

TRANSITION METAL PROMOTED OXIDATION AND

REDUCTION REACTIONS

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by

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ABSTRACT

Transition metal promoted oxidation and reduction reactions

Two areas of organotransition metal chemistry and their potential application to organic transformations are discussed.

The synthesis of cations of the type $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{L})_2(\text{CO})]^+$, $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)(\text{L})_2(\text{CO})]^+$, $[\text{Fe}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{L})_2(\text{CO})]^+$ (where $(\text{L})_2 = (\text{CO})_2$, $(\text{PPh}_3)(\text{CO})$, $(\text{PMe}_3)(\text{CO})$, $(\text{PPh}_3)_2$, (diphos) and $(\text{PMe}_3)_2$) and $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{L})_3(\text{CO})]^+$ (where $(\text{L})_3 = (\text{PPh}_3)(\text{CO})_2$, (diphos)(CO) and (triphos)), many of them novel, is described. Investigations into the site of nucleophilic attack on the cations using hydride as a probe and the effect of varying the overall charge distribution of the cation are discussed. Hydride attack on a carbonyl ligand leads to the formation of metal formyl moieties and their detection by low temperature ^1H n.m.r. spectroscopy is described; furthermore, the fate of the metal formyls was found to be dependent upon the nature of the other ligands in the complex. A new criterion for establishing the stereoselectivity of nucleophilic attack on $\eta^5\text{-C}_5\text{H}_5$ ligands is proposed. Hydride attack on an $\eta^5\text{-C}_5\text{H}_4\text{CH}_3$ ligand was discovered to be regioselective occurring at the carbon atom alpha to the methyl-bearing carbon. The direct oxidation of alkenes to epoxides by hydrogen peroxide was shown to be catalysed by some of the metal carbonyl cations.

The use of organotitanium reagents to convert *vic*-dibromides and epoxides to alkenes is discussed. $(\text{C}_5\text{H}_5)_2\text{TiCl}_2$ was shown to catalyse both a sodium amalgam debromination of disubstituted *vic*-dibromides and a zinc debromination of mono and disubstituted *vic*-dibromides. The latter reaction was developed into a synthetically useful procedure. Reduction of $(\text{C}_5\text{H}_5)_2\text{TiCl}_2$ by both sodium amalgam and zinc dust gave reagents which deoxygenated epoxides. Investigations into the regioselectivity and chemoselectivity of these reagents are discussed. During the synthesis of molecules containing both *vic*-dibromide and epoxide functionalities, a novel cyclisation was discovered which may have relevance to the biosynthesis of certain marine natural products.

Acknowledgements

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Abbreviations

diphos	bis 1,2-(diphenylphosphino)ethane ($\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$)
DMF	dimethylformamide
DMSO	dimethylsulphoxide
ϵ	dielectric constant
ESCA	electron spectroscopy for chemical analysis
mCPBA	meta-chloroperbenzoic acid
SCE	standard calomel electrode
THF	tetrahydrofuran
triphos	di(2-diphenylphosphinoethyl)phenylphosphine ($\text{PPh}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2$)

Infra-red spectroscopy

br	broad
m	medium
s	strong
sh	shoulder
vs	very strong
w	weak

N.m.r. spectroscopy

br	broad
d	doublet
m	multiplet
s	singlet
t	triplet

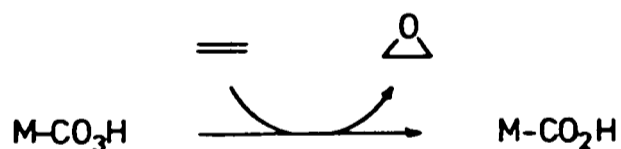
Foreword

Investigations into the use of organotransition metal complexes to effect transformations of organic molecules have led to the discovery of remarkable reactions which are unparalleled in traditional organic chemistry.¹ Although metal complexes have been employed as both catalytic and stoichiometric reagents, the former use is of more instant appeal for organic synthesis. This thesis discusses two areas of organotransition metal chemistry and their potential application to organic transformations.

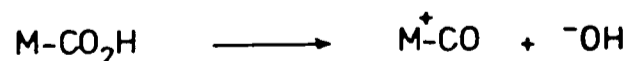
Section I is concerned with the generation of peroxymetallacarboxylic acids, an unknown class of compound, by nucleophilic addition of the hydroperoxide anion to a metal carbonyl cation.



Oxidation of an alkene to an epoxide generates a metallacarboxylic acid.



These are known to dissociate to a metal carbonyl cation and hydroxide,² thus completing a cycle which is catalytic in metal carbonyl cation.



Section I.1 discusses the synthesis of some potential catalysts *i.e.* organo-iron and organo-molybdenum cations with at least one carbonyl ligand. Formation of a peroxymetallacarboxylic acid is dependent upon attack of the hydroperoxide ion on the metal carbonyl cation occurring only at the carbonyl ligand.

Section I.2 investigates the regioselectivity of the cations synthesised in Section I.1 towards nucleophiles using hydride as a model nucleophile. Section I.3 examines the potential of the cations for catalysing the oxidation of alkenes to epoxides.

Section II looks at the use of low-valent organo-titanium complexes to reduce *vic*-dibromides to alkenes.

Sections I and II are discrete.

S E C T I O N I

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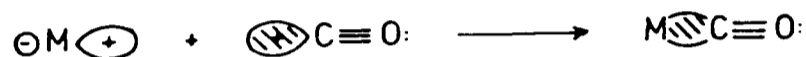
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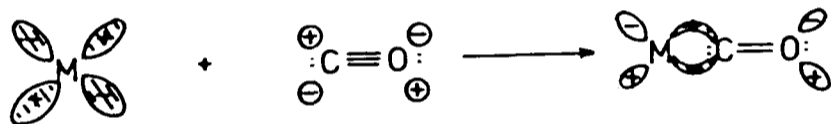
I.1.1 Introduction

The physical and chemical properties of organotransition metal complexes can be finely tuned in many ways. Some of the effects of replacing carbon monoxide ligands with phosphine ligands³ and of methylating an $\eta^5\text{-C}_5\text{H}_5$ ligand are outlined below.

The bonding of carbon monoxide to a transition metal involves two distinct interactions a) overlap of a filled carbon σ orbital with a σ -type orbital on the metal atom,



and b) overlap of a filled $d\pi$ metal orbital with an empty $p\pi$ antibonding orbital on carbon monoxide.



This bonding is synergic since the movement of metal electrons into CO orbitals will tend to make the ligand negative and hence to increase its basicity *via* the σ orbitals of carbon; however the movement of electrons to the metal in the σ bond tends to make the CO positive thus enhancing the acceptor strength of the π orbitals. These processes have important chemical consequences, affecting electron and orbital availability at both carbon and metal centres, stabilising metals in low formal oxidation states and modifying the bonding and behaviour of other ligands present.

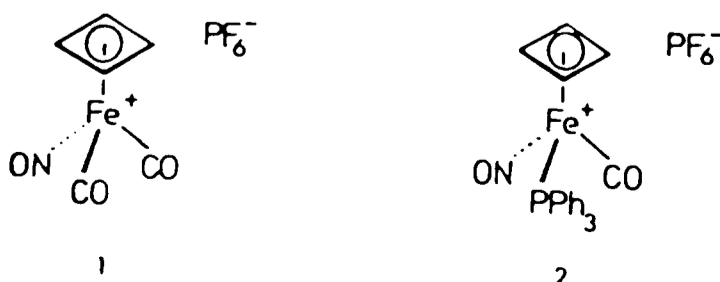
As the extent of π -donation from metal to CO increases, the metal-carbon bond becomes stronger and the carbon-oxygen bond becomes weaker. Thus, if some CO groups are replaced by ligands with low π -acceptor ability, the CO groups that remain

accept $d\pi$ electrons from the metal to a greater extent to counteract the accumulation of negative charge on the metal. Hence the carbon-oxygen bond is weakened and this is reflected in the stretching frequencies in the infra-red which are to a good approximation specific group frequencies. They are also sharp, sensitive to environment and generally intense.

The bonding between a tertiary phosphine and a transition metal also involves two components, a) overlap of a filled phosphorus σ orbital with a σ -type orbital on the metal atom, and b) overlap of a filled $d\pi$ metal orbital with an empty $3d$ phosphorus orbital. Similarly the bonding between an unsaturated hydrocarbon and a transition metal involves two interactions, a) the unsaturated hydrocarbon donates electrons from its π orbital to the metal, and b) the metal donates d electrons into the π^* orbital of the olefin.

Tertiary phosphines are net donors *i.e.* interaction a) is stronger than interaction b). Unsaturated hydrocarbons may be net donors or net acceptors; the relative strengths of the two types of bonding depend on the complex. Some of the effects on the properties of transition metal complexes of replacing a CO ligand with a tertiary phosphine ligand are outlined below.

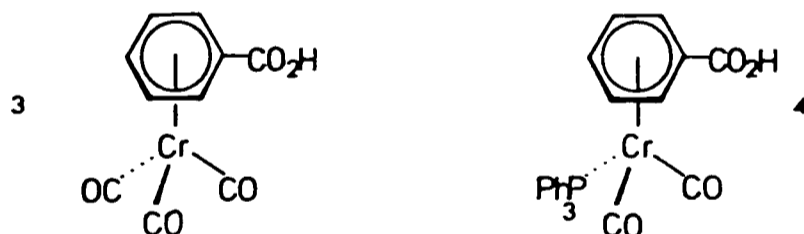
The rate constant for the addition of triphenylphosphine to the cyclobutadiene ring of (1) is $44000 \pm 1700 \text{ M}^{-1} \text{ s}^{-1}$ whereas the rate constant for the addition of triphenylphosphine to the cyclobutadiene ring of (2) is $1740 \pm 70 \text{ M}^{-1} \text{ s}^{-1}$. These rates reflect the increased electron density on the hydrocarbon



ligand of (2) that results from phosphine substitution.⁴ The increased electron density on the η^4 -C₄H₄ ligand of (2) shields the protons attached to the ligand and as a result the protons of (2) resonate at δ 5.40 whereas the protons of the η^4 -C₄H₄ ligand of (1) resonate at δ 6.14.⁵

The infra-red stretching frequencies of the carbonyls in the iron complex [Fe(PPh₃)(CO)₄] are 2 051, 1 978 and 1 945 cm⁻¹ whereas the stretching frequency of the carbonyls in the complex [Fe(PPh₃)₂(CO)₃] is 1 892 cm⁻¹.⁶ This reflects donation of electron density from the phosphine ligand to the π^* orbitals of the carbon monoxide ligands.

The pKa of the chromium complex (3) is 4.77 whereas the pKa of (4) is 6.15;⁷ this is the result of the net donating effect of the tertiary phosphine ligand destabilising the anion of (4) relative to the anion of (3).



The increased electron density at the metal centre resulting from phosphine substitution may not all be deposited on the carbonyl ligands and/or the hydrocarbon ligands. Mössbauer studies have shown that the influence of phosphine ligands on the electron density at the nucleus of the metal atom increases with decreasing CO content.⁸

The steric properties of tertiary phosphines affect the chemistry of their co-ordination compounds; they may determine stereochemistry, structure, rate and equilibria of dissociation

reactions *etc.* Some angles of ligand cones (defined by a conic surface with apex at the metal atom which can just enclose the van der Waals surface of all ligand atoms over all rotational orientations about the metal-phosphorus bond) of tertiary phosphines are given in Table 1.

Table 1 Phosphine ligand cone angles

<u>Ligand</u>	<u>Cone angle</u>
PMe ₃	118°
PPh ₃	145°
diphos	123°

It is of note that the smaller the ligand cone angle, the greater the competitive binding ability of the ligand when steric interference between ligands becomes significant.

Replacement of the $\eta^5\text{-C}_5\text{H}_5$ ligand by the $\eta^5\text{-C}_5(\text{CH}_3)_5$ ligand in certain bis and mono cyclopentadienyl complexes of transition metals produces significant changes in chemical reactivity, stability, sensitivity to oxidation *etc.* The effects of methyl substitution have been attributed to both the electronic and steric changes that are a result of replacing a hydrogen atom with a methyl group; the electron-releasing effects of the five methyl groups should strengthen the metal-ring bond by increasing the electron density (and hence the effective "basicity") in the ring donor orbitals.

Some examples of the change in properties that accompany permethylation of an $\eta^5\text{-C}_5\text{H}_5$ ligand are given below.

a) The rhodium complex $[\text{Rh}(\eta^5\text{-C}_5(\text{CH}_3)_5)\text{Cl}_2]_2$ has a strong metal-ring bond which survives acidic and basic conditions as well as reducing and oxidising conditions; its solubility is

good and it is easy to crystallise. In contrast the metal-ring bond in $[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}_2]_n$ is readily cleaved by a variety of reagents; the polymeric species is insoluble in all but powerfully co-ordinating solvents and is amorphous.⁹

b) In contrast to the $\eta^5\text{-C}_5\text{H}_5$ analogues, attempts to substitute the CO ligands of the decamethylmetallocene dicarbonyls $[\text{M}(\eta^5\text{-C}_5(\text{CH}_3)_5)_2(\text{CO})_2]$ (M=Ti, Zr, Hf) with phosphines and phosphites under both thermal and photochemical conditions have thus far proved to be unsuccessful.¹⁰

c) Dicyclopentadiene reacts with molybdenum hexacarbonyl to give the dimer $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]_2$ (5) with three carbon monoxide groups for each molybdenum atom. In contrast to this behaviour, 1,2,3,4,5-pentamethylcyclopentadiene was found to react with molybdenum hexacarbonyl to give $[\text{Mo}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{CO})_2]_2$ with only two carbon monoxide groups for each molybdenum atom. It was concluded that the greater steric requirements of the $\eta^5\text{-C}_5(\text{CH}_3)_5$ ligand more severely limit the number of carbon monoxide groups that can be attached to the metal atom.¹¹

d) Permethylation of the $\eta^5\text{-C}_5\text{H}_5$ ligands in a complex generally raises its melting point. For example $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]$ is a liquid at room temperature (m.p. -22°C) whereas $[\text{Co}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{CO})_2]$ is a crystalline solid (m.p. 56°C).¹¹

e) ESCA studies of titanocenes, zirconocenes, hafnocenes and ferrocenes have shown that permethylation of the $\eta^5\text{-C}_5\text{H}_5$ ligand results in a dramatic electronic effect reflected by the binding energies of the inner shell electrons of the metal. The studies conclude that permethylation of two cyclopentadienyl ligands is approximately equivalent to a one electron reduction of the complexed metal.¹²

This chapter outlines the synthesis of cations belonging to the four series described by the generalised cations in Fig. 1; the cations were required for the studies discussed in Section I.2 and I.3.

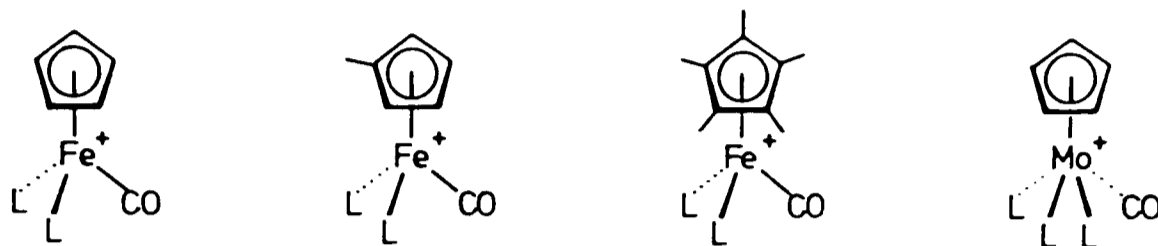


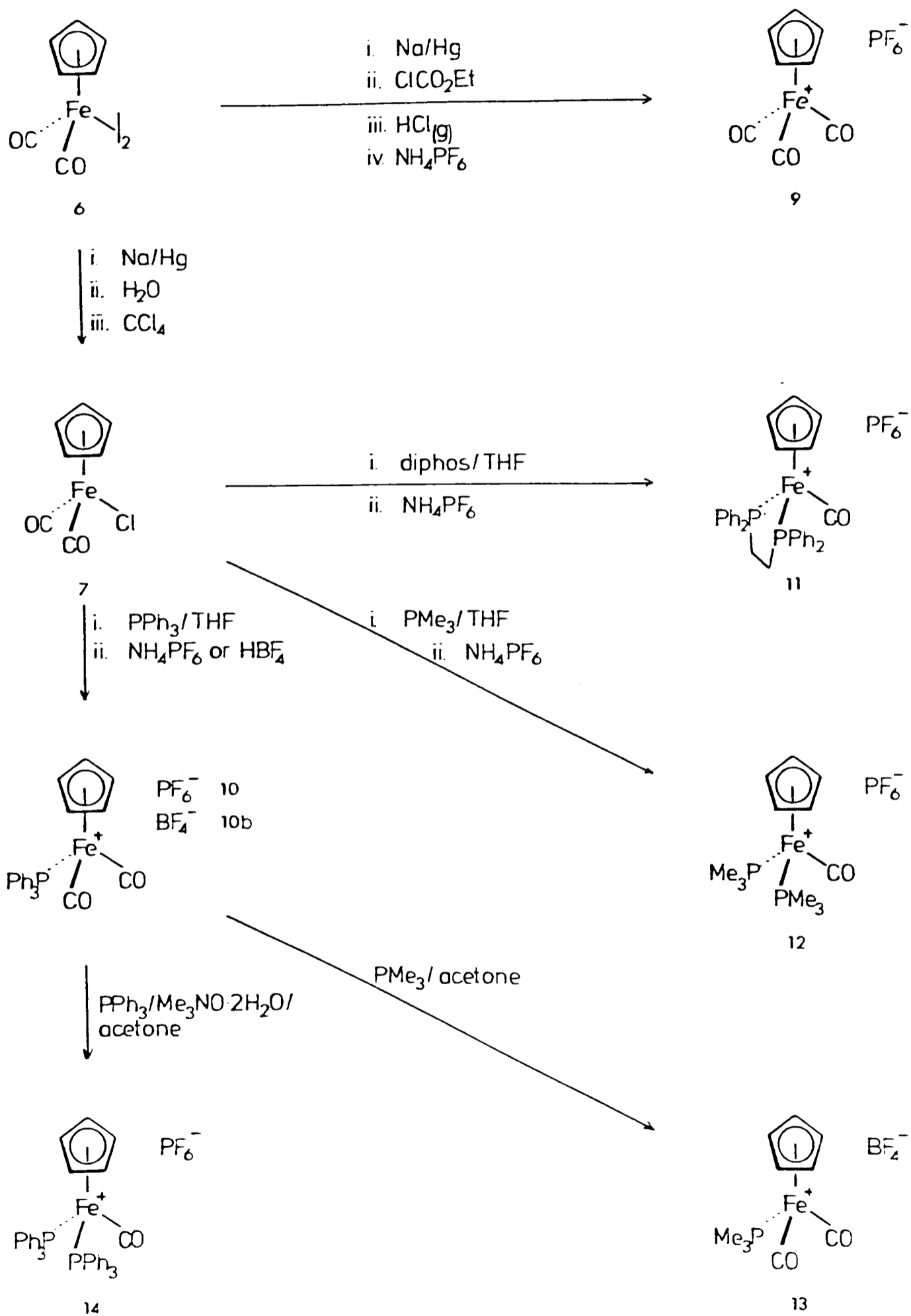
Fig. 1

L = CO, tertiary phosphine

Although a literature search revealed methods for synthesising some of the iron cations in the $\eta^5\text{-C}_5\text{H}_5$ series, and some of the molybdenum cations, only the tricarbonyl cation in the $\eta^5\text{-C}_5(\text{CH}_3)_5$ series had been reported; none of the cations in the $\eta^5\text{-C}_5\text{H}_4\text{CH}_3$ series were known.

It was postulated that the carbonyl stretching mode absorption frequencies, the ^1H chemical shifts of the hydrocarbon ligands and the ^{31}P shifts of the phosphine ligands would provide information about the electron density distribution in these complexes.

Scheme 1 Synthesis of cationic $\eta^5\text{-C}_5\text{H}_5$ complexes of iron



I.1.2 Synthesis of cationic $\eta^5\text{-C}_5\text{H}_5$ complexes of iron

The routes used to synthesise $\eta^5\text{-C}_5\text{H}_5$ complexes of iron are summarised in Scheme 1.

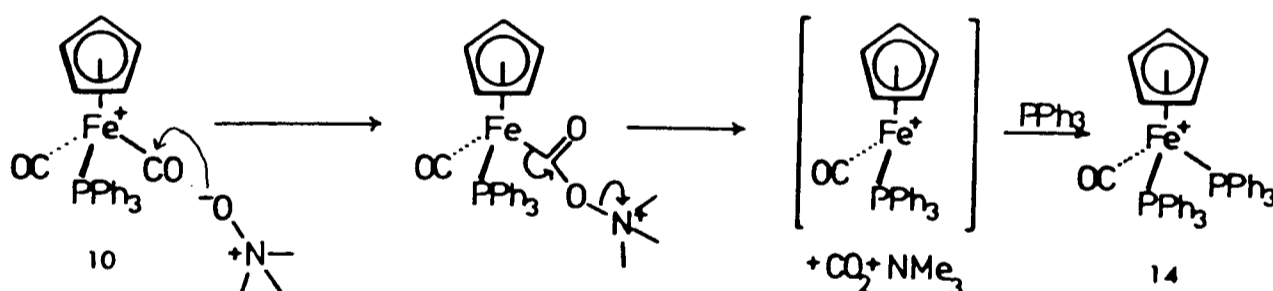
$[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]_2$ (6) was converted to $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Cl}]$ (7) by a known procedure;¹³ reductive cleavage of the dimer (6) by 2% sodium amalgam leading to $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]\text{Na}$, followed by protonation gave the highly unstable hydride $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{H}]$ (8). Radical halogenation by carbon tetrachloride gave (7) in good yield (66%). $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]_2$ (6) was also converted to $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]\text{PF}_6$ (9) by a literature procedure;¹⁴ treatment of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]\text{Na}$ with ethyl chloroformate followed by hydrogen chloride gas gave $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]\text{Cl}$ (9a). Anion exchange using ammonium hexafluorophosphate led to isolation of (9) in moderate yield (39%).

Heating $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Cl}]$ (7) in tetrahydrofuran with triphenylphosphine gave the monosubstituted complex $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{CO})_2]\text{Cl}$ (10a), whereas the thermolysis product of (7) and the bidentate phosphine diphos was the disubstituted complex $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{diphos})(\text{CO})]\text{Cl}$ (11a); substitution of the second carbonyl ligand for a phosphine in the latter case is aided by the 'chelate effect'. Heating (7) with the reactive trimethylphosphine led to the disubstituted product $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{PMe}_3)_2(\text{CO})]\text{Cl}$ (12a) as a result of the high nucleophilicity and low steric demands of this phosphine. Anion exchange with ammonium hexafluorophosphate gave the known salts (10), (11) and (12) in good yields (70-75%).

The problem of preventing disubstitution by trimethylphosphine in order to synthesise the monosubstituted cation

was circumvented by the novel procedure of stirring $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{CO})_2]\text{BF}_4$ (10b) with trimethylphosphine in acetone at 20 °C for an hour to give the monosubstituted salt $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{PMe}_3)(\text{CO})_2]\text{BF}_4$ (13) in 80% yield.

Formation of the disubstituted triphenylphosphine complex $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2(\text{CO})]\text{PF}_6$ (14) from $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{CO})_2]\text{PF}_6$ (10) has been reported in the literature;¹⁵ the method uses aluminium tribromide to facilitate the substitution of a carbon monoxide ligand for the phosphine and gives a poor yield of (14) (19%). A communication by Davies¹⁶ presented preliminary results demonstrating the use of Me_3NO hydrate as an oxidising agent sufficiently nucleophilic to remove two molecules of carbon monoxide from the tricarbonyl complex (9). Use of this reagent indeed provided an easy route to the disubstituted complex (14) from the monosubstituted complex (10) in 70% yield. A mechanism for this reaction is given below.



The infra-red spectra, mass spectra and ^1H n.m.r. and ^{31}P -(^1H) n.m.r. spectra of the yellow, crystalline, air-stable salts discussed in this section were recorded (Table 2, p 84) and compared with literature data where available (references in Table 2). The mass spectra all contained molecular ion peaks. The carbonyl stretching mode absorption frequencies, the ^1H chemical shifts of the $\eta^5\text{-C}_5\text{H}_5$ ligand and the ^{31}P chemical shifts of the phosphine ligands are given in Table 3.

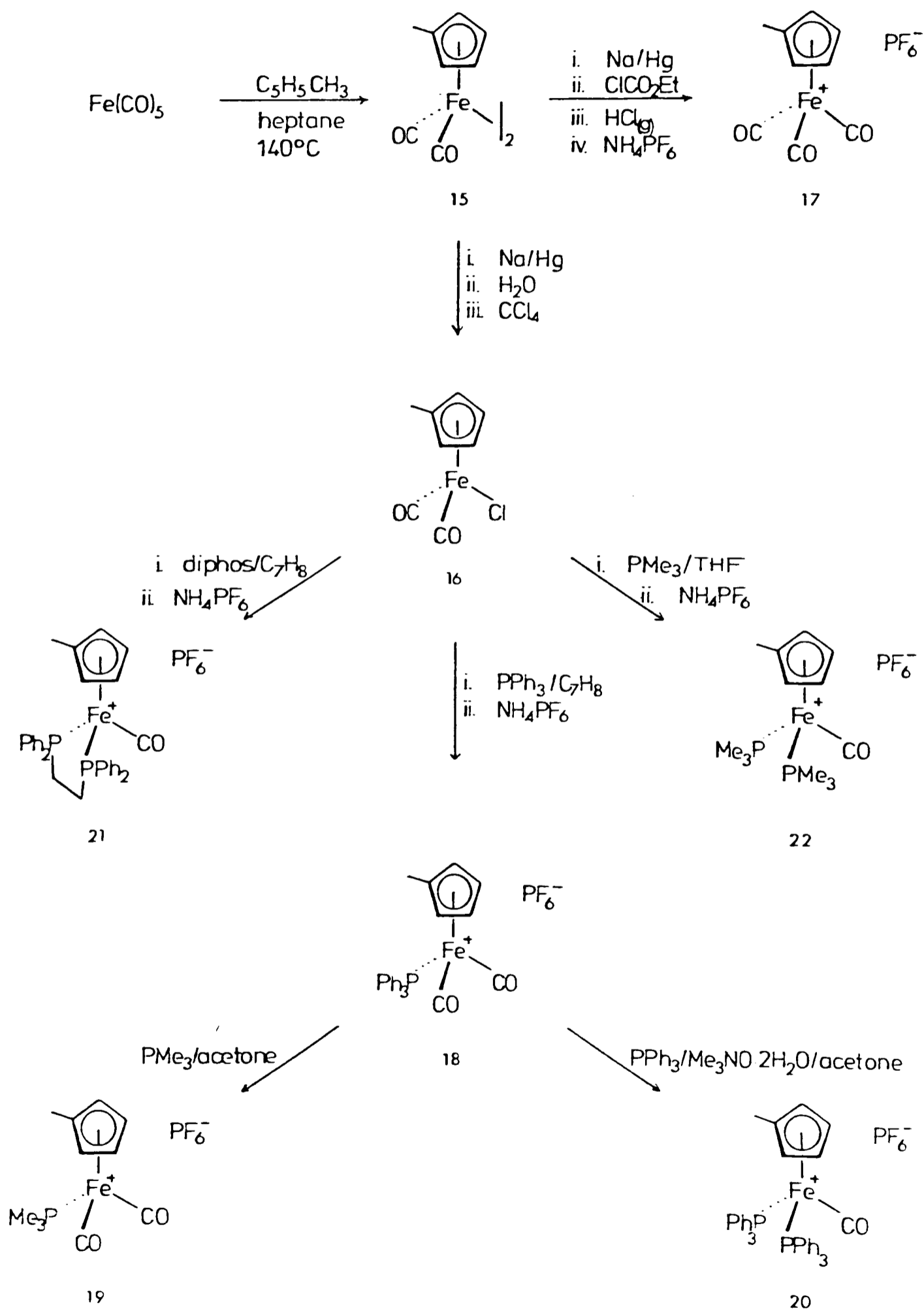
Table 3 Selected spectroscopic data for $\eta^5\text{-C}_5\text{H}_5$ cationic complexes of iron

<u>Compound</u>		$\nu_{\text{max.}}$ (cm^{-1})	δ C_5H_5	δ P
$[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]\text{PF}_6$	(9)	2 125, 2 070	6.1	
$[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{CO})_2]\text{PF}_6$	(10)	2 065, 2 020	5.6	59.8
$[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{PMe}_3)(\text{CO})_2]\text{BF}_4$	(13)	2 050, 1 995	5.5	30.8†
$[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2(\text{CO})]\text{PF}_6$	(14)	1 980	4.8	56.6
$[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{diphos})(\text{CO})]\text{PF}_6$	(11)	1 975	5.1	91.6
$[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{PMe}_3)_2(\text{CO})]\text{PF}_6$	(12)	1 945	5.1	25.6

† This value was recorded using the hexafluorophosphate salt.

The carbonyl stretching frequencies decrease with increasing phosphine substitution due to the inferior π -acceptor ability of phosphines relative to carbonyls. Although the data suggest that trimethylphosphine is a net donor of electron density relative to triphenylphosphine (a result of increased σ donation and/or reduced π -acceptor ability), it is apparent that the degree of substitution has a more profound effect on the carbonyl stretching frequency. Likewise, the protons of the $\eta^5\text{-C}_5\text{H}_5$ ligand are shielded dramatically with increasing phosphine substitution (an average of 0.55 ppm per phosphine), but show no consistent shielding/deshielding effect as the phosphine is varied within a given degree of substitution. The chemical environment of the phosphorus nucleus appears to be dominated by the alkyl and/or aryl groups attached to it. However, a deshielding effect is apparent on moving from a disubstituted complex to a monosubstituted complex.

Scheme 2 Synthesis of cationic $\eta^5\text{-C}_5\text{H}_4\text{CH}_3$ complexes of iron



I.1.3 Synthesis of cationic $\eta^5\text{-C}_5\text{H}_4\text{CH}_3$ complexes of iron

Although the syntheses of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)(\text{CO})_2]_2$ (15)¹⁷ and $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)(\text{CO})_2\text{Cl}]$ (16)¹⁸ were carried out 25 and 15 years ago respectively, cationic derivatives of triphenylphosphine, trimethylphosphine and diphos were unknown. The routes used to synthesise such derivatives are summarised in Scheme 2.

$[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)(\text{CO})_2]_2$ (15) was synthesised from freshly-cracked methylcyclopentadiene, iron pentacarbonyl and heptane, and conversion to $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)(\text{CO})_2\text{Cl}]$ (16) was carried out by the method used for $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Cl}]$ (7). Complexes (15) and (16) are more air-sensitive than the corresponding $\eta^5\text{-C}_5\text{H}_5$ compounds; it was important to use freshly-cracked methylcyclopentadiene in order to obtain pure crystalline samples of these compounds.

The salts $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)(\text{CO})_3]\text{PF}_6$ (17), $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)(\text{PPh}_3)(\text{CO})_2]\text{PF}_6$ (18), $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)(\text{PMe}_3)(\text{CO})_2]\text{PF}_6$ (19), $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)(\text{PPh}_3)_2(\text{CO})]\text{PF}_6$ (20), $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)(\text{diphos})(\text{CO})]\text{PF}_6$ (21) and $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)(\text{PMe}_3)_2(\text{CO})]\text{PF}_6$ (22) were prepared by analogous methods to those used for the corresponding $\eta^5\text{-C}_5\text{H}_5$ complexes; the reactions proceeded smoothly in good yield (76-93%).

The novel, yellow, crystalline, air-stable salts discussed in this section were fully characterised by infra-red spectroscopy, ^1H n.m.r. and ^{31}P -(^1H) n.m.r. spectroscopy, mass spectrometry and elemental microanalysis (Tables 4a and 4b, p 88, 89). The mass spectra all contained molecular ion peaks. The carbonyl stretching mode absorption frequencies, the ^1H chemical shifts of the $\eta^5\text{-C}_5\text{H}_4\text{CH}_3$ ligand (for numbering system, see Fig. 2) and the ^{31}P chemical shifts of the phosphine ligands are

given in Table 5.

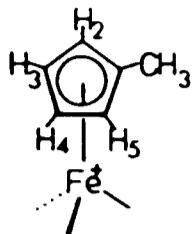


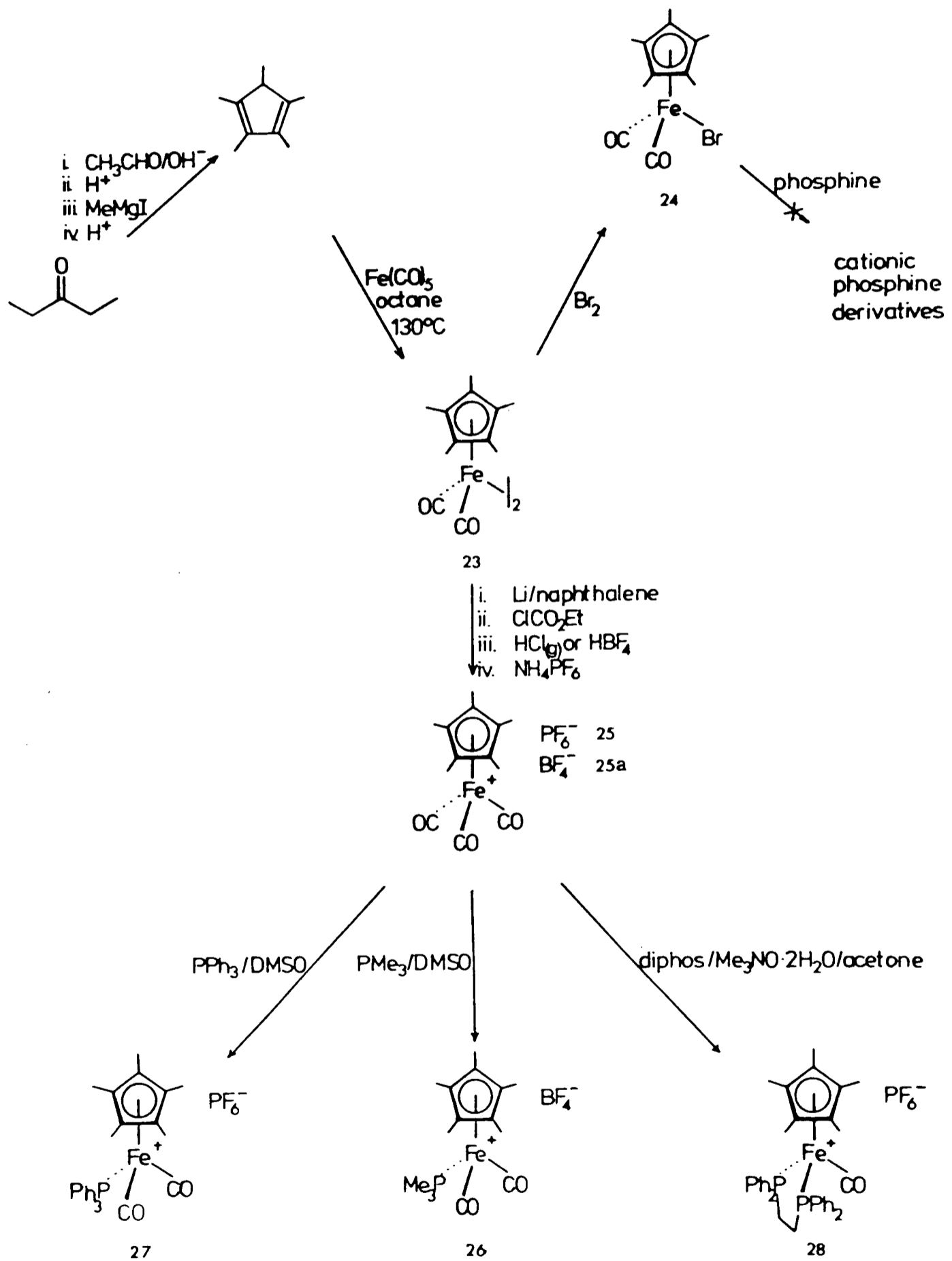
Fig. 2

Table 5 Selected spectroscopic data for η^5 -C₅H₄CH₃ cationic complexes of iron

<u>Compound</u>		<u>$\nu_{\text{max.}}$ (cm⁻¹)</u>	<u>δ H_{3,4}</u>	<u>δ H_{2,5}</u>	<u>δ C₅H₄CH₃</u>	<u>δP</u>
[Fe(η^5 -C ₅ H ₄ CH ₃)(CO) ₃]PF ₆	(17)	2 130,2 095	6.03	5.96	2.30	
[Fe(η^5 -C ₅ H ₄ CH ₃)(PPh ₃)(CO) ₂]PF ₆	(18)	2 070,2 015	5.57	5.37	2.18	63.2
[Fe(η^5 -C ₅ H ₄ CH ₃)(PMe ₃)(CO) ₂]PF ₆	(19)	2 055,2 010	5.53	5.51	2.16	31.9
[Fe(η^5 -C ₅ H ₄ CH ₃)(PPh ₃) ₂ (CO)]PF ₆	(20)	1 955	4.82	4.47	1.98	57.3
[Fe(η^5 -C ₅ H ₄ CH ₃)(diphos)(CO)]PF ₆	(21)	1 960	5.30	4.69	1.96	91.7
[Fe(η^5 -C ₅ H ₄ CH ₃)(PMe ₃) ₂ (CO)]PF ₆	(22)	1 950	5.12	4.87	2.07	27.3

The carbonyl stretching frequencies of the η^5 -C₅H₄CH₃ compounds decrease with increasing phosphine substitution in a similar manner to the carbonyl stretching frequencies of the η^5 -C₅H₅ compounds. Again, although the $\nu_{\text{max.}}$ values demonstrate that trimethylphosphine is a net donor of electron density relative to triphenylphosphine, the effect is slight relative to the effect of increasing substitution. The three sets of protons of the η^5 -C₅H₄CH₃ ligand are shielded with increasing phosphine substitution. However, no consistent shielding/deshielding effect is observed as the phosphines are varied within a given degree of substitution. The deshielding effect on the phosphorus nucleus on moving from a disubstituted complex to a monosubstituted complex is again apparent.

Scheme 3 Synthesis of cationic $\eta^5\text{-C}_5(\text{CH}_3)_5$ complexes of iron



I.1.4 Synthesis of cationic $\eta^5\text{-C}_5(\text{CH}_3)_5$ complexes of iron

$[\text{Fe}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{CO})_2]_2$ (23)¹⁹ and $[\text{Fe}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{CO})_2\text{Br}]$ (24)²⁰ were synthesised 17 and 10 years ago respectively and (24) has been converted to $[\text{Fe}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{CO})_3]\text{PF}_6$ (25) using 40 atmospheres of carbon monoxide and aluminium trichloride at 60 °C.²¹ At the outset of this study cationic derivatives of triphenylphosphine, trimethylphosphine and diphos were unknown; however $[\text{Fe}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{PMe}_3)(\text{CO})_2]\text{BF}_4$ (26) has recently been reported in the literature.²² The routes used to synthesise the cationic derivatives are summarised in Scheme 3.

Dicyclopentadiene and di(methylcyclopentadiene) are inexpensive, commercially available materials which are used liberally in the synthesis of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]_2$ (6) and $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)(\text{CO})_2]_2$ (15); these syntheses give low yields with respect to the diene. Commercially available 1,2,3,4,5-pentamethylcyclopentadiene however is prohibitively expensive, and tedious methods of synthesis have restricted its use as a ligand in organometallic chemistry. A recent communication²³ presented a relatively simple, inexpensive, four-step conversion of pentan-3-one and acetaldehyde to $\text{C}_5(\text{CH}_3)_5\text{H}$ making moderate quantities of $\text{C}_5(\text{CH}_3)_5\text{H}$ readily available. $\text{C}_5(\text{CH}_3)_5\text{H}$ prepared by this method was heated with iron pentacarbonyl and octane at 130 °C for 60 h to give $[\text{Fe}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{CO})_2]_2$ (23) in 73% yield based on $\text{C}_5(\text{CH}_3)_5\text{H}$. Although $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]\text{Na}$ can be produced from sodium amalgam reduction of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]_2$ (6), sodium amalgam reduction of (23) does not give $[\text{Fe}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{CO})_2]\text{Na}$ because of the more negative reduction potential of (23) relative to (6). ($E_{\frac{1}{2}} = -1.80\text{V/SCE}$ in DMF and $\text{Bu}_4\text{N}^+\text{Br}^-$

i.e. 0.36V more negative than (6)). This reflects the relative electron donating properties of C_5H_5 and $C_5(CH_3)_5$. Conversion of (23) into $[Fe(\eta^5-C_5(CH_3)_5)(CO)_2CH_3]$ by potassium mirror reduction followed by treatment with methyl iodide in 80% yield demonstrates that potassium efficiently reduces (23). However attempts to make $[Fe(\eta^5-C_5(CH_3)_5)(CO)_2Cl]$ by replacing 2% sodium amalgam with sodium/potassium alloy in the methods used for synthesis of $[Fe(\eta^5-C_5H_5)(CO)_2Cl]$ (7) and $[Fe(\eta^5-C_5H_4CH_3)(CO)_2Cl]$ (16) gave a very poor yield (15%) of the chloride. Cleavage of the metal-metal bond of (23) using bromine to give an alternative halogen derivative $[Fe(\eta^5-C_5(CH_3)_5)(CO)_2Br]$ (24) proceeded smoothly, but attempts to isolate cationic phosphine derivatives by heating (24) with a range of phosphines in a range of solvents all failed. This is attributed to the increase of electron density on the metal caused by permethylation of the $\eta^5-C_5H_5$ ligand. It is of note that a recent kinetic study on the substitution of $[M(\eta^5-C_5H_5)(CO)_2]$ ($M=Rh,Co$) and $[M(\eta^5-C_5(CH_3)_5)(CO)_2]$ with phosphines, phosphites and isocyanides showed that the reaction was generally retarded in the permethylated case, *e.g.* tributylphosphine reacts 100 times faster with $[Rh(\eta^5-C_5H_5)(CO)_2]$ than with $[Rh(\eta^5-C_5(CH_3)_5)(CO)_2]$ and whereas the two carbonyls of $[Co(\eta^5-C_5H_5)(CO)_2]$ are readily replaced by phosphites and isocyanides, only one carbonyl of $[Co(\eta^5-C_5(CH_3)_5)(CO)_2]$ can be replaced by these ligands.²⁴

Synthesis of the phosphine substituted cations was finally achieved by stepwise oxidative decarbonylation of $[Fe(\eta^5-C_5(CH_3)_5)(CO)_3]PF_6$ (25) (or $[Fe(\eta^5-C_5(CH_3)_5)(CO)_3]BF_4$ (25a)). The high pressure carbonylation used previously in the preparation of (25) was obviated by reduction of $[Fe(\eta^5-C_5(CH_3)_5)(CO)_2]_2$ (23)

using lithium naphthalenide (a more convenient reducing agent than either sodium/potassium alloy or a potassium mirror) to produce $[\text{Fe}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{CO})_2]\text{Li}$, treatment of this lithium salt with ethyl chloroformate, hydrogen chloride gas (or tetrafluoroboric acid) and finally anion exchange using ammonium hexafluorophosphate. Yields of (25) and (25a) were erratic (<39%) and this, coupled with the reduced supply of 1,2,3,4,5-pentamethylcyclopentadiene relative to dicyclopentadiene and di(methylcyclopentadiene), meant that the synthesis of the phosphine substituted cations derived from $\text{C}_5(\text{CH}_3)_5\text{H}$ was carried out on a much smaller scale than the synthesis of cations derived from $(\text{C}_5\text{H}_6)_2$ and $(\text{C}_5\text{H}_5\text{CH}_3)_2$. The communication by Davies¹⁶ demonstrating the use of Me_3NO hydrate as an oxidising agent sufficiently nucleophilic to remove two molecules of carbon monoxide from the tricarbonyl complex $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]\text{PF}_6$ (9), also demonstrates that DMSO selectively oxidises one molecule of carbon monoxide from (9) *i.e.* it is insufficiently nucleophilic to attack a carbonyl ligand which has been deactivated by an electron donating phosphine. Stirring $[\text{Fe}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{CO})_3]\text{PF}_6$ (25) with triphenylphosphine in DMSO indeed gave a good yield (78%) of $[\text{Fe}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{PPh}_3)(\text{CO})_2]\text{PF}_6$ (27) and stirring $[\text{Fe}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{CO})_3]\text{BF}_4$ (25a) with trimethylphosphine in DMSO also gave a good yield (81%) of $[\text{Fe}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{PMe}_3)(\text{CO})_2]\text{BF}_4$ (26). Addition of Me_3NO hydrate to a mixture of (25) and diphos in acetone gave consistently low yields of $[\text{Fe}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{diphos})(\text{CO})]\text{PF}_6$ (28).

The novel, yellow, crystalline, air-stable salts $[\text{Fe}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{PPh}_3)(\text{CO})_2]\text{PF}_6$ (27) and $[\text{Fe}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{PMe}_3)(\text{CO})_2]\text{BF}_4$ (26) were fully characterised by infra-red spectroscopy, ^1H n.m.r. and ^{31}P -(^1H) n.m.r. spectroscopy, mass spectrometry and elemental microanalysis. The novel, yellow, amorphous salt $[\text{Fe}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{diphos})(\text{CO})]\text{PF}_6$ (28) was characterised by infra-red spectroscopy, ^1H n.m.r. and ^{31}P -(^1H) spectroscopy and mass spectrometry. The infra-red spectrum, mass spectrum and ^1H n.m.r. spectrum of $[\text{Fe}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{CO})_3]\text{PF}_6$ (25) were recorded and compared with literature data (Tables 6a and 6b, p 93, 94). The mass spectra all contained molecular ion peaks. The carbonyl stretching mode absorption frequencies, the ^1H chemical shifts of the $\eta^5\text{-C}_5(\text{CH}_3)_5$ ligand and the ^{31}P chemical shifts of the phosphine ligands are given in Table 7.

Table 7 Selected spectroscopic data for $\eta^5\text{-C}_5(\text{CH}_3)_5$ cationic complexes of iron

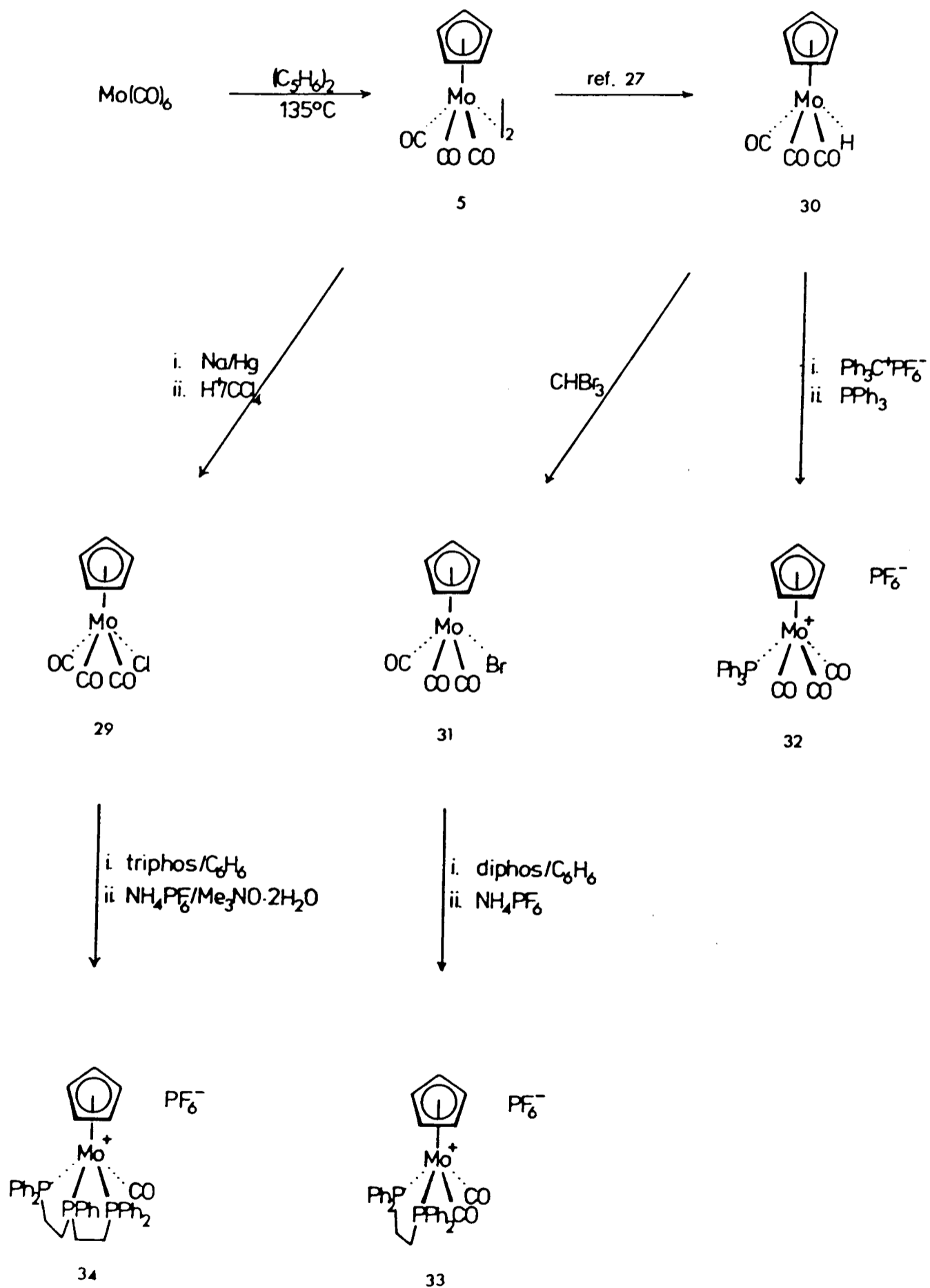
<u>Compound</u>		<u>$\nu_{\text{max.}}$ (cm^{-1})</u>	<u>δ $\text{C}_5(\text{CH}_3)_5$</u>	<u>δP</u>
$[\text{Fe}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{CO})_3]\text{PF}_6$	(25)	2 105, 2 040	2.2	
$[\text{Fe}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{PPh}_3)(\text{CO})_2]\text{PF}_6$	(27)	2 040, 1 987	1.85	61.6
$[\text{Fe}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{PMe}_3)(\text{CO})_2]\text{BF}_4$	(26)	2 070, 1 995	2.08	28.5
$[\text{Fe}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{diphos})(\text{CO})]\text{PF}_6$	(28)	1 940	1.42 [†]	86.3 [†]

† Data obtained on tetrafluoroborate salt.

