Some aspects of organonitrogen transition metal complexes

Clark, John Andrew

Clark, John Andrew (1982) *Some aspects of organonitrogen transition metal complexes*, Durham theses, Durham University. Available at Durham E-Theses Online: http://etheses.dur.ac.uk/7414/

SOME ASPECTS OF ORGANONITROGEN TRANSITION METAL COMPLEXES

by

JOHN ANDREW CLARK, B.Sc. (SHEFFIELD)

A Thesis submitted for the degree of Doctor of Philosophy in
the University of Durham

October 1982

To Helen and my parents

"The search for truth is one way difficult and one way easy, for it is certain that one can neither find it completely nor miss it wholly".

Aristotle

ACKNOWLEDGEMENTS

I wish to express my sincere gratitude to Dr. M. Kilner, under whose supervision this research was carried out, for his constant encouragement and valuable advice. My thanks are also due to Dr. A.J. Banister, Dr. Z.V. Hauptman and Dr. N.R.M. Smith for invaluable discussions with regards to experimental procedures and to Mrs. Dianne Chrystal for typing this thesis.

I am indebted to the Science Research Council for a research studentship.

J.A. CLARK
DURHAM 1982

DECLARATION

The work described in this thesis was carried out in the University of Durham between October 1979 and September 1982. It has not been submitted, either wholly or in part, for a degree in this or any other University and is the original work of the author except where acknowledged by reference.

Some Aspects of Organonitrogen Transition Metal Complexes

ABSTRACT

Attempts to introduce amidino ligands into Transition metal carbonyl and non carbonyl systems are described, and a new synthetic route to transition metal methyleneamino complexes is explored.

Reaction of lithiodiaryl -acetamidines and -benzamidines with $Re(CO)_5X$ (X = Cl,Br) produced carbamoyl type complexes, $Re(CO)_4$(CONR-CR'-NR) containing a bidentate carbamoyl-amidino ligand. These complexes could be decarbonylated, forming the chelated amidino complexes $Re(CO)_4$(RN-CR'-NR) by heating.

The chelated amidino complexes were also prepared by the direct action of lithioamidines on the rhenium carbonylhalide dimer $[Re(CO)_4X]_2$, and by the reaction of n-butyllithium with the simple two electron donor monodentate amidine complexes, $Re(CO)_4$(Amidine)X.

Complexes containing ortho-metallated diaryl -formamidino, -acetamidino and -benzamidino ligands were prepared by the action of the parent amidine on $Re(CO)_5X$ or $Re(CO)_4$(Amidine)X in refluxing monoglyme. These complexes also contained a simple two electron donor monodentate amidine. The acetamidine and formamidine derivatives formed six membered ortho-metallate rings, the benzamidines forming either five or six membered ring complexes. In contrast, refluxing $Re(CO)_4$(Amidine)X with PPh_3 in monoglyme produced a chelated amidino species, $Re(CO)_3(PPh_3)$(RN-CR'-NR).

The reaction mechanisms for the formation of the above complexes, and their probable bonding modes are discussed. Interconversions between many of the species were possible.

$FeCl_3$ reacts with lithiodiarylamidines to produce $[Fe(amidino)_3]_n$ type complexes. The acetamidines and formamidines form monomeric complexes (with a probable tris chelate structure), and the benzamidine forms both a monomeric and an oligomeric/polymeric complex. $FeCl_2$ reacts similarly with lithiumdi-p-tolylacetamidine, both monomeric and oligomeric/polymeric $[Fe(amidine)_2]_n$ species being produced. The complexes are paramagnetic,the Fe(III) species have magnetic moments thatsuggest they contain five unpaired electrons.

Nucleophilic attack by n-butyllithium at the carbon atom of $[CpMo(CO)(AsPh_3)(NCPh)]^+$ did not produce a methyleneamino complex. Free nitrile was liberated in the reaction, and dimeric molybdenum complexes were produced.

CONTENTS

PAGE

CHAPTER ONE: INTRODUCTION

CHAPTER TWO: EXPERIMENTAL

CHAPTER THREE: RHENIUM CARBAMOYL COMPLEXES

......CONTINUED

CHAPTER FOUR: RHENIUM CARBONYL COMPLEXES CONTAINING A MONODENTATE AMIDINE LIGAND

CHAPTER FIVE: RHENIUM CARBONYL COMPLEXES CONTAINING A BIDENTATATE THREE ELECTRON DONOR AMIDINO LIGAND

CHAPTER SIX: RHENIUM CARBONYL COMPLEXES CONTAINING AN ORTHO-METALLATED AMIDINE LIGAND

CHAPTER SEVEN: IRON AMIDINO COMPLEXES

......CONTINUED

CHAPTER 1

INTRODUCTION

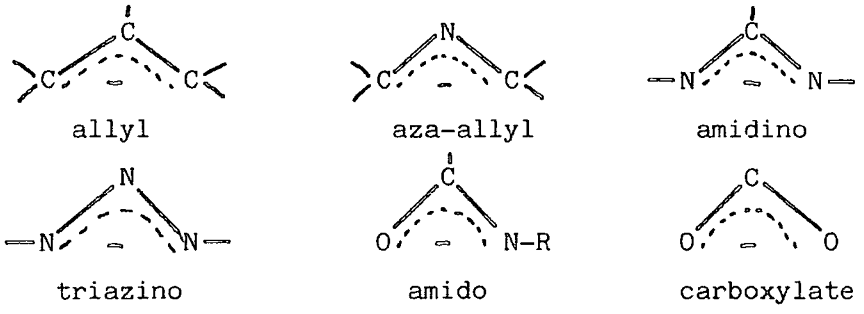
1.0 PREFACE

The scope and extent of organometallic transition metal chemistry has increased rapidly over the last 20 years, resulting in, amongst other things, improved industrial processes, and a better understanding of some naturally occurring ones. The thermal stability of many organometallics has undoubtably contributed to the advances made, and to the uses to which organometallics have been put. This stability is due in part to the so-called "synergic" bonding that results between transition metals and carbonyl or π bonded organic groups. The organic group donates charge to the metal through either a σ-bonded lone pair or from the π bond of an unsaturated molecule; the metal in turn simultaneously back donates from its non-bonding d orbitals to the ligand non-bonding and /or antibonding π^* orbitals. Each process has the effect of mutually increasing the other, and also helps to reduce excessive build up of charge on the metal, thus helping stabilize low oxidation states of the metal. Replacement of the carbonyl group by a ligand not capable of accepting back donation from the metal (e.g. NH_3) leads to excessive charge build up on the metal, up to the point where the remaining carbonyls can accept no more charge from the metal. At this point further substitution is prevented. e.g. $Cr(CO)_6 + \text{liq. } NH_3 \xrightarrow{120°C} Cr(CO)_3(NH)_3 + 3CO$. If the ligand has available vacant π or d orbitals then the dissipation of the excess electronic charge is not the sole responsibility of the carbonyl groups and further substitution may take place.

The importance of organonitrogen groups in transition metal chemistry has been recognised for many years, particularly in the field of homogeneous catalysis, where organonitrogen-metal intermediates are postulated. Interest has also been shown in the bonding modes of unsaturated carbon-nitrogen and nitrogen - nitrogen multiple bonded systems, and it is in this respect that the pseudo allyl groups and in particular the amidino group is investigated.

1.1 Pseudo Allyl Systems

The isoelectronic relationship between allyl and carboxylate groups was in the past overlooked because of the wildly different properties of the two series of derivatives. Allyl groups (when donating three electrons to the metal) lie with the three carbon atoms in a plane above that of the metal atom [1], whereas carboxylate groups form a chelate ring with the metal atom in the same plane as the O-C-O skeleton [2]. It is now realised that the two groups represent the extreme ends of an isoelectronic series generally known as pseudo -allyls. In this series the skeletal atoms (together with its attached atom or group) have been replaced by one or more hetero atoms i.e. nitrogen, oxygen, phosphorus or sulphur. The isoelectronic series containing nitrogen and oxygen is shown below (Fig. 1.1).



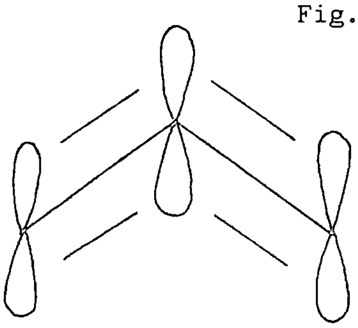
allyl aza-allyl amidino

triazino amido carboxylate

Fig. 1.1.

These groups can in certain circumstances all adopt a delocalised form of bonding, where the three Π electrons lie in p orbitals of the three atom skeleton (Fig. 1.2).

Fig. 1.2



The main difference between allyls and pseudo allyls, is that by the introduction of a hetero atom, or atoms, the number of co-ordination possibilities of the pseudo allyl group increases with respect to the allyl group. As in the cases stated above (Fig. 1.1), the hetero atom has a lone pair of electrons through which co-ordination to the metal may occur. Furthermore, it may be possible that the ligand may be bonded via a combination of σ and Π bonds resulting in a wide variety of bonding modes.

The chemistry of the pseudo allyl metal complexes is slowly being expanded and there are now examples of each pseudo allyl system with metals of groups I, II, IV and also of the transition metals.

1.2 Metal-Allyl complexes

Organometallic compounds containing the allyl C_3H_5 moiety have been known for many years, one of the earliest being allyl magnesium bromide [3] . The number of compounds containing this group has grown rapidly, and must now number several thousand. The nature of the metal allyl bond was in dispute for a long time, until it was realised that the allyl group could bond in a non classical manner, and may also be fluxional. It has now been established by x-ray crystallographic and nuclear magnetic resonance techniques that the allyl-metal bond can be of four types:-

a) σ-allyl

A terminal carbon atom is σ bonded to the metal atom with a localised double bond between the two remaining carbon atoms.

e.g. $(\sigma\text{-}C_3H_5)Mn(CO)_5$ [4]

$(\sigma\text{-}C_3H_5)CpMo(CO)_3$ [5]

b) μ-allyl

The allyl group bridges between two metal atoms, being σ-bonded to the first metal atom through a terminal carbon atom, and to the second metal atom by the interaction of the allyl double bond with the metal orbitals.

e.g. $(\mu\text{-}C_3H_5)_4$ Mo [6] and $[(\mu C_3H_5)PtCl)]_4$ [7]

c) Π-allyl

Here the bonding between the three carbon atoms is delocalised; it forms a multicentric bond with the metal. The three carbon atoms of the allyl group are in a plane above that of the metal, with all metal––carbon distances being approximately equal. The metal receives three electrons from the ligand.

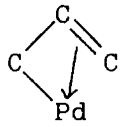
e.g. $(\Pi\text{-}C_3H_5)Fe(CO)_3Cl$ [8] and $(\pi\text{-}C_3H_5)Mn(CO)_4$ [9]

The allyl group may be an isolated three carbon system, it may have substituent R groups on any of the carbon atoms, or it may form part of a hydrocarbon ring system.

d) σ, Π -allyl

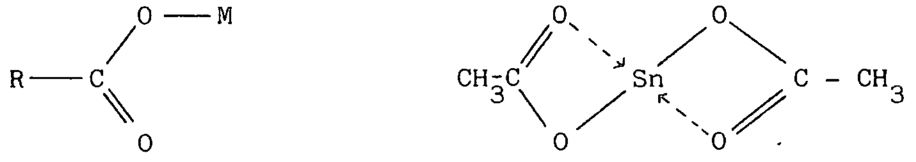
The allyl group is bonded to the metal using a combination of σ and π bonds.

e.g. $(\Pi C_4H_7)PdCl(PPh_3)$ [10]



1.3. Metal Carboxylato Complexes

This is undoubtably the most studied of all the psuedo allyl groups and has been reviewed by Oldham [11]. The carboxylato-group usually acts as a one electron monodentate ligand using only one of the two available atoms to bond to the metal, e.g. $CO(O_2CCH_3)_24H_2O$ [9] and $W(\Pi\text{-}C_5H_5)(CO_3)(O_2CR)$ [12]. (Fig. 1.3.a). The purely monodentate nature of some similar complexes is disputed and an unsymmetrical bidentate structure has been suggested for dialkyltindiacetates, $R_2Sn(OAc)_2$(Fig. 1.3.b) [13].



a b

Fig. 1.3.

A third mode is the chelating σ,σ attached delocalised carboxylato group (Fig. 1.4.) which has been found for $Zn(O_2CCH_3)_2 2H_2O$, [12] $(\Pi C_6H_6)Mo(C_5H_5)(O_2CR)$ [13] , and $IrHCl(O_2CR)L_2$ [14].

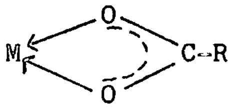


Fig. 1.4.

Bridging carboxylato groups are also know (Fig. 1.5.), and the metals

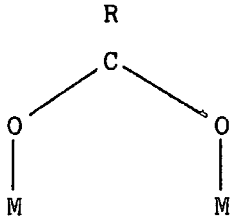


Fig. 1.5.

may be the same, e.g. $M_2(O_2CR)_4$ (M=CrMo) [15] or different, as in $(PPH_3)_2(CO)IrAg(O_2CR)$ [16].

The type of bonding so far not observed for the carboxylato group is the pseudo Π allyl arrangement (Fig. 1.6.).

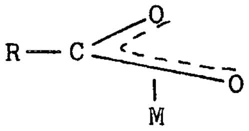


Fig. 1.6

1.4. Amidines and Metallated Amidines

1.4.1. Amidines

The amidine group (Fig. 1.7.) was first synthesised by Gerhardt in 1858 when he reacted aniline and N-phenylbenzimidyl chloride [17]

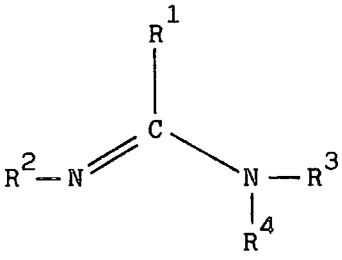


Fig. 1.7

$C_6H_5C(Cl){=}NC_6H_5{+}C_6H_5NH_2 \longrightarrow C_6H_5N{=}C(C_6H_5)NHC_6H_5.HCl$

In general the amidine is named after the acid or amide which may be obtained from it after hydrolysis. Thus when R^1=H, the group is known as formamidine, and similarly when R^1=Me, acetamidine; R^1=Et, proprioamidine; R^1=Ph, benzamidine etc. It is worth noting however that while most workers in the field still call these compounds amidines, the chemical literature now lists them under their systematic names, i.e. as the amide of the corresponding imidic acids [18]. Thus when R^1=H the group is know as methanimidamide, R^1=Me, ethanimidamide etc.

1.4.2. Physical Properties

Amidines are generally colourless or pale yellow stable liquids or solids. The low molecular weight compounds are moisture sensitive, and are often stored as the hydrochloride, from which the amidine is easily recovered.

Unsubstituted amidines are monoacidic bases. They form well crystallized salts:- sulphates, chlorides, acetates, nitrates, carbonates etc. The basic strengths of the amidines vary with substitution. Bernthsen [19] noticed that N,N'-diphenylbenzamidine reacts neutral to litmus in alcoholic solution. The latter is a weaker base than ammonia whereas

N,N'-diphenylacetamidine is a stronger base than ammonia. It can also be concluded that benzamidine and acetamidine are stronger bases than ammonia since the hydrochlorides can be obtained directly from solutions that contain an excess of ammonia.

Monosubstituted and N,N' disubstituted amidines are capable of exhibiting tautomerism (Fig. 1.8.). The many early attempts to synthesise separate isomers [20-24] failed, and in only one case [25] were the two isomers observed. Even these isomers however form identical salts.

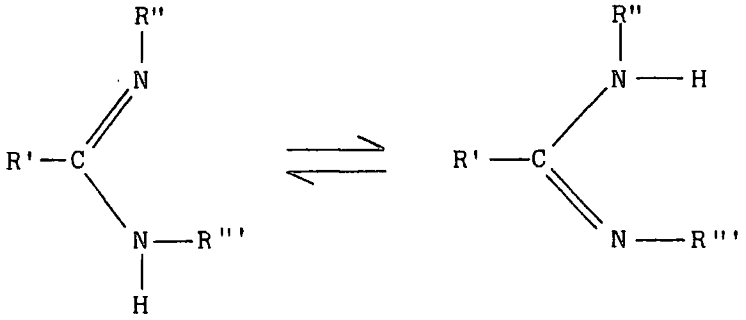


Fig. 1.8

Rotational isomerism about the C-N single bond also occurs [26].

1.4.3. Preparation

There are now many general preparations for amidines in the literature, the particular method depending upon whether a formamidine, acetamidine, or benzamidine etc., is required, and whether it is to be mono, di or tri substituted. Some examples of the methods of preparation are given below:-

$\mathrm{RCONHR' + PCl_5 \longrightarrow RC(Cl){=}NR' \xrightarrow{R''NH_2} R''NH{-}C(R){=}NR'(HCl)}$ [27]

$\mathrm{PhCCl_3 + 4PhNH_2 \longrightarrow PhN{=}CPh{-}NHPh(HCl) + 2PhNH_3Cl}$ [28]

$\mathrm{RC(OEt){=}NH(HCl) + 2R'NH_2 \longrightarrow R'NH{-}CR{=}NR' + NH_4Cl + EtOH}$ [29]

$\mathrm{RC(OEt)_3 + 2R'NH_2 \longrightarrow R'N{-}CR{=}NR' + 3EtOH}$ [30] [31]

$\mathrm{RCSNR'_2 + R''{-}NH_2 \longrightarrow R'_2N{-}CR{=}NR'' + H_2S}$ [32]

$\mathrm{RCN + KNH_2 \longrightarrow H_2N{-}CR{=}NK \xrightarrow{HCl} H_2N{-}CR{=}NH(HCl) + KCl}$ [33]

$\mathrm{PhCH{=}NPh + NaNH_2 \longrightarrow H_2N{-}C(Ph){=}NPh}$ [34]

$RN{=}C{=}NR + R'MgBr \longrightarrow RN{=}CR'{-}NRMgBr \xrightarrow[NH_4Cl]{H_2O} RN{=}CR'{-}NHR$ [35]

The organic chemistry of the amidines has been reviewed by R.I. Shriner and F.W. Neumann [36] , but this is now rather dated.

1.4.4. Amidino-Metal Complexes

Amidino-metal complexes have been known for almost as long as amidines. In 1878 Pinner reported the synthesis of the silver salts, and also a platinum chloride complex. [37]

The group (1a) salts are known and are usually prepared from the parent amidine [38 - 41].

$RN{=}CR'{-}NHR'' + KNH_2 \xrightarrow{NH_3} RN{=}CR'{-}N(K)R'' + NH_3$ [38]

$RN{=}CR'{-}NHR'' + KOBu^t \longrightarrow RN{=}CR'{-}N(K)R'' + Bu^tOH$ [39]

$RN{=}CR'{-}NHR'' + Bu^nLi \longrightarrow RN{=}CR{-}N(Li)R'' + Bu^nH$ [40]

$2RN{=}CR'{-}NHR'' + 2Na \longrightarrow 2RN{=}CR'(Na)R'' + H_2$ [41]

They can however be produced by the action of metal amines on nitriles.

$RCN + KNH_2 \longrightarrow H_2N{-}CR{=}N(K)$ [42]

These compounds, unlike the analogous acetate salts are extremely sensitive to atmospheric moisture; they are prepared under anhydrous conditions, and generally used "in situ".

$R{-}N{-}CR'{-}NR''(Li) + H_2O \longrightarrow R{-}N{=}CR'{-}NR''H + LiOH$

When symmetrical amidines are used a mixture of isomeric salts results, because in solution the lithio-amidines are associated, and react as though they are a mixture of R'N(Li)-CR=NR" and R'N=CR-N(Li)R" [36]. The group (11a) salts are also known and are similarly moisture sensitive.

$R_2NCN + R'MgBr \longrightarrow R_2NCR'{=}NMgBr$ [43]

$2RCN + Ca(NH_2)_2 \longrightarrow (H_2N{-}CR{=}N)_2Ca$ [44]

The group (1b) metal amidines are made by the reaction of metal acetates with the amidines.

$M(CH_3COO) + RN{=}CR'{-}NHR'' \longrightarrow RN{=}CR'{-}N(M)R'' + CH_3COOH$

M = Ag or Cu [45,46].

These compounds are much more stable than their group 1a counterparts, and the copper derivative shows no tendancy to oxidation by air even when moist.

The transition metal derivatives vary in their stability to withstand hydrolysis, they are generally made by one of the following methods:-

a) By the reaction of the free amidine with the metal carbonyl, causing the displacement of the carbonyl groups.

e.g. $2M(CO)_6 + 4ArNHC(Ph){=}NAr \longrightarrow M_2[PhC(NAr)_2]_4 + 12CO + 4[H]$

M = Mo, Cr [47].

b) By the reaction of the free amidine with a metal halide.

e.g. $(Cp)Mo(CO)_3Cl + 2ArNHC(CH_3){=}NAr \longrightarrow CpMo(CO)_2[CH_3C(NAr)_2]$
$+ CH_3C(NHAr)_2Cl$ [48]

$(Bu^t_4N)^+_2(Re_2Cl_8)^{2-} + 4ArNHC(Ph){=}NAr \longrightarrow$
$[ReCl_2(PhC(NAr)_2)]_2 + 2(Bu^tN)Cl + 2PhC(NHAr)_2Cl$ [49].

c) By the interaction of metal halides with group 1a metal salts.

e.g. $K(HC(NAr)_2) + CpMo(CO)_3Cl \longrightarrow CpMo(HC(NAr)_2)(CO)_2 + KCl + CO$ [50].

$Li(CH_3C(NAr)_2) + Mn(CO)_5Br \longrightarrow Mn(CO)_4(CONArC(CH_3)NAr) + LiBr$ [40].

d) By the displacement of silver halides from silver amidines and metal chlorides.

e.g. $Ag(HC(NAr)_2) + CpMo(CO)_3Cl \longrightarrow CpMo(CO)_2(HC(NAr)_2) + AgCl + CO$ [16].

The group 4a amidines are also known, they are unstable colourless or yellow liquids, or solids. They are prepared by the reaction of lithium amidines on the alkyl metal chlorides.

e.g. $(R'{-}N{-}C(Ph){=}NR'')Li + Me_3MCl \longrightarrow LiCl + R'{-}N{-}C(Ph){-}NR''{-}MMe_3$ [52].

M = Si,Ge,Sn,Pb.

1.4.5 Structural Considerations

There are five possible bonding modes that have been proposed for metal-amidino systems. These are monodentate, pseudo Π-allylic, chelate, bridging and for N,aryl substituted amidines, ortho metalate chelate.

a) Monodentate: One nitrogen is σ bonded to the metal, the other nitrogen is not attached; it has a localised double bond to the central carbon atom (Fig. 1.9).

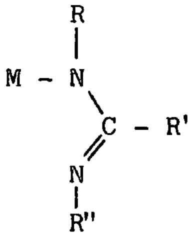


Fig. 1.9

In the solution the nitrogens may interchange through a fluxional process.

b) Pseudo Π allyl: This structure has a Π allylic arrangement with the N-C-N skeleton in a separate plane to the metal (Fig 1.10).

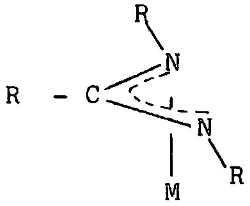


Fig.1.10

c) Chelate: In this case the N-C-N skeleton and the metal atom are all in the same plane. This class can be subdivided as follows:-

i) amidine is σ,σ-attached to the metal; the bonding is delocalised (Fig. 1.11a).

ii) one nitrogen σ bonds to the metal, whilst the localised double bond interacts with the metal's orbitals (Fig. 1.11b).

iii) one nitrogen σ-bonds to the metal, whilst the other donates to the metal via its lone pair of electrons (Fig. 1.11c).

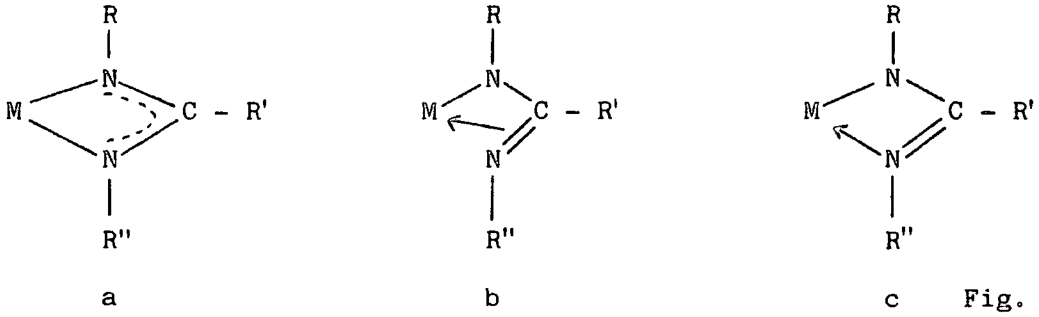


Fig. 1.11

d) Bridging: Here the chelate ring is extended by the incorporation of another atom. This atom can either be another metal, the amidine forming a metal-metal bridge (Fig. 1.12a), or else an inserted group such as a carbonyl giving a carbamoyl type complex (Fig. 1.12b).

a Fig. 1.12 b

e) Orthometalled: If one of the N substituents is aryl, orthometallation may occur, forming a fairly stable six membered ring (Fig. 1.13).

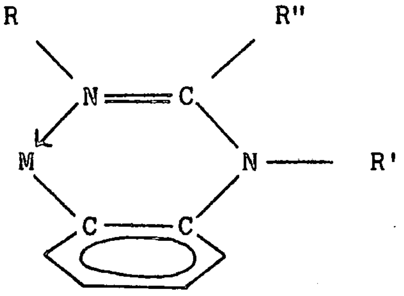


Fig. 1.13

If R" group is an aryl substituent, o-metallation to this ring can occur to produce a five membered ring.

In addition, the free amidine can also be attached to the metal via the lone pairs on either of the nitrogen atoms.

1.4.6. Monodentate Complexes

This is the prevalent type of bonding for the non transition metals. The group IV metals have been shown to undergo tautomerism with mono or N,N'-disubstituted amidines [52] (Fig. 1.14).

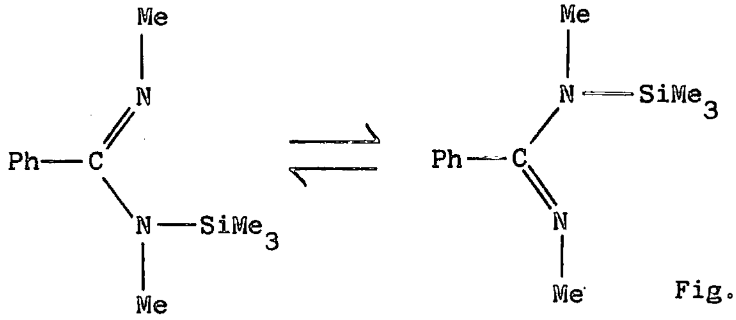


Fig. 1.14

Monodentate transition metal amidines are comparatively rare, perhaps because of the availablility of the second nitrogen atom to displace a ligand on the metal by chelating or bridging between two metals. As yet X-ray data is not available for monodentate transition metal amidines, although a few compounds have been assigned this structure on the basis of the similarity of the spectroscopic data which is available for the analogous triazene complexes [53,54]. Examples of monodentate transition metal complexes are *trans*-$Pd(PPh_3)_2Cl(PhN\text{-}CH\text{=}Ph)$ and *cis*-$Pt(PPh_3)_2(Cl)(PhN\text{-}CH\text{=}NPh)$[54]. Neutral amidine monodentate complexes have also been reported for Mo but these compounds then react further with the loss of CO etc., to produce the $Mo_2(PhNCHNPh)_4$ species.

$$Mo(CO)_6 + (PhNH\text{-}CH\text{=}NPh) \xrightarrow{h\nu} Mo(CO)_5(PhNH\text{-}CH\text{=}NPh) + CO$$

and $$Mo(CO)_6 + 2(PhNH\text{-}CH\text{=}NPh) \xrightarrow{h\nu} Mo(CO)_4(PhNH\text{-}CH\text{=}NPh)_2 + 2CO$$

$$2Mo(CO)_4(PhNH\text{-}CH\text{=}NPh)_2 \longrightarrow Mo_2(PhN\text{-}CH\text{-}NPh)_4 + 4H + 8CO \quad [55]$$

1.4.7. Chelate Complexes

Because of the relatively small size of the chelate ring, i.e. only four membered, there will always be steric strain and distortion of the valency angles. The number of chelated amidine complexes therefore is not large, the amidine often prefering to bridge between two metals. So far much of the work has been performed using formamidines, where the central N-$\hat{C}$-N angle is at a maximum. This angle decreases in the order R=H >Ph >CH_3> $C\text{-}(CH_3)_3$, and it is postulated that by the incorporation of a more bulky substituent on the carbon atom the preference for forming monomeric chelate complexes will increase.

The first chelated amidino complexes were those formed by the thermal decarbonylation of the carbamoyl product of the reaction between tetracarbonylmanganesebromide and lithium N,N'-diphenylbenzamidine [56]. This work was later extended to include the N,N'-diarylacetamidines, and the decarbonylation step was achieved by u.v. irradiation[40] (Fig. 1.15).

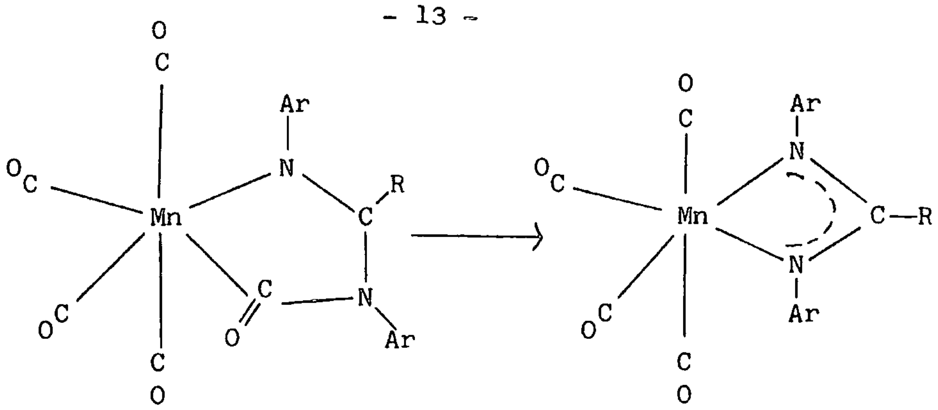


Fig. 1.15

At the time this compound was first made, it was unclear what type of bonding was occuring. The chemistry of the chelating amidino-group was then extended by the sythesis of a series of cyclopentadienylmolybdenumdicarbonyl amidines via direct reaction of benzamidines or acetamidines with cyclopentadienylmolybdenumtricarbonylchloride [48-57], or by decarbonylation of the carbamoyl formed when using lithioamidines. By now the spectroscopic evidence was mounting in favour of a delocalised σ,σ-type of chelated amidine (Fig. 1.16).

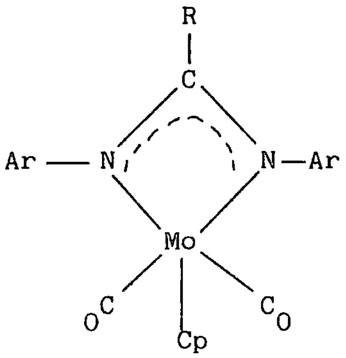


Fig. 1.16

This type of bonding was confirmed when X-ray crystallography showed that the Mo-N bond lengths were almost equal, and shorter than the Mo-C distance. The N-C distances were also found to be approximately equal [58].

The literature has since been further expanded with the analogous chromium and formamidine complexes [50] made by the reaction of the cyclopentadienyl-chromium tricarbonylchloride with potassium, silver, and copper amidines, or the free amidine and u.v. irradiation. Substitution of the carbonyls by triphenylphosphine, -arsine and -stibine has also been achieved [59].

The anionic group (VIa) compounds which are isostructural and isoelectronic to the manganese compounds above have also been made using the potassium salt of dialkyl or diaryl formamidine and $NEt_4^+[M(CO)_5Cl]^-$[50]. Bis (N,N'-di-ptolylacetamidine) paladium II complexes have been made, they have been shown by X-ray crystallography to contain chelated amidines [58] (Fig. 1.17).

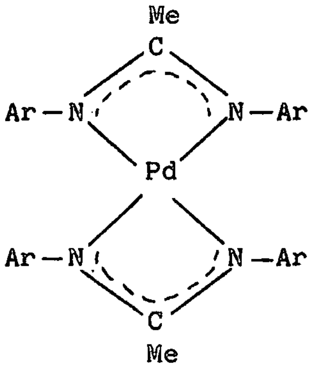


Fig. 1.17

Molecular weight experiments suggest that the analogous formamidine compound is dimeric, containing amidino bridges (cf. triazene complex)[53] (Fig. 1.18) .

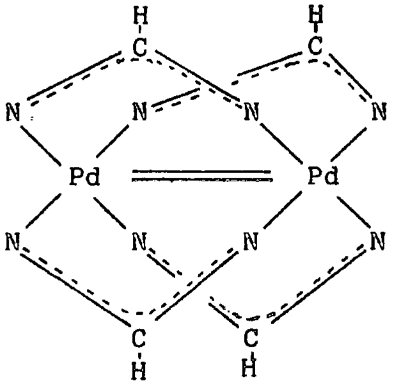
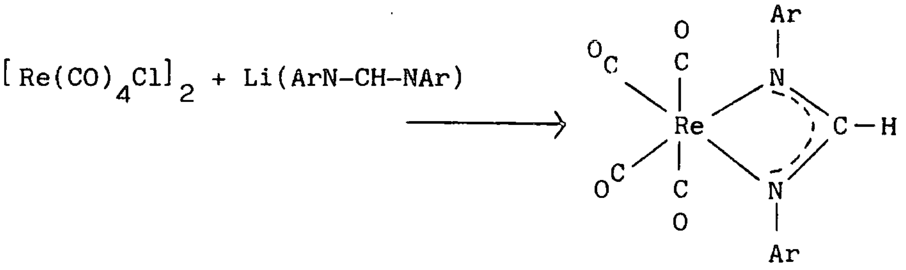


Fig. 1.18

This is perhaps evidence that by increasing the size of the carbon atom substituent from H to CH_3 the C-N-C angle is reduced enough for chelate formation to occur in the acetamidines.

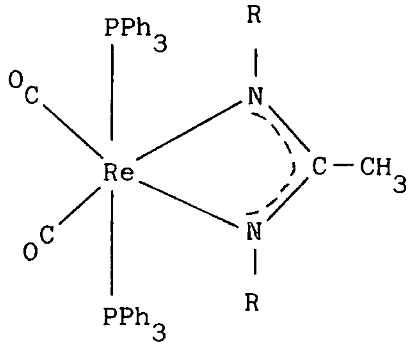
Chelated amidines have recently been reported for the reaction between rheniumtetracarbonylchloride dimer and lithium formamidines [61].



These compounds can also be made from the decarbonylation of the carbamoyl product obtained by using rheniumpentacarbonyl chloride, in place of the dimer. They are assigned the chelate structure on the basis of ^{13}C n.m.r. and i.r. data.

Another recently reported chelating amidino complex is shown below, prepared by the action of Li-formamidine on $Re(CO)_3(PPh_2)Cl$ [62]. Again it is assigned the chelate structure by comparison to the analogous triazene complex [63].

e.g.



The problem of small ring size and the subsequent steric strain is often overcome by the adoption of extra atoms in the chelate. These can be of three types:-

1) Carbamoyl type When a carbonyl group is inserted into a metal-nitrogen bond the resulting complex is know as a carbamoyl. There are numerous examples of this type in the literature [64-66]. With amidines, a carbonyl is inserted between one nitrogen and the metal, the other nitrogen being bonded directly to the metal, giving a five membered ring (Fig. 1.15). Several examples of these carbamoyl complexes have already been mentioned, as they are often the initial product of the reaction between group (1a) metal amidines, with metal carbonyl halides [40,56,61].

2) Orthometallation When at least one of the N substituents is aryl,

orthometallation can occur. The amidine is still bidentate, so a stable six membered ring is formed. One of the first examples of this was the product formed by the reaction of mercuric acetate with N,N'-di-p-tolyl formamidine (Fig. 1.19) [45].

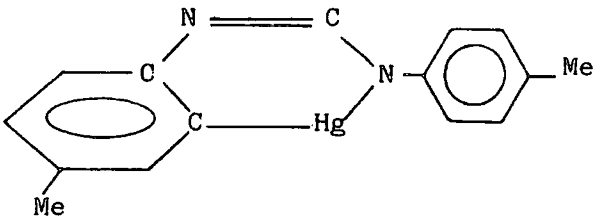


Fig. 1.19

There are not many examples of this type of bonding to transition metals, one example however, is the product formed by the reaction of potassium-tetrachloropalladite with N,N'-diphenylacetamidine to give the chloro bridged dimer [67], shown below (Fig. 1.20).

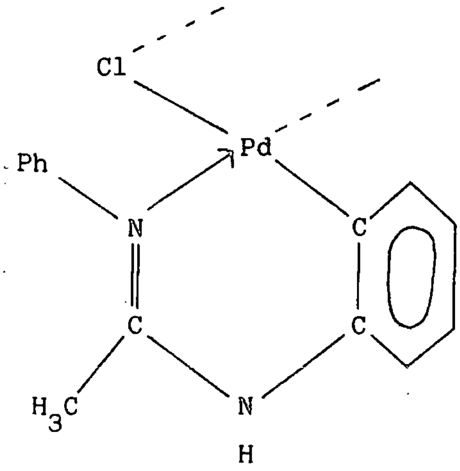


Fig. 1.20

The chlorine bridges can be replaced by an allyl, cyclopentadienyl, or even a second amidino group, which gives the unusual mixed chelate - orthometallate complex (Fig. 1.21).

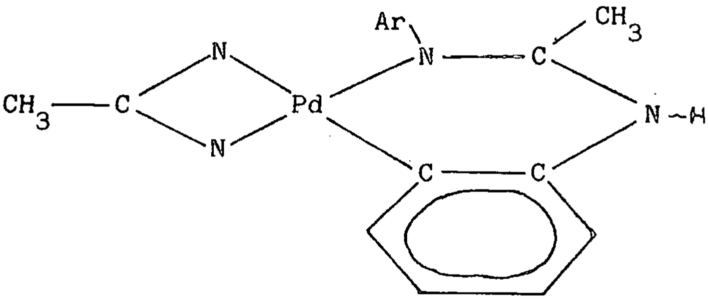


Fig. 1.21

3) Bridging This is the most popular way that the amidino group overcomes ring strain. Here the amidine incorporates another metal into the ring giving an amidino-bridge between the two metal atoms. The metal atoms may be the same or different. The first metal amidino bridged complex was that formed by the reaction of copper (II) acetate with N,N'-di-2-anthraquinonylformamidine [68] . This compound was originally formulated as a monomer, but later work suggested it to be a tetramer (Fig. 1.22) [45].

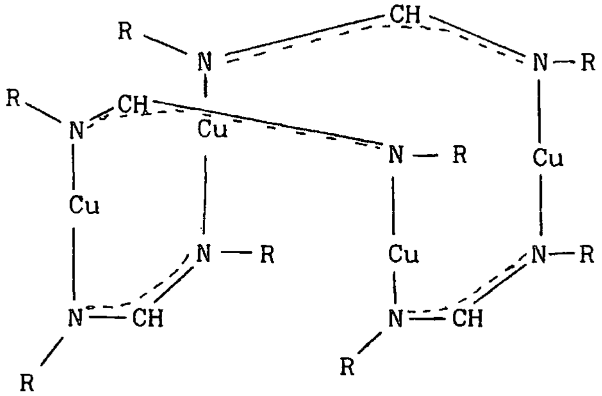
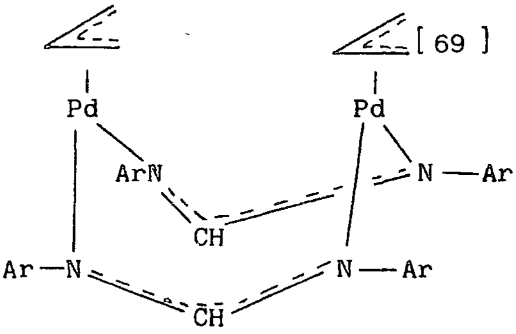


Fig. 1.22

More recently a number of transitition metal aminino bridging complexes have been made. Some examples of the preparation and range of amidino bridged complexes are:-

i. $[Pd(C_3H_5)Cl]_2$ + 2Li(ArNCHNAr) $\longrightarrow$

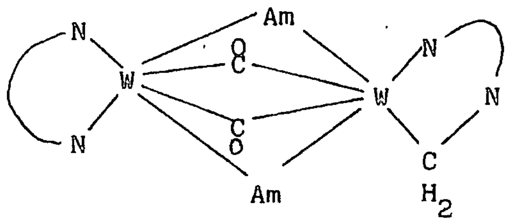


[69]

ii. $M(CO)_6$ + 4(PhNH-C(Ph)=NPh) $\longrightarrow$ $M_2(\mu$-PhNC(Ph)NPh$)_4$ + 4[H]

M = Mo,Cr [55]

iii. $W(CO)_6$ + 4(PhNH-CH=NPh) $\longrightarrow$



[70]

iv. $[Re_2Cl_8]^{2-}$ + 2PhNH–C(Me)=NPh $\longrightarrow$ $Re_2(\mu$-PhNC(Me)NPh$)_2Cl_4$ [49]

v. $[Re_2Cl_8]^{2-}$ + 4MeNH–C(Ph)–NMe $\longrightarrow$ $Re_2(\mu$-MeNC(Ph)NMe$)_4$ [49]

vi. $Pd(NCCH_3)_2Cl_2$ + 4Li(CH(NAr$)_2$) $\longrightarrow$ $Pd_2(\mu$-CH(NAr$)_2)_4$ [53]

vii. $Ir(CO)_3Cl$ + Li(HC(NAr$)_2$) $\longrightarrow$ $Ir(CO)_4(\mu$-CH(NAr$)_2)_2$ [71]

Bridging can also take place via a different metal atom, an interesting example of this is the compounds formed by the reaction

$(COD)RhCl_2$ + Hg(ArN–CH–NAr) $\longrightarrow$ (COD)(μ-ArNCHNAr)RhHgCl

The product is shown to be fluxional, the amidines exchanging their bonding roles [72] (Fig. 1.23).

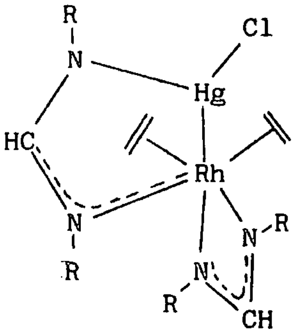
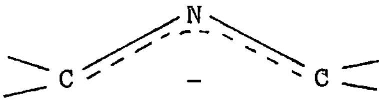


Fig. 1.23

1.5. 2-Aza-Allyls and Metallated 2-Aza-Allyls

Aldimines (RCH=NR') and ketimines (RR"C=NR') where $R'=CHR^{2}R$ on removal of a proton form the 2-aza-allyl group which is an interesting intermediate between the allyl and amidino groups.

e.g.



2-aza-allyl

So far there are not many metallated 2-aza-allyl complexes known. Group (1a) metal aldimines are known however, and are made in the same way as the group (1a) metal amidines.

e.g. $Ph_2CHN{=}CHPh + KNH_2 \longrightarrow Ph_2CHNC(K)Ph + Ph_2(K)NCHPh + NH_3$ [73]

$PhCH_2N{=}CHPh + NaNH_2 \longrightarrow PhCH(Na)NCHPh + NH_3$ [74]

$PhCH_2N{=}CHPh + LiNEt_2 \longrightarrow PhCH(Li)N{=}CHPh + EtNH$ [75]

$P.N[CH(Me)_2]_2 + {}^{n}BuLi \longrightarrow Me_2C(Li)N{=}CMe_2 + BuH$ [76]

In common with the amidino-metal complexes these compounds are extremely moisture sensitive, and are therefore not generally isolated, but prepared and used "in situ".

The group (IVb) metal aldimines are also known. They are prepared by the reaction of the group (1a) complexes with the triorganometal chlorides.

e.g. $RCH(Li)N{=}CHR' + R^2{}_3MCl \longrightarrow RCH(MR^2{}_3)N{=}CHR' + LiCl$ [77]

$M = Si, Ge, Sn.$

As in the allyl compounds the spectroscopic data can only be explained by assuming conjugative interaction between the metal and the N=C bond.

The only examples of transition metal 2-aza-allyl complexes are those formed by the novel reaction of lithium ketimines on group (VIa) cyclopentadienylmetalcarbonylchlorides.

e.g. $CpM(CO)_3Cl + LiN{=}C(Ar)_2 \longrightarrow CpM(CO)_2(Ar_2CNCAr_2) + LiCl + LiNCO$

$M = Mo, W$ [78-80]

An obvious synthetic route to these compounds is the reaction between $Li(Ar_2CNCAr_2)$ and $CpM(CO)_3Cl$. For the tetraaryl derivative the only recoverable product is $[CpM(CO)_3]_2$[81], there is however some spectroscopic evidence that the metallated 2-aza-allyl product is formed when using the diaryl derivative, Li(PhHCNCHPh) [81].

