THE FORMATION AND APPLICATION TO ORGANIC SYNTHESIS OF TITANIUM COMPLEXES

by

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A thesis submitted for the degree of
MASTER OF PHILOSOPHY

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December 1990

ACKNOWLEDGEMENTS

I am sincerely grateful to my two supervisors; Dr Derek Pletcher and Dr Richard Whitby who have been more than helpful through out this project.

I would also like to acknowledge the Department of Chemistry for providing the finances to enable me to complete this degree.

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UNIVERSITY OF SOUTHAMPTON

ABSTRACT

FACULTY OF SCIENCE

CHEMISTRY

Master of Philosophy

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Three monocyclopentadienyl titanium dichloride alkoxide complexes have been prepared; $CpTiCl_2(O^iPr)$, $CpTiCl_2$(menthoxide), and $CpTiCl_2[OPh(^iPr)]$. Each was isolated as a crystalline solid and characterised by proton nmr spectroscopy.

The electrochemical behaviour of these three $CpTiCl_2(OR)$ complexes was investigated by cyclic voltammetry in THF/Bu_4NBF_4 solutions. The electrochemistry appeared dependant on concentration so experiments were carried out on solutions of different $CpTiCl_2(OR)$ concentration. The cyclic voltammograms obtained for each of the three $CpTiCl_2(OR)$ complexes were similar but the reduced titanium species varied in stability. A mechanism involving reactions of both the starting species and the major reduced species with trace amounts of water is proposed.

The preparation of monocyclopentadienyl titanium dichloride aminoalkoxide complexes where both the oxygen and the nitrogen of the aminoalcohol are co-ordinated to the metal, thereby creating a five co-ordinate titanium species, was investigated.

LIST OF ABBREVIATIONS & SYMBOLS

BSA	bis(trimethysilyl)acetamide
^{n}Bu	normal butyl
^{t}Bu	tertiary butyl
c	concentration of species
Cp	cyclopentadienyl
DMF	dimethylformamide
DMSO	dimethylsulphoxide
E	potential vs a reference electrode
e.e	enantiomeric excess
Ep	peak potential - superscripted a or c to denote anodic or cathodic process respectively (V)
ΔEp	peak separation (mV)
ESR	electron spin resonance
Et	ethyl
HMPA	hexamethlyphosphoramide
Ip	peak current density - superscripted a or c to denote anodic or cathodic process respectively (mAcm^{-2})
IR	infra-red
Me	methyl
nmr	nuclear magnetic resonance. Nmr signals are quoted as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad).
^{i}Pr	iso propyl
TMS	tetramethylsilane
ν	potential sweep rate (mVs^{-1})
τ	transition time (s)

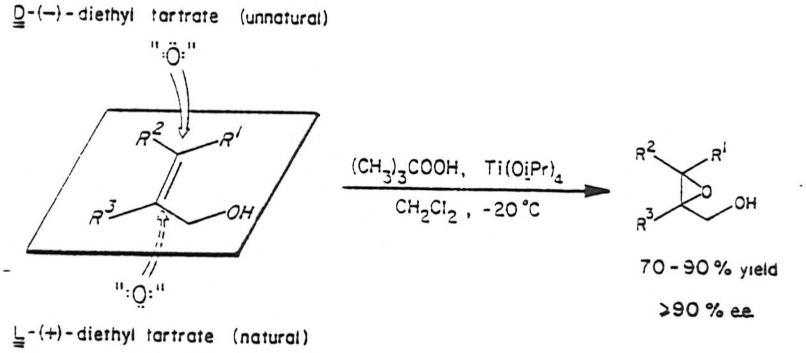
1. INTRODUCTION

1.1 The use of transition metals in asymmetric synthesis.

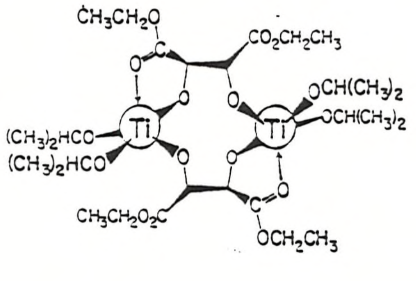
Asymmetric synthesis is an important part of synthetic organic chemistry. Commercially it is important to the agrochemical and pharmaceutical industries where perhaps only one enantiomer of a product is active. Also natural product synthesis relies heavily on the ability to develop convergent syntheses involving asymmetric compounds. Generally, in a convergent synthesis two compounds are made separately then brought together to form the product. If either or both of these are asymmmetric compounds then only one diastereomer of the product dominates. This saves on both the resolution of the product and chemical material since none is wasted on the unwanted isomer. Within the field of asymmetric synthesis perhaps the most desirable and most challenging aim is that of catalytic asymmetric synthesis. Here one chiral catalyst molecule can be used to create many chiral product molecules in a similar way to that of enzymes in biological systems. In industrial scale production of single enantiomers, catalytic processes often have a distinct economic advantage over stoichiometric ones. It is possibly cheaper to be able to use a relatively small amount of a compound, ie the catalyst, than to use stoichiometric amounts of all reagents and, of course, the catalyst may be recovered and used again.

Transition metal compounds have long been used for catalytic purposes because of the metal's ability to hold differing oxidation states. This includes the use of chiral organotransition metal complexes in catalytic asymmetric synthesis. One of the most familiar examples of this is the

Sharpless epoxidation where the reaction of an allylic alcohol with ^{t}Bu-hydroperoxide in the presence of Ti(O^{i}Pr)$_4$ and diethyltartrate forms an epoxy alcohol of high enantiomeric purity. This reaction was first introduced in 1980 using stoichiometric amounts of the substrate and reagents. It seemed that the epoxide oxygen added to one face of the olefinic substrate if (+)-diethyltartrate was used and to the other if (-)-diethyltartrate was used. This is shown in scheme I proposed by Katsuki and Sharpless(1a,b). The catalyst is believed to be a dimeric species; [Ti(O^{i}Pr)$_2$(tartrate)]$_2$ with a 10-membered ring structure, 1. Scheme II summarizes the proposed catalytic pathway and highlights the transfer of chirality from the Ti-tartrate complex to the allylic alcohol.(1b)



Scheme I



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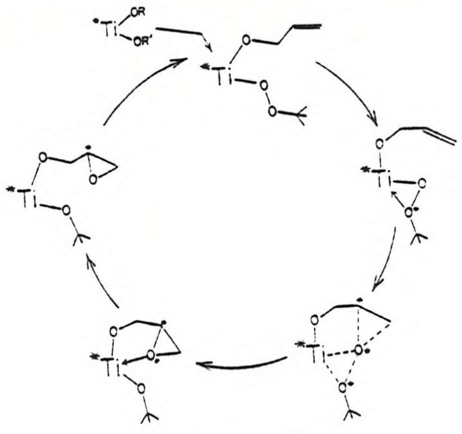


Scheme II

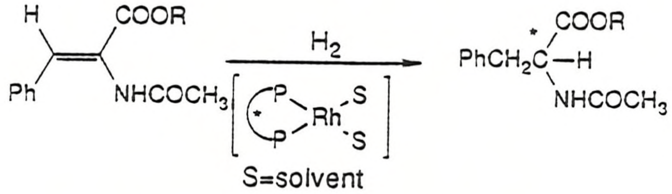
A variety of allylic alcohols were used, yields were in the range 70 - 87% and enantiomeric excesses were found to be ≥90%.

By 1987 Sharpless et al had investigated ways of making this asymmetric epoxidation catalytic. It was found that by the addition of molecular sieves (3 or 4Å) to the reaction mixture catalytic amounts (5 -10 mol %) of the diethyltartrate/$Ti(O^iPr)_4$ system could be used without significant loss in product yield and in some cases enantiomeric excesses (e.e.s)[†] of >98% were achieved[*]. The role of the molecular sieves is to protect the titanium catalyst form adventitious water in the reaction mixture(2). The mechanism of the reaction involves the in situ incorporation of a chiral ligand (the tartrate) into the co-ordination sphere of the metal, the peroxide also co-ordinates and asymmetry is induced into the substrate molecule.(3)

[†] The enantiomeric excess is the amount of one single enantiomer produced expressed as a percentage of the overall product yield.

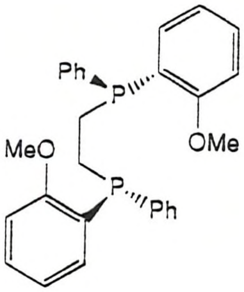
[*] Transubstituted allyl alcohols typically gave the highest e.e. The e.e.s achieved for cis-disubstituted allyl alcohols were the lowest being between 80 & 86%. Other systems investigated (unsym-disubstituted, trisubstituted and low molecular weight allyl alcohols) gave e.e.s in the range 90 - >98%. Although for the trisubstituted case better e.e.s were found with stoichiometric conditions.

Other notable asymmetric transformations using organotransition metal complexes include the use of rhodium complexes containing chiral diphosphine ligands in the asymmetric hydrogenation of prochiral olefinic substrates, a representation of which is given in Eq. 1(4). Enantiomeric excesses exceeding 95% can be obtained in such reactions.

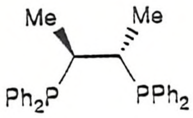


Eq. 1

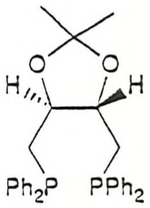
$\overset{\frown}{P^*P}$ depicts a chiral chelating diphosphine ligand such as DIPAMP(5) (2), CHIRAPHOS(6) (3), or DIOP(7) (4).



2. DIPAMP.



3. CHIRAPHOS



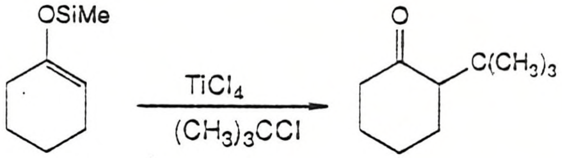
4. DIOP

These rhodium based systems seem to be limited to the preparation of amino acids. Similar ruthenium complexes have, however been developed and used for the enantioselective hydrogenation of allylic alcohols(8).

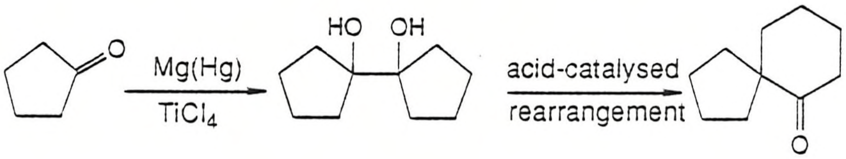
A publication by Ojima, Clos and Bastos(9) outlines recent advances in the use of transition metal complexes mentioned here along with many others for a variety of catalytic asymmetric reactions including carbon-carbon bond forming reactions.

1.2 Titanium in organic synthesis.

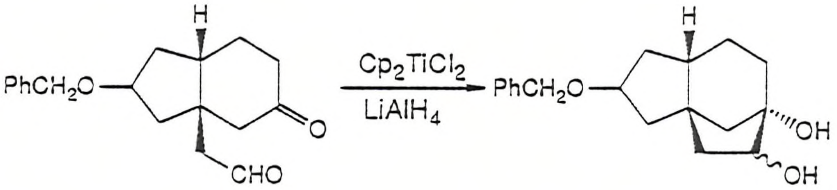
Titanium is a familiar reagent to organic synthesis. The epoxidation of allylic alcohols by the Ti(O^{i}Pr)$_4$/Diethyltartrate system has already been mentioned. Other reactions include the use of TiCl$_4$ as a Lewis acid with silyl enol ethers (Eq. 2)(10), the reductive coupling of aldehydes and ketones, both inter- and intramolecular, by low-valent titanium (Eq.s 3 & 4)(11.12,13) and the erythro selective aldol condensations using titanium enolates (Eq 5)(14).



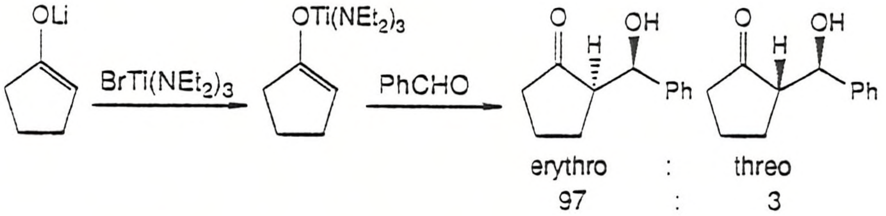
Eq 2



Eq 3

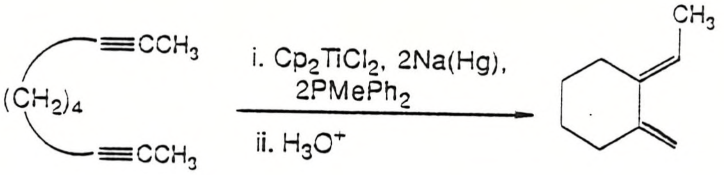


Eq 4



Eq 5

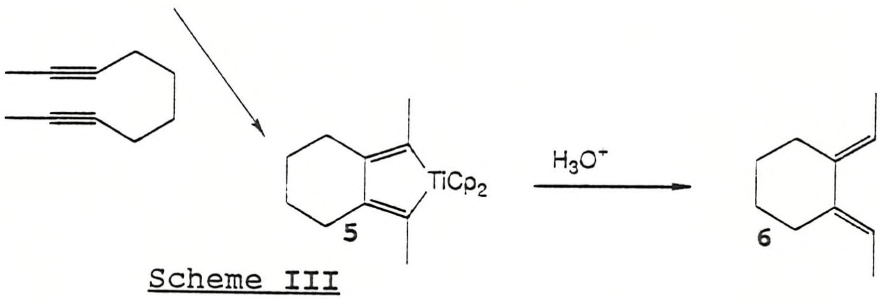
However, one of the most interesting areas of work with titanium, as far as this project is concerned, is the reaction of dicyclopentadienyltitanium dichloride (Cp$_2$TiCl$_2$) in the presence of a reductant and alklyphosphorus compounds, with unsaturated hydrocarbons such as enynes (Eq 6) and diynes.



Eq 6

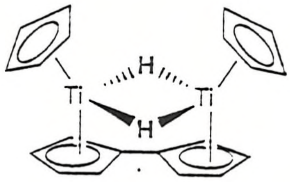
Parshall and co-workers(15) proposed that the intermediate in this type of reaction was a titanocycle. Reactions with diynes went through the intermediate titanocycle (**5**), which, on hydrolysis, gave the exocyclic diene (**6**), scheme **III**.

$Cp_2TiCl_2 + 2Na(Hg) \xrightarrow{PMePh_2} Cp_2Ti(PMePh_2)_2 + 2Na$



Scheme III

When reducing Cp_2TiCl_2 to the 'Cp_2Ti' moiety as occurs in this case, there is a danger of hydrogen abstraction giving a dimeric species (7)(16). This is why alkylphosphines are employed to stabilize the titanium(11) making the co-ordinatively saturated $Cp_2Ti(PR_3)_2$ complex which is formally a 18 electron complex. 18 electron complexes are unfavourable for titanium(17) as one of the orbitals has an energy unsuitable for ligand bonding, hence one of the phosphines is very labile. 16 electron complexes of titanium are more common.



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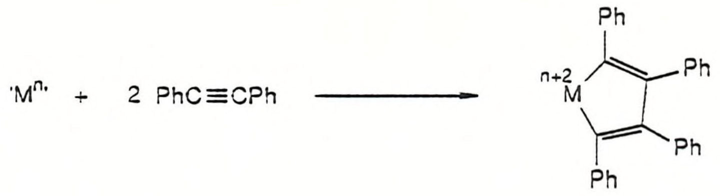
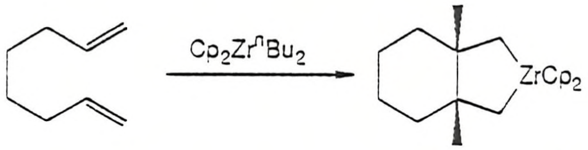
The diyne cyclisation shown in scheme **111** was developed from the known reductive dimerisation of diphenylacetylene with a variety of transition metal reagents (M) including Cp_2Ti (Eq 7)(18).

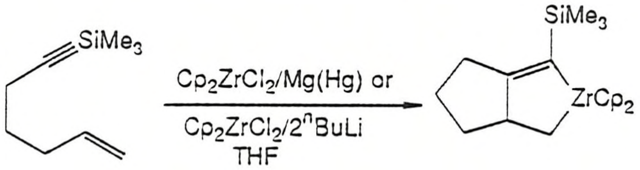


Eq 7

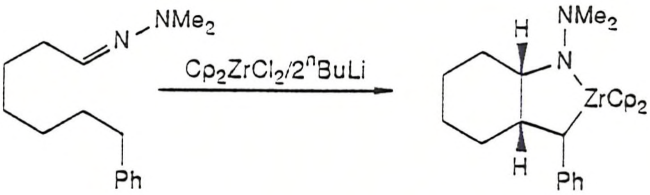
This reaction has been developed for both cyclopentadienyl titanium and zirconium reagents. Intramolecular coupling of 1,6- and 1,7-dienes (Eq 8)$^{(19)}$, 1,6- and 1,7-enynes (Eq 9)$^{(20,21)}$ and diynes$^{(20,21)}$ is achieved by reducing the Cp_2MCl_2 complex in the presence of suitable ligands to stabilize the 'Cp_2M' unit. Similar intramolecular couplings with heteroatom analogues, such as hydrazones, has also been developed (Eq 10)$^{(22)}$ as has the intramolecular coupling of ketones to alkenes and alkynes (Eqs 11 & 12) induced by the titanocene complex$^{(23)}$.



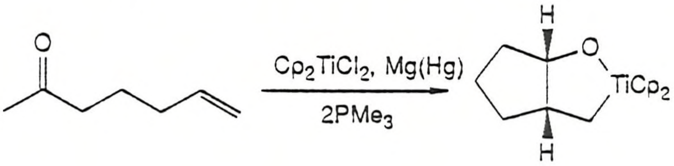
Eq 8



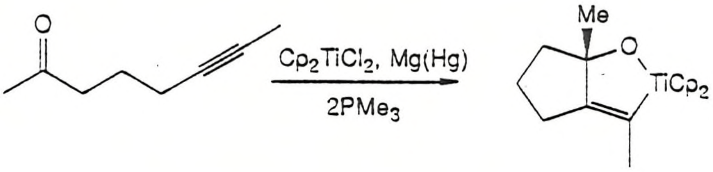
Eq 9



Eq 10



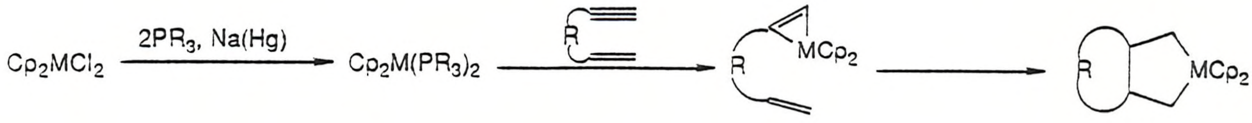
Eq 11



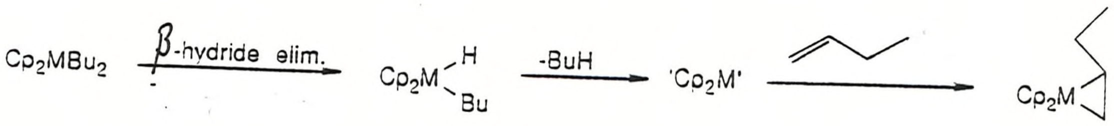
Eq 12

Negishi et al have shown that the combination of Cp_2ZrCl_2 with 2 molar equivalents of n-butyllithium provides a clean and convenient method for generating a zirconocene equivalent in situ(24). This can also be generated by a procedure involving Cp_2ZrCl_2 and amalgamated magnesium metal(25). As previously shown (Eq 6) a titanocene equivalent can be generated by a sodium amalgam in the presence of alkylphosphine ligands.

