MECHANISTIC ORGANOMETALLIC CHEMISTRY

A thesis submitted

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for the Degree of Doctor of Philosophy

by

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ABSTRACT

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Mechanistic Organometallic Chemistry

A number of organometallic transformations related to proposed elementary steps in the reductive polymerization of carbon monoxide are discussed.

The use of isonitrile as model ligands for carbon monoxide, with which they are isoelectronic, is proposed. Investigations show that alkyl migration to isonitrile is preferred over migration to carbon monoxide. Iminoformyl products due to hydride migration to isonitrile are not, however, observed.

Syntheses of a range of cationic complexes of the type $[(\eta^5\text{-}C_5H_5)M(L)_2(CNR)]^+$, $[(\eta^5\text{-}C_9H_7)Ru(L)_2(CNR)]^+$ and $[(\eta^5\text{-}C_9H_7)M(L)_2(CO)]^+$ (M = Fe, Ru; L = CO, phosphine) are described. In two cases, addition of hydride to the isonitrile cations is followed by protonation on work-up to give aminocarbene complexes. These are inert to further reduction under the conditions employed. The majority of isonitrile cations lose the isonitrile ligand to give good yields of metal hydride complexes. A mechanism involving ring-slippage of the hydrocarbon ligand is implicated. Hydride addition to $\eta^5\text{-}C_9H_7$ complexes results, in the majority of cases, in loss of the hydrocarbon ligand from the complex and recovery of indane.

Evidence for the intermediacy of metal formyl complexes in a number of hydride donation reactions is presented. These formyl complexes are formed from carbonyl hydride complexes either under moderate CO pressure or in THF solution. Hydride complexes lacking a carbonyl ligand are found to be inert.

Finally, two reactions, one involving an alkyl migration reaction catalyzed by silver(I) salts, and the other involving the reduction of a metal acyl ligand to metal alkyl, are combined to demonstrate a model for carbon chain growth at a metal centre. The synthesis of an iron pentanoyl complex, followed by a decomplexation reaction, gives pentanoic acid in which all the carbon atoms are potentially directly derived from carbon monoxide. This is the first synthesis of a single homologous acid from carbon monoxide.

To my father

ACKNOWLEDGEMENTS

I would like to thank my supervisor, Dr. S.G. Davies, for his help and advice throughout the course of this work. I am also grateful to colleagues in the laboratory for providing such an agreeable working atmosphere. I am particularly indebted to Drs. Paul Beckett, Kevin Sutton and Mark Whittaker, who proof-read this thesis. Thanks are also due to Kevin Sutton for obtaining the X-ray crystal structure for me, and to Lesley Woods for typing the manuscript so efficiently.

I must also acknowledge the help of Dr. David Pippard and Dr. Mike Preece at the B.P. Research Centre, Sunbury-on-Thames. The British Petroleum Company p.l.c. are gratefully acknowledged for generous financial support.

CONTENTS

ABBREVIATIONS

R	alkyl or aryl group
X	halide
M	metal moiety
L	2-electron donor ligand
Cp	η^5-cyclopentadienyl
In	η^5-indenyl
THF	tetrahydrofuran
DMSO	dimethylsulphoxide
OEP	octaethylporphyrin
dppm	bisdiphenylphosphinomethane
dppe	1,2-bisdiphenylphosphinoethane
dppp	1,3-bisdiphenylphosphinopropane
dmpe	1,2-bisdimethylphosphinoethane
cdpe	*cis*-1,2-bisdiphenylphosphinoethene
tripod	1,1,1-tris(diphenylphosphinomethyl)ethane
IR	infra-red
NMR	nuclear magnetic resonance
s	singlet
d	doublet
t	triplet
m	multiplet
br	broad
m/z	mass-to-charge ratio
E.I.	electron impact technique
F.D.	field desorption technique
F.I.	field ionization technique

CHAPTER 1

INTRODUCTION

1.1 Organometallic Complexes as Catalysts

Over the last thirty years, a considerable effort has been devoted to the study of complexes formed between metals and organic ligands. This has greatly broadened the range of subtlety of chemical transformations available to the organic chemist, both in the laboratory and in industry. Coordination of an organic moiety to a metal may cause dramatic changes in its pattern of reactivity. These changes may be used to effect reactions not otherwise feasible.

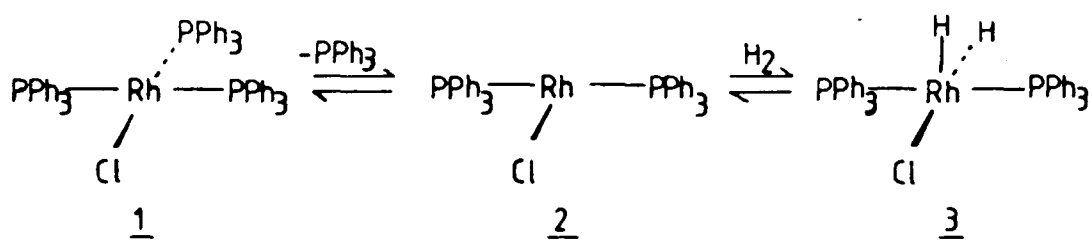
Organometallic complexes have an increasingly large role as stoichiometric intermediates in organic synthesis[1,2,3]. They may be used as protecting groups, for example shielding alkene or acetylene functionalities; to stabilize otherwise unstable intermediates such as cyclobutadiene[4], cyclohexyne[5] or cyclohexadieneone[6]; or to fundamentally change the reactivity of an organic group, as seen for example in the wide and varied chemistry of arylchromiumtricarbonyl complexes[1,2]. Despite the great synthetic usefulness and greater potential of such stoichiometric complexes, the versatility of organometallic complexes as catalysts remains paramount. Many large-scale industrial processes, producing in some cases over a million tons of product per annum, rely on such catalysts. Examples include hydroformylation of alkenes to aldehydes (the "oxo" reaction) and subsequent reduction to alcohols, Wacker oxidation of ethylene to acetaldehyde, Ziegler-Natta polymerization of olefins, and the carbonylation of methanol to acetic acid (see below).

The above examples all employ soluble, homogeneous catalysts. These in general require milder conditions, show greater efficiency and much greater selectivity than heterogeneous catalysts. An example of the tremendous selectivity obtainable with such systems is given in the cyclooligomerization of butadiene with nickel complexes. Nickel-olefin complexes catalyze trimerization to give cyclododecatriene, whereas substitution of the catalyst with phosphines leads to dimerization to give cyclooctadiene with greater than 95% selectivity[7].

Another significant advantage of homogeneous catalysts is the relative ease with which catalytic pathways may be studied. Solid-phase, heterogeneous catalysts are ill-defined, non-stoichiometric compounds, and mechanistic interpretation is hindered by complications such as influence of pore volume or rate control by mass transfer. Study of the elementary reactions within the coordination sphere of well-defined soluble complexes, with possible isolation or spectroscopic identification of intermediates, has allowed elucidation of the mechanisms of many homogeneously catalyzed reactions. It is assumed that the same, or closely analogous, elementary reactions occur at heterogeneous catalyst surfaces. In this way the study of homogeneous systems is hoped to lead also to improvements in heterogeneous catalysts.

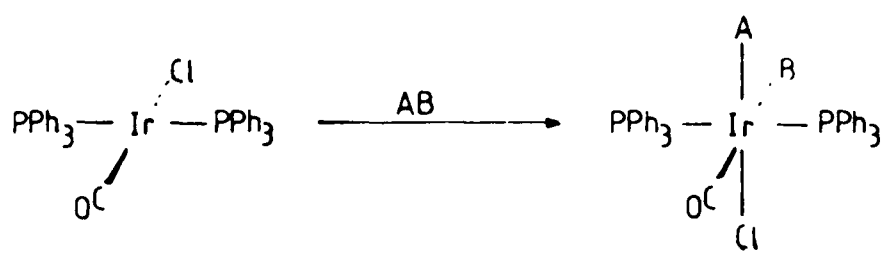
The ability of transition metal complexes to catalyze reactions is fundamentally dependent on the ability of the metal to change its coordination number. The majority of stable organometallic complexes have a closed-shell, eighteen-electron structure, but structures with as few as fourteen electrons are implicated in catalysis. Given this ability, the key reactions leading to catalytic activity are as follows:

i) Ligand coordination and dissociation. Ligands bonded to many complexes are appreciably labile and may dissociate to give coordinatively unsaturated species. Thus the first step in hydrogenation using Wilkinson's catalyst 1 has been shown[8] to involve dissociation of phosphine to give a fourteen-electron intermediate 2. Such reactions are, of course, reversible; coordination by a different ligand will lead to an overall S_N1-type substitution.



1 2 3

ii) Addition and elimination reactions. Coordination of a molecule AB to an unsaturated metal centre may lead to a [M](A)(B) species. Thus the intermediate 2 reacts rapidly with dihydrogen to give the rhodium dihydro species 3. A wide range of molecules AB have been shown to react in this fashion with Vaska's complex 4[9], examples including H_2, HCl, Cl_2, RI, R_3SiH, R_3SnCl, $HgCl_2$ and many others.



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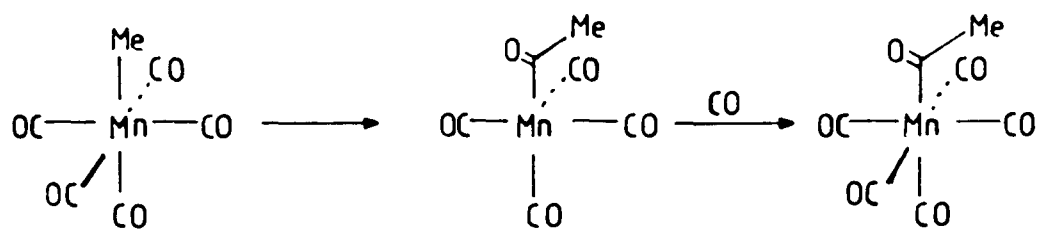
Elimination reactions, the reverse of the above behaviour, are proposed as the product-forming steps in many catalytic cycles.

iii) Ligand migration. This process involves the combination of a σ-bonded ligand with a coordinatively bound ligand at the same metal centre, forming a new ligand. The most important examples involve CO, as in the CO-induced methyl migration shown for 5[10], or alkenes, as shown by 6[11].



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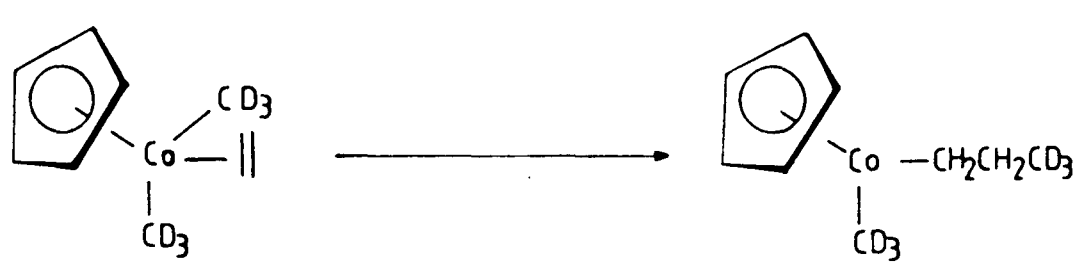

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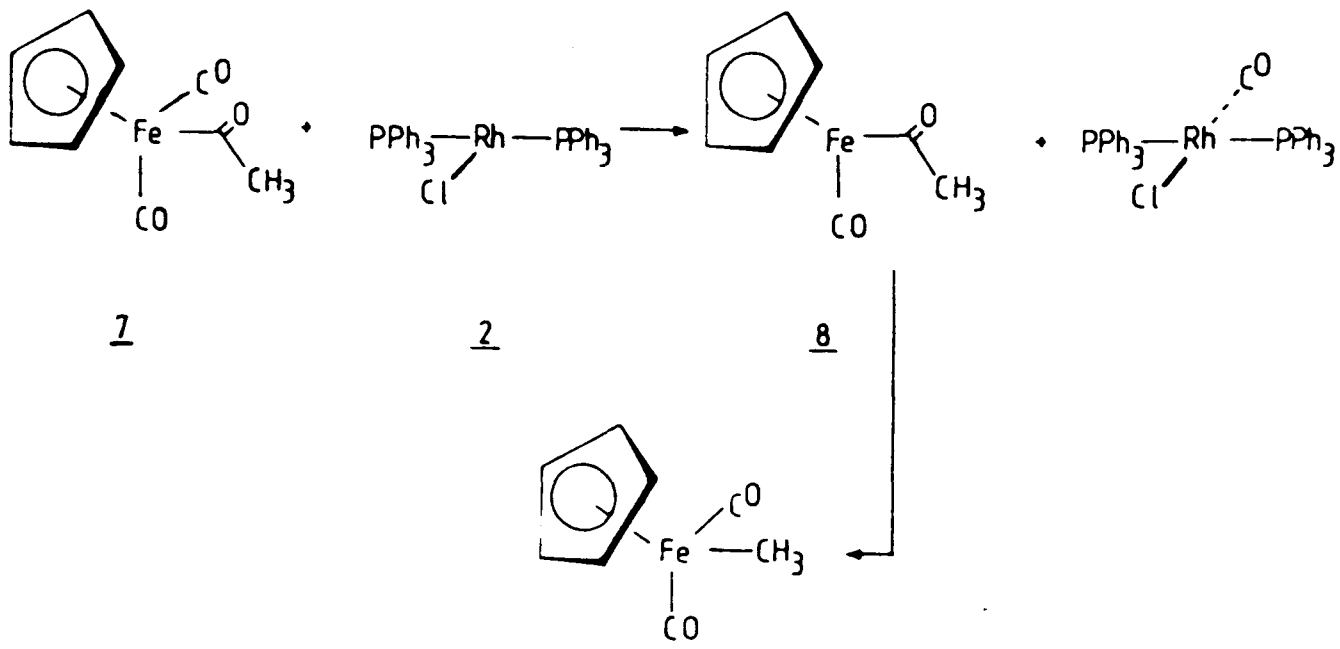
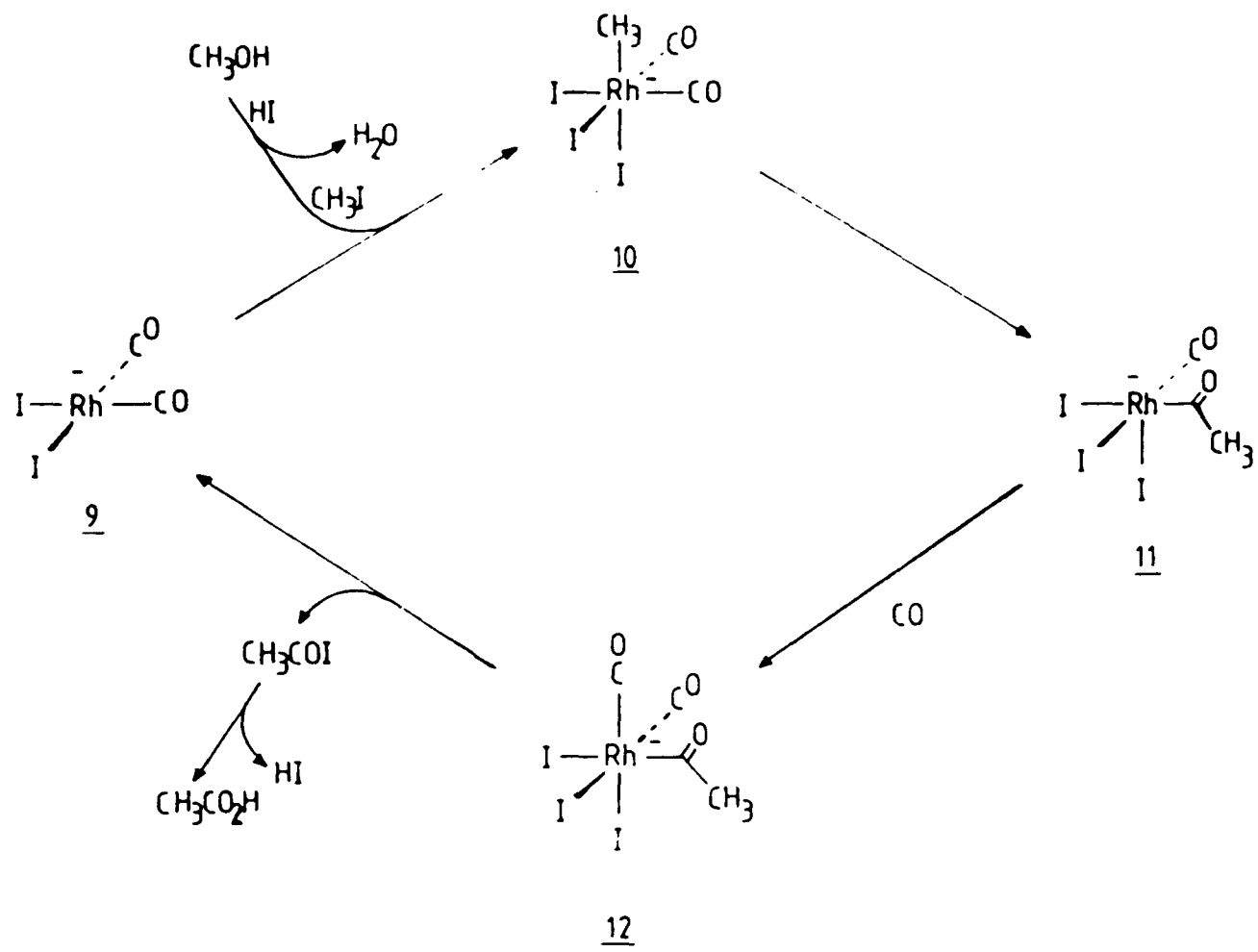
Many other groups take part in such migration reactions, including thiocarbonyls[12,14], carbenes[13,14], sulphur dioxide[15] and isonitriles[15,16]. Again, the reverse of this reaction is well documented. For example, the iron acetyl complex 7 is decarbonylated with the aid of Wilkinson's catalyst in its dissociated form 2. The unsaturated species 8 is an intermediate[17].



These features are well illustrated in a real catalytic cycle by the rhodium-catalyzed conversion of methanol to acetic acid in the Monsanto process, which accounts for over one million tons of acetic acid production per year. The mechanism of this conversion has been elucidated[18], and the major reactions occurring are shown in Scheme 1.

The role of iodide in the reaction is clearly to generate methyl iodide, which reacts with the complex 9 by an addition reaction, forming the short-lived intermediate 10, This addition has been identified as the rate-determining step. Methyl migration follows, and then association of another CO molecule to unsaturated 11 gives the saturated spe cies 12. Elimination of acetyl iodide regenerates 9. The acetyl iodide is hydrolyzed to the final product, acetic acid, with re-liberation of the iodide promoter. The anionic nature of 9 enhances its nucleophilicity, and hence its reactivity toward methyl iodide.



Scheme 1

Simplified Mechanism of the Monsanto Acetic Acid Process

1.2 The Catalyzed Reduction of Carbon Monoxide in Industry

The industrial reduction of carbon monxide using heterogeneous catalysts has been in operation since the early part of this century. Methane and methanol are the major products. Development of such processes was forced on pre-war Germany, possessing large coal stocks but little oil, and catalytic synthesis of hydrocarbons via the Fischer-Tropsch process became vital during World War Two.

The oil embargo of the early nineteen seventies pushed previously low oil prices up steeply. One consequence of this was to focus industrial and scientific attention on research towards coal-based energy sources. At present the only large-scale Fischer-Tropsch syntheses are carried out in South Africa, but political as well as commercial considerations may well require such production capacity elsewhere in the near future.

The major problem associated with the Fischer-Tropsch synthesis at present is its low selectivity. Saturated and unsaturated hydrocarbon products range from methane and ethylene to hydrocarbon waxes, together with variable amounts of aromatic and oxygenated species. Such low selectivity is a general feature of heterogeneous processes due to the large number of different catalytic sites available at a solid surface.

For greater commercial viability, selectivity must be improved, and it is here that homogeneous catalysis could have an important role. The advantages of milder reaction conditions and more facile heat transfer would also be gained. The problem of separation of products from the reaction mixture in homogeneous systems is, however, severe.

At present the only industrially important syntheses of alcohol or hydrocarbon products from carbon monoxide outside

South Africa are the heterogeneously catalyzed methane and methanol syntheses. Methane, or substitute natural gas, production has had a varied history as natural gas production and demand have changed. Methanol production via Cu/ZnO catalysts is, however, practised on a large scale. Homogeneous catalysts for this process are in fact less selective, producing for example methyl formate and ethylene glycol as well as methanol. Studies of such systems have, however, been of great benefit in proposing reaction mechanisms[19].

Current developments in the production of CO-based feedstocks or fuel sources employ both homogeneous and hetergeneous catalysts. Methanol, produced from CO, is already used in the production of acetic acid as described above. Other possible products from methanol are ethanol, via a homologation using soluble cobalt catalysts[20]; ethylene, either via dehydration of ethanol or cracking of methanol[21]; and, in a new but extremely promising process, hydrocarbons produced over a zeolite catalyst[22]. A plant employing this technology to convert methane to hydrocarbons has been constructed in New Zealand[23].

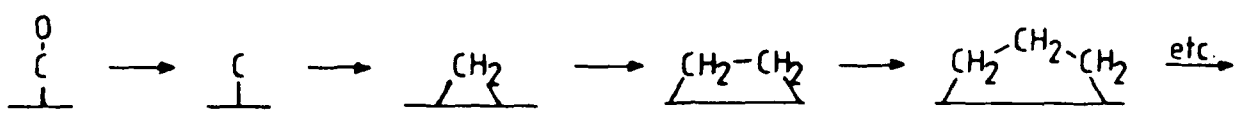
A very attractive two-carbon product often formed in low yields in the Fischer-Tropsch reaction is ethylene glycol. In higher yield this would be a very desirable product. The Union Carbide Corporation have disclosed that rhodium carbonyl systems under very high pressure (ca. 3000 atm.) catalyze the production of ethylene glycol with a selectivity of up to 70%. Few details have been released[24,28], although polynuclear clusters containing up to twelve rhodium atoms seem to be implicated. Extremely high pressures are required to shift the equilibium from methanol to ethylene glycol. These very high pressures prevent the process from being commercially viable.

1.3 Mechanisms for Carbon Monoxide Reduction

The number of reaction mechanisms and variations which have been put forward for reduction of carbon monoxide is very great. A large number of reviews, many partisan toward one mechanism or another, have appeared[25-33]. In heterogeneous systems, it is quite possible that more than one mechanism operates under a given set of conditions, and consequently it is not feasible to talk of a single "correct" mechanism.

It is useful here to briefly discuss three suggestions, two involving carbide or carbene intermediates, and the third involving alkyl migration to metal-bound carbon monoxide.

i) Carbide mechanism. The original proposal of Fischer and Tropsch[34] was that carbon monoxide is dissociated on the metal surface of a heterogeneous catalyst. This forms a metal carbide layer which is hydrogenated to give products. Much conflicting evidence for [27] and against[26] this mechanism has been presented. Hydrogenation of the carbide species to CH_x (x = 1-4) would be followed by association of these fragments to oligomeric hydrocarbons (Scheme 2).

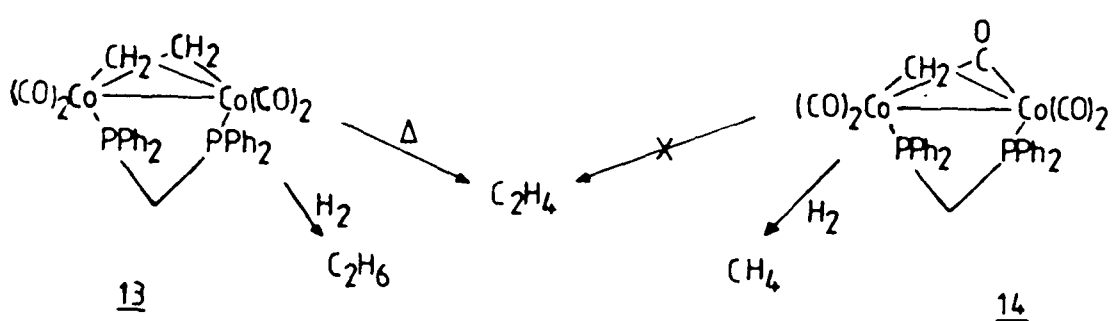


Scheme 2

Outline of Carbide Mechanism

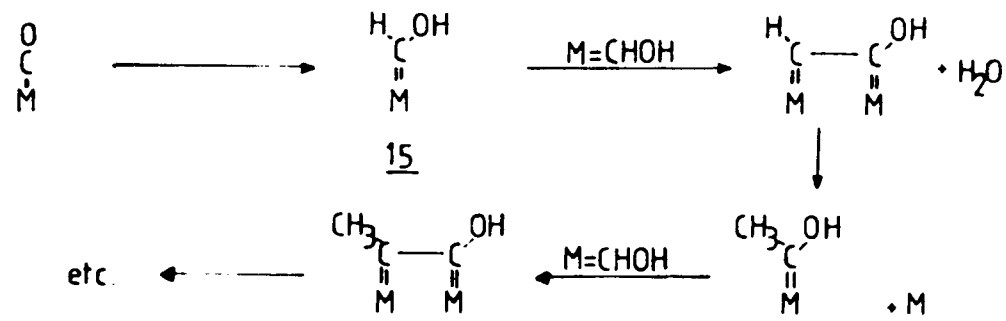
Modelling studies of such fragments have been carried out[35]. Diazomethane is decomposed by Fischer - Tropsch active metals to ethylene in high yield, indicating dimerization of methylene

species. The same reaction performed in the presence of H_2 led to a range of hydrocarbons up to C_{18}. The dimerization of methylene groups has been observed in the binculear complex 13[36]. Heating this led to production of ethylene, and hydrogenation of it to ethane. The monomethylene complex 14 on the other hand did not eliminate ethylene, and gave only methane on hydrogenation.



Although such dimerization has been established for small clusters, the large mobility required of CH_x species on metal surfaces in order to oligomerize has not been demonstrated. Henrici-Olivé and Olivé [26] argue that, although such species may form and be incorporated into growing alkyl chains, they can only account for a small proportion of product. Evidence is also given that alkenes and alcohols are formed by a common route. Since methanol formation from $^{13}C^{16}O$ and $^{12}C^{18}O$ labelled carbon monoxide has been shown[37] to proceed in a non-dissociative manner to give predominantly $^{13}CH_3{}^{16}OH$ and $^{12}CH_3{}^{18}OH$, the carbide mechanism is dismissed as a minor contributor.

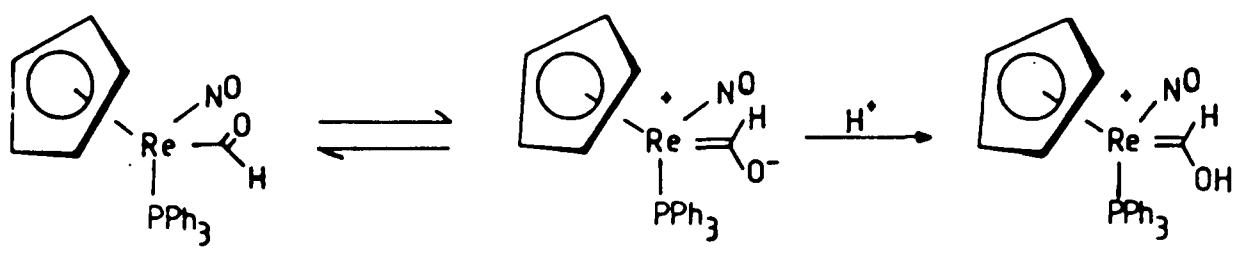
ii) Carbene mechanism. This mechanism involves the combination of metal-bound carbene species. It was proposed[38] to explain the unbranched or 2-methyl branched nature of carbon chains formed in the Fischer-Tropsch reaction. It is outlined in Scheme 3.



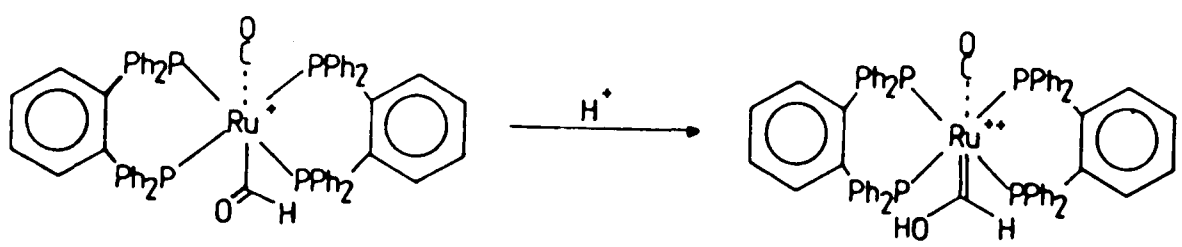
Scheme 3

Outline of Carbene Mechanism

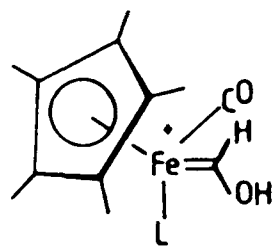
Again, mobility of surface species, which is required for them to be able to combine, has not been shown. Indeed, hydroxycarbene species such as 15 have been isolated on very few occasions. Protonation of formyl complexes 16 and 18, for example, gave 17[39] and 19[40] respectively. NMR evidence for the unstable iron complexes 20 (L = CO, PMe_3) has been presented[41]. In no case has the coupling of such carbene species been reported, and the mechansim has foundered somewhat for lack of supporting evidence.



16 17



18 19



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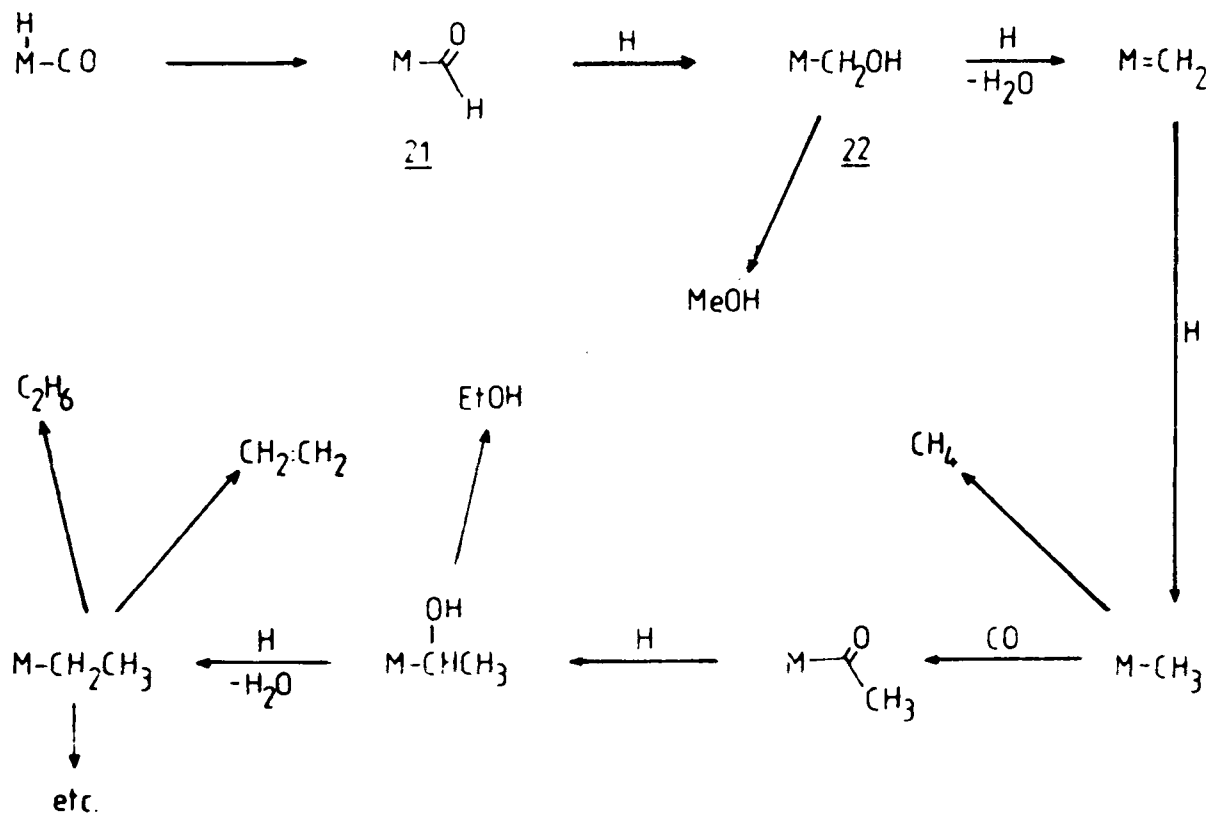
iii) Alkyl migration mechanism. As its name implies, this mechanism depends upon alkyl migration to a metal-bound carbonyl for chain growth, followed by a reduction step to give an alkyl group one carbon atom longer. The formation of oxygenated species may also be explained by this mechanism. A summary of the steps is set out in Scheme 4.



Scheme 4

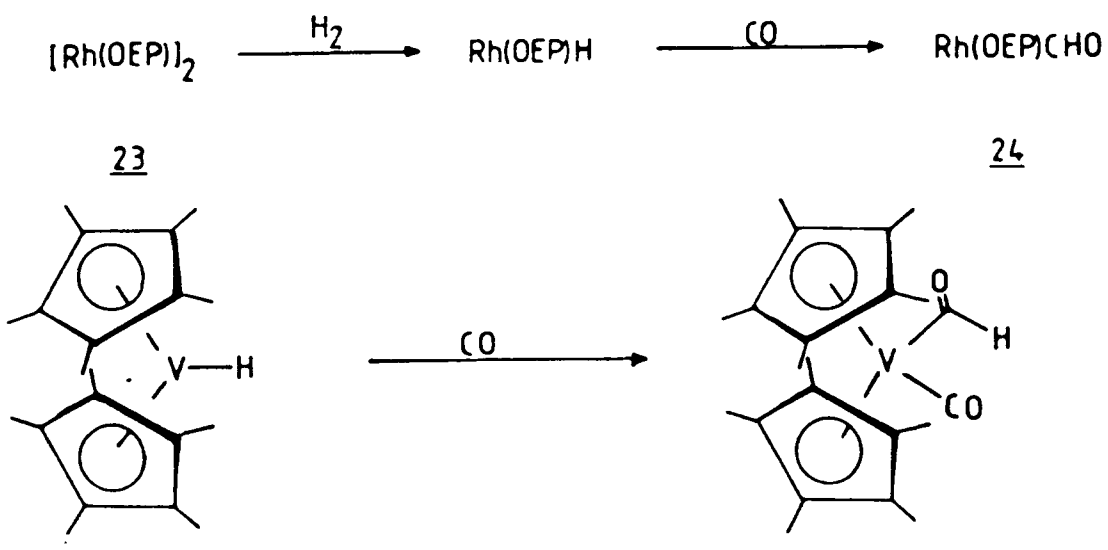
Outline of Alkyl Migration Mechanism

This reaction mechanism focuses on a single metal centre, unlike the previous two suggestions, and is therefore applicable to mononuclear homogeneous catalysis. It is eminently suitable for modelling studies, and also for the design of relatively simple catalyst systems.

Most of the steps shown in Scheme 4 have been demonstrated in model complexes, and intermediates, especially the usually less-stable formyl and hydroxymethyl complexes 21 and 22, have been prepared, characterized and studied. Such studies are considered in the next section.

1.4 Model Complexes for Catalytic Intermediates

The first step in the mechanism outlined in Scheme 4 is the migration of hydride to a carbonyl ligand to give a metal formyl complex. Such a process appears to occur in the reaction of the rhodium octaethylporphyrin (OEP) complex 23 with H_2 and CO[42]. The actual mechanism of formation of formyl 24 is uncertain, although an intramolecular hydride migration seems unlikely. A brief report of the formation of 26 from hydride 25 and gaseous CO has appeared[43]. Infra-red data alone were given in support of structure 26.



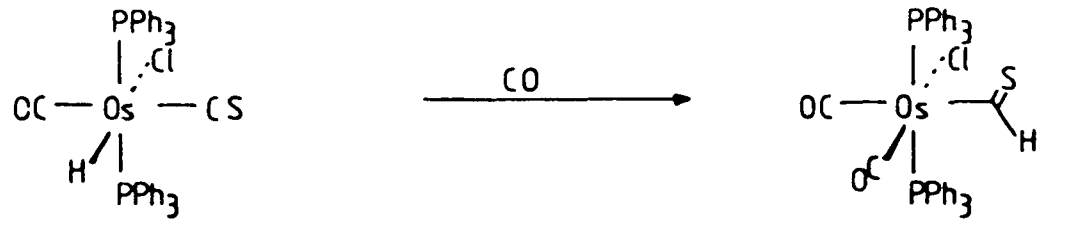
23 24

25 26

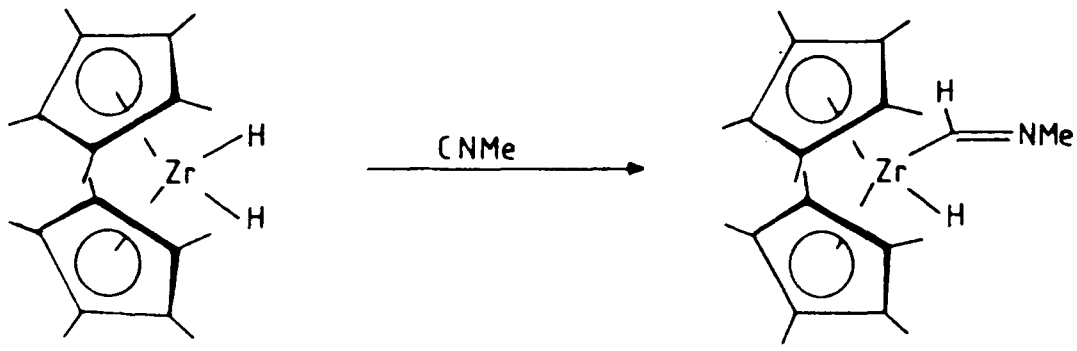
These are the only isolated η^1-formyl complexes to date for which this mechanism is proposed. The thermodynamics of this migration have been speculated upon[44,45]. The general conclusion is that the reaction is very unfavourable, due mainly to the strong metal-hydride bond which must be broken. The greater M-H bond dissociation energy compared with that for metal alkyls M-R has been offered to explain the fact that, whereas alkyl migration to CO is commonly encountered, hydride migration is not.

Certainly hydride migration reactions to molecules other

than CO are known[44]. The osmium thioformyl 28, for example, is formed from 27 by simple stirring under CO[46], and the imino-formyl 30 similarly on treatment of 29 with methyl isonitrile[47].



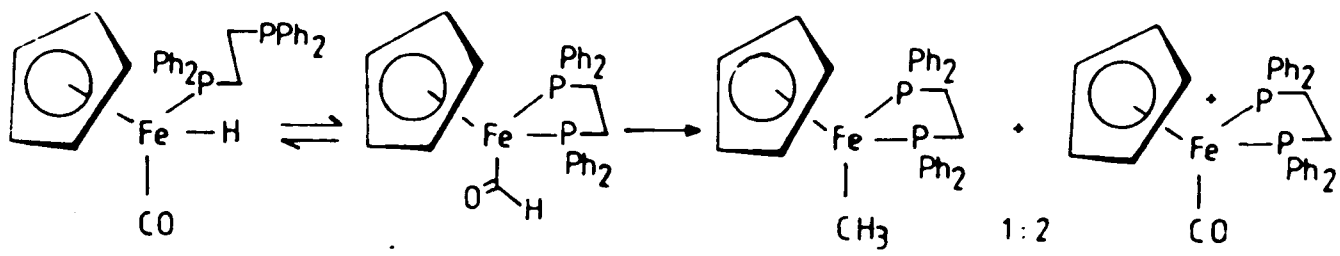
27 28



29 30

Many formyl complexes have been indirectly prepared by hydride addition to metal carbonyl complexes. These preparations have been reviewed[48]. Such formyl complexes are in general extremely unstable at room temperature, decomposing by a reverse migration to give carbonyl hydride complexes[49]. This decomposition makes detailed study difficult in practice.

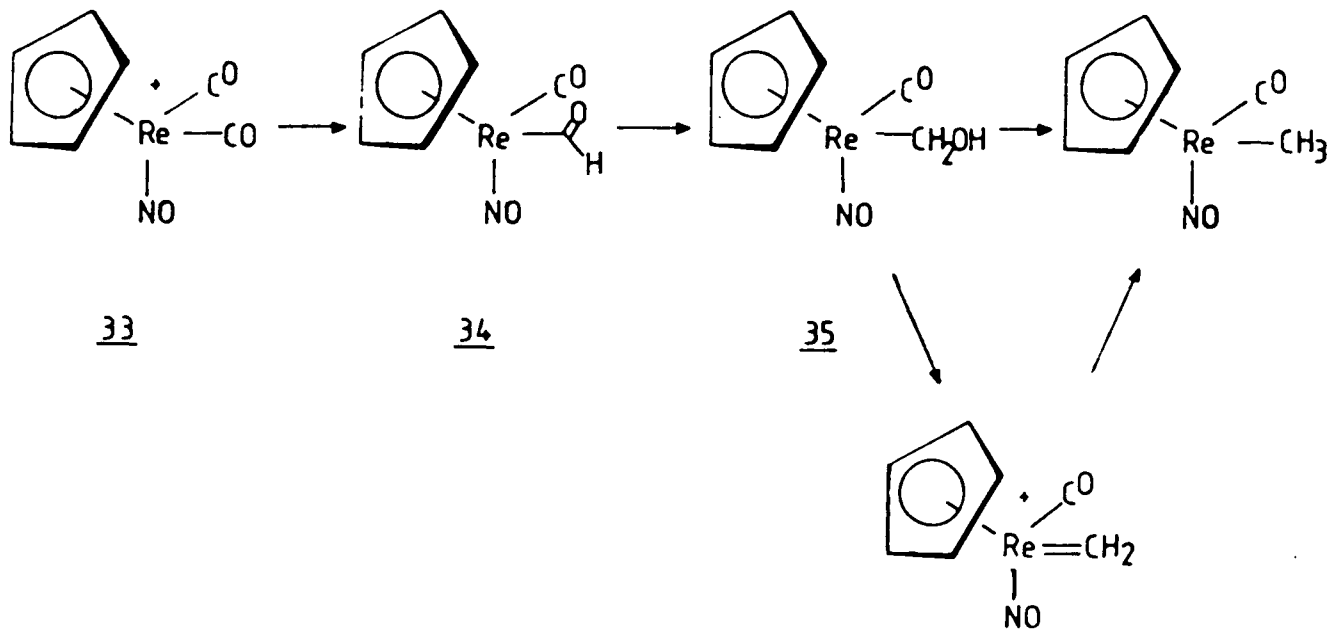
The iron carbonyl hydride 31 has been shown[50] to exist in equilibrium with formyl 32. In THF solution, disproportionation to the methyl complex occurs. This is in accord with Scheme 4; presumably two molecules of 30 act as the hydride donors necessary for further reduction of a third. This is the only example of the formation of a methyl complex directly from a carbonyl hydride complex.



31 32

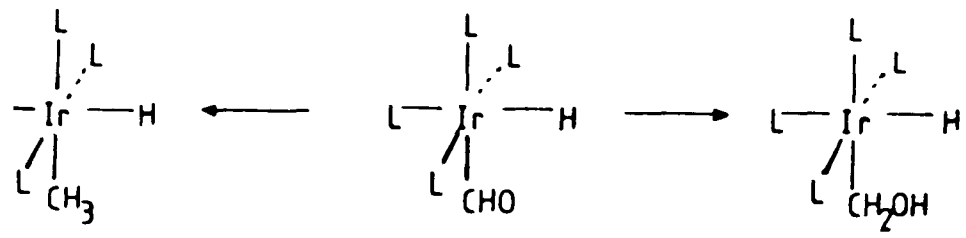
Two examples of stable formyl complexes have been exploited in detailed modelling studies.

The cationic rhenium complex 33 was thus reduced[51,52] to the fairly stable formyl 34, which was isolated and further reduced to hydroxymethyl 35. Finally, reduction of 35 to the methyl complex was achieved. The intermediacy of the methylene complex 36 is assumed but has not been proven.



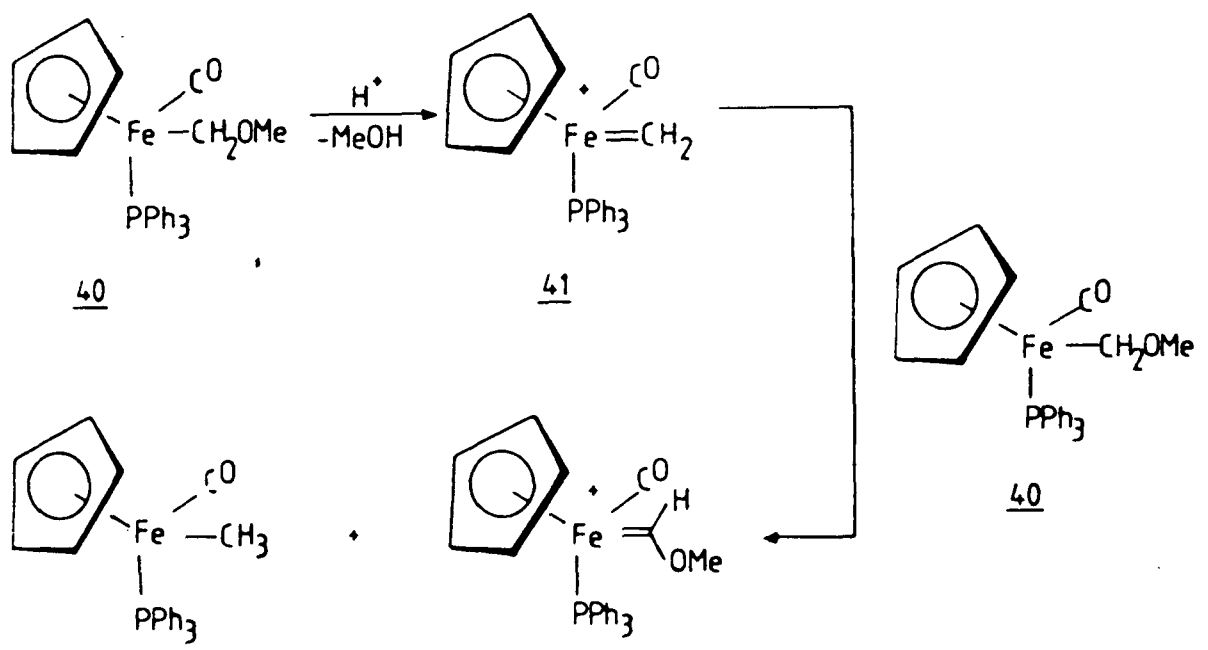
33 34 35 36

In a similar fashion, the stable iridium formyl complex 37 (L = PMe_3) has been shown to reduce to hydroxymethyl 38 and to methyl 39[53]. The intermediacy of 38 in the formation of 39 was assumed, but not proven.



39 37 38

A related study[54] has shown that protonation of the methoxymethyl complex 40 leads to the methylene cation 41. This acts to abstract hydride from a second molecule of 40 to give the methyl complex together with the methoxycarbene.



40 41 40

These modelling studies have shown that the intermediates indicated in Scheme 4 can be formed, and do interconvert to give overall reduction of bound carbon monoxide to methyl. The paucity of information about their formation and decomposition, and questions such as to the source of hydrogen shown in Scheme 4, means that much more work is needed before applications to real systems can be foreseen.

1.5 Objectives

The model systems described above for the reduction of carbon monoxide according to the alkyl migration mechanism have depended for their utility on chance observation of stable formyl complexes, which can be subjected to further reduction. The use of isoelectronic isonitriles as models for carbon monoxide is proposed. This will exploit the observed greater stability of iminoformyls over formyl complexes. It is hoped therefore to observe intermediates in an analogous reduction series.

The relationship between carbonyl hydride and formyl complexes will also be examined, together with the intermediacy of such formyl complexes in reduction reactions. In particular, the hydride-donating ability of formyl complexes will be studied.

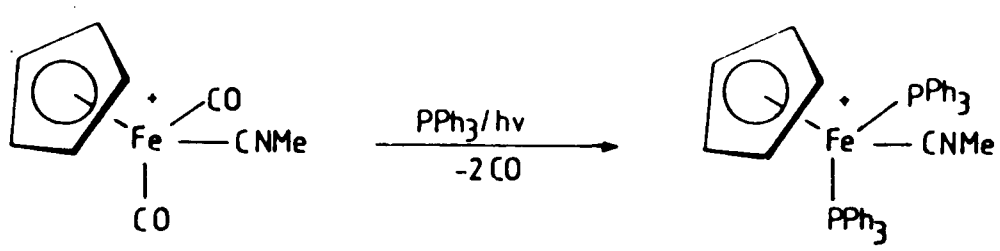
CHAPTER 2

ISONITRILE LIGANDS AS MODELS FOR CARBON MONOXIDE

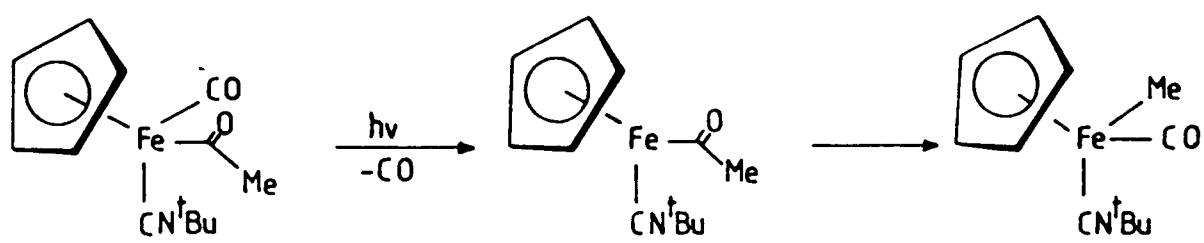
2.1 Isonitriles as Ligands

The isonitrile ligand CNR is isoelectronic with the carbonyl ligand CO and, like CO, is well established as a two-electron donor in many metal complexes. The major difference[55] between the two lies in the relative importance of σ- and π-bonding interactions. Isonitriles are stronger σ-donors, but tend to be weaker π-acceptors. This has been used to explain the existence of cationic metal isonitrile complexes such as $[Fe(CNMe)_6]^{2+}$, the carbonyl analogues of which are unknown[55].

Several comparative studies of carbonyl and isonitrile ligands have been reported. The lability of carbonyl ligands in cationic complexes, for example, appears to be much greater. This is explained[56] in terms of the lower electron density at the metal available for π-bonding to the ligand. This effect is more important for carbonyl than for isonitrile and so CO is more labile. Thus complex 41, on photolysis in the presence of triphenylphosphine, gives a high yield of 42, in which the carbonyl ligands only have been displaced. This selective lability is lost in many neutral complexes[57,58], although it is still operative, for example, in decarbonylation of 43 to give 44[58].


CO
Fe
CNMe
CO
PPh3/hv
-2 CO
PPh3
Fe
CNMe
PPh3

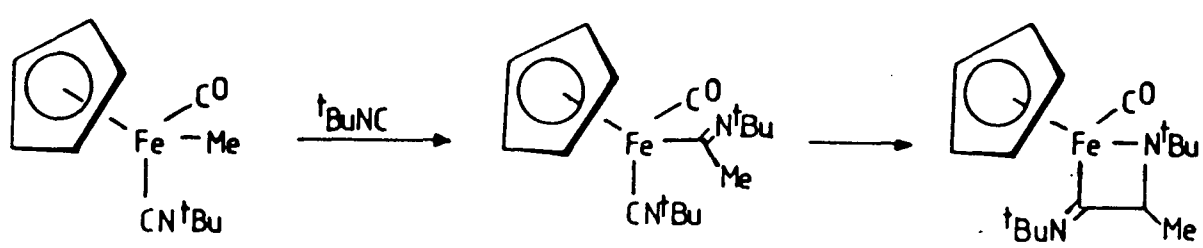
41 42


CO
Fe
O
Me
CN^tBu
hv
-CO
Fe
O
Me
CN^tBu
Me
Fe
CO
CN^tBu

43 44

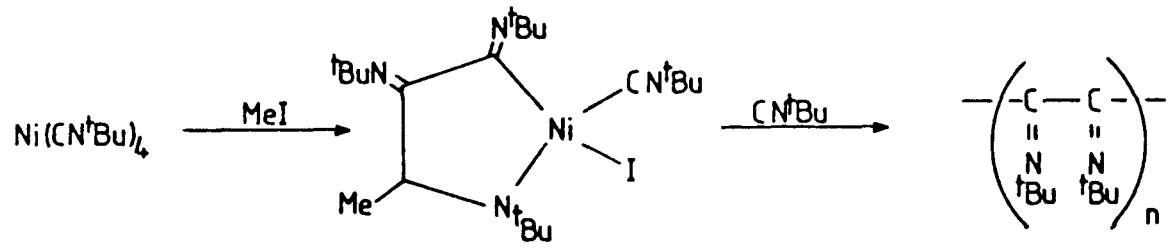
2.2 Alkyl Migration to Isonitriles

The migration of alkyl groups to isonitrile ligands appears to be extremely favourable. Multiple migrations are not infrequent. The iron complex 44, on refluxing with free *t*-butyl isonitrile, undergoes a double migration to give the product 46, presumably via 45[58].