There is also some spectroscopic evidence that a manganese derivative is possible, derived from the reaction between $Ph_2C{-}N{-}C(Cl)Ph_2$ and $Mn(CO)_5Br$. Other synthetic routes such as $(ClMg)Ph_2C{-}N{=}CP_2 + Mn(CO)_5Br$;

$Ph_2C=N-C(Cl)Ph_2$ + $Na(Mn(CO)_5)^-$, do not produce the desired product [82]. The bonding in the compound $CpMo(CO)_2((ptolyl)_2CNC(potlyl)_2)$ has been examined by X-ray crystallography, and shown to bond in an aza-allene fashion, (Fig. 1.24)[83].

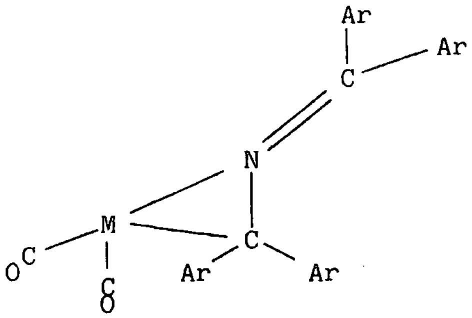


Fig. 1.24

In solution however, the i.r. and variable temperature n.m.r. data suggests that σ,π-type bonding is occurring, with interchange between the two isomers, (Fig. 1.25) [80].

Fig. 1.25

1.6 Triazenes and Metallated Triazenes

Compounds containing an unsaturated chain of three nitrogen atoms, R'-N=N-NR"R"'are called triazenes (or diazoamines), they are members of the pseudo allyl compounds. Triazenes were discovered by Griess [84] in 1860 and now a wide variety of triazenes with differing R',R" and R"'groups are known [85]. Of special interest are those triazenes where R"'is a hydrogen atom which can be replaced to form the triazinido-group. Triazenes are generally stable yellow solids.

Metal compounds of the triazenido-anion have been known as long as the parent triazenes [33] and have been the subject of a good deal of attention over the years [86-89, 44].

The group (la) metal triazenes are prepared in a similar way to the metal amidines, e.g.

$R{-}N{=}N{-}NHR' + Bu^{n}Li \longrightarrow Li(RN_3R') + Bu^{n}H$ [38]

$R{-}N{=}N{-}NHR' + NaH \longrightarrow Na(RN_3R') + H_2$ [90]

$R{-}N{=}N{-}NHR' + KNH_2 \longrightarrow K(RN_3R') + NH_3$ [38]

Transition metal derivatives are generally made by the interaction of metal halides with group la salts [90], displacement of silver halides from silver triazenes [91] , or by the reaction of the diorganotriazenes with a substituted metal, followed by elimination of hydrogen [44]. e.g.

$CpMo(CO)_3Cl + Na(PhN_3Ph) \longrightarrow CpMo(CO)_2(PhN_3Ph){+}NaCl{+}CO$ [90]

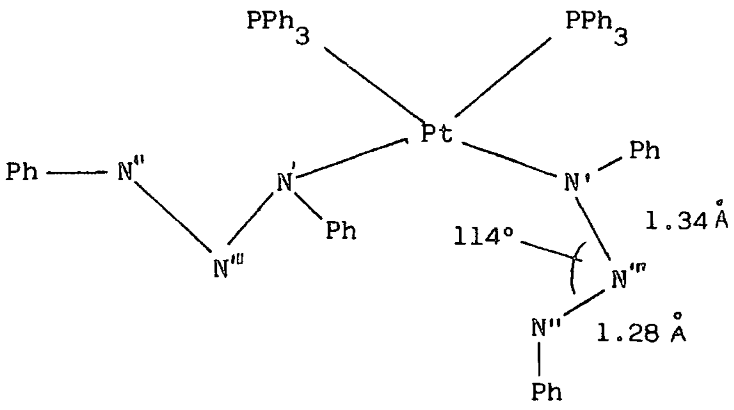
$FeCl_3 + 3Ag(PhN_3Ph) \longrightarrow Fe(PhN_3Ph)_3{+}3AgCl$ [42]

$Pd(PPh_3)_4 + 2(PhN{=}N{-}NPh) \longrightarrow Pd(PPh_3)_2(PhN_3Ph)_2 + 2PPh_3 + H_2$ [44]

Four different types of bonding have been proposed for the triazenido ion, they have been established by X-ray crystallography [92-94,89] . These are:- monodentate, chelate, and bridging (two types) (Fig. 1.9, 1.11a, 1.12a and 1.26).

Monodentate

e.g. $Pt(PPh_3)_2(PhN_3Ph)_2$ (Fig. 1.26a) [92]



It is noted that the N - N bond adjacent to the metal is longer than the one remote from the metal, 1.34 and 1.28Å respectively, giving a canonical structure of M - N ÷ N = N. If these bond lengths are compared to the N - N single and double bond lengths of, 1.44 Å and 1.24 Å, it is evident that there is a significant degree of delocalisation. The $\widehat{\mathrm{NNN}}$ angle is 114°.

Chelate

e.g. $CpMo(CO)_2(ArN_3Ar)$ [93].

The triazene is found to bond with all three nitrogens in the same plane as the metal. The nitrogen - nitrogen bond lengths are approximately equal (1.29 and 1.32 Å) implying a fully delocalised system. The $\widehat{\mathrm{NNN}}$ angle is reduced to 101°.

Bridging

eg. a) $Ni_2(\mu ArN_3Ar)_4$ [89].

In this complex all the N ÷ M bond lengths are approximately equal (1.93 A), as are the N - N bonds, (1.32 A). This emphasises the truly delocalised bonding for the N_3 skeleton, and that the bonding must be taking place through the lone pairs of the terminal nitrogens in a σ,σ-fashion. The ring strain apparent in the chelate system is no longer evident, the $\widehat{\mathrm{NNN}}$ angle being 115°

eg. b) $(PPh_3)(CO)(Rh)(MeN_3Me)CuCl$ [94] (Fig. 1.26b)

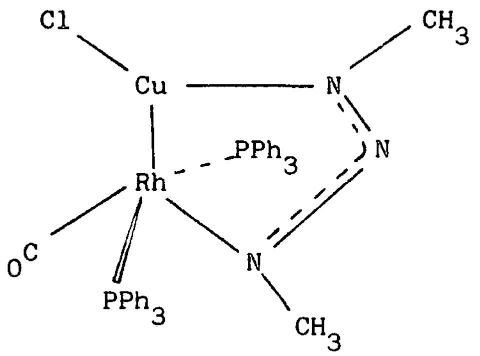


Fig. 1.26b

Again the ring strain is reduced, this time by the incorporation of another metal atom into the chelate ring.

The triazenido ligand shows a marked tendency for donation of the lone pair of electrons on both terminal nitrogen atoms. The few complexes that contain the monodentate triazenido ligand in the solid state all exhibit fluxional behaviour in solution, a chelated triazenido ligand being an intermediate bonding mode.

1.7. Rhenium Carbonyl Chemistry

Most of the work in this thesis involves the reactions of various rhenium carbonyl and amidine species. A brief synopsis of the typical chemistry of the rhenium carbonyl species of relevance to this work is given below.

Rhenium carbonyl [$Re_2(CO)_{10}$] is an air stable, sweet smelling white crystalline solid. It is slightly soluble in most organic solvents, and in contrast to manganese carbonyl [$Mn_2(CO)_{10}$] , it is stable when exposed to air in solution.

The pentacarbonyl halides of rhenium and manganese are easily formed by the reaction of halogens with the parent carbonyl in a suitable solution. The stability of these halogen derivatives is in the order $I > Br > Cl$ and $Re > Mn$ [95]. These compounds lose carbon monoxide when heated in an inert solvent, forming the halogen bridged dimers [$M(CO)_4X$] $_2$ [96]. Rhenium also gives a highly reactive tetramer [$Re(CO)_3X$] $_4$ [97]. The pentacarbonyl halides undergo substitution reaction when refluxed or irradiated with amines. The monosubstituted derivative is not isolated, as it is more reactive than the parent halide i.e.

$$Re(CO)_5X \xrightarrow[-\ CO]{+\ Amine} Re(CO)_4(Amine)X \xrightarrow[-\ CO]{Amine} Re(CO)_3(Amine)_2X \quad [98] .$$

Further substitution is not possible since with three essentially non Π-electron accepting ligands present the metal — carbon multiple bond is at a maximum. With the manganesepentacarbonylchloride, a similar reaction leads to the carbamoyl product, $Mn(CO)_4(CONHR)(NH_2R)$ [99] .

The reaction of $[Re(CO)_4X]_2$ (X=Cl,Br) with amines proceeds under much milder conditions than for the pentacarbonyl halides, providing a route to the monosubstituted $Re(CO)_4(Amine)X$ complexes.

Both manganese and rheniumpentacarbonylhalides form anions with sodium amalgam. The salts can be isolated, but are generally used "in situ" to produce alkyl or acyl derivatives by reaction with an alkyl or acyl halide e.g.

$$Mn(CO)_5Na + CH_3I \longrightarrow Mn(CO)_5CH_3 + NaI \qquad [100]$$

$$Re(CO)_5Na + CH_3COCI \longrightarrow Re(CO)_5(COCH_3) + NaCl \qquad [101]$$

A similar reaction with allyl halides produces the σ-bonded complex $(\sigma\text{-}C_3H_5)Mn(CO)_5$ [4] for manganese, but the Π-bonded complex $(\Pi C_3H_5)Re(CO)_4$ [102] for rhenium. The Π-bonded manganese complex is produced by heating the σ-bonded derivatives to 70°C. The σ-bonded rhenium complex has not been observed.

$Mn(CO)_5Br$ reacts with lithio-amidines [40,61] to give the carbamoyl species $Mn(CO)_4$(COAmidine), which can be decarbonylated by heating or u.v. irradiation to give the bidentate amidino complex $Mn(CO)_4$(Amidine). A similar reaction has been found for $Re(CO)_5Cl$ and lithioformamidines[61]. The product $M(CO)_4$ (formamidine) can also be formed directly by the reaction of lithio formamidines on the dimeric tetracarbonylmetalchlorides. The chelated triazene complexes Mn or $Re(CO)_4(ArN_3Ar)$ are also known, and are prepared by the action of $Na(ArN_3Ar)$ on the pentacarbonylbromide [90]. The mono and bis-triphenyt phosphine derivatives are also known [130,62]. The only evidence for a monodentate triazenido or amidino-bonded ligands is from the reaction between $Mn(CO)_4$(PhNC(Ph)NPh) and CO at high temperature and carbon monoxide pressure, in this instance a species identified by i.r. spectroscopy, $Mn(CO)_5$(PhNC(Ph)NPh) was observed, but it reverted to $Mn(CO)_4$(PhNC(Ph)NPh) on release of the pressure [40].

CHAPTER 2

EXPERIMENTAL

2.1.Notation

In this thesis a shorthand notation for amidines has been employed, i.e. DPTAAH = N,N' -di(p-tolyl) acetamidine. The H suffix denotes that the amidine is the parent amidine with a N - H group. If the final H is omitted the shorthand refers to the amidino group, i.e. DPTAA = N,N' - di(p-tolyl) acetamidino group.

In complexes where orthometallation is believed to have occured, this is signified by the prefix o-met.

Only N,N' symmetrically disubstituted amidines were used, these are listed below, together with their abbreviations.

N,N' -diphenylacetamidine	DPAAH
N,N' -di(p-tolyl)acetamidine	DPTAAH
N,N' -diphenylbenzamidine	DPTBAH
N,N' -di(p-tolyl)benzamidine	DPTBAH
N,N' -diphenylformamidine	DPFAH

In addition, when an amidine is referred to generally it is abbreviated to AmH and its derivative to Am.

2.2 Techniques

2.2.1. General Methods

All solvents were rigorously degassed before use. Reactions were carried out in twin-necked flasks, under an atmosphere of pure dry nitrogen. Solutions were transferred by syringe against a counter current of nitrogen. For the more air sensitive materials single Schlenk tubes fitted with suba seals were used, solutions being transferred from one tube to another via Schlenk needles and positive nitrogen pressure. A glove box was used for the manipulation of air sensitive solids.

2.2.2. Nitrogen Supply

The nitrogen supplied to the bench was the boil off from the departments liquid nitrogen plant, which after being passed over a heated copper catalyst has an oxygen content of less than 10 p.p.m. The supply was bubbled through concentrated H_2SO_4 at the bench, and delivered to a multiplet outlet system. A constant pressure of nitrogen was maintained in the system by connecting one outlet to an oil bubbler. These conditions were adequate for the rhenium amidine chemistry, but not for the iron amidine work. This demanded that the nitrogen was further dried by the addition of P_4O_{10} towers to the supply, and the residual oxygen removed by the inclusion of a heated copper catalyst in the line immediately before the multiple outlet system.

2.2.3. Vacuum Line

A vacuum line connected to a rotary vacuum pump capable of maintaining a vacuum of 10^{-2} torr was fitted with two way taps connected to the nitrogen supply, enabling the apparatus to be alternatively degassed and filled with nitrogen, creating and maintaining an inert atmosphere.

2.2.4. Glove Box

The pure dry nitrogen atmosphere in the glove box was maintained by continuously recycling it through a P_4O_{10} column and over a heated copper catalyst. Nitrogen, as supplied above was used to flush out the transfer port. All external tubing was of p.v.c. or glass. This atmosphere was suitable for brief manipulations of the iron complexes, but was not suitable for lengthy operations, decomposition of the compounds occuring. The iron complexes needed to be stored as sealed samples in the glove box if decomposition was not to occur.

2.2.5. Chromatography

Column chromatography was employed in many of the syntheses, as was the less precise practice of filtering solutions through about 4 cm. of alumina. The alumina used was supplied by Woelm Pharmaceutical, and was rated Brockman activity III.

2.3. Instrumentation

2.3.1. Mass spectroscopy

Mass spectra were obtained on a A.E.I. MS9 mass spectrometer operating at 70 e.V. with an accelerating potential of 8 kV. , and a source temperature of 200°C. The samples were mounted on an inert ceramic and were introduced by direct insertion into the ion source. Perfluorokerosine (P.F.K.) was often introduced simultaneously to the sample to provide a means of calibration.

2.3.2. Infra red spectroscopy

Infra-red spectra in the range 4,000 - 250 cm^{-1} were recorded on a Perkin-Elmer 456 prism grating spectrophotometer. In general both nujol mulls and solution spectra were recorded. For the mulls, KBr plates were used, and for solutions a cell with NaCl windows and a 0.1 mm space was employed. In addition, the progress of many of the reactions was followed by the monitering of the carbonyl stretching frequencies in the region 2,200 - 1600 cm^{-1}. For the very air sensitive iron complexes an isolation cell was used, but without much success.

2.3.3. Nuclear magnetic resonance spectroscopy

Proton n.m.r. spectra at 60 M.Hz. were recorded on a Varian E.M. 360L spectrometer in $CDCl_3$ solution using $(CH_3)_4Si$ as an internal reference.

Carbon - 13 spectra were recorded on a Bruker HX90E spectrometer modified for F.T. operation using a Nicolet B.N.C. 12 computer. Samples were dissolved in $CDCl_3$ and $(CH_3)_4Si$ was employed as an internal reference.

In order to obtain a reasonable spectrum a pure sample of about 200 mg was required, unfortunately this was not always possible.

The Bruker HX90 E spectrometer was also occasionally used for proton n.m.r. at 90 M.Hz. when better resolution of the spectrum obtained from the Varian was required.

2.3.4. Raman Spectroscopy

Raman spectra of solid samples in the range 4,000 - 200 cm^{-1} were recorded on a Cary 82 180° geometry laser Raman spectrometer utilising a Spectrophysics 164 argon ion laser source.

2.3.5. Melting Points

Melting points were determined using a Reichert hot-stage polarizing microscope or a Gallenkamp capillary melting point instrument.

2.4. Analytical Methods

2.4.1. Carbon, Hydrogen and Nitrogen

C,H, and N determinations were carried out by the departmental microanalyst using a Perkin-Elmer 240 Elemental Analyser.

2.4.2. Halogens

Analyses of chlorine and bromine were performed by the departmental microanalyst using the conventional method of oxygen flask combustion followed by potentiometric titration of the halogen ion.

2.4.3. Metals

Analyses of Mo and Fe were performed by the departmental analyst using a Perkin-Elmer 403 A.A. spectrometer. Analyses of Re were not performed as reliable results could not be provided from the amount of sample available.

2.5. Preparation and Purification of Starting Materials

2.5.1. Hydrocarbon solvents and ether were dried over freshly extruded sodium wire.

2.5.2. Monoglyme and T.H.F. were dried by refluxing for 48 hours over potassium, then distilled under nitrogen, and stored over freshly extruded sodium wire.

2.5.3. Dichloromethane was distilled under nitrogen, and stored over activated 3A molecular sieve.

2.5.4. Carbontetrachloride and chloroform were dried by refluxing for 48 hours over P_4O_{10} then distilled under nitrogen onto activated 3A molecular sieve.

2.5.5. $Re_2(CO)_{10}$ was used as supplied by Strem Chemicals. Its infra-red spectra was recorded for comparative purposes.

Nujol $\nu(CO)$ 2075m 2075m 2017vs 1978s cm^{-1}.

CH_2Cl_2 $\nu(CO)$ 2017s 2010vs 1968s cm^{-1}.

2.5.6. $Re(CO)_5Br$ was prepared according to Abel et al [104] using a suspension of $Re_2(CO)_{10}$ in CCl_4 with a 30% excess of Br_2. Greater yields and quicker reaction times were however obtained by the following method. To a solution of $Re_2(CO)_{10}$ (2.000g, 3.06 m mole) in monoglyme (50ml) was added Br_2 (1 ml, 19.46 m mole) a white precipitate forming immediately. The mixture was stirred at room temperature for one hour to ensure complete reaction, then reduced in volume by 50% by evacuation. The monoglyme/Br_2 solution was then syringed off, and the off-white powder washed with ether (4 x 5 ml). The pure white powder was dried under vacuum, (yield 90%).

Nujol $\nu(CO)$ 2152w 2079shw 2062s 2040vs 1976 s 1964 s cm^{-1}.

CH_2Cl_2 $\nu(CO)$ 2044vs 1982m cm^{-1}.

2.5.8. $[\underline{Re(CO)_4Br}]_2$, the bromine bridged dimer was prepared according to Abel et al [104] , by the decarbonylation of $Re(CO)_5Br$ in a refluxing petroleum fraction (b.pt 100°C) for one hour. The product a white precipitate is pure enough to use without further purification. It is noted however, that prolonged refluxing results in the formation of the tetrameric $[Re(CO)_3Br]_4$ species [105].

Nujol ν (CO) 2114m 2040s 2019s 1996vs 1968vs 1930s cm^{-1}.

CH_2Cl_2 insoluble.

2.5.9. $[\underline{Re(CO_4)Cl}]_2$ was prepared in the same manner as the bromide dimer. It was an off-white colour.

Nujol ν (CO) 2120w 2064sh 2027sh 1998s 1970s 1930s cm^{-1}.

CH_2Cl_2 insoluble.

2.5.10 $\underline{Re(CO_4)(PPh_3)Br}$ was prepared according to Attwood and Brown [106] by stirring together $[Re(CO)_4Br]_2$ and PPh_3 in a 1:2 molar ratio in CCl_4 for two days at room temperature. Reaction is complete when $[Re(CO)_4Br]_2$ is no longer visible as a precipitate in the CCl_4 solution. The product forms small hard white crystals.

Nujol ν (CO) 2100s 2010vs 1987vs 1931vs 1887s cm^{-1}.

CCl_4 ν (CO) 2103m 2019s 2003vs 1942s cm^{-1}.

2.5.11 $\underline{Re(CO)_4(AsPh_3)Br}$ was prepared in a similar way to 2.5.10 Gentle heating to 50°C ensured complete reaction in 3 hours. The product was a white powder.

Nujol ν (CO) 2101s 2012vs 1990vs 1931vs 1888s cm^{-1}.

CCl_4 ν (CO) 2104m 2019vs 2008vs 1942s cm^{-1}.

2.5.12 DPAAH: A mixture of triethylorthoacetate (81.0g, 0·5 mole.), aniline (93.0g, 1.0 mole) and glacial acetic acid (2.5 ml) was refluxed for two hours. The unreacted starting materials and ethanol were removed by distillation at 47 mm/Hg at an oil bath temperature of 225°C. The residual liquid solidified on cooling. The product was recrystallised from hot toluene, washed with pet-ether (60°-80°) and dried on the vaccum line giving small white crystals, (yield 76%).

2.5.13 DPTAAH: A mixture of p-toluidine (107g, 1.0 mole)triethylorthoacetate (81g, 0.5 mole) and glacial acetic acid (2.5 ml) was refluxed for two hours. Ethanol and unreacted starting materials were then removed by distillation at 47mm/Hg. at an oil bath temperature of 240°C. The residual liquid solidified on cooling. Recrystallisation from toluene/hexane gave white crystals which were dried under vacuum (yield 80%).

2.5.14 DPBAH: To N-phenylbenzamide (11.10g, 56.3m mole) and PCl_5(12.00g, 57.55 m mole) was added toluene (105 ml) and the mixture refluxed for 2½ hours. The solution was allowed to cool, and a solid developed. To this was added a mixture of aniline (8.0 ml) in toluene (105 ml). The resulting mixture was refluxed for 6 hours. The solution was then allowed to cool giving a white precipitate which was washed with hexane and then recrystallised from pyridine/water to give white crystals (yield 40%).

2.5.15 DPTBAH To benzoyl-p-toluidine (5.23g, 24.7 m mole) and PCl_5 (5.68g, 27.2 m mole) was added toluene (50 ml) and the mixture refluxed for 2 hours. A solution of p-toluidine (3.98g, 37.19 m mole) in toluene (50ml) was then added and the whole was refluxed for four hours. On cooling the product separates, it was collected and recrystallised from pyridine water, forming white crystals, (yield = 30%).

2.5.16 DPFAH was used as supplied by Aldrich.

2.5.17 All other chemical reagents were used as supplied by the manufacturers.

2.6. The measurement of magnetic moments by n.m.r. spectroscopy

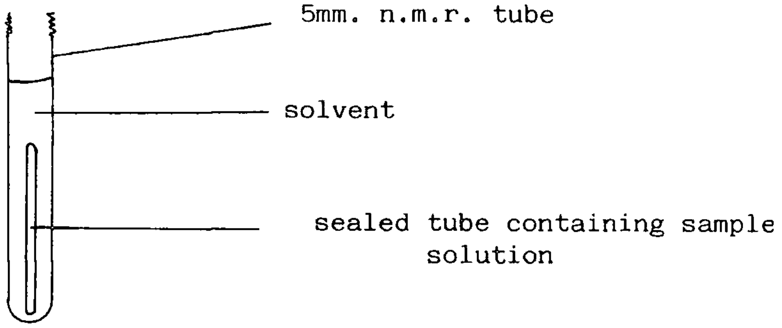
The position of a given proton resonance in a molecule is dependent upon the bulk susceptibility of the medium in which it is found. The shift of a proton resonance line of an inert substance due to the presence of a paramagnetic species is given by the theoretical expression:-

$$\frac{\delta\nu}{\nu_o} = \frac{2\pi}{3}\left(\chi_v - \chi_v^{\prime}\right) \qquad [107]$$

where $\delta\nu$ is the shift, ν_o is the applied field, χ_v is the volume susceptibility of the solution containing the paramagnetic species and $\chi_v^{\prime}$ is the volume susceptibility of the reference solution.

In order to measure $\delta\nu$ both the solution and the solvent must be contained within a single n.m.r. tube. The simplest way to do this is to put the solution in a narrow sealed tube, and insert this into a n.m.r. tube. The n.m.r. tube is then filled with solvent.

e.g.



The mass susceptibility, of the dissolved substance is given by the expression:-

$$\chi = \frac{3\,\delta\nu}{2\,\pi\nu_o\,m} + \chi_o + \chi_o\,\frac{(d_o - d_s)}{m} \qquad [108]$$

where $\delta\nu$ is the frequency separation between the two lines in Hz, ν_o the operating frequency of the spectrometer, m is the mass of substance in 1ml of solution, χ_o is the mass susceptibility of the solvent, and d_o and d_s are the densities of the solvent and solution respectively.

A problem was encountered with this method when measuring the magnetic moments of $Fe(DPAA)_3$ and $Fe(DPTAA)_3$ caused by the air sensitive nature of the complexes. The need to seal the sample tube efficiently once filled with the sample solution and removed from the glove box led to the use of melting point capillaries which were very easily sealed in a hot flame. Unfortunately the large differences in solution volumes exposed to ν_0 by this method led to large discrepancies in the signal strength from the annular solvent and the solution contained within the capillary, resulting in the solvent masking the solution signal.

The problem was solved in 2 ways:-

a) Two capillaries were used, one containing solvent, the other containing solution, the signals were now of equal strength. CCl_4 was used as a medium to support the two capillaries in the n.m.r. tube.

b) When using the Bruker spectrometer a deuterium lock is required. In this case the single capillary method was used, the annular CH_2Cl_2 solvent being replaced by a mixture of 98% CD_2Cl_2 and 2% CH_2Cl_2. Again this resulted in the signal strengths being approximately equal.

The susceptibilities measured for a given material will consist of contributions from paramagnetic and diamagnetic susceptibilities which directly oppose each other, the former being the greater. Complexes with a large number of diamagnetic atoms per paramagnetic atom (such as $Fe(DPAA)_3$ must be corrected for diamagnetism in order to obtain the true paramagnetic susceptibility. Fortunately diamagnetic susceptibilities are additive, and a fairly accurate figure is arrived at for the ligand by simply totaling the sum of diamagnetic susceptibilities [109]

From standard diamagnetic susceptibility tables it is calculated that χm (DPAA) = 120 X 10^{-6}/g atom and χm(DPTAA) = 144 X 10^{-6}/g atom.

This method was validated before use using $Cr(acac)_3$ and $Fe(acac)_3$ solutions in CH_2Cl_2.

PREFACE TO CHAPTERS 3, 4, 5, and 6

These chapters are concerned with the complexes formed between rhenium carbonyl species and amidines. For convenience the work has been divided into four separate chapters, each being primarily concerned with a separate type of rhenium-amidine bonding. These are, carbamoyls, simple two electron donor derivatives, three electron donor chelates, and finally ortho-metalated complexes. Many of the reactions produced a mixture of products of more than one class, but it was generally possilbe to isolate the major product from each reaction. The conditions reported, unless otherwise stated were those found to yield the maximum yield of the desired product.

The reader is reminded of the shorthand notation used to identify the different N,N'-symmetrically disubstituted amidines.

i.e. DPAAH = $PhN{=}C(CH)_3{-}NHPh$

DPTAAH = $(p\text{-tolyl})N{=}C(CH)_3{-}NH(p\text{-tolyl})$

DPBAH = $PhN{=}C(Ph){-}NHPh$

DPTBAH = $(p\text{-tolyl})N{=}C(Ph){-}NH(p\text{-tolyl})$

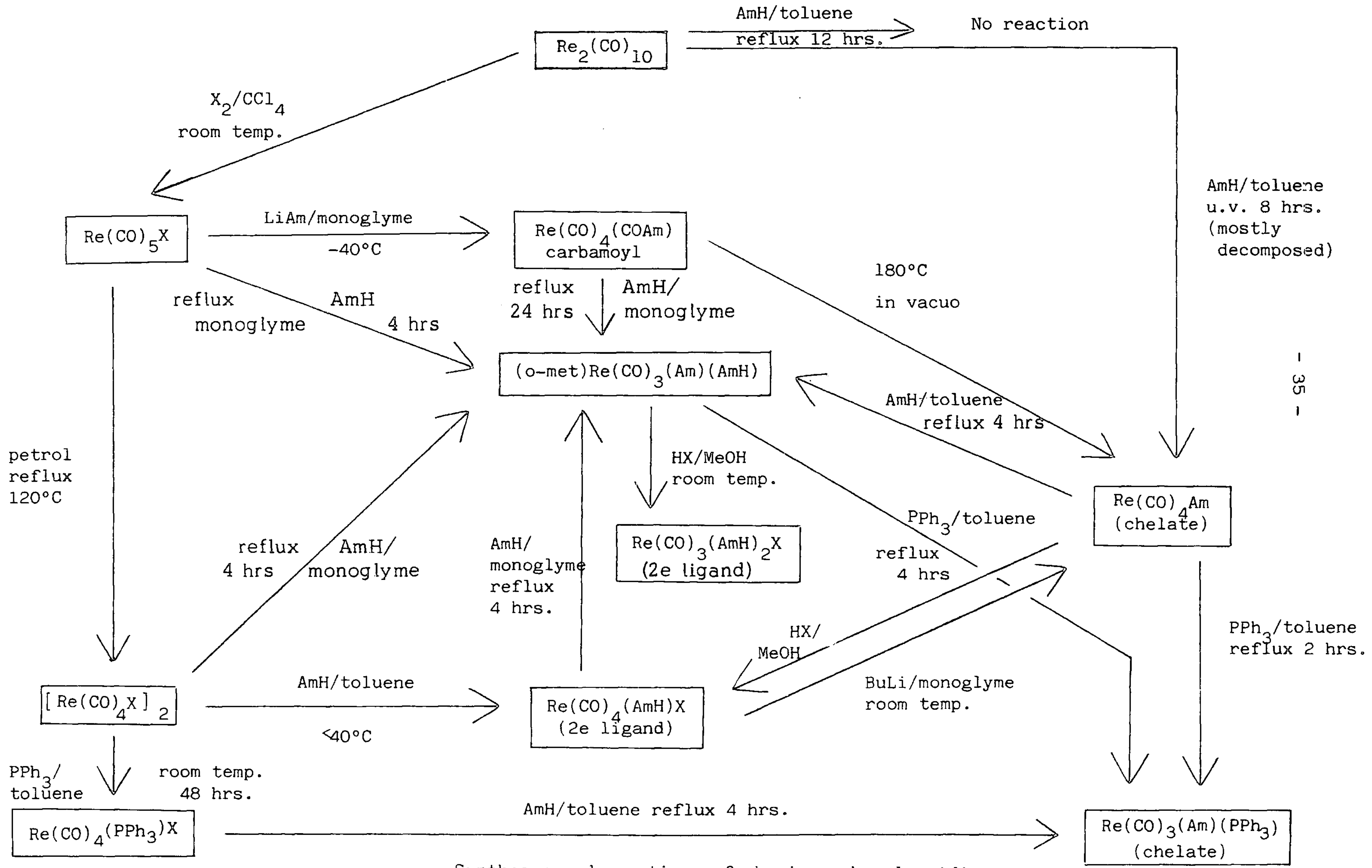
DPFAH = $PhN{=}C(H){-}NHPh$

If the final H is omitted the shorthand refers to the amidino-group

i.e. DPAA = $[PhN \overset{\text{---}}{=} C(CH_3) \overset{\text{---}}{=} NPh]^-$

AmH and Am are non specific abbreviations, they refer to the parent amidine and the amidino-group respectively.

Under suitable reaction conditions many of the rhenium-amidine products described in Chapters 3,4,5 and 6 could be converted to other types of rhenium-amidine complexes. It was thought useful to include at this stage a flow diagram showing all the rheniumcarbonyl-amidine products and the reactions and interconversions discussed in the following chapters.



Syntheses and reactions of rheniumcarbonyl-amidine complexes

CHAPTER 3

Rhenium Carbamoyl Complexes

3.1. INTRODUCTION

In this Chapter the synthesis and reactions of several new rhenium carbamoyl amidino systems are described. Kilner [40] has shown that complexes of the empirical formula $Mn(CO)_5(RN-CR'-NR)$ are produced when $Mn(CO)_5Br$ is reacted with lithio-amidines in an ether solvent. The available evidence suggests that they have the carbamoyl structure $Mn(CO)_4(CONR-CR'=NR)$ and that they decarbonylate on heating or ultra violet irradiation to produce the manganese tetracarbonyl amidino species $Mn(CO)_4(RN-CR'-NR)$. Diaryl-benzamidino and -acetamidino carbamoyl complexes of manganese have been prepared in this way. Recently diaryl formamidino carbamoyl complexes of rhenium have been made in a similar fashion [61], and further evidence gained for the carbamoyl type structure.

It is relevant to note that the carbon substituent of the amidino-group can have a profound effect on the structure adopted by the amidino group in complexes. The object of this work was to synthesise acetamidino and benzamidino carbamoyl complexes of rhenium, to compare and contrast their properties with those of the manganese and formamidino analogues, and to investigate the simple reactions of the complexes formed.

3.2. EXPERIMENTAL

3.2.1. Reaction of $Re(CO)_5Br$ with LiDPTAA

TO a solution of DPTAAH (0.293g, 1.23m mole) in ether (35ml) frozen to 77K was added n-butyllithium (1.23m mole in hexane solution) and the mixture allowed to warm to room temperature. After stirring at this temperature for 15 minutes the suspension formed was refrozen to 77K and a suspension of $Re(CO)_5Br$ (0.500g, 1.23m mole) in ether (5ml) added.

The mixture was allowed to reach room temperature where it formed a pale yellow solution. After stirring for an additional two hours a white precipitate began to form. An infra red spectrum of the solution still showed Re(CO)$_5$Br to be present, so stirring was continued for a further 48 hours, but this did not result in any further changes taking place. The white precipitate was encouraged to form by cooling to -16°C for 24 hours, then collected by filtration of the reaction mixture and dried. The solid was dissolved in CH$_2$Cl$_2$, and the solution filtered through alumina (one inch column) to remove LiBr. Crystallisation was induced by the addition of ether and cooling. The product Re(CO)$_4$(CODPTBA) was obtained as a white crystalline solid (yield 0.216g, 31%).

<u>Analyses</u>. Found:	C,44.70; N,5.15; H,3.17
Re(CO)$_4$(CODPTAA) requires	C,44.75; N,4.97; H,3.04%
<u>Melting point</u>	158°C (with decomposition).

<u>Infra red spectra</u>

ν(CO) CH$_2$Cl$_2$ 2090m 1990sh 1983vs 1948vs cm^{-1}

ν(CO) Nujol 2081m 1988vs 1980vs 1970vs 1924vs cm^{-1}

ν(CO) Carbamoyl, Nujol 1665s cm^{-1}

<u>Raman spectrum</u>

ν(CO) Solid sample, 2080s 1980vs 1927s cm^{-1}

<u>^{1}H n.m.r. spectrum</u>

(CDCl$_3$) 7.1m(8) 2.40s(6) 1.87(3) δ.

<u>Mass Spectrum</u>: The product [^{187}Re(CO)$_4$(CODPTAA)]$^+$ was found at m/e 564, with daughter ions corresponding to the stepwise loss of five carbonyl units being observed at m/e 536, 508, 480, 452 and 424. Metastable peaks were not observed. The ion of highest mass in the spectrum occured at m/e 1014 corresponding to [Re$_2$(CO)$_6$(DPTAA)$_2$]$^+$. It also showed stepwise

loss of carbonyl grups with daughter ions being recorded at m/e 958, 930, 902, 874 and 846. Three further ions were distinguishable, those of $[Re(CO)_2(DPTAA)]^+$ $[Re(CO)(DPTAA)]^+$ and $[Re(DPTAA)]^+$ at m/e 665, 637 and 609 respectively.

The above reaction was also tried in T.H.F. in an attempt to increase the yield of the pure product. After mixing the LiDPTAA and $Re(CO)_5Br$ at 77K a mixture of products was detected by infra red spectroscopy as the solution warmed to room temperature. Absorptions were recorded at:- 2095w, 2085w, 2005vs, 1992vs, 1973vs, 1948m 1902vs, 1885sh and 1862vs cm^{-1}. Heating this solution to the reflux temperature caused the formation of the orthometallate complex, $Re(CO)_3(DPTAA)(DPTAAH)$ ((CO):1994vs, 1878vs, 1860vs cm^{-1} Nujol). This product will be discussed separately in Chapter 6.

The reaction was repeated once more using an excess of LiDPTAA in T.H.F. On this occasion a red solution formed having infra red absorptions at 1930vs, 1893vs and 1862vs cm^{-1}, on prolonged stirring overnight however, absorptions corresponding to the original product $(Re(CO)_4(CODPTAA)$ reappeared at 2095w, 1975vs and 1862cs cm^{-1}. Addition of further LiDPTAA again produced the new product, and this process was found to be indefinitely repeatable. The new product could not be isolated, solutions yielding only the original carbamoyl product described above.

3.2.2. $Re(CO)_5Br$ with LiDPAA

To a solution of DPAAH (0.517g, 2.46m mole) in monoglyme (50ml) frozen to 77K was added n-butyllithium (2.46m mole in hexane solution) and the mixture allowed to warm to room temperature, where it was stirred for an additional 15 minutes. The pale yellow solution formed was refrozen to 77K, then finely powdered $Re(CO)_5Br$ (1.00g, 2.46m mole) added to it. The mixture was slowly warmed to room temperature and stirred for a further 2½ hours. An infra red spectrum of the solution at this stage appeared to show more than one product. Absorptions at 2095w, 1979vsbr, and 1948s cm^{-1} were assigned to the expected product $Re(CO)_4$(CODPAA), but further absorptions occurred at 2006s, 1902s and 1862s cm^{-1}. The solution was reduced in volume to 4ml, hexane added (1ml) and the mixture cooled in the freezer. A white precipitate developed which was separated and shown by infra red spectroscopy to be a mixture of $Re(CO)_5Br$ and a hydroscopic solid (LiBr). The mother liquor was then evaporated at reduced pressure and the residue extracted with CH_2Cl_2(10ml). The resulting solution was filtered through alumina (one inch column) and reduced in volume before ether was added. The product $Re(CO)_4$(CODPAA) crystallized as white needles (yield 0.423g, 32%). The addition of hexane to the remaining solution precipitated a mixture of the product and ortho-metallated $Re(CO)_3$(DPAA)(DPAAH) (See Chapter 6 for preparation and characterisation of this compound).

Data for $Re(CO)_4$(CODPAA)

Analyses. Found:	C,42.65;	N,5.33,	H,2.47
$Re(CO)_4$(CODPAA) required	C,42.60;	N,5.23;	H,2.43%

Melting point 123.5°C

Infra red spectra

ν(CO)	CH_2Cl_2	2096w	1990sh	1987vs	1942m	cm^{-1}
ν(CO)	Nujol	2090m	1994vs	1967vs	1932vs	cm^{-1}

ν(CO) carbamoyl Nujol; 1671s cm^{-1}

Raman spectrum

ν(CO) solid sample: 2095w, 2076s, 1979vs, 1947m 1918w cm^{-1}

'H n.m.r. spectrum

($CDCl_3$) 7.38(10), 1.86s(3) δ

Mass Spectrum: The ion of highest mass occurred at m/e 536 corresponding to the parent ion $[^{187}Re(CO)_4(CODPAA)]^+$. Fragmentation by the stepwise loss of 5 carbonyl groups was indicated by daughter ions at m/e 508, 480,452, 424 and 396. Evidence for the early fragmentation of the amidine group was not observed, neither were metastable peaks.

3.2.3. Reaction of $Re(CO)_5Br$ with LiDPBA

To a solution of DPBAH(0.669g, 2.46m mole) in monoglyme (50ml) frozen to 77K was added n-butyllithium (2.46m mole in hexane solution) and the mixture allowed to warm to room temperature, where it was stirred for an additional 15 minutes. The yellow solution formed was refrozen to 77K, then finely powdered $Re(CO)_5Br$ (1.00g, 2.46m mole) added to it. The mixture was slowly warmed to room temperature and stirred for a further 2½ hours. An infra red spectrum showed new carbonyl absorptions at 2096w, 1995sh, 1980vs, 1950m, 1896m and 1871m cm^{-1} indicating that a mixture of products had been produced. The solution was reduced in volume to ca. 10ml by evaporation at reduced pressure causing the precipitation of a cream solid. The solid was collected by filtration, dissolved in CH_2Cl_2 (10ml) and the resulting soution filtered through alumina (one inch column). After evaporating to 4ml, ether (2ml) was added and the product $Re(CO)_4$(CODPBA) precipitated by cooling to -16°C (yield 0.268g, 18.3%). When further reduced in volume the remaining mother liquor produced a yellow gum. An infra red spectrum of this gum showed it to contain $Re(CO)_5Br$, $Re(CO)_4$(CODPBA), (o-met) $Re(CO)_3$(DPBA)(DPBAH) and DPBAH.

Data for $Re(CO)_4$(CODPBA)

Analyses. Found:	C,48.00; N,4.68; H,2.54
$Re(CO)_4$(CODPBA) requires	C,48.22; N,4.68; H,2.51%
Melting point	123°C (with decomposition)

Infra-red spectra

(CO)	CH_2Cl_2	2098m	1997sh	1987vs	1947s cm^{-1}		
(CO)	Nujol	2096m	2022vs	1988vs	1969vs	1937vs	1913vs cm^{-1}

(CO) carbamoyl, Nujol: 1655 cm^{-1}

Raman spectrum

(CO) solid sample, 2095vs 1999vs 199ovs 1946vs 1912vs cm^{-1}

Mass Spectrum: The ion at highest mass occurred at m/e 570 corresponding not to the parent ion but $[^{187}Re(CO)_4(DPBA)]^+$. Fragmentation occurred by the stepwise loss of 4 carbonyl groups, with daughter ions at 542,514,485 and 458. Metastable peaks were not observed.

3.2.4. Reaction of $Re(CO)_5Br$ with LiDPTBA

To a solution of DPTBAH (0.369g, 1.23m mole) in monoglyme (50ml) frozen to 77K was added n-butyllithium (1.23m mole in hexane solution). The mixture was slowly warmed to room temperature and stirred for an additional 15 minutes. The yellow solution formed was then refrozen to 77K and finely powdered $Re(CO)_5Br$ (0.500g, 0.23m mole) added to it. As the monoglyme melted an intense yellow soltuion was formed; this was stirred at room temperature for 1½ hours. The solvent was then removed by evaporation at reduced pressure. The residue was extracted with CH_2Cl_2 (10ml), filtered through alumina (one inch column) and then reduced to ca. 4ml by evaporation. Addition of hexane (2ml) and cooling to -16°C caused precipitation of the product $Re(CO)_4$(CODPTBA) as a white powder (yield 0.167, 21.7%).

Analyses. Found:	C,49.94: N,4.49; H,3.10
$Re(CO)_4$(CODPTBA) requires	C,49.91: N,4.48; H,3.06%

Infra red spectra

ν(CO)	CH_2Cl_2	2093w	2000sh	1988vs	1948s	cm^{-1}		
ν(CO)	Nujol	2093m	2008sh	1989vs	1973vs	1938vs	1921vs	cm^{-1}

ν(CO) carbamoyl, Nujol: 1650s cm^{-1}

Raman spectrum was not obtained as the sample fluoresced.

Mass Spectrum: The parent ion $[^{187}Re(CO)_4(CODPTBA)]^+$ at m/e 626 was not detected. $[^{187}RE(CO)_4(DPTBA)]^+$ appeared at m/e 598 followed by daughter ions at m/e 570, 542, 514 and 486 corresponding to the stepwise loss of four carbonyl groups. The highest mass recorded in the spectrum occurred at m/e 1138 corresponding to $[Re_2(CO)_6(DPTBA)_2]^+$ from which the stepwise loss of six carbonyl groups to $[Re_2(DPTBA)_2]^+$ at m/e 970 was clearly observed. Other species detected were $[^{187}Re((DPTBA)(DPTBAH)(CO)_3]^+$ at m/e 869, and ions corresponding to the stepwise loss of three carbonyl groups to $[^{187}Re(DPTBA)(DPTBAH)]^+$ at m/e 785.

3.2.5 Reactions of $Re(CO)_5Cl$ with Lithioamidines

$Re(CO)_5Cl$ was used in place of the bromide in analogous reactions with LiDPAA, LiDPTAA, LiDPBA and LiDPTBA. The products $Re(CO)_4(CONR-CR'=NR)$ were similarly formed but yields were not improved.

3.2.6. Reaction of $Re(CO)_5Br$ with LiDPFA

The reaction procedure was identical to 3.2.3. The product $Re(CO)_4$ (CODPFA) forms white crystals from a CH_2Cl_2/ether solution (yield 51%).

