Synthesis and Reactivity of Titanium Cyclopentadienyl Imido Amidinate Complexes

by

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Abstract

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This Thesis describes the preparation and characterisation of a range of titanium imido complexes supported by a cyclopentadienyl-amidinate ligand set. Reactivity studies of these complexes towards unsaturated organic species are presented.

Chapter 1 reviews transition metal complexes containing imido, cyclopentadienyl, and amidinate ligands, with an emphasis on recent work.

Chapter 2 describes the synthesis and characterisation of titanium cyclopentadienyl imido amidinate complexes, along with precursor complexes which have not been previously reported. X-ray crystal structures of four imidotitanium species are described.

Chapter 3 describes the reactivity of titanium cyclopentadienyl imido amidinate complexes towards carbon dioxide. An unprecedented reaction with two molecules of carbon dioxide is reported for the arylimido complexes. X-ray crystal structures of two of the arylimido dicarboxylate products are described. The kinetics of the insertion of the second molecule of carbon dioxide are investigated and reported.

Chapter 4 describes the reactivity of titanium cyclopentadienyl imido amidinate complexes towards isocyanates and carbodiimides. The X-ray crystal structures of two N, O- bound ureate complexes are described. A new series of reactions involving two molecules of *p*-tolyl isocyanate with arylimido complexes is reported. Reactions of isocyanates with carbamate complexes are also reported.

Chapter 5 explores the reactivity of titanium cyclopentadienyl imido amidinate complexes towards sulfur-containing substrates. Comparisons are drawn with the reactivity towards oxygen-bearing homologues. X-ray crystal structures of two bridging sulfido complexes are described.

Chapter 6 discusses the reactivity of titanium cyclopentadienyl imido amidinate complexes towards substrates containing only one unsaturated linkage. Reactions with organic carbonyls and terminal alkynes are found to afford equilibria rather than isolable products.

Chapter 7 details full experimental procedures for all syntheses and reactions described in the text.

Chapter 8 contains characterising data for all new compounds reported.

Full tables of crystallographic data for all new crystallographically characterised complexes described herein are presented in **Appendices A – H, J – M**.

Appendix I contains kinetics data relating to work discussed in Chapter 3.

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'And we know that in all things God works for the good of those who love him, who have been called according to his purpose.'

- Romans, 8 v 28

'After this I looked and there before me was a great multitude that no-one could count, from every nation, tribe, people and language, standing before the throne and in front of the Lamb. They were wearing white robes and were holding palm branches in their hands. And they cried out in a loud voice:
"Salvation belongs to our God, who sits on the throne, and to the Lamb."'

- Revelation 7 v 9 - 10

Abbreviations

General

Å	Angstrom
APCI	Atmospheric Pressure Chemical Ionisation
Ar	aryl
atm	atmosphere
^{t}Bu	*tert*-butyl
°C	degrees Celsius
C_5H_5	cyclopentadienyl
C_5H_4Me	methylcyclopentadienyl
C_5Me_5	pentamethylcyclopentadienyl
ca.	*circa*, about
cf.	compared with
cod	cycloocta-1,5-dienyl
Cy	cyclohexyl
d	day(s)
E.I.	Electron Impact
F.I.	Field Ionisation
GC	Gas Chromatography
h	hour(s)
Me	methyl
Me_4taa	tetramethyldibenzotetraaza[14]annulene dianion
Me_8taa	octamethyldibenzotetraaza[14]annulene dianion
MS	Mass Spectrometry

min	minute(s)
(N_2N_{py})	$MeC(2\text{-}C_5H_4N)(CH_2NSiMe_3)_2$
OTf	CF_3SO_3
Ph	phenyl
phen	1,10-phenanthroline
^{i}Pr	*iso*-propyl
^{n}Pr	*n*-propyl
py	pyridine
salen	bis(salicylaldimine)
sec	second(s)
THF	tetrahydrofuran
Tol	*p*-tolyl, $4\text{-}C_6H_4Me$
TPP	5,10,15,20-tetraphenylporphyrin dianion
TTP	5,10,15,20-tetratolylporphyrin dianion
vs	versus

Nuclear Magnetic Resonance spectroscopic data

br	broad
$^{13}C\text{-}\{^{1}H\}$	proton-decoupled ^{13}C
COSY	COrrelation SpectroscopY
d	doublet
δ	chemical shift in ppm
DEPT	Distortionless Enhancement by Polarisation Transfer
INEPT	Insensitive Nucleus Enhancement by Polarisation Transfer

J	coupling constant
HMBC	Heteronuclear Multiple Bond Connectivity
HMQC	Heteronuclear Multiple Quantum Coherence
Hz	Hertz
m	multiplet
MHz	Megahertz
NMR	Nuclear Magnetic Resonance
nOe	nuclear Overhauser effect
NOESY	Nuclear Overhauser Effect SpectroscopY
ppm	parts per million
qt	quartet
s	singlet
sept	septet
t	triplet

Infrared spectroscopic data

br	broad
cm^{-1}	wavenumber
IR	Infrared
m	medium
ν	frequency
s	strong
sh	shoulder
w	weak

Note about numbering of literature compounds described in this Thesis

Literature compounds described in this Thesis are numbered **1.x**, **2.x**, **3.x**, **4.x**, **5.x**, **6.x** according to the Chapter in which they occur. The new compounds described in this Thesis are numbered **1 – 70**.

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{OC(O)N(-2,6-$C_6H_3Me_2$)C(O)O}{MeC(N^iPr)$_2$} (31)

Appendix H – X-ray Structure Analysis of Ti(η-C_5H_4Me)

{OC(O)N(-2,6-$C_6H_3Me_2$)C(O)O}{PhC($NSiMe_3$)$_2$} (32)

Appendix I – Data from rates studies of insertion of CO_2 into

Ti(η-C_5Me_5){N(4-C_6H_4X)C(O)O}{MeC(N^iPr)$_2$}

(X = CF_3, Me, NMe_2)

Appendix J – X-ray Structure Analysis of Ti(η-C_5Me_5)

{N(-2,6-$C_6H_3Me_2$)C(N-2,6-$C_6H_3Me_2$)O}{MeC(N^iPr)$_2$} (41)

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{N(-2,6-$C_6H_3Me_2$)C(N-4-C_6H_4Me)O}{MeC(N^iPr)$_2$} (42)

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(μ-S){PhC($NSiMe_3$)$_2$}]$_2$ (58)

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CHAPTER 1

Introduction

1.1 General introduction

This Thesis is concerned with the synthesis and reactivity of titanium imido complexes supported by cyclopentadienyl-amidinate ligand sets.

Transition metal complexes with metal-ligand multiple bonds have attracted considerable attention over recent years. A desire for a more complete understanding of their structure and reactivity has prompted a rapid growth in the number and range of complexes which have been discovered and studied. Many of these complexes have been found to have important applications in areas such as organic synthesis,[1,2] industrial catalysis,[3] atom transfer reactions,[4] and in biological systems.[5] Many excellent and comprehensive reviews have been written, and the reader is directed towards these for a more extensive discussion on the subject.[1,3,4,6-11]

A metal-ligand multiple bond is one in which the ligand binds to the metal through one σ- bond and one or more π- bonds. The donation of the π- electrons by heteroatoms to the metal acts to stabilise high oxidation states, and is commonly observed for the early transition metals. In some respects, the double bond (one σ and one π component) and triple bond (one σ and two π components) are analogous to olefinic or acetylenic linkages. In the cases of alkylidene and alkylidyne ligands, the bond orders are invariably two and three respectively, but for oxo and imido ligands, the assignment of bond order is not straightforward. The metal-ligand bond order in a particular complex is dependent on the electronic and symmetry requirements of the metal centre, as

well as the nature of other ligands around the metal; thus in oxo and imido complexes, the bond order can range between the two extremes.[12-18]

The following Section will concentrate on the imido ligand, as it is complexes of this moiety which are the main focus of this Thesis. Subsequent Sections will review the cyclopentadienyl and amidinate ligands, as they form the ancillary ligand environment around the titanium centre in the work reported. Unlike cyclopentadienyl ligands, amidinates have been relatively underdeveloped as supporting ligands for transition metal chemistry until comparatively recently.

1.2 THE IMIDO LIGAND

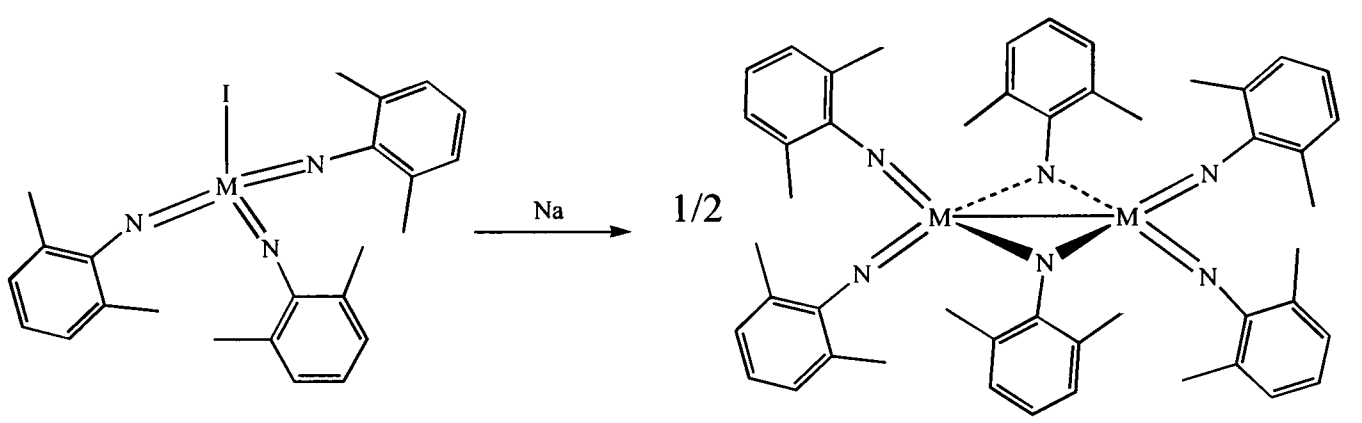
The first reported transition metal-imido complex was $Os(N^tBu)O_3$ (**1.1**) in 1959.[19] Since then, much work has been carried out investigating the nature and reactivity of the metal-imido bond. This Section will briefly explore some aspects of the work that has been reported on transition metal imido complexes. For a more comprehensive overview, readers are directed towards the reviews mentioned above.

The Section will begin by considering the bonding characteristics of the imido ligand, before moving on to the methods of synthesis used to make transition metal imido complexes, and then proceed to cover the techniques used to characterise those compounds. The Section will then conclude with the applications of imido complexes in biologically and industrially important

processes. The reactivity of imido complexes towards unsaturated substrates will be dealt with in subsequent Chapters.

1.2.1 BONDING CHARACTERISTICS OF THE IMIDO LIGAND

The imido ligand is able to act as both a terminal ligand or as a bridging ligand. Clark and Bryan have reported the compounds $M_2(N\text{-}2,6\text{-}C_6H_3Me_2)_4(\mu\text{-}N\text{-}2,6\text{-}C_6H_3Me_2)_2$ (M = Tc (**1.4**), Re (**1.5**)), in which the imido group can be seen acting as both as a bridging and a terminal ligand[17] (Equation 1.1).



M = Tc **1.2**, Re **1.3** M = Tc **1.4**, Re **1.5**

Equation 1.1

In terminal imido complexes, there exist three possible extremes of bonding, in which the hybridisation about the nitrogen atom can vary, as can the bond order. These three extremes are shown in Figure 1.1.

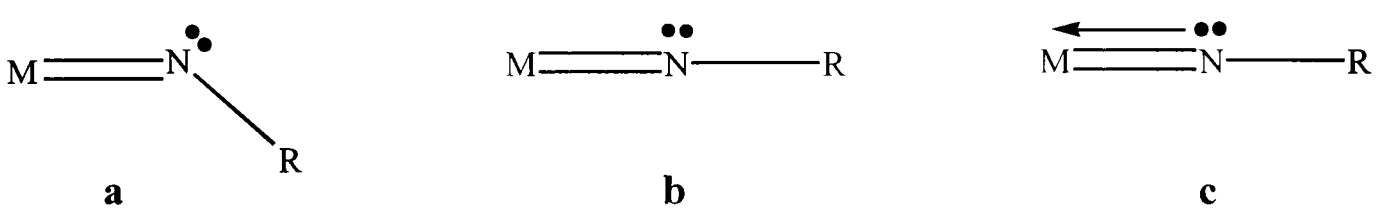


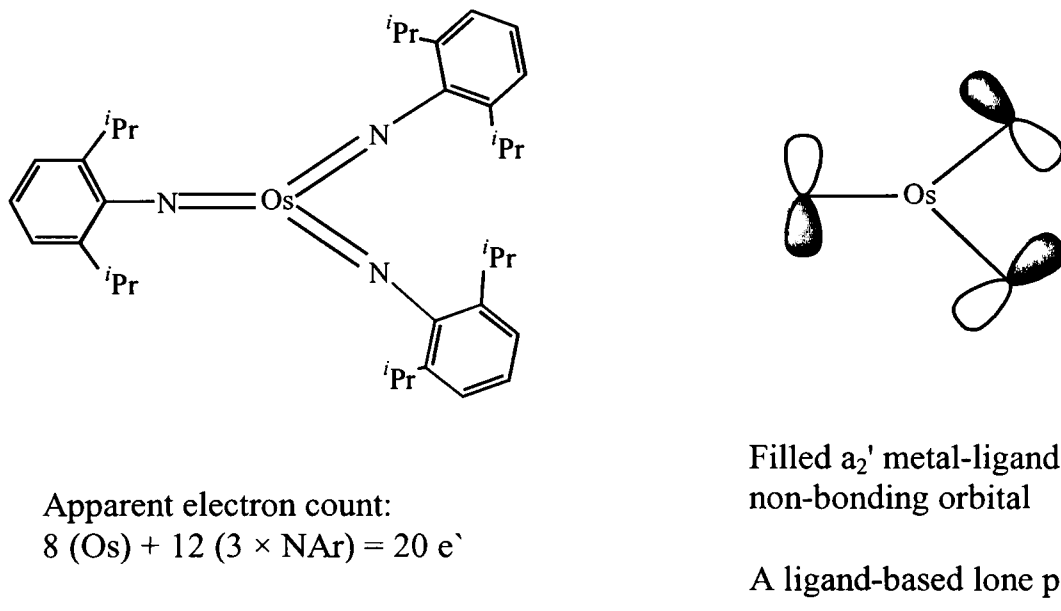
Figure 1.1 – Possible bonding mode of the imido ligand in transition metal complexes

Strähle reports the distinction between cases **a** and **c** by classifying **a** as an imido complex, and **c** as a nitrene complex.[12] In recent times, the distinction between these two terms has been dropped; both are now referred to as imido complexes, as per standard IUPAC nomenclature.[20]

In case **a**, the nitrogen atom is formally sp^2 hybridised, with a localised lone pair which cannot be donated to the metal centre. The metal-imido linkage is "bent" at nitrogen, with the nitrogen forming a double bond to the metal through one σ and one π interaction. In this instance, the nitrogen can be considered to be a 2 electron donor to the metal centre. This type of coordination is exceptionally rare; additionally, the expected bond angle of 120 ° for sp^2 hybridisation is significantly exceeded. An example of this mode of coordination is the complex $Mo(NPh)_2(S_2CNEt_2)_2$ **(1.6)**[21,22] in which the angle about one of the imido nitrogens is 139.4(4) °. It is now accepted that imido ligands with M–N–C angles as low as 150 ° may still be able to donate four electrons to the metal.

In the second case, that of **b** above, the metal-imido linkage is linear, but the lone pair of electrons is still localised in an orbital which is predominantly ligand based. This situation arises, despite the nitrogen now being formally *sp* hybridised, due to a severe disparity in either energy or symmetry between the ligand π orbitals and the π-acceptor orbitals on the metal. Thus, the nitrogen is donating less than four electrons to the metal; in the limiting case only two are available for bonding.[23] The complex $Mo(N\text{-}2,6\text{-}C_6H_3{}^iPr_2)_2(S_2CNEt_2)_2$ **(1.7)** bears two imido fragments which are best considered linear, and each donate three electrons to the metal.[24] Another example of this mode of bonding is the

planar tris(imido) complex Os(N-2,6-$C_6H_3{}^iPr_2)_3$ (**1.8**) reported by Schrock.[25] All three imido linkages are linear, and thus could be argued to give rise to a formal electron count of 20 at osmium. The dilemma is resolved when the symmetry of the relevant orbitals is taken into consideration. One of the linear combinations of atomic orbitals used is made up from p_x orbitals on the metal; this has a_2' symmetry and so has no match with the metal orbitals in the D_{3h} point group (See Figure 1.2). Each imido group can therefore be considered to donate 3 electrons to the metal. Theoretical investigations of the electronic structure of this and related compounds have been carried out in more detail.[15,26]



Apparent electron count:
8 (Os) + 12 (3 × NAr) = 20 e`

Filled a_2' metal-ligand non-bonding orbital

A ligand-based lone pair

Figure 1.2 – Description of ligand-based non-bonding orbital in Os(N-2,6-$C_6H_3{}^iPr_2)_3$ (**1.8**)

In the third case depicted in Figure 1.1, the imido linkage is linear and the nitrogen can be considered to be donating four electrons to the metal centre. This is by far the most common mode of coordination for the imido ligand, and consists of one σ and 2 π interactions between the ligand and the metal. Formally, the metal-ligand bond has an order of three in imido complexes of

this type. Most metal-imido linkages in this Thesis will be written 'M=NR' for ease of representation, but this does not serve to imply a bond order of two.

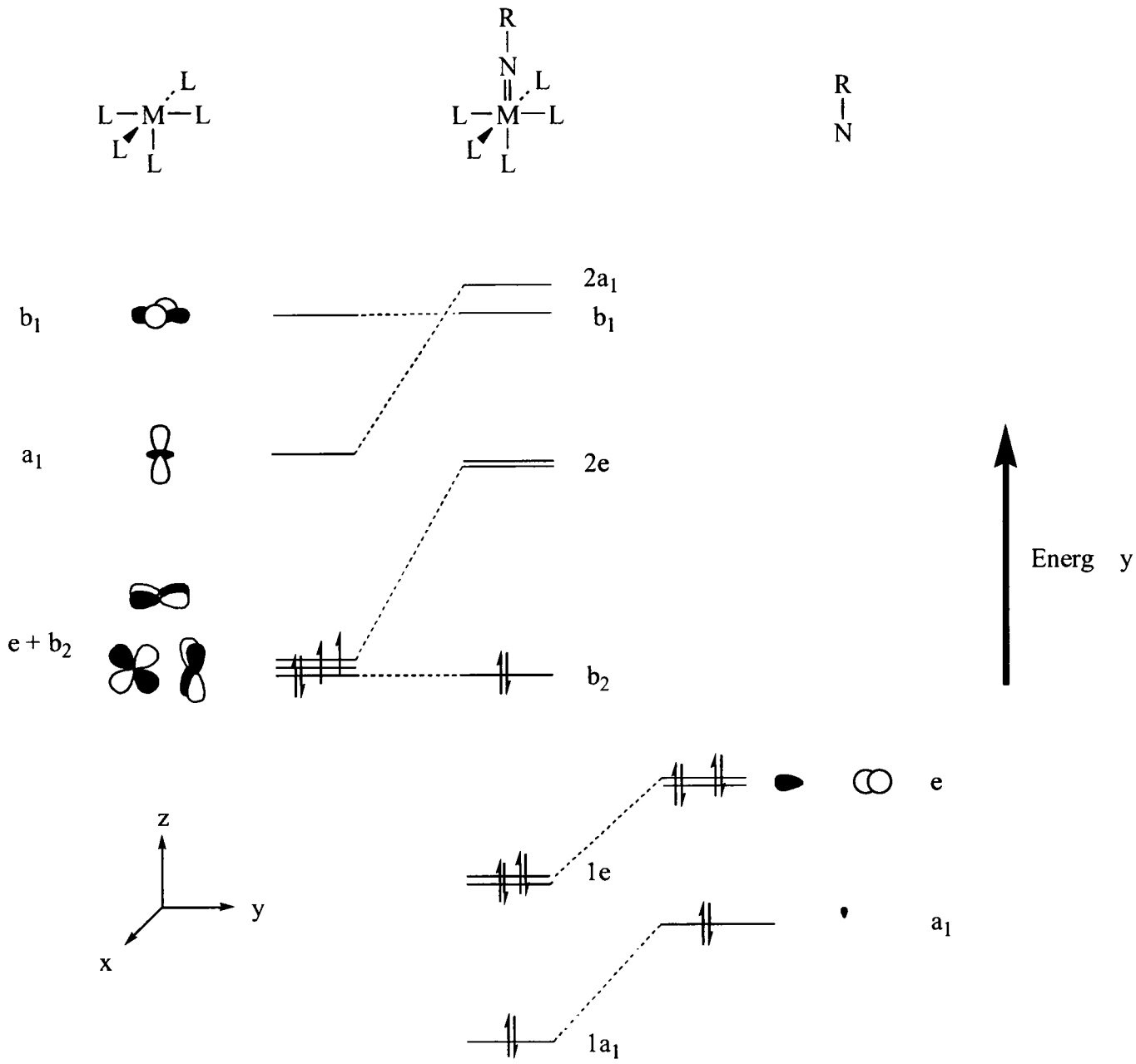


Figure 1.3 – Stylised fragment Frontier Molecular Orbital interaction diagram for a d^2 $M(NR)L_5$ complex derived from Extended Huckel Molecular Orbital theory. The tie-lines reflect the major fragment molecular orbital contributions to the molecular orbitals of the resultant complex

Figure 1.3 depicts the stylised molecular orbital diagram for a transition metal-imido complex (d^4 metal centre) of the form $M(NR)L_5$, where L is a σ-donor ligand. The diagram illustrates the formal $\sigma^2\pi^4$ triple bond, and that the imido NR group is formally a 2- ligand. It also shows that the metal based d_π-orbitals are raised in energy, suggesting that low d electron counts would be preferred for imido complexes. This is indeed found to be the case; the majority of

transition metal-imido complexes are found to have d^0, d^1 or d^2 electronic configurations.

1.2.2 SYNTHESIS OF IMIDO COMPLEXES

A variety of methods exist for the synthesis of transition metal-imido complexes. This Section reviews the most important methods; for a more comprehensive study the reader is pointed towards some excellent discussions in the literature.[1,6,27,28]

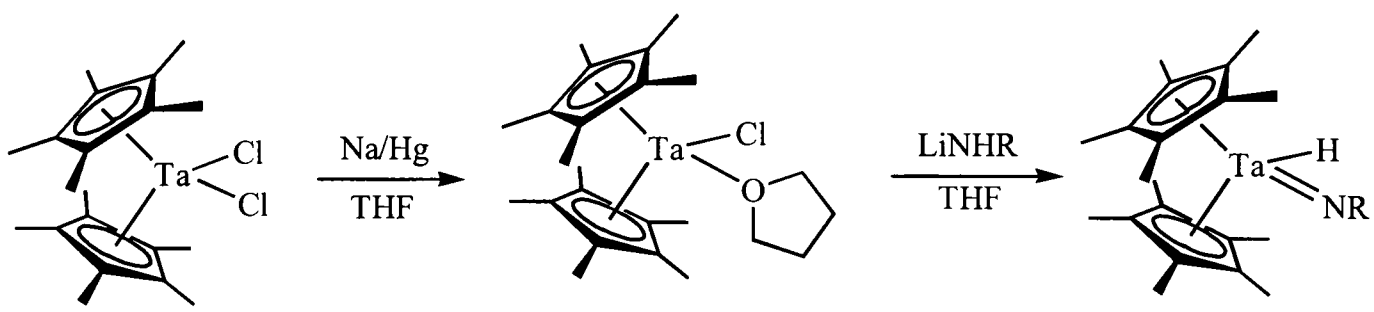
1.2.2.1 AMINES, AMIDES AND SILYLAMINES

The earliest route to transition metal-imido complexes, this method involves the cleavage of an N–H or N–Si bond, with transfer of the proton or silicon to an acceptor group such as an oxide, a chloride, or an alkyl. Some examples are given in Equations 1.2 and 1.3.[19,29,30]

$$OsO_4 + {}^tBuNH_2 \longrightarrow Os(N^tBu)O_3$$

1.1

Equation 1.2



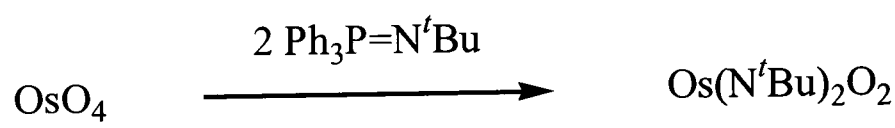
1.9 **1.10**

R = ^{t}Bu **1.11**
Ph **1.12**

Equation 1.3

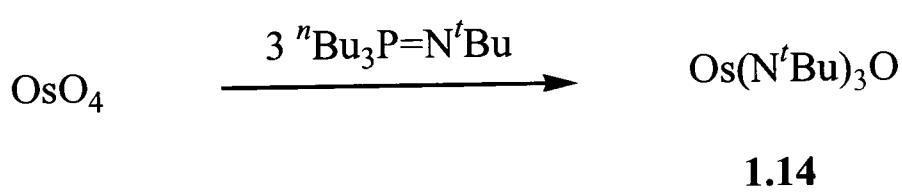
1.2.2.2 METATHESIS OF OTHER MULTIPLE BONDS

Reaction between metal-ligand multiple bonds and unsaturated substrates can effect redistribution of the ligands *via* [2 + 2] cycloaddition. In the case where the substrate contains an element-nitrogen double bond, such as carbodiimides (RNCNR) or isocyanates (RNCO), the metathesis can result in the formation of a metal-imido functionality. Examples are given in Equations 1.4 – 1.7.[31-38]



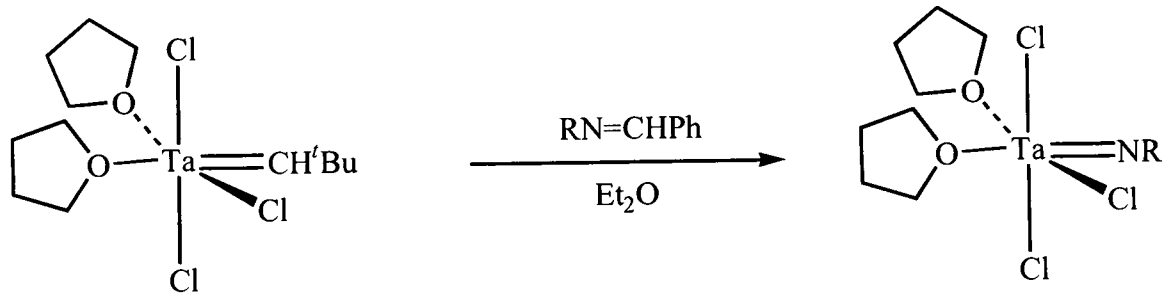
1.13

Equation 1.4



1.14

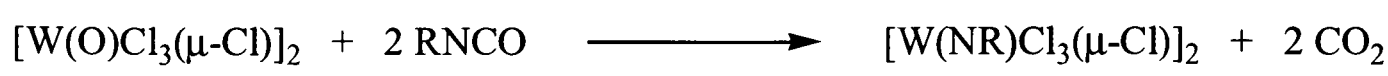
Equation 1.5



1.15

R = Me **1.16**
^{t}Bu **1.17**
Ph **1.18**

Equation 1.6

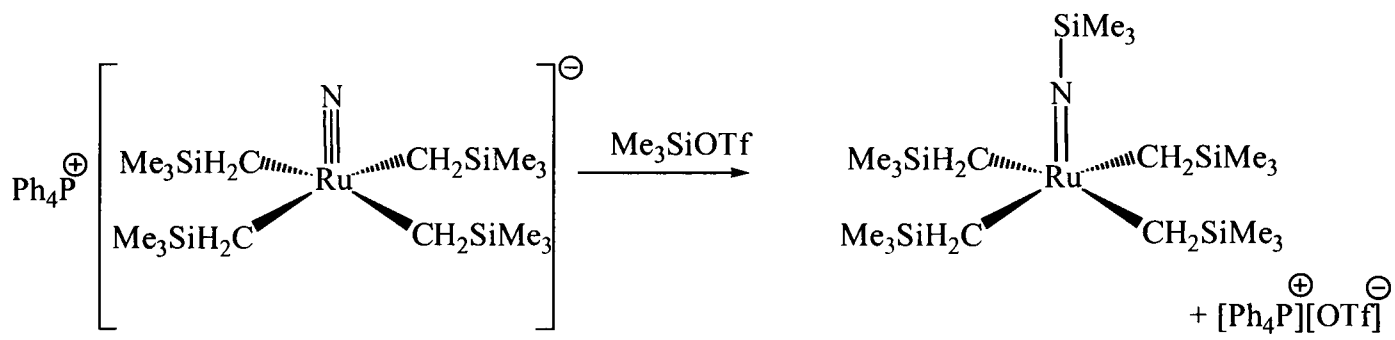


1.19

Equation 1.7

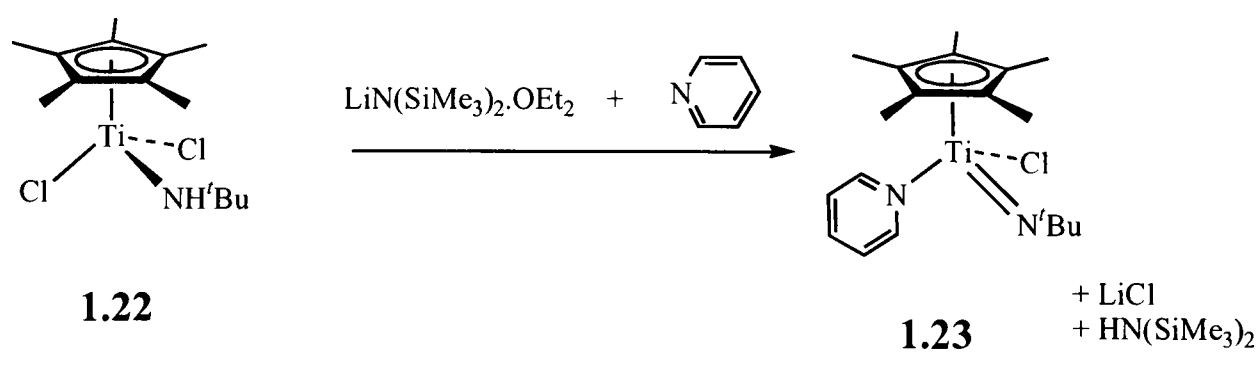
1.2.2.3 NITRIDO AND AMIDO SPECIES

Imido species can be produced by alkylation of a nitrido precursor, and from amido species *via* base promoted elimination. Two examples are given in Equations 1.8 and 1.9.[39-42]



1.20 **1.21**

Equation 1.8

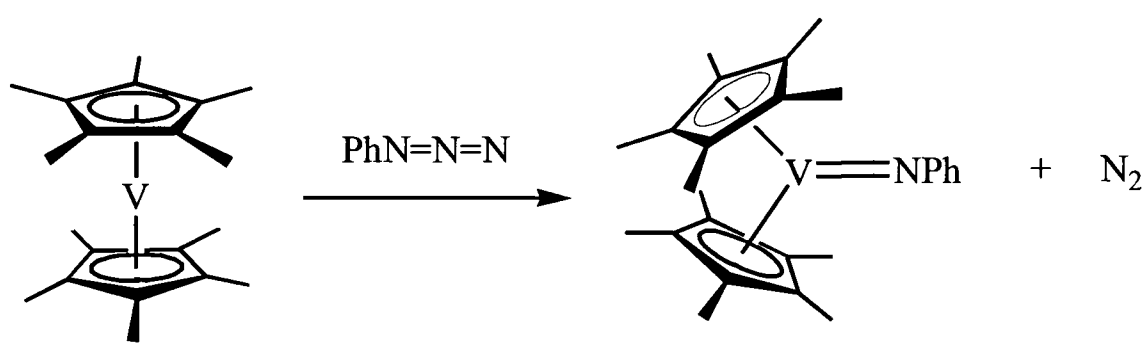


1.22 **1.23**

Equation 1.9

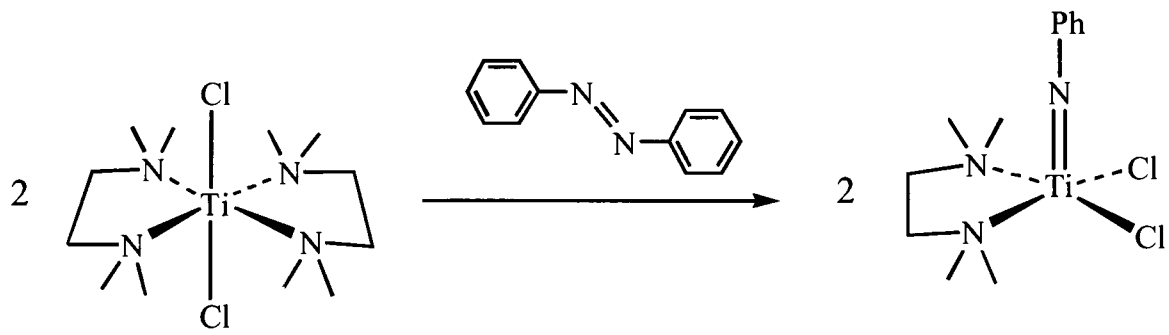
1.2.2.4 ORGANIC AZIDES AND OTHER AZO SPECIES

The elimination of N_2 provides a strong thermodynamic driving force for the formation of imido complexes from the reactions between a metal complex and an organic azide, resulting in oxidation of the metal. Other azo species may also be employed; two examples are given in Equations 1.10 and 1.11.[43-45]



1.24 **1.25**

Equation 1.10



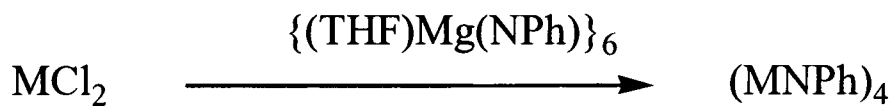
1.26 **1.27**

Equation 1.11

1.2.2.5 IMIDO TRANSFER REAGENTS

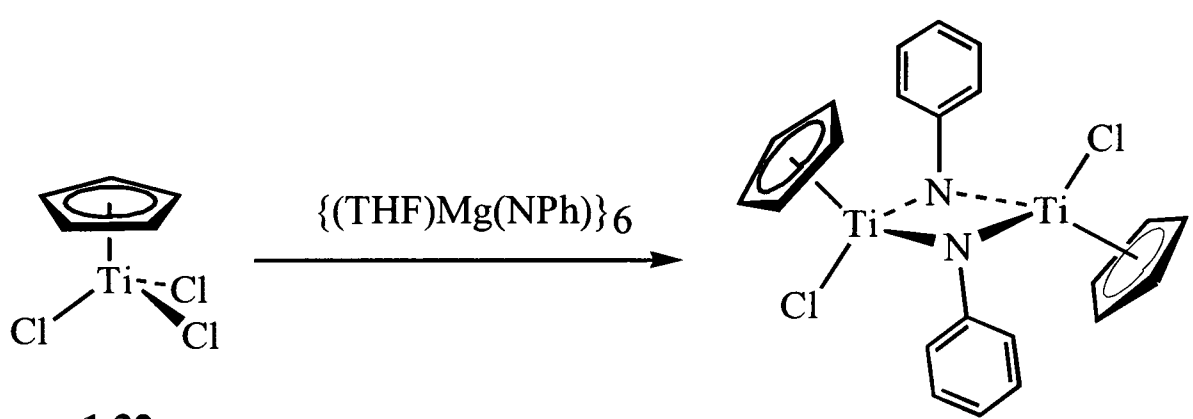
The use of organometallic imido complexes as a source of the imido ligand has been explored. Power *et al.* have reported the use of the hexameric reagent

{(THF)Mg(NPh)}$_6$ (**1.28**) in successful imido transfer reactions on both main group[46] and transition metals,[47] as indicated in Equations 1.12 and 1.13:



M = Ge **1.29**
Sn **1.30**
Pb **1.31**

Equation 1.12



1.32

1.33

Equation 1.13

1.2.3 CHARACTERISATION OF IMIDO COMPLEXES

Transition metal-imido complexes have been characterised by the full gamut of analytical techniques. Special mention will be made in this Section of two of the potentially most informative techniques: NMR and IR.

1.2.3.1 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

For diamagnetic complexes, the use of NMR spectroscopy can provide invaluable spectroscopic evidence for the structure and bonding in transition

metal-imido species. Of particular use is ^{1}H NMR spectroscopy for species containing hydrocarbyl fragments; this is typically the most common technique for initial identification. Characteristic resonances for the organic group bound to the nitrogen can be observed, proving a useful structural handle. However, the chemical shifts of these groups relative to those of the uncoordinated amine are dependent on the other ligands coordinated to the metal centre, and so do not necessarily correspond to the acidity of the protons.

^{13}C NMR spectroscopy has also been used extensively to study the organic group. In the case of *tert*-butylimido complexes, a term called $\Delta\delta$ has been coined, where $\Delta\delta$ is the difference between the chemical shifts of C_α and C_β (where C_α is the quaternary carbon, and C_β the methyl carbons). It has been proposed that $\Delta\delta$ gives a measure of the electron density at nitrogen; the larger the value of $\Delta\delta$, the lower the electron density on the nitrogen atom.[27,48] This proposal is corroborated by analysis of various imido complexes, and comparing their $\Delta\delta$ values with their observed reactivity.[48] Thus $Os(N^tBu)O_3$ (**1.1**), which exhibits electrophilic reactivity at nitrogen, has a $\Delta\delta$ of 55 ppm, while the more nucleophilic main group phosphaimine $Ph_3P{=}N^tBu$ has $\Delta\delta$ value of 16 ppm. Although the value of $\Delta\delta$ gives a qualitative rather than a quantitative measure of the reactivity of the imido nitrogen, it is nevertheless a very useful parameter. Investigation of a series of titanium *tert*-butylimido tris(pyrazolyl)hydroborate complexes revealed the relative donor abilities of the ligands, and showed that they were less effective donors to the metal centre than η-C_5H_5 or η-C_5Me_5.[49]

In addition to these nuclei, some spectroscopic studies have been attempted using nitrogen as the nucleus of interest. This has not found wide applicability however, as the more abundant ^{14}N nucleus has a nuclear spin quantum number (I) of 1, and therefore possesses a quadrupole moment. As a result, only highly symmetrical molecules are suitable for study, since in other systems quadrupolar broadening prevents any useful information being extracted.[50] The ^{15}N nucleus has a spin quantum number of ½, but a very low natural abundance (0.37%). A few studies have been conducted using this nucleus, either by using the INEPT (Insensitive Nucleus Enhancement by Polarisation Transfer) pulse sequence,[50-52] or else by isotopic enrichment (which is very costly).[34,53] It has been observed that the nitrogen atom is more shielded in imido complexes (-80 to +10 ppm) (relative to nitromethane) than in nitrido complexes (+40 to +190 ppm). LeNy and Osborn conducted a study of a series of imidotungsten complexes, which showed that the ^{14}N resonance is only sharp for linear imido linkages; this is consistent with the electron density about the imido group being highly axially symmetrical.[54] An extensive study into imido complexes of the late transition metals of the third row by Bradley *et al.* has discovered a fluxional process between bent and linear modes in solution. They have also shown however that in contrast to N=O and N=NR ligands, deshielding on bending is small for the imido ligand, and the nitrogen chemical shift ranges are not distinct for bent and linear geometries. As a result, nitrogen NMR is not able to distinguish between these two modes.[52]

Metal atom NMR has not been widely used as an analytical technique, but some studies on ^{51}V and ^{183}W nuclei have been conducted. Maatta *et al.* reported that

the derivatives of the *p*-tolylimido complex V(N-4-C_6H_4Me)Cl_3 (**1.34**) display an "inverse halogen dependence", in which the metal centre becomes increasingly shielded as σ-donor ligands are replaced with more electronegative and π-donor ligands.[55,56] ^{183}W studies by Faller *et al.* on the series of complexes W(η-C_5Me_5)(O)(E)Me (E = S (**1.35**), O (**1.36**), NPh (**1.37**)) have shown that as the multiply bonded ligand E is changed from S to O to NPh, the metal centre is increasingly shielded, suggesting that the imido ligand is the best π-donor.[57] More recent ^{51}V NMR studies have demonstrated that 2,6-diisopropylphenylimido ligands donate more electron density to the metal centre than *tert*-butylimido ligands.[58]

The bridging imido complex [Mo(η-C_5H_5)O]$_2$(μ-Te)(μ-NC_6H_5) (**1.38**) was recently characterised[59] by techniques including ^{125}Te NMR spectroscopy, another example in which metal atom NMR spectroscopy has been used in the characterisation of an imido species.

1.2.3.2 Infrared spectroscopy

IR spectroscopy has been found to be of limited use in the characterisation of imido complexes of the transition metals. The main problem is that the ν(M=N) mode may be coupled to the ν(N–C) stretch. Furthermore, vibrations due to the organic group itself, as well as other modes within the molecule may cause complications. Most imido complexes are found to have bands between 1100 – 1350 cm^{-1} and 900 – 1000 cm^{-1}. Unequivocal assignment of these bands has proven extremely difficult. Osborne and Trogler studied the IR spectra of natural abundance V(η-C_5Me_5)$_2$(NPh) (**1.25**) and the ^{15}N enriched analogue

$V(\eta\text{-}C_5Me_5)_2(^{15}NPh)$ (**1.25b**), and concluded that the ν(N–C) mode in $V(\eta\text{-}C_5Me_5)_2(NPh)$ occurs at 1130 cm^{-1} and the ν(M=N) mode at 934 cm^{-1}.[13] However, after studying the series $V(NX)Cl_3$ (X = Cl (**1.39**), Br (**1.40**), I (**1.41**)), Dehnicke and Strähle suggested that coupling to the other metal-ligand vibrations in the molecule results in the *higher* energy mode being associated with the ν(M=N) stretch.[12] In addition, they propose that in organoimido complexes, the ν(M=N) will be at higher energy, giving an absorption in the range 1200 – 1300 cm^{-1}.

Studies of Raman spectra suggest that the two bands are due to symmetric and antisymmetric vibrations of the entire M–N–C linkage.[60] As a consequence of all of these factors, clear assignment of IR spectra is not usually possible.

1.2.4 APPLICATIONS OF IMIDO CHEMISTRY

Imido complexes have been shown to be important in a number of biologically and industrially important processes. Imido complexes are used as Ring Opening Metathesis Polymerisation (ROMP) catalysts,[3,61] Ziegler-Natta polymerisation catalysts,[58,62,63] as catalysts in the synthesis[64] and metathesis[65] of carbodiimides, in Metal Organic Chemical Vapour Deposition (MOCVD),[66] and in the oxyammination and diammination of olefins.[67] It has also been suggested that imido complexes are intermediates in the enzymatic fixation of nitrogen.[5]

1.3 THE CYCLOPENTADIENYL LIGAND

Of all the ligands used in transition metal chemistry, the monoanionic cyclopentadienyl-based set are surely the most widely studied. The η^5 coordination mode of the ligand, which donates one electron from each carbon atom to the metal centre, was first determined in 1952 for ferrocene ($Fe(\eta\text{-}C_5Me_5)_2$) **(1.42)**,[68,69] winning the researchers Fischer and Wilkinson the Nobel Prize in Chemistry in 1973,[70] and since then an enormous amount of research has been carried out on complexes bearing this ligand. The chemical stability of the ligand, the high steric protection it affords a metal centre, and its potential for modification, have all contributed to this research interest. The discovery that cationic metallocene complexes such as $[Zr(\eta\text{-}C_5H_5)_2Me]^+$ **(1.43)** are extremely active olefin polymerisation catalysts has provided strong incentive for further studies of these systems.

This Section provides a brief overview of the cyclopentadienyl ligand, beginning with its synthesis and characterisation, and discussing some of the relevant features which relate to the chemistry reported in this Thesis. The Section concludes with some recent developments discussed in the literature. Of necessity, this will be confined to work which is directly relevant to that discussed in subsequent Chapters. For a more detailed discussion of the chemistry of this class of ligand, the reader is directed towards reviews in the literature[71-74]

1.3.1 SYNTHESIS OF THE CYCLOPENTADIENYL LIGAND

Two cyclopentadienyl ligands were used as ancillary ligands in the complexes reported in this Thesis. These were the methylcyclopentadienyl (C_5H_4Me) and pentamethylcyclopentadienyl (C_5Me_5) ligands.

$Li(C_5H_4Me)$ was formed by cracking the commercially available methylcyclopentadiene dimer $[C_5H_5Me]_2$, and reacting the monomeric C_5H_5Me formed with *n*-butyllithium to afford the lithium salt $Li(C_5H_4Me)$. The bulkier $Li(C_5Me_5)$ reagent was not synthesised in this way, as the dimer does not exist. The monomer C_5Me_5H is available, but is photosensitive, and expensive. Several methods involving inexpensive reagents have been devised over the years,[75-79] but the method used was that developed by Jutzi *et al.*[78] The main difference between C_5Me_5 and C_5H_4Me is steric bulk, but C_5Me_5 is also a stronger electron donor than C_5H_4Me.

1.3.2 CHARACTERISATION OF THE CYCLOPENTADIENYL LIGAND IN COMPLEXES

When complexed, the cyclopentadienyl ligand, in common with many other cyclic polyene ligands, exhibits stereochemical nonrigidity in solution. The barrier to rotation about the metal-ring centroid axis is very small, and at room temperature, the ^1H and ^{13}C-$\{^1H\}$ NMR spectra of complexed C_5H_5 and C_5Me_5 contain only a single resonance. In the case of complexed C_5H_4Me, rapid rotation does not make all sites on the ring magnetically equivalent, and this allows more information about the complex to be obtained. It was for this

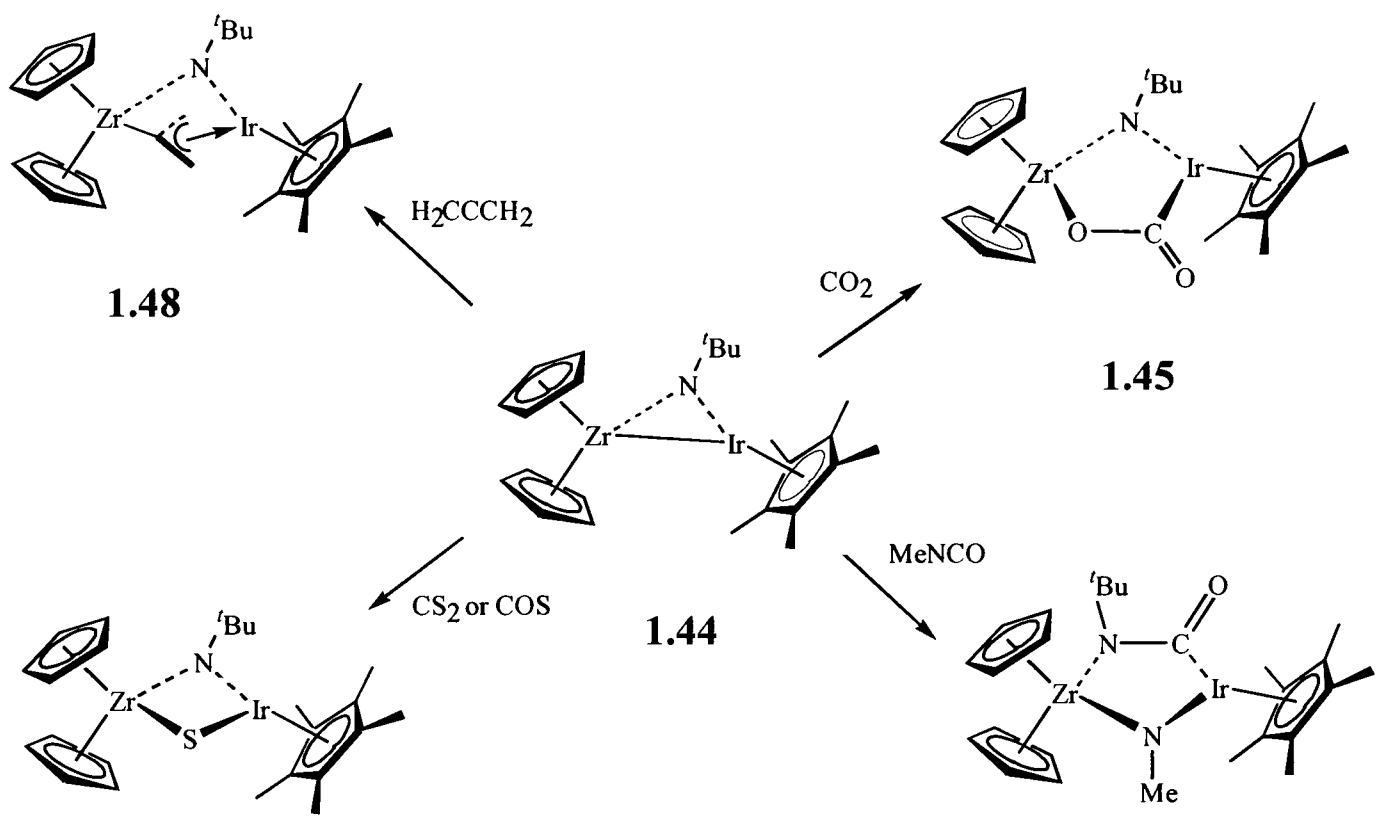
reason that the C_5H_4Me ligand was used, rather than the more common C_5H_5 ligand.

1.3.3 RECENT WORK INVOLVING THE CYCLOPENTADIENYL LIGAND

As mentioned above, the cyclopentadienyl ligand has been used extensively in organometallic chemistry over the last fifty years, and most of this work is beyond the scope of this introduction. In this Section, only material which is relevant to the work described in subsequent Chapters will be discussed.

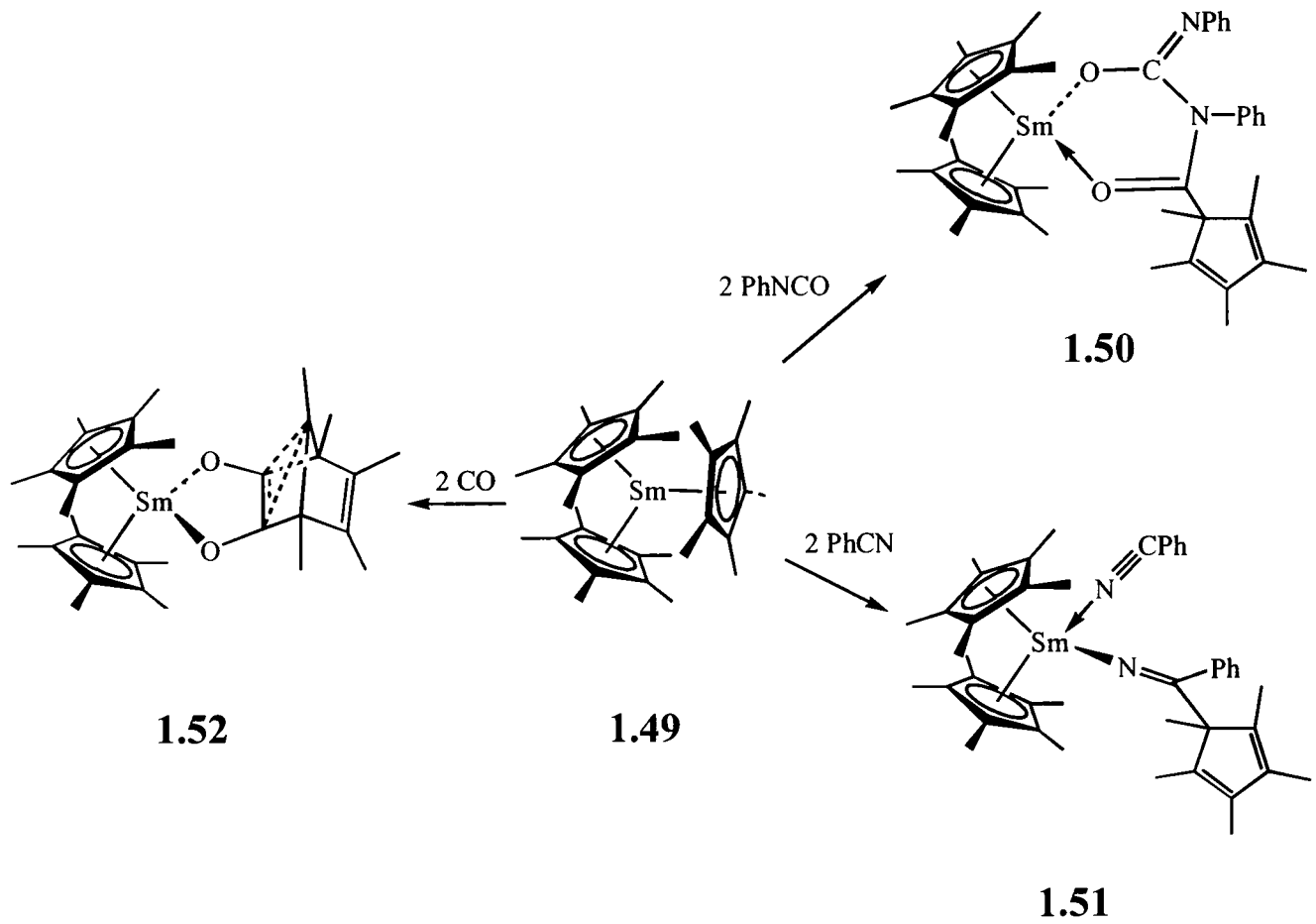
The cyclopentadienyl ligand has been used to support metal-imido complexes of many transition metal complexes, including titanium,[80-85] zirconium,[86] vanadium,[43,87] niobium,[88,89], tantalum,[63,88,90] molybdenum,[16,91-95] tungsten,[16,95-97] and iridium.[98] Stabilisation of a uranium(IV) imido complex has also been achieved.[99] Attaching groups such as $SiMe_3$[100] and C_6F_5[101] to the cyclopentadienyl rings to modify the electronic properties has also been attempted. Complexes involving *ansa*-bridges, whether between two cyclopentadienyl groups[74,100,102-104] or between a cyclopentadienyl ring and a group such as an arene,[105] an amide,[106,107] or an imido moiety[108,109] are still an active avenue of research, with the focus on olefin polymerisation catalysis.

In conclusion, a few unusual examples of complexes supported by cyclopentadienyl ligands will be mentioned. A bimetallic imido complex $Zr(\eta\text{-}C_5H_5)_2(\mu\text{-}N^tBu)Ir(\eta\text{-}C_5Me_5)$ (**1.44**) was reported by Bergman[110] which was found to be very reactive towards unsaturated substrates, as shown in Scheme 1.1.



Scheme 1.1 – Reactions of $Zr(\eta\text{-}C_5H_5)_2(\mu\text{-}N^tBu)Ir(\eta\text{-}C_5Me_5)$ **(1.44)** with unsaturated substrates

The extremely crowded complex tris(pentamethylcyclopentadienyl)samarium **(1.49)** has been prepared, and despite its steric saturation displays varied reaction chemistry.[111] Some examples are given in Scheme 1.2. It is noteworthy that for this complex, the cyclopentadienyl ligand adopts uncharacteristic reactivity patterns since it is usually an inert spectator ligand. Other examples of C-H bond activation of the methyl groups in pentamethylcyclopentadienyl ligands have been reported, but are rare.[103]



Scheme 1.2 – Reactions of $Sm(\eta\text{-}C_5Me_5)_3$ (**1.49**) with some unsaturated axially cylindrical substrates

1.4 THE AMIDINATE LIGAND

Amidines, $\{R^1C(NR^2)(NR^3R^4)\}$, are isoelectronic with carboxylic acids, and form a large number of transition metal derivatives, with the metals varying from early metals in high oxidation states to the later metals in lower oxidation states. The related allyl group often bonds to metals using its π-system, but the amidine, like carboxylic acids, prefers to bond through the heteroatom lone pairs, giving other coordination possibilities. The amidinate chemistry of the transition metals has been reviewed recently by Barker and Kilner (on amidines)[112] and Edelmann (on benzamidine).[113]

Amidines were first synthesised by Gerhardt[114] in 1858 by the reaction of aniline with *N*-phenylbenzimidyl chloride, and are named after the acid or amide obtained by hydrolysis. Thus when R^1 = Me, the compound is an acetamidine and when $R^1 = C_6H_5$ a benzamidine. Amidines act as monodentate, two-electron donors *via* the more basic and less sterically hindered imino lone pair, to form simple adducts such as $CoCl_2(AmH)_2$ (**1.53**) and $PdCl_2(AmH)_2$ (**1.54**), where AmH = amidine. However, a much more interesting group is formed if the R^4 group is displaced to form the mono-anionic amidinate group $\{R^1C(NR^2)(NR^3)\}^-$, which is isoelectronic with the allyl and carboxylato ligands (Figure 1.4)

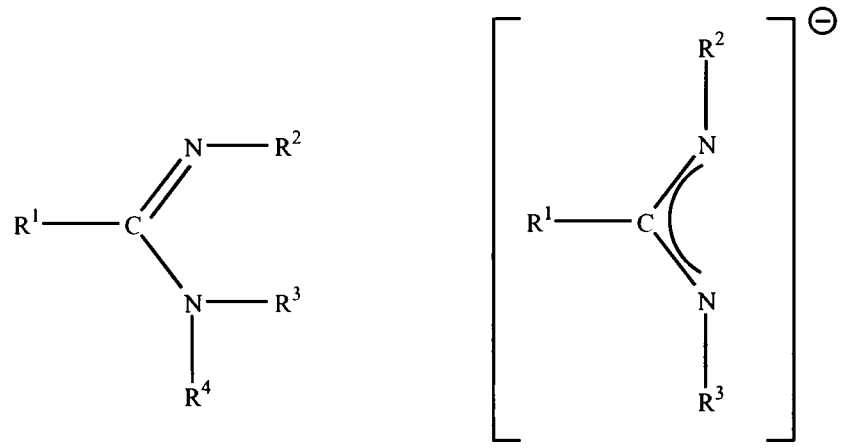


Figure 1.4 – Structure of the amidine and amidinate moieties

Amidinate ligands have been shown to be useful in place of cyclopentadienyl ligands in the stabilisation of transition metal complexes. They are hard, three electron donors,[115] and give rise to complexes with electron-deficient metal centres, allowing the isolation of cationic Lewis acidic compounds. The steric and electronic properties of the ligand can be altered by variation of the substituents R^1, R^2, and R^3, affording a wide range of available properties. As a

result, there have been examples reported of amidinates with very bulky substituents,[116-119] pendant arms in the R^2 position bearing additional donor groups,[120-123] bridged amidinate ligands (linked through R^2),[124-126] and asymmetrical substituents (*i.e.* R^2 R^3).[127,128] This latter group will be discussed later in this Section.

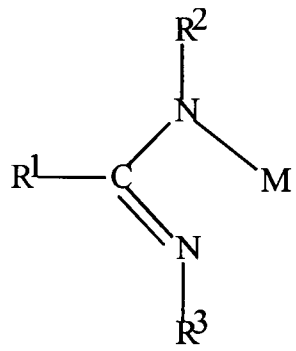
Of particular interest have been the benzamidinate ligands, of the form $\{ArC(NR^2)(NR^3)\}^-$ (Ar = Ph, substituted Ph). Their steric demands are considered to lie between those of the η-C_5H_5 and η-C_5Me_5 ligands,[115,129] although the shape of the ligand sphere is very different. Benzamidinate complexes are often found to possess excellent solubility, and generally form highly crystalline complexes.

Many early transition metal amidinate complexes have now been well established to form active catalyst systems for olefin polymerisation. The high degree of variation of the ligands gives rise to a wide range of polymer products.[130-136] In addition to olefin polymerisation, amidinate complexes have been reported as catalysts for phenyl isocyanate cyclisation,[137] isomerisation of olefins,[138] and disproportionation of cyclic olefins.[138]

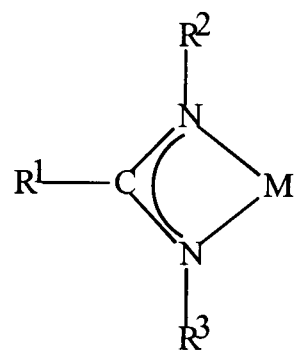
1.4.1 BONDING CHARACTERISTICS OF THE AMIDINATE LIGAND

The amidinate ligand can adopt a wide variety of possible binding modes, as shown in Figure 1.5. The nature of the bonding is strongly influenced by the steric properties of the amidinate ligand.[139,140] Many of these have been

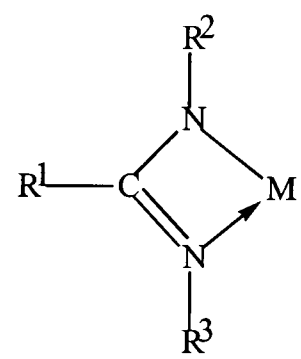
characterised by X-ray crystallography while others remain only postulated. The binding modes are:



a



b



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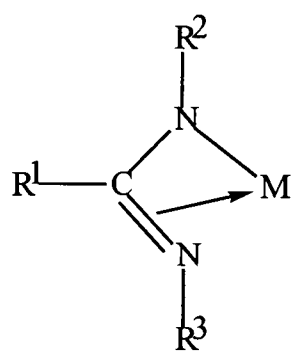
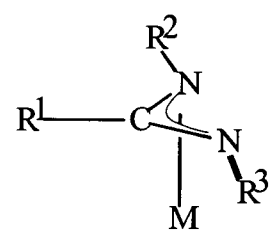
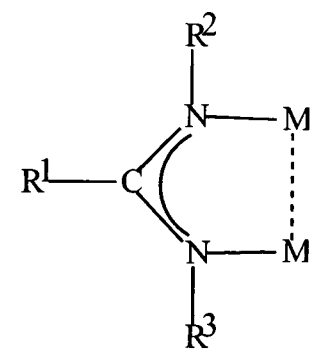


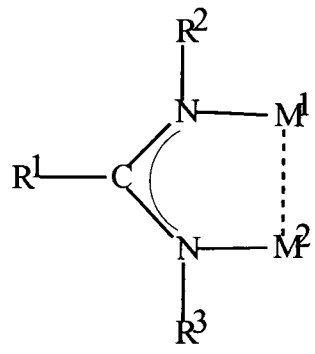
d



e



f



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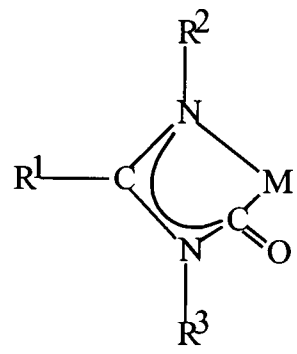

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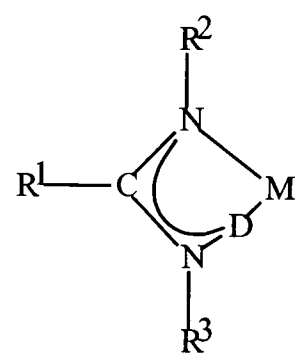

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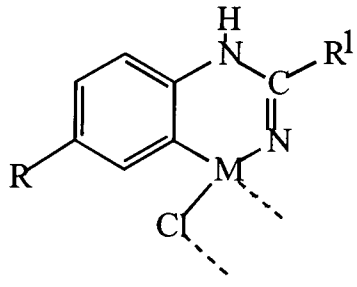

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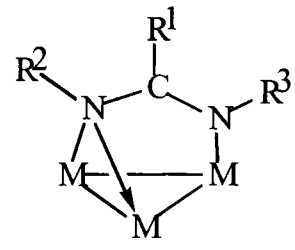

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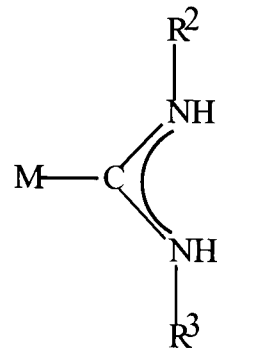


l

Figure 1.5 – Binding modes of the amidinate ligand in transition metal chemistry

a) Monodentate. One of the nitrogen atoms is σ-bonded to the metal centre while the other, which is double-bonded to the central carbon, remains unattached. Two examples have been structurally characterised by single crystal X-ray diffraction.

b), c), and d) Chelate complexes. The small size of the four-membered M(NCN) ring introduces steric strain and distortion of the valence angles. The class may be subdivided as follows: *b)* σ,σ- symmetrical attachment, where the NCN bonding is delocalised; *c)* σ,σ- unsymmetrical attachment, in which both nitrogen atoms bond to the metal centre but one bonds formally *via* the imine lone pair of electrons, leading to asymmetry in both the N–M and N–C bond lengths; *d)* one nitrogen binds as an imine while there is also an interaction from the delocalised double bond (no examples of this binding mode have yet been structurally characterised). Modes *c)* and especially *b)* are favoured when the R^1 substituent in the backbone position is bulky, thus making bridging difficult.

e) η^3-Allyl. This type of amidinate linkage is very rare, and has only been recently reported in the case of the complexes $Ru(\eta\text{-}C_5Me_5)\{MeC(N^iPr)_2\}Ru(\eta\text{-}C_5Me_5)X$ (X = Cl (**1.55**), Br (**1.56**)). These complexes have been structurally characterised.[141]

f), g) Bridging. This often coincides with metal-metal bonding, and is favoured if the R^1 substituent is small, especially H or Me. The metals may be the same (*f*) or different (*g*).

h), i) Carbamoyl/insertion complexes. The insertion of a carbonyl group into the M–N amidinate bond results in the formation of a carbamoyl complex, such as

$Ru(CO)_4\{C(O)N(Ph)C(Ph)N(Ph)\}$ (**1.57**).[142] Insertion of CH_2 and C_6H_5CN has also been found.

j) Ortho-metallation. Ortho-metallation may occur if a nitrogen substituent is an aryl group, to afford a stable six-membered metallacycle. This has been established for $Pd(\eta\text{-}C_5H_5)\{MeC_6H_3N(H)C(Me)N\text{-}4\text{-}C_6H_4Me\}$ (**1.58**),[143] though for the complex $Re(CO)_3\{N(Ph)C(C_6H_4)N(H)(Ph)\}\{PhNC(Ph)NHPh\}$ (**1.59**) a five-membered ring is indicated by spectroscopic methods.[144]

k) Cluster-capping. In the case of the structurally characterised complex $Os_3(\mu\text{-}H)(CO)_9\{PhC(NPh)(NH)\}$ (**1.60**),[145] the amidinate ligand caps one triangular face of osmium atoms, thus formally donating five electrons to the cluster.

l) Carbene. Such complexes are only included for completeness, since this binding mode should be regarded as a carbene, and not as an amidinate complex.

The protonated amidine ligand forms the cation in simple salts such as $[PhC(NH_2)_2]^+[Re(CO)_4(MeCO)_2]^-$ (**1.61**),[146] the structure of which has been determined by single crystal X-ray diffraction.

1.4.2 SYNTHETIC ROUTES TO TRANSITION METAL AMIDINATE COMPLEXES

The Section will firstly describe the synthetic routes used in the synthesis of amidinate ligands and amidines, before describing methods of synthesising transition metal complexes containing these ligands.

1.4.2.1 PREPARATION OF AMIDINE AND AMIDINATE LIGANDS

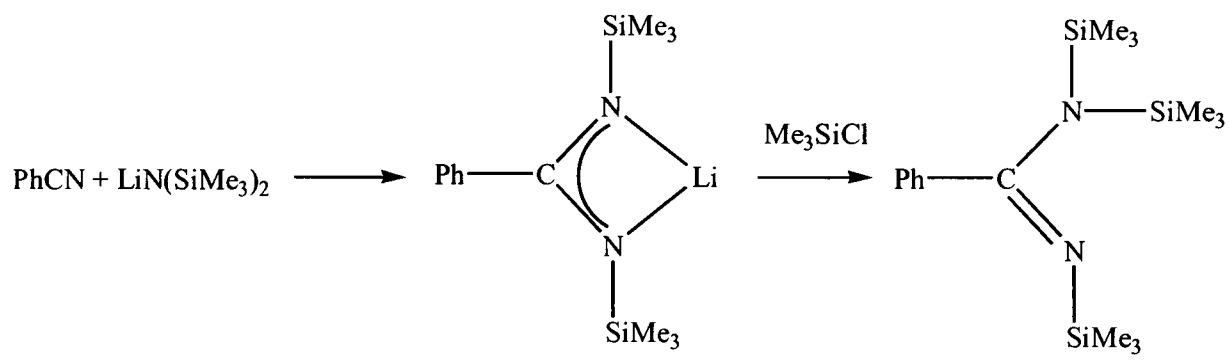
A large number of methods have been developed for the synthesis of these compounds; only the most important will be outlined here. A number of literature sources are available with more comprehensive surveys.[147,148]

1.4.2.1.1 PREPARATION FROM NITRILES

Three types of reaction are used.

a) Addition of metal amides to nitriles

The first example of a silyl benzamidinate was discovered by Sanger in 1973[149] *via* the treatment of benzonitrile with lithium bis(trimethylsilyl)amide, followed by reaction with trimethylsilyl chloride to give the silylated amidine. (Equation 1.14).



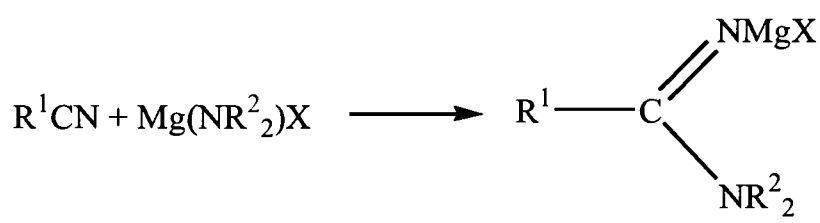
1.62

Equation 1.14

This route produces a symmetrically disubstituted amidinate (*e.g.* **1.62**) only if the amide used is an alkali metal bis(trimethylsilyl)amide, and the nitrile is either aromatic or fluorinated. Use of an asymmetrical metal amide affords an

unsymmetrical amidinate product. This enables the facile synthesis of pendant arm amidinate ligands.[120,122,123]

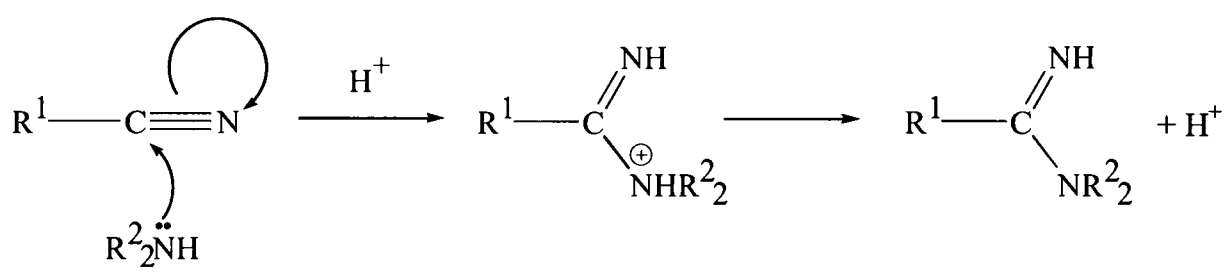
If an organomagnesium amido derivative is used, the product is an unsymmetrically disubstituted amidinate (Equation 1.15).



Equation 1.15

b) Addition of salts of ammonia or amines to nitrile

Theoretically the reaction scheme is as shown in Equation 1.16.

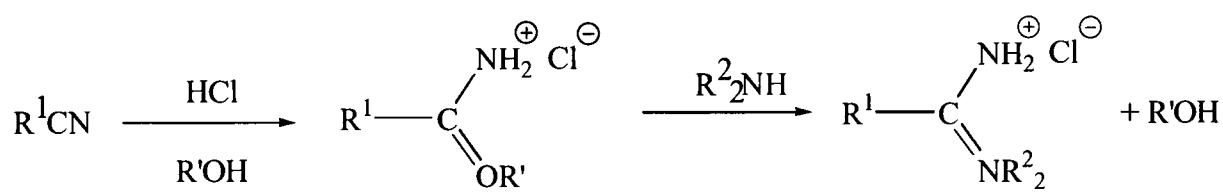


Equation 1.16

Ammonia and free amines give a direct addition only with nitriles which are activated by an electron withdrawing R' group on the α-carbon. Ammonium salts can be condensed with nitriles under a variety of conditions, but these are often very specific to a particular reaction.

c) Formation of an imidoester which subsequently reacts with ammonia or an amine (Pinner method)

Nitriles resist condensation with bases containing nitrogen, but with alcohols they easily form imidoesters which can then be transformed into amidines (Equation 1.17).

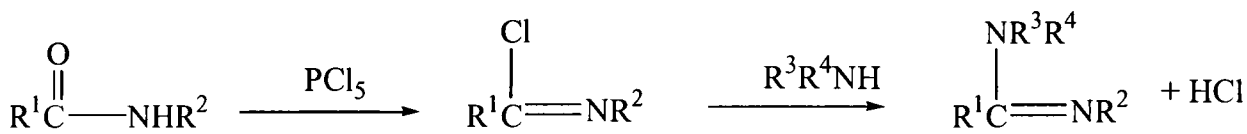


Equation 1.17

1.4.2.1.2 PREPARATION FROM AMIDES AND THIOAMIDES

a) Condensation of amides and amines in the presence of a halogenating agent

As shown in Equation 1.18, if monosubstituted amides are used, a variety of amidines can be formed depending on the choice of amine used for the second step.

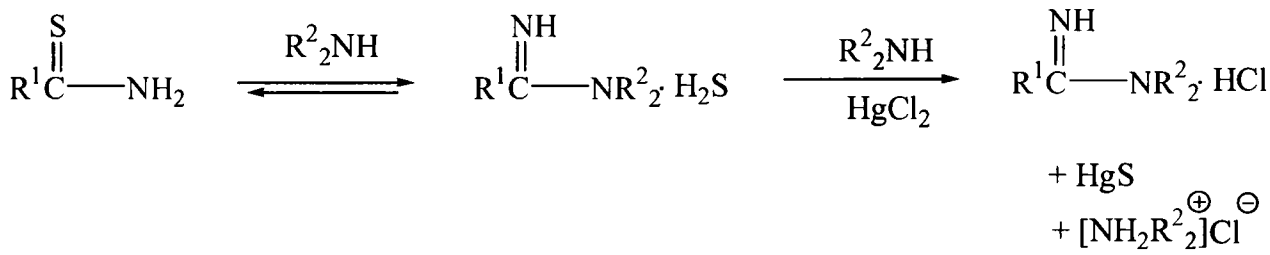


Equation 1.18

This method can also be used for disubstituted amides, but the lack of stability of N-unsubstituted imidochlorides (R' = H) makes the route unattractive for unsubstituted amides.

b) Synthesis from thioamides

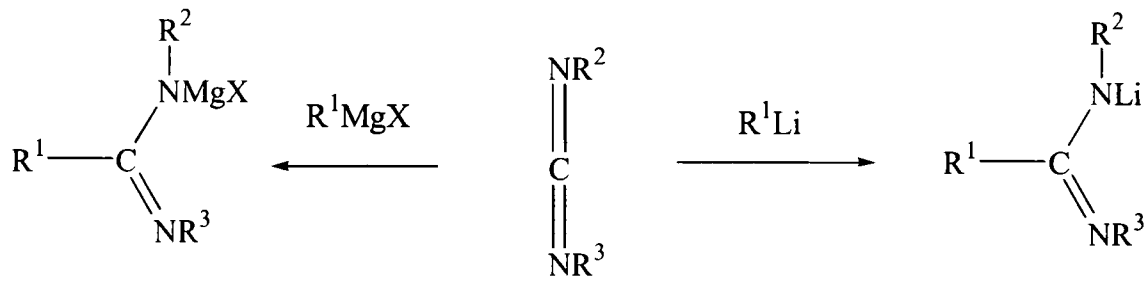
Condensation of ammonia or an amine with a thioamide leads to the formation of the H_2S salt of an amidine (Equation 1.19). The H_2S can then be removed using a mercury salt.



Equation 1.19

1.4.2.1.3 PREPARATION FROM CARBODIIMIDES

This method is particularly useful for the preparation of symmetrically disubstituted amidinates, and enables the R^1 and R^2 / R^3 groups to be varied easily. The addition of an alkali metal alkyl or Grignard reagent to a carbodiimide leads to simple addition of the alkyl to the central carbon atom (Equation 1.20).



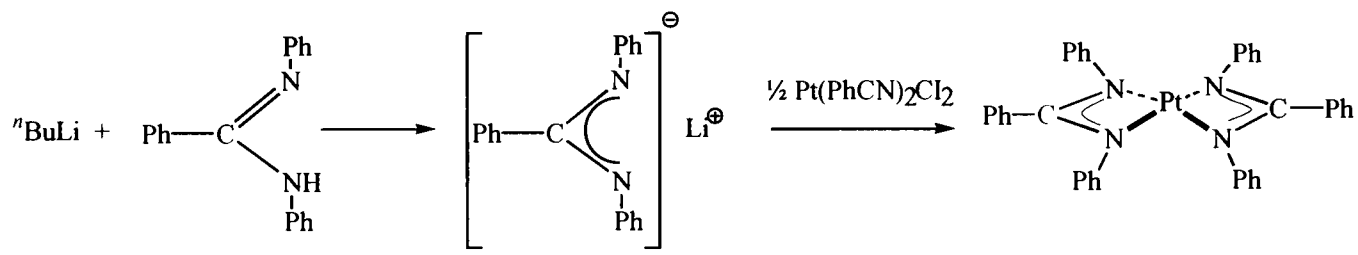
Equation 1.20

1.4.2.2 PREPARATION OF TRANSITION METAL AMIDINATE COMPLEXES

Five methods have been used in the synthesis of transition metal amidinate complexes.

a) Reaction of a metal amidinate with a metal halide

This is the most commonly used route for the preparation of transition metal amidinate complexes, and involves the elimination of MHal to form the desired complex. Most usually involve the use of a lithiated amidinate. The metallated amidinate may be generated *in-situ*, or else isolated and purified prior to reaction. A typical example is shown in Equation 1.21.[150]

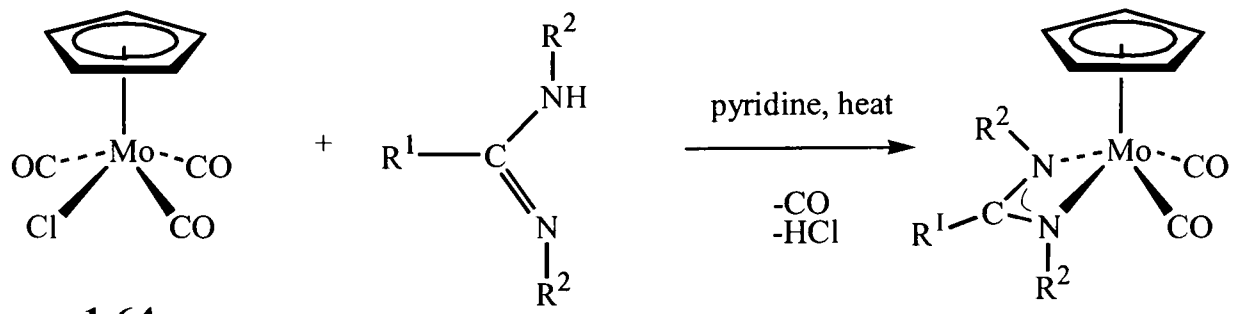


Equation 1.21

Alternatively, another Group 1 metal derivative may be used, (*e.g.* $K\{R^1C(NR^2)(NR^3)\}$), or silver or copper amidinates.[151]

b) Reaction of an amidine with a metal halide

Treatment of a suitable metal halide with an amidine in the presence of base yields the amidinate complex[152] (Equation 1.22). Alternatively, two equivalents of amidine can be used, giving the metal amidinate complex and amidine hydrochloride salt.[153]

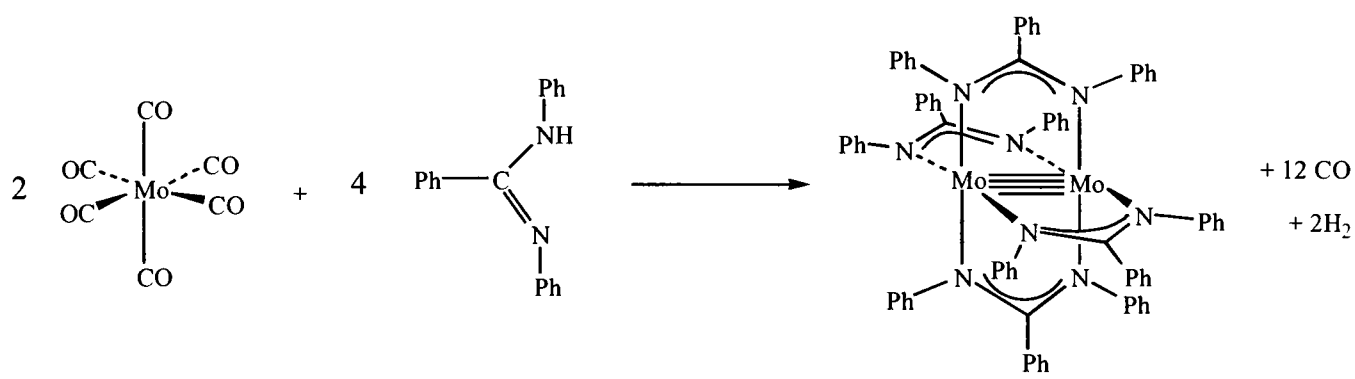


1.64 **1.65**

Equation 1.22

c) Reaction of an amidine with a metal carbonyl in air

This is not a commonly used route as it is rather limited. A rare example is given in Equation 1.23.[154]

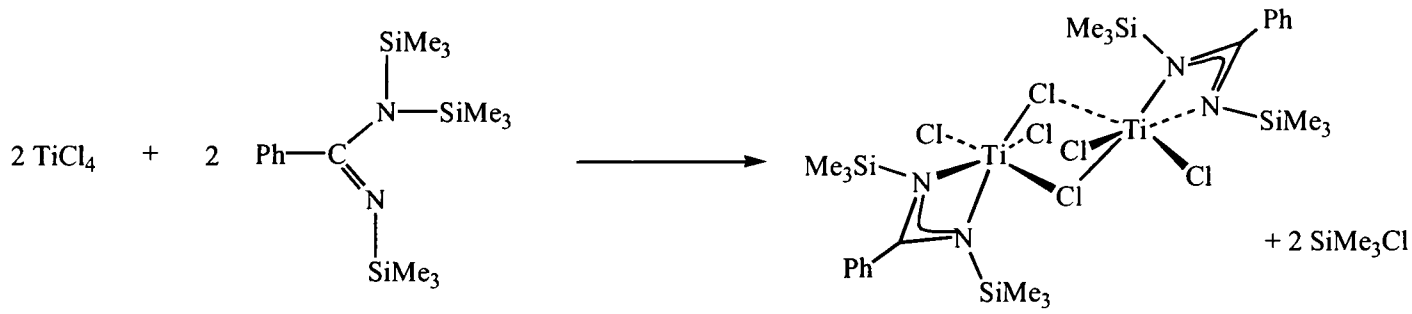


1.66 **1.67**

Equation 1.23

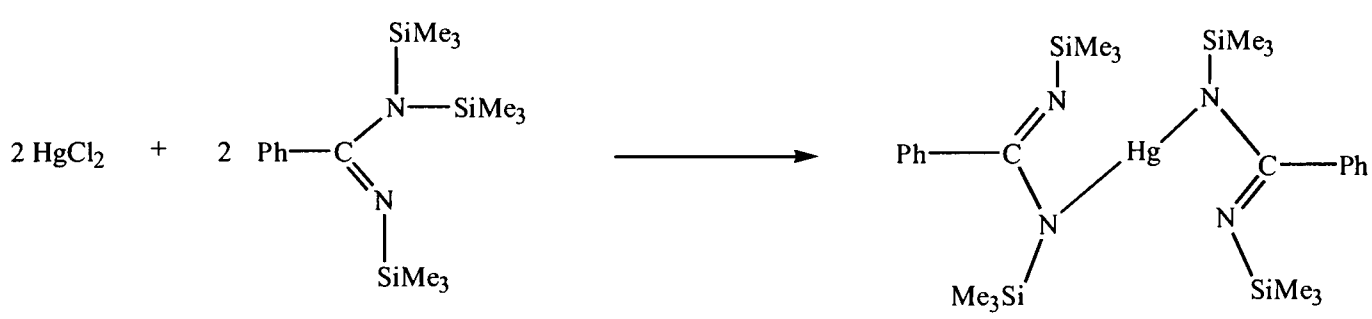
d) Reaction of a silyl-amidine with a metal halide

This route is more often used for the main group metals, and involves the elimination of trimethylsilyl chloride. However, this route has been used successfully to produce several transition metal complexes, as shown in Equations 1.24 and 1.25.



