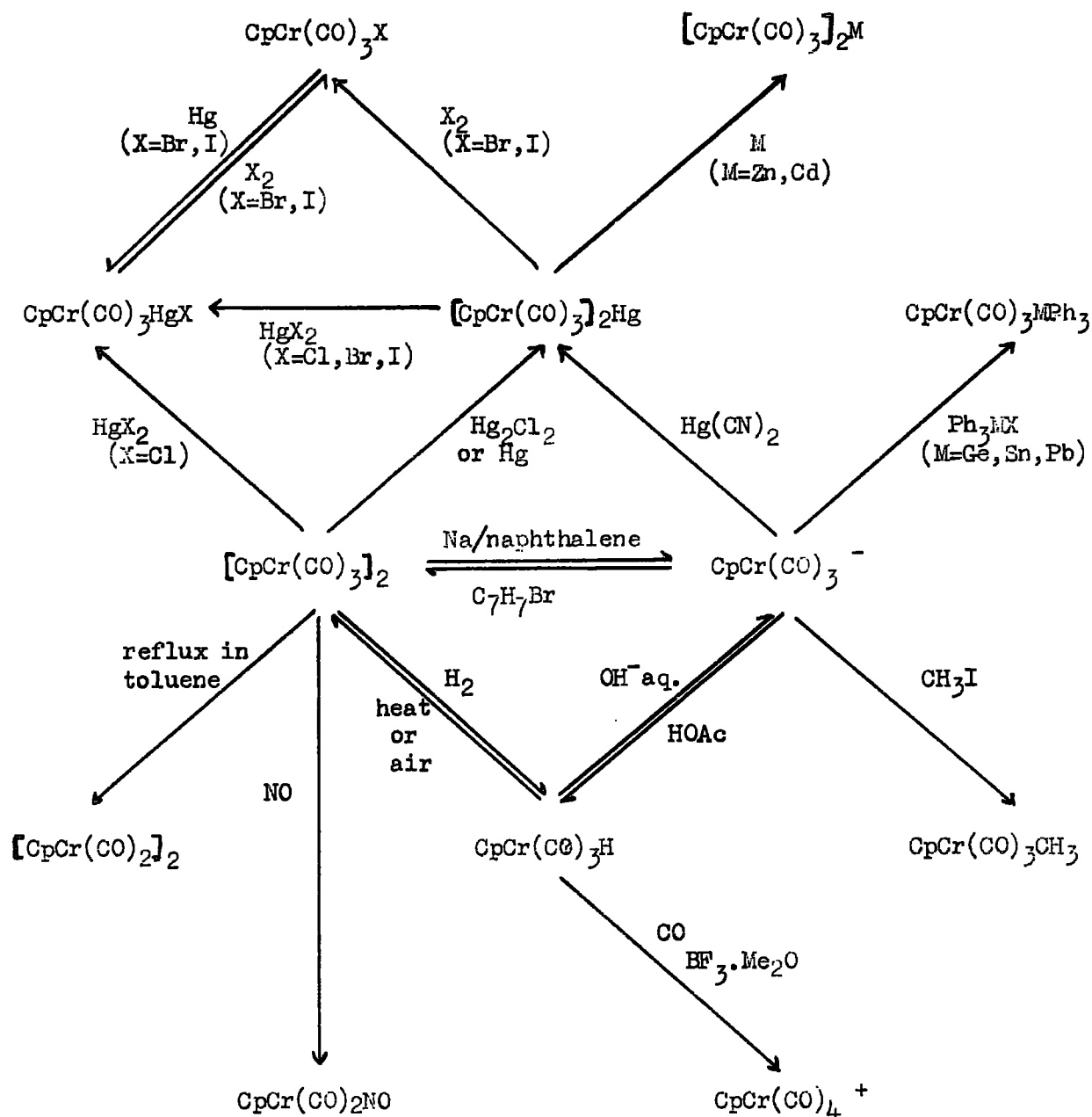


Fig. 2.1 Some of the more important reactions of cyclopentadienyl chromium carbonyl complexes.

$\text{CpM}(\text{CO})_3\text{R}$ (R = alkyl, aryl) is $\text{CpCr}(\text{CO})_3\text{CH}_3$ and this is thermally unstable. For M = Mo, W, however, a variety of complexes are known. The chromium complex $\text{CpCr}(\text{CO})_3\text{Me}$ may be prepared in low yield from $\text{CpCr}(\text{CO})_3^-$ by reaction with methyl iodide in THF.⁴⁰

$\text{CpCr}(\text{CO})_3\text{CH}_3$ reacts with a number of phosphines, L, to give acyl complexes $\text{CpCr}(\text{CO})_2\text{LCOCH}_3$ (L = PPh_3 , $\text{P}(\text{p-CH}_3\text{OC}_6\text{H}_4)_3$, PPhMe_2).⁴¹ This is the only well-defined example of the so-called "carbon monoxide insertion" reaction for cyclopentadienyl chromium alkyls.

3. Complexes with chromium-metal or metalloids bonds

Cyclopentadienyl chromium carbonyl complexes containing chromium-metal or metalloids bonds are too numerous to describe in detail, and so only a brief outline will be given.

(a) Zinc, cadmium and mercury

Of the complexes $[\text{CpCr}(\text{CO})_3]_2\text{M}$ (M = Zn, Cd, Hg), the mercury derivative is the most well known and studied. It can be prepared from the anion $\text{CpCr}(\text{CO})_3^-$ as described before or from the reaction between $[\text{CpCr}(\text{CO})_3]_2$ and Hg or Hg_2Cl_2 in THF.³¹ $[\text{CpCr}(\text{CO})_3]_2\text{Zn}$ and $[\text{CpCr}(\text{CO})_3]_2\text{Cd}$ can be prepared from $[\text{CpCr}(\text{CO})_3]_2\text{Hg}$ by metal exchange reactions.⁴²

All three complexes are yellow crystalline solids. The mercury derivative, being the only air-stable one, is a very useful starting material for the preparation of a whole range of related complexes. Reaction of $[\text{CpCr}(\text{CO})_3]_2\text{Hg}$ with X_2 (X = Br, I) in CH_2Cl_2 gives purple crystalline $\text{CpCr}(\text{CO})_3\text{X}$,⁴³ which is unstable, particularly in solution or in the air. With a deficiency of X_2 , both $\text{CpCr}(\text{CO})_3\text{X}$ and $\text{CpCr}(\text{CO})_3\text{HgX}$ are formed. The latter can also be

obtained by reaction of HgX_2 in acetone with $[\text{CpCr}(\text{CO})_3]_2\text{Hg}$,⁴³
or, for $\text{X} = \text{Cl}$ only, by reaction of HgCl_2 with $[\text{CpCr}(\text{CO})_3]_2$.³¹

(b) transition metals

Some complexes containing chromium-chromium bonds have already been mentioned, notably $[\text{CpCr}(\text{CO})_3]_2$. There are a series of complexes related to this dimer, in which one of the chromium atoms is replaced by a transition metal, and which contain a chromium-transition metal bond. Examples are $[\text{Cp}(\text{CO})_3\text{CrMo}(\text{CO})_3\text{Cp}]$ and $[\text{Cp}(\text{CO})_3\text{CrW}(\text{CO})_3\text{Cp}]$.⁴⁴

Apart from compounds of the above type, the number of cyclopentadienyl chromium carbonyl complexes containing chromium-transition metal bonds is very small, being mainly confined to the copper, silver and gold group. The complexes $[\text{CpCr}(\text{CO})_3]_2\text{M}^-$ ($\text{M} = \text{Cu}, \text{Ag}$) may be obtained from the reaction between $\text{CpCr}(\text{CO})_3^-$ and CuCl or AgNO_3 .⁴⁵ A similar gold complex is not known although $\text{CpCr}(\text{CO})_3\text{AuPPh}_3$ may be prepared from $\text{CpCr}(\text{CO})_3\text{H}$ and Ph_3PAuCl in THF.³⁰ In this case the corresponding copper and silver derivatives are too unstable to be isolated.

(c) group III

The only compounds in this category are the two thallium complexes, $\text{CpCr}(\text{CO})_3\text{Tl}$ and $[\text{CpCr}(\text{CO})_3]_3\text{Tl}$. They are prepared by the reaction of $\text{CpCr}(\text{CO})_3\text{Na}$ with either thallium (I) nitrate or thallium (III) chloride respectively.⁴⁶ The reaction of $[\text{CpCr}(\text{CO})_3]_2$ with thallium metal gives a mixture of the two complexes.⁴⁷

(d) group IV

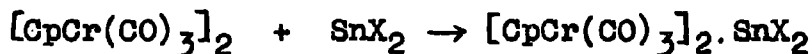
The vast majority of cyclopentadienyl chromium carbonyl

complexes containing chromium-metal or metalloids bonds, which have so far been prepared, are with group IV elements. The anion, $\text{CpCr}(\text{CO})_3^-$, is the most convenient starting material for the preparation of many of these complexes. It reacts with Ph_3MX ($\text{M} = \text{Ge}, \text{Sn}, \text{Pb}$; $\text{X} = \text{halogen}$) to give yellow or yellow-green $\text{CpCr}(\text{CO})_3\text{MPh}_3$.⁴⁸ Analogous methyl derivatives are also formed by the reaction of Me_3MBr ($\text{M} = \text{Ge}, \text{Sn}$) with $\text{CpCr}(\text{CO})_3^-$.^{49, 50} The mixed methyl chloro complex $\text{CpCr}(\text{CO})_3\text{GeMe}_2\text{Cl}$ can be obtained from GeMe_2Cl_2 . Photolysis gives the dimeric $[\text{CpCr}(\text{CO})_2\text{GeMe}_2]_2$ in low yield.⁵¹ All these complexes are generally fairly unstable, decomposing readily in the presence of air or water.

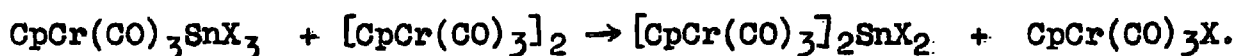
A number of silicon derivatives may be similarly prepared from $\text{CpCr}(\text{CO})_3^-$ e.g. $\text{CpCr}(\text{CO})_3\text{SiH}_3$, $\text{CpCr}(\text{CO})_3\text{SiMe}_2\text{H}$, $\text{CpCr}(\text{CO})_3\text{SiMeClH}$ and $\text{CpCr}(\text{CO})_3\text{SiCl}_2\text{H}$ using SiH_3Br ,^{52, 53} SiMe_2HCl ,⁵⁴ SiMeHCl_2 ⁵⁵ and SiHCl_3 ⁵⁵ respectively. The hydrogen in each of the latter three compounds may be replaced by a chlorine on treatment with carbon tetrachloride.⁵⁴ The silicon-chromium bond in $\text{CpCr}(\text{CO})_3\text{SiH}_3$ is readily cleaved by HCl at room temperature to give $\text{CpCr}(\text{CO})_3\text{H}$ and SiH_3Cl .^{52, 53}

The dimer, $[\text{CpCr}(\text{CO})_3]_2$, is also a useful starting material for the preparation of complexes with group IV elements. It reacts with R_3SnH ($\text{R} = \text{PhCH}_2, \text{Ph}$) in benzene at 80° to give $\text{CpCr}(\text{CO})_3\text{SnR}_3$ and $\text{CpCr}(\text{CO})_3\text{H}$.³³ Reaction with SnX_2 ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$) is brought about by heating or u.v. irradiation in a suitable solvent and gives a mixture of $[\text{CpCr}(\text{CO})_3]_2\text{SnX}_2$ and $\text{CpCr}(\text{CO})_3\text{SnX}_3$ ⁴⁴. The former compound contains a Cr-Sn-Cr unit. The percentage yield of the dichromium product decreases in the series $\text{F} > \text{Cl} > \text{Br} > \text{I}$. Indeed for $\text{X} = \text{F}$, only $[\text{CpCr}(\text{CO})_3]_2\text{SnF}_2$ is formed. There are two main

mechanisms involved in this reaction. The "direct" route involves insertion of SnX_2 into the chromium-chromium bond of $[\text{CpCr}(\text{CO})_3]_2$,



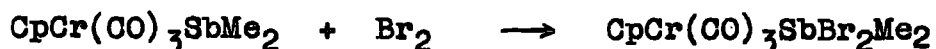
The "indirect" route gives, firstly, a mixture of $\text{CpCr}(\text{CO})_3\text{X}$ and $\text{CpCr}(\text{CO})_3\text{SnX}_3$. The $\text{CpCr}(\text{CO})_3\text{X}$ decomposes under the reaction conditions whereas the $\text{CpCr}(\text{CO})_3\text{SnX}_3$ reacts further with $[\text{CpCr}(\text{CO})_3]_2$ to give $[\text{CpCr}(\text{CO})_3]_2 \cdot \text{SnX}_2$,



The importance of the "indirect" route increases in the series $\text{F} < \text{Cl} < \text{Br} < \text{I}$ and is also more important for the u.v. irradiation than for the thermal reaction. Similar complexes containing three different metals may also be obtained e.g. $[\text{CpCr}(\text{CO})_3]_2$ reacts with $\text{Cp M}(\text{CO})_3 \text{SnX}_3$ ($\text{M} = \text{Mo}, \text{W}; \text{X} = \text{Cl}, \text{Br}, \text{I}$) to give $[\text{CpCr}(\text{CO})_3][\text{CpM}(\text{CO})_3]\text{SnX}_2$.⁴⁴

(e) group V

A number of cyclopentadienyl chromium carbonyl complexes containing arsenic and antimony are known. They are most conveniently prepared from the anion, $\text{CpCr}(\text{CO})_3^-$, by reaction with compounds of the type R_2MX (where $\text{R} =$ alkyl group; $\text{M} = \text{As}$ or Sb ; $\text{X} =$ halogen). E.g. Me_2SbBr gives $\text{CpCr}(\text{CO})_3\text{SbMe}_2$.⁵⁶ Reaction of this product with $\text{W}(\text{CO})_5$. THF or (norbornadiene) $\text{W}(\text{CO})_4$ results in the expansion of the coordination of the antimony to give $\text{CpCr}(\text{CO})_3\text{Me}_2\text{Sb} \rightarrow \text{W}(\text{CO})_5$ or $[\text{CpCr}(\text{CO})_3\text{Me}_2\text{Sb} \rightarrow]_2\text{W}(\text{CO})_4$ respectively. Reaction of $\text{CpCr}(\text{CO})_3\text{SbMe}_2$ with bromine in cyclohexane gives $\text{CpCr}(\text{CO})_3\text{SbBr}_2\text{Me}_2$.⁵⁷



This is an oxidative-addition reaction, there being no cleavage of

the element-metal or element-carbon bond as in related systems.

