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**A STUDY OF SOME NOVEL CATIONIC
COMPLEXES OF THE GROUP 4 METALS AND
THEIR APPLICATIONS IN ZIEGLER-NATTA
CATALYSIS.**

Mark L. Butcher

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the degree of
Doctor of Philosophy.

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Declaration.

The work submitted in this thesis is my own and was conducted in the Chemistry Department at the University of Warwick. The X-ray crystallography was performed by Prof. Mary McPartlin, Dr. Ian Scowen (University of North London) and Dr. Michael Drew (University of Reading). The sections involving computer-based molecular modelling techniques were conducted with the aid of Dr Ramdas (BP International, Sunbury) and those containing polymerisation studies with the help of Mr. John Graham (BP International, Grangemouth).

Publications.

Cationic titanium(IV) complexes *via* halide abstraction from CpTiCl_3 : crystal and molecular structure of $[\text{CpTi}(\text{MeCN})_5][\text{SbCl}_6]_3 \cdot 2\text{MeCN}$.

G R Willey, M L Butcher, M McPartlin, and I J Scowen, *J. Chem. Soc., Dalton Trans.*, 1994, 305.

Halide abstraction reactions of antimony(V) chloride and CpMCl_3 (M = Zr, Hf): crystal and molecular structure of $[\text{CpHf}(\text{MeCN})_6][\text{SbCl}_6]_3$.

G R Willey, M L Butcher, M McPartlin, and I J Scowen, *J. Chem. Soc., Dalton Trans.*, (manuscript in preparation).

Abstract.

The reactions between antimony(v) chloride and the monocyclopentadienyl metal trichlorides of Group 4 (CpMCl_3 for $M = \text{Ti, Zr and Hf}$) in acetonitrile solution have afforded new hexachloroantimonate salts. These cationic metal-containing products have been isolated and characterised using IR, ^1H NMR, elemental analysis, and in two cases, X-ray crystallography. The analogous pentamethylcyclopentadienyl (Cp^*) systems have also been investigated, with largely similar results.

Depending on the stoichiometry employed in the reaction, the relevant *mono-*, *di-* and *tri-*cationic complexes can be formed *via* halide exchange. For the $\text{Cp/Cp}^*\text{TiCl}_3$ series, a 1:1 or 2:1 ratio of $\text{Sb}:\text{Ti}$ affords $[\text{CpTiCl}_2(\text{MeCN})_3][\text{SbCl}_6]$ and $[\text{CpTiCl}(\text{MeCN})_4][\text{SbCl}_6]_2$ respectively. A ratio of 1:6 is required to yield pure $[\text{CpTi}(\text{MeCN})_5][\text{SbCl}_6]_3$. The 16-electron, pseudo-octahedral geometry of the latter complex was confirmed by X-ray analysis.

A similar situation is found in the analogous Zr and Hf cases. However, the formation of the triply-charged complexes is accompanied by an expansion in coordination number about the metal centre; X-ray crystallographic studies revealed the 18-electron $[\text{CpZr}(\text{MeCN})_6][\text{SbCl}_6]_3$ to exhibit a pseudo-pentagonal bipyramidal geometry.

The reactivity of the CpTi^{3+} salt towards a variety of both neutral and anionic species has been investigated. In acetonitrile solution, the complex reacts with amines to give insoluble mixtures of partially substituted products. Adduct formation with ethers and trimethylphosphine is slow and only occurs when non-coordinating solvents are employed. The complex reacts with inorganic salts to reform neutral CpTiX_3 compounds by simple anion exchange.

The Ziegler-Natta catalytic activity of the cationic series has been studied. In the presence of methylaluminumoxane cocatalysts, the complexes polymerise ethene but their activity is inversely proportional to the charge on the metal.

Abbreviations

Cp	cyclopentadienyl
Cp*	pentamethylcyclopentadienyl
Cp'	methylcyclopentadienyl
Ind	indenyl
hal	halogen
M	metal
R	alkyl, aryl
Me	methyl
Bu	butyl
Ph	phenyl
$^{15}\text{O}_5$	1,4,8,11,13-pentaoxycyclopentadecane
THF	tetrahydrofuran
THT	tetrahydrothiophene
acac	acetylacetonate
hfac	hexafluoroacetylacetonate
bipy	bipyridyl
tmeda	tetramethylethylenediamine
MAO	methylaluminoxane
2-MP	2-methylpropane
IR	infra-red
NMR	nuclear magnetic resonance
UV	ultraviolet
MW	molecular weight
MWD	molecular weight distribution
MI	melt index
MO	molecular orbital
PE	potential energy

CHAPTER 1:

INTRODUCTION

1.1: The chemistry of titanium, zirconium and hafnium.

The chemistry displayed by the Group 4 elements and their compounds is wide and varied. It is not possible to give an extensive review which covers all aspects of early transition metal chemistry in this report. For this reason, the properties of titanium, zirconium and hafnium have only been examined in a general sense, being introduced to the text where appropriate. An excellent overview of Group 4 chemistry is provided in the relevant sections of the standard texts by Cotton and Wilkinson,^{1a} and Greenwood and Earnshaw.^{1b}

Titanium, zirconium and hafnium are generally regarded as the first of the transition metals. The low effective nuclear charge of the elements results in the predominance of the maximum oxidation state, i.e. M(IV). However, complexes of M(III) and, to a lesser extent, M(II) are also well known. Recent work, particularly by Ellis *et al*,² has demonstrated that even lower oxidation states can be formed under suitable conditions; a series of complexes based on the M(II), (0), (-1) and (-2) configuration have been stabilised by the use of strong π -acceptor ligands such as carbonyls and phosphines.

As the ionisation energy required to form the M^{4+} ion is so high [Ti (91.1), Zr (77.4), Hf (79.4 kJ mol⁻¹)], compounds are essentially covalent in nature although cationic species are known. The synthesis of this latter class of complex forms the main subject of this project. The M(IV) oxidation state behaves as a hard Lewis acid³ and consequently there is a predominance of complexes containing similarly hard basic ligands (O- and N-donors). Softer ligands (S-, P-, and As-donors) are more usually found in lower valent metal species.

The variety in Group 4 chemistry is also evident in the geometry displayed in their compounds. As would be expected, the most common coordination number is 6 but a full range between 3 and 8 have been observed. Examples of complexes with various combinations of oxidation state and coordination number are given in the texts outlined above.

1.1.1: Titanium vs. zirconium and hafnium.

As within other groups of the transition metals, the second- and third-row elements are distinct from their 3d congeners. The main differences stem from the increase in atomic size (Table 1.1).

Table 1.1: The relative sizes of the Group 4 metals.

	atomic radius/ Å	ionic radius /Å
Ti	1.36	0.68
Zr	1.45	0.74
Hf	1.44	0.75

The effect of the lanthanide contraction on the size of atomic Hf is well illustrated by these figures. This results in Zr and Hf enjoying very similar chemical properties. In general, equivalent complexes of Zr and Hf are isostructural and only show slight differences in aspects such as solubility or melting point.

The larger, less polarising elements have more basic oxides and a complex aqueous chemistry (their compounds possess a greater resistance to hydrolysis). There are also many examples of high coordination numbers in the complexes of Zr and Hf.

In contrast to Ti, the M(III) state is limited to non-aqueous conditions for Zr and Hf as water is readily reduced. Most examples of this oxidation state are found in complexes which contain the cyclopentadienyl ligand. The greater ease of reduction of Ti(IV) is demonstrated by differences in chemical behaviour. An example of this is found in the reaction of Cp_2MCl_2 with LiPPh_2 ; Ti affords $[\text{Cp}_2\text{Ti}(\text{PPh}_2)]_2$ whereas Zr yields $[\text{Cp}_2\text{Zr}(\text{PPh}_2)_2]$.⁴

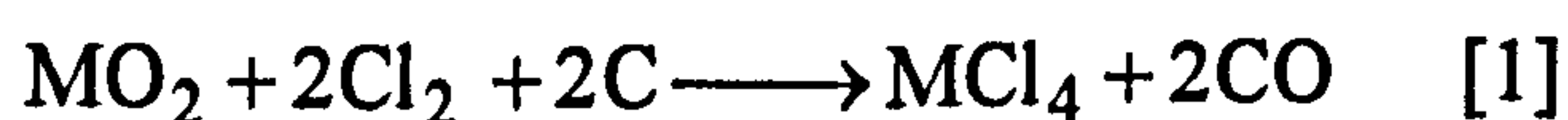
1.2: The Group 4 halides.

Of the compounds of Group 4, the most chemically versatile are those which contain (metal-halogen) bonds. Such species are found in a variety of oxidation states both in binary form and more complex systems. However, it is those based on M(IV) which are of special interest; they are excellent starting materials for a huge range of compounds.

1.2.1: The tetrahalides (MCl₄).

The 12 parent compounds are all well characterised. In the gas phase⁵ they share a monomeric, tetrahedral structure. At first glance their stability is somewhat surprising since this configuration implies an 8-electron count. In fact there is a considerable amount of *pπ-dπ* character involved in the (M-Hal) bond.

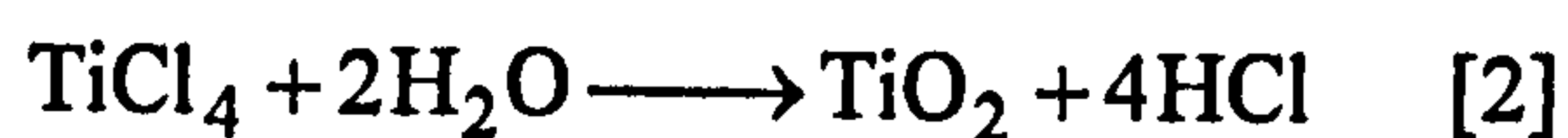
Of the various halogeno species, it is the tetrachlorides that are most useful and widely studied. They can be prepared in a number of ways, but usually the metal oxide is treated with chlorine gas at elevated temperatures (*ca.* 900 °C) in the presence of a reducing agent such as charcoal [equation 1].



The other halides can then be prepared by treating the relevant tetrachloride with the appropriate hydrogen halide.

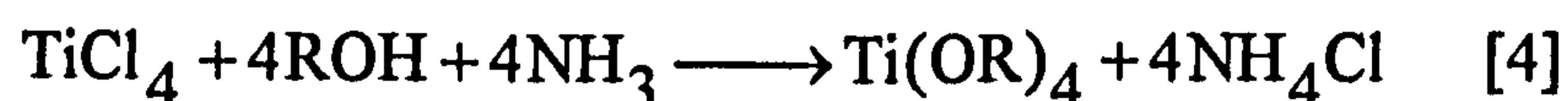
In contrast to the Zr and Hf analogues, TiCl₄ is a liquid at room temperature. In the solid state, ZrCl₄ and HfCl₄ are polymeric with zigzag chains of edge-sharing [MCl₆] octahedra;⁶ TiBr₄ retains its tetrahedral structure due to its smaller size.⁷

All of the tetrahalides are extremely hygroscopic and are readily hydrolysed. In air, TiCl_4 fumes to form TiO_2 [2], whereas ZrCl_4 and HfCl_4 afford their stable oxychlorides [3].



These reactions give an insight to the reasons why the normal salts of Ti(IV) cannot be prepared from aqueous solutions. Even with Zr(IV) and Hf(IV), highly acidic conditions are required to form salts such as $\text{Zr}(\text{NO}_3)_4$.

Other solvolytic reactions are also common to the tetrachlorides. Various compounds containing protic hydrogens, such as alcohols and amines react with TiCl_4 with the condensation of HCl. However, a HCl scavenger is normally employed to ensure complete reaction [4].



Group 4 halides are generally powerful Lewis acids and as such have found uses as catalysts in many organic syntheses.⁸ The tetrachlorides form adducts with a range of neutral ligands such as THF,⁹ MeCN,¹⁰ PPh_3 ,¹¹ and 1,4-thioxane,¹² although Zr and Hf show a high preference for O- and N- donors. These adducts are normally octahedral *cis*- MCl_4L_2 species; the mono-adducts form dimers with chloride bridges.

Complexes are also formed in a reaction with halide anions. The hexachloro salt, $\text{K}_2[\text{TiCl}_6]$,¹³ has been characterised as have the Zr and Hf analogues. However, the latter compounds are much more difficult to prepare.

Similar fluorozirconates and fluorohafnates can be prepared but display considerable variety; anions up to $[\text{MF}_8]^{4-}$ have been recovered.

The tetrachlorides provide an excellent route to lower valent metal species. Most examples of Zr(III) and Hf(III) complexes are prepared *via* the reduction of MCl_4 . In fact, TiCl_3 is prepared by the reaction of TiCl_4 with H_2 gas at high temperature [5].



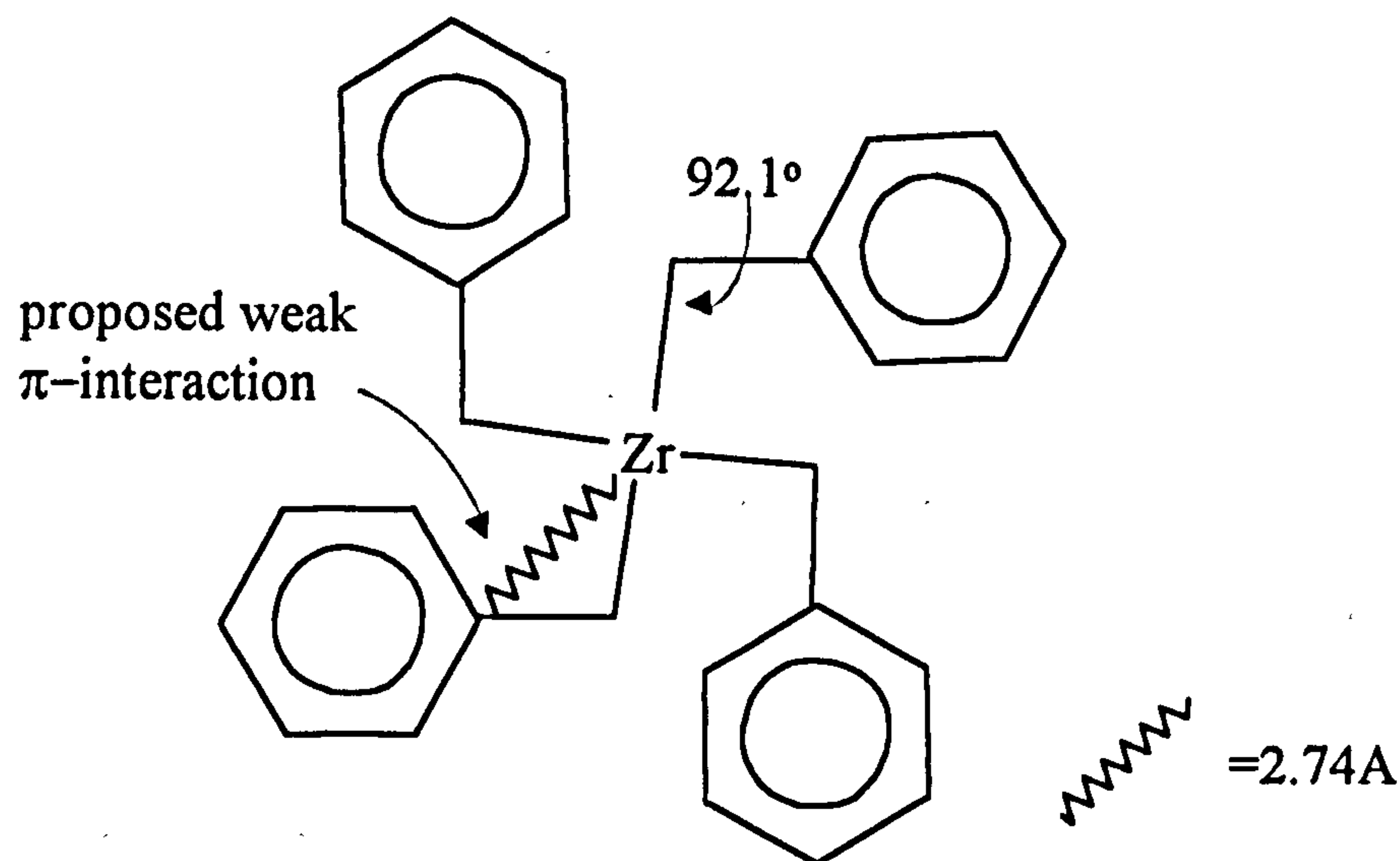
However, for the purposes of this thesis, the most relevant quality of the tetrachlorides is the ease with which they can be used in the synthesis of organometallic compounds. Indeed, the (M-Cl) bond provides the starting point for the synthesis of a large range of metal derivatives. For this reason, almost all of the halide systems covered from this point forward will be chloride derivatives.

1.3: The organometallic chemistry of Group 4.

Before the 1950s this area of chemistry for Ti, Zr and Hf was largely unexplored. Early experiments had not anticipated the sensitive nature of their target compounds. Research interest in general organometallic chemistry was then spurred by two landmark discoveries; the polymerisation of ethene over a $\text{TiCl}_3\text{-AlEt}_3$ catalyst, and the isolation of ferrocene. Improved handling procedures for air- and thermally-sensitive materials eventually resulted in the expansion of Group 4 organometallic chemistry. The commercial importance of such work prompted an explosion of research interest; according to Cardin *et al*,¹⁴ by 1984 the number of well characterised organo-Zr and -Hf compounds alone exceeded 1700.

Early synthetic studies, such as the preparation of TiMe_4 (which decomposes above -40°C),¹⁵ lead to the belief that the (M-C) σ -bond was intrinsically weak. However, it is now generally agreed that it is not the relative bond strength that is the cause of thermal instability in such compounds: studies have revealed that their sensitive nature is due to the combination of high electron deficiency with low energy pathways to decomposition. This theory is well illustrated by the synthesis of the $\text{M}(\text{CH}_2\text{Ph})_4$ series.¹⁶ On close inspection of the $\text{Zr}(\text{CH}_2\text{Ph})_4$ structure,¹⁷ it is clear that the non-perfect tetrahedral angle in the methylene groups serve to help stabilise the metal centre; extra electron density is gained from a weak π -interaction with the benzene ring (Figure 1.1). Perhaps more importantly, the steric bulk of the ligands provides excellent protection to the Zr centre.

Figure 1.1: Diagrammatic description of $\text{Zr}(\text{CH}_2\text{Ph})_4$.



In a series of experiments, Lappert *et al*¹⁸ decided to investigate the synthesis and characterisation of homoleptic alkyls of several metals across the periodic table. In the review of this work, it was concluded that there are various mechanisms which contribute to (M-C) bond decomposition. For the Group 4 compounds, the most prevalent of these involves β -hydrogen elimination from the alkyl group. With this in mind, a number of stable complexes containing R-groups without protons in the β -position have been prepared. These include $\text{M}(\text{CH}_2\text{CMe}_3)_4$, $\text{M}(\text{CH}_2\text{SiMe}_3)_4$ and heteroleptic derivatives such as $\text{Zr}[\text{CH}(\text{SiMe}_3)_2]_3\text{Cl}$.¹⁹

The number of Group 4 organometallic compounds which contain π -bonded C-donors is very large thanks to the use of cyclopentadienyl-based ligands. However, apart from these anionic "multi-dentate" ligands, simple π -bonding interactions between neutral species and the Group 4 metals are rare. This type of (M-L) bonding is only observed in lower valent metal complexes such as the series of arene and diene derivatives prepared by Green *et al*.²⁰

1.3.1: The Cyclopentadienyl Ligand, "Cp⁻."

Any ligand which can supply large amounts of electron density will form strong bonds with the electron deficient metals of Group 4. Formed by the deprotonation of cyclopentadiene, the aromatic cyclopentadienide anion (C₅H₅⁻ or Cp as it is commonly referred to) is an excellent example of such a ligand; up to 6 π -electrons are available for donation to a metal centre.

In addition to this electronic effect, the steric bulk of the 5-membered ring also infers stability. Consequently, compounds containing at least one (M-Cp) moiety have been extensively used for the Group 4 elements; derivatives are much more stable towards heat and air/moisture hydrolysis.

As would be expected, the most stable bonding mode of a Cp ring with the early transition metals is that involving η^5 -donation. In this configuration each carbon atom is equidistant from the metal centre. This is often called the π -bonding mode for obvious reasons. However, other configurations are known, notably the η^1 -mode which basically involves a (M-C) σ -bond. This latter arrangement is only found in complexes which contain acute steric constraints.

1.3.2: Substituted Cp groups.

If the hydrogen atoms of the Cp ring are substituted for other groups, the chemistry of any subsequent metal complex may be very different. Substituents are usually alkyl groups but others such as halogens, cyanides and even metals have been reported. An important class of compounds is derived from the indenyl anion which can be described as a Cp ring fused to a benzene molecule.

Not surprisingly it is complexes which contain *pentasubstituted* Cp rings which show the most significant changes in chemical properties. The most widely used of this type of ligand is pentamethylcyclopentadiene (henceforth Cp*).

The substitution of Cp* for Cp in transition metal complexes generally results in changes in reactivity, solubility, sensitivity to redox and ease of recrystallisation; these changes are usually for the better. For example, the dimeric complex $[\text{RhCpCl}_2]_2$ is known to be amorphous, highly insoluble and its (Rh-Cl) bond is easily cleaved. By comparison, the Cp* analogue, $[\text{RhCp}^*\text{Cl}_2]_2$, is stable and, following facile recrystallisation, its crystal structure has been determined.²¹

The reasons for these changes derive from both steric (due to the large shielding nature of the Cp* ring) and electronic factors. The molecular orbital bonding model breaks the (M-Cp*) interaction into 3 components:²²

- a) A σ -bond from the full A orbitals on the ring to an empty metal d-orbital,
- b) Two orthogonal π -bonds from the donation of 2 orthogonal E_1 orbitals into empty d-orbitals on the metal,
- c) Up to 2 orthogonal δ -bonds from back donation from the metal to the empty E_2 ring set.

Replacing the Cp hydrogens with electron-withdrawing substituents such as halogens has the effect of decreasing the electron density of the A and E_1 orbitals; the (M-Cp) bond is therefore reduced in strength. This point is well illustrated by the reaction of FeCl_2 with pentacyanocyclopentadienide, $[\text{C}_5(\text{CN})_5]^-$: instead of the expected ferrocene analogue $[\eta^5\text{-C}_5(\text{CN})_5]_2\text{Fe}$, the highly unstable, ionic iron(II) pentacyanocyclopentadienide $[\text{C}_5(\text{CN})_5]_2\text{Fe}$ is recovered.²³

Conversely, when electron releasing substituents (such as methyl groups) are bonded to the ring, increased electron density in the A and E orbitals results in a stronger metal-ring interaction. This view of the stabilising effect is very simplistic. A number of more detailed experiments have been reported which attempt to give a more quantitative view of the effect. These include MO

calculations,²⁴ PE spectroscopy,²⁵ ESCA studies,²⁶ cyclic voltammetry,²⁷ and NQR measurements.²⁸

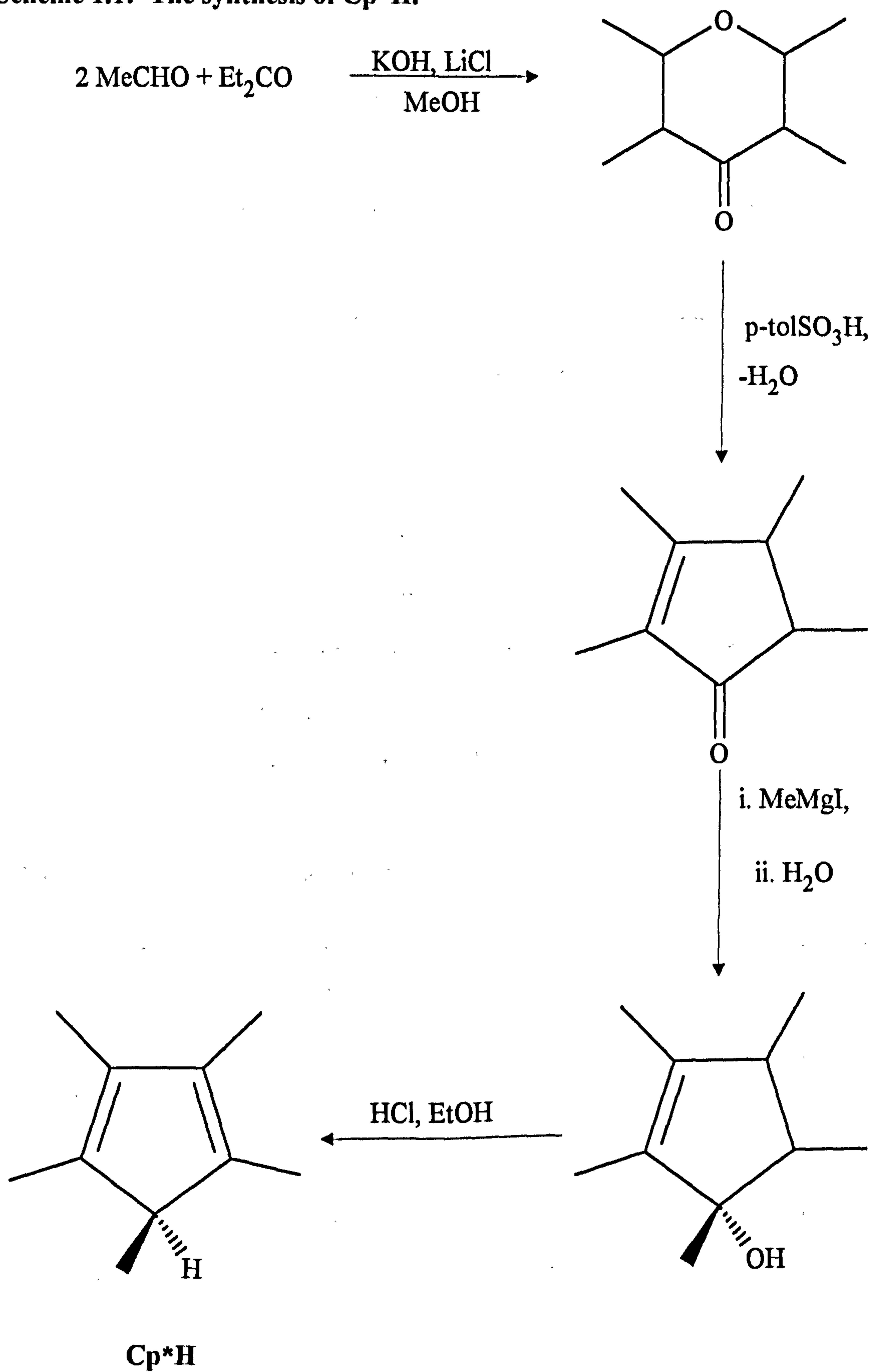
PE spectroscopy is used to measure the core and valence ionisation potentials, which allows for the separation of the various inductive and orbital overlap effects. The shifts in the valence ionisation energies on the methylation are comparatively large, thus showing that the electronic effects are at least as important as the steric influences.

In the ESCA study, a series of Group 4 metallocene derivatives (Cp_2MX_2 , where $\text{Cp} = \text{C}_5\text{H}_5$, C_5Me_5 or mixtures of both and $\text{X} = \text{halogen}$) were investigated. It was found that variation of the halide has no effect on the binding energies of the inner shell electrons. However, increased methylation of the ring has a drastic effect. The report concluded, "the substitution of two Cp^* ligands for Cp ligands has an electronic effect approaching that of a one electron reduction of the metal."

1.3.3: Preparation of Pentamethylcyclopentadiene, Cp^*H

The first convenient synthetic route was reported in 1960 by de Vries.²⁹ This method has gradually been fine-tuned to give better yields; the presently preferred scheme is shown in **Scheme 1.2**. This three step synthesis only gives small quantities of Cp^*H for the starting materials consumed,³⁰ but is still the pick of numerous other synthetic approaches.³¹ However, the most recent method published, which begins with a mixture of *cis*- and *trans*-but-2-ene,³¹ is a one-pot reaction and is said to proceed in a 50% yield. Unfortunately this synthesis has not been verified during the process of this study.

Scheme 1.1: The synthesis of Cp*H.



1.4: Cyclopentadienyl complexes of Group 4.

In the M(IV) oxidation state, Ti, Zr, and Hf can each accommodate up to four Cp rings. Again, the most useful complexes are those which also contain (Metal-Halogen) bonds. The combination of stabilising Cp groups and labile (M-Cl) bonds has resulted in a huge range of derivative chemistry. The following sections describe the four groups of Cp complexes. As this report centres on the CpMCl₃ series, a more detailed account is given for these complexes.

1.4.1: CpMCl₃.

The monocyclopentadienyl metal trichlorides are formally 12 electron compounds. They are all therefore, more reactive than their Cp₂MCl₂ counterparts. Nevertheless, the presence of the single ring does infer stability to the metal centre. Both Cp and Cp* analogues are known for all three elements; some of their properties are summarised in Table 1.2.

Table 1.2: Properties of the CpMCl₃ series.

Complex	colour	melting point / °C	structure ref
CpTiCl ₃	orange/yellow	208-211	piano stool ^{32, 33}
Cp*TiCl ₃	red	225-227	piano stool
CpZrCl ₃	white	237(d)	polymeric ³³
Cp*ZrCl ₃	white	subl.160/0.001Torr	polymeric
CpHfCl ₃	white	125(d)	polymeric
Cp*HfCl ₃	white	subl.140/0.001Torr	polymeric

The Ti compounds are coloured due to charge transfer from the chloride ligands. This is one of a number of differences between the Ti species and the heavier analogues. Firstly, the Ti compounds are only moderate Lewis acids. Adducts are only formed with a few powerful ligands (most examples are bidentate).³⁴ In contrast to this the Zr and Hf complexes are extremely good Lewis acids and their chemical behaviour is similar to the tetrachlorides. The 16-electron, octahedral adducts that are readily formed with a variety of ligands are easier to handle than their more electron deficient parents.

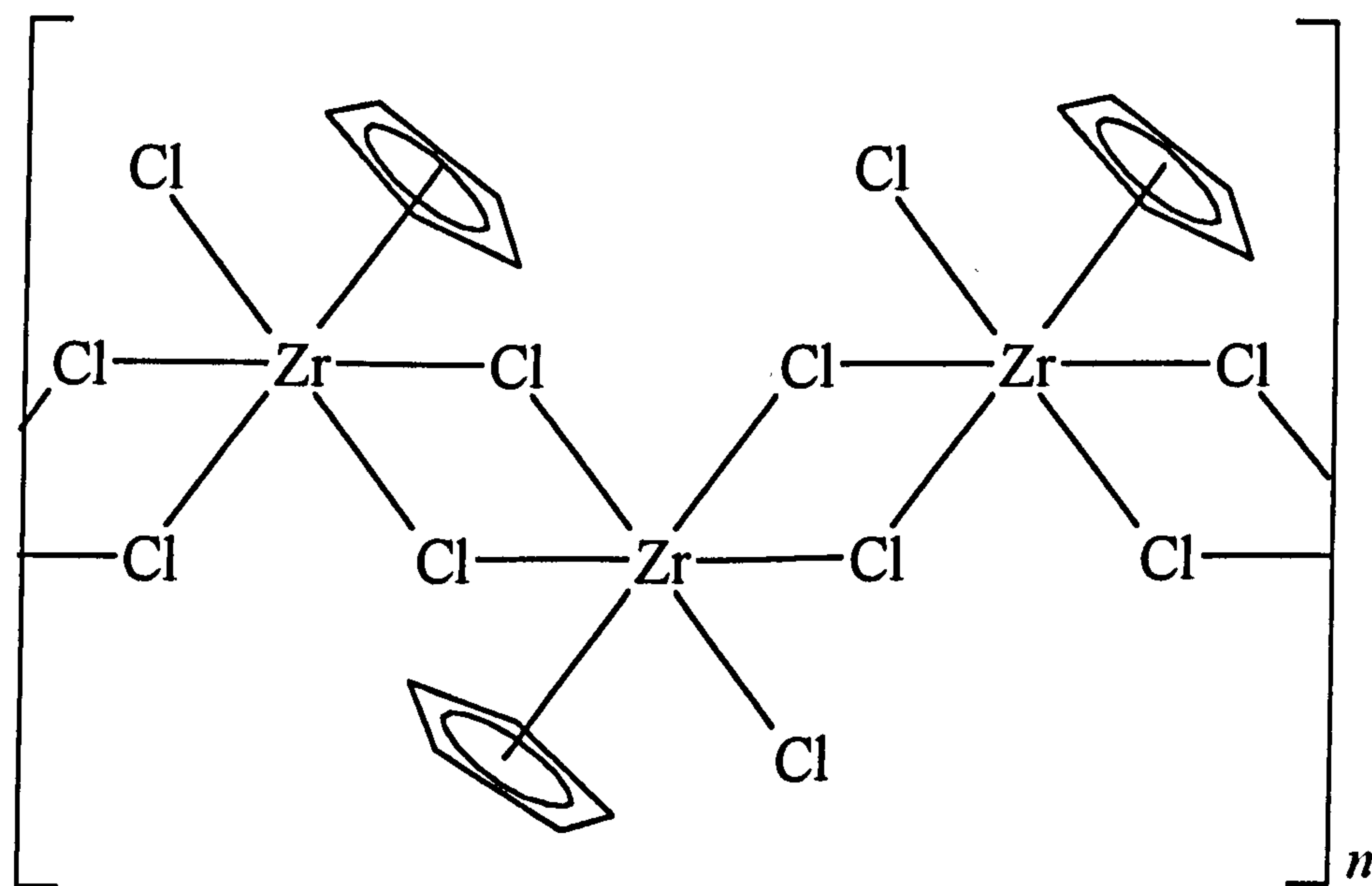
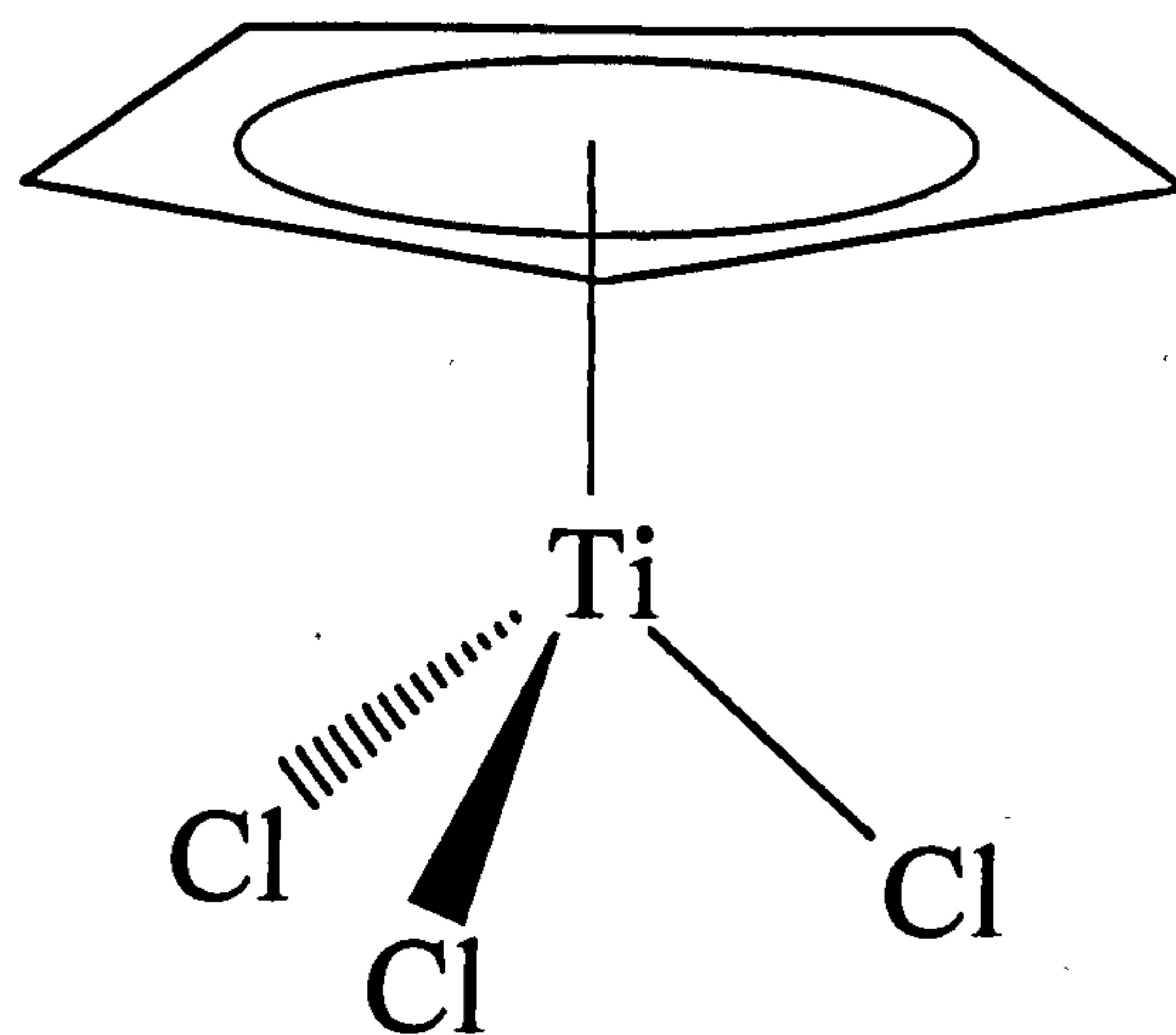
This difference in reactivity is reflected in the structures of the Ti and Zr compounds (Figure 1.2). Whilst the Ti species exhibits a monomeric, "piano-stool" geometry, the Zr structure is similar to that of ZrCl₄, involving edge sharing octahedra in a polymeric chain. This shows that there is a need for more than 12 electrons around these metal centres. The Ti complex must gain electron density from the full p-orbitals of the chlorine atoms in the form of π -bonds to gain stability.

It is only recently that the CpMCl₃ series could be prepared in analytically pure form in good yields. The problems arise because treatment of the tetrachlorides with the normal reagents (LiCp, NaCp, MgCp₂ etc.) results in the formation of the thermodynamically preferred Cp₂MCl₂ series, even when an excess of MCl₄ is employed.

Before 1980 the most convenient synthesis of CpTiCl₃ involved a redistribution reaction [6] between TiCl₄ and Cp₂TiCl₂.³⁵ The problem with this approach is the separation of the product from the reaction mixture; some of the starting materials always remain unchanged. Purification by sublimation seems to give the best results.



Figure 1.2: The structures of CpMCl_3 for Ti and Zr.



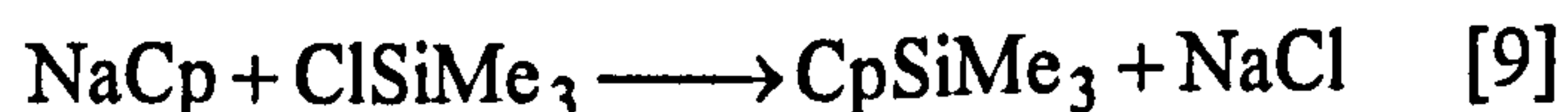
Another early method utilising Cp_2TiCl_2 is the displacement of one Cp ring with chlorine gas.³⁵ The problem with this approach is the control of the reaction; too much chlorine results in the displacement of both rings [7].



The publication of a new approach by Cardoso *et al*³⁶ greatly improved the synthesis of CpTiCl_3 . Their method involved the reaction of trimethylsilylcyclopentadiene (Me_3SiCp) with TiCl_4 [8]. This silicon based reagent was found to be a much milder source of the Cp^- anion. Monocyclopentadienyl metal chlorides of Ti, Nb and Ta were all recovered in excellent yield.



Other advantages of this approach include short reaction times and simple work-up procedures; as the by product ClSiMe_3 is a liquid, the complexes can simply be filtered from the reaction solvent. More importantly there is no formation of Cp_2TiCl_2 , regardless of conditions and reaction times. The CpSiMe_3 is easily prepared from NaCp [9].

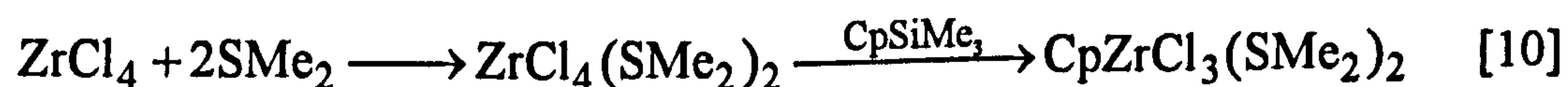


Shortly after Cardoso's breakthrough, Royo *et al*³⁷ applied the synthetic route to the Cp^*MCl_3 series. They found that using Cp^*SiMe_3 all three analogous compounds could be prepared in excellent yield. Previously the best way of preparing Cp^*TiCl_3 was by HCl oxidation of $\text{Cp}^*\text{TiCl}_2(\text{THF})$.³⁸ The latter is prepared using TiCl_3 and LiCp . Yields were low in this messy procedure.

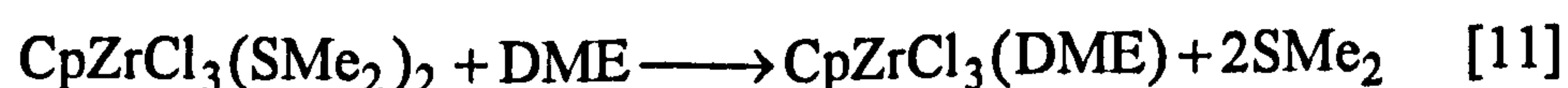
In the case of Zr and Hf, the higher stability of the M(IV) oxidation state permits the use of Cp*Li and MCl₄ in the preparation of the Cp*MCl₃ complexes.³⁹ The problem with this method is the separation of the product from the LiCl by-product: the required sublimation (160 °C, 10⁻⁴ Torr, 2 days) is accompanied by substantial decomposition.

In view of these preparations, it is somewhat surprising that the CpMCl₃ compounds for Zr and Hf could not be prepared using an analogous procedure. Before 1990, the most widely used method for the synthesis of CpZrCl₃ involved the free radical chlorination of Cp₂ZrCl₂.⁴⁰ Over-chlorination results in ZrCl₄ in this exacting preparation. The published synthesis of the Hf analogue was even worse. After the treatment of excess HfCl₄ with Cp₂Mg, the CpHfCl₃(THF)₂ adduct was recovered in only 25% yield.⁴¹ Purification involved multiple recrystallisations to be rid of the HfCl₄ and Cp₂HfCl₂ contaminants. It was therefore a bonus when Lund and Livinghouse⁴² modified Cardoso's procedure to include CpMCl₃ for Zr and Hf.

Lund and Livinghouse discovered that the addition of dimethylsulphide (Me₂S) to ZrCl₄ prior to the CpSiMe₃ resulted in the formation of CpZrCl₃(Me₂S)₂ in almost quantitative yields [10]. Without the Me₂S, the reaction results in a mixture of intractable solids.



A stronger ligand is then added (originally 1,2-dimethoxyethane, DME) to aid purification and isolation of a stable adduct of the desired complex [11].



The Hf analogue can be prepared in a similar fashion although it is necessary to employ the slightly more reactive tribuylstannylcyclopentadiene (CpSnBu₃) to supply the Cp ring. The use of this type of tin reagent has been reported before.⁴³

Reactions of CpMCl₃.

The reactions of this series can usually be labelled under one of three categories :

a) Adduct formation (mentioned previously),

b) HCl elimination,

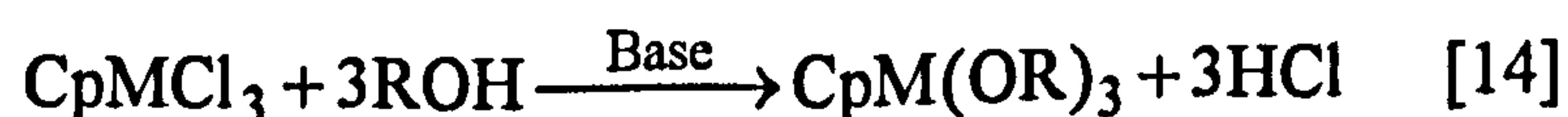


c) Salt elimination.



Perhaps the most important of these reactions is hydrolysis. Stringent anhydrous conditions have to be employed when performing syntheses so that any reaction with water is avoided. Controlled hydrolyses have been performed under a range of conditions for most of the CpMCl₃ series. Partial hydrolysis can result in discrete dimeric species with (M-O-M) bridges⁴⁴ whereas full, base catalysed hydrolysis gives complex metal-oxo cage structures whose exact configurations vary considerably depending on reactant and reaction conditions.^{45, 46}

Alcoholysis is another common HCl elimination reaction. In the presence of a base to act as scavenger for HCl, the CpMCl₃ series will react with alcohols to form either trisalkoxide [14] derivatives⁴⁷ or mixed halo-alkoxides [15].



Analogous complexes have also been reported for the thioalkoxides⁴⁸ but these are very air and heat sensitive.

By far the most important salt elimination reactions are those which are used in the preparation of metal alkyl species. Treatment of the Cp*MCl₃ series with lithium alkyls (LiR) results in some of the most stable Group 4 (M-R) complexes yet discovered [16].⁴⁹

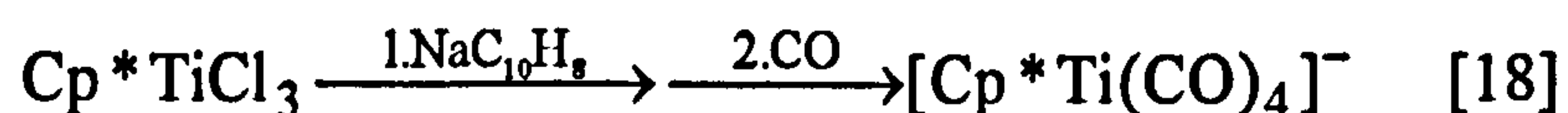


Similarly, if treated with Cp salts (LiCp, NaCp etc.) CpMCl₃ compounds go on to form the higher Cp₂MCl₂ range. This has been utilised in the synthesis of "mixed ring" metallocene based complexes. A good example of this is given in the publication of Rausch *et al*;⁵⁰ CpCp*TiCl₃ is prepared using Cp*TiCl₃ and TiCp, [17].



The salt elimination method is also used to prepare triscarboxylate species CpM(O₂CR)₃. Potassium carboxylates are normally used⁴² but some derivatives such as the tribenzoate are better prepared with the silver salt⁵¹. A similar reaction with dialkylamino salts can yield a range of CpM(NR₂)₃ complexes.

Perhaps the most elegant examples of these salt elimination reactions are those devised by Ellis *et al*⁵² for the synthesis of low valent metal carbonyls. The Cp*MCl₃ complexes are first reduced with alkali metal naphthalenides at low temperatures under an atmosphere of argon. Carbon monoxide is then added to produce a variety of complexes depending on the particular conditions. An example of one such reaction is given in equation [18]. The formal Ti(0) species is isolated as an anion with a variety of salts.



When compared to the Cp_2MCl_2 systems, there are many areas in which the chemistry of the CpMCl_3 series remains unexplored. Now that their syntheses are much better developed, the compounds offer themselves as ideal starting materials for a range of research activity. In this project they have been utilised in the synthesis of some new cationic Group 4 complexes.

1.4.2: Cp_2MCl_2 .

These compounds were the first Cp derivatives of Group 4 to be discovered; Cp_2TiCl_2 was first reported in a patent⁵³ in 1952 and Cp_2ZrCl_2 in a paper by Wilkinson and Birmingham⁵⁴ the following year. The ease of preparation coupled with the high stability of their derivatives has made the "metallocene dichloride" systems the most extensively studied of the Group 4 metals. An extensive review of the chemistry derived from this series is not possible in this report. An excellent overview can be found in the text by Wailes, Coutts and Weingold.⁷

The 16-electron Cp_2MCl_2 complexes are the most thermodynamically favoured of the Cp/Group 4 metal series. For this reason, they are easily prepared. Usually this involves the treatment of MCl_4 with 2 moles of a Cp^- salt. Sources of the latter that have been used include CpMgBr ,⁵³ LiCp ,⁵⁵ TiCp ,⁵⁶ and PbCp_2 .⁵⁷ However, the best synthetic route is described by King⁵⁸ and sees the use of NaCp with MCl_4 in 1,2-DME [19].

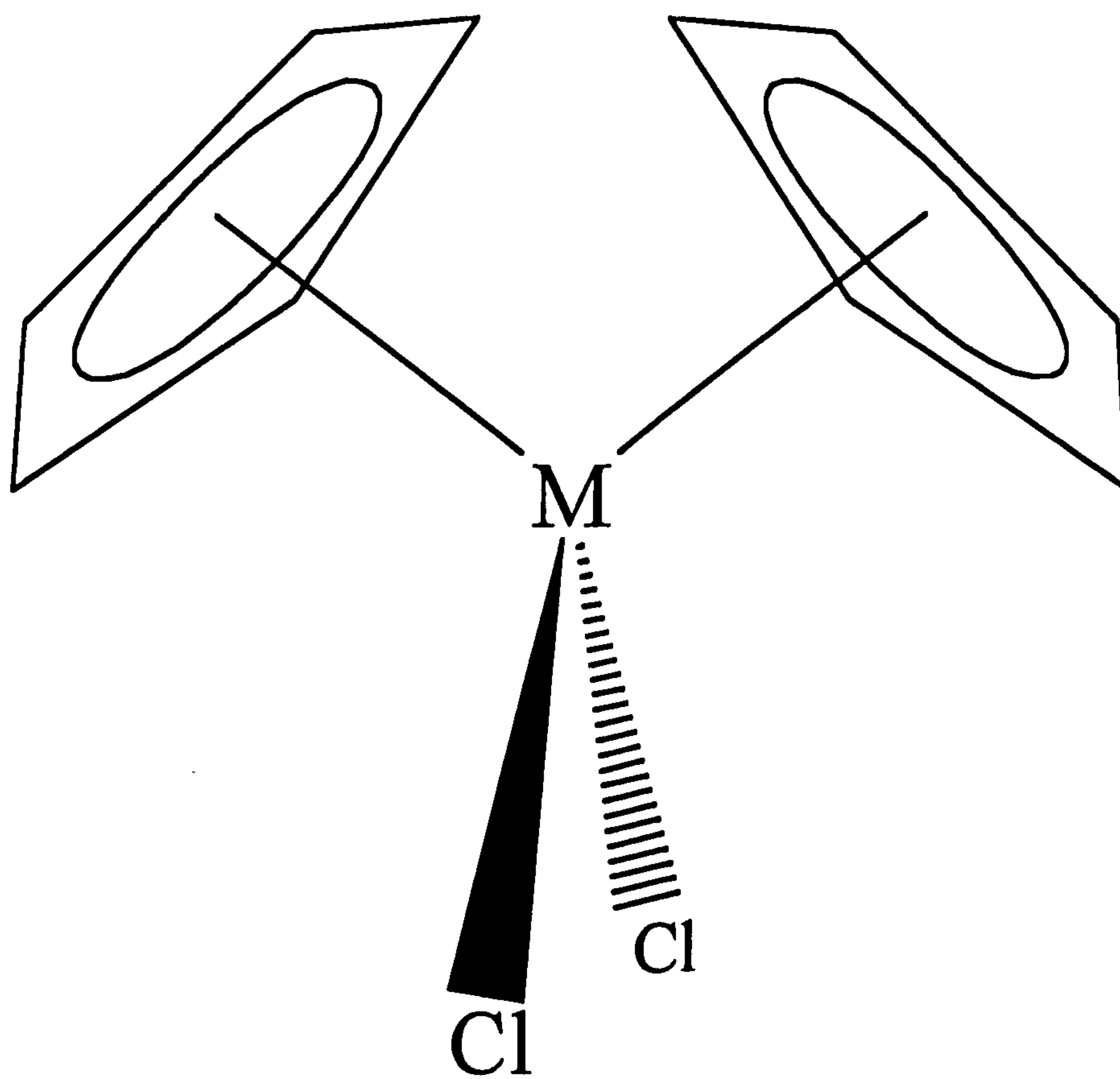


These methods can also be expanded to cover the synthesis of the analogous $\text{Cp}^*_2\text{MCl}_2$ compounds.