The carbonyl stretching frequencies of the $\eta^5\text{-C}_5(\text{CH}_3)_5$ compounds decrease with increasing phosphine substitution in a similar manner to the carbonyl stretching frequencies of the $\eta^5\text{-C}_5\text{H}_5$ and $\eta^5\text{-C}_5\text{H}_4\text{CH}_3$ compounds. The protons of the

$\eta^5\text{-C}_5(\text{CH}_3)_5$ ligand are shielded with increasing phosphine substitution.

Scheme 4 Synthesis of cationic $\eta^5\text{-C}_5\text{H}_5$ complexes of molybdenum



I.1.5 Synthesis of cationic $\eta^5\text{-C}_5\text{H}_5$ complexes of molybdenum

The routes used to synthesise $\eta^5\text{-C}_5\text{H}_5$ complexes of molybdenum are summarised in Scheme 4.

$[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]_2$ (5)²⁵ and $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\text{Cl}]$ (29)²⁶ were prepared by standard literature procedures; reductive cleavage of the dimer by sodium amalgam led to $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]\text{Na}$. Subsequent protonation gave the hydride (30) which on radical halogenation by carbon tetrachloride gave $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\text{Cl}]$ (29) in good yield (65%). Alternatively $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\text{H}]$ (30) could be efficiently (88%) converted to $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\text{Br}]$ (31) by radical bromination using bromoform.²⁶

Treatment of (30)²⁷ with tritylhexafluorophosphate at $-30\text{ }^\circ\text{C}$ gave the 16-electron intermediate $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]\text{PF}_6$ which was readily attacked by triphenylphosphine to provide an excellent route to $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{CO})_3]\text{PF}_6$ (32)²⁸ in 77% yield. The thermolysis product of (31) and diphos was the disubstituted complex $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{diphos})(\text{CO})_2]\text{Br}$ (33a) and the thermolysis product of (29) and the tridentate ligand triphos was also a disubstituted complex; addition of Me_3NO hydrate led to the required trisubstituted complex $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{triphos})(\text{CO})]\text{Cl}$. Anion exchange with ammonium hexafluorophosphate gave the known salt $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{diphos})(\text{CO})_2]\text{PF}_6$ (33) and the novel salt $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{triphos})(\text{CO})]\text{PF}_6$ (34) in 64% and 30% yields respectively.

The novel, yellow, crystalline, air-stable salt $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{triphos})(\text{CO})]\text{PF}_6$ (34) was fully characterised by infra-red spectroscopy, ^1H n.m.r. and ^{31}P -(^1H) n.m.r. spectroscopy, mass spectrometry and elemental microanalysis. The infra-red

spectra, mass spectra and ^1H n.m.r. and ^{31}P -(^1H) n.m.r. spectra of $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{CO})_3]\text{PF}_6$ (32) and $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{diphos})(\text{CO})_2]\text{PF}_6$ (33) were recorded and compared with literature data where available (Table 8, p 98). The mass spectra all contained isotope patterns corresponding to the molecular ion. The carbonyl stretching mode absorption frequencies, the ^1H chemical shifts of the $\eta^5\text{-C}_5\text{H}_5$ ligand and the ^{31}P chemical shifts of the phosphine ligands are given in Table 9.

Table 9 Selected spectroscopic data for $\eta^5\text{-C}_5\text{H}_5$ cationic complexes of molybdenum

<u>Compound</u>		<u>$\nu_{\text{max.}}$ (cm^{-1})</u>	<u>$\delta_{\text{C}_5\text{H}_5}$</u>	<u>δ_{P}</u>
$[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{CO})_3]\text{PF}_6$ (32)		2 060, 1 995, 1 960	6.05	44.1
$[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{diphos})(\text{CO})_2]\text{PF}_6$ (33)		1 990, 1 920	5.08	77.5
$[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{triphos})(\text{CO})]\text{PF}_6$ (34)		1 863	5.0	105.5, 88.7

Again, the carbonyl stretching frequencies of the compounds decrease with increasing phosphine substitution and the protons of the $\eta^5\text{-C}_5\text{H}_5$ ligands are shielded with increasing phosphine substitution. The details of the ^{31}P -(^1H) n.m.r. spectrum of (34) are given in Fig. 3; the presence of two signals in the spectrum reveals a plane of symmetry in the cation.

^1P , $\delta = 88.7$, d, $J = 35$ Hz

^{31}P , $\delta = 105.5$, t, $J = 35$ Hz

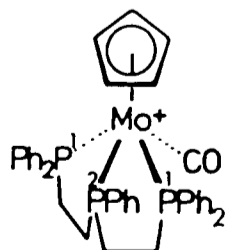


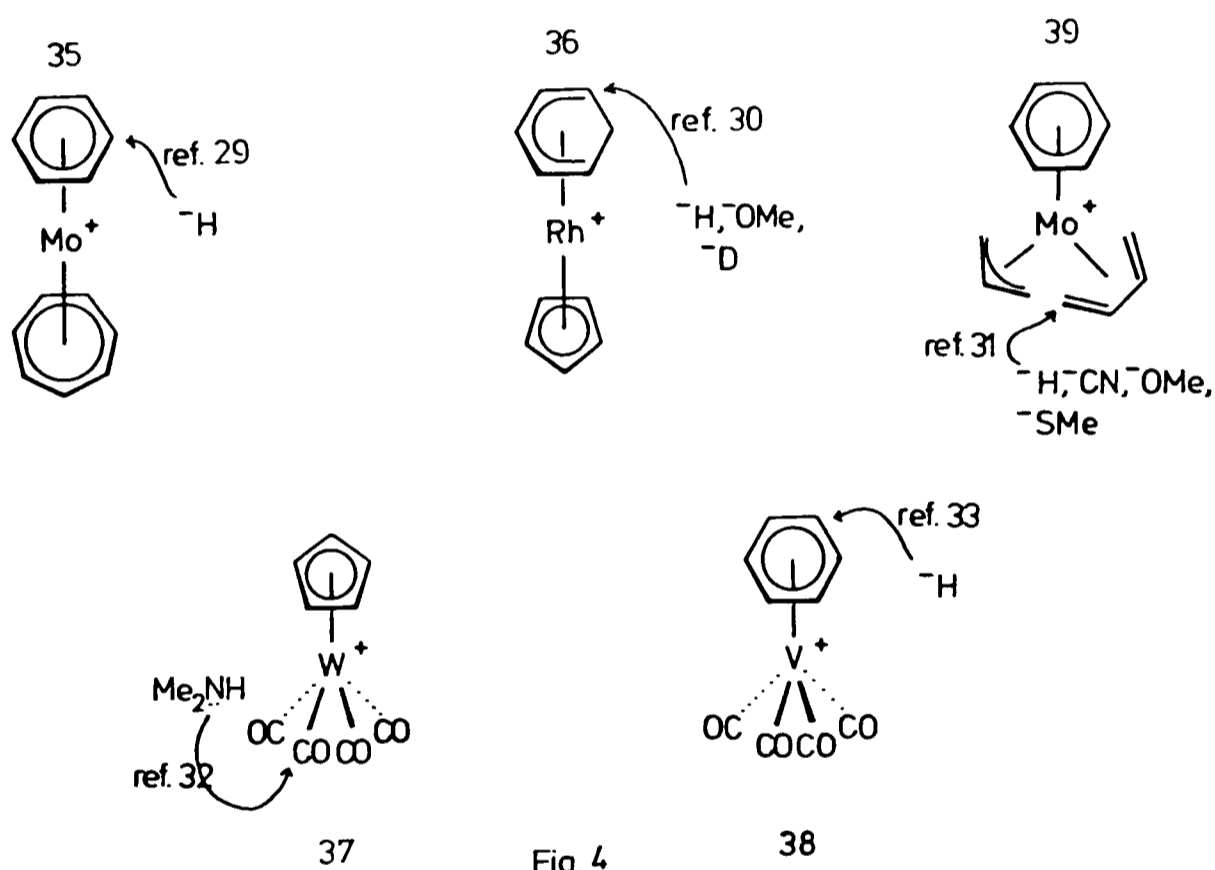
Fig. 3

I.1.6 Conclusions

The cations, many of them novel, used in the studies described in Sections I.2 and I.3 and depicted in a generalised form on p 6 have been synthesised. The carbonyl stretching mode absorption frequencies reflect the increased electron density available at the metal for π -donation resulting from replacement of carbonyl groups with phosphines and permethylation of the $\eta^5\text{-C}_5\text{H}_5$ ligand. The increase in electron density available at the metal as a result of phosphine substitution is also reflected in the ^1H chemical shifts of the $\eta^5\text{-C}_5\text{H}_5$, $\eta^5\text{-C}_5\text{H}_4\text{CH}_3$ and $\eta^5\text{-C}_5(\text{CH}_3)_5$ ligands. The ^{31}P chemical shifts of the phosphine ligands revealed little.

I.2.1 IntroductionRegioselectivity of nucleophilic attack on transition metal cations

Nucleophilic addition to 18-electron organotransition metal cations is a fundamental reaction in organometallic chemistry. A number of 18-electron cationic complexes are illustrated in Fig. 4.



There is more than one possible site in each cation at which nucleophilic attack may occur, *i.e.* (35) may be attacked at the η^6 -C₆H₆ ligand and the η^7 -C₇H₇ ligand, (36) may be attacked at three positions on the η^5 -C₆H₇ ligand and at the η^5 -C₅H₅ ligand *etc.* Cations (37) and (38) may be attacked at the hydrocarbon ligands and at the carbon atoms of the carbonyl ligands. (The metal is eliminated as a possible site of attack as it is co-ordinatively and electronically saturated.)

Generally however, nucleophilic addition to 18-electron organotransition metal cations is regiospecific and the arrows in Fig. 4 indicate the position of attack by the named nucleophiles. A number of simple rules have been proposed which, if used sequentially, predict the position of attack of a nucleophile on unsaturated hydrocarbon ligands in 18-electron organotransition metal cations for reactions that are kinetically rather than thermodynamically controlled.³⁴

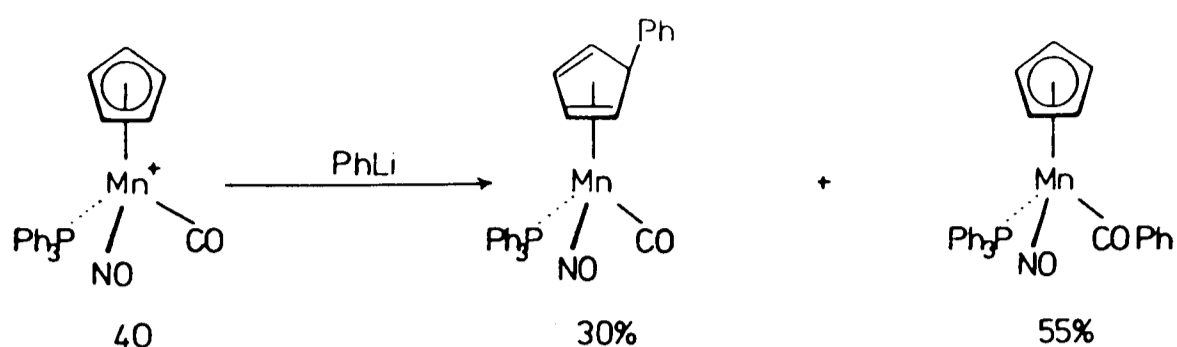
Rule 1. Nucleophilic attack occurs preferentially at even[†] co-ordinated polyenes which have no unpaired electrons in their homo's.

Rule 2. Nucleophilic addition to open[†] co-ordinated polyenes is preferred to addition to closed polyenes.

Rule 3. For even open polyenes nucleophilic attack at the terminal carbon atom is always preferred, for odd open polyenyls attack at the terminal carbon atom occurs only if the remainder of the metal complex is strongly electron withdrawing.

It is apparent that the position of nucleophilic attack on cations (35), (36) and (39) in Fig. 4 is governed by these rules and in general, the position of nucleophilic addition to any 18-electron organotransition metal cation containing unsaturated ligands can be predicted using the rules.

† The terms even and odd refer to the parity of the ligand *hapto* number. Ligands which are cyclically conjugated and those which are not are described as closed and open respectively.



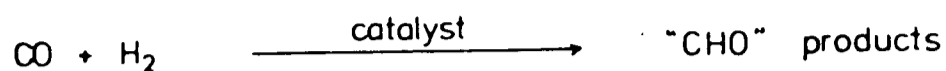
The site of nucleophilic attack on cations containing $\eta^5\text{-C}_5\text{H}_5$ and carbonyl ligands has not been rationalised and no systematic study has been undertaken on the effect of replacing carbonyl ligands with tertiary phosphines and substituting hydrogen atoms with methyl groups on the $\eta^5\text{-C}_5\text{H}_5$ ligand. In order to discover the site of nucleophilic attack on the transition metal cations synthesised in Section I.1, a model study was proposed using hydride as the nucleophile. It was of interest to determine whether a) increasing tertiary phosphine content and b) increasing methylation of the $\eta^5\text{-C}_5\text{H}_5$ ligand would influence the site of nucleophilic attack.

If hydride attacks the cations to be studied at a carbon monoxide ligand, a metal formyl species will be produced; metal formyls are postulated intermediates in the catalytic reduction of carbon monoxide (Fischer-Tropsch Synthesis and related reactions).

The Fischer-Tropsch Synthesis and related reactions

The Fischer-Tropsch Synthesis and related reactions are an attractive alternative to the refinement of crude oil as a source of chemical feedstocks. They involve the catalytic conversion of synthesis gas (a mixture of carbon monoxide and hydrogen produced by burning coal in the presence of oxygen and

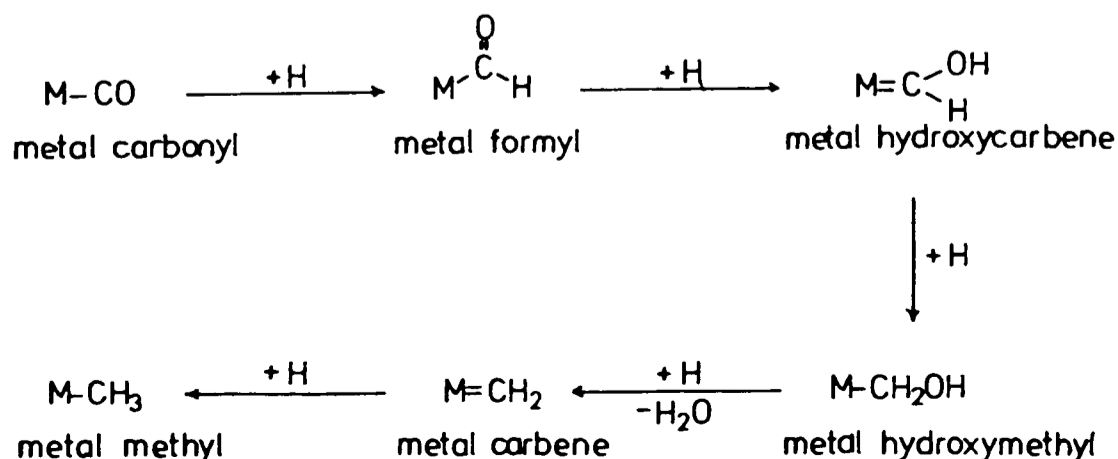
steam) into a range of organic molecules containing carbon, hydrogen and oxygen.



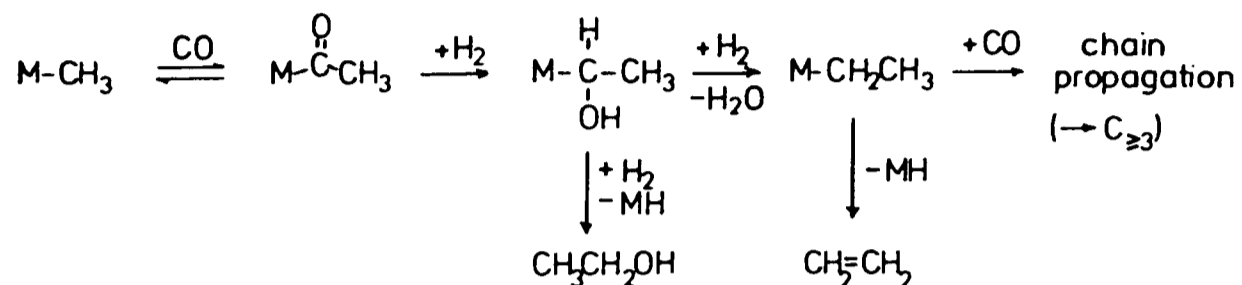
Economically, the Fischer-Tropsch Synthesis could only compete with crude oil as a source of chemical feedstocks if the selectivity of the process was improved or if crude oil was scarce and coal was comparatively cheap; the latter requirements are met in South Africa and indeed the process is applied commercially there to synthesise hydrocarbons. Research into producing an increase in selectivity of the Synthesis is currently popular and it is generally agreed that the development of new catalysts, in particular homogeneous catalysts with their increased potential for selectivity, deserves primary attention.³⁶

Elucidation of the mechanism of the reduction of carbon monoxide may well aid the design of new catalysts. Any mechanism proposed must account for the fact that the primary products are alkenes and alcohols (saturated hydrocarbons arise independently from alkene hydrogenation).

The currently most popular mechanism is based upon carbon monoxide insertion into a metal carbon bond as the fundamental chain growth step.³⁷ According to this mechanism a metal-bound carbon monoxide molecule is reduced *via* a metal formyl species to a methyl group attached to the metal.

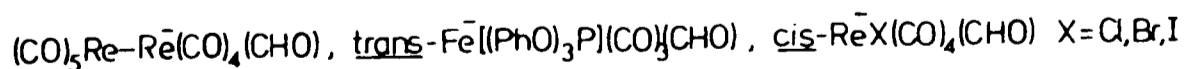


Carbon monoxide insertion followed by stepwise reduction of the resulting metal acetyl gives intermediates which are precursors to ethanol and ethene. Further carbon monoxide insertion results in chain propagation and the formation of higher homologues.



Metal formyls

As catalyst-bound formyls are believed to be the initial intermediates in the conversion of carbon monoxide and hydrogen mixtures to organic products, a study of their basic chemistry may provide some insight into catalytic reaction pathways. The first metal complex containing a formyl ligand to be isolated was the anionic species $[\text{Fe}(\text{CO})_4(\text{CHO})]^-$, prepared in 1973 by the reaction of $[\text{Fe}(\text{CO})_4]^{2-}$ with formic acetic anhydride.³⁸ Subsequently, a number of anionic formyl complexes were prepared by the reaction of neutral metal carbonyls with powerful hydride donors. Most of the formyls synthesised were unstable, decomposing below room temperature; examples that proved stable enough for isolation are shown below.^{39, 40, 41}

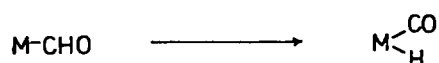


Hydridic reagents required forcing conditions to reduce formyl ligands on anionic complexes and so attention was turned towards the synthesis of neutral formyl complexes whose chemistry might resemble more closely that of catalyst-bound formyls. The

first neutral formyl complex $\text{OsCl}(\text{PPh}_3)_2(\text{CO})(\text{CN-}p\text{-C}_6\text{H}_4\text{CH}_3)(\text{CHO})$ was isolated⁴² in 1978 and other examples shown below are now known.^{43, 44, 45}

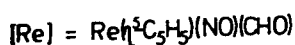
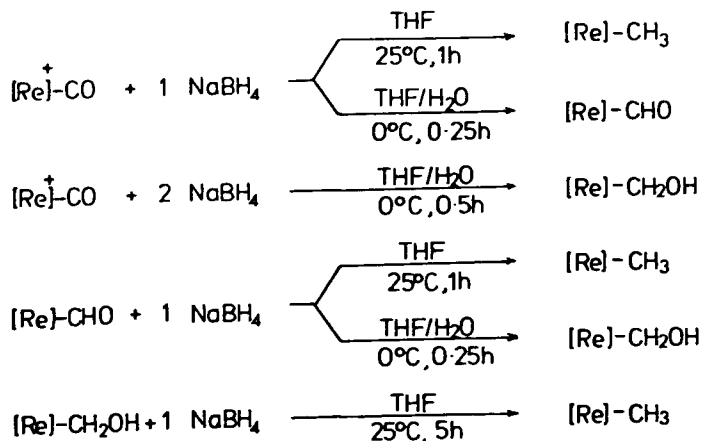


Metal formyls generally remain elusive however due to their thermodynamic instability with respect to a carbonyl hydride species.



The kinetic stability of the rare examples of isolated metal formyls is attributed to ligand dissociation being an unfavourable process in these compounds. Dissociation from the electronically saturated centres is required before decomposition to the thermodynamically stable carbonyl hydride can occur.

The isolation of $[\text{Re}(\eta^5\text{-C}_5\text{H}_5)(\text{NO})(\text{PPh}_3)(\text{CHO})]$ was achieved as a result of a study which demonstrated the stepwise reduction of co-ordinated carbon monoxide to a methyl ligand.⁴⁴ Reduction of $[\text{Re}(\eta^5\text{-C}_5\text{H}_5)(\text{NO})(\text{CO})_2]\text{BF}_4$ using sodium borohydride under various reaction conditions led to the isolation of complexes with formyl, hydroxymethyl and methyl ligands.

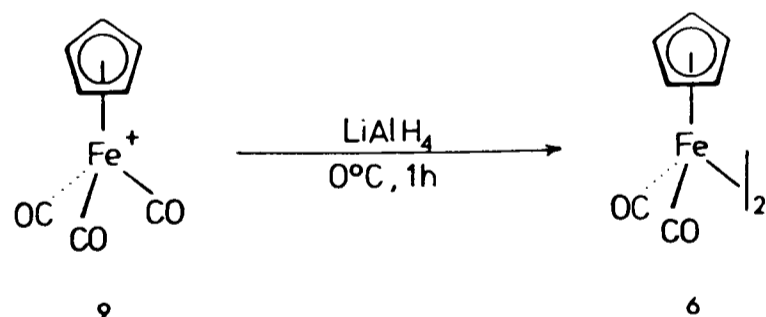


Objectives 2

If regioselective addition of hydride to a carbonyl ligand of the cations synthesised in Section I.1 was achieved, the resultant metal formyl may undergo further reaction. Decomposition to the thermodynamically favoured carbonyl hydride may occur, or further reduction of the carbon monoxide ligand to hydroxymethyl, methyl *etc.* is possible. It was of interest to determine whether varying the tertiary phosphine content (and the nature of the phosphine) and methylating the $\eta^5\text{-C}_5\text{H}_5$ ligand would affect the stability and fate of a metal formyl.

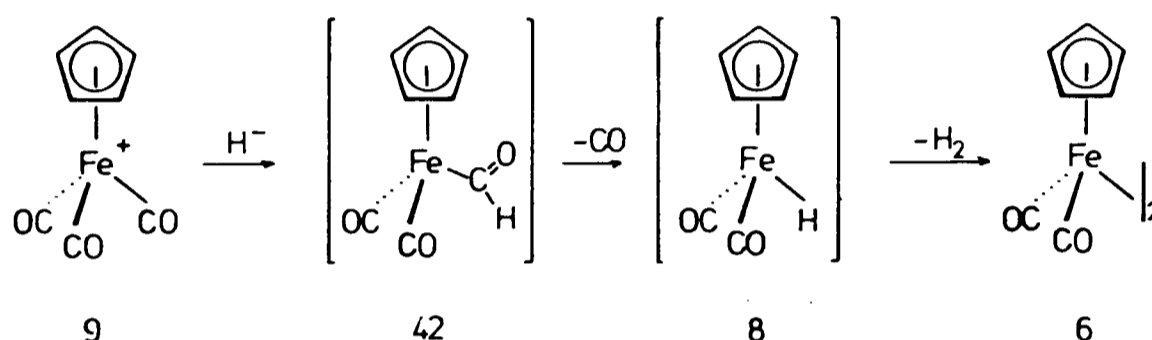
I.2.2 Hydride reduction of cationic $\eta^5\text{-C}_5\text{H}_5$ iron complexes

The yellow crystalline salt $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]\text{PF}_6$ (9) was stirred with an excess of LiAlH_4 at 0°C in tetrahydrofuran. After one hour, water was added to the resultant yellow-brown solution to hydrolyse any remaining LiAlH_4 . The solvent was removed under reduced pressure and the residue extracted with diethyl ether to give a red solution. (The residue was colourless, indicating that the cation had been completely converted into a neutral species.) The diethyl ether solution was dried and removal of solvent gave a red solid which was identified as $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]_2$ (6) by comparison of its infra-red and ^1H n.m.r. spectra with those of an authentic sample. (The infra-red spectrum contained three strong bands in the carbonyl region at 2010 and 1965 cm^{-1} due to terminal carbonyls and at 1785 cm^{-1} due to bridging carbonyls; the ^1H n.m.r. spectrum contained a singlet at $\delta 4.2$.)



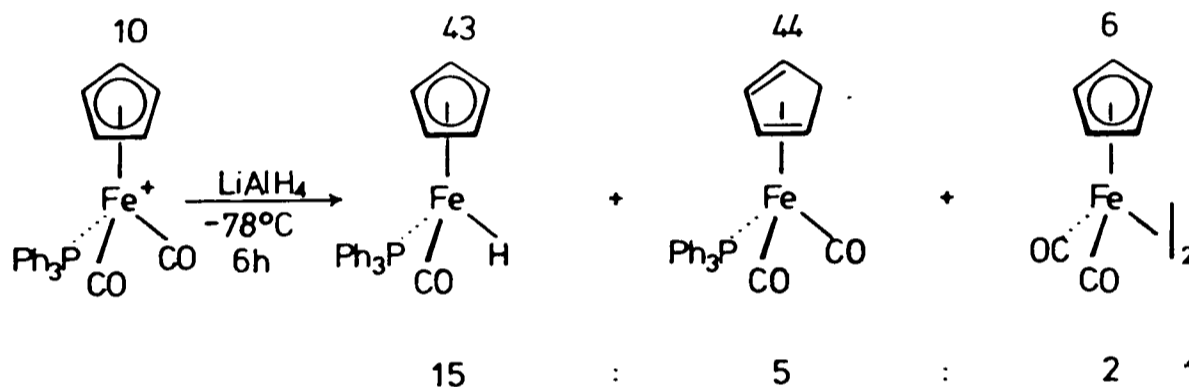
There was no evidence for the formation of any of the diene $[\text{Fe}(\eta^4\text{-C}_5\text{H}_6)(\text{CO})_3]$ (41) which would result from nucleophilic attack on the $\eta^5\text{-C}_5\text{H}_5$ ligand. This result is consistent with the isolation of (6) only from the reduction of (9) with NaBH_4 at -20°C .⁴⁶ It is known that $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{H}]$ (8), formed by the action of NaBH_4 on $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Cl}]$ (7), is thermally unstable at room temperature decomposing to (6) and hydrogen.⁴⁷

and it has been shown that vigorous conditions (heating at 140 °C for 4 hours) are required to convert the stable isolable diene (41) into (6).⁴⁸ It would seem reasonable therefore that initial attack of hydride occurs on the carbon monoxide ligand rather than on the $\eta^5\text{-C}_5\text{H}_5$ ligand to give the metal formyl (42) which decomposes to the carbonyl hydride (8) by loss of a carbon monoxide ligand; decomposition of (8) leads to the observed product (6).

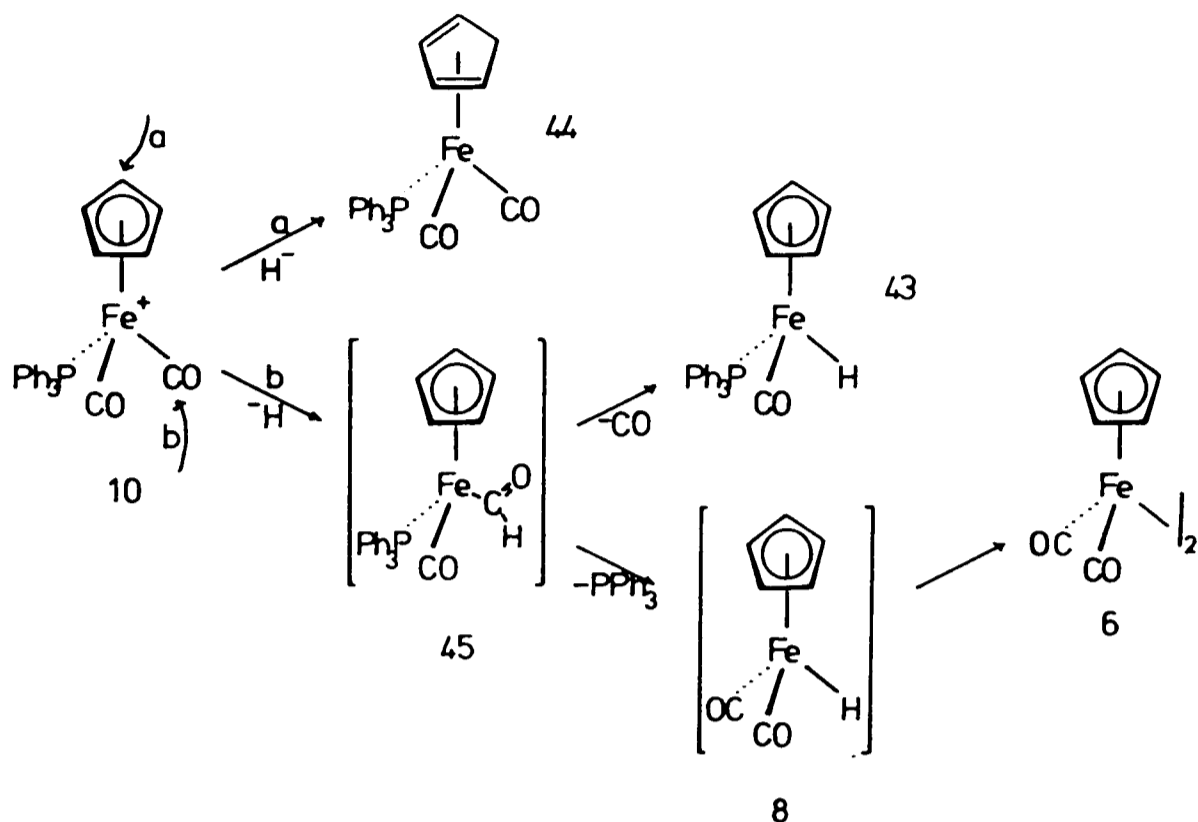


The yellow crystalline salt $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{CO})_2]\text{PF}_6$ (10) was stirred with an excess of LiAlH_4 at -78 °C for 6 hours in tetrahydrofuran. Hydrolysis, removal of solvent and extraction with diethyl ether gave colourless extracts indicating that there were no reduction products present in the residue. The experiment was repeated using a 1:1 mixture of dichloromethane and tetrahydrofuran to solubilise the cation and this time the extracts were yellow-brown. After drying the combined extracts, removal of the solvent produced an air-sensitive brown oil which was identified as a 15:5:2 mixture of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{CO})\text{H}]$ (43), $[\text{Fe}(\eta^4\text{-C}_5\text{H}_6)(\text{PPh}_3)(\text{CO})_2]$ (44) and $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]_2$ (6) respectively by comparison of its infra-red and ^1H n.m.r. spectra with those of authentic samples. The metal hydride (43) gave rise to a characteristic high-field doublet at $\delta -12.8$ ($^2J_{\text{PH}} = 74\text{Hz}$) due to the hydrogen bonded to iron and a singlet at $\delta 4.2$ due to the protons of the $\eta^5\text{-C}_5\text{H}_5$ ligand.

The diene (44) was identified by resonances at δ 5.1 and 2.8 due to $H_{2,3}$ and H_{endo} and at δ 2.2 due to $H_{1,4}$ and H_{exo} . (See Section I.2.6 for assignment of diene protons) and (6) was identified by the three characteristic strong bands in the infra-red spectrum at 2 000, 1 970 and 1 785 cm^{-1} and a singlet in the ^1H n.m.r. spectrum at δ 4.05. Integration of the resonances due to the diene protons against the resonances due to the $\eta^5\text{-C}_5\text{H}_5$ ligands of (6) and (43) gave the ratio of products.

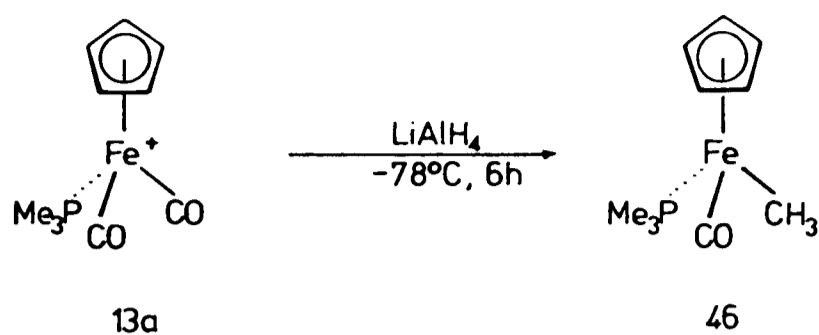


Replacement of a carbonyl ligand with the electron donating triphenylphosphine feeds electrons onto the $\eta^5\text{-C}_5\text{H}_5$ ligand and the carbon monoxide ligand; the extent of this donation is reflected in the extent of attack at each site (assuming addition is irreversible) and it appears that nucleophilic attack at the carbon monoxide is favoured over nucleophilic attack at the $\eta^5\text{-C}_5\text{H}_5$ ligand by a factor of 3.4. Attack at the carbon monoxide ligand gives rise to the formyl (45) which decomposes either by loss of carbon monoxide to form (43) or by loss of phosphine to give (8) and ultimately the observed (6). The former pathway is favoured over the latter pathway by a factor of 7.5.

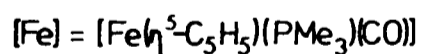
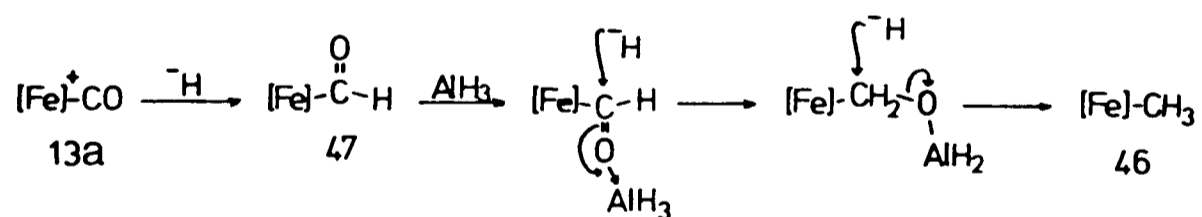


It is of note that reduction of (10) with NaBH₄ at -10 °C gave (44) in 75% yield and (6) in 7-8% yield.⁴⁶ This suggests that attack on carbon monoxide is kinetically favoured over attack on the η⁵-C₅H₅ ligand.

The reduction of [Fe(η⁵-C₅H₅)(PMe₃)(CO)₂]PF₆ (13a) was carried out by S. D. Moon, a co-worker.⁴⁹ The cation (13a) was treated with excess LiAlH₄ in tetrahydrofuran at -78 °C for 6 hours and subsequently quenched with water. Removal of solvent, extraction of the residue with toluene followed by the removal of toluene led to an orange oil which was shown to be [Fe(η⁵-C₅H₅)(PMe₃)(CO)CH₃] (46).

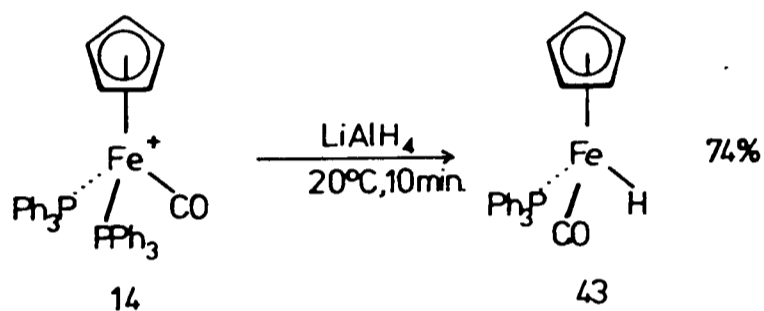


The reduction of (13a) in CD_2Cl_2 at low temperature was monitored by ^1H n.m.r. spectroscopy. On warming a mixture of (13a), LiAlH_4 and CD_2Cl_2 from -78°C to -60°C , a characteristic metal formyl proton resonance appeared at δ 15.4 (d, $^3J_{\text{PH}} = 5\text{Hz}$). Reduction of (13a) to (46) reveals that strong donation of electron density from trimethylphosphine favours attack on the carbon monoxide ligand. It also stabilises the resultant metal formyl (47) with respect to decomposition *via* carbon monoxide loss or phosphine loss. The stability of the metal formyl (47) allows further Lewis acid catalysed attack by hydride to give the product (46).

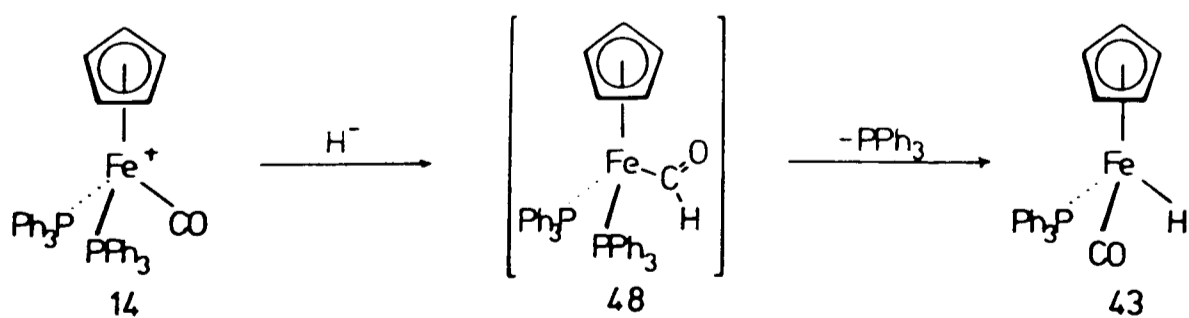


The orange crystalline salt $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2(\text{CO})]\text{PF}_6$ (14) was treated with LiAlH_4 at 20°C for 10 minutes. After hydrolysis of the resultant yellow solution, removal of solvent and extraction with diethyl ether gave a yellow solution which was filtered through alumina and the solvent evaporated to give an air-sensitive yellow powder. The infra-red spectrum of the powder contained a terminal carbonyl stretch at 1930 cm^{-1} ;

the ^1H n.m.r. spectrum contained a characteristic iron hydride doublet at $\delta -13.0$ ($^2J_{\text{PH}} = 75\text{Hz}$) indicating that only one phosphine remained bound to the iron, a singlet at $\delta 4.2$ due to an $\eta^5\text{-C}_5\text{H}_5$ ligand and a multiplet at $\delta 7.7\text{-}6.9$ due to phenyl protons. The compound was assigned as $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{CO})\text{H}]$ (43) and this was confirmed by comparison of the above data with literature data.⁵⁰ [The carbonyl hydride (43) was previously synthesised by the action of triphenylphosphine on $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{H}]$ (8).]^{50a}

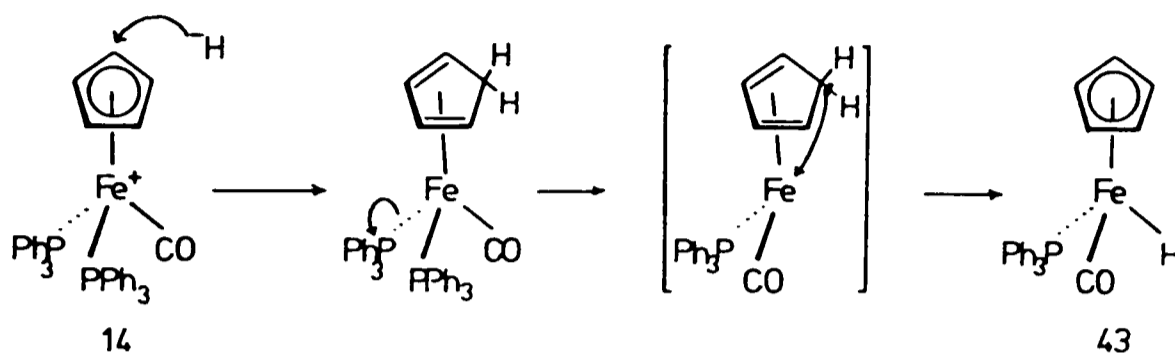


The effect of two electron donating phosphine ligands on the charge distribution in the cation (14) directs nucleophilic attack to the carbonyl ligand even at room temperature. (There was no evidence for nucleophilic addition to the $\eta^5\text{-C}_5\text{H}_5$ ligand.) The resultant metal formyl (48) decomposes by loss of triphenylphosphine.



The reduction of (14) was repeated using LiAlD_4 in order to ascertain that the carbon monoxide ligand was indeed the site of

attack. If the alternative mechanism outlined in Scheme 6 is valid then the use of LiAlD_4 as the reducing agent will lead to deuterium incorporation into the $\eta^5\text{-C}_5\text{H}_5$ ligand.



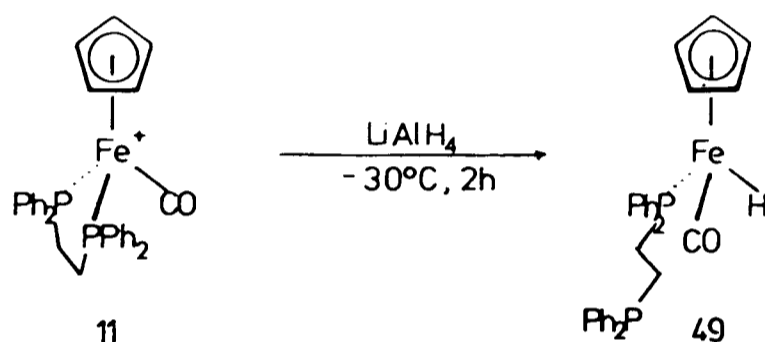
Scheme 6

The product of the LiAlD_4 reduction $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{CO})\text{D}]$ (43a) contained less than 1% of the protio-compound (43) as shown by ^1H n.m.r. spectroscopy and no detectable deuterium incorporation into the $\eta^5\text{-C}_5\text{H}_5$ moiety as shown by ^2H n.m.r. spectroscopy. The ^2H n.m.r. spectrum of (43a) contained a doublet at $\delta -12.8$ ($^2J_{\text{PD}} = 11.4\text{Hz}$) and the mass spectrum of (43a) contained a molecular ion peak. Isolation of (43a) in 84% yield eliminates the mechanism postulated in Scheme 6.

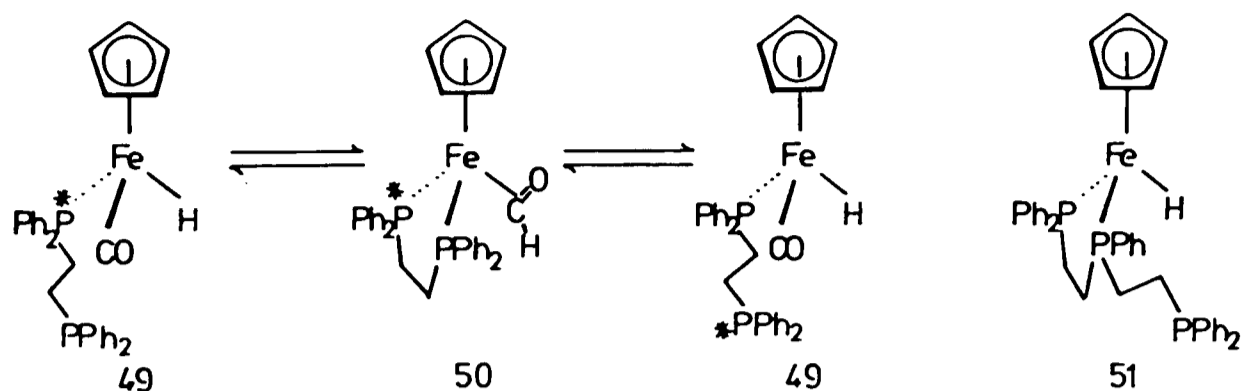
Decomposition of formyl (48) to the carbonyl hydride (43) requires prior dissociation of a triphenylphosphine ligand as the metal centre is electronically and co-ordinatively saturated. It was postulated that if the dissociation also occurred to an appreciable extent in cation (14) then the two triphenylphosphine ligands in (14) might be exchanged for a diphos ligand. The chelating properties of the diphos ligand provide an entropic driving force for such an exchange. A solution of (14) and diphos in tetrahydrofuran-dichloromethane (1:1) was monitored by ^{31}P n.m.r. spectroscopy. After 18 hours at 20°C no phosphine exchange had occurred. This result is consistent

with the phosphine being more tightly bound in cations than in neutral complexes.

Extensive studies into the reduction of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{diphos})(\text{CO})]\text{PF}_6$ (11) were carried out by co-workers Dr. S. J. Simpson, Dr. O. Watts and J. Hibberd.⁵¹ Treatment of cation (11) with excess LiAlH_4 in dichloromethane-tetrahydrofuran (1:1) or neat tetrahydrofuran at -30°C for 2 hours followed by hydrolysis and work-up led to a microcrystalline yellow solid which was shown to be $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{diphos})(\text{CO})\text{H}]$ (49).

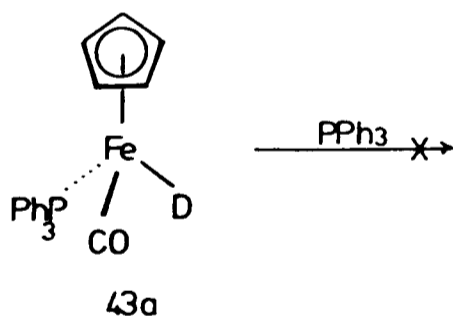


The reduction of (11) in $[\text{}^2\text{H}_8]$ tetrahydrofuran at low temperature was monitored by ^1H n.m.r. spectroscopy. On warming a mixture of (11), LiAlH_4 and $[\text{}^2\text{H}_8]$ tetrahydrofuran from -78°C to -70°C , a metal formyl resonance appeared at δ 11.53; the resonance rapidly disappeared above -50°C . It is of note that the carbonyl hydride (49) was used to demonstrate the existence of an equilibrium between the carbonyl hydride (49) and the formyl species (50). ^{31}P N.m.r. saturation-transfer experiments clearly demonstrated that the co-ordinated and unco-ordinated phosphorus atoms were rapidly equilibrating in (49) but not in the phosphine hydride (51). Exchange via the formyl (50) is the only possible mechanism available to (49) that is unavailable to (51).



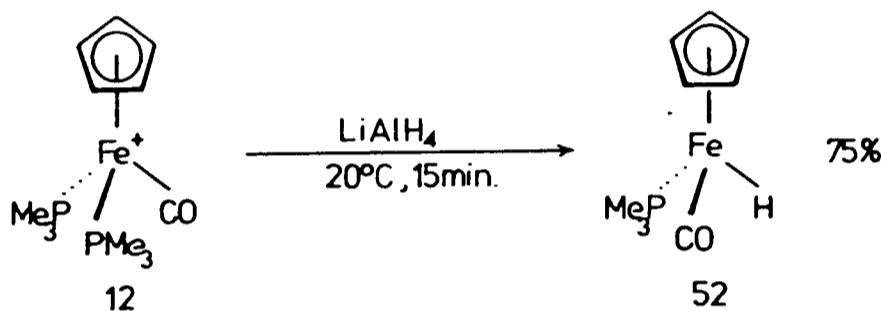
This was the first demonstration of an equilibrium between a formyl and a carbonyl hydride; such an equilibrium is considered to be an essential feature of the Fischer-Tropsch reaction.

Insertion of carbon monoxide into a metal-deuterium bond promoted by free triphenylphosphine (*i.e.* reversal of formyl decomposition) was attempted with $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{CO})\text{D}]$ (43a). Stirring (43a) in toluene saturated with triphenylphosphine for 3 days at 0 °C and 3 days at 20 °C gave no new products as shown by ^{31}P spectroscopy.