Thermal or solvolytic decomposition of the product gives $\text{CpCr}(\text{CO})_3\text{Br}$,



showing that halogen-cleavage in such element-transition metal compounds must be regarded as an addition-elimination process.

Reaction of $\text{CpCr}(\text{CO})_3^-$ with Me_2AsCl in a non-polar medium gives orange $\text{CpCr}(\text{CO})_3\text{AsMe}_2$,⁵⁸ which is unexpectedly stable. It may be quaternised, using methyl iodide, to form the pale yellow salt $[\text{CpCr}(\text{CO})_3\text{AsMe}_3]^+ \text{I}^-$.

With the dihalogen compound, MeSbBr_2 , $\text{CpCr}(\text{CO})_3^-$ reacts to form a complex containing a Cr-Sb-Cr bond, i.e. $[\text{CpCr}(\text{CO})_3]_2\text{SbMe}$.⁵⁹ Similarly, mixed transition metal compounds such as $[\text{CpCr}(\text{CO})_3][\text{CpM}(\text{CO})_3]\text{SbMe}$ (M = Mo, W) may also be obtained.

4. Complexes with chromium - non-metal bonds

Examples of cyclopentadienyl chromium carbonyl complexes containing chromium bonded to most of the non-metals can be found. Some of the more interesting elements involved are phosphorus, the halogens and nitrogen. The latter, in the form of nitrosyl complexes, will be discussed in the next section.

Substitution of carbonyl groups by phosphine ligands is a very common reaction for these complexes e.g. $[\text{CpCr}(\text{CO})_3]_2$ reacts with PPh_3 in ethanol to give $[\text{CpCr}(\text{CO})_2\text{PPh}_3]_2$.³¹ Other phosphines give similar though less stable products. On heating in a suitable solvent, $[\text{CpCr}(\text{CO})_3]_2\text{Hg}$ reacts with phosphines and phosphites to give complexes of the type $[\text{CpCr}(\text{CO})_2\text{L}]_2\text{Hg}$ (L = $\text{P}(\text{OMe})_3$, PPh_3 , $\text{P}(\text{OPh})_3$).⁴³

The halides, $\text{CpCr}(\text{CO})_3\text{X}$ ($\text{X} = \text{Br}, \text{I}$), prepared from $[\text{CpCr}(\text{CO})_3]_2\text{Hg}$ and X_2 ,⁴³ are very unstable. The chloride is not known. Reaction with mercury metal, as a suspension in THF, reforms the chromium-mercury bond to give $\text{CpCr}(\text{CO})_3\text{HgX}$.³¹

The most well-known complex of this type containing a chromium-sulphur bond is $\text{CpCr}(\text{CO})_2(\text{S}_2\text{CNet}_2)$. This, also, may be obtained from $[\text{CpCr}(\text{CO})_3]_2\text{Hg}$, by reaction with $(\text{Et}_2\text{NCS})_2\text{S}_2$ in benzene.⁶⁰ $[\text{CpCr}(\text{CO})_3\text{Hg}(\text{S}_2\text{CNet}_2)]$ is formed additionally.

5. Nitrosyl complexes

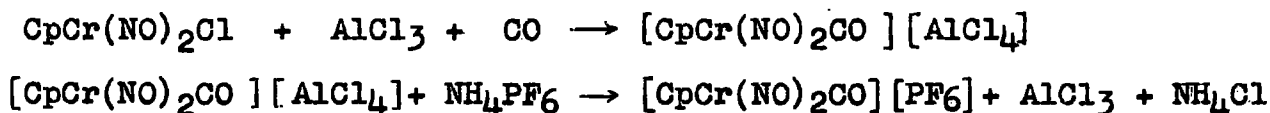
The most important cyclopentadienyl chromium mixed nitrosyl-carbonyl complex is $\text{CpCr}(\text{CO})_2\text{NO}$. It may be prepared from $[\text{CpCr}(\text{CO})_3]_2$ by reaction with NO in benzene⁶¹ or from $\text{CpCr}(\text{CO})_3^-$ by reaction with N-methyl-N-nitroso-ptoluenesulphonamide in ether.⁶² If $\text{CpCr}(\text{CO})_3^-$ is treated with NOCl in THF, a mixture of $[\text{CpCr}(\text{CO})_3]_2$ and $\text{CpCr}(\text{CO})_2\text{NO}$ is formed⁶³. Excess NOCl results in the conversion of the $\text{CpCr}(\text{CO})_2\text{NO}$ to $\text{CpCr}(\text{NO})_2\text{Cl}$.

$\text{CpCr}(\text{CO})_2\text{NO}$ reacts thermally or photochemically with PPh_3 to give $\text{CpCr}(\text{CO})(\text{NO})\text{PPh}_3$.^{64,65} Further substitution to $\text{CpCr}(\text{NO})(\text{PPh}_3)_2$, in the presence of excess PPh_3 , is difficult. Photolysis of $\text{CpCr}(\text{CO})_2\text{NO}$ in cyclooctene solution also results in the substitution of one carbonyl group forming $\text{CpCr}(\text{CO})(\text{NO})(\text{C}_8\text{H}_{14})$.⁶⁶ The π -bonded cycloolefin in this compound may be replaced by various monodentate ligands, L, to give $\text{CpCr}(\text{CO})(\text{NO})(\text{L})$ ($\text{L} = \text{C}_2\text{H}_2, \text{C}_2\text{H}_4, \text{C}_2(\text{COOMe})_2, \text{C}_{12}\text{H}_8, \text{C}_7\text{H}_{10}, \text{C}_4\text{H}_2\text{O}_3$).⁶⁶⁻⁶⁸

$\text{NaN}(\text{SiMe}_3)_2$ attacks one of the carbonyl groups of $\text{CpCr}(\text{CO})_2\text{NO}$

to give $\text{CpCr}(\text{CO})(\text{NO})\text{CN}^-$. This can be characterised as the olive-green monohydrate $\text{NaCpCr}(\text{CO})(\text{CN})(\text{NO})\cdot\text{H}_2\text{O}$,⁷⁰ in which the hydration water is bound to the nitrosyl group by hydrogen bonds. Phenyl lithium also attacks a carbonyl group of $\text{CpCr}(\text{CO})_2\text{NO}$, forming $\text{CpCr}(\text{CO})(\text{NO}) [\text{C}(\text{OLi})(\text{Ph})]$. This in turn reacts with $[\text{Me}_3\text{O}]\text{BF}_4$ in H_2O to give $\text{CpCr}(\text{CO})(\text{NO}) [\text{C}(\text{OMe})(\text{Ph})]$.⁷¹

A somewhat unrelated nitrosyl complex is the cation $[\text{CpCr}(\text{NO})_2\text{CO}]^+$. It may be prepared from the reaction of a mixture of $\text{CpCr}(\text{NO})_2\text{Cl}$ and AlCl_3 (1:3) with carbon monoxide under pressure.⁷² On removal of the benzene solvent and hydrolysis with concentrated NH_4PF_6 solution, $[\text{CpCr}(\text{NO})_2\text{CO}][\text{PF}_6]$ is formed,



6. Complexes with substituents on the cyclopentadienyl ring

Cyclopentadienyl chromium carbonyl complexes in which there are substituents on the cyclopentadienyl ring are quite numerous but do not fall within the scope of this review. However, for comparative purposes, a brief outline will be given.

$\text{AlCl}_3/\text{CH}_3\text{COCl}$ attacks the cyclopentadienyl ring of the nitrosyl complex $\text{CpCr}(\text{CO})_2\text{NO}$ to give the red acetyl derivative $\text{CH}_3\text{COC}_5\text{H}_4\text{Cr}(\text{CO})_2\text{NO}$.⁷⁶ Reaction of $\text{Cr}(\text{CO})_6$ or $(\text{MeCN})_3\text{Cr}(\text{CO})_3$ with $\text{Me}_5\text{C}_5\text{COCH}_3$ (5-acetyl - 1,2,3,4,5 - pentamethyl - cyclopentadiene) gives the air-stable green complex $[\text{h}^5\text{-Me}_5\text{C}_5\text{Cr}(\text{CO})_2]_2$,^{73,74} which is isoelectronic with $[\text{CpCr}(\text{CO})_2]_2$. Although the pentamethyl cyclopentadienyl complex, $[\text{h}^5\text{-Me}_5\text{C}_5\text{Cr}(\text{CO})_3]_2$, analagous to $[\text{CpCr}(\text{CO})_3]_2$, is not known, a whole range of its derivatives have been prepared.⁷⁵ Examples are $\text{h}^5\text{-Me}_5\text{C}_5\text{Cr}(\text{CO})_3^-$, $[\text{h}^5\text{-Me}_5\text{C}_5\text{Cr}(\text{CO})_3]_2\text{Hg}$, $\text{h}^5\text{-Me}_5\text{C}_5\text{Cr}(\text{CO})_3\text{X}$. (X = $\text{SnPh}_3, \text{HgCl}, \text{I}$) and $\text{h}^5\text{-Me}_5\text{C}_5\text{Cr}(\text{CO})_2\text{NO}$.

C. Metal - ligand bonding

1. Cyclopentadienyl group

In the cyclopentadienyl metal complexes considered in this review, the metal is effectively equidistant from all five carbon atoms of the cyclopentadienyl ring. The bonding is most conveniently discussed in terms of the LCAO-MO approximation. Thus, assuming a regular pentagon for the cyclopentadienyl ring, the π -molecular orbitals which are formed from the set of p_{π} -orbitals of the ring may be represented as shown in figure 2.2. There are five MO's, lowest in energy being orbital (e) which is strongly bonding. In addition there are two degenerate pairs of orbitals, one pair (c,d) weakly bonding and the highest in energy (a,b) antibonding.

The bonding between ligand and metal consists of two interrelated electron donations. Electron density is transferred from the cyclopentadienyl group to the chromium via overlap of filled ring molecular orbitals on the ligand (c,d,e) with vacant orbitals of appropriate symmetry on the metal. A simultaneous feeble back donation process operates from the filled metal orbitals to empty antibonding molecular orbitals (a,b) on the cyclopentadienyl group. Undoubtedly other ligand-metal orbital interactions also play some part in the overall bonding but are less important.

2. Carbonyl group

The nature of the bonding involving the carbonyl group and transition metals has been discussed briefly in chapter 1. Bonds between transition metals and carbon monoxide and related ligands involve the overlap of a filled ligand orbital with a vacant metal orbital of appropriate symmetry and the simultaneous back donation of electron density from filled metal orbitals to empty π - antibonding

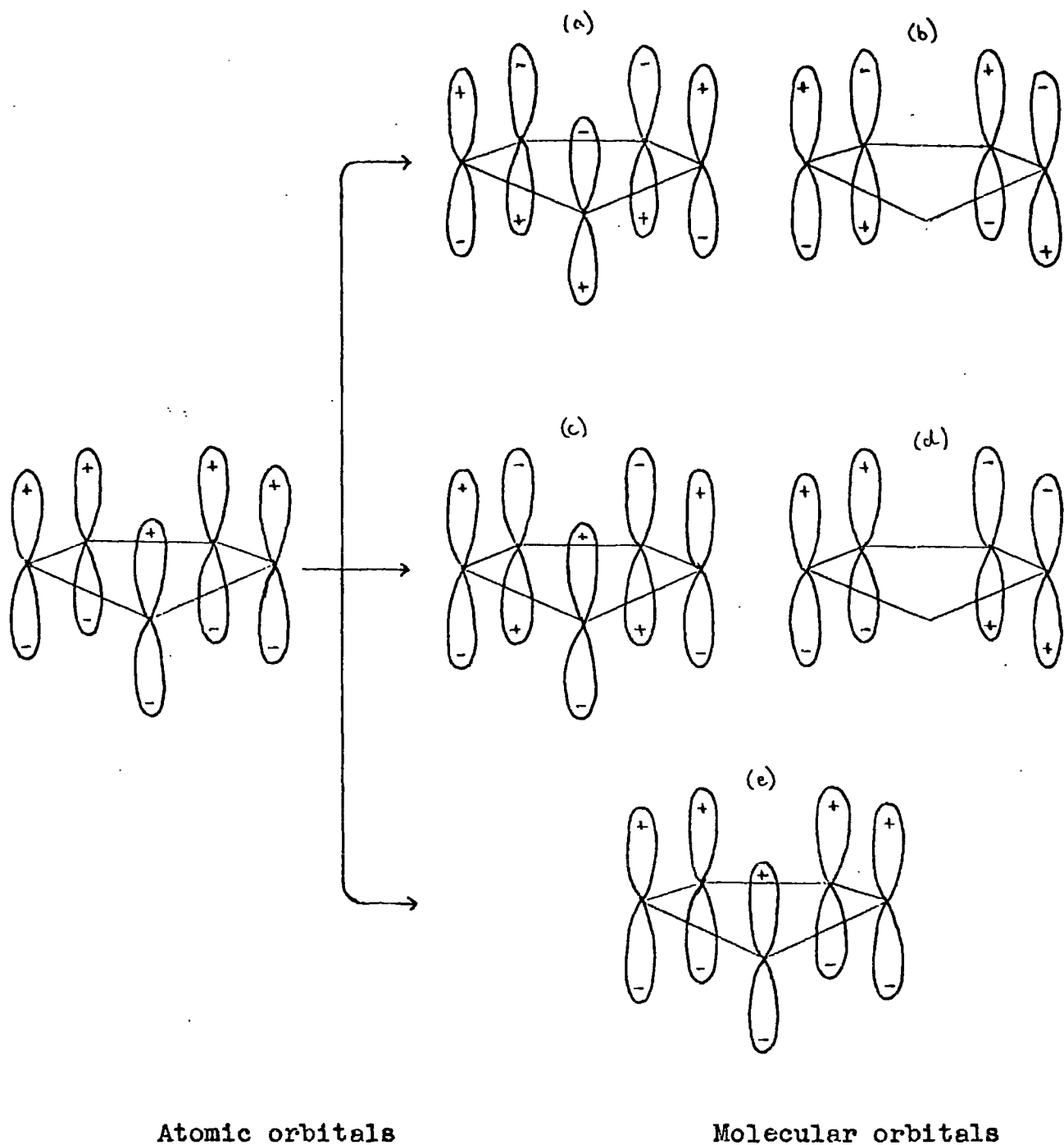
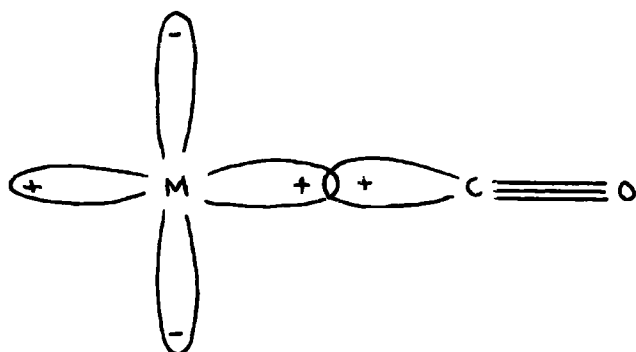


Fig. 2.2 π - molecular orbitals available for bonding between the cyclopentadienyl group and a transition metal.

