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Studies of the Co-ordination Chemistry of Guanidines with Transition Metals

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A talk to a group of children.

Bear in mind that the wonderful things you learn in your schools are the work of many generations, produced by enthusiastic effort and infinite labour in every country of the world. All this is put into your hands as your inheritance in order that you may receive it, honor it, add to it and one day faithfully hand it on to your children. Thus do we mortals achieve immortality in the permanent things which we create in common.

If you always keep that in mind you will find a meaning in life and work and acquire the right attitude towards other nations and ages.

Albert Einstein

Carl Seeling, *Ideas and Opinions*, (Wings Books, New York)

Declaration

The work contained in this thesis has not been submitted elsewhere for any other degree or qualification, and unless otherwise referenced it is the author's own work.

To my Family

Acknowledgements

I wish to express my gratitude to the Brazilian Agency CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico) for the financial support of a research studentship over the last four years.

My sincere thanks go to Dr. Melvyn Kilner for his supervision throughout the project. I would also like to thank Dr. Michael Richardson for his encouragement towards the idea of working for a high degree in England since we met in Brazil.

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Finally, I thank all Brazilians, foreigners and British citizens who helped me with their sincere friendship during the last four years.

J. R. S. Maia
Durham November, 1994.

Studies of the Co-ordination Chemistry of Guanidines with Transition Metals

J. R. S. Maia, Ph.D. Thesis, 1994

Abstract

This work involves the characterisation of reaction products of transition metals from the 1st, 2nd and 3rd rows of the Periodic Table with guanidines and their lithiated derivatives. Physical methods such as infrared spectroscopy, ^1H, ^{13}C and ^{19}F nuclear magnetic resonance spectroscopy, microanalysis, and conductivity measurements have been used to characterise the materials. The transition metal compounds used in this work can be divided into two groups: (*i*) metal carbonyls and (*ii*) metal halides. The metal carbonyls group consists of $[M(CO)_5L]$ (M = Mn, L = Br; M = Cr, Mo, W, L = CO), $[Mo(Cl)L(CO)_3]$ ($L = \eta\text{-}C_5H_5$) and $[MoL(CO)_3][BF_4]$ ($L = \eta\text{-}C_7H_7$), and the metal halide group consists of MCl_2 (M = Pd, Pt), $MLCl_2$ (M = Pd and $L = C_8H_{12}$), K_2MCl_4 (M = Pd, Pt) and WCl_4. Studies have involved two substituted guanidines, 1,2,3-triphenylguanidine and *syn*-1,2-diphenylguanidine and the lithiated derivative of 1,2,3-triphenylguanidine.

The reactions were undertaken using a variety of conditions. The type of solvent, temperature and molar ratio are important parameters, particularly for the complexes of manganese. Similar conditions were explored for the complexes of palladium, platinum, chromium, molybdenum, tungsten and arylmolybdenum derivatives. Carbonyl complexes of the type $[Mn(Br)(CO)_3L_2]$ (L = 1,2,3-triphenylguanidine), $[Mn(Br)(CO)_4L]$ (L = 1,2,3-triphenylguanidine), $[Mo(\eta\text{-}C_5H_5)L(CO)_2]$ (L = 1,2,3-triphenylguanidino) and complexes of the type $[M_2Cl_4L_2]$ (M = Pd, Pt; L = 1,2,3-triphenylguanidine, *syn*-1,2-diphenylguanidine), $[Pt_2Cl_4L_3]$ (L = *syn*-1,2-diphenylguanidine), $[Pt_2Cl_4L_2L^1]$ (L = *syn*-1,2-diphenylguanidine, L^1 = N,N'-diphenylurea), $[Pt_2Cl_2L_2L^1{}_2]$ (L = *syn*-1,2-diphenylguanidino, L^1 = *syn*-1,2-diphenylguanidine), $[PtCl_2L]$ (L = HNC(Me)NHC(Me)NH) and $[PdCl_2(C_8H_{12})L]$ (L = 1,2,3-triphenylguanidine, *syn*-1,2-diphenylguanidine), were isolated. A product containing BF_3 was isolated, and the bonding of the BF_3 studied.

The guanidine ligand adopts various bonding modes towards transition metals, and studies have been directed towards determining the mode adopted in each of the new complexes synthesised. Guanidines are found to act as strong σ-bonding ligands, having consequences on the remaining ligands. Comparison is made throughout with the related amidine ligands. Mechanisms of reactions, consistent with experimental data, are discussed throughout the thesis.

Abbreviations

bipy	2,2'-bipyridine
CI	Chemical ionization
COD	1,5-cyclooctadiene
$DPGH_3$	*Syn*-1,2-diphenylguanidine
$DPGH_2$	*Syn*-1,2-diphenylguanidino-anion
$DPGH_4$	*Syn*-1,2-diphenylguanidinium cation
DTB	N,N'-di-p-tolylbenzamidino-anion
DPA	N,N'-diphenylacetamidino-anion
DTF	N,N'-di-p-tolylformamidino-anion
DPT	N,N'-diphenyltriazeno-anion
DTBH	N,N'-di-p-tolylbenzamidine
DPAH	N,N'-diphenylacetamidine
DTFH	N,N'-di-p-tolylformamidine
DPTH	N,N'-diphenyltriazine
dppm	bis(diphenylphosphino)methane
DMG	dimethylglyoximato anion
dppp	2,6-bis(diphenylphosphino)pyridine
dppe	1,2-bis(diphenylphosphino)ethane
dmp	2,4-dimethyl-6-hydroxypyrimidino-anion
EI	Electron ionization
FAB	Fast atom bombardment
p-tolyl	*p*-methylphenyl group
py	pyridine
salen	N,N'-ethylenebis(salicylideneaminato)
$TPGH_2$	1,2,3-triphenylguanidine
TPGH	1,2,3-triphenylguanidino-anion
$TPGH_3$	1,2,3-triphenylguanidinium cation
TMEDA	N,N,N',N'-tetramethylethylenediamine
THF	Tetrahydrofuran
TCE	s-tetrachloroethane
trpy	tripyridine

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Chapter One

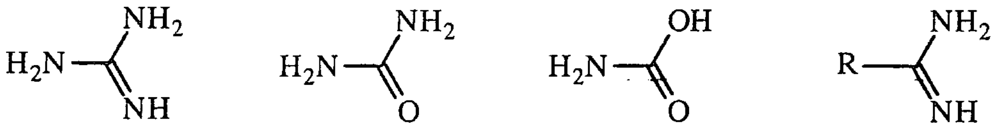
Guanidines and Related Compounds

Introduction

This chapter is concerned with a short review of the preparation, properties and reactions of guanidines and their derivatives (section A), and emphasises the similar chemistry of guanidines and amidines (section B). In section C the chemistry of guanidines and amidines towards transition metals is surveyed.

Guanidine is related to many other organic molecules as illustrated in Figure 1.1. It may be regarded as the imide of urea (**2**), and derived from carbamic acid (**3**) by replacement of O, and OH groups by NH and NH_2 groups respectively. When the R group of an amidine (**4**) is NH_2, the compound is named guanidine (**1**).

Free guanidine is very hygroscopic[1] and crystalline material melts at 48-49°C. It is very basic with pK_a value of 13.6, and absorbs carbon dioxide.



1 2 3 4

Figure 1.1 Guanidine and related compounds

Guanidine and its derivatives have been known to show various biological properties, and thus, have been studied in the field of pharmacology. These compounds have been used in chemotherapy of illnesses such as hypertension and diabetes[1].

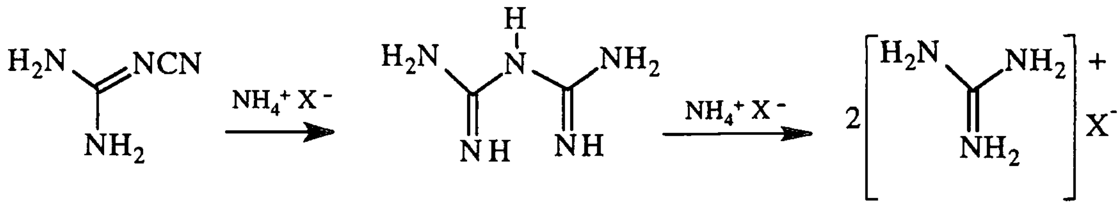
A. Preparation of Guanidines and Guanidine Derivatives[1]

1. Synthesis of Guanidines

Guanidines have been prepared as salts from reaction between ammonium salts and cyanoguanidines, cyanamide and thiourea. These three methods are discussed below.

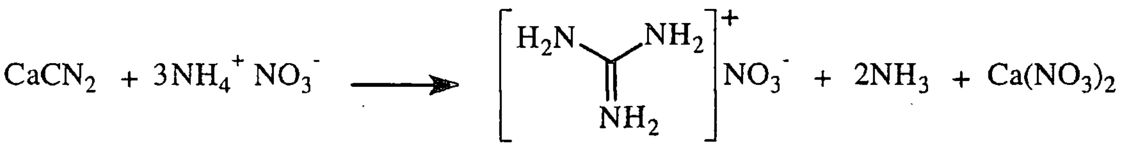
1.1 Addition of Ammonium Salts to Cyanoguanidines

This method involves a fusion of cyanoguanidine with two molar equivalents of an ammonium salt[2-4], and is the common process used in the industrial preparation of guanidine salts[5,6]. The yield of the reaction is about 80-95% at 160 - 260°C, the precise temperature depending on the ammonium salt used. However, Davis *et al*[7] do not recommend this method in the preparation of guanidinium nitrate due to the potential danger involved in the fusion of nitrate compounds. The reaction below is an example of this synthetic method.



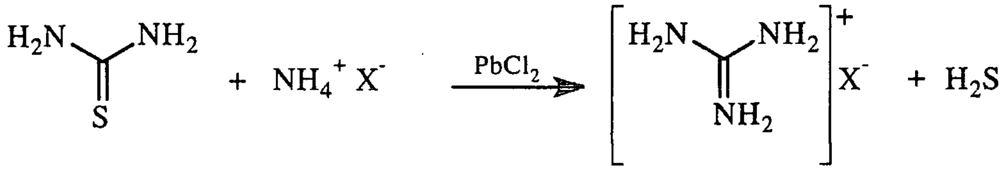
1.2 Addition of Ammonium Salts to Cyanamide

This method is also a fusion reaction between calcium cyanamide and an ammonium salt in a molar ratio of 1:3 respectively. Guanidinium nitrate[8] can be prepared by this reaction in 75% yield at 100°C (see reaction below).



1.3 Preparation of Guanidine Salts Catalysed by Lead(II) Chloride

Guanidine salts can also be prepared by heating thiourea with an excess of an ammonium salt in the presence of a molar equivalent of lead(II) chloride at 300°C in 95% yield[6]. This preparation requires the mixture to be heated in an autoclave. The reaction is illustrated below.

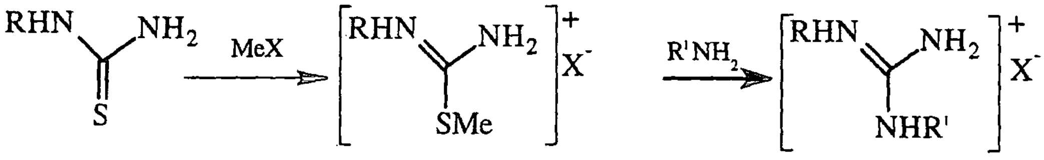


2. Synthesis of Substituted Guanidines

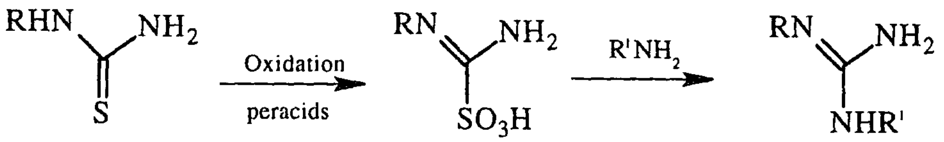
The preparation of substituted guanidines involves a variety of starting materials. The substituted alkyl- and arylguanidines have been obtained from thiourea, urea, and carbodiimide, among other reactants. Alkylation and arylation of guanidines can also be achieved to some extent. Some of these methods are described in this section.

2.1 Reactions Involving Thiourea

One of the reactions involving thiourea to synthesise substituted guanidines is the preparation of an S-methylisothiuronium salt, $[H_2NC(SMe)NHR]X$ as an intermediate. Methyl iodide or dimethyl sulphate reacts with an alkyl- or arylthiourea to produce such isothiuronium salts which can be isolated. Further reaction with an alkyl- or arylamine gives the corresponding alkyl- or arylguanidinium salt (see equation below). The last reaction requires temperatures of 60-80°C to achieve good yields[9,10]. Several alkyl-substituted guanidines have been prepared by this method in 40-50% yield[11,12].

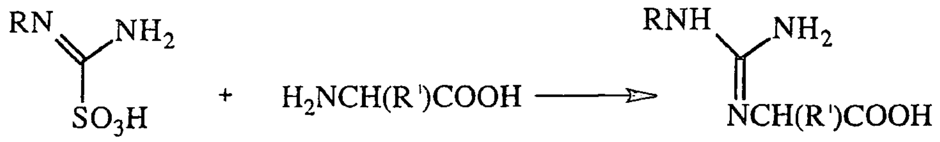


Another method named, "oxidation of thiourea" is the reaction of alkyl- or arylthioureas with peracids to give aminoiminomethanesulfonic acids, $H_2NC(SO_3H)NR$ which are isolated in 50-80% yield. Further reaction between this intermediate and alkyl- or arylamines at room temperature produces substituted guanidines[13,14].



Guanidino-acids are also prepared from thiourea either via the reaction of aminoiminomethanesulfonic acids or via the reaction of S-methylisothiuronium salts with amino acids[13], but the former method is preferred.

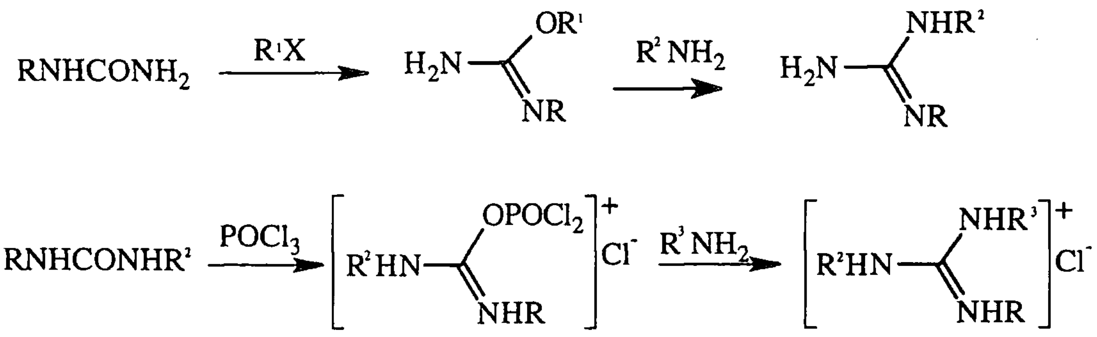
The yield of the latter intermediate is not as good as the yield of the sulphonic acid from the oxidation of thiourea.



The S-methylisothiuronium salt method also provides the 3(R)- and 3(S)-hydroxy-(2S) arginines in good yield for pharmaceutical use by reaction between the corresponding β-hydroxyornithines[15] and S-methylisothiourea.

2.2 Reactions Involving Urea

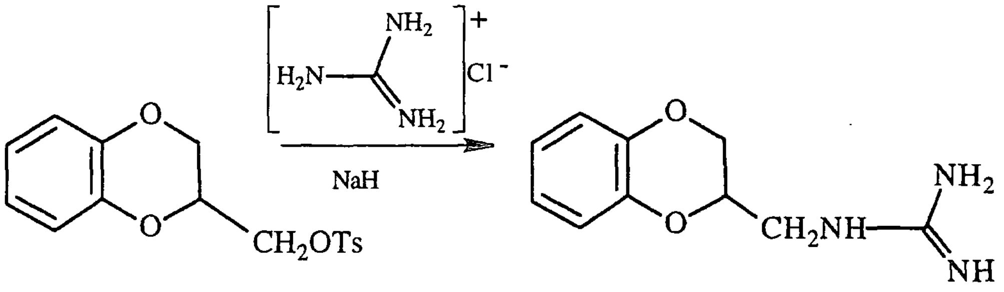
Ureas react with amines through different intermediates, depending on the reactants used to activate the urea. One method involves the conversion of urea to O-alkylisourea, and its subsequently reaction with amines. The second is the reaction of urea with $POCl_3$ and amines *in situ*. These reactions are illustrated below.



Substituted guanidines[14,16,17], and also amidines, have been prepared by the O-alkylisourea method. The direct preparation of trisubstituted guanidinium chloride is also known by reaction of N,N'-disubstitued ureas with phosgene. A second molecule of urea instead of an amine is necessary to complete the reaction.

2.3 Alkyl and Arylderivatives of Guanidine

Alkylation and arylation of guanidines often leads to a mixture of products, especially if a simple alkyl halide is used in the preparation of the alkylated derivatives. A monosubstituted compound can be prepared by reaction of guanidine with a sterically hindered tosylate[18] (see below). Arylation of guanidines seems to be more productive using a strongly-electrophilic pyridine, such as 1-chloro-3-nitro-pyridine.



2.4 Activation by Aluminium(III) Chloride and Nitric Acid

The reaction of 3,5-dimethyl-1-guanylpyrazole (**5**) nitrate with amines produces substituted guanidinium salts[19]. Aluminium(III) chloride is also used to activate the electrophilic attack of guanidine sulphonates (**6**) towards aromatic hydrocarbons[20]. Examples are given in Figure 1.2 .

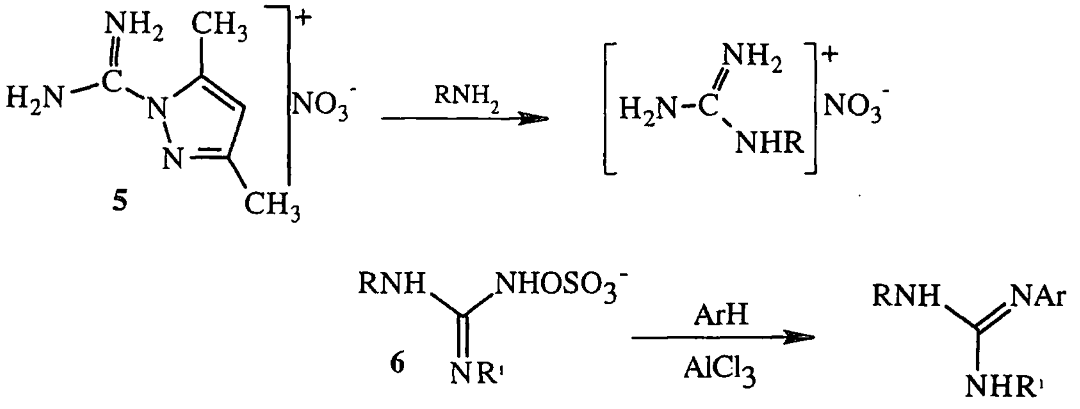


Figure 1.2 Preparation of substituted guanidines by $AlCl_3$ or HNO_3 activation

2.5 Reactions Involving Isocyanide and Carboimidate Derivatives

Penta-, tetra- and trisubstituted guanidines are prepared by reaction of isocyanide dichlorides with amines[21,22]. An intermediate chloride (**7**) is produced first (see Figure 1.3), and further reaction with amines leads to the substituted guanidines. Some of these chloride intermediates can be isolated.

S,S'-dimethyl-N-sulphonyliminodithiocarboimidates (**8**), which are easily prepared from the reaction of sulphonylamide with carbon disulphide in the presence of alkali, followed by quenching with MeI, react with amines to produce N-sulphonylisothioureas[23] (**9**) (see Figure 1.3) in 50-80% yield. Further reaction of N-sulphonylisothioureas with amine produces N-sulphonylguanidines (**10**). This method is similar to the S-methylisothiuronium process described before.

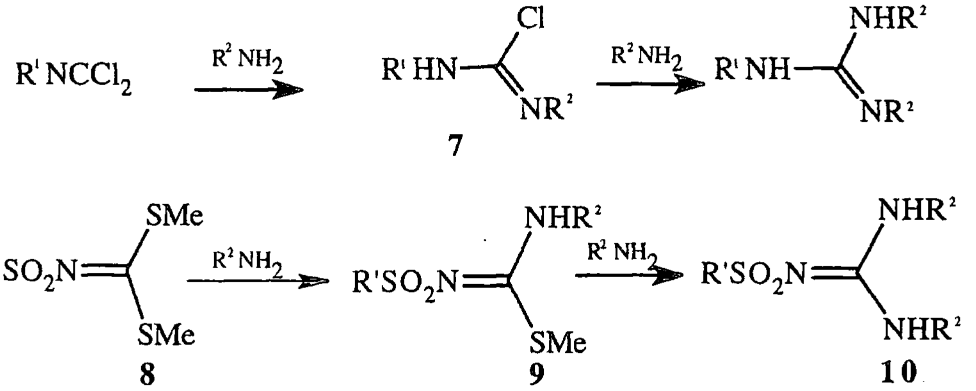


Figure 1.3 Reactions involving isocyanide and carboimidate derivatives

3. Basicity of Guanidines

The guanidinium ion is very stable due to π-electron delocalisation which involves the delocalisation of the positive charge[24-27] on the nitrogen atoms. All three resonance structures are equivalent and this may influence the stability of the guanidinium ion. Due to the delocalisation of electrons between the carbon and nitrogen atoms in guanidine or guanidinium ions, the C-N bonds all have some double bond character. Substitution into guanidine or the guanidinium ion changes the character of all of the C-N bonds.

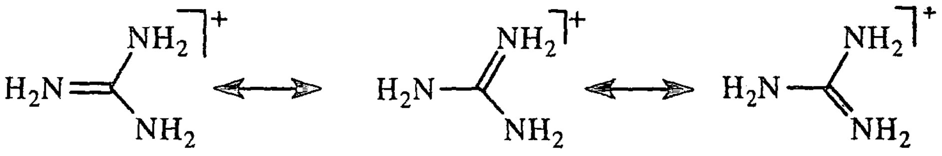


Figure 1.4 Resonance structures for the guanidinium ion

Methyl-substituted guanidines[11] have pK_a values in the range of 13.4 to 13.9. Since the parent guanidinium salt in water at 25°C has a pK_a value of 13.6, the methyl groups do not influence very much the basicity of methyl-substituted guanidines. Methyl groups are well known as electron donor groups in organic chemistry and the idea of having donation of electrons towards the nitrogen atoms of guanidine also supports the high pK_a value for methyl substituted guanidines.

The base strengthening effect is well observed by comparing the effect on pK_a for monosubstituted guanidinium salts of groups like $-NO_2$ and -OMe. Some examples are shown in Table 1.1 for monosubstituted guanidinium salts of the type $[RNH=C(NH_2)NH_2]X$.

Table 1.1
pK_a of monosubstituted guanidinium salts in water.

$[RNH=C(NH_2)NH_2]X$ R	pK_a .(25°C)
NH_2	11.04
Ph	10.77
NHPh	8.26
NO_2	-0.98

Taylor *et al* and Charton *et al*[28,29] have suggested that if the group R is an electron acceptor, the amino tautomer of the guanidine predominates, and if R is an electron donor group the imino tautomer is considered either predominant or the two isomers are present in comparable amounts. Figure 1.5 shows the two possible forms of tautomerism for phenylguanidine.

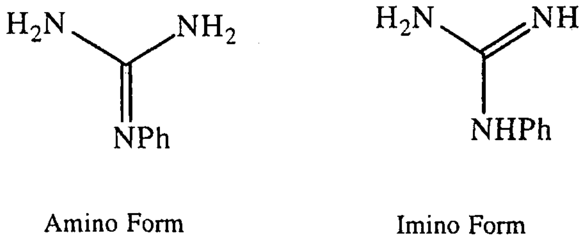


Figure 1.5 Tautomerism of Substituted Guanidines

Table 1.2 gives some pK_a value of substituted 2-phenyl-1,1,3,3-tetramethylguanidine salts in water[17] and in acetonitrile[28] where the group R is the substituent on the phenyl group.

Table 1.2
pK_a of substituted guanidinium salts in water and acetonitrile at 25°C

$[RC_6H_4NHC(NMe_2)NMe_2]X$ R	pK_a (In acetonitrile)	pK_a (in water)	ΔpK_a (acetonitrile-water)
4-OMe	21.00	12.57	8.43
2-OMe	21.00	12.19	8.81
4-Me	20.90	12.37	8.53
H	20.60	12.18	8.42
4-Cl	19.68	11.70	7.98
$3-CF_3$	19.09	--.--	
$4-CF_3$	19.00	11.36	7.64
2-Cl	18.80	11.20	7.60
4-CN	18.37	10.95	7.42
$4-NO_2$	17.82	9.78	8.04

In both solvents the basicity increases with the electron donation property of the substituent and is dependent on its position on the phenyl ring. The ΔpK_a values for the salts having electron withdrawing and electron donor groups, such as -4-NO_2 and -4-OMe respectively are very close for the same solvents. However, the pK_a for the same substituent increases when the solvent changes due to the dissociation of the guanidinium hydrochloride. This means the compound with -4-NO_2 or -4-OMe as substituent is more acidic in water than in acetonitrile.

B. Comparison of Amidines and Guanidines

1. General Aspects

Acid-base properties of amidines are closely related to tautomerism, hydrogen bonding and formation of complexes. Patai *et al*[1], classified amidines according to: unsubstituted, monosubstituted, symmetrically N,N'-disubstituted, unsymmetrically N,N'-disubstituted, N,N-disubstituted and trisubstituted amidines. Trisubstituted amidines do not exist in two or more tautomeric forms in contrast with the other types. In the case of unsubstituted and symmetrical N,N'-disubstituted amidines, the tautomerization can be neglected because both tautomeric forms are identical. However, Patai *et al*[1] have mentioned that when the pK_a values of amidines are considered, tautomerization should be taken into account even for the amidines that have identical tautomeric forms.

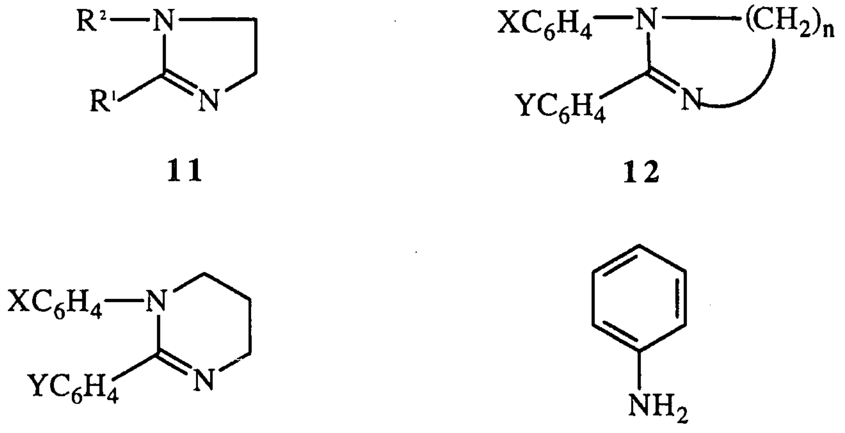
2. Basicity of Trisubstituted Amidines

Basicity of amidines can be greatly affected by the substituent on the three possible NCN sites to which they may be bonded, both nitrogen atoms and the functional carbon atom. Phenylamidines that have substituent groups on the phenyl ring at the amino nitrogen atom presumably cannot conjugate with the planar group -N=CN- because of the saturation of the adjacent CN bond. Conjugation, however, can occur with substituents on the phenyl ring at the imino nitrogen atom.

Several researchers have studied the effect of substitution on the basicity of amidines in a variety of solvents, such as methanol, ethanol, water, acetonitrile and water-ethanol mixtures. The pK_a values have been measured in such conditions, and the effect of groups at the functional carbon atom[30], at the imino nitrogen atom[31] and at the amino nitrogen atom[32-34] determined. The strongest influence on basicity occurs for substituents at the imino nitrogen atom, followed by substitution at the carbon atom, and finally by substitution at the amino nitrogen atom.

The conclusion about the protonation site of amidines was achieved by comparison of the pK_a values of imidazolines (**11**) with those of the corresponding arylamines (**14**). Fernández *et al*[32,33] and Perillo *et al*[34] have noticed that the pK_a values of imidazolines were a few units higher than the arylamines. It is concluded that the imino nitrogen atom should be the protonation site of amidines. Comparison of the pK_a values of the homologous cyclic amidines (**12**; see Figure 1.6) have shown that the basicity depends to a considerable degree on the ring size, decreasing in the order tetrahydropyrimidines (**13**)> tetrahydrodiazepines (**12**, n = 4)> hexahydrodiazocines (**12**, n = 5)> imidazolines (**11**)> aniline (**14**). Figure 1.6 illustrates some examples of cyclic amidines.

Guanidines can be regarded as amidines containing an amino group at the carbon atom, and thus, by analogy, they may have similar chemical properties when considering the protonation site.



11 **12**

13 **14**

Figure 1.6 Structures of cyclic N-arylamidines and arylamine

3. Tautomerism and Hydrogen Bonding

According to NMR studies[35] tautomerization is very fast in amidines. The proton exchange occurs several times per second. The tautomeric equilibrium constant depends on the substituent groups, and in the case of identical substituent groups the equilibrium constant is equal to unity. Compounds with two different tautomeric forms have the equilibrium shifted towards the tautomer containing the electron withdrawing substituent at the imino nitrogen atom, or in other words the less basic tautomer predominates in the equilibrium mixture. A substance which has three identical tautomeric forms, such as guanidine, yields a common conjugated acid. In such a tautomeric equilibrium for substituted guanidines, again the least basic tautomer predominates. Trisubstituted guanidines have the least basic tautomer similar to amidines, that is, the one with the strongest electron-withdrawing substituent at the imino nitrogen atom.

According to Clement *et al*[36], who studied the tautomeric equilibria of N,N'-diphenylguanidine by ^{15}N NMR, the tautomer containing the phenyl ring at the imino nitrogen atom predominates in the mixture. Figure 1.7 shows the tautomeric equilibria of N,N'-diphenylguanidine.

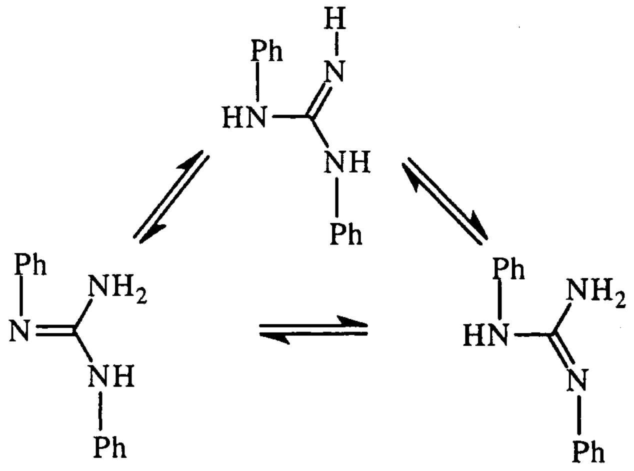


Figure 1.7 Tautomeric equilibria of N,N'-diphenylguanidine

Intermolecular hydrogen bonding between amidine molecules, or between amidine and other molecules, may facilitate the prototropic tautomerism equilibria. Halliday *et al*[35] have reported ^1H NMR and infrared studies of N,N'-dimethylacetamidine, for which tautomers occurred through a hydrogen-bonded cyclic dimer as presented in Figure 1.8 below.

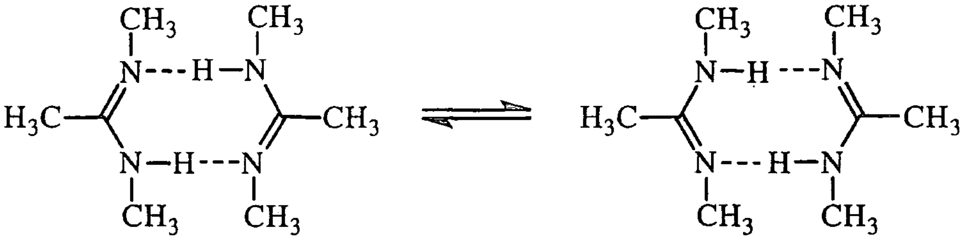


Figure 1.8 Tautomeric equilibria through a hydrogen-bonded cyclic dimer

Complete association was found for the neat amidine (see Figure 1.8), and the authors[35] observed that dilution may affect the lifetime of tautomers in equilibrium since the rate constant of tautomerization was different for different solvents at several concentrations. According to Patai *et al*[37], in solvents of low dielectric constant such as hexane, dimerization through hydrogen bonding was deduced because the infrared stretching frequency assigned to ν(C=N) of amidines shows a strong dependence on the solvent. The ν(C=N) band of N,N'-diethylacetamidine, for instance, observed at 1675 cm^{-1} in dioxane solution, has shifted to 1592 cm^{-1} in hexane. The band observed in dioxane was assigned to the single amidine molecule hydrogen bonding to the dioxane molecule.

C. Coordination of Amidine and Guanidine Ligands

1. Coordination Chemistry of the Guanidine Ligand

Coordination chemistry involving guanidines and metals such as sodium or lithium is not common, though recently, colourless crystals of $[Li_4Na_2(N{=}C(NMe_2)_2)_6]$[38] were characterised by X-ray diffraction. This compound was very similar to $[Li_4Na_2(N{=}C(Ph)Bu^t)_6]$[39] concerning synthesis, composition and structure. These heterobimetallics were air- and moisture-sensitive. The structure is centrosymmetric with a $(NaN)_2$ ring sandwiched between two $(LiN)_2$ rings. Nitrogen and sodium centres within the central ring were five- and four coordinated. The guanidine was attached to the lithium through the imino and amino nitrogen atoms in a bidentate bonding mode.

Another lithium derivative of tetramethylguanidine[40] was isolated in 1968, and determined by cryoscopy to be dimeric in benzene solution. Complexes involving transition metals such as cobalt(II), palladium(II), nickel(II) and chromium(II) have been prepared using tetramethylguanidine by Longhi *et al*[41]. All complexes are shown by infrared studies to have the transition metal ions bonded through the imine group, since the position of the band $\nu(C{=}N)$ band shifted towards lower wave numbers. It was concluded that the monodentate bonding was via the imino nitrogen donor site.

Under slightly basic conditions (pH=8.5 to 10.5) the complex $[PtCl(trpy)]^+$ has been used for complexation[42] with guanidinium salts and arginine. The study is related to the binding of platinum(II) to L-arginine in the tuna cytochrome *c*. The high reactivity was explained by the structural environment in the cytochrome *c*. The complexes have similar structures as illustrated in Figure 1.9 below.

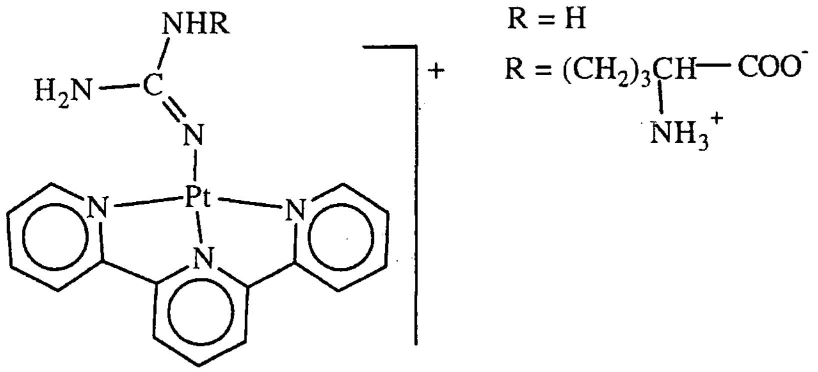
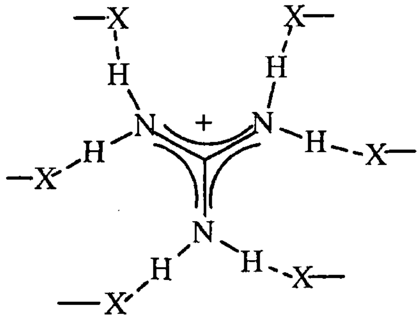


Figure 1.9 Structure of $[Pt(trpy)NC(NH_2)(NHR)]^+$

Structures of compounds containing the guanidinium ion have been determined by X-ray diffraction, and show the guanidinium ion encapsulated[43,44] in a cage of $[GaF_6]^{3-}$, $[PdCl_4]^{2-}$ or $[AuCl_4]^-$ units. They have hydrogen bonded frameworks with participation of all hydrogen atoms of the guanidine cation towards the chloride and fluoride ions. Encapsulated guanidinium ions with all hydrogen atoms involved in hydrogen bonding towards oxygen atoms were found by X-ray crystallography studies in the case of $\{[Ni(salen)]_3[C(NH_2)_3]\}(BPh_4)$ 2THF[45]. Two more examples of complexes that contain a guanidinium ion are $\{[Cr(C_2O_4)_3][C(NH_2)_3]_3\}$ H_2O[46], and guanidinium molybdate, reported by Ozeki *et al*[47]. The latter has hydrogen bonding between the guanidinium cation and the oxygen atoms of the tetrahedral group $[MoO_4]^{2-}$. The Mo-O bond distance increases with the number of interacting hydrogen atoms: 1.757(3), 1.762(3) and 1.776(3) Å for two, three and four interacting hydrogen atoms, respectively.

The possible bonding modes of guanidine and its anionic derivatives to metals are shown in Figure 1.10 below.

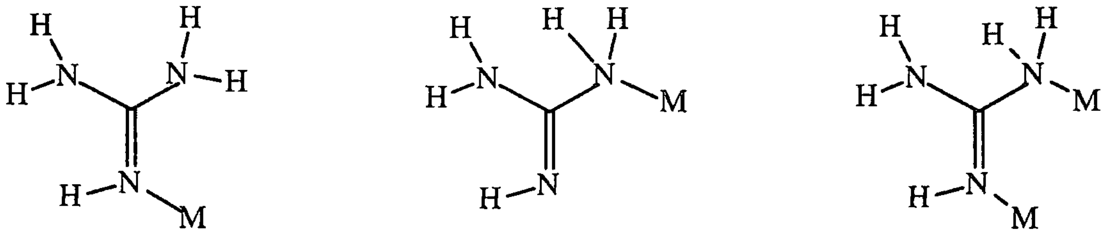
A. Bonding Mode of the Guanidinium Cation



X = OR, NR_2, F, Cl

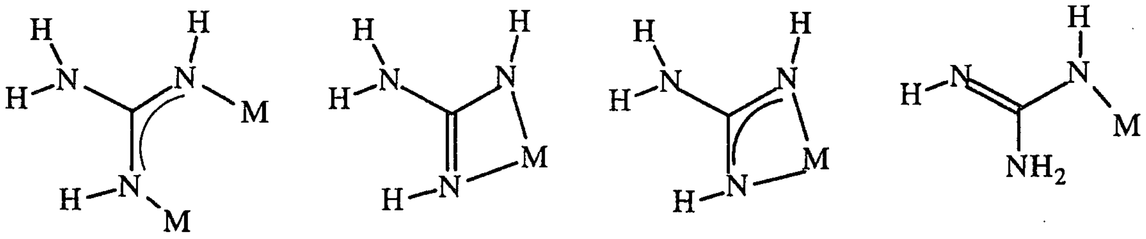
Hydrogen Bonding involving the Guanidinium ion

B. Bonding Modes of Guanidines



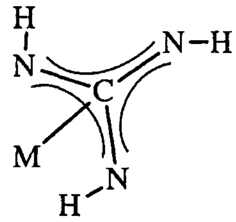
Monodentate Mode | Monodentate Mode | Bridging Mode

C. Bonding Modes of the Guanidino-anion



Bridging Mode | Chelate Mode | Chelate Mode | Monodentate Mode

D. Bonding Mode of the Guanidino-dianion



Sandwich Mode

Figure 1.10 Possible Bonding Modes of Guanidines, Guanidino-anion and Guanidino-dianion

2. Coordination Chemistry of Amidine Ligands

2.1. Metal-Amidine Bonding Modes

Amidines can bind to main group metals and transition metals in many different bonding modes. At least five bonding modes are theoretically accepted, as described before. Two examples of the monodentate mode have been characterised by X-ray crystallography, [Pt{$C_6H_3(CH_2NMe_2)_2$}(*p*-tolyl)NC(H)N(*p*-tolyl)][48] and [Hg(Ph)(*p*-tolylbenzamidine)][48].

Chelate complexes were also identified by X-ray crystallographic studies of $[Pt(PhNC(Ph)NPh)_2]$[49] in which the four-membered ring has delocalised π-electrons. A similar example was found in the case of $[TaCl_2(C_6H_{11}NC(Me)NC_6H_{11})_2(Me)]$ which has a four-membered ring with a localised double bond between the carbon and the nitrogen atoms[50].