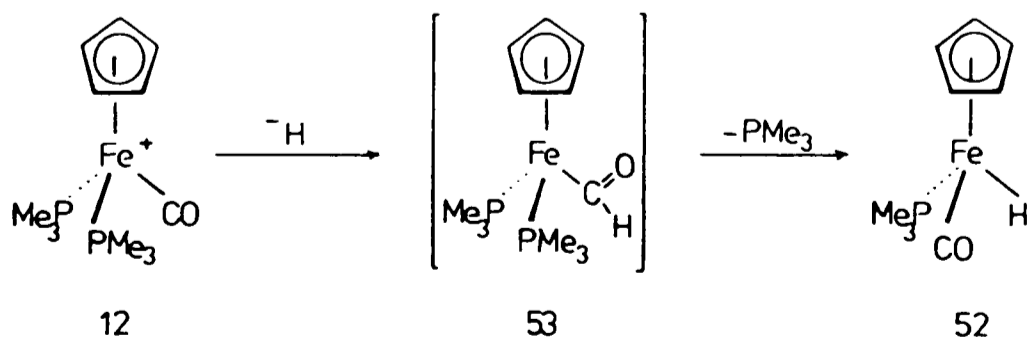


The yellow crystalline salt $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{PMe}_3)_2(\text{CO})]\text{PF}_6$ (12) was treated with LiAlH_4 at 20 °C for 15 minutes. Hydrolysis, removal of solvent and extraction with diethyl ether led to a yellow solution. Filtration through alumina and removal of solvent gave air-sensitive yellow crystals which gave an infra-red spectrum containing one terminal carbonyl stretch at 1 920 cm^{-1} . The ^1H n.m.r. spectrum of the crystals contained a characteristic iron hydride doublet at $\delta -14.0$ ($^2J_{\text{PH}} = 10\text{Hz}$)

indicating that only one phosphine remained bound to the iron, a doublet at δ 4.2 ($^3J_{\text{PH}} = 1\text{Hz}$) due to an $\eta^5\text{-C}_5\text{H}_5$ ligand coupled to one phosphorus atom and a doublet at δ 0.95 ($^2J_{\text{PH}} = 10\text{Hz}$) due to the protons of a trimethylphosphine ligand. The compound was assigned as $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{PMe}_3)(\text{CO})\text{H}]$ (52) and this was confirmed by comparison of the above data with literature data.^{50a} [The carbonyl hydride (52) was previously synthesised by the action of trimethylphosphine on $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{H}]$ (8).^{50a}]

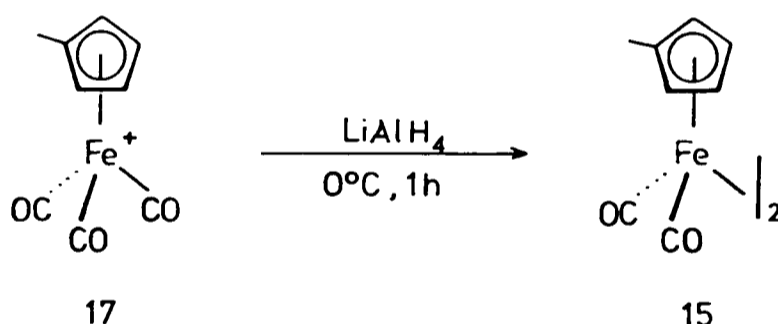


Once again it is evident that the effect of two electron donating phosphine ligands on the charge distribution in the cation (12) directs nucleophilic attack to the carbonyl ligand even at room temperature. (There was no evidence for hydride attack at the $\eta^5\text{-C}_5\text{H}_5$ ligand.) The resultant metal formyl (53) decomposes to the carbonyl hydride (52) by loss of trimethylphosphine.



I.2.3 Hydride reduction of cationic $\eta^5\text{-C}_5\text{H}_4\text{CH}_3$ iron complexes

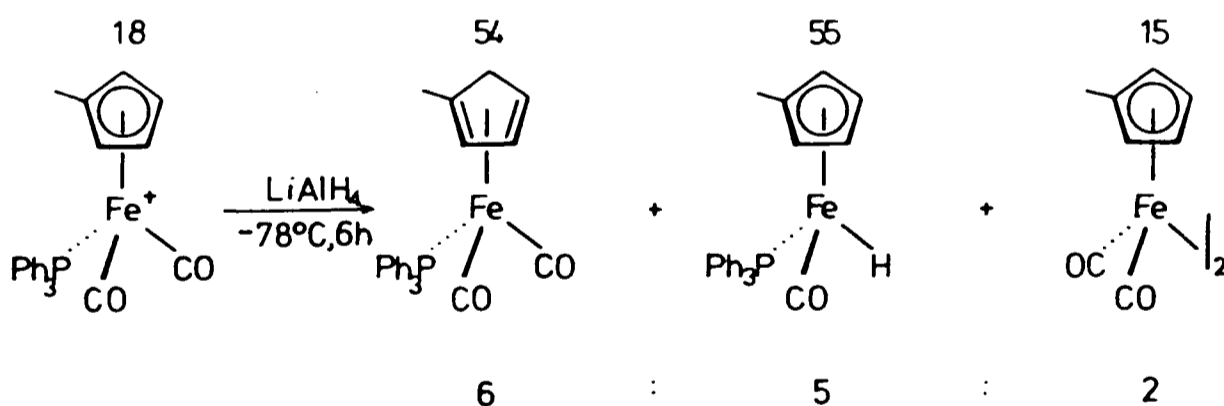
Treatment of the crystalline yellow salt $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)(\text{CO})_3]\text{PF}_6$ (17) with excess LiAlH_4 at 0°C in tetrahydrofuran for one hour led to a yellow-brown solution; hydrolysis followed by work-up gave a red solid. The infra-red spectrum of the solid contained three bands in the carbonyl region, two at 2005 and 1955 cm^{-1} due to terminal carbonyls and one at 1780 cm^{-1} due to bridging carbonyls; the ^1H n.m.r. spectrum of the solid contained a broad singlet at $\delta 4.5$ due to the diene protons of an $\eta^5\text{-C}_5\text{H}_4\text{CH}_3$ ligand and a singlet at $\delta 2.05$ due to the methyl protons of an $\eta^5\text{-C}_5\text{H}_4\text{CH}_3$ ligand. Identification of the red solid as $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)(\text{CO})_2]_2$ (15) was confirmed by comparison of the data above with the data of an authentic sample.



This result is analogous to the result obtained for the reduction of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]\text{PF}_6$ (9).

The yellow crystalline salt $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)(\text{PPh}_3)(\text{CO})_2]\text{PF}_6$ (18) was stirred with an excess of LiAlH_4 at -78°C for 6 hours in tetrahydrofuran. Hydrolysis and work-up led to the isolation of an air-sensitive yellow-brown solid which was identified as a 6:5:2 mixture of $[\text{Fe}(1\text{-methyl-}\eta^4\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{CO})_2]$ (54), $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)(\text{PPh}_3)(\text{CO})\text{H}]$ (55) and $[(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)(\text{CO})_2]_2$ (15) respectively by comparison of its infra-red and ^1H n.m.r. spectra with those of samples prepared by alternative routes. The

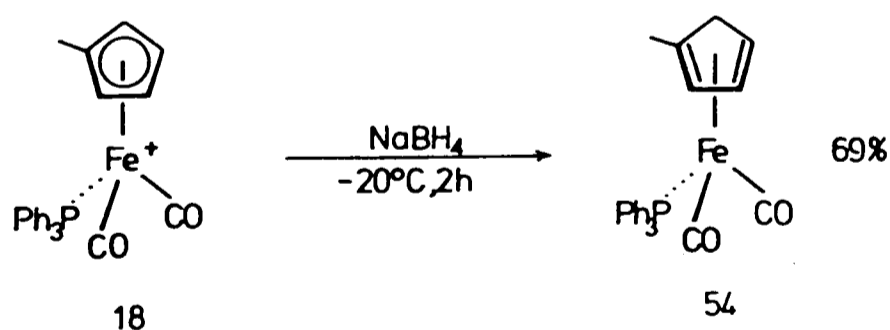
metal hydride (55) gave rise to a characteristic high-field doublet at δ -12.72 (${}^2J_{\text{PH}}=80\text{Hz}$) due to the hydrogen bonded to iron and was further identified by the presence of four one-proton singlets at δ 4.35, 4.25, 4.10 and 3.95 and a three-proton singlet at δ 1.85 due to the protons of the $\eta^5\text{-C}_5\text{H}_4\text{CH}_3$ ligand. The diene (54) was identified by resonances at δ 5.15 and 4.70 due to H_2 and H_3 , a doublet at δ 2.75 due to H_{endo} , a triplet at δ 2.40 due to H_{exo} a singlet at δ 1.85 due to H_4 and a singlet at δ 1.53 due to the methyl group at C-1 of the diene. (See Section I.2.6 for assignment of diene protons.) The dimer (15) was identified by the three characteristic strong bands in the infra-red spectrum at 2 010, 1 965 and 1 775 cm^{-1} and a singlet in the ${}^1\text{H}$ n.m.r. spectrum at δ 1.95 due to the methyl protons of the $\eta^5\text{-C}_5\text{H}_4\text{CH}_3$ ligand. Integration of the resonances due to the methyl group on the hydrocarbon ligand of each compound gave the ratio of products.



The lack of regiospecificity in this reaction is analogous to the result obtained for the reduction of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{CO})_2]\text{PF}_6$ (10).

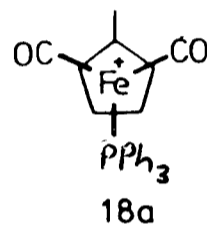
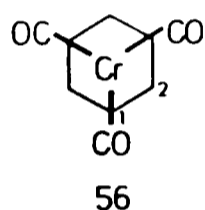
Although nucleophilic attack of (18) by hydride at -78°C showed no regiospecificity with respect to the η^5 -hydrocarbon ligand and the carbonyl ligands, the ${}^1\text{H}$ n.m.r. spectrum indicated that addition to the $\eta^5\text{-C}_5\text{H}_4\text{CH}_3$ ligand had only occurred at one

of three possible sites of reaction. A reduction was performed at $-20\text{ }^{\circ}\text{C}$ therefore, in order to direct nucleophilic addition towards the $\eta^5\text{-C}_5\text{H}_4\text{CH}_3$ ligand and to ascertain whether or not the regioselectivity observed above is maintained at $-20\text{ }^{\circ}\text{C}$. The salt $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)(\text{PPh}_3)(\text{CO})_2]\text{PF}_6$ (18) was treated with NaBH_4 at $-20\text{ }^{\circ}\text{C}$ for 2 hours in tetrahydrofuran. Hydrolysis and subsequent work-up led to the isolation of a yellow oil which gave an infra-red spectrum containing two strong bands in the terminal carbonyl region at 1975 and 1920 cm^{-1} . The ^1H n.m.r. spectrum of the solid contained only the resonances attributed to (54) (see p 43). On the basis of this data, the compound was assigned as $[\text{Fe}(1\text{-methyl-}\eta^4\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{CO})_2]$ (54). (See Section I.2.6 for assignment of diene protons and position of methyl group). The ^{31}P -(^1H) n.m.r. spectrum of (54) contained a singlet at $\delta 71.6$. The novel η^4 -diene complex (54) was further characterised by low and high resolution mass spectrometry.

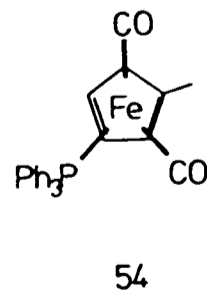
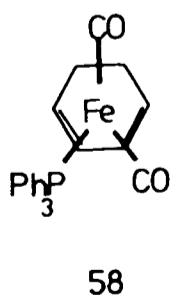
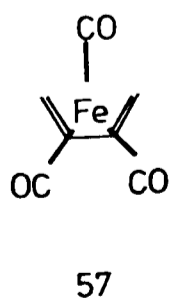


There are no literature examples of nucleophilic attack on an $\eta^5\text{-C}_5\text{H}_4\text{CH}_3$ ligand. (The only example of nucleophilic attack on a cation containing an $\eta^5\text{-C}_5\text{H}_4\text{CH}_3$ moiety and a carbonyl ligand is the reaction of the cation $[\text{Mn}(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)(\text{CO})_2(\text{NO})]\text{PF}_6$ with primary alkylamines where the nucleophile adds to a carbonyl ligand.⁵²) The result depicted above demonstrates that

hydride addition to 1-methyl-substituted η^5 -hydrocarbon ligands occurs regiospecifically at C-2. Although attack at C-1 can be discounted due to the steric hindrance of the methyl group the preference for attack at C-2 over C-3 is more difficult to rationalise. It has been calculated using extended Hückel molecular orbital theory and qualitative considerations from perturbation theory⁵³ that in $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)(\text{CO})_3]$ (56) the carbon atoms of the $\eta^6\text{-C}_6\text{H}_6$ ligand which are eclipsed with respect to the carbonyl groups *i.e.* C₁ are more susceptible to nucleophilic attack than those which are not *i.e.* C₂.



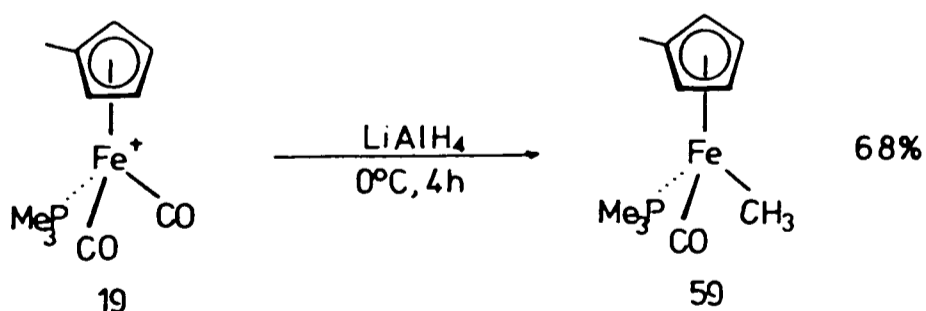
The most stable conformation of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)(\text{PPh}_3)(\text{CO})_2]\text{PF}_6$ (18) would be (18a) and the observed position of nucleophilic attack corresponds to addition to an eclipsed carbon. Alternatively, the regiospecificity of hydride attack may be explained in terms of product stability. It is well established that the preferred conformation of an $\text{Fe}(\eta^4\text{-diene})(\text{CO})_3$ compound is (57)⁵⁴ and the structure of the triphenylphosphine substituted η^4 -diene $[\text{Fe}(\eta^4\text{-C}_6\text{H}_8)(\text{PPh}_3)(\text{CO})_2]$ (58) is similar.⁵⁵



The most stable conformer of the observed product *i.e.* the η^4 -diene resulting from hydride attack at C-2 (54) is predicted therefore to be more stable than any of the conformers of the

η^4 -diene that would result from hydride attack at C-3.

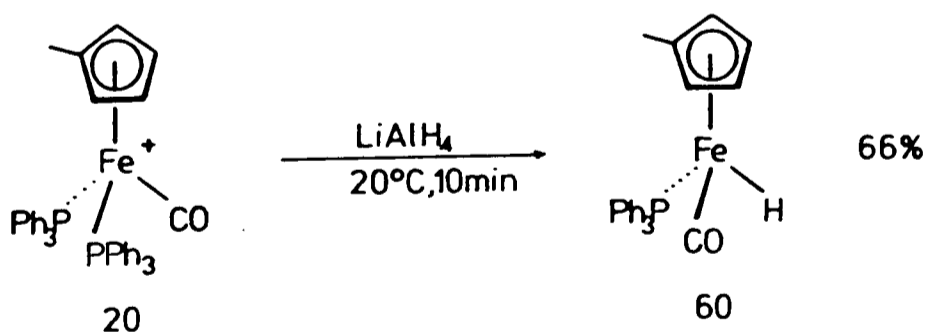
The yellow crystalline salt $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)(\text{PMe}_3)(\text{CO})_2]\text{PF}_6$ (19) was treated with excess LiAlH_4 in tetrahydrofuran at 0°C for 4 hours. Hydrolysis and subsequent work-up led to the isolation of an air-sensitive yellow solid at -30°C which became an amber oil at room temperature. The oil gave an infrared spectrum containing a broad carbonyl stretch at 1900 cm^{-1} . The ^1H n.m.r. spectrum of the amber oil contained a doublet at $\delta -0.1$ ($^3J_{\text{PH}}=7\text{Hz}$) which is characteristic of an iron methyl group and indicated that the compound still contained a tertiary phosphine ligand; the ^1H n.m.r. spectrum also contained a multiplet at $\delta 4.3\text{-}3.9$ due to the diene protons of an $\eta^5\text{-C}_5\text{H}_4\text{CH}_3$ ligand, a singlet at $\delta 1.9$ due to the methyl protons of an $\eta^5\text{-C}_5\text{H}_4\text{CH}_3$ ligand and a doublet at $\delta 1.0$ ($^2J_{\text{PH}}=9\text{Hz}$) due to the methyl protons of a trimethylphosphine ligand. On the basis of this data, the compound was assigned as $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)(\text{PMe}_3)(\text{CO})\text{CH}_3]$ (59). The ^{31}P -(^1H) n.m.r. spectrum of the oil contained a singlet at $\delta 42.0$. The novel complex (59) was further characterised by low and high resolution mass spectrometry.



The reduction of (19) in $[\text{}^2\text{H}_8]$ tetrahydrofuran and CD_2Cl_2 (1:2) at low temperature was monitored by ^1H n.m.r. spectroscopy. A mixture of (19), LiAlH_4 , $[\text{}^2\text{H}_8]$ tetrahydrofuran and CD_2Cl_2 was examined at -70°C , -40°C and 0°C ; there was no signal corresp-

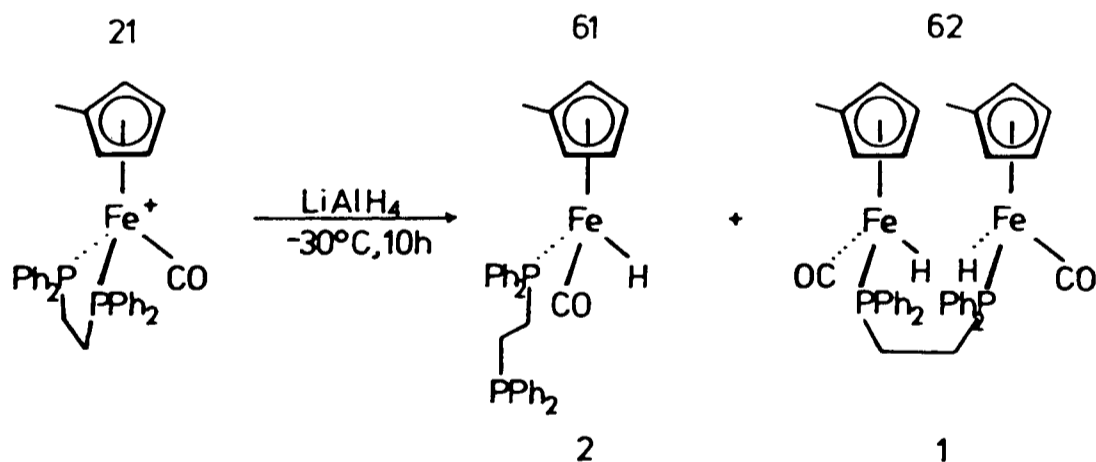
onding to a metal formyl proton at any of these temperatures.

The orange crystalline salt $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)(\text{PPh}_3)_2(\text{CO})]\text{PF}_6$ (20) was treated with excess LiAlH_4 in tetrahydrofuran-dichloromethane (1:1) at 20 °C for 10 minutes. Hydrolysis, followed by a standard work-up procedure led to the isolation of an air-sensitive yellow gum. The infra-red spectrum of the gum contained a terminal carbonyl stretch at $1\,930\text{ cm}^{-1}$; the ^1H n.m.r. spectrum of the gum contained a characteristic iron hydride doublet at $\delta -12.70$ ($^2J_{\text{PH}}=83\text{Hz}$) indicating that only one phosphine remained bound to the iron, four one-proton singlets at $\delta 4.35, 4.25, 4.10$ and 3.98 and a three-proton singlet at $\delta 1.85$ due to an $\eta^5\text{-C}_5\text{H}_4\text{CH}_3$ ligand and a multiplet at $\delta 7.8\text{-}7.0$ due to phenyl protons. On the basis of this data, the compound was assigned as $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)(\text{PPh}_3)(\text{CO})\text{H}]$ (60). The ^{31}P -(^1H) n.m.r. spectrum of the compound contained a singlet at $\delta 89.0$. The novel hydride (60) was further characterised by low and high resolution mass spectrometry.



The yellow crystalline salt $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)(\text{diphos})(\text{CO})]\text{PF}_6$ (21) was treated with excess LiAlH_4 in tetrahydrofuran-dichloromethane (1:1) at $-30\text{ }^\circ\text{C}$ for 10 hours. Hydrolysis followed by a standard work-up procedure led to the isolation of an air-sensitive yellow powder. The infra-red spectrum of the powder contained a broad terminal carbonyl stretch at $1\,923\text{ cm}^{-1}$; the ^1H n.m.r. spectrum of the powder contained two

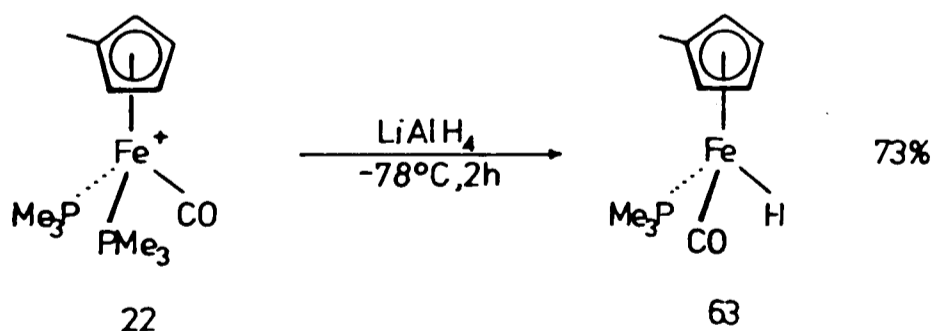
characteristic iron hydride doublets at δ -13.08 (${}^2J_{\text{PH}}=74\text{Hz}$) and δ -13.12 (${}^2J_{\text{PH}}=75\text{Hz}$) in a ratio of 1:2, a multiplet at δ 4.3-3.8 and two singlets at δ 1.87 and δ 1.85 in a ratio of 1:2 assigned to two $\eta^5\text{-C}_5\text{H}_4\text{CH}_3$ ligands and multiplets at δ 7.5-6.9 and δ 2.7-2.2 assigned to diphos ligands. On the basis of this data, the powder was assigned as a mixture of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)(\text{diphos})(\text{CO})\text{H}]$ (61) and $[(\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)(\text{CO})\text{H})_2(\mu\text{-diphos})]$ (62). The ${}^{31}\text{P}$ -(${}^1\text{H}$) n.m.r. spectrum revealed that (61) was the major product. The metal-bound phosphorus atom of (61) gave rise to a doublet centred at δ 82.8 (${}^3J_{\text{PP}}=38\text{Hz}$) and the unbound phosphorus atom of (61) gave rise to a doublet at δ -15.5 (${}^3J_{\text{PP}}=38\text{Hz}$) whereas the two metal-bound phosphorus atoms of (62) gave rise to a singlet at δ 82.8. The presence of (61) in the product was confirmed by low and high resolution mass spectrometry.



The analogous $\eta^5\text{-C}_5\text{H}_5$ compound $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{diphos})(\text{CO})\text{H}]$ (49) is known to disproportionate *via* phosphine exchange to $[(\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\text{H})_2(\mu\text{-diphos})]$ and free diphos.⁵¹ The reduction of (21) in $[{}^2\text{H}_8]$ tetrahydrofuran and CD_2Cl_2 (1:2) at low temperature was monitored by ${}^1\text{H}$ n.m.r. spectroscopy. A mixture of (21), LiAlH_4 , $[{}^2\text{H}_8]$ tetrahydrofuran and CD_2Cl_2 was examined at

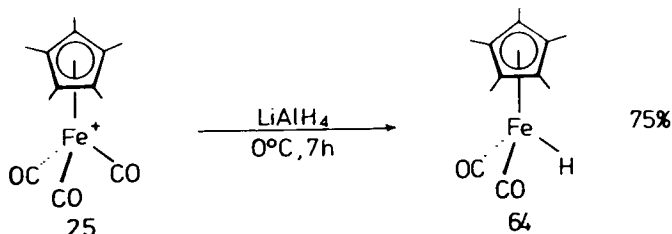
-70 °C, -40 °C and 20 °C; there was no signal corresponding to a metal formyl proton at any of these temperatures. A doublet at δ -13.56 ($^2J_{\text{PH}}=76\text{Hz}$) assigned to a metal hydride appeared at -40 °C and persisted to 20 °C.

The yellow crystalline salt $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)(\text{PMe}_3)_2(\text{CO})]\text{PF}_6$ (22) was treated with LiAlH_4 at -78 °C for 2 hours in tetrahydrofuran. Hydrolysis and subsequent work-up led to the isolation of an air-sensitive yellow oil which gave an infrared spectrum containing a broad carbonyl stretch at 1905 cm^{-1} . The ^1H n.m.r. spectrum of the oil contained a characteristic iron hydride doublet at δ -14.1 ($^2J_{\text{PH}}=84\text{Hz}$) indicating that only one phosphine remained bound to the iron, a multiplet at δ 4.3-4.0, a singlet at δ 1.9 due to the protons of an $\eta^5\text{-C}_5\text{H}_4\text{CH}_3$ ligand and a doublet at δ 1.0 ($^2J_{\text{PH}}=9\text{Hz}$) due to the methyl protons of a trimethylphosphine ligand. On the basis of this data, the compound was assigned as $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)(\text{PMe}_3)(\text{CO})\text{H}]$ (63). The ^{31}P -(^1H) n.m.r. spectrum of (63) contained a singlet at δ 39.9. The hydride (63) was further characterised by low and high resolution mass spectrometry.



I.2.4 Hydride reduction of cationic $\eta^5\text{-C}_5(\text{CH}_3)_5$ iron complexes

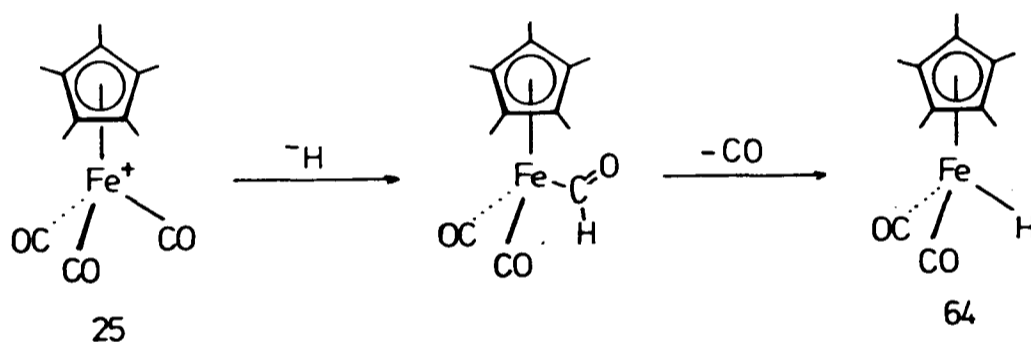
The yellow crystalline salt $[\text{Fe}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{CO})_3]\text{PF}_6$ (25) was treated with excess LiAlH_4 at 0°C for 7 hours in tetrahydrofuran. Hydrolysis and subsequent work-up led to the isolation of air-sensitive cream-coloured crystals which gave an infra-red spectrum containing two strong bands in the carbonyl region at 1995 and 1935 cm^{-1} due to terminal carbonyls. There were no bands in the bridging carbonyl region of the spectrum. The ^1H n.m.r. spectrum of the crystals contained a characteristic singlet at $\delta -11.6$ due to an iron hydride and a singlet at $\delta 1.6$ due to the protons of an $\eta^5\text{-C}_5(\text{CH}_3)_5$ moiety. On the basis of the above data, the compound was assigned as $[\text{Fe}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{CO})_2\text{H}]$ (64).



There was no evidence for the formation of a diene compound which would result from nucleophilic attack on the $\eta^5\text{-C}_5(\text{CH}_3)_5$ ligand. Hydride (64) was stable with respect to the dimer $[\text{Fe}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{CO})_2]_2$ (23) at room temperature in the absence of air. Isolation of the hydride (64) contrasts strongly with the results obtained on reduction of the $\eta^5\text{-C}_5\text{H}_5$ and $\eta^5\text{-C}_5\text{H}_4\text{CH}_3$ analogues of (25) when only isolation of the corresponding dimers proved possible. It appears that the electron donating properties and the steric properties of the $\eta^5\text{-C}_5(\text{CH}_3)_5$ ligand

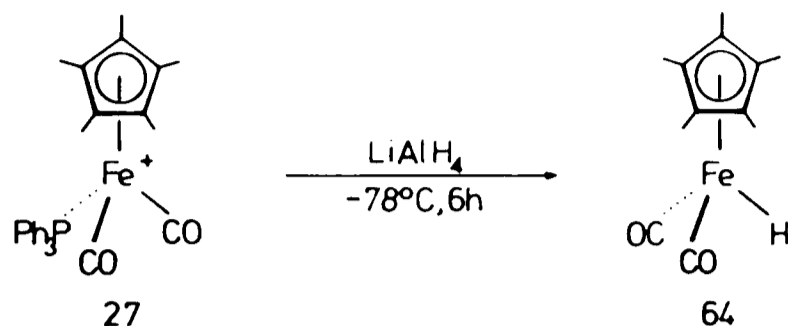
stabilise (64) with respect to dimerisation.

The reduction of (25) in [$^2\text{H}_8$] tetrahydrofuran and CD_2Cl_2 (1:2) at low temperature was monitored by ^1H n.m.r. spectroscopy. A mixture of (25), LiAlH_4 , [$^2\text{H}_8$] tetrahydrofuran and CD_2Cl_2 was warmed from -78°C to -67°C and its ^1H n.m.r. spectrum recorded. The spectrum contained two resonances at δ 13.86 and 13.43 due to metal formyl protons and a resonance at δ -11.38 due to a metal hydride. These results strongly support the mechanism which involves nucleophilic attack by hydride at a carbonyl ligand to give a metal formyl which decomposes to a carbonyl hydride by loss of a carbon monoxide ligand.

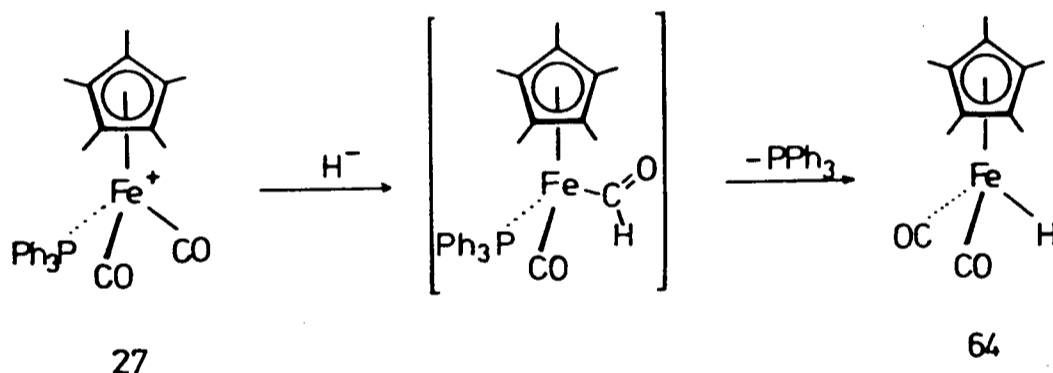


The yellow microcrystalline salt $[\text{Fe}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{PPh}_3)(\text{CO})_2]\text{PF}_6$ (27) was stirred with excess LiAlH_4 at -78°C for 6 hours in tetrahydrofuran. Hydrolysis and subsequent work-up led to the isolation of an orange solid which gave an infrared spectrum that contained two strong bands in the carbonyl region at 1995 and 1935 cm^{-1} due to terminal carbonyls. The ^1H n.m.r. spectrum of the solid contained a characteristic singlet at δ -11.8 due to an iron hydride in a molecule without a tertiary phosphine ligand, a singlet at δ 1.6 due to the protons of an $\eta^5\text{-C}_5(\text{CH}_3)_5$ ligand and a multiplet at δ 7.6-7.0. The orange solid was assigned as a mixture of $[\text{Fe}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{CO})_2\text{H}]$ (64) and triphenylphosphine by comparison of the data

given above with the data of samples obtained by alternative routes.



There was no evidence for the formation of a diene compound which would result from nucleophilic hydride attack on the $\eta^5\text{-C}_5(\text{CH}_3)_5$ ligand. Nucleophilic attack must occur at the carbon monoxide ligand only to give an iron formyl species which decomposes to (64) by loss of triphenylphosphine.

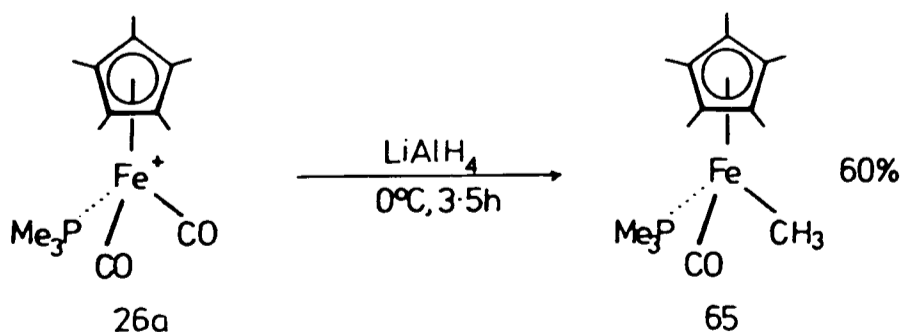


Monitoring the reduction of (27) at low temperature failed to produce any evidence for the existence of a formyl species as an intermediate in this reaction.

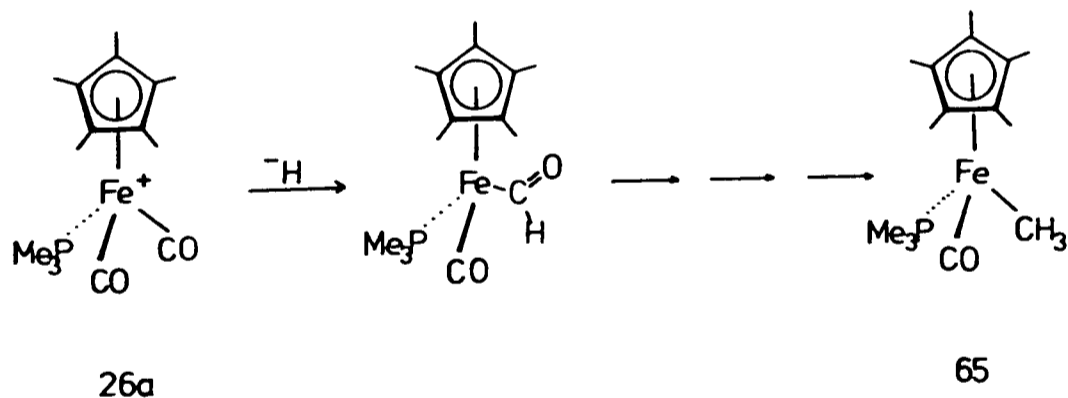
The formation of (64) as the only discernible product from the reduction of (27) contrasts with the results of the reductions of the $\eta^5\text{-C}_5\text{H}_5$ and $\eta^5\text{-C}_5\text{H}_4\text{CH}_3$ analogues of (27). These compounds exhibited no regioselectivity in their reaction with hydride undergoing attack at the η^5 -hydrocarbon ligand and the carbon monoxide; they also showed no specificity in ligand loss as the intermediate formyl decomposed to carbonyl hydride. The increased electron density of the $\eta^5\text{-C}_5(\text{CH}_3)_5$

ligand due to the five methyl groups will direct nucleophiles to the carbon monoxide ligand; furthermore the increased electron density will be relayed to the metal centre and to the π -accepting carbon monoxide ligand thus strengthening the metal carbon bond. (The poor π -acceptor triphenylphosphine will not receive any extra electron density from the $\eta^5\text{-C}_5(\text{CH}_3)_5$ ligand.) This accounts for the specific loss of triphenylphosphine in preference to carbon monoxide.

The yellow salt $[\text{Fe}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{PMe}_3)(\text{CO})_2]\text{PF}_6$ (26a) was stirred with LiAlH_4 at 0°C for 3.5 hours in tetrahydrofuran. Hydrolysis and subsequent work-up led to the isolation of a yellow air-sensitive solid which gave an infra-red spectrum containing a weak band at 1895 cm^{-1} indicating the presence of a terminal carbonyl ligand. The ^1H n.m.r. spectrum of the yellow solid contained a doublet at $\delta -0.3$ ($^3J_{\text{PH}}=7\text{Hz}$) characteristic of an iron methyl in a compound containing one tertiary phosphine ligand, a singlet at $\delta 1.55$ due to the methyl protons of an $\eta^5\text{-C}_5(\text{CH}_3)_5$ moiety and a doublet at $\delta 0.95$ ($^2J_{\text{PH}}=9\text{Hz}$) due to the protons of a trimethylphosphine ligand. On the basis of the data given above, the yellow solid was assigned as $[\text{Fe}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{PMe}_3)(\text{CO})\text{CH}_3]$ (65)!

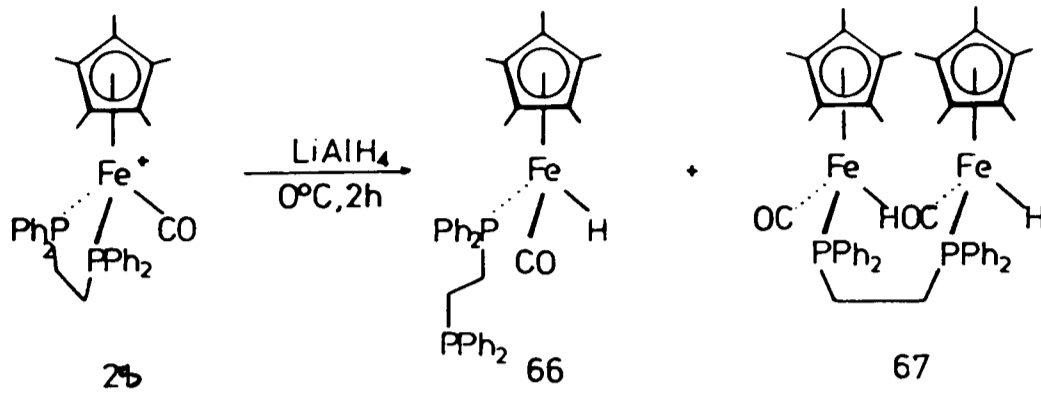


The reduction of (26a) in [$^2\text{H}_8$] tetrahydrofuran and CD_2Cl_2 (1:2) at low temperature was monitored by ^1H n.m.r. spectroscopy. A mixture of (26a), LiAlH_4 , [$^2\text{H}_8$] tetrahydrofuran and CD_2Cl_2 was warmed from -78°C to -60°C . The ^1H n.m.r. spectrum of the mixture was recorded; the spectrum contained a resonance at δ 14.50, which was assigned to a metal formyl proton and a doublet at δ -0.44 ($^3J_{\text{PH}}=7\text{Hz}$) assigned to the protons of the metal methyl group in the product of the reaction (65). These results are consistent with those obtained on reduction of the $\eta^5\text{-C}_5\text{H}_5$ and $\eta^5\text{-C}_5\text{H}_4\text{CH}_3$ analogues of (26a) *i.e.* nucleophilic attack occurs regiospecifically at a carbon monoxide ligand to produce a metal formyl species which is sufficiently stable to undergo further reduction to a metal methyl complex.



The yellow salt $[\text{Fe}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{diphos})(\text{CO})]\text{PF}_6$ (28) was treated with excess LiAlH_4 in tetrahydrofuran at 0°C for 2 hours. Hydrolysis followed by a standard work-up procedure led to the isolation of an air-sensitive yellow powder. The ^1H n.m.r. spectrum of the powder contained two characteristic iron hydride doublets at δ -13.21 ($^2J_{\text{PH}}=74\text{Hz}$) and δ -13.26 ($^2J_{\text{PH}}=74\text{Hz}$), two singlets at δ 1.65 and δ 1.64 assigned to two $\eta^5\text{-C}_5(\text{CH}_3)_5$ ligands and multiplets at δ 7.8-7.0 and δ 2.6-2.2 assigned to diphos ligands. On the basis of this data, the

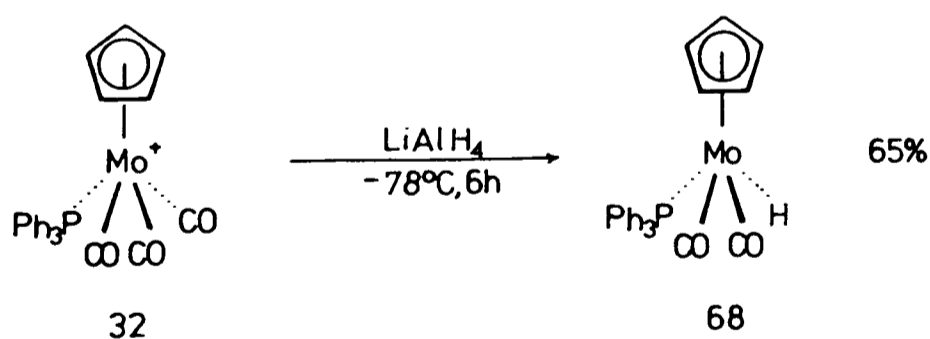
powder was assigned as a mixture of $[\text{Fe}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{diphos})(\text{CO})\text{H}]$ (66) and $[\text{Fe}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{CO})\text{H}]_2(\mu\text{-diphos})$ (67).



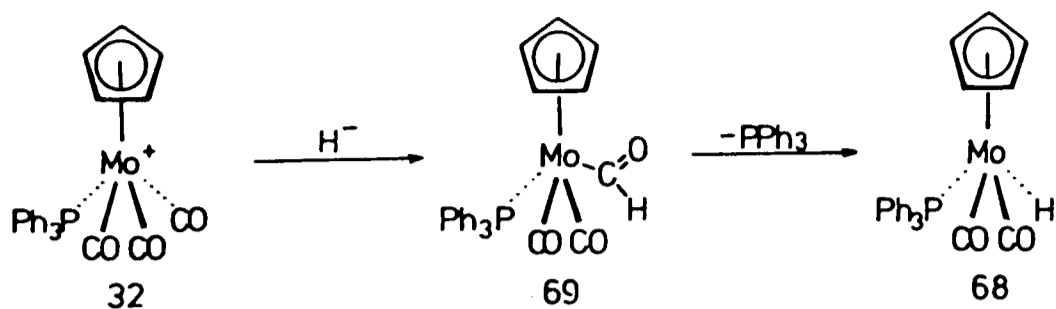
This result is analogous to the result obtained on reduction of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)(\text{diphos})(\text{CO})]\text{PF}_6$ (21).

I.2.5 Hydride reduction of cationic $\eta^5\text{-C}_5\text{H}_5$ molybdenum complexes

The yellow crystalline salt $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{CO})_3]\text{PF}_6$ (32) was treated with LiAlH_4 in tetrahydrofuran at -78°C for 6 hours. Hydrolysis and subsequent work-up led to the isolation of a yellow air-sensitive solid which gave an infra-red spectrum that contained two strong bands at 1945 and 1865 cm^{-1} due to terminal carbonyl ligands. The ^1H n.m.r. spectrum of the yellow solid contained a doublet at $\delta -5.1$ ($^2J_{\text{PH}}=50\text{Hz}$) characteristic of a molybdenum hydride and indicating that the complex contained a tertiary phosphine ligand, a singlet at $\delta 4.75$ due to an $\eta^5\text{-C}_5\text{H}_5$ ligand and a multiplet at $\delta 7.7\text{-}6.9$ due to a triphenylphosphine ligand. On the basis of the above data, the yellow powder was assigned as $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{CO})_2\text{H}]$ (68) and this assignment was confirmed by comparison of the above data with literature data.⁵⁶ (The carbonyl hydride (68) was previously synthesised by the action of triphenylphosphine on $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\text{H}]$ (30).⁵⁶)



There was no evidence for the formation of any diene resulting from nucleophilic attack on the $\eta^5\text{-C}_5\text{H}_5$ ligand. Attack of hydride on (32) is regiospecific therefore and the formyl resulting from hydride attack on a carbon monoxide ligand decomposes by loss of carbon monoxide rather than triphenylphosphine.



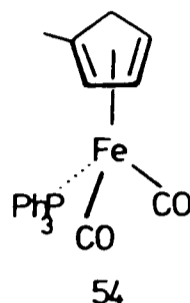
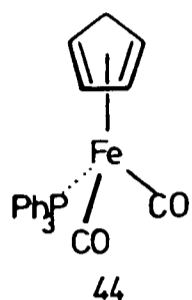
It is of note that sodium borohydride reduction of (32) at 0 °C leads to complete reduction of a carbon monoxide ligand to a methyl group giving $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{CO})_2\text{Me}]$ as the product in low yield.⁵⁷ Recently, reduction of (32) with NaBH_4 in methanol led to the isolation of $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{CO})_2(\text{CHO})]$ (69).⁵⁸ The formyl was labile in solution at room temperature converting cleanly to $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\text{H}]$ (30) within a few minutes by loss of triphenylphosphine.

Attempts to reduce $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{diphos})(\text{CO})_2]\text{PF}_6$ (33) and $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{triphos})(\text{CO})]\text{PF}_6$ (34) at -78 °C and at room temperature using LiAlH_4 and more powerful reducing agents such as LiBET_3H and Red-Al^\dagger all failed to give an identifiable product. This is consistent with the failure of $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2(\text{CO})_2]\text{PF}_6$ to react with NaBH_4 at room temperature.⁵⁷

† $[(\text{CH}_3\text{OCH}_2\text{CH}_2\text{O})_2\text{AlH}_2]\text{Na}$

I.2.6 Assignment of the ^1H n.m.r. spectra of compounds containing an η^4 -diene ligand

The η^4 -dienes (44) and (54) were components of the mixtures produced on reduction by LiAlH_4 of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{CO})_2]\text{PF}_6$ (10) and $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)(\text{PPh}_3)(\text{CO})_2]\text{PF}_6$ (18) respectively.



The ^1H n.m.r. resonances of these compounds were assigned as follows. The diene (44) was synthesised by sodium borohydride reduction of (10) at $-20\text{ }^\circ\text{C}$ ^{46, 59} (performing the reduction at $-20\text{ }^\circ\text{C}$ directs nucleophilic attack to the $\eta^5\text{-C}_5\text{H}_5$ ligand of (10) and away from the carbon monoxide ligand). The 300 MHz ^1H n.m.r. spectrum of pure (44) contained two multiplets at δ 7.5 and 7.0 assigned to the protons of the triphenylphosphine ligand, a two proton singlet at δ 5.13 assigned to H_2 and H_3 on the basis that these two protons have more sp^2 character than protons H_1 and H_4 , a one proton unresolved multiplet at δ 2.78, a two proton singlet at δ 2.27 assigned to protons H_1 and H_4 and a one proton triplet at δ 2.24. Nucleophilic addition to cyclopentadienyl ligands bonded to 18-electron cations proceeds *via* an $\text{S}_{\text{N}}2$ with inversion mechanism *i.e.* the nucleophile attacks the unco-ordinated face of the cyclopentadienyl ligand to yield *exo* 5-substituted η^4 -cyclopentadiene complexes.³⁴ The cation (10) was reduced with NaBD_4 at $-20\text{ }^\circ\text{C}$ for 2 hours. Work-up gave $[\text{Fe}(5\text{-exo-}\eta^4\text{-C}_5\text{H}_5\text{D})(\text{PPh}_3)(\text{CO})_2]$ (44a) as a yellow

powder. The infra-red spectrum of (44a) contained three weak bands at 2 080, 2 060 and 2 015 cm^{-1} assigned to the stretching mode of the CD_{exo} bond, and two strong bands at 1 965 and 1 900 cm^{-1} due to the two carbonyl ligands. The ^1H n.m.r. spectrum of (44a) resembled that of (44) apart from the absence of the triplet at δ 2.24. This resonance was assigned to H_{exo} therefore and the unresolved multiplet at δ 2.78 was assigned to H_{endo} .

The resonance due to H_{exo} in (44) is a triplet as a result of coupling to H_{endo} and to the co-ordinated phosphorus atom ($^2J_{\text{HH}}=10.5\text{Hz}$, $J_{\text{PH}}=10.5\text{Hz}$). The resonance due to H_{endo} in (44) is an unresolved multiplet. Long range spin-spin coupling between nuclei occurs over four bonds between atoms in a 'W' arrangement. In cyclopentadiene complexes H_{exo} but not H_{endo} is in the required geometric arrangement with any co-ordinated phosphorus atoms for such long range coupling to be expected, assuming rotation about the diene-metal bond.

Coupling between H_{exo} and a co-ordinated phosphorus atom is seen in other diene complexes (see Table 10) and can be used as a reliable tool in the assignment of the stereochemistry of 5-substituted η^4 -cyclopentadiene transition metal complexes. ⁶⁰ Previously the most common criterion for assigning the stereochemistry of 5-substituted η^4 -cyclopentadiene complexes has been the presence or absence of an infra-red absorption at *ca.* 2 750 cm^{-1} attributed to C-H_{exo} . This absorption was however initially misassigned to C-H_{endo} and this has resulted in its subsequent history being rather confused. In the infra-red spectrum of each of the cyclopentadiene complexes in Table 10, the absorption at *ca.* 2 750 cm^{-1} ascribed to C-H_{exo} was

Table 10

Characteristic spectroscopic data for cyclopentadiene iron and ruthenium complexes⁶⁰

Complex	δ /p.p.m.						$\nu(\text{C-H}_{\text{exo}}) / \text{cm}^{-1}$	$\nu(\text{C-D}_{\text{exo}}) / \text{cm}^{-1}$
	H _{1,4}	H _{2,3}	H _{endo}	H _{exo}	$^2J_{\text{H}_{\text{exo}}\text{H}_{\text{endo}}}$ / Hz	$J_{\text{PH}_{\text{exo}}}$ / Hz		
[Fe(η^4 -C ₅ H ₆)(PPh ₃)(CO) ₂] (44)	2.27	5.13	2.78	2.24 (t)	10.5	10.5	2 730	2 080m, 2 060m, 2 015w
[Fe(η^4 -C ₅ H ₆)(diphos)(CO)]	2.43	4.89	3.03	2.75 (dt)	10.0	9.3	2 740	2 060m, 2 040m
[Ru(η^4 -C ₅ H ₆)(PPh ₃) ₂ (CO)]	2.13	5.26	2.51	2.94 (dt)	10.4	19.7	2 750	2 075w, 2 065m
[Ru(η^4 -C ₅ H ₆)[MeC(CH ₂ Ph) ₂] ₃]	2.59	5.85	3.54	4.01 (dq)	9.0	14.2	2 715	2 050m, 2 020m, 1 995w
[Ru(η^4 -C ₅ H ₆)[PhP(CH ₂ CH ₂ Ph) ₂] ₂]	2.90	5.36	2.58	3.57 (ddt)	10.3	8.1 18.8	2 750	2 045m, 2 015m

absent from the spectra of the corresponding *exo* deuterides. It had, however, been replaced by a C-D_{*exo*} absorption at *ca.* 2 040 cm⁻¹ (see Table 10). The agreement between the H_{*exo*} and H_{*endo*} assignments on the basis of ¹H_{*exo*}-³¹P coupling and the H_{*exo*} infra-red absorptions allows renewed confidence to be placed in the use of the latter for the determination of the stereochemistry of 5-substituted cyclopentadiene complexes.