All six complexes in the series exhibit the same structure. It is best described as a distorted tetrahedral geometry with the Cp rings being regarded as sterically demanding unidentate ligands (**Figure 1.3**).

Obviously the bond lengths and angles vary slightly from metal to metal and the use of Cp* also has an effect but the basic geometry is maintained throughout the series.

Figure 1.3: The Structure of Cp_2MCl_2 .



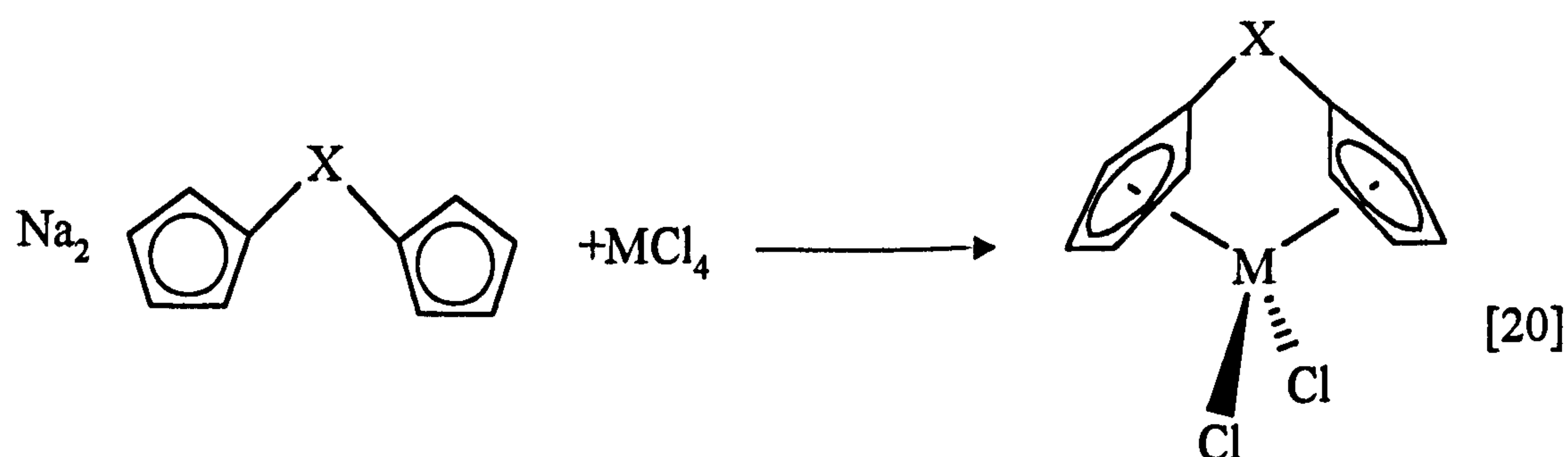
The addition of substituents to a Cp ring can result in three groups of Cp_2MCl_2 derivatives:

- a) $\text{Cp}'\text{Cp}'\text{MCl}_2$ (Two *identical* rings),
- b) $\text{CpCp}'\text{MCl}_2$ (Two *different* rings),
- c) $(\text{Cp-X-Cp})\text{MCl}_2$ (Two rings *chemically joined together via X*).

Type a) represents the simplest and most common type of derivative. An example of this is $\text{Cp}^*_2\text{TiCl}_2$. These complexes are easily synthesised by the method described above.

Compounds in class b) provide a route into chiral metal species after the substitution of one chloride ligand.⁵⁹ Type b) complexes are prepared using the reaction of the desired CpMCl_3 system with an equivalent of the $\text{Cp}'\text{Na}$ salt [17].⁴⁵

In the synthesis of type c), the two rings are joined together before double-deprotonation and complexation with the Group 4 metal [20]. There are a number of different bridging groups X reported in the literature such as $(-\text{CH}_2-)$, $(-\text{SiMe}_2-)$, $(-\text{C}_2\text{H}_4-)$ etc.



These ansa-metallocenes as they are known, have proved to be excellent Ziegler-Natta catalysts; in the presence of methylaluminoxane (MAO), isotactic polypropylenes are produced.⁶⁰ Metallocene dichloride based catalysts have been central to polymerisation research since Ziegler's initial discovery in 1953.

The reactions of the Cp_2MCl_2 series can generally be divided into two categories: salt or HCl elimination. Unlike their CpMCl_3 analogues, they do not form neutral adducts. The range of synthetic studies on the Cp_2MCl_2 systems is too large to document fully here. The most important of these include hydrolysis, alcoholysis, aminolysis, redox, alkylation and metallocycle formation. An excellent overview of these and other reactions is given in the literature.⁶¹

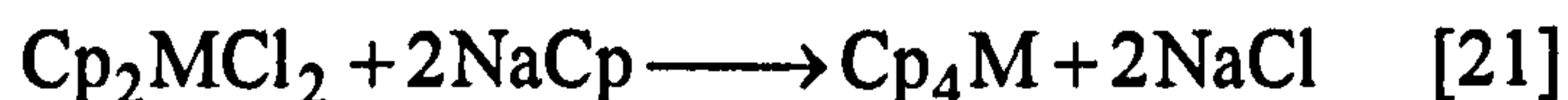
1.4.3: Cp_3MCl .

These compounds are the most unstable of the Cp series. The Ti analogue was first obtained from the reaction between CpMgCl and Cp_2TiCl_2 by Calderon *et al.* As analytical data could not be obtained, the proposed formulation was based on NMR evidence.⁶² The Zr and Hf species were identified shortly afterwards.⁶³ There are no analogous Cp^* complexes, presumably because of their inherent steric crowding. However, the methylcyclopentadienyl (Cp') derivative has been isolated and NMR data of this complex suggests a structure best described as $[\text{ZrCl}(\eta^5\text{-C}_5\text{H}_4\text{Me})_2(\eta^1\text{-C}_5\text{H}_5)]$. The only single crystal X-ray data obtained from this type of complex is from a derivative: $[\text{Cp}_3\text{Zr}(\text{HAlEt}_3)]$. In this example, the rings are all in a η^5 -configuration.⁶⁴

The reactivity of these systems remains largely unexplored mainly because of their inherent instability. Reactions can generally be divided into two groups: protic loss of the η^1 -ring and Cl-substitution.¹⁴

1.4.4: Cp₄M

The first example of this type of compound was Cp₄Ti, reported in 1963.⁶⁵ It was closely followed by the Zr and Hf analogues.^{66, 67} All three complexes are best prepared from Cp₂MCl₂ and two moles of NaCp [21].



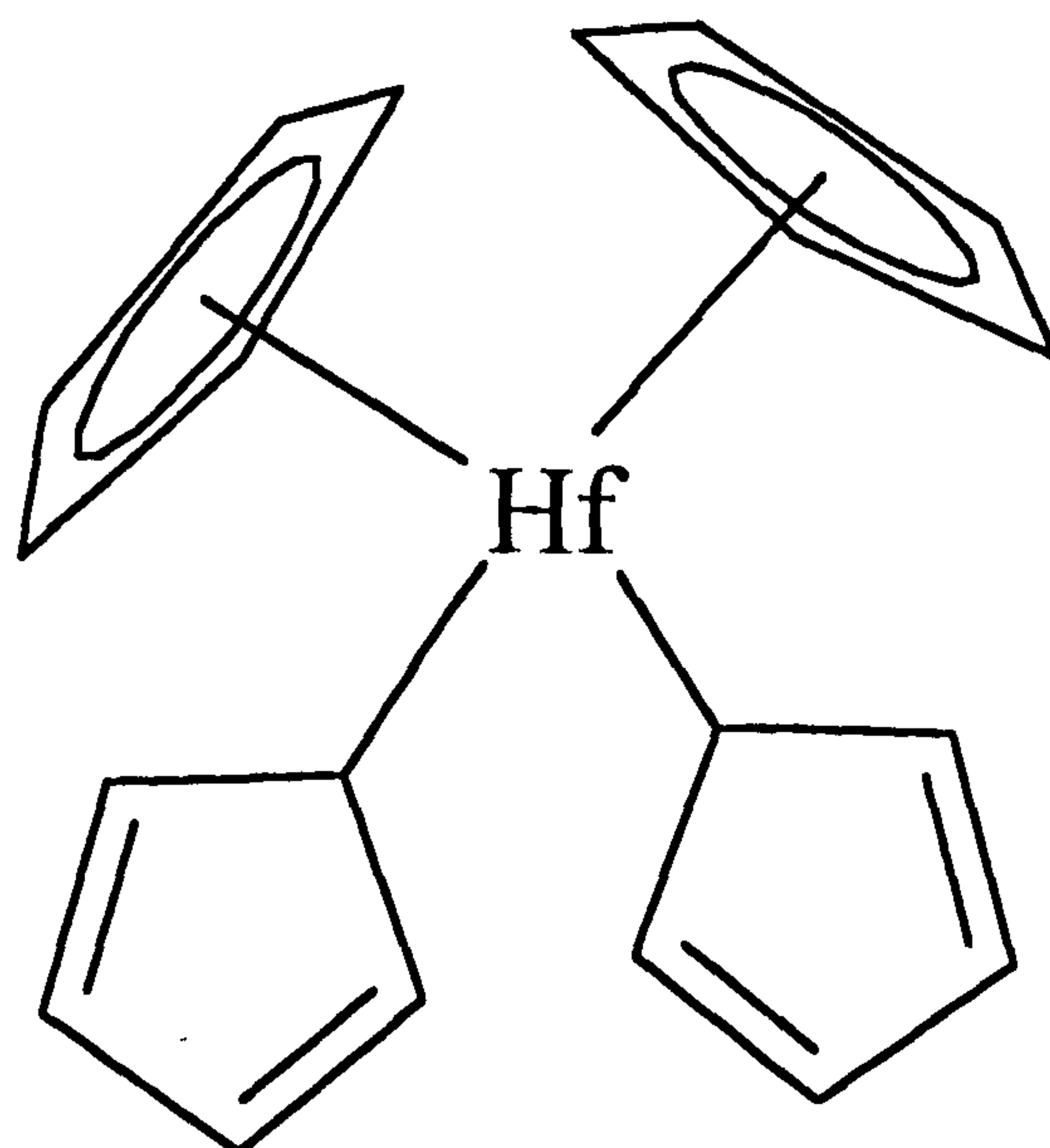
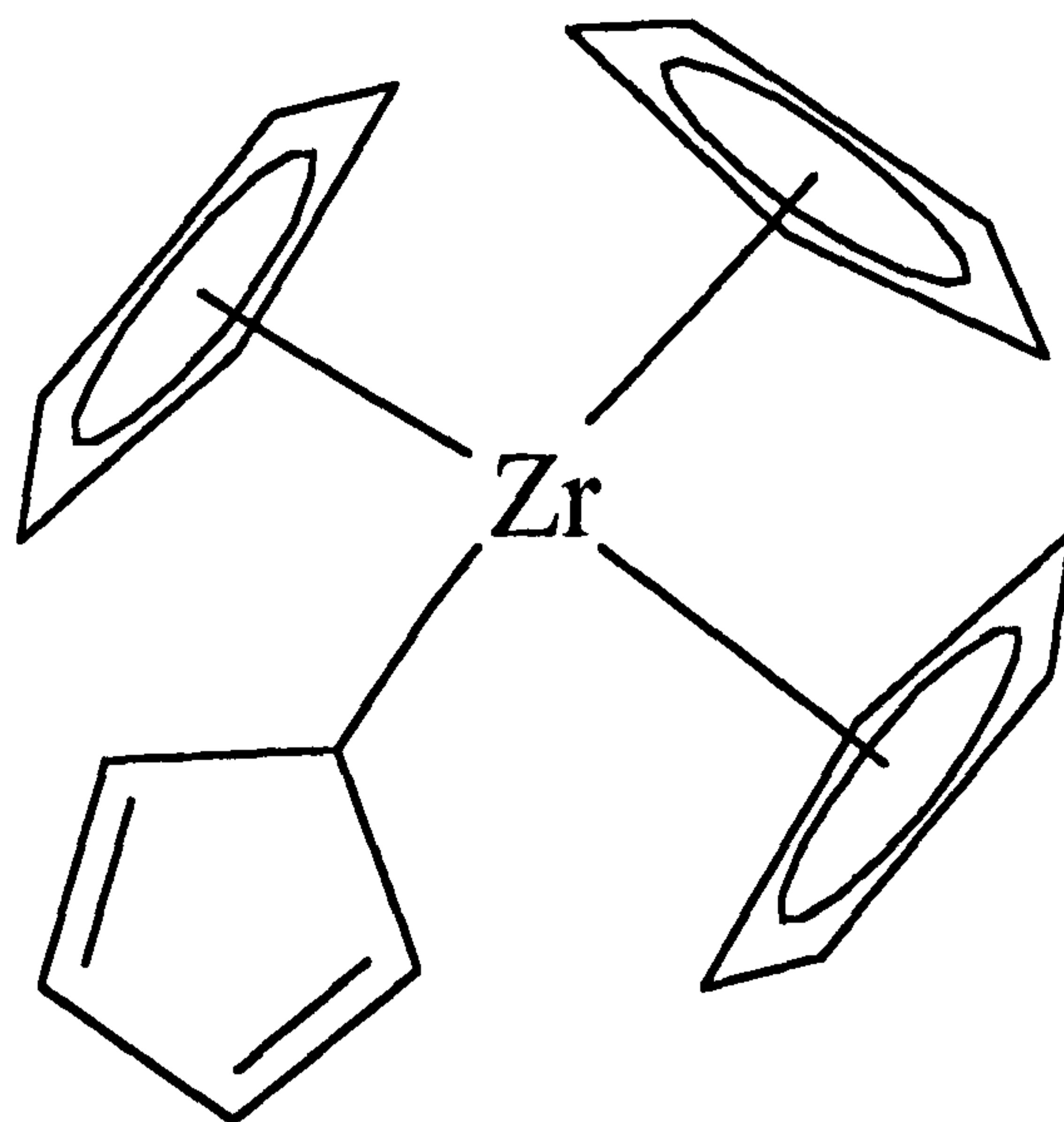
The crystal structures of these three compounds were quite surprising. Whilst the Ti⁶⁸ and Hf⁶⁹ species adopt a [M(η⁵-C₅H₅)₂(η¹-C₅H₅)₂] configuration, the Zr analogue has the [Zr(η⁵-C₅H₅)₃(η¹-C₅H₅)] structure.⁷⁰ The latter complex is formally 20-electron but the (Cp-Zr) bond lengths are appreciably longer than usual, suggesting that each ring donates less than 6 electrons. This rare example of structural inequality between Zr and Hf is illustrated in Figure 1.4. It is thought to be due to the slightly smaller size of the Hf centre.

In solution, NMR studies have shown that there are two fluxional processes which result in one broad singlet in the room temperature spectrum (Cp₄Ti,⁶² Cp₄Hf⁶⁷): the rings rotate and interchange between the η⁵- and η¹-bonding modes.

Reactions of the Cp₄M systems are usually based upon the protic cleavage of the more weakly η¹-bound rings. A range of reagents will effect this loss such as alcohols (yielding Cp₂M(OR)₂), halogens (yielding Cp₂MX₂) and hydrogen halides (yielding Cp₂MX₂).

Once again steric bulk precludes the formation of the Cp* analogues although (C₅H₄Me)₄Zr has been isolated. Even in this example, the final chlorine substitution proved difficult to achieve.⁶³

Figure 1.4: The structures of Cp_4Zr and Cp_4Hf .



1.5: Cationic complexes of Group 4.

The compounds of Group 4 are predominantly covalent. One of the first challenges to synthetic chemists was therefore the preparation of some stable ionic species. This area of research was later fuelled by Shilova's cationic model of Ziegler-Natta olefin polymerisation catalysis (section 4.6).

Since then, the literature has seen many examples of ionic systems based on Group 4 cations. Despite the various methods of preparation, the cationic centres share similar properties. The most important of these is the extreme Lewis acid character that they exhibit. For this reason, the majority of complexes consist of the charged metal centre surrounded by the maximum number of stabilising ligands. Once again, Cp groups have been utilised with great effect in lowering the reactivity of such species.

Preparation.

There are 3 general methods used in the synthesis of cationic species:

- a) halide abstraction reactions,
- b) oxidation of low valent metal species using silver salts,
- c) protolysis of metal-alkyl complexes.

1.5.1: Halide abstraction.

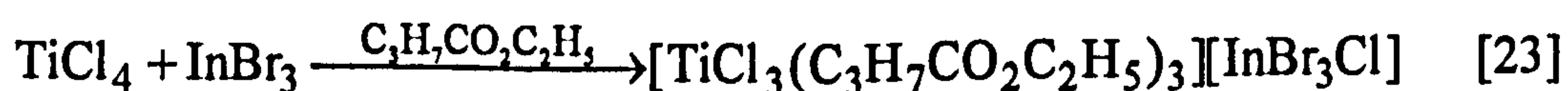
The first example of a cationic Group 4 complex was reported in 1956 when Gutmann⁷¹ recovered a sample of $[\text{ZrCl}_3(\text{POCl}_3)][\text{SbCl}_6]$. As the postulated structure of this product was based purely on elemental analysis, his team went on to investigate the analogous Ti system⁷² with similar results. Further evidence for the existence of the cationic model was gained by Adolfsen⁷³ who performed electrolytic experiments on $[\text{TiCl}_3(\text{POCl}_3)][\text{SbCl}_6]$.

The synthesis of these new cationic systems was effected by the use of antimony(v) chloride (SbCl₅) with the parent MCl₄ in the presence of 3 moles of the POCl₃ ligand. The mechanism of this process involves the transfer of a chloride ion from the metal to the SbCl₅ followed by the ligation of the POCl₃ to the metal centre [22].



The halide transfer reaction can be regarded as a competition between two Lewis acids; the weaker Lewis acid becomes the cationic centre. Subsequent studies concentrated on the use of alternative halide abstraction reagents. In a paper which documented the use of iron(III) chloride in the TiCl₄/POCl₃ system, Gutmann postulated that a number of Ti species could exist in solution.⁷⁴ These included TiCl₃⁺, TiCl₅⁻, TiCl₆²⁻ and also many neutral chloro-bridged intermediates depending on the particular combination of Lewis acids.

In an attempt to categorise the reactants in terms of Lewis acid strength, Lysenko⁷⁵ took mixtures of different metal chlorides to produce ion pairs. One example of these, involving indium tribromide (InBr₃), yielded a new Ti cation containing ethyl butyrate ligands [23].

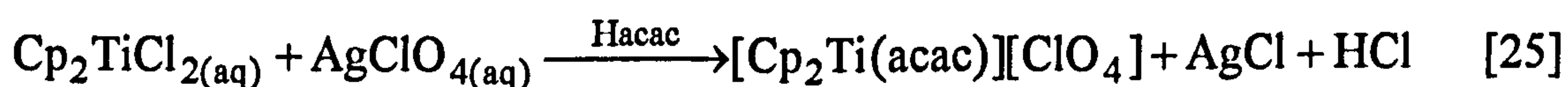


Some halide abstraction reagents are also reducing agents and thus with Ti, cationic M(III) complexes have been recovered. This is well illustrated by the reaction between tin(II) chloride (SnCl₂) and TiCl₄ in THF [24]. The crystal structure of the cation produced shows that the *trans*-configuration is preferred.⁷⁶



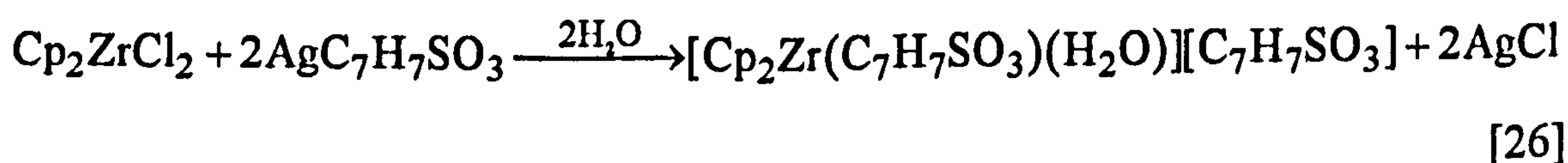
Halide abstraction reactions involving Zr and Hf complexes are rare and examples are almost exclusively limited to Cp-containing species. One curious exception is the Zr cation reported by Troganov *et al.*⁷⁷ They found that a small amount of $[\text{ZrBr}_3(\text{MeCN})_4][\text{ZrBr}_5(\text{MeCN})]$ can be formed by auto-ionisation of ZrBr_4 in MeCN solution.

The use of metallocene dihalides of Group 4 has promoted a huge range of halide abstraction reactions. The great advantage of metallocene-based systems is that some can be made under aqueous conditions. One of the earliest examples of a titanocene-based cation, $[\text{Cp}_2\text{Ti}(\text{acac})][\text{ClO}_4]$ was synthesised using Cp_2TiCl_2 and silver perchlorate (AgClO_4) in water [25].⁷⁸ A variety of ligands can be used to stabilise the metal centre.



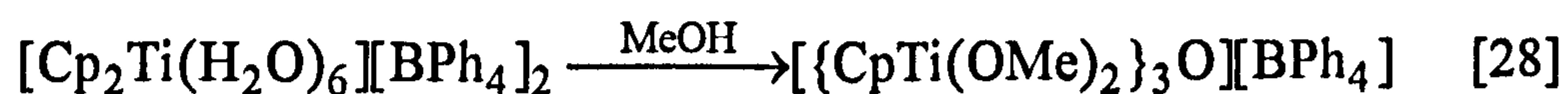
It was suggested that the reaction begins with the formation of $\text{Cp}_2\text{TiOH}^+_{(\text{aq})}$. More recent evidence for this was gained by Thewalt *et al.*⁷⁹ Using another silver salt (AgCF_3SO_3) with $\text{Cp}^*_2\text{TiCl}_2$ in wet THF, they recovered $[\text{Cp}^*_2\text{Ti}(\text{OH})(\text{H}_2\text{O})][\text{CF}_3\text{SO}_3]$ and $[\text{Cp}^*_2\text{Ti}(\text{H}_2\text{O})_2][\text{CF}_3\text{SO}_3]_2$.

In fact, with aqueous solutions of Cp_2MCl_2 it is not necessary to employ both an anion salt and a stabilising diketone; one or the other will produce a cationic centre. This is well illustrated by the work of Lasser [26],⁸⁰ and of Kakkar *et al* [27].⁸¹



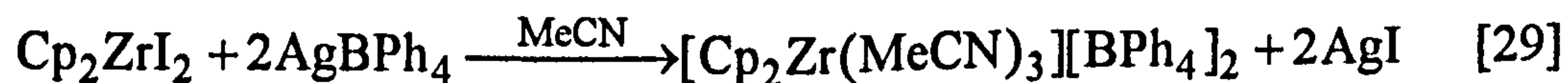
The latter type of complex, containing free chloride ions, has not been isolated but subsequent anion exchange reactions can be performed to yield the related salts.

When water is used as the reaction solvent, there is always the possibility of forming (M-O-M) oxo-bridged species. This has resulted in the isolation of both bi- and tri-metallic cluster compounds which carry a cationic charge. Thewalt reports⁸² that the reaction of Cp_2TiCl_2 with $\text{Na}[\text{S}_2\text{O}_6]$ in water yields $[\{\text{Cp}_2\text{Ti}(\text{H}_2\text{O})\}_2\text{O}][\text{S}_2\text{O}_6]$ whose structure is illustrated in **Figure 1.5**. Aslan *et al*⁸³ published a structure of $[\{\text{CpTi}(\text{OMe})_2\}_3\text{O}][\text{BPh}_4]$, (**Figure 1.6**) which they had prepared from $[\text{Cp}_2\text{Ti}(\text{H}_2\text{O})_6][\text{BPh}_4]_2$ and methanol. This reaction is unusual in that it sees the substitution of a Cp ligand under facile conditions [28].



Metallocene-based cations have been prepared in a number of other solvents by the halide abstraction method. Those most commonly used are also good ligands; THF and MeCN. However, non-coordinating solvents have also been used. These include liquid SO_2 and $\text{CH}_2\text{Cl}_2/\text{CHCl}_3$ mixtures. The latter was employed by Berhalter and Thewalt⁸⁴ with $\text{Cp}_2\text{TiCl}_2/\text{SnCl}_4$ in the presence of various chelating nitrile ligands. Interestingly, in the cations produced, the nitrile ligands were only bound in a mono-dentate fashion.

In coordinating solvents, a number of halide abstraction reagents have been used, mostly with metallocene-based systems. The most common example of these agents consist of silver salts, usually containing non-coordinating anions. An example is given in equation [29].⁸⁵



Other metal salts have also been used, including TIPF_6 [30],⁸⁸ and NaBPh_4 [31].⁸⁷

Figure 1 5: Thewalt's structure of $[\{\text{Cp}_2\text{Ti}(\text{H}_2\text{O})\}_2\text{O}]^{2+}$.

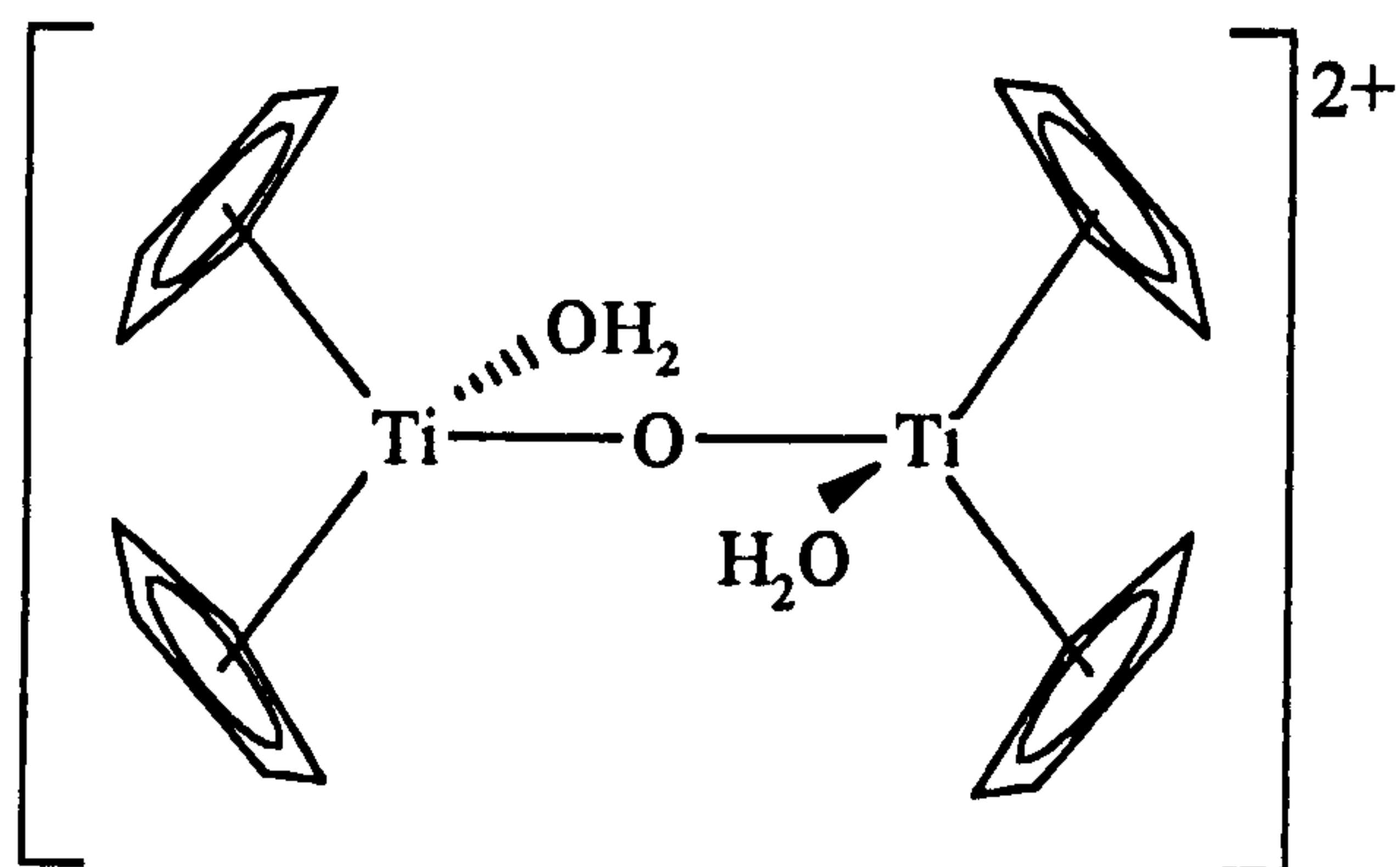
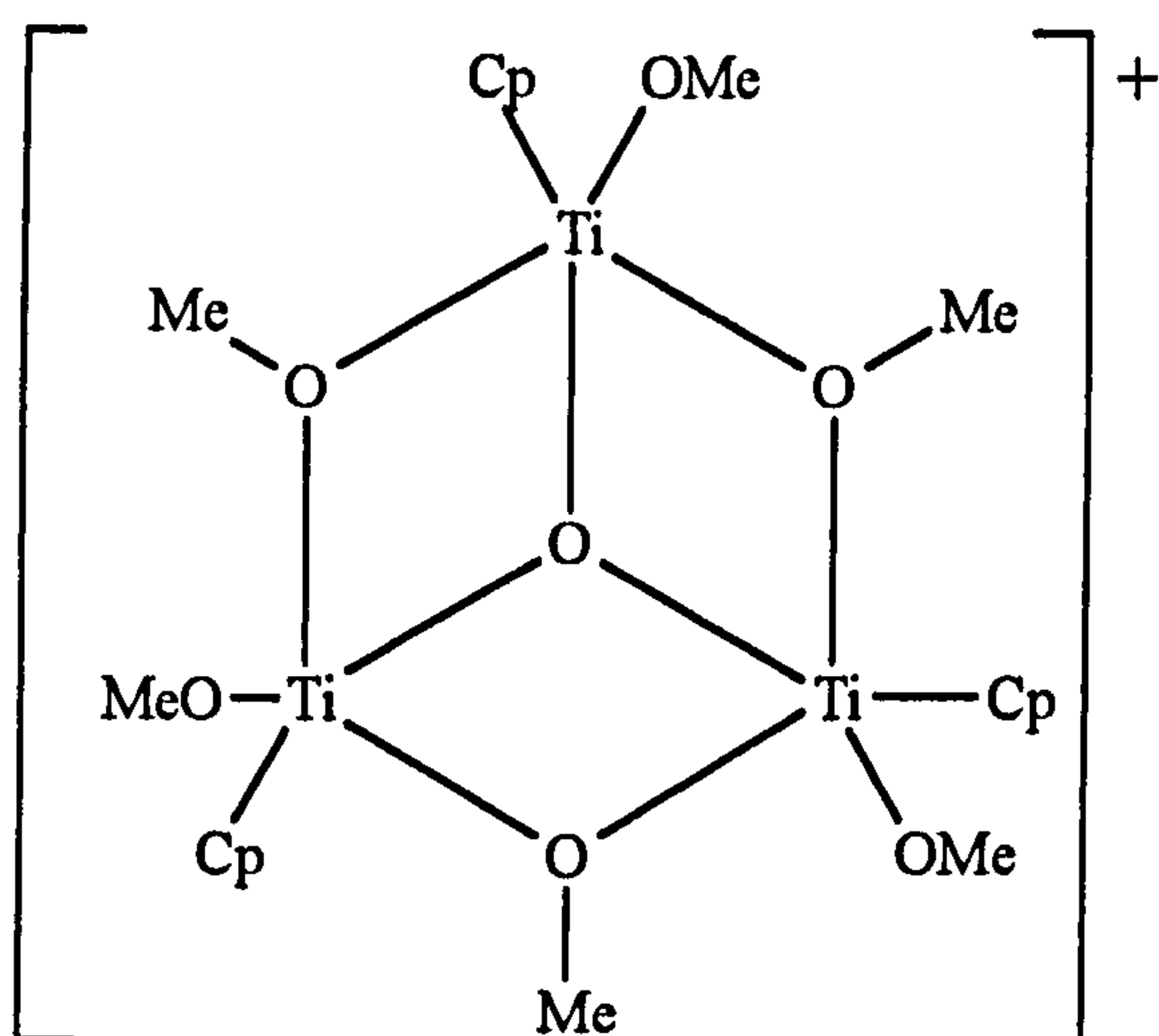


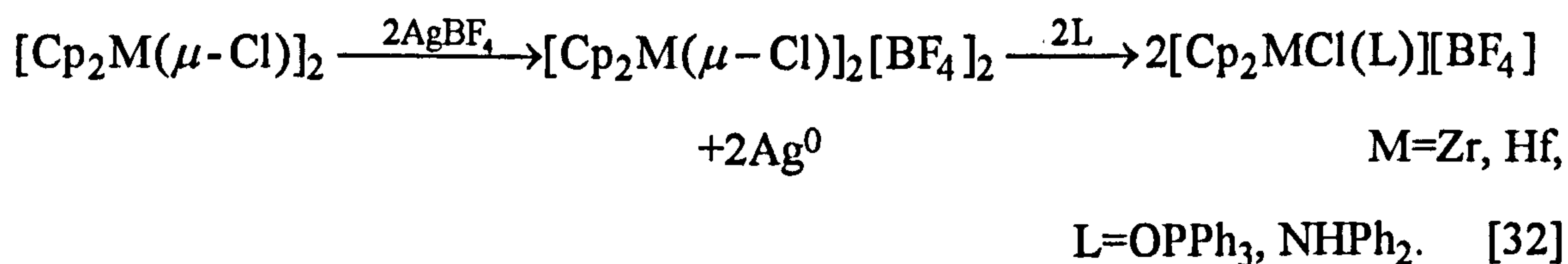
Figure 1.6: Aslan's trimetallic $[\{\text{CpTi}(\text{OMe})_2\}_3\text{O}]^+$ structure.



Equation [31] illustrates a rare example of halide abstraction from a mono-Cp/Group 4 complex. In view of the vast quantity of metallocene cations reported, it is somewhat surprising that this area remains largely unexplored. This thesis thus examines the halide transfer reactions between SbCl_5 and the CpMCl_3 series.

1.5.2: Oxidation of low valent metal species.

The first example of this method of cation generation was reported by Cuenca and Royo in 1985.⁸⁸ It involves the reaction of either Ag(I) or Tl(I) salts with the $[\text{Cp}_2\text{M}(\mu\text{-Cl})]_2$ complexes of Zr and Hf followed by the addition of a ligand [32].



If a bidentate ligand such as bipy is added in the final stage, a bimetallic dication is formed.

A similar preparation for the $[\text{Cp}^*_2\text{TiMe}(\text{THF})][\text{BPh}_4]$ was later reported by Bochmann *et al.*⁸⁹ This group used the oxidation of Cp^*TiMe by AgBPh_4 in THF solution [33].



Although not strictly a metal oxidation, another redox reaction using AgBPh_4 has been utilised to prepare a cationic Zr-alkyl complex. In this example the Ag(I) "oxidises" a (Zr-R) bond.⁹⁰ Again, the THF adduct is recovered [34].



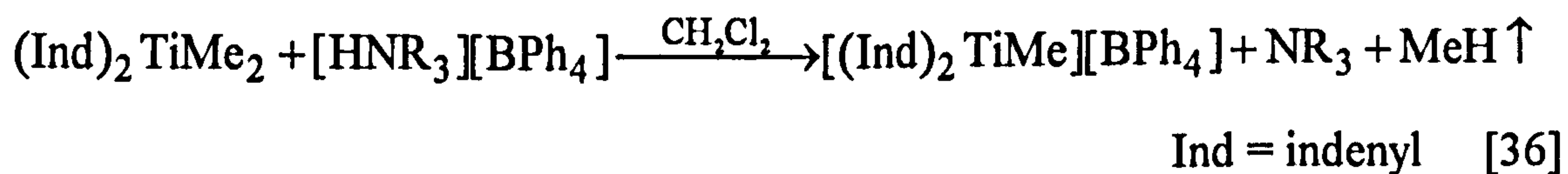
This type of one electron reduction generally works for a variety of zirconocene-based systems. However, the only Ti cations produced in this way derive from very reactive (Ti-R)-containing species.

1.5.3: Protonolysis of (M-R) bonding.

The first example of this synthetic approach was published by Bochmann *et al* in 1986.⁹¹ Their method involved the treatment of Cp_2TiMe_2 with the weakly acidic NH_4PF_6 salt in THF. The cation was formed at room temperature with the evolution of CH_4 gas [35].



Subsequent studies concentrated on the replacement of the acid with one whose conjugate base was less coordinating. It was discovered⁹² that the use of bulkier ammonium reagents such as $[\text{HNMe}_2\text{Ph}][\text{BPh}_4]$ was ideal; 14-electron, cationic complexes could be formed in the absence of both ligands and basic counter anions [36].



These 14 electron complexes are extremely reactive and make good Ziegler-Natta catalysts. Their high electrophilic nature lead Bochmann to postulate a number of structural possibilities. These are shown in **Figure 1.7**.

In solution, there is likely to be a mixture of these conformations depending on solvent, anion, metal etc. However, in a similar reaction performed by Hlatky *et al*⁹³ an interesting zwitterion was recovered [37]. This species probably resulted *via* the $[\text{Cp}_2\text{ZrMe}]^+$ moiety.

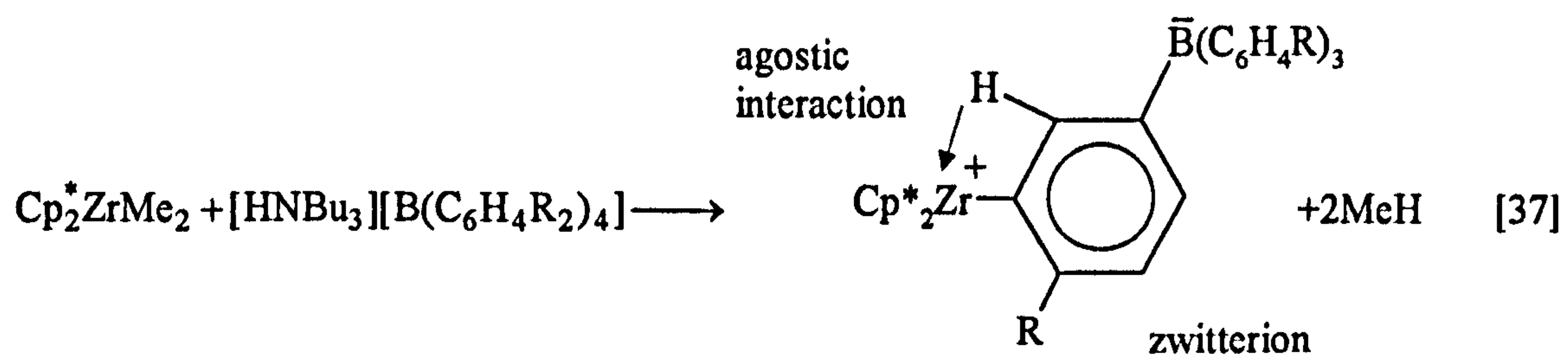
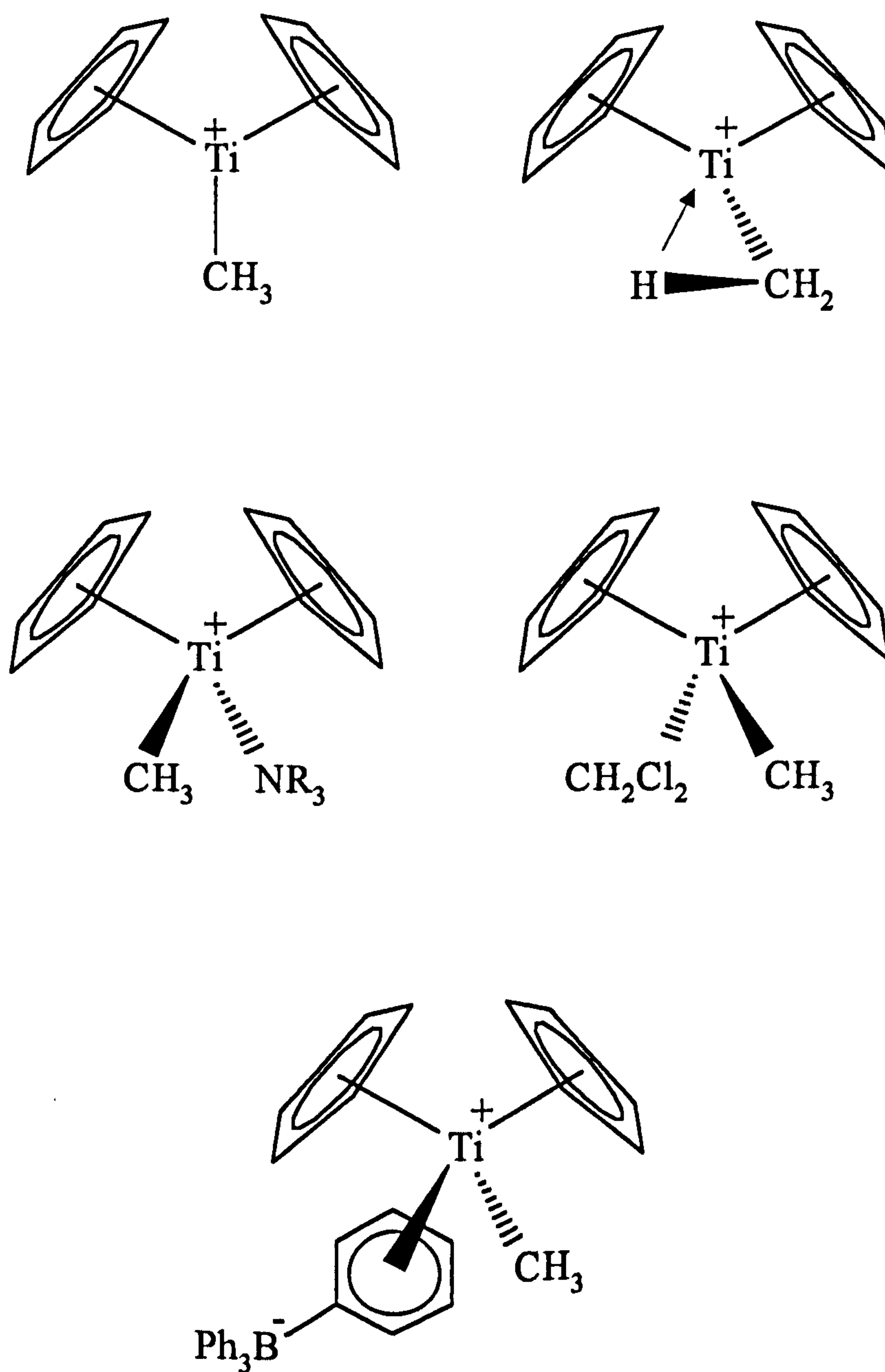


Figure 1.7: Bochmann's postulated structures of $[(\text{Ind})_2\text{TiMe}][\text{BPh}_4]$.⁹²



Indenyl groups drawn as Cp⁻ for clarity.

1.6: Antimony(v) chloride.

Under normal conditions, SbCl_5 is a colourless liquid that decomposes at its boiling point. As the compound is readily hydrolysed (fuming in air), manipulations must be conducted under an inert atmosphere. Preparation involves the treatment of SbCl_3 with Cl_2 gas. The general chemistry of the compound is well documented in the literature.⁹⁴

In both the solid and gas phase SbCl_5 exhibits a regular trigonal bipyramidal geometry.⁹⁵ Evidence for the expected Cl-bridged, dimeric octahedral structure is confined to low temperature studies.⁹⁶

The reactions of SbCl_5 are of a wide variety. It is a powerful oxidant ($\text{Sb}^{\text{V}} \rightarrow \text{Sb}^{\text{III}}$) and has been used as a chlorinating agent. As with other covalent halides, reaction with water gives oxides or oxohalides. Similarly, related species are recovered from reactions with alcohols. An important feature of SbCl_5 chemistry is its tendency to achieve a coordination number of 6. This results in a powerful Lewis acid character; adducts are generated with both neutral and anionic ligands. Neutral octahedral complex formation is readily achieved with a variety of common ligands⁹⁷ such as ethers, esters, nitriles, trisalkylamines, and phosphines. In fact, SbCl_5 has also been used to stabilise otherwise unstable ligands. A good example of this is given by the cyclooctasulfur monoxide complex, $(\text{S}_8\text{O})\text{SbCl}_5$.⁹⁸ However, the most widely studied reactions of SbCl_5 involve the formation of anionic species, $[\text{SbCl}_5\text{X}]^-$, especially those formed *via* halide abstraction mechanisms.

1.6.1: Halide abstraction reactions of SbCl₅.

The high Lewis acidity of SbCl₅ results in the facile formation of complex anions, particularly with halide donors. In this way, ionic compounds have been formed from both organic and inorganic precursors although metallic species are the most widely studied. The simplest example of this type of reaction is given in equation [38].⁹⁹



Here the product is obviously stable in a distinct anion/cation configuration but it is a rare example. More often, it is necessary to carry out the reaction in the presence of a ligand to stabilise the cation formed *via* halide transfer. This is best achieved by employing a coordinating solvent in the reaction. A good example of this type of process is given in equation [39] and uses MeCN.



Under these conditions, a whole range of metal cations have been synthesised. Some of these are shown in **Table 1.3**. Other ligands that have been employed in the reaction include POCl₃,⁷¹ and esters.⁷⁵ Unfortunately, THF cannot be used as it polymerises in the presence of both SbCl₅ and related anion salts.¹⁰³

From **Table 1.3** it is apparent that halide abstraction from metal tri- and tetrachloride systems becomes more complex. For example, so far only the monocation has been recovered from the TiCl₄/SbCl₅/MeCN system. In some ways this is not surprising; the removal of a Cl⁻ ion from an already cationic covalent species will be difficult on electrostatic grounds alone.

Table 3: Ionic species prepared via SbCl₅ halide abstraction in MeCN.

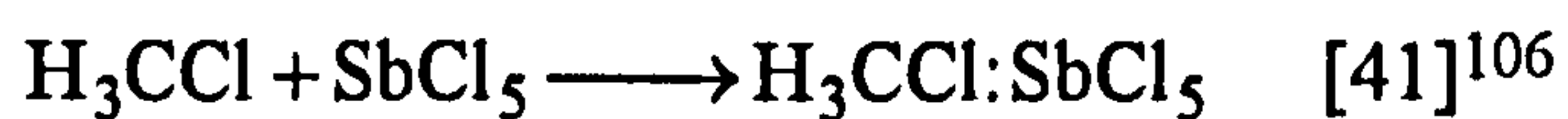


MCl _x	n	product	reference.
LiCl	1	[Li(MeCN) ₄][SbCl ₆]	99
AgCl	1	[Ag(MeCN) ₄][SbCl ₆]	99
MnCl ₂	2	[Mn(MeCN) ₆][SbCl ₆] ₂	99
CuCl ₂	2	[Cu(MeCN) ₇][SbCl ₆] ₂	99
AlCl ₃	3	[Al(MeCN) ₉][SbCl ₆] ₃	100
InCl ₃	3	[In(MeCN) ₉][SbCl ₆] ₃	100
FeCl ₃	3	[FeCl(MeCN) ₅][SbCl ₆] ₂	100
BiCl ₃	3	[BiCl ₂ (MeCN) ₆][SbCl ₆]	100
TiCl ₄	1	[TiCl ₃ (MeCN) ₃][SbCl ₆]	101
Cp ₂ TiCl ₂	2	[Cp ₂ Ti(MeCN) ₂][SbCl ₆] ₂	102
Cp ₂ ZrCl ₂	2	[Cp ₂ Zr(MeCN) ₃][SbCl ₆] ₂	102
Cp ₂ HfCl ₂	2	[Cp ₂ Hf(MeCN) ₃][SbCl ₆] ₂	102

Halide abstraction from organic and other non-metal halide systems has proven to be even more difficult. In general, ionic products are only formed when there is some inherent stability involved in the cation produced [40], [41].