1.68

Equation 1.24

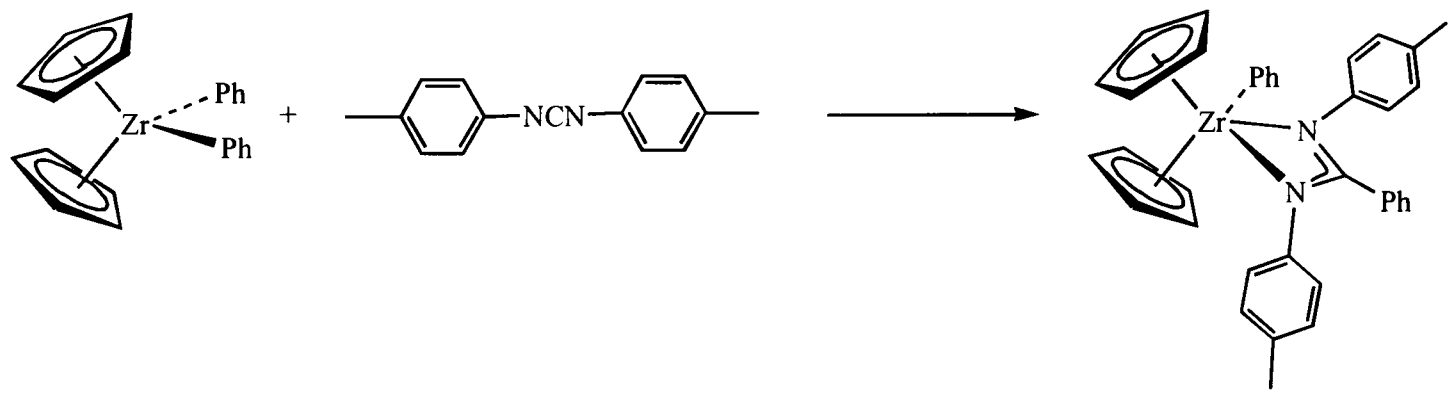


1.69

Equation 1.25

e) Reaction of a carbodiimide with a metal alkyl complex

Carbodiimides have been found to undergo insertion into metal-alkyl bonds to give amidinate complexes. This route has long been employed in the preparation of metal complexes with small alkyl groups,[155,156] but only a few benzamidinate complexes have been synthesised using this method (Equation 1.26).[157,158] Reaction with asymmetric carbodiimides affords the corresponding asymmetric amidinate complex.[126-128]



1.70

Equation 1.26

1.4.3 CHARACTERISATION OF THE AMIDINATE LIGAND

1.4.3.1 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

NMR spectroscopy is a very useful tool in the characterisation of amidinate complexes, due to the organic substituents normally present at the nitrogen and carbon atoms of the NCN unit. A number of solution studies of complexes containing monodentate amidinates indicate the occurrence of a fluxional intramolecular process involving a chelated intermediate (Figure 1.6).[112] There are also many examples of complexes in which chemically inequivalent (in the solid state structure) groups on the nitrogen atoms of an amidinate ligand are interconverted by dynamic processes in solution.[113]

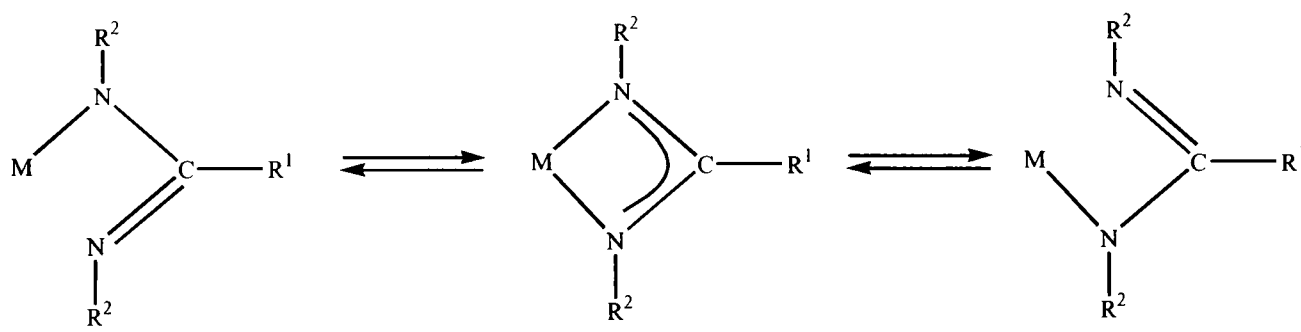


Figure 1.6 – Proposed mechanism for monodentate amidinate interconversion

1.4.3.2 INFRARED SPECTROSCOPY

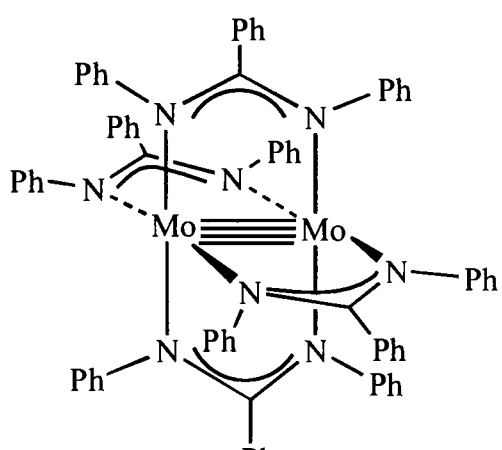
Infrared data are presented in most papers, but there has been relatively little analysis of these data. A rationalisation of the bands in *N,N'*- diaryl amidinate complexes has been carried out by Kilner *et al.*,[150] who designated bands in the *ca.* 1640 cm^{-1} region (assigned to $\nu_{asym}(NCN)$) and *ca.* 1588 cm^{-1} (assigned to $\nu(C=N)$) as "amidine I bands". "Amidine II" absorptions are described as a complex mixture of $\nu(C–N)$ and $\delta(N–H)$ modes, and are found in the region 1390 – 1520 cm^{-1}. Also of note is the "amidine III band" which may be described as a complex mixtures of $\nu(C–N)$, $\delta(N–H)$, and $\nu(C–C)$ vibrations, and occurs around 1240 – 1400 cm^{-1}.

1.4.4 RECENT WORK INVOLVING THE AMIDINATE LIGAND

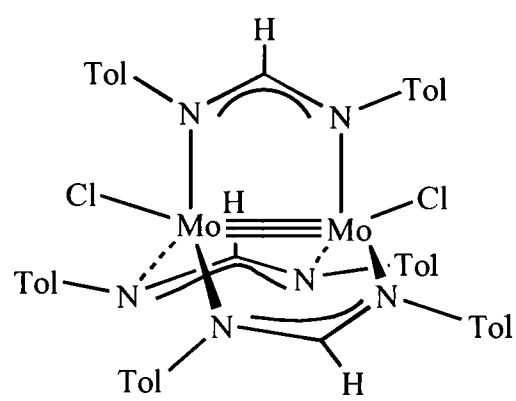
This Section will cover some of the more recent developments in the field of transition metal amidinate chemistry. Work reported before 1994 will not be covered as this has already been thoroughly reviewed.[113,150]

Interest in the Group 3 metals is fuelled by the importance of such complexes in the homogeneous catalysis of C–H, C–C, and C–X bond formation. Teuben *et al.* have prepared a number of bis(benzamidinato)yttrium complexes and have been able to demonstrate that complexes such as $[Y\{PhC(NSiMe_3)_2\}_2(\mu\text{-}H)]_2$ **(1.71)** can insert unsaturated substrates, and activate C–H bonds in such substrates, resulting in oligomerisation.[115,159]

Cotton *et al.* have recently described a series of new tetra- and triply- bonded dinuclear lantern complexes, of cobalt, iron, niobium, and molybdenum.[160-167] This includes an efficient route to triply-bonded dimolybdenum compounds.[167] The tetragonal lantern structure (**1.67**, Figure 1.7) is common in dinuclear transition metal complexes, in which the metals are bridged by four ligands, but triply-bridged lantern complexes have proved much harder to prepare. An example of such a triply-bridged complex is the molybdenum (II, III) complex $Mo_2\{\mu\text{-}HC(N\text{-}4\text{-}C_6H_4Me)_2\}_3Cl_2$ (**1.72**), as shown below (Figure 1.7).



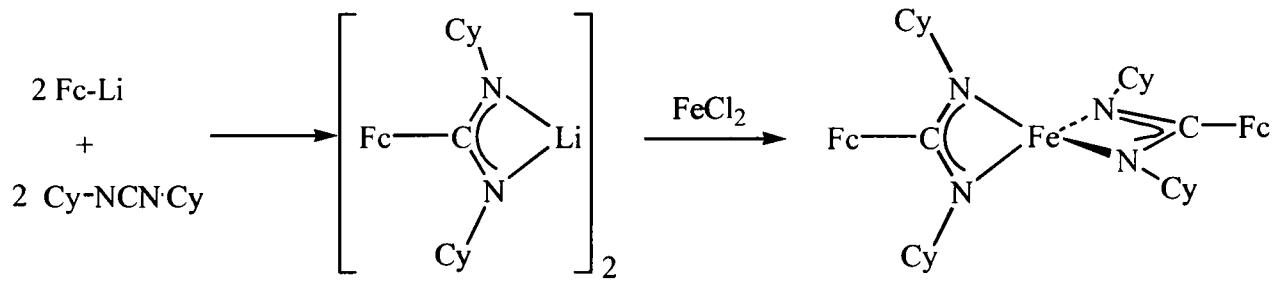
1.67



1.72

Figure 1.7 – Dinuclear complexes of molybdenum containing metal-metal bonds of bond order 4 (**1.67**) and 3½ (**1.72**)

An interesting new amidinate ligand containing a ferrocene unit has recently been synthesised by Arnold *et al.*[168] The reaction of ferrocenyllithium with dicyclohexylcarbodiimide, followed by reaction with $FeCl_2$ gave the new trimetallic complex $Fe\{FcC(NCy)_2\}_2$ (**1.73**) as shown in Equation 1.27. There is no electronic interaction between the iron centres, due to the orthogonality of the ferrocenyl and NCN units of the amidinate ligand.



1.73

(Fc = Fe(η-C_5H_5)(η-C_5H_4))

Equation 1.27

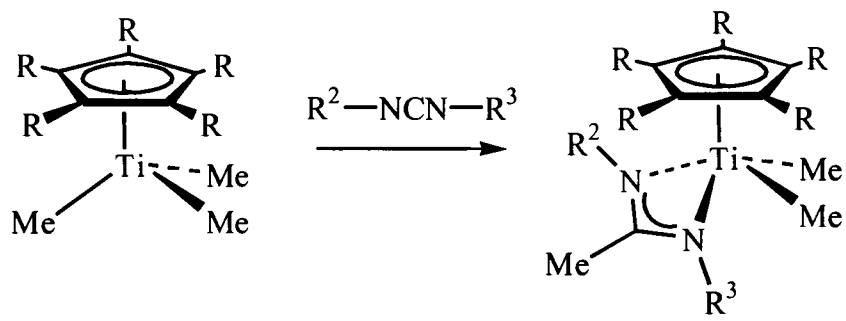
Amidinate ligands have been used as ancillary ligands to support imido complexes of transition metals, including titanium,[169-171] zirconium,[172] niobium,[173] and tantalum.[174]

1.4.5 USES OF A CYCLOPENTADIENYL-AMIDINATE LIGAND SET

The possibility of combining the cyclopentadienyl and amidinate ligands to form a new supporting ligand environment has been investigated. By far the most intensively studied complexes have been those of Group 4, owing to the similarities with the metallocene complexes, and the potential for Ziegler-Natta type polymerisation catalysts.

Green *et al.* first reported the complexes M(η-C_5R_5){$PhC(NSiMe_3)_2$}Cl_2 (R = H, M = Ti (**1.74**), Zr (**1.75**), Hf (**1.76**); R = Me, M = Ti (**1.77**), Zr (**1.78**)) in 1993[175] and since then a number of studies on these complexes have been undertaken, mainly focussing on their potential for olefin polymerisation catalysis.[176-179] More recently, Sita *et al.* have reported the facile synthesis of a varied library of complexes of the form Ti(η-C_5R_5){$MeC(NR^2)(NR^3)$}Me_2 (**1.79**

– **1.88**), by reaction of Ti(η-C_5R_5)Me_3 with a range of carbodiimides (Equation 1.28).[128]



R	R^2	R^3	
H	Cy	Cy	**1.79**
H	^{t}Bu	2,6-$C_6H_3Me_2$	**1.80**
H	^{t}Bu	Et	**1.81**
H	^{t}Bu	^{i}Pr	**1.82**
H	^{t}Bu	Cy	**1.83**
H	^{t}Bu	Ph	**1.84**
Me	Cy	Cy	**1.85**
Me	^{t}Bu	Et	**1.86**
Me	^{t}Bu	^{i}Pr	**1.87**
Me	^{t}Bu	Cy	**1.88**

Equation 1.28

The group has also synthesised and studied chiral complexes such as *meso*-(*R*,*S*)- and (*R*,*R*)- Ti(η-C_5R_5){MeC(N-1-phenylethyl)$_2$}Me_2 (R = H, (*R*,*S*) (**1.89**), (*R*,*R*) (**1.90**); R = Me, (*R*,*S*) (**1.91**), (*R*,*R*) (**1.92**)).[127]

In addition to these titanium complexes, much work has recently been published on zirconium cyclopentadienyl-amidinate dimethyl complexes. Structural characterisation[180] and stability studies[181] have been carried out on these systems, and variation of the amidinate ligand has been demonstrated to have a pronounced effect on the catalytic activity of these complexes towards olefins, including 1-hexene[182] and vinylcyclohexene,[183] and the cyclopolymerisation of nonconjugated dienes.[184]

In addition to complexes of the Group 4 metals, the cyclopentadienyl-amidinate ligand set has been used to support complexes of vanadium,[185] niobium,[186] tantalum,[186,187] ruthenium,[141,188] and iridium.[189] Transition metal imido complexes bearing a cyclopentadienyl-amidinate supporting ligand set have only been reported in the case of titanium. These are $Ti(\eta\text{-}C_5R_5)(N^tBu)\{PhC(NSiMe_3)_2\}$ (R = H (**1.93**), Me (**1.94**)).[190,191] The reactivity of these imido complexes has not been investigated.

1.5 Aim and Objectives of this Thesis

The study of the titanium imido bond continues to be an active avenue of investigation, and the facile modification of the cyclopentadienyl-amidinate ligand set provides considerable scope for its use as a supporting framework. The aim of the work described in this Thesis was to synthesise new titanium imido complexes supported by cyclopentadienyl-amidinate ligands, and to explore their reactivity towards unsaturated substrates.

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CHAPTER 2

Synthesis of Titanium Cyclopentadienyl Imido Amidinate Complexes

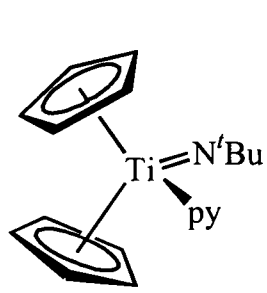
2.1 OVERVIEW

This Chapter explores the synthesis and characterisation of some new imidotitanium complexes supported by a cyclopentadienyl-amidinate auxiliary ligand set. It begins by introducing some work previously carried out in the Mountford group leading up to the development of the cyclopentadienyl-amidinate auxillary ligand set (Section 2.2). The rest of the Chapter is divided into two parts. The first part discusses the new *tert*-butylimido titanium complexes (Section 2.3), their syntheses (Section 2.3.1), and characterisation (Section 2.3.2). The second part deals with the new arylimido titanium complexes (Section 2.4), their syntheses (Section 2.4.1) and characterisation (Section 2.4.2).

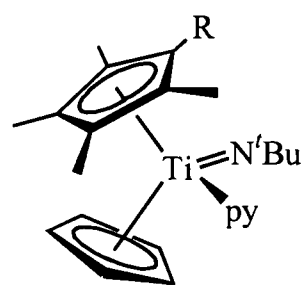
2.2 INTRODUCTION

This Section briefly summarises the recent developments in titanium imido chemistry which gave rise to the use of the cyclopentadienyl-amidinate ligand set as a supporting environment for imidotitanium reactivity studies.

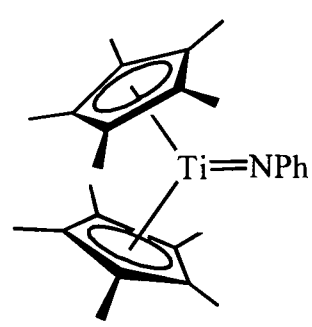
The bis(cyclopentadienyl) ligand set has been shown to stabilise monomeric Group 4 imido complexes, such as **2.1** – **2.4**.[1,2]



2.1

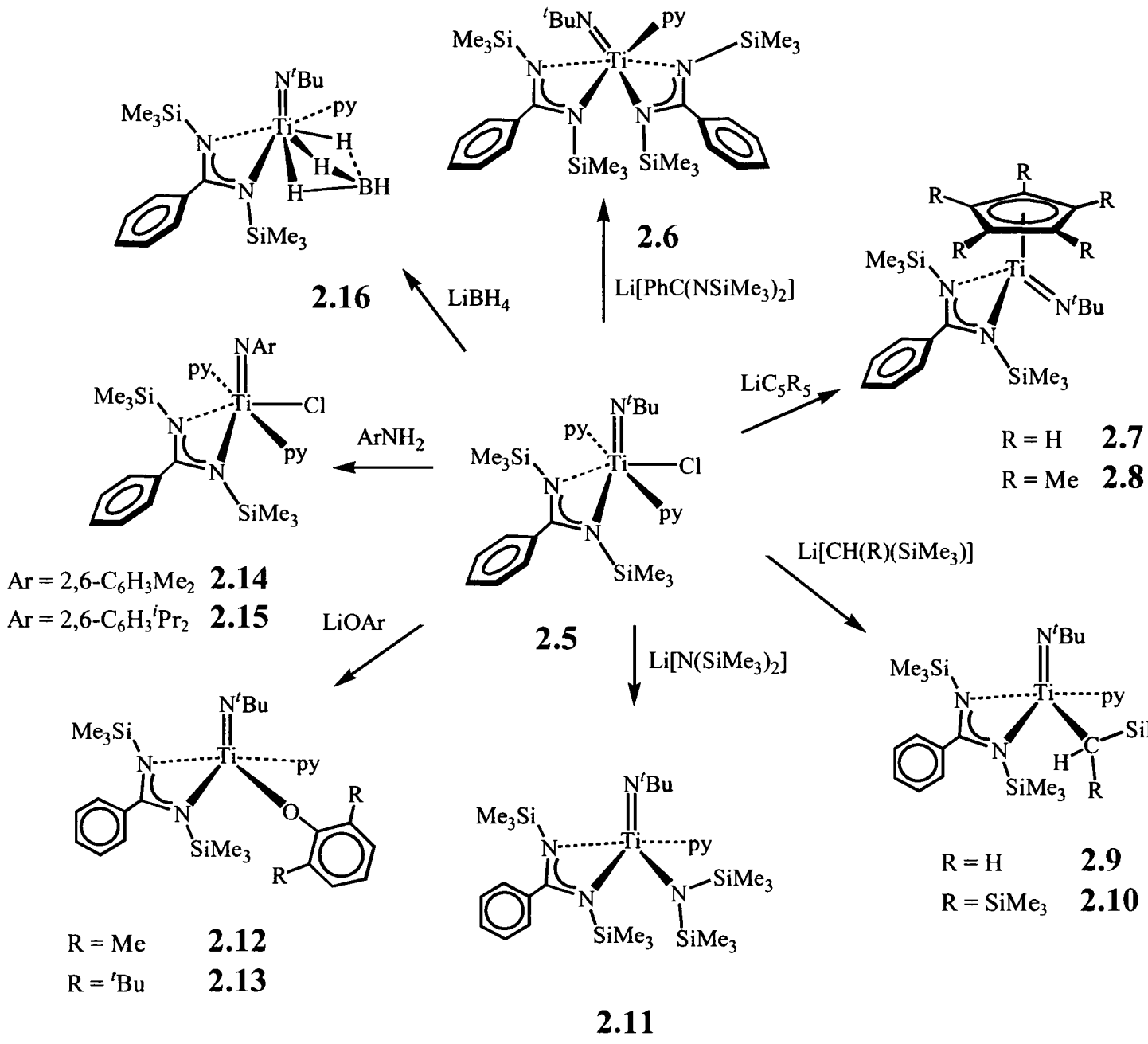


2.2 R = Me
2.3 R = Et



2.4

Another ligand found to be effective at stabilising the monomeric imido group is the amidinate *N,N'*-bis(trimethylsilyl)benzamidinate. A wide variety of imidotitanium complexes supported by this ligand have been synthesised, and a selection **(2.5 – 2.16)** are given in Scheme 2.1.[3-5]



Scheme 2.1 – Amidinate-supported imidotitanium complexes

The reactivity of the imido linkage in these and other[6] amidinate-supported complexes has never been explored.

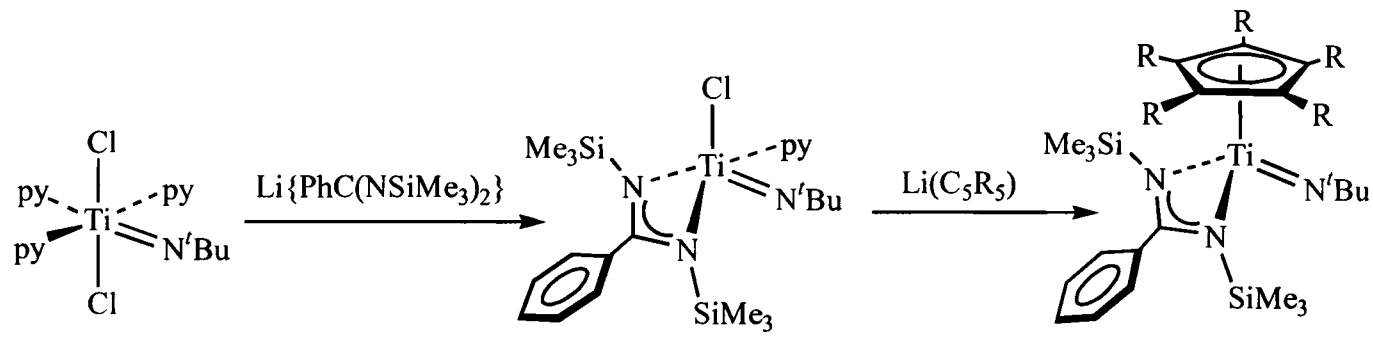
The potential for combining the cyclopentadienyl and amidinate ligands to form a supporting group has recently been explored in the context of olefin polymerisation catalysts, and the possibility of widely varying the electronic and steric properties of the ligand set has been demonstrated.[7-11] In addition to this desirable flexibility, the possibility of varying the N-substituent of the imido group presents a further dimension of reactivity which can be explored.

2.3 TITANIUM *TERT*-BUTYLIMIDO COMPLEXES

This Section describes the synthesis of novel *tert*-butylimido titanium complexes, bearing a cyclopentadienyl and an amidinate moiety as the ancillary ligand set.

2.3.1 SYNTHESIS OF TITANIUM *TERT*-BUTYLIMIDO COMPLEXES

The compound $Ti(N^tBu)Cl_2(py)_3$ **(2.17)**, which was first synthesised by Mountford *et al.*,[12] has proven to be a highly versatile point of entry into the chemistry of titanium imido complexes.[13] It was from this starting material that the first of the titanium imido complexes bearing a cyclopentadienyl-amidinate ancilliary ligand set was synthesised, *via* metathesis of the starting complex with the lithium salt of the amidinate, followed by the introduction of the cyclopentadienyl fragment (Equation 2.1).[4]



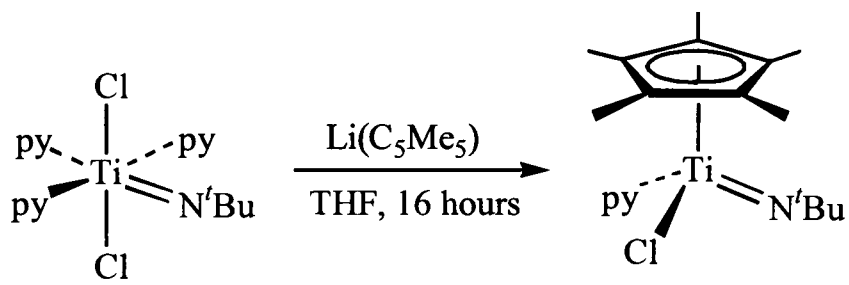
2.17 **2.5** R = H **2.7**, R = Me **2.8**

Equation 2.1

Another route involving $Ti(N^tBu)Cl_2(py)_3$ is to assemble the ancillary ligand set in the reverse order, *i.e.* to react the starting complex first with the appropriate lithium cyclopentadienide, followed by reaction with the lithium amidinate. This second pathway to the final product was found to give **2.8** in higher yield than the first route.[4] In attempting the synthesis of complexes bearing an *N,N'*-di-*iso*-propylacetamidinate ligand (*vide infra*), it was found that reaction of $Ti(N^tBu)Cl_2(py)_3$ with lithium *N,N'*-di-*iso*-propylacetamidinate resulted in a mixture of amidinate-containing products, possibly indicating that the reactivity of the $Ti(N^tBu)\{MeC(N^iPr)_2\}Cl(py)_n$ (n = 2 or 3) species formed is comparable to that of $Ti(N^tBu)Cl_2(py)_3$. For these reasons, the second route to the cyclopentadienyl imido amidinate products was favoured, and used exclusively.

The bonding nature of the imido group in the product of the reaction between $Ti(N^tBu)Cl_2(py)_3$ and the lithium cyclopentadienides is found to depend on both the steric properties of the cyclopentadienide and the reaction conditions used. This will be discussed in the following two subsections.

2.3.1.1 SYNTHESIS OF PENTAMETHYLCYCLOPENTADIENYL TITANIUM *TERT*-BUTYLIMIDO COMPLEXES

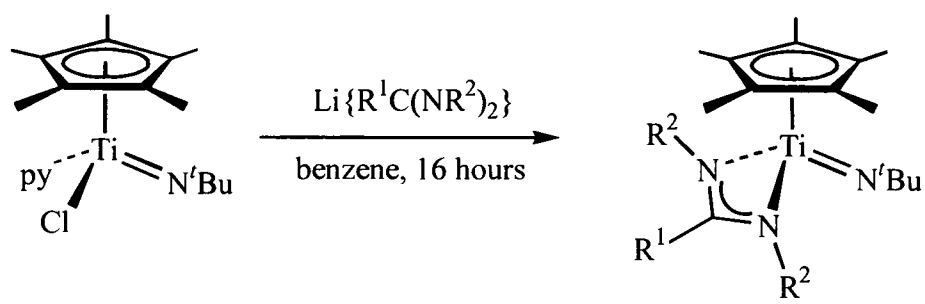


2.17 **2.18**

Equation 2.2

Reaction of Ti(N^{t}Bu)Cl$_2$(py)$_3$ with Li(C$_5$Me$_5$) afforded the known compound Ti(η-C$_5$Me$_5$)(N^{t}Bu)Cl(py) (**2.18**)[1] as a dark red powder in excellent yield (typically > 90 %). Heating this compound to assist in the removal of solvent had no effect on the stability of the product.

Reaction of Ti(η-C$_5$Me$_5$)(N^{t}Bu)Cl(py) with the lithium amidinates Li{PhC(NSiMe$_3$)$_2$} and Li{MeC(N^{i}Pr)$_2$} afforded the complexes Ti(η-C$_5$Me$_5$)(N^{t}Bu){PhC(NSiMe$_3$)$_2$} (**1**)[1] and Ti(η-C$_5$Me$_5$)(N^{t}Bu){MeC(N^{i}Pr)$_2$} (**2**) in excellent yield (both > 95 %), as shown in Equation 2.3.



2.18

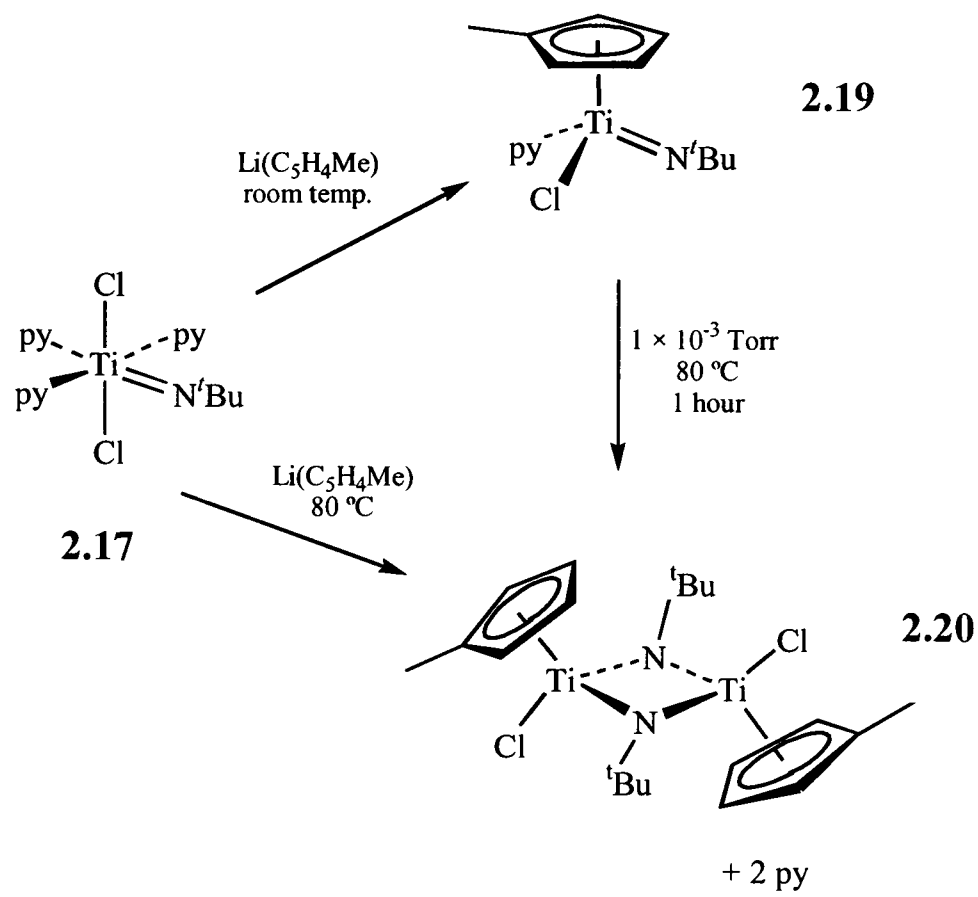
R^1 = Ph, R^2 = SiMe$_3$ **1**
R^1 = Me, R^2 = ^{i}Pr **2**

Equation 2.3

Compound **1** was obtained as a red powder, and **2** as a darker red waxy solid. Further purification was found to be unnecessary.

2.3.1.2 SYNTHESIS OF METHYLCYCLOPENTADIENYL TITANIUM *TERT*-BUTYLIMIDO COMPLEXES

In contrast to the C_5Me_5 systems, reaction of $Ti(N^tBu)Cl_2(py)_3$ (**2.17**) with $Li(C_5H_4Me)$ affords products which depend strongly on the reaction conditions (see Scheme 2.2).



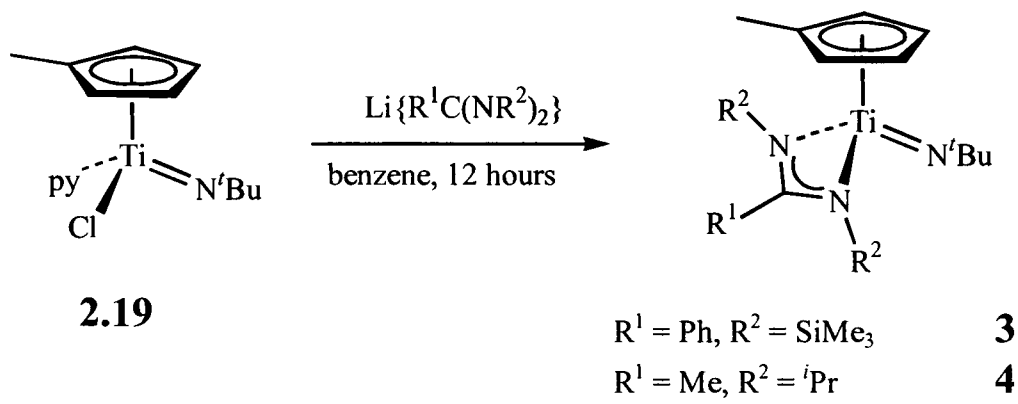
Scheme 2.2 – Reaction of $Ti(N^tBu)Cl_2(py)_3$ (**2.17**) with $Li(C_5H_4Me)$

When the volatiles were removed under reduced pressure at room temperature, the product was afforded as the red monomeric terminal imido species $Ti(\eta\text{-}C_5H_4Me)(N^tBu)Cl(py)$ (**2.19**) (typically 90 % yield), analogous to the reaction with $Li(C_5Me_5)$. When the volatiles were removed under

reduced pressure at 80 °C, the product was afforded as the pyridine-free dimeric complex $[Ti(\eta\text{-}C_5H_4Me)(\mu\text{-}N^tBu)Cl]_2$ (**2.20**) (yield: 90 %). This complex is also formed on heating $Ti(\eta\text{-}C_5H_4Me)(N^tBu)Cl(py)$ to 80 °C at 1×10^{-3} Torr for 1 hour. These species have been previously reported.[1]

2.3.1.2.1 REACTIVITY OF TERMINAL MONOMERIC *VERSUS* BRIDGING DIMERIC IMIDO SPECIES

The reactivity of **2.19** and **2.20** towards the lithium amidinates $Li\{R^1C(NR^2)_2\}$ (R^1, R^2 = Ph, $SiMe_3$; Me, ^{i}Pr) was found to be crucially dependent on the presence of pyridine. Thus, $Ti(\eta\text{-}C_5H_4Me)(N^tBu)Cl(py)$ reacted cleanly with $Li\{PhC(NSiMe_3)_2\}$ and $Li\{MeC(N^iPr)_2\}$ at room temperature to afford the cyclopentadienyl imido amidinate species $Ti(\eta\text{-}C_5H_4Me)(N^tBu)\{PhC(NSiMe_3)_2\}$ (**3**, > 95 % isolated yield) and $Ti(\eta\text{-}C_5H_4Me)(N^tBu)\{MeC(N^iPr)_2\}$ (**4**, > 95 % isolated yield) respectively (Equation 2.4)



2.19

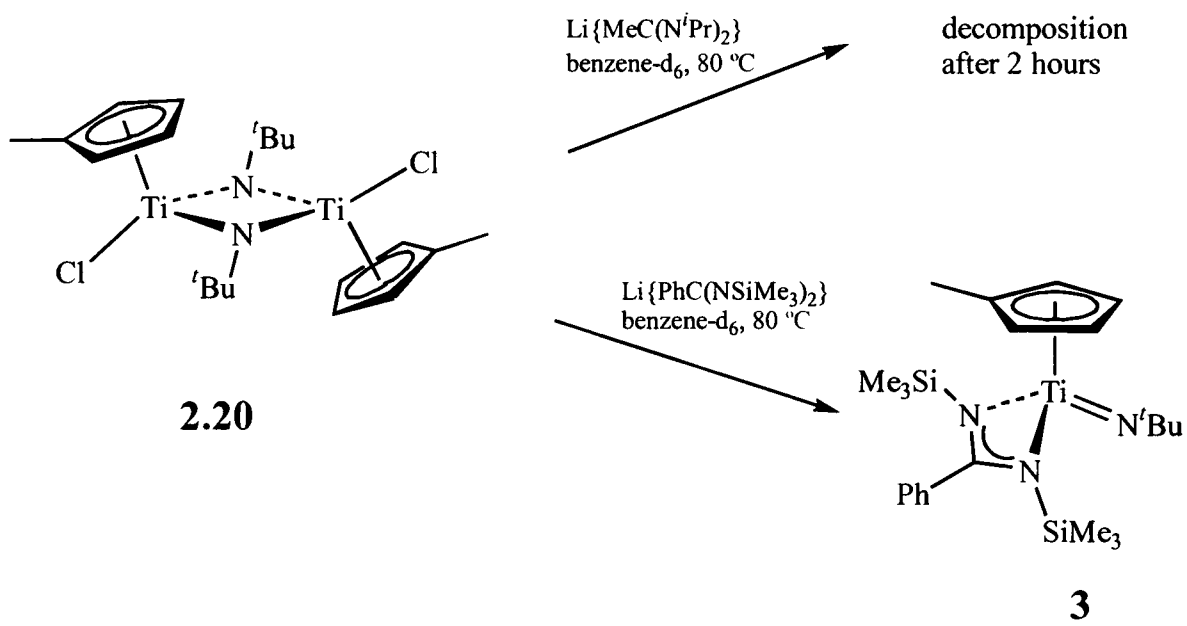
R^1 = Ph, R^2 = $SiMe_3$ **3**

R^1 = Me, R^2 = ^{i}Pr **4**

Equation 2.4

Compound **3** was obtained as a red solid, while **4** was produced as a red oil. Attempts to triturate or sublime **4** to afford a solid product proved unsuccessful.

Reaction of the dimeric precursor with lithium amidinates in benzene did not occur at room temperature. At 80 °C, reaction occurred as given in Scheme 2.3.



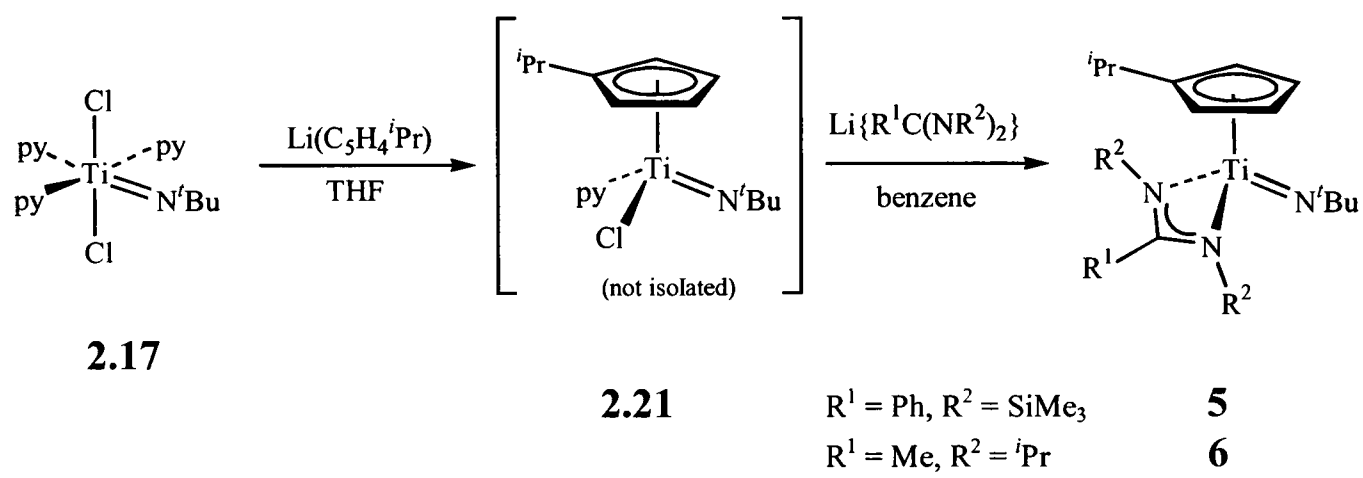
Scheme 2.3 – Reaction of $[Ti(\eta\text{-}C_5H_4Me)(\mu\text{-}N^tBu)Cl]_2$ **(2.20)** with lithium amidinates

In-situ NMR tube scale experiments showed the formation of a dimeric intermediate presumed to be $Ti(\eta\text{-}C_5H_4Me)\{PhC(NSiMe_3)_2\}(\mu\text{-}N^tBu)_2$ $Ti(\eta\text{-}C_5H_4Me)Cl$, although this species was not isolated. The need for more forcing reaction conditions is ascribed to the lack of a labile ligand in the coordination sphere of the metal, requiring the amidinate to attack a more crowded centre. In the reaction of **2.19**, the pyridine molecule can dissociate from the complex to give an intermediate with a lower coordination number, facilitating approach of the amidinate.

2.3.1.3 SYNTHESIS OF *ISO*-PROPYLCYCLOPENTADIENYL TITANIUM *TERT*-BUTYLIMIDO COMPLEXES

The pair of complexes $Ti(\eta\text{-}C_5H_4{}^iPr)(N^tBu)\{PhC(NSiMe_3)_2\}$ **(5)** and $Ti(\eta\text{-}C_5H_4{}^iPr)(N^tBu)\{MeC(N^iPr)_2\}$ **(6)** were also synthesised using the same

methodology, but the intermediate species Ti(η-$C_5H_4{}^iPr$)(N^{t}Bu)Cl(py) (**2.21**) was not isolated. **2.21** has been previously isolated and characterised.[1] Purification of **5** and **6** was performed *via* tube sublimation, affording the products as a red powder (120 °C, 2 × 10^{-5} Torr, 3 hours, 50 % yield) and a red oil (80 °C, 2 × 10^{-5} Torr, 3 hours, 65 % yield) respectively (Equation 2.5).



2.17

2.21

R^1 = Ph, R^2 = SiMe$_3$ **5**

R^1 = Me, R^2 = ^{i}Pr **6**

Equation 2.5

2.3.2 CHARACTERISATION OF TITANIUM *TERT*-BUTYLIMIDO COMPLEXES

Compounds **1** – **6** were fully characterised by ^{1}H and ^{13}C-{^{1}H} NMR, and IR spectroscopies, EI mass spectrometry, and elemental analysis. In addition, Ti(η-C_5H_4Me)(N^{t}Bu){PhC(NSiMe$_3$)$_2$} (**3**) was structurally characterised by single crystal X-ray diffraction. Full characterising data are given in Chapter 8 and Appendix A.

2.3.2.1 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPIC STUDIES

Compounds **1** – **6** were characterised by ^{1}H and ^{13}C-{^{1}H} NMR spectroscopy. In addition, Ti(η-C_5Me_5)(N^{t}Bu){PhC(NSiMe$_3$)$_2$} (**1**) and Ti(η-C_5H_4Me)

(N^tBu){$PhC(NSiMe_3)_2$} (**3**) were studied in the presence of pyridine using low temperature ^1H NMR spectroscopy.

2.3.2.1.1 DISCUSSION OF NMR SPECTRA

The ^1H and ^{13}C-{^1H} NMR spectra of **1** – **6** are all sharp and well resolved at room temperature. As they all conform to one of two patterns, discussion will be confined to two examples, Ti(η-C_5Me_5)(N^tBu){$MeC(N^iPr)_2$} (**2**) and Ti(η-C_5H_4Me)(N^tBu){$PhC(NSiMe_3)_2$} (**3**), which serve to illustrate the features of all six.

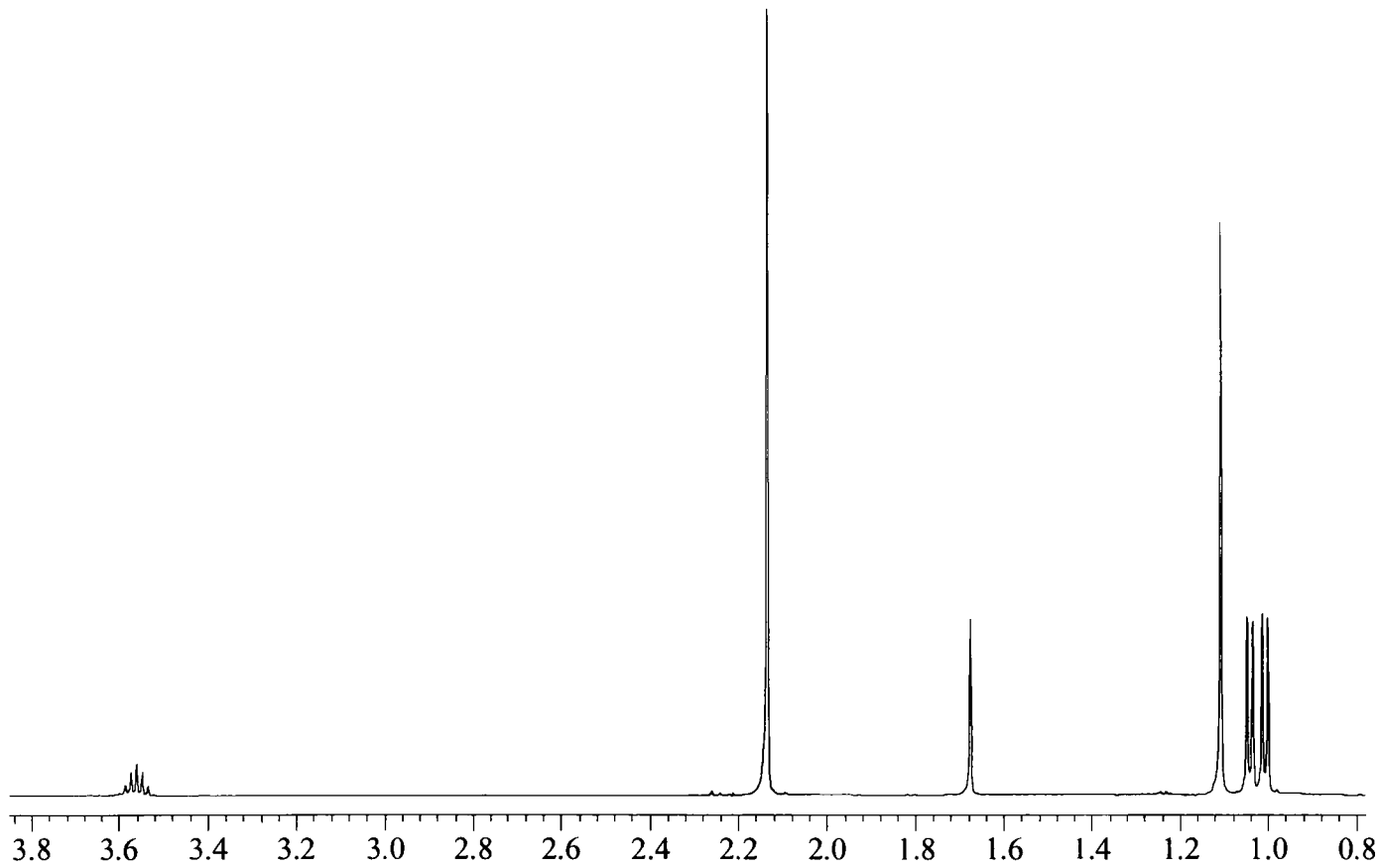


Figure 2.1 – 500.0 MHz ^1H NMR spectrum of Ti(η-C_5Me_5)(N^tBu){$MeC(N^iPr)_2$} (**2**) in benzene-d_6

In the ^1H NMR spectrum of **2** in benzene-d_6 (Figure 2.1), the singlet at 1.10 ppm (integration 9 H) corresponds to the *tert*-butyl group of the imido moiety. The singlet at 2.13 ppm (integration 15 H) is assigned to the 15 equivalent protons on the C_5Me_5 ligand. The apparent septet at 3.56 ppm (integration 2

H) is assigned to the methine protons of the *iso*-propyl groups on the amidinate, while the (pair of) doublets at 1.04 and 1.01 ppm (integration 6 H each) are assigned to the diastereotopic methyl protons of the same groups. The peak at 1.68 ppm (integration 3 H) is assigned to the methyl protons on the backbone of the amidinate. This pattern of peaks is typical for the $MeC(N^iPr)_2$ ligand in all three complexes **2**, **4**, and **6**, and is consistent with the molecule possessing C_s symmetry in solution.

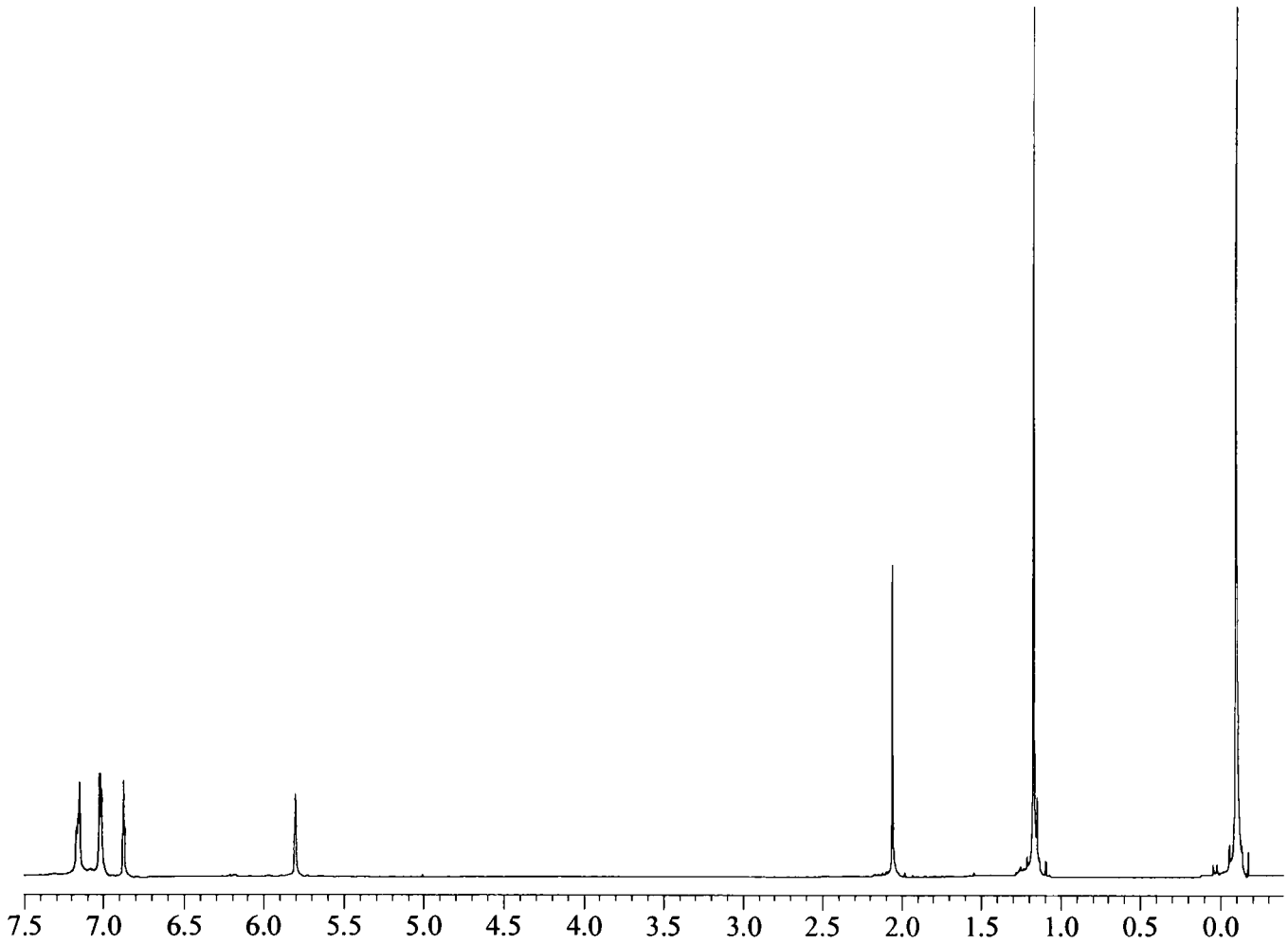


Figure 2.2 – 500.0 MHz ^{1}H NMR spectrum of $Ti(\eta\text{-}C_5H_4Me)(N^tBu)\{PhC(NSiMe_3)_2\}$ (**3**) in benzene-d_6

The ^{1}H NMR spectrum of **3** (Figure 2.2) displays singlets at 1.17 ppm (integration 9 H) and 2.06 ppm (3 H) which correspond to the *tert*-butyl group of the imido and the methyl group of the C_5H_4Me ligand respectively. The resonances at 6.78 ppm (integration 2 H) and 5.80 ppm (integration 2 H) are assigned respectively to the β- and α- protons (with respect to the methyl

group) of the C_5H_4Me ligand, and this assignment was confirmed by an nOe experiment, irradiating on the methyl resonance. The benzamidinate ligand produces a singlet for the two equivalent $SiMe_3$ groups (-0.10 ppm, integration 18 H), a multiplet for the *ortho-* and *para-* protons (7.16 ppm, integration 3 H), and a multiplet further upfield for the *meta-* protons (7.03 ppm, integration 2 H).

As has been mentioned previously, the difference in chemical shift between C_α and C_β ($\Delta\delta$) of the *tert*-butyl group of the imide gives a measure of the electron density at nitrogen.[14,15] Comparison of $\Delta\delta$ for complexes **1** – **6** reveals only slight variation across the series, as shown in Table 2.1.

Table 2.1 – Compounds **1** – **6** in order of increasing $\Delta\delta$

Compound	Supporting Ligands	C_α	C_β	$\Delta\delta$
4	C_5H_4Me, $MeC(N^iPr)_2$	66.81	32.88	**33.93**
6	$C_5H_4{}^iPr$, $MeC(N^iPr)_2$	66.91	32.85	**34.06**
1	C_5Me_5, $PhC(NSiMe_3)_2$	67.13	32.96	**34.17**
3	C_5H_4Me, $PhC(NSiMe_3)_2$	66.95	32.74	**34.21**
2	C_5Me_5, $MeC(N^iPr)_2$	66.03	31.80	**34.23**
5	$C_5H_4{}^iPr$, $PhC(NSiMe_3)_2$	67.04	32.69	**34.35**

The $\Delta\delta$ range (34.4 – 33.9) is comparable to the values found for some other previously reported *tert*-butylimido titanium complexes dissolved in benzene-d_6,[16] which are given in Table 2.2.

Table 2.2 – Values of Δδ for some literature compounds

Compound	C_α	C_β	Δδ
$Ti(\eta\text{-}C_5Me_5)(N^tBu)Cl(py)$ (**2.18**)	68.5	32.5	**36.0**
$Ti(\eta\text{-}C_5H_5)_2(N^tBu)(py)$ (**2.1**)	69.0	32.2	**36.8**
$Ti(\eta\text{-}C_5Me_5)(\eta\text{-}C_5H_5)(N^tBu)(py)$ (**2.2**)	68.7	33.0	**35.2**

The data show a clear trend of decreasing Δδ (*i.e.* increasing nucleophilicity of the imido nitrogen) upon replacing one of the cyclopentadienyl ligands of the titanocene compounds (**2.1**) and (**2.2**) with an amidinate ligand. This suggests that the amidinate has a stronger donor ability than the cyclopentadienyl ligand. However, no clear trend can be seen within the compounds **1** – **6**. This suggests that the effect on the electron density at the imido nitrogen by the supporting ligand set cannot be simply reduced to the sum of a cyclopentadienyl contribution and an amidinate contribution.

2.3.2.1.2 Low temperature NMR studies

The pseudo four-coordinate titanium imido systems **1** – **6** are formally 16 valence electron compounds, suggesting that coordination of a good σ- donor Lewis base such as pyridine may be favoured at low temperature. The synthetic pathway used in their synthesis involved the removal of pyridine under reduced pressure at room temperature, so *in-situ* NMR tube scale studies of the stoichiometric reaction between the complexes $Ti(\eta\text{-}C_5Me_5)(N^tBu)\{PhC(NSiMe_3)_2\}$ (**1**) and $Ti(\eta\text{-}C_5H_4Me)(N^tBu)\{PhC(NSiMe_3)_2\}$ (**3**) and pyridine were carried out at low temperature in dichloromethane-d_2.

It was found that at -90 °C in the absence of pyridine, no significant change was observed in the ^{1}H NMR spectrum of either compound. Upon addition of one equivalent of pyridine to the sample of **1** the spectrum remained unchanged, even upon cooling to -95 °C. Upon addition of one equivalent of pyridine to the sample of **3**, the room temperature ^{1}H NMR spectrum remained unchanged. Upon cooling to -90 °C, however, coordination of pyridine to the complex was observed (see Figure 2.3 below).

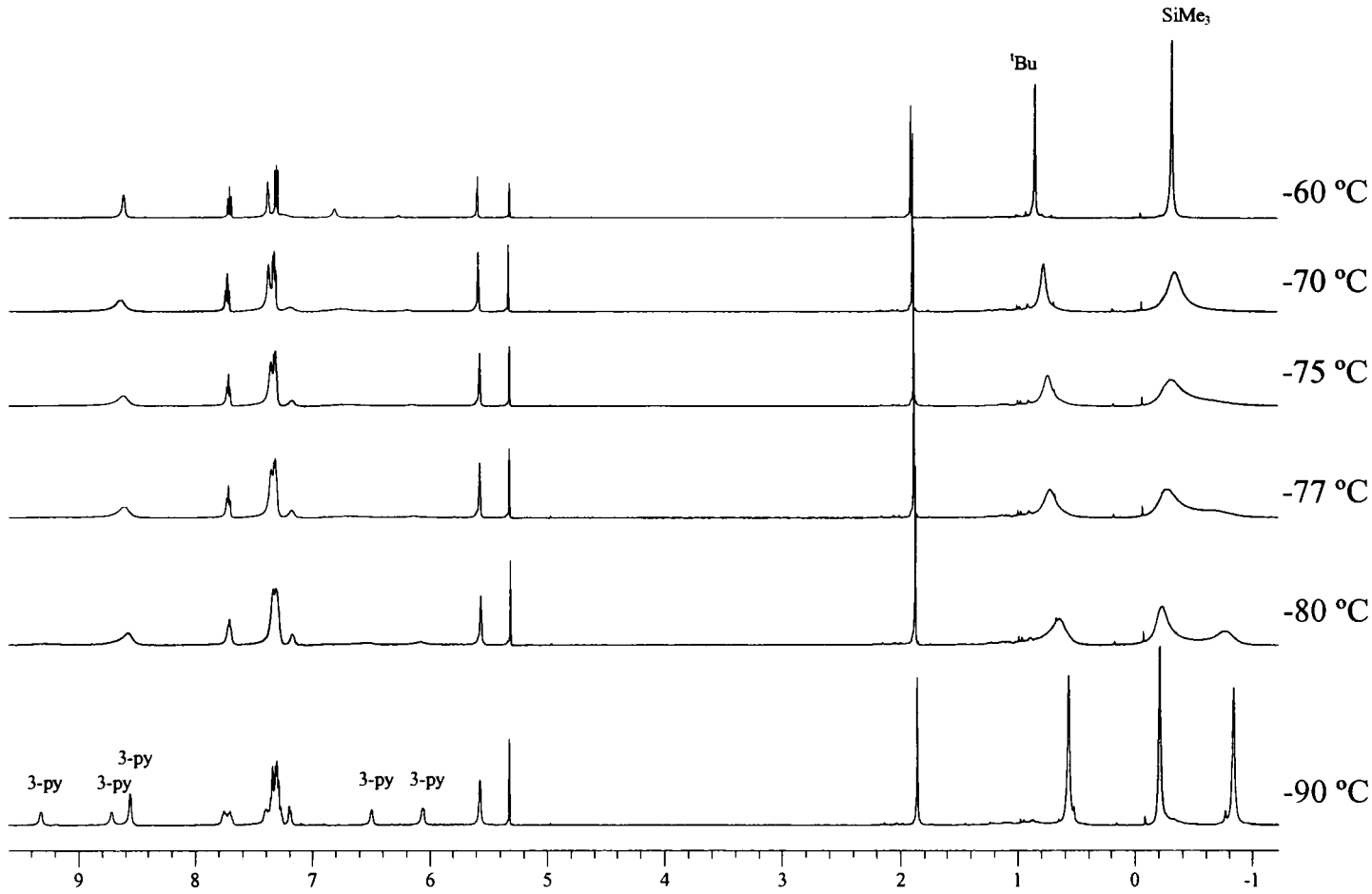
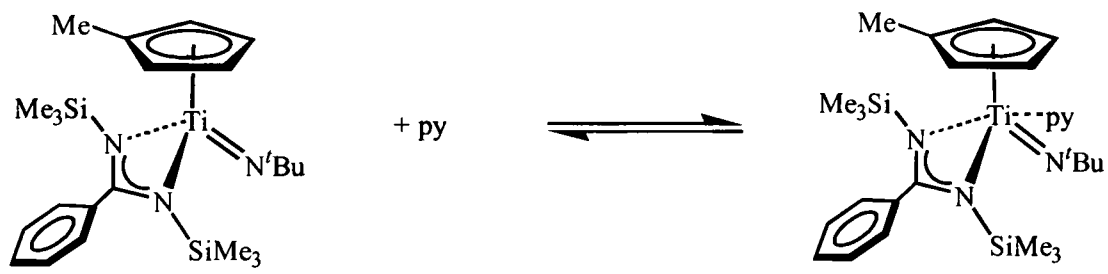


Figure 2.3 – Low temperature 500.0 MHz ^{1}H NMR spectra of $Ti(\eta\text{-}C_5H_4Me)(N^tBu)\{PhC(NSiMe_3)_2\}$ (**3**) in dichloromethane-d_2 the presence of pyridine

It can be clearly seen from the decoalesence of the $SiMe_3$ singlet at -0.26 ppm (-60 °C) to give a pair of singlets at -0.21 ppm and -0.84 ppm (-90 °C) that at low temperature, pyridine forms an adduct with **3** in which the C_s symmetry of the molecule is removed. This is illustrated in Equation 2.6.



3 **3-py**

Equation 2.6

Figure 2.3 shows how **3** is in dynamic equilibrium with **3-py** as the temperature is lowered. Both complexes are clearly present at -79 °C by comparison with the static spectra of both complexes. At room temperature the only species present is **3**, as the TΔS term promoting the dissociation of **3-py** is dominant. At -90 °C, **3-py** is the favoured species, with ΔH_f (Ti–N) the dominating factor. The broadening of the peaks above -90 °C cannot be used to extract kinetic parameters, as has been done for other imidotitanium complexes.[3] This is due to the overlap of peaks from **3** and **3-py**, which prevents determination of their relative concentrations.

It is noteworthy that between -80 °C and -90 °C the resonances from the coordinated pyridine in **3-py** are observed to decoalesce and sharpen, indicating the freezing out of the rotation about the Ti–N bond. This suggests a degree of steric crowding around the metal centre, which is consistent with the observation that the more crowded Ti(η-C_5Me_5)(N^{t}Bu){PhC(NSiMe_3)$_2$} (**1**) does not form the analogous complex **1-py**, even at -95 °C.

2.3.2.2 X-RAY CRYSTAL STRUCTURE OF Ti(η-C_5H_4Me)(N^tBu) {$PhC(NSiMe_3)_2$} (3)

A red crystal of **3** suitable for analysis by single crystal X-ray diffraction was grown from a saturated solution in pentane at -30 °C. The data were collected and the structure solved by Dr. L. H. Rees of this department. Figure 2.4 shows the molecular structure, and Table 2.3 summarises some important bond lengths and angles. Full details are provided in Appendix A.

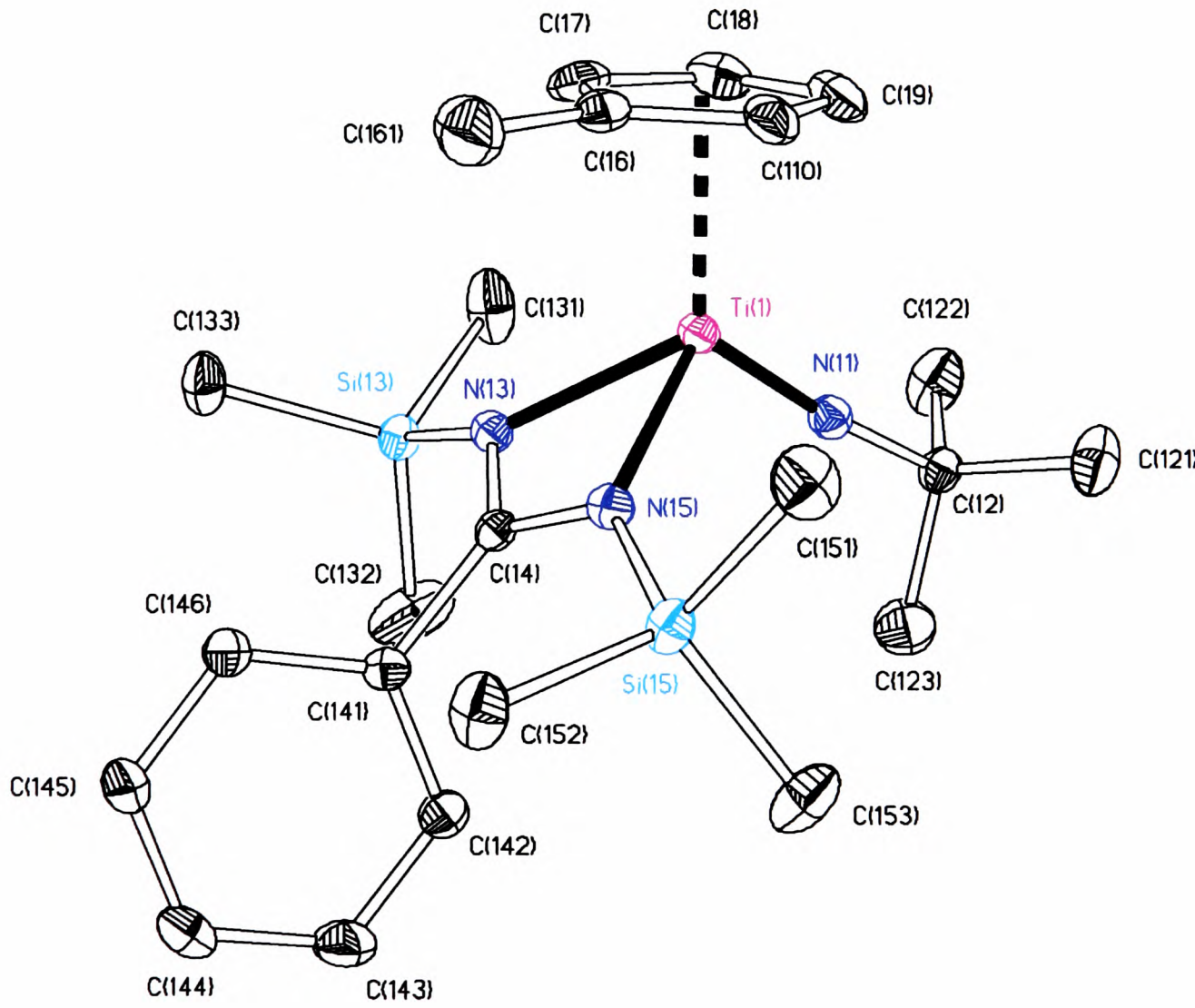


Figure 2.4 – Thermal ellipsoid plot (30 % probability) of Ti(η-C_5H_4Me)(N^tBu){$PhC(NSiMe_3)_2$} (**3**). H atoms are omitted for clarity

Table 2.3 – Selected bond lengths (Å) and angles (°) for

$Ti(\eta\text{-}C_5H_4Me)(N^tBu)\{PhC(NSiMe_3)_2\}$ (**3**)

Ti(1) – $Cp_{(cent)}$	2.082	Ti(1) – N(11) – C(12)	174.28(19)
Ti(1) – N(11)	1.708(2)	$Cp_{(cent)}$ – Ti(1) – N(11)	124.7
Ti(1) – N(13)	2.098(2)	$Cp_{(cent)}$ – Ti(1) – N(13)	118.6
Ti(1) – N(15)	2.111(2)	$Cp_{(cent)}$ – Ti(1) – N(15)	119.7
		N(11) – Ti(1) – N(13)	105.6(1)
		N(13) – Ti(1) – N(15)	65.04(8)

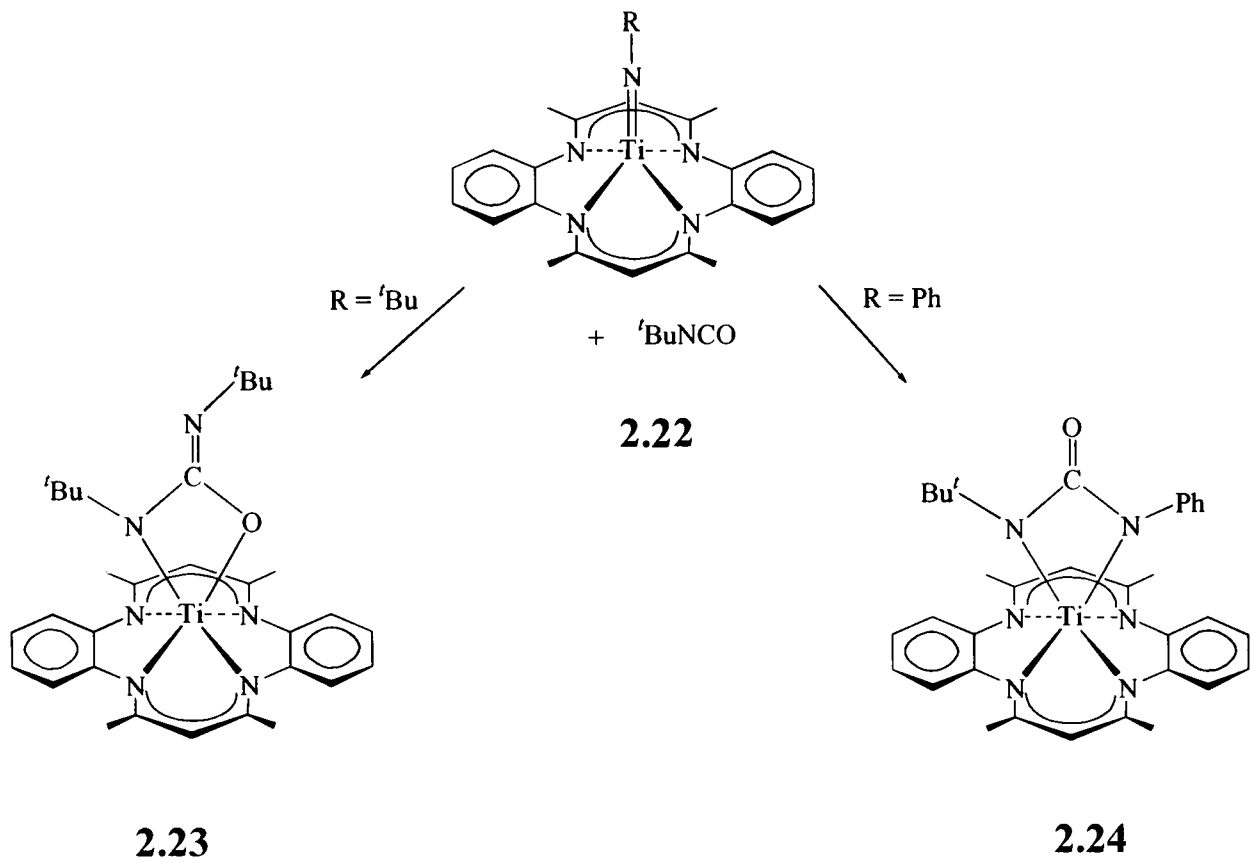
The compound adopts a three-legged piano stool structure, as is typical for half-sandwich complexes. The $Cp_{(cent)}$–Ti bond length is typical of bond lengths found for other cyclopentadienyl-titanium(IV) complexes (2.0 – 2.1 Å).[17,18] The amidinate ligand binds symmetrically to titanium, with bond lengths within the range found for other titanium (IV) benzamidinate complexes (1.986(2) – 2.194(2) Å for six examples[19-22]). The methyl group of the cyclopentadienyl ligand points over the amidinate, away from the imido group. This reflects the greater steric demand of the imido moiety which, with a bond length of 1.708(2) Å, is much closer to the metal centre than the amidinate. The imido bond length falls within the range found for other imidotitanium complexes (1.68 – 1.77 Å)[13,23] The angle about the imido nitrogen is 174.28(19) °, demonstrating that the nitrogen is donating all four available electrons to titanium. Again, this value is typical of that found for other imidotitanium complexes.[13]

2.3.3 CONCLUSIONS

It has previously been shown that *tert*-butylimido complexes of titanium bearing a cyclopentadienyl-amidinate auxiliary ligand set can be synthesised by simple salt metathesis reactions of $Ti(N^tBu)Cl_2(py)_3$ with lithium salts of the ligands. The work reported in this Chapter has developed this chemistry, both by improving the yield of the synthesis using an alternative route, and by extending the range of known compounds. In addition, the reaction between $Ti(\eta\text{-}C_5H_4Me)(N^tBu)\{PhC(NSiMe_3)_2\}$ (**3**) and pyridine has been studied at low temperatures.

2.4 TITANIUM ARYLIMIDO COMPLEXES

It has been shown that the imido N- substituent can play a crucial role in determining the reactivity of titanium imido species. One example of this is the reaction of the tetraazaannulene-supported imidotitanium complexes $Ti(NR)(Me_4taa)$ (H_2Me_4taa = tetramethyldibenzotetraaza[14]annulene; R = ^{t}Bu, Ph) with *tert*-butyl isocyanate (Scheme 2.4).[24] It was therefore decided to synthesise cyclopentadienyl imido amidinate complexes bearing an arylimido functionality, to explore the differences in reactivity, if any, between the two classes of complex.



Scheme 2.4 – Reaction of Ti(NR)(Me_4taa) (R = ^{t}Bu, Ph) with ^{t}BuNCO

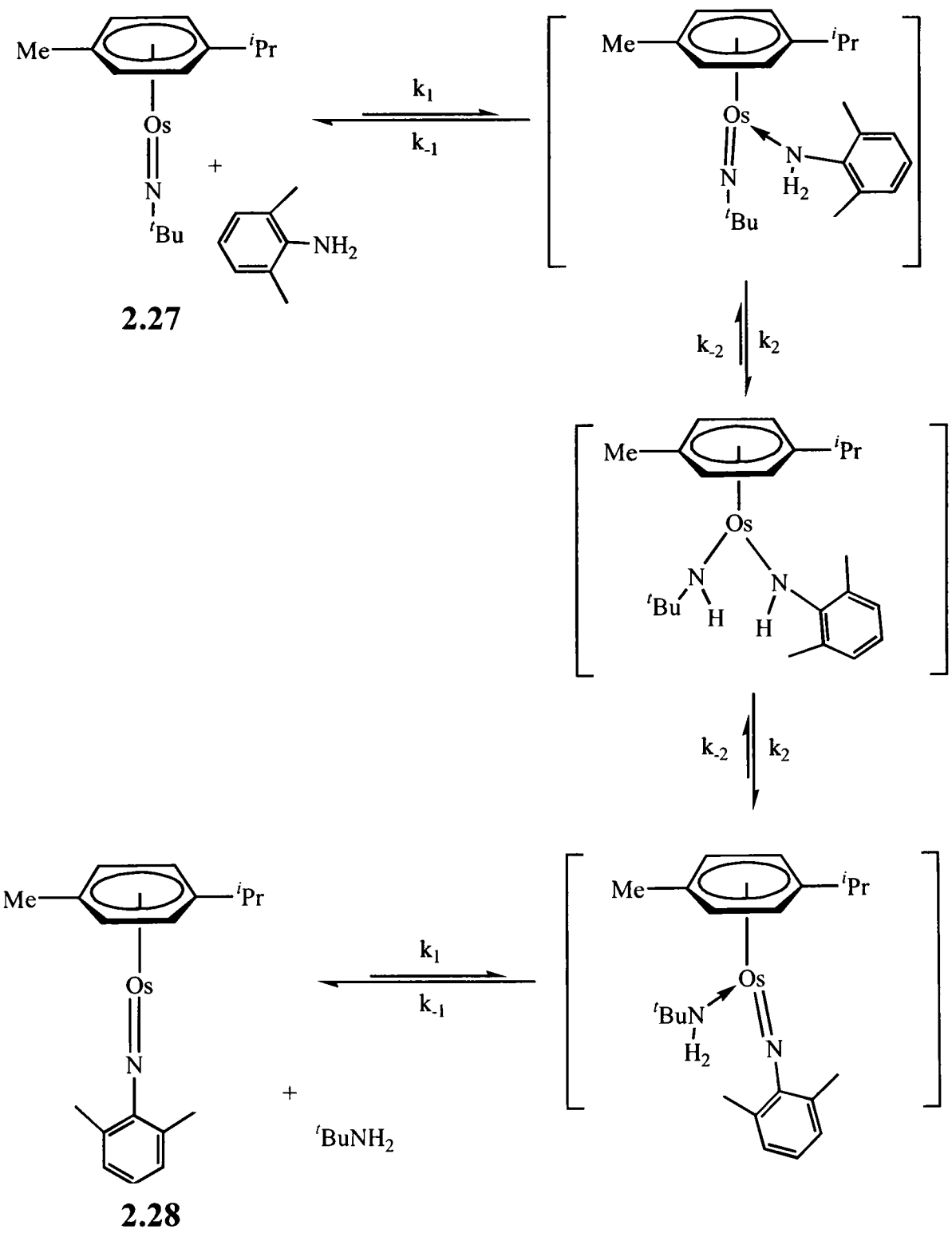
2.4.1 SYNTHESIS OF TITANIUM ARYLIMIDO COMPLEXES

Two main synthetic routes were employed in the synthesis of the arylimido titanium species. These were (i) amine-imido exchange reactions with *tert*-butylimido titanium complexes already bearing cyclopentadienyl-amidinate ancillary ligands, and (ii) assembly of the ancillary ligand set onto arylimido titanium species of the form $Ti(NR)Cl_2(py)_3$ (R = 2,6-$C_6H_3Me_2$, 4-C_6H_4Me) *via* lithium salt metathesis.

2.4.1.1 AMINE-IMIDO EXCHANGE OF Ti(η-C_5R_4Me)(N^{t}Bu){$R^1C(NR^2)_2$} (R = H, Me, R^1, R^2 = Ph, $SiMe_3$; Me, ^{i}Pr)

Bergman *et al.*, first reported the phenomenon of amine-imido exchange in 1991.[25] These researchers showed that the late transition metal imido complex

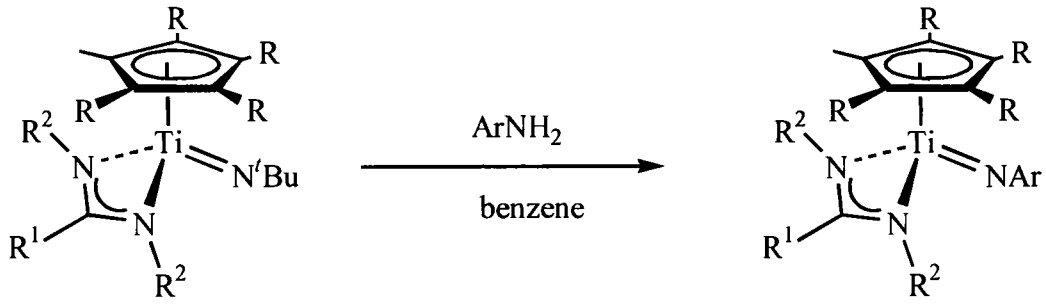
Ir(η-C_5Me_5)(N^{t}Bu) (**2.25**) reacts with one equivalent of 2,6-dimethylphenyl-aniline to give the arylimido species Ir(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$) (**2.26**) and *tert*-butylamine as a by-product. Subsequent mechanistic studies conducted on the reaction between the isolobal and isoelectronic osmium complex Os(Cym)(N^{t}Bu) (**2.27**) (Cym = η-*p*-cymene) and arylamines[26] demonstrated that the reaction shows a first order dependence in both the imido starting species and the arylamine. Bergman proposed a mechanism for the reaction which proceeds *via* a bis(amide) intermediate, as shown in Scheme 2.5.



Scheme 2.5 – Amine-imido exchange mechanism for Os(Cym)(N^{t}Bu) (**2.27**) with arylamines

In the first step, the aniline forms a donor complex with the alkyl imide. The greater basicity of the alkyl amide compared to an aryl amide allows proton transfer to form the bis(amide) intermediate. A second proton transfer results in another donor complex, this time between the arylimide and the amine. Loss of the donor amine affords the arylimido product. When the reaction was monitored by ^{1}H NMR spectroscopy, no intermediates were observed. There are many examples of similar reactivity for other metal imides in the literature,[27-29] in particular for *tert*-butylimido titanium complexes.[30,31] The kinetics of these exchange reactions have not been studied, but it is proposed that they proceed *via* analogous bis(amide) intermediates.

As the exchange reactions for *tert*-butylimido titanium complexes are generally found to yield clean products, the first route chosen to attempt the synthesis of arylimido species involved this method. Reactions of compounds **1** – **4** with arylamines were found to form the corresponding arylimido complexes and *tert*-butylamine (Equation 2.7). Table 2.4 summarises which compounds have been synthesised.



Compound	R	R^1	R^2
1	Me	Ph	$SiMe_3$
2	Me	Me	^{i}Pr
3	H	Ph	$SiMe_3$
4	H	Me	^{t}Pr

Ar = 2,6-$C_6H_3Me_2$

4-C_6H_4Me

(see Table 2.4 for details)

Equation 2.7

Table 2.4 – Summary of amine-imido exchange reactions

tert-butylimido complex	Arylamine	Reaction product
$Ti(\eta\text{-}C_5Me_5)(N^tBu)\{PhC(NSiMe_3)_2\}$ **(1)**	$H_2N\text{-}2,6\text{-}C_6H_3Me_2$	No reaction after 24 hrs at 80 °C
$Ti(\eta\text{-}C_5Me_5)(N^tBu)\{PhC(NSiMe_3)_2\}$ **(1)**	$H_2N\text{-}4\text{-}C_6H_4Me$	Decomposition upon heating at 80 °C
$Ti(\eta\text{-}C_5Me_5)(N^tBu)\{MeC(N^iPr)_2\}$ **(2)**	$H_2N\text{-}2,6\text{-}C_6H_3Me_2$	$Ti(\eta\text{-}C_5Me_5)(N\text{-}2,6\text{-}C_6H_3Me_2)\{MeC(N^iPr)_2\}$ **(7)**
$Ti(\eta\text{-}C_5Me_5)(N^tBu)\{MeC(N^iPr)_2\}$ **(2)**	$H_2N\text{-}4\text{-}C_6H_4Me$	$Ti(\eta\text{-}C_5Me_5)(N\text{-}4\text{-}C_6H_4Me)\{MeC(N^iPr)_2\}$ **(8)**
$Ti(\eta\text{-}C_5Me_5)(N^tBu)\{MeC(N^iPr)_2\}$ **(2)**	$H_2N\text{-}4\text{-}C_6H_4CF_3$	$Ti(\eta\text{-}C_5Me_5)(N\text{-}4\text{-}C_6H_4CF_3)\{MeC(N^iPr)_2\}$ **(9)**
$Ti(\eta\text{-}C_5Me_5)(N^tBu)\{MeC(N^iPr)_2\}$ **(2)**	$H_2N\text{-}4\text{-}C_6H_4NMe_2$	$Ti(\eta\text{-}C_5Me_5)(N\text{-}4\text{-}C_6H_4NMe_2)\{MeC(N^iPr)_2\}$ **(10)**
$Ti(\eta\text{-}C_5H_4Me)(N^tBu)\{PhC(NSiMe_3)_2\}$ **(3)**	$H_2N\text{-}2,6\text{-}C_6H_3Me_2$	$Ti(\eta\text{-}C_5H_4Me)(N\text{-}2,6\text{-}C_6H_3Me_2)\{PhC(NSiMe_3)_2\}$ **(11)**
$Ti(\eta\text{-}C_5H_4Me)(N^tBu)\{PhC(NSiMe_3)_2\}$ **(3)**	$H_2N\text{-}4\text{-}C_6H_4Me$	$Ti(\eta\text{-}C_5H_4Me)(N\text{-}4\text{-}C_6H_4Me)\{PhC(NSiMe_3)_2\}$
$Ti(\eta\text{-}C_5H_4Me)(N^tBu)\{MeC(N^iPr)_2\}$ **(4)**	$H_2N\text{-}2,6\text{-}C_6H_3Me_2$	$Ti(\eta\text{-}C_5H_4Me)(N\text{-}2,6\text{-}C_6H_3Me_2)\{MeC(N^iPr)_2\}$ **(12)**
$Ti(\eta\text{-}C_5H_4Me)(N^tBu)\{MeC(N^iPr)_2\}$ **(4)**	$H_2N\text{-}4\text{-}C_6H_4Me$	$Ti(\eta\text{-}C_5H_4Me)(NH^tBu)(NH\text{-}4\text{-}C_6H_4Me)\{MeC(N^iPr)_2\}$

2.4.1.1.2 DISCUSSION OF AMINE-IMIDO EXCHANGE REACTIONS

The amine-imido exchange process has been proposed to occur *via* an associative mechanism. The arylamine coordinates to the metal centre, proton transfer occurs to give a bis(amide) intermediate, followed by a further proton transfer step and extrusion of *tert*-butylamine. It is to be expected therefore

that the steric requirements of the environment around the metal centre, and those of the arylamine, will greatly influence the process.