Bridging modes have been characterised by X-ray crystallography[51] in $[Mo_2(PhNC(Ph)NPh)_4]$. Delocalised π electrons also occurred for this type of ligand bonding mode. For the same stoichiometry of the molybdenum compound above, that is a ratio of two metals to four ligands, the structure of a heterobimetallic complex of platinum and mercury was determined by X-ray crystallography in the work of Duisenberg *et al*[52].

Amidines reacts with metal carbonyl compounds to produce carbamoyl complexes which can be described as complexes that have a carbon monoxide molecule between the metal and the nitrogen atom of a chelating or monodentate amidino-group. An example of this type of complex is the rhenium carbonyl $[Re(CON(Ph)C(Ph)NPh)(CO)_4]$[53]. Instead of having carbon monoxide inserted between the metal and the nitrogen atom of the amidino ligand, CH_2 and PhCN have also been found[54,55]. The nucleophilic attack at the nitrile of $[PtCl_2(PhCN)_2]$ by Li(NHC(Ph)NH) has produced a complex that has the formulation $[Pt(HNC(Ph)NC(Ph)NH)_2]$ in which the chelating ligand forms a six-membered ring. The structure of the latter has been characterised by X-ray crystallography[54,56].

Another type of bonding mode, found in complexes that have amidines as ligands, was the *ortho*-metallated mode, a type of bonding mode not exclusive to amidines. A wide range of organic ligands can form this kind of bonding mode, and they have been found in a variety of complexes which have different central atoms in their coordination mode, such as palladium and manganese[54,57,58]. Furthermore, reasonable stability was found for complexes that have a six-membered ring formed by aryl group *ortho*-metallation, as in $[Pd(\eta\text{-}C_5H_5)(p\text{-tolyl})NHC(Me)N(p\text{-}MeC_6H_3)]$[54]. Clark *et al*[59] have also detected five-membered ring complexes of rhenium by spectroscopic methods in studying the complexation of rhenium carbonyls with diphenylbenzamidines.

The amidino ligand was also found in $[Os_3(\mu\text{-}H)(PhNC(Ph)NH)(CO)_9]$ to act as a five electron donor ligand lying over a triangle of osmium atoms. The complex structure was determined by X-ray crystallography[60]. The molecular structure of the osmium complex is illustrated in Figure 1.11 below.

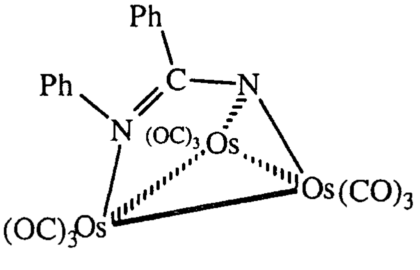
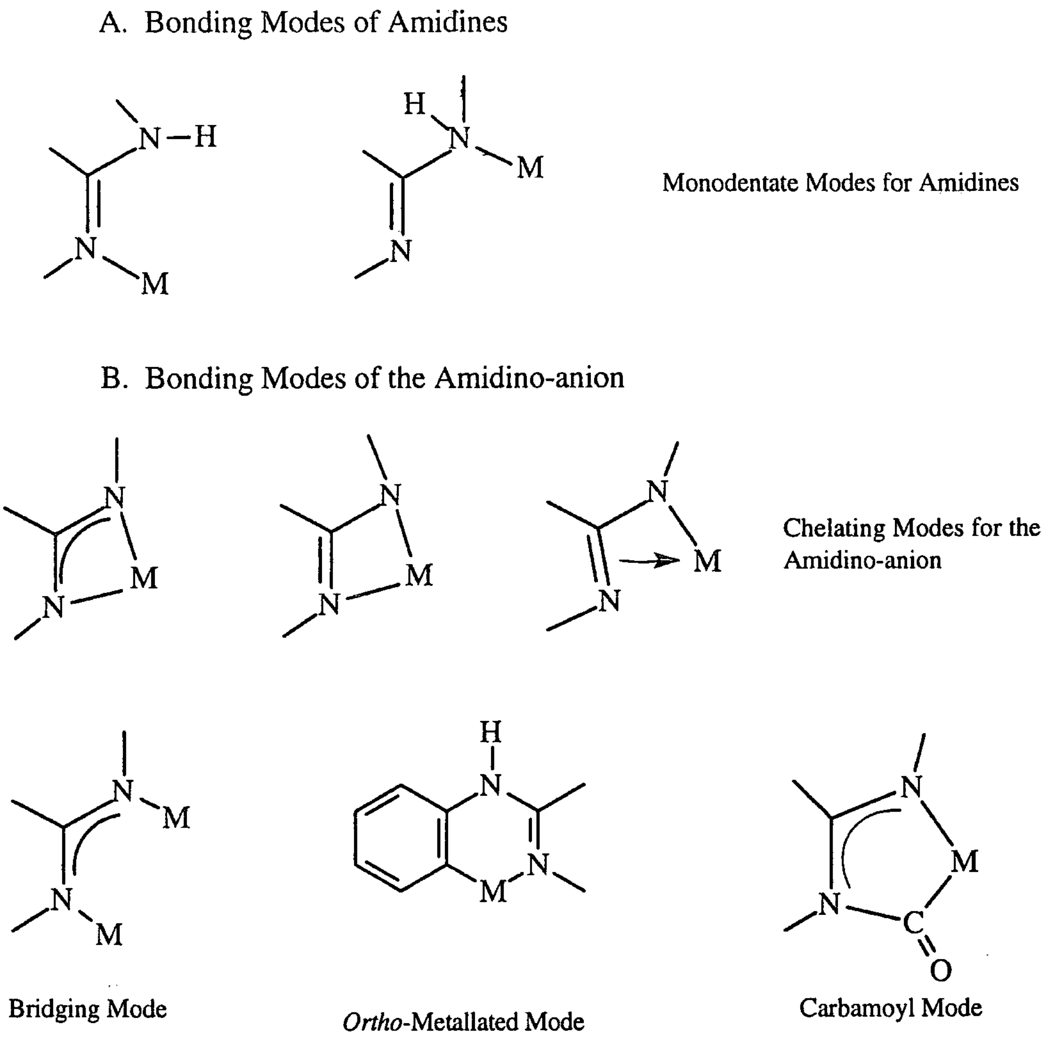


Figure 1.11 Structure of $[Os_3(\mu\text{-}H)(PhNC(Ph)NH)(CO)_9]$
(Hydrogens not located)

The most common and known bonding modes of amidines and derivatives are displayed in Figure 1.12. The chelating modes, bridging modes and carbamoyl modes have been shown to be the preferred modes for amidines towards transition metals. The carbamoyl mode, for instance, has been assigned for complexes of manganese and rhenium as shown in the next section.



A. Bonding Modes of Amidines

Monodentate Modes for Amidines

B. Bonding Modes of the Amidino-anion

Chelating Modes for the Amidino-anion

Bridging Mode

Ortho-Metallated Mode

Carbamoyl Mode

Figure 1.12 Possible Bonding Modes of Amidines and the Amidino-anion

2.2. Preparation of Amidine Transition Metal Complexes

2.2.1. Reactions Involving Lithiated Amidines and Metal Halides

The lithiated amidine is prepared *in situ*[49] and a yellow solution is often obtained. These materials are air- and moisture-sensitive[39]. Another alternative method is to use another element of the group, such as potassium[61], in place of lithium. The reactions using lithioamidines are illustrated in Figure 1.13 below.

$$\text{n-ButylLi} + \text{PhN(H)C(Ph)NPh} \xrightarrow{\text{THF/0°C}} \text{PhN(Li)C(Ph)NPh}$$

$$2\ \text{Li(PhNC(Ph)NPh)} + [\text{Pt(PhCN)}_2\text{Cl}_2] \xrightarrow{\text{THF/-196°C}} [\text{Pt(PhNC(Ph)NPh)}_2] + 2\ \text{LiCl} + 2\text{PhCN}$$

$$\text{K(ArNC(H)NAr)} + [\text{Mo(Cl)}(\eta\text{-C}_5\text{H}_5)(\text{CO})_3] \longrightarrow$$

$$\longrightarrow [\text{Mo}(\eta\text{-C}_5\text{H}_5)(\text{ArNC(H)NAr})(\text{CO})_2] + \text{KCl} + \text{CO}$$

Figure 1.13 Reactions of Lithiated Amidines and Metal halides

2.2.2. Reactions Involving Amidines and Metal Halides

The stoichiometry required in this process is one mole of metal halide to two moles of amidine. Gaylani *et al*[62,63] have reported the preparation of $[\text{Mo}(\eta\text{-C}_5\text{H}_5)(\text{PhNC(Me)NPh})(\text{CO})_2]$ in toluene at about 50°C. The guanidine hydrochloride separates out in this solvent completely after 9.5 hours. The reaction is summarised in Figure 1.14.

$$[\text{Mo(Cl)}(\eta\text{-C}_5\text{H}_5)(\text{CO})_3] + 2(\text{PhN(H)C(Me)NPh}) \longrightarrow$$

$$\longrightarrow [\text{Mo}(\eta\text{-C}_5\text{H}_5)(\text{PhNC(Me)NPh})(\text{CO})_2] + [\text{PhNHC(Me)NHPh}]^+\ \text{Cl}^- + \text{CO}$$

Figure 1.14 Preparation of $[\text{Mo}(\eta\text{-C}_5\text{H}_5)(\text{PhNC(Me)NPh})(\text{CO})_2]$

2.2.3. Reaction Involving Metal Carbonyls and Amidines

Metal carbonyls such as $[\text{M(CO)}_6]$ (M=Cr, Mo), when refluxed with amidines in n-heptane for several hours form complexes of the type

$[M_2(R^1NC(R)NR^1)_4]$ (R^1=Ph; R=Ph). These reactions are considered later in more detail in section 3.1.

2.2.4. Miscellaneous Reactions

Various additional methods to prepare amidine complexes have been reported. One of them, for instance, involves the reaction of silver or copper amidines with metal halides[61] such as $[Mo(Cl)(\eta\text{-}C_5H_5)(CO)_3]$. Gambarotta *et al*[64] have reported the use of metal hydride and carbodiimide as reactants to produce metal formamidino-complexes. The reaction of metal alkyls with amidines has also been reported by Cotton *et al*[65], and the reaction of ammonia with coordinated nitriles by Bradley *et al*[66].

3. Transition Metal Complexes of Amidines

3.1 Complexes with Chromium, Molybdenum and Tungsten

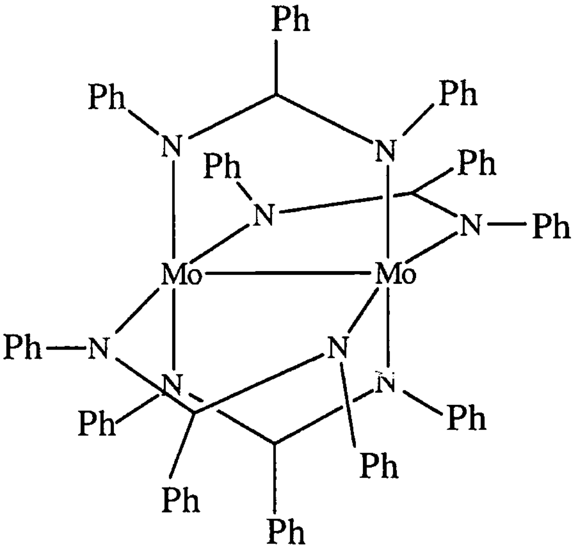
Many researchers have used metal hexacarbonyl complexes as starting materials in reactions with amidines and lithioamidines to produce dinuclear complexes of general formula $[M_2L_4]$ (M= Cr, Mo, W; L= N,N'-disubstituted formamidino-, acetamidino- and benzamidino-groups). The reaction pathway can be envisaged as in Figure 1.15 below.

$$2[M(CO)_6]+ 4\ R'NHC(R)NR' \xrightarrow{[O]} [M_2(R'NC(R)NR')_4]+ 12CO+2H_2O$$

Figure 1.15 Reaction pathway of $[M(CO)_6]$ with amidines
($R = H, CH_3, Ph; R'= Ph, p$-tolyl)

Roode *et al*[55,67,68] have investigated reactions involving formamidines and hexacarbonyl complexes. The preparation with tungsten yielded a complex formulated as $[W_2(\mu\text{-HC(NR)}_2)_2(\text{RNC(H)NR(CH}_2))(\mu\text{-CO})_2)]$ instead of the expected $[W_2(\text{amidino})_4]$. The complex was characterised later by X-ray crystallography studies[55,69] which showed the $-CH_2-$ group to be inserted between the metal and the nitrogen of the chelating formamidino group. Two bridging carbonyl groups, and two bridging formamidino groups are also present. The complexes $[M_2(\text{formamidino})_4]$ (M= Mo, Cr)[68] were also reacted with an excess of molybdenum and chromium hexacarbonyls to afford the complexes, $[Mo_2(HC(NR)_2)_2(HC(NR)_2.Mo(CO)_3)_2]$, $[Mo_2(HC(NR)_2)_3(HC(NR)_2.Mo(CO)_3)]$ and $[Cr_2(HC(NR)_2)_3(RNC(H)NR).Cr(CO)_3]$. The fragment $[M(CO)_3]$ is attached to one of the aromatic rings. A monomer-dimer equilibrium was observed in solution for the complexes above, and it seemed to be very dependent of the group R.

Dinuclear complexes of molybdenum with benzamidines have been characterised crystallographically[51] as illustrated below. A red material was obtained in the reactions of chromium or tungsten carbonyls with benzamidines. The insoluble chromium product was formulated as $[Cr_2(\text{amidino})_4]$, but the tungsten product was not fully characterised.



Potassium formamidines[70] have also been used in reactions with $NEt_4[M(Cl)(CO)_5]$, in a molar ratio 1:1, to afford complexes formulated as $[M(HC(NR)_2)(CO)_4]^-$ (M= Cr, Mo or W; R= aryl, t-butyl). The carbamoyl derivative $NEt_4[M(CO)_4(OCN(Me)C(H)NMe)]$ (M= Cr, Mo, W) was obtained in reactions of $[MeNC(H)NMe]^-$ with $NEt_4[M(Cl)(CO)_5]$. The terminal carbonyl groups have exhibited fluxionality as indicated by ^{13}C NMR. Substitution reactions also occurred when the carbamoyl complex was heated with triphenylphosphine or pyridine to afford the *fac*-$NEt_4[M(RNC(H)NR)(CO)_3L]$ (M= Mo, W; L= PPh_3, py).

Cotton *et al*[71-73] have reported the X-ray characterisation of complexes prepared by the reaction of lithioamidines with acetate-metal complexes of chromium, molybdenum and tungsten. Some of the dinuclear complexes were formulated as $[Cr_2(MeNC(Ph)NMe)_4]$; $[W_2(PhNC(Me)NPh)_2(dmp)_2]$. Roode *et al*[74,75] have investigated cyclopentadienyl amidino-complexes by a number of routes, and carbamoyl complexes were separated by chromatography. The use of symmetrically substituted potassium formamidines in the reactions has produced complexes formulated as $[M(\eta\text{-}C_5H_5)(RNC(H)NR)(CO)_2]$ and $[M(\eta\text{-}C_5H_5)(OCN(R)C(H)NR)(CO)_2]$ (M= Cr, Mo, W). Terminal CO exchange was observed on the NMR time scale for the complex formulated as $[W(\eta\text{-}C_5H_5)(OCN(Ph)C(H)NPh)(CO)_2]$; the others were stereochemically rigid. Product relative molar ratios were found to be highly dependent on the molar ratios of the starting materials.

Complexes such as $[M(\eta\text{-}C_5H_5)(p\text{-tolyl})NC(H)N(p\text{-tolyl})(CO)L]$ (M= Mo, W; L= PPh_3, $AsPh_3$, $SbPh_3$, $P(OMe)_3$) were also prepared by the reaction of $[M(Cl)(\eta\text{-}C_5H_5)(CO)L_2]$ with $K[(p\text{-tolyl})NC(H)N(p\text{-tolyl})]$. Reactions of metal cyclopentadienyl complexes of molybdenum and tungsten were also investigated by Inglis *et al*[76-78] and Gaylani *et al*[63] .

Carbamoyl complexes formulated as $[Mo(\eta\text{-}C_5H_5)(OCN(R^1)C(R)NR^1)(CO)_2]$ (R= H, Me, Ph; R^1= Ph, H, *p*-tolyl) were achieved as products of reaction between [Mo(Cl)(η-C_5H_5)$(CO)_3$] with lithioamidines. In contrast, dicarbonyl complexes formulated as [Mo(amidino)(η-C_5H_5)$(CO)_2$] were the reaction products of [Mo(Cl)(η-C_5H_5)$(CO)_3$] with N,N'-disubstituted amidines. Dicarbonyl complexes were also obtained by the reaction of [Mo(Cl)(η-C_5H_5)$(CO)_2$(PPh_3)] with lithioamidines. The mechanism to afford the carbamoyl complexes, presumably, occurred by nucleophilic attack at the carbonyl group attached to the metal. On the other hand, the dicarbonyl complexes could be formed by nucleophilic attack at the metal centre.

Brunner *et al*[79-83] have reported the characterisation of molybdenum cyclopentadienyl amidino-complexes which were optically active. The reactions were performed between [Mo(Cl)(η-C_5H_5)$(CO)_3$] and N,N'-disubstituted amidines in pyridine, and a dicarbonyl complex formulated as [Mo(amidino)(η-C_5H_5)$(CO)_2$] was obtained. Similar results were achieved by Gaylani *et al*[62] using lithiodiphenylacetamidine in ether.

Brunner *et al*[79,83] have also investigated the reaction of lithiated amidines, carbon disulphide and [Mo(Cl)(η-C_5H_5)$(CO)_3$] which has afforded the products shown in Figure 1.16 below. Diastereoisomeric pairs of enantiomers were separated by fractional crystallisation. In these reactions an asymmetric centre at the molybdenum was generated.

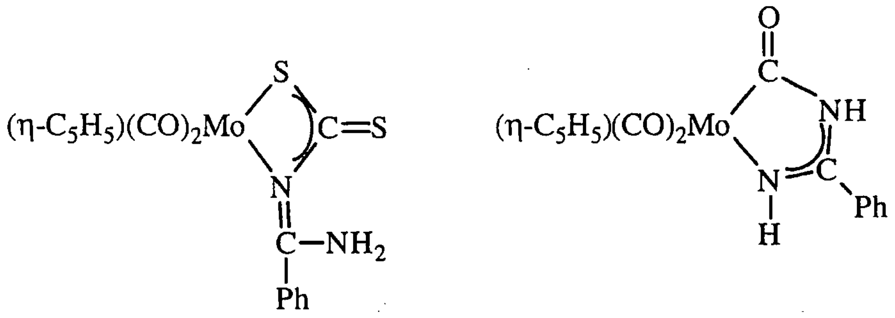


Figure 1.16 Products of the reaction CS_2+[Mo(Cl)(η-C_5H_5)$(CO)_3$] +Li(NHC(Ph)NH)

3.2 Complexes with Manganese and Rhenium

Reaction between $[Mn(X)(CO)_5]$ (X= Cl, Br or I) and lithioamidines produced carbamoyl complexes, $[Mn(OCN(R^1)C(R)NR^1)(CO)_4]$, as reported by Inglis *et al*[78,84,85]. The carbamoyl complexes synthesised by Inglis can be decarbonylated by U.V. irradiation to form tetracarbonyl complexes formulated as $[Mn(N(R^1)C(R)NR^1)(CO)_4]$. The carbamoyl complexes can also be decarbonylated by heating up to 150°C. Inglis *et al* observed the formation of the first pentacarbonyl complex, $[Mn(PhNC(Ph)NPh)(CO)_5]$, under high pressure of carbon monoxide.

Reactions of monomeric and dimeric carbonyl halides, $[Mn(X)(CO)_5]$ and $[Mn(X)(CO)_4]_2$, with formamidines were investigated by Abel *et al*[86]. The products were formulated as $[Mn(amidino)(CO)_4]$ similar to the products obtained by the reaction of monomeric and dimeric rhenium carbonyl halides. Cotton *et al*[87] reported reactions of N,N'-diphenylacetamidine or N,N'-dimethylbenzamidine with tetrabutylammonium octachlorodirhenate which afforded $[Re_2Cl_4(PhNC(Me)NPh)_2]$ and $[Re_2Cl_2(MeNC(Ph)NMe)_4]$. The complexes were characterised by X-ray crystallography.

Clark *et al*[53,59] have investigated several reactions of rhenium carbonyl complexes with diarylamidines. A six-membered *ortho*-metallated complex was prepared by the reaction of $[Re(Br)(CO)_5]$ with arylformamidines, acetamidines and benzamidines in refluxing monoglyme. An intermediate formulated as $[Re(Br)(R^1NC(R)NMeR^1)(CO)_3(PPh_3)]$ was observed when a trisubstituted amidine was used as reactant. Carbamoyl complexes and their decarbonylation were also reported by Clark.

Forsellini *et al*[88] have reported reactions of $[Re(Cl)(CO)_3(PPh_3)_2]$ with Li(RNC(H)NR) (R= *p*-tolyl, Ph, *p*-ClC_6H_4 and *o*-FC_6H_4) in refluxing THF to afford complexes which have the general formula $[Re(RNC(H)NR)(CO)_2(PPh_3)_2]$.

Infrared bands in the region 1620 to 1218 cm^{-1} were assigned to the -NCN- delocalised system. The amidino-group was symmetrically bonded to the metal as shown by X-ray crystallography studies of the complex formulated as $[Re(RNC(H)NR)(CO)_2(PPh_3)_2]$.

3.3 Complexes with Cobalt, Rhodium and Iridium

Minghetti *et al*[89] have performed reactions by direct addition of different N,N'-diarylformamidines ArNHC(H)NAr to metal salts. No reaction with cadmium bromide, zinc bromide, cobalt chloride, $[Rh(Cl)(CO)_2]_2$ or silver fluoroborate occurred when the group Ar was *p*-nitrophenyl. However, when the group Ar was *p*-tolyl, complexes were obtained, such as $[Co(amidine)_2Cl_2]$, $[amidinium][CoCl_4]$, $[Rh(Cl)(amidine)(CO)_2]$ and $[Ag(amidine)_2][BF_4]$.

Rigby *et al*[90] and Piraino *et al*[91] have reported the preparation of $[Rh(Cl)(\eta\text{-}C_5Me_5)(R^1NC(R)NR^1)]$ (R= H or Me; R^1= Ph, *p*-tolyl) from $[Rh_2Cl_4(\eta\text{-}C_5Me_5)_2]$ with amidines in the presence of base. Another method used the silver and potassium amidine derivatives. Carbamoyl complexes can be prepared in these reactions, formed by insertion of carbon monoxide into the M-N bond of the complex to afford $[Rh(Cl)(\eta\text{-}C_5Me_5)(OCN(p\text{-tolyl})C(R)N(p\text{-tolyl}))]$.

The synthesis of $[Rh(diene)L]_2$ (diene= COD, norbornadiene; L= amidino) complexes were reported by Piraino *et al*[92]. The dimeric complexes have the formamidino-group as a bidentate bridging ligand towards the metal. The complexes were reactive with carbon monoxide, dppe and PPh_3 displacing the diene ligand to yield complexes formulated as $[Rh(R^1NC(H)NR^1)(CO)_2]$, $[Rh(dppe)_2]^+$ and $[Rh(R^1NC(H)NR^1)(PPh_3)_2]$. The complex $[Rh(COD)L]_2$ also reacted with CS_2, SO_2, PhNCS and PhNCO with replacement of the cyclooctadiene ligand to produce mixtures of complexes, except in the case of CS_2, which led to isolation of a red-black complex, formulated as $[Rh(CS_2)_2(R^1NC(H)NR^1)]_n$ (R^1= *p*-tolyl).

Abel *et al*[93] and Connelly *et al*[94] have investigated the reaction of $[Rh(CO)_2Cl]_2$ with $Li(R^1NC(R)NR^1)$ (R= H or Me; R^1= Ph, ClC_6H_4). Figure 1.17 shows the proposed structure for the product.

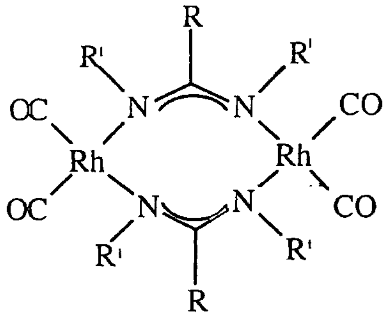


Figure 1.17 Proposed structure of $[Rh_2(amidino)_2(CO)_4]$

When R= H an intermediate was formed, but its separation was not possible. Presumably the intermediate was mononuclear $[Rh((XC_6H_4)NC(H)N(XC_6H_4))(CO)_2]$ (X= F or Cl) which can detach the chelate ligand to form bridged dimers such as the one in Figure 1.17.

Iridium complexes, similar to the rhodium complexes above, have been synthesised and their reactivity investigated[93,95].

3.4 Complexes with Nickel, Palladium and Platinum

Treatment of $[Ni(Cl)(\eta\text{-}C_5H_5)(PPh_3)]$ with lithiobenzamidine afforded a brown , insoluble powder[76]. The analytical data, combined with the stability, insolubility of the material, and its polymeric nature, have suggested the product formula $[Ni(\eta\text{-}C_5H_5)(PhNC(Ph)NPh)]_n$. The material was very resistant to chemical attack, and the IR spectrum of the compound indicated that the amidino-group is coordinated to the metal centre in a bridging mode. Bradley *et al*[96] have reported the synthesis and characterisation of a product formulated as $[Ni((p\text{-}O_2NC_6H_4)NC(H)N(p\text{-}NO_2C_6H_4))_2(py)_4]$

Stephenson *et al*[97] have determined the structure of the platinum complex, $[Pt(CH_3C(NH_2)NH)_2(NH_3)_2]2Cl(H_2O)$. Reactions of lithioamidines and amidines with platinum and palladium compounds were reported[49,98] to form a variety of complexes which have their nature closely related to the amidine substituents, the metal, and the synthetic route used in the chemical reaction. Lithioamidines reacted with $[MCl_2(PhCN)_2]$ (M=Pt, Pd) to afford complexes, such as [Pt(amidino)$_2$], [Pd(amidino)$_2$], and [Pd$_2$(amidino)$_4$]. Barker *et al*[49] have also reported X-ray crystallography studies of $[Pt(PhNC(Ph)NPh)_2]$ which has symmetrical bidentate groups.

Spectroscopic methods such as NMR have shown that palladium complexes[98] were monomeric when the starting material was *trans*-$[PdCl_2(PPh_3)_2]$ and the ligand bonded to the metal was the formamidino-anion. Dimeric species were obtained by replacing *trans*-$[PdCl_2(PPh_3)_2]$ with $[PdCl_2(NCCH_3)_2]$. Barker *et al*[99] have suggested the structure in Figure 1.18 as a possibility for dimeric $[Pd_2(PhNC(H)NPh)_4]$.

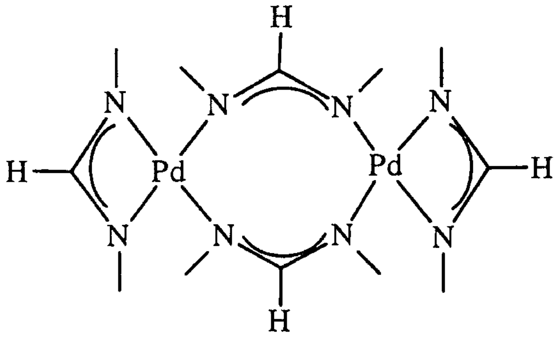


Figure 1.18 Suggested strucuture of a palladium dimer derivative of formamidine

^1H NMR spectroscopy at -5°C has indicated fluxionality for the palladium derivative of the *p*-tolyl-formamidino-anion. ^{13}C NMR at low temperatures (-80°C) has indicated a bridging benzamidino-anion for the palladium complexes $[\{Pd[R^1NC(Ph)NR^1]_2\}_n]$[99] ($R^1$= Ph or *p*-tolyl). Species having bridging or chelate groups could also be detected by variable temperature ^{19}F NMR spectroscopy when the substituent at the carbon atom was the phenyl group and the substituent at the nitrogen atom was the *p*-FC_6H_4 group. Mass spectral studies have indicated palladium acetamidino-complexes to be monomeric and the benzamidino-derivatives to be dimeric.

Ortho-metallated complexes of platinum and palladium prepared by the reaction of K_2MCl_4 with N,N'-diarylamidines have been investigated. The dark green complexes have the chloride ions bridging the metal centre. These bridges can be cleaved to form monomeric species[54,100] by a variety of reagents.

The lithioamidine, Li(NHC(Ph)NH) reacted in diethyl ether with $[PtCl_2(PhCN)_2]$ to afford $[Pt(NHC(Ph)NC(Ph)NH)_2]$ the structure of which was determined crystallographically (shown in Figure 1.19 below).

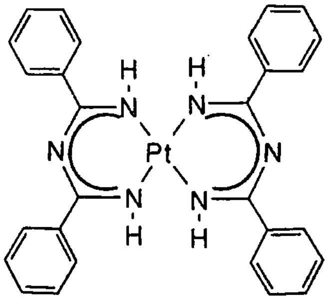


Figure 1.19 Structure of $[Pt(HNC(Ph)NC(Ph)NH)_2]$

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Chapter Two

Studies of Bromopentacarbonylmanganese(I) with 1,2,3-Triphenylguanidine

Introduction

The work presented in this chapter concerns the use of 1,2,3-triphenylguanidine ($TPGH_2$) in reactions with the metal carbonyl, $[Mn(Br)(CO)_5]$. In the first chapter the possible bonding modes of guanidine towards a metal centre were described and one of the aims here was to study the possible bonding modes of this trisubstituted guanidine towards *soft* centres, such as manganese(I), and the reactivity of the complexes formed. Reactions under a variety of conditions have been undertaken in order to gain insight into the ligand properties of $TPGH_2$, particularly, the possible interchanges between the various bonding types.

A. Experimental Work

All experimental work was undertaken using a nitrogen atmosphere. Solutions were added by syringe against a counter current of this gas.

1. Synthesis of Bromopentacarbonylmanganese(I)

Decacarbonyldimanganese (5.0g/ 12mmol) was dissolved in degassed dichloromethane(50ml) at 0°C. A solution of bromine (2.5g/ 15.7mmol/ 0.87ml) in dichloromethane (20 ml) was then added drop by drop to the cold solution of the carbonyl reactant, and the mixture allowed to warm slowly to room temperature. Some of the solid product separated inside the flask, and the reaction mixture was stirred for a further 1 hour at room temperature. The final dark red solution was evaporated *in vacuo* to produce a dry orange residue, which was redissolved in the minimum of degassed dry dichloromethane. Addition of dry hexane caused the separation of the orange yellow product which was removed by filtration, washed with dry pentane and dried under vacuum. $[Mn(Br)(CO)_5]$ was identified by infrared spectroscopy by reference to literature data[1]. Analysis (see Table 2.1). Yield: 6.4g {90% based on $[Mn_2(CO)_{10}]$}.

2. Reaction of Bromopentacarbonylmanganese(I) with 1,2,3-Triphenylguanidine in Toluene Solution

Bromopentacarbonylmanganese(I) (0.54g/ 1.96mmol) was dissolved in dry toluene(40ml) and solid 1,2,3-triphenylguanidine (0.30g /1.04mmol) was then added to the solution against a counter flow of nitrogen. The mixture was heated between 45°-50°C, and stirred overnight. An orange, homogeneous solution was produced after this time. Some of the bromopentacarbonylmanganese(I) separated after cooling the mixture overnight in the fridge, and was removed by filtration. Removal of half the solvent from the filtrate under reduced pressure, addition of hexane, and cooling the mixture to -5°C, gave the product $[Mn(Br)(CO)_4TPGH_2]$ as an air-stable, yellow solid, which was stable also in hydrocarbon solution. Yield: 0.36g (65% based on $TPGH_2$). Analysis - see Table 2.1

3. Reaction of Bromopentacarbonylmanganese(I) with 1,2,3-Triphenylguanidine in Hexane Solution

Bromopentacarbonylmanganese(I) (0.52g/ 1.9mmol) was put into a flask together with 1,2,3-triphenylguanidine (1.09g/ 3.8mmol) under a nitrogen atmosphere, and dry degassed hexane (45ml) was added. The mixture was heated overnight at between 45-50°C. Gas was evolved during the reaction time and a yellow solid separated. The solid product $[Mn(Br)(CO)_3(TPGH_2)_2]$ was separated by filtration under a nitrogen atmosphere, then dried *in vacuo*. Yield:1.12g {75% based on $[Mn(Br)(CO)_5]$}. Analysis - see Table 2.1.

4. Reaction of Bromopentacarbonylmanganese(I) with 1,2,3-Triphenylguanidine in Diethyl ether/ Dichloromethane or Diethyl ether/Chloroform Mixtures

A different product was produced by reacting $[Mn(Br)(CO)_5]$ (0.54g/ 2.0 mmol) with $TPGH_2$ (0.59g/ 2.1mmol) in diethyl ether/chloroform (2:1; 40ml) or diethyl ether/dichloromethane (2:1; 40ml) at room temperature. The mixture was left stirring at room temperature for 24 hours to complete the reaction, and at the end of this time a homogeneous orange solution was produced. The solvent was removed *in vacuo* and dry degassed hexane (30ml) was added to the orange residue. The new mixture was heated in the range 40-60°C overnight. The yellow-orange solution produced after this time was filtered through Celite 521 at room temperature, leaving behind an orange-yellow residue. On evaporation of the filtrate *in vacuo* to smaller bulk, a yellow solid separated, which was removed by filtration, washed with hexane and dried *in vacuo.* The product, designated product A, gave the analytical data recorded in Table 2.1. The stability of the material towards air was greater in the solid state, compared with solutions in hydrocarbon solvents. Yield: 0.61g.

The same material was produced when a mixture of hexane/diethyl ether/chloroform was used as the reaction solvent, the initial room temperature stage being eliminated. The reaction was monitored by infrared spectroscopy. Also the same final product was achieved using a stoichiometry of two ligands to one metal complex. Another attempt at the preparation of the same product was made as follows.

4.1 Reaction of [Mn(Br)$(CO)_4$TPGH_2] and Triethylamine

The compound [Mn(Br)$(CO)_4$TPGH_2] (0.25g /0.46mmol) was heated with triethylamine (0.12g /0.5mmol) at 40°C in a mixture of diethyl ether/chloroform (2:1) during 12 hours. Dichloromethane works very well in place of chloroform. The reaction was monitored by infrared spectroscopy which gave, at the end of 12 hours an I.R. spectrum identical with that of the previous material (section A). The final product was extracted with dry degassed hexane, and the complex isolated by removing solvent slowly from the filtered extract under vacuum. Removal of the yellow solid by filtration, and washing with hexane, before drying *in vacuo* gave, according to infrared spectroscopy, the same product A as that reported in the previous section. Yield: 0.12g.

5. Irradiation of Filtrate from Reaction 3

The filtrate of the reaction 3, was left at room temperature exposed to the sunlight for two days under a nitrogen atmosphere. The yellow solution became dark and was filtered through Celite 521. A clear yellow solution was obtained, which was cooled to -20°C. A yellow material separated after two days in a very poor yield. Attempted recrystallisation led to decomposition of the yellow material. Infrared spectroscopy (section B4) suggests the complex to be [Mn(TPGH)(CO)$_4$].

Table 2.1

Analytical results and melting points of the manganese carbonyl complexes

		Found	(Calc)	%		
Product Formula	C	H	N	Br	Mn	mp (°C)
[Mn(Br)(CO)$_5$]	22.17	0.00	0.00	31.09		
	(21.85)	(0.00)	(0.00)	(29.20)		
[Mn(Br)(CO)$_4$TPGH$_2$]	51.39	3.11	7.68	14.43		115-117
	(51.71)	(3.21)	(7.87)	(14.96)	(10.28)	
[Mn(Br)(CO)$_3$(TPGH$_2$)$_2$]	60.09	4.26	10.46	10.02		68-71
	(62.05)	(4.32)	(10.59)	(10.07)	(6.92)	
Product A	66.23	4.54	10.75	*	8.80	
[Mn$_2$(TPGH)$_2$(CO)$_6$(TPGH$_2$] requires	(66.49)	(4.34)	(11.08)	(0.00)	(9.65)	
[Mn(Br)(CO)$_3$(TPGH$_2$)$_2$].TPGH$_2$ requires	(66.67)	(4.76)	(11.66)	(7.39)	(5.08)	
[Mn(Br)(CO)$_3$(TPGH$_2$)$_2$].0.5TPGH$_2$ requires	(64.71)	(4.54)	(11.21)	(8.53)	(5.86)	

* Analysis for bromine was not undertaken

B. Results and Discussion

1. The Tetracarbonyl Complex $[Mn(Br)(CO)_4TPGH_2]$

Bromopentacarbonylmanganese(I) reacts with 1,2,3-triphenylguanidine in toluene at 50°C in a molar ratio of 1:1 under a nitrogen atmosphere to form the orange yellow product $[Mn(Br)(CO)_4TPGH_2]$. This organometallic complex was obtained irrespective of the amount of metal carbonyl used in its preparation. The introduction of a molecule of 1,2,3-triphenylguanidine led to the loss of one molecule of carbon monoxide. In principle, the 1,2,3-triphenylguanidine can bind to the metal through the amino-, and imino-groups or through two nitrogen atoms, in a monodentate or bidentate bonding mode, acting as a 2, or 4-electron donor to satisfy the 18-electron rule. Infrared spectroscopy of a Nujol mull showed four medium to strong metal carbonyl stretching frequencies in the range 2100 to 1900 cm^{-1} at 2100, 2030, 2000 and 1960 cm^{-1}, which suggests terminal carbonyl groups attached to the metal. This pattern of ν(CO) frequencies is consistent with Br and monodentate $TPGH_2$ ligands in *cis*-positions of a $[Mn(X)(Y)(CO)_4]$-type complex, or two nitrogens of a bidentate ligand in a *cis*-$[Mn(X)_2(CO)_4]$-type complex. The patterns of carbonyl stretching frequencies expected for complexes having various formulations and stereochemistries are discussed in Appendix B. For *cis*-complexes of the type $[MnX_2(CO)_4]$ and $[Mn(X)(Y)(CO)_4]$ (X, Y= monodentate ligands), four ν(CO) stretching frequencies, one of weak intensity and three of strong intensity, are expected, whereas for the corresponding *trans*-complexes, a maximum of two ν(CO) stretching frequencies (one of weak intensity, if observed, and one of strong intensity) are expected. The general shift of ν(CO) in this complex towards low frequency by comparison with ν(CO) for [Mn(Br)(CO)$_5$] (see Table 2.2) reflects the increase in the strength of the M-C bond especially for carbon monoxide in the *trans* position to the nitrogen atoms of the ligand[2,3]. The result is typical for replacement of a carbonyl group in [Mn(Br)(CO)$_5$] by a stronger σ-donating ligand such as an amine or imine. Two weak bands were also observed in the range 3100 to 3400 cm^{-1} at 3400 and 3160 cm^{-1}, assigned to ν(N-H) stretching frequencies, which in the free 1,2,3-triphenylguanidine occurred as a single, sharp band of medium intensity at 3365 cm^{-1}.

Table 2.2

Infrared absorptions of [Mn(Br)(CO)$_5$] and the manganese derivatives of TPGH$_2$†

Product Formula		ν(CO)/cm^{-1}	ν(N-H)/cm^{-1}	ν(CN)/cm^{-1}
[Mn(Br)(CO)$_5$]	CHCl$_3$	2080w, 2050s 2005s		
	Nujol	2140s, 1950s‡		
[Mn(Br)(CO)$_4$TPGH$_2$]	Nujol	2100m, 2030s 2000s, 1960s	3400w 3160w	1620m 1605m
[Mn(Br)(CO)$_3$(TPGH$_2$)$_2$]	Nujol	2010s, 1920s, 1895s	3380w	1620m
	KBr	2005s, 1920m, 1890s	3250s(br)	1625s
Product A	KBr	2005s, 1915s 1895s	3390s	1620s
	Nujol	2005s, 1925s 1900s	3395s	1625m
[Mn(TPGH)(CO)$_4$]	Nujol	2093m; 2010s 1990s; 1933s	3375w	1601w

‡ - broad absorption; L= TPGH; ν(CN) for the free ligand occurs at 1636 cm^{-1}

† - Features of the IR spectra of the new complexes are illustrated across the page.

The data for the ν(CO) stretching frequencies of the complex [Mn(Br)(CO)$_4$TPGH$_2$] (Tables 2.2 and 2.3) correlate with the ν(CO) data of [Mn(X)(CO)$_4$L] (L= phosphines, etc.; X= Br)[2] (Table 2.3) and for [Mn(L-L)(CO)$_4$] (L-L = amidino) complexes[4-7] (Table 2.3).