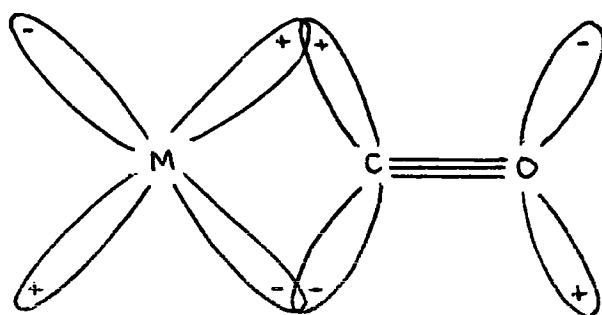
orbitals of the ligand. The C-O bond is thus weakened relative to uncomplexed carbon monoxide, and this is borne out by infrared studies of a number of transition metal carbonyl complexes.⁷⁷ A simplified diagram of this simultaneous donation and back-donation is shown in figure 2.3.

3. Nitrosyl group

Bonding of the nitrosyl group to a transition metal in the types of complexes under consideration is similar to that of the carbonyl group though slightly more complex. The nitric oxide molecule contains one more electron, located in a π -antibonding orbital, than carbon monoxide and in most cases may be formally regarded as a three-electron donor when complexed to transition metals. This three-electron donation may be thought of as the transfer of one electron to the metal, the resulting nitrosonium ion being isoelectronic with carbon monoxide and bonding similarly.⁷⁸ In these complexes the M-N-O bond is linear. Complexes containing bent M-N-O bonds (with no carbonyl analogues) are also known. In the extreme cases, only a σ -bond is formed and then the nitrosyl group may be regarded as a one-electron donor.



Metal-carbon σ -bond (forward bond)



Metal - carbon π -bond (back bond)

Fig. 2.3.

The "synergic effect" operative in bonding
between carbon monoxide and a transition metal, M.

D. Structure, Bonding and physical properties of some representative complexes.

1. Simpler cyclopentadienyl chromium carbonyl complexes

(a) $[\text{CpCr}(\text{CO})_3]_2$

Many reactions of $[\text{CpCr}(\text{CO})_3]_2$ imply that the Cr-Cr bond is weaker than the corresponding Mo-Mo and W-W bonds in the related complexes $[\text{CpMo}(\text{CO})_3]_2$ and $[\text{CpW}(\text{CO})_3]_2$. The strength of this metal-metal bond and also the bond lengths observed result from a balance of the attractive bonding forces between the metal atoms with the repulsive forces between "adjacent ligands" coordinated to the different metal atoms. The structure of $[\text{CpCr}(\text{CO})_3]_2$ is similar to its molybdenum counterpart, $[\text{CpMo}(\text{CO})_3]_2$, and it is unlikely that the "adjacent ligand" interactions would allow the Cr-Cr bond in $[\text{CpCr}(\text{CO})_3]_2$ to be markedly shorter than the already long Mo-Mo bond in $[\text{CpMo}(\text{CO})_3]_2$. Thus the constraints imposed by the structure prevent the optimum overlap of orbitals and the result is a weak Cr-Cr bond. The consequences of these "adjacent ligand" interactions may be eliminated either by cleavage of the Cr-Cr bond or by insertion of another atom (e.g. Hg) between the two $\text{CpCr}(\text{CO})_3$ - moieties. Therefore, these types of reaction take place much more readily than with $[\text{CpMo}(\text{CO})_3]_2$. The thermal decomposition of $[\text{CpCr}(\text{CO})_3]_2$ to $[\text{CpCr}(\text{CO})_2]_2$ also results in the reduction of the "adjacent ligand" interactions by the loss of two carbonyl groups and the adoption of a trans structure.

Hence, as expected, the crystal structure of $[\text{CpCr}(\text{CO})_3]_2$ ⁷⁹ reveals a long Cr-Cr bond. It is in fact 0.06 Å⁰ longer than the Mo-Mo bond in $[\text{CpMo}(\text{CO})_3]_2$. The $[\text{CpM}(\text{CO})_3]_2$ molecule is exceptionally sterically crowded and interaction between the ligands is

very significant. For a given M-M distance these repulsions are more severe when M = Cr than when M = Mo because the various Cr-ligand distances are shorter than the corresponding Mo-ligand distances. This results in a longer and weaker metal-metal bond in $[\text{CpCr}(\text{CO})_3]_2$ than in $[\text{CpMo}(\text{CO})_3]_2$.

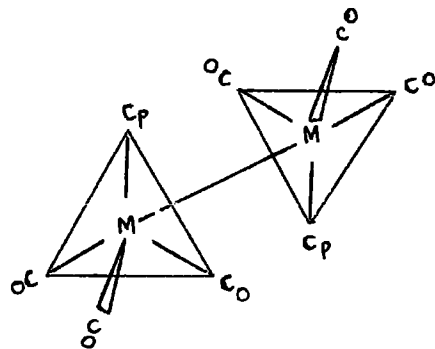
The i.r. spectrum of $[\text{CpCr}(\text{CO})_3]_2$ ^{31,85} indicates a centrosymmetric trans structure in the solid state, whereas in solution this isomer is in equilibrium with a gauche species (see fig. 2.4.). In very polar solvents such as DMF or DMSO, $[\text{CpCr}(\text{CO})_3]_2$ ionises completely to $[\text{CpCr}(\text{CO})_3\text{S}]^+$ and $[\text{CpCr}(\text{CO})_3]^-$ (where S is a coordinated solvent molecule). The presence of $[\text{CpCr}(\text{CO})_3]^-$ is confirmed by the two absorption bands at approximately 1770 and 1880 cm^{-1} (cf. $[\text{Et}_4\text{N}][\text{CpCr}(\text{CO})_3]$ in DMSO; $\nu_{\text{CO}} = 1768, 1878 \text{ cm}^{-1}$). Neither $[\text{CpMo}(\text{CO})_3]_2$ nor $[\text{CpW}(\text{CO})_3]_2$ ionise in these solvents.

Proton n.m.r.⁷⁹ shows that $[\text{CpCr}(\text{CO})_3]_2$ exists as a solvent- and temperature-dependent mixture of anti and gauche rotamers. In addition, the line width of the signal (in both non-polar and polar solvents) shows a reversible broadening on increasing the temperature. This is most easily explained by the presence of small concentrations of paramagnetic species in equilibrium with the normal diamagnetic isomers. These paramagnetic species may result from the dissociation of $[\text{CpCr}(\text{CO})_3]_2$ into stable $\text{CpCr}(\text{CO})_3$ radicals, i.e. a temperature-dependent equilibrium of the type,

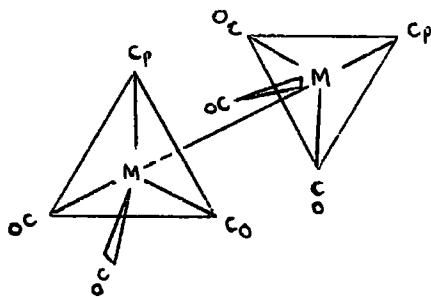


is indicated, in keeping with the extraordinary length of the Cr-Cr bond.

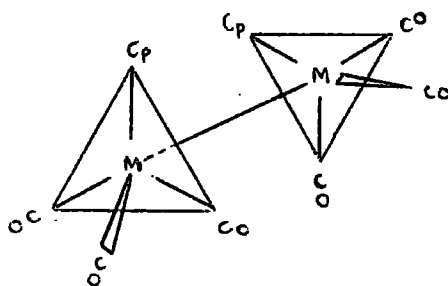
The mass spectrum of $[\text{CpCr}(\text{CO})_3]_2$ ^{80,81 (table 2.1)} exhibits no



anti rotamer



gauche rotamer



gauche rotamer

Fig 2.4 The three staggered configurations of $[\text{CpCr}(\text{CO})_3]_2$.

Table 2.1

Mass spectrum of $[\text{CpCr}(\text{CO})_3]_2$

Chromium-containing ions of intensity ≥ 1

Ion	Relative Intensity (based on $\text{CpCr}^+=100$)
$\text{CpCr}(\text{CO})_3\text{H}^+$	10
$\text{CpCr}(\text{CO})_3^+$	11
$\text{CpCr}(\text{CO})_2\text{H}^+$	6
$\text{CpCr}(\text{CO})_2^+$	23
$\text{CpCr}(\text{CO})\text{H}^+$	17
$\text{CpCr}(\text{CO})^+$	26
CpCr^+	100
$\text{C}_3\text{H}_3\text{Cr}^+$	25
$\text{Cr}(\text{CO})^+$	17
Cr^+	220

ions containing two chromium atoms in marked contrast to the spectrum of $[\text{CpMo}(\text{CO})_3]_2$. Since ions of the type $\text{Cp}_2\text{Cr}_2(\text{CO})_n^+$ ($n = 0 \dots 4$) observed in the spectra of $[\text{CpCr}(\text{CO})_3]_2\text{M}$ ($\text{M} = \text{Zn}, \text{Cd}, \text{Hg}$)⁴² (table 2.2) seem to have considerable stability, it is likely that the weak Cr-Cr bond in $[\text{CpCr}(\text{CO})_3]_2$ breaks before ionisation in the mass spectrometer. Indeed, the sublimation temperature of $[\text{CpCr}(\text{CO})_3]_2$ ($\sim 1000^\circ$, 0.1 mm.Hg)⁸¹ is much lower than that of $[\text{CpMo}(\text{CO})_3]_2$ ($\sim 150^\circ$, 0.1mm.Hg). Thus, it is very likely that the dimeric $[\text{CpCr}(\text{CO})_3]_2$ dissociates to monomeric $\text{CpCr}(\text{CO})_3$ during the process of vaporisation and ionisation which occur prior to observing the mass spectrum. Further evidence for this is the fact that the peak of highest m/e value in the mass spectrum of $[\text{CpCr}(\text{CO})_3]_2$ corresponds to $\text{CpCr}(\text{CO})_3\text{H}^+$. Formation of $\text{CpCr}(\text{CO})_3\text{H}$ may occur if the radicals obtained by vaporisation of $[\text{CpCr}(\text{CO})_3]_2$ abstract protons from other species available in the mass spectrometer.

(b) $\text{CpCr}(\text{CO})_3\text{H}$

$\text{CpCr}(\text{CO})_3\text{H}$ is a volatile yellow crystalline compound, very soluble in organic solvents such as benzene and ether. It is unstable even at room temperature, the chromium-hydrogen bond being readily broken e.g. by oxidation or heat to give $[\text{CpCr}(\text{CO})_3]_2$ or by the effect of alkali to give $\text{CpCr}(\text{CO})_3^-$. It is a powerful reducing agent and a weak acid.

The n.m.r. spectrum of $\text{CpCr}(\text{CO})_3\text{H}$ in C_6H_{12} ^{82,84} shows two singlets at 5.22 and 15.46 γ corresponding to C_5H_5 and $\text{Cr}-\underline{\text{H}}$ respectively. Calculations by Lohr and Lipscomb⁸³ have shown that 90% of the high field shift for M-H in $\text{CpM}(\text{CO})_3\text{H}$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) is due to the presence of an excess of negative charge on the hydrogen, and that the increase in γ (M-H) with increasing atomic

weight of M is due to increasing electron density on the hydrogen.

(c) CpCr(CO)₃⁻

The anion, CpCr(CO)₃⁻, is a base of medium strength. It is protonated by aqueous acetic acid but not by water. For the series of anions CpM(CO)₃⁻ (M = Cr, Mo, W), the nucleophilicity increases on descending group VI.⁸⁶⁻⁸⁸ Thus, the second order rate constant for reaction with methyl iodide follows the order, CpCr(CO)₃⁻ < CpMo(CO)₃⁻ < CpW(CO)₃⁻.⁸⁸ CpCr(CO)₃⁻ forms a number of adducts with Lewis acids. These may be bonded directly to the chromium atom, e.g. with H⁺ and CH₃⁺, or through the oxygen atoms of one of the carbonyl groups, e.g. with AlPh₃ and Al(THF)₃³⁺.⁸⁹

2. Complexes with chromium-metal or metalloids bonds

(a) Zinc, cadmium and mercury

[CpCr(CO)₃]₂Hg is a yellow crystalline solid which is fairly soluble in organic solvents. The chromium-mercury bond is remarkably stable, a concentration of 1% sodium amalgam in THF at 25° being insufficient to break it. In addition, only slight decomposition occurs when [CpCr(CO)₃]₂Hg is sublimated (130°, 0.1mm Hg).³⁶

The i.r. spectrum of [CpCr(CO)₃]₂Hg⁸⁵ in the solid state is best interpreted in terms of a single isomer with a skew configuration of CpCr(CO)₃ groups about the linear Cr-Hg-Cr system. The i.r. spectra for the zinc and cadmium analogues⁴² indicate that they adopt a similar configuration. In DMF, however, conductivity and i.r. data shows that [CpCr(CO)₃]₂Zn is largely dissociated.⁹⁰ Thus, whereas the complex [CpCr(CO)₃]₂ has a centrosymmetrical trans

structure, the conformations of its derivatives $[\text{CpCr}(\text{CO})_3]_2\text{X}$ vary with the nature of the bridging ligand X.⁸⁵ For the cationic complexes where X = H or I, the structure is centrosymmetric, for X = Zn, Cd or Hg, a skew configuration with a linear Cr-X-Cr arrangement is indicated; yet for X = GeR_2 , SnR_2 or PbR_2 , a bent Cr-X-Cr system is observed.

The mass spectra of the complexes $[\text{CpCr}(\text{CO})_3]_2\text{M}$ (M = Zn, Cd, Hg) are characterised by substantial loss of the metal, M.⁴² (table 2.2) The spectrum of the zinc complex shows a considerably greater proportion of ions with Cr-M bonds still intact, suggesting that the Zn-Cr bond in $[\text{CpCr}(\text{CO})_3]_2\text{Zn}$ is significantly stronger than the Cd-Cr bond in $[\text{CpCr}(\text{CO})_3]_2\text{Cd}$ or the Hg-Cr bond in $[\text{CpCr}(\text{CO})_3]_2\text{Hg}$.