As discussed before, the mechanism proposed for these intramolecular couplings involves the reduction of the metal centre and the consequential stabilisation of the M(II) state by phosphine ligands giving a 18 electron complex. This then goes on to react with the chosen enyne yielding a metallocycle where the metal, M, is formally in the +4 oxidation state and its co-ordination sphere contains 16 electrons (scheme IV)(20) Where n-butylithium is used as the reducing agent the stabilisation of the M(II) state is by the alkene produced from the β-hydride elimination reaction that occurs when the butyl groups are co-ordinated to the metal centre (scheme V).(23)

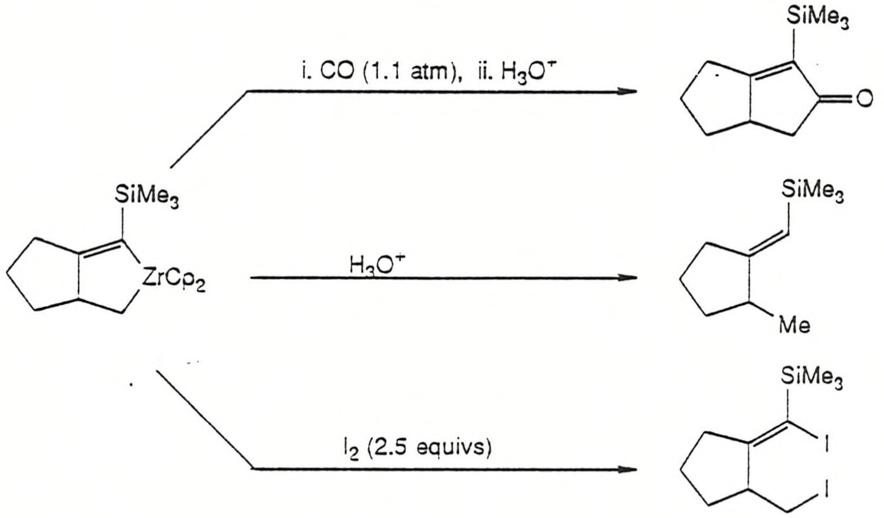


Scheme IV

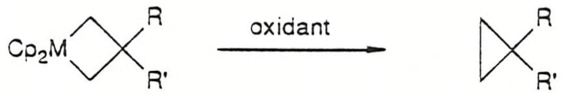


Scheme V

It is important to be able to elaborate the metallocycle into useful organic products. So far, reactions have been limited to hydrolysis, halogenation and reaction with carbon monoxide yielding bicyclic ketones, (scheme VI). Although in a recent paper Burk and co-workers(26) suggested that oxidative cleavage of titanium and zirconium metallocycles would provide new routes to hetero- and carbocycles. One of the examples reported was the oxidation by a variety of oxidising agents, including electrolysis, of titanacyclobutanes resulting in the quantitative production of the corresponding cyclopropanes (Eq 13).



Scheme VI

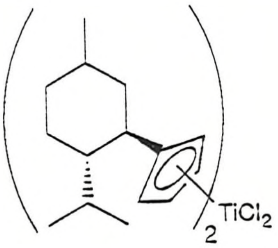


Eq 13

The failure of the metallocycle to react with carbonyl compounds or halides must be due, at least in part, to the stability of the Cp_2M unit within the metallocycle and/or steric hindrance around it. As a comparison alkyl-titanium trialkoxides react readily with aldehydes and ketones as do alkyl, aryl and alkenyl zirconium trialkoxides(27).

1.3 Chiral Complexes

By using chiral metal(11) complexes, as opposed to the symmmetric Cp_2M ones, asymmetric cyclisations should be able to be developed. Chiral cyclopentadiene ligands have been developed and used to make analogues of Cp_2TiCl_2. Dimenthylcyclopentadienyl titanium dichloride (**8**) is an example, this, with one equivalent of $NaH_2Al(OCH_2CH_2OMe)$ generates a hydrogenation catalyst. Asymmetric reduction of 2-phenyl-1-butene at room temperature under 1 atm of hydrogen yielded 2-phenylbutane; but only with 15% enantiomeric excess(28). Other chiral Cp_2TiCl_2 complexes include **9**(29), **10** and **11**. Both **10** and **11** have been employed in the asymmetric hydrogenation of 2-phenyl-1-butene giving e.e.s of 33%(30). and 68%(31) respectively, at room temperature.



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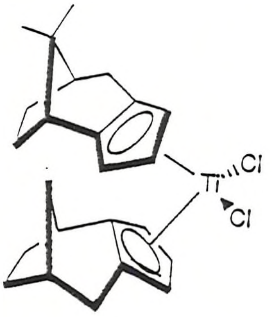

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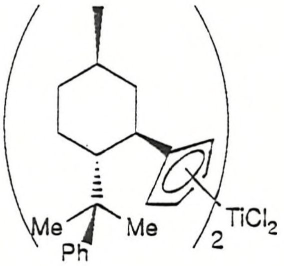

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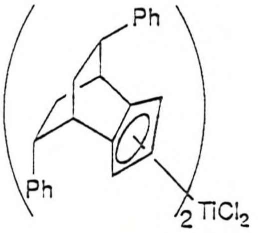

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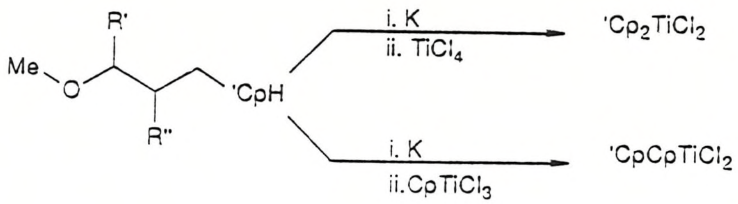
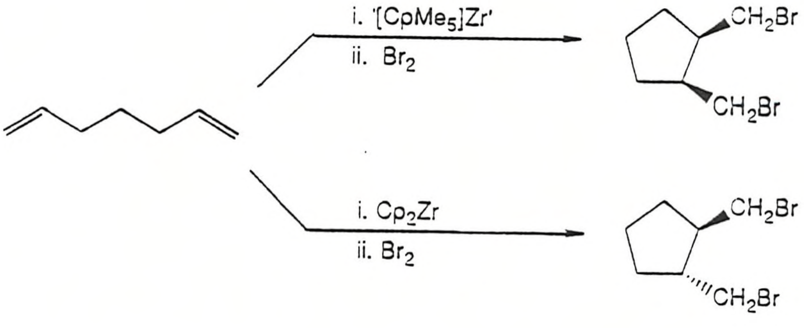
Huang et al reported the synthesis and crystal structures of a new family of chiral cyclopentadienyl titanium complexes which have chiral side chains containing an ethereal oxygen atom; $'Cp_2TiCl_2$ and $'CpCpTiCl_2$ where $'Cp= CH_3OCH(R')CH(R'')Cp$, scheme **VII**. The ethereal oxygen atom in the side chain does not co-ordinate to the metal atom in these cases(32).



Scheme VII

The centres of chirality in these complexes are distant from the metal centre so any asymmetric induction would be expected to be accomplished by steric effects.

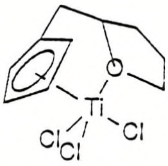
The use of monocyclopentadienyl complexes extends the scope for asymmetric reagents. The only example of the use of a low valent monocyclopentadienyl complex in a similar way to that shown for dicyclopentadienyl complexes is that of $[C_5(CH_3)_5]ZrCl_3$ with 1,6-heptadiene with sodium amalgam as the reducing agent. This was followed by bromination to yield cis-1,2-bis(bromomethyl)cyclopentane in 78% isolated yield (99% cis by GLC). The same diene on reaction with $Cp_2ZrCl_2/^nBuLi$ gave predominantly the trans dibromide (97%), scheme **VIII**$^{(19b)}$.



Scheme VIII

Interestingly the pentamethylcyclopentadienyl ligand is employed in this case. This could be due to the danger of H abstraction as mentioned previously for 'Cp$_2$Ti'. Another reason may be the increased electron density in the ring, due to the inductive effect of the methyl groups and since 'CpTiCl' is only an 10e$^-$ unit, this may help its stability.

Another monocyclopentadienyl titanium complex of particular interest is the tetrahydrofurfurylcyclopentadienyl titanium trichloride (**12**) reported by Qian and co-workers(33). They reported the synthesis of **12**, determined its crystal structure and found that the ethereal oxygen atom in the THF moiety chelates with the titanium atom. The same chelation does not occur in the diTHF-Cp analogue nor, as previously mentioned, in the dicyclopentadienyl complexes with an ethereal oxygen in the side chain. In the complex **12** because the oxygen takes part in the co-ordination, the electron count of the titanium is 14. This is also achieved in the complexes $CH_3OCH_2CH_2CpTiCl_3$ and (cyclo-$C_4H_7H_2$)$CpTiCl_3$(32). With the oxygen co-ordination, the chiral atom is brought nearer to the reaction centre of the organometallic molecule and this may lead to higher enantiomeric excesses.



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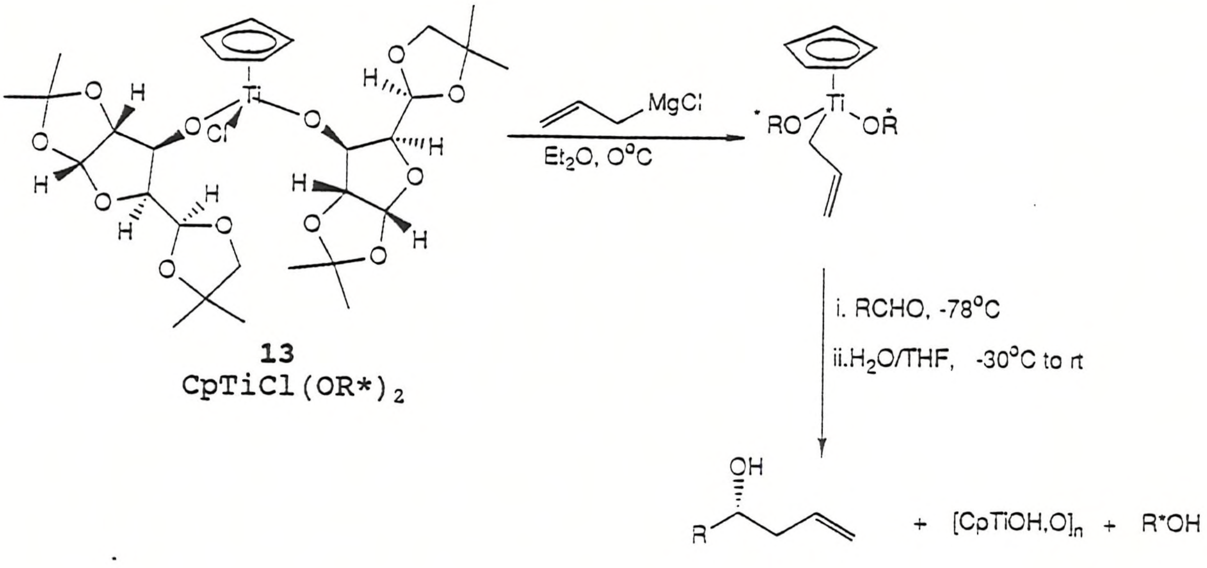
Riediker and Duthaler employed chiral alkoxy ligands into monocyclopentadienyl titanium complexes in the shape of glucose compounds. Complex **13** was prepared from $CpTiCl_3$, 1,2:5,6-isopropylidene-α-D-glucofuranose and triethylamine and then used in the enantioselective allylation of carbonyl compounds, scheme **IX.**(34)



13
CpTiCl(OR*)$_2$

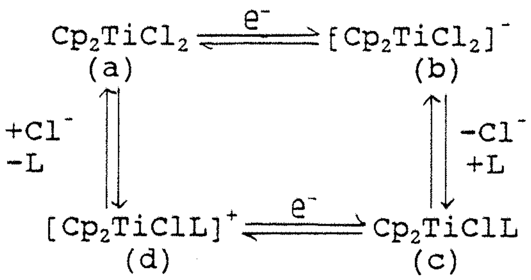
Scheme IX

1.4 Electrochemical Behaviour of Cyclopentadienyl Titanium Complexes.

Where the cyclopentadienyl titanium complexes, previously mentioned, are employed in organic synthesis the oxidation - reduction reactions probably constitute the most important stages. Hence the need to investigate such reactions and the necessity to establish a detailed account of the reduction process.

The reduction of Cp_2TiCl_2 and some derivatives has been studied extensively and a wealth of electrochemical data exists on this topic.(35-43) The interpretation of such data however, is the subject of some controversy.

Cp_2TiCl_2 shows three cathodic waves ($E_{\frac{1}{2}}$ = -0.80, -2.10 and -2.38V vs SCE). Two basic sequences have been proposed to account for the reduction reactions of cyclopentadienyl titanium compounds (schemes **X** and **XI**). The first (scheme **X**) describes the fast, but reversible loss of a chloride ion after electron uptake, this is then replaced by a neutral ligand (which can be a solvent molecule).(35)



Scheme X

In THF, with Bu_4NPF_6 as the supporting electrolyte, process a→b gives all the characteristics of a reversible system. However, in DMF, no reverse anodic peak is obtained unless a chloride salt is used as the supporting electrolyte. A new anodic peak at more positive potentials corresponding to the process c→d is seen in DMF with Bu_4NPF_6 and a coupled cathodic peak seen on the second sweep. When dimethylphenylphosphine is added to a solution of Cp_2TiCl_2 in THF, at slow sweep rates anodic waves for both b→a and c→d are observed. At increased sweep rates however, only the process c→d is observed. DMF binds more strongly to the metal than THF so the reaction c→b does not occur in the time scale of the experiment ~~of the experiment~~ and the only anodic wave seen is that for c→d. Dimethylphenylphosphine binds more strongly than THF, but not as strongly as DMF, so at slow sweep rates there is time for the reaction c→b to take place hence an anodic wave for b→a is seen along with one for c→d. Then at fast sweep rates c→b does not have time to occur and only one anodic wave, that of c→d, is observed.

These observations and the ESR studies of the product obtained after a one electron reduction of Cp_2TiCl_2 in THF (the ESR spectrum of this product was identical to that of chemically prepared Cp_2TiCl in the same solvent) led Mugnier et al(35) to conclude that a chloride ion is eliminated rapidly after the uptake of an electron by Cp_2TiCl_2. This is an opinion shared by a number of other researchers in this field$^{(36,37,38,39)}$ and seems to be supported by the electrochemistry of Cp_2TiCl. A solution of Cp_2TiCl in THF exhibits two cathodic waves, $E_{1/2}$=-2.12 and -2.42 V vs SCE, which are very similar to the second and third waves of Cp_2TiCl_2 and in the presence of Cl^- the oxidation of Cp_2TiCl leads to the formation of the dichloride$^{(40)}$.

Scheme **XI** was proposed by El Murr and Chaloyard$^{(41)}$. They too examined the electrochemical behaviour of Cp_2TiCl_2 in THF with Bu_4NBF_6 as the supporting electrolyte and observed three reduction waves. The first of these waves is highly reversible and the other two only slightly reversible becoming irreversible at slow scan rates (25 mVs^{-1}). At very slow scan rates (1 mVs^{-1}) the first wave still shows complete reversibility indicating that the one electron reduction of Cp_2TiCl_2 affords a stable radical anion; $[Cp_2TiCl_2]^-$. A cyclic voltammogram of $[Cp_2TiCl_2]$ in the presence of PMe_2Ph showed the original first cathodic wave had become irreversible and a new anodic wave had appeared at more positive potentials, scheme **XII**.

$$Cp_2TiCl_2 \overset{e^-}{\rightleftharpoons} [Cp_2TiCl_2]^-$$

$$\begin{tikzcd}
{[Cp_2TiCl_2]^-} \arrow[r, "e^-"] & {[Cp_2TiCl_2]^{2-}} \arrow[r, "e^-"] \arrow[d] & {[Cp_2TiCl_2]^{3-}} \\
 & {[Cp_2TiCl]^- + Cl^-} &
\end{tikzcd}$$

Scheme XI

$$Cp_2TiCl_2 + PMe_2Ph + e^- \rightleftharpoons [Cp_2TiCl_2(PMe_2Ph)]^-$$

Scheme **XII**

El Murr and Chaloyard also examined the Cp_2TiCl_2 system in DMF$^{(42)}$ and obtained identical cyclic voltammograms to those reported by Mugnier et al$^{(35)}$ when the concentration of Cp_2TiCl_2 was 2mM. An increase in concentration to 10mM produced a reversible system even at slow sweep rates (25 mVs^{-1}), Mugnier and co-workers saw no reversible system on their 2mM solution whatever the sweep rate (50 mVs^{-1} to 100 mVs^{-1}). No free chloride ion was detected by El Murr and Chaloyard until the potential of the second electron transfer system of Cp_2TiCl_2 was reached. They also claim that the ESR spectrum of the reduced species is that of the monoanion not Cp_2TiCl as previously mentioned. The discrepancies between the two sets of results is blamed, by El Murr and Chaloyard, on the low concentration of Cp_2TiCl_2 that Mugnier used and impurities in the DMF.

The reduction of Cp_2TiCl_2 under carbon monoxide is cited as evidence for $[Cp_2TiCl_2]^-$(43). $Cp_2TiCl(CO)$ cannot be prepared from $(Cp_2TiCl)_2$(44) and neither does CO react with the monomer, Cp_2TiCl.(45) However, under CO pressure, a drastic change in the cyclic voltammetry of Cp_2TiCl_2 in THF, with Bu_4NPF_6 as the supporting electrolyte, occurs. The second two, well known cathodic peaks disappear, the reversibility of the first decreases and two new cathodic peaks appear at about -1.7 and -2.8V (vs SCE). This indicates that a reaction with CO follows the addition of the first electron to Cp_2TiCL_2. Bulk electrolysis of Cp_2TiCl_2 under CO pressure performed at -1.8V (vs SCE) confirmed the formation of $Cp_2Ti(CO)_2$ and scheme **XIII** was proposed.(43)

$$Cp_2TiCl_2 + e^- \rightleftharpoons [Cp_2TiCl_2]^-$$
$$[Cp_2TiCl_2]^- + CO \rightleftharpoons [Cp_2Ti(CO)Cl_2]^-$$
$$[Cp_2Ti(CO)Cl_2]^- + e^- + CO \longrightarrow Cp_2Ti(CO)_2 + 2Cl^-$$

Scheme XIII

A more recent study(46) reported the identification by ESR of the species obtained upon reduction of Cp_2TiCl_2 in THF by both chemical and electrochemical methods. Cp_2TiCl_2 is reduced chemically to the dimer $(Cp_2TiCl)_2$, but in donor solvents, such as THF, the solvated monomer $Cp_2TiCl(THF)$, is present. Samuel and Vedel compared the ESR spectra of this solvated monomer with that of the product of the one electron electrochemical reduction of Cp_2TiCl_2 under the same conditions (solvent, temperature, concentration). They found that the isotopic spectra of the two compounds were practically the same, (g and hyperfine splitting values were the same for both), the only slight difference being in the bandwidths ($\Delta B(Cp_2TiCl_2)=2.0G$, $\Delta B(Cp_2TiCl(s))=4.2G$). In the frozen solution study, however, the two compounds gave identical spectra. This led to the conclusion that they were the same species. In other words, the electrochemical reduction yielded only the monohalide and not the radical anion. Samuel and Vedel concluded that the differences in the isotopic line shape were due to trace amounts of water in the THF, which cannot be removed by conventional chemical treatment. This conclusion arose from their discovery that the use of pre-electrolysed THF (to remove the trace amounts of water) produced identical ESR spectra for both species.

If it is the case that the $1e^-$ reduction of Cp_2TiCl_2 is followed by rapid loss of Cl^-, then the perfect reversibility (at all scan rates) of this reduction is not wholly explained. This perfect reversibility relies on the fact that those lost chloride ions are still available, at the re-oxidation potential, to be picked up to regenerate the starting material.

Other cyclopentadienyl titanium complexes have been studied. The electrochemical behaviour of $CpTiCl_3$ and $(\pi-(CH_3)_5C_5)TiCl_3$ has been reported by Gubin and Smirnova(38). Both complexes show three one-electron reduction waves, each one corresponding to the reduction of successive Ti-Cl bonds.

Chaloyard et al(47) looked at alkyl and aryloxy cyclopentadienyl complexes: Cp_2TiR_2, $Cp_2Ti(OAr)_2$, $Cp_2Ti(OSiR_3)_2$, $CpTi(OAr)_3$ and $CpTi(OSiR_3)_3$. For these complexes the first electron transfer reaction leads to a d^1 Ti^{111} radical anion which is chemically unstable and rearranges giving the corresponding neutral monocyclopentadienyl Ti^{111} complex, scheme **XIV**.