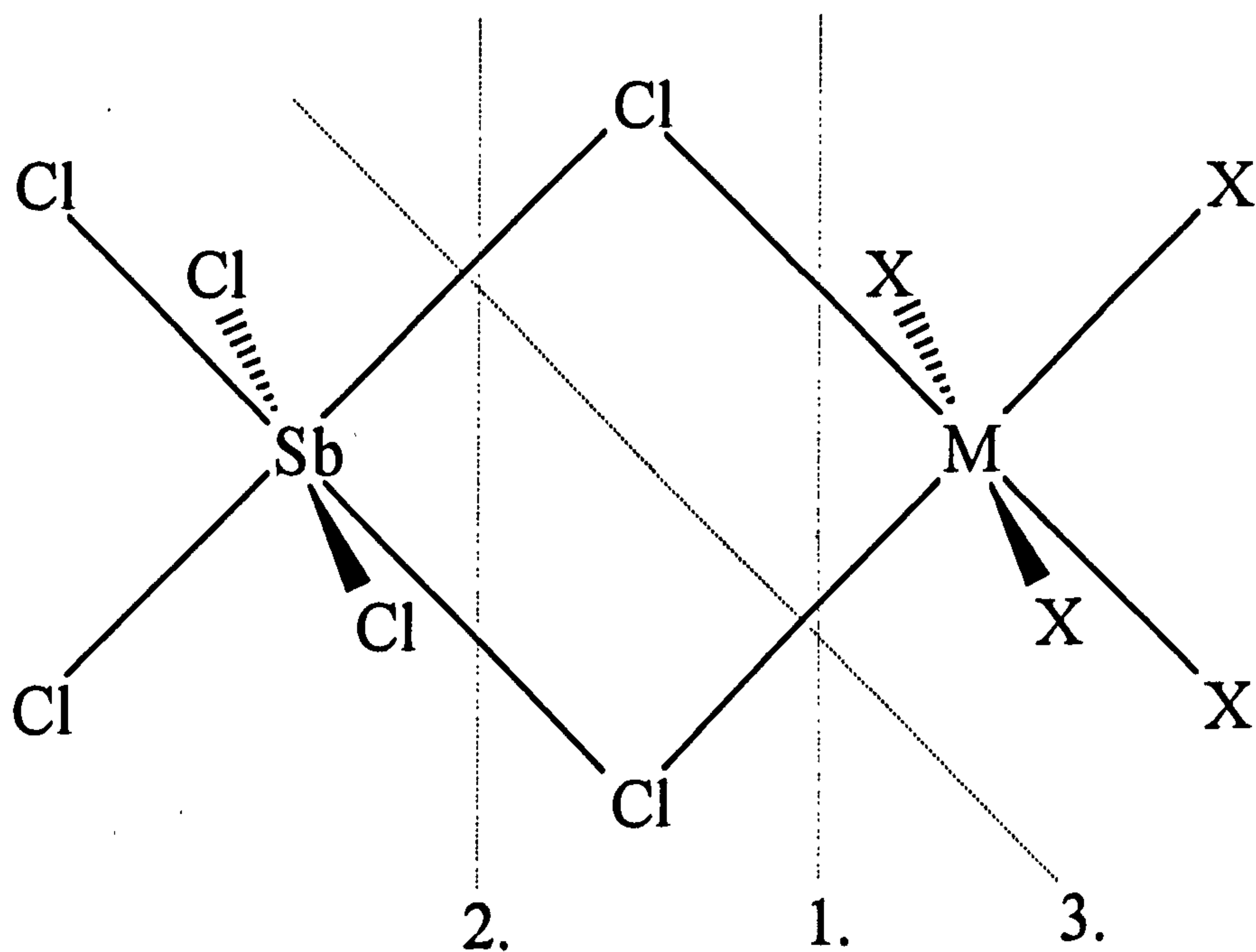
The vast majority of these types of reactions result in the formation of simple adducts [42].



1.6.2. Mechanisms of Halide Transfer.

Halide transfer almost certainly proceeds *via* a halogen bridged intermediate. One such species is illustrated in **Figure 1.8**. In this instance, the intermediate has been drawn in an edge-sharing, doubly bridged conformation. However, it could equally be apex-sharing (1 bridge) or face-sharing (3 bridges) depending on the properties of the donating metal centre.

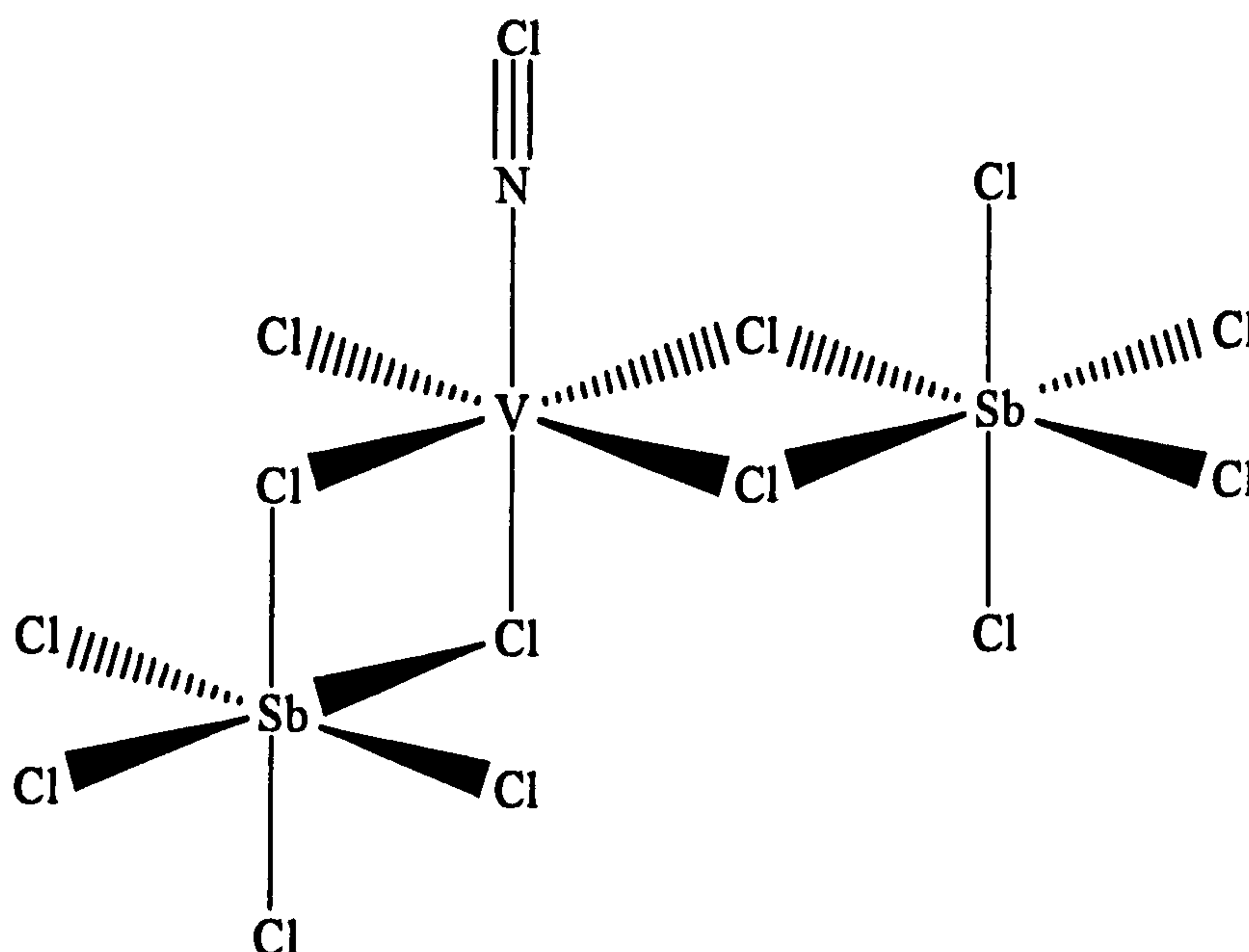
Figure 1.8: Postulated Intermediate of Halide Exchange.



If the postulated species exists in MeCN solution, cleavage can occur along one of three axes depending on the relative Lewis acid strengths of the two centres. Normally, route A is followed to form a cationic species and the SbCl_6^- anion. However, if the second metal centre is the more powerful Lewis acid, cleavage along B results with the formation of an SbCl_4^- salt. A rare example of this occurs in the reaction between SbCl_5 and SbF_5 ,¹⁰⁷ the latter being an extremely powerful Lewis acid. Cleavage C would be found in cases of balanced Lewis acid character. This route represents the retro step in a $\text{SbCl}_5/\text{SbCl}_6^-$ equilibrium. Evidence for such an equal balance of Lewis acids has yet to be found.

The first concrete evidence for the existence of these halogen-bridged intermediates was published in 1979 when Lorcher *et al*¹⁰⁸ investigated the $\text{VCl}_3(\text{NCl})/\text{SbCl}_5$ system. The structure of the product that they isolated was quite unexpected and is shown in **Figure 1.9**.

Figure 1.9: The molecular structure of $\text{VCl}_3(\text{NCl}) \cdot 2\text{SbCl}_5$.



CHAPTER 2.

RESULTS AND DISCUSSION.

2.1: Preparation of the CpMCl₃ series.

2.1.1: CpTiCl₃.

This compound was prepared using the method of Cardoso *et al.*³⁶ Recrystallisation from hot toluene gave the orange/yellow title compound in excellent (90%) yield. Some spectroscopic and analytical data are summarised in **Table 2.1**. These properties have been adequately discussed before in the literature.^{36,109}

2.1.2: CpMCl₃(MeCN)₂ for M = Zr and Hf.

An adaptation of the method used by Lund and Livinghouse⁴² was used in these syntheses. The DME adducts that they reported proved to be unsuitable for our investigations. For this reason, MeCN was substituted for the DME in the final stage of the reaction [42]. It was also found that the tin-centred reagent, CpSn(Bu)₃ was the most suitable source of the ring for both Hf and Zr.



The 16-electron adducts that were recovered were found to be ideal sources of the CpM moiety. The compounds are moderately soluble in CH₃CN, CH₂Cl₂ and toluene but insoluble in Et₂O and hydrocarbons. Their high solubility in hot MeCN provides an excellent medium for recrystallisation. Some important physical and spectroscopic properties are given in **Table 2.1**.

The 250 MHz ¹H NMR spectra of the two complexes show similar features. In CD₃CN solution, the Cp signal is a sharp singlet in both cases: for Zr it is found at 6.50 ppm and Hf at 6.40 ppm. This is surprising given that there are three possible geometrical isomers of the CpMCl₃L₂ moiety. The rapid ligand/solvent exchange (no detectable coordinated CH₃CN after 5 minutes)

suggests that the Cp signal may be time averaged. Unfortunately, low temperature studies are precluded by the high freezing point of the CD₃CN solvent.

The IR spectra also exhibit similar properties. In the solid state, three of the four characteristic bands due to the Cp group are seen¹¹⁰ with the fourth being masked by the Nujol. The coordinated MeCN is immediately recognisable from the doublet arising at *ca.* 2300 cm.⁻¹ There are several theories as to why the frequency of this (C≡N) stretch should rise upon coordination to a metal centre;¹¹¹ most other ligands, such as carbonyls, ethers, ketones, etc. show a negative shift. Purcell reports that the increase in the force constant of the (C≡N) bond can be explained using MO calculations.¹¹²

The low energy region of the IR spectra is complex. Between 200-400 cm.⁻¹ there are a number of bands due to (M-Cl), (Cp-M) and one due to MeCN. Unfortunately this rules out any studies on the (solid state) symmetry around the metal centres arising from the various (M-Cl) stretches. For this reason, we await a single crystal X-ray structure determination of CpZrCl₃(MeCN)₂. From analogy with the CpZrCl₃(DME) structure,¹¹³ the expected configuration is given in **Figure 2.1**.

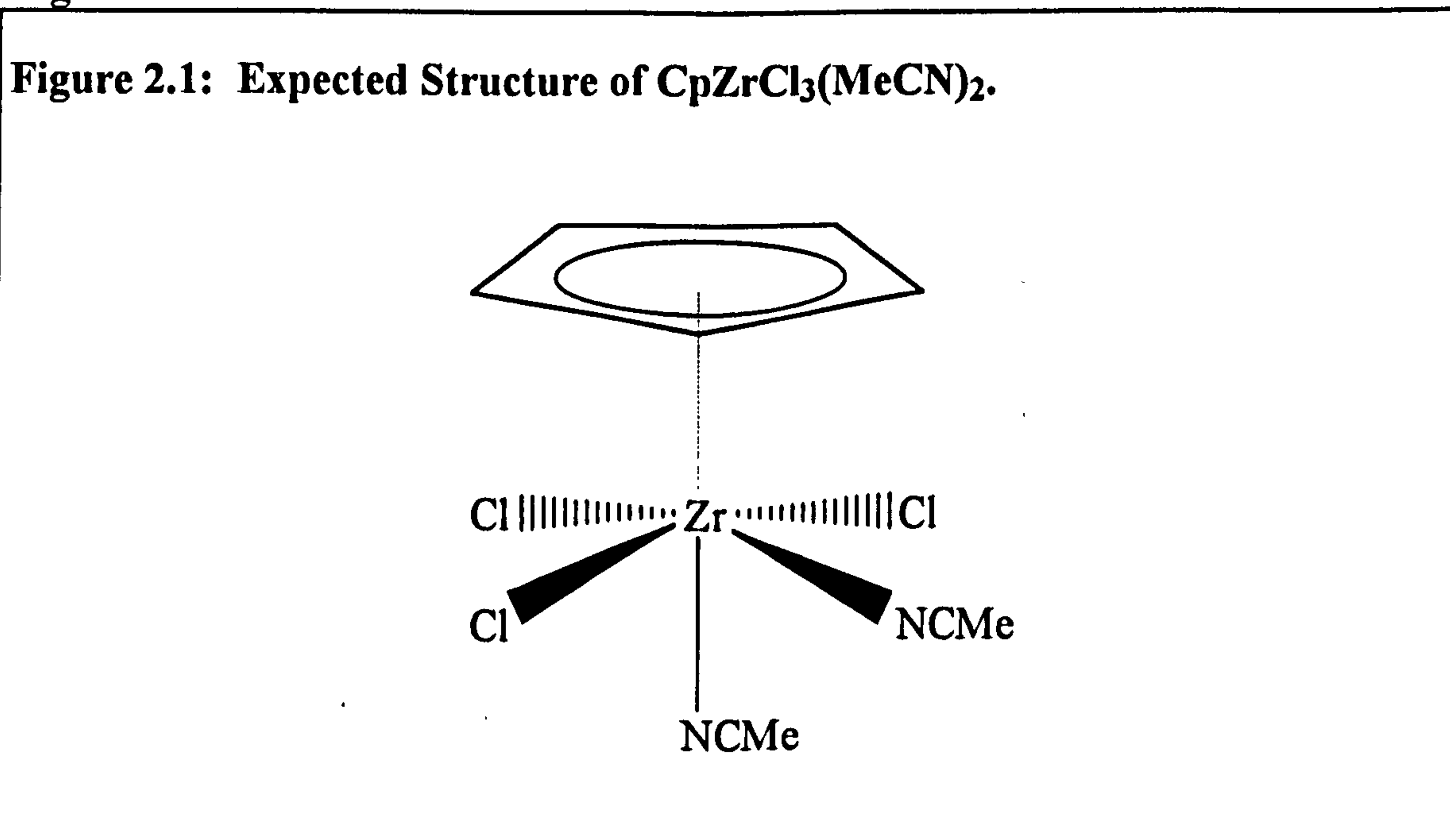


Table 2.1: Selected physical and spectroscopic data for the CpMCl₃ series.

	CpTiCl ₃	CpZrCl ₃ (MeCN) ₂	CpHfCl ₃ (MeCN) ₂
Colour	yellow/orange	white	white
Melting point/°C	208-211	130(decomposes)	125(decomposes)
Microanalysis			
C H N	27.38 2.30 -	31.35 3.22 8.13	25.02 2.57 6.49
(calc/obs)	27.59 2.39 -	30.44 3.24 8.50	25.61 2.71 6.41
¹H NMR (250 MHz) (CD ₃ CN solution) δ/ppm	7.20	6.50	6.40
IR (nujol), v/cm⁻¹			
Cp			
(C-H) stretch	3080(w)	3090(w)	3090(w)
(C-H) deform.	1017(m)	1022(m)	1020(m)
(C-C) deform.	835(s)	811(m)	815(m)
MeCN	-		
(C≡N) stretch		2315(s)	2315(s)
		2290(s)	2290(s)
(C-C) stretch		940(m)	940(m)
(M-Cl) and(M-Cp)	460(m)	400(m)	300(m, br)
combinations.	415(s)	341(m)	
	330(w, br)	320(m)	
		295(m)	
		212(m)	

2.2: Preparation of the Cp*MCl₃ series.

2.2.1: Cp*TiCl₃.

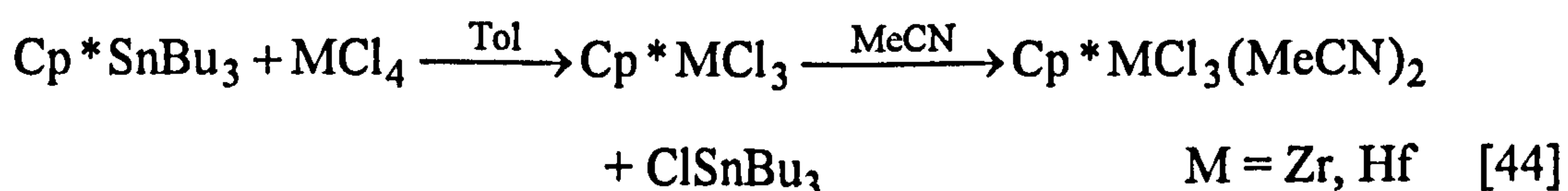
The method of Royo *et al*³⁷ was used to prepare the title complex in excellent yield. Some spectroscopic and analytical data are summarised in Table 2.2.

2.2.2: Cp*MCl₃(MeCN)₂ for M = Zr and Hf.

Early attempts to synthesise Cp*MCl₃ using Cp*Li and MCl₄ proved to be unsuccessful; the products recovered from these reactions were extremely air sensitive and difficult to purify. It was therefore decided to adapt the method of Green *et al*.⁴³ This involved the synthesis of Cp*SnBu₃ as the Cp* donating agent. The tin compound was recovered in good yield and purified *via* distillation [43].



The desired complexes were then formed under facile conditions [44].



The complexes recovered proved to be very much improved in terms of air sensitivity. Their properties mirror the unmethylated analogues with the extra stability inferred by the Cp* ring. Table 2.2 illustrates some physical and spectroscopic data. In general the spectra are similar to those of the Cp analogues; one singlet in the ¹H NMR and similar absorbances in the IR. The only major differences to occur are observed in the latter and are due to the replacement of the protons on the ring with methyl groups; the band at *ca.* 810 cm⁻¹ disappears in the Cp* compounds and the region below 400 cm⁻¹ is reduced in complexity.

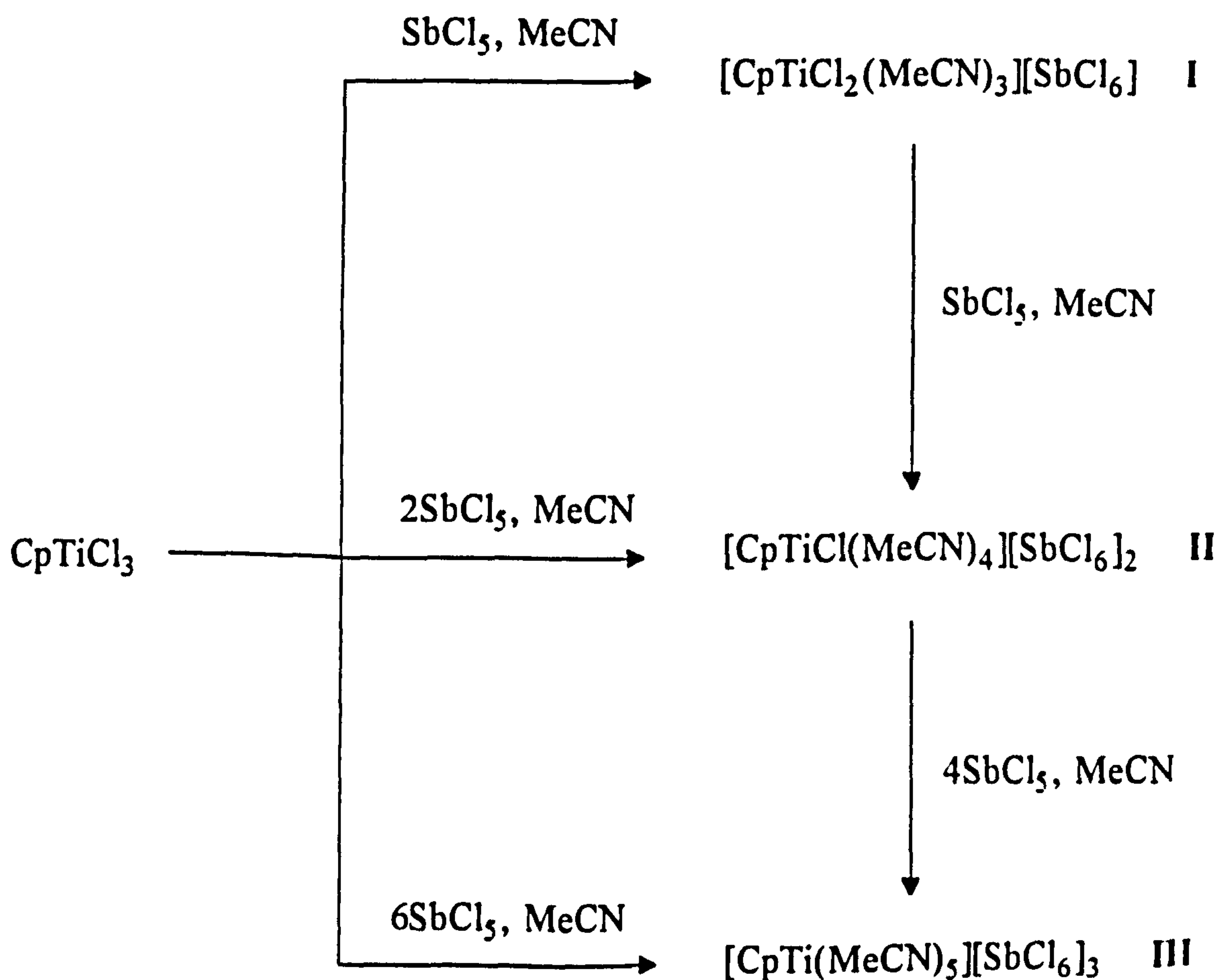
Table 2.2: Selected physical and spectroscopic properties of the CpM*Cl₃ series.**

	Cp*TiCl ₃	Cp*ZrCl ₃ (MeCN) ₂	Cp*HfCl ₃ (MeCN) ₂
Colour	red	white	white
melting point/°C	225-226	150(decomposes)	155(decomposes)
microanalysis			
C H N	41.49 5.23 -	40.52 5.11 6.75	33.48 4.22 5.58
(calc/obs))	40.93 5.03 -	40.16 5.00 6.58	33.52 4.21 5.49
¹H NMR (250 MHz) (CD ₃ CN solution) δ/ppm	2.41	2.03	2.11
IR (nujol), v/cm⁻¹			
Cp*	1020(m)	1030(m)	1020(m)
MeCN	-		
(C≡N) stretch		2295(s)	2300(s)
		2270(s)	2275(s)
(C-C) stretch		935(m)	936(m)
(M-Cl) and (M-Cp*)	458(s)	410(m)	408(w)
combinations	408(s)	357(m)	344(m)
	335(br, m)	303(m)	298(m)
		265(w)	280(m)
			267(w)

2.3.: Halide abstraction from CpTiCl₃.

In an investigation of the possible extent of cation formation, chloride ions were sequentially removed from CpTiCl₃ using SbCl₅ in MeCN solution. Using this method, three new cationic complexes of Ti(IV) have been isolated in excellent yield (scheme 2.1).

Scheme 2.1



Analytically pure compounds are recovered by the removal of the solvent *in vacuo* followed by washing with CH₂Cl₂. Characterisation follows from analytical, spectroscopic (Table 2.3) and in the case of III an X-ray crystal structure determination (section 2.3.2). Complex III is the first example of a tricationic titanium species.

Table 2.3: Properties of the CpTiⁿ⁺ series.

	[CpTiCl ₂ (MeCN) ₃] ⁺ I	[CpTiCl(MeCN) ₄] ²⁺ II	[CpTi(MeCN) ₅] ³⁺ III
Colour	red	pale blue	purple/blue
microanalysis			
C H N	20.59 2.20 6.55	15.91 1.75 5.71	13.63 1.53 5.30
(calc/obs)	20.62 2.24 6.50	15.90 1.68 5.62	13.89 1.65 5.33
¹H NMR (250 MHz) (CD ₃ CN solution) δ/ppm	7.40	7.53	7.69 (high temps only)
IR (nujol), v/cm⁻¹			
Cp			
(C-H) stretch	3110(w)	3115(w)	3110(w)
(C-H) deformation	1025(m)	1025(m)	1025(m)
(C-C) deformation	850(w)	852(w)	861(w)
MeCN			
(C≡N) stretch	2321(s)	2321(s)	2319(s)
	2295(s)	2295(s)	2285(s)
(Ti-Cl)	440(w)	440(w, br)	-
	430(w, br)		
(Sb-Cl)	345(vs)	345(vs)	345(vs)

The complexes recovered are soluble in polar organic solvents such as MeCN and Me₂CO but insoluble in most others. Solvents must be rigorously pre-dried as red brown **I**, pale blue **II** and purple blue **III** are all extremely sensitive to hydrolysis, especially when in solution. For this reason, anaerobic conditions are essential; standard Schlenk techniques under an atmosphere of N₂ or Ar were found to be adequate. The complexes are also thermally sensitive and all decompose before melting. This may well be due to the loss of some coordinated MeCN which is so vital to the stability of the cationic centre.

The best method of purification involves recrystallization from MeCN/CH₂Cl₂ although conditions must be carefully monitored. If pure complex **II** is recrystallized, crystals of both **I** and **II** are recovered. A very small excess of SbCl₅ must be added to ensure a full yield of **II**. When pure **III** is used, a larger excess of SbCl₅ is required to avoid **II** and **I**. However, recrystallisation of **I** is straightforward.

These observations are consistent with the reaction stoichiometries required in the formation of **I**, **II** and **III** (above scheme). To generate the triply charged cation **III** it was found that a healthy excess of SbCl₅ is required. (Ti:Sb≈1:6). Similarly, whilst **II** can be obtained in sequence from **I** using one equivalent of SbCl₅, the formation of **III** from **II** is only effected by the use of an excess (4 molar) of SbCl₅.

The ¹H NMR spectra of the series are very informative and go some way towards explaining these curious stoichiometries. At room temperature, the spectrum of **I** recorded in CD₃CN exhibits two singlets: one at δ7.40 due to the Cp ring protons and the other at δ1.95 for uncoordinated MeCN. In fact, in the spectra of all three complexes, the lack of a signal due to coordinated MeCN is indicative of rapid ligand/solvent exchange. This makes the measurement of the integral signals difficult; the MeCN signal appears in the middle of the septet due to the CHD₂CN present in the solvent.

When pure **II** is dissolved in CD_3CN , the ^1H NMR spectrum surprisingly exhibits three Cp resonances at $\delta 7.15$, 7.40 and 7.53 . At first, the two higher field signals were thought to be due to hydrolysis but after stringent drying of the solvent, this idea was proved incorrect. In fact, species **II** decomposes in an equilibrium with **I**. The signal at $\delta 7.15$ may be due to a halogen-bridged intermediate. On the addition of an excess of SbCl_5 to this equilibrium mixture, the three resonances collapse to one at $\delta 7.45$. This signal has again been attributed to an intermediate. Upon warming this solution to 76°C , the single resonance is retained but with a conspicuous downfield shift to $\delta 7.69$; it is this which has been assigned to the trication **III**. Similarly, the room temperature spectrum of **III** feature four of these resonances at $\delta 7.15$, 7.40 , 1.53 and 7.45 . Again, these collapse to the singlet at $\delta 7.69$ as the temperature is raised to 76°C . These observations are consistent with the reaction profile illustrated in **Scheme 2.2**.

These results show that in this particular system, there is a very delicate electronic balance between the various species. It is obvious that the removal of the final chloride ion from the Ti centre requires an extra input of energy. This either comes from the heat of crystallization when **III** drops out of solution, or a rise in temperature. The excess SbCl_5 is required to push the equilibrium towards the trication precursor.

The downfield shift of the characteristic Cp resonance on going from the neutral CpTiCl_3 through **I**, **II**, and **III** is a direct reflection of the increasing cationic charge. The postulated intermediates **A** and **B** are depicted as doubly-halogen-bridged species involving edge-edge sharing of (pseudo) octahedral, solvated CpTi and Sb units. However, these intermediates could equally involve triply bridged, face-face arrangements (**C** and **D**) or a single apex-apex interaction (**E** and **F**). These conformations are illustrated in **Figure 2.2**.

Scheme 2.2: Postulated reaction profile of $\text{CpTiCl}_3 + n\text{SbCl}_6$

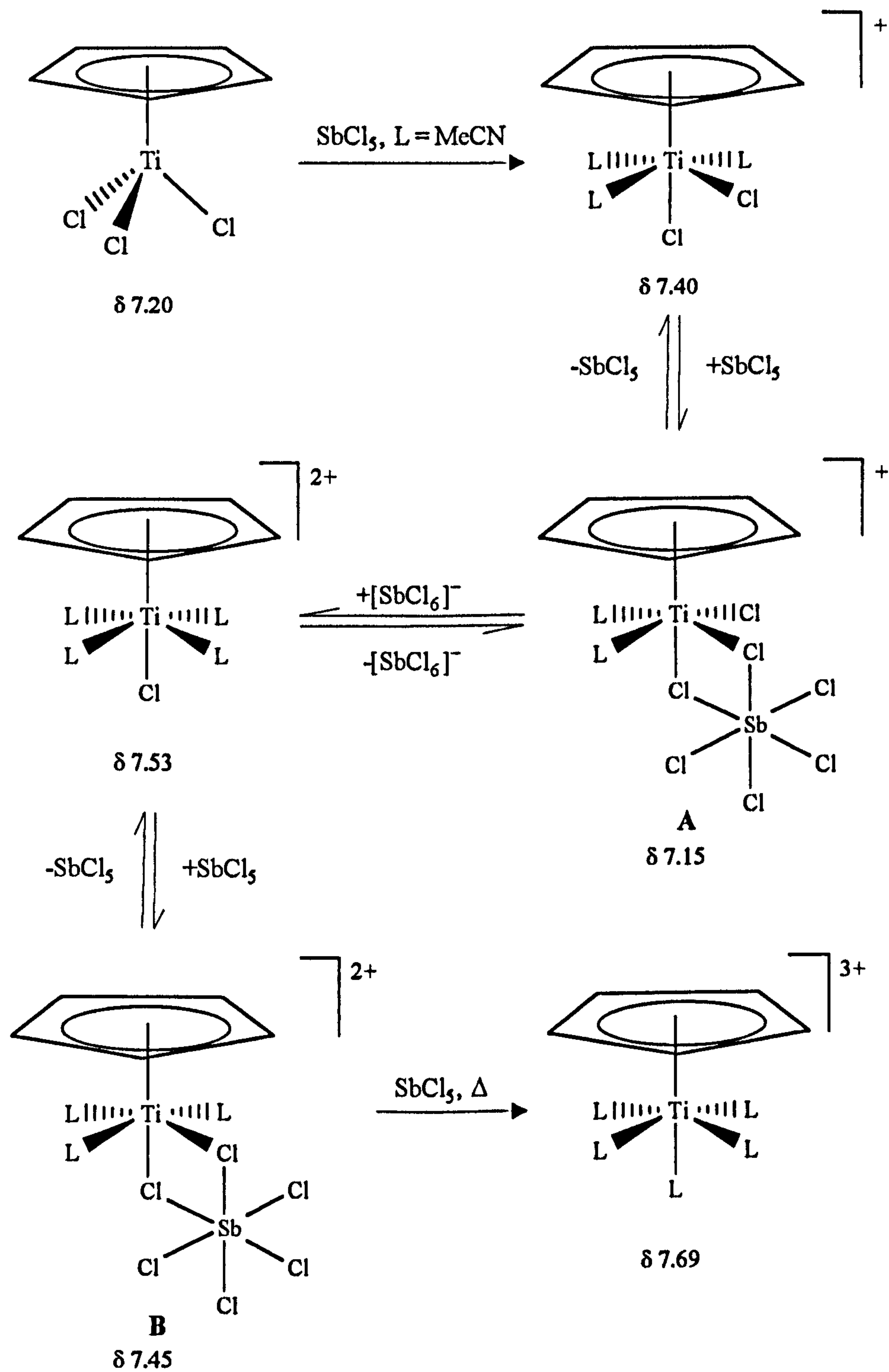
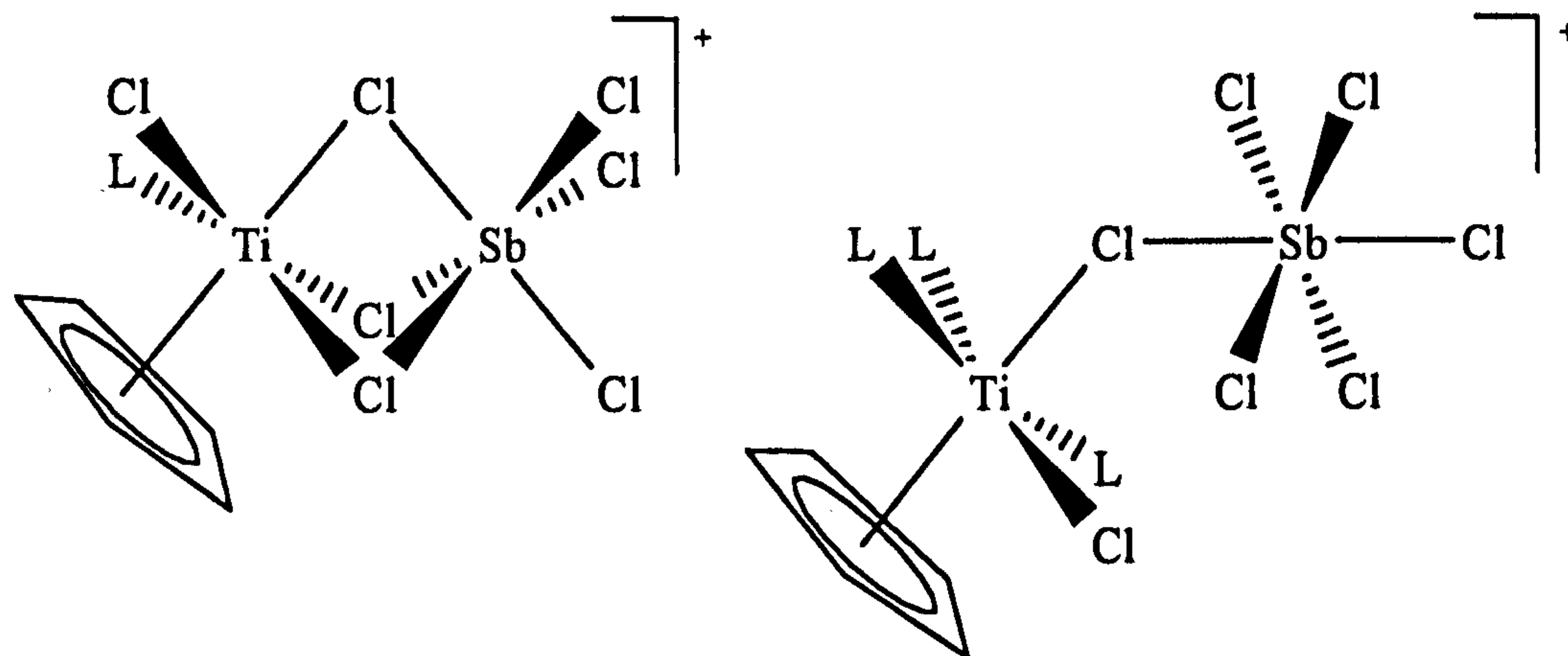
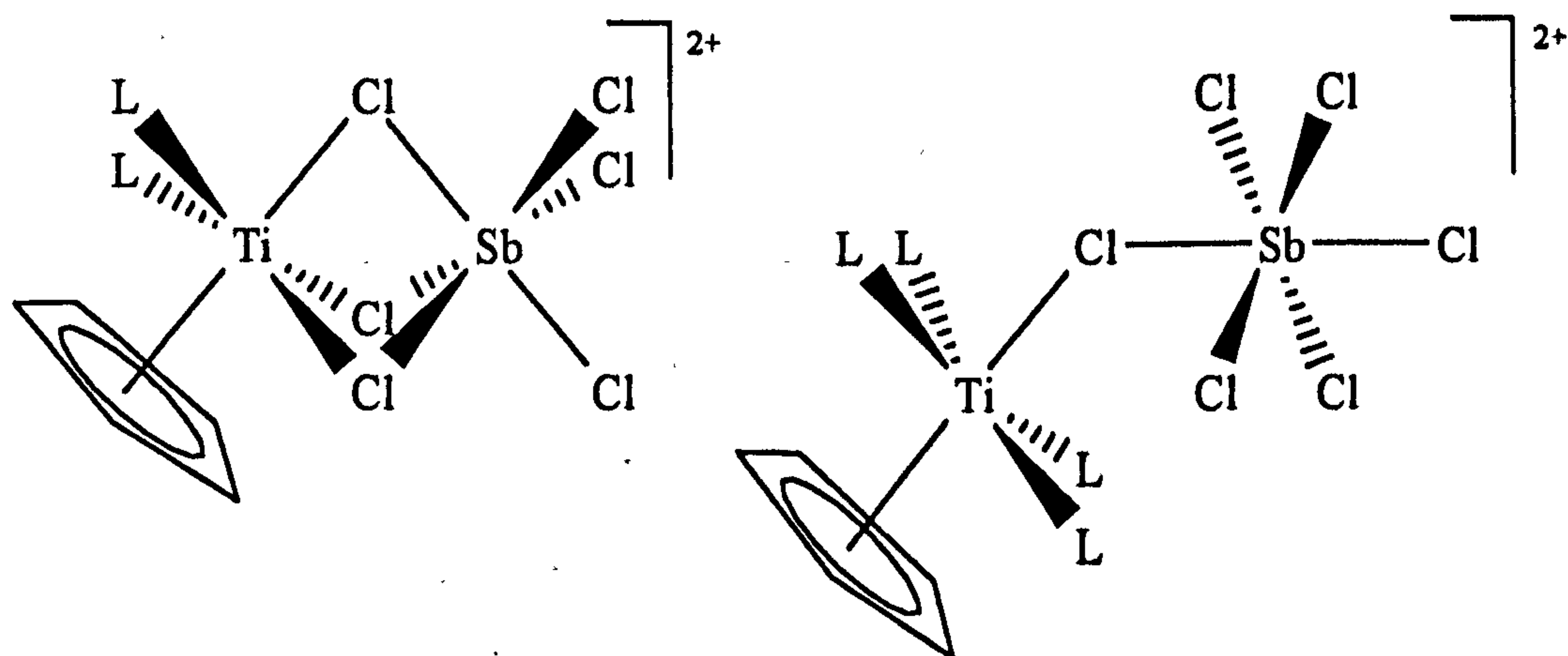


Figure 2.2: Postulated structures of the possible intermediates.



C

E



D

F

All attempts in the recovery of the intermediates in a pure, solid form were unsuccessful. It was hoped that they could be "trapped" by recrystallisation from MeCN/CH₂Cl₂ in the presence of a large excess of KSbCl₆. We assumed that the presence of excess anion would have the effect of pushing the equilibria towards the intermediates. However, in all cases, only the discrete ionic complexes were recovered. It is for this reason that it was decided to try some molecular modelling techniques to help estimate the bridging structures involved (section 2.3.1).

It is interesting that the resonances due to these intermediates are found at a higher field than their parent cations. This points to the possession of an increased electron density around the Ti centre in the intermediate moieties. It is assumed that this, in turn, arises from the extra π -donation of the Cl atoms in the postulated doubly-bridged structures.

In contrast to the complicated ¹H NMR, the IR spectra of the three cations are all very similar. The sharp doublet at ν 2321, 2291 (I), 2319, 2291 (II) and 2320, 2291 cm⁻¹ (III) is indicative of the coordinated MeCN; the shift to higher energy (34-40 cm⁻¹) with respect to free ligand is typical for such solvated cationic species. It is perhaps surprising that there is no relationship between the charge of the metal centre and the force constant of the (C \equiv N) bond; the stretches are roughly constant. This is also true of the characteristic bands of the Cp group which remain unchanged from those in CpTiCl₃. In all cases, the low energy region of the spectra is dominated by an intense, broad band at *ca.* 348 cm⁻¹ due to the SbCl₆ anion (*cf.* [K][SbCl₆] ν (Sb-Cl)F_{1u}(ν_3)346 cm⁻¹).¹¹⁴ Unfortunately, this absorbance covers the area in which the (Ti-Cl) and (Ti-Cp) stretches appear, precluding their assignment.

The UV spectra, recorded in MeCN, are also similar for all three cations. An intense charge transfer band is seen around λ_{max} 36,800 cm⁻¹ which is diagnostic of the SbCl₆⁻ anion in solution.¹⁰²

2.3.1: Molecular modelling of the chloride-bridged intermediates.

The relationship between structure, reactivity, strain energy and steric hindrance has long been recognised in qualitative terms. A quantitative measure of the effect is much more difficult to achieve. With the evolution of high powered computers, good semi-quantitative analysis is now possible. Molecular mechanics calculations can provide an idealised structure for any given molecule. Using approximated interatomic distances and angles (often gained from the parameters of similar compounds) as a starting point, calculations based on Force Field models result in a potential energy value for the optimum structure;¹¹⁵ the lower the PE value, the more "sterically favourable" the configuration. A comparison of this figure with those of known systems can then give an idea of the probable stability of the compound under scrutiny. The calculations take account of both bonding and non-bonding interactions between the atoms of the compound.

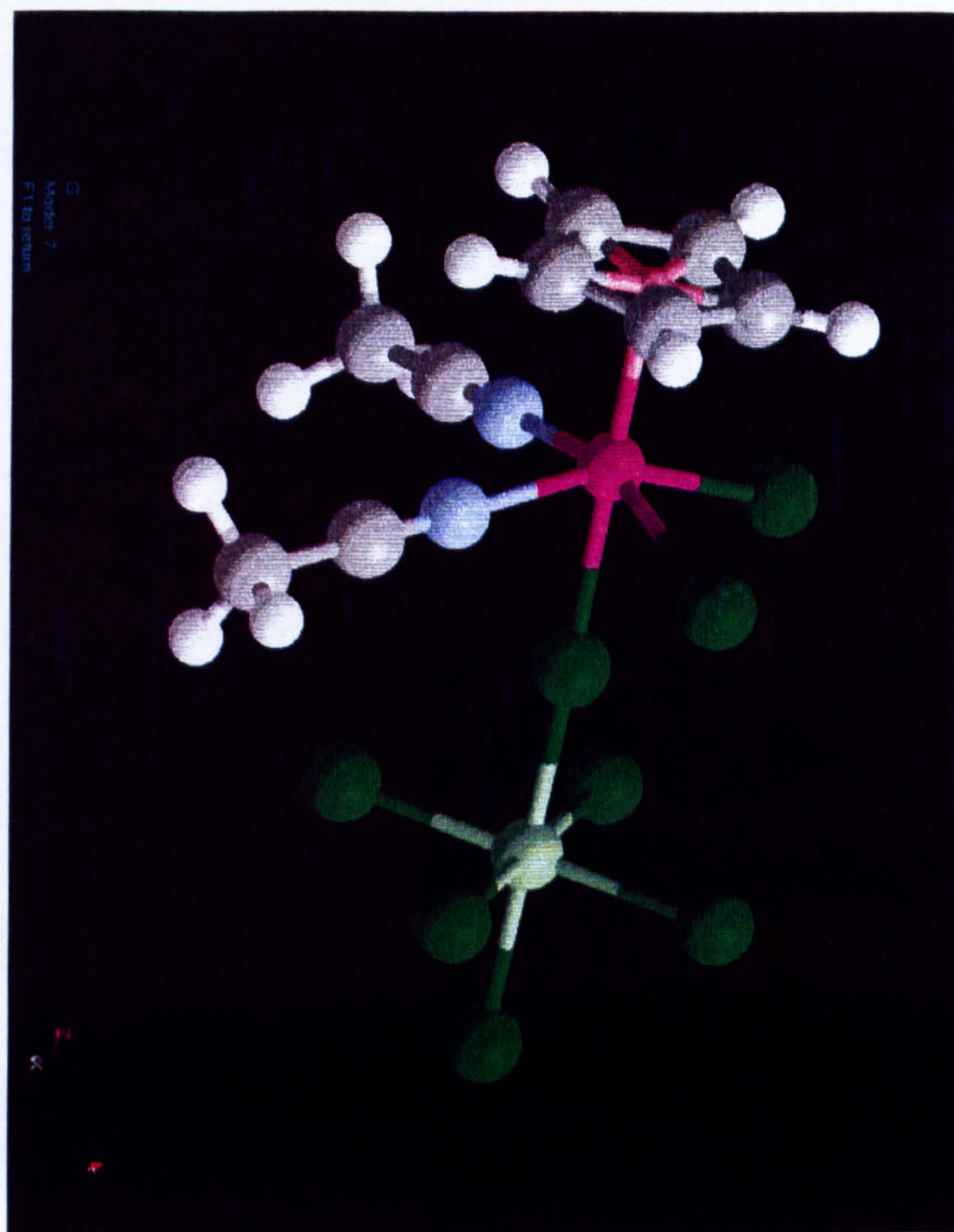
In this way, hypothetical structures can be "built" and investigated using data from other systems. By this method, the PE values of the postulated intermediates of the halide exchange reactions have been estimated. This was achieved with the aid of Dr. D. Ramdas and the facilities provided by BP Chemicals Ltd. at the Sunbury Research Centre. The structures were assembled using bond length and angle data of the trication III (next section).

Not surprisingly, the results of this study suggest that the most sterically favoured intermediates involve the single (apex-apex) Cl-bridge. The models of the three possible intermediate structures are shown pictorially in **Figures 2.3, 2.4, and 2.5.**

The main disadvantages of this type of molecular modelling are amply evident in this study. When some intermediates are known to exist in the doubly-bridged conformation, it is obvious that electronic effects that are almost impossible to forecast are sometimes just as important as steric considerations. The

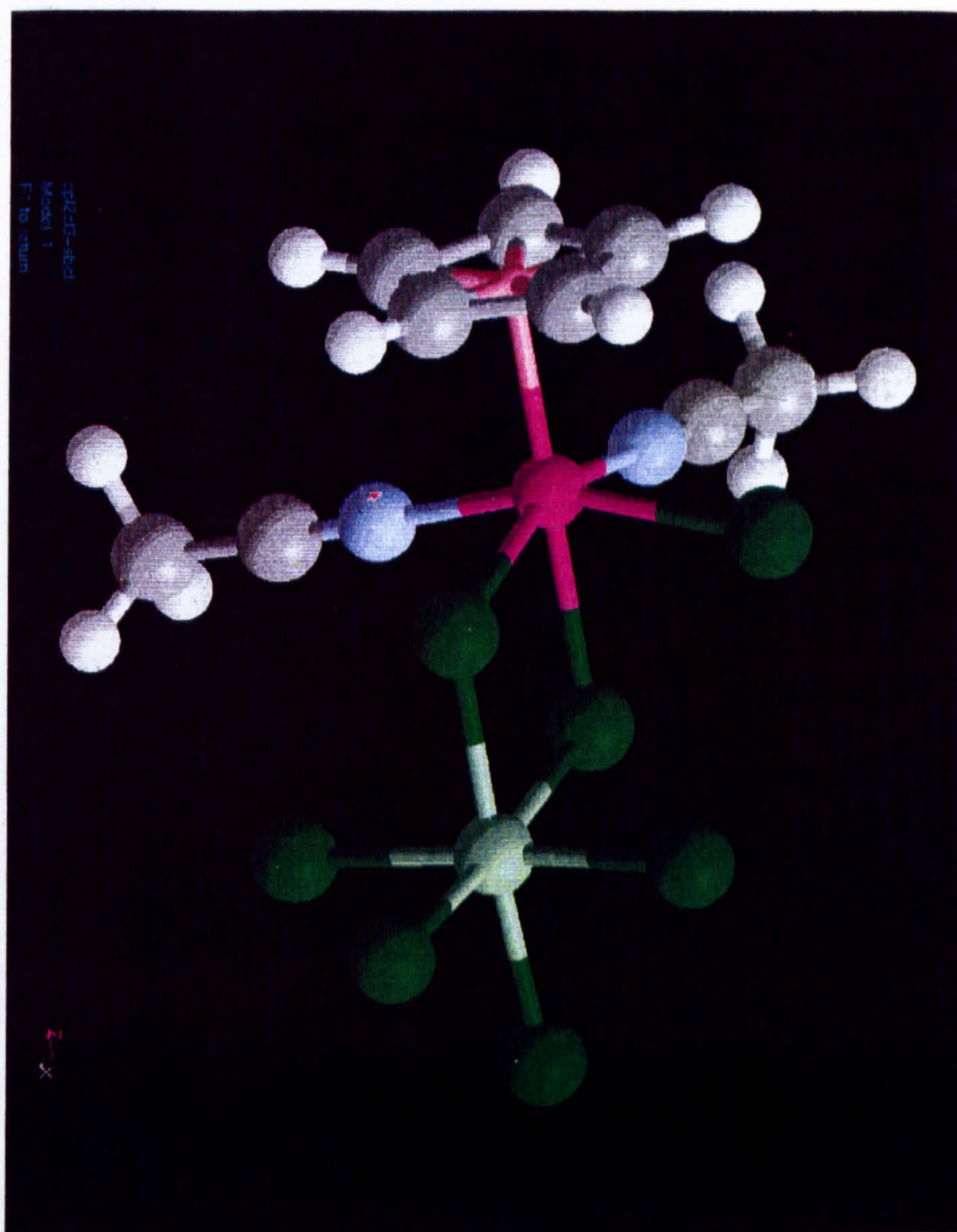
program used in this experiment would predict an (apex-apex) interaction as a direct result of the lack of electronic factors in the Force Field calculations.

Figure 2.3: Molecular model of the postulated (apex-apex) intermediate.