(b) Transition metals

Infrared spectral data for the complexes $[\text{Cp}_2\text{M}][\text{CpCr}(\text{CO})_3]$ (M = Co, Cr, V, Ti)³³ are shown in table 2.3. For M = Co and Cr, the ν_{CO} frequencies are similar to those for the ionic compounds $\text{CpCr}(\text{CO})_3^- \text{Na}^+$ and $\text{CpCr}(\text{CO})_3^- \text{Et}_4\text{P}^+$ suggesting a very polar metal-chromium bond. However, there is a distinct increase in frequency of the carbonyl stretching vibration in the compounds $[\text{Cp}_2\text{V}][\text{CpCr}(\text{CO})_3]$ and $[\text{Cp}_2\text{Ti}][\text{CpCr}(\text{CO})_3]$, evidence for a considerably more covalent metal-chromium bond. The shift to shorter wavelengths of the carbonyl bands may be explained by the decreased negative charge of the chromium atom.

Similarities between the infrared spectra of $[\text{CpM}(\text{CO})_3]_2\text{Ag}^-$ salts⁴⁵ and their neutral $[\text{CpM}(\text{CO})_3]_2\text{Hg}$ (M = Cr, Mo, W) analogues imply that the two series are isostructural with linear M-Ag-M and M-Hg-M systems. The lower ν_{CO} frequencies of the silver anions are attributed to their negative charge.

Table 2.2

Mass spectra of $[\text{CpCr}(\text{CO})_3]_2\text{M}$ (M = Zn, Cd, Hg)

Metal - containing ions of intensity ≥ 1

Ion	Relative Intensity (based on $\text{CpCr}^+ = 100$)		
	M = Zn	M = Cd	M = Hg
$\text{MCp}_2\text{Cr}_2(\text{CO})_6^+$	58	2	4
$\text{MCpCr}(\text{CO})_3^+$	5	1	-
$\text{MCpCr}(\text{CO})^+$	5	-	-
MCpCr^+	-	1	-
M^+	7	13	42
$\text{Cp}_2\text{Cr}_2(\text{CO})_4^+$	1	-	-
$\text{Cp}_2\text{Cr}_2(\text{CO})_3^+$	48	1	1
$\text{Cp}_2\text{Cr}_2(\text{CO})_2^+$	12	-	-
$\text{Cp}_2\text{Cr}_2(\text{CO})^+$	19	1	1
Cp_2Cr_2^+	51	2	4
Cp_2Cr^+	145	6	10
$\text{CpCr}(\text{CO})_3^+$	8	12	11
$\text{CpCr}(\text{CO})_2^+$	33	17	19
$\text{CpCr}(\text{CO})^+$	36	24	24
CpCrC^+	4	1	-
CpCr^+	100	100	100
Cr^+	93	95	90

Table 2.3

Infrared spectral data for some CpCr(CO)₃X complexes

Complex	V _{co} C.m. ⁻¹			Ref.
Na ⁺ CpCr(CO) ₃ ⁻ (KBr)	1876		1695	91,92
Et ₄ P ⁺ CpCr(CO) ₃ ⁻ (Nujol)	1892		1765	55
[Cp ₂ Co][CpCr(CO) ₃]	1888		1765	33
[Cp ₂ Cr][CpCr(CO) ₃] (Nujol)	1890	1881	1767	33,91
[Cp ₂ V][CpCr(CO) ₃]	2020	1928	1840	33
[Cp ₂ Ti][CpCr(CO) ₃]	2020	1930	1870	33
CpCr(CO) ₃ SiH ₃ (Nujol)	1995	1943	1918	93
CpCr(CO) ₃ CH ₃ (KBr)	2006	1938sh.		91

(C) Group III

The infrared spectrum of $\text{CpCr}(\text{CO})_3\text{Tl}$ in THF ⁴⁶ shows three strong carbonyl bands, consistent with C_3 symmetry and similar to the spectra of $\text{CpCr}(\text{CO})_3\text{MR}_3$ ($M = \text{Ge, Sn, Pb}$). The presence of a chromium-thallium bond means that all three bands are shifted to a higher frequency relative to those of $\text{CpCr}(\text{CO})_3^-$. However, the relatively small increase in frequency compared with that observed in the tin (IV) or mercury (II) covalent derivatives indicates that the metal-metal bond is fairly polar.

(d) Group IV

The x-ray structure of $\text{CpCr}(\text{CO})_3\text{MR}_3$ ($M = \text{Sn, Pb; R = Ph}$)⁹⁴ shows, as expected, that the two groups $\text{CpCr}(\text{CO})_3$ and MR_3 are joined only by a chromium-metal bond. The environment about the metal M is tetrahedral with the chromium atom displaying 7 - coordination (assuming the occupation of three coordination bonds by the cyclopentadienyl group). The chromium-metal bond is approximately the same length as the sum of the metal radii, suggesting partial double bond character. The mass spectra of some similar complexes ($M = \text{Ge, Sn; R = Me}$) has also been studied.⁹⁵

The expected structure of $[\text{CpCr}(\text{CO})_3]_2\text{SnCl}_2$ with Sn(II) chloride inserted into the chromium-chromium bond of $[\text{CpCr}(\text{CO})_3]_2$ is confirmed by a recent crystal structure determination.⁹⁶ The corresponding distances and angles in each $\text{CpCr}(\text{CO})_3$ group are the same and show little variation from those in $[\text{CpCr}(\text{CO})_3]_2$. The environment about the tin atom is distorted tetrahedral.

The i.r. and n.m.r. spectra of $[\text{CpCr}(\text{CO})_2\text{GeMe}_2]_2$ ⁵¹ are consistent with a trans-bridged structure (see fig. 2.5).

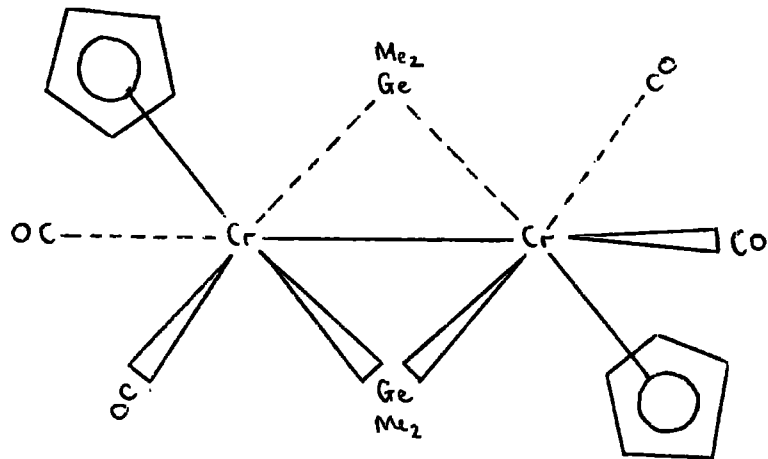


Fig. 2.5 Trans-bridged structure of $[\text{CpCr}(\text{CO})_2\text{GeMe}_2]_2$

3. Complexes with chromium-non-metal bonds

Derivatives of this type are very common. For example there is a whole range of phosphine complexes. Very useful information on the structure and isomerisation of such compounds may be obtained from i.r. and n.m.r. data.

An interesting series of phosphine complexes is $\text{CpCr}(\text{CO})_2(\text{L})\text{COCH}_3$ ($\text{L} = \text{PPh}_3, \text{P}(\text{p-CH}_3\text{OC}_6\text{H}_4)_3, \text{PPhMe}_2$)⁴¹, containing an acyl carbonyl group. These complexes have a distorted square pyramidal structure with the cyclopentadienyl group occupying the apical position and the terminal carbonyl groups trans to one another in the basal plane. The assignments are made on the basis of their ¹H n.m.r. spectra (table 2.4). The cyclopentadienyl resonances all appear as doublets due to P-H coupling. The PPhMe_2 derivative shows a doublet for the ligand methyl protons ($\delta = 1.88$ ppm, $J_{\text{PH}} = 8.5$ Hz) indicating that the molecule possesses a plane of symmetry and therefore exists as the trans isomer in solution. These observations parallel those made for analogous molybdenum acyl complexes. The two strong terminal carbonyl stretching bands and the characteristic acetyl carbonyl stretching band at approx 1640 cm^{-1} in the i.r. spectra of these complexes (table 2.5) support their formulation as acetyl derivatives. Comparison of both the proton n.m.r. and i.r. spectra of the chromium complexes with the corresponding molybdenum acetyl derivatives suggests that there is considerably greater electron density at the metal atom in the former. In the n.m.r. spectra the C_5H_5 chemical shifts are 0.4-0.5 ppm upfield relative to the molybdenum analogues whereas in the i.r. spectra the terminal carbonyl stretching frequencies are uniformly $10\text{-}20 \text{ cm}^{-1}$ lower for the chromium complexes.

Table 2.4

¹H-NMR spectral data for CpCr(CO)₂(L)COCH₃ in acetone - d₆

L	C ₅ H ₅ group		COCH ₃ group
	δ C ₅ H ₅ ppm.	JPH Hz.	δ COCH ₃ ppm.
PPh ₃	4.58 (doublet)	2.0	2.5
P(p-CH ₃ OC ₆ H ₄) ₃	4.60 (doublet)	2.1	2.5
PPhMe ₂	4.48 (doublet)	2.1	2.5

Table 2.5

IR spectral data for CpCr(CO)₂(L)COCH₃ in CCl₄

L	V _{CO} cm ⁻¹		
PPh ₃	1932 s	1856 vs	1644 m
P(p-CH ₃ OC ₆ H ₄) ₃	1929 s	1850 vs	1642 m
PPhMe ₂	1924 s	1841 vs	1643 m

The infrared spectrum of $[\text{CpCr}(\text{CO})_3]_2\text{Mn}(\text{py})_4$ (py = pyridine)⁹⁷ shows three strong absorptions in the carbonyl stretching region at 1902, 1805 and 1652 cm^{-1} (nujol mull), one conspicuously lower than the other two. The corresponding molybdenum complexes $[\text{CpMo}(\text{CO})_3]_2\text{Mn}(\text{py})_4$ and $[\text{CpMo}(\text{CO})_3]_2\text{Mg}(\text{py})_4$ show similar absorptions at 1905, 1818 and 1650 cm^{-1} and 1918, 1828 and 1667 cm^{-1} respectively. X-ray diffraction studies indicate that the magnesium atom in $[\text{CpMo}(\text{CO})_3]_2\text{Mg}(\text{py})_4$ is in an octahedral environment, coordinated by four equatorial pyridine ligands and two axial oxygen atoms, one from each $\text{CpMo}(\text{CO})_3$ group. The C-O bond in the bridging Mo-C-O-Mg group is longer than that in the terminal carbonyl groups. By analogy with the spectral assignments for the complex $[\text{CpMo}(\text{CO})_3]_2\text{Mg}(\text{py})_4$ the band at 1652 cm^{-1} in the spectrum of $[\text{CpCr}(\text{CO})_3]_2\text{Mn}(\text{py})_4$ is attributed to a C-O group bridging between chromium and manganese and coordinated to the latter via the oxygen atom. The two high frequency absorptions are associated with terminal carbonyl groups.

4. Nitrosyl complexes

$\text{CpCr}(\text{CO})_2\text{NO}$ is the simplest mixed carbonyl-nitrosyl of cyclopentadienyl chromium. Mass spectral evidence⁹⁸ (table 2.6) suggests that the carbonyl groups are eliminated more easily than the nitrosyl group, and hence less strongly bound. This is also borne out by the reactions of $\text{CpCr}(\text{CO})_2\text{NO}$. Triphenylphosphine, for example, replaces a carbonyl group, in preference to the nitrosyl group, to give $\text{CpCr}(\text{CO})(\text{NO})(\text{PPh}_3)$.^{64,65} The reaction stops at the monosubstitution stage⁹⁹ because the substitution of the strong π -acceptor carbonyl group by triphenylphosphine results in an increase in electron density at the chromium atom. The

Table 2.6

Primary ions in the mass spectrum of CpCr(CO)₂NO

Ion	Relative Intensity (based on CpCr ⁺ = 100)
CpCr(CO) ₂ (NO) ⁺	26.
CpCr(CO)(NO) ⁺	21
CpCr(NO) ⁺	13
CpCr(CO) ⁺	2.0
CpCr ⁺	100
C ₃ H ₂ Cr ⁺	4.5
Cr ⁺	80

carbonyl group in the monosubstitution product $\text{CpCr}(\text{CO})(\text{NO})(\text{PPh}_3)$ is thus more strongly bound, due to increased $\text{M} \rightarrow \text{C}$ back-bonding, and hence more difficult to replace, than the carbonyl groups in $\text{CpCr}(\text{CO})_2\text{NO}$.

The nucleophiles, $\text{NaN}(\text{SiMe}_3)_2$ ⁷⁰ and PhLi ⁷¹ both attack a carbonyl group of $\text{CpCr}(\text{CO})_2\text{NO}$ in preference to the less acidic nitrosyl group.

A study of the changes induced in the infrared spectrum of CH_2Cl_2 solutions of $\text{CpCr}(\text{CO})_2\text{NO}$ by the addition of various Lewis acids $\text{Ln}(\text{MeC}_5\text{H}_4)_3$ ($\text{Ln} = \text{Sm}, \text{Ho}$)⁶² (table 2.7) verifies that, in $\text{CpCr}(\text{CO})_2\text{NO}$, the nitrosyl group is a better Lewis base than the carbonyl groups. The existence of an isonitrosyl ($\text{Cr}-\text{N}-\text{O}-\text{Ln}$) linkage is confirmed by the band at 1635 cm^{-1} . The formation of the isonitrosyl group weakens the $\text{N}-\text{O}$ bond since the lanthanide metal withdraws electron density from the oxygen atom. In addition the $\text{Cr}-\text{N}$ bond is strengthened due to increased back donation from filled chromium orbitals into π -antibonding orbitals of the $\text{N}-\text{O}$ group. The two carbonyl bands in the infrared spectrum of the adduct are shifted to high frequency relative to those in the uncomplexed $\text{CpCr}(\text{CO})_2\text{NO}$. This is due to the fact that the presence of the stronger π -acceptor $-\text{NO}(\text{C}_5\text{H}_4\text{Me})_3$ group in the adduct reduces the extent of π -bonding between the chromium atom and the terminal carbonyl groups resulting in weaker $\text{Cr}-\text{C}$ bonds and therefore stronger $\text{C}-\text{O}$ bonds.