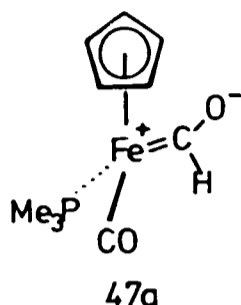
The η⁴-diene compound [Fe(1-methyl-η⁴-C₅H₅)(PPh₃)(CO)₂] (54) was one of the products of the reduction of [Fe(η⁵-C₅H₄CH₃)(PPh₃)(CO)₂]PF₆ (18) by LiAlH₄ at -78 °C and was also synthesised by the action of NaBH₄ on (18) at -20 °C (see Section I.2.3). The position of the methyl group on the diene ligand of (54) was determined from its ¹H n.m.r. spectrum. This contained the following resonances due to the hydrocarbon ligand: a one-proton singlet at δ 5.17, a broad one-proton singlet at δ 4.67, a one-proton doublet at δ 2.77 (J=10Hz), a one-proton triplet at δ 2.40 (J=10Hz), a one-proton singlet at δ 1.86 and a three-proton singlet at δ 1.53 readily assigned to the methyl group. By comparison of these resonances with the resonances in Table 10 for η⁴-C₅H₆ ligands, it was apparent that the singlets at δ 5.17 and 4.67 were due to protons H₂ and H₃. The triplet at δ 2.40 was assigned to H_{*exo*} as H_{*exo*} is expected to show spin-spin coupling to H_{*endo*} and the phosphorus atom of the phosphine ligand (²J_{HH}=10Hz, J_{PH}=10Hz). The doublet at δ 2.77 was assigned to H_{*endo*}; in this case the spin-spin coupling of this proton to H_{*exo*} was resolved. These assignments led to the conclusion that the diene was substituted at C-1 *i.e.* in the terminal position of the diene and that the singlet at δ 1.86 was due to H₄.

I.2.7 Conclusions

The site of hydride attack on the 18-electron organo-transition metal cations synthesised in Section I.1 has been determined. By performing the reactions at low temperature, attack is directed towards the carbonyl ligand in all cases except for the cations with one triphenylphosphine ligand *i.e.* $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{CO})_2]\text{PF}_6$ (10) and $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)(\text{PPh}_3)(\text{CO})_2]\text{PF}_6$ (18) which are attacked at the η^5 -hydrocarbon ligand to give an η^4 -diene complex even at -78°C . Attack can be directed specifically towards the carbonyl ligand in a monosubstituted triphenylphosphine cation by permethylating the η^5 -hydrocarbon ligand. Cations monosubstituted with the strong electron donating phosphine, trimethylphosphine, undergo regiospecific nucleophilic attack at a carbonyl ligand at 0°C and cations disubstituted with either triphenylphosphine or trimethylphosphine undergo regiospecific nucleophilic attack at a carbonyl ligand at room temperature.

The fate of the formyl produced in these reactions by hydride attack on a carbon monoxide ligand is dependant on the degree of phosphine substitution, the nature of the phosphine and the nature of the η^5 -hydrocarbon ligand. Apart from directing nucleophiles away from the η^5 -hydrocarbon ligand and towards the carbonyl ligand, permethylation of the $\eta^5\text{-C}_5\text{H}_5$ ligand in complexes monosubstituted with triphenylphosphine leads to the decomposition of the formyl by specific loss of triphenylphosphine. This contrasts with the $\eta^5\text{-C}_5\text{H}_5$ and $\eta^5\text{-C}_5\text{H}_4\text{CH}_3$ analogues where the formyl decomposes by loss of triphenylphosphine or carbon monoxide. Formyl species formed from cations monosubstituted with the powerfully electron

donating phosphine trimethylphosphine are stabilised to further reduction; this may be a result of a large contribution from the canonical (47a).

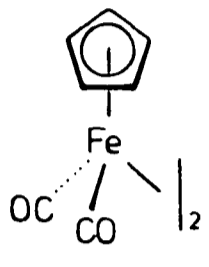
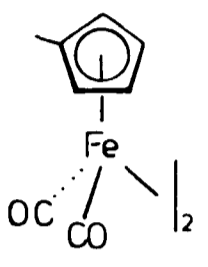
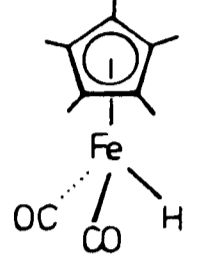
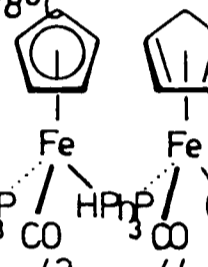
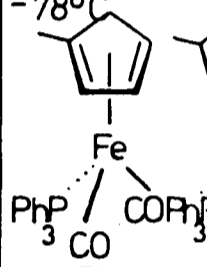
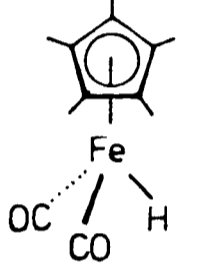
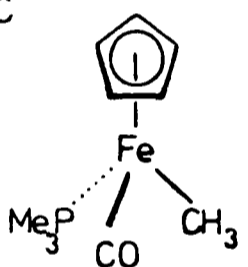
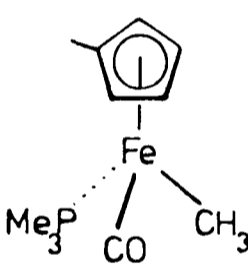
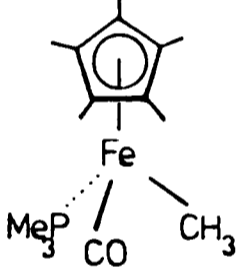
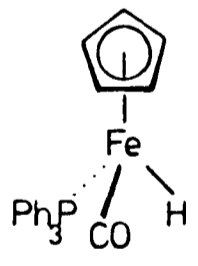
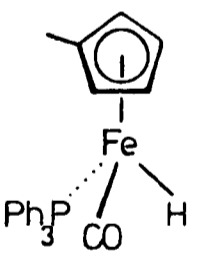
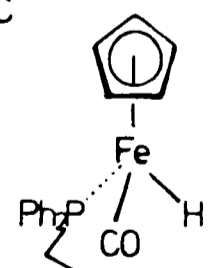
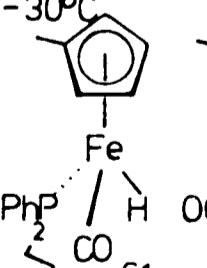
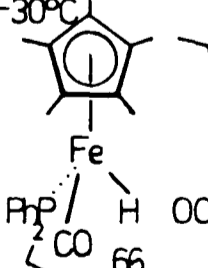
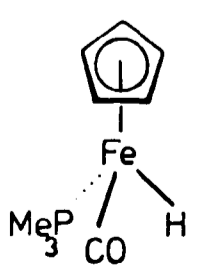
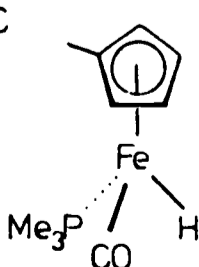


When two phosphine ligands are present in the formyl species, the stabilisation from canonicals related to (47a) is outweighed by the destabilising steric influence of the two bulky phosphines. Decomposition of the formyl to carbonyl hydride with concomitant loss of phosphine is accelerated by relief of steric crowding.

The results are summarised in Table 11.

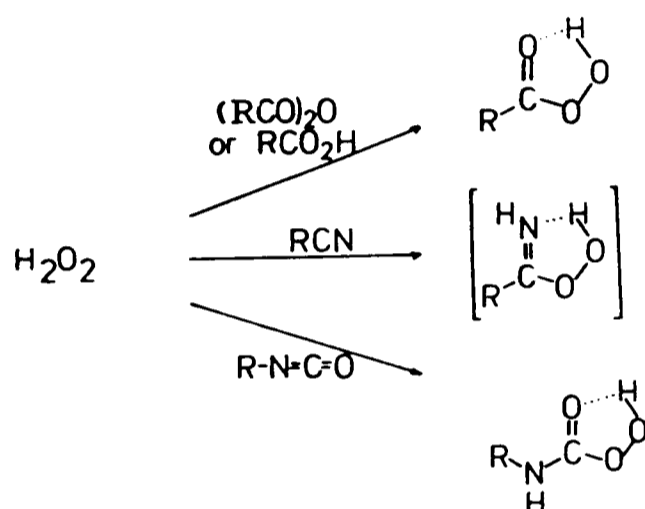
Table 11

Summary of products of LiAlH_4 reductions of iron cations

$\eta^5\text{-C}_5\text{R}_s$ Other ligands	$\eta^5\text{-C}_5\text{H}_5$	$\eta^5\text{-C}_5\text{H}_4\text{CH}_3$	$\eta^5\text{-C}_5(\text{CH}_3)_5$
Fe^+ OC CO CO	0°C  6	0°C  15	0°C  64
Fe^+ PPh CO CO	-78°C  43 15	-78°C  54 6	-78°C  64
Fe^+ PMe3 CO CO	-78°C  46	0°C  59	0°C  65
Fe^+ PPh3 CO CO	20°C  43	20°C  55	
Fe^+ PPh2 CO CO	-30°C  49	-30°C  61 2	-30°C  66
Fe^+ PMe3 CO CO	20°C  52	-78°C  63	

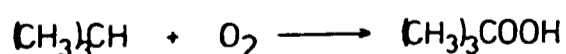
I.3.1 Introduction

The incorporation of simple sources of oxygen e.g. molecular oxygen itself or hydrogen peroxide into isolated alkenes to give epoxides traditionally requires two steps.[†] Oxidation of carboxylic acids or anhydrides,^{6 2} nitriles^{6 3} and isocyanates^{6 4} with hydrogen peroxide gives peroxy-carboxylic acids, peroxy-carboximidic acids and peroxy-carbamic acids respectively.



These intermediates, acting as electrophilic oxygen atom equivalents, oxidise alkenes to epoxides.

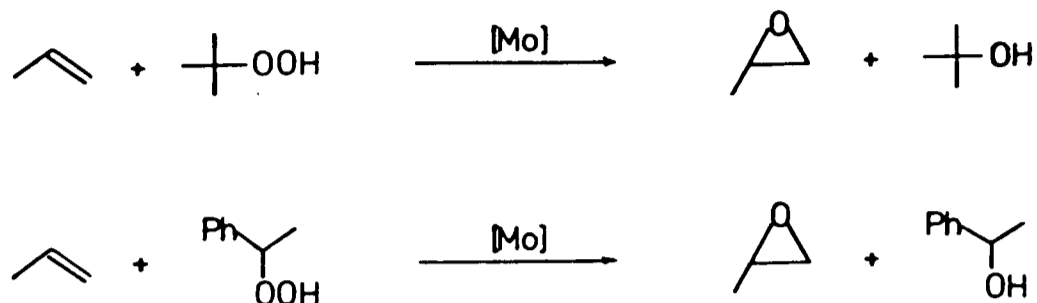
Propylene oxide is manufactured on an industrial scale by the metal-catalysed oxidation of propylene with an alkyl hydroperoxide. The alkyl hydroperoxide is available from the autoxidation of an appropriate hydrocarbon e.g. *tert*-butyl hydroperoxide is available from isobutane autoxidation.



† An exception to this generalisation is the commercial preparation of ethylene oxide in which ethylene is reacted with oxygen over a supported silver catalyst at elevated temperatures (250 °C).

^{6 1} The oxidation of propylene and higher alkenes under these conditions unfortunately leads to very low yields of epoxides .

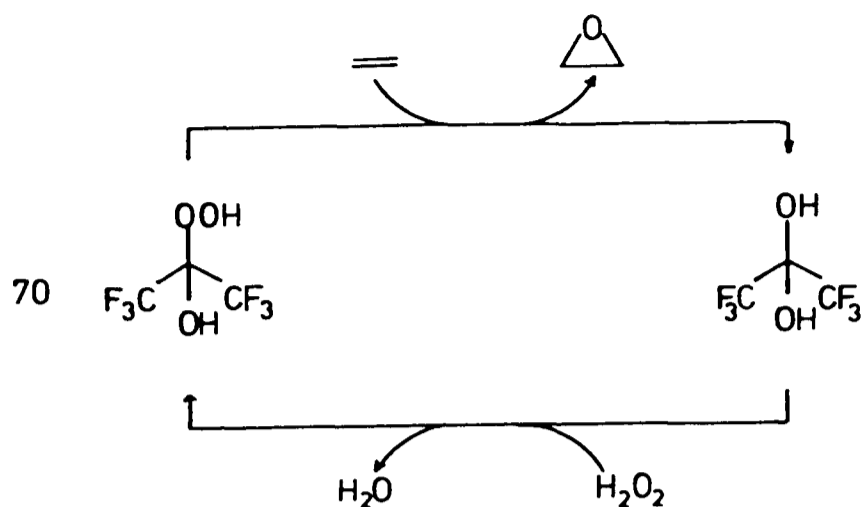
Processes employing molybdenum catalysts with both *tert*-butyl hydroperoxide and ethylbenzene hydroperoxide are used.^{6 5}



The *tert*-butyl alcohol coproduct is dehydrated to isobutene which can be sold or recycled after hydrogenation and the phenylmethylcarbinol coproduct is dehydrated to styrene which can be sold or recycled. The economics of these processes are closely related to the price obtainable for the coproduct and this restriction is very limiting. The alkyl hydroperoxide however, is a relatively inexpensive epoxidising agent, prepared by oxidation of a cheap hydrocarbon; it is less explosive and corrosive than organic peracids.

Catalysis of the direct oxidation of alkenes to epoxides by hydrogen peroxide would lead to an inexpensive and safe industrial process with water as the only coproduct. There has been much interest in discovering/designing a catalyst for this process; compounds which have shown some catalytic activity are discussed below.

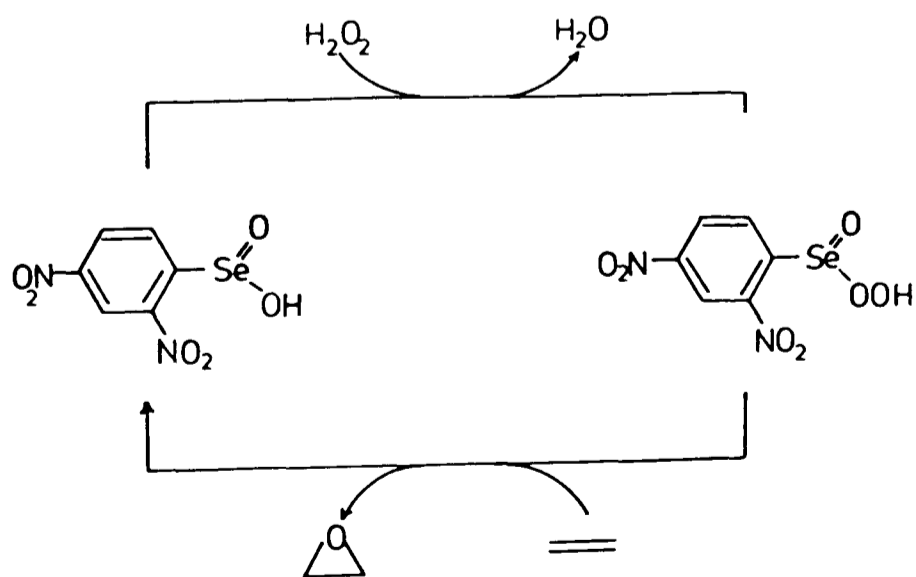
2-Hydroperoxyhexafluoro-2-propanol (70), prepared by the reaction of hexafluoroacetone and concentrated hydrogen peroxide, was shown to undergo the catalytic cycle shown in Scheme 7.



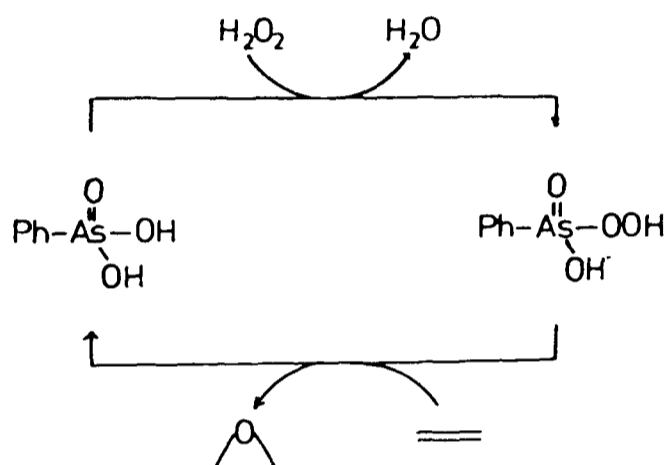
Scheme 7

The catalyst (70) performed 6.5 turnovers with 2 equivalents of 90% hydrogen peroxide over 24 hours at 83 °C. Similarly, 1,1,3,3-tetrachloroacetone performed 5 turnovers with 2 equivalents of 50% hydrogen peroxide over 24 hours at 61 °C.⁶⁶

2,4-Dinitrophenylseleninic acid achieved 19 turnovers with 2 equivalents of 30% hydrogen peroxide over 19.5 hours at room temperature.⁶⁷ A perselenious acid is thought to be the active epoxidising species.

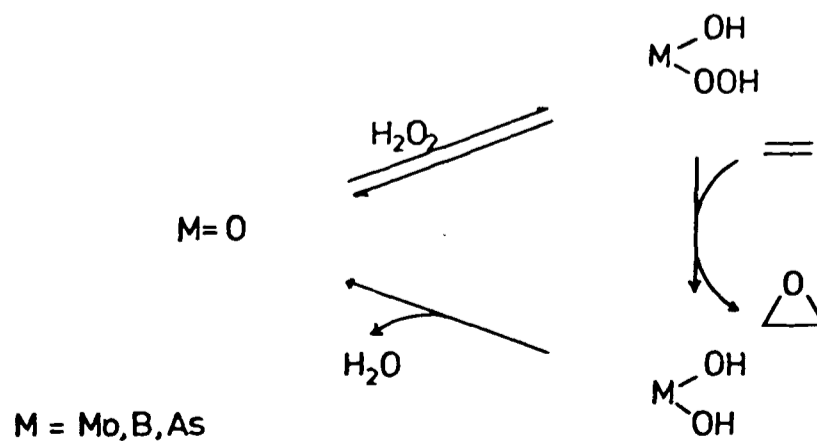


The exchange process between hydrogen peroxide and a carboxylic acid requires strong acid catalysis; generally it is incompatible with the epoxide product and isolation of the intermediate percarboxylic acid is necessary. The *in situ* formation of perselenious acids however, occurs under very mild conditions. Similarly, phenylarsonic acid has been shown to be a catalyst.^{6 8}



15 turnovers of the catalyst were achieved with 2 equivalents of 30% hydrogen peroxide over 22 hours at 70 °C. Arsonated polystyrene resins showed similar catalytic reactivity and were quantitatively recovered by simple filtration.

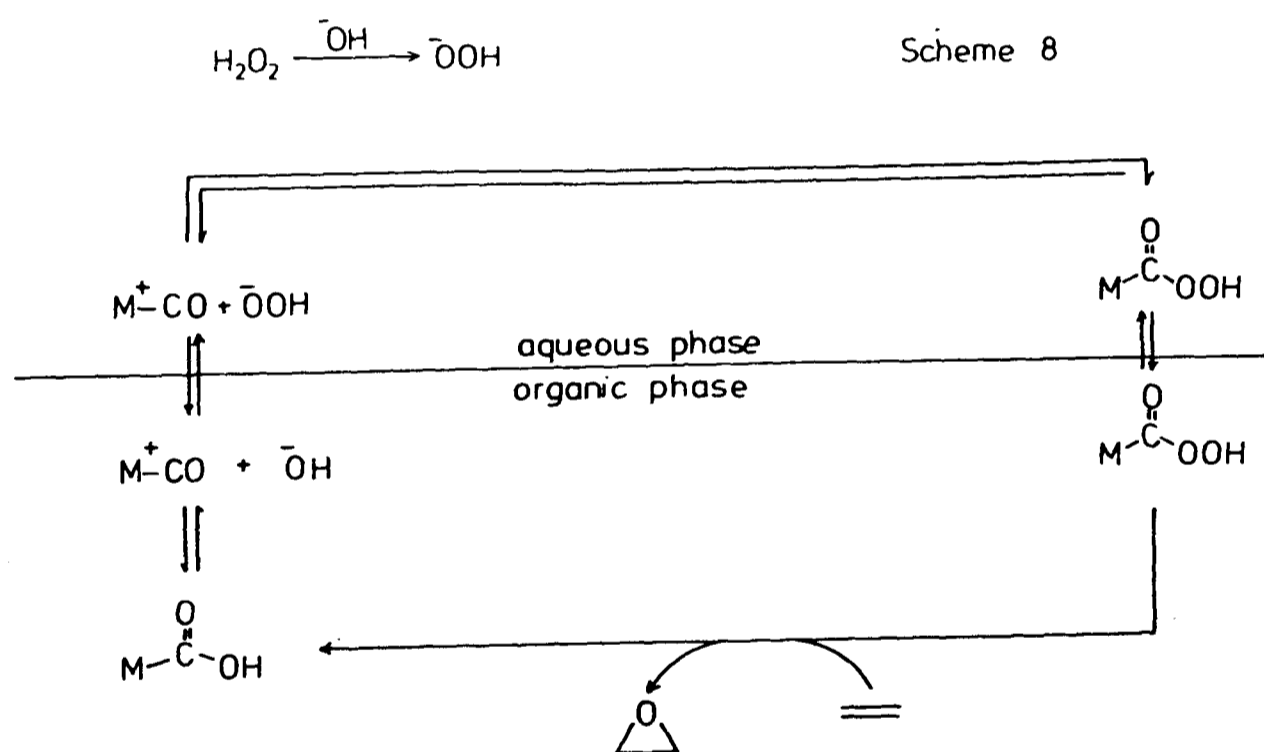
It has been demonstrated that molybdenum, boron and arsenic oxides act as epoxidation catalysts under rather severe conditions.^{6 9}



Typically, addition of 70% hydrogen peroxide to dioxane, cyclohexene and the catalyst at 80 °C with continuous removal of water by azeotropic distillation gave a catalytic turnover "high enough for an industrial process".

Objective

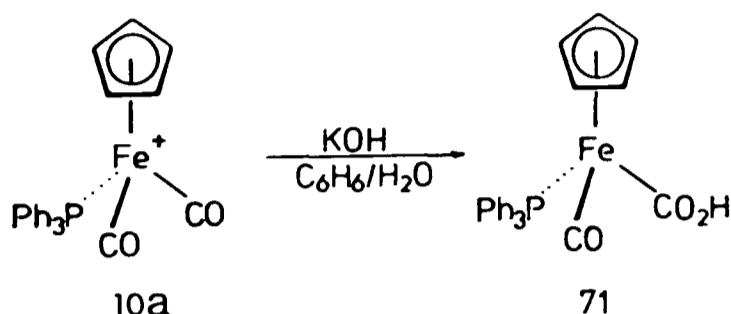
Transition metal cations with at least one carbonyl ligand are potential epoxidation catalysts. A biphasic catalytic cycle is illustrated in Scheme 8.



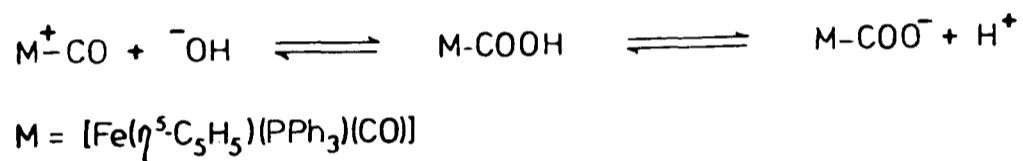
It is proposed that the metal carbonyl cation is attacked in the aqueous phase by a hydroperoxide ion to form a peroxymetal-lacarboxylic acid. This neutral species will move into the organic phase containing the olefinic substrate. Epoxidation of the olefin gives a metallacarboxylic acid which dissociates to the metal carbonyl cation and hydroxide ion (Scheme 8 is catalytic in hydroxide ion). The charged cation then moves into

the aqueous phase to complete the cycle.

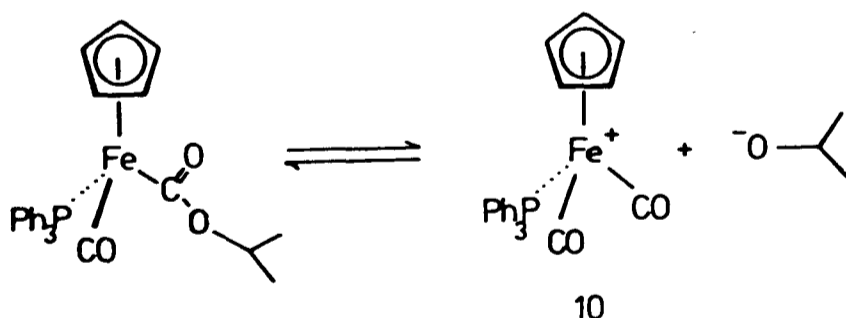
Although peroxymetallacarboxylic acids are unknown, the metallacarboxylic acid (71) has been formed by the addition of hydroxide ion to a metal carbonyl cation.²



The acid (71) may be readily induced to ionise in two ways depending on conditions.



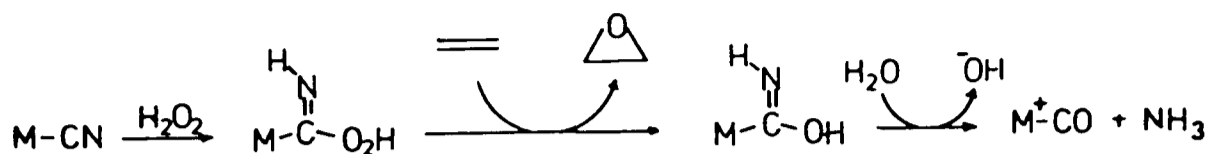
The cleavage of the carbon-oxygen bond which is unprecedented in organic carboxylic acids is observed in esters derived from (71); this was elegantly demonstrated on the isopropyl ester of (71).



In acetone ($\epsilon=21$), the two methyl groups of the isopropyl moiety are diastereotopic and appear as two separate doublets due to the attachment of this fragment to the chiral iron atom in the covalent form. In formamide ($\epsilon=109$) however, the methyl groups appear as a single doublet indicating separation of the isopropyl fragment from the chiral iron atom.²

It is proposed that a metal nitrile compound may enter the

catalytic cycle in Scheme 8 by its conversion to a metal carbonyl cation (Scheme 9).



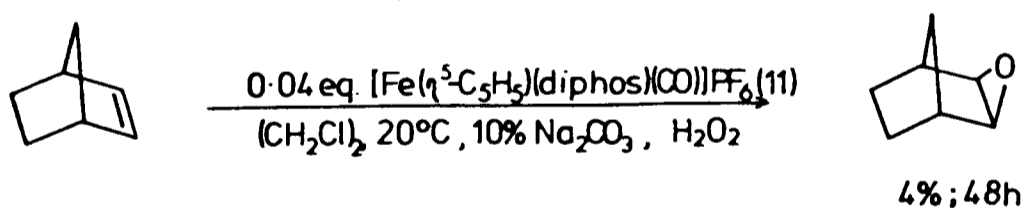
Scheme 9

The success of the cycle illustrated in Scheme 8 relies on fine tuning of the equilibria involved. The partitioning of the metal carbonyl cation and the peroxymetallacarboxylic acid between the aqueous and organic phases for example may be controlled by varying the polarity of the remaining ligands on the metal. The dissociation of the metallacarboxylic acid to metal carbonyl cation has already been demonstrated to be dependent on solvent polarity (see above). The results discussed in Section I.2 demonstrate that nucleophilic attack on metal carbonyl cations may be controlled by altering the other ligands in the complex. It was proposed to investigate the potential of the cations synthesised in Section I.1 to act as catalysts for the direct epoxidation of alkenes by hydrogen peroxide.

I.3.2 Epoxidation

The results discussed in Section I.2 suggest that nucleophilic attack on the cations synthesised in Section I.1 is directed away from the η^5 -hydrocarbon ligand and towards the carbon monoxide ligand at room temperature by the presence of two tertiary phosphine ligands.

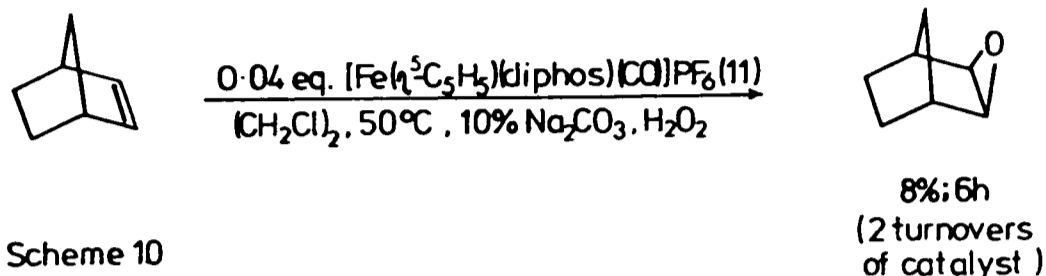
An excess of 85% hydrogen peroxide was added dropwise to a rapidly stirred biphasic mixture of bicyclo [2.2.1] hept-2-ene (norbornene), $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{diphos})(\text{CO})]\text{PF}_6$ (11) (25:1), dichloroethane and 10% aqueous sodium carbonate. After one hour, analysis by gas chromatography revealed that a small quantity of *exo*-norbornene oxide had been produced. Further analysis showed that after 17.5 hours the amount of *exo*-norbornene oxide present in the reaction mixture was equivalent to one third of the amount of the iron cation (11) used and after 48 hours the quantity of *exo*-norbornene oxide present was equivalent to the amount of cation used.



Further stirring did not increase the amount of epoxide present in the reaction mixture. Thus, although an alkene had been oxidised to an epoxide, the reaction did not appear to be catalytic with respect to the cation under these conditions.

The experiment was repeated with the reaction mixture carefully maintained at 50 °C. After 2 hours, decomposition of the 85% hydrogen peroxide was complete and analysis by gas chromatography showed that the ratio of norbornene oxide produced to iron cation used was 3:4. Addition of 30% hydrogen peroxide

followed by vigorous stirring at 50 °C for a further 4 hours increased the ratio of *exo*-norbornene oxide produced to iron cation used from 3:4 to 2:1 *i.e.* the catalyst had performed 2 turnovers in 6 hours.[†]



Although $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{diphos})(\text{CO})]\text{PF}_6$ (11) "catalysed" the oxidation of norbornene to *exo*-norbornene oxide, the turnover rate of the catalyst was low and the lifetime of the catalyst short; furthermore, a reduction in reaction temperature from 50 °C to room temperature is desirable to retard the decomposition of hydrogen peroxide.

The counter-ion of the iron cation (11) was changed from hexafluorophosphate to chloride. This should enhance the solubility of the complex in the aqueous phase thus increasing contact between the cation and hydrogen peroxide. (It also tests the hypothesis that the hexafluorophosphate anion is catalysing the oxidation.) 85% Hydrogen peroxide was added to a biphasic mixture of norbornene, $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{diphos})(\text{CO})]\text{Cl}$ (11a) (25:1), dichloroethane and 10% aqueous sodium carbonate. Analysis by gas chromatography after 48 hours revealed that the ratio of *exo*-norbornene oxide produced to cation used was 1:3.

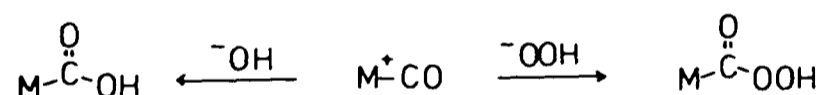
† Although 2 turnovers in 6 hours was normally observed, occasionally turnovers in the range 5-10 occurred both in Oxford and at Laporte Industries Limited in Widnes.

Further attempts were made to improve the result given in Scheme 10 and the variations that were tried are outlined below.

The solvents used (in order of increasing dielectric constant) included benzene, toluene, tetrahydrofuran, dichloroethane, methanol and dimethylformamide. The variation in dielectric constant alters the degree of ionisation of the peroxymetallacarboxylic acid and affects the partitioning of the metal cation and the peroxymetallacarboxylic acid between the aqueous and organic phases. Solvents miscible with water increase the contact between the metal cation and the hydrogen peroxide.

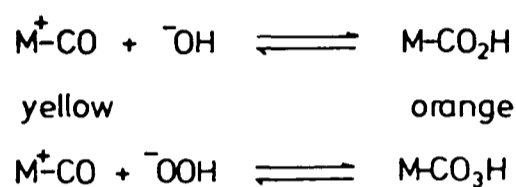
A number of alkenes were used as the substrate: cyclohexene, norbornene, allyl bromide, allyl acetate and allyl alcohol.

It was postulated that the catalytic cycle would be extremely sensitive to the pH of the system. Nucleophilic attack of hydroperoxide ion on the cation will compete with nucleophilic attack of hydroxide ion.

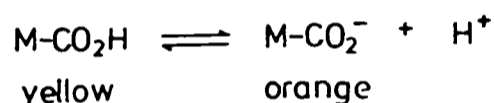


Measurement of rate constants for attack by hydroperoxide and hydroxide ions on several substrates reveals that the hydroperoxide ion is more reactive than hydroxide ion by a factor sometimes larger than 10^4 , in spite of its much lower basicity⁷⁰ ($\text{pK}_a(\text{H}_2\text{O}_2) = 11.6^{71}$). Although a high pH (>10) would favour attack of the hydroperoxide ion, a high pH is incompatible with the product epoxide. An optimum pH should lie between 7 and 9 with the higher nucleophilicity of the hydroperoxide ion with respect to the hydroxide ion counterbalancing its lower concentration in this range. The following bases were used in the reaction mixture: sodium carbonate, sodium hydrogen carbonate, sodium hydroxide, sodium oxide, sodium acetate, sodium methoxide and

triethylamine. An initial biphasic mixture of cation, alkene, solvent and hydrogen peroxide was yellow. Increasing the pH from 4 to 9 by addition of base resulted in a rapid distinct colour change to orange at pH 9 which was readily reversed by addition of hexafluorophosphoric acid to pH 6. This pH dependent colour change could be repeated indefinitely. Repeated attempts to isolate the orange species failed. The colour change may be associated with one of three equilibria *i.e.* addition of a nucleophile to a carbon monoxide ligand.



or dissociation of the metallacarboxylic acid



30% Hydrogen peroxide is an attractive reagent for industrial processes due to its stability relative to more concentrated solutions. Reduction of the water content of the hydrogen peroxide will reduce competition from hydroxide ion for the cation, making hydroperoxide ion attack and peroxy metallacarboxylic acid formation more favourable. The hydrogen peroxide sources used were 85% hydrogen peroxide, an anhydrous solution of hydrogen peroxide in diethyl ether (prepared by drying a mixture of 85% hydrogen peroxide and diethyl ether over sodium sulphate and calcium sulphate) and a complex of urea and hydrogen peroxide (prepared by crystallisation of urea from 30% hydrogen peroxide⁷²).

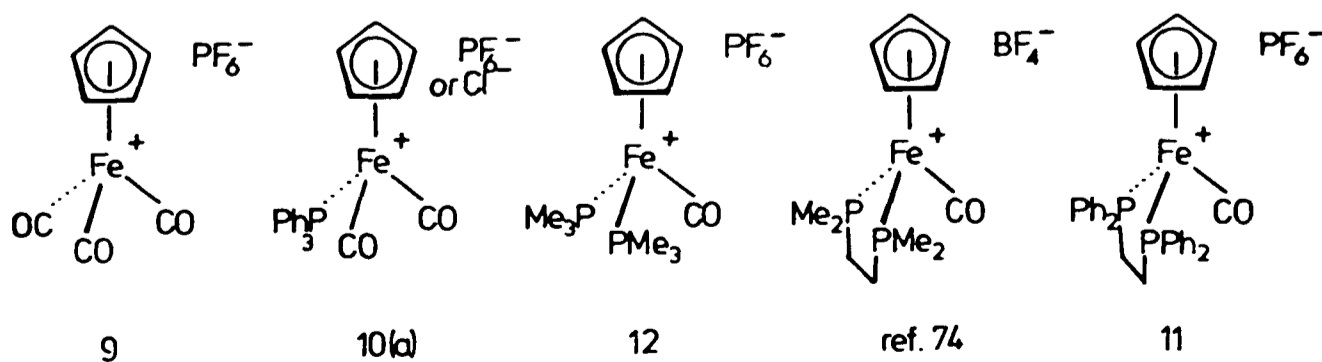
In order to increase the contact between the organic phase and the aqueous phase, the reaction mixture was subjected to sonication.

None of the variations on the original reaction mixture discussed above gave a better yield of epoxide or an improved number of turnovers of the catalyst and the majority produced no epoxide at all.

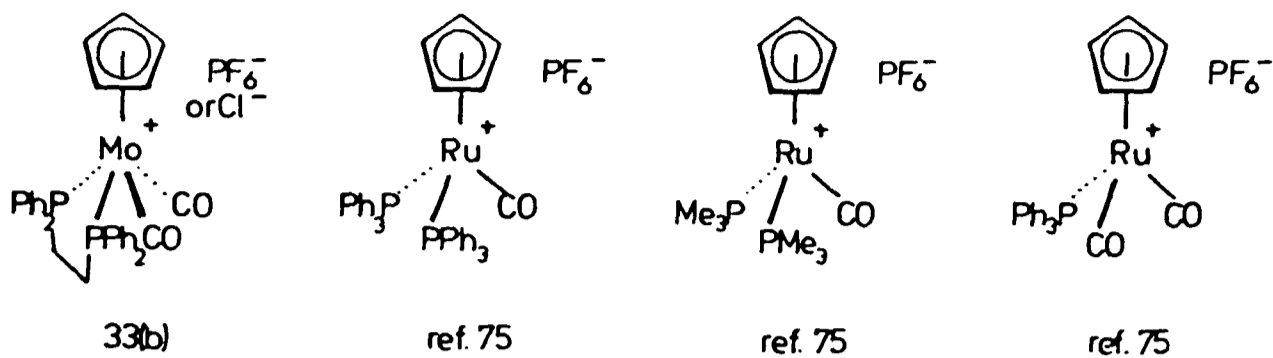
Attempts to improve on the oxidation of norbornene achieved with $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{diphos})(\text{CO})]\text{PF}_6$ (11) and sodium carbonate in dichloroethane at 50 °C included testing many transition metal compounds for catalytic activity.

It was postulated that metal nitrile compounds may enter the catalytic cycle as a result of their conversion to metal carbonyl cations (see Scheme 9). A biphasic mixture of norbornene, $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{CN}]^{73}$ (25:1), dichloroethane, 30% hydrogen peroxide and 8% sodium hydrogen carbonate was carefully heated to 70 °C. After 2 hours the ratio of *exo*-norbornene oxide produced to ruthenium compound used was 1:3. Further heating did not increase the yield of epoxide. A reaction mixture containing $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{diphos})\text{CN}]^{73}$ failed to produce any epoxide.

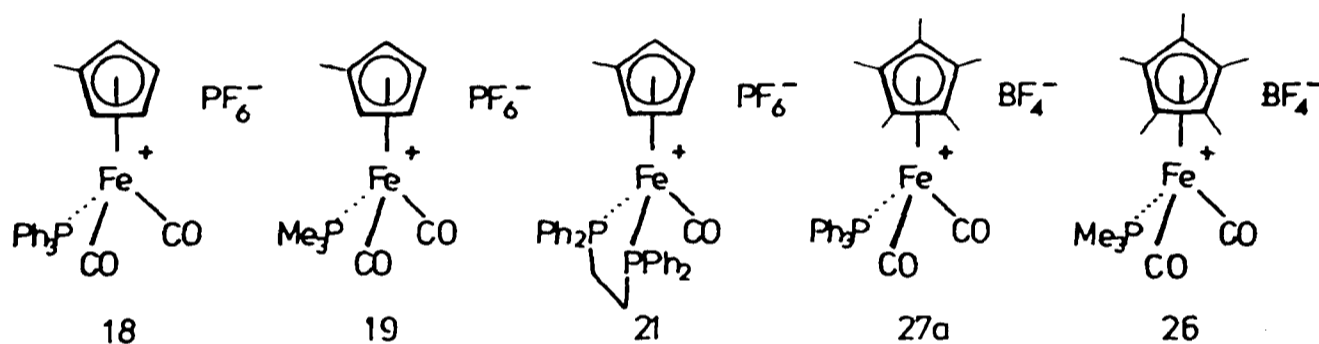
The degree of tertiary phosphine substitution and the nature of the phosphine in the potential metal carbonyl catalyst were changed in order to vary the rate of nucleophilic attack by the hydroperoxide ion. Some of the compounds tested are illustrated below:



The metal centre was varied:



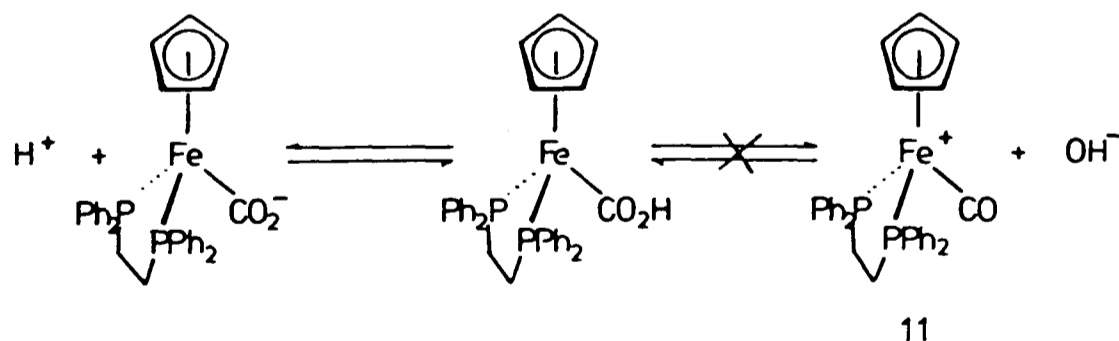
Substitution of the hydrogen atoms of the η^5 -hydrocarbon by methyl groups will alter the electronic, steric and solubility properties of the cation. The following compounds were tested for catalytic activity:



None of these cations gave a better yield of epoxide or an improved number of turnovers than $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{diphos})(\text{CO})]\text{PF}_6$ (11). The majority produced no epoxide at all.

I.3.3 Conclusions

A reaction mixture containing $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{diphos})(\text{CO})]\text{PF}_6$ (11), norbornene (1:25), base and hydrogen peroxide produced *exo*-norbornene oxide in 4% yield in 48 hours at 20 °C after which time no more epoxidation occurred. At 50 °C the yield was 8% in 6 hours. Under the former conditions, the production of one equivalent of epoxide relative to cation present suggests that a peroxymetallacarboxylic acid is indeed being formed although the rate of epoxidation is slow. The rate of epoxidation of alkenes by organic peracids is increased by the presence of electron withdrawing groups *e.g.* $\text{CF}_3\text{CO}_3\text{H} > \text{HCO}_3\text{H} > \text{CH}_3\text{CO}_3\text{H} > \text{C}_6\text{H}_5\text{CO}_3\text{H}$. The $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{diphos})]$ moiety is relatively electron rich and this would account for the low rate of epoxidation. As only one equivalent of epoxide is formed at 20 °C, the catalytic cycle is not operating; presumably the metallacarboxylic acid is not dissociating back to the carbonyl cation and hydroxide ion. Deprotonation of the acid under the basic conditions of the reaction may provide an explanation for this.



Heating the reaction to 50 °C allows the catalytic cycle to operate; increasing the temperature presumably favours dissociation back to cation and increases the epoxidation rate.

It appears that a fine balance of conditions is required

to achieve a higher catalytic turnover and epoxidation rate. Whilst an electron rich cation directs nucleophilic attack to a carbon monoxide ligand, the resultant electron rich peracid is a poor epoxidising agent. Although a base is required to generate the peroxy-metallacarboxylic acid, the basic conditions promote deprotonation of the metallacarboxylic acid thus retarding its dissociation back to cation.

Experimental

General

All reactions involving transition metal complexes were performed under an atmosphere of nitrogen, using standard vacuum line and Schlenk techniques, unless otherwise stated.⁷⁶

Reagents and solvents

Tetrahydrofuran and *toluene* were distilled from sodium benzophenone ketyl under nitrogen. *Dichloromethane* was distilled from calcium hydride under nitrogen. *DMSO* was heated (100 °C) over calcium hydride for 6 h, then distilled under reduced pressure (80 °C, 15 mm Hg) from a small quantity of fresh calcium hydride. *Methanol* was distilled before use. *Diethyl ether* was peroxide free and dried over sodium wire. *Light petroleum* refers to the fraction boiling between 40 °C and 60 °C. 2% Sodium amalgam is w/w.

Infra-red spectra were recorded on Perkin-Elmer 257 and Pye-Unicam SP3 instruments and calibrated against a polystyrene standard.

¹H N.m.r. spectra were recorded on Hitachi-Perkin-Elmer R24B (60 MHz), Brüker WH90 (90 MHz), Brüker AM250 (250 MHz) and Brüker WH300 (300 MHz) instruments. Tetramethylsilane was used as an internal standard where appropriate.

²H N.m.r. spectra were recorded on a Brüker WH300 (46.07 MHz) instrument and referenced to internal C₆D₆.

³¹P N.m.r. spectra were recorded on Brüker WH90 (36.43 MHz),

Brüker AM250 (101.2 MHz) and Brüker WH300 (121.5 MHz) instruments. Spectra were referenced to external polyphosphoric acid and were fully proton decoupled.

^{13}C N.m.r. spectra were recorded on a Brüker AM250 (62.89 MHz) instrument. Spectra were fully proton decoupled and referenced to internal CDCl_3 .

Mass spectra were recorded on a VG Micromass ZAB 1F instrument. Where applicable they are related to the most abundant isotope of molybdenum, ^{98}Mo .

Elemental microanalyses were carried out by Dr. F. B. Strauss.

Column chromatography was performed using deactivated (Grade V) basic alumina.

Experimental for Section I.1[Fe(η^5 -C₅H₅)(CO)₂Cl] (7)

Tetrahydrofuran (100 ml) was added to a mixture of [Fe(η^5 -C₅H₅)(CO)₂]₂ (6) (4.00 g, 11.3 mmol) and 2% Na/Hg (1.00 g of Na, 43 mmol). After stirring for 16 h at 20 °C, the solution was decanted and H₂O added (1 ml). The solvent was removed under reduced pressure, the residue extracted with light petroleum (3 x 20 ml) and the extracts added to a rapidly stirred mixture of CCl₄ (5 ml) and light petroleum (5 ml). Concentration and cooling to -30 °C gave red crystals of (7), 3.17 g (66%); ν_{\max} . (Nujol) 2 050s (CO), 1 995s (CO) cm⁻¹; ¹H n.m.r. (60 MHz, CDCl₃) δ 5.1 (s, C₅H₅). Lit.⁷⁷: ν_{\max} . (CCl₄) 2 050vs (CO) and 2 010vs (CO).

[Fe(η^5 -C₅H₅)(CO)₃]PF₆ (9)

Tetrahydrofuran (100 ml) was added to a mixture of [Fe(η^5 -C₅H₅)(CO)₂]₂ (6) (2.00 g, 5.65 mmol) and 2% Na/Hg (0.50 g of Na, 22 mmol). After stirring for 16 h at 20 °C, the solution was decanted and cooled to -78 °C. ClCO₂Et (5.0 ml, 52 mmol) was added and the solution stirred at -78 °C for 1 h and 20 °C for 1 h. The solvent was removed under reduced pressure and the residue extracted with light petroleum (4 x 20 ml) to give a yellow-brown solution which was treated with HCl gas for 20 min at 0 °C. The yellow crystals produced were collected by filtration and suspended in methanol (30 ml) containing NH₄PF₆ (2.50 g, 15 mmol) for 30 min. Removal of the solvent under reduced pressure, extraction with acetone (3 x 20 ml), concentration (20 ml) and addition of diethyl ether gave yellow crystals of (9), 1.54 g (39%). See Table 2, p 84.

[Fe(η^5 -C₅H₅)(PPh₃)(CO)₂]PF₆ (10)

A mixture of [Fe(η^5 -C₅H₅)(CO)₂Cl] (7) (1.00 g, 4.71 mmol) and PPh₃ (1.30 g, 4.96 mmol) in tetrahydrofuran (30 ml) was heated under reflux for 2 h. The yellow crystals produced were collected by filtration and suspended in methanol (30 ml) containing NH₄PF₆ (1.20 g, 7.1 mmol) for 30 min. Removal of the solvent under reduced pressure, extraction with dichloromethane (2 x 20 ml), concentration (10 ml) and addition of diethyl ether gave yellow crystals of (10), 1.83 g (70%). See Table 2, p 84.

[Fe(η^5 -C₅H₅)(PMe₃)(CO)₂]BF₄ (13)

[Fe(η^5 -C₅H₅)(PPh₃)(CO)₂]BF₄ (10b) (0.050 g 0.10 mmol) and PMe₃ (0.2 ml, 2.0 mmol) were stirred in acetone (10 ml) for 1 h at 20 °C. The solvent was removed under reduced pressure and the residue washed with toluene (2 x 5 ml) to give (13) as a yellow powder, 0.028 g (80%). See Table 2, p 84.

[Fe(η^5 -C₅H₅)(PPh₃)₂(CO)]PF₆ (14)

A mixture of [Fe(η^5 -C₅H₅)(PPh₃)(CO)₂]PF₆ (10) (2.00 g, 3.43 mmol), PPh₃ (1.00 g, 3.82 mmol) and Me₃NO.2H₂O (0.84 g, 7.5 mmol) in acetone (70 ml) was stirred for 1 h at 20 °C. The solvent was removed under reduced pressure and the orange residue extracted with dichloromethane (3 x 20 ml) and concentrated (5 ml). Chromatography on alumina [dichloromethane-toluene (1:1)] gave an orange band which on concentration gave orange crystals of (14), 2.00 g (70%). See Table 2, p 84.