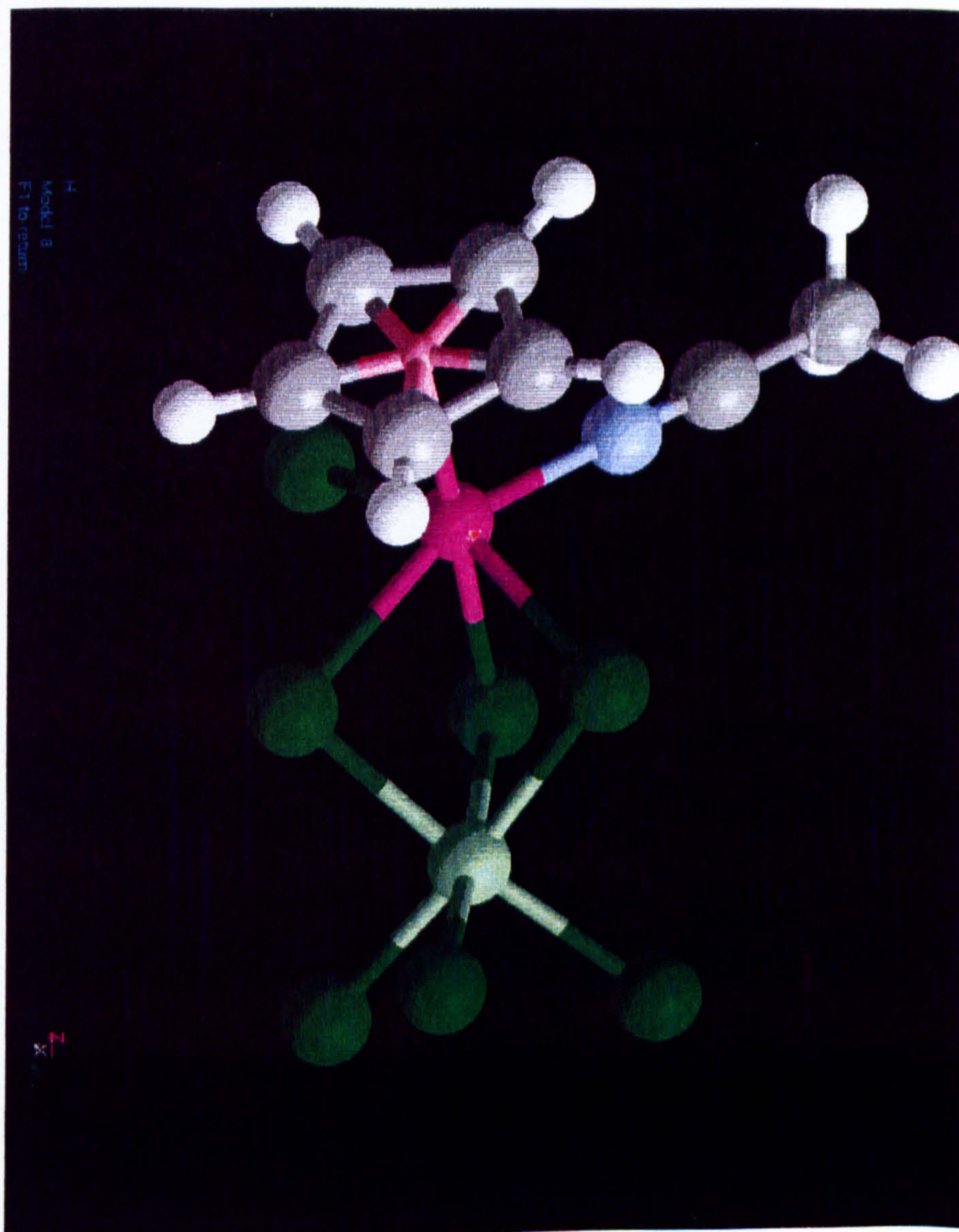
Calculated PE value = 44.77 kcal mol⁻¹

Figure 2.4: Molecular model of the postulated (edge-edge) intermediate.



Calculated PE value = 147.79 kcal mol⁻¹

Figure 2.5: Molecular model of the postulated (face-face) intermediate.



Calculated PE value = 253.67 kcal mol⁻¹

2.3.2: The X-ray crystal structure of [CpTi(MeCN)₅][SbCl₆]₃ 2MeCN (III).

The crystal and molecular structure of the title complex was determined by Dr I J Scowen at the University of North London. The chosen purple-blue crystal of **III** was sealed in a Lindemann tube under an atmosphere of argon and data obtained via a Phillips PW1100 four-circle diffractometer by the method described in the literature.¹¹⁶

Crystal data: C₁₉H₂₆Cl₁₈N₇Sb₃Ti, M = 1403.72, monoclinic, space group Cc, a = 19.650(4), b = 19.182(4), c = 12.958(3) Å, β = 91.612(3)°, Z = 4, U = 4882.27 Å³, D_c = 1.910 g cm⁻³, F(000) = 2 680, μ(Mo-Kα) = 27.1 mm⁻¹, R=0.03.

The structure of the bis(MeCN) solvate of complex **III** shows a discrete [CpTi(MeCN)₅]³⁺ cation, three SbCl₆⁻ counter anions and two non-associated (and disordered) MeCN molecules in the asymmetric unit (**Figure 2.6**). Selected bond lengths and angles are given in **Table 2.4**. The cation is 6-coordinate; the metal coordination sphere comprises of five N-bonded MeCN ligands and an η⁵-bonded Cp anion, and shows significant distortion from idealised octahedral geometry (**Figure 2.7**).

The Cp ring is symmetrically bonded to the metal with a ring centroid-Ti distance (2.04Å) comparable to those found for neutral CpTiCl₃ (2.01Å)³³ and cationic [Cp₂TiCl(C₃H₂N₂)]⁺ (2.00, 2.03Å).⁸⁴ The four "equatorial" nitrogen atoms are coplanar to within 0.01Å. The metal lies 0.46Å above the N₄ equatorial plane and consequently N-Ti-N angles between these ligands and the MeCN *trans* to the Cp ring are in the range 76.7(4)-77.8(4)°, significantly smaller than the ideal. This can be attributed to steric effects between the bulky Cp ligand and the equatorial ligands.

The (Ti-N) bond lengths in the equatorial plane, in the range 2.089(11)-2.098(10) Å, are significantly shorter than those in the 6-coordinate

$[\text{TiCl}_3(\text{MeCN})_3]^+$ monocation¹⁰¹ and in 4-coordinate titanocenes featuring N-bonded nitrile ligands.^{117,118} This shortening may be attributed to the markedly higher charge of the trication centre in **III**. Interestingly, the bond length to the nitrogen *trans* to the Cp ring in the Ti(IV) coordination sphere [Ti-N(5) 2.185(12) Å] is significantly longer than the equatorial Ti-N distances and is attributed to a *trans* influence from the η^5 -Cp ligand. Since this appears to be the first example of an octahedral CpTi(IV)-MeCN complex, suitable comparisons with related complexes are not possible.

The hexachloroantimonate(V) counter anions possess geometries close to ideal octahedral; observed bond angles lie in the range 88.6(4)-91.1(4)°, within 2° of the ideal, and (Sb-Cl) bond lengths in the range 2.321(5)-2.365(4) Å.

The structure of **III** corresponds to a 16-electron count for the Ti centre. A survey of the Cambridge Crystallographic Database reveals a distinct lack of other octahedral, cationic CpTi-based complexes. The closest example to this particular series has been synthesised by Winter *et al.*¹¹⁹ the structure of the triflate salt, $[\{\eta^5\text{-C}_5(\text{SiMe}_3)_2\text{H}_3\}\text{Ti}(\text{acac})_2][\text{CF}_3\text{SO}_3]$, features the 5-coordinate CpTi-based cation with a formal 14-electron configuration. An octahedral geometry only results when the triflate anion enters the empty coordination site at the Ti centre thus removing the formal positive charge.

Figure 2.6: The asymmetric unit of $[\text{CpTi}(\text{MeCN})_5][\text{SbCl}_6]_3 \cdot 2\text{MeCN}$ (III).

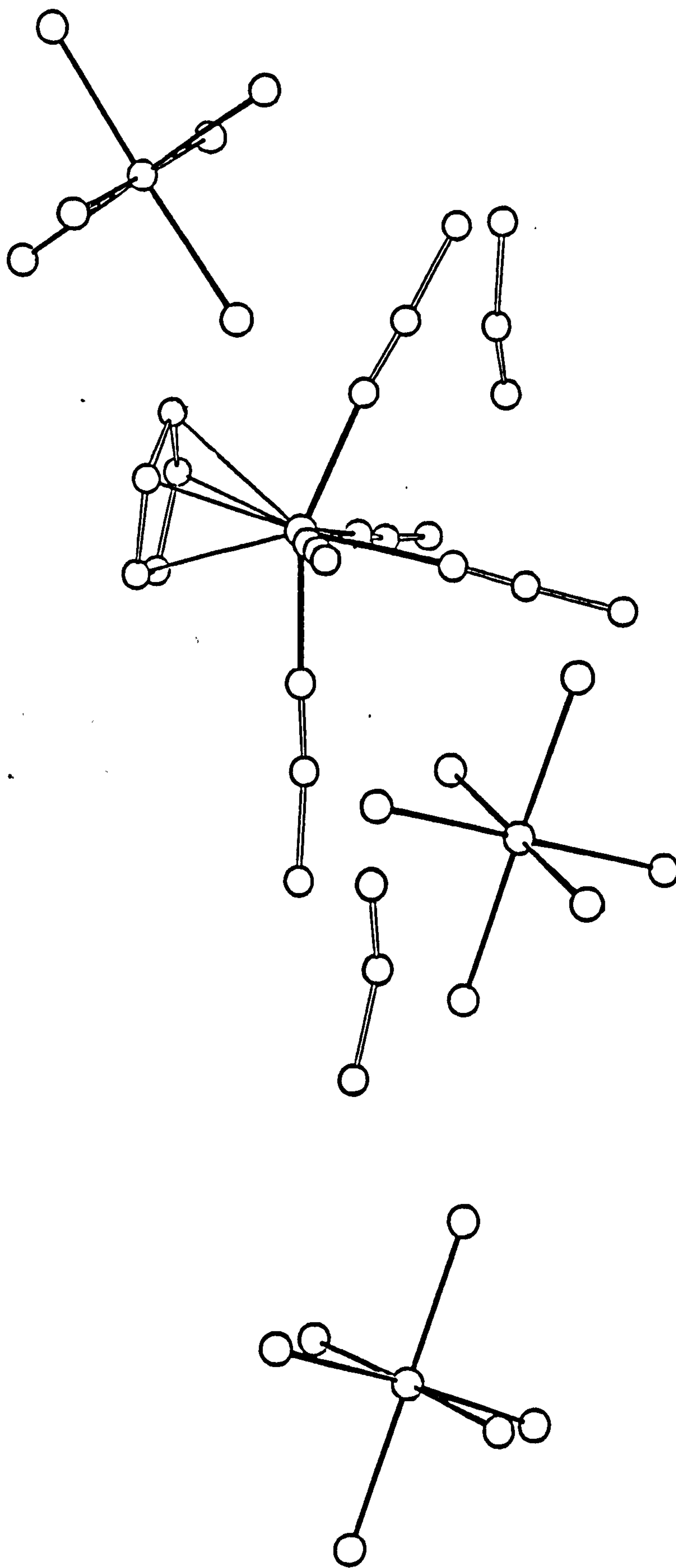


Figure 2.7: View of the discrete $[\text{CpTi}(\text{MeCN})_5]^{3+}$ cation.

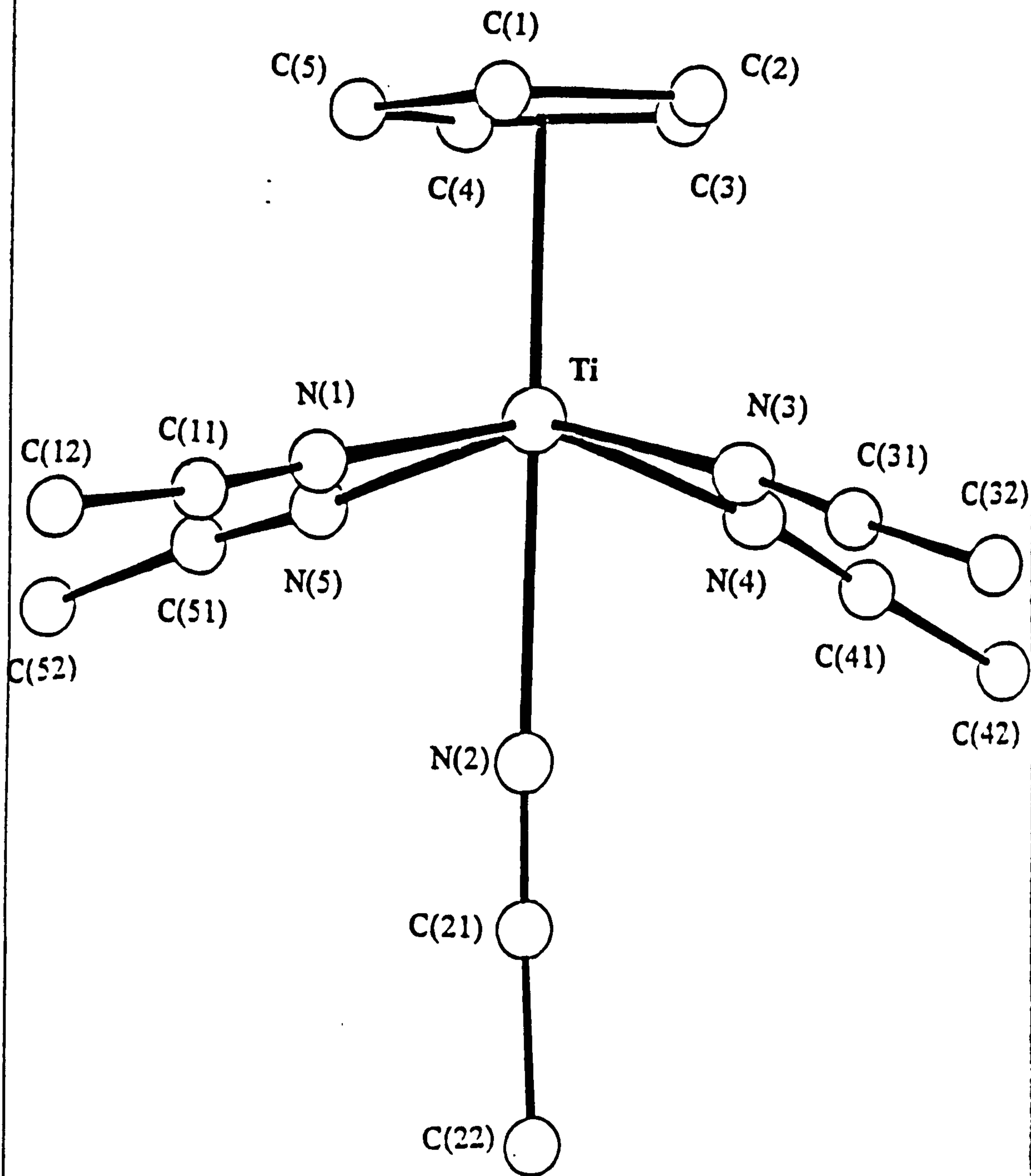


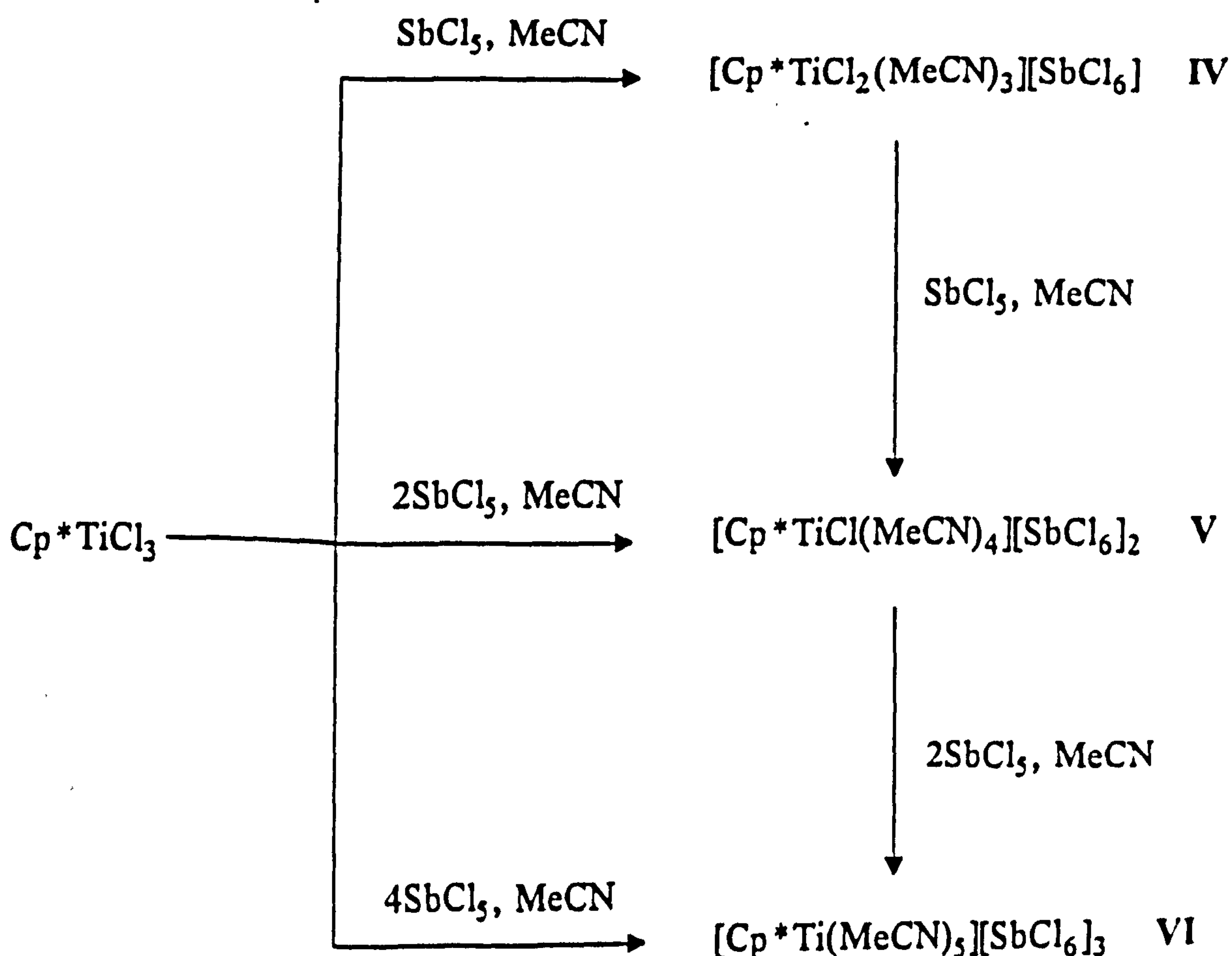
Table 2.4: Selected bond lengths (Å) and angles (°) for [CpTi(MeCN)₅][SbCl₆]₃.

Ti-N(1)	2.092(11)	Ti-N(2)	2.098(10)
Ti-N(3)	2.089(11)	Ti-N(4)	2.094(11)
Ti-N(5)	2.185(12)	Ti-C(1)	2.36(2)
Ti-C(2)	2.37(2)	Ti-C(3)	2.40(2)
Ti-C(4)	2.38(2)	Ti-C(5)	2.32(2)
N(1)-C(11)	1.12(2)	C(11)-C(12)	1.45(2)
N(2)-C(21)	1.11(2)	C(21)-C(22)	1.45(2)
N(3)-C(31)	1.11(2)	C(31)-C(32)	1.47(2)
N(4)-C(41)	1.13(2)	C(41)-C(42)	1.48(2)
N(5)-C(51)	1.10(2)	C(51)-C(52)	1.39(2)
C(1)-C(2)	1.42(2)	C(1)-C(5)	1.40(2)
C(2)-C(3)	1.37(2)	C(3)-C(4)	1.46(2)
C(4)-C(5)	1.41(2)		
N(2)-Ti-N(1)	85.6(4)	N(2)-Ti-N(5)	76.7(4)
N(4)-Ti-N(1)	88.2(4)	N(4)-Ti-N(5)	77.8(4)
N(4)-Ti-N(2)	156.6(4)	N(3)-Ti-N(1)	154.8(4)
N(3)-Ti-N(5)	77.4(4)	N(3)-Ti-N(2)	88.0(4)
N(3)-Ti-N(4)	87.2(4)	N(5)-Ti-N(1)	77.5(4)
C(11)-N(1)-Ti	178(1)	C(21)-N(2)-Ti	175(1)
C(31)-N(3)-Ti	175(1)	C(41)-N(4)-Ti	179(1)
C(51)-N(5)-Ti	176(1)	N(1)-C(11)-C(12)	176(2)
N(2)-C(21)-C(22)	176(1)	N(3)-C(31)-C(32)	179(2)
N(4)-C(41)-C(42)	178(2)	N(5)-C(51)-C(52)	177(2)
C(5)-C(1)-C(2)	107(1)	C(3)-C(2)-C(1)	111(1)
C(4)-C(3)-C(2)	107(1)	C(5)-C(4)-C(3)	107(1)
C(4)-C(5)-C(1)	109(1)		

2.4: Halide abstraction from Cp*TiCl₃.

Stepwise chloride abstraction from Cp*TiCl₃ using SbCl₅ in MeCN yielded three new cationic species (Scheme 2.3). The preliminary work on this system was conducted jointly with Dr F Palaços during a collaborative study with the University of Madrid.

Scheme 2.3.



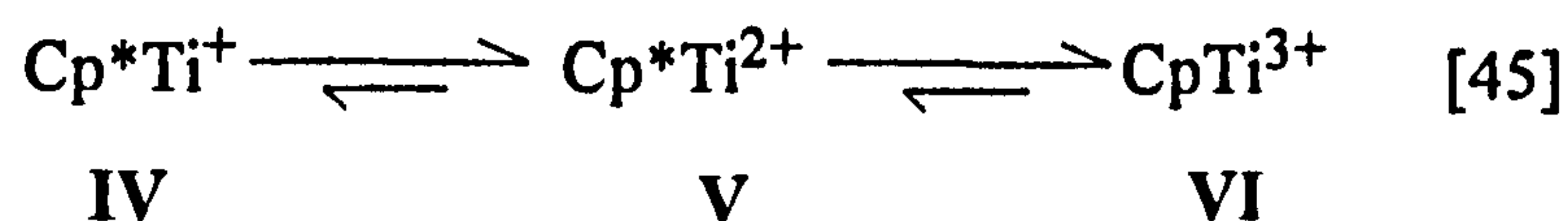
All of the complexes are insoluble in the common laboratory solvents except MeCN and Me₂CO which must be carefully dried. Recrystallisation from MeCN/CH₂Cl₂ results in analytically pure solids. Some physical and spectroscopic data are summarised in Table 2.5.

Table 2.5: Selected physical and spectroscopic data for the SbCl_6^- salts of the $\text{Cp}^*\text{Ti}^{n+}$ series.

	$[\text{Cp}^*\text{TiCl}_2(\text{MeCN})_3]^+$ IV	$[\text{Cp}^*\text{TiCl}(\text{MeCN})_4]^{2+}$ V	$[\text{Cp}^*\text{Ti}(\text{MeCN})_5]^{3+}$ VI
Colour	dark red	dark green	light green
Microanalysis			
C H N	27.00 3.41 5.91	20.55 2.59 5.33	17.26 2.18 5.03
(calc./obs.)	25.97 3.27 6.09	20.32 2.40 5.30	17.20 2.13 4.98
$^1\text{H NMR}$, δ/ppm . (250 MHz) (CD_3CN solution)	2.37	2.40	2.50
IR (nujol), ν/cm^{-1}			
Cp*	1025(m)	1020(m)	1025(m)
($\text{C}\equiv\text{N}$) stretch	2315(s)	2310(s)	2310(s)
	2280(s)	2296(s)	2280(s)
(Sb-Cl) stretch	345(vs)	345(vs)	344(vs)

As in the analogous CpTi series, the mono- (IV) and dication (V) were formed using the appropriate stoichiometric quantities of Cp^*TiCl_3 and SbCl_5 whilst the trication VI requires an excess of the Lewis acid. However, it is noticeable that this excess (4-fold) was significantly lower than that required in the synthesis of CpTi^{3+} (III) (6-fold).

In fact, the whole reaction scheme is much less equilibrium-based than that of the CpTi analogue. This is shown in the ^1H NMR and in the recrystallisation of V when very little IV is recovered [45].



The ^1H NMR of this cationic series is very simple; complex IV gives one Cp signal, complex V gives two (one of which is due to IV) and complex VI gives three (for all three distinct cations). There is no evidence for any chloro-bridged intermediates and the retro reactions from each cation is very small. In contrast to its Cp analogue, the trication VI does exist in solution at room temperature. Ligand-solvent exchange is still very rapid in CD_3CN with no coordinated CH_3CN detectable after 5 minutes.

Interestingly, on going from the neutral parent species to the monocation, a slight drop is seen in the chemical shift of the Cp signal. This is probably due to the electron density afforded by the three extra MeCN ligands. After this initial reaction, an increase in the charge of the metal is accompanied by a downfield shift in the Cp resonance as usual.

It is clear from these observations that the Cp* group facilitates the formation of cationic species. It may well be that the extra electron density supplied lowers the Lewis acidity of the metal centre, thus weakening the (Ti-Cl) bonds. The absence of any intermediates can be explained by the steric bulk of the Cp* which discourages any bimetallic interaction.

Other than the factors discussed above, the general properties and spectra of the Cp^*M^{n+} series reflect those of the CpM^{n+} situation. The IR spectra include bands for coordinated MeCN, the Cp* group and the SbCl_6^- anion. Again, all of the complexes decompose before melting and are extremely sensitive to hydrolysis.

2.5: Halide abstraction from $\text{CpMCl}_3(\text{MeCN})_2$ for $\text{M} = \text{Zr}$ and Hf .

As a useful comparison with the CpTiCl_3 system, the title compounds were treated sequentially with equimolar, MeCN solutions of SbCl_5 . The products of these reactions proved to be difficult to identify. Initially it was assumed that halide abstraction would yield 6-coordinate, pseudo-octahedral metal complexes as in the analogous Ti-based series. Using this assumption, spectroscopic and elemental analysis results suggested that the tricationic complexes could not be formed. However, this assignment was disproved when a crystal, grown from a MeCN solution of the proposed Hf-based "dication" in the presence of excess SbCl_5 , was the subject of an X-ray analysis; its structure was found to involve $[\text{CpHf}(\text{MeCN})_6][\text{SbCl}_6]_3$. Thus, whilst the relevant mono- and di- cations can be formed in facile (stoichiometric) conditions, the tricationic complexes are only formed during recrystallisation in the presence of a large excess of SbCl_5 . There is no evidence of the CpM^{3+} moieties in solution, even at elevated temperatures.

Scheme 2.4 describes the reaction profile.

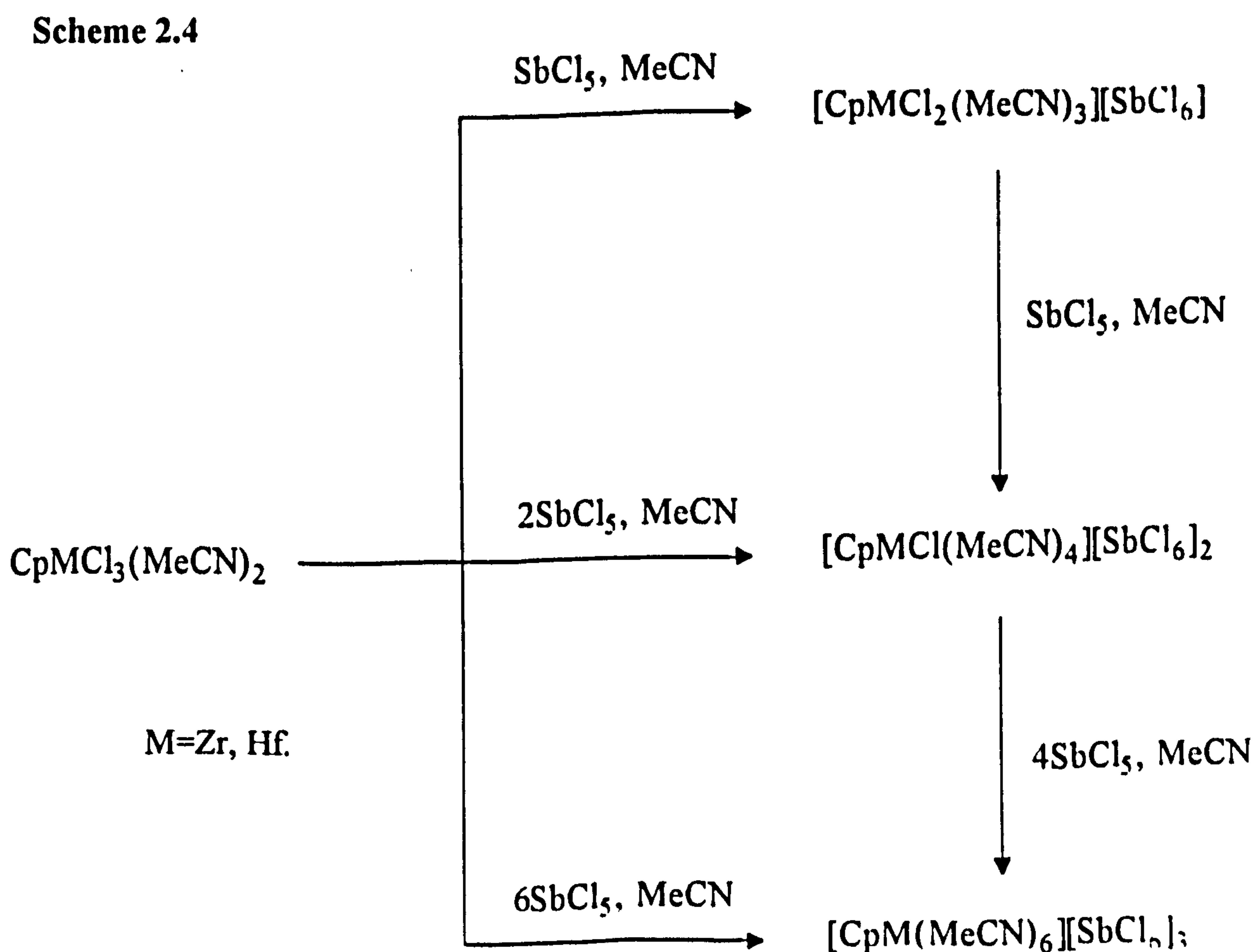


Table 2.6: Properties of the CpMⁿ⁺ series for M=Zr and Hf.

	colour	microanalysis			IR, v/cm ⁻¹		¹ H NMR, δ/ppm	
		(calc/obs)			(nujol)		(CD ₃ CN sol ⁿ)	
		C	H	N	v(C≡N)	v(Sb-Cl)	Cp	MeCN
[CpZrCl ₂ (MeCN) ₃] ⁺ VII	off- white	19.29 18.58	2.06 2.33	6.14 5.72	2315 2285	346	6.69	2.53(br.)
[CpZrCl(MeCN) ₄] ²⁺ VIII	white	15.23 15.35	1.68 1.98	5.47 5.75	2320 2290	345	6.86	2.54(br.)
[CpZr(MeCN) ₆] ³⁺ IX	white	14.52 14.52	1.65 1.62	5.98 5.78	2320 2290	345	6.85	2.53(br.)
[CpHfCl ₂ (MeCN) ₃] ⁺ X	off- white	17.11 16.91	1.83 1.93	5.44 5.51	2315 2290	345	6.52	2.57(br.)
[CpHfCl(MeCN) ₄] ²⁺ XI	white	14.04 13.85	1.54 1.62	5.04 5.36	2320 2290	344	6.66	2.57(br.)
[CpHf(MeCN) ₆] ³⁺ XII	white	13.67 13.56	1.56 1.73	5.63 5.93	2320 2290	345	6.65	2.57(br.)

The six cationic complexes generally exhibit similar properties both physical and spectroscopic. Some of these are summarised in **Table 2.6**. The cations are only soluble in very polar solvents, most notably MeCN in which they form yellow-brown solutions. They all share a moisture and heat sensitive nature, especially in solution. In the solid state, the Hf-based series slowly decompose at room temperature over a period of weeks. All of the complexes decompose at similar temperatures (80-110°C). To increase their life span, they are best stored in the refrigerator under an atmosphere of argon.

The IR spectra of the six complexes are all very similar. Absorbances that are characteristic of coordinated MeCN, the Cp group and the SbCl_6^- anion are all observed. The fact that these all occur at similar wavenumbers suggests that the relevant bond strengths do not vary with sequential cation formation. It is noteworthy that the region below 400 cm^{-1} is considerably simplified in all cases when compared to the neutral parent compounds. The individual (M-Cl) bond stretches are most probably drowned by the broad, intense band at 345 cm^{-1} which is due to the anion.

Prior to the X-ray crystal structure determination of **XII**, the only evidence for the existence of the trications lay in the yields recorded for the $\text{CpMCl}_3\text{L}_2 + 6\text{SbCl}_5$ reactions. The extremely high values corresponded to over 100% production of the appropriate dications. However, the absence of a suitable signal in the NMR coupled with "poor" elemental analysis results led us to doubt the existence of the trications.

The measured C, H and N values of the products of the $\text{CpZrCl}_3\text{L}_2 + 6\text{SbCl}_5$ reaction are much closer to the theoretical figures for the dication **VIII** than those of the expected trication $[\text{CpZr}(\text{MeCN})_5][\text{SbCl}_6]_3$. It is only when the values are calculated for the 7-coordinate **IX** that the formation of a trication becomes feasible (**Table 2.7**). The Hf-based series shows a similar pattern.

**Table 2.7: Elemental compositions of the various possible products of
CpZrCl₃(MeCN)₂ + 6SbCl₅.**

	C	H	N
[CpZrCl(MeCN) ₄][SbCl ₆] ₂	15.23	1.68	5.47
[CpZr(MeCN) ₅][SbCl ₆] ₃	13.20	1.48	5.13
[CpZr(MeCN) ₆][SbCl ₆] ₃	14.52	1.65	5.89
Actual product recovered	15.35	1.98	5.75

Once that the 7-coordinate nature of the trication becomes apparent, the number of MeCN ligands around the mono- and dication must be brought into question. The relevant elemental analysis results strongly suggest that these complexes do exhibit pseudo-octahedral geometries but this is not conclusive. For this reason, we await a crystal structure determination of the Hf dication **XI**.

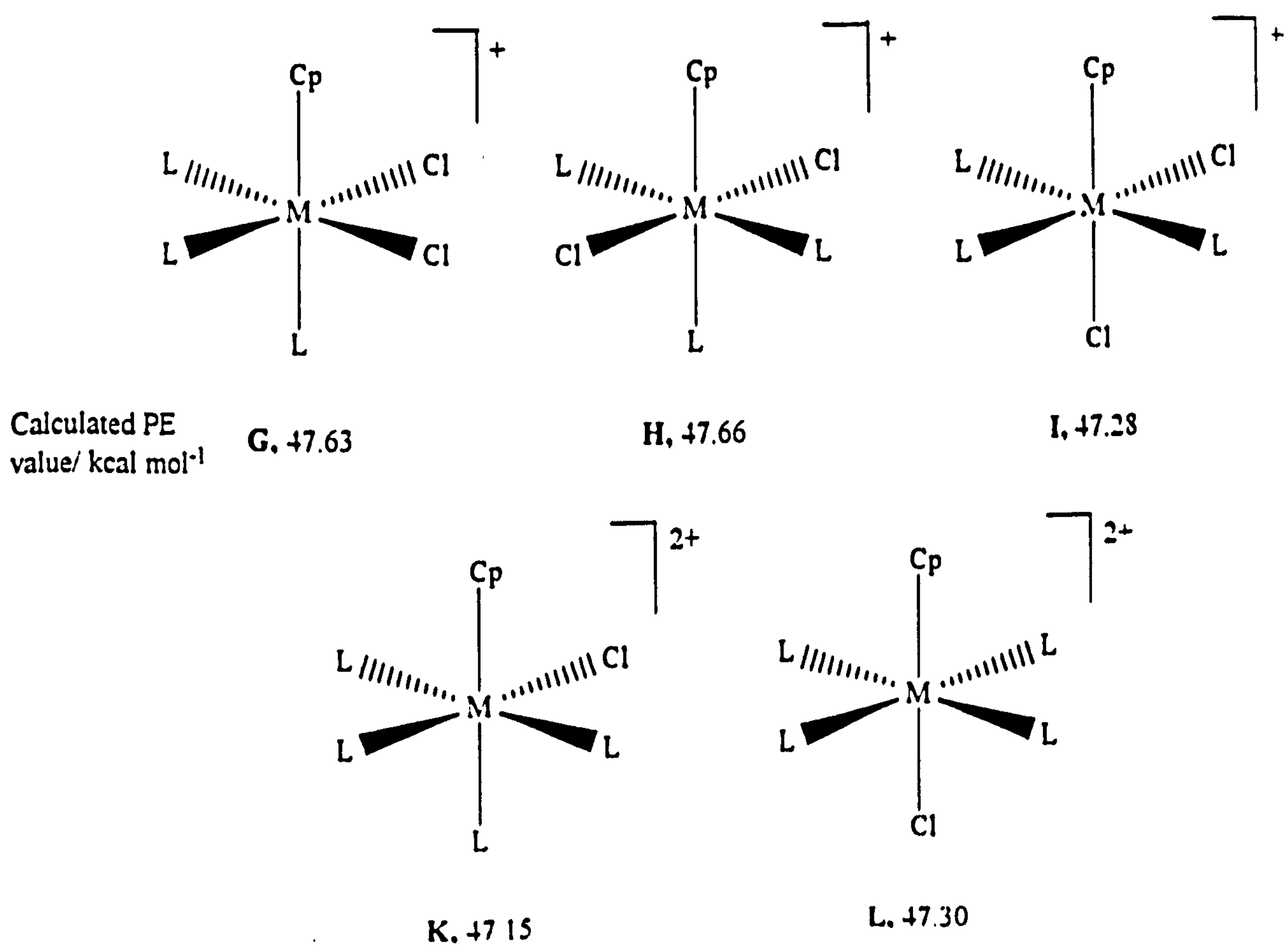
The ¹H NMR spectra of the complexes are very interesting. As in the analogous Ti-based system, the triply-charged cations are thought not to exist in solution, even at high temperatures (up to 76°C). When the spectra are recorded in the presence of excess SbCl₅, a resonance is seen at a field very close to that of the appropriate dication; there is no characteristic downfield shift for CpM³⁺. This could be due to the extra electron density afforded by the 7-coordinate metal centre, but is more likely to show the non-existence of the trications in solution. This signal could be due to a Cl-bridged intermediate similar to those proposed in the Ti system earlier.

The most notable feature in the spectra of the mono- and dicationic complexes is the presence of signals due to coordinated MeCN. At room temperature in CD₃CN solution, broad resonances in the region around δ 2.5ppm are observed for all four complexes. Solvent-ligand exchange is thus considerably slower than in both the neutral parent species and the analogous Ti-based series. The coordinated MeCN is washed into solution over a period of hours rather than seconds although labilisation occurs with an increase in temperature.

This inert nature of the complexes at ambient temperatures results in the possibility of viewing isomeric species in solution. These geometrical isomers are illustrated in **Figure 2.8** along with their postulated chemical shifts. If a solution of recrystallized cation is studied, then initially only the most favoured isomer is seen as a singlet in the ¹H NMR. New signals then appear as isomerisation occurs. However, if freshly prepared (i.e. not recrystallized) the resonances due to the mono- and di- cations are split into three and two respectively at 23°C. As the signals cannot be labelled with absolute certainty, some computer based molecular modelling calculations were carried out to aid in their assignment. The calculations were based upon the steric requirements of the relative configurations using bond lengths and angles measured in the structures of other, similar complexes. Results in the form of potential energy values were then correlated with the intensities of the Cp signals of the isomers; the lower the PE value, the more sterically favourable the conformation and hence the higher integral value in the NMR. This method of assignment is not perfect since electronic effects are neglected in the calculations used by the computer. They are only introduced by way of the bond lengths employed; there may be more important (electronic) considerations in the real situation.

Figure 2.8: The chemical shift of the Cp group in the relative configurations of the $[\text{CpMCl}_2\text{L}_3]^+$ and $[\text{CpMClL}_4]^{2+}$ complexes for $\text{M}=\text{Zr}$ and Hf .

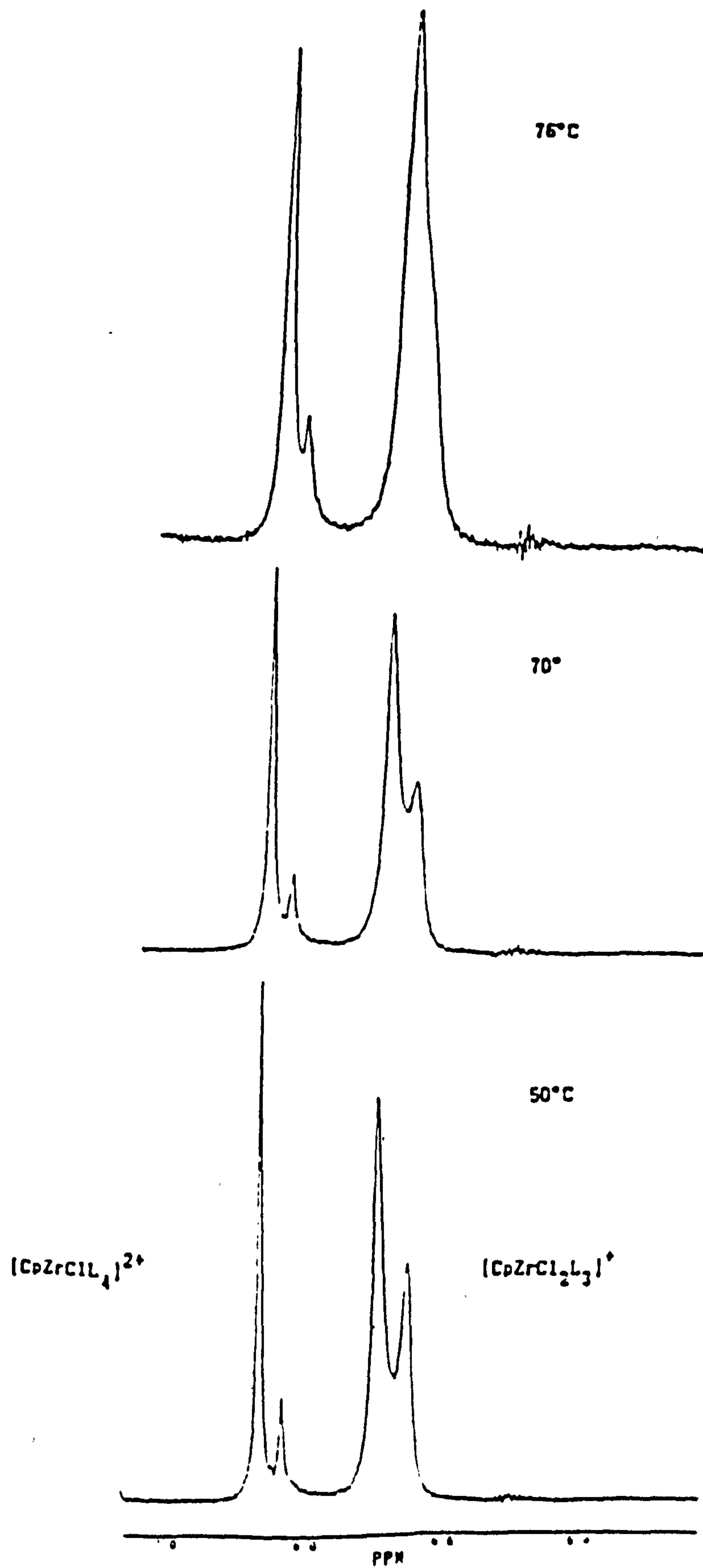
species	^1H NMR (CD_3CN solution) Cp δ/ppm .	
	Zr	Hf
H	6.64	6.48
I	6.69	6.52
G	6.73	6.57
K	6.84	6.66
L	6.87	6.68



At elevated temperatures, the systems become much more labile. This is illustrated in two ways by the ^1H NMR spectra: the signal due to coordinated MeCN disappears as the rate of ligand exchange increases and the isomeric Cp resonances begin to coalesce. Some higher temperature spectra are reproduced in **Figure 2.9**. They show a mixture of the CpZr^+ and CpZr^{2+} complexes in CD_3CN solution. It is noticeable that the monocation isomerises faster than its doubly-charged analogue. The increase in charge seems to be accompanied by an increase in the (M-L) bond strength.

The conclusions of these solution studies represent a considerable change from those reported before. In his review of cationic dicyclopentadienyl Group 4 metal-alkyl complexes, Jordan¹²⁰ reports that such species are normally extremely labile with respect to solvent exchange. It is postulated that the reason for the inert nature of complexes **VII** to **XII** lies in the electron deficiency resulting from the lack of a second Cp group. This results in very strong (MeCN-M) bonding. This simplistic argument can also be used to explain the 7-coordinate structure of the CpM^{3+} trications: the extremely hard tricationic metal centre requires extra electron density in the form of 6 MeCN ligands.

Figure 2.9: Variable temperature ^1H NMR spectra of a mixture of $[\text{CpZrCl}_2\text{L}_3]^+$ and $[\text{CpZrClL}_4]^{2+}$.



2.5.1: The X-ray crystal structure of $[\text{CpHf}(\text{MeCN})_6][\text{SbCl}_6]_3$ (XII).

The crystal and molecular structure of the title complex was determined by Dr. Michael Drew at the University of Reading. The chosen colourless crystal of XII was sealed in a Lindemann tube under an atmosphere of argon.

Crystal data: $\text{C}_{35}\text{H}_{48}\text{Cl}_{36}\text{Hf}_2\text{N}_{12}\text{O}_4\text{Sb}_6$, $M=1403.72$, monoclinic, space group $P2_1/n$, $a=22.627(5)$, $b=18.956(5)$, $c=22.699(5)$ Å, $\beta=98.80(10)^\circ$, $Z=4$, $U=9621(8)$ Å³, $D_c=2.106$ gcm⁻³, $F(000)=5716$, $\mu(\text{Mo-K}\alpha)=27.1$ mm⁻¹, $R=0.08$.

The asymmetric unit of complex XII consists of two independent $[\text{CpHf}(\text{MeCN})_6]^{3+}$ cations, six SbCl_6^- counter anions and four non-associated small molecules (labelled H_2O for crystallographic purposes). This is illustrated in **Figure 2.10**. Selected bond lengths and angles involved in the cations are given in **Tables 2.8** and **2.9** respectively.

Although the Hf is formally 11-coordinate, a better description is achieved when the Cp group is regarded as unidentate; the stereochemistry is then based on that of a pentagonal bipyramid. The metal coordination sphere thus comprises of five N-bonded MeCN ligands in the equatorial plane, with the Cp group and the remaining MeCN occupying the axial positions (**Figure 2.11**). There is however, a significant distortion from idealised geometry, mainly because of the steric bulk of the Cp ring. This distortion is such as to maintain approximate C_{5v} symmetry.

The Cp ring is symmetrically bonded to the metal with (C-Hf) distances that lie in the range 2.34-2.53 Å and average 2.43 Å. These values are significantly smaller than those reported both for hafnocene derivatives (*e.g.* Cp_2HfMe_2 , 2.50 Å)¹²¹ and the only other monocyclopentadienyl Hf complex, $\text{CpHf}(1,2,3\text{-Me}_3\text{allyl})(1,2\text{-Me}_2\text{butadiene})$ which has an average (Hf-C) distance of 2.49 Å.¹²² This shortening is quite surprising given the 7-coordinate nature of the metal centre.

The Cp ring has a staggered conformation with respect to the five equatorial nitrogen atoms. The latter are approximately coplanar, with the metal centred at 0.43 Å above the plane. The N-Hf-N angles between these equatorial nitrogens and that *trans* to the Cp ring are consequently smaller than the ideal, and lie in the range 73.8-80.5°. The (Hf-N) bond lengths are between 2.21 and 2.28 Å with an average of 2.27 Å. Unfortunately, since this appears to be the first example of a complex containing (Hf-nitrile) bonding, suitable comparisons are not possible.

The SbCl_6^- counter anions possess geometries close to ideal octahedral; the observed bond angles lie in the range 87.7-92.8° and (Sb-Cl) bond lengths in the range from 2.28-2.34 Å.

Complexes of the generic type $[\text{CpMX}_a\text{L}_{5-a}]^{(3-a)+}$ [where $a = 2, 1$ (and 0 for $M = \text{Ti, III}$)] have a formal 16-electron classification with a 6-coordinate, pseudo-octahedral metal geometry; the title complex XII features a 7-coordinate Hf centre. This expansion in coordination number on going from CpHf^{2+} to CpHf^{3+} is seen, in simple terms, as a result of the increased Lewis acidity coincident with the removal of the chloride ligand. Structure XII is the first example of a 7-coordinate Hf complex to contain a Cp ligand. However, similar geometries are exhibited by some Zr complexes which feature three anionic, bidentate ligands such as $\text{CpZr}(\text{hfac})_3$ ¹²³ and $\text{CpZr}(\text{S}_2\text{CNMe}_2)_3$.¹²⁴ The number of structures which involve a formal positive charge on an Hf centre is similarly limited; to date, only those of $[\text{Cp}^*_2\text{HfMe}(\text{THT})][\text{BPh}_4]$ ¹²⁵ and $[\{(9\text{N}_3)\text{Hf}(\text{acac})_2\}_2\text{O}][\text{ClO}_4]_2$ ¹²⁶ have been reported.

Figure 2.10: The asymmetric unit of $[\text{CpII}(\text{MeCN})_6][\text{SbCl}_6]_3$.