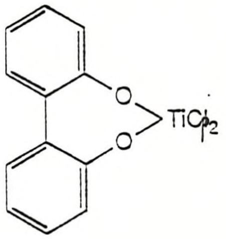
$$[Cp_2TiX_2]^{\cdot -} \longrightarrow CpTiX_2 + Cp^-$$

$$[CpTiX_3]^{\cdot -} \longrightarrow CpTiX_2 + X^-$$

X = aryl or aryloxy

Scheme XIV

Reduction of the same compounds by sodium naphthalenide in THF (in the presence of the supporting electrolyte for a fair comparison) produced solutions which gave the same ESR spectral and electrochemical behaviour. This indicates the formation of the same final products. Chemical reduction of complex **14** however, generated the corresponding anion which was stable enough to be detected by ESR techniques, but did eventually rearrange to the neutral monocyclopentadienyl species. Cyclic voltammetry on **14** showed an anodic peak at -0.2V (vs SCE) characteristic of the cyclopentadienyl anion indicating that the rearrangement shown in scheme **XIV** is correct.



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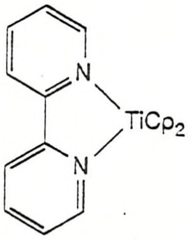


15

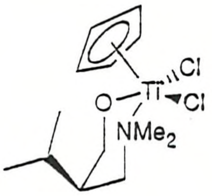
Cp_2Tibipy, **15** (bipy = 2,2'-bipyridine), formally a Ti^{II} species, has been reported to exhibit three reversible one-electron reduction steps and one oxidation step on the cyclic voltammogram time scale(48). The stability of this complex towards electron addition and abstraction is surprising given the reactive nature of the species (it is very air- and moisture-sensitive). Whether the first reduction is metal or ligand centred is not known, the oxidation of **15** is thought to generate free bipyridine.

1.5 Project Aims.

As explained earlier the chiral titanium complexes that have been prepared only induce asymmetry in their reactions by steric effects. High levels of chiral induction are more likely to be achieved when the metal centre itself is chiral and there is both steric and electronic influence. The types of chiral complex which will be most effective in this remains to be discovered.

This project concentrates on the synthesis of monocyclopentadienyl titanium complexes starting with the introduction of alkoxy ligands into the co-ordination sphere of the metal then moving on to amino alcohols.

In chiral amino alcohol monocyclopentadienyl titanium complexes such as **16** and **17** the Cp group will provide facial selectivity and the amino alcohol both steric and electronic asymmetry. The configuration shown for such complexes is only speculation. It is thought that the nitrogen will co-ordinate to the titanium centre since without it, the electron count is only 12 and co-ordination of the nitrogen is intramolecular leading to a more stable 14 electron complex.



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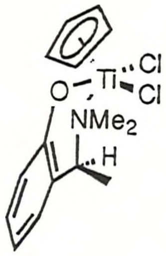

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Since the use of these complexes in organic synthesis relies on their oxidation and reduction, their behaviour under oxidising and reducing conditions needs to be investigated. The proposal was to do this by carrying out cyclic voltammetry on their solutions offering one approach to investigating the chemistry of the active Ti species.

In addition, electrolysis of these complexes may be one way in which the active Ti^{II} species can be generated, ie electrochemical, rather than chemical reduction of a Ti^{IV} species.

2. EXPERIMENTAL SECTION

2.1 Organic Chemistry.

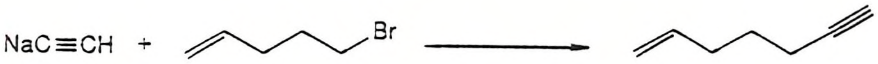
Unless otherwise stated all experiments were carried out in a fume cupboard under an argon atmosphere. All chemicals were supplied by Aldrich except o-dimethylaminomethylphenol which was obtained from Apin Chemicals Ltd. Diethylether and benzene were distilled from Na/benzophenone as was hexane after drying with conc.H_2SO_4 (neutralized with Na_2CO_3) and $MgSO_4$. Dichloromethane and xylene were distilled from CaH_2.

Nmr spectra were obtained from either a JOEL FX90 or a JOEL GX270 FT nmr spectrometer and IR spectra from a Perkin-Elmer 1600 FT-IR spectrophotometer.

5-Bromo-1-pentene.

5-Bromo-1-pentene was prepared in 45% yield by heating 1,5-dibromopentane (115.02 g, 500 mmol) to 170°C then adding HMPA (100 ml) dropwise with further heating to 195°C until all the product distilled over. The product was redistilled (b.p. 127-129°C).

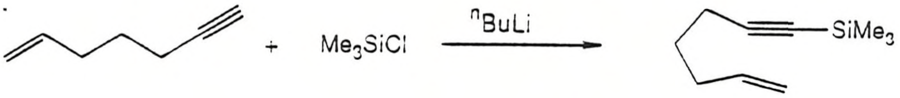
1-hepten-6-yne.(49)



Sodium acetylide was prepared first by adding sodium (10 g, 0.4 mol) to liquid ammonia (500 ml) with $Fe(NO_3)_3.xH_2O$ (200 mg) and allowing to stir for ½ hr. Then to this suspension of $NaNH_2$ in liquid ammonia triphenylmethane (0.25 g) was added and a red colour appeared. Acetylene was introduced with efficient stirring until this red colour disappeared. To this solution of sodium acetylide DMSO (100 ml) was carefully added then the 1-bromopent-4-ene added dropwise. The reaction mixture was left stirring for 1½ hrs then poured carefully onto 500 ml of crushed ice. The product was extracted into pentane, this washed with dil. HCl acid and left drying over $MgSO_4$ overnight. After filtering, the pentane was distilled off leaving the crude product which was also distilled, giving a clear liquid (17 g) - 60% yield.

^{1}Hnmr (90 MHz, $CDCl_3$) 5.6-6.1(1H, m), 5.0-5.3(2H, m), 1.0-2.5(7H, m).

7-(Trimethylsilyl)-1-hepten-6-yne.(20)



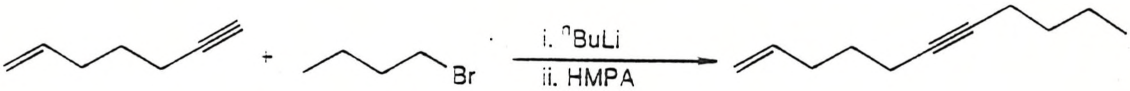
1-hepten-6-yne (3.71 g, 39.5 mmol) and dry distilled THF (80 ml) were placed in a flask under an Ar atmosphere and cooled to about -20°C. ⁿBuLi (1 equiv) was added to the flask then (trimethylsilyl)chloride (1.2 equiv) added slowly. The reaction mixture was quenched with $NaHCO_3$ solution and the product extracted into pentane, this then washed twice with water and once with NaCl solution. After drying with $MgSO_4$ the pentane was distilled off and the product Kugelrohr distilled. 7-(trimethylsilyl)-1-hepten-6-yne was obtained in 58% yield

IR(neat) 2176s, 1642m,1249s.

^{1}Hnmr (360MHz, $CDCl_3$) 5.7-5.9(1H, m), 5.0-5.1(2H, m), 2.2-2.3(2H, m), 2.1-2.2(2H, m), 1.6-1.7(2H, m), 0.03-0.07(9H, m).

^{13}Cnmr (90MHz, $CDCl_3$) 138d, 115t, 34t, 29t, 20t, 0.0q.

1-undecene-6-yne.



ⁿButyllithium (1.6 mmol) was added to a solution of 1-hepten-6-yne (1.52 g, 1.6 mmol) in THF at -20°C and left stirring for 30 mins. 1-Bromobutane (1 equiv.) was added with HMPA (2 equivs.)

and the reaction mixture left stirring for 2½ hours at 0°C, then poured into cold water and the product extracted into pentane. The pentane washed well with water, dried over $MgSO_4$ then distilled off leaving 1.5 g of product (a clear liquid). Thus giving a 63% yield.

Bicyclisation of enynes using Cp_2ZrCl_2 .(20)

a). Using Cp_2ZrCl_2, ^nBuLi.

Cp_2ZrCl_2 (0.65 g, 2.2 mmol) was placed in a 25 ml R.B. flask with a side arm tap with dry, distilled THF (7 ml). ^nBuLi (2 equiv) was added dropwise and the contents of the flask stirred for 1hr at -78°C. The (trimethylsilyl)heptenyne (1 equiv) was then added and the mixture was allowed to warm up to room temperature slowly and stirred for 6 hours. The mixture was then quenched with 2M HCl and extracted with pentane. The pentane then washed with $NaHCO_3$ and NaCl and dried over $MgSO_4$. The pentane was distilled off and the product run through a column (eluant: pet. ether 40-60) then kugelrohr distilled to afford 0.09g (25% yield) of 1-[(trimethylsilyl)methylene]-2-methlycyclopentane, **18**.

b). Using Cp_2ZrCl_2, Mg, $HgCl_2$.

Using the same aparatus as the previous experiment, ground Mg (0.35 g, 14.4 mmol) was placed in the flask and dried by evacuation. THF (3 ml) and a THF solution (1.35mM) of $HgCl_2$ (1.1 ml, 1.5 mmol) were added to the flask and left stirring for ½hr. After allowing the contents of the flask to settle the THF was removed and the flask evacuated to dry the grey solid left. Cp_2ZrCl_2 (0.5 g, 1.7 mmol) was added, then the (trimethylsilyl)heptenyne (0.25g, 1.5 mmol) in THF with the flask in an ice bath. The reaction mixture was left stirring overnight. The mixture was quenched with 2M HCl then extracted with pentane. The pentane washed with $NaHCO_3$ and NaCl then dried over $MgSO_4$ and the pentane removed by distillation. The product was run through a column as before and kugelrohr distilled to give 0.04g (15%

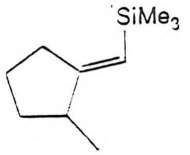
yield) of **18**.

IR(neat) 1621m, 1247s.

^{1}Hnmr (360MHz, $CDCl_3$) 0.1(9H,s),1.1(3H,d,J 6.6Hz),1.2-2.5(7H,m),5.25 (1H,dt,J 2.38Hz).

^{13}Cnmr (90MHz, $CDCl_3$) 0.0, 14.5, 19.0, 24.5, 30.0, 33.0, 35.0, 42.0, 116, 168.

This experiment was also carried out once using $ZrCl_4$ as a replacement for Cp_2ZrCl_2 and another time using Cp_2TiCl_2 neither of which gave the desired product.



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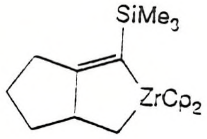

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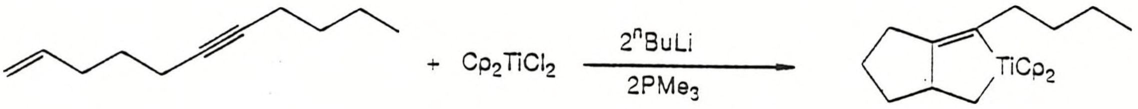
The reaction with ^{n}BuLi, Cp_2ZrCl_2 and the trimethylsilylheptenyne was carried out again, this time isolating the metallocycle; 3,3-bis(cyclopentadienyl)-2-(trimethylsilyl)-3-zirconabicyclo-[3.3.0]oct-1-ene, **19**. Two nmr samples were taken, one in $CDCl_3$ and one in D_6-benzene. In $CDCl_3$ the product appears to revert back to starting material.

^{1}Hnmr (270MHz, C_6D_6) 0.15(9H,s),1.0-2.5(9H,m),5.8(5H,s),5.9(5H,s).

^{13}Cnmr (90MHz,C_6D_6) 1.4, 20.7, 33.6, 38.6, 41.4, 42.8, 109.2, 110.7, 152.1, 186.4.

3,3-bis(cyclopentadienyl)-2-^{n}butyl-3-titanabicyclo[3.3.0]-oct-1-ene (20).



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Titanocene dichloride (0.25 g, 1 mmol) was dissolved in 5 ml THF and cooled to -70°C. To this 2 equivalents of ^nBuLi were carefully added followed by 2 equivalents of trimethylphosphine and the reaction mixture left stirring for 1 hr at room temperature. 1-undecene-6-yne (0.15 g, 1 mmol) was then added with further stirring for 1 hr. The solvent was then removed in vacuo and the product extracted into hexane, this solution removed to another flask and the hexane vacuum distilled off giving a dark red solid in 91% yield (0.3 g).

^1H nmr (270MHz, $CDCl_3$) 5.5 (5H, s), 5.6 (5H, s).

Monocyclopentadienyltitanium Trichloride, $CpTiCl_3$.(50)

To Cp_2TiCl_2 (12g, 0.0.48 mol) in xylene (90 ml), $TiCl_4$ (14.5 ml, 0.136 mol) was added and the mixture refluxed under an argon atmosphere for 2½ hours. The mixture was then allowed to cool down to room temperature and left overnight to allow yellow crystals to form. The xylene was then decanted off with a constant stream of argon going through the flask. The crystals were washed with a further 20 ml of xylene then with hexane (4 x 20 ml) and then dried under vacuum. Benzene (60 ml) was added and heated to boiling to dissolve all the solid, decolourizing charcoal was added and the mixture filtered hot. $CpTiCl_3$ (6.9g) recrystallized from the bright yellow filtrate giving a 65% yield.

^1H nmr (90 MHz, $CDCl_3$) 7.0 (5H, s).
(c.f. Cp_2TiCl_2 ^1H nmr (90 MHz, $CDCl_3$) 6.5(5H, s).)

MonoctclopentadienyltitaniumDichloride(2,6-di-isopropyl)-phenoxide, $CpTiCl_2[OPh(^iPr)_2]$ (21).

$CpTiCl_3$ (0.24 g, 1.1 mmol) was dissolved in diethylether (12 ml), 2,6-diisopropylphenol, $[(CH_3)CH]_2C_6H_3OH$, was added and the mixture stirred for 2 mins. Triethylamine (1.1 mmol) as a solution in ether was added dropwise and the reaction left stirring overnight, then filtered and the residue ($Et_3N.HCl$) washed with ether (2 x 5 ml). The washings added to the filtrate and the solvent removed in vacuo leaving a dark orange solid. The product was recrystallized from hexane giving the title compound (orange crystals) in 72% yield.

^1H nmr (270 MHz, $CDCl_3$) 7.0-7.2 (3H, m), 6.65 (5H, s), 3.21-3.28 (2H, septet, J=6.7 Hz), 1.22-1.25 (6H, d, J=6.7 Hz).

MonocyclopentadienyltitaniumDichlorideMenthoxide,
$CpTiCl_2[OC_6H_8(CH_3).CH(CH_3)_2]$ (22).

$CpTiCl_3$ (0.22 g, 1 mmol) and menthol (0.156 g, 1 mmol) were dissolved in diethylether (12 ml), triethylamine (1.1 mmol) as a solution in ether was added dropwise. The reaction mixture was left stirring overnight, filtered and the residue washed with ether (3 x 5 ml). The washings were added to the filtrate and the ether removed in vacuo. The resultant yellow solid was dissolved in boiling hexane (8 ml), the solution cooled in ice and fine yellow crystals came out. A second crop was obtained by concentrating the solution down by evacuation giving an overall yield of 50%.

The title compound was also prepared from the silyl ether of menthol; to a solution of menthol (1.56 g, 0.01 mol) in acetonitrile (16 ml) bis(trimethylsilyl)acetamide, BSA (3ml) was added and the mixture refluxed at 90°C overnight. After being allowed to cool down to room temperature the solvent was removed in vacuo, the remaining oil was kugelrohr distilled giving a quantiatve yield of (trimethylsilyl)menthoxy ether.

^1H nmr (270 MHz, $CDCl_3$) 0.85(6H, d), 0.7(3H, d), 0.2(9H, s)

IR (film) 1250(s), 842(s), 750(m) cm^{-1}.

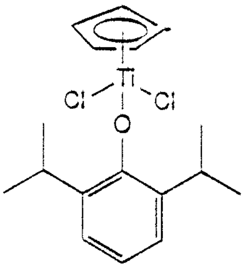
The (trimethylsilyl)menthoxyether (0.41 g, 1.8 mmol) and CH_2Cl_2 (5 ml) were mixed, then a solution of $CpTiCl_3$ (0.40 g, 1.8 mmol) in CH_2Cl_2 (7 ml) was added and left stirring overnight. The solvent was removed in vacuo, hexane (7 ml) added to the resultant yellow solid, heated to boiling and filtered hot. The filtrate was allowed to cool to afford fine yellow crystals of the title compound in 60% yield.

^1H nmr (90 MHz, $CDCl_3$) 6.7(5H, s), 4.4-4.7(1H, m), 1.3-2.5(8H, m), 0.95-1.1(6H, d), 0.90(3H, d).

MonocyclopentadienyltitaniumDichlorideIsopropoxide, $CpTiCl_2[OCH(CH_3)_2]$ (23).

$CpTiCl_3$ (0.22 g, 1 mmol) was dissolved in diethylether (12 ml), isopropanol (0.075 ml, 1 mmol) added and the mixture stirred for 2 mins. Triethylamine (1.1 mmol) as a solution in ether was added dropwise and the reaction mixture left stirring overnight, then filtered and the residue washed with ether (2 x 5 ml). The washings added to the filtrate and the solvent removed in vacuo leaving a yellow solid. To this, hexane (8 ml) was added and heated to boiling, then left overnight to give fine yellow crystals in 50% yield.

^1H nmr (270 MHz, $CDCl_3$) 6.7 (5H, s), 4.8-5.0 (1H, septet), 1.3-1.4 (6H, d).



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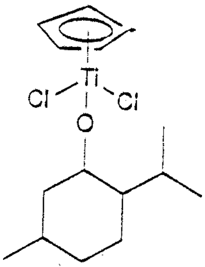

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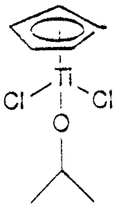

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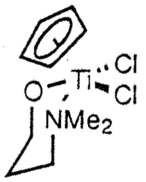
MonocyclopentadienyltitaniumDichloride(3-dimethyl-1-propoxide), $CpTiCl_2[O(CH_2)_3NMe_2]$ (24).



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Attempts at making this compound involved three different methods. In the first attempt the sodium salt of the aminoalcohol was added to a solution of $CpTiCl_3$ in THF, this was unsuccessful. In the second attempt triethylamine was employed with the aminoalcohol in Et_2O as for the alcohols:

$CpTiCl_3$ (0.22 g, 1 mmol) was dissolved in ether (12 ml), the 3-dimethylamino-1-propanol was added. The reaction stirred for 2 mins before triethylamine was added dropwise and the reaction mixture left stirring overnight. The mixture was then filtered and the residue washed with ether (3 x 5 ml).

Variations of the above procedure included adding the triethylamine before the aminoalcohol and leaving the reaction stirring for only 2 hrs. Proton nmr spectra were taken on the products from all the reactions, none of them strongly indicated a single product and often the resolution was poor. The data here represents the best resolved spectrum.

^1H nmr (270 MHz, $CDCl_3$) 6.5-6.55 (<5H, s), 4.5-4.8 (2H, 3t, J=6,6,6 Hz), 2.62-2.72 (2H, t, J=7 Hz), 2.3-2.5 (6H, 3s), 1.85-1.95 (2H, quintet).

^{13}C nmr (270 MHz, $CDCl_3$) 117.6 (s), 116.7 (s), 77.9 (t), 55.7 (t), 44.6 (q), 30.2 (t).

Thirdly the silylether of the aminoalcohol was prepared and used with a dichloromethane solution of $CpTiCl_3$:

To a mixture of 3-dimethylamino-1-propanol (2 ml, 0.17 mol) in acetonitrile (17 ml) bis(trimethylsilyl)acetamide (3.46 ml, 0.014 mol) was added and refluxed overnight. The solvent was removed in vacuo and the resultant oil run down a column (packing material - basic alumina grade 3, eluant - ether : petrol (bp 40-60°C), 3:7). The fractions were monitored by t.l.c. (I_2 staining), after removing the solvent 1.63 g (66% yield) of the silylether was recovered.

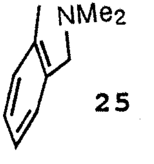
^{1}H nmr (270 MHz, $CDCl_3$) 3.6(2H, t), 2.3(2H,t), 2.2(6H, s), 1.7(2H, quintet), 0.1(9H, s).

^{13}C nmr (270 MHz, $CDCl_3$) 61.1, 56.6, 45.7, 31.0, -0.3.