Table 2

Characterisation of cationic η^5 -C₅H₅ complexes of Fe by infra-red spectroscopy, mass spectrometry, ¹H n.m.r. and ³¹P-(¹H) n.m.r. spectroscopy

Compound	$\nu_{\text{max.}}$ (cm ⁻¹)	m/z[M] ⁺	¹ H n.m.r. ¹			³¹ P-(¹ H) n.m.r.	
			Solvent	δ C ₅ H ₅	δ Phosphine		Solvent
⁴ 8 [Fe(η^5 -C ₅ H ₅)(CO) ₃]PF ₆ (9)	2 125s (CO) 2 070s (CO)	205	(CD ₃) ₂ CO	6.1, s		(CH ₃) ₂ CO	
¹ 5 [Fe(η^5 -C ₅ H ₅)(PPh ₃) ₂ (CO) ₂]PF ₆ (10)	2 065s (CO) 2 020s (CO)	439	(CD ₃) ₂ CO	5.6, 5H, d, ³ J _{PH} =1Hz	7.7-7.2, 15H, m, aryl-H.	(CH ₃) ₂ CO	59.8
⁷ 8 [Fe(η^5 -C ₅ H ₅)(PMe ₃) ₂ (CO) ₂]BF ₄ (13)	2 050s (CO) 1 995s (CO)	253	(CD ₃) ₂ SO	5.5, 5H, d, ³ J _{PH} =1Hz	1.8, 9H, d, ² J _{PH} =11 Hz, PMe ₃ .	(CH ₃) ₂ CO	30.8 ²
¹ 5 [Fe(η^5 -C ₅ H ₅)(PPh ₃) ₂ (CO)]PF ₆ (14)	1 980s (CO)	818	(CD ₃) ₂ SO	4.8, 5H, t, ³ J _{PH} =1Hz	7.5-6.9, 30H, m, aryl-H	CH ₂ Cl ₂ /THF	56.6
⁷ 9 [Fe(η^5 -C ₅ H ₅)(diphos)(CO)]PF ₆ (11)	1 975s (CO)	547	(CD ₃) ₂ CO	5.1, 5H, t, ³ J _{PH} =1Hz	8.2-7.2, 20H, m, aryl-H; 3.2-2.8, 4H, m, CH ₂ .	(CH ₃) ₂ CO	91.6
⁷ 8 [Fe(η^5 -C ₅ H ₅)(PMe ₃) ₂ (CO)]PF ₆ (12)	1 945s (CO)	301	(CD ₃) ₂ CO	5.1, 5H, t, ³ J _{PH} =1Hz	1.7, 18H, X' ₉ A'AX ₉ , ² J _{PH} + ⁴ J _{PH} =11Hz, PMe ₃	(CH ₃) ₂ CO	25.6

1. ¹H n.m.r. data is given in the following order: δ , intensity, multiplicity, coupling constant.

2. This value was recorded using the hexafluorophosphate salt.

[Fe(η^5 -C₅H₅)(diphos)(CO)]PF₆ (11)

A mixture of [Fe(η^5 -C₅H₅)(CO)₂Cl] (7) (1.00 g, 4.71 mmol) and diphos (2.25 g, 5.65 mmol) in tetrahydrofuran (30 ml) was heated under reflux for 2 h. The yellow precipitate produced was collected by filtration and suspended in methanol (30 ml) containing NH₄PF₆ (1.15 g, 6.8 mmol) for 30 min. Removal of the solvent under reduced pressure, extraction with dichloromethane (2 x 20 ml), concentration (10 ml) and addition of diethyl ether gave yellow crystals of (11), 2.45 g (75%). See Table 2, p 84.

[Fe(η^5 -C₅H₅)(PMe₃)₂(CO)]PF₆ (12)

[Fe(η^5 -C₅H₅)(CO)₂Cl] (7) (3.00 g, 14.1 mmol) and PMe₃ (2.1 ml, 21 mmol) in tetrahydrofuran (100 ml) were heated under reflux for 4 h. The yellow precipitate was collected by filtration and suspended in methanol (50 ml) containing NH₄PF₆ (3.40 g, 20.1 mmol) for 30 min. Removal of the solvent under reduced pressure and extraction with dichloromethane (2 x 35 ml) gave a yellow solution. Concentration (30 ml) and addition of diethyl ether gave yellow crystals of (12), 4.47 g (71%).

[Fe(η^5 -C₅H₄CH₃)(CO)₂]₂ (15)

Freshly cracked C₅H₅CH₃ (40 g, 0.5 mol), Fe(CO)₅ (40 ml) and heptane (40 ml) were heated (oil bath temperature, 140 °C) for 16 h. The red-brown solution obtained was concentrated (80 ml), added to a column of alumina and washed with light petroleum (6 x 75 ml) until the washings were colourless. Addition of dichloromethane (300 ml) developed a red band which was collected; removal of solvent under reduced pressure gave

purple crystals of (15), 12.76 g (13% based on $C_5H_5CH_3$); $\nu_{max.}$ (CCl_4) 2 060m (CO), 2 010s (CO), 1 955s (CO), 1 920sh,w (CO) and 1 780s (CO); 1H n.m.r. (60MHz, $CDCl_3$) δ 4.5 (4H, s, $H_{2,3,4,5}$) and 2.05 (3H, s, $C_5H_4CH_3$); m.p. 98-99 °C. Lit.¹⁷ : $\nu_{max.}$ (CCl_4) 2 050m (CO), 1 999vs (CO), 1 953vs (CO), 1 923sh,m (CO), 1 791sh,m (CO) and 1 779vs (CO); m.p. 98-99 °C.

$[Fe(\eta^5-C_5H_4CH_3)(CO)_2Cl]$ (16)

$[Fe(\eta^5-C_5H_4CH_3)(CO)_2Cl]$ (16) was prepared by the route previously described for $[Fe(\eta^5-C_5H_5)(CO)_2Cl]$ (7). Yield 52%; $\nu_{max.}$ (CCl_4) 2 055s (CO) and 2 015s (CO); 1H n.m.r. (60MHz, $CDCl_3$) δ 4.9 (2H, s, $H_{3,4}$), 4.7 (2H, s, $H_{2,5}$) and 2.0 (3H, s, $C_5H_4CH_3$). Lit.⁸⁰ : $\nu_{max.}$ (CH_2Cl_2) 2 053s (CO) and 2 006s (CO); 1H n.m.r. ($CDCl_3$) δ 4.93 and 4.73 ($H_{2,3,4,5}$).

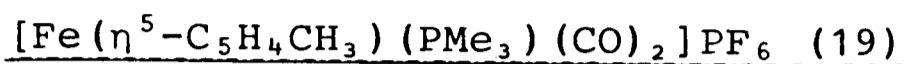
$[Fe(\eta^5-C_5H_4CH_3)(CO)_3]PF_6$ (17)

$[Fe(\eta^5-C_5H_4CH_3)(CO)_3]PF_6$ (17) was prepared by the route previously described for $[Fe(\eta^5-C_5H_5)(CO)_3]PF_6$ (9). Yield 93%. See Tables 4a and 4b, p 88, 89.

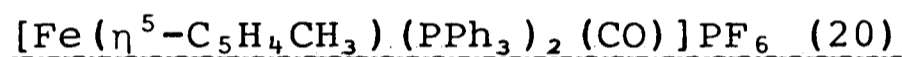
$[Fe(\eta^5-C_5H_4CH_3)(PPh_3)(CO)_2]PF_6$ (18)

A mixture of $[Fe(\eta^5-C_5H_4CH_3)(CO)_2Cl]$ (16) (0.50 g, 2.21 mmol) and PPh_3 (0.64 g, 2.44 mmol) was stirred in toluene (50 ml) at 25 °C for 5 h. The yellow precipitate produced was collected by filtration, washed with toluene (10 ml) and suspended in methanol (40 ml) containing NH_4PF_6 (0.56 g, 3.31 mmol) for 30 min. Removal of the solvent under reduced pressure and extraction with dichloromethane (2 x 20 ml) gave a yellow solution. Concentration (10 ml) and addition to rapidly stirred diethyl

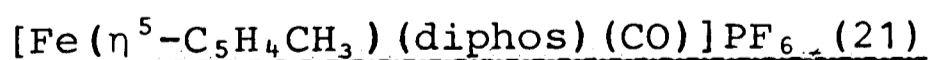
ether (150 ml) produced a fine precipitate; crystallisation from dichloromethane-diethyl ether gave yellow crystals of (18), 1.00 g (76%). See Tables 4a and 4b, p 88, 89.



A mixture of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)(\text{PPh}_3)(\text{CO})_2]\text{PF}_6$ (18) (0.40 g, 0.67 mmol) and PMe_3 (0.2 ml, 2.0 mmol) in acetone (20 ml) was stirred for 1 h at 20 °C. The solvent was removed under reduced pressure and the residue washed with diethyl ether (2 x 10 ml). Crystallisation from dichloromethane-diethyl ether at -30 °C gave yellow crystals of (19), 0.24 g (89%). See Tables 4a and 4b, p 88, 89.



A mixture of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)(\text{PPh}_3)(\text{CO})_2]\text{PF}_6$ (18) (1.00 g, 1.67 mmol), PPh_3 (0.88 g, 3.36 mmol) and $\text{Me}_3\text{NO}\cdot 2\text{H}_2\text{O}$ (0.56 g, 5.05 mmol) in acetone (70 ml) was stirred for 2 h at 20 °C. The solvent was removed under reduced pressure and the brown residue dissolved in dichloromethane (70 ml); this solution was washed with water (3 x 20 ml) and dried over magnesium sulphate. Filtration, concentration (10 ml) and addition to rapidly stirred diethyl ether (150 ml) gave an orange crystalline precipitate of (20), 1.13 g (81%). See Tables 4a and 4b, p 88, 89.



A mixture of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)(\text{CO})_2\text{Cl}]$ (16) (0.50 g, 2.21 mmol) and diphos (0.97 g, 2.44 mmol) in toluene (60 ml) was heated under reflux for 5 h. The yellow precipitate produced was collected by filtration, washed with toluene (10 ml) and

Table 4a

Characterisation of cationic $\eta^5\text{-C}_5\text{H}_4\text{CH}_3$ complexes of Fe by infra-red spectroscopy, mass spectrometry and elemental microanalysis

Compound	$\nu_{\text{max.}}$ (cm^{-1})	m/z [M] ⁺	Elemental microanalysis data ⁺ (%)
$[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)(\text{CO})_3]\text{PF}_6$ (17)	2 130s (CO) 2 095s (CO)	219	C, 29.47(29.71); H, 2.19(1.94); P, 8.70(8.51).
$[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)(\text{PPh}_3)(\text{CO})_2]\text{PF}_6$ (18)	2 070s (CO) 2 015s (CO)	453	C, 52.02(52.19); H, 3.90(3.71); P, 10.26(10.35).
$[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)(\text{PMe}_3)(\text{CO})_2]\text{PF}_6$ (19)	2 055s (CO) 2 010s (CO)	267	C, 31.94(32.06); H, 3.88(3.92).
$[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)(\text{PPh}_3)_2(\text{CO})]\text{PF}_6$ (20)	1 955s (CO)	687	
$[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)(\text{diphos})(\text{CO})]\text{PF}_6$ (21)	1 960s (CO)	561	C, 55.89(56.11); H, 4.67(4.43); P, 13.10(13.15).
$[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)(\text{PMe}_3)_2(\text{CO})]\text{PF}_6$ (22)	1 950s (CO)	315	C, 34.12(33.91); H, 5.46(5.43); P, 19.85(20.22).

+ Found (Required)

Table 4b

Characterisation of cationic $\eta^5\text{-C}_5\text{H}_4\text{CH}_3$ complexes of Fe by ^1H n.m.r. and $^3\text{P-}(\text{H})$ n.m.r. spectroscopy

Compound	^1H n.m.r. †						$^3\text{P-}(\text{H})$ n.m.r.	
	Solvent	δ $\text{H}_{3,4}$	δ $\text{H}_{2,5}$	δ $\text{C}_5\text{H}_4\text{CH}_3$	δ Phosphine	Solvent	δ P	
(17)	$(\text{CD}_3)_2\text{CO}$	6.03, 2H, 't'	5.96, 2H, 't'	2.30, 3H, s				
(18)	$(\text{CD}_3)_2\text{CO}$	5.57, 2H, br s	5.37, 2H, br s	2.18, 3H, s	7.8-7.5, 15H, m, aryl-H	$(\text{CH}_3)_2\text{CO}$	63.2	
(19)	$(\text{CD}_3)_2\text{CO}$	5.53, 2H, s	5.51, 2H, s	2.16, 3H, s	1.88, 9H, d, $^2\text{J}_{\text{PH}}=11$ Hz, PMe ₃	$(\text{CH}_3)_2\text{CO}$	31.9	
(20)	$(\text{CD}_3)_2\text{CO}$	4.82, 2H, s	4.47, 2H, s	1.98, 3H, s	8.0-7.3, 30 H, m, aryl-H.	$(\text{CD}_3)_2\text{CO}$	57.3	
(21)	$(\text{CD}_3)_2\text{CO}$	5.30, 2H, br s	4.69, 2H, br s	1.96, 3H, s	7.9-7.4, 20 H, m, aryl-H; 2.96-2.90, 4H, m, CH ₂	$(\text{CH}_3)_2\text{CO}$	91.7	
(22)	$(\text{CD}_3)_2\text{CO}$	5.12, 2H, br s	4.87, 2H, br s	2.07, 3H, br s	1.68, 18H, X ⁹ A'AX ₉ , $^2\text{J}_{\text{PH}} + ^4\text{J}_{\text{PH}} = 11$ Hz, PMe ₃	$(\text{CH}_3)_2\text{CO}$	27.3	

† ^1H n.m.r. data is given in the following order: δ , intensity, multiplicity.

suspended in wet acetone (30 ml) containing NH_4PF_6 (0.56 g, 3.31 mmol). $\text{Me}_3\text{NO}\cdot 2\text{H}_2\text{O}$ (0.49 g, 4.41 mmol) was added and the mixture stirred for 2 h. Removal of the solvent under reduced pressure and extraction with dichloromethane (2 x 30 ml) gave a yellow solution which was washed with water, decanted and dried over magnesium sulphate. Filtration, concentration (10 ml) and addition to rapidly stirred diethyl ether produced a fine, pale yellow precipitate; crystallisation from dichloromethane-diethyl ether gave yellow crystals of (21), 1.27 g (81%). See Tables 4a and 4b, p 88, 89.

$[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)(\text{PMe}_3)_2(\text{CO})]\text{PF}_6$ (22)

Addition of PMe_3 (0.5 ml, 5.0 mmol) to a solution of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)(\text{CO})_2\text{Cl}]$ (16) (0.25 g, 1.10 mmol) in tetrahydrofuran (30 ml) produced a yellow precipitate instantaneously. After stirring for 4 h at 25 °C, the solid was collected by filtration and suspended in methanol (30 ml) containing NH_4PF_6 (0.25 g, 1.48 mmol) for 30 min. Removal of the solvent under reduced pressure and extraction with dichloromethane (2 x 20 ml) gave a yellow solution. Concentration (10 ml) and slow addition of diethyl ether gave yellow crystals of (22), 0.41 g (80%). See Tables 4a and 4b, p 88, 89.

$[\text{Fe}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{CO})_2]_2$ (23)

$\text{C}_5(\text{CH}_3)_5\text{H}$ (2.20 g, 16.18 mmol), $\text{Fe}(\text{CO})_5$ (10.00g, 51.02 mmol) and octane (50 ml) were heated (oil bath temperature 130 °C) for 60 h. The resultant deep red solution was cooled (0 °C) and the red-purple crystalline precipitate isolated by filtration. Extraction with dichloromethane (10 x 30 ml)

followed by removal of solvent under reduced pressure gave red-purple crystals of (23), 2.93 g (73% based on $C_5(CH_3)_5H$); ν_{max} . (Nujol) 1 940s (CO) and 1 745s (CO) cm^{-1} ; 1H n.m.r. (60MHz, $CDCl_3$) δ 1.65 (s, $C_5(CH_3)_5$). Lit.¹¹: ν_{max} . (cyclohexane) 1 932s (CO) and 1 764s (CO); 1H n.m.r. (CS_2) δ 1.62 (s, $C_5(CH_3)_5$).

$[Fe(\eta^5-C_5(CH_3)_5)(CO)_2Br]$ (24)

Br_2 (0.15 g, 0.94 mmol) in chloroform (10 ml) was added slowly (15 min) to a stirred solution of $[Fe(\eta^5-C_5(CH_3)_5)(CO)_2]_2$ (23) (0.40 g, 0.81 mmol) in chloroform (20 ml) and dichloromethane (10 ml) at 0 °C. After stirring at 20 °C for 3 h, the solution was washed with aqueous sodium thiosulphate solution (10 ml) and water (2 x 10 ml) and dried over magnesium sulphate. Filtration and removal of the solvent under reduced pressure gave deep violet crystals of (24), 0.40 g (76%); ν_{max} . (Nujol) 2 015s (CO) and 1 975s (CO) cm^{-1} ; 1H n.m.r. (60 MHz, $(CD_3)_2CO$) δ 1.9 (s, $C_5(CH_3)_5$). Lit.²⁰: ν_{max} . (cyclohexane) 2 033s (CO) and 1 978s (CO); 1H n.m.r. ($CDCl_3$) δ 1.83 (s, $C_5(CH_3)_5$).

$[Fe(\eta^5-C_5(CH_3)_5)(CO)_3]PF_6$ (25)

Li metal (0.056 g, 8.0 mmol) was added to naphthalene (1.038 g, 8.1 mmol) in tetrahydrofuran (40 ml) giving a green solution after 1 min. After stirring for 30 min, a solution of $[Fe(\eta^5-C_5(CH_3)_5)(CO)_2]_2$ (23) (1.00 g, 2.02 mmol) in tetrahydrofuran (40 ml) was added and the resultant brown solution stirred for a further 4 h. $ClCO_2Et$ (4.0 g, 41.8 mmol) was added and the solution stirred at 20 °C for 16 h. The solvent was removed under reduced pressure and the residue extracted with light petroleum (4 x 20 ml) to give a brown solution* which was

treated with HCl gas for 20 min at 0 °C. The yellow powder was collected by filtration and suspended in methanol (20 ml) containing NH_4PF_6 (0.50 g, 2.96 mmol) for 30 min. Removal of the solvent under reduced pressure, extraction with acetone (3 x 10 ml), concentration (10 ml) and addition of diethyl ether gave yellow crystals of (25), 0.65 g (39%). See Tables 6a and 6b, p 93, 94.

$[\text{Fe}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{CO})_3]\text{BF}_4$ (25a)

$[\text{Fe}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{CO})_3]\text{BF}_4$ (25a) was prepared by the method previously described for $[\text{Fe}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{CO})_3]\text{PF}_6$ (25) up to the point marked *, when $\text{HBF}_4 \cdot \text{OMe}_2$ was added to the light petroleum solution. The yellow precipitate of (25a) produced was collected in an analogous manner to that used for (25). Yield 29%.

$[\text{Fe}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{PPh}_3)(\text{CO})_2]\text{PF}_6$ (27)

PPh_3 (0.040 g, 0.153 mmol) was added to a stirred solution of $[\text{Fe}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{CO})_3]\text{PF}_6$ (25) (0.060 g, 0.143 mmol) in DMSO (10 ml). After stirring for 1 h, water (15 ml) was added, the solution extracted with dichloromethane (3 x 20 ml) and the extracts dried over magnesium sulphate. Filtration, removal of solvent under reduced pressure and washing with hot toluene (3 x 15 ml) gave pure yellow crystals of (27), 0.073 g (78%). See Tables 6a and 6b, p 93, 94.

$[\text{Fe}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{PMe}_3)(\text{CO})_2]\text{BF}_4$ (26)

Excess PMe_3 (0.1 ml, 1.0 mmol) was added to a stirred solution of $[\text{Fe}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{CO})_3]\text{BF}_4$ (25a) (0.060 g, 0.166 mmol)

Table 6a

Characterisation of cationic $\eta^5\text{-C}_5(\text{CH}_3)_5$ complexes of Fe by infra-red spectroscopy, mass spectrometry and elemental microanalysis

<u>Compound</u>	<u>ν_{max} (cm⁻¹)</u>	<u>m/z [M]⁺</u>	<u>Elemental microanalysis data[†] (%)</u>
$^{21}\text{[Fe}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{CO})_3\text{]PF}_6$ (25)	2 105s (CO) 2 040s (CO)		
$[\text{Fe}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{PPh}_3)(\text{CO})_2]\text{PF}_6$ (27)	2 040s (CO) 1 987s (CO)	509	C, 55.88 (55.04); H, 4.75 (4.59)
$[\text{Fe}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{PMe}_3)(\text{CO})_2]\text{BF}_4$ (26)	2 070s (CO) 1 995s (CO)	323	C, 43.84 (43.90); H, 6.06 (5.85); P, 7.84 (7.56).
$[\text{Fe}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{diphos})(\text{CO})]\text{PF}_6$ (28)	1 940m (CO)	617	

[†] Found (Required)

Table 6b

Characterisation of cationic $\eta^5\text{-C}_5(\text{CH}_3)_5$ complexes of Fe by ^1H n.m.r. and ^{31}P -(^1H) n.m.r. spectroscopy

Compound	^1H n.m.r. †			^{31}P -(^1H) n.m.r.	
	Solvent	δ $\text{C}_5(\text{CH}_3)_5$	δ Phosphine	Solvent	δ P
(25)	$(\text{CD}_3)_2\text{CO}$	2.2, s			
(27)	$(\text{CD}_3)_2\text{CO}$	1.85, 15 H, s	7.9-7.5, 15 H, m, aryl-H.	$(\text{CH}_3)_2\text{CO}$	61.6
(26)	$(\text{CD}_3)_2\text{CO}$	2.08, 15 H, s	1.78, 9 H, d, $^2J_{\text{PH}} = 11$ Hz, PMe_3	$(\text{CH}_3)_2\text{CO}$	28.5
(28) ‡	$(\text{CD}_3)_2\text{CO}$	1.42, s	8.0-7.2, m, aryl-H; 2.8-2.4, m, CH_2 .	$(\text{CD}_3)_2\text{CO}$	86.3

† ^1H n.m.r. data is given in the following order: δ , intensity, multiplicity.

‡ These measurements were performed on the tetrafluoroborate salt.

in DMSO (10 ml). After stirring for 10 min, water (15 ml) was added, the solution extracted with dichloromethane (3 x 20 ml) and the extracts dried over magnesium sulphate. Filtration, concentration (5 ml) and addition to rapidly stirred diethyl ether (150 ml), gave a pale yellow powder. Crystallisation from dichloromethane-diethyl ether gave yellow crystals of pure (26), 0.055 g (81%). See Tables 6a and 6b, p 93, 94.

$[\text{Fe}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{PMe}_3)(\text{CO})_2]\text{PF}_6$ (26a)

$[\text{Fe}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{PMe}_3)(\text{CO})_2]\text{PF}_6$ (26a) was prepared by the method previously described for $[\text{Fe}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{PMe}_3)(\text{CO})_2]\text{BF}_4$ (26) except $[\text{Fe}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{CO})_3]\text{PF}_6$ (25) was used in place of $[\text{Fe}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{CO})_3]\text{BF}_4$ (25a). Yield 45%.

$[\text{Fe}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{diphos})(\text{CO})]\text{PF}_6$ (28)

A mixture of $[\text{Fe}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{CO})_3]\text{PF}_6$ (25) (0.082 g, 0.20 mmol), diphos (0.083 g, 0.21 mmol) and $\text{Me}_3\text{NO}\cdot 2\text{H}_2\text{O}$ (0.10 g, 0.90 mmol) in acetone (50 ml) was stirred for 20 h at 20 °C. The solvent was removed under reduced pressure and the residue dissolved in dichloromethane (50 ml); this solution was washed with water (3 x 10 ml) and dried over magnesium sulphate. Filtration, concentration (5 ml) and addition to rapidly stirred diethyl ether (200 ml) gave a pale yellow precipitate of (28), 0.033 g (22%). See Tables 6a and 6b, p 93, 94.

$[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\text{Cl}]$ (29)

Tetrahydrofuran (100 ml) was added to a mixture of $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]_2$ (5) (4.00 g, 8.16 mmol) and 2% Na/Hg (1.00 g of Na, 43 mmol). After stirring for 16 h at 20 °C,

the solution was decanted onto a rapidly stirred mixture of $\text{CH}_3\text{CO}_2\text{H}$ (1 ml) and CCl_4 (9 ml). The solvent was removed under reduced pressure, dichloromethane (20 ml) added and the solution filtered through alumina (5 cm). Concentration followed by the addition of diethyl ether gave red crystals of (29), 2.98 g (65%); ν_{max} . (Nujol) 2 020s (CO), 1 970s (CO) and 1 930sh (CO) cm^{-1} ; ^1H n.m.r. (60 MHz, CDCl_3) δ 5.6 (s, C_5H_5). Lit.²⁶: ν_{max} . (CCl_4) 2 055vs (CO), 1 980vs (CO) and 1 960vs (CO).

$[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\text{Br}]$ (31)

A solution of $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\text{H}]^{27}$ (30) (4.14 g, 16.83 mmol) in dichloromethane (50 ml) was added to a rapidly stirred mixture of CHBr_3 (10 ml) and dichloromethane (10 ml). After stirring at 20 °C for 2 h, the solution was concentrated (30 ml) and light petroleum was added to give red needle crystals of (31), 4.81 g (88%); ν_{max} . (Nujol) 2 050s (CO), 1 970s (CO) and 1 935s (CO) cm^{-1} ; ^1H n.m.r. (60 MHz, CDCl_3) δ 5.65 (s, C_5H_5). Lit.²⁶: ν_{max} . (CCl_4) 2 049vs (CO), 1 977vs (CO) and 1 958vs (CO).

$[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{CO})_3]\text{PF}_6$ (32)

Addition of a cooled (-30 °C) solution of $\text{Ph}_3\text{C}^+\text{PF}_6^-$ (0.96 g, 2.47 mmol) in dichloromethane (20 ml) to rapidly stirred $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\text{H}]^{27}$ (30) (0.61 g, 2.48 mmol) at -30 °C gave a suspension of purple crystals. After adding PPh_3 (0.65 g, 2.48 mmol), the mixture was allowed to warm to 20 °C giving (32) as a pale yellow crystalline precipitate. Addition of diethyl ether (10 ml) gave further crystals of $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{CO})_3]\text{PF}_6$ (32), 1.24 g (77%). See Table 8, p 98.

[Mo(η^5 -C₅H₅)(diphos)(CO)₂]PF₆ (33)

A mixture of [Mo(η^5 -C₅H₅)(CO)₃Br] (31) (1.00 g, 3.08 mmol) and diphos (1.84 g, 4.62 mmol) in benzene (40 ml) was heated under reflux for 4 h. The crystalline, yellow precipitate produced was collected by filtration and suspended in methanol (30 ml) containing NH₄PF₆ (0.75 g, 4.4 mmol) for 30 min. Removal of the solvent under reduced pressure, extraction with dichloromethane (3 x 15 ml), concentration (15 ml) and addition of diethyl ether gave yellow crystals of (33), 1.50 g (64%). See Table 8 p 98.

[Mo(η^5 -C₅H₅)(triphos)(CO)]PF₆ (34)

A mixture of [Mo(η^5 -C₅H₅)(CO)₃Cl] (29) (1.00 g, 3.57 mmol) and triphos (2.75 g, 5.15 mmol) in benzene (40 ml) was heated under reflux for 8 h. Evaporation of solvent under reduced pressure gave a yellow solid which was suspended in wet acetone (30 ml) containing NH₄PF₆ (0.60 g, 3.68 mmol). Me₃NO.2H₂O (0.60 g, 5.41 mmol) was added and the mixture stirred for 6 h. After removal of the acetone under reduced pressure, the residue was extracted with dichloromethane (3 x 15 ml), the combined extracts concentrated (5 ml) and chromatographed on alumina (dichloromethane). A red band developed and was eluted with acetone/NH₄PF₆ producing a red solution which was concentrated (5 ml) and added to rapidly stirred diethyl ether (150 ml) to give a yellow powder. Crystallisation from dichloromethane-diethyl ether gave yellow crystals of pure (34), 0.92 g (30%). See Table 8, p 98.

Table 8

Characterisation of cationic $\eta^5\text{-C}_5\text{H}_5$ complexes of Mo by infra-red spectroscopy, mass spectrometry,elemental microanalysis and ^1H n.m.r. and ^{31}P -(^1H) n.m.r. spectroscopy

Compound	$\nu_{\text{max.}}$ (cm^{-1})	m/z [M] ⁺	Elemental microanalysis data ⁺ (%)
28 $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{CO})_3]\text{PF}_6$ (32)	2 060s (CO) 1 995s (CO) 1 960s (CO)	509 (^{98}Mo)	
81 $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{diphos})(\text{CO})_2]\text{PF}_6$ (33)	1 990s (CO) 1 920s (CO)	617 (^{98}Mo)	
$[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{triphos})(\text{CO})]\text{PF}_6$ (34)	1 863s (CO)	725 (^{98}Mo)	C, 55.19(55.30); H, 4.49(4.38); P, 13.95(14.28).
^1H n.m.r. [†]			
Compound	δ C_5H_5	δ Phosphine	δ P
(32)	Solvent (CD_3) ₂ CO 6.05, 5H, s	7.7-7.2, 15 H, m, aryl-H	Solvent (CH_3) ₂ CO 44.1
(33)	(CD_3) ₂ CO 5.08, 5H, s	7.8-7.5, 20 H, m, aryl-H; 3.4-3.2, and 2.6-2.4, 4 H, m, CH_2 .	(CH_3) ₂ CO 77.5
(34)	(CD_2)Cl ₂ 5.0, 5H, 't', $^3J_{\text{PH}} = 1$ Hz	7.2-6.4, 25 H, m, aryl-H; 2.6-1.4, 8 H, m, CH_2 .	(CH_3) ₂ CO 105.5, t, J=35 Hz, Mo-PPH; 88.7, d, J= 35 Hz, Mo-PPH ₂ .

[†] ^1H n.m.r. data is given in the following order: δ , intensity, multiplicity.⁺ Found (Required).

Experimental for Section I.2Reduction of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]\text{PF}_6$ (9) with LiAlH_4

LiAlH_4 (0.2 g, 5.2 mmol) was added to a cooled ($-78\text{ }^\circ\text{C}$) slurry of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]\text{PF}_6$ (9) (0.200 g, 0.57 mmol) in tetrahydrofuran (20 ml); the mixture was warmed and stirred at $0\text{ }^\circ\text{C}$ for 1 h to give a yellow-brown solution. After addition of H_2O (0.5 ml) at $-78\text{ }^\circ\text{C}$, the products were warmed to $0\text{ }^\circ\text{C}$ and the solvent removed under reduced pressure. Extraction with diethyl ether (2 x 10 ml) gave a red solution which was dried over magnesium sulphate. Filtration, followed by removal of solvent under reduced pressure, gave a red solid identified as $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]_2$ (6) by comparison of its infra-red and ^1H n.m.r. spectra with those of an authentic sample.

Reduction of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{CO})_2]\text{PF}_6$ (10) with LiAlH_4

LiAlH_4 (0.2 g, 5.2 mmol) was added to a cooled ($-78\text{ }^\circ\text{C}$) slurry of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{CO})_2]\text{PF}_6$ (10) (0.200 g, 0.34 mmol) in dichloromethane-tetrahydrofuran (1:1, 20 ml); the mixture was stirred at $-78\text{ }^\circ\text{C}$ for 6 h. After addition of H_2O (1 ml) the products were warmed to $20\text{ }^\circ\text{C}$ and the solvent removed under reduced pressure. Extraction with diethyl ether (2 x 10 ml) gave a yellow-brown solution which was dried over magnesium sulphate. Filtration, followed by removal of solvent under reduced pressure gave a brown oil which was identified as a 15:5:2 mixture of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{CO})\text{H}]$ (43), $[\text{Fe}(\eta^4\text{-C}_5\text{H}_6)(\text{PPh}_3)(\text{CO})_2]$ (44)^{60, 46} and $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]_2$ (6) by comparison of its infra-red and ^1H n.m.r. spectra with those of authentic samples.

Reduction of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{CO})_2]\text{PF}_6$ (10) with NaBD_4

A slurry of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{CO})_2]\text{PF}_6$ (10) (1.20 g, 2.06 mmol) in tetrahydrofuran (50 ml) was cooled with stirring. NaBD_4 (0.5 g, 13 mmol) was added and the mixture stirred at -20°C for 2 h. 30-40 Light petroleum (50 ml) was added to the resultant yellow solution which was cooled (-10°C) and D_2O (5 ml) added. The 30-40 light petroleum layer was decanted and the tetrahydrofuran layer extracted with 30-40 light petroleum (2 x 20 ml). The extracts were combined and the solvent removed under reduced pressure to give $[\text{Fe}(5\text{-exo-}\eta^4\text{-C}_5\text{H}_5\text{D})(\text{PPh}_3)(\text{CO})_2]$ (44a) as a yellow powder, 0.51 g (68%); ν_{max} . (Nujol) 2 085w, 2 060w, 2 015w (CD_{exo}), 1 965s (CO) and 1 900s (CO) cm^{-1} ; ^1H n.m.r. (300 MHz, C_6D_6) δ 7.5 and 7.0 (15H,m,aryl-H), 5.15 (2H,s, $\text{H}_{2,3}$), 2.77 (1H,s, H_{endo}) and 2.28 (2H,s, $\text{H}_{1,4}$). Data for $[\text{Fe}(\eta^4\text{-C}_5\text{H}_6)(\text{PPh}_3)(\text{CO})_2]$ (44)^{60, 46}: ν_{max} . (Nujol) 2 730w (CH_{exo}), 1 978s (CO) and 1 920s (CO); ^1H n.m.r. (C_6D_6) δ 7.5 and 7.0 (15H,m,aryl-H), 5.13 (2H,s, $\text{H}_{2,3}$), 2.78 (1H,s, H_{endo}), 2.27 (2H,s, $\text{H}_{1,4}$) and 2.24 (1H,t, $^2\text{J}_{\text{HH}}=10.5$ Hz, $\text{J}_{\text{PH}}=10.5$ Hz, H_{exo}).

Reduction of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2(\text{CO})]\text{PF}_6$ (14) with LiAlH_4

A solution of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2(\text{CO})]\text{PF}_6$ (14) (0.20 g, 0.25 mmol) in tetrahydrofuran-dichloromethane (1:1; 30 ml) was cooled (-78°C) with stirring. LiAlH_4 (0.1 g, 2.6 mmol) was added and the mixture warmed to 20°C ; the orange-yellow mixture became yellow on stirring for 10 min at 20°C . After dropwise addition of H_2O (1 ml) at -78°C , the products were warmed to 20°C and the solvents removed under reduced pressure. Extraction into diethyl ether (3 x 10 ml), concentration (5 ml) and filtration through alumina (5 cm) gave a bright yellow solution which on

evaporation gave $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{CO})\text{H}]$ (43) as a yellow powder, 0.075 g (74%); $\nu_{\text{max.}}(\text{C}_6\text{H}_{14})$ 1 930s (CO) cm^{-1} ; ^1H n.m.r. (60 MHz, C_6D_6) δ 7.7-6.9 (15H, m, aryl-H), 4.2 (5H, s, C_5H_5) and -12.7 (1H, d, $^2J_{\text{PH}}=74$ Hz, Fe-H). Lit.⁵⁰: $\nu_{\text{max.}}(\text{C}_6\text{H}_6)$ 1 923s (CO) cm^{-1} ; ^1H n.m.r. (C_6D_6) δ 4.08 (5H, d, $^3J_{\text{PH}}=1$ Hz, C_5H_5) and -13.0 (1H, d, $^2J_{\text{PH}}=75$ Hz, Fe-H).

Reduction of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2(\text{CO})]\text{PF}_6$ (14) with LiAlD_4

The method was analogous to that above but using LiAlD_4 followed by D_2O (yield 84%). The product $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{CO})\text{D}]$ (43a) contained less than 1% of the protio-compound (43) as shown by ^1H n.m.r. spectroscopy and no detectable deuterium incorporation into the $\eta^5\text{-C}_5\text{H}_5$ moiety as shown by ^2H n.m.r. spectroscopy; $\nu_{\text{max.}}(\text{C}_6\text{H}_6)$ 1 915s (CO) cm^{-1} ; ^1H n.m.r. (300 MHz, C_6D_6) δ 7.7-6.9 (15H, m, aryl-H) and 4.25 (5H, d, $^3J_{\text{PH}}=1$ Hz, C_5H_5); ^2H n.m.r. (46.07 MHz, C_6H_6) δ -12.8 (d, $^2J_{\text{PD}}=11.4$ Hz); ^{31}P - ^1H n.m.r. (36.43 MHz, C_6H_6) δ 88.2 (t, $^2J_{\text{PD}}=11.0$ Hz); m/z 413 $[\text{M}]^+$.

Attempted phosphine exchange in $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2(\text{CO})]\text{PF}_6$ (14)

A solution of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2(\text{CO})]\text{PF}_6$ (14) (0.040 g, 0.049 mmol) and diphos (0.050 g, 0.191 mmol) in tetrahydrofuran-dichloromethane (1:1; 0.7 ml) was kept at 20 °C for 18 h. Monitoring the reaction mixture by ^{31}P n.m.r. spectroscopy showed that no phosphine exchange had occurred.

Attempted insertion of CO into the metal-deuterium bond of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{CO})\text{D}]$ (43a) using excess PPh_3

A solution of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{CO})\text{D}]$ (43a) (0.030 g,

0.073 mmol) and PPh_3 (0.040 g, 0.153 mmol) in toluene (0.7 ml) was kept at 0 °C for 3 days and at 20 °C for a further 3 days. Monitoring of the reaction mixture by ^{31}P n.m.r. spectroscopy showed that no reaction had occurred.

Reduction of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{PMe}_3)_2(\text{CO})]\text{PF}_6$ (12) with LiAlH_4

A slurry of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{PMe}_3)_2(\text{CO})]\text{PF}_6$ (12) (0.200 g, 0.45 mmol) and LiAlH_4 (0.1 g, 2.6 mmol) in tetrahydrofuran (30 ml) was stirred at 20 °C for 15 min. The yellow solution was cooled to -78 °C and after dropwise addition of H_2O (1 ml) the products were warmed to 20 °C and the solvents removed under reduced pressure. Extraction into diethyl ether (3 x 10 ml), concentration (5 ml) and filtration through alumina (5 cm) gave a yellow solution which on evaporation gave $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{PMe}_3)(\text{CO})\text{H}]$ (52) as yellow crystals, 0.075 g (75%); $\nu_{\text{max.}}$ (C_6H_{14}) 1 920s (CO) cm^{-1} ; ^1H n.m.r. (60 MHz, C_6D_6) δ 4.2 (5H, d, $^3\text{J}_{\text{PH}} = 1\text{Hz}$, C_5H_5), 0.95 (9H, d, $^2\text{J}_{\text{PH}} = 10\text{Hz}$, CH_3) and -14.0 (1H, d, $^2\text{J}_{\text{PH}} = 80\text{Hz}$, Fe-H). Lit.^{50a}: $\nu_{\text{max.}}$ ($\text{C}_{16}\text{H}_{34}$) 1 925s (CO) cm^{-1} ; ^1H n.m.r. (C_6D_6) δ 4.32 (5H, s, C_5H_5), 0.92 (9H, d, $^2\text{J}_{\text{PH}} = 10\text{Hz}$, CH_3) and -14.84 (1H, d, $^2\text{J}_{\text{PH}} = 84\text{Hz}$, Fe-H).

Reduction of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)(\text{CO})_3]\text{PF}_6$ (17) with LiAlH_4

The reduction of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)(\text{CO})_3]\text{PF}_6$ (17) with LiAlH_4 was performed in an analogous manner to the reduction of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]\text{PF}_6$ (9) with LiAlH_4 . The product was a red solid which was identified as $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)(\text{CO})_2]_2$ (15) by comparison of its infra-red and ^1H n.m.r. spectra with those of an authentic sample.

Reduction of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)(\text{PPh}_3)(\text{CO})_2]\text{PF}_6$ (18) with LiAlH_4

LiAlH_4 (0.2 g, 5.2 mmol) was added to a cooled (-78°C) slurry of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)(\text{PPh}_3)(\text{CO})_2]\text{PF}_6$ (18) (0.200 g, 0.33 mmol) in tetrahydrofuran (20 ml); the mixture was stirred at -78°C for 6 h. After addition of H_2O (1 ml), the products were warmed to 20°C and the solvent removed under reduced pressure. Extraction with diethyl ether (2 x 10 ml) gave a yellow solution which was dried over magnesium sulphate. Filtration, followed by removal of solvent under reduced pressure, gave a yellow brown solid which was identified as a 6:5:2 mixture of $[\text{Fe}(1\text{-methyl-}\eta^4\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{CO})_2]$ (54), $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)(\text{PPh}_3)(\text{CO})\text{H}]$ (55) and $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)(\text{CO})_2]_2$ (15) by comparison of its infra-red and ^1H n.m.r. spectra with those of samples prepared by alternative routes.

Reduction of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)(\text{PPh}_3)(\text{CO})_2]\text{PF}_6$ (18) with NaBH_4

A slurry of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)(\text{PPh}_3)(\text{CO})_2]\text{PF}_6$ (18) (1.00 g, 1.67 mmol) in tetrahydrofuran (50 ml) was cooled with stirring. NaBH_4 (0.5 g, 13 mmol) was added and the mixture stirred at -20°C for 2 h. 30-40 Light petroleum (50 ml) was added to the resultant yellow solution which was cooled (-10°C) and H_2O (5 ml) added. The 30-40 light petroleum layer was decanted and the tetrahydrofuran layer extracted with 30-40 light petroleum (2 x 20 ml). The extracts were combined and the solvent removed under reduced pressure to give $[\text{Fe}(1\text{-methyl-}\eta^4\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{CO})_2]$ (54) as a yellow oil, 0.52 g (69%); $\nu_{\text{max.}}$ (C_6H_{14}) 1 975s (CO) and 1 920s (CO) cm^{-1} ; ^1H n.m.r. (300 MHz, C_6D_6) δ 7.5 and 7.0 (15H, m, aryl-H), 5.17 (1H, s, H_2 or H_3) 4.67 (1H, brs, H_2 or H_3) 2.77 (1H, d, $^2J_{\text{HH}}=10\text{Hz}$, H_{endo}), 2.40 (1H, 't', $^2J_{\text{HH}}=10\text{Hz}$, $J_{\text{PH}}=10\text{Hz}$, H_{exo}), 1.86 (1H,

s, H₄) and 1.53 (3H, s, C-CH₃); ³¹P-[¹H] n.m.r. (101.2MHz, C₆D₆) δ 71.6; m/z 454 [M]⁺, (Found: 426.0836, C₂₅H₂₃FeOP[M-CO]⁺ requires 426.0836).

Reduction of [Fe(η⁵-C₅H₄CH₃)(PMe₃)(CO)₂]PF₆ (19) with LiAlH₄

LiAlH₄ (0.5 g, 13.0 mmol) was added to a cooled (-78 °C) slurry of [Fe(η⁵-C₅H₄CH₃)(PMe₃)(CO)₂]PF₆ (19) (0.750 g, 1.82 mmol) in tetrahydrofuran (90 ml); the mixture was warmed and stirred at 0 °C for 4 h. After addition of H₂O (2 ml) at -78 °C, the products were warmed to 20 °C and the solvent removed under reduced pressure. Extraction with diethyl ether (2 x 30 ml) gave a yellow solution which was dried over magnesium sulphate. Filtration, followed by removal of solvent under reduced pressure, gave [Fe(η⁵-C₅H₄CH₃)(PMe₃)(CO)CH₃] (59) as a yellow solid at -30 °C and an amber oil at 20 °C, 0.314 g (68%); ν_{max.} (C₆H₆) 1900br, s (CO) cm⁻¹; ¹H n.m.r. (60MHz, C₆D₆) δ 4.3-3.9 (4H, m, H_{2,3,4,5}), 1.9 (3H, s, C₅H₄CH₃), 1.0 (9H, d, ²J_{PH}=9Hz, PMe₃) and -0.1 (3H, d, ³J_{PH}=7Hz, Fe-CH₃); ³¹P-[¹H] n.m.r. (101.2MHz, C₆H₆) δ 42.0; m/z 426 [M]⁺, (Found: 426.0836, C₂₅H₂₃FeOP requires 426.0836).

Attempted low temperature generation of [Fe(η⁵-C₅H₄CH₃)(PMe₃)(CO)(CHO)] (53)

LiAlH₄ (0.003 g) in [²H₈] tetrahydrofuran (0.2 ml) was added to a cooled (-78 °C) saturated solution of [Fe(η⁵-C₅H₄CH₃)(PMe₃)(CO)₂]PF₆ (19) in CD₂Cl₂ (0.4 ml) in an n.m.r. tube. After allowing the contents of the n.m.r. tube to re-cool to -78 °C the two layers were mixed and the n.m.r. tube transferred to the pre-cooled probe (-70 °C) of the WH300 spectrometer. There was no signal corresponding to a metal formyl proton at -70 °C, -40 °C or 0 °C.

Reduction of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)(\text{PPh}_3)_2(\text{CO})]\text{PF}_6$ (20) with LiAlH_4

A solution of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)(\text{PPh}_3)_2(\text{CO})]\text{PF}_6$ (20) (0.50 g, 0.60 mmol) in tetrahydrofuran-dichloromethane (1:1; 30 ml) was cooled (-78 °C) with stirring. LiAlH_4 (0.2 g, 5.2 mmol) was added and the mixture warmed to 20 °C; the orange mixture became yellow on stirring for 10 min at 20 °C. After addition of H_2O (1 ml) at -78 °C, the products were warmed to 20 °C and the solvents removed under reduced pressure. Extraction into diethyl ether (3 x 10 ml), concentration (5 ml) and filtration through alumina (5 cm) gave a bright yellow solution which on evaporation gave $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)(\text{PPh}_3)(\text{CO})\text{H}]$ (55) as a yellow gum, 0.194 g (66%); $\nu_{\text{max.}}(\text{C}_6\text{H}_{14})$ 1 930s (CO) cm^{-1} ; ^1H n.m.r. (300MHz, C_6D_6) δ 7.8-7.0 (15H, m, aryl-H), 4.35, 4.25, 4.10 and 3.98 (4 x 1H, 4 x s, $\text{H}_2, 3, 4$ and 5), 1.85 (3H, s, $\text{C}_5\text{H}_4\text{CH}_3$) and -12.70 (1H, d, $^2J_{\text{PH}} = 83\text{Hz}$, Fe-H); ^{31}P - ^1H n.m.r. (101.2MHz, C_6H_6) δ 89.0; m/z 254 $[\text{M}]^+$, (Found: 254.0519, $\text{C}_{11}\text{H}_{19}\text{FeOP}$ requires 254.0519).

Reduction of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)(\text{diphos})(\text{CO})]\text{PF}_6$ (21) with LiAlH_4

A solution of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)(\text{diphos})(\text{CO})]\text{PF}_6$ (21) (0.350 g, 0.50 mmol) in tetrahydrofuran-dichloromethane (1:1, 50 ml) was cooled (-78 °C). LiAlH_4 (0.3 g, 7.8 mmol) was added and the mixture stirred for 2 h at -78 °C. Storage at -30 °C with occasional agitation (10 h) gave a yellow solution which was treated with H_2O (1 ml) and allowed to warm to 20 °C. The solvent was removed under reduced pressure and the residue extracted with diethyl ether (3 x 15 ml) to give a yellow solution which was dried over magnesium sulphate. Filtration, followed by removal of solvent under reduced pressure, gave a yellow microcrystalline solid identified as a 2:1 mixture of $[\text{Fe}(\eta^5\text{-$

$C_5H_4CH_3$) (diphos) (CO)H] (61) and $[(Fe(\eta^5-C_5H_4CH_3)(CO)H)_2(\mu-diphos)]$ (62); ν_{max} . (Nujol) 1 923s (CO) cm^{-1} ; 1H n.m.r. (300 MHz, C_6D_6) δ 7.5-6.9 (m, aryl-H), 4.3-3.8 (m, $H_{2,3,4,5}$), 2.7-2.2 (m, $-CH_2-$), 1.87 (s, $C_5H_4CH_3$) 1.85 (s, $C_5H_4CH_3$), -13.08 (d, $^2J_{PH}=74Hz$) and -13.12 ($^2J_{PH}=75Hz$); ^{31}P - $[^1H]$ n.m.r. (101.2MHz, C_6H_6) δ 82.8 (s, Fe-P of (62)) 82.8 (d, $^3J_{PP}=38Hz$, Fe-P of (61)) and -15.5 (d, $^3J_{PP}=38Hz$, $FePCH_2CH_2P$ of (61)), m/z (Found: 240.0368, $C_{10}H_{17}FeOP$ requires 240.0366).

Attempted low temperature generation of $[Fe(\eta^5-C_5H_4CH_3)(diphos)(CHO)]$

$LiAlH_4$ (0.003 g) in $[^2H_8]$ tetrahydrofuran (0.2 ml) was added to a cooled (-78 °C) saturated solution of $[Fe(\eta^5-C_5H_4CH_3)(diphos)(CO)]PF_6$ (21) in CD_2Cl_2 (0.4 ml) in an n.m.r. tube. After allowing the contents of the n.m.r. tube to re-cool to -78 °C, the two layers were mixed and the n.m.r. tube transferred to the pre-cooled probe (-70 °C) of the WH300 spectrometer. On warming the sample to -40 °C a signal appeared in the spectrum at δ -13.56 (d, $^2J_{PH}=76Hz$, Fe-H); there was no signal corresponding to a metal formyl proton. The signal at δ -13.56 persisted as the sample was warmed to 20 °C.

Reduction of $[Fe(\eta^5-C_5H_4CH_3)(PMe_3)_2(CO)]PF_6$ (22) with $LiAlH_4$

A slurry of $[Fe(\eta^5-C_5H_4CH_3)(PMe_3)_2(CO)]PF_6$ (22) (0.400 g, 0.86 mmol) in tetrahydrofuran (40 ml) was cooled to -78 °C, $LiAlH_4$ (0.2 g, 5.2 mmol) added and the mixture stirred for 2 h at -78 °C to give a yellow solution. After addition of H_2O (1 ml), the products were warmed to 20 °C and the solvents removed under reduced pressure. The residue was extracted with diethyl ether

(2 x 20 ml) and dried over magnesium sulphate; filtration followed by removal of the solvent under reduced pressure gave $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)(\text{PMe}_3)(\text{CO})\text{H}]$ (63) as a yellow oil, 0.153 g (73%); $\nu_{\text{max.}}$ (C_6H_6) 1 905br,s (CO) cm^{-1} ; ^1H n.m.r. (60MHz, C_6D_6) 4.3-4.0 (4H, m, $\text{H}_{2,3,4,5}$), 1.9 (3H, s, $\text{C}_5\text{H}_4\text{CH}_3$), 1.0 (9H, d, $^2J_{\text{PH}}=9\text{Hz}$ and -14.1 (1H, d, $^2J_{\text{PH}}=84\text{Hz}$); m/z 534 $[\text{M}-\text{CO}]^+$, (Found: 534.1318, $\text{C}_{32}\text{H}_{32}\text{FeP}_2$ requires 534.1329).