For the complex, [Mn(Br)$(CO)_4$TPGH_2], one of the two ν(N-H) stretching frequencies occurs at lower frequency, and may be related to the nitrogen-hydrogen group attached to the manganese atom[8,9], and the other one at higher frequency may be related to a free N-H group by comparison with the ν(NH) assigned for the free ligand. Various possible structures are consistent with these particular results and are shown in Figure 2.1.

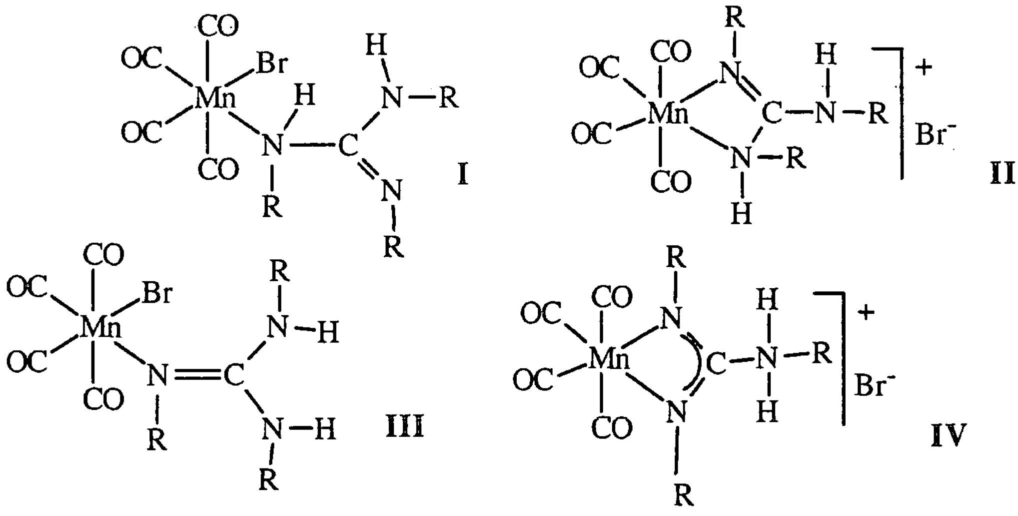


Figure 2.1 Possible structures for[Mn(Br)$(CO)_4$TPGH_2]

In the structures in Figure 2.1 the ligand is attached to the metal in four different bonding modes. Both the monodentate mode **I** and the bidentate mode **II** of the ligand have a nitrogen-hydrogen group bonded to the metal and another free. The modes **I** and **II** are consistent with the ν(N-H) data found for the complex, but **II** is not consistent with the solubility of the material. [Mn(Br)$(CO)_4$TPGH_2] was very soluble in toluene and slightly soluble in hexane, properties inconsistent with an ionic formulation. Since toluene and hexane are apolar solvents it is expected that the non-ionic complexes, **I** and **III** would dissolve in both solvents, whereas the ionic complexes, **II** and **IV** are unlikely to be soluble in hexane. Thus the ionic structures **II** and **IV** are most unlikely to be the structures adopted. Structure **IV**, having a quaternary nitrogen atom, is included as a possibility because the two ν(N-H) stretching frequencies can be explained in terms of symmetrical and unsymmetrical ν(NH_2) stretching frequencies. However, quaternary ν(NH_2) stretching frequencies are expected to be broad, and since no broad absorption occurs in the spectrum of the complex, proposed structure **IV** is unlikely. Therefore the structures **I** and **III** are the preferred structures for the complex $[Mn(Br)(CO)_4TPGH_2]$. The structure **III** would be the choice considering that the imino-nitrogen atoms are stronger Lewis donors than amino-nitrogens, though the observed ν(N-H) stretching frequencies are more consistent with the structure **I**. The two structures (**I** and **III**) are tautomers and will be in equilibrium with each other in solution.

Table 2.3

Infrared absorptions of tetracarbonyl complexes[2,4-7]

Complex	$\nu(CO)^t/cm^{-1}$	$\nu(C{=}O)/cm^{-1}$
$[Mn(CO(Ph)NC(Me)NPh)(CO)_4]^b$	2085m; 2004s; 1986vs; 1972vs	1694m
$[Mn(PhNC(Ph)NPh)(CO)_4]^b$	2093w; 2010m; 1995s; 1950s	
$[Re(PhNC(Me)NPh)(CO)_4]^d$	2110w; 1992vs; 1978vs; 1940vs	
$[Mn(TPGH)(CO)_4]^d$	2093m; 2010s; 1990s; 1933s	
$[Mn(NO_3)(CO)_4AsPh_3]^d$	2097m; 2044s; 1965s; 1939s	
$[Mn(NO_3)(CO)_4PPh_3]^d$	2100w; 2050s; 1970s; 1940s	
$[Mn(Br)(CO)_4PPh_3]^c$	2101m; 2012s; 1965s	
$[Mn(Br)(CO)_4(P(OC_6H_5)_3)]^c$	2101m; 2020s; 1972s	
$[Mn(Br)(CO)_4TPGH_2]^d$	2100m; 2030s; 2000s; 1960s	

b-Cyclohexane solution; c-chloroform; d-Nujol mull; t- Terminal carbonyl frequencies

Mass spectral studies were attempted on the manganese complexes using EI, CI and FAB techniques, but in all cases no manganese containing ions were detected. The manganese complexes appeared to be unstable to dissociation under the conditions used. A variety of temperatures and source voltages was used in the attempts to detect manganese containing ions.

2. The Tricarbonyl Complex $[Mn(Br)(CO)_3(TPGH_2)_2]$

The reaction of $[Mn(Br)(CO)_5]$ with two molar equivalents of 1,2,3-triphenylguanidine produced $[Mn(Br)(CO)_3(TPGH_2)_2]$. This complex separated from the hexane solution at 50°C. The reaction occurs slowly with the separation of an insoluble pale yellow material and evolution of gas. The product is not air stable, and leads to the hydrobromide of the guanidine when exposed to air. In principle, the guanidine can bind to the metal in a monodentate or bidentate bonding mode when it acts as a 2- or 4-electron donor to satisfy the 18-electron rule. The composition of the product is consistent with the molar ratio of the reactants used.

The infrared spectrum of the product exhibited three strong terminal carbonyl absorptions in the range 2100 to 1800 cm^{-1} in a Nujol mull at 2010, 1920 and 1895 cm^{-1} (Table 2.2), consistent with the *fac* isomer[10] for which a pattern of three strong absorptions is expected (see Appendix B). *Mer* isomers show a pattern of one weak and two strong $\nu(CO)$ absorptions. The $\nu(N\text{-}H)$ stretching frequencies were assigned to a weak absorption at 3350 cm^{-1}, and another broad absorption in the range 3100 to 2800 cm^{-1}. The broad absorption is typical for amine and imine hydrochlorides or hydrobromides, e.g. guanidinium bromide, due to hydrogen bonding, and the $\nu(NH)$ absorption was undoubtedly broad in a KBr disc (see Table 2.2). This broad infrared band suggests ionic character for the organometallic product.

The ionic nature of the product complex was confirmed by electrical conductivity measurements. Various organic solvents have been used previously for conductivity measurements[11], the criteria most relevant to the selection of a solvent being the dielectric constant, viscosity, specific conductivity, ease of purification, and donor capacity towards metals ions. Carbonyl complexes have been characterised in solvents such as nitrobenzene[12-16] or nitromethane[17,18] (see Table 2.4), and for most purposes a specific conductivity of 2×10^{-6} $ohm^{-1}cm^{-1}$ for the pure solvent is adequate for nitromethane. Several cyclopentadienyl complexes involving iron, manganese, and tungsten as the metal centre, and $[PF_6]^-$ as the counter ion, were characterised in nitromethane[19,20], and this same solvent has been used for carbonyl complexes[17,18,21] including the complexes in this work. Some manganese carbonyl complexes have been characterised in acetone as well[22]. However, dissociation of complexes in nitromethane without coordination of the solvent was found by Farina *et al*[23]. Data presented in Tables 2.4 and 2.5 indicate that $[Mn(Br)(CO)_3(TPGH_2)_2]$ is a 1:1 electrolyte in nitromethane solution.

Table 2.4

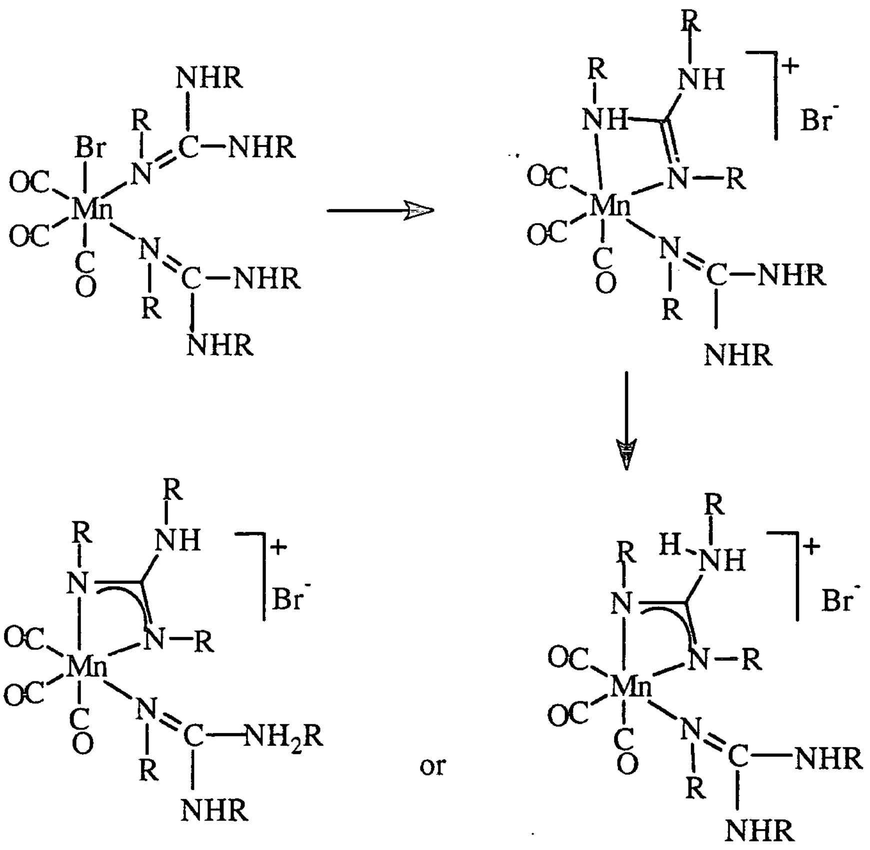
Electrical conductivity data for freshly prepared solutions of various compounds.

Product Formula	RMM	weight g/25 cm^3	Molar Conc. $mol.dm^{-3}$ (x 10^3)	$ohm^{-1}\ cm^2\ mol^{-1}$
$[(n\text{-}C_4H_9)_4N]Br$				90.8^a
$[(C_6H_5)_4As]_2(S_2C_2N_2)$				202.0^b
$TPGH_2.HCl$	323	0.0092	1.13	88.5
$SnCl_2.2H_2O$	189	0.0176	3.12	12.1
$[Mn(Br)(CO)_3(TPGH_2)_2]$	793	0.0212	1.11	90.9

Conductivity measurements in nitromethane; Specific conductivity, $\kappa = 5.54 \times 10^{-7}\ ohm^{-1}cm^{-1}$; Data from the literature[11], a- 1:1 electrolyte and b- 2:1 electrolyte in nitromethane;

On the basis of the positive evidence for the presence of a $[Mn(CO)_3]$ moiety, NH_2 and/or NH groups, and evidence for the complex being a 1:1 electrolyte, the structure shown in Figure 2.5, V, is proposed. Consistent with this structure were failed attempts to detect a ν(M-Br) vibrational frequency in the range 200 to 350 cm^{-1} using Nujol mulls and CsI windows. Structure **V** can be envisaged as the transformation product of $[Mn(Br)(CO)_3(TPGH_2)_2]$ (Figure 2.4, **VI**) formed from $[Mn(Br)(CO)_4TPGH_2]$ by displacement of a carbonyl group by a further $TPGH_2$ molecule. Such stepwise substitution reactions are well known for phosphine ligands[4,24]. The two strong σ-donating ligands will labilise the Mn-Br bond, leading to loss of the bromide ion, just as the nitrate ion is lost readily from

$[Mn(NO_3)(CO)_3(bipy)]$ complexes with nitrogen bases, e.g.. pyridine[25]. The following reaction scheme may be envisaged.



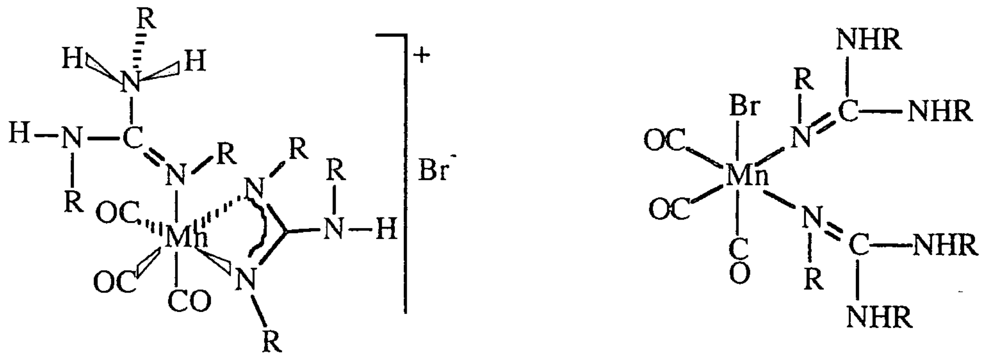
Coordinated guanidine acts as the proton base, promoting loss of HBr from the coordination complex. For the related amidine complexes, displacement of HBr requires the presence of additional base to absorb the HBr, e.g.

$$[Re(Br)(CO)_4(R'NHC(R)NR')] + R'NHC(R)NR' \longrightarrow$$

$$\longrightarrow [Re(CO)_4(R'NC(R)NR')] \quad + \; [R'NHC(R)NHR']Br$$

$(R=CH_3, Ph; R' = Ph, p\text{-tolyl})$

The high basicity of guanidines may be responsible for the retention of the displaced proton in the complex unit. From the data collected it is not possible to say which of the non-coordinated nitrogen atoms is quaternised.



V VI

Figure 2.2 Possible structures for[$Mn(Br)(CO)_3(TPGH_2)_2$] (R=Ph)

3. Product A

The reaction of [$Mn(Br)(CO)_5$] with 1,2,3-triphenylguanidine in a solvent mixture, such as dichloromethane/diethyl ether, chloroform/diethyl ether at room temperature, or dichloromethane/ diethyl ether/hexane at 40°C, gave a yellow product designated product A. It was prepared on several occasions and gave consistent analytical data. The nature of the product did not depend on the molar ratio of the reactants used nor on the reaction conditions. The same product was produced using a variety of different molar ratios of reactants. Good correspondence between the analytical data found and calculated percentage compositions occurred only for a metal:CO:$TPGH_2$ ratio of 2:6:3. Data for two formulations containing bromine are given in Table 2.1, and differ in the amount of guanidine in the lattice, Alternatively, the product may be considered to contain no bromine but a guanidino- ligand. Unfortunately, close correspondence does not occur between the data found and data for a likely complex.

The infrared spectrum of the product in a Nujol mull showed three strong absorptions in the range 2100 to 1900 cm^{-1} at 2005, 1915 and 1895 cm^{-1} that are assigned to terminal carbonyls, and a sharp strong absorption at 3350 cm^{-1} assigned to the ν(N-H) stretching frequency. The pattern, position and relative intensity of the carbonyl absorptions resemble closely those observed for $[MnBr(CO)_3(TPGH_2)_2]$ (see page facing Table 2.2), and suggests that product A contains this complex. However, the analytical data indicates that this complex is not the only component of the material which requires also the presence of a high carbon, hydrogen and nitrogen containing compound. Product A is produced using various stoichiometries of $[MnBr(CO)_5]$ and $TPGH_2$, and in hydrocarbon solvents both $[MnBr(CO)_4(TPGH_2)]$ and $[MnBr(CO)_3(TPGH_2)_2]$ may be synthesised. The latter complex is air reactive in solution and gives the guanidinium bromide on storage, It is conceivable, therefore, that in polar solvents additional free guanidine is produced during storage by decomposition, and becomes associated with the isolated product. On the evidence available, however, it is not possible to be categorical about the identity of product A, though there are distinct pointers relating it to $[MnBr(CO)_3(TPGH_2)_2]$.

Table 2.5

Expected molar conductivity† ranges for different electrolyte types in different solvents[11]

	Electrolyte Type			
Solvent	1:1	2:1	3:1	4:1
Nitromethane	75-95	150-180	220-260	290-330
Nitrobenzene	20-30	50-60	70-82	90-100
Acetone	100-140	160-200		
Acetonitrile	120-160	220-300	340-420	

† - molar conductivity ($ohm^{-1}cm^{2}mol^{-1}$) at molar concentration of $10^{-3}M$.

4. Evidence for the Formation of the Tetracarbonyl Complex, $[Mn(TPGH)(CO)_4]$

The yellow solution produced in the preparation of [Mn(Br)(CO)$_3$(TPGH$_2$)$_2$] from [Mn(Br)(CO)$_5$] with TPGH$_2$, was left under a nitrogen atmosphere for two days exposed to the sunlight and a new complex was isolated having an infrared spectrum reminiscent of [Mn(PhNC(Ph)NPh)(CO)$_4$] (see Table 2.3). Interestingly, the ν(CO) stretching frequencies were of higher energy than those of [Mn(Br)(CO)$_3$(TPGH$_2$)$_2$], and consistent with a smaller number of guanidines in the complex. The available data are consistent with the formation of [Mn(TPGH)(CO)$_4$], which is formed also in the reaction between [Mn(Br)(CO)$_5$] and the lithio-guanidine (see Chapter Three). Here, [Mn(TPGH)(CO)$_4$] may arise via the formation of the intermediate [Mn(Br)(CO)$_4$TPGH$_2$]. The nitrogen ligand in [Mn(TPGH)(CO)$_4$] needs to act as a 3-electron donor to satisfy the 18-electron rule, and four absorptions of carbon monoxide are expected for such a *cis* complex according to point group theory for C_{2v} symmetry (see Appendix B). The same pattern for tetracarbonyl complexes, such as [Mn(TPGH)(CO)$_4$], has been found by Inglis *et al*[5,7] and Clark *et al*[6] for the products of reaction of [Mn(Br)(CO)$_5$] (M= Mn, Re) with lithioamidines (see Table 2.3). The infrared spectrum of the complex [Mn(TPGH)(CO)$_4$] exhibited four medium to strong carbonyl absorptions in the region of 2100 to 1900 cm^{-1} (see Table 2.2), plus a sharp medium band about 3400 cm^{-1} which is assigned to the ν(N-H) stretching frequency. Unfortunately, [Mn(TPGH)(CO)$_4$] was formed here in solution in insufficient amount to allow full characterisation.

Table 2.2 summarises the infrared data for the manganese complexes described in previous sections. All compounds showed a slight shift of ν(CN) towards lower frequency which is an indication of TPGH$_2$ coordination through the imino-nitrogen, since in the free ligand the ν(CN) occurred about 1635 cm^{-1}. However, the ν(CN) is difficult to assign in compounds such as TPGH$_2$, due to the presence of other absorptions such as ν(C=C) from aromatic rings in the same region of the spectrum.

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Chapter Three

Studies of the Reaction of Bromopentacarbonylmanganese(I) with Lithio-1,2,3-triphenylguanidine and with a Mixture of Boron Trifluoride Etherate and 1,2,3-Triphenylguanidine

Introduction

This chapter presents work concerning the coordination of the guanidino-ligand to manganese carbonyl moieties. Several reactions involving the lithiated derivative of $TPGH_2$ and $[Mn(Br)(CO)_5]$ as starting materials were carried out under different conditions in order to understand the chemical behaviour of the ligand as an anion in its reactions towards the metal centre. Also, a comparative study between the lithium cation and BF_3 as bromide acceptors was performed using the same reaction conditions.

A. Experimental Work

1. Reaction of Bromopentacarbonylmanganese(I) with Lithio-guanidine in the Presence of Tetramethylethylenediamine

TMEDA (0.27g/ 2.3 mmol), in THF (5 ml), was frozen in liquid nitrogen and *n*-butyllithium (1.62M in hexane/ 0.15g/ 2.3 mmol) was added to the solid. The mixture was allowed to warm to room temperature to complete the reaction. After stirring for 30 minutes at room temperature, the yellow solution was frozen again in liquid nitrogen and a solution of $TPGH_2$ (0.67g/ 2.3 mmol) in THF (20ml) was added to the flask at low temperature. Again, the mixture was allowed to warm to room temperature and stirred for 45 minutes before $[Mn(Br)(CO)_5]$ (0.64g/ 2.3 mmol), dissolved in THF (20ml), was added dropwise into the yellow solution of lithio-guanidine at low temperature (CO_2 bath). After dropwise addition of the metal complex solution, the mixture was kept at low temperature for a further 2 hours and then warmed to room temperature. The THF was removed *in vacuo*, and the gum which appeared at the bottom of the flask was dissolved in dry, degassed, diethyl ether. The solvent was removed from the filtered solution *in vacuo* after 5 minutes stirring at room temperature. The diethyl ether procedure was repeated until an orange-yellow solid appeared inside the flask. Attempts to extract the orange solid with a mixture of diethyl ether/petroleum ether (1:7) did not succeed because at low temperature an oil separated from the solution. After drying the solid, dry degassed petroleum ether (60-80°) was added into the flask to extract the product at room temperature, and a yellow solution was obtained after filtration through Celite 521. No solid separated out of this solution after cooling, and the solvent was removed to obtain a yellow solid which was not air stable. The experiment was carried out under a nitrogen atmosphere. The product was shown to be [Mn(TPGH)$(CO)_4$] by elemental analyses (see Table 3.1) and infrared spectroscopy. Yield: 0.47g {45% based on [Mn(Br)$(CO)_5$]}.

2. Reaction of Bromopentacarbonylmanganese(I) with 1,2,3-Triphenylguanidine using Trifluoroboron Etherate (1:1:1 ratio)

$BF_3.OEt_2$ (0.26g/ 1.84 mmol) was added to a THF (10ml) solution of [Mn(Br)$(CO)_5$] (0.5g/ 1.81 mmol) at room temperature. The system was left stirring for a further hour without any change in colour. The mixture was heated and a THF (10 ml) solution of $TPGH_2$ (0.54g/ 1.87 mmol) was added dropwise into the hot mixture (75°C). The system was allowed to reflux overnight. The yellow solution became dark orange and returned to yellow when the system cooled. The THF was removed under reduced pressure at room temperature and the residual gum was extracted with diethyl ether three times before filtering the extracts. A white crystalline material separated from the diethyl ether, and the yellow filtrate was evacuated again to remove the diethyl ether. Toluene (20ml) was then added to the light yellow solid and produced a yellow solution plus a little more of the white material. After another filtration through Celite 521, the clear yellow solution was cooled overnight to afford orange crystals plus white needles. They were removed by filtration. From the filtrate in toluene, yellow-gold crystals separated overnight in the freezer. The experiment was carried out in a nitrogen atmosphere. The yield of the white material, $TPGH_2.BF_3$, was 0.42g [65% based on $BF_3.OEt_2$] but the yield of the yellow gold product was small. The latter product was shown to be a mixture of $TPGH_2.BF_3$ (see section A5) and [$Mn_2(CO)_{10}$] by elemental analyses, infrared, and ^1H NMR spectroscopy. The orange crystals, obtained from the toluene solution, were identified by IR spectroscopy of a Nujol mull as unreacted [Mn(Br)$(CO)_5$].

3. Reaction of Bromopentacarbonylmanganese(I) with 1,2,3-Triphenylguanidine and Trifluoroboron Etherate (1:2:1 ratio)

$BF_3.OEt_2$ (0.26g/ 1.84 mmol) was added to a solution of $[Mn(Br)(CO)_5]$ (0.5g/ 1.81 mmol) in THF (20ml) at room temperature. The system was allowed to stir for a further hour. A THF solution (10ml) of $TPGH_2$ (1.06g/ 3.68 mmol) was then added dropwise into the hot mixture (75°C), and the system heated to the reflux temperature overnight. The hot dark orange THF solution was then subjected to reduced pressure and the hot solvent removed. After removing the solvent completely, the yellow residue was allowed to reach room temperature. Recrystallisation from diethyl ether gave a yellow solid, designated product B. Yield: 1.05g. Analyses are recorded in Table 3.1.

4. Reaction of Bromopentacarbonylmanganese(I) with Lithio-1,2,3-triphenylguanidine

A solution of $[Mn(Br)(CO)_5]$ (0.5g/ 1.81 mmol) in THF (15ml) was heated to about 70°C, then LiTPGH (0.12g/ 1.82 mmol) in THF (15ml) was added dropwise to the solution. The orange colour of the hot solution became intense dark orange with the addition of the lithium compound. The system was heated to the reflux temperature for 4 hours. The colour of the solution was still orange even when the system reached room temperature. After removing the solvent *in vacuo*, dry toluene (35ml) was added to extract the product from the gum formed. The mixture was then heated again to about 50°C for a further 1.5 hours, causing a light brown solid to separate. Filtration through Celite 521 produced a clear yellow-gold filtrate. The toluene was replaced by diethyl ether and the orange solution was kept in a freezer overnight at -20°C. No crystals separated from the solution. The solvent was removed under reduced pressure, and a yellow solid obtained. The yellow solid was soluble in dichloromethane, hexane and petroleum ether, but decomposed in air at room temperature in the dark. The product was shown to be [Mn(TPGH)$(CO)_4$] by analytical data (see Table 3.1).Yield: 0.53g {65% based on [Mn(Br)$(CO)_5$]}.

5. Reaction of 1,2,3-Triphenylguanidine with Trifluoroboron Etherate

$TPGH_2$ (0.5g/ 1.74 mmol) was dissolved in a mixture of THF/monoglyme (1:1, 20ml) at room temperature and $BF_3.OEt_2$ (0.24g/ 1.70 mmol) was added to the solution. After 1 hour stirring at room temperature, the solvent mixture was removed *in vacuo*, and replaced by diethyl ether. A white material separated immediately and was left stirring in diethyl ether at room temperature for a further two hours. After filtration, the white solid, $TPGH_2.BF_3$, was dried. Yield: 0.61g [85% based on $BF_3.OEt_2$]. [Found: C, 62.60; H, 4.79; N, 10.95. $C_{19}H_{17}BF_3N_3$ requires C, 64.22; H, 4.79; N, 11.83%].

6. Reaction of Bromotetracarbonyl-1,2,3-triphenylguanidinemanganese(I) with n-Butyllithium

The complex [Mn(Br)$(CO)_4$$TPGH_2$] was prepared as described in Chapter Two. After crystallisation, [Mn(Br)$(CO)_4$$TPGH_2$] (0.24g/ 0.44 mmol) was dissolved in dry, degassed monoglyme (15 ml). The solution was frozen and LiBu (0.028g/ 0.43 mmol/ 1.31 M in hexane) added to the flask. The mixture was allowed to warm to room temperature, and was frozen again. The procedure of freezing/thawing was repeated three times before the solution was left to stir at room temperature for a further 1.5 hours. The colour of the solution by the end of the reaction time was dark orange-red. No solid separated from the solution even after leaving the final solution at -20°C. The monoglyme was then removed *in vacuo* and a mixture of toluene/hexane was used to redissolve the yellow residue. After filtration, the solution was left at room temperature under a nitrogen atmosphere for 24 hours and a yellowish material separated. However, the colour of the solution did not change. The solution was filtered, the solvent was removed *in vacuo* and a gum was formed at the bottom of the flask. On leaving the gum overnight under vacuum, part of the yellow material changed colour from yellow to brown. The dark solid was redissolved in diethyl ether, the extract filtered, and from the yellow solution a solid was obtained in a very poor yield (< 50 mg). This solid seemed to decompose during the process of purification, decreasing even more the yield. The product was characterised as the previously prepared material, product A, on the basis of analytical data (see Table 3.1), and infrared spectroscopy.

7. Reaction of Bromopentacarbonylmanganese(I) with TMEDA

The complex $[Mn(Br)(CO)_5]$ (0.64g/ 2.3 mmol) was dissolved in THF (20ml) at room temperature under a nitrogen atmosphere. After 5 minutes, TMEDA (0.27g/ 2.3 mmol) was added to the flask which was warmed to 30-34°C. The solution became orange and it was kept stirring for a further 2 hours. The solvent was removed *in vacuo*, and the orange yellow product, $[Mn(Br)(CO)_3TMEDA]$, dried under reduced pressure. The product was identified by analyses and infrared spectroscopy by reference to literature data[1,2]. Yield: 0.67g {80% based on $[Mn(Br)(CO)_5]$}.

Table 3.1

Data for the manganese complexes obtained using LiTPGH and BF_3/$TPGH_2$

Product Formula	Found(Calcd.)% C	H	N	Br	F	mp.(°C)
Product A[a]	65.59	6.99	8.11	*		
$[Mn(Br)(CO)_3(TPGH_2)_2].0.5TPGH_2$ requires	(64.71)	(4.54)	(11.21)	(8.53)		
$[Mn(Br)(CO)_3(TPGH_2)_2].TPGH_2$ requires	(66.67)	(4.76)	(11.66)	(7.39)		
$[Mn(TPGH)(CO)_4]$	61.68	4.54	8.56			
	(60.92)	(3.53)	(9.27)			
$[Mn(TPGH)(CO)_3]$ requires	(62.12)	(3.80)	(9.87)			
Product B	53.08	4.65	8.43	10.60	8.36	75-78
$[Mn_2(Br)_2(CO)_6(TPGH_2)_3(BF_3)_2]$ requires	(52.72)	(3.55)	(8.79)	(11.15)	(7.91)	

a - Product of reaction of $[Mn(Br)(CO)_4TPGH_2]$ with LiBu (very little material to analyse, section A6).

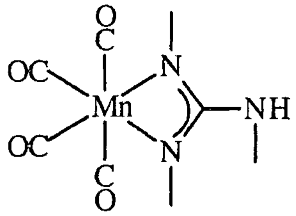
* - Analysis of bromine was not attempted.

B. Results and Discussion

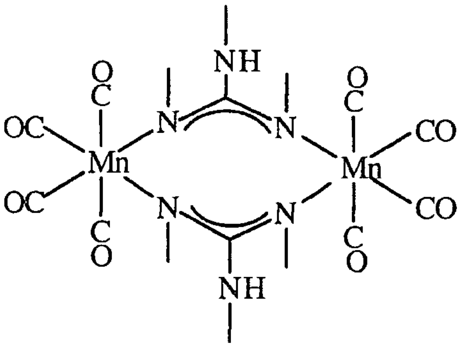
1. Complex [Mn(TPGH)(CO)$_4$]

The same complex was produced following three slightly different procedures: (*i*) reaction of bromopentacarbonylmanganese(I) with lithio-1,2,3-triphenylguanidine in THF at low temperature using TMEDA in a molar ratio of 1:1:1 (section A1), (*ii*) reaction in THF of lithio-1,2,3-triphenylguanidine, without TMEDA, with bromopentacarbonylmanganese(I) at 70°C in a molar ratio of 1:1 (section A4), and (*iii*) dehydrobromination of [Mn(Br)(CO)$_4$TPGH$_2$] (section A6; section B4). The product seems to be formed irrespective of the presence of TMEDA or the temperature at which the lithio-reactions were performed. Again the 1,2,3-triphenylguanidino-group binds to the metal as a 3-electron donor to satisfy the 18-electron rule of a single metal, or bridge between metals.

The compound [Mn(TPGH)(CO)$_4$] in hexane solution exhibited four ν(CO) stretching frequencies in the region of 2100 to 1900 cm^{-1} at 2092w, 2011s, 1991s, and 1949s cm^{-1}. The similarity of this spectrum compared with the spectrum of the corresponding amidino-complex, [Mn(PhNC(Ph)NPh)(CO)$_4$], is striking (Table 3.2), and since the analytical data are consistent with a complex of this type, the complex is formulated as [Mn(TPGH)(CO)$_4$]. Possible structures are shown below, having the guanidino-group either bidentate or bridging two manganese atoms. The guanidino-group acts as a 3-electron donor in each case. The amidino complex has a structure similar to the mononuclear complex. Similarities also occur between [Mn(TPGH)(CO)$_4$] and [Mn(X)(CO)$_4$]$_2$ (X=Cl, Br, I) complexes in which the halogens bridge the two manganese atoms. The infrared spectra in the carbonyl stretching region are compared in Table 3.2. The infrared data are consistent with both monomeric and dimeric structures and on the basis of the data available it is not possible to differentiate between the two possibilities.



monomer



dimer

Analytical data recorded in Table 3.1 indicate that the tricarbonyl complex [Mn(TPGH)$(CO)_3$], is also consistent with the carbon, hydrogen and nitrogen contents found. However, such a formulation requires either the TPGH ligand to provide an additional two electrons through bridging (see Figure 2.3, structure **VIII**), or for a metal-metal double bond to be formed. When the guanidino-ligand acts as a five electron donor, the third nitrogen may become involved to produce a $[Mn(CO)_3L_2L^1]$ type complex in a polymeric structure, but this can be eliminated by the non-$[Mn(CO)_3]$ type pattern of ν(CO) stretching frequencies (see Appendix B) observed for the product. The weight of evidence available favours the [Mn(TPGH)$(CO)_4$] empirical formulation. Interestingly, some, but not all samples, of the isolated material showed an additional medium intensity absorption at 1919 cm^{-1}, ascribed to an impurity.

The IR spectrum of a hydrocarbon solution of [Mn(TPGH)$(CO)_4$] was monitored after the material was exposed to air, and four ν(CO) absorptions remained (see Table 3.3). Also, the yellow gold colour became slightly brown over 24 hours exposed to air, which suggested decomposition of the material. The infrared spectrum taken again after the elimination of the brown material showed the original four carbonyl stretching frequencies in solution and in the solid state (see Table 3.3). The brown decomposition material was not identified but it was insoluble in hydrocarbon solvents.

Table 3.2

Carbonyl stretching frequencies for several manganese complexes[3,4]

Product Formula	ν(CO)/cm^{-1}
$[Mn(Cl)(CO)_4]_2$	2104w; 2045s; 2012m; 1977m
$[Mn(Br)(CO)_4]_2$	2099w; 2042s; 2011m; 1975m
$[Mn(I)(CO)_4]_2$	2087w; 2033s; 2009m; 1976m
$[Mn(TPGH)(CO)_4]$	2092w; 2011s; 1991s; 1949s
$[Mn(PhNC(Ph)NPh)(CO)_4]$	2096w; 2017s; 1996s; 1955s

2. The Boron Trifluoride Adduct of $TPGH_2$

Bromopentacarbonylmanganese(I) reacted with 1,2,3-triphenylguanidine in a 1:1 reaction mixture in the presence of $BF_3.OEt_2$ in THF (20ml) at the reflux temperature. A dark orange colour was obtained at the end of the reaction time. However, the colour changed to pale yellow when the reaction mixture cooled, and a white material started to precipitate. Extraction of the pale yellow solid with diethyl ether or toluene gave only decacarbonyldimanganese and $TPGH_2.BF_3$ as products, the latter being the main component. The infrared spectrum of the yellow residue exhibited three strong ν(CO) frequencies at 2138, 2050 and 1991 cm^{-1} which cannot be assigned at present, and do not relate to any complex isolated in this work.

Table 3.3

Infrared data for compounds prepared in this work (frequencies in cm^{-1})

Product Formula	Solvent	ν(CO)	ν(NH)	ν(CN)	ν(BF)
$TPGH_2$	Nujol		3374m	1636s	
$TPGH_2.HCl$	Nujol		3427m†	1635s	
$TPGH_2.BF_3$	Nujol		3346s	1638s	1078s
Product A	Nujol	2013s; 1914s 1893s	3385s	1623s	
$[Mn(TPGH)(CO)_4]$	Hexane	2092w; 2011s 1991s; 1949s	3396m	1602m	
	Nujol	2090w; 2010 1990s; 1955s			
Product B	Nujol	2090w; 2012s 1984m‡; 1930s*	3301m†	1637s	1075s
	KBr	2090w; 2016s 1984m‡; 1933s	3373s†	1640s	1083s
$[Mn(Br)(CO)_3TMEDA]$	Nujol	2015s; 1919s 1894s			

† - broad absorption; ‡ - shoulder; * - broad.

The complex, decacarbonyldimanganese, was identified by infrared[5] spectroscopy, showing its typical three strong carbonyl absorptions in the range 2050 to 1950 cm^{-1} in hexane and dichloromethane solutions.

The infrared spectrum of $TPGH_2.BF_3$ shows a strong absorption at about 3346 cm^{-1}, assigned to ν(N-H). Also strong absorptions in the range 900 to 1130 cm^{-1} at 916, 1007, 1078 and 1109 cm^{-1} are assigned to ν(B-F) absorptions, and others in the range of 800 to 500 cm^{-1} are correlated to ν(B-N)[6-8] absorptions. In addition, typical (C-H) out-of-plane vibrational frequencies for a benzene substituted ring[9] occur in the same region. Overlap of absorption regions is one of the difficulties in assigning vibrational modes in the range 800 to 500 cm^{-1}.

The ^{19}F NMR of $TPGH_2.BF_3$ exhibited a singlet peak at -149.1 ppm which is an indication that all fluorine atoms are magnetically equivalent in the adduct, and that J_{BF} is very small, since no coupling is resolved. A singlet is also observed for $Me_3N.BF_3$ (see Table 3.4), but trifluoroboron adducts of ethylamine and piperidine[10,11] exhibit quartets in a variety of solvents. ^{19}F NMR signals for BF_3 adducts of nitrogen bases occur in the range of -142.4 to -164.1 ppm (see Table 3.4). These adducts do not undergo hydrolysis easily at room temperature to form ions such as $[BF_4]^-$, $[BF_3OH]^-$ and $[(RNH_2)_2BF_2]^+$. The authors[10,11] have reported little change over a period of 4 days, when monitored by ^{19}F NMR in hygroscopic solvents such as acetone or dimethyl sulphoxide. Hydrolysis was also not observed in the case of the adduct $TPGH_2.BF_3$ at room temperature.

The ^1H NMR spectrum of $TPGH_2.BF_3$ in CD_3CN exhibited a multiplet centred at 7.3 ppm, within the typical chemical shift range of aromatic compounds, a broadened peak at 8.1, and a very weak broad peak at 2.2 ppm, the last two peaks being assigned to the N-H groups. The broadness of these peaks is probably due to the quadrupole relaxation[12] associated with $^{14}N(I=1)$. It is well known that the solvent affects the chemical shift of N-H peaks; for example, the N-H chemical shift of $TPGH_2$ occurs at 5.4 ppm in $CDCl_3$ whereas in CD_3CN it is at 6.5 ppm. The higher frequency shift of the N-H signal in the more polar solvent is an indication of hydrogen bonding, and is associated with hydrogen bonding for a variety of different nitrogen compounds[13-15]. Nowick *et al*[13] and Tinkler *et al*[14] reported high frequency shifts for N-H protons of 1,2-diaminoethane diureas and sulphonyl-benzamidines and -guanidines. Nowick *et al*[13], for example, concluded that 1,2-diaminoethane diureas exhibit a substantially higher degree of intramolecular hydrogen bonding than the homologous derivatives of 1,3-diamino propane. The peak for the hydrogen bonded N-H group was estimated to appear 2.5 ppm higher in frequency than the signal for a non-hydrogen bonded N-H group. The chemical shift allows the estimation of the relative populations of hydrogen-bonded conformers and non-hydrogen-bonded conformers for this family of compounds. For example, $NCCH_2CH_2N(R)(CH_2)_3N(R)Ph$ (5.62 ppm, $CDCl_3$; R= $-C(O)NHCH_3$) exhibits for the H-bonded N-H group a signal 1.3 ppm to higher frequency than that of $(CH_3CH_2)_2NC(O)NHCH_3$ (4.32 ppm, $CDCl_3$). This high frequency shift corresponds to 52% of the molecules having intramolecular hydrogen bonding of the type N-H··O.