$CpTiCl_3$ (0.22 g, 1 mmol) was dissolved in CH_2Cl_2 (5 ml) then (trimethylsilyl)-3-dimethylamino-1-propylether (0.18 g, 1.03 mmol) was added with a further 2 ml CH_2Cl_2. The mixture was left stirring for 4 hours, the solvent removed in vacuo leaving a thick orange oil which did not dissolve in boiling hexane.

^{1}H nmr (270 MHz, $CDCl_3$) 6.7(5H, s), 4.8(2H, br), 3.2(2H, m), 2.8(6H, d), 2.2(2H, br).

MonocyclopentadienyltitaniumDichloride(Dimethylaminomethylphenoxide), $CpTiCl_2[OPh(CH_2NMe_2)]$ (25).



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Attempts to prepare this compound involved both the triethylamine and silylether methods.

To a solution of $CpTiCl_3$ (0.25 g, 1.14 mmol) and o-dimethylaminomethylphenol (0.17 g,1,14 mmol) in Et_2O (24 ml) triethylamine (2.5 ml of 0.5 M in Et_2O, 1.25 mmol) was added dropwise. A precipitate was seen immediatly, and the yellow solution darkened a little. The mixture was left stirring overnight, filtered and the residue washed with Et_2O (2 x 10 ml). The Et_2O was removed in vacuo leaving a yellow solid and a thick orange oil. This was all redissolved in Et_2O and a sample taken for proton nmr analysis.

^1H nmr (90 MHz, $CDCl_3$) 6.5-7.5 (9H, m), 3.8-4.1 (2H, br m), 2.5 (6H, s). (Poorly resolved spectrum).

(Trimethylsilyl)-o-dimethylaminomethylphenyl ether, was prepared by adding BSA (1.42 ml, 6.1 mmol) to dimethylamino-methylphenol (0.91 g, 6.06 mmol) in acetonitrile (10 ml) and refluxed for 3½ hours. The solvent was removed in vacuo and the product kugelrohr distilled.

^1H nmr (270 MHz, $CDCl_3$) 6.7-7.3(4H, m), 3.2(2H, s), 2.2(6H, s), 0.2(9H, s).

To a solution of $CpTiCl_3$ (0.22 g, 1 mmol) in CH_2Cl_2 (10 ml) the silylether (0.25 g, 1mmol), was added and the mixture left stirring overnight. A thick orange oil was left after removal of the solvent.

^1H (270 MHz, $CDCl_3$) 6.8-7.4(4H, m), 6.6(5H, s), 4.1-4.2(2H, 2d), 2.6-2.7(6H, 2d).

2.2 ELECTROCHEMISTRY.

Cyclic voltammetry was carried out on THF solutions of Cp_2TiCl_2, $CpTiCl_3$, $CpTiCl_2(O^iPr)$, $CpTiCl_2$(menthoxide) and $CpTiCl_2[OPh(^iPr)_2]$ in a three electrode, two compartment cell (fig. 2.2a). The secondary electrode was a platinum wire loop and the reference electrode placed within a Luggin capillary whose tip was positioned adjacent to the surface of the working electrode which was a glassy carbon disc (area = 0.07 cm^2). Because organo-titanium complexes are known to be unstable in moist conditions experiments were carried out inside a glove box (argon atmosphere) as an extra precaution. The THF was distilled from Na/benzophenone and stored over molecular seives before use, the supporting electrolyte having been previously dissolved in it. The supporting electrolyte in each case was tetrabutyl-ammoniumtetrafluoroborate (Bu_4NBF_4) prepared by neutralising a concentrated solution of Bu_4NHSO_4 with NaOH then adding an equimolar amount of $NaBF_4$. The mixture was then filtered, the residue (Bu_4NBF_4) recrystallized from aqueous ethanol and the crystals dried in a vacuum oven.

Cyclic voltammograms at a variety of sweep rates were obtained using a Hi-Tek model DT2101 potentiostat, a Hi-Tek model PPR1 waveform generator and a Gould model 60 000 X-Y chart recorder.

Cyclic voltammetry was also carried on a THF solution of Cp_2TiCl_2 (9 mM) with an excess of diphenylacetylene added. Bu_4NBF_4 was again the supporting electrolyte.

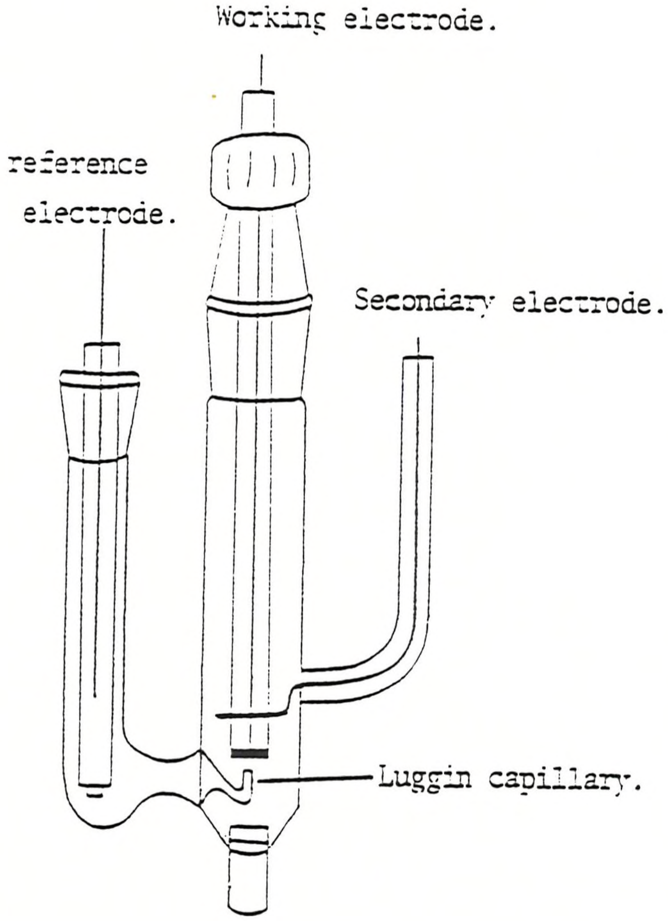


Figure 2.2a
Cyclic voltammetry cell

3. RESULTS AND DISCUSSION - ORGANIC CHEMISTRY

3.1 Bicyclisation of enynes.

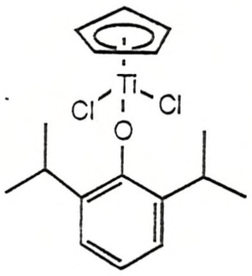
The organic work for this project started off by repeating the bicyclisation reactions of enynes with zirconocene and titanocene reagents reported by Negishi et al(20) and RajaBabu et al.(21) There is scope for asymmetric induction in these reactions if the metallocene can be replaced by a chiral metal complex. The ultimate aim is to discover suitable metal complexes for this, so the racemic metallocycles **19** and **20** were prepared to provide a comparison for further work.

19

20

3.2 $CpTiCl_2(OR)$ Complexes.

After the bicyclisation of enynes work concentrated on preparing metal complexes. Monocyclopentadienyl titanium complexes were chosen as a starting point. This was because it was thought that keeping one cyclopentadienyl titanium ligand would help maintain some stability on the complex since formally it is a $6e^-$donor. Monocyclopentadienytitanium-trichloride was prepared by literature methods(50) and used to make monocyclopentadienyl-titanium-dichloride-alkoxide complexes; $CpTiCl_2(OR)$. Riediker and Duthaler(34) reported the synthesis of $CpTiCl(OR^*)_2$ from $CpTiCl_3$, where R^* is a chiral glucose moiety, using triethylamine as the base to remove a proton from the alcohol and to mop up the HCl. $CpTiCl_2(O^iPr)$ (**23**), which has been previously prepared by a different method,(51) and the new complexes $CpTiCl_2[OPh(^iPr)_2]$ (**21**) and $CpTiCl_2$(menthoxide) (**22**) were prepared using this triethylamine method. A 1.1 molar equivalent of Et_3N was added to a 1:1 mixture of $CpTiCl_3$ and the alcohol, in ether. An immediate precipitate of $Et_3N.HCl$ was observed and could be filtered off. Each of the $CpTiCl_2(OR)$ complexes were recrystallized from hexane; $CpTiCl_2(O^iPr)$ is a yellow powder, $CpTiCl_2$(menthoxide) forms small yellow crystals and $CpTiCl_2[OPh(^iPr)_2]$ forms larger orange crystals. $CpTiCl_2$(menthoxide) was also made from $CpTiCl_3$ and the silylether of menthol (section 4.3).



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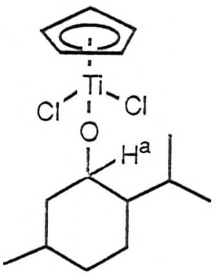

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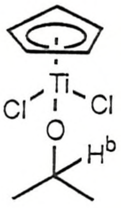

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The proton nmr of these $CpTiCl_2(OR)$ complexes all display a 5H singlet at about 6.7 ppm corresponding to the five equivalent hydrogens of the cyclopentadienyl ligand. In $CpTiCl_2(O^iPr)$ the hydrogen on the carbon atom next to the oxygen (H^a in **23**) has shifted to δ 4.9 which is about 2 ppm downfield compared to the starting alcohol. In $CpTiCl_2$(menthoxide) the downfield shift for the corresponding hydrogen (H^b in **22**) is 1 ppm. For $CpTiCl_2[OPh(^iPr)_2]$ there is a slight shift downfield for the aromatic protons; from 6.8-7.1 ppm in di-isopropylphenol to 7.0-7.2 ppm in the complex (**21**).

These $CpTiCl_2(OR)$ complexes are, of course, not chiral at the metal centre but their behaviour on reduction is of interest and could possibly be used as a guideline for other similar complexes. The electrochemical behaviour of THF solutions of the three $CpTiCl_2(OR)$ complexes, **21**, **22**, and **23**, is discussed in sections 4.5, 4.6, 4.7 and 4.8.

3.3 $CpTiCl_2(O-R-NMe_2)$ Complexes.

Having successfully prepared some $CpTiCl_2(OR)$ complexes, experimental work moved on to trying to incorporate amino alcohol ligands into the co-ordination sphere of the titanium (discussed in section 1.5). It was hoped that steric and electronic asymmetry at the metal centre would be achieved by having both the oxygen and nitrogen of the aminoalcohol bound to the titanium (fig. 3.3a).

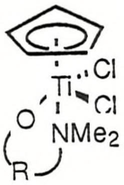
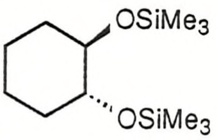


Fig. 3.3a

The first aminoalcohol tried was a simple straight-chain one; 3-dimethylamino-1-propanol. After unsuccessful attempts to react $CpTiCl_3$ with the sodium salt of the aminoalcohol the triethylamine method used by Riediker and Duthaler$^{(34)}$ was tried. $CpTiCl_3$ and $HO(CH_2)_3NMe_2$ were mixed together in ether, before any triethylamine had been added a cream precipitate had formed in the reaction mixture. It was suspected that this was $HO(CH_2)_3NMe_2.HCl$. Had it been the expected complex it is likely that it would have been yellow or orange. For this salt to form, at least some of the aminoalcohol must have co-ordinated to the metal and displaced a chloride ion. A sample was taken at this stage for proton nmr analysis, but the spectrum obtained was very poorly resolved and not very helpful. Triethylamine was then added to the reaction mixture and the amount of precipitate increased. Once the mixture was filtered and the solvent removed a thick orange oil and a pale yellow solid were left. The proton nmr data for the product of this reaction is presented in table 3.3a and discussed later. Attempts to recrystallize the product from hexane were unsuccessful. Results were not improved by varying the order of addition of reagents.

Similar observations were made when the same procedure was adopted with o-dimethylaminomethylphenol.

In view of the work published by Galeffi et al (52) where a bidentate zirconium trichloride alkoxide (**27**) was prepared from the bis(trimethylsilyl)ether (**26**) it was decided to make the trimethylsilyl ethers of the two aminoalcohols that were being used, and then reacting them with $CpTiCl_3$. In this reaction (Eq. 14) the byproduct, trimethylsilylchloride, can be removed <u>in vacuo</u>. The products from both the (trimethylsilyl)-dimethylamino-propylether and the (trimethylsilyl)-o-dimethylaminophenyl ether with $CpTiCl_3$, were thick orange oils, insoluble in hexane, and their proton nmr data is also discussed later.



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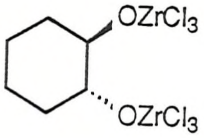
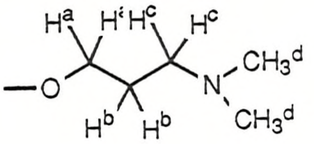


27

$$CpTiCl_3 + Me_3SiO\text{-}R\text{-}NMe_2 \xrightarrow{CH_2Cl_2} CpTiCl_2(O\text{-}R\text{-}NMe_2) + Me_3SiCl \qquad \text{Eq 14}$$

Table 3.3a +3.3b summarize~~s~~ the proton nmr data for the starting materials and products for each of the two types of reaction tried.

Figure 3.3b shows the ^1H nmr spectra obtained for the product of the reaction of $HO(CH_2)_3NMe_2$ with $CpTiCl_3$ in the presence of triethylamine. It can be seen that a mixture of compounds were present in the sample. H^a shows three triplets, H^d shows three singlets and the signal for H^c has a shoulder and possibly another, much smaller, triplet at slightly lower δ values (2.60 ppm). The major cyclopentadienyl peak integrates to less than 5H and there are other signals in that region. What the different compounds in the sample are, is very difficult to tell from the data available, the possibilities include compounds with different numbers of aminoalcohol ligands attached to the titanium centre, compounds where both oxygen and nitrogen, either from the same or different molecules, are co-ordinated to titanium and compounds where only oxygen co-ordinates. The downfield shift, compared to the starting material, of ≈1 ppm observed for the H^a signal of the major product gives a strong indication that oxygen is bound to the titanium. Smaller downfield shifts are observed for H^c and H^d (0.2 and 0.3 respectively for the major product) suggesting that nitrogen may also be bound to titanium but not as strongly as oxygen.



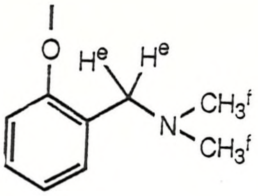
H	$HO(CH_2)_3$-NMe_2	$CpTiCl_2$-$(O(CH_2)NMe_2)$ (from amino-alcohol)	Me_3SiO-$(CH_2)_3$-NMe_2	$CpTiCl_2$-$(O(CH_2)_3NMe_2)$ (from silyl ether)
H^a	3.7(2H,t)	4.5-4.8(2H,3t)	3.6(2H,t)	4.8(2H,br)
H^b	1.6(2H,quin)	1.85-1.95(2H, quintet)	1.7(2H,quin)	2.2(2H,br)
H^c	2.5(2H,t)	2.62-2.72(2H,t)	2.3(2H,t)	3.2(2H,q)
H^d	2.2(6H,s)	2.3-2.5(6H,3s)	2.2(6H,s)	2.8(6H,d)
Cp	-	6.5(<5H,s) & other signals.	-	6.7(<5H,s) & other signals.
		Fig. 3.3b		Fig.3.3c

Table 3.3a.

Figure 3.3c shows the ^1H nmr spectrum obtained from the product of the reaction between $CpTiCl_3$ and $Me_3SiO(CH_2)_3NMe_2$. Clearly it is much cleaner than the spectrum seen in figure 3.3b although some of the peaks are broad. The main differences between the spectrum in fig. 3.3c and the spectrum of the major product in fig.3.3b are the differences in the downfield shifts observed for H^c and H^d. H^a has again shifted approximately 1ppm downfield compared to the starting material but the shifts observed for H^c and H^d are now 0.9 and 0.6 respectively. Because the spectra are otherwise quite similar it is likely that the same compound is present in both samples. The differences that are observed could arise from the fact that both samples were referenced to $CHCl_3$ not TMS, which is the standard for δ values to be quoted from, or from the differences in acidity of the two samples due to the separate reaction conditions.

In figure 3.3c the broadness of some of the peaks probably arises from rapid changes in conformation of the compound. The H^c signal which appears as a quartet is really likely to be a poorly resolved doublet of triplets. The methyl groups on the nitrogen give two singlets indicating that they are in different environments which is what would be expected if the compound had the configuration shown in fig. 3.3a. The sharp singlet at δ 2 is due to BSA impurity in the sample, which arises from the excess used in the experiment.

Table 3.3b summarizes the data for the dimethylaminomethylphenyl case.



H	$HOPh.CH_2$-NMe_2	$CpTiCl_2$-($OPh.CH_2NMe_2$) (from amino-alcohol)	Me_3SiO-$Ph.CH_2$-NMe_2	$CpTiCl_2$-($OPh.CH_2NMe_2$) (from silyl-ether)
H^{Ar}	6.4-7.0(4H,m)	6.5-7.5(9H,m)*	6.7-7.3(4H,m)	6.8-7.4(4H,m)
H^e	3.4(2H,s)	3.8-4.1(2H,br)	3.4(2H,s)	4.1-4.2(2H,2d)
H^f	2.0(6H,s)	2.5(6H,s)	2.2(6H,s)	2.6-2.7(6H,2d)
Cp	-	*included in H^{Ar} signal	-	6.6(5H,s)
		Fig. 3.3d		Fig. 3.3e

Table 3.3b

Similar differences to those observed in table 3.3a, between the proton shifts for the products of the two types of reaction are also seen here. Figure 3.3d shows a spectrum run on a 90 MHz spectrometer hence the much poorer resolution although downfield shifts for H^e and H^f of about 0.4 ppm compared to the stating material, are evident. Because of the poor resolution it is difficult to tell whether a similar mixture of products to that seen in fig. 3.3c was present in the sample. Figure 3.3e is a better resolved spectrum, the downfield shifts for H^e and H^f are 0.7 and 0.5 ppm respectively compared to the starting silylether. The occurance of this shift again indicates that there is some nitrogen - titanium co-ordination. BSA impurity is also seen in this spectrum at δ 2.

The conclusions made from the results of the experiments of

$CpTiCl_3$ with aminoalcohol moieties can only be that there is evidence to suggest a product of the conformation shown in figure 3.3a is formed. Both types of reaction conditions seemed to give rise to this product, although there still remain differences in their proton nmr data that are yet to be fully explained.

3.4 Further Work.

Since some $CpTiCl_2(OR)$ complexes have been prepared it would be of interest to see if they can couple to 1,6- or 1,7-enynes in the way Cp_2TiCl_2 does.

Further work must involve a deeper investigation into the differences in the proton nmr data from the two different methods of preparing $CpTiCl(O\text{-}R\text{-}NMe_2)$ complexes. Isolation of a pure product from the reactions of $CpTiCl_3$ and aminoalcohols or their silylethers is desirable so a method of purifying the thick oil must be discovered. Once this has been achieved then reactions with dienes, diynes or enynes can be tried and the possibility of chiral induction looked at.