Reduction of $[\text{Fe}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{CO})_3]\text{PF}_6$ (25) with LiAlH_4

LiAlH_4 (0.1 g, 2.6 mmol) was added to a cooled ($-78\text{ }^\circ\text{C}$) slurry of $[\text{Fe}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{CO})_3]\text{PF}_6$ (25) (0.050 g, 0.12 mmol) in tetrahydrofuran (20 ml); the mixture was warmed and stirred at $0\text{ }^\circ\text{C}$ for 7 h. After addition of H_2O (0.5 ml) at $-78\text{ }^\circ\text{C}$, the products were warmed to $20\text{ }^\circ\text{C}$ and the solvent removed under reduced pressure. Extraction with diethyl ether (2 x 10 ml) gave a pale orange solution which was dried over magnesium sulphate. Filtration, followed by removal of solvent under reduced pressure, gave an orange solid from which cream-coloured crystals of $[\text{Fe}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{CO})_2\text{H}]$ (64) sublimed, 0.022 g (75%); $\nu_{\text{max.}}$ (C_6D_6) 1 995s (CO) and 1 935s (CO) cm^{-1} ; ^1H n.m.r. (60MHz, C_6D_6) δ 1.6 (15H, s, $\text{C}_5(\text{CH}_3)_5$) and -11.6 (1H, s, Fe-H).

Low temperature generation of $[\text{Fe}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{CO})_2(\text{CHO})]$

LiAlH_4 (0.003 g) in $[\text{H}_8]$ tetrahydrofuran (0.2 ml) was added to a cooled ($-78\text{ }^\circ\text{C}$) saturated solution of $[\text{Fe}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{CO})_3]\text{PF}_6$ (25) in CD_2Cl_2 (0.4 ml) in an n.m.r. tube. After allowing the contents of the n.m.r. tube to re-cool to $-78\text{ }^\circ\text{C}$,

the two layers were mixed and the n.m.r. tube transferred to the pre-cooled probe (-67 °C) of the WH300 spectrometer. The ^1H n.m.r. spectrum at this temperature showed the presence of resonances at δ 13.86, 13.43 (Fe-CHO) and -11.38 (Fe-H).

Reduction of $[\text{Fe}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{PPh}_3)(\text{CO})_2]\text{PF}_6$ (27) with LiAlH_4

LiAlH_4 (0.1 g, 2.6 mmol) was added to a cooled (-78 °C) slurry of $[\text{Fe}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{PPh}_3)(\text{CO})_2]\text{PF}_6$ (27) (0.180 g, 0.28 mmol) in tetrahydrofuran (20 ml); the mixture was stirred at -78 °C for 6 h. After addition of H_2O (0.5 ml), the products were warmed to 20 °C and the solvent removed under reduced pressure. Extraction with diethyl ether (2 x 10 ml) gave an orange solution which was dried over magnesium sulphate. Filtration followed by removal of solvent under reduced pressure gave an orange solid which was identified as a mixture of $[\text{Fe}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{CO})_2\text{H}]$ (64) and PPh_3 by ^1H n.m.r. and i.r. spectroscopy.

Attempted low temperature generation of $[\text{Fe}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{PPh}_3)(\text{CO})(\text{CHO})]$

LiAlH_4 (0.003 g) in $[\text{}^2\text{H}_8]$ tetrahydrofuran (0.2 ml) was added to a cooled (-78 °C) saturated solution of $[\text{Fe}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{PPh}_3)(\text{CO})_2]\text{PF}_6$ (27) in CD_2Cl_2 (0.4 ml) in an n.m.r. tube. After allowing the contents of the n.m.r. tube to re-cool to -78 °C, the two layers were mixed and the n.m.r. tube transferred to the pre-cooled probe (-65 °C) of the WH300 spectrometer. The ^1H n.m.r. spectrum at this temperature showed the presence of a resonance at δ -12.15 (Fe-H); no resonances attributable to a formyl proton were detected.

Reduction of $[\text{Fe}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{PMe}_3)(\text{CO})_2]\text{PF}_6$ (26a) with LiAlH_4

LiAlH_4 (0.1 g, 2.6 mmol) was added to a cooled ($-78\text{ }^\circ\text{C}$) slurry of $[\text{Fe}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{PMe}_3)(\text{CO})_2]\text{PF}_6$ (26a) (0.050 g, 0.11 mmol) in tetrahydrofuran (20 ml); the mixture was warmed and stirred at $0\text{ }^\circ\text{C}$ for 3.5 h. After addition of H_2O (0.5 ml) at $-78\text{ }^\circ\text{C}$, the products were warmed to $20\text{ }^\circ\text{C}$ and the solvent removed under reduced pressure. Extraction with diethyl ether (2 x 10 ml) gave a yellow solution which was dried over magnesium sulphate. Filtration, followed by removal of solvent under reduced pressure gave $[\text{Fe}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{PMe}_3)(\text{CO})\text{CH}_3]$ (65) as a yellow solid, 0.020 g (60%); $\nu_{\text{max.}}$ (Nujol) $1\ 895\text{w}$ (CO) cm^{-1} ; ^1H n.m.r. (60MHz, C_6D_6) δ 1.55 (15H, s, $\text{C}_5(\text{CH}_3)_5$), 0.95 (9H, d, $^2\text{J}_{\text{PH}} = 9\text{Hz}$, PMe_3) and -0.3 (3H, d, $^3\text{J}_{\text{PH}} = 7\text{Hz}$, Fe-CH_3).

Low temperature generation of $[\text{Fe}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{PMe}_3)(\text{CO})(\text{CHO})]$

LiAlH_4 (0.003 g) in [$^2\text{H}_8$] tetrahydrofuran (0.2 ml) was added to a cooled ($-78\text{ }^\circ\text{C}$) saturated solution of $[\text{Fe}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{PMe}_3)(\text{CO})_2]\text{PF}_6$ (26a) in CD_2Cl_2 (0.4 ml) in an n.m.r. tube. After allowing the contents of the n.m.r. tube to re-cool to $-78\text{ }^\circ\text{C}$, the two layers were mixed and the n.m.r. tube transferred to the pre-cooled probe ($-60\text{ }^\circ\text{C}$) of the WH300 spectrometer. The ^1H n.m.r. spectrum at this temperature showed the presence of resonances at δ 14.50 (Fe-CHO) and δ -0.44 (d, $^3\text{J}_{\text{PH}} = 7\text{Hz}$, Fe-CH_3).

Reduction of $[\text{Fe}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{diphos})(\text{CO})]\text{PF}_6$ (28) with LiAlH_4

LiAlH_4 (0.1 g, 2.6 mmol) was added to a cooled ($-78\text{ }^\circ\text{C}$)

slurry of $[\text{Fe}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{diphos})(\text{CO})]\text{PF}_6$ (28) (0.040 g, 0.046 mmol) in tetrahydrofuran (20 ml); the mixture was warmed to 0 °C and stirred for 2 h. After addition of H_2O (0.5 ml) at -78 °C, the products were warmed to 20 °C and the solvent removed under reduced pressure. Extraction with diethyl ether (2 x 10 ml) gave a yellow solution which was dried over magnesium sulphate. Filtration, followed by removal of solvent under reduced pressure gave a yellow solid identified as a mixture of $[\text{Fe}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{diphos})(\text{CO})\text{H}]$ (66) and $[\text{Fe}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{CO})\text{H}]_2(\mu\text{-diphos})$ (67); ^1H n.m.r. (300 MHz, C_6D_6) δ 7.8-7.0 (m, aryl-H), 2.6-2.2 (m, $-\text{CH}_2-$), 1.65 and 1.64 (2xs, $\text{C}_5(\text{CH}_3)_5$) and -13.21 and -13.26 (2xd, $^2J_{\text{PH}}=74\text{Hz}$).

Reduction of $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{CO})_3]\text{PF}_6$ (32) with LiAlH_4

LiAlH_4 (0.2 g, 5.2 mmol) was added to a cooled (-78 °C) slurry of $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{CO})_3]\text{PF}_6$ (32) (0.200 g, 0.31 mmol) in tetrahydrofuran (30 ml); the mixture was stirred at -78 °C for 6 h. After addition of H_2O (0.5 ml), the products were warmed to 20 °C and the solvent removed under reduced pressure. Extraction with diethyl ether (2 x 15 ml) gave a pale yellow solution which was dried over magnesium sulphate. Filtration, followed by removal of solvent under reduced pressure, gave $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{CO})_2\text{H}]$ (68) as a yellow solid, 0.096 g (65%); $\nu_{\text{max.}}$ (C_6H_6) 1 945s (CO) and 1 865s (CO) cm^{-1} ; ^1H n.m.r. (300MHz,

C_6D_6) δ 7.7-6.9 (15H, m, aryl-H), 4.75 (5H, s, C_5H_5) and -5.1 (1H, d, $^2J_{PH}=50\text{Hz}$, Mo-H). Lit.⁵⁶ : ν_{max} . (cyclohexane) 1991 vs (CO) and 1876 vs (CO); 1H n.m.r. (300MHz, $CDCl_3$) δ 5.06 (5H, s, C_5H_5) and -5.56 (1H, d, $^2J_{PH}=48\text{Hz}$).

Attempted reduction of $[Mo(\eta^5-C_5H_5)(\text{diphos})(CO)_2]PF_6$ (33)

The reductions were performed in an analogous manner to previous reductions.

<u>Reducing agent</u>	<u>Solvent</u>	<u>Temp. ($^{\circ}C$)</u>	<u>Time (h)</u>	<u>Result</u>
$LiAlH_4$	THF- CH_2Cl_2 (1:1)	20	1	(33) recovered.
$LiAlH_4$	THF- CH_2Cl_2 (1:1)	20	24	Low yield of intractable reduction products.
$LiBEt_3H$	THF	-78	2	No ether-soluble products obtained.
Red-Al*	Toluene	20	16	Low yield of intractable products.

* $[(CH_3OCH_2CH_2O)_2AlH_2]Na$

Attempted reduction of $[Mo(\eta^5-C_5H_5)(\text{triphos})(CO)]PF_6$ (34)

The reductions were performed in an analogous manner to previous reductions.

<u>Reducing agent</u>	<u>Solvent</u>	<u>Temp ($^{\circ}C$)</u>	<u>Time (h)</u>	<u>Result</u>
$LiAlH_4$	THF- CH_2Cl_2 (1:1)	20	4	No ether-soluble products obtained.
$LiAlH_4$	THF	20	6	No ether-soluble products obtained.

Experimental for Section I.3

These experiments were not carried out under an atmosphere of nitrogen.

1 [Fe(η^5 -C₅H₅)(diphos)(CO)]PF₆ (11)

85% H₂O₂ (0.5 cm³, 17 mmol) was added dropwise to a rapidly stirred mixture of norbornene (0.176 g, 1.87 mmol), [Fe(η^5 -C₅H₅)(diphos)(CO)]PF₆ (11) (0.052 g, 0.075 mmol, dichloroethane (5 cm³) and 10% w/v sodium carbonate solution (0.2 ml, 0.19 mmol). The reaction was followed by gas chromatography; after 17.5 hours 2.7 mg of *exo*-norbornene oxide were present in the reaction mixture and after 48 hours, 8.0 mg of *exo*-norbornene oxide were present.

The experiment was repeated at 50 °C. Analysis by gas chromatography after 2 hours showed that 6.0 mg of *exo*-norbornene oxide were present in the reaction mixture. 30% H₂O₂ (2 cm³, 20 mmol) was added and the reaction mixture stirred at 50 °C for a further 4 hours; yield of *exo*-norbornene oxide, 16.7 mg (8%).

2 [Fe(η^5 -C₅H₅)(diphos)(CO)]Cl (11a)

85% H₂O₂ (0.5 cm³, 17 mmol) was added dropwise to a rapidly stirred mixture of norbornene (0.176 g, 1.87 mmol), [Fe(η^5 -C₅H₅)(diphos)(CO)]Cl (11a) (0.044 g, 0.075 mmol), dichloroethane (5 cm³) and 10% w/v sodium carbonate solution (0.2 ml, 0.19 mmol). The reaction was followed by gas chromatography; after 48 hours, 2.8 mg of *exo*-norbornene oxide were present in the reaction mixture.

3 $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{CN}]^{73}$

30% H_2O_2 (4 cm^3 , 39 mmol) was added dropwise to a rapidly stirred mixture of norbornene (0.198 g, 2.11 mmol), $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{CN}]$ (0.044 g, 0.075 mmol), dichloroethane (25 cm^3) and 8% w/v sodium hydrogen carbonate solution (4 cm^3 , 3.8 mmol). The reaction mixture was maintained at 70 °C and analysed by gas chromatography; after 2 hours, 2.7 mg of *exo*-norbornene oxide were present in the reaction mixture.

The experiments above exemplify the method used for all the investigations undertaken in Section I.3.

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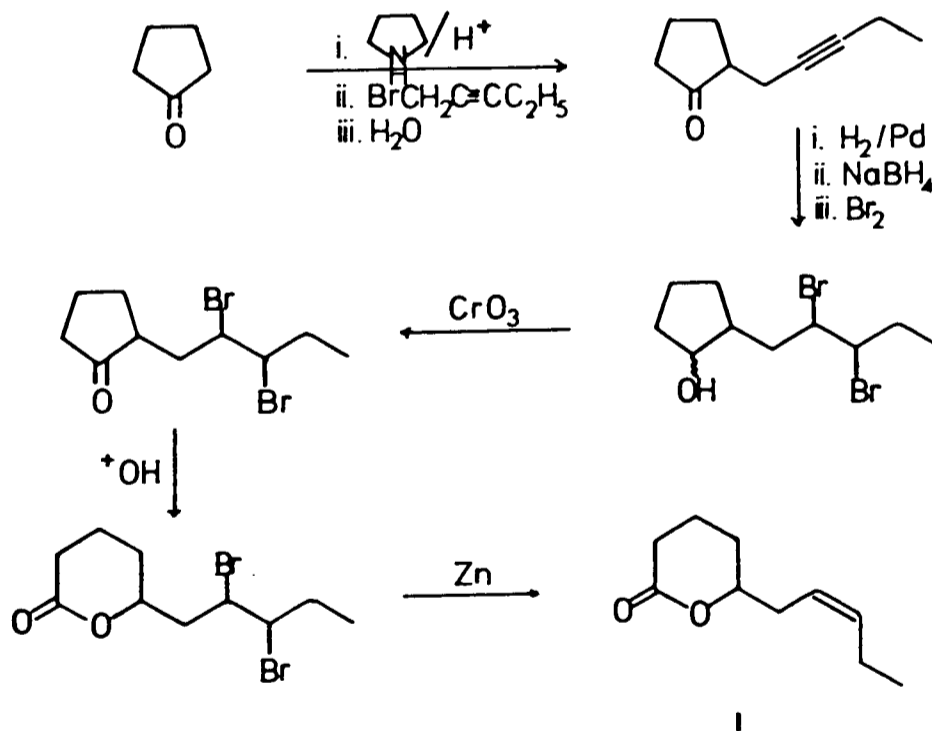
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II.1 Introduction

Bromine as an olefin protecting agent

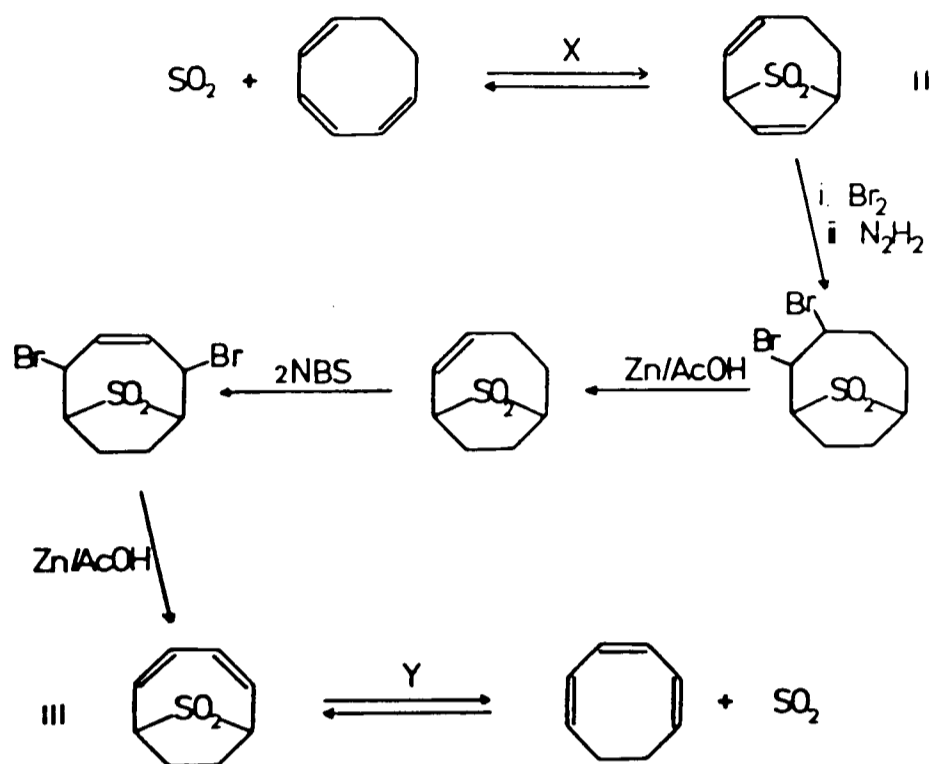
Alkenes are susceptible to oxidation and reduction, and they also undergo addition reactions with a variety of reagents. There are many illustrations in the literature of bromine being used as a protecting agent for the alkene and being removed at some later stage of the synthesis; three examples are:-

a) During the synthesis of the natural product "essence of jasmin" (I), bromine is used to protect an alkene against chromic acid oxidation and a Baeyer-Villiger oxidation with perbenzoic acid.¹



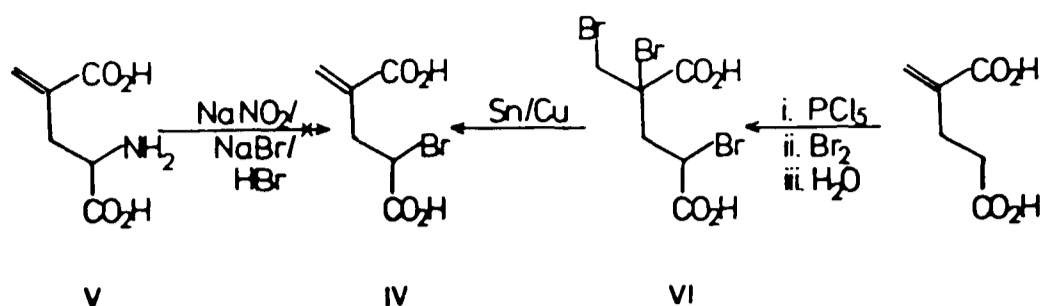
b) In an investigation into the application of the Woodward-Hoffmann rules to the decomposition of sulphur dioxide adducts of cyclo-octatriene, 9-thiabicyclo [4.2.1] nona-2,7-diene 9,9-dioxide (II) and 9-thiabicyclo [4.2.1] nona-2,4-diene

9,9-dioxide (III) were synthesised as shown.²



It was assumed that the sulphur dioxide molecule is a π^2 component and that because of the geometry of the cyclooctatriene ring, both components are suprafacial; therefore process X is thermally allowed whilst process Y is thermally disallowed. The ratio of the rate of decomposition of (II) to the rate of decomposition of (III) was found to be 60,000 at 180 °C.

c) Preparation of α -methylene- γ -bromoglutaric acid (IV) by diazotisation of γ -methyleneglutamic acid (V) in the presence of sodium bromide was complicated by lactone formation. Selective debromination of the tribromide (VI) (readily prepared by bromination of α -methyleneglutaryl chloride) with a tin/copper couple provided a solution to this problem.³



Present debromination methods

A successful protecting agent must satisfy three primary requirements: a) quantitative addition, b) quantitative removal, c) addition and removal must take place under mild conditions. Treatment of an alkene with bromine generally results in a 90-100% yield of the corresponding *vic*-dibromide; in contrast, debromination under mild conditions and in good yields has proved difficult.

Traditionally zinc/acetic acid, zinc/alcohol⁴ and sodium/liquid ammonia⁵ systems have been used and in some cases give good yields *e.g.* debromination of cholesterol dibromide with zinc/acetic acid.⁶ Yields are often moderate however with zinc/alcohol, the presence of acetic acid may bring about unwanted side reactions such as the acetylation of alcohol functions, and although excellent yields are generally obtained with sodium/liquid ammonia, the method is limited *e.g.* phenyl groups are susceptible to Birch reduction.

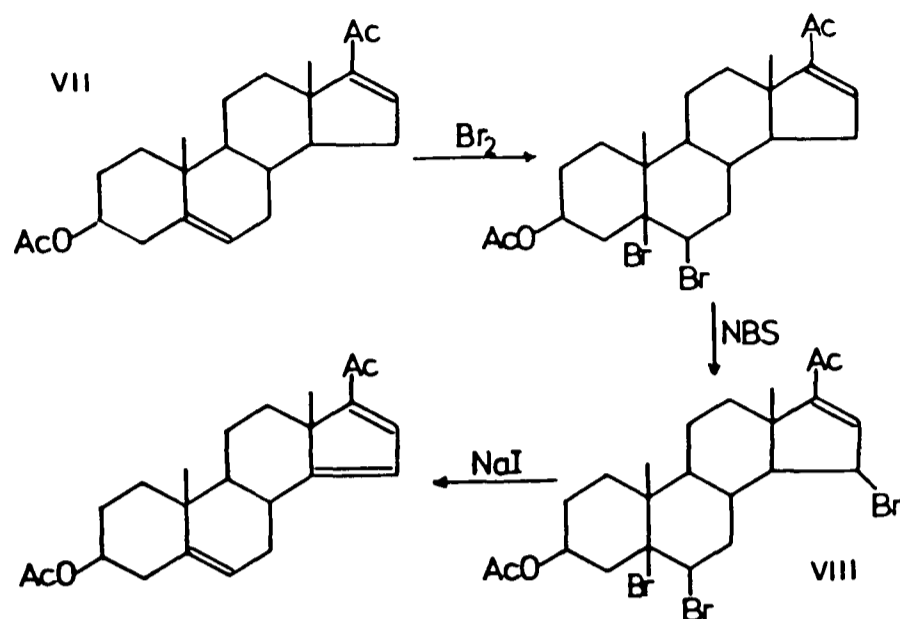
The debromination of 1 α :2 β -dibromocholestane by zinc/acetic acid provides a typical example of the conditions employed.⁷ A solution of the dibromide in acetic acid was heated to boiling, zinc dust was added in portions and the solution was heated under reflux for 1.5 hours; cholest-1-ene was produced after work-up in 75% yield.

Many methods have been reported in the literature as alternatives to zinc/acetic acid, zinc/alcohol and sodium/liquid ammonia. Some representative examples are given below.

a) Sodium dihydronaphthylide is an increasingly useful synthetic reagent, partially because it forms homogeneous solutions in polar ethers; surface adsorption is therefore not required and subsequent surface reactions, perhaps leading to undesired materials, do not occur. Sodium dihydronaphthylide and sodium dihydrobiphenylide have both been used to debrominate cyclododecene dibromide, cyclo-octene dibromide and 1,2-dibromoheptane in excellent yields.⁸ Preparation of these reagents involves stirring the required amount of clean sodium metal with a solution containing a 2-10 fold excess of the aromatic reagent in dry dimethoxyethane for 24-48 hours at room temperature under an inert atmosphere. This long preparation combined with a two hour addition of reagent to the dibromide and a long work-up procedure, makes this method of debromination of *vic*-dibromides unattractive.

Disodium phenanthrene has also been used in debromination reactions.⁹

b) Sodium iodide in acetone has been used successfully for debromination of *vic*-dibromides; it has found particular use deprotecting double bonds at the end of synthetic sequences for modifying steroids. For example, in the scheme below, which introduces an extra double bond into 16-dehydropregnenolene acetate (VII), debromination is achieved by heating the tribromide (VIII) and sodium iodide in acetone at reflux under a nitrogen atmosphere for 3 hours.¹⁰



c) Chromous chloride has been used in debromination steps; for example, stirring 5,6-dibromopregnanedione in acetone with an aqueous solution of chromous chloride at 26 °C for 2 hours gave a 90% yield of progesterone. (Stirring the dibromide with sodium iodide in ethanol for 10 hours at room temperature gave a 65% yield of product, and treatment of the dibromide with zinc dust in acetic acid gave waxy progesterone together with an unknown by-product.)¹¹

The conversion of 1,2-dibromoethane to ethene can be carried out quantitatively within 15 minutes using a reagent in which the chromous ion is complexed with ethylenediamine or related ligands; the solubility of this reagent in organic solvents accounts for its increased reactivity when compared with chromous chloride.¹² The purple chromium complex is prepared by dilution of an aqueous solution of chromous chloride with dimethylformamide followed by addition of ethylenediamine; all operations are carried out in the absence of air.

d) Debromination of stilbene dibromide has been achieved using tetrakis(triphenylphosphine)palladium (0);¹³ equimolar amounts of stilbene dibromide and the palladium complex were heated in anhydrous benzene under argon at 80 °C for 2 hours. After an arduous extraction procedure to free the product of organometallic impurities, an 80% yield of stilbene was obtained.

e) A novel reagent has been used to obtain 1-undecene from 1,2-dibromoundecane.¹⁴ Melting potassium over graphite under argon gives a lamellar compound, potassium graphite; when a solution of anhydrous ferric chloride in tetrahydrofuran is added dropwise to a stirred suspension of potassium graphite in tetrahydrofuran, a fast and exothermic reaction takes place affording iron graphite as a black powder. This reagent effected 50% debromination in 16 hours at 70 °C but addition of a little degassed water increased the reactivity of the reagent to give a yield of 95% in 3 hours.

f) Aqueous sodium sulphide or sodium hydrogen sulphide with trioctylmethylammonium chloride as a phase transfer agent produces a two-phase reduction system which converts *vic*-dibromides to alkenes in excellent yields.¹⁵ The reaction, which may be performed using benzene as the organic solvent or with neat alkene, takes one hour at room temperature and does not reduce esters or other carbonyl groups present in the substrate. Low yields were obtained with the dibromides of terminal alkenes as substitution reactions seemed to predominate.

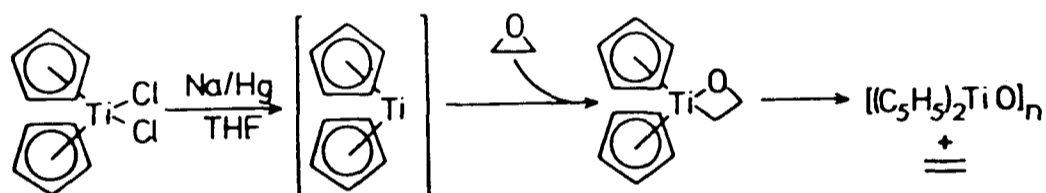
g) Debromination of a range of *vic*-dibromides has been achieved with a titanium (II) reagent.¹⁶ This is prepared by adding lithium aluminium hydride to a slurry of titanium (III) chloride or titanium (IV) chloride in tetrahydrofuran under

nitrogen. After stirring the resultant black slurry for 30 minutes, a solution of the *vic*-dibromide was added over a 30 minute period; heating under reflux for 8 hours and work-up gave the alkene in good yield.

A similar reagent prepared from vanadium (III) chloride and lithium aluminium hydride has also been used in debromination reactions.¹⁷

Objectives

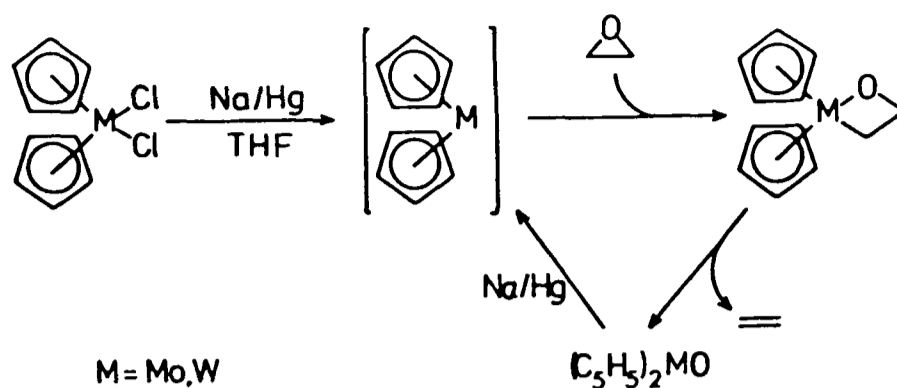
It has been demonstrated that reduction of dicyclopentadienyl titanium (II) dichloride with sodium amalgam produces a low-valent reactive titanocene[†] which can be used to deoxygenate epoxides.¹⁸



For example, a 1% solution of propene oxide in tetrahydrofuran containing $(C_5H_5)_2TiCl_2$ (1.1 equivalents) was vigorously stirred under nitrogen at 20 °C with sodium amalgam (2%, excess); after 16 hours the yield of propene was greater than 95%.

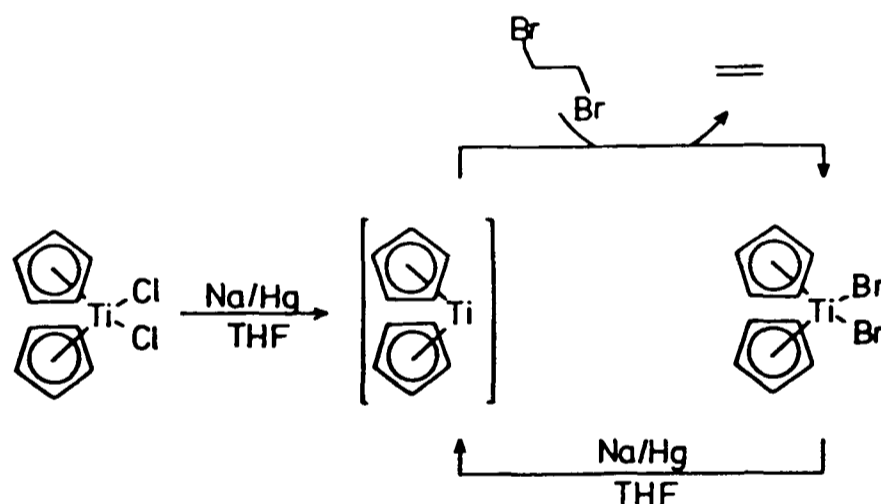
Use of the corresponding molybdenum or tungsten complexes leads to a system which is catalytic as the resultant oxides $(C_5H_5)_2MO$ (M=Mo,W) can be reduced by sodium amalgam back to the active reducing species $(C_5H_5)_2M$.

† Titanocene is used throughout to describe $(C_5H_5)_2Ti$.



These reactions were followed until 250 equivalents (relative to M) of propene oxide had been deoxygenated.

It was proposed that titanocene could be used to catalytically debrominate *vic*-dibromides.

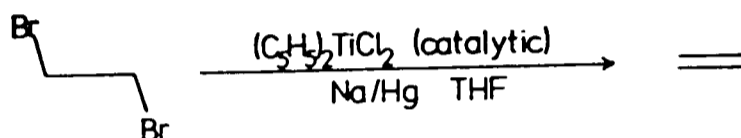


The active reducing species $[(C_5H_5)_2Ti]$, acting as a homogeneous catalyst, might be expected to a) increase the selectivity (and therefore the yields) of the debromination reaction by eliminating side reactions which take place on the surface of the metal in a heterogeneous reaction, and b) reduce the temperature and time necessary for debromination.

II.2 Na/Hg/ (C₅H₅)₂TiCl₂ systems for debromination and de-epoxidation

Na/Hg and catalytic quantities of (C₅H₅)₂TiCl₂ as a debromination system

Initial investigations into the proposal that low-valent titanocenes should debrominate *vic*-dibromides were carried out using catalytic amounts of titanocene dichloride [(C₅H₅)₂TiCl₂] over excess 2% sodium amalgam.

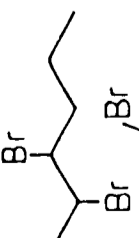
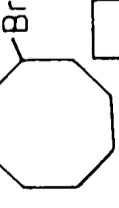
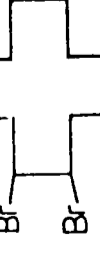
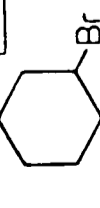
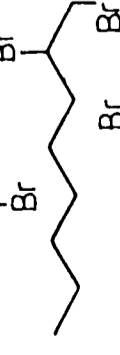
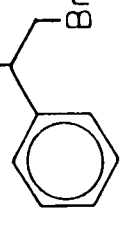


In a typical experiment, sodium was added to rapidly stirred mercury to form on cooling, solid 2% sodium amalgam. Addition of 2,3-dibromohexane, one third of an equivalent of titanocene dichloride and tetrahydrofuran led to a red solution of titanocene dichloride over the amalgam. The solution was degassed thoroughly and the reaction proceeded under a nitrogen atmosphere with stirring throughout. Simultaneously, a control experiment was performed without the titanocene dichloride. The reactions were followed by gas chromatography and yields were determined by calibration of the chromatograph with hex-2-ene. After 3.5 hours, all the 2,3-dibromohexane had been converted to hexene by the system containing titanocene dichloride; completion of this conversion was accompanied by a change in the colour of the reaction mixture from brown to indigo. The control system had converted <5% of the dibromide to alkene.

The results obtained with a number of *vic*-dibromides and the corresponding control reactions are given in Table I. Entries 1-4 illustrate that titanocene dichloride can catalyse the

Table I

Debromination of vic-dibromides with 2% sodium amalgam/(C₅H₅)₂TiCl₂ system and a 2% sodium amalgam control

Entry	<u>vic-Dibromide</u>	<u>Alkene</u>	<u>2% Sodium amalgam/(C₅H₅)₂TiCl₂ system</u>		<u>Sodium amalgam control</u>		
			<u>Yield (%)^A</u>	<u>Time (hr)</u>	<u>(C₅H₅)₂TiCl₂:vic-dibromide</u>	<u>Yield (%)^A</u>	<u>Time (hr)</u>
1.		Hexenes ^B	100	3.5	1:3	<5	3.5
2.		Cyclo-octene	100	1.25	1:5	20	3
3.		Cyclododecenes	100	23	1:5	45	23
4.		Cyclohexene	100	1.5	1:5	10	1.5
5.		Octene	20	2.5	1:5	100	2.5
6.		Styrene	10	1.5	1:3	75	1.5
			50	1.5	1:20		

A Yields measured by gas chromatography.

B Separation of isomeric alkenes was not undertaken at this stage.

reductive debromination of *vic*-dibromides by sodium amalgam. However, the presence of the titanium compound appears to inhibit the debromination of the dibromides of terminal olefins by sodium amalgam. (Entries 5 and 6.)

Cyclo-octene dibromide was debrominated on a preparative scale in order to develop an isolation procedure; efficient separation of alkene from the titanium residues proved difficult and cyclo-octene was isolated only in moderate yield (66%).

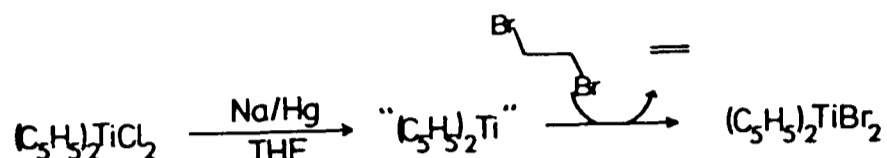
The stereochemical consequences of the bromination/debromination procedure were investigated using cyclododecene. A mixture of cyclododecenes (*cis:trans*, 35:65) was brominated in carbon tetrachloride at 0 °C. The dibromides were debrominated using the $(C_5H_5)_2TiCl_2$ /sodium amalgam and the sodium amalgam systems. The catalysed reduction gave a *cis:trans* ratio of 57:43 and the uncatalysed reduction gave a *cis:trans* ratio of 44:56. Thus, although enhancement of the concentration of *cis* isomer had occurred in both cases, these results give little insight into the mechanism of debromination and into whether elimination of bromine is occurring in a *syn* or *anti* fashion.

"Titanocene"[†] as a debromination reagent

As the sodium amalgam present in the reaction vessel appeared to be competing in the debromination process in some cases, it

† "Titanocene" is used throughout to describe the product obtained on reducing $(C_5H_5)_2TiCl_2$ with sodium amalgam in tetrahydrofuran.

seemed appropriate to remove the active titanium species from the sodium amalgam before use, thus allowing rates of reaction, stereochemical observations etc. to be accredited to the titanium reagent alone. This necessitated the reduction of stoichiometric amounts of $(C_5H_5)_2TiCl_2$ to "titanocene"; however the titanium should be recoverable as $(C_5H_5)_2TiBr_2$.

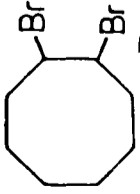
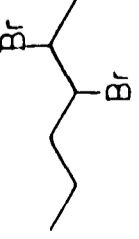
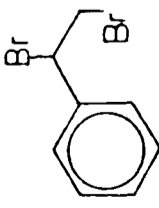
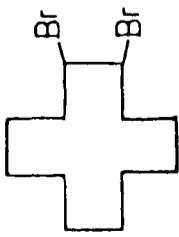
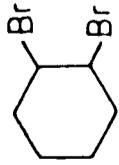


Stock solutions of "titanocene" were prepared by shaking $(C_5H_5)_2TiCl_2$ in tetrahydrofuran over 2% sodium amalgam in a nitrogen atmosphere; the initial red solution of $(C_5H_5)_2TiCl_2$ turned brown, black-yellow and finally black. The colour changes were sharp and formation of the black-yellow colour was accompanied by evolution of heat. Vigorous stirring led to formation of the final inky black solution within 15 minutes; this solution was stored over the sodium amalgam.

A typical reductive debromination using "titanocene" was carried out as follows. Cyclo-octene dibromide was added to tetrahydrofuran and the solution degassed thoroughly. 1.1 equivalents (based on titanium) of the "titanocene" solution were transferred in a syringe under a blanket of nitrogen to the rapidly stirred cyclo-octene dibromide solution. The resultant deep red-black solution was analysed by gas chromatography and the yield of cyclo-octene measured by comparison with standard solutions of cyclo-octene used to calibrate the chromatograph beforehand. The results obtained for a number of *vic*-dibromides are recorded in Table II. Entry 1 was also performed under an atmosphere of argon; 1.1 equivalents of "titanocene" gave a 50% yield of hexenes in one minute.

Table II

Debromination of vic-dibromides using "titanocene"

Entry	<u>vic-Dibromide</u>	Alkene	Effect of addition of 1.1 equivalents ^A		Effect of addition of further 1.1	
			<u>Yield (%)^B</u>	<u>Time (minutes)</u>	<u>equivalents^A of "titanocene" to vic-dibromide</u>	<u>Time (minutes)</u>
1		Cyclo-octene	55	1	90	1
2		Hexenes ^C	50	3	85	1
			50	15		
3		Styrene	100	2		
4		Cyclododecenes	60	1	90	1
			60	30		
5		Cyclohexene	25	2	50 ^D	1
			30	30		

A 1.1 equivalents based on titanium.

B Yields measured by gas chromatography.

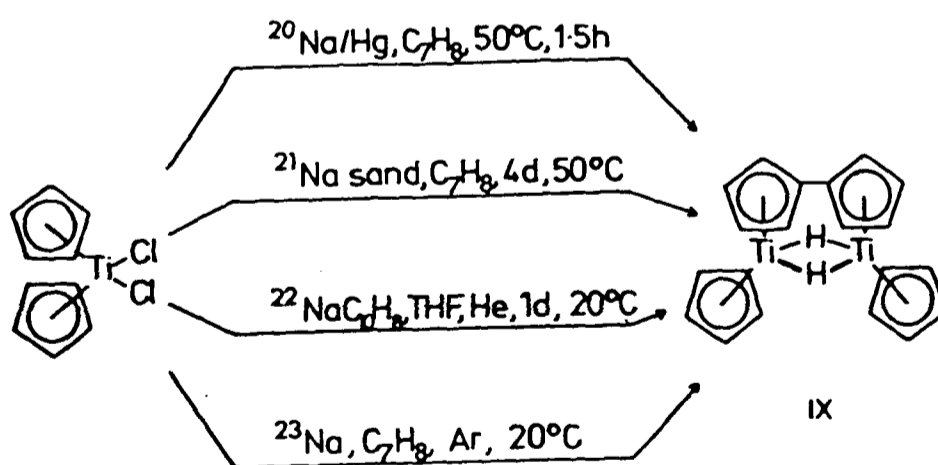
C Separation of isomeric alkenes was not undertaken at this stage.

D A further 1.1 equivalents of titanocene gave a 66% yield within 2 mins; cyclohexane was produced in 12% yield.

The organometallic product of the debromination reaction was isolated by concentration and cooling of the final red-black solution obtained by addition of 1.1 equivalents of "titanocene" to cyclo-octene dibromide; this gave three crops of red-violet crystals which analysis by ^1H n.m.r. spectroscopy and mass spectrometry showed to be predominantly (>90%) $(\text{C}_5\text{H}_5)_2\text{TiBr}_2$. The remaining material was $(\text{C}_5\text{H}_5)_2\text{TiBrCl}$. The yield of the mixture defined above was 51% based on recovery of titanocene halides.

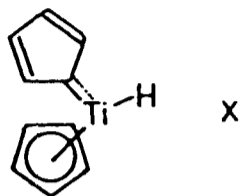
The nature of "titanocene"

Titanocene $(\text{C}_5\text{H}_5)_2\text{Ti}$, although frequently referred to in the literature has never actually been isolated as a discrete chemical compound.¹⁹ Attempted routes to titanocene include the reduction of $(\text{C}_5\text{H}_5)_2\text{TiCl}_2$ with Group 1A metals and conditions reported in the literature for performing this reduction with sodium are summarised below.

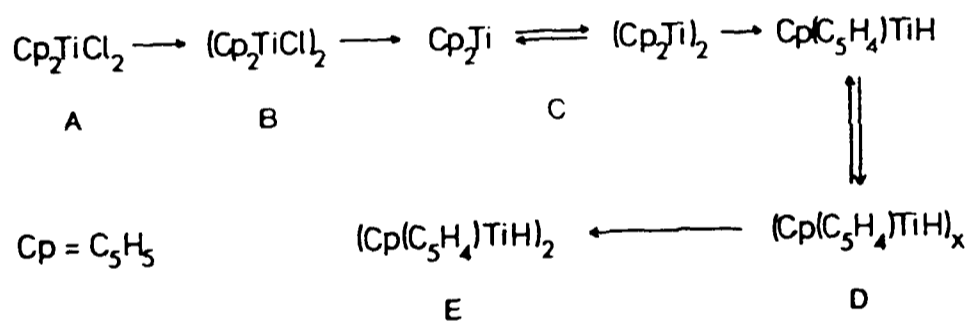


The formation of hydride (IX) (whose structure remained a mystery for some time) in these reduction reactions has been reasonably explained by assuming the formation of a $(\text{C}_5\text{H}_5)_2\text{Ti}$ "carbenoid" intermediate in these reactions. Carbenes are known

to rearrange by an α -hydrogen abstraction process to yield an olefin. By analogy, the highly co-ordinatively unsaturated titanium (II) centre in $(C_5H_5)_2Ti$ could extract hydrogen from a C_5H_5 ligand to yield a titanafulvene-hydride structure (X) which could then dimerise to (IX).²¹

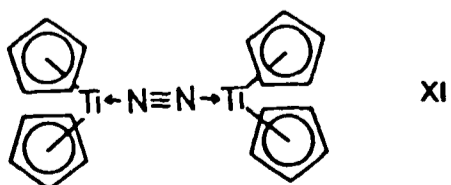


The reduction of $(C_5H_5)_2TiCl_2$ by sodium in toluene under argon has been followed by visible and infra-red spectroscopy;²³ the sequence of compounds in Scheme I was proposed to explain the results.



Scheme I

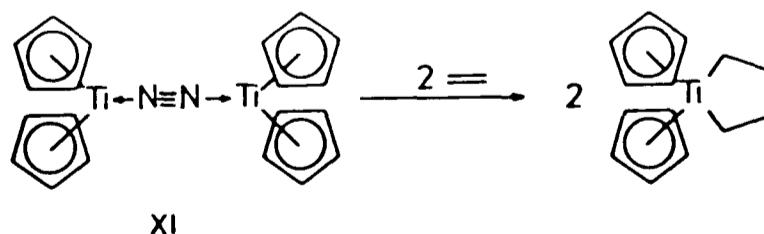
Under nitrogen, only A, B and C could be detected in turn, following which a black precipitate appeared. Whereas A, B, D and E in solution do not react with nitrogen, C (prepared under argon) reacts rapidly and reversibly with nitrogen below 3 °C forming a dark blue complex with the proposed structure (XI).



Discussion

The isolation of $(C_5H_5)_2TiBr_2$ from the reaction mixture in approximately the same yield as the yield of alkene suggests that active titanocene $(C_5H_5)_2Ti$ is the debrominating agent in these reactions. (The experiment conducted under argon demonstrates that formation of a dinitrogen adduct is unnecessary for the success of the reaction.) The low yields obtained with 1.1 equivalents of the reagent (Table II) suggest that a) the black solution obtained on reduction of $(C_5H_5)_2TiCl_2$ with sodium amalgam is in fact a mixture of "over-reduced" and "under-reduced" $(C_5H_5)_2Ti$ *i.e.* species B and E in Scheme I, and b) the highly unstable nature of this solution results in its rapid decomposition after removal from the sodium amalgam.

The inhibition of catalytic activity in Table I (Entries 5 and 6) can be explained by co-ordination of two molecules of the alkene produced to the $(C_5H_5)_2Ti$, followed by formation of a titanium metallacyclopentane. (A metallacyclopentane has been postulated as the product of the reaction between $[(C_5H_5)_2Ti]_2 \cdot N_2$ (XI) and ethylene.²⁴)



When 1.1 equivalents of reagent are added to the *vic*-dibromide of a terminal alkene (Table II, Entry 3), the concentrations of alkene and $(C_5H_5)_2Ti$ will never be simultaneously high enough to permit co-ordination of two molecules of alkene.

The high yield obtained in the reaction of the *vic*-dibromide of styrene (Table II, Entry 3) suggests i) a mechanism involving the development of charge at the α position of styrene and ii) that b) is a reasonable explanation of the moderate yields obtained with the other *vic*-dibromides in Table II.

Stereochemical consequences of "titanocene" debromination

The stereochemical consequences of bromination followed by the "titanocene" debromination were investigated on three systems:- a) *cis* and *trans* cyclododecenes b) diethyl maleate and diethyl fumarate and c) *cis* and *trans* but-2-enes.

a) *Cis* and *trans* cyclododecenes. The brominated mixture of cyclododecenes (*cis:trans* 35:65) used previously (p 11) was debrominated using 1.1 equivalents of "titanocene"; a slight enhancement of the concentration of *cis* isomer occurred, giving a *cis:trans* ratio of 50:50.

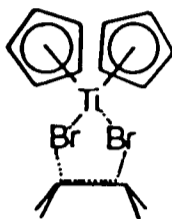
b) Diethyl maleate and diethyl fumarate. Debromination of *meso* 2,3-dibromodiethyl succinate with 1.1 equivalents of "titanocene" at 20 °C and at -30 °C gave only diethyl fumarate (analysis by gas chromatography). A mixture of *meso* and *dl* 2,3-dibromodiethyl succinates was also debrominated by "titanocene" at -30 °C and -78 °C to give diethyl fumarate only; finally addition of diethyl maleate to these reaction mixtures gave diethyl fumarate as the only product, indicating that under all these conditions of debromination, diethyl maleate is isomerised to the more stable diethyl fumarate.

c) *Cis* and *trans* but-2-enes. The results of debromination of *dl* and *meso* 2,3-dibromobutanes using "titanocene" are summarised

in Table III.

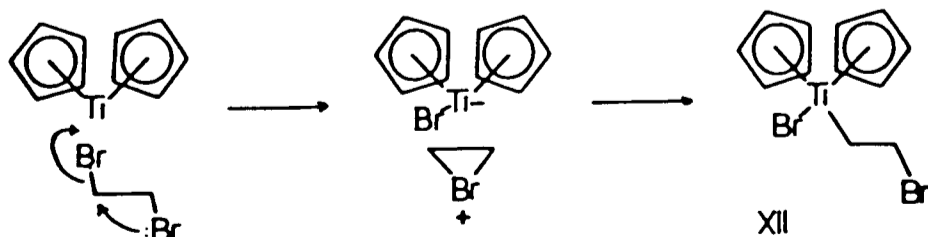
A mechanism for "titanocene" debromination

Initially it was postulated that debromination should occur in a concerted manner through a cyclic transition state represented below.



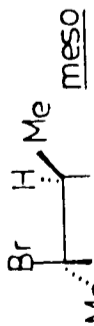
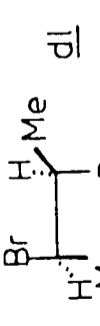
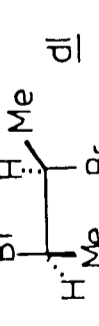
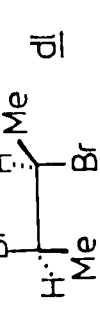
This leads to stereospecific *syn* elimination and therefore a bromination/debromination procedure could be used as a method for isomerisation of *trans* alkenes to *cis* alkenes, a useful synthetic conversion. However the results obtained using the *vic*-dibromides of *cis* and *trans* but-2-ene demonstrate that *anti* elimination of bromine is the predominant stereochemical pathway of the reaction. A mechanism to account for these results is discussed below.