Analyses. Found: C,40.90; N,5.61; H,2.21

$Re(CO)_4$(CODPFA) requires C,41.44; N,5.73; H,2.13%

Infra red spectra

ν(CO)	CH_2Cl_2	2098m	1996sh	1990vs	1948s	cm^{-1}
ν(CO)	Nujol	2108w	2000sh	1977vs	1940vs	cm^{-1}
ν(CO)	hexane	2097w	1996m	1987vs	1962s	cm^{-1}
ν(CO)	carbamoyl	hexane:	1700vw	cm^{-1}		
ν(CO)	carbamoyl	Nujol :	1675s	cm^{-1}		

3.2.7. Decarbonylation reactions of $Re(CO)_4$(CODPTAA)

i) $Re(CO)_4$(CODPTAA) (0.042g) was heated to 155°C at a pressure of 0.01 torr for one hour. The sample appeared unchanged, and an infra red spectrum confirmed this. The temperature was then gradually increased to 180°C, causing the sample to gradually turn yellow, and a yellow deposit to form on a cold finger (6°C) inserted in the flask. The sublimate was identified by infra red spectroscopy as $Re(CO)_4$(DPTAA) (ν(CO) absorptions at 2101w, 1991vs, 1975vs, 1938s, 1915w-msh cm^{-1} Nujol)

Extraneous ν(CO) absorptions at 2084s and 1928s cm^{-1} were also observed.

ii) $Re(CO)_4(CODPTAA)$ (0.078g) was dissolved in T.H.F. (5ml) forming a colourless solution which was refluxed for four hours without any change in the (CO) adsorptions being detected. The T.H.F. was then removed "in vacuo", replaced by monoglyme (5ml), and refluxed for a further two hours. Again no change could be detected in the infra red spectrum. The solution was then transferred to a silica flask and irradiated with ultra violet light for 2½ hours forming a brown solution. Infra-red spectroscopy showed much decomposition to have occurred, and the formation of at least one unidentified carbonyl species (ν(CO) absorptions 2008m, 1994m, 1912m and 1890m cm^{-1}). A solid product was not obtained due to gum formation and the small scale of the reaction.

3.2.8. Reaction of $Re(CO)_4(CODPTAA)$ with DPTAAH

To a solution of $Re(CO)_4(CODPTAA)$ (0.016g, 0.109m mole) in monoglyme (10ml) was added DPTAAH (0.026g., 0.109m mole) and the colourless solution refluxed for two hours, no change in the infra red spectrum being observed. The solution was then refluxed for a total of 33 hours, by which time it was apparent that (o-met)$Re(CO)_3$(DPTAA)(DPTAAH) was slowly being formed (ν(CO) absorptions at 2008vs, 1892vs, and 1885vs cm^{-1}. (See Chapter 6 for a description of this complex). To speed up the reaction the solution was transferred to a Carius tube and heated "in vacuo" to 140°C for 15 hours. Unfortunately this caused decomposition of both the original carbonyl species and the ortho-metallated product.

3.2.9. Reaction of $Re(CO)_4(CODPTAA)$ with PPh_3

To a solution of $Re(CO)_4$(CODPTAA) (0.065g, 0.115m mole) in monoglyme (10ml) was added PPh_3 (0.030g, 0.115m mole) and the solution refluxed for 4 hours. New ν(CO) absorptions at 2022vs, 1917vs and 1898vs cm^{-1} had appeared after this time, but the reaction was not judged to be complete until refluxing had continued for a total of 27 hours. The solution was then reduced in volume by evaporation causing precipitation of the product Re(CO)$_3$(DPTAA)(PPh$_3$) (yield 80%).

Analyses. Found: C,57.76: N,4.16: H,3.63

Re(CO)$_3$(DPTAA)(PPh$_3$) requires C,57.46; N,4.66; H,3.74%

Infra red spectrum

ν(CO)	CH_2Cl_2	2018vs	1914vs	1888vs	cm^{-1}
ν(CO)	Nujol	2010vs	1907vs	1883vs	cm^{-1}

3.2.10 Reactions of Re(CO)$_4$(CODPAA), Re(CO)$_4$(CODPBA) and Re(CO)$_4$(COTBA)

i) These carbamoyl complexes were also decarbonylated (see 3.2.7i) when heated strongly under vacuum. Decarbonylation was not observed in solution even after prolonged refluxing in monoglyme.

ii) Re(CO)$_3$(PPh$_3$)(Am) complexes were formed in similar reactions to 3.2.9. when Re(CO)$_4$(COAm) complexes are refluxed in monoglyme with an equimolar amount of PPh$_3$. These complexes are described in more detail in Chapter 5.

iii) When refluxed in monoglyme for long periods (24 hours or more) with the parent amidine all the carbamoyls complexes showed signs in the infra red spectrum of the ortho-metallated species (o-met)Re(CO)$_3$(Am)(AmH) being produced (see 3.2.8.).

3.3. DISCUSSION

$Re(CO)_5X$ (X=Cl,Br) complexes were found to form carbamoyl complexes of the general formula $Re(CO)_4(COAm)$ when reacted with lithiumdiarylbenzamidines and lithiumdiarylacetamidines in monoglyme or ether solutions. These products are white, indefinitely air stable solids which decompose over a period of months in solutions exposed to air. The yield of product isolated was low, 20-30%, although the reactions themselves were more efficient, (an estimated 60% from solution infra red of the reaction mixture). Considerable difficulty was encountered in increasing the recovered yield due to the presence of the starting material $Re(CO)_5X$, amidine, and secondary products such as (o-met) $Re(CO)_3(Am)(AmH)$.

Several methods of product isolation were tried, including chromatography (in a wide variety and combination of solvents), sublimation and fractional crystallization. A good separation could not be achieved between the product and the parent amidine by chromatography, and sublimation was only successful for $Re(CO)_4(CODPTAA)$, where the impurities sublimed. The other carbamoyl complexes melted at approximately the temperature that the parent amidine sublimed (ca. 125°C), and the resulting melt decomposed with the formation of $Re(CO)_4(Am)$ and (o-met)$Re(CO)_3(Am)(AmH)$. Fractional crystallization from a CH_2Cl_2 solution proved to be the most reliable way of obtaining the pure crystalline product. Attempts to increase the yield by forcing further precipitation resulted in samples contaminated with $Re(CO)_5X$ and (o-met)$Re(CO)_3(Am)(AmH)$.

The reaction of lithiumdiphenylformamidine with $Re(CO)_5Br$ in monoglyme produced a greater yield, 50% being collected. This is comparable to the previously reported method [61] using $Re(CO)_5Cl$, where the reaction took place in ether and the product was extracted using boiling hexane. It is assumed that the large difference in solubility of the parent formamidine and the carbamoyl product leading to easier separation accounts for the increased yield.

The complexes are assigned the carbamoyl structure $Re(CO)_4(COAm)$ (Fig. 3.3.1.) on the basis of the infra red and ^{13}C n.m.r. data. Unfortunately a crystal structure was not performed on any of the

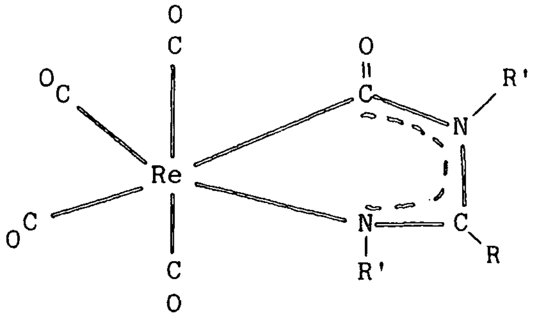


Fig. 3.3.1.

complexes, but this should be possible as the compounds easily form microcrystalline solids.

The general formulation of the complexes as $Re(CO)_5(Am)$ is confirmed by elemental analysis, and mass spectroscopy also provides evidence for the $Re(CO)_5(Am)$ moiety for the acetamidino complexes. For the benzamidino complexes however, the ion of highest m/e value appears to be $[^{187}Re(CO)_4(Am)]^+$; this is possibly due to thermal decomposition of the sample material and selective volatility of the product molecules. None of the samples have a fragment corresponding to AmCO, indicating that the carbamoyl C-N bond is broken before the fragmentation of the molecule There is no evidnece of a Re(CO)x (x=1-5) species (indicating that the amidine is not easily cleaved from the rhenium), nor of any metastable peaks.

The spectroscopic evidence for the carbamoyl type structure is reviewed below:-

Infra red spectra. In solution the complexes $Re(CO)_4(COAm)$ show four terminal metal carbonyl stretching frequencies in the 2100-1940 cm^{-1} region of the spectrum. These all have the pattern (in decreasing cm^{-1})

w, s, vs, vs, which is typical of a cis substituted octahedral tetracarbonyl species. A monodentate amidino pentacarbonyl species would be expected to show a carbonyl pattern of vw, vs, vw, s (i.e. similar to the precursor Re(CO)$_5$Br). The absence of any absorption in the 3400-3000 cm^{-1} region of the Nujol spectrum indicates the lack of an N-H stretch, and an amidino species can therefore be assumed to be present.

The differences in the infra red spectra of the complexes and the parent amidine are shown in table 3.3.1. below. All absorptions are due to the various modes of the ν(-C=ONR-CR'=NR) vibrations, the most significant of them being the band at ca. 1650-1670 cm^{-1}, which is assigned to the ν(CO,carbamoyl) stretch, and the band at ca. 1570-1580 cm^{-1} which is similar to that observed for delocalised chelate systems [62] . This lower frequency band is assigned the νas(N-C-N) stretch, and is approximately 40-50 cm^{-1} lower than the similar vibration of the parent

Table 3.3.1. A Comparison of the i.r. absorptions in the region 1670-1200 cm^{-1} of the carbamoyl complexes Re(CO)$_4$(COAm) and their parent amidines

Amidine used	Re(CO)$_4$(COAm) ν(CONR-CR'=NR)*			parent amidine ν(NR=CR'-NHR)*			
DPTAAH	1665s	1583s	1500ms	1630s	1587s		1522ms
	1268s	1206vw		1511m	1320w	1272w	1219w
DPAAH	1671s	1578s	1488ms	1630s	1586s	1535m	1490w
	1424m	1270s	1210w	1443m	1332w	1320wm	
DPTBAH	1650s	1574s	1502w	1616s	1588s	1522m	1500m
	1400ms	1331w	1282m	1400m	1333ms	1226w	
DPBAH	1655s	1569s	1491m	1624s	1585w	1528s	1482m
	1400m	1282s		1440m	1328m	1220w	

*cm^{-1} Nujol

amidine. As for the delocalised chelate complexes (Chapter 5), this reduction in frequency can be viewed as either due to back donation to the π^* antibonding orbitals of the formally imino nitrogen, or to the perturbation of the vibration caused by bonding to the heavy rhenium atom.

Raman Spectra. In general the Raman spectra compliments that of the infra red. The new bands (w.r.t. the parent amidine) are shown in Table 3.3.2. The weak band at about 1660-1670 cm^{-1} is assigned to the carbamoyl $\nu(C=O)$ stretch, and the medium intensity band at about 1270-1286 cm^{-1} (which also appears in the infra-red spectra) is thought to be characteristic of a delocalised chelating ligand[62].

Table 3.3.2. Raman active bonds observed for $Re(CO)_4(COAm)$ not present in the free amidine

Complex	new Raman bonds* cm^{-1}	
$Re(CO)_4$(CODPTAA)	1670w	1274m
$Re(CO)_4$(CODPAA)	1673w	1275m
$Re(CO)_4$(CODPTBA)	1663w	1286m
$Re(CO)_4$(CODPBA)	1661w	1286m

* solid sample

^{1}H n.m.r. spectra. Unfortunately the proton n.m.r. of the para-tolyl derivatives showed no differences in the para-tolyl methyl signals. The possibility of a rapid exchange process occurring was investigated by cooling a $Re(CO)_4$(CODPTAA) solution to -60°C and recording its spectrum. No change was observed, and it is concluded that the molecule is static, with the para-tolyl methyl groups being too far removed from the unsymmetrical bonding of the amidino nitrogen atoms to be sensitive to the differing bonding situations. This was the tentative conclusion reached for the anlaogous $Mn(CO)_4$(COAm) complexes[40], and the ^{13}C n.m.r.

data (below) would seem to confirm this.

<u>^{13}C n.m.r. spectra</u> Due to the greater chemical shifts involved with ^{13}C n.m.r. spectroscopy the different environments of the aryl groups in $Re(CO)_4$(CODPA) were easily detected by ^{13}C n.m.r. The data for this complex is given in Fig. 3.3.2. (shifts in p.p.m. relative to T.M.S.). Unfortunately sufficient pure samples of the other carbamoyl species were not available, so only the spectrum of $Re(CO)_4$(CODPAA) was recorded. It is assumed that the DPTAA, DPBA and DPTBA derivatives would show similar ^{13}C n.m.r. spectra on the basis of their almost identical infra red spectra.

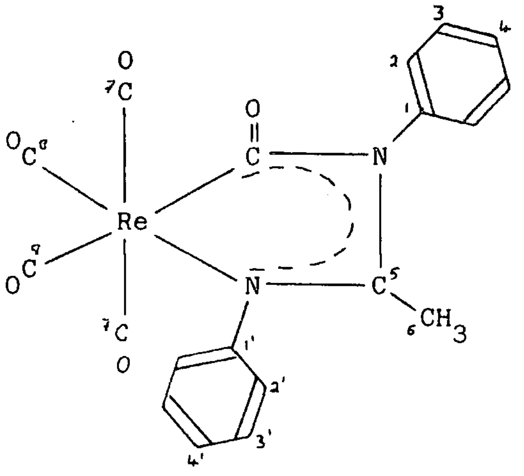


Fig. 3.3.2.

1,1' = 152.61 138.79
2,2' = 123.38 122.77
3,3' = 129.53 129.79
4,4' = 126.54 124.20
5 = 167.60
6 = 16.84
7 = 193.35
8,9 = 188.80 186.28
10 = 176.74

The above spectrum is only consistent with a carbamoyl type of bonding, as a monodentate $Re(CO)_5$(Am) species (Fig. 3.3.3.) would be expected to show only 3 types of carbonyl carbon nuclei in the ratio 2:2:1.

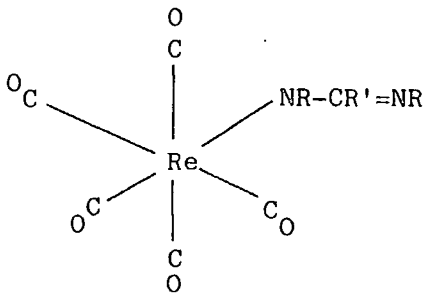


Fig. 3.3.3.

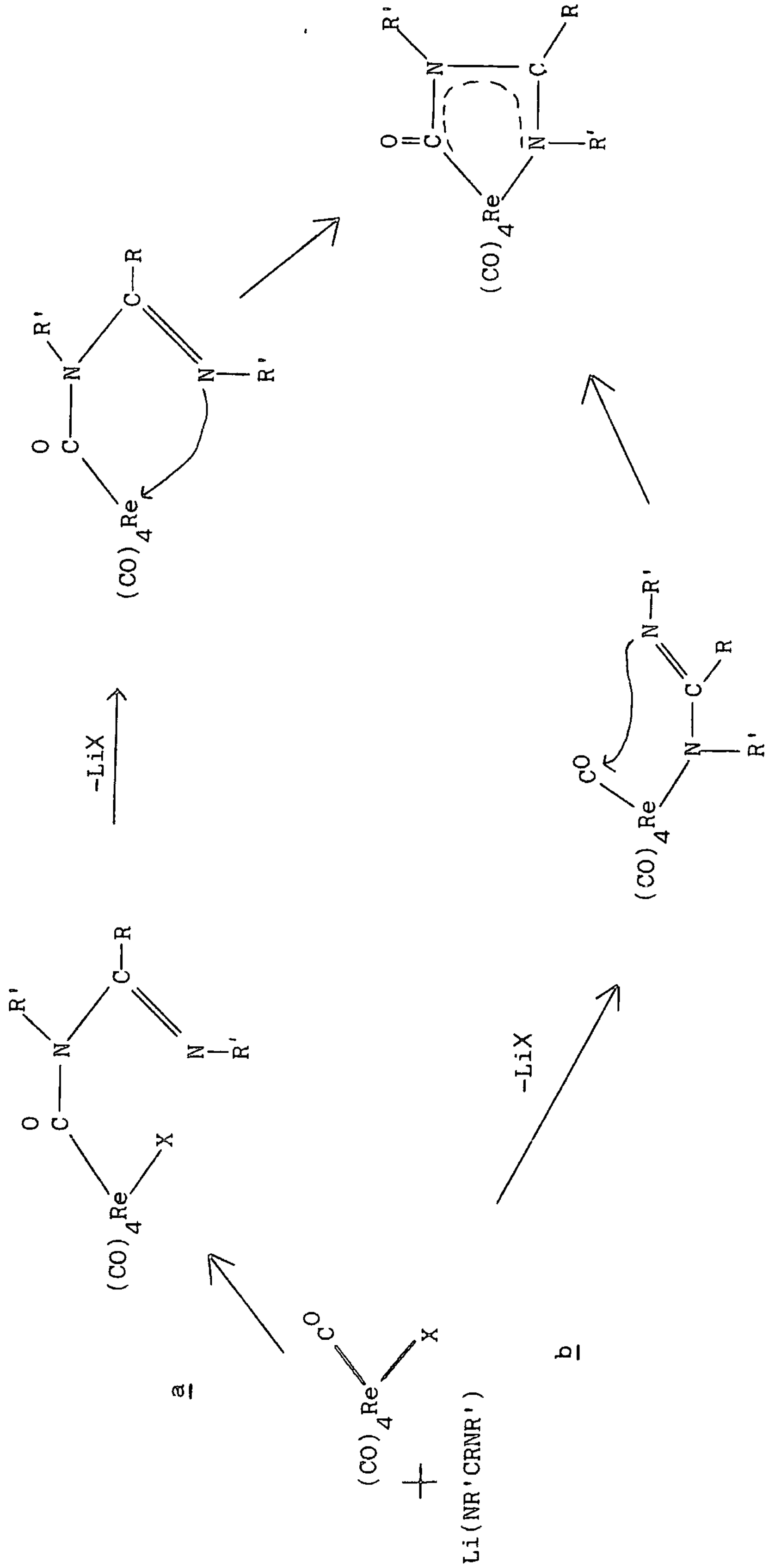
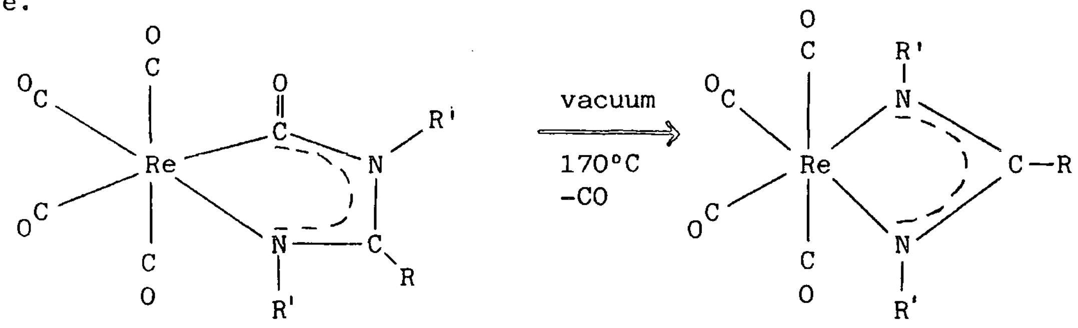


Fig. 3.3.4

The initial formation of carbamoyl complexes can take place via one of two routes. These are:- a) nucleophilic attack by the amidino ion at the carbon of the carbonyl group, followed by elimination of lithium halide, and the now vacant coordination site being taken up by the imino nitrogen; b) metathetical elimination of lithium halide from the complex, followed by nucleophilic attack of the imino nitrogen on an adjacent carbonyl group. These pathways are illustrated in Fig. 3.3.4. Route(a)is favoured, as it is known that other carbamoyls are formed by initial attack, by for example an amine, at a carbonyl group [110].

In common with the $Mn(CO)_4(COAM)$ complexes [40] (Am=DPAA,DPBA,DPTAA, DPTBA) complexes and the $Re(CO)_4(CONR\text{-}C\underline{H}\text{-}NR)$ complexes [61] the $Re(CO)_4(COAm)$ complexes also undergo decarbonylation to the tetracarbonyl chelate type complex on heating. Unlike the manganese complexes however this only

i.e.

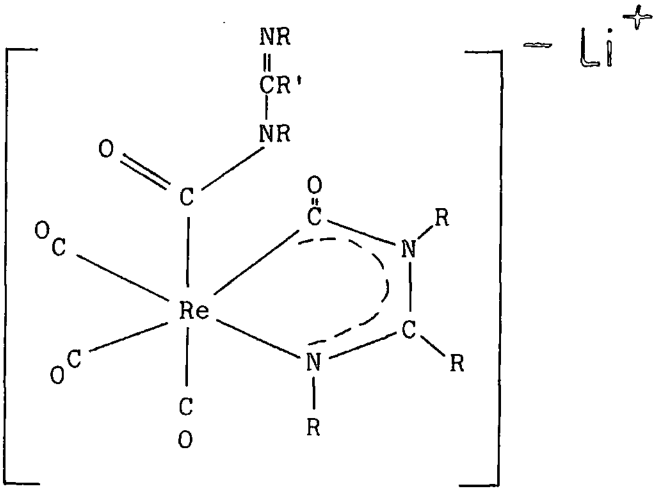


took place in the solid state, and was not achieved by heating in solution, perhaps because the reflux temperature of the solvent (monoglyme) was too low. Decarbonylation was also achieved under prolonged u.v. irradiation, this produced a mixture of products, probably $Re(CO)_4Am$ and $(o\text{-}met)Re(CO)_3(Am)(AmH)$ (See Chapter 6), and a good deal of decomposition.

The slow reaction of $Re(CO)_4(CODPAA)$with PPh_3 appears to be straightforward; a carbonyl group is displaced by PPH_3 and the amidino group becomes bidentate chelate. In view of the reluctance of carbamoyls to decarbonylate in refluxing monoglyme it is probable that the reaction proceeds via metathetical substitution of a carbonyl group, the new carbamoyl product then decarbonylates further forming the chelated amidino product Re(CO)$_3$(PPh$_3$)(Am). e.g. Re(CO)$_4$(COAm)+PPh$_3$ $\xrightarrow[-CO]{90°C}$ Re(CO)$_3$(PPh$_3$)(COAm) $\xrightarrow[-CO]{90°C}$ Re(CO)$_3$(PPh$_3$)(Am).

The formation of the (o-met) Re(CO)$_3$(Am)(AmH) complexes when Re(CO)$_4$(COAm) complexes are refluxed with the parent amidine, AmH, is unusual as one of the amidines ortho-metallates. It is also a slow reaction and probably proceeds initially by metathetical substitution of a carbonyl by AmH. A possible mechanism for this reaction is discussed in Chapter 6, which deals exclusively with the ortho-metallated products.

The reaction of excess LiDPTAA with Re(CO)$_5$Br gave a red solution, with ν(CO) absorptions in T.H.F. at 1903s, 1893s and 1862s cm^{-1}. The low values of ν(CO) suggest that an anionic species is formed. The complex partially reverts to Re(CO)$_4$(CODPTAA) when stirred overnight suggesting that the complex has not lost its carbonyl groups. This evidence is consistent with the formation of a complex of the type Li$^+$[Re(CO)$_3$(CODPTAA)$_2$]$^-$, having one amidino group in a ring (c.f. Re(CO)$_4$(CODPTAA)), with the other forming a unidentate carbamoyl group (Fig. 3.3. 5)



(Fig. 3.3.5.)

The slow reverse reaction was probably caused by consumption of the lithioamidine through air or moisture diffusing into the apparatus, or through reaction with the solvent.

e.g.

$$\mathrm{Re(CO)_5Br + LiAm \longrightarrow Re(CO)_4(COAm) + LiBr}$$

air stable soln.

$$\mathrm{Re(CO)_4(COAm) \xrightleftharpoons[{[O]}]{LiAm} [Re(CO)_3(COAm)_2]^- Li^+}$$

air sensitive soln.

The presence of $Re_2(CO)_6(Am)_2$ and (o-met)$Re(CO)_3(Am)(AmH)$ in the mass spectrum of the DPTAA and DPTBA carbamoyl derivatives was possibly due to small fractions of stable impurities in the samples, or to thermal decomposition products in the heated source. The ortho-metallated complexes have been made independently and are described in Chapter 6, the $Re_2(CO)_6(Am)_2$ complexes have not however been synthesised. If the ion of highest m/e value represents the parent ion, the most likely structure for this complex is one involving two amidino bridges, and a Re=Re double bond (Fig. 3.3.6.)

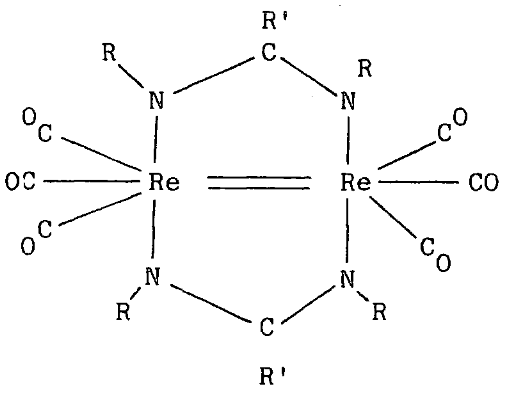


Fig. 3.3.6.

CHAPTER 4

Rhenium Carbonyl Complexes Containing a Monodentate Amidine Ligand

4.1. INTRODUCTION

As part of a systematic survey of the reactions between amidines and rhenium carbonyl complexes it was essential to explore the simple two electron ligand properties of the amidines.

The capacity of amidines to act as simple two electron donor ligands with transition metals was first demonstrated by the formation of the Pd and Pt complexes $(NH_2CRHN)_2MCl_2$ by the reaction of $(NH_3)_2MCl_2$ with RCN[115]. More recent work suggests that the complexes $Mo(CO)_5(AmH)$ and $Mo(CO)_4(AmH)_2$ are formed as intermediates in the photochemical reaction of $Mo(CO)_6$ with DPFAH, which gives $Mo_2(DPFA)_4$ as the final product [55].

The reaction of $Re(CO)_5X$ (X=Cl,Br) with an amine NH_2R (R=Me,Et etc) produces the disubstituted product $Re(CO)_3(NH_2R)_2X$ [98], this is in contrast to the reaction of $Mn(CO)_5X$ (X=Cl,Br) with NH_2R (R=Me,Et etc) where a carbamoyl product $Mn(CO)_4(CONHR)$ [99] is formed.

Rhenium carbonyl complexes containing a two electron donor amidine ligand appeared to be produced as secondary products in the reactions designed to produce chelated amidino systems. A complete study of these complexes was therefore initiated in order to fully characterise these complexes. It was hoped that these complexes could provide valuble information on the nature of the simple two electron amidine —— rhenium bond, and also provide an alternative precursor for other rhenium amidine systems.

4.2. EXPERIMENTAL

4.2.1. Reaction of $[Re(CO)_4Br]_2$ with DPTAAH

$[Re(CO)_4Br]_2$ (0.500g, 0.661m mole) was suspended in toluene (40ml) and to it added DPTAAH (0.315g, 1.322m mole). The resulting mixture was stirred at 38-40°C for 16 hours by which time all trace of the ν(CO) dimer had dissappeared from the i.r. spectrum. The pale yellow solution was reduced in volume (to 10ml) by vacuum, and the product precipitated by the addition of hexane (5ml) and cooling. The product an air stable white crystalline solid was washed with hexane, and dryed (yield 0.67g, 83%).

Analyses. Found: C,39.20; N,4.50: H,3.00; Br,12.80:

$Re(CO)_4$(DPTAAH)Br requires C,38.95; N,4.54; H,2.92; Br,12.96%

Melting point 113°C (with decomposition).

'H n.m.r. Spectrum

$CDCl_3$ (δ) 7.10m (8) 2.38, 2.35(6), 1.77s(3).

Mass spectrum: The parent ion was not observed; peaks were recorded at m/e 537, 509, 481, 453, and 425 corresponding to $[^{187}Re(CO)_4(DPTAAH]^+$ and the subsequent stepwise loss of 4 carbonyl groups. The highest intensity peak in the isotopic distribution pattern for $[^{187}Re\ Br(CO)_4]^+$ was observed at m/e 378, and peaks corresponding to the loss of 1, 2 and 4 carbonyls were also observed at m/e 350,322 and 266.

4.2.2. Reaction of $[Re(CO)_4Br]_2$ with DPAAH

Reaction procedure and conditions were identical to 4.2.1. The product is white crystalline solid (yield 80%).

Analyses. Found: C,36.45; N,4.70; H,2.40; Br,13.44:

$Re(CO)_4$(DPAAH)Br requires C,36.72; N 4.76; H,2.28; Br, 13.5%

Melting point 115°C (with decomposition).

'H n.m.r. Spectrum

$CDCl_3$ (δ) 7.27m(10) 1.83s(3).

Mass Spectrum: The parent ion was not observed; peaks were recorded at m/e 509, 481, 453, 425 and 397 corresponding to $[^{187}Re(CO)_4(DPAAH)]^+$ and the stepwise loss of 4 carbonyl groups.

4.2.3. Reaction of $[Re(CO)_4Br]_2$ with DPTBAH

Reaction procedure and conditions were identical to 4.2.1. The product was a white crystalline solid (yield 70%).

Analyses. Found: C,143.94; N,4.01; H,2.98; Br,12.95:

$Re(CO)_4(DPTBAH)Br$ requires C,44.24; N,4.13; H,2.95; Br,11.78%

Melting point 112°C (with decomposition).

'H n.m.r. Spectrum

$CDCl_3(\delta)$ 7.03s 6.83s 2.19s.

Mass Spectrum: The parent ion was not observed; peaks were recorded at m/e 599, 571, 543, 515 and 487 corresponding to $[^{187}Re(CO)_4(DPTBAH)]^+$ and the subsequent stepwise loss of 4 carbonyl groups.

4.2.4. Reaction of $[Re(CO)_4Br]_2$ with DPBAH

Reaction procedure and conditions were identical to 4.2.1. The product was a white crystalline solid (yield 70%).

Analyses. Found: C,42.31; N,4.15; H,2.56; Br,12.40:

$Re(CO)_4(DPBAH)Br$ requires C,42.48; N,4.31; H,2.45; Br,12.29%

Melting point 124°C (with decomposition).

Mass Spectrum: The parent ion was not observed; peaks were recorded at m/e 571, 543, 515, 487 and 459 corresponding to $[^{187}Re(CO)_4(DPBAH)]^+$ and the subsequent stepwise loss of 4 carbonyl groups.

4.2.5. Reaction of $[Re(CO)_4Br]_2$ with DPFAH

Reaction procedure and conditions were identical to 4.2.1. The product was a white powder (yield 60%).

Analyses. Found: C,34.49; N,4.52; H,1.93; Br, 14.16:

$Re(CO)_4(DPFAH)Br$ requires C,35.55; N,4.88; H,2.09; Br,13.91%

Melting Point 125°C (with decomposition).

Mass Spectrum: The parent ion was not observed; peaks were recorded at m/e 495, 467, 439, 411 and 383 corresponding to $[^{187}Re(CO)_4(DPFAH)]^+$ and the subsequent loss of 4 carbonyl groups.

4.2.6. Reaction of $[Re(CO)_4Br]_2$ with ptolylN(Me)-C(Me)=Nptolyl(=DPTAAMe)

$[Re(CO)_4Br]_2$ (0.500g, 0.661m mole) was suspended in monoglyme (40ml), and to it was added DPTAAMe (0.333g, 1.322m mole). The mixture was stirred at 38°C for 120 hours giving a pale yellow solution, and a trace of white precipitate. The solution was filtered, reduced in volume, hexane added and placed in the freezer. An i.r. spectrum of the white precipitate showed it to be unreacted dimer. The mother liquor produced a white crystalline precipitate and a yellow gum, the white crystals were separated and recrystallized from a toluene/hexane solution. The yellow gum was shown to be predominantly DPTAAMe (yield of white crystals 0.202g, 24%).

Analyses. Found: C,39.59; N, 4.42; H,3.35; Br 12.75:

$Re(CO)_4(DPTAAMe)Br$ requires C,39.99; N,4.44; H,3.17; Br,12.68%

Melting point 90°C (with decomposition).

^{1}H n.m.r. Spectrum

$CDCl_3$ (δ) 7.47s(6) 7.37s(2) 3.90s(3) 2.47s(3) 2.41s(3) 2.07s(3)

Mass Spectrum: The peak at highest mass assignable to the sample occured at m/e 495 corresponding to $[^{187}Re(DPTAAMe)(CO)_2]^+$, the stepwise loss of two carbonyls was noted, with peaks at m/e 467 and 439. The sample was seen to be contaminated with $[Re(CO)_3Br]_4$ which gave a very strong and distinct mass spectrum.

4.2.7. Reaction of $[Re(CO)_4Cl]_2$ with DPTAAH

$Re(CO)_4Cl_2$ (0,500g, 0.749m mole) wassuspended in toluene and to it added DPTAAH (0.356g, 1.498m mole). The mixture was then stirred at 55°C for 23 hours, giving a pale yellow solution and a faint white precipitate. This precipitate was shown by i.r. to be unreacted dimer. The solution was filtered, reduced in volume by evaporation to about 5ml and cooled to -10°C. A white precipitate was produced, which was collected by removing the solution by syringe, washing with hexane and pumping dry (yield 0.471g, 55%).

Analyses. Found: C,41.69; N,4.74; H,2.74; Br, 6.23:

$Re(CO)_4(DPTAAH)Br$ requires C,41.98; N,4.89: H,2.97; Br, 6.21%

Melting point 112°C (with decomposition).

'H n.m.r. Spectrum

$CDCl_3$ (δ) 7.12m(8) , 2.38 + 2.36(6), 1.76s(3).

Mass Spectrum: The parent ion was not observed: peaks were recorded at m/e 537, 509, 481, 453 and 425 corresponding to $[^{187}Re(DPTAAH)(CO)_4]$ and the subsequent loss of 4 carbonyl groups.

4.2.8. Reaction of $[Re(CO)_4Cl]_2$ with DPAAH

Reaction procedure and conditions were identical to 4.2.7. The product is a white powder (yield 53%).

Analyses. Found C,40.12; N,5.18; H,2.60; Cl,6.58:

$Re(DPAAH)(CO)_4Br$ requires C,39.70; N,5.14; Cl,6.53%

Melting point 110°C (with decomposition).

'H n.m.r Spectrum

$CDCl_3$ (δ) 7.23m(10) 1.80s(3)

Mass Spectrum: The parent ion was not observed; peaks at m/e 509, 481, 453, 425, and 397 were recorded due to $[^{187}Re(CO)_4DPAAH]^+$ and the subsequent loss of 4 carbonyl groups. Metastable peaks were recorded at m/e 455 and 427 arrising from the $[^{187}Re(CO)_4(DPAA)]^+ \longrightarrow [^{187}Re(CO)_3(DPAAH)]^+$ and $[^{187}Re(CO)_3(DPAAH)]^+ \longrightarrow [^{187}Re(CO)_2(DPAAH)]^+$ fragmentations.

4.2.9. Reaction of $[Re(CO)_4Cl]_2$ with DPTBAH

Reaction conditions and procedure were identical to 4.2.7. The product is a white powder (yield 50%).

Analyses. Found: C,47.60; N,4.48; H, 3.80; Cl,5.64:

$Re(CO)_4(DPTBAH)Cl$ requires. C,47.34; N,4.42; H,3.44; Cl,5.60%

Melting point. 125°C (with decomposition).

'H n.m.r. Spectrum

$CDCl_3$ (δ) 7.12s(4) 6.93s(4) 2.27s(6)

Mass Spectra: The parent ion was not recorded, the spectrum being identical to 4.2.3.

4.2.10 Reaction of $[Re(CO)_4Cl]_2$ with DPBAH

Reaction conditions and procedure were identical to 4.2.7. The product is a white powder (yield 54%).

Analyses.	Found,	C,45.80;	N,4.66;	H,2.74;	Cl,5.90
$Re(CO)_4$(DPBAH)Cl requires		C,45.57;	N,4.62;	H,2.64;	Cl,5.86%

Melting point 124°C (with decomposition)

'H n.m.r. Spectrum was not recorded.

Mass Spectra: The parent ion was not recorded, the spectra was identical to 4.2.4.

4.2.11 Photochemical Reactions of $Re(CO)_5Br$ with DPTAAH

a) $Re(CO)_5Br$ (0.500g, 1.23m mole) was suspended in toluene (40ml) in a silica flask, and to it added DPTAAH (0.293g 1.23m mole). The mixture was stirred under u.v. irradiation for 35 minutes forming a yellow solution. An i.r. spectra showed new ν(CO) cm^{-1} absorbtions at 2112w, 2014vs, 1989s and 1947vs cm^{-1}, as well as a band at 2050m cm^{-1} belonging to unreacted $Re(CO)_5Br$. The solution was reduced in volume to about 25ml in vacuo, when a white solid began to precipitate. The precipitate was allowed to develop by standing the solution overnight in the freezer. The solution was then filtered, and the precipitate was identified as $Re(CO)_5Br$ by its i.r. spectrum. The solution was further reduced in volume to about 5ml, when precipitation again began to occur. The product was collected as a yellow-white solid. Its i.r. spectrum showed ν(CO) stretching frequencies (Nujol) at 2102w, 2000vs, 1980vs, 1938m and 1917vs cm^{-1} and ν(N-H) at 3228w cm^{-1}.

In an attempt to purify the sample the solid was sublimed in vacuo at 130°C. This resulted in three products being obtained i) a slight yellow deposit high on the cold finger, identified as $Re(CO)_4$(DPTAA) by its i.r. spectrum, ν(CO)(Nujol) 2.00w, 1992vs, 1977vs, 1938vs cm^{-1} ; ii) a white crystalline solid lower down the cold finger, identified as $Re(CO)_4$ (DPTAAH)Br by its i.r. spectrum, ν(CO)(Nujol) 2101w, 2002vs, 1981vs, 1918s and ν(N-H) (Nujol) 3228 cm^{-1} ; iii) a yellow residue in the flask, identified by i.r. as being a crude sample of (o-met)$Re(CO)_3$(DPAA) (DPAAH), ν(CO) 2002vs, 1887vsbr, cm^{-1} and ν(N-H) at 3344m cm^{-1} .(Nujol) From the i.r. spectra of the original crude product it was evident that the predominant product of the reaction was $Re(CO)_4$(DPTAAH)Br with some $Re(CO)_4$(DPTAA) also present. The yellow residue of (o-met)$Re(CO)_3$(DPAA) (DPAAH), the major product after the sublimation, was produced by the decomposition of $Re(CO)_4$(DPTAAH)Br.

b) $Re(CO)_5Br$ (0.500g, 1.23m mole) was suspended in toluene (50ml) in a silica flask and to it added DPTAAH (0.586g, 2.46m mole). The mixture was stirred under u.v. irradiation for 30 minutes, new ν(CO)'s being observed at 2112w, 2014vs, 1989vs and 1947vs; $Re(CO)_5Br$ was also identified by a ν(CO) at 2050 cm^{-1}. The solution was filtered through 1.5 inches of alumina removing much of the unreacted $Re(CO)_5Br$. The solution was reduced in volume in vacuo to about 10ml and left to stand to encourage separation of a white powder. This was also identified by i.r. as $Re(CO)_5Br$. The solution was then refiltered through a 1 inch alumina column and eluted with toluene (20ml), an i.r. spectrum now showed that all $Re(CO)_5Br$ had been removed. The solution was reduced in volume to about 10ml, hexane (5ml) was added and the product $Re(CO)_4$(DPTAAH)Br formed as white crystals (yield 0.191g, 25%). This was then recrystallised from a toluene/Hexane solution.

c) $Re(CO)_5Br$ and DPTAAH in a 1:3 molar ratio, under prolonged irradiation gave (o-met)$Re(CO)_3$(DPTAA)(DPTAAH), (see Chapter 6).

4.2.12 Sublimation of $Re(CO)_4(AmH)X$ Species

It was found that all of the $Re(CO)_4(AmH)X$ species described in this chapter could be sublimed by heating in vacuo to 100°C. The product, always a pure white crystalline solid was collected on a water cooled (8°C) cold finger. Above 100°C decomposition occured, the major product being (o-met) $Re(CO)_3(Am)(AmH)$.

4.2.13 Decarbonylation of $Re(CO)_4(DPTAAH)Br$

$Re(CO)_4(DPTAAH)Br$ (0.010g) was placed in a Carius tube and heated in vacuo to 150°C for 5 hours. On cooling a yellow glass like solid was produced. An i.r. spectrum of this solid showed $\nu(CO)$ stretching frequencies at 2102w, 1990s, 1975m, 1938s, 2002vs and 1885vs,br cm^{-1}; and $\nu(N-H)$ at 3,340vw cm^{-1}, indicating the presence of both $Re(CO)_4(DPTAA)$ and (o-met)$Re(CO)_3(DPTAA)(DPTAAH)$.

4.2.14 Reaction of $Re(CO)_4(AmH)X$ with LiBu

The reaction between $Re(CO)_4(AmH)X$ (X=Br,Cl) and n-butyllithium producing the $Re(CO)_4(Am)$ species can take place in a variety of solvents (ether, monoglyme, toluene and hexane). Experimental details are given in Chapter 5.

4.2.15 Reaction of $Re(CO)_4(AmH)X$ with AmH

The reaction between $Re(CO)_4(AmH)X$ (X=Br,Cl) and an amidine in refluxing monoglyme produces the (o-met)$Re(CO)_3(Am)(AmH)$ species. Experimental details are given in Chapter 6.

4.2.16 Low Temperature 'H n.m.r. Spectral Study of $Re(CO)_4(DPTAAH)Br$

The proton n.m.r. spectra of $Re(CO)_4(DPTAAH)Br$ was recorded at ambient temperature, then at -20°C and -40°C. No significant change in the spectra was recorded, in particular a single proton resonance due to νN-H was not observed.

4.3. DISCUSSION

The complexes formulated Re$(CO)_4$(AmH)X (X=Cl,Br) were easily formed in good yield by the reaction of the dimer molecular $[Re(CO)_4X]_2$ with diaryl benzamidines, acetamidines and formamidines in monoglyme solution. At room temperature the reaction proceeded very slowly and gentle heating was necessary for convenient reaction times (16 hours). The reaction temperature was critical because above a threshold value (about 40°C for the bromide and 55°C for the chloride) a second product, (o-met)Re$(CO)_3$(Am(AmH) began to form.

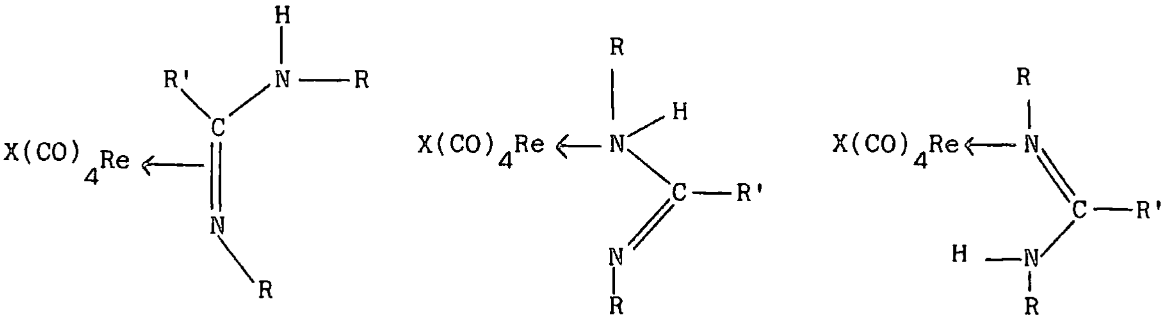
The u.v. reaction between a 1:1 molar ratio of Re$(CO)_5$Br and DPTAAH in toluene also produced the product Re$(CO)_4$(DPTAAH)Br as well as a small amount of Re$(CO)_4$Am. A second reaction with 2 moles of DPTAAH per Re$(CO)_5$Br did not produce Re$(CO)_4$(Am) and AmH(HBr) or Re$(CO)_3$$(AmH)_2$Br as wished, the only product being Re$(CO)_4$(AmH)Br.

The complexes Re$(CO)_4$(AmH)X are all pure-white crystalline solids of moderately good solubility in organic solvents. They are indefinitely stable in air, both as a solid and in solution. In vacuo they all sublime slowly onto a cold finger maintained at 6°C when heated to 100°C. Above this temperature they decompose to give Re$(CO)_4$(Am), (o-met)Re$(CO)_3$(Am)(AmH) and other unidentified noncarbonyl species.

The formulation of the complex as Re$(CO)_4$(AmH)X from the analytical data is strongly supported by spectroscopic methods. The infra-red spectra clearly shows 4 terminal carbonyl stretching frequencies (Table 4.1), consistent with a cis substituted rhenium tetracarbonyl species. The infra-red spectra also shows a broad weak ν(N-H) stretch at about 3220 cm^{-1} (c.f. free amidine ν(N-H) about 3280 cm^{-1}) indicating the presence of a rhenium bound amidine molecule which is probably substantially hydrogen bonded.

In the mass spectrometer, the parent ion is not observed for any of the complexes; a peak corresponding to the daughter ion $[Re(CO)_4(AmH)]^+$ was always observed followed by further peaks corresponding to the stepwise loss of four carbonyl groups. The spectrum of $Re(CO)_4(DPTAAH)Br$ showed that a second fragmentation pattern was possible; here an ion corresponding to $[^{\overset{187}{185}}Re\ ^{\overset{79}{81}}Br(CO)_4]^+$ was observed at m/e 378 followed by daughter ions corresponding to the loss of four carbonyl groups. Metastable peaks were only observed for one of the series, $Re(CO)_4(DPAAH)Cl$. These peaks arose from the $[Re(CO)_4(DPAA)]^+ \longrightarrow [Re(CO)_3(DPAA)]^+$ and $[Re(CO)_3(DPAA)]^+ \longrightarrow [Re(CO)_2(DPAA)]^+$ fragmentations, and not from the parent ion.