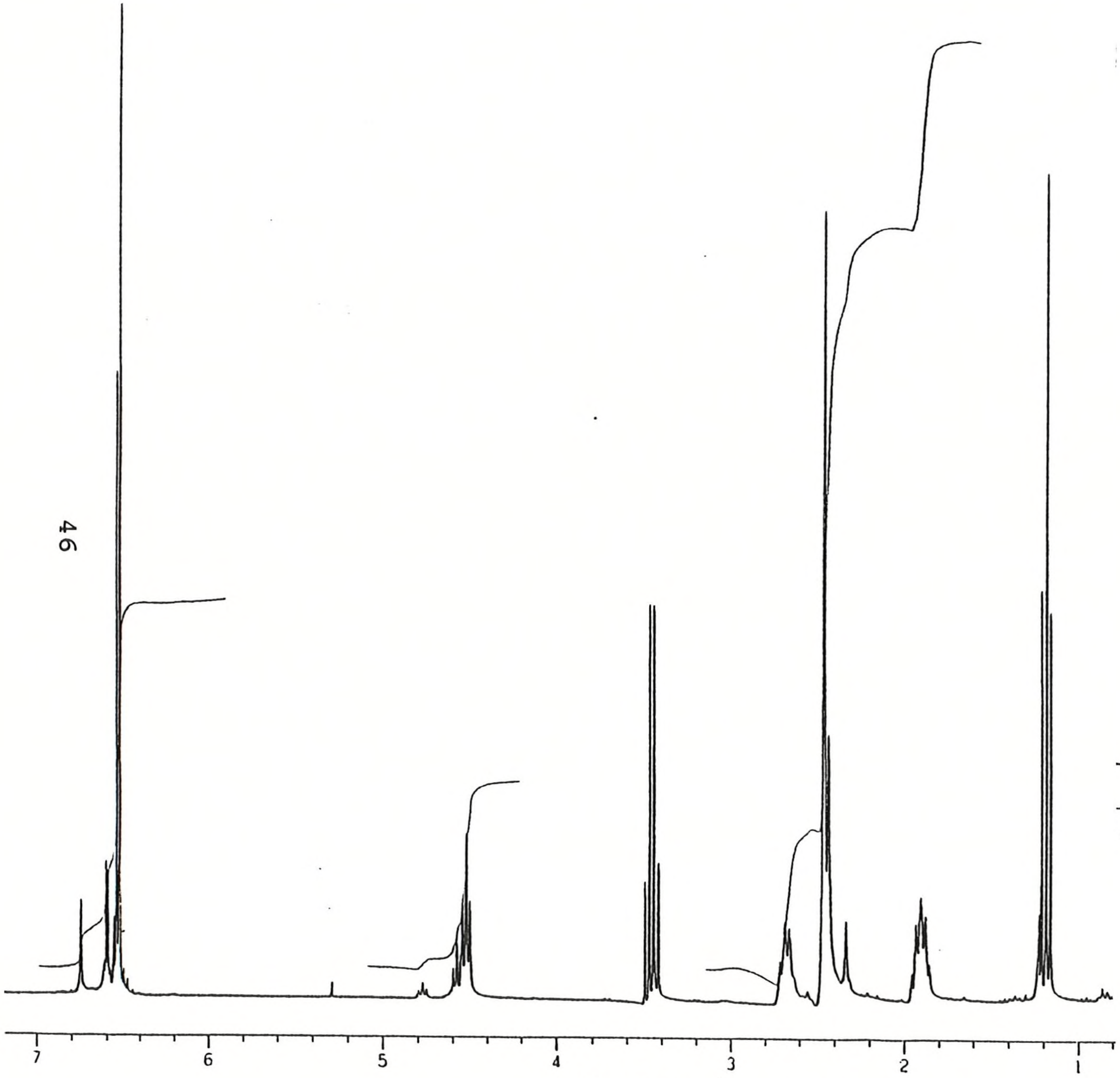


Fig. 3.3b

^{1}H nmr spectrum for $CpTiCl_2[O(CH_2)_2NMe_2]$ - Et_3N method.

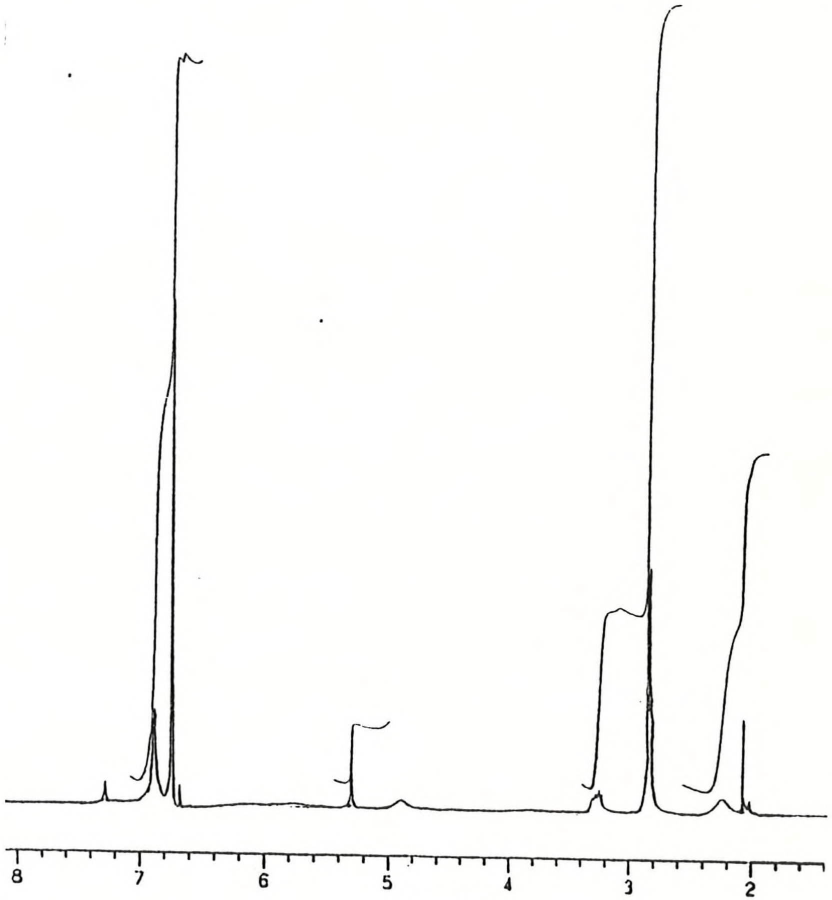


Fig. 3.3c

^{1}H nmr spectrum for $CpTiCl_2[O(CH_2)_2NMe_2]$ - silylether method.

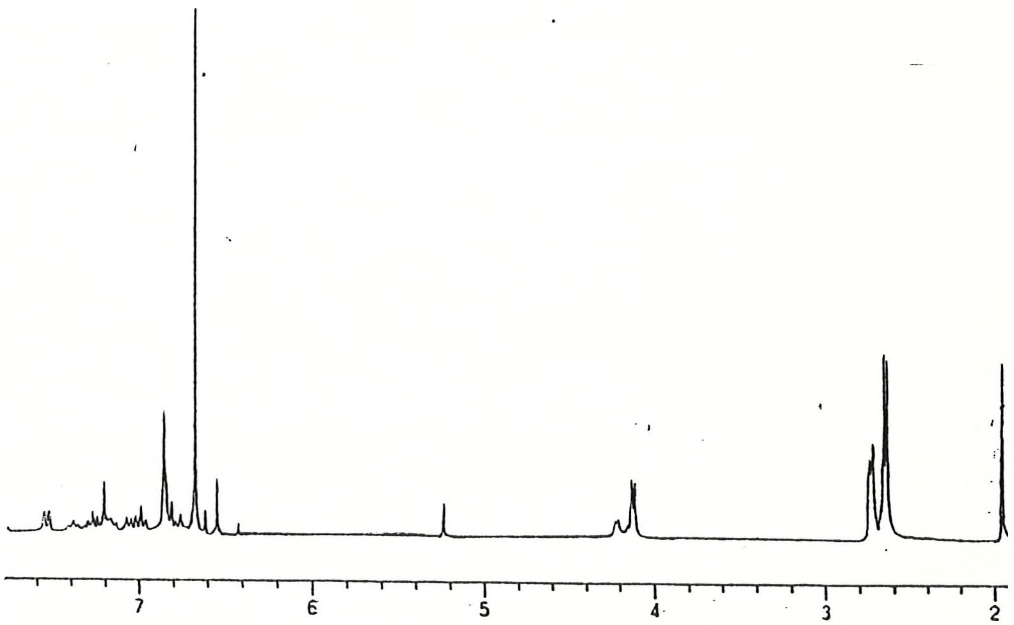


Fig. 3.3e

^{1}H nmr spectrum for CpTiCl$_2$[OPh(CH$_2$NMe$_2$)] - silylether method.

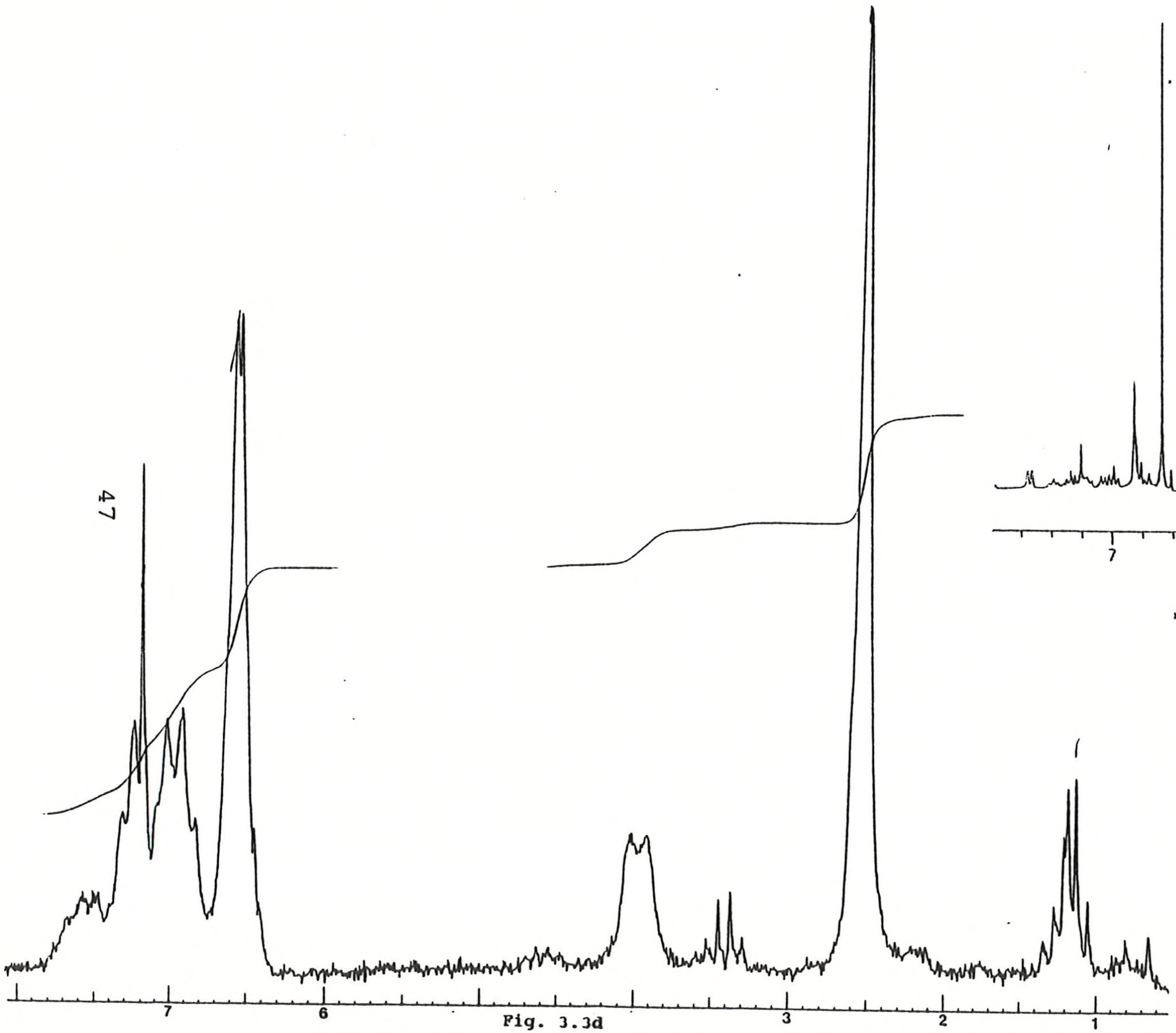


Fig. 3.3d

^{1}H nmr spectrum for CpTiCl$_2$[OPh(CH$_2$NMe$_2$)] - Et$_3$N method.

4. RESULTS AND DISCUSSION - ELECTROCHEMISTRY.

4.1 Introduction.

The electrochemical behaviour of the available organo-titanium complexes was investigated by cyclic voltammetry of their solutions in THF/Bu_4NBF_4. Because the chemistry of these complexes in organic synthesis involves redox reactions it was felt worthwhile to investigate the potential where reduction occurs and the stability of the reduced species. Cyclic voltammetry offered one approach to this. Initially the cyclic voltammetry of Cp_2TiCl_2 and $CpTiCl_3$ was investigated and compared to literature data, then the three $CpTiCl_2(OR)$ complexes were investigated.

4.2 Cyclic voltammetry of Cp_2TiCl_2.

Figure 4.2a shows a cyclic voltammogram recorded at 300 mVs^{-1} between the limits -0.6 V and-2.1 V vs ferrocene for a THF solution of Cp_2TiCl_2 (6.1 mM) with Bu_4NBF_4 (0.2 M) as the supporting electrolyte. It shows the first one electron transfer for Cp_2TiCl_2 at -1.28 V (**A**); this process displays complete reversibility; ΔEp=60 mV and $Ip^A/Ip^{A'}$=1.0. A cyclic voltammogram recorded under the same conditions but with extended limits (-0.6 to -3.06 V vs ferrocene) is shown in figure 4.2b. A second cathodic peak (**B**) is observed at -2.56 V, this also appears to be a $1e^-$ reduction but is irreversible indicating that the dianion has rapid chemistry. The third $1e^-$ cathodic peak reported by Mugnier et al(35) is not seen under these conditions. Otherwise the cyclic voltammograms presented here are comparable with the literature.(35,41,42)

The mechanism of the electrochemical reduction of Cp_2TiCl_2 has been the subject of much discussion in the literature (section 1.4). The central argument is whether the radical anion, produced from the first one electron reduction is stable (Eq. 15) or whether it rapidly and reversibly loses a chloride ion (Eq.16). The data presented here offers no solution to the argument and it is difficult to distinguish between the two proposed mechanisms. The data is presented here to allow comparisons with the data for other titanium complexes.

$$Cp_2TiCl_2 + e^- \rightleftharpoons [Cp_2TiCl_2]^- \qquad \text{Eq 15}$$

$$[Cp_2TiCl_2]^- \rightleftharpoons [Cp_2TiCl] + Cl^- \qquad \text{Eq 16}$$

Cyclic voltammetry was also used to look at the behaviour of $[Cp_2TiCl_2]^-$ with diphenylacetylene. In view of the work carried out with Cp_2TiCl_2 and carbon monoxide (section 1.4) where a reaction of CO follows the addition of the first electron to Cp_2TiCl_2(43), it was thought that a similar reaction may occur between $[Cp_2TiCl_2]^-$ and diphenylacetylene. There was no evidence of this however, the cyclic voltammogram for Cp_2TiCl_2 (9 mM) remained unchaged by the addition of an excess of diphenylacetylene.

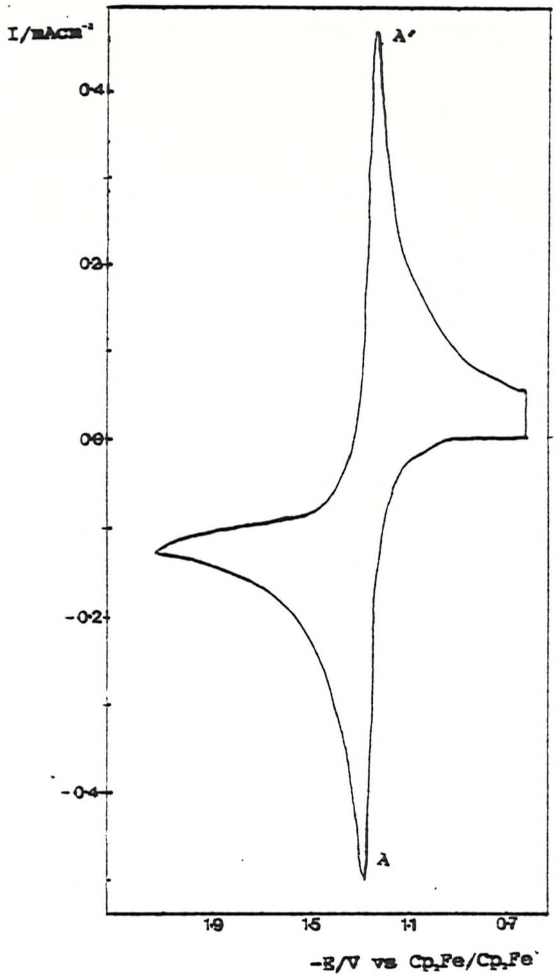


Fig. 4.2a

Cyclic voltammogram recorded at 300 mVs^{-1} between -0.6 and -2.1 V vs ferrocene for a THF solution of Cp_2TiCl_2 (6.1 mM) with Bu_4NBF_4 (0.2 M).

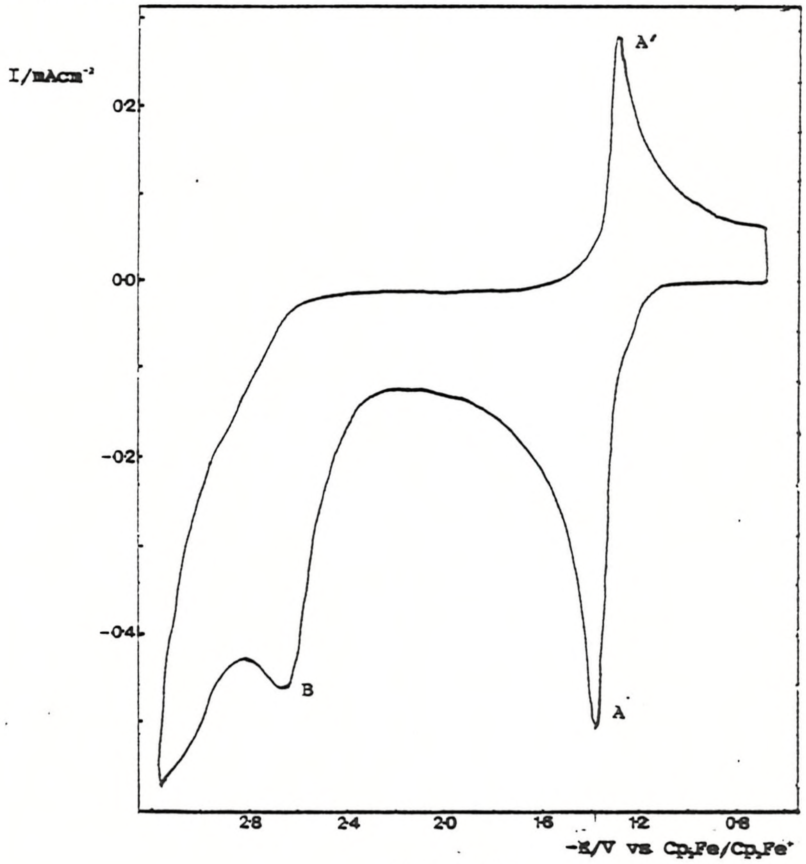


Fig. 4.2b

Cyclic voltammogram recorded at 300 mVs^{-1} between -0.6 and -3.06 V vs ferrocene for a THF solution of Cp_2TiCl_2 (6.1 mM) with Bu_4NBF_4 (0.2 M).

4.3 Cyclic Voltammetry of $CpTiCl_3$.

Figure 4.3a shows a cyclic voltammogram recorded at 300 mVs^{-1} between -0.2 V and -1.0 V vs ferrocene for a THF solution of $CpTiCl_3$ (16 mM) with Bu_4NBF_4 (0.2 M) as the supporting electrolyte. A cathodic peak (**C**) is observed at -0.84 V with a coupled anodic peak (**C'**). The **C/C'** couple displays complete reversibility; $\Delta Ep=60$ mV and $Ip^{C}/Ip^{C'}=1.0$. When the potential limits are extended (-0.2 to -2.86 V vs ferrocene) a second cathodic peak (**D**) is seen at -2.7 V but no coupled anodic peak (fig. 4.3b). Hence the electrochemistry of $CpTiCl_3$ and Cp_2TiCl_2 is essentially identical, with a reversible $1e^-$ reduction followed by the addition of a second electron at more negative potentials to give a very unstable species.

Gubin and Smirnova(46) reported three cathodic waves at -0.87, -1.60 and -2.04 V vs SCE in their polarographic study of $CpTiCl_3$ in DMF (2 mM). Clearly the behaviour reported here is simpler. A third, smaller, cathodic peak (**E**) is seen in figure 4.3c where a cyclic voltammogram was run on a 7.4 mM solution of $CpTiCl_3$ using THF not stored over molecular sieves and an SCE reference. The lower concentration of $CpTiCl_3$ and the higher ratio of $[H_2O]/[CpTiCl_3]$ may cause additional chemistry leading to the third reduction process. Similar effects would explain the results of the Russian workers.