44 45 46

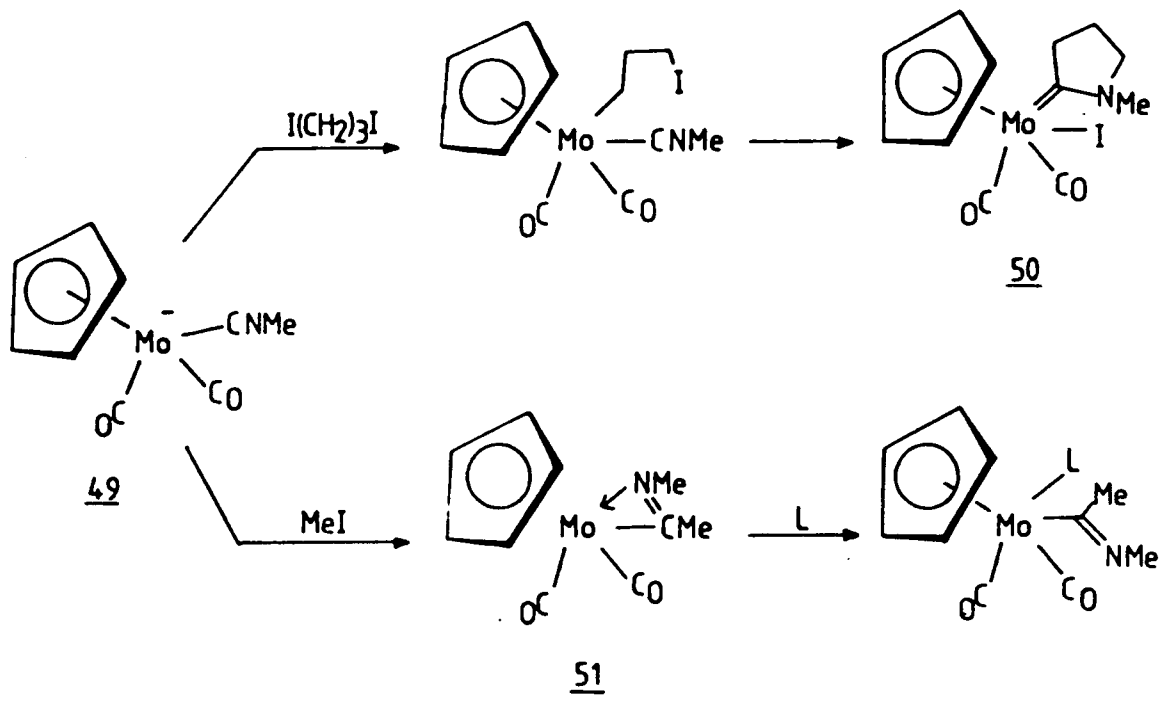
Such multiple migration leads to oligomerization of isonitrile in the nickel complex 47. Further treatment with isonitrile gives a polymer with the repeating unit 48[59].



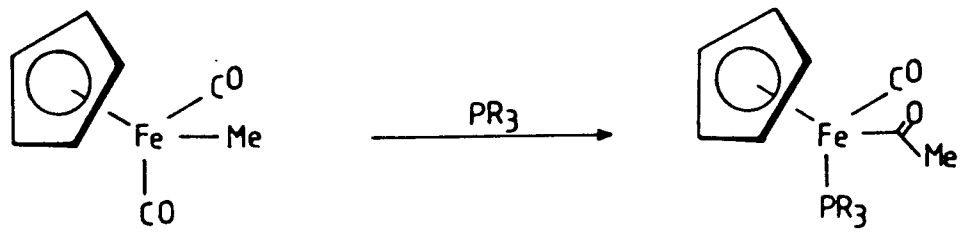
47 48

In studies of migration reactions involving metals coordinating both carbonyl and isonitrile ligands, products due only to migration to isonitrile have been seen[60,61,62]. Complex 45 was isolated in 10% yield on heating 44 in a sealed tube with *t*-butyl isonitrile at 70°C for 30h, on this occasion without further migration[60]. The molybdenum complex 49 gave a product 50 due solely to migration of the iodoalkyl unit to isonitrile[61]. A similar reaction with methyl iodide gave an iminoacyl intermediate 51 which was trapped with a variety of ligands L

(L = PPh_3, $P(OMe)_3$, tetracyanoethylene)[62].



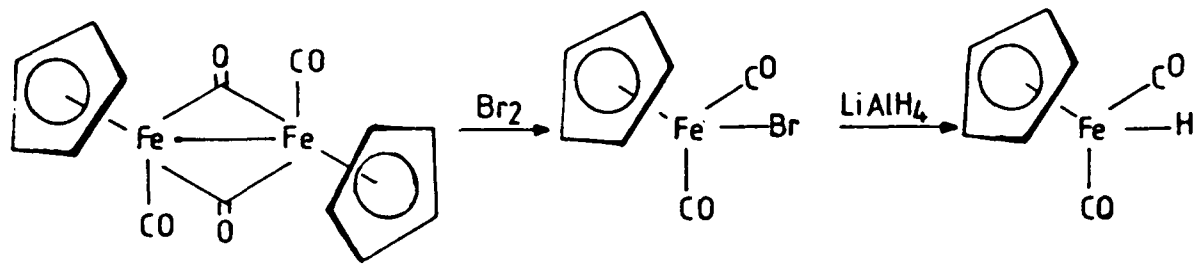
It would appear that alkyl migration occurs exclusively to isonitrile in complexes containing both isonitrile and carbonyl ligands. It was decided to test this hypothesis using a system analogous to the well-known[63] phosphine-induced migration in complex 52 to give acetyl complex 53.



52 53

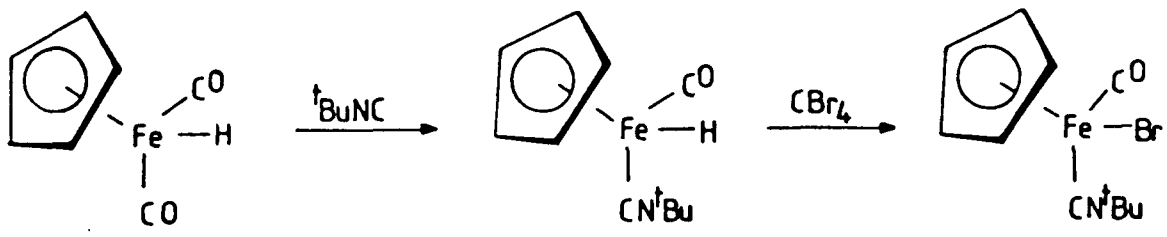
Complex 44, formally derived from 52 by replacement of one carbonyl ligand with *t*-butyl isonitrile, was therefore prepared as above (section 2.1) by photolysis of acetyl complex 43. Complex 44, and the related *n*-butyl complex 59, were also prepared by alkyl lithium displacement of bromide from bromo-complex 58. Cleavage of the dimer 54, prepared in high yield from

dicyclopentadiene and iron pentacarbonyl, with bromine gives the bromide 55. Displacement of bromide with hydride was achieved with $LiAlH_4$ at -30°C to give the thermally unstable hydride 56.



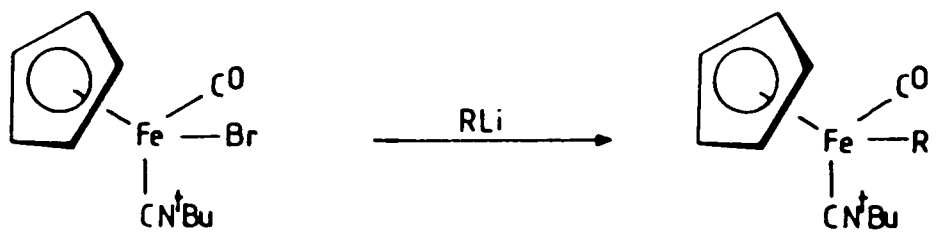
54 55 56

The lability of ligands in carbonyl hydride complexes such as 56 is well documented. An explanation, involving hydride migration to give a formyl group, coordination of an incoming ligand, and reverse migration with loss of carbonyl, has been proposed[64]. Replacement of only one carbonyl ligand was found to occur by addition of excess *t*-butyl isonitrile to a light petroleum solution of 56 at 0°C. The hydride 57 could be isolated as a moderately stable yellow oil, and was characterized by NMR and IR spectroscopy and high-resolution mass spectrometry.



56 57 58

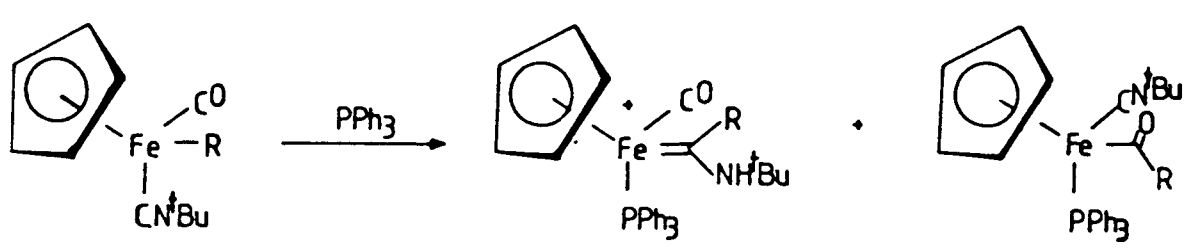
Bromination of hydride 57 with carbon tetrabromide was achieved in quantitative yield to give the known[65] bromide 58. Reaction of complex 58 with methyl or *n*-butyl lithium in THF at -78°C gave the alkyl complexes 44 and 59 in moderate yields.



58

44 R=Me
59 R=^{n}Bu

Complexes 44 and 59 were refluxed in acetonitrile with one equivalent of triphenylphosphine for 18h. Chromatography led to isolation of the aminocarbenes 60a,b, formed by protonation of initially produced iminoacyl, together with small amounts of the acyls 61a,b. Migration was therefore not completely specific to isonitrile.

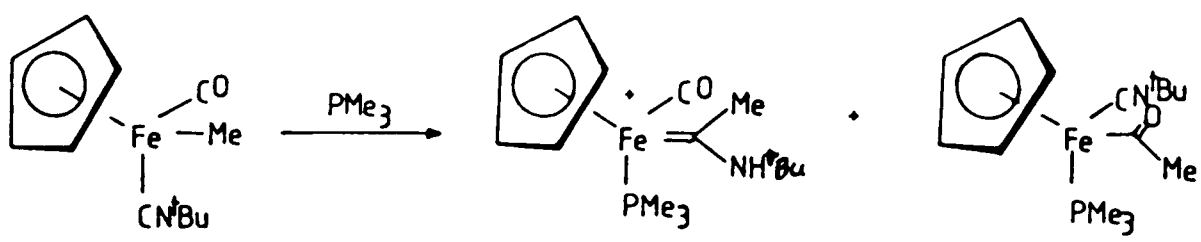


44 R=Me
59 R=^{n}Bu

60a R=Me
60b R=^{n}Bu

61a R=Me
61b R=^{n}Bu

Ratios found were 60a:61a, 29:1; 60b:61b, 2.5:1; with overall chemical yields of 42% and 40% respectively. Refluxing complex 44 with trimethylphosphine similarly gave aminocarbene 62 in high (69%) yield, together with a small amount (0.6%) of a compound assigned as the acyl 63 by ^{1}H NMR spectroscopy.



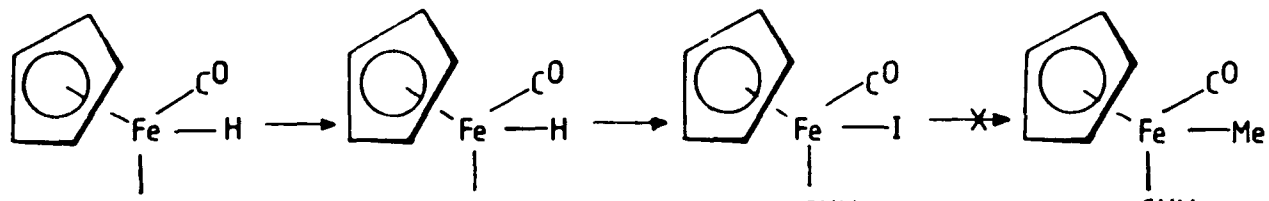
44

62

63

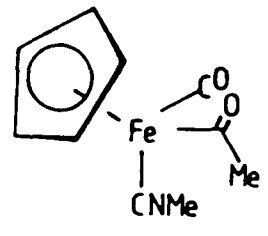
IR spectra of the aminocarbene complexes 60a,b and 62 showed a complete absence of the isonitrile stretch at 2120 cm^{-1}, and new sharp peaks at ca. 3300 cm^{-1} assigned to the NH group. For acyl complexes 61a,b carbonyl stretches at 1920 cm^{-1} were replaced by acyl carbonyl peaks at around 1570 cm^{-1}.

Repetition of these migration reactions using methyl isonitrile in place of *t*-butyl isonitrile could not be attempted, as syntheses of the alkyl complex 66 proved unsuccesful. The hydride 64, prepared in a similar fashion to 57 above, proved to be quite unstable, darkening in about one minute at 0°C. It was transformed to the stable, known[66] iodide 65 by treatment with 1,2-diiodoethane. Treatment of this iodide with methyl lithium, methyl magnesium iodide or $Me_2CuCNLi_2$ failed to give 66.



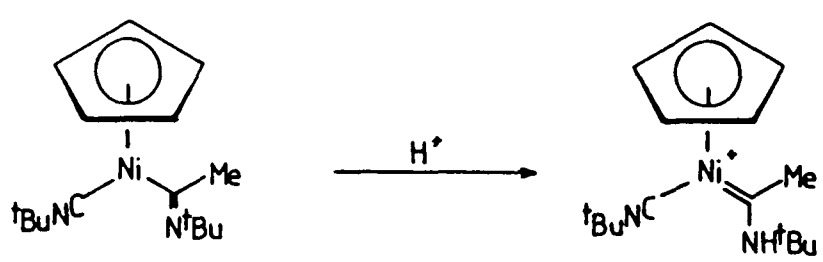
56 64 65 66

Other syntheses attempted included decarbonylation of the known acetyl 67, or deprotonation of 64 with *n*-butyl lithium followed by alkylation with methyl iodide or methyl tosylate. Neither of these methods yielded any of the desired complex 66.



67

It is of interest that the work-up procedures employed for iminoacyls 60a,b and 62, involving simply chromatography on alumina, led to N-protonated aminocarbenes. Such protonation was not observed in the works cited above. It is known, however, that the iminoacyl nitrogen is strongly basic. Alkylation and protonation have several times been reported. Treatment of iminoacyl complex 68 with HBF_4, for example, gave the amino-carbene complex 69[67].

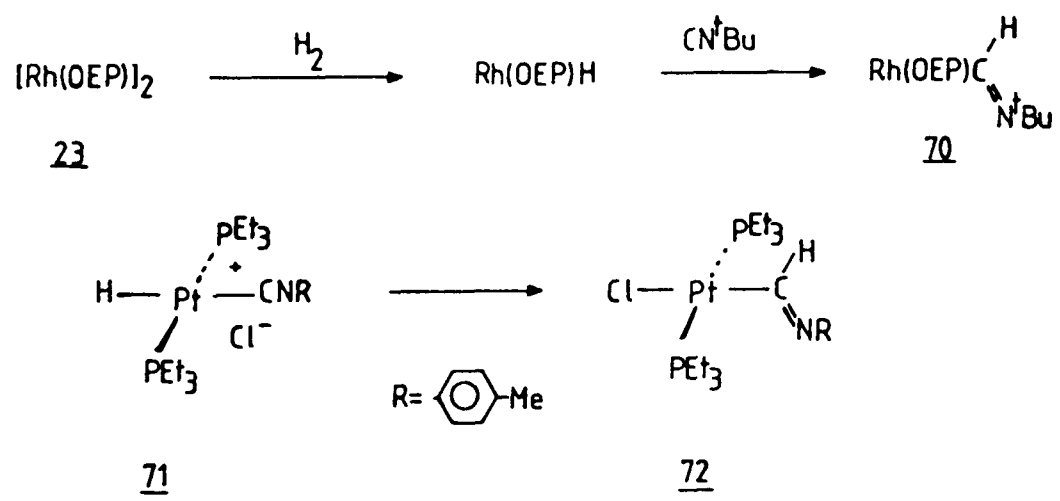


68 69

Finally, it should be noted that the stability of imino-acyls is such that, although decarbonylation of acyls to alkyl carbonyl complexes is well known, similar reverse migration reactions have never been reported for iminoacyls.

2.3 Hydride Migration to Isonitriles

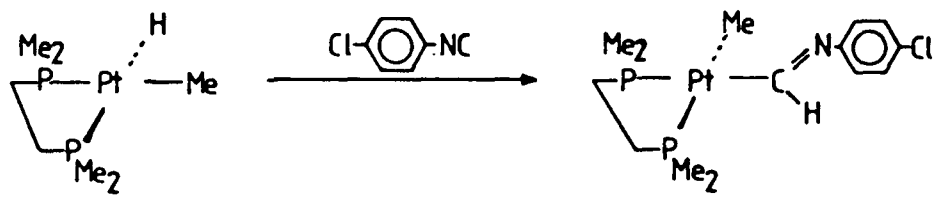
As was remarked in section 1.4, the migration of hydride to metal-bound isonitriles is well documented. In addition to the example already quoted[48], an analogue 70 of the rhodium octaethylporphyrin formyl complex 24 has been prepared[68]. The platinum salt 71 has been shown to convert in non-polar solvents to the iminoformyl complex 72[69].



23 70

71 72

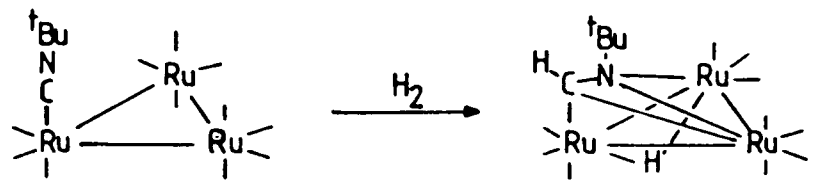
A migration of hydride in preference to methyl was seen in the reaction of platinum complex 73 with *p*-chlorophenyl isonitrile[70]. The iminoformyl 74 was the exclusive product, no migration of methyl being seen.



73 74

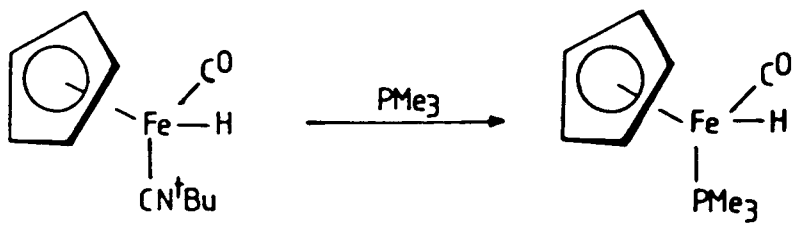
Iminoformyl groups bound to more than one metal centre have also been prepared[71]. For example, treatment of the ruthenium cluster $Ru_3(CO)_{11}(CNtBu)$, 75 with dihydrogen gave the μ^3, η^2-iminoformyl complex 76[71]. For clarity, carbonyl ligands have

been omitted from the diagram.



75 76

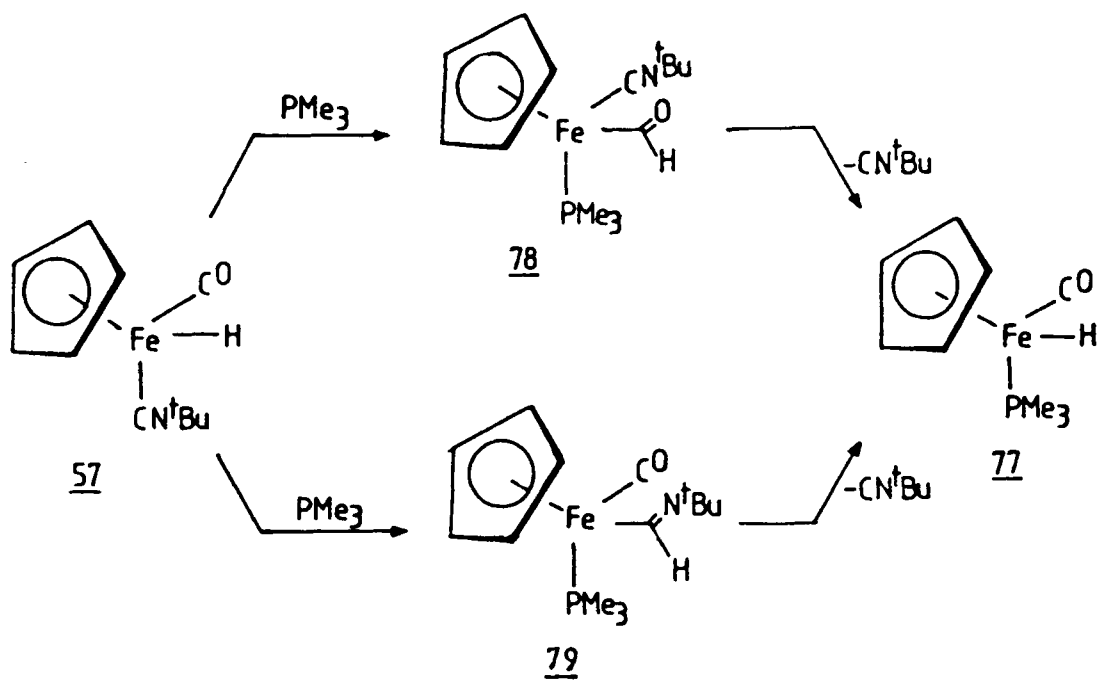
Hydride migration to isonitriles thus appears to be a quite facile process. It was hoped that such a migration might be achieved for the stable complex 57 with the aid of phosphines. An acetonitrile solution of 57 was therefore stirred with triphenylphosphine. No reaction resulted at room temperature, and rapid decomposition occurred on heating. Similar reaction at room temperature with trimethylphosphine led to displacement of the isonitrile ligand, producing the known phosphine hydride complex 77.



57 77

Two mechanisms in particular may be envisaged for this substitution. Hydride migration to carbonyl to give the formyl 78, followed by loss of isonitrile and reverse migration of hydride is a possibility. Hydride migration to isonitrile would give iminoformyl 79, which would decompose via an overall α-elimination with loss of isonitrile. The above results would lead us to expect migration to isonitrile, and 79 as the likely intermediate. The fate of intermediates such as 79 will be

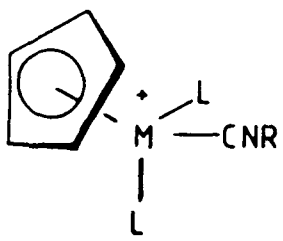
further discussed in Chapter 4.



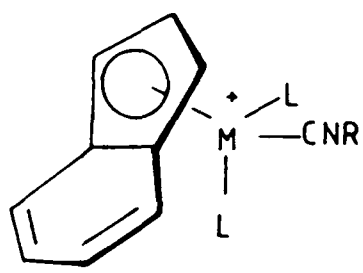
CHAPTER 3

PREPARATION OF CATIONIC CARBONYL AND ISONITRILE COMPLEXES

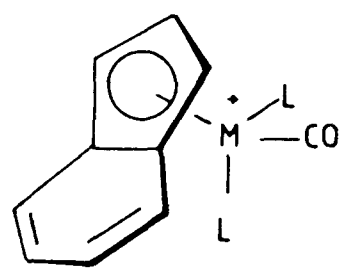
As stated in section 1.4, metal formyl complexes have been prepared by hydride donation to metal carbonyl complexes. It was hoped that, in an analogous fashion, hydride donation to a series of cationic isonitrile complexes might yield iminoformyl complexes suitable for further study. This work confines itself to "piano-stool" complexes of the type 80 or 81, with M as iron or ruthenium, and L as carbonyl or phosphine ligands. Cyclopentadienyl is one of the hydrocarbon ligands least susceptible to nucleophilic attack[1], and it is therefore expected that hydride donation will be directed to the isonitrile ligand. η^5-indenyl carbonyl complexes of the type 82 are also considered.



80



81

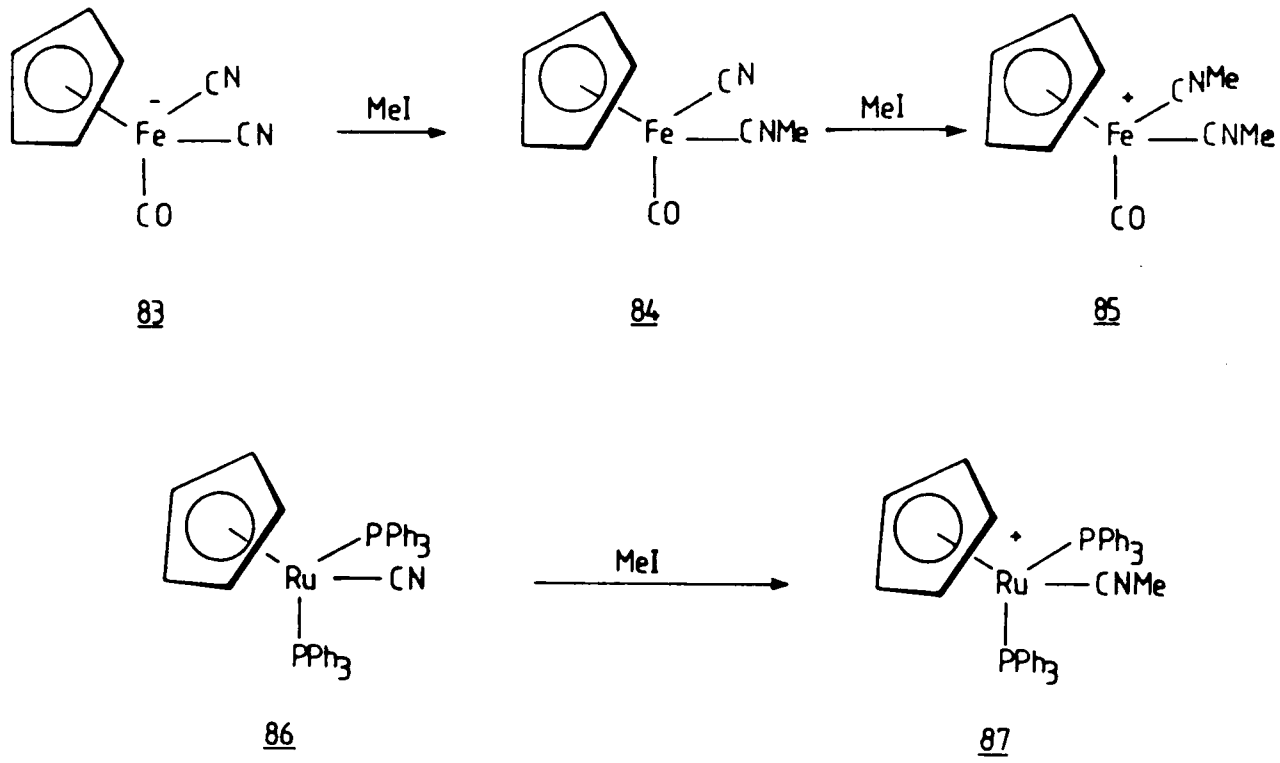


82

3.1 Preparation of η^5-cyclopentadienyl isonitrile complexes

Methods employed in the literature for the synthesis of cationic isonitrile complexes of the type 80 fall into three major categories[55].

i) Alkylation of [M]-CN. This is perhaps the most common route to cationic isonitrile complexes. The first such complexes were prepared by this route[72]. Reaction of the anionic dicyano complex 83 with methyl iodide gave first monomethylated 84, and then the dimethylated cation 85. Similarly the ruthenium isonitrile complex 87 was prepared[73] by methylation of cyano complex 86. This reaction was further studied in work by Baird and Davies[74], in which a number of iron and ruthenium cyano complexes were alkylated by, for example, methyl iodide, allyl bromide, benzyl bromide or 2-iodoethanol.

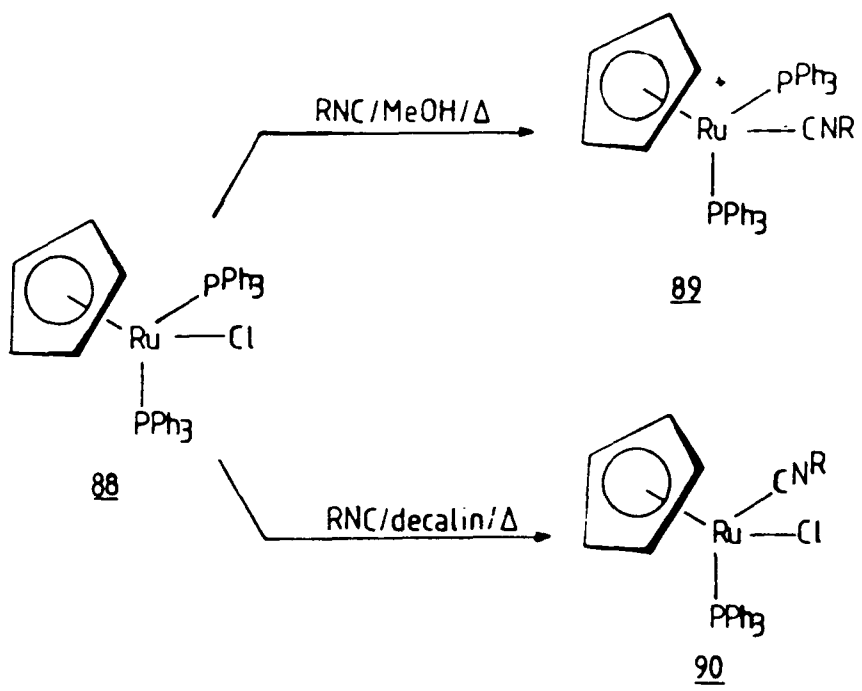


83 84 85

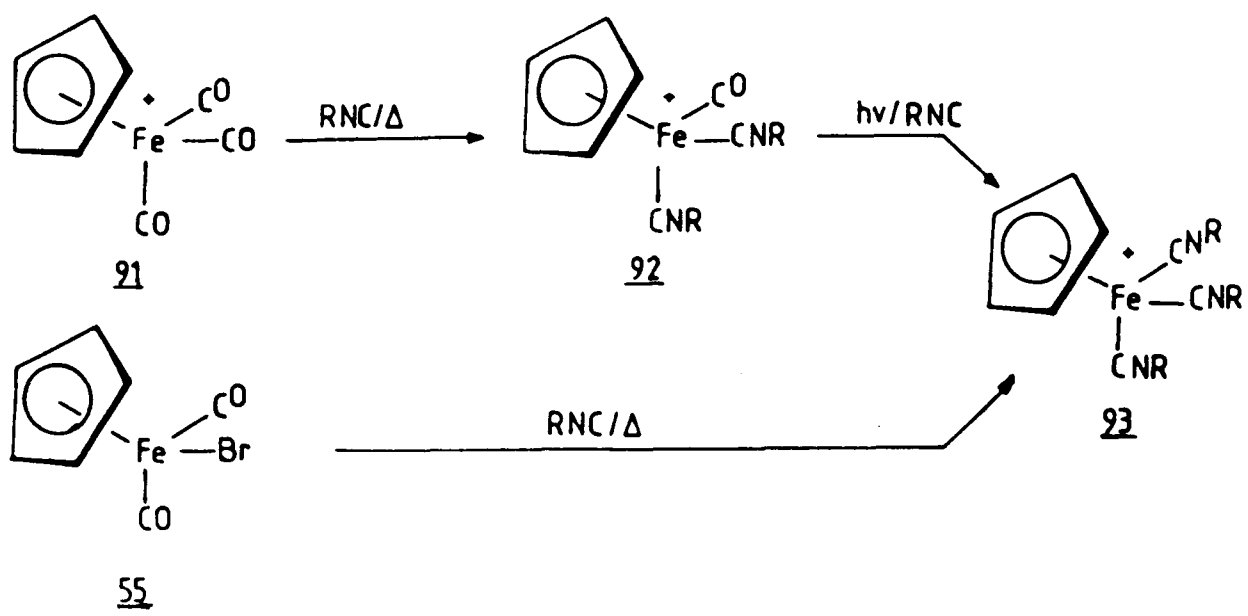
86 87

ii) The utility of the alkylation reaction as a preparative method is limited, as cyano complexes are usually prepared from halides by reaction with potassium cyanide, and then alkylated, giving a two-step preparation. It is possible in many instances

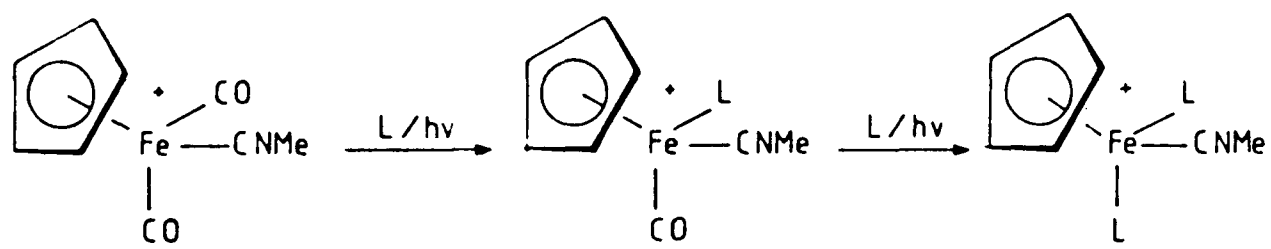
to displace halide directly with free isonitrile in one step. Yields are therefore usually much better. A range of complexes 89, analogous to the methyl isonitrile complex 87 (above), were prepared[73] in this fashion from the chloro complex 88 on reflux with isonitrile CNR (R = *t*-butyl, cyclohexyl, *p*-tolylsulphonyl) in methanol. Reaction in non-polar solvents, however, gave products 90 due to displacement of triphenylphosphine.



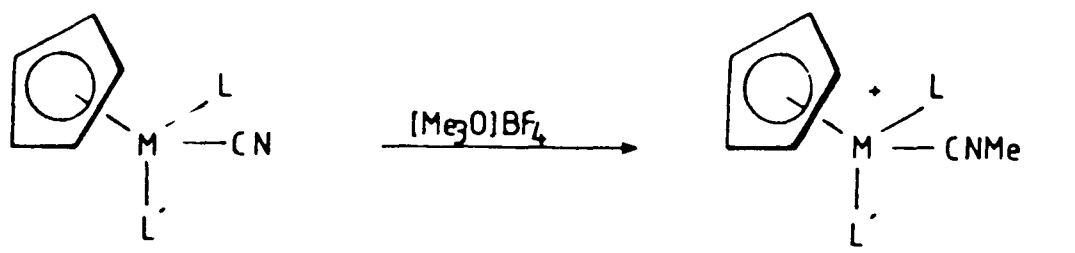
iii) A third method which has been employed involves the thermal or photochemical displacement of a carbonyl ligand by isonitrile. Thus refluxing complex 91 in THF with methyl or *t*-butyl isonitrile was found[75] to give the disubstituted complexes 92. Displacement of the remaining carbonyl ligand was achieved upon ultra-violet irradiation to give the trisubstituted complexes 93. These latter complexes have also been prepared[65,76] by reaction of the bromo complex 55 with isonitrile under reflux.



As explained in section 2.1, cationic complexes containing both carbonyl and isonitrile ligands undergo displacement reactions with selective loss of carbonyl. This selectivity has been employed in the synthesis of complexes of the type 94, by irradiation of complex 41 in the presence of ligands L = PPh_3, $AsPh_3$, $SbPh_3$, MeCN, ethylene or pyridine[56]. Further irradiation led to complexes of the type 95 in several cases.



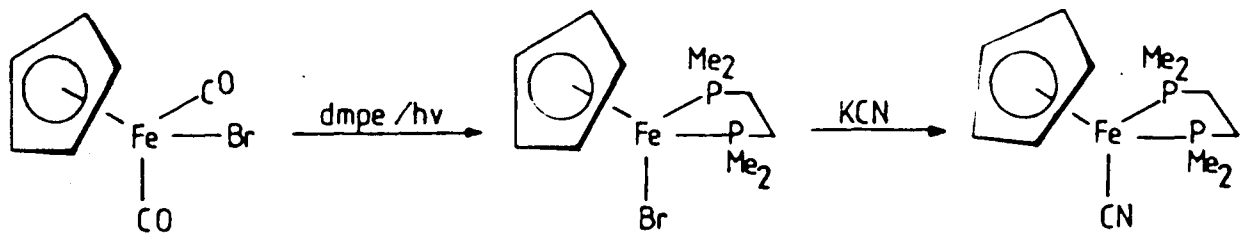
Syntheses of a few of the complexes required in this study have thus been reported. Literature procedures were followed for the syntheses of cationic complexes 97[77], 98[74] and 99[78] from the corresponding cyano complexes 96.



96

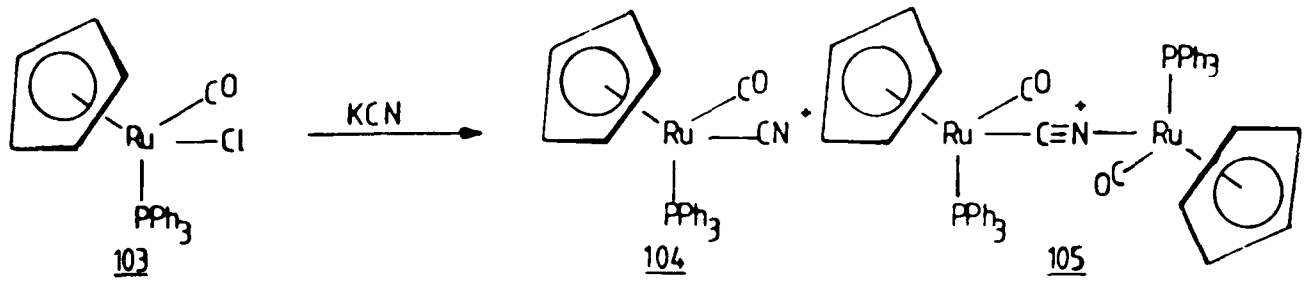
97 M = Fe; L = PPh_3; L' = CO
98 M = Fe; L,L' = dppe
99 M = Ru; L = PPh_3; L' = CO
100 M = Fe; L,L' = dmpe

The novel complex 100 was correspondingly prepared via the known bromide 101, itself prepared[79] by photolysis of complex 55 with dmpe in benzene. Reaction of complex 101 with potassium cyanide in methanol gave the cyano complex 102 as orange needles. Methylation as above gave isonitrile complex 100 in 88% yield, characterized by NMR and IR spectroscopy, mass spectrometry and elemental analysis.



55 101 102

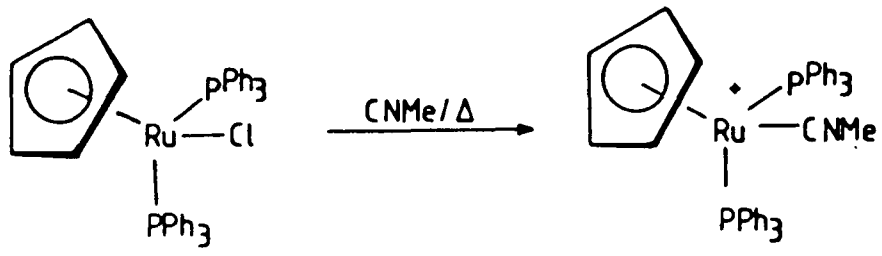
An interesting side-reaction was observed during the synthesis of the ruthenium complex 99. Heating the chloride 103 in methanol with potassium cyanide gave, as well as the desired cyano complex 104, a dimeric compound formulated as 105, and formed in 41% yield. Presumably complex 105 is formed due to a competition for the chloro complex 103 between cyanide and cyano complex 104.



103 104 105

^{1}H NMR spectroscopy indicated that both possible diastereomers of 105 were present in equal proportions. The compound gave an IR absorbtion at 2140 cm^{-1} due to the C-N linkage. This is consistent with similar cyano-bridged iron and ruthenium dimers previously reported[80].

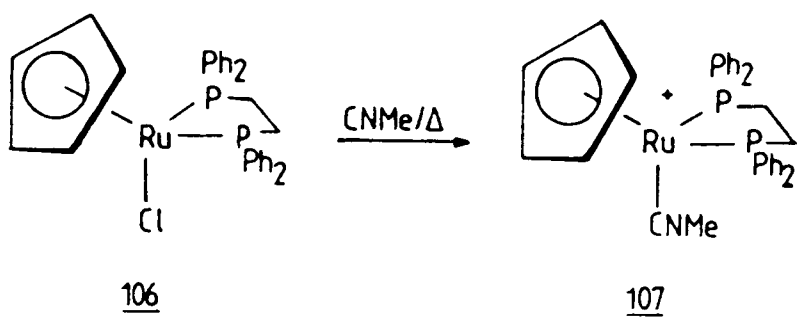
Direct reaction of methyl isonitrile with the ruthenium chloro complex 88 was used to prepare complex 87. As expected, the change from a two-step to a one-step preparation resulted in a large gain in yield. Conversion of complex 88 to 87 via the cyano intermediate 86 has been reported to proceed in 38% overall yield[73]. Refluxing a methanol solution of 88 with one equivalent of methyl isonitrile in the presence of NH_4PF_6, however, gave complex 87 in 92% yield.



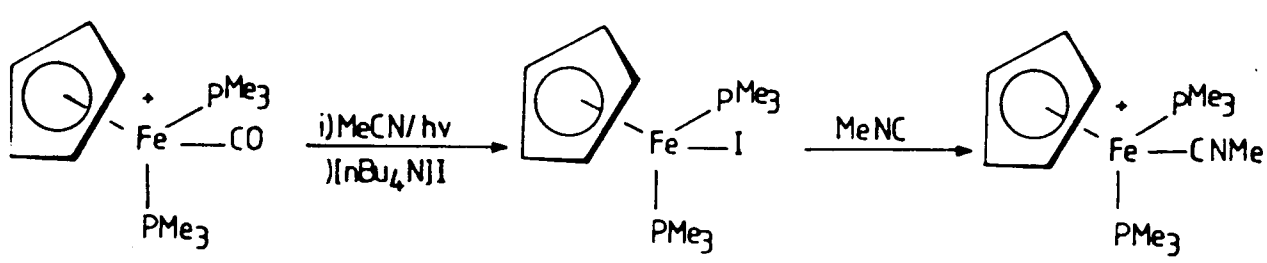
88 87

Two novel cationic complexes were also prepared by this route. The dppe-substituted ruthenium complex 106 reacts with methyl isonitrile under identical conditions to complex 88 to give the product 107 in 62% yield. The iron iodo complex 109

was prepared in moderate yield by a literature procedure[81] involving ultra-violet irradiation of cation 108 in acetonitrile, followed by refluxing with [nBu$_4$N]I in THF. Complex 109 was found to react with methyl isonitrile at room temperature to give the novel cation 110 in 94% yield.

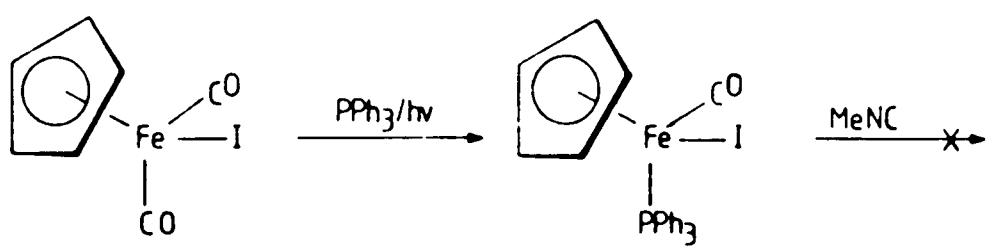


106 107



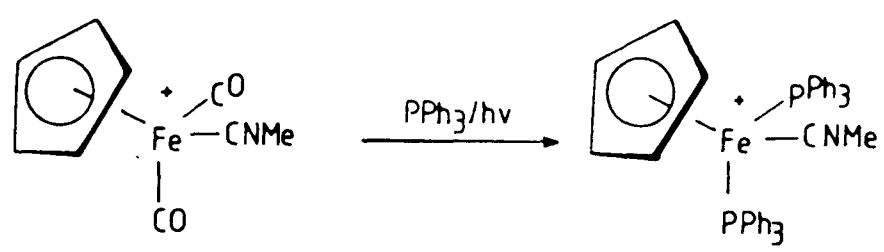
108 109 110

Attempts to extend this method to the synthesis of cations 97 and 99 were unsuccessful. Refluxing complex 103, or the iodo complex 112, prepared by visible light irradiation of complex 111 with triphenylphosphine, with methyl isonitrile and NH_4PF_6 in methanol gave starting materials only. Presumably the lower electron density at the metal caused by the presence of only one phosphine ligand disfavours dissociation of the halide, preventing reaction from occurring.

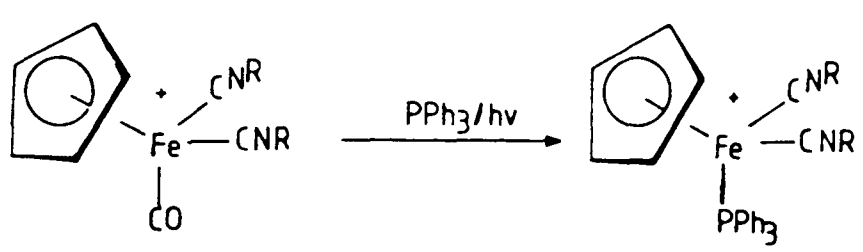


111 112

The displacement of carbonyl ligands on irradiation of carbonyl isonitrile cations noted above was used in the preparation of the known complexes 42 and 113 by the literature route[56]. The novel complex 114 was produced in an entirely analogous fashion in 73% yield from 92.



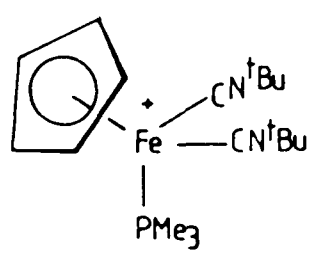
41 42



92

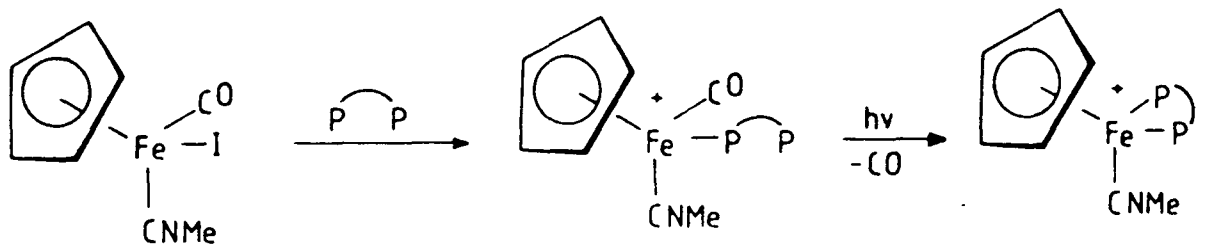
113 R=Me
114 R=^{t}Bu

Attempts to repeat these reactions with the more electron-rich ligand trimethylphosphine were not successful. This phosphine reacted with displacement of both isonitrile and carbonyl ligands, and intractable mixtures of various cationic species were formed. The trimethylphosphine complex 115 was, however, formed unexpectedly during the work described in section 5.2.



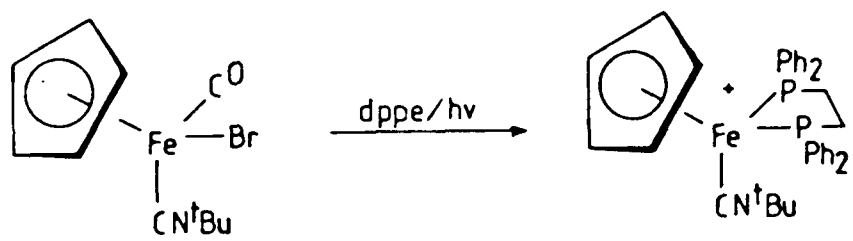
115

This displacement reaction was adapted for the synthesis of a series of complexes with chelating bisphosphines. Such phosphines might be expected to displace iodide from the iodo complex 65 to generate the intermediate 116. Irradiation of this should result in preferential loss of the carbonyl ligand. This reaction was found to occur readily, and complexes 117, 118 and 119 were prepared in this manner in yields of 36 to 48%.



65 116 117 P_2=dppm; 118 P_2=dppp; 119 P_2=cdpe

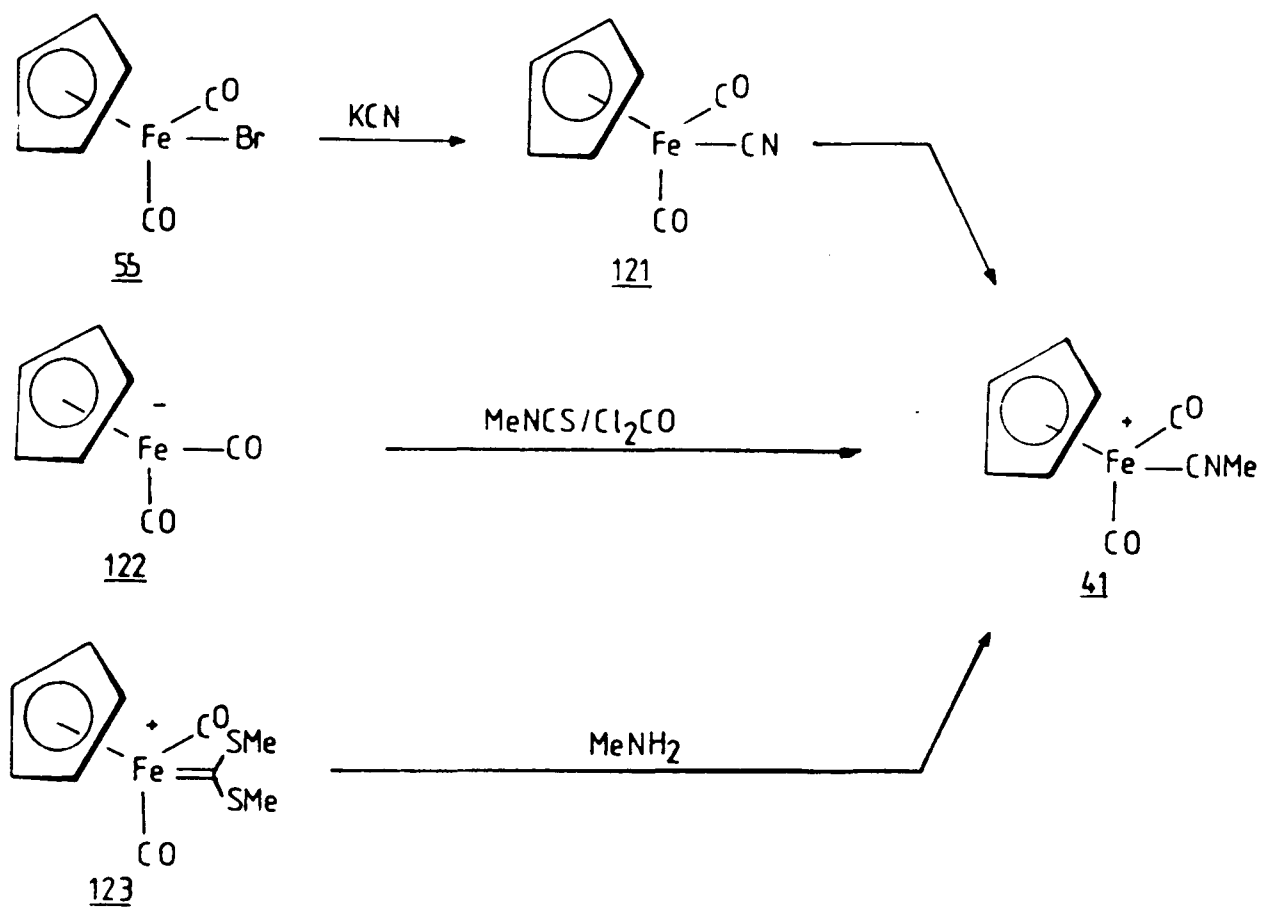
In a similar manner the *t*-butyl isonitrile complex 120 was prepared from bromo complex 58 and dppe. No carbonyl absorbtions could be detected for these bisphosphine complexes in the infrared spectrum, all showing instead strong isonitrile absorbtions in the region 2175-2125 cm^{-1}.



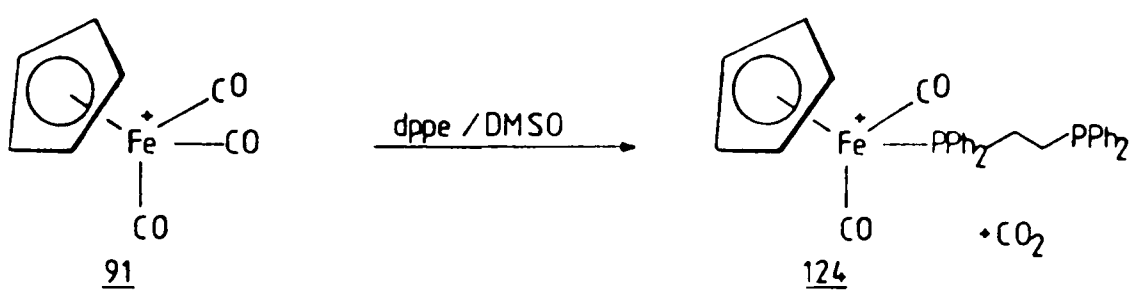
58 120

The dicarbonyl isonitrile complex 41 was first prepared[82] by methylation of the corresponding cyano complex 121. An early report[83] describes the synthesis of this cyano complex from bromo complex 55 and potassium cyanide in 46% yield. This synthesis has, however, repeatedly failed to give any product in our laboratory[84]. Other reported preparations of complex 41

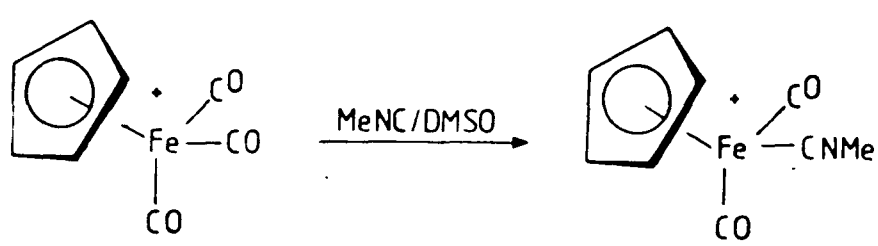
include the reaction of the anion 122, derived from $[CpFe(CO)_2]_2$ 54, with MeNCS in the presence of phosgene[85]; and treatment of the thiocarbene 123 with anhydrous methylamine[86].



As these latter two preparations are somewhat inconvenient, a new synthesis of complex 41 was devised. A report by Davies[87] showed that one carbonyl ligand could be removed from tricarbonyl cation 91 by oxidation with dimethylsulphoxide. Thus complex 124 had been prepared by performing the reaction in the presence of excess dppe.