In the reactions involving Ti(η-C_5Me_5)(N^{t}Bu){PhC(NSiMe_3)$_2$} (**1**), it was found that prolonged heating in the presence of the arylamine afforded little or no product, with increasing quantities of decomposition species observed by ^{1}H NMR spectroscopy. This is easily understood from the principles laid out above, and such lack of reactivity is not without precedent.[32]

The reduced steric bulk of the acetamidinate ligand in Ti(η-C_5Me_5)(N^{t}Bu){MeC(N^{i}Pr)$_2$} (**2**) provides an environment in which the exchange reaction is favoured for arylamines, giving rise to compounds **7** – **10** (see Table 2.4). All reactions proceed cleanly at room temperature to give the desired product in 90 – 95 % isolated yield. As expected, the reaction with 2,6-dimethylaniline requires more time to go to completion than do those with 4-substituted arylamines (*ca.* 6 hours cf. *ca.* 10 minutes). Compound **7** was structurally characterised by single crystal X-ray diffraction. (See Section 2.4.2.1)

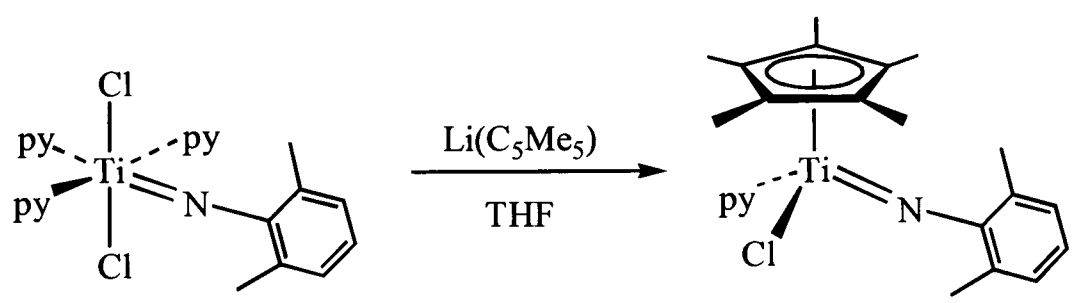
Ti(η-C_5H_4Me)(N-2,6-$C_6H_3Me_2$){PhC(NSiMe_3)$_2$} (**11**) and Ti(η-C_5H_4Me)(N-4-C_6H_4Me){PhC(NSiMe_3)$_2$} were both found to form after *ca.* 6 hours reaction time. Due to time constraints, and on the basis of product purity, it was decided to scale up only compound **11**, which was isolated and fully characterised (58 % recrystallised yield).

Reaction of Ti(η-C_5H_4Me)(N^{t}Bu){MeC(N^{i}Pr)$_2$} (**4**) with 2,6-dimethylaniline afforded Ti(η-C_5H_4Me)(N-2,6-$C_6H_3Me_2$){MeC(N^{i}Pr)$_2$} (**12**) as a green oil within 10 minutes (71 % sublimed yield). However, reaction of **4** with *p*-toluidine to give the analogous *p*-tolylimido complex did not afford the expected imido species. The peaks in the ^{1}H NMR spectrum of the reaction mixture are broad, and indicate the formation of a fluxional bis(amide) complex Ti(η-C_5H_4Me)(NH^{t}Bu)(NH-4-C_6H_4Me){MeC(N^{i}Pr)$_2$}. Attempts to force the complex to extrude *tert*-butylamine by heating, addition of pyridine, or tube sublimation under high vacuum were unsuccessful. This stabilisation of a bis(amide) complex has been observed for reactions of other Group 4 imides with amines.[23,33] It arises due to insufficent steric protection around the metal centre, causing the extrusion of *tert*-butylamine to become less favoured. The compound was not isolated and characterised.

2.4.1.2 Syntheses from Ti(NAr)Cl_2(py)$_3$

This method was found to be much more restricted in scope than the amine-imido exchange route.

2.4.1.2.1 Complexes from Ti(N-2,6-$C_6H_3Me_2$)Cl_2(py)$_3$



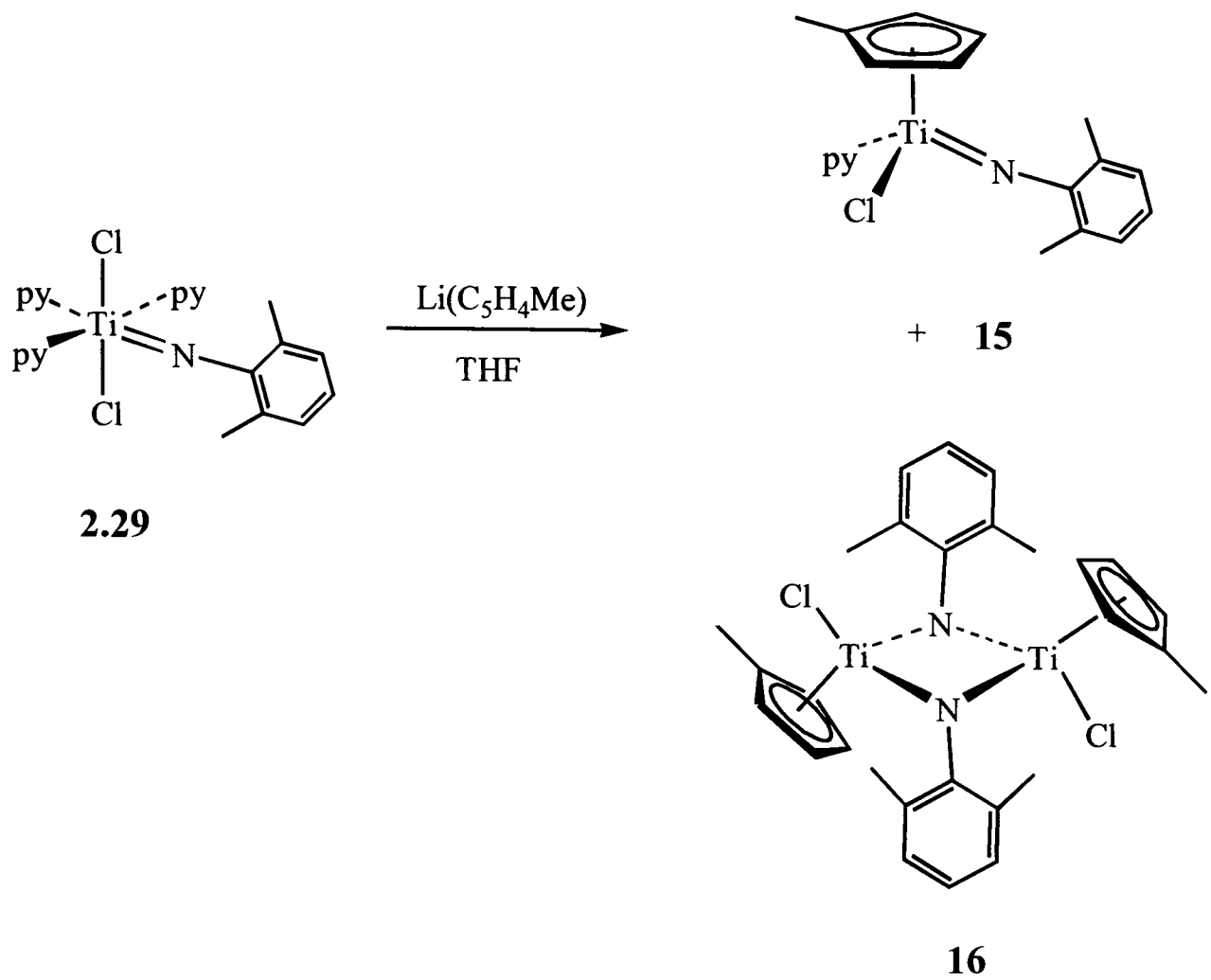
2.29 **13**

Equation 2.8

Reaction of the previously characterised complex $Ti(N\text{-}2,6\text{-}C_6H_3Me_2)Cl_2(py)_3$ (**2.29**)[31] with $Li(C_5Me_5)$ in refluxing THF afforded the complex $Ti(\eta\text{-}C_5Me_5)(N\text{-}2,6\text{-}C_6H_3Me_2)Cl(py)$ **(13)** in high yield (87 % crude, 64 % recrystallised) after 1 hour, as shown in Equation 2.8. This compound has been structurally characterised (see Section 2.4.2.2 below).

Reaction of **13** with $Li\{PhC(NSiMe_3)_2\}$ or $Li\{MeC(N^iPr)_2\}$ in refluxing benzene for 2 hours gave the compounds $Ti(\eta\text{-}C_5Me_5)(N\text{-}2,6\text{-}C_6H_3Me_2)\{PhC(NSiMe_3)_2\}$ **(14)** and $Ti(\eta\text{-}C_5Me_5)(N\text{-}2,6\text{-}C_6H_3Me_2)\{MeC(N^iPr)_2\}$ **(7)**. The crude compounds were found to have impurities present. Purification proved difficult, owing to the high solubility of **7** and **14** in pentane, and neither sublimed readily even under high vacuum conditions (1×10^{-5} Torr, 120 °C). However, though lower yielding (**7** obtained in 16 % recrystallised yield; **14** obtained in 30 % recystallised yield), this route did afford a pathway to the synthesis of **14**, which was found to be inaccessible using the amine-imido exchange method. Compound **14** has been fully characterised by ^1H and $^{13}C\text{-}\{^1H\}$ NMR, and IR spectroscopies, elemental analysis and EI mass spectrometry, and has also been structurally characterised (see Section 2.4.2.3).

Reaction of $Ti(N\text{-}2,6\text{-}C_6H_3Me_2)Cl_2(py)_3$ with $Li(C_5H_4Me)$ did not proceed as cleanly as the C_5Me_5 case. The reaction produced a mixture of two products, as shown in Equation 2.9 below.



2.29

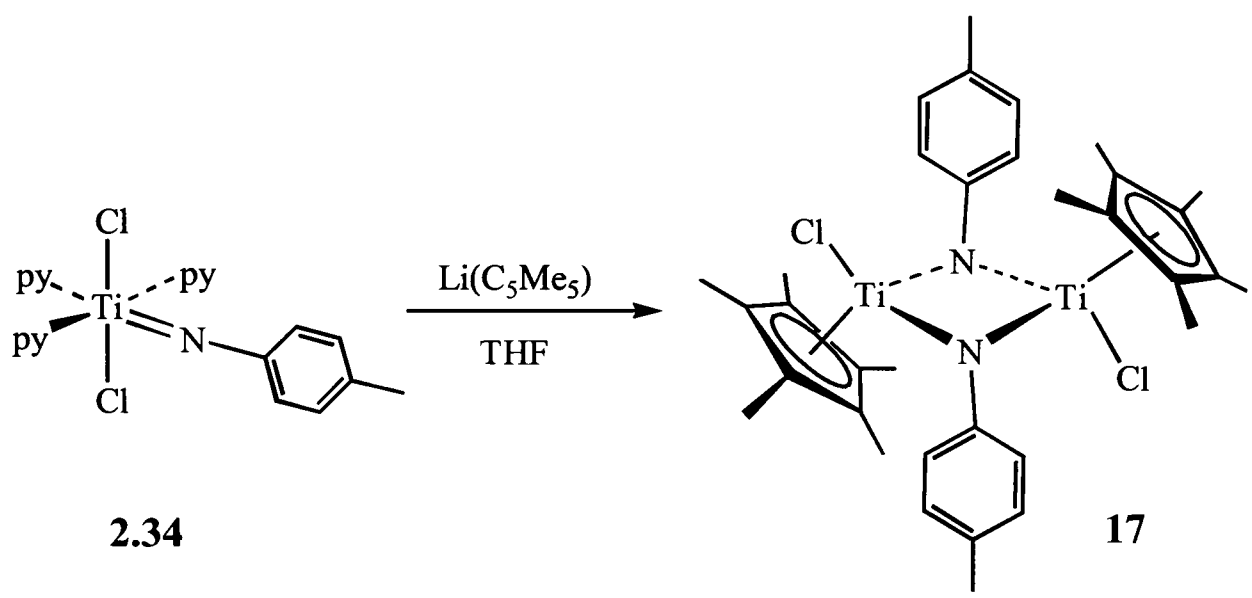
16

Equation 2.9

The ^{1}H NMR spectrum of the crude product contained peaks consistent with the two species **15** and **16**. Complex **15** is analogous to the complex Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$)Cl(py) **(13),** while **16** is the dimeric product formed upon dissociation of pyridine. These products are analogous to the previously reported complexes Ti(η-C_5H_4R)(N^{t}Bu)Cl(py) (R = H (**2.30**), Me (**2.31**)) and [Ti(η-C_5H_4R)(N^{t}Bu)Cl]$_2$ (R = H (**2.32**), Me (**2.33**)), which are interconverted by addition or removal of pyridine.[1,16] All attempts to separate and characterise the compounds proved unsuccessful. Some **15** was found to lose pyridine and dimerise to give **16** even when solvent was removed at -30 °C. However, some pyridine was always found to remain trapped in the solid, preventing complete formation of **16**. Attempts to sublime the compound under high vacuum resulted in decomposition. A peak at consistent with **16** (*m/z* = 674, $[M]^+$) was detected in the EI mass spectrum.

2.4.1.2.2 COMPLEXES FROM Ti(N-4-C_6H_4Me)$Cl_2(py)_3$

Reaction of Ti(N-4-C_6H_4Me)$Cl_2(py)_3$ (**2.34**)[31] with Li(C_5Me_5) in refluxing THF overnight exclusively gave the dimeric imido product [Ti(η-C_5Me_5)(μ-N-4-C_6H_4Me)Cl]$_2$ (**17**) (80 % yield) as shown in Equation 2.10:

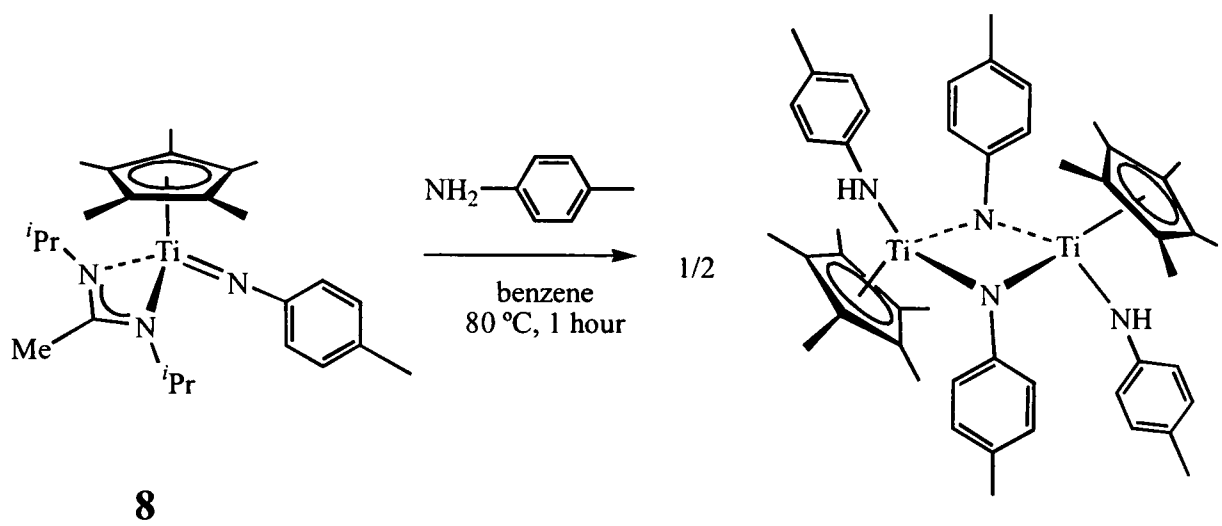


2.34 **17**

Equation 2.10

Compound **17** was found to be poorly soluble in most solvents. Reaction of **17** with the lithium salts of the amidinates, even in the presence of an excess of pyridine, afforded no reaction. When heated, only decomposition products were evident in the ^{1}H NMR spectra of the reactions.

A related complex, [Ti(η-C_5Me_5)(μ-N-4-C_6H_4Me)(NH-4-C_6H_4Me)]$_2$ (**18**), was formed on reaction of **8** with one equivalent of *p*-toluidine (50 % recrystallised yield), as shown in Equation 2.11.



8 **18**

Equation 2.11

Compounds **17** and **18** were fully characterised by ^{1}H, ^{13}C-{^{1}H} and IR spectroscopies. A peak at ν = 3303 cm^{-1} in the IR spectrum of **18** was consistent with the amide proton. A parent ion peak was detected in the EI mass spectrum of **17** (*m/z* = 647, $[M]^+$) and in the FI mass spectrum of **18** (*m/z* = 788, $[M]^+$).

Reaction of Ti(N-4-C_6H_4Me)$Cl_2(py)_3$ with Li(C_5H_4Me) afforded only a mixture of products which were poorly soluble and were not identified.

2.4.2 CHARACTERISATION OF TITANIUM ARYLIMIDO COMPLEXES

Compounds **7** – **15** were fully characterised by ^{1}H and ^{13}C-{^{1}H} NMR, and IR spectroscopies, EI mass spectrometry, and elemental analysis. In addition, compounds Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$){MeC(N^{i}Pr)$_2$} (**7**), Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$)Cl(py) (**13**), and Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$){PhC($NSiMe_3$)$_2$} (**14**) were structurally characterised by single crystal X-ray

diffraction. The NMR spectra of the terminal imido compounds conformed to the same patterns as discussed for the *tert*-butylimido complexes **1** – **6**; free rotation of the imido N-substituent was observed for all aryl imido species investigated.

2.4.2.1 X-RAY CRYSTAL STRUCTURE OF $Ti(\eta\text{-}C_5Me_5)(N\text{-}2,6\text{-}C_6H_3Me_2)\{MeC(N^iPr)_2\}$ (7)

A green-brown crystal suitable for analysis by single crystal X-ray diffraction was obtained by slow cooling of a saturated solution in pentane to -30 °C, using a toluene bath. The data were collected and the structure solved by Dr. A. R. Cowley of this department. Figure 2.5 shows the molecular structure of **7**, and Table 2.5 summarises some important bond lengths and angles. Full details are provided in Appendix B.

Table 2.5 – Selected bond lengths (Å) and angles (°) for $Ti(\eta\text{-}C_5Me_5)(N\text{-}2,6\text{-}C_6H_3Me_2)\{MeC(N^iPr)_2\}$ (7)

$Ti(1) - Cp_{(cent)}$	2.085	Ti(1) – N(3) – C(9)	168.9(2)
Ti(1) – N(1)	2.094(2)	$Cp_{(cent)}$ – Ti(1) – N(3)	121.4
Ti(1) – N(2)	2.099(2)	$Cp_{(cent)}$ – Ti(1) – N(2)	119.5
Ti(1) – N(3)	1.738(2)	$Cp_{(cent)}$ – Ti(1) – N(1)	119.1
C(1) – N(1)	1.335(4)		
C(1) – N(2)	1.339(4)		

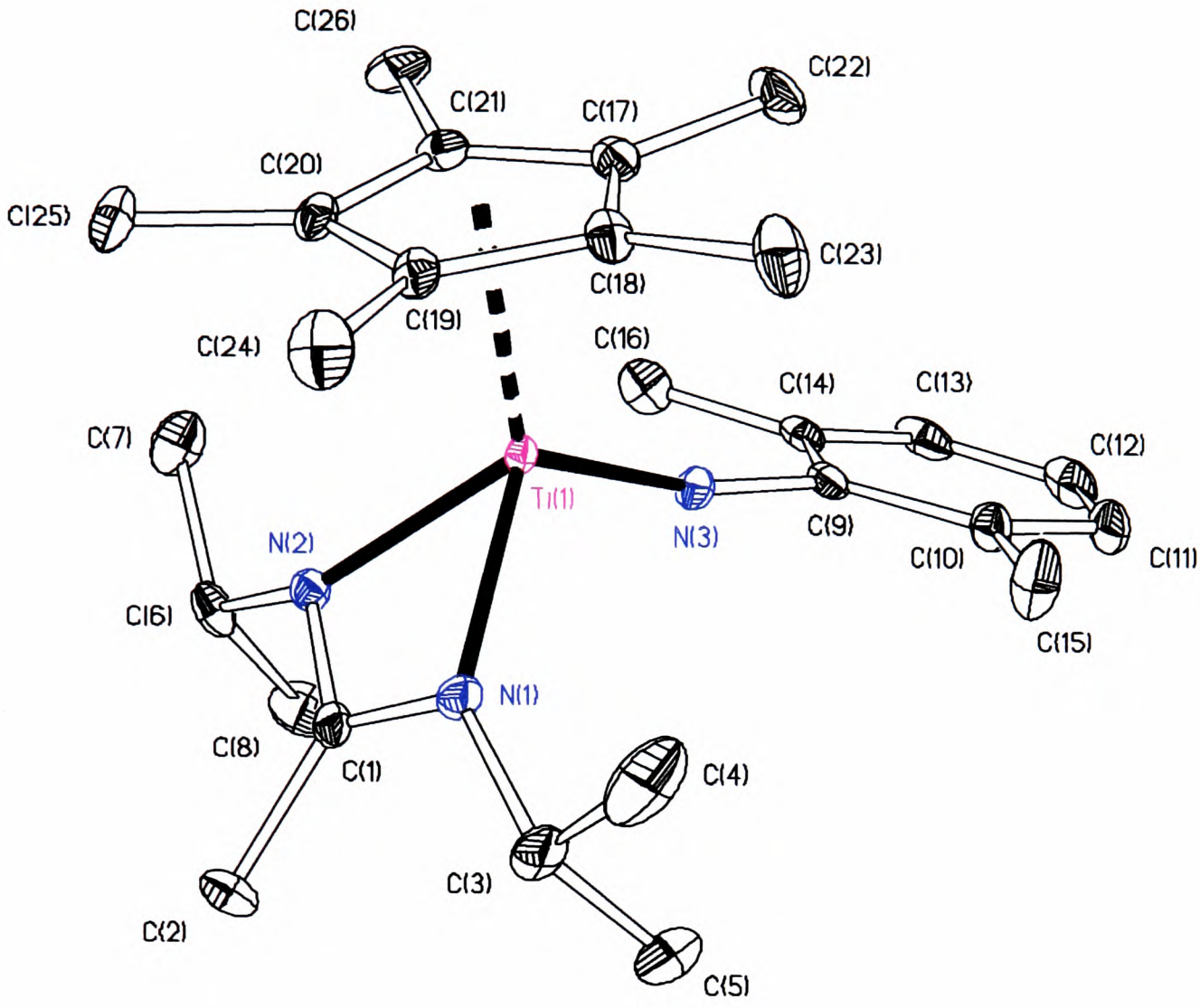


Figure 2.5 – Thermal ellipsoid plot (30 % probability) of Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$){$MeC(N^iPr)_2$} (7). H atoms are omitted for clarity

2.4.2.2 X-RAY CRYSTAL STRUCTURE OF Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$)Cl(py) (13)

A dark brown crystal suitable for analysis by single crystal X-ray diffraction was obtained from a solution in dichloromethane-d_2 layered with pentane. The data were collected and the structure solved by Dr. A. R. Cowley of this department. Figure 2.6 shows the molecular structure of **13**, and Table 2.6 summarises some important bond lengths and angles. Full details are provided in Appendix C.

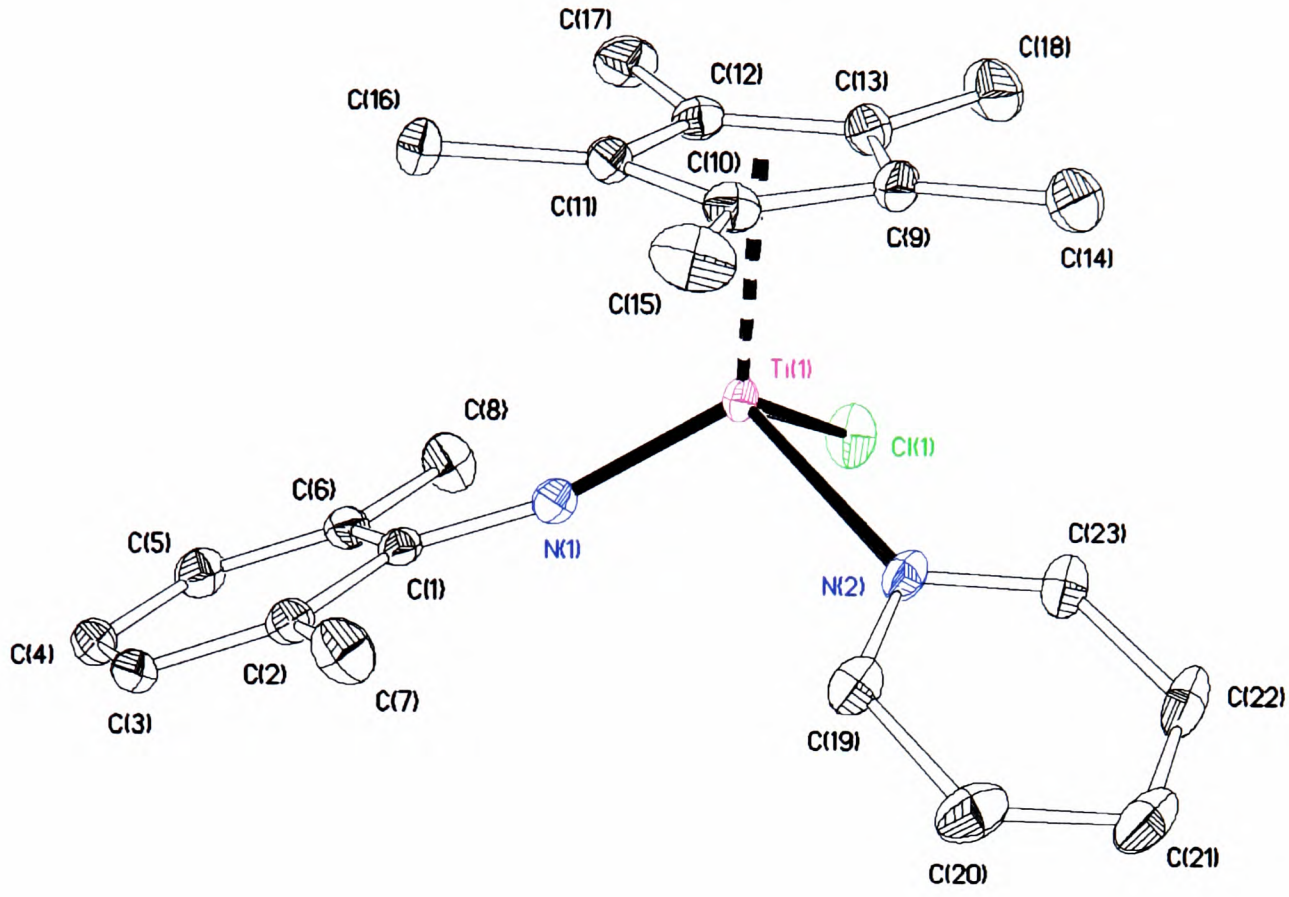


Figure 2.6 – Thermal ellipsoid plot (30 % probability) of Ti(η-C_5Me_5) (N-2,6-$C_6H_3Me_2$)Cl(py) (**13**). H atoms are omitted for clarity

Table 2.6 – Selected bond lengths (Å) and angles (°) for Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$)Cl(py) (**13**)

Ti(1) – $Cp_{(cent)}$	2.062	Ti(1) – N(1) – C(1)	167.2 (2)
Ti(1) – N(1)	1.754 (3)	$Cp_{(cent)}$ – Ti(1) – Cl(1)	115.9
Ti(1) – N(2)	2.177 (3)	$Cp_{(cent)}$ – Ti(1) – N(1)	121.8
Ti(1) – Cl(1)	2.345 (1)	$Cp_{(cent)}$ – Ti(1) – N(2)	110.2

2.4.2.3 X-RAY CRYSTAL STRUCTURE OF Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$) {$PhC(NSiMe_3)_2$} (14)

A red crystal suitable for analysis by single crystal X-ray diffraction was obtained by slow cooling of a saturated solution in pentane. The data were collected by the author, and the structure solved by Dr. P. Mountford. Figure

2.7 shows the molecular structure of **14**, and Table 2.7 summarises some important bond lengths and angles. Full details are provided in Appendix D.

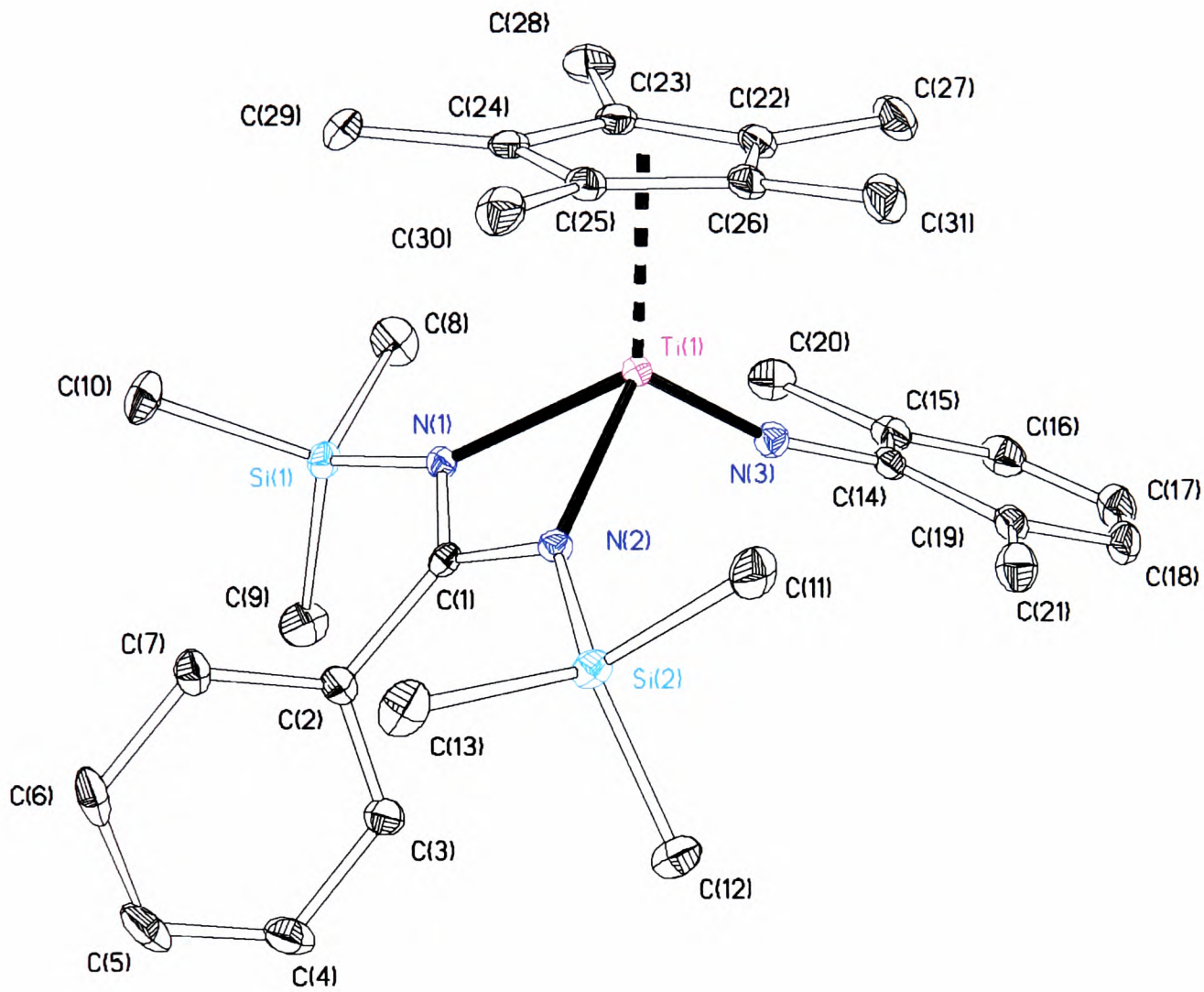


Figure 2.7 – Thermal ellipsoid plot (30 % probability) of Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$) {$PhC(NSiMe_3)_2$} (**14**). H atoms are omitted for clarity

Table 2.7 – Selected bond lengths (Å) and angles (°) for Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$) {$PhC(NSiMe_3)_2$} (**14**)

Ti(1) – $Cp_{(cent)}$	2.079	Ti(1) – N(3) – C(14)	165.9(2)
Ti(1) – N(1)	2.134(2)	$Cp_{(cent)}$ – Ti (1) - N(3)	121.8
Ti(1) – N(2)	2.107(2)	$Cp_{(cent)}$ – Ti(1) - N(2)	119.6
Ti(1) – N(3)	1.748(2)	$Cp_{(cent)}$ – Ti(1) - N(1)	120.5
C(1) – N(1)	1.327(4)		
C(1) – N(2)	1.346 (4)		

2.4.2.4 DISCUSSION AND COMPARISON OF THE CRYSTAL STRUCTURES

All three complexes adopt a three-legged piano stool structure. The $Cp_{(cent)}$–Ti bond lengths are all typical of those found for other cyclopentadienyl-titanium(IV) complexes (2.0 – 2.1 Å).[17,18] As expected, the Ti=N imido bond is found to be shorter than the bonds to the nitrogens of amidinate (complexes **8** and **14**) or pyridine (**13**) ligands. The imido bond is found to be longer in all three aryl systems ($Ti–N_{imido}$: 1.738(2) – 1.754(2) Å) than was found for $Ti(\eta\text{-}C_5H_4Me)(N^tBu)\{PhC(NSiMe_3)_2\}$ (**3**) ($Ti–N_{imido}$: 1.708 (2) Å) or the complex $Ti(\eta\text{-}C_5Me_5)(N^tBu)Cl(py)$ (**2.18**) ($Ti–N_{imido}$: 1.754 (3) Å).[34] This is consistent with the electron density being delocalised throughout the aryl ring of the arylimido complexes, reducing the bond order of the imido linkage. $Ti(\eta\text{-}C_5Me_5)(N\text{-}2,6\text{-}C_6H_3Me_2)\{MeC(N^iPr)_2\}$ (**8**) has the shortest imido bond of the three aryl complexes ($Ti–N_{imido}$: 1.738 (2) Å), with $Ti(\eta\text{-}C_5Me_5)(N\text{-}2,6\text{-}C_6H_3Me_2)Cl(py)$ (**13**) having the longest bond (1.754 (3) Å). This is consistent with the steric properties of the supporting ligands.

Comparison of the structures of $Ti(\eta\text{-}C_5Me_5)(N^tBu)Cl(py)$ (**2.18**)[34] and $Ti(\eta\text{-}C_5Me_5)(N\text{-}2,6\text{-}C_6H_3Me_2)Cl(py)$ (**13**) reveals a shortening of $Cp_{(cent)}$–Ti (2.062 cf. 2.091 Å), $Ti–N_{pyridyl}$ (2.177(3) cf. 2.195(3) Å), and Ti–Cl (2.345(1) cf. 2.359(2) Å) bonds upon substitution of the *tert*-butyl group for 2,6-dimethylphenyl. This is consistent with the longer arylimido bond causing less steric crowding at the metal centre.

All values for the imido bond lengths fall within the reported range for imidotitanium species (1.68 – 1.77 Å).[13,23] The Ti–N–C angle subtended at the imido nitrogen is greater in the *tert*-butyl complex **3** (174.28(19) °) than in the

aryl complexes (range: 165.9(2) – 168.9(2) °). The greatest deviation from linearity is observed for Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$){PhC($NSiMe_3$)$_2$} (**14**), with the most linear bond being found in Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$) {MeC(N^iPr)$_2$} (**8**). Again, this difference between the *tert*-butyl- and aryl-imido complexes can be rationalised in terms of a lower π-donation from the nitrogen to titanium in the arylimido complexes, owing to delocalisation throughout the aryl ring. All bond angles are consistent with the imido group acting as a linear, four electron donor to the metal centre. The amidinate ligand is found to bind symmetrically to the metal. Ti(η-C_5Me_5) (N-2,6-$C_6H_3Me_2$){PhC($NSiMe_3$)$_2$} (**14**) displays a slight binding asymmetry ($Ti–N_{amidinate}$: 2.134(2) and 2.107(2) Å), which may be attributable to crystal packing forces. The $Ti–N_{amidinate}$ bond lengths are all typical of the values reported in the literature (mean: 2.148 Å, range: 2.056 – 2.395 Å for 30 compounds).[17,18]

2.4.3 Discussion of Arylimido Complexes

It can be seen that synthesis of the cyclopentadienyl-amidinate supported aryl imido species **7** – **12** from Ti(NAr)$Cl_2(py)_3$ is a much less general method than amine-imido exchange from their *tert*-butyl imido homologues. The only case in which it is the preferred route is in the synthesis of Ti(η-C_5Me_5) (N-2,6-$C_6H_3Me_2$){PhC($NSiMe_3$)$_2$} (**14**), which cannot be synthesised by exchange from Ti(η-C_5Me_5)(N^tBu){PhC($NSiMe_3$)$_2$} (**1**). This is presumably due to the high degree of steric protection afforded to the metal centre by the ancillary ligands.

The complex Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$)Cl(py) (**13**) can be isolated readily, and has been fully characterised (see Section 2.4.1.2.1 above). In contrast, attempts to synthesise and isolate the analogous Ti(η-C_5H_4Me)(N-2,6-$C_6H_3Me_2$)Cl(py) (**15**) were unsuccessful. In all cases, a mixture of **15** and the dimeric, pyridine-free complex [Ti(η-C_5H_4Me)(μ-N-2,6-$C_6H_3Me_2$)Cl]$_2$ (**16**) was obtained. NMR experiments confirmed that these two compounds readily interconvert as a function of pyridine concentration; however, the removal of pyridine under reduced pressure is sufficient to cause decomposition of some of the monomer to dimer. This was found to be the case even when volatiles were removed under reduced pressure at low temperature (-30 °C). Obtaining the pure dimer was complicated by the ability of the solid to trap pyridine within its matrix, thereby making removal of all the pyridine very difficult. As a result of this, and the fact that the *tert*-butylimido systems bearing the C_5H_4Me ligand (complexes **3** and **4**) undergo exchange readily with 2,6-dimethylaniline, no further attempts were made to isolate and characterise these intermediates.

The synthesis of arylimido complexes with cyclopentadienyl and amidinate supporting ligands from Ti(N-4-C_6H_4Me)Cl_2(py)$_3$ was found to be even less successful. Even $(C_5Me_5)^-$ does not provide sufficient steric protection to prevent loss of pyridine and dimerisation to form [Ti(η-C_5Me_5)(μ-N-4-C_6H_4Me)Cl]$_2$ (**17**). Unlike [Ti(η-C_5H_4Me)(μ-N-2,6-$C_6H_3Me_2$)Cl]$_2$ (**16**) which, when formed in the presence of pyridine, is in equilibrium with monomeric Ti(η-C_5H_4Me)(N-2,6-$C_6H_3Me_2$)Cl(py) (**15**), the dimer **17** shows no propensity to form a pyridine-adduct at room temperature.

A sample of $[Ti(\eta\text{-}C_5Me_5)(\mu\text{-}N\text{-}4\text{-}C_6H_4Me)Cl]_2$ was dissolved in 680 µl dichloromethane-d_2. After running a series of low temperature ^1H NMR spectra as standards for comparison, two molar equivalents of pyridine were added to the tube. Low temperature ^1H NMR measurements showed that as the temperature is lowered, some degree of association is observed, indicating formation of a weakly-bound pyridine adduct (sharpening of pyridyl peaks indicated by *, Figure 2.8). However, since thermal energy at room temperature is easily sufficient to cause dissociation of this adduct, isolation of **17** can be afforded without the problems encountered for $[Ti(\eta\text{-}C_5H_4Me)(N\text{-}2,6\text{-}C_6H_3Me_2)Cl]_2$.

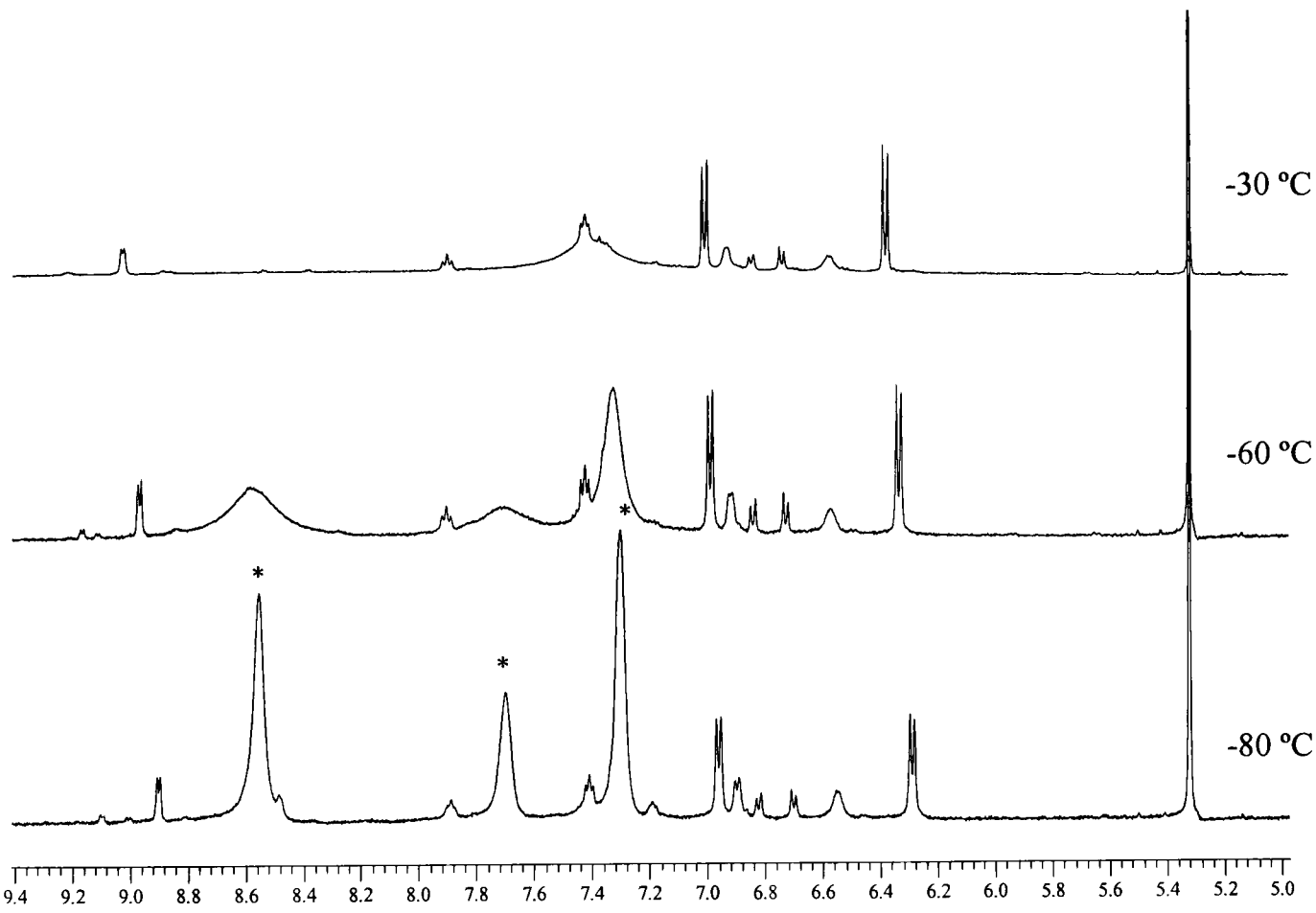


Figure 2.8 – Low temperature 500.0 MHz ^1H NMR spectra of $[Ti(\eta\text{-}C_5Me_5)(\mu\text{-}N\text{-}4\text{-}C_6H_4Me)Cl]_2$ (**17**) in dichloromethane-d_2 in the presence of pyridine

This lack of reactivity of the dimeric imido complex **17** compared with that of the related monomeric species Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$)Cl(py) (**13**) resembles the difference in reactivity between the dimeric [Ti(η-C_5H_4Me)(N^{t}Bu)Cl] (**2.20**) and monomeric Ti(η-C_5H_4Me)(N^{t}Bu)Cl(py) (**2.19**) (Section 2.3.1.2) Both steric and electronic factors may be responsible for this difference. As with the *tert*-butyl congeners, it can be argued that although both **13** and **17** are pseudo-four coordinate, the pyridine of **13** is inherently more labile than the chloride of **17**, giving access to a less crowded intermediate, the pyridine-free species Ti(η-C_5Me_5)(N^{t}Bu)Cl, which would be highly reactive.

Similarly, the imido nitrogen of the monomeric imide is formally *sp* hybridised, able to donate 4 electrons to the metal centre. By contrast, the imido nitrogen of the dimer **17** is forced to adopt sp^2 hybridisation, and can therefore only donate a maximum of 1½ electrons to each metal centre, the lone pair being localised on the heteroatom. Each metal centre is therefore more electron deficient in the dimer, and so could be argued to hold the ligands closer, restricting approach of nucleophiles such as the amidinate ion.

Reaction of Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$){MeC(N^{i}Pr)$_2$} (**7**) with a second equivalent of *p*-toluidine to give [Ti(η-C_5Me_5)(μ-N-4-C_6H_4Me)(NH-4-C_6H_4Me)]$_2$ (**18**) was an unexpected reaction, which had been anticipated to give the bis(amide) complex Ti(η-C_5Me_5)(NH-4-C_6H_4Me)$_2${MeC(N^{i}Pr)$_2$}. Instead of undergoing coordination of the amine followed by proton transfer (analogous to the amine-imido exchange

reaction pathway, Scheme 2.5), the *p*-toluidine protonates the amidinate, giving the amido-imido complex **18** as the product.

NMR experiments have shown that the displaced amidine is able to coordinate to the dimer, resulting in a loss of symmetry in the *iso*-propyl arms of the molecule (See Figure 2.9).

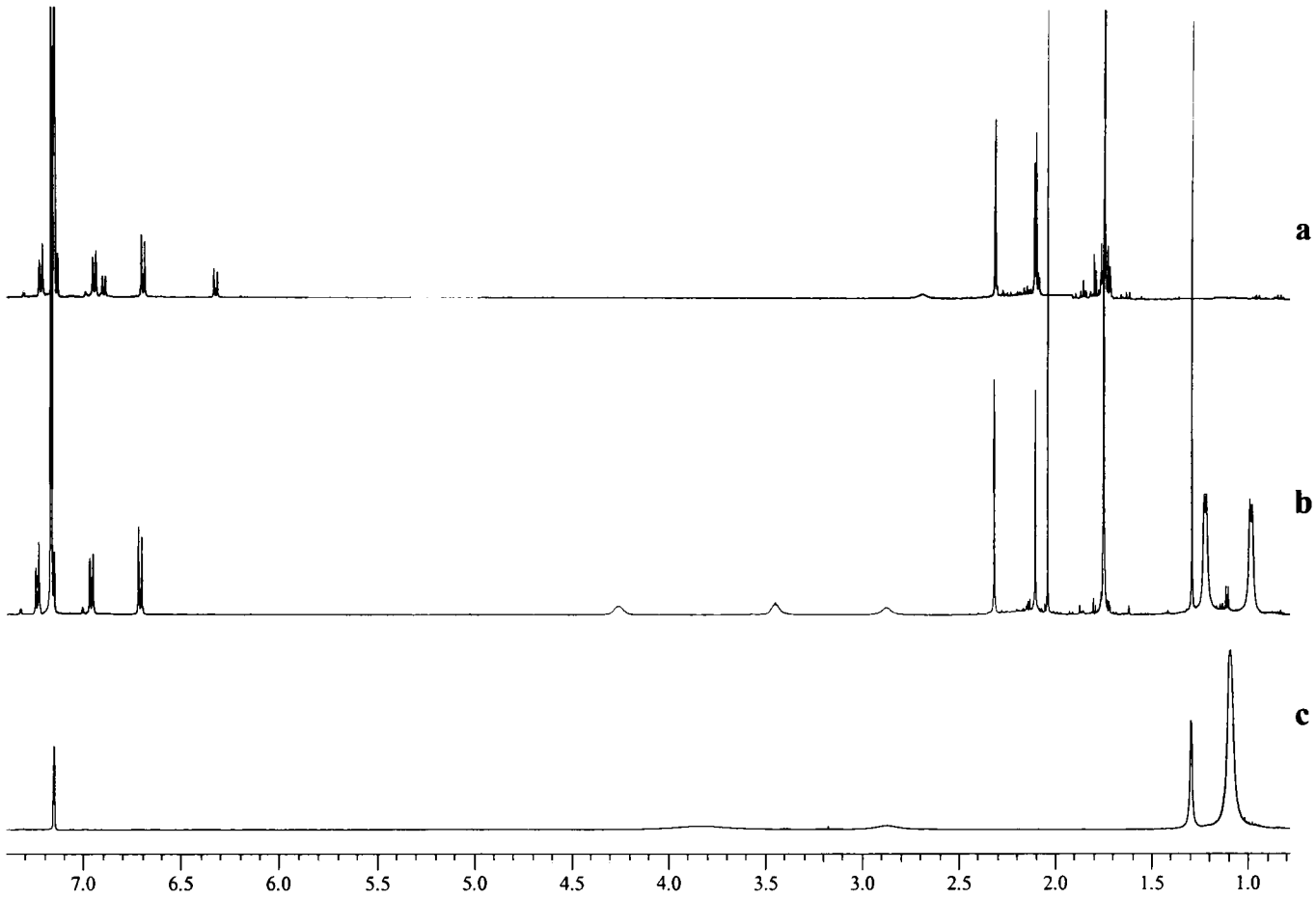


Figure 2.9 – Interaction of **18** with MeC(N^{i}Pr)(NH^{i}Pr) in benzene-d_6

a: 500.0 MHz ^{1}H NMR spectrum of [Ti(η-C_5Me_5)(μ-N-4-C_6H_4Me)(NH-4-C_6H_4Me)]$_2$ (**18**)

b: 500.0 ^{1}H NMR spectrum of 18 in the presence of *N,N'*-di-*iso*-propylacetamidine

c: 500.0 MHz ^{1}H NMR spectrum of *N,N'*-di-*iso*-propylacetamidine

It can be seen that on addition to the imido complex **18**, the ^{1}H NMR resonances of the amidine (**c**) sharpen, and the symmetry of the molecule is split (**b**). The ease of crystallisation of **18** (**a**) from a reaction mixture containing MeC(N^{i}Pr)(NH^{i}Pr) demonstrates the weak binding between the

amidine and the metal complex. A possible explanation for this behaviour is hydrogen bonding between the protons on the amide, and the proton on the amidine, as indicated in Figure 2.10.

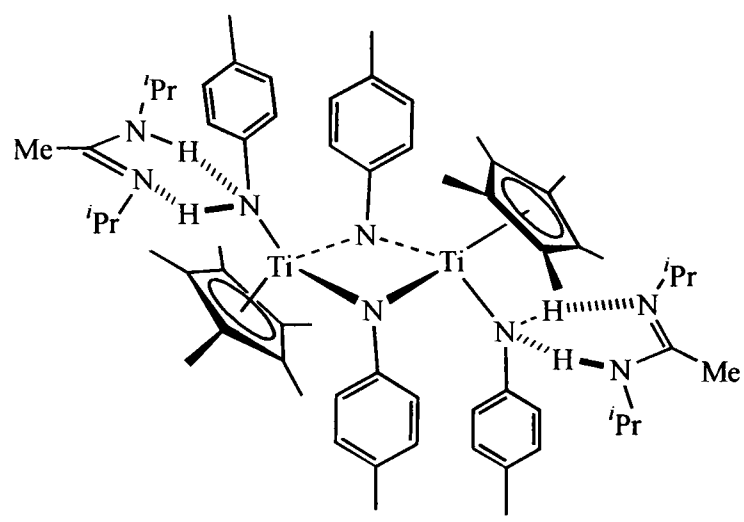


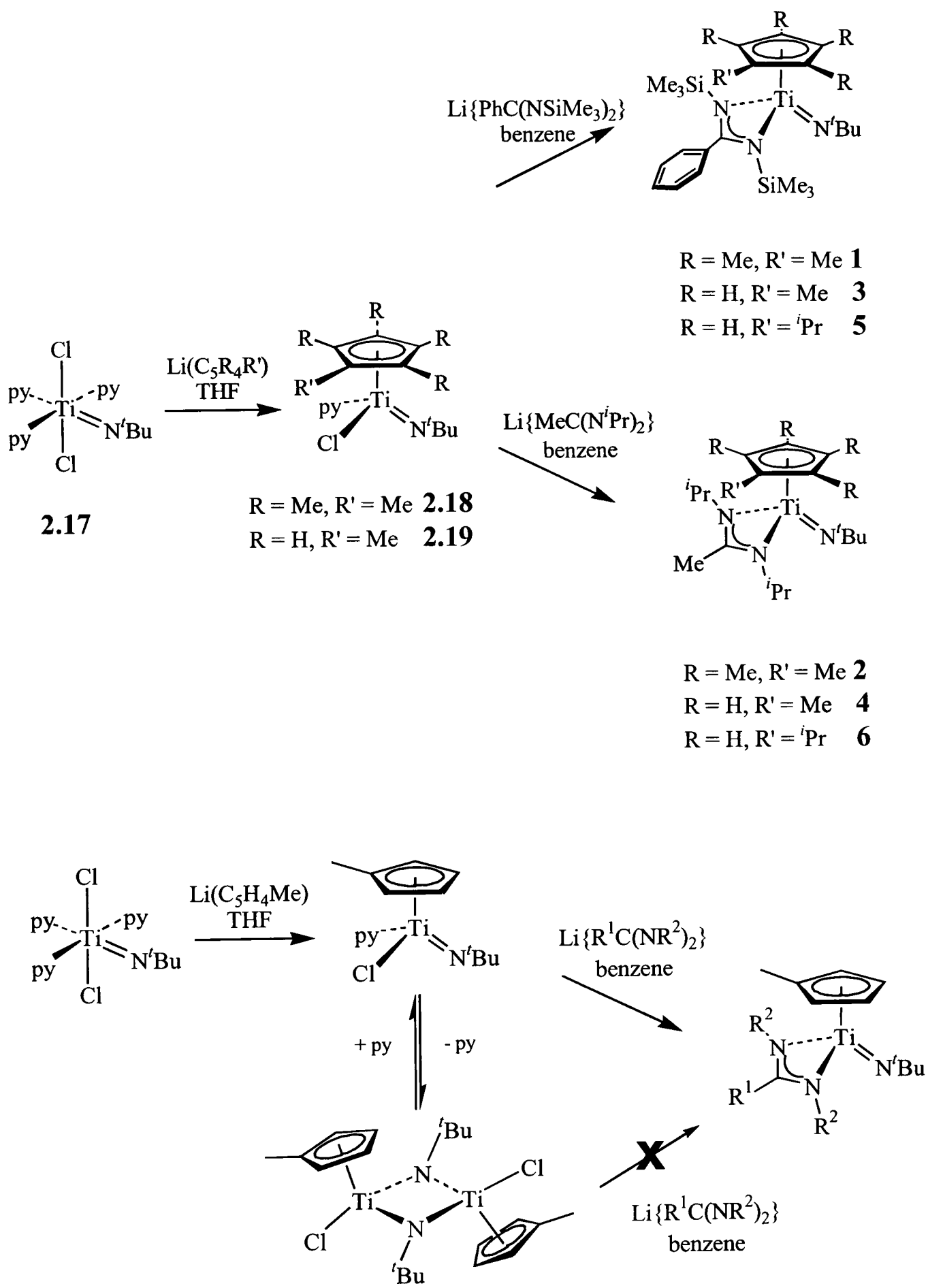
Figure 2.10

Another possibility is a dimeric molecule in which the titanium centres are bridged by the amido ligands, with the imido groups terminal. This species is less likely to be formed, however, as Group 4 imido-amido complexes are typically found to bridge through the imido moiety.

2.5 SUMMARY

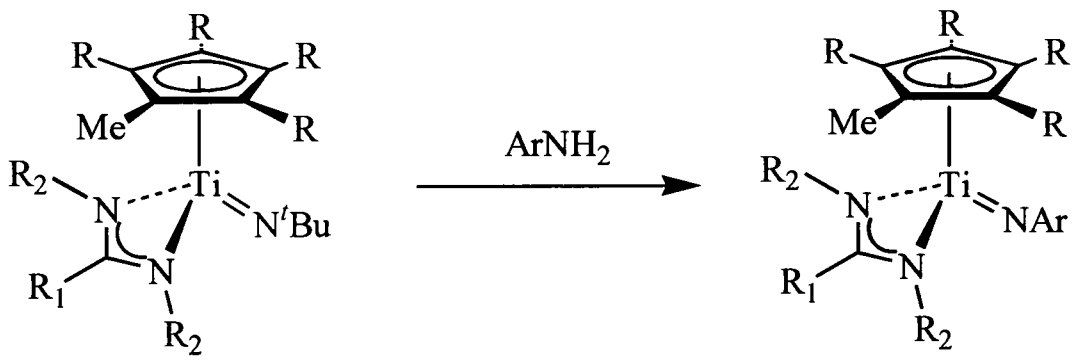
The synthesis and characterisation of new *tert*-butylimido species supported by a cyclopentadienyl-amidinate ligand set (compounds **1 – 6**) are described in Section 2.3. It has been shown that these compounds are all synthesised in high yield using the same synthetic strategy, and that there is a marked difference in the reactivity of monomeric species Ti(η-C_5H_4Me)(N^{t}Bu)Cl(py)

(**2.19**) compared to the dimeric species $[Ti(\eta\text{-}C_5H_4Me)(\mu\text{-}N^tBu)Cl]_2$ (**2.20**). The reactivity is summarised in Scheme 2.6.



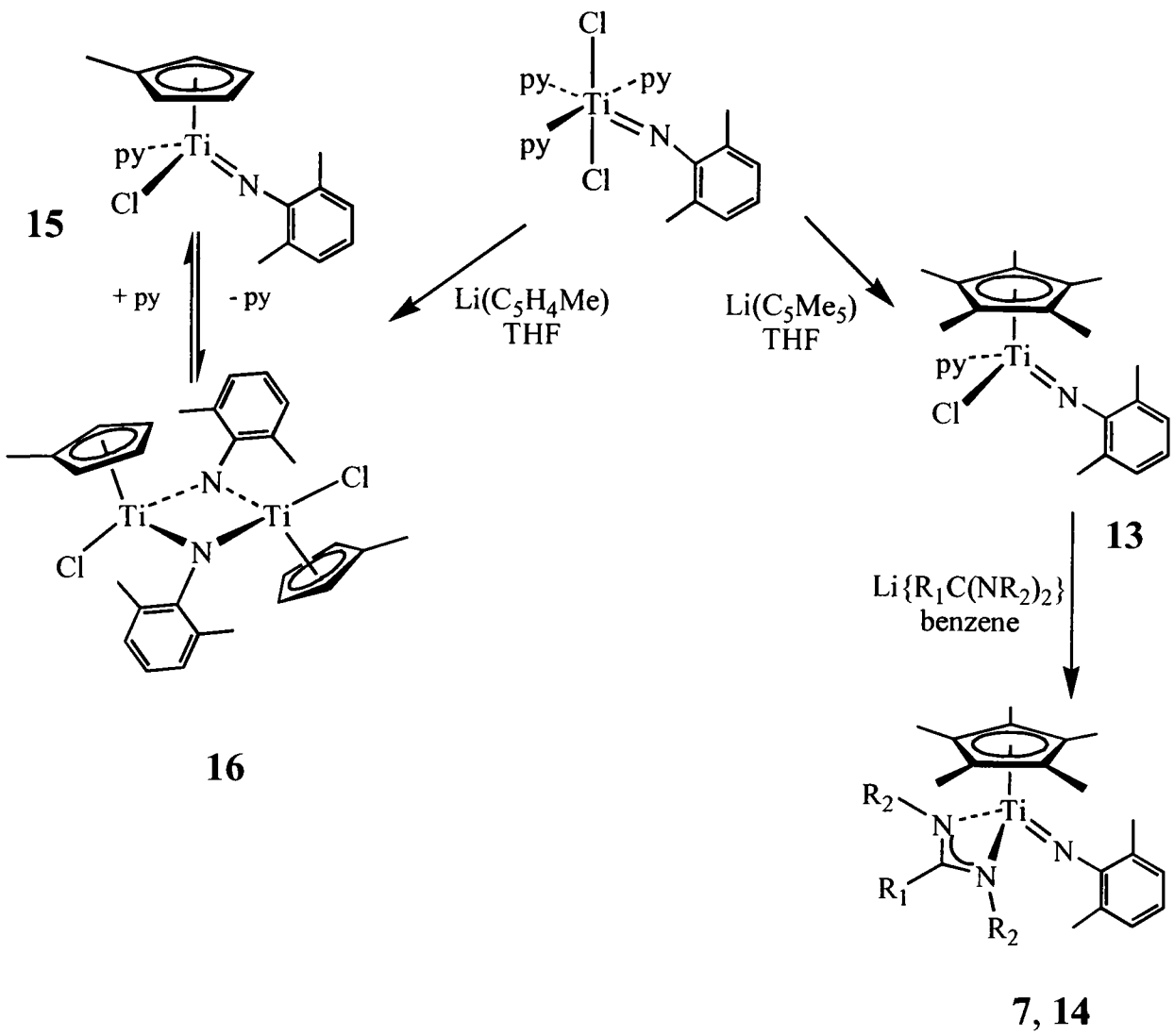
Scheme 2.6 – Summary of synthetic methodology of titanium cyclopentadienyl *tert*-butylimido amidinate complexes

The synthesis and characterisation of new arylimido complexes supported by cyclopentadienyl and cyclopentadienyl-amidinate ancillary ligands are described in Section 2.4. It has been shown that the best synthetic strategy depends on the steric requirements of both the ancillary ligands and the imido N-substituent; generally amine-imido exchange of a cyclopentadienyl *tert*-butylimido amidinate complex gives better results, although the more crowded species Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$){$PhC(NSiMe_3)_2$} (**14**) is only afforded by assembling the cyclopentadienyl-amidinate supporting ligands around the arylimido starting complex Ti(N-2,6-$C_6H_3Me_2$)$Cl_2(py)_3$. As with the *tert*-butylimido complex [Ti(η-C_5H_4Me)(μ-N^{t}Bu)Cl]$_2$ (**2.20**), it was found that the bridging imido complex [Ti(η-C_5H_4Me)(μ-N-4-C_6H_4Me)Cl]$_2$ (**17**) is not synthetically useful. The reactivity of the arylimido complexes described in this Chapter is summarised in Scheme 2.7 – 2.9.

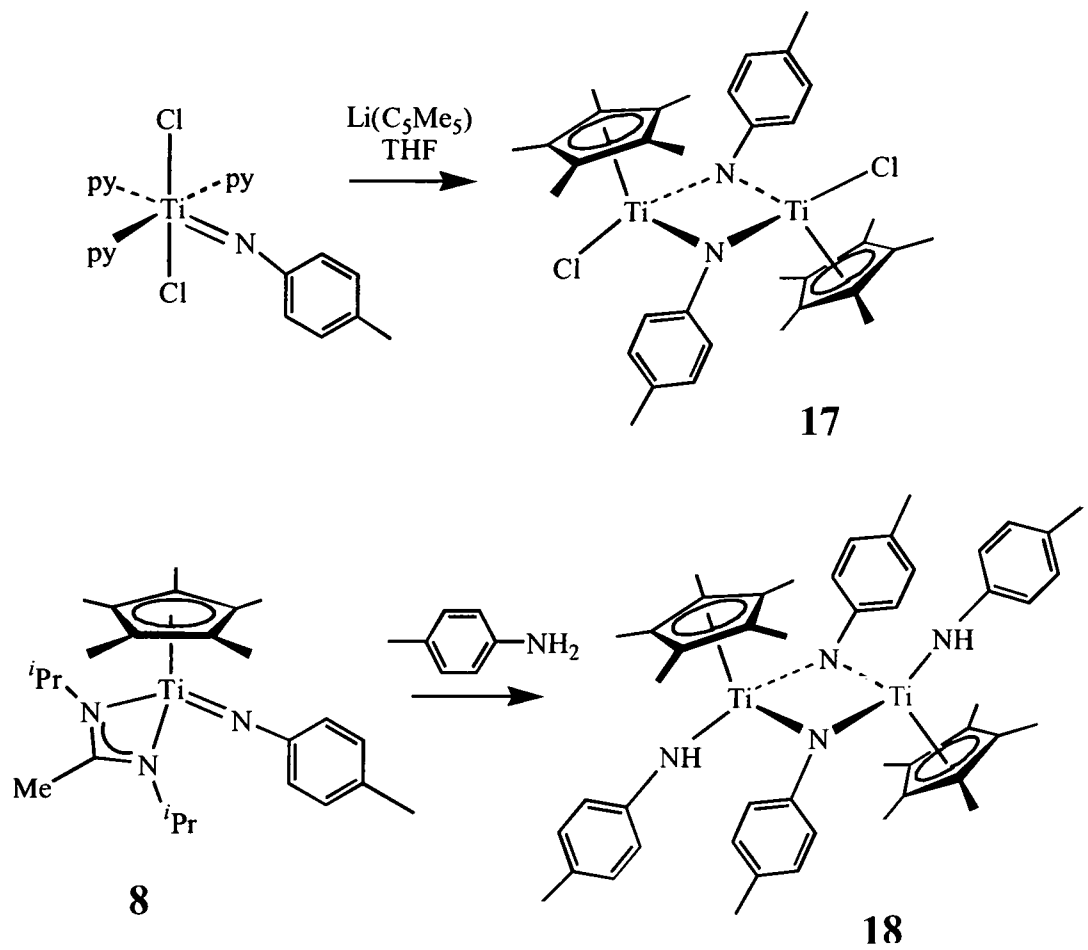


Compound	R	R_1	R_2	Ar
7	Me	Me	^{i}Pr	2,6-$C_6H_3Me_2$
8	Me	Me	^{i}Pr	4-C_6H_4Me
9	Me	Me	^{i}Pr	4-$C_6H_4CF_3$
10	Me	Me	^{i}Pr	4-$C_6H_4NMe_2$
11	H	Ph	$SiMe_3$	2,6-$C_6H_3Me_2$
12	H	Me	^{i}Pr	2,6-$C_6H_3Me_2$

Scheme 2.7 – Synthesis using amine-imido exchange reaction on *tert*-butylimido precursors



Scheme 2.8 – Synthesis of titanium 2,6-dimethylphenylimido complexes



Scheme 2.9 – Synthesis of titanium *p*-tolylimido complexes

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CHAPTER 3

Reactions of Titanium Cyclopentadienyl Imido Amidinate Complexes With Carbon Dioxide

3.1 Overview

This Chapter explores the reactivity of titanium cyclopentadienyl imido amidinate complexes towards carbon dioxide. It begins by reviewing previously reported reactivity of some organometallic complexes towards carbon dioxide, including some mechanistic investigations that have been carried out (Section 3.2). The next Section (Section 3.3) discusses the reactivity of the *tert*-butylimido titanium complexes supported by a cyclopentadienyl-amidinate ligand set. The reactivity of the arylimido homologues is discussed in Section 3.4. Part of this work has recently been published.[1-3]

3.2 Introduction

The reactivity of organometallic compounds with carbon dioxide has been a well-studied phenomenon, which has received much attention in recent years. This Section summarises work which has investigated the reactivity of carbon dioxide with Group 4 metal imides. It begins by discussing other relevant studies, in which the mechanism of carbon dioxide activation is explored, and provides an introduction to the reactivity studies carried out with imidotitanium complexes (both *tert*-butyl- and aryl- imido) supported by the cyclopentadienyl-amidinate ancillary ligand set.

Carbon dioxide is produced in abundance in the environment, both by biological processes and as an industrial by-product. The potential uses of

CO_2 as a C_1 building block for chemical synthesis are limited, however, owing to its tremendous thermodynamic stability. As a result, considerable interest has been shown in recent years in systems that will activate CO_2. For more comprehensive reviews, the reader is directed towards some excellent discussions in the literature.[4-8]

3.2.1 MECHANISTIC STUDIES OF CO_2 REACTIONS WITH METAL COMPLEXES

Floriani has shown that the zirconocene complex $[Zr(\eta\text{-}C_5H_5)_2(H)(Cl)]_n$ (**3.1**) is effective in stoichiometrically reducing CO_2 to formaldehyde and methanol.[9] More recently, interest has been shown in the catalytic coupling of CO_2 with epoxides to form polycarbonates, using zinc bis(salicylaldiminato) complexes,[10] zinc(II) and iron(II) bridging cyanide complexes,[11] and some Cr(III) salen (salen = bis(salicylaldimine)) complexes.[12] Despite this plethora of catalytic systems for the activation of CO_2, comparatively little study of the mechanism behind the activation has been undertaken, although a recent review does discuss some theoretical studies that have been carried out.[13]

3.2.1.1 REACTION WITH CO_2 *VIA* LIGAND EXCHANGE

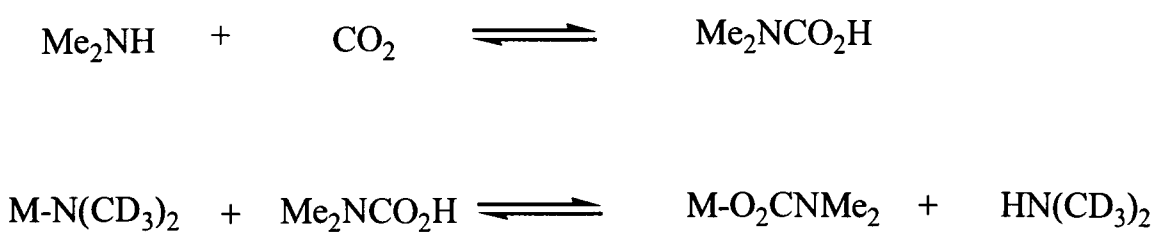
In studies conducted on the metal phenoxide complexes $[M(CO)_5OPh]^-$ (M = Cr (**3.2**), W (**3.3**)), Darensbourg *et al.* showed that CO_2 readily undergoes insertion into the metal-oxygen bond of the phenoxide to afford the corresponding metal pentacarbonyl phenyl carbonate complexes $[M(CO)_5OC(O)Ph]^-$ (M = Cr (**3.4**), W (**3.5**)).[14]. They propose that CO_2 acts as an electrophile, interacting initially at the lone pair on the phenoxide. The

carbonate product was found to decompose back to the starting phenoxide upon the removal of the CO_2 atmosphere. Similar studies involving COS and CS_2 were also carried out by this group;[14,15] these results will be discussed in Chapter 5 of this Thesis.

Similar reactivity towards CO_2 had been previously found for the complexes $M(NMe_2)_n$ (M = Ti (**3.6**), Zr (**3.7**), V (**3.8**), n = 4; M = Nb (**3.9**), Ta (**3.10**), n = 5).[16] Reaction with excess CO_2 afforded the corresponding dimethylcarbamates $M(OC(O)NMe_2)_n$, in which a molecule of CO_2 was found to insert into each metal-amide bond. It was also discovered by the use of labelling experiments that the dimethylcarbamate products undergo facile CO_2 exchange. Chisholm went on to study the mechanism of the reaction, and concluded that for CO_2 exchange:[17]

a) extrusion of CO_2 from the carbamate ligand does not occur;
b) the exchange process occurs *via* attack of a second molecule of CO_2;
c) this attack is not on the carbamate ligand coordinated to the metal, but on a molecule of adventitious amine.

Studies on the mechanism for the initial insertion of CO_2 led Chisholm to conclude that the reaction of $M(NMe_2)_n$ with CO_2 is catalysed by the presence of trace free amine, as shown in Equation 3.1.

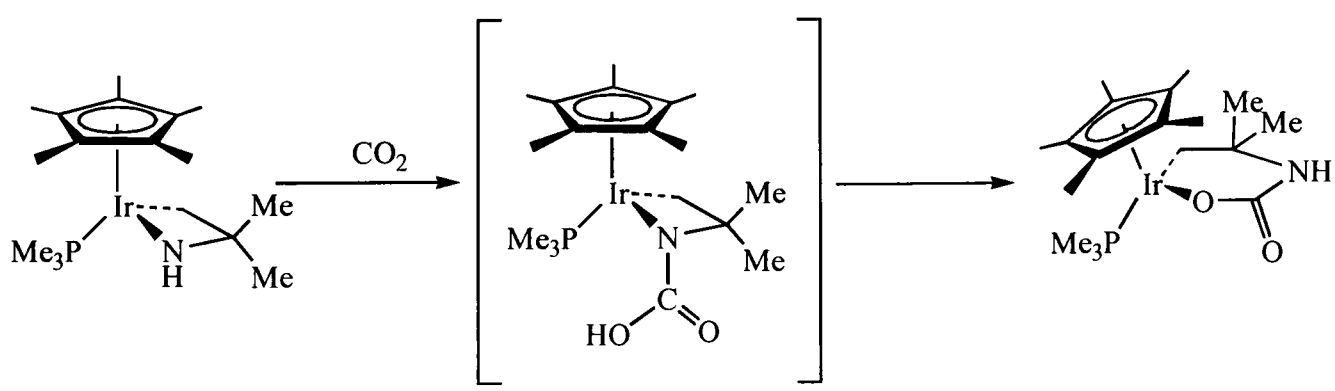


Equation 3.1

Thus, the mechanism for insertion of CO_2 into the metal-amide bond of the $M(NMe_2)_n$ complexes involves attack of trace free amine on CO_2 to afford a molecule of dimethylcarbamic acid. This then undergoes a ligand exchange (protonolysis) reaction, liberating a molecule of dimethylamine and forming the metal-carbamate bond. A study by Darensbourg *et al.*[18] on the insertion of CO_2 into the tungsten-nitrogen bond of the anionic W(0) complex $[Na]^+[W(CO)_4(2\text{-}NH\text{-}NC_5H_4)]^-$ **(3.11)** proved mechanistically inconclusive, owing to the same uncertainty regarding trace free amine.

3.2.1.2 REACTION WITH CO_2 *VIA* FORMAL INSERTION

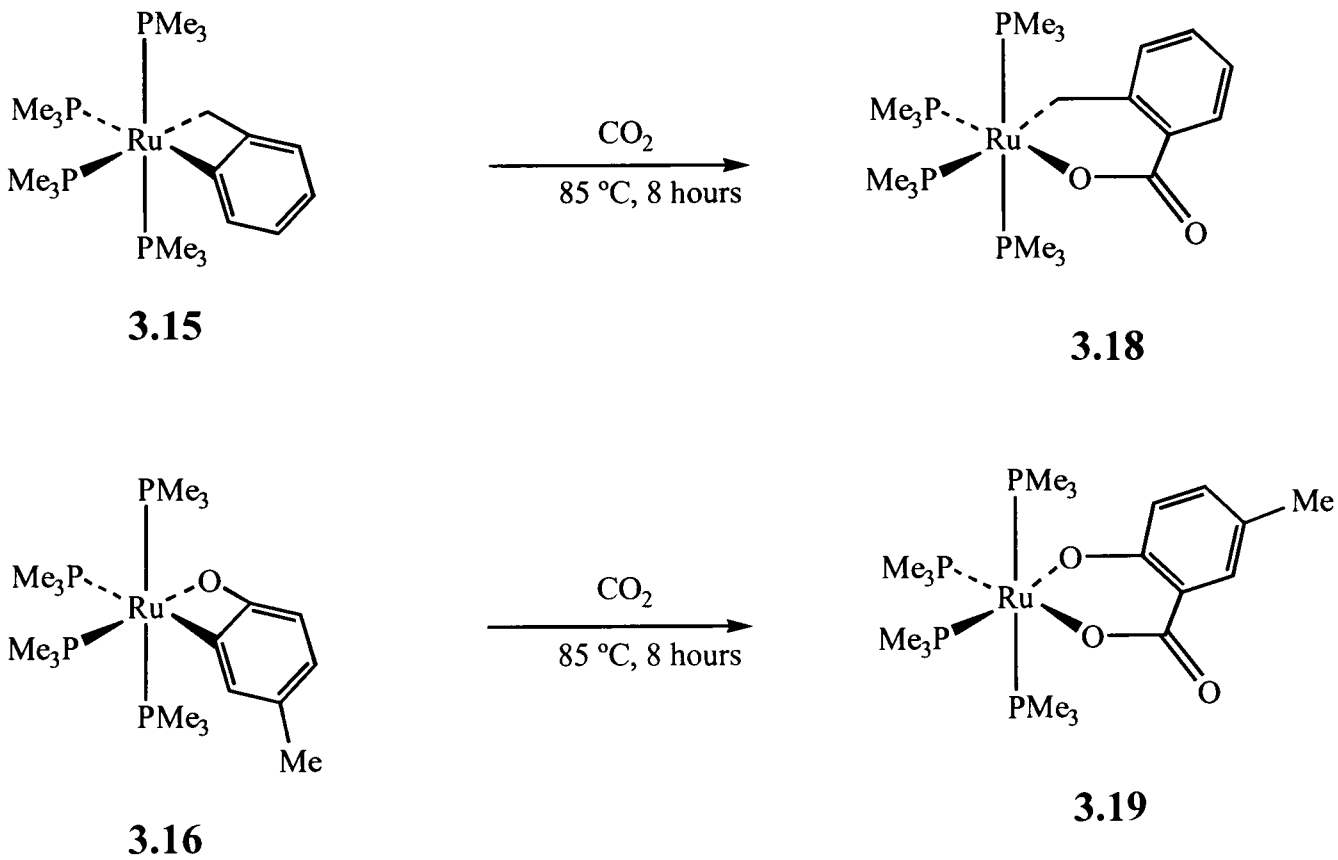
In 1988, Bergman reported the reaction of a cyclopentadienyl iridium complex $Ir(\eta\text{-}C_5Me_5)\{\eta^2\text{-}N(H)C(Me)_2C(H_2)\}(PMe_3)$ **(3.12)** with carbon dioxide.[19] The reaction is summarised in Equation 3.2:



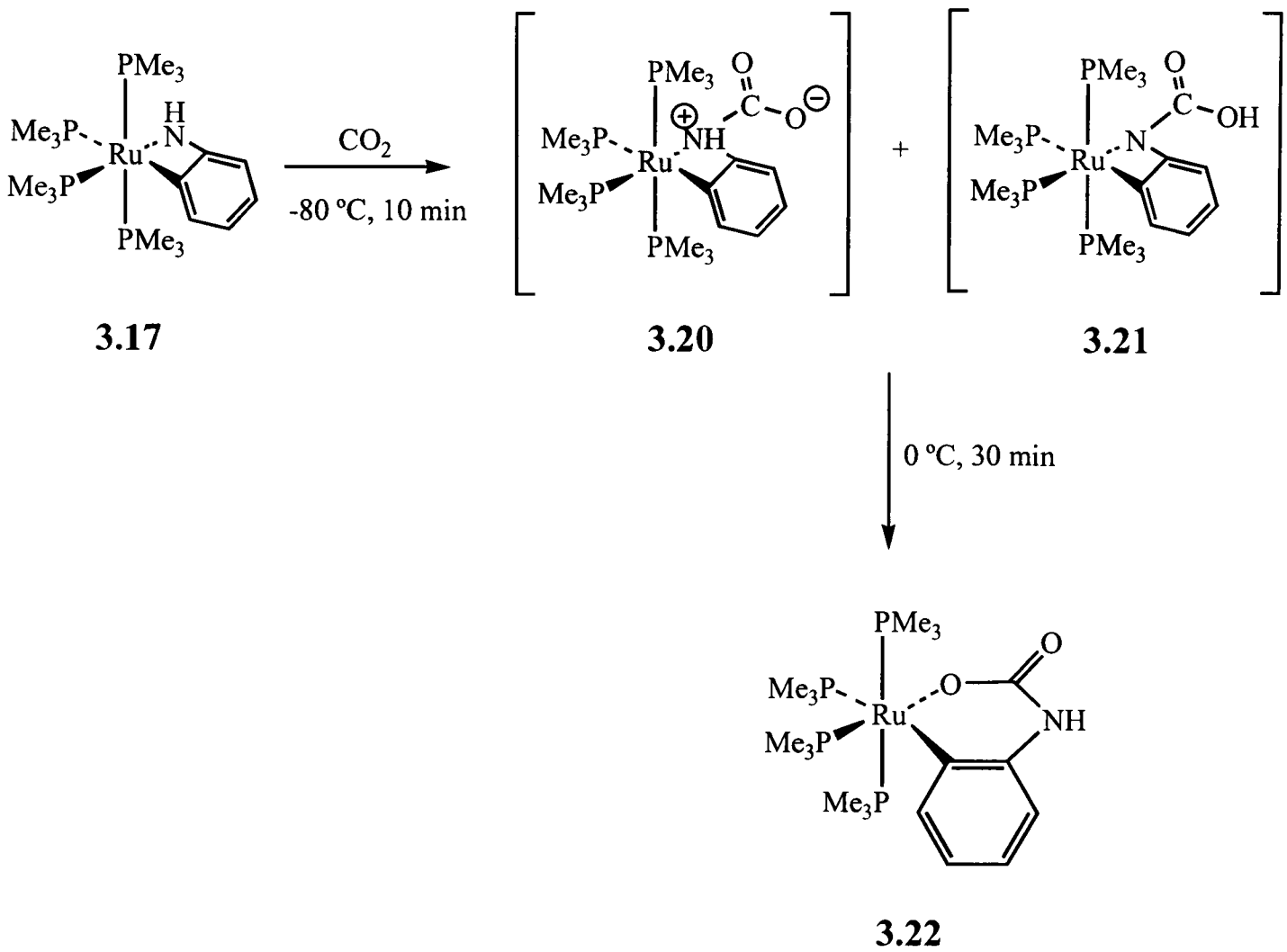
Equation 3.2

The iridium metallacycle **3.12** reacted immediately on exposure to CO_2 to produce complex **3.13**, which was identified by ^1H NMR spectroscopy. This carbamic acid derivative is formed by attack of the nucleophilic nitrogen of the amide on carbon dioxide. Though detectable, **3.13** was found to be too unstable to isolate, quickly rearranging to give a second product, **3.14**, which can be isolated. Bergman has proposed the structure of the intermediate **3.13** by analogy with the isolable product formed by reaction of the parent metallacycle **3.12** with *tert*-butyl isocyanate.

In subsequent work, the group reported the reaction of ruthenium metallacycles of the form $Ru(PMe_3)_4(\eta^2\text{-}2\text{-}X\text{-}5\text{-}C_6H_3R)$ (X, R = CH_2, H (**3.15**); NH, H (**3.16**); O, Me (**3.17**)) with CO_2.[20] They found that the reactivity with CO_2 varied with X, as shown in Schemes 3.1 and 3.2:



Scheme 3.1 – Reaction of $Ru(PMe_3)_4(\eta^2\text{-}2\text{-}X\text{-}5\text{-}C_6H_3R)$ complexes with CO_2

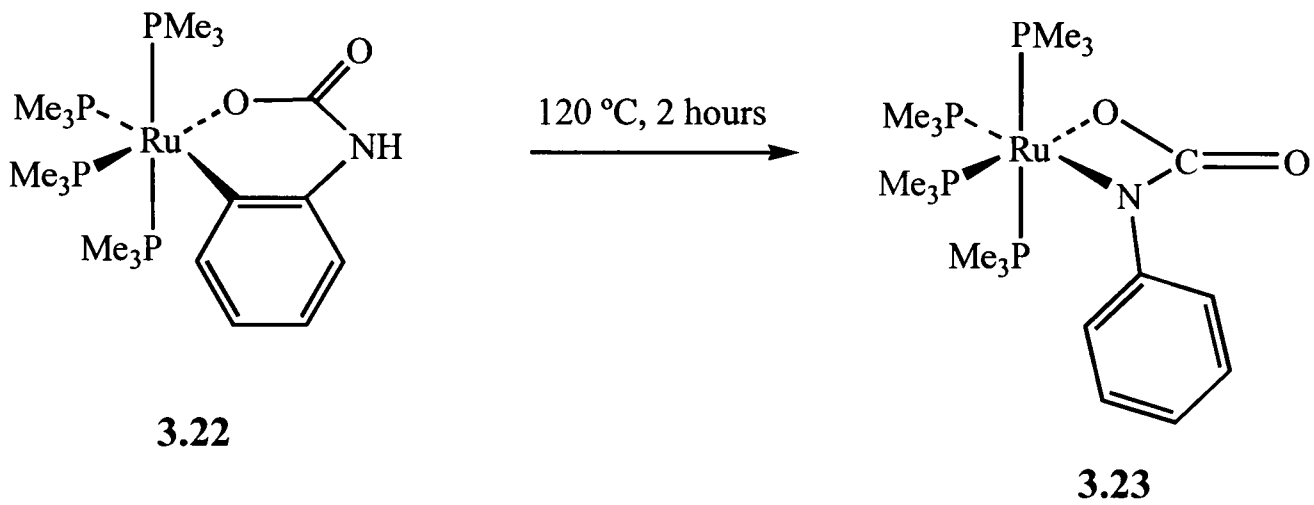


3.17 **3.20** **3.21**

3.22

Scheme 3.2 – Reaction of $Ru(PMe_3)_4(\eta^2\text{-}2\text{-}NH\text{-}5\text{-}C_6H_4)$ (**3.17**) with CO_2

The reactions of $Ru(PMe_3)_4(\eta^2\text{-}CH_2C_6H_4)$ (**3.15**) and $Ru(PMe_3)_4(\eta^2\text{-}OC_6H_3Me)$ (**3.16**) with CO_2 require elevated temperatures, and result in the insertion of CO_2 into the metal-aryl carbon bond. No other reaction is observed. By contrast, the amide derivative $Ru(PMe_3)_4(\eta^2\text{-}NHC_6H_4)$ (**3.17**) reacts very rapidly with CO_2 even at -80 °C to afford at least two coordinated amide-CO_2 adducts (**3.20**, **3.21**), which rearrange to give the final product (**3.22**) as a formal insertion into the metal-nitrogen bond. It was also found that heating **3.22** caused a further reaction, the molecule undergoing ring contraction to give a carboxamide complex **3.23** as shown in Equation 3.3.[20]



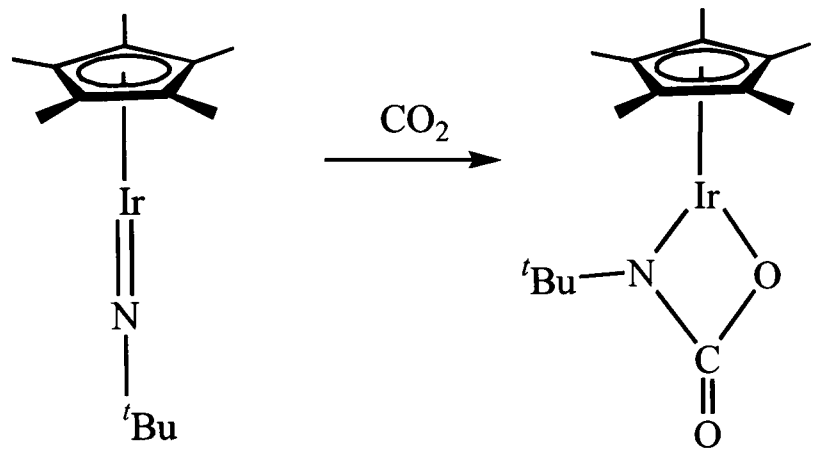
3.22 **3.23**

Equation 3.3

The nature of the amido group used in these experiments removes the possibility of trace amines catalysing the reaction; mechanistic certainty is therefore much improved compared to the work by Chisholm and Darensbourg cited earlier. It is therefore clear that two mechanisms for the insertion of CO_2 into metal-nitrogen amide bonds exist. One involves catalysis by free amine followed by ligand exchange, the other by direct attack of the electrophilic carbon of CO_2 on the nitrogen lone pair.