In order that the rhenium atom maintains an inert gas configuration of 18 electrons in its outer shell the amidine molecule is required to donate to it two electrons. There are three possible sources for these electrons in the amidine molecule; (Fig. 4.3.1.)i) the C=N double bond ii) the amino nitrogen's lone pair iii) the imino nitrogens lone pair. A variation on the latter could involve a fluxional situation where co-ordination via a nitrogen lone pair changes from one nitrogen to the second nitrogen atom with a concomitant change in the position of the proton and the double bond.



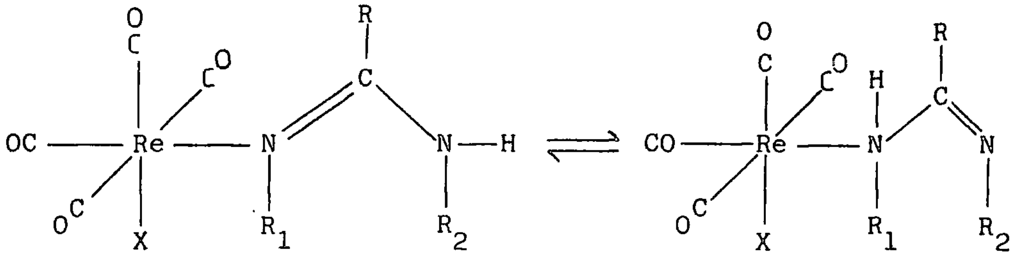
i (π-type) ii (amino) iii (imino)

Fig. 4.3.1

The first example, that of a Πbonded rhenium amidine complex is thought unlikely to occur when lone pairs on the nitrogen atoms are available.

If such a complex existed, it would be expected to show signs of fluxionality, the proton undergoing 1,3 shifts with a corresponding change in the position of the C=N double bond. This would lead to the equivalence of the R groups in ^{13}C n.m.r. spectroscopy, which is not observed (Table 4.2.). Both the amino and imino bonding modes are emirentnly possible, the choice depending upon which nitrogen atom forms the stronger Re-N bond. The lone pair on the imino nitrogen is more basic, and might be expected to form a stronger σ bond to the rhenium. In addition, if bonded through the imino nitrogens lone pair the Π* anti-bonding orbitals of the N=C double bond become available for back donation from the metals d orbitals, thus forming a very stable Re-N bond. The imino type bonding is thus the one most likely to be occurring in the solid state. In solution however, if the energy difference between the imino and amino type bonding is not large, a fluxional molecule might result. This type of fluxionality would not necessarily lead to the equivalence of the R_1 and R_2 groups in the ^{13}C n.m.r. spectra as the nitrogen atoms do not actually have to change positions, one R group can remain close to the metal, and the other remote. Broadening of the two distinct sets of signals would result.

e.g.



This is in contrast to Pd/Pt chemistry where the ends of AmH do exchange and a complete fluxional process is observed.

A low temperature ^{1}H n.mr. study of $Re(CO)_4$(DPTAAH)Br failed to locate the N-H proton, and it is assumed that the nitrogen quadrupole is responsible for severe broadening of the signal.

Once again proton n.m.r. failed to clealy distinguish between the two p-tolyl methyl environments, only for $Re(CO)_4(DPTAAH)X$ was a difference observed and this was very small (Br-0.03δ ;Cl=0.02δ). This underlines the caution that must be employed when making deductions about the symetry of a molecule by reference to the p-tolyl methyl signals. The ^{13}C n.m.r. spectra however, (table 4.2.), because of the greater chemical shifts involved in ^{13}C n.m.r. spectroscopy clearly showed that the aryl groups were in different chemical environments. Three carbonyl groups were also observed in the ^{13}C n.m.r. spectra, which is concurrent with a cis - substituted tetracarbonyl species. It is interesting to note that the central carbon atom of the N-C-N skeleton has a chemical shift about 16δ downfield from the free amidine, at approximately the same value as for the carbamoyl $Re(CO)_4(COAm)$, and chelate $Re(CO)_4(Am)$ complexes. This indicates a similar environment in each case, and is probably due to a similar degree of delocalisation in each complex.

The principal differences between $Re(CO)_4(AmH)X$ and AmH in the i.r. spectra (in the ν(N-C-N) region) are shown in Table 4.3. The most significant difference observed is the reduction in the ν(N-C-N) asymmetric stretch by 25-35 cm^{-1} on complexation. This reduction in the ν (N-C-N) stretch is thought to be a result of the Π* antibonding orbitals of the imino nitrogen being partially filled by back donation from the metal's d orbitals. It could however be caused by the perturbation induced on the (N-C-N) system by the heavy rhenium atom.

The Raman spectra (table 4.4) compliments the infra-red.

The formation of the complexes $Re(CO)_4(AmH)X$ from $[Re(CO)_4X]_2$ and AmH probably takes place in two steps. In solution an equilibrium $[Re(CO)_4X]_2$ $\rightleftharpoons$ $2Re(CO)_4X$ is though to exist, which is normally well to the left. Gentle heating in the presence of a ligand causes the reaction of the labile

$Re(CO)_4X$ species to form the stable product $Re(CO)_4(AmH)X$. It was found that the bromide products were formed more easily by this route than the chloride ones. This was due to the relative solubility of the halogen dimers, the chloride dimer being practically insoluble at room temperature.

The very slow reaction of DPTAAMe with $[Re(CO)_4Br]_2$ can be partially attributed to steric effects, and the difficulty of the amino-nitrogen atom approaching close enough to the rhenium atom for bond formation to occur. The protonated amidines can attack by either of the nitrogen atoms, facile proton transfer occuring once the amidine is co-ordinated to the metal. With DPTAAMe however, the amino nitrogen atom is effectively shielded from the rhenium atom by the presance of the bulky CH_3 and p-tolyl groups making attack via the amino nitrogen less likely.

The $[Re(CO)_3Re]_4$ detected as an impurity in the mass spectra of $Re(CO)_4(DPTAAMe)Br$ is formed during the extended period of heating (5 days at 38°) necessary to form the product. It is known that refluxing $Re(CO)_5Br$ (in petrol at 100°C) for short periods causes decarbonylation and dimerisation to occur forming $[Re(CO)_4Br]_2$, and that further decarbonylation occurs [113] after a prolonged period of refluxing (12 hours) to produce $[Re(CO)_3Br]_4$. From the present work it is now apparent that this product can be produced under milder conditions over a suitably long period of time.

The photochemical reaction of $Re(CO)_5Br$ and DPTAAH also proceeds via the intermediary of the labile $Re(CO)_4Br$ species, formed by the decarbonylation of $Re(CO)_5Br$. The $Re(CO)_4Br$ species formed can react either with, CO to reform the $Re(CO)_5Br$ species; another $Re(CO)_4Br$ unit to form the dimer; or with the amidine to form the product. The reaction was thought not to proceed via the intermediary of $[Re(CO)_4Br]_2$ as reaction times for the reaction of the dimer with DPTAAH at room temperature are much much longer.

Prolonged irradiation led to the elimination of a second carbonyl group and the formation of ortho-metallated complex (o-met)$Re(CO)_3(Am)(AmH)$ and other non carbonyl products. A mechanism for the formation of this complex is given in Chapter 6.

$Re(CO)_4(AmH)X$ complexes can be used as precursors for other rhenium amidine systems. It was found that hydrocarbon or ether solutions of $Re(CO)_4(AmH)X$ could be converted to the chelated amidino-complex $Re(CO)_4(Am)$ by the addition of an equimolar amount of n-butyllithium, (Eqn 4.1.). This reaction is discussed further in Chapter 5. The ortho metallated species (o-met)$Re(CO)_3(Am)(AmH)$ is formed when $Re(CO)_4(AmH)X$ is refluxed in monoglyme, or irradiated in toluene for an extended period of time in the presence of free amidine, (eqn. 4.2). This reaction is discussed in more detail in Chapter 6.

Eqn. 4.1. $Re(CO)_4(AmH)X + BuLi \longrightarrow Re(CO)_4(Am) + LiX + BuH$

Eqn. 4.2. $Re(CO)_4(AmH)X + 2AmH \longrightarrow (o\text{-}met)Re(CO)_3(Am)(AmH) + AmH(HX)$

Table 4.1.

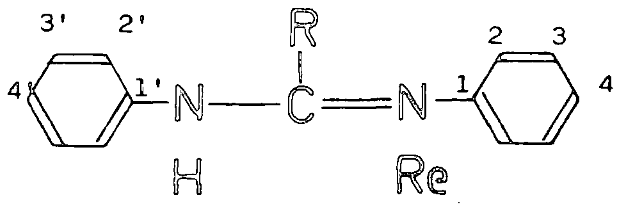
Infrared Spectral Data for $Re(CO)_4(AmR)X$ Complexes ($R-H,CH_3;X=Cl,Br$)

COMPOUND		ν (CO) cm^{-1}				ν (NH) (Nujol)
		1m	2vs	3vs	4vs	
$Re(CO)_4(DPTAAH)Br$	a	2102	2002	1918	1918	3228w br
	b	2122	2022	1919	1949	
$Re(CO)_4(DPAAH)Br$	a	2104	1993	1984	1924	3210w br
	b	2108	2012	1986	1936	
$Re(CO)_4(DPTBAH)Br$	a	2110	2020	1991	1911	3210w br
	b	2108	2013	1985	1913	
$Re(CO)_4(DPBAH)Br$	a	2100	2010	1982	1912	3230w br
	b	2121	2020	1992	1939	
$Re(CO)_4(DPFAH)Br$	a	2102	2018	1982	1910	3228w br
	b	2120	2018	1994	1941	
$Re(CO)_4(DPTAAMe)Br$	a	2102	2002	1969	1910	-
	b	2100	2006	1972	1911	
$Re(CO)_4(DPTAAH)Cl$	a	2104	2002	1980	1913	3222w br
	b	2115	2018	1985	1931	
$Re(CO)_4(DPAAH)Cl$	a	2104	1996	1982	1922	3220 br
	b	2108	2012	1986	1932	
$Re(CO)_4(DPTBAH)Cl$	a	2104	2016	1990	1922	3210w br
	b	2108	2015	1986	1931	
$Re(CO)_4(DPBAH)Cl$	a	2104	2020	1986	1918	3224w br
	b	2110	2017	1986	1913	

(a=Nujol mull b=CH_2Cl_2 solution)

TABLE 4.2. ^{13}C n.m.r. Spectra of $Re(CO)_4(AmH)X$ Complexes

COMPLEX	Aromatic Carbons				Carbonyls		ptolyl Me	R= Me	N-C=N	R=phenyl			
	C/C'	C_2/C_2'	C_3/C_3'	C_4/C_4'	2CO	CO				a	b	c	d
$Re(CO)_4(DPAAH)Cl$	153.71 138.24	124.33 124.98	130.05 130.83	126.93 130.83	187.14	185.29 187.94	-	17.88	169.31	-	-	-	-
$Re(CO)_4(DPTAAH)Cl$	157.48 141.76	123.68 123.81	130.05 130.05	125.38 129.38	186.59	184.82 187.47	21.00 21.00	17.36	168.93	-	-	-	-
$Re(CO)_4(DPTAAH)Br$	157.41 141.95	123.66 124.57	130.02 130.02	125.82 130.68	186.55	184.82 187.47	20.87 20.87	17.10	168.88	-	-	-	-
$Re(CO)_4(DPBAH)Cl$	151.73 140.02	124.59 125.37	130.53 130.18	126.93 129.66	186.20	185.69 187.37	-	-	167.64	122.14	128.03	128.62	123.68
$Re(CO)_4(DPBAH)Br$	153.00 136.76	124.81 125.46	130.33 129.03	125.72 130.72	185.70	185.03 186.68	-	-	168.24	122.14	128.25	128.70	123.83
$Re(CO)_4(DPTBAH)Cl$	150.98 135.88	125.11 122.14	129.40 129.01	135.57 134.82	186.20	185.68 187.50	20.61 20.61	-	168.66	123.45	129.92	130.44	129.68
$Re(CO)_4(DPTBAH)Br$	150.90 135.57	125.17 122.18	130.76 130.11	134.53 135.18	186.78	185.34 185.74	20.80 20.80	-	168.06	123.61	128.16	129.20	129.59
$Re(CO)_4(DPFAH)Br$	154.57 137.78	123.61 123.09	129.98 129.59	125.30 127.12	185.61	183.62 186.26	-	-	159.10	-	-	-	-



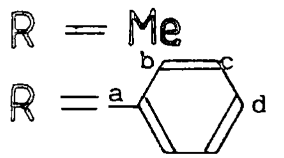


TABLE 4.3.

Differences in ν(N-C=N)* between free Amidines and the Complexes

$Re(CO)_4(AmH)X$

Amidine	Free Amidine ν(N-C=N)	$Re(CO)_4(AmH)Cl$ ν(N-C=N)	$Re(CO)_4(AmH)Br$ ν(N-C=N)
DPTAAH	1630s 1587s 1320w 1272w 1219w	1610s 1580s 1390m 1210w 1210w	1608s 1578s 1392m
DPAAH	1630s 1586s 1535m 1333w 1220w	1598s 1574s 1505m 1213w	1599s 1574s 1506m 1213w
DPTBAH	1616m 1588s 1522m 1333m 1218w	1602s 1595s 1665m 1500s 1208w	1595m 1565s 1500s 1208w
DPBAH	1624s 1585s 1528m 1440m 1328m 1221	1598s 1565s 1398m 1204w	1596s 1565s 1395m 1203w
DPFAH	1670s 1500s 1480s 1208w		1630s 1575m 1499m 1205w

* Nujol

Raman Spectra in the range 1650-1200 cm^{-1} for Re(CO)$_4$(AmR)X Complexes. (R=H,CH$_3$;X=Cl,Br)

TABLE 4.4.

Complex	Observed Raman bonds cm^{-1}										
Re(CO)$_4$(DPAAH)Cl	1600	1585	1506	1476	1431	1362	1315	1293	1241	1217	
Re(CO)$_4$(DPAAH)Br	1603	1585	1505	1476	1430	1362	1315	1295	1242	1217	
Re(CO)$_4$(DPTAAH)Cl	1616	1602	1521	1450	1408	1381	1316	1291	1243	1212	
Re(CO)$_4$(DPTAAH)Br	1617	1602	1522	1450	1407	1380	1316	1290	1243	1212	
Re(CO)$_4$(DPTBAH)Cl	1609	1601	1568	1518	1468	1453	1402	1318	1295	1245	1214
Re(CO)$_4$(DPTBAH)Br	1613	1603	1570	1519	1499	1464	1403				
Re(CO)$_4$(DPBAH)Cl	1600	1572	1507	1477	1426	1315	1297	1239	1220		
Re(CO)$_4$(DPBAH)Br	1604	1572	1508	1477	1426	1315	1298	1240	1220		
Re(CO)$_4$(DPFAH)Br	1642	1604	1503	1495	1478	1419	1364	1315	1212		
Re(CO)$_4$ (DPTAAMe)Br	1613	1610	1520	1492	1295	1213					

CHAPTER 5

Rhenium Carbonyl Complexes Containing a Bidentate Three Electron Donor Amidino-Ligand

5.1. INTRODUCTION

So far this thesis has examined two types of rhenium-amidine bonding, that of the carbamoyl group, where a rhenium-amidine ring complex is formed with the inclusion of a carbonyl group, and that of the simple two electron donor amidine ligand. Both of these types of complex are air stable, and the rhenium-amidine bond is under little or no strain.

The initial work with transition metal carbonyl amidine systems has been performed using molybdenum, tungsten, manganese, palladium and platinum systems. The reaction of $CpMo(CO)_3Cl$ with lithio amidines produces the carbamoyl complex $CpMo(CO)_2(COAm)$, whereas when it is refluxed with N,N'-disubstituted amidines, $CpMo(CO)_2(Am)$ was produced [48]. The latter species has been shown by x-ray crystalography to contain a σ,σ- symetrically bonded chelated amidine group [58] . The carbamoyl decarbonylates on heating or u.v. irradiation to produce the chelated amidino complex, but much decomposition occurs.

When this work was extended to other transition metal carbonyls it was found that $Mn(CO)_5Br$ also formed carbamoyl complexes when reacted with lithio amidines. These carbamoyls are air sensitive solids, and are readily converted to the chelated amidino systems in fairly good yield by the loss of a carbonyl group by refluxing, or u.v. irradiation in an inert solvent. Unfortunately these complexes proved too air sensitive for a comprehensive study, and only basic information was obtained.

The recently reported synthesis of $Re(CO)_4$ (formamidino) complexes shows as expected that the rhenium complexes are more air stable than the manganese analogues. The evidence from these formamidino complexes indicates the presence of symmetrically bonded amidino groups, and by comparison with the known structure of $CpMo(CO)_2(Am)$, a symmetrical σ,σ- bonding arrangement is proposed [61].

This work extends the field to include rhenium carbonyl acetamidino- and benzamidino- complexes and some of their simple reactions. New routes to these complexes are explored with some success.

The reaction of the parent N,N'-disubstituted amidines with $Mn(CO)_5Br$ has not been reported. When $Re(CO)_5Br$ is refluxed with the parent N,N'-disubstituted amidines a complicated reaction occurs. This work is reported separately in chapter 6.

5.2. EXPERIMENTAL

5.2.1. Reaction of $[Re(CO)_4Br]_2$ with LiDPBA

A solution of LiDPBA in monoglyme was prepared by freezing to -196°C a solution of DPBAH (0.955g, 3.46m mole) in monoglyme (40ml) and to it adding n-butyl lithium (3.46m mole in hexane). The mixture was allowed to warm to room temperature and was then stirred for 15 minutes. The LiDPBA solution was then transferred by syringe onto solid $[Re(CO)_4Br]_2$ (1.309g, 1.73m mole) and the mixture stirred. After 30 minutes the white suspension had disappeared, and a clear yellow solution resulted. The solution was evaporated to dryness (using ether additions to reduce gum formation), the residue extracted with toluene (25ml), and the clear yellow solution filtered through alumina (one inch column). This solution was then evaporated to small volume (5ml) and left in the freezer to crystallise. A white product separated which was identified by i.r. spectroscopy as $Re(CO)_4(DPBAH)Br$. Hexane (5ml) was then added to the mother liquor, and yellow crystals formed on cooling. This product, $Re(CO)_4(DPBA)$ was recrystallized from toluene (yield 0.42g, 21%).

Data for $Re(CO)_4(DPBA)$

Analyses. Found: C,48.53; N,4.83; H,2.57:

$Re(CO)_4(DPBA)$ requires C,48.53; N,4.92; H,2.64%

Melting point 148°C

Infra-red spectra

ν (CO) cm^{-1}	CH_2Cl_2	2117w	2005vs	1981vs	1947vs
ν (CO) cm^{-1}	Nujol	2110w	1995vs	1973vs	1918vs

Mass spectrum: The peak at highest m/e value was the parent ion $[^{187}Re(CO)_4(DPBA)]^+$ at m/e 570. Daughter ions occured at m/e values 542,514,486, and 458 corresponding to the stepwise loss of the 4 carbonyl groups. Metastable peaks were not observed.

5.2.2. Reaction of $[Re(CO)_4Br]_2$ with LiDPTBA

The reaction conditions and procedure were identical to 5.2.1. The crude product contained $Re(CO)_4(DPTBA)$, $Re(CO)_4(DPTBAH)Br$ and an isomer of (o-met)$Re(CO)_3(DPTBA)(DPTBAH)$(ν (NH) 3335w cm^{-1}, ν (CO) 2018vs, 1919vs, 1873vs cm^{-1}), all identified by i.r. spectroscopy. This crude product was recrystallised from a toluene/hexane solution giving yellow crystals of $Re(CO)_4(DPTBA)$ (yield 20%).

Analyses. Found: C,49.93; N,4.64; H,3.25:

$Re(CO)_4(DPTBA)$ requires C,50.23; N,4.69; H,3.18%

Melting point 114°C

Infra-red spectra

ν (CO) cm^{-1}	CH_2Cl_2	2103w	2002vs	1947vs	1930vs
ν (CO) cm^{-1}	Nujol	2106w	2000vs	1978vs	1911vs

'H n.m.r. spectrum

$CDCl_3$ 6.95(1), 6.74(1), 6.45(5/2), 6.61(2), 2.18(3) δ .

Mass spectrum: The peak at highest m/e value was the parent ion $[^{187}Re(CO)_4(DPTBA)]^+$ at m/e 598. Daughter ions occured at m/e values 570, 542, 514, and 486, corresponding to the stepwise loss of the four carbonyl groups. No metastable peaks were observed.

5.2.3. Reaction of $[Re(CO)_4Cl]_2$ with LiDPBA

The reaction conditions and procedure were identical to 5.2.1. The product was shown by i.r. spectroscopy to be $Re(CO)_4(DPBA)$ (yield 28%).

5.2.4. Reaction of $[Re(CO)_4Cl]_2$ with LiDPTBA

The reaction conditions and procedure were identical to 5.2.1. The product was shown by i.r. spectroscopy to be $Re(CO)_4(DPTBA)$ (yield 19%).

5.2.5. Reaction of $[Re(CO)_4Cl]_2$ with LiDPAA

A solution of LiDPAA in monoglyme was prepared by freezing to -196°C a solution of DPAAH (0.315g,1.50m mole) in monoglyme (25ml) and to it adding n-butyllithium (1.50 m mole in hexane). The mixture was allowed to warm to room temperature and was then stirred for 15 minutes. The LiDPAA solution was then transferred by syringe onto solid $[Re(CO)_4Cl]_2$ (0.500g,0.75m mole) and the mixture stirred for one hour giving a pale yellow solution. After evaporation to dryness (using ether additions to prevent gum formation) the residue was extracted with toluene (15ml) and the pale yellow solution filtered through alumina (1" column). The solution was then evaporated to low volume ($5cm^3$) and placed in the freezer to crystallise. A crude product containing $Re(CO)_4(DPAA)$,$Re(CO)_4(DPAAH)Br$ and (o-met) $Re(CO)_3(DPAA)(DPAAH)$ (all identified by i.r. spectroscopy) was precipitated. Hexane (2ml) was added to the mother liquor, which on standing produced yellow crystals of $Re(CO)_4(DPAA)$. These crystals were recrystallized twice from a hexane solution, (yield after 1st recrystallization, 1.54g, 20%).

Analyses. Found:	C,42.59;	H,2.40;	N, 5.49:
$Re(CO)_4(DPAA)$ requires	C,42.59;	H,2.56;	N, 5.52%
Melting point	146°C		

Infra-red spectra

ν (CO) cm^{-1}	CH_2Cl_2	2114w	1998vs	1976vs	1933vs
ν (CO) cm^{-1}	Nujol	2110w	1992vs	1978vs	1940vs

^1H n.m.r. spectrum

$CDCl_3$ 7.25, 7.13, 6.93, 6.8(10) 2.07(3) δ .

Mass Spectrum: The peak at highest m/e value was the parent ion $[^{187}Re(CO)_4(DPAA)]^+$ at m/e 508. Daughter ions were also observed at m/e values 480, 455, 424 and 396, corresponding to the stepwise loss of the 4 carbonyl groups. No metastable ions were observed.

5.2.6. Reaction of $[Re(CO)_4Cl]_2$ with LiDPTAA

The reaction procedure and conditions were identical to 5.2.5. The product was recrystallized twice from hexane giving yellow crystals. (Yield after first re-crystallization 18%).

Analyses.	Found:	C,45.71;	N,5.28;	H, 3.26:
$Re(CO)_4$(DPTAA) requires		C,44.84;	N,5.23;	H, 3.18%
Melting point		140°C.		

Infra-red Spectra

ν(CO) cm^{-1}	CH_2Cl_2	2110w	2000vs	1976vs	1932vs
ν(CO) cm^{-1}	Nujol	2000w	1992vs	1977vs	1938vs

^{1}H n.m.r. Sprectrum

$CDCl_3$ 6.87, 6.73(8), 2.30(6), 2.03(3) δ .

Mass Spectrum: The peak at highest m/e value was the parent ion $[^{187}Re(CO)_4(DPTAA)]^+$ at m/e 536. Daughter ions occured at m/e values 508, 480, 452 and 424, corresponding to the stepwise loss of the four carbonyl groups. No metastable peaks were observed.

5.2.7. Reaction of $Re_2(CO)_{10}$ with DPTBAH

$Re_2(CO)_{10}$ (0.788g, 1.21m mole) was dissolved in toluene (20ml) and to it added DPTBAH (0.725g, 2.42m mole). The solution was refluxed for 12 hours, and although the solution became dark brown, the ν(CO) region of the i.r. spectrum remained unchanged.

The solution was transfered to a silica flask and irradiated with u.v. light from a high pressure mercury lamp for two hours, the ν(CO) stretching frequencies remained unchanged. Further irradiation, for a total of 8 hours produced a very dark solution,which contained no ν(CO) stretching frequencies, and a light grey precipitate on the walls of the flask. An i.r. spectrum of this precipitate showed it to contain neither amidine nor carbonyls and it was discarded.

The solution was evaporated at reduced pressure to about 5ml, ether (2ml) added and then placed in the freezer overnight. A mustard coloured precipitate was produced, this was recrystallised from a CH_2Cl_2/hexane solution giving just enough material for an i.r. spectrum. The spectrum showed the product to be $Re(CO)_4$(DPTBA).

5.2.8. Reaction of $Re(CO)_4$(DPBAH)Br with n-butyl lithium

A solution of $Re(CO)_4$(DPBAH)Br (0.743g, 1.14m mole) in monoglyme (40ml) was frozen to -196°C. To it was added a hexane solution of n-butyl lithium (1.14m mole), and the mixture allowed to reach room temperature, it was then stirred for 30 minutes forming a yellow solution. The solvent was then removed by evaporation, the residue extracted with toluene (40ml) and filtered. Evaporation of this solution to low volume (5ml) and cooling produced the product $Re(CO)_4$(DPBA) (identical to that produced in 5.2.1.) as yellow crystals (yield 0.402g 62%). The remaining mother liquor produced some more yellow crystals which were shown by i.r. spectroscopy to be an orthometallate tricarbonyl species, (ν(NH)3335m cm^{-1}; ν (CO) 2018w,1919vs,1873vs cm^{-1} Nujol). There was insufficient sample for further analysis.

5.2.9. Reaction of $Re(CO)_4$(DPTBAH)Br with n-butyl lithium

Reaction conditions and procedure were identical to 5.2.8. The product $Re(CO)_4$(DPTBA) is the same as that described in 5.2.2 (yield 60%). Two other yellow crystalline products were produced in this reaction. They co-crystallized after $Re(CO)_4$(DPTBA) on the addition of hexane, and were identified as the two isomers of (o-met)$Re(CO)_3$(DPTBA)(DPTBAH) by their infra-red spectra. The preparation of these complexes is described in Chapter 6.

5.2.10 Reaction of $Re(CO)_4(DPAAH)Br$ with n-butyl lithium

Reaction conditions and procedure were identical to 5.2.8. The product $Re(CO)_4(DPAA)$ was contaminated by (o-met)$Re(CO)_3(DPAA)(DPAAH)$, and had to be recrystallized from hexane three times to produce a pure sample (yield 30%). It was identical to that produced in 5.2.5.

5.2.11 Reaction of $Re(CO)_4(DPTAAH)Br$ and n-butyl lithium

Reaction conditions and procedure were identical to 5.2.8. The product $Re(CO)_4(DPTAA)$ was contaminated with (o-met)$Re(CO)_3(DPTAA)(DPTAAH)$, and had to be recrystallised from hexane three times to produce a pure sample (yield 24%). It was identical to that described in 5.2.6.

5.2.12 Reactions of $Re(CO)_4(AmH)Cl$ with n-butyl lithium

Reactions 5.2.8. - 5.2.11 were repeated using the chloride precursor. The products were identical to those described for the bromide, and in similar yields.

5.2.13 Reaction of $Re(CO)_4(DPBA)$ with Hydrobromic Acid

$Re(CO)_4(DPBA)$ (0.100g, 1.75m mole) was suspended in methanol (10ml). Hydrobromic acid (0.3ml, 47%, 1.75m mole) was added dropwise, the solid changing colour from yellow to white. The solvent was then syringed off, and the solid dryed under vacuum. An i.r. spectrum showed it to be $Re(CO)_4(DPBAH)Br$.

5.2.14 Reaction of $Re(CO)_4(PPh_3)Br$ with DPTAAH

$Re(CO)_4(PPh_3)Br$ (0.500g, 0.78m mole) was dissolved in toluene (40ml) and to it added DPTAAH (0.371g, 1.56m mole). The mixture was refluxed for 4 hours, until all the $\nu(CO)$'s of the reactant had disappeared. The solvent was then evaporated at reduced pressure to ¼ of its volume, then ether (10ml) added and the solution placed in the freezer. After 16 hours a white powdery precipitate had gathered, this was collected and dried. It was shown by ^1H n.m.r. and i.r. spectroscopy to be DPTAAH(HBr). To the remaining solution pentane (10ml) was added causing the precipitation of hard white crystals of $Re(CO)_3(PPh_3)_2Br$ (.151g, ν(CO) 1938vs, 1884vs Nujol). The mother liquor was then removed by evaporation at reduced pressure, and the residue extracted with carbontetrachloride (10ml). Solvent evaporation and cooling produced the product $Re(CO)_3(PPh_3)$(DPTAA). It was recrystallized from carbontetrachloride/pentane, giving a white powder (yield 0.19g, 31%).

Analyses. Found: C,57.77; N,3.65; H,4.20:

$Re(CO)_3(PPh_3)$(DPTAA) requires C,57.76; N,3.63, H, 4.16%

Melting point 196°C (with decomposition).

Infra-red spectra

ν(CO) cm^{-1}	CH_2Cl_2	2018vs	1914vs	1882vs
ν(CO) cm^{-1}	Nujol	2012vs	1907vs	1883vs

'H n.m.r. spectrum

$CDCl_3$ (δ) Aromatic protons: 7.20(6), 7.10(2), 6.92(1), 6.60(1), 6.47(1).

Me groups: 2.31s(2), 1.45d(1)(J=4Hz).

Massspectrum: The peak at highest m/e value was the parent ion $[^{187}Re(PPh_3)(DPTAA)(CO)_3]^+$ at m/e 770. The following fragmentations were observed:-

$$\begin{tikzcd}
 & 742 \arrow[r, "-CO"] & 714 \arrow[r, "-CO"] & 686 \arrow[dr, "-PPh_3"] & \\
{[Re(PPh_3)(DPTAA)(CO)_3]^+} \atop 770 \arrow[ur, "-CO"] \arrow[dr, "-PPh_3"'] & & & & {Re(DPTAA)^+} \atop 424 \\
 & 508 \arrow[r, "-CO"'] & 480 \arrow[r, "-CO"'] & 452 \arrow[ur, "-CO"'] &
\end{tikzcd}$$

metastable ions were not observed.

5.2.15 Reaction of $Re(CO)_4(PPh_3)Br$ with DPAAH

The reaction conditions and procedure were identical to 5.2.13. The product $Re(CO)_3(PPh_3)$(DPAA) was collected as an off-white solid (45% yield).

Analyses Found: C,56.71; N,3.80: H,3.80:

$Re(CO)_3(PPh_3)$(DPAA) requires C,56.66; N,3.77; H,3.77%

Melting point 196°C (with decomposition).

Infra-red spectra

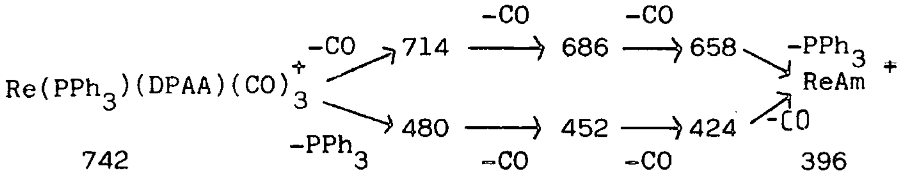
ν(CO) cm^{-1}	CH_2Cl_2	2019vs	1912vs	1888vs
ν(CO) cm^{-1}	Nujol	2016vs	1909vs	1885vs

<u>'H n.m.r. spectrum</u> $CDCl_3$ (δ) Methyl: 1.62d(J=4Hz).

Aromatics: 7.13(5) 6.75(1) 6.61(1).

Mass spectrum: The parent ion was not observed, the peak at highest m/e value occured at m/e 714 corresponding to $[Re(PPh_3)(DPAA)(CO)_2]^+$.

The following fragmentations were observed:-



(not observed)

the initial loss of carbonyl being the favoured route.

5.2.15 Reaction of $Re(CO)_4(PPh_3)Br$ with DPTBAH

The reaction conditions and procedure were identical to 5.2.13. The product $Re(CO)_3(PPh_3)(DPTBA)$ was recrystallized from a CH_2Cl_2/hexane solution as an off-white solid (yield 38%). $Re(CO)_3(PPh_3)_2Br$ was also collected in 20% yield.

Analyses. Found: C,61.55; N,3.35; H,4.20;

$Re(CO)_3(PPh_3)(DPTBA)$ requires C,60.67, N,3.37; H,4.09%

Melting point 190°C (with decomposition).

Infra-red spectra

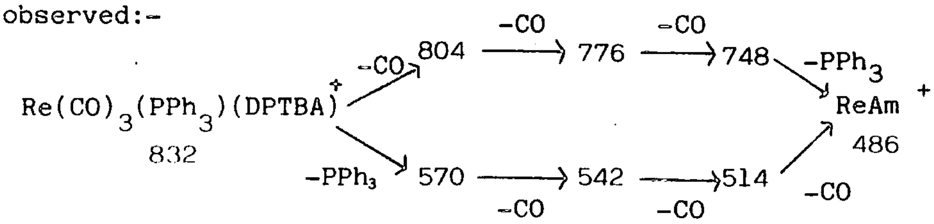
ν (CO) cm^{-1} CH_2Cl_2 2021vs 1917vs 1890vs

ν (CO) cm^{-1} Nujol 2019vs 1918vs 1907vs 1899vs 1887vs

'H n.m.r. spectrum $CDCl_3$ (δ) Methyl: 2.19

Aromatics: 7.40(1), 7.25(4), 7.17(3), 6.87(4), 6.63(1), 6.3(1).

Mass spectrum The peak at highest mass is the parent ion $[^{187}Re(CO)_3(PPh_3)(DPTBA)]^+$ at m/e 832. The following fragmentations were observed:-



the initial loss of carbonyl being the favoured route. Metastable peaks at m/e 721.0 and 695.9 were also observed, due to the $[Re(PPh_3)(Am)(CO)_2]^+ \rightarrow [Re(PPh_3)(Am)(CO)]^+$ and $[Re(PPh_3(Am)(CO)]^+ \longrightarrow [Re(PPh_3)(Am)]^+$ fragmentations.

5.2.17 Reaction of $Re(CO)_4(PPh_3)Br$ with DPBAH

The reaction conditions and procedure were identical to 5.2.13. The product $Re(CO)_3(PPh_3)(DPBA)$ was recrystallized as an off-white powder from a CH_2Cl_2/hexane solution (yield 42%). $Re(CO)_3(PPh_3)_2Br$ was also produced.

Analyses Found: C,59.92; N,3.64; H,3.83:

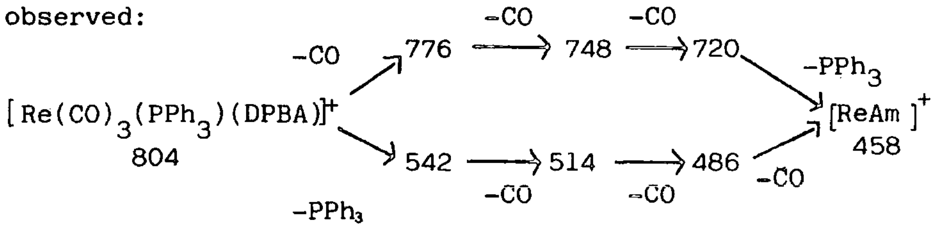
$Re(CO)_3(PPh_3)(DPBA)$ requires C,59.81; N,3.49; H,3.74%

Melting point 192°C (with decomposition).

Infra-red spectra

ν (CO)	CH_2Cl_2 cm^{-1}	2020vs	1917vs	1888vs
ν (CO)	Nujol cm^{-1}	2022vs	1911vs	1894vs

Mass spectrum The peak at highest m/e value was the parent ion $[^{187}Re(CO)_3(PPh_3)(DPBA)]^+$ at m/e 804. The following fragmentations were observed:



the initial loss of carbonyl being the favoured route. Metastable peaks were also observed at m/e 748.9, 721.0 and 693.0 corresponding to the $[Re(PPh_3)(Am)(CO)_3]^+ \longrightarrow [Re(PPh_3)(Am)CO)_2]^+$, $[Re(PPh_3)(Am)(CO)_2]^+ \longrightarrow [Re(PPh_3)(Am)(CO)]^+$, and $[Re(PPh_3)(Am)(CO)]^+ \longrightarrow [Re(PPh_3)(Am)]^+$ fragmentations.

5.2.18 Reaction of $Re(CO)_4(AsPh_3)Br$ with DPTAAH

$[Re(CO)_4Br]_2$ (0.500g, 0.66m mole) was sitrred with $AsPh_3$ (0.405g, 1.32m mole) in CCl_4 (40ml) at 50°C for 2½ hours. An i.r. spectrum of the solution showed that $Re(CO)_4(AsPh_3)Br$ had formed in good yield. To this solution was added DPTAAH (0.62g, 2.64m mole) and the solution refluxed until an i.r. spectrum indicated that the reaction was complete (3 hours). Removal of the solvent by evaporation at reduced pressure led to the formation of a gum, toluene (4ml) was added to form a solution, then the solution was cooled in the freezer. A white solid was precipitated, this was shown by i.r. and n.m.r. spectroscopy to be DPTAAH(HBr). The mother liquor was returned to the freezer and an off white solid precipitated. This was recrystallized from a CH_2Cl_2/hexane solution giving a white powder (yield 0.143g 13%).

Analyses Found: C,54.70; N,3.50; H,4.02:

$Re(CO)_3(AsPh_3)(DPTAA)$ requires C,54.61; N,3.44; H,3.94

Melting point 185°C.

Infra-red spectra

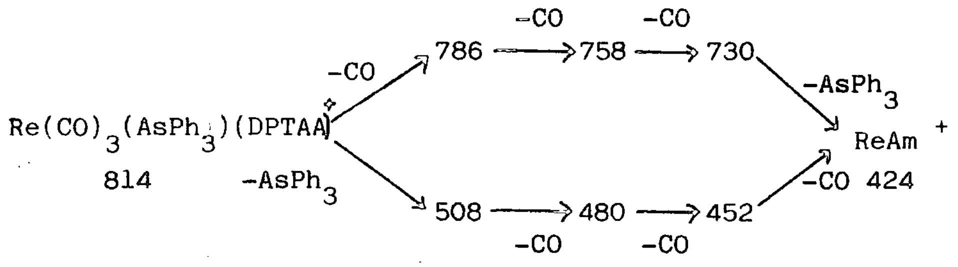
ν(CO)	cm^{-1}	CH_2Cl_2	2021vs	1910vs	1892vs
ν(CO)	cm^{-1}	Nujol	2015vs	1906vs	1887vs

^1H n.m.r. spectrum $CDCl_3$ (δ) Methyls: 2.31s(2) 1.63s(1)

Aromatics: 7.07 (m).

Mass Spectrum: The peak at highest mass was the parent ion $[^{187}Re(CO)_3(AsPh_3)(DPTAA)]^+$ at m/e 814.

The following fragmentations were observed.



5.2.19 Reaction of $Re(CO)_3(PPh_3)Br$ with DPTAAMe

$Re(CO)_4(PPh_3)Br$ (0.200g, 0.31m mole) was dissolved in toluene (10ml) and to it added DPTAAMe (0.079g, 0.31m mole). This mixture was then refluxed for a total of 21 hours when the i.r. spectrum indicated that all the $Re(CO)_4(PPh_3)Br$ had reacted, a white precipitate was evident on the walls of the flask. The solution was filtered. An i.r. spectrum showed the precipitate to be hydroscopic, it contained neither amidine nor carbonyl groups and was not investigated further as there was insufficient sample. Evaporation and cooling of the solution produced a precipitate of trans $Re(CO)_3(PPh_3)_2Br$. The remaining solution could not be successfully crystallized due to gum formation although several solvents were tried, (including CH_2Cl_2, ether, monoglyme and pentane). An i.r. spectrum in CH_2Cl_2 showed ν(CO)'s at 2020s and 1904s(broad), I believed this to be a crude sample of $Re(CO)_3(PPh_3)$(DPTAAMe)Br.

5.2.20 Reaction of $Re(CO)_4$(DPBA) with PPh_3

$Re(CO)_4$(DPBA) (0.120g,0.21m mole) was dissolved in toluene (20ml) and to it added PPh_3 (0.060g 0.21m mole). The solution was then refluxed until an i.r. spectrum showed that the reaction was complete (2 hours). The solution was cooled, evaporated to half its volume and pentane (5ml) added. White crystals of $Re(CO)_3(PPh_3)$(DPBA) formed on cooling (yield 0.12g 67%).

5.2.21 Reaction of $Re(CO)_4$(DPTAA) with PPh_3

$Re(CO)_4$(DPTAA) (0.100g, 0.18m mole) was dissolved in toluene (20ml) and to it added PPh_3 (0.049g 0.19m mole). The solution was refluxed for 2 hours, then the solvent removed by evaporation at reduced pressure. An i.r. spectra of the crude product showed it to be $Re(CO)_3(PPh_3)$(DPTAA).

5.2.22 Reaction of $Re(CO)_4$(DPBA) with DPBAH

$Re(CO)_4$(DPBA) (0.205g, 0.36m mole) was dissolved in toluene (12ml) and to it added DPBAH (0.098g, 0.36m mole). The solution was then refluxed for 4 hours, evaporated at reduced pressure to about 3ml, a few drops of hexane added and set in the freezer. This produced yellow crystals of (o-met)$Re(CO)_3$(DPBA)(DPBAH), (yield 0.20g, 66%). The product is described fully in section 6.2.4. Addition of more pentane produced a second yellow crystalline product. This was believed to be a second isomer of (o-met)Re$(CO)_3$(DPBA(DPBAH) (c.f. section 6.2.5.). It was recrystallized from pentane.

Data for the second isomer of (o-met)Re$(CO)_3$(DPBA)(DPBAH)

Analyses. Found: C,62.01; N,7.02; H,4.06:

(o-met)Re$(CO)_3$(DPBA)(DPBAH) requires C,60.52; N,6.88; H,3.81%

Mass Spectrum: This was identical to isomer described in 6.2.4.

Infra-red spectrum

ν(CO) Nujol 2016vs 1912vs 1873vs cm^{-1}.

ν(N-H)Nujol 3341m cm^{-1}.

5.2.23 Reaction of Re$(CO)_4$(DPTBA) with DPTBAH

Re$(CO)_4$(DPTBA) (0.100g, 0.17m mole) was dissolved in monoglyme (10ml) and to it added DPTAAH (0.050g, 0.17m mole). The solution was then refluxed for 4 hours, then the solvent removed by evaporation at reduced pressure. An i.r. spectrum in CH_2Cl_2 showed that (o-met)Re$(CO)_3$(DPTBA) (DPTBAH) was produced. (ν(NH) CH_2Cl_2 3340 cm^{-1};ν(CO) CH_2Cl_2 2012vs, 1895vs,1882vs). The product is described fully in section 6.2.5.

5.2.24 Reactions of Re$(CO)_4$(DPAA) and Re$(CO)_4$(DPTAA) with DPAAH and DPTAAH

These reactions were performed on a very small scale in the same manner as 5.2.22. The products were not isolated. Infra-red spectra in CH_2Cl_2 showed the products to be (o-met)Re$(CO)_3$(Am)(AmH) as described in sections 6.2.1. and 6.2.3.