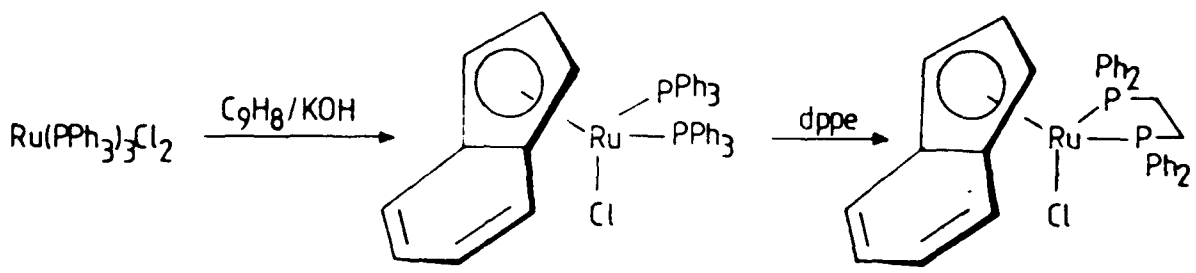
Following this method, preparation of complex 41 was achieved by stirring a solution of cation 91 with one equivalent of methyl isonitrile and excess dimethylsulphoxide in acetone at room temperature. Yields of complex 41 were around 37%, the remainder being unreacted 91. The two cationic complexes were separated by simple extraction with dichloromethane, in which complex 91 is insoluble.



91 41

3.2 Preparation of η^5-indenyl ruthenium complexes

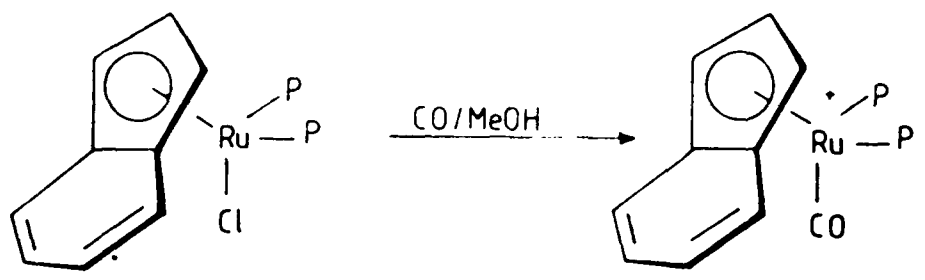
A recent report[88] described the syntheses of the η^5-indenyl ruthenium complexes 125 and 126. Addition of potassium hydroxide to a refluxing mixture of $Ru(PPh_3)_3 Cl_2$, 127[89] and indene in ethanol produced complex 125 in 78% yield. Heating a toluene solution of complex 125 with dppe resulted in phosphine displacement to give complex 126.



127 125 126

Replacement of chloride in complex 125 with carbon monoxide had also been achieved by bubbling dry CO gas through a solution of complex 125 containing sodium perchlorate.

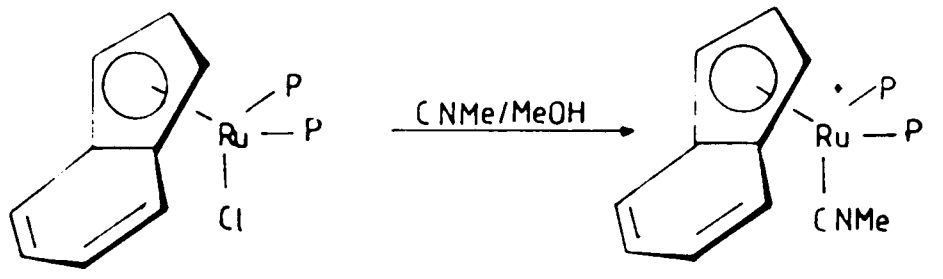
This replacement was here achieved by a slightly different method. A solution of complex 125 in methanol containing NH_4PF_6 was stirred under 3 atmospheres pressure of CO in a Fischer-Porter bottle. A colour change from red to yellow over three hours indicated that reaction to give complex 128 was complete. This method was also used for the novel carbonyl complex 129. These two products showed the expected carbonyl absorbtions in the IR spectrum at 1990 and 1970 cm^{-1} respectively.



125 P = PPh_3
126 P_2 = dppe

128 P = PPh_3
129 P_2 = dppe

The novel isonitrile complexes 130 and 131 were prepared in a similar fashion by room-temperature reaction of complexes 125 and 126 with methyl isonitrile in methanol containing NH_4PF_6. The reaction was again monitored by its colour, a change from red to yellow indicating that reaction was complete.



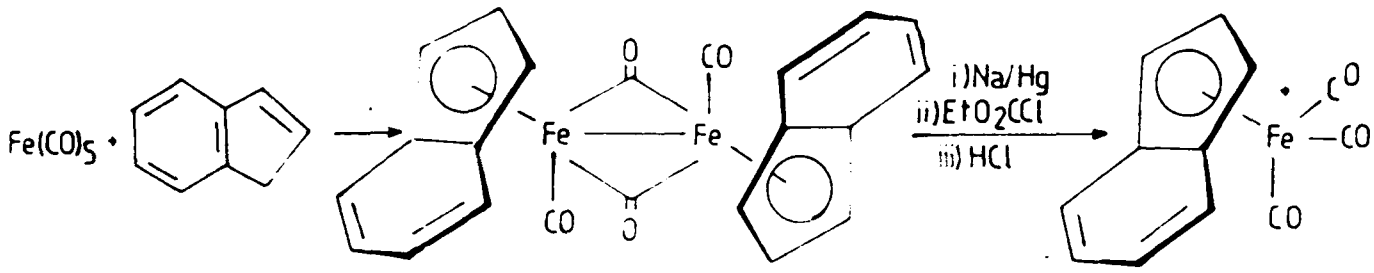
125 $P = PPh_3$
126 P_2 = dppe

130 $P = PPh_3$
131 P_2 = dppe

Unfortunately, contamination of chloro complex 126 with a small amount of its precursor 125 resulted in contamination of complex 131 with a small amount of complex 130. A correct elemental analysis could not therefore be obtained for complex 131, and mass spectroscopy revealed the presence of complexes 130 and 131. All other spectroscopic techniques, including IR, ^1H NMR, ^{31}P NMR and ^{13}C NMR spectroscopy, indicated that complex 131 was indeed the product.

3.3 Preparation of η^5-indenyl iron complexes

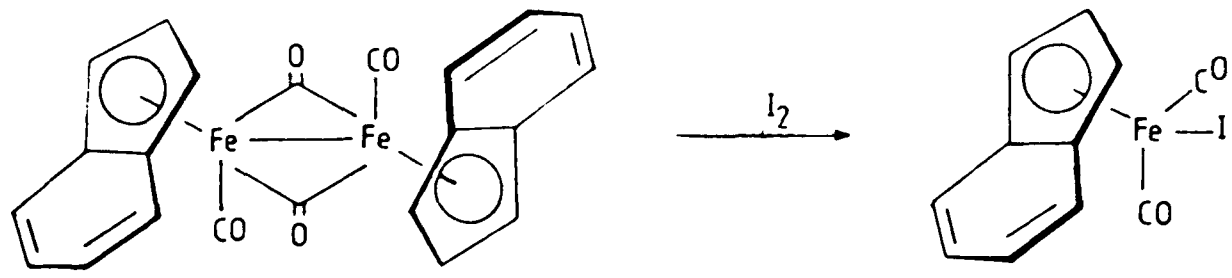
The five indenyl iron complexes which were prepared in this work are all derived from the dimeric complex 132. This dimer is prepared[90] analogously to the cyclopentadienyl dimer 54 by refluxing iron pentacarbonyl together with indene. Yields obtained were very low, in the range 1-5%.



132 133

Only one of these cationic complexes has been previously reported. Complex 133 has been prepared[91] analogously to the cyclopentadienyl complex 91[92] by cleavage of dimer 132 with sodium amalgam and treatment with ethyl chloroformate and hydrogen chloride gas.

The cleavage of dimer 132 with sodium amalgam was not found to occur readily. Reaction with iodine to give the iodo monomer 134[93] however proceeded in very high yield. Substitution of complex 134 for dimer 132 in the above synthesis of 133 gave a moderate (17%) overall yield.



132 134

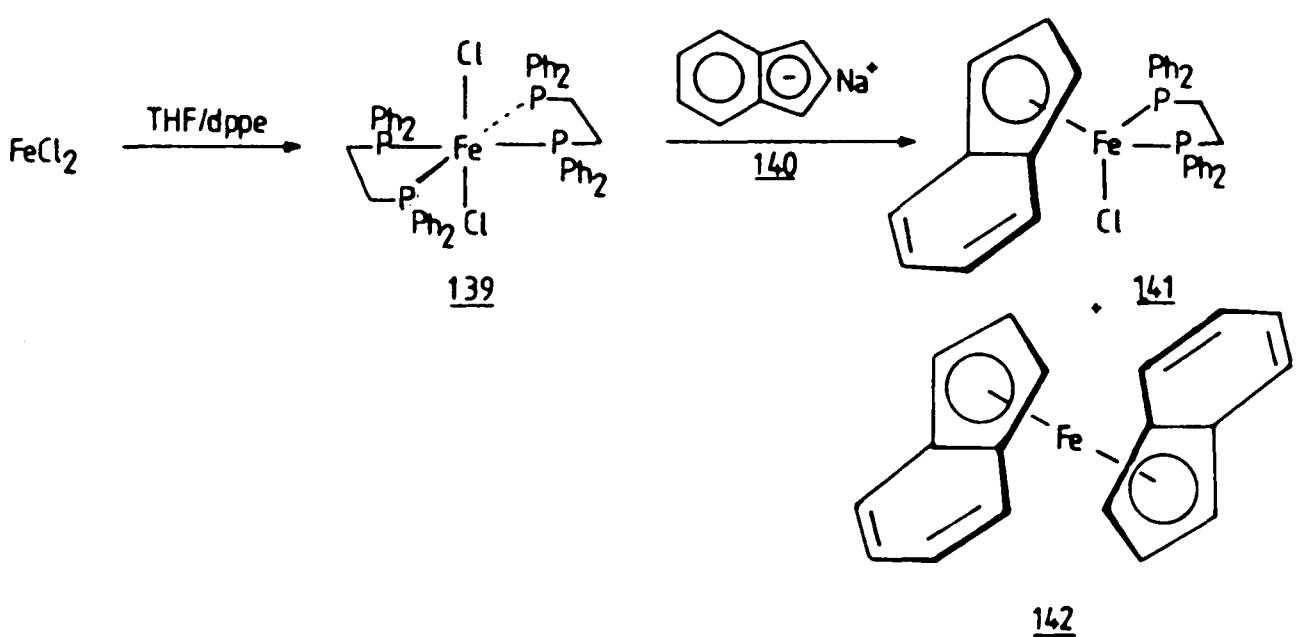
A recent report[94] showed that displacement of iodide from complex 134 with a limited range of phosphines and phosphites

could be achieved in light petroleum under reflux. We found this reaction to be extremely facile in methanol containing NH_4PF_6. In the presence of one equivalent of phosphine, complex 135 was formed at reflux, and 136 at room temperature. Refluxing with excess phosphine gave the bisphosphine complexes 137 and 138 in good yield.

134

135 L = PPh_3, L´= CO
136 L = PMe_3, L´ = CO
137 L = L´ = PMe_3
138 L, L´ = dppe

Because of the disappointing yields obtained for formation of the dimer 132, an alternative synthesis of complex 138 was attempted. Heating anhydrous $FeCl_2$ in THF followed by refluxing with dppe gives a complex of probable structure 139. It was hoped that indenyl sodium 140 would react with this complex to give the chloro-complex 141, which might then be carbonylated by reaction with gaseous CO.



139

141

142

In fact, reaction of complex 139 with indenyl sodium 140 gave a large quantity of diindenyliron, 142. This was not separable from complex 141. Carbonylation of the mixture with 3 atmospheres pressure of CO in methanol gave a small quantity of a cationic complex, separable by chromatography. This was identified as complex 138 by comparison with an authentic sample The diindenyliron 142 was identified by comparison with a sample prepared from $FeCl_2$ and indenyl sodium[95].

The yield of complex 138 by this route was only 2.6%, making it unsuitable for preparative purposes.

3.4 Summary of Preparations

i) Table 1. Preparation of η^5-cyclopentadienyl complexes, $CpMLL'L''^+$.

Compound No.	M	L,L',L''	Method (a,e)	Prepared from		Lit. ref.
97	Fe	CO, PPh_3, CNMe	A(f)	$CpFe(CO)(PPh_3)CN$	96	77
98	Fe	dppe, CNMe	A(f)	CpFe(dppe)CN	96	74
100	Fe	dmpe, CNMe	A(f)	CpFe(dmpe)CN	102	(c)
110	Fe	$2PMe_3$, CNMe	B	$CpFe(PMe_3)_2I$	109	(c)
42	Fe	$2PPh_3$, CNMe	C	$CpFe(CO)_2CNMe^+$	41	56
117	Fe	dppm, CNMe	D	CpFe(CO)(CNMe)I	65	(c)
118	Fe	dppp, CNMe	D	CpFe(CO)(CNMe)I	65	(c)
119	Fe	cdpe, CNMe	D	CpFe(CO)(CNMe)I	65	(c)
120	Fe	dppe, CN^tBu	D	$CpFe(CO)(CN^tBu)I$	58	(c)
113	Fe	PPh_3, 2CNMe	E	$CpFe(CO)(CNMe)_2^+$	92	56
114	Fe	PPh_3, $2CN^tBu$	E	$CpFe(CO)(CN^tBu)_2^+$	92	(c)
115	Fe	PMe_3, $2CN^tBu$	(b)	$CpFe(CO)(PMe_3)H$	77	(c)
41	Fe	2CO, CNMe	F	$CpFe(CO)_3^+$	91	(d)
99	Ru	CO, PPh_3, CNMe	A(f)	$CpRu(CO)(PPh_3)CN$	104	78
87	Ru	$2PPh_3$, CNMe	B	$CpRu(PPh_3)_2Cl$	88	(d)
107	Ru	dppe, CNMe	B	CpRu(dppe)Cl	106	(c)

(a) A: $[M]\text{-}CN + Me_3O^+BF_4^-$
B: $[M]\text{-}X + MeNC + NH_4PF_6$
C: $[M]\text{-}(CO)_2^+ + PPh_3 + h\nu$
D: $[M](CO)Cl + P_2 + h\nu$
E: $[M]\text{-}CO^+ + PPh_3 + h\nu$
F: $[M]\text{-}CO^+ + CNMe + DMSO$

(b) See section 5.2.

(c) Novel complex: characterized by IR, ^1H NMR, ^{31}P NMR spectroscopy, mass spectrometry and elemental analysis.

(d) Previously reported complex, prepared by novel route.

(e) Isolated as PF_6^- salts unless otherwise stated.

(f) Isolated as BF_4^- salts.

Table 2 Preparation of η^5-indenyl complexes, $InMLL'L''^+$.

Compound No.	M	L,L',L''	Method (a,b)	Prepared from		Lit. ref.
133	Fe	3CO	A	$[InFe(CO)_2]_2$	132	91
135	Fe	PPh_3, 2CO	B	$InFe(CO)_2I$	134	(c)
136	Fe	PMe_3, 2CO	B	$InFe(CO)_2I$	134	(c)
137	Fe	$2PMe_3$, CO	B	$InFe(CO)_2I$	134	(c)
138	Fe	dppe, CO	B	$InFe(CO)_2I$; $FeCl_2(dppe)_2$	134 139	(c)
128	Ru	$2PPh_3$, CO	C	$InRu(PPh_3)_2Cl$	125	88
129	Ru	dppe, CO	C	InRu(dppe)Cl	126	(c)
130	Ru	$2PPh_3$, CNMe	C	$InRu(PPh_3)_2Cl$	125	(c)
131	Ru	dppe, CNMe	C	InRu(dppe)Cl	126	(d)

(a) A: 134 + Na/Hg, $ClCO_2Et$, HCl.
B: [M]-X + PR_3
C: [M]-X + CNMe or CO.

(b) All compounds isolated as PF_6^- salts.

(c) Novel complex, characterized by IR, ^1H NMR, ^{31}P NMR, ^{13}C NMR spectroscopy, mass spectrometry and elemental analysis.

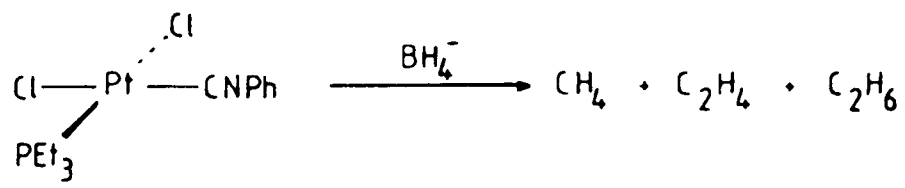
(d) Novel complex, characterized by IR, ^1H NMR, ^{31}P NMR ^{13}C NMR spectroscopy and mass spectrometry.

CHAPTER 4

REDUCTION OF CATIONIC CARBONYL AND ISONITRILE COMPLEXES

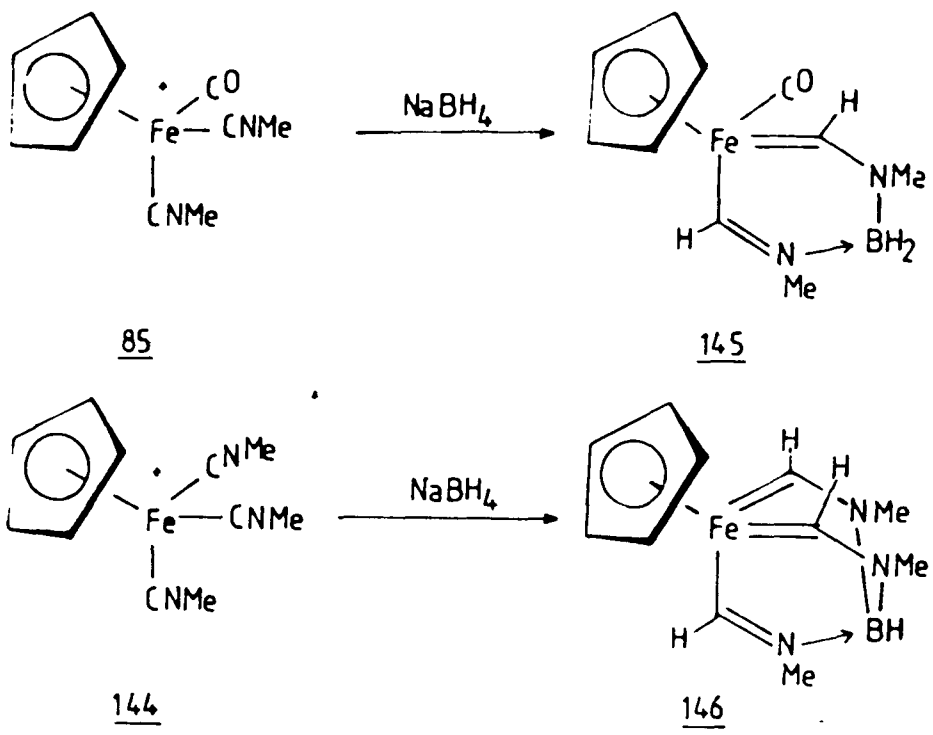
4.1 Introduction

Very little work has been reported to date on the reduction of coordinated isonitriles. A number of reports have appeared of enzymatic reduction of methyl, ethyl and phenyl isonitriles with nitrogenase enzymes, giving methane and other hydrocarbons up to propane. Coordination of isonitrile to a metal atom within the enzyme is considered to be a vital step[96]. Such a reduction is also found to occur with a molybdate catalyst system which mimics the action of nitrogenases[97]. Borohydride reduction of isonitrile in the platinum complex 143 is reported to give methane, ethylene and ethane[98]. No mechanisms were advanced for these reductions.



143

The only reported examples of isonitrile reductions to give a reduced metal-coordinated species are given by the iron complexes 41, 85 and 144[99]. Sodium borohydride reduction of the latter two complexes gave species assigned the structures 145 and 146, with boron hydride units attached to the reduced ligands.

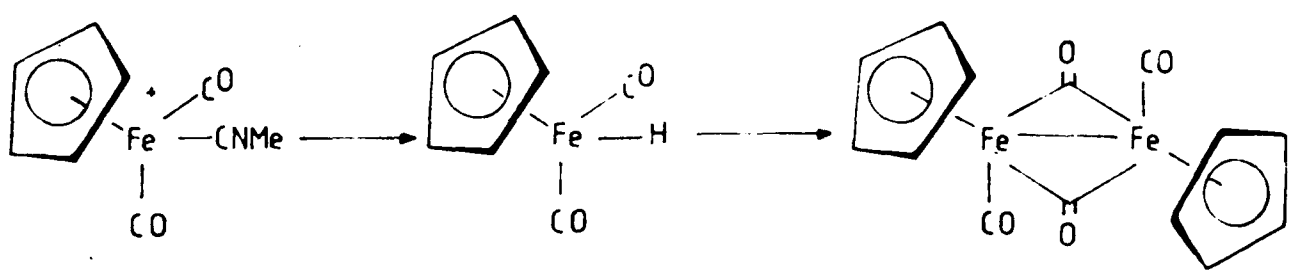


85 145

144 146

A number of resonance structures can be drawn for each of these. The two complexes, each of which contains iminoformyl units, were characterized by ^{1}H NMR and ^{11}B NMR spectroscopy. No further reactions of either were reported, apart from replacement of boron-bound hydrogen with fluorine for complex 145.

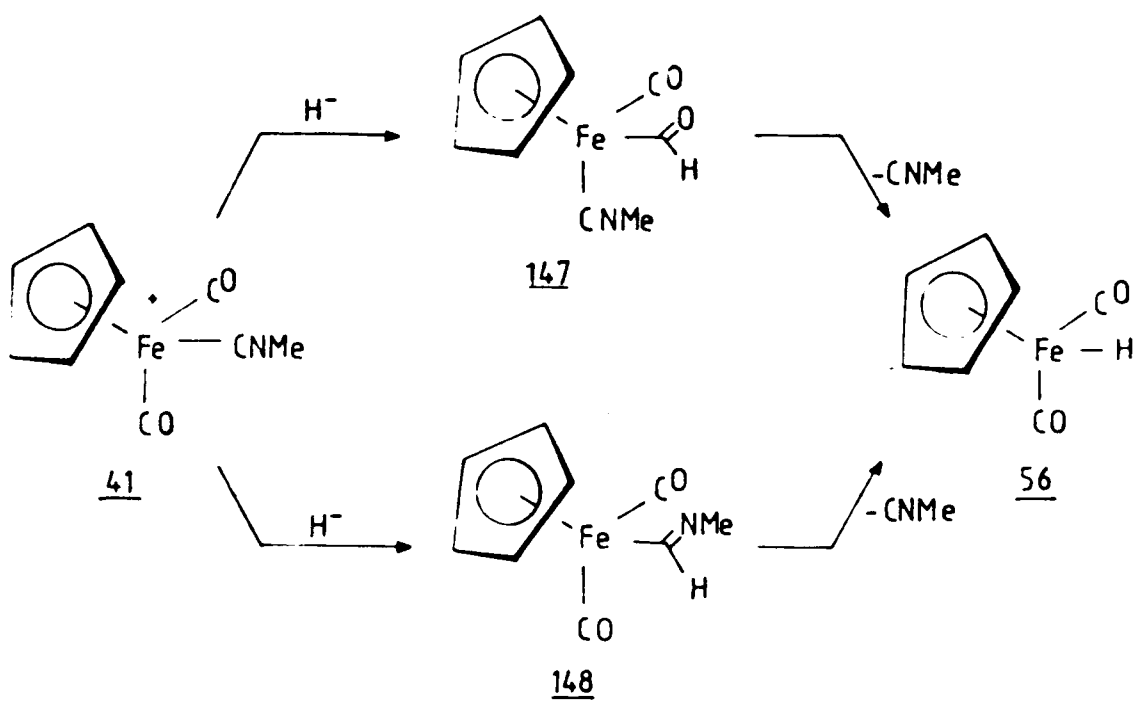
Complex 41 reacted in a different manner, the major product being the dimer $[CpFe(CO)_2]_2$, 54. This is presumably formed by thermal decomposition of the mononuclear hydride 56[100].



41 56 54

No mechanism was suggested for this reaction. Two mechanisms in particular may be advanced. Hydride attack may occur at the carbonyl ligand to give the formyl intermediate 147. Loss of isonitrile and hydride migration to the metal would give hydride

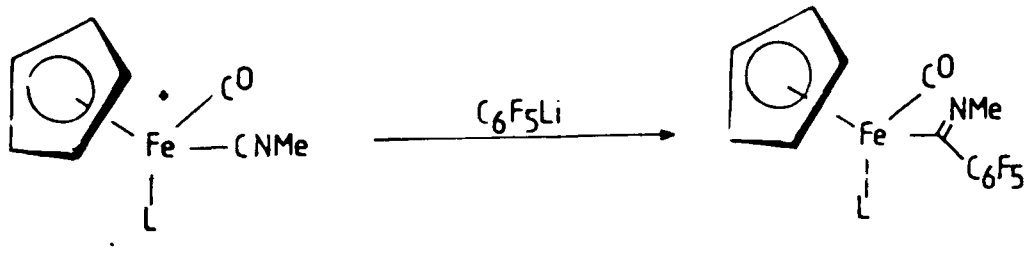
complex 56. Alternatively, hydride attack at the isonitrile ligand would give the iminoformyl intermediate 148. This may dissociate by an α-elimination mechanism, with loss of isonitrile, giving the hydride 56.



The intermediates 147 and 148 bear a strong resemblance to the intermediates 78 and 79 involved in section 2.3. It was shown there that the more likely intermediate is the iminoformyl 74, due to the experimental observation that hydride migration to isonitrile is more facile than to carbonyl ligands. This may not apply to nucleophilic attack by external hydride.

Very few examples of nucleophilic attack at complexes containing both carbonyl and isonitrile ligands have been reported. The hydride reductions of complexes 41 and 85 above provide two such. A study has also been made of the reaction of these complexes with pentafluorophenyl lithium[101]. Products due to attack at the cyclopentadienyl ring were found in small quantities, but in each case the major product was due to attack at the isonitrile ligand. No products due to attack at carbonyl were detected. It would thus appear that nucleophiles attack the isonitrile ligand

in preference to the carbonyl ligand.



41 L=CO
85 L=CNMe

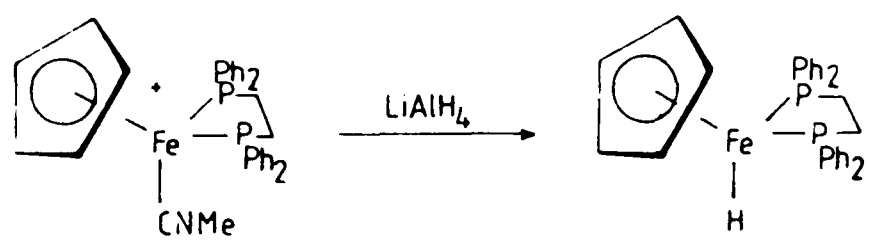
As stated in section 1.4, many metal formyl complexes have been prepared by reduction of cationic carbonyl complexes. It was therefore hoped that analogous iminoformyl complexes might be prepared by hydride donation to cationic isonitrile complexes.

4.2 Hydride Addition to Phosphine Isonitrile Complexes

Standard conditions were employed for the reduction of isonitrile and carbonyl complexes. These had already been proven in a previous study of hydride addition to various metal carbonyl species[49]. Lithium aluminium hydride was used as the hydride source in large excess (approx. 5 molar equivalents). The cationic complex was dissolved in THF under N_2, cooled to $-78^{o}C$ in an acetone-dry ice bath, and the $LiAlH_4$ added as a powder. The reaction temperature was then adjusted as required and the reaction mixture stirred for an appropriate time. Quenching was performed by addition of water to the mixture, which had previously been re-cooled to $-78^{o}C$. Removal of solvent under reduced pressure was followed by extraction of products with appropriate solvents, usually diethyl ether for uncharged complexes.

Reduction of complex 98 was carried out by this method. No reaction occurred at $-78^{o}C$, the starting complex being extracted from the quenched reaction mixture. At $-30^{o}C$, only a very small quantity of product was obtained. Reduction at room temperature over 18h, however, gave an excellent yield of the metal hydride

complex 149. No other organometallic products were seen, but the unmistakeable odour of methyl isonitrile was detected. This indicated that isonitrile had been expelled without reduction.



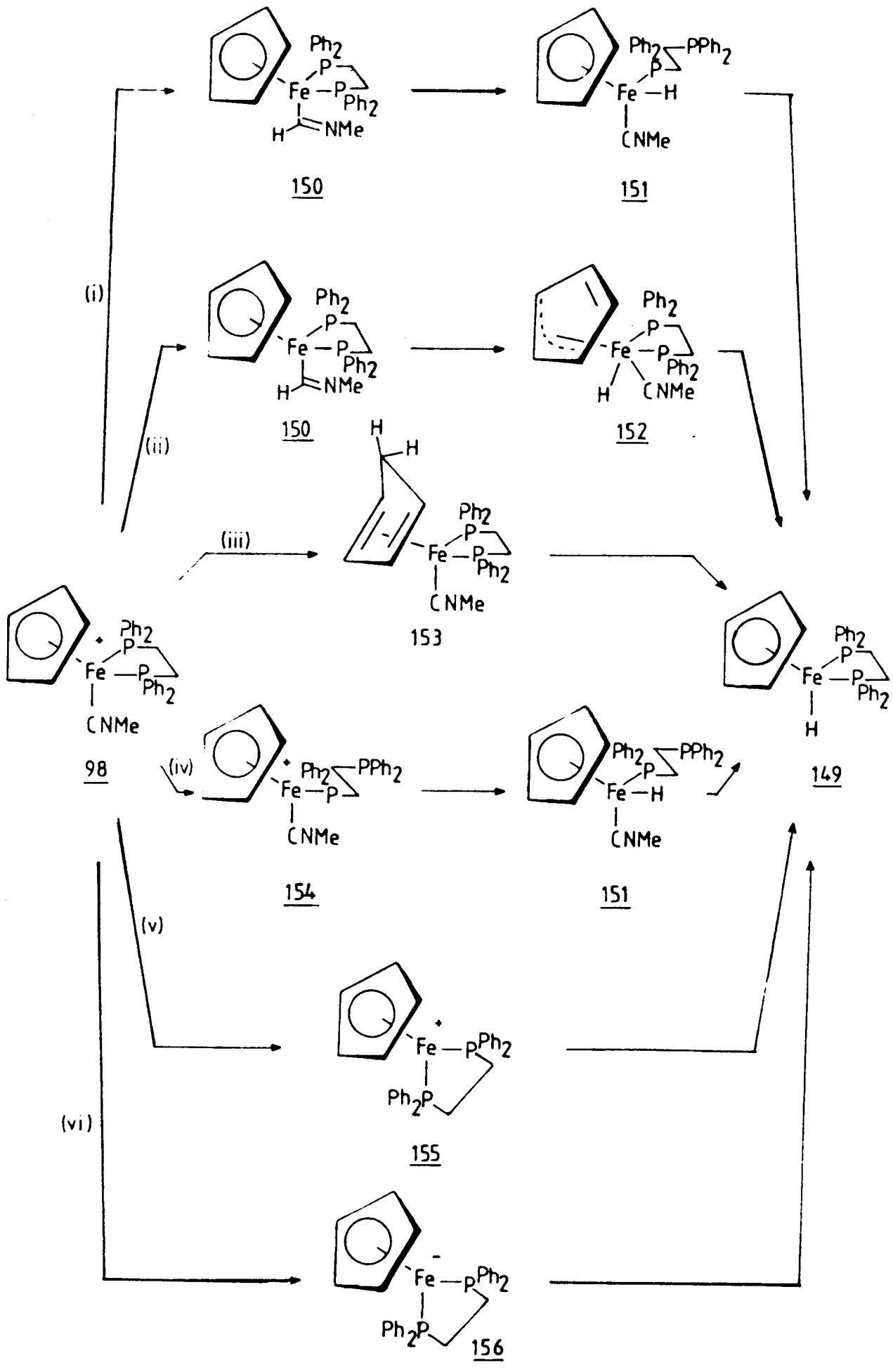
98 149

Several mechanisms may be proposed to rationalize the conversion of complex 98 to the hydride 149. These are illustrated in scheme 5.

i) Hydride attack at the electrophilic isonitrile carbon atom would give the iminoformyl complex 150. If this is formed, it is presumably unstable to a reverse migration reaction to give an isonitrile hydride complex. Such a migration requires a vacant coordination site at the metal. This site might be formed by dissociation of one phosphine group to give the pendant phosphine complex 151. Hydride migration, followed by displacement of the isonitrile ligand by the pendant phosphine group, would give the hydride product 149.

ii) A second possibility for formation of a vacant coordination site is a "ring-slippage" of the η^5-cyclopentadienyl ligand. It is possible for this ligand to rearrange to an η^3-moiety with an unbound alkene group. The intermediate complex 152 would then react with isonitrile displacement by the alkene group to give hydride 149.

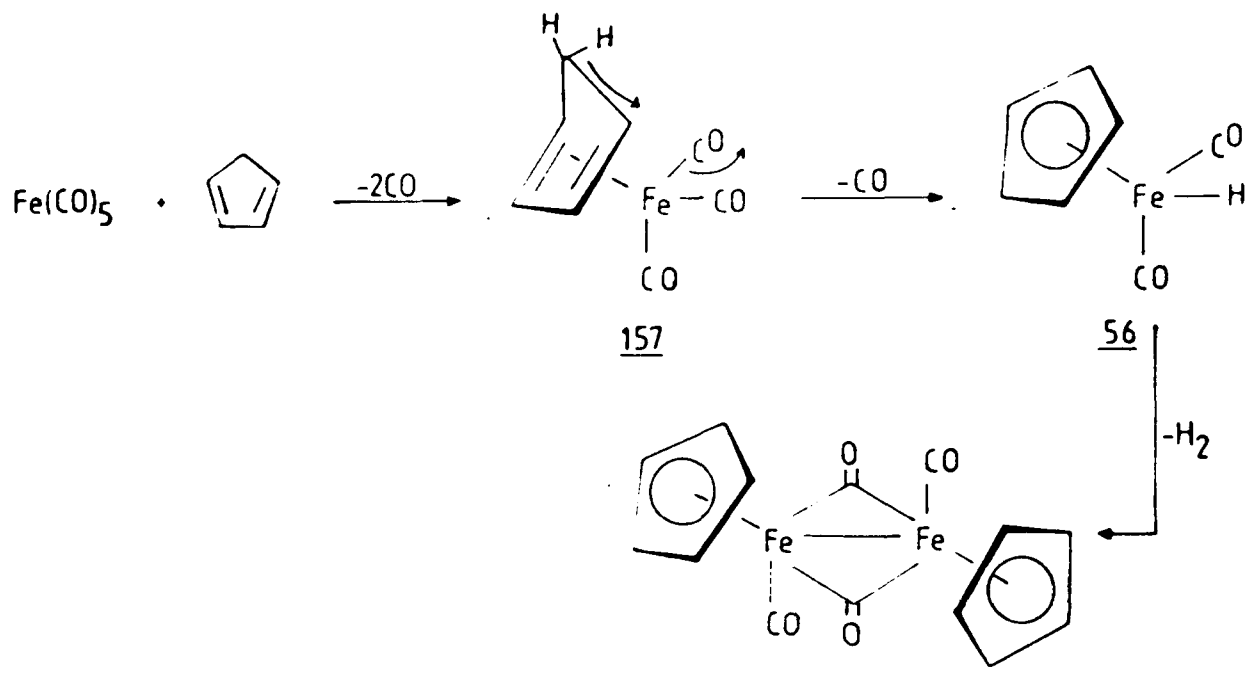
iii) Hydride attack at the cyclopentadienyl ring would give the η^4-cyclopentadiene complex 153. Dissociation of the isonitrile ligand, accompanied by hydride migration from the hydrocarbon ring



SCHEME 5

Mechanisms for Reduction of [CpFe(dppe)CNMe]$^{+}$, 98.

to the metal, would give the hydride product 149. This hydride migration step is similar to that assumed in the synthesis of $[CpFe(CO)_2]_2$, 54. Iron pentacarbonyl and cyclopentadiene react to give complex 157 as an intermediate. Loss of carbon monoxide and hydride migration from the ring gives complex 56, which decomposes to dimeric 54[100].



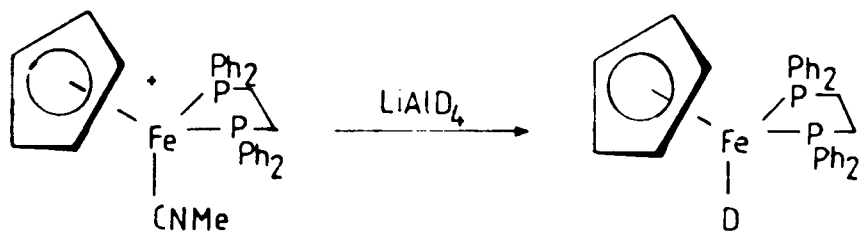
iv) Predissociation of one phosphine group would give the cationic intermediate 154. This complex may be attacked by hydride directly at the metal. The intermediate thus formed is identical to complex 151, and would decompose in the same fashion to hydride complex 149.

v) Predissociation of the isonitrile ligand to give complex 155 would also allow direct hydride attack at the metal. In this case, complex 149 would be formed without further rearrangement.

vi) Reduction and loss of the isonitrile ligand may leave an anionic intermediate such as 156. Protonation of this complex on work-up would give hydride 149.

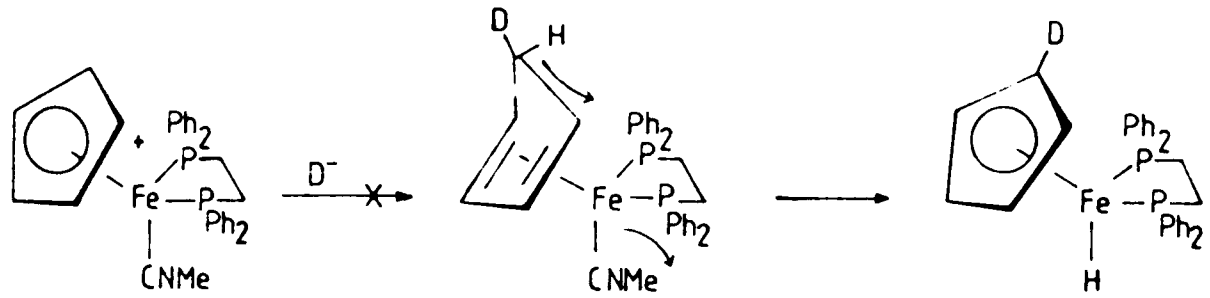
It was found possible to discount two of these alternatives

by a repetition of the reduction under identical conditions, but with lithium aluminium deuteride as the reducing agent. ^{1}H and ^{2}H NMR spectroscopy showed the product to be entirely composed of the metal deuteride complex 158.



98 158

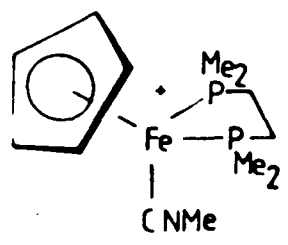
Mechanism (iii) proposed above would proceed with *exo*-deuteride attack at the cyclopentadienyl ring to give the *exo*-deuterated intermediate 159. Only the *endo*-hydrogen is available for migration to the metal in an intramolecular process. The product via this route would thus have been the ring-deuterated hydride complex 160. No trace of this complex was detected.



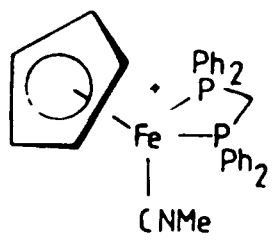
98 159 160

Work-up was in this case performed with unlabelled water. As no metal hydride 149 was detected, it is possible also to discount mechanism (vi).

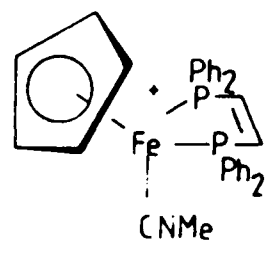
Mechanisms (i) and (iv) in scheme 5 require dissociation of one end of the chelating bisphosphine. Reduction of complexes 100, 117, 118 and 119, containing different phosphine ligands, was carried out.



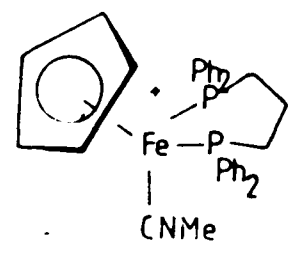
100



117



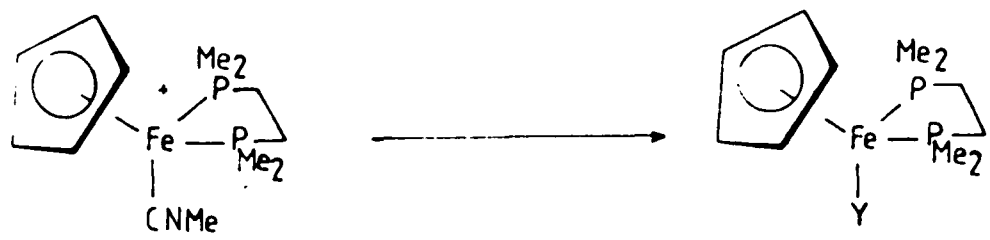
119



118

Complex 100 contains the much more basic, and therefore strongly coordinated, dmpe ligand, and dissociation is unlikely. Complexes 117 and 119 are sterically constrained from dissociation to pendant phosphine complexes. The large-ring chelate complex 118 was included for comparison.

Reduction of complex 100 was performed under conditions identical to those for complex 98 above. The sole isolated product was the hydride 161, showing a triplet in the ^{1}H NMR spectrum at δ-17.4. The yellow crystals of this hydride proved highly unstable, darkening over a few hours even under N_2 at -30°C. Repetition of the reduction using lithium aluminium deuteride gave the iron deuteride complex 162 as determined by ^{2}H NMR spectroscopy. There was no evidence of deuterium incorporation elsewhere in the complex.

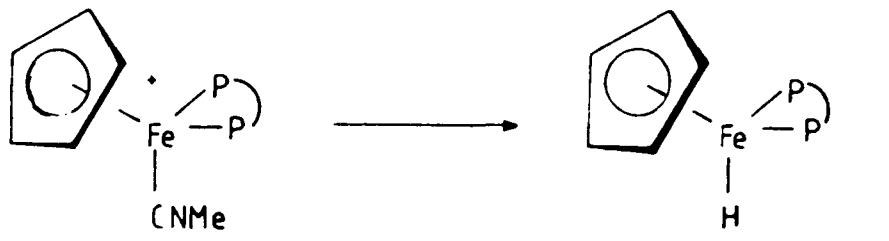


100

161 Y=H
162 Y=D

Complex 117 was reduced at -30°C over a period of 18h. Work-up and extraction with diethyl ether gave a yellow powdery solid which showed a triplet by ^{1}H NMR spectroscopy at δ-12.0,

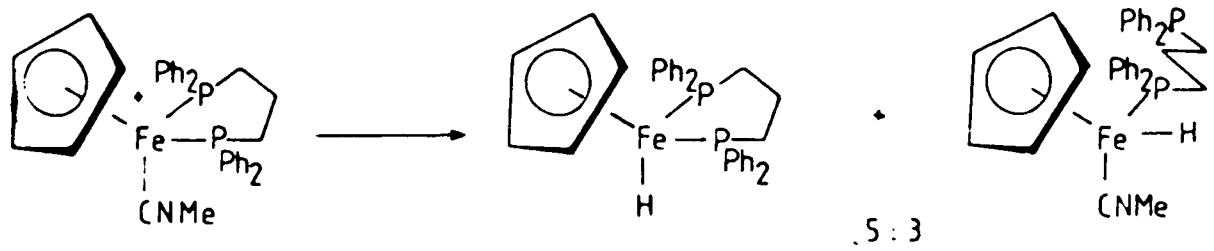
consistent with the structure 163. Similarly, complex 119, reduced at room temperature, gave a highly unstable yellow oil which showed a triplet by ^{1}H NMR spectroscopy consistent with the structure 164.



117 P_2 = dppm
119 P_2 = cdpe

163 P_2 = dppm
164 P_2 = cdpe

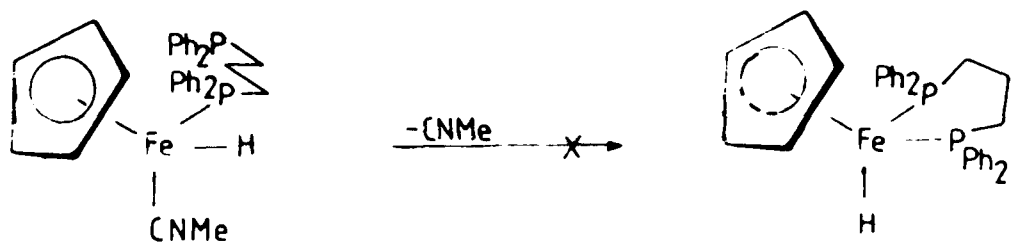
No products due to phosphine dissociation were detected for these chelating phosphine complexes. Reduction of complex 118 at -30°C, however, gave a mixture of two products. ^{1}H NMR spectroscopy showed a doublet at δ-13.4 and a triplet at δ-15.9, in the ratio 3:5. Resonances due to metal-bound phosphine at δ67 and δ26 and to unbound phosphine at δ-21 were seen in the ^{31}P NMR spectrum. This is consistent with products of structures 165 and 166. Phosphine dissociation would thus appear to have occurred in this case.



118 165 166

According to mechanism (i) in scheme 5 above, complex 166 would be an intermediate in the formation of hydride complex 165. The isolated mixture of complexes was stirred at room temperature in THF solution for 5 days, but no change occurred in the ^{1}H NMR spectrum of the mixture. It appears that complex

166 is not converted to hydride 165 under these conditions.



166 165

It is concluded that the pendant phosphine complex 166 is probably formed via a mechanism separate from that which is responsible for formation of hydride 165.

A further test for phosphine dissociation during such reduction was made with complexes 42 and 110, each of which contain two tertiary phosphine ligands. If one of these were to dissociate, especially the very bulky triphenylphosphine ligand, reassociation would be unlikely and products should contain only one phosphine ligand.

Room-temperature reduction of bistriphenylphosphine complex 42 gave, on work-up and ether extraction, an unstable orange oil. This oil showed a triplet in the ^{1}H NMR spectrum at δ-13.3, indicating the bisphosphine hydride complex 167.

42 R=Ph
110 R=Me

167 R=Ph, Y=H
168 R=Ph, Y=D
169 R=Me, Y=H

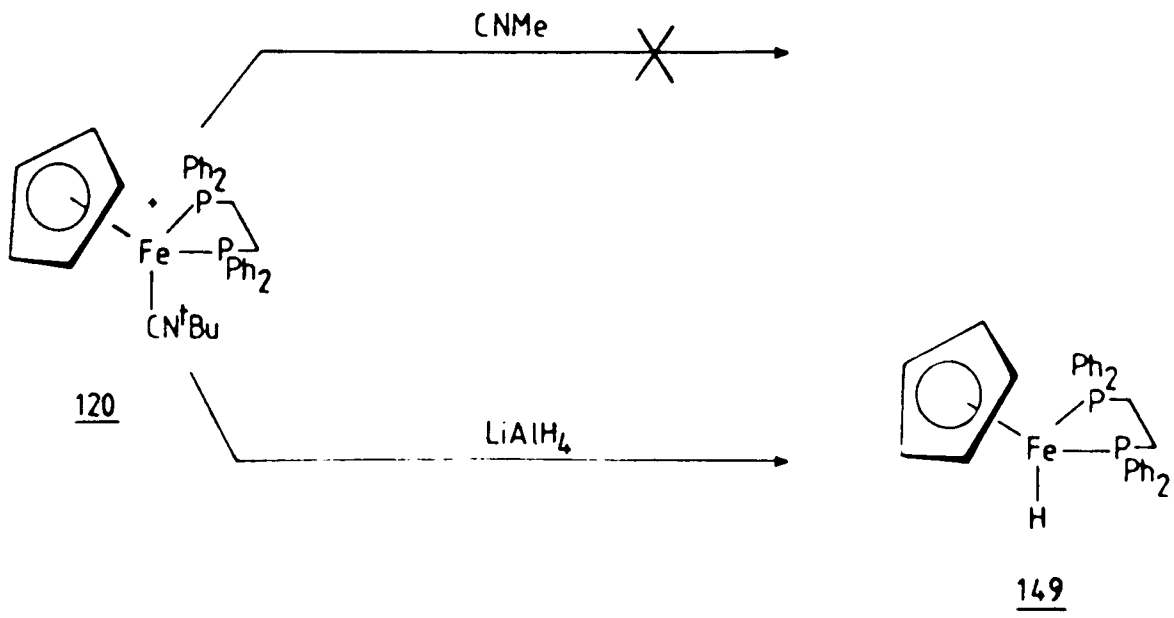
Repetition of this reduction using lithium aluminium deuteride gave the iron deuteride complex 168 without deuterium incorporation into the cyclopentadienyl ring. Reduction of the trimethylphosphine complex 110 with lithium aluminium hydride similarly gave a low yield of the known[102] bisphosphine hydride

complex 169, identified by comparison with literature data.

It appears therefore that loss of the isonitrile group from these complexes is achieved without dissociation of phosphine at any stage in the reaction.

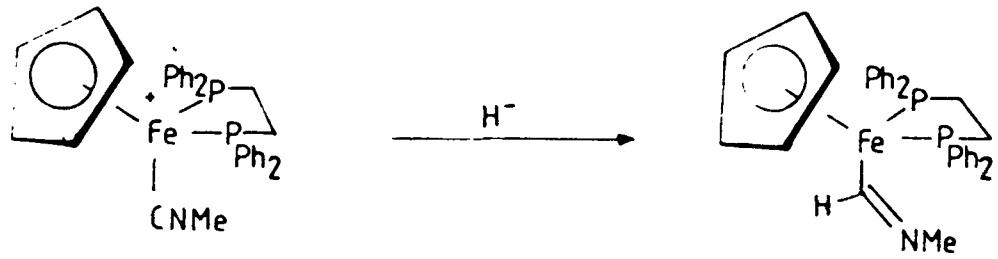
Mechanism (v) in scheme 5 requires the dissociation of isonitrile as its first step. If this mechanism were operating then the dissociated intermediate 155 should be in equilibrium with starting complex 98 even in the absence of $LiAlH_4$.

An attempt was made to trap the intermediate 155 by addition of a 10-fold excess of *t*-butyl isonitrile to a solution of complex 98 in THF. No exchange was observed between the two isonitriles on stirring at room temperature for 5 days, and complex 98 was recovered unchanged, as determined by the integration for the methyl group relative to that for cyclopentadienyl in the ^1H NMR spectrum. The reverse reaction was also attempted; that is, a solution of the *t*-butyl isonitrile complex 120 was stirred in THF solution with excess methyl isonitrile. Again, no reaction resulted and complex 120 was recovered unchanged. It therefore seems unlikely that mechanism (v) in scheme 5, which requires prior dissociation of isonitrile, is involved in the reaction of these complexes with $LiAlH_4$.



Complex 120 was reduced with $LiAlH_4$ under conditions identical to those for complex 98 above. Once again, a high yield of the hydride complex 149 was obtained.

An attempt was made to detect reaction intermediates by low-temperature ^1H NMR spectroscopy. A solution of 20mg of complex 98 in 300µl CD_2Cl_2 was cooled to -78°C in an NMR tube. A solution of 5mg $LiAlH_4$ in 250µl d^8 THF was filtered into the tube, and the mixture allowed to warm up over 1h. NMR spectra were recorded at intervals of 10°C. At -50°C a small peak appeared at δ10.5. This peak grew steadily with increasing temperature and on standing at -20°C for 30 minutes. A triplet structure was apparent, with a proton-phosphorus coupling of 4.7 Hz. This, and the low-field position of the peak, is consistent with the iminoformyl structure 150.



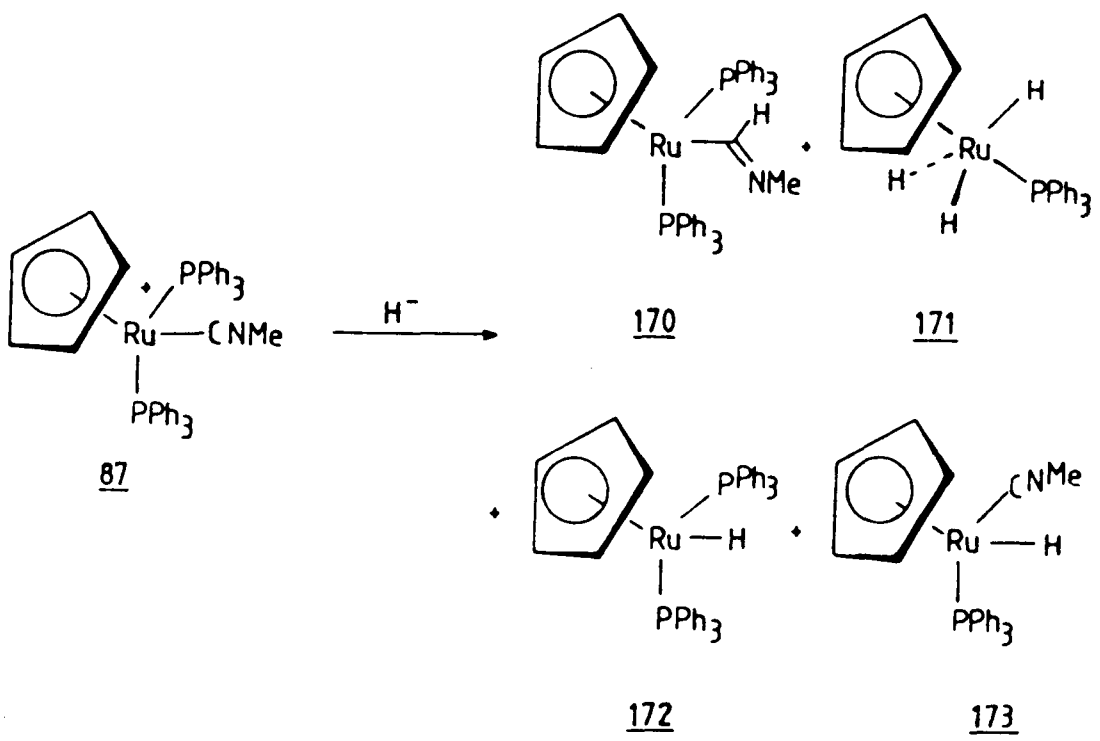
98 150

Contrary to expectation, the iminoformyl resonance did not diminish on standing at room temperature for 1h. No peak due to metal hydride was seen up to this point. The reaction mixture was quenched by addition of a drop of water. A further spectrum showed that the iminoformyl peak had disappeared The spectrum was unfortunately too broad for the presence or absence of metal hydride species to be confirmed.