Temperature-dependent ^1H n.m.r. measurements on $\text{CpCr}(\text{CO})(\text{NO})(\text{CH} \equiv \text{CH})$ ⁶⁷ indicate intramolecular mobility of the π -bonded C_2H_2 ligand in solution. At low temperatures, the ligand appears to assume a favoured rotameric position, whilst above room temperature

Table 2.7

CpCr(CO)₂NO/Lewis Acid adducts in CH₂Cl₂ Solutions

Infrared spectra in the CO and NO stretching regions

Lewis Acid	Vco cm ⁻¹				VNO cm ⁻¹	
		2018 s	1973 s	1945 s	1692 s	1635s
-		2018 s	1973 s	1945 s	1692 s	
Sm(MeC ₅ H ₄) ₃	2038 s	2018 s	1973 s	1945 s	1692 s	1635s
Ho(MeC ₅ H ₄) ₃	2038 s	2018 s	1973 s	1945 s	1692 s	1635s
> 2 Ho (MeC ₅ H ₄) ₃	2038 s	2018 s	1973 s	1945 s	1692 s	1635s

a propeller-like rotation of the C_2H_2 group about the $Cr-C_2H_2$ bond axis takes place. Depending on the solvent, the free activation enthalpy, ΔG^\ddagger , of the C_2H_2 rotation varies between about 12 and 14 Kcal/mole.

Similar measurements on $CpCr(CO)(NO)(CH_2 = CH_2)$ ⁶⁸ indicate that the ethylene ligand undergoes a hindered rotation about the $Cr-C_2H_4$ bond axis. In this case the activation barrier for the rotation, ΔG^\ddagger_{238} , is approximately 11-12 Kcal/mole.

5. Complexes with substituents on the cyclopentadienyl ring

Of the cyclopentadienyl chromium carbonyl complexes of this type, most work has been done on the pentamethyl derivative, $[h^5-Me_5C_5Cr(CO)_2]_2$. Its crystal structure^{100,101} shows that it is an unbridged binuclear π -complex with a short metal-metal multiple bond and four terminal carbonyl groups. The cyclopentadienyl rings are trans w.r.t. the chromium-chromium axis and staggered w.r.t. each other, the methyl groups being bent from the cyclopentadienyl plane. The carbonyl groups are staggered w.r.t. the chromium-chromium axis. $[h^5-Me_5C_5Cr(CO)_2]_2$ is diamagnetic implying that it contains a triple metal-metal bond if the effective atomic number rule is not to be broken. The chromium-chromium distance of 2.28 Å lies between that reported for chromium II acetate (2.36 Å)¹⁰² and that for $(C_3H_5)_4Cr_2$ (1.97 Å)¹⁰³ both of which are reputed to contain quadruple bonds, and compares with the distance of 3.28 Å for the very long chromium-chromium bond in $[CpCr(CO)_3]_2$ ⁷⁹.

All the reactions⁷⁵ of $[h^5-Me_5C_5Cr(CO)_2]_2$ involve cleavage of the metal-metal bond. In addition, intramolecular carbon monoxide transfer is often observed. This is most probably due to the close

proximity of the carbonyl groups to the metal atom to which they are not bonded. The overall structure makes the triple bond rather inaccessible to attack by large groups, although this is not the case with small molecules such as nitric oxide. Its mass spectrum⁷⁴ shows a number of bimetallic ions in contrast to that for $[\text{CpCr}(\text{CO})_3]_2$,^{80,81} in keeping with its greater bond order.

CHAPTER 3

THE SYNTHESIS AND PROPERTIES OF SOME

NEW KETIMINO - DERIVATIVES OF CHROMIUM

In this chapter the synthesis and properties of some new dialkyl and di-aryl ketimino complexes of chromium are described.

A. Experimental

1. Preparation of $h^5-C_5H_5Cr(CO)_3Br$

$h^5-C_5H_5Cr(CO)_3Br$ was prepared from $[h^5-C_5H_5Cr(CO)_3]_2Hg$ by a modification of the method of Manning and Thornhill.⁴³ Thus, $[h^5-C_5H_5Cr(CO)_3]_2Hg$ (3.0 g., 5 mmole) was dissolved in chloroform (50 ml.) to give a yellow solution, which was frozen in liquid nitrogen. A solution of bromine (0.27 ml., 5 mmole) in chloroform (10 ml.) was syringed onto this, and the mixture allowed to warm to 0°. The solvent was removed under vacuum (0°, 0.05 mm.Hg) and the residue extracted with cold ether (70 ml., 0°). The ether extract was filtered (the sinter was kept cold by a jacket of cotton wool soaked in liquid nitrogen) to give a purple solution and a yellow solid, identified by i.r. spectroscopy as $h^5-C_5H_5Cr(CO)_3Br$ and $h^5-C_5H_5Cr(CO)_3HgBr$ respectively.⁴³ The purple $h^5-C_5H_5Cr(CO)_3Br$ solution was immediately frozen in liquid nitrogen.

2. Reaction of $h^5-C_5H_5Cr(CO)_3Br$ with R_2CNLi (R = Ph, p-tolyl or t-butyl)

A solution of the lithioketimine (5 mmole) in ether (10 ml.) was added to the ether solution of $h^5-C_5H_5Cr(CO)_3Br$ (5 mmole), frozen at -196°. The mixture was allowed to warm to room temperature with stirring, and left at room temperature for 1 hour, the colour changing from purple to dark green. After filtering, the solvent was removed under vacuum (room temperature, 0.05 mm Hg). The residue was extracted with toluene and filtered to give a dark green solution and a blue precipitate, the latter showing a positive lithium flame test. The toluene was removed under vacuum (room temperature, 0.05 mm Hg).

and the residue extracted with hexane. A large amount of bluish-green material remained in the flask and would not extract with hexane. This was identified by i.r. spectroscopy as the dimer, $[\text{h}^5\text{-C}_5\text{H}_5\text{Cr}(\text{CO})_3]_2$.⁸⁵

The hexane extract was filtered and then evaporated to dryness (room temperature, 0.05 mm Hg). The product was sublimated under vacuum (0.01 mm Hg) onto a cold finger cooled by an ice-salt mixture, and identified by mass spectroscopy as $[\text{h}^5\text{-C}_5\text{H}_5\text{Cr}(\text{CO})_2 (\text{N}:\text{CR}_2)]$ (R = Ph, p-tolyl or Bu^t). Under these conditions, the temperatures required for sublimation were as follows:- for R = Ph, approx. 75°; for R = p-tolyl, approx 85°; and for R = Bu^t, approx. 40°.

The phenyl and para-tolyl derivatives were contaminated with the corresponding ketone, i.e. benzophenone or di-p-tolyl ketone, and so were obtained as green oils. It was not possible to separate the product from the ketone by varying the temperature of sublimation. The ketones may well be thermal decomposition products of the ketimino-chromium complexes.

The t-butyl derivative was obtained as green leaf-like crystals. The only other volatile product of the reaction was the azine, $\text{Bu}_2^t\text{CNNCBu}_2^t$, (identified by mass spectroscopy), which was removed by a prior sublimation (room temperature, 0.01 mm Hg.).

Properties: All three complexes readily dissolved in most organic solvents to give green solutions which decomposed slowly, even at -25°. For this reason, it was not possible to crystallise the complexes from hexane or toluene. The green crystals of $\text{h}^5\text{-C}_5\text{H}_5\text{Cr}(\text{CO})_2 (\text{N}:\text{C Bu}_2^t)$ melted at 92-3° with decomposition. They were stable in air for short periods. The action of water on the complex $\text{h}^5\text{-C}_5\text{H}_5\text{Cr}(\text{CO})_2 (\text{N}:\text{CPh}_2)$ caused some (but not complete)

decomposition to a non-carbonyl species.

Infrared spectra: All three complexes showed two strong sharp absorptions in the carbonyl stretching region (table 3.1). The two ν_{CO} bands observed for a solution of $h^5-C_5H_5Cr(CO)_2(N:CBu_2^t)$ in pentane showed no splitting on cooling from room temperature to -100° , and no new bands were seen. An absorption at 1626 cm^{-1} for the $h^5-C_5H_5Cr(CO)_2(N:CBu_2^t)$ complex (nujol mull) can be assigned to $\nu_{C=N}$.

Mass Spectra: The parent ion $[h^5-C_5H_5Cr(CO)_2(N:CR_2)]^+$ was observed for all three complexes. The major chromium-containing ions are listed in table 3.2. In addition, peaks were observed for the following organic fragments:- for the complex $h^5-C_5H_5Cr(CO)_2(N:CPh_2)$ at m/e 181 (Ph_2CNH^+), 180 (Ph_2CN^+), 104 ($PhCNH^+$), 103 ($PhCN^+$) 90.5 (Ph_2CNH^{2+}), 77(Ph^+) and 51.5 ($PhCN^{2+}$), and for the complex $h^5-C_5H_5Cr(CO)_2(N:CBu_2^t)$ at m/e 84 (Bu^tCNH^+) and 57(Bu^{t+}). The spectrum of $h^5-C_5H_5Cr(CO)_2\{N:C(ptolyl)_2\}$ was not recorded below m/e 120.

1H n.m.r. spectra: The data for $h^5-C_5H_5Cr(CO)_2(N:CBu_2^t)$ is shown in table 3.3. Two singlets with intensity ratio 5:9, corresponding to $h^5-C_5H_5$ and Bu^t protons respectively, were observed in all solvents. There was no splitting of these peaks on cooling solutions in toluene from ambient to -26° or on cooling solutions in CS_2 from ambient to -60° .

Analyses for chromium:

$h^5-C_5H_5Cr(CO)_2(N:CBu_2^t)$ Found, 16.15%; Expected, 16.59%.

None of the complexes could be crystallised from a hydrocarbon solvent. In addition the products obtained by sublimation, in particular the phenyl and para-tolyl derivatives, were contaminated and did not give satisfactory analysis figures.

3. Reaction of $h^5-C_5H_5Cr(CO)_2(N:CBu_2^t)$ with PPh_3

A solution of $\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{CO})_2 (\text{N}:\text{C}_2\text{Bu}^t)$ in hexane was heated under reflux for 2 hours with a solution of triphenylphosphine in the same solvent. There was no change in the positions of the ν_{CO} absorptions in the i.r. spectrum. Similarly, there was no reaction in toluene after refluxing for 5 hours, nor in monoglyme.

Table 3.1

Infrared spectral data for $\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{CO})_2 (\text{N:CR}_2)$

complexes: Vco bands

R	Solvent	Vco cm^{-1}	
Ph	Hexane	1979	1912
P-tolyl	Hexane	1976	1909
Bu ^t	Hexane	1965	1891
Bu ^t	Ether	1960	1884
Bu ^t	CS ₂	1956	1878
Bu ^t	Nujol Mull	1961	1886

Table 3.2

Mass spectral data for $h^5-C_5H_5Cr(CO)_2(N:CR_2)$

complexes; Cr - containing ions

Ion	R = Bu ^t		R = Ph		R = p-tolyl			
	m/e	R.I.	m*	Fragment Lost	m/e	R.I.	m/e	R.I.
$h^5-C_5H_5Cr(CO)_2N:CR_2^+$	313	28	259.5	CO	353	11	381	14
$h^5-C_5H_5Cr(CO)N:CR_2^+$	285	16			231.8	CO	325	8
$h^5-C_5H_5CrN:CR_2^+$	257	100					297	100
$h^5-C_5H_5CrNCR^+$	200	344			-	-	-	-
$h^5-C_5H_5CrR^+$	-	-			194	186	-	-
$h^5-C_5H_5Cr(CO)N:CR_2^{2+}$	-	-			162.5	1	-	-
$Cr(NCR)^+$	135	72			155	19	-	-
$h^5-C_5H_5CrN:CR_2^{2+}$	-	-			148.5	4	162.5	4
$h^5-C_5H_5Cr^+$	117	156			117	33		
Cr^+	52	44			52	102		

R.I. = Relative Intensity

Table 3.3

N.M.R. data for $\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{CO})_2(\text{N:CBu}_2^t)$

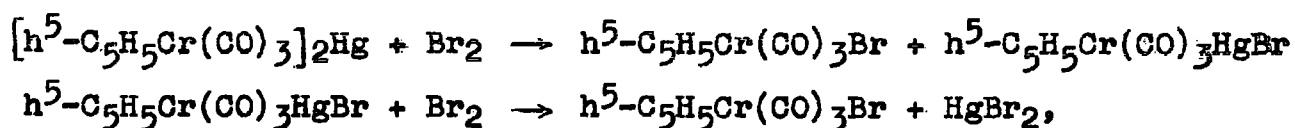
Solvent	Temperature	τ (C5H5)	τ (Bu ^t)
C_6D_6	Ambient	5.40	9.14
Toluene	Ambient	5.39	9.12
Toluene	-26°	5.53	9.22
CS_2	Ambient	4.39	8.30
CS_2	-60°	4.72	8.67

B. Discussion

1. The preparation of $h^5-C_5H_5Cr(CO)_3Br$

To achieve the best yields of $h^5-C_5H_5Cr(CO)_3Br$, the initial addition of bromine to $[h^5-C_5H_5Cr(CO)_3]_2Hg$ was done at -196° . This ensured that, on warming, the reactants were fully mixed before the temperature for reaction was reached, since above this temperature even a slight local excess of bromine was sufficient to cause considerable decomposition of the product. Throughout the preparation the temperature was not allowed to go above 0° , due to the unstable nature of solutions of $h^5-C_5H_5Cr(CO)_3Br$.⁴³

In addition, sufficient bromine was used to cleave one of the Hg-Cr bonds in $[h^5-C_5H_5Cr(CO)_3]_2Hg$ only. $h^5-C_5H_5Cr(CO)_3HgBr$ was thus formed as a by-product (and subsequently used in a later reaction). If enough bromine was used for the reaction,



to go to completion,

the $HgBr_2$ formed, being soluble in ether, reacted with the lithio ketimine, in the subsequent reaction, in preference to $h^5-C_5H_5Cr(CO)_3Br$. As $h^5-C_5H_5Cr(CO)_3HgBr$ is insoluble in ether, it could be removed from the reaction mixture by filtration, and so did not interfere.

2. The dicarbonyl complexes $h^5-C_5H_5Cr(CO)_2(N:CR_2)$

$h^5-C_5H_5Cr(CO)_3Br$ reacts with lithio ketimines, $LiNCR_2$ (R = Ph, p-tolyl, Bu^t)

(R = Ph, p-tolyl, Bu^t), to form the dicarbonyl products $h^5-C_5H_5Cr(CO)_2(N:CR_2)$. There was no evidence for the formation of complexes

containing the 2-aza-allyl group as had been the case for the reaction of $h^5-C_5H_5Mo(CO)_3Cl$ with Ph_2CNLi .^{7,15}

The introduction of a methyleneamino group into the π -cyclopentadienyl chromium complex thus results in the loss of one molecule of carbon monoxide. The methyleneamino group may act either as a three-electron donor and conserve the noble gas configuration of the metal, or as a one-electron donor in which case the noble gas configuration is broken. I.r. spectroscopy together with a comparison with the molybdenum and tungsten analogues, $[h^5-C_5H_5M(CO)_2(N:CR_2)]$ ($M = Mo, W$), leads us to believe that the group is behaving as a 3-electron donor to a single metal.