5.3. DISCUSSION

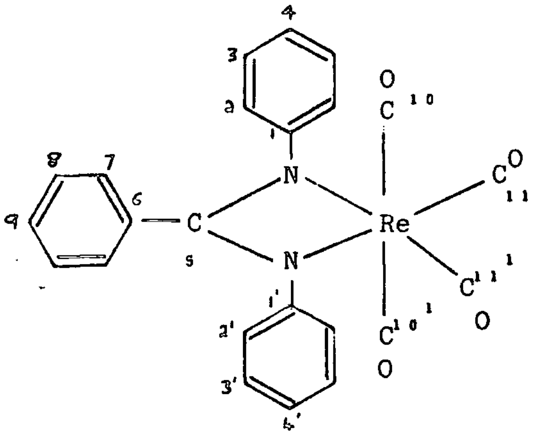
Compounds of the formula Re$(CO)_4$(Am) were prepared by the reaction of $[Re(CO)_4X]_2$ (X=Cl,Br) with lithio-diarylacetamidines and lithio-diarylbenzamidines in monoglyme solution. These compounds were bright yellow, air stable solids (m.pt. ca. 140°) which formed yellow air stable solutions in organic solvents. They were shown by spectroscopic methods to be identical with the decarbonylation products of Re$(CO)_4$(COAm) complexes (Chapter 3). Although monitoring of the reaction solution by infra-red spectroscopy indicated that the product was formed in good yield, only about 20% of the product was recovered from the reaction. This was due mainly to the fact that two other products were produced in the reaction, ($Re(CO)_4(AmH)X$ and an ortho-metallated species $Re(CO)_3(Am)(AmH)$), and the ensuing problems of product isolation. The formation of the ortho-metallated species consumes two amidine molecules, and so has a greater effect on the % yield. The solubility of unreacted free amidine (formed from protonation of the amidino-ion), (o-met)$Re(CO)_3(Am)(AmH)$, and the product $Re(CO)_4(Am)$ were very similar in a range of solvents making separation by fractional crystallization extremely difficult. Seeding of the solutions and the relative concentrations of the species in solution appeared to be very important, as a solution containing both $Re(CO)_4(Am)$ and (o-met)$Re(CO)_3(Am)(AmH)$ could produce a precipitate of either of the products first, or as more frequently happened a mixture of the two. As both of the complexes form bright yellow crystalline solids, it was extremely difficult to obtain conditions ideal for the preferential crystallization of one product. Chromatography of the reaction mixture using silica gel or alumina columns was not justified due to excessive loss through retention of the product on the column using a whole range of organic solvents.

In order to simplify the procedure for the isolation of the product, some of the reactions were repeated using toluene and hexane solutions. The work up proved not to be significantly different to that described for the monoglyme reactions, nor were yields or product ratios affected. A more efficient route to the pure product than the two established methods (i.e. decarbonylation of $Re(CO)_4(COAm)$ and $Re(CO)_4X_2$+LiAm) was therefore sought. No reaction accured between $Re_2(CO)_{10}$ and DPTBAH in refluxing toluene. Ultra-violet irradiation of the solution caused decomposition of the carbonyl, although a small yield of $Re(CO)_4$(DPTAA) was produced. This was not a viable method of synthesis.

Addition of an equimolar amount of n-butyllithium to a solution of $Re(CO)_4(AmH)X$ (X=Cl,Br) in monoglyme (or hydrocarbon solvent) also produced the compound $Re(CO)_4Am$. Monitoring the reaction mixture by infra-red spectroscopy proved to be impossible for this reaction because of the extreme similarity between the solution spectra of $Re(CO)_4Am$ and $Re(CO)_4(AmH)Br$. This method of synthesis also produced the ortho-metallated derivative, leading to the previously stated problems of product isolation. Although the yields recorded were slightly better than via the $[Re(CO)_4)X]_2$ route, the necessary presynthesis of $Re(CO)_4(AmH)X$ makes this route unfavourable.

The evidence for the formulation of these complexes is derived from the analytical data, and infra-red and mass spectrometry. All of the compounds analyse correctly for $Re(CO)_4(Am)$ complexes. The infra-red spectra contain four terminal carbonyl stretching frequencies consistent with a di-substituted tetracarbonyl moiety, which on initial inspection appear the same as for the complexes $Re(CO)_4(AmH)X$. In solution it was difficult to tell them apart, the major difference occuring for the second lowest frequency band (1985-1995 cm^{-1} for $Re(CO)_4(Am)X$; 1975-1985 cm^{-1} for $Re(CO)_4(Am)$). Fortunately other differences were apparent in the Nujol spectra. In addition to the difference in the solution spectra the low frequency carbonyl occurred at 1930 cm^{-1} for $Re(CO)_4(Am)$, about 10 cm^{-1} higher than that of $Re(CO)_4(AmH)X$; also the ν(N-H) vibration of the $Re(CO)_4(AmH)X$ complexes at about 3222 cm^{-1} was no longer present in $Re(CO)_4(Am)$ complexes. All of the compounds exhibited molecular ions of 4 carbonyl groups. It is concluded therefore that $Re(CO)_4(Am)$ is the correct formulation of the complex, and if the complex is to obey the 18 electron rule, the amidino-group must supply the rhenium atom with three electrons.

In Chapter one, it was suggested that such complexes might be bonded with either a pseudo πallylic-type of bonding, or a chelate-type. In addition three different types of chelate bonding were proposed (Fig. 1.4.5.), including symetricalσ,σ(with delocalised electrons), unsymetricalσ,σ(with a localised double bond), and σ , Π -bonding (with a C=N double bond). The 'H n.m.r. spectra shows the magnetic equivalence of p-tolyl methyl groups in these complexes, but this evidence has proved misleading for the carbamoyl complexes in this work and elsewhere. The ^{13}C n.m.r. spectrum was obtained for $Re(CO)_4(DPBA)$ (Fig. 5.3.1.) (insufficiently pure samples were available for the other species), and showed the equivalence of the aryl carbon atoms, and two pairs of carbonyls. The spectrum did not show any appreciable



1=1^{1} =145.97
2=2^{1} =123.74
3=3^{1} =128.55
4=4^{1} =122.96

10=10^{1} = 189.77
11=11^{1} = 186.78

6= 123.68
7= 128.94
8= 129.98
9= 132.71

5= 165.00

Fig. 5.3.1.

change when re-run at -60°C, eliminating the possibility of dynamic equivalence due to rapid interchange of bonding mode. The equivalence of the N-Aryl groups in the ^{13}C n.m.r. spectrum eliminate the possibility of a localised C=N double bond, and therefore the unsymmetrical σ,σ - and σ , Π-types of bonding. Which of the remaining structures, that of the pseudo- Πallyl or chelate type bonding cannot be resolved without a crystal structure being performed, but in view of the information available for other amidino-complexes (Chapter 1), the chelate structure appears most likely, Fig. 5.3.2.

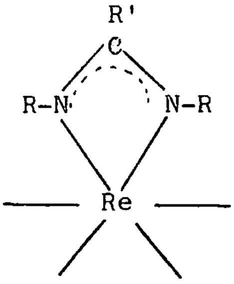


Fig. 5.3.2.

The infra-red absorption associated with the N-C-N skeleton are listed in table 5.3.1.

Table 5.3.1.

Complex	i.r. absorptions associated with the N-C-N skeleton (cm^{-1} Nujol)				
$Re(CO)_4(DPAA)$	1590m	1575w	1495s	1475s	1412s
	1364m	1312w	1297w		
$Re(CO)_4(DPTAA)$	1606w	1570vw	1502s	1490s	1475s
	1412s	1368m	1315w	1293w	
$Re(CO)_4(DPBA)$	1590m	1570w	1525w	1490s	1475sh
	1425s	1365w	1273w		
$Re(CO)_4(DPTBA)$	1606w	1569w	1502s	1432s	1365w
	1298w	1272w			

Compared to the spectra for the free amidines (page 47) the band at about 1600 cm^{-1} represents a lowering (of about 20 cm^{-1}) of the high frequency vibration attributed to the ν(N-C-N) asymetric stretch. The symetric stretch is similarly lowered, with the absorption now occurring at about 1500 cm^{-1}. These changes are similar to those observed for other Re-Amidine systems (Chapters 3 and 4) and can be interpreted as either the population of the π^* antibonding orbitals of a delocalised amidine group, or as a perturbation on the N-C-N system induced by bonding to the Re atom.

The formation of the complexes from $Re(CO)_4X_2$ and lithio-amidines can be assumed not to take place via attack at a carbonyl as there is no evidence of carbamoyls being formed. Two remaining routes for reaction are possible, i.e. where LiX is eliminated as either a first or second step, (Fig 5.3.2.). It is not possible to predict which of the reaction routes is followed.

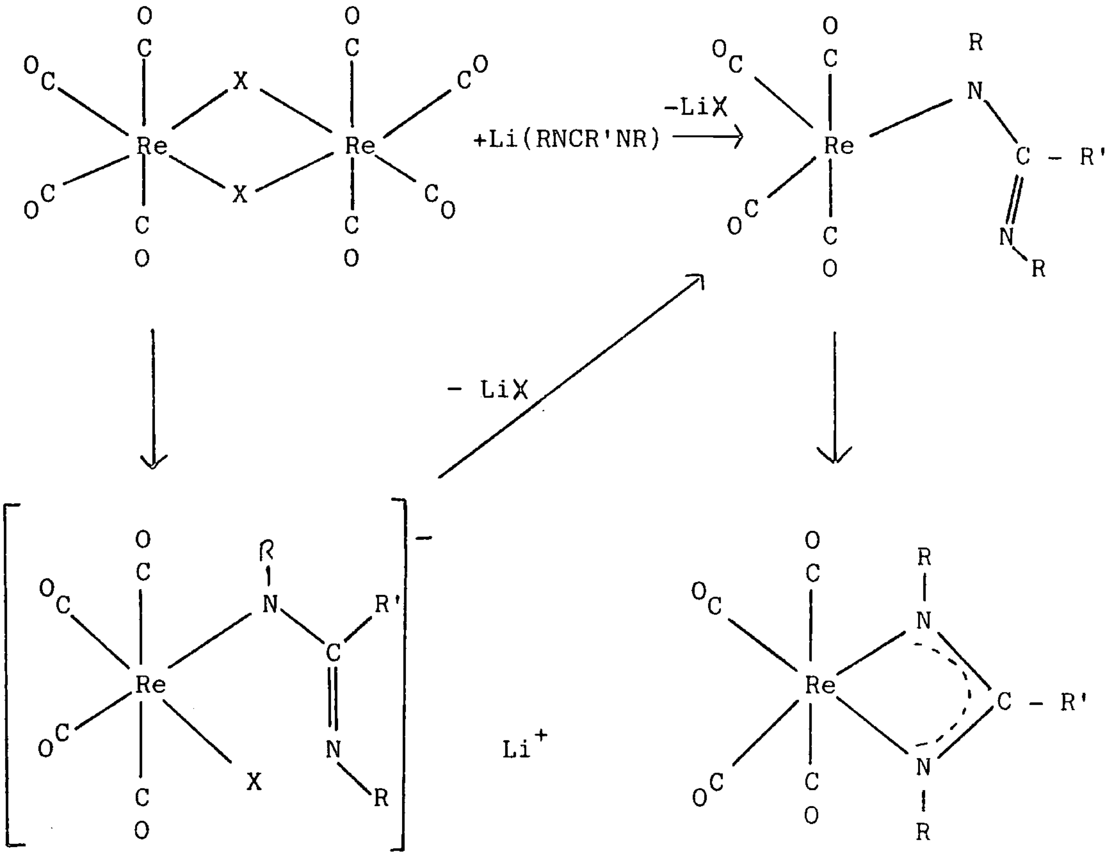


Fig. 5.3.2.

The formation of $Re(CO)_4Am$ from the reaction of $Re(CO)_4(AmH)X$ and n-butyl lithium can also take place via two routes:- a) the initial removal of the proton from the amino group followed by elimination of HX; or b) the elimination of LiX followed by nucleophilic attack at the metal by the amino nitrogen and the removal of a proton by the Bu group. (Fig. 5.3.3.)

The reaction of $Re(CO)_4Am$ with HBr forming cis-$Re(CO)_4(AmH)Br$ is probably a direct reversal of route(b) overleaf. After protonation of the nitrogen, the amino group then leaves the metal, leaving a vacant co-ordination site

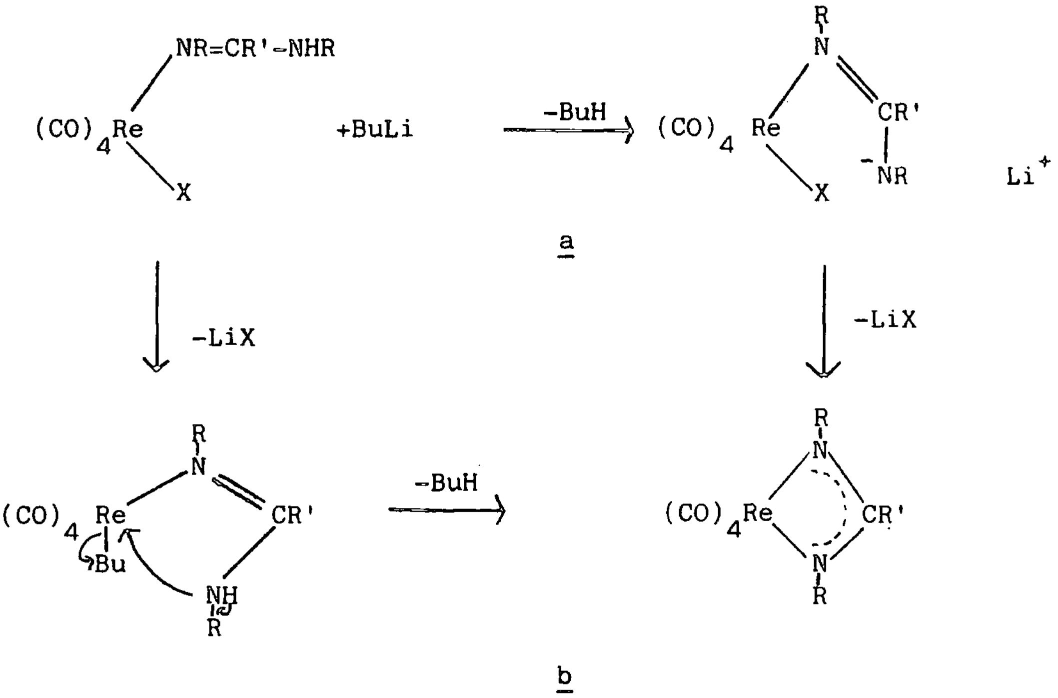


Fig. 5.3.3.

for nucleophilic attack by the bromine to occur. An SN_2 type of reaction is judged not to have occurred, as this normally requires the nucleophile to enter trans to the leaving group, resulting in the formation of the trans isomer. It may be possible to prepare other cis-substituted rhenium amidine complexes by reacting $Re(CO)_4(Am)$ with compounds containing an acidic proton, e.g. HF,HI,HNO_3,HCOOH,C_6H_5OH etc.

The reaction of $Re(CO)_4(Am)$ with AmH in refluxing monoglyme (or toluene) is unusual, as the product $Re(CO)_3(Am)(AmH)$ contains an ortho-metalated amidino group. These compounds, and their reactions are described separately in Chapter 6, together with the obvious question; which group ortho-metalates; the amidine originally bound to the metal, or the incoming amidine?

The reaction of $Re(CO)_4(Am)$ with PPh_3 in refluxing toluene to form $Re(CO)_3(Am)(PPh_3)$ is of little note as it is a straightforward substitution of a carbonyl group. It is however interesting in the context of the above reaction, i.e. it does not promote the formation of a ortho-metallated product. The ortho-metallation reaction above cannot therefore be merely the result of non-carbonyl ligand being bound to the metal.

The compounds $Re(CO)_3(Am)(PPh_3)$ containing a three electron donor amidine ligand were more easily obtained from the reaction between $Re(CO)_4(PPh_3)Br$ and the free amidines AmH, in refluxing toluene. The notable aspect of this reaction is that the amidine becomes a bidentate three electron donor ligand even though a neutral amidine species was used (c.f. LiAm needed to form $Re(CO)_4(Am)$ when using $[Re(CO)_4X]_2$). The reaction proceeds in fairly good yield (about 40%), the products being white air stable crystalline solids with melting points around 195°C. Only the facial isomer is observed having three metal carbonyl stretching frequencies at about 2020, 1917, and 1890 cm^{-1}. The analogous reaction using DPTAAMe is very slow, the reaction pathway being effectively blocked by the substitution of a Me group for the amino proton. The tricarbonyl product detected by i.r. spectroscopy is probably $Re(CO)_3(AmMe)(PPh_3)Br$. In the mass spectrometer, the parent ion is observed for all but the DPAA complex, where $[Re(CO)_2(Am)(PPh_3)]^+$ is the ion of highest mass. The stepwise loss of the carbonyls and the PPh_3 group is clearly visible, the initial loss of the carbonyls being the marginally preferred route.

'H n.m.r. spectroscopy showed that the two para-tolyl methyl groups of the DPTAA and DPTBA derivatives to be in identical chemical environments, but this was not confirmed by ^{13}C n.m.r. spectroscopy, as there was not enough of the samples available. The C-Me group of the acetamidines was found to be split by 4Hz., this was attributed to long range P-H coupling. The subsequent synthesis of $Re(CO)_3(AsPh_3)(Am)$ which did not show such splitting confirmed this.

The infra-red absorptions in the ν(N-C-N) region of the spectrum (1650 - 1200 cm^{-1}) are listed in table 5.3.2. This shows similar absorptions to those observed for the $Re(CO)_4(Am)$ complexes, and a similar type of delocalised chelate bonding is proposed (Fig. 5.3.4).

Table 5.3.2.

Complex	i.r. absorptions associated with the NCN skeleton (cm^{-1} Nujol)					
$Re(CO)_3(PPh_3)(DPAA)$	1590w	1500m	1475m	1429w	1410m	1218m
$Re(CO)_3(PPh_3)(DPTAA)$	1600vw	1500m	1475m	1429wm	1413m	1408w
	1358wm	1288w	1222m			
$Re(CO)_3(PPh_3)(DPBA)$	1588w	1576w	1495m	1485m	1468m	1430s
	1375m	1312w	1275w	1212w		
$Re(CO)_3(PPh_3)(DPTBA)$	1603w	1565w	1500m	1465m	1425s	1408w
	1310w	1295w	1268w	1215w		

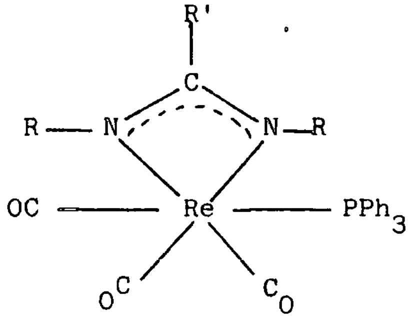


Fig. 5.3.4.

The reaction mixture contained two moles of AmH per mole of $Re(CO)_4(PPh_3)Br$; this was to provide a 'sink' for the eliminated HBr, without introducing a second Lewis base to the mixture which might complicate the reaction. A possible reaction mechanism for the formation of $Re(CO)_4(Am)(PPh_3)$ from $Re(CO)_4(PPh_3)Br$ and AmH is illustrated overleaf (Fig. 5.3.5.). The formation of substantial amounts (20%) of trans $Re(CO)_3(PPh_3)_2Br$ in the reaction indicates that a second process can occur, i.e. the initial elimination of PPh_3 from $Re(CO)_4(PPh_3)Br$. The liberated PPh_3 is then free

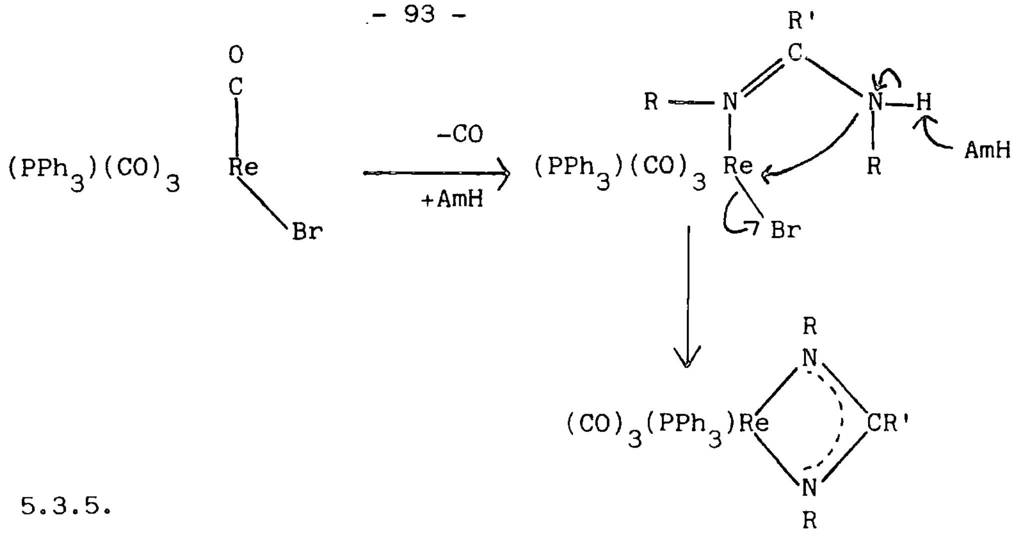


Fig. 5.3.5.

to react with $Re(CO)_4(PPh_3)Br$ to form the stable $Re(CO)_3(PPh_3)_2Br$ complex. The labile $Re(CO)_4$(solvent)Br species also formed probably reacts with amidine to form (o-met)$Re(CO)_3$(Am)AmH). This species was not detected however.

The reaction did not produce a complex containing an ortho-metalated amidino group (c.f. reflux of AmH with $Re(CO)_5Br$, $[Re(CO)_4X]_2$ and $Re(CO)_4$(AmH)X), the reason for this is not clear as it seems to be the desired thermodynamic product in the above reactions. Three possibilities for this are:- a) once the product $Re(CO)_3(PPh_3)$(Am) is formed it is very stable (m.pt. 190°C) and does not react further; b) an ortho-metalated ligand may have more steric interactions with <u>cis</u> PPh_3 than a chelated one; steric interactions in the chelate o-metalate transition-state prevent this process occuring. The first example appears to be most likely, as molecular models show that the o-metallated product has less steric interactions than the chelted one, and also in view of the reaction between (o-met)$Re(CO)_3$(Am)(AmH) and PPh_3 which produces the chelated amidino $Re(CO)_3(PPh_3)$(Am) complex (see Chapter 6).

Preliminary work suggests that facial isomers of $Re(CO)_3(PPh_3)$(AmH)X can be produced by reaction of $Re(CO)_3(PPh_3)$(Am) with HX i.e. HCl, HBr, HI, HF, HNO_3, HCOOH and C_6H_5OH etc.

CHAPTER 6

Rhenium Carbonyl Complexes Containing An Ortho-Metallated Amidine Ligand

6.1. INTRODUCTION

The reactions of $[Re(CO)_4X]_2$ and $Re(CO)_4(AmH)X$ (X=Cl,Br) with lithio amidines and n-butyllithium respectively produce the chelating amidino-complexes $Re(CO)_4(Am)$, but the products are recovered in low yield.

As it is known that the chelated amidino-complex $CpMo(CO)_2(Am)$ [57] is formed in good yield when $CpMo(CO)_3Cl$ is refluxed in monoglyme with the parent amidine, a similar reaction was tried using $Re(CO)_5Br$ and DPTAAH. In this instance a more complex reaction took place, resulting in the formation of an ortho-metallated rhenium amidine complex.

This Chapter describes the ortho-metallation reactions occuring for diaryl -acetamidines, -benzamidines and -formamidines and discusses the mechanisms by which these processes might occur. In addition attention is drawn to some novel transformations, i.e. that of a chelated amidino-group to an ortho-metallated one, and vice-versa. Explanations for these transformations are also proposed.

6.2. EXPERIMENTAL

6.2.1. Reaction of $Re(CO)_5Br$ with 2DPTAAH

To a suspension of $Re(CO)_5Br$ (1.00g, 2.46m mole) in monoglyme (40ml) was added DPTAAH (1.72g, 4.92m mole) and the mixture refluxed for 6 hours. Infra-red spectra however showed that the reaction was completed after 2½ hours. The monoglyme was removed by evaporation, and the residue extracted with toluene (10ml) and placed in the freezer. After 5 days a precipitate was collected (1.263g) which was found to consist of two crystalline products, one yellow [(o-met)Re$(CO)_3$(Am)(AmH)] and the other white [Re$(CO)_3$$(AmH)_2$Br] . The mother liquor was evaporated to form a gummy residue, extracted with CCl_4, and pentane added. Precipitates of Re$(CO)_4$(DPTAAH)Br and DPTAAH(HBr) were collected.

The mixture of yellow and white precipitates were heated in vacuo; a faint sublimate of DPTAAH appeared on the cold finger at 145°C. The sublimate was removed, the cold finger cleaned and reinserted, and the temperature raised. The solid did not sublime, but melted at 190°C, a yellow deposit gradually forming on the cold finger. This product did not give a clean i.r. spectrum and so it was recrystallized from toluene/pentane giving yellow crystals. An i.r. spectrum of the residue from the attempted sublimation showed only the yellow product to be present. Experiment 6.2.7. using Re$(CO)_5$Cl suggests that the white product initially formed was Re$(CO)_3$$(DPTAAH)_2$Br.

i) Yellow product

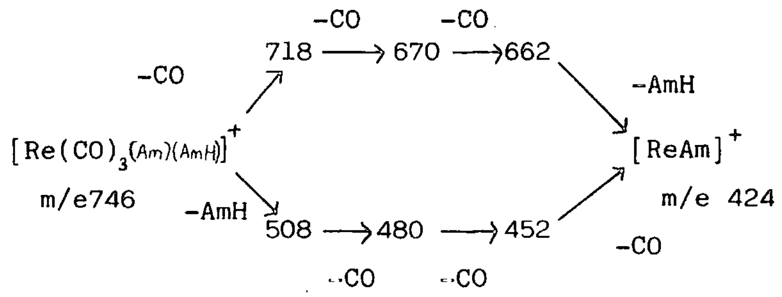
Analyses. Found: C,56.46; N,4.71; H,7.20:

(o-met)Re$(CO)_3$(DPTAA)(DPTAAH) requires C,56.36; N,4.70; H,7.51%

Infra-red spectra

ν(CO)	CH_2Cl_2	2015vs	1887vs broad		cm^{-1}
ν(CO)	Nujol	2002vs	1887vs	1878vs	cm^{-1}
ν(N-H)	CH_2Cl_2	3348w;	Nujol	3346m	cm^{-1}

Mass Spectrum: The parent ion [^{187}Re$(CO)_3$(DPTAA)(DPTAAH)]$^+$ was detected at m/e 746. Subsequent fragmentation was by either the loss of AmH or carbonyl. i.e.



[$Re_2$$(CO)_6$$(Am)_2$]$^+$ (see section 3.2.4.) was also observed to the high mass of the product.

'H n.m.r.

($CDCl_3$) aromatics : 6.78m.

methyls: 2.28(3), 2.17(1), 2.08(1), 1.68(1).

ii) White product ($Re(CO)_3(DPTAAH)_2Br$)

Infra-red spectrum

ν(CO)	Nujol	2020vs	1905vs	1890vs	cm^{-1}
ν(N-H)	Nujol	3210w	cm^{-1}		

Mass Spectrum: The mass spectrum was identical to $Re(CO)_3(Am)(AmH)$ above.

6.2.2. Reaction of $Re(CO)_5Br$ with 8DPTAAH

The reaction procedure was similar to 6.2.1., on this occasion $Re(CO)_5Br$ and DPTAAH were used in a 1:8 molar ratio, i.e. a large excess of DPTAAH. The product was identical to the yellow material in 6.2.1. A yield of 60% was successfully separated from DPTAAH(HBr) produced and DPTAAH by fractional crystallization of the reaction solution.

6.2.3. Reaction of $Re(CO)_5Br$ with 3DPAAH

$Re(CO)_5Br$ (0.885g, 2.18m mole) was suspended in monoglyme (50ml) and to it added DPAAH (1.372g, 6.54m mole). The mixture was refluxed for a total of 5½ hours by which time the reaction (which was being monitered by i.r. spectroscopy) appeared to be complete. The pale green solution was allowed to cool, then the monoglyme removed by evaporation, and the residue extracted with toluene (10ml). Pentane (2ml) was added to this solution, and the mixture placed in the freezer overnight. A pale yellow solid was precipitated form this solution, it was shown to be a tricarbonyl species and so was recrystallised from toluene/pentane (yield 0.85g).

To the mother liquor pentane (5ml) was added. This resulted in a yellow gum being formed. The solution was separated from the gum, reduced in volume and left to crystallise. It produced a white powder (0.505g) which was shown by i.r. spectroscopy to be a mixture of the tricarbonyl product and DPAAH(HBr). The yellowy gum was extracted with CCl_4 (30ml); crystallisation produced samples of both $Re(CO)_4$(DPAAH)Br and DPAAH(HBr).

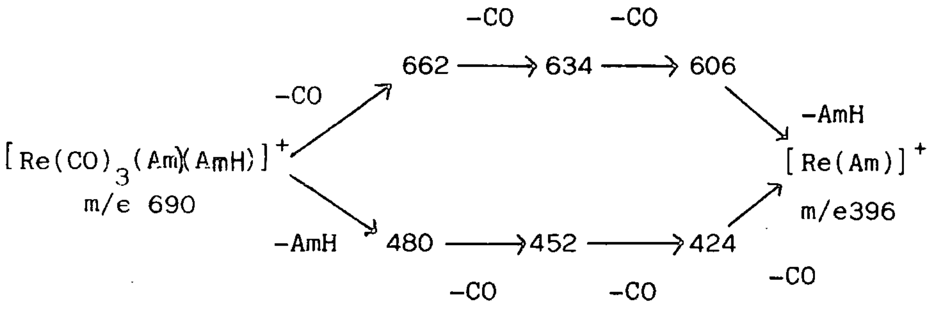
Analyses. Found C,54.06; N,8.10; H,4.14:

(o-met)$Re(CO)_3$(DPAA)(DPAAH) requires C,53.98; N,8.13; H,3 92%

Infra-red Spectra

ν(CO)	CH_2Cl_2	2012vs	1890vs broad,		cm^{-1}
ν(CO)	Nujol	2002vs	1894vs	1979vs	cm^{-1}
ν(N-H)	CH_2Cl_2	3343w	Nujol	3342m	cm^{-1}

Mass Spectrum: The parent ion$[^{187}Re(CO)_3(DPAA)(DPAAH)]^+$ was detected at m/e 690. Daughter ions corresponding to the stepwise loss of AmH and carbonyl were observed i.e.



$[Re_2(CO)_6(Am)_2]^+$ was also observed to the high mass of the product. Metastable peaks were not observed.

'H n.m.r.

(CDCl$_3$) aromatics: 7.26m, δ.

methyls: 2.10(1), 1.68(1), δ.

6.4.2. Reaction of $Re(CO)_5Br$ with 3DPBAH

The reaction conditions and procedure were identical to 6.2.3. The product (o-met)$Re(CO)_3$(DPBA)(DPBAH) was collected as yellow crystals (yield 60%).

Analyses. Found C,61.02; N,6.80; H,3.92:

(o-met)$Re(CO)_3$(DPBA)(DPBAH) requires C,60.52; N,6.88; H,3.81%

Infra-red Spectrum

ν(CO) CH_2Cl_2: 2018vs, 1898vs, 1885vs cm^{-1}.

ν(CO) Nujol: 2010vs, 1880vs broad cm^{-1}.

ν(N-H) CH_2Cl_2: 3341w. Nujol: 3340m cm^{-1}.

Mass Spectrum: The parent ion $[^{187}Re(CO)_3(DPBA)(DPBAH)]^+$ was observed at m/e 814. Daughter ions corresponding to the stepwise loss of AmH and carbonyls were also noted.

i.e.

$$\begin{tikzcd}
 & 786 \arrow[r, "-CO"] & 758 \arrow[r, "-CO"] & 730 \arrow[dr, "-AmH"] & \\
{[Re(CO)_3(Am)(AmH)]^+} \atop {m/e\ 814} \arrow[ur, "-CO"] \arrow[dr, "-AmH"'] & & & & {[Re(Am)]^+} \atop {m/e\ 458} \\
 & 542 \arrow[r, "-CO"'] & 514 \arrow[r, "-CO"'] & 486 \arrow[ur, "-CO"'] &
\end{tikzcd}$$

$[Re_2(CO)_6(Am)_2]^+$ was also observed to the high mass of the product.

6.2.5. Reaction of $Re(CO)_5Br$ with 3DPTBAH

To a suspension of $Re(CO)_5Br$ (0.851g, 2.09m mole) in monoglyme (40ml) was added DPTBAH (1.884g, 6.27m mole) and the mixture refluxed for 4 hours The monoglyme was removed by evaporation, and the residue extracted with toluene (10ml) forming a clear yellow solution. Addition of pentane (3ml) caused the deposition of a yellow gum, which was redissolved by evaporating off the pentane. Addition of ether (5ml) also caused gum formation, so the flask was set in the freezer for 3 days to allow the gum to fully develop. The solution was then removed from the gum, and filtered through alumina (1 inch column). Evaporation to low bulk and the addition of pentane caused precipitation to occur. The yellow solid produced was shown by i.r. spectroscopy to be (o-met)$Re(CO)_3(Am)(AmH)$ containing impuritites of $Re(CO)_4(AmH)Br$ and a second tricarbonyl species (ν(CO) 2014vs 1905vs 1896vs cm^{-1} Nujol), possibly $Re(CO)_3(AmH)_2Br$. The mixture was heated in vacuo in an attempt to sublime out the impurities or product. The solid however, melted at 180°C, and a yellow deposit slowly began to form on a cold finger when heated to 190°C. The small sample on the cold finger was shown to be pure (o-met)Re$(CO)_3$(Am)(AmH) by i.r. spectroscopy. It was being produced very slowly however and so the residue of the melt was recrystallized from toluene/pentane. Yellow crystals (0.515g, 28%) of (o-met)Re$(CO)_3$(Am)(AmH) were collected from this solution.

The yellow gum reported above was heated to 70°C and pumped under vacuum for 2 hours. It was then allowed to cool to room temperature and the residue scraped from the flask as crisp yellow flakes. An infra-red spectrum showed it to contain a new tricarbonyl species. It was recrystallized twice from ether/pentane, the first crystallization removing DPTBAH(HBr), and the second forming yellow crystals of the product, (0.13g). Analysis showed it to be a second isomer of (o-met)Re$(CO)_3$(Am)(AmH).

Analyses.

first isomer,	Found:	C,62.12;	N,6.44;	H,4.48.
second isomer,	Found:	C,62.43;	N,6.38;	H,4.87.
(o-met)Re$(CO)_3$(DPTBA)(DPTBAH)	requires	C,62.56;	N,6.40;	H,4.89%

Infra-red spectra

first isomer

ν(CO)	CH_2Cl_2:	2012vs,	1895vs,	1882vs	cm^{-1}.
ν(CO)	Nujol:	2010vs,	1890vs,	1877vs	cm^{-1}.
ν(N-H)	CH_2Cl_2:	3340w.	Nujol: 3340m		cm^{-1}.

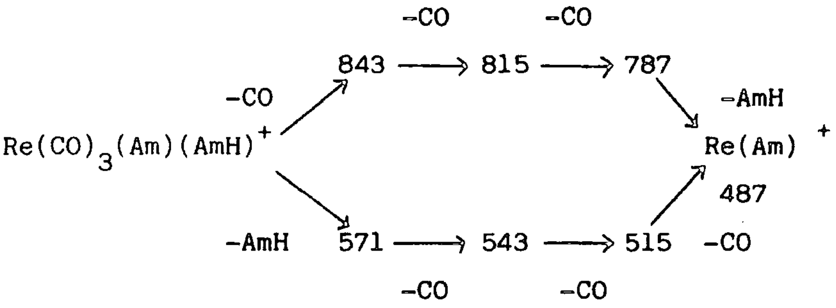
second isomer

ν(CO)	CH_2Cl_2:	2016vs,	1916vs,	1868vs	cm^{-1}.
ν(N-H)	CH_2Cl_2:	3332w cm^{-1}.			

'H n.m.r. spectra $CDCl_3$

first isomer:	aromatics 6.89m;	methyls 2.20(3)	2.09(1)	(δ)
second isomer:	aromatics 6.83m;	methyls 2.17(3)	2.07(1)	(δ)

Mass spectra: The mass spectra of both isomers were identical. the parent ion $[^{187}Re(CO)_3(DPTBA)(DPTBAH)]^+$ was observed at m/e 871. Daughter ions corresponding to the stepwise loss of AmH and the carbonyls were also observed i.e.



$[Re_2(CO)_6(Am)_2]^+$ was also observed to the high mass of the product. Metastable peaks were not observed.

6.2.6. Reaction of $[Re(CO)_4Br]_2$ with 6DPFAH

A mixture of $[Re(CO)_4Br]_2$ (0.500g, 0.661m mole) and DPFAH (0.777g, 3.966m mole) in monoglyme (30ml) was refluxed for 1½ hours forming a pale yellow solution. The solvent was then removed by evaporation and the residue extracted with toluene (10ml). The addition of pentane (4ml) and cooling produced yellow crystals of (o-met)$Re(CO)_3$(DPFA)(DPFAH). These were recrystallized from a toluene/pentane solution. (yield 0.421g, 48%).

Analyses. Found: C,52.65; N,8.49; H,3.50:

(o-met)$Re(CO)_3$(DPFA)(DPFAH) requires C,52.63; N,8.47; H,3.48%

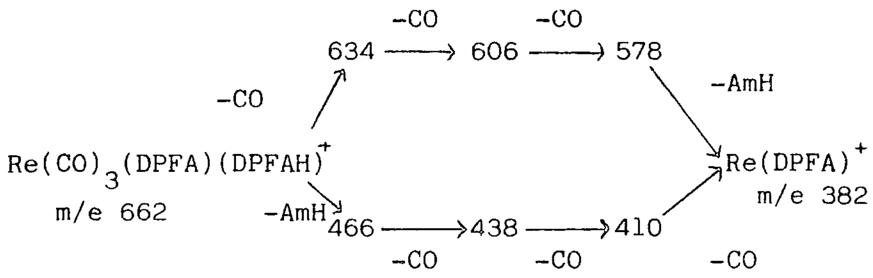
Infra-red spectra

ν(CO) CH_2Cl_2: 2020vs, 1885vs broad cm^{-1}.

ν(CO) nujol: 2015vs, 1900vs, 1878vs cm^{-1}.

ν(N-H) CH_2Cl_2: 3365w. nujol: 3348m cm^{-1}.

Mass spectrum: The parent ion $[^{187}Re(CO)_3(DPFA)(DPFAH)]^+$ was observed at m/e 662. Daughter ions corresponding to the stepwise loss of DPFAH and carbonyls were observed i.e.



Re(CO)$_6$Am$_2$ was also observed to the high mass of the product.

Metastable peaks were not observed.

6.2.7. Reaction of Re(CO)$_5$Cl with 3DPTAAH

A mixture of Re(CO)$_5$Cl (0.500g, 1.38m mole) and DPTAAH (0.987g, 4.15m mole) in monoglyme (40ml) was refluxed for 6 hours giving a pale yellow solution. The solvent was then removed by evaporation giving a gummy yellow residue. The residue was washed with hot hexane (2 x 20ml, 50°C), the pale yellow hexane washings were combined and the solution reduced in volume to 10ml by evaporation and placed in the freezer.

The undissolved residue was extracted with CHCl$_3$(10ml) forming a pale yellow solution and hexane added to it. This produced a pale yellow precipitate, (1.010g). An i.r. spectrum of this precipitate (ν(CO) 2022vs 2010vs 1885vs broad; ν(N-H) 3344m 3215w 3170w cm^{-1} Nujol) showed it to contain more than one species. The solid was recrystallised from petroleum-ether (100°-120°, 40ml) by refluxing for one hour and filtering the solution whilst hot (temperature greater than 90°C). A white powder precipitated (0.416g) which was identified as Re(CO)$_3$(DPTAAH)$_2$Cl. The remaining solution was shown to contain (o.met)Re(CO)$_3$(DPTAA)(DPTAAH) by i.r. spectroscopy. It was not further purified.

The hexane washings of the original yellow residue produced yellow crystals (o-met)Re(CO)$_3$(DPAA)(DPAAH) (0.259g) after one week in the freezer.

Data for $Re(CO)_3(DPTAAH)_2Cl$

Analyses. Found: C,53.82; N,7.18; H,4.60; Cl,4.60:

$Re(CO)_3(DPTAAH)_2Cl$ requires c,53.73; N,7.16; H,4.68; Cl,4.54%

Infra-red spectra

ν(CO)	CH_2Cl_2:	2022vs	1895vs broad		cm^{-1}
ν(CO)	Nujol:	2022vs	1904vs	1888vs	cm^{-1}
ν(N-H)	Nujol:	3210w	3150w		cm^{-1}

'H n.m.r. spectrum

$CDCl_3$ (δ) aromatics 7.09 7.03(8);

N-H 6.02 5.90(1); methyls 2.33(6) 1.63(3)

Mass spectrum: The parent ion$[^{187}Re(CO)_3(DPTAAH)_2Cl]^+$ was observed as a very weak peak at m/e 782. Loss of HCl was almost immediate, this formed $Re(CO)_3(DPTAA)(DPTAAH)$ and the remaining spectrum was identical to (o-met)$Re(CO)_3(DPTAA)(DPTAAH)$ as described in 6.2.1.

6.2.8. Reaction of $Re(CO)_5Cl$ with 2DPTAAH

This reaction was identical to 6.2.7. in all aspects apart from the molar ratios of the reactants. It did not form $Re(CO)_3(DPTAAH)_2Cl$ exclusively, but also (o-met)$Re(CO)_3(DPTAA)(DPTAAH)$ and $Re(CO)_4(DPTAAH)Cl$. The products were isolated by fractional crystallization, and were identified by their infra-red spectra which compared favourably with previously prepared samples.

6.2.9. Reaction of $Re(CO)_5Br$ with 3DPTAAMe

A mixture of $Re(CO)_5Br$ (0.500g, 1.23m mole) and DPTAAMe (0.931g, 3.69m mole) in monoglyme (40ml) was refluxed for 6 hours (no further change of ν(CO) occurred after 2½ hours) forming an orange solution. On cooling a white precipitate (0.212g) formed, shown by infra-red spectroscopy to be DPTAAMe(HBr). The solvent was then removed by evaporation and the gummy residue extracted with toluene (10ml). Cooling and the addition of pentane did not produce a precipitate. The solution was chromatographed on an alumina column (15 x 2cm) using toluene as eluent. Evaporation of the fractions produced only DPTAAMe. The column was washed with CH_2Cl_2 but the carbonyl product was not recovered. The alumina was then soxhleted with monoglyme for 5 hours, and the resulting pale yellow solution evaporated to a few mls. Addition of pentane caused the precipitation of a powdery white product which was recrystallized from toluene/pentane (yield .113g).

Analyses. Found: C,57.65; N,7.44; H,5.32:

(o-met)Re$(CO)_3$(DPTAAMe)(DPTAAMe) requires C,57.42; N,7.24; H,5.04%

Infra-red spectra

ν(CO) CH_2Cl_2: 2018vs, 1900vs, 1875vs cm^{-1}.

ν(CO) Nujol: 2018vs, 1900vs broad cm^{-1}.

Mass spectrum: The parent ion O-metallated $[^{187}Re(CO)_3(DPTAAMe)(DPTAAMe)]^+$ was observed at m/e 774. Fragmentation was complex with initial loss of CH_2 or CO; the principal daughter ions and their assignments are listed below.

m/e	Loss	ion
774	-	parent
760	CH_2	$Re(CO)_3(AmMe)(AmH)^+$
719	2(CO)	$Re(CO)(AmMe)(AmMe)^+$
702	2(CO)+MeH	$Re(CO)(AmMe)(Am-H)^+$
675	3(CO)+MeH	$Re(AmMe)(Am-H)^+$
508	AmMe+CH_2	$Re(CO)_3(Am)^+$
424	AmMe+CH_2+3(CO)	$Re(Am)^+$

Metastable peaks were not observed.

6.2.10 Reaction of (o-met)$Re(CO)_3$(DPTAA)(DPTAAH) with PPh_3

A mixture of (o-met)$Re(CO)_3$(DPTAA)(DPTAAH) (0.100g, 0.13m mole) and PPh_3 (0.035g, 0.13m mole) was dissolved in toluene (10ml) and stirred at room temperature for 24 hours. An infra-red spectrum of the solution showed that the broad ν(CO) at 1870-90 cm^{-1} had been replaced by two sharp ν(CO)'s at 1915 and 1892 cm^{-1}. Evaporation and cooling produced the chelated amidino product $Re(CO)_3(DPTAA)(PPh_3)$ as an off-white powder (0.08g, 80%). It was identified by its infra-red and 'H n.m.r. spectra which were identical to that described for $Re(CO)_3(DPTAA)(PPh_3)$ in Section 5.2.14.

6.2.11 Reactions of (o-met)$Re(CO)_3$(Am)(AmH) with PPh_3

The ortho-metallated complexes (o-met)$Re(CO)_3$(Am)(AmH) (where Am=DPAA, DPTBA and DPBA) were treated with an equimolar amount of PPh_3 as in 6.2.10 above. Infra-red spectra of the products showed that the chelated amidino complexes $Re(CO)_3(Am)(PPh_3)$ had formed. These products are fully described in Chapter 5.

6.2.12 Reaction of (o-met)$Re(CO)_3$(DPTAA)(DPTAAH) with HBr.

A small sample of (o-met)$Re(CO)_3$(DPTAAH) (about 0.01g) was suspended in MeOH (10ml) and hydrobromic acid (47%) was added by dropwise addition with stirring until the rhenium complex changed colour from yellow to white. The solvent was then syringed off the precipitate and the solid dried under vaccuum. The infra-red spectra showed it to be $Re(CO)_3(DPTAAH)_2Br$

6.2.13 Reactions of $Re(CO)_4$(COAm) or $Re(CO)_4$(Am) with AmH

The formation of ortho-metallated products by these routes are described previously in sections 3.2.10 and 5.2.22-24.