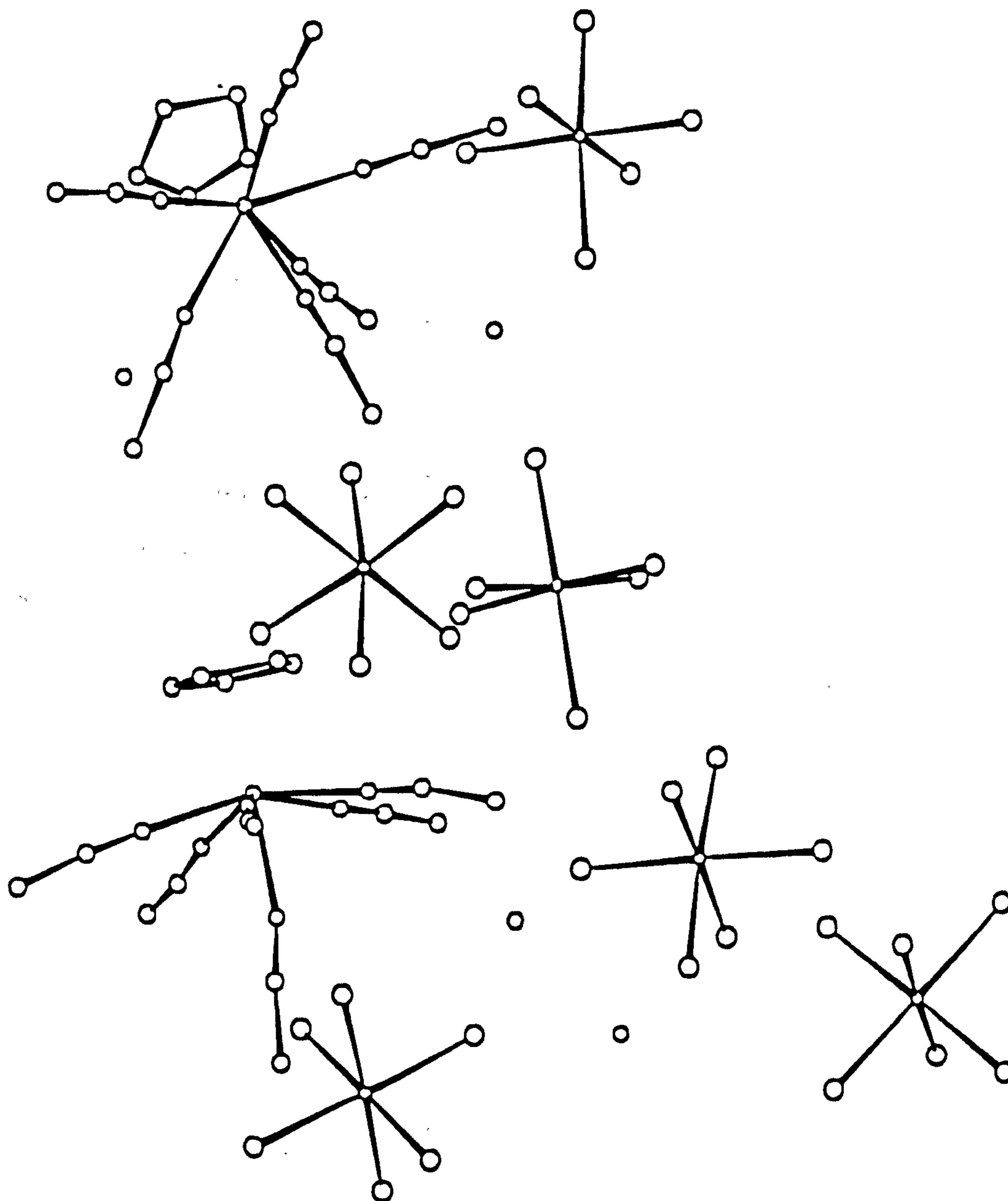


Figure 2.11: View of the discrete $[\text{CpHf}(\text{MeCN})_6]^{3+}$ cation.

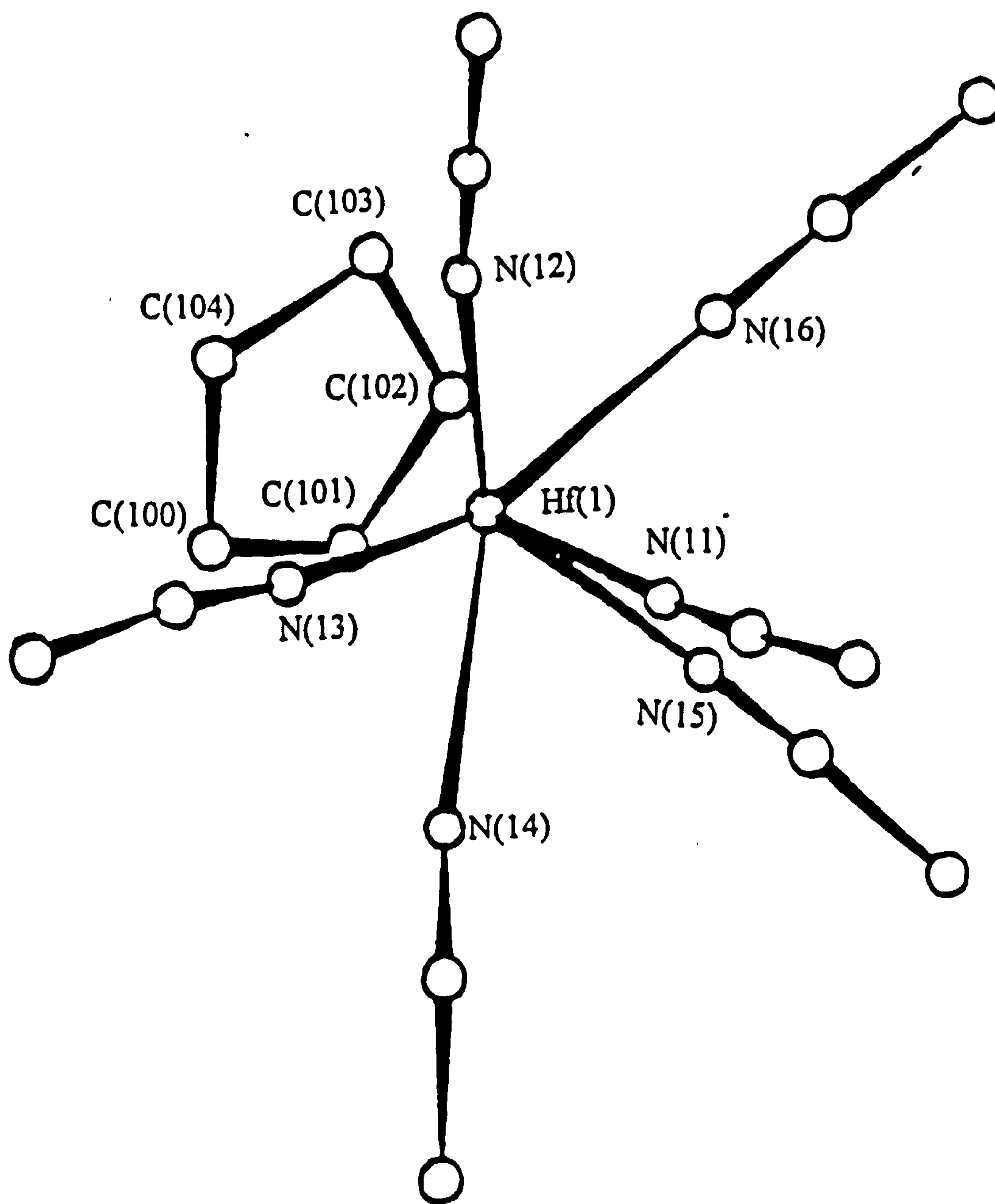


Table 2.8: Selected bond lengths (Å) in the [CpHf(MeCN)₆]³⁺ cation.

Hf(1)-N(11)	2.27(2)
Hf(1)-N(12)	2.281(13)
Hf(1)-N(13)	2.28(2)
Hf(1)-N(14)	2.211(14)
Hf(1)-N(15)	2.26(2)
Hf(1)-N(16)	2.27(2)
Hf(1)-C(100)	2.41(3)
Hf(1)-C(101)	2.53(2)
Hf(1)-C(102)	2.50(4)
Hf(1)-C(103)	2.39(2)
Hf(1)-C(104)	2.47(3)
Hf(2)-N(21)	2.30(2)
Hf(2)-N(22)	2.274(12)
Hf(2)-N(23)	2.23(2)
Hf(2)-N(24)	2.26(2)
Hf(2)-N(25)	2.24(2)
Hf(2)-N(26)	2.37(3)
Hf(2)-C(200)	2.43(3)
Hf(2)-C(201)	2.34(4)
Hf(2)-C(202)	2.46(3)
Hf(2)-C(203)	2.38(2)
Hf(2)-C(204)	2.42(4)

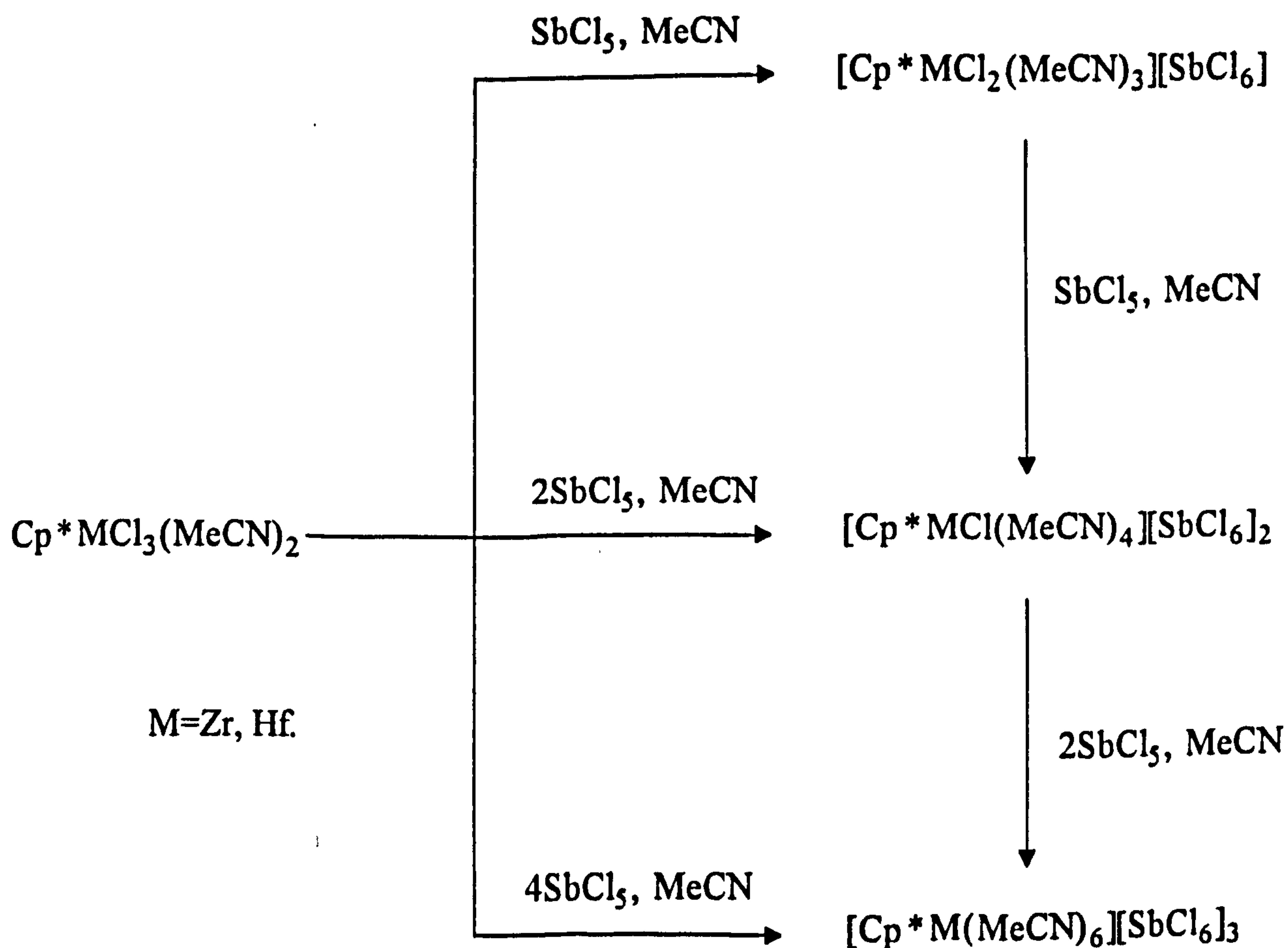
Table 2.9: Selected bond angles (°) in the [CpHf(MeCN)₆]³⁺ cation.

N(14)-Hf(1)-N(15)	71.2(7)	N(23)-Hf(2)-N(25)	137.5(9)
N(14)-Hf(1)-N(16)	138.0(8)	N(23)-Hf(2)-N(24)	68.4(9)
N(15)-Hf(1)-N(16)	69.2(8)	N(25)-Hf(2)-N(24)	72.5(10)
N(14)-Hf(1)-N(11)	79.9(7)	N(23)-Hf(2)-N(22)	70.9(7)
N(15)-Hf(1)-N(11)	79.5(7)	N(25)-Hf(2)-N(22)	137.6(9)
N(16)-Hf(1)-N(11)	80.5(8)	N(24)-Hf(2)-N(22)	137.0(7)
N(14)-Hf(1)-N(13)	69.4(6)	N(23)-Hf(2)-N(21)	77.9(8)
N(15)-Hf(1)-N(13)	135.4(7)	N(25)-Hf(2)-N(21)	78.9(7)
N(16)-Hf(1)-N(13)	137.6(7)	N(24)-Hf(2)-N(21)	79.0(7)
N(11)-Hf(1)-N(13)	73.8(8)	N(22)-Hf(2)-N(21)	79.4(7)
N(14)-Hf(1)-N(12)	140.1(6)	N(23)-Hf(2)-C(20)	81.9(14)
N(15)-Hf(1)-N(12)	136.9(7)	N(25)-Hf(2)-C(20)	127.6(9)
N(16)-Hf(1)-N(12)	70.6(6)	N(22)-Hf(2)-C(20)	109.5(12)
N(11)-Hf(1)-N(12)	79.8(6)	N(24)-Hf(2)-C(20)	77.5(7)
N(13)-Hf(1)-N(12)	72.1(6)	N(21)-Hf(2)-C(20)	153.3(9)
N(14)-Hf(1)-C(103)	130.3(6)	N(23)-Hf(2)-N(26)	134.2(7)
N(15)-Hf(1)-C(103)	110.7(8)	N(25)-Hf(2)-N(26)	70.2(9)
N(16)-Hf(1)-C(103)	77.2(8)	N(24)-Hf(2)-N(26)	137.2(9)
N(11)-Hf(1)-C(103)	149.6(6)	N(22)-Hf(2)-N(26)	69.0(6)
N(13)-Hf(1)-C(103)	110.4(8)	N(21)-Hf(2)-N(26)	73.9(9)
N(12)-Hf(1)-C(103)	73.5(6)	N(26)-Hf(2)-C(20)	109.6(14)
N(14)-Hf(1)-C(100)	75.6(10)	N(23)-Hf(2)-C(20)	127.1(12)
N(15)-Hf(1)-C(100)	106.7(11)	N(25)-Hf(2)-C(20)	74.6(7)
N(16)-Hf(1)-C(100)	128.5(9)	N(24)-Hf(2)-C(20)	99.0(13)
N(11)-Hf(1)-C(100)	150.9(9)	N(22)-Hf(2)-C(20)	116.5(11)
N(13)-Hf(1)-C(100)	83.0(9)	N(21)-Hf(2)-C(20)	152.7(9)
N(12)-Hf(1)-C(100)	109.8(11)	N(26)-Hf(2)-C(20)	90.7(14)
N(14)-Hf(1)-C(104)	109.5(8)	N(23)-Hf(2)-C(20)	99.0(2)
N(15)-Hf(1)-C(104)	131.5(8)	N(25)-Hf(2)-C(20)	84.0(2)
N(16)-Hf(1)-C(104)	106.4(9)	N(24)-Hf(2)-C(20)	71.9(9)
N(11)-Hf(1)-C(104)	148.9(8)	N(22)-Hf(2)-C(20)	129.0(2)
N(13)-Hf(1)-C(104)	81.9(8)	N(21)-Hf(2)-C(20)	149.4(11)
N(12)-Hf(1)-C(104)	74.5(7)	N(26)-Hf(2)-C(20)	122.8(12)
N(14)-Hf(1)-C(102)	109.6(10)	N(23)-Hf(2)-C(20)	78.0(10)
N(15)-Hf(1)-C(102)	82.1(11)	N(25)-Hf(2)-C(20)	114.1(9)
N(16)-Hf(1)-C(102)	77.4(12)	N(24)-Hf(2)-C(20)	84.0(2)
N(11)-Hf(1)-C(102)	155.2(12)	N(22)-Hf(2)-C(20)	100.9(11)
N(13)-Hf(1)-C(102)	130.8(12)	N(21)-Hf(2)-C(20)	154.3(12)
N(12)-Hf(1)-C(102)	103.1(10)	N(26)-Hf(2)-C(20)	131(2)
N(14)-Hf(1)-C(101)	80.3(8)	N(23)-Hf(2)-C(20)	114.6(13)
N(15)-Hf(1)-C(101)	79.1(8)	N(25)-Hf(2)-C(20)	103.4(12)
N(16)-Hf(1)-C(101)	104.3(9)	N(24)-Hf(2)-C(20)	131.5(9)
N(11)-Hf(1)-C(101)	154.5(7)	N(22)-Hf(2)-C(20)	78.7(9)
N(13)-Hf(1)-C(101)	113.5(9)	N(21)-Hf(2)-C(20)	149.0(9)
N(12)-Hf(1)-C(101)	125.6(7)	N(26)-Hf(2)-C(20)	77.9(12)

2.6: Halide abstraction from $\text{Cp}^*\text{MCl}_3(\text{MeCN})_2$ for $\text{M}=\text{Zr}$ and Hf .

As described previously, the substitution of Cp^* for Cp usually results in the formation of more stable complexes. With this in mind, the synthesis of the triply charged cations of Zr and Hf were attempted using the title compounds. The existence of 7-coordinate tricationic metal complexes is based purely on elemental analysis results. Efforts in the growth of crystals suitable for X-ray structure measurement have so far been fruitless. Once again, ^1H NMR studies have revealed only the mono- and dicationic complexes in solution, even at high temperature (scheme 2.5).

Scheme 2.5.



Some physical and spectroscopic properties of compounds XIII→XVIII are summarised in Table 2.10. In general, these properties almost exactly mirror those of the analogous Cp complexes. The only exception to this lies in the ^1H NMR, in which the spectra are considerably simplified.

Table 2.10: Selected Physical and Spectroscopic Properties of SbCl_6^- salts of the Cp^*M^{n+} series.

	Colour	Microanalysis			IR, ν/cm^{-1}		^1H NMR, δ/ppm (CD_3CN soln) Cp
		(calc/obs)			(nujol)		
		C	H	N	$\nu(\text{C}\equiv\text{N})$	$\nu(\text{SbCl})$	
$[\text{Cp}^*\text{ZrCl}_2(\text{MeCN})_3]^+$ XIII	pale yellow	25.45 23.69	3.21 3.17	5.57 4.52	2315 2290	345	2.09
$[\text{Cp}^*\text{ZrCl}(\text{MeCN})_4]^{2+}$ XIV	white	19.74 19.68	2.49 2.49	5.12 5.05	2315 2295	344	2.15
$[\text{Cp}^*\text{Zr}(\text{MeCN})_6]^{3+}$ XV	white	17.90 17.79	2.25 2.29	5.69 5.54	23.20 2290	345	2.15
$[\text{Cp}^*\text{HfCl}_2(\text{MeCN})_3]^+$ XVI	cream	22.81 21.50	2.88 2.73	4.99 4.88	2315 2290	345	2.16
$[\text{Cp}^*\text{HfCl}(\text{MeCN})_4]^{2+}$ XVII	white	18.28 17.99	2.31 2.21	4.74 4.68	2320 2295	345	2.23
$[\text{Cp}^*\text{Hf}(\text{MeCN})_6]^{3+}$ XVIII	white	16.90 16.84	2.13 2.17	5.38 5.32	2320 2290	345	2.23

Surprisingly, the cations show a high lability in CD₃CN solution. This is demonstrated by the absence of the coordinated MeCN signal and the lack of resonances due to the isomeric species. It would seem that the presence of the Cp* group has a marked effect on the solvent exchange rate of the cations. It is debatable whether the complexes exhibit geometrical isomerism at all; it could be that the steric bulk of the Cp* precludes the formation of all but the most energetically stable configurations. Given the more labile nature of these Cp*-based systems, it is perhaps surprising that a signal due to the trications could not be identified in the NMR. Even when in the presence of excess SbCl₅ at 76°C, only the resonance attributed to the relevant dications was observed in all cases.

The microanalytical data from this series lends further credence to the existence of 6-coordinate metal centres in the mono- and dicationic complexes. The steric crowding around the metal centres in the trications must be quite intense with the bulky Cp* ligand involved.

2.7: Halide abstraction from CpNbCl₄(MeCN).

The results of the halide exchange reactions of the Group 4 CpMCl₄/SbCl₅ series were very interesting. As the formation of triply-charged species is obviously possible, it was decided to investigate the analogous Group 5 CpMCl₄ reactions. In this case there is an *a priori* possibility of forming quadruply charged metal species. However, electrostatic considerations suggested that complete halide transfer may not be possible.

Unfortunately, any research on d⁰ Group 5 chemistry is restricted to niobium and tantalum; vanadium(v) is only stable in O- and F-donor complexes, VCl₅ rapidly disproportionates to form VCl₄ and Cl₂. A literature survey surprisingly reveals an absence of work in simple halide abstraction reactions. The only cationic d⁰ Nb and Ta species that have been reported are those containing (M-R) bonding such as [Cp₂Nb(CH₂SiMe₃)₂][BF₄].¹²⁷ This, combined with the simple procedures involved in the preparation of CpMCl₄ provides an obvious opportunity for a new area of research.

2.7.1: Preparation of CpNbCl₄

The title complex was prepared in good yield (76%) using the method of Green *et al* [46].¹²⁸



Some important chemical and physical properties of the product are summarised in Table 2.11 along with those of the adduct CpNbCl₄(MeCN) which was synthesised and recrystallised as a method of purification.

Table 2.11: Selected properties of CpNbCl₄ and CpNbCl₄(MeCN).

	CpNbCl ₄	CpNbCl ₄ (MeCN)
Colour	deep red	red
Microanalysis		
C H N	20.03 1.68	24.66 2.37 4.11
(calc/obs)		25.77 2.53 4.11
¹H NMR (250 MHz) (CD ₃ CN solution) δ/ppm	-	7.26
IR (nujol), v/cm⁻¹		
Cp		
(C-H) stretch	3100(w)	3110(w)
(C-H) deform	1020(w)	1025(w)
(C-C) deform	850(s)	845(m)
MeCN		
(C≡N) stretch	-	2290(s)
		2315(s)
(C-C) stretch	-	940(w)
(M-Cl) and (M-Cp)	345(br. m)	370(w)
combinations	280(br. m)	350(br. m)
		290(br. s)

The complex was purified by recrystallisation from the minimum amount of hot MeCN. The adduct formed in this way shows the familiar absorbances in the IR which are characteristic of the Cp group and coordinated MeCN along with (Nb-Cl) stretches at low frequency. In solution, both complexes are extremely sensitive to hydrolysis; the NMR spectra in CD₃CN exhibit a sharp singlet due to the Cp group at δ 7.26 and a broader resonance at δ 7.17 which has been assigned to the hydrolysis product [47].



Ligand exchange is again rapid with no coordinated MeCN detectable in CD₃CN solution after 5 minutes.

2.7.2: Reaction with SbCl₅.

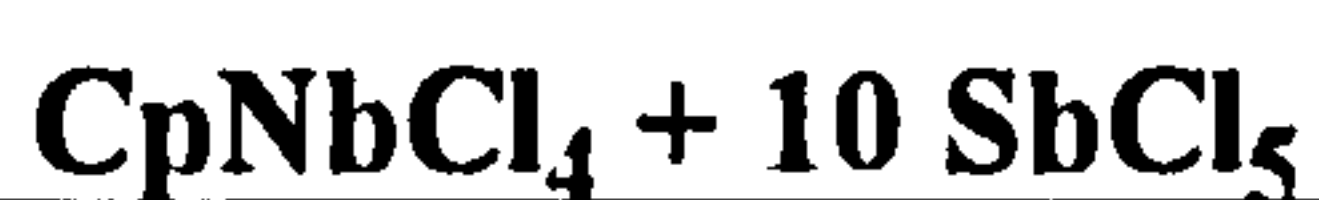
This system was not analysed in any great depth. It was decided just to establish the maximum extent of halide abstraction that is possible. Consequently, a solution of CpNbCl₄(MeCN) was treated with a 10 molar excess of SbCl₅. The spectroscopic and physical properties of the product of this reaction are given in **Table 2.12**.

The product was recrystallised from MeCN/CH₂Cl₂ in the presence of excess SbCl₅ to give bright red blocks which have been the subject of an X-ray analysis. The results of this study are essential as, once again, formulation of the product is uncertain from the analysis figures. The "best-fit" is for the 6-coordinate [CpNbCl(MeCN)₄][SbCl₆]₃ although the presence of a quadruply-charged, 7-coordinate cation is not beyond the realms of reason (**Table 2.13**). A more detailed study is obviously required.

The ¹H NMR spectrum of CpNbCl₄/SbCl₅ (*ca.* 1:10) in CD₃CN shows a singlet at δ 7.49 and coordinated MeCN at δ 2.59. This mirrors the analogous Zr

and Hf reactions and shows an inert solvent exchange. The lack of resonances associated with isomeric species suggests a bridging intermediate exists under these conditions at room temperature. The possibility of discrete CpNb^{4+} moieties surviving in solution is very unlikely on electrostatic considerations alone.

Table 2.12: Selected physical and spectroscopic properties of



Colour	bright red
IR, ν/cm^{-1}	
(nujol)	
$\nu(\text{C}\equiv\text{N})$	2290
	2315
$\nu(\text{Sb-Cl})$	345
$^1\text{H NMR, } \delta/\text{ppm}$	
($\text{CD}_3\text{CN soln.}$)	
Cp	7.49
MeCN	2.59

Table 2.13: Elemental compositions of the various possible products of



	C	H	N
$[\text{CpNbCl}_2(\text{MeCN})_3][\text{SbCl}_6]_2$	12.93	1.38	4.12
$[\text{CpNbCl}_2(\text{MeCN})_4][\text{SbCl}_6]_2$	14.70	1.62	5.28
$[\text{CpNbCl}(\text{MeCN})_4][\text{SbCl}_6]_3$	11.47	1.26	4.12
$[\text{CpNbCl}(\text{MeCN})_5][\text{SbCl}_6]_3$	12.84	1.44	5.00
$[\text{CpNb}(\text{MeCN})_6][\text{SbCl}_6]_4$	11.71	1.33	4.83
Actual product recovered	11.99	1.36	4.17

Addendum.

We now have some preliminary results from the crystallographic study of the product from the $\text{CpNbCl}_4/\text{xSbCl}_5$ reaction. So far, the structure has only been refined to $R=0.13$. Consequently accurate bond lengths and angles are not available. However, the asymmetric unit has been determined and shows exciting features. The unit consists of two distinct cations, $[\text{CpNbCl}(\text{MeCN})_4]^{3+}$ and $[\text{CpNb}(\text{MeCN})_6]^{4+}$, with seven $[\text{SbCl}_6]^-$ counter anions. Views of the two cations are shown in **Figure 2A**. In cyclopentadienylniobium chemistry, this is the first example of a structure which contains two differently charged metal species.

The synthesis of this particular crystal can only be ascribed to good fortune. It would seem that the formation of pure $[\text{CpNb}(\text{MeCN})_6][\text{SbCl}_6]_4$ is dependant upon a threshold level of SbCl_5 in the mother liquor. In our preparation, the insufficient quantity of SbCl_5 has resulted in the formation of a mixture of cationic products.

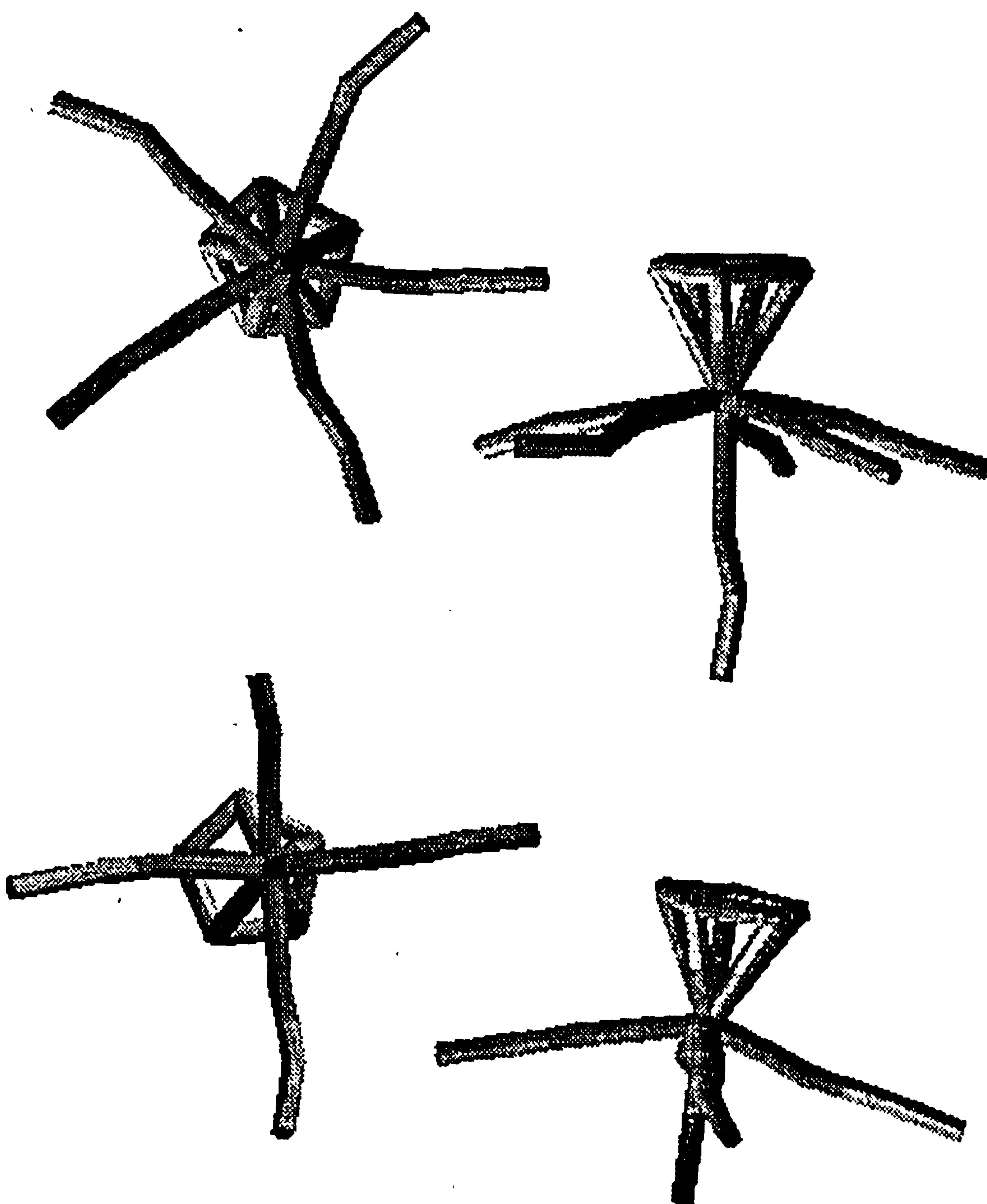
The CpNb^{4+} cation is isostructural and isoelectronic with the trications of Zr and Hf. The 7-coordinate metal centre implies an 18-electron configuration. Again, the "equatorial" MeCN ligands lie in a plane slightly below the Nb centre due to the steric bulk of the Cp group.

The CpNb^{3+} cation exhibits pseudo-octahedral geometry with a coordination sphere comprising of four MeCN ligands and a chloride anion in the *trans* position to the Cp ring. If the Cp group is regarded as unidentate, the cation possesses approximate C_{4v} symmetry.

All of the available evidence now points directly to $[\text{CpNbCl}(\text{MeCN})_4]^{3+}$ cation being isoelectronic with the dications of Group 4. It would appear that the final chloride abstraction from the CpMCl_x series [for $M=\text{Zr}$, Hf ($x=3$) and Nb ($x=4$)] is accompanied by an increase in the metal coordination number. As an increase in positive charge is normally associated with a decrease in ionic radius, there must be some inherent stabilising effect involved in the final (M-Cl)

interaction. This stability most probably arises from a stronger $p\pi-d\pi$ interaction. It would be interesting to chart the relative sizes of the (M-Cl) bonds in the CpNb-CpNb⁺-CpNb²⁺-CpNb³⁺ series. One would expect a decrease in the (Nb-Cl) bond dimension along the series, thus providing better orbital overlap for the π -bonding. This is an obvious area for further work.

Figure 2A: Views of the [CpNbCl(MeCN)₄]³⁺ and [CpNb(MeCN)₆]⁴⁺ cations.



2.8: Reactions of the CpMⁿ⁺ complexes.

2.8.1: MeCN Substitution.

Originally it was hoped that the replacement of the MeCN ligands in the cationic complexes I→XVIII would be a facile procedure with a variety of neutral ligands. In fact, the success of these type of reaction proved to be limited because of unexpected experimental problems.

N-Donor Ligands.

As the solubility of the cations is so good in MeCN, the solvent offers itself as an ideal medium in which to carry out reactivity studies. To assess the compatibility of other N-donor ligands with CpTi³⁺, CpZr²⁺ and CpHf²⁺, the relevant cations were treated with triethylamine (NEt₃) or tetramethylethylenediamine (TMEDA). Equations [48]→[51] summarise the reactions attempted.



In all cases, the addition of the amine ligand results in the immediate precipitation of highly insoluble solids. These proved to be insoluble in all common laboratory solvents and even the appropriate ligands used in excess. Unfortunately, this precluded purification and resulted in inaccurate characterisation. Elemental analysis results were inconsistent with any of the theoretical values for the species formed by sequential MeCN replacement. The IR

spectra of the four samples recovered all exhibit similar features, namely, bands associated with coordinated amines¹²⁹ and MeCN together with the SbCl_6^- anion. These observations are consistent with the formation of mixtures of partially substituted complexes. This is true of the products even if larger excesses of ligand are employed with increased reaction times.

O-Donor Ligands.

The interaction of O-donor ligands with the Group 4 cations was investigated using CpTi^{3+} , CpZr^{2+} and CpHf^{2+} with diethyl ether and acetone. Initial experiments involving the use of MeCN as the reaction solvent gave entirely negative results; no substitution occurs even with a healthy excess of ligand after 5 days. Given the classically hard nature of the O-donors, it is perhaps surprising that adducts did not form under these conditions. In fact, such complexes are only formed if the MeCN solvent is removed from the reaction.

When the cations were stirred as a suspension in the appropriate ligands used as solvent, they slowly become sparingly soluble as MeCN substitution occurs. In the case of CpTi^{3+} , this is accompanied by a blue to yellow colour change. However, the presence of coordinated MeCN in the IR spectrum of all of the products shows that there is incomplete substitution even after reaction times of 5 days.

As the use of O-donors in this way gave promising if not perfect results, it was decided to attempt full substitution by employing the crown ether 1,4,8,11,13-pentaoxacyclopentadecane ($^{15}\text{O}_5$). It was hoped that the use of this ligand would promote reaction *via* the macrocyclic effect. The ligand was stirred with CpTi^{3+} as a toluene suspension over a period of 5 days. A pale yellow solid was recovered. Reactions with the Zr- and Hf-based cations were avoided as other groups have reported evidence of unusual "ring opening" of crown-ethers under similar conditions.¹³⁰

The solubility of all of these O-donor adducts that were recovered is basically limited to MeCN in which the original species reform. The Et₂O and Me₂CO adducts do show a very slight solubility in the parent solvent, but not enough to allow for the measurement of informative NMR spectra.

The elemental analyses of these O-donor adducts were variable in quality although the products of the CpTi³⁺ series did yield interesting results. The observed C, H and N content of the solids obtained from the Et₂O, Me₂CO and ¹⁵O₅ reactions all show remarkably good agreement with the theoretical values for the [CpTiL₄(MeCN)][SbCl₆]₃ adducts (Table 2.14). This suggests that the cations may retain at least one MeCN ligand in any attempted substitution although the impure nature of the solids must be taken into account with this assignment.

Table 2.14: Reaction of [CpTi(MeCN)₅][SbCl₆]₃ with neutral O-donors.

	Possible Product (SbCl ₆ salt)	Theoretical Composition			Observed Microanalysis		
		C	H	N	C	H	N
Et ₂ O	[CpTi(Et ₂ O) ₄ (MeCN)] ³⁺	19.00	3.33	0.96	18.78	3.21	1.05
Me ₂ CO	[CpTi(Me ₂ CO) ₄ (MeCN)] ³⁺	16.41	2.33	1.01	16.40	2.25	1.07
¹⁵ O ₅	[CpTi(¹⁵ O ₅)(MeCN)] ³⁺	14.82	2.05	1.02	14.62	1.89	1.10

b. IR spectra.

Reaction: CpTi ³⁺ + ligand	Bands exhibited by products (nujol), ν/cm^{-1}
Et ₂ O	2320(s), 2295(s), 1600(m), 1185(m), 1140(m), 1084(m), 1005(s), 983(s), 866(s), 820(s), 740(s), 345(vs).
Me ₂ CO	2319(s), 2295(s), 1659(s), 1630(s), 1245(s), 1080(s), 829(m), 538(m), 345(vs).
¹⁵ O ₅	2322(s), 2290(s), 1275(w), 1250(w),, 1120(w), 1103(m), 1090(m), 1060(s), 1030(m), 980(s), 940(m), 910(m), 830(m), 710(s), 345(vs).

P- and S-Donor Ligands.

The reactivity of the CpTi³⁺ cation was investigated with the ligands PMe₃, PPh₃ and SMe₂. The P-donors (6 molar excess) were stirred with the cation as a toluene suspension and the SMe₂ used neat as the reaction solvent. It was found that only PMe₃ yields new compounds in this way, with a pale pink solid being recovered from the reaction. The IR spectrum of this product exhibits bands for both coordinated MeCN and PMe₃¹³¹ along with the SbCl₆⁻ anion. Elemental analysis results were inconsistent with any of the theoretical values derived from sequential ligand substitution.

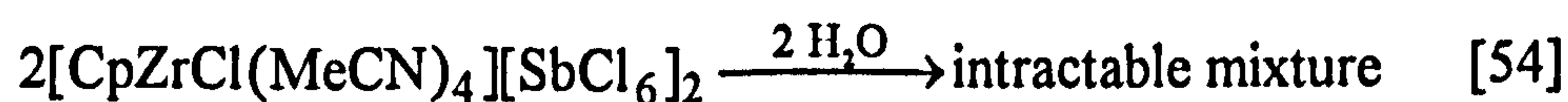
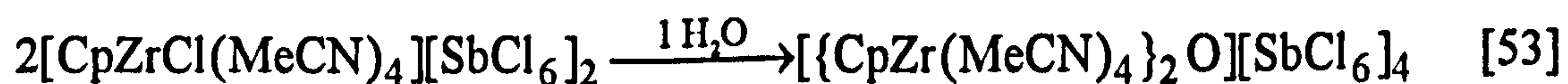
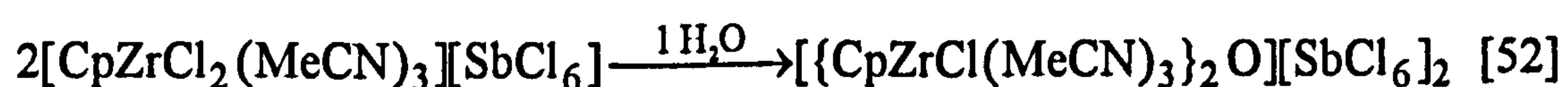
The product was found to be completely insoluble in all common laboratory solvents including MeCN. Perhaps significantly, the parent cation does not reform as with the O-donor adducts discussed previously. This suggests that there may be other competing processes, such as some kind of Sb/P redox couple.

It is interesting that a reaction does occur with PMe₃ but not with the softer PPh₃ ligand. This may be attributed to the electron donating effect of the methyl groups on the P- centre in the more reactive PMe₃. No such effect is present in the SMe₂ analogous ligand as no reaction is seen to occur even when vast excesses are employed.

2.8.2: Hydrolysis.

The complexes I→XVIII all exhibit an extreme sensitivity towards hydrolysis and rapidly decompose in air to give yellow or brown oils. Attempts to characterise these oils were unsuccessful. However, it is evident that they contain a number of different compounds. It was therefore decided to carry out hydrolysis reactions in a controlled manner using accurate concentrations of water as MeCN solutions. Using this approach, the reactions can be monitored much more closely.

When water is added to MeCN solutions of I→XVIII there seem to be two distinct reaction pathways. The first of these involves simple attack of any (M-Cl) bonding with the elimination of HCl to give discrete oxygen-bridged, binuclear cationic complexes [52, 53]. However, the second type of process yields a wide range of products and is very difficult to follow. This reaction probably involves the deprotonation of coordinated H₂O to give (M-OH) species and "HSbCl₆". It then becomes possible to envisage a wide range of metal complexes which could arise from the decomposition of these initial products. These points are best illustrated by a comparison of the results gained from the systems studied, given in equations [52]→[55].



It is obvious from these reactions that simple (M-Cl) hydrolysis is preferred; the second type of reaction only takes place when there are no such

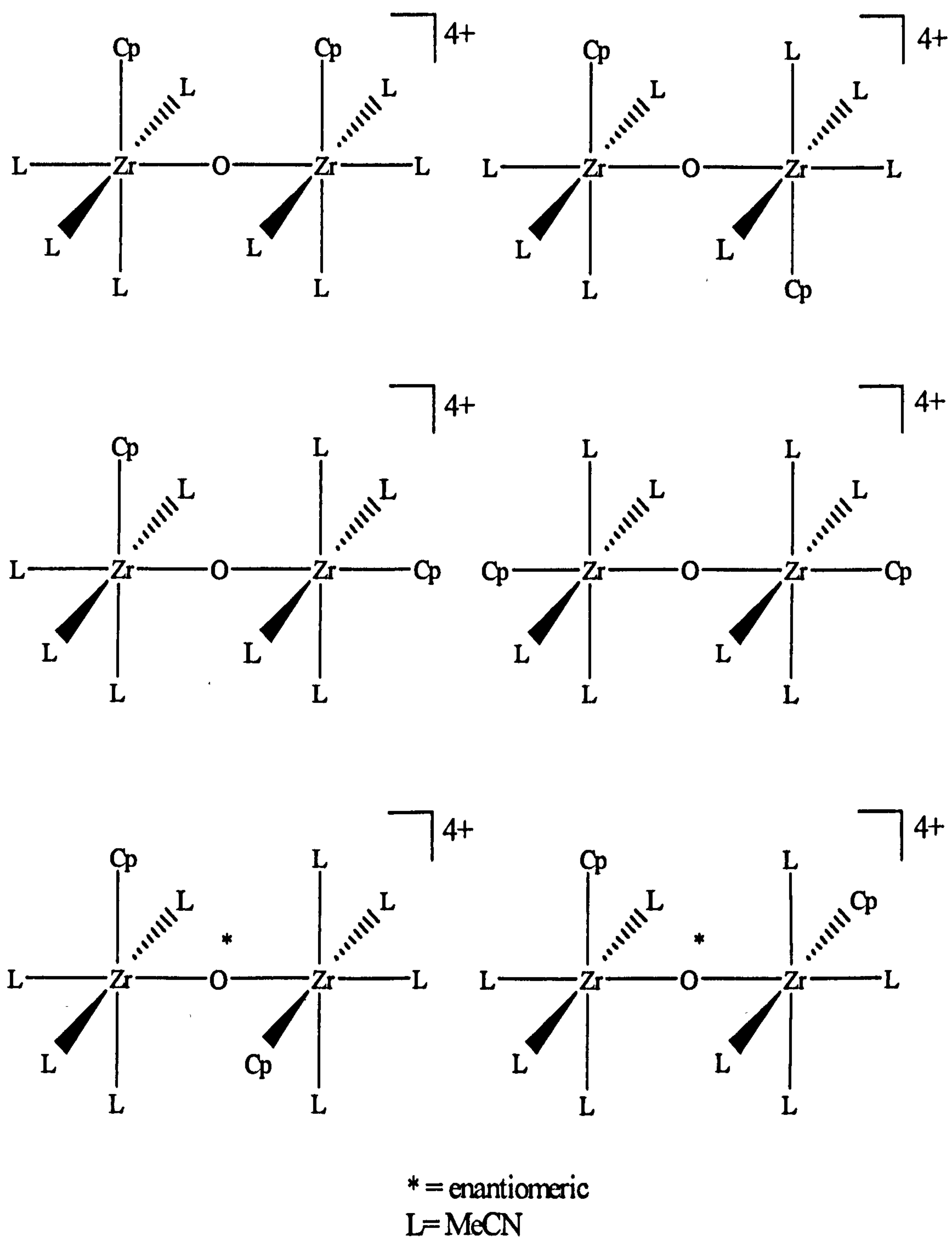
bonds available. In the latter case, as in reactions [54, 55] it proved impossible to characterise the products in any of the systems that were studied. These mixtures all exhibit similar properties to the oils which result from air hydrolysis: insolubility and IR spectra dominated by bands in the region 700-800 cm^{-1} . This suggests the presence of a variety of complexes which contain (M-O-M) bonding.

In contrast to the results of full hydrolysis, those gained from the partial reactions were very informative. The best example of this is given by the $\text{CpZr}^{2+}/\frac{1}{2}\text{H}_2\text{O}$ system. The interpretation of the results of this experiment apply equally well to the analogous CpTi^{2+} and Cp^*M^{2+} cases but is much easier to present. The latter systems were studied to a much lesser extent due to the lack of solution equilibria which confuse the Ti-based series, and the more sensitive handle that Cp provides in the NMR.

Treatment of $[\text{CpZrCl}(\text{MeCN})_4][\text{SbCl}_6]_2$ in MeCN solution with 0.5 equivalents of H_2O results in the formation of a white solid which analyses for $[\{\text{CpZr}(\text{MeCN})_4\}_2\text{O}][\text{SbCl}_6]_4$, in good yield [46]. However, it should be noted that the analysis is inconclusive on its own as both reactant and product have very similar theoretical composition. The complex is completely insoluble in common organic solvents except MeCN. Even here, its solubility is noticeably lower than that of the parent dication. In the IR, the bands characteristic of coordinated MeCN, the Cp group and SbCl_6^- anion are joined by an intense, broad absorbance at 730 cm^{-1} , characteristic of the (Zr-O-Zr) moiety.¹³²

The ^1H NMR spectrum of this species is very interesting. As with the parent dication, the coordinated MeCN is observed indicating a low lability. Resonances due to the presence of isomeric species are also seen as an unresolved multiplet centred at $\delta 6.7$. Assuming a linear (Zr-O-Zr) bridge as in other similar cases,¹³³ there will be a considerable π -character involved in the bonding. This rules out any rotation about the (Zr-O) bonds and results in the possibility of six geometrical isomers, two of which being a pair of enantiomers (Figure 2.12).

Figure 2.12: The geometrical isomers of $[\{\text{CpZr}(\text{MeCN})_4\}_2\text{O}][\text{SbCl}_6]_4$.

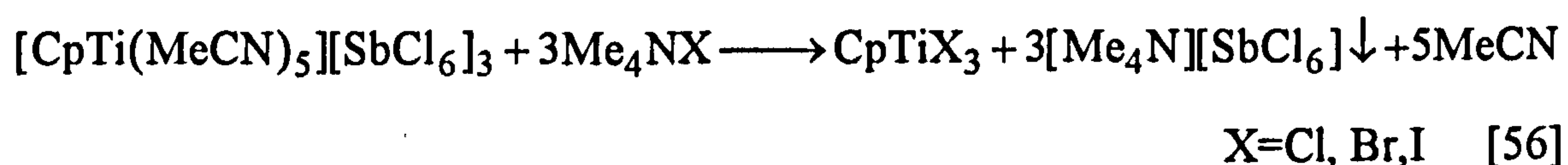


The complex should thus exhibit 5 bands in the ^1H NMR. Hydrolysis of the monocations yields an even higher number of isomeric species and leads to what is best described as a very broad multiplet in the NMR, centred at $\delta 6.6$.

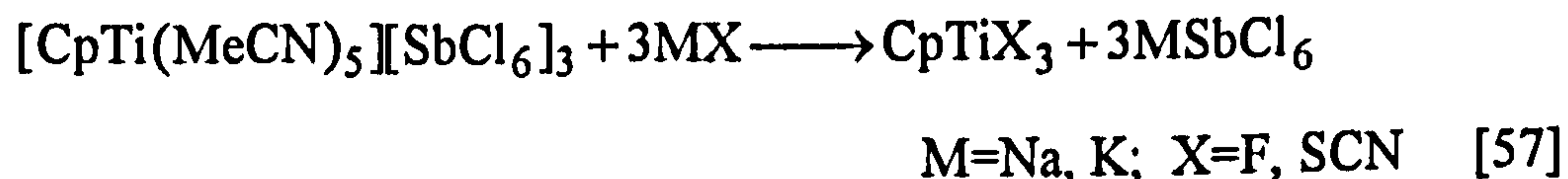
2.8.3: Reactions of $[\text{CpTi}(\text{MeCN})_5][\text{SbCl}_6]_3$ with inorganic salts.

Ionic reactions of the whole CpM^{n+} series were not carried out. Instead, a number of such investigations were carried out on the Ti trication **III**. It is assumed that the cationic compounds **I**→**XVIII** would all react in a similar fashion to the title complex but this cannot be guaranteed. This area obviously lends itself for further study.

The Ti trication **III** reacts with a variety of halide salts to regenerate the neutral CpTiX_3 species [56]. It was found that the use of toluene as the reaction solvent combined with the relevant tetramethylammonium salt greatly improves recovery of the product. In most cases the CpTiX_3 produced stays in solution whilst the antimonate is deposited as a solid.



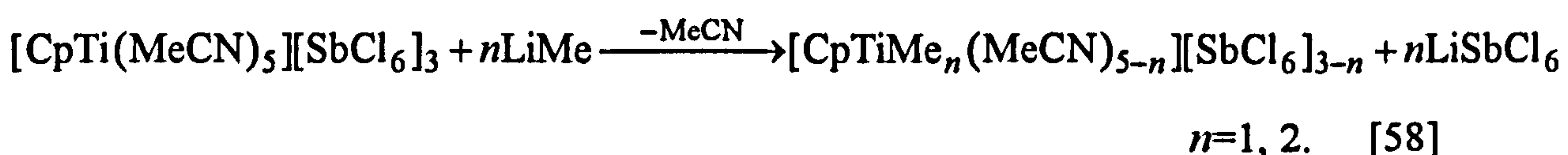
The products of these reactions were identified by the comparison of their melting points with those reported in the literature.¹³⁴ Salts other than those of Me_4N also react in this way but the work-up procedures are sometimes more difficult. Using sodium or potassium salts, the fluoride and thiocyanide derivatives can be synthesised [57].