$(C_5H_5)_2Ti$ has carbenoid character in so much as it has at least one low energy unfilled orbital and at least one high energy filled orbital.²⁵ The first step of the mechanism involves insertion of the titanium carbene into a carbon-bromine bond to give the titanium alkyl species (XII).



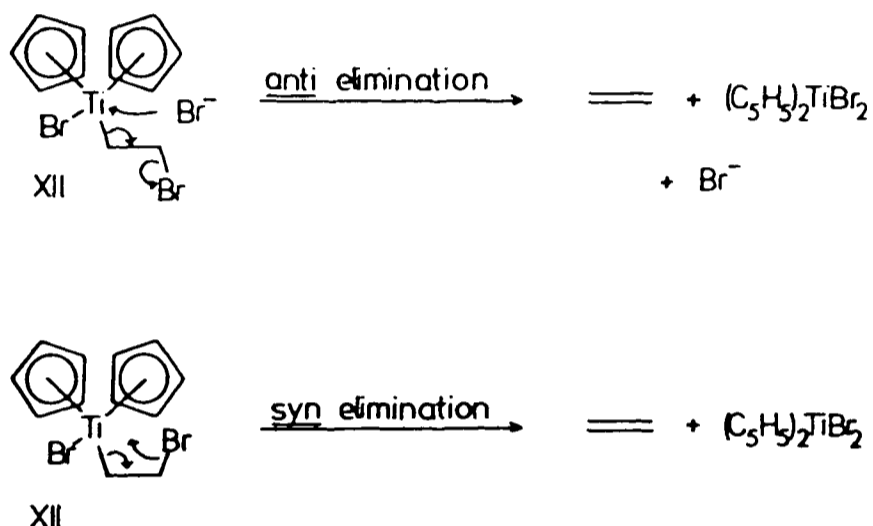
As titanocene is effectively an electron deficient carbene (14 electron species), it is envisaged that the insertion proceeds

Table IIIResults of debromination of dl and meso 2,3-dibromobutanes using "titanocene"

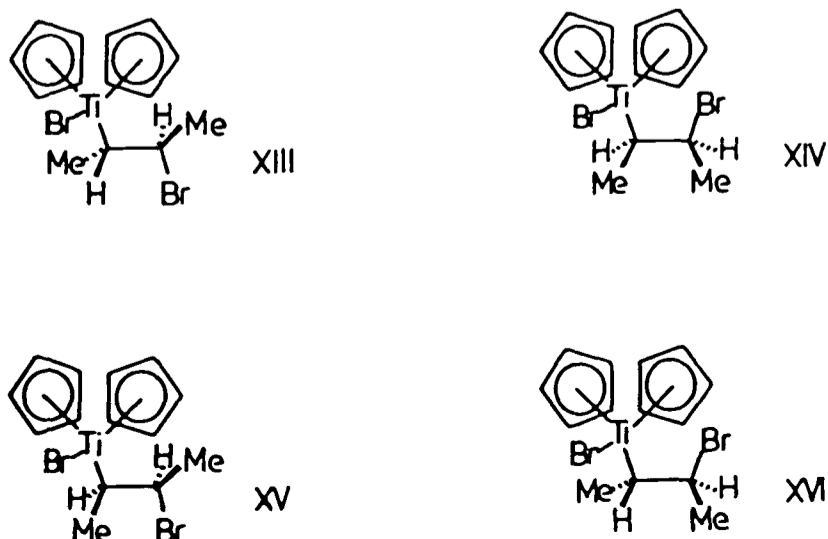
<u>Entry</u>	<u>vic-Dibromide</u>	<u>Temperature (°C)</u>	<u>trans But-2-ene:cis but-2-ene</u> *	<u>Comments</u>
1.	 meso	20	>95:5	
2.	 dl	20	40:60	
3.	 dl	-30	10:90	10% of products is but-1-ene.
4.	 dl	-78	<1:99	40% unknown by-product.

* Ratios determined by gas chromatography.

through an intimate ion pair, in which the donation of two electrons into the low-lying vacant orbital of titanium by the bromine atom has occurred before the donation of the two electrons from the high energy filled orbital on titanium to the carbon atom. The titanium alkyl (XII) proceeds to break down *via* two routes:



In the case of the titanium alkyl intermediate derived from *meso* 2,3-dibromobutane (Table III, Entry 1), the conformation required for *anti* elimination puts the two methyl groups anti-periplanar (XIII), whereas the conformation required for *syn* elimination requires the two methyl groups to be eclipsing (XIV). Hence we see highly selective *anti* elimination.



Anti elimination of bromine from *dl*-2,3-dibromobutane requires the conformation (XV) in which the two methyl groups are gauche whereas *syn* elimination puts them anticlinal (XVI). Hence the energy difference in the two transition states will be narrower in the *dl* case than in the *meso*, and selectivity will fall. See Table III, Entry 2. On reduction of the temperature, the number of molecules possessing sufficient energy to react by the higher energy pathway will decrease and selectivity will improve. See Table III, Entries 3 and 4.

"Titanocene" as a de-epoxidation reagent

As debromination of *vic*-dibromides took place almost instantaneously using " $(C_5H_5)_2Ti$ ", it was of interest to determine whether or not this reagent would convert epoxides to alkenes as rapidly.

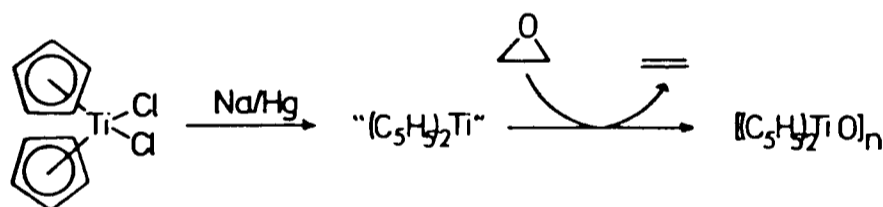
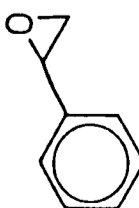
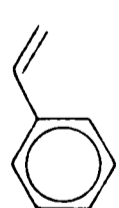
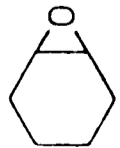



Table IV describes the results obtained with two epoxides. The de-epoxidation was performed in an analogous fashion to the debrominations carried out with "titanocene"; however, addition of the black "titanocene" to the epoxide solution produced a bright orange precipitate of titanium oxides rather than the deep red-black solutions obtained in the debromination reactions.

The results indicate that $(C_5H_5)_2Ti$ rapidly deoxygenates epoxides. The poor yield of alkene obtained from cyclohexene oxide is due to the production of cyclohexane. (The cyclohexene system appears to be susceptible to over-reduction - Table II, Entry 5.) An excess of " $(C_5H_5)_2Ti$ " and water has been shown to

Table IV

Conversion of epoxides to alkenes using "titanocene"

<u>Entry</u>	<u>Epoxide</u>	<u>Alkene</u>	<u>Effect of addition of 1.1 equivalents^A of "titanocene" to epoxide</u>	<u>Yield (%)^B</u>	<u>Time (minutes)</u>	<u>Effect of addition of further 1.1 equivalents^A of "titanocenes" to epoxide</u>	<u>Yield (%)^B</u>	<u>Time (minutes)</u>
1			60	2	85	2		
2			25	5	50 ^C	2		

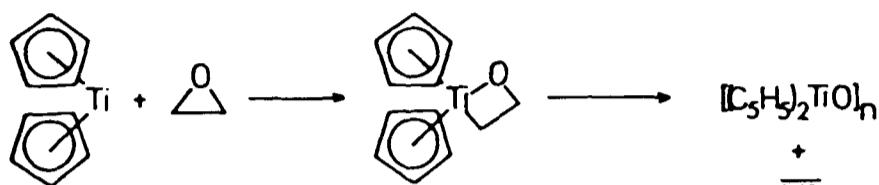
A 1.1 equivalents based on titanium.

B Yields measured by gas chromatography.

C The remaining 50% of epoxide was converted to cyclohexane.

reduce epoxides to alkanes.²⁶

The mechanism of deoxygenation is thought to involve insertion of the titanium carbene into a carbon-oxygen bond to give a metalla-oxacyclobutane followed by decomposition of the metallacycle to alkene and a polymeric titanium oxide species.¹⁸

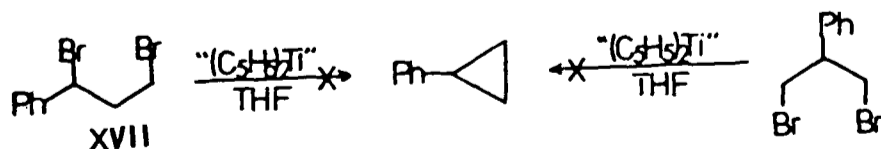


Cyclo-octene oxide was de-epoxidised to cyclo-octene on a preparative scale. Two equivalents of $(C_5H_5)_2TiCl_2$ were used and most of the resultant heavy orange precipitate was finally removed by filtration through celite; two distillations gave a 65% yield of pure cyclo-octene.

Miscellaneous reactions performed with "titanocene"

1. The rapid debromination of *vic*-dibromides by "titanocene" indicated that it might be possible to effect dehalogenation of other classes of compound containing two halogen atoms. Three reactions were attempted:

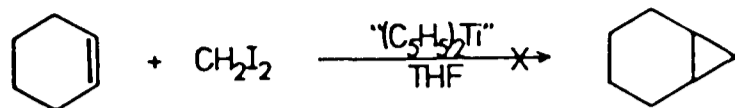
a) Debromination of 1,3-dibromoalkanes. Prolonged exposure of 1-phenyl-1,3-dibromopropane (XVII) and 1,3-dibromo-2-phenylpropane to "titanocene" failed to produce any phenylcyclopropane.



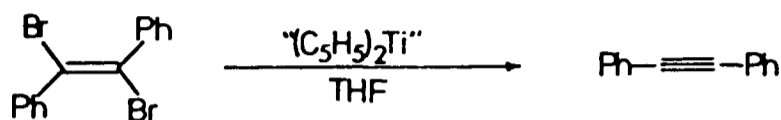
1-phenyl-3-bromopropane was isolated in low yield from the reaction of (XVII).

b) Deiodination of di-iodomethane. Addition of di-iodomethane

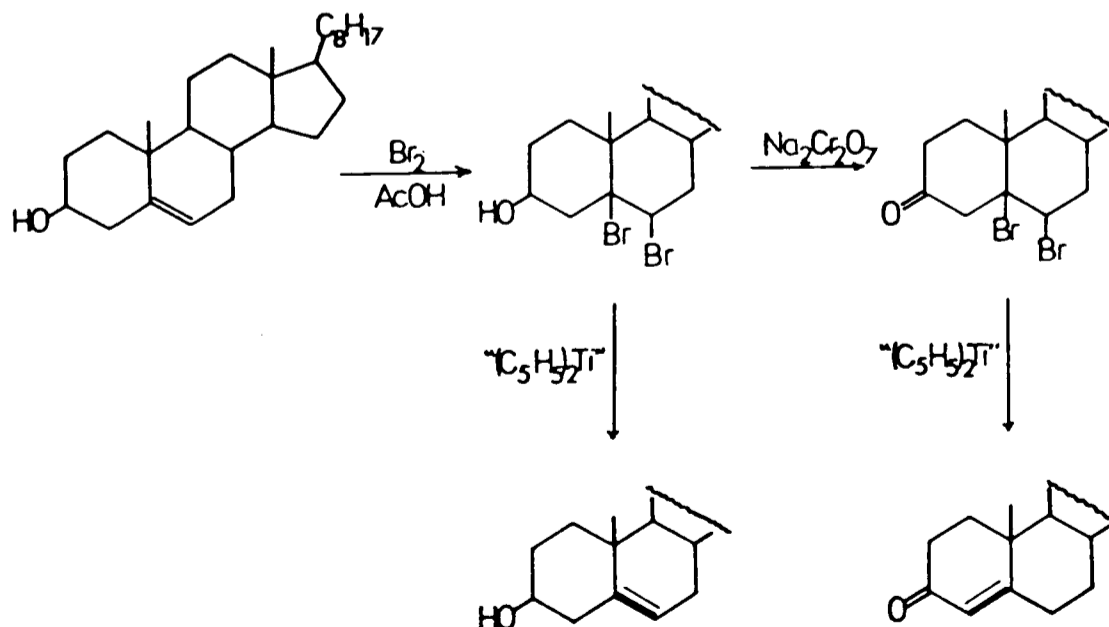
and cyclohexane to "titanocene" failed to produce any norcarane.



c) Debromination of diphenylacetylene dibromide. Addition of "titanocene" to diphenylacetylene dibromide gave a good yield (85%) of diphenylacetylene within 15 minutes.



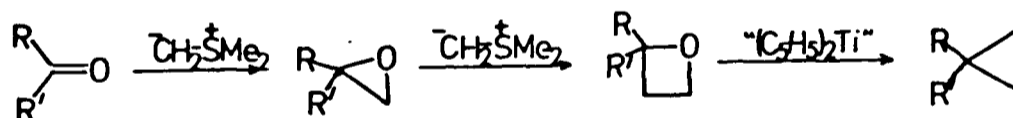
2. Bromination/debromination has been used as a method for purifying steroids. For example, purification of cholesterol through the dibromide completely eliminates cholestanol, 7-dehydrocholesterol and cholest-7-en-3-ol.⁶ Isolation of lanosterol (the non-saponifiable portion of wool fat which contains four closely related compounds) has been achieved by a bromination/debromination route.^{2,7} "Titanocene" was used to debrominate cholesterol dibromide and the dibromide of cholest-5-en-3-one.



"Titanocene" debromination of cholesterol dibromide gave cholesterol in good yield. As "titanocene" debrominates under mild, essentially neutral conditions, it was anticipated that debromination of the dibromide of cholest-5-en-3-one would give the unconjugated cholest-5-en-3-one in contrast to some existing methods of debromination;⁶ the presence of an absorption at 238 nm in the ultra-violet spectrum of the product however indicated that conjugation of the double bond had indeed occurred to form cholest-4-en-3-one.

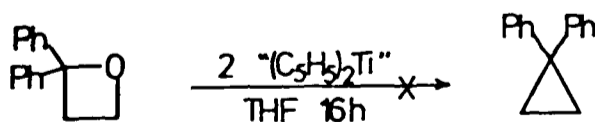
N.B. Debromination of cholesterol dibromide and the dibromide of cholest-5-en-3-one can only occur by elimination of bromine in an *anti* fashion.

3. The high affinity of "titanocene" for an oxygen atom suggested that Scheme 2 might provide a synthesis of cyclopropanes from ketones and epoxides.



Scheme 2

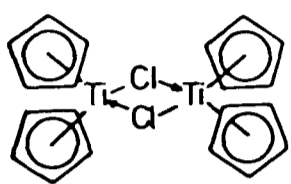
However, treatment of 2,2-diphenyloxetane with two equivalents of "titanocene" for 16 hours did not give 1,1-diphenylcyclopropane.



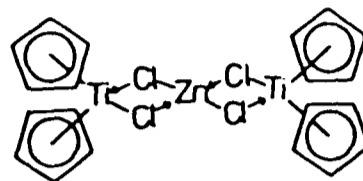
II.3 Zn/(C₅H₅)₂TiCl₂ systems for debromination and de-epoxidation

The Zn reduction product of (C₅H₅)₂TiCl₂

Reduction of (C₅H₅)₂TiCl₂ with zinc dust in various solvents gives green solutions of either (XVIII) or (XIX).



XVIII

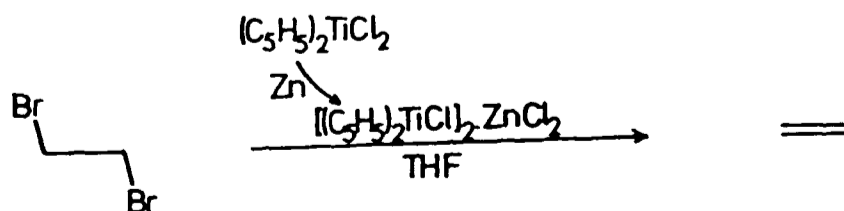


XIX

The green crystals obtained from the reaction mixtures in both toluene²⁸ and tetrahydrofuran²⁹ gave a zinc analysis corresponding to compound (XIX). Recrystallisation from diethyl ether of the product obtained from a reduction performed in tetrahydrofuran gave (XVIII). The absence of zinc from this product was demonstrated by a negative dithizone test.³⁰ It was postulated that if the complex produced in this reduction (probably [(C₅H₅)₂TiCl]₂.ZnCl₂) converted *vic*-dibromides to alkenes, then this debromination may be more efficient than the "titanocene" reduction due to the greater stability of the titanium (III) compound.

[(C₅H₅)₂TiCl]₂.ZnCl₂ as a debromination reagent

The use of [(C₅H₅)₂TiCl]₂.ZnCl₂ to debrominate *vic*-dibromides was investigated using stoichiometric quantities of titanium.



Stock solutions of [(C₅H₅)₂TiCl]₂.ZnCl₂ were prepared by efficient stirring of (C₅H₅)₂TiCl₂ in tetrahydrofuran over zinc dust

(activated by washing with dilute hydrochloric acid, water and diethyl ether) under a nitrogen atmosphere. After 15 minutes the red colour of $(C_5H_5)_2TiCl_2$ was replaced by the emerald green of $[(C_5H_5)_2TiCl]_2 \cdot ZnCl_2$; this solution could be stored indefinitely over the zinc dust.

In a procedure similar to the one used for following reductive debrominations with "titanocene" (see p 12), known quantities of $[(C_5H_5)_2TiCl]_2 \cdot ZnCl_2$ solution were added to well-stirred solutions of the *vic*-dibromide and the conversion of dibromide to alkene analysed by gas chromatography. After several minutes, red crystals were observed in the reaction mixture. The results obtained using a number of *vic*-dibromides are recorded in Table V.

The organometallic product was isolated by concentration and cooling of the reaction mixture obtained by addition of 2.2 equivalents of $[(C_5H_5)_2TiCl]_2 \cdot ZnCl_2$ to 2,3-dibromohexane; this gave three crops of red crystals which analysis by 1H n.m.r. spectroscopy and mass spectrometry showed to be only $(C_5H_5)_2TiCl_2$. The yield was 65% based on $(C_5H_5)_2TiCl_2$.

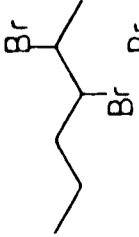

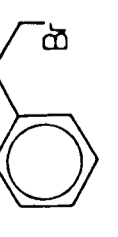
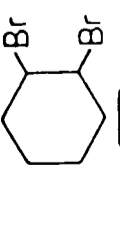
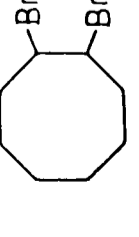
Discussion

$[(C_5H_5)_2TiCl]_2 \cdot ZnCl_2$ is a more efficient debrominating agent than $(C_5H_5)_2Ti$ *i.e.* 1.1 equivalents of $[(C_5H_5)_2TiCl]_2 \cdot ZnCl_2$ give yields in the order of 65-95% (Table V) whereas 1.1 equivalents of $(C_5H_5)_2Ti$ typically give yields in the order of 25-60%. Yields based on the quantity of $(C_5H_5)_2TiCl_2$ used in the reaction though, are comparable.

Entries 1 and 2 in Table V demonstrate that $[(C_5H_5)_2TiCl]_2 \cdot ZnCl_2$ does not cause significant isomerisation of alkenes. This

Table V

Debromination of vic-dibromides using $[(C_5H_5)_2TiCl]_2 \cdot ZnCl_2$

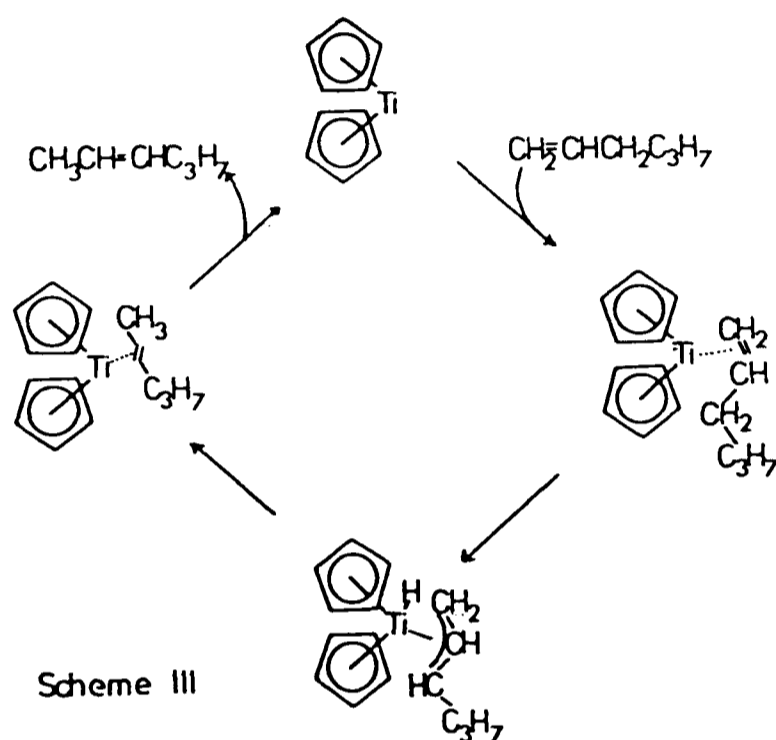
<u>Entry</u>	<u>vic-Dibromide</u>	<u>Alkene</u>	<u>Effect of addition of 0.55 equivalents^A of $[(C_5H_5)_2TiCl]_2 \cdot ZnCl_2$ to vic-dibromide</u>	<u>Effect of addition of further 0.55 equivalents^A of $[(C_5H_5)_2TiCl]_2 \cdot ZnCl_2$ to vic-dibromide</u>	<u>Time (minutes)</u>	<u>Yield (%)^B</u>	<u>Time (minutes)</u>	<u>Yield (%)^B</u>
1		Hex-2-ene ^C	50	95	1	95	2	95
2		Hex-1-ene ^C	45	75	1	75	2	75
3		styrene	45	85	1	85	1	85
4		Cyclohexene	33	75	2	75	3	75
5		Cyclo-octene		65		65	2	65

A 1.1 equivalents based on titanium.

B Yields measured by gas chromatography.

C <5% isomerisation occurred.

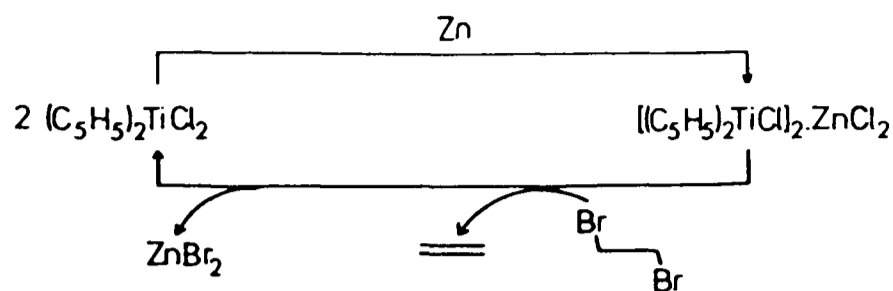
is in contrast to $(C_5H_5)_2Ti$ which has been shown to catalyse the isomerisation of 1-alkenes to 2-alkenes.³¹ However, the isomerisation requires two vacant co-ordination sites on titanium (Scheme III) and this requirement is clearly not met by $[(C_5H_5)_2TiCl]_2 \cdot ZnCl_2$.



Isolation of 65% $(C_5H_5)_2TiCl_2$ as the organometallic product of this debromination supports the hypothesis that the green solution obtained from stirring $(C_5H_5)_2TiCl_2$ over zinc dust is predominantly $[(C_5H_5)_2TiCl]_2 \cdot ZnCl_2$.

Zn dust and catalytic quantities of $(C_5H_5)_2TiCl_2$ as a debromination system

Scheme IV predicts that $(C_5H_5)_2TiCl_2$ should catalyse the reductive elimination of bromine from vic-dibromides by zinc.



Scheme IV

Catalytic amounts of $(C_5H_5)_2TiCl_2$ (*vic*-dibromide: $(C_5H_5)_2TiCl_2$, 5:1) were added to tetrahydrofuran solutions of *vic*-dibromide and zinc dust, and the slurry stirred vigorously under a nitrogen atmosphere; the initial red supernatant turned green within five minutes. When the reaction was complete, the tetrahydrofuran was removed under reduced pressure and the residue extracted with 30-40 light petroleum. After removal of this solvent, the product was purified by either distillation or crystallisation. A control was conducted in some cases; 1H n.m.r. analysis of the residue resulting from the removal of the tetrahydrofuran revealed the extent of the reaction. The results are recorded in Table VI.

These results demonstrate that $(C_5H_5)_2TiCl_2$ can be used to catalyse zinc debrominations in tetrahydrofuran. Debromination takes place in good yields at room temperature within thirty minutes for *di*-substituted alkenes and four hours for *mono*-substituted alkenes.

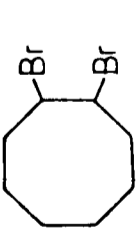

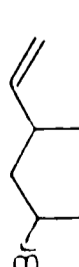
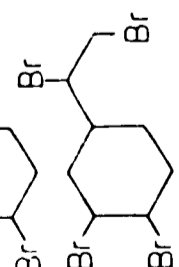
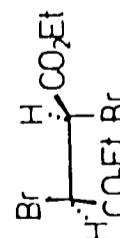
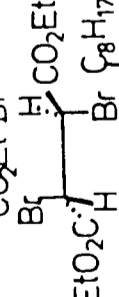
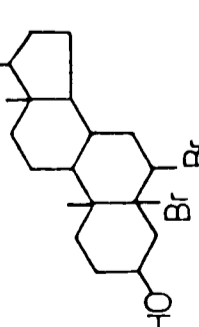
A mechanism for $[(C_5H_5)_2TiCl]_2.ZnCl_2$ debromination

The stereochemical consequences of bromination followed by debromination using $[(C_5H_5)_2TiCl]_2.ZnCl_2$ were investigated using *dl* and *meso* 2,3-dibromobutanes. The results summarised in Table VII, suggest a mechanism involving *anti* elimination

Table VI

Debromination of vic-dibromides to alkenes by zinc dust

Comparison of titanium-catalysed system and uncatalysed system

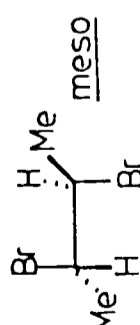
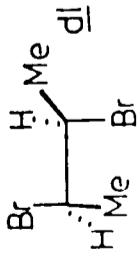
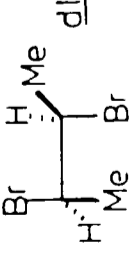
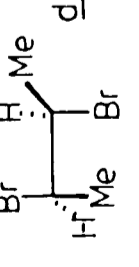
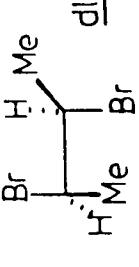
Entry	vic-Dibromide	Alkene	(C ₅ H ₅) ₂ TiCl ₂ /Zn/THF		Zn/THF (control)	
			Yield (%) ^A	Time (hours)	Yield (%) ^B	Time (hours)
1		Cyclo-octene	74	‡	<5	‡
2		Oct-1-ene	66	4	<5	4
3		4-Vinyl-1-cyclohexene	81	‡	<10	‡
4		4-Vinyl-1-cyclohexene	69	2‡		
5		Diethyl fumarate	74	‡		
6		Diethyl fumarate	78	‡	>95	‡
7		Cholesterol	68	‡	<5	‡

A Isolated yields.

B ¹H n.m.r. yields.

Table VII

Results of debromination of dl and meso 2,3-dibromobutanes using [(C₅H₅)₂TiCl]₂·ZnCl₂ and the (C₅H₅)₂TiCl₂ catalysed zinc system

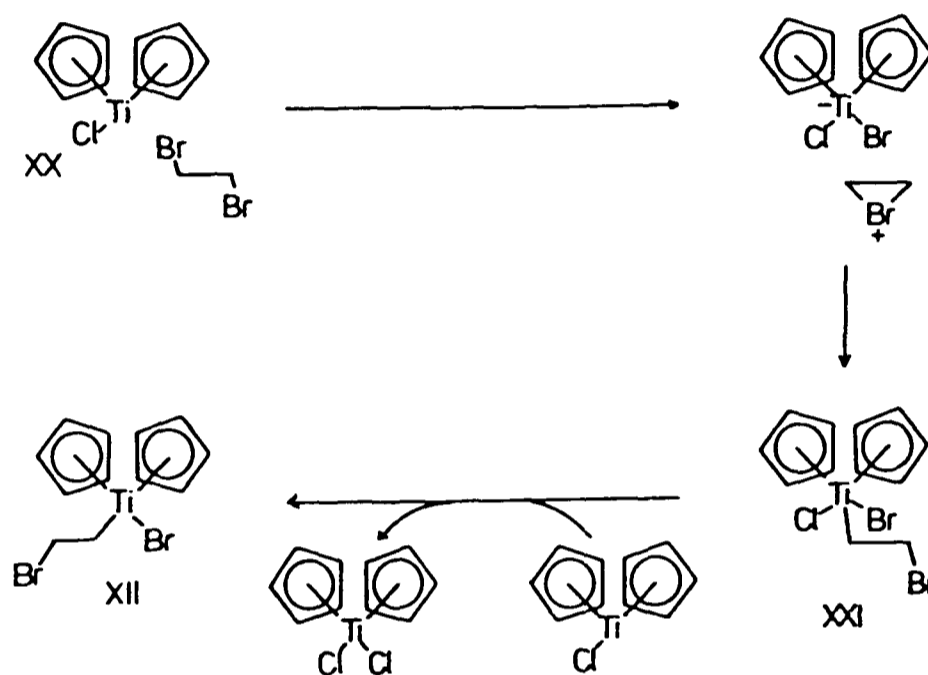
<u>Entry</u>	<u>vic-Dibromide</u>	<u>Conditions</u>	<u>trans But-2-ene: cis but-2-ene^A</u>
1	 $\text{Br} \quad \text{H} \quad \text{Me}$ $\quad \quad \quad \quad $ $\text{C} - \text{C}$ $\quad \quad \quad \quad $ $\text{Me} \quad \text{H} \quad \text{Br}$ meso	Zinc dust with catalytic ^B amounts of (C ₅ H ₅) ₂ TiCl ₂ ; 20 °C	>95:5
2	 $\text{Br} \quad \text{H} \quad \text{Me}$ $\quad \quad \quad \quad $ $\text{C} - \text{C}$ $\quad \quad \quad \quad $ $\text{H} \quad \text{Me} \quad \text{Br}$ dl	Zinc dust with catalytic ^B amounts of (C ₅ H ₅) ₂ TiCl ₂ ; 20 °C	25:75
3	 $\text{Br} \quad \text{H} \quad \text{Me}$ $\quad \quad \quad \quad $ $\text{C} - \text{C}$ $\quad \quad \quad \quad $ $\text{H} \quad \text{Me} \quad \text{Br}$ dl	Dibromide added to stoichiometric amounts of [(C ₅ H ₅) ₂ TiCl] ₂ ·ZnCl ₂ ; -20 °C	15:85
4	 $\text{Br} \quad \text{H} \quad \text{Me}$ $\quad \quad \quad \quad $ $\text{C} - \text{C}$ $\quad \quad \quad \quad $ $\text{H} \quad \text{Me} \quad \text{Br}$ dl	Stoichiometric amounts of [(C ₅ H ₅) ₂ TiCl] ₂ ·ZnCl ₂ added to dibromide; -20 °C	15:85
5	 $\text{Br} \quad \text{H} \quad \text{Me}$ $\quad \quad \quad \quad $ $\text{C} - \text{C}$ $\quad \quad \quad \quad $ $\text{H} \quad \text{Me} \quad \text{Br}$ dl	Zinc dust with catalytic ^B amounts of [(C ₅ H ₅) ₂ TiCl] ₂ ·ZnCl ₂ ; -20 °C	15:85

A Ratios determined by gas chromatography.

B Ti:vic-dibromide, 1:5.

of bromine.

The mechanism proposed for the reduction of *vic*-dibromides to alkenes by $[(C_5H_5)_2TiCl]_2 \cdot ZnCl_2$ is outlined below. The titanium (III) species (XX) inserts into a carbon-bromine bond to give (XXI).



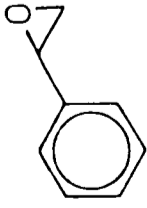
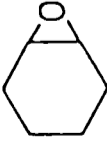

Further reaction with $(C_5H_5)_2TiCl$ gives the titanium alkyl (XII); this can then eliminate the product alkene in a *syn* or *anti* fashion as proposed for the mechanism of debromination by $(C_5H_5)_2Ti$ (see p 20). Isolation of $(C_5H_5)_2TiCl_2$ from the reaction mixture (see p 27) can be explained in terms of halogen exchange between the zinc and titanium; stirring $(C_5H_5)_2TiBr_2$ with zinc chloride in tetrahydrofuran gave exclusively $(C_5H_5)_2TiCl_2$.

$[(C_5H_5)_2TiCl]_2 \cdot ZnCl_2$ as a de-epoxidation reagent

The conversion of epoxides to alkenes by $[(C_5H_5)_2TiCl]_2 \cdot ZnCl_2$ was investigated. Table VIII describes the results obtained

Table VIII

Conversion of epoxides to alkenes using [(C₅H₅)₂TiCl]₂·ZnCl₂

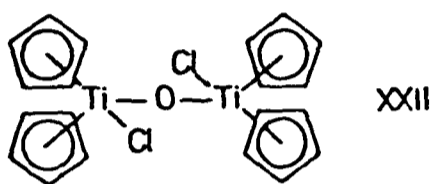
<u>Entry</u>	<u>Epoxide</u>	<u>Alkene</u>	<u>Effect of addition of 0.55 equivalents^A of [(C₅H₅)₂TiCl]₂·ZnCl₂ to epoxide</u>	<u>Effect of addition of further 0.55 equivalents^A of [(C₅H₅)₂TiCl]₂·ZnCl₂ to epoxide</u>	<u>Yield (%)^B</u>	<u>Time (minutes)</u>	<u>Yield (%)^B</u>	<u>Time (minutes)</u>
1		Styrene	15	2	20	3	34	
2		Cyclohexene	42	1	70	3		
3		Hexene ^C			50	5		

A 1.1 equivalents based on titanium.

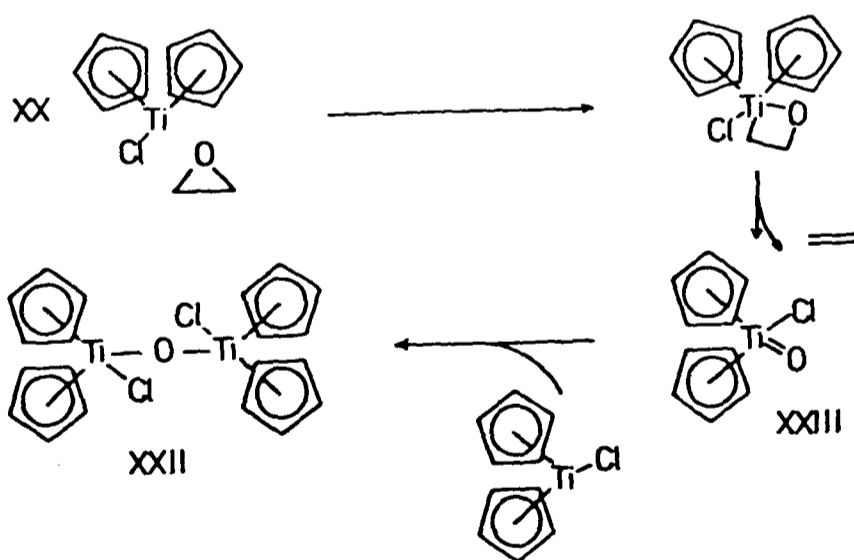
B Yields measured by gas chromatography.

C Separation of isomeric alkenes was not undertaken.

with three epoxides. The de-epoxidation was performed in an analogous manner to the debrominations carried out with $[(C_5H_5)_2TiCl]_2 \cdot ZnCl_2$; however addition of the green $[(C_5H_5)_2TiCl]_2 \cdot ZnCl_2$ to the epoxide solution produced orange crystals rather than the red crystals obtained in the debromination reaction. The crystals produced in the reaction between $[(C_5H_5)_2TiCl]_2 \cdot ZnCl_2$ and cyclohexene oxide were identified as the oxygen bridged dimer (XXII).³²



The results show that $[(C_5H_5)_2TiCl]_2 \cdot ZnCl_2$ deoxygenates epoxides in low to moderate yields. A mechanism for this reaction is proposed below.



After insertion of the titanium (III) species (XX) into a carbon-oxygen bond, elimination of alkene gives a titanium oxide (XXIII). Further reaction with another equivalent of $(C_5H_5)_2TiCl$ (XX) leads to the isolated oxygen bridged dimer (XXII).

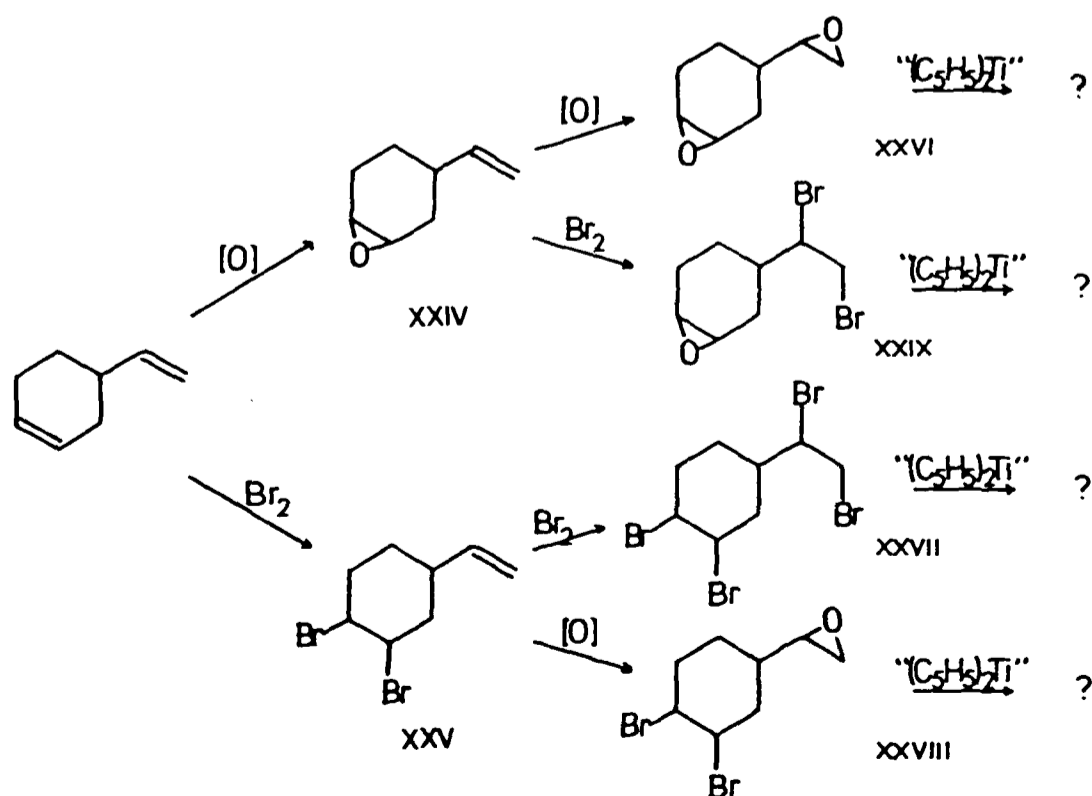
II.4 Investigations into the selectivity of Na/Hg/(C₅H₅)₂TiCl₂ systems and Zn/(C₅H₅)₂TiCl₂ systems towards vic-dibromides and epoxides

Having found that both "titanocene" and [(C₅H₅)₂TiCl]₂.ZnCl₂ debrominated vic-dibromides and removed the oxygen atom from epoxides, it was of interest to discover whether these reagents showed any selectivity in their reactivity towards a molecule containing both vic-dibromide and epoxide functionalities and whether the reagents would exhibit any preference for either the vic-dibromide/epoxide of a di-substituted double bond or the vic-dibromide/epoxide of a mono-substituted double bond.

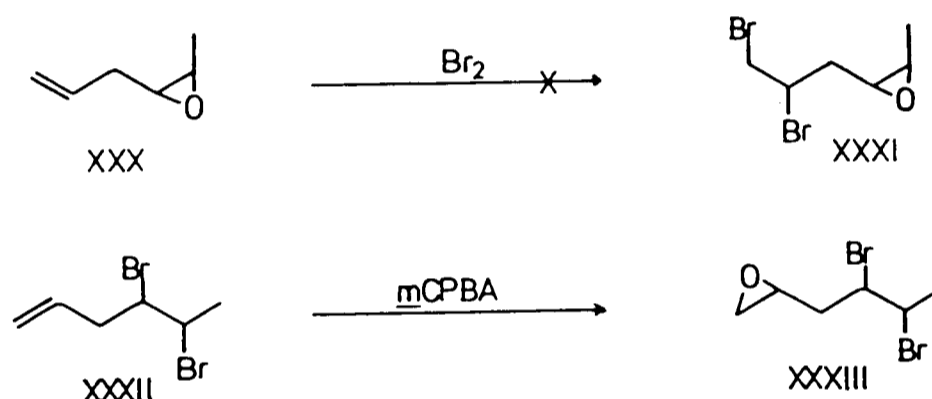
(Selective deprotection of the di-substituted double bond would produce the epoxide/vic-dibromide of the less reactive double bond, a synthetically useful reaction.)

A novel bromine-assisted cyclisation

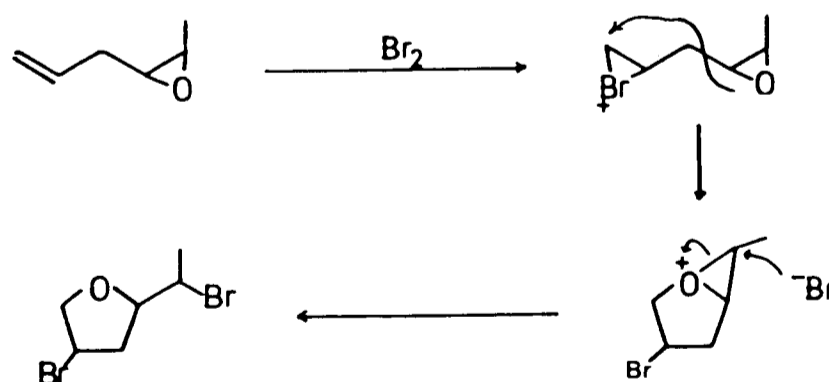
4-Vinylcyclohex-1-ene was used to investigate the reactions of "(C₅H₅)₂Ti" depicted in the proposed reaction scheme below.



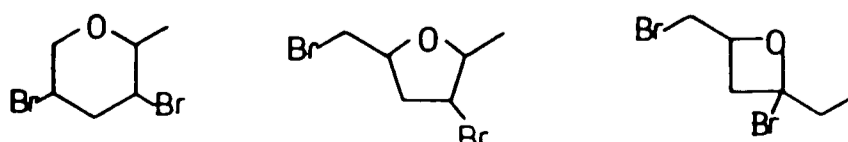
The epoxidations and brominations proceeded smoothly to produce compounds (XXIV), (XXV), (XXVI), (XXVII), and (XXVIII). However, attempted bromination of the *mono*-substituted double bond of (XXIV) repeatedly gave a product whose ^1H n.m.r. spectrum did not contain any resonances corresponding to the protons attached to the carbon atoms of the epoxide which should still be present in (XXIX). Similarly, attempted bromination of the *mono*-substituted double bond of (XXX) did not give the expected product (XXXI), whereas epoxidation of (XXXII) with $m\text{CPBA}$ gave (XXXIII) in good yield.



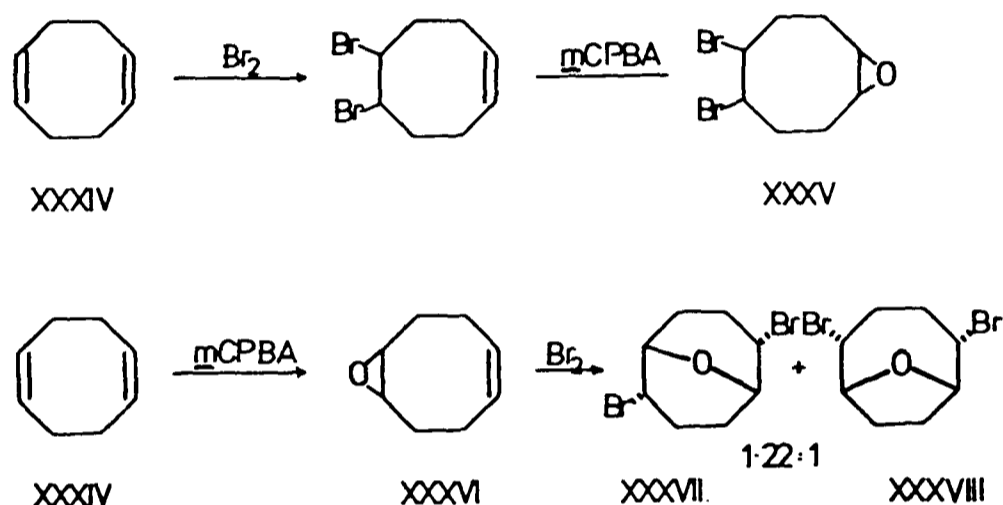
It was proposed that bromination caused opening of the epoxide to give cyclic ethers, e.g.



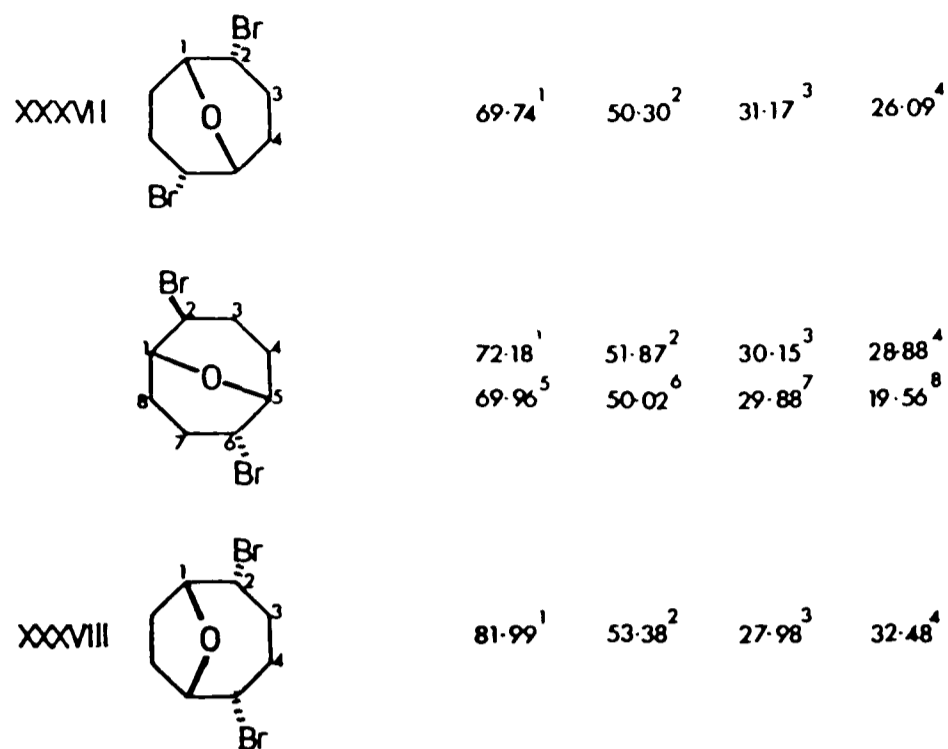
Three other cyclic ethers (discounting stereoisomers) are theoretical products of this type of reaction.



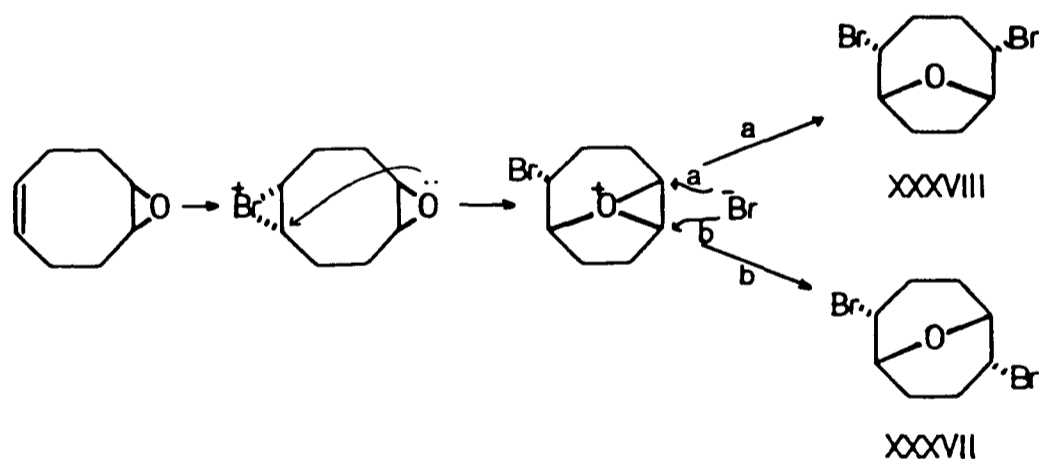
1,5-Cyclo-octadiene (XXXIV) was used to verify this proposal. Bromination of (XXXIV) followed by epoxidation with *m*CPBA gave the expected product (XXXV). Oxidation of (XXXIV) with *m*CPBA to give (XXXVI) followed by bromination, produced a 1.22:1 mixture of *trans, trans*-isomers of 2,6-dibromo-9-oxabicyclo [3.3.1] nonane (XXXVII) and 2,5-dibromo-9-oxabicyclo [4.2.1] nonane (XXXVIII).