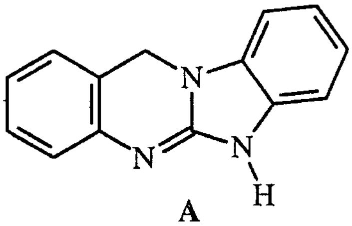
Table 3.4

^{19}F NMR data (ppm) for various compounds in different solvents[10,11,16-22]

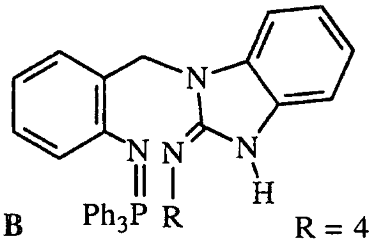
Product Formula	Solvent	δ(BF_3)	δ(BF_3Br)	δ(BF_2Br)	δ(BF_2Br_2)	δ(BF_4)
Product B†	$CDCl_3$	-149.5s				
$C_2H_5NH_2.BF_3$[10,11]	$(CD_3)_2CO$	-150.39q				
$C_5H_{10}NH.BF_3$[11]	$(CD_3)_2CO$	-156.94q				
$TPGH_2.BF_3$†	$CDCl_3$	-149.1s				
$4\text{-}MeC_5H_4N.BF_3$[21]	$CFCl_3$	-142.4s				
$Me_3N.BF_3$[21]	$CFCl_3$	-164.1s				
$4\text{-}MeC_5H_4N.BF_2Br$[21]	$CFCl_3$			-117.3q		
$[\eta\text{-}C_4H_9)_4N][BF_2Br_2]$[17]	$CH_2Cl_2/CFCl_3$				-88.2q	
$[\eta\text{-}C_4H_9)_4N][BF_3Br]$[17]	$CH_2Cl_2/CFCl_3$		-113.8s			
$Et_2O.BF_3$	$CDCl_3$	-153.5s				
$Me_2O.BF_2Br$[22]	$CFCl_3$				-123.9q	
$[\{VO(salen)\}_2(\mu\text{-}F)][BF_4]$[16]	CD_3CN					-152.2s
$[In(PhCH_2)_2][BF_4]$[18]	CD_3CN					-151.2s
$[Xe(4\text{-}FC_6H_4)][BF_4]$[20]	CD_3CN/CH_2Cl_2					-149.2s
$[Ru(F)(CO)_2(PPh_3)(H_2O)][BF_4]$[19]	$CFCl_3$					-149.3s
$[\eta\text{-}C_4H_9)_4N][BF_4]$[17]	$CH_2Cl_2/CFCl_3$					-151.3s

s - singlet; q - quartet; † - This work; $Et_2O.BF_3$ is the external reference; L = $TPGH_2$.

The chemical shift observed for the adduct $TPGH_2.BF_3$ (peak at 8.1 ppm, 2H) is probably due to intramolecular bonding of the type N-H··F by comparison with the peak at 6.5 ppm (CD_3CN) and 5.4 ppm($CDCl_3$) of $TPGH_2$. However, intermolecular hydrogen bonding of the type N-H··N cannot be disregarded since the position of the peaks found for $TPGH_2$ is already an indication of this type of bonding[9] in both $CDCl_3$ and CD_3CN. In addition, intermolecular hydrogen bonding of the type N-H··F may also occur. Cunningham *et al*[23] have characterised N-aryl-N'-cyanoguanidines by NMR in $(CD_3)_2SO$ solution and found that the N-H proton resonates at high frequency, 8.84 ppm and 9.04 ppm for $4\text{-}MeOC_6H_4NHC(NH_2)NCN$ and $PhNHC(NH_2)NCN$ respectively. However, no evidence was found for prototropic tautomerism or general exchange of the NH hydrogens since change in peak broadening or chemical shift was not observed at any temperature. The author attributed this to the very low basicity and acidity of the cyanoguanidines. Molina *et al*[24] have characterised cyclic guanidines by X-ray crystallography. The crystal structure of compound **A** below consists of dimers formed by N-H··N hydrogen bonds. The N-H resonance occurred at 10.31 ppm in $(CD_3)_2SO$ and at 9.83 ppm for the compound **B** in $CDCl_3$. Thus the broad signal at 8.1 ppm for $TPGH_2.BF_3$ in CD_3CN solution is confidently assigned to a hydrogen bonded N-H group.



A



B

R = $4\text{-}FC_6H_4$

The broad weak peak observed at 2.2 ppm for the adduct $TPGH_2.BF_3$ is an indication that the N-H protons may be taking part in an exchange process at room temperature. The broadness of this peak suggests a compound which is exchanging N-H protons at room temperature probably via an associative process as illustrated in Figure 3.2. Interestingly, the hydrochloride of $TPGH_2$ also shows in $CDCl_3$ a broad peak at 2.0 ppm but no N-H signal at high frequency. Thus, the 2.2 ppm signal of $TPGH_2.BF_3$ may arise from N-H groups involved in a tautomeric equilibrium[25].

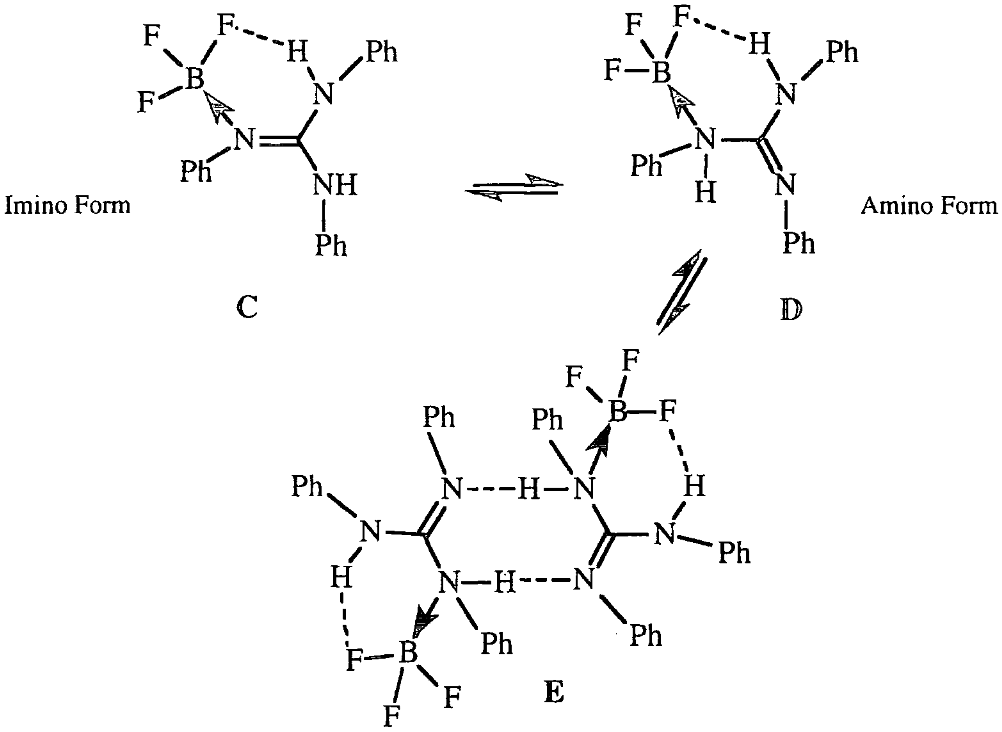


Figure 3.2 Amino and Imino tautomers of the adduct $TPGH_2.BF_3$

It is concluded that the broad signal at 8.1 ppm arises from hydrogen bonded N-H groups (hydrogen bonded to either fluorine or nitrogen as in **C**, **D** and **E**, Figure 3.2) and the weaker signal at 2.2 ppm is probably due to non-hydrogen bonded N-H groups in tautomers **C** and **D**.

3. Product B

Bromopentacarbonylmanganese(I) in the presence of BF_3, was reacted with 1,2,3-triphenylguanidine in a 1:1:2 molar ratio in THF at the reflux temperature. The order in which the reactants were mixed was the bromopentacarbonylmanganese(I), the trifluoroboron etherate followed by the addition of the guanidine. Excess of trifluoroboron etherate was avoided. The colour of the reaction solution was dark orange after the reaction. The yellow product, obtained after removing the hot solvent, was air sensitive, and it was observed that after long storage at low temperature, decomposition also occurred leading to a white material. Repeated analyses of the yellow product indicated the following apparent composition $[Mn_2(Br)_2(CO)_6(TPGH_2)_3(BF_3)_2]$. The empirical ratio of N:Br is 9:2 indicating $3TPGH_2$:2Br. The theoretical compositions for a variety of formulations are compared below with the analytical data found. The formulations are based on 18-electron manganese(I) centres.

Analytical data and theoretical composition for manganese complexes containing BF_3

Product Formula	C	H	N	Br	F
Found	53.08	4.65	8.43	10.60	8.36
$[Mn_2(Br)_2(CO)_6(TPGH_2)_3(BF_3)_2]$	52.68	3.55	8.78	11.15	7.94
$[Mn_2(Br)_2(CO)_7(TPGH_2)_3(BF_3)_2.]$	52.50	3.48	8.61	10.93	7.79
$[Mn_2(Br)_2(CO)_6(TPGH_2)_3)(BF_3)]$	55.30	3.73	9.22	11.70	4.17
$[Mn_2(Br)_2(CO)_6(TPGH_2)_2(BF_3)]$	48.88	3.14	7.77	14.81	5.27

The infrared spectrum of product B exhibited in a Nujol mull three strong carbonyl absorptions in the range 2100 to 1900 cm^{-1} at 2090w, 2012s, and 1930s cm^{-1} plus a shoulder at 1984 cm^{-1} of medium intensity. The ν(N-H) stretching frequency occurred as a broad medium absorption centred at 3301 cm^{-1}. The broadness of the latter was confirmed in the range 3400 to 2700 cm^{-1} by scanning the same material in a KBr disc. The infrared spectrum of product B also exhibited in the range 1000 to 1200 cm^{-1}, a broad absorption assigned to a ν(B-F) stretching frequency[26] (see Table 3.3). Compounds containing the $[BF_4]^-$ anion and adducts such as $CH_3CN.BF_3$ are reported[7,8,26] to have ν(B-F) stretching frequencies in the same range. The nature of the bonding of BF_3 in the product is of particular interest since two likely possibilities exist, (i) coordination via a free nitrogen of a guanidine ligand, or (ii) coordination to a bromide ion as $[BF_3Br]^-$. Infrared spectroscopy does not allow a distinction to be made between these two possibilities.

The ν(CN) vibrational modes usually occur in the range of 1660 to 1480 cm^{-1} and the identification of such absorptions is often difficult due to the large variations in intensity and the closeness to the ν(C=C) stretching region. An indication of complexation through an imino-nitrogen atom of $TPGH_2$ would be the shift of the ν(CN) band towards low frequency, but in this work data were not easy to collect because of overlapping bands and assignment difficulty. However, the supposed ν(CN) stretching frequency assigned for product B at 1637 cm^{-1} was not noticeably different from that of the adduct, $TPGH_2.BF_3$ (1638 cm^{-1}), and free $TPGH_2$ (1636 cm^{-1}). Similar assignments have been made by Martínez *et al*[27] in studies of BF_3/imidazole derivatives. In both the imidazole and guanidine-BF_3 derivatives, coordination to BF_3 will be via the imino-nitrogen atoms. It is conceivable that in product B the BF_3 may be bonded through amino-nitrogen atoms (see Figure 3.2; amino form) if further coordination of the guanidine occurs to manganese. Comparison of the ν(CN) frequencies of the manganese complex, $TPGH_2.BF_3$ and $TPGH_2$ shows little difference. Thus, coordination has little effect on the ν(CN) frequencies of guanidines and ν(CN) data provide no useful structural information.

For product B, in the infrared spectral range 500 to 800 cm^{-1}, two medium to strong absorptions at 752 and 691 cm^{-1} can be assigned undoubtedly to the C-H out-of-plane vibration for the monosubstituted phenyl rings of $TPGH_2$. The same absorptions can be found in the spectrum of $TPGH_2$ and $TPGH_2.BF_3$ scanned in Nujol or a KBr disc. Compared with the spectrum of $TPGH_2$, additional absorptions due to ν(B-N) stretching vibrations are observed in the 500 to 800 cm^{-1} region for both $TPGH_2.BF_3$ and product B. However, the precise ν(B-N) frequency cannot be assigned with certainty due to overlapping in this region with the (C-H) out of plane absorptions from the phenyl groups. Thus, BF_3 is bound to the guanidine as shown by NMR. No ν(M-Br) absorption was observed for product B using a CsI disc in the range 300 to 200 cm^{-1}.

The ^{19}F NMR shows the fluorine of product B to resonate as a singlet to high frequency (see Table 3.4) of the external reference, $Et_2O.BF_3$ which has also a single peak. The chemical shift difference between these two materials scanned in the same solvent, deuterated chloroform, was 4.0 ppm. The singlet peak suggests that all fluorine atoms are magnetically equivalent in product B and this particular feature excludes any structure in which the BF_3 group does not remain intact. Thus halide exchange[17] reactions such as $2[BF_3Br]^- \longrightarrow [BF_4]^- + [BF_2Br_2]^-$ which occur readily at room temperature are excluded. The purpose of adding BF_3 to the reaction medium was to assist removal of the bromide ion as $[BF_3Br]^-$. However, formation of this ion can be readily eliminated from consideration by the ^{19}F NMR spectrum of the product complex. A signal in the -114 ppm region[17] due to $[BF_3Br]^-$ was absent, as was a signal in the -88 ppm region due to the $[BF_2Br_2]^-$ anion[17]. Similarly, occurrence of a guanidine.BF_2Br adduct is also eliminated (see Table 3.4) by the absence of a signal about -117 ppm found for $4\text{-}CH_3C_5H_4N.BF_2Br$[21].

The observed ^{19}F NMR signal for product B (at -149.5 ppm) is very close to that observed for $TPGH_2.BF_3$ (at -149.1 ppm), and nitrogen-boron bonding is consequently deduced for product B. A variety of amine.BF_3 adducts have ^{19}F NMR signals in the -142 to -164 ppm region and it is concluded that the BF_3 is bonded in the manganese complex to a nitrogen atom of a guanidine. The ^{19}F NMR signals for complexes containing $[BF_4]^-$ occur in the same region (-149 to -152 ppm, see Table 3.4) but this is not thought to be present in the manganese complex because disproportionation of BF_3 would be required for its formation, for example via

$$4Br^- + 4BF_3 \longrightarrow 4[BF_3Br]^- \longrightarrow [BF_{4-x}Br_x]^- \longrightarrow 3[BF_4]^- + [BBr_4]^-.$$

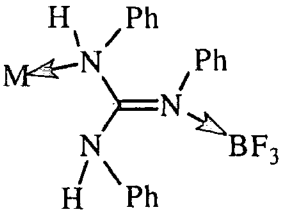
Such a process would lead to the formation of various fluorine containing species of the type $[BF_{4-x}Br_x]^-$. Since only one signal was observed, and this is very close to that for [guanidine.BF_3], it is concluded that BF_3 is coordinated to a guanidine nitrogen atom,

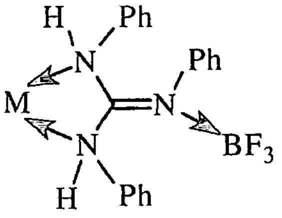
The ^1H NMR for product B in $CDCl_3$ shows a peak centred at 7.3 ppm within the typical chemical shift region of aromatic groups such as phenyl. Two broad peaks at 8.91 and 2.03 ppm are assigned to the N-H groups of the ligand. Similar broad peaks were also observed for the adduct $TPGH_2.BF_3$ at 8.1 and 2.2 ppm. The peak at 8.9 ppm is an indication of hydrogen-bonded conformers and the one at 2.03 ppm an indication of proton exchange at room temperature as discussed previously for the adduct $TPGH_2.BF_3$ (8.1 and 2.2 ppm, CD_3CN). Hydrogen bonding between the fluoride and N-H hydrogens may be a strong factor in the structure adopted. Thus, the NMR results show a close similarity between $TPGH_2.BF_3$ and product B, and it is again concluded that BF_3 is bonded to nitrogen of a guanidine, and that the anion $[BF_3Br]^-$ is not formed in the reaction.

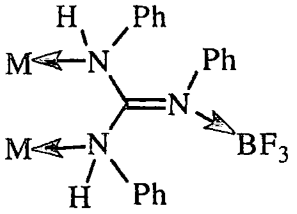
Electrical conductivity measurements conducted in nitromethane solutions of $TPGH_2.BF_3$ and of product B gave data which demonstrated that reaction with the nitromethane solvent had plainly occurred. This conclusion was confirmed by ^{19}F NMR spectroscopy in deuteronitromethane for product B. The spectrum in the latter solvent [δ_F(ppm) -139.1s, -150.2s] contrasted markedly with that measured in $CDCl_3$ [δ_F(ppm) -149.5s]. Further investigation of the reaction with nitromethane was not undertaken.

Although product B appears to have the composition $[Mn(Br)_2(CO)_6(TPGH_2)_3(BF_3)_2]$, its precise nature can not be deduced from the structural data obtained. Unfortunately, crystals suitable for an X-ray crystallographic study could not be obtained. Clearly, product B and [$TPGH_2.BF_3$] have closely similar infrared and NMR data, and there is no doubt that the [BF_3] molecule is bound to a nitrogen atom of a guanidine. However, the nature of the presence of [$TPGH_2.BF_3$] in product B has not been deduced, and can be the subject only of speculation. It may be present as a consistent impurity, or as part of a mixed lattice compound. Alternatively, since the guanidine ligand will bond to

BF_3 using only one of the three nitrogen donor atoms, it is conceivable that the same guanidine could also coordinate to manganese as shown below.







However, there is no evidence at present to support the idea that $[TPGH_2.BF_3]$ can act as a donor to a Lewis acid centre, and interestingly, in this work there was no evidence for the formation of $[TPGH_2.2BF_3]$. In the absence of diagnostic structural data, further conclusions can not therefore be made.

4. The Reaction of $[Mn(Br)(CO)_4TPGH_2]$ with n-Butyllithium

Product A (see chapter 2) is believed to be the main product of reaction between $[Mn(Br)(CO)_4TPGH_2]$ and LiBu. The LiBu was added at low temperature (-196°C) in a molar ratio of 1:1 and the mixture then allowed to warm to room temperature. All solvents were degassed, and the colour of the solution at the end of the reaction time was dark orange-red. LiBr was removed by filtration of the orange-red hydrocarbon extracts of the yellow residue obtained after removing the reaction solvent.

The infrared of the product exhibited six carbonyl absorptions in the range 2100 to 1900 cm^{-1} at 2093w, 2045w, 2011s, 1992s, 1951s, and 1921w cm^{-1} in hexane solution. Three of them were weak in intensity and the other three very strong. Four of these absorptions at 2093w, 2011s, 1992s and 1951s cm^{-1} indicate the formation of the desired product, $[Mn(TPGH)(CO)_4]$ (see Table 2.2, Chapter

Two). An additional weak absorption at 1921 cm^{-1}, referred to previously (at 1919 cm^{-1}), was also observed. The reaction product decomposed under vacuum at room temperature affording a further product which exhibited one very weak band at 2044 cm^{-1}, and three strong carbonyl absorptions at 2013, 1914 and 1893 cm^{-1} in the infrared spectrum. Also a sharp absorption at 3400 cm^{-1} was detected, similar to those observed in the spectrum of Product A (see Table 2.2 Chapter Two). This manganese complex is probably the main product of decomposition, but analytical data suggest that the material isolated was impure (see Table 3.1).

5. Other Aspects Involving the Manganese Complexes

The work described in this chapter is concerned with introducing the guanidino-group into manganese carbonyl complexes. Two approaches have been used, (*i*) using lithioguanidines to eliminate lithium bromide from $[Mn(Br)(CO)_5]$, and (*ii*) using BF_3 as a bromide extractor in attempts to produce $[BF_3Br]^-$.

Several of the complexes synthesised show three carbonyl stretching frequencies consistent with the *fac*-$[M(CO)_3]$ arrangement of groups (see Appendix B), though the difference between the pattern of ν(CO) absorptions for this moiety, and that expected for *cis*-$[M(CO)_4XY]$ type complexes, amounts only to an additional high frequency weak absorption. This weak absorption is not always detected. Thus, it is not always possible, using IR spectroscopy, to differentiate between *fac*-$[M(CO)_3]$ and *cis*-$[M(CO)_4]$ species. *Trans*-carbonyl groups compete with each other for the electron density on the metal due to the fact that they bond to the same *d* orbitals of the metal. The symmetrical stretching frequency for *trans*-carbonyls will have weak intensity whereas the asymmetrical stretching frequency will have strong intensity. This is a general rule which applies to all such groupings (see Appendix B).

The canonical-forms of $[TPGH_2.BF_3]$ are shown in Figure 3.3.

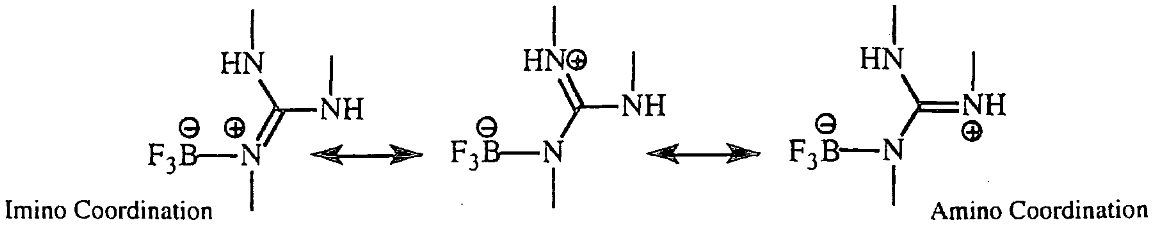


Figure 3.3 Canonical forms for the adductTPGH$_2$.BF$_3$

The bond through the imino nitrogen to the Lewis acid BF_3 should affect the availability of the lone pair from the amino nitrogen for bonding to the metal ion. Also the amino form of the adduct in Figure 3.5 would reduce the electron density on the other nitrogen atoms by the inductive effect. Imino coordination prevents delocalization of the positive charge over the other coplanar nitrogen atoms which is favourable for the stability of the adduct. However, in both situations the basicity of the $TPGH_2$ would be reduced, leading to a weaking of the ligand as a good σ-donor. Competition between the metal and BF_3 will occur for the nitrogen lone pairs, and since nitrogen ligands are predominantly σ-donors, imino-nitrogen-BF_3 bonds are likely to be formed. Thus, it is the amino-nitrogen donor centres which will be available for further coordination to the metal.

Interestingly, the reactions were performed using 1:1:1 or 1:1:2 stoichiometries of $[Mn(Br)(CO)_5]$:BF_3 etherate:$TPGH_2$. An excess of BF_3 etherate led to formation of gums after removal of the reaction solvent *in vacuo*, and was avoided at all costs. The 1:1:2 reaction led to a $TPGH_2$ derivative whereas the 1:1:1 reaction led only to by-products. Thus the second mole of guanidine has an important participation concerning the stabilisation of the final product at room temperature in diethyl ether solution.

The reactions undertaken using lithium reagents and BF_3 etherate are summarised in Figure 3.6. The product prepared following the reaction pathway 3 in Figure 3.6 did not show any dependence on temperature. The final product was the same whether the preparation followed the technique using TMEDA at low temperature, or without TMEDA but at high temperature. It was anticipated that TMEDA would coordinate to the lithium forming [Li(TPGH)TMEDA], thereby reducing the degree of clustering of the lithio-reagent and increasing its reactivity, but the expected benefit was not realised. TMEDA is itself a very strong base and it will compete with the anion [TPGH] for coordination to the manganese centre. However, $[Mn(Br)(CO)_3TMEDA]$ was not isolated as a by-product in the reaction pathway 3, nor was there evidence for its formation. The infrared spectrum of an authentic sample exhibits a pattern of three strong ν(CO) absorptions typical of a *fac*-isomer (see Table 3.3 and Appendix B), but such absorptions were not observed in the infrared of the product.

The idea of using BF_3 in the reaction medium was based upon the possible formation of the anion $[BF_3Br]^-$ as a means of removing Br^- from the starting complex. The BF_3 was introduced as the etherate $Et_2O.BF_3$. Even if $[BF_3Br]^-$ is initially formed in solution, its lifetime should not be very long if a better σ-donor ligand, such as $TPGH_2$ competes for the Lewis acid, BF_3. A further theoretical possibility is the binding of BF_3 to the oxygen of one of the CO groups attached to the metal, but this would be less favourable than binding to the free nitrogen of a guanidine, considering that CO is a soft base and BF_3 is a hard acid. This is extremely unlikely however.

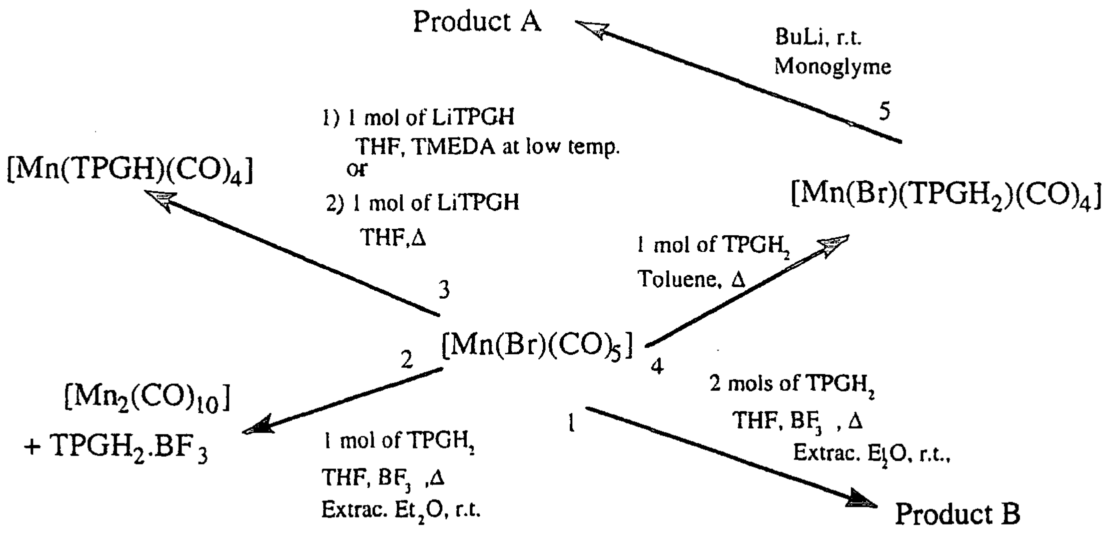


Figure 3.5 Summary of the reactions involving lithium reagents and BF_3 etherate

Interestingly, in the reactions involving BF_3, the dimer $[Mn_2(CO)_{10}]$ was isolated as a by-product of the reaction pathway 2, possibly via a radical process. The starting material $[Mn(Br)(CO)_5]$ did not contain this complex as an impurity, as it was well characterised and in its preparation, excess of bromine was used to ensure complete reaction of $[Mn_2(CO)_{10}]$. Traces of $[Mn_2(CO)_{10}]$ are not uncommon in reactions of halocarbonyls with amine or imine derivatives, and often form when the carbonyl products are labile in solution. Once formed, the rate of combination of $[Mn(CO)_5]^{\cdot}$ radicals to form $[Mn_2(CO)_{10}]$ is high, according to Zhang *et al*[28] and other researchers such as Kidd *et al*[29] and Walker *et al*[30].

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Chapter Four

Studies of Mo-Arene Complexes with 1,2,3-Triphenylguanidine and Amidines

Introduction

This chapter presents the work involving substituted amidines and 1,2,3-triphenylguanidine as ligands in reactions with cycloheptatriene and cycloheptatrienyl carbonyl complexes of molybdenum. Guanidines and amidines have in principle a close chemical relationship which is discussed in Chapter One. This similarity is explored in the new ligand-coordination chemistry undertaken with cycloheptatriene, cycloheptatrienyl and cyclopentadienylmolybdenum systems.

A. Experimental Work

1. Reaction of Cycloheptatrienyltricarbonylmolybdenum(0) Tetrafluoroborate with Lithio-N,N'-di-*p*-tolylbenzamidine

$[Mo(\eta-C_7H_7)(CO)_3][BF_4]$ (0.24g/ 0.67 mmol) was suspended in dry THF(15ml). A Li[(*p*-tolyl)NC(Ph)N(*p*-tolyl)] (0.67 mmol) (see Appendix A) solution in THF(15ml) was transferred by syringe onto the metal complex at -40°C (acetone-CO_2 bath) under a nitrogen atmosphere. The mixture was stirred for 2.5 hours to complete the reaction. The THF was removed under reduced pressure until 2.0 ml of solvent remained. Petroleum ether (30 ml, 60-80^o) was added to the THF remaining in the flask, causing some white precipitate to separate. After filtration, the solution was kept in the freezer overnight and a yellow solid material separated. More THF was added to redissolve this material and the flask was returned to the freezer. The yellow solid material separated again. After filtration to remove the yellow material, the filtrate was stirred for two days at room temperature before putting it back in the freezer. From the filtrate an orange-yellow solid of $[Mo(C_7H_7DTB)(CO)_3]$ crystallised. Yield: 0.16g {45% based on $[Mo(\eta-C_7H_7)(CO)_3][BF_4]$}. Analyses - see Table 4.1

Instead of THF, a THF/monoglyme mixture worked well as the solvent and following the procedure above. Toluene, instead of petroleum ether, was also suitable as the solvent to extract the product. However, in THF/monoglyme the orange-yellow colour of the final solution was more intense than in THF alone. Using both conditions some red product appeared, but it was not enough to characterise by infrared spectroscopy or microanalysis.

2. Reaction of Cycloheptatrienyltricarbonylmolybdenum(0) Tetrafluoroborate with Lithio-N,N'-diphenylacetamidine in the Presence of TMEDA

N,N'-diphenylacetamidine (0.18g/ 0.9 mmol) was dissolved in dry monoglyme (20ml) together with TMEDA (0.20g/ 1.7 mmol) under a nitrogen atmosphere. The mixture was frozen in liquid nitrogen and butyl-lithium (0.056g/ 0.9 mmol-1.635 M in hexane sol.) was transferred by syringe into the flask. After warming and leaving the mixture stirring at room temperature for 1 hour the yellow solution was transferred by syringe onto $[Mo(\eta\text{-}C_7H_7)(CO)_3][BF_4]$ (0.30g/ 0.8 mmol) cooled to -196°C. The reactants were, firstly, allowed to reach -40°C for thirty minutes and, subsequently, the mixture was warmed to room temperature. The colour of the reaction was yellow at the beginning, passing through red-orange at room temperature. Finally, the solution became dark after stirring for a further hour. The monoglyme was removed *in vacuo* and dry degassed toluene was added to the powder residue at the bottom of the flask. From the resultant orange solution, which was subsequently filtered, some yellow-gold crystals of $[Mo(CO)_4TMEDA]$ appeared after cooling at -10°C. IR spectra and analytical data were consistent with data for an authentic sample prepared from $[Mo(CO)_6]$ and TMEDA. Yield: 0.16g {60% based on $[Mo(\eta\text{-}C_7H_7)(CO)_3][BF_4]$}. Analyses - see Table 4.1

3. Reaction of Cycloheptatrienyltricarbonylmolybdenum(0) Tetrafluoroborate with Lithio-N,N'-di-*p*-tolylformamidine

The same technique was used as described above in reaction 1. The differences were: (*i*) the reaction was carried out in monoglyme; (*ii*) when the solvent was removed under reduced pressure and degassed toluene was added to the orange gum to extract the product. The colour of the solution changed, passing through orange to black. Filtration through Celite 521 was undertaken, but the colour of the supernatant liquid remained black. The solution was left at room temperature for a long time and a black solid separated. Another filtration was done and an orange solution obtained. From the orange solution a red material in poor yield (< 10 mg) was separated after cooling at low temperature. The analyses and infrared spectrum (Table 4.2) of the red material identified it as $[Mo(C_7H_8)(CO)_3]^1$. [Found; C, 44.91; H, 2.61; N, 0.00. $C_{10}H_8MoO_3$ requires C, 45.79; H, 3.07; N, 0.00%]

4. Reaction of Cycloheptatrienyltricarbonylmolybdenum(0) Tetrafluoroborate with Lithio-N,N'-diphenylacetamidine

4.1. Using Monoglyme as Solvent.

A solution of Li[(PhNC(Me)NPh)] in dry monoglyme (20ml) was transferred by syringe to a suspension of $[Mo(\eta\text{-}C_7H_7)(CO)_3][BF_4]$ in monoglyme (20ml) at -40°C. After 24 hours stirring the solution, a yellow material separated. The mixture was allowed to warm to room temperature, then, after 1 hour, filtration yielded a yellow product, which was washed with petroleum ether (60-80°) in which it was insoluble. More degassed petroleum ether was added to the filtrate, and the solution was heated at 35-40°C in a water bath for approximately 1.5 hour. A white hygroscopic product, thought to be $LiBF_4$, separated after cooling the mixture at -20°C. Further cooling gave another dark material in the flask, but no further material was isolated. The yellow solid product, thought to be impure $[Mo(C_7H_7DPA)(CO)_3]$, changed colour from yellow to slightly brown when exposed to air. [Found:(For sample weighed in air) C, 50.92; H, 4.48; N, 4.04; Mo, 8.31; Li, 2.04. (For sample weighed in a nitrogen glove box) C, 50.70; H, 4.30; N, 3.92. $C_{24}H_{20}N_2MoO_3$ requires C, 60.12; H, 4.17; N, 5.84%].

4.2. Using THF as Solvent.

The same method described in reaction 1 for Li[(*p*-tolyl)NC(Ph)N(*p*-tolyl)] was used for Li[(PhNC(Me)NPh)] in THF. At the stage when approximately 2.0 ml of THF were left in the flask, and petroleum ether (60-80°) was added into the reaction solution, a black solid precipitated quickly.[Found: C, 43.23; H, 4.19; N, 3.00%]. From the filtrate a second solid product was obtained after cooling. [Found: C, 78.34; H, 6.56; N, 12.12%]. The data did not correspond to any reasonable complex, and it was concluded that a mixture of compounds had been isolated.

5. Reaction of Cycloheptatrienyltricarbonylmolybdenum(0) Tetrafluoroborate with Lithio-N,N'-diphenylacetamidine in a Solvent Mixture

A suspension of Li[(PhNC(Me)NPh)] (0.18g/ 0.9 mmol) in dry degassed diethyl ether (20ml) was transferred by syringe into a flask which contained another suspension of $[Mo(\eta\text{-}C_7H_7)(CO)_3][BF_4]$ (0.30g/ 0.8 mmol) in monoglyme (5.0ml) cooled to -196°C. The mixture was allowed to freeze and warm up three times before leaving at 0°C for a further 2 hours. Some more monoglyme was added to the flask to help the reactants to dissolve.

The solvent was removed *in vacuo* to leave an orange gum at the bottom of the flask. A solid separated after attempting an extraction with diethyl ether. After filtering the resulting mixture, the solvent was removed from the filtrate *in vacuo* again and replaced by dry, degassed toluene. Solid separated once more. Filtration of the toluene extract through Celite 521 was undertaken, then on cooling the filtrate, a pale yellow powder separated. No other material was obtained from the supernatant liquid, even on reducing the volume of the solution and keeping the flask at low temperature for long storage. The procedure was carried out under a nitrogen atmosphere. Analysis of the pale yellow product suggests the presence of a major impurity such as $LiBF_4$. [Found: C, 37.44; H, 3.09; N, 3.83. $C_{24}H_{20}N_2MoO_3$ requires C, 60.12; H, 4.17; N, 5.84%].

6. Reaction of Cycloheptatrienyltricarbonylmolybdenum(0) Tetrafluoroborate with Lithio-1,3-diphenyltriazene

A dark wine coloured solution of Li[(PhNNNPh)] (0.23g/ 1.5 mmol) in monoglyme was transferred by syringe to a suspension of $[Mo(\eta\text{-}C_7H_7)(CO)_3][BF_4]$ (0.53g/ 1.5 mmol) in monoglyme at -195°C. The mixture was left at low temperature overnight under a nitrogen atmosphere and an orange solution appeared after that time. The solvent was removed *in vacuo* and dry petroleum ether added to extract the orange gum. The whole extraction was done at low temperature and an orange solution obtained. After that the solution was filtered through Celite 521, and kept at low temperature. Yellow-gold crystals started to separate in the flask, but attempts at growing them to larger crystals for a further 24 hours led to decomposition of the material. The initial orange colour changed to dark green. A solution of the green material was very stable for a long time even at room temperature. The isolated dark green solid [Found: C, 56.19; H, 4.31; N, 9.34%] was also very stable at room temperature, but was not characterised fully. The IR spectrum in a Nujol mull indicated that the carbonyl and the cycloheptatrienyl groups had been lost from the starting material. The green solution was returned to the freezer for seven days and changed to a yellow colour, depositing a black solid.

7. Reaction of Chlorocyclopentadienyltricarbonylmolybdenum(II) with 1,2,3-Triphenylguanidine

Chlorocyclopentadienyltricarbonylmolybdenum(II) (0.68g/ 2.4 mmol) was dissolved in dry diethyl ether (10ml) under a nitrogen atmosphere. A solution of $TPGH_2$ (1.40g/ 4.9 mmol), in the same solvent (10ml), was added dropwise into the metal complex solution at 35-40°C. After complete addition of $TPGH_2$ the mixture was heated to the reflux temperature for a further hour. The mixture was allowed to cool to room temperature and stirring was continued for two days. A white material separated, and was removed by filtration through Celite 521. A red wine filtrate was obtained. The diethyl ether was removed *in vacuo* and a red solid, $[Mo(\eta\text{-}C_5H_5)(TPGH)(CO)_2]$, obtained, which was recrystallised from toluene/hexane mixtures. The complex was soluble in toluene, halogenated solvents and hexane, but the product decomposed when kept for a long time in solution even at low temperature. For analyses, and infrared spectrum see Table 4.1 and Table 4.2. Yield: 0.91g {75% based on $[Mo(\eta\text{-}C_5H_5)(CO)_3Cl]$}.

Table 4.1

Data for starting materials and for the molybdenum carbonyl complexes prepared

	Found(Calcd.)%			
Product Formula	C	H	N	mp.(°C)
DPAH	80.01 (79.96)	6.67 (6.71)	13.23 (13.32)	
DTBH	84.65 (83.65)	6.90 (6.71)	9.13 (9.33)	
$[Mo(CO)_4TMEDA]$	37.11 (37.05)	5.18 (4.97)	8.17 (8.64)	
$[Mo(C_7H_7DTB)(CO)_3]$	64.86 (65.27)	4.69 (4.59)	4.68 (4.91)	
$[Mo(\eta\text{-}C_5H_5)(TPGH)(CO)_2]$	60.44 (62.03)	4.81 (4.21)	7.93 (8.35)	121-124

B. Results and Discussion

1. The Tricarbonyl Complex [Mo(C_7H_7DTB)(CO)$_3$]

Lithio-N,N'-di-*p*-tolylbenzamidine reacts with [Mo(η-C_7H_7)(CO)$_3$][BF$_4$] in THF at -40°C under a nitrogen atmosphere in a molar ratio 1:1. The product is not air stable, and decomposition readily occurs, depending on the reaction conditions. No loss of carbon monoxide was observed during its synthesis.

The complex [Mo(C_7H_7DTB)(CO)$_3$] showed in its infrared spectrum (Table 4.2) three carbonyl vibrational frequencies in the range 1800 to 1950 cm^{-1} at 1925s, 1840s and 1800s cm^{-1} in a Nujol mull. These vibrational frequencies resembled those of the first starting material [Mo(C_7H_8)(CO)$_3$] though moved to lower frequency, which suggested that donation of electrons density from the new ligand system was increased compared with η^6-C_7H_8 to the [Mo(CO)$_3$] moiety. The infrared spectrum of the complex [Mo(C_7H_7DTB)(CO)$_3$] did not exhibit evidence for the presence of the [BF$_4$]$^-$ group as no ν(B-F) absorption was detected in the IR spectrum in the range 1100 to 1000 cm^{-1}.

The starting material [Mo(η-C_7H_7)(CO)$_3$][BF$_4$] reacts in different ways towards nucleophiles. The attack may occur at the ring, at the metal or at the carbon monoxide bonded to the metal. Attack at the metal occurs with nucleophiles such as PPh$_3$, PPh$_2$Me, AsPh$_3$ etc., and attack at the ring with nucleophiles such as MeO$^-$, I$^-$ and CN$^-$.

The similarity between the ν(CO) stretching frequencies of the complex [Mo(C_7H_7DTB)(CO)$_3$] with those of the starting material

$[Mo(C_7H_8)(CO)_3]$ indicates that N,N'-di-*p*-tolylbenzamidino attack has occurred at the ring.

There are two possible positions for the nucleophile to attack the ring and act as a ring substituent, at the axial position or *exo* and at the equatorial position or *endo*. Nucleophiles in general prefer the *exo* position since steric effects are minimal. Figure 4.1 shows possible structures for the complex $[Mo(C_7H_7DTB)(CO)_3]$.