6.2.3. DISCUSSION

When $Re(CO)_5Br$ is refluxed in monoglyme with an amidine [RN=C(R')NHR = AmH; Am = DPAA,DPTAA,DPBA,DPTBA or DPFA] the complexes $Re(CO)_3(Am)(AmH)$ are formed in good yield. This formulation is derived on the evidence of elemental analysis, infra-red and mass spectroscopy.

In order that the complexes fulfil the 18 electron rule, the amidine groups must contribute a total of five electrons to the rhenium atom. This is achieved by one amidine group donating three electrons and the other two. The existence of a medium intensity infra-red absorption at about 3340 cm^{-1} for each of the complexes indicates the presence of an N-H moiety. Moreover, the unusually sharp nature of this band and its relatively high frequency indicates that it is not due to the N-H vibration of the amino N-H in a bound amidine molecule c.f. $Re(CO)_4(NR=CR'-NHR)X$ (Chapter 4). An unusually strong N-H absorption at this same frequency has been attributed to an ortho-metallated amidino group in the complex $[Pd(Am)Cl]_n$ [47](Fig. 1.20), and it is believed that a similar six membered ortho-metallated amidino-ring complex is formed with one of the amidine groups in $Re(CO)_3(Am)(AmH)$. These complexes are hereafter referred to as (o-met)$Re(CO)_3(Am)(AmH)$ to distinguish this type of amidine-rhenium bonding from other types.

The existence of three terminal metal-carbonyl vibrations in the infra-red spectra of these complexes indicates a facial isomer is formed, and the acetamidine and formamidine derivatives are therefore assigned the following structure (Fig. 6.3.1.). The major product from the reaction using DPTBAH, and the only product from the reaction using DPBAH are also assigned a similar six membered ortho-metallated ring structure (in preference to a five membered ortho-metallated ring, via the C-Ph substituent) because of the similarity between their carbonyl stretching frequencies and those of the acetamidine and formamidine derivatives.

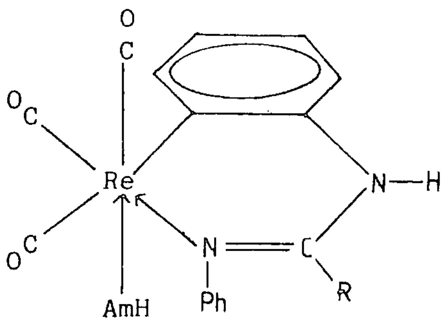


Fig. 6.3.1.

A second product was isolated from the reaction of $Re(CO)_5Br$ with DPTBAH. It also has a distinctive N-H absorption, but this occurs at 3332 cm^{-1}, a slightly lower value than that observed for the six membered ortho-metallated rings. The three carbonyl stretching frequencies are markedly different to those of the six-membered ortho-metallated ring complex (o-met)$Re(CO)_3$(DPTBA)(DPTBAH) which is produced as the major product. This second product is thought to contain a five membered ortho-metallated amidino group, the ortho-metallation now occurring through the phenyl substituent on the central carbon atom of the amidine (Fig. 6.3.2.)

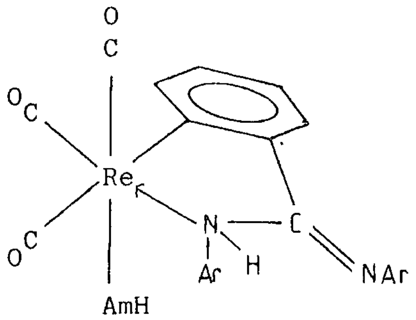


Fig. 6.3.2.

The analogous DPBA derivative was not observed in the reaction of $Re(CO)_5Br$ with DPBAH, but was isolated as a minor product in the reaction of $Re(CO)_4$(DPBA) with DPBAH (See 5.2.21).

The proton n.m.r. spectra of all the para-tolyl ortho-metallated species described above (both five and six membered rings) show just two CH_3 resonances attributable to the para-tolyl methyl groups, in the ratio 3:1. It must be assumed that the two electron bound amidine molecule and the para-tolyl group on the ortho-metallated amidino group remote from the metal, have co-incidental overlap of para-tolyl Me resonances; the unique Me resonance being due to the Me group on the ortho-metallated aromatic ring. The acetamidine derivatives show two more CH_3 resonances; these are due to the different environments of the central $C-CH_3$ groups.

The infra-red spectra of both the five and six membered ortho-metallated ring complexes in the ν(N-C-N) region of the spectrum are complicated, with many broad ill defined peaks. The highest frequency bands (assigned to the ν(N-C-N) asymmetric stretch) are listed in table 6.3.1. together with the corresponding band of the parent amidine. It is not possible to ascertain which group gives rise to this band, but a

Table 6.3.1. The highest frequency absorptions associated with the (N-C-N) vibrations of (o-met)Re$(CO)_3$(Am)(AmH) and the parent amidines.

Amidine used	Highest frequency ν(N-C-N)cm^{-1} ‡ (o-met)Re$(CO)_3$(Am)(AmH)		ν(N-C-N)asym cm^{-1} ‡ parent amidine
DPAAH	(6)	1595	1630
DPTAAH	(6)	1592	1630
DPFAH	(6)	1645	1665-1670
DPBAH	(6)	1605	1624
DPTBAH	(6)	1600	1616
DPBAH	(5)	1605	1624
DPTBAH	(5)	1605	1616

(5),(6); denotes size of ortho-metallated ring complex.

‡ Nujol

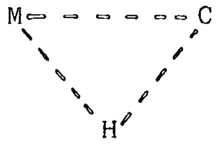
significant decrease from that of the parent amidine is apparent. In common with the other rhenium amidino-species in this thesis this $\Delta\nu$ is attributed to:- a) the perturbation of the -N-C-N- caused by the heavy rhenium atom; b) a slight degree of $d \rightarrow \pi^*$ back bonding from the rhenium to amidine ligand; or c) a combination of the above.

The reaction of $Re(CO)_5Br$ with 2DPTAAH also produced a trace of a second tricarbonyl species, but enough sample for positive identification was not isolated. When this reaction was repeated with an excess of DPTAAH this second product was not observed. Evidence for similar complexes was not detected in the reactions of $Re(CO)_5Br$ with the other amidines. However, a very similar species was isolated from the reaction of $Re(CO)_5Cl$ with three mole equivalents of DPTAAH. The product showed three carbonyl stretching frequencies in the infra-red spectrum, two methyl resonances (ratio2:1) in the 'H n.m.r. spectrum and analysed correctly for $Re(CO)_3(DPTAAH)_2Cl$. The mass spectrum confirmed this formulation and the complex is assigned a facially substituted type structure containing two two-electron donor amidine molecules on the basis of the infra-red and 'H n.m.r. data. This complex and the now identified bromide derivative are important when considering the reaction route and mechanism for the formation of (o-met)$Re(CO)_3$(Am)(AmH) from $Re(CO)_5X$ (X=Cl,Br).

Another important reaction in this respect is that of the trisubstituted amidine, DPTAAMe, with $Re(CO)_5Br$. It also forms an orthometallate product, $Re(CO)_3$(o-met)(AmMe)(AmMe), identified by analysis, mass spectroscopy and by comparison of its infra-red spectrum with (o-met)$Re(CO)_3$(DPTAA)(DPTAAH). This reaction demonstrates that the amino proton need not enter into the ortho-metallation reaction.

Current thinking on the mechanism of intra-molecular aromatic substitution involves a process mimicking classical electrophilic aromatic substitutions. This process is undoubtedably helped by the ability of the ortho-proton of the aryl group to approach the metal very closely, perhaps with the formation of a three centre intermediate.

i.e.



The proposed mechanism for the formation of the six membered ortho-metallate species from Re(CO)$_5$Br (orCl) is shown in Figure 6.3.3. and involves the presynthesis of Re(CO)$_3$(AmH)$_2$Br by metathetical

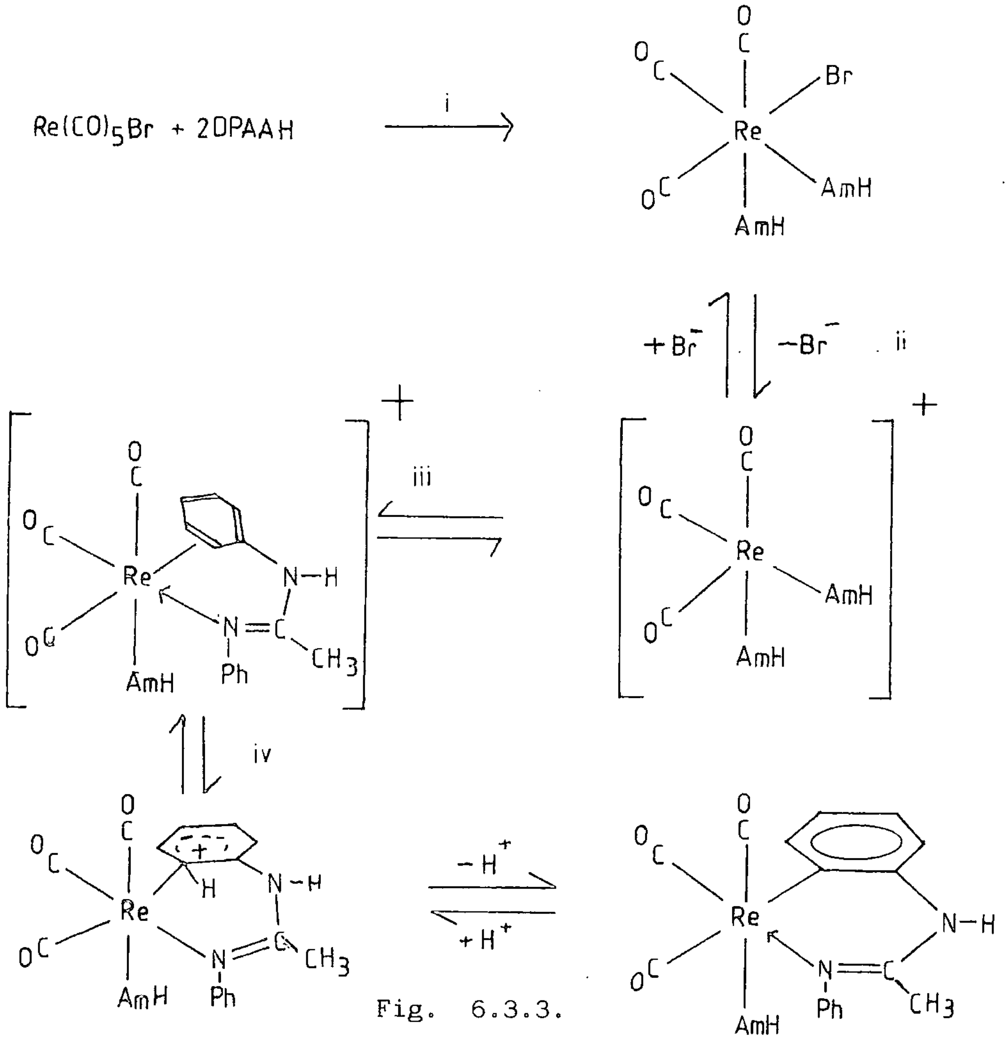


Fig. 6.3.3.

substitution of two carbonyls. This presynthesis is a valid step as the normal product of the reaction of $Re(CO)_5Br$ with an amine is $Re(CO)_3(Amine)_2Br$ [98] , and the intermediates $Re(CO)_3(DPTAAH)_2X$ (X=Cl,Br) have been isolated in the ortho-metallation reaction when using DPTAAH. The following steps, the elimination of Br^- and the formation of a metal-arene complex, followed by the formation of a carbonium ion, and then the final elimination of H^+ are similar to those proposed for the formation of a 5-membered ortho-metallated product from $[PdCl_4]^{2-}$ with Ar-N=N-Ar [114]. The reversible nature of the reaction was demonstrated by the action of hydrobromic acid on a suspension of (o-met)$Re(CO)_3$(DPTAA)(DPTAAH) in methanol. This caused the formation of $Re(CO)_3(DPTAAH)_2Br$ and indicates the route by which the other rhenium-tricarbonyldiamidinehalide complexes can be synthesised.

The formation of some five membered ortho-metallate ring complex when DPTBAH was refluxed with $Re(CO)_5Br$ is thought to follow a similar reaction route to the acetamidines (Fig. 6.3.3.). In this instance, the C-Ph group is also able to take up a position where the ortho-proton approaches the metal very closely, facilitating electrophilic substitution by the metal. Five membered ortho-metallate ring systems are generally much more common than six membered ring systems, minimum steric strain being the argument usually forwarded for this. The acetamidines and formamidines in this study are only able to form six membered rings, but the benzamidines are able to form both five and six membered rings, the six membered ring being most favoured. It is possible that a substantial degree of stabilization can occur for these six membered ring systems by the formation of a pseudo-aromatic delocalised ring of electrons (Fig. 6.3.4.), although the crystal structure of (o-met AmH) PdCp showing a puckered ring type of arrangement makes this unlikely [58].

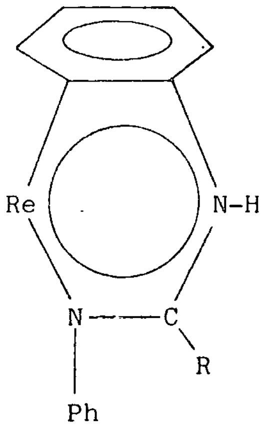


Fig. 6.3.4.

During the initial preparations of the two electron donor amidine Re(CO)$_4$(AmH)Br (Chapter 4) complexes from (Re(CO)$_4$Br)$_2$ and AmH it was discovered that substantial amounts of (o-met)Re(CO)$_3$(Am)(AmH) complexes formed if the mixture was heated above 40°C. The mechanism for this reaction is assumed to be identical as that described in Fig. 6.3.3., for the reaction of Re(CO)$_5$Br and AmH. In this case the first metathetical substitution of CO by AmH has already taken place.

The reactions of Re(CO)$_4$(Am) and Re(CO)$_4$(COAm) with AmH in refluxing toluene also produce ortho-metallated products (see Chapters 3 and 5), decarbonylation to the chelate product probably occurring first for the carbamoyl complex. These reactions may proceed via a similar route to that shown in Fig. 6.3.3., the initial steps being the metathetical substitution of carbonyl by AmH, and the protonation (from the solvent or other amidine species) of one end of the chelated amidine. Formation of a π -arene complex could then follow, resulting in electrophilic substitution by the metal and the eventual return of the proton to the solvent (or amidine species) (Fig. 6.3.5.A).

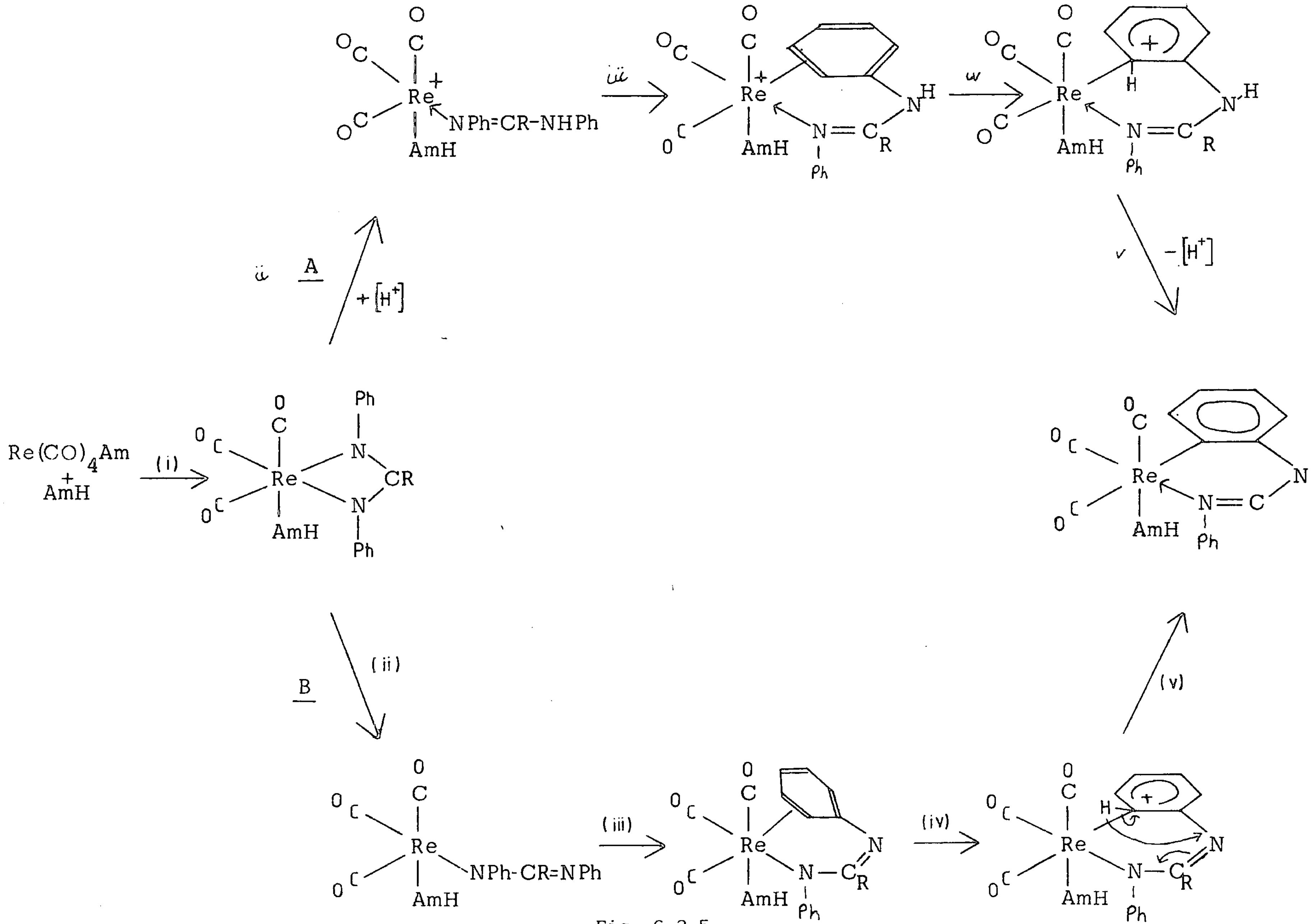

Re(CO)$_4$Am
+
AmH
(i)
A
+[H$^+$]
ii
iii
iv
v
−[H$^+$]
B
(ii)
(iii)
(iv)
(v)
NPh=CR-NHPh
NPh-CR=NPh
AmH
Re
CR
N
Ph
R
H

Fig. 6.3.5.

Alternatively an interesting reaction involving a 1–3 shift of the ortho proton to the nitrogen atom might occur. This reaction scheme is mechanistically described in Figure 6.3.5.B.

It is difficult to determine the extent steric crowding has on the formation of the ortho-metallated complexes in preference to the chelated amidino type complexes. It was found that ortho-metallation only occurred when two amidine groups were bound to the metal, and not when a combination of amidine and PPh_3 groups were present. Molecular models show that both the chelated amidino complexes $Re(CO)_3(Am)L$ ($L=AmH$, PPh_3) show strong interactions between the ligands in certain configurations. However, it is likely that steric interactions in the intermediate complexes $Re(CO)_3(AmH)(L)X$ ($L=AmH,PPh_3$) are more important. The diamidine complex can show a much greater degree of steric interaction, causing one of the aryl groups to approach the metal closely.

The formation of chelated amidino complexes in preference to the ortho-metallated complexes for $Re(CO)_3(Am)(AmH)$ is perhaps more rationally explained by considering the electron donor-acceptor properties of the amidine and PPh_3 ligands. The hypothetical $Re(CO)_3(PPh_3)$ moiety is able to accept a chelating amidino group containing two essentially σ-donating $N \rightarrow Re$ bonds, as the resulting charge on the metal can be dissipated in both the metal → carbonyl $d \rightarrow \pi^*$, and metal → phosphorus $d \rightarrow d\pi$ orbitals. On the other hand, the hypothetical $Re(CO)_3(AmH)$ moiety already has one essentially σ-donating ligand. The addition of a σ,σ bonded chelating ligand would result in an unacceptable build up of charge on the rhenium atom as it would be unable to dissipate all the charge accumulated by three essentially σ-bonded ligands amongst its remaining three carbonyl groups. This argument is borne out by the observation that $Re(CO)_5Br$ only forms disubstituted derivatives when reacted with amine ligands.

i.e. $Re(CO)_5Br + Amine \longrightarrow Re(CO)_3(Amine)_2Br + 2CO$ [98] .

The above considerations and the proven reversibility of the ortho-metallation reaction with hydrobromic acid are also useful in considering the reaction of ortho-metallated $Re(CO)_3(Am)(AmH)$ complexes with PPh_3 to give the chelated amidino complexes $Re(CO)_3(Am)(PPh_3)$. Protonation of the ortho-metallated species could occur in solution, resulting in the reversal of reaction steps IV and V in figure 6.3.3. until the π -arene complex is reached. Metathetical substitution of the aryl group of PPh_3 may then occur, steric crowding then causing the elimination of AmH. The formation of the stable chelate complex then follows by nucleophilic attack by the amino nitrogen at the metal and the elimination of a proton. An alternative mechanism might again involve a proton in a 1,3 shift. If the steps iii to v of Figure 6.3.5.B are reversible the complex $Re(CO)_3(AmH)(PPh_3)(NPh-CR=NPh)$ containing a monodentate amidino ligand could easily be formed. Steric crowding of the facially substituted complex may then cause the nucleophilic substitution of AmH by the imino nitrogen of the monodentate amidino group resulting in the stable, chelated amidino complex, $Re(CO)_3(Am)(PPh_3)$.

CHAPTER 7

Iron Amidino Complexes

7.1. INTRODUCTION

This chapter describes a study of some simple iron compounds with amidines and lithioamidines. The general introduction cited examples of chelated and bridged amidino systems [40,48,56-62, 68-71] , and this work has extended the range to include rhenium-carbonyl acetamidines and benzamidines. Unpublished work by Kilner and Pietrzykowski has shown that copper forms a range of amidino complexes involving both copper (+I) and (+II). The cuprous complexes, although synthesised by a new route are the same as those reported by Bradley[45 }. The cupric complexes are made by the reaction of lithioamidines on $CuCl_2$ in monoglyme. A range of these cupric complexes has been made using diaryl -formamidines, -acetamidines and -benzamidines. They are all air stable purple solids that decompose quickly in solution if air is admitted. A recent crystal structure of one of them, $Cu(DPAA)_2$ [116] , has shown it to be dimeric with four bridging amidino ligands. The complex is diamagnetic, and is shown to have a Cu-Cu single bond.

Iron is known to form stable complexes with β-diketones, $Fe(acetylacetone)_3$ [117] is one such example (Fig. 7.1.1). It is an air stable monomeric

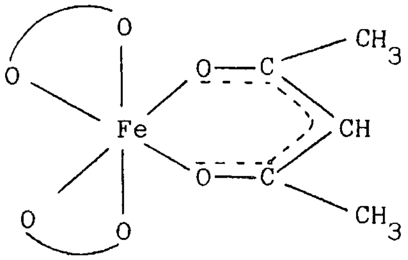


Fig. 7.1.1.

species that is soluble in most organic solvents. The complex is bright red in colour and is paramagnetic having five unpaired electrons. Trisdiphenyltriazeneiron(III) is also known; it is an unstable black purple solid prepared by the action of silverdiphenyltriazene on anhydrous $FeCl_3$. The complex is believed to be monomeric, but has not been further investigated since its synthesis in 1963 [42].

The crystal structure of trisdiphenyltriazene cobalt(III) [89] has been performed, and the diphenyltriazene ligands (Ph-N-N-N-Ph = dpt.) are found to be delocalised chelate (Fig. 7.1.2). In this complex the triazenido ligand has a small $N\hat{Co}N$ angle of 65° (c.f. 90° for perfect octahedron), and a strained $N\hat{N}N$ angle of 105°. This is in contrast to the monodentate triazenido complexes Cu(dpt) [118] and $Ni(dpt)_4$ [119] which have $N\hat{N}N$ angles of 116.0° and 115.8° respectively; and the bridged triazenido complex $Cu_2(dpt)_2$ [120] which has also an unstrained $N\hat{N}N$ angle of 116°.

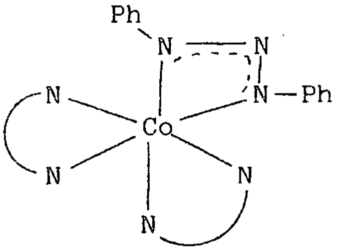


Fig. 7.1.2

In the light of the $Fe(acac)_3$ and $Fe(dpt)_3$ complexes, the synthesis of $Fe(Am)_3$ complexes therefore seemed a distinct possibility. It was thought worthwhile to investigate various synthetic pathways into iron-amidino complexes to see if differing types of iron-amidino bonds resulted, and to investigate whether the bonding mode was dependent upon the type of amidine used (i.e. formamidine, benzamidine, acetamidine) or the presence of other ligands.

The triazenido complexes of cobalt have shown that considerable ring strain is present when bonding takes place in a chelate fashion. It was of interest to see if different amidino groups could also accommodate such a distortion of the valency angles or whether bridging or ortho-metallated species necessarily resulted.

7.2. EXPERIMENTAL

7.2A REACTIONS IN SOLUTION

7.2A.1 Reaction of $FeCl_3$ with 3LiDPAA

A solution LiDPAA was prepared by dissolving DPAAH (3.912g, 18.609m mole) in monoglyme (20ml), freezing to 77K, and then adding n-butyllithium (18.609m mole in hexane solution). The flask was then warmed to room temperature and stirred for about 15 minutes. The pale yellow solution thus formed, was slowly added to a stirred solution of anhydrous $FeCl_3$ (1.000g, 6.203m mole) in monoglyme (10ml), occasionally cooling the reaction vessel by dipping it in liquid nitrogen. The $FeCl_3$ solution darkened as soon as the LiDPAA was added, gradually changing colour from yellow to blue-green to navy blue. After all the LiDPAA had been added the solution was stirred at room temperature for 30 minutes to ensure complete reaction. The monoglyme was removed in vacuo, the residue extracted with toluene (40ml), filtered to remove LiCl, and then crystallized by reducing the solution to low volume and the addition of hexane. The product $Fe(DPAA)_3$ which formed navy blue plate like crystals was washed with hexane and pumped dry (yield 3.12g, 74%). Samples for analysis were recrystallized from $CHCl_2$/hexane.

Analyses.	Found	C,73.98;	N,12.32;	H,5.74;	Fe,7.96
$Fe(DPAA)_3$ requires		C,73.78	N,12.29;	H,5.76;	Fe,8.17%
Melting point		Decomposition at 134°C under nitrogen			

Infra-red and 'H n.m.r. spectra

Decomposition by reaction with air prevented the infra-red spectrum of $Fe(DPAA)_3$ from being recorded. The 'H n.m.r. spectrum could not be recorded due to severe broadening of the signals caused by paramagnetic iron(III).

Mass spectrum: The observed spectrum above m/e 208 consisted of just three peaks; $[Fe(DPAA)_3]^+$ at m/e 683, $[Fe(DPAA)_2]^+$ at m/e 464 and $[DPAAH]^+$ at m/e 209. Metastable peaks were not observed.

7.2A.2. Reaction of $FeCl_3$ with 3 LiDPTAA

Experimental procedure was identical to 7.2A.1. The product, also a navy blue crystalline solid was collected in 75% yield.

Analyses. Found:	C,74.90; N,10.95; H,6.65; Fe,7.60:
$Fe(DPTAA)_3$ requires	C,75.08; N,10.95; H,6.70; Fe,7.27%
Melting point	Decomposition at 110°C under nitrogen

Infra red and 'H n.m.r. spectra:- as for $Fe(DPAA)_3$, 7.2A.1

Mass Spectrum: The observed spectrum above m/e 237 consisted of just four peaks; $[Fe(DPTAA)_3]^+$ at 767, $[Fe(DPTAA)_2]^+$ at m/e 530, $[Fe(DPTAA)]^+$ at m/e 293 and $[DPTAAH]^+$ at m/e 238. Metastable peaks were not observed.

7.2A.3 Reaction $FeCl_3$ with 3LiDPBA

A solution of LiDPBA was prepared by dissolving DPBAH (1.508g, 5.55m mole) in monoglyme (25ml) freezing to 77K and then adding n-butyllithium (5.55m mole in hexane solution). The mixture was warmed to room temperature and stirred for about 15 minutes. The yellow solution thus formed was then slowly added to a solution of anhydrous $FeCl_3$ (0.300g, 1.85m mole) in monoglyme (10ml), occasionally cooling the reaction vessel by dipping it in liquid nitrogen. The pale blue solution that formed immediately on addition of the LiDPBA to the $FeCl_3$ gave way to a green solution after about 30 seconds; a green precipitate was then deposited. The mixture was stirred at room temperature for an additional 30 minutes, then filtered giving a red solution and a bright green precipitate. The green precipitate was washed with toluene (4x10ml), dried, washed with water (4x5ml), and finally dried in vacuo giving the product $[Fe(DPBA)_3]_n$ as a bright green powder (yield 1.204g, 75%). The red solution was concentrated by evaporation, but decomposed (by slow infusion of air) to an orange gum before a crystalline product could be isolated.

Data for $[Fe(DPBA)_3]_n$

Analyses. Found: C,78.40; N,9.60; H,5.02; Fe,5.23:
$[Fe(DPBA)_3]n$ requires C,78.42; N,9.62; H,5.06; Fe,6.28%

Melting point Decomposition at 95°C under nitrogen

Infra red spectrum (KBr disc)

3050w 3024vw 1624s 1588vs 1576m 1530vs
1490shm 1483s 1450shw 1443s 1438s 1419m 1330m
1272w 1242w 1221m 1172w 1152w 1105m 1075w
1026m 998vw 920w 895vw 832vw 792w 779m
768wm 759s 744m 700s 694shs 540w 520wm
505w

'H n.m.r. spectrum: could not be recorded as the product was insoluble.

Mass spectrum: The iron containing ions are tabulated below, the major peak in the spectrum being DPBA at m/e 271.

ion	m/e	%	fragment lost
$Fe(DPBA)_3^+$	869	28	
$Fe(DPBA)_2^+$	598	100	DPBA
$Fe(DPBA)(PhNCPhNH_2)^+$	523	7	C_6H_3
$Fe(DPBA)(Ph_2N)^+$	495	16	$C-NH_2$
$Fe(DPBA)(PhN)^+$	418	10	C_6H_5
$Fe(DPBA)(Ph)^+$	404	17	N
$Fe(DPBA)^+$	327	73	C_6H_5

Magnetic Moment. The complex was found to be paramagnetic, having a magnetic moment of 5.47B.M. (as measured on a Gouy balance).

7.2A.4 Reaction of $FeCl_3$ with 3LiDPFA

A solution of LiDPFA was prepared by dissolving DPFAHH (3.546g, 18.609m mole) in monoglyme (30ml), freezing to 77K, and adding n-butyllithium. The mixture was warmed to room temperature and stirred for 15 minutes. The pale yellow solution thus formed was then slowly added to a stirred solution of anhydrous $FeCl_3$ (1.000g, 6.203m mole) in monoglyme (10ml), occasionally cooling the reaction vessel by dipping it in liquid nitrogen. There was an immediate colour change yellow to dark red on mixing the two solutions, no further change was observed after stirring for 30 minutes. The monoglyme was removed in vacuo giving a red-black residue which was extracted with CCl_4 (40ml), filtered, reduced in volume by evaporation (to 10ml) and hexane (10ml) added. The product $[Fe(DPFA)_3]_n$ a red-black powder was collected by filtration (yield 3.07g, 77%).

Analyses. Found:	C,73.08;	N,13.21;	H,5.19;	Fe,8.65:
$Fe(DPFA)_3$ requires	C,73.00;	N,13.10;	H,5.14;	Fe,8.74%

Melting point Decomposition at 85°C under nitrogen

Infra red and 'H n.m.r. spectra: as for $Fe(DPAA)_3$, 7.2A.1

Mass spectrum : The highest m/e value recorded was 252, corresponding to $[Fe(DPFA)]^+$. The strongest peak in the spectrum at m/e 195 was assigned to DPFA.

7.2A.5 Reaction of $FeCl_2$ with 2 LiDPAA

To a solution of anhydrous $FeCl_3$ (0.300g, 1.84m mole) in monoglyme (10ml) was added n-butyllithium (1.848m mole in hexane solution) forming an oily brown deposit. To this was added a solution of Li(DPAA), prepared by the addition of n-butyllithium (3.696m mole in hexane solution) to DPAAH(0.776g, 3.696m mole) in monoglyme (10ml) at 77K. This produced a brown solution which was stirred at 20°C overnight. The solvent was removed in vacuo and the brown residue washed with toluene (10ml) giving a navy blue solution and a brown gum. The blue solution was evaporated to dryness and a mass spectrum obtained of the product. The gum could not be induced to crystallize and was not investigated further.

Mass spectrum: The parent ion was found at m/e 683, the next peaks occurring at m/e 464 and 209. This is identical to the $Fe(DPAA)_3$ spectra; the complex is presumably formed by incomplete reduction of the $FeCl_3$ species.

7.2A.6 Reaction of $FeCl_2$ with 2LiDPTAA

A solution of LiDPTAA was prepared by the addition of n-butyllithium (27.900m mole in hexane solution) to a solution of DPTAAH (6.612g, 27.900m mole) in monoglyme frozen to 77K. The mixture was warmed to room temperature and stirred for about 15 minutes. This solution was slowly added to a suspension of anhydrous $FeCl_2$ (1.772g, 13.950m mole) in monoglyme (10ml), cooling occasionally by dipping the reaction into liquid nitrogen. A brown precipitate in a red-brown solution formed and persisted as the mixture was stirred overnight. Filtration produced a red solution and a brown precipitate. The red solution was concentrated by evaporation, and hexane added. A crimson solid precipitated. It was collected by filtration and washed with hexane (yield 1.56g). The brown precipitate was found to be insoluble in CH_2Cl_2, monoglyme, and toluene. After being washed with these solvents it was dried in vacuo (yield 5.42g). An attempt to recrystallize the brown precipitate by refluxing in monoglyme failed as the solid was not soluble.

Data for red solid

Analyses.	Found:	C,71.31;	N,11.16;	H,8.86:
$Fe(DPTAA)_2$	requires,	C,72.45;	N,10.56;	H,6.41:
$Fe(DPTAA)_2$(monoglyme)	requires,	C,69.67;	N,9.03;	H,7.10%

Melting point. Decomposition at 108°C under nitrogen

Infra-red and 'H n.m.r. spectra

Decomposition of the sample to the free amidine occurred when the Nujol spectra of the complex was recorded. The use of an isolation cell did not prevent decomposition occurring. Severe broadening of the 'H n.m.r. resonances by paramagnetic Fe(II) species prevented the 'H n.m.r. from being recorded.

Mass spectrum: The peak at highest m/e value was at 237, corresponding to $[DPTAA]^+$. The sample was introduced at several source temperatures 80-200°C but a parent ion could not be observed.

Data for brown powder

Analyses .	Found	C,71.80;	N,9.89;	H,7.20
$[Fe(DPTAA)_2]n$ requires		C,72.45;	N,10.56;	H,6.41%

Melting point Decomposition at 109°C under nitrogen.

Infra red and 'H n.m.r. spectra Material is not soluble in any suitable solvent, so no n.m.r. measurements or solution infra-red were possible. Nujol mulls decomposed, only the spectrum of the parent amidine was recorded.

Mass spectrum: The spectrum was identical to the red solid described above.

7.2A.7 Reaction of $Fe(DPTAA)_3$ with NO

Nitric oxide was bubbled through a solution of $Fe(DPTAA)_3$(0.400g, 0.52m mole) in monoglyme (20ml) causing the colour to change from navy blue to orange brown. Concentration of the solution and addition of hexane caused the precipitation of a red brown solid. Further concentration brought about the crystallisation of a yellow product. Recrystallisation from a monoglyme/hexane solution yielded 0.213g of yellow needle like crystals. The red-brown solid, which decomposed in air producing NO_2

was washed with CCl_4, then recrystallized from its purple solution in CH_2Cl_2 to give an air sensitive purple solid (yield 0.102g). Solutions of the purple solution decomposed slowly, even under nitrogen, giving a yellow solution from which the yellow crystals could be collected. N.B. The reaction was also performed using CCl_4 as solvent. The same products were isolated.

Data for yellow crystals

Analyses. Found: C,71.33; N,15.37; H,6.46:

DPTAA(NO) requires, C,71.89; N,15.72; H,6.41%

'H n.m.r. spectrum (CD_2Cl_2)

Methyls: 2.30s, 2.38s 2.63s (1:1:1)

Aromatics: 7.24 7.08 6.90 6.81 6.64 6.5(2:2:2:1:2:1)

Mass spectrum: The parent ion $[DPTAA(NO)]^+$ was observed at m/e 267 Loss of NO gave the daughter $[DPTAA]^+$ at m/e 237.

Infra red spectra (Nujol mull) 1668m, 1605sh, 1490m, 1443w, 1412w, 1390m, 1373ms, 1240br,ms, 1220m, 1165w, 1142s, 849w, 824m, 809w, 753m, 732m, 719m, 695w, 552w, 222w, cm^{-1}.

Data for purple solid Analytical data were inconsistent, typical results being:-

Fe, 4.80; C,65.54; H,3.63; N,14.20%

$Fe(DPTAA)_3NO$ requires C,72.27; H,6.40; N,12.30; Fe, 7.03%

$Fe(DPTAA)_3(NO)_4$ requires C,64.94; H,5.75; N,15.78; Fe, 6.13%

$Fe(DPTAA)_2NO$ requires C,68.57; H,6.07; N,12.50, Fe,10.00%

Mass spectrum: A peak at m/e 413 occurred for one scan, but could not be repeated. It was possibly due to $[Fe(DPTAA)(NO)_4]^+$ or $[Fe(DPTAA)(NO)(monoglyme)]^+$; or perhaps it was a spurious peak. All other scans showed ions at m/e 267 and 237 corresponding to $[DPTAA(NO)]^+$ and $[DPTAA]^+$.

Infra red spectrum. A Nujol mull decomposed in the spectrometer, only the spectrum of DPTAAH was recorded.

'H n.m.r. spectrum The compound decomposed in $CDCl_3$. Only signals due to DPTAAH and DPTAA(NO) were observed in the spectrum.

7.2A.8 DPTAAH + NO (no reaction)

DPTAAH (0.50g, 2.110m mole) was dissolved in monoglyme and nitric oxide was bubbled through for 5 minutes. The saturated solution was then stirred under an atmosphere of nitric oxide for one hour at 20°C. The solvent was then evaporated, and the resulting white solid collected. 'H n.m.r. i.r. and C,H,and N analyses showed it to be pure DPTAAH.

To see if oxygen had any effect on the reaction, the procedure was repeated, this time air was deliberately injected into the solution. Again, there was no apparent reaction.

7.2A.9. $[Fe(DPTAA)_2]_n$ + NO (no reaction)

$[Fe(DPTAA)_2]_n$ (0.5g) was suspended in monoglyme (20ml) and nitric oxide bubbled through for ten minutes. The suspension was then stirred under an atmosphere of nitric oxide for one hour at 20°C. Filtration of the suspension recovered the unreacted brown powder.

7.2A.10 Reaction of $Fe(DPTAA)_3$ with sodium amalgam

A solution of $Fe(DPTAA)_3$ (0.100g, 0.130m mole) in T.H.F. (20ml) was added to a sodium amalgam (0.03g Na in 10ml Hg), and the mixture violently shaken. Decomposition of $Fe(DPTAA)_3$ occurred, the amidine forming an orange gum. The reaction was not studied further.

7.2A.11 $Fe(DPTAA)_3$ + PPh_3 (no reaction)

To a solution of $Fe(DPTAA)_3$ (0.400g, 0.521m mole) in monoglyme (20ml) was added PPh_3 (0.137g, 0.521m mole) and the mixture refluxed for four hours. There was no apparent reaction.

A similar reaction was tried using toluene as solvent, no reaction occurred when stirred for four hours at 80°C, but when refluxed, $Fe(DPTAA)_3$

decomposed forming a yellow gum. A product could not be isolated.

7.2A.12 Fe(DPTAA)$_3$ + bipyridine (no reaction)

To a solution of Fe(DPTAA)$_3$ (0.456g, 0.594m mole) in monoglyme (10ml) was added bipyridine (92.7mg, 0.594m mole) and the solution refluxed for three hours with no apparent reaction.

7.2A.13 Fe(DPTAA)$_3$ + hex-1-ene (no reaction)

To a solution of Fe(DPTAA)$_3$ (0.400g, 0.521m mole) in monoglyme (20ml)was added hex-1-ene (43.7mg, 0.521m mole) and the solution refluxed for four hours with no apparent reaction.

7.2A.14 Fe(DPTAA)$_3$ + iodine (no reaction)

To a solution of Fe(DPTAA)$_3$ (0.460g, 0.599m mole) in monoglyme (20ml) was added iodine (0.152g, 0.599m mole) the colour changing from navy blue to green. No further change occurred on refluxing for one hour. Addition of hexane to the solution caused the decomposition of an iodine containing yellow gum, the mother liquor reverting to its former blue colour. No reaction had occurred, the initial colour change being due to blue and yellow species in solution.

7.2A.15 Fe(DPTAA)$_3$ + NH$_3$ (no reaction)

Ammonia was bubbled through a solution of Fe(DPTAA)$_3$ (0.300g, 0.391m mole) in monoglyme (20ml) for ten minutes. There was no apparent reaction.

7.2A.16 Reaction of FeCl$_3$ with DPTAAH

To a suspension of anhydrous FeCl$_3$ (0.210g, 1.230m mole) in toluene (20ml) was added a solution of DPTAA (1.550g, 7.380m mole) in toluene (40ml) and the mixture stirred for 30 minutes at room temperature. A yellow gum was deposited on the walls of the flask but no product could be isolated. The reaction was not further studied.

7.2A.17 Fe(acetylacetone)$_3$ + DPAAH (no reaction)

Fe(acac)$_3$ (0.500g, 1.417m mole) was dissolved in monoglyme (10ml) and to it a solution of DPTAAH (0.893g, 4.251m mole) in monoglyme (10ml) was slowly added. No reaction occurred, the solution was then refluxed for four hours without any apparent change.

7.2A.18 Reaction of Fe(DPTAA)$_3$ + Et$_2$OBF$_3$

To a solution of Fe(DPTAA)$_3$ (0.300g, 0.391m mole) in monoglyme (20ml) was added freshly distilled Et$_2$OBF$_3$ (0.05ml, 0.391m mole) causing the solution to turn a red-brown colour. Attempts to crystallize the product failed, and air sensitive brown gum being formed. The reaction was not studied further.

7.2.B. Reactions in the absence of a solvent

7.2B.1 Fe(acetylacetone)$_3$ + DPTAAH (no reaction)

Fe(acac)$_3$ (0.153g, 0.434m mole) and DPTAAH (0.302m mole) were ground together forming an orange powder. The powder was then placed in a Carius tube, evacuated, sealed and heated to 95°C for 18 hours. A fused red solid was produced on cooling which was extracted with toluene (40ml) and the solution filtered. Crystallization of the reactants was achieved by the addition of hexane. These were identified by i.r. spectroscopy. T.l.c. of the components of the remaining solution, using CH_2Cl_2 as eluent, showed that no other species were present.

7.2B.2 Fe(Cp)$_2$ + DPTAAH (no reaction)

The procedure was identical to reaction 7.2B.1 given above. A fused yellow solid was formed from which Fe(Cp)$_2$ was extracted using hexane. The white solid remaining was shown to be the free amidine.

7.2B.3 Reaction of FeCI$_3$ with DPTAAH

FeCI$_3$ (0.174g, 1.072m mole)and DPTAAH (1.531g, 6.432m mole) were ground together forming an orange powder. The powder was then placed in a Carius tube, evacuated, sealed and heated to 95°C for eight hours. The red solid produced was extracted with toluene (20ml), and the solution evaporated to low bulk, forming a brown gum. T.l.c. using CH_2Cl_2 as solvent showed the product to consist of four fractions: i) yellow, ii) red-brown, iii) brown and iv) brown. Chromatography of the product on grade 3 alumina using CH_2Cl_2 as eluent extracted the yellow fraction, which was shown to be DPTAAH by i.r. spectroscopy. The red-brown material decomposed on the column, and the two brown species could not be removed from the column using a whole range of solvents and solvent mixtures.

7.2B.4 Reaction of $FeCl_2$ with DPTAAH

$FeCl_2$ (0.135g, 1.061m mole) and DPTAAH (1.010g, 4.246m mole) were ground together forming an off-white powder. The powder was placed in a Carius tube, evacuated, sealed and heated to 95°C for four hours. On cooling, an orange glass-like solid was formed; this was extracted with CH_2Cl_2 (30ml), the solid only forming a solution after being immersed in CH_2Cl_2 overnight. An unidentified grey residue was left undissolved. The solvent was removed from the orange solution in vacuo, and the residue soxhleted first with hexane (which removed excess DPTAAH (0.203g)), then ether, giving an orange solution from which an orange solid precipitated on cooling (2.39g). This powder was recrystallized from a monoglyme/hexane solution giving a white solid DPTAA(HCl) and an orange powder.