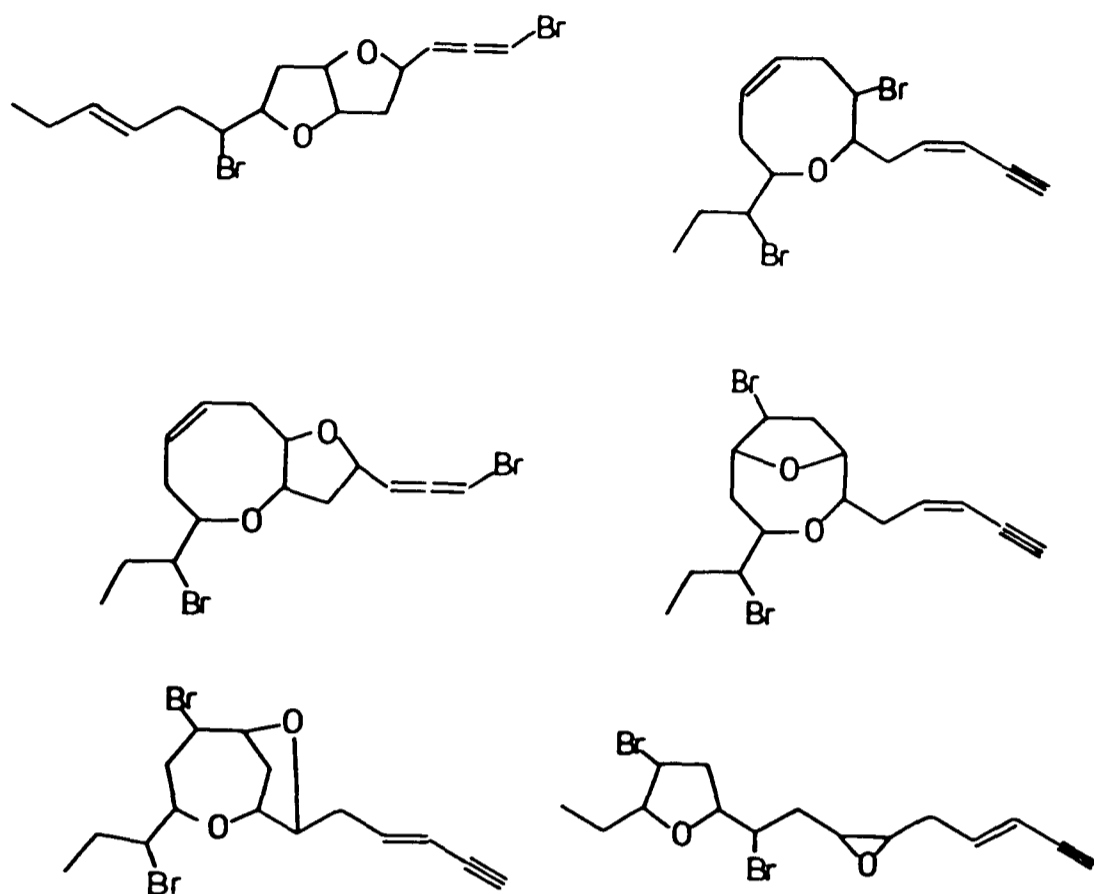
Although the ¹H n.m.r. spectrum of the mixture of (XXXVII) and (XXXVIII) indicated that there was no epoxide functionality present, the proton-decoupled ¹³C spectrum finally determined which bicyclic ethers had been formed. In order to indicate the power of ¹³C n.m.r. spectroscopy to differentiate between compounds of this type, the resonances of three possible products of the reaction are given overleaf.³³



A mechanism for this cyclisation, which presumably involves a bromonium ion intermediate, is shown below.



It is of interest that dibrominated sesquiterpenes containing ether linkages have been isolated from the red alga genus *Laurencia*.³⁴ Examples include the compounds whose structures are shown overleaf.



In the light of the above results it is postulated that these products may all be formed from a precursor such as (XXXIX) by a biosynthetic pathway involving bromine-assisted cyclisations of epoxides to cyclic ethers.



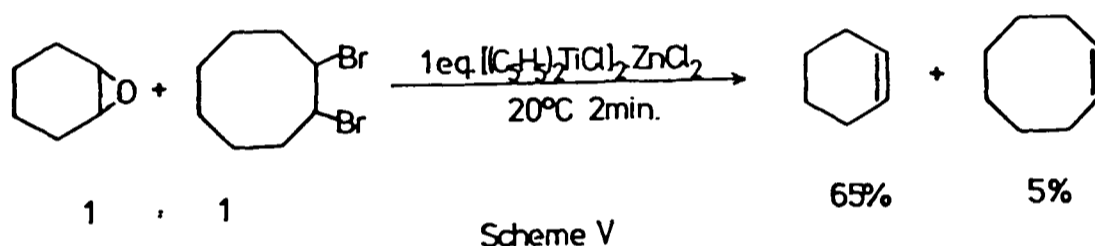
XXXIX

Attempted investigation of chemoselectivity of "titanocene"

Treatment of compounds (XXVI), (XXVII) and (XXVIII) with 1.1 equivalents of "titanocene" at $-78\text{ }^{\circ}\text{C}$, $-30\text{ }^{\circ}\text{C}$ and room temperature failed to produce consistent results.

Chemoselectivity of $[(C_5H_5)_2TiCl]_2 \cdot ZnCl_2$

Initial investigations into the selectivity of $[(C_5H_5)_2TiCl]_2 \cdot ZnCl_2$ towards *vic*-dibromides and epoxides were encouraging (see Table IX). One equivalent of the reagent was added to a 1:1 mixture of the *vic*-dibromide and the epoxide at $-78^\circ C$, and the resultant slurry kept at $-20^\circ C$ for several hours. The results show a clear preference for reduction of the epoxide over reduction of the *vic*-dibromide; this selectivity was confirmed in a competition experiment, performed at room temperature and analysed by gas chromatography, which gave the result depicted in Scheme V.



The selectivity can be explained in terms of a pre-reaction association of $(C_5H_5)_2TiCl$ (XX) with either a *vic*-dibromide molecule or an epoxide molecule - see Scheme VI.

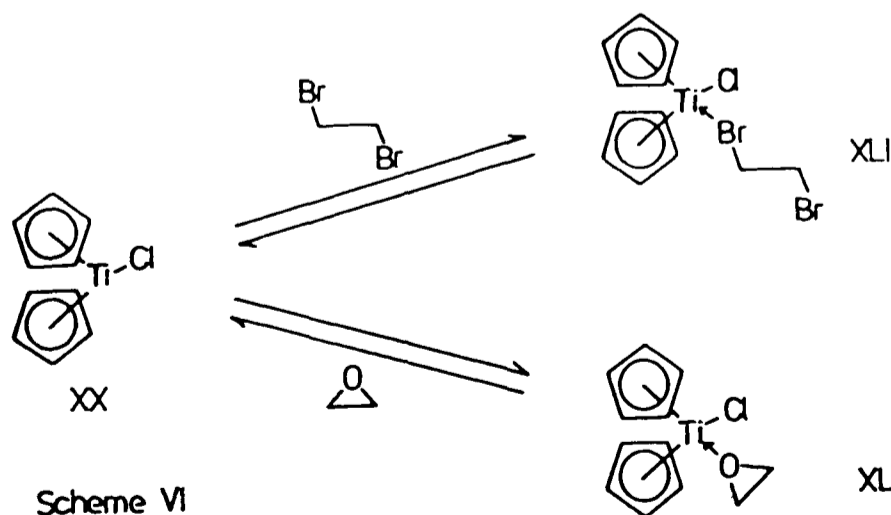
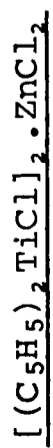


Table IX

Results of competition experiments on 1:1 mixtures of vic-dibromides and epoxides using one equivalent of



<u>Entry</u>	<u>Epoxide</u>	<u>vic-Dibromide</u>	<u>Conditions</u>	<u>Results</u> [†]
1	Cyclo-octene oxide	Cyclo-octene dibromide	-20 °C, 3.5 hours	Preference for epoxide shown; difficult to quantify accurately.
2	1,2-epoxydodecane	1,2-dibromododecane	-20 °C, 3.5 hours	Epoxide:vic-Dibromide:Olefin <0.005:4:1

† The organometallic product was removed from the reaction mixture by standard procedures, and the ¹H n.m.r. of the crude organic product recorded.

The greater affinity of titanium for oxygen than for bromine leads to a higher concentration of (XL) than (XLI), and hence the titanium (III) species (XX) will insert preferentially into the carbon-oxygen bond leading to the observed selectivity.

The low yields of alkene obtained in these competition experiments (Table IX and Scheme V) and the initial investigations into the reaction of epoxides with $[(C_5H_5)_2TiCl]_2 \cdot ZnCl_2$ (Table VI), indicate that the reduction of epoxides by this reagent is inefficient in comparison with its reduction of *vic*-dibromides (Table V). Utilisation of the good selectivity observed in Scheme V for synthetic purposes requires an improvement in these yields.

The yield of hex-1-ene from 1,2-epoxyhexane was improved from 50% using 1.1 equivalents of $[(C_5H_5)_2TiCl]_2 \cdot ZnCl_2$ (Table VIII, Entry 3) to 65% using 2 equivalents of $[(C_5H_5)_2TiCl]_2 \cdot ZnCl_2$. It was demonstrated that $[(C_5H_5)_2TiCl]_2O$ (XXII) can be converted back to $(C_5H_5)_2TiCl_2$ in 77% yield by stirring with concentrated hydrochloric acid for 20 minutes in dichloromethane.

Regioselectivity of $[(C_5H_5)_2TiCl]_2 \cdot ZnCl_2$

Investigations into the selectivity of $[(C_5H_5)_2TiCl]_2 \cdot ZnCl_2$ towards derivatives of cyclohexene and hex-1-ene were undertaken. After addition (at room temperature) of one equivalent of $[(C_5H_5)_2TiCl]_2 \cdot ZnCl_2$ to a 1:1 cyclohexene derivative: hex-1-ene derivative solution in tetrahydrofuran, the resultant mixture was analysed by gas chromatography. These results, recorded in Table X, reveal that $[(C_5H_5)_2TiCl]_2 \cdot ZnCl_2$ selectively

Table X

Results of experiments to determine the selectivity of [(C₅H₅)₂TiCl]₂, .ZnCl₂, towards derivatives of cyclohexene and hex-1-ene

<u>Entry</u>	<u>Cyclohexene derivative</u>	<u>Hex-1-ene derivative</u>	<u>Yield^A of cyclohexene (%)</u>	<u>Yield^A of hexene^B (%)</u>	<u>4</u>
1	Epoxide	Epoxide	66	10	4
2	<i>vic</i> -Dibromide	<i>vic</i> -Dibromide	45	25	4
3	<i>vic</i> -Dibromide	Epoxide	40	33	
4	Epoxide	<i>vic</i> -Dibromide	75	5	

A Yields determined by gas chromatography.

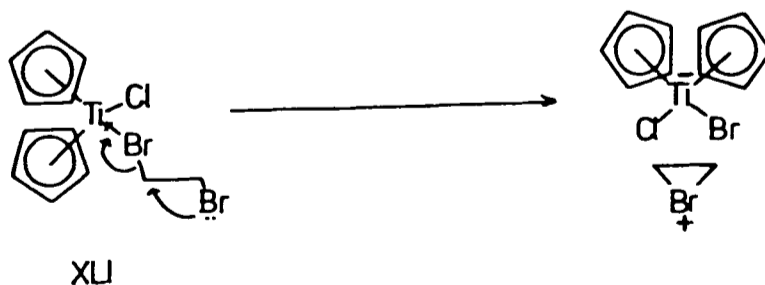
B Separation of isomeric hexenes was not undertaken.

reduces the *di*-substituted derivatives of cyclohexene over the *mono*-substituted derivatives of hex-1-ene. This selectivity dominates its preference for reduction of an epoxide rather than reduction of a *vic*-dibromide (Table X, Entry 3).

These results suggest that the rate determining step of both de-epoxidation and debromination using $[(C_5H_5)_2TiCl]_2 \cdot ZnCl_2$ involves a transition state which is stabilised to a greater extent by 1,2 dialkyl substitution than by monoalkyl substitution.

It is proposed that co-ordination of the oxygen atom of the epoxide to titanium is the rate determining step in de-epoxidation (see Scheme VI), and that the adduct of cyclohexene oxide, stabilised by the inductive effect of two alkyl groups, is of lower energy content than the adduct of 1,2-epoxyhexane, stabilised by the inductive effect of one alkyl group. This leads to a lower transition state energy for the addition of cyclohexene oxide to titanium and hence the selectivity observed in Table X, Entry 1.

Regarding the bromonium ion forming step in the debromination reaction as the rate determining step accounts for the selectivity observed in Table X, Entry 2.



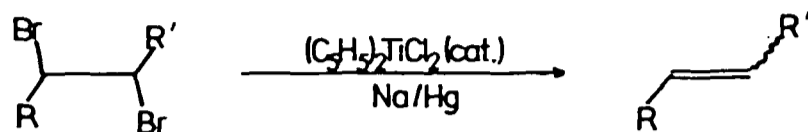
The *di*-substituted bromonium ion of cyclohexene, stabilised by the inductive effect of two alkyl groups, will be of lower energy content than the *mono*-substituted bromonium ion of hex-1-ene, stabilised by the inductive effect of one alkyl group.

The selectivities in Table X, Entries 3 and 4 result from

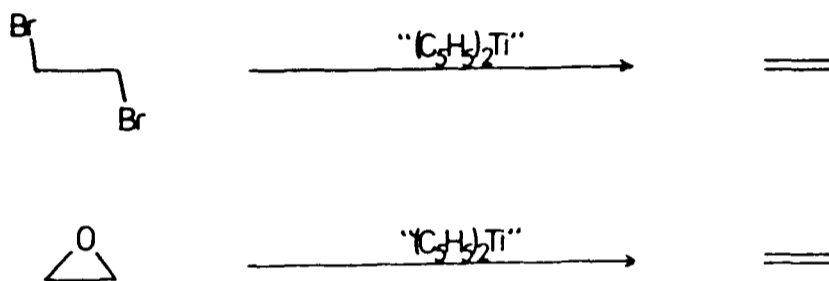
a super-position of the effects explained here on the preference of $(C_5H_5)_2TiCl$ (XX) for de-epoxidation over debromination rationalised previously (p 41).

II.5 Conclusions

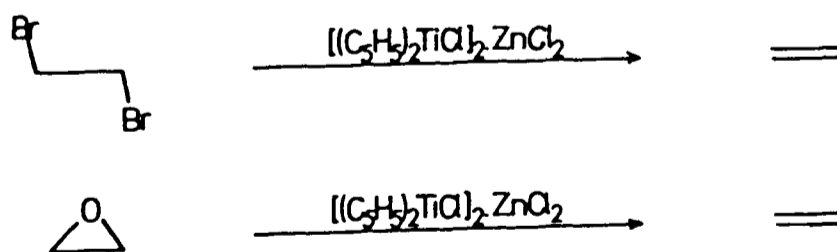
It has been demonstrated that $(C_5H_5)_2TiCl_2$ catalyses a Na/Hg debromination of *di*-substituted *vic*-dibromides.



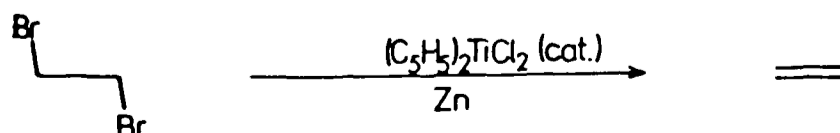
Reduction of $(C_5H_5)_2TiCl_2$ with Na/Hg in the absence of a *vic*-dibromide produces an unstable black solution of "titanocene" which debrominates *mono* and *di*-substituted *vic*-dibromides and deoxygenates epoxides within several minutes. It has been shown that the debromination proceeds with *anti* stereoselectivity.



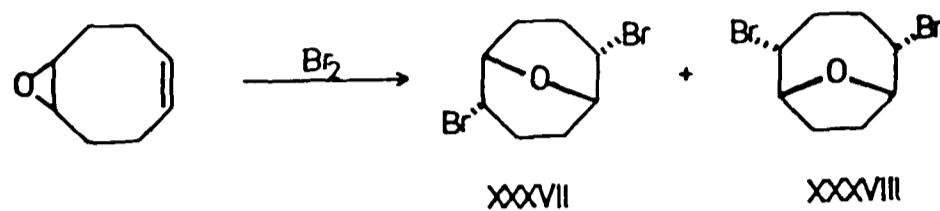
Reduction of $(C_5H_5)_2TiCl_2$ with zinc dust produces a relatively stable titanium (III) species $[(C_5H_5)_2TiCl]_2 \cdot ZnCl_2$, which also rapidly deoxygenates epoxides and debrominates *vic*-dibromides. It was demonstrated that the debromination proceeds with *anti* stereoselectivity.



$(C_5H_5)_2TiCl_2$ was shown to catalyse a zinc debromination of *vic*-dibromides. The mild conditions and short reaction times required make $(C_5H_5)_2TiCl_2$ an attractive additive to the classical zinc debromination procedure.



During the synthesis of molecules containing both *vic*-dibromide and epoxide functionalities, a novel cyclisation was discovered which may be involved in the biosynthesis of certain marine natural products.



Finally, $[(\text{C}_5\text{H}_5)_2\text{TiCl}]_2 \cdot \text{ZnCl}_2$ was shown to preferentially deoxygenate epoxides in the presence of *vic*-dibromides and to preferentially deoxygenate/debrominate cyclohexene derivatives in the presence of hex-1-ene derivatives.

Experimental

For general experimental procedure, see p 80 , Section I.

In Section II, light petroleum is of boiling range 30-40 °C.

Zinc dust was activated by treatment with dilute hydrochloric acid for one minute. The dust was then washed with water (x2) and acetone (x2), and dried.

Analytical gas chromatography was carried out using a Pye Unicam 104 instrument with a column 5 ft. long x 4 mm bore. The analyses of mixtures of butenes were performed using a column packed with celite coated with 5% silver nitrate. The remaining analyses were conducted using a column packed with Chromosorb W.HP 100/120 mesh coated with 15% Carbowax 6000.

The following compounds were synthesised by standard procedures:

a) 1,2-Dibromoalkanes

d1 2,3-Dibromobutane, *meso* 2,3-dibromobutane, *meso* 2,3-dibromodiethylsuccinate, 1,2-dibromohexane, 2,3-dibromohexane, 4,5-dibromohex-1-ene (XXXII), cyclohexene dibromide, 1,2-dibromo-octane, cyclo-octene dibromide, 5,6-dibromocyclo-oct-1-ene, 1,2-dibromo-4-vinyl-cyclohexane (XXV), 4-vinyl-cyclohex-1-ene tetrabromide (XXVII), styrene dibromide, 1,2-dibromododecene cyclododecene dibromide, diphenylacetylene dibromide and stilbene dibromide were prepared by the addition of bromine to the parent unsaturated compound in carbon tetrachloride at 0 °C.³⁵

d1 2,3-Dibromodiethylsuccinate was prepared by the addition of bromine to the parent alkene in diethyl ether at 0 °C.³⁶

Cholesterol dibromide was derived from cholesterol using an acetic acid/sodium acetate/bromine mixture and cholest-5-en-3-one dibromide was prepared by sodium dichromate oxidation of cholesterol dibromide.⁶

b) Epoxides

1,2-Epoxyhexane, 4,5-epoxyhex-1-ene (XXX), 1,2-epoxy-4,5-dibromohexane (XXXIII), cyclohexene oxide, cyclo-octene oxide, 5,6-epoxycyclo-oct-1-ene (XXXVI), 1,2-dibromo-5,6-epoxycyclo-octane (XXXV), 1,2-epoxy-4-vinyl-cyclohexane (XXIV), 4-vinyl-cyclohex-1-ene diepoxide (XXVI), 1,2-dibromo-4-vinyl-cyclohexane epoxide (XXVIII), styrene oxide, 1,2-epoxydodecane and cyclododecene oxide were prepared by addition of *m*CPBA to the parent alkene in chloroform at 0 °C.³⁷

c) 1,3-Dibromoalkanes

1-Phenyl-1,3-dibromopropane (XVII) was prepared from 1-phenyl-3-bromopropane by treatment with *N*-bromosuccinimide in carbon tetrachloride.³⁸

1,3-Dibromo-2-phenylpropane was prepared by successive treatment of 1,3-dicarboethoxy-2-phenylpropane with LiAlH₄, methanesulphonyl chloride/pyridine and lithium bromide/acetone.

d) Oxetanes

2,2-Diphenyloxetane was synthesised by addition of two equivalents of dimethyloxosulphonium methylide to acetophenone.³⁹

1. Debromination of vic-dibromides with a Na/Hg/(C₅H₅)₂TiCl₂ system and a Na/Hg control

Tetrahydrofuran (20 ml) was added to a mixture of 2% sodium amalgam (0.25 g of sodium, 11 mmol), cyclo-octene dibromide (0.500 g, 1.85 mmol) and (C₅H₅)₂TiCl₂ (0.092 g, 0.37 mmol).

In a control experiment, tetrahydrofuran (20 ml) was added to a mixture of 2% sodium amalgam (0.25 g of sodium, 11 mmol) and cyclo-octene dibromide (0.500 g, 1.85 mmol). The reactions were stirred efficiently with a magnetic stirrer and monitored by gas chromatography.

The above procedure was also carried out using 2,3-dibromohexane, cyclododecene dibromide, cyclohexene dibromide, 1,2-dibromo-octane and styrene dibromide. The results are given in Table I, p10.

2. Preparative scale debromination of cyclo-octene dibromide

2% Sodium amalgam (2.0 g of sodium, 87 mmol), cyclo-octene dibromide (10.0 g, 37.0 mmol), $(C_5H_5)_2TiCl_2$ (0.921 g, 3.70 mmol) and tetrahydrofuran (100 ml) were stirred efficiently for 4 h; the initial red mixture became brown and finally blue. The final solution was decanted and filtered through celite. Removal of the solvent under reduced pressure and extraction with light petroleum (5 x 15 ml) gave a yellow solution. Removal of the solvent under reduced pressure followed by flash micro-distillation gave cyclo-octene, 2.69 g (66%) which was identified by comparison of its 1H n.m.r. spectrum with that of an authentic sample.

3. The stereochemical consequences of bromination/debromination of a mixture of *cis* and *trans* cyclododecenes using a Na/Hg/ $(C_5H_5)_2TiCl_2$ system and a Na/Hg control

A mixture of cyclododecenes (*cis:trans*, 35:65) was brominated in carbon tetrachloride at 0 °C. The resultant dibromides were debrominated using the procedure described in Experiment 1.

The catalysed reaction gave a *cis:trans* ratio of 57:43 and the uncatalysed reaction gave a *cis:trans* ratio of 44:56 as measured by gas chromatography.

4. Debromination of *vic*-dibromides using "titanocene"

Tetrahydrofuran (70 ml) was added to 2% sodium amalgam (1.0 g of sodium, 43 mmol) and $(C_5H_5)_2TiCl_2$ (3.493 g, 14.08 mmol). With vigorous shaking (15 min), the initial red solution turned brown, black-yellow and finally black. 5 ml (1.00 mmol based on titanium) of this solution were removed in a syringe under a blanket of nitrogen and added to a rapidly stirred solution of cyclo-octene dibromide (0.248 g, 0.91 mmol) in tetrahydrofuran (5 ml). The extent of debromination was determined by gas chromatography. A further 5 ml of the titanocene solution was added to the reaction mixture and the extent of the reaction again monitored by gas chromatography.

The above procedure was also carried out with 2,3-dibromohexane, styrene dibromide, cyclododecene dibromide and cyclohexene dibromide. The results are given in Table II, p 13.

5. Debromination of 2,3-dibromohexane using "titanocene" under an atmosphere of argon

2,3-Dibromohexane was debrominated using "titanocene" using the procedure given in Experiment 4 except the nitrogen atmosphere was replaced by an argon atmosphere; 1.1 equivalents of "titanocene" gave a 50% yield of alkene after one minute.

6. Isolation of the organometallic product from a "titanocene" debromination

2% Sodium amalgam (0.5 g of sodium, 22 mmol), $(C_5H_5)_2TiCl_2$ (1.000 g, 4.03 mmol) and tetrahydrofuran (50 ml) were shaken vigorously for 30 min. to give a black solution which was decanted onto a rapidly stirred solution of cyclo-octene dibromide (1.000 g, 3.70 mmol) in tetrahydrofuran (20 ml). The resultant brown slurry separated to a red solution and fine yellow precipitate. Filtration, followed by concentration (10 ml) and cooling ($-30\text{ }^\circ\text{C}$) for 16 h gave red-violet crystals; repeated filtration, concentration and cooling ($-30\text{ }^\circ\text{C}$) for 16 h gave a further two crops of red-violet crystals. The 1H n.m.r. spectrum (60 MHz, $CDCl_3$) contained two singlets at δ 6.7 and 6.65 in a ratio 19:1 which were assigned to $(C_5H_5)_2TiBr_2$ and $(C_5H_5)_2TiBrCl$ respectively (Lit.⁴⁰: $(C_5H_5)_2TiBr_2$ ($CDCl_3$) δ 6.70, $(C_5H_5)_2TiCl_2$ ($CDCl_3$) δ 6.57). These assignments were confirmed by the presence of molecular ion isotope patterns in the mass spectrum corresponding to $(C_5H_5)_2TiBr_2$ and $(C_5H_5)_2TiBrCl$. The infra-red spectrum was consistent with the assignments. Yield (based on recovery of titanocene halide) 0.690 g (51%).

7. The stereochemical consequences of bromination/debromination of a mixture of *cis* and *trans* cyclododecenes using "titanocene"

A mixture of cyclododecenes (*cis:trans*, 35:65) was brominated in carbon tetrachloride at $0\text{ }^\circ\text{C}$. The resultant dibromides were debrominated using the procedure described in Experiment 4. The resultant *cis:trans* ratio was 50:50 as measured by gas chromatography.

8. The stereochemical consequences of debromination of *dl*

and meso 2,3-dibromodiethyl succinates using "titanocene"

meso 2,3-Dibromodiethyl succinate was debrominated using the procedure described in Experiment 4 producing diethyl fumarate only. The reaction was repeated with the solution of dibromide cooled (-78 °C) before the addition of the "titanocene". The resultant mixture was stored at -30 °C for 16 h; analysis by gas chromatography showed that the sole product was diethyl fumarate. Analogous experiments using a mixture of *meso* and *dl* 2,3-dibromodiethyl succinates at -30 °C (16 h) and -78 °C (16 h) produced diethyl fumarate only. Addition of diethyl maleate to the reaction mixture resulted in its isomerisation to diethyl fumarate.

9. The stereochemical consequences of debromination of *dl* and *meso* 2,3-dibromobutanes using "titanocene"

dl and *meso* 2,3-Dibromobutanes were debrominated using the procedure described in Experiment 4; the gas in the reaction vessel was analysed by gas chromatography after 30 min. *dl* 2,3-Dibromobutane was also treated with "titanocene" at -30 °C and -78 °C and the gas in the reaction vessel analysed after 3 h in both cases. The results are given in Table III, p 19.

10. Conversion of epoxides into alkenes using "titanocene"

Tetrahydrofuran (70 ml) was added to 2% sodium amalgam (1.0 g of sodium, 43 mmol) and $(C_5H_5)_2TiCl_2$ (3.493 g, 14.08 mmol). With vigorous shaking, the initial red solution turned brown, black-yellow and finally black. 5 ml (1.00 mmol based on titanium) of this solution were removed in a syringe under

a blanket of nitrogen and added to a rapidly stirred solution of styrene oxide (0.109 g, 0.91 mmol) in tetrahydrofuran (5 ml). The extent of deoxygenation was determined by gas chromatography. A further 5 ml of the titanocene solution was added to the reaction mixture and the extent of the reaction again monitored by gas chromatography. The above procedure was also carried out with cyclohexene oxide. The results are given in Table IV, p 22.

11. Preparative scale conversion of cyclo-octene oxide to cyclo-octene using "titanocene"

Tetrahydrofuran (150 ml) was added to 2% sodium amalgam (2.0 g of sodium, 87 mmol) and $(C_5H_5)_2TiCl_2$ (8.98 g, 36.0 mmol). With vigorous shaking (20 min), the initial red solution turned brown, black-yellow and finally black; the final colour change was accompanied by evolution of heat. The "titanocene" solution was decanted onto a rapidly stirred solution of cyclo-octene oxide (2.27 g, 18.0 mmol) in tetrahydrofuran (30 ml) producing a yellow precipitate. Addition of light petroleum (300 ml) followed by filtration through celite gave a pale yellow solution. Removal of solvents by distillation at atmospheric pressure followed by two flash microdistillations at reduced pressure gave cyclo-octene, 1.29 g (65%) which was identified by comparison of its 1H n.m.r. spectrum with that of an authentic sample.

12a. Attempted debromination of 1-phenyl-1,3-dibromopropane (XVII) using "titanocene"

Tetrahydrofuran (75 ml) was added to 2% sodium amalgam

(0.75 g of sodium, 33 mmol) and $(C_5H_5)_2TiCl_2$ (4.00 g, 16.1 mmol). With vigorous shaking (20 min), the initial red solution turned brown, black-yellow and finally black. The "titanocene" solution was decanted onto rapidly stirred 1-phenyl-1,3-dibromopropane (XVII) (4.00 g, 14.4 mmol) in tetrahydrofuran (10 ml). The solvent was removed under reduced pressure from the resultant yellow-brown slurry and the residue extracted with light petroleum (5 x 30 ml). Removal of solvent under reduced pressure followed by flash microdistillation gave 1-phenyl-3-bromopropane, 0.20 g (7%), identified by comparison of its 1H n.m.r. spectrum with that of an authentic sample.

12b. Attempted debromination of 1,3-dibromo-2-phenylpropane using "titanocene"

Tetrahydrofuran (75 ml) was added to 2% sodium amalgam (0.25 g of sodium, 11 mmol) and $(C_5H_5)_2TiCl_2$ (0.928 g, 3.74 mmol). With vigorous shaking (15 min), the initial red solution turned brown, black-yellow and finally black. After decanting the "titanocene" solution off the sodium amalgam, 1,3-dibromo-2-phenylpropane (0.80 g, 2.88 mmol) was added slowly (10 min) with efficient stirring. The solvent was removed under reduced pressure and the residue extracted with light petroleum (3 x 20 ml). Removal of solvent under reduced pressure followed by flash microdistillation failed to give an identifiable product.

13. Attempted deiodination of di-iodomethane with "titanocene"

Tetrahydrofuran (70 ml) was added to 2% sodium amalgam (0.5 g of sodium, 22 mmol) and $(C_5H_5)_2TiCl_2$ (2.50 g, 10.1 mmol).

With vigorous shaking (30 min), the initial red solution turned brown, black-yellow and finally black. After decanting the "titanocene" solution off the sodium amalgam, di-iodomethane (2.45 g, 9.1 mmol) and cyclohexene (0.75 g, 9.1 mmol) were added. Stirring at 20 °C for 8 h and heating under reflux for 3 h did not produce any new compound as shown by gas chromatography analysis.

14. Debromination of diphenylacetylene dibromide using "titanocene"

Tetrahydrofuran (80 ml) was added to 2% sodium amalgam (0.25 g of sodium, 11 mmol) and $(C_5H_5)_2TiCl_2$ (0.74 g, 3.0 mmol). With vigorous shaking (20 min), the initial red solution turned brown, black-yellow and finally black. The "titanocene" solution was added to an efficiently stirred slurry of diphenylacetylene dibromide (0.50 g, 1.5 mmol) in tetrahydrofuran (50 ml). After stirring for 15 min, the solvent was removed under reduced pressure and the residue extracted with light petroleum (3 x 30 ml). Removal of the solvent under reduced pressure gave white needle crystals, which analysis by infra-red spectroscopy showed to be diphenylacetylene only, 2.24 g (85%); m.p. 58-59.5 °C (Lit.⁴¹: 60 °C).

15a. Debromination of cholesterol dibromide using "titanocene"

Tetrahydrofuran (70 ml) was added to 2% sodium amalgam (0.25 g of sodium, 11 mmol) and $(C_5H_5)_2TiCl_2$ (1.00 g, 4.03 mmol). Vigorous shaking (20 min) produced a black solution of "titanocene" which was decanted onto a rapidly stirred mixture of cholesterol dibromide (1.00 g, 1.83 mmol) and tetrahydrofuran (20 ml). After stirring for 5 min, the solvent

was removed under reduced pressure and the residue extracted with light petroleum (3 x 30 ml). The solvent was removed under reduced pressure, the residue dissolved in diethyl ether, washed with dilute hydrochloric acid (10 ml), 0.1 M sodium hydroxide (10 ml) and water (3 x 20 ml), and dried over magnesium sulphate. Filtration and removal of the solvent under reduced pressure gave a white solid which was crystallised from diethyl ether/methanol. The white needle crystals were identified as cholesterol by comparison of their ^1H n.m.r. spectrum, melting point and mass spectrum with those of an authentic sample. Yield 0.493 g (70%).

15b. Debromination of the dibromide of cholest-5-en-3-one using "titanocene"

Tetrahydrofuran (70 ml) was added to 2% sodium amalgam (0.25 g of sodium, 11 mmol) and $(\text{C}_5\text{H}_5)_2\text{TiCl}_2$ (1.00 g, 4.03 mmol). Vigorous shaking (20 min) produced a black solution of "titanocene" which was decanted onto a rapidly stirred mixture of cholest-5-en-3-one dibromide (1.00 g, 1.84 mmol) and tetrahydrofuran (20 ml). After stirring for 5 min, the solvent was removed under reduced pressure and the residue extracted with light petroleum (3 x 30 ml). The solvent was removed under reduced pressure to give a white solid which was recrystallised from diethyl ether/methanol. The white crystals produced an absorption in the ultra-violet spectrum at 238 nm which was identical with the absorption produced in the ultra-violet spectrum of an authentic sample of cholest-4-en-3-one.

16. Attempted deoxygenation of 2,2-diphenyloxetane with "titanocene"

Tetrahydrofuran (70 ml) was added to 2% sodium amalgam (0.5 g of sodium, 22 mmol) and $(C_5H_5)_2TiCl_2$ (1.18 g, 4.76 mmol). Vigorous shaking (15 min) produced a black solution of "titanocene" which was decanted onto an efficiently stirred solution of 2,2-diphenyloxetane (0.50 g, 2.38 mmol) in tetrahydrofuran (20 ml). After stirring for 16 h, the solvent was removed under reduced pressure and the residue extracted with light petroleum (3 x 20 ml). Removal of the solvent under reduced pressure gave an oil whose 1H n.m.r. spectrum contained no identifiable product.

17. Debromination of vic-dibromides using $[(C_5H_5)_2TiCl]_2.ZnCl_2$

Tetrahydrofuran (140 ml) was added to activated zinc dust (3.0 g, 46 mmol) and $(C_5H_5)_2TiCl_2$ (6.944 g, 28.00 mmol). With efficient stirring, the initial red solution turned emerald green. 5 ml (1.00 mmol based on titanium) of this mixture were filtered onto a rapidly stirred solution of 2,3-dibromohexane (0.222 g, 0.910 mmol) in tetrahydrofuran (5 ml). The resultant red solution was analysed by gas chromatography to determine the extent of debromination. A further 5 ml of the $[(C_5H_5)_2TiCl]_2.ZnCl_2$ solution was added to the reaction mixture producing a red crystalline precipitate; the extent of the reaction was again monitored by gas chromatography.

The above procedure was also carried out with 1,2-dibromohexane, styrene dibromide, cyclohexene dibromide and cyclo-octene dibromide. The results are given in Table V, p 28.

18. Isolation of the organometallic product from a $[(C_5H_5)_2TiCl]_2 \cdot ZnCl_2$ debromination

The red crystalline precipitate produced in Experiment 17 was collected by filtration; repeated concentration, cooling ($-30\text{ }^\circ\text{C}$) for 16 h and filtration gave two further crops of red crystals. The ^1H n.m.r. spectrum (60 MHz, $CDCl_3$) contained one singlet at δ 6.55 which was assigned to $(C_5H_5)_2TiCl_2$. (Lit.⁴⁰: $(C_5H_5)_2TiCl_2$ ($CDCl_3$) δ 6.57). This assignment was confirmed by a molecular ion isotope pattern in the mass spectrum corresponding to $(C_5H_5)_2TiCl_2$. The infra-red spectrum was consistent with the assignment. M.p. $285-7\text{ }^\circ\text{C}$ (Lit.⁴²: $287-91\text{ }^\circ\text{C}$). Yield of $(C_5H_5)_2TiCl_2$, 0.320 g (65%).

19. Debromination of vic-dibromides to alkenes by zinc dust. Comparison of titanium-catalysed system and uncatalysed system

Activated zinc dust (1.5 g, 23 mmol), $(C_5H_5)_2TiCl_2$ (0.368 g, 1.48 mmol), cyclo-octene dibromide (2.000 g, 7.40 mmol) and tetrahydrofuran (30 ml) were stirred for 30 min. The resultant emerald green mixture was filtered in air and the solvent removed under reduced pressure to give an orange oil which was extracted with light petroleum (5 x 20 ml). Removal of solvent under reduced pressure followed by flash microdistillation gave cyclo-octene, 0.60 g (74%) which was identified by comparison of its ^1H n.m.r. spectrum with that of an authentic sample.

The above procedure was also carried out with 1,2-dibromooctane, 1,2-dibromo-4-vinyl-cyclohexane (XXV), 4-vinyl-cyclohex-

1-ene tetrabromide (XXVII), *dl* 2,3-dibromodiethylsuccinate, *meso* 2,3-dibromodiethylsuccinate and cholesterol dibromide. The results are given in Table VI, p 31.

In a control experiment, activated zinc dust (0.75 g, 12 mmol), cyclo-octene dibromide (1.000 g, 3.70 mmol) and tetrahydrofuran (30 ml) were stirred for 30 min. The mixture was filtered in air and the solvent removed under reduced pressure. The ^1H n.m.r. spectrum of the residue indicated that the ratio of cyclo-octene dibromide to cyclo-octene was >95:5.

The above procedure was also carried out with 1,2-dibromooctane, 1,2-dibromo-4-vinyl-cyclohexane (XXV), *meso* 2,3-dibromodiethylsuccinate and cholesterol dibromide. The results are given in Table VI, p 31.

20. The stereochemical consequences of debromination of *dl* and *meso* 2,3-dibromobutanes using $[(\text{C}_5\text{H}_5)_2\text{TiCl}]_2 \cdot \text{ZnCl}_2$ and the $(\text{C}_5\text{H}_5)_2\text{TiCl}_2$ -catalysed zinc system

dl and *meso* 2,3-Dibromobutanes were debrominated using the titanium-catalysed zinc system described in Experiment 19; the gas in the reaction vessel was analysed after 1 h. *dl* 2,3-Dibromobutane was also debrominated using the titanium-catalysed zinc system at -20°C ; the gas in the reaction vessel was analysed after 3 h. Debromination of *dl* 2,3-dibromobutane was also performed using the procedure described in Experiment 17 at -20°C and the procedure was inverted by adding *dl* 2,3-dibromobutane to $[(\text{C}_5\text{H}_5)_2\text{TiCl}]_2 \cdot \text{ZnCl}_2$ at -20°C ; the gas in the reaction vessel was analysed after 3 h. The results are given in Table VII, p 32.

21. Addition of excess ZnCl_2 to $(\text{C}_5\text{H}_5)_2\text{TiBr}_2$

A mixture of $(\text{C}_5\text{H}_5)_2\text{TiBr}_2$ (0.100 g, 0.30 mmol), zinc chloride (0.2 g, 1.47 mmol) and tetrahydrofuran (10 ml) were stirred for 3 h. Repeated concentration, cooling ($-30\text{ }^\circ\text{C}$) for 16 h and filtration gave two crops of red crystals. The ^1H n.m.r. spectrum (60 MHz, CDCl_3) contained one singlet at δ 6.55 which was assigned to $(\text{C}_5\text{H}_5)_2\text{TiCl}_2$. (Lit.⁴⁰ : $(\text{C}_5\text{H}_5)_2\text{TiCl}_2$ (CDCl_3) δ 6.57). This assignment was confirmed by a molecular ion isotope pattern in the mass spectrum corresponding to $(\text{C}_5\text{H}_5)_2\text{TiCl}_2$. The infra-red spectrum was consistent with this assignment. M.p. $289\text{-}90\text{ }^\circ\text{C}$ (Lit.⁴² : $287\text{-}91\text{ }^\circ\text{C}$). Yield of $(\text{C}_5\text{H}_5)_2\text{TiCl}_2$, 0.048 g (65%).

22. Conversion of epoxides into alkenes using $[(\text{C}_5\text{H}_5)_2\text{TiCl}]_2 \cdot \text{ZnCl}_2$

Tetrahydrofuran (140 ml) was added to activated zinc dust (3.0 g, 46 mmol) and $(\text{C}_5\text{H}_5)_2\text{TiCl}_2$ (6.944 g, 28.00 mmol). With efficient stirring (15 min), the initial red solution turned emerald green. 5 ml (1.00 mmol based on titanium) of this solution were filtered onto a rapidly stirred solution of cyclohexene oxide (0.089 g, 0.91 mmol) in tetrahydrofuran (5 ml). The resultant orange solution was analysed by gas chromatography to determine the extent of de-epoxidation. A further 5 ml of the $[(\text{C}_5\text{H}_5)_2\text{TiCl}]_2 \cdot \text{ZnCl}_2$ solution was added to the reaction mixture producing an orange crystalline precipitate; the extent of the reaction was again monitored by gas chromatography.

The above procedure was also carried out with styrene oxide and 1,2-epoxyhexane. The results are given in Table VIII, p 34.

23. Isolation of the organometallic product from a $[(C_5H_5)_2TiCl]_2 \cdot ZnCl_2$ de-epoxidation

The orange crystalline precipitate produced in Experiment 22 was collected by filtration and shown to be $[(C_5H_5)_2TiCl]_2O$ (XXII), 0.180 g (41%); ν_{max} . (Nujol) 3 095w, 1 028m, 1 021m, 1 010m, 872m, 850sh, 838sh, 820s, 801sh, 762sh and 730br,s cm^{-1} ; 1H n.m.r. (60 MHz, $CDCl_3$) δ 6.3; m.p. 221 °C; m/z 377 (^{48}Ti , ^{35}Cl) $[M-C_5H_5]^+$ (Lit.³² ν_{max} . (mineral oil) 3 085, 1 024, 1 016, 1 006, 867sh, 845sh, 831sh, 810s, 795sh, 753sh and 720br,s cm^{-1} ; 1H n.m.r. $[(CD_3)_2CO]$ δ 6.35; m.p. 230 °C).

24. Bromination of 5,6-epoxycyclo-oct-1-ene (XXXVI)

Bromine (1.55 g, 9.7 mmol) in carbon tetrachloride (30 ml) was added (1 h) to a cooled (0 °C), stirred solution of 5,6-epoxycyclo-oct-1-ene (XXXVI) (1.00 g, 8.1 mmol) in carbon tetrachloride (30 ml). After stirring for a further hour, the solution was washed with 2% sodium thiosulphate (50 ml), water (3 x 20 ml) and dried over magnesium sulphate. Removal of solvent under reduced pressure gave a colourless oil, which was identified as a 1:1.22 mixture of *trans, trans*-isomers of 2,6-dibromo-9-oxabicyclo [3.3.1] nonane (XXXVII) and 2,5-dibromo-9-oxabicyclo [4.2.1] nonane (XXXVIII); ν_{max} . (Nujol) 1 052s and 1 038s (C-O-C) cm^{-1} ; 1H n.m.r. (300 MHz, $CDCl_3$) δ 4.63-3.99 (4H, m, $\text{>C} \begin{smallmatrix} \text{H} \\ \text{Br} \end{smallmatrix}$ and $\text{>C} \begin{smallmatrix} \text{O} \\ \text{H} \end{smallmatrix}$), 2.57-2.07 (8H, m, >CH_2); ^{13}C -(1H) n.m.r. (62.89 MHz, $CDCl_3$) δ 81.89, 69.65, 53.36, 50.29, 32.42, 31.09, 27.94 and 26.03; m/z 282, 284, 286 in ratio 1:2:1 $[M]^+$. Yield 1.94 g (85%). (Lit. data for 2,6-dibromo-9-oxabicyclo [3.3.1] nonane (XXXVII)^{33,43}: ν_{max} . (Vaseline) 1 050 (C-O-C) cm^{-1} ; 1H n.m.r. (CCl_4) δ 4.7-4.0 (4H, m, $\text{>C} \begin{smallmatrix} \text{H} \\ \text{Br} \end{smallmatrix}$ and $\text{>C} \begin{smallmatrix} \text{O} \\ \text{H} \end{smallmatrix}$),

2.4-1.8 (8H, m, $>CH_2$); $^{13}C-(^1H)$ n.m.r. (62.89 MHz, $CDCl_3$)
 δ 69.74, 50.30, 31.17 and 26.09. Lit. data for 2,5-dibromo-
 9-oxabicyclo [4.2.1] nonane (XXXVIII)³³: $^{13}C-(^1H)$ n.m.r.
 ($CDCl_3$) δ 81.99, 53.38, 32.48 and 27.98.)

25. Competition experiments on 1:1 mixtures of vic-dibromides and epoxides using one equivalent of $[(C_5H_5)_2TiCl_2]_2 \cdot ZnCl_2$; analysis by 1H n.m.r. spectroscopy

Tetrahydrofuran (50 ml) was added to activated zinc dust (1.0 g, 15 mmol) and $(C_5H_5)_2TiCl_2$ (1.000 g, 4.03 mmol). With efficient stirring (15 min), the initial red solution turned emerald green; this solution was filtered onto an efficiently stirred mixture of 1,2-dibromododecane (0.661 g, 2.02 mmol) and 1,2-epoxydodecane (0.371 g, 2.02 mmol) in tetrahydrofuran (50 ml) at $-78^\circ C$. After storing at $-20^\circ C$ for 3.5 h, the solvent was removed under reduced pressure and the residue extracted with light petroleum (3 x 30 ml). Removal of the solvent under reduced pressure gave a colourless liquid which was analysed by 1H n.m.r. spectroscopy and shown to be a $<0.005:4:1$ mixture of 1,2-epoxydodecane, 1,2-dibromododecane and dodec-1-ene.

The above procedure was also carried out with cyclo-octene dibromide and cyclo-octene oxide. The results are given in Table IX, p 42.

26. Competition experiment on cyclohexene oxide and cyclo-octene dibromide using one equivalent of $[(C_5H_5)_2TiCl_2]_2 \cdot ZnCl_2$

Tetrahydrofuran (20 ml) was added to activated zinc dust (1.0 g, 15 mmol) and $(C_5H_5)_2TiCl_2$ (1.210 g, 4.88 mmol). With

efficient stirring (15 min), the initial red solution turned emerald green; this solution was filtered onto an efficiently stirred mixture of cyclohexene oxide (0.239 g, 2.44 mmol), cyclo-octene dibromide (0.659 g, 2.44 mmol) and tetrahydrofuran (20 ml). The resultant red solution produced an orange precipitate after 15 min and the mixture was analysed for alkenes by gas chromatography. $[(C_5H_5)_2TiCl]_2 \cdot ZnCl_2$ had converted 65% of cyclohexene oxide to cyclohexene and 5% of cyclo-octene dibromide to cyclo-octene.

27. De-epoxidation of 1,2-epoxyhexane using two equivalents of $[(C_5H_5)_2TiCl]_2 \cdot ZnCl_2$

Tetrahydrofuran (30 ml) was added to activated zinc dust (2.0 g, 31 mmol) and $(C_5H_5)_2TiCl_2$ (2.956 g, 11.92 mmol). With efficient stirring (20 min), the initial red solution turned emerald green; this solution was filtered onto an efficiently stirred solution of 1,2-epoxyhexane (0.298 g, 2.98 mmol) in tetrahydrofuran (10 ml). The resultant mixture was analysed by gas chromatography; 65% of 1,2-epoxyhexane had been converted to hexene (separation of isomeric alkenes was not undertaken in this experiment).

28. Action of concentrated hydrochloric acid on $[(C_5H_5)_2TiCl]_2O$ (XXII)

$[(C_5H_5)_2TiCl]_2O$ (XXII) (0.080 g, 0.18 mmol), concentrated hydrochloric acid (0.5 ml) and dichloromethane (20 ml) were stirred for 20 min; the initial orange solution turned red after 3 min. After washing with water (2 x 10 ml), the solution was dried over magnesium sulphate. Filtration followed by concentration

and cooling (-30 °C) for 16 h gave two crops of red crystals. The ^1H n.m.r. spectrum (60 MHz, CDCl_3) contained one singlet at δ 6.55 which was assigned to $(\text{C}_5\text{H}_5)_2\text{TiCl}_2$. (Lit.⁴⁰ : $(\text{C}_5\text{H}_5)_2\text{TiCl}_2$ (CDCl_3) δ 6.57). This assignment was confirmed by a molecular ion isotope pattern in the mass spectrum corresponding to $(\text{C}_5\text{H}_5)_2\text{TiCl}_2$. The infra-red spectrum was consistent with this assignment. M.p. 287-9 °C (Lit.⁴² : 287-91 °C). Yield of $(\text{C}_5\text{H}_5)_2\text{TiCl}_2$ 0.069 g (77%).

29. Experiments to determine the selectivity of $[(\text{C}_5\text{H}_5)_2\text{TiCl}]_2 \cdot \text{ZnCl}_2$ towards derivatives of cyclohexene and hex-1-ene

Tetrahydrofuran (20 ml) was added to activated zinc dust (1.0 g, 15 mmol) and $(\text{C}_5\text{H}_5)_2\text{TiCl}_2$ (1.476 g, 5.95 mmol). With efficient stirring (15 min), the initial red solution turned emerald green; this solution was filtered onto an efficiently stirred mixture of cyclohexene oxide (0.292 g, 2.98 mmol), 1,2-dibromohexane (0.727 g, 2.98 mmol) and tetrahydrofuran (20 ml). The resultant solution was analysed for alkenes by gas chromatography after 3 min.

The above procedure was also carried out with cyclohexene oxide v. 1,2-epoxyhexane, cyclohexene dibromide v. 1,2-dibromohexane, cyclohexene dibromide v. 1,2-epoxyhexane. The results are given in Table X, p 44.

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