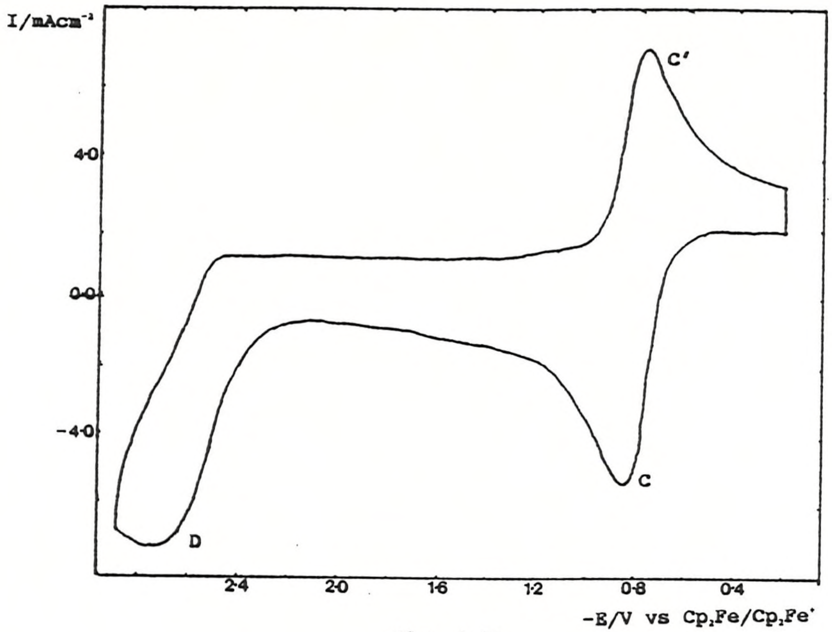


Fig. 4.3b

Cyclic voltammogram recorded at 300 mVs^{-1} between -0.2 and -2.86 V vs ferrocene for a THF solution of $CpTiCl_3$ (16 mM) with Bu_4NBF_4 (0.2 M).

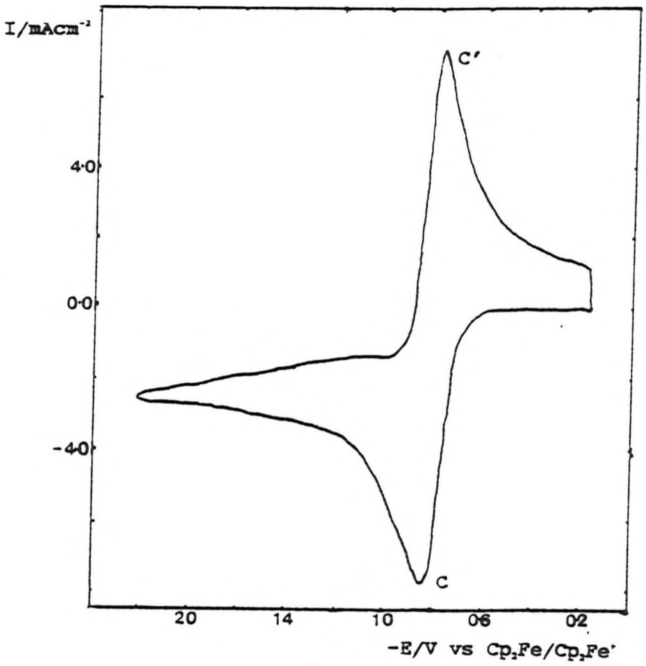


Fig. 4.3a

Cyclic voltammogram recorded at 300 mVs^{-1} between -0.2 and -1.0 V vs ferrocene for a THF solution of $CpTiCl_3$ (16 mM) with Bu_4NBF_4 (0.2 M).

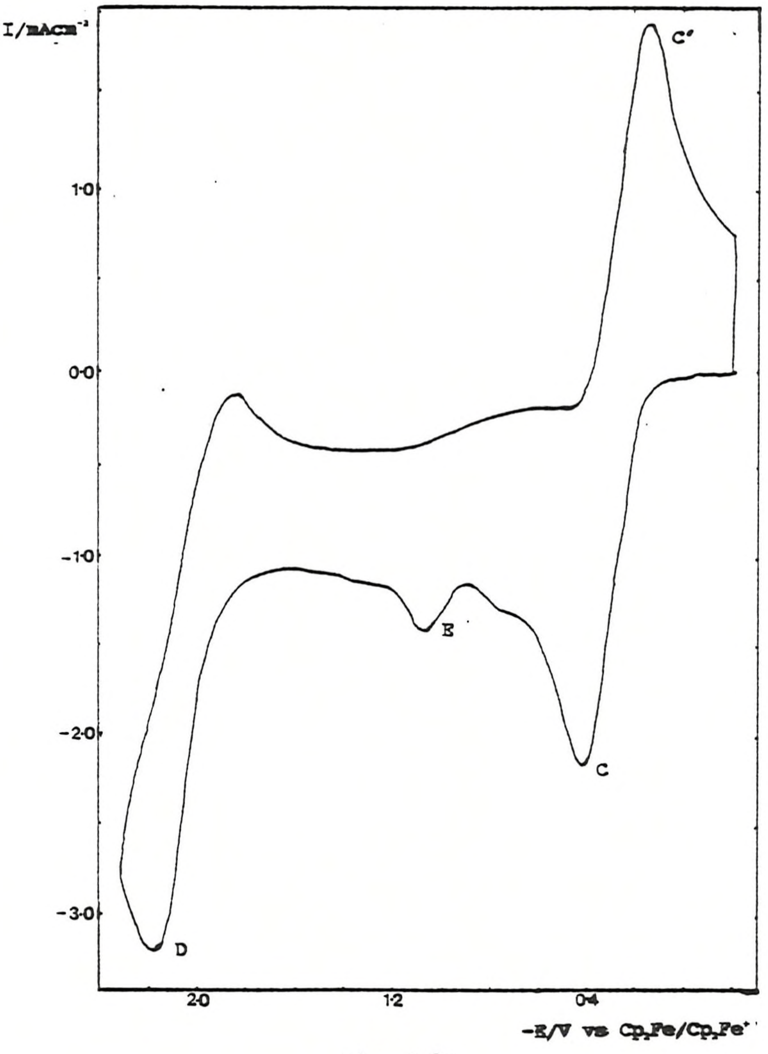


Fig. 4.3c

Cyclic voltammogram recorded at 300 mVs^{-1} between 0.2 and -2.3 V vs SCE for a THF solution of CpTiCl$_3$ (7.4 mM) with Bu$_4$NBF$_4$ (0.2 M).

4.4 The Electrochemical Behaviour of $CpTiCl_2(OR)$ Complexes.

Cyclic voltammograms were run in THF/Bu_4NBF_4 solutions for the three $CpTiCl_2(OR)$ complexes prepared from $CpTiCl_3$ (section 2.1). From the cyclic voltammograms shown in figures 4.5a and 4.5b (5.3 mM and 23 mM $CpTiCl_2[OPh(^iPr)_2]$) it is clear that the electrochemistry is somewhat dependant on concentration, so experiments were carried out on solutions of different $CpTiCl_2(OR)$ concentration.

4.5 Cyclic Voltammetry of $CpTiCl_2[OPh(^iPr)]$.

Figure 4.5c shows a cyclic voltammogram recorded at 800 mVs^{-1} between the limits -0.4 and -1.6 V vs ferrocene for a THF solution of $CpTiCl_2[OPh(^iPr)_2]$ (23 mM) with Bu_4NBF_4 (0.2 M) as the supporting electrolyte. This cyclic voltammogram is similar in appearance, except for the minor peaks **H** and **G**, to that for a reversible one electron transfer with a sharp cathodic peak (**F**) at -1.16 V and a coupled anodic peak (**F'**). ΔEp for the **F/F'** system is 60 mV indicating that the reduced species is stable on the timescale of the experiment, $Ip^F/Ip^{F'} \approx 1.0$. A small cathodic peak (**G**) can be seen at -0.86 V and a small anodic one (**H**) appears at about the same potential. When a sweep rate of 36 mVs^{-1} is employed between the same limits (fig. 4.5d) the cathodic peaks **F**, which displays a sweep rate dependence, and **G**, which is independent of sweep rate, appear again but there has been a remarked change in the anodic peaks. **F'** has decreased in size, $Ip^F/Ip^{F'}$ is now only 0.68 and peak **H** is clearly more pronounced. This indicates that the species obtained from the reduction during peak **F** undergoes some chemical change most extensive at slow sweep rates.

Figure 4.5a shows a cyclic voltammogram recorded under the same conditions as above except the $CpTiCl_2[OPh(^iPr)_2]$ concentration is now only 5.3 mM. The potential limits are -0.2 to -2.4 V vs ferrocene (fig. 4.5b shows the cv for 23 mM $CpTiCl_2[OPh(^iPr)_2]$ with comparable limits). It can clearly be seen that both **G** and **H** are more pronounced, **F'** has almost disappeared and peak **J**, which is just noticeable in figure 4.5b, has increased considerably. The indication here is that the chemical change undergone by the species created during peak **F** is almost complete, hence a very small **F'** peak, and that this species is further reduced at the potential of peak **J**.

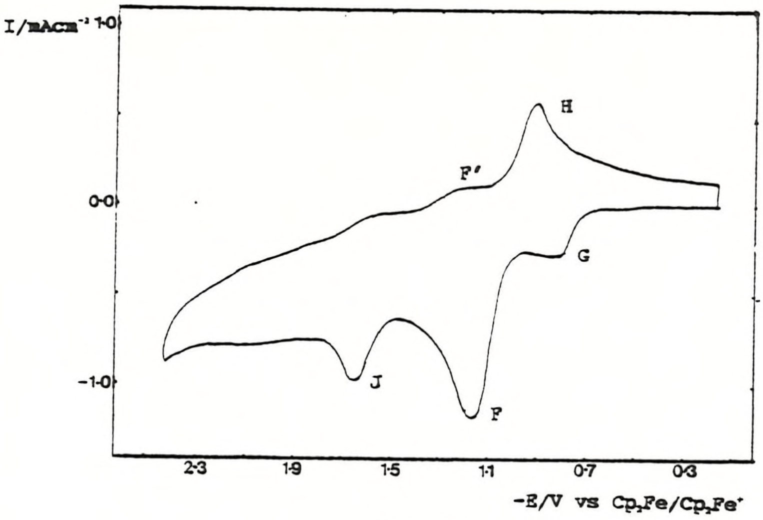


Fig. 4.5a

Cyclic voltammogram recorded at 300 mVs^{-1} between -0.2 and -2.4 V vs ferrocene for a THF solution of CpTiCl$_2$[OPh(^{i}Pr)$_2$] (5.3 mM) with Bu$_4$NBF$_4$ (0.2 M).

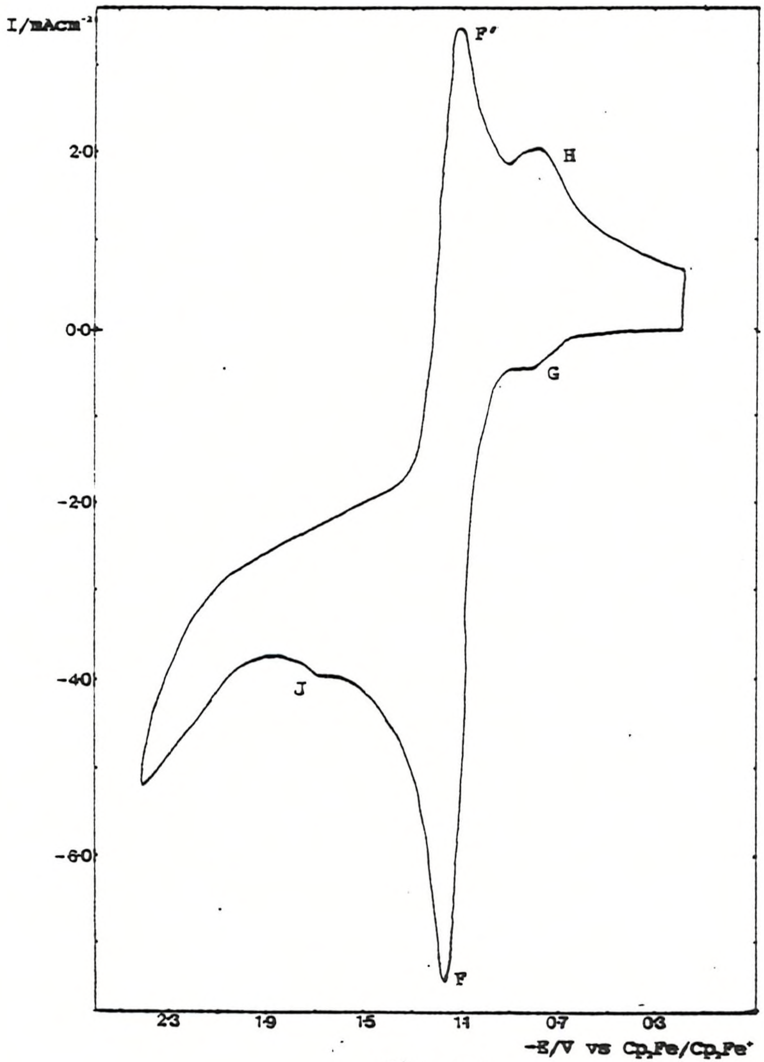


Fig. 4.5b

Cyclic voltammogram recorded at 300 mVs^{-1} between -0.2 and -2.4 V vs ferrocene for a THF solution of CpTiCl$_2$[OPh(^{i}Pr)$_2$] (23 mM) with Bu$_4$NBF$_4$ (0.2 M).

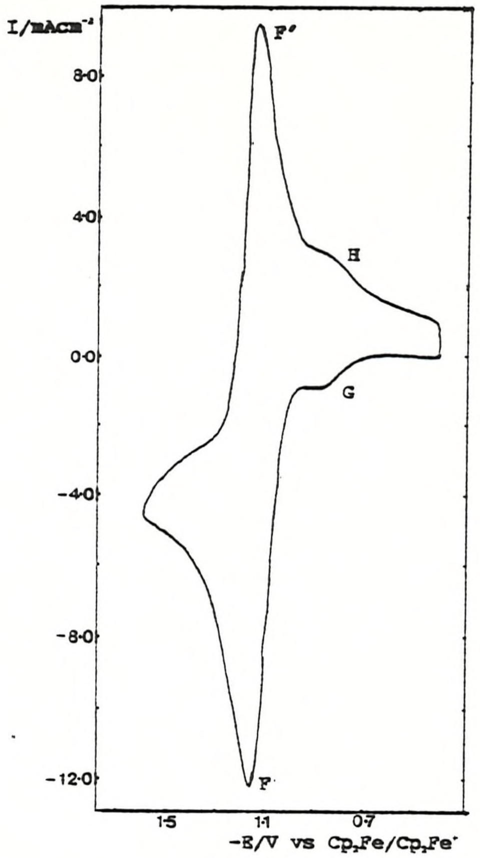


Fig. 4.5c

Cyclic voltammogram recorded at 800 mVs^{-1} between -0.4 and -1.6 V vs ferrocene for a THF solution of CpTiCl$_2$[OPh(^{i}Pr)$_2$] (23 mM) with Bu$_4$NBF$_4$ (0.2 M).

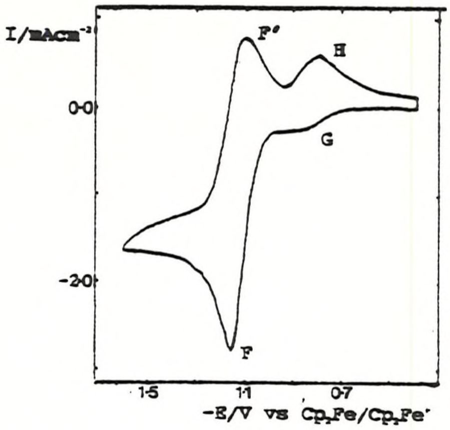


Fig. 4.5d

Cyclic voltammogram recorded at 36 mVs^{-1} between -0.4 and -1.6 V vs ferrocene for a THF solution of CpTiCl$_2$[OPh(^{i}Pr)$_2$] (23 mM) with Bu$_4$NBF$_4$ (0.2 M).

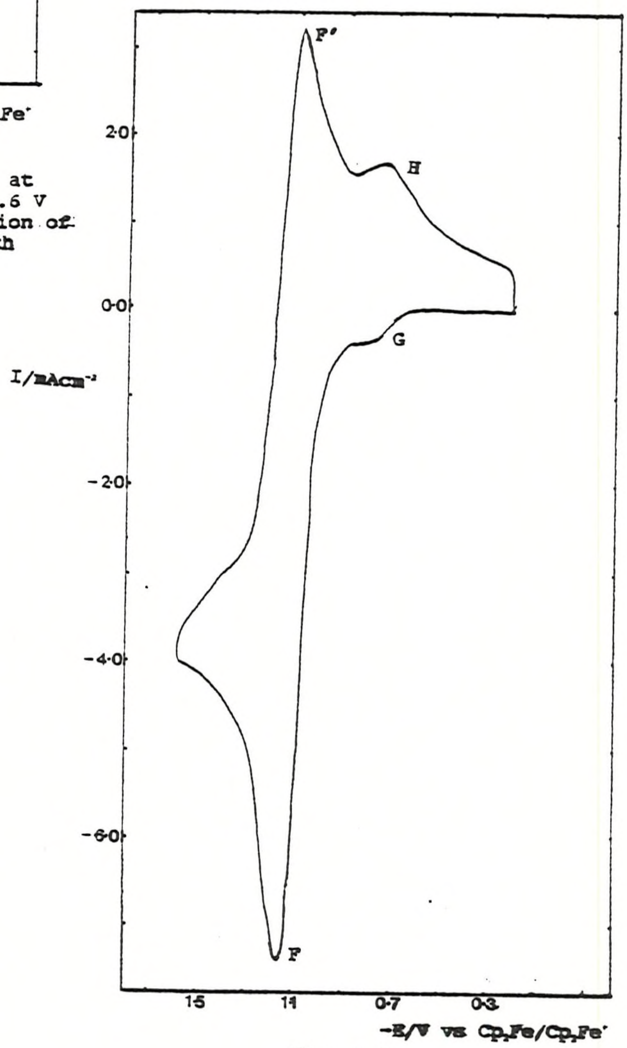


Fig. 4.5e

Cyclic voltammogram recorded at 300 mVs^{-1} between -0.3 and -1.6 V vs ferrocene for a THF solution of CpTiCl$_2$[OPh(^{i}Pr)$_2$] (23 mM) with Bu$_4$NBF$_4$ (0.2 M).

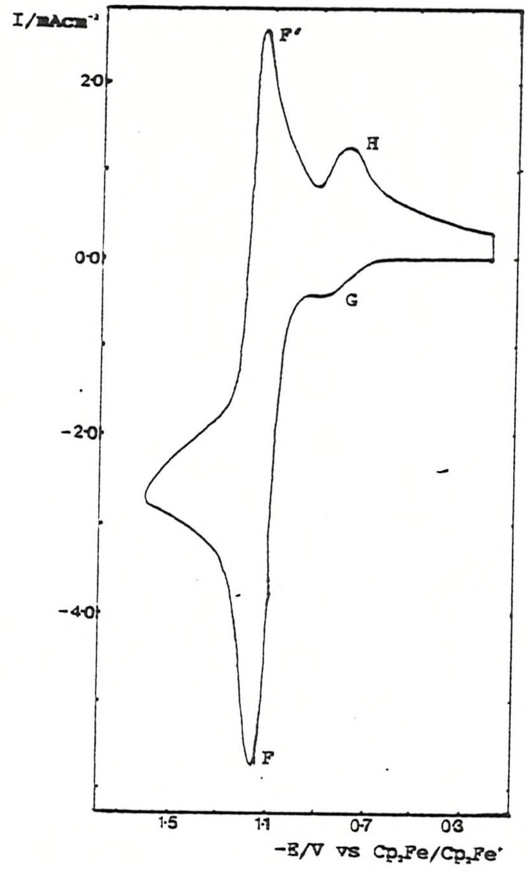


Fig. 4.5f

Cyclic voltammogram recorded at 150 mVs^{-1} between -0.2 and -1.6 V vs ferrocene for a THF solution of CpTiCl$_2$[OPh(^{i}Pr)$_2$] (23 mM) with Bu$_4$NBF$_4$ (0.2 M).