Reactions involving other sources of halide anions proved to be less successful. It was found that chloride exchange only occurs with sufficiently ionic compounds; no reaction was observed with Bu_3SnCl or chlorinated solvents.

2.8.4: Reaction of [CpTi(MeCN)₅][SbCl₆]₃ with lithium methyl.

In an attempt to produce potential Ziegler-Natta catalysts, the Ti-based trication **III** was treated with LiMe. It was hoped that the reaction would generate the [CpTiMe(MeCN)₄]²⁺ and [CpTiMe₂(MeCN)₃]⁺ cations with 1 and 2 molar ratios of LiMe respectively [58].

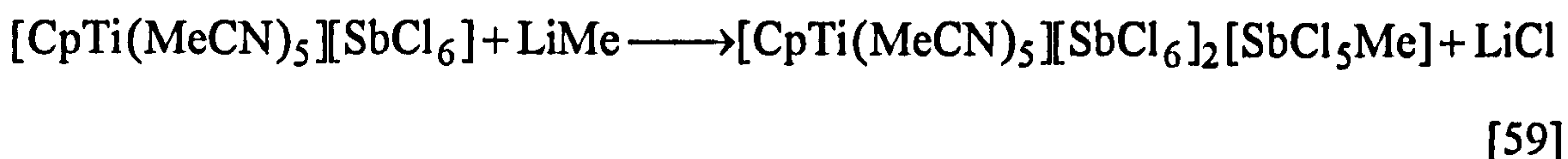


Unfortunately this did not turn out to be the case. Treatment of blue **III** in MeCN with LiMe results in the instantaneous formation of a red solution and a thin white precipitate. The lack of any "organic" bands in the IR spectrum of this solid is consistent with the formation of LiCl. Removal of the MeCN from the remaining solution yields a deep red oil. Only after thorough washing with hexane followed by prolonged pumping is this oil converted to a manageable red/brown solid. Solubility of this sample is restricted to MeCN and attempts in recrystallisation proved to be fruitless.

The formulation of the red/brown solid is open to conjecture; microanalytical data points to the existence of a mixture of compounds. The ¹H NMR in CD₃CN solution gives a complex spectrum. In the region δ7.1-7.4 a large number of unidentified signals suggests severe decomposition. Perhaps significantly, these resonances include two at δ7.2 and 7.4 which could be due to CpTiCl₃ and [CpTiCl₂(MeCN)₃]⁺ respectively. Another important observation from the spectrum is the absence of any signals in the δ0-1 region. By analogy with the results of other workers, it can be assumed that the mixture does not contain any (Ti-Me) bonding {cf. δ0.69 for [Cp₂TiMe(MeCN)][BPh₄]}.⁸⁹

In the IR, the red solid exhibits characteristic absorbances for the Cp group, coordinated MeCN and an intense band at 345 cm⁻¹ due to the (Sb-Cl) stretch. In

addition to these, a new signal is observed at 545 cm.⁻¹ As the presence of (Ti-Me) bonding has been ruled out, this absorbance could well be due to (Sb-Me) stretching; the IR spectrum of SbCl₂Me₃¹³⁵ shows band at 577 and 538 cm.⁻¹ It would seem that alkylation of the Sb centre is the outcome of the reaction [59].

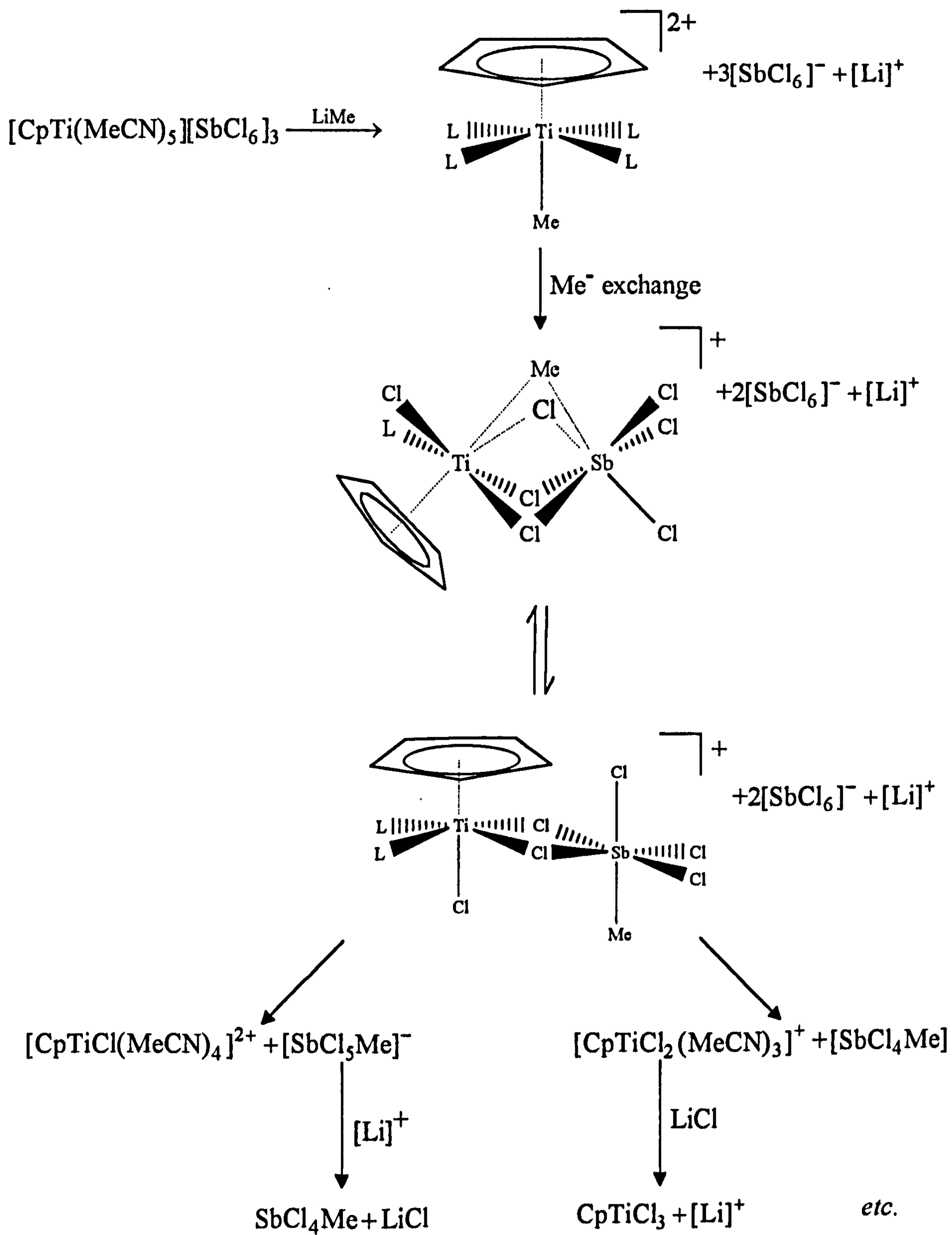


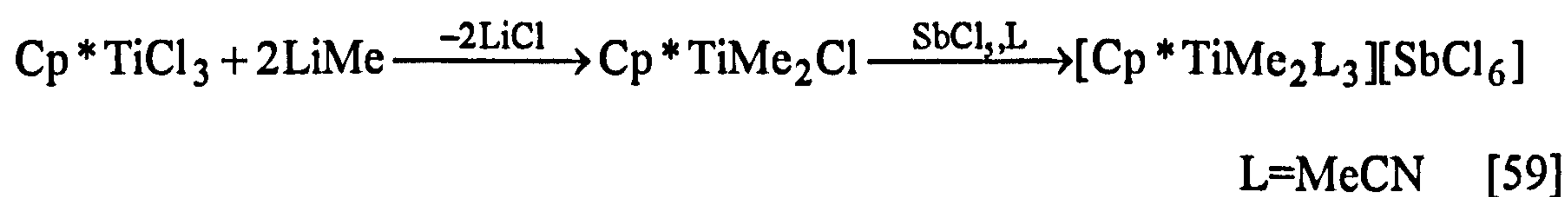
At first glance, this reaction looks improbable. The attack of the negatively charged methyl group on the SbCl₆⁻ anion is electrostatically unlikely. However, in view of the cation/anion bridging interactions described earlier, it is possible to postulate a feasible mechanism for Sb-alkylation. One such idea is illustrated in **Scheme 2.6**.

It is likely that the initial reaction does indeed involve the attack of the methyl group on the Ti-centre. In the cationic system there is a predominance of equilibria between the distinct cation/anion formulation and the Cl-bridged intermediates. So, on the formation of the latter type of complex, it may be possible for the methyl group to migrate to the Sb-centre in exchange for a Cl-ligand. It is then possible to envisage a number of decomposition processes that result in the range of products. The formation of CpTiCl₃ and LiCl can both be explained in this manner.

In retrospect it might have been better to carry out the analogous reactions of the Cp*Ti³⁺ system so that the extra stability offered by the Cp* and the lack of solution equilibria could be used to full effect. In fact, the excellent stability and ease of preparation of Cp*TiMe₂Cl⁴⁹ provides an alternative synthetic route to cationic alkyl species, *i.e.* alkylation before halide abstraction [59]. The unstable nature of CpTiMe₂Cl precludes this in the current example.

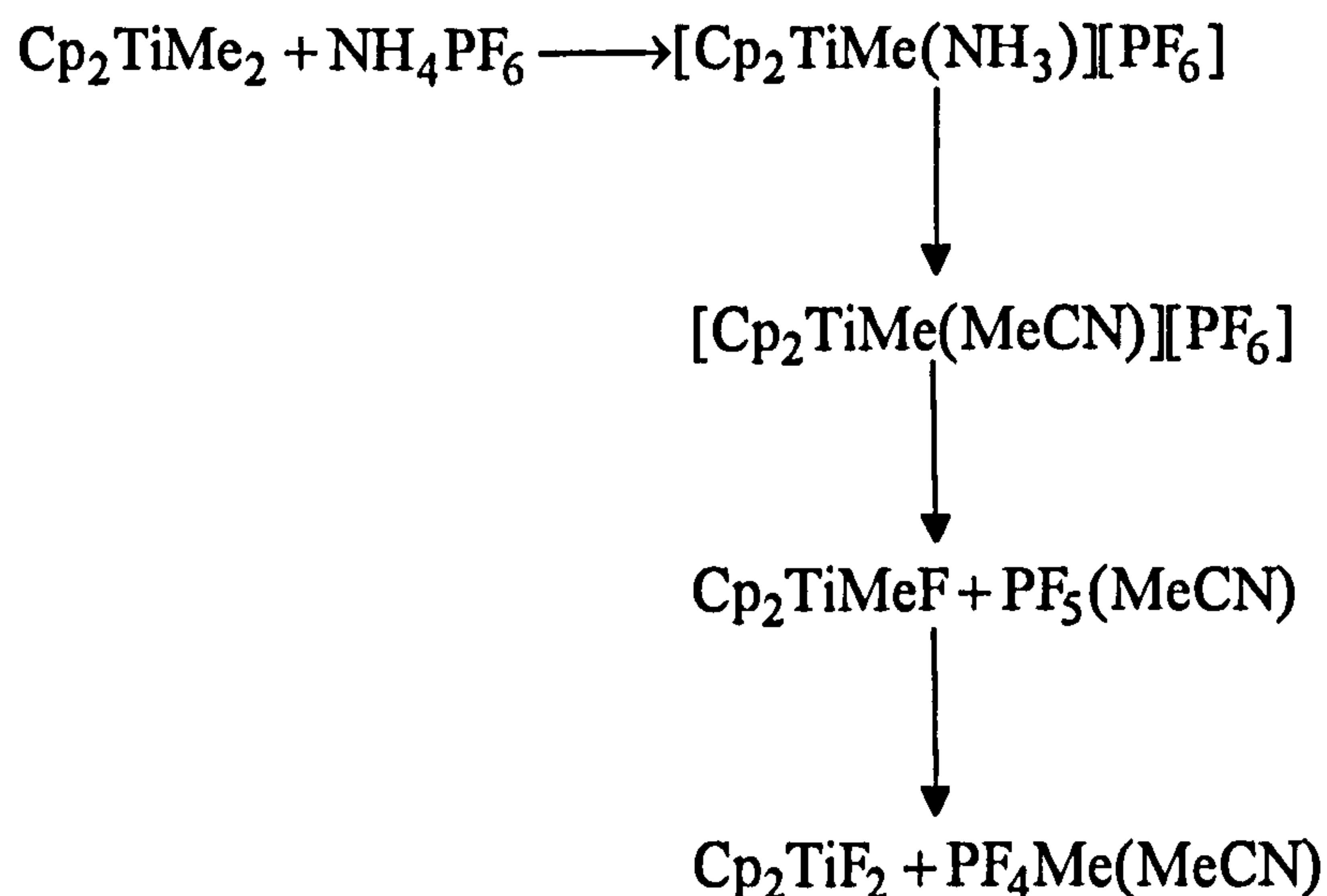
Scheme 2.6: Proposed mechanism for $[\text{CpTiMe}(\text{MeCN})_4]^{2+}$ decomposition.





This is obvious ground for future work. If the product shown in [59] could be isolated, the mechanism proposed for the failure of the trication alkylation reaction would be disproved. However, results from other workers suggest that there may be a problem with the SbCl_6^- anion irrespective of the synthetic approach. Similar difficulties have been reported when the hexafluorophosphate anion (PF_6^-) is employed. Bochmann *et al*¹³⁶ report that in MeCN solution, the $[\text{Cp}_2\text{TiMe}(\text{NH}_3)][\text{PF}_6]$ salt gradually decomposes (scheme 2.7) to form Cp_2TiF_2 .

Scheme 2.7: The decomposition of $[\text{Cp}_2\text{TiMe}(\text{NH}_3)][\text{PF}_6]$.



The behaviour of these Ti complexes is mirrored by related Zr species [60].⁹⁰



CHAPTER 3

EXPERIMENTAL.

3.1: General.

Manipulations of materials were carried out using a conventional Schlenk system and a dinitrogen filled glove-box except when stated otherwise. All solvents were dried over the appropriate agent (Table 3.1) and distilled under dinitrogen directly before use.

Table 3.1: The drying of solvents.

Solvent	Drying agent
acetonitrile	calcium hydride/potassium pentoxide
acetone	calcium hydride
dichloromethane/chloroform	calcium hydride
tetrahydrofuran/diethyl ether	sodium-potassium alloy/benzophenone
hexane/pentane	calcium hydride
toluene	sodium metal

3.1.1: Instrumentation.

IR: recorded as nujol mulls (unless otherwise stated) between caesium iodide plates on a Perkin Elmer 580b spectrometer.

¹H NMR: recorded on a Bruker AC250 spectrometer.

UV: recorded in quartz cells using a Shimadzu 365 instrument.

Elemental analyses were performed by Medac Ltd., Brunel University, Uxbridge, Middlesex.

3.2: The synthesis of 1,2,3,4,5-pentamethylcyclopentadiene.

The title compound is prepared by a synthetic route which involves three sequential reactions. It is recommended that the product formed after step 2 be stored for use as a Cp*H precursor. As the desired compound slowly decomposes, even in the refrigerator, best results are obtained when Cp*H is freshly prepared.

3.2.1: Preparation of 2,3,5,6-tetrahydro-2,3,5,6-tetramethyl- γ -pyrone.

A multinecked, 5 litre, R B flask equipped with overhead mechanical stirrer and ice-cooled dropping funnel was placed in a water bath kept at 30°C. To the flask was added 3-pentanone (516g, 6mol), potassium hydroxide (112g, 2mol), methanol (750ml), and lithium chloride (17g, 0.4mol).

Once up to the water bath temperature, the vigorously stirred mixture was treated with ice cold acetaldehyde (1 litre, 17mol) at a rate of about 1ml per minute over a period of 24 hours. After the first 2 hours, the solution became light red in colour. By the time of complete addition, the mixture takes the appearance of a crimson oily liquid.

At this point, the reaction was neutralised with hydrochloric acid (200ml, 30%, 2mol) and the resulting mixture transferred to a separating funnel. The red organic layer was separated and washed with distilled water (2 x 200ml). The resulting light red liquid was then distilled under reduced pressure (14 Torr) through a 20cm vigreux column into a 2-litre flask. The clear solvents were collected first at room temperature before a pale yellow fraction at up to 100°C. During this process, the oil bath was maintained at 150°C and the contents of the flask magnetically stirred. After the distillation, a thick red syrup remained in the flask. It is recommended that this be removed from the flask whilst hot as on cooling, a immovable glass is formed.

The yellow distillate contains the required product, but at this stage NMR spectroscopy reveals large amounts of impurities. It is therefore suggested that the liquid be redistilled. In the presence of anti-bumping granules with magnetic stirring, the title compound is recovered at 68-72°C in 370g yield (~36%).

IR/cm⁻¹: 1720(s), ν (C=O); 1160(s), ν (C-O-C).

¹H NMR(CDCl₃) δ /ppm: 0.92(d, 6Hz)6H; 1.30(d, 6Hz)6H; 2.10(d x q)2H; 3.25(d x q)2H.

3.2.2: Preparation of 2,3,4,5-tetramethylcyclopent-2-enone.

A 250ml R B flask was charged with p-toluenesulphonic acid (45g, 0.24mol), the pyrone made above (370g, 2.4mol) and benzene (150ml). After fitting the flask with a Dean-Stark trap and condenser, the mixture was refluxed for 30 hours. The resulting elimination of water (47ml) was collected after a low boiling organic by-product. Upon cooling, a sticky, dark brown solution remained in the flask.

This solution was first treated with small portions of sodium carbonate (50g, 0.46mol) to neutralise the acidic conditions. Water (200ml) was then added and the mixture transferred to a separating funnel. The black organic layer was separated and washed with more water (2 x 200ml). The resultant black liquid was then distilled under reduced pressure through a 20cm vigreux column with the addition of anti-bumping granules and magnetic stirring. The title compound was collected as a very pale yellow liquid at 70-75°C/15Torr in 190g yield (59%) after 2 other lower boiling fractions. The stable nature of this compound makes it ideal as a "bottled" precursor to Cp*H which is itself, much more prone to decomposition.

IR/cm⁻¹: 1700(s) ν (C=O); 1650(s) ν (C=C).

¹H NMR (CDCl₃) δ /ppm: 1.14(d, 5Hz)3H; 1.25(d, 5Hz)3H; 1.70(s, sh.)3H; 2.05(s, br.)3H; 2.2-2.8(m)2H.

3.2.3: Preparation of 1,2,3,4,5-pentamethylcyclopentadiene (Cp*H).

A 1 litre 3-necked flask was fitted with a pressure-equalised dropping funnel and a reflux condenser connected to a dry nitrogen supply. After flushing the apparatus with nitrogen, the flask was charged with oven dried magnesium turnings (13.4g, 0.55mol), diethyl ether (200ml) and a magnetic follower.

To this stirred mixture was added methyl iodide (36ml, 0.57mol) at a rate to sustain a gentle reflux (dropwise after the first 5ml). An ice bath can be used to control the reaction if it becomes too fast. When the addition was complete, the resulting grey/brown solution was then stirred for a further 3 hours. At this point any excess magnesium metal can be destroyed by the cautious addition of a saturated aqueous solution of ammonium chloride (as required).

The Grignard solution was then treated dropwise with an ethereal (300ml) solution of the cyclopentenone (40g, 0.3 mol) prepared in the previous section. The resulting mixture was refluxed at low heat for 3 hours. On cooling, the contents of the flask separated into a yellow organic layer and a thick, white slurry. It is possible to work up the reaction at this point to yield the pentamethylcyclopentenol but it is suggested that it is more productive to proceed directly to the Cp*H in a "one-pot" synthesis.

The layered system gained above was cautiously treated with small portions of ice until the vigorous hydrolysis was seen to cease. Consequent addition of water (300ml) and concentrated hydrochloric acid (50ml) with rigorous shaking yielded two clear layers. These were transferred to a separating funnel and the aqueous component discarded. After washing with water (2 x 100ml), the organic layer was dried over anhydrous magnesium sulphate. Filtration followed by removal of the solvent *in vacuo* yielded a deep yellow liquid. This was then distilled under reduced pressure through a 20cm vigreux column to yield pale yellow Cp*H (15.6g, 40%) at 55°C/14 Torr.

IR/cm⁻¹: 2900(m, 3 bands); 1660(m); 1640(m); 1390(s).

¹H NMR (CDCl₃) δ/ppm: 2.14(m)1H; 1.75(s,br)12H; 0.95(d,8Hz)3H.

3.3: Preparation of sodium cyclopentadienide (NaCp).

A 1 litre Schlenk tube was charged with sodium amide (7.8g, 0.2mol) and THF (500ml). The resulting suspension was then thoroughly degassed *via* 3 freeze-pump-thaw cycles and connected to an argon supply with an outlet valve (bubbler). In the meantime, a commercial sample of dicyclopentadiene was "cracked," with the monomer being collected at the still head (40°C) of the boiling dimer.

The stirred THF suspension was treated dropwise with the freshly prepared CpH (13.2g, 0.2mol) to give a slightly exothermic reaction. Formation of a pale red/brown solution was accompanied by the evolution of hydrogen gas. It should be noted that this solution is extremely sensitive to the presence of oxygen; the colour arises from the decomposition product formed by contact with the air. Strictly anaerobic conditions must be followed throughout the preparation. The reaction mixture was stirred for 1 hour to ensure completion.

Removal of the solvent *in vacuo* yielded a pale pink solid. This was then further pumped at room temperature to eliminate any traces of ammonia. The NaCp was used as prepared without purification. The solid must be stored under an atmosphere of argon at all times.

3.3.1: Preparation of NaCp*.

The title compound was prepared using an analogous procedure to that above. Freshly prepared Cp*H (13.6g, 0.1mol) and sodium amide (3.9g, 0.1mol) yield pale yellow NaCp*. The yellow colour is again due to the product arising from oxygen contamination.

3.4: Preparation of trimethylsilylcyclopentadiene (CpSiMe₃).



To the NaCp (0.2mol) prepared in the previous section was added degassed THF (200ml). The resulting solution was magnetically stirred and treated dropwise with trimethylsilyl chloride (21.7g,0.2mol) via a pressure-equalised dropping funnel. This addition prompted a decolourisation of the solution with the precipitation of a gelatinous solid (NaCl).

Filtration of this mixture proved to be a difficult procedure. The best method involved suction filtration through celite on a large sinter-containing vessel equipped with an argon inlet. This process takes up to 24 hours and some of the solid always contaminates the filtrate. Providing that the vast majority is removed, this is not a problem.

The cloudy yellow solution was then transferred to a 250ml R B flask equipped with magnetic follower. Careful removal of the THF under reduced pressure (*ca.* 20 Torr) gives a sticky yellow liquid. Distillation *in vacuo* yields pure CpSiMe₃ (21.5g, 78% based on CpH) as a pale yellow liquid (b.pt. 36°C, 13 Torr).

3.4.1: Cp*SiMe₃, CpSnBu₃ and Cp*SnBu₃.

These three compounds are all prepared using similar procedures to that described for CpSiMe₃. Obviously the relevant NaCp and ClSiMe₃ are substituted with the appropriate Cp* or ClSnBu₃ analogues. Table 3.1 gives the experimental details of the four preparations. It should be noted that some decomposition occurs in the distillation of both tin-centred complexes due to the high temperatures involved. All four liquids should be stored under an argon atmosphere. The tin reagents tend to darken in colour with age.

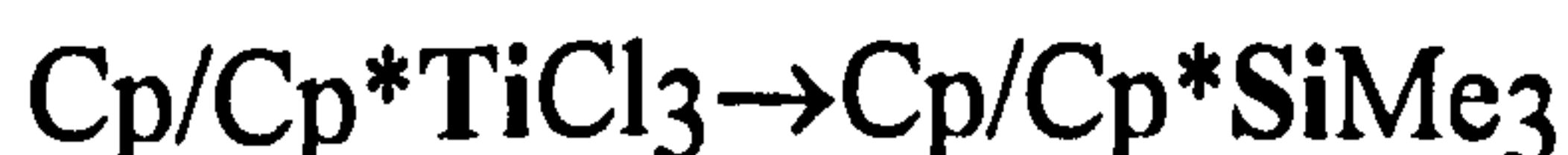
Table 3.2: Experimental details of the CpER₃ syntheses.

Preparation	Reagents	B.pt.	Yield
CpSiMe ₃	ClSiMe ₃ (21.7g) + NaCp (0.2mol)	36°C/13 Torr	21.5g, 78%
Cp*SiMe ₃	ClSiMe ₃ (10.9g) + NaCp* (0.1mol)	100°C/10 Torr	16.9g, 81%
CpSnBu ₃	ClSnBu ₃ (65.1g) + NaCp (0.2mol)	145°C/0.1 Torr	46.2g, 65%
Cp*SnBu ₃	ClSnBu ₃ (32.6g) + NaCp* (0.1mol)	169°C/0.1 Torr	25.9g, 61%

3.5: Preparation of monocyclopentadienyl metal chlorides

for Ti, Zr, Hf and Nb

Synthesis of the title compounds and their Cp* analogues involves straight forward procedures which are all similar in nature. Although there are a number of reactants which can be used to effect each preparation, experiment has shown that there are optimum conditions for the particular complexes. Generally, the Ti-species are best prepared using the Si-based reagents whilst the Sn analogues give better results for the heavier metals:



3.5.1: Preparation of CpTiCl₃.

An oven-dried schlenk tube equipped with magnetic follower was charged with toluene (100ml) and titanium tetrachloride (9.5g, 0.05mol). To this stirred solution, trimethylsilylcyclopentadiene (6.9g, 0.05mol) was added dropwise from a pressure-equilised dropping funnel. An instantaneous reaction results in the gradual colour change of red to yellow. After the complete addition, the solution was stirred for a further 30 minutes. Removal of around half of the solvent *in vacuo* then precipitates a yellow, microcrystalline solid of the title compound. This was collected by filtration, washed with hexane (2 x 30ml) and pumped dry. The yield at this stage was 9.6g (88%). The solid can be recrystallised from the minimum amount of hot acetonitrile.

3.5.2: Preparation of Cp*TiCl₃.

This complex is prepared using Cp*SiMe₃ (10.4g, 0.05mol) and TiCl₄ (9.5g, 0.05mol), in an analogous procedure to that above. The product is recovered as a microcrystalline red solid in a 12.4g yield (86%).

3.5.3: Preparation of CpZrCl₃(MeCN)₂.

A schlenk tube equipped with magnetic follower was charged with zirconium tetrachloride (11.65g, 0.05mol) and dichloromethane (100ml). To this stirred suspension at 0°C was added dimethyl sulphide (6.20g, 0.1mol). The resultant cloudy solution was filtered to be rid of any insoluble hydrolytic species. This clear yellow solution was then treated dropwise with tributylstannylcyclopentadiene (17.76g, 0.05mol) whereupon a solid immediately began to form. The reaction mixture was stirred for 2 hours at room temperature.

Acetonitrile (30ml) was then added and the solvent subsequently reduced *in vacuo* to a volume of ca. 20ml. The suspension was transferred to a fritted funnel, washed with cold acetonitrile (2 x 20ml) and dried under vacuum to afford the title compound as a white solid in 11.2g yield (65%). The complex can be further purified by recrystallisation from hot acetonitrile.

3.5.4: Preparation of $\text{Cp}^*\text{HfCl}_3(\text{MeCN})_2$.

This complex is prepared in an analogous procedure to that above using hafnium tetrachloride (16.02g, 0.05mol), tributylstannylcyclopentadiene (17.76g, 0.05mol) and dimethyl sulphide (6.20g, 0.1mol). It is recovered in 12.7g yield (59%) as a white solid. Again, recrystallisation from hot acetonitrile affords the pure title compound.

3.5.5: Preparation of $\text{Cp}^*\text{MCl}_3(\text{MeCN})_2$ for $\text{M}=\text{Zr}$ and Hf .

The title compounds were prepared using similar procedures. The relative amounts of the reactants employed are given in Table 3.2.

Table 3.3: Experimental details of the $\text{Cp}^*\text{MCl}_3(\text{MeCN})_2$ syntheses for $\text{M}=\text{Zr}$ and Hf .

	colour	MCl_4 (0.02mol)	Cp^*SnBu_3 (0.02mol)	Yield
$\text{Cp}^*\text{ZrCl}_3(\text{MeCN})_2$	white	4.66g	8.51g	6.22g (75%)
$\text{Cp}^*\text{HfCl}_3(\text{MeCN})_2$	white	6.41	8.51g	7.33g (73%)

A stirred suspension of the relevant metal chloride in dichloromethane (50ml) was treated with tributylstannylcyclopentadiene whereupon a white solid immediately began to form. The reaction mixture was stirred for a further 2 hours.

Acetonitrile (20ml) was then added and the reaction mixture was subsequently concentrated to a volume of *ca.* 20ml. The title compounds are recovered via filtration, washed with cold acetonitrile (2 x 20ml) and pumped dry. Both complexes can be recrystallised from hot acetonitrile.

3.5.6: Preparation of CpNbCl₄.

To a stirred suspension of niobium pentachloride (5.40g, 0.02mol) in toluene (100ml) was added tributylstannylcyclopentadiene (7.10g, 0.02mol). A deep red solid was seen to form instantaneously. After continued stirring for 2 hours, the solvent was reduced *in vacuo* to *ca.* 20ml. The bright red title compound was recovered by filtration, washed with hexane (2 x 20ml) and pumped dry. At this stage the yield recorded was 4.56g (76%).

As with the analogous Zr and Hf systems, adduct formation in acetonitrile is very fast. It should be noted that the title complex seems to be even more sensitive to hydrolysis than the Group 4 complexes. When recrystallised from warm acetonitrile, the red platelets of the required adduct are always formed in the company of a small amount of yellow crystals. The latter are due to the hydrolysis product [CpNbCl₃(MeCN)]₂O.

3.6: Halide abstraction reactions of the CpMCl₃ series.

3.6.1: Preparation of [CpTiCl₂(MeCN)₃][SbCl₆] I.

A bright orange, chilled solution (0°C) of CpTiCl₃ (1.56g, 7.1mmol) in acetonitrile (50ml) was treated dropwise with SbCl₅ (2.12g, 7.1mmol) in a similar solvent (30ml). This addition was accompanied by an immediate darkening of the orange solution. The reaction was then stirred for 4 hours to ensure completion. Removal of the solvent from the resultant brown solution *in vacuo* gave a dark red solid. This was washed with dichloromethane (4 x 30ml) and then hexane (30ml) before being pumped dry for 2 hours. The red solid was recrystallised from an acetonitrile/dichloromethane solution (*ca.* 30/70) to give red/brown cubes of the title compound (3.96g, 87%).

3.6.2: Preparation of [CpTiCl(MeCN)₄][SbCl₆]₂ II.

Method (a). A chilled solution of CpTiCl₃ (0.97g, 4.4mmol) in acetonitrile (50 ml) was treated dropwise with a solution of SbCl₅ (2.64g, 8.8mmol) in acetonitrile (25ml). On the addition, the solution immediately darkens to give a brown colour. As the resultant mixture is stirred over a further 2 hours this colour gradually takes on an olive green appearance. Removal of the solid *in vacuo* provides a blue/black powder. This was washed with dichloromethane (4 x 30ml) and hexane (30ml) before being pumped dry. At this stage, the title compound can be used as pure (3.94g, 91%). If the blue/grey solid is recrystallised from acetonitrile/dichloromethane, a mixture (*ca.* 50/50) of red and pale blue crystals are obtained. The former consist of the monocation I whilst the latter are pure II. Both sets of crystals are suitable for X-ray analysis.

Method (b). A cooled red brown solution of I (4.36g, 6.8mmol) in acetonitrile (100ml) was treated with SbCl₅ (2.03g, 6.8mmol) in acetonitrile (50ml). Over a period of 2 hours at room temperature, the resultant solution became olive green in colour. Removal of the solvent *in vacuo* gave a blue/grey solid which was subsequently washed with dichloromethane (4 x 30ml) and hexane (30ml). After pumping the product for 2 hours, it can be used as pure II (5.94g, 89%). Recrystallisation from acetonitrile/dichloromethane again yields a mixture of I and II.

3.6.3: Preparation of [CpTi(MeCN)₅][SbCl₆]₃ III.

An ice-cold solution of CpTiCl₃ (0.56g, 2.6mmol) in acetonitrile (50ml) was treated dropwise with a solution of SbCl₅ (4.57g, 15mmol) in acetonitrile (30ml). The resulting solution assumed a deep blue colour over a period of 4 hours with stirring at room temperature. Subsequent removal of the solvent *in vacuo* yielded a pale blue/black solid. After washing with dichloromethane (6 x 40ml) and hexane (30ml) followed by drying *in vacuo* the solid appears as a pale violet solid. At this stage the yield of III is 2.79g (83%). The title compound can be recrystallised from an acetonitrile/dichloromethane mixture (ca. 40/60) doped with SbCl₅ to give purple/blue blocks.

3.6.4: Preparation of [CpZrCl₂(MeCN)₃][SbCl₆] VII.

To a chilled, stirred solution of CpZrCl₃(MeCN)₂ (1.00g, 2.9mmol) in acetonitrile (50ml) was added SbCl₅ (0.87g, 2.9mmol) in the same solvent (30ml) from a pressure equalised dropping funnel. The resultant yellow/ brown solution was stirred at room temperature for a further 2 hours to ensure the completion of the reaction. Removal of the solvent *in vacuo* gives a dirty white solid. This was

washed with dichloromethane (4 x 30ml) and then hexane (30ml) before before being pumped to dryness under vacuum. The white solid recovered in this way analyses for the title compound. Without further purification, the yield is 1.55g (78%).

The only successful method that was discovered for the recrystallisation of the complex involved the use of an acetonitrile/toluene mixture at -30°C. However, the bright yellow crystals produced in this way proved to be extremely sensitive at room temperature. They must be filtered from the solvent mixture at low temperature and washed with toluene immediately. Even then, the small amount of decomposition that takes place precludes their use in crystallographic studies.

3.6.5: Preparation of $[\text{CpZrCl}(\text{MeCN})_4][\text{SbCl}_6]_2$ VIII.

To a stirred acetonitrile solution (50ml) of $\text{CpZrCl}_3(\text{MeCN})_2$ (0.56g, 1.6mmol) was added SbCl_5 (0.97g, 3.2mmol) in the same solvent (30ml) via pressure equalised dropping funnel. The resultant yellow/brown solution was stirred for a further 2 hours. After the removal of the solvent *in vacuo*, the product was washed with dichloromethane (4 x 30ml) and hexane (30ml). Pumping dry under vacuum then yields the title compound as a white powder (1.28g, 77%).

Recrystallisation from acetonitrile/dichloromethane gives small colourless diamond shaped crystals which are suitable for X-ray analysis. These should be kept under an argon atmosphere preferably at low temperature to prevent the darkening of their colour which leads to substantial decomposition.

3.6.6: Preparation of $[\text{CpZr}(\text{MeCN})_6][\text{SbCl}_6]_3$ IX.

An acetonitrile solution (50ml) of $\text{CpZrCl}_3(\text{MeCN})_2$ (0.50g, 1.5mmol) was treated with SbCl_5 (2.60g, 8.7mmol) and stirred for 24 hours. Solvent was then removed *in vacuo* from the resulting yellow/brown solution until precipitation of the excess $\text{SbCl}_5(\text{MeCN})$ began to occur. At this point, dichloromethane (150ml) was added to redissolve the solid before precipitating the title complex. In this way, it is certain that the product recrystallises in the presence of a large excess of SbCl_5 . The solid was then filtered from the reaction and washed thoroughly with more dichloromethane (6 x 40ml) and then hexane (30ml). After drying *in vacuo*, the white microcrystalline product was isolated in 1.55g (76%) yield. The lower yield is probably due to the formation of some $[\text{CpZrCl}(\text{MeCN})_4][\text{SbCl}_6]_2$ which then contaminates the product.

3.6.7: Preparation of $[\text{CpHfCl}_2(\text{MeCN})_3][\text{SbCl}_6]$ X.

A chilled, stirred solution of $\text{CpHfCl}_3(\text{MeCN})_2$ (0.60g, 1.4mmol) in acetonitrile (50ml) was treated dropwise with SbCl_5 (0.42g, 1.4mmol) in the same solvent. The resulting yellow/brown solution was then stirred at room temperature for 2 hours. Removal of the solvent *in vacuo* revealed a dirty white solid. This was washed with dichloromethane (4 x 30ml) and hexane (30ml) to give the title complex (0.80g, 75%). Studies in the purification of this compound proved to be fruitless; mixtures of acetonitrile with the common laboratory solvents were tried, but did not yield a crystalline sample.

3.6.8: Preparation of $[\text{CpHfCl}(\text{MeCN})_4][\text{SbCl}_6]_2$ XI.

To a stirred acetonitrile solution (50ml) of $\text{CpHfCl}_3(\text{MeCN})_2$ (0.54g, 1.2mmol) was added SbCl_5 (0.75g, 2.5mmol) in the same solvent. The resulting yellow/brown solution was then stirred for a further 2 hours at room temperature. Removal of the solvent *in vacuo* yields an off-white solid. After washing this solid with dichloromethane (4 x 30ml) and hexane (30ml), drying under vacuum produces a cleaner-looking white powder. This analyses for the title compound (1.04g, 72%).

Recrystallisation from acetonitrile/dichloromethane gives excellent, colourless, diamond shaped crystals which are suitable for X-ray analysis.

3.6.9: Preparation of $[\text{CpHf}(\text{MeCN})_6][\text{SbCl}_6]_3$ XII.

A mixture of $\text{CpHfCl}_3(\text{MeCN})_2$ (0.50g, 1.2mmol) and SbCl_5 (2.07g, 6.9mmol) in acetonitrile (80ml) was stirred for 24 hours. The reaction solvent was then concentrated *in vacuo* until the excess $\text{SbCl}_5(\text{MeCN})$ began to precipitate from solution. Subsequent addition of dichloromethane (150ml) redissolved the $\text{SbCl}_5(\text{MeCN})$ before precipitating the title complex. The solid was removed by filtration, washed well with dichloromethane (6 x 40ml) and hexane (30ml) before being pumped to dryness. The white microcrystalline product was isolated in 1.23g (71%) yield. It probably contains a trace quantity of the dication X.

3.7: Halide abstraction from the Cp*MCl₃ series.

3.7.1: Preparation of [Cp*TiCl₂(MeCN)₃][SbCl₆] IV.

A chilled solution of Cp*TiCl₃ (0.60g, 2.1mmol) in acetonitrile was treated with SbCl₅ (0.62g, 2.1mmol) dissolved in the same solvent (30ml). The resultant orange solution was stirred for 2 hours. Removal of the solvent *in vacuo* revealed an orange/red solid. This was washed with dichloromethane (4 x 30ml) and hexane (30ml) before being pumped dry under vacuum. Recrystallisation from acetonitrile/ dichloromethane yields the title compound as a microcrystalline orange solid (1.21g, 82%).

3.7.2: Preparation of [Cp*TiCl(MeCN)₄][SbCl₆]₂ V.

To an ice-cold, stirred solution of Cp*TiCl₃ (0.43g, 1.5mmol) in acetonitrile (50ml) was added SbCl₅ (0.89g, 3.0mmol) in the same solvent (30ml). The colour of the solution changed from red to green/black on this addition. Stirring was continued for a further 2 hours. Removal of the solvent *in vacuo* then revealed a dark green solid. This was washed with dichloromethane (4 x 30ml) and hexane (30ml) before being pumped dry under vacuum. The title complex was thus recovered as a dark green powder (1.17g, 75%).

Recrystallisation from acetonitrile/dichloromethane gives a dark green microcrystalline solid with a trace amount of the orange coloured IV viewable only with the aid of a microscope.

3.7.3: Preparation of $[\text{Cp}^*\text{Ti}(\text{MeCN})_5][\text{SbCl}_6]_3$ VI.

A stirred solution of Cp^*TiCl_3 (0.40g, 1.4mmol) was treated dropwise with a 4 molar excess of SbCl_5 (1.65g, 5.5mmol) dissolved in the same solvent. During this addition the solution changes from red to dark green and then gradually lightens in colour. After 4 hours of stirring at room temperature, the solvent was removed *in vacuo* from this light green solution to reveal a similarly coloured solid. After washing with dichloromethane (6 x 40ml) and hexane (30ml), the solid was dried under vacuum. At this stage, pale green VI is recovered in 1.63g (85%) yield.

Recrystallisation from acetonitrile/dichloromethane gives pale green blocks which are suitable for X-ray analysis.

3.7.4: Preparation of $[\text{Cp}^*\text{ZrCl}_2(\text{MeCN})_3][\text{SbCl}_6]$ XIII.

To a stirred solution of $\text{Cp}^*\text{ZrCl}_3(\text{MeCN})_2$ (0.45g, 1.1mmol) in acetonitrile (50ml) was added SbCl_5 (0.32g, 1.1mmol) in the same solvent. The resultant lemon yellow solution was then stirred at room temperature for 2 hours. Removal of the solvent *in vacuo* revealed an orange solid. This was washed with dichloromethane (4 x 30ml) and hexane (30ml) before being pumped to dryness. At this stage, the yellow solid analyses for the title compound and is recovered in 0.65g (79%) yield. Attempts in recrystallisation proved to be unsuccessful.

3.7.5: Preparation of $[\text{Cp}^*\text{ZrCl}(\text{MeCN})_4][\text{SbCl}_6]_2$ XIV.

A stirred solution of $\text{Cp}^*\text{ZrCl}_3(\text{MeCN})_2$ (0.42g, 1.0mmol) in acetonitrile (40ml) was treated dropwise with SbCl_5 (0.61g, 2.0mmol) dissolved in the same solvent (20ml). The resultant lemon yellow solution was stirred at room temperature for a further 2 hours. Subsequent removal of the solvent *in vacuo* gave a yellow solid. This was washed with dichloromethane (4 x 30ml) and hexane (30ml) and then pumped dry. The pale yellow solid recovered in this way analyses for the title compound, yield 0.94g(85%). Recrystallisation from acetonitrile/dichloromethane affords a white microcrystalline solid.

3.7.6: Preparation of $[\text{Cp}^*\text{Zr}(\text{MeCN})_6][\text{SbCl}_6]_3$ XV.

A mixture of $\text{Cp}^*\text{ZrCl}_3(\text{MeCN})_2$ (0.50g, 1.2mmol) and SbCl_5 (2.16g, 7.2mmol) in acetonitrile (60ml) was stirred at for 24 hours. The resultant bright yellow solution was then concentrated *in vacuo* to ca. 10ml, whereupon the excess $\text{SbCl}_5(\text{MeCN})$ precipitated out. The addition of dichloromethane (150ml) redissolves this solid but subsequently precipitates the title complex. This was collected by filtration, washed with dichloromethane (6 x 40ml) and pumped dry *in vacuo*. The pale yellow solid recovered in this way analyses for the trication XV; the yield of the preparation being 1.40g (79%).

3.7.7: Preparation of $[\text{Cp}^*\text{HfCl}_2(\text{MeCN})_3][\text{SbCl}_6]$ XVI.

To a cooled, stirred solution of $\text{Cp}^*\text{HfCl}_3(\text{MeCN})_2$ (0.45g, 0.9mmol) in acetonitrile (30ml) was added SbCl_5 (0.27g,0.9mmol) in the same solvent (20ml). The resulting lemon yellow solution was stirred for a further 2 hours. Removal of the solvent *in vacuo* revealed a brick red solid. Washing this solid with dichloromethane (4 x 30ml) and hexane (30ml) followed by drying *in vacuo* affords the tan coloured title compound in 0.60g (79%) yield.

3.7.8: Preparation of $[\text{Cp}^*\text{HfCl}(\text{MeCN})_4][\text{SbCl}_6]_2$ XVII.

An ice-cold stirred solution of $\text{Cp}^*\text{HfCl}_3(\text{MeCN})_2$ (0.40g, 0.8mmol) in acetonitrile (40ml) was treated dropwise with SbCl_5 (0.48g, 1.6mmol) dissolved in the same solvent (20ml). The resulting lemon yellow solution was stirred at room temperature for 2 hours. Subsequent removal of the solvent *in vacuo* gave a yellow solid. This was washed with dichloromethane (4 x 30ml) then hexane (30ml) and pumped dry. In this way, the cream title compound was recovered in 0.76g (81%) yield. Recrystallisation from acetonitrile/dichloromethane affords a microcrystalline off-white solid.

3.7.9: Preparation of $[\text{Cp}^*\text{Hf}(\text{MeCN})_6][\text{SbCl}_6]_3$ XVIII.

A mixture of $\text{Cp}^*\text{HfCl}_3(\text{MeCN})_2$ (0.50g, 1.0mmol) and SbCl_5 (1.79g, 6.0mmol) in acetonitrile (50ml) was stirred for 24 hours. The resultant yellow solution was concentrated to a volume of *ca.* 10ml whereupon the excess $\text{SbCl}_5(\text{MeCN})$ began to precipitate from solution. The addition of dichloromethane (150ml) redissolved this solid and then precipitated the desired title complex. The product was collected by filtration, washed with dichloromethane (6 x 40ml) and the dried *in vacuo*. The yield of the off white product was found to be 1.21g (78%).

3.8: Halide abstraction from $\text{CpNbCl}_4(\text{MeCN})$.

To investigate the possible extent of cation formation, the title compound was treated with a 10 molar excess of SbCl_5 . A mixture of $\text{CpNbCl}_4(\text{MeCN})$ (0.40g, 1.2mmol) and SbCl_5 (3.59g, 12mmol) was stirred at 60°C for 24 hours. After allowing the resultant orange solution to cool, the solvent was removed *in vacuo* to reveal a similarly coloured solid. This was washed with dichloromethane (6 x 40ml) then hexane (30ml) and pumped dry. At this point, the solid recovered (1.27g) represents a 78% yield for the trication $[\text{CpNbCl}(\text{MeCN})_4][\text{SbCl}_6]_3$.

3.9: MeCN substitution reactions of the cationic CpMⁿ⁺ series.

3.9.1: N-donors (NEt₃ and TMEDA).

A general procedure was followed for both title ligands in combination with the CpTi³⁺, CpZr²⁺ and CpHf²⁺ cationic complexes. Experimental details for each reaction can be found in Table 3.4.

To a cooled solution of the relevant cation in MeCN was added a 6 molar excess of the appropriate ligand. This addition invariably resulted in the immediate precipitation of "dirty" solids. After stirring for 2 days these solids were filtered from the liquors, washed with MeCN (2 x 30ml) then hexane (20ml) and pumped dry *in vacuo*. Characterisation by IR and elemental analysis were inconclusive but suggested the presence of mixtures containing partially substituted products.

Table 3.4: Experimental details of N-donor substitution reactions.

CpM ⁿ⁺	Ligand added	Product colour	Yield
[CpTi(MeCN) ₅][SbCl ₆] ₃ 0.41g, 0.3mmol	NEt ₃ 0.19g, 1.9mmol	orange-brown	0.35g
[CpTi(MeCN) ₅][SbCl ₆] ₃ 0.42g, 0.3mmol	TMEDA 0.11g, 1.0mmol	brown	0.35g
[CpZrCl(MeCN) ₄][SbCl ₆] ₂ 0.37g, 0.4mmol	NEt ₃ 0.22g, 2.2mmol	cream	0.30g
[CpHfCl(MeCN) ₄][SbCl ₆] ₂ 0.31g, 0.3mmol	TMEDA 0.10g, 0.8mmol	off-white	0.22g

3.9.2: O-Donors.

Et₂O and Me₂CO.

The cations CpTi³⁺, CpZr²⁺ and CpHf²⁺ were slurried in the title solvents (20ml) and stirred at room temperature for 5 days. It was noted that the Ti-based cation changed from blue to yellow over the first few minutes and seems to become more soluble. The latter was also true of the Zr- and Hf-based systems but all three reactions never become fully soluble. Removal of the solvents *in vacuo* afforded yellow (for Ti) and white (Zr, Hf) solids.

The reaction of [CpTi(MeCN)₅][SbCl₆]₃ with ¹⁵O₅

To a suspension of the Ti-based trication (0.29g, 0.2mmol) in toluene (20ml) was added ¹⁵O₅ (0.1g, 0.4mmol). The colour of the resultant mixture was seen to change from blue to yellow over a period of 10 minutes. Subsequent stirring for 5 days resulted in the formation of a fine yellow powder. After decanting the reaction solvent, the solid was washed with hexane (3 x 20ml) and pumped dry. Attempts at recrystallisation proved unsuccessful due to the low solubility of the product in all but MeCN in which the parent species reform. Evidence from IR and elemental analysis suggest the product may be [CpTi(¹⁵O₅)(MeCN)][SbCl₆]₃. Based on this, the solid recovered (0.21g) represents a 71% yield.

3.9.3: P- and S-Donors.

The reaction of $[\text{CpTi}(\text{MeCN})_5][\text{SbCl}_6]_3$ with PMe_3 .

An ice-cold suspension of the title complex (0.41g, 0.3mmol) in toluene (20ml) was treated dropwise with a commercial solution of PMe_3 in toluene (1.9ml, 1M, 1.9mmol). An instantaneous reaction results in the formation of a pink solid. After stirring this suspension for 2 days, the solid was filtered from the reaction, washed with hexane and pumped dry. The pale pink solid was recovered in 0.43g yield but characterisation proved to be impossible.

Attempted reaction of $[\text{CpTi}(\text{MeCN})_5][\text{SbCl}_6]_3$ with PPh_3 .

To a stirred suspension of the title complex (0.35g, 0.3mmol) in toluene (20ml) was added PPh_3 (0.42g, 1.6mmol) as a solution in the same solvent (20ml). Even after the mixture had been stirred for 5 days, the blue colour of the title complex was seen to remain. Recovery of the solid by filtration followed by the measurement of its ^1H NMR spectrum confirmed that no reaction had taken place.

Attempted reaction of $[\text{CpTi}(\text{MeCN})_5][\text{SbCl}_6]_3$ with SMe_2 .

A pure sample of the trication (0.38g, 0.3mmol) was suspended in SMe_2 (20ml) and stirred for 5 days. The absence of any reaction was again confirmed by the recovery of the blue solid via filtration and the subsequent measurement of its ^1H NMR spectrum. Even if the reaction is refluxed, no reaction occurs.

3.10: Hydrolysis of the CpMⁿ⁺ series.