Table 4.2

Infrared absorptions of the molybdenum complexes studied

Product Formula	Solvent	$\nu(CO)/cm^{-1}$	$\nu(C\text{-}H)/cm^{-1}$	$\nu(B\text{-}F)/cm^{-1}$
$[Mo(C_7H_8)CO)_3]$	Nujol	1970s; 1910s; 1860s	3040w	
$[Mo(\eta\text{-}C_7H_7)(CO)_3][BF_4]$	Nujol	2076s; 2027s; 2001s	3080w	1100m;1050s; 1035s
$[Mo(CO)_4TMEDA]$	CH_2Cl_2	2020s; 1890s; 1900s# 1830s		
	Nujol	2010s; 1875s‡; 1820s‡		
$[Mo(C_7H_7DTB)(CO)_3]$	Nujol	1925s; 1840s; 1800s	3035w	
$[Mo(Cl)(\eta\text{-}C_5H_5)(CO)_3]$	Nujol	2040s, 1985s; 1940s		
	CCl_4	2060s, 1990s; 1970s		
$[Mo(\eta\text{-}C_5H_5)(TPGH)(CO)_2]$	Nujol	1935s; 1830s	3380w†	
	Et_2O	1915s; 1857s		

†- This absorption corresponds to the ν(N-H) from the 1,2,3-triphenylguanidino ligand. ‡ -broad. # -shoulder

The ^1H NMR spectrum for the complex $[Mo(C_7H_7DTB)(CO)_3]$ exhibited a doublet of doublets at 5.2 ppm, a doublet of triplets at 6.2 ppm, a triplet at 6.7 ppm, another slightly broad peak at 7.1 ppm and a multiplet centred at 7.25 ppm. The spectrum also exhibited two peaks at low frequency [1H,s, at 2.0 ppm, and 1H,s, at 2.3 ppm] assigned to the *exo* and *endo* hydrogens respectively by analogy to the *exo* and *endo* hydrogens of the η^4-cycloheptatriene cobalt complex, $[Co(C_7H_8)(PMe_3)_3][BPh_4]$, reported by Carvalho *et al*[2]. Another intense peak at 2.2 ppm is assigned to the methyl groups of DTB. Pauson *et al*[3] have reported the characterisation of substituted η^4-cycloheptatriene complexes of chromium which were envisaged as having the metal bonded to four of the carbon atoms of the cycloheptatriene. However, the peaks assigned to the *exo* and *endo* hydrogens of the complexes studied by Pauson occur at 2.0 ppm and about 3.0 ppm respectively, in contrast with the results found in this work for the molybdenum complex. Figure 4.2 shows structures for $[Mo(C_7H_7DTB)(CO)_3]$ consistent with the ^1H NMR data.

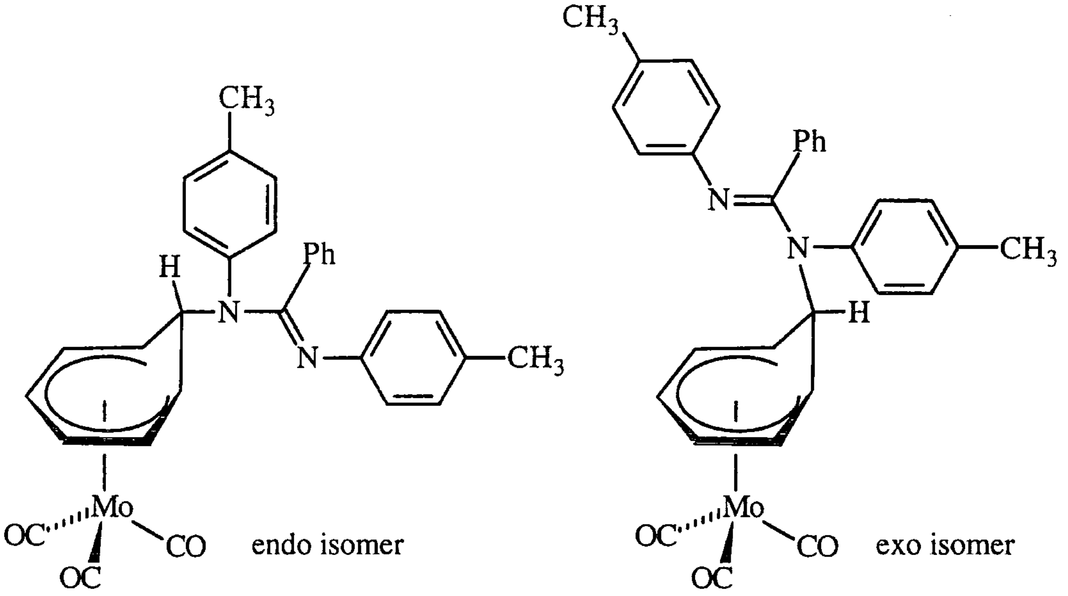


Figure 4.1 Possible structures for $[Mo(C_7H_7DTB)(CO)_3]$

Structure **II** remains the most likely structure as **I** requires hydrogen migration. However, the two peaks found for the complex, which are assigned to the *endo* and *exo* protons by reference to the spectrum of $[Mo(C_7H_8)(CO)_3]$ [*exo* 1H,d, at 2.4 ppm, and *endo* 1H,m, at 3.01 ppm] suggests strongly the structure **I**. The structure of $[Co(C_7H_8)(PMe_3)_3][BPh_4]$, obtained by X-ray crystallography[2], is similar to structure **I**, and is supportive of structure **I** for the $[Mo(C_7H_7DTB)(CO)_3]$ complex because the ^1H NMR spectrum of $[Co(C_7H_8)(PMe_3)_3][BPh_4]$ shows two peaks [1H,br, at 2.0 ppm, and 1H,s, at 2.2 ppm] assigned to *exo* and *endo* hydrogens respectively of the CH_2 group. These chemical shifts are close to the ones found for the complex $[Mo(C_7H_7DTB)(CO)_3]$.

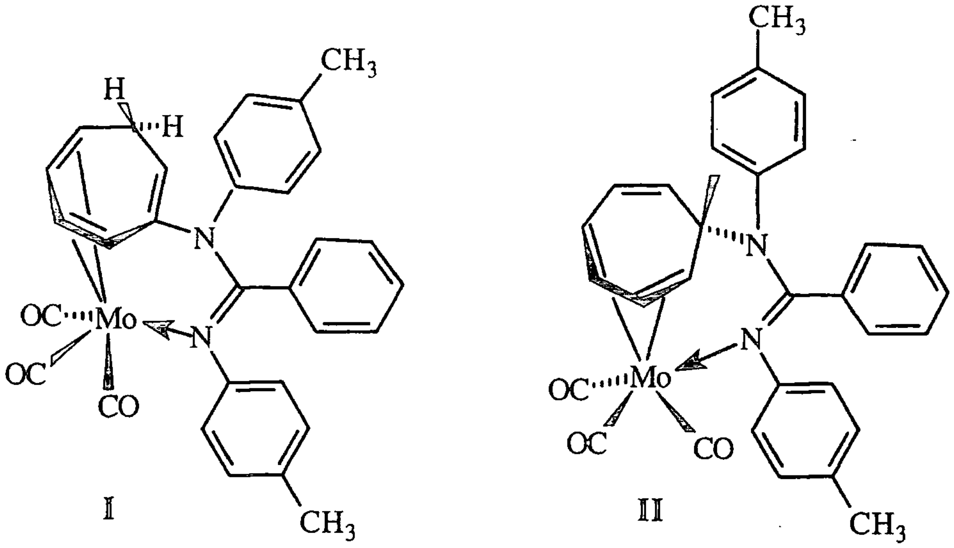


Figure 4.2 Alternative structures for the complex $[Mo(C_7H_7DTB)(CO)_3]$

2. The Tetracarbonyl Complex $[Mo(CO)_4TMEDA]$

This complex was obtained as the product when the reaction of $[Mo(\eta\text{-}C_7H_7)(CO)_3][BF_4]$ with lithio-N,N'-diphenylacetamidine was attempted in the presence of TMEDA in monoglyme at room temperature. The material is yellow-gold and indefinitely air stable. The TMEDA is a four electron chelate donor ligand towards the metal, and the metal satisfies the 18-electron rule. The complex has a *cis* geometry.

The infrared spectrum of solids isolated from the reaction mixture did not show any evidence for the presence of the PhNC(Me)NPh ligand. Important vibrations, such as ν(C-H) stretching, and ν(C=C) stretching for the phenyl groups were missed in the range 3000 to 3060 cm^{-1} and 1600 to 1500 cm^{-1} respectively. No evidence for the ν(C-H) stretching for the cycloheptatrienyl groups were found.

According to Cotton *et al*[4] complexes of the type $[M(CO)_4L_2]$ (M= Cr, Mo or W; L= Ph_3P) should have one doubly degenerate E_u carbonyl vibrational mode active in the infrared if it is a *trans* complex and four active infrared absorptions in the case of a *cis* complex (see Appendix B). The infrared of [Mo(CO)$_4$TMEDA] was identical to that of an authentic sample[5] and consistent with a *cis* complex, though only three vibrational frequencies of carbon monoxide were detected in a Nujol mull at 2010, 1875 and 1820 cm^{-1} (Table 4.2). It was very difficult to identify four carbonyl absorptions due to the broad absorption in the range of 1900 to 2000 cm^{-1}. However, in a solution of dichloromethane, an additional shoulder appeared about 1900 cm^{-1} (see Table 4.2). Similar tetracarbonyl molybdenum complexes have been characterised by infrared and Raman spectroscopy[6].

The ^{1}H NMR spectrum of [Mo(CO)$_4$TMEDA] exhibited two singlets. The singlet peak at 2.8 ppm is assigned to the four CH$_3$ groups attached to the nitrogen atoms of TMEDA due to its intensity which was correlated to twelve hydrogen atoms, and another singlet (relative intensity, 4) at 2.7 ppm which is assigned to the backbone CH$_2$ groups of the ligand. The spectrum is very simple due to the high symmetry of [Mo(CO)$_4$TMEDA]. Again no peaks at high frequency in the region 7.0 to 9.0 ppm, typical for aromatic rings were observed.

3. The Carbonyl Complexes from the Reaction of [Mo(η-C$_7$H$_7$)(CO)$_3$]$^+$ with Lithio-N,N'-diphenylacetamidine, Lithio-N,N'-di-*p*-tolylformamidine and Lithio-1,3-diphenyltriazene

Lithio-N,N'-diphenylacetamidine and lithio-N,N'-di-*p*-tolylformamidine react with [Mo(η-C$_7$H$_7$)(CO)$_3$][BF$_4$] under various reaction conditions leading to products which have uncertain composition. In the case of lithio-1,3-diphenyltriazene a dark green solid was produced. However, in the infrared spectrum, obtained using a Nujol mull, no ν(CO) stretching frequencies, or absorptions due to the η-C_7H_7 group, were detected. Thus complete decomposition had occurred.

The yellow material synthesised from lithio-N,N'-diphenylacetamidine, exhibited three broad ν(CO) bands in its infrared spectrum at 1985, 1925 and 1800 cm^{-1} (Nujol mull) and a weak band at 2035 cm^{-1}. Two shoulders occurred at 1840 and 1910 cm^{-1}. The absorptions assigned to the ligand were also very weak throughout the range of 1600 to 400 cm^{-1}. The spectrum did not show clear evidence of bands which could be assigned to ν(B-F) as occurs for $[Mo(\eta\text{-}C_7H_7)(CO)_3][BF_4]$ in the region of 1000-1100 cm^{-1}. Unfortunately the product complex was not identified as the analytical data did not correspond to any realistic formulation. However, the infrared data clearly show that the complex has the $[Mo(CO)_3]$ moiety containing a strongly electron donating group, as the carbonyl absorptions had shifted to low frequency. Indeed, noticeable similarities occur with the ν(CO) data for $[Mo(C_7H_7DTB)(CO)_3]$ (Table 4.2), and it is conceivable that the DPA complex is also of this type.

4. The Dicarbonyl Complex $[Mo(\eta\text{-}C_5H_5)(TPGH)(CO)_2]$

Chlorocyclopentadienyltricarbonylmolybdenum(II) reacts with 1,2,3-triphenylguanidine in a molar ratio 1:1 at 30°C in diethyl ether. The red product $[Mo(\eta\text{-}C_5H_5)(TPGH)(CO)_2]$ is not air stable in the solid state, must be stored under a nitrogen atmosphere, and decomposes under a nitrogen atmosphere in hydrocarbon solvents irrespective of the temperature. 1,2,3-Triphenylguanidine hydrochloride was observed as a by-product of the preparative reaction, and the introduction of the 1,2,3-triphenylguanidino-group led to the loss of one molecule of carbon monoxide. The guanidino-group acts as a three electron donor ligand to satisfy the 18-electron rule.

The infrared spectrum of the complex [Mo(η-C_5H_5)(TPGH)$(CO)_2$] exhibited two strong carbonyl absorptions in the range of 1800 to 1950 cm^{-1} at 1935 and 1830 cm^{-1}. The weak vibrational band centred at 3380 cm^{-1} was assigned to the ν(N-H) stretching vibration which occurs in the same range as the ν(N-H) for the non-bonded nitrogen of $TPGH_2$ in other coordination complexes. The data are consistent with TPGH acting as a 3-electron chelate donor to the molybdenum atom. A possible structure for this complex can be envisaged (see Figure 4.3) by analogy with work of Inglis *et al*[7] and Gaylani *et al*[8] on cyclopentadienyl complexes of general formulation [Mo(η-C_5H_5)(L)$(CO)_2$] (L= amidino).

The ^1H NMR spectrum for the complex [Mo(η-C_5H_5)(TPGH)$(CO)_2$] exhibited a multiplet centred at 6.91 ppm assigned to the phenyl hydrogens of the TPGH group and a single peak (at 5.53 ppm) which is assigned to the hydrogens of the cyclopentadienyl group - a single peak is also observed in the spectrum of the starting material, [Mo(Cl)(η-C_5H_5)$(CO)_3$]. Deuterated chloroform (+1%TMS) was used as the solvent for the NMR spectra. The N-H proton signal was not detected, possibly because of broadness.

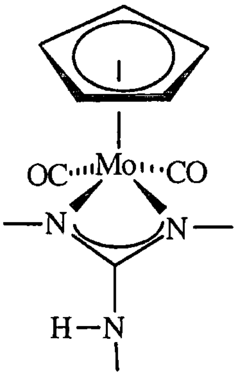


Figure 4.3 Proposed structure of [Mo(η-C_5H_5)(TPGH)$(CO)_2$]

5. Other Aspects Involving the Molybdenum Complexes

Both the starting materials in this work have an aryl ligand bonded to the metal through its π molecular orbitals. $[Mo(\eta\text{-}C_7H_7)(CO)_3][BF_4]$ and $[Mo(Cl)(\eta\text{-}C_5H_5)(CO)_3]$ (see Table 4.3) exhibit an increase in the average ν(CO) compared with $[Mo(C_7H_8)(CO)_3]$, consistent with an increase in the net positive charge on the metal. Structural studies have shown a short distance between the metal and the cycloheptatrienyl ring in the complex $[Mo(\eta\text{-}C_7H_7)(CO)_3][BF_4]$[9]. The preparation of this complex involves a hydride abstraction from the cycloheptatriene ring. The induced positive charge on the ring is partially transferred to the metal, but the cycloheptatrienyl is considered to retain a partial positive charge[10].

Table 4.3

Carbonyl stretching frequencies for molybdenum tricarbonyl complexes

Product Formula	Solvent	ν(CO)/cm^{-1}	Average ν(CO)
$[Mo(C_7H_8)(CO)_3]$	Nujol	1970s; 1910s; 1860s	1913
$[Mo(C_7H_7DTB)(CO)_3]$	Nujol	1925s; 1840s; 1800s	1855
$[Mo(\eta\text{-}C_7H_7)(CO)_3][BF_4]$	Nujol	2076s; 2027s; 2001s	2034
$[Mo(Cl)(\eta\text{-}C_5H_5)(CO)_3]$	CCl_4	2060s; 1990s; 1970s	2006

Nucleophilic addition[11] and carbonyl substitution reactions by Lewis bases have been studied in organometallics such as $[M(\eta\text{-}C_7H_7)(CO)_3]^+$ (M= Mo, W). The conditions of the reaction seem to be very important in obtaining a product with the nucleophile attached either to the ring or to the metal. The amounts of the ligand and the strength of the nucleophile also contribute to the type of product formed. The complexes $[M(C_7H_7P(Pr^i)_3)(CO)_3][BF_4]$ (M= Mo,W), for example, were prepared at low temperature in a molar ratio 1:1. However, at room temperature the product isolated had the formulation of $[M(CO)_3L_3]$, (L= $P(Pr^i)_3$).

The three carbonyl stretching frequencies for the complex with one phosphine attached to the ring occurred at 1880, 1925 and 1980 cm^{-1} (M= Mo) and at 1860, 1920 and 2000 cm^{-1} (M= W). According to Salzer *et al*[11] hard bases, neutral or anionic, tend to react at the carbocyclic ring and *soft* bases at the metal by CO substitution under mild conditions. Increase of temperature favours the displacement of the carbocyclic ring.

Monosubstituted complexes of the type $[Mo(\eta\text{-}C_7H_7)(CO)_2L][PF_6]$ (L=$P(OPh)_3$, PPh_3, PPh_2Me, $PPhMe_2$, $AsPh_3$, $SbPh_3$) have been reported by Isaacs *et al*[12] using conditions to favour the attack by the nucleophile at the metal. All the dicarbonyl monosubstituted complexes reported by Isaacs *et al* were prepared from $[Mo(\eta\text{-}C_7H_7)(CO)_3]^+$ in refluxing ethanol. The intermediates were subsequently reduced by reaction with $NaBH_4$ to afford $[Mo(C_7H_8)(CO)_2L]$. An interesting observation made was that the solvent plays a critical part in these reactions. When 98% ethanol (and *ca* 2% benzene) was used, yields were minimal in some reactions and zero in others. The presence of water (from 95% ethanol) was necessary for most of the reactions. Alkyl lithium, in tetrahydrofuran or diethyl ether, reacted with the dicarbonyl derivatives, $[Mo(\eta\text{-}C_7H_7)(CO)_2L][PF_6]$, affording complexes of formula $[Mo(C_7H_7R)(CO)_2L]$ (R=Me, L=phosphines). On the other hand, the reaction with $[Mo(\eta\text{-}C_7H_7)(CO)_3]^+$ and methyl lithium resulted in decomposition. The products with a methyl group attached to the ring exhibit ^1H NMR chemical shift for the ring protons similar to values for $[Mo(C_7H_8)(CO)_3]$, with the *endo* proton at 2.5 ppm. Figure 4.4 shows the possible paths for nucleophilic attack, either at the cycloheptatrienyl ring or at the metal.

Powell *et al*[13] have reported the kinetics of the nucleophilic attack of sodium methoxide in methanol at -15°C on the cycloheptatrienyl ring of $[M(\eta\text{-}C_7H_7)(CO)_3][BF_4]$ (M=Cr, Mo, W). The kinetics show that reaction at the ring occurs in two steps. The fast initial reaction produces two species (**III** and **IV**, Figure 4.5) which in the case of chromium are not detected. The slower step leads to the irreversible formation of the 7-*exo*-methoxycycloheptatriene product (V). The species were proposed to be an ionic pair (III) with the charge centred on the metal, or a carboxymethyl derivative (IV), arising from the attack of methoxide on the CO group.

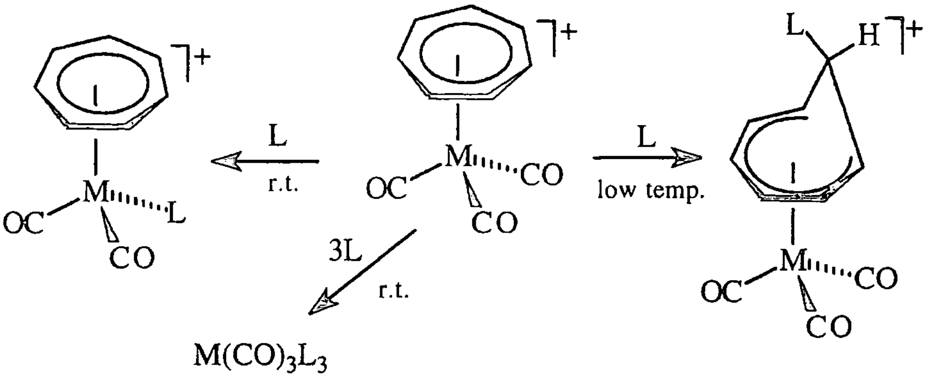


Figure 4.4 Reactions involving $[M(\eta\text{-}C_7H_7)(CO)_3][BF_4]$ (M=Mo,W). L=phosphines

The rate constants κ_1 and κ_{-1} were large compared with κ_2 in the case of molybdenum and tungsten. It was not possible to measure the rate constant for chromium according to Powell *et al*[13] because the fast initial step merged into the second slower step.

The same cationic starting materials $[M(\eta\text{-}C_7H_7)(CO)_3]^+$ reacted with iodide[14] ions in acetone at 0°C to produce a dicarbonyl derivative formulated as $[M(I)(\eta\text{-}C_7H_7)(CO)_2]$ (M=Mo, W). This reaction also proceeds in two steps where the fast initial step, according to the author, favoured the formation of two intermediates, the ion pair $[M(\eta\text{-}C_7H_7)(CO)_3]I$, and $[M(C_7H_7I)(CO)_3]$. The slower step consisted of the replacement of CO groups by the acetone molecules and subsequently acetone by the iodide to produce the dicarbonyl product.

Addition of hydride to the cycloheptatrienyl ring was reported by Faller *et al*[15]. The ratio of *endo* and *exo* addition was found to be 28:72 when the deuterated complex, $[Mo(C_7H_7D)(CO)_3]$, was prepared from borodeuteride. When borodeuteride was replaced by cyanoborodeuteride an even lower specificity was found, 40:60. The proposed mechanism of addition involves the attack of the hydride at a carbonyl group first, followed by a second step which involves the hydride migration onto the ring. The chemical shifts for the *endo* and *exo* protons occurred at 3.1 ppm and 2.2 ppm respectively for chromium complexes formulated as $[Cr(C_7H_7R)(CO)_3]$ (R=H, Me, CN, Ph).

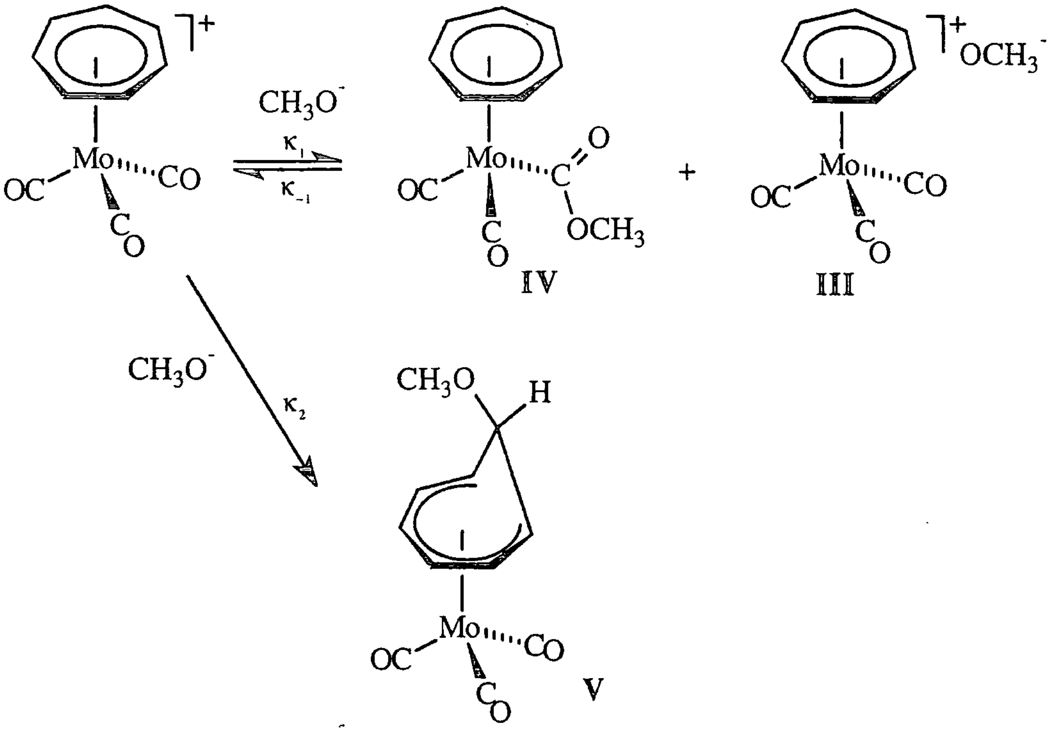


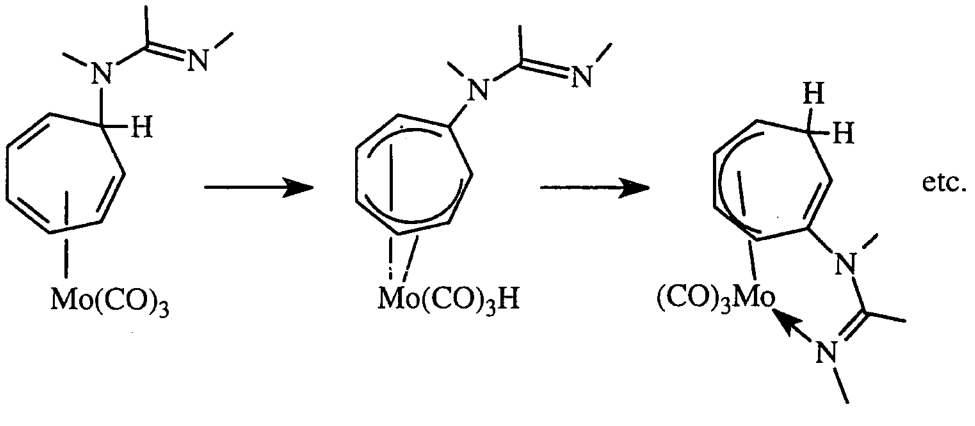
Figure 4.5 Reaction scheme for the formation of $[Mo(C_7H_7OMe)(CO)_3]$ at low temperature

The nitrogen ligands in the complexes $[Mo(C_7H_7DTB)(CO)_3]$ and $[Mo(\eta\text{-}C_5H_5)(L)(CO)_2]$ (L = TPGH), prepared in this work, seem to have strong σ-donor effects as measured by the shift of ν(CO) frequencies towards low frequency compared with those of the starting complexes (see Table 4.2). Unfortunately it was not possible to study the complex $[Mo(C_7H_7DTB)(CO)_3]$ by X-ray crystallography because the crystallisation of the product did not give suitable crystals for this purpose. The ν(CO) data available for this complex suggests the structure **I** or **II** shown in Figure 4.2. Recently Hadley *et al*[16] reported the structures of a homologous series of cycloheptatriene complexes of chromium, tungsten and molybdenum. The X-ray diffraction studies showed that the hydrogen atoms vicinal to the CH_2 group of the cycloheptatriene were not coplanar with the other ring hydrogen atoms. The bond angles involving the hydrogens bonded to the carbon C9 and C4 (Figure 4.6) and the chromium are lower than the angles for other ring hydrogens, and result as a consequence of the non-planar position of the CH_2 group of the cycloheptatriene. Replacing one of these CH_2 hydrogen atoms by a nitrogen of DTB, can be envisaged to give the structures presented in Figure 4.1.

In the present work involving amidines and a guanidine, attachment of the nitrogen to the ring is thought to precede coordination of the second nitrogen to the metal. The latter process will result in the ring changing its mode of attachment to the metal (see scheme below). The ring formally becomes tetrahapto-bonded. No evidence of fluxional changes relating to the bonding of the ring to the metal was observed.

There are two ways that the metal can receive the electronic density of the ligand to shift the average ν(CO) in the direction of low frequency. One is direct bonding between the molybdenum and the nitrogen atom of the nucleophile DTB; the other is through modification to the π-donor properties of the ring. The former is thought to occur because of the extensive lowering of the average ν(CO) stretching frequencies (Table 4.3).

The attack of the nucleophile DTB at the planar cycloheptatrienyl ring leads to an N-C bond, as shown in Figure 4.1. The *exo* isomer is the preferred position for nucleophiles in general. According to the work of Hadley *et al*[16], the cycloheptatriene forms a pseudo ring between the six coplanar carbon atoms if the distance between the carbon C4 and C9 (Figure 4.6) is <2.1Å. The complexes $[M(C_7H_8)(CO)_3]$ (M= Cr, Mo, W) reported by Hadley *et al*[16] had the distance between these carbons >2.3Å presumably due to the size of the metal. Also a CO group is placed below the group CH_2 as shown by the X-ray crystallography for the chromium complex (see Figure 4.6). If a bulky ligand such as DTB is bonded to the cycloheptatriene at the *exo*-methano carbon (Figure 4.1, *exo*-isomer), a steric interaction between the boat conformation and the phenyl groups of this ligand may occur. If the DTB is bonded at the *endo*-methano carbon (Figure 4.1, *endo*-isomer), the lone pair at a nitrogen atom may bind to the metal. The carbon monoxide placed below the >CH-DTB group will provide steric difficulty for the attack of a DTB nitrogen atom towards the metal since these groups are coplanar, but if the proton from >CH-DTB migrates to the vicinal carbon, a gap will open and the attack of DTB towards the metal may occur. Therefore the structure **I** (Figure 4.2) is a very realistic possibility and is consistent with the data. The nitrogen atom from DTB would not then be coplanar with the hydrogens of the cycloheptatriene ring. In addition, structure **I** in Figure 4.2 also follows the 18-electron rule. Models show that the nitrogen group in either the *endo* or *exo*-positions (Figure 4.1) will be too distant from the metal centre for a pendant nitrogen to coordinate strongly to the metal as shown in **II**, Figure 4.2. However, isomerization of the complex from the *exo*-isomer, the normal product of nucleophilic attack at the ring, to **I**, Figure 4.2, will provide stability to the chelate system, by relieving the ring strain. This process could be achieved via a π-allyl-intermediate involving oxidation of molybdenum(0) to molybdenum(II), a well established mechanism of isomerization particularly favoured by iron carbonyls. This is illustrated below.



The complex [Mo(η-C_5H_5)(TPGH)$(CO)_2$] most certainly has the TPGH bonded directly to the metal because substitution on the cyclopentadienyl ring is unlikely under the conditions used. Electrophilic attack on the ring is the usual reaction pathway to produce substitution on the cyclopentadienyl ring, not nucleophilic attack. The difference of about 24 cm^{-1} found for the lowest frequency carbonyl bands of the complex [Mo(η-C_5H_5)(TPGH)$(CO)_2$] in Nujol mull and in diethyl ether suggests solvent effects or different structures in the solid state and in solution. In fact the complex was not stable in hydrocarbon solution at low temperature or at room temperature under a nitrogen atmosphere. A very slow decomposition also occurred in diethyl ether. The 18-electron rule holds for the complex shown in Figure 4.3, and also for a dimer having bridging guanidino-groups.

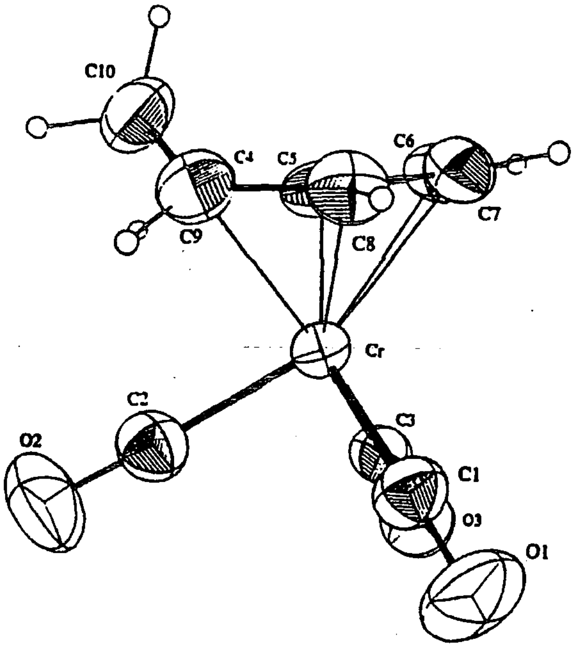


Figure 4.6 ORTEP drawing of [Cr(η^6-C_7H_8)$(CO)_3$] showing the flattened boat conformation of the cycloheptatriene (Reference 16).

Interestingly, during the preparation of [Mo(η-C_5H_5)(TPGH)$(CO)_2$] in diethyl ether, precipitation of the $TPGH_2$.HCl occurred slightly above room temperature. Coordination of $TPGH_2$ to molybdenum increases the acidity of a N-H hydrogen to such an extent that proton loss occurs. A second molecule of $TPGH_2$ acts as a proton base. A similar reaction has been reported by Gaylani *et al*[8] using N,N'-diphenylacetamidine as the ligand. When reactions were carried out at higher temperatures, the brown product formed was shown by IR spectroscopy to be a non-carbonyl derivative, and was not studied further.

Several procedures used in the current work, involving the synthesis of amidine derivatives, such as LiDPT, LiDPA and LiDTF, were developed following the ideas of other researchers[13,14,17-23]. One important finding in this work was the presence of traces of lithium in the products. Attempts were made to remove possible lithium containing impurities, and involved changing the solvent, the use of a lithium chelate ligand and the use of a mixture of solvents, but such methods did not provide always a means of removing all traces of lithium. Attempts were also made to increase the reactivity of the lithium reagent using TMEDA and aid the removal of lithium by increasing the solubility of the lithium tetrafluoroborate by-product in solvent mixtures[17,24]. In the present work, the use of TMEDA is shown to make the reaction more complex, because the complex $[Mo(CO)_4TMEDA]$ was separated from the reaction as a by-product.

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Chapter Five

Studies of the Hexacarbonyls of Chromium, Molybdenum and Tungsten with 1,2,3-Triphenylguanidine

Introduction

Amidines and lithio-amidines react with metal carbonyls such as $[M(CO)_6]$ (Cr, Mo or W) to form dimeric complexes such as $[M(amidino)_2]_2$. Such reactions and the metal complexes formed, involving a variety of substituted amidines as ligands, are discussed in Chapter One.

Several reactions of $TPGH_2$ and LiTPGH with the hexacarbonyls of chromium, molybdenum and tungsten, and tungsten tetrachloride are the subject of study in this chapter. All the reactions were performed with the system exposed to the air, to permit oxidation of the metal(0) to metal(II), except when tungsten tetrachloride was the starting material.

A. Experimental Work

1. Reaction of Hexacarbonylchromium(0) with 1,2,3-Triphenylguanidine

Hexacarbonylchromium(0) (0.71g / 3.21 mmol) was mixed with dried petroleum ether (40 ml,100-120°) and $TPGH_2$ (1.88g / 6.55 mmol) added. The mixture was heated at the reflux temperature in air for 48 hours. A dark green material separated, and was removed by filtration in the air and washed with dried hexane. The dark green solid is soluble in chlorinated solvents, and slightly soluble in diethyl ether. Analytical data are recorded in the table below. Yield: 0.76g {26% of crude product based on $[Cr(CO)_6]$}.

Microanalyses of the dark green material

		% Found		
Reaction Product	Recrystallisation Solvent	C	H	N
Crude material		73.05	6.85	11.17
First recrystallisation	$Et_2O/CHCl_3$	76.10	5.79	13.38
Second recrystallisation	$CHCl_3$	66.81	4.76	11.83
$[Cr_2(TPGH)_4]$ requires		73.07	5.12	13.46
$[Cr(TPGH)_3]$ requires		75.16	5.27	13.84

Note: The second recrystallisation was attempted after the material had been exposed to air in the solid state for a long period. The sample was dissolved in chloroform, the solution filtered and the solvent removed *in vacuo*. The IR spectrum of the sample in carbon tetrachloride did not exhibit bands that could be assigned to $CHCl_3$ [ν(C-H) at 3000 cm^{-1}] as a contaminant.

2. Reaction of Hexacarbonylmolybdenum(0) with 1,2,3-Triphenylguanidine

Hexacarbonylmolybdenum(0) (0.51g/ 1.93 mmol) was mixed with dried petroleum ether (40ml,100-120°) and $TPGH_2$ (1.13g / 3.93 mmol). Air was bubbled through the system which was kept at the reflux temperature and open to the air for 24 hours. A dark brown material separated, and was removed by filtration in the air and washed with dried hexane. The dark brown solid gave a red solution in chlorinated solvents, aromatic hydrocarbons, methanol and acetonitrile. It was slightly soluble in diethyl ether. Recrystallisation was undertaken in chloroform solution. Analytical data are recorded in the table below. Yield: 0.21g {29% of the crude product based on $[Mo(CO)_6]$}.

Microanalyses of the brown material

		% Found		
Reaction Product	Recrystallisation Solvent	C	H	N
Crude material		63.97	4.57	12.19
First recrystallisation	$CHCl_3$	60.70	4.72	10.64
$[Mo_2(TPGH)_4]$ requires		68.36	4.79	12.59

Note: The first recrystallisation was attempted after a long exposure of the solid material to air. The sample was dissolved in chloroform, the solution filtered and the solvent removed *in vacuo.* The IR spectrum of the sample in carbon tetrachloride did not exhibit bands that could be assigned to $CHCl_3$ [v(C-H) at 3000 cm^{-1}] as a contaminant.

3. Reaction of Hexacarbonylmolybdenum(0) with 1,2,3-Triphenylguanidine in hot benzene solution

Hexacarbonylmolybdenum(0) (0.51g / 1.93 mmol) was dissolved in hot benzene (10 ml). A benzene solution of $TPGH_2$ (1.13g / 3.93 mmol) was then added, drop by drop, into the metal carbonyl solution at 63°C. The colour of the solution changed in 30 min. from colourless to dark brown. The temperature was allowed to reach the benzene boiling point and the system was left opened to air under reflux for 24 hours. The dark brown yellow colour persisted after that time. The solvent was removed under vacuum. The residual brown powder was extracted with dried hexane, producing a yellow solution and a brown powder residue. Both materials were soluble in aromatic hydrocarbons. Yellow-gold crystals of $[Mo(CO)_4(TPGH_2)]$ were obtained from the yellow hexane solution after cooling to 6°C. Yield: 95mg {10% based on $[Mo(CO)_6]$}. Analyses - see Table 5.1

The brown powder was identified by microanalyses and IR spectroscopy as the same brown powder as that produced in the previous reaction (section A3) using petroleum ether (100-120°) as the reaction medium.

4. Reaction of Hexacarbonyltungsten(0) with 1,2,3-Triphenylguanidine

Hexacarbonyltungsten(0) (0.67g/ 1.93 mmol) was mixed with dried petroleum ether (40 ml,100-120°) and $TPGH_2$ (1.12g / 3.93 mmol). The system was heated at the reflux temperature in air for 24 hours. The colour of the mixture became initially green, passing through yellow, and finally became red after 21 hours of refluxing. The yellow-orange solid which separated in the flask was removed by filtration and washed with hexane. During the hot filtration the colour of the solution changed from red to yellow-orange. The filtrate was heated again for a further 24 hours. The colour of the reaction mixture became red again and a red solid separated in the flask. The red solid was removed by filtration, washed with hexane and recrystallised in chloroform. Analytical data are recorded in the table below. Yield of the yellow orange solid: 0.27g{11% based on $[W(CO)_6]$} and for the red solid < 50mg.

Microanalyses of the red and yellow-orange materials†

		% Found		
Reaction Product	Recrystallisation Solvent	C	H	N
Yellow orange		70.33	5.33	12.37
Red material	$CHCl_3$	36.51	3.05	6.01
$[W_2(TPGH)_4]$ requires		60.31	4.23	11.11
$[W(TPGH)_4]$ requires		68.72	4.81	12.65

† - These Materials will be discussed further in section B3

5. Reaction of Tetrachlorotungsten(IV) with Lithio-1,2,3-triphenylguanidine

Tetrachlorotungsten(IV) (0.75g / 2.30 mmol) was put into a flask under a nitrogen atmosphere. The flask was transferred from the glove box to the vacuum line where it was connected again to a nitrogen atmosphere. A freshly prepared yellow THF solution of LiTPGH (6.50 mmol), having been stirred at room temperature for 30 min, was added, drop by drop, into the flask. During the addition of the LiTPGH, the flask was kept at -196°C. The mixture was then allowed to warm to room temperature and left overnight. After this time, the THF was removed *in vacuo* and dry hexane was used to extract the product. A suspension of a green material was obtained in hexane and the mixture was filtered in air, the pale yellow filtrate being discarded. A sample of the green material was dissolved in chloroform and a white material separated after a few minutes at room temperature. A filtration was done through a microfilter and a red solution obtained. Two materials were obtained after recrystallisation at low temperature, a pale orange solid and dark crystals of WCl_4.

Microanalyses of the material

Reaction Product	Recrystallisation Solvent	% Found C	H	N
Green crude material		53.22	4.50	9.84
Pale orange solid	$CHCl_3$	65.91	5.93	12.23
$[W_2(TPGH)_4]$		60.31	4.23	11.11
$[W(TPGH)_3]$		65.64	4.61	12.09

Table 5.1 shows some possibilities of molecular formula for the products synthesised in reactions 1-4 consistent with the analytical data found.