A comparison of the infrared spectral data for the complexes, $[h^5-C_5H_5M(CO)_2(N:CR_2)]$ ($M = Cr, Mo, W$; $R = Ph, p\text{-tolyl}, Bu^t$), is shown in tables 3.4 and 3.5. All complexes show two strong sharp carbonyl absorptions characteristic of a dicarbonyl species at relatively low frequencies compared with the starting materials. Loss of carbon monoxide and the consequent increase in π -bonding between the metal and the 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 consistent with the methyleneamino group acting as a three-electron donor.^{104,105}

For $[h^5-C_5H_5M(CO)_2NCR_2]$ ($M = Cr, Mo, W$), the frequencies of the two carbonyl absorptions decrease in the series $Cr > Mo > W$. This should be in keeping with the M-C bond strengths increasing in the order $Cr < Mo < W$. This trend is generally (but not always) reflected throughout the chemistry of carbonyl complexes of metals

Infrared spectral data for $\eta^5\text{-C}_5\text{H}_5\text{M}(\text{CO})_2(\text{N}:\text{CR}_2)$ complexes

Table 3.4.

M	R	Solvent	Vco cm ⁻¹		Ref.
Cr	Ph	Hexane	1979	1912	This work
Cr	p-tolyl	Hexane	1976	1909	This work
Cr	Bu ^t	Hexane	1965	1891	This work
Cr	Bu ^t	CS ₂	1956	1878	This work
Mo	Bu ^t	Hexane	1967	1883	8
W	Bu ^t	MeC ₆ H ₁₁	1954	1867	8
Mo	p-tolyl	CS ₂	1965	1883	11
W	p-tolyl	CS ₂	1948	1866	11

Table 3.5

M	R	Solvent	Vcn cm ⁻¹	Ref.
Cr	Bu ^t	Nujol	1626	This work
Mo	Bu ^t	Nujol	1618	8
W	Bu ^t	Nujol	1620	8
	^t Bu ₂ CNH	Nujol	1610	108

of the chromium triad. The inertness to substitution of $W(CO)_6$ relative to $Mo(CO)_6$ and $Cr(CO)_6$ is well documented¹⁰⁶ and has been attributed to the lanthanide contraction affording an inordinately strong W-C bond.¹⁰⁷

For $[h^5-C_5H_5Cr(CO)_2(NCR_2)]$ ($R = Ph, p\text{-tolyl}, tBu$), the frequencies of the two carbonyl absorptions decrease in the series $Ph > p\text{-tolyl} > Bu^t$. The Bu^t group donates more electron density than do the $p\text{-tolyl}$ or phenyl groups resulting in an increased M-C bond strength and a decreased C-O bond strength.

On cooling a pentane solution of $h^5C_5H_5Cr(CO)_2(N:CBu_2^t)$ down from room temperature to $-100^\circ C$, the two ν_{CO} bands observed showed no splitting and no new bands were seen. This is in contrast to the corresponding molybdenum system, $h^5-C_5H_5Mo(CO)_2(N:CBu_2^t)$, where reversible i.r. and 1H n.m.r. spectral changes in the temperature range 28° to -45° were reported.⁶ These changes were interpreted in terms of conformational changes about the multiple metal-nitrogen bond. The structure of the molybdenum complex is shown in fig.3.1. Steric properties of the Bu^t groups require the Mo-N-C unit to be approximately linear. The solid state and low temperature forms are thought on the basis of their i.r. data to be the same conformer, the most sterically favourable staggered form (A).

The d-orbitals involved in the $d\pi - p\pi$ bonding will be of similar energies and rotation about the $Mo = N$ bond should be a low energy process. The high temperature form may be either the staggered conformer (B) or the form with free rotation.

The tungsten system, $h^5-C_5H_5W(CO)_2(N:CBu_2^t)$, like the chromium system, did not show these reversible i.r. and 1H n.m.r. spectral

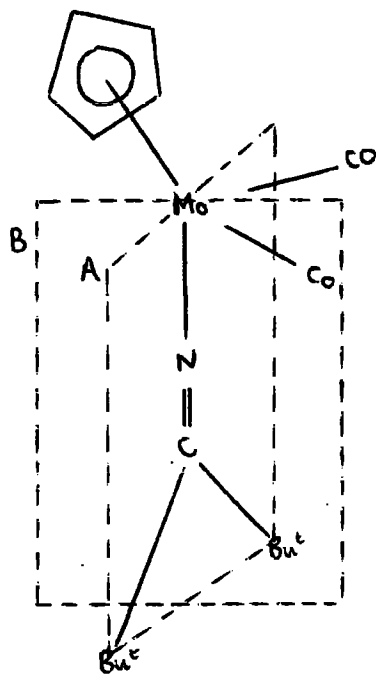


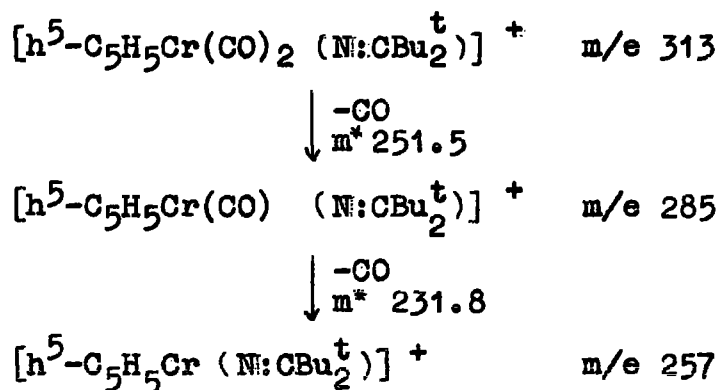
Fig. 3.1 Structure of $h^5-C_5H_5Mo(CO)_2(N:CBu_2^t)$ showing two possible conformers.

changes. It is thought 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 cyclopentadienyl group. Interconversion of tungsten conformers appears to be rapid at the temperatures of the measurements, and a time-averaged signal is observed.

The C = N stretching frequencies for all three complexes, $[h^5-C_5H_5M(CO)_2(N:CBu_2^t)]$ ($M = Cr, Mo, W$) remain little changed from that of the free methyleneamine at 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 $X = ^+CR_2, BR_2^+, BeR^+, Al(NCR_2)_2$ and $SiMe_3$.¹⁰⁹⁻¹¹¹ As the coordinating element becomes heavier, $\Delta\nu$, the difference between 'VCN' for the complex and VCN for the free methyleneamine, becomes less,¹⁰⁹ and the small changes for transition-metal derivatives are in keeping with this trend. Thus the overall process of $\sigma, p_\pi-d_\pi$, and $d_\pi-\pi^*$ bonding leaves VCN little changed from that of the methyleneamine. The first two types of interaction produce electron donation to, and the last electron withdrawal from the metal. The process of σ and lone-pair donation causes VCN to move to higher energy,¹⁰⁹ and since VCN for transition-metal derivatives remains little changed, $d_\pi-\pi^*$ bonding may effectively balance the donation process.

The mass spectra of the three complexes $h^5-C_5H_5Cr(CO)_2N:CR_2$ ($R = Ph, p\text{-tolyl}, Bu^t$) all showed the presence of the parent ion and

peaks corresponding to the loss of one or both carbonyl groups from it. There was a number of differences between the spectra of the three compounds, however. The most intense peak in the spectrum of the Bu^t complex was for the ion [C₅H₅Cr(NCBu^t)]⁺ (m/e 200). The corresponding ions were not seen for the Ph and p-tolyl complexes. For the Ph complex, the most intense peak was for [C₅H₅CrPh]⁺, whereas there was no evidence for the corresponding ions in the spectra of the ^tBu and p-tolyl complexes. The presence of two metastable peaks at m/e 251.5 and 231.8 in the spectrum of h⁵-C₅H₅Cr(CO)₂(N:CBu^t) confirmed the stepwise loss of carbon monoxide from the parent ion,



The ¹H n.m.r. spectrum of h⁵-C₅H₅Cr(CO)₂(N:CBu^t) showed single signals for Bu^t and h⁵-C₅H₅ in positions typical of such groups. On cooling solutions in toluene to -26° and solutions in CS₂ to -60°, these signals moved to high field. However, there was no splitting of the peaks. The signals in CS₂ were considerably downfield compared to those in toluene and C₆D₆. There is a possibility that reaction occurred between the complex and the carbon disulphide solvent. This could not be investigated further, however, due to the highly unstable nature of solutions of the complex in this solvent.

CHAPTER 4

THE SYNTHESIS AND PROPERTIES OF A

NEW AMIDINO - DERIVATIVE OF IRON

In this chapter the synthesis and properties of a new amidine complex of iron is described. The attempted isolation and identification of the intermediate in the preparation is also described.

A. Experimental

1. Reaction of $\text{Fe}(\text{CO})_4\text{I}_2$ with $(\text{ptolyl})\text{NLi}\cdot\text{CMe:N}(\text{ptolyl})$

A suspension of the lithioamidine (10 mmole) in ether (20 ml.) was added to a solution of $\text{Fe}(\text{CO})_4\text{I}_2$ (4.22g., 10 mmole) in ether (100 ml.), frozen at -196° . The mixture was allowed to warm to room temperature, with stirring, and left at room temperature for 1 hour, the colour changing from brown to very dark green. After filtering, the solvent was removed under vacuum (20° , 0.05 mm.Hg). The residue was extracted with toluene and filtered to give a very dark green solution and a little grey precipitate, the latter showing a positive lithium flame test. The product would not crystallise from toluene. Addition of hexane brought down a sludge. This was filtered off, washed with hexane and dried under vacuum (20° , 0.01 mm. Hg) to give a yellow powder.

Properties: The yellow powder dissolved in solvents such as ether, monoglyme, toluene and carbon tetrachloride but not in hexane or pentane to give greenish-yellow solutions which did not decompose on standing. The solid was air-stable but very hygroscopic.

Infrared spectrum: Absorptions in the carbonyl stretching region are shown in table 4.1.

Mass spectrum: The mass spectrum (70° , 12 eV) of the yellow powder showed a strong peak at m/e 238 corresponding to the amidine ligand $[(\text{ptolyl})\text{NH}\cdot\text{CMe:N}(\text{ptolyl})]^+$. The only iron containing fragments

observed were at m/e 56 corresponding to $[\text{Fe}]^+$ and m/e 420 corresponding to $[\text{Fe} \{(\text{ptolyl}) \text{N.CMe:N} (\text{ptolyl})\} \text{I}]^+$.

2. Reaction of the yellow powder with alumina

A dark green solution of the yellow powder in toluene, prepared as above, was reacted with excess alumina. On mixing thoroughly, the colour changed from dark green to deep orange. The mixture was filtered, the toluene removed under vacuum (20° , 0.05 mm.Hg) and the residue extracted with hexane and filtered to give an orange solution. An i.r. spectrum showed the presence of a small amount of $\text{Fe}(\text{CO})_5$ in addition to a new unknown species. The solution was reduced in volume (20° , 0.05 mm. Hg) and cooled to -25° . A mass of orange needles were obtained. These were filtered off, washed with cold hexane and dried (20° , 0.01 mm.Hg), and identified by mass spectroscopy and analyses as $\text{Fe}(\text{CO})_4 \{(\text{ptolyl})\text{NH.CMe:N}(\text{ptolyl})\}$.

Properties: The orange crystals were extremely air-sensitive. They dissolved in most organic solvents to give orange solutions, which decomposed on standing. Solutions in hydrocarbon solvents decomposed slowly, solutions in CS_2 within a day and solutions in CCl_4 within minutes. Non-carbonyl species were formed. Refluxing or u.v. irradiating a solution of the complex (0.02 g.) in hexane (10 ml.) resulted in its decomposition to a non-carbonyl species, with the formation of a little $\text{Fe}(\text{CO})_5$, as indicated by i.r. spectroscopy. The orange crystals decomposed below 80° when heated in a sealed tube.

Infrared spectrum: The main absorptions in the i.r. spectrum of $\text{Fe}(\text{CO})_4 \{(\text{ptolyl})\text{NH.CMe:N}(\text{ptolyl})\}$ in various solvents are shown in table 4.2. The four carbonyl absorptions were all very sharp. On leaving the orange crystals in the glove box for a few days, the i.r. spectrum (nujol mull) changed slightly, the three carbonyl absorptions below 2000 cm^{-1} developing shoulders on the low frequency side.

Table 4.1

Infrared spectral data for the yellow powder obtained from the reaction of $\text{Fe}(\text{CO})_4\text{I}_2$ with $(\text{ptoly}1\text{NLi.CMe:Nptoly}1)$

Solvent	$\nu_{\text{CO}} \text{ cm}^{-1}$				
	KBr disc	1963s		2032s	
Toluene	1963s	2018m	2038s	2052s	2098s
Ether	1967s	2018m	2034s	2054s	2098s
CCl_4	1970s	2020s	2042s	2056s	2098s

Table 4.2

Infrared spectral data for $\text{Fe}(\text{CO})_4$, $(\text{ptoly}1\text{NH.CMe:Nptoly}1)$

Solvent	$\nu_{\text{CO}} \text{ cm}^{-1}$	Absorptions in the 1550-1650 cm^{-1} region	$\nu_{\text{NH}} \text{ cm}^{-1}$
		Nujol mull	
Hexane	1931s, 1950s, 1968s, 2057m,	1603m, 1621m	
CS_2	1925s, 1943s, 1962s, 2056m		

Mass Spectrum: The major ions in the mass spectrum (70°) of $\text{Fe}(\text{CO})_4(\text{ptoly1NH.CMe:Nptoly1})$ are listed in table 4.3. The parent ion, $[\text{Fe}(\text{CO})_4(\text{ptoly1NH.CMe:Nptoly1})]^+$, and all four ions, $[\text{Fe}(\text{CO})_n(\text{ptoly1NH.CMe:Nptoly1})]^+$ ($n = 0, 1, 2, 3$), corresponding to stepwise loss of CO groups, were observed.