3.2.2 REACTION OF CO_2 WITH METAL IMIDO COMPLEXES

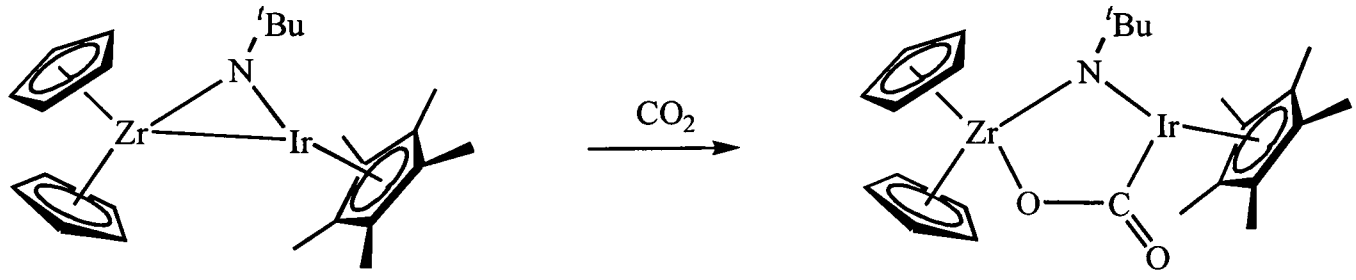
Armor[21] first reported the reaction of an imidotitanium complex $[Ti(C_5H_5)_2(\mu\text{-}NH)]_2H$ with CO_2 to give a carbamate product, though neither the starting material nor the product were fully characterised. The first fully characterised product (**3.25**) was formed from reaction of $Ir(\eta\text{-}C_5Me_5)(N^tBu)$ (**3.24**) with CO_2, as shown in Equation 3.4.[22]



3.24 **3.25**

Equation 3.4

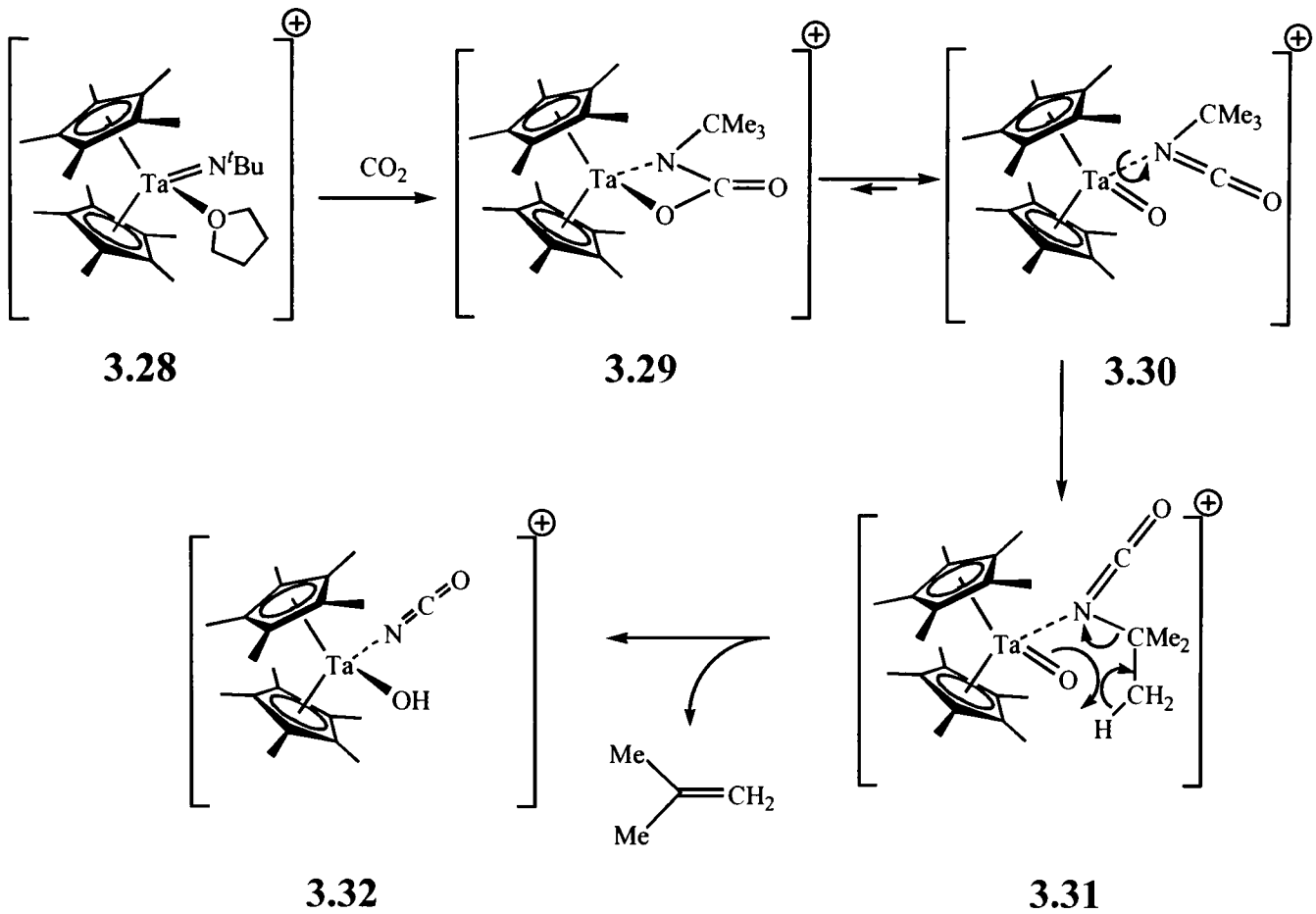
Bergman[23] also reported the direct addition of CO_2 into the metal-metal bond in the bimetallic bridging imido system $(C_5H_5)_2Zr(\mu\text{-}N^tBu)Ir(C_5Me_5)$ as shown in Equation 3.5.



3.26 **3.27**

Equation 3.5

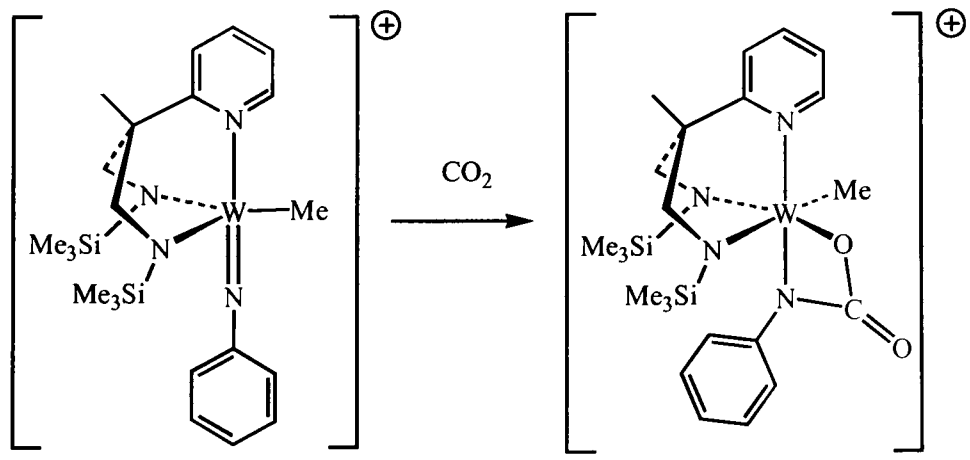
Bercaw has reported the reaction between the cationic species $[Ta(C_5Me_5)_2(N^tBu)(THF)]^+$ and CO_2, which gives isobutylene and the isocyanate complex $[Ta(C_5Me_5)_2(OH)(NCO)]^+$.[24] A possible mechanism, going *via* an expected (though unobserved) carbamate intermediate (**3.29**), has been suggested, and is shown in Scheme 3.3.



3.28 **3.29** **3.30** **3.31** **3.32**

Scheme 3.3 – Reaction of $[Ta(C_5Me_5)_2(N^tBu)(THF)]^+$ with CO_2

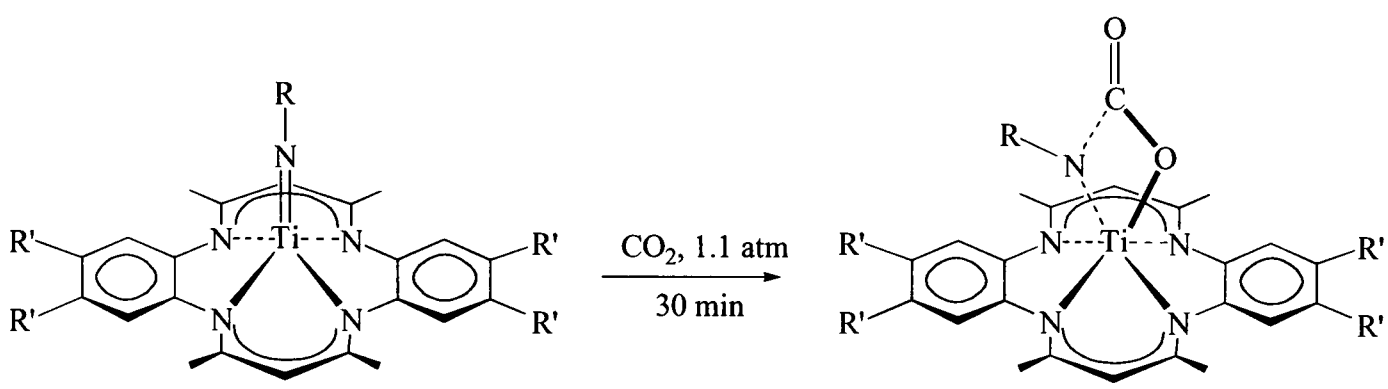
The reaction of another cationic imido species $[W(N_2N_{py})(NPh)(Me)]^+$ (N_2N_{py} = $MeC(2\text{-}C_5H_4N)(CH_2NSiMe_3)_2$) with CO_2 has very recently been investigated.[25] The product was a formal [2 + 2] cycloadduct between the imido group and CO_2, rather than insertion into the metal-carbon bond of the alkyl group, as shown in Equation 3.6.



3.33 **3.34**

Equation 3.6

Recent work in the Mountford group has investigated the reactivity of tetraazamacrocycle-supported Group 4 imido systems towards CO_2.[26] These systems undergo irreversible [2 + 2] cycloaddition reactions to give N, O-bound carbamate products, as shown in Equation 3.7.



	R	R'	
3.35	^{t}Bu	H	**3.36**
3.37	4-C_6H_4Me	H	**3.38**
3.39	NPh_2	H	**3.40**
3.41	^{t}Bu	Me	**3.42**
3.43	4-C_6H_4Me	Me	**3.44**
3.45	NPh_2	Me	**3.46**

Equation 3.7

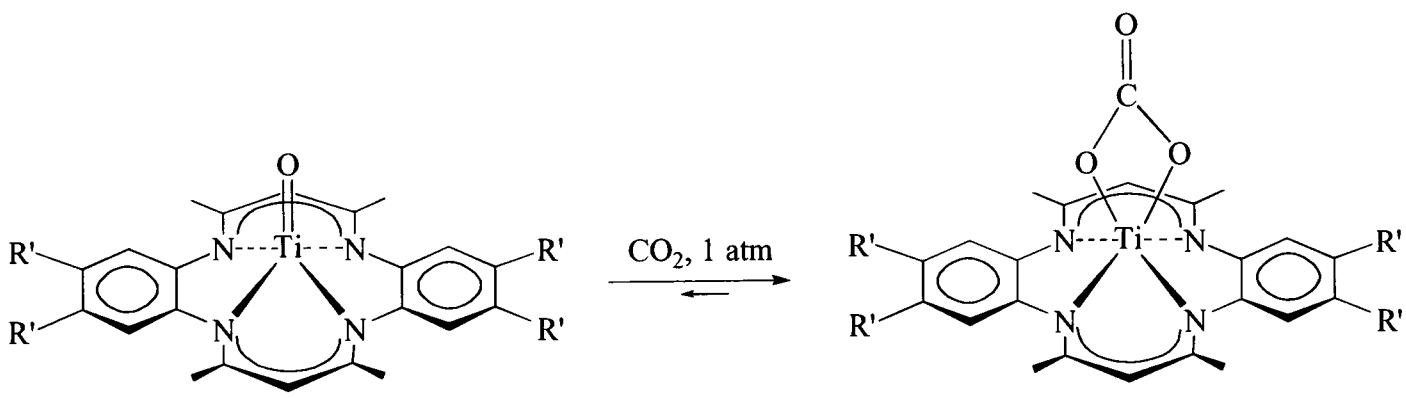
The cycloaddition complexes with R = ^{t}Bu, 4-C_6H_4Me were found to be light sensitive in both solution and the solid state, decomposing over a matter of days to give the terminal oxo species and free isocyanate. By contrast, a chloroform-d solution of Ti{N(^{t}Bu)C(O)O}(Me_8taa) (H_2Me_8taa = octamethyldibenzotetraaza[14]annulene) showed no evidence for decomposition after 5 days stored in the dark. The molecular structure of **3.38** has been determined by single crystal X-ray diffraction studies, and will be discussed in Section 3.3.1.1.

The complex $Ta(C_5Me_5)Cl_2(N^tBu)$ **(3.47)** reported by Royo,[27] reacted with CO_2 to give an oxo product and free isocyanate, without any intermediates being observed.

3.2.3 REACTION OF CO_2 WITH METAL OXO COMPLEXES

The reaction of terminal oxo species with CO_2 has also been reported. Goedkin[28] found that reaction of $Ti(O)(Me_4taa)$ (H_2Me_4taa = tetramethyldibenzotetraaza[14]annulene) **(3.48)** with CO_2 at 0 °C and 2 atm pressure afforded a product which was not fully characterised, due to the ease of reversibility of the reaction.

Geoffroy investigated the reaction of the related complex $Ti(O)(Me_8taa)$ with CO_2, and reported the analogous apparent [2 + 2] cycloaddition reaction that was later found for the imido systems.[29,30] The resulting system incorporates a (η^2-O, O'- bound) carbonate ligand, as shown in Equation 3.8.



3.49 **3.50**

Equation 3.8

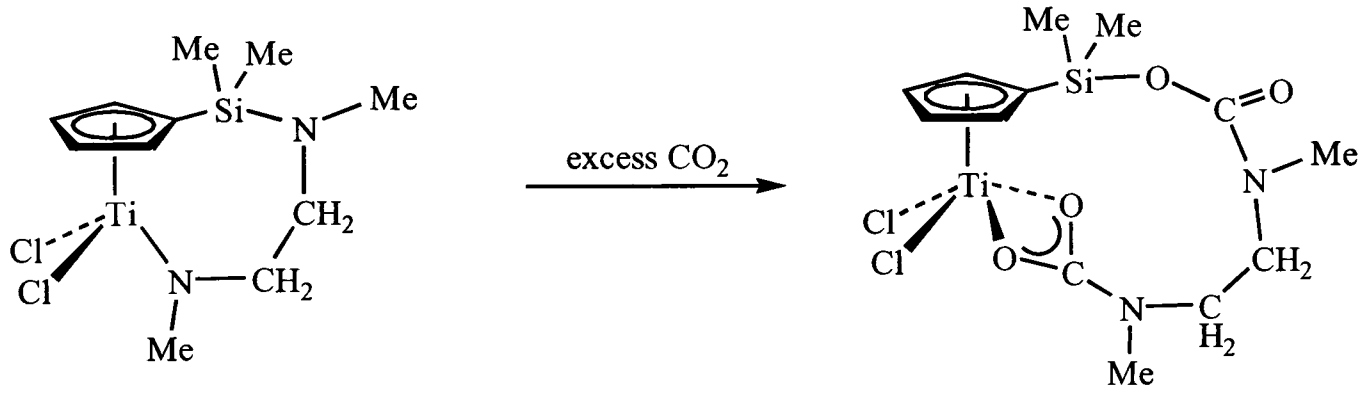
The carbonate ligand has also been formed in the reaction of the complex $Re(\eta\text{-}C_5Me_5)(O)Cl_2$ **(3.51)** with Ag_2CO_3 to afford $Re(\eta\text{-}C_5Me_5)(O)\{O_2C(O)\}$

(**3.52**). This complex was found to be thermally unstable, evolving CO at 200 °C to afford the oxo complex $Re(\eta\text{-}C_5Me_5)O_3$ (**3.53**).[31]

3.2.4 REACTION OF CO_2 WITH METAL AMIDO COMPLEXES

The reaction between metal amido complexes and CO_2 has been well-studied, and some of the work by Chisholm, Darensbourg, and Bergman was discussed above in Section 3.2.1.

Royo *et al.* have reported the reaction of two molecules of CO_2 at two different sites in the linked cyclopentadienyl-amido titanium complex $Ti\{\eta^5\text{-}C_5H_4SiMe_2NMe(CH_2)_2\text{-}\eta\text{-}NMe\}Cl_2$.[32] The reaction is summarised in Equation 3.9.

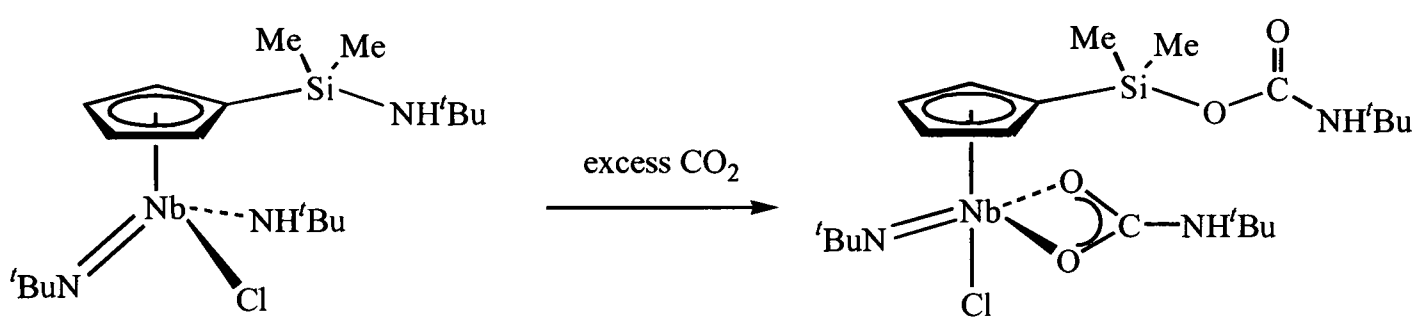


3.54 **3.55**

Equation 3.9

Heating **3.55** causes elimination of 1,3-dimethyl-2-imidazolidinone and CO_2, to form the complexes $[Ti\{\mu\text{-}(SiMe_2O\text{-}\eta^5\text{-}C_5H_4)\}Cl_2]_2$ as the major and $(TiCl_2)_2(\mu\text{-}O)\{\mu\text{-}(\eta^5\text{-}C_5H_4)_2\text{-}SiMe_2O\}$ as the minor components of the product. Although the insertion of CO_2 into the M–N bond has been proposed as the first step in the analogous reactions of amide derivatives of titanium,

zirconium,[33] germanium, and tin,[34-36] such carbamate intermediates have not been observed. The group also reported similar reactivity with a niobium imido complex, Nb{η^5-$C_5H_4SiMe_2(NH^tBu)$}(N^tBu)Cl(NH^tBu) (**3.56**), which inserts CO_2 in an identical fashion, as shown in Equation 3.10.[37] In this study, it was found that the N–Si and Nb–N_{amide} bonds were reactive, while the imido group remained unchanged, even after heating.



3.56 **3.57**

Equation 3.10

3.2.5 Reaction of CO_2 with metal alkoxo complexes

The reaction between metal alkoxide complexes and CO_2 has also been investigated, and the mechanistic studies of the phenoxide systems $[M(CO)_5(OPh)]^-$ (M = Cr (**3.2**), W (**3.3**)) have already been discussed in Section 3.2.1 above. These reactions are typical of metal-alkoxo complex reactions with CO_2, in which insertion (often reversible) of CO_2 into the metal-carbon bond.

3.2.6 Conclusion

Reaction of transition metal complexes with CO_2 has been found to afford a variety of isolable products. The remainder of this Chapter explores the

products formed by reaction of titanium cyclopentadienyl imido amidinate complexes with CO_2.

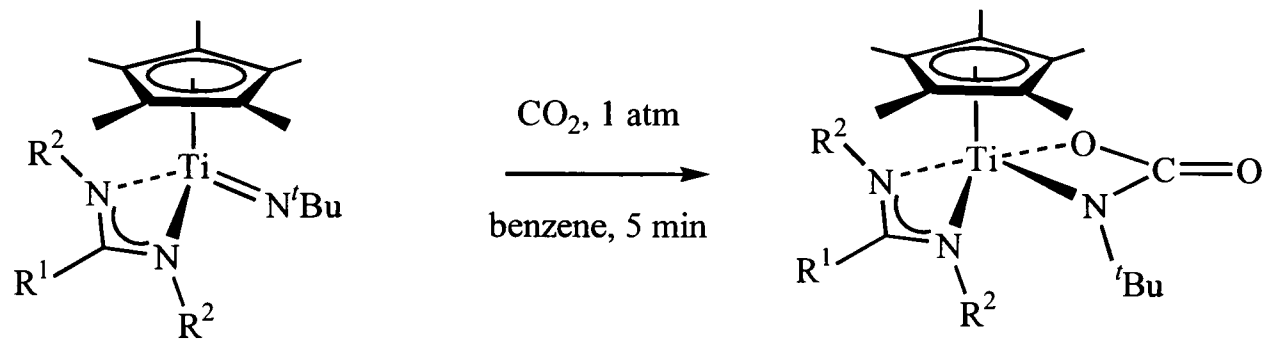
3.3 REACTIONS OF TITANIUM CYCLOPENTADIENYL *TERT*-BUTYLIMIDO AMIDINATE COMPLEXES WITH CO_2

The reaction of tetraazaannulene-supported titanium *tert*-butylimido species with CO_2 were found to afford isolable carbamate products.[26] The reaction of the more reactive imidotitanium complex $Ti(N_2N_{py})(N^tBu)(py)$ (**3.58**) with CO_2 has also been investigated by Mountford *et al.*, but all attempts to isolate a stable product were unsuccessful.[38] This can be ascribed in part to the lower steric protection afforded the metal centre by the (N_2N_{py}) supporting ligand. However, the main reason is probably the availability of the nucleophilic lone pairs of electrons on the amido nitrogens of (N_2N_{py}). In the Me_ntaa (n = 4, 8) systems, the lone pairs are delocalised, limiting the possible side-reactions that could occur. The cyclopentadienyl-amidinate ligand set was anticipated to give greater steric protection than (N_2N_{py}), and the amidinate nitrogens possess delocalised lone pairs. It was therefore expected that the products of reaction would be more stable than those of N_2N_{py}-supported complexes.

3.3.1 REACTIONS OF $Ti(\eta\text{-}C_5Me_5)(N^tBu)\{R^1C(NR^2)_2\}$ WITH CO_2

Samples of $Ti(\eta\text{-}C_5Me_5)(N^tBu)\{PhC(NSiMe_3)_2\}$ (**1**) and $Ti(\eta\text{-}C_5Me_5)(N^tBu)\{MeC(N^iPr)_2\}$ (**2**) were dissolved in benzene, and exposed to CO_2 at a pressure of 1 atm. Immediate reaction was indicated by a colour change from dark red to a deep cherry red. Removal of volatiles under reduced pressure

afforded the carbamate compounds $Ti(\eta\text{-}C_5Me_5)\{N(^tBu)C(O)O\}\{PhC(NSiMe_3)_2\}$ (**19**) (95 % yield) and $Ti(\eta\text{-}C_5Me_5)\{N(^tBu)C(O)O\}\{MeC(N^iPr)_2\}$ (**20**) (65 % yield) respectively, as shown in Equation 3.11.



	R^1	R^2	
1	Ph	$SiMe_3$	**19**
2	Me	^iPr	**20**

Equation 3.11

The compounds **19** and **20** have been characterised by ^1H and $^{13}C\text{-}\{^1H\}$ NMR, and IR spectroscopies, and elemental analysis. Neither compound was found to give a molecular ion in its mass spectrum, using either EI or FI techniques. The ^1H NMR spectra of these molecules shows the loss of the plane of symmetry on formation of the adduct, as shown in Figure 3.1 for **19**.

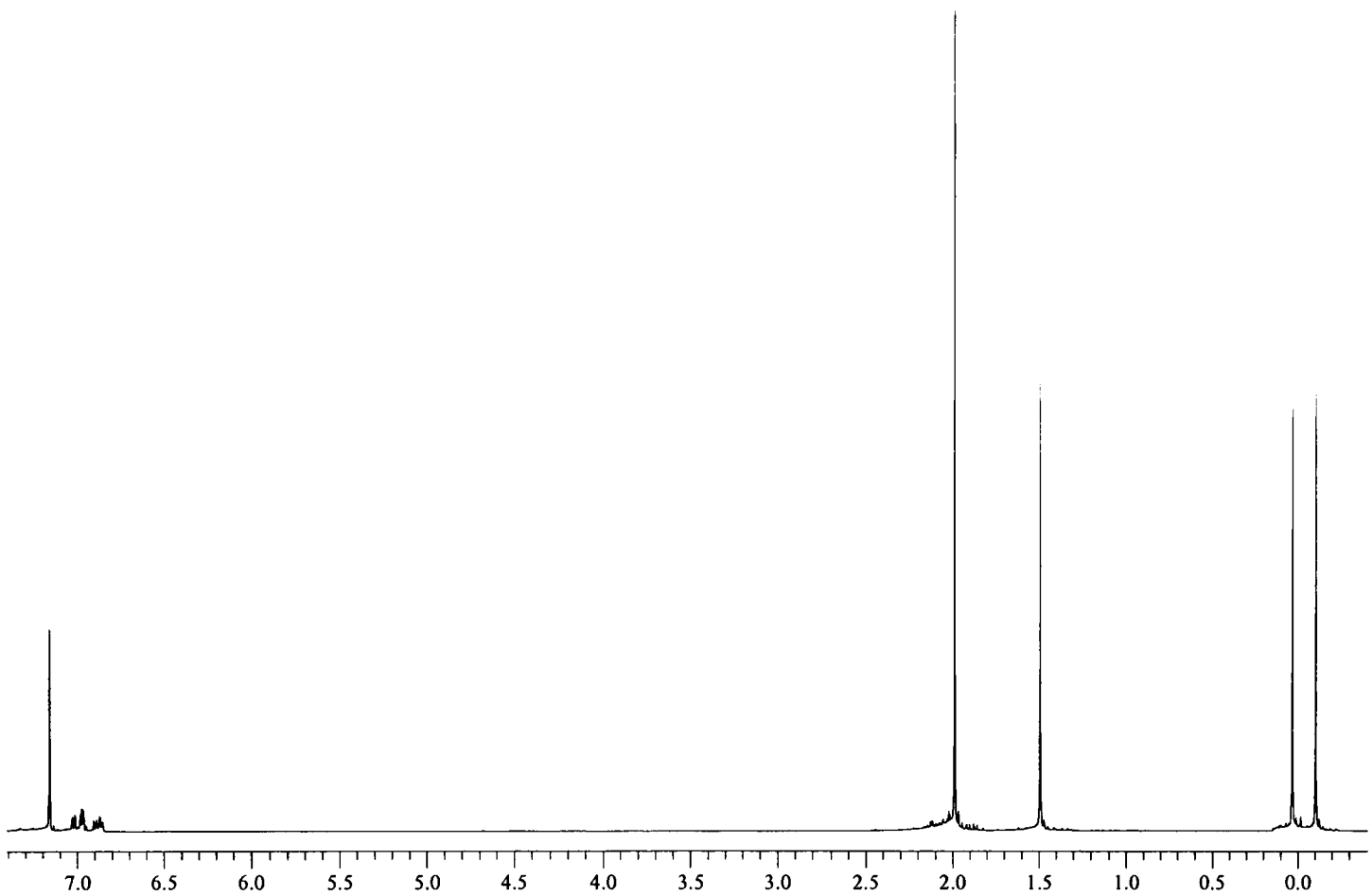


Figure 3.1 – 500.0 MHz ^{1}H NMR spectrum of Ti(η-C_5Me_5){N(^{t}Bu)C(O)O}{PhC(NSiMe$_3$)$_2$} (**19**) in benzene-d_6

A series of ^{1}H nOe experiments were conducted on **19**. They revealed that the resonance at 0.03 ppm can be assigned to the $SiMe_3$ group adjacent to the *tert*-butyl group of the carbamate. They also showed that the methyl protons on the pentamethylcyclopentadienyl ring are spatially close to the aryl protons of the benzamidinate, suggesting that the molecule possesses a four-legged piano stool structure.

The IR spectra of **19** and **20** show intense new stretches at 1660 cm^{-1} and 1662 cm^{-1} respectively. These are consistent with the incorporation of a new carbonyl unit into the molecule (cf. ν = 1636 – 1657 cm^{-1} for Me$_n$taa carbamate complexes,[26] 1708 cm^{-1} for Ir(η-C_5Me_5){N(^{t}Bu)C(O)O} (**3.25**),[22]

1626 cm^{-1} for $Mo(\eta\text{-}C_5H_5)_2\{N(Ph)C(O)O\}$ (**3.59**),[39] and 1728 cm^{-1} for $Re(\eta\text{-}C_5Me_5)(O)\{N(Ph)C(O)O\}$ (**3.60**)[40].

Concurrent with this work, a study into the reactivity of the related pendant arm functionalised amidinate complex $Ti(\eta\text{-}C_5Me_5)(N^tBu)\{PhC(NSiMe_3)(NCH_2CH_2CH_2NMe_2)\}$ (**3.61**) was carried out by Catherine Boyd (a Part II student) under my direct supervision. Reaction of **3.61** with CO_2 under conditions identical to those used in the synthesis of **19** and **20** yielded $Ti(\eta\text{-}C_5Me_5)\{N(^tBu)C(O)O\}\{\kappa^2\text{-}PhC(NSiMe_3)(NCH_2CH_2CH_2NMe_2)\}$ (**3.62**). A peak was detected in the IR spectrum of the product at 1666 cm^{-1}, consistent with the incorporation of a carbonyl functional group. A crystal of **3.62** suitable for an X-ray diffraction study was grown from a saturated solution in benzene. X-ray diffraction data were collected by the author, and the structure solved by Dr. P. Mountford. The molecular structure is given in Figure 3.2, and some selected bond distances and angles are given in Table 3.1 below:

Table 3.2 – Selected bond lengths (Å) and angles (°) for $Ti(\eta\text{-}C_5Me_5)\{N(^tBu)C(O)O\}\{PhC(NSiMe_3)(NCH_2CH_2CH_2NMe_2)\}$ (**3.62**)

$Ti(1) - Cp_{(cent)}$	2.058	$Cp_{(cent)}$-Ti(1)-N(1)	119.3
Ti(1) – N(1)	2.087(5)	$Cp_{(cent)}$-Ti(1)-N(2)	108.7
Ti(1) – N(2)	2.131(4)	$Cp_{(cent)}$-Ti(1)-N(4)	129.3
Ti(1) – N(4)	1.991(5)	$Cp_{(cent)}$-Ti(1)-O(1)	109.0
Ti(1) – O(1)	1.971(4)		

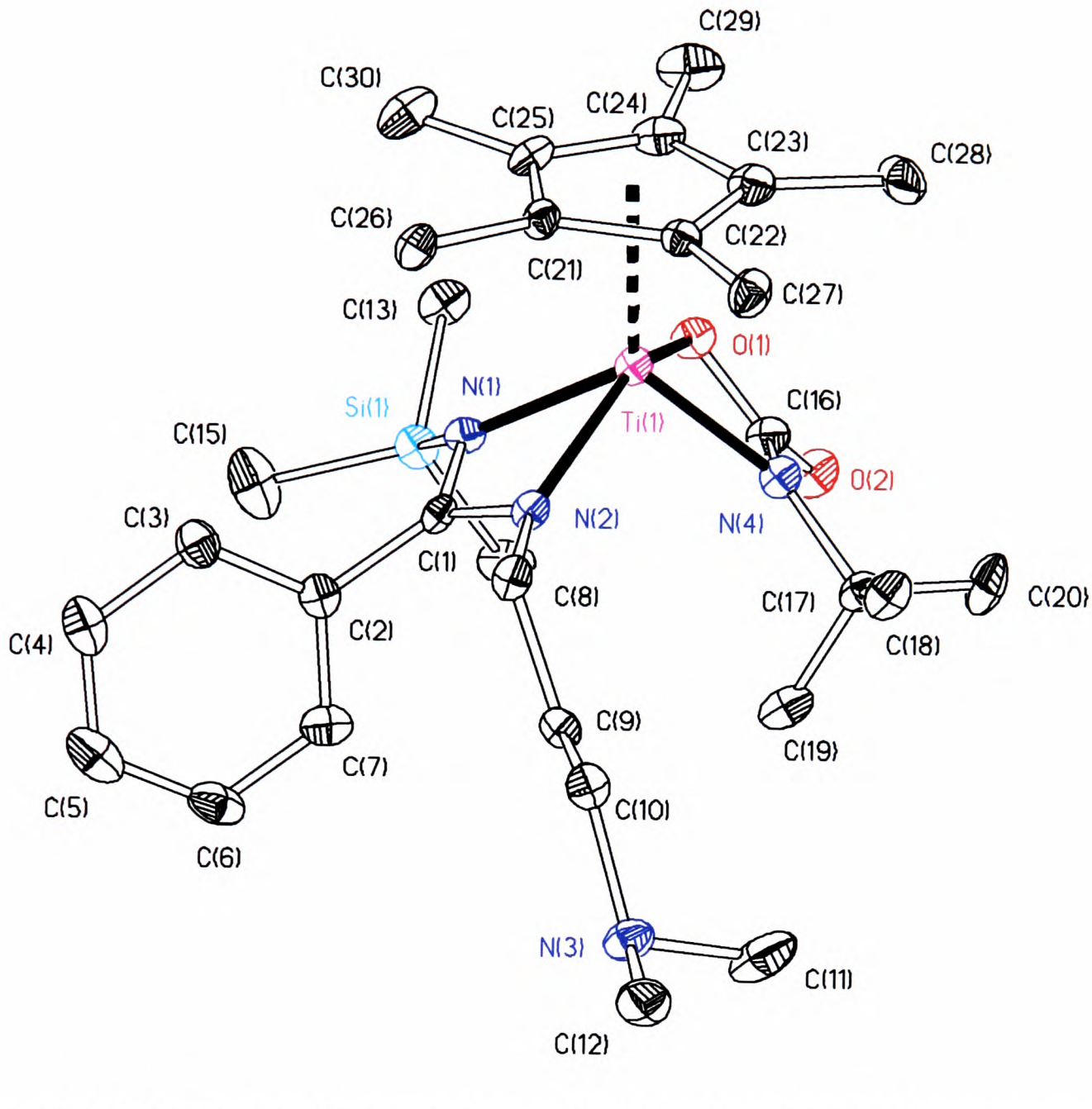


Figure 3.2 - Thermal ellipsoid plot (30 % probability) of Ti(η-C_5Me_5){N(^{t}Bu)C(O)O} {κ^2-PhC(NSiMe$_3$)(NCH$_2$CH$_2$CH$_2$NMe$_2$)} (**3.62**). H atoms are omitted for clarity

3.3.1.1 Comparison of the X-ray crystal structures of Ti{N(-4-C_6H_4Me)C(O)O}(Me_4taa) (3.38) and Ti(η-C_5Me_5){N(^{t}Bu)C(O)O}{κ^2-PhC(NSiMe$_3$)(NCH$_2$CH$_2$CH$_2$NMe$_2$)} (3.62)

The molecular structure of Ti{N(-4-C_6H_4Me)C(O)O}(Me_4taa) (**3.38**) has been determined by single crystal X-ray diffraction, and is given in Figure 3.3.[26]

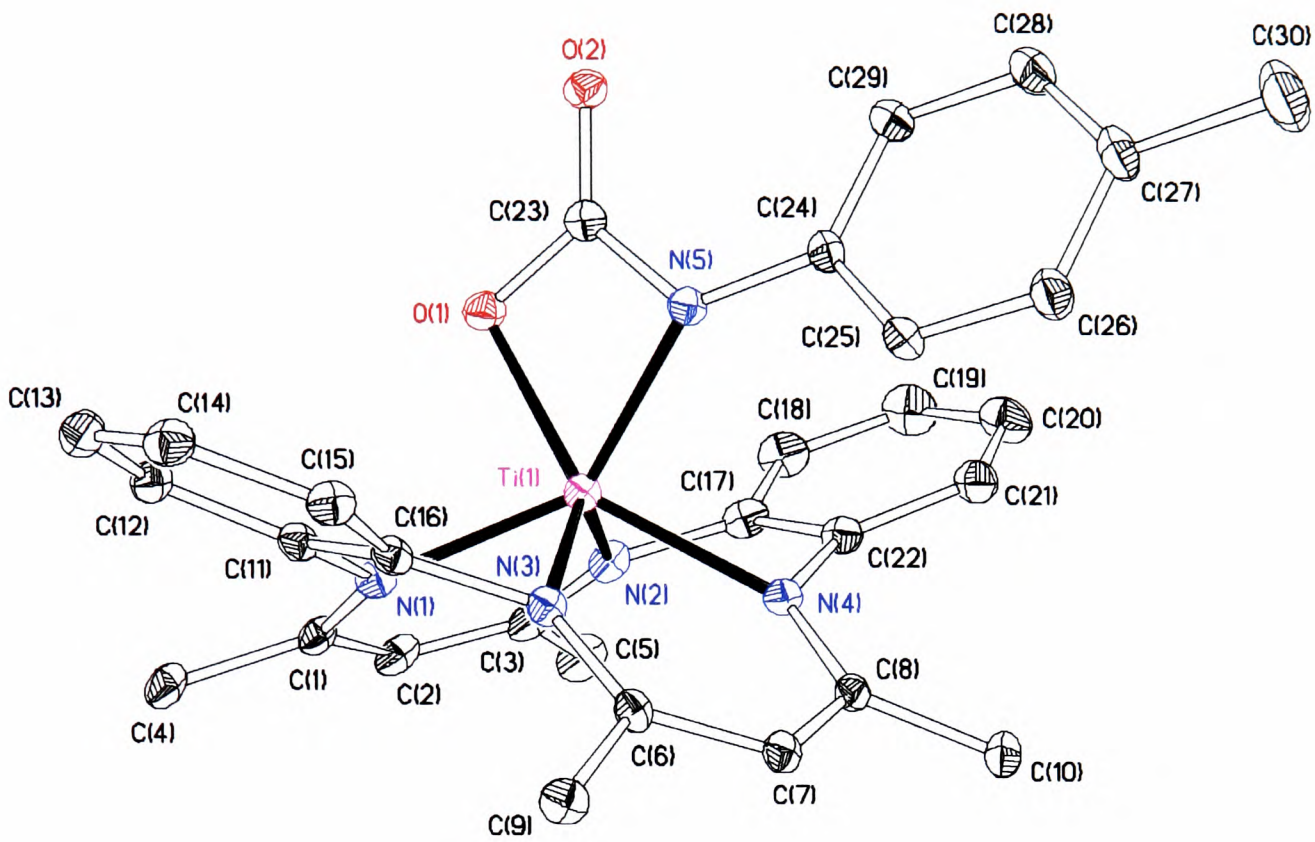


Figure 3.3 - Thermal ellipsoid plot (30 % probability) of Ti{N(-4-C_6H_4Me)C(O)O}(Me_4taa) (**3.38**). H atoms omitted for clarity

The internal C=O, C–O, and C–N distances of the carbamate moieties of the two complexes are compared in Figure 3.4.

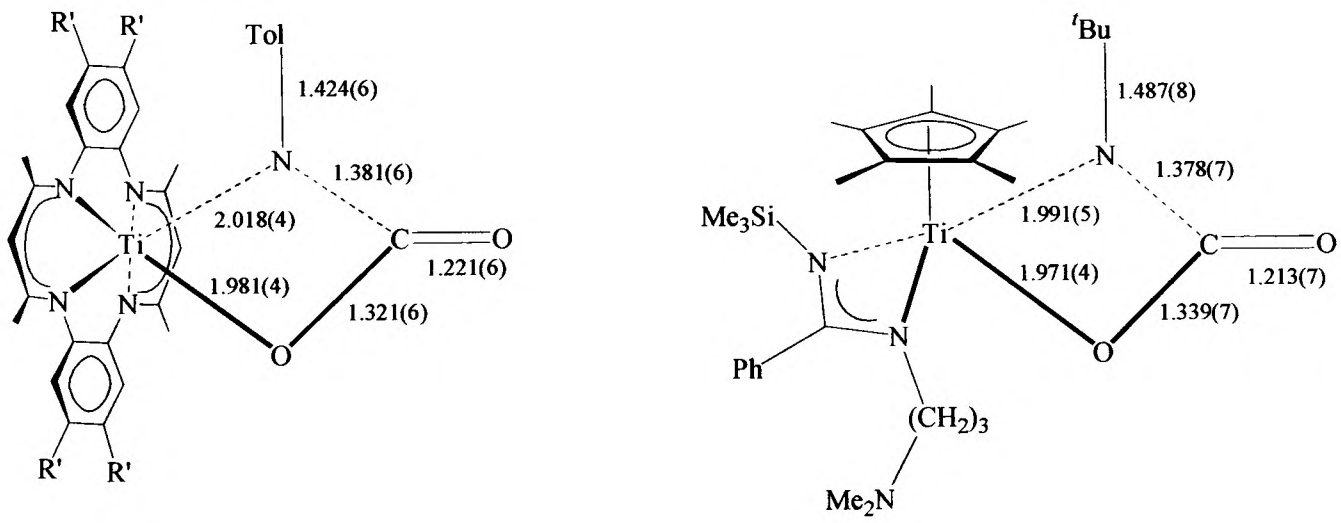


Figure 3.4 – Comparison of bond lengths in carbamate complexes **3.38** and **3.62**

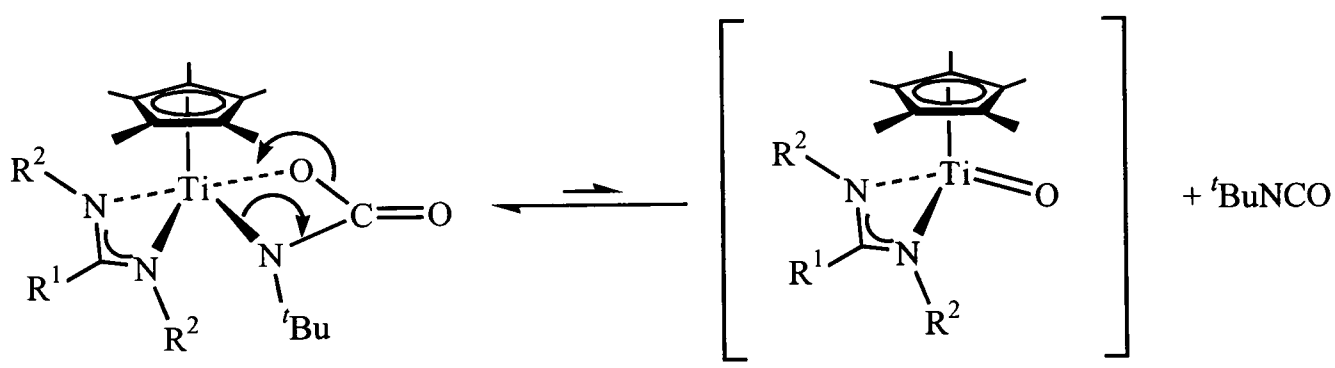
The bond lengths for the carbamate moieties of both complexes are comparable to the corresponding average values of 1.196 (range ± 0.024), 1.344 (range ± 0.024) and 1.38 (range ± 0.014) Å found for three other crystallographically characterised carbamate complexes: Ir(η-C_5Me_5){N(^{t}Bu)C(O)O} (**3.25**),[22] Mo(η-C_5H_5)$_2${N(Ph)C(O)O} (**3.59**),[39] and Re(η-C_5Me_5)(O){N(Ph)C(O)O} (**3.60**),[40] These latter three carbamate complexes were synthesised by reaction of terminal oxo complexes with isocyanates. Reaction of Ir(η-C_5Me_5)(N^{t}Bu) with CO_2 was also found to afford **3.25**, as has been discussed above.

The Ti–N bond of the carbamate group is longer in **3.38** than **3.62** (2.018(4) Å cf. 1.991(5) Å respectively). This can be rationalised by considering that the N^{t}Bu group is more basic, and so a better electron donor than N-4-C_6H_4Me. The steric bulk of the macrocyclic ligand is greater than that of the cyclopentadienyl-amidinate ligand set, and so the nitrogen would also be expected to lie at a greater distance on steric grounds. The N–R bond of the carbamate group is shorter in **3.38** (1.424(6) Å cf. 1.487(8) Å), which is due to the difference in hybridisation of the carbon bound to the nitrogen (sp^2 in **3.38**, sp^3 in **3.62**). As well as the possible π-electron interaction of the aryl ring of **3.38** with the carbamate nitrogen causing an increase in bond order (and thus shortening the N–R bond), the greater steric bulk of the *tert*-butyl group in **3.62** might be expected to lengthen the N–R bond.

3.3.1.2 REACTIONS OF THE CARBAMATE COMPLEXES

$Ti(\eta\text{-}C_5Me_5)\{N(^tBu)C(O)O\}\{R^1C(NR^2)_2\}$ (19, 20)

The cycloaddition products **19** and **20** are unstable in solution, and decompose to form $[Ti(\eta\text{-}C_5Me_5)(\mu\text{-}O)\{PhC(NSiMe_3)_2\}]_2$ (**21**) (53 % isolated yield) and $[Ti(\eta\text{-}C_5Me_5)(\mu\text{-}O)\{MeC(N^iPr)_2\}]_2$ (**22**) (70 % isolated yield) respectively, with the concomitant formation of *tert*-butyl isocyanate. It is proposed that the mechanism for this process involves a retrocyclisation, as described in Scheme 3.4.



R^1, R^2 = Ph, $SiMe_3$ **19**
Me, ^{i}Pr **20**

R^1, R^2 = Ph, $SiMe_3$ **21**
Me, ^{i}Pr **22**

Scheme 3.4 – Proposed decomposition pathway of $Ti(\eta\text{-}C_5Me_5)\{N(^tBu)C(O)O\}\{R^1C(NR^2)_2\}$ **(19, 20)**

The rates of decomposition of **19** and **20** are strongly dependent on the ancillary ligand set. Complete decomposition of Ti(η-C_5Me_5) {N(^{t}Bu)C(O)O}{MeC(N^{i}Pr)$_2$} (**20**) occurs in benzene-d_6 solution at room temperature in 4 hours, even in the absence of light. In the case of Ti(η-C_5Me_5){N(^{t}Bu)C(O)O}{PhC(NSiMe$_3$)$_2$} (**19**), with the more bulky PhC(NSiMe$_3$)$_2$ ligand, complete decomposition is not observed until 5 days have elapsed. The stability of these carbamate complexes is thus somewhat lower than the tetraaza[14]annulene-supported systems, which are found to be photosensitive, but stable for long periods in solution in the absence of light.[26]

An alternative synthesis of **22** was carried out by reaction of the parent imido complex Ti(η-C_5Me_5)(N^{t}Bu){MeC(N^{i}Pr)$_2$} (**2**) with a stoichiometric amount of water. Hydrolysis results in an immediate colour change from red to amber, and yields **22** and *tert*-butylamine as expected; however, the reaction does not proceed as cleanly as that with CO_2, presumably owing to the moisture sensitivity of the remaining ligands. High dilution of the H_2O reagent is necessary, and even then other products of hydrolysis are noted in the ^{1}H NMR spectrum of the product. This is in contrast to other systems, in which hydrolysis of the imido function to give oxo complexes has been found to proceed cleanly.[41-43]

Compounds **21** and **22** have been fully characterised by ^{1}H and ^{13}C-{^{1}H} NMR, and IR spectroscopies, and elemental analysis. No parent ion is observed in the EI or FI mass spectrum of either compound. However, both compounds have been structurally characterised. Full details are given in

Chapter 8 and Appendix E. The crystal structures are discussed in subsections 3.3.1.3 and 3.3.1.4 below.

The absence of a terminal Ti=O stretch in the range 850 - 930 cm^{-1} in the IR spectra[28,30,44,45] of **21** and **22** points to a dimeric oxo structure; this was confirmed by structural determination of the compounds (*vide infra*). The extrusion of the isocyanate indicates the formation of an intermediate terminal oxo complex as indicated in Scheme 3.4, but no evidence for this is observed in the NMR spectra of *in-situ* experiments. Instead, the complex self-traps, dimerising to give the final product.

The formation of dimeric oxo species illustrates another difference between the cyclopentadienyl-amidinate and tetraazamacrocyclic ligand sets. In the case of the Ti(N^{t}Bu)(Me_ntaa) (n = 4, 8) complexes, reaction with H_2O gives the oxo complexes Ti(O)(Me_ntaa) (n = 4, 8) which are monomeric, with terminal Ti=O bonds which are reactive towards unsaturated substrates such as isocyanates.[26,30] By comparison, the oxo complexes **21** and **22** exhibit no such reactivity, and are inert towards species such as aldehydes, amines, azobenzene, carbodiimides (alkyl and aryl), carbon dioxide, imines, isocyanates (alkyl and aryl), ketones, and nitrosobenzene. This difference in reactivity between monomeric and dimeric species mirrors that found for the imido ligand, and is attributed to the multiple bond character and M=E (E = O, NR) bond polarity of the terminal species.

3.3.1.3 X-RAY CRYSTAL STRUCTURE OF

$[Ti(\eta\text{-}C_5Me_5)(\mu\text{-}O)\{PhC(NSiMe_3)_2\}]_2$ (21)

An amber crystal suitable for analysis by single crystal X-ray diffraction was obtained from a saturated solution in benzene. The data were collected by the author, and the structure solved by Dr. P. Mountford. Figure 3.5 shows the molecular structure of **21**. Ambiguity in assigning the space group of the crystal prevented a more thorough analysis of the data.

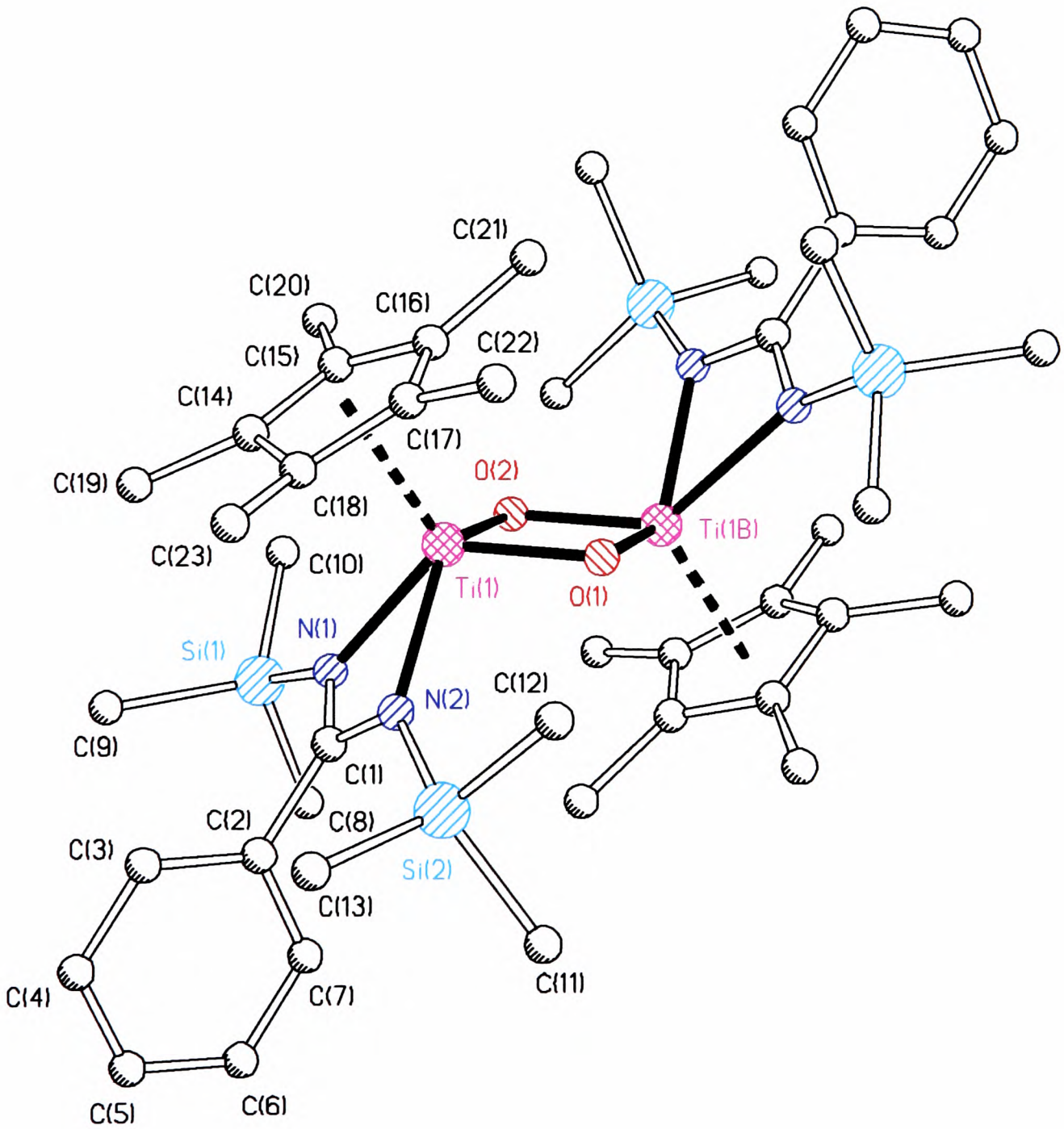


Figure 3.5 – X-ray crystal structure of $[Ti(\eta\text{-}C_5Me_5)(\mu\text{-}O)\{PhC(NSiMe_3)_2\}]_2$ (**21**). H atoms omitted for clarity

3.3.1.4 X-RAY CRYSTAL STRUCTURE OF $[Ti(\eta\text{-}C_5Me_5)(\mu\text{-}O)\{MeC(N^iPr)_2\}]_2$ (22)

An amber crystal suitable for analysis by single crystal X-ray diffraction was obtained from a saturated solution in benzene. The data were collected by the author, and the structure solved by Dr. P. Mountford. Figure 3.6 shows the molecular structure of **22**, and Table 3.4 summarises some important bond lengths and angles. Full details are provided in Appendix E.

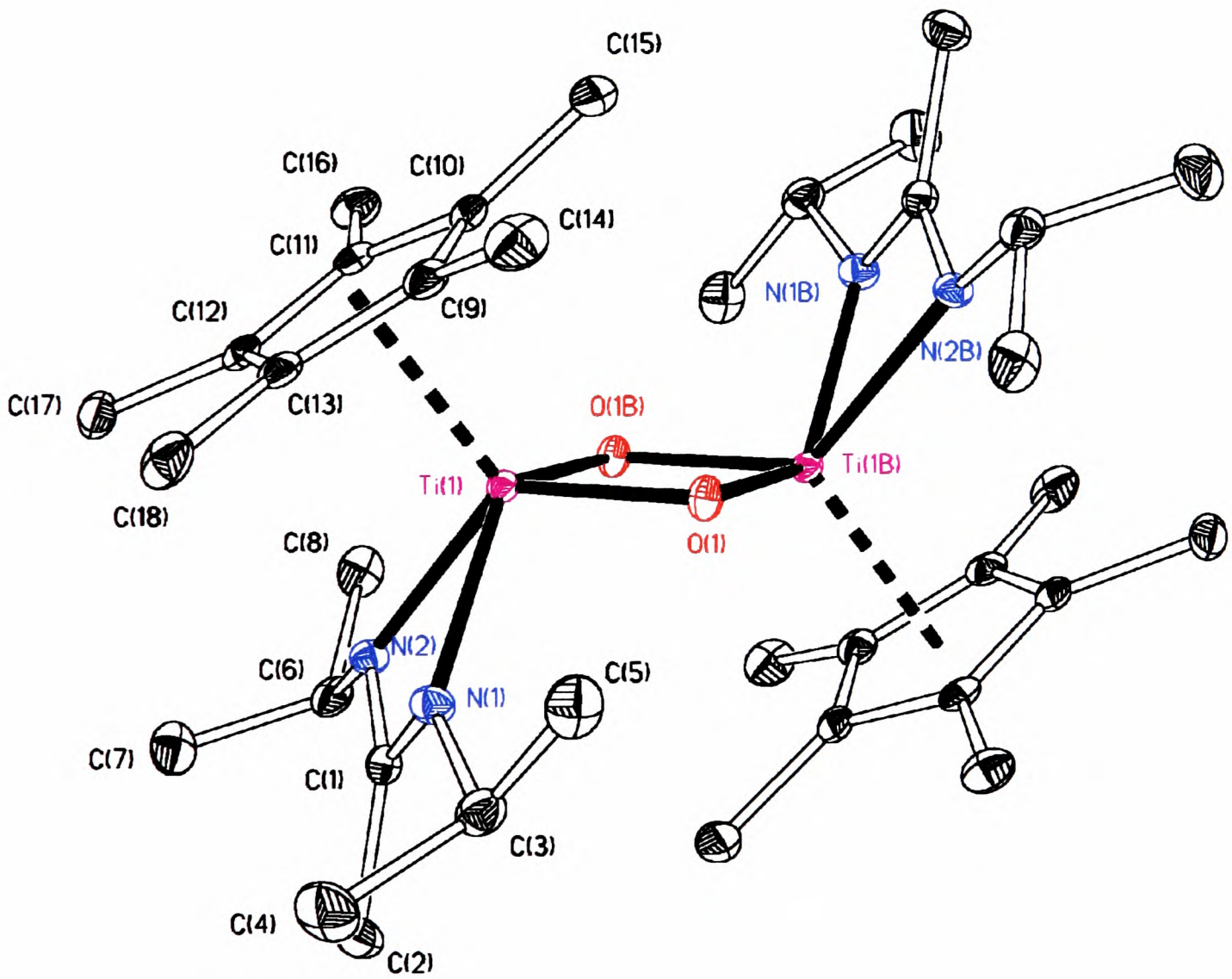


Figure 3.6 - Thermal ellipsoid plot (30 % probability) of $[Ti(\eta\text{-}C_5Me_5)(\mu\text{-}O)\{MeC(N^iPr)_2\}]_2$ (**22**). H atoms omitted for clarity

Table 3.4 – Selected bond lengths (Å) and angles (°) for $[Ti(\eta\text{-}C_5Me_5)(\mu\text{-}O)\{MeC(N^iPr)_2\}]_2$ **(22)**

Ti(1) – $Cp_{(cent)}$	2.13	$Cp_{(cent)}$ – Ti(1) – O(1)	117.8
Ti(1) – O(1)	1.855(2)	$Cp_{(cent)}$ – Ti(1) – O(1B)	115.9
Ti(1) – O(1B)	1.869(2)	$Cp_{(cent)}$ – Ti(1) – N(1)	109.4
Ti(1) – N(1)	2.188(3)	$Cp_{(cent)}$ – Ti(1) – N(2)	110.0
Ti(1) – N(2)	2.168(3)	Ti(1) – O(1) – Ti(1B)	98.59(9)
		O(1) – Ti(1) – O(1B)	81.41(9)
		O(1) – Ti(1) – N(1)	89.9(1)
		O(1B) – Ti(1) – N(2)	90.3(1)
		N(1) – Ti(1) – N(2)	60.7(1)

3.3.1.5 Discussion of the Crystal Structures

Comparison of the X-ray crystal structure of **22** with that of the arylimido complex $Ti(\eta\text{-}C_5Me_5)(N\text{-}2,6\text{-}C_6H_3Me_2)\{MeC(N^iPr)_2\}$ (**7**) shows that the $Ti–Cp_{(cent)}$ and $Ti–N_{amidinate}$ bond lengths are longer in the bridging oxo complex than in the imide ($Ti–Cp_{(cent)}$ = 2.13 Å cf. 2.085 Å, $Ti–N_{amidinate}$ = 2.178 ± 0.01 Å cf. 2.097 ± 0.003 Å). This is consistent with the increased steric crowding about the metal centres in **22** relative to **7**. The Ti–O bond lengths (1.862 ± 0.07 Å) are typical of those reported in the literature for other Ti(IV) complexes (1.858 ± 0.08 Å for 15 compounds[46,47]). They are not quite identical, a feature that is likely to be caused by packing forces within the crystal. As with **7**, the $Ti–Cp_{(cent)}$ and $Ti–N_{amidinate}$ bond lengths are also consistent with values reported in the literature for other Ti(IV) complexes.

3.3.2 REACTION OF $Ti(\eta\text{-}C_5H_4Me)(N^tBu)\{R^1C(NR^2)_2\}$ WITH CO_2

This Section describes the reactions of complexes bearing the smaller methylcyclopentadienyl ligand in place of a pentamethylcyclopentadienyl ligand.

A sample of $Ti(\eta\text{-}C_5H_4Me)(N^tBu)\{PhC(NSiMe_3)_2\}$ (**3**) was dissolved in benzene-d_6, and exposed to CO_2 at a pressure of *ca.* 0.5 atm. Immediate reaction was indicated by a colour change from red to a deep cherry red. ^1H NMR studies revealed that within 5 minutes, *ca.* 80 % of the parent imido complex had been consumed, and a new set of resonances indicated the formation of a carbamate complex analagous to **19**. However, at room temperature in the dark, the complex was observed to decompose over about 30 minutes, as shown in Figure 3.7 below.

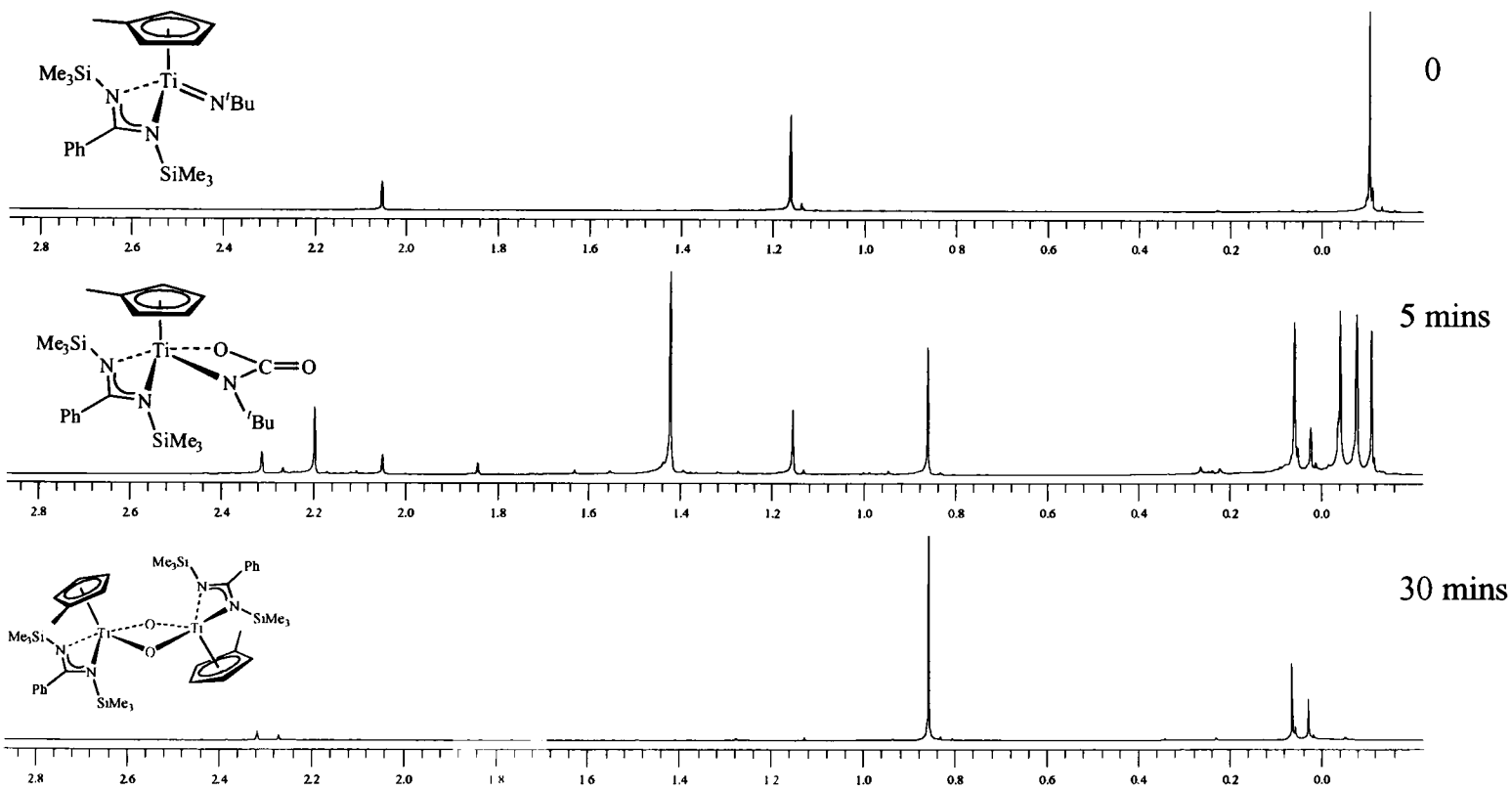
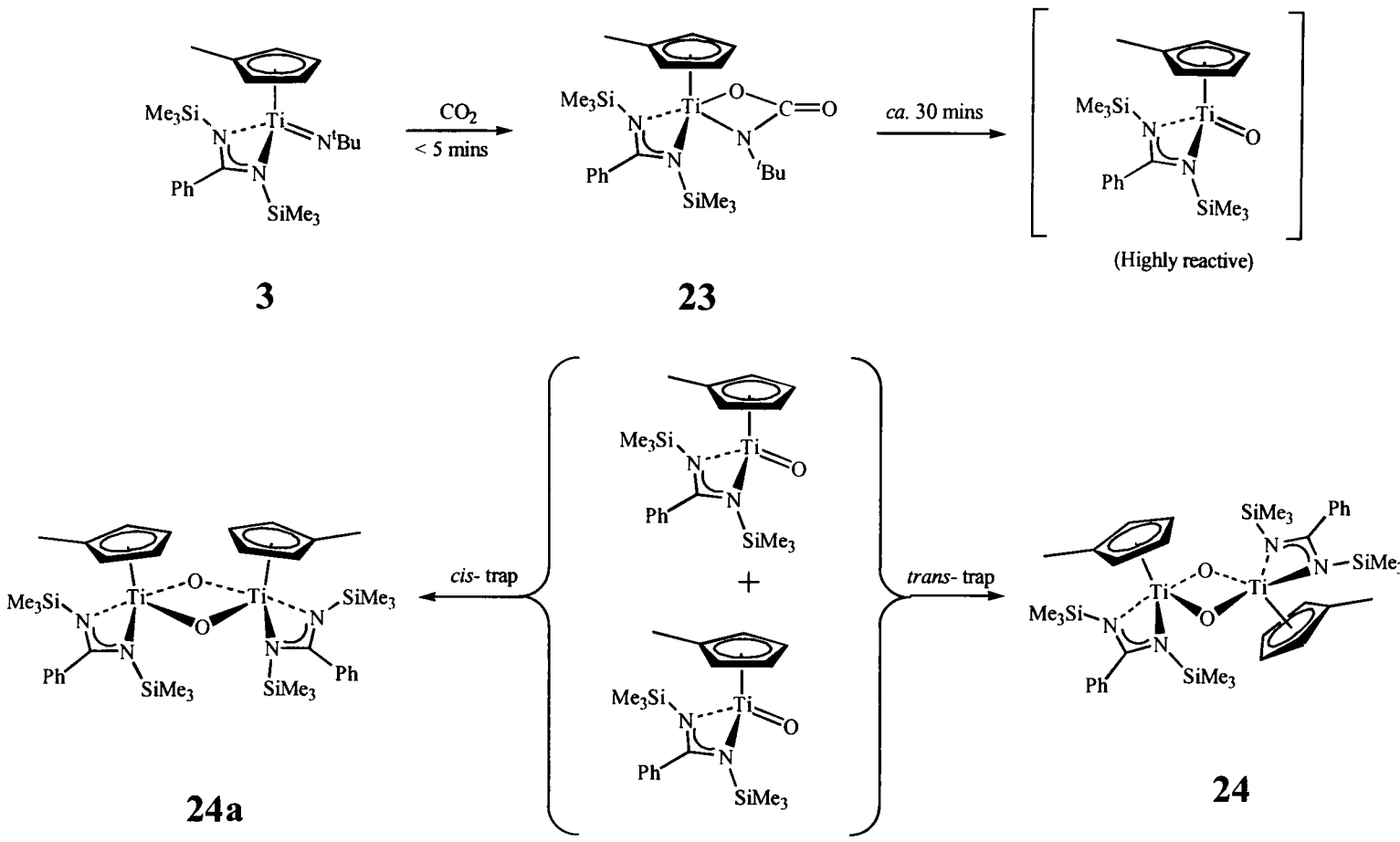


Figure 3.7 – 500.0 MHz ^1H NMR spectra of reaction between $Ti(\eta\text{-}C_5H_4Me)(N^tBu)\{PhC(NSiMe_3)_2\}$ (**3**) and CO_2 in benzene-d_6 at time *t*

The new resonance in the final product at 0.88 ppm was assigned to *tert*-butyl isocyanate, by comparison with the ^{1}H NMR spectrum of a pure sample of *tert*-butyl isocyanate. Removal of volatiles under reduced pressure followed by re-dissolution in benzene-d_6 caused the loss of the peak, without affecting any of the other resonances in the spectrum. By analogy with complexes **21** and **22**, it would be expected that the final product of this reaction would be the dimeric oxo species $[Ti(\eta\text{-}C_5H_4Me)(\mu\text{-}O)\{PhC(NSiMe_3)_2\}]_2$. However, closer inspection of the ^{1}H NMR spectrum revealed twice as many peaks as expected for the formation of a single product. It was also found that upon heating to 80 °C for 1 hour, half the peaks were converted cleanly into the others, with the resultant ^{1}H NMR spectrum that predicted for the oxo species. On the basis of these observations, it is proposed that the reaction of the imido complex **3** with CO_2 does indeed produce the analogous carbamate intermediate (**23**), but that this is too unstable to be isolated as a pure compound. Extrusion of *tert*-butyl isocyanate produces the transient monomeric species $Ti(\eta\text{-}C_5H_4Me)(O)\{PhC(NSiMe_3)_2\}$, which owing to the lower steric crowding of the monomethylcyclopentadienyl ligand *versus* the pentamethyl congener is able to self-trap in one of two ways, as shown in Scheme 3.5.



Scheme 3.5 – Mechanism of reaction between Ti(η-C_5H_4Me)(N^{t}Bu){PhC($NSiMe_3$)$_2$} (**3**) and CO_2

The transient monomeric oxo species self-traps to form two possible isomers: one which is structurally analogous to the form adopted by **21** and **22**, and possesses C_{2h} symmetry; the other having C_{2v} symmetry. One of these two forms, found to be the *trans* isomer (*vide infra*) is the thermodynamic product, and upon heating conversion of the *cis* isomer to the *trans* is observed.

The other possibility, that the extra peaks in the NMR do not correspond to a *cis* isomer but are due to the monomeric oxo species, can be discounted. Only one product is observed in the formation of **21** and **22**, yet the stability of the corresponding monomeric oxo complex is expected to be greater on steric arguments. Secondly, conversion of the peaks does not follow the exponential rate that would correspond to the dimerisation of a monomeric oxo species.

All the carbamate must decompose to give the terminal oxo species initially, and after 15 minutes the majority of the peaks present in the ^{1}H NMR spectrum correspond to the *trans* dimer. After a further hour, there is no change in the ratio of peaks, demonstrating that the minor peaks present cannot be the monomer. Thirdly, the formation of two isomeric bridging oxo species is not without precedent. Hogarth has reported the molybdenum complexes Mo(η-C_5H_4Me)(μ-NPh)$_2$(O)$_2$ (**3.63**) and Mo(η-C_5H_4Me)(μ-NPh)(μ-O)(NPh)(O) (**3.63a**) which are structural isomers, although these are not found to interconvert.[48] Bergman has reported isomerism in the compounds [Zr(η-C_5H_5)$_2$(O)]$_x$, where the value of x is dependent on reaction conditions.[49] The *trans* isomer **24** has been isolated as a pure species, and crystallographically characterised. The *cis* isomer cannot be readily separated from the mixture, and has only been characterised spectroscopically. It is given the designation **24a**. The isolated yield of **24 / 24a** was 91 %.

3.3.2.1 X-RAY CRYSTAL STRUCTURE OF [Ti(η-C_5H_4Me)(μ-O){PhC(NSiMe$_3$)}]$_2$ (24)

An amber crystal suitable for analysis by single crystal X-ray diffraction was obtained from a saturated solution in benzene. The data were collected and the structure solved by Dr. L. H. Rees of this department. Figure 3.8 shows the molecular structure of **24**, and Table 3.5 summarises some important bond lengths and angles. Full details are provided in Appendix F.

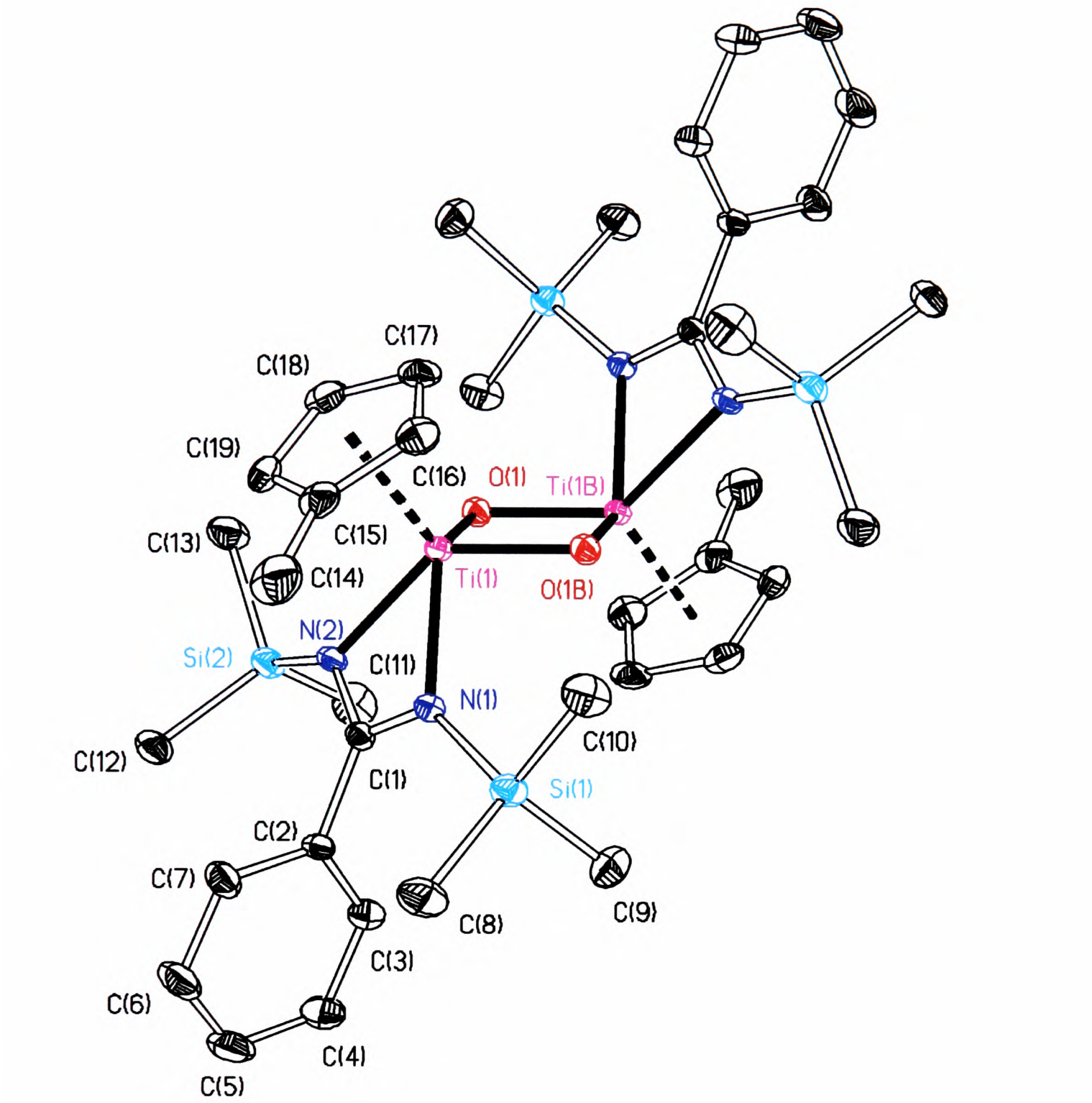


Figure 3.8 - Thermal ellipsoid plot (30 % probability) of [Ti(η-C_5H_4Me)(μ-O){$PhC(NSiMe_3)_2$}]$_2$ (**24**). H atoms omitted for clarity

Table 3.5 – Selected bond lengths (Å) and angles (°) for [Ti(η-C_5H_4Me)(μ-O){$PhC(NSiMe_3)_2$}]$_2$ (**24**).

Ti(1) – $Cp_{(cent)}$	2.087	$Cp_{(cent)}$ – Ti(1) – O(1)	117.7
Ti(1) – O(1)	1.8417(8)	$Cp_{(cent)}$ – Ti(1) – O(1B)	115.5
Ti(1) – O(1B)	1.8588(8)	$Cp_{(cent)}$ – Ti(1) – N(1)	111.2
Ti(1) – N(1)	2.1538(9)	$Cp_{(cent)}$ – Ti(1) – N(2)	109.2

Ti(1) – N(2)	2.1630(9)	Ti(1) – O(1) – Ti(1B)	97.01(4)
		O(1) – Ti(1) – O(1B)	82.99(4)
		O(1) – Ti(1) – N(2)	88.02(4)
		O(1B) – Ti(1) – N(1)	89.03(3)
		N(1) – Ti(1) – N(2)	62.21(4)

A comparison between the crystal structures of **24** and its parent imido complex **3** reveals a lengthening of the Ti–$N_{amidinate}$ bond distances (average bond length increases from 2.105(2) Å to 2.1584(9) Å) upon replacement of the terminal imido with the bridging oxo ligand. This follows from the increase of steric crowding around the metal centre on dimerising; the same reasoning explains the tightening of the Cp_{cent}–Ti–$N_{amidinate}$ bond angles (average angle decreases from 119.2 ° to 110.2 °), as the auxillary ligands are forced closer together. Steric repulsion is also presumed to be the major factor causing bond lengths to be shorter in **24** than in **22** (2.087 cf. 2.13 Å for $Cp_{(cent)}$–Ti, 2.1584 (mean value) cf. 2.178 Å for Ti–$N_{amidinate}$, and 1.85025 cf. 1.862 for Ti–O).

The factors governing the ratio of the isomers **24** and **24a** formed was investigated by systematically varying conditions and monitoring the reaction using ^{1}H NMR spectroscopy. It was found that neither CO_2 pressure, nor concentration of the solution, nor substituting chloroform (as a more polar solvent) for benzene had any effect on the *cis* : *trans* ratio of the two μ- oxo products. Raising the temperature to 45 °C for 1 hour promoted the formation of the *trans* form as expected, but conducting the reaction of **3** with CO_2 at

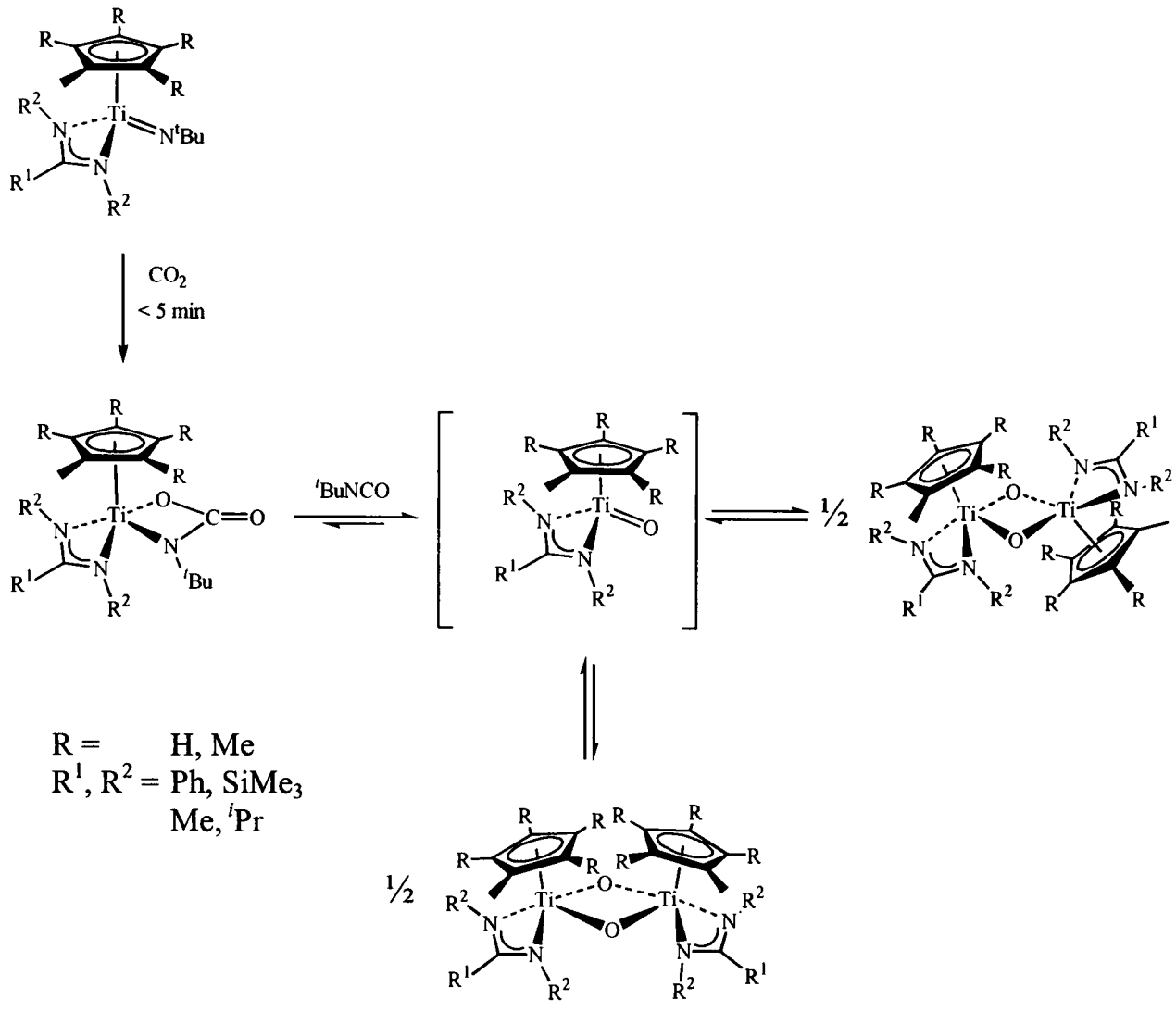
5 °C resulted only in an increase in the amount of impurities present relative to the room temperature reaction after 1 hour.