Table 5.1

Molecular formula approximation for the products obtained in this work

Reaction	Product Formula	Colour	Found(Calcd.)% C	H	N
3	$[Mo(CO)_4(TPGH_2)]$	Yellow-gold	55.91 (55.88)	3.36 (3.26)	8.05 (8.50)
4	$[W(TPGH)_4]$	Yellow-orange	70.33 (68.72)	5.33 (4.81)	12.37 (12.65)
5	$[W(TPGH)_3]$	Pale orange	65.91 (65.64)	5.93 (4.61)	12.23 (12.09)
1	$[Cr(TPGH)_3]$	Dark green	76.10 (75.16)	5.79 (5.27)	13.38 (13.84)
1	"[Cr(TPGH)]"	Dark green	66.81 (67.45)	4.76 (4.73)	11.83 (12.42)
2	"[Mo(TPGH)]"	Brown	60.70 (59.69)	4.72 (4.22)	10.64 (10.99)

B. Results and Discussion

1. The Triphenylguanidine/Chromium Complexes

Hexacarbonylchromium(0) reacts with 1,2,3-triphenylguanidine in petroleum ether at 110°C to form [Cr(TPGH)$_3$]. The reaction does not follow the molar ratio 1:2 as expected. The oxidation of chromium goes further than the oxidation state +2 and leads to the formation of a green compound, the colour of which is typical of chromium(III) compounds. This green compound decomposes when exposed to air for a long period leading to a material corresponding to the formulation "[Cr(TPGH)]". The complex [Cr(TPGH)$_3$] is not ionic, and the most likely structure will have three TPGH ligands chelating to the metal. The chromium centre will be hexacoordinated by the nitrogen atoms of the ligands.

The complexes obtained in this work did not exhibit any absorptions that could be assigned to ν(CO) stretches. All CO molecules were lost with the introduction of the ligand. The infrared of the crude chromium product exhibited two bands assigned to ν(N-H) at 3379 and 3352 cm^{-1}, which occurred at 3372 and 3285 cm^{-1} (see Table 5.2) after recrystallisation in chloroform. Also, very weak bands were observed in the range 1500 to 1600 cm^{-1} usually assigned to carbamoyl complexes. The presence of these absorptions suggests a possible contamination by a carbamoyl complex though aromatic and C=N compounds also have characteristic frequencies in this region.

According to Cotton *et al*[1] the decomposition of the dinuclear [Cr$_2$(DTF)$_4$] (DTF= di-*p*-tolylformamidino) in dichloromethane was considered to be due to an oxidative addition of dichloromethane to the dichromium core, perhaps to afford the edge-sharing bioctahedral dichromium(III) complex formulated as

$[Cr_2(\mu\text{-}Cl)_2(\mu\text{-}DTF)_2(\eta^2\text{-}DTF)_2]$. However, no such process appears to occur for the present complexes, where formation of chromium(III) oxides seems to account more for the large decrease in the guanidine content on ageing in air.

In the current work several reactions were investigated with the system exposed to air because of the need to allow oxidation of the metal from 0 to +2, since formation of complexes of the type $[M_2(amidino)_4]$ was anticipated by comparison with the amidine ligands[1,2]. However, $[Cr_2(TPGH)_4]$ was not detected. Some possible structures for $[Cr(TPGH)_3]$ are illustrated in Figure 5.1.

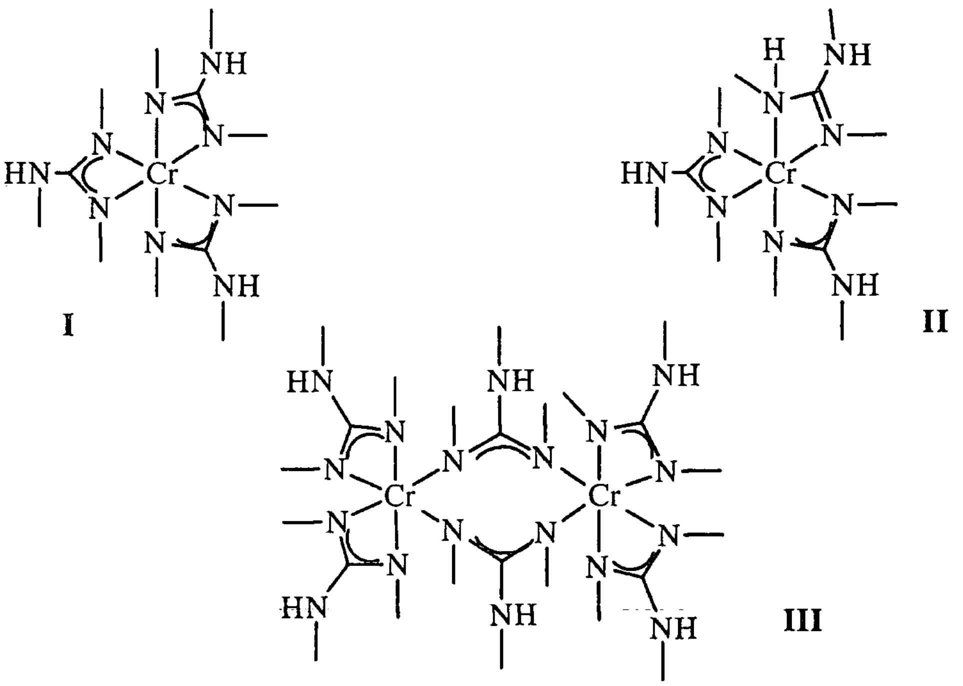


Figure 5.1 Some possible structures for $[Cr(TPGH)_3]$

2. The Triphenylguanidine/Molybdenum Complexes

Hexacarbonylmolybdenum(0) reacts with 1,2,3-triphenylguanidine to form products the nature of which depends on the temperature. A brown complex was obtained by the reaction in petroleum ether (100-120°) at the reflux temperature. The molar ratio of the metal to guanidine in the brown product did not follow the stoichiometry used in the reactants. A yellow-gold product was also obtained from the reaction in benzene at the reflux temperature. Again the product molar ratio did not follow the reactants molar ratio, and the introduction of a molecule of 1,2,3-triphenylguanidine into the complex led to the loss of two molecules of carbon monoxide. The $TPGH_2$ is thus acting as a four-electron donor to satisfy the 18-electron rule. The yellow-gold product, $[Mo(CO)_4(TPGH_2)]$ is air-sensitive and decomposes to the brown material when exposed to air.

The infrared spectrum of the brown product did not exhibit any vibrational mode that could be assigned to ν(CO) stretching. All CO molecules were lost in forming this product. However, carbonyl stretching frequencies (see Table 5.2) occurred in the region of 1900 to 2100 cm^{-1} at 2071, 1981, 1937 and 1889 cm^{-1} for the complex prepared in benzene under reflux conditions and formulated as $[Mo(CO)_4(TPGH_2)]$. Weak bands were also exhibited for the brown complex formulated as "[Mo(TPGH)]" in the 1500 to 1600 cm^{-1} region as for the chromium complex. For both yellow-gold and brown products, a band was exhibited in the region 3100 to 3400 cm^{-1} assigned to the ν(N-H) stretching frequency.

Table 5.2

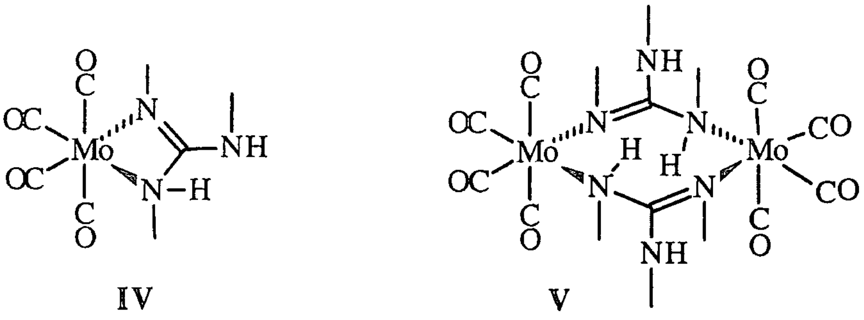
Infrared data of the Cr, Mo and W complexes synthesised in this work

Product Formula		ν(C=N)/cm^{-1}	ν(NH)/cm^{-1}	ν(CO)/cm^{-1}	Others
$[Mo(CO)_4(TPGH_2)]$	CH_2Cl_2	1625s	3386w	2071m;1981s 1937s; 1889s	
$[W(TPGH)_4]$	Nujol	1630s	3380w		
$[Cr(TPGH)_3]$	Nujol	1610s	3285w; 3372w		
"[Cr(TPGH)]"	Nujol	1591s	3362w		1650w
"[Mo(TPGH)]"	Nujol	1593s	3377w		1643w
$[W(TPGH)_3]$	Nujol	1612s	3373m		

Roode *et al*[3] have followed reactions of [M(CO)$_6$] (Cr, Mo) and formamidine in refluxing heptane by infrared spectroscopy. Disubstituted intermediate products were identified and represent the last substitution step before the complete loss of all CO groups. In the work currently undertaken, reactions with TPGH$_2$ and [Mo(CO)$_6$] were investigated using different conditions. A reaction was performed in petroleum ether (100-120°) and another reaction in benzene, both under reflux conditions. No evidence of carbon monoxide attached to the metal was observed at the end of the reaction in petroleum ether. After many attempts, the reaction seemed to produce better results when air was bubbled into the flask regardless of having the system exposed to air through the condenser. The reaction performed in benzene, however, showed the presence of an intermediate carbonyl [Mo(CO)$_4$(TPGH$_2$)], demonstrating the stepwise formation of the final non-carbonyl product. The brown solid obtained using both sets of conditions suggests strongly that [Mo(CO)$_4$(TPGH$_2$)] is an intermediate in the formation of "[Mo(TPGH)]". The yellow carbonyl complex isolated in the benzene preparation changes colour from yellow to a brown solid when exposed to air, and the brown solid from which [Mo(CO)$_4$(TPGH$_2$)] is extracted is shown to be "[Mo(TPGH)]".

Magee *et al*[4] have described phosphine substitution reactions of [M(CO)$_6$] (Cr, Mo or W) in diglyme at high temperature (160°C). The IR spectrum in the carbonyl stretching region for the yellow air-sensitive product [Mo(CO)$_4$(TPGH$_2$)], obtained in this work in hot benzene, is in general agreement with that found for *cis*-[Mo(CO)$_4$L$_2$] complexes, such as *cis*-[Mo(CO)$_4$(PPh$_3$)$_2$], reported by Shamir *et al*[5] (see also Appendix B).

Two possible structures for the tetracarbonylmolybdenum derivative can be envisaged as shown in Figure 5.2 below. It is important to note that structures **IV** and **V** conform to the 18-electron rule. However, the lack of stability found in this work for the complex formulated as [Mo(CO)$_4$(TPGH$_2$)], in the presence of air, is in contrast with the stability of most *cis*-[Mo(CO)$_4$L$_2$] complexes, though many, such as $[Mo(CO)_4(MeCN)_2]$ disproportionate rapidly in solution. Oxygen has a catalytic effect on many reactions by oxidising the complex to form a 17-electron radical complex, which reacts rapidly leading to further substitution. This may be the process by which hydrogen is lost from the ligand and the metal is oxidised. According to Kapko *et al*[6], $TPGH_2$ may also photodegrade in air.


IV

V

Figure 5.2 Possible structures for $[Mo(CO)_4(TPGH_2)]$

3. The Triphenylguanidine/Tungsten Complexes

Two products were obtained by the reaction of hexacarbonyltungsten(0) with 1,2,3-triphenylguanidine in petroleum ether (100-120°) at the reflux temperature. Neither of these products has carbon monoxide in their composition since no ν(CO) stretching frequency was exhibited in their infrared spectrum. These products seemed to be dependent on the temperature and the molar ratio of the reactants. The yellow-orange product exhibited one band at 3380 cm^{-1} which is assigned to the ν(N-H) stretching frequency. This product seems to be air sensitive because the colour changed from yellow-orange to a very pale colour when the sample was exposed to air. A red material obtained as a by-product from the same reaction did not exhibit any band in the region that could be assigned to ν(N-H) stretching. On the other hand, it exhibited extra absorptions in the range 600 to 800 cm^{-1} where bands related to the substitution on the benzene ring have been assigned for organic compounds. For example, two strong bands about 690 and 753 cm^{-1} have been correlated to the monosubstitution on the benzene ring for $TPGH_2$ or $DPGH_3$ in this work. Possibly the sample of the yellow-orange material had the red by-product (see section A4) as an impurity. The molecular formula $[W(TPGH)_4]$ presented in Table 5.1 is the only formula that approximates closely to the analytical data of the material. The reaction was carried out in a molar ratio 1:2 (metal complex: guanidine), and in this case, the stoichiometric pathway was not followed in the chemical reaction. Thus, the red by-product material may contain a high metal content, but this was not determined. Extra bands at low frequency (600 to 800 cm^{-1}) in the infrared spectrum of the red by-product may be an indication of ring substitution. Also, a new band at 975 cm^{-1} which appeared after heating the system for 24 hours suggests the formation of a compound having a W=O bond.

Many attempts at reacting $[W(CO)_6]$ with $TPGH_2$ in hot toluene and in hot benzene were unsuccessful. A slight amount of a pale yellow material was all that was obtained. However, the analytical and infrared spectroscopic data indicated that the major component of this pale yellow material was the starting material.

Cotton *et al*[1] have reported the preparation of the dinuclear complex $[M_2(amidino)_4]$ by reacting metal halides such as $CrCl_2$ and WCl_4 or metal carbonyls such as $[W(CO)_6]$ with amidines and lithio-amidines in THF or hydrocarbon solvents. Sodium amalgam was mixed with a suspension of WCl_4 to produce the anion $[W_2Cl_8]^{4-}$ which was the starting material to react with the lithio-amidine at -30°C. According to the authors, it was important to add the lithio-amidine at low temperature to avoid the formation of WCl_2 and consequently to avoid an oil as the product. The yield of the reactions was about 45%. According to Cotton *et al* [1,2] the reaction involving $[W(CO)_6]$ and N,N'-diphenylbenzamide under reflux was not successful, in spite of good results for the reaction of benzamidine with $[Mo(CO)_6]$ in refluxing petroleum ether. Electronic spectroscopy of the complexes reported by Cotton *et al*[1,2] showed a strong charge-transfer band assigned as an n→π* transition at a high energy (294 nm). As part of the current study, a reaction between Li(TPGH) and WCl_4 was investigated using slightly different conditions. No sodium amalgam was used throughout the process. The recrystallisation process employed chloroform, affording a red-orange solution. At this point LiCl was removed by filtration. Pale orange crystals were obtained from slow evaporation of the red chloroform solution at room temperature but they were not well formed crystals suitable for X-ray diffraction studies. The final product is formulated as $[W(TPGH)_3]$ on the basis of analytical data on samples recrystallised from chloroform.

The absorption assigned to ν(CN) for the coordinated TPGH for all complexes in this work also shifted slightly to low frequency, e.g. between 1591 and 1630 cm^{-1} (see Table 5.2), compared with 1636 cm^{-1} in the free ligand. This was observed for all complexes irrespective of the bonding type of the ligand, but provides no structural information on the nature of the bonding.

Reactions of $[M(CO)_6]$ (Cr, Mo, W) with 1,2,3-triphenylguanidine led to different type products depending on the metals and the reaction conditions used. 1,2,3-triphenylguanidine seems not to form stable $[M_2(guanidino)_4]$-complexes with these metals, but reacts further with the oxygen and/or water in the atmosphere, leading to $[M(guanidino)_3]$-type complexes.

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Chapter Six

Complexes of Palladium(II) and Platinum (II) with 1,2,3-Triphenylguanidine and 1,2-Diphenylguanidine

Introduction

In this chapter, work concerning the coordination chemistry of $TPGH_2$ and $DPGH_3$ towards palladium(II) and platinum(II) compounds is presented. Many researchers have reported the characterisation of coordination complexes involving these two metals with a wide variety of ligands, including those containing heteroatoms such as nitrogen, sulphur and phosphorus. In exploring the coordination chemistry of guanidines, a wealth of different types of complexes of palladium(II) and platinum(II) is expected.

A. Experimental Work

1. Reaction of [$PdCl_2$(COD)] with 1,2,3-Triphenylguanidine in Acetonitrile

The [$PdCl_2$(COD)] (0.41g/ 1.4 mmol) prepared as described by Drew[1] was dissolved in acetonitrile (20ml) at room temperature. $TPGH_2$ (0.43g / 1.5 mmol), dissolved in a minimum volume of acetonitrile, was poured slowly into the metal complex solution, causing the colour of the solution to change immediately from yellow to a red wine colour. After a few seconds the solution changed to dark orange. The reaction was left stirring overnight at room temperature. The acetonitrile was removed *in vacuo*, and the yellow-orange residue was suspended in diethyl ether before filtering the mixture in air. The solid product was washed with diethyl ether and dried. On the basis of elemental analysis (see Table 6.1) the complex is formulated as [$PdCl_2$(COD)$TPGH_2$]. Yield: 0.61g {75% based on [$PdCl_2$(COD)]}.

2. Reaction of [$PdCl_2$(COD)] with *syn*-1,2-Diphenylguanidine in Acetonitrile/Dichloromethane

The procedure described above in reaction 1 was used. The reaction took place in a mixture of dichloromethane/acetonitrile (1:1, 20ml) at 35°C. A yellow coloured solution was formed when the $DPGH_3$ (0.31g/ 1.5 mmol) in acetonitrile (10ml) was poured into the metal complex solution. A yellow product separated by removing half of the solvent, and was removed by filtration. Removing more solvent from the filtrate under reduced pressure gave a pale orange material which was removed by filtration. This process was repeated and a further pale orange material obtained. The various fractions of the product were labelled as samples 1, 2 and 3. Table 6.1 gives the analytical results of the product, which is believed to be [$PdCl_2$(COD)$DPGH_3$]. Yield of the crude product: 0.57g {80% based on [$PdCl_2$(COD)]}.

3. Reaction of Platinum(II) Chloride with 1,2,3-Triphenylguanidine in Acetonitrile

$PtCl_2$ (0.37g/ 1.39 mmol) was mixed with acetonitrile (20 ml) and heated at 60°C. After the compound had dissolved completely, a solution of $TPGH_2$ (0.41g / 1.42 mmol), also in acetonitrile (10 ml), was poured into the solution of the metal compound, and the mixture heated at the reflux temperature for 2 hours. The acetonitrile was then removed under reduced pressure. The dry orange solid was suspended in diethyl ether and the mixture filtered in air. Further diethyl ether (20ml) was used to wash the solid before it was dried *in vacuo*. Elemental analysis (see Table 6.2) and IR data showed the complex to be [$Pt_2Cl_4(TPGH_2)_2$]. Yield: 0.65g [85% based on $PtCl_2$].

4. Reaction of Platinum(II) Chloride with *syn*-1,2-Diphenylguanidine in Acetonitrile

This product was obtained using the procedure described in reaction 3, with some minor modifications as described below. The solution of $DPGH_3$(0.29g/ 1.42 mmol) in acetonitrile (10ml) was left exposed to air for thirty minutes before adding to the metal solution. A pale yellow-green solid separated from the reaction mixture and the mixture was left overnight at the reflux temperature in an attempt to dissolve it. The pale yellow-green solid did not, however, dissolve. The solid was removed by filtration in air, and washed with diethyl ether. From the filtrate a pale yellow solid was obtained after reducing the volume of solvent *in vacuo*. After separation by filtration, this material was washed thoroughly with diethyl ether, before drying in the air. Diethyl ether was also the solvent to wash the product. Analysis identified the yellow-green solid as [$PtCl_2$(NHC(Me)NHC(Me)NH)] [Yield: 0.1g (20% based on $PtCl_2$)] and the pale yellow solid as [$Pt_2Cl_4(DPGH_3)_2$(PhNH(CO)NHPh)] [Yield: 0.61g (75% based on $PtCl_2$)]. Analytical data are given in Table 6.2.

5. Reaction of Palladium(II) Chloride with *syn*-1,2-Diphenylguanidine in Acetonitrile

This product was prepared using the procedure described in reaction 3 with minor modifications. Palladium(II) chloride (0.37g/ 2.10 mmol) was heated at 60°C in acetonitrile until it was dissolved completely, and a solution of $DPGH_3$ (0.45g/ 2.15 mmol) in acetonitrile (10ml), freshly prepared, was added. An orange-red material was obtained. The product was shown by elemental analyses to be [$Pd_2Cl_4(DPGH_3)_2$] (see Table 6.2). Yield: 0.65g [80% based on $PdCl_2$].

6. Reaction of Palladium(II) Chloride with 1,2,3-Triphenylguanidine in Acetonitrile

This product was also prepared using the procedure described in section 3, with only minor modifications. Palladium(II) chloride (0.37g/ 2.10 mmol) was heated at 60°C in acetonitrile until it was dissolved completely, and a solution of $TPGH_2$ (0.61g/ 2.15 mmol) in acetonitrile (10ml), freshly prepared, was added. A red wine coloured material was obtained. The product was shown by elemental analyses to be [$Pd_2Cl_4(TPGH_2)_2$](see Table 6.2). Yield: 0.82g [85% based on $PdCl_2$].

7. Reaction of $[PtCl_2(NCPh)_2]$ with *syn*-1,2-Diphenylguanidine

The $[PtCl_2(NCPh)_2]$ (0.15g/ 0.31 mmol), prepared according to the method of Marr *et al*[2] was suspended in dry toluene (20ml) at room temperature. $DPGH_3$ (0.13g/ 0.62 mmol), dissolved in toluene (10ml), was poured into the solution of the metal compound at room temperature, and the mixture heated at about 65°C for 24 hours. The colour of the solution became orange. A yellow solid was separated from the hot solution by filtration, and a further orange solid was obtained from the filtrate by removing the solvent under reduced pressure. The solids were washed with diethyl ether. Elemental analyses (see Table 6.2) showed the orange product to be $[Pt_2Cl_2(DPGH_2)_2(DPGH_3)_2]$ {yield: 0.11g(55% based on $[PtCl_2(NCPh)_2]$)} and the yellow product to be $[Pt_2Cl_4(DPGH_3)_3]$ {yield: 77mg (35% based on $[PtCl_2(NCPh)_2]$)}.

8. Purification of the Complexes

The palladium complex $[Pd_2Cl_4(DPGH_3)_2]$ was purified from acetonitrile and the other complexes from dichloromethane, except for the yellow-green product of the reaction of $DPGH_3$ with $PtCl_2$ in acetonitrile, which was very insoluble and could not be recrystallised. The purification procedure used is described below.

A sample of the complex was dissolved in the appropriate solvent and the solution filtered through a filterglassfrit, number four, to remove insoluble materials. The solvent was removed under reduced pressure and a mixture of dichloromethane and diethyl ether (1:6) was added to the gum remaining. The system was stirred vigorously until a solid separated. Another filtration was performed and the product washed with diethyl ether. Analytical data for the derivatives of palladium and platinum with $TPGH_2$ and $DPGH_3$ are shown in Table

6.1 and Table 6.2 below. The products were vacuum dried at 60°C for 8 hours to remove the lattice trapped solvent, dichloromethane or acetonitrile.

Table 6.1

Data for the complexes resulting from [$PdCl_2$(COD)] reactions

Product Formula	Colour	Found(Calcd.)% C	H	N	Cl	mp.(°C)
[$PdCl_2$(COD)$TPGH_2$]	Orange	55.87	4.65	7.94	12.79	180d
		(56.64)	(5.06)	(7.34)	(12.41)	
[$PdCl_2$(COD)$DPGH_3$]		(50.78)	(5.04)	(8.46)	(14.31)	145d
Sample 1	Yellow	51.15	4.91	9.44	14.66	
Sample 2	Pale Orange	50.81	5.10	9.92	13.05	
Sample 3	Pale Orange	50.85	5.15	10.21	13.14	

d - decomposition point

Table 6.2

Data for the palladium and platinum complexes

Product Formula	Colour	Found(Calcd.)% C	H	N	Cl	mp.(°C)
[$Pd_2Cl_4(DPGH_3)_2$]	Orange-red	40.11	3.39	10.55	19.45	155d
		(40.20)	(3.35)	(10.82)	(18.29)	
[$Pd_2Cl_4(TPGH_2)_2$]	Red wine	49.22	3.86	9.06	15.58	165d
		(49.13)	(3.66)	(9.05)	(15.30)	
[$Pt_2Cl_4(TPGH_2)_2$]	Orange	41.16	2.86	7.80	11.46	230d
		(41.25)	(3.10)	(7.60)	(12.84)	
[$Pt_2Cl_4(DPGH_3)_2L$]	Pale Yellow	40.47	3.48	10.65	11.74	240d
		(40.17)	(3.34)	(10.81)	(12.19)	
[$PtCl_2L^1$]	Yellow Green	13.06	2.40	11.38		330d
		(13.15)	(2.48)	(11.51)		
[$Pt_2Cl_4(DPGH_3)_3$]	Orange	40.16	3.36	10.33		
		(40.17)	(3.34)	(10.81)		
[$Pt_2Cl_2(DPGH_2)_2(DPGH_3)_2$]	Yellow	48.04	3.36	11.10		
		(47.89)	(3.86)	(12.89)		

d-decomposition point; L - PhNH(CO)NHPh; L^1- (HNC(CH_3)NHC(CH_3)NH)

B. Results and Discussion

1. Complex [$Pt_2Cl_4(TPGH_2)_2$]

Platinum(II) chloride reacts in a molar ratio 1:1 with 1,2,3-triphenylguanidine in acetonitrile at the reflux temperature. The solution of 1,2,3-triphenylguanidine was prepared a few minutes before mixing with the metal halide solution in hot acetonitrile. An orange solid was obtained from the orange solution after 2 hours heating at the reflux temperature. The product, [$Pt_2Cl_4(TPGH_2)_2$], is air stable, and is soluble in dichloromethane, chloroform and acetonitrile producing orange solutions in these solvents. The complex was shown to be a 2:1 electrolyte (see Table 6.3) in nitromethane solution.

The infrared spectrum in dichloromethane, or collected using a CsI disc, exhibited a medium band at low frequency at 330 cm^{-1} assigned to ν(Pt-Cl), and two others of weak to very weak intensity at 540 and 500 cm^{-1} assigned to ν(Pt-N). The ν(CN) stretching frequency also shifted slightly towards low frequency (see Table 6.4) compared with the free ligand $TPGH_2$. A broad band was observed in the range 3000 to 3300 cm^{-1} which was assigned to the coordinated N-H bond. The broadness of this band in the solid state and in solution suggests hydrogen bonding involving the N-H group.

2. Complex [$Pd_2Cl_4(TPGH_2)_2$]

Palladium(II) chloride reacts in a molar ratio 1:1 with 1,2,3-triphenylguanidine in acetonitrile at the reflux temperature. The solution of 1,2,3-triphenylguanidine was prepared a few minutes before mixing with the metal halide solution in hot acetonitrile. A red wine coloured solid was obtained from the red solution after 2 hours heating at the reflux temperature. The product, $[Pd_2Cl_4(TPGH_2)_2]$, is air stable, and is soluble in dichloromethane, chloroform and acetonitrile producing an orange-red solution in these solvents. The complex was shown to be a 2:1 electrolyte (see Table 6.3) in nitromethane solution.

The infrared spectra in dichloromethane, and in a CsI disc, exhibited a medium intensity band at low frequency at 335 and 330 cm^{-1} respectively assigned to ν(Pd-Cl), and two others of weak to very weak intensity at 530 and 500 cm^{-1} assigned to ν(Pd-N). The ν(CN) stretching frequency also shifted slightly towards low frequency (see Table 6.4). A broad band was observed in the range 3000 to 3300 cm^{-1} which can be assigned to the coordinated N-H group. The broadness of this band in the solid state and in solution suggested again hydrogen bonding between the N-H group and chloride attached to the metal, or other nitrogen atoms.

Table 6.3

Electrical conductivity measurements of the palladium and platinum complexes

Product Formula	RMM	weight (g) $g/25\ cm^3$	Molar Conc. $mol\ dm^{-3}$ (x 10^3)	$ohm^{-1}\ cm^2\ mol^{-1}$
$[Pt_2Cl_4(TPGH_2)_2]$	1106	0.0296	1.07	168.2
$[Pd_2Cl_4(TPGH_2)_2]$	928	0.0290	1.25	160.0
$[Pd_2Cl_4(DPGH_3)_2]$	776	0.0244	1.26	158.7
$[PdCl_2(COD)TPGH_2]$	572	0.0159	1.11	47.6
$[Pt_2Cl_2(DPGH_2)_2(DPGH_3)_2]$	1303	0.0364	1.12	178.5
$[Pt_2Cl_4(DPGH_3)_3]$	1165	0.0279	1.12	89.3

Conductivity Measurements in Nitromethane, $\kappa = 5.54 \times 10^{-7}\ \Omega^{-1}\ cm^{-1}$.

Table 6.4

Infrared absorptions for palladium and platinum complexes

Product Formula	Solvent	ν(C=N)/cm^{-1}	ν(M-N)/cm^{-1}	ν(M-Cl)/cm^{-1}
$[Pt_2Cl_4(TPGH_2)_2]$	CH_2Cl_2	1620s	540vw;500w	330m
	CsI	1625s	535vw; 500w	330m
$[Pd_2Cl_4(DPGH_3)_2]$	Nujol	1630s	*	325m
	CsI	1630s	495w	330m
$[Pd_2Cl_4(TPGH_2)_2]$	CH_2Cl_2	1625s	530vw; 500w	335m
	CsI	1620s	520vw; 500w	330m
$[Pt_2Cl_4(DPGH_3)_2L]$	CH_2Cl_2	1665m^a;1635s	525w; 500w	325m
	CsI	1660m^a;1630s	535w; 500w	325m
$[PtCl_2(HNC(Me)NHC(Me)NH)]$	Nujol	1672s; 1668s	505m	325s;310s
	CsI	1670s	505s	323s; 310s
$[Pt_2Cl_4(DPGH_3)_3]$	CsI	1630s	*	315s
$[Pt_2Cl_2(DPGH_2)_2(DPGH_3)_2]$	CsI	1630s	495m	325m
$[PdCl_2(COD)TPGH_2]$	Nujol	1625s	505m	330s

* Difficult to establish; L-PhNH(CO)NHPh; a-shoulder assigned as ν(CO) from PhNH(CO)NHPh

3. Complex $[Pd_2Cl_4(DPGH_3)_2]$

Palladium(II) chloride reacts in a molar ratio 1:1 with 1,2,3-triphenylguanidine in acetonitrile at the reflux temperature. The solution of 1,2,3-triphenylguanidine was prepared a few minutes before mixing with the metal halide solution in hot acetonitrile. An orange-red solid was obtained from the orange-red solution after two hours at the reflux temperature. The product is air stable, and is not soluble in dichloromethane but forms a gum when in contact with this solvent. It is, however, soluble in acetonitrile and nitromethane producing orange-red solutions. The complex was shown to be a 2:1 electrolyte (see Table 6.3) in nitromethane solution.

The infrared spectra in a Nujol mull, and in a CsI disc, exhibited a medium intensity band at low frequency at 325 and 330 cm^{-1} respectively, assigned to the ν(Pd-Cl). A weak band at 495 cm^{-1} was assigned to ν(Pd-N); the same band was difficult to assign in Nujol mull. The ν(CN) stretching frequency also shifted slightly towards low frequency (see Table 6.4) compared with the free ligand. A broad band was observed in the range 3000 to 3300 cm^{-1} which is assigned to the coordinated N-H groups. The broadness of this band in the solid state suggests hydrogen bonding between the N-H group and chloride or other nitrogen atoms. Close similarities were found in the data for the three related complexes $[Pd_2Cl_4(DPGH_3)_2]$, $[Pd_2Cl_4(TPGH_2)_2]$ and $[Pt_2Cl_4(TPGH_2)_2]$

4. The Yellow-Green Product from the $PtCl_2/DPGH_3$ Reaction

Platinum(II) chloride reacts in a molar ratio 1:1 with *syn*-1,2-diphenylguanidine in acetonitrile at the reflux temperature to produce this yellow-green material. The solution of guanidine was prepared about half an hour before mixing with the solution of the metal halide in hot acetonitrile. A yellow-green solid was obtained from solution after 2 hours heating at the reflux temperature, and further heating did not dissolve the solid. The product is air stable, and is insoluble in dichloromethane, chloroform and acetonitrile.

The infrared spectra in a Nujol mull or collected using a CsI disc, exhibited two strong bands at low frequency at 325 and 310 cm^{-1} assigned to the ν(Pt-Cl). A medium to strong band at 505 cm^{-1} was assigned to ν(Pt-N). The infrared spectra of this product exhibited, in a Nujol mull, two strong bands at 1672 and 1668 cm^{-1} assigned to the ν(CN) stretching frequencies, but in CsI only one is exhibited at 1670 cm^{-1}. These frequencies are very close to the ν(C=N) or ν(C=O) absorptions of imines, and ν(C=O) of ureas. Sharp bands were observed in the range 3000 to 3300 cm^{-1} which are assigned to the N-H group.

Analytical data obtained (Table 6.2) correspond to those required for $[PtCl_2(HNC(CH_3)NHC(CH_3)NH)]$, but the precise identity of the complex cannot be deduced on the basis of the data collected. Possible structures are discussed later.

5. Complex $[Pt_2Cl_4(DPGH_3)_2(PhNH(CO)NHPh)]$

Platinum(II) chloride reacts in a molar ratio 1:1 with *syn*-1,2-diphenylguanidine in acetonitrile in air at the reflux temperature. The solution of guanidine was prepared about half an hour before it was mixed with the solution of the metal halide in hot acetonitrile. After removal of the yellow-green precipitate by filtration (discussed above, section 4), a pale yellow solid was obtained by removing the solvent under reduced pressure.

The infrared spectrum of the product in dichloromethane solution and CsI disc, exhibited at low frequency a medium intensity absorption at 325 cm^{-1} assigned to a ν(Pt-Cl) stretching frequency. Two weak absorptions were also detected at 525 and 500 cm^{-1} and assigned to ν(Pt-N) stretching frequencies. The ν(C=N) assigned for the complex had shifted slightly towards low frequency compared with the free ligand, but in this case it was difficult to assign the band due to overlap with an extra absorption at higher frequency (at 1655 cm^{-1}) due to the ν(C=O) of a urea. Williams *et al*[3] have reported the ν(C=O) stretching frequencies for ureas of general formula RNH(CO)NHR (R=Ph) at about 1660 cm^{-1} and Allaf *et al*[4] have reported the same frequency for free diphenylurea.

The ^{13}C NMR spectrum of the complex exhibits peaks in the region typical for aromatic carbons at 119, 123, 126, 128, 129, 134, 144 and 153 ppm. An extra peak occurs at 174 ppm which is assigned to δ(CO) of ureas following the work of Williams *et al*[3]. According to Allaf *et al*[4] palladium and platinum complexes formulated as $[MCl_2(PhNHC(S)NHPh)]_2$ (M=Pd, Pt) have the sulphur bonded to the metal and exhibit the chemical shift of δ(CS) at 152.9 ppm for the platinum complex and 152.7 ppm for the palladium complex. For the free thiourea PhNHC(S)NHPh the chemical shift of δ(CS) occurred at 179.6 ppm. The authors[4] also found peaks for the coordinated thiourea at 139, 129, 128, 125 ppm which correspond to the aromatic carbons. In the spectrum of the complex formulated as

$[Pt_2Cl_4(DPGH_3)_2(PhNH(CO)NHPh)]$ the peak at 153 ppm may be due to the carbon bonded to the three nitrogens of the *syn*-1,2-diphenylguanidine and the other signal at 174 ppm to the carbonyl carbon of PhNHC(O)NHPh ligand bonded to the metal through the nitrogen atoms. This interpretation is consistent with the work of Allaf *et al*[4] who found that PhNHC(O)NHPh does not bind metals, such as palladium and platinum through the oxygen atom. The other ^{13}C NMR peaks found for the complex $[Pt_2Cl_4(DPGH_3)_2(PhNH(CO)NHPh)]$ are difficult to assign because they belong to both *syn*-1,2-diphenylguanidine and PhNHC(O)NHPh bonded to the platinum ion through the nitrogen atoms.

6. Complex $[PdCl_2(COD)TPGH_2]$

1,2,3-triphenylguanidine reacts with $[PdCl_2(COD)]$ in a molar ratio 1:1 in acetonitrile at room temperature. The solution of 1,2,3-triphenylguanidine was prepared a few minutes before mixing it with the orange solution of the $[PdCl_2(COD)]$. The colour changed immediately to red-wine and in a few seconds later became orange again. An orange-yellow solid was obtained as the product, which is soluble in dichloromethane, acetonitrile and nitromethane.

The infrared spectra of the complex $[PdCl_2(COD)TPGH_2]$ exhibited at low frequency a strong band at 330 cm^{-1} which was assigned to the ν(Pd-Cl). Another band of medium intensity at 500 cm^{-1} was assigned to ν(Pd-N). A broad ν(N-H) absorption was also observed for the complex in the range 3000 to 3300 cm^{-1}.

The ^1H NMR of the complex $[PdCl_2(COD)TPGH_2]$ exhibited two low frequency signals at 1.59 and 2.37 ppm which can be assigned to the $-CH_2$ groups of the coordinated 1,5-cyclooctadiene by comparison with the signals found for the starting material $[PdCl_2(COD)]$ at 2.20 ppm. Two signals at 5.98 and 6.30 ppm were also exhibited in the spectrum of the complex $[PdCl_2(COD)TPGH_2]$ and are assigned to the -CH groups of the coordinated 1,5-cyclooctadiene by comparison with the signal at 6.34 ppm of the starting material [$PdCl_2$(COD)]. In addition, the ^1H NMR spectrum of the complex [$PdCl_2$(COD)$TPGH_2$] exhibited a multiplet centred at 7.4 ppm typical of aromatic hydrogen atoms which are assigned to the phenyl groups of 1,2,3-triphenylguanidine, and a peak also occurs at 8.55 ppm in the same spectrum, the high frequency position for N-H suggesting hydrogen bonding according to Williams *et al*[3] and Sanders *et al*[5]. The hydrogen bonding in this case could be intramolecular of the type N-H···Cl, intermolecular of the type N-H···N or both. Therefore the ^1H NMR shows the 1,5-cyclooctadiene is still bonded to the metal in the complex. However, the product [$PdCl_2$(COD)$TPGH_2$] may have the 1,5-cyclooctadiene acting as a chelate ligand or a monodentate ligand towards the palladium centre. Figure 6.1 illustrates some possible structures for the complex [$PdCl_2$(COD)$TPGH_2$]. Electrical conductivity measurements (Table 6.3) suggest that the complex has a molar conductivity between that expected from a non-electrolyte (0 $ohm^{-1}cm^2mol^{-1}$) and for a 1:1 electrolyte (75-95 $ohm^{-1}cm^2mol^{-1}$). This could arise from reaction of a molecular complex, such as **B**, with the solvent to displace chloride ions from the complex, to form an ionic compound such as **D**.

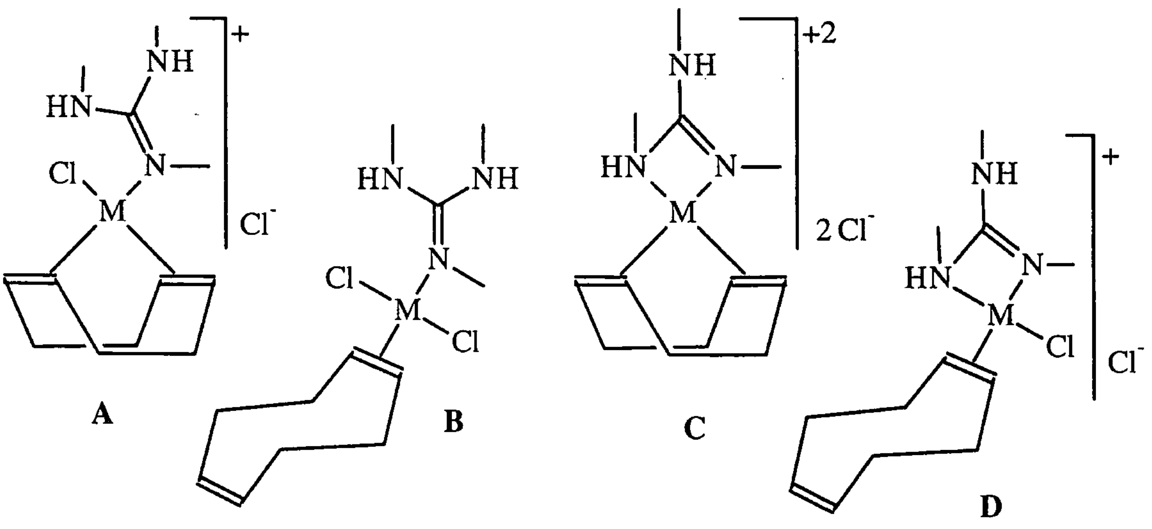


Figure 6.1 Structures for the complex [$PdCl_2$(COD)$TPGH_2$]

7. Complex [$PdCl_2$(COD)DPGH_3]

Syn-1,2-diphenylguanidine reacts with [$PdCl_2$(COD)] in a 1:1 molar ratio in a mixture of dichloromethane/acetonitrile at 35°C to form [$PdCl_2$(COD)DPGH_3]. The solution of the ligand *syn*-1,2-diphenylguanidine was prepared a few minutes before mixing with the orange solution of [$PdCl_2$(COD)]. The colour of the reaction mixture did not change when the solution of the ligand was added, and two solids, a pale orange and a yellow solid, were obtained as products.