It would appear from these results that reduction of these bisphosphine isonitrile complexes proceeds via an iminoformyl intermediate. This intermediate may be stabilized by coordination

to the strong Lewis acid AlH_3. In any case, it is not stable to the work-up procedures employed, and decomposes with loss of isonitrile to the metal hydride.

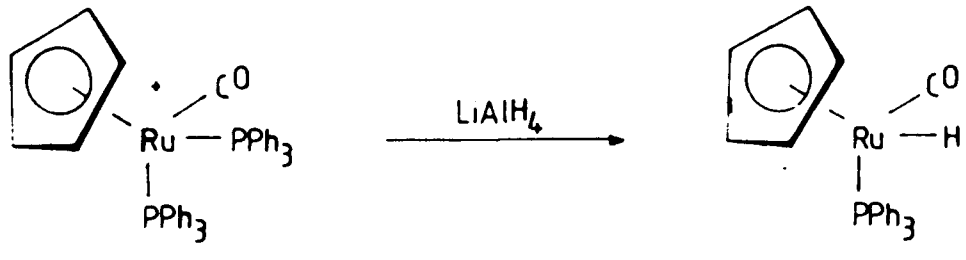
Two ruthenium complexes were also subjected to reduction under the standard conditions given above. The bistriphenylphosphine complex 87 was reduced at -30°C. Work-up and extraction with diethyl ether gave a yellow oil in moderate yield. Four compounds were identified by their ^1H NMR signals: iminoformyl 170 (δ10.9, t), and hydrides 171 (δ-9.8, d), 172 (δ-11.2, t) and 173 (δ-11.5, d). The ratio 170:171:172:173 was approximately 25:5:1:10.



The iminoformyl 170 would appear to be relatively stable to work-up, and is the major product obtained. It did not prove possible, however, to obtain a pure sample. It is of interest that iminoformyl 170 would appear to decompose with loss of phosphine rather than of isonitrile. The reason for this is unclear, but may for instance be due to a weak ruthenium-phosphine bond. The product expected by analogy with the iron cases above, hydride 172, is thus only a minor component. This hydride, and

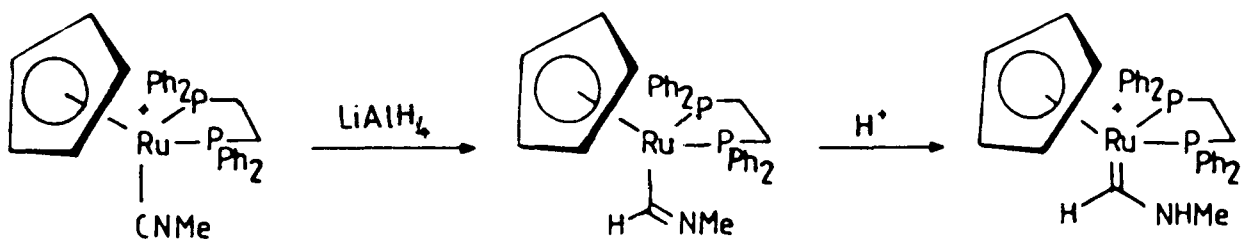
the product of further reduction, the trihydride 171, are known compounds[103]. For identification of the isonitrile hydride complex 173 see section 4.3.

The decomposition of the iminoformyl complex 170 with loss of phosphine is analogous to the behaviour of the corresponding carbonyl compound. Complex 174 has been reported[104] to be reduced by $LiAlH_4$ at -78°C to the carbonyl hydride complex 175.



174 175

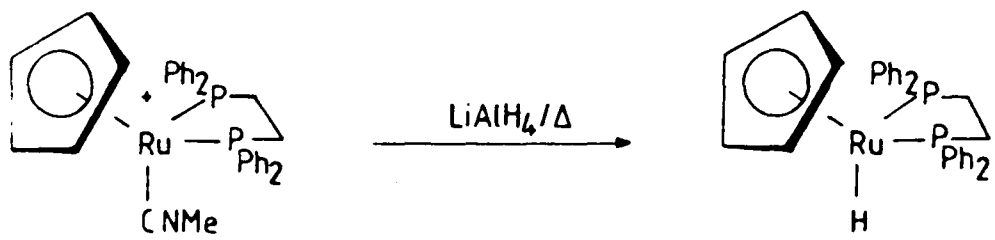
The ruthenium dppe complex 107 was reduced at -30°C as above. Work-up and extraction with diethyl ether gave a low yield of a greenish-yellow solid exhibiting a broad singlet in the ^1H NMR spectrum at δ11.4, consistent with the iminoformyl complex 176. Further extraction with THF, followed by crystallization by diffusion of hexane into a dichloromethane solution of the extract, gave pale yellow rod-like crystals. These were identified as the N-protonated iminoformyl, aminocarbene complex 177, formed in 66% yield.



107 176 177

The aminocarbene 177 is presumably formed by protonation of iminoformyl 176 on work-up with water. Complex 177 crystallized together with one mole of dichloromethane of crystallization, these crystals being stable enough to allow elemental analysis. The carbene proton was visible by ^{1}H NMR spectroscopy as a multiplet at δ9.3, and the N-bound proton as a broad singlet at δ8.7. The carbene carbon appeared in the ^{13}C NMR spectrum at δ239.

Repetition of this reduction in refluxing THF led to a moderate yield of the known[80] hydride 178 as the only organometallic product. An attempt to show that conversion of the iminoformyl 176 to the hydride 178 occurs under these conditions was made. A mixture of aminocarbene 177 with one equivalent of base was heated to reflux in THF. Complete decomposition occurred. All attempts to isolate the neutral iminoformyl 176 by deprotonation of aminocarbene 177 were unsuccessful, no stable neutral species being identified.



107 178

Although reduction of complex 107 to the iminoformyl 176 does occur, it would appear that the iminoformyl is unstable in this form. Protonation at the basic nitrogen occurs readily to give the stable aminocarbene complex 177.

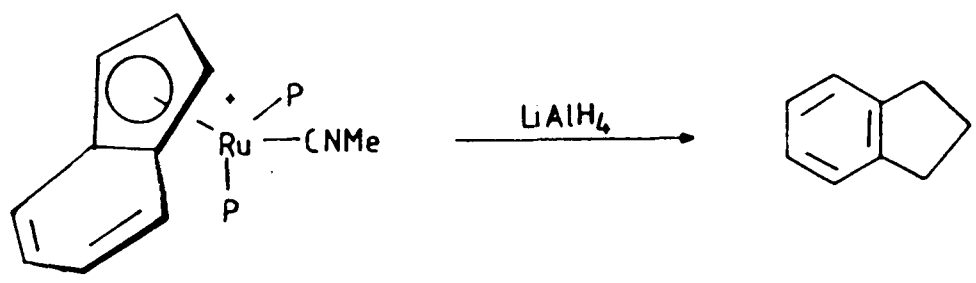
Treatment of the aminocarbene complex 177 with $LiAlH_4$ failed to give any products due to further reduction.

It would appear that hydride reduction of these phosphine

isonitrile complexes is proceeding with initial hydride attack at isonitrile. Two possible fates of the iminoformyl intermediate were considered in scheme 5 above. Decomposition by phosphine dissociation has been shown not to occur. This leaves mechanism (ii) in scheme 5, in which ring slippage to an η^3-form occurs.

It is not simple to demonstrate that such a mechanism is operating. It was decided to make use of the "indenyl effect"[105], by which ring-slippage from η^5-indenyl to an η^3-form is relatively facile due to the ability of the ligand to retain an aromatic structure. Such a ring-slippage might be expected to cause the ruthenium dppe complex 131 to be reduced directly to the corresponding hydride, which for the cyclopentadienyl case 107 required elevated temperature.

Reduction of 131, and of the related bistriphenylphosphine complex 130, was performed at -30°C. Work-up and extraction with diethyl ether did not lead to isolation of any ruthenium species. Indane, 179 was the sole organic or organometallic product observed. The fate of the ruthenium was not determined. Lithium aluminium hydride did not reduce indene to indane in the absence of ruthenium complexes, and so a hydrogenation via some ruthenium hydride complex seems likely.



130 P=PPh_3
131 P_2=dppe

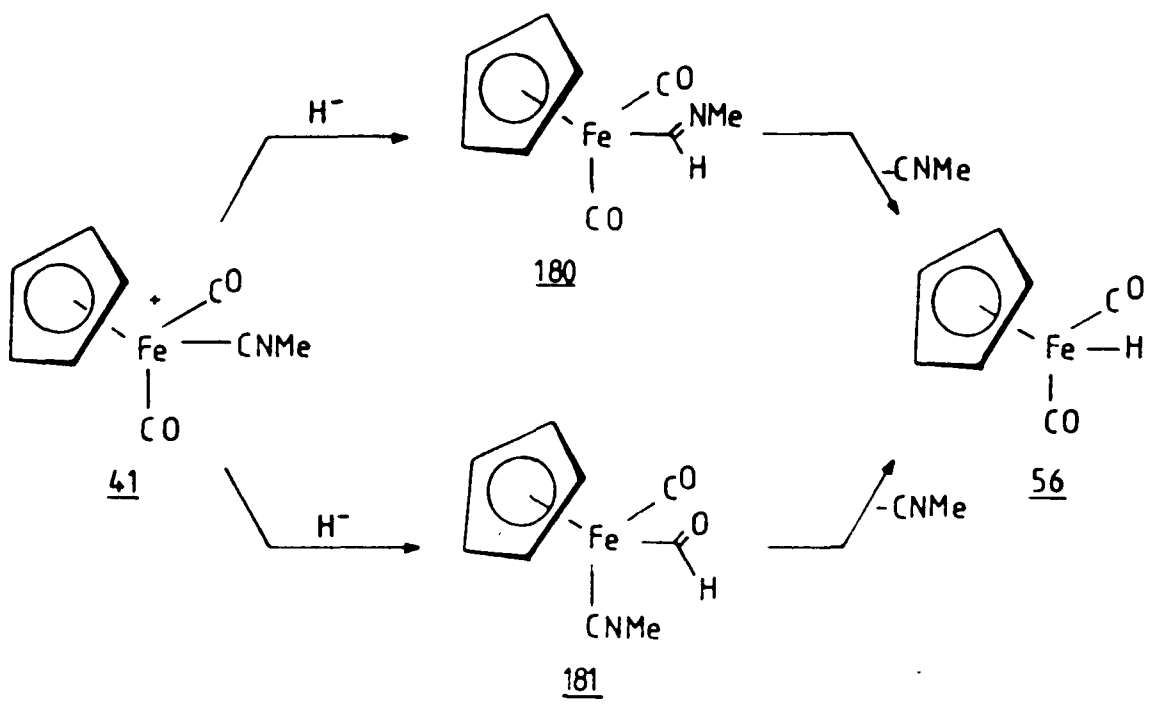
179

Several reports[91,106] have concluded that the indenyl-metal bond is considerably weaker than the cyclopentadienyl-metal bond in corresponding complexes. This conclusion is based on the evidence of CO stretching frequencies and Mössbauer isomer shifts. This weakening is presumably great enough that the ligand is deta ched under the reaction conditions.

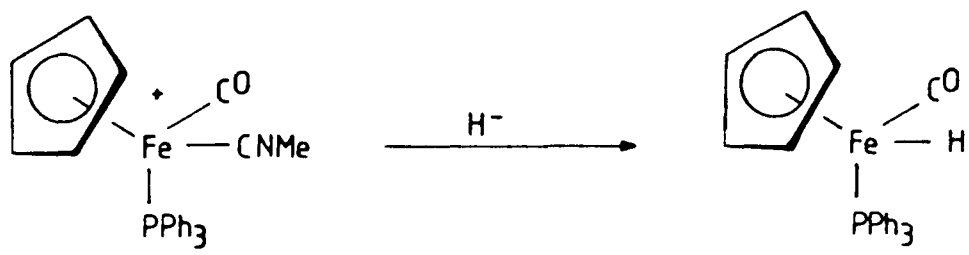
4.3 Hydride Addition to Carbonyl Isonitrile Complexes

Addition of hydride to a number of complexes containing both carbonyl and isonitrile ligands was carried out. From the examples quoted in section 4.1, nucleophilic attack might be expected at the isonitrile rather than the carbonyl ligands; hence iminoformyl intermediates are once again expected as primary products.

Reduction of the dicarbonyl isonitrile complex 41 proceeded smoothly over 1h with darkening of the solution from pale yellow to dark red. The only organometallic product isolated on work-up was the dimer $[CpFe(CO)_2]_2$, 54, identified by ^1H NMR and IR spectroscopy. This is presumably formed by decomposition of the dicarbonyl hydride complex 56, which dimerizes with loss of dihydrogen[100]. This result is in accord with that reported in section 4.1 for the borohydride reduction of complex 41[99]. The hydride 56 may be formed via the iminoformyl 180 in a manner analogous to the bisphosphine hydrides observed in the previous section. Alternatively, hydride attack at a carbonyl ligand would give the formyl complex 181. Decomposition with loss of isonitrile and hydride migration to the metal would give hydride complex 56. However, there is no precedent for such selective attack at carbonyl.

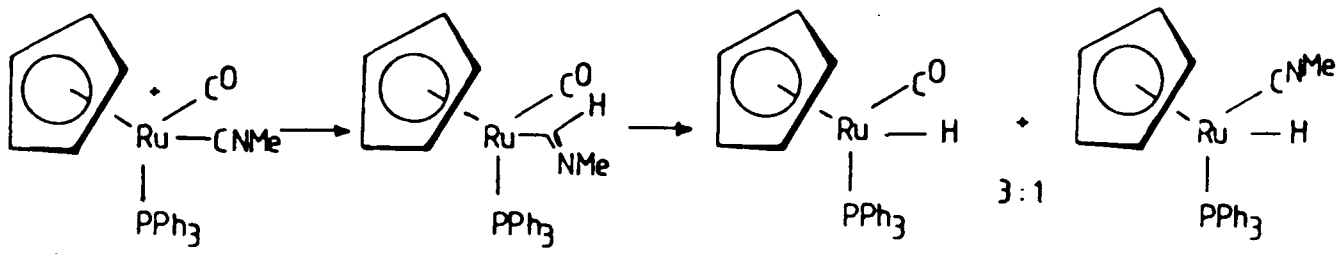


The reduction of complex 97 was performed in a similar fashion. Reduction over 2h gave an 80% yield of the hydride 182. Once again, this result may be explained with either formyl or iminoformyl intermediates, and the position of nucleophilic attack remains unclear.



97 182

The reduction of the ruthenium analogue 99 of complex 97 proceeded smoothly at -30°C to give a high yield of ether-soluble material. ^{1}H NMR and ^{31}P NMR spectroscopy showed this to be a 3:1 mixture of the two hydrides 184 and 173.

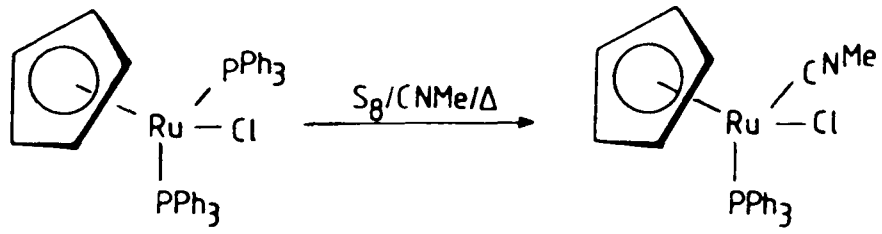


99 183 184 173

Formation of the major product, carbonyl hydride complex 184, may be explained by a mechanism identical to that for the iron bisphosphine complexes in the previous section. The iminoformyl intermediate 183 may also decompose with loss of a carbonyl ligand to give the isonitrile hydride complex 173. This decomposition is comparable with that of the bistriphenylphosphine iminoformyl 170 (section 4.2), proceeding with loss of phosphine to give the isonitrile hydride 173.

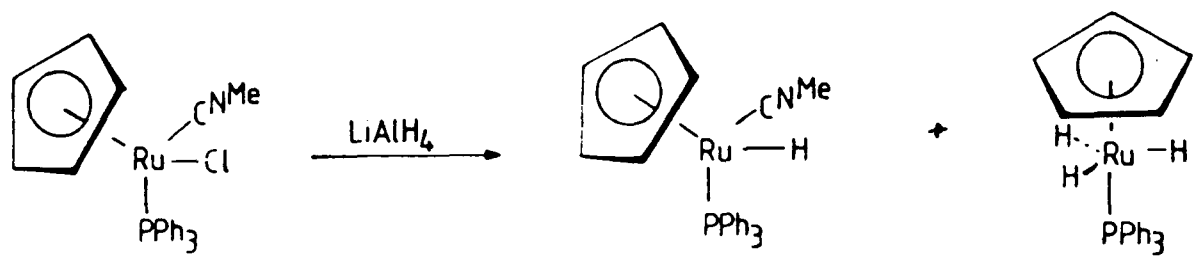
Complex 184 has been previously reported, and was identified by comparison of its spectroscopic data with those in the literature. Complex 173, however, was previously unknown, and synthesis by an independent route was carried out in order to confirm its identity.

A recent report[107] described the replacement of one triphenylphosphine ligand in complex 88 with carbon monoxide. Elemental sulphur was used to remove the phosphine as Ph_3PS, and replacement with carbon monoxide was effected under moderate CO pressure. This reaction was successfully adapted to prepare the isonitrile complex 185. Complex 88 was heated at reflux in benzene with excess sulphur and methyl isonitrile for 8h. Chromatography of the reaction mixture gave complex 185 in 65% yield, characterized by IR and NMR spectroscopy, mass spectrometry and elemental analysis.



88 185

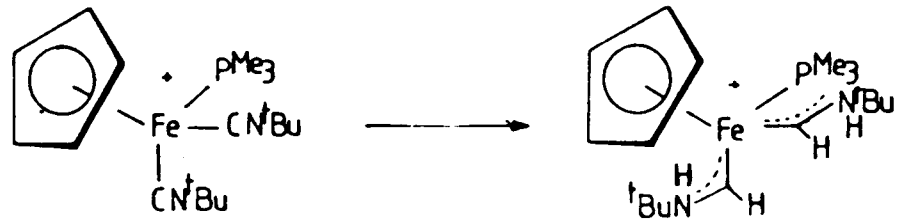
Replacement of the chloride ligand in complex 183 by hydride did not occur on reflux with sodium methoxide in methanol, nor with lithium triethylborohydride. Reaction with $LiAlH_4$ in THF gave the expected hydride 173 together with a small amount of the trihydride 171. A single recrystallization from diethyl ether gave the pure hydride 173 as a greenish-yellow solid in 54% yield. ^1H NMR spectroscopy showed a doublet at δ-11.3 due to the hydride ligand, and an absorbtion at 2105 cm^{-1} in the IR spectrum was assigned to the isonitrile ligand. High-resolution mass spectrometry gave a correct mass for the molecular ion.



185 173 171

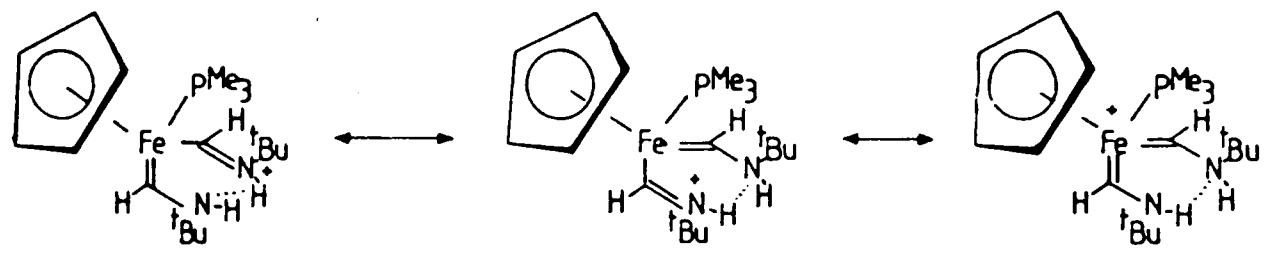
4.4 Hydride Addition to Bisisonitrile Complexes

The trimethylphosphine isonitrile complex 115 was reduced with excess $LiAlH_4$ at room temperature. The reaction mixture was quenched and chromatographed on alumina to give a single, cationic product. This product showed no isonitrile stretch in the IR spectrum, but a sharp peak at 3360 cm^{-1} apparently due to an NH group. In the ^1H NMR spectrum, a doublet appeared at δ 11.2, together with a broad doublet with the same coupling constant at δ 10.1. The compound was assigned the doubly protonated bisiminoformyl structure 186. Crystals were obtained by diffusion of hexane into a dichloromethane solution of the complex. These crystals were moderately stable, melting at 135°C with decomposition. Elemental analysis supported the structure 186.



115 186

Since it is possible for this complex to form a six-membered ring by hydrogen bonding, similar to the sturcture of 145 shown in section 4.1, the structure, 186(b), represented by the resonance structures shown, was initially assumed.



186b

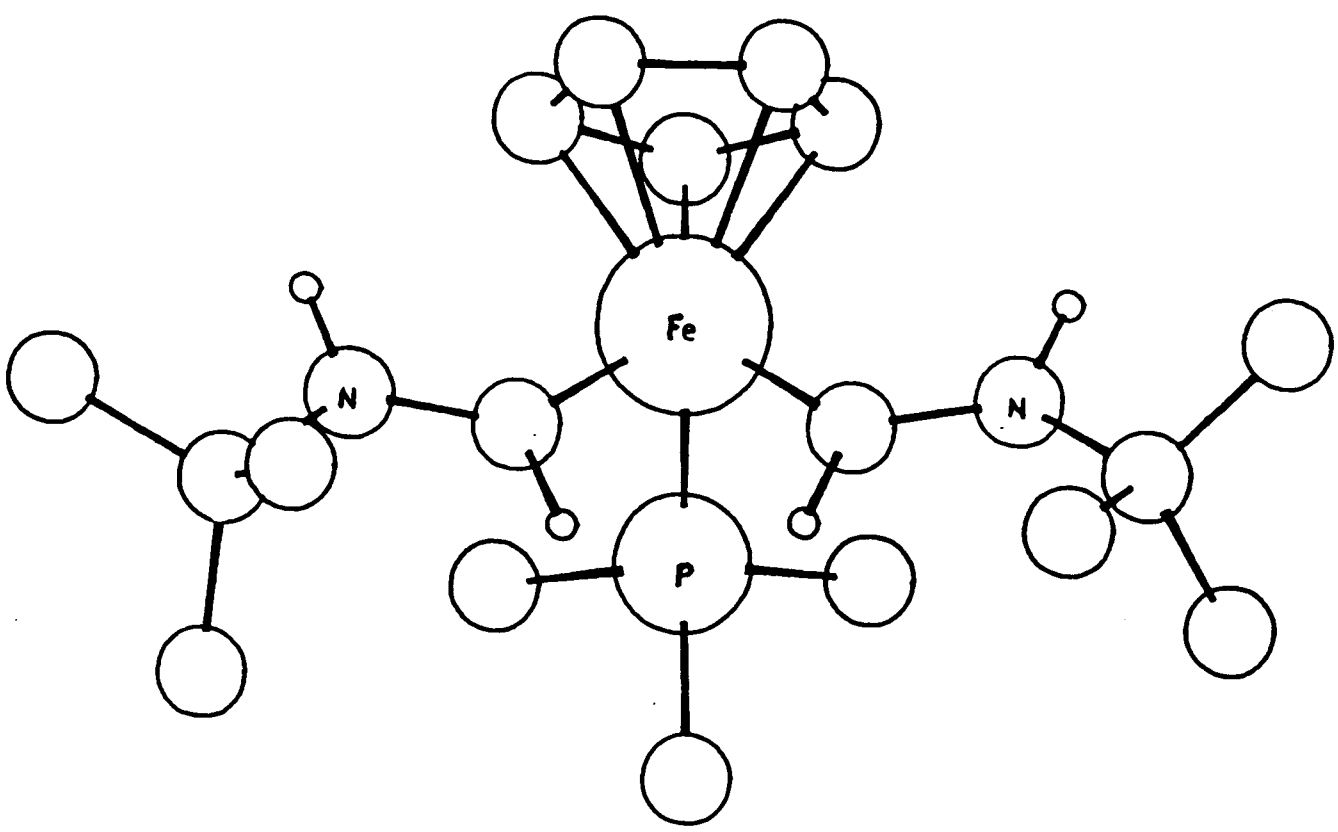
A single crystal of this complex was submitted for an X-ray crystal structure determination. Three views of the structure determined in this way are shown in figure 1. Selected bond lengths and angles are also given.

It can be seen from figure 1 that the six-membered ring structure 186(b) is not applicable. The complex is pseudo-octahedral, with the cyclopentadienyl ligand occupying three coordination sites, the angles between other ligands being approximately 90^{o}.

The N-C-Fe-C-N system is almost planar, as shown by the torsional angles given. The Fe-C bond lengths are much shorter than is common for iron-alkyl systems (approx. 2.0-2.1Å), and the C-N bond lengths are intermediate between a single (1.4-1.5 Å) and a double (1.2 Å) C-N bond. All these factors support a structure for complex 186 with the positive charge delocalized over the N-C-Fe-C-N system.

The molecule does not possess a plane of symmetry due to a rotation of the *t*-butyl groups. This apart, the molecule is symmetrical about a plane through C(7)-Fe-P-C(16). The PF_6^- counterion has been omitted from figure 1 for clarity. Further structural details and experimental procedure for this determination can be found in the appendix.

Attempts to further reduce complex 186 with $LiAlH_4$, BH_3.THF or $NaBH_4$ were unsuccessful. Deprotonation of complex 186 with potassium *t*-butoxide gave a neutral, ether-soluble yellow species showing a singlet in the ^1H NMR spectrum at δ 11.1. This is presumed to be due to the iminoformyl-aminocarbene complex 187. Proton transfer allows the two ligands to exchange roles, and an averaged NMR signal is obtained. This neutral species was highly unstable, and no further reactions could be attempted.



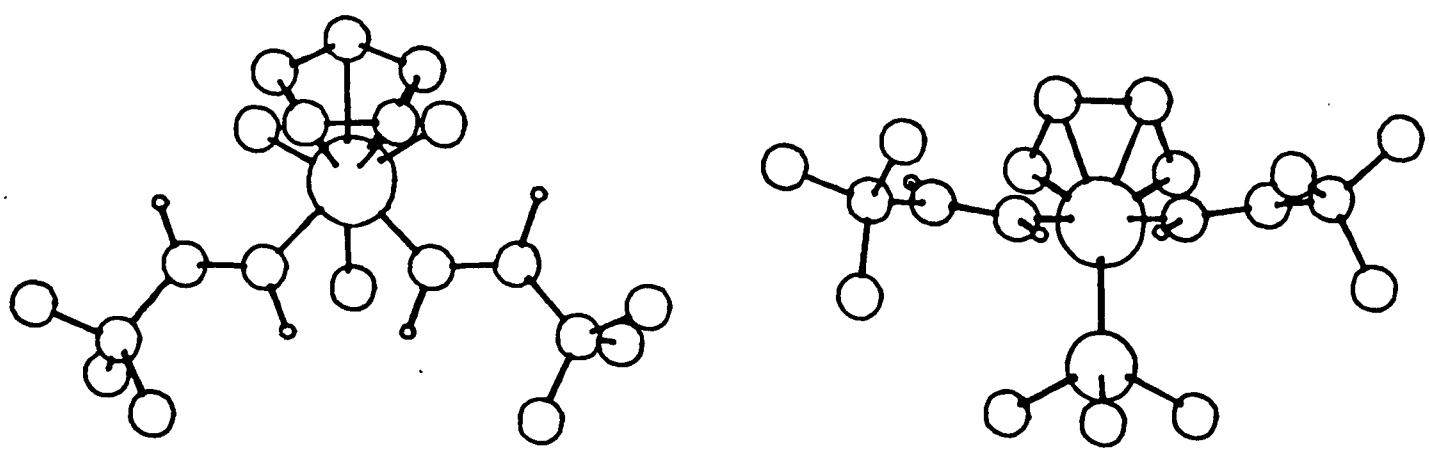
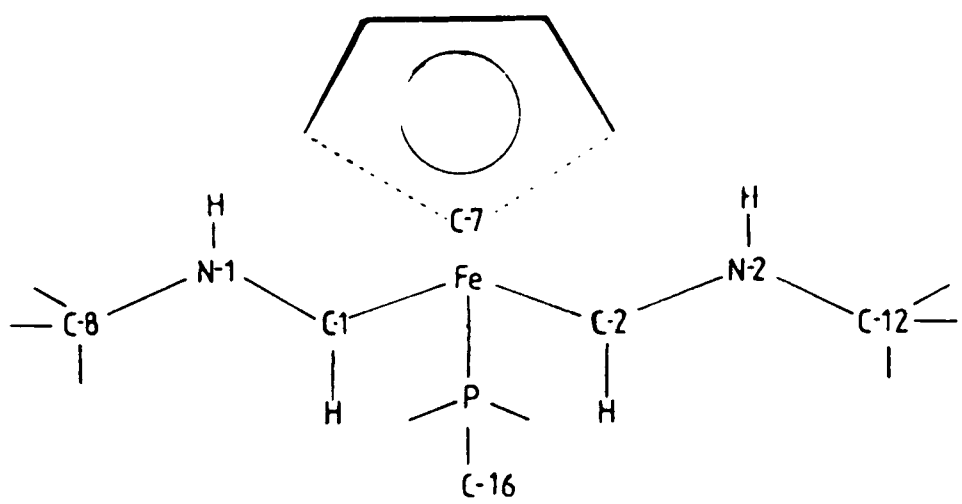


Figure 1



Selected Bond Lengths

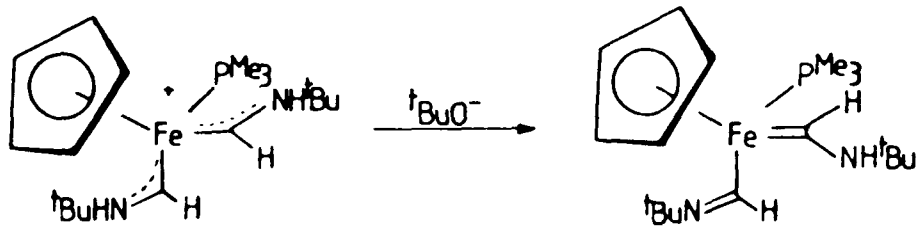
Fe-P	2.173(2)Å	C(1)-N(1)	1.313(7)Å
Fe-C(1)	1.834(6)Å	C(2)-N(2)	1.307(7)Å
Fe-C(2)	1.833(6)Å		

Selected Bond Angles

C(1)-Fe-P	89.7(2)°	N(1)-C(1)-Fe	131.6(4)°
C(2)-Fe-P	89.6(2)°	N(2)-C(2)-Fe	131.0(4)°
C(1)-Fe-C(2)	89.2(2)°	C(8)-N(1)-C(1)	127.3(5)°
		C(12)-N(2)-C(2)	129.6(5)°

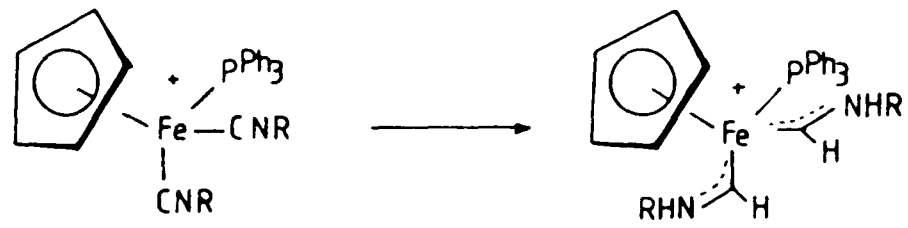
Torsional Angles

N(1)-C(1)-Fe-C(2)	+166°
N(2)-C(2)-Fe-C(1)	-168°
C(7)-Fe-P-C(16)	+179°



186 187

Two cations similar to complex 115 but containing the triphenylphosphine ligand were reduced under conditions identical to those employed for complex 115. In both cases, low yields of unstable cationic products were obtained. Attempts to crystallize these complexes were unsuccessful. In both cases ^{1}H NMR spectroscopy showed doublets at around δ 11. These complexes were assigned structures 188 and 189. A mass spectrum of complex 188 confirmed the structure, showing a molecular ion peak plus a peak due to loss of triphenylphosphine.



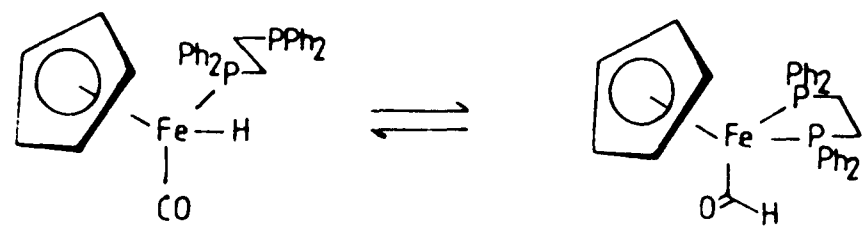
113 R= Me
114 R=tBu

188 R= Me
189 R=tBu

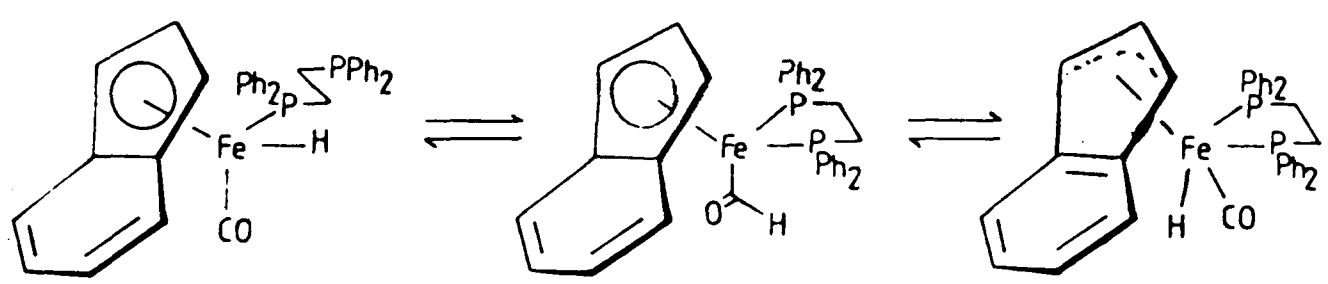
4.5 Hydride Addition to η^5-Indenyl Carbonyl Complexes

In addition to the study of hydride addition to cationic isonitrile complexes, the reactions of various carbonyl complexes containing the η^5-indenyl ligand were studied. Previous work[49] has shown that η^5-cyclopentadienyl complexes, and mono-and permethylated cyclopentadienyl derivatives, undergo hydride attack at the carbonyl group in almost all cases, giving unstable formyl complexes. These formyl complexes decomposed to carbonyl hydride complexes, or were further reduced to methyl complexes. It was hoped therefore that a study of η^5-indenyl complexes may shed further light on the subject by giving more information about the stability and fate of the formyl species.

As described in section 1.4, the iron carbonyl hydride complex 31 has been shown[50] to be in equilibrium with the formyl species 32. The presence of the indenyl group raises the possibility of further structures for the equivalent intermediates 190 and 191, such as structure 192. The reduction of the dppe cation 138 is therefore of particular interest.



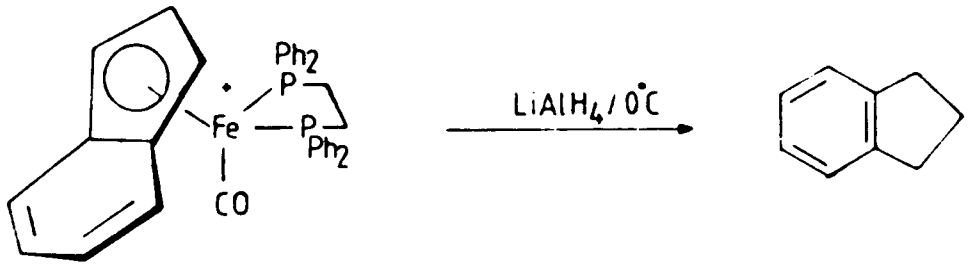
31 32



190 191 192

Attempted reduction of complex 138 with $LiAlH_4$ at -78°C resulted in isolation of starting materials only. At -30°C, a deep blue colour developed, and a deep blue material, only sparingly soluble in diethyl ether, was extracted with THF. This material reverted to a yellow oil on standing under N_2 at room temperature for a few minutes. This yellow oil proved to be the starting complex 138. The intense colour and spontaneous decomposition of the extract suggest a one-electron reduction of complex 138 to a radical species unstable at room temperature.

Reduction at 0°C proceeded with generation of a deep blue colour which reverted to yellow on quenching. Extraction with diethyl ether gave a quantity of indane, 179, identified by comparison with a commercial sample. No organometallic complexes were identified.

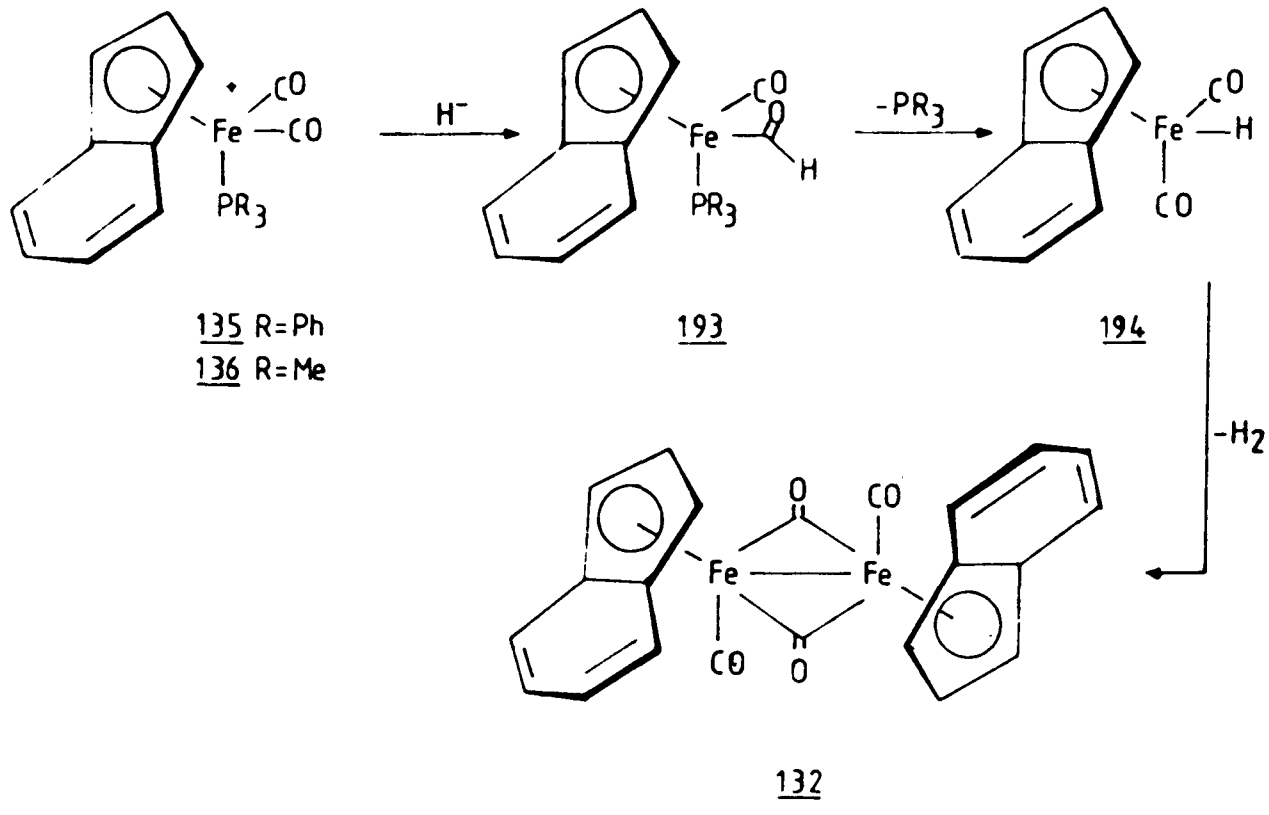


138 179

The relative weakness of the indenyl-metal bond, as discussed in section 4.2 above, is presumably responsible for the lability of this ligand in these reductions.

Organometallic products were observed on reduction of monophosphine complexes 135 and 136. In both cases the dimer 132 was the only observed product, formed in 79% yield from complex 135, and around 20% yield from complex 136. This dimer presumably results from decomposition of the dicarbonyl hydride complex 194, by analogy with the cyclopentadienyl complex 56[100] The hydride 194 may in turn be generated by loss of phosphine

from the intermediate formyl complex 193.

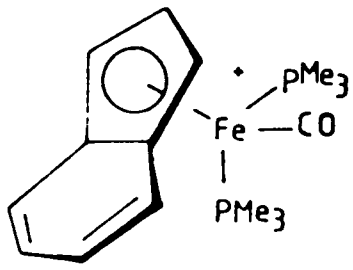


132

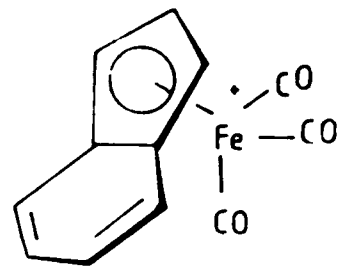
The phosphine hydride complexes which could be derived by loss of a carbonyl ligand from formyl 193 were not observed. The selective loss of phosphine from this complex is not in accord with results obtained for the analogous cyclopentadienyl systems[49]. Loss of phosphine may be rationalized in terms of relief of steric crowding at iron, the indenyl ligand being much more bulky than cyclopentadienyl.

The bistrimethylphosphine complex 137 yielded a yellow crystalline ether extract on reduction at room temperature. Full characterization of this complex was not possible. ^{1}H NMR spectroscopy shows the lack of an indenyl ligand, and reveals an $Fe(PMe_3)_2H$ moiety. Several carbonyl stretches are visible in the IR spectrum. Mass spectrometry shows only an $Fe(PMe_3)_2$ fragment.

Reduction of the tricarbonyl iron cation 133 resulted in complete decomposition, and no organometallic products could be identified.

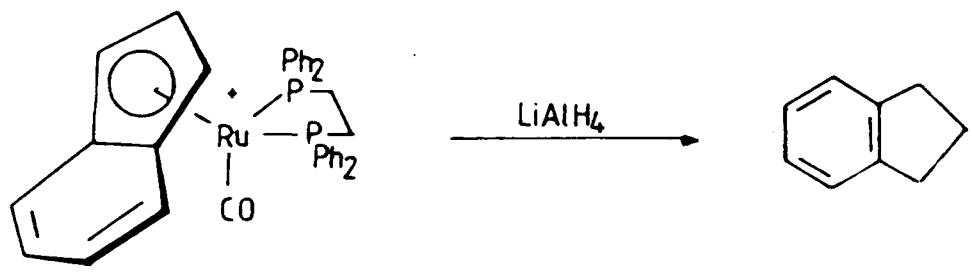


137



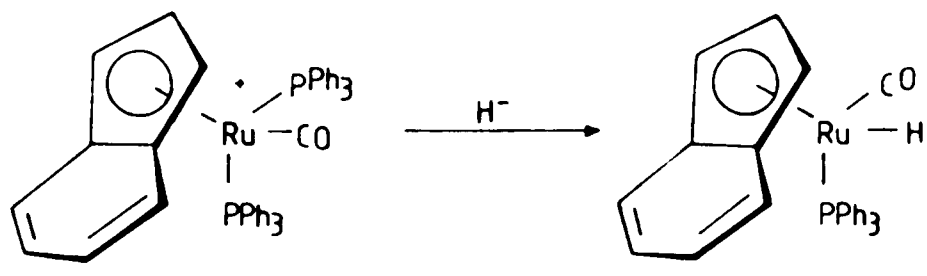
133

The ruthenium dppe complex 129 yielded indane on reduction at -30°C. Several complex multiplets were also observed in the ^{1}H NMR spectrum in the range δ-6 to -8.5, indicative of ruthenium polyhydride species. It was not possible, however, to isolate any of these species.



129 179

The bistriphenylphosphine complex 128 was reduced smoothly at -78°C to the hydride complex 195, isolated in 85% yield. This is the product expected by analogy with the cyclopentadienyl system[104]. It was obtained as a yellow oil, characterized by ^{1}H NMR spectroscopy, showing a doublet due to hydride at δ-13.4; by IR spectroscopy, showing a carbonyl absorbtion at 1945 cm^{-1}; and also by ^{31}P NMR and ^{13}C NMR spectroscopy and mass spectroscopy.

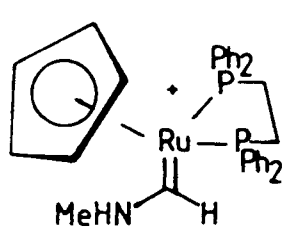


128 195

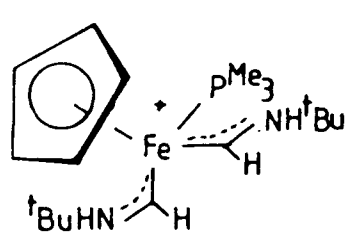
It is not clear why, of the four ruthenium indenyl complexes prepared and reduced, complex 128 alone retained the indenyl ligand to give a characterizable organometallic product.

4.6 Conclusions

The primary products on addition of hydride to cationic isonitrile complexes of iron and ruthenium are iminoformyl complexes. If carbonyl ligands are also present, the direction of attack is not clear. The iminoformyl complexes are not generally sufficiently stable to be isolated, and are destroyed on work-up of the reaction mixture. In two cases, however, the products survived this treatment. These were both protonated on work-up to give the aminocarbene and charge-delocalized structures 177 and 186.

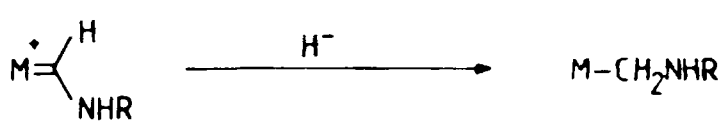


177



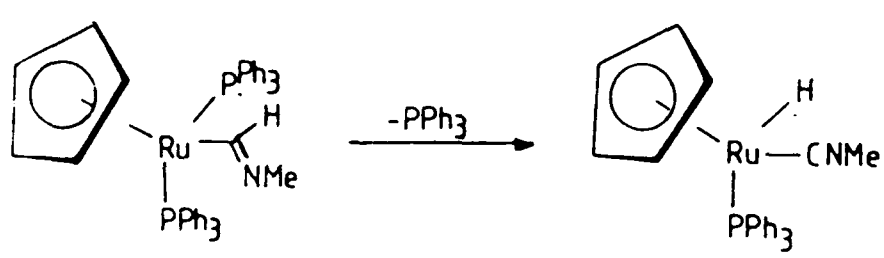
186

To pursue the analogy between reduction of isonitriles and of carbonyls, an aminocarbene complex should add a further hydride to give an aminomethyl complex 196, comparable to the hydroxymethyl 22 described in scheme 4, section 1.3. This type of hydride addition was not achieved for complexes 177 and 186.



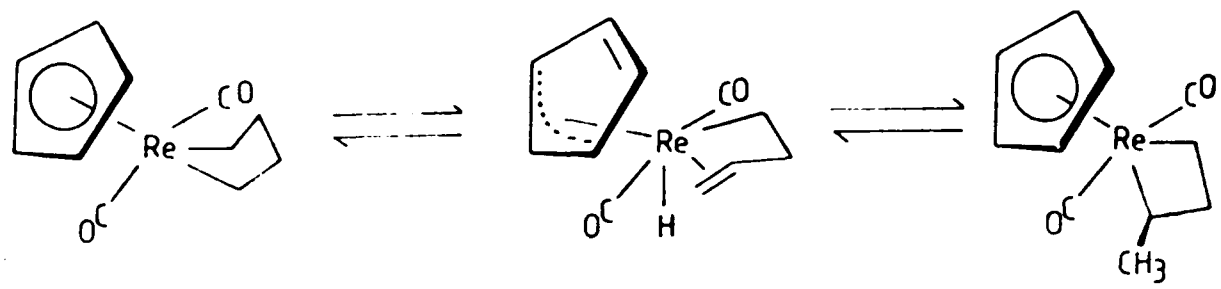
196

Other iminoformyl complexes decomposed with hydride migration to the metal and loss of isonitrile. A vacant coordination site is required at the metal in order for the hydride to be able to migrate. With the exception of the ruthenium iminoformyl complex 170, which loses phosphine and retains isonitrile to give complex 173 as a major product, this vacant coordination site is not formed by loss of a two-electron ligand.

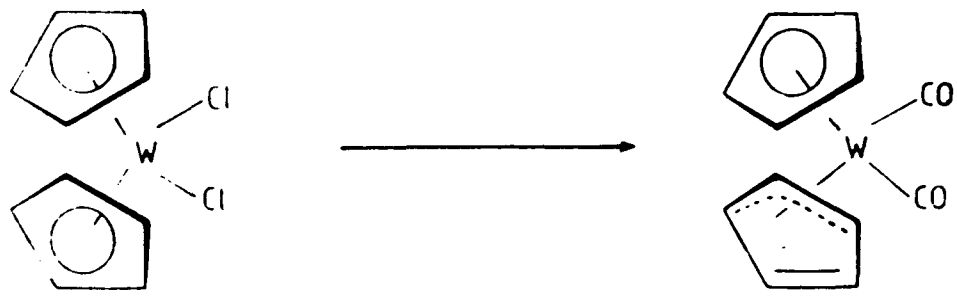


170 173

An alternative mechanism is for the η^5-cyclopentadienyl ligand to slip to an η^3-ligand, creating a vacant coordination site in the process. This mechanism had previously been invoked to explain reactions requiring metal coordination sites, such as the rearrangement of the rhenium complex 197 to the four-membered ring complex 199[108]. This rearrangement occurs without exchange of coordinated CO with added labelled ^{13}CO. The η^3-ligand in intermediate 198 is offered to explain this result. Reduction of dicyclopentadienyl tungsten dichloride under CO pressure gave the complex 200. A crystal structure shows the η^3-ligand to be bent by 20^o from planarity[109].



197 198 199



200

It was hoped that decomposition via such ring-slippage would be accelerated by replacement of cyclopentadienyl with indenyl, due to the "indenyl effect"[105]. However, the weak indenyl-metal bond caused loss of the ligand under the reaction conditions employed. The hydrocarbon was recovered as indane, showing that ligand loss was accompanied by a hydrogenation.

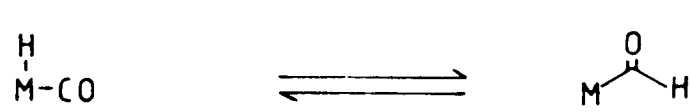
Hydride addition to indenyl carbonyl complexes again resulted in loss of the indenyl ligand in most cases. The three cases where this did not occur gave carbonyl hydride complexes with loss of a phosphine ligand. Where a choice of ligands was available, phosphine was lost selectively, presumably in order to relieve steric crowding at the metal.

CHAPTER 5

METAL FORMYL SPECIES FROM CARBONYL HYDRIDE COMPLEXES AS REACTION INTERMEDIATES

5.1 Introduction

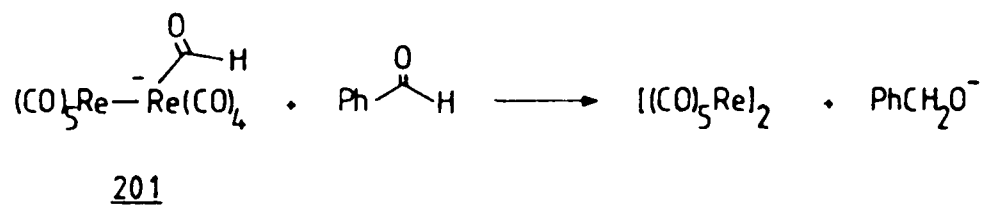
A large number of unstable metal formyl complexes have been prepared by stoichiometric addition of hydride donors to metal carbonyl complexes. It has been suggested that some may also be formed by hydride migration to coordinated CO[42,43,50]. Although this latter reaction is thermodynamically very unfavourable, only a small amount of the formyl 21 is required in the equilibrium mixture in order for further reaction to proceed.



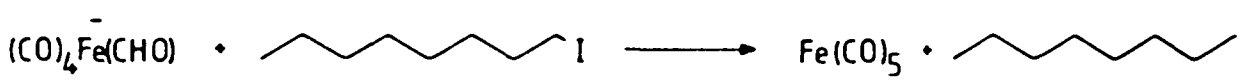
21

In this section, a number of reactions are examined which rely on the establishment of such an equilibrium in order to supply metal formyl species for further reaction. The fate of these metal formyls and the nature of their reactivity is of interest.

Many reports have been made of the hydride-donating ability of metal formyl groups. Most of these have involved anionic formyl complexes, themselves formed by hydride addition to neutral metal carbonyl species. Examples of such hydride donation include the reduction of benzaldehyde to benzyl alcohol by the binuclear formyl 201[110], and production of octane from octyl iodide with formyl 202[111].

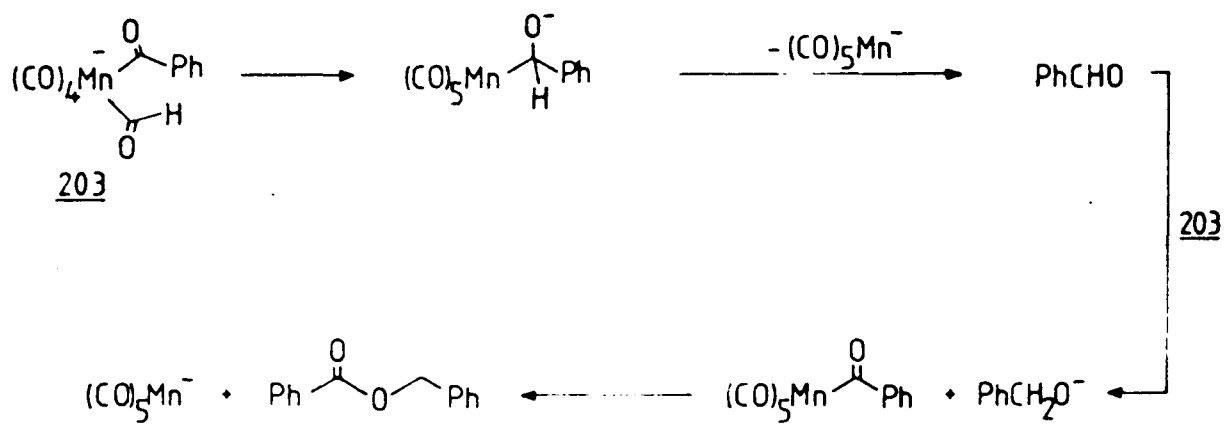


201



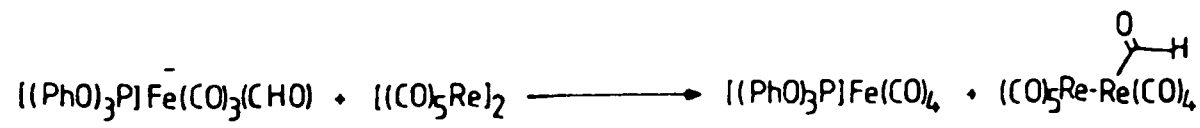
202

An interesting example involves the formyl acyl complex 203, which produces benzyl benzoate as the eventual product[112]. This is a variant of the Cannizzaro reaction with formyl acting as the hydride donor in this case.