Data for orange powder

Analyses. Found: C,57.06; N,8.52; H,5.64; Cl,21.09; Fe,6.62:

$[FeCl_6]^{3-}[DPTAAH_2]^+_3$ requires C,58.43; N,8.52; H,5.83; Cl,21.56; Fe,5.66%

Melting point Decomposition at 65°C under nitrogen

Infra red spectrum (Nujol) New absorptions w.r.t. DPTAAH were recorded at:- 1640s, 1640m, 818m and 808 cm^{-1}. The following absorptions were missing from the spectrum of DPTAAH:- 1630s, 1588s, 1530s, 1322m, 1233m, 838m, 827m, and 815m cm^{-1}.

The 'H n.m.r. spectrum could not be recorded due to severe broadening of the signal.

Mass spectrum: The ion at highest mass was $[DPTAAH]^{+}$ at m/e 238. No iron containing species was identified.

7.2B.5. Attempted sublimation of $Fe(DPAA)_3$

A sample of $Fe(DPAA)_3$ known to be contaminated slightly with DPAAH was heated in vacuo to 110°C with a cold finger maintained at 6°C inserted in the flask. After 16 hours a pure-white crystalline solid had collected on the cold finger, this was shown by analyses and i.r. spectroscopy to be the DPAAH. The residue, a dark blue solid was collected; attempts to re-crystallise this solid from monoglyme, toluene and ether led to decomposition. Analyses and mass spectroscopy were performed on the residue.

Analyses.	Found:	C,71.48;	N,12.09;	H,5.65;	Fe,10.2:
$Fe(DPAA)_2$ requires		C,71.03;	N,11.84;	H,5.28;	Fe,11.84:
$Fe(DPAA)_3$ requires		C,73.79;	N,12.30;	H,5.71;	Fe,8.19%

The experiment was repeated, the following analyses being obtained on the product:-

C,69.90; N,10.68; H,5.80; Fe,11.80%

Mass Spectrum: The ion of highest mass was $[DPAA]^{+}$ at m/e 209.

7.2C Measurements of magnetic moments

7.2C.1. $Fe(DPAA)_3$

$Fe(DPAA)_3$ (0.1014g) was placed in a 10ml volumetric flask and carefully diluted to the mark with CH_2Cl_2. A melting point tube sealed at one end was filled with this solution using a microsyringe. The tube was covered with "parafilm", and then permanently sealed by passing through a CH_4/O_2 flame. A similar tube was prepared using neat CH_2Cl_2. (These operations took place with the vigorous exclusion of air and moisture, which would certainly have decomposed the samples immediately). The two sample tubes were then inserted into a 5mm n.m.r. tube, to which CCl_4

was added to hold the samples in position. The 'H n.m.r. spectrum in the CH_2Cl_2 region was then run on a 60 MHz. instrument. The difference in the frequency ($\Delta\nu$) of the proton resonance of CH_2Cl_2 in the solution and the pure solvent was measured. The experiment was repeated using five different melting point tubes prepared from the original $Fe(DPAA)_3$ solution.

Results

weight of sample = 0.1014g

weight of sample/cm^3 = 0.0104g

density of solution = 1.13145g/cm^3

density of CH_2Cl_2 = 1.3266g/cm^3

temperature = 308K

$\chi o = -0.549 \times 10^{-6}$ c.g.s.units

Sample	$\Delta\nu$(Hz)
1	16.8
2	16.9
3	16.8
4	16.8
5	16.7

Average $\Delta\nu$ = 16.8Hz.

Applying the formula described in Chapter 2 (page 32)

$$\chi = \frac{-3\ \Delta\nu}{2\pi\nu\ \ m} + \chi o + \chi o \left(\frac{do-ds}{m} \right) \qquad [107,108]$$

$$\chi = 1.4388 \times 10^{-5} \quad \text{and} \quad \chi m = 9.8273 \times 10^{-3}$$

The molar susceptibility, χm, should now be corrected for diamagnetism by adding the diamagnetic susceptibility of the DPAA ligands (see page 33). i.e. 3 x 120 x 10^{-6}g atom c.g.s. units. This gives $\chi' m = 1.0193 \times 10^{-2}$.

$$\mu\ eff. = 2.84\ \sqrt{\chi' mT}$$

$$\underline{\mu\ eff. = 5.03 B.M.}$$

7.2C.2 $Fe(DPTAA)_3$

The method was identical to that used for $Fe(DPAA)_3$ above, except that a 90MHz. machine was employed.

Results

weight of sample = 0.1408g

weight of sample/cm^3 = 0.01408g

density of solution = 1.3145g/cm^3

temperature 298K

$\chi o = -0.549 \times 10^{-6}$ c.g.s. units.

Sample	$\Delta\nu$(Hz)
1	29.343
2	29.348
3	29.342
4	29.340
5	29.343

Average $\Delta\nu$ = 29.343Hz

Applying the formula:

$$\chi = \frac{-3\ \Delta\nu}{2\Pi\nu \quad m} + \chi o + \chi o \left(\frac{do-ds}{m}\right)$$

$\chi = 1.1750 \times 10^{-5}$ c.g.s.; $\chi m = 9.0129 \times 10^{-3}$ c.g.s. χm is corrected for diamagnetic susceptibility of the DPTAA ligands. i.e. $3 \times 144 \times 10^{-6}$g/atom c.g.s. units. This gives $\chi'_m = 9.4447 \times 10^{-3}$ c.g.s.

$\mu_{eff} = 4.76$B.M.

7.2C.3 Variation of μ_{eff} for $Fe(DPTAA)_3$ with Temperature

The magnetic moment of one of the samples of $Fe(DPTAA)_3$ from 7.2C.2. above was measured at different temperatures.

Results

Temp(K)	$\Delta\nu$(Hz)	μ_{eff}	$^1/_T \times 10^{-3}$	$\chi'_m \times 10^{-3}$
313	26.41	4.65	3.195	8.597
298	29.34	4.75	3.356	9.378
285	30.52	4.73	3.509	9.719
273	32.87	4.78	3.663	10.398
248	38.15	4.88	4.032	11.924

7.2C.5 $[Fe(DPBA)_3]_n$

The standard Gouy method was performed on this complex. μ_{eff} was found to be 5.47B.M.

7.3. DISCUSSION

Most of the complexes described in this chapter proved to be extremely sensitive to moisture and oxygen, both in solution and in the solid state. Great care was therefore needed to exclude both at all stages of the preparations, isolations, and subsequent investigations (see Chapter 2 for general experimental conditions and techniques used).

The reaction between LiDPAA and $FeCl_3$ in monoglyme proceeded smoothly to the navy-blue product $Fe(DPAA)_3$ without any apparent intermediate stage. The complex is thought to be monomeric, having the tris chelate structure of $Co(dpt)_3$ (Fig. 7.1.2.). The evidence for this is the good solubility in most organic solvents and the $[Fe(DPAA)_3]^+$ ion at highest mass (m/e 683) in the mass spectrum. The complex decomposes immediately in solution, or in the solid state, when in contact with air or moisture. The products of this decomposition are the free amidine and an orange coloured hygroscopic iron hydroxy species. The complex formed when using LiDPTAA and $FeCl_3$ is entirely analogous to the compound described above.

In the mass spectrometer the complexes $Fe(DPAA)_3$ and $Fe(DPTAA)_3$ fragmented by the loss of the whole amidine ligand at once, i.e. $[Fe(Am)_3]^+ \longrightarrow [Fe(Am)_2]^+ \longrightarrow [Fe(Am)]^+$. Great difficulty was encountered in observing the parent ion, it was only observed when the source temperature was approximately 100°C. The intensity of the iron containing peaks was in the order $[Fe(Am)_2]^+ > [Fe(Am)]^+ > [Fe(Am)_3]^+$. Ions relating to a di-iron species were looked for but not observed.

The ease with which the compounds decomposed in air prevented good i.r. spectra from being recorded. The complexes appeared to decompose even when exposed to the atmosphere of the glove box (including a special high quality box with a combined O_2/H_2O level of less than 2 p.p.m.) the resulting Nujol mulls (prepared using sodium dried Nujol) producing only the spectra of the free amidines. The use of a special isolation cell, with 'O' rings to prevent air reaching the sample did not improve the spectra obtained.

The 'H n.m.r. spectra could not be recorded due to the presence of paramagnetic iron species, it did however prove to be a useful method of determining the magnetic moments of the complexes. These were measured using the method described by Deutsch and Poling [108] which has been summarised in Chapter 2. The magnetic moments measured by this method were 5.03B.M. and 4.76B.M. for $Fe(DPAA)_3$ and $Fe(DPTAA)_3$ respectively. The number of unpaired electrons in the complexes is therefore calculated to be approximately four. This result implies that:-
i) there is a high spin - low spin crossover mechanism operating; or
ii) the iron is in a +II oxidation state; or iii) the experiment is inaccurate.

The first postulate was closely examined in view of the proven high spin - low spin phenomenon existing for the isoelectronic and isostructural tris dithiocarbamatoiron(III) molecule, $Fe(dtc)_3$. This complex has a trigonally distorted octahedral configuration of six

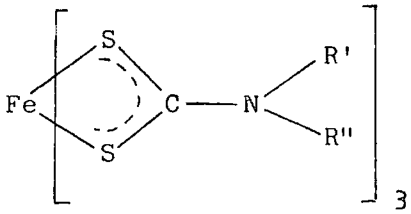


Fig. 7.3.1.

$\widehat{SFeS} < 90°$

sulphur atoms (Fig. 7.3.1.). Mössbauer spectroscopy has shown that the distortion does not greatly change the electronic states from that of pure O_h symmetry, and calculations have shown that magnetic properties are insensitive to the small splittings caused by this distortion [121]. The magnetic properties can thus be interpreted on the basis of pure O_h

symmetry. Hence the ground states for high and low spin configurations are respectively $^6A_{1g}$ $(t^3_{2g}\ e^2)$ and $^2T_{2g}$ (t^5_{2g}). With most R groups the $^2T_{2g}$ state lies several hundred cm^{-1} below the $^6A_{1g}$ state, thus at low temperature the μ_{eff} tends towards the value 2.1B.M. which is characteristic of the t^5_{2g} configuration. As the temperature rises the molecules begin to populate the high spin state and the μ_{eff} rises following a sigmoidal curve that approaches an asymptotic limit. This limiting value will be less than μ_{eff} for a high spin complex as it will never be possible to excite all the molecules into a high spin state. This behaviour is demonstrated graphically below (Fig. 7.3.2.) [122]

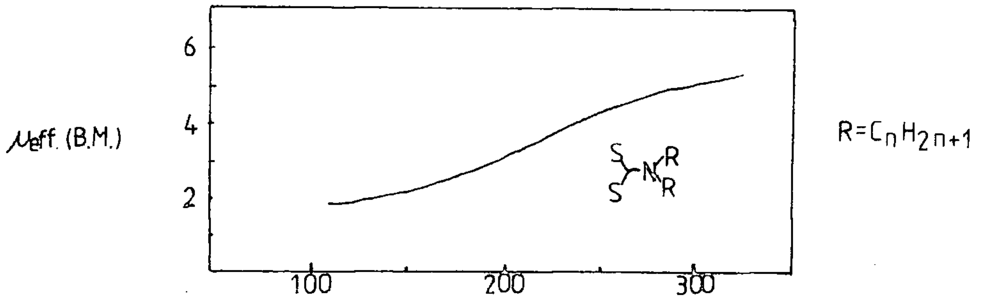


Fig. 7.3.2.

for a typical case where the energy difference between the high and low spin states is within the range 50-150 cm^{-1}.

The variable temperature measurements performed on the Fe(DPTAA)$_3$ complex gave a fairly constant value of μ_{eff} between the two extremes of temperature (Fig. 7.3.3); whilst a plot of the molar susceptibility (χm)

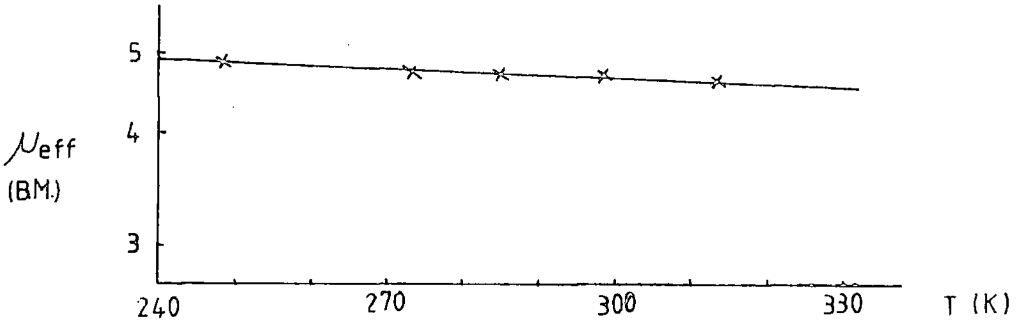


Fig. 7.3.3.

versus the reciprical of temperature demonstrates the adherence of the complex to the Curie-Weiss Law, $\chi m = \frac{C}{T \ \theta}$ where C = Curie constant, T = absolute temperature, θ = Weiss constant) (Fig. 7.3.4.) The

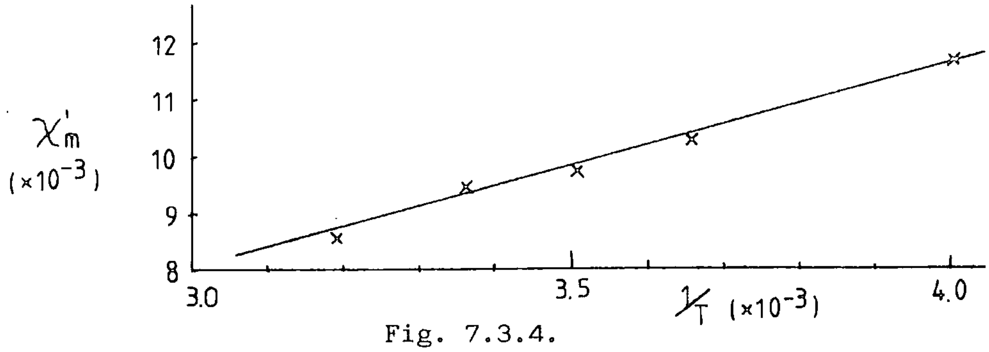


Fig. 7.3.4.

adherence to this law indicates that the observed magnetic moment is not due to a high spin - low spin crossover effect.

That the complexes Fe(DPAA)$_3$ and Fe(DPTAA)$_3$ contain Fe(II) rather than Fe(III) also appears unlikely in view of the different types of complexes produced when starting from an Fe(II) precursor (see later).

The remaining explanation of the observed magnetic moment is that the experiment is inaccurate. The general applicability of the method was examined using the air stable Fe(acac)$_3$ and Cr(acac)$_3$ complexes; three different concentrations of Cr(acac)$_3$ solution being used. Values of μ_{eff} of 5.91B.M. for Fe(acac)$_3$, and 3.86, 3.95 and 3.89B.M. for Cr(acac)$_3$ ere obtained which compare well with the experimental moments of 5.95B.M. for Fe(acac)$_3$ [117]and 3.86B.M. for Cr(acac)$_3$ [123].

The reason for the low values of the magnetic moments of the Fe(DPAA)$_3$ and Fe(DPTAA)$_3$ complexes compared to other Fe(III) species is probably due to partial decomposition of the complex. If the slightest amount of moisture is present in the CH$_2$Cl$_2$ solution some of the complex will decompose . As long as the decomposition products do not remain in solution, this will lead to less Fe(III) species in solution than allowed for by the weighings. This will have the effect of lowering the calculated magnetic moment.

The dark red complex formed on addition of LiDPFA to $FeCl_3$ in monoglyme is also tentatively formulated as monomeric $Fe(DPFA)_3$, with a tris chelate type structure. There is little concrete evidence for this, the exceptionally good solubility in organic solvents being the reason that this type of structure is preferred to an oligomeric or polymeric structure. The complex appeared even more unstable than the acetamidine derivatives, and was not studied further.

The reaction of LiDPBA with $FeCl_3$ is interesting, as it was the only reaction of $FeCl_3$ with a lithioamidine that appeared to give more than one product. In this reaction a solution containing a very unstable red species and an air stable green solid were produced. The green solid analysed correctly for $Fe(DPBA)_3$, but its insolubility in organic solvents and stability to air and water suggest a different structure to that assigned to the acetamidine and formamidine complexes. The parent ion in the mass spectrometer however was $[Fe(DPBA)_3]^+$ and there was no sign of any di-iron species in the spectrum. The complex is paramagnetic, with a measured μ_{eff} of 5.47 B.M. (Gouy method); there is probably a large error here due to the difficulty of evenly packing the sample and the amount of sample available), giving the number of unpaired electrons as approximately 4.6. The solubility suggests that it is an oligomeric or polymeric species, and the mass spectra and magnetic properties are in keeping with a product having no formal Fe-Fe bond. An amidine bridged oligomer/polymer structure is therefore suggested for this complex. The red species produced in the reaction was not identified but it's solubility, deep colour and sensitivity to air suggests a close analogy to the monomeric $Fe(DPAA)_3$ and Fe(DPFA) species previously described.

The complexes $(Fe(Am)_3)_n$ were involatile, and could not be sublimed even when heated to about 100°C in vacuo. Above this temperature decomposition occurred, free amidine being produced which sublimed from the residue. One attempt at purification of $Fe(DPAA)_3$ (contaminated with DPAAH) by sublimation produced a blue black residue and a good deal of DPAAH. More DPAAH was sublimed than was thought to be present as impurity, and the possibility of decomposition to an orthometallate species (Fig. 7.3.5.) which preserves the (+III) oxidation state of the iron, was examined.

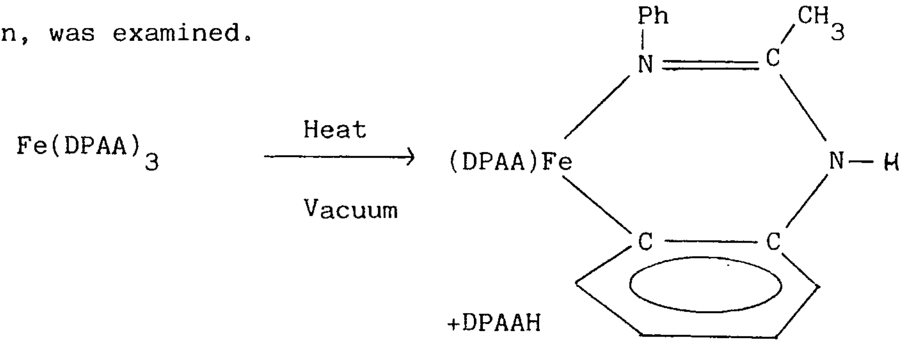


Fig. 7.3.5.

An orthometallate derivative might be expected to have a fairly strong peak at m/e 264 corresponding to the $[(o\text{-met})\ Fe(DPAA)]^+$ ion, but the ion at highest mass in the spectrum was $[DPAA]^+$ at m/e 209. The analytical data for the residue was close to $Fe(DPAA)_2$, but not too far removed from the precursor $Fe(DPAA)_3$. Recrystallisation led to decomposition and it was eventually concluded that the residue was undecomposed $Fe(DPAA)_3$ and an unknown iron species.

Reactions were also performed using $FeCl_2$ and LiDPTAA. Reduction of $FeCl_3$ to $FeCl_2$ by n-butyllithium was not wholly successful, therefore commercially prepared $FeCl_2$ was used. Two products were isolated from this reaction, an insoluble brown powder (73%) and a soluble crimson solid (21%). Both products analysed correctly for $[Fe(DPTAA)_2]_n$ and the crimson product was shown to be paramagnetic by 'H n.m.r. Both samples were extremely sensitive to air, and the infra red spectra could not be recorded, the mass spectra showing only $[\mathrm{DPAA}]^+$ and its subsequent fragmentation. On the evidence available it seems likely that the red product is monomeric, or dimeric with amidine bridges, and the brown powder polymeric.

The sensitivity of the complexes described so far made them extremely difficult to study. A systematic investigation was therefore initiated to discover whether reduction, electrophilic or nucleophilic reagents had any effect on the stability of $Fe(DPTAA)_3$.

Refluxing $Fe(DPTAA)_3$ in monoglyme with a series of reagents including PPh_3, I_2, hex-1-ene and bipyridine did not result in reaction if the solvents were scrupulously dried and oxygen rigorously excluded. If these conditions were not met, decomposition of the iron complex occurred Reactions did not occur when ammonia was bubbled through a monoglyme solution of $Fe(DPTAA)_3$.

When treated with a sodium amalgam, $Fe(DPTAA)_3$ decomposed to a yellow gum. An air sensitive brown gum was formed when $Fe(DPTAA)_3$ was reacted with Et_2OBF_3 but this was not investigated further.

A reaction that did produce an identifiable product was that of nitric oxide with a solution of $Fe(DPTAA)_3$ in monoglyme. This produced a red brown solution, from which a brown solid which decomposed in air evolving NO_2 was precipitated. Recrystallisation from its purple solution in CH_2Cl_2 gave a purple solid which was not properly identified. Solutions of this solid decomposed, even with the exclusion of air, giving a yellow solution from which yellow needles of $(p\text{-tolyl})N{=}C(CH_3)N(NO)(p\text{-tolyl})$ were crystallised and conclusively identified. Although the reaction was repeated several times consistent analytical data for the purple complex could not be obtained. The ^1H n.m.r. spectrum however showed it to contain paramagnetic iron. The ion at m/e 413 in the mass spectrum was not repeatable, it may have been due to a

[Fe(DPTAA)(NO)$_4$]$^+$ or [Fe(DPTAA)(monoglyme)(NO)]$^+$ species. Nitrosoamines can be formed by the action of nitric oxide on amine solutions in organic solvents, the nitrosation taking place through the intermediacy of N_2O_3 or N_2O_4 formed by the presence of oxygen in the reaction mixture [124]. Attempts to prepare the nitrosoamidine by the action of NO on DPTAAH failed, even when air was admitted. The formation of the nitrosoamidine must therefore be occurring on the metal in solutions of Fe(DPTAA)$_3$. It is probable that initial attack occurs at the metal by NO to donate one electron. In such a case the NO will have a bent configuration. One of the amidino groups may then become monodentate, the NO changing from a bent one electron donor to a linear three electron donor. The NO which can now be regarded as bonding NO$^+$ can then be nucleophilically attacked by the uncoordinated nitrogen of the amidino group (Fig. 7.3.6), (nucleophilic attack on coordinated NO [125,126,127]). The Fe(DPTAA)$_2$(DPTAA(NO)) species thus formed could not be isolated, but goes on to react further or decompose giving DPTAA(NO) and DPTAAH as the only identifiable products of the reaction.

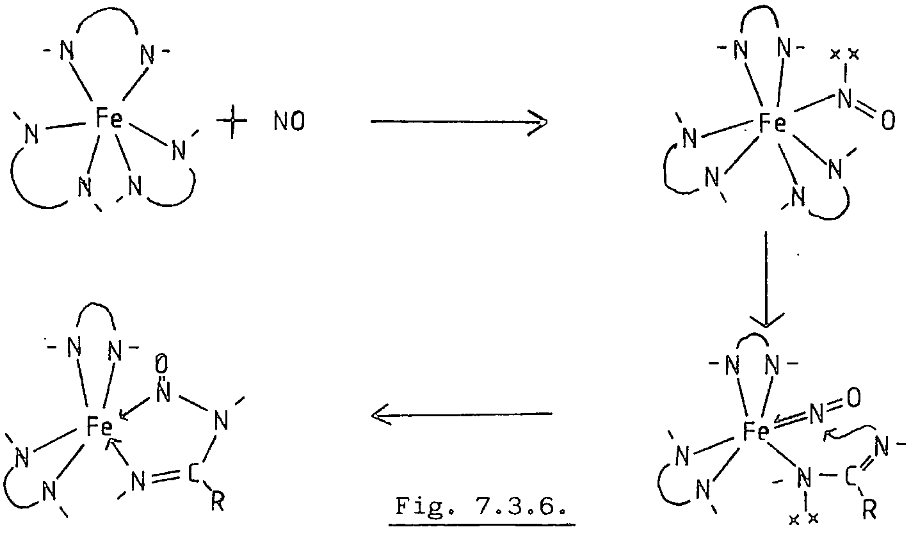


Fig. 7.3.6.

Treatment of the brown powder [Fe(DPTAA)$_2$]$_n$ with nitric oxide did not cause a similar reaction. The unreacted brown powder was recovered.

Alternative pathways to iron amidino complexes were explored, these included refluxing $Fe(acac)_3$ with DPTAAH in monoglyme, and a series of Carius tube reactions using DPTAAH and $Fe(acac)_3$,$FeCl_3$, $FeCp_2$, and $FeCl_2$. In all but the $FeCl_2$ case the only products recovered were the starting materials. The $FeCl_2$ reaction led to the isolation of an orange powder formulated by chemical analysis to be $FeCl_3$(DPTAAH.HCl$)_3$ and an unidentified grey precipitate (possibly metallic iron). A possible structure for the iron complex is given below (Fig. 7.3.7.).

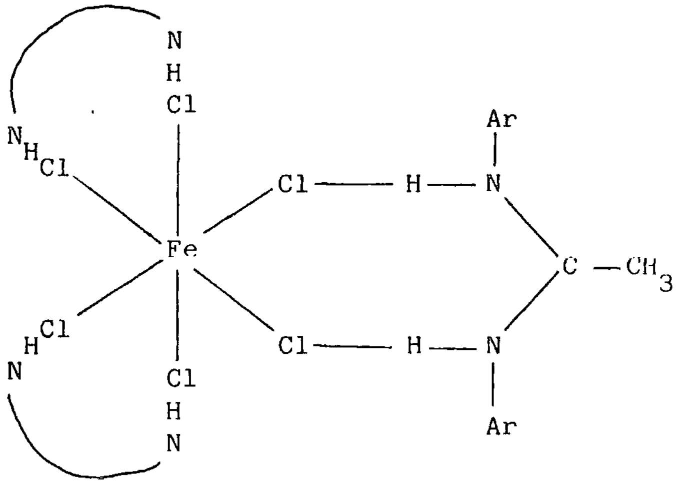


Fig. 7.3.7.

The i.r. spectrum of this compound shows an increase in the ν_{as}(N-C=N) from 1630 to 1640 cm^{-1} w.r.t. DPTAAH, and is very similar to DPTAAH(HCl).

7.4. CONCLUSION

$FeCl_3$ reacts smoothly with lithioamidines forming brightly coloured iron-trisamidino complexes. The formamidino and acetamidino complexes are believed to be monomeric and are extremely air sensitive. The benzamidine reaction produces two products, which are tentatively assigned monomeric and oligomeric/polymeric structures, the oligomer/polymer being unusual, in that it is stable to both air and water.

The complexes are parmagnetic, and the $Fe(DPTAA)_3$ derivative has been shown to obey the Curie-Weiss law. The measured magnetic moments of

$Fe(DPAA)_3$ and $Fe(DPTAA)_3$ are less than those expected for high spin Fe(III) species, but this is probably due to their instability in solution and consequently the difficulty of preparing standard solutions. The air stable oligomer/polymer $[Fe(DPBA)_3]_n$ has a measured magnetic moment closer to that predicted for a complex containing 5 unpaired electrons.

$FeCl_2$ also undergoes reaction with LiDPTAA, two products, both formulated as $Fe(DPTAA)_2$ being formed. These are believed to be a monomer and an oligomeric/polymeric species. Both were extremely air sensitive and could not be investigated further.

Reactions of various iron compounds with DPTAAH in the absence of a solvent did not appear to produce iron-amidino species. A strange reaction with $FeCl_2$ did occur however, the products being $FeCl(DPTAAH.HCl)_3$ and metallic iron.

The Fe $(acetamidine)_3$ derivatives were resistant to nucleophilic substitution by donor ligands, but decomposition occurred when treated with a sodium amalgam or reacted with Et_2OBF_3. Reaction did occur with nitric oxide however, though the iron containing product was not identified. It decomposed easily forming NO_2 and amidine in the solid state, and nitrosoamidine and amidine when in solution.

It is noted that Δo for $Fe(DPAA)_3$ Fe(DPTAA) and $[Fe(DPBA)_3]_n$ must be quite small as the iron adopts a high spin configuration. The value of Δo would be expected to be large if a significant degree of Π back bonding to the metal takes place, It is concluded therefore that the amidine to metal bond is basically of the σ,σ-type, with little iron to amidine Π back bonding.

APPENDIX I

A preliminary investigation into the syntheses of molybdenum - methylene-amino complexes by nucleophilic attack on molydenum nitriles

A1.1 INTRODUCTION

As part of this group's continuing interest in transition metal-nitrogen ligand complexes the methylene amino-group $-N{=}CR_2$ has been studied in some depth [128-132]. The methyleneamino group can be considered to be isoelectronic with nitric oxide ($\cdot N{=}O$) which has been shown to act as a one or three electron donor ligand [133] in transition metal complexes. As a one electron donor the N atom is sp^2 hybridised and a bent M-N-O skeleton results; when acting as a three electron donor the N atom is sp hybridised, and it now also participates in π-bonding to the metal, a linear M-N-O skeleton being observed (Fig. A1.1.1.)

1 electron donor 3 electron donor

Fig. A1.1.1

In addition, the three electron donor NO ligand can be bridging. This situation is formally quite analogous to that for bridging halogen atoms. (Fig. A1.1.2)

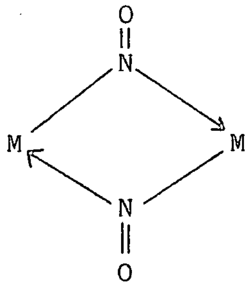


Fig. A1.1.2.

Similar bonding modes have been proposed for the methylene-amino group, and there is strong evidence in favour of the three electron donor linear

($CpMo(CO)_2(NC(t\text{-}butyl)_2)$) [131], and bridging ($[Fe(CO)_3(NCPh_2)]_2$) [134] types of co-ordination.

The methyleneamino group has the additional possibility of an "olefin-type" interaction, which has been observed for some vinyleneamine [135] and cyanamide [136] systems.

The successful syntheses of transition metal-methyleneamino complexes have been by the following routes:-

i)	$Fe(CO)_5 + Ph_2CNNCPh_2$	[134]
ii)	$CpM(CO)_3Cl + R_2CNSiMe_3$	[128]
iii)	$CpM(CO)_3Cl + R_2CNLi$	[128]

(M=Mo,W)

The first method worked well for $Fe(CO)_5$, but with $[CpM(CO)_3]_2$ (M=Mo,W) only the starting materials were recovered. For the $CpM(CO)_2(NCR_2)$ complexes the second route was the most successful; a monomer being isolated for the tungsten reaction and both monomer and dimer (containing $-NCR_2$ bridges) being isolated for the molydenum reaction, the dimer being the predominant product. The third route generally caused a complex reaction to occur, with the formation of π-allyl/allene complexes e.g. $CpMo(CO)_2(R_2C\text{-}N\text{=}CR_2)$, but could be induced to give the monomeric methyleneamino-complexes by the incorporation in the reaction mixture of added substrates such as $R_2C\text{=}O$, PhCN, and PhNCO [132].

The compound $CpMo(CO)_2(NCBu^t_2)$ [130] was prepared by route (iii) above; interestingly this did not lead to the π-allyl/allene type of complex resulting from Ph_2CNLi. A crystal structure of the methyleneamino complex [131] revealed that the M-N-C skeleton is approximately linear having an angle of 171.8° and a short Mo-N bond length of 1.87Å compared with a "normal" single bond distance of 2.32Å in <u>cis</u>-$Mo(CO)_3$(dien). The evidence in favour of a three electron donor methyleneamino group in this complex is quite strong i.e:- i) the complex requires three electrons from the methyleneamino group to satisfy the 18 electron rule; ii) the presence of only two carbonyl groups, and the failure to add a further neutral donor ligand even under forcing conditions; iii) the short Mo-N bond length implying multiple bonding; and iv) the approximate linearity of the M-N-C skeleton. It must be noted however that the linearity of this skeleton may be facilitated by the bulky tertiary butyl groups and hence the three electron donor nature of the methyleneamino-group cannot yet be assumed to apply in all cases.

Further evidence for the three electron donor linearly bonded structure of the methyleneamino group in $CpMo(CO)_2(NC\ Bu^t_2)$ was obtained by observing its temperature dependent 'H n.m.r. and i.r. spectra [130]. This also concludes that the tertiary butyl methyleneamino group is linearly bonded to the molybdenum, and a slightly hindered rotation about the Mo-N bond gives rise to the temperature dependent spectra.

The tungsten complex $CpW(CO)_2(NCPh_2)$ dimerises with the loss of carbonyls to $[CpW(CO)(NCPh_2)]_2$ on heating, whereas the analogous molybdenum complex is stable to above its melting point and does not appear to decarbonylate. The molybdenum dimer $[CpMo(CO)_2(NCPh_2)]_2$ however, is extremely difficult to isolate as under the conditions favourable for the formation of the tungsten dimer ($Ph_2CNSiMe_3$ route) the reaction predominantly gave the $[CpMo(CO)(NCPh_2)]_2$ complex.

Substituents on the methyleneamino-group considerably influence the type of complex formed in the reaction between methyleneamino derivatives and transition metal carbonyls. For instance $Ph_2CNSiMe_3$ produces $[CpMo(CO)_2(NCPh_2)]_2$ + $[CpMo(CO)(NCPN)]_2$ with $[CpMo(CO)_2Cl]$ but $LiNCPh_2$ gives the above in very low yield, the major product being $CpMo(CO)(Ph_2CNCPh_2)$. With $Bu^t_2CNSiMe_3$ or Bu^t_2CNLi with $CpMo(CO)_3Cl$ however, the only product formed is $CpMo(CO)_2(NCBu^t_2)$. An investigation as to whether this was due solely to steric effects led to the synthesis of $CpMo(CO)_2(NC(Ph)(Bu^t))$ by both the silyl and lithio routes. It was envisaged that the decreased size of the methyleneamino group might allow the formation of a dinuclear bridged species or a π -allyl/allene type of complex; further reactions with differing R groups might reveal the answer.

In contrast to the diphenyl- and ditertiarybutyl- methyleneamino-complexes ($CpMo(CO)_2(NCR_2)$) already described, the mixed phenyl-tertiarybutyl complex does react with PPh_3 to give $CpMo(CO)(PPh_3)(NC(Ph)(Bu^t))$. The fact that a substitution and not an addition occurs suggests that both complexes contain 18 electrons and that the methyleneamino group is a three electron donor. $CpMo(CO)_2(NC(Ph)(Bu^t))$ shows no changes in its infra-red spectrum (hexane) from -40° ⟶ 50°C, but it is not clear whether this is due to a single preferred conformation or free rotation about a linear M-N bond.

The chemistry of the $CpMo(CO)_2(NCRR')$ complexes is still relatively unexplored, a more efficient route to these complexes being a prerequisite for further study. This work was devoted to exploring a new synthetic route, and it was hoped that a range of methyleneamino complexes with differing R and R' groups could be produced. The method explored was that of nucleophilic attack by a carbanion on co-ordinated nitriles.

It has been postulated for [cis-Co(ethylenediamine)$_2$(NCCH$_2$NH$_2$)Cl]$^{2+}$ that coordination via the lone pair of the nitrile enhances the susceptibility of the nitrile carbon to nucleophilic attack [137]; the complex is found to isomerise by such a nucleophilic attack to one containing the tridentate amide ligand $NH_2CH_2C(NH_2)CH_2CH_2NH_2$ in near neutral or basic solutions. Other examples of nucleophilic attack on a co-ordinated nitrile is that of NH_3 on cis-$Cl_2Pt(NCMe)_2$ which produces the diamine-diamidine product trans-$[(NH_3)_2Pt(NH{=}C(CH_3){-}NH_2)_2]^{2+}Cl_2$ [138]. Similar types of reaction occur for carbonyls, and it has been demonstrated that a useful method of producing transition metal carbamoyl complexes is the reaction of cationic carbonyl complexes with a nucleophile.

e.g.

$$CpMo(CO)_4^{+} + NHRR' \longrightarrow CpMo(CO)_3{:}\,C(=O)NRR'$$ [139]

The related alkoxy-carbonyls are also produced in a similar reaction using alcohols or lithium alkoxides.

e.g.

$$CpMo(CO)_4^{+} + MeOH \longrightarrow CpMo(CO)_3{:}C(=O)OMe$$ [139]

The synthesis of other metal carbonyl complexes via cationic precursors has also proved useful using π -coordinated olefin ligands with both bases and anionic carbon nucleophiles [140].

e.g. i) $CpMo(CO)_3(C_2H_4)^{+} + L \longrightarrow CpMo(CO)_3(CH_2CH_2L)^{+}$

ii) $CpMo(CO)_3(C_2H_4)^{+} + R^{-} \longrightarrow CpMo(CO)_3(CH_2CH_2R)$

The synthesis of molybdenum-methyleneamino complexes from nitrile complexes therefore seemed feasible, the reaction undergoing the following type of process:-

Initial attack by the nucleophile causes the transfer of an electron pair from the C≡N bond to the nitrogen atom, and the simultaneous transfer of an electron to the metal forming a neutral complex. The nitrogen atom may now remain sp hybridised, donating its electron pair to the metal, causing the loss of one of its neutral ligands and the formation of a three electron donor methyleneamino complex (Fig. Al. 1.3a). Alternatively, the nitrogen's orbitals may rehybridise to a sp^2 state, forming a lone pair on the nitrogen atom. This lone pair may remain uncoordinated or else be donated to another metal atom forming a bridged methyleneamino complex (Fig. Al.1.3)

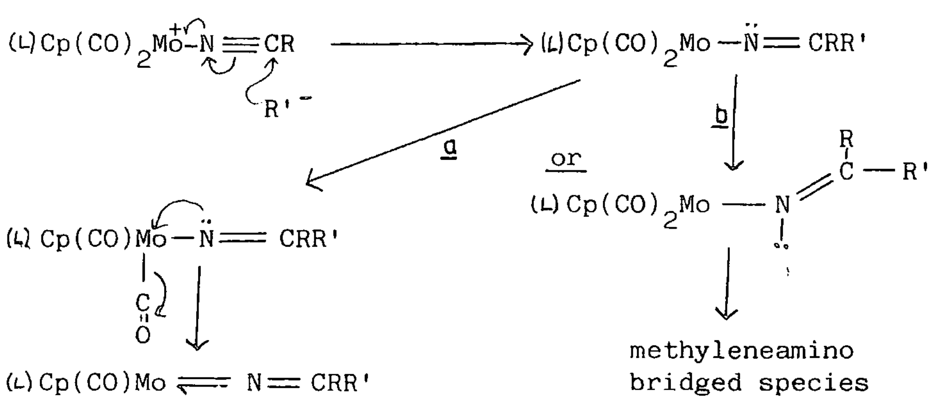


Fig.Al.1.3

A1.2 EXPERIMENTAL

A1.2.1 $CpMo(CO)_3Cl$ was prepared according to Fischer [141]. It was recrystallized from a chloroform/hexane solution, and the red crystals were stored under nitrogen in the freezer.

A1.2.2 $CpMo(CO)_3Cl + PhCN \xrightarrow{AlCl_3}$ no reaction.

$CpMo(CO)_3Cl$ (0.400g, 1.43m mole) was dissolved in CH_2Cl_2 (10ml) and $AlCl_3$ (0.190g, 1.43m mole) carefully added under nitrogen. To this solution was added a solution of PhCN (0.147g, 1.43m mole) and the mixture refluxed for 16 hours. NH_4PF_6 (0.233g, 1.43m mole) was dissolved in water (10ml) and this solution added to the organic mixture. The flask was vigorously shaken, the aqueous layer removed and the organic layer washed with water (2 x 10ml). The solvent was then removed by evaporation in vacuo and the residue dried. Extraction of the residue gave a clear red solution showing only the carbonyl stretching frequencies attributable to $CpMo(CO)_3Cl$. Crystallization by the addition of hexane produced red crystals of $CpMo(CO)_3Cl$, identified by i.r. spectroscopy.

A1.2.3 $CpMo(CO)_3Cl+MeCN \xrightarrow{AlCl_3}$ no reaction.

This reaction was performed in the same manner as A1.2.2. Only the starting material $CpMo(CO)_3Cl$ was recovered.

A1.2.4. $CpMo(CO)_3Cl+PhCN \xrightarrow{AlCl_3}$ decomposition.

$CpMo(CO)_3Cl$ (0.400g, 1.43m mole) was dissolved in toluene (40ml) and to it added $AlCl_3$ (0.190g, 1.43m mole) and PhCN (0.300g, 2.91m mole). The resulting red solution was refluxed for 2½ hours, a black oil and a black solution forming. The toluene was removed by evaporation, and the resultant black oil extracted with CH_2Cl_2 (10ml). An i.r. spectrum of this solution showed no carbonyl stretching frequencies and decomposition was assumed to have occured.

A1.2.5. Reaction of $CpMo(CO)_3Cl$ with $AsPh_3$

$CpMo(CO)_3Cl$ (3.055g, 10.91m mole) was dissolved in toluene (150ml) and $AsPh_3$

(5.00g, 16.3m mole) added. (When refluxing toluene was used, decomposition to black oil occurred). The resulting orange solution was heated to 60°C for 8 hours, then filtered whilst hot and allowed to crystallize on cooling. The resulting orange crystals of $CpMo(CO)_2(AsPh_3)Cl$ were washed with hexane and dried under vacuum (yield 93%). The solid product was stable in air for short periods, but solutions quickly decomposed if air was admitted.

Analyses. Found: C,53.79; H,4.08

$CpMo(CO)_2(AsPh_3)Cl$ requires, C,53.71; H,3.58%

Melting point 160°C (with decomposition)

Infra red Spectra

$\nu(CO)$ cm^{-1} Nujol: 1946vs 1855vs

$\nu(CO)$ cm^{-1} CH_2Cl_2 1970vs 1880vs

'H n.m.r. spectrum

$(CDCl_3)$ C_6H_5, 7.65s(15); Cp, 5.65s(5) δ

A1.2.6 $CpMo(CO)_2(AsPh_3)Cl+PhCN \xrightarrow{AlCl_3} [CpMo(CO)_2(AsPh_3)(NCPh)]^+ [AlCl_4]^-$

$CpMo(CO)_2(AsPh_3)Cl$ (4.600g, 8.23m mole) was dissolved in CH_2Cl_2 (25ml) and to it added $AlCl_3$ (2.194g, 16.47m mole) and PhCN (1.695g, 16.45m mole). The solution was stirred at 20°C for 16 hours. A solution of NH_4PF_6 (1.500g, 9.20m mole) in water (15ml) was carefully added, and the flask vigorously shaken. The greenish aqueous layer was then removed, and the dark red organic solution was washed with water (5 x 10ml). The solution was evaporated to dryness, yellow crystals appearing as the volume was reduced. The yellow crystals of $[CpMo(CO)_2(AsPh_3)(NCPh)]^+ [PF_6]^-$ produced were washed with toluene (5 x 10ml) to remove residual $CpMo(CO)_2(AsPh_3)Cl$ and then recrystallized from CH_2Cl_2/hexane (yield 82%).

Analyses. Found: C,49.97; N,1.68; H,3.58:

$[CpMo(CO)_2(AsPh_3)(NCPh)]^+ [PF_6]^-$ requires, C,49.80; N,1.82; H,3.24%

Infra red spectra

$\nu(CO)$ cm^{-1} Nujol: 1989vs 1970m,sh 1920vs 1894m

$\nu(CO)$ cm^{-1} CH_2Cl_2: 1997vs 1918vs

$\nu(CN)$ cm^{-1} Nujol: 2248w ; $\nu(PF_6)$ cm^{-1} Nujol: 844vs broad

A1.2.7. Reaction of $[CpMo(CO)_2(AsPh_3)(NCPh)]^+$ $[PF_6]^-$ with n-BuLi

A suspension of $[CpMo(CO)_2(AsPh_3)(NCPh)]^+$ $[PF_6]^-$ (4.00g. 5.19m mole) in T.H.F. was frozen to 77K and to it added nBuLi (5.19m mole in hexane solution). The flask was warmed to room temperature, the mixture forming an orange solution as it melted. The mixture was then stirred for two hours at room temperature and then filtered giving a red solution (an odour of PhCN was detected) and a pink slurry. The slurry was washed with toluene and dried under vacuum to give a flesh coloured powder. This powder was shown to be $LiPF_6$ (contaminated slightly by a red product) by infra red spectroscopy. The red solution was then evaporated to about 6ml and ether (2ml) added. A red gum formed.* The remaining solvent was removed by evaporation and the residue washed with toluene (3 x 10ml) producing a crimson precipitate and a red solution.

The toluene washings were combined and evaporated to low volume ($5cm^3$), ether (2ml) was added and the solution set in the freezer. Red crystals of $Cp_2Mo_2(CO)_5(AsPh_3)$ were collected and dried under vacuum (yield 0.155g).

The crimson precipitate was found to be insoluble in a whole range of organic solvents and could not be recrystallized. It was therefore washed with acetone (3 x 5ml), water (3 x 5ml) and acetone (3 x 5ml) to remove impurities. After pumping dry a crimson powder formulated as $[CpMo(CO)_2(AsPh_3)]_2$ was collected (yield 0.565g, 17%).