Exposure to CO_2 at a pressure of 1 atm of a sample of Ti(η-C_5H_4Me)(N^{t}Bu){$MeC(N^iPr)_2$} (**4**) in benzene-d_6 resulted in an extremely fast reaction. The red solution deepened in colour to a deep cherry red for *ca.* 5 seconds, before lightening to dark amber. The ^{1}H NMR spectrum recorded after 3 minutes reaction time revealed no resonances attributable to **4**, and indicated the formation of *tert*-butyl isocyanate and two isomeric oxo species, of the formula [Ti(η-C_5H_4Me)(μ-O){$MeC(N^iPr)_2$}]$_2$ (58 % isolated yield). By analogy with the benzamidinate species, the *trans* isomer is designated **25**, and the *cis* isomer **25a**. Separation of **25** from **25a** was possible by recrystallisation. The *trans* isomer was successfully crystallised from the reaction mixture and characterised; the *cis* isomer could not be separated by this method, but was spectroscopically characterised.

Alternative synthesis of **25** and **25a** was attempted by controlled hydrolysis, using a solution of H_2O in THF. As in the case of hydrolysis of **2**, the reaction was found to afford the corresponding oxo species, but not cleanly.

3.3.3 EFFECT OF VARYING CYCLOPENTADIENYL-AMIDINATE SUBSTITUENTS

The reaction of the titanium cyclopentadienyl *tert*-butylimido amidinate species **1** – **4** with CO_2 is summarised in Scheme 3.6



Scheme 3.6 – Reaction of *tert*-butylimido titanium complexes supported by cyclopentadienyl-amidinate ligand sets with CO_2

Reactions of all four complexes Ti(η-C_5Me_5)(N^{t}Bu){PhC(NSiMe$_3$)$_2$} (**1**), Ti(η-C_5Me_5)(N^{t}Bu){MeC(N^{i}Pr)$_2$} (**2**), Ti(η-C_5H_4Me)(N^{t}Bu){PhC(NSiMe$_3$)$_2$} (**3**), and Ti(η-C_5H_4Me)(N^{t}Bu){MeC(N^{i}Pr)$_2$} (**4**) with CO_2 resulted in an immediate reaction to form the corresponding carbamate complex. The stability of the carbamate was found to be strongly dependent on the supporting ligands. The cycloadduct Ti(η-C_5Me_5){N(^{t}Bu)C(O)O}{PhC(NSiMe$_3$)$_2$} (**19**) was easily isolated and fully characterised, being stable in benzene-d_6 solution for a number of hours. Ti(η-C_5Me_5){N(^{t}Bu)C(O)O}{MeC(N^{i}Pr)$_2$} (**20**) was also isolable, but decomposed more rapidly in solution. Upon moving to the sterically less crowded C_5H_4Me supported

systems, decomposition of the carbamate occurs more rapidly still. $Ti(\eta\text{-}C_5H_4Me)\{N(^tBu)C(O)O\}\{PhC(NSiMe_3)_2\}$ (**23**) undergoes substantial decomposition to the bridging oxo species **24** / **24a** within 5 minutes of reaction when the reaction is carried out at 1 atm pressure CO_2, precluding its isolation. The homologous complex $Ti(\eta\text{-}C_5H_4Me)\{N(^tBu)C(O)O\}\{MeC(N^iPr)_2\}$ is not observed in the reaction of **4** with CO_2, completely decomposing within 3 minutes under identical conditions to the other reactions.

These observations indicate that the stability of the carbamates is correlated with the steric factors of the ancillary ligand set, and are consistent with the ordering of steric bulk being C_5Me_5 > C_5H_4Me and $PhC(NSiMe_3)_2$ > $MeC(N^iPr)_2$. It has been previously proposed from other studies that $PhC(NSiMe_3)_2$ is intermediate in steric bulk between C_5Me_5 and C_5H_4Me,[50] but the position of $MeC(N^iPr)_2$ in this series cannot be unambiguously stated.

Decomposition of the carbamate is proposed to proceed *via* a retrocyclisation (pre-equilibrium), extruding *tert*-butyl isocyanate, and forming a highly reactive transient monomeric oxo species. This species rapidly dimerises to form the observed corresponding bridging oxo complex. Only the *trans* isomer of $[Ti(\eta\text{-}C_5Me_5)(\mu\text{-}O)\{PhC(NSiMe_3)_2\}]_2$ (**21**) and $[Ti(\eta\text{-}C_5Me_5)(\mu\text{-}O)\{MeC(N^iPr)_2\}]_2$ (**22**) is observed in this reaction, and this is attributed to the unfavourable steric crowding which would be present in a cisoid isomer. The complexes $[Ti(\eta\text{-}C_5H_4Me)(\mu\text{-}O)\{PhC(NSiMe_3)_2\}]_2$ (**24** / **24a**) and $[Ti(\eta\text{-}C_5H_4Me)(\mu\text{-}O)\{MeC(N^iPr)_2\}]_2$ (**25** / **25a**) do not experience such

crowding, and thus form mixtures of both the *trans* and the *cis* isomers. It was noted that the ratio of isomers initially formed is closer to 1 : 1 for **25 / 25a** (typically 5 : 3) than for **24 / 24a** (typically 4 : 1). This is consistent with steric arguments, which would tend to favour the *trans* isomer over the *cis* for the more bulky $PhC(NSiMe_3)_2$ ligand; the smaller $MeC(N^iPr)_2$ ligand inducing less strain in a cisoid configuration.

In contrast to the case of **24 / 24a**, in which the minor *cis* isomer converts to the *trans* form upon heating to 80 °C for 1 hour, it was found that heating had little effect on the ratio of *cis* : *trans* isomer of the oxo species **25 / 25a**. A benzene-d_6 solution of **25 / 25a** heated to 80 °C for 3 hours had no effect on the isomer ratio present. Prolonged heating (3 days at 80 °C) began to effect conversion of the *cis* isomer to its *trans* congener, but after 5 days there was still a *cis* : *trans* ratio of 1 : 6. This suggests that either i) the less crowded dimeric $[Ti(\eta\text{-}C_5H_4Me)(\mu\text{-}O)\{MeC(N^iPr)_2\}]_2$ system is more stable than $[Ti(\eta\text{-}C_5H_4Me)(\mu\text{-}O)\{PhC(NSiMe_3)_2\}]_2$, or ii) the difference in steric crowding between *cis* and *trans* isomers is smaller in $[Ti(\eta\text{-}C_5H_4Me)(\mu\text{-}O)\{MeC(N^iPr)_2\}]_2$.

It can also be argued that the larger auxiliary ligands destabilise the dimeric oxo species, and so require less forcing conditions to effect the isomerism. Thus, in the C_5H_4Me- supported oxo systems where isomerism is observed, the monomeric intermediate $Ti(\eta\text{-}C_5H_4Me)(O)\{PhC(NSiMe_3)_2\}$ would be expected to form at a lower temperature than $Ti(\eta\text{-}C_5H_4Me)(O)\{MeC(N^iPr)_2\}$. Once formed, the greater thermodynamic driving force of cisoid repulsion

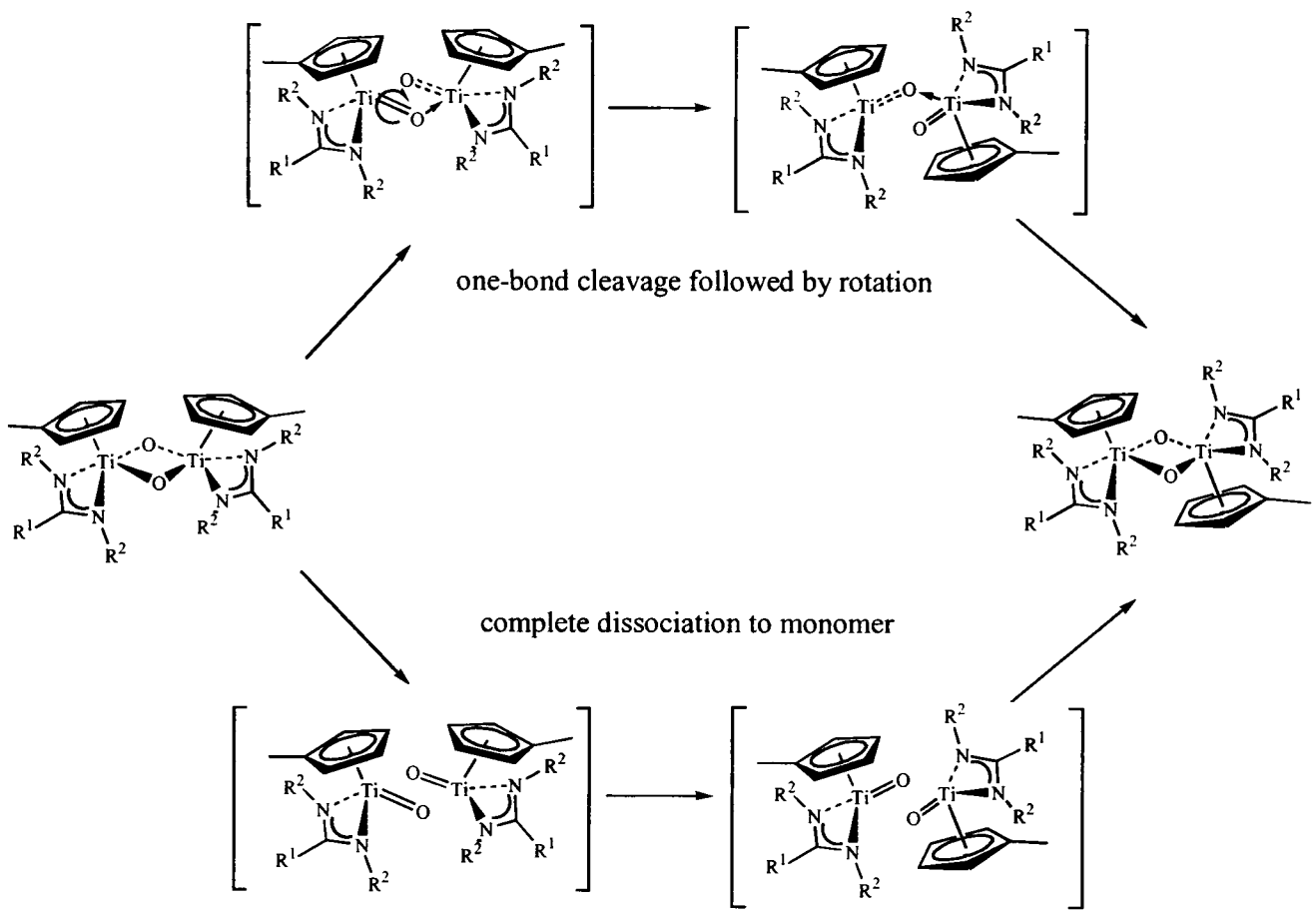
would favour recombination to **24**. As a result, it might be expected that the monomer formed from **21** would be most easily formed, but that formation of a cisoid dimer is thermodynamically disfavoured. The cisoid dimer $[Ti(\eta\text{-}C_5Me_5)(\mu\text{-}O)\{MeC(N^iPr)_2\}]_2$ (**22a**) is formed preferentially when the oxo species are formed from reaction of the parent imido species with nitrosobenzene, and it is found to decompose rapidly to the trans isomer **22** (this reactivity is discussed in Chapter 6 of this Thesis). Although these observations support this argument, the hypothesis cannot be demonstrated as no evidence for a monomeric species can be observed in the ^1H NMR spectra of these reactions, even when observing the decomposition of the carbamate species at low temperatures.

Addition of three equivalents of 4-*tert*-butylpyridine to a sample of **24** in an attempt to further stabilise the monomer as an adduct $Ti(\eta\text{-}C_5H_4Me)(O)(NC_5H_4{}^tBu)\{PhC(NSiMe_3)_2\}$ did not cause any change in the ^1H NMR spectrum. Heating an equimolar mixture of $[Ti(\eta\text{-}C_5Me_5)(\mu\text{-}O)\{MeC(N^iPr)_2\}]_2$ and **24** / **24a** resulted in complete conversion of **24a** into **24**, but no peaks corresponding to a mixed dimer of the form $Ti(\eta\text{-}C_5H_4Me)\{PhC(NSiMe_3)_2\}(\mu\text{-}O)_2Ti(\eta\text{-}C_5H_5)\{MeC(N^iPr)_2\}$ were observed.

3.3.4 MECHANISTIC STUDY OF *CIS* – *TRANS* ISOMERISATION

An alternative argument for the mechanism of *cis* to *trans* isomerisation can be forwarded; namely that rather than complete dissociation to generate discrete monomers followed by recombination, only one Ti–O bond breaks,

and a rotation occurs about the remaining Ti–O linkage. Reforming the broken bond at this point effects the observed isomerisation (Scheme 3.7):



Scheme 3.7 – Possible mechanisms for *cis* – *trans* isomerisation *via* Ti–O bond cleavage

The principle of microscopic reversibility suggests that the complete dissociation pathway is the more likely, since the initial dimer formation must arise through reaction between two monomers. Nevertheless, the second mechanism is possible. In order to differentiate between the two, it was decided to try a crossover experiment similar to that attempted using $[Ti(\eta\text{-}C_5Me_5)(\mu\text{-}O)\{MeC(N^iPr)_2\}]_2$ (**22**) and $[Ti(\eta\text{-}C_5H_4Me)(\mu\text{-}O)\{PhC(NSiMe_3)_2\}]_2$ (**24** / **24a**), but with two compounds which were structurally more closely related. By minimising the structural differences between the two oxo complexes involved in the crossover experiment,

differences in rate of reaction would be minimised, increasing the likelihood of a crossover product being formed.

Exposure of a solution of $Ti(\eta\text{-}C_5H_4{}^iPr)(N^tBu)\{PhC(NSiMe_3)_2\}$ (**5**) in benzene to CO_2 at a pressure of 1 atm resulted in an immediate colour change from red to a deep cherry. This lightened over a period of *ca.* 1 hour to brown. Volatiles were removed under reduced pressure to afford the product as a brown powder (yield 84 %). ^1H NMR spectroscopy confirmed this to be the *trans* and *cis* oxo products $[Ti(\eta\text{-}C_5H_4{}^iPr)(\mu\text{-}O)\{PhC(NSiMe_3)_2\}]_2$ **26** and **26a** respectively, in a ratio of 4 : 1. Heating a sample of the product in solution to 80 °C for 1 hour afforded complete conversion of **26a** to **26**, which was characterised by ^1H and $^{13}C\text{-}\{^1H\}$ NMR, and IR spectroscopies. The crossover experiment was carried out using equimolar amounts of **24** / **24a** and **26** / **26a** in benzene-d_6, and following the reaction by ^1H NMR spectroscopy. It was found that after heating the reaction mixture to 80 °C, the peaks corresponding to **24a** and **26a** disappeared, and a new series of peaks (indicated by *) had grown in, that could be assigned to the mixed oxo species $Ti(\eta\text{-}C_5H_4Me)(PhC(NSiMe_3)_2\}(\mu\text{-}O)_2Ti(\eta\text{-}C_5H_4{}^iPr)\{PhC(NSiMe_3)_2\}$. The ratio of final products (**24** : **26** : mixed oxo) is *ca.* (1 : 1 : 2), as would be expected statistically. The ^1H NMR spectrum recorded after heating is given in Figure 3.9 below.

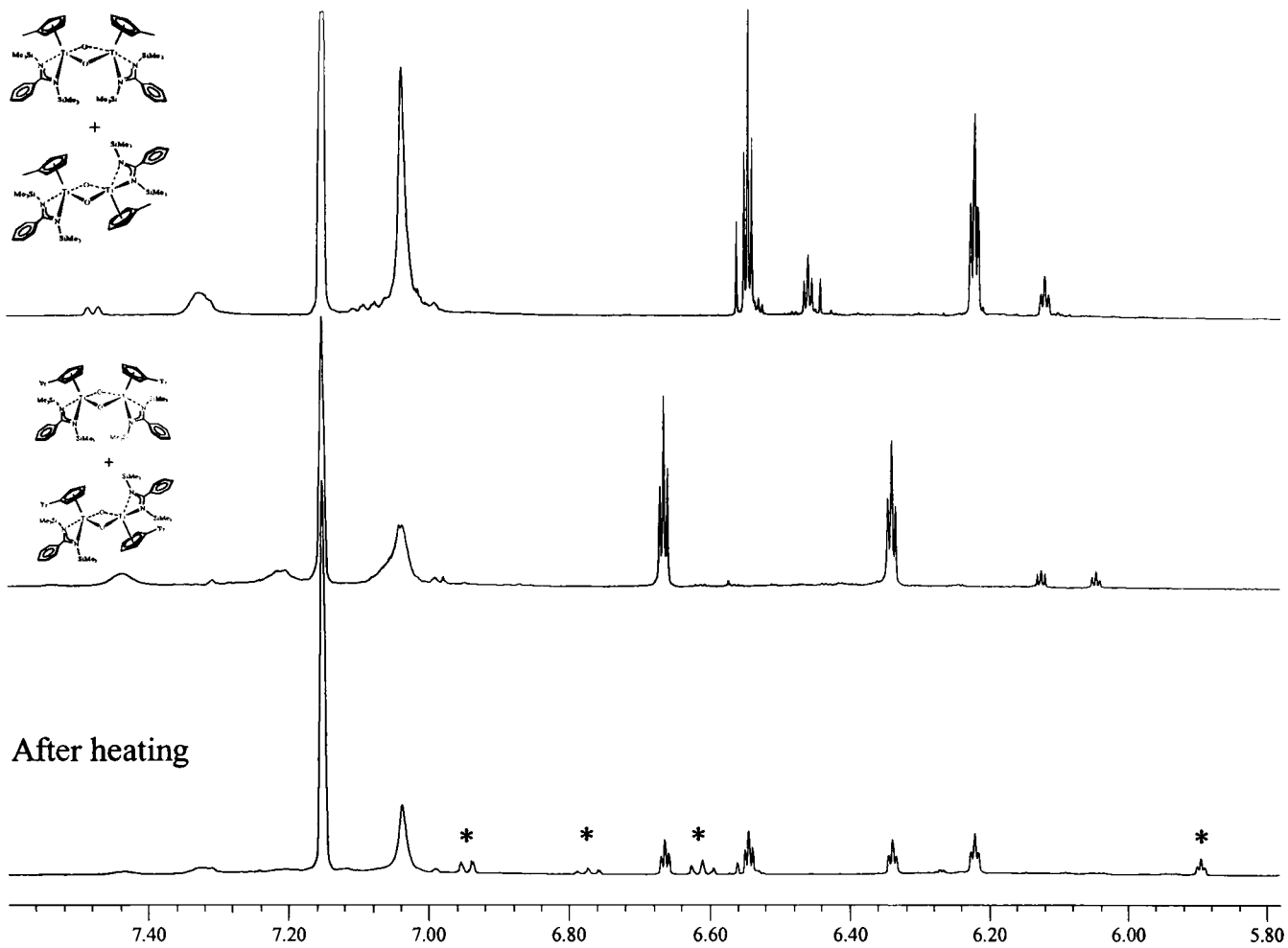
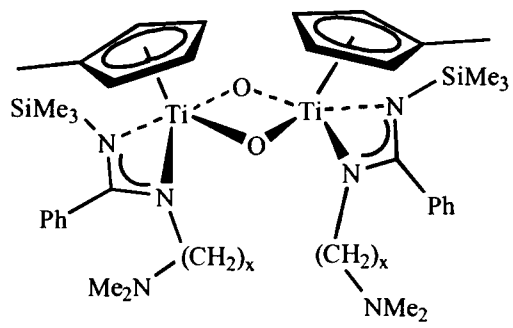
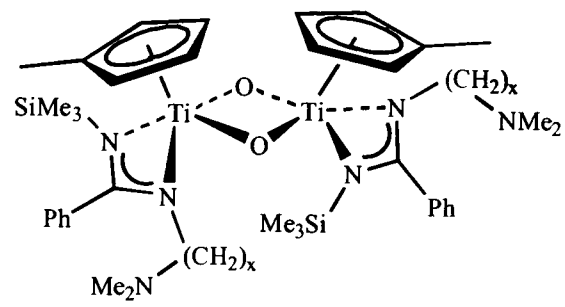


Figure 3.9 – 500.0 MHz ^{1}H NMR spectra of crossover experiment between **24 / 24a** and **26 / 26a** in benzene-d_6

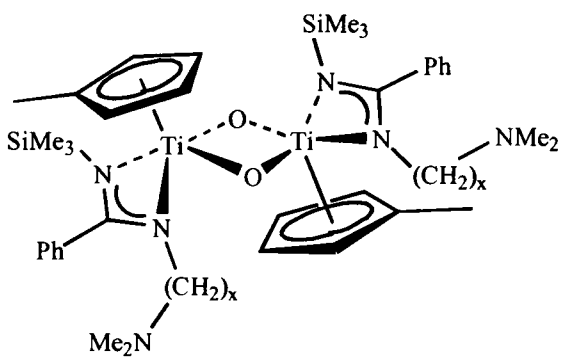
This demonstrates that the isomerisation does occur *via* a transient monomeric oxo complex. Work carried out concurrently by Catherine Boyd under my direct supervision has attempted to trap the transient monomeric oxo species by use of a pendant amine arm on the amidinate ligand.[51] This has not proven successful in preventing dimerisation. However, the use of an unsymmetrical amidinate ligand has corroborated the result of the crossover experiment, and furthermore shows that the dimer-monomer-dimer mechanism (Scheme 3.7) is the only mechanism by which isomerisation takes place. With the oxo complexes $[Ti(\eta\text{-}C_5H_4Me)(\mu\text{-}O)\{\kappa^2\text{-}PhC(NSiMe_3)N(CH_2)_x(NMe_2)\}]_2$ (x = 2, 3), there exist four possible isomers, as shown in Figure 3.10 below:



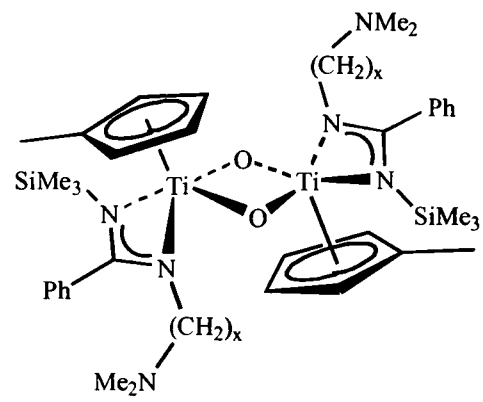
C_s - *cis* isomer



C_2 - *cis* isomer



C_2 - *trans* isomer



C_i - *trans* isomer

Figure 3.10 – Possible isomers of $[Ti(\eta\text{-}C_5H_4Me)(\mu\text{-}O)\{\kappa^2\text{-}PhC(NSiMe_3)N(CH_2)_x(NMe_2)\}]_2$

(x = 2, 3)

Only two isomers are observed in the ^1H NMR spectrum; crystallographic characterisation has proved that one isomer is the C_i - *trans* molecule. The other is presumed to be *cis*- with respect to the methylcyclopentadienyl ligands by analogy with **24** / **24a**, namely the C_2 - *cis* isomer.

It follows that if the one-bond cleavage mechanism is operating at all, the C_i - *trans* species can be formed from the C_s - *cis* isomer. We know however that the mechanism involving the monomer (i.e. two-bond cleavage) is operating, and thus the C_i - *trans* molecule must be formed from the C_2 - *cis* isomer, which is more likely to be favoured than the C_s - *cis* isomer on steric grounds. Hence, more than two first-formed isomers will be apparent in the ^1H NMR

spectrum if both mechanisms are operating. This is not the case; the presence of only two isomers supporting the view that the one-bond cleavage mechanism does not occur.

Another possibility for isomerism exists, which takes into account all the available data. This is that the mechanism involves exchange of the cyclopentadienyl ligands, with the $Ti_2(\mu\text{-}O)_2$ unit remaining intact after it has formed in the initial dimerisation process. Cyclopentadienyl exchange processes have been well-documented in the literature.[52-54] Such a process would give the results observed, and would be indistinguishable from the discrete monomer mechanism proposed above.

3.3.5 Conclusions

The formation of a $Ti_2(\mu\text{-}O)_2$ unit represents a strong thermodynamic sink. In contrast to the potential reactivity of Ti=O bonds mentioned previously, the oxo species **21 – 22, 24 – 26** display a total lack of reactivity towards cycloaddition or metathesis reactions, and are typically the final product in reactions of imido species with oxygen-containing substrates (these reactions will be mentioned elsewhere in this Thesis). As a result, attempts have been made to stabilise the monomeric oxo species for isolation and further study. None of these attempts have proved successful, suggesting that the cyclopentadienyl-amidinate ligand set may not inherently possess sufficient steric bulk to prevent dimerisation. This is in contrast to the metallocene complex $Ti(\eta\text{-}C_5Me_5)_2(O)(py)$ **(3.64)** which has been isolated and shown to possess high reactivity towards unsaturated substrates.[44,55] The related species

$Zr(\eta\text{-}C_5H_5)_2(O)$ and $Zr(\eta\text{-}C_5Me_5)(O)$ have both been generated, but are too reactive to isolate. In contrast to the transient $Ti(\eta\text{-}C_5R_4Me)(O)\{R^1C(NR^2)_2\}$ (R = H, Me; R^1, R^2 = Ph, $SiMe_3$, Me, ^{i}Pr) oxo species, the transient zirconocene complexes are not trapped as dimers, preferring to activate C–H bonds in solvent molecules or undergoing cycloaddition reactions with unsaturated substrates such as alkynes.[56-58]

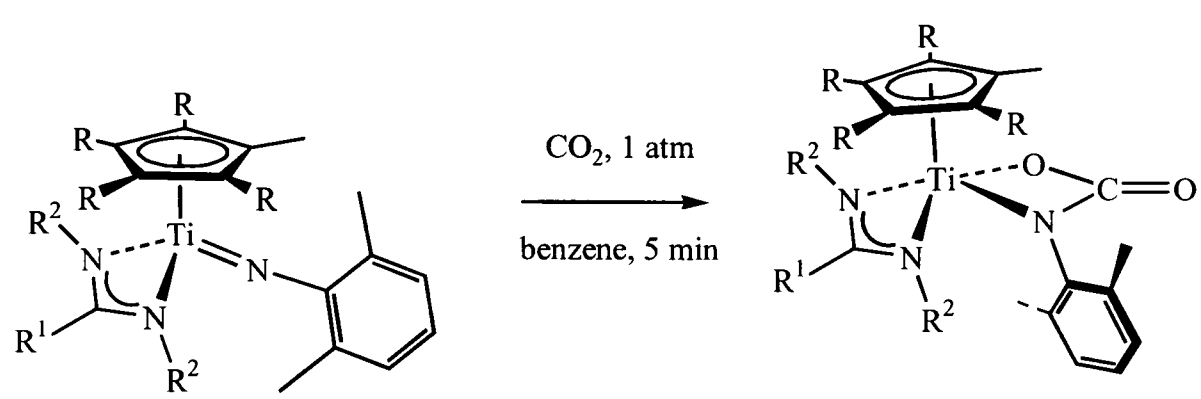
3.4 REACTIONS OF TITANIUM CYCLOPENTADIENYL ARYL IMIDO AMIDINATE COMPLEXES WITH CO_2

Previous studies into the chemistry of organometallic imido species have demonstrated pronounced differences in reactivity upon substitution of *tert*-butyl by aryl groups on the imido function.[26] It seemed appropriate therefore to investigate the reactivity of titanium arylimido complexes supported by cyclopentadienyl-amidinate ligands towards CO_2, and compare the results with those of the *tert*-butyl systems.

3.4.1 REACTION OF $Ti(\eta\text{-}C_5R_4Me)(N\text{-}2,6\text{-}C_6H_3Me_2)\{R^1C(NR^2)_2\}$ WITH CO_2

Samples of $Ti(\eta\text{-}C_5Me_5)(N\text{-}2,6\text{-}C_6H_3Me_2)\{MeC(N^iPr)_2\}$ (**7**), $Ti(\eta\text{-}C_5H_4Me)(N\text{-}2,6\text{-}C_6H_3Me_2)\{PhC(NSiMe_3)_2\}$ (**11**), $Ti(\eta\text{-}C_5H_4Me)(N\text{-}2,6\text{-}C_6H_3Me_2)\{MeC(N^iPr)_2\}$ (**12**), and $Ti(\eta\text{-}C_5Me_5)(N\text{-}2,6\text{-}C_6H_3Me_2)\{PhC(NSiMe_3)_2\}$ (**14**) were dissolved in benzene-d_6 and exposed to CO_2 at a pressure of 1 atm. An

immediate colour change to cherry red showed that reaction was occurring within seconds. ^{1}H NMR spectra of the reactions recorded after 5 minutes showed complete conversion to the corresponding carbamate complexes Ti(η-C_5Me_5){N(-2,6-$C_6H_3Me_2$)C(O)O}{MeC(N^{i}Pr)$_2$} (**27**), Ti(η-C_5H_4Me){N(-2,6-$C_6H_3Me_2$)C(O)O}{PhC(NSiMe$_3$)$_2$} (**28**), Ti(η-C_5H_4Me){N(-2,6-$C_6H_3Me_2$)C(O)O}{MeC(N^{i}Pr)$_2$} (**29**), Ti(η-C_5Me_5){N(-2,6-$C_6H_3Me_2$)C(O)O}{PhC(NSiMe$_3$)$_2$} (**30**) respectively, as shown in Equation 3.12.



	R	R^1	R^2	
7	Me	Me	^{i}Pr	**27**
11	H	Ph	SiMe$_3$	**28**
12	H	Me	^{i}Pr	**29**
14	Me	Ph	SiMe$_3$	**30**

Equation 3.12

3.4.1.1 Discussion of carbamate complexes

The reaction of the 2,6-dimethylphenylimido complexes with CO_2 follows the same initial reaction pathway as the *tert*-butylimido complexes discussed earlier. Reaction occurs within 5 minutes to afford the carbamate product, where one molecule of CO_2 has undergone a formal [2 + 2] cycloaddition to

the imido moiety. This is again identified by the loss of symmetry of the R^2 groups on the amidinate ligand in the ^1H and ^{13}C-{^1H} NMR spectra, and the appearance of an absorption in the IR spectrum in the range 1667 – 1671 cm^{-1}, indicative of a ν(C=O) stretch. However, in contrast to the *tert*-butylimido systems, the cycloadduct is more stable and is isolable for the C_5H_4Me systems **28** and **29** as well as for those of C_5Me_5.

The ^1H NMR spectra of complexes **27** and **30** in benzene-d_6 show that neither molecule is fluxional at room temperature; two distinct and sharp resonances assignable to the *ortho*- methyl groups on the aryl ring (3.23 and 3.05 ppm, and 2.28 and 2.26 ppm respectively) indicating restricted rotation. In contrast, the complexes **28** and **29** (bearing the smaller C_5H_4Me ligand) show evidence for fluxionality at room temperature. This fluxionality occurs by two processes. At room temperature, **28(29)** shows a single resonance at 2.14 (s) (1.97 (s)) ppm for the *ortho*- methyl groups of the aryl ring, and a single resonance for the two R^2 groups on the amidinate at -0.27 (s) (1.16 (d)) ppm. Upon cooling to -20 °C (-20 °C) the resonance assigned as the R^2 group of the amidinate decoalesces to give two (four) resonances at -0.22 (s), -0.48 (s) (1.11 (d), 1.09 (d), 0.95 (d), 0.23 (d)) ppm. Upon cooling to -50 °C (-20 °C) the resonance assigned as the *ortho*- methyl groups decoalesces to give two singlets at 2.13, 2.04 (2.09, 1.77) ppm (Figure 3.11).

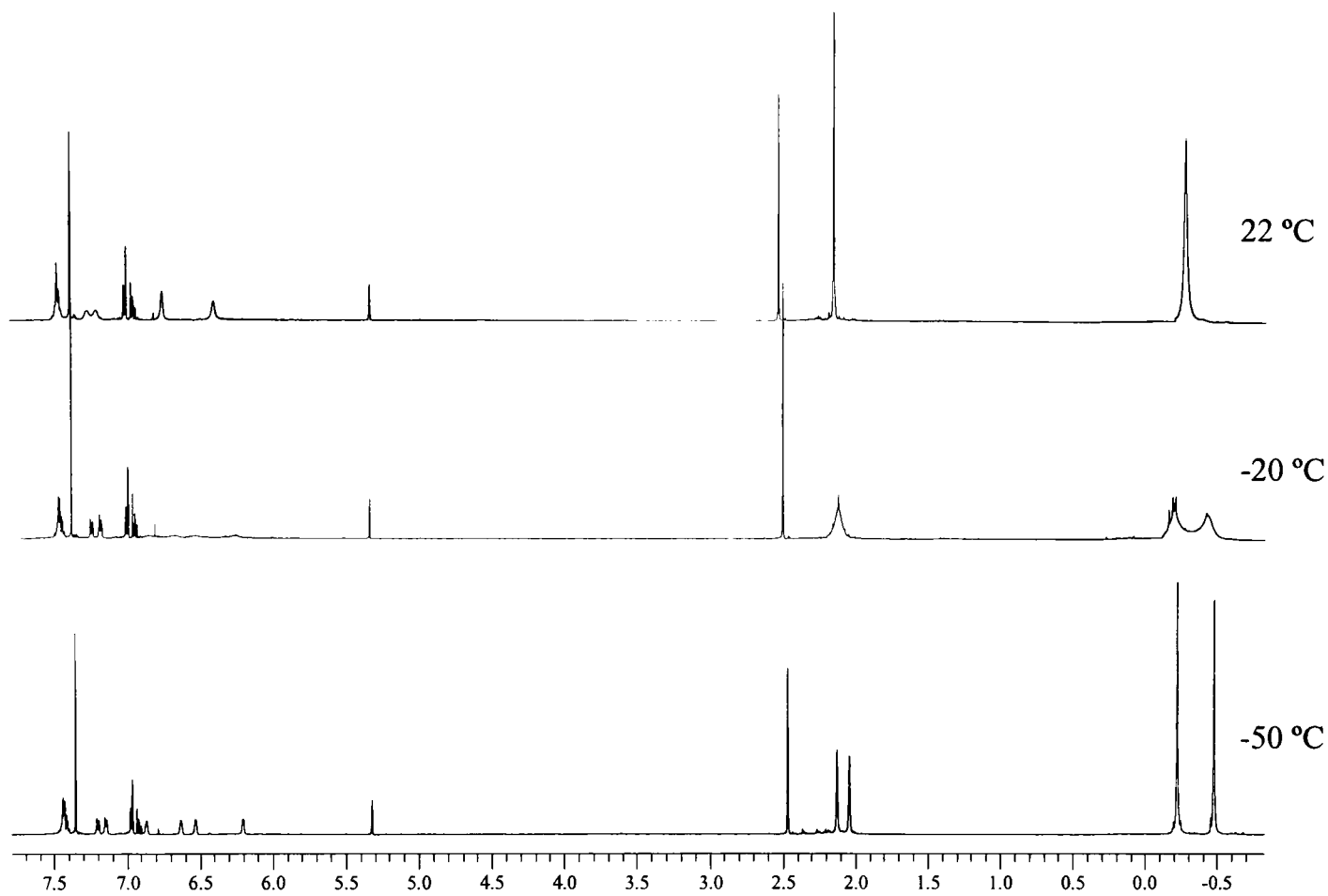


Figure 3.11 – 500.0 MHz variable temperature ^{1}H NMR spectra of $Ti(\eta\text{-}C_5H_4Me)\{N(\text{-}2,6\text{-}C_6H_3Me_2)C(O)O\}\{PhC(NSiMe_3)_2\}$ (**28**) in dichloromethane-d_2

The first fluxional process, frozen out at -20 °C, is unlikely to correspond to rotation of the amidinate, since amidinate rotation has only been observed for complexes of larger metals such as zirconium.[59] Rotation of the $\{N(\text{-}2,6\text{-}C_6H_3Me_2)C(O)O\}$ moiety about the titanium centre is more probable, and has been reported in the complex $Ti\{N(4\text{-}MeC_6H_4)C(O)O\}(Me_4taa)$ (**3.27**).[26] The second process is rotation about the $N–C_{aryl}$ bond of the carbamate group.

On standing in benzene-d_6 solution, complexes **27** – **30** were found to slowly undergo decomposition over a period of days, but unlike their *tert*-butyl counterparts, this decomposition did not yield the dimeric oxo complexes **21** –

22, **24** – **25** and the corresponding isocyanate. Instead, the reaction gave only a mixture of unidentified products, suggesting that the retrocyclisation mechanism observed for **19** and **20** to form the oxo species $[Ti(\eta\text{-}C_5Me_5)(\mu\text{-}O)\{PhC(NSiMe_3)_2\}]_2$ (**21**) and $[Ti(\eta\text{-}C_5Me_5)(\mu\text{-}O)\{MeC(N^iPr)_2\}]_2$ (**22**) is no longer competitive relative to alternative decomposition pathways. The slower rate of decomposition of the aryl carbamate complexes could suggest a faster pre-equilibrium step relative to their *tert*-butyl congeners (see Scheme 3.4, p 119).

Upon standing in benzene-d_6 solution under a CO_2 atmosphere however, complexes **27** – **29** were found to undergo further reaction to cleanly yield new products **31** - **33** in quantitative yield. Figure 3.12 shows the ^1H NMR spectrum of a sample of **27** exposed to CO_2.

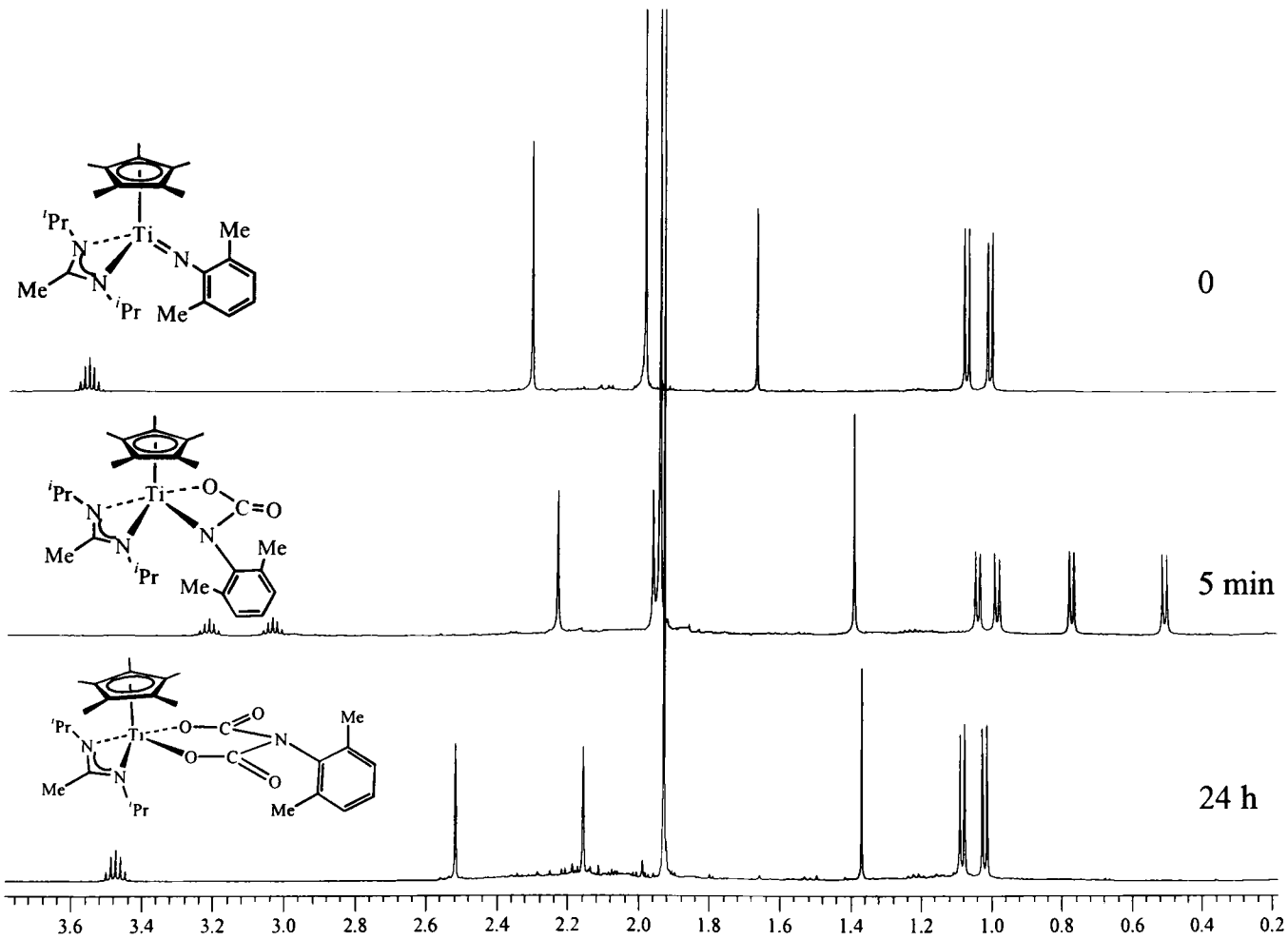
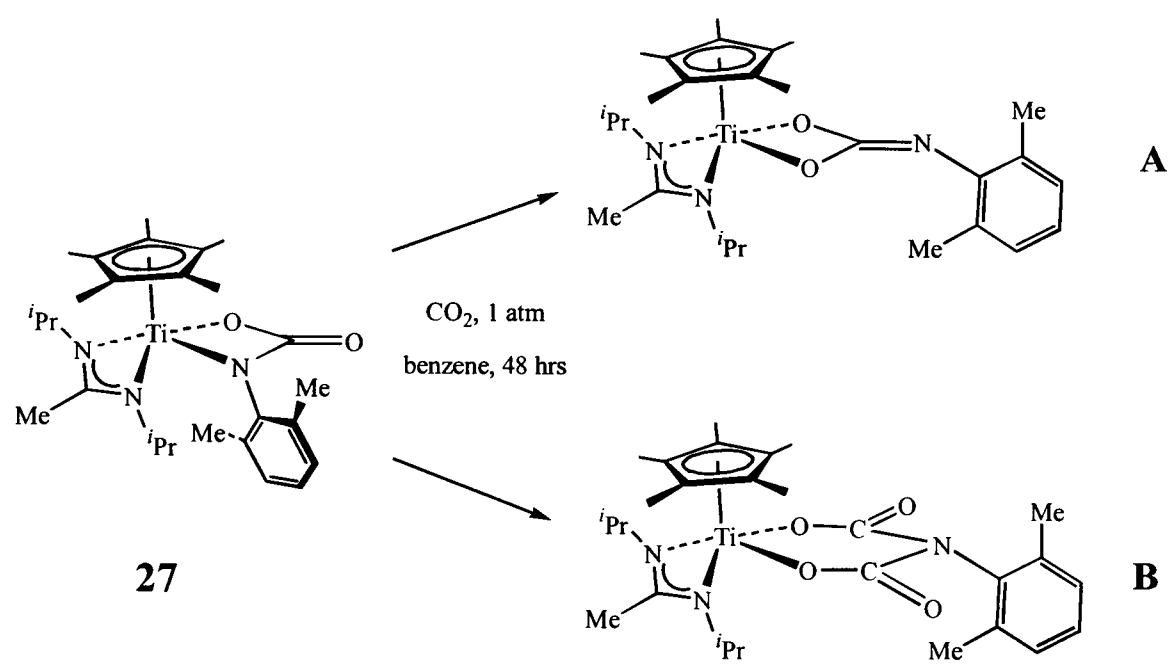


Figure 3.12 – 500.0 MHz ^1H NMR spectra of $Ti(\eta\text{-}C_5Me_5)(N\text{-}2,6\text{-}C_6H_3Me_2)\{MeC(N^iPr)_2\}$ (**7**) reaction with CO_2 in benzene-d_6 at time *t*

Two possibilities might in principle account for this observation. Either the carbamates **27 - 29**, which have already been shown to be more stable towards retrocyclisation to the give the corresponding oxo product, are able to rearrange to form a more symmetrical O, O'- bound complex, or a second molecule of CO_2 is reacting with the carbamate (see Scheme 3.8).



Scheme 3.8 – Possible products from reaction of $Ti(\eta\text{-}C_5Me_5)(N(\text{-}2,6\text{-}C_6H_3Me_2)C(O)O\}\{MeC(N^iPr)_2\}$ (**27**)

Rearrangement of a carbamate from (N, O- bound) to (O, O'- bound) chelation may be possible. However, it is unlikely here as this reactivity is not observed in the absence of further CO_2.

In addition to the evidence for structure **B** coming from this observation, the IR data also strongly suggest the incorporation of another carbonyl unit in the new molecule. Compound **27** has one band in the IR at 1669 cm^{-1} corresponding to the $\nu(C{=}O)$ stretching mode, while the new compound

exhibits IR absorptions at 1694 cm^{-1} and 1651 cm^{-1}. The final conclusive evidence for structure **B** comes from X-ray crystal structure determination (*vide infra*).

3.4.1.2 SYNTHESIS AND CHARACTERISATION OF THE COMPLEXES

Ti(η-C_5R_4Me){OC(O)N(-2,6-$C_6H_3Me_2$)C(O)O}{$R^1C(NR^2)_2$} (31 – 33)

Solutions of complexes Ti(η-C_5Me_5){N(-2,6-$C_6H_3Me_2$)C(O)O}{$MeC(N^iPr)_2$} (**27**), Ti(η-C_5H_4Me){N(-2,6-$C_6H_3Me_2$)C(O)O}{$PhC(NSiMe_3)_2$} (**28**) and Ti(η-C_5H_4Me){N(-2,6-$C_6H_3Me_2$)C(O)O}{$MeC(N^iPr)_2$} (**29**) in benzene were left standing under a CO_2 atmosphere for 24 hours. During this time, the colour of the solutions darkened from red to brown. Removal of volatiles under reduced pressure at the end of this time afforded the products as brown powders in varying yield (33 % – 82 %; the low yield owing to problems of recovery) and good purity. All three compounds were fully characterised by ^1H, ^{13}C-{^1H} NMR, IR, and elemental analysis. Compounds **31** and **33** displayed a parent ion peak in the EI mass spectrum (*m/z* = 531, 475, $[M]^+$ respectively) while in the cases of **31** and **32**, single crystals were obtained of sufficient quality to allow structural determination to be carried out.

3.4.1.2.1 X-RAY CRYSTAL STRUCTURE OF

Ti(η-C_5Me_5){OC(O)N(2,6-$C_6H_3Me_2$)C(O)O}{$MeC(N^iPr)_2$} (31)

A red crystal of **31** suitable for analysis by single crystal X-ray diffraction was obtained from a saturated solution in benzene. The data were collected and the

structure solved by Dr. A. R. Cowley of this department. Figure 3.13 shows the molecular structure of **31**, and Table 3.6 summarises some important bond lengths and angles. Full details are provided in Appendix G.

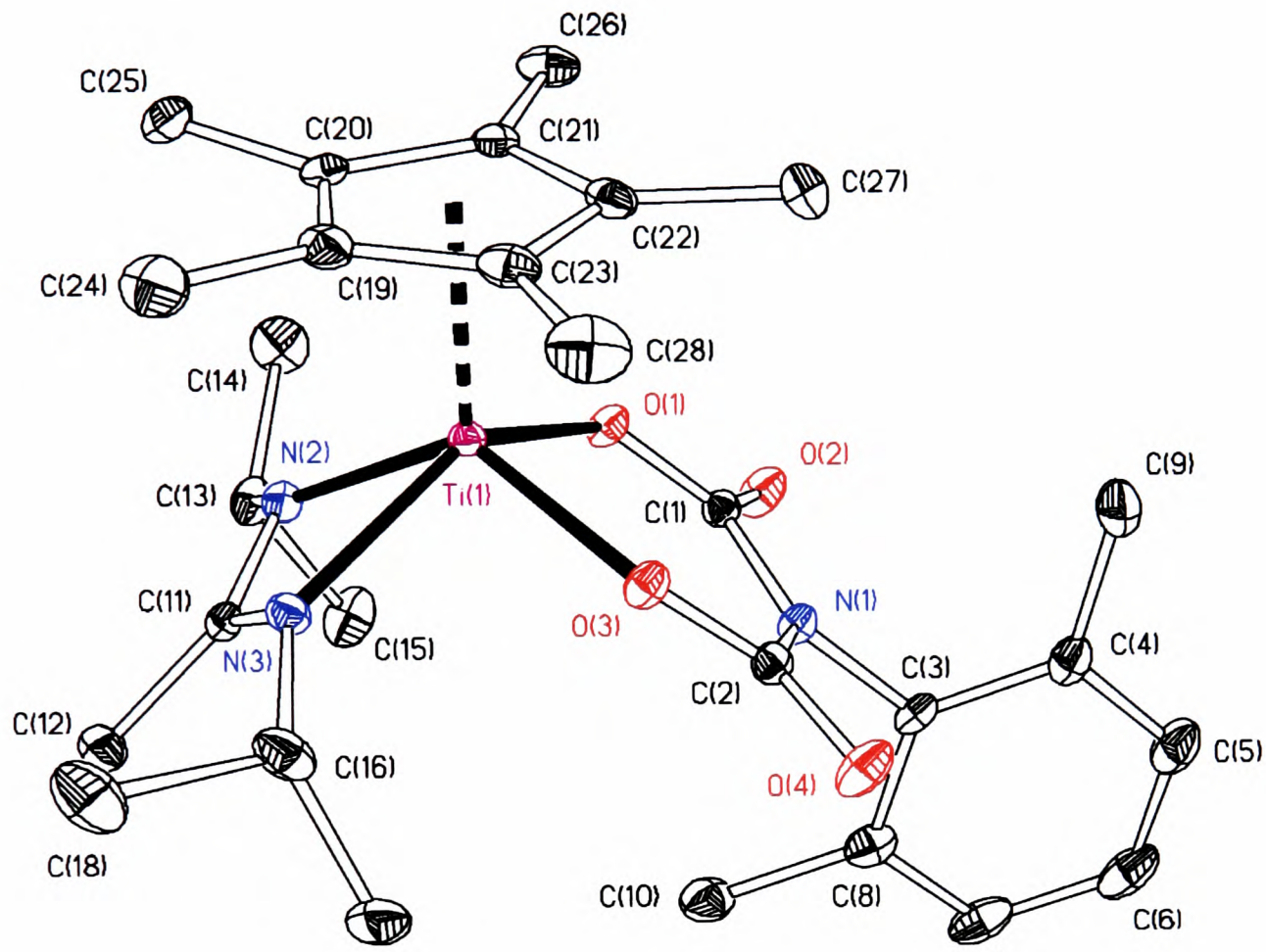


Figure 3.13 – Thermal ellipsoid plot (30 % probability) of Ti(η-C_5Me_5) {OC(O)N(-2,6-$C_6H_3Me_2$)C(O)O}{$MeC(N^iPr)_2$} (**31**). H atoms omitted for clarity

Table 3.5 – Selected bond lengths (Å) and angles (°) for Ti(η-C_5Me_5) {OC(O)N(-2,6-$C_6H_3Me_2$)C(O)O}{$MeC(N^iPr)_2$} (**31**)

Ti(1) – $Cp_{(cent)}$	2.046	$Cp_{(cent)}$ – Ti(1) – O(1)	110.8
Ti(1) – O(1)	1.932(2)	$Cp_{(cent)}$ – Ti(1) – O(3)	112.2
Ti(1) – O(3)	1.931(2)	$Cp_{(cent)}$ – Ti(1) – N(2)	118.9
Ti(1) – N(2)	2.064(2)	$Cp_{(cent)}$ – Ti(1) – N(3)	111.8
Ti(1) – N(3)	2.071(2)	O(1) – Ti(1) – O(3)	83.38(6)

N(2) – Ti(1) – N(3)	64.09(7)
O(1) – Ti(1) – N(2)	88.70(7)
O(3) – Ti(1) – N(3)	87.71(7)

3.4.1.2.2 X-RAY CRYSTAL STRUCTURE Ti(η-C_5H_4Me) {OC(O)N(-2,6-$C_6H_3Me_2$)C(O)O}{PhC($NSiMe_3$)$_2$} (32)

A yellow crystal of **32** suitable for analysis by single crystal X-ray diffraction was obtained from a saturated solution in benzene. The data were collected by the author, and the structure solved by Dr. P. Mountford. Figure 3.14 shows the molecular structure of **32**, and Table 3.6 summarises some important bond lengths and angles. Full details are provided in Appendix H.

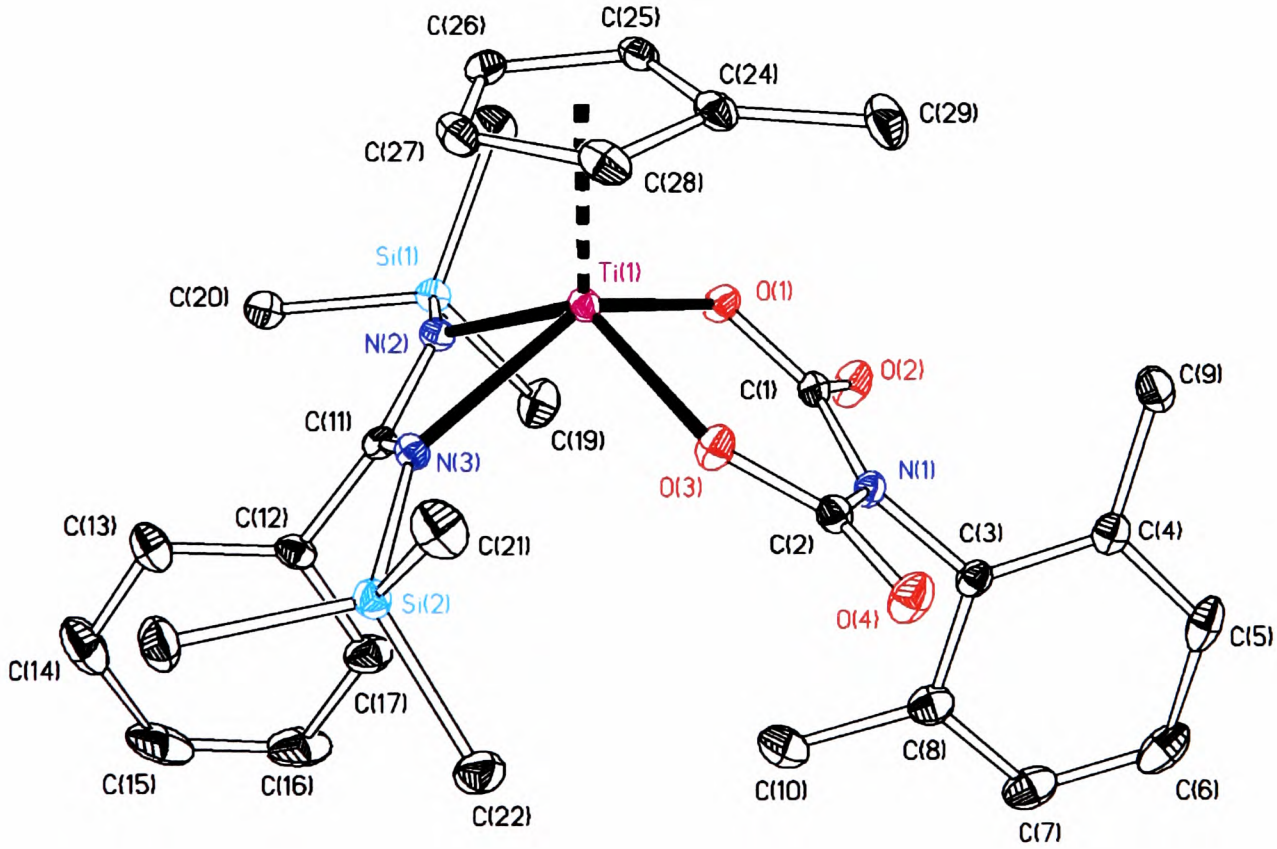


Figure 3.14 – Thermal ellipsoid plot (30 % probability) of Ti(η-C_5H_4Me) {OC(O)N(-2,6-$C_6H_3Me_2$)C(O)O}{PhC($NSiMe_3$)$_2$} (**32**). H atoms omitted for clarity

Table 3.6 – Selected bond lengths (Å) and angles (°) of Ti(η-C_5H_4Me)(OC(O)N(-2,6-$C_6H_3Me_2$)C(O)O}{PhC($NSiMe_3$)$_2$} (**32**)

Ti(1) – $Cp_{(cent)}$	2.026	$Cp_{(cent)}$ – Ti(1) – O(1)	110.9
Ti(1) – O(1)	1.925 (2)	$Cp_{(cent)}$ – Ti(1) – O(3)	113.1
Ti(1) – O(3)	1.915 (2)	$Cp_{(cent)}$ – Ti(1) – N(2)	117.2
Ti(1) – N(2)	2.079 (3)	$Cp_{(cent)}$ – Ti(1) – N(3)	115.7
Ti(1) – N(3)	2.095 (3)	O(1) – Ti(1) – O(3)	83.6 (1)
		N(2) – Ti(1) – N(3)	64.9 (1)
		O(1) – Ti(1) – N(2)	86.6 (1)
		O(3) – Ti(1) – N(3)	86.3 (1)

3.4.1.2.3 COMPARISON OF THE STRUCTURES OF 31 AND 32

Both complexes **31** and **32** adopt a four-legged piano stool structure. In contrast to the structures of Ti(η-C_5H_4Me)(N^{t}Bu){PhC($NSiMe_3$)$_2$} (**3**) and the oxo species [Ti(η-C_5H_4Me)(μ-O){PhC($NSiMe_3$)$_2$}]$_2$ (**24**), the methyl group of the C_5H_4Me ligand in **32** is directed away from the amidinate ligand, indicating the lower steric requirements of the arylimido dicarboxylate ligand. A comparison of the bond lengths and angles of these two complexes shows very little difference between them. All bond lengths around the metal are comparable to those found in other Ti(IV) complexes.[46,47] The slight shortening of the bonds around titanium in **32** are consistent with the reduced steric bulk of the cyclopentadienyl ligand.

3.4.1.3 Discussion of insertion of second CO_2 molecule

The insertion of a second molecule of CO_2 into a metal carbamate to give an arylimido dicarboxylate is without precedent in the literature. The closest related chemistry reported in the literature is the proposed reversible insertion of phenyl isocyanate into the titanium tetraazaannulene ureate species Ti{N(-4-C_6H_4Me)C(O)N(Ph)}(Me_4taa) to give the transient (unobserved) adduct Ti{N(Ph)C(O)N(-4-C_6H_4Me)C(O)N(Ph)}(Me_4taa).[26] This is discussed in more depth in Chapter 4.

Arylimido dicarboxylates have not been previously reported as ligands in metal coordination chemistry, although derivatives have been long established in the organic literature.[60] Reaction between metal complexes and two molecules of CO_2 have been reported previously, but reaction has always taken place at two different sites within the molecule,[32,37] or else has resulted in the formation of an unsymmetrical η^2-C(O)OC(O)O ligand, in which the metal is bound through one C and one O atom.[61] It was demonstrated that in the exchange reactions of CO_2 with carbamate complexes derived from $M(NMe_2)_n$ (M = Ti, Zr, V, n = 4; M = Nb, Ta, n=5), attack of the second CO_2 molecule did not occur directly on the carbamate, but on trace free amine.[17] This new reactivity would seem to arise through the direct reaction of the carbamate with CO_2, thereby demonstrating the direct attack of CO_2 on the ligand bound to the metal. Imido complexes studied previously in the Mountford group have been found either to (i) react stoichiometrically with CO_2 to give an isolable cycloaddition product, or else (ii) react to give decomposition products. The former case is favoured by the more sterically

crowded macrocyclic ligands,[26] while the more open tripodal dianionic ligands tend to give decomposition products.[62]

It is proposed that the cyclopentadienyl-amidinate ligand set, falling in the steric middle ground between these two extremes, is sufficiently open to allow reaction of the cycloadduct with CO_2 to occur, but sufficiently crowded to stabilise the product formed. Thus, it may be that insertion of a second molecule of CO_2 occurs rapidly with less crowded systems such as $Ti(N^tBu)(N_2N_{py})$, but then decompose to unidentifiable products due to insufficient steric protection.

A qualitative comparison of the rate at which the second molecule of CO_2 reacts with the cycloadducts **27** – **30** follows the pattern expected on steric grounds under otherwise identical conditions. Reaction of $Ti(\eta\text{-}C_5H_4Me)\{N(\text{-}2,6\text{-}C_6H_3Me_2)C(O)O\}\{MeC(N^iPr)_2\}$ (**29**) with the second molecule of CO_2 is complete in *ca.* 12 hours. For $Ti(\eta\text{-}C_5H_4Me)\{N(\text{-}2,6\text{-}C_6H_3Me_2)C(O)O\}\{PhC(NSiMe_3)_2\}$ (**28**) it is *ca.* 24 hours, and for $Ti(\eta\text{-}C_5Me_5)\{N(\text{-}2,6\text{-}C_6H_3Me_2)C(O)O\}\{MeC(N^iPr)_2\}$ (**27**) after *ca.* 2 days. Insertion of a second molecule of CO_2 does eventually occur with the most crowded cycloadduct, $Ti(\eta\text{-}C_5Me_5)\{N(\text{-}2,6\text{-}C_6H_3Me_2)C(O)O\}\{PhC(NSiMe_3)_2\}$ (**30**), but takes several days at room temperature, and is not obtained pure. These observations are consistent with the more sterically crowding ligands retarding the rate of reaction, with the cyclopentadienyl ligand being the most important contributing factor.

Exposure of a sample of Ti(η-C_5Me_5)(N^{t}Bu){MeC(N^{i}Pr)$_2$} (**2**) dissolved in benzene-d_6 to CO_2 at a higher overall pressure (2 atm) for 24 hours revealed some peaks in the ^{1}H NMR spectrum consistent with insertion of CO_2 into the carbamate complex Ti(η-C_5Me_5){N(^{t}Bu)C(O)O}{MeC(N^{i}Pr)$_2$} (**20**), suggesting that the *tert*-butyl homologues can also undergo this reaction. However, the majority of the proton resonances were attributable to the oxo dimer [Ti(η-C_5Me_5)(μ-O){MeC(N^{i}Pr)$_2$}]$_2$ (**22**). No resonances assigned to the parent imido species were present, and the new product was not found to decompose to **22** on standing in solution. No further attempt was made to isolate or characterise this product.

In order to explore more fully the chemistry of this second addition of CO_2, a comparison was carried out on systems possessing different *para*- substituents on the arylimido group.

3.4.2 Reactions of Ti(η-C_5Me_5)(N-4-C_6H_4X){MeC(N^{i}Pr)$_2$} (X = CF_3, Me, NMe_2) with CO_2

It has been shown that replacing the *tert*-butyl group with a 2,6-dimethylphenyl substituent radically alters the reactivity observed for the imido complexes. A further avenue of investigation was to vary the electronic nature of the aryl ring, while keeping its steric character as constant as possible. This offered the possibility of revealing more information about the mechanism of the insertion of CO_2 into the carbamate. For this reason, three complexes of the form Ti(η-C_5Me_5)(N-4-C_6H_4X){MeC(N^{i}Pr)$_2$} (X = CF_3,

Me, NMe_2) were synthesised; the X substituent is in the *para* position to remove any possible steric differences at the active site.

3.4.2.1 SYNTHESIS OF Ti(η-C_5Me_5)(N-4-C_6H_4X){$MeC(N^iPr)_2$} COMPLEXES

The three *para*- substituents (CF_3, Me, NMe_2) were chosen on the basis of their strongly differing Hammett parameters, σ.[63] These are given in Table 3.7 below.

X	σ
p- CF_3	0.53
p- CH_3	-0.14
p- NMe_2	-0.63

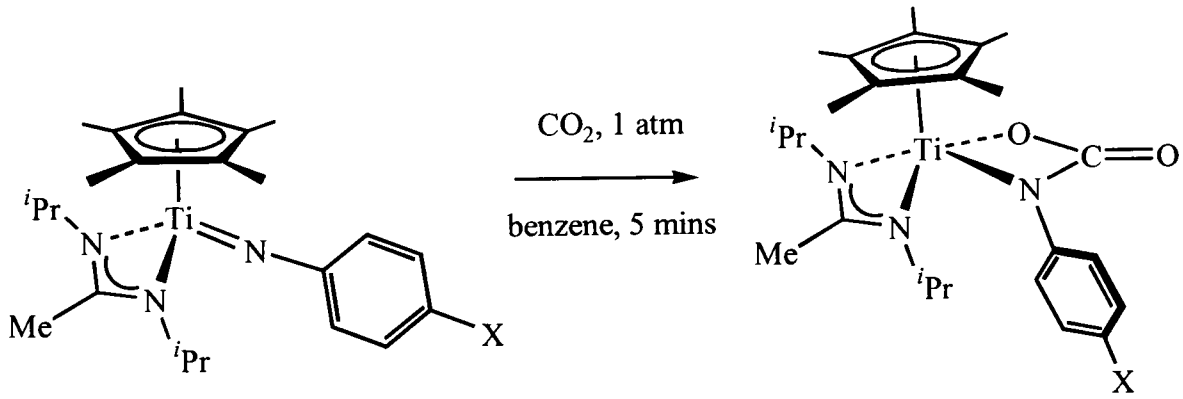
Table 3.7 – Hammett parameters σ for the 4- substituted aryl groups[63]

The Hammett parameter is an empirically measured property of an aryl substituent, and gives a measure of the capacity of the group to donate or sequester electron density from the ring.[63] It has been used to probe the nature of transition states for chemical reactions involving aryl substituents. Though determined from organic rather than organometallic species, the Hammett parameter nevertheless provides a means of gaining a basis set of systems with different electronic properties.[64,65]

The syntheses of the three complexes Ti(η-C_5Me_5)(N-4-C_6H_4Me){$MeC(N^iPr)_2$} (**8**), Ti(η-C_5Me_5)(N-4-$C_6H_4CF_3$) (**9**) and Ti(η-C_5Me_5)(N-4-$C_6H_4NMe_2$){$MeC(N^iPr)_2$} (**10**) are detailed in Chapter 2.

3.4.2.2 REACTIONS OF Ti(η-C_5Me_5)(N-4-C_6H_4X){$MeC(N^iPr)_2$} WITH CO_2 (ONE EQUIVALENT)

Samples of Ti(η-C_5Me_5)(N-4-C_6H_4Me){$MeC(N^iPr)_2$} (**8**), Ti(η-C_5Me_5)(N-4-$C_6H_4CF_3$) (**9**) and Ti(η-C_5Me_5)(N-4-$C_6H_4NMe_2$){$MeC(N^iPr)_2$} (**10**) were dissolved in benzene and exposed to CO_2 at a pressure of 1 atm. Immediate colour change to cherry red showed that reaction was occurring. Removal of volatiles under reduced pressure within 30 seconds afforded the carbamate complexes Ti(η-C_5Me_5){N(-4-C_6H_4Me)C(O)O}{$MeC(N^iPr)_2$} (**34**), Ti(η-C_5Me_5){N(-4-$C_6H_4CF_3$)C(O)O}{$MeC(N^iPr)_2$} (**35**) and Ti(η-C_5Me_5){N(-4-$C_6H_4NMe_2$)C(O)O}{$MeC(N^iPr)_2$} (**36**) respectively in quantitative 100 % yield, as shown in Equation 3.13.



X	Compound
Me	**34**
CF_3	**35**
NMe_2	**36**

Equation 3.13

All three carbamates have been fully characterised by ^1H, $^{13}C\{^1H\}$ NMR, and IR spectroscopies, and elemental analysis. The ^1H NMR spectra of the

complexes adopt the same pattern as that of Ti(η-C_5Me_5){N(-2,6-$C_6H_3Me_2$)C(O)O}{MeC(N^{i}Pr)$_2$} (**27**), the loss of the plane of symmetry giving rise to four doublets between 0.44 and 1.35 ppm, and two virtual septets between 3.3 and 3.7 ppm assigned to the amidinate. The IR spectra of the three complexes show absorptions at 1672 cm^{-1} (**34**), 1655 cm^{-1} (**35**), and 1656 cm^{-1} (**36**) corresponding to the ν(C=O) stretch, with no overall trend being evident.

3.4.2.3 Comparison of Ti(η-C_5Me_5){N(-4-C_6H_4X)C(O)O}{MeC(N^{i}Pr)$_2$} with Ti(η-C_5R_4Me){N(-2,6-$C_6H_3Me_2$)C(O)O}{MeC(N^{i}Pr)$_2$} species

The synthesis of the 4-substituted carbamates Ti(η-C_5Me_5){N(-4-C_6H_4X)C(O)O}{MeC(N^{i}Pr)$_2$} (X = Me (**34**), CF_3 (**35**), NMe_2 (**36**)) was found to be more difficult than that of Ti(η-C_5Me_5){N(-2,6-$C_6H_3Me_2$)C(O)O}{MeC(N^{i}Pr)$_2$} (**27**), Ti(η-C_5H_4Me){N(-2,6-$C_6H_3Me_2$)C(O)O}{PhC($NSiMe_3$)$_2$} (**28**), Ti(η-C_5H_4Me){N(-2,6-$C_6H_3Me_2$)C(O)O}{MeC(N^{i}Pr)$_2$} (**29**) and Ti(η-C_5Me_5){N(-2,6-$C_6H_3Me_2$)C(O)O}{PhC($NSiMe_3$)$_2$} (**30**), due to the ease with which insertion of the second molecule of CO_2 takes place in the 4-substituted aryl complexes. Contamination of the samples with the imido starting material, or the arylimido dicarboxylate product was frequently observed, and the exposure of CO_2 had to be carefully regulated to afford clean products. In the case of Ti(η-C_5Me_5){N(-4-C_6H_4Me)C(O)O}{MeC(N^{i}Pr)$_2$} (**34**), a clean sample was obtained using a volumetrically calibrated gas manifold, and condensing

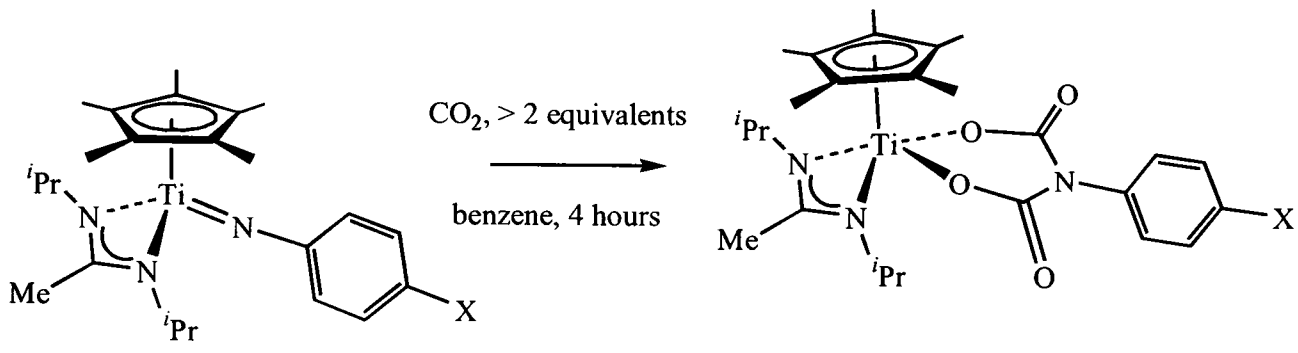
exactly 1 equivalent of CO_2 onto a frozen solution of the parent imido species. However, this method was often found to be unreliable. The preferred synthetic route was thus the exposure of the imido complexes to CO_2 at 1 atm pressure followed by rapid removal of excess reagent under reduced pressure.

The possibility of the carbamate being able to rearrange to an O, O -bound ligation mode (similar to the type reported by Strähle[66] and Royo[32] for species derived from amido precursors) was tested by observing the effect of heating a sample of **34**. The compound **34** was selected due to its greater longevity than the *tert*-butyl congeners in benzene-d_6 solution. Additionally, its high reactivity towards further CO_2 addition suggested that it would be amongst the most likely candidates for Ti–N bond cleavage; a necessary step in a potential rearrangement.

A sample of Ti(η-C_5Me_5){N(-4-C_6H_4Me)C(O)O}{MeC(N^{i}Pr)$_2$} (**34**) was dissolved in benzene-d_6 and heated to 80 °C for 6 hours. At the end of this time, the ^{1}H NMR spectrum of the reaction mixture showed complete decomposition of the complex to the dimeric oxo complex [Ti(η-C_5Me_5)(μ-O){MeC(N^{i}Pr)$_2$}]$_2$ (**22**), and [(4-C_6H_4Me)NCO]$_3$. The trimerisation of *p*-tolyl isocyanate to give [(4-C_6H_4Me)NCO]$_3$ on heating has been reported previously.[67] At room temperature, decomposition was observed to take place slowly over a period of 3 days to give a mixture of unidentified products.

3.4.2.4 REACTIONS OF Ti(η-C_5Me_5)(N-4-C_6H_4X){$MeC(N^iPr)_2$} WITH CO_2 (TWO EQUIVALENTS)

Samples of Ti(η-C_5Me_5)(N-4-C_6H_4Me){$MeC(N^iPr)_2$} (**8**), Ti(η-C_5Me_5)(N-4-$C_6H_4CF_3$) (**9**) and Ti(η-C_5Me_5)(N-4-$C_6H_4NMe_2$){$MeC(N^iPr)_2$} (**10**) were dissolved in benzene and exposed to CO_2 at a pressure of 1 atm. Immediate colour change to cherry red showed that reaction was occurring. All solutions were left under a CO_2 atmosphere for at least 4 hours, before the volatiles were removed under reduced pressure to afford the arylimido dicarboxylate complexes Ti(η-C_5Me_5){OC(O)N(-4-C_6H_4Me)OC(O)}{$MeC(N^iPr)_2$} (**37**), Ti(η-C_5Me_5){OC(O)N(-4-$C_6H_4CF_3$)OC(O)}{$MeC(N^iPr)_2$} (**38**) and Ti(η-C_5Me_5){OC(O)N(-4-$C_6H_4NMe_2$)OC(O)}{$MeC(N^iPr)_2$} (**39**) respectively (54 % – 62 % isolated yield), as shown in Equation 3.14.



X	Compound
Me	**37**
CF_3	**38**
NMe_2	**39**

Equation 3.14

Compounds **37** – **39** have been characterised by ^1H, ^{13}C-{^1H} NMR and IR spectroscopies, and by elemental analysis. In addition, the parent ion of

complex **39** was detected in a high resolution EI mass spectrum (*m/z* found(calculated) = 546.2689(546.2686), $[M]^+$). The NMR spectra of compounds **37** – **39** follow the same pattern as that of Ti(η-C_5Me_5){OC(O)N(-2,6-$C_6H_3Me_2$)C(O)O}{MeC(N^{i}Pr)$_2$} (**7**), the *iso*-propyl groups on the amidinate being related by symmetry, and giving rise to a pair of doublets in the range 1.11 – 1.05 ppm, and a virtual septet in the range 3.41 – 3.43 ppm. The IR spectra of the complexes show no overall trend, with two absorptions at 1698, 1656 cm^{-1} (**37**), 1704, 1658 cm^{-1} (**38**), and 1698, 1653 cm^{-1} (**39**), corresponding to the in-phase and out-of-phase ν(C=O) stretches.

3.4.2.5 Effect of *para*- substituent X in Ti(η-C_5Me_5){N(-4-C_6H_4X)C(O)O}{MeC(N^{i}Pr)$_2$} (X = CF_3, Me, NMe_2) on rate of insertion of CO_2

The rapid reaction of the carbamate complexes Ti(η-C_5Me_5){N(-4-C_6H_4Me)C(O)O}{MeC(N^{i}Pr)$_2$} (**34**), Ti(η-C_5Me_5){N(-4-$C_6H_4CF_3$)C(O)O}{MeC(N^{i}Pr)$_2$} (**35**) and Ti(η-C_5Me_5){N(-4-$C_6H_4NMe_2$)C(O)O}{MeC(N^{i}Pr)$_2$} (**36**) with CO_2 makes them convenient to study in real time at room temperature using ^{1}H NMR spectroscopy. A series of pseudo-first order rate studies were carried out on the three complexes, using the procedure described below.

Samples of the parent imido complexes Ti(η-C_5Me_5)(N-4-C_6H_4Me){MeC(N^{i}Pr)$_2$} (**8**), Ti(η-C_5Me_5)(N-4-$C_6H_4CF_3$){MeC(N^{i}Pr)$_2$} (**9**), and Ti(η-C_5Me_5)(N-4-$C_6H_4NMe_2$){MeC(N^{i}Pr)$_2$} (**10**) at the same

concentration were prepared in benzene-d_6, and exposed to CO_2 at a pressure of 1.6 atm (> 10 equivalents CO_2). They were then immediately transferred into the magnet of a Varian Unity 500 NMR spectrometer, with the temperature being maintained at a constant 18 °C. 1,4-dimethoxybenzene was used as an internal standard to ensure the concentration of the reactant and product species present in solution could be independently verified during the experiment. As expected, all of the imido complexes **8** – **10** were consumed to form the corresponding carbamate complexes **34** – **36** within 2 minutes, before any of the arylimido dicarboxylate products were detected. This confirmed that the insertion of CO_2 into the carbamate complexes was independent of the formation of the carbamates.

In each of the three cases, the reaction progress was monitored *via* ^{1}H NMR spectroscopy. The relative concentrations of the carbamate and arylimido dicarboxylate complexes were measured from each spectrum, and the results fitted to a first order exponential relationship. In order to increase the confidence of the study, each experiment was repeated, and the results of all six experiments collated.

3.4.2.6 RESULTS AND DISCUSSION OF RATES EXPERIMENTS

The results of the six experiment runs are given in full in Appendix I. Figures 3.15 – 3.17 below show the reaction of the carbamates to give the corresponding arylimido dicarboxylates as a function of time.

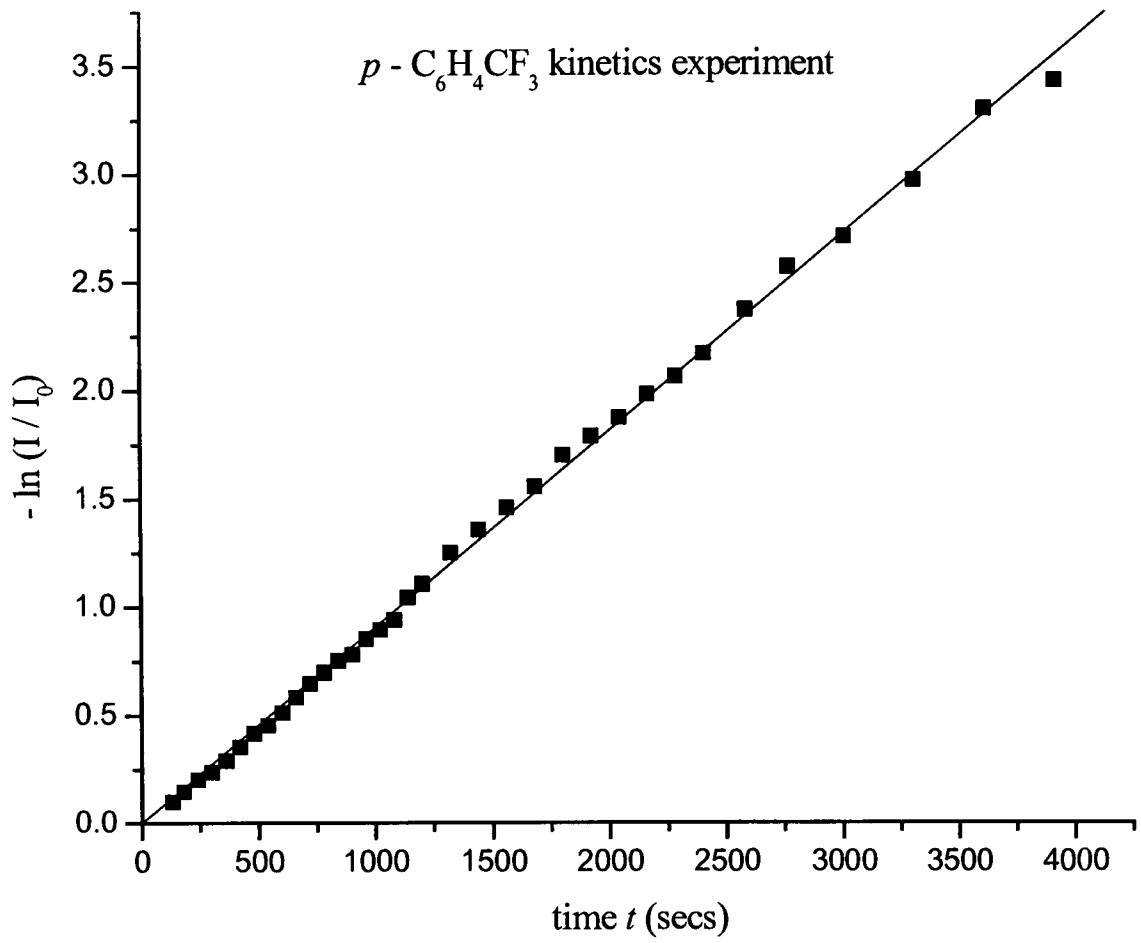


Figure 3.15 – Decay of Ti(η-C_5Me_5){N(-4-$C_6H_4CF_3$)C(O)O}{MeC(N^{i}Pr)$_2$} (**35**) under pseudo-first order conditions with excess CO_2 as a function of time

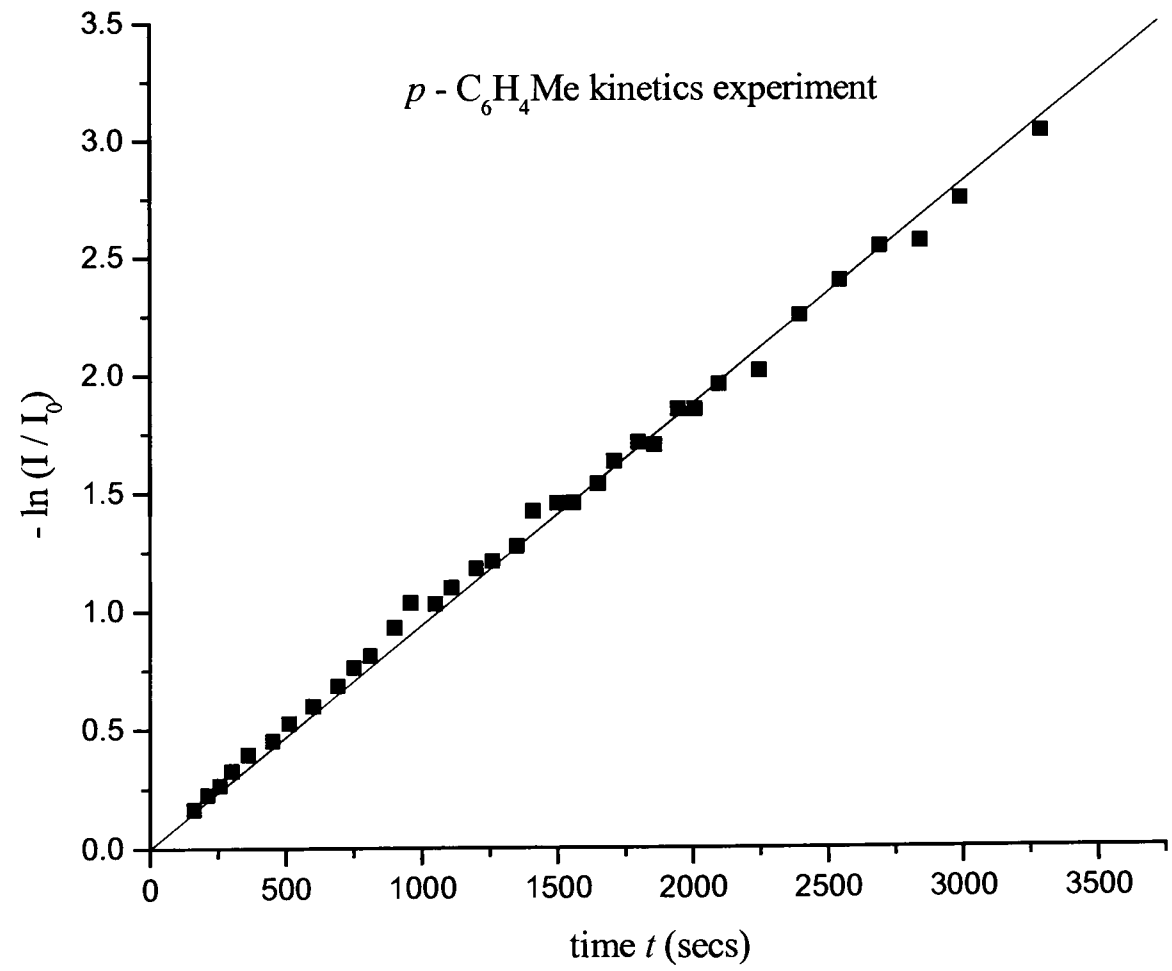


Figure 3.16 – Decay of Ti(η-C_5Me_5){N(-4-C_6H_4Me)C(O)O}{MeC(N^{i}Pr)$_2$} (**34**) under pseudo-first order conditions with excess CO_2 as a function of time

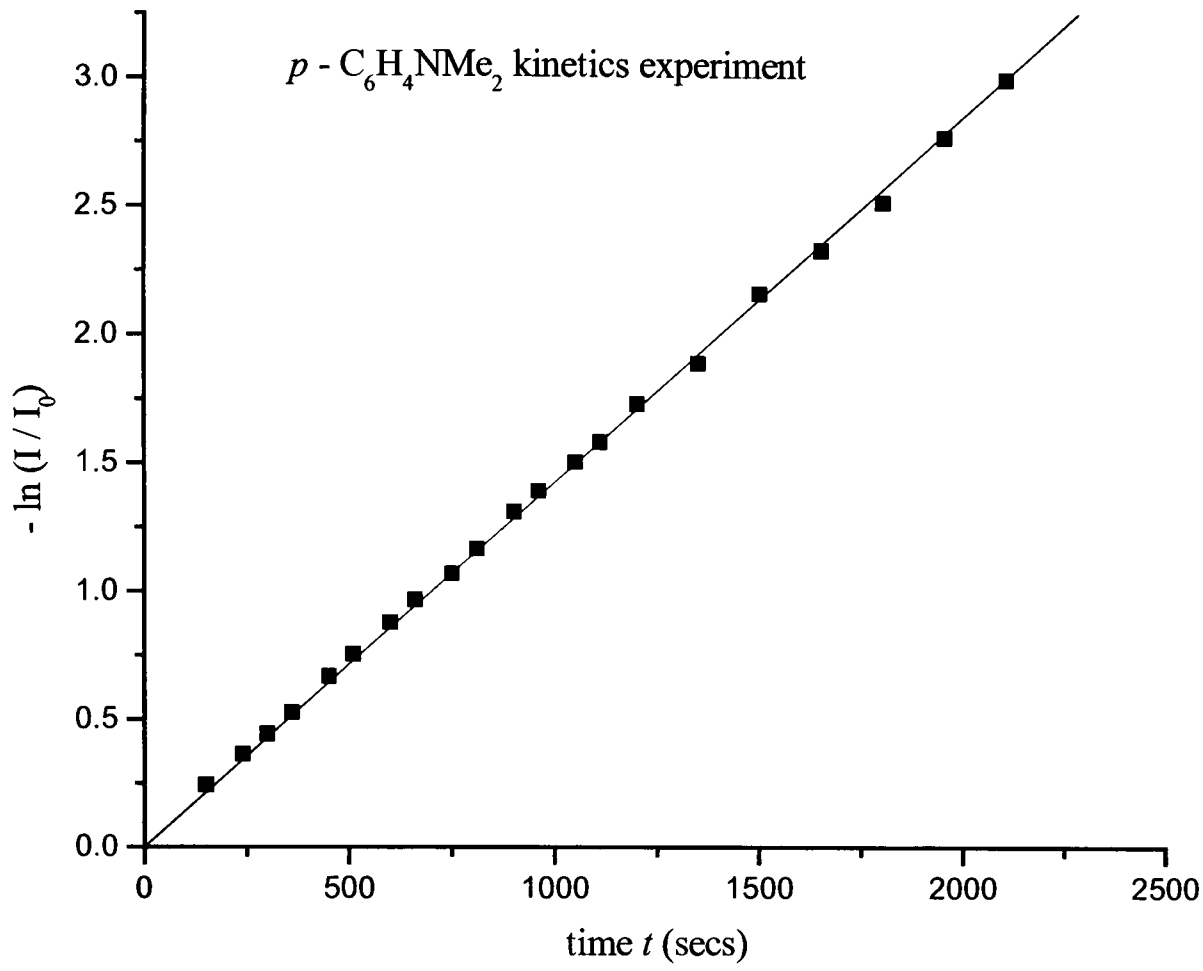


Figure 3.17 – Decay of Ti(η-C_5Me_5){N(-4-$C_6H_4NMe_2$)C(O)O}{MeC(N^iPr)$_2$} (**36**) under pseudo-first order conditions with excess CO_2 as a function of time

Table 3.7 summarises the information which can be extracted from the data shown above.