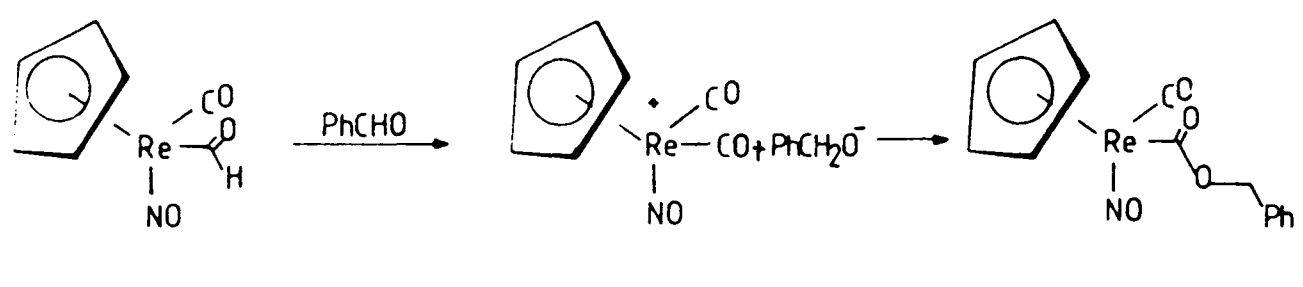
203

Hydride donation at carbonyl ligands is also known, forming new formyl complexes. Complex 204, being a stronger hydride donor than complex 201, attacks dirhenium decacarbonyl[113].

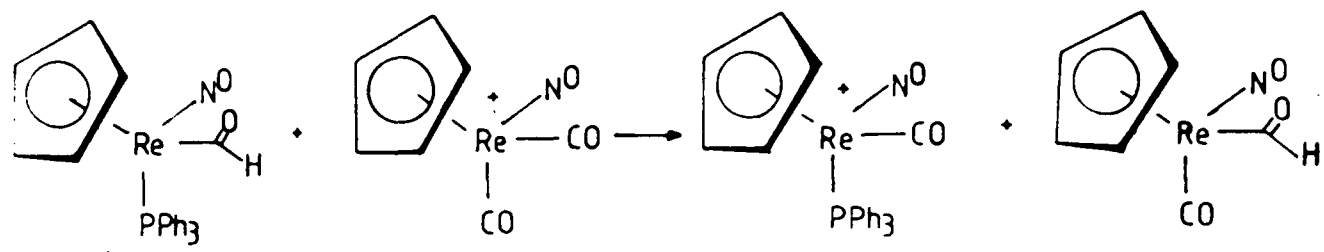


204 201

A few cases of hydride donation by neutral formyl complexes have been reported. The rhenium formyl 34 reduces benzaldehyde to benzyl alcohol, which then attacks the simultaneously formed cationic complex 33[52]. The formyl complex 34 may itself be formed from cation 33 by hydride donation from the phosphine-containing formyl 16[114].



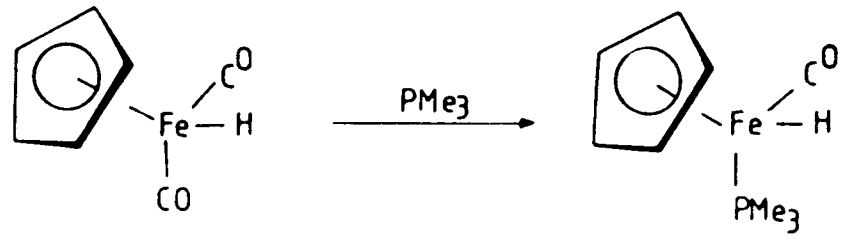
34 33



16 33 34

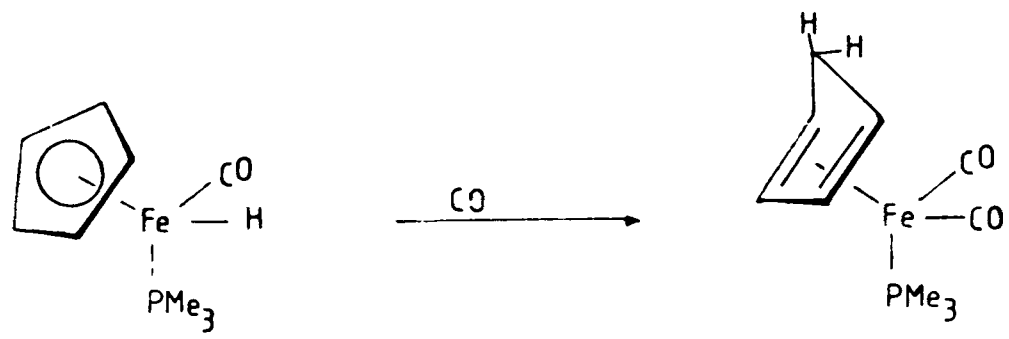
5.2 Autoreduction of $CpFe(PMe_3)(CO)H$, 77

The phosphine hydride complex 77 may be prepared in simple fashion by treatment of the dicarbonyl hydride complex 56 with trimethylphosphine[115]. It is a yellow crystalline solid which may be stored for months under nitrogen at low temperature.



56 77

Toluene or THF solutions of complex 77 undergo reaction with gaseous CO. At one atmosphere pressure, reaction was slow, but at 3 atmospheres pressure of CO, stirring for 18h gave two products after chromatography. One was identified as $[CpFe(CO)_2]_2$, 54, produced in very small quantities. The major product, obtained in 89% yield, was identified as the dicarbonyl diene complex 205.

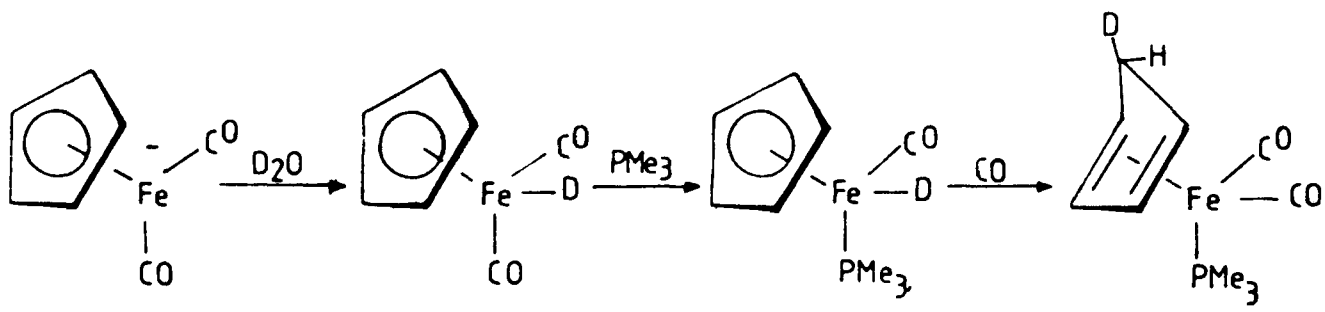


77 205

The structure of 205 was confirmed by IR, ^1H NMR ^{31}P NMR and ^{13}C NMR spectroscopy and high-resolution mass spectrometry. A study of the stereochemistry of η^4-cyclopentadiene complexes related to complex 205 had previously been made[116]. Only H_{exo} was found to be in the correct geometrical relationship to show long-range coupling to phosphorus in the ^1H NMR spectrum. The resonance in the ^1H NMR spectrum of complex 205 at δ 2.41 was thus

ascribed to H_{exo} by its coupling to phosphorus (J = 6.3 Hz). A geminal coupling of 10.7 Hz between H_{exo} and H_{endo} was also seen.

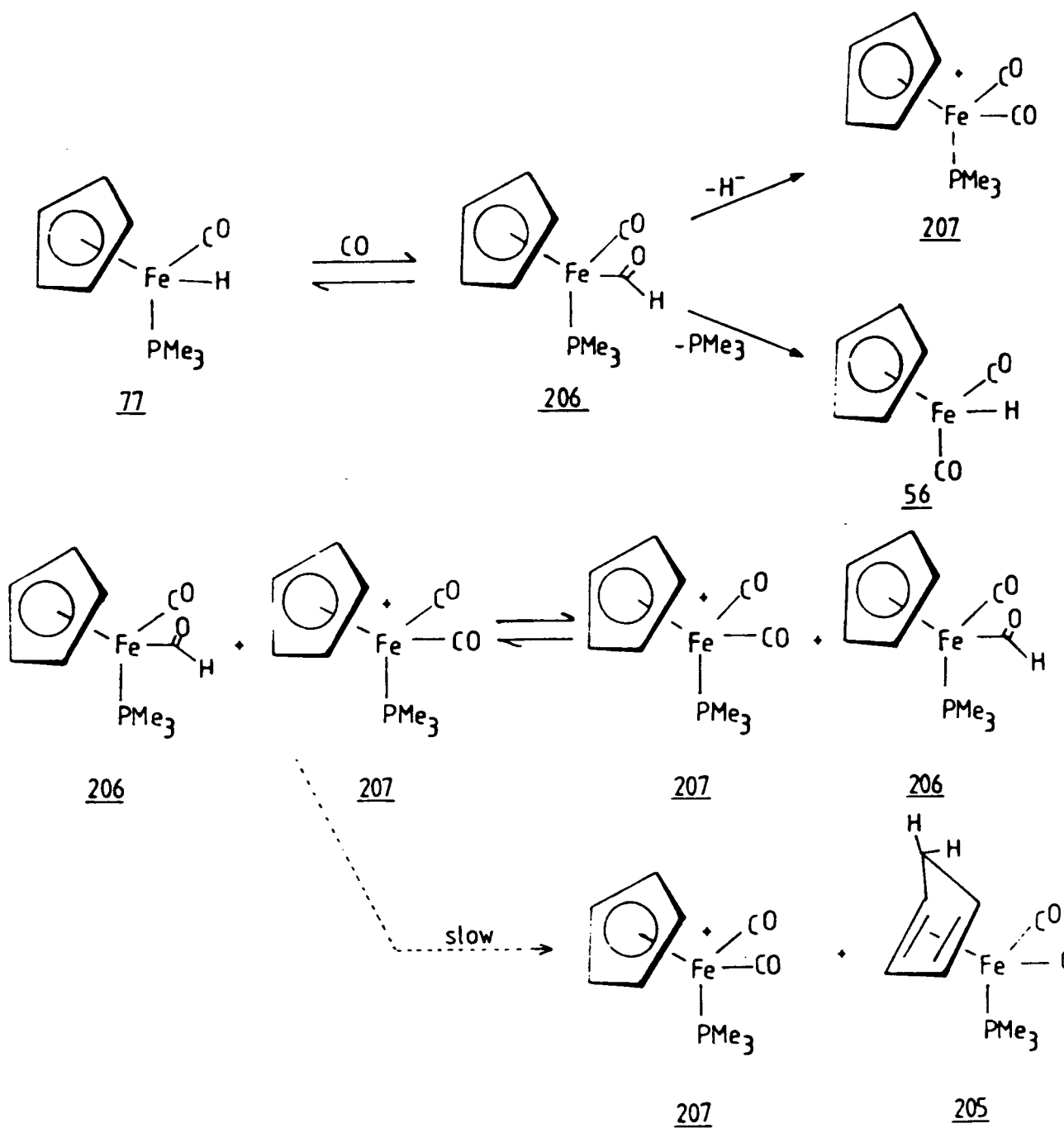
The iron deuteride 77a was prepared by reaction of the anion 122 with D_2O, followed by treatment with trimethylphosphine. This complex was stirred in toluene solution under 3 atmospheres pressure of CO as above. The product obtained, complex 205a, was exclusively deuterated on the *exo*-face. The characteristic ^1H NMR signal at δ 2.41 due to H_{exo} was absent, and that due to H_{endo} was now a broad multiplet due to coupling to deuterium. ^2H NMR spectroscopy showed a single broad resonance at δ 2.36 due to D_{exo}. The IR absorbtion at 2760 cm^{-1} assigned to C-H_{exo} in complex 205 had shifted to 2040 cm^{-1}.



122 77a 205a

The *exo*-position of deuterium in complex 205a shows that the transfer of hydride in this reaction must be intermolecular in nature. A simple intramolecular migration of deuterium from the metal to the ring would have resulted in the *endo*-deuterio complex.

A mechanism is proposed to explain the intermolecular nature of this reaction, and is illustrated in scheme 6.



Scheme 6

Prosposed Mechanism for Formation of $(C_5H_6)Fe(PMe_3)(CO)_2$, 205

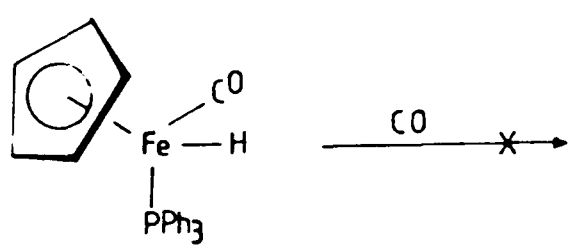
The first step in this mechanism involves hydride migration to CO to give a formyl species. The resulting vacant coordination site is taken by an external CO molecule. In order to initiate the reaction, an unspecified hydride acceptor is required in order to allow the production of a catalytic quantity of cation 207.

One possible candidate for this role is molecular oxygen. By analogy with the hydride donation reactions of formyls outlined in section 5.1, formyl 206 might be expected to attack cation 207. Hydride donation to complex 207 would be expected[49] to occur predominantly at coordinated CO. In this case, complexes 206 and 207 merely exchange identities and no overall reaction results. A small degree of hydride donation to cyclopentadienyl may be postulated, leading to irreversible formation of the eventual product, complex 205. A further molecule of cation 207 is produced in this step.

The formation of $[CpFe(CO)_2]_2$, 54 may be explained as due to loss of phosphine from the formyl 206. The dicarbonyl hydride 56 thus formed in known to dimerize to complex 54 very readily[100].

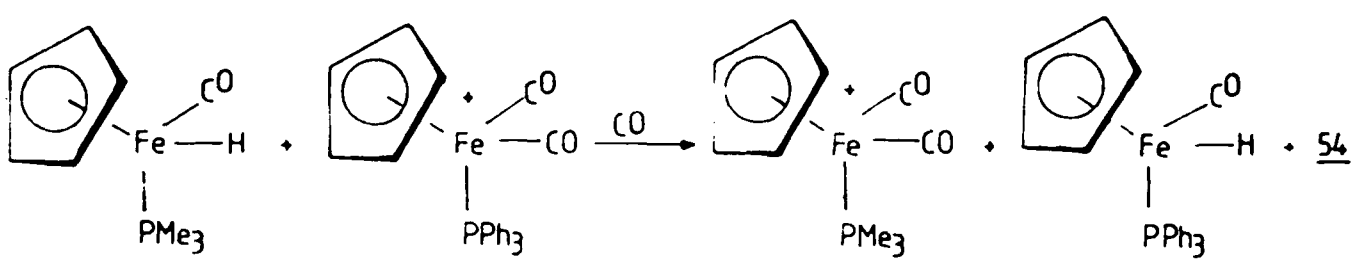
In support of this mechanism is the observation that formation of complex 205 is completely suppressed by the presence of $LiAlH_4$. Only starting complex 77 is isolated in this case. Presumably $LiAlH_4$ acts by mopping up any cation 207 formed, thus preventing formation of complex 205.

The analogous reaction for the triphenylphosphine complex 208 was not observed. Stirring a solution of complex 208 in THF under CO pressure led to isolation of starting material only.



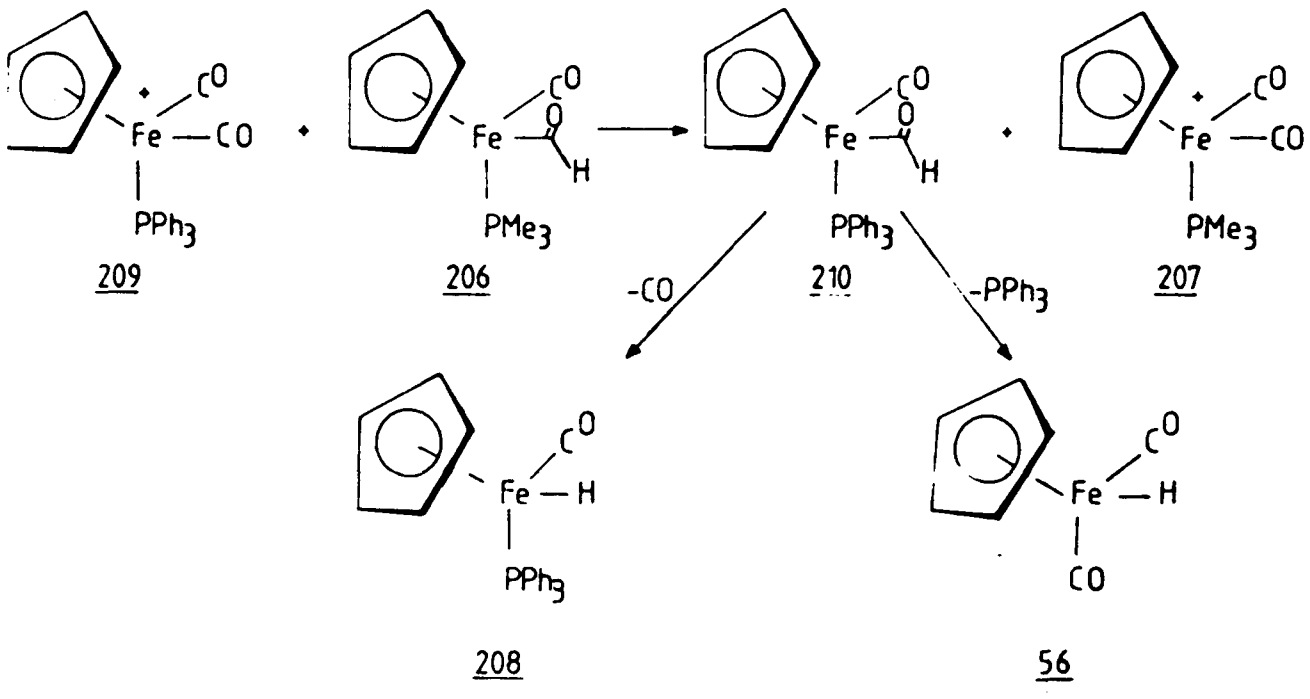
208

According to the mechanism proposed in Scheme 6, another hydride acceptor added to the reaction mixture might be expected to compete with cation 207. The more electrophilic cation 209, containing the less basic ligand triphenylphosphine in place of trimethylphosphine, was chosen for this purpose. A mixture of complexes 77 and 209 in THF under CO pressure did not form any diene 205. Chromatography gave three products. Hydride 208 was formed in 73% yield from cation 209, and was accompanied by a small quantity of $[CpFe(CO)_2]_2$, 54. A high yield of cation 207 was also isolated.

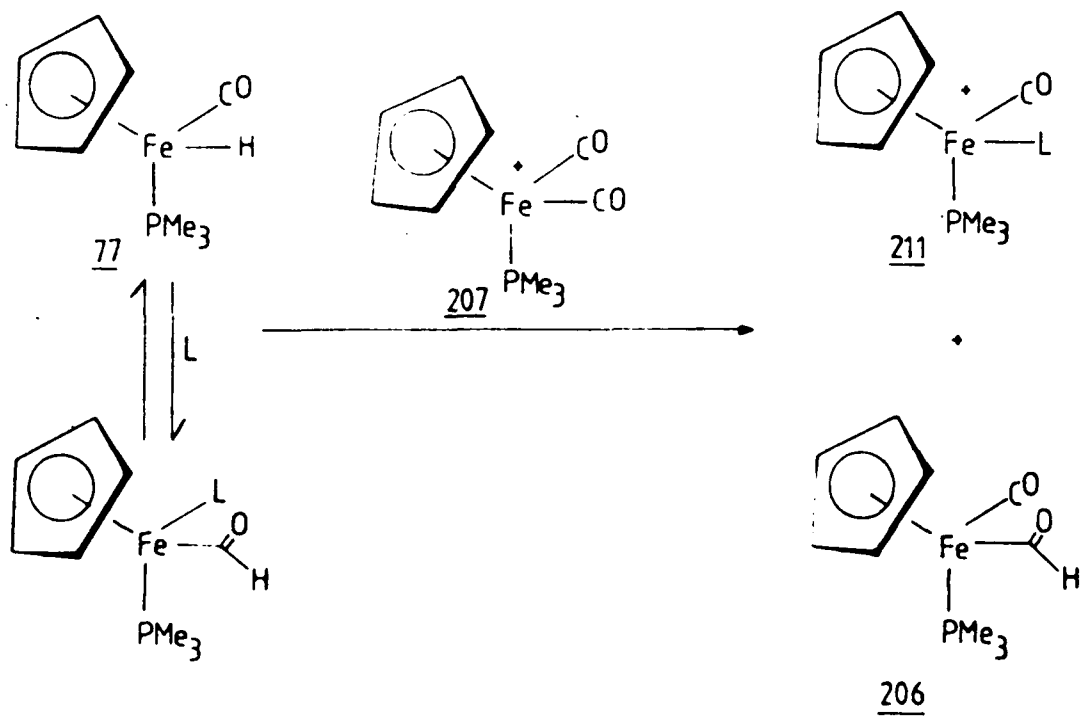


77 209 207 208 54

This result is consistent with hydride attack by the formyl 206 occurring selectively at the carbonyl ligand of cation 209. The intermediate formyl complex 210 would then decompose with loss of CO to give complex 208. Loss of triphenylphosphine may occur to a small extent, leading to the unstable hydride 56 which decomposes to give the dimer 54. Complexes 208 and 54 have been reported on reduction of cation 209 with $LiAlH_4$[49].



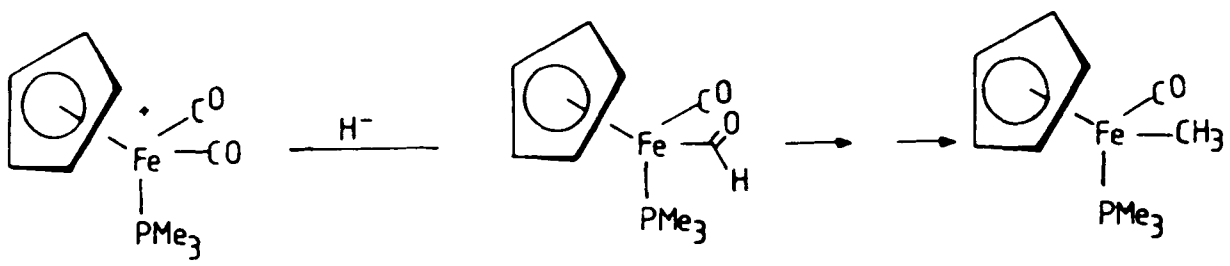
Attempts were made to show that the equilibrium between complex 77 and a formyl derivative could be established with two-electron donor ligands other than CO. Thus addition of PPh_3, PMe_3 or *t*-BuNC to a mixture of complexes 77 and 207 would, if successful, give cationic products of the form 211.



Addition of *t*BuNC to a mixture of complex 77 and 207 failed to give any isolable neutral species. An unidentifiable mixture of more than 4 cationic complexes was obtained.

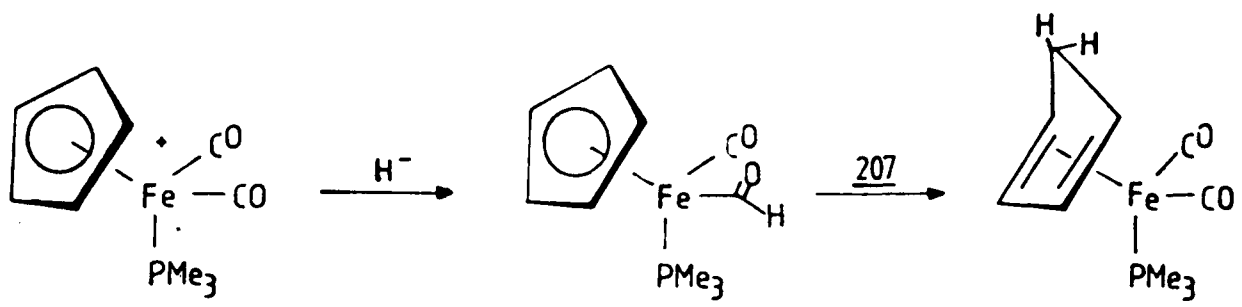
The same reaction with PPh_3 failed to give any products containing this ligand. Reaction in the presence of PMe_3 did give the expected mixture of complexes 77 and 211 (L = PMe_3). A control experiment, however, demonstrated that this latter complex is also formed by treatment of cation 207 with PMe_3. The result is therefore not conclusive.

The formyl complex 206 presumed as the intermediate in this reaction is identical to the initial product of hydride addition to cation 207. Excess hydride has previously been shown[117] to further reduce complex 207 to the methyl complex 212. Addition of less than one equivalent of hydride, however, should give a mixture of formyl 206 and unchanged cation 207. These should react as in scheme 6 to form the diene 205.



207 206 212

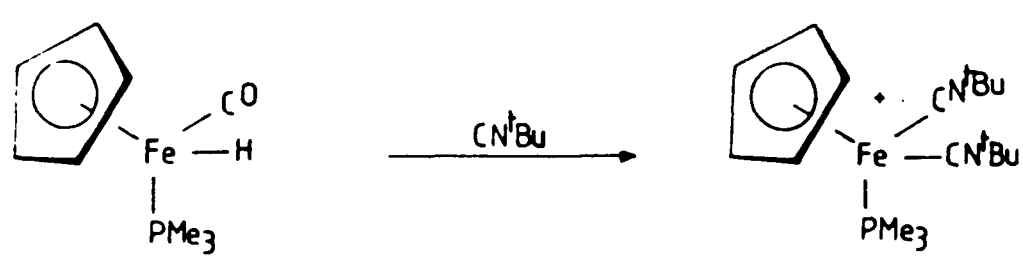
Addition of half a molar equivalent of $LiAlH_4$ to cation 207 resulted in a good yield of methyl complex 212, the $LiAlH_4$ being capable of utilizing more than one hydride per molecule. However, use of K-Selectride (potassium tri*sec*butylborohydride), which has only one available hydride, gave the expected mixture of diene 205 and a small quantity of $[CpFe(CO)_2]_2$, 54. This result is consistent with cation 207 being an intermediate in the reaction of hydride 77 with CO.



207 206 205

The reaction of hydride 77 with two-electron donor ligands other than CO was studied in the absence of added cations. Complex 77 is quite stable towards added phosphines and indeed is prepared with an excess of trimethylphosphine present. Triphenylphosphine also has no effect. This may be a steric effect, crowding at the iron centre being too severe for easy approach of a relatively large phosphine. Ethylene also leaves complex 77 unchanged. Isonitriles, however, are linear molecules which present much the same profile to the metal as does CO, and should not be much more sterically demanding despite the terminal alkyl group.

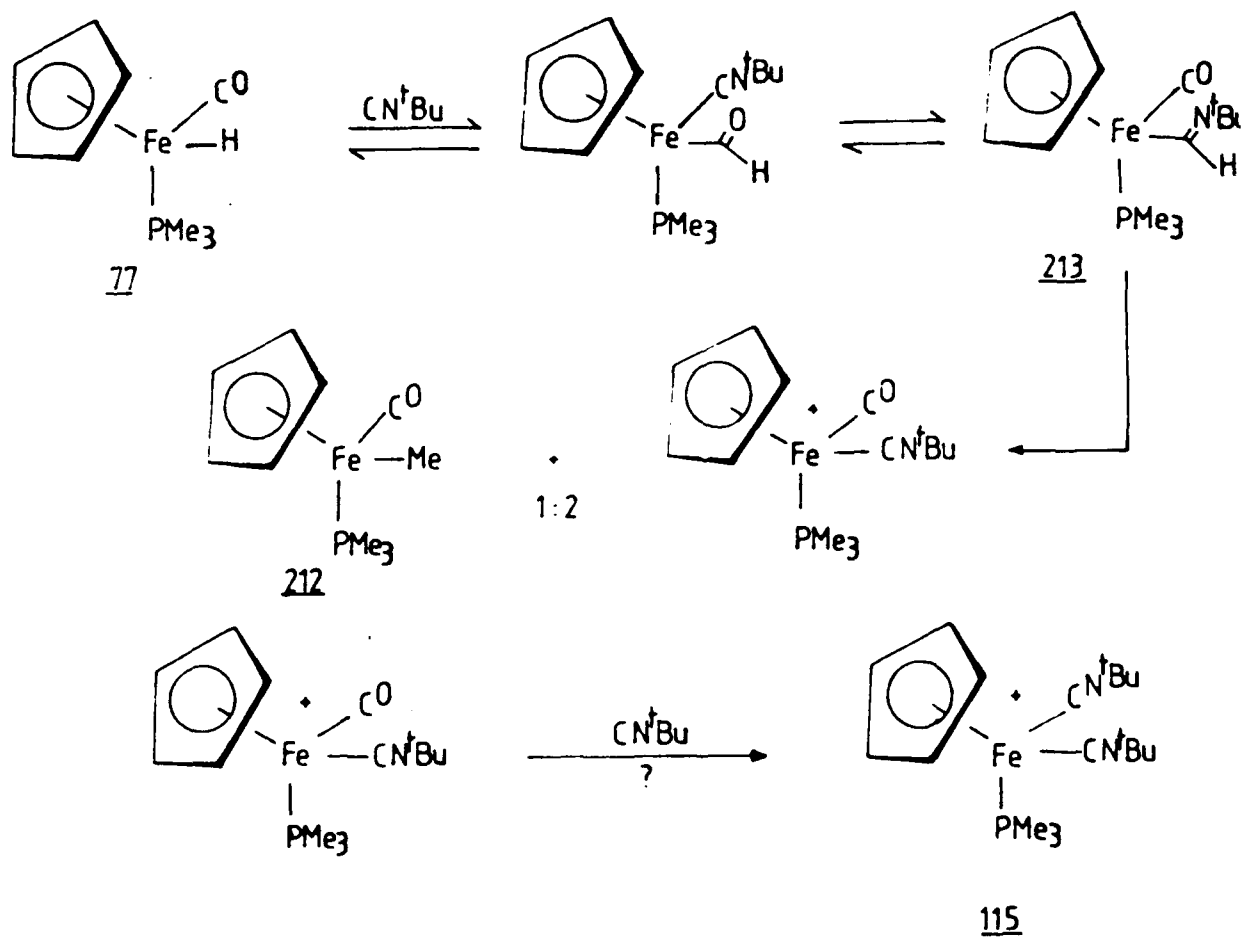
A solution of complex 77, on stirring with excess *t*-butyl isonitrile in toluene over 18h developed a heavy yellow precipitate. This was characterized as the bisisonitrile phosphine complex 115, isolated in 58% yield. The yellow crystals showed two absorbtions in the IR spectrum at 2140 and 2110 cm^{-1} ascribed to the isonitrile ligands.



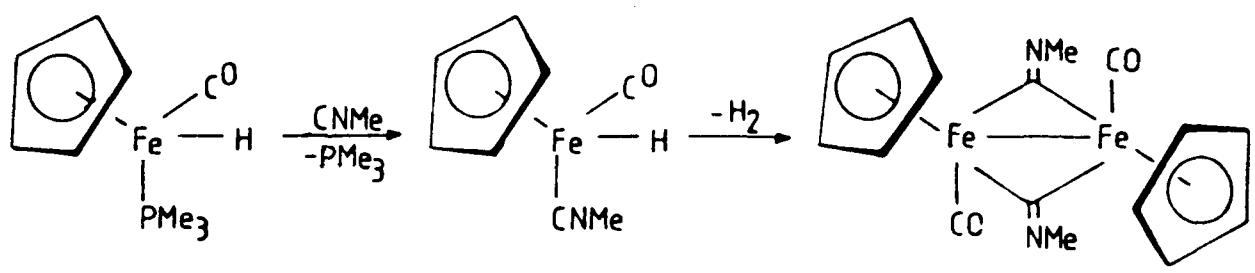
77 115

Attempts to isolate other products were not successful. ^1H NMR spectroscopy of the supernatant from the reaction mixture was not informative. Mass spectrometry showed the presence of methyl complex 212; a molecular ion plus fragments due to consecutive losses of methyl, carbonyl and trimethylphosphine were observed.

The presence of a methyl group indicates that the hydride ligand in complex 77 completely reduces a carbonyl or isonitrile ligand. Such a process would give a maximum yield of complex 115 of 67%. A possible mechanism, shown below, involves disproportionation of an iminoformyl complex 213 in a manner analogous to that described for formyl 32 (section 1.4). That was the only example of the disproportionation of a carbonyl hydride complex to give a methyl species. This new reaction would appear to provide a second example of such a process. It is unclear at which stage the remaining carbonyl ligand is exchanged for isonitrile.



This reaction does not follow the same course with methyl isonitrile. Stirring a solution of complex 77 with methyl isonitrile in toluene gave no precipitate. Chromatography led to isolation of a small quantity of the dimer 214 only. This presumably arises from replacement of trimethylphosphine with methyl isonitrile to give the unstable hydride 64, which dimerizes in a fashion similar to the dicarbonyl hydride 56. The dimer 214 was identified by ^{1}H NMR and IR spectroscopy and mass spectrometry.



77 64 214

An attempt was made to observe the formyl intermediate 206 shown in scheme 6 directly by high pressure ^{1}H NMR spectroscopy. A high pressure of CO should shift the initial equilibrium between complexes 77 and 206 towards the formyl complex.

A sample of complex 77 in a titanium pressure vessel was placed in the magnetic field. The vessel was pressurized to 50 atmospheres with CO. No reaction occurred, as monitored by ^{1}H NMR spectroscopy, over 60h. This was presumably due to mixing difficulties as the sample could not be stirred or spun. The vessel was then pressurized to 300 atmospheres with CO, and data collection performed for a total of 17 500 pulses.

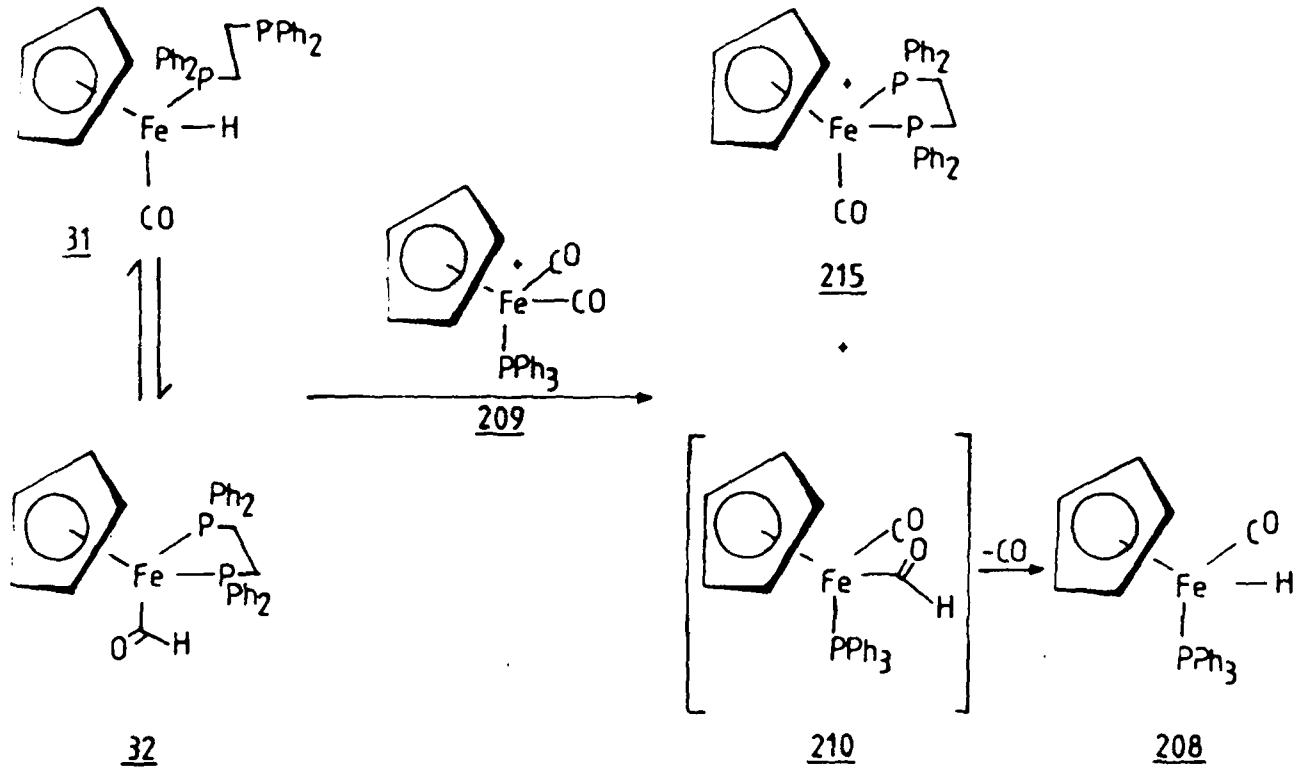
Even with this large data collection, taking approximately 7 hours, the spectrum obtained had a very poor signal to noise ratio, due mainly to the fact that the sample was not spinning. A resonance was observed in the low field region, as expected

for a formyl group, at δ 18.45. This resonance was, however, only about twice the height of the noise level, and so the result should be viewed with some caution.

It is hoped to repeat this experiment under more favourable conditions at a future date. If this confirms the formyl resonance at δ 18.45, this will be the first observation of a metal formyl species formed from a carbonyl hydride complex as a reaction intermediate.

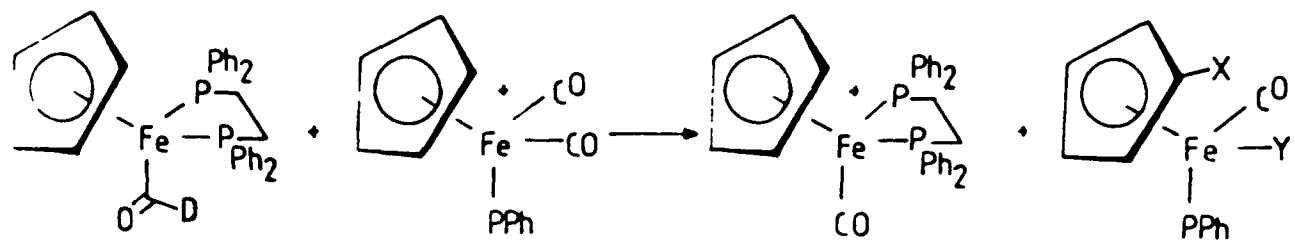
5.3. Hydride Donation via Metal Formyl Species

In the previous section a reaction mechanism was postulated in which a metal formyl complex acts as a hydride donor. Attack by hydride occurred almost exclusively at the carbonyl ligand of a cationic complex. In order to demonstrate that this is a general reaction, an analogous hydride donation was performed using formyl complex 32. This complex is known to be in equilibrium with the readily-prepared carbonyl hydride complex 31[50]. External CO is not required, as the incoming group is the unbound end of the pendant phosphine ligand. Complex 32 was thus found to reduce cation 209 smoothly in THF solution under N_2. The products obtained were the cation 215 and the carbonyl hydride 208, produced by loss of CO from formyl 210.



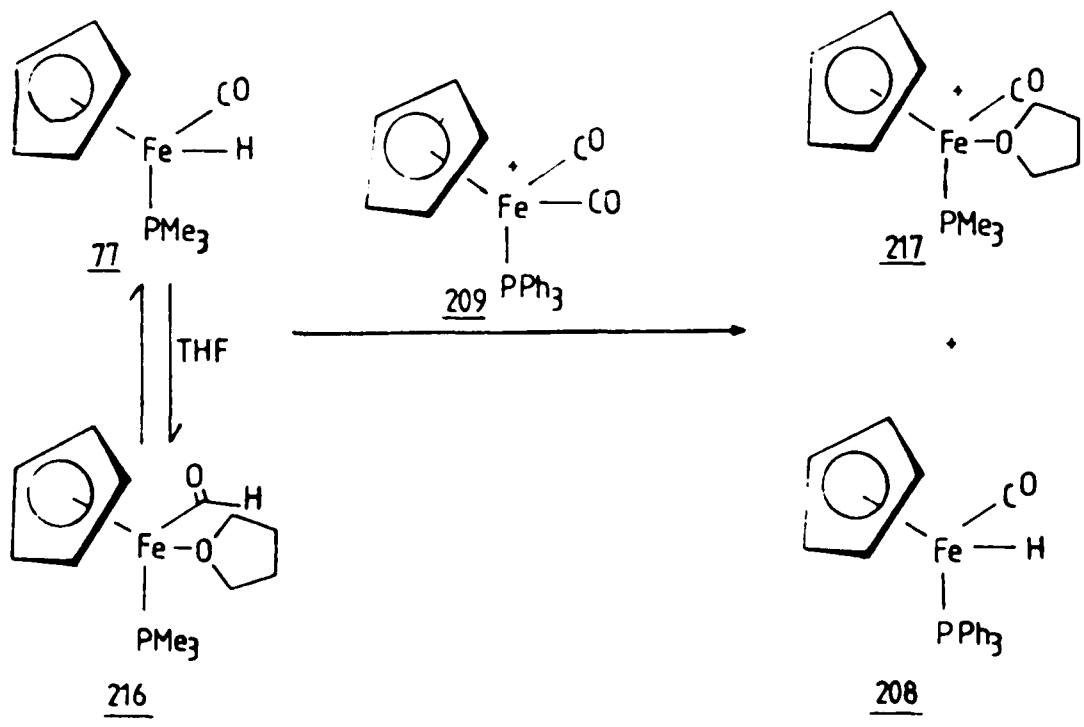
In order to demonstrate that hydride attack is occurring at the carbonyl ligand of cation 209, the reaction was repeated using the deuterio-formyl complex 32a. Attack at the cyclopentadienyl ligand would result in an *exo*-deuterio diene complex. Migration of the *endo*-hydrogen to metal would then give the ring-labelled complex 208b. No such labelling was observed, and

the product was the metal deuteride 208a without any deuterium incorporation elsewhere, as determined by ^{1}H NMR and ^{2}H NMR spectroscopy. This confirmed the specificity of hydride attack at CO.



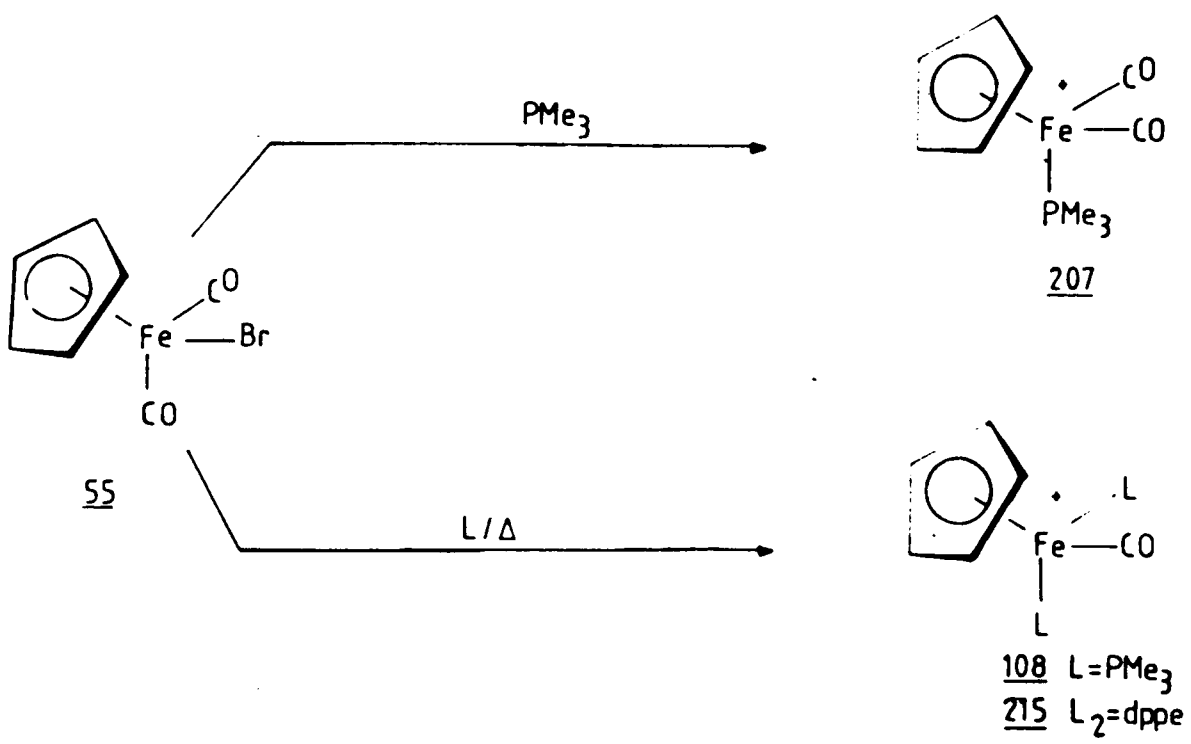
32a 209 215 208a X=H, Y=D
208b X=D, Y=H

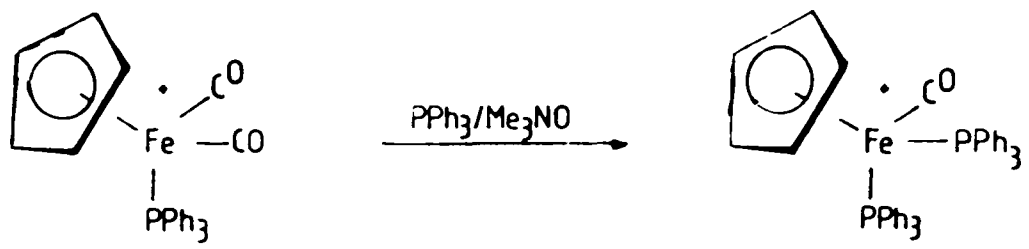
The reaction described in section 5.2 between hydride 77 and cation 209 employed CO to form the formyl complex 206. A similar reaction was found to occur in THF under nitrogen, in the absence of CO. Stirring the two reactants together under these conditions gave a high yield of hydride 208. The cationic product also formed could not be identified. This was presumably an unstable solvate of the form 217. This result indicates either that hydride donation from complex 77 is possible without an intermediate formyl, or that a molecule of THF is capable of reacting to give an intermediate formyl 216.



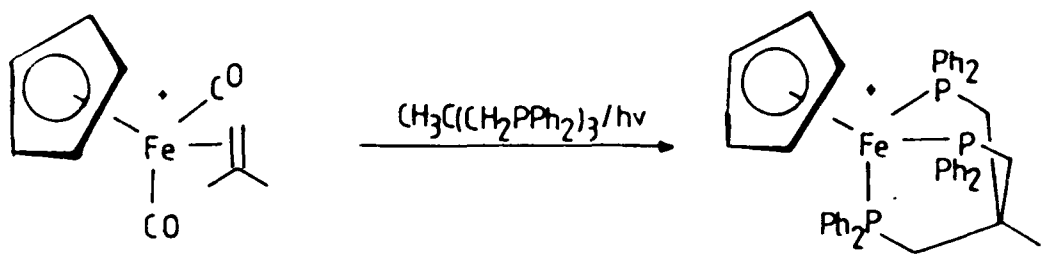
The scope of this reaction was assessed by testing the reaction of a number of metal hydride complexes with a range of cationic metal species. Six carbonyl cations $[CpFe(CO)LL']^+$ (L,L' = CO, phosphines) were selected together with the isonitrile cations 97 and 98 and the cyclopentadienyl iron tripod cation 218 (tripod = $CH_3C(CH_2PPh_2)_3$).

Syntheses of $[CpFe(CO)_3]PF_6$, 41; $[CpFe(PPh_3)(CO)(CNMe)]BF_4$, 97 and $[CpFe(dppe)(CNMe)]BF_4$, 98 have already been described (Chapter 3). The monophosphine cation 207 was prepared by reaction of trimethylphosphine with the bromide 55. Diphosphine cations 108, 215 and 219 were prepared by literature procedures[49], the first two by refluxing bromide 55 with the appropriate phosphine, and the latter at room temperature using trimethylamine-N-oxide to remove a carbonyl ligand. The tripod cation 218 was prepared according to the literature method[118] by visible-light photolysis of the isobutylene complex 220 until no carbonyl absorbtion could be detected by IR spectroscopy.



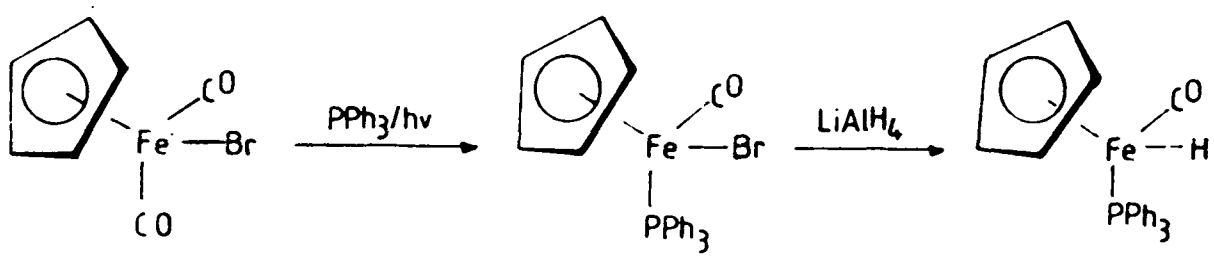


209 219



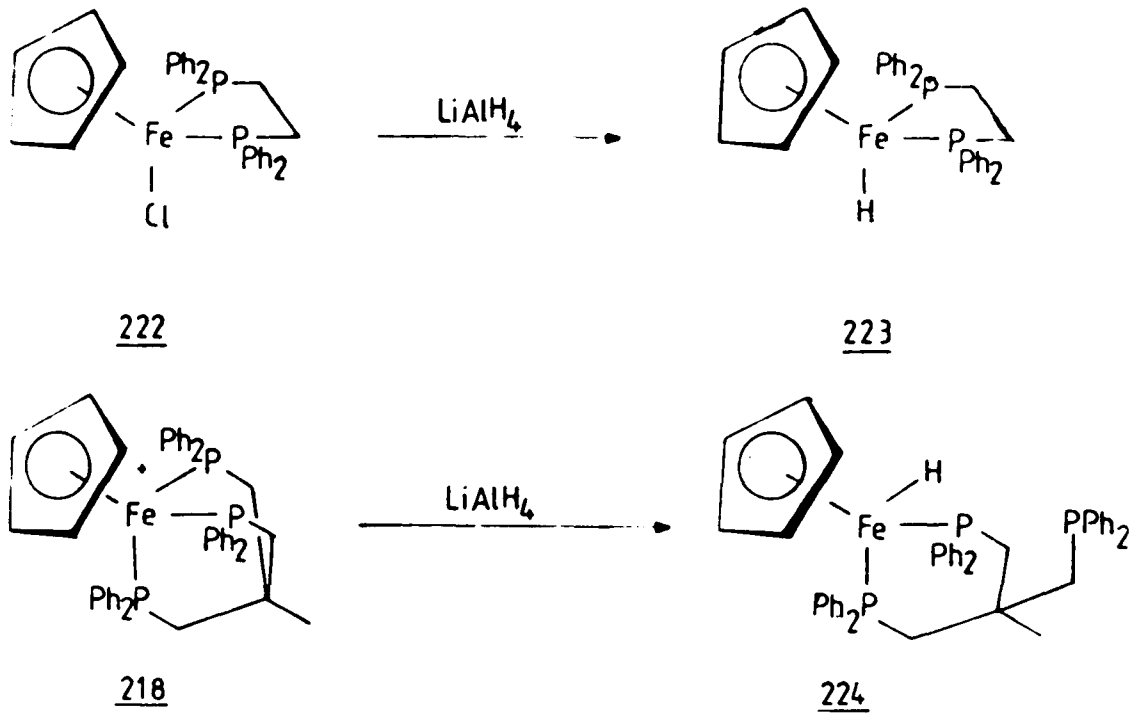
220 218

Five metal hydride complexes were also prepared. The carbonyl hydride complexes 31[50] and 77[115] were prepared by literature procedures. Hydride 208 was prepared by treatment of the bromide 221 with $LiAlH_4$.



55 221 208

Two hydride complexes without carbonyl ligands were also prepared. The dppe hydride 223 was prepared by treatment of the appropriate chloro complex 222 with $LiAlH_4$[50]. Similar treatment of tripod cation 218 gave the pendant phosphine hydride 224[118].



The nine cationic iron complexes 91, 97, 98, 108, 207, 209, 215, 218 and 219 were each in turn treated with each of the five iron hydride complexes 31, 77, 208, 223, and 224 in THF under nitrogen. Only reactions attributable to hydride transfer from iron hydride to carbonyl or isonitrile ligands were observed. In seven cases the product of such hydride transfer would be expected[49] to be indistinguishable from the starting material. These cases were therefore excluded, and a total of thirty-eight reaction mixtures were thus monitored.

Reactions were performed by mixing equimolar amounts of iron hydride and cationic complexes and dissolving the mixture in THF under N_2. The mixtures were stirred at room temperature (18h) and solvents removed. Filtration through a short alumina column allowed recovery of neutral and cationic species.

The results of these reactions are given in Table 3.