All of the cationic species I→XVIII can be hydrolysed in a controlled manner using an accurately known solution of water in pre-dried MeCN. The experimental procedure described below for the CpZr²⁺ cation was applied to other members of the series employing the quantities outlined in Table 3.5.

Stock Solution Used (0.1M): H₂O (0.18g, 10mmol) in MeCN (100ml).

3.10.1: Preparation of [{CpZr(MeCN)₄}₂O][SbCl₆]₄ XX.

A stirred solution of [CpZrCl(MeCN)₄][SbCl₆]₂ (0.50g, 0.5mmol) in dry MeCN (30ml) was treated dropwise with an aliquot of the stock solution (2.44ml, 0.25mmol H₂O). After the reaction had been stirred for 4 hours, the solvent was removed in vacuo and the solid produced washed with dichloromethane (2 x 30ml). The off-white powder was then pumped dry for 2 hours, thus ensuring the removal of any HCl. In this way, the title complex was recovered in 0.43g (89%) yield. However, the purity of the sample cannot be guaranteed due to the delicate balance of stoichiometries involved in the preparation.

Analysis: calculated for C₂₆H₃₄N₈OZr₂Sb₄Cl₂₄, C 15.65; H 1.72; N 5.61.

Found, C 15.55; H 1.60; N 5.71.

Table 3.5: Experimental details of CpMⁿ⁺ hydrolysis reactions.

Reactant	Stock Solution	Product Yield
[CpZrCl ₂ (MeCN) ₃][SbCl ₆] 0.50g, 0.7mmol	3.65ml (0.35mmol H ₂ O)	0.39g
[CpHfCl(MeCN) ₄][SbCl ₆] ₂ 0.40g, 0.4mmol	1.80ml (0.2mmol H ₂ O)	0.35g
[Cp*ZrCl(MeCN) ₄][SbCl ₆] ₂ 0.40g, 0.40mmol	1.83ml (0.2mmol H ₂ O)	0.34g

3.11: The reactions of $[\text{CpTi}(\text{MeCN})_5][\text{SbCl}_6]_3$ with inorganic salts.

A common methodology was used with a number of Me_4N^+ , Na^+ and K^+ salts. This involved the addition of the title complex as a solid to an excess of the appropriate salt in a toluene suspension. Under glove-box conditions employing test-tube quantities, the reactions go to completion after a few minutes of shaking. In the majority of cases, the desired Ti-based complexes remain solvated whilst the counter-products are deposited from solution. The two exceptions to this rule, namely the products of the NaF and KSCN reactions, are only soluble when the toluene is heated. The solutions bearing the relevant Ti complexes were then decanted from the reaction mixtures. Removal of the solvent *in vacuo*, followed by washing with hexane (20ml) afforded the compounds described in Table 3.6. These were identified by a comparison of their melting points with the literature values.¹³⁴

Table 3.6: Experimental details of the reactions between CpTi^{3+} and various inorganic salts.

Salt	Product	Colour	Melting Point/ $^{\circ}\text{C}$	
			measured	Lit. value
Me_4NCl	CpTiCl_3	orange-yellow	206-209	208-211
Me_4NBr	CpTiBr_3	orange	195-196	197-199
Me_4NI	CpTiI_3	deep red	143-145	148-150
NaF	CpTiF_3	v.pale yellow	138(d)	140(d)
KSCN	$\text{CpTi}(\text{SCN})_3$	brick red	157-162	161-163

3.12: The reaction of $[\text{CpTi}(\text{MeCN})_5][\text{SbCl}_6]_3$ with lithium methyl.

An ice-cold, stirred solution of CpTi^{3+} (0.75g, 0.6mmol) in MeCN (40ml) was treated dropwise with a commercial solution of LiMe in Et_2O (0.57ml, 1M, 0.6mmol). The solution immediately turns bright red and, after 2 hours, a thin white precipitate is observed. Careful filtration using Celite filter-aid gives a clear, red solution. Analysis (IR) of the white solid indicates the presence of LiCl.

Removal of the solvent from the solution affords a thick red oil. This was stirred with hexane for 24 hours. The hexane washings were then decanted and the oil pumped under full vacuum for 2 days. The waxy red-brown solid that was recovered is soluble in MeCN but all attempts at recrystallisation resulted in the formation of oils. Characterisation of the red solids proved to be inconclusive.

CHAPTER 4

INTRODUCTION TO ZIEGLER-NATTA POLYMERISATION

4.1: Historical origins.

In 1953 Professor Karl Ziegler and his team of co-workers stumbled upon a reaction which was to revolutionise the plastics industry.

Whilst investigating the oligomerisation of ethene over triethylaluminium, it was noticed that a trace quantity of nickel in the reactor increased the productivity. Subsequent experiments¹³⁷ demonstrated that other transition metals gave similar results. The use of zirconium acetylacetonate filled the autoclave with a high molecular weight, linear polyethylene. Titanium tetrachloride was found to be even more active.

Natta suggested that the transition metal halides were activating the ethene molecules prior to their insertion into the aluminium alkyl bonds and applied the principle to propene oligomerisation. In March 1954, using a titanium tetrachloride/triethylaluminium catalyst, Natta and his co-workers succeeded in synthesising the first crystalline polypropylene.¹³⁸

Up until this time polyolefin polymerisation could only be achieved under the high temperatures (150°-230°) and pressures (1000-3000 atm.) of the free-radical process. The polymers produced by this method contain highly branched hydrocarbon chains which pack poorly to give materials of low density. In contrast to this, Ziegler-Natta materials are usually of high density due to the highly linear polymeric chains. The development of the catalytic process eventually led to Ziegler and Natta being jointly awarded the Nobel Prize for Chemistry in 1963.

4.2: Scope of the reaction.

A Ziegler-Natta catalyst can be defined as the product of two components: an early transition metal compound (generally termed the "catalyst") and a hydride, alkyl or aryl derivative of Groups 1-3 (the "cocatalyst"). The most widely used (and studied) systems are those which combine Group 4 metal chlorides with aluminium alkyl cocatalysts.

A typical reaction involves the mixing of catalyst, cocatalyst and monomer in an inert solvent under a pressure of 8-10 atm. at temperatures up to 120°C (although some systems are active at room temperature and atmospheric pressure). The catalyst may or may not be soluble although in the former case, the metal centre will only stay in solution for the first few chain propagation steps.

The great advantage of Ziegler-Natta systems lies in the ease with which they can be "fine-tuned" to produce polymers of predetermined physical properties. The particular choice of catalyst (metal centre, oxidation state, ligand set, etc.), cocatalyst and reaction conditions results in a wide range of possible polymer structures.

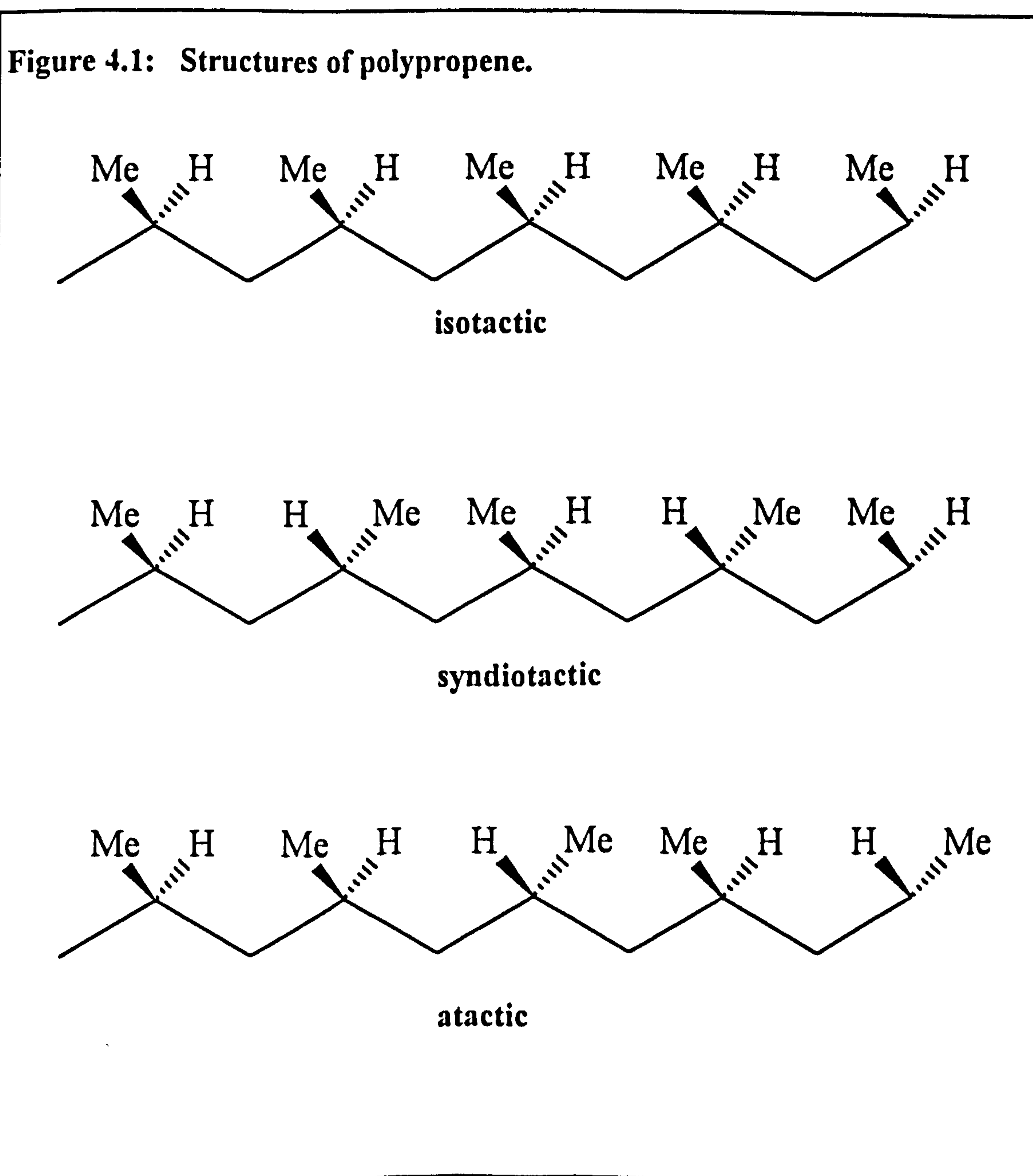
Comonomers may also be added to the reaction mixture and hydrogen gas can be used to terminate chain growth, thus providing a handle to limit the molecular weight of polymer produced.

The activity of a catalytic system is usually measured in terms of productivity, i.e. mass of polymer produced per mole of catalyst employed.

4.3: Structure and properties of polyolefins.

In contrast to the polymers produced *via* free radical processes, those made under Ziegler-Natta conditions are linear molecules which approach the ideal $(CR_2CR_2)_n$ configuration.

When higher alkenes are used as feedstock, the stereochemistry of the developing polymer can be controlled. For example, in propene polymerisation, the preferred, more crystalline isotactic and syndiotactic forms can be obtained whilst avoiding the random atactic form (Figure 4.1).



Despite the intensive research that has centred around Ziegler-Natta catalytic systems, there are no definitive unequivocal polymerisation mechanisms which fully describe how stereoselectivity is achieved. However, investigation of the properties of resultant polymers can often give useful pointers to the mechanism of their synthesis. The bulk properties of polyolefins broadly depend on two variables: average molecular weight and the degree of linearity of the polymeric chains.

4.3.1: Molecular weight (MW) and molecular weight distribution (MWD).

Polyethylene produced over Ziegler-Natta catalysts exhibit polydispersity i.e. the bulk polymer is composed of chains which cover a range of molecular weight. Of all the many scales used to describe the bulk polymer, two are most useful:¹³⁹

a) Number average molecular weight (\bar{M}_n) defined as, " the sum of the products of the molar mass of each fraction multiplied by it's mole fraction."

$$\bar{M}_n = \frac{\sum_{n_i} M_i}{\sum_{n_i}}$$

where n_i denotes the number of molecules with molecular weight M_i . Techniques such as osmometry, which measures colligative solution properties, can be used to determine \bar{M}_n . It can also be calculated *via* end group analysis; ^{13}C NMR and IR measurements can both be used to detect the number of end chain methyl groups. These techniques also give an indication of the extent of branching which is normally very low in this type of polymer.

b) Weight average molecular weight (\overline{M}_w), defined as, "the sum of the products of the molar mass of each fraction multiplied by its weight fraction."

$$\overline{M}_w = \frac{\sum w_i M_i}{\sum n_i}$$

where W_i is the total weight of all molecules of molecular weight M_i . Techniques which rely on molecular size such as ultracentrifugation can be used to determine \overline{M}_w .

The molecular weight distribution of a polymer sample is measured by Gel Permeation Chromatography in which the solvated molecules are eluted from a column depending on their size. In the absence of this technique, a numerical value of MWD can be calculated from the ratio $\overline{M}_w/\overline{M}_n$. This ratio is called the Polydispersity Index.

The determination of MW and MWD often involves difficult slow procedures. However, one point measurements can be taken to give more rapid, if less accurate, indications of these properties.

The Melt Index is one such measure of \overline{M}_w ; low MI values indicate a high MW and are inversely proportional roughly to the equation $MI \propto MW^{-4}$.

MI determination involves measuring the flow rate of molten polymer through a standard die at 463K under a load of 2.16 kg. The actual MI value is then calculated as the average weight of polymer extruded in 10 minutes. Similarly, the High Load Melt Index (HLMI) is recorded under a 21.6kg load. It is a general rule with polyethylene that the ratio of HLMI to MI increases as molecular weight distribution broadens. Typical values of Melt Index Ratio (MIR) in commercial polyethenes lie in the range 30 - 120.

4.4: Mechanisms of Ziegler-Natta catalysis.

Despite many years of intensive research, there are no definitive polymerisation mechanisms. Nevertheless, it is generally agreed that there are two key steps: complexation of the alkene to the active metal centre followed by insertion of this monomer into the growing polymer chain.

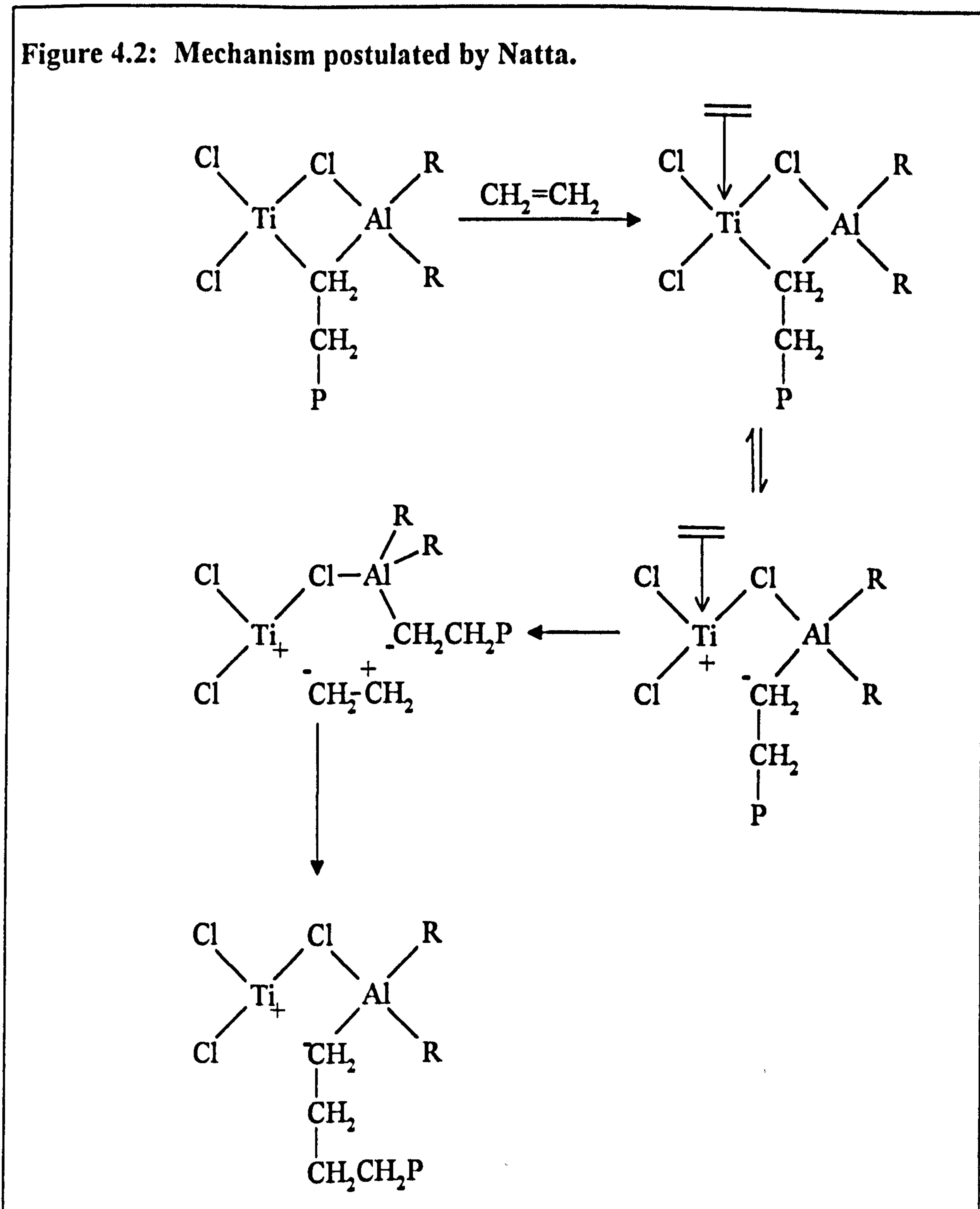
It is the exact nature of the active species which is the central point of discussion. Detailed mechanistic proposals fall into two main categories; those with propagation occurring at the aluminium (often termed Bimetallic) and those involving the transition metal centre.

4.4.1: Bimetallic mechanism theories.

Most of the evidence gained from early studies pointed toward this type of active centre. Previous work with Aluminium in the Aufbau reaction lead Natta¹⁴⁰ to propose that polymer growth occurred *via* alkene insertion into an (Al-R) bond (Figure 4.2).

Patat and Sinn¹⁴¹ proposed a similar mechanism in which the alkene becomes partially bonded between the transition metal and the methylene group of the last unit added to the polymer chain.

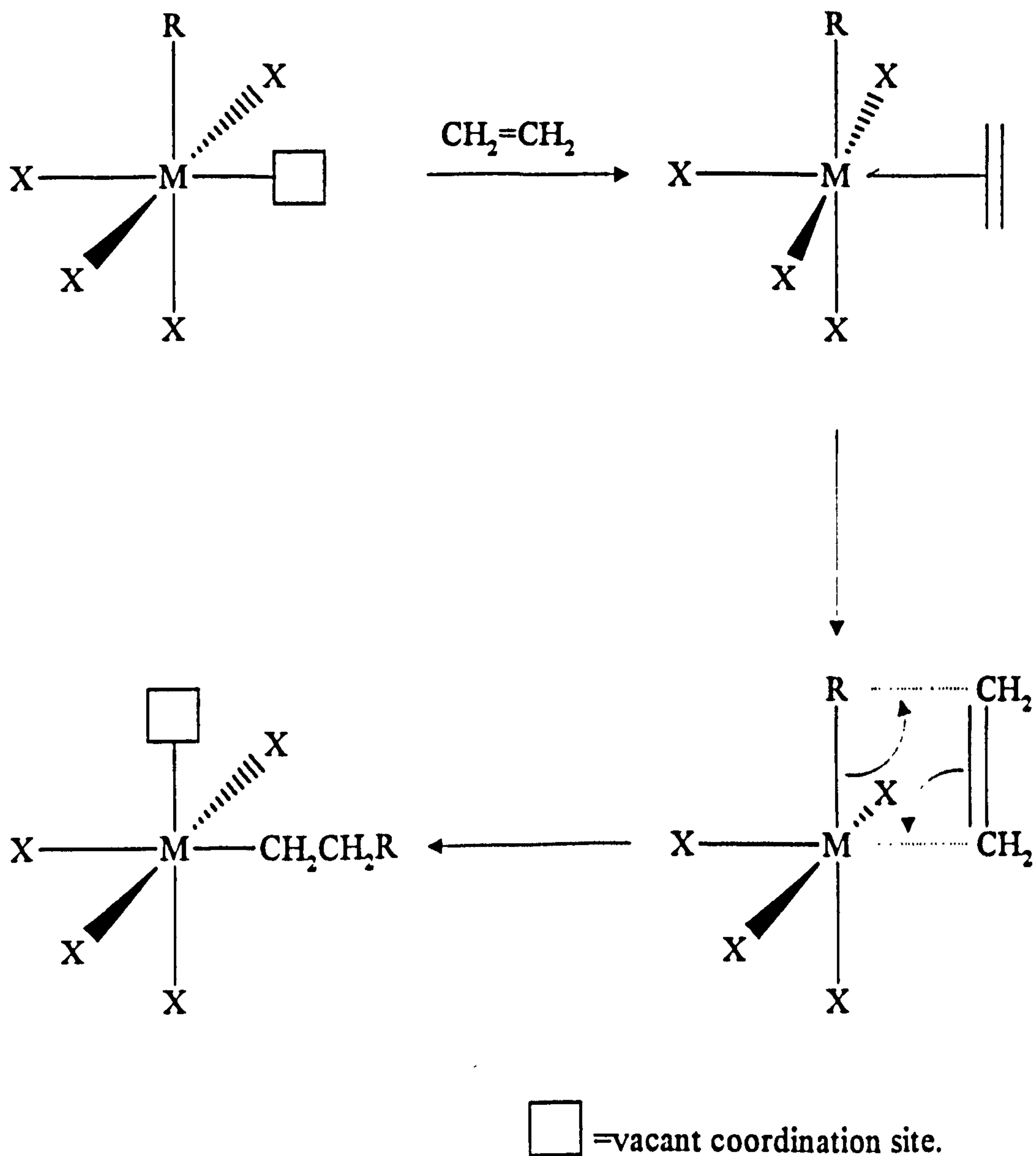
Figure 4.2: Mechanism postulated by Natta.



4.4.2: Transition metal-alkyl insertion theories.

Most experimental evidence points to the mechanism proposed by Cossee and Arlman.¹⁴² This widely accepted theory involves an octahedral transition metal centre with one alkyl group and one vacant coordination site due to the loss of another of its five ligands (Figure 4.3).

Figure 4.3: Mechanism proposed by Cossee and Arlman.



Polymer chain growth is achieved when the alkyl group migrates to the alkene which coordinates at the vacant site *via* a four membered ring transition state. The original geometry is then regenerated by vacant site/polymer chain exchange. This explains the regular stereochemistry of the polymer.

Green *et al*¹⁴³ suggested that the key reaction could proceed *via* transition metal carbene intermediates rather than by insertion (Figure 4.4). This mechanism was later modified to involve agostic transition metal species (Figure 4.5) after Grubbs¹⁴⁴ demonstrated that α -elimination in the parent metal alkyl was unlikely. Brookhart¹⁴⁵ has since shown that these (3c-2e) species do exist in the "resting states" during olefin polymerisation.

Figure 4.4: Mechanism proposed by Green and Ivin.

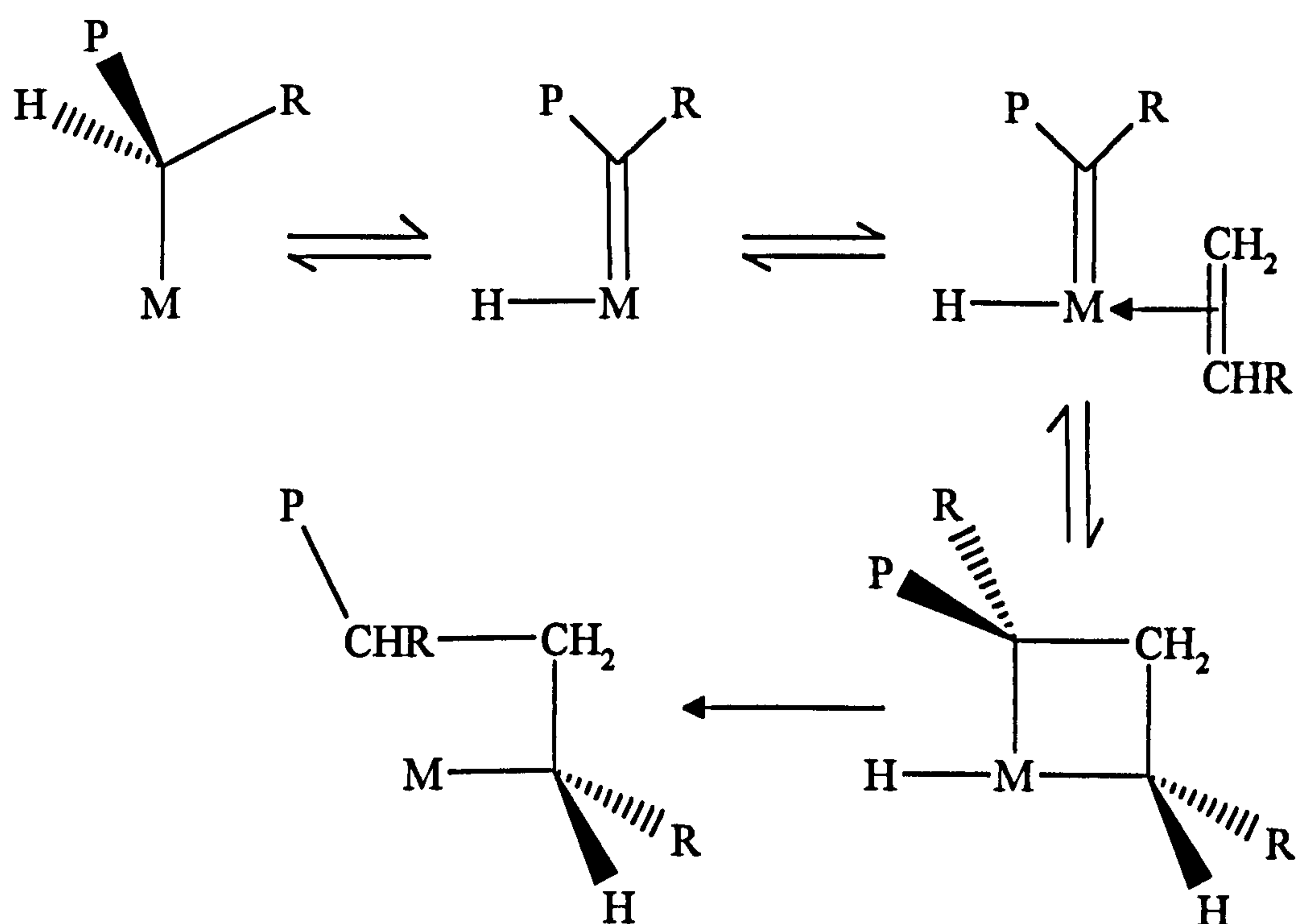
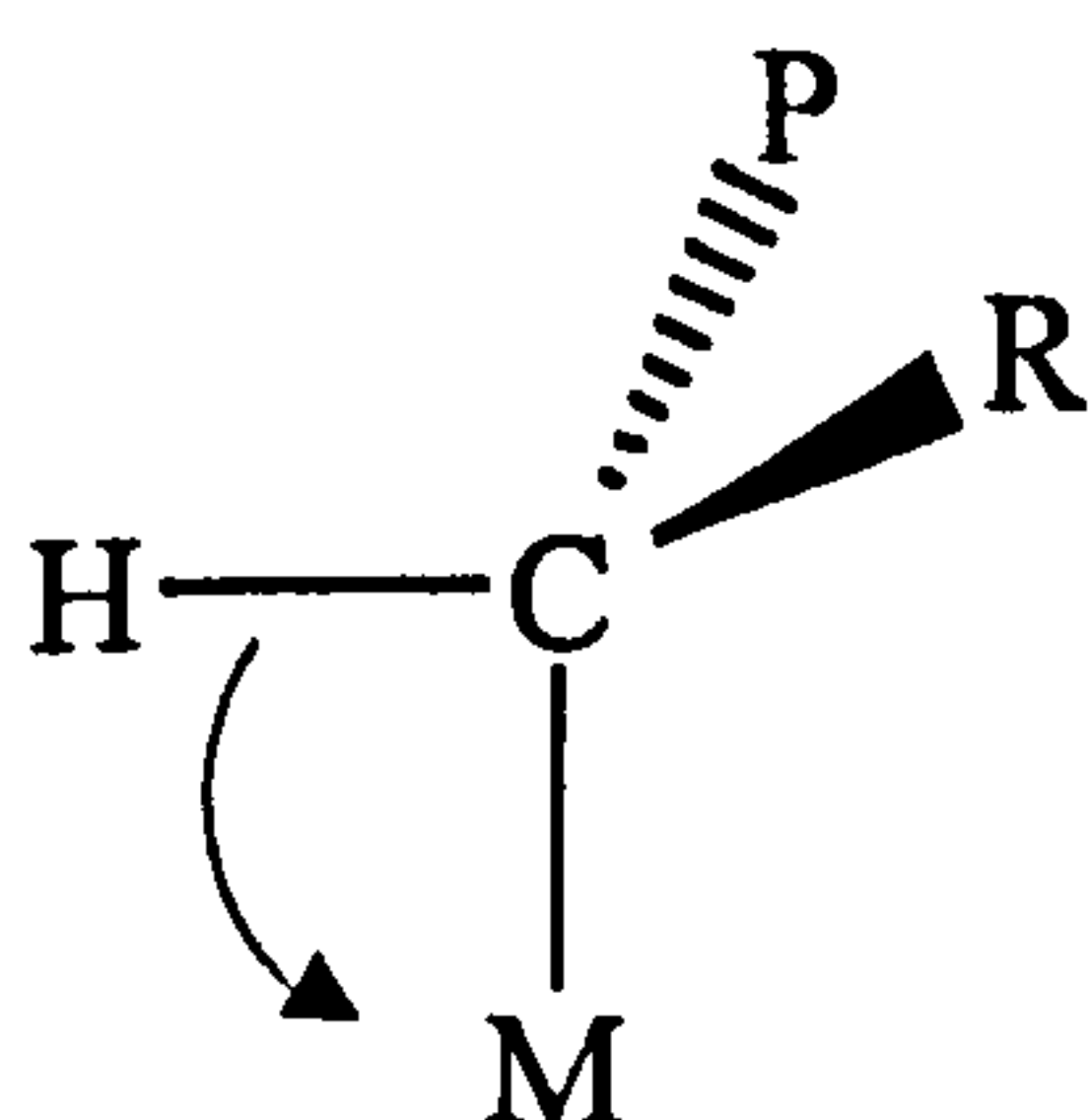


Figure 4.5: Agostic active centre proposed by Green.

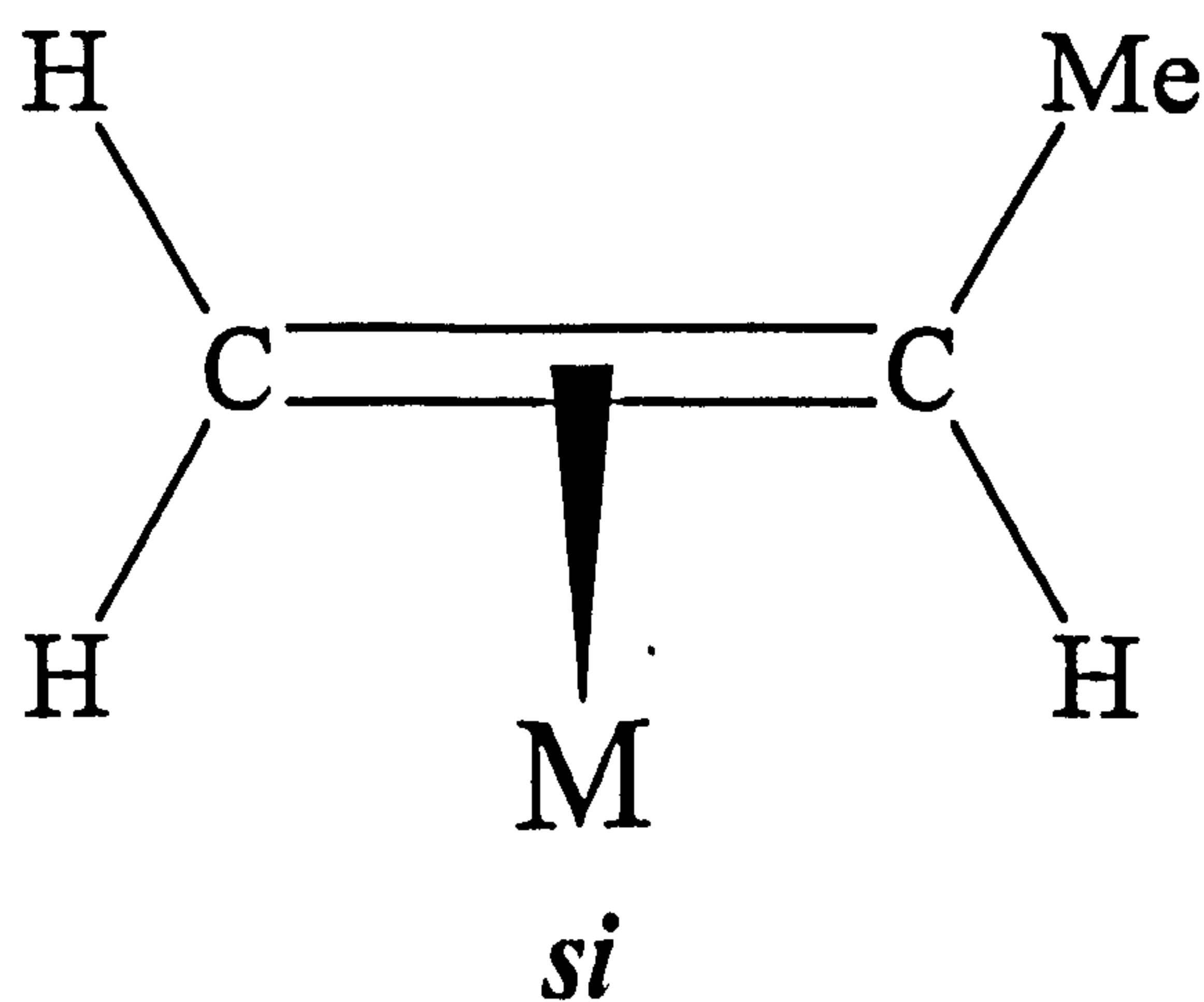
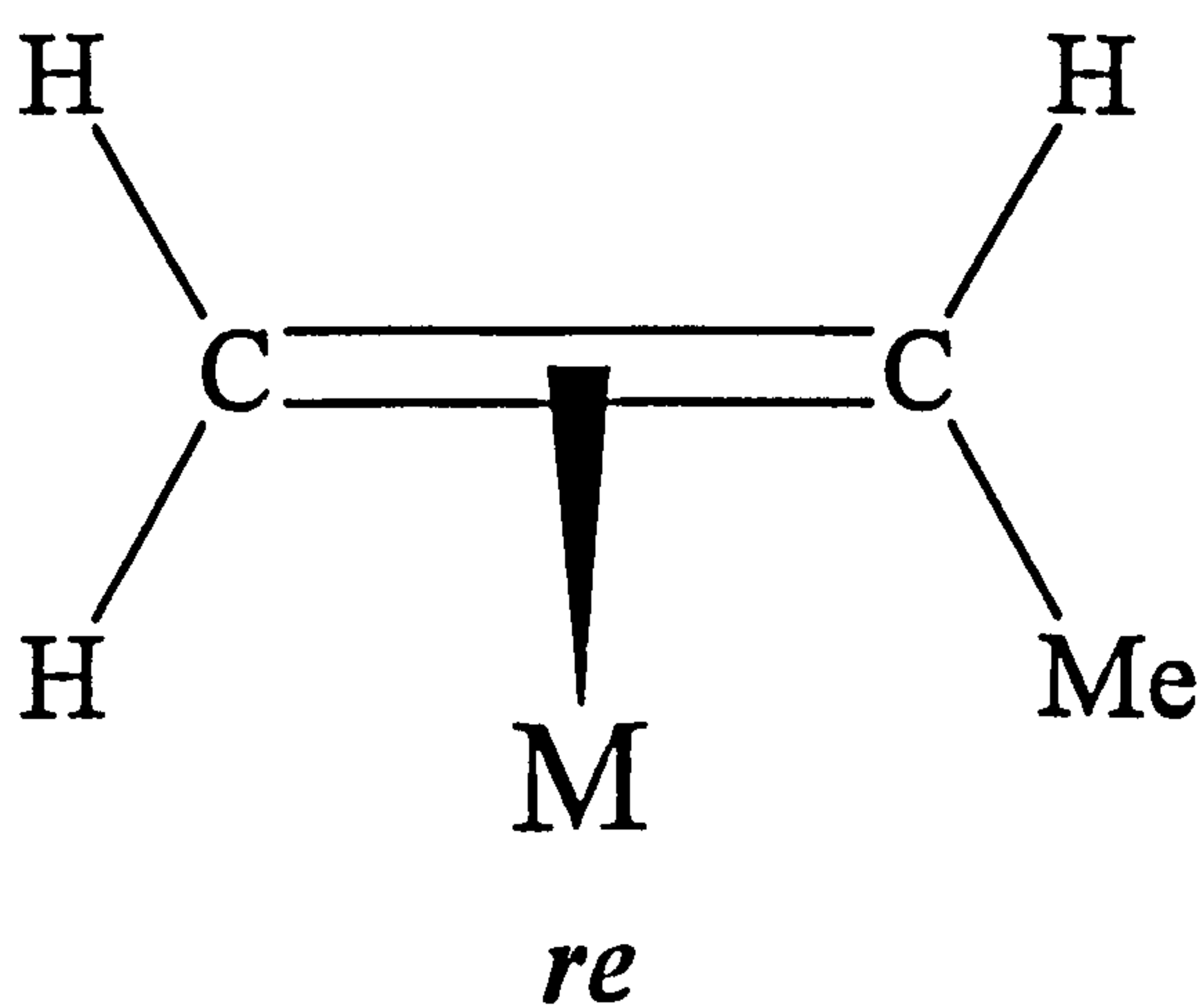


4.5: Mechanisms of stereochemical control.

The proposals for the causes of stereospecificity are based on considerations of steric interactions at the active catalytic centre.

Firstly, upon coordination, a prochiral 1-alkene, such as propene can give rise to two isomers¹⁴⁶ as shown in Figure 4.6.

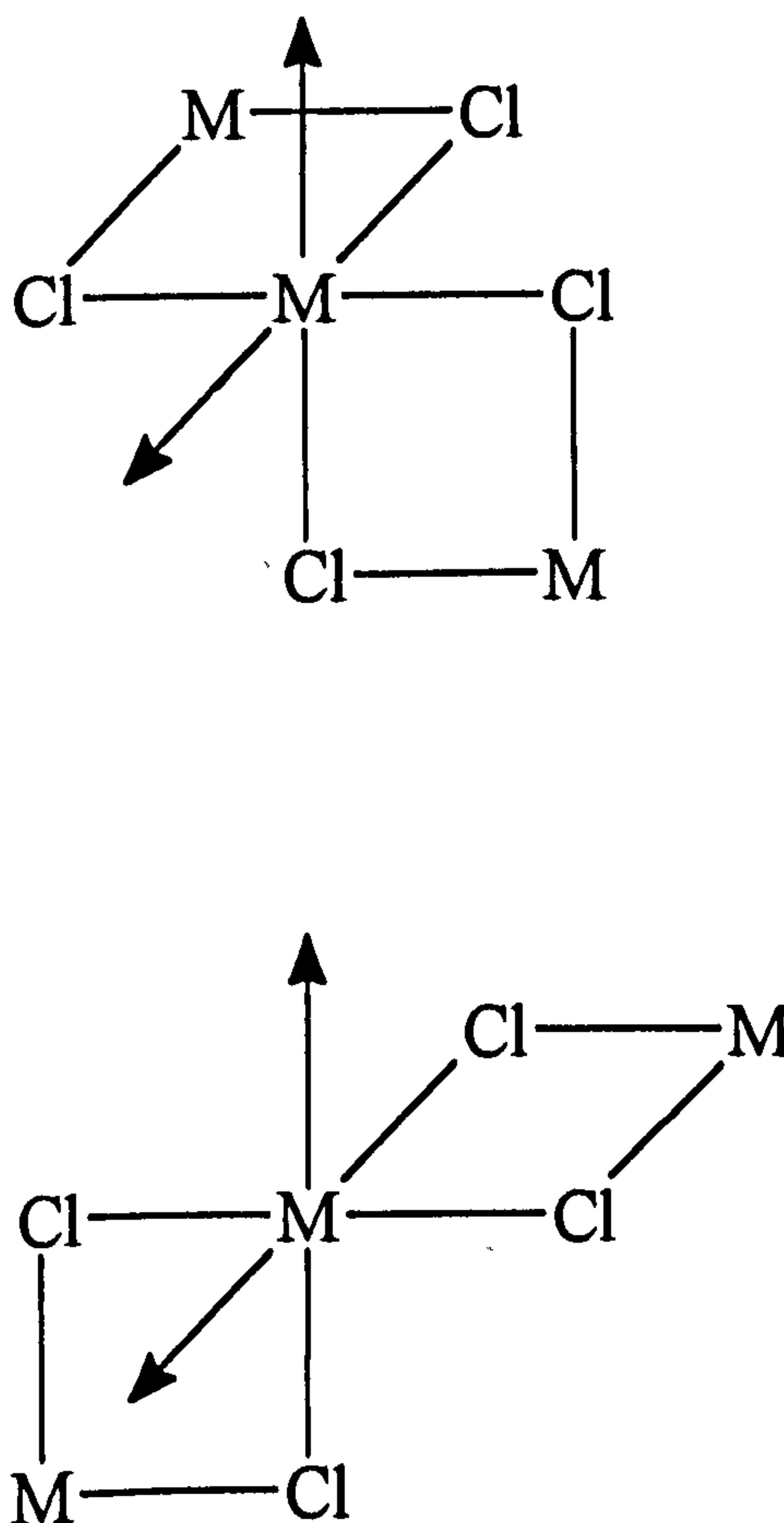
Figure 4.6: Enantiomeric forms of a propene-metal moiety.



If the other ligands around the metal are not symmetrical then one of these isomers may be favoured. In this case, an isotactic polymer will be formed. Syndiotactic polymers would be formed by alternate insertions of *si*- and *re*-coordinated monomers.

Another element of chirality may lie in the catalytic site itself. A schematic example of a heterogeneous catalyst proposed by Arlman¹⁴⁷ is shown in **Figure 4.7**.

Figure 4.7: Chiral sites on the surface of a catalyst.



The arrows represent the vacant positions that are available for the incoming monomer.

4.6: Homogeneous Ziegler-Natta catalysis.

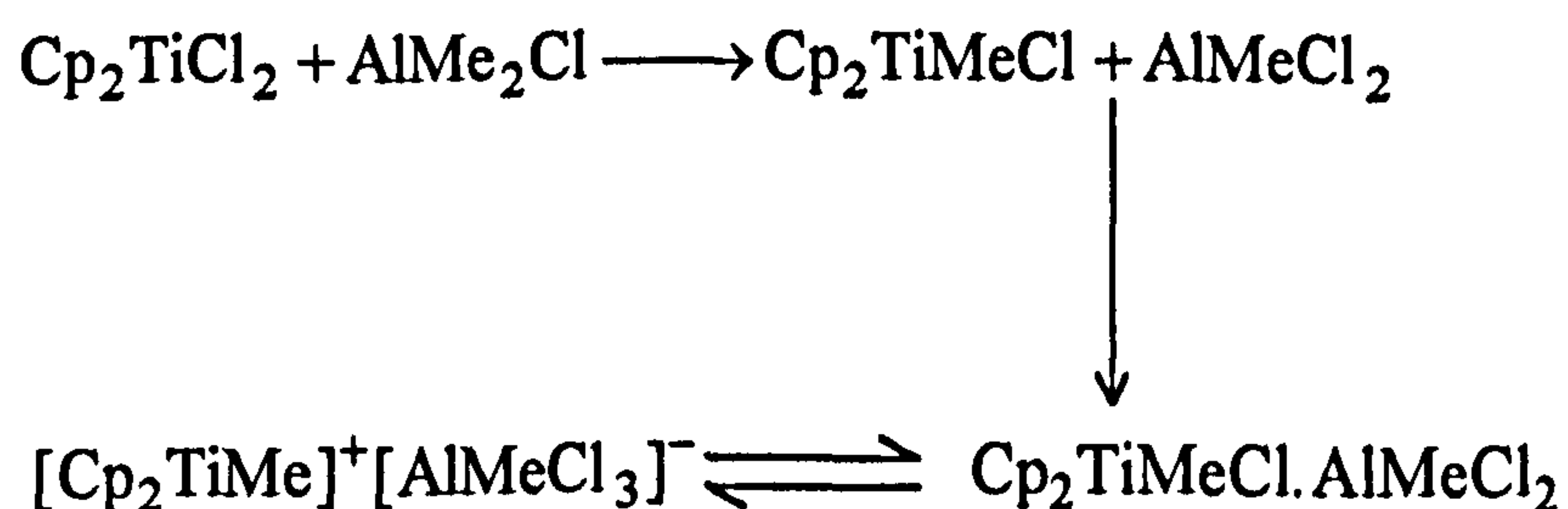
In the early 1960s, it was suggested by Shilov¹⁴⁸ that the active centre in heterogeneous catalysis involves a cationic transition metal cation. In an attempt to prove this, he went on to study the model system $\text{Cp}_2\text{TiCl}_2/\text{AlMe}_2\text{Cl}$, which was soluble in the reaction solvent. It was hoped that such homogeneous systems would avoid the problems associated with surface properties and particle size of earlier systems. The model was found to show catalytic activity and thus a new field of research began.

Since then, intensive research and development has resulted in homogeneous catalysis being the most versatile route to polymers with controlled structures.

4.6.1: Mechanisms of homogeneous catalysis.

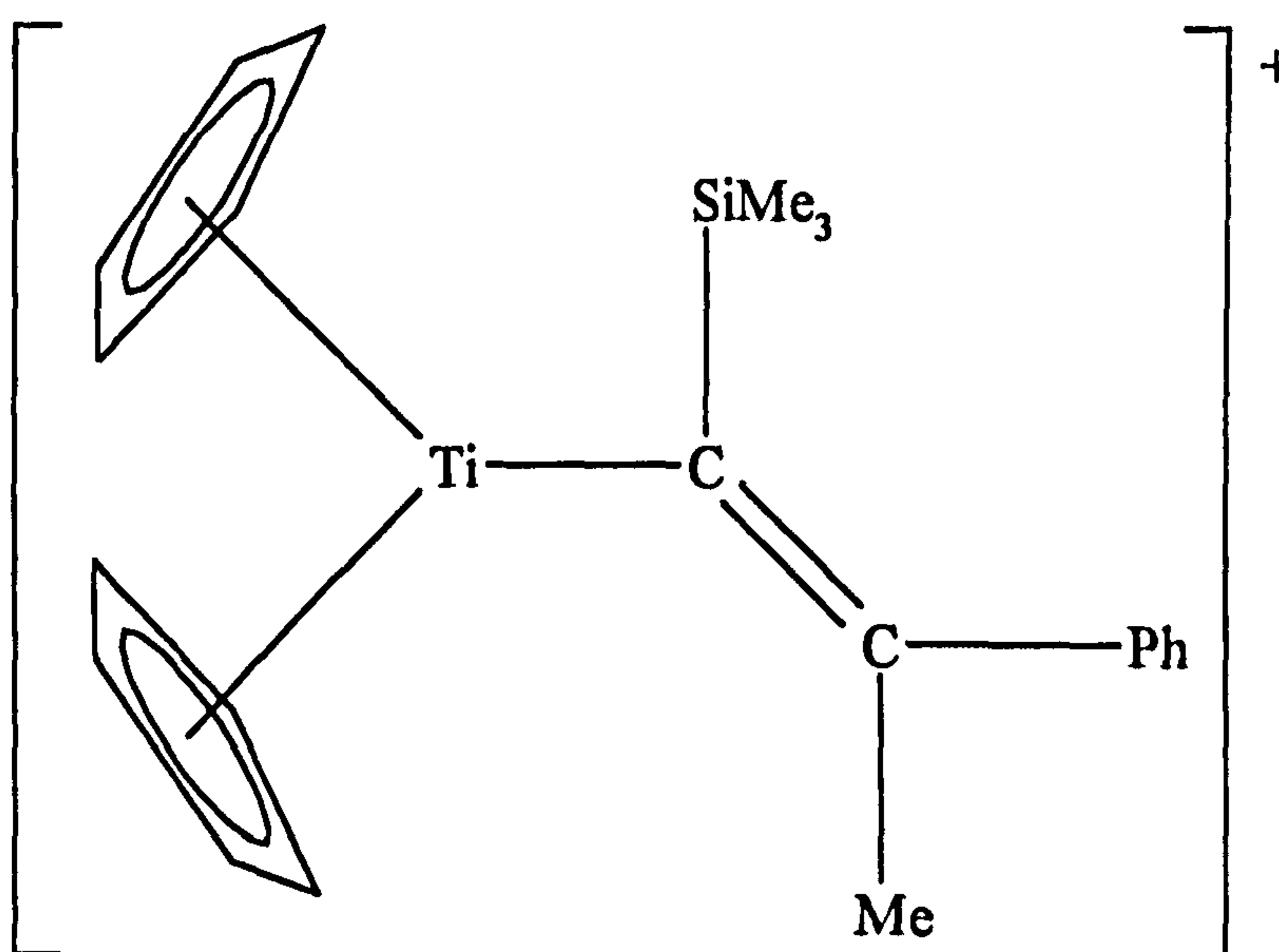
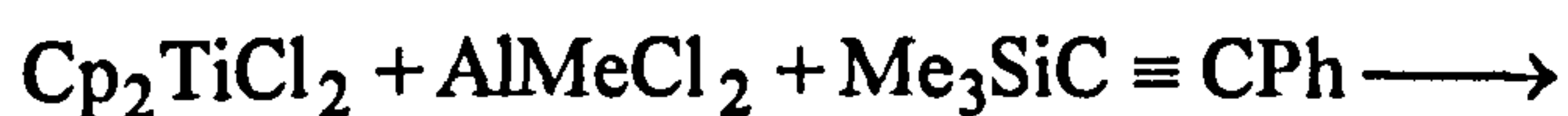
Shilov's work with $\text{Cp}_2\text{TiCl}_2/\text{AlMe}_2\text{Cl}$ included the detection using electro dialysis of positive ions in the reaction mixture. It led him to propose that the insertion step occurred on a titanium cation¹⁴⁹ formed *via* halide abstraction (Figure 4.8).