Table 3.7 – Values of k_{obs} and $t_{½}$ extracted from analysis of kinetic data for conversion of carbamate complexes **36** **36** to arylimido dicarboxylate complexes **37** - **39**

X	K_{obs} (s^{-1})	$t_{½}$ (s)
p- CF_3	$9.3(1) \times 10^{-4}$	745
p- Me	$9.0(1) \times 10^{-4}$	770
p- NMe_2	$14.2(2) \times 10^{-4}$	480

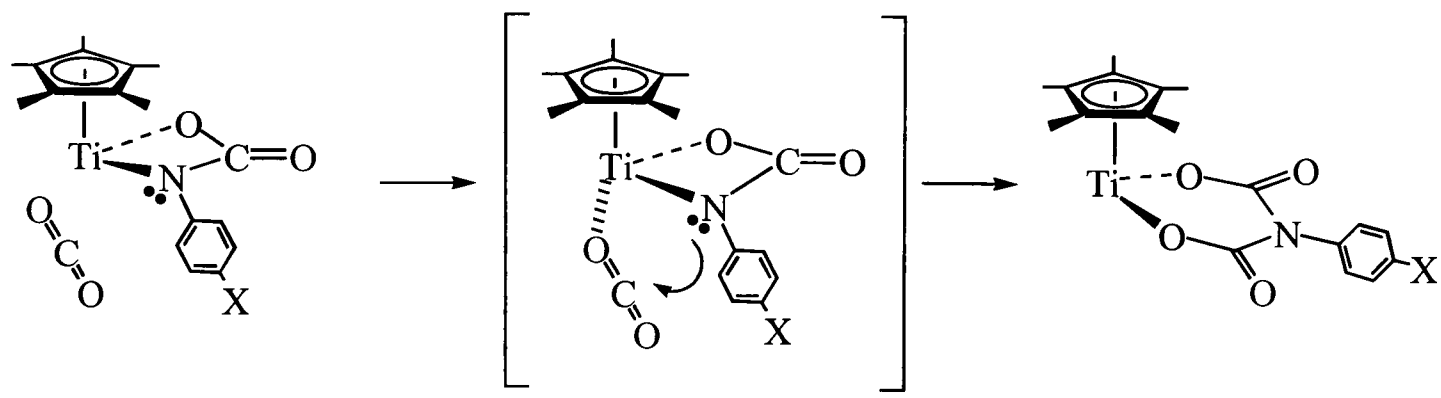
It can be seen that no significant effect is observed on substitution of *p*- CF_3 with *p*- Me. However, substitution with the *p*- NMe_2 group substantially increases the rate of reaction of the carbamate with CO_2.

These observations warrant further analysis. The lack of a retardation of reaction rate in the CF_3 system can be attributed to one of two phenomena:

i) That two opposing factors affect the rate of second insertion; i.e. the electron donating properties of the ring are balanced against the electron withdrawing properties of the metal centre.

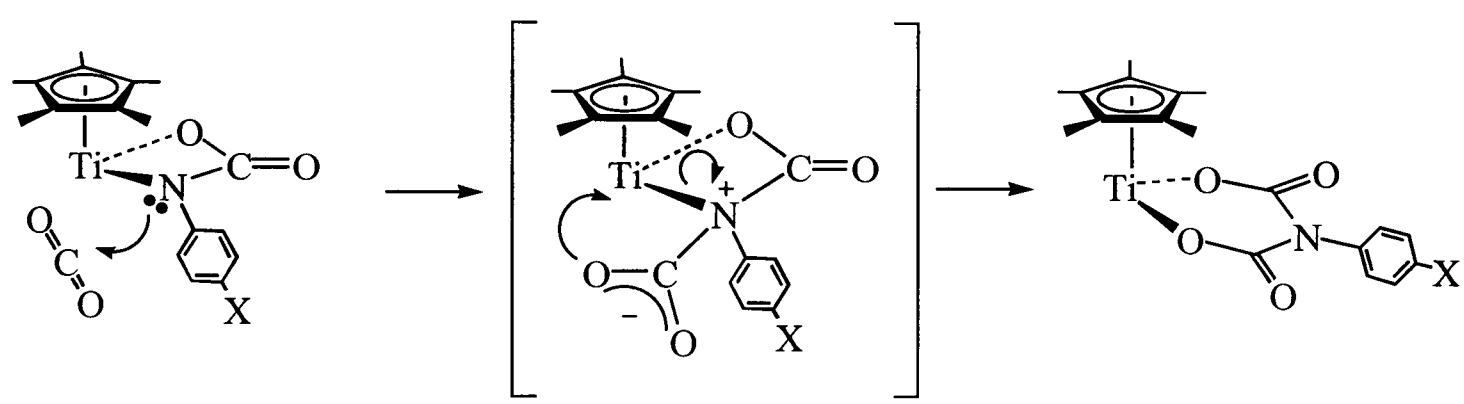
ii) That the Hammett parameter for the CF_3 group does not reflect a true value in this organometallic system.

As has already been mentioned, the Hammett parameter is empirically determined from measurements made on systems without a metal centre, and may not hold for metal-containing compounds.[63] However, it seems more likely in this case that the rate determining step is dependent on both the nucleophilicity of the lone pair on nitrogen, and on the electrophilicity of the titanium. It follows that as the aryl ring gets more electron-rich, the nucleophilicity of the nitrogen will increase. However, at some point this may cause an increase in electron density at the titanium, which may act to inhibit the pre-coordination of the CO_2, as indicated in Equation 3.15 below, which illustrates the likely reaction mechanism involved in the formation of the final complex.



Equation 3.15

Another possible mechanism, which does not involve the precoordination of CO_2 to the metal centre, is given in Equation 3.16.



Equation 3.16

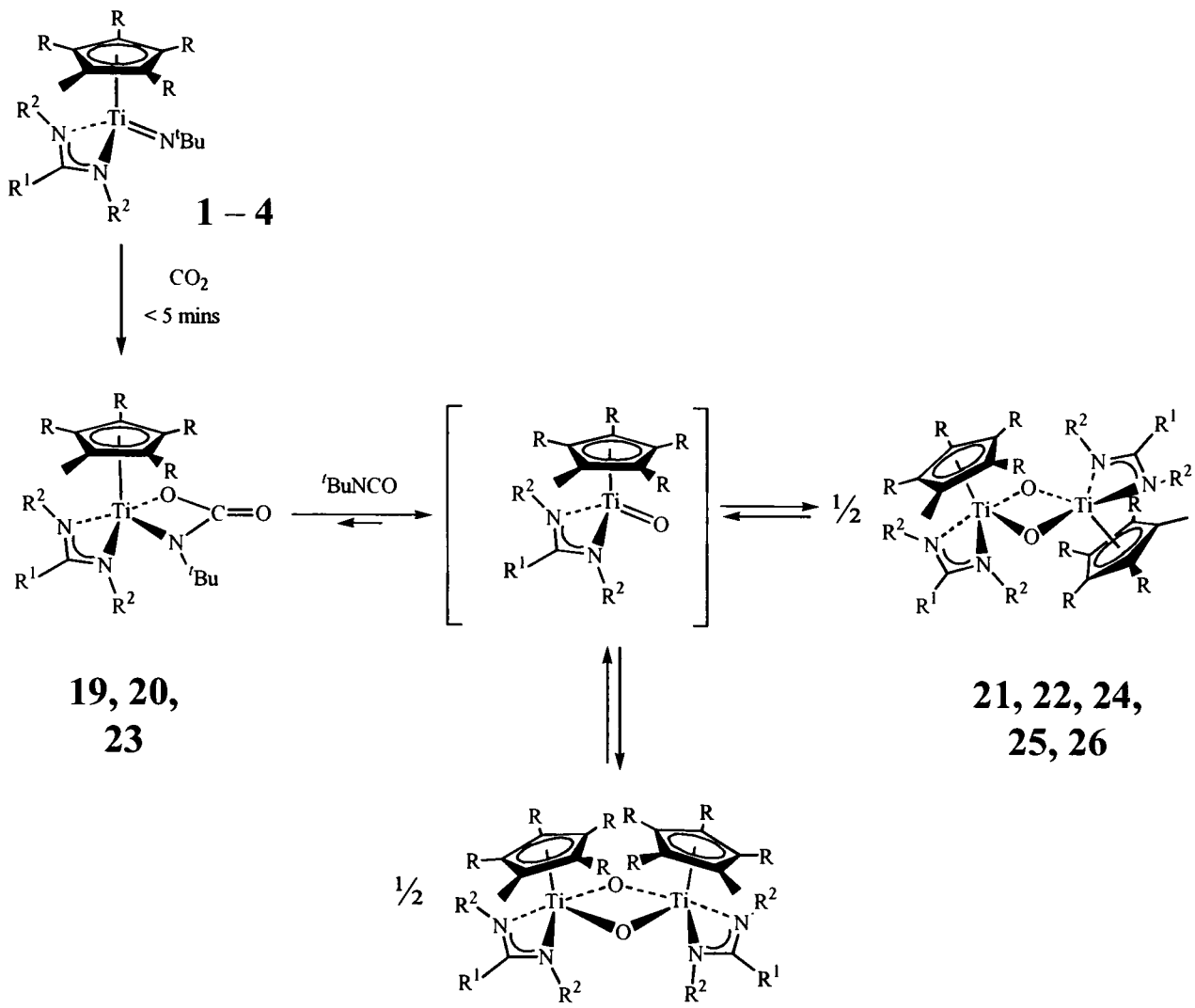
However, the dramatic increase in the rate of insertion of *p*-tolyl isocyanate into the Ti–N bond of both carbamates and ureates relative to CO_2 (discussed in Chapter 4) supports the view that precoordination of the substrate prior to attack of the nitrogen lone pair is occuring, and thus that the mechanism given in Equation 3.15 is more probable.

The rate enhancement observed in the case of the *p*- NMe_2 system is significant, and indicates nucleophilic attack of the carbamate nitrogen on CO_2 is the rate-determining step of the insertion.

In the reaction of the iridium amido species Ir(η-C_5Me_5) {η^2-N(H)C(Me)$_2$C(H_2)}(PMe_3) (**3.12**) with CO_2 by Bergman[19] cited earlier, evidence for transient species was observed in the ^{1}H NMR spectrum of the reaction mixture at low temperature. In an attempt to identify the possible intermediate in the above reaction scheme, a sample of Ti(η-C_5Me_5)(N-4-C_6H_4Me){MeC(N^{i}Pr)$_2$} (**8**) was dissolved in an aliquot of toluene-d_8, cooled to -78 °C and exposed to CO_2 at a pressure of 1 atm. The reaction was monitored by ^{1}H NMR spectroscopy at -80 °C, and followed from the starting imido species through to the final product. At this temperature, complete consumption of Ti(η-C_5Me_5)(N-4-C_6H_4Me) {MeC(N^{i}Pr)$_2$} (**8**) to form Ti(η-C_5Me_5){N(-4-C_6H_4Me)C(O)O}{MeC(N^{i}Pr)$_2$} (**34**) was observed before any peaks corresponding to Ti(η-C_5Me_5){OC(O)N(-4-C_6H_4Me)C(O)O}{MeC(N^{i}Pr)$_2$} (**37**) became visible. No evidence was found for any intermediates, indicating that they are highly unstable.

3.5 SUMMARY

This Chapter has described and discussed the reaction of Ti(η-C_5R_4Me)(N^{t}Bu){R^{1}C(NR^2)$_2$} with CO_2. It has been seen that the imido species react rapidly *via* a formal [2 + 2] cycloaddition to give a carbamate complex, which then undergoes retrocyclisation to afford *tert*-butyl isocyanate and the corresponding oxo dimer [Ti((η-C_5R_4Me)(μ-O){R^{1}C(NR^2)$_2$}]$_2$, as shown in Scheme 3.9.



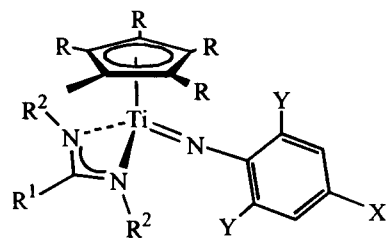
R	R^1	R^2	Imido	Carbamate	Oxo dimer
Me	Ph	$SiMe_3$	**1**	**19**	**21**
Me	Me	^{i}Pr	**2**	**20**	**22**
H	Ph	$SiMe_3$	**3**	**23***	**24 / 24a**
H	Me	^{i}Pr	**4**	Not observed	**25 / 25a**
H	Ph	$SiMe_3$	**5**	-	**26 / 26a**

* = not isolated

Scheme 3.9 – Reactivity of titanium cyclopentadienyl *tert*-butylimido amidinate complexes with CO_2

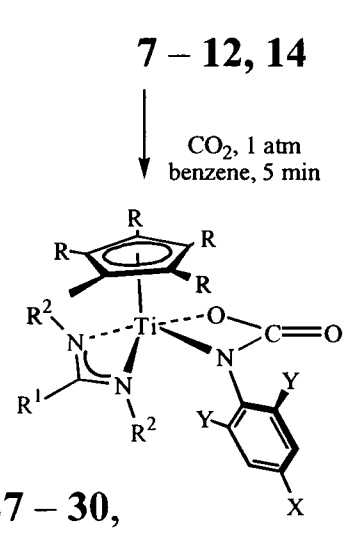
The stability of the carbamate is dependant on the ancillary ligand set, with the more crowding C_5Me_5 ligand affording the most stable carbamates, and $PhC(NSiMe_3)_2$ affording greater stability than $MeC(N^iPr)_2$.

The imido N-substituent is found to have a profound effect on the reactivity of the carbamate. Whereas the *tert*-butyl carbamates undergo retrocyclisation to give a bridging oxo product and *tert*-butyl isocyanate, the aryl carbamates are found to react with a further molecule of CO_2 in an unexpected and unprecedented manner to give products in which the $Ti–N_{carbamate}$ bond has been cleaved, and CO_2 formally inserted. This reactivity is shown in Scheme 3.10.



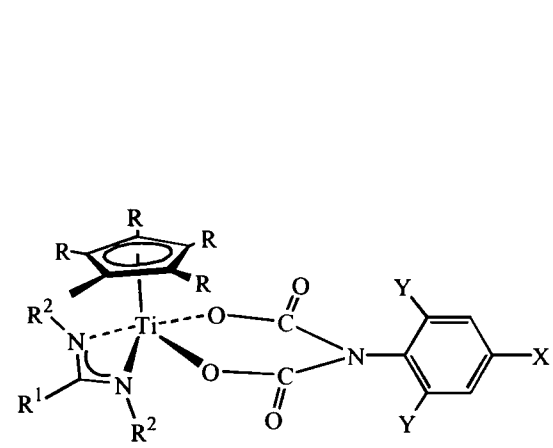
7 – 12, 14

CO_2, 1 atm
benzene, 5 min



27 – 30, 34 – 36

CO_2, 1 atm
benzene, 4 hours



31 – 33, 37 – 39

R	R^1	R^2	X	Y	Imido	Carbamate	Arylimido dicarboxylate
Me	Me	^{i}Pr	H	Me	**7**	**27**	**31**
Me	Me	^{i}Pr	Me	H	**8**	**34**	**37**
Me	Me	^{i}Pr	CF_3	H	**9**	**35**	**38**
Me	Me	^{i}Pr	NMe_2	H	**10**	**36**	**39**
H	Ph	$SiMe_3$	H	Me	**11**	**28**	**32**
H	Me	^{i}Pr	H	Me	**12**	**29**	**33**
Me	Ph	$SiMe_3$	H	Me	**14**	**30**	Not isolated

Scheme 3.10 – Reactivity of titanium cyclopentadienyl arylimido amidinate complexes with CO_2

The OC(O)N(Ar)C(O)O fragment so formed (derived formally from the dianionic conjugate base of azamalonic acid) has not been structurally characterised previously, and represents a new type of ligand.

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CHAPTER 4

Reactivity Towards Nitrogen Heterocumulenes

4.1 OVERVIEW

This Chapter focuses on the reactivity of titanium cyclopentadienyl imido amidinate complexes with nitrogen-containing heterocumulenes.

In the first Section, a survey of the reactivity of isocyanates and carbodiimides with organometallic compounds is given, with particular focus on systems that are directly comparable to the title complexes. Subsequent Sections will discuss the reactivity of the titanium cyclopentadienyl imido amidinate complexes with alkyl and aryl isocyanates, and alkyl and aryl carbodiimides. Comparisons between the reactivity of these unsaturated substrates and that with CO_2 will be drawn where appropriate. Part of this work has recently been communicated.[1]

4.2 INTRODUCTION

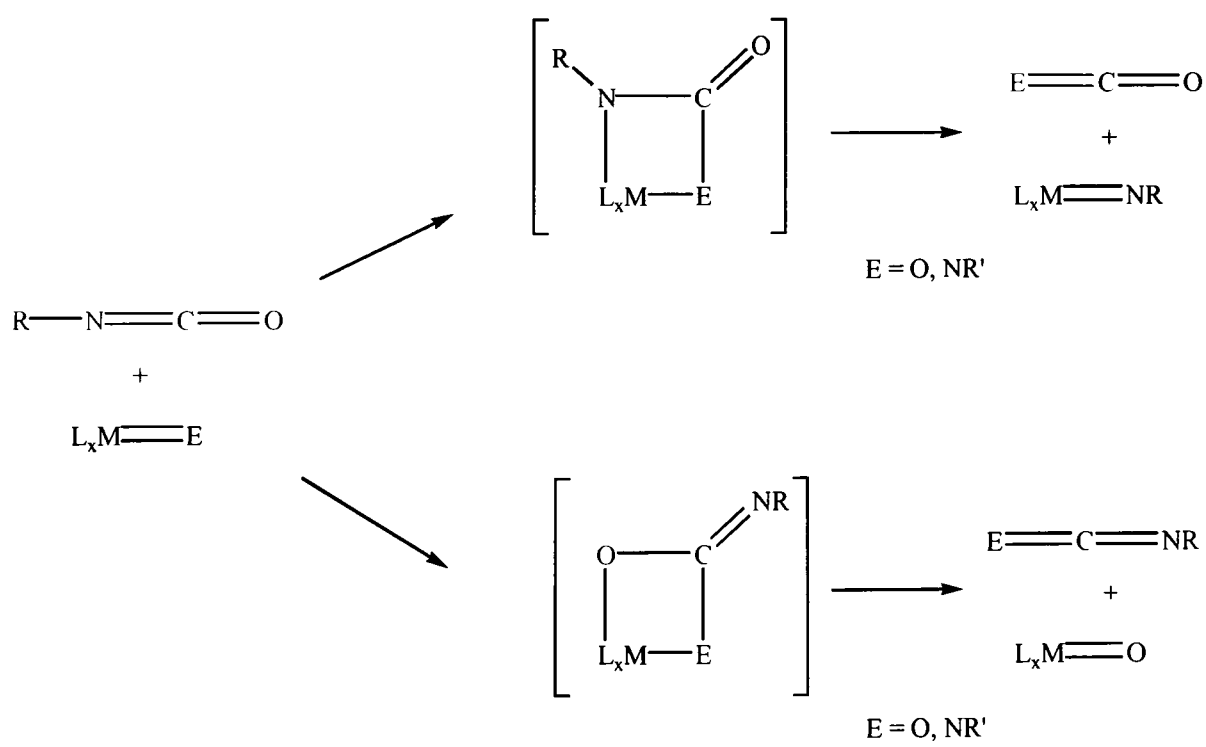
The background discussion will be divided into two sections. The reactivity with isocyanates (RNCO) will be dealt with in the first, while the second section will focus on the reactivity with carbodiimides (RNCNR). Naturally, the discussion will tend to focus on work directly relevant to the chemistry of the titanium imido bond. For a more comprehensive overview, the reader is directed towards more extensive discussions in the literature.[2,3]

4.2.1 ISOCYANATE CHEMISTRY

The use of isocyanates in the synthesis of metal imido complexes is now very well established. Typically, a metal complex bearing a terminal oxo linkage

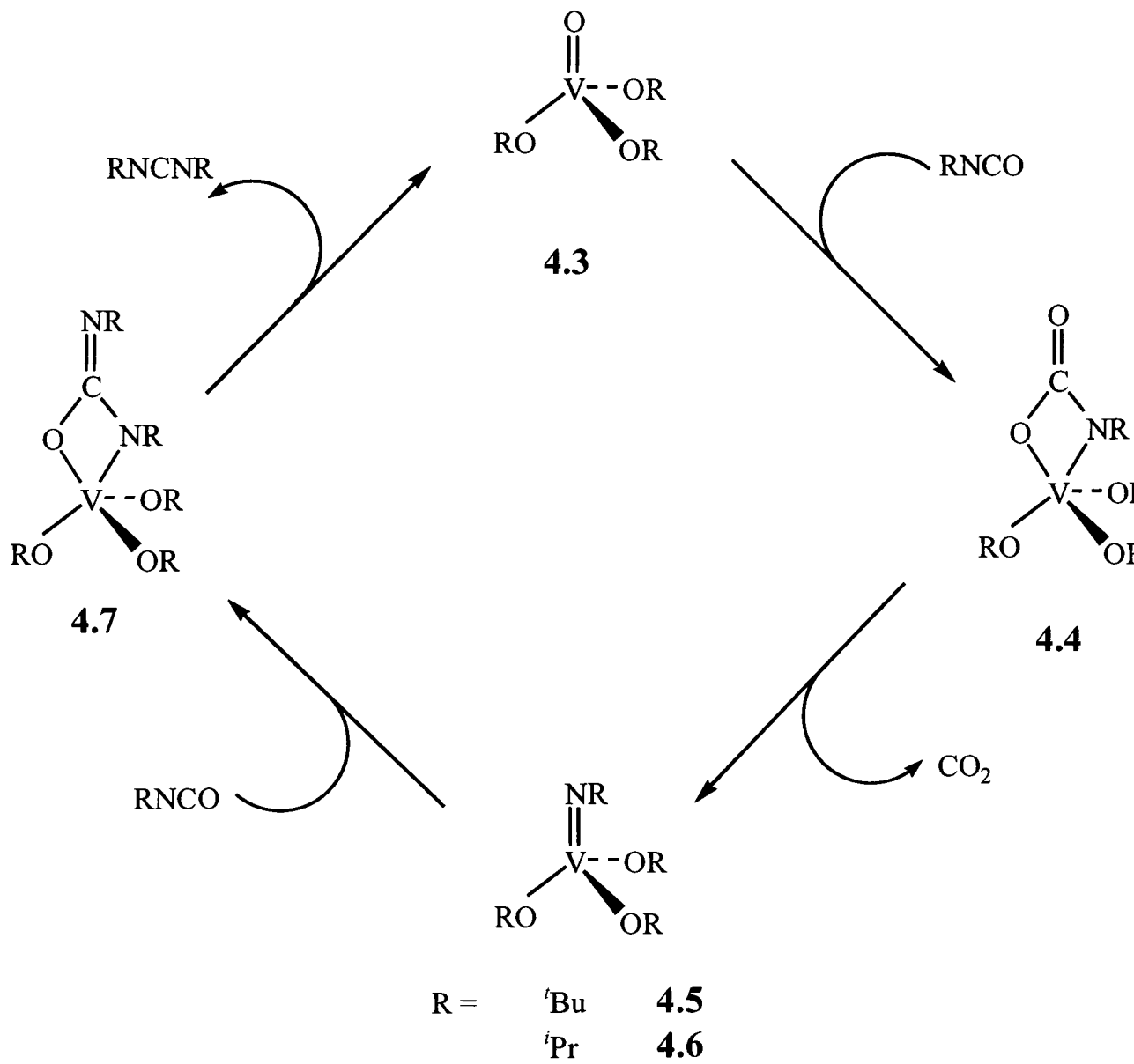
undergoes metathesis with an isocyanate to generate a metal imido species and CO_2. This type of reactivity has been reported for many different metal systems, including those of titanium,[4] zirconium,[5] vanadium,[6,7] molybdenum,[8,9] tungsten,[10,11] technetium,[12] and osmium.[13] In addition, metathesis of imido bonds with isocyanates to effect imido exchange has been found to occur in some cases, for instance in the case of *p*-tolyl isocyanate with $[Mo(\eta\text{-}C_5H_4Me)(NPh)(\mu\text{-}NPh)]_2$ (**4.1**).[14] Alternatively, Bergman *et al.* have shown that the reaction of the terminal imido species $Zr(\eta\text{-}C_5H_5)_2(N^tBu)(THF)$ (**4.2**) with *tert*-butyl isocyanate affords polymeric zirconium oxides and 1,3-di-*tert*-butylcarbodiimide,[5] showing that the reactive moiety of the isocyanate depends on the chemical nature of the organometallic species.

The reaction is believed to proceed *via* a formal [2 + 2] cycloaddition of the isocyanate to the metal-ligand multiple bond, giving a metallacycle which can undergo retrocyclisation to afford the products (Scheme 4.1).



Scheme 4.1 – Reaction of metal-ligand multiple bond with isocyanate

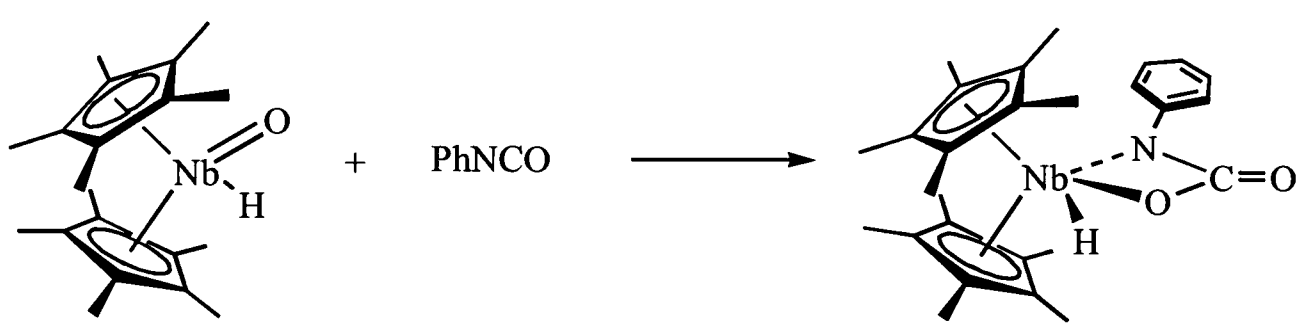
The catalytic cycle reported by Birdwhistell[15] in which phenyl isocyanate is converted to *N,N'*-diphenylcarbodiimide *via* vanadium oxo and imido species, was proposed to proceed *via* this mechanism. This system involves the cycloaddition of a vanadium oxo species with phenyl isocyanate to give a carbamate, which then extrudes CO_2 to give an imido complex. This undergoes cycloaddition with another molecule of phenyl isocyanate, followed by extrusion of *N,N'*-diphenylcarbodiimide to give the initial vanadium oxo species. This cycle is summarised in Scheme 4.2.



Scheme 4.2 – Vanadium catalysed condensation of phenylisocyanate to *N,N'*-diphenylcarbodiimide

More recent reactivity studies have provided further evidence by isolating and characterising various carbamate and ureate complexes corresponding to intermediates in this scheme.

Wachter *et al.*[16] reported the reaction of the monomeric oxoniobocene complex $Nb(\eta\text{-}C_5Me_5)_2(O)H$ (**4.8**) with phenyl isocyanate to give an isolable carbamate complex which was structurally characterised. The reaction is summarised in Equation 4.1.



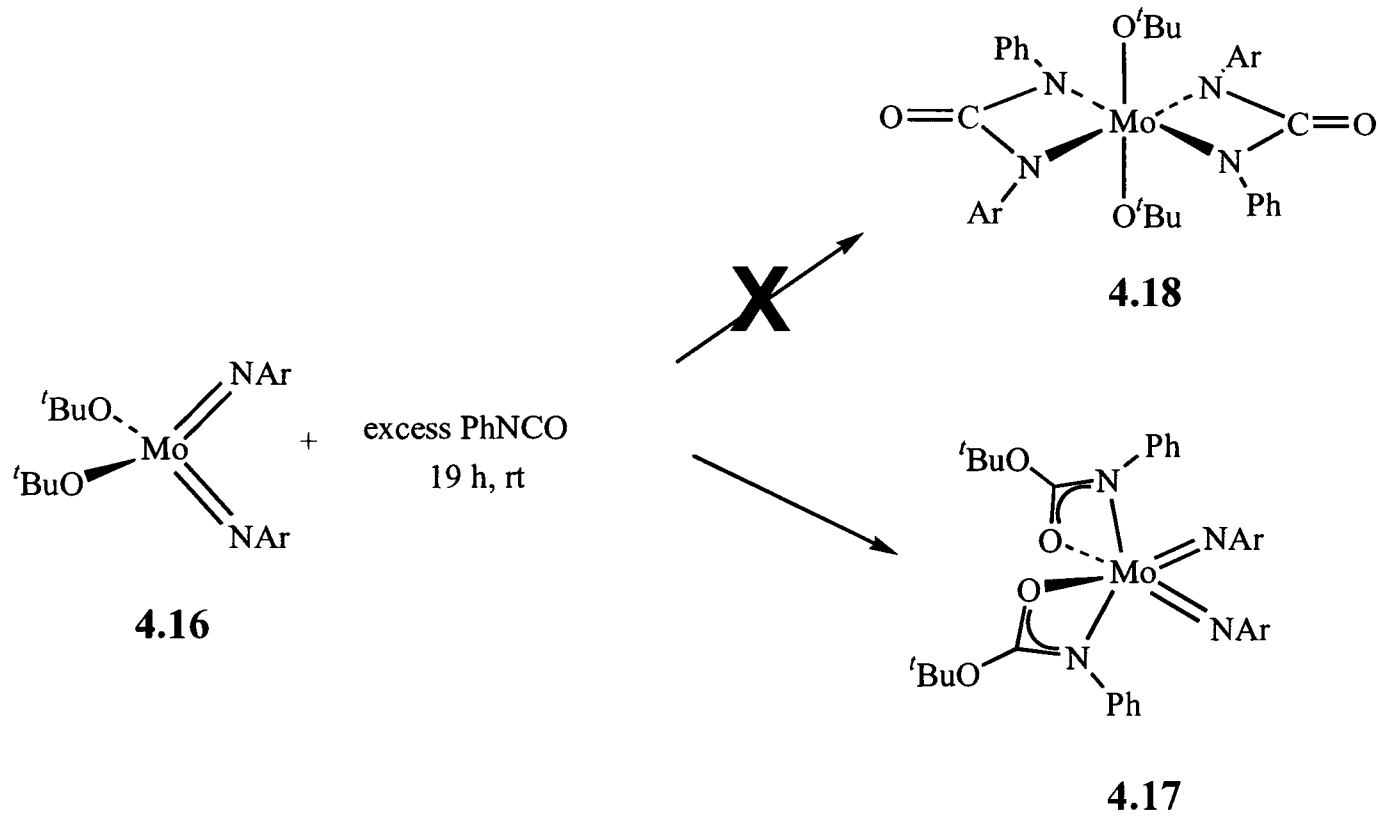
4.8 **4.9**

Equation 4.1

Although formally a [2 + 2] cycloaddition, the group suggested that the process is not concerted; reaction most likely taking place *via* nucleophilic attack of the oxo ligand on the electrophilic carbon atom of the isocyanate to give a zwitterionic intermediate. This intermediate would then undergo ring closure to form the metallacycle, with the relative strength of the C=O bond compared to the C=N determining the nature of the final product. However, the dearth of information available precludes the unambiguous assignment of the mechanism at this time.

The molybdenum complex Mo(η-C_5H_5)$_2${N(Ph)C(O)O} (**4.11**) was obtained and structurally characterised by Jernakoff *et al.*[17] by the analogous reaction of the oxo species Mo(η-C_5H_5)$_2$(O) (**4.10**) with phenyl isocyanate. The structurally characterised complex Ir(η-C_5Me_5){N(^{t}Bu)C(O)O} (**4.13**) was similarly prepared by addition of *tert*-butyl isocyanate to the dimeric species [Ir(η-C_5Me_5)(O)]$_2$ (**4.12**),[18] as was Re(η-C_5Me_5)(O){N(Ph)C(O)O} (**4.15**) by treatment of [Re(η-C_5Me_5)(O)(μ-O)]$_2$ (**4.14**) with phenyl isocyanate.[19]

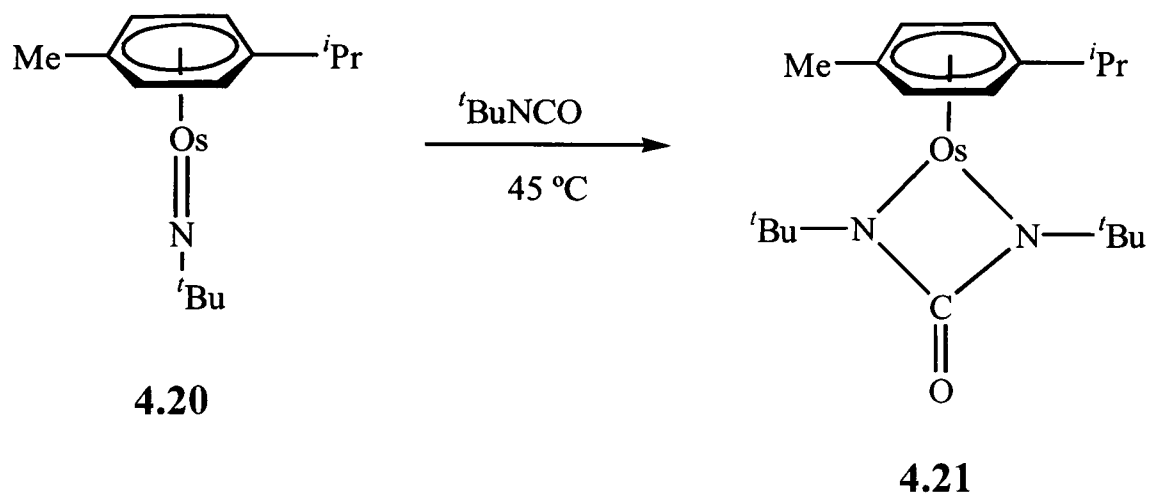
Reaction of the bis(imido) complex Mo(N-2,6-$C_6H_3{}^i$Pr$_2$)$_2$(O^{t}Bu)$_2$ (**4.16**) with phenyl isocyanate was found to afford a bis(carbamate) complex Mo(N-2,6-$C_6H_3{}^i$Pr$_2$)$_2${N(Ph)C(O)O(^{t}Bu)}$_2$ (**4.17**),[20] and not the diureate complex originally reported (**4.18**)[21] as shown in Scheme 4.3.



Scheme 4.3 – Reaction of Mo(N-2,6-$C_6H_3{}^i$Pr$_2$)$_2$(O^{t}Bu)$_2$ (**4.16**) with phenyl isocyanate

The dimeric species $[Mo(\eta\text{-}C_5H_4Me)(\mu\text{-}NPh)_2]_2$ **(4.19)** undergoes imido ligand exchange on reaction with isocyanates.[22-24] Thus, the reactivity expressed by seemingly similar complexes is seen to be less predictable than expected.

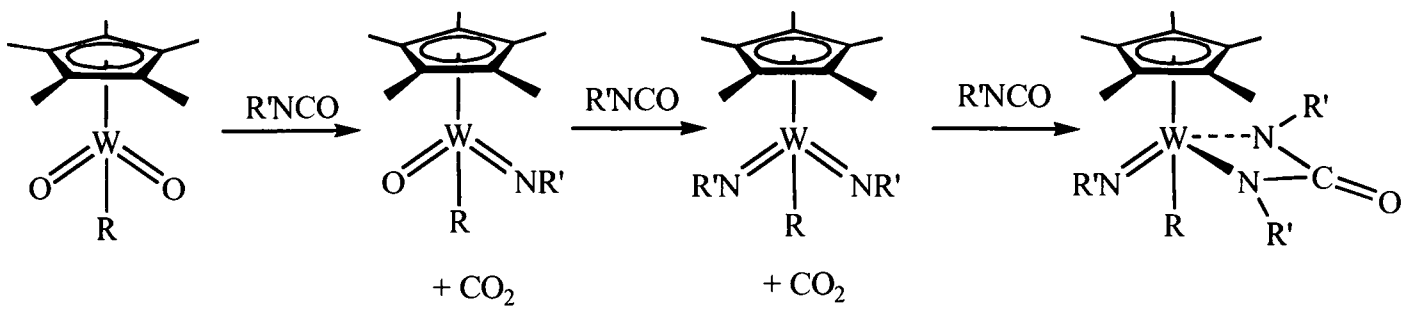
Bergman reported the osmium species $Os(\eta\text{-}Cym)(N^tBu)$ (Cym = *p*-cymene) **(4.20)** reacts with *tert*-butyl isocyanate to afford the ureate complex $(Cym)Os\{(N^tBu)_2CO\}$ **(4.21)**[25] as shown in Equation 4.2 below.



4.20 **4.21**

Equation 4.2

Combining the metathesis and cycloaddition reactions of isocyanates, Legzdins and Trotter[26] reported the reaction of $W(\eta\text{-}C_5Me_5)(O)_2(CH_2SiMe_3)$ **(4.22)** with *p*-tolyl isocyanate, firstly to sequentially replace the oxo ligands with imido groups, before forming an N, N'- bound ureate (see Equation 4.3).



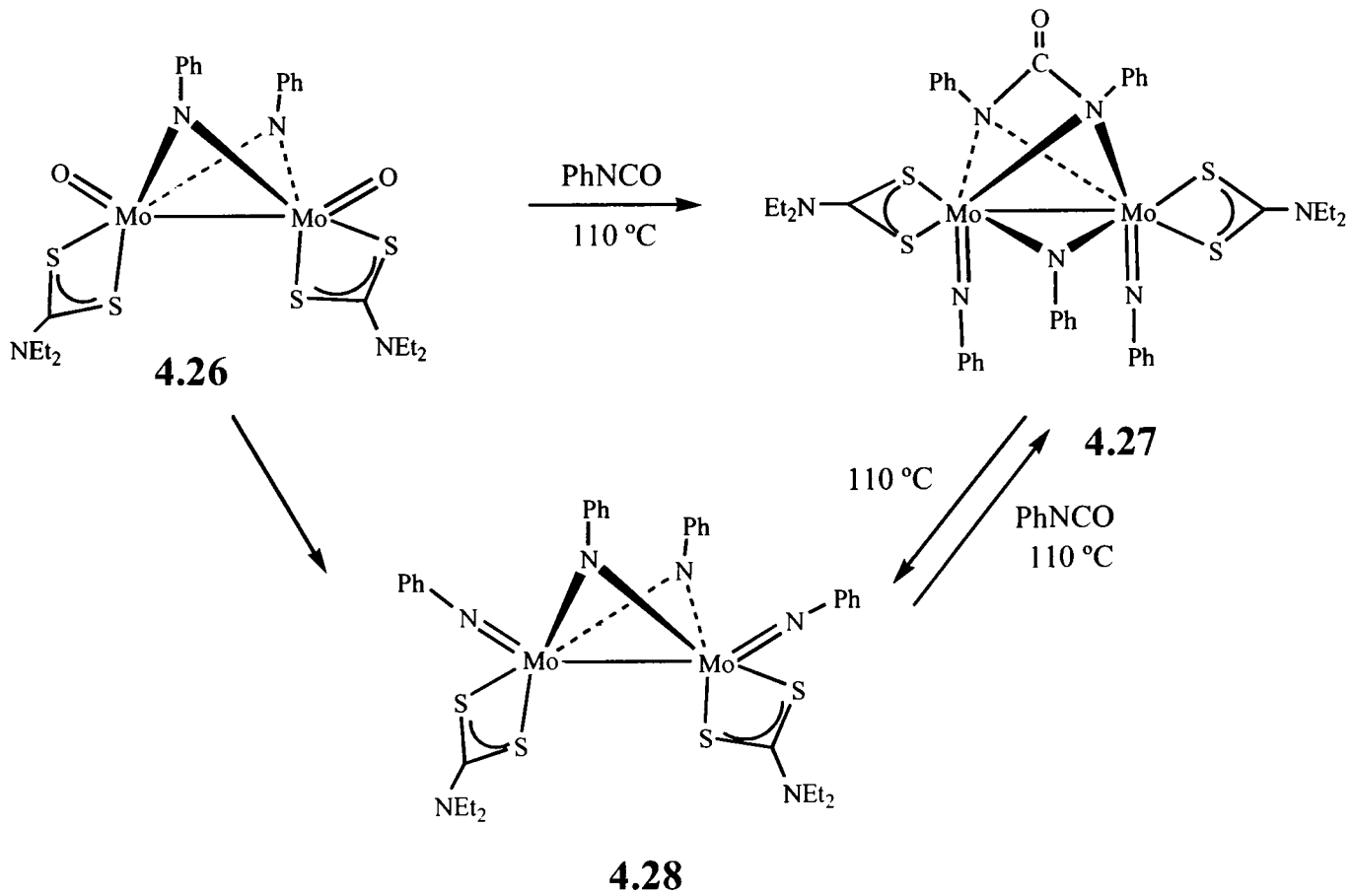
4.22 **4.23** **4.24** **4.25**

R = CH_2SiMe_3

R' = 4-C_6H_4Me

Equation 4.3

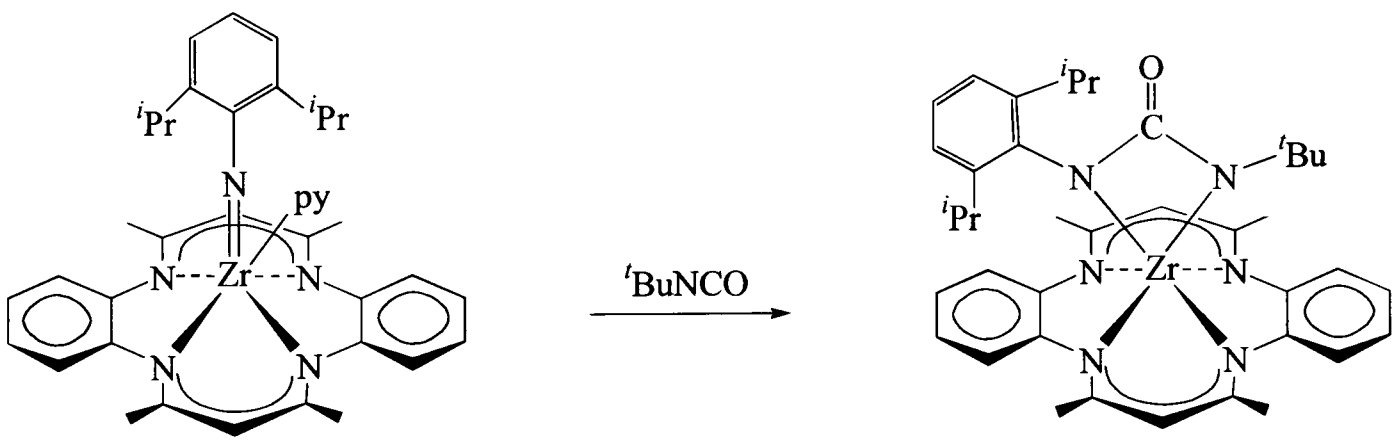
Similarly, Hogarth showed metathesis and reversible insertion of phenyl isocyanate into the species $[Mo(O)(S_2CNEt_2)(\mu\text{-NPh})]_2$ (**4.26**) to give the complex $Mo_2(NPh)_2(S_2CNEt_2)_2(\mu\text{-NPh})\{\mu\text{-PhNC(O)NPh}\}$ (**4.27**), as shown in Scheme 4.4.[27]



Scheme 4.4 – Reaction of $[Mo(O)(S_2CNEt_2)(\mu\text{-NPh})]_2$ (**4.26**) with phenyl isocyanate

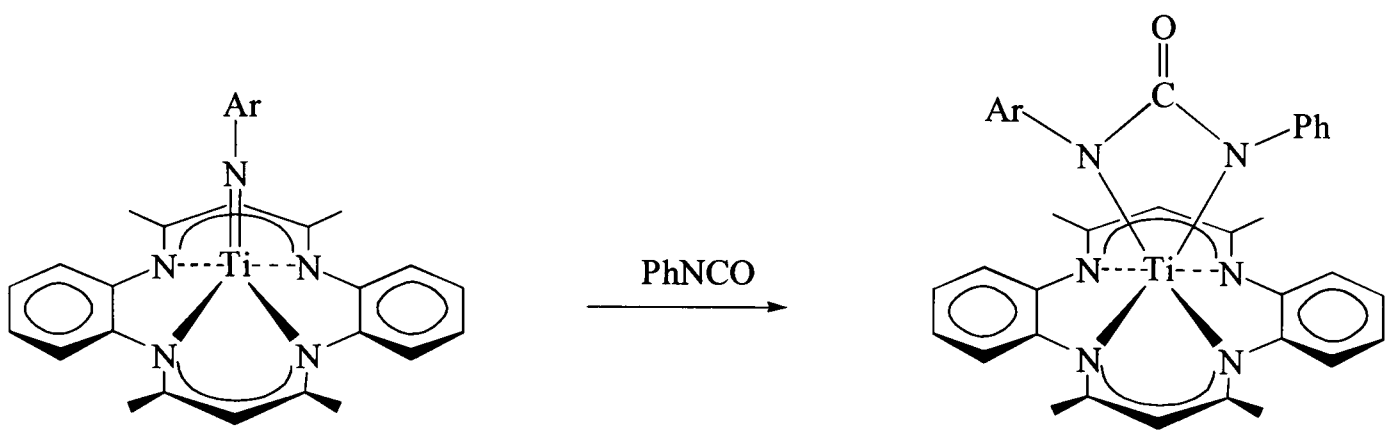
A number of studies have been carried out on Group 4 terminal imido species. In particular, complexes possessing tetraaza macrocyclic ligands have been proven to form a number of stable cycloaddition products which have been fully characterised.[28]

Treatment of the zirconium imido complex Zr(Me$_4$taa)(N-2,6-C$_6$H$_3$^{i}Pr$_2$)(py) (Me$_4$taa = tetramethyldibenzotetraaza[14]annulene) (**4.29**) with an equivalent of *tert*-butyl isocyanate gives the structurally characterised N, N'-bound ureate Zr(Me$_4$taa){N(-2,6-C$_6$H$_3$^{i}Pr$_2$)C(O)N(^{t}Bu)} (**4.30**) (Equation 4.4).[29] The analogous reactivity was found for the titanium species Ti(Me$_4$taa)(NAr) (Ar = Ph (**4.31**), 4-C$_6$H$_4$Me (**4.33**) (Equation 4.5).[29]



4.29 **4.30**

Equation 4.4



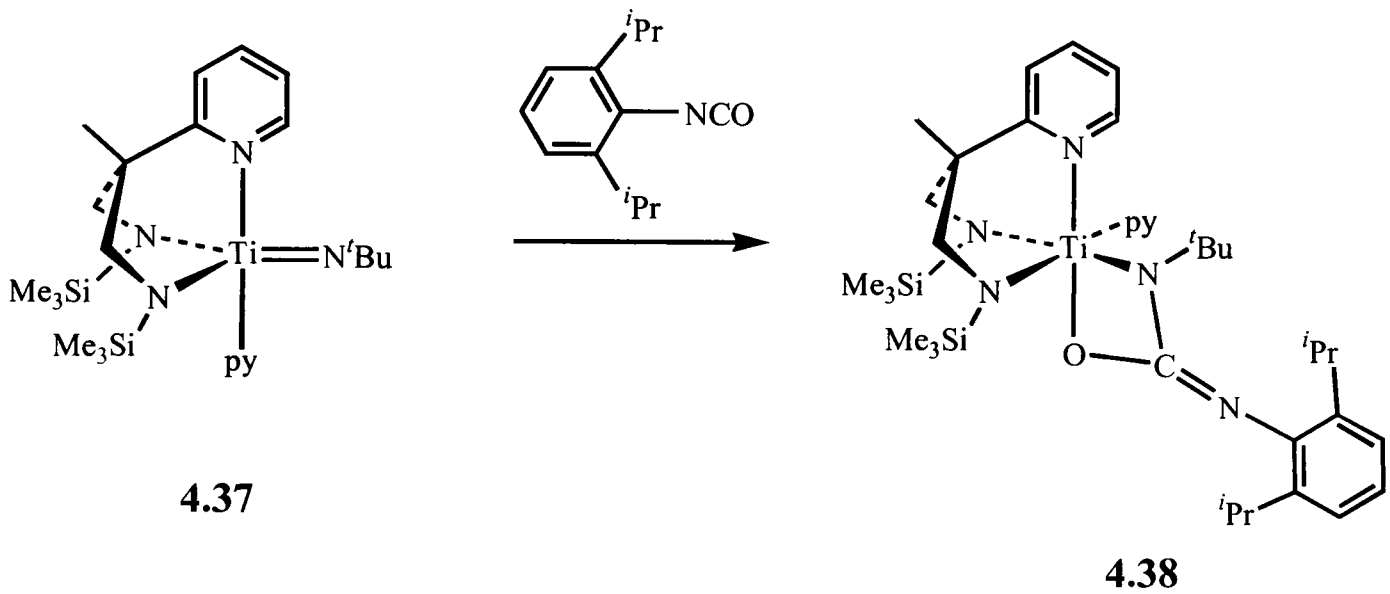
	Ar	
4.31	Ph	**4.32**
4.33	4-C_6H_4Me	**4.34**

Equation 4.5

In addition, it was found that in the presence of excess phenyl isocyanate, the unsymmetrical ureate complex Ti(Me_4taa){N(Ph)C(O)N(-4-C_6H_4Me)} (**4.34**) is converted into the symmetrical Ti(Me_4taa){N(Ph)C(O)N(Ph)} (**4.32**) species, with the loss of *p*-tolyl isocyanate.[29,30] This reactivity of the ureate will be addressed later in this Chapter.

In addition, the reaction of the oxo species Ti(Me_4taa)(O) (**4.35**) with *p*-tolyl isocyanate was found to yield the N, O- bound carbamate complex Ti(Me_4taa){N(-4-C_6H_4Me)C(O)O} (**4.36**) in a manner analogous to the reaction of CO_2 with the *p*-tolylimido species Ti(Me_4taa)(N-4-C_6H_4Me).[30] In contrast, the analogous reaction with *tert*-butyl isocyanate was found to be much slower, demonstrating the considerably different reactivity of the N-aryl- and N-*tert*-butyl- substituted heterocumulenes.

Studies were also carried out on the less sterically crowded titanium imido system bearing the diamido pyridine ligand (N_2N_{py}) (N_2N_{py} = $Me(C)(2\text{-}C_5H_4N)(CH_2NSiMe_3)_2$).[31-33] In this work, reaction with 2,6-di-*iso*-propyl isocyanate was found to occur readily, to give an isolable cycloaddition product (Equation 4.6). The resulting ureate was found to bind to the metal in an N, O- chelating mode, in contrast to that of the macrocycle-based imides.[31,33]

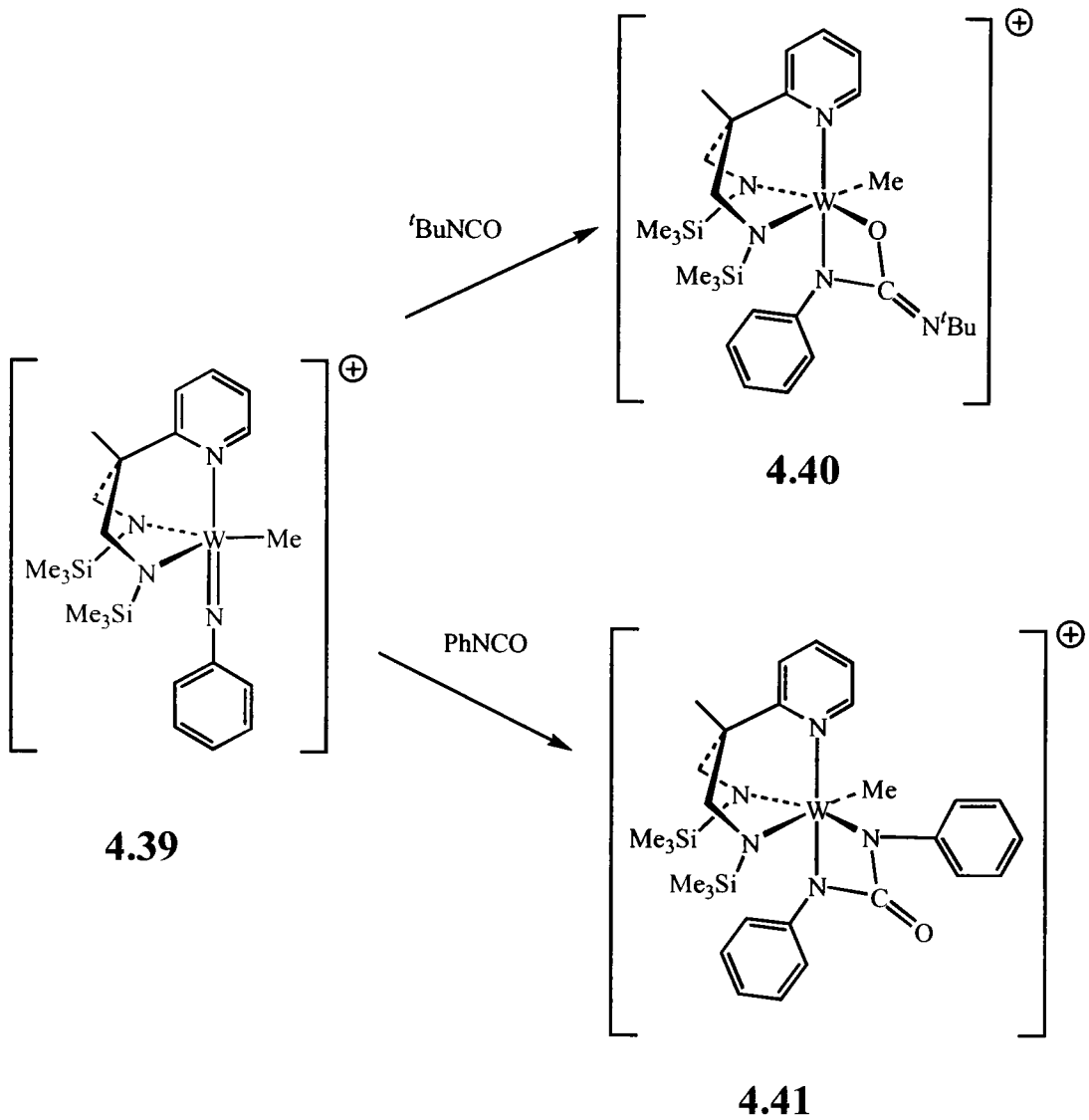


Equation 4.6

Reactions with less bulky heterocumulenes such as CO_2, *tert*-butyl- and phenyl- isocyanates gave only intractable mixtures.[33] This result, the only reported example of a titanium imide yielding an N, O- bound ureate on reaction with an isocyanate, again shows that the ligand environment surrounding the metal centre can radically affect the chemistry of the imide.

Recent work has been carried out using the (N_2N_{py}) ligand to support a cationic tungsten imido complex, $[W(N_2N_{py})(NPh)Me]^+$ (**4.39**).[34] Reactions of this species with *tert*-butyl- and phenyl- isocyanates were found to afford

stable cycloaddition products, in which the binding mode is dependent on the isocyanate used (Scheme 4.5).



4.40

4.39

4.41

Scheme 4.5 – Reactions of $[W(N_2N_{py})(NPh)Me]^+$ (**4.39**) with isocyanates

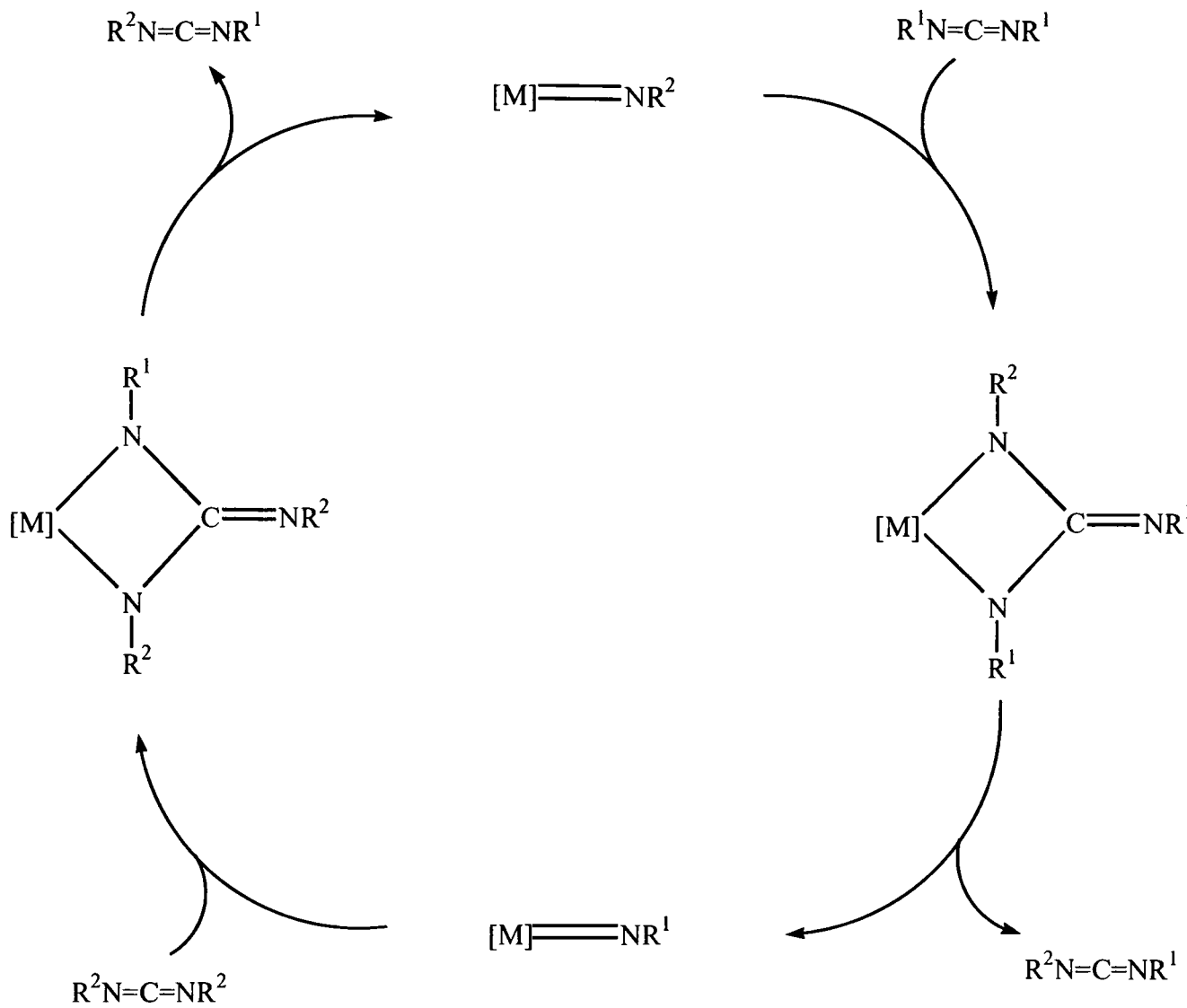
The reactivity of titianium imido complexes supported by cyclopentadienyl-amidinate ligands were shown in Chapter 3 to be intermediate between the macrocycle- and the (N_2N_{py})- supported imido systems in their reactivity towards CO_2. The reactions with isocyanates were therefore of considerable interest.

4.2.2 CARBODIIMIDE CHEMISTRY

One of the major uses of carbodiimides developed earlier in this Thesis is their use in the synthesis of the amidinate ligand by insertion into metal-alkyl bonds.[35,36] In this Section, attention will be focussed on the reactivity of carbodiimides towards the imido ligand.

The reactions of metal complexes with carbodiimides have not been explored as extensively as those of the isocyanates. However, a few examples serve to illustrate that their mode of activity lies along similar lines.

Weiss *et al.*[37] reported the catalytic use of tungsten(VI) complexes in the metathesis of carbodiimides. Following on from his report of vanadium oxo and imido species catalysing the condensation of phenyl isocyanate to give *N,N'*-diphenylcarbodiimide,[15] Birdwhistell later reported that the same systems act as catalysts for the metathesis of symmetrical into unsymmetrical carbodiimides.[38] He concluded that the oxo species are precatalysts, and that they undergo reaction with the carbodiimides to give the active vanadium imido species and isocyanate. Thus, the predicted mechanism in both the tungsten and vanadium systems involves the formal [2 + 2] cycloaddition of the carbodiimide to the imido bond, followed by a retrocyclisation to give an imido complex and an unsymmetrical carbodiimide (Scheme 4.6).



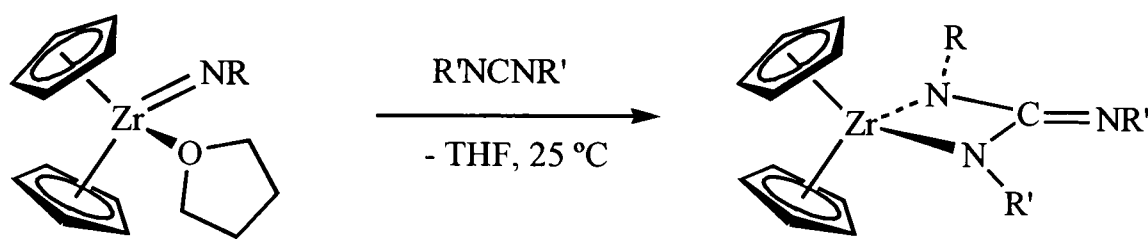
(M = V, W)

Scheme 4.6 – Transition metal-imido catalysed metathesis of carbodiimides

The first example of a stable monomeric triazatrimethylene methane transition metal complex was reported by Henderson in 1996.[39] Treatment of $PtCl_2$(cod) (cod = cycloocta-1,5-diene) (**4.42**) with one equivalent of *N,N',N''*-triphenylguanidine, PhNHC(NPh)NHPh was found to give the complex Pt(cod){N(Ph)C(NPh)N(Ph)} (**4.43**) in excellent yield, which was structurally characterised.

The imidozirconocene complexes $Zr(\eta\text{-}C_5H_5)_2$(NR)(THF) (R = ^{t}Bu (**4.44**), 2,6-$C_6H_3Me_2$ (**4.45**), 2,6-$C_6H_3{}^iPr_2$ (**4.46**)) have been studied in great detail by Bergman.[40,41] It was found that they reacted with a number of symmetrical

carbodiimides to afford stable metallacyclic products which could be isolated and characterised, as shown in Equation 4.7:



R = ^{t}Bu **4.44**

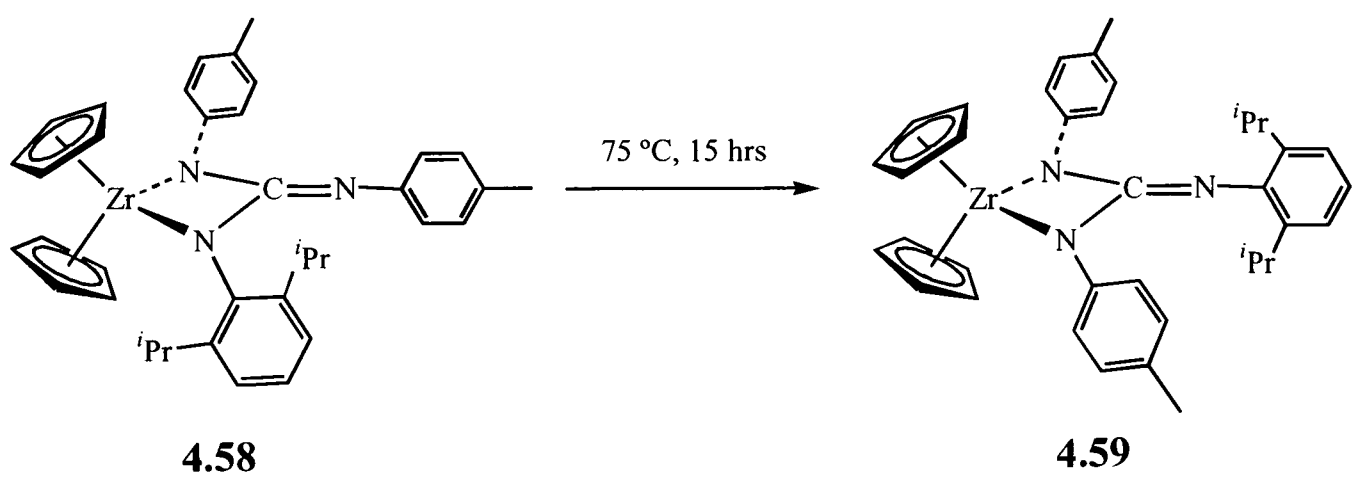
2,6-$C_6H_3Me_2$ **4.45**

2,6-$C_6H_3{}^{i}Pr_2$ **4.46**

R	R'
^{t}Bu	^{i}Pr **(4.47)**, Cy **(4.48)**, 4-C_6H_4Me **(4.49)**, $SiMe_3$ **(4.50)**
2,6-$C_6H_3Me_2$	^{i}Pr **(4.51)**, Cy **(4.52)**, 4-C_6H_4Me **(4.53)**, $SiMe_3$ **(4.54)**, ^{t}Bu **(4.55)**
2,6-$C_6H_3{}^{i}Pr_2$	^{i}Pr **(4.56)**, Cy **(4.57)**, 4-C_6H_4Me **(4.58)**

Equation 4.7

Rearrangement to a less sterically crowded product was observed upon heating a solution of one of the 2,6-di-*iso*-propyl arylimido adducts, as shown in Equation 4.8.

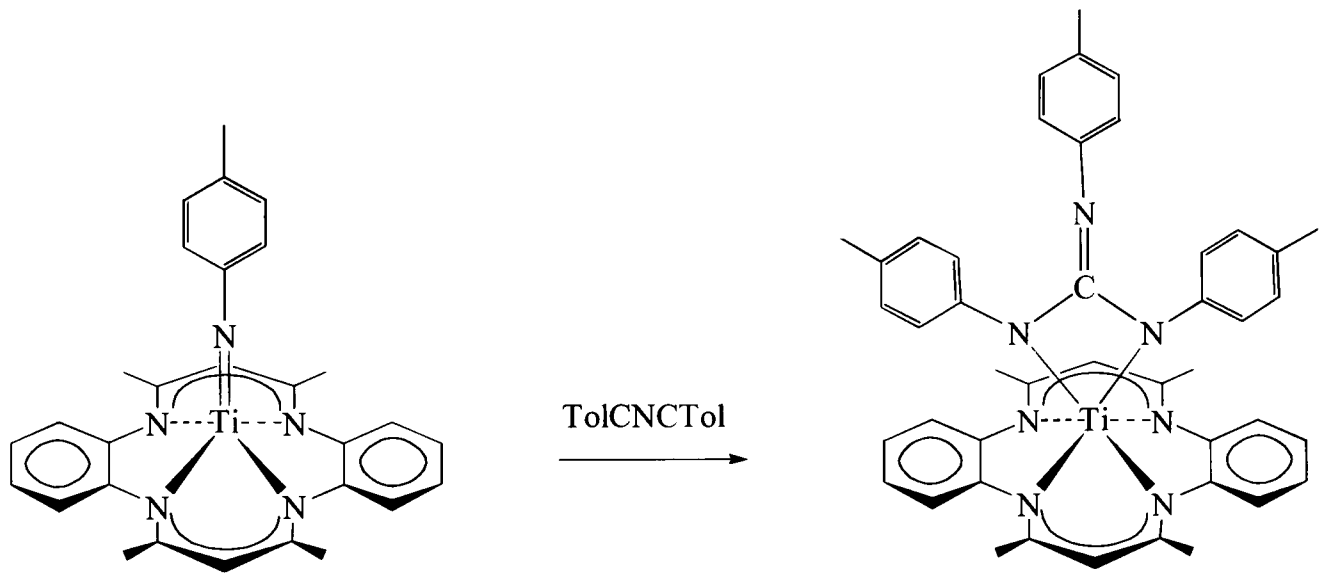


4.58 **4.59**

Equation 4.8

This group also demonstrated the preparation of unsymmetrical carbodiimides by further reaction of the metallacycle products with additional carbodiimide substrates to give metathesised products.[40] They concluded that the steric factors associated with both the imido fragment and the carbodiimide were highly significant.

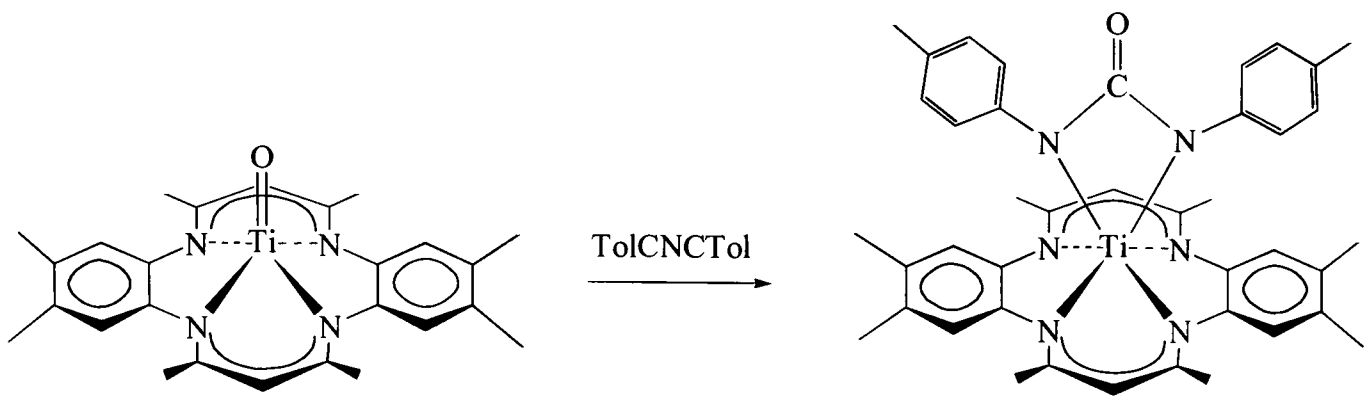
In the case of titanium imido complexes, the tetraaza[14]annulene-supported tolylimido complexes were found to form stable adducts with di-*p*-tolylcarbodiimide (Equation 4.9).[42]



4.33 **4.60**

Equation 4.9

Interestingly, reaction with the terminal oxo species Ti(Me_4taa)(O) (**4.35**) afforded the N, N'- bound ureate isomer, rather than the N, O- bound form as might have been predicted (Equation 4.10).[30]



4.35 **4.32**

Equation 4.10

The product was independently synthesised by reaction of $Ti(Me_4taa)(N\text{-}4\text{-}C_6H_4Me)$ with *p*-tolyl isocyanate (Section 4.2.1). Rearrangement of the N, O- bound isomer to the N, N'- bound form could either occur *via* a two step process (extrusion of *p*-tolyl isocyanate followed by cycloaddition of *p*-tolyl isocyanate to the resulting tolylimido complex) or by rupture of the Ti–O bond followed by rotation about the C–N bond in the ligand. The overall reaction amounts to the insertion of carbodiimide into the Ti=O multiple bond.

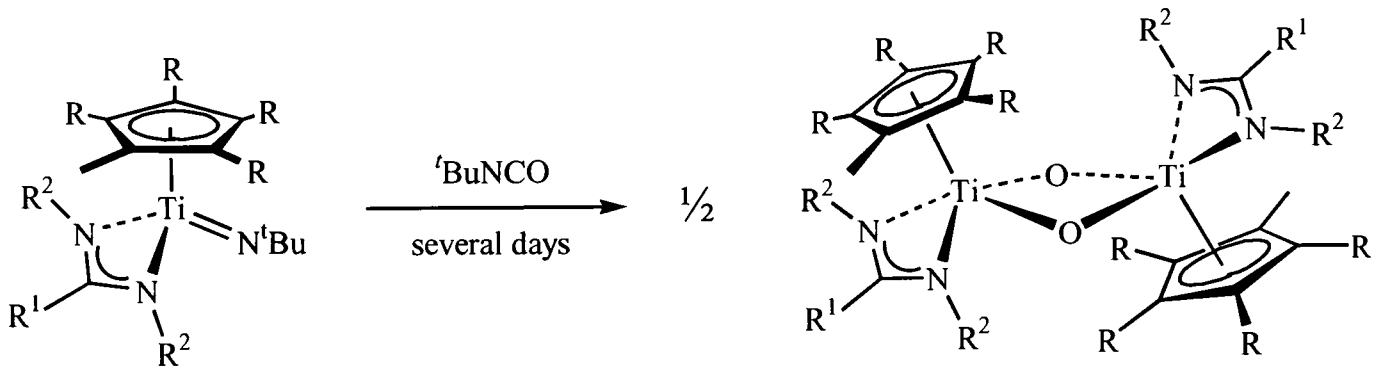
Reactions with the more sterically open $Ti(N_2N_{py})(NR)$ systems were not found to afford any tractable products; the enhanced reactivity of these systems compared to the macrocyclic imido complexes is presumed to result in further reaction to give decomposition products. As with isocyanate reactions therefore, the reactivity of the cyclopentadienyl-amidinate supported imidotitanium complexes was of considerable interest.

4.3 REACTIONS OF TITANIUM CYCLOPENTADIENYL *TERT*-BUTYLIMIDO AMIDINATE COMPLEXES WITH ISOCYANATES

This Section describes the reactivity of titanium cyclopentadienyl *tert*-butylimido amidinate compounds with both *tert*-butyl- and aryl- isocyanates. Of particular interest was the comparison between this reactivity and that exhibited towards CO_2 discussed in the preceding Chapter.

4.3.1 REACTIONS WITH *TERT*-BUTYL ISOCYANATE

Samples of Ti(η-C_5Me_5)(N^{t}Bu){PhC(NSiMe$_3$)$_2$} (**1**), Ti(η-C_5Me_5)(N^{t}Bu){MeC(N^{i}Pr)$_2$} (**2**), Ti(η-C_5H_4Me)(N^{t}Bu){PhC(NSiMe$_3$)$_2$} (**3**) and Ti(η-C_5H_4Me)(N^{t}Bu){MeC(N^{i}Pr)$_2$} (**4**) were dissolved in benzene-d_6 and treated with one equivalent of *tert*-butyl isocyanate, and the reaction monitored by ^{1}H NMR spectroscopy. The reaction proceeded as shown in Equation 4.11:



	R	R^1	R^2	
1	Me	Ph	SiMe$_3$	**21**
2	Me	Me	^{i}Pr	**22**
3	H	Ph	SiMe$_3$	**24 / 24a**
4	H	Me	^{i}Pr	**25 / 25a**

Equation 4.11

4.3.1.1 DISCUSSION OF REACTIVITY WITH *TERT*-BUTYL ISOCYANATE

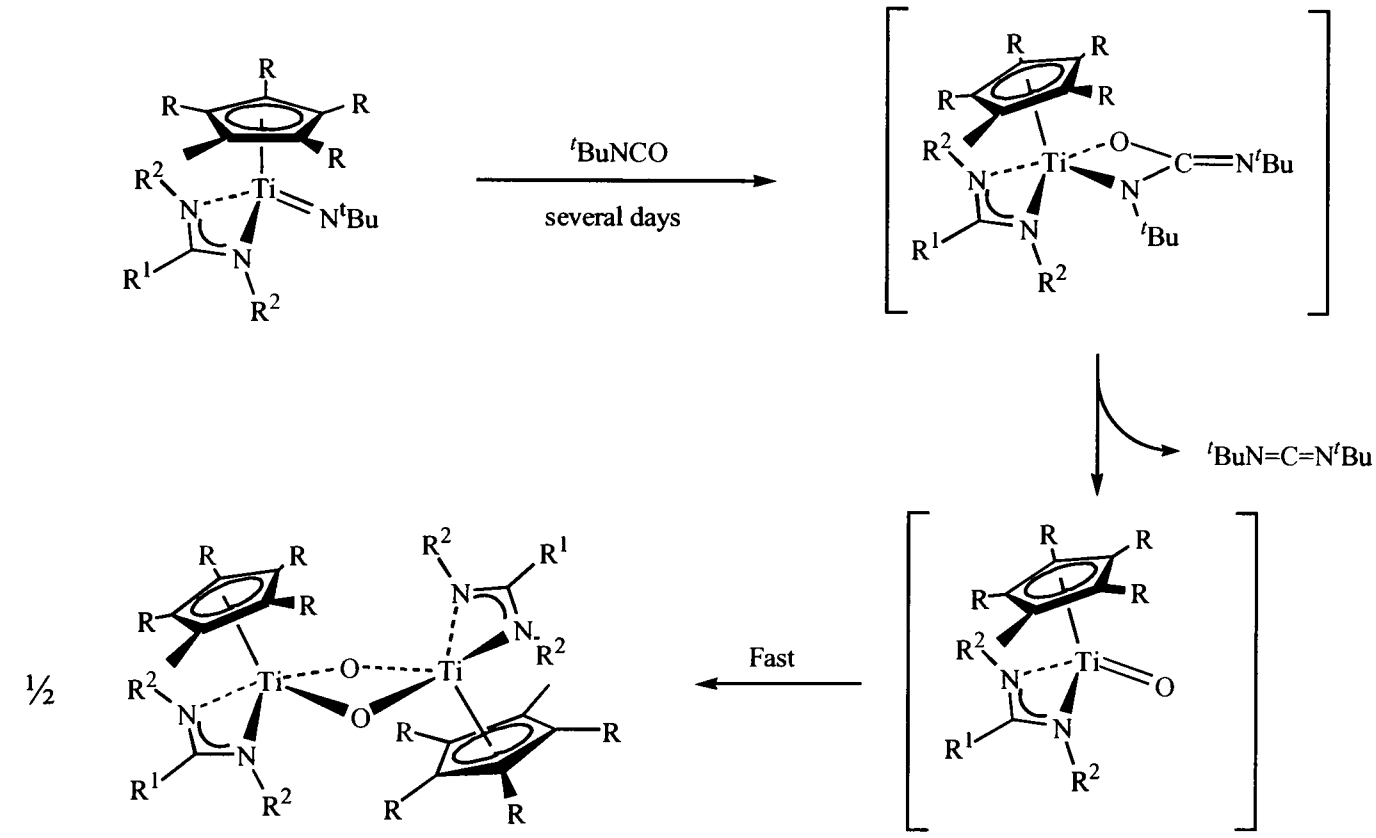
The products of the reaction were characterised by ^{1}H NMR spectroscopy and APCI mass spectrometry. Comparison with ^{1}H NMR spectra of the previously prepared oxo species **21** – **22**, **24** – **25** confirmed the identity of the titanium-containing products; the isomers **24** / **24a** and **25** / **25a** were formed in the same ratios as with the reactions of the imido complexes with CO_2. The organic by-product, 1,3-di-*tert*-butylcarbodiimide, was identified by comparison with the ^{1}H NMR spectrum of pure 1,3-di-*tert*-butylcarbodiimide obtained from commercial sources, and from the observation of a parent ion peak (m/z = 177, $[M+Na]^+$) in the APCI mass spectrum.

An attempt was made to synthesise **24** / **24a** on a preparative scale using this method. However, although purity of the final organometallic product was found to be good by ^{1}H NMR, separation from the organic by-product was found to be very difficult, owing to the solubility of the oxo species in pentane (isolated yield: 33 %).

The rate at which the reaction proceeded was found to vary considerably. Ti(η-C_5Me_5)(N^{t}Bu){PhC(NSiMe$_3$)$_2$} (**1**) reacted very slowly, with a half-life of more than 18 days at room temperature. The other complexes reacted more quickly, with Ti(η-C_5H_4Me)(N^{t}Bu){PhC(NSiMe$_3$)$_2$} (**3**) taking *ca.* 4 days, and Ti(η-C_5Me_5)(N^{t}Bu){MeC(N^{i}Pr)$_2$} (**2**) taking *ca.* 2 days for half the parent imido complex to be consumed. Complete consumption of Ti(η-C_5H_4Me)(N^{t}Bu){MeC(N^{i}Pr)$_2$} (**4**) was observed after 8 days. It was noted that the reactions with *tert*-butyl isocyanate were considerably slower

than those with CO_2, in which the parent imide reacted immediately to form a carbamate intermediate, which then decomposed to give the oxo species and isocyanate by-product.

By analogy with the reaction with CO_2, the reaction is presumed to occur *via* formal [2 + 2] cycloaddition to give a metallacyclic intermediate, which then undergoes a retrocyclisation, to extrude the organic product and form a transient monomeric oxo complex (see Scheme 4.7).