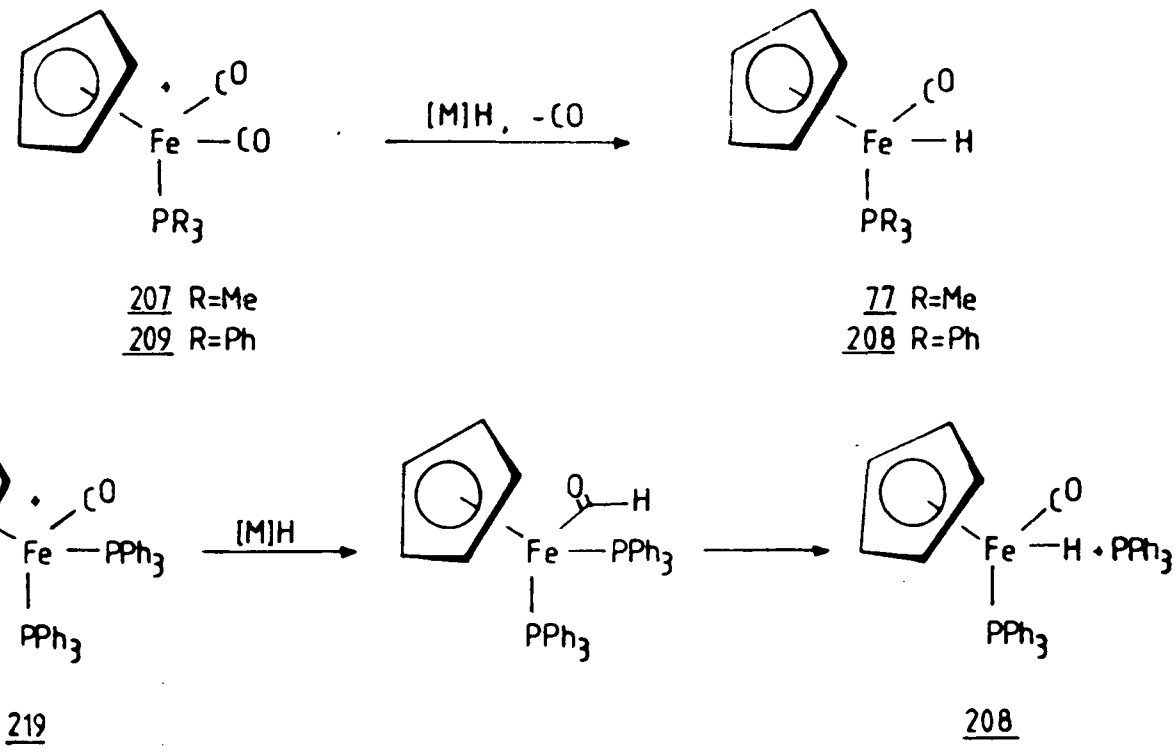
In only ten cases was reaction found to occur. Hydride donation to cations 207 and 209 led to isolation of the carbonyl

Table 3. Hydride Donation to Cationic Iron Complexes

$[CpFeLL'L'']^+$ L,L'L''	CpFeLL'H L,L'				
	P-dppe, CO 31	PMe_3, CO 77	PPh_3, CO 208	dppe 223	P,P'-tripod 224
tripod 218	X	X	X	X	-
$2PMe_3$, CO 108	X	-	X	X	X
dppe, CNMe 98	X	X	X	X	X
dppe, CO 215	-	X	X	X	X
PMe_3, 2CO 207	✓	-	X	X	X
$2PPh_3$, CO 219	✓	✓	-	X	X
PPh_3, CO, CNMe 97	✓	✓	-	X	X
PPh_3 2CO 209	✓	✓	-	X	X
3CO 91	✓	✓	✓	X	X

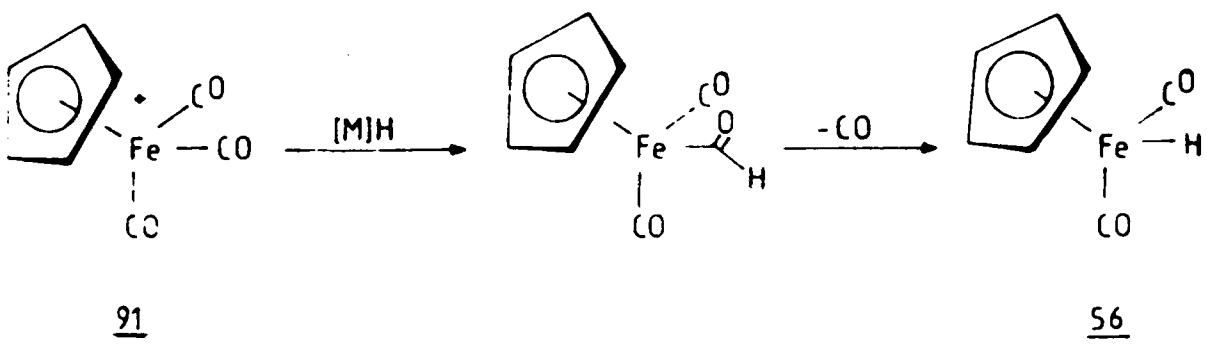
X:No reaction, starting materials recovered
✓:Products due to hydride donation recovered

hydride complexes 77 and 208, as explained in section 5.2. In a similar fashion, hydride donation to cation 219 gave a mixture of hydride complex 208 and triphenylphosphine.



Hydride donation to the isonitrile cation 97 gave products identical to those obtained on its reduction with $LiAlH_4$ (section 4.3); namely the carbonyl hydride complex 208 plus methyl isonitrile. The latter was readily identified by its characteristic odour.

The observed product on reduction of the iron tricarbonyl cation 91 was the dicarbonyl iron dimer $[CpFe(CO)_2]_2$, 54. Once again, this was presumed to be formed from the dicarbonyl hydride complex 56[100], which in turn may have been produced by loss of CO from the intermediate formyl species.



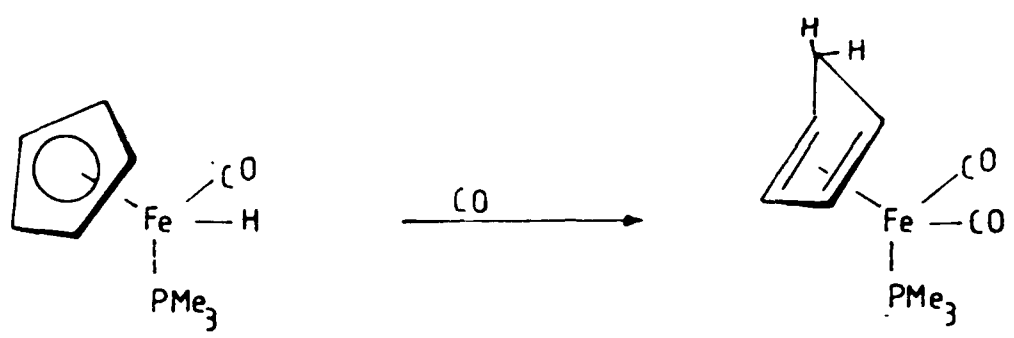
The nine cationic complexes are arranged in table 3 in approximate order of decreasing basicity of the three ligands L, L' and L''. It can be seen that hydride donation only occurs from hydride complexes with more basic ligands to cationic complexes with less basic ligands. This shows that, as might be expected, electron-donating ligands increase the hydride donating ability of the complexes.

The results for the two phosphine hydride complexes 223 and 224 require explanation. These complexes contain basic phosphine ligands which might be expected to make them powerful hydride donors. Complex 224 might also be expected to lose hydride in order to allow closure of the chelating phosphine cage. In no cases, however, were any products due to hydride donation from these complexes observed. Both hydride complexes were quite inert, and starting materials were recovered unchanged.

This lack of reactivity may be ascribed to the lack of a carbonyl ligand. The need for a carbonyl ligand in order for hydride donation to occur lends strong support to the hypothesis made above that hydride donation occurs via an intermediate formyl complex.

5.4. Conclusions

It has been shown that an intermolecular hydride transfer process is responsible for the transformation of the carbonyl hydride complex 77 into the diene 205. A mechanism involving a cationic intermediate as the hydride acceptor is proposed.

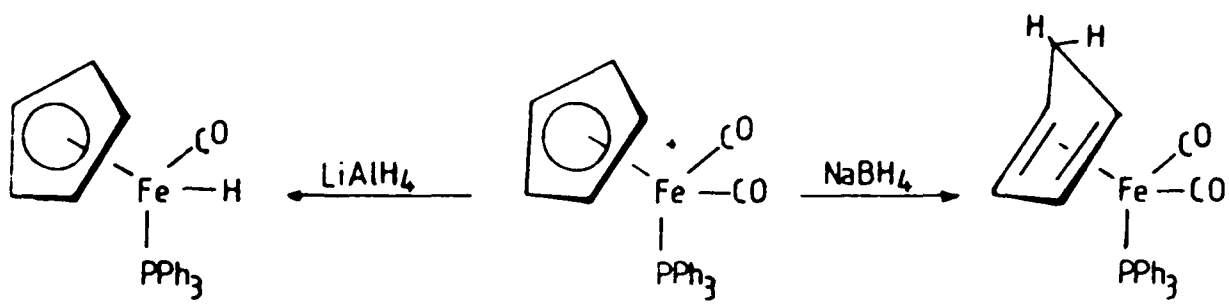


77 205

Support for the proposed cationic intermediate is given by the fact that this reaction is totally suppressed by $LiAlH_4$. Other cationic complexes can also act as hydride acceptors, and the reaction illustrated above was shown to be one particular example of a much more general reaction.

All of the carbonyl hydride complexes examined behaved as hydride donors. Two complexes not containing carbonyl ligands, however, proved inert to such reaction. It is postulated that hydride donation takes place via metal formyl species formed by migration of hydride to carbonyl under the influence of an incoming species such as CO or solvent. Hydride complexes without a carbonyl ligand cannot give rise to a formyl species, and therefore cannot be activated to donate hydride.

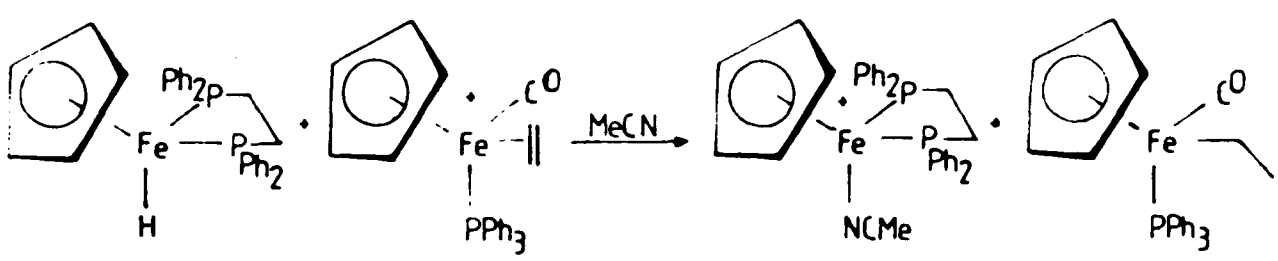
This proposal may be used to account for the different products observed in a previous study[49] on reduction of cation 209 with $LiAlH_4$ and with $NaBH_4$. The major product obtained with $LiAlH_4$ was hydride 208, whereas with $NaBH_4$ diene complex 225 was formed in 75% yield.



208 209 225

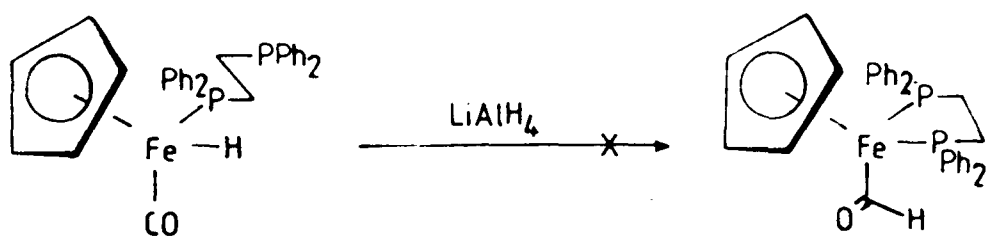
Reaction between $LiAlH_4$ and cation 209 is fast, and the cation is rapidly transformed into the formyl species. This decomposes mainly with loss of CO to give hydride 208. Sodium borohydride is, however, only sparingly soluble in THF. A considerable concentration of the cation 209 is therefore present as the formyl species is formed. Reaction between this cation and the formyl complex therefore predominates over decomposition of the formyl. This situation is analogous to that shown in Scheme 6 (section 5.2) for the trimethylphosphine complexes. Diene 225, as the only species formed irreversibly in this reaction, is the eventual product.

Several examples of hydride donation via metal formyl complexes were given in section 5.1. It is much more difficult, however, to find unambiguous examples of hydride donation from metal hydrides without the intervention of a formyl species. The iron hydride complex 223 has been shown to reduce the cationic ethylene complex 226 in acetonitrile solution[119].



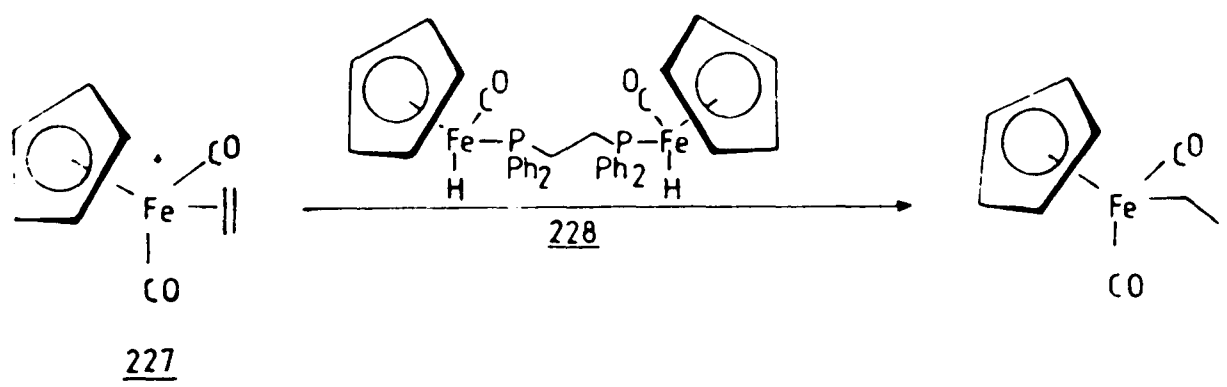
223 226

This reduction is one of the very few examples of hydride reduction which cannot occur via a formyl. Reduction via early transition metal (Zr, Nb, V) hydrides is known, but such reductions have been shown to occur via a radical process[120]. The pendant phosphine complex 31 does not disproportionate in the presence of $LiAlH_4$[50]. Presumably, Lewis acid coordination to the unbound phosphine moiety prevents formation of the formyl 32, and disproportionation via hydride donation cannot occur.



31 32

Other reductions, such as that of the ethylene ligand in cation 227 by the binuclear complex 228[121], are quite consistent with hydride donation via formyl complexes. This indicates that such a mechanism may well be more general than the particular cases studied here.



More indirect evidence for such a mechanism is given by the behaviour of the two related ruthenium cluster complexes $K[HRu_3(CO)_{11}]$ and $K[HRu_3(CO)_9(dppe)]$. These would appear to function as hydride donors only under a carbon monoxide atmosphere[122,124]. In the light of the results above, it might be suggested that the actual hydride donors are formyl complexes

$K[Ru_3(CO)_{11}(CHO)]$ and $K[Ru_3(CO)_9(dppe)(CHO)]$.

Recent reports have put forward the suggestion that metal formyl formation, as a first step in catalysis, may be achieved by hydride transfer [40,124]. Although such a process would be as thermodynamically disfavoured as hydride migration, it was proposed in order to overcome the necessity for the rarely-observed hydride migration to carbonyl, and thus provide a mechanism with greater precedent. The hydride donors used in these studies were the two ruthenium cluster complexes above. It is quite possible, therefore, that what is in fact observed is a hydride transfer from one formyl group, attached to the ruthenium cluster, to a carbonyl ligand on the target molecule.

It has been shown in this chapter that metal formyl species can be formed from carbonyl hydride complexes. Although such formyl complexes were not observed directly, it was demonstrated that their formation as intermediates is necessary in order to explain the products obtained.

CHAPTER 6

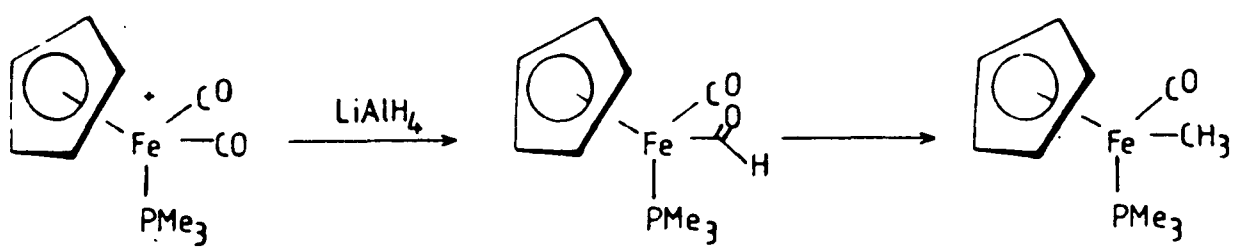
REDUCTIVE POLYMERIZATION OF CARBON MONOXIDE

6.1 Introduction

In section 1.3, a mechanism was outlined for reductive polymerization of carbon monoxide by a series of migration-reduction reactions, as illustrated in Scheme 4. The first step in this mechanism involves hydride migration to a carbonyl ligand to form a formyl complex. This process was demonstrated in Chapter 5.

Although the mechanism of reduction of formyl to methyl is unclear, a disproportionation of formyl has been demonstrated, and a trimolecular mechanism postulated[50]. In that case, formyl species are acting as the hydride sources necessary for reduction.

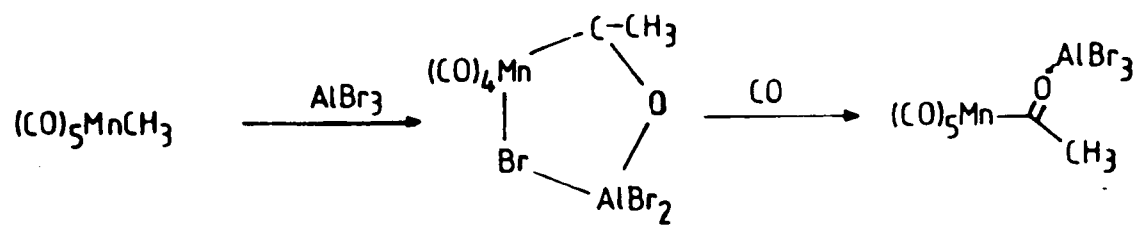
The reduction of the triphenylphosphine carbonyl cation 209 gives products ascribed to ligand loss from the intermediate formyl complex[49]. Cation 207 is reduced cleanly to the methyl complex 212.[117] The intermediate formyl complex 206 was detected by low-temperature ^1H NMR spectroscopy[49].



207 206 212

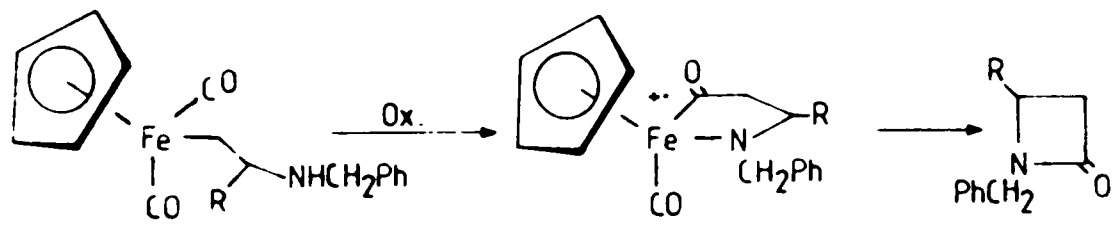
The migration of alkyl groups in complexes such as 212 is normally very slow in the presence of moderate pressures of carbon monoxide. Various catalysts have been used to promote such reactions. Strong Lewis acids such as BF_3 or $AlBr_3$ induce

migration under very mild conditions. Intermediates such as complex 229 have been isolated[125].



229

One-electron oxidizing agents have also been used in this way[126]. It would appear that oxidation of the metal reduces the bond strength to carbonyl, possibly by a reduction in the metal-carbonyl back-donation contribution. This then favours the formation of an acyl complex. An example is given by the one-electron oxidation of the β-amino iron complex 230, which promotes a migration to carbonyl and decomplexation of a β-lactam[127].

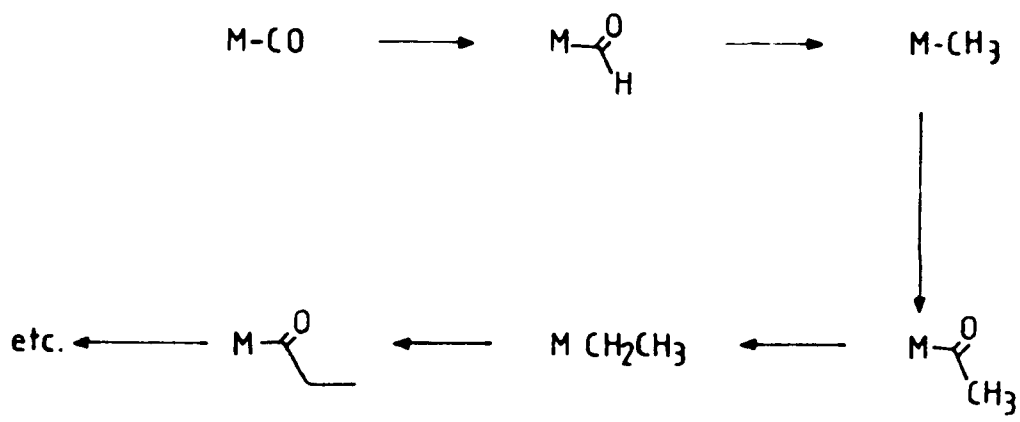


230

The reduction of a range of cyclopentadienyl iron acyl complexes to the corresponding alkyl complexes has been reported[128]. The reducing agent was diborane, or one of a number of borane complexes. These reductions were found to be more facile with strongly electron-donating ligands attached to iron.

Although the mechanism of this reduction is not clear, it was decided to use it to model the reduction of bound oxygenated species according to Scheme 4 (section 1.3). The reduction, combined with a catalytic alkyl migration, would give a simplified

migration-insertion sequence as shown in Scheme 7.



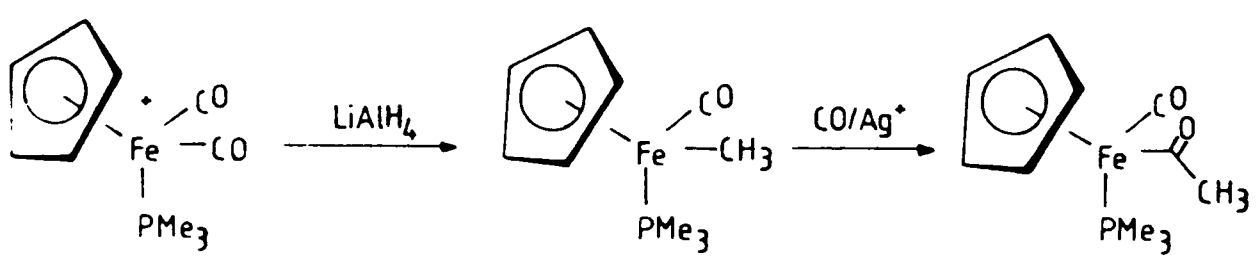
Scheme 7

Simple Model for Migration-Reduction Mechanism.

6.2 Synthesis of CO-derived Pentanoic Acid

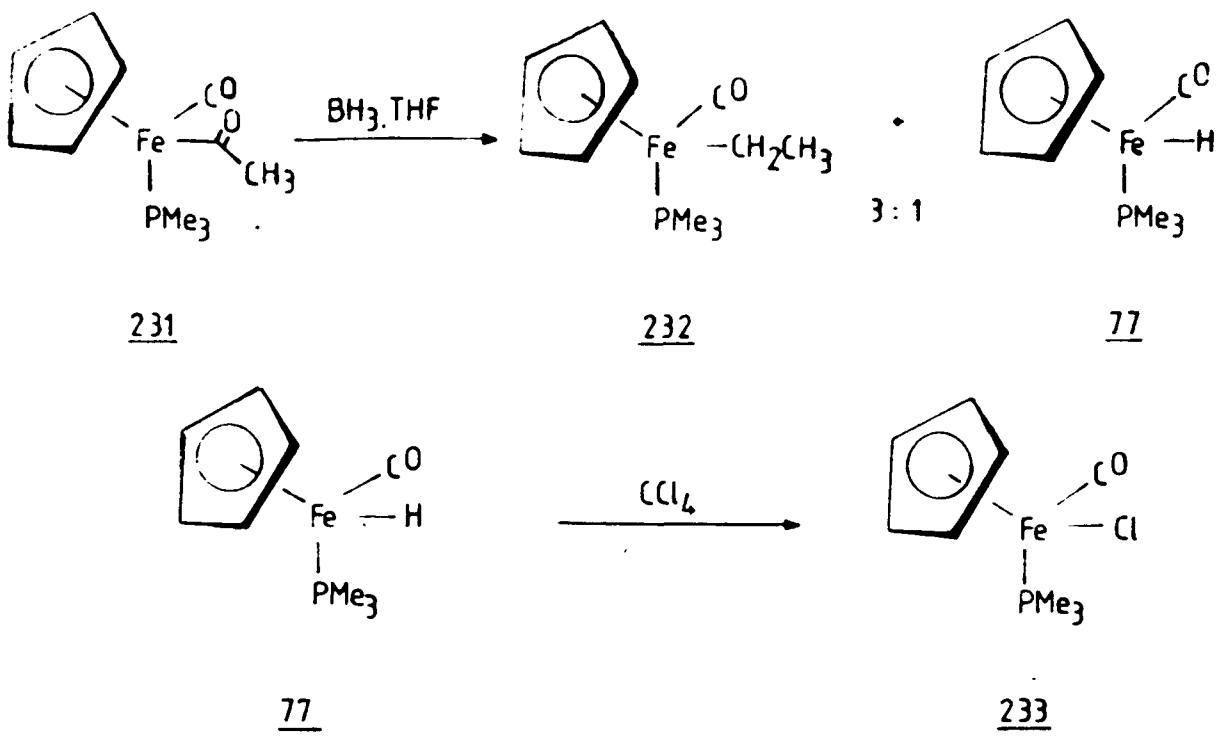
The reduction of cation 207 with $LiAlH_4$ was achieved in high (76%) yield by the literature method[117] to give methyl complex 212. Attempts were then made to perform a methyl migration under carbon monoxide to give an acetyl complex.

A catalytic quantity of $AgBF_4$ was found to be most satisfactory for this purpose. A sample of the methyl complex 212, stirred in THF under one atmosphere pressure of carbon monoxide in the presence of 2 mole % $AgBF_4$, led cleanly to acetyl complex 231 in high (90%) yield.



207 212 231

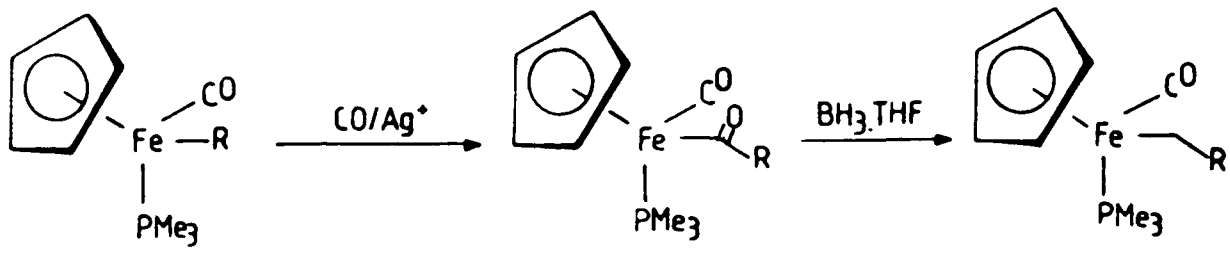
Reduction of the acetyl functionality was achieved using a BH_3.THF complex. Room-temperature reaction of complex 231 with an excess of the reducing agent gave a 3:1 mixture of the ethyl complex 232 and the hydride 77. This hydride was removed by reaction with carbon tetrachloride to give chloro complex 233[115]. A simple filtration through alumina with light petroleum gave a pure sample of ethyl complex 232 in 60% yield from methyl complex 212.



231 232 77

77 233

Treatment of ethyl complex 232 with $AgBF_4$ and CO gave propanoyl complex 234. Reduction of this with BH_3.THF followed by work-up and further treatment with $AgBF_4$ and CO gave butanoyl complex 236. One further repetition gave pentanoyl complex 238.



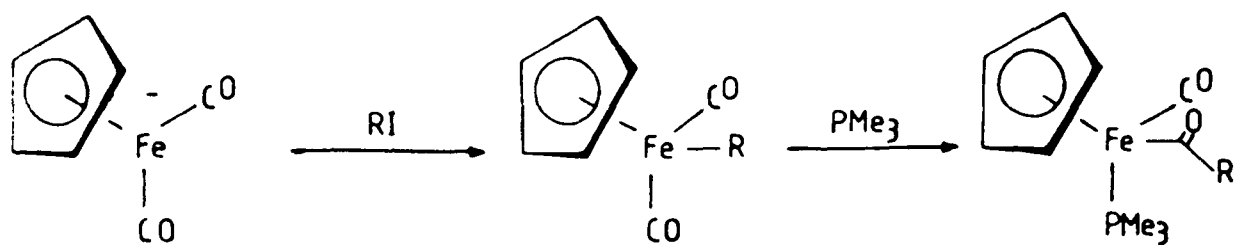
212 R=Me
232 R=Et
235 R=^{n}Pr
237 R=^{n}Bu

231 R=Me
234 R=Et
236 R=^{n}Pr
238 R=^{n}Bu

232 R=Me
235 R=Et
237 R=^{n}Pr

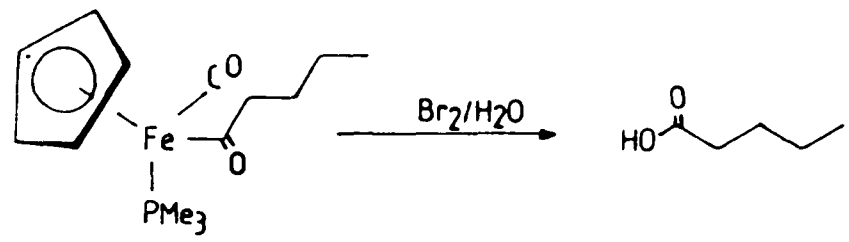
The acyl complexes 234, 236 and 238 were independently synthesized from the corresponding alkyl complexes of the type 239. Alkylation of the iron anion 122 with the appropriate alkyl iodide followed by reflux with trimethylphosphine gave the

required acyl complexes. These complexes were obtained as waxes which were characterized by ^{1}H NMR and IR spectroscopy and high resolution mass spectrometry.



122 239 234 R=Et; 236 R=^{n}Pr; 238 R=^{n}Bu

The organic ligand was decomplexed from the pentanoyl complex 238 by reaction with bromine in aqueous THF. The product, pentanoic acid, 240, was isolated in 70% yield. This was identified by ^{1}H NMR and IR spectroscopy and mass spectrometry and shown to be entirely free from any higher or lower homologues.



238 240

The final product in this model study is a single five-carbon molecule in which all carbon atoms are potentially derived directly from carbon monoxide.

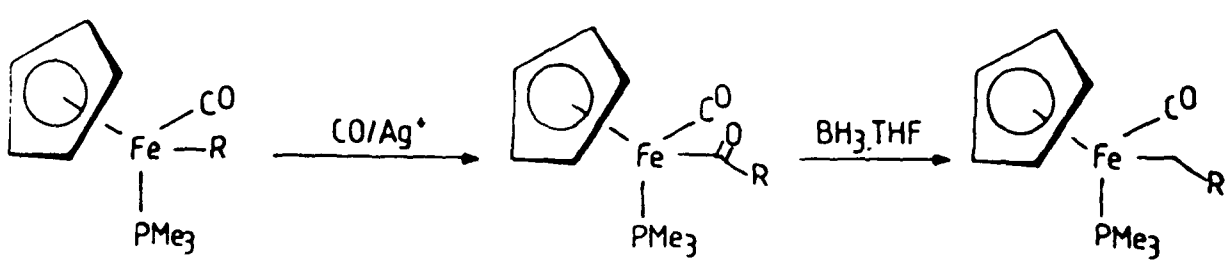
Attempts were made to combine the migration and reduction steps to give a one-pot process. The silver (I) catalyst is not stable in the presence of borane, and so a simple mixing of reactants is not possible.

Addition of the strong Lewis acid BF_3.to a mixture of the methyl complex 212 and BH_3.THF under carbon monoxide failed to give any reaction products. Borane is itself a Lewis acid,

although somewhat weaker than BF_3. An attempt was made to use borane both as the reducing agent and as the Lewis acid. A mixture of the methyl complex 212 and BH_3.THF was stirred under 100 atmospheres pressure of carbon monoxide for 6h. No reaction was observed, and complex 212 was recovered unchanged.

6.3 Conclusions

A cycle of CO-addition and reduction has been demonstrated for carbon chains attached to an iron centre. Alkyl migration to CO under the influence of a silver (I) catalyst allowed preparation of the acyl complexes 231, 234, 236 and 238 from the corresponding alkyl complexes. These were themselves prepared by reduction of the preceeding acyl complex in the series by a borane complex, leading to a carbon chain growth.



212 R=Me
232 R=Et
235 R=^{n}Pr
237 R=^{n}Bu

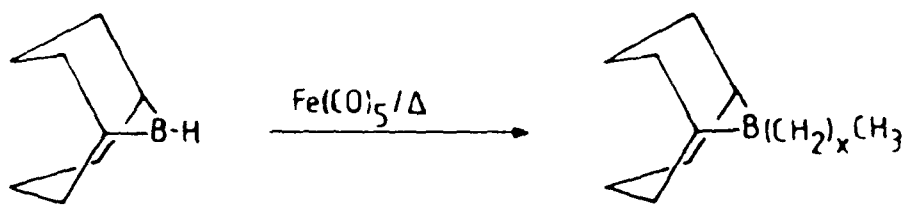
231 R=Me
234 R=Et
236 R=^{n}Pr
238 R=^{n}Bu

232 R=Me
235 R=Et
237 R=^{n}Pr

The methyl group in complex 212 may be formed from a carbonyl ligand by $LiAlH_4$ reduction. The building of a carbon chain in which each carbon atom is derived from carbon monoxide is thus demonstrated. Treatment of the pentanoyl complex 238 with bromine and water gave pentanoic acid free from any higher or lower homologues. This is the first demonstration of the synthesis of an acid as a single product from carbon monoxide.

The CO-addition and reduction steps in this study are isolated and observed separately. These steps are the ones assumed in an independent study by Schriver *et.al.*[129]. A range of hydrocarbons up to C_4 were observed on mixing $(CO)_5MnMe$ or $CpFe(CO)_2Me$ with carbon monoxide and diborane. A related study has been reported involving heating 9-BBN, 241 with iron penta-

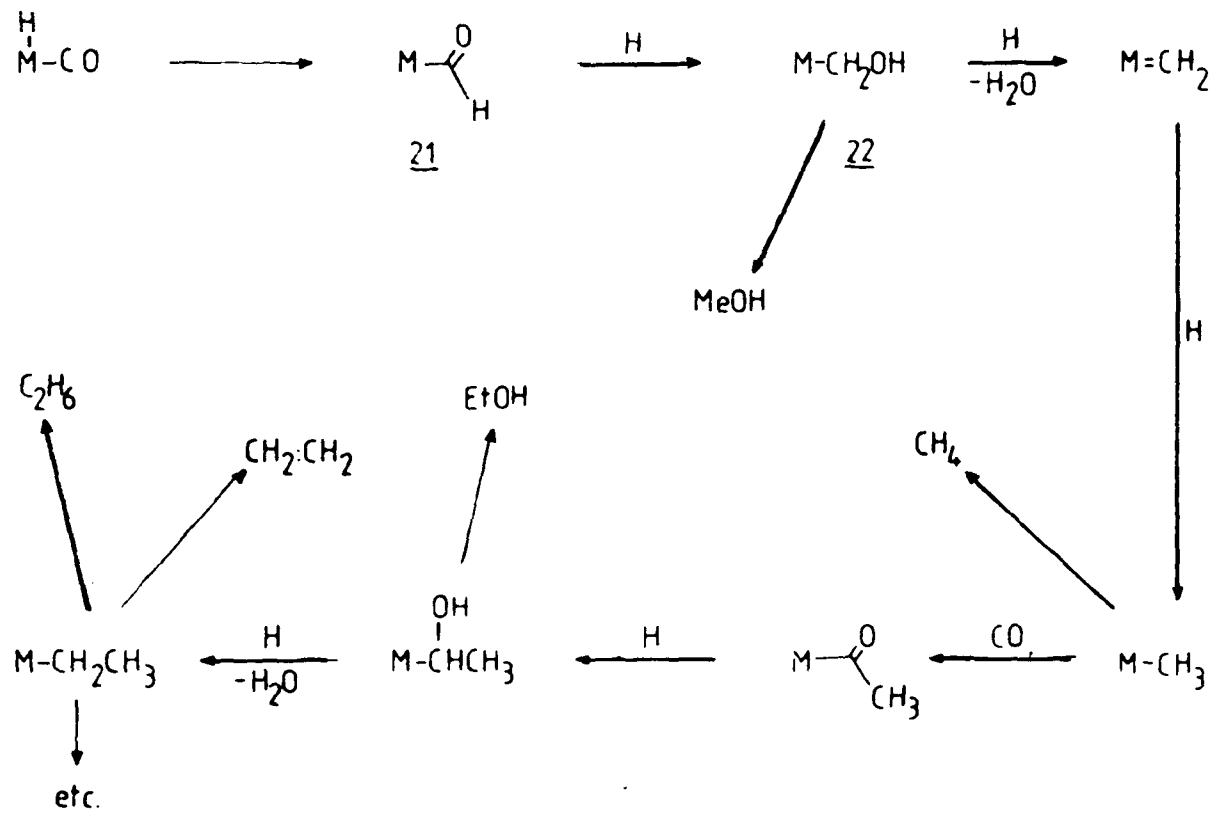
carbonyl. The products were boron-bound alkyl species of the type 242 with carbon chain lengths up to C_{10}[130].



241 242 x=0-9

CONCLUSION

One of the many mechanisms proposed for the reductive polymerization reaction of carbon monoxide involves stepwise reduction via the intermediates depicted in Scheme 4. Some modelling studies of these intermediates have previously been performed.



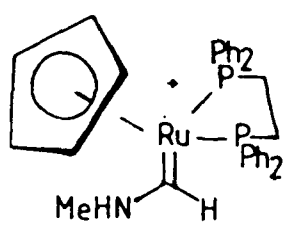
Scheme 4

The aim of the work reported here was to extend these model studies and to create a novel model system using isonitriles in place of carbon monoxide.

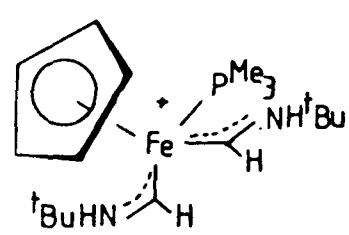
Hydride addition to cationic metal isonitrile complexes resulted, in the most part, in isolation of metal hydride complexes in which the isonitrile ligand had been lost. The mechanism by which isonitrile is lost is not clear. A cyclopenta-

dienyl ring slippage (η^5 to η^3) may be involved.

Two examples of reduced isonitrile complexes were obtained in protonated form on work-up, as the cationic aminocarbene complex 177 and the complex 186 which has a charge-delocalized structure. Further reduction of these complexes was unsuccessful.

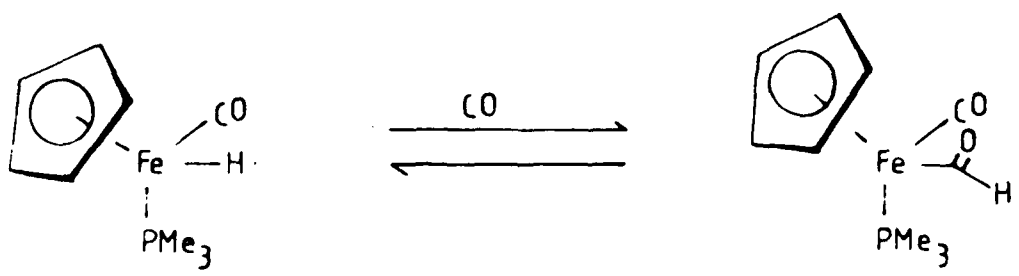


177

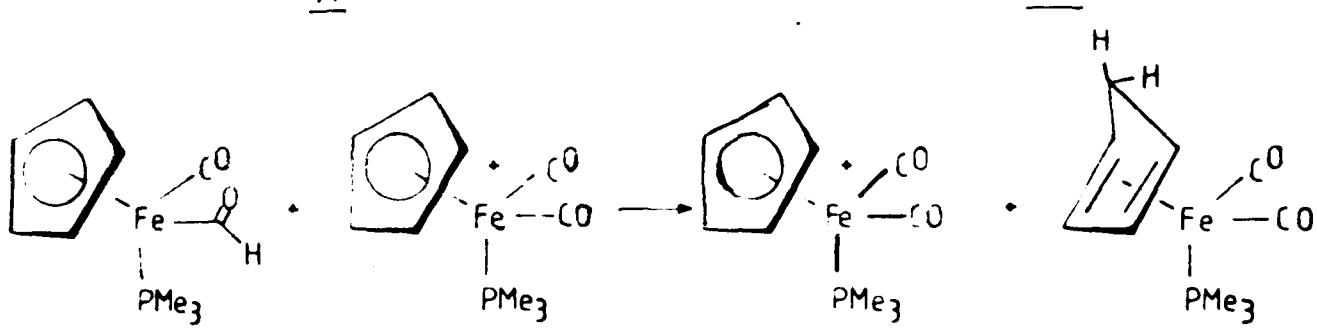


186

A study was also made of the reaction between hydride complex 77 and carbon monoxide. Interaction of these species gives the intermediate formyl 206 via a hydride migration reaction. This formyl was not observed directly, but acted as a hydride donor to the intermediate cation 207 to give the eventual product, diene complex 205.



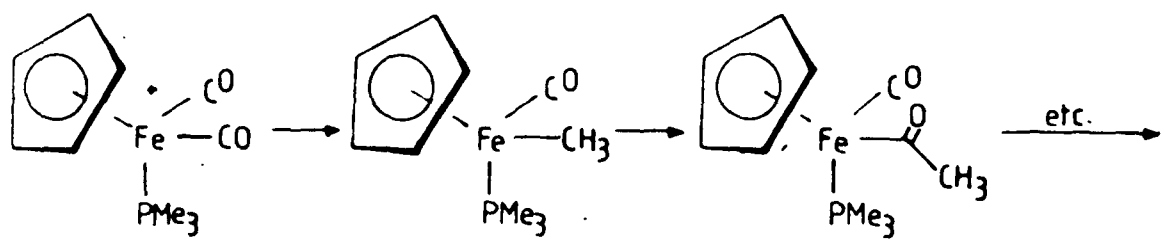
77 206



206 207 207 205

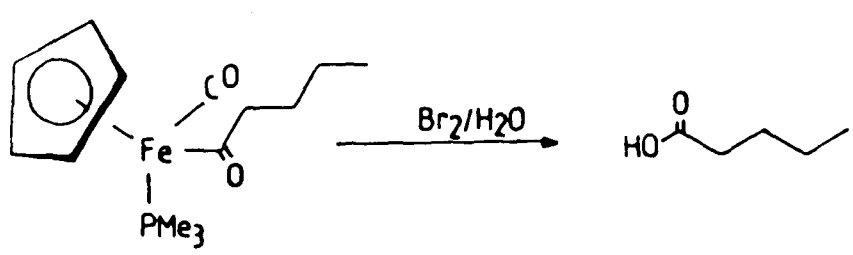
Carbonyl hydride complexes such as 77 were also shown to act as hydride donors in the absence of external carbon monoxide. Solvent molecules are responsible for the establishment of equilibria between these complexes and formyl structures analogous to 206. Metal hydride complexes not containing carbonyl ligands, and therefore unable to form formyl complexes, were found to be inert to hydride donation under the conditions employed. This supports the hypothesis that hydride donation occurs via a formyl intermediate.

A study was performed of alkyl-to-CO migration and reduction reactions at an iron centre. Reduction of a carbonyl ligand of the cationic complex 207 to methyl, followed by a migration induced by $AgBF_4$ in the presence of CO gave the acetyl complex 231. Reduction of the acetyl group to ethyl, followed by addition of a further CO molecule and further reduction demonstrated the growth of a carbon chain at the metal centre.



207 212 231

This chain growth was continued to give the five-carbon pentanoyl 237, which was treated with bromine and water to give pentanoic acid, 239.



238 240

The pentanoic acid is entirely free from lower or higher homologues. This is the first demonstration of the synthesis of a single oligomeric acid from CO.

The mechanistic steps demonstrated in this thesis have all required external sources of hydride, or metal hydrides derived from such sources. Future work should consider the generation of active metal hydride complexes by the interaction of suitable metal precursor complexes with dihydrogen. The inclusion of such hydride generation in the carbonyl systems described above would then be followed by the design of real catalytic systems.

EXPERIMENTAL

General

All reactions were carried out under a nitrogen atmosphere unless otherwise stated. Standard vacuum line and Schlenk techniques were used throughout[131].

Reagents and Solvents

THF was distilled from sodium benzophenone ketyl under nitrogen. *Dichloromethane* was distilled from calcium hydride under nitrogen. *Methanol* was distilled from magnesium methoxide. *Light petroleum* refers to that fraction boiling between 40°C and 60°C. *Indene* was technical grade, filtered through alumina and distilled from alumina under reduced pressure. *Methyl isonitrile*[132], t-*butyl isonitrile*[133], *dppe*[134], $CpFe(PPh_3)(CO)CN$[135] and $CpFe(CO)_2I$[136] were prepared by literature methods.

Chromatography was carried out on grade I (active) alumina unless otherwise stated.

Infra-red spectra were obtained as nujol mulls on a Perkin-Elmer 297 instrument and were calibrated against a polystyrene standard.

NMR Spectra were obtained on Perkin-Elmer R24B (^1H, 60MHz), Brucker WH300 (^1H, 300MHz) or Brucker AM250 (^2H, 38.39MHz; ^{13}C, 62.89MHz; ^{31}P, 101.2MHz) instruments. High-pressure NMR spectra were obtained on a Brucker WH200 (^1H, 200MHz) instrument at the University of Liverpool.

Mass spectra were recorded on a VG Micromass ZAB 1F instrument, using fast atom bombardment techniques unless otherwise stated. Where relevant they are related to the ruthenium isotope ^{102}Ru.

Melting points were obtained on a Kofler block and are uncorrected.

Elemental microanalyses were carried out by the University of Manchester and by Mrs. V. Lamburn (Dyson Perrins Laboratory).

Photolytic reactions were carried out using a Hanovia 125W medium pressure mercury arc lamp in a quartz reaction vessel.

Experimental for Chapter 2

Trimethylphosphine

Methyl iodide (310ml, 5mole) was added to a stirred suspension of magnesium (121.6g, 5mole) in diethyl ether (1.5l) over 3h. The mixture was cooled in ice water and a solution of triphenylphosphite (348ml, 1.33mole) in diethyl ether (100ml) added over 2h. The mixture was heated under reflux (2h) and then distilled into hydrochloric acid (18% HCl; 500ml) until the residue started to smoke. The mixture was stirred (18h), allowed to settle and the ether layer discarded. The aqueous layer was heated ($70^{o}C$) and a solution of sodium hydroxide (200g, 5mole) in water (450ml) added dropwise to distil out the product. This was collected in a trap cooled to $0^{o}C$ and stored over potassium hydroxide pellets. Yield 76g (75%).

$[CpFe(CO)_2]_2$, 54

$Fe(CO)_5$ (450g, 2.3mole) and dicyclopentadiene (1.5kg, 11.4 mole) were mixed and heated under reflux (24h). The mixture was cooled and filtered, and the dark-red crystals washed with light petroleum (3 x 400ml) and dried under reduced pressure at $70^{o}C$ to give 54 (300g, 74%); ν_{max} 1 960, 1 760 cm^{-1} (lit.[137]:1 945, 1 765 cm^{-1}); ^{1}H NMR ($CDCl_3$): δ 4.75 (s).

$CpFe(CO)_2Br$, 55

A solution of $[CpFe(CO)_2]_2$, 54 (100g, 0.28mole) in dichloromethane (250ml) was cooled (0^oC) and a solution of bromine (22.4g, 0.28mole) in dichloromethane (100ml) added over 1h with stirring. The solution was allowed to warm to room temperature and stirred (3h). It was then washed with saturated aqueous sodium thiosulphate (200ml) and water (200ml) and dried ($MgSO_4$). Filtration and removal of solvent gave red crystals of 55 (110g, 90%); ν_{max} 2025, 2005 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.03 (s).

$CpFe(CO)_2H$, 56

A solution of $CpFe(CO)_2Br$, 55 (4.0g, 15.6mmole) in diethyl ether (60ml) was cooled (-30^oC) and $LiAlH_4$ (0.75g, 22mmole) added. The mixture was stirred (1h; -30^oC) and quenched with water (2ml). Solvents were removed under reduced pressure, and yellow $CpFe(CO)_2H$, 56 extracted with light petroleum (2 x 50ml). This petrol solution was used immediately.

$CpFe(CO)(CNtBu)H$, 57

The solution of $CpFe(CO)_2H$, 56 prepared above was treated with *t*BuNC (1.4g, 16.9mmole) at 0^oC. The mixture was filtered through celite and chromatographed (grade V alumina). Elution with light petroleum:diethyl ether (3:1) gave yellow crystals of 57 (1.22g, 34%); ν_{max} 2075, 1945 (CO), 1870 (FeH) cm^{-1}; ^1H NMR (C_6D_6) δ 4.5 (5H, s, C_5H_5), 1.1 (9H, s, *t*Bu), -12.2 (1H, s, FeH); m/z 233.0504 (calculated for $C_{11}H_{15}FeNO$ 233.0503).

CpFe(CO)(CNMe)H, 64

Substitution of MeNC for *t*BuNC in the above preparation gave 64 as a highly unstable yellow oil (58% yield); ^{1}H NMR (C_6D_6) δ 4.5 (5H, s, C_5H_5), 2.5 (3H, s, Me), -12.2 (1H, s, FeH).

CpFe(CO)(CN*t*Bu)Br, 58

A solution of CpFe(CO)(CN*t*Bu)H (2.12g, 9.1mmole) in light petroleum (40ml) was filtered into a solution of carbon tetrabromide (3.02g, 9.1mmole) with stirring at 0°C, A red precipitate formed immediately. After 3h this was collected by filtration. Recrystallization (dichloromethane/hexane) gave 58 (2.84g, quantitative yield); ν_{max} 2155 (CN), 1990 (CO) cm^{-1} (lit.[65]:2160, 1990); ^{1}H NMR (C_6D_6) δ 4.1 (5H, s, C_5H_5), 1.0 (9H, s, *t*Bu) (lit.[65]: δ4.25, 0.97); m/z (F.I.) 311, 131 (M^+).

CpFe(CO)(CNMe)I, 65

Treatment of CpFe(CO)(CNMe)H, 64 with 1,2-diiodoethane as for the preparation of 58 gave green crystals of 65 (25% yield); ν_{max} 2180 (CN), 1985 (CO) cm^{-1} (lit.[66]:2180, 1985); ^{1}H NMR ($CDCl_3$) δ 4.7 (5H, s, C_5H_5), 3.55 (3H, s, Me) (Lit.[66]: δ 4.75, 3.58); m/z (F.I.) 317 (M^+).

CpFe(CO)(CN*t*Bu)Me, 44

Method A: A solution of $[CpFe(CO)_2]_2$ (4g, 11.3mmole) in THF (100ml) was stirred with a 1% sodium amalgam (1g Na) (18h). The solution was decanted onto methyl iodide (3ml, 48mmole) and stirred (1h). Solvents were removed under reduced pressure, and the residue filtered through alumina with light petroleum. The filtrate was heated with *t*BuNC (3g, 36mmole) in THF (80ml) under reflux (18h). The mixture was cooled, chromatographed (light

petroleum:benzene 5:1) and dissolved in benzene (100ml). Photolysis (12h) followed by chromatography (light petroleum:benzene 5:1) gave yellow crystals of 44 (1.51g, 27%); ν_{max} 2120 (CN), 1920 (CO) cm^{-1} (Lit.[133]:2118, 1922); ^1H NMR ($CDCl_3$) δ 4.6 (5H, s, C_5H_5), 1.5 (9H, s, *t*Bu), -0.05 (3H, s, Me) (lit.[133]:δ 4.62, 1.44, -0.06).

Method B: A solution of CpFe(CO)(CN*t*Bu)Br, 58 (306mg, 0.98 mmole) in THF (30ml) was cooled to -78°C and methyl lithium (1.4M; 0.8ml, 1.12mmole) added. The solution was stirred (-78°C, 1h), quenched with methanol (1ml) and chromatographed (light petroleum:benzene 5:1) to give 44 (85mg, 35%).

CpFe(CO)(CN*t*Bu)*n*Bu, 59

Replacement of methyl lithium with *n*butyl lithium in Method B above gave 59 (41%); ν_{max} 2100 (CN), 1920 (CO) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.5 (5H, s, C_5H_5), 1.5 (9H, s, *t*Bu), 1.0-0.0 (9H, m, *n*Bu).

Reaction of CpFe(CO)(CN*t*Bu)Me, 44 with triphenylphosphine

CpFe(CO)(CN*t*Bu)Me, 44 (0.5g, 2.0mmole) was heated under reflux with triphenylphosphine (0.53g, 2.0mmole) in acetonitrile (24h). Chromatography gave two fractions. Elution with dichloromethane followed by recrystallization (dichloromethane/hexane) gave $CpFe(PPh_3)(CN{t}Bu)COMe$, 61a (15mg, 1.5%); m.p. 146-147°C; ν_{max} 2035 (CN), 1565 (CO) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.6-7.2 (15H, m, PPh_3), 4.17 (5H, d, J_{PH} = 0.9Hz, C_5H_5), 2.36 (3H, s, Me), 1.25 (9H, s, *t*Bu); ^{31}P NMR ($CDCl_3$) δ 79.2; m/z 509 (M^+). Found: C 70.8, H 6.4, N 2.75, P 6.2; $C_{30}H_{32}FeNOP$ requires: C 70.7, H 6.3, N 2.75, P 6.1%.