Analyses: Found, Fe, 13.1, 14.1; C, 58.8; H, 3.0; N, 7.1
 $\text{FeC}_{20}\text{H}_{18}\text{N}_2\text{O}_4$ requires Fe, 13.8; C, 59.1; H, 4.5; N, 6.9

^1H n.m.r. spectrum: The n.m.r. spectrum of $\text{Fe}(\text{CO})_4(\text{ptoly1NH.CMe:Nptoly1})$ in deuterobenzene showed broadish peaks at $2.11\tau(0.6)$ and 3.78 and $3.86\tau(\text{total } 7.2)$ and sharp peaks at $8.55\tau(6.9)$ and $9.40\tau(3)$

3. Reaction of $\text{Fe}(\text{CO})_4(\text{ptoly1 NH.CMe:Nptoly1})$ with N-bromo succinimide

A solution of $\text{Fe}(\text{CO})_4(\text{ptoly1NH.CMe:Nptoly1})$ (0.01 g.) in toluene (5 ml) was stirred with a solution of N-bromo succinimide (0.005 g.) in the same solvent (20 ml.). No reaction was detected by i.r. spectroscopy.

4. Reaction of $\text{Fe}(\text{CO})_4\text{I}_2$ with alumina

A solution of $\text{Fe}(\text{CO})_4\text{I}_2$ (0.4g., 1 mmole) in hexane (50 ml.) was stirred with excess alumina. The dark red solution became very pale yellow. I.r. spectroscopy identified the product as $\text{Fe}(\text{CO})_5$.

Table 4.3

Mass spectral data for Fe(CO)₄ (ptoly1NH.CMe:Nptoly1)

Ion	M/e	R.I.	M*	Frag- ment Lost
[Fe(CO) ₄ (ptoly1NH.CMe:Nptoly1)] ⁺	406	2.5		
[Fe(CO) ₃ (ptoly1NH.CMe:Nptoly1)] ⁺	378	4.5		
[Fe(CO) ₂ (ptoly1NH.CMe:Nptoly1)] ⁺	350	0.25		
[Fe(CO)(ptoly1NH.CMe:Nptoly1)] ⁺	322	32		
[Fe(ptoly1NH.CMe:Nptoly1)] ⁺	294	100	268.4	CO
[ptoly1NH.CMe:Nptoly1] ⁺	238	61		
[ptoly1NCMe] ⁺	132	71		
[ptoly1NHC] ⁺	118	3		
[ptoly1NH ₂] ⁺	107	6.5		
[ptoly1] ⁺	91	12		
[Fe] ⁺	56	0.5		

R.I. = Relative Intensity

B. Discussion

$\text{Fe}(\text{CO})_4\text{I}_2$ reacts with $(\text{ptolyl})\text{NLi}.\text{C}(\text{CH}_3):\text{N}(\text{ptolyl})$ to give an unidentified yellow powder which reacts in turn with alumina to give $\text{Fe}(\text{CO})_4\{(\text{ptolyl})\text{N}(\text{H})\text{C}(\text{CH}_3)\text{N}(\text{ptolyl})\}$. For the noble gas configuration of the metal to be conserved, the neutral amidine ligand must be regarded as a two-electron donor. There have been very few examples of metal carbonyl complexes containing a neutral amidine ligand reported. The chromium complex, $\text{Cr}(\text{CO})_3\{\text{PhN}(\text{H})\text{C}(\text{Ph})\text{NPh}\}$ ²¹ has the amidine group acting as an arene, with a bond from one of the phenyl groups to the metal atom. In this case, the neutral amidine acts as a 6-electron donor. The complexes $[(\text{NO})_2\text{M}\{\text{H}_2\text{NC}(\text{Ph})\text{NPh}\}]^+$ ($\text{M} = \text{Fe}, \text{Co}$)¹¹² also contain a neutral amidine group. The mode of attachment is not clear however.

Some possible modes of attachment of the neutral amidine ligand, acting as a 2-electron donor to a metal, are shown in fig. 4.1. Structure (D) is ruled out for $\text{Fe}(\text{CO})_4\{(\text{ptolyl})\text{N}(\text{H})\text{C}(\text{CH}_3)\text{N}(\text{ptolyl})\}$ as it is not compatible with the complex showing a VNH absorption.

$\text{Fe}(\text{CO})_4\{(\text{ptolyl})\text{N}(\text{H})\text{C}(\text{CH}_3)\text{N}(\text{ptolyl})\}$ is an extremely air-sensitive orange crystalline solid. Its infrared spectrum showed four sharp carbonyl absorptions, the general appearance of the carbonyl-stretching region being indicative of a tetracarbonyl species. The VNH absorption occurred at 3246 cm^{-1} (nujol mull). The infrared spectrum of $\text{Cr}(\text{CO})_3\{\text{PhN}(\text{H})\text{C}(\text{Ph})\text{N}(\text{Ph})\}$ ²¹ showed a weak peak at 3405 cm^{-1} (CH_2Cl_2 solution) corresponding to VNH but shifted some 100 cm^{-1} to higher frequency from that in the free amidine. A nujol mull infrared spectrum of $\text{Fe}(\text{CO})_4\{(\text{ptolyl})\text{N}(\text{H})\text{C}(\text{CH}_3)\text{N}(\text{ptolyl})\}$ changed slightly after the crystals were left at room temperature under nitrogen for a few days, the three carbonyl absorptions below 2000 cm^{-1} developing

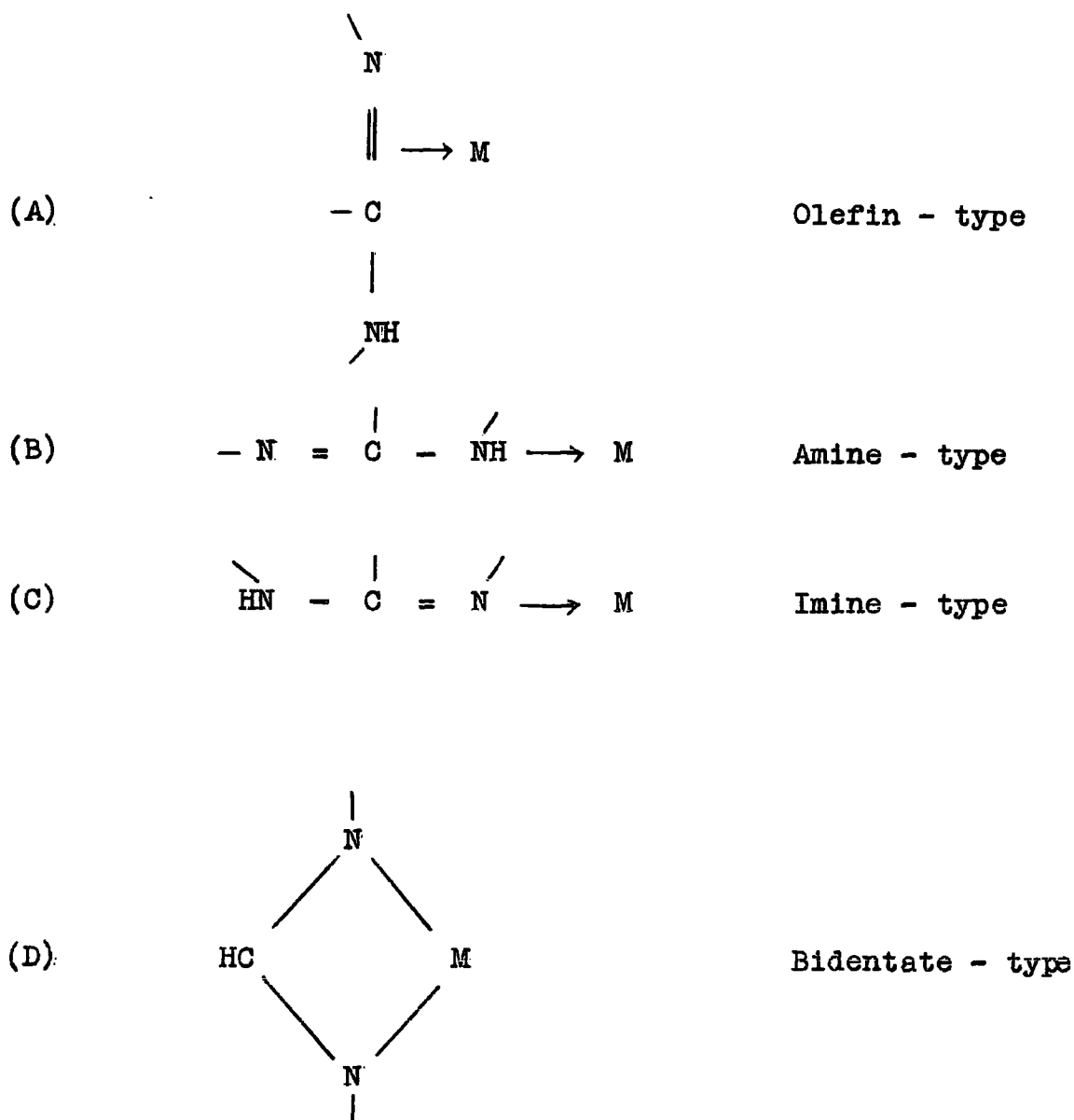
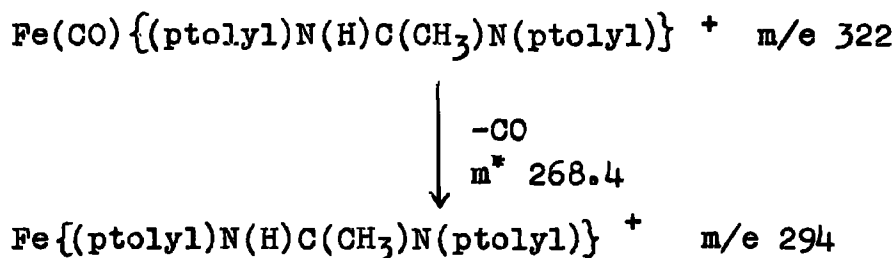


Fig 4.1 Some possible modes of attachment of the neutral amidine ligand, $\text{RN} = \text{C}(\text{R}') - \text{NHR}$, acting as a two-electron donor to a metal (Groups R and R' are not shown).

shoulders on the low-frequency side. The new species is possibly an isomeric form of the first.

The mass spectrum of $\text{Fe}(\text{CO})_4 \{(\text{ptolyl})\text{N}(\text{H})\text{C}(\text{CH}_3)\text{N}(\text{ptolyl})\}$ showed the presence of the parent ion and peaks corresponding to the loss of 1, 2, 3 or 4 carbonyl groups from it. The most intense peak in the spectrum was for $[\text{Fe}\{(\text{ptolyl})\text{N}(\text{H})\text{C}(\text{CH}_3)\text{N}(\text{ptolyl})\}]^+$, i.e. the parent ion less four carbonyl groups. The only observed metastable peak was for the following transition,



The ^1H n.m.r. spectrum of $\text{Fe}(\text{CO})_4 \{(\text{ptolyl})\text{N}(\text{H})\text{C}(\text{CH}_3)\text{N}(\text{ptolyl})\}$ in C_6D_6 showed peaks at 9.40γ (3), 8.55γ (6.9), 3.86 and 3.78γ (total 7.2) and 2.11γ (0.6). A n.m.r. spectrum of the free amidine, $(\text{ptolyl})\text{NH}\cdot\text{C}(\text{CH}_3):\text{N}(\text{ptolyl})$, in C_6D_6 as a comparison showed peaks at 8.71γ (3), 8.09γ (6.1), 4.47γ (0.6), and 3.15 and 3.09γ (total 7.5). Tentative assignments of these peaks are given in table 4.4.

The yellow powder obtained from the reaction of $\text{Fe}(\text{CO})_4\text{I}_2$ with $(\text{ptolyl})\text{NLi}\cdot\text{C}(\text{CH}_3):\text{N}(\text{ptolyl})$ may be an iron carbonyl iodide amidino-complex such as $\text{Fe}(\text{CO})_4\text{I}\{(\text{ptolyl})\text{NC}(\text{CH}_3)\text{N}(\text{ptolyl})\}$ or $\text{Fe}(\text{CO})_3\text{I} - \{(\text{ptolyl})\text{NC}(\text{CH}_3)\text{N}(\text{ptolyl})\}$. There is not a lot of evidence to support this however, although the mass spectrum did show a peak corresponding to $[\text{FeI}\{(\text{ptolyl})\text{NC}(\text{CH}_3)\text{N}(\text{ptolyl})\}]^+$.

The yellow powder reacts with alumina to give $\text{Fe}(\text{CO})_4 \{(\text{ptolyl}) - \text{N}(\text{H})\text{C}(\text{CH}_3)\text{N}(\text{ptolyl})\}$. It is possible that a free radical mechanism

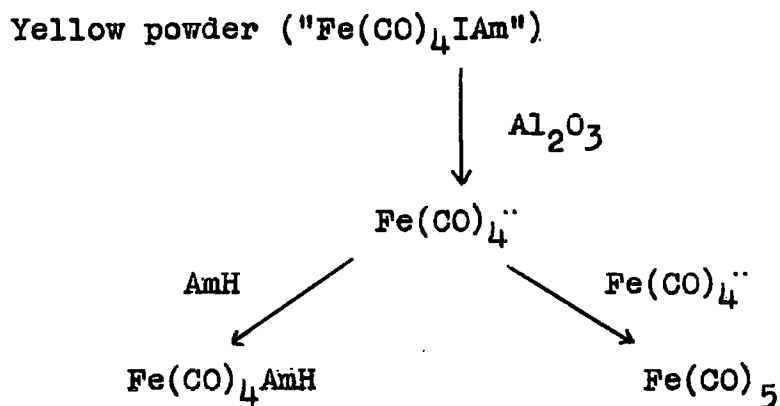
Table 4.4

N.M.R. data in C₆D₆ for [Fe(CO)₄(ptolyl)N(H)C(CH₃)N(ptolyl)]
and [(ptolyl)NH.C(CH₃):N(ptolyl)] and tentative assignments

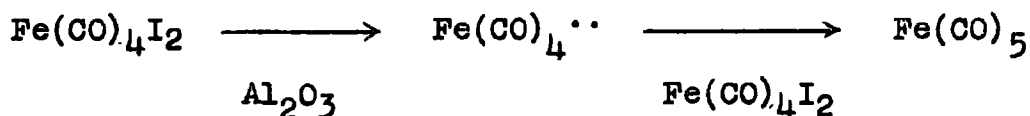
Tentative Assignment	Expected Relative Intensity	[Fe(CO) ₄ (ptolyl)N(H)-C(CH ₃)N(ptolyl)] . γ values and relative intensities	[(ptolyl)NH.C(CH ₃):N(ptolyl)] . γ values and relative intensities
>NC(CH ₃)N -	3	9.40 (3)	8.71 (3)
p-tolyl group terminal CH ₃	6	8.55 (6.9)	8.09 (6.1)
p-tolyl group ring C - <u>H</u>	8	3.86 3.78 (7.2)	3.15 3.09 (7.5)
<u>N</u> - <u>H</u>	1	2.11 (0.6)	4.47 (0.6)

Relative intensities are based on an intensity of 3, taken for the >NC(CH₃)N - peak.