The infrared spectra of the complex [$PdCl_2$(COD)DPGH_3] exhibited at low frequency a weak intensity band at 295 cm^{-1} and another medium intensity band at 315 cm^{-1}, assigned to the ν(Pd-Cl) stretching frequencies of a *cis*-$PdCl_2$ moiety. The ν(Pd-N) was difficult to assign due to very weak absorptions in the range 490 to 530 cm^{-1}. A broad absorption was also observed for the complex in the range 3000 to 3300 cm^{-1} which was assigned to the ν(N-H) stretching frequency. Hydrogen bonding of the type mentioned before is indicated.

The ^1H NMR spectrum of the product [$PdCl_2$(COD)DPGH_3] showed signals at 6.32 ppm and at 2.28 ppm, and by comparison with the starting material [$PdCl_2$(COD)], it suggests that the product has the 1,5-cyclooctadiene bonded to the metal ion. Peaks at 7.19 ppm also confirm that the ligand *syn*-1,2-diphenylguanidine is in the product. The spectrum also exhibits additional peaks at 2.81, 2.49, 2.10, 1.93, 1.53 and 1.29 ppm which suggests the formation of more than one species. Some variations occur between ^1H NMR spectra for samples 1, 2 and 3 (Table 6.1) though the main features remain the same for all samples. It is conceivable that a mixture of isomers may exist in solution, including *cis* and *trans*-isomers as well as various conformational isomers associated with the relative positions of guanidine and 1,5-cyclooctadiene ligands.

8. Complex $[Pt_2Cl_4(DPGH_3)_3]$

Syn-1,2-diphenylguanidine reacts in a 1:2 molar ratio with $[PtCl_2(NCPh)_2]$ in toluene at 65°C over 24 hours to form $[Pt_2Cl_4(DPGH_3)_3]$. An orange solid was obtained in poor yield after removing the solvent under reduced pressure and after the yellow complex, $[Pt_2Cl_2(DPGH_2)_2(DPGH_3)_2]$, was also removed. The infrared spectrum of $[Pt_2Cl_4(DPGH_3)_3]$ in a CsI disc exhibited a strong band at 315 cm^{-1} assigned to a ν(Pt-Cl) stretching frequency. The band ν(Pt-N) was difficult to assign due to overlap of absorptions in the region of 490 to 530 cm^{-1}. The infrared spectrum also exhibited a broad absorption in the range 3000 to 3400 cm^{-1}, assigned to a ν(N-H) stretching frequency, which in appearance was reminiscent of the bands assigned to ν(N-H) stretching frequencies of hydrochlorides, as found before in the work involving $[Mn(Br)(CO)_5]$ and 1,2,3-triphenylguanidine (see Chapter Two). The ionic nature of the complex was confirmed by electrical conductivity measurements in nitromethane solution, where conductivity of a 1:1 electrolyte was found (Table 6.3).

9. Complex $[Pt_2Cl_2(DPGH_2)_2(DPGH_3)_2]$

Syn-1,2-diphenylguanidine reacts in a molar ratio 1:2 with $[PtCl_2(NCPh)_2]$ in toluene at 65°C over 24 hours. A yellow product separated in hot toluene after 24 hours and filtration of the mixture gave $[Pt_2Cl_2(DPGH_2)_2(DPGH_3)_2]$. The infrared spectrum of the product in a CsI disc exhibited a medium band at 325 cm^{-1} assigned to ν(Pt-Cl) and another medium band at 495 cm^{-1} assigned to ν(Pt-N) stretching frequencies. The ionic nature of the complex was also confirmed by electrical conductivity measurements (Table 6.3). Table 6.4 gives a summary of the infrared spectroscopic data for the complexes.

10. Other Aspects Involving the Palladium and Platinum Complexes

The low frequency vibrations of complexes have been studied in the region of 600 to 200 cm^{-1}, the region associated with metal-halogen and metal-nitrogen stretching frequencies for transition metal complexes. Halogen ligands are the most common in coordination chemistry and the terminal ν(M-X) stretching bands appear in the regions of 750 to 500 cm^{-1} for M-F; 400 to 200 cm^{-1} for M-Cl; 300 to 200 cm^{-1} for M-Br, and 200 to 100 cm^{-1} for M-I. According to Nakamoto[6,7] several factors govern the ν(M-X) frequencies. For instance, the ν(M-X) is higher, the higher the oxidation state of the metal or as the coordination number of the metal decreases. The electronegativity difference between the metal and the halide ligand also governs the position of ν(M-X) if the halogen is significantly more electronegative than the metal. This explain in particular the high range of ν(M-F) frequencies in comparison with the other halides. The vibrational modes for bridging halides, however, are lower in energy than the terminal ν(M-X) stretching frequencies. As an illustration, the *trans*-planar $[M_2X_4L_2]$ (M=Pd, Pt; X= Cl, Br; L= PMe_3, PPh_3) complexes exhibit three infrared active modes: one $\nu(M\text{-}X_t)$ terminal and two bridging modes $\nu(M\text{-}X_b)$. The higher frequency band for the bridging modes is claimed by Nakamoto[6,7] to correspond to the halide *trans* to halide whereas the lower frequency mode corresponds to halide *trans* to the ligand L since the latter ν(M-X) (X=halide) is sensitive to the nature of the ligand. For platinum and palladium complexes[6,7] the $\nu(M\text{-}Cl_t)$ is assigned in the range of 370 to 340 cm^{-1} and $\nu(M\text{-}Cl_b)$ is assigned in the range of 335 to 290 cm^{-1} and 300 to 235 cm^{-1}. Strong coupling is expected among these modes because they belong to the same symmetry species[6,7]. Figure 6.2 shows two structures for planar complexes of the type $[M_2X_4L_2]$.

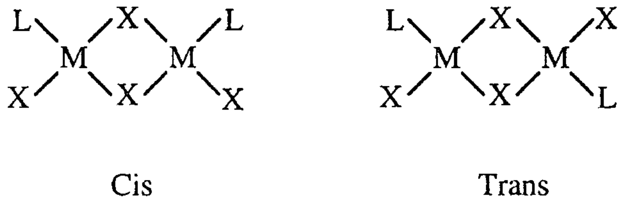


Figure 6.2 Stereochemistry for complexes of general formula $[M_2X_4L_2]$
(M= Pt, Pd; X= Cl, Br; L= PMe_3, PPh_3)

The metal-nitrogen stretching frequency also depends on the nature of the other ligands in the complex. *Cis* and *trans* complexes of the type $[M(NH_3)_2Cl_2]$ (M= Pd, Pt) have been studied by During *et al*[8]. The stretching frequencies ν(M-N) were assigned in the region of 528 to 436 cm^{-1}. However, the ν(M-N) stretching band[6] may shift towards low frequency if a ligand of strong *trans*-influence is placed in the position *trans* to the M-N bond. For complexes of the type $[M(en)_3]^{2+}$ (M= Cu, Ni, Mn, Zn) the ν(M-N) has also been assigned in the range of 550 to 400 cm^{-1} [9]. Harvey *et al*[10] have reported that platinum complexes, involving 2,2'-bipyridine as the ligand, exhibit weak bands at 240 and 230 cm^{-1} assigned to ν(M-N), and Rutherford *et al*[11] have assigned ν(M-N) bands for the cobalt complexes $[Co(X)(DMG)_2(py)]$ (X= halide) at 512 and 453 cm^{-1} based on ^{15}N and py-d_5 isotope shifts.

For all complexes, except $[PtCl_2(HNC(CH_3)NHC(CH_3)NH)]$, in Nujol mulls, dichloromethane solutions and CsI discs, just one band about 325 cm^{-1} was observed and assigned to ν(M-Cl). $[PtCl_2(HNC(CH_3)NHC(CH_3)NH)]$ exhibited two bands in the region 300 to 330 cm^{-1} (see Table 6.2). Another band about 500 cm^{-1} was also observed and assigned to ν(M-N).

Cis and *trans* isomers of Pd(II) and Pt(II) ions are often distinguished by use of far-infrared spectroscopy (low frequency) in the absence of other physical methods such as X-ray crystallography. Bruno *et al*[12] have reported for instance the X-ray diffraction crystallography of a square-planar palladium dichloride complex in which the metal is bonded to the phosphorus atom of a $(Pr^n)_3P$ ligand and the nitrogen atom of a 4-pyridinecarbaldehydephenylhydrazone in *trans* positions. The stereochemistry of square-planar complexes can be observed by the number of bands correlated to ν(M-X) (X= halide) at low frequency. In the case of the Bruno's complex[12], only one band was observed at low frequency at 350 cm^{-1} suggesting that the chloride ligands are in *trans* positions. Recently, ν(M-Cl) absorptions bands have been assigned to the *trans* arylamine[13] complexes, $[PdCl_2(NH_2Ph)_2]$ in the region 300 to 330 cm^{-1}. The *cis* complexes exhibit two bands as in the case of the *cis*-$[PtCl_2(MeCN)_2]$ reported by Rochon *et al*[14], one due to the symmetrical stretch, and the other due to the asymmetrical stretch of the *cis*-MCl_2 moiety. The *trans* and *cis* ν(M-Cl) bands can be easily assigned because of their strong intensity. Complexes with both bridging halides and terminal halides (see Figure 6.2) exhibit three bands at low frequency as mentioned by Alkins *et al*[15].

Metal halides have been extensively used as reactants in various solvents. Faraglia *et al*[16,17] have reported the synthesis of complexes of palladium and platinum derivatives of dithioesters and N-alkyl-O-ethylthiocarbamates using metal halides as reactants,. In the case of dithioesters the metal halide was suspended in a minimum volume of benzene and stirred overnight affording reaction products with the general molecular formula of $[PdX_2L]$ (X= Cl, Br). The complexes were characterised as having *cis* square-planar and a halide bridged square-planar geometry respectively by the number of bands exhibited in their infrared spectra at low frequency. Reactions in a 1:2 molar ratio involving N-alkyl-O-ethylthiocarbamates and platinum(II) halides in diethyl ether gave $[PtXL_3]X$ (X= Cl, Br)[16], which reacted slowly with further platinum(II) halide to form the yellow insoluble 1:2 adduct, $[PtX_2L_2]$. An adduct with the general molecular formula $[PdL_4]X_2$ was also prepared in a 1:4 molar ratio in dry benzene.

Demertzi *et al*[18] also used halides of platinum and palladium to prepare complexes of benzothiazoles. The reactions were performed in a 1:1 and 1:2 molar ratio, dissolving the metal halide in a 0.5N HCl solution with gentle heating, followed by the addition of the ligand dissolved in aqueous 50% acetic acid. The mixture was stirred at 80°C for ten minutes, then at room temperature for 1 hour, producing separation of the products formulated as $[MX_2L_2]$ and $[MX_2L]_2$ (M= Pd, Pt). Strong to medium intensity bands were assigned to $\nu(M\text{-}X_t)$ stretching for the *cis* and *trans* complexes at about 325 cm^{-1} [16-18]. Also a medium to weak intensity band was assigned in the same range to the $\nu(M\text{-}X_b)$ stretching frequencies for the bridged complexes. Other researchers[19,20] found medium to weak intense bands assigned to ν(M-X) terminal and bridging halides for complexes of palladium(II) and platinum(II) with $Ph_2P(CH_2)_nPPh_2$ (n = 1, 2 or 3), benzimidazole and benzothiazole ligands. However, Cornock *et al*[21] have reported a strong band at 300 cm^{-1} assigned to the bridging chloride complex $[PdCl(S_2CNEt_2)]_2$.

In the current work the halides of platinum(II) and palladium(II) were first completely dissolved in hot acetonitrile, before the addition of the ligand dissolved in the appropriate solvent. The ligand solution was prepared a few minutes before mixing the reactants. Presumably the starting material for the reactions involving $TPGH_2$ and $DPGH_3$ as ligands was the complex *cis*-$[PtCl_2(NCMe)_2]$, the product of reaction between $PtCl_2$ and acetonitrile, or *trans*-$[PdCl_2(NCMe)_2]$ in the case of $PdCl_2$. *Cis*-palladium(II) complexes with monodentate ligands undergo easy isomerization to the *trans* isomer because of the greater thermodynamic stability of *trans* palladium complexes[13,22].

The stoichiometry of the reactions in the current work was 1:1, which led to reaction products with a general molecular formula of $[M_2Cl_4L_2]$ (M= Pd, Pt; L= $TPGH_2$, $DPGH_3$)(see Table 6.2). The infrared spectrum at low frequency exhibited a single medium band about 325 cm^{-1}, which was assigned to the ν(M-Cl) by reference to literature data for M-Cl complexes[7]. Figure 6.3 shows some possible structures for $[M_2Cl_4L_2]$ complexes.

The structure **III** and **IV** should exhibit a single strong band due to the *trans* chloride atoms and according to the infrared data in Table 6.2 for the complexes of general formulation [$M_2Cl_4L_2$] (M= Pd, Pt; L= $TPGH_2$, $DPGH_3$) this possibility has to be excluded since only medium to weak bands were exhibited at low frequency. Also, the conductivity measurements (see Table 6.3) did not agree with the structure III since the complexes are 2:1 electrolytes. The infrared data at low frequency (see Table 6.4) and the conductivity measurements (see Table 6.3) suggests the structures I and II as the closest possibilities to represent the complexes formulated as [$M_2Cl_2L_2$]2Cl.

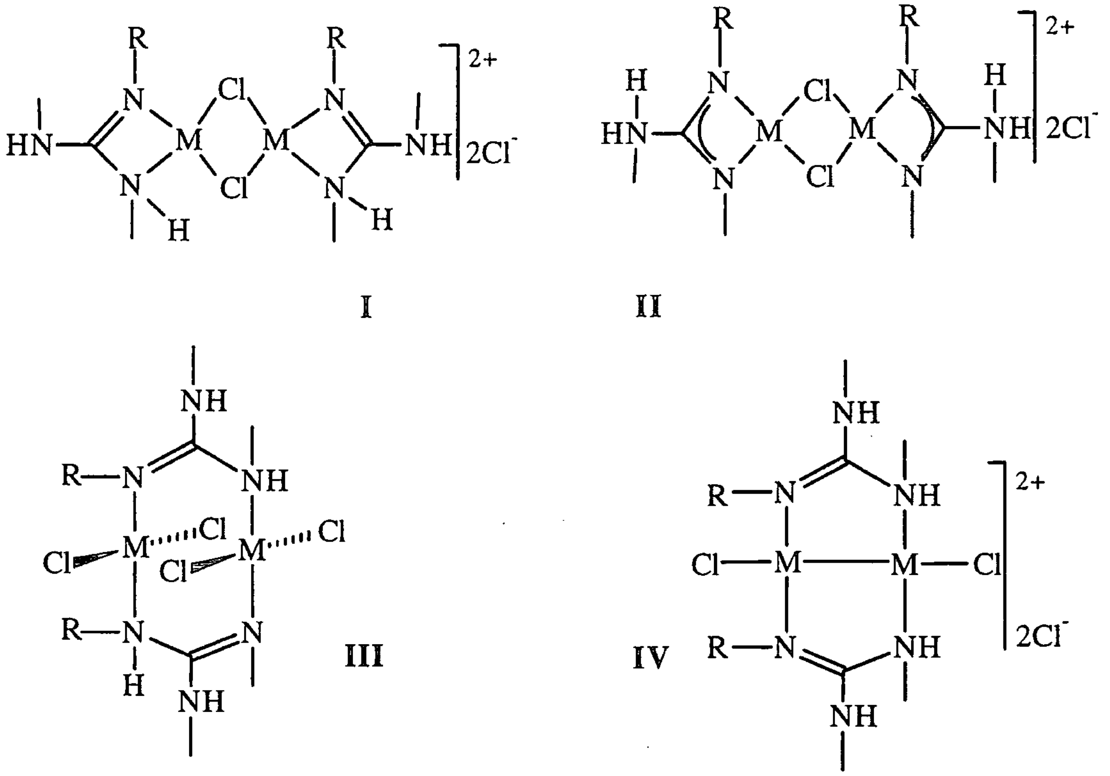
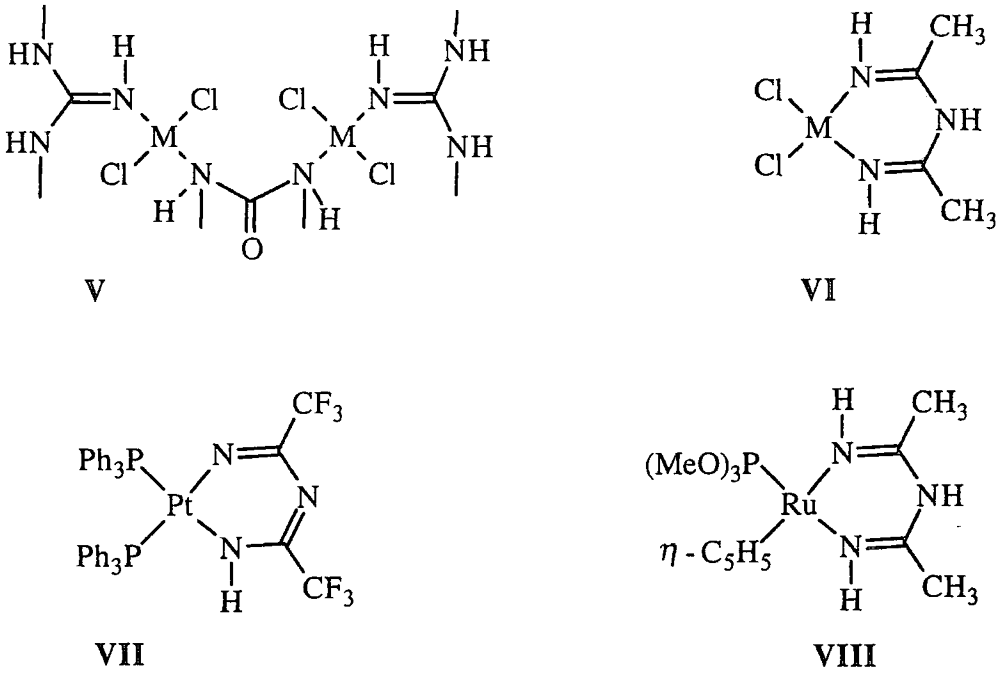


Figure 6.3 Possible structures for [$M_2Cl_4L_2$] (M=Pd, Pt; L=$TPGH_2$; $DPGH_3$)
R= H, Ph

The reaction involving $PtCl_2$ and $DPGH_3$ (*syn*-1,2-diphenylguanidine) apparently takes a different chemical pathway in the presence of water from the atmosphere, the final products being identified as having the molecular formulae [$Pt_2Cl_4(DPGH_3)_2(PhNHCONHPh)$] and [$PtCl_2(NHC(Me)NHC(Me)NH)$]. The infrared for the latter complex exhibits a strong double ν(M-Cl) (see Table 6.2) band typical for the *cis*-$[MCl_2L_2]$ complexes of transition metals. The former complex, which contains diphenylurea in its composition according to the ^{13}C NMR data and the infrared spectrum in the range of 1660 to 1600 cm^{-1}, also exhibited a medium band assigned to ν(M-Cl) at low frequency. Similar complexes to *cis*-$[PtCl_2(NHC(Me)NHC(Me)NH)]$, prepared in this work, have been reported by Bland *et al*[23] and Robinson *et al*[24] for platinum and ruthenium. In these complexes, X-ray diffraction studies have shown the metal atom bonded to the nitrogen atoms of the ligand in a six membered ring, together with two triphenylphosphines in *cis* positions to the metal (structures **VII** and **VIII**; Figure 6.4). The structures **V** and **VI** (Figure 6.4), represent possible structures for the products $[Pt_2Cl_4(DPGH_3)_2(PhNHCONHPh)]$ and $[PtCl_2(NHC(Me)NHC(Me)NH)]$ respectively, prepared in this work. Complexes **VII** and **VIII** also exhibited strong bands assigned to ν(C=N) and weak bands assigned to ν(N-H) as found in the present work for $[PtCl_2(NHC(Me)NHC(Me)NH)]$, complex **VI** (Figure 6.4). For $[Pt_2Cl_4(DPGH_3)_2(PhNHCONHPh)]$, complex **V** (Figure 6.4), the observed medium intensity of the band assign to ν(Pt-Cl) is not as intense as that expected for *trans*-MCl_2 groups. Once this complex is separated in the solid state it does not redissolve in strongly polar solvents such as nitromethane, and therefore no conductivity data were collected for this complex.

The complex **VI** was not soluble in acetonitrile, dichloromethane and other solvents such as water, even on warming. The formation of this type of complex occurred only when $PtCl_2$ was used as the starting material. The formation of the *trans* or *cis*-$[PtCl_2(NCMe)_2]$ as intermediates of the reaction, helps to explain the reaction leading to the products **V** and **VI**. Stephenson *et al*[25] have reported in 1962 a reaction between $[PtCl_2(NCMe)_2]$ and an excess of ammonia, which produced an ionic complex which was characterised by X-ray diffraction as having two ammonia groups in *trans* position to the metal with two acetamidines bonded to the metal through the imine nitrogen atoms. The complex **VI**, obtained in this work, suggests the formation of ammonia as a product of hydrolysis during the preparation involving $PtCl_2$ and the ligand $DPGH_3$ in hot acetonitrile. Hydrolysis of imines RC=NH to produce carbonyl and amine groups is well established in organic chemistry[26].



V

VI

VII

VIII

Figure 6.4 Possible reaction products from $[PtCl_2(NCCH_3)_2]$ and $DPGH_3$ (V, VI) and relevant structures from the literature (refs. 23 and 24).

Allaf *et al*[4] have reported studies of Pt(II) and Pd(II) complexes with N,N-disubstituted thioureas (1:1 molar ratio) as ligands. According to Allaf *et al* many attempts were tried to react the urea analogues RNHC(O)NHR (R = Ph) with K_2MCl_4 (M = Pd or Pt) in ethanol to produce $[MCl_2L]_2$, but the experiments were not successful. The thiourea complexes prepared by Allaf *et al* were non-electrolytes, had terminal ν(M-Cl) bands at about 300 cm^{-1} of medium intensity, and had ν(M-N) absorptions at about 520 cm^{-1}.

Considering the chemistry related to tautomerism of nitrogen ligands, such as amidines, $DPGH_3$ has three tautomeric forms in equilibrium according to Clement *et al*[27]. One of these tautomers which may give an important contribution in releasing ammonia into the reaction system can be envisaged as shown in Figure 6.5 below.

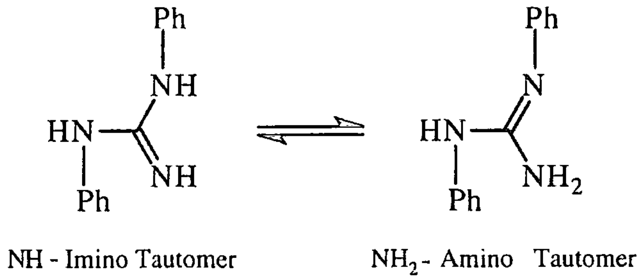


Figure 6.5 Possible tautomeric equilibrium of $DPGH_3$

Some bonding aspects need to be considered about the attachment of diphenylguanidines to metals, and their subsequent hydrolysis. Firstly, the metal may bind $DPGH_3$ through the imine nitrogen since this nitrogen is the most basic nitrogen towards the metal centre. Secondly, solvent water[13] or atmospheric water may take part in the hydrolysis of the C=N bond. Thirdly, the ammonia produced in the medium would be free to react with the unreacted starting material *cis*-$[PtCl_2(NCMe)_2]$. Two possible reaction pathways for the liberation of ammonia into the system can be envisaged as shown in Figure 6.6 below.

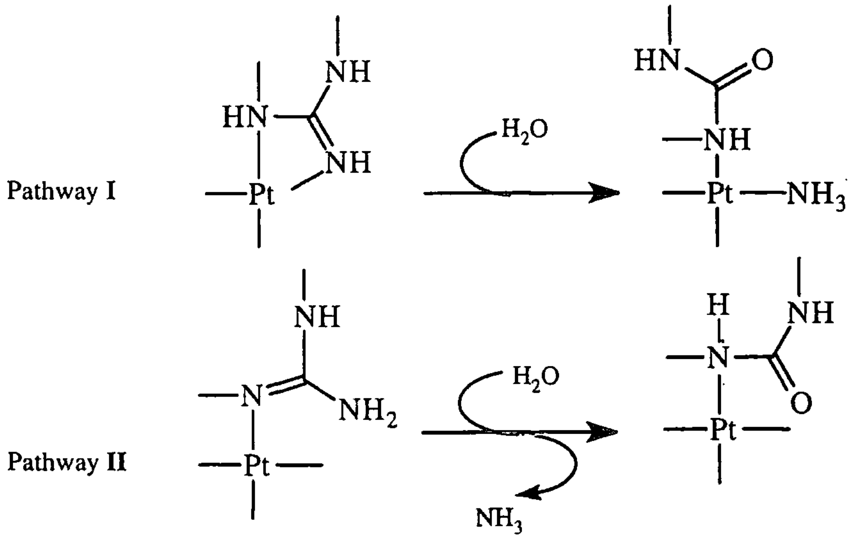
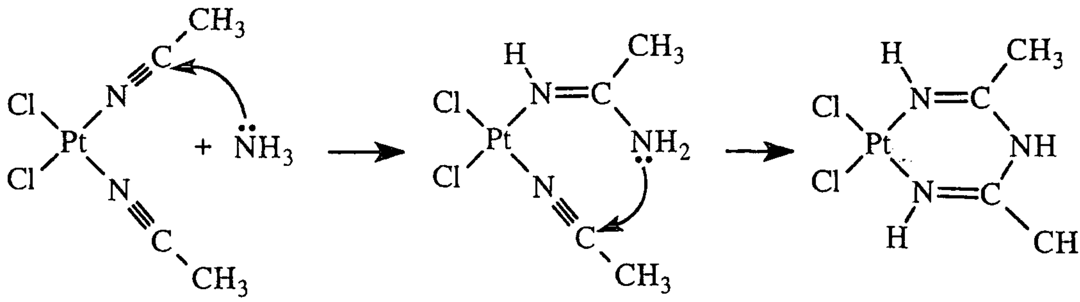


Figure 6.6 Nucleophilic attack of water towards coordinated $DPGH_3$

The pathway **II** suggested that the amino tautomer of the ligand $DPGH_3$ would drive the reaction towards the products since free ammonia would be released into the system. However, the pathway **I** could also release ammonia depending on the *trans effect* of acetonitrile, the chloride groups or the ligand $DPGH_3$. A mechanism that can explain the formation of **VI** in Figure 6.4 is shown below. Stephenson *et al*[25] have reported a nucleophilic attack at the carbon of the acetonitrile for the reaction of $[PtCl_2(NCMe)_2]$ and excess ammonia. Barker *et al*[28] have also reported a reaction of lithio-benzamidine with $[PtCl_2(NCMe)_2]$ in diethyl ether with similar results involving nucleophilic attack at the carbon of the coordinated nitrile to form $[Pt(HNC(Ph)NC(Ph)NH)_2]$. A similar reaction sequence can be envisaged here for the reaction involving platinum(II) and NH_3, derived from $DPGH_3$.

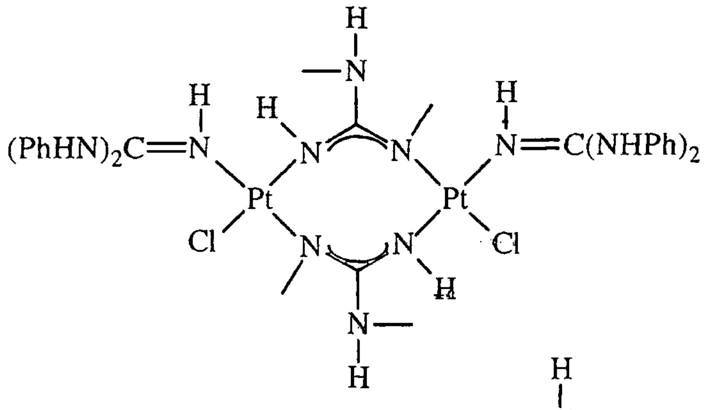


The compounds $[MCl_2(NCPh)_2]$, MCl_2 and K_2MCl_4 {M = Pd, Pt) have been used as starting material in reactions involving amidines and lithio-amidines. Dimeric, monomeric and oligomeric palladium derivatives of lithio-amidines have also been studied by Barker *et al*[29-31]. The crystal structure of the complex, $[Pd(p\text{-}MeC_6H_5NC(Me)NC_6H_5Me\text{-}p)_2]$ for instance, shows the nitrogen atoms of the acetamidine bonded symmetrically to the palladium atom as a bidentate ligand. Dimeric and monomeric nickel complexes with amidino-groups were identified in the solid state as well as in solution, in contrast with platinum complexes which were monomeric in the solid state and in solution. Reactions involving free amidines and $[PdCl_2(NCPh)_2]$ as starting material, in a 2:1 stoichiometry form complexes with a general molecular formula of $[PdCl_2(amidine)_2]$.

In the current work the complex $[PtCl_2(NCPh)_2]$ reacted with $DPGH_3$ in hot toluene in a 1:2 molar ratio to form complexes formulated as $[Pt_2Cl_4(DPGH_3)_3]$ and $[Pt_2Cl_2(DPGH_2)_2(DPGH_3)_2]$ (see Table 6.2). The product $[Pt_2Cl_2(DPGH_2)_2(DPGH_3)_2]$ exhibited in its infrared spectrum at low frequency a medium band assigned to the ν(Pt-Cl) stretching frequency. The conductivity measurements for this complex were consistent with a 1:2 electrolyte (see Table 6.3). In addition, the product was not soluble in toluene even when the system was hot. No one structure is consistent with the presence of platinum-chloride bonds and the complex being a 1:2 electrolyte. However, the data are explained by the complex having structure **IX** (Figure 6.7) in the solid state, but structure **X** in solution. Chloride ions are considered to be displaced from the platinum complex, **IX**, in nitromethane solution, a process which has been observed before[32], to form complex **X**, a 1:2 electrolyte.

$$\begin{tikzcd}
\underset{\textbf{IX}}{[Pt_2Cl_2(DPGH_2)_2(DPGH_3)_2] + \text{solvent}(S)} \arrow[r, shift left] & {[Pt_2(DPGH_2)_2(DPGH_3)_2(S)_2]^{2+}\ 2Cl^-} \arrow[l, shift left] \arrow[dl] \\
\underset{\textbf{X}}{[Pt(DPGH_2)_2(DPGH_3)_2]^{2+} + 2Cl^-} &
\end{tikzcd}$$

Possible displacement of $[DPGH_2]^-$, in place of Cl^-, is considered very unlikely.



IX

X

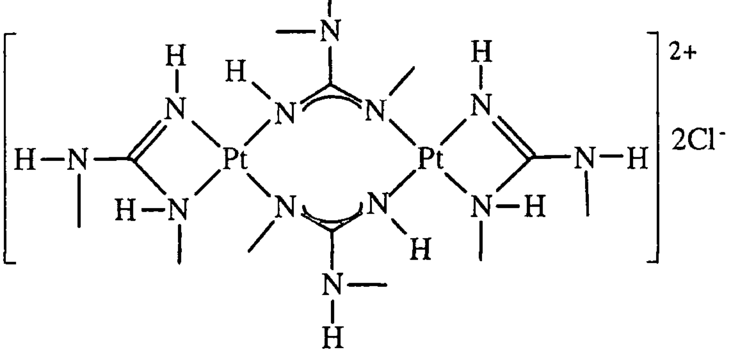
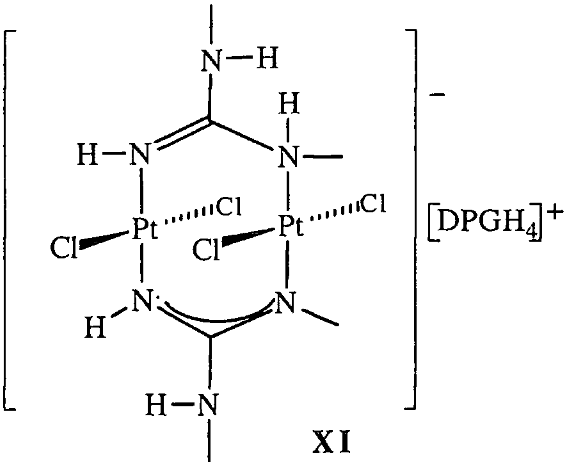


Figure 6.7 Possible structures for the complex [$Pt_2Cl_2(DPGH_2)_2(DPGH_3)_2$]

The product [$Pt_2Cl_4(DPGH_3)_3$] exhibited a strong band at low frequency which was assigned to ν(Pt-Cl) and a broad band at high frequency in the region of 3100 to 3300 cm^{-1}, similar to the ν(N-H) of hydrochlorides (Table 6.4). The bands at high frequency suggest an ionic product. The conductivity measurements for this product (see Table 6.3) are compatible with a 1:1 electrolyte in nitromethane solution. The combined results suggest the structure **XI**, shown in Figure 6.8 below, as the most probable structure.

The loss of HCl from the reaction of [$PtCl_2(NCPh)_2$] with $DPGH_3$ to form [$Pt_2Cl_2(DPGH_2)_2(DPGH_3)_2$] can be explained by the strong intermolecular hydrogen bonding, which according to Demertzi *et al*[18] would help the elimination of HCl upon heating in solution. Therefore, by analogy with amidines[33], it is not surprising that guanidines have this peculiar chemical property of elimination of hydrogen chloride in hydrocarbon solvents.

The complex $[PdCl_2(COD)]$ was also used in the current work as a starting material, and reactions using a similar starting complex are illustrated by the work of Guimerans *et al*[34], who synthesised *cis*-$[PtCl_2(dapm)]$ by reacting 1 mol of $[PtCl_2(COD)]$ with 2 mol of $(Ph)_2AsCH_2P(Ph)_2$ in dichloromethane, followed by precipitation of the complex with ether.



XI

Figure 6.8 A possible structure for the product $[Pt_2Cl_4(DPGH_3)_3]$

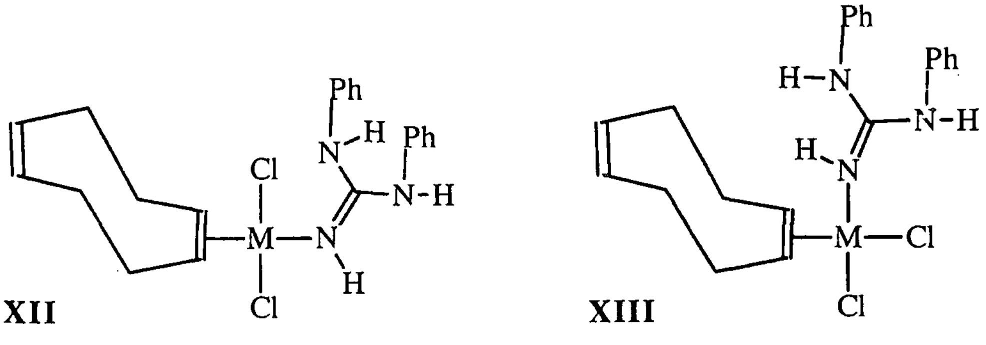
Dimerization and oligomerization were observed by Wood *et al*[35] in reactions involving the starting material $[PdCl_2(COD)]$ and 2,6-bis(diphenylphosphino)pyridine (molar ratio 1:1) in dichloromethane at room temperature. According to the author mixtures were detected by ^{31}P NMR after 20 minutes of mixing the reactants when platinum, instead of palladium, was the metal centre. The product was slowly isolated over a period of days from solution, apparently in the form of a variety of polymers. Dimers of platinum were characterised by X-ray diffraction. Other workers[36] have studied related systems using the same type of starting material, $[PtCl_2(COD)]$, with $Ph_2PCH_2CH_2OMe$ and $Ph_2PCH_2CH_2NMe_2$ in a molar ratio 1:2. A *cis*-complex formulated as $[PtCl_2(Ph_2PCH_2CH_2OMe)_2]$ was detected by ^{31}P NMR, and $[PtCl(Ph_2PCH_2CH_2NMe_2)_2]Cl$ was precipitated with ether.

Cornock *et al*[21] have reported a pale yellow platinum complex from the reaction of $Na[S_2CNEt_2].3H_2O$ and $[Pt(COD)Cl_2]$ in dichloromethane and formulated as $[Pt(S_2CNEt_2)_2(COD)Cl]$. This complex was prepared using a 1:1 molar ratio and was too insoluble for NMR spectroscopy. Its infrared spectrum exhibited a band at 310 cm^{-1} which was assigned to a ν(Pt-Cl) stretching mode. The complex was suggested by Cornock *et al*[21] to have the 1,5-cyclooctadiene as a bridged ligand.

In the current work involving $[PdCl_2(COD)]$ as starting material and $TPGH_2$ or $DPGH_3$ as ligands, reactions were investigated in a molar ratio 1:1 at room temperature or at a slightly higher temperature in acetonitrile or in a mixture of solvents. Complexes of the type $[PdCl_2(COD)(guanidine)]$ (guanidine=$TPGH_2$, $DPGH_3$) were isolated (see Table 6.1). For the Pd/$TPGH_2$ complex, the infrared spectrum (Table 6.4) has a band at 330 cm^{-1}, a typical ν(PdCl) stretching frequency for a *trans* complex because of its strong intensity. The conductivity measurements for the complex given in Table 6.3 indicate that it is a non-electrolyte, in keeping with coordination of both chloro-ligands to the metal. The COD and $TPGH_2$ ligands act as 2-electron donor ligands in *trans* positions, thereby minimising steric interactions. The ^1H NMR spectrum contains signals at 2.37 and 6.30 ppm which indicate that the 1,5-cyclooctadiene ligand is attached to the metal. Thus the ligand $TPGH_2$ displaces one attachment of the 1,5-cyclooctadiene from the metal in acetonitrile.

Inspection of the infrared spectrum of the reaction product $[PdCl_2(COD)DPGH_3]$ did not establish clearly the stereochemistry of the product. A medium band at 315 cm^{-1} may be assigned to ν(Pd-Cl) for *trans* chlorides but another weak band at 295 cm^{-1} makes for uncertainty. It seems that both *cis* and *trans* complexes may be formed in the reaction. The low frequency of the ν(Pd-Cl) absorption at 295 cm^{-1} for $[PdCl_2(COD)DPGH_3]$ may relate to the *trans* 1,5-cyclooctadiene ligand because a large difference in electronegativity of atoms in *trans* positions shifts the band to low frequency. Although the absorption position at 295 cm^{-1} is in the range normally found for terminal chlorides, its low intensity is unusual[7]. Figure 6.9 shows the two structures for the [$PdCl_2$(COD)$DPGH_3$] complex.

Taking account of the changes in pK_a values when replacing N-H groups by NPh groups etc. of guanidine, $NH_2C(NH)NH_2$, $DPGH_3$ is expected to be a better base than $TPGH_2$, and to be more reactive in Lewis acid/base reactions. $DPGH_3$ is expected to be a stronger ligand than $TPGH_2$ in coordination to metals in their usual oxidation states. An important consequence of strong coordination is polarisation of the ligand, which may cause (i) an increase in the acidity of N-H protons, and their ready loss from the ligand, and (ii) increased susceptibility of the ligand towards nucleophilic attack. Conversion of guanidines to guanidino-anion is a result of (i), whereas an increase in susceptibility towards attack by water and the generation of the urea, PhNHCONHPh, is a consequence of (ii). The differences in basicities between $DPGH_3$ and $TPGH_2$, provide an explanation for the ready degradation of $DPGH_3$ to the corresponding urea, in the presence of platinum(II) but not of $TPGH_2$.



Trans *Cis*

Figure 6.9 Structures for [$PdCl_2$(COD)($DPGH_3$)].

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Conclusion

Guanidines are electron rich molecules which, in principle, can bind to metal centres acting as a 2, 4 or 6-electron donors, and the guanidino-group can act as a 1, 3 or 5-electron donor in metal complexes. When bound as a chelate ligand, 4-membered rings are formed, so some strain exists in this mode of attachment. For guanidines this may be relieved to a small extent by loss of hydrogen to form the guanidino-ligand.

In this work the coordination properties of two guanidines, $TPGH_2$ and $DPGH_3$, have been explored in complexes having metals in low oxidation states, e.g.. manganese(I), chromium(0), molybdenum(0), tungsten(0), and in normal oxidation states, e.g.. palladium(II), platinum(II). Carbon monoxide is displaced from chromium, molybdenum and tungsten carbonyls in the presence of guanidines, leading to products which have the guanidine or the guanidino-group bonding in a monodentate, bidentate or bridging bonding modes. Guanidines, adopting different bonding modes, have been found attached to the same metal centre.