Elution with acetone/NH_4PF_6 followed by recrystallization (dichloromethane/hexane) gave yellow crystals of $[CpFe(PPh_3)(CO)C(NH{t}Bu)Me]PF_6$, 60a (533mg, 40%); m.p. 210°C (dec); ν_{max} 3335 (NH),

1955 (CO), 840 (PF_6^-) cm^{-1}; ^1H NMR (d^6-acetone) δ 9.0 (1H, s, NH), 7.8-7.2 (15H, m, PPh_3), 4.98 (5H, d, J_{PH} = 1.3Hz, C_5H_5), 3.10 (3H, s, Me), 1.27 (9H, s, *t*Bu); ^{31}P NMR (d^6 acetone) δ 69.6; m/z 510 (M^+). Found: C 55.1, H 5.2, N 2.1, P 9.2; $C_{30}H_{33}F_6FeNOP_2$ requires: C 55.0, H 5.1, N 2.1, P 9.4%.

Reaction of CpFe(CO)(CN*t*Bu)Me, 44 with trimethylphosphine

Reaction as above but with trimethylphosphine in place of triphenylphosphine gave two fractions by chromatography. Elution with dichloromethane:ethyl acetate (5:1) gave CpFe(PMe_3)(CN*t*Bu)COMe, 63 (4mg, 0.6%); ^1H NMR ($CDCl_3$) δ 4.10 (5H, s, C_5H_5), 2.31 (3H, s, Me), 1.65 (9H, s, *t*Bu), 1.50 (9H, d, J_{PH} = 10Hz, PMe_3).

Elution with acetone/NH_4PF_6 followed by recrystallization (dichloromethane/hexane) gave yellow crystals of [CpFe(PMe_3)(CO)C(NH*t*Bu)Me]PF_6, 62 (658mg, 69%); m.p. 166-167°C; ν_{max} 3358 (NH), 1930 (CO), 840 (PF_6^-) cm^{-1}; ^1H NMR (d^6 acetone) δ 5.00 (5H, d, J = 1.4Hz, C_5H_5), 3.01 (3H, s, Me), 1.63 (9H, d, J = 10Hz, PMe_3), 1.57 (9H, s, *t*Bu); ^{31}P NMR (d^6 acetone) δ 31.4; m/z 324 (M^+). Found: C 38.5, H 5.8, N 2.9, P 13.2; $C_{15}H_{27}F_6FeNOP_2$ requires: C 38.4, H 5.8, N 3.0, P 13.2%.

Reaction of CpFe(CO)(CN*t*Bu)*n*Bu, 59 with triphenylphosphine

Reaction as above but with 59 in place of 44 gave two fractions by chromatography. Elution with ethyl acetate followed by recrystallization (dichloromethane/hexane) gave yellow crystals of CpFe(PPh_3)(CN*t*Bu)CO*n*Bu (175mg, 11.4%); mp 129-130°C; ν_{max} 2010 (CN), 1585 (CO) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.5-7.2 (15H, m, PPh_3), 4.16 (5H, d, J_{PH} = 1.2Hz, C_5H_5), 2.89-2.53 (2H, m, $COCH_2$), 1.25 (9H, s, *t*Bu), 1.12-1.04 (4H, m, CH_2CH_2), 1.78 (3H, t, J_{HH} = 7Hz, CH_3); ^{31}P NMR ($CDCl_3$) δ 78.9; m/z 551 (M^+). Found: C 71.7,

H 7.25, N 2.6, P 5.6; $C_{33}H_{38}FeNOP$ requires: C 71.9, H 6.95, N 2.5, P 5.6%.

Elution with acetone/NH_4PF_6 followed by recrystallization (dichloromethane/hexane) gave yellow crystals of [$CpFe(PPh_3)(CO)C(NHtBu)nBu]PF_6$ (555mg, 29%); ν_{max} 3330 (NH), 1965 (CO), 840 (PF_6^-) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 8.7 (1H, s, NH), 7.7-7.0 (15H, m, PPh_3), 4.71 (5H, d, J_{PH} = 1.1Hz, C_5H_5), 3.3-3.2, 2.8-2.7 (2H, AB system, $CNCH_2$), 2.1-1.4 (4H, m, CH_2CH_2), 1.15 (9H, s, *t*Bu), 0.99 (3H, t, J_{HH} = 7.2Hz, CH_3); ^{31}P NMR (d^6 acetone) δ 69.8; m/z 552 (M^+).

Attempted Preparations of CpFe(CO)(CNMe)Me, 66

Method A: A solution of CpFe(CO)(CNMe)I, 65 (913mg, 2.9 mmole) in THF (30ml) was cooled to -78°C and treated with methyl lithium (1.4M; 2.2ml, 3.1mmole). The mixture was stirred (-78°C, 1h) and quenched with methanol. Chromatography failed to yield any 66.

Similar treatment of 65 with $Me_2CuCNLi_2$, or with MeMgI at room temperature, failed to give any 66.

Method B: A solution of CpFe(CO)(CNMe)COMe, 67[134] in benzene (100ml) was photolysed (7h). Chromatography failed to yield any 66.

Method C: A solution of CpFe(CO)(CNMe)H, 64 (0.95g, 5mmole) in THF (20ml) was cooled to -78°C and treated with *n*BuLi (1.6M; 3.5ml, 5.1mmole). The solution darkened. This mixture was stirred (-78°C, 30min) and methyl iodide (2ml, 32mmole) added. Chromatography gave CpFe(CO)(CNMe)I, 65 (685mg, 43%). Similar reaction using methyl tosylate as the methylating agent failed to yield any 66.

Reaction of CpFe(CO)(CN*t*Bu)H, 57 with PMe_3

A mixture of CpFe(CO)(CN*t*Bu)H, 57 (450mg, 1.9mmole) and trimethylphosphine (0.3ml, 3mmole) in acetonitrile (30ml) was stirred at room temperature (20h). Removal of solvents under reduced pressure left a yellow oil identified as $CpFe(PMe_3)(CO)H$, 77 by comparison with an authentic sample.

Experimental for Chapter 3

$[CpFe(CO)_3]PF_6$, 91

This complex was prepared by a variation of the literature method[92]. A solution of $[CpFe(CO)_2]_2$, 54 (4g, 11.3mmole) in THF (100ml), was stirred with a 1% sodium amalgam (1g Na; 18h). The solution was decanted, cooled (-78°C) and treated with ethyl chloroformate (8ml, 84mmole). The mixture was allowed to warm to room temperature and was stirred (1h). Solvents were removed under reduced pressure, and the residue extracted with light petroleum (2 x 50ml). Hydrogen chloride gas was bubbled through these extracts (15min) to form a pink precipitate, which was washed with dichloromethane (100ml) in a soxhlet apparatus for 2½h. The bright yellow solid remaining was stirred with NH_4PF_6 (3g, 18mmole) in methanol (75ml), solvents removed under reduced pressure and the residue extracted with acetone (2 x 40ml). The volume of these extracts was reduced (10ml) and diethyl ether (100ml) added to give yellow crystals of $[CpFe(CO)_3]PF_6$, 91 (4.5g, 57%); ν_{max} 2132, 2070 (CO) cm^{-1} (lit.[92]:2120, 2068); ^1H NMR (d^6 acetone) δ 6.1 (s, C_5H_5).

$[CpFe(PPh_3)(CO)(CNMe)]BF_4$, 97

A solution of $CpFe(PPh_3)(CO)CN$[135] (1.96g, 4.5mmole) in dichloromethane (40ml) was treated with $[Me_3O]BF_4$ (0.75g, 5mmole) and the mixture stirred at room temperature (2h). The volume of the solution was reduced (7ml) and diethyl ether (100ml) added to give a yellow precipitate of $[CpFe(PPh_3)(CO)(CNMe)]BF_4$, 97 (2.33g, 98%); ν_{max} 2220 (CN), 1970 (CO), 1045 (BF_4^-) cm^{-1} (lit[77]:

2194, 1999 cm^{-1}): ^1H NMR (d^6 acetone) δ 7.6-7.1 (15H, m, PPh_3), 5.1 (5H, s, C_5H_5) 3.3 (3H, s, Me) (lit.[77]; δ 7.5-6.5, 5.10, 3.24).

[CpFe(dppe)(CNMe)]BF_4, 98

Reaction as above but with CpFe(dppe)CN[74] in place of $CpFe(PPh_3)(CO)CN$ gave [CpFe(dppe)(CNMe)]BF_4, 98 (92%); ν_{max} 2150 (CN), 1045 (BF_4^-) cm^{-1} (lit.[74]: 2150, 1050 cm^{-1}); ^1H NMR (d^6 acetone) δ 7.7-7.1 (20H, m, Ar), 4.5 (5H, s, C_5H_5), 2.8 (3H, s, Me), 2.5-2.3 (4H, m, CH_2CH_2) (lit.[74]: δ 7.7-7.2, 4.53, 2.74, 2.64-2.43).

Reaction between $CpRu(PPh_3)(CO)Cl$, 103 and potassium cyanide

A mixture of $CpRu(PPh_3)(CO)Cl$, 103[138] (1.10g, 2.24mmole) and potassium cyanide (0.70g, 10.5mmole) in methanol (50ml) was heated under reflux (72h). Chromatography, on elution with dichloromethane:ethyl acetate (1:1) gave a yellow material which was treated with NH_4PF_6 in acetone and recrystallized from dichloromethane/hexane to give yellow needles of [$(CpRu(PPh_3)(CO))_2(\mu\text{-}CN)]PF_6$ (0.45g, 41%) as a 1:1 mixture of diastereomers; m.p. >250°C; ν_{max} 2140 (CN), 1965 (CO), 840 (PF_6^-) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.6-7.3 (30H, m, Ar), 4.79, 4.76, 4.72, 4.71 (10H, 4 x s, C_5H_5); ^{31}P NMR (d^6 acetone) δ 48.7 (s), 48.2 (s), 46.8 (s), 46.1 (s); m/z (F.D.) 939 (M^+). Found:C 53.9, H 3.7, N 1.2, P 8.2; $C_{49}H_{40}F_6NO_2P_3Ru_2$ requires: C 54.3, H 3.7, N 1.3, P 8.5%.

Elution with ethyl acetate gave yellow crystals of $CpRu(PPh_3)(CO)CN$, 104 (0.22g, 21%); ν_{max} 2100 (CN), 1960 (CO) cm^{-1} (Lit.[78]: 2104, 1980 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.45 (15H, m, PPh_3), 5.00 (5H, s, C_5H_5) (lit.[78]: 7.41, 4.99); m/z (F.D.) 483 (M^+).

[CpRu(PPh_3)(CO)(CNMe)]BF_4, 99

A solution of CpRu(PPh_3)(CO)CN, 104 (222mg, 0.46mmole) in dichloromethane (20ml) was treated with [Me_3O]BF_4 (100mg, 0.67 mmole) and the mixture stirred at room temperature (3h). The volume of the solution was reduced (4ml) and diethyl ether (100ml) added to give an off-white precipitate of [CpRu(PPh_3)(CO)(CNMe)]BF_4, 99 (203mg, 76%); ν_{max} 2220 (CN), 2005 (CO), 1050 (BF_4^-) cm^{-1} (lit.[78]: 2217, 2001 cm^{-1}); ^1H NMR (d^6 acetone) δ 7.59 (15H, m, PPh_3), 5.54 (5H, s, C_5H_5), 3.40 (3H, s, Me) (lit.[78]: δ 7.62, 5.56, 3.37); m/z 498 (M^+).

CpFe(dmpe)Br, 101

A mixture of CpFe($CO)_2$Br, 55 (1.0g, 3.9mmole) and 1,2-bisdimethylphosphinoethane (0.65ml, 3.9mmole) in benzene (150ml) were irradiated with UV light (4h). Filtration of the dark solution and removal of solvents gave black CpFe(dmpe)Br, 101 (716mg, 52%); ^1H NMR ($CDCl_3$) δ 4.3 (5H, s, C_5H_5), 2.0-1.6 (4H, m, CH_2CH_2), 1.3 (12H, m , PMe_2).

[CpFe(dmpe)(CNMe)]BF_4, 100

A solution of CpFe(dmpe)Br, 101 (702mg, 2.0mmole) and potassium cyanide (700mg, 10mmole) in methanol (30ml) was stirred (1h). Solvent was removed and the orange residue extracted with dichloromethane (2 x 20ml) to give CpFe(dmpe)CN, 102 (445mg, 75%); ν_{max} 2045 (CN) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.23 (5H, t, J_{PH} = 1.5Hz, C_5H_5), 1.79-1.45 (4H, m, CH_2CH_2), 1.25 (12H, m, PMe_2); m/z (E.I.) 297 (M^+).

A solution of this complex (531mg, 1.79mmole) in dichloromethane was treated with [Me_3O]BF_4 (350mg, 2.36mmole) and stirred at room temperature (18h). Chromatography, eluting with 1%

methanol in dichloromethane, followed by recrystallization from dichloromethane/hexane gave yellow needles of [CpFe(dmpe)(CNMe)]BF_4, 100 (586mg, 88%); m.p. >250°C; ν_{max} 2125 (CN), 1048 (BF_4^-) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.47 (5H, t, J_{PH} = 1.6Hz, C_5H_5), 3.44 (3H, t, J_{PH} = 1.2Hz, Me), 1.9-1.3 (4H, m, CH_2CH_2), 1.63-1.58 (12H, m, PMe_2); ^{31}P NMR (d^6 acetone) δ 76.08; m/z 312 (M^+). Found: C 39.33, H 6.14, N 3.36, P 15.2; $C_{13}H_{24}BF_4FeNP_2$ requires: C 39.13, H 6.06, N 3.51, P 15.5%.

[CpRu(PPh_3)$_2$(CNMe)]PF_6, 87

A solution of CpRu(PPh_3)$_2$Cl, 88[138] (2.0g, 2.8mmole) and NH_4PF_6 (1.5g, 9.2mmole) in methanol (50ml) was treated with methyl isonitrile (0.5ml, 9.1mmole) and heated to reflux (3h). Solvents were removed and the residue extracted with dichloromethane (40ml). The volume of the solution was reduced (10ml) and light petroleum (100ml) added to give [CpRu(PPh_3)$_2$(CNMe)]PF_6, 87 (2.23g, 92.3%); ν_{max} 2160 (CN), 840 (PF_6^-) cm^{-1} (lit.[74]:2160 cm^{-1}); ^1H NMR ($CDCl_3$) δ 7.2 (30H, m, Ar), 4.7 (s, 5H, C_5H_5), 3.4 (3H, s, Me) (lit.[74]: δ7.2, 4.7, 3.4).

[CpRu(dppe)(CNMe)]PF_6, 107

Reaction as above but with CpRu(dppe)Cl, 106[138] in place of CpRu(PPh_3)$_2$Cl, 88 gave [CpRu(dppe)(CNMe)]PF_6 (62%); m.p. 235-236°C; ν_{max} 2165 (CN), 840 (PF_6^-) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.7-7.2 (20H, m, Ar), 4.94 (5H, s, C_5H_5), 2.66 (3H, t, J_{PH} = 1.4Hz, Me), 2.65-2.57 (4H, m, CH_2CH_2); ^{31}P NMR (d^6 acetone) δ 76.4; m/z 606 (M^+). Found: C 52.7, H 4.2, N 1.8, P 12.2; $C_{21}H_{22}F_6NP_3Ru$ requires: C 52.8, H 4.3, N 1.9, P 12.4%.

[$CpFe(PMe_3)_2(CNMe)]PF_6$, 110

A solution of $CpFe(PMe_3)_2I$, 109[81] (350mg, 0.88mmole) and NH_4PF_6 (300mg, 1.8mmole) in methanol (20ml) was treated with methyl isonitrile (50µl, 0.91mmole) and the mixture stirred at room temperature (4h). Solvents were removed and the residue extracted with dichloromethane (2 x 20ml). Addition of hexane gave yellow crystals of [$CpFe(PMe_3)_2(CNMe)]PF_6$, 110 (378mg, 94%); m.p. 181-182°C; ν_{max}2135 (CN), 840 (PF_6^-) cm^{-1}; ^1H NMR (d^6 acetone) δ 4.6 (5H, t, J_{PH} = 1Hz, C_5H_5), 3.55 (3H, s, Me), 1.55 (18H, m, PMe_3); ^{31}P NMR (d^6 acetone) δ 27.98; m/z 314 (M^+). Found: C 34.07, H 5.87, N 2.95; $C_{13}H_{26}F_6FeNP_3$ requires: C 34.01, H 5.71, N 3.05%.

Attempted displacement reactions using methyl isonitrile

A solution of $CpFe(CO)_2I$, 111[136] (1.77g, 5.82mmole) and triphenylphosphine (1.52g, 5.82mmole) in benzene (40ml) was subjected to visible-light photolysis (0°C; 15min). Solvent was removed to give green $CpFe(PPh_3)(CO)I$, 112 in quantitative yield. This was suspended in methanol (20ml) together with NH_4PF_6 (1.2g, 7.4mmole) and methyl isonitrile (0.5ml, 9mmole) added. The mixture was heated under reflux (3h). Removal of solvents gave a residue which failed to yield any [$CpFe(PPh_3)(CO)(CNMe)]PF_6$.

Similar treatment of $CpRu(PPh_3)(CO)Cl$, 103 failed to yield any [$CpRu(PPh_3)(CO)(CNMe)]PF_6$.

[$CpFe(CO)_2(CNMe)]PF_6$, 41

To a well-stirred mixture of [$CpFe(CO)_3]PF_6$, 91 (1.5g, 4.3 mmole) and methyl isonitrile (230µl, 4.3mmole) in acetone (20ml) was added DMSO (1ml, 14.1mmole) and the mixture stirred at room temperature (24h). Solvent was removed under reduced pressure

and the residue washed with diethyl ether. Extraction with dichloromethane (2 x 30ml) and removal of solvent under reduced pressure gave $[CpFe(CO)_2(CNMe)]PF_6$, 41 (0.58g, 37%); ν_{max} 2220 (CN), 2065, 2020 (CO) cm^{-1} (lit.[82]: 2224, 2075, 2022); ^1H NMR (d^6 acetone) δ 5.8 (5H, s, C_5H_5), 3.8 (3H, s, Me)(lit.[82]: δ 5.8, 3.8).

$[CpFe(PPh_3)_2(CNMe)]PF_6$, 42

A solution of $[CpFe(CO)_2(CNMe)]PF_6$, 41 (580mg, 1.6mmole) and triphenylphosphine (4.19g, 16mmole) in dichloromethane (200ml) was irradiated with UV light (3h). Solvents were removed and the residue chromatographed. Elution with dichloromethane gave orange $[CpFe(PPh_3)_2(CNMe)]PF_6$, 42 (870mg, 66%); ν_{max} 2150 cm^{-1} (lit.[56]: 2149 cm^{-1}); ^1H NMR (d^6 acetone) δ 7.5-7.1 (30H, m, Ar), 4.5 (5H, s, PPh_3), 3.8 (3H, s, Me)(lit.[56]: δ 7.43-7.28, 4.46, 3.74).

$[CpFe(PPh_3)(CNMe)_2]PF_6$, 113

Reaction as above but with $[CpFe(CO)(CNMe)_2]PF_6$, 92[75] in place of $[CpFe(CO)_2(CNMe)]PF_6$, 41 gave $[CpFe(PPh_3)(CNMe)_2]PF_6$, 113 (75%); ν_{max} 2180, 2150 (CN) cm^{-1} (lit.[56]: 2185, 2153 cm^{-1}); ^1H NMR (d^6 acetone) δ 7.4 (15H, m, PPh_3), 4.7 (5H, s, C_5H_5), 3.2 (6H, s, Me) (lit.[56]: δ 7.60-7.49, 4.71, 3.31).

$[CpFe(PPh_3)(CNtBu)_2]PF_6$, 114

Reaction as above but with $[CpFe(CO)(CNtBu)_2]PF_6$, 92[75] in place of $[CpFe(CO)_2(CNMe)]PF_6$, 41 gave $[CpFe(PPh_3)(CNtBu)_2]PF_6$, 114 (73%); m.p. 186-188°C; ν_{max} 2155, 2125 (CN) cm^{-1}; ^1H NMR (d^6 acetone) δ 7.5 (15H, m, PPh_3), 4.68 (5H, d, J_{PH} = 1.0Hz, C_5H_5), 1.25 (18H, s, *t*Bu); ^{31}P NMR (d^6 acetone) δ 71.8; m/z 549 (M^+).

Found: C 57.24, H 5.77, N 3.96; $C_{33}H_{38}F_6FeN_2P_2$ requires: C 57.07, H 5.52, N 3.96%.

[CpFe(dppm)(CNMe)]PF_6, 117

A solution of CpFe(CO)(CNMe)I, 65 (1.0g, 3.2mmole) and bisdiphenylphosphinomethane (1.21g, 3.2mmole) in dichloromethane (150ml) was irradiated with UV light (2h). Solvent was evaporated and the residue dissolved in methanol (30ml) with NH_4PF_6 (1.5g, 9.2mmole) and stirred (1h). Removal of solvent under reduced pressure and chromatography, eluting with 1% methanol in dichloromethane, followed by recrystallization from dichloromethane/hexane, gave [CpFe(dppm)(CNMe)]PF_6, 117 (1.06g, 49%); m.p. 200°C (dec.); ν_{max} 2155 (CN), 840 (PF_6^-) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 7.7-7.1 (20H, m, Ar), 4.7, 3.8 (2H, 2 x m, CH_2), 4.66 (5H, s, C_5H_5), 2.80 (3H, s, Me); ^{31}P NMR (d^6 acetone) δ 32.78; m/z 546 (M^+). Found: C 55.76, H 4.47, N 2.07; $C_{32}H_{30}F_6FeNP_3$ requires: C 55.59, H 4.37, N 2.03%.

[CpFe(dppp)(CNMe)]PF_6, 118

Reaction as above but with 1,3-bisdiphenylphosphinopropane in place of dppm gave [CpFe(dppp)(CNMe)]PF_6, 118 (36%); m.p. 174-175°C (dec.); ν_{max} 2145 (CN), 840 (PF_6^-) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 7.6-7.1 (20H, m, Ar), 4.41 (5H, t, J_{PH} = 1.3Hz, C_5H_5), 3.56 (3H, t, J_{PH} = 1.4Hz, Me), 2.6-1.3 (6H, m, $CH_2CH_2CH_2$); ^{31}P NMR (d^6 acetone) δ 56.04; m/z 574 (M^+). Found: C 56.66, H 4.61, N 1.98; $C_{34}H_{34}F_6FeNP_3$ requires: C 56.77, H 4.76, N 1.95.

[CpFe(cdpe)(CNMe)]PF_6, 119

Reaction as above but with *cis*-1,2-bisdiphenylphosphinoethene in place of dppm gave [CpFe(cdpe)(CNMe)]PF_6, 119 (36%);

m.p. >250°C; ν_{max} 2175 (CN), 840 (PF_6^-) cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.0-7.2 (22H, m, Ar plus CH:CH), 4.49 (5H, t, J_{PH} = 1.4Hz, C_5H_5), 2.62 (3H, s, Me); ^{31}P NMR (d^6 acetone) δ 101.1; m/z 558 (M^+). Found: C 56.40, H 4.23, N 1.99; $C_{33}H_{36}F_6FeNP_3$ requires: C 56.35, H 4.30, N 1.99%.

[CpFe(dppe)(CN*t*Bu)]PF_6, 120

Reaction as above but with CpFe(CO)(CN*t*Bu)Br, 58 and 1,2-bisdiphenylphosphinoethane in place of CpFe(CO)(CNMe)I, 65 and dppm gave [CpFe(dppe)(CN*t*Bu)]PF_6, 120 (74%); m.p. 134°C; ν_{max} 2125 (CN), 840 (PF_6^-) cm^{-1}; ^1H NMR (d^6 acetone) δ 8.00-7.45 (20H, m, Ar), 4.78 (5H, t, J_{PH} = 1.4Hz, C_5H_5), 2.9-2.5 (4H, m, CH_2CH_2), 0.81 (9H, s, *t*Bu); ^{31}P NMR (d^6 acetone) δ 95.44; m/z 602 (M^+). Found: C 57.63, H 5.18, N 2.11; $C_{36}H_{36}F_6FeNP_3$ requires: C 57.85, H 5.12, N 1.87%.

InRu(PPh_3)$_2$Cl, 127

A mixture of Ru(PPh_3)$_3$$Cl_2$, 127[89] (3.52g, 3.67mmole) and indene (7ml, 60mmole) in ethanol (35ml) was brought to reflux and a solution of potassium hydroxide (210mg, 3.67mmole) in ethanol (20ml) added rapidly via a dropping funnel. The mixture was heated under reflux (5h), cooled in ice water and filtered. The residue was extracted with dichloromethane (30ml) and methanol (100ml) added to the extracts. Red crystals formed on standing, which were washed with methanol (10ml) and ether (10ml) to give InRu(PPh_3)$_2$Cl, 127, (2.12g, 74%): ^1H NMR ($CDCl_3$) δ 7.0 (34H, m, Ar), 4.6 (1H, t, J_{HH} = 3Hz, H_2), 3.9 (2H, d, J_{HH} = 3Hz, $H_{1,3}$) (lit.[88]: δ 7.0, 4.6, 3.9).

InRu(dppe)Cl, 126

A solution of $InRu(PPh_3)_2Cl$, 125 (1.20g, 1.55mmole) and dppe (0.65g, 1.63mmole) in toluene (120ml) was heated under reflux (24h). Solvents were removed under reduced pressure and the residue chromatographed. Elution with ethyl acetate gave InRu(dppe)Cl, 126 (465mg, 47%); ^1H NMR ($CDCl_3$) δ7.3 (24H, m, Ar), 4.9 (1H, s, H_2), 4.5 (2H, s, $H_{1,3}$), 2.4 (4H, m, CH_2CH_2) (lit.[88]: δ 7.3, 4.9, 4.5, 2.4).

$[InRu(PPh_3)_2(CO)]PF_6$, 128

A solution of $InRu(PPh_3)_2Cl$, 125 (915mg, 1.18mmole) and NH_4PF_6 (700mg, 4.3mmole) in methanol (20ml) was pressurized to 3 atm. with carbon monoxide in a Fischer-Porter bottle and stirred (3h). Solvents were removed under reduced pressure, the residue extracted with dichloromethane and hexane added to give yellow crystals of $[InRu(PPh_3)_2(CO)]PF_6$, 128 (601mg, 56%); ν_{max} 1970 (CO) cm^{-1} (lit.[88]: 1970 cm^{-1}); ^1H NMR ($CDCl_3$) δ 7.4-6.9 (34H, m, Ar), 5.49 (1H, t, J_{HH} = 2.6Hz, H_2), 5.32 (2H, d, J_{HH} = 2.6Hz, $H_{1,3}$) (lit.[88]: δ 7.3-6.9, 5.46, 5.28); m/z 769 (M^+).

$[InRu(dppe)(CO)]PF_6$, 129

Reaction as above but with InRu(dppe)Cl, 126 in place of $InRu(PPh_3)_2Cl$, 125 gave $[InRu(dppe)(CO)]PF_6$, 129 (76%); ν_{max} 1990 (CO), 840 (PF_6^-) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.7-7.0 (20H, m, Ar), 7.2 (2H, m, $H_{5,6}$), 6.9 (2H, m, $H_{4,7}$), 5.54 (2H, d, J_{HH} = 2.8Hz, $H_{1,3}$), 5.30 (1H, t, J_{HH} = 2.8Hz, H_2), 2.85-2.49 (4H, m, CH_2CH_2); ^{31}P NMR (d^6acetone) δ 73.9; ^{13}C NMR (d^6 acetone) δ 200.5 (t, J_{PC} = 24Hz, CO), 135.5-124.8 (m, Ar), 109.9 (s, $C_{3a,7a}$), 98.5 (s, C_2), 75.6 (s, $C_{1,3}$), 29.3 (m, CH_2CH_2). Mass spectrometry showed the presence of $[InRu(PPh_3)_2(CO)]PF_6$, 128 (m/z 769) as

well as m/z 643 (M^+).

[$InRu(PPh_3)_2(CNMe)]PF_6$, 130

A solution of $InRu(PPh_3)_2Cl$, 125 (317mg, 0.41mmole) and NH_4PF_6 (100mg, 0.61mmole) in methanol (25ml) was treated with methyl isonitrile (55µl, 1.0mmole) and stirred at room temperature (3h). The mixture was filtered, the residue extracted with dichloromethane (20ml) and hexane added to the extracts to give yellow needles of [$InRu(PPh_3)_2(CNMe)]PF_6$, 130 (320mg, 85%); m.p. >250°C; ν_{max} 2155 (CN), 840 (PF_6^-) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.4-6.8 (30H, m, Ar), 7.01 (2H, m, $H_{5,6}$), 6.31 (2H, m, $H_{4,7}$), 5.42 (1H, t, J_{HH} = 2.7Hz, H_2), 4.92 (2H, d, J_{HH} = 2.7Hz, $H_{1,3}$), 3.33 (3H, s, Me); ^{31}P NMR (d^6 acetone) δ 45.13; ^{13}C NMR (d^6 acetone) δ 136-124 (m, Ar), 109.8 (s, $C_{3a,7a}$), 96.4 (s, C_2), 75.4 (s, $C_{1,3}$), 31.1 (s, Me); m/z 782 (M^+). Found: C 60.65, H 4.29, N 1.48; $C_{47}H_{40}F_6NP_3Ru$ requires: C 60.91, H 4.35, N 1.51%.

[$InRu(dppe)(CNMe)]PF_6$, 131

Reaction as above but with InRu(dppe)Cl, 126 in place of $InRu(PPh_3)_2Cl$, 125 gave [$InRu(dppe)(CNMe)]PF_6$, 131 (36%); m.p. 240-241°C; ν_{max} 2175 (CN), 840 (PF_6^-) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.6-7.1 (20H, m, Ar), 7.45 (2H, m, $H_{5,6}$), 7.00 (2H, m, $H_{4,7}$), 5.27 (2H, d, J_{HH} = 2.7Hz, $H_{1,3}$), 5.09 (1H, t, J_{HH} = 2.7Hz, H_2), 2.60 (3H, s. Me), 2.50-2.45 (4H, m, CH_2CH_2); ^{31}P NMR (d^6 acetone) δ 78.23; ^{13}C NMR (d^6 acetone) δ 138-124 (m, Ar), 108.5 (s, $C_{3a,7a}$), 95.9 (s, C_2), 72.1 (s, $C_{1,3}$), 30.7 (s, Me), 28.0 (m, CH_2CH_2); m/z 656 (M^+). Found: C 55.20, H 4.24, N 1.75; $C_{37}H_{34}F_6NP_3Ru$ requires: C 55.50, H 4.28, N 1.75%.

$[InFe(CO)_2]_2$, 132

A mixture of indene (27ml, 0.23mole), iron pentacarbonyl (15ml, 0.11mole) and heptane (27ml) was heated (140°C; 5h). The mixture was cooled and chromatographed. Elution with diethyl ether:dichloromethane (1:1) gave $[InFe(CO)_2]_2$, 132 (1.24g, 4.5%); ν_{max} 1950, 1795 (CO)cm $^{-1}$ (lit.[90]: 1951, 1790 cm^{-1}).

$InFe(CO)_2I$, 134

$[InFe(CO)_2]_2$, 132 (473mg, 1.04mmole) was dissolved in chloroform (20ml). A solution of iodine (300mg, 1.18mmole) in chloroform (20ml) was added dropwise over 10min. with stirring at room temperature. The mixture was stirred for a further 30min., solvents removed under reduced pressure and the residue chromatograghed (silica gel). Elution with dichloromethane gave black $InFe(CO)_2I$, 134 (720mg, 97%); ν_{max} 2040, 2000 (CO) cm^{-1} (lit.[93]: 2038, 1997 cm^{-1}).

$[InFe(CO)_3]PF_6$, 133

A solution of $InFe(CO)_2I$, 134 (1.8g, 5.1mmole) in THF (40ml) was treated with a 1% sodium analgan (0.6g Na; 3h). The solution was decanted, cooled to -78°C and ethyl chloroformate (6ml, 63mmole) added. The mixture was stirred at room temperature (18h), solvents removed under reduced pressure and the residue extracted with light petroleum (3 x 50ml). These extracts were treated with hydrogen chloride gas (15min) and the yellow precipitate washed with diethyl ether (50ml) and suspended in methanol (30ml) containing NH_4PF_6 (500mg, 3mmole). Removal of solvents under reduced pressure and extraction of the residue with dichloromethane (2 x 30ml) gave $[InFe(CO)_3]PF_6$, 133 (346mg, 17%); ν_{max} 2120, 2075 (CO) cm^{-1} (lit.[91]: 2117, 2072).

[$InFe(PPh_3)(CO)_2]PF_6$, 135

A solution of $InFe(CO)_2I$, 134 (2.35g, 6.6mmole), triphenylphosphine (1.75g, 6.6mmole) and NH_4PF_6 (1.6g, 10mmole) in methanol (60ml) was heated under reflux (3h). Solvent was removed under reduced pressure and the residue dhromatgraphed. Elution with 1% methanol in dichloromethane, followed by recrystallization from dichloromethane/hexane, gave [$InFe(PPh_3)(CO)_2]PF_6$, 135 (3.82g, 91%); m.p. 199-200°C; ν_{max} 2040, 2000 (CO), 840 (PF_6^-) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.6-7.1 (19H, m, Ar), 5.80 (2H, d, J_{HH} = 2.6Hz, $H_{1,3}$), 4.91 (1H, t, J_{HH} = 2.6Hz, H_2); ^{31}P NMR (d^6 acetone) δ 62.99; ^{13}C NMR (d^6 acetone) δ211.7 (d, J_{PC} = 24Hz, CO), 134-126 (m, Ar), 131.8 (d, J_{PC} = 51Hz, C_{ipso}), 105.9 (s, $C_{3a,7a}$), 95.7 (s, C_2), 78,3 (s, $C_{1,3}$); m/z 489 (M^+). Found: C 55.06, H 3.29; $C_{29}H_{22}F_6FeO_2P_2$ requires: C 54.92, H 3.50%.

[$InFe(PMe_3)_2(CO)]PF_6$, 137

Reaction as above but with trimethylphosphine (2 equivalents) in place of triphenylphosphine gave [$InFe(PMe_3)_2(CO)]PF_6$, 137 (39%); m.p. 195°C; ν_{max} 1937 (CO), 840 (PF_6^-) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 7.56 (2H, m, $H_{5,6}$), 7.43 (2H, m, $H_{4,7}$), 5.22 (2H, d, J_{HH} = 2.6Hz, $H_{1,3}$), 5.10 (1H, d, J_{HH} = 2.6Hz, H_2), 1.46 (18H, m, PMe_3); ^{31}P NMR (d^6 acetone) δ 21.4; ^{13}C NMR (d^6 acetone) δ217.8 (t, J_{PC} = 25Hz, CO), 130.1 (s, $C_{5,6}$), 126.4 (s, $C_{4,7}$), 104.0 (s, $C_{3a,7a}$), 90.4 (s, $C_{1,3}$), 75.3 (s, C_2), 20.1 (t, J_{PC} = 17Hz, PMe_3); m/z 351 (M^+). Found: C 38.74, H 5.11; $C_{16}H_{25}F_6FeOP_3$ requires: C 38.74, H 5.08%.

[$InFe(dppe)(CO)]PF_6$, 138

Method A: Reaction as above but with dppe in place of triphenylphosphine gave [$InFe(dppe)(CO)]PF_6$, 138 (86%); m.p. 108-

110°C; ν_{max} 1967 (CO), 840 (PF_6^-) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.8-7.0 (24H, m, Ar), 5.30 (2H, d, J_{HH} = 2.7Hz, $H_{1,3}$), 5.16 (1H, t, J = 2.7Hz, H_2) 2.6-2.4 (4H, m, CH_2CH_2); ^{31}P NMR (d^6 acetone) δ 89.0; ^{13}C NMR (d^6acetone) δ 133-126 (m, Ar), 104.0 (s, $C_{3a,7a}$), 92.1 (s, C_2), 73.9 (s, $C_{1,3}$), 26.2 (m, CH_2CH_2); m/z 597 (M^+). Found: C 58.09, H 4.52; $C_{36}H_{31}F_6FeOP_3$ requires: C 58.24, H 4.21%.

Method B: Anhydrous iron (II) chloride (5.0g, 39mmole) was heated to reflux in THF (150ml; 2h). Solvents were removed under reduced pressure, the residue taken up in toluene (120ml) and heated to reflux (3½h) with dppe (15.25g, 38mmole). The solution was cooled (20°C) and a solution of indenyl sodium, prepared by refluxing indene (4ml, 35mmole) with sodium pieces (1.0g, 43mmole) in THF (20ml) for 24h, added at room temperature. The dark solution was filtered and solvents removed under reduced pressure. ^1H NMR indicated a mixture of dppe and In_2Fe, 142 by comparison with authentic samples.

This mixture was suspended in methanol with NH_4PF_6 (1.3g, 8mmole) in a Fischer-Porter bottle, pressurized to 3 atmospheres with carbon monoxide and stirred (18h). Solvents were removed under reduced pressure, the residue extracted with dichloromethane (30ml) and diethyl ether (100ml) added to give a precipitate of $[InFe(dppe)(CO)]PF_6$, 138 (656mg, 2.6%).

$[InFe(PMe_3)(CO)_2]PF_6$, 136

A solution of $InFe(CO)_2I$, 134 (1.08g, 3.05mmole) and NH_4PF_6 (600mg, 3.7mmole) in methanol (50ml) was cooled to -78°C with stirring, and trimethylphosphine (0.30ml, 3.0mmole) added. The solution was warmed to room temperature and stirred (18h). Solvents were removed under reduced pressure and the residue chromatographed. Elution with 1% methanol in dichloromethane,

followed by recrystallization from dichloromethane/hexane gave $[InFe(PMe_3)(CO)_2]PF_6$, 136 (720mg, 53%); m.p. 160-163°C; ν_{max} 2040, 2005 (CO), 840 (PF_6^-) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 7.68 (2H, m, $H_{5,6}$), 7.55 (2H, m, $H_{4,7}$), 5.79 (2H, d, J_{HH} = 2.7Hz, $H_{1,3}$), 5.33 (1H, t, J_{HH} = 2.7Hz, H_2), 1.68 (9H, d, P_{PH} = 11.4Hz, PMe_3); ^{31}P NMR (d^6acetone) δ 35.93; ^{13}C NMR (d^6 acetone) δ 210.8 (d, J_{PC} = 26Hz, CO), 132.3 (s, $C_{5,6}$), 126.4 (s, $C_{4,7}$), 105.9 (s, $C_{3a,7a}$), 94.5 (s, C_2), 76.3 (s, $C_{1,3}$), 19.5 (d, J_{PC} = 35Hz, PMe_3); m/z 303 (M^+). Found: C 37.39, H 3.59; $C_{14}H_{16}F_6FeO_2P_2$ requires: C 37.53, H 3.60%.

In_2Fe, 142

A mixture of indene (10ml, 87mmole) and sodium pieces (2.5g, 109mmole) in THF (50ml) was heated under reflux (24h). The mixture was cooled (0°C) and decanted slowly into a suspension of anhydrous iron (II) chloride (4.5g, 35mmole) at 0°C. The mixture was warmed to room temperature and stirred (3h). Solvents were removed under reduced pressure and the residue extracted with benzene (150ml). Methanol (100ml) was added to the extracts which on storage at 0°C (4h) gave black crystals of In_2Fe, 142 (0.18g, 8%); ^1H NMR ($CDCl_3$) δ 6.7 (4H, s, Ar), 4.6 (2H, d, J_{HH} = 2.5Hz, $H_{1,3}$), 4.0 (1H, t, J_{HH} = 2.5Hz, H_2) (lit.[139]: 411.7, 275.8, 241.9 Hz, at 60MHz, equivalent to δ 6.86, 4.60, 4.03).

Experimental for Chapter 4

Standard Reduction Conditions

A sample of the cationic complex (typically 200mg) was dissolved in THF (20ml) and cooled to -78°C using a dry ice-acetone bath. Lithium aluminium hydride (approx. 5 molar equivalents) was added and the reaction temperature adjusted as required. The mixture was stirred for the required time, and recooled to -78°C. Water (typically 0.5ml) was added, the reaction mixture allowed to warm to room temperature, and solvents removed under reduced pressure. Neutral complexes were extracted with diethyl ether. Further extractions if required were performed with THF or acetone, until the residues were colourless.

Reduction of [CpFe(dppe)(CNMe)]BF_4, 98

Reduction of [CpFe(dppe)(CNMe)]BF_4, 98 (200mg, 0.31mmole) (-78°C; 6h) followed by work-up and extraction with acetone (20ml) gave starting material only.

Repetition of this reduction (-30°C; 18h) followed by work-up and extraction with diethyl ether gave a very small quantity of a yellow solid.

A further repetition (room temperature; 18h) followed by work-up and extraction with diethyl ether (2 x 20ml) gave CpFe(dppe)H, 149 (130mg, 80%); identified by comparison with an authentic sample. The distinctive odour of methyl isonitrile was detected during work-up.

Repetition of this reduction but using lithium aluminium deuteride gave CpFe(dppe)D, 160; ^2H NMR (C_6H_6) δ -16.01 (t, J_{PD} = 11 Hz).

Reduction of [CpFe(dmpe)(CNMe)]BF_4, 100

Reduction of [CpFe(dmpe)(CNMe)]BF_4, 100 (150mg, 0.38mmole) (room temperature; 18h) followed by work-up and extraction with diethyl ether gave yellow crystals assigned as CpFe(dmpe)H, 161 (100mg, 97%); ^{1}H NMR (C_6D_6) δ 4.2 (5H, br s, C_5H_5), 2.2-1.0 (4H, m, CH_2CH_2), 1.0 (12H, m, PMe_2), -17.4 (1H, t, J_{PC} = 78 Hz, FeH).

Repetition of this reduction but using lithium aluminium deuteride gave CpFe(dmpe)D, 162; ^{2}H NMR (C_6H_6) δ -17.4 (t, J_{PD}= 11.5Hz).

Reduction of [CpFe(dppm)(CNMe)]PF_6, 117

Reduction of [CpFe(dppm)(CNMe)]PF_6, 117 (400mg, 0.58mmole) (-30°C; 18h) followed by work-up and extraction with diethyl ether (2 x 30ml) gave a yellow solid assigned as CpFe(dppm)H, 163 (250mg, 85%); ^{1}H NMR (C_6D_6) δ 7.9-6.8 (30H, m, Ar), 4.5 (5H, s, C_5H_5), 4.2-3.0 (2H, m, CH_2), -12.0 (1H, t, J_{PH} = 70 Hz, FeH).

Reduction of [CpFe(cdpe)(CNMe)]PF_6, 119

Reduction of [CpFe(cdpe)(CNMe)]PF_6, 119 (236mg, 0.33mmole) (room temperature; 18h) followed by work-up and extraction with diethyl ether (30ml) gave an unstable yellow oil assigned as CpFe(cdpe)H, 169 (100mg, 58%); ^{1}H NMR (C_6D_6) δ 8.0-6.8 (32H, m, Ar plus CH:CH), 4.2 (5H, br s, C_5H_5), -16.2 (1H, t, J_{PH} = 75 Hz, FeH).

Reduction of [CpFe(dppp)(CNMe)]PF_6, 118

Reduction of [CpFe(dppp)(CNMe)]PF_6, 118 (1.03g, 1.43mmole) (-30°C; 36h) followed by work-up and extraction with diethyl ether (50ml) gave a yellow oil (208mg), assigned as a mixture of CpFe(dppp)H, 165 and CpFe(dppp)(CNMe)H, 166 in the ratio 5:3;

^{1}H NMR (C_6D_6) δ 7.8-6.6 (m, Ar), 4.1 (br s, C_5H_5), 3.3 (s, Me), 2.2-0.8 (m, $CH_2CH_2CH_2$), -13.4 (d, J_{PH} = 75 Hz, FeH), -15.9 (t, J_{PH} = 80 Hz, FeH); ^{31}P NMR (C_6D_6) δ 67, 26, -21.

Further extraction with THF gave starting material.

Attempted reaction of CpFe(dppp)(CNMe)H, 166

The unseparated mixture of CpFe(dppp)H, 165 and CpFe(dppp)(CNMe)H, 166 (208mg) was dissolved in THF and allowed to stand (room temperature; 4 days). No reaction occurred as monitored by ^{1}H NMR spectroscopy.

Reduction of [$CpFe(PPh_3)_2(CNMe)]PF_6$, 42

Reduction of [$CpFe(PPh_3)_2(CNMe)]PF_6$, 42 (250mg, 0.03mmole) (room temperature, 18h) followed by work-up and extraction with diethyl ether (2 x 20ml) gave an unstable orange oil assigned as $CpFe(PPh_3)_2H$, 167 (50mg, 26%); ^{1}H NMR (C_6D_6) δ 8.2-6.9 (30H, m, PPh_3), 4.0 (5H, br s, C_5H_5), -13.3 (1H, t, J_{PH} = 74 Hz, FeH); ^{31}P NMR (d^6 benzene) δ 85, -8 (free PPh_3).

Repetition of this reduction but using lithium aluminium deuteride gave $CpFe(PPh_3)_2D$, 168; ^{2}H NMR (C_6H_6) δ -13.2 (t, J_{PD} = 11 Hz).

Reduction of [$CpFe(PMe_3)_2(CNMe)]PF_6$, 110

Reduction of [$CpFe(PMe_3)_2(CNMe)]PF_6$, 110 (100mg, 0.22mmole) (room temperature, 18h) followed by work-up and extraction with diethyl ether (30ml) gave $CpFe(PMe_3)_2H$, 169 (25mg, 42%); ^{1}H NMR (C_6D_6) δ4.0 (5H, br s, C_5H_5), 1.1 (18H, m, PMe_3), -16.2 (1H, t, J_{PH} = 76 Hz, FeH) (lit.[102]: δ 4.06, 1.12, -16.2).

Reaction of [CpFe(dppe)(CNMe)]BF_4, 98 with *t*-butyl isonitrile

A sample of [CpFe(dppe)(CNMe)]BF_4, 98 (90mg, 0.14mmole) in THF (10ml) was treated with *t*-butyl isonitrile (0.5ml, 4.5mmol) and the mixture stirred (room temperature; 5 days). Removal of solvents under reduced pressure gave starting material only.

Reaction of [CpFe(dppe)(CN*t*Bu)]PF_6, 120 with methyl isonitrile

Repetition of the above reaction but with [CpFe(dppe)(CN*t*Bu)] PF_6, 120 and methyl isonitrile gave starting material only.

Reduction of [CpFe(dppe)(CN*t*Bu)]PF_6, 120

Reduction of [CpFe(dppe)(CN*t*Bu)]PF_6, 120 (400mg, 0.53mmole) (room temperature; 18h) followed by work-up and extraction with diethyl ether (30ml) gave CpFe(dppe)H, 149 (200mg, 72%); identified by comparison with an authentic sample.

Low-temperature NMR reduction of [CpFe(dppe)(CNMe)]BF_4, 98

A solution of [CpFe(dppe)(CNMe)]BF_4, 98 (20mg, 0.03mmole) in CD_2Cl_2 (300µl) was cooled to -78°C in an NMR tube, and a solution of lithium aluminium hydride (5mg, 0.15mmole) in d^8 THF (250µl) added. The mixture was allowed to warm over 1h, and ^1H NMR spectra were recorded at 10°C intervals between -70°C and -20°C. At -50°C a signal appeared at δ 10.5, which became more intense on warming and on standing (-20°C, ½h). The signal had a triplet structure (J_{PH} = 4.7 Hz).

The solution was stood at room temperature (1h). The signal at δ 10.5 was unchanged. Water (approx. 100µl) was added, whereupon the signal at δ 10.5 disappeared, and the spectrum broadened considerably.

Reduction of [$CpRu(PPh_3)_2(CNMe)]PF_6$, 87

Reduction of [$CpFe(PPh_3)_2(CNMe)]PF_6$, 87 (440mg, 0.50mmole) (-30^oC; 4h) followed by work-up and extraction with diethyl ether (30ml) gave a yellow oil (160mg) identified as a 25:5:1:10 mixture of $CpRu(PPh_3)_2CHNMe$, 170, ^1H NMR (d^6 benzene) δ 10.9 (t, J_{PH} = 7.3 Hz, CHN); $CpRu(PPh_3)H_3$, 171, ^1H NMR (C_6D_6) δ -9.8 (d, J_{PH} = 20 Hz, RuH) (lit.[103] δ -9.8); $CpRu(PPh_3)_2H$, 172; and CpRu (PPH_3)(CNMe)H, 173. The latter two compounds were identified by comparison with authentic samples.

Reduction of [$CpRu(dppe)(CNMe)]PF_6$, 107

Reduction of [$CpRu(dppe)(CNMe)]PF_6$, 107 (300mg, 0.40mmole) (-30^oC; 18h) followed by work-up and extraction with diethyl ether gave a greenish-yellow solid assigned as CpRu(dppe)CHMe, 176 (20mg, 8%); ^1H NMR (C_6D_6) δ 11.4 (1H, br s, CHN), 8.1-6.9 (20H, m, Ar), 5.0 (5H, s, C_5H_5), 2.0 (4H, m, CH_2CH_2).

Further extraction with THF (30ml) followed by crystallization from dichloromethane/hexane gave pale yellow rods of [$CpRu(dppe)(CHNHMe)]PF_6.CH_2Cl_2$, 178 (185mg, 55%); m.p. 105^oC (dec.); ν_{max} 3375 (NH), 1690 (CN), 1550 (Ph), 840 (PF_6^-) cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.3 (1H, m, RuCH), 8.7 (1H, br s, NH), 7.5-7.0 (20H, m, Ar), 5.3 (2H, s, CH_2Cl_2), 4.92 (5H, s, C_5H_5), 2.7-2.5 (4H, m, CH_2CH_2), 2.50 (3H, d, J = 4.5Hz, Me); ^{31}P NMR (d^6 acetone) δ 83.87; ^{13}C NMR (d^6 acetone) δ 239.3 (s, RuCH), 134-129 (m, Ph), 87.7 (s, C_5H_5), 68.3 (s, CH_2Cl_2), 44.3 (s, NMe), 27.0 (m, CH_2CH_2); m/z 608 (M^+). Found: C 48.70, H 4.47, N 1.64; $C_{34}H_{36}Cl_2F_6NP_3Ru$ requires: C 48.76, H 4.33, N 1.67%.

Repetition of this reduction but in THF under reflux gave CpRu(dppe)H, 178 (36%); ^1H NMR (C_6D_6) δ 8.0-6.8 (20H, m, Ar), 4.9 (5H, s, C_5H_5), 2.3-1.0 (4H, m, CH_2CH_2), -13.2 (1H, t, J_{PH} =

34 Hz, RuH) (lit.[80]: δ 7.3, 4.8, 2.0, -12.9).

Deprotonation of [CpRu(dppe)(CHNHMe)]PF_6, 177

A sample of [CpRu(dppe)(CHNHMe)]$PF_6.CH_2Cl_2$, 177 (112mg, 0.13 mmole) in THF (10ml) was treated with *n*-butyl lithium (1.5M; 1.10 ml, 0.15mmol) and the mixture heated under reflux (2h). Complete decomposition occurred and no products were isolated.

Reduction of [InRu(dppe)(CNMe)]PF_6, 131

Reduction of [InRu(dppe)(CNMe)]PF_6, 131, (150mg, 0.19mmole) (-30°C; 24h) followed by work-up and extraction with diethyl ether (30ml) gave indane, 179, identified by comparison with an authentic sample.

Reduction of [InRu(PPh_3)$_2$(CNMe)]PF_6, 130

Reduction as above but with [InRu(PPh_3)$_2$(CNMe)]PF_6, 130 in place of [InRu(dppe)(CNMe)]PF_6, 131 gave indane 179.

Reduction of [CpFe(CO)$_2$(CNMe)]PF_6, 41

Reduction of [CpFe(CO)$_2$(CNMe)]PF_6, 41 (210mg, 0.58mmol) (room temperature; 18h) followed by work-up and extraction with diethyl ether (20ml) gave [CpFe(CO)$_2$]$_2$, 54 (87mg, 85%) identified by comparison with an authentic sample.

Reduction of [CpFe(PPh_3)(CO)(CNMe)]BF_4, 97

Reduction of [CpFe(PPh_3)(CO)(CNMe)]BF_4, 97 (100mg, 0.19mmole) (room temperature; 2h) followed by work-up and extraction with diethyl ether (20ml) gave CpFe(PPh_3)(CO)H, 182 (60mg, 80%), identified by comparison with an authentic sample.

Reduction of [$CpRu(PPh_3)(CO)(CNMe)]BF_4$, 99

Reduction of [$CpRu(PPh_3)(CO)(CNMe)]BF_4$, 99 (178mg, 0.30mmole) (-30°C; 24h) followed by work-up and extraction with diethyl ether (30ml) gave a mixture of $CpRu(PPh_3)(CO)H$, 184 and $CpRu(PPh_3)$ (CNMe)H, 173 in the ratio 3:1.

$CpRu(PPh_3)(CNMe)Cl$, 185

A mixture of $CpRu(PPh_3)_2Cl$, 88 (500mg, 0.69mmol), sulphur (100mg, 3.1mmole) and methyl isonitrile (0.10ml, 1.8mmole) in benzene (30ml) were heated under reflux (8h). The mixture was chromatographed. Elution with ethyl acetate gave bright yellow $CpRu(PPh_3)(CNMe)Cl$, 185 (225mg, 65%); m.p. 175-176°C; ν_{max} 2120 (CN) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.7-7.2 (15H, m, PPh_3), 4.53 (5H, s, C_5H_5), 3.04 (3H, s, Me); ^{31}P NMR ($CDCl_3$) δ 49.34; m/z (F.D.) 505, 507 (M^+). Found: C 59.64, H 4.57, N 2.77; $C_{25}H_{23}ClNPRu$ requires: C 59.47, H 4.59, N 2.77.