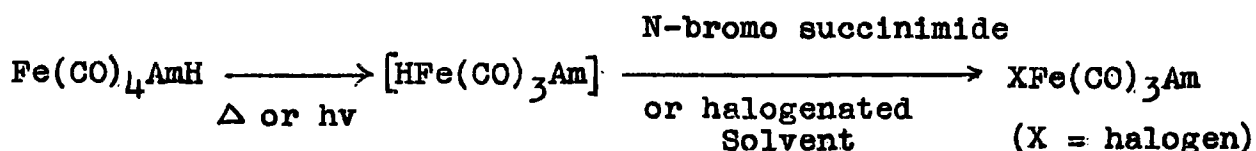
is involved, and that the alumina breaks up the yellow complex into $\text{Fe}(\text{CO})_4$ radicals. These could then pick up free amidine molecules to give $\text{Fe}(\text{CO})_4\{(\text{ptolyl})\text{N}(\text{H})\text{C}(\text{CH}_3)\text{N}(\text{ptolyl})\}$. Alternatively, the $\text{Fe}(\text{CO})_4$ radicals could react with one another to give $\text{Fe}(\text{CO})_5$, identified as a minor product of the reaction. Thus possible mechanisms are as follows [where $\text{Am} = (\text{ptolyl})\text{NC}(\text{CH}_3)\text{N}(\text{ptolyl})$, $\text{AmH} = (\text{ptolyl})\text{N}(\text{H})\text{C}(\text{CH}_3)\text{N}(\text{ptolyl})$],



As a comparison, $\text{Fe}(\text{CO})_4\text{I}_2$ was treated with alumina and $\text{Fe}(\text{CO})_5$ was obtained. Again, this is most easily explained by a free radical mechanism e.g.,



A number of reactions were carried out with $\text{Fe}(\text{CO})_4\{(\text{ptolyl})\text{N}(\text{H})\text{C}(\text{CH}_3)\text{N}(\text{ptolyl})\}$ in the hope that they might throw some light on its structure. The purpose of these reactions was to bring about a rearrangement of the $\text{Fe}(\text{CO})_4\{(\text{ptolyl})\text{N}(\text{H})\text{C}(\text{CH}_3)\text{N}(\text{ptolyl})\}$ to produce a species containing the amidine ligand acting as a 3-electron donor e.g,



However, these attempts were unsuccessful. Refluxing or u.v. irradiating a solution of the complex in hexane resulted in considerable decomposition, with the formation of a little $\text{Fe}(\text{CO})_5$, again probably by a free radical mechanism. Reaction with CCl_4 resulted in rapid decomposition to a non-carbonyl species. There was no reaction with N-bromo succinimide in toluene.

The reaction of $\text{Fe}(\text{CO})_4\text{I}_2$ with the lithioamidine, $(\text{ptolyl})\text{NLi}.\text{C}(\text{CH}_3):\text{N}(\text{ptolyl})$, and subsequent reaction of the product with alumina is thus quite complex and rather different from the reaction of $\text{Fe}(\text{CO})_4\text{I}_2$ with lithioketimines. In the latter case, complexes of the type $[\text{Fe}(\text{CO})_3\text{N}:\text{CRR}']_2$ and $[\text{Fe}_2(\text{CO})_6\text{I}(\text{NCRR}')]_2$ (where $\text{RR}' = \text{Ph}_2, \text{p-tolyl}_2$ or Ph Bu^t) are formed when $\text{Fe}(\text{CO})_4\text{I}_2$ is treated with $\text{RR}'\text{CNLi}$ in ether at ambient temperature.^{9,14}

APPENDICES

Appendix 1

Exploratory investigations of the reaction of lithioamidines with
 $h^5-C_5H_5Cr(CO)_3Br$

A. Experimental

Reaction of $h^5-C_5H_5Cr(CO)_3Br$ with $RNLi.CR':NR$ (i) R = p-tolyl,
R' = Me; (ii) R = Me, R' = Ph

A suspension of the lithioamidine (5 mmole) in ether (20 ml.) was added to an ether solution of $h^5-C_5H_5Cr(CO)_3Br$ (5 mmole), prepared as in chapter 3, and frozen at -196° . The mixture was allowed to warm to room temperature with stirring, and left at room temperature for one hour, the colour changing from purple to dark green. The solvent was removed under vacuum (20° , 0.05 mm.Hg). The residue was only slightly soluble in hexane to give, on filtering, a green solution and leaving a large quantity of greenish material in the flask. This was mainly $[h^5-C_5H_5Cr(CO)_3]_2$,⁸⁵ as identified by i.r. spectroscopy.

For (i) (R' = Me, R = p-tolyl), the i.r. spectrum of the green hexane extract was very similar to that obtained for the ketimine complexes, $h^5-C_5H_5Cr(CO)_2(N:CR_2)$ (R = Ph, p-tolyl, Bu^t), showing two strong sharp carbonyl absorptions at 1892 and 1964 cm^{-1} . For (ii) (R = Me, R' = Ph), however, the i.r. spectrum of the hexane extract showed the presence of only a very small amount of carbonyl-containing product.

The solvent was removed under vacuum (20° , 0.05 mm.Hg) from the hexane extract. A mass spectrum of the residue showed only the presence of the amidine ligand.

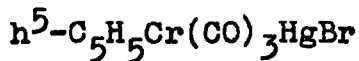
B. Discussion

It was not possible to isolate any well-defined amidino-chromium complexes from the above reactions. However, there is infrared spectral evidence for the formation of a new carbonyl species from the reaction between $h^5-C_5H_5Cr(CO)_3Br$ and $\{(ptoly1)NLi-CMe:N(ptoly1)\}$. The two strong sharp carbonyl absorptions in the i.r. spectrum of this species are very similar in position and intensity to those for the ketimine complexes, $h^5-C_5H_5Cr(CO)_2(N:CR_2)$ ($R = Ph, p-toly1, Bu^t$), prepared in chapter 3. Hence it is likely that the species formed is of a similar structure e.g. $h^5-C_5H_5Cr(CO)_2\{(ptoly1)N-C(Me)N(ptoly1)\}$. This would also be in keeping with the corresponding molybdenum and tungsten systems.¹⁹ $h^5-C_5H_5M(CO)_3Cl$ ($M = Mo, W$) reacts smoothly with lithio-amidines, $RNLi.CR':NR$, to form complexes of composition $h^5-C_5H_5M(CO)_2\{RNC(R')NR\}$, which show two strong sharp carbonyl absorptions in their i.r. spectra. In these complexes, the amidino-group acts as a 3-electron-donor-ligand. A comparison of the i.r. data in the ν_{CO} stretching region for the above complexes is shown in the following table:-

Complex	Solvent	$\nu_{CO} \text{ cm}^{-1}$	
" $h^5-C_5H_5Cr(CO)_2\{(p-toly1)NC(Me)N(ptoly1)\}$ "	Hexane	1964	1892
$h^5-C_5H_5Mo(CO)_2\{PhNC(Ph)NPh\}$	CCl_4	1970	1890
$h^5-C_5H_5Mo(CO)_2\{(p-toly1)NC(Ph)N(p-toly1)\}$	$(CH_2Cl)_2$	1956	1868
$h^5-C_5H_5W(CO)_2\{PhNC(Ph)NPh\}$	$(CH_2Cl)_2$	1965	1877
$h^5-C_5H_5W(CO)_2\{(p-toly1)NC(Ph)N(p-toly1)\}$	$(CH_2Cl)_2$	1949	1852

Appendix 2

Exploratory investigations of the reactions between Ph₂CNLi and



A. Experimental

1. Preparation of h⁵-C₅H₅Cr(CO)₃HgBr

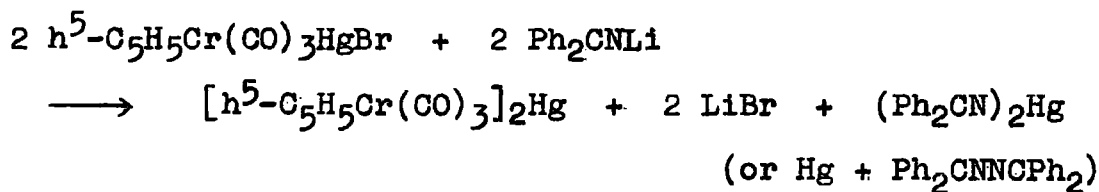
h⁵-C₅H₅Cr(CO)₃HgBr was prepared from [h⁵-C₅H₅Cr(CO)₃]₂Hg by the method of Mays and Robb.¹¹³ Thus, a solution of [h⁵-C₅H₅Cr(CO)₃]₂Hg (1.51 g., 2.5 mmole) in acetone (50 ml.) was stirred at room temperature with a solution of HgBr₂ (0.91 g., 2.5 mmole) in the same solvent (30 ml.). The solvent was removed under vacuum (20°, 0.05 mm.Hg) to give h⁵-C₅H₅Cr(CO)₃HgBr as a yellow solid.

2. Reaction of h⁵-C₅H₅Cr(CO)₃HgBr with Ph₂CNLi

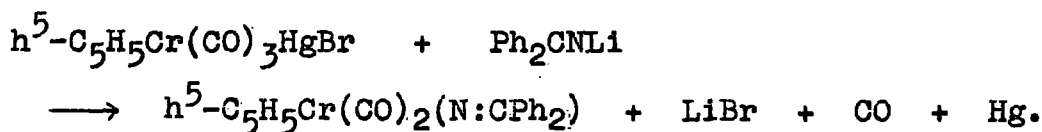
A solution of Ph₂CNLi (5 mmole) in ether (10 ml.) was added to a suspension of h⁵-C₅H₅Cr(CO)₃HgBr (5 mmole) in the same solvent (80 ml.) frozen at -196°. The mixture was allowed to warm to room temperature, with stirring, the colour changing from orange to yellow-brown. On filtering, a yellow solid and a yellow-brown solution were obtained. The yellow solid was mainly [h⁵-C₅H₅Cr(CO)₃]₂Hg⁸⁵ as shown by i.r. spectroscopy. It also contained a little h⁵-C₅H₅Cr(CO)₂(N:CPh₂) (identified by mass spectroscopy). The i.r. spectrum of the yellow-brown solution showed four peaks in the carbonyl stretching region, at 1879(s), 1897(m), 1952(s) and 1980(m) cm⁻¹. The nature of the carbonyl compound(s) present could not be determined, however.

B. Discussion

In the reaction of $h^5-C_5H_5Cr(CO)_3HgBr$ with Ph_2CNLi , there is no evidence for the formation of a chromium-mercury ketimine complex such as $h^5-C_5H_5Cr(CO)_3Hg(Ph_2CN)$. The major product of the reaction is $[h^5-C_5H_5Cr(CO)_3]_2Hg$, which could be formed according to,



$h^5-C_5H_5Cr(CO)_2(N:CPh_2)$ is a minor product of the reaction. A possible equation for its formation is as follows,



There was limited mass spectral evidence for the formation of $Ph_2CNNCPh_2$ but no evidence for any free metallic mercury.

Appendix 3

Experimental details and starting materials

1. General Techniques

All the reactions described were carried out in an atmosphere of pure, dry nitrogen in two-necked round-bottomed flasks. Air-sensitive solids were handled in a glove box. Liquids and solutions were transferred as required, by syringe, against a counter current of nitrogen.

2. Nitrogen supply

Nitrogen was drawn off from a tank containing liquid nitrogen and delivered to a multiple outlet system. Traces of oxygen were removed by passing the gas through a tower containing copper at 400°. A constant pressure of nitrogen was maintained in the system by connecting one outlet to an oil bubbler.

3. Glove box

The purity of the nitrogen atmosphere in the glove box was maintained by continuously recycling it through a trap cooled with liquid air to remove volatile material, a tower containing copper at 400° to remove traces of oxygen and a tower containing phosphorus pentoxide to remove traces of moisture. All external tubing was of polythene, and the gloves used were made of "Butasol" rubber.

4. Solvents

Solvents were degassed on the vacuum line before use and stored under nitrogen. Hydrocarbon solvents and diethyl ether were dried over extruded sodium wire. Chlorocarbon solvents and carbon disulphide were dried over molecular sieve. Monoglyme was freshly distilled, under nitrogen, from LiAlH_4 .

5. Starting materials

$[\eta^5\text{-C}_5\text{H}_5\text{Cr(CO)}_3]_2\text{Hg}$,³⁶ $\text{Fe(CO)}_4\text{I}_2$,¹¹⁴ $(\text{ptolyl})_2\text{CNH}$,¹¹⁵
 Ph_2CNH ,¹¹⁶ $(\text{ptolyl})\text{NH.C(CH}_3)_2\text{N(ptolyl)}$ ¹¹⁷ and MeNH.CPh:NMe were prepared by methods described in the literature.

Solutions of lithioketimines¹¹⁸ were prepared by adding a solution of n-butyl lithium to a frozen solution of the appropriate ketimine or amidine at -196° . The mixtures were stirred at room temperature for about 20 minutes before use.

Di-t-butyl ketiminolithium¹⁰⁸ was also prepared by adding a solution of t-butyl lithium to a frozen solution of t-butyl cyanide at -196° , and then stirring the mixture at room temperature for approximately 20 minutes.

Alumina was activated by heating under vacuum (100° , 0.01 mm.Hg) for two hours.

All other starting materials were of standard reagent grade.

6. Instrumentation

(a) Infrared spectra

Infrared spectra in the range $4000 - 250 \text{ cm}^{-1}$ were recorded on a Perkin-Elmer 457 grating spectrometer. Samples were in the form of mull, KBr discs or solutions in a suitable solvent, as appropriate.

(b) Nuclear magnetic resonance spectra

Proton magnetic resonance spectra were recorded on a Varian A56/60D spectrometer, fitted with a variable temperature controller, and operating at 60 MHz/sec. Samples were in the form of solutions

in carbon disulphide, toluene or perdeuterobenzene, as appropriate. The external reference standard was tetramethylsilane.

(c) Mass spectra

Mass spectra were recorded on a A.E.I. MS9 mass spectrometer at 70 eV (except where otherwise stated in the text) and an accelerating potential of 8 kV, with a source temperature between ambient and 220^o (depending on the sample) and electromagnetic scanning. Samples were introduced by direct insertion into the ion source.

7. Analytical methods

Carbon, hydrogen and nitrogen were determined using a Perkin - Elmer 240 Elemental Analyser. Chromium and iron were determined using a Perkin - Elmer 403 atomic absorption spectrophotometer.

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