The complex $[Mn(Br)(CO)_4(TPGH_2)]$ is an example in which the guanidine ligand acts as a 2-electron donor. Guanidine acting as a 4-electron donor was found for the palladium complexes $[Pd_2Cl_4(TPGH_2)_2]$ and $[Pd_2Cl_4(DPGH_3)_2]$. In this work no examples of complexes have been synthesised in which the guanidine ($TPGH_2$ or $DPGH_3$) is known with certainty to act as a 6-electron donor, though materials formulated as "[Cr(TPGH)]" and "[Mo(TPGH)]" have been isolated.

Complexes were prepared using several reaction conditions, involving changes in parameters such as the stoichiometry, temperature, solvent polarity etc. Protonated $TPGH_2$ was observed in various reactions and its formation depended of the parameters mentioned above. Loss of hydrogen as HBr or HCl into the reaction mixture occurred from $TPGH_2$ complexes, converting the ligand into the guanidino-group which adopts bidentate or bridging bonding modes towards the metal centres.

Loss of HBr was observed in the preparation of complexes such as $[Mn(TPGH)(CO)_4]$, and $[Mo(\eta\text{-}C_5H_5)(TPGH)(CO)_2]$. These complexes have the guanidino group acting as a 3-electron donor in a bidentate bonding mode. No examples of complexes having the guanidino-group acting as 5-electron donor were observed.

The substitution of carbon monoxide in $[Mn(X)(CO)_5]$ and $[Mo(Cl)(\eta\text{-}C_5H_5)(CO)_3]$ complexes by the guanidines were fast reactions to produce the complexes $[Mn(Br)(CO)_3(TPGH_2)_2]$ and $[Mo(\eta\text{-}C_5H_5)(TPGH)(CO)_2]$ Interestingly, the preparation of the latter complex proceeds through the intermediate $[Mo(Cl)(\eta\text{-}C_5H_5)(TPGH)(CO)_2]$ and the loss of hydrogen halide occurs much faster for this complex than for the manganese complexes. Therefore the conversion of $TPGH_2$ into TPGH is highly influenced by the strength of the metal/ Lewis base interaction, in association with the reaction conditions. The effect of coordination of guanidines to metal centres, on the chemistry of guanidines, is further illustrated by the increased susceptibility of $DPGH_3$ to nucleophilic attack. Traces of water hydrolyse the ligand to form the corresponding urea complex, with loss of ammonia, which itself acts as a nucleophile towards acetonitrile bound in the starting complex, $[PtCl_2(NCMe)_2]$. The complex $[PtCl_2(HNC(Me)NHC(Me)NH)]$ results. Decomposition due to air/ moisture was a problem which led to low yields, and formation of urea complexes for example. Guanidines seem to be activated by the transition metals towards nucleophilic attack due to the electron donation to the metal.

Many of the reactions involving guanidines proved to be complex, and gave mixtures of products. The susceptibility of coordinated guanidines towards nucleophilic attack also produced difficulties because the complexes tended to degrade on storage and in the presence of moisture. Coordinating solvents were generally used for the reactions and these themselves were regarded as potential nucleophiles, since solutions even at low temperatures had a low storage life. Attempts to obtain products by recrystallisation from polar solvents, involved many filtrations of the solutions to remove decomposition materials separating over a matter of days. This area of chemistry is quite complex and produces difficulties in obtaining pure materials by recrystallisation. Complexes often undergo extensive decomposition in solution. Attempts to form crystals suitable for X-ray crystallography studies were not successful.

Appendix A: Starting Complexes, Lithium Reagents and Physical Methods used.

A. Preparation and Characterisation of Starting Complexes

1. Reaction of Hexacarbonylmolybdenum(0) with Cycloheptatriene

Hexacarbonylmolybdenum(0) (3.00g/ 14.7 mmol) was put into a flask which contained 60 ml of di-n-butylether under a nitrogen atmosphere. Freshly distilled cycloheptatriene (1.4g /15 mmol) was added to the mixture, which was heated at the reflux temperature over twelve hours. The solvent was removed *in vacuo* from the dark red solution and the brown residue extracted with petroleum ether (60-80°). Some unreacted hexacarbonylmolybdenum(0) appeared during the evaporation of the solvent. A dark red crystalline material $[Mo(CO)_3(C_7H_8)]$ separated after cooling the solution. Yield: 2.06g {66% based on $[Mo(CO)_6]$}. Cotton[1] and co-workers synthesised the same complex in refluxing n-octane for over 8 hours. The extraction of the brown residue was through a Soxhlet apparatus with n-pentane. The author[1] reported a 58% yield.[Found: C, 45.79; H, 3.07. $C_{10}H_8MoO_3$ requires C, 44.28; H, 2.95%]; IR absorptions: ν_{max}/cm^{-1}(Nujol mull) 1970s, 1910s and 1860s (CO); δ_C(100 MHz; $CDCl_3$; $SiMe_4$) 27 (1C, CH_2), 60 (2C, 1,6 CH), 97 (2C, 2,5 CH) and 102 (2C, 3,4 CH)ppm. This complex was also identified by Faller *et al*[2] using ^1H NMR.

2. Reaction of Cycloheptatrienetricarbonylmolybdenum(0) with Triphenylmethyl Tetrafluoroborate

The $[Mo(CO)_3(C_7H_8)]$ (1.5g/ 5.5 mmol) was dissolved in 10 ml of dry dichloromethane and a solution of $[Ph_3C][BF_4]$ (2.0g/ 6.0 mmol) was added to the solution by syringe at room temperature. An orange solid appeared inside the flask immediately. The suspension was stirred for a further fifteen minutes and the mixture filtered. The orange solid was washed twice (2 x 20ml) with dry dichloromethane before drying under reduced pressure. Red-orange crystals of $[Mo(\eta\text{-}C_7H_7)(CO)_3][BF_4]$ were obtained by recrystallisation of the orange solid from an acetone solution at 10°C. Yield: 1.38g {70% based on $[Mo(CO)_3(C_7H_8)]$}. [Found: C, 33.70; H, 1.91. $C_{10}H_7BF_4MoO_3$ requires C, 33.56; H, 1.97%]; IR absorptions: ν_{max}/cm^{-1}(Nujol mull) 2076s, 2027s and 2001s (CO); δ_H(100 MHz; $CDCl_3$; $SiMe_4$) 6.2 (7H, s, CH), δ_C(100 MHz; $CDCl_3$; $SiMe_4$) 116 (7C, CH), 156(3C, CO)ppm. Characterisation of this complex was reported by Harvey *et al*[3].

3. Reaction of Triphenylcarbinol with Fluoroboric Acid[4]

Triphenylcarbinol (4.5g/ 17 mmol), contained in a flask, was dissolved in about 45 ml of acetic anhydride by warming in a hot water bath (80-100°C). The flask was then cooled to 20°C and fluoroboric acid (4.5 ml / 38 mmol, 48%) was added, drop by drop. A yellow material started to precipitate when the acid was completely added to the solution. The mixture was left in an ice bath for 30 minutes to allow the yellow crystals to settle, which were then separated by filtration, washed with three portions (3 x 10ml) of cold dry, diethyl ether and dried under a nitrogen atmosphere. The product $[Ph_3C][BF_4]$ was identified by comparison of its IR spectrum with that of an authentic sample. Yield: 4.86g [80% based on Triphenylcarbinol].

4. Reaction of Hexacarbonylmolybdenum(0) with Cyclopentadienylsodium

Sodium metal (1.38g/ 60 mmol) was put into a flask under a nitrogen atmosphere. THF (150ml) was added, followed by freshly distilled cyclopentadiene (5.0g/ 75 mmol/ 14ml). The flask was covered with aluminium foil during the reaction between sodium metal and cyclopentadiene. A pink solution was formed after the sodium metal dissolved completely. Hexacarbonylmolybdenum(0) (13g/ 77 mmol) was then added to the pink solution against a counter current of nitrogen, and the mixture was heated to the reflux temperature for 15 hours, forming a yellowish solution. After cooling to room temperature the yellowish solution was treated with 8.0 ml of glacial acetic acid (6.3g/ 105 mmol/ 99.8%) and the mixture was left stirring at room temperature for a further two hours. The solvent was removed under reduced pressure and carbon tetrachloride (200ml) was added to the residue to produce a dark red solution. The dark red solution was then transferred to a separating funnel, and 200 ml of water added to remove the sodium acetate. After separation of the two phases, and drying of the organic solvent layer over calcium chloride, the solvent was removed from the dark red solution under reduced pressure. The solid was washed with dry hexane. Yield: 19g {90% based on $[Mo(CO)_6]$}. [Found: C, 34.37; H, 1.93. $C_8H_5ClMoO_3$ requires C, 34.25; H, 1.80%]; IR absorptions: $\nu_{max}/cm^{-1}(CCl_4)$ 2060s, 1990s and 1970s (CO); δ_H(100 MHz; $CDCl_3$; $SiMe_4$) (5H,s,6.4)ppm[5].

The preparation of the $[Mo(Cl)(\eta\text{-}C_5H_5)(CO)_3]$ involves a hydride[5,6] intermediate complex which forms by protonation of the metal in $[Mo(\eta\text{-}C_5H_5)(CO)_3]^-$ using acid. An improvement was achieved in the synthesis of $[Mo(Cl)(\eta\text{-}C_5H_5)(CO)_3]$ as follows. Firstly, an excess of acetic acid was added to the carbonylate salt in solution, and the mixed solvents removed *in vacuo*. The equilibrium in this situation favours the formation of the hydride complex. This procedure was found preferable to removal of the solvent prior to the addition of the acid. Secondly, the hydride complex is reacted with excess of carbon tetrachloride which was found to be the best chlorinating agent. It was a rapid reaction, and this solvent gave the product in solution. Consequently the product was easily separated from by-products such as sodium acetate which is insoluble in the solvent mixture.

5. Synthesis of *trans*-$[PdCl_2(NH_2Ph)_2]$ from K_2PdCl_4 Salt

K_2PdCl_4 (0.51g / 1.5 mmol) was dissolved in the minimum amount of water, and aniline (0.28g / 3.1 mmol) was then added at room temperature. A yellow solid separated out after a few minutes of stirring. The solid was removed by filtration in the air, and washed with water before drying. The product was identified by elemental analyses as $[PdCl_2(NH_2Ph)_2]$. Yield: 0.48g [85% based on K_2PdCl_4]. [Found: C, 39,65; H, 3.47; N, 7.55. $C_{12}H_{14}N_2Cl_2Pd$ requires C, 39.77; H, 3.86; N, 7.73%], ν_{max}/cm^{-1}(Nujol mull) 330s (Pd-Cl).

Trans-$[PtCl_2(NH_2Ph)_2]$ was prepared similarly using K_2PtCl_4 (0.51g / 1.22 mmol) and aniline(0.28g / 3.1 mmol). [Found: C, 31.58; H, 3.07; N, 6.02. $C_{12}H_{14}N_2Cl_2Pt$ requires C, 31.87; H, 3.12; N, 6.17%], ν_{max}/cm^{-1}(Nujol mull) 335s (Pt-Cl)

6. Synthesis of *trans*-$[PdCl_2(NH_2Ph)_2]$ from $PdCl_2$

Palladium(II) chloride (0.5g / 2.84 mmol) was mixed with dried acetonitrile (20ml) and the suspension was heated to about 80°C. After the metal compound dissolved completely, aniline (0.34g / 3.7 mmol) was then added to the hot solution. The reaction time was about 2 hours at the reflux temperature. After this time the solvent was removed in part *in vacuo*, and an orange-yellow material separated. Filtration gave an orange-yellow solid, which was washed with diethyl ether before drying *in vacuo*. On further evaporation of the solution under reduced pressure, more orange-yellow material was produced. After removal by filtration, it was washed with diethyl ether and dried. The product was identified as $[PdCl_2(NH_2Ph)_2]^7$. Yield: 0.76g [75% based on $PdCl_2$]. [Found: C, 39,75; H, 3.57; N, 7.65. $C_{12}H_{14}N_2Cl_2Pd$ requires C, 39.77; H, 3.86; N, 7.73%], v_{max}/cm^{-1}(Nujol mull) 330s (Pd-Cl).

7. Synthesis of *cis*-$[PtCl_2(NH_2Ph)_2]$

K_2PtCl_4 (0.51g / 1.22 mmol) was dissolved in the minimum amount of water/methanol, and aniline (0.28g / 3.1 mmol) added to the solution. The *cis*-platinum/aniline complex separated after a few minutes stirring at room temperature, but the mixture was stirred for a further 4 hours. The pale orange solid was then separated by filtration in the air and washed with diethyl ether before drying. The product was identified as $[PtCl_2(NH_2Ph)_2]$. Yield: 0.41g [75% based on K_2PtCl_4]. [Found: C, 31.68; H, 3.08; N, 6.10. $C_{12}H_{14}N_2Cl_2Pt$ requires C, 31.87; H, 3.12; N, 6.17%], v_{max}/cm^{-1}(Nujol mull) 345s, 330s (Pt-Cl).

Attempts were made to react the palladium(II) and platinum(II) complexes (prepared as in reaction 5, 6 and 7) with Cl_2CNPh but the reactions were not successful, and the preparation of complexes such as $[MCl_2(PhNHC(NPh)NHPh)]$ by this route was abandoned.

B. Lithium Reagents

All alkyl lithium reagents used were taken from previously opened containers available from commercial suppliers, i.e. Aldrich Chemical Company.

1. Titration Procedure

A flame dried, two necked, 50 ml Erlenmeyer flask containing a magnetic stirring bar and a few crystals of 1,10-phenanthroline was fitted with a B24 size, rubber serum cap and an appropriate glass vacuum tap. The flask was flushed with dry nitrogen gas and 10 ml of sodium dried toluene added by syringe through the septum and against a counter flow of nitrogen. The stirred solution was then charged with 5 ml of alkyl lithium solution, accurately measured by syringe, producing a deep red colour.

Using a 10 ml burette with the delivery section pushed through the septum, a one molar solution of secondary butyl alcohol in dry xylene was added dropwise until a sharp colour change from red to clean golden yellow was observed in the continuously stirred solution.

2. Synthesis of Lithio-amidines

N,N'-di-*p*-tolylbenzamidine (0.23g / 0.76 mmol) was dissolved in dry THF (15 ml) under a N_2 atmosphere. The solution was frozen in liquid nitrogen and butyllithium (0.049g/ 0.76 mmol; 1.6 M hexane sol.) was added. The mixture was allowed to warm to room temperature and a yellow solution was produced after one hour of stirring. The same reaction was achieved using monoglyme instead of THF. (*All the lithium amidine and guanidine derivatives were prepared using the same technique*).

C. Physical Methods Used

1. Infrared Spectroscopy

The samples were ground with Nujol and placed between CsI or KBr windows. The KBr and CsI discs were prepared by grinding the samples with dried KBr or CsI powder and subjected to pressure. The infrared equipment used was a PERKIN ELMER FTIR 1600 and also a PERKIN ELMER 580B.

2. Nuclear Magnetic Resonance Spectroscopy

The spectra were obtained in deuterated chloroform or deuterated acetonitrile. The spectrometers used were a BRUKER AC 250 and a VARIAN VXR 400S.

3. Conductivity Measurements

The samples were weighted into a graduated container of 25 ml volume to which nitromethane was added up to the mark. The solution was placed in a beaker of 25 ml and the conductivity read using a PTI-18 CONDUCTIVITY METER. The electrolytic cell used platinum electrodes.

4. Microanalysis

For microanalyses, the department services were used. The CHN analyses were performed using a CARLO ERBA EMAsyst 1106. The metal analyses were performed using a PERKIN ELMER 5000 atomic analyser and the halogen analyses by titration against silver nitrate for bromine or chlorine and against sodium hydroxide (0.02 N) for fluorine.

1. F. A. Cotton, J. A. McCleverty, J. E. White, R. B. King, A. F. Fronzaglia, and M. B. Bisnette, *Inorg. Synth.,* **28**, 45, (1990).
2. J. W. Faller, *Inorg. Chem.,* **19**, 2857, (1980).
3. P. D. Harvey, I. S. Butler, and D. F. R. Gilson, *J. Chem. Soc. Chem. Commun.,* **26**, 32, (1987).
4. *University of Durham 3H laboratory script,*
5. J. J. Eisch and R. B. King, Eds.,*"Organometallic Syntheses"*, vol. 1, (Academic Press, New York, 1965).
6. J. Kleinberg, Ed.,*"Inorganic Synthesis"*, vol. 7, (McGraw-Hill Book Company, Inc., New York, 1963).
7. J. R. S. Maia and C. A. L. Filgueiras, *Transition Met. Chem.,* **17**, 228, (1992).

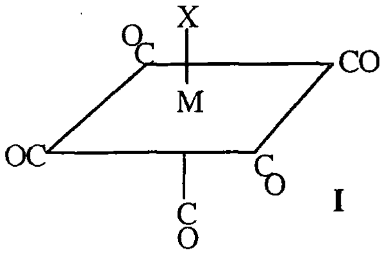
Appendix B: Group Theory and Metal Carbonyls.

A. Infrared Spectra and Molecular Structure

Group theory and molecular symmetry have found wide application in predicting the C-O stretching vibrations of metal carbonyls. They have application mainly in stereochemical problems, and by considering the various arrangements of the ligands and the symmetry of the molecules concerned, the expected infrared spectrum in the carbonyl stretching region can be determined. A comparison of the actual spectrum with that theoretically derived for each isomer leads to the true structure of the molecule.

By the choice of a certain system of coordinates to define the molecule, it is possible to consider certain vibrations of the molecule separately. When cartesian coordinates of the individual atoms are used, the entire motion of the molecule is considered, including both the stretching and bending modes of vibration plus the modes of translation and rotation. However, in the study of metal carbonyl complexes, for example, it is only the stretching modes of the C-O bonds which are of interest, and through the use of the C-O bond vectors themselves as coordinates, the motion of these groups along the axes of these bonds can be considered alone. All other motion of the molecule including the bending modes of the C-O groups is disregarded, so that the molecular vibrations deduced by the use of group theory and molecular symmetry are the stretching modes of the C-O groups only.

In describing the procedure, the manganese pentacarbonyl halides will be used to illustrate each step. These compounds have the following elements of symmetry: E C_4 $2\sigma_v$ $2\sigma_d$ which can be deduced from the structure **I** below.



I

The pentacarbonyl halides belong, therefore, to the C_{4v} point group, associated with which are the following symmetry operations: E $2C_4$ C_2 $2\sigma_v$ $2\sigma_d$. When the symmetry operations are applied to the molecule, the various carbonyl groups, and, therefore, the coordinates will change position in space, and in a similar way to the cartesian method, all these transformations can be represented by a matrix. Since it is only the diagonal element of this matrix which is characteristic of the operation, all coordinates which transform into other coordinates contribute zero to the character of the operation. In other words, coordinates (or carbonyl groups, for example), which do not move, contribute 1, and those that do move contribute zero to the character. The procedure, therefore, involves simply the counting of the number of carbonyl groups, which remain unmoved with respect to the original C-O axes, under the symmetry operations of the particular point group. By determining the character of the matrix for each symmetry operation, the reducible representation Γstr. is obtained, which is reduced, with the aid of character tables, to a sum of irreducible representations. Each irreducible representation having a mode of translation as its basis will be infrared active, and so give rise to an absorption band.

For the manganese pentacarbonyl halides, therefore, by applying the symmetry operations of the C_{4v} point group, the following reducible representations Γstr., are obtained as shown in Table B1.

Table B1

	E	C_2	$2C_4$	$2\sigma_d$	$2\sigma_v$
Γstr.	5	1	1	1	3
Γstr.	$2A_1 + E + B_2$				

In other words, under the C_2 symmetry operation, only one carbonyl group remains unaltered, and under σ_v, reflection in a plane of symmetry across the diagonal in structure **I**, three carbonyl groups are unchanged. The reducible representation is then reduced by inspection, using the character table for the C_{4v} point group, which is reproduced[1,2] in Table B2, to the sum of the irreducible representations, $2A_1 + E + B_2$. Only A_1 and E have modes of translation as their bases, so for the pentacarbonyl halide compounds three infrared active stretching vibrations are predicted ($2A_1 + E$).

Table B2

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$	
A_1	1	1	1	1	1	T_z
A_2	1	1	1	-1	-1	R_z
B_1	1	-1	1	1	-1	
B_2	1	-1	1	-1	1	
E	2	0	-2	0	0	$(T_x, T_y); (R_x, R_y)$

The intensity of the bands cannot be obtained from group theory, but the relative intensity can be assessed from a consideration of the particular vibrations involved, which are illustrated for the pentacarbonyl halides in Figure B1.

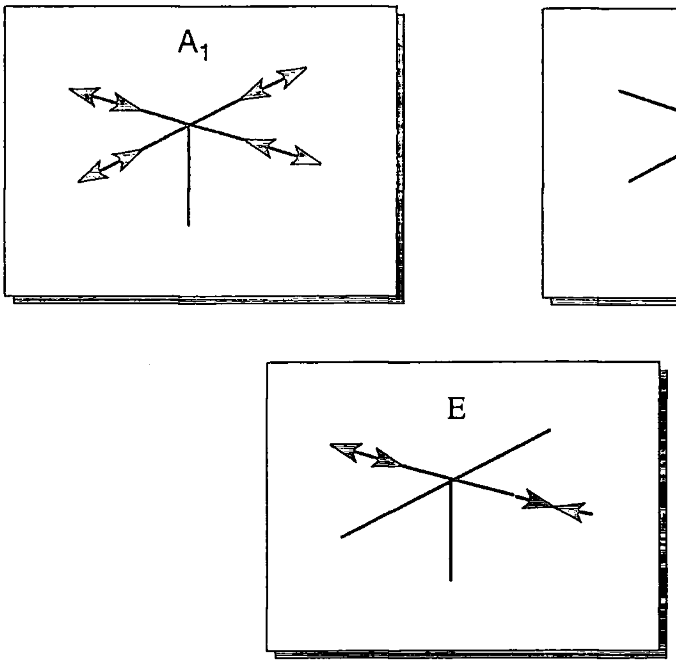
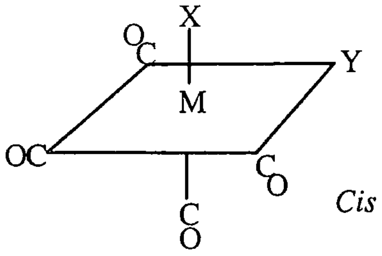


Figure B1 Theoretical vibrational modes for the pentacarbonyl halides

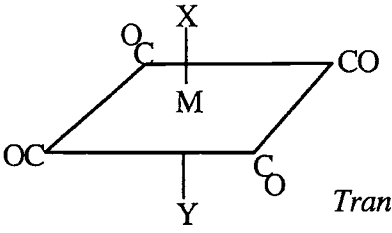
The two A_1 vibrations are made up from the stretching mode of the unique carbonyl group and the symmetrical breathing mode of the other four. Associated with the former vibration is a significant dipole moment change, hence the absorption band in the infrared spectrum will be intense. However the latter vibration is almost forbidden, but can have a small intensity due to the non-coplanarity of the radial carbonyl groups. However, since the two vibrations under discussion are of the same symmetry type, they can enter into Fermi resonance with each other, and some of the intensity of the strongly allowed vibration can be transferred to the other. Orgel[3] estimates that the strongly allowed E vibration will account for about 80% of the total intensity of absorption, whilst the A_1 vibration involving the stretching mode of the unique carbonyl group will account for almost all of the remaining 20% of the intensity. For compounds of the type [$M(X)(CO)_5$] (X= halide groups), three bands are therefore expected, one of very strong intensity, one of slightly less intensity, and a third of much weaker intensity. The majority of compounds of the type $[M(X)(CO)_5]$ show the three predicted fundamental absorption bands. As the size of the metal is decreased, or the size of group X increased, the weak band increases in intensity. This band, which is due to the symmetrical stretching mode of the four *cis* carbonyl groups, cannot be observed if the four groups are coplanar, but appears and increases in intensity as the repulsive forces between the halide group and the four *cis* carbonyl groups become stronger, and force the four carbonyl groups out of the plane. Consequently, the growth in intensity of the weak band is in the directions Re ---> Mn and Cl ---> I.

B. Application to Compounds of the Type $[M(X)(Y)(CO)_4]$

Two structures are possible for a molecule of this form, one with the groups X and Y in *cis* positions to each other, and the other with the ligands in *trans* positions, as shown below.



Cis



Trans

Four stretching frequencies are predicted for the *cis* but only two for the *trans* structure. The predicted vibrations for the *cis* isomer are shown in Figure B2. The A' vibration, i, will be of low intensity because of the small dipole moment change, but the other three vibrations will be high intensity. However, the weak intensity band may become more intense by entering into Fermi resonance with the other vibrations of the same symmetry species, but one absorption band will always be weaker than the others.

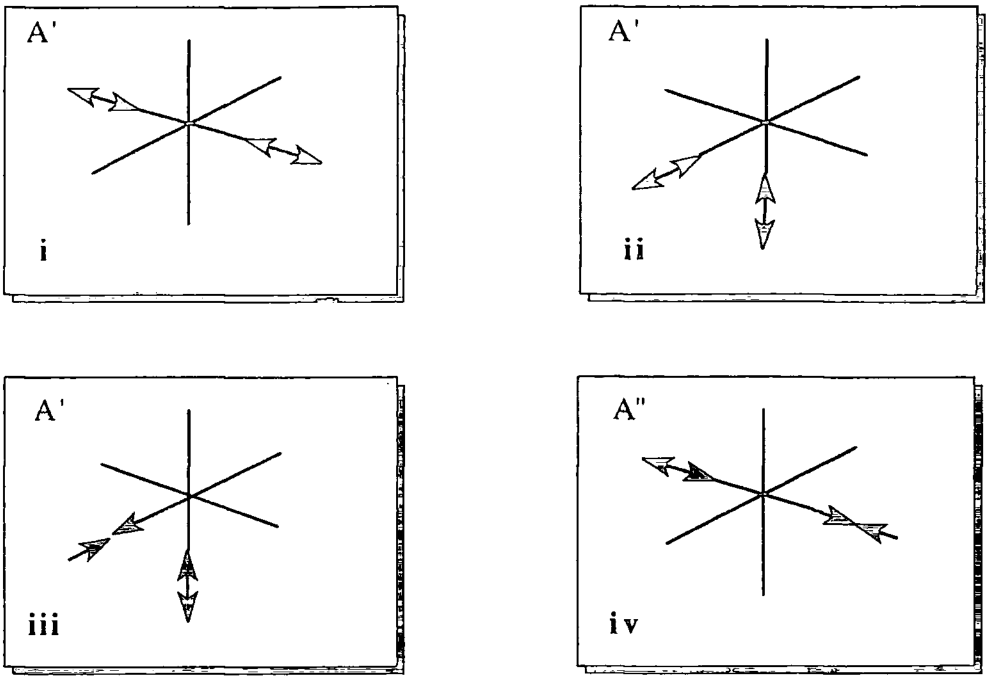


Figure B2 Theoretical vibrational modes for *cis* -[M(X)(Y)(CO)$_4$]-type complex (X, Y = monodentate ligands)

For the *trans* isomer, the A_1 vibration, the symmetrical breathing mode of the four planar carbonyl groups, will be of low intensity because of the low dipole moment change, but the E vibration will be of high intensity. Thus, one weak and one intense band are predicted for the *trans* isomer. The infrared spectrum of the product will, therefore, differentiate between the isomers. The predicted vibrations for the *trans* isomer are shown in Figure B3.

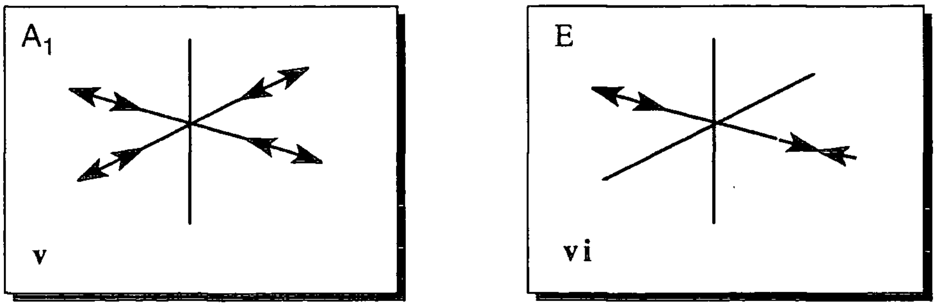
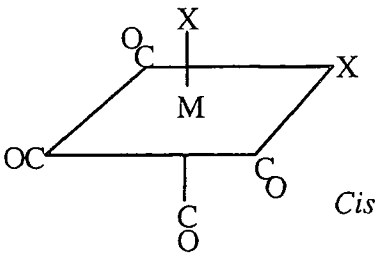


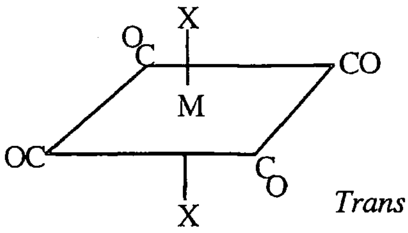
Figure B3 Theoretical vibrational modes for the *trans* -[M(X)(Y)(CO)$_4$]-type complex (X, Y = monodentate ligands)

C. Application to Compounds of the Type $[M(X)_2(CO)_4]$

Two structures are again possible for compounds of this type, a *cis* and a *trans* isomer. The structures are shown below. The *cis* isomer will show four bands and the *trans* only one band in the infrared spectrum, which enables a distinction to be made between the isomers.



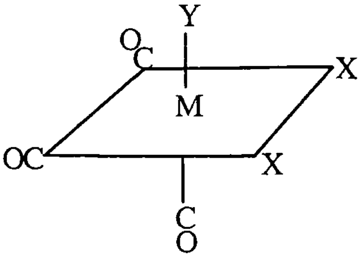
Cis



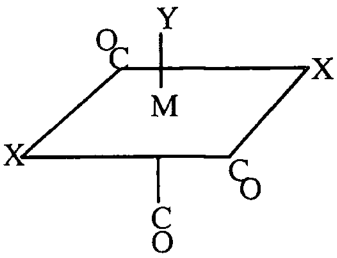
Trans

D. Application to Compounds of the Type $[M(X)_2(Y)(CO)_3]$

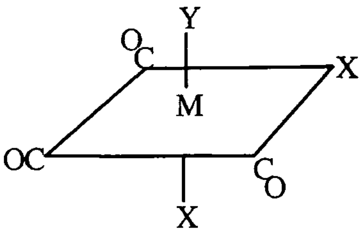
Three structures are possible for a molecule of this type, as shown below. Three infrared bands are predicted for each isomer. For the *fac* isomer, each stretching vibration as shown in Figure B4, produces a large change in dipole moment, so all three vibrations will be of strong intensity.



fac



mer (I)



mer (II)

However, for the *mer*(I) and *mer*(II) isomers, the symmetrical stretch of the pair of *mer*(I) carbonyl groups produces only a very small dipole moment change, and results in a band of low intensity. Two strong and one weak bands should, therefore, be found for a molecule of these *mer* structures.

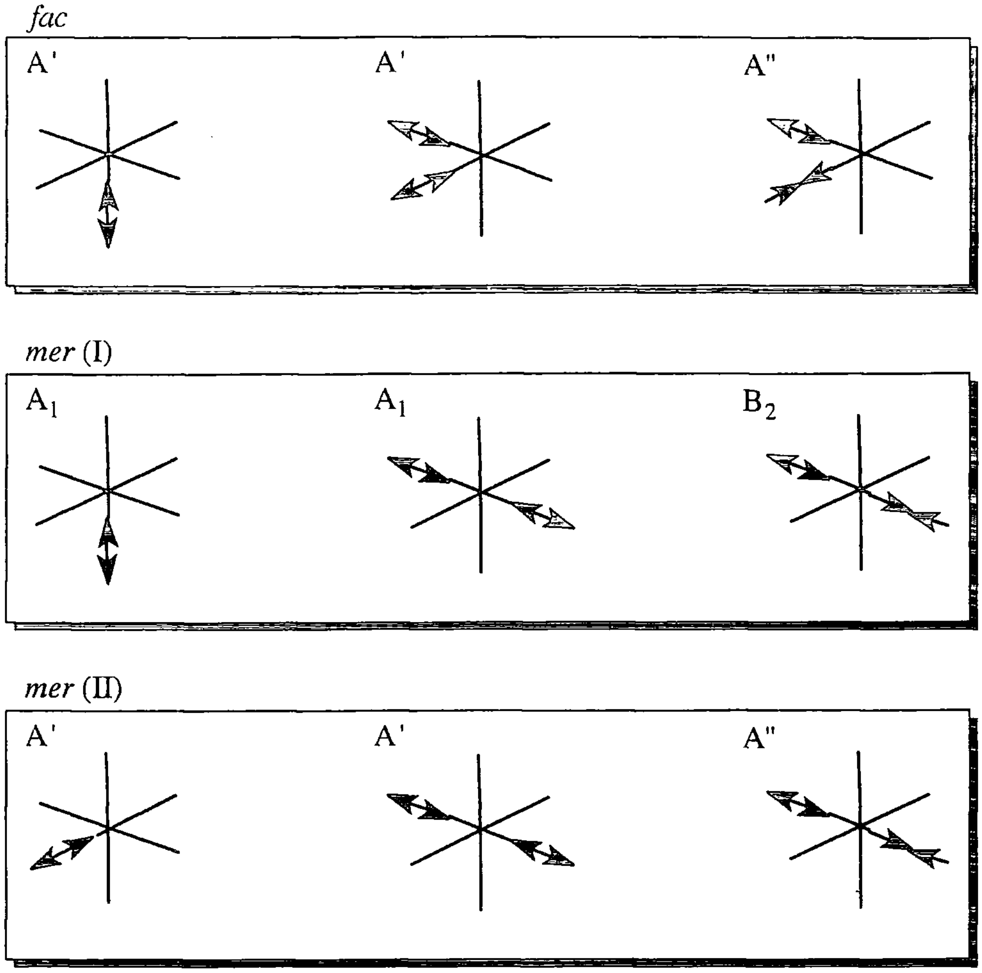


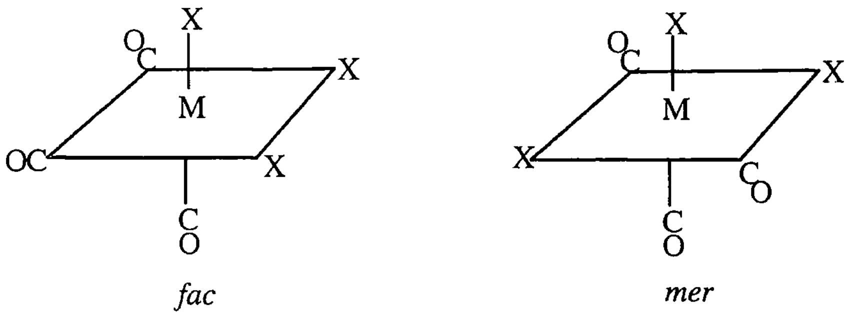
Figure B4 Theoretical vibrational modes for [$M(X)_2(Y)(CO)_3$]-type complex (X, Y = monodentate ligands)

The low intensity band will appear at high frequencies, since the carbonyl groups involved in the vibration are in competition with each other for π-bonding with the metal. Consequently, the bond order of the C-O bonds will not be notably reduced on introduction of the X/Y ligands into the molecule. Thus the *fac* isomer can be differentiated from the other two.

In the compounds being considered, group Y is regarded as an electronegative group, such as a halide, which π-bonds to the metal to a lesser extent than the carbonyl groups and, say, the organic ligands X. For the *mer*(I) isomer, therefore, the carbonyl group *trans* to group Y will be more strongly bonded to the metal than the other carbonyl groups. Thus the A_1 vibration, involving the stretching of this unique carbonyl group, will occur at lower frequency than the comparable A' vibration of the *mer*(II) isomer, which involves the carbonyl group *trans* to the more strongly π-bonding organic ligand X. These isomers can be distinguished, therefore, through the separation of the two intense bands.

E. Application to Compounds of the Type $[M(X)_3(CO)_3]$

Only two isomers are possible for a molecule of this type, a *fac* isomer having all the carbonyl groups in *cis* positions to each other, and a second isomer, having a pair of *trans* carbonyl groups, which will be referred to as the *mer* isomer as shown below.



Two bands are predicted for the *fac* isomer, and as shown in Figure B5, both vibrations have a large associated dipole moment change, which will result in two intense bands. The *mer* isomer will show three bands; two bands will be strong, and the one at high frequency will be weak. Distinction between the isomers is, therefore, based solely on the presence of one weak band, thereby limiting the use of the technique to this type of complex. However, the examples quoted in

Table B3 show no evidence for a weak band at high frequency, and so have been assigned as *fac* isomers, which are the expected structures, considering *trans-effect* arguments.

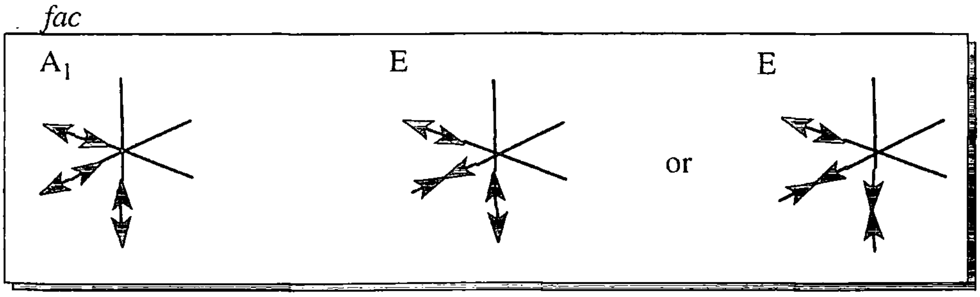


Figure B5 Theoretical vibrational modes for $[M(X)_3(CO)_3]$-type complex (X = monodentate ligand)

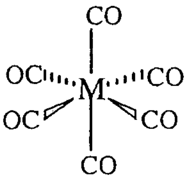
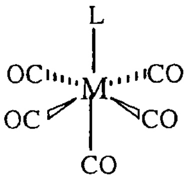
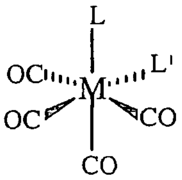
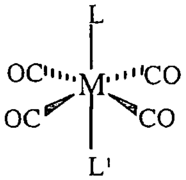
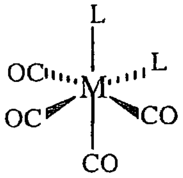
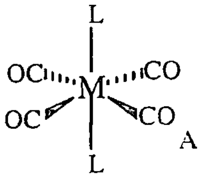
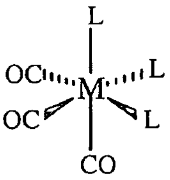
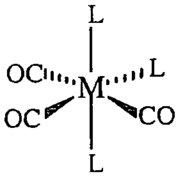
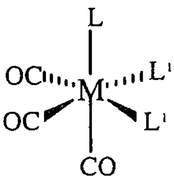
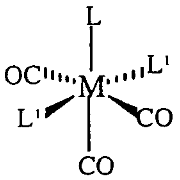
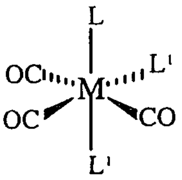
Table B3[4]

Compound	$\nu(CO)/cm^{-1}$	Assignment
$[Cr(CO)_3(dien)]$	1881s; 1735s‡	*fac*
$[Mo(CO)_3(dien)]$	1883s; 1723s‡	*fac*
$[Mo(CO)_3(Ph_2PCl)_3]$	1977s; 1885s	*fac*
$[Mo(CO)_3(PhPCl_2)_3]$	2016s; 1943s	*fac*

‡ - Broad absorption; dien - diethylenetriamine

Table B4 summarises the point group, the Γstretches, and the predicted number of IR active bands for metal carbonyls concerned in this work.

Table B4

Complex	Number and Modes of IR-active Bands ν(CO)	Point Group	Complex	Number and Modes of IR-active Bands ν(CO)	Point Group	Complex	Number and Modes of IR-active Bands ν(CO)	Point Group
 $[M(CO)_6]$	1 T_{1u}	O_h	 $[M(L)(CO)_5]$	3 $2A_1+E+B_2$	C_{4v}			
 cis - $[M(L)(L')(CO)_4]$	4 $3A' + A''$	C_s	 trans - $[M(L)(L')(CO)_4]$	2 $A_1 + B_2 + E$	C_{4v}			
 cis - $[M(L)_2(CO)_4]$	4 $2A_1 + B_1 + B_2$	C_{2v}	 trans - $[M(L)_2(CO)_4]$	1 $A_{1g} + B_{2g} + E_u$	D_{4h}			
 fac - $[M(L)_3(CO)_3]$	2 $A_1 + E$	C_{3v}	 mer - $[M(L)_3(CO)_3]$	3 $2A_1 + B_2$	C_{2v}			
 fac - $[M(L)(L')_2(CO)_3]$	3 $2A' + A''$	C_s	 mer - $[M(L)(L')_2(CO)_3]$	3 $2A_1 + B_2$	C_{2v}	 mer - $[M(L)(L')_2(CO)_3]$	3 $2A' + A''$	C_s

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