Scheme 4.7 – Proposed mechanism for reaction of titanium cyclopentadienyl *tert*-butylimido amidinate complexes with *tert*-butyl isocyanate

As a result of the slower rate of cycloadduct formation compared to the CO_2 cases, the only peaks visible in the ^{1}H NMR spectra of the reactions are those corresponding to the parent imide and the final products. The only exception is the reaction between Ti(η-C_5H_4Me)(N^{t}Bu){MeC(N^{i}Pr)$_2$} (**4**) and *tert*-butyl

isocyanate. In this instance, some extra peaks are visible during the reaction, which can be assigned to the N, O- bound ureate intermediate. This suggests that in this case, either i) the cycloadduct forms more quickly, or ii) it is intrinsically more stable than its more bulky ureate congeners. While the former explanation is undoubtedly true, the instability of the corresponding carbamate in the CO_2 reaction suggests that the reason is at least in part due to enhanced stability of the ureate. This may be due to the lower steric bulk of the ancillary ligands producing less strain in the metallcycle, although why the reverse appears to be true for the carbamates is not easily explained. Another possibility is that of an equilibrium existing between the parent imido complex, the 1,3-di-*tert*-butylcarbodiimide by-product, and the corresponding cycloadduct. This seems unlikely however, given the lack of reactivity of **4** towards the less bulky 1,3-di-*iso*-propylcarbodiimide (*vide infra*).

It can be seen therefore that the bridging oxo species **21** – **22**, **24** – **25** are unreactive towards both *tert*-butyl isocyanate and 1,3-di-*tert*-butylcarbodiimide, in contrast to the reactions of the terminal titanium oxo species supported by macrocyclic ligands.[29,30] It should further be noted at this point that the mode of cycloaddition of the isocyanate to form an N, O- bound ureate is in contrast to the formation of the N, N'- binding motif of the macrocycle-supported imidotitanium systems.[29,30] The cyclopentadienyl-amidinate supporting ligand set clearly favours the isomer formed by the tripodal dianionic systems discussed above.

4.3.2 REACTIONS WITH ARYL ISOCYANATES

The reactivity of aryl isocyanates with *tert*-butylimido complexes was investigated by studying the reaction between 2,6-dimethylphenyl isocyanate and two representative imido species, Ti(η-C_5Me_5)(N^{t}Bu){MeC(N^{i}Pr)$_2$} (**2**) and Ti(η-C_5H_4Me)(N^{t}Bu){PhC(NSiMe$_3$)$_2$} (**3**). Samples were dissolved in benzene-d_6, one equivalent of 2,6-dimethylphenyl isocyanate added to each, and the reactions monitored using ^{1}H NMR spectroscopy.

4.3.2.1 DISCUSSION OF REACTIVITY WITH ARYL ISOCYANATES

Reaction in both instances was notably different from the *tert*-butyl isocyanate cases. Reaction was found to occur more rapidly; with half the parent imido complex being consumed within 24 hours for Ti(η-C_5Me_5)(N^{t}Bu){MeC(N^{i}Pr)$_2$} (**2**), and within 12 hours for Ti(η-C_5H_4Me)(N^{t}Bu){MeC(N^{i}Pr)$_2$} (**3**). In addition, both systems showed evidence of the ureate cycloaddition product in the ^{1}H NMR spectrum; as a minor product in the case of **2**, but as a major consitituent of the reaction mixture after 12 hours in **3**. (Figure 4.1)

Isolating the intermediates of these reactions was not possible, as the decomposition to give the bridging oxo species and mixed carbodiimide by-product is well advanced before the imido starting material is consumed (See Figure 4.1; the identity of the mixed *N*-*tert*-butyl-*N'*-2,6-dimethyl-phenylcarbodiimide by-product was proposed by analogy with the reaction of *tert*-butyl isocyanate, and confirmed by the presence of a protonated parent

ion peak in the APCI mass spectrum (m/z = 203, $[M+H]^+$), and from GC-MS (m/z = 202, $[M]^+$)).

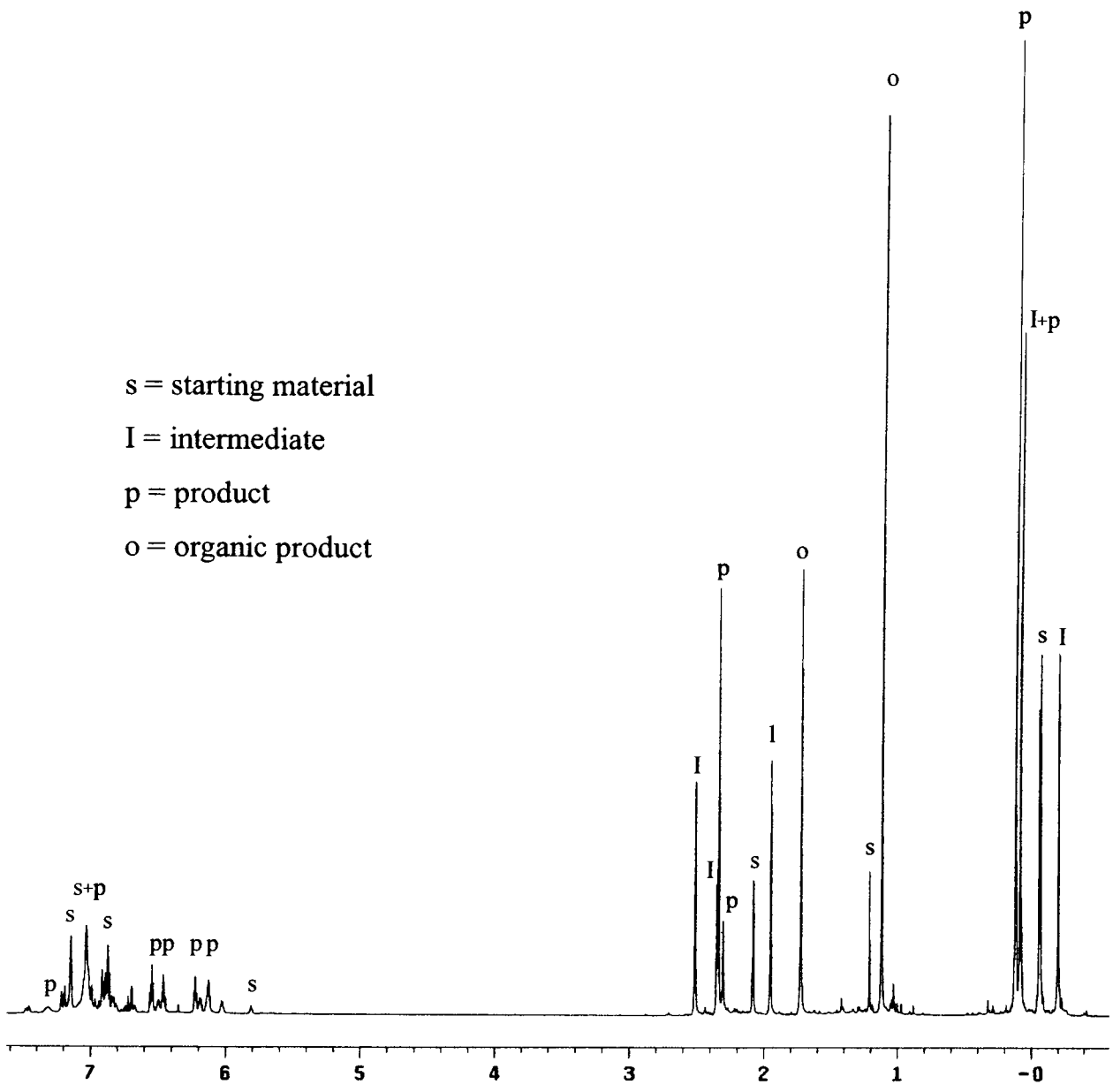


Figure 4.1 – 300.1 MHz ^{1}H NMR spectrum of the reaction of Ti(η-C_5H_4Me)(N^tBu){$PhC(NSiMe_3)_2$} (**3**) with 2,6-dimethylphenyl isocyanate in benzene-d_6 after 12 hours

An independent series of experiments was carried out, in which the oxo species [Ti(η-C_5Me_5)(μ-O){$MeC(N^iPr)_2$}]$_2$ (**22**) and [Ti(η-C_5H_4Me)(μ-O){$MeC(N^iPr)_2$}]$_2$ (**25**) were shown to be unreactive towards *p*-tolyl isocyanate, and [Ti(η-C_5H_4Me)(μ-O){$PhC(NSiMe_3)_2$}]$_2$ (**24**) was found to be unreactive towards 2,6-dimethylphenyl isocyanate. This confirms the stability of the dimeric oxo species with regard to unsaturated substrates.

The above reactions demonstrate the enhanced stability of the cycloadducts derived from aryl isocyanates. Rather than pursue more reactions with *tert*-butyl imidotitanium species, it was felt more appropriate to investigate the reactivity of arylimido systems in the hope of synthesising more stable, isolable adducts.

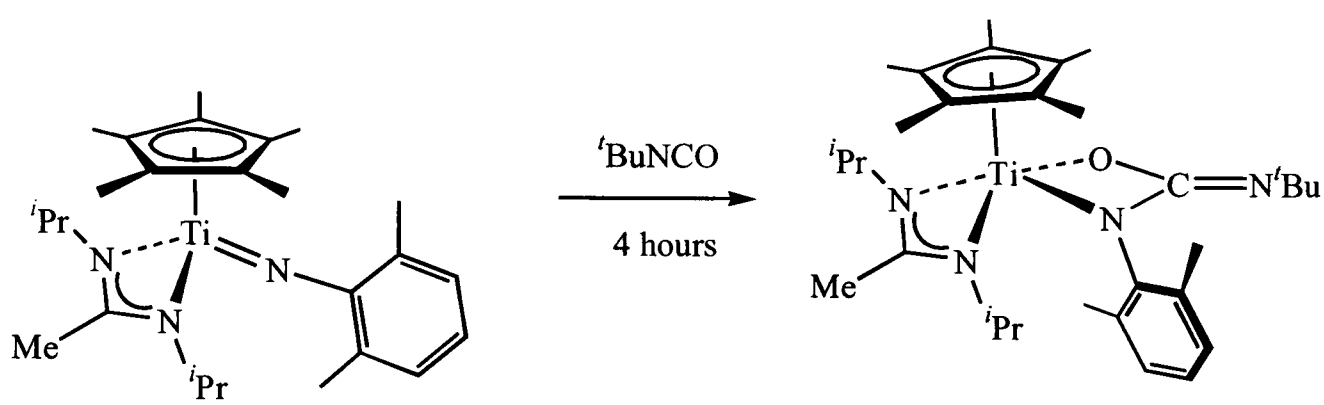
4.4 REACTIONS OF TITANIUM CYCLOPENTADIENYL ARYLIMIDO AMIDINATE COMPLEXES WITH ISOCYANATES

This Section describes the reactivity of arylimido title compounds with both *tert*-butyl- and aryl- isocyanates. It compares and contrasts this reactivity with that of the *tert*-butyl analogues, and also with the reactivity of the imido species with CO_2.

4.4.1 REACTIONS WITH *TERT*-BUTYL ISOCYANATE

Samples of the complexes Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$){MeC(N^{i}Pr)$_2$} (**7**), Ti(η-C_5Me_5)(N-4-C_6H_4Me){MeC(N^{i}Pr)$_2$} (**8**) and Ti(η-C_5H_4Me)(N-2,6-$C_6H_3Me_2$){PhC(NSiMe$_3$)$_2$} (**11**) were dissolved in benzene-d_6 and treated with one equivalent of *tert*-butyl isocyanate. The reactions were monitored by ^{1}H NMR spectroscopy. In the case of the reaction with **7**, the ureate intermediate Ti(η-C_5Me_5){N(-2,6-$C_6H_3Me_2$)C(N^{t}Bu)O}{MeC(N^{i}Pr)$_2$} (**40**) was found to be stable enough to isolate it under preparative conditions (yield 27 % due to handling problems), and it was characterised by ^{1}H and ^{13}C-{^{1}H} NMR, and IR spectroscopies. The compound did not give a parent

ion in either EI and FI mass spectrometry, and satisfactory microanalysis could not be obtained; nevertheless the structure of the complex (Equation 4.12) could be inferred from the NMR evidence, and by analogy to other ureate complexes (*vide infra*).



7 **40**

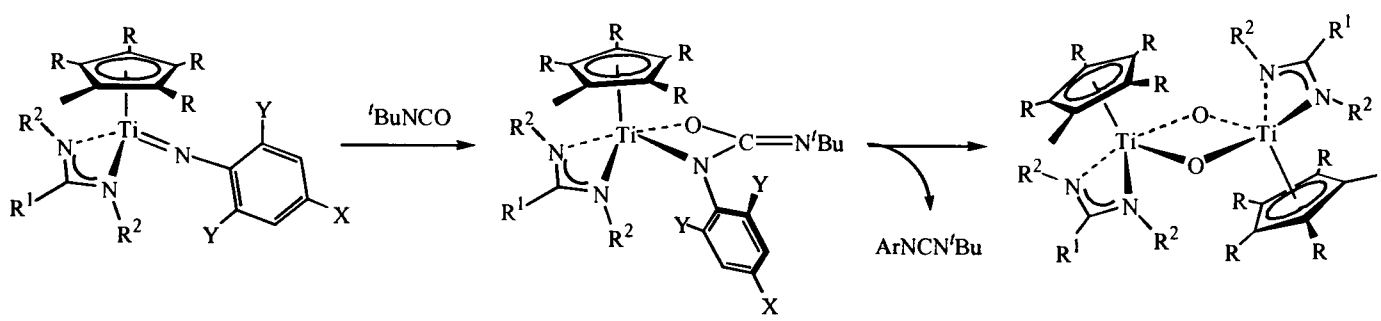
Equation 4.12

4.4.1.1 DISCUSSION OF REACTIVITY WITH *TERT*-BUTYL ISOCYANATE

The reaction of $Ti(\eta\text{-}C_5Me_5)(N\text{-}2,6\text{-}C_6H_3Me_2)\{MeC(N^iPr)_2\}$ (**7**) with *tert*-butyl isocyanate was found to be rapid compared with the previous isocyanate reactions, with a colour change from green to red occuring within 40 minutes, and peaks assignable to the ureate being detectable after 10 minutes. The half-life for the reaction was found to be *ca.* 40 minutes, and the ureate could be isolated after *ca.* 4 hours. Decomposition to the dimeric oxo species $[Ti(\eta\text{-}C_5Me_5)(\mu\text{-}O)\{MeC(N^iPr)_2\}]_2$ (**22**) and *N*-*tert*-butyl-*N'*-2,6-dimethyl-phenylcarbodiimide was observed after *ca.* 12 hours in solution.

The reaction of $Ti(\eta\text{-}C_5Me_5)(N\text{-}4\text{-}C_6H_4Me)\{MeC(N^iPr)_2\}$ (**8**) with *tert*-butyl isocyanate was found to be faster, with a colour change from green to red

occurring within 10 minutes, and peaks corresponding to the ureate appearing in the ^{1}H NMR spectrum within minutes. However, the adduct was less stable than **40**, and decomposed within 3 hours to the dimeric oxo species and *N-tert*-butyl-*N'-p*-tolylcarbodiimide, before all the imide had been consumed (Equation 4.13).



	R	R^1	R^2	X	Y	
8	Me	Me	^{i}Pr	Me	H	**22**
11	H	Ph	$SiMe_3$	H	Me	**22**

Equation 4.13

Again, the carbodiimide was identified by the presence of a parent ion peak in the APCI mass spectrum (*m/z* = 211, $[M+Na]^+$). Additionally, the peaks assigned to the adduct were not as sharp as those of **40**, suggesting some fluxionality of the molecule in solution. This prevented spectroscopic characterisation of the adduct, since it was not possible to obtain the complex as a pure compound. A similar situation was found for the product of the reaction between Ti(η-C_5H_4Me)(N-2,6-$C_6H_3Me_2$){$PhC(NSiMe_3)_2$} (**11**) and *tert*-butyl isocyanate, which also showed evidence for a ureate intermediate, but which was too unstable to isolate and characterise (Equation 4.13). The identity of the *N-tert*-butyl-*N'*-2,6-dimethylphenylcarbodiimide by-product

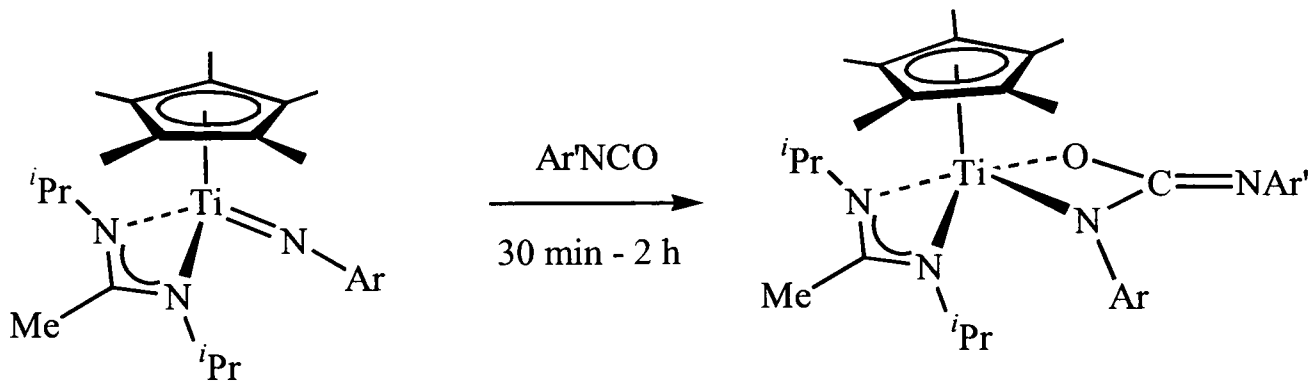
was confirmed by comparison of the ^{1}H NMR spectrum with the reaction products of Ti(η-C_5Me_5)(N^{t}Bu){MeC(N^{i}Pr)$_2$} (**2**) and Ti(η-C_5H_4Me)(N^{t}Bu){PhC(NSiMe$_3$)$_2$} (**3**) with 2,6-dimethylphenyl isocyanate, and also by detection of a protonated parent ion peak in the APCI mass spectrum (*m/z* = 203, $[M+H]^+$).

It can be seen that reaction of *tert*-butyl isocyanate with arylimido complexes is much faster than the corresponding *tert*-butylimido homologues, yielding detectable ureate intermediates. As with the case of the aryl isocyanates reacting with *tert*-butylimides, however, the ureates tend to decompose before the imido species have been consumed, preventing the isolation of the adducts. The exception to this is in the case of Ti(η-C_5Me_5){N(-2,6-$C_6H_3Me_2$)C(N^{t}Bu)O}{MeC(N^{i}Pr)$_2$} (**40**), which can be isolated. This stability may be due to the greater steric bulk around the titanium centre, which perhaps raises the energy required to bring the atoms forming the metallacycle into co-planarity to effect retrocyclisation. The crystal structures of analogous aryl isocyanate-based ureate complexes have been determined, and indicate a substantial deviation from planarity in the crystal structure of the complexes (see Section 4.4.2.3)

4.4.2 Reactions with aryl isocyanates

Two aryl isocyanates were used to investigate the reactivity of the arylimido titanium complexes: 2,6-dimethylphenylisocyanate and *p*-tolyl isocyanate.

Samples of Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$){MeC(N^{i}Pr)$_2$} (**7**) and Ti(η-C_5Me_5)(N-4-C_6H_4Me){MeC(N^{i}Pr)$_2$} (**8**) were dissolved in benzene or pentane, and treated with one equivalent of the isocyanates at room temperature to afford the stable ureate complexes Ti(η-C_5Me_5){N(-2,6-$C_6H_3Me_2$)C(N-2,6-$C_6H_3Me_2$)O}{MeC(N^{i}Pr)$_2$} (**41**) (84 % isolated yield), Ti(η-C_5Me_5){N(-2,6-$C_6H_3Me_2$)C(N-4-C_6H_4Me)O}{MeC(N^{i}Pr)$_2$} (**42**) (85 % isolated yield), Ti(η-C_5Me_5){N(-4-C_6H_4Me)C(N-2,6-$C_6H_3Me_2$)O}{MeC(N^{i}Pr)$_2$} (**43**) (67 % isolated yield), and Ti(η-C_5Me_5){N(-4-C_6H_4Me)C(N-4-C_6H_4Me)O}{MeC(N^{i}Pr)$_2$} (**44**) (41 % recrystallised yield), as shown in Equation 4.14.

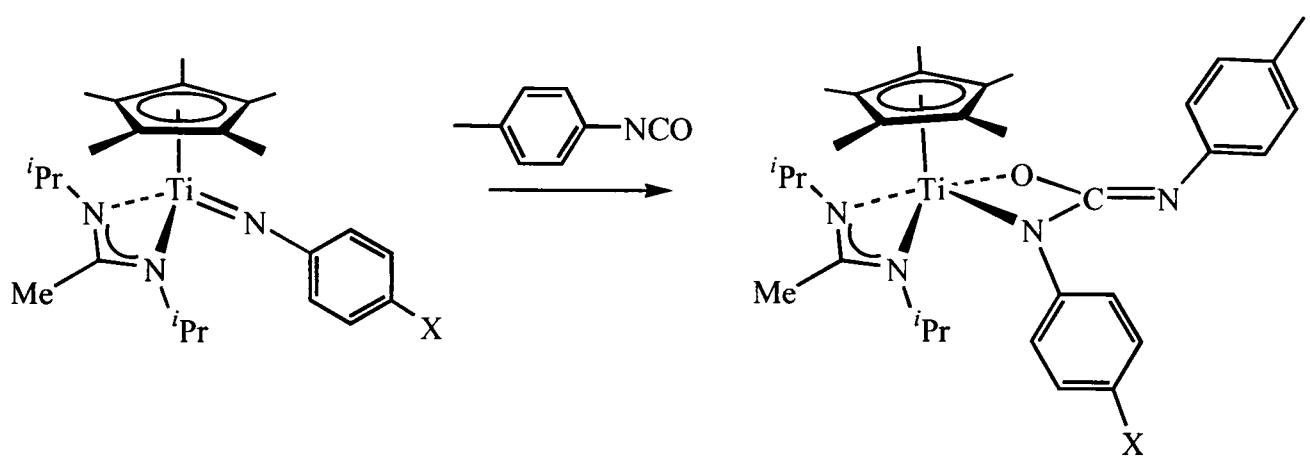


	Ar	Ar'	
7	2,6-$C_6H_3Me_2$	2,6-$C_6H_3Me_2$	**41**
	2,6-$C_6H_3Me_2$	4-C_6H_4Me	**42**
8	4-C_6H_4Me	2,6-$C_6H_3Me_2$	**43**
	4-C_6H_4Me	4-C_6H_4Me	**44**

Equation 4.14

Similar reactivity was observed for samples of Ti(η-C_5Me_5)(N-4-$C_6H_4CF_3$){MeC(N^{i}Pr)$_2$} (**9**) and Ti(η-C_5Me_5)(N-4-$C_6H_4NMe_2$){MeC(N^{i}Pr)$_2$} (**10**), which were each reacted with one equivalent of *p*-tolyl isocyanate in benzene

to afford the ureate complexes Ti(η-C_5Me_5) {N(-4-$C_6H_4CF_3$)C(N-4-C_6H_4Me)O}{MeC(N^{i}Pr)$_2$} (**45**) (57 % yield due to handling problems) and Ti(η-C_5Me_5){N(-4-$C_6H_4NMe_2$)C(N-4-C_6H_4Me)O} {MeC(N^{i}Pr)$_2$} (**46**) (71 % yield) (Equation 4.15).



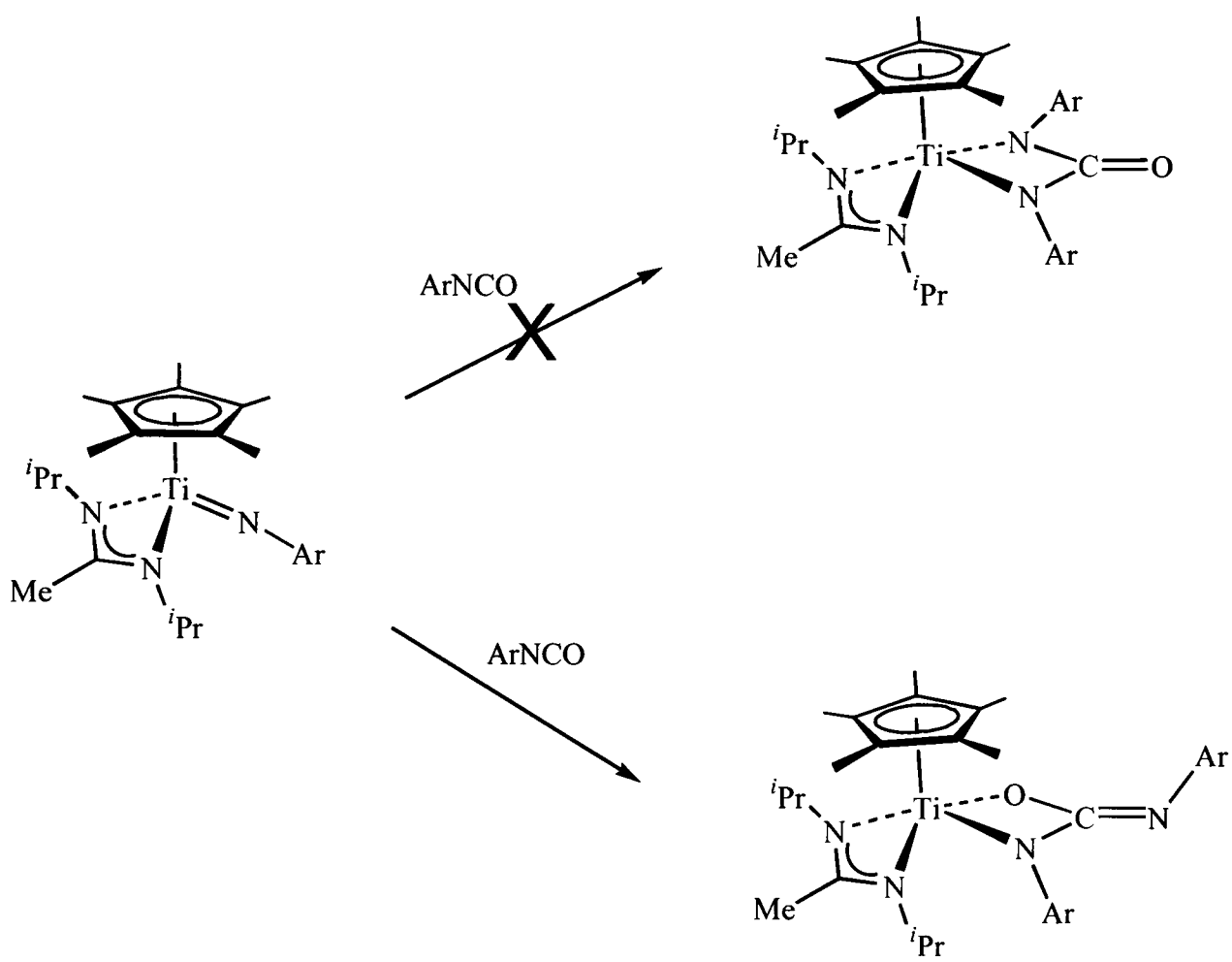
X	Compound
Me	**44**
CF_3	**45**
NMe_2	**46**

Equation 4.15

The products **41** – **46** were all characterised by ^{1}H and ^{13}C-{^{1}H} NMR and IR spectroscopies. Satisfactory elemental analysis was obtained for all compounds except **42**. Parent ion peaks were detected in the EI mass spectra of **41** (*m/z* = 591, $[M]^+$) and **44** (*m/z* = 562, $[M]^+$). Single crystals of complexes **41** and **42** suitable for X-ray diffraction studies were obtained, and the structures were determined (see Section 4.4.2.1 and 4.4.2.2).

The N, O- binding motif of complexes **41** – **46** in solution is evidenced by the lack of symmetry of the amidinate ligands in the complexes **41** and **44**, as shown by their ^{1}H and ^{13}C-{^{1}H} NMR spectra. An N, N'- bound complex

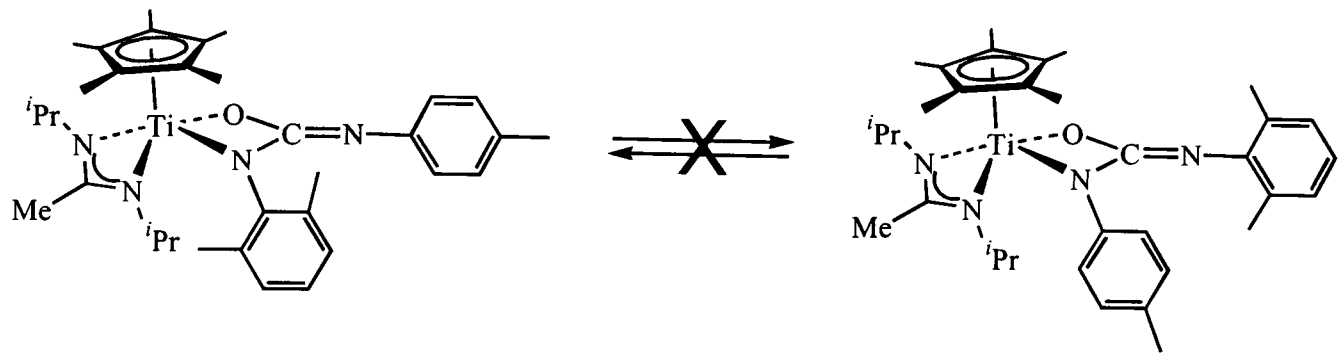
would have a mirror plane, and would result in equivalent resonances for the two *iso*-propyl groups (Scheme 4.8).



Scheme 4.8 – Possible isomers for reaction of $Ti(\eta\text{-}C_5Me_5)(NAr)\{MeC(N^iPr)_2\}$ with ArNCO (Ar = 2,6-$C_6H_3Me_2$ (**7**, **41**), 4-C_6H_4Me (**8**, **44**))

Both complexes **41** and **44** show four doublets for the methyl groups of the *iso*-propyl arms of the amidinate, and two virtual septets assigned as the methine resonances, demonstrating the N, O- binding motif.

Complexes **42** and **43** demonstrate the robust nature of the ureate ligand. If the ligand were labile, it would be possible for interconversion between the two complexes, as indicated in Equation 4.16.



42 **43**

Equation 4.16

Figure 4.2 shows the ^{1}H NMR spectra of complexes **42** and **43**. It can be seen that the two complexes display different resonances, and that neither sample contains impurities corresponding to the other.

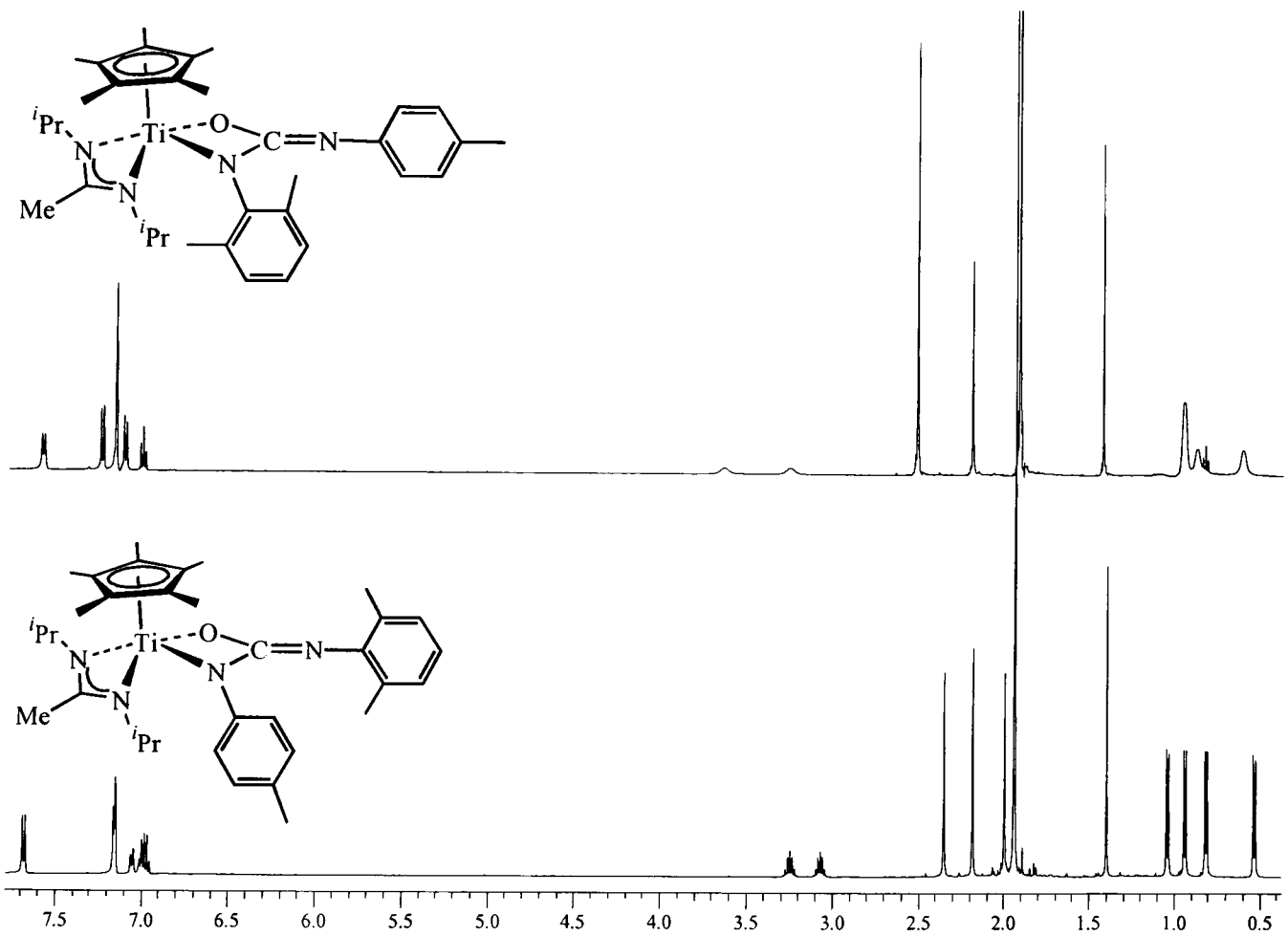


Figure 4.2 – 500.0 MHz ^{1}H NMR spectra of Ti(η-C_5Me_5) {N(-2,6-$C_6H_3Me_2$)C(N-4-C_6H_4Me)O} {MeC(N^{i}Pr)$_2$} (**42**) and Ti(η-C_5Me_5) {N(-4-C_6H_4Me)C(N-2,6-$C_6H_3Me_2$)O} {MeC(N^{i}Pr)$_2$} (**43**) in benzene-d_6

The IR spectra of the ureate complexes possess strong absorptions at 1610 cm^{-1} ($Ti(\eta\text{-}C_5Me_5)\{N(\text{-}2,6\text{-}C_6H_3Me_2)C(N\text{-}2,6\text{-}C_6H_3Me_2)O\}\{MeC(N^iPr)_2\}$ (**41**)), 1655 cm^{-1} ($Ti(\eta\text{-}C_5Me_5)\{N(\text{-}2,6\text{-}C_6H_3Me_2)C(N\text{-}4\text{-}C_6H_4Me)O\}\{MeC(N^iPr)_2\}$ (**42**)), 1616 cm^{-1} ($Ti(\eta\text{-}C_5Me_5)\{N(\text{-}4\text{-}C_6H_4Me)C(N\text{-}2,6\text{-}C_6H_3Me_2)O\}\{MeC(N^iPr)_2\}$ (**43**)), and 1609 cm^{-1} ($Ti(\eta\text{-}C_5Me_5)\{N(\text{-}4\text{-}C_6H_4Me)C(N\text{-}4\text{-}C_6H_4Me)O\}\{MeC(N^iPr)_2\}$ (**44**)), which correspond to the ν(C=N) stretch. These are lower than the ν(C=O) absorptions of $Ti(\eta\text{-}C_5Me_5)\{N(\text{-}2,6\text{-}C_6H_3Me_2)C(O)O\}\{MeC(N^iPr)_2\}$ (**27**) (1669 cm^{-1}) and $Ti(\eta\text{-}C_5Me_5)\{N(\text{-}4\text{-}C_6H_4Me)C(O)O\}\{MeC(N^iPr)_2\}$ (**34**) (1672 cm^{-1}). Unambiguous assignment of the N, O-binding of the ureate from the IR data was not possible, however, as the range of these values overlaps with that of the ν(C=O) stretch determined for the N, N'-bound complexes $Ti(Me_4taa)\{N(Ph)C(O)N(Ph)\}$ (**4.32**), $Ti(Me_4taa)\{N(Ph)C(O)N(\text{-}4\text{-}C_6H_4Me)\}$ (**4.34**) and $Ti(Me_4taa)\{N(\text{-}4\text{-}C_6H_4Me)C(O)N(\text{-}4\text{-}C_6H_4Me)\}$ (**4.63**) (1626 – 1630 cm^{-1}).[30]

A sample of $Ti(\eta\text{-}C_5Me_5)(N\text{-}2,6\text{-}C_6H_3Me_2)\{PhC(NSiMe_3)_2\}$ (**14**) was treated with one equivalent of 2,6-dimethylphenyl isocyanate to form the ureate complex $Ti(\eta\text{-}C_5Me_5)\{(N\text{-}2,6\text{-}C_6H_3Me_2)C(N\text{-}2,6\text{-}C_6H_3Me_2)O\}\{PhC(NSiMe_3)_2\}$ (**47**) in > 95 % yield. Complex **47** was characterised by ^1H, $^{13}C\text{-}\{^1H\}$ NMR and IR spectroscopies. The ^1H NMR spectrum is shown in Figure 4.3.

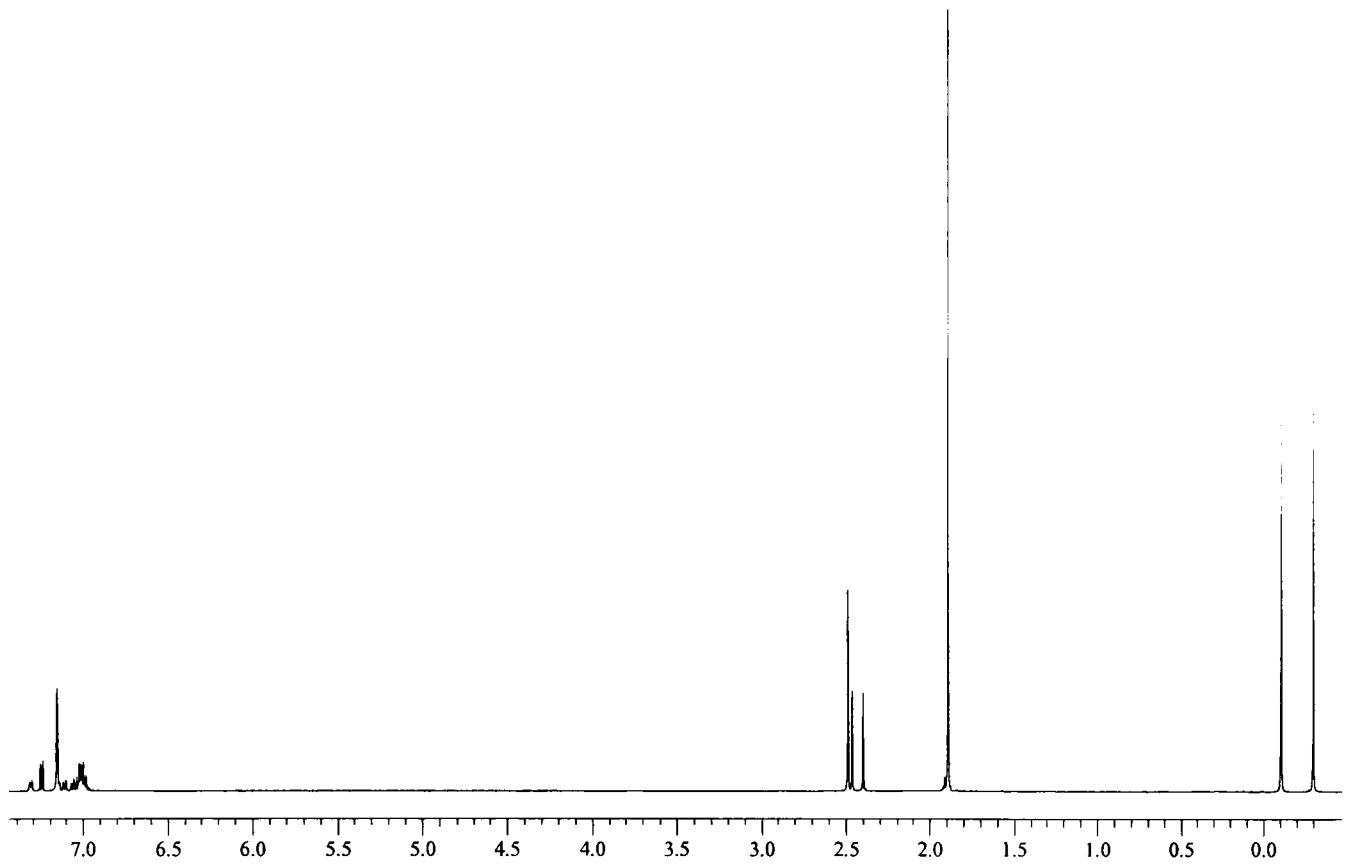


Figure 4.3 – 500.0 MHz ^{1}H NMR spectrum of Ti(η-C_5Me_5) {N(-2,6-$C_6H_3Me_2$)C(N-2,6-$C_6H_3Me_2$)O} {PhC($NSiMe_3$)$_2$} (**47**) in benzene-d_6

The reaction is slower than for Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$){MeC(N^{i}Pr)$_2$} (**7**), as expected on steric grounds. It does indicate, however, the high reactivity of the Ti–N_{imido} bond towards aryl isocyanates, as **14** is the most crowded cyclopentadienyl imido amidinate complex of titanium investigated.

4.4.2.1 X-RAY CRYSTAL STRUCTURE OF Ti(η-C_5Me_5) {N(-2,6-$C_6H_3Me_2$)C(N-2,6-$C_6H_3Me_2$)O}{MeC(N^{i}Pr)$_2$} (41)

A brown needle crystal of **41** suitable for analysis by single crystal X-ray diffraction was grown from a slowly cooled solution in benzene. The data were collected by the author, and the structure solved by Dr. P. Mountford.

Figure 4.4 shows the molecular structure, and Table 4.1 summarises some important bond lengths and angles, and shows the bisecting angles calculated for different least-squares planes described by atoms in the molecule. Full details are provided in Appendix J.

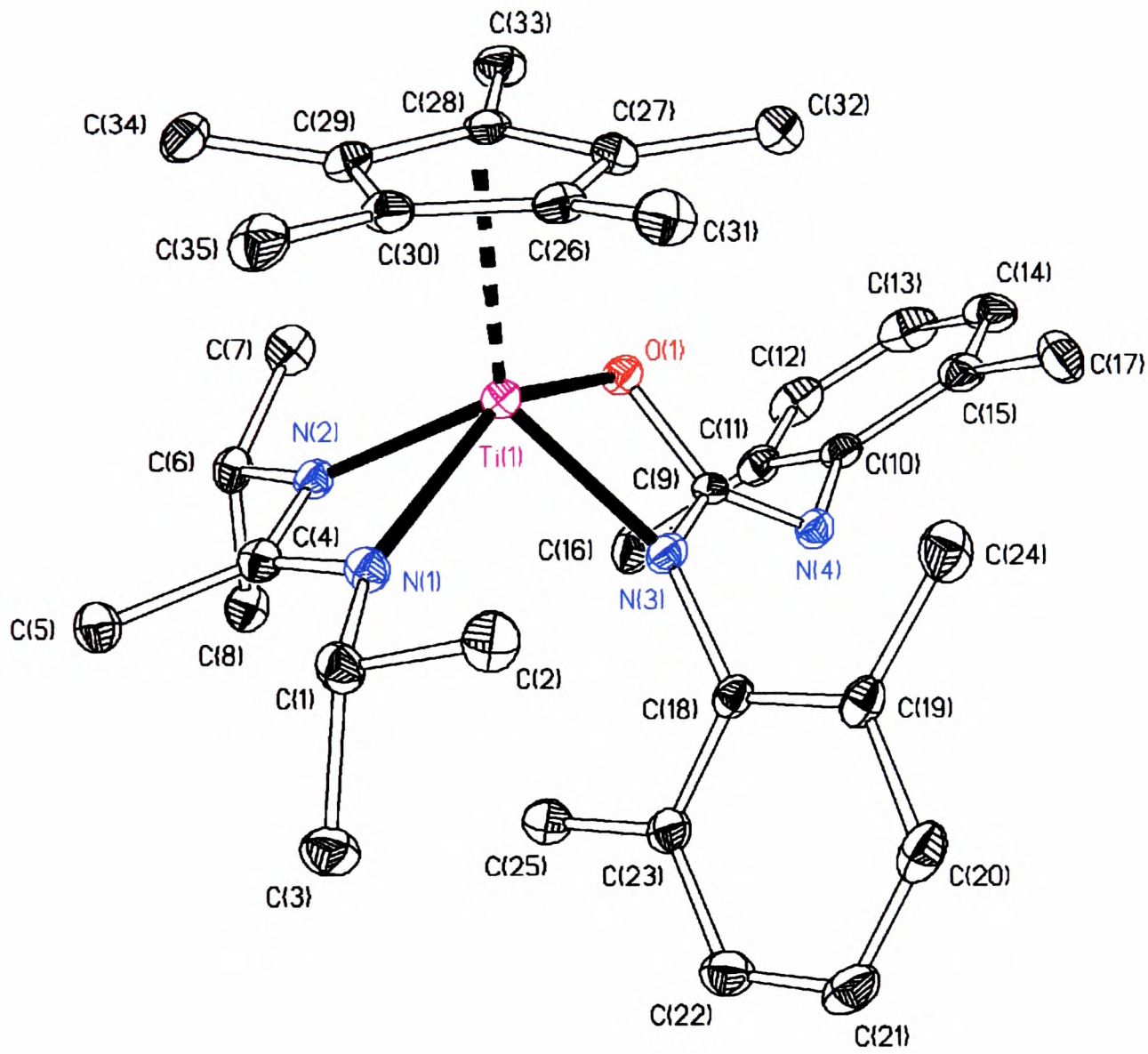


Figure 4.4 – Thermal ellipsoid plot (30 % probability) of Ti(η-C_5Me_5) {N(-2,6-$C_6H_3Me_2$)C(N-2,6-$C_6H_3Me_2$)O}{$MeC(N^iPr)_2$} (**41**). H atoms omitted for clarity

Table 4.1 – Selected bond lengths (Å) and angles (°) for Ti(η-C_5Me_5) {N(-2,6-$C_6H_3Me_2$)C(N-2,6-$C_6H_3Me_2$)O}{MeC(N^{i}Pr)$_2$} (**41**)

Ti(1) – $Cp_{(cent)}$	2.094	$Cp_{(cent)}$ – Ti(1) – N(1)	112.2
Ti(1) – N(1)	2.149(3)	$Cp_{(cent)}$ – Ti(1) – N(2)	114.7
Ti(1) – N(2)	2.027(3)	$Cp_{(cent)}$ – Ti(1) – N(3)	136.1
Ti(1) – N(3)	1.995(3)	$Cp_{(cent)}$ – Ti(1) – O(1)	104.1
Ti(1) – O(1)	1.981(3)		
N(3) – C(9)	1.383(5)		
O(1) – C(9)	1.343(4)		
N(4) – C(9)	1.283(5)		
N(4) – C(10)	1.431(5)		

Plane 1	Plane 2	Angle subtended
$Cp_{(cent)}$ – Ti(1) – C(4)	N(1) – Ti(1) – N(2)	87.6
$Cp_{(cent)}$ – Ti(1) – C(4)	N(3) – Ti(1) – O(1)	63.5

4.4.2.2 X-RAY CRYSTAL STRUCTURE OF Ti(η-C_5Me_5) {N(-2,6-$C_6H_3Me_2$)C(N-4-C_6H_4Me)O}{MeC(N^{i}Pr)$_2$} (42)

A red prism of **42** suitable for analysis by single crystal X-ray diffraction was grown from a saturated solution in pentane. The data were collected by the author, and the structure solved by Dr. P. Mountford. Figure 4.5 shows the molecular structure, and Table 4.2 summarises some important bond lengths and angles, and shows the bisecting angles calculated for different least-squares planes described by atoms in the molecule. Full details are provided in Appendix K.

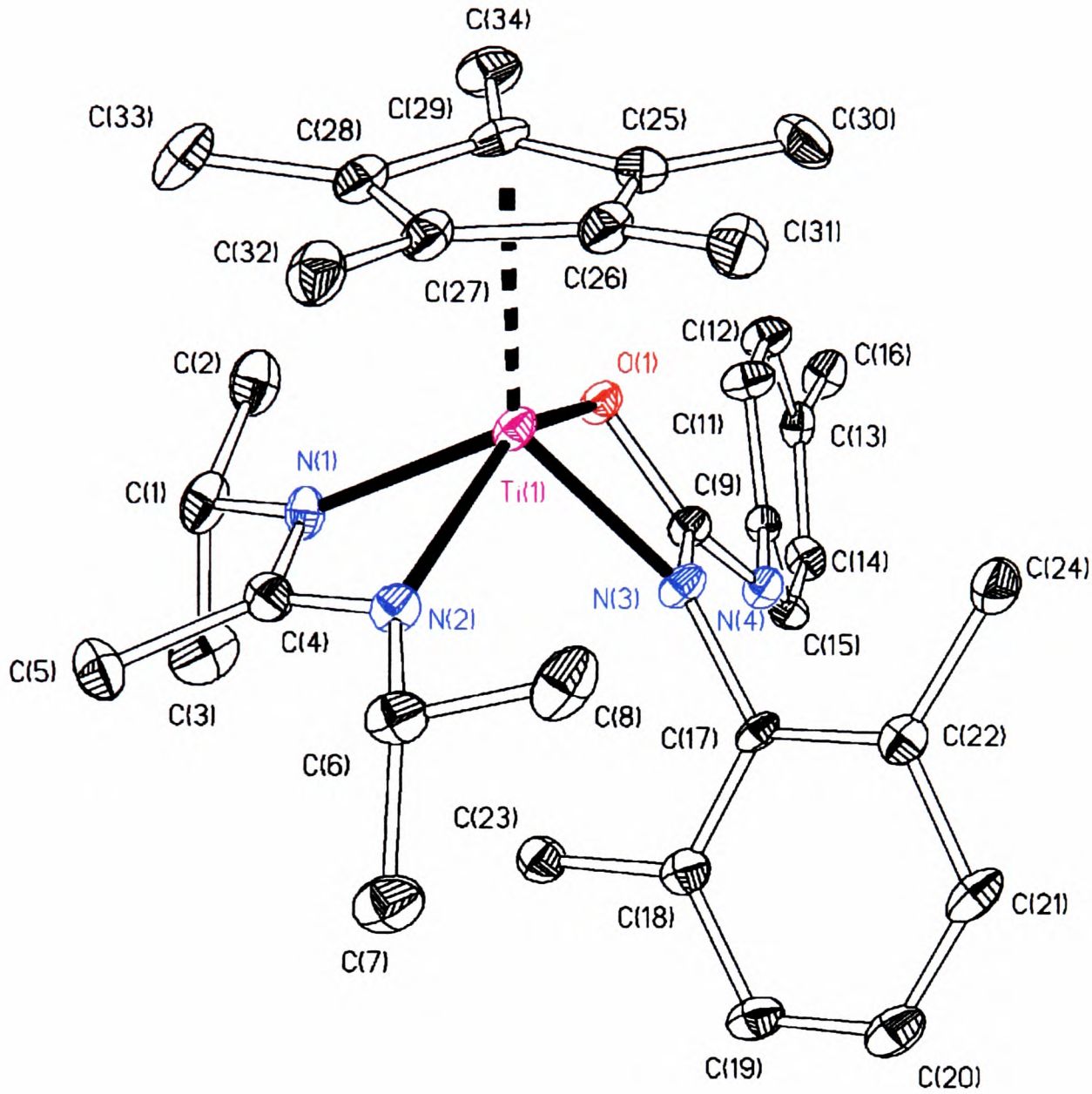


Figure 4.5 – Thermal ellipsoid plot (30 % probability) of Ti(η-C_5Me_5) {N(-2,6-$C_6H_3Me_2$)C(N-4-C_6H_4Me)O}{MeC(N^{i}Pr)$_2$} (**42**). H atoms omitted for clarity

Table 4.1 – Selected bond lengths (Å) and angles (°) for Ti(η-C_5Me_5) {N(-2,6-$C_6H_3Me_2$)C(N-4-C_6H_4Me)O}{MeC(N^{i}Pr)$_2$} (**42**)

Ti(1) – $Cp_{(cent)}$	2.106	$Cp_{(cent)}$ – Ti(1) – N(1)	115.2
Ti(1) – N(1)	2.024(5)	$Cp_{(cent)}$ – Ti(1) – N(2)	111.7
Ti(1) – N(2)	2.150(5)	$Cp_{(cent)}$ – Ti(1) – N(3)	135.7
Ti(1) – N(3)	1.994(4)	$Cp_{(cent)}$ – Ti(1) – O(1)	105.4
Ti(1) – O(1)	1.973(4)		

N(3) – C(9)	1.387(6)
O(1) – C(9)	1.347(6)
N(4) – C(9)	1.283(7)
N(4) – C(10)	1.420(6)

Plane 1	Plane 2	Angle subtended
$Cp_{(cent)}$ – Ti(1) – C(4)	N(1) – Ti(1) – N(2)	86.9
$Cp_{(cent)}$ – Ti(1) – C(4)	N(3) – Ti(1) – O(1)	67.2

4.4.2.3 COMPARISON OF THE STRUCTURES OF 41 AND 42

The crystal structures of Ti(η-C_5Me_5){N(-2,6-$C_6H_3Me_2$)C(N-2,6-$C_6H_3Me_2$)O}{MeC(N^{i}Pr)$_2$} (**41**) and Ti(η-C_5Me_5){N(-2,6-$C_6H_3Me_2$)C(N-4-C_6H_4Me)O}{MeC(N^{i}Pr)$_2$} (**42**) confirm the N, O- binding motif of the ureate ligand. The $Cp_{(cent)}$–Ti length is lengthened in the ureates relative to the imido starting material (2.094 and 2.106 Å cf. 2.085 Å), and the average $Cp_{(cent)}$–Ti(1)–$N_{amidinate}$ angles are decreased slightly (113.5 ° cf. 119.3 °), consistent with an increase in steric crowding around the metal centre.

Further, the structures demonstrate an interesting deviation from the geometry normally associated with four-legged piano stool complexes. This can be seen in the large $Cp_{(cent)}$–Ti(1)–N(3) angle subtended (136.1 ° and 135.7 ° respectively), but is even more obvious when considering the angle between the planes described by {$Cp_{(cent)}$–Ti(1)–C(4)} and {N(3)–Ti(1)–O(1)}. In an ideal system, this angle is 90 °, but in these cases the angle is much lower (63.5 ° and 67.2 ° respectively). This twisting of the plane of the ureate ligand is caused by the steric interactions between the methyl groups on the aryl ring

on N(3) and those on the cyclopentadienyl ring. A further steric effect can be seen in the orientation of the second aryl ring: the more crowded 2,6-dimethylphenyl group in **40** lies flat, whereas the less crowded *p*-tolyl group of **41** lies upright. The bond lengths C(9)–N(4) and N(4)–C(10) are equivalent between the two systems (within error), indicating that this has no electronic effect. This distortion is also evident in the amidinate ligand, which is bound asymmetrically to the metal (Ti(1)–N(1), Ti(1)–N(2): 2.094(2), 2.099(2) Å in the parent imido complex; 2.149(3), 2.027(3) Å and 2.150(5), 2.024(5) Å for **41** and **42** respectively). The short bond distances (2.027(3) and 2.024(5) Å) are the shortest titanium(IV)-amidinate bond distances reported (80 compounds),[43,44] with the exception of the complex Ti{C($SiMe_2$N(2-N-5-C_5H_3Me)$_3$}Cl (**4.61**) (2.019 Å).[45]

4.4.3 Conclusions

The rate of reaction of the arylimido species Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$){MeC(N^iPr)$_2$} (**7**) and Ti(η-C_5Me_5)(N-4-C_6H_4Me){MeC(N^iPr)$_2$} (**8**) with aryl isocyanates is much faster than the reactions of the *tert*-butylimido complex Ti(η-C_5Me_5)(N^tBu){MeC(N^iPr)$_2$} (**2**), and faster also than the reaction of the arylimido species **7** and **8** with *tert*-butyl isocyanate. This is in agreement with steric arguments. Formation of the *p*-tolyl isocyanate cycloaddition products **42** and **44** were found to be complete within 30 minutes, whilst formation of the more crowded adduct Ti(η-C_5Me_5){N(-2,6-$C_6H_3Me_2$)C(N-2,6-$C_6H_3Me_2$)O}{MeC(N^iPr)$_2$} (**41**) was found to have a half-life of *ca.* 15 minutes.

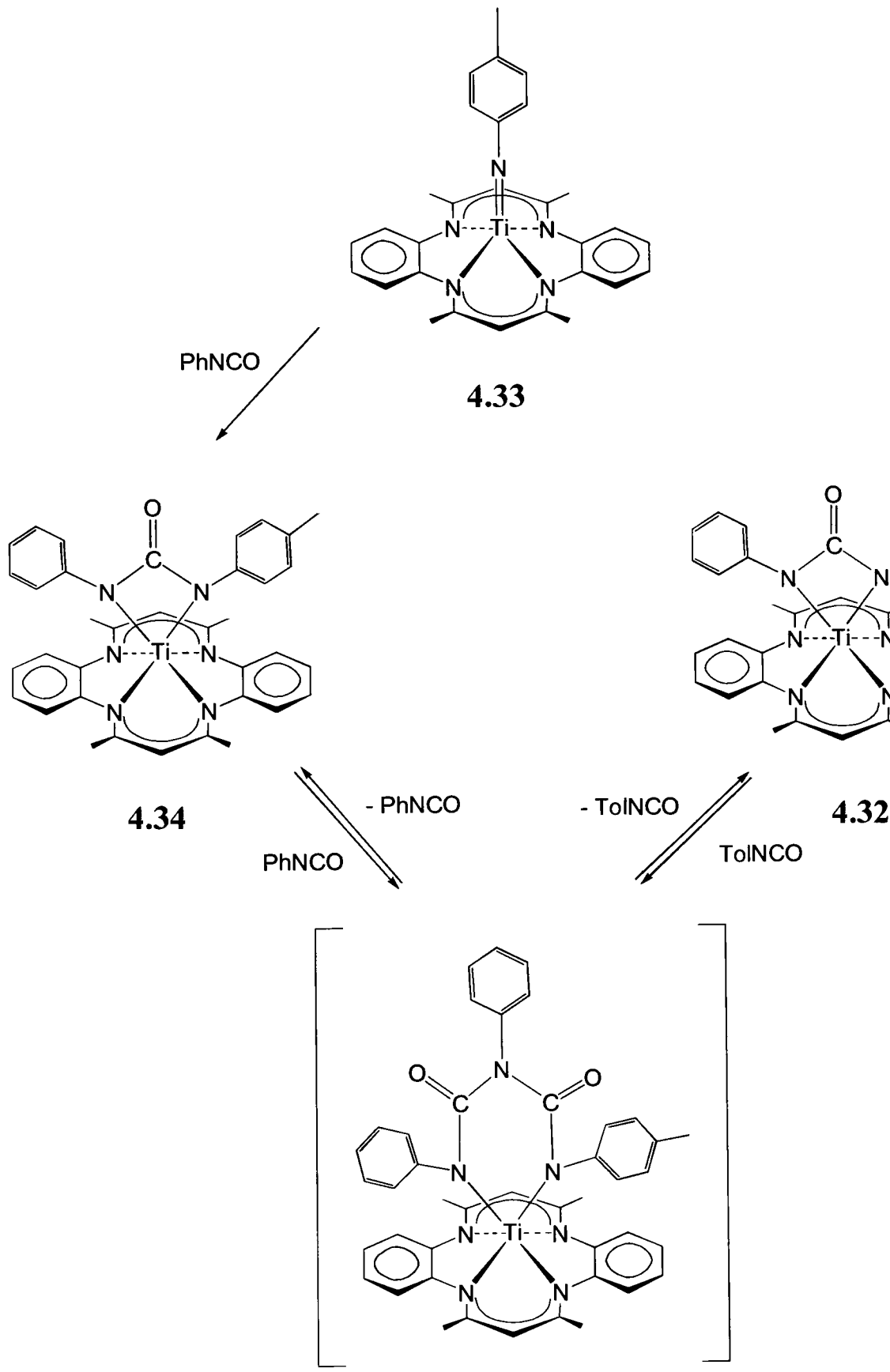
The enhanced reaction rate of these reactions is nevertheless considerably slower than the cycloaddition of CO_2 to give the carbamate complexes discussed in the previous Chapter. Although this can initially be explained in terms of concentration effects, and on steric grounds (CO_2 being much smaller than isocyanate), work described later in this Chapter will require a more detailed answer, and this will be discussed in more depth in Section 4.5.

Interconversion from Ti(η-C_5Me_5){N(-2,6-$C_6H_3Me_2$)C(N-4-C_6H_4Me)O}{$MeC(N^iPr)_2$} (**42**) to Ti(η-C_5Me_5){N(-4-C_6H_4Me)C(N-2,6-$C_6H_3Me_2$)O}{$MeC(N^iPr)_2$} (**43**) was not observed. Although the degree of steric crowding about the metal centre in **42** is higher than in **43**, the barrier to breaking to Ti–N and Ti–O bonds is large enough to allow facile isolation of each isomer.

4.5 FURTHER REACTIONS OF TITANIUM CYCLOPENTADIENYL ARYLIMIDO AMIDINATE COMPLEXES WITH ISOCYANATES

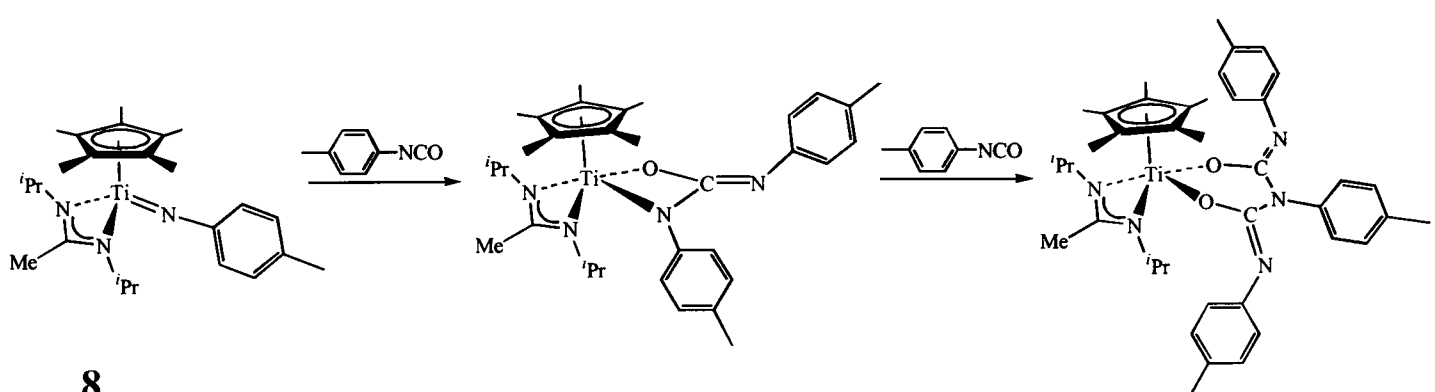
An interesting aspect of the behaviour of the Me_4taa- supported imidotitanium complexes previously studied is their behaviour in the presence of excess isocyanate. It was reported that Ti(Me_4taa)(N-4-C_6H_4Me) (**4.33**) reacted with excess phenyl isocyanate to afford both the expected ureate Ti(Me_4taa){N(-4-C_6H_4Me)C(O)N(Ph)} (**4.34**) and the unexpected complex Ti(Me_4taa){N(Ph)C(O)N(Ph)} (**4.32**).[30] It was subsequently shown that the isolated ureate Ti(Me_4taa){N(-4-C_6H_4Me)C(O)N(Ph)} (**4.34**) did indeed react with phenyl isocyanate over 5 days to give Ti(Me_4taa){N(Ph)C(O)N(Ph)} (**4.32**) and *p*-tolyl isocyanate. ^{1}H NMR crossover experiments eliminated

Ti(Me_4taa)(NPh) (**4.31**) as an intermediate, thus indicating that the (phenyl isocyanate – *p*-tolyl isocyanate) exchange proceeds *via* an associative mechanism involving a biuret-type species (Scheme 4.9).[30,42]



Scheme 4.9 – Proposed mechanism for isocyanate exchange *via* biuret intermediate (unobserved)[30]

In studies carried out on the *tert*-butyl- and 2,6-dimethylphenyl- imido complexes, addition of more than one equivalent of isocyanate (alkyl or aryl) had no effect on the products of the reaction. In the case of *p*-tolyl imido species however, further reaction was observed to yield a product in which a second molecule of isocyanate is inserted into the former Ti–N_{imido} bond (directly analogous to the behaviour of the arylimido complexes with CO_2). This reactivity is summarised in Equation 4.17.



Equation 4.17

It can be seen that this behaviour parallels that of the transient biuret species proposed for the Me_4taa exchange chemistry. In this case however, it is proposed that the new ligand binds in an O, O' - chelating fashion.

4.5.1 Synthesis and characterisation of Ti(η-C_5Me_5) {OC(N-4-C_6H_4Me)N(-4-C_6H_4X)C(N-4-C_6H_4Me)O}{MeC(N^{i}Pr)$_2$} (X = Me (48), CF_3 (49), NMe_2 (50))

A sample of Ti(η-C_5Me_5)(N-4-C_6H_4Me){MeC(N^{i}Pr)$_2$} (**8**) was dissolved in benzene and treated with two equivalents of *p*-tolyl isocyanate to afford the

biuret complex Ti(η-C_5Me_5){OC(N-4-C_6H_4Me)N(-4-C_6H_4Me)C(N-4-C_6H_4Me)O}{$MeC(N^iPr)_2$} (**48**) (51 % isolated yield). Reaction of a sample of the ureate Ti(η-C_5Me_5){N(-4-C_6H_4Me)C(N-4-C_6H_4Me)O}{$MeC(N^iPr)_2$} (**44**) in benzene-d_6 with one equivalent of *p*-tolyl isocyanate also gave **48** as the product, as indicated in Equation 4.17.

In order to investigate the effect that the electronic nature of the aryl ring might have on the kinetics of insertion of the second molecule of isocyanate, compounds Ti(η-C_5Me_5)(N-4-$C_6H_4CF_3$){$MeC(N^iPr)_2$} (**9**) and Ti(η-C_5Me_5)(N-4-$C_6H_4NMe_2$){$MeC(N^iPr)_2$} (**10**) were treated with two equivalents of *p*-tolyl isocyanate to afford the biuret complexes Ti(η-C_5Me_5){OC(N-4-C_6H_4Me)N(-4-$C_6H_4CF_3$)C(N-4-C_6H_4Me)O}{$MeC(N^iPr)_2$} (**49**) (59 % isolated yield) and Ti(η-C_5Me_5){OC(N-4-C_6H_4Me)N(-4-$C_6H_4NMe_2$)C(N-4-C_6H_4Me)O}{$MeC(N^iPr)_2$} (**50**) (71 % isolated yield) respectively. These compounds were also formed by reaction of the respective ureate complexes (**45** and **46**) with one equivalent of *p*-tolyl isocyanate. It was noted that the treatment of **8** with an excess of *tert*-butyl isocyanate did not afford any ureate insertion product.

Complexes **48** – **50** were characterised by ^1H, ^{13}C-{^1H} NMR, and IR spectroscopies, and by elemental analysis. The ^1H and ^{13}C-{^1H} NMR spectra of the three complexes are consistent with a plane of symmetry in the molecules, giving rise to one virtual septet (range 3.41 – 3.44 ppm) and two doublets (range 0.82 – 0.92) in the ^1H NMR spectra. In the case of Ti(η-C_5Me_5){OC(N-4-C_6H_4Me)N(-4-C_6H_4Me)C(N-4-C_6H_4Me)O}

{$MeC(N^iPr)_2$} (**48**), resonances assigned to the *para*- methyl groups of the aryl rings occurred at 2.17 ppm and 2.05 ppm in the ratio 2:1.

The IR spectra of the complexes contained two absorptions at 1655, 1572 cm^{-1} (**48**), 1628, 1577 cm^{-1} (**49**) and 1716, 1570 cm^{-1} (**50**). These are consistent with the in-phase and out-of-phase ν(C=N) stretches of the biuret, although the possibility of the complexes rearranging to the alternative N, N'-bound biuret isomer (Figure 4.6, isomer **B**) cannot be discounted, as the identity of the stretches cannot be unambiguously assigned as ν(C=O) or ν(C=N). Further reactivity studies confirmed, however, that the complexes bind in an O, O'- fashion (*vide infra*).

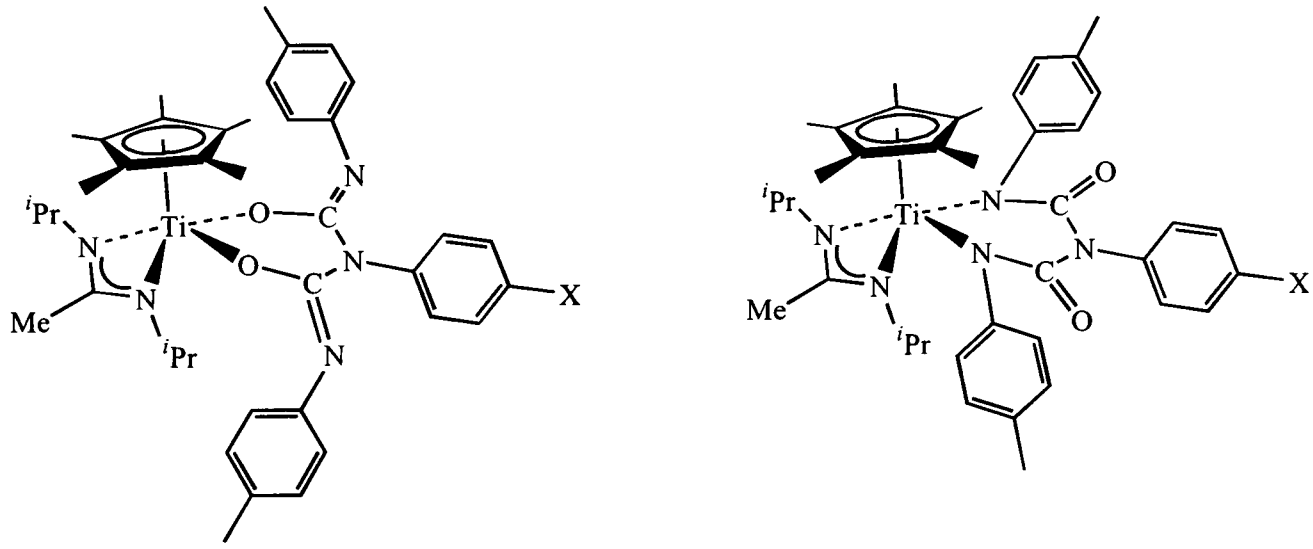
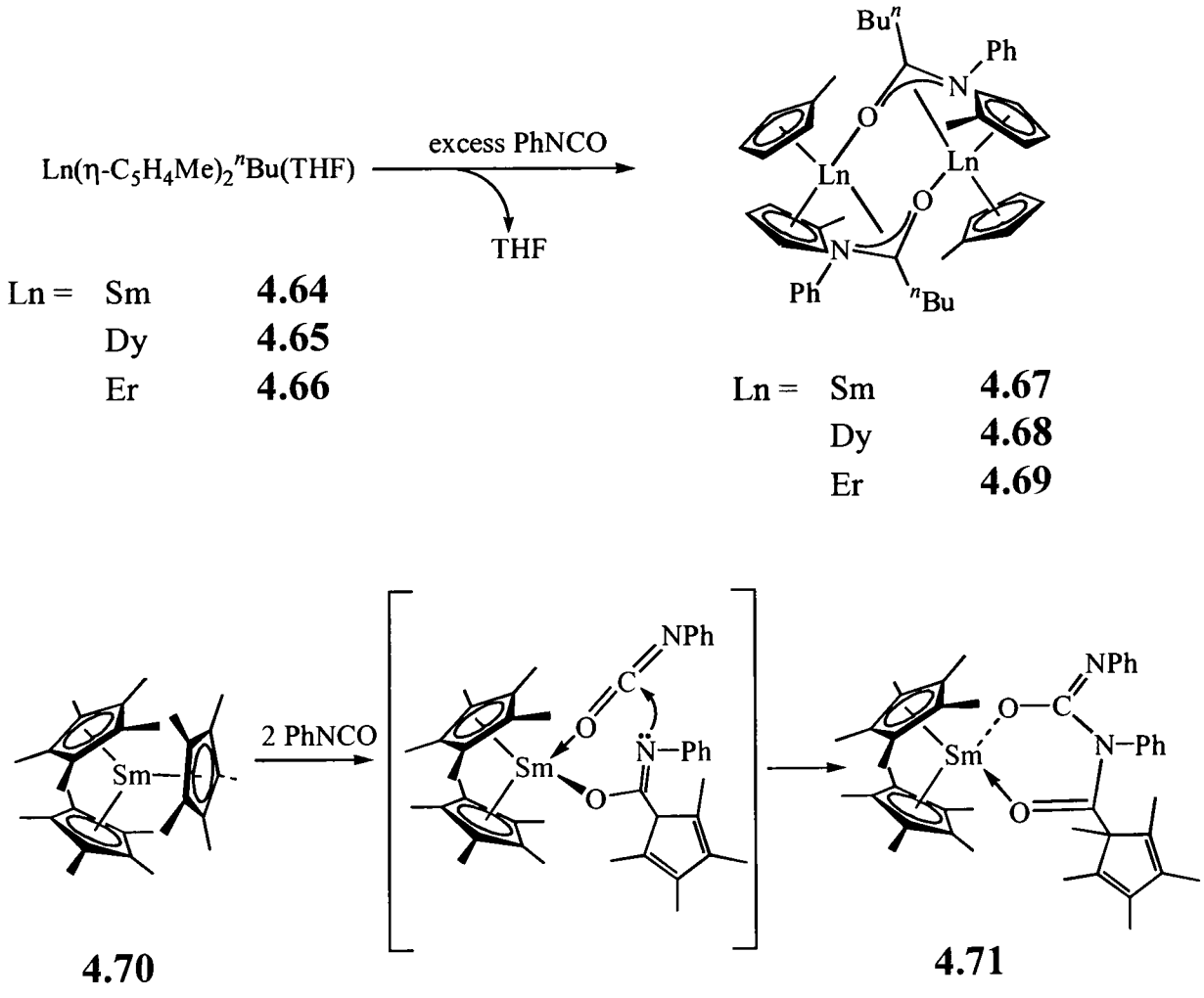


Figure 4.6 – Possible structural isomers of complexes **48** – **50**.

4.5.2 DISCUSSION OF REACTIVITY TOWARDS SECOND MOLECULE OF ISOCYANATE

The reaction of an organometallic complex with two equivalents of isocyanate to give an isolable product is extremely rare. The exchange reactions of the

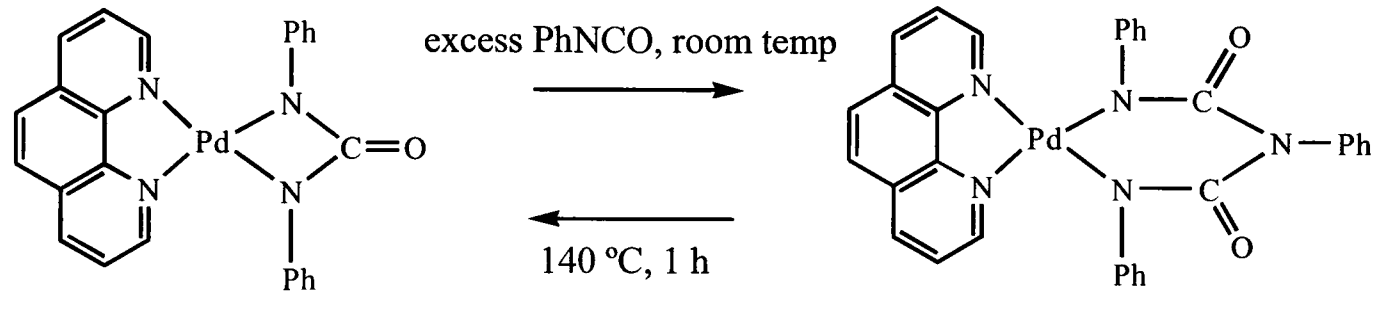
ureates of the Me_4taa- supported imidotitanium species detailed above (**4.32** – **4.33**) were proposed to pass through a biuret intermediate (**4.62**), but this was never observed directly. One example of a stable molecule in which two molecules of isocyanate have been added can be found in the alkyl-insertion chemistry of the extremely crowded $Sm(\eta\text{-}C_5Me_5)_3$ molecule. In contrast to the reaction of an excess of phenyl isocyanate with $Ln(\eta\text{-}C_5H_4Me)_2R(THF)$ (Ln = Sm (**4.64**), Dy (**4.65**), Er (**4.66**); R = *n*-butyl),[46] in which the product formed is the dimeric $[Ln(\eta\text{-}C_5H_4Me)_2\{OC(R)NPh)]_2$ (Ln = Sm (**4.67**), Dy (**4.68**), Er (**4.62**); R = *n*-butyl), where only one molecule of phenyl isocyanate has reacted, $Sm(\eta\text{-}C_5Me_5)_3$ (**4.63**) is found to react immediately with excess phenyl isocyanate to form a product in which two molecules have been inserted.[47] This is summarised in Scheme 4.10.



Scheme 4.10 – Reaction of lanthanide complexes **4.64** – **4.66**, **4.70** with excess PhNCO

Although $Sm(\eta\text{-}C_5Me_5)_3$ (**4.70**) reacts with two molecules of phenyl isocyanate, the resemblance to the reactivity of the $Ti(\eta\text{-}C_5Me_5)(N\text{-}4\text{-}C_6H_4X)\{MeC(N^iPr)_2\}$ series (X = Me, CF_3, NMe_2) ends there.

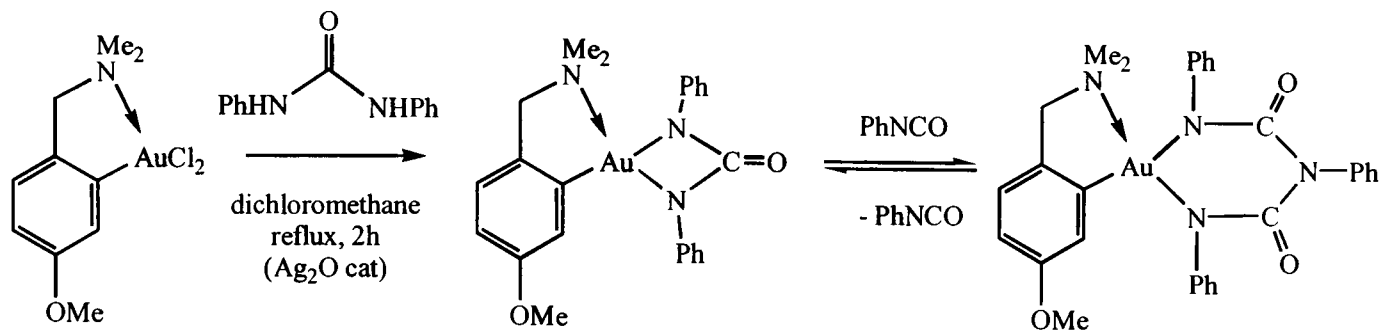
Osborn[48] reported the synthesis of the six-membered metallacycle $Pd\{N(Ph)C(O)N(Ph)C(O)N(Ph)\}(phen)$ (phen = 1,10-phenanthroline) (**4.72**), as shown in Equation 4.18. Exchange reactions with *p*-tolyl isocyanate also revealed total exchange of the phenyl isocyanate groups.



4.72 **4.73**

Equation 4.18

Another related system is that of the cyclometallated gold complex $Au\{C_6H_3(CH_2NMe_2)\text{-}2\text{-}(OMe)\text{-}5\}$ (**4.74**). This complex reacts with *N,N'*-diphenylurea to give a ureate complex, which is found to undergo reaction with phenyl isocyanate to afford a biuret product, as shown in Equation 4.19.[49] The biuret product **4.76** was found to readily de-insert phenyl isocyanate in solution to regenerate the ureate precursor **4.75**, but could be isolated as a crystalline solid and characterised.



4.74 **4.75** **4.76**

Equation 4.19

These systems are mentioned due to the structural similarities they possess with complexes **48** – **50**. However, the obvious point should be made that although the new chelating ligand formed in these reactions is formally a homologue of those found in **48** – **50**, it is neither synthesised by the same reaction pathway, nor bound to the metal in an O, O'- manner.

4.5.3 KINETICS OF REACTION WITH SECOND MOLECULE OF *P*-TOLYL ISOCYANATE

The effect of increasing the steric bulk of the aryl substituent on the imido function by replacing the *p*-tolyl with a 2,6-dimethylphenyl group was found to completely inhibit the reactivity of the ureate towards a second molecule of *p*-tolyl isocyanate. Another avenue of investigation was to alter the electronic properties of the aryl ring by changing the *para*- substituent, and observe the effect this had on the rate of reaction.

As with the kinetic study of complexes $Ti(\eta\text{-}C_5Me_5)(N\text{-}4\text{-}C_6H_4X)\{MeC(N^iPr)_2\}$ (X = Me (**8**), CF_3 (**9**), NMe_2 (**10**)) reported in Chapter 3, it was

found that reaction of the imide to form the cycloadduct was complete within 3 minutes in all cases. Since formation of the ureate starting material of interest was rapid, for convenience the same procedure was used as in the pseudo-first order kinetics study of CO_2 second insertion (*i.e.* that of reacting the parent imido complexes with a 10-fold excess of the reagent).

4.5.3.1 SERIES 1

A first series of experiments were conducted, in which 0.01 mmol of complexes Ti(η-C_5Me_5)(N-4-C_6H_4X){$MeC(N^iPr)_2$} (X = Me (**8**), CF_3 (**9**), NMe_2 (**10**)) were dissolved in a known amount of benzene-d_6, with 1,4-dimethoxybenzene added as an internal standard. These solutions were loaded into NMR tubes fitted with Teflon valves. To these tubes were added 10-fold excesses of *p*-tolyl isocyanate, and the progress of the reaction monitored using ^1H NMR spectroscopy.

The first measurement made on each sample confirmed that the reaction had gone to completion (*i.e.* total conversion to Ti(η-C_5Me_5){OC(N-4-C_6H_4Me) N(4-C_6H_4X)C(N-4-C_6H_4Me)O}{$MeC(N^iPr)_2$} (X = Me (**48**), CF_3 (**49**), NMe_2 (**50**)) had occurred) within 2¼ minutes.

4.5.3.2 SERIES 2

A second series of experiments was attempted, using low temperature techniques. Owing to the possibility that at low temperature the formation of the ureates Ti(η-C_5Me_5){N(-4-C_6H_4X)C(N-4-C_6H_4Me)O}{$MeC(N^iPr)_2$} (X = Me (**44**), CF_3 (**45**), NMe_2 (**46**)) may complicate the analysis of the data, the ureates were used as the starting materials.

0.01 mmol of complexes **44** – **46** were dissolved in a known amount of toluene-d_8, and 1,4-dimethoxybenzene added as an internal standard. The solutions were loaded into NMR tubes fitted with Teflon valves, and were then cooled to -35 °C. When the solutions had reached thermal equilibrium, they were charged with 10-fold excesses of *p*-tolyl isocyanate. They were immediately transferred using a cold bath (-30 °C) to an NMR spectrometer which had been pre-cooled to -30 °C. The rate of reaction was monitored using ^{1}H NMR. All reactions were found to be complete within 3 minutes.

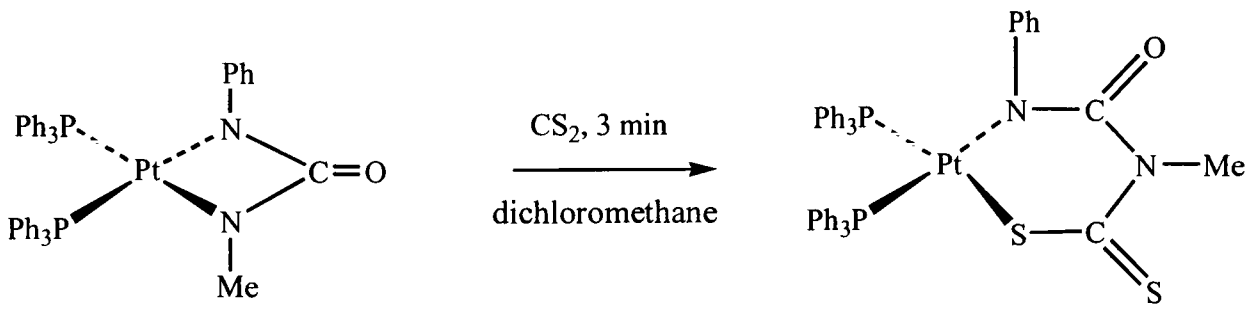
4.5.3.3 Conclusions

It is clear that both the reaction between the *p*-tolylimido species and *p*-tolyl isocyanate, and between the ureate products and *p*-tolyl isocyanate are rapid. Lack of formation of **48** – **50** in the reaction between **8** – **10** and one equivalent of *p*-tolyl isocyanate suggests that the formation of the ureate is the faster step. This mirrors the reactivity of the imido complexes *versus* the carbamate complexes towards CO_2, as described in the preceeding Chapter.