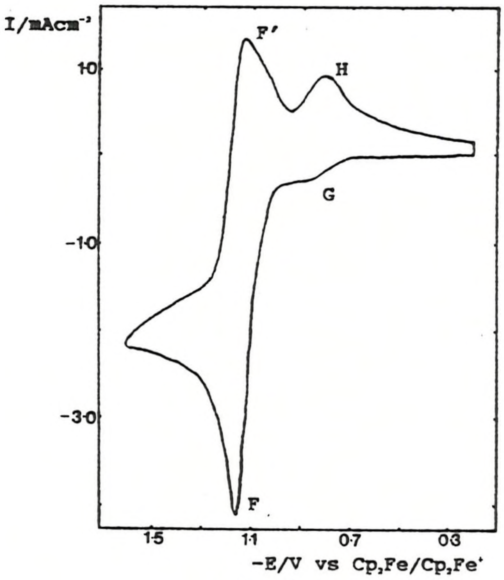


Fig. 4.5g

Cyclic voltammogram recorded at 75 mVs^{-1} between -0.2 and -1.6 V vs ferrocene for a THF solution of CpTiCl$_2$[OPh(^{i}Pr)$_2$] (23 mM) with Bu$_4$NBF$_4$ (0.2 M).

4.6 Cyclic Voltammetry of $CpTiCl_2$(menthoxide).

Figure 4.6a shows a cyclic voltammogram recorded at 600 mVs^{-1} between the limits -0.4 and -1.6 V vs ferrocene for a THF solution of $CpTiCl_2$(menthoxide) (22 mM) with Bu_4NBF_4 (0.2 M) as the supporting electrolyte. A cathodic peak, **K**, occurs at -1.36 V which has a coupled anodic peak, **K'**, the peak separation of this couple being 60 mV. Another much smaller cathodic peak (**L**) is seen between -0.8 and -0.9 V and a second anodic peak (**M**) occurs at -0.82 V. **K/K'** look similar to a reversible couple, but it is clear from the presence of peak **M** that some chemical change is occurring to the reduced species generated at **K**. **M** is the peak corresponding to the oxidation of this species. When the sweep rate is brought down to 75 mVs^{-1} it would appear that the chemical change is complete since no **K'** peak is seen (fig. 4.6b). $Ip^K/Ip^{K'}$ did not reach unity at any of the sweep rates used. The fastest sweep rate, 1000 mVs^{-1}, produced $Ip^K/Ip^{K'}=0.73$. Repetitive sweeps were performed between the limits -0.4 and -1.6 V at 300 mVs^{-1} to see if peak **L** increased in size, there was no evidence of this (fig. 4.6c).

When the potential limits were extended (-0.4 to -2.4 V vs ferrocene) a slight shoulder (**N**) on peak **K** at about -1.7 V can be seen for the same 22 mM $CpTiCl_2$(menthoxide) solution at a sweep rate of 300 mVs^{-1} (fig. 4.6d). When the same experiment is carried out on a 4.3 mM solution of $CpTiCl_2$(menthoxide) this shoulder has become a well resolved peak (fig. 4.6e). In this experiment also, the anodic peak **K'** has disappeared.

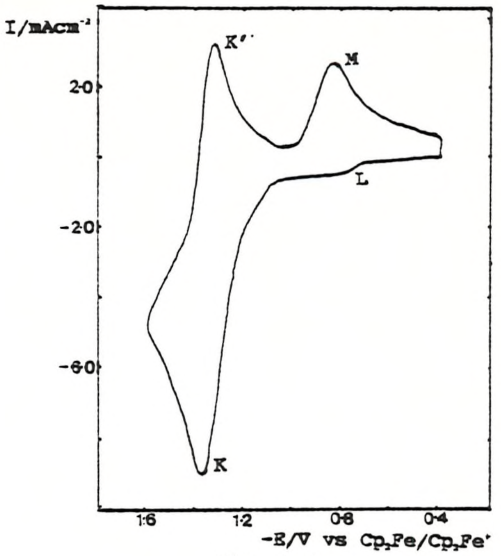


Fig. 4.6a

Cyclic voltammogram recorded at 600 mVs^{-1} between -0.4 and -1.6 V vs ferrocene for a THF solution of CpTiCl$_2$(menthoxide) (22 mM) with Bu$_4$NBF$_4$ (0.2 M).

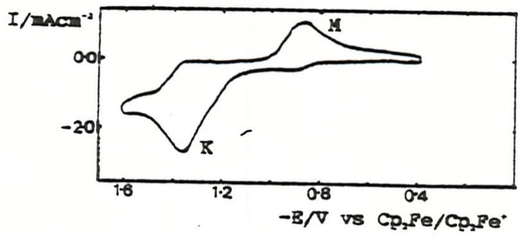


Fig. 4.6b

Cyclic voltammogram recorded at 75 mVs^{-1} between -0.4 and -1.6 V vs ferrocene for a THF solution of CpTiCl$_2$(menthoxide) (22 mM) with Bu$_4$NBF$_4$ (0.2 M).

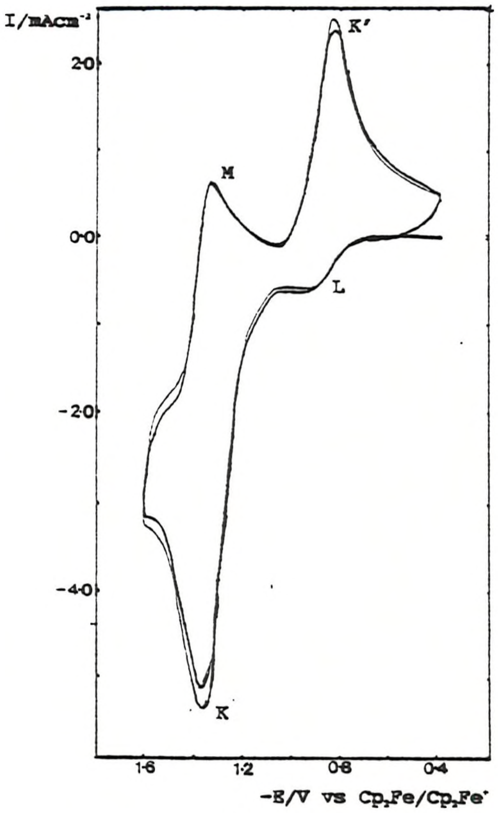


Fig. 4.6c

Cyclic voltammogram recorded repetitively at 300 mVs^{-1} between -0.4 and -1.6 V vs ferrocene for a THF solution of CpTiCl$_2$(menthoxide) (22 mM) with Bu$_4$NBF$_4$ (0.2 M).

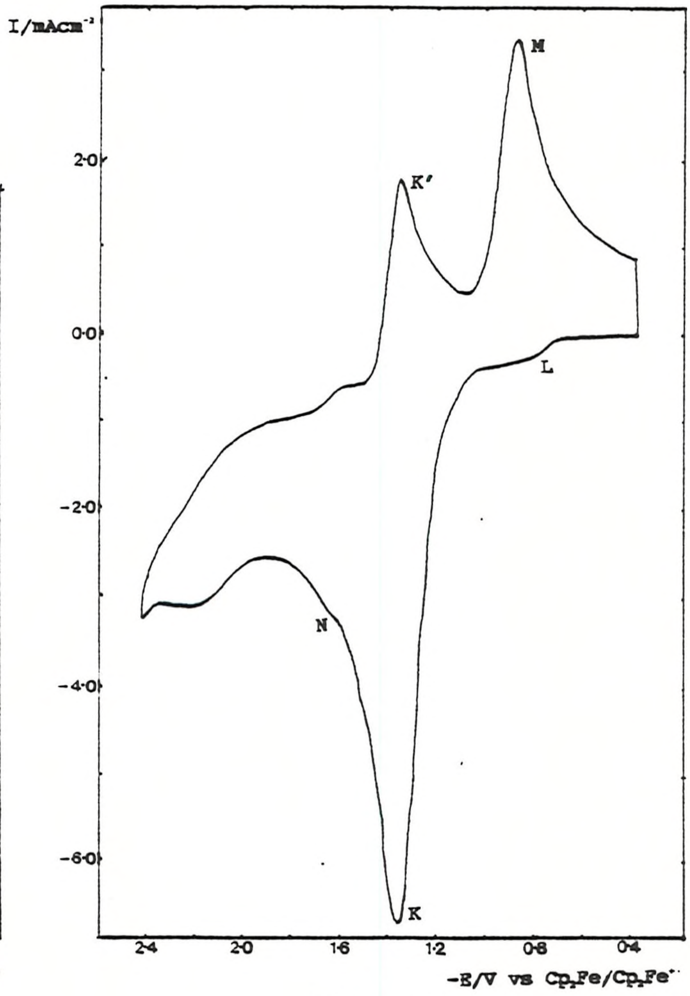


Fig. 4.6d

Cyclic voltammogram recorded at 300 mVs^{-1} between -0.4 and -2.4 V vs ferrocene for a THF solution of CpTiCl$_2$(menthoxide) (22 mM) with Bu$_4$NBF$_4$ (0.2 M).

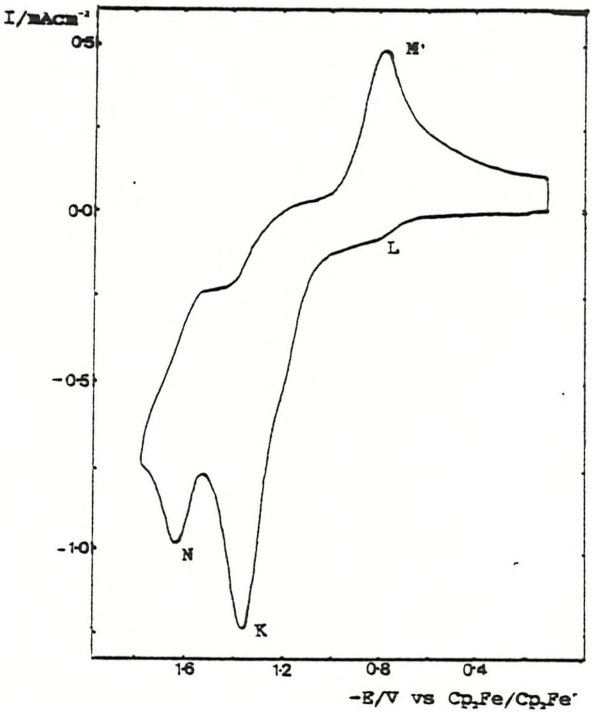


Fig. 4.6e

Cyclic voltammogram recorded at 300 mVs^{-1} between -0.4 and -1.8 V vs ferrocene for a THF solution of $CpTiCl_2$(menthoxide) (4.3 mM) with Bu_4NBF_4 (0.2 M).

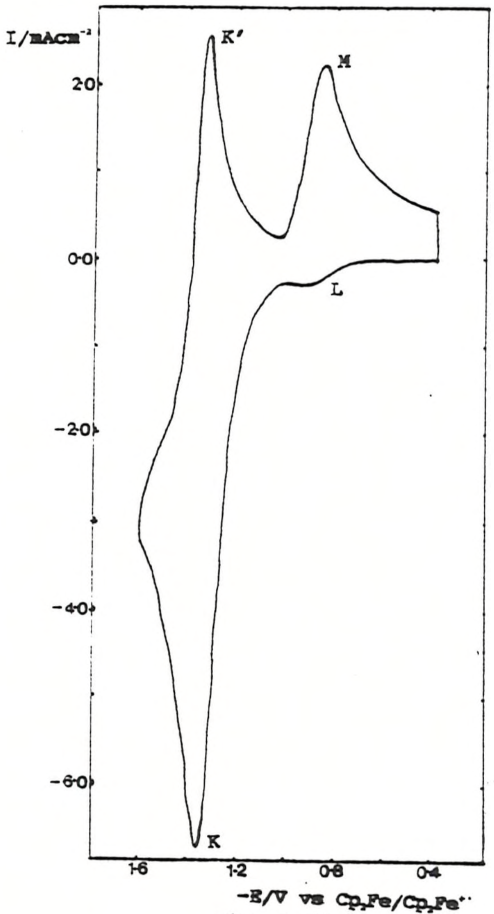


Fig. 4.6f

Cyclic voltammogram recorded at 300 mVs^{-1} between -0.4 and -1.6 V vs ferrocene for a THF solution of $CpTiCl_2$(menthoxide) (22 mM) with Bu_4NBF_4 (0.2 M).

4.7 Cyclic Voltammetry of $CpTiCl_2(O^iPr)$.

Figure 4.7a shows a cyclic voltammogram recorded at 600 mVs^{-1} between -0.2 and -1.6 V vs ferrocene for a THF solution of $CpTiCl_2(O^iPr)$ (19 mM) with Bu_4NBF_4 (0.2 M) as the supporting electrolyte. As with $CpTiCl_2[OPh(^iPr)_2]$ and $CpTiCl_2$(menthoxide) two cathodic peaks are seen, one of them , small and broad (peak **Q** at about 0.88 V) and the other large and sharp (**P**). This large one for $CpTiCl_2(O^iPr)$ occurs at -1.32 V, and unlike the other two complexes, does not have a coupled anodic peak to resemble a reversible system. At very fast sweep rates (3 Vs^{-1}), although the cyclic voltammogram is very noisy, the beginnings of a peak corresponding to the reverse of **P** can be seen (fig. 4.7b). A large anodic peak (**R**) at -0.8 V is seen on figure 5.7a, again indicating that a chemical change is taking place in the reduced species produced at **P**, the product of which is oxidised at **R**. No increase in **Q** was observed on repetitive sweeps.

Again a third cathodic peak (**S**) is observed if the potential limits are extended (-0.2 to -1.68 V vs ferrocene, fig. 4.7c) and this peak is more pronounced when the concentration of $CpTiCl_2(O^iPr)$ is lowered to 2.1 mM (fig. 4.7d).

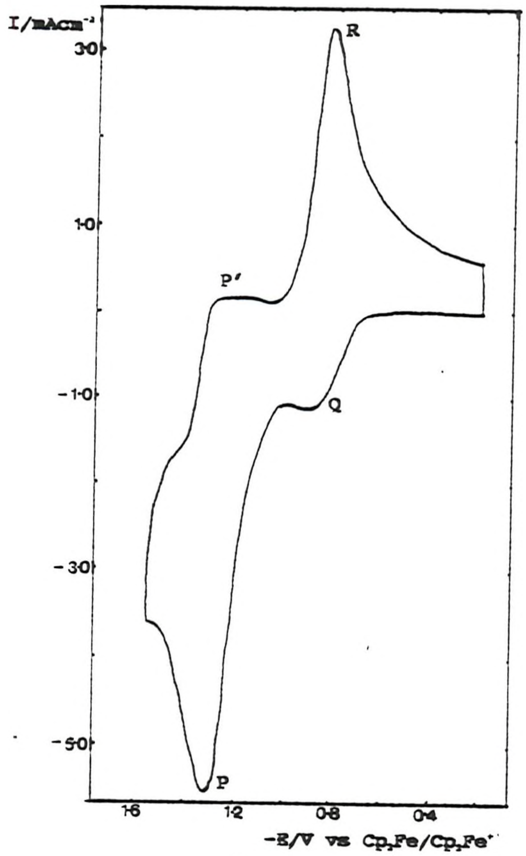


Fig. 4.7a

Cyclic voltammogram recorded at 600 mVs^{-1} between -0.2 and -1.6 V vs ferrocene for a THF solution of CpTiCl$_2$(O^{i}Pr) (19 mM) with Bu$_4$NBF$_4$ (0.2 M).

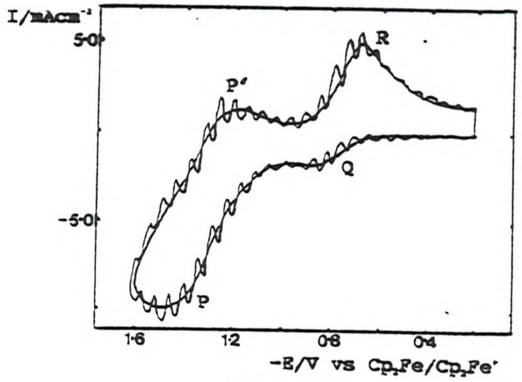


Fig. 4.7b

Cyclic voltammogram recorded at 3 Vs^{-1} between -0.2 and -1.6 V vs ferrocene for a THF solution of CpTiCl$_2$(O^{i}Pr) (19 mM) with Bu$_4$NBF$_4$ (0.2 M).

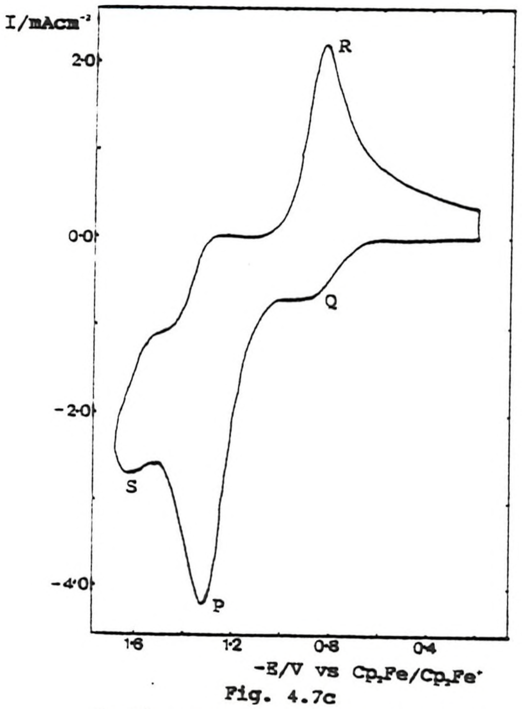


Fig. 4.7c

Cyclic voltammogram recorded at 300 mVs^{-1} between -0.2 and -1.68 V vs ferrocene for a THF solution of CpTiCl$_2$(O^{i}Pr) (19 mM) with Bu$_4$NBF$_4$ (0.2 M).

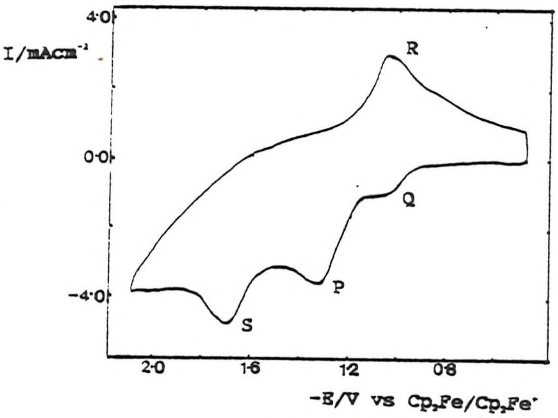


Fig. 4.7d

Cyclic voltammogram recorded at 300 mVs^{-1} between -0.5 and -2.3 V vs ferrocene for a THF solution of CpTiCl$_2$(O^{i}Pr) (2.1 mM) with Bu$_4$NBF$_4$ (0.2 M).

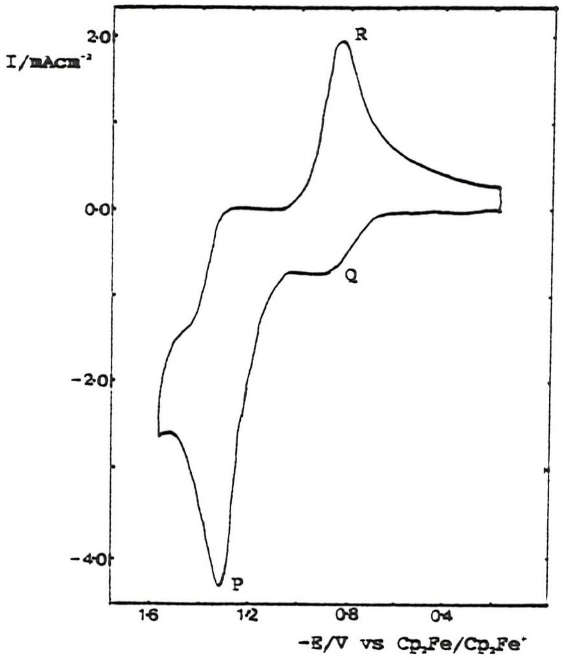


Fig. 4.7e

Cyclic voltammogram recorded at 300 mVs^{-1} between −0.2 and −1.6 V vs ferrocene for a THF solution of CpTiCl$_2$(O^{i}Pr) (19 mM) with Bu$_4$NBF$_4$ (0.2 M).

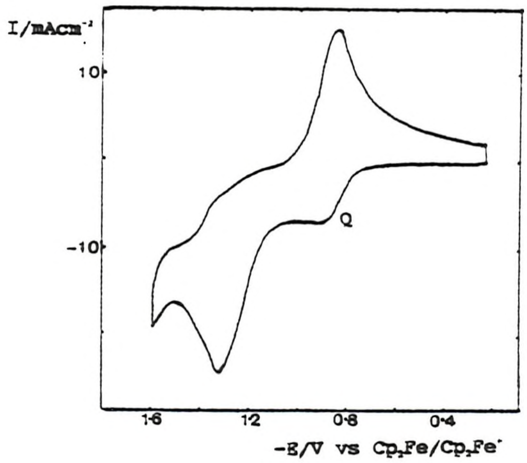


Fig. 4.7f

Cyclic voltammogram recorded at 150 mVs^{-1} between −0.2 and −1.6 V vs ferrocene for a THF solution of CpTiCl$_2$(O^{i}Pr) (19 mM) with Bu$_4$NBF$_4$ (0.2 M).