$CpRu(PPh_3)(CNMe)H$, 173

A solution of $CpRu(PPh_3)(CNMe)Cl$, 185 (100mg, 0.20mmole) in THF (20ml) was treated with lithium aluminium hydride (30mg, 0.88 mmole) and the mixture stirred (room temperature, 18h). ^1H NMR spectroscopy indicated a mixture of $CpRu(PPh_3)(CNMe)H$, 173 and $CpRu(PPh_3)H_3$, 171 after work-up. Recrystallization from diethyl ether gave $CpRu(PPh_3)(CNMe)H$, 173 (50mg, 54%); ν_{max} 2105 (CN) cm^{-1}; ^1H NMR (C_6D_6) δ 7.8-7.0 (15H, m, PPh_3), 5.0 (5H, s, C_5H_5), 2.3 (3H, s, Me), -11.3 (1H, d, J_{PH} = 36 Hz, RuH); ^{31}P NMR (d^6 benzene) δ 70.5; m/z (E.I.) 471.0685 (calculated for $C_{25}H_{24}NPRu$ 471.0683).

Reduction of [$CpFe(PMe_3)(CNtBu)_2]PF_6$, 115

Reduction of [$CpFe(PMe_3)(CNtBu)_2]PF_6$, 115 (226mg, 0.44mmole) (room temperature; 18h) followed by work-up and chromatography, eluting with 2% methanol in ethyl acetate, gave [$CpFe(PMe_3)(CHNHtBu)_2]PF_6$, 186 (189mg, 83%); m.p. 135°C (dec.); ν_{max} 3360 (NH), 840 (PF_6^-) cm^{-1}; ^1H NMR (d^6 DMSO) δ 11.18 (2H, d, J_{HH} = 18.6 Hz, FeCH), 10.08 (2H, br d, J_{HH} = 18.6 Hz, NH), 4.56 (5H, s, C_5H_5), 1.28 (18H, s, *t*Bu), 1.17 (9H, d, J_{PH} = 9.4 Hz, PMe_3); ^{31}P NMR (d^6 acetone) δ 37.3; ^{13}C NMR (d^6 acetone) δ 199.8 (d, J_{PC} = 32 Hz, Fe-C), 85.4 (s, C_5H_5), 60.7 (s, $\underline{C}Me_3$), 29.4 (s, $C\underline{Me}_3$), 19.4 (d, J_{PC} = 30 Hz, PMe_3); m/z 367 (M^+). Found: C 41.9, H 7.1, N 5.15; $C_{18}H_{36}F_6FeN_2P_2$ requires: C 42.2, H 7.1, N 5.45. An X-ray structure determination was performed (see Appendix).

Reduction of [$CpFe(PPh_3)(CNMe)_2]PF_6$, 113

Reduction as above but wtih [$CpFe(PPh_3)(CNMe)_2]PF_6$, 113 in place of [$CpFe(PMe_3)(CNtBu)_2]PF_6$, 115 gave an unstable yellow oil assigned as [$CpFe(PPh_3)(CHNHMe)_2]PF_6$, 188 (61%); ^1H NMR (CD_2Cl_2) δ 11.16 (2H, d, J_{HH} = 18.7 Hz, FeCH), 8.30 (2H, br d, J_{HH} = 18.7 Hz, NH), 7.5-7.2 (15H, m, PPh_3), 4.50 (5H, s, C_5H_5), 3.12 (3H, d, J = 4.6 Hz, Me); m/z 469 (M^+).

Reduction of [$CpFe(PPh_3)(CNtBu)_2]PF_6$, 114

Reduction as above but with [$CpFe(PPh_3)(CNtBu)_2]PF_6$, 114 in place of [$CpFe(PMe_3)(CNtBu)_2]PF_6$, 115 gave a highly unstable yellow oil which showed a broad singlet by ^1H NMR spectroscopy at δ 10.5.

Reduction of [$InFe(dppe)(CO)]PF_6$, 138

Reduction of [$InFe(dppe)(CO)]PF_6$, 138 (250mg, 0.34mmole) (-78^oC; 5h) followed by work-up and extraction with THF (20ml) gave starting material only.

Repetition of the reduction (-30^oC; 18h) and extraction with diethyl ether (3 x 30ml) gave a dark blue extract which changed colour to yellow over a period of 10mins. The resulting yellow oil was shown to be starting material.

Repetition of the reduction (0^oC; 3h) and extraction with diethyl ether (20ml) gave indane, 179, identified by comparison with an authentic sample.

Reduction of [$InFe(PPh_3)(CO)_2]PF_6$, 135

Reduction of [$InFe(PPh_3)(CO)_2]PF_6$, 135 (273mg, 0.48mmole) -78^oC; 6h) followed by work-up and extraction with diethyl ether gave [$InFe(CO)_2]_2$, 132 (108mg, 79%), identified by comparison with an authentic sample.

Reduction of [$InFe(PMe_3)(CO)_2]PF_6$, 136

Reduction of [$InFe(PMe_3)(CO)_2]PF_6$, 136 (250mg, 0.56mmole) (-78^oC; 6h) followed by work-up and extraction with diethyl ether gave [$InFe(CO)_2]_2$, 132 (25mg, 20%).

Reduction of [$InFe(PMe_3)_2(CO)]PF_6$, 137

Reduction of [$InFe(PMe_3)_2(CO)]PF_6$, 137 (250mg, 0.50mmole) (room temperature; 1h) followed by work-up and extraction with diethyl ether gave a yellow crystalline solid (60mg); ν_{max} 1972, 1925, 1890 cm^{-1}; ^1H NMR (C_6D_6) δ 1.2 (18H, m, $2PMe_3$), -9.7 (1H, t, J_{PC} = 75 Hz, FeH); m/z 208 ($Fe(PMe_3)_2$).

Reduction of [$InFe(CO)_3]PF_6$, 133

Reduction of [$InFe(CO)_3]PF_6$, 133 (150mg, 0.38mmole) (room temperature; 2h) resulted in complete decomposition. No organic or organometallic products were observed.

Reduction of [$InRu(dppe)(CO)]PF_6$, 129

Reduction of [$InRu(dppe)(CO)]PF_6$, 129 (400mg, 0.51mmole) (-30^oC; 18h) followed by work-up and extraction with diethyl ether (20ml) gave indane, 179. ^1H NMR spectroscopy also revealed several sets of complex multiplets in the range δ -6 to -8.5.

Reduction of $InRu(PPh_3)_2(CO)\ PF_6$, 128

Reduction of $InRu(PPh_3)_2(CO)\ PF_6$, 128 (255mg, 0.28mmole) (-78^oC; 3h) followed by work-up and extraction with diethyl ether (30ml) gave $InRu(PPh_3)(CO)H$, 195 (120mg, 85%); ν_{max} 1945 (CO) cm^{-1}; ^1H NMR (C_6D_6) δ 7.5-6.8 (19H, m, Ar), 6.75 (1H, t, J_{HH} = 2.7 Hz, H_2), 6.25 (2H, d, J_{HH} = 2.5 Hz, $H_{1,3}$), -13.4 (1H, d, J_{PH} = 30 Hz, RuH); ^{31}P NMR (C_6D_6) δ 60.19; ^{13}C NMR (C_6D_6) δ 206.5 (d, J_{PC} = 15 Hz, CO), 139-121 (m, Ar), 112.4 (s, $C_{3a,7a}$), 90.8 (s, C_2), 74.0 (s, $C_{1,3}$); m/z (E.I.) 508 (M^+).

Experimental for Chapter 5

$CpFe(PMe_3)(CO)H$, 77

A solution of $CpFe(CO)_2Br$, 55 (6.6g, 25.7mmole) in diethyl ether (120ml) was cooled (-30°C) and treated with $LiAlH_4$ (1.8g, 53mmole). The mixture was stirred (-30°C; 1h), allowed to warm (-20°C) and trimethylphosphine (5ml, 50mmole) added. The solution was stirred (-20°C; 30min) and water (5ml, 280mmole) added. Solvents were removed under reduced pressure and the residue extracted wtih light petroleum (4 x 40ml) to give $CpFe(PMe_3)(CO)H$, 77 (4.47g, 77%); ν_{max} 1928 (CO), 1851 (FeH) cm^{-1} (lit.[115]:1925 cm^{-1}; ^1H NMR (C_6D_6) δ 4.26 (5H, d, J_{PH} = 1.3 Hz, C_5H_5), 0.99 (9H, d, J_{PH} = 9.3 Hz, PMe_3), -14.24 (1H, d, J_{PH} = 81 Hz, FeH) (lit.[115]: δ 4.32, 0.92, 14.84).

$CpFe(PMe_3)(CO)D$, 77a

A solution of $[CpFe(CO)_2]_2$, 54 (4.0g, 11.3mmole) in THF (100ml) was treated with a 1% sodium amalgam (1g Na; 18h). The solution was decanted and treated with D_2O (0.6ml, 33mmole). Solvents were removed under reduced pressure and the residue extracted with light petroleum (3 x 30ml). The extracts were cooled (-20°C) and trimethylpnosphine (2ml, 20mmole) added. The mixture was stirred (-20°C; 30min) and the supernatant filtered off. The residue was extracted with light petroleum (20ml) and this extract added to the filtrate. Removal of solvents gave $CpFe(PMe_3)(CO)D$, 77a (1.48g, 29%); ν_{max} 1928 (CO), 1349 (FeD) cm^{-1}; ^2H NMR (C_6H_6) δ -14.43 (d, J_{PD} = 12.2 Hz).

Reaction of $CpFe(PMe_3)(CO)H$, 77 with CO

A solution of $CpFe(PMe_3)(CO)H$, 77 (0.40g, 1.77mmole) in THF (40ml) in a Fischer-Porter bottle was put under 3 atm. pressure of CO and stirred (room temperature; 18h). Chromatography (grade V alumina) gave two fractions.

Elution with light petroleum gave $(\eta^4\text{-}C_5H_5)Fe(PMe_3)(CO)_2$, 205 (0.40g, 89%); ν_{max} 2760 (CH_{exo}), 1970, 1910 (CO) cm^{-1}; ^1H NMR (C_6D_6) δ 4.95 (2H, m, $H_{2,3}$), 2.75 (1H, d, J_{HH} = 10.7 Hz, H_{endo}), 2.41 (1H, dd, J_{HH} = 10.7 Hz, J_{PH} = 6.3 Hz, H_{exo}), 2.37 (2H, m, $H_{1,4}$), 0.70 (9H, d, J_{PH} = 8.7 Hz, PMe_3); ^{31}P NMR (C_6D_6) δ 25.1; ^{13}C NMR (C_6D_6) δ 219.4 (d, J_{PC} = 15 Hz, CO), 83.0 (s, $C_{2,3}$), 48.3 (s, $C_{1,4}$), 45.4 (s, C_5), 19.8 (d, J_{PC} = 27 Hz, PMe_3); m/z (E.I.) 254.0155 (calculated for $C_{10}H_{15}FeO_2P$ 254.0159).

Elution with light petroleum:diethyl ether (5:1) gave $[CpFe(CO)_2]_2$, 54 (30mg, 9.6%).

Repetition of the reaction with $CpFe(PMe_3)(CO)D$, 77a gave $(5\text{-}exo\text{-}\eta^4C_5H_5D)Fe(PMe_3)(CO)_2$, 205a; ν_{max} 2040 (FeD) cm^{-1}; ^1H NMR (C_6D_6) δ 4.95 (2H, m, $H_{2,3}$), 2.74 (1H, br m, H_{endo}), 2.35 (2H, m, $H_{1,4}$), 0.70 (9H, d, J_{PH} = 8.7 Hz, PMe_3); ^2H NMR (C_6H_6) δ 2.36 (br m, D_{exo}).

$CpFe(PPh_3)(CO)H$, 208

A mixture of $CpFe(CO)_2Br$, 55 (1.5g, 5.8mmol) and triphenylphosphine (1.5g, 5.8mmol) in benzene (50ml) were cooled (0°C) and irradiated with visible light (15min). Solvent was removed to give a quantitative yield of $CpFe(PPh_3)(CO)Br$, 221. A solution of this complex (1.8g, 3.7mmole) in THF (30ml) was cooled (-20°C) and treated with $LiAlH_4$ (500mg, 14.7mmole). The mixture was stirred (1h) and water (1ml, 55mmole) added. Chromatography (grade V alumina), eluting with light petroleum: diethyl ether (5:1) gave $CpFe(PPh_3)(CO)H$, 208 (1.0g, 66%); ^1H NMR (C_6D_6) δ 7.5

-7.0 (15H, m, PPh_3), 4.2 (5H, s, C_5H_5), -12.8 (1H, d, J_{PH} = 75 Hz, FeH) (lit.[119]: δ 7.2, 4.27, -12.8).

Reaction of $CpFe(PPh_3)(CO)H$, 208 with CO

A sample of $CpFe(PPh_3)(CO)H$, 208 was treated with CO as for $CpFe(PMe_3)(CO)H$, 77 above. Chromatography gave only starting material.

$[CpFe(PMe_3)(CO)_2]PF_6$, 207

A solution of $CpFe(CO)_2Br$, 55 (3.4g, 13.2mmole) and NH_4PF_6 (2.2g, 13.5mmole) in methanol (40ml) was cooled (-78°C) and trimethylphosphine (1.3ml, 13mmole) added. The solution was allowed to warm to room temperature and stirred (18h). Solvents were removed under reduced pressure and the residue extracted with acetone (2 x 40ml). The acetone was removed and this residue washed with water (100ml). The water was removed by filtration and the residue dried by azeotroping residual water away with benzene (3 x 20ml), to give yellow crystals of $[CpFe(PMe_3)(CO)_2]PF_6$, 207 (2.80g, 53%); ^1H NMR (d^6 acetone) δ 5.6 (5H, d, J_{PH} = 1.0 Hz, C_5H_5), 1.8 (9H, d, J_{PH} = 11.0 Hz, PMe_3) (lit.[49]: δ 5.5, 1.8).

Reaction of $CpFe(PMe_3)(CO)H$, 77 with $[CpFe(PPh_3)(CO)_2]PF_6$, 209

A solution of $CpFe(PMe_3)(CO)H$, 77 (200mg, 0.88mmole) and $[CpFe(PPh_3)(CO)_2]PF_6$, 209[140] (520mg, 0.89mmole) in THF in a Fischer-Porter bottle was put under 3 atm. pressure of CO and stirred (room temperature; 18h). The solution was chromatographed (grade V alumina). Elution with light petroleum:diethyl ether (10:1) gave $CpFe(PPh_3)(CO)H$, 208 (360mg, 73%). Elution with diethyl ether gave $[CpFe(CO)_2]_2$, 54 (30mg, 19%). Elution with acetone gave $[CpFe(PMe_3)(CO)_2]PF_6$, 207 (280mg, 80%). All compounds were identified by comparison with authentic samples.

Attempted reactions of $CpFe(PMe_3)(CO)H$, 77, with ligands L

A mixture of $CpFe(PMe_3)(CO)H$, 77 (200mg, 0.88mmole) and $[CpFe(PMe_3)(CO)_2]PF_6$, 207 (350mg, 0.88mmole) in THF (40ml) was treated with *t*-butyl isonitrile (0.5ml, 4.5mmole) and the mixture stirred (18h). Removal of solvents followed by extraction with diethyl ether did not give any identifiable products. Extraction with acetone gave an intractable mixture of compounds.

Repeating this reaction with triphenylphosphine in place of *t*-butyl isonitrile failed to give any triphenylphosphine-containing products as determined by ^1H NMR. Repeating this reaction with trimethylphosphine in place of *t*-butylisonitrile gave a mixture of $CpFe(PMe_3)(CO)H$, 77 and $[CpFe(PMe_3)_2(CO)]PF_6$, 108 identified by comparison with authentic samples. Treatment of $[CpFe(PMe_3)(CO)_2]PF_6$, 207 with excess trimethylphosphine in THF also gave complex 108.

Hydride addition to $[CpFe(PMe_3)(CO)_2]PF_6$, 207

A solution of $[CpFe(PMe_3)(CO)_2]PF_6$, 207 (800mg, 2.01mmole) in THF (20ml) was cooled (-78^oC) and $LiAlH_4$ (38mg, 0.90mmole) added. The mixture was allow to warm to room temperature and stirred (18h). Quenching with water was followed by chromatography. Elution with light petroleum:diethyl ether (1:1) gave $CpFe(PMe_3)(CO)Me$, 121 (173mg, 36%). Elution with acetone gave starting material.

Repetition of the above reaction but with K-Selectride (potassium tri*sec*butylborohydride) in place of $LiAlH_4$ gave a mixture of $(\eta^4\text{-}C_5H_6)Fe(PMe_3)(CO)_2$, 205 (71%) and $[CpFe(CO)_2]_2$, 54, (10%).

Reaction of $CpFe(PMe_3)(CO)H$, 77 with *t*BuNC

A mixture of $CpFe(PMe_3)(CO)H$, 77 (400mg, 1.77mmole) and *t*-butyl isonitrile (2ml, 18mmole) in toluene (40ml) was stirred (room temperature; 18h). A yellow precipitate formed, which was separated by filtration.

Removal of solvent from the filtrate gave a yellow gum; m/z (E.I.) 240 (M^+), 225 (M^+-Me), 197 (M^+-Me, CO), 121 (M^+-Me, CO, PMe_3) indicates $CpFe(PMe_3)(CO)Me$.

The precipitate was treated with NH_4PF_6 in aqueous acetone and recrystallized (dichloromethane/hexane) to give yellow crystals of $[CpFe(PMe_3)(CNtBu)_2]PF_6$, 115 (520mg, 58%); m.p. 151°C; ν_{max} 2140, 2110 (CN), 840 (PF_6^-) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 4.58 (5H, d, J_{PH} = 1.8 Hz, C_5H_5), 1.48 (9H, d, J_{PH} = 10 Hz, PMe_3), 1.47 (18H, s, *t*Bu); ^{31}P NMR (d^6 acetone) δ 35.0; m/z 363 (M^+). Found: C 42.51, H 6.33, N 5.38, P 12.0; $C_{18}H_{32}F_6FeN_2P_2$ requires: C 42.54, H 6.35, N 5.51, P 12.19.

Reaction of $CpFe(PMe_3)(CO)H$, 77 with MeNC

Reaction as above but with methyl isonitrile in place of *t*-butyl isonitrile followed by chromatography of the reaction mixture gave as the only organometallic product $[CpFe(CO)(CNMe)]_2$, 214 (20%); ν_{max} 1970, 1920, 1700 cm^{-1} (lit.[141]: 1971, 1926, 1697 cm^{-1}); ^1H NMR ($CDCl_3$) δ 4.7 (5H, s, C_5H_5), 3.7 (3H, s, Me) (Lit.[141]: δ 4.71, 367); m/z (F.D.) 380 (M^+).

High-pressure NMR reaction of $CpFe(PMe_3)(CO)H$, 77 with CO

A sample of $CpFe(PMe_3)(CO)H$, 77 (150mg, 0.66mmole) in THF (3ml) was placed in a titanium pressure vessel and pressurized to 50 atm. with CO. Monitoring the reaction by ^1H NMR showed no reaction to occur over 60h. The pressure was increased to 300 atm.

and NMR data collected for 17 500 pulses. A broad resonance in the low-field region at δ 18.45 appeared. The signal-to-noise ratio was too low to be certain of this resonance.

CpFe(dppe)(CO)H, 31[50]

A solution of [CpFe(dppe)(CO)]PF_6, 215 (1.55g, 2.24mmole) in THF:dichloromethane (1:1; 50ml) was cooled (-30°C) and $LiAlH_4$ (0.25g, 7.35mmole) added. The mixture was allowed to react (-30°C; 18h), water (1ml, 55mmole) added and solvents removed under reduced pressure. Extraction of the residue with diethyl ether (2 x 50ml) gave CpFe(dppe)(CO)H, 31 (0.90g, 73%); ν_{max} 1910 (CO), 1875 (FeH) cm^{-1} (lit.[50] 1910, 1880 cm^{-1}); ^1H NMR (C_6D_6) δ 7.5-6.5 (20H, m, Ar), 4.1 (5H, s. C_5H_5), 2.7-2.1 (4H, m, CH_2CH_2), -13.2 (1H, d, J_{PH} = 75 Hz, FeH) (lit.[50]: δ 7.7-6.5, 4.15, 2.7-2.1, -13.23).

Repetition of the above reaction but with $LiAlD_4$ and D_2O in place of $LiAlH_4$ and water gave CpFe(dppe)(CO)D, 31a; ^2H NMR (C_6H_6) δ -13.2 (d, J_{PD} = 11.2 Hz).

Reaction between CpFe(dppe)(CO)H, 31 and [CpFe(PPh_3)$(CO)_2$]PF_6, 209

A mixture of CpFe(dppe)(CO)H, 31 (420mg, 0.77mmole) and [CpFe(PPh_3)$(CO)_2$]PF_6, 209 (450mg, 0.77mmole) in THF (30ml) was stirred (room temperature; 18h). Chromatography (grade V alumina), eluting with light petroleum:diethyl ether (5:1) gave CpFe(PPh_3)(CO)H, 208 (220mg, 69%). Elution with diethyl ether gave [$CpFe(CO)_2]_2$, 54 (10mg, 7%). Elution with acetone gave [CpFe(dppe)(CO)]PF_6, 215 (450mg, 85%). All these products were identified by comparison with authentic samples.

Repetition of the above reaction but with CpFe(dppe)(CO)D, 31a in place of CpFe(dppe)(CO)H, 31 gave CpFe(PPh_3)(CO)D, 208a as

the only deuterium-containing product; ^{2}H NMR (C_6H_6) δ -12.8 (d, J_{PD} = 11.4 Hz).

[$CpFe(PMe_3)_2(CO)]PF_6$, 108[49]

A mixture of $CpFe(CO)_2Br$, 55 (3.40g, 13.2mmole) and trimethylphosphine (4ml, 40mmole) in THF (100ml) was heated under reflux (4h). Removal of solvent and treatment with NH_4PF_6 (2.5g, 15mmole) in aqueous acetone, followed by removal of solvents and extraction with dichloromethane (2 x 50ml) gave [$CpFe(PMe_3)_2$ $(CO)]PF_6$, 108 (3.29g, 56%); ν_{max} 1945 (CO) cm^{-1} (lit.[49]:1945 cm^{-1}); ^{1}H NMR (d^6 acetone) δ 5.1 (5H, t, J_{PH} = 1.0 Hz, C_5H_5), 1.7 (18H, m, PMe_3) (lit.[49]: δ 5.1, 1.7).

[$CpFe(dppe)(CO)]PF_6$, 215[49]

Repetition of the above reaction but with dppe in place of trimethylphosphine gave [$CpFe(dppe)(CO)]PF_6$, 215 (69%); ν_{max} 1975 (CO) cm^{-1} (lit.[49]:1975 cm^{-1}); ^{1}H NMR (d^6 acetone) δ 8.0-7.2 (20H, m, Ar), 5.1 (5H, t, J_{PH} = 1.0 Hz, C_5H_5), 3.2-2.8 (4H, m, CH_2CH_2) (lit.[49]: δ 8.2-7.2, 5.1, 3.2-2.8).

[$CpFe(PPh_3)_2(CO)]PF_6$, 219[49]

A mixture of [$CpFe(PPh_3)(CO)_2]PF_6$, 209 (2.00g, 3.42mmole), trimethylamine-N-oxide dihydrate (0.84g, 7.57mmole) and triphenylphosphine (1.0g, 3.82mmole) in acetone (70ml) was stirred (1h) and chromatographed (grade V alumina). Elution with toluene:ethyl acetate (1:1) gave [$CpFe(PPh_3)_2(CO)]PF_6$, 219 (0.69g, 25%); ν_{max} 1980 (CO) cm^{-1} (lit.[49]:1980 cm^{-1}); ^{1}H NMR (d^6 acetone) δ 7.7-6.9 (30H, m, PPh_3), 4.8 (5H, t, J_{PH} = 1.0 Hz, C_5H_5) (lit.[49]: δ 7.5-6.9, 4.8).

[CpFe(tripod)]PF_6, 218[118]

A solution of $[CpFe(CO)_2]_2$, 54 (4.0g, 11.3mmole) in THF (100ml) was treated with a 1% sodium amalgam (1g Na; 18h). The solution was decanted, cooled (-78°C) and 3-chloro-2-methyl-1-propene (9ml, 91mmole) added. The mixture was allowed to warm to room temperature with stirring, solvents removed and the residue extracted with diethyl ether (150ml). Solvent was removed and the residue taken up in THF (15ml) and cooled (0°C). Addition of aqueous HPF_6 (60%; 3ml, 20mmole) immediately followed by addition of diethyl ether (150ml), gave a yellow precipitate of $[CpFe(CO)_2(isobutylene)]PF_6$ (5.03g, 60%).

A mixture of this complex (1.00g, 2.65mmole) and tripod (1.63g, 2.62mmole) in 1,2-dichloroethane was irradiated with visible light (6h). Chromatography, eluting with dichloromethane: ethyl acetate (2:1) gave $[CpFe(tripod)]PF_6$, 218 (1.92g, 82%); ^1H NMR (d^6 acetone) δ 7.5-6.7 (30H, m, Ar), 5.1 (5H, m, C_5H_5), 2.7-2.4 (6H, m, CH_2P), 1.6 (3H, s, Me) (lit.[118]: δ 7.6-6.7, 5.05, 2.7-2.4, 1.65).

CpFe(dppe)H, 223[50]

A solution of CpFe(dppe)Cl, 222 (1.0g, 1.80mmole) in THF (50ml) was cooled (-78°C) and treated with $LiAlH_4$ (330mg, 9.7mmole). The mixture was warmed (0°C) and stirred (2h). Addition of water (2ml, 110mmole), removal of solvents under reduced pressure, and extraction with diethyl ether (2 x 40ml) gave CpFe(dppe)H (735mg, 79%); ^1H NMR (C_6D_6) δ 8.0-6.8 (20H, m, Ar), 4.1 (5H, s, C_5H_5), 2.2-1.7 (4H, m, CH_2CH_2), -16.1 (1H, t, J_{PH} = 75 Hz, FeH) (lit.[50]: δ 8.0-6.8, 4.15, 2.3-1.7, -16.1).

CpFe(tripod)H, 224[118]

A solution of [CpFe(tripod)]PF_6, 218 (500mg, 0.56mmole) in THF (30ml) was treated with $LiAlH_4$ (70mg, 2.06mmole) and the mixture stirred (room temperature; 3h). Addition of water (0.5ml, 27mmole), removal of solvents under reduced pressure and extraction with diethyl ether (2 x 20ml) gave CpFe(tripod)H, 224 (330mg, 79%) as a mixture of two diastereomers (ca. 3:2); ^1H NMR (C_6D_6) δ 8.0-6.8 (30H, m, Ar), 3.92 (s, C_5H_5, major isomer), 3.88 (s, C_5H_5, minor isomer), 3.0-2.0 (6H, m, CH_2), 0.3 (3H, m, Me), -16.0 (t, J_{PH} = 69 Hz, FeH, minor isomer), -16.1 (t, J_{PH} = 69 Hz, FeH, major isomer) (lit.[118]: δ 8.0-6.8, 3.93, 3.88, 2.9-1.9, 0.29, -16.00, -16.14).

Reaction of Metal hydrides with cationic complexes.

A mixture of the metal hydride (typically 100mg) and an equimolar amount of the cationic complex in THF (20ml) were stirred (room temperature; 18h). Removal of solvents was followed by chromatography on a short (10 cm) column. Elution with diethyl ether gave the neutral product. Elution with acetone gave the cationic product. Results are shown in table 3.

In twenty-eight cases, marked (X) in table 3, no reaction occurred and starting materials were recovered.

In the remaining ten cases, marked (✓) in table 3, no identifiable cationic product was recovered for reactions involving CpFe(PMe_3)(CO)H, 77 or CpFe(PPh_3)(CO)H, 208. Reactions involving CpFe(dppe)(CO)H, 31 resulted in recovery of [CpFe(dppe)(CO)]$^+$ salts.

Reactions involving [CpFe(PMe_3)$(CO)_2$]PF_6, 207 led to recovery of CpFe(PMe_3)(CO)H, 77. Reactions involving [CpFe$(PPh_3)_2$(CO)]PF_6, 219, [CpFe(PPh_3)(CO)(CNMe)]BF_4, 97 or [CpFe(PPh_3)$(CO)_2$]PF_6, 209

Table 3. Hydride Donation to Cationic Iron Complexes

$[CpFeLL'L'']^+$ L,L'L''	CpFeLL'H L,L'				
	P-dppe, CO 31	PMe_3, CO 77	PPh_3, CO 208	dppe 223	P',P'-tripod 224
tripod 218	X	X	X	X	-
$2PMe_3$, CO 108	X	-	X	X	X
dppe, CNMe 98	X	X	X	X	X
dppe, CO 215	-	X	X	X	X
PMe_3, 2CO 207	✓	-	X	X	X
$2PPh_3$, CO 219	✓	✓	-	X	X
PPh_3, CO, CNMe 97	✓	✓	-	X	X
PPh_3 2CO 209	✓	✓	-	X	X
3CO 91	✓	✓	✓	X	X

X:No reaction, starting materials recovered
✓:Products due to hydride donation recovered

led to recovery of $CpFe(PPh_3)(CO)H$, 208. In the case of complex 97 the odour of methyl isonitrile was also detected. Reactions involving $[CpFe(CO)_3]PF_6$, 91 led to recovery of $[CpFe(CO)_2]_2$, 54.

Experimental for Chapter 6

Reduction of [CpFe(PMe_3)$(CO)_2$]PF_6, 207[117]

Treatment of a suspension of [CpFe(PMe_3)$(CO)_2$]PF_6, 207 (750mg, 1.88mmole) in THF (50ml) at -78°C with $LiAlH_4$ (200mg, 5.88mmole) followed by stirring (6h), addition of water (1ml, 55mmole), removal of solvents under reduced pressure and extraction with diethyl ether (2 x 30ml) gave CpFe(PMe_3)(CO)Me, 212 (341mg, 76%), identified by comparison with an authentic sample.

Carbonylation of CpFe(PMe_3)(CO)R

A solution of CpFe(PMe_3)(CO)Me, 212 (510mg, 2.13mmole) in dichloromethane (20ml) was put under a CO atmosphere and treated with $AgBF_4$ (10mg, 0.05mmole). The black mixture was stirred (30min), solvents removed under reduced pressure and the residue filtered through alumina. Washing with light petroleum removed any starting material. Washing with diethyl ether gave CpFe(PMe_3)(CO)COMe, 231 (510mg, 90%), identified by comparison with an authentic sample.

Treatment of alkyl complexes CpFe(PMe_3)(CO)R (R = Et, 232; *n*Pr, 235; *n*Bu, 237) in an identical fashion gave the acyl complexes CpFe(PMe_3)(CO)COR (R = Et, 234; *n*Pr, 236; *n*Bu, 238) in similar yields; identified by comparison with authentic samples.

Reduction of CpFe(PMe_3)(CO)COR

A solution of CpFe(PMe_3)(CO)COMe, 231 (520mg, 1.94mmole) in THF (10ml) was treated with BH_3.THF (1M; 10ml, 10mmole) and the mixture stirred (1h). Addition of methanol (2ml, 50mmole) and carbon tetrachloride (1ml, 10mmole) followed by filtration through

alumina with light petroleum gave $CpFe(PMe_3)(CO)Et$, 231 (325mg, 66%); ν_{max} 1895 (CO) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.3 (5H, s, C_5H_5), 1.4 (9H, d, J_{PH} = 10 Hz, PMe_3), 1.2 (3H, br s, CH_3), 0.4 (2H, m, CH_2); m/z (E.I.) 254 (M^+).

Repetition of this reduction with $CpFe(PMe_3)(CO)COEt$, 234 gave $CpFe(PMe_3)(CO)nPr$, 235 (60%); ν_{max} 1895 (CO) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.3 (5H, s, C_5H_5), 1.3 (9H, d, J_{PH} = 10 Hz, PMe_3), 1.8-0.7 (7H, m, *n*Pr); m/z (E.I.) 268 (M^+).

Repetition of this reduction with $CpFe(PMe_3)(CO)CO*n*Pr$, 236 gave $CpFe(PMe_3)(CO)nBu$, 237 (52%); ν_{max} 1890 (CO) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.3 (5H, s, C_5H_5), 1.3 (9H, d, J_{PH} = 10 Hz, PMe_3), 1.7-0.6 (9H, m, *n*Bu); m/z (E.I.) 282 (M^+).

Preparation of $CpFe(PMe_3)(CO)COR$

A solution of $[CpFe(CO)_2]_2$, 54 (2.0g, 5.6mmole) in THF (60ml) was treated with a 1% sodium amalgam (0.5g Na; 18h) and the solution decanted onto excess ethyl iodide. The mixture was stirred (90min) and chromatographed, eluting with light petroleum. The yellow eluate was heated to reflux with trimethylphosphine (2ml, 20mmole) in toluene (10ml; 16h). Chromatography, eluting with diethyl ether, gave $CpFe(PMe_3)(CO)COEt$, 234 (2.37g, 75%); ν_{max} 1900, 1595 (CO) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.45 (5H, d, J_{PH} = 1.4 Hz, C_5H_5), 3.0-2.7 (2H, m, CH_2), 1.34 (9H, d, J_{PH} = 9.7 Hz, PMe_3), 0.88 (3H, t, Me); m/z (E.I.) 282.0472 (calc. for $C_{12}H_{19}FeO_2P$ 282.0472).

Repetition of this reaction but with *n*-propyl iodide in place of ethyl iodide gave $CpFe(PMe_3)(CO)CO*n*Pr$ 236 (72%); ν_{max} 1903, 1590 (CO) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.45 (5H, d, J_{PH} = 1.1 Hz, C_5H_5), 3.0-2.7 (2H, m, $COCH_2$), 1.7-1.2 (2H, m, CH_2), 1.36 (9H, d, J_{PH} = 9.7 Hz, PMe_3), 0.84, (3H, t, Me); m/z (E.I.) 296.0628 (calc. for

$C_{13}H_{21}FeCO_2P$: 296.0628).

Repetition of this reaction but with *n*-butyl iodide in place of ethyl iodide gave $CpFe(PMe_3)(CO)CO\textit{n}Bu$, 238 (64%) ν_{max} 1900, 1590 (CO) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.44 (5H, d, J_{PH} = 1.4 Hz, C_5H_5), 3.0-2.7 (2H, m, $COCH_2$), 1.7-1.1 (4H, m, CH_2CH_2), 1.34 (9H,d, J_{PH} = 9.8 Hz, PMe_3), 0.86 (3H, t, Me); m/z (E.I.) 310.0785 (calc. for $C_{14}H_{23}FeO_2P$: 310.0784).

Decomplexation of $CpFe(PMe_3)(CO)CO\textit{n}Bu$, 238

A solution of $CpFe(PMe_3)(CO)CO\textit{n}Bu$, 238 (1.0g, 3.2mmole) in THF (8ml) and water (1ml) was treated with bromine (0.5g, 3.2mmole) and stirred (30min). The solution was washed with saturated aqueous sodium thiosulphate (10ml), solvents removed, and aqueous sodium hydroxide (2M; 20ml) added. The mixture was filtered and the residues washed with sodium hydroxide (2 x 10ml). The filtrate was acidified with hydrochloric acid to pH3 and extracted with diethyl ether (6 x 20ml). The ether layer was dried ($MgSO_4$) and solvents removed to give pentanoic acid (233mg, 70%), identified by comparison with an authentic sample.

Attempted Carbonylation using BF_3

A mixture of $CpFe(PMe_3)(CO)Me$, 212 (120mg, 0.50mmole) and BH_3.THF (1M; 3ml, 3mmole) in THF (10ml) was put under a CO atmosphere and $BF_3.Et_2O$ (0.07ml, 0.57mmole) added. The mixture was stirred under CO (6h). Chromatography led to isolation of $CpFe(PMe_3)(CO)Me$, 212 only.

Attempted High-Pressure Carbonylation

This reaction was performed using high-pressure apparatus at the B.P. Research Centre, Sunbury-on-Thames. A mixture of

$CpFe(PMe_3)(CO)Me$, 212 (380mg, 1.58mmole) and BH_3.THF (1M; 10ml, 10mmole) in THF (80ml) was put under a CO pressure of 100 atm. and stirred (6h). Quenching with methanol (3ml, 75mmole) followed by chromatography led to isolation of $CpFe(PMe_3)(CO)Me$, 212 only.

APPENDIX

Cell parameters and reflection intensities for the X-ray crystal structure analysis presented in this thesis were measured with graphite monochromated Cu-Kα radiation on an Enraf-Nonius CAD4 diffractometer operating in the $\omega/2\theta$ scan mode for an orange crystal having dimensions 0.65 x 0.41 x 0.24 mm. The cell parameters were determined by least-squares refinement of the setting angles of 25 accurately centred reflections having $26^{o}<\theta<28^{o}$. The scan range (ω) was calculated from [0.8 + 0.14 tanθ] and the scan speed varied from 0.9 to 6.7^{o} min^{-1} depending upon the intensity. Reflections were scanned in the range $0<\theta<60^{o}$. Three standard reflections measured every hour showed no appreciable variation with time. The data were corrected for Lorentz, polarisation and absorption effects[142] (relative transmission factors 1.00-1.93) and equivalent reflections were merged to give 3775 unique reflections (R_{merg} 0.029) of which 2214 were considered to be observed $I>3\sigma(I)$ and used in the structure analysis.

Crystal Data, $C_{18}H_{36}F_{6}N_{2}P_{2}Fe$, M = 512.281, monoclinic, a = 13.366 (2), b = 18.515(2), c = 10.308(2)Å, β = 92.85(2)^{o}, U = 2547.8Å^{3}, z = 4, D_{calc} = 1.34 M_{gm}^{-3}, μ(Cu-Kα) 64.48 cm^{-1}, space group $P2_{1/n}$ (established from systematic absences). The structure was solved by Patterson function and electron density Fourier synthesis. During the final stages of refinement, "soft" Waser constraints[143] were applied to the bond lengths of the C(12)-C(15) *t*-butyl group. Final full-matrix least squares refinement included parameters for atomic positions, temperature factors (anisotropic for non-

hydrogen atoms), an overall scale factor and an extinction parameter. All hydrogen atoms were allowed to "ride" on their respective parent atoms and were assigned chemically reasonable temperature factors. The refinement was terminated when all shifts were less than 0.1 σ with R = 0.056, R_w = 0.063, GOF = 1.15. The weight for each reflection was calculated from the Chebyshev series $w = [11.45\ t_0(x) - 12.82t_1(x) + 8.97t_2(x) - 3.56t_3(x)]$ where $X = F_{obs}/F_{max}$[144]. Final difference Fourier synthesis showed no significant residual electron density and a detailed analysis failed to reveal any systematic errors. All calculations were performed with the CRYSTALS package on the Chemical Crystallography Laboratory DEC VAX 11/750 computer. Atomic scattering factors were taken from International Tables, Vol. IV[145]. Final atomic positional coordinates with e.s.d.'s in parentheses are listed in Table I, bond lengths in Table II and bond angles in Table III.

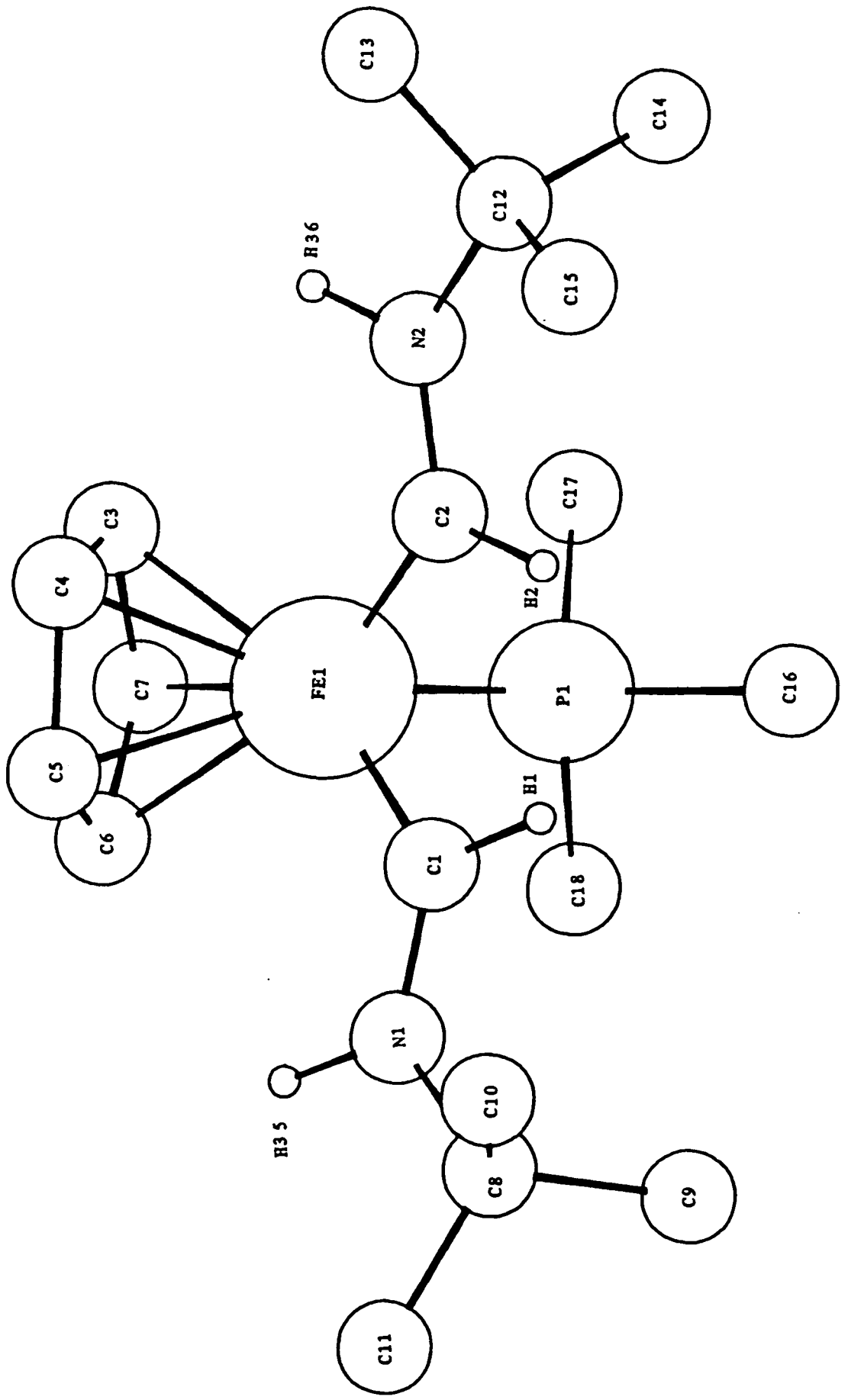

C13
C14
C12
H36
C15
N2
C2
C17
C3
C4
H2
C7
FE1
P1
C16
C5
H1
C6
C1
C18
N1
H35
C10
C8
C9
C11

Table I

Atomic Positional Coordinates with
Estimated Standard Deviations in Parentheses

Atom	x/a	y/b	z/c	U(iso)
FE(1)	0.16957(7)	-0.15191(5)	0.06500(8)	0.0432
P(1)	0.3300(1)	-0.16772(9)	0.0539(2)	0.0604
C(16)	0.3739(6)	-0.2246(5)	-0.0751(8)	0.0821
C(17)	0.3898(6)	-0.2092(5)	0.1992(8)	0.0962
C(18)	0.4015(6)	-0.0850(5)	0.029(1)	0.1002
N(1)	0.1471(4)	-0.0763(3)	-0.1787(4)	0.0542
N(2)	0.1311(4)	-0.3015(2)	0.1136(5)	0.0536
C(1)	0.1594(4)	-0.1359(3)	-0.1107(5)	0.0497
C(2)	0.1499(4)	-0.2486(3)	0.0346(5)	0.0477
C(3)	0.1356(7)	-0.1457(4)	0.2639(6)	0.0637
C(4)	0.0474(6)	-0.1447(4)	0.1839(7)	0.0640
C(5)	0.0502(6)	-0.0834(4)	0.1028(7)	0.0680
C(6)	0.1392(6)	-0.0463(3)	0.1321(6)	0.0584
C(7)	0.1930(6)	-0.0854(4)	0.2310(7)	0.0694
C(8)	0.1354(5)	-0.0695(3)	-0.3231(5)	0.0532
C(9)	0.2359(6)	-0.0880(4)	-0.3793(6)	0.0723
C(10)	0.0540(6)	-0.1199(5)	-0.3762(7)	0.0842
C(11)	0.1087(6)	0.0088(4)	-0.3521(6)	0.0716
C(12)	0.1086(6)	-0.3776(3)	0.0848(6)	0.0676
C(13)	0.040(1)	-0.4051(6)	0.188(1)	0.1358
C(14)	0.2060(8)	-0.4196(5)	0.108(1)	0.1455
C(15)	0.067(1)	-0.3887(6)	-0.0533(8)	0.1321
P(2)	0.2310(2)	-0.3363(1)	0.5453(2)	0.071
F(1)	0.1634(8)	-0.3015(6)	0.4451(9)	0.204
F(2)	0.1682(7)	-0.4028(4)	0.536(1)	0.201
F(3)	0.2977(9)	-0.3627(6)	0.442(1)	0.221
F(4)	0.2970(7)	-0.3710(8)	0.642(1)	0.223
F(5)	0.1658(8)	-0.3056(7)	0.644(1)	0.214
F(6)	0.2959(7)	-0.2694(4)	0.553(1)	0.192
H(1)	0.1642(4)	-0.1828(3)	-0.1673(5)	0.080(7)
H(2)	0.1546(4)	-0.2642(3)	-0.0629(5)	0.080(7)
H(3)	0.1556(7)	-0.1851(4)	0.3336(6)	0.080(7)
H(4)	-0.0108(6)	-0.1827(4)	0.1859(7)	0.080(7)
H(5)	-0.0058(6)	-0.0684(4)	0.0329(7)	0.080(7)
H(6)	0.1635(6)	0.0013(3)	0.0881(6)	0.080(7)
H(7)	0.2630(6)	-0.0716(4)	0.2747(7)	0.080(7)
H(35)	0.1369(4)	-0.0307(3)	-0.1236(4)	0.080(7)
H(36)	0.1312(4)	-0.2841(2)	0.2180(5)	0.080(7)
H(8)	0.2905(6)	-0.0527(4)	-0.3391(6)	0.199(9)
H(9)	0.2322(6)	-0.0827(4)	-0.4809(6)	0.199(9)
H(10)	0.2550(6)	-0.1414(4)	-0.3541(6)	0.199(9)
H(11)	0.0740(6)	-0.1738(5)	-0.3565(7)	0.199(9)
H(12)	0.0455(6)	-0.1124(5)	-0.4771(7)	0.199(9)
H(13)	-0.0138(6)	-0.1081(5)	-0.3335(7)	0.199(9)
H(14)	0.0386(6)	0.0201(4)	-0.3150(6)	0.199(9)
H(15)	0.1054(6)	0.0178(4)	-0.4528(6)	0.199(9)
H(16)	0.1631(6)	0.0428(4)	-0.3074(6)	0.199(9)
H(17)	-0.028(1)	-0.3773(6)	0.176(1)	0.199(9)
H(18)	0.027(1)	-0.4608(6)	0.179(1)	0.199(9)
H(19)	0.073(1)	-0.3941(6)	0.280(1)	0.199(9)
H(20)	0.2336(8)	-0.4154(5)	0.205(1)	0.199(9)
H(21)	0.1950(8)	-0.4742(5)	0.084(1)	0.199(9)
H(22)	0.2576(8)	-0.3968(5)	0.047(1)	0.199(9)
H(23)	0.118(1)	-0.3684(6)	-0.1186(8)	0.092(9)
H(24)	0.056(1)	-0.4441(6)	-0.0701(8)	0.092(9)
H(25)	-0.001(1)	-0.3614(6)	-0.0667(8)	0.092(9)
H(26)	0.4525(6)	-0.2271(5)	-0.0679(8)	0.199(9)
H(27)	0.3444(6)	-0.2767(5)	-0.0650(8)	0.199(9)
H(28)	0.3504(6)	-0.2035(5)	-0.1660(8)	0.199(9)
H(29)	0.3701(6)	-0.1804(5)	0.2819(8)	0.199(9)
H(30)	0.4679(6)	-0.2083(5)	0.1927(8)	0.199(9)
H(31)	0.3654(6)	-0.2629(5)	0.2062(8)	0.199(9)
H(32)	0.3711(6)	-0.0582(5)	-0.054(1)	0.199(9)
H(33)	0.4766(6)	-0.0983(5)	0.015(1)	0.199(9)
H(34)	0.3978(6)	-0.0511(5)	0.110(1)	0.199(9)

Table II

Bond Lengths [Angstroms] with
Estimated Standard Deviations in Parentheses

FE(1)	P(1)	2.173(2)
FE(1)	C(1)	1.834(6)
FE(1)	C(2)	1.833(6)
FE(1)	C(3)	2.125(6)
FE(1)	C(4)	2.094(6)
FE(1)	C(5)	2.090(7)
FE(1)	C(6)	2.119(6)
FE(1)	C(7)	2.118(7)
P(1)	C(16)	1.816(7)
P(1)	C(17)	1.831(8)
P(1)	C(18)	1.831(8)
N(1)	C(1)	1.313(7)
N(1)	C(8)	1.495(7)
N(2)	C(2)	1.307(7)
N(2)	C(12)	1.469(8)
C(3)	C(4)	1.40(1)
C(3)	C(7)	1.40(1)
C(4)	C(5)	1.411(9)
C(5)	C(6)	1.39(1)
C(6)	C(7)	1.42(1)
C(8)	C(9)	1.528(9)
C(8)	C(10)	1.515(9)
C(8)	C(11)	1.520(9)
C(12)	C(13)	1.52(1)
C(12)	C(14)	1.53(1)
C(12)	C(15)	1.51(1)
P(2)	F(1)	1.485(7)
P(2)	F(2)	1.489(7)
P(2)	F(3)	1.500(8)
P(2)	F(4)	1.445(7)
P(2)	F(5)	1.484(7)
P(2)	F(6)	1.513(7)

Table III

Bond Angles [Degrees] with
Estimated Standard Deviations in Parentheses

C(1)	FE(1)	P(1)	89.7(2)
C(2)	FE(1)	P(1)	89.6(2)
C(2)	FE(1)	C(1)	89.2(2)
C(3)	FE(1)	P(1)	108.5(2)
C(3)	FE(1)	C(1)	159.3(3)
C(3)	FE(1)	C(2)	100.5(3)
C(4)	FE(1)	P(1)	147.1(2)
C(4)	FE(1)	C(1)	123.1(3)
C(4)	FE(1)	C(2)	93.0(3)
C(4)	FE(1)	C(3)	38.9(3)
C(5)	FE(1)	P(1)	148.9(2)
C(5)	FE(1)	C(1)	93.8(3)
C(5)	FE(1)	C(2)	121.3(3)
C(5)	FE(1)	C(3)	65.5(3)
C(5)	FE(1)	C(4)	39.4(3)
C(6)	FE(1)	P(1)	110.3(2)
C(6)	FE(1)	C(1)	99.6(3)
C(6)	FE(1)	C(2)	158.1(3)
C(6)	FE(1)	C(3)	65.3(3)
C(6)	FE(1)	C(4)	65.4(3)
C(6)	FE(1)	C(5)	38.7(3)
C(7)	FE(1)	P(1)	90.8(2)
C(7)	FE(1)	C(1)	134.8(3)
C(7)	FE(1)	C(2)	136.0(3)
C(7)	FE(1)	C(3)	38.7(3)
C(7)	FE(1)	C(4)	65.1(3)
C(7)	FE(1)	C(5)	65.2(3)
C(7)	FE(1)	C(6)	39.1(3)
C(16)	P(1)	FE(1)	118.2(3)
C(17)	P(1)	FE(1)	113.9(3)
C(17)	P(1)	C(16)	102.2(4)
C(18)	P(1)	FE(1)	114.7(3)
C(18)	P(1)	C(16)	101.0(4)
C(18)	P(1)	C(17)	104.9(5)
C(8)	N(1)	C(1)	127.3(5)
C(12)	N(2)	C(2)	129.6(5)
N(1)	C(1)	FE(1)	131.6(4)
N(2)	C(2)	FE(1)	131.0(4)
C(4)	C(3)	FE(1)	69.4(4)
C(7)	C(3)	FE(1)	70.4(4)
C(7)	C(3)	C(4)	107.5(6)
C(3)	C(4)	FE(1)	71.7(4)
C(5)	C(4)	FE(1)	70.1(4)
C(5)	C(4)	C(3)	108.2(7)
C(4)	C(5)	FE(1)	70.4(4)
C(6)	C(5)	FE(1)	71.8(4)
C(6)	C(5)	C(4)	108.4(7)
C(5)	C(6)	FE(1)	69.5(4)
C(7)	C(6)	FE(1)	70.4(4)
C(7)	C(6)	C(5)	107.5(6)
C(3)	C(7)	FE(1)	70.9(4)
C(6)	C(7)	FE(1)	70.5(4)
C(6)	C(7)	C(3)	108.4(7)
C(9)	C(8)	N(1)	107.9(5)
C(10)	C(8)	N(1)	110.2(5)
C(10)	C(8)	C(9)	110.7(6)
C(11)	C(8)	N(1)	106.7(5)
C(11)	C(8)	C(9)	110.0(6)
C(11)	C(8)	C(10)	111.1(6)
C(13)	C(12)	N(2)	107.7(6)
C(14)	C(12)	N(2)	106.9(6)
C(14)	C(12)	C(13)	104.8(9)
C(15)	C(12)	N(2)	112.4(6)
C(15)	C(12)	C(13)	114.1(9)
C(15)	C(12)	C(14)	110.4(9)
F(2)	P(2)	F(1)	89.6(6)
F(3)	P(2)	F(1)	90.7(7)
F(3)	P(2)	F(2)	92.2(6)
F(4)	P(2)	F(1)	179.2(9)
F(4)	P(2)	F(2)	90.0(7)
F(4)	P(2)	F(3)	88.7(8)
F(5)	P(2)	F(1)	87.2(7)
F(5)	P(2)	F(2)	90.7(6)
F(5)	P(2)	F(3)	176.4(7)
F(5)	P(2)	F(4)	93.4(8)
F(6)	P(2)	F(1)	90.6(6)
F(6)	P(2)	F(2)	179.1(6)
F(6)	P(2)	F(3)	86.9(6)
F(6)	P(2)	F(4)	89.8(6)
F(6)	P(2)	F(5)	90.1(6)

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