It is also clear that the ureate reacts more quickly with *p*-tolyl isocyanate than the corresponding carbamate does with CO_2. Whether this is due to enhanced reactivity of the ureate species, or the isocyanate substrate will be explored in the next Section.

4.6 MIXED SECOND (INSERTION) PRODUCTS OF ARYLIMIDO COMPLEXES

Given the propensity for both the carbamate series (**27 – 30**, **34 – 36**) and the ureate series (**44 – 46**) of complexes to undergo further reaction with excess substrate to give isolable products of insertion, it seemed reasonable to extend the range of this chemistry by attempting to synthesise compounds containing both CO_2 and isocyanate moieties. Insertion of other substrates into ureate complexes has been reported for some late-transition metal complexes. Henderson has reported the reaction of the N, N'- bound platinum ureate complex $Pt\{N(Me)C(O)N(Ph)\}(PPh_3)_2$ (**4.77**) with carbon disulfide to yield the product of insertion into the Pt–NMe bond, as shown in Equation 4.20. The complex has been crystallographically characterised.[50]



4.77 **4.78**

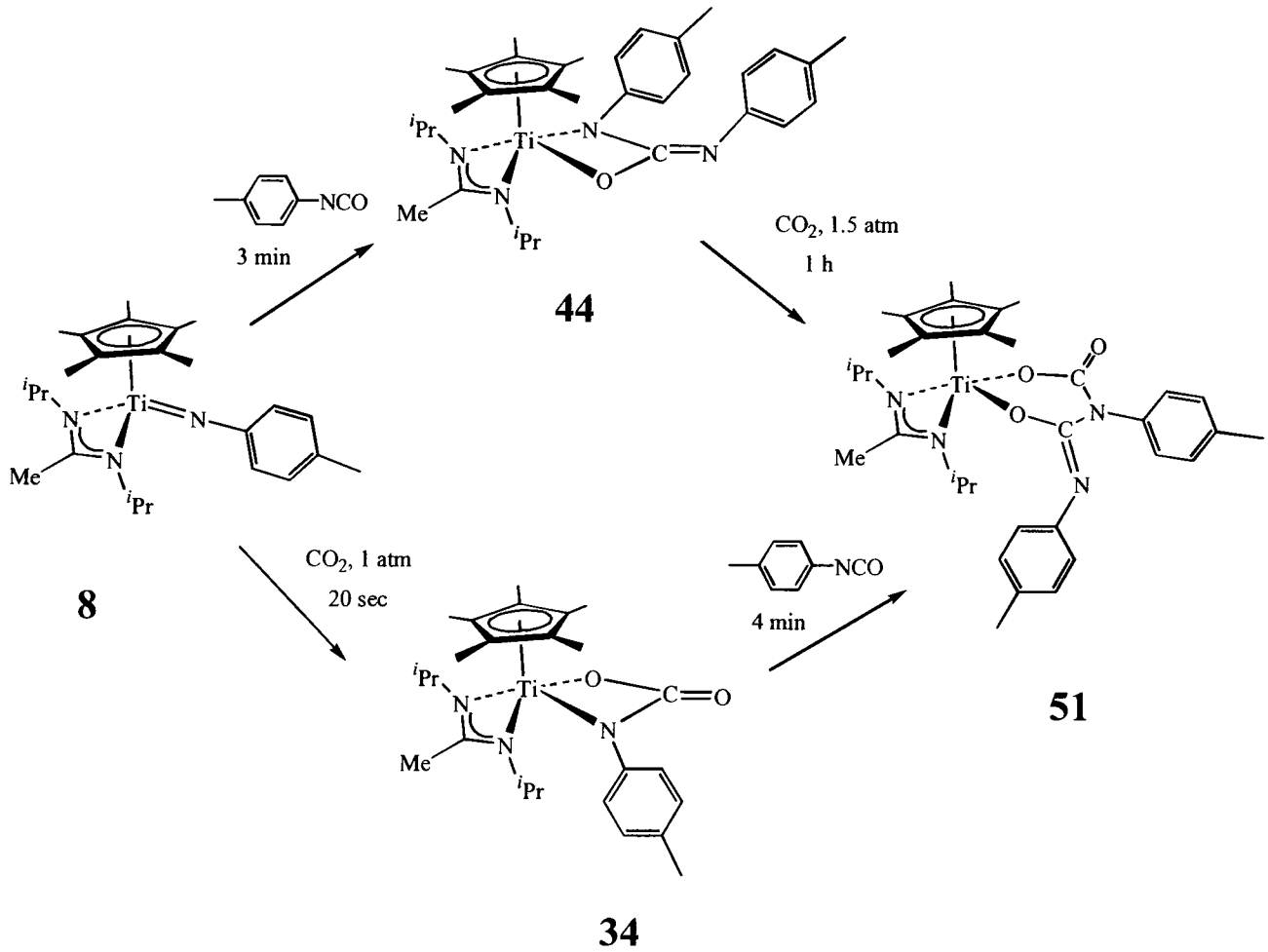
Equation 4.20

Initially, this was done to further investigate the difference between the rate of reaction of $Ti(\eta\text{-}C_5Me_5)\{N(\text{-}4\text{-}C_6H_4Me)C(O)O\}\{MeC(N^iPr)_2\}$ (**34**) and $Ti(\eta\text{-}C_5Me_5)\{N(\text{-}4\text{-}C_6H_4Me)C(N\text{-}4\text{-}C_6H_4Me)O\}\{MeC(N^iPr)_2\}$ (**44**). It was

felt that synthesising the cross-product between these two molecules would shed light on the cause of this difference.

4.6.1 SYNTHESIS AND CHARACTERISATION OF Ti(η-C_5Me_5) {OC(O)N(-4-C_6H_4Me)C(N-4-C_6H_4Me)O}{$MeC(N^iPr)_2$} (51)

The synthesis of this compound was achieved through two different routes. Exposure of a solution of Ti(η-C_5Me_5){N(-4-C_6H_4Me)C(N-4-C_6H_4Me)O}{$MeC(N^iPr)_2$} (**44**) in benzene-d_6 to CO_2 (1.5 atm), and reaction of a benzene-d_6 solution of Ti(η-C_5Me_5){N(-4-C_6H_4Me)C(O)O}{$MeC(N^iPr)_2$} (**34**) with one equivalent of *p*-tolyl isocyanate both gave the mixed second (insertion) complex Ti(η-C_5Me_5){OC(O)N(-4-C_6H_4Me)C(N-4-C_6H_4Me)O}{$MeC(N^iPr)_2$} (**51**), as shown in Scheme 4.11.



Scheme 4.11 – Synthetic pathways used in the formation of complex Ti(η-C_5Me_5){OC(O)N(-4-C_6H_4Me)C(N-4-C_6H_4Me)O}{$MeC(N^iPr)_2$} (**51**)

Both routes were found to go in quantitative yield by ^{1}H NMR spectroscopy. The synthesis was scaled up *via* the second route (i.e. using **34** as intermediate), and the product characterised by ^{1}H and ^{13}C-{^{1}H} NMR, and IR spectroscopies. Satisfactory elemental analysis was obtained for the complex. The ^{1}H NMR spectrum of **51** is fully consistent with the proposed structure, and resembles the pattern found for complexes **34** and **44**, with two virtual septets at 3.47 and 3.38 ppm, and four doublets at 1.10, 1.09, 0.89 and 0.86 ppm indicating the asymmetrical environment of the amidinate ligand. The IR spectrum contains two stretches as 1681 cm^{-1} and 1618 cm^{-1}, consistent with the in-phase and out-of-phase stretches of the ν(C=O) and ν(C=N) modes (cf. 1698, 1656 cm^{-1} for Ti(η-C_5Me_5){OC(O)N(-4-C_6H_4Me)C(O)O}{MeC(N^{i}Pr)$_2$} (**37**) and 1655, 1572 cm^{-1} for Ti(η-C_5Me_5){OC(N-4-C_6H_4Me)N(-4-C_6H_4Me)C(N-4-C_6H_4Me)O}{MeC(N^{i}Pr)$_2$} (**48**)).

4.6.2 Comparison of the rates of formation of 51

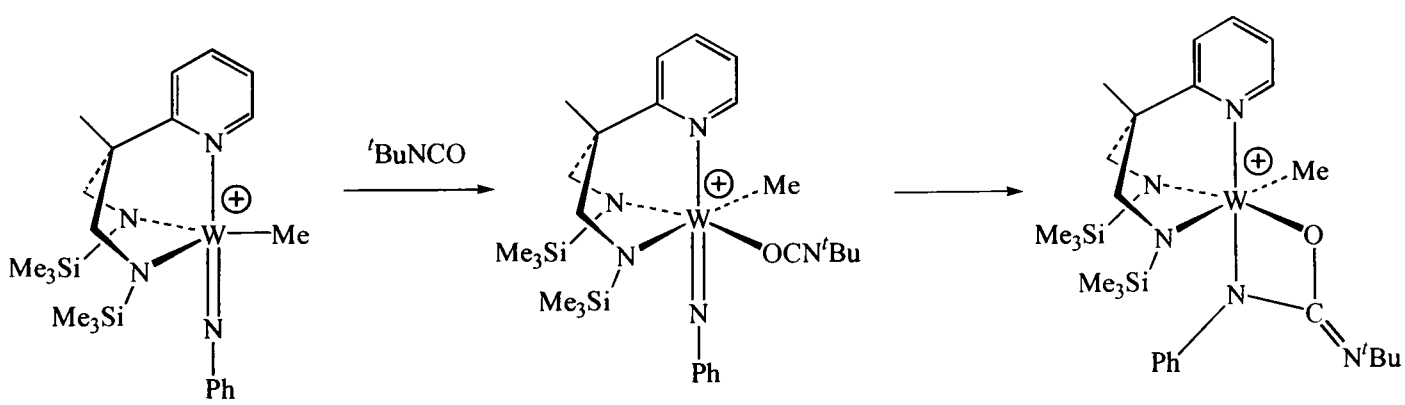
The extent of reaction was monitored by ^{1}H NMR spectroscopy. As indicated in Scheme 4.11, the reaction of the carbamate with *p*-tolyl isocyanate was found to be much faster than that of the ureate with CO_2. The reaction of the ureate with *p*-tolyl isocyanate was previously shown to be much faster than that of the carbamate with CO_2, indicating that it is the substrate which causes the difference in rate.

There are two possibilities which can account for this observation:

i) The amount of CO_2 dissolved in solution, and thus available for reaction, is very low, and thus the rate observed does not reflect the true reactivity.

ii) The reaction passes through a pre-coordination step, which the more polar isocyanate is able to achieve more rapidly than the apolar CO_2 molecule.

Of these two possibilities, the second is more likely. The rapidity of formation of the carbamates on exposure of the imido starting materials to CO_2 reveals that the concentration of CO_2 present in solution is sufficient for immediate reaction to a suitably reactive complex. The formation of **51** from the carbamate demonstrates that the carbamate is such a reactive species. This argument lends further support to the assertion made in Chapter 3, that the second (insertion) reaction begins with, or is assisted by, a pre-coordination of the substrate to the metal centre. This has been observed in the reaction of the cationic tungsten complex $[W(N_2N_{py})(NPh)Me]^+$ **(4.39)** with *tert*-butyl isocyanate, as shown in Equation 4.21.[34]



4.39 **4.79** **4.40**

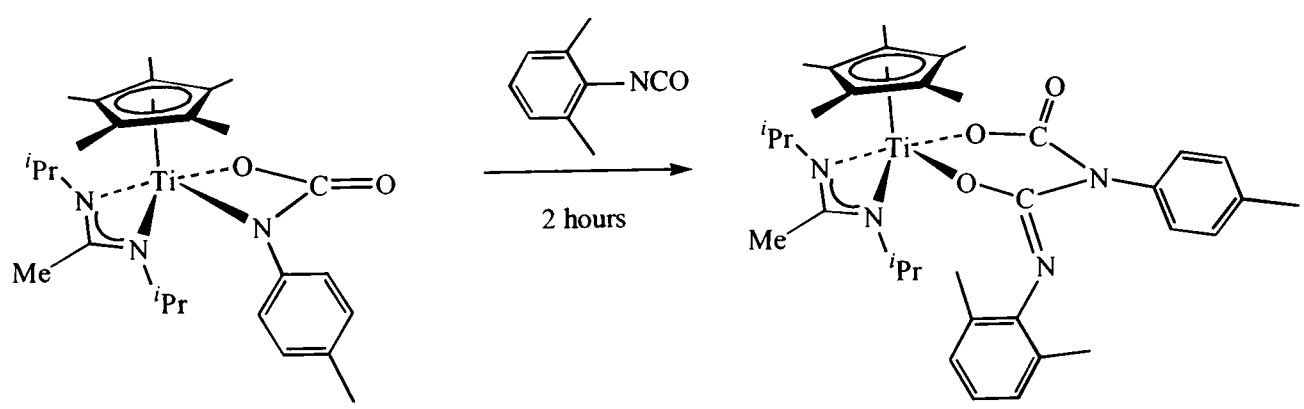
(observed at -60 °C)

Equation 4.21

4.6.3 FURTHER MIXED SECOND (INSERTION) PRODUCTS OF ARYLIMIDO COMPLEXES

As has already been stated, all reactions involving Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$){$MeC(N^iPr)_2$} (**7**) as the starting precursor failed to produce second (insertion) products; the only exception was found to be the double CO_2-derived species Ti(η-C_5Me_5){OC(O)N(-2,6-$C_6H_3Me_2$)C(O)O}{$MeC(N^iPr)_2$} (**31**). This is presumably due to the steric barrier associated with the methyl groups in the *ortho-* positions on the ring. Heating the reaction mixture of the carbamate Ti(η-C_5Me_5){N(-2,6-$C_6H_3Me_2$)C(O)O}{$MeC(N^iPr)_2$} (**27**) and *p*-tolyl isocyanate to 80 °C for 2 hours did not afford any product, and longer periods of heating simply gave unidentified decomposition products.

Reaction of 2,6-dimethylphenyl isocyanate with Ti(η-C_5Me_5){N(-4-C_6H_4Me)C(O)O}{$MeC(N^iPr)_2$} **34** in benzene-d_6 afforded the mixed second (insertion) product Ti(η-C_5Me_5){OC(O)N(-4-C_6H_4Me)C(N-2,6-C_6H_3Me)O}{$MeC(N^iPr)_2$} (**52**) in quantitative yield, as shown in Equation 4.22.



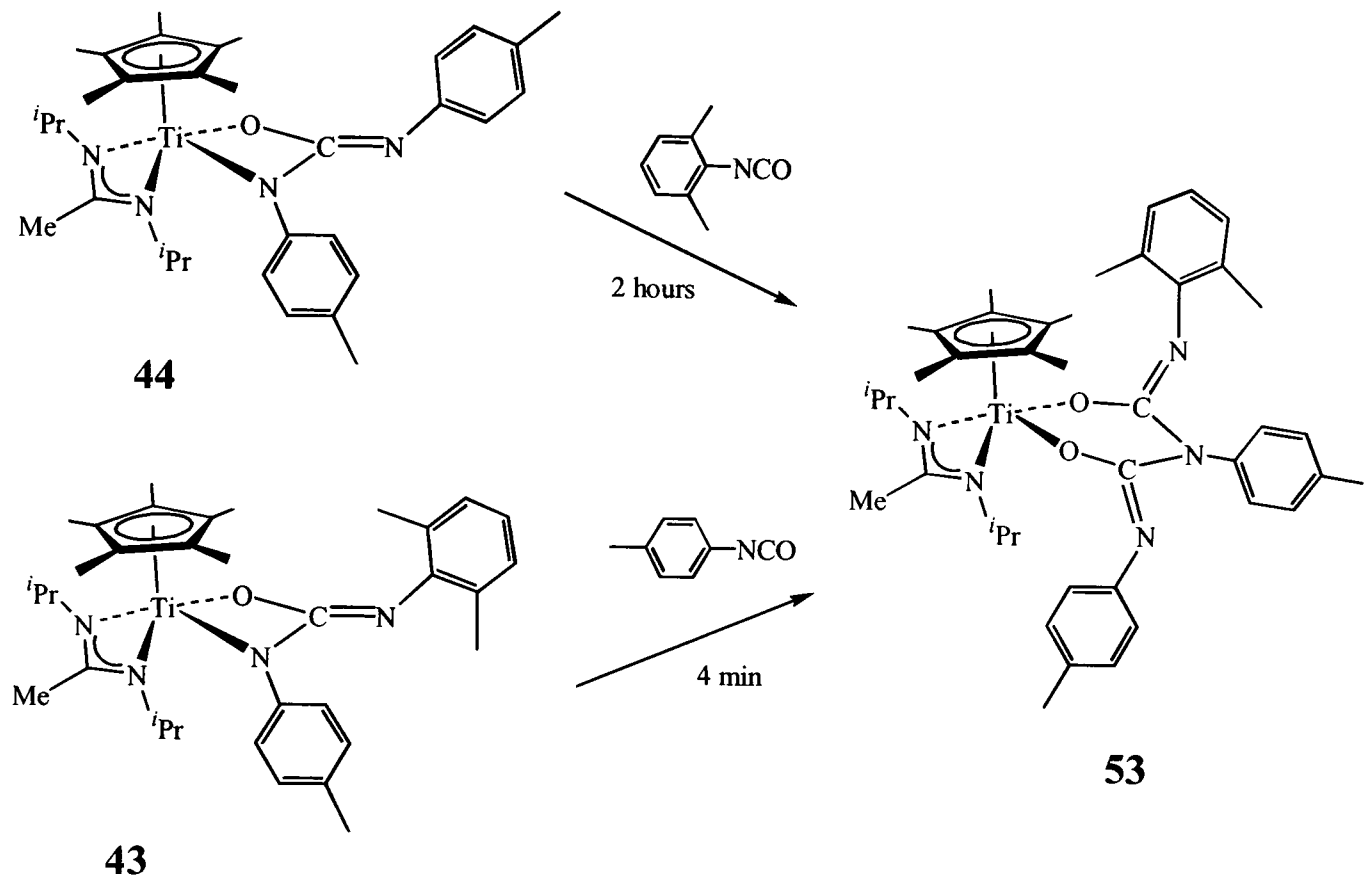
34 **52**

Equation 4.22

This compound was characterised by ^{1}H and ^{13}C-{^{1}H} NMR, and IR spectroscopies. Satisfactory elemental analysis was also obtained for the complex. The NMR data were fully consistent with the proposed structure, with two virtual septets at 3.37 and 3.02 ppm, and four doublets at 1.15, 1.08, 0.85, and 0.58 ppm in the ^{1}H NMR spectrum corresponding to the amidinate ligand. In addition, the methyl groups of the 2,6-dimethylphenyl group were assigned as two singlets at 2.29 and 2.11 ppm, indicating that the ring was not free to rotate in the molecule. Resonances at 7.03 and 6.93 ppm were assigned as the two inequivalent *meta*- protons of the ring, and 6.87 ppm as the *para* proton. The tolyl group gave only two aryl resonances (7.53 and 7.13 ppm) indicating free rotation in solution at room temperature.

The IR spectrum of **52** showed absorptions at 1680 cm^{-1} and 1620 cm^{-1}, corresponding to the in-phase and out-of-phase stretches of the ν(C=O) and ν(C=N) modes. These are very close to the values found for the homologous complex $Ti(\eta\text{-}C_5Me_5)\{OC(O)N(\text{-}4\text{-}C_6H_4Me)C(N\text{-}4\text{-}C_6H_4Me)O\}MeC(N^{i}Pr)_2\}$ (**51**) (1681, 1618 cm^{-1}).

In addition to the mixed CO_2 / isocyanate complexes **51** and **52**, it was possible to synthesise the mixed isocyanate / isocyanate complex $Ti(\eta\text{-}C_5Me_5)\{OC(N\text{-}4\text{-}C_6H_4Me)N(\text{-}4\text{-}C_6H_4Me)C(N\text{-}2,6\text{-}C_6H_3Me_2)O\}$ $\{MeC(N^{i}Pr)_2\}$ (**53**). This was carried out through two possible pathways, as illustrated in Scheme 4.12.



44

43

53

Scheme 4.12 - Synthetic pathways used in the formation of complex Ti(η-C_5Me_5) {OC(N-4-C_6H_4Me)N(-4-C_6H_4Me)C(N-2,6-$C_6H_3Me_2$)O} {MeC(N^{i}Pr)$_2$} (**53**)

The complex was scaled up using the second route (reaction of Ti(η-C_5Me_5) {N(-4-C_6H_4Me)C(N-2,6-$C_6H_3Me_2$)O} {MeC(N^{i}Pr)$_2$} (**43**) with *p*-tolyl isocyanate, 82 % isolated yield), and was characterised by ^{1}H and ^{13}C-{^{1}H} NMR, and IR spectroscopies. Satisfactory elemental analysis was obtained for the complex. The ^{1}H and ^{13}C-{^{1}H} NMR spectra of **53** adopts the same pattern as that of the mixed CO_2 / isocyanate complex Ti(η-C_5Me_5) {OC(O)N(-4-C_6H_4Me)C(N-2,6-$C_6H_3Me_2$)O} {MeC(N^{i}Pr)$_2$} (**52**), with virtual septets in the ^{1}H NMR spectrum at 3.50, 3.05 ppm assigned as the inequivalent methine protons and doublets at 1.06, 1.01, 0.91, and 0.61 ppm assigned as the methyl groups of the amidinate ligand. The methyl groups of the 2,6-dimethylphenyl ring are inequivalent (2.35, 2.07 ppm) and the two *p*-tolyl methyl groups give rise to two singlets at 2.23 and 2.14 ppm. Free

rotation of the isocyanate-derived 2,6-dimethylphenyl ring is once again hindered, as for **52**. The IR spectrum has two absorptions at 1637 cm^{-1} and 1597 cm^{-1}, similar to the values found for Ti(η-C_5Me_5){OC(N-4-C_6H_4Me) N(-4-C_6H_4Me)C(N-4-C_6H_4Me)O}{$MeC(N^iPr)_2$} (**48**) (1655 cm^{-1}, 1572 cm^{-1}), which correspond to the in-phase and out-of-phase ν(C=N) stretches.

The route involving the more bulky 2,6-dimethylphenyl isocyanate (Scheme 4.12, top) was found to be much slower than the *p*-tolyl isocyanate method. This follows the pattern predicted on the basis of steric interaction.

Following on from this, an attempt was made to investigate the difference in rate of reaction of 2,6-dimethylphenyl isocyanate with the ureates Ti(η-C_5Me_5){N(-4-C_6H_4X)C(N-4-C_6H_4Me)O}{$MeC(N^iPr)_2$} (X = Me (**44**), CF_3 (**45**), NMe_2 (**46**)). This was not pursued however, as preliminary studies indicated no significant difference in rate upon changing the X substituent of the aryl group. This shows that the interaction between the ureates and 2,6-dimethylphenyl isocyanate is dominated by steric rather than electronic factors, as would be reasonably expected.

4.7 ATTEMPTED SYNTHESES OF LESS-HINDERED TITANIUM CYCLOPENTADIENYL ALKYLIMIDO AMIDINATE COMPLEXES

The reactions of the *tert*-butyl- and aryl- imidotitanium complexes supported by a cyclopentadienyl-amidinate ligand set with CO_2 and isocyanates have been shown to give very different products. The lack of insertion of CO_2 into

the carbamate complexes Ti(η-C_5Me_5){N(^{t}Bu)C(O)O}{PhC(NSiMe$_3$)$_2$} (**19**) and Ti(η-C_5Me_5){N(^{t}Bu)C(O)O}{MeC(N^{i}Pr)$_2$} (**20**), and the preferential formation of the corresponding dimeric oxo species [Ti(η-C_5Me_5)(μ-O){PhC(NSiMe$_3$)$_2$}]$_2$ (**21**) and [Ti(η-C_5Me_5)(μ-O){MeC(N^{i}Pr)$_2$}]$_2$ (**22**) may be due to the steric crowding of the *tert*-butyl group preventing insertion of a further molecule of substrate.

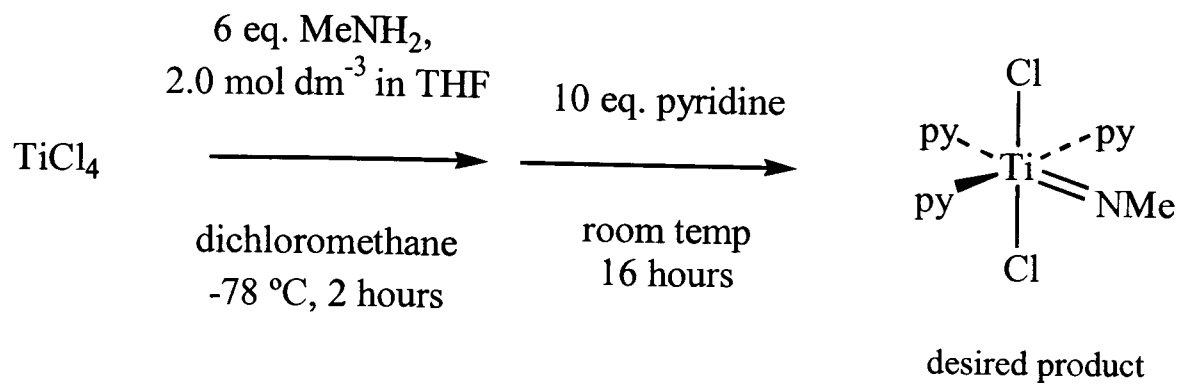
To investigate the steric effect of the *tert*-butyl group, attempts were made to synthesise two less hindered titanium alkylimido complexes, in which the *tert*-butyl group was replaced with methyl or *n*-propyl.

4.7.1 ATTEMPTED SYNTHESIS OF METHYLIMIDO COMPLEXES

Two synthetic strategies were employed in attempting to synthesis methylimido complexes, to which could be attached the cyclopentadienyl and amidinate ligands.

4.7.1.1 ATTEMPTED SYNTHESIS OF Ti(NMe)Cl$_2$(py)$_3$

The first approach involved the reaction of titanium(IV) tetrachloride, methylamine, and pyridine in dichloromethane, in a manner directly analogous to that used in the synthesis of Ti(N^{t}Bu)Cl$_2$(py)$_3$ (Equation 4.23).



Equation 4.23

The product obtained after filtering and removal of volatiles was a red powder which, once isolated, proved insoluble in most solvents. Attempts to characterise the compound failed, but it is presumed to be an oligomeric complex by analogy with work carried out by Cloke *et al.*[51]

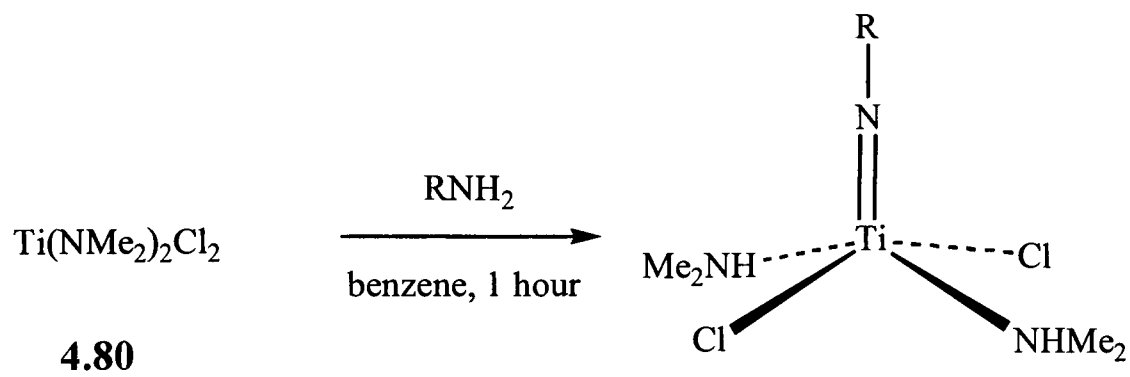
Attempts to react the product onwards with the lithium salts of the C_5Me_5 and $MeC(N^iPr)_2$ ligands failed to give any tractable product.

4.7.1.2 ATTEMPTED SYNTHESIS OF $Ti(NMe)Cl_2(NHMe_2)_2$

The second route was based on work carried out on the precursor complex $Ti(NMe_2)_2Cl_2$ (**4.80**).

Choukroun[52,53] recently published the synthesis of the terminal vanadium imido complex $V(N\text{-}2,6\text{-}C_6H_3{}^iPr_2)Cl_2(NHMe_2)_2$ (**4.81**) from the reaction of $V(NMe_2)_4$ (**4.82**) with 2,6-di-*iso*-propylamine followed by treatment with an excess of trimethylsilyl chloride. The titanium complex $Ti(NMe_2)_4$ (**4.83**)[54] can be reacted with a stoichiometric amount of $TiCl_4$ to give the complex $Ti(NMe_2)_2Cl_2$,[55] which is found to be an effective synthon for the formation of various imido species. It has been found that reaction of this complex with an

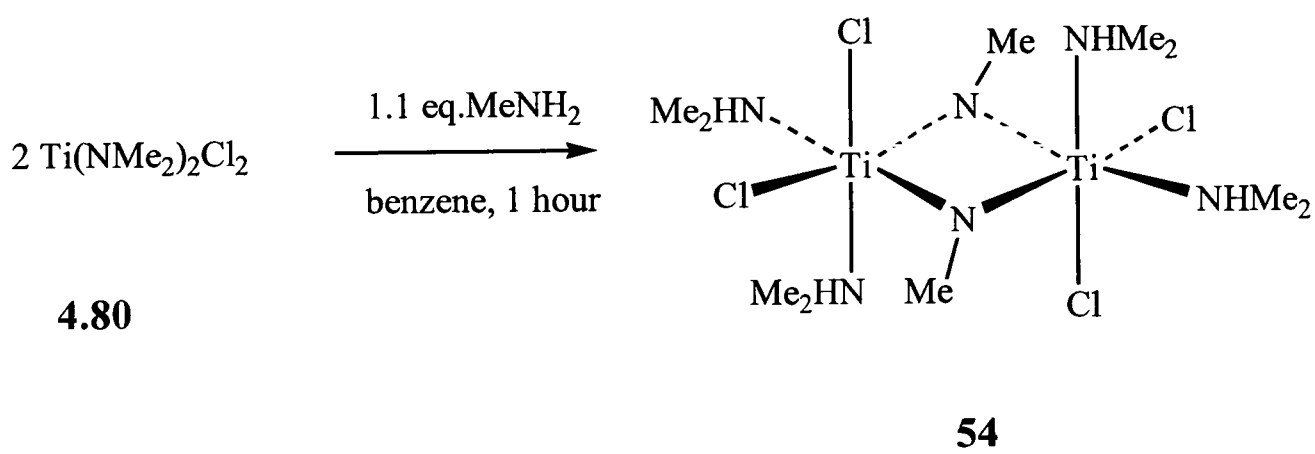
equivalent of an amine RNH_2 yields monomeric imido complexes $Ti(NR)Cl_2(NHMe_2)_2$ in good yield[56] (Equation 4.24).



R =		
	^{i}Pr	**4.84**
	Ph	**4.85**
	4-C_6H_4F	**4.86**
	4-C_6F_4H	**4.87**

Equation 4.24

Upon reaction with $MeNH_2$ as a solution in THF, the product was afforded as a poorly soluble red powder $[Ti(\mu\text{-}NMe)Cl_2(NHMe_2)_2]_2$ (**54**) (60 % yield). (Equation 4.25).



54

Equation 4.25

The complex was characterised by ^{1}H and ^{13}C-{^{1}H} NMR and IR spectroscopies. Elemental analysis was also obtained. The NMR data are fully consistent with the structure proposed for the complex. The two methylimido groups are magnetically equivalent, giving rise to a single peak at 4.26 ppm in the ^{1}H NMR spectrum. The four dimethylamide ligands give rise to two distinct doublets in the ^{1}H NMR spectrum (2.92 and 2.69 ppm), indicating the inequivalent environments. This is in contrast to the monomeric complexes **4.84 – 4.87**, in which one doublet is observed. The IR spectrum possesses an absorption peak at 3171 cm^{-1}, consistent with the N–H stretching mode of the amide ligands.

Attempts to use compound **54** to synthesise a complex of the form $Ti(\eta\text{-}C_5Me_5)(NMe)Cl(NHMe_2)$, or by the simultaneous addition of pyridine form $Ti(\eta\text{-}C_5Me_5)(NMe)Cl(py)$ were unsuccessful. The only products formed were insoluble, and presumed to be oligomeric. Attempts to react these products *in-situ* to form $Ti(\eta\text{-}C_5Me_5)(NMe)\{MeC(N^{i}Pr)_2\}$ in either THF or benzene proved similarly unsuccessful.

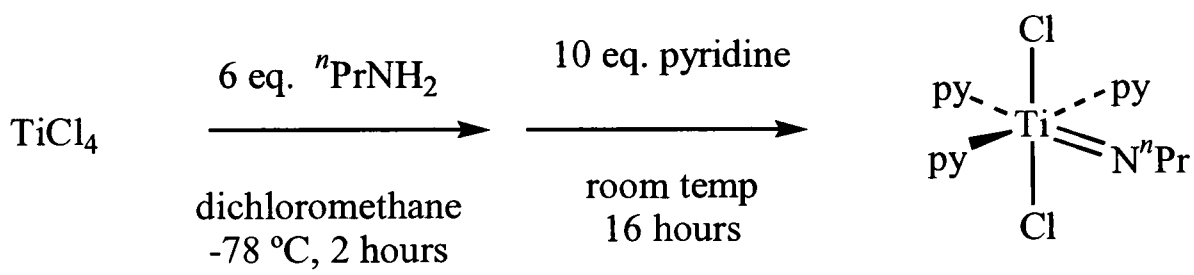
4.7.2 ATTEMPTED SYNTHESIS OF *N*-PROPYLIMIDO COMPLEXES

It seemed possible that the failure to synthesise the methylimido systems was due at least in part to the lack of solubility of the reaction products. It was therefore decided to attempt the synthesis of *n*-propylimido complexes, as these should exhibit greater solubility, without significantly increasing the

steric crowding around the imido nitrogen. Again, two synthetic strategies were employed.

4.7.2.1 ATTEMPTED SYNTHESIS OF $Ti(N^nPr)Cl_2(py)_3$

This approach involved the reaction of titanium(IV) tetrachloride, *n*-propylamine, and pyridine in dichloromethane, in a manner directly analogous to that used in the synthesis of $Ti(N^tBu)Cl_2(py)_3$, as shown in Equation 4.26.

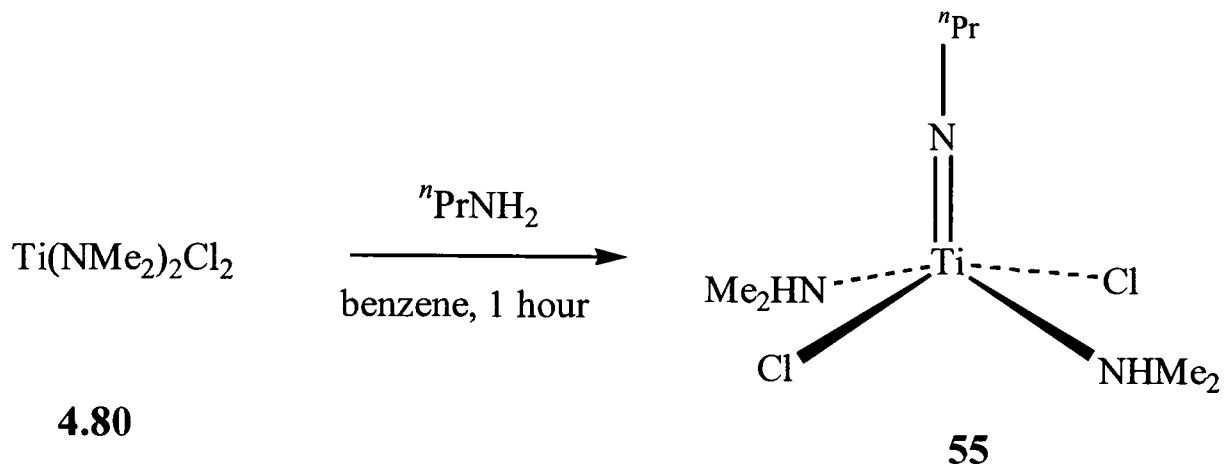


Equation 4.26

In contrast to the successful *tert*-butylimido[57] and unsuccessful methylimido syntheses (Section 4.7.1.1), this reaction mixture was not cloudy, but a clear red solution. The hydrochloride salts which form as a by-product of the reaction, and which are normally removed by filtration, are apparently soluble in the reaction mixture in the *n*-propylamine case, thus rendering ineffective the workup procedure to isolate the product. Further attempts to remove the hydrochloride salts were not pursued, owing to the constraints of time.

4.7.2.2 SYNTHESIS OF $Ti(N^nPr)Cl_2(NHMe_2)_2$

Reaction of $Ti(NMe_2)_2Cl_2$ (**4.80**) with an equivalent of *n*-propylamine in benzene gave the expected complex $Ti(N^nPr)Cl_2(NHMe_2)_2$ (**55**) in good yield (63 %, Equation 4.27).



4.80 **55**

Equation 4.27

Complex **55** showed good solubility in benzene-d_6, and was characterised by ^1H and ^{13}C-{^1H} NMR, and IR spectroscopies. The ^1H NMR spectrum contains resonances at 3.13, 1.35, and 0.97 which are assigned as the *n*-propyl group, and only one resonance at 2.27 ppm for the methyl groups of the dimethylamide ligand. The NMR data are consistent with those found for the complexes $Ti(NR)(NHMe_2)_2Cl_2$ (R = ^{i}Pr (**4.78**), Ph (**4.79**), 4-C_6H_4F (**4.80**), 4-C_6F_4H (**4.81**)). The IR spectrum shows an absorption at 3169 cm^{-1}, corresponding to the N–H stretching mode of the amide ligands.

The synthetic methodology from here proceeded in two ways: (i) direct reaction of **55** with $Li(C_5Me_5)$ to give a product which could be reacted with $Li\{MeC(N^iPr)_2\}$ to give the desired complex $Ti(\eta\text{-}C_5Me_5)(N^nPr)$

{MeC(N^{i}Pr)$_2$}, and (ii) conversion of **55** to a pyridine adduct Ti(N^{n}Pr)Cl$_2$(py)$_3$ before assembly of the ancillary ligand set.

4.7.2.2.1 ATTEMPTED REACTION OF Ti(N^{n}Pr)Cl$_2$(NHMe$_2$)$_2$ WITH Li(C$_5$Me$_5$)

It was found that reaction of Ti(N^{n}Pr)Cl$_2$(NHMe$_2$)$_2$ (**55**) with Li(C$_5$Me$_5$) did not occur at room temperature, and that upon heating the reaction mixture decomposed to unidentified products. Adding five equivalents of pyridine to a sample of **55** resulted in a colour change from red to amber, but following the addition of the Li(C$_5$Me$_5$) the ^{1}H NMR spectrum again indicated complete decomposition. It is possible that the protons on the amide ligands in **55** may be acidic enough to attack Li(C$_5$Me$_5$), in which case isolation of the amide-free precursor would be necessary.

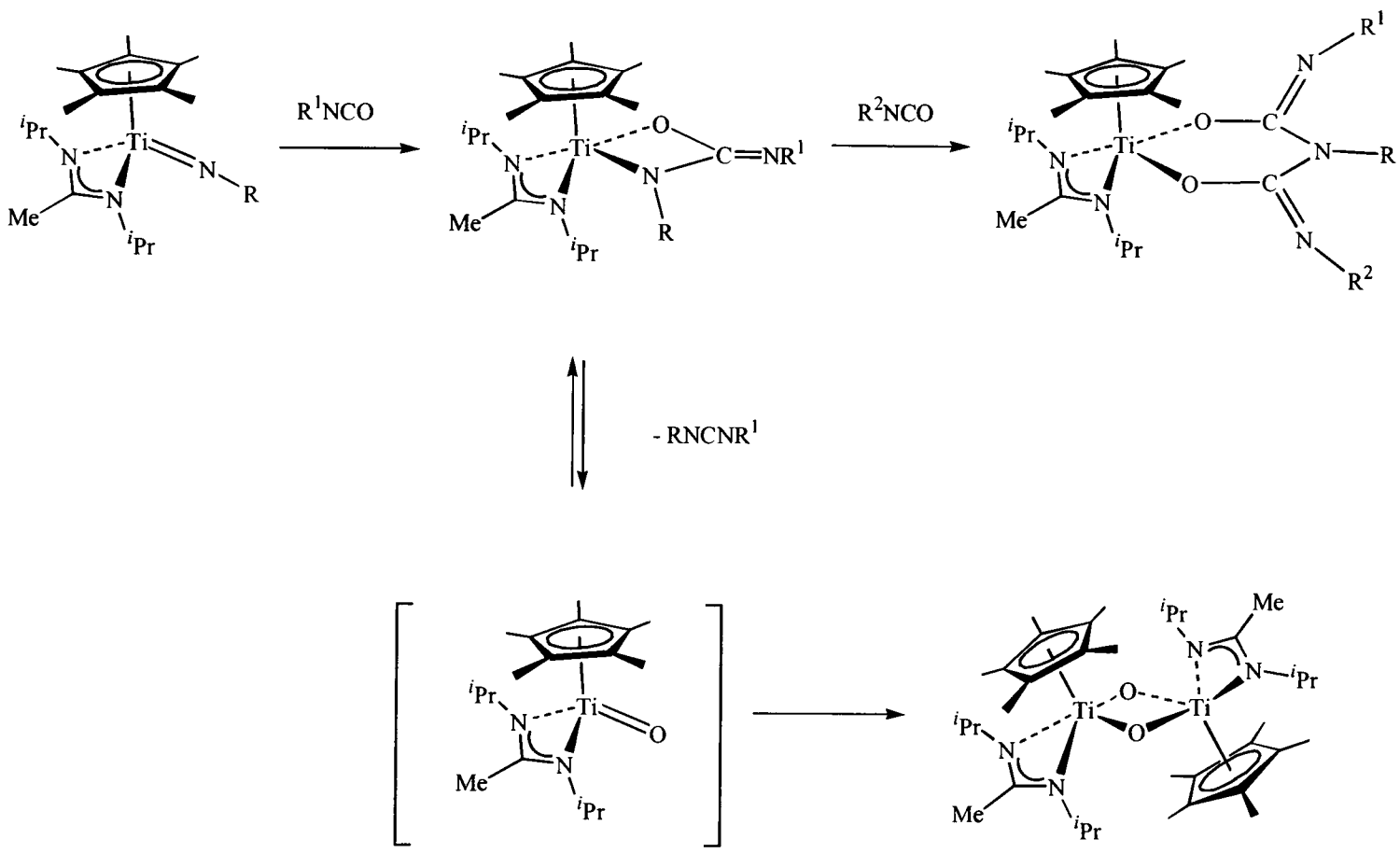
4.7.2.2.2 ATTEMPTED SYNTHESIS OF Ti(N^{n}Pr)Cl$_2$(py)$_3$

A sample of Ti(N^{n}Pr)Cl$_2$(NHMe$_2$)$_2$ (**55**) was dissolved in neat pyridine to afford an amber coloured solution. All volatiles were removed under reduced pressure, and the residue extracted into benzene-d$_6$. The product was found to be poorly soluble, and the ^{1}H NMR spectrum not consistent with the single product Ti(N^{n}Pr)Cl$_2$(py)$_3$. Peaks present in the range 3.6 – 0.8 ppm indicated the continued presence of dimethylamido ligands.

Reaction of this mixture with Li(C$_5$Me$_5$) and Li{MeC(N^{i}Pr)$_2$} in an attempt to form the desired product Ti(η-C$_5$Me$_5$)(N^{n}Pr){MeC(N^{i}Pr)$_2$} were unsuccessful.

4.8 CONCLUSIONS

It has been shown that the products of reaction between titanium cyclopentadienyl imido amidinate complexes and isocyanates become more stable as alkyl substituents are replaced by aryl groups. This is summarised in Scheme 4.13 and Table 4.5.



Scheme 4.13 – Summary of reactions between titanium cyclopentadienyl imido amidinate complexes with isocyanates

Table 4.5 – Summary of reactions of titanium imido complexes supported by cyclopentadienyl - amidinate ancillary ligand set with isocyanates

Imido Group	Isocyanate	Typical Reaction
^{t}Bu	^{t}BuNCO	Slow reaction to give dimeric oxo and di-*tert*-butylcarbodiimide No evidence of ureate intermediate
	ArNCO	More rapid reaction to give dimeric oxo and mixed carbodiimide Evidence for ureate intermediate, but not isolable
2,6-$C_6H_3Me_2$	^{t}BuNCO	Even more rapid reaction – intermediate isolable in some cases, but final product remains dimeric oxo and mixed carbodiimide
	ArNCO	Stable ureate adduct formed. Complexes stable with respect to ligand rearrangement to less strained configuration
4-C_6H_4Me	^{t}BuNCO	Still more rapid reaction giving oxo and mixed carbodiimide Ureate intermediate observed, but not isolable
	ArNCO	Very rapid reaction to give stable ureate adducts Can display insertion of CO_2, ArNCO into ureate

This insertion of isocyanate into the ureates and carbamates, like the insertion of CO_2 into carbamates described in Chapter 3 of this Thesis, has not been previously reported. It represents a new synthetic methodology for the formation of highly functionalised organic molecules from an arylimido complex. It could be envisaged that this chemistry could be developed into a catalytic process using arylamines provided some mechanism could be established for the removal of the new chelating ligand, possibly using trimethylsilyl chloride.

Investigation was carried out into the syntheses of less crowded titanium imido species, for comparison with the reactivity of the *tert*-butyl complex $Ti(\eta\text{-}C_5Me_5)(N^tBu)\{MeC(N^iPr)_2\}$ **(2)** with CO_2 and isocyanates. These were found to be very difficult to synthesise, and the desired products bearing a cyclopentadienyl-amidinate supporting framework were not obtained.

4.9 REACTION OF TITANIUM CYCLOPENTADIENYL IMIDO AMIDINATE COMPLEXES WITH CARBODIIMIDES

This Section will deal with the reaction of titanium cyclopentadienyl imido amidinate complexes with carbodiimides. Reactions of *tert*-butylimides will be considered in the first case, followed by the reactions of arylimido complexes.

4.9.1 REACTION OF TITANIUM CYCLOPENTADIENYL *TERT*-BUTYLIMIDO AMIDINATE COMPLEXES WITH ALKYL CARBODIIMIDES

Samples of $Ti(\eta\text{-}C_5Me_5)(N^tBu)\{PhC(NSiMe_3)_2\}$ **(1)**, $Ti(\eta\text{-}C_5Me_5)(N^tBu)\{MeC(N^iPr)_2\}$ **(2)**, $Ti(\eta\text{-}C_5H_4Me)(N^tBu)\{PhC(NSiMe_3)_2\}$ **(3)**, and $Ti(\eta\text{-}C_5H_4Me)(N^tBu)\{MeC(N^iPr)_2\}$ **(4)** were dissolved in benzene-d_6 and treated with one equivalent of 1,3-di-*iso*-propylcarbodiimide. The reaction mixtures were monitored using ^1H NMR spectroscopy. No reaction was observed, even after heating the samples for 5 hours at 80 °C.

4.9.2 REACTION OF A TITANIUM CYCLOPENTADIENYL *TERT*-BUTYLIMIDO AMIDINATE COMPLEX WITH AN ARYL CARBODIIMIDE

A sample of $Ti(\eta\text{-}C_5Me_5)(N^tBu)\{MeC(N^iPr)_2\}$ (**2**) was dissolved in benzene-d_6 and treated with one equivalent of 1,3-di-*p*-tolylcarbodiimide. The reaction was monitored using ^1H NMR spectroscopy. No reaction was observed, even after heating the sample for 7 hours to 80 °C.

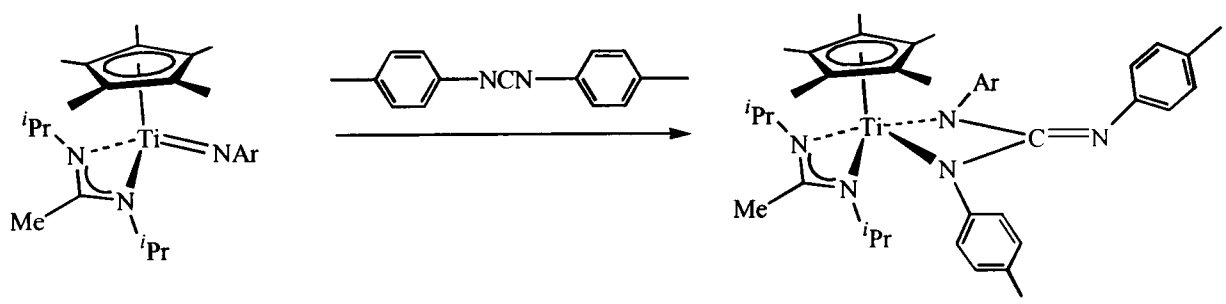
4.9.3 REACTION OF A TITANIUM CYCLOPENTADIENYL ARYLIMIDO AMIDINATE COMPLEX WITH AN ALKYL CARBODIMIDE

A sample of $Ti(\eta\text{-}C_5Me_5)(N\text{-}4\text{-}C_6H_4Me)\{MeC(N^iPr)_2\}$ (**8**) was dissolved in benzene-d_6 and treated with one equivalent of 1,3-di-*iso*-propylcarbodiimide. The reaction was monitored using ^1H NMR spectroscopy. No reaction was observed, even after heating the sample to 80 °C for 12 hours.

4.9.4 REACTION OF TITANIUM CYCLOPENTADIENYL ARYLIMIDO AMIDINATE COMPLEXES WITH ARYL CARBODIIMIDES

A sample of $Ti(\eta\text{-}C_5Me_5)(N\text{-}4\text{-}C_6H_4Me)\{MeC(N^iPr)_2\}$ (**8**) was dissolved in benzene-d_6 and treated with one equivalent of 1,3-di-*p*-tolylcarbodiimide. An immediate colour change from dark green to dark brown was observed. The reaction was monitored using ^1H NMR spectroscopy, which showed complete consumption of the imide after 1 hour to give a new product, $Ti(\eta\text{-}C_5Me_5)\{N(\text{-}4\text{-}C_6H_4Me)C(N\text{-}4\text{-}C_6H_4Me)N(\text{-}4\text{-}C_6H_4Me)\}\{MeC(N^iPr)_2\}$ (**56**) in quantitative yield.

A sample of Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$){$MeC(N^iPr)_2$} (**7**) was dissolved in benzene-d_6 and treated with one equivalent of 1,3-di-*p*-tolylcarbodiimide. The reaction was monitored using ^1H NMR spectroscopy, which showed complete consumption of the imide after 24 hours to give a new product, Ti(η-C_5Me_5){N(-2,6-$C_6H_3Me_2$)C(N-4-C_6H_4Me)N(-4-C_6H_4Me)}{$MeC(N^iPr)_2$} (**57**) in quantitative yield. These reactions are summarised in Equation 4.28.



	Ar	
8	4-C_6H_4Me	**56**
7	2,6-$C_6H_3Me_2$	**57**

Equation 4.28

Both complexes have been characterised by ^1H and ^{13}C-{^1H} NMR and IR spectroscopies, and elemental analysis. Complex **56** has C_s symmetry, and this structure is supported by the ^1H NMR data, which shows one virtual septet at 3.69 ppm, and two doublets at 1.02 and 0.73 ppm corresponding to the amidinate, and two singlets at 2.11 and 2.02 ppm (ratio 2 : 1) for the methyl groups on the aryl rings.

By contrast, **57** has C_1 symmetry, as shown by the two virtual septets (3.89, 3.11 ppm) and four doublets (1.15, 1.06, 0.89, 0.31 ppm) for the amidinate ligand, and three singlets (2.26, 2.19, 2.07 ppm, ratio 1: 2: 1) for the freely

rotating aryl groups. Both molecules show an absortion peak in their IR spectrum at 1655 cm^{-1}, corresponding to the ν(C=N) stretching mode.

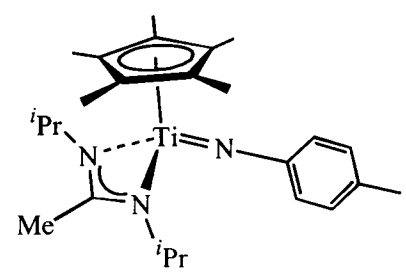
4.9.5 DISCUSSION OF REACTIVITY OF TITANIUM CYCLOPENTADIENYL IMIDO AMIDINATE COMPLEXES WITH CARBODIIMIDES

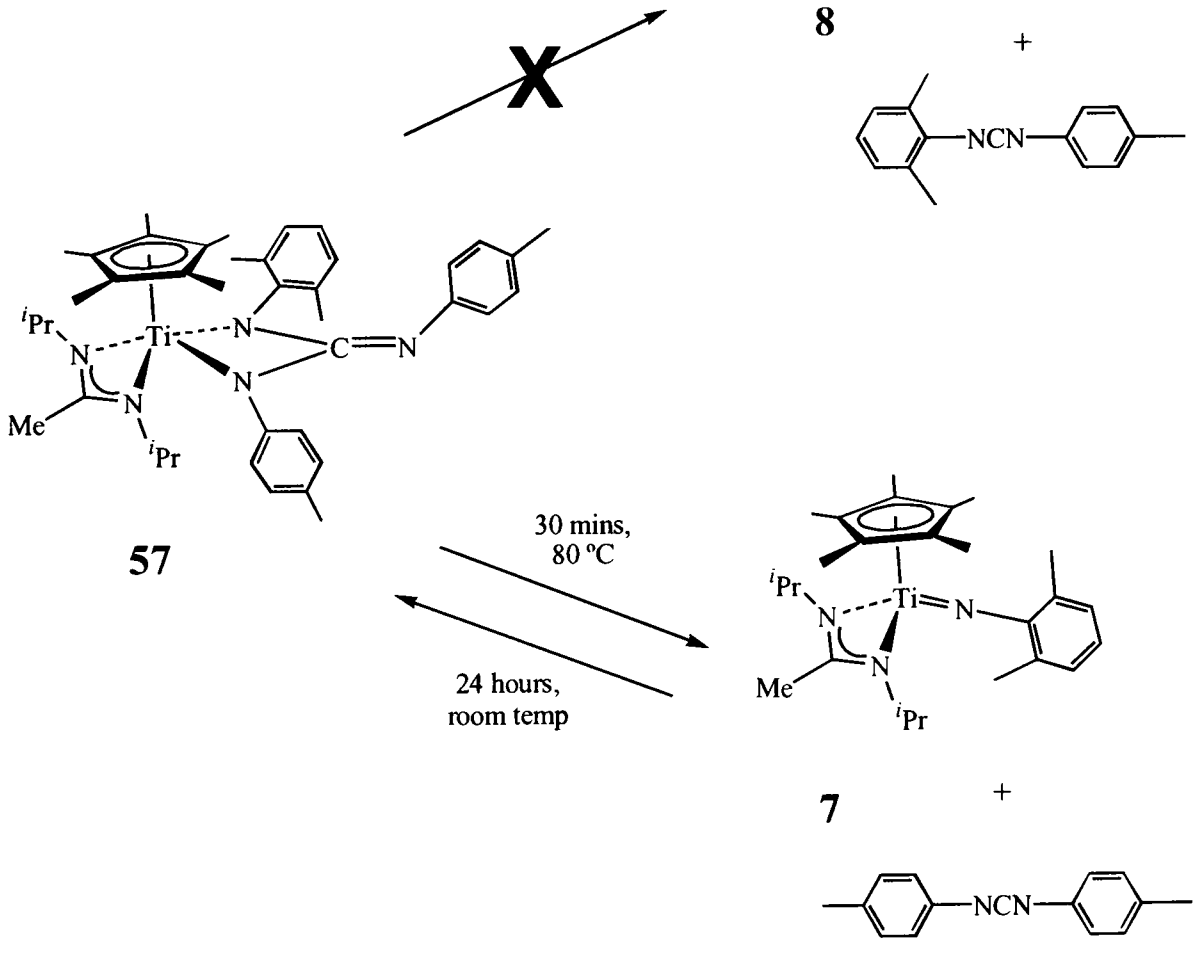
In contrast to the isocyanate, in which the reactive linkage is found to be terminal, the reactive bond of the carbodiimide is necessarily internal. It is clear that steric influences have a great effect on the reaction between the imidotitanium species and carbodiimides. In the case where the imido N-substituent is *tert*-butyl, no reaction is observed with alkyl or aryl carbodiimides, and this can be attributed to the high degree of strain necessary to bring the C=N bond of the carbodiimide close enough to the metal centre to effect reaction.

The reaction of Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$){$MeC(N^iPr)_2$} (**7**) and Ti(η-C_5Me_5)(N-4-C_6H_4Me){$MeC(N^iPr)_2$} (**8**) with 1,3-di-*p*-tolylcarbodiimide to give the stable adducts Ti(η-C_5Me_5){N(-4-C_6H_4Me)C(N-4-C_6H_4Me)N(-4-C_6H_4Me)}{$MeC(N^iPr)_2$} (**56**) and Ti(η-C_5Me_5){N(-2,6-$C_6H_3Me_2$)C(N-4-C_6H_4Me)N(-4-C_6H_4Me)}{$MeC(N^iPr)_2$} (**57**) is analogous to the reactivity of the Me_4taa-supported imidotitanium species reported by Mountford *et al.*[30] In contrast to the terminal oxo complex Ti(Me_8taa)(O) (**4.82**), which reacts with 1,3-di-*p*-tolylcarbodiimide to afford the ureate complex Ti(Me_8taa){N(-4-C_6H_4Me)C(N-4-C_6H_4Me)O} (**4.83**), the dimeric

complex $[Ti(\eta\text{-}C_5Me_5)(\mu\text{-}O)\{MeC(N^iPr)_2\}]_2$ (**22**) was found to be completely unreactive towards the carbodiimide even when heated to 80 °C for 16 hours.

The stability of the adduct is also comparable to the zirconocene systems reported by Bergman.[40,41] In these systems, rearrangement to a less sterically crowded arrangement occurs upon heating. By contrast, the triazatrimethylene methane complex **57** undergoes retrocyclisation after 30 mins at 80 °C to give the parent imido species $Ti(\eta\text{-}C_5Me_5)(N\text{-}2,6\text{-}C_6H_3Me_2)\{MeC(N^iPr)_2\}$ (**7**) and 1,3-di-*p*-tolylcarbodiimide, as shown in Scheme 4.14.





Scheme 4.14 – Effect of heating on triazatrimethylene methane complex $Ti(\eta\text{-}C_5Me_5)\{N(\text{-}2,6\text{-}C_6H_3Me_2)C(N\text{-}4\text{-}C_6H_4Me)N(\text{-}4\text{-}C_6H_4Me)\}\{MeC(N^iPr)_2\}$ (**57**)

This result is not what might be expected on steric grounds, as the product is the more sterically hindered 2,6-dimethylphenyl imido species. No trace of the products from the alternative retrocyclisation were detected by ^{1}H NMR spectroscopy. Such systems would therefore seem ill-suited as catalysts for the conversion of symmetrical to unsymmetrical carbodiimides, unlike those of Bergman.[40]

4.10 Conclusions

Steric factors have been shown to be very important in determining the reactivity of the titanium cyclopentadienyl imido amidinate complexes with carbodiimides. In cases where either the imido group or the carbodiimide possesses alkyl substituents, no reactivity is observed. Aryl groups on both reactants gives rise to the formation of triazatrimethylene methane titanium complexes, which are stable but which undergo retrocyclisation upon heating to afford clean starting materials.

4.11 Summary

It has been shown in this Chapter that the titanium imido linkage supported by a cyclopentadienyl-amidinate supporting ligand set displays a range of reactivity towards nitrogen-containing heterocumulenes. This reactivity is crucially dependent on the identity of the imido N-substituent, and also steric factors. A variety of ureate species have been synthesised and characterised. A novel type of reactivity involving complete cleavage of a titanium-imido bond

with insertion of two molecules of *p*-tolyl isocyanate has been demonstrated. Extension of this reaction to afford adducts of insertion of two different substrates has been explored. Reaction with carbodiimides to give stable triazatrimethylene methane species has also been demonstrated; a dearth of which have been reported in the literature.

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CHAPTER 5

Reactivity Towards Sulfur Containing Substrates

5.1 Overview

This Chapter focuses on the reactions between titanium cyclopentadienyl imido amidinate complexes and substrates containing sulfur. It begins by briefly introducing the chemistry of sulfur-containing substrates with metal complexes (Section 5.2), and then describes the reactivity of titanium cyclopentadienyl imido amidinate complexes towards COS (Section 5.3), CS_2 (Section 5.4), H_2S (Section 5.5), and isothiocyanates (Section 5.6).

5.2 Introduction

This Section provides a brief review of the chemistry of sulfur-containing substrates with metal complexes. Of necessity, this survey will focus on chemistry related to that of the titanium imido complexes, and will not touch upon much of the chemistry that is known about metal-sulfide complexes. For a more in-depth discussion, the reader is directed towards some excellent reviews in the literature.[1-3]

The overview will be split into parts, each of which will address the reactivity of one of the substrates or classes of substrate of interest. Comparisons will be drawn where appropriate with oxygen-based substrate reactivity. Later Sections will describe the reaction of the title complexes with the sulfur compounds in the order given above, and results will be tied in with relevant findings from previous Chapters.

5.2.1 REACTIONS OF COS AND CS_2 WITH METAL COMPLEXES

Comparison between the reactions and products of reaction of CO_2 and CS_2 has often shown considerable differences between the two substrates. Chisholm[4] reported the reaction of $W_2(NMe_2)_6$ (**5.1**) with both excess CO_2 and excess CS_2 to give the N, N-dialkylcarbamate and N, N-dithiocarbamate complexes $W_2(O_2CNMe_2)_6$ (**5.2**) and $W_2(S_2CNMe_2)_6$ (**5.3**) respectively. In contrast to the diamagnetic nature of $W_2(O_2CNMe_2)_6$ however, $W_2(S_2CNMe_2)_6$ was found to be paramagnetic.

Subsequently, Yamamoto[5] compared the reaction of a series of alkyl copper complexes $RCu(PPh_3)_2$ (R = Me (**5.4**), Et (**5.5**), ^{n}Pr (**5.6**), ^{i}Bu (**5.7**)) with CO_2 and CS_2. The reactions are summarised in Equations 5.1 and 5.2.

$$RCu(PPh_3)_2 \xrightarrow{\text{excess } CO_2} (\eta^2\text{-}RCO_2)Cu(\eta^1\text{-}CO_2)(PPh_3)_2$$

Equation 5.1

$$RCu(PPh_3)_2 \xrightarrow{\text{excess } CS_2} (\eta^1\text{-}RCSS)Cu(PPh_3)_2$$

Equation 5.2

Although insertion into the metal-alkyl bond occurred for both substrates, only CO_2 was found to also coordinate to the copper. Assignment of the coordination modes of the carboxylate and thiocarboxylate ligands was made on the basis of IR data.

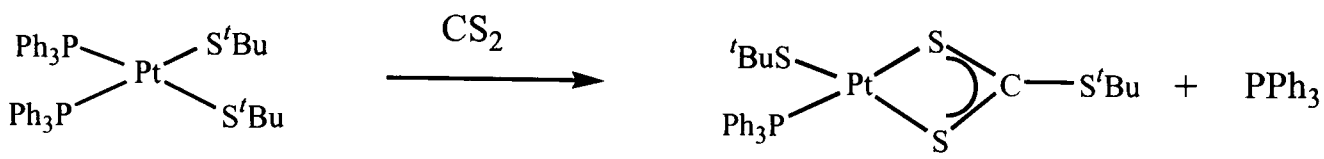
Experiments carried out by Darensbourg *et al.*[6] on $[M(CO)_5(OPh)]^-$ complexes (M = Cr (**5.8**), W (**5.9**)) showed that that they underwent facile insertion reactions of CO_2, COS and CS_2 into the metal-phenoxide oxygen bond. The relative rates of reaction were $CS_2 > COS > CO_2$, and it was found that the COS and CS_2 insertions were irreversible, in contrast to the instability of the CO_2 insertion product. Mechanistic studies on the related complex $[W(CO)_5(O\text{-}2,6\text{-}C_6H_3Ph_2)]^-$ (**5.10**)[7] showed that CO_2 was unreactive even at high pressures, while COS reacted rapidly and irreversibly to give the monothiocarbonate product $[W(CO)_5\{SC(O)O\text{-}2,6\text{-}C_6H_3Ph_2\}]^-$ (**5.11**), in which the C=S bond of COS had been attacked in preference to C=O. These authors concluded that the difference in reactivity was due to inherent differences in the bonding nature of the sulfur atom *vs* that of the oxygen atom, and that the transition state is lowered in energy as a result for the COS-aryloxide interaction compared to the CO_2-aryloxide interactions. They thus concluded that COS is not a good model for CO_2 when conducting activation studies.

However, it is not always the case that COS mirrors the reactivity of CS_2 more than that of CO_2. Reactions of the complexes *cis*- $Pt(PPh_3)_2(SH)_2$ (**5.12**) and *cis*- $Pt(PPh_3)_2(S^tBu)_2$ (**5.13**) with CS_2 were reported to form the metallacyclic products $Pt(PPh_3)_2(\eta^2\text{-}S_2CS)$ (**5.14**) and $Pt(PPh_3)(S^tBu)(\eta^2\text{-}S_2CS^tBu)$ (**5.15**) respectively, as shown in Equations 5.3 and 5.4.[8] No reaction was observed between either starting material and COS or CO_2.



5.12 **5.14**

Equation 5.3



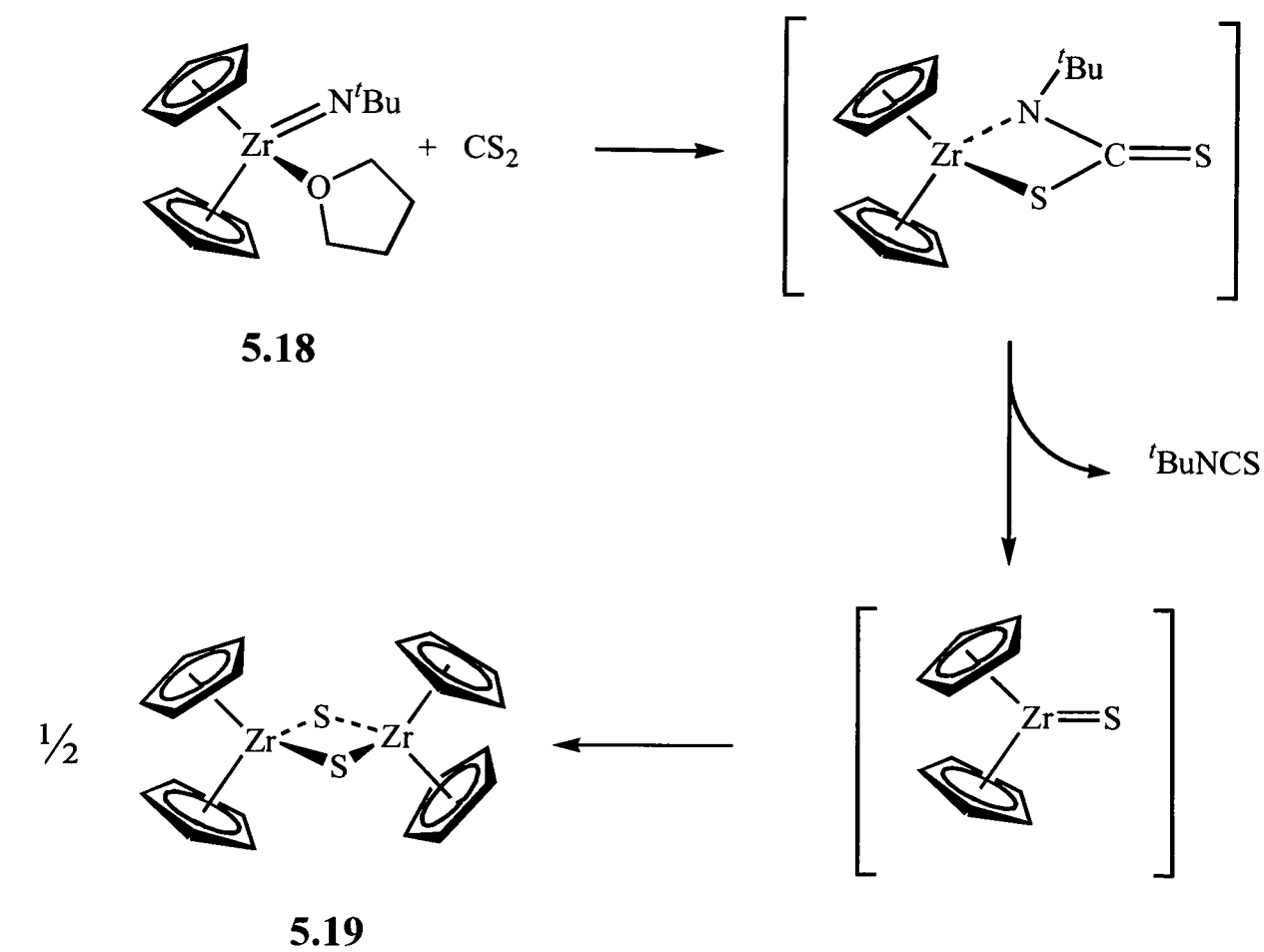
5.13 **5.15**

Equation 5.4

The reactions of COS or CS_2 with imido species have been little studied. The earliest study was carried out by West *et al.* on the paramagnetic chromium species Cr(TPP)N(-4-C_6H_4Me) (TPP = 5, 10, 15, 20 – tetraphenylporphyrin dianion) (**5.16**),[9] and showed the propensity of the imido group to undergo atom-transfer, yielding *p*-tolyl isothiocyanate and a product presumed to be a sulfido species. Identification of this product was complicated by the paramagnetic nature of the metal centre. More recently, Woo *et al.*[10] synthesised and characterised the related sulfido species Ti(TTP)(S) (TTP = *meso*-5,10,15,20-tetra-*p*-tolylporphyrinato dianion) (**5.17**) from the reaction of Ti(TTP)(η^2-3-hexyne) with CS_2.

Bergman[11] has shown that the zirconocene imido complex Zr(η-C_5H_5)$_2$(N^{t}Bu)(THF) (**5.18**) reacts immediately with CS_2 to afford the sulfido-bridged dimer [Zr(η-C_5H_5)$_2$(μ-S)]$_2$ (**5.19**) and *tert*-butyl isothiocyanate.

The most likely mechanism for this imido transfer reaction involves cycloaddition of CS_2 to the Zr=N^{t}Bu bond, followed by retrocyclisation to afford the isolated products, as shown in Scheme 5.1.

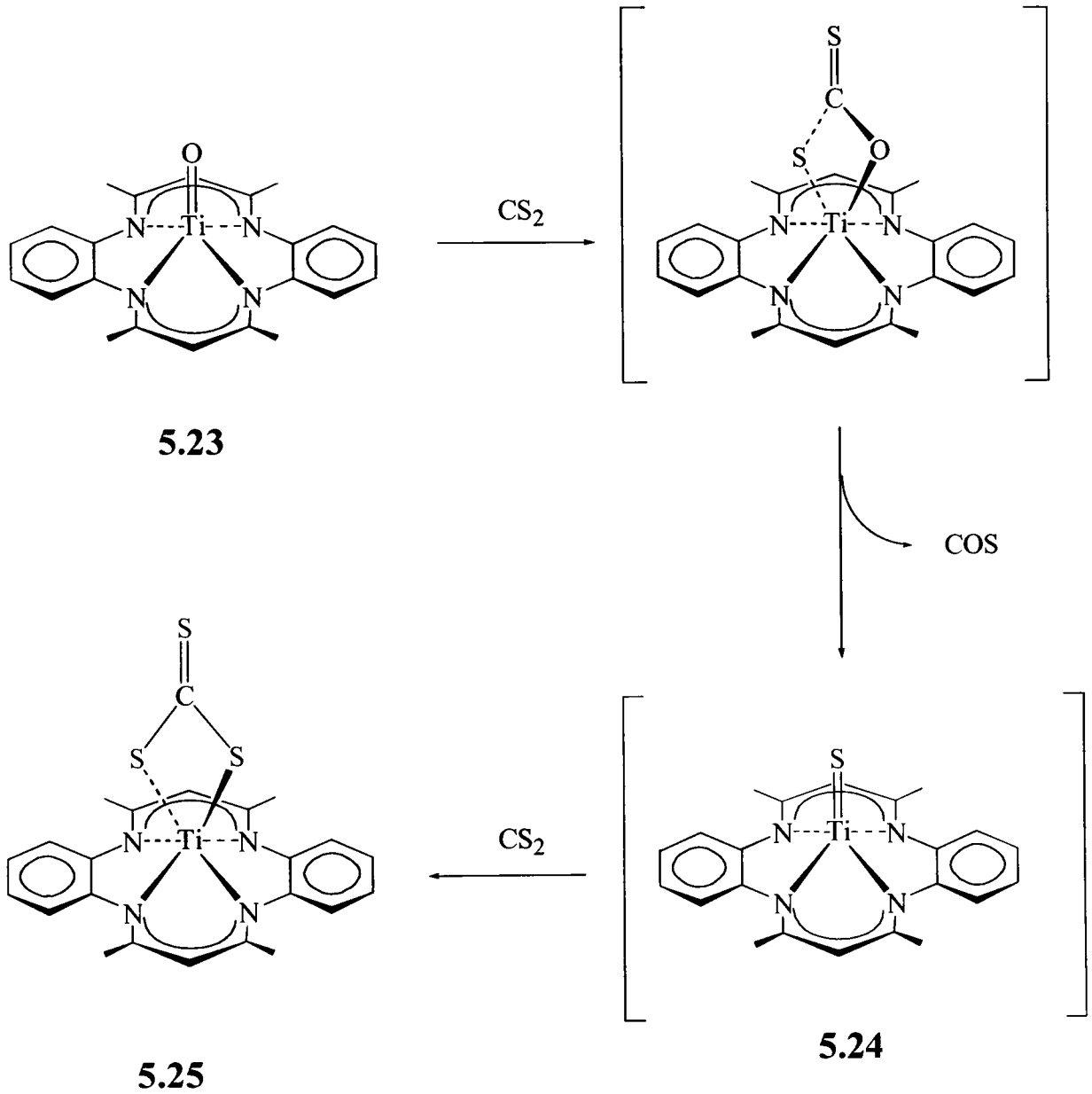


5.18 **5.19**

Scheme 5.1 – Reaction of $Zr(\eta\text{-}C_5H_5)_2(N^tBu)(THF)$ **(5.18)** with CS_2

The bis(pentamethylcyclopentadienyl) terminal sulfido species $Zr(\eta\text{-}C_5Me_5)_2(S)(py)$ **(5.20)** has been synthesised by Bergman, but by an alternative route involving dehydrohalogenation of $Zr(\eta\text{-}C_5Me_5)_2(SH)(I)$ **(5.21)** in the presence of pyridine.[12,13] It was the first report of a structurally characterised Group 4 sulfido compound. More recently, Arnold has reported the reaction of the titanium dinitrogen complex $[Ti\{PhC(NSiMe_3)_2\}]_2(\mu\text{-}N_2)$ with S_8 in the presence of pyridine and mercury to afford the structurally characterised terminal sulfido complex $Ti\{PhC(NSiMe_3)_2\}_2(S)(py)$ **(5.22)**.[14]

An interesting result is obtained from the reaction of CS_2 with the titanium oxo complex Ti(Me$_4$taa)(O) (**5.23**). The reaction occurs in two steps: first, a molecule of CS_2 reacts with the oxo *via* a cycloaddition / retrocyclisation mechanism to afford the terminal sulfido species Ti(Me$_4$taa)(S) (**5.24**) and COS. The second step involves cycloaddition of a second molecule of CS_2 to give the final product. This mechanism was confirmed by the independent reaction of Ti(Me$_4$taa)(S) with CS_2,[15] and is illustrated in Scheme 5.2.



5.23 **5.24** **5.25**

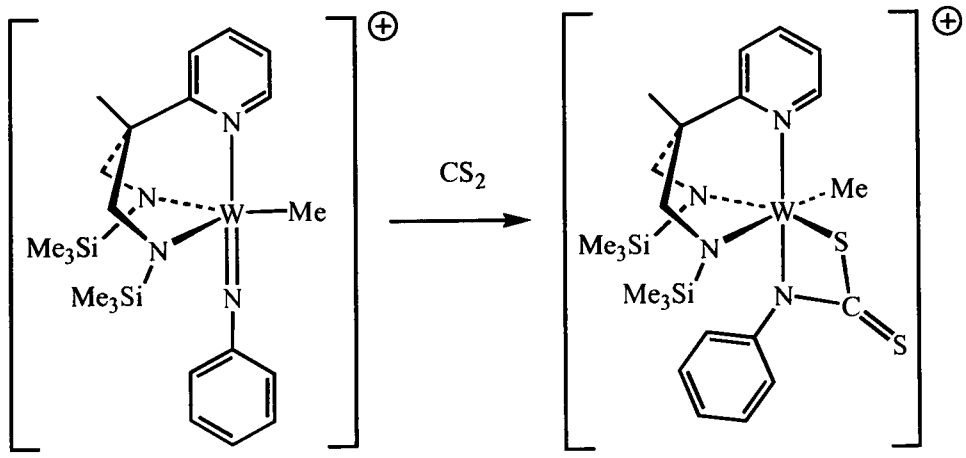
Scheme 5.2 – Reaction of Ti(Me$_4$taa)(O) (**5.23**) with CS_2

It was later shown that Ti(Me$_4$taa)(O) reacts more quickly with COS than CS_2, to afford the terminal sulfido complex Ti(Me$_4$taa)(S) and CO_2 by an

analogous apparent cycloaddition / retrocyclisation process.[16] This again shows that the formation of a strong C=O bond (in CO_2) provides the thermodynamic driving force for replacing Ti=O by Ti=S.

Interestingly, the complex $Ti(N_2N_{py})(N^tBu)(py)$ (N_2N_{py} = $(MeC(2\text{-}C_5H_4N)(CH_2NSiMe_3)_2)$ (**5.26**), in which the titanium centre is less sterically shielded that in macrocyclic systems, is found to be unreactive towards CS_2.[17] This contrasts strongly with its pronounced reactivity with stoichiometric CO_2 to afford a mixture of unidentified products.

The reaction of the cationic species $[W(N_2N_{py})(NPh)Me]^+$ (**5.27**) with CS_2 gives the cycloaddition product $[W(N_2N_{py})\{N(Ph)C(S)S\}Me]^+$ (**5.28**), analogous to the reaction of **5.27** with CO_2 (Equation 5.5).[18]



5.27 **5.28**

Equation 5.5

5.2.2 REACTIONS OF H_2S WITH METAL COMPLEXES

Reactions with H_2S tend to be more complicated than those with COS or CS_2, due to its ability to act as a Brønsted acid. This enables H_2S to react at a wider range of ligand sites, and thus tends to give mixtures of products.

The imidotitanocene complex $Ti(\eta\text{-}C_5H_5)_2(N^tBu)(py)$ (**5.29**) reacts with one equivalent of H_2S to afford the bridging dimeric complex $[Ti(\eta\text{-}C_5H_5)_2(\mu\text{-}S)]_2$ (**5.30**) and *tert*-butylamine.[19] This complex was found to react further with excess H_2S to afford the bis(thiol) complex $Ti(\eta\text{-}C_5H_5)_2(SH)_2$ (**5.31**), the synthesis of which had been previously reported by reaction of $Ti(\eta\text{-}C_5H_5)_2Cl_2$ with H_2S.[20] It was also found that stoichiometric reaction of $Ti(\eta\text{-}C_5H_5)_2(N^tBu)(py)$ with $Ti(\eta\text{-}C_5H_5)_2(SH)_2$ yielded $[Ti(\eta\text{-}C_5H_5)_2(\mu\text{-}S)]_2$ as a clean product along with *tert*-butylamine.

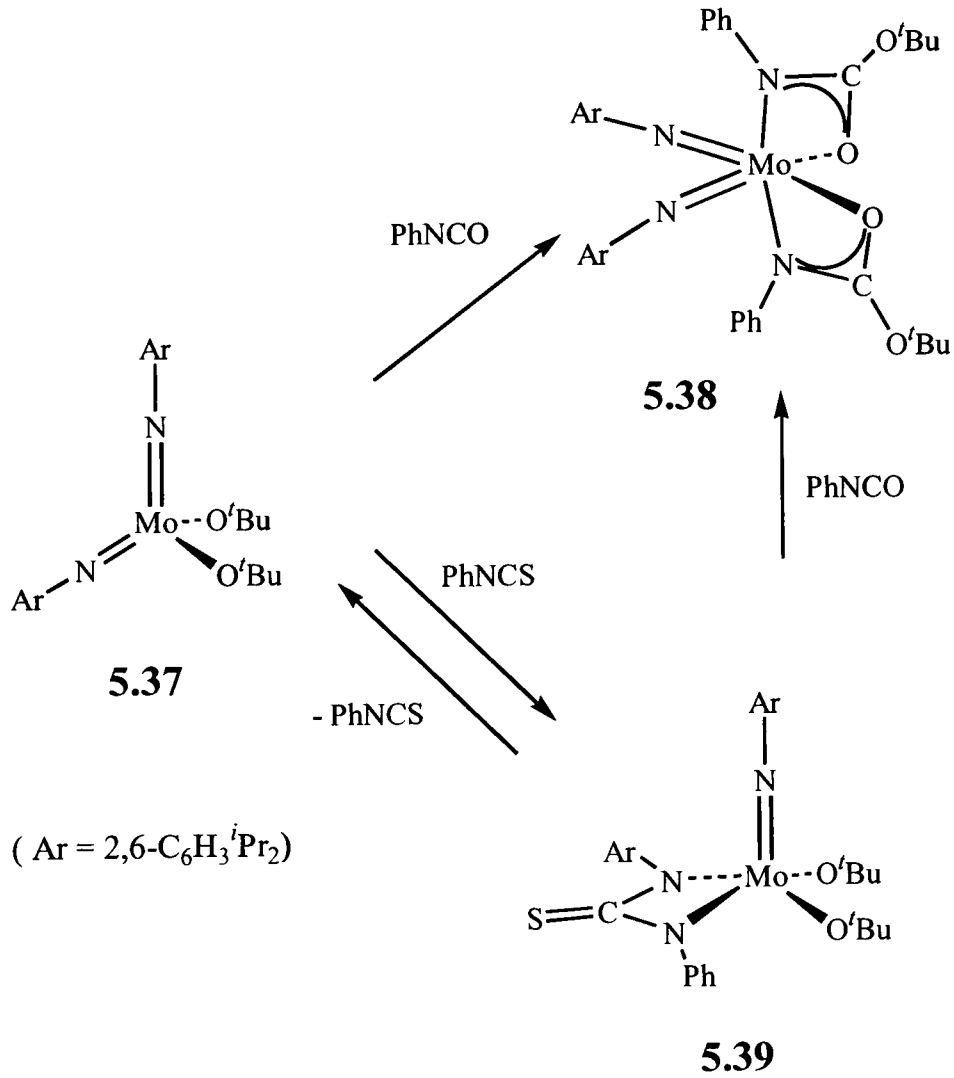
However, the use of H_2S as a means of sulfide formation is not of general applicability. Reaction of the ethylene complex $Ti(\eta\text{-}C_5Me_5)_2(\eta^2\text{-}C_2H_4)$ (**5.32**) with one equivalent of H_2S affords the terminal sulfide $Ti(\eta\text{-}C_5Me_5)_2(S)(py)$ (**5.33**) in low yield, with significant quantities of $Ti(\eta\text{-}C_5Me_5)_2(SH)_2$ (**5.34**).[21]

The most stable supporting ligand sets reported for reactions of H_2S with Group 4 metals have been the Me_ntaa (n = 4, 8) ligands. Reaction of the complex $Ti(Me_4taa)(N^tBu)$ (**5.35**) with excess H_2S afforded the sulfido product $Ti(Me_4taa)(S)$ (**5.36**) cleanly and rapidly.[22] This complex had been previously reported, but synthesised *via* a different route.[23]

5.2.3 REACTIONS OF ISOTHIOCYANATES WITH METAL COMPLEXES

There has been a dearth of studies carried out on isothiocyanates, particularly in view of the reports published on the chemistry of the isocyanates. It is noteworthy, however, that where reactions have been carried out, they do not typically proceed in the same fashion as those of their oxygen-bearing congeners.