Figure 4.8: Shilov's Mechanism



Initially, direct proof of the existence of this cationic species was difficult to find, but in 1985 Eisch *et al*¹⁵⁰ isolated the insertion product formed between a bulky alkyne and a homogenous catalytic system (Figure 4.9).

Figure 4.9: Insertion product isolated by Eisch.

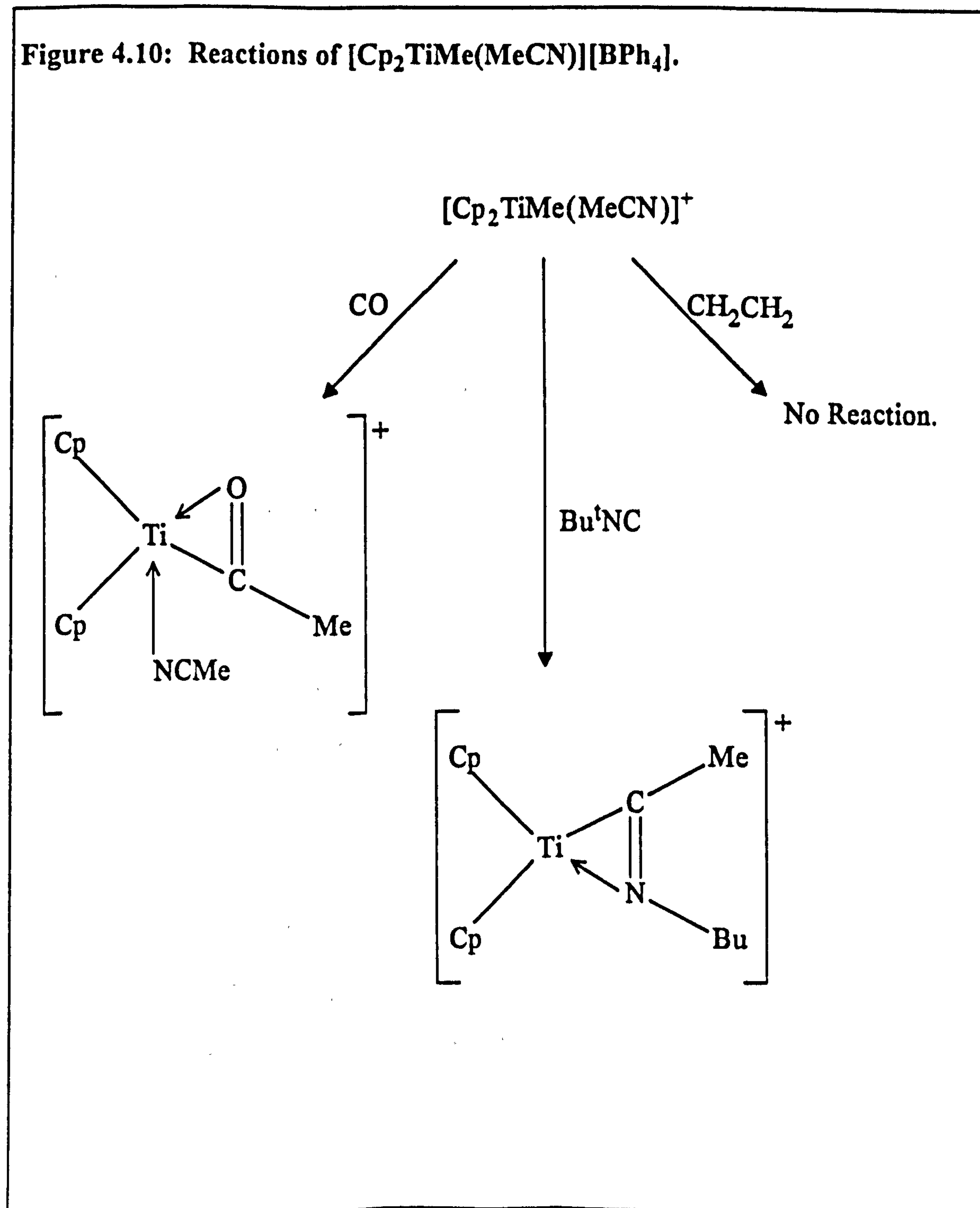


NMR studies lead them to suggest that the active species was $[\text{Cp}_2\text{TiMe}][\text{AlCl}_4]$ although this species itself was spectroscopically undetectable.

Shilov's work suggests that the aluminium cocatalyst supplies the transition metal with its alkyl group and then abstracts a halide anion to form the cationic centre. In view of this, much interest has been centred on the synthesis of cationic metal alkyls in the absence of aluminium activators.

Bochman and Wilson¹⁵¹ isolated two salts of $[\text{Cp}_2\text{TiMe}]^+$ from Cp_2TiMe_2 but the counter anions employed prohibited catalytic activity and any attempt at solvolysis. The use of Cp_2TiClMe and NaBPh_4 proved to be more successful in that the acetonitrile adduct $[\text{Cp}_2\text{TiMeL}]^+$ produced was found to undergo insertion reactions with a variety of substrates.¹⁵² However, this compound was also unreactive towards alkenes and alkynes (Figure 4.10).

Figure 4.10: Reactions of $[\text{Cp}_2\text{TiMe}(\text{MeCN})][\text{BPh}_4]$.



The inactivity of this cationic alkyl was blamed on the strongly coordinating MeCN. This led Bochmann to generate such species without extra ligands. The 14-electron $[\text{Cp}_2\text{TiMe}][\text{BPh}_4]$ was found to catalyze the polymerization of ethene.¹⁵³ Since then, research has centered on the production of catalysts which contain anions of very weak basicity; it has been shown that the anions compete with the alkenes for coordination during polymerization to lower the productivity. Latest examples such as $[\text{Cp}_2\text{Zr}(\text{CH}_2\text{Ph})][\text{B}(\text{C}_6\text{F}_5)_4]$ are very active catalysts.¹⁵⁴

Jordan *et al*¹⁵⁵ has conducted similar experiments using analogous Zr and Hf complexes. The activity of Group 4 catalysts seems to follow the general trend,



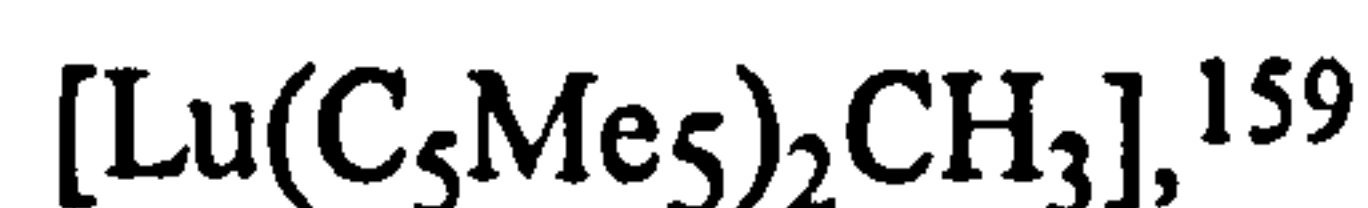
Several other experiments have given support to the cationic intermediate model. These include:

*Kinetic Studies,¹⁵⁶

*Isotope Effect measurements,¹⁵⁷

*Electrochemical measurements,¹⁵⁸

*The direct observation of propene insertion into the (M-R) bond in



*MO calculations,¹⁶⁰

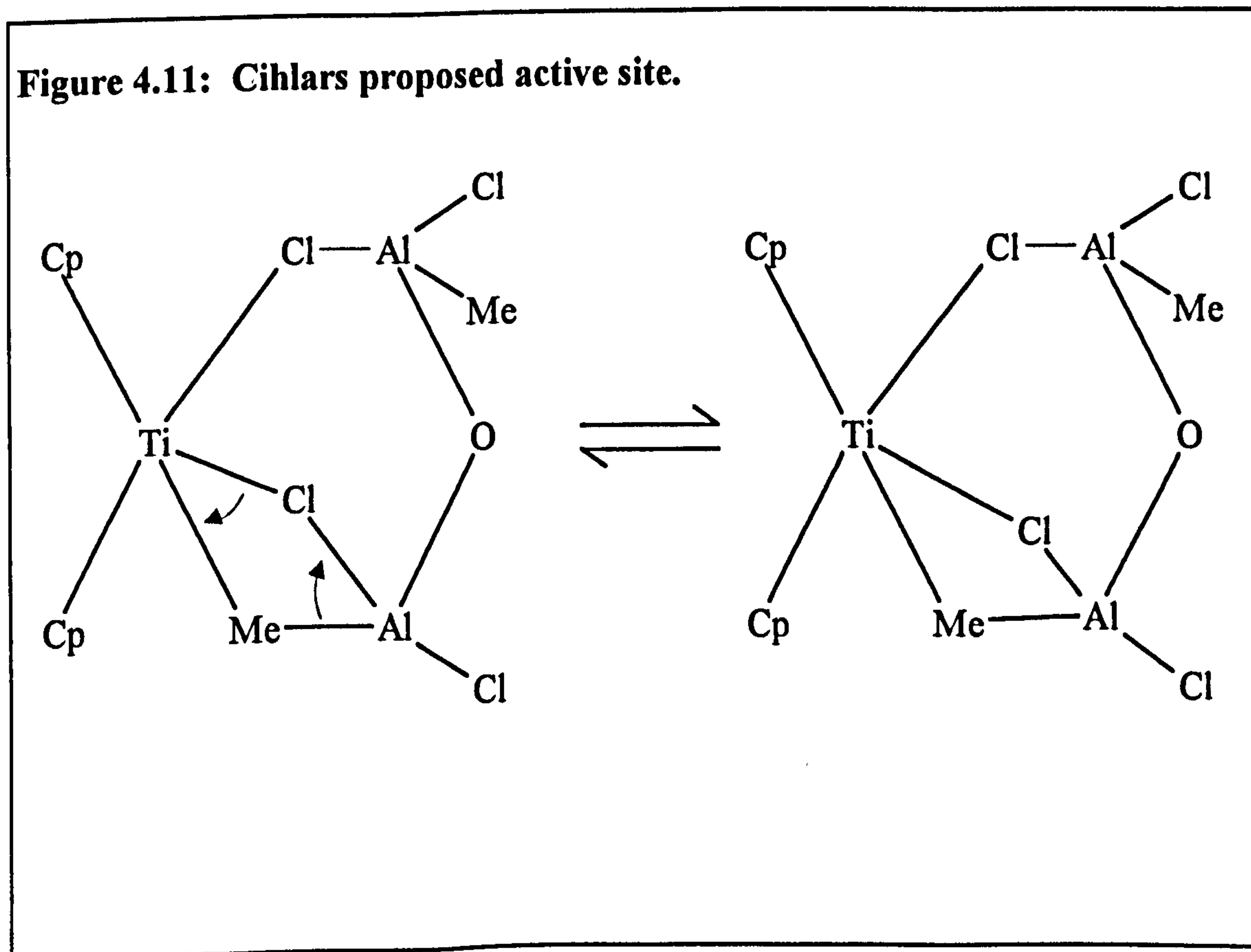
*The synthesis of the zwitterionic η^6 -arene zirconium tris(hydrocarbyl) and its subsequent positive catalysis results.¹⁶¹

4.1.2: Effect of cocatalyst.

For many years, homogeneous catalyst were ignored due to their extremely low activities when compared to the heterogeneous systems. Water is known to be a poison in the latter class of reactions.¹⁶²

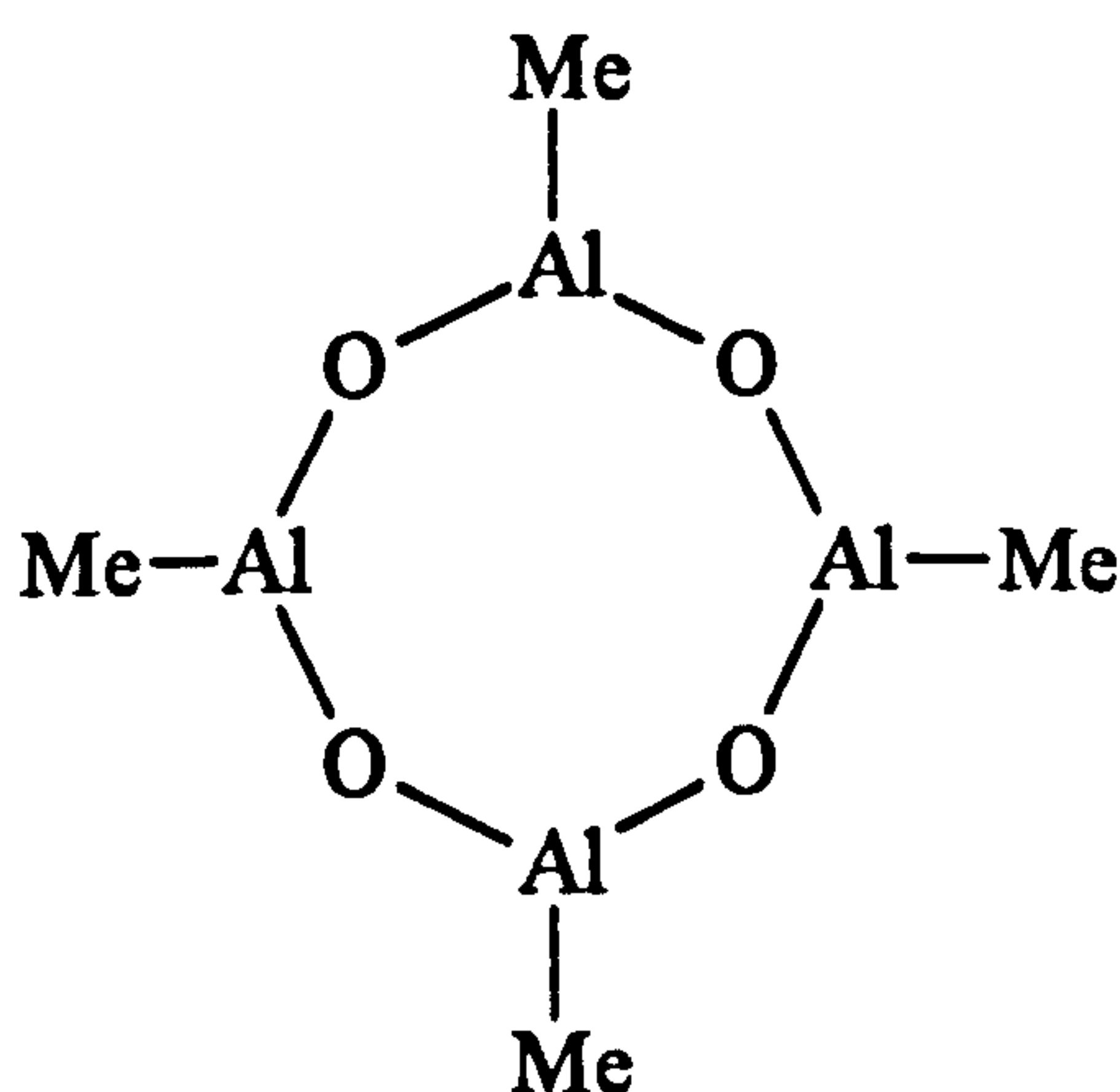
It was, therefore, surprising when Breslow¹⁶³ reported that the addition of water to a number of titanocene related catalysts had a markedly good effect on their activity. Kaminsky¹⁶⁴ then discovered that halide free systems, such as $\text{Cp}_2\text{TiMe}_2/\text{AlMe}_3$ which were previously inactive, also became extremely productive in the presence of water. These halide free catalysts were found to have longer lifetimes of maximum activity with little ageing processes observed for up to 20 hours.

Cihlar¹⁶⁵ proposed that this increase in activity was due to the higher Lewis acidity of the hydrolysed aluminium cocatalysts (**Figure 4.11**).



The presence of (Al-O-Al) moieties seems to play a key role in achieving cocatalyst activity although their precise structures have been subject to debate. Proposals range from linear¹⁶⁶ to cyclic configurations such as those of Kaminsky (Figure 4.12).¹⁶⁷ It is only recently that the first crystal structure of an aluminoxane has confirmed the presence of cyclic cage-like configurations.¹⁶⁸

Figure 4.12: Structure of methylaluminoxane proposed by Kaminsky.

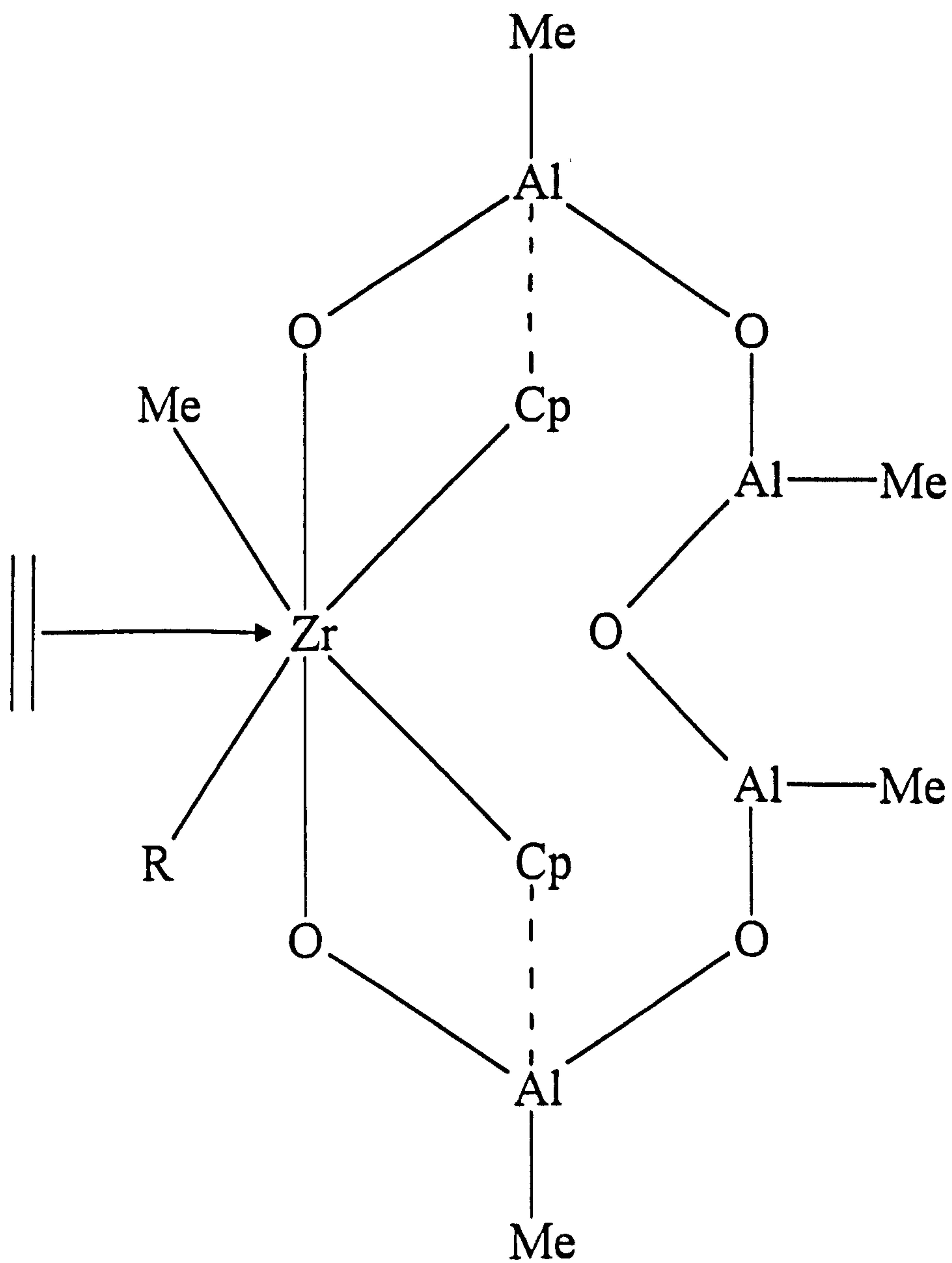


These oligomeric aluminoxanes, as they are known, are synthesised by the hydrolysis of the parent aluminium trialkyl. Typically AlMe_3 is treated with a stoichiometric amount of a hydrated inorganic sulphate.¹⁶⁹ Experiment has shown that the aluminoxane must reach a critical degree of hydrolysis to obtain high activity.

The main disadvantage of the use of Methylaluminoxane (MAO) is the large amounts required; reaction rates have been found to depend quadratically on cocatalyst concentration. Typical polymerisation reactions are normally run with $[\text{M}]/[\text{Al}]$ ratios of 1:1000 and upwards.¹⁶⁹

The precise role of the aluminoxane in the active site is uncertain with many unproven theories. The most elegant of these, suggested by Kaminsky¹⁷⁰ involves a very complex active site as shown in Figure 4.13.

Figure 4.13: The active centre proposed by Kaminsky.



CHAPTER 5.

**ZIEGLER-NATTA POLYMERISATION OVER THE
CpMⁿ⁺ SERIES.**

5.1: Ethene Polymerisation Catalysis over the CpMⁿ⁺ series.

Using the facilities provided by BP Chemicals Ltd at their research centre in Grangemouth, the Ziegler-Natta activity of the CpMⁿ⁺ series was investigated. Studies were performed with both MAO and AlEt₃ cocatalysts. By employing constant reaction conditions a simple quantitative comparison of the catalytic properties of the various cations was performed.

Polymerisation experiments were carried out in a stirred stainless steel autoclave. All of the reactions were performed using 2-methylpropane solvent (1litre) with an ethene pressure of 400psi at 60°C. Experiments with AlEt₃ used a M/Al ratio of 1/30 whilst those with MAO required a 1:800 cocatalyst concentration. The activities of each system were measured in terms of polymer produced per mmole of catalyst per hour.

5.2: Catalysis with AlEt₃.

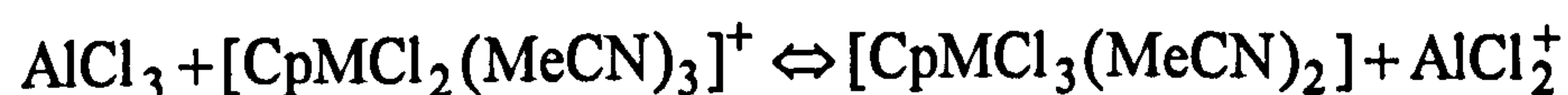
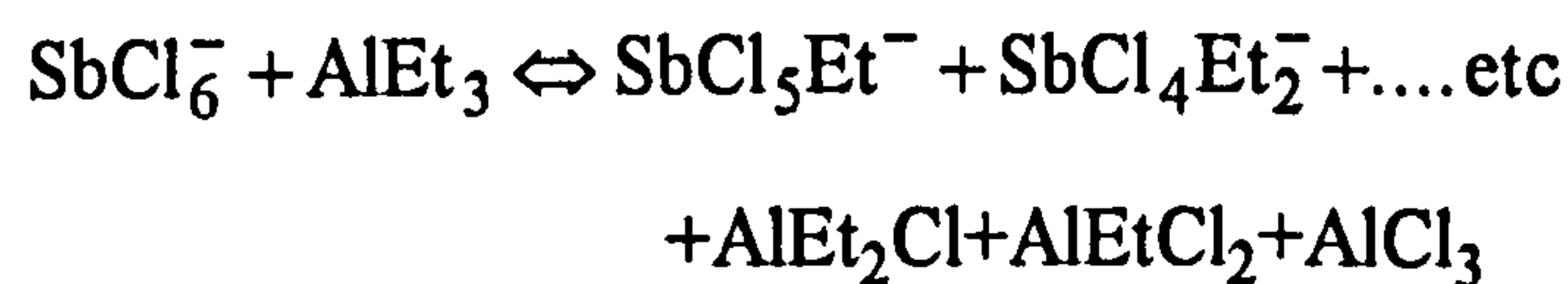
One of the biggest disadvantages of the metallocene based soluble catalysts is their inactivity with all but high concentrations of aluminoxane cocatalysts. The reason normally given for this is the higher Lewis acidity of the bulky, non-coordinating cage structures of the anions formed after halide abstraction. It was therefore hoped that the use of pre-formed cationic species would lead to catalytic activity with relatively low CpMⁿ⁺/AlEt₃ ratios. Unfortunately, this did not turn out to be the case. The only system to yield measurable quantities of polythene was the CpTi⁺/AlEt₃/C₂H₄ reaction, and even then the productivity recorded was very low (11g polymer/mmol Ti/hr).

Reasons for the failure of these systems can only be estimated. The most probable cause of their inactivity lies in the presence of competing side processes which serve to poison the potential catalysts. Of these, the most obvious involve the interaction between both the MeCN and SbCl₆⁻ with the active metal centre. The (M-Cl-Sb) intermediates reported in section 2.3 may be even more

predominant in the non-coordinating 2-methylpropane solvent. This would greatly reduce the chances of any ethene complexation at the catalytic centre. The slight activity displayed by the CpTi⁺ system could then be attributed to its more labile ligand exchange reactions.

A further complication may arise from the decomposition of the active sites *via* the alkylation of the SbCl₆⁻ anions. In view of the attempted reactions with LiMe (section 2.8.4), this process may be very important. A postulated mechanism of decomposition is outlined in scheme 5.1.

Scheme 5.1: Possible decomposition mechanisms of the CpMⁿ⁺ catalysts.



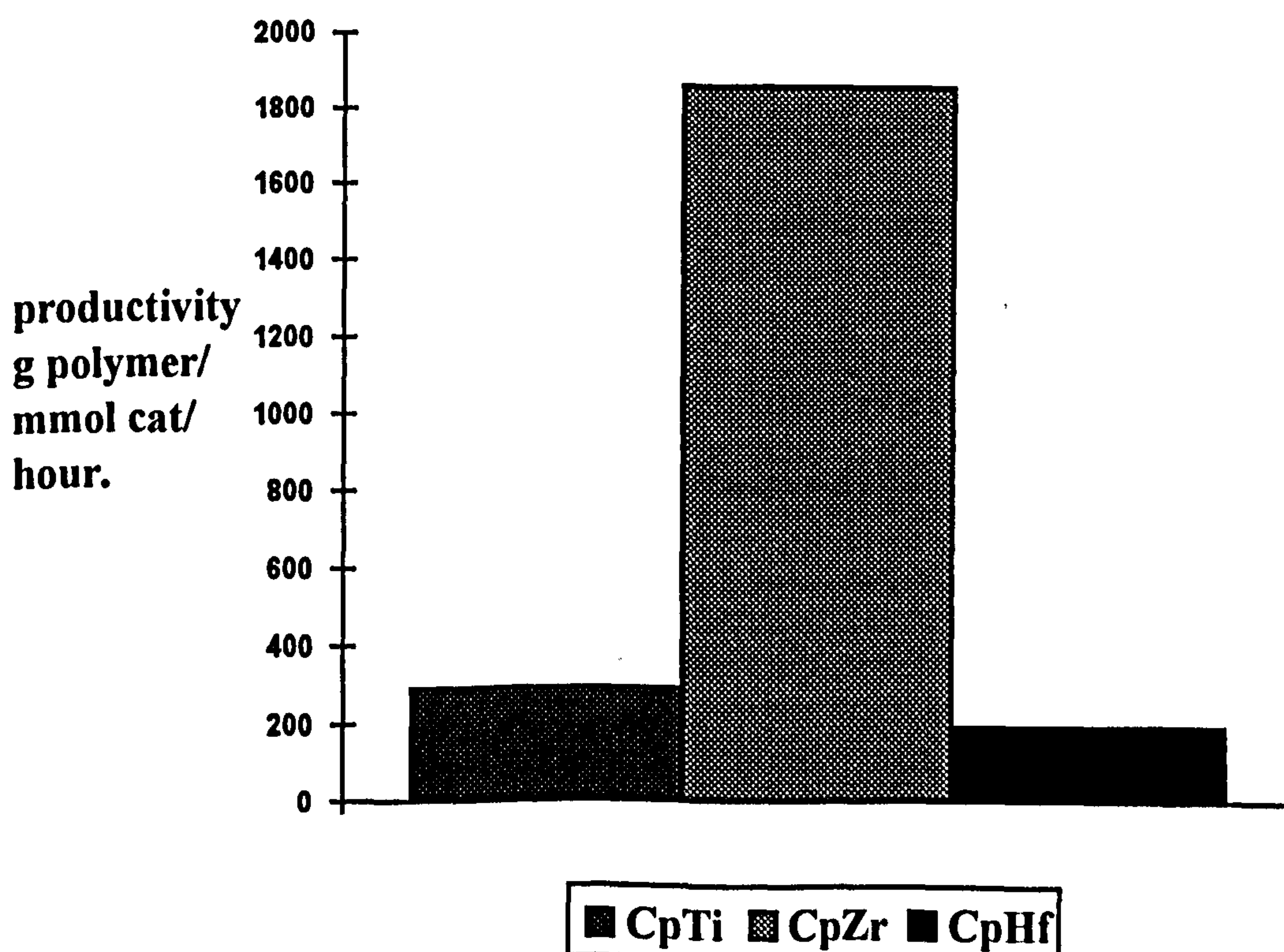
In this scheme, the number of "active" alkyl groups is greatly reduced whilst more and more Cl⁻ ions become available for recombination with the transition metal centre. It would be interesting to repeat these experiments with a larger excess of AlEt₃. If a larger amount of alkyl groups were provided, the systems should eventually become active. Unfortunately, this approach ultimately defeats the purpose of the use of these cationic complexes as catalysts. An alternative way forward would be to investigate the activity of the cations in the absence of the SbCl₆⁻ anion. This could be achieved using a more innocent anion such as BPh₄⁻.

5.3: Catalysis with MAO.

With metallocene-based catalysts, extremely high activities have been reported using MAO as cocatalyst. It was therefore decided to conduct polymerisation reactions over the CpMCl_3 series and the cations derived thereof under similar conditions.

Generally, the results obtained for these experiments were much better than those gained using AlCl_3 . However, the activities recorded were all still much lower than those of commercial catalysts. Once again, the presence of the SbCl_6^- anion seems to present a problem; the best catalysts proved to be the parent CpMCl_3 compounds. Table 5.1 illustrates the relative activities of the neutral series.

Table 5.1: Productivity of ethene polymerisation over $\text{CpMCl}_3(\text{MeCN})_2/\text{MAO}$.



It is obvious that the Zr-based systems are the most active catalysts of Group 4. Ethene polymerisation over $\text{CpZrCl}_3(\text{MeCN})_2$ was so rapid that a large uncontrollable exotherm accompanied the reaction. This resulted in the enforced termination of the process after only 25 minutes for safety reasons. Had better heat transfer equipment been available, the reaction may have yielded an even higher productivity. Of all of the systems that were studied, this was the only catalyst to achieve an activity which approaches those found in modern commercial processes.

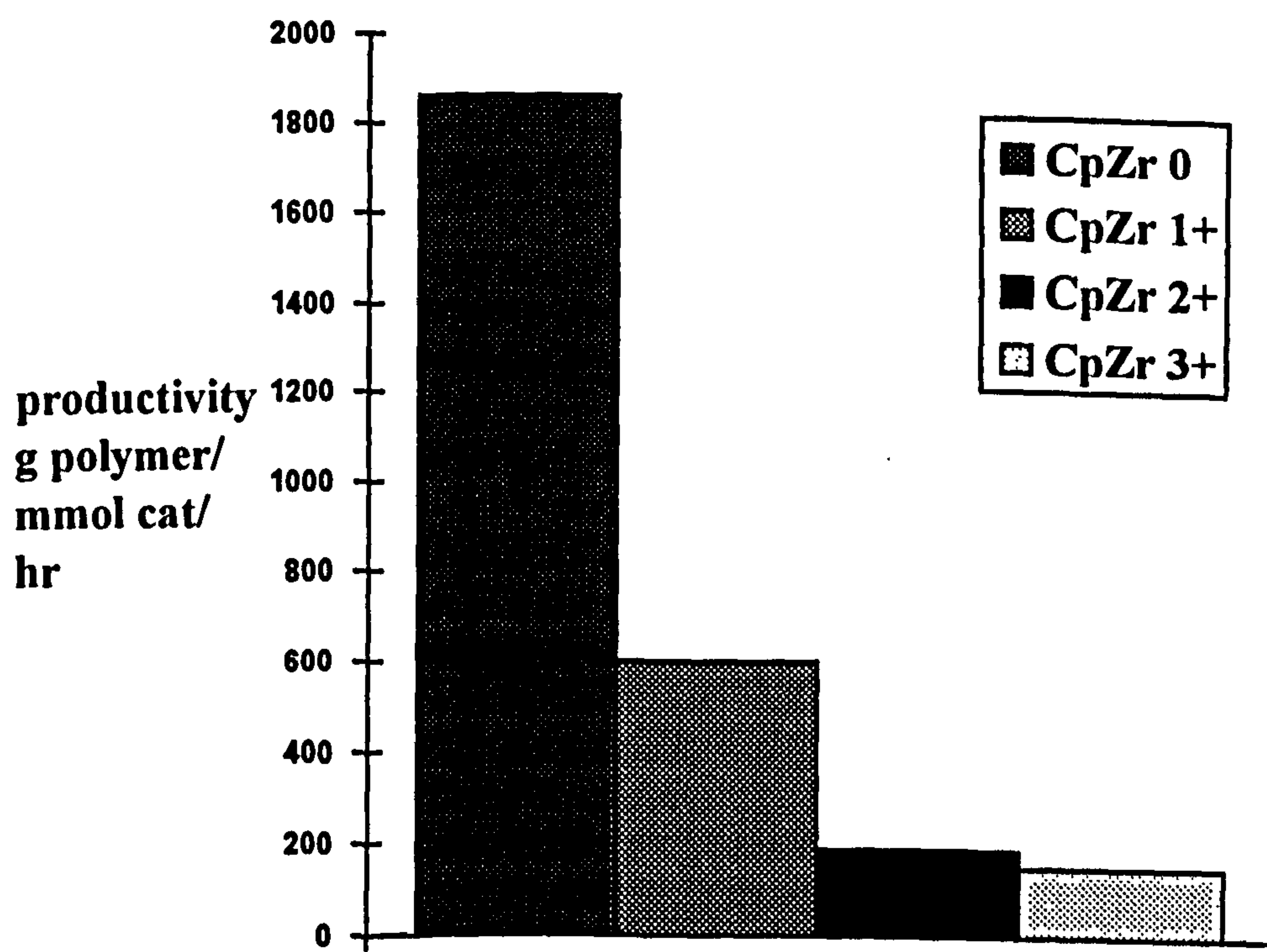
Perhaps the most surprising aspect of these results is the low activity of the analogous Hf system. It would be expected that the Ti-based catalyst would be the least effective despite its lack of MeCN ligands. The latter seem to have a pronounced effect on the activity of the Hf complex. Why this MeCN/C₂H₄ competition should not be so important in the Zr-case is rather curious.

As the Zr-based catalysts are so much more active, studies on the effect of cationic charge were centred on the CpZr^{n+} series. The results of these are illustrated in **Table 5.2**.

These results tie in well with those gained from the AlEt_3 experiments. It is now clear that the SbCl_6^- anion presents a major problem to catalytic activity. Previous studies with metallocene-based catalysts have shown that the rates of polymerisation depend quadratically on the concentration of the aluminoxane.¹⁶⁷ Therefore, if a small quantity of MAO is "used up" in side reactions with SbCl_6^- , the effect on the productivity will be much pronounced. This argument fits the pattern observed in these experiments and explains the inactivity of the AlEt_3 systems; the concentration of "active" alkyl groups is of paramount importance.

On top of these decomposition reactions there is also the extra mole of MeCN ligands which accompany a rise in cationic charge. This factor will also lower the *a priori* rate of polymerisation as the ethene must compete for coordination at the metal centre.

Table 5.2: Ethene polymerisation over the CpZrⁿ⁺ series/MAO.



5.4: Polythene properties.

As a preliminary investigation of the properties of the polymers produced over the CpM/MAO catalysts, samples were subjected to Melt Indices measurement. The results of both MI and HLMI studies indicated polythene of extremely high molecular weight, too high to undergo more accurate analysis. This is reflected in the insolubility of the samples in the solvents used normally for solution viscosity, gel permeation chromatography and ¹³C NMR. In an attempt to produce a polymer of measurable properties, a further reaction using the CpZr⁺/MAO system was carried out in the presence of H₂ gas. This controlled the molecular weight of the polythene produced and allowed the further structural investigations. The results of these measurements are consistent with a conventional linear polythene of normal molecular weight distribution.

5.5: Experimental aspects of polymerisation.

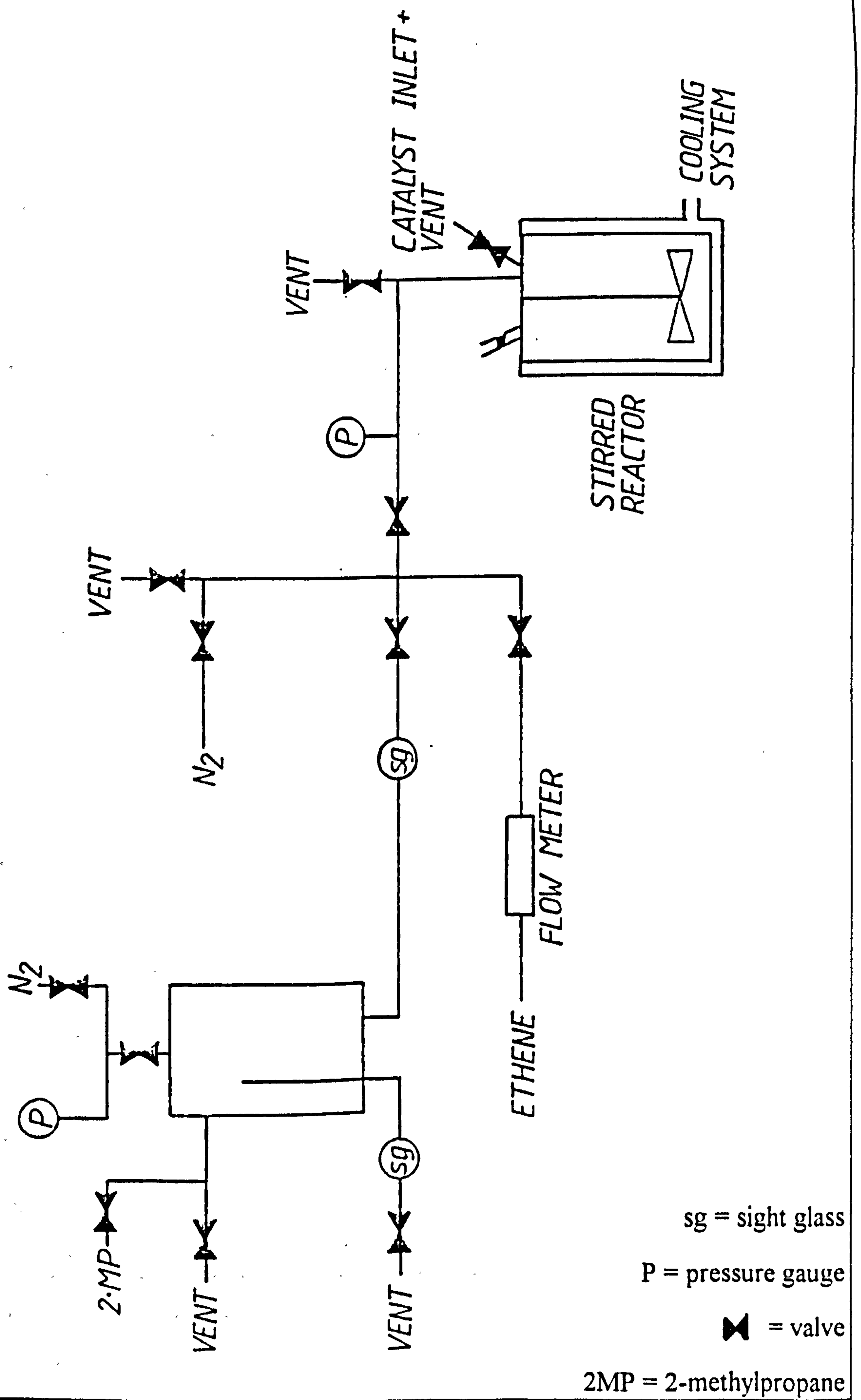
Polymerisation reactions were carried out in a specialist bench scale reactor. The system is pictorially illustrated in **Figure 5.1**. The stainless steel autoclave was equipped with a mechanical stirrer (350RPM) and a water/steam heat exchange mechanism. Using a computer to control the latter device it was possible to maintain the temperature of the autoclave at a predetermined 60°C.

After flushing the apparatus with dry N₂, catalyst was added to the reactor in the form of a solution whilst the reactor was set to reach the required reaction temperature. Details of the relevant quantities and concentrations of these solutions can be found in **Table 5.3**. 2-methylpropane (1 litre) was then added as diluent under a high pressure of N₂ and the mechanical stirrer started. On reaching the set 60°C, ethene was admitted slowly until the required reactor pressure was reached (600psi). During the reaction, the ethene was supplied on demand to keep the pressure constant.

Any polymerisation activity could be followed by a number of measurements. Active systems are usually accompanied by an exotherm which has the effect of raising the temperature of the autoclave. This in turn leads to a drop in the coolant temperature. As these figures were initially equal, this "cross-over point" is taken as being the commencement of the polymerisation reaction. The process was then monitored for the remainder of the time scale (usually for 1 hour after crossover) by means of both ethene consumption and temperature changes.

When the CpZrCl₃(MeCN)₂/ MAO mixture was used as catalyst, the initial exotherm was too large for the coolant system to handle. In this case the reaction was terminated after 25 minutes for safety reasons. This was achieved by "flashing off" the mixture of gases through the safety valve. However, in all other experiments, polymerisation was terminated by cutting off the ethene supply and slowly venting the autoclave.

Figure 5.1: The bench-scale polymerisation reactor.



After allowing the apparatus to return to room temperature, the top of the vessel was carefully removed. On meeting the air, the polymer produced is seen to fume gently as the remains of the catalytic species hydrolyse. Once this HCl emission ceases, the polymer is collected and weighed. The activity of each catalyst was measured in terms of the amount of polymer produced. The units of this measurements thus read as g polymer/mmol catalyst/hour.

Table 5.3: The relative quantities used in catalytic experiments.

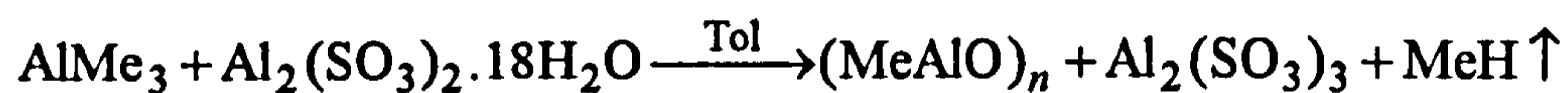
catalyst	moles	cocatalyst/moles		M:Al	Ethene /psi	polymer yield	
		AlEt ₃	MAO			/g.	/gmmol ⁻¹ hr ⁻¹
CpTiCl ₃	6.6x10 ⁻⁵	2.0x10 ⁻³	-	1:30	400	no reaction	
CpTiCl ₂ ⁺	1.8x10 ⁻⁴	5.6x10 ⁻³	-	1:30	600	2	11
CpZrCl ₂ ⁺	1.5x10 ⁻⁴	4.4x10 ⁻³	-	1:30	600	no reaction	
CpHfCl ₂ ⁺	1.3x10 ⁻⁴	3.9x10 ⁻³	-	1:30	600	no reaction	
CpTiCl ₃	6.8x10 ⁻⁵	-	0.05	1:800	600	20	292
CpZrCl ₂ L ₂	5.8x10 ⁻⁵	-	0.05	1:800	600*	45	1860
CpHfCl ₃ L ₂	4.6x10 ⁻⁵	-	0.04	1:800	600	9	194
CpZrCl ₂ ⁺	5.8x10 ⁻⁵	-	0.05	1:800	600	35	603
CpZrCl ₂ ²⁺	5.8x10 ⁻⁵	-	0.05	1:800	600	11	188
CpZr ³⁺	5.8x10 ⁻⁵	-	0.05	1:800	600	9	153
CpZrCl ₂ ⁺ +H ₂ (5 psi)	5.8x10 ⁻⁵	-	0.05	1:800	600	17	300

* Reaction terminated before full reactor pressure was reached (25 minutes).

L = MeCN

MAO methylaluminoxane.

5.5.1: Preparation of methylaluminoxane (MAO).



A 1 litre RB flask equipped with magnetic follower was charged with hydrated aluminium sulphite and flushed with nitrogen gas. After placing in an ice bath, the flask was linked to a commercial container of trimethylaluminium in toluene (1 litre, 2M) *via* transfer needle. The nitrogen pressure of the R B flask was then gently lowered so that a few drops of the AlMe_3 solution fell on the sulphite. A vigorous reaction ensued with the emission of heat and methane gas. The pressure of the system was allowed to dissipate *via* an exit needle. It is important that this needle does not block up with the solid which is blown around in the flask. Small aliquots of the AlMe_3 solution continued to be added at a rate to keep the reaction under control. Initially the reaction is much more active than when enough solution has been added so as to drown the solid. When this has been achieved (*ca.* 2 hours), the remainder of the AlMe_3 can be added continuously.

The resulting mixture was then allowed to warm to room temperature where upon it was stirred for 24 hours. The reaction continued to release methane and heat.

Finally, the clear toluene solution of the title compound was separated from the solid sulphite by filtration and stored under nitrogen. This clear solution was used in polymerisation reactions as MAO (2M) despite the small quantity of solvent which is lost during preparation.

CHAPTER 6

CONCLUSIONS

6.1: Summary.

The halide abstraction properties of SbCl_5 in acetonitrile solution provides an effective synthetic route to cationic complexes of the early transition metals. The use of this reagent has yielded charged derivatives of the CpMCl_3 series of Group 4. Depending on the stoichiometrical amounts employed in the reaction, all three metals can be isolated in mono-, di-, and tricationic form.

The chemistry of these new complexes is dominated by their extreme Lewis acid character, which increases with cationic charge. This is demonstrated by their ligand exchange reactions: all show a high preference for classically hard donors, especially N-donors. Unfortunately, this high Lewis acidity cannot be harnessed in terms of Ziegler-Natta activity, probably because of the presence of the SbCl_6^- counter anion. There is significant evidence, especially for $\text{M}=\text{Ti}$, for a preponderance of cation/anion interaction in solution. The complexes do show a high reactivity toward other anionic species, reforming neutral compounds with a range of negatively charged ligands.

At first glance, the substitution of Cp^* for Cp seems to have little effect on the outcome of the halide abstraction process; the various methylated/unmethylated analogous species all share the same conformations. However, on close inspection, it is clear that the Cp^* group has a labilising effect on the cationic complexes. This is demonstrated by a much faster ligand/solvent exchange in the Cp^*M^{n+} series as a whole, and the presence of a suitable signal for $\text{Cp}^*\text{Ti}^{3+}$ in the room temperature ^1H NMR spectrum. The signal for CpM^{3+} is only observed above 50°C . Structurally, it would be expected that the Cp^* group increases the distortion of the ideal geometry around the metal centres. It is hoped that future work will include X-ray analysis of the Cp^*M^{n+} series to confirm this.

Despite the simple nature of the overall synthetic approach, the studies have revealed a number of interesting points in the general area of bonding and

electronics. Also, some significant differences have arisen between the behaviour of the Ti-based complexes and their heavier Group 4 analogues.

Although not conclusive, there is some evidence to suggest that there is a definite intermediate involved in the $\text{CpMCl}_3\text{-SbCl}_5$ reactions. It is possible to envisage some kind of Cl-bridging interaction. Previous studies, such as the work of Lorcher *et al*¹⁰⁸ suggests that SbCl_5 prefers (edge-edge) sharing of octahedra in its reaction with metal chlorides. This may explain why the proposed intermediates are much more prevalent in the CpTi^{n+} series than those of Zr and Hf; perhaps the larger size of the latter metals infers extra strain on the double bridge, making it energetically unfavourable. A similar argument can be invoked for the lack of intermediates in the $\text{Cp}^*\text{Ti}^{n+}$ system.

The energetics of the proposed halide abstraction mechanism are very interesting. Simplistically, the energy produced in bond formation must outweigh that required for bond making, including the "ionisation" of the metal centre. Clearly, as the charge on the metal centre increases, the energy required to remove Cl^- anions should rise progressively in the ideal case. Solution studies have shown that this balance is satisfied up to the dication stage for all three Group 4 elements. However, the transition between CpM^{2+} and CpM^{3+} is not so clear cut.

In the room temperature ^1H NMR spectra of the trications, only $\text{Cp}^*\text{Ti}^{3+}$ shows a signal conducive with its 3+ charge; the remainder exhibit the resonances of their lesser charged precursors. Why this should be so is uncertain. One reasonable proposition involves the formation of ion pairs which are so tightly bound that the Cl-bridges once more come to prominence. An extra input of energy (in the form of heat or lattice energy) is then required to form the discrete tricationic centres.

It would be interesting to find out when the possibility of halide abstraction ends because of these simple energy requirements. For this reason, future work could look at the reactions of SbCl_5 with the d^0 chlorides of Groups 5 and 6.

An accurate description of the bonding involved in the cationic complexes is similarly complex. Simple electron counting results in 16 for the octahedral and 18 for the 7 coordinate metal complexes. The actual bonding can thus only be evaluated in Molecular Orbital Theory terminology. This model is itself complicated by the presence of ligands which are both π -donors (Cl^- , Cp, MeCN) and π -acceptors (Cp, MeCN).

The problems involved in the evaluation of the electronic configurations come to a head with the transition from CpM^{2+} to CpM^{3+} for Zr and Hf. All of the experimental evidence points to an increase in coordination number at this point. Why should this happen when the Ti analogue remains octahedral? At first glance, the smaller size of the Ti centre would seem important. However, an increase in charge at a metal centre is usually accompanied by a decrease in size and (M-L) bond length. It could be argued that this would actually discourage an increase in coordination number in the CpM^{3+} cations of Zr and Hf. As the latter do exhibit 7 coordinate structures, the presence of the extra ligand can be attributed to their increased Lewis acid character arising from the lack of a π -donating Cl^- ion. The whole system obviously contains a delicate balance of electronic and steric factors.

6.2: References.

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