*When the experiment was repeated this gum was extracted with boiling CH_2Cl_2, the red solution was filtered, and the crimson precipitate collected. The CH_2Cl_2 solution was then chromatographed on a silica gel column (using CH_2Cl_2 as eluant) giving first a red and then an orange fraction. These fractions were crystallized by evaporation and the products identified as $Cp_2Mo_2(CO)_5(AsPh_3)$ and $CpMo(CO)_2(AsPh_3)Cl$ respectively by their infra red spectra.

Data for $Cp_2Mo_2(CO)_5(AsPh_3)$

Analyses. Found: C,52.54; H,3.28; Mo,26.7

$Cp_2Mo_2(CO)_5(AsPh_3)$ requires, C,51.56; H,3.26; Mo,25.00%

Infra red spectra

ν(CO) CH_2Cl_2 1968vs 1896vs broad 1885vs 1812vs cm^{-1}

ν(CO) Nujol 1967vs 1902vs 1888vs 1873vs 1818s cm^{-1}

'H n.m.r. spectrum

($CDCl_3$) Cp's, 4.83s(5) 5.10s(5) C_6H_5, 7.46s(15) δ

(a small Cp peak at 5.29 indicates the presence of $[CpMo(CO)_3]_2$).

Mass spectrum The parent ion $[Cp_2Mo_2(CO)_5(AsPh_3)]^+$ was not observed. The peak at highest mass occurred at m/e 462 corresponding to $[Mo_2Cp_2(CO)_5]^+$. Daughter ions corresponding to the stepwise loss of the five carbonyl groups were also observed at m/e 434, 406,378, 350 and 322. $[AsPh_3]^+$, $[AsPh_2]^+$ and $[AsPh]^+$ were the most intense peaks in the spectrum at m/e 306, 229, and 152 respectively.

Data for $[CpMo(CO)_2(AsPh)]_2$

Analyses. Found: C,55.50; H,3.61; Mo,21.3; As 13.80:

$[CpMo(CO)_2(AsPh_3)]_2$ requires, C,57.30; H,3.82; Mo,18.3; As, 14.34%

Infra red spectrum

ν(CO) Nujol: 1843vs 1828vs cm^{-1}

Mass Spectrum: The parent ion $[Cp_2Mo_2(CO)_4(AsPh_3)_2]^+$ was not observed. The peak at highest mass occurred at m/e 434 corresponding to $[Mo_2Cp_2(CO)_4]^+$. Daughter ions corresponding to the stepwise loss of the four carbonyl groups were observed at m/e 406,378,350 and 322. $[AsPh_3]^+$, $[AsPH_2]^+$ and $[AsPh]^+$ were the most intense peaks in the spectrum at m/e 306,229 and 152 respectively.

A1.2.8. Decomposition of $[CpMo(CO)_2(AsPh_3)]_2$

$[Cp_2Mo(CO)_2(AsPh_3)]_2$ (0.132g, 0.126m mole) was suspended in toluene (15ml) and stirred at 50°C for two hours. The resulting red solution was filtered, leaving a brown non-carbonyl residue. The solution was concentrated by evaporation to 2ml, and a drop of hexane was added to it. Red crystals of

$Cp_2Mo_2(CO)_5(AsPh_3)$ were collected (0.07g), which were identified by their infra red spectrum.

Infra red spectrum

ν(CO) Nujol: 1967vs 1902vs 1888vs 1873vs 1818s cm^{-1}

A1.2.9. Reaction of $Cp_2Mo_2(CO)_5(AsPh_3)$ with CH_2Cl_2

$Cp_2Mo_2(CO)_5(AsPh_3)$ (0.022g) was dissolved in CH_2Cl_2 (10ml) and refluxed for two hours. The infra red spectrum showed four new carbonyl stretching frequencies at 2059m, 1978vs broad, 1970vs and 1880vs cm^{-1}. These were attributed to $CpMo(CO)_3Cl$ and $CpMo(CO)_2(AsPh_3)Cl$ respectively.

A1.2.10 Reaction of $[CpMo(CO)_2(AsPh_3)(NCPh)]^+ [PF_6]^-$ with LiOMe

To a suspension of $[CpMo(CO)_2(AsPh_3)(NCPh)]^+ [PF_6]^-$ (1.380g, 1.68m mole) in T.H.F. (10ml) frozen to 77K was added LiOMe (1.68m mole in methanol) and the mixture allowed to warm to room temperature forming an orange solution. The solution was stirred for a further 10 minutes and then the THF evaporated leaving a brown gum. The gum was extracted with acetone (5ml) and pumped dry to give a fawn non-carbonyl containing precipitate. The dark red-brown solution was reduced in volume to 3ml and hexane(2ml) added. The solution produced dark red crystals of $Cp_2Mo_2(CO)_5(AsPh_3)$ identified by infra red spectroscopy.

A1.2.11 Reaction of $[CpMo(CO)_2(AsPh_3)(NCPh)]^+ [PF_6]^-$ with a sodium amalgam

Sodium amalgam was prepared containing 0.5g of sodium in 10ml of mercury. To this was added T.H.F. (20ml) and $[CpMo(CO)_2(AsPh_3)(NCPh)]^+ [PF_6]^-$ 91.300g, 1.68m mole). The mixture was then vigorously shaken, the T.H.F. layer becoming a brown-red colour. The amalgam was removed from the flask via a drain tap, residual droplets being removed with the aid of clean mercury (2 x 3ml). The T.H.F. solution was filtered, and then the solvent removed by evaporation. The brown gummy residue was extracted with toluene forming a red solution and an off-white precipitate. The precipitate was dried under vacuum, and shown by infra red spectroscopy to be $Na^+PF_6^-$.

The red solution did not crystallise on concentration; the toluene was therefore evaporated and the red solid extracted with CH_2Cl_2. The infra red spectrum of this solution was recorded, and the red product identified as $Cp_2Mo_2(CO)_5(AsPh_3)$.

Infra red Spectrum

$\nu(CO)$ CH_2Cl_2: 1968vs 1896vs broad 1885vs 1821vs cm^{-1}

Reaction of $[CpMo(CO)_3]_3$ with $AsPh_3$

A solution of $[CpMo(CO)_3]_2$ (0.564g, 1.15m mole) and $AsPh_3$ (0.450, 1.47m mole) in T.H.F. (25ml) was refluxed for 70 hours. No appreciable change in the carbonyl stretching frequencies was noted after this period. The solution was transferred to a silica flask, and irradiated with a 1K.W. u.v. lamp placed 60cm. from it for 8 hours. The T.H.F. was then removed by evaporation, and the residue extracted with $CHCl_3$(10ml). Ether (20ml) was added to this solution causing the precipitation of the starting material. Further crystals were obtained on cooling, and shown by infra red spectroscopy to be a mixture of starting material and product. The remaining solution (containing most of the product) was chromatographed on a silica gel column (12" x 1") using $CHCl_3$/hexane 1:1 eluant. The products were eluted as a continuous red band, and were collected in three fractions, each producing dark red crystals on evaporation. Infra red spectra identified the first fraction as $[CpMo(CO)_3]_2$ and the second as $Cp_2Mo_2(CO)_5AsPh_3$. The yield of $Cp_2Mo_2(CO)_5AsPh_3$ was 0.426g (48.2%); and the recovered amount of $[CpMo(CO)_3]_2$ was 0.223g.

A1.3. RESULTS AND DISCUSSION

The reaction of cyclopentadienyl carbonyl halides with a halogen acceptor such as $AlCl_3$ and a donor molecule are known to give ionic carbonyl species of the type $[CpMo(CO)_3L]^+ [AlCl_4]^-$ and $[CpM(CO)_2L_2]^+[AlCl_4]^-$ (M=Mo,W; halide = Cl) Complexes where L=nitrile (NCMe,NCPh etc) were therefore chosen as the substrate for the syntheses of methyleneamino-complexes by nucleophilic attack of R^- groups. Barnett et al [142] have made the unstable $[CpMo(CO)_2(NCMe)_2]^+ [AlCl_4]^-$ complex but this easily decomposes. For this reason, and also because the coordination of two nitrile groups to the molybdenum might complicate subsequent reactions it was thought not to be a suitable starting material. The mononitrile complex $[CpMo(CO)_3(NCR)]^+[AlCl_4]^-$ (R=Me,Ph) could not be prepared by Barnett and my attempts also failed.

By replacing a carbonyl ligand on the $CpMo(CO)_3Cl$ moiety by another ligand such as PPh_3 or $AsPh_3$ the lability of the Mo–Cl bond is expected to increase due to the large σ-donor and poor Π-acceptor properties of these ligands. $AsPh_3$ was chosen in preference to PPh_3 for this substitution as it forms the monosubstituted derivative *cis*-$CpMo(CO)_2(AsPh_3)Cl$ whereas PPh_3 forms a mixture of mono and disubstituted products, $CpMo(CO)_2(PPh_3)Cl$ and $CpMo(CO)(PPh_3)_2Cl$, under both thermal and photochemical conditions [142]. The orange $CpMo(CO)_2(AsPh_3)Cl$ produced by the reaction of $CpMo(CO)_3Cl$ with an excess of $AsPh_3$ in toluene at 50°C for eight hours is identical to that described by Barnett [142], but was achieved in less than half the reaction time and in a much greater yield (93% vs. 32%).

The complex $[CpMo(CO)_2(AsPh_3)(NCPh)]^+ [AlCl_4]^-$ smoothly formed when $CpMo(CO)_2(AsPh_3)Cl$ was stirred with a two molar excess of $AlCl_3$ and PhCN in dichloromethane at room temperature overnight. The cation was precipitated as bright yellow crystals of $[CpMo(CO)_2(AsPh_3)(NCPh)]^+$ $[PF_6]^-$ by the addition of NH_4PF_6. This complex is relatively air stable in the solid state, but quickly decomposes in solutions exposed to air. Although the doubling of infra red absorptions in the solid state spectrum indicated that more than one isomer might exist (doubling could be merely solid state effects) it was decided not to try and further purify the sample. The subsequent reaction $[CpMo(CO)_2(AsPh_3)(NCPh)]^+[AlCl_4]^-$ with a nucleophile would hopefully lead to the formation of a three electron donor nitrogen ligand and the expulsion of a carbonyl or the $AsPh_3$ group. The product of this reaction presumably being the same whether a cis- or trans-substituted cationic precursor is used.

nButyllithium was chosen as the nucleophilic species for the reaction with $[CpMo(CO)_2(AsPh_3)(NCPh)]^+[PF_6]^-$ initially in order to prove the validity of the method before the more useful but expensive phenyllithium and tertiarybutyllithium species were used. The reaction did not produce any of the expected products ($[CpMo(CO)_{2-x}(AsPh_3)_x(NCPhBu)]_n$ (n=1,2) (x=0,1) or $CpMo(CO)_2(AsPh_3)(NCPhBu)$); instead non-nitrogen containing species were isolated, and the odour of PhCN in the reaction mixture suggested that PhCN was lost "intact" from the metal. The recovered products were identified as $(\Pi-C_5H_5)_2Mo_2(CO)_5(AsPh_3)$ (Fig.A1.3.1) and $(\Pi-C_5H_5)_2Mo_2(CO)_4(AsPh_3)_2$ (Fig. A1.3.2) by a combination of elemental analyses, infra red, 'H n.m.r. and mass spectroscopy, and by comparison with the analogous PPh_3 derivatives [143, 144]. Neither of the parent ions were observed in the mass spectrometer, both complexes appearing to lose $AsPh_3$ extremely easily. The ions $[CpMo_2(CO)_5]^+$ and $[Cp_2Mo_2(CO)_4]^+$ however were clearly visible for pentacarbonyl and tetracarbonyl complexes respectively, together with the daughter ions representing the stepwise

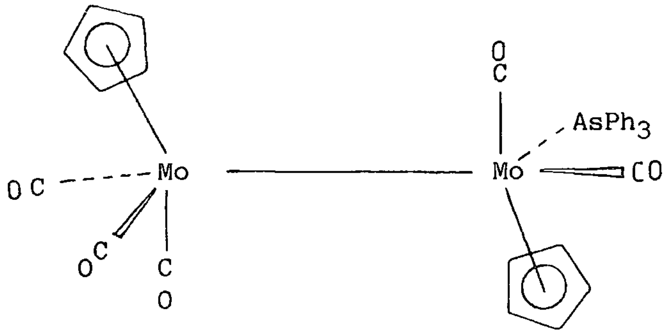


Fig. A1.3.1.

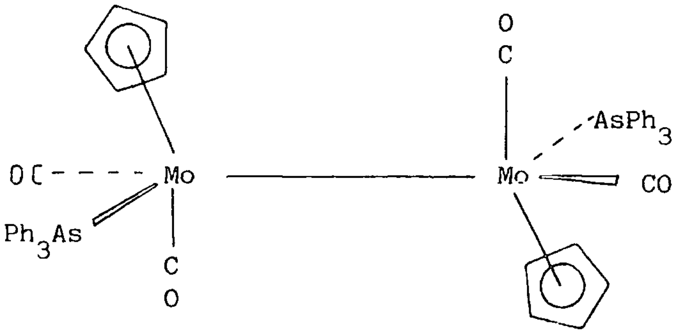


Fig. A1.3.2.

loss of the carbonyls. For both complexes the most intense peaks in the spectrum were those corresponding to $AsPh_3^+$, $AsPh_2^+$ and $AsPh^+$. The spectroscopic data for these complexes are summarised in table A1.3.1. together with the data for the previously reported analogous PPh_3 complexes. [144].

Table A1.3.1

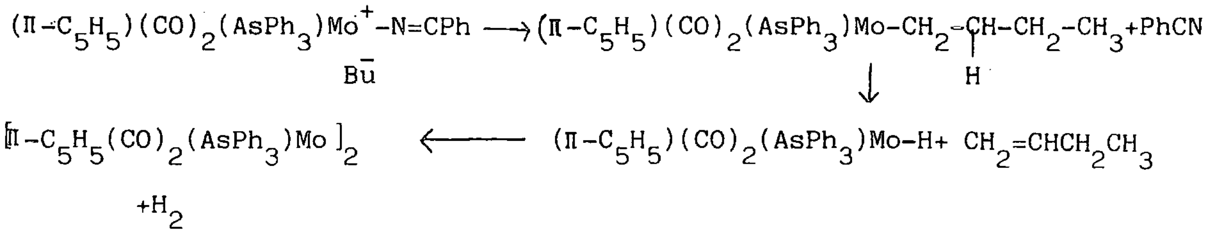
Spectroscopic data for $Cp_2Mo_2(CO)_5L$ and $Cp_2Mo_2(CO)_4L_2$ ($L=PPh_3, AsPh_3$)

Complex	colour	ν(CO)† (cm^{-1})	'H n.m.r.‡ (δ)
$Cp_2Mo_2(CO)_5(AsPh_3)$	red	1967vs 1902vs 1888vs 1873vs 1818s	4.83(5) 5.10(5) 7.46.(15)
$Cp_2Mo_2(CO)_5(PPh_3)$	red	1968vs 1905vs 1886vs 1873vs 1816s	4.73(5)5.11(5) 7.44(15)
$Cp_2Mo_2(CO)_4(AsPh_3)_2$	crimson	1843s 1828vs	insufficiently soluble
$Cp_2Mo_2(CO)_4(AsPh_3)_2$	red	1853sh 1830s	"

† Nujol mull ‡ $CDCl_3$ solution

When CH_2Cl_2 was used to extract the product from the reaction residue an additional product $CpMo(CO)_2(AsPh_3)Cl$ was recovered in substantial yield (17%). Further reactions showed that $Cp_2Mo_2(CO)_5(AsPh_3)$ could be formed from $Cp_2Mo(CO)_4(AsPh_3)_2$ by gentle heating in toluene, non-carbonyl decomposition products also being produced. $Cp_2Re_2(CO)_5(AsPh_3)$ decomposes to $CpMo(CO)_3Cl$ and $CpMo(CO)_2(AsPh_3)Cl$ when refluxed in CH_2Cl_2. These additional reactions show that all the products isolated from the reaction of n-BuLi with $[CpMo(CO)_2(AsPh_3)(NCPh)]^+[PF_6]^-$ can be explained by the decomposition of the initially formed $Cp_2Mo_2(CO)_4(AsPh_3)_2$ species, but this does not rule out the possibility of $Cp_2Mo_2(CO)_5(AsPh_3)$ being formed directly as a product of the reaction.

A possible reaction scheme might therefore involve nucleophilic attack by Bu^- not at the nitrile, but at the positively charged molybdenum atom. The molybdenum -alkyl complex thus formed may then undergo a β-elimination reaction resulting in the formation of the metal hydride and but-1-ene (no direct evidence for the production of but-1-ene was obtained). The metal hydride will readily thermally decompose resulting in the formation of $Cp_2Mo_2(CO)_4(AsPh_3)_2$ This reaction scheme is illustrated in Fig. A1.3.3.



$$(\Pi\text{-}C_5H_5)(CO)_2(AsPh_3)\underset{Bu^-}{Mo^+}\text{-}N{=}CPh \longrightarrow (\Pi\text{-}C_5H_5)(CO)_2(AsPh_3)Mo\text{-}CH_2\text{-}\underset{H}{CH}\text{-}CH_2\text{-}CH_3 + PhCN$$

$$\big\downarrow$$

$$[\Pi\text{-}C_5H_5(CO)_2(AsPh_3)Mo]_2 + H_2 \longleftarrow (\Pi\text{-}C_5H_5)(CO)_2(AsPh_3)Mo\text{-}H + CH_2{=}CHCH_2CH_3$$

Fig. A1.3.3.

This reaction scheme offers an alternative explanation of the formation of $CpMo(CO)_2(AsPh_3)Cl$ when the reaction residue is extracted with CH_2Cl_2. It is expected that any metal hydride present would be converted to the chloride on the addition of CH_2Cl_2 (c.f. formation of $CpMo(CO)_3Cl$ from $CpMo(CO)_3H + CH_2Cl_2$[141]).

The reaction was repeated using LiOMe as the nucleophilic species to determine whether the reaction scheme was valid for other nucleophilic species. In this case β-elimination of a proton from the initial product would result in the formation of the metal hydride and formaldehyde ($CH_2=O$). Unfortunately $Cp_2Mo_2(CO)_4(AsPH_3)_2$ was not recovered from this reaction, the only carbonyl product being $Cp_2Mo_2(CO)_5(AsPh_3)$. It is not clear whether all the $Cp_2Mo_2(CO)_4(AsPh_3)_2$ formed in the reaction decomposed, or whether another type of reaction e.g. reduction was occurring. In a separate experiment $[CpMo(CO)_2(AsPH_3)(NCPh)]^+ [PF_6]^-$ was treated with a sodium amalgam with the aim of bringing about a reduction. The only carbonyl product recovered was $Cp_2Mo_2(CO)_5(AsPh_3)$, a good deal of decomposition being evident. It is not clear how this product forms, but it is probable that $Na^+ [CpMo(CO)_2(AsPh_3)]^-$ or $CpMo(CO)_2(AsPh_3)$ are involved as intermediates in the process, free PhCN being liberated.

To further validate the formulation of $Cp_2Mo_2(CO)_5(AsPh_3)$, produced in the above reactions, a direct method of synthesis was devised. $[CpMo(CO)_3]_2$ when refluxed with a slight molar excess of $AsPh_3$ in T.H.F. did not bring about a reaction. When irradiated with u.v. light however a good yield (80%) of $Cp_2Mo_2(CO)_5(AsPh_3)$ was recovered. This was identical to the similarly formulated product isolated as the result of the reactions using $[CpMo(CO)_2(AsPh_3(NCPh)]^+ [PF_6]^-$ described above.

A1.4. CONCLUSION

Nucleophilic attack by BuLi on the cationic $[CpMo(CO)_2(AsPh_3)(NCPh)]^+$ species did not result in the formation of molybdenum-methyleneamino complexes. A reaction involving the formation of a molybdenum-butyl species probably resulted, this species then undergoing a β-elimination reaction resulting in the formation of a metal hydride and but-1-ene.

The hydride then decomposes (thermally or in the presence of air) to give a mixture of $Cp_2Mo_2(CO)_4(AsPh_3)_2$ and $Cp_2Mo_2(CO)_5(AsPh_3)$. A method of preparing the pentacarbonyl derivative directly is described.

It is possible that the molybdenum atom in the $[Cp\ Mo(CO)_2(AsPh_3)(NCPh)]^+$ species was made more attractive to the nucleophile by the overall positive charge on the complex, resulting in attack not at the carbon of the nitrile, but at the metal itself. Future work might therefore be conducted using a nucleophilic species that cannot approach the metal closely for steric reasons e.g. tertiarybutyl-lithium, or else a neutral substrate such as $CpMo(CO)_2(NCPh)Cl$.

APPENDIX TWO

Departmental colloquia, Chemical Society lectures and first-year induction course for post-graduate students.

(*denotes those attended)

1. University of Durham chemistry Colloquia 1979-82

*21 November 1979	Dr. J. Muller (University of Bergen),"Photochemical reactions to ammonia".
*28 November 1979	Dr. B. Cox (University of Stirling), "Macrobicyclic cryptate complexes: dynamics and selectivity".
* 5 December 1979	Dr. G.C. Eastmand (University of Liverpool), "Synthesis and properties of some multicomponent polymers".
*12 December 1979	Dr. C.I. Ratcliffe, "Rotor motions in solids".
*18 December 1979	Dr. K.E. Newman (University of Lausanne), "High pressure multinuclear n.m.r. in the elucidation of mechanism in fast simple inorganic reactions".
*30 January 1980	Dr. M. Barrow (University of Edinburgh), "The structures of some simple inorganic compounds of silicon and germamium-pointers to structural trends in group IV".
6 February 1980	Dr. J.M.E. Quirke (University of Durham), "Degradation of chlorophyll in sediments".
*23 April 1980	B.Grievson BSc. (University of Durham), "Halogen radiopharmaceuticals".
14 May 1980	Dr. R. Hutton (Waters Associates), "Recent developments in multi-milligram and multi-gram scale preparative high performance liquid chromatography".
21 May 1980	Dr. T.W. Bentley (University of Swansea), "Medium and structural effects on solvolytic reactions".
*10 July 1980	Professor D Des Marteau (University of Heidelberg), "New developments in organonitrogen fluorine chemistry".

19 September 1980	Dr. C.D. Wagner (University of Berkeley, California), "Identification of chemical states by special features in ESCA".
*8 October 1980	Professor T. Fehlner (Notre Dame University, Indiana, U.S.A.), "Metalloboranes - cages or co-ordination compounds".
*15 October 1980	Dr. R. Alder (University of Bristol), "Doing chemistry inside cages - medium ring bicyclic molecules".
*12 November 1980	Dr. M. Gerloch (University of Cambridge), "Magneto-chemistry is about chemistry".
*19 November 1980	Dr. T. Gilchrist (University of Liverpool), "Nitroso-olefins as synthetic intermediates".
*3 December 1980	Dr. J.Connor (University of Manchester),"Thermo-chemistry of transition metal compounds".
*18 December 1980	Dr. R.F. Evans, (University of Brisbane, Australia), "Some recent communications to the editor of Australian Journal of failed chemistry".
*4 February 1981	Professor S.F.A. Kettle (University of East Anglia), "Variations in the molecular dance at the crystal ball".
25 February 1981	Dr. K. Bowden (University of Essex), "The transmission of polar effects of substituents".
*4 March 1981	Dr. S. Cradock (University of Edinburgh), "Pseudo-linear pseudohalides".
11 March 1981	Dr. J.F. Stoddart (I.C.I.Ltd/University of Sheffield), "Stereochemical principles in the design and function of synthetic molecular receptors".
*17 March 1981	Professor W. Jencks (Brandeis University, Massachusetts, "When is an intermediate not an intermediate"?
*18 March 1981	Dr. P.J. Smith (International Tin Research institute), "Organotin compounds - a versatile class of organmetallic derivatives".

6 May 1981	Professor M. Szwarc F.R.S. (University of California), "Mechanisms of ionic polymerisation, living and dormant polymers".
10 June 1981	Dr. J. Rose (I.C.I. Plastic Division), "New engineering plastics".
*17 June 1981	Dr. P. Moreau (University of Montpellier), "Recent results in perfluroorganometallic chemistry".
*24 June 1981	Dr. S.A.R. Knox (University of Bristol), "Co-ordination and reactivity of organic species at dinuclear metal centres".
26 June 1981	Professor A.P. Schaap (Office of U.S. Naval Research, London), "Mechanisms of chemiluminescence and photooxygenation".
14 October 1981	Professor E. Kluk (University of Katowice), "Chemiluminescence & Photooxidation".
28 October 1981	Dr.R.J.H. Clark (University College, London): Resonance Raman spectroscopy".
6 November 1981	Dr. W. Moddenman (Monsato Labs, St. Louis, Missouri): "High energy materials".
18 November 1981	Prof. M.J. Perkins (Chelsea College): "Spin trapping and Nitroxide radicals".
*25 November 1981	Dr. M. Baird (University of Newcastle),"Intramolecular reactions of carbenes and carbenoids".
*2 December 1981	Dr. G. Beamson (University of Durham), "Photoelectron spectroscopy in a strong magnetic field".
*30 November 1981	Dr. B.T. Heaton (University of Kent), "N.M.R. studies of carbonyl clusters".
*20 January 1982	Dr. M.R. Bryce, (University of Durham), "Organic metals".

27 January 1982	Dr. D.L.H. Williams, (University of Durham), "Nitrosation & nitrosoamines".
*3 Februry 1982	Dr. D. Parker (University of Durham), "Modern methods of determining enantiomeric purity".
*10 February 1982	Dr. D. Pethrick (University of Strathclyde), "Conformation of small and large molecules".
17 February 1982	Prof.D.T. Clark (University of Durham), "Studies of surfaces by ESCA".
*24 February 1982	Dr. L. Field (University of Oxford), "Application of N.M.R to biosynthestic studies on penicillin".
3 March 1982	Dr. P. Bamfield (I.C.I. Organics), "Computer aided design in synthetic organic chemistry".
*17 March 1982	Prof. R.J. Haines (University of Cambridge/ Natal), "Clustering around Ru,Fe and Rh."
7 April 1982	Dr. A. Pensak (Dupont, USA), "Computer aided synthesis".
5 May 1982	Dr. G. Tennant (University of Edinburgh), "The aromatic nitro group in heterocyclic reactions".
7 May 1982	Dr. C.D. Garner (University of Manchester), "Molybdenum centres in enzymes".
26 May 1982	Dr. A. Welch (University of Edinburgh), "Conformation and distortion in Carbometallo-boranes".

2. Durham University Chemical Society Lectures 1979-1982

*18 October 1979	Dr. G. Cameron (University of Aberdeen), "Synthetic polymers - twentieth century polymers".
*25 October 1979	Professor P. Gray (University of Leeds), "Oscillatory combustion reactions".
*1 November 1979	Dr. J. Ashby (I.C.I. Toxicological Laboratory), "Does chemically-induced cancer make chemical sense".

*8 November 1979	J.H. Turnbull (R.M.C. Shrievenham), "Luminescence of drugs.
*15 November 1979	Professor E.A.V. Ebsworth (University of Edinburgh), "Stay still, you brute: the shape of simple silyl complexes".
24 January 1980	Professor R.J.P. Williams (University of Oxford), "On first looking into biology's chemistry".
14 February 1980	Professor G. Glamen (University of Salford), "A yarn with a new twist - fibres and their uses".
*21 February 1980	Dr. M.L.H. Green (University of Oxford), "Synthesis of highly reactive organic compounds using metal vapours".
28 February 1980	Professor S.F.A. Kettle (University of East Anglia), "Molecular shape, structure and chemical blindness".
*6 March 1980	Professor W.D. Ollis (University of Sheffield), "Novel molecular rearrangements".
*16 October 1980	Dr. D. Maas (University of Salford), "Reactions a go-go".
*23 October 1980	Professor T.M. Sugden (University of Cambridge), "Reactions in flames".
30 October 1980	Professor N. Grassie (University of Glasgow), "Inflammability hazards in commercial polymers".
* 6 November 1980	Professor A.G. Sykes (University of newcastle), "Metalloproteins: an inorganic chemists approach".
13 November 1980	Professor N.N. Greenwood (University of Leeds), "Metalloborane chemistry".
*4 December 1980	Rev. R. Lancaster, "Fireworks".
22 January 1981	Professor E.A. Dawes (University of Hull), "Magic and mystery through the ages".
*29 January 1981	Mr. H.J.F. Maclean (I.C.I. Agricultural Division), "Managing in chemical industry in the 1980's".

*5 February 1981	Professor F.G.A. Stone (University of Bristol), "Chemistry of carbon to metal triple bonds".
12 February 1981	Dr. I. Fleming (University of Cambridge), "Some uses of silicon compounds in organic synthesis".
*7 May 1981	Professor M. Gordon (University of Essex), "Do scientists have to count"?
*22 October 1981	Dr. P.J. Corish (Dunlop), "What would life be like without rubber".
*29 October 1981	Miss J.M. Croyn (University of Durham),"Chemistry in Archeology".
12 November 1981	Professor A.I. Scott (University of Edinburgh", "An organic chemist's view of life through the N.M.R. tube".
19 November 1981	Professor B.L. Shae (University of Leeds), "Big rings and metal-carbon bond formation".
3 December 1981	Dr. W.O. Ord (Northumbria Water Authority), "The role of the scientist in a regional water authority".
28 January 1982	Professor I. Fells (University of Newcastle), "Balancing the energy equations".
*11 February 1982	Prof. R.K. Harris (University of East Anglia), "N.M.R. in the 1980's".
25 February 1982	Professor R.O.C. Norman (University of York) "Turning points and challenges for the organic chemist".
*4 March 1982	Dr. R. Whyman (I.C.I. Runcorn),"Making metal clusters work".

3. First year induction course

Series of lecture arranged by the department for the benefit of the postgraduate students.

Department organisation	Dr. E.J.F. Ross
Safety matters	Dr. M.R. Crampton
Electrical appliances and infrared spectroscopy	Mr. R.N. Brown
Chromatography and microanalysis	Mr. T.F. Holmes
Library facilities	Mr. W.B. Woodward (Keeper of Science books)
Atomic absorptiometry and inorganic analysis	Mr. R. Coult
Mass spectrometry	Dr. M. Jones
N.m.r. spectroscopy	Dr. R.S. Matthews
Glassblowing techniques	Mr. W.H. Fettis and Mr. R. Hart

REFERENCES

1 W.R.McClellan, H.H.Hoehn,H.N.Crips, E.L.Muetterties and B.W.Howk, J.A.C.S., 83, (1961), 1603.

2 R.B. King and R.N. Kapoor, J. Organometal. Chem., 15 (1968),457.

3 W.G. Young and J.D. Roberts, J.A.C.S., 68, (1946), 1472.

4 H.L.Clarke and N.J.Fitzpatrick, J.Organometal.Chem., 40, (1972), 379.

5 M. Cousins and M.L.H. Green, J.Chem.Soc., (1963), 889

6 F.A. Cotton and J.R. Pipal, J.A.C.S., 93, (1971), 5441.

7 G. Raper and W.S. McDonald, J.Chem.Soc. Dalton, (1972), 265

8 B.M.Mikhailov, Organometal.Chem. Revs., 8 (1972), 1.

9 J.N. Van Niekerk and F.R.L. Schoeing,Acta. Cryst., 6, (1953), 609.

10 K.Vrieze, A.P. Praat and P. Cossee, J. Organometal. Chem. 12, (1968), 533.

11 C. Oldham, Prog.Inorg.Chem., 10, (1968), 223.

12 A. Davidson, W.McFarlane, L.Pratt and G. Wilkinson, J.Chem.Soc (1962), 3653

13 Y. Maeda, and R. Okawara, J.Organometal.Chem. 10, (1967), 247

14a J.N.Van Niekerk, F.R.L.Shoening and J.F. de Wet, Acta. Cryst., 6 (1953), 501.

14b M.L.H. Green, L.L. Mitchard, W.E. Silverthorn, J.Chem.Soc. Dalton, (1973) , 1403.

15 F.A. Cotton, Chem.Soc.Revs., 4, (1975), 27.

16 J. Kuyper, L.G. Hubert-Pfazgraf, P.C. Keijzer and K.Vrieze. J.Organometal.Chem. 108, (1976), 271.

17 C. Gerhardt, Annalen. 108, (1858), 219.

18 Chem.Abs. 9th Coll.Index Guide, (1972-76), 42G

19 A.Bernthsen, Annalen, 192, (1878), 1.

20 H. Von Pechman, Berichte, 28, (1895), 869.

21 H. Von Pechman, Berichte, 28, (1895), 2362

22 W. Markwald, Annalen, 286, (1895), 343.

23 H.Von Pechman, Berichte, 30, (1897), 1779.

24 J.B. Cohen and J. Marshall, J.Chem.Soc., (1910), 328.

25 R. Burtles and K.L.Pyman, J.Chem.Soc., (1923), 361.

26 D.C. Prevorsek, J.Physical Chem., 66,(1962), 769.

27 O.Dimroth, M.Eble and W.Gruhl, Berichte, 40,(1907), 2390.

28 O. Dimroth, Berichte, 36, (1903), 909.

29 S.N. Danilov, L.N. Yastrebav and L.N. Borova, Zhur.Obs. ei Khim.40, (1970), 2248; C. Abs. 72, (1970), 12326K.

30 E.C. Taylor and W.A. Ehrhart, J. Org.Chem., 28, (1963), 1108.

31 R.H. DeWolfe, J. Organometal.Chem., 27, (1962), 490.

32 O. Dimroth, Berichte, 40, (1907), 2376.

33 P. Greiss, Annalen, 137, (1866), 53.

34 W. Beckh and J.Tafel, Berichte, 27, (1894), 2315.

35 L. Meunier and E. Despartment, Compt.Rend., 144,(1907), 273.

36 R.L.Shriner and F.W. Neumann Chem.Revs., 35, (1944), 351.

37 A. Pinner and F. Klein, Berichte, 11,(1878), 4.

38 W.H. Knoth, Inorg. Chem., 12, (1973), 38.

39 L. Meunier, Compt. Rend., 136, (1903), 758,

40 T. Inglis, M. Kilner, T. Reynoldson and E.E.Robertson, J.Chem.Soc. Dalton, (1975), 924.

41 W. Seidel and H.J. Marke, Z.Anorg.Chem., 416, (1975), 83.

42 F.E. Brinckman and H.S. Haiss, Chem & Ind., (1963), 1124.

43 F.E. Brinckman and H.S. Haiss, U.S.Patent 3, 437,651; C. Abs. 70 (1969), P115335a.

44 K.R. Laing, S.D. Robinson and M.F. Uttley, J.Chem.Soc., Dalton, (1974), 1205.

45 W. Bradley and I. Wright, J.Chem.Soc., (1956), 641.

46 S. Candeloro de Sanctis, L.Toniolo, T. Boschi, Inorg.Chim.Acta, 12, (1975), 251.

47 F.A. Cotton, T.Inglis, M. Kilner and T. Webb, Inorg.Chem., 14, (1975), 2023.

48 B. Gaylani and M. Kilner, J. Less Common Metals, 54, (1977), 175.

49 F.A. Cotton, W.H. Isley and W. Kaim, Inorg.Chem., 19, (1980), 2360.

50 W.H. DeRoode, M.L.Beckes, A. Oskam and K. Vrieze, J.Organometal Chem., 142, (1977), 337.

51 J. Kuyper, L.G. Hubert-Pfalzgraf, P.C.Keijzer and K. Vrieze, J.Organometal. Chem., 108, (1976), 271.

52 O.J. Scherer and P. Hornig, Chem. Berichte 101, (1968), 2533.

53 L. Toniolo, G. Deganello, P.L. Sandrini and G. Bombieri, Inorg. Chim.Acta, 15, (1975), 11

54 L. Toniolo, A. Immirizi, V.Croatto and G. Bombieri, Inorg.Chim.Acta, 19, (1976), 209.

55 W.H. DeRoode and K. Vrieze, J. Organometal.Chem., 135, (1977), 183.

56 T. Inglis, M. Kilner and T. Reynoldson, J. Chem.Soc. Chem. Comm., (1972), 774.

57 T. Inglis and M. Kilner, J.Chem.Soc. Dalton, 10, (1975), 930.

58 M. Kilner and S. Wallwork, personal communication, unpublished results.

59 W.H.DeRoode, J. Berke,A.Oskam and K. Vrieze, J. Organometal.Chem. 165, (1978), 307.

60 E. Pfeiffer and K. Olie, Cryst.Struct.Comm., 4, (1975), 605.

61 E.W. Abel and S.J. Skittral, J. Organometal.Chem. 185, (1980), 391.

62 R. Rossi, A. Duatti, L.Magon and L. Tonido, Inorg.Chim.Acta , 48, (1981), 243.

63 A. Casellato, R. Graziani, R. Rossi, L.Magon and L.Toniolo, Inorg. Chim.Acta, 52, (1981), 119.

64 R.J. Angelici, Accs. of Chem.Res., 5, (1972), 335.

65 R.J. Angelici and D.L. Denton, Inorg.Chim.Acta, 2, (1968), 3.

66 R.J. Angelici and H.E. Kruse, J. Organometal.Chem., 22, (1970), 461.

67 N.D. Cameron and M. Kilner, J. Chem.Soc.Chem Comm.,(1975), 687.

68 W. Bradley and E. Leete, J.Chem. Soc., (1951), 2147.

69 L. Toniolo, T. Boschi and G. Deganello. J. Organometal. Chem., 93, (1975), 405.

70 W.H.DeRoode and K. Vrieze, J. Organometal.Chem., 145, (1978), 207.

71 E.W. Abel and S.J. Skittral, J. Organometal.Chem., 193, (1980), 389.

72 P.I. Van Vliet, G. Van Koten and K. Vrieze, J. Organometal.Chem., 188, (1980), 301.

73 C.R. Hauser, I.C. Flur, S.W. Kantor, J.A.C.S. 71, (1949), 294.

74 T. Kauffman, G. Bessner, E.Koppelmann, D. Kuhlmann, A. Schott and H. Schrecken, Angew.Chem.Internat.Ed., 7, (1968), 131.

75 T. Kauffman, Angew.Chem.Internat.Ed., 13, (1974), 627.

76 H.R. Keable, PhD. Thesis Univ. of Durham (1972), 155.

77 E. Popowski, A. Hahn and H. Kelling, J. Organometal. Chem., 110, (1976), 295.

78 K. Farmery, M. Kilner and C. Midcalf, J. Chem.Soc., (A), (1970), 2279.

79 H.R. Keable and M. Kilner, J.Chem.Soc., Dalton, (1972), 153.

80 H.R. Keable and M. Kilner, J.Chem.Soc., Dalton, (1972), 1535.

81 H.R. Keable, Ph.D. Thesis. Univ. of Durham , (1972), 153.

82 C.A. Payling, Ph.D. Thesis, Univ. of Durham (1969), 138.

83 H.M.M. Shearer and J.D. Sowerby, communicated in ref 81.

84 P. Griess, Annalen, 121, (1862), 258.

85 Beilstein's Handbuch der Organischen Chemie, Springer Verlag, Berlin, part 16/1, (1974), 643.

86 O. Dimroth, Berichte, 39, (1906), 3905, and 38, (1905) 670

87 F.P. Dwyer, J.A.C.S., 63, (1941), pages 78 and 81

88 C.M. Harris, B.F. Hoskins and R.L. Martin, J.Chem.Soc, (1959), 3728.

89 M. Corbett and B.F. Hoskins, J.A.C.S., 89, (1967), 1530, and J.Chem.Soc., Chem Comm., (1968), 1602.

90 R.B. King and N.C. Nainan, Inorganic Chem., 14, (1975), 271.

91 F.E. Brinckman and H.S. Haiss, Chem and Ind., (1963), 1124.

92 L.D. Brown and J.A. Ibers, J.A.C.S., 98, (1976), 1597.

93 E. Pfeiffer and K. Olie, Cryst. Struct.Comm., 4, (1975), 605.

94 R.T. Kops, A.R. Overbeek and H. Schenk, Cryst.Struct, Comm., 5, (1976), 125.

95 T.A. Manuel, Ad. in Organometal.Chem., 3, (1965), 181.

96 M.E. El Sayed and H.D. Kaesz, Inorg.Chem., 2, (1963), 158.

97 R. Colton and J.E. Garrard, Aust. J. Chem., 26, (1973), 1781.

98 E.W. Abel, G.B. Hargreaves and G. Wilkinson, J. Chem.Soc. (1958), 3149.

99 R.J. Angelici and D.L. Denton, Inorg. Chem.Acta, 2, (1968), 3

100 R.B. King, Ad. in Organometal Chem., 2, (1964), 157.

101 H.D. Kaesz, R.B. King, and F.G.A. Stone, Z.Naturforsch, 15B, (1960), 763.

102 E.W. Abel and S. Moorhouse, Angew,Chem., 10, (1971), 339.

103 E. W. Abel and I.D.H. Towle, J. Organometal. Chem., 155, (1978), 299.

104 E.W. Abel, G.W. Hargreaves and G. Wilkinson, J. Chem.Soc., (1958), 3149.

105 R. Calton and J.E. Garrard Aust.J.Chem., 26, (1973), 1781.

106 J.D. Atwood and T.L. Brown, J.A.C.S., 98, (1976), 3155.

107 D.F. Evans, J. Chem Soc., (1959), 2003.

108 J.L. Deutsh and S. M. Poling, J. Chem.Ed., 46, (1969), 167.

109 J. Lewis and R.G. Wilkins, "Modern Co-ord. Chem.". Interscience 1960, pp.403.

110 R.J. Angelici and D.L. Denton, Inorg.Chim.Acta, 2, (1968), 3.

111 R.J. Angelici and H.E. Kruse, J.Organometal. Chem., 22 , (1970), 461.

112 D.C. Prevorsek, J. Phys. Chem, 16, (1962), 769.

113 R. Colton and J.E. Garrard, Aust. J. Chem., 26, (1973), 1781.

114 G.W. Parshall, Accounts Chem. Res., 3, (1970), 139.

115 F.R. Hartley, "The Chem. of Pt. and Pd, with particular reference to complexes of the elements", London, Applied Science, (1973).

116 J. Halfpenny and M. Kilner, personal communication.

117 L. Cambi and L. Szego, Berichte, 64, (1931), 2591.

118 I.D. Brown and P. Dunitz, Acta. Cryst., 14, (1961), 480.

119 H. Corbett and B.F. Hoskins, Chem.Comm., (1968), 1602.

120 J.E. Conner, G.A. Janusonis and E.R. Corey, Chem. Comm., (1968), 445.

121 A.H. Ewald, R.L. Martin, E. Sinn and A.H. White, Inorg.Chem., 8, (1969), 1837.

122 F.A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry". (3rd Ed.,) Interscience, (1972), pp 569.

123 B.N. Figgis, J. Lewis and F. Mabbs, J. Chem.Soc., (1961), 3138.

124 B.C. Challis, S.A. Kyrtopoulos, J. Chem.Soc. Perkin I, (1979), 299.

125 B.F.G. Johnson, J.A. MacCleverty, Progr. Inorg. Chem., 7, (1966), 277

126 P.G. Douglas, R.D. Feltham and H.G. Metzger, J.A.C.S., 93, (1971), 84.

127 F. Bottomley, W.V.F. Brooks, S.G. Clarkson and S.B. Tong, Chem. Comm., (1973), 919.

128 K. Farmery, M. Kilner and C. Midcalf. J. Chem. Soc (A), (1970), 2279.

129 M. Kilner and C. Midcalf, Chem. Comm., (1970), 552.

130 M. Kilner and C. Midcalf, J.Chem.Soc. Dalton, (1971), 292.

131 H.M.M. Shearer and J.D. Sowerby, J. Chem.Soc.Dalton, (1973), 2629.

132 H.R. Keable, M. Kilner and E.E. Robertson, J. Chem Soc., Dalton, (1974), 639.

133 F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", (3rd Edition), Interscience, (1972), pp. 713.

134 D. Bright and O.S. Mills, Chem. Comm., (1967), 245.

135 S. Otsuka, T. Yoshida and N.A. Nakamura, Inorg. Chem., 6., (1967), 20.

136 H. Bock, Angew. Chem. Int.Ed., 1, (1962), 550.

137 D.A. Buckingham, B.M. Sargeson, A. Zenella, J.A.C.S, 94, (1972), 1007.

138 N.C. Stephenson, J. Inorg. and Nucl, Chem., 24,(1962), 801.

139 R.J. Angelici, Accs. of Chem.Res., 5, (1972), 335,

140 W.H. Knoth, Inorg. Chem, 14, (1975), 1566.

141 E.O. Fischer, Inorg. Synth., 7, (1963), 136.

142 P.M. Treichel, K.W. Barnett, and R.L. Shubkin, J. Organometal. Chem., 7, (1967), 449.

143 K.W. Barnett, and P.M. Treichel, Inorg. Chem., 6, (1967), 294.

144 R.J. Haines, R. Nyholm and M.H.B.Stiddard, J. Chem.Soc. (A), (1968), 43.