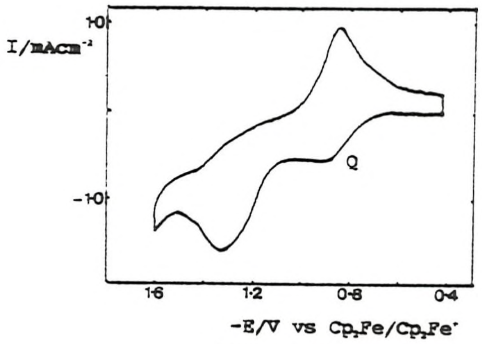


Fig. 4.7g

Cyclic voltammogram recorded at 150 mVs^{-1} between −0.2 and −1.6 V vs ferrocene for a THF solution of CpTiCl$_2$(O^{i}Pr) (19 mM) with Bu$_4$NBF$_4$ (0.2 M).

4.8 Comparison of, and mechanism for, the electrochemical behaviour of $CpTiCl_2(OR)$ complexes.

The cyclic voltammograms obtained for each of the three $CpTiCl_2(OR)$ complexes clearly show definite similarities indicating that the mechanism of the reduction and oxidation processes in each case is the same.

The $Ip/\nu^{\frac{1}{2}}c$ ratio for the first major reduction peak for each complex has been calculated (table 4.8a) from the plots shown in figures 4.8a, b and c. The fact that the three values are almost identical indicates that the same number of electrons are involved in each reduction and this is independent of whether the product is stable. It will be assumed that this number is one.

cv fig.	complex	sweep rate (mVs^{-1})	$-Ep^c$ (V)	ΔEp (mV)	$Ip^c/\nu^{\frac{1}{2}}c$	Ip^a/Ip^c
4.5e	$CpTiCl_2$-[$OPh(^iPr)_2$]	300	1.16	60	17.7	0.7
4.6f	$CpTiCl_2$-(menthoxide)	300	1.36	60	17.0	0.5
4.7e	$CpTiCl_2$-(^iOPr)	300	1.32	-	18.6	-

Table 4.8a

Table 4.8a; all potentials are quoted against ferrocene as an internal reference.

Using figures 4.5a and 4.5b, scheme **XV** describes a basic mechanism to account for the major reduction peak (**F**), its coupled oxidation peak (**F'**), the other oxidation peak (**H**) and the other reduction peak (**J**) seen at more negative potentials than **F**, which is only really prominent when **F'** is small or absent.

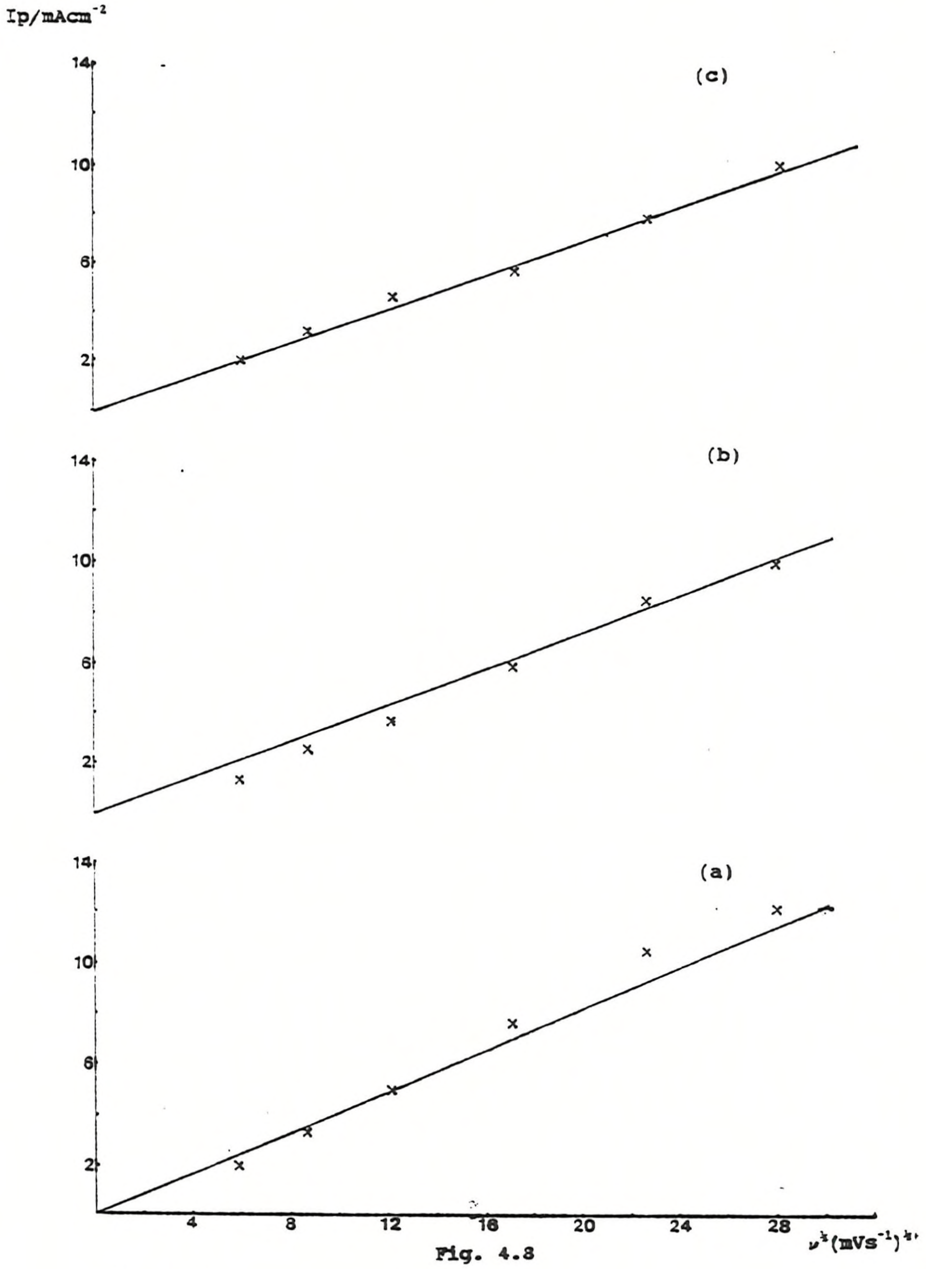
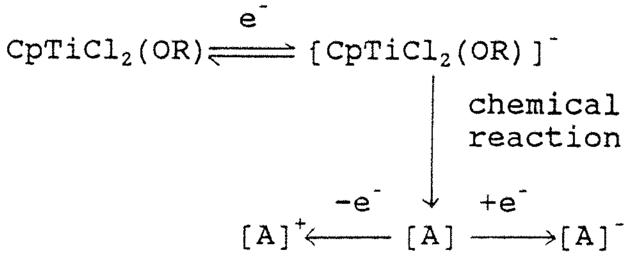


Fig. 4.8

Plot of Ip vs $\nu^{1/2}$ for the major reduction peak in the cyclic voltammetry of THF solutions of a) CpTiCl$_2$[OPh(^{i}Pr)$_2$] (23 mM), b) CpTiCl$_2$(menthoxide) (22 mM), c) CpTiCl$_2$(O^{i}Pr) (19 mM).



Scheme **XV**

In order to simplify the discussion to will be assumed that the major reduced species is the anion $[CpTiCl_2(OR)]^-$ and that any loss of Cl^- from this is a wholly reversible process. It is impossible from the data available, to ascertain whether this really is the case or not.

The reversible one electron transfer process; $CpTiCl_2 \rightleftharpoons [CpTiCl_2]^-$ gives rise to the couple **F/F'**. $[CpTiCl_2(OR)]^-$, however, is not perfectly stable and undergoes a chemical reaction producing compound [A]. When the potential is swept to more negative values peak **J**, corresponding to the reduction of [A] is seen. Because [A] is not as easily reduced as $CpTiCl_2(OR)$, the major reduction peak is not an ece process. An ece process involves the product of the chemical reaction undergone by the initial reduced species, [A] in this case, being at least as readily reduced as the starting compound, $CpTiCl_2$ here.(53) Peak **H**, corresponding to the oxidation of [A] is observed on the anodic sweep.

The chemical reaction of the reduced species varies in rate between the three complexes. This can be seen by comparing the cyclic voltammograms shown in figures 4.5e ($CpTiCl_2[OPh(^iPr)_2]$), 4.6f ($CpTiCl_2$(menthoxide)) and 4.7e ($CpTiCl_2(O^iPr)$). The anodic peak of the reversible couple decreases in size from **F'** (fig. 4.5e) to **K'** (fig. 4.6f) and is non-existent for **P'** (fig. 4.7e), although **P'** is just visible at 3 Vs^{-1}. At the same time the size of the second anodic peak corresponding to the oxidation of [A] (the product of the chemical reaction of $[CpTiCl_2(OR)]^-$) increases from **H** (fig. 4.5e) to **M** (fig. 4.6f) to **R** (fig. 4.7e) where it is the only anodic peak observed. This leads to the conclusion that the rate of reaction $[CpTiCl_2]^- \rightarrow [A]$ decreases for the three $CpTiCl_2(OR)$ systems in the order:

$$CpTiCl_2(O^iPr) > CpTiCl_2(\text{menthoxide}) > CpTiCl_2[OPh(^iPr)_2]$$

Table 4.8b shows the rate constants calculated from a plot of Ip^a/Ip^c vs log $k\tau$ (τ is the time taken to scan from $E_{½}$ to the sweeping potential),(53) and supports the trend shown above.

	$CpTiCl_2[OPh(^iPr)_2]$	$CpTiCl_2$(menthoxide)	$CpTiCl_2(O^iPr)$
k (s^{-1})	0.2	0.8	>4.0

Table 4.8b

At higher concentrations of $CpTiCl_2[OPh(^iPr)_2]$ (fig. 4.5b) peaks **H** and **J** are small, indicating that $[CpTiCl_2[OPh(^iPr)_2]^-$ is quite stable. This stability seems to diminish at lower concentrations since **H** and **J** are more prominent and **F'** has disappeared (fig. 4.5a).

A similar pattern is seen with the $CpTiCl_2$(menthoxide) system. The cathodic peak **N**, corresponding to the reduction $[A] \rightarrow [A]^-$ is more prominent for the lower concentration experiment (fig. 4.6e). At higher concentrations (fig. 4.6d) peak **N** does clearly decrease and can only just be noticed as a shoulder on peak **K**. The $CpTiCl_2(O^iPr)$ system also displays similar behaviour (figs. 4.6c & d).

If the chemical reaction that occurs with the major reduced species involves attack of either the solvent or the electrolyte on $[CpTiCl_2(OR)]^-$, the rate of reaction would be first order with respect to $[CpTiCl_2(OR)]^-$ and the rate would therefore be higher for a higher concentration of $CpTiCl_2(OR)$. This is the opposite to what is observed. The concentration dependence that is observed indicates that the reaction of $[CpTiCl_2(OR)]^-$ involves something that is there in low concentration. Even though steps were taken to make the conditions as dry as possible the solutions may still contain trace amounts of water. Samuel and Vedel(46) report that trace amounts of water in THF, which cannot be removed by conventional chemical treatment, affect the results of their studies on Cp_2TiCl_2.

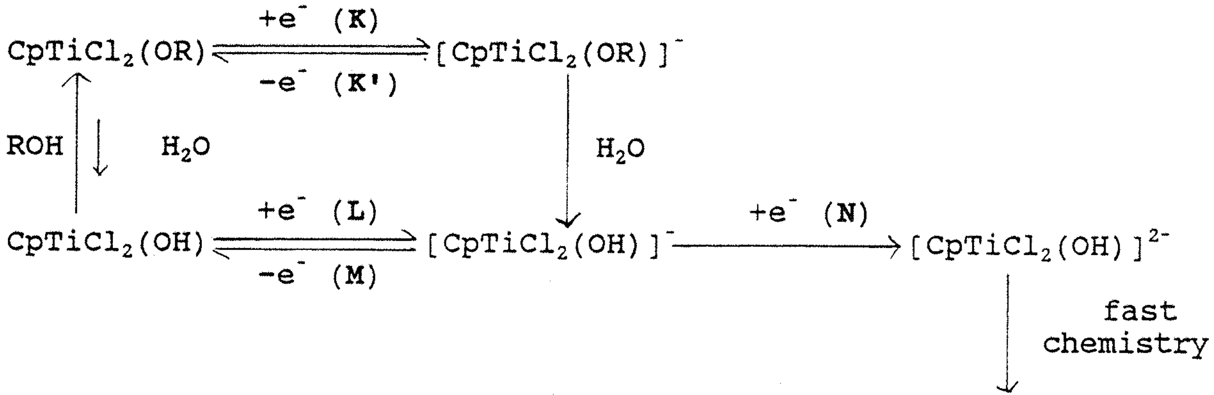
Another feature of all these cyclic voltammograms is the presence of a small cathodic peak which occurs at less negative potentials than the major reduction peak; at around -0.86 V in each case. This indicates that the starting species undergoes a chemical reaction, the product of which is the same for each of the complexes and is in low concentration (hence the small peak) and is more easily reduced than the starting species. This "extra" cathodic peak displays certain characteristics:

i. It appears relatively large when the $[CpTiCl_2(OR)]^-$ ion is unstable, ie, when the major reduction peak has little or no reverse anodic peak. For example, the ratio **F/G** (fig. 4.5a) is ≈3 where no **F'** peak is seen, whereas the same ratio is ≈12 (fig. 4.5b) where **F** is clearly present.

ii. When relatively large it shows a sweep rate (ν) dependence (figs. 4.7a, e, f & g), but not a $\nu^{\frac{1}{2}}$ dependence indicating that the process to which it corresponds is not wholly diffusion controlled.

iii. When small it is independent of sweep rate (figs. 4.5c, e, f & g).

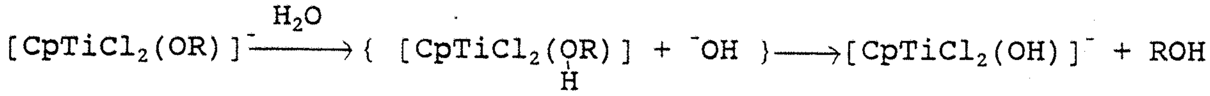
Scheme **XVI** shows a possible mechanism to account for the observations made, the $CpTiCl_2$(menthoxide) system (figs. 4.6a-f) is used as an example.



Scheme **XVI**

The major electron transfer process is the one electron reduction (peak **K**) of $CpTiCl_2(OR)$ to the monoanion. This would appear to be a wholly reversible process but for the chemical reactions that occur due to the presence of water.

The $[CpTiCl_2(OR)]^-$ anion is unstable in the presence of water and reacts to form $[CpTiCl_2(OH)]^-$. This reaction is likely to proceed via protonation of the alkoxy ligand then exchange between this and ^-OH (Eq 15). This hydroxy anion can be further reduced (peak **N**), if potentials are swept far enough, to the dianion which undergoes rapid chemistry so no coupled anodic peak is seen. The oxidation of the hydroxy anion back to $CpTiCl_2(OH)$ is represented by peak **M**. The slower the sweep rate the more chance water has of reacting with the $[CpTiCl_2(OR)]^-$ so the larger the oxidation peak (**M**) of $[CpTiCl_2(OH)]^-$ appears (fig. 4.6b). Also the lower the concentration of $CpTiCl_2(OR)$ the more marked the effect of water is and so electron transfer processes involving the product of the chemical reaction (peaks **N** and **M**) are more dominant (fig. 4.6e)



$$[CpTiCl_2(OR)]^- \xrightarrow{H_2O} \{\ [CpTiCl_2(\underset{H}{O}R)] + {}^-OH\ \} \longrightarrow [CpTiCl_2(OH)]^- + ROH$$

Eq 15

The water in solution also reacts with the starting species, forming the hydroxide complex, $CpTiCl_2(OH)$, but the equilibrium lies well towards $CpTiCl_2(OR)$ (Eq 16). This hydroxide complex is more readily reduced than the alkoxide and so a reduction peak (**L**) is observed at less negative potentials than **K**. This reduction peak appears larger when the $[CpTiCl_2(OR)]^-$ anion is less stable, ie when the anion is more readily attacked by water. It is likely that the more the anion is susceptible to attack by water then the more the neutral species is also, so this reduction peak (**G**, **L** or **Q**) is larger for the most unstable species. The rate of reaction of the alkoxy anion with water went in the order $[CpTiCl_2(O^iPr)]^-$ > $[CpTiCl_2(menthoxide)]^-$ > $[CpTiCl_2[OPh(^iPr)]]^-$. The ratios Ip^Q/Ip^P (fig. 4.7e), Ip^L/Ip^K (fig. 4.6f) and Ip^G/Ip^F (fig. 4.5e) also descend in this order (0.13, 0.05 & 0.04 respectively) supporting the argument that $CpTiCl_2(O^iPr)$ is the most unstable to water and $CpTiCl_2[OPh(^iPr)]$ the least.

$$\mathrm{CpTiCl_2(OR)} \overset{H_2O}{\rightleftharpoons} \mathrm{CpTiCl_2(OH)} \qquad \text{Eq 16}$$

The first reduction peak at -0.86 V vs ferrocene shows the classical behaviour for a ce reaction (scheme **XVII**)$^{(53)}$. When the rate of reaction (Eq 16) is slow only a small peak is observed and is independent of scan rate (peak **G**, figs. 4.5), but when the rate increases the peak becomes larger and displays a sweep rate dependence (peak **Q**, figs. 4.7).

ce reaction:

$$\mathrm{CpTiCl_2(OR)} \overset{H_2O}{\rightleftharpoons} \mathrm{CpTiCl_2(OH)}$$

$$\mathrm{CpTiCl_2(OH)} \pm e^- \rightleftharpoons \mathrm{[CpTiCl_2(OH)]^-}$$

$CpTiCl_2(OR)$ is not electroactive in the potential range of interest but is in equilibrium with $CpTiCl_2(OH)$ which is.

Scheme **XVII**

Peak **M** always has a greater current density than **L** because more $[CpTiCl_2(OH)]^-$ forms once $[CpTiCl_2(OR)]^-$ is present. If **L** and **M** are coupled reduction and oxidation processes then it would not be unreasonable to expect the current density of **L** to reach that of **M** on a repetitive scan. Figure 4.6c shows that this is not the case, **L** remains constant in size. This is due to the fact that once $CpTiCl_2(OH)$ has been formed (after peak **M**), in the presence of ROH, it reacts to give the starting material, $CpTiCl_2(OR)$, again. This reaction is in equilibrium and the re-establishment of this equilibrium is faster than the time it takes to sweep from **M** to **L** at a sweep rate of 300 mVs^{-1}. At faster sweep rates, with repetitive sweeps, an increase in **L** may be observed.

4.9 Further Work.

To examine the validity of the mechanism proposed in scheme **XVI** it will be necessary to do the experiments under perfectly dry conditions. Samuel and Vedel$^{(46)}$ dried their THF/Bu_4NPF_6 solution by electrolyzing it with a cathodic current for about two hours prior to use. If experiments under perfectly dry conditions produce cyclic voltammograms for each complex displaying a wholly reversible one electron transfer with no other cathodic or anodic peaks anywhere in the potential region of this transfer, then work must move on to using solutions containing a known amount of water. Solutions with equal concentrations of complex and water should be subjected to cyclic voltammetry experiments. If all the complex reacts with all the water then a cyclic voltammogram containing peaks corresponding to the oxidation and reduction of $CpTiCl_2(OH)$ only should be obtained. Isolation of $CpTiCl_2(OH)$ from the reaction of $CpTiCl_2(OR)$ with water would give further evidence to support scheme **XVI**.

It is proposed to investigate the electrochemical behaviour of $CpTiCl_2$(aminoalcohol) complexes, symmetric and asymmetric, once they have been isolated.

An investigation into the behaviour of electrochemically generated $[CpTiCl_2(OR)]^-$ with organic molecules such as the dienes, diynes and enynes mentioned in section 1 is also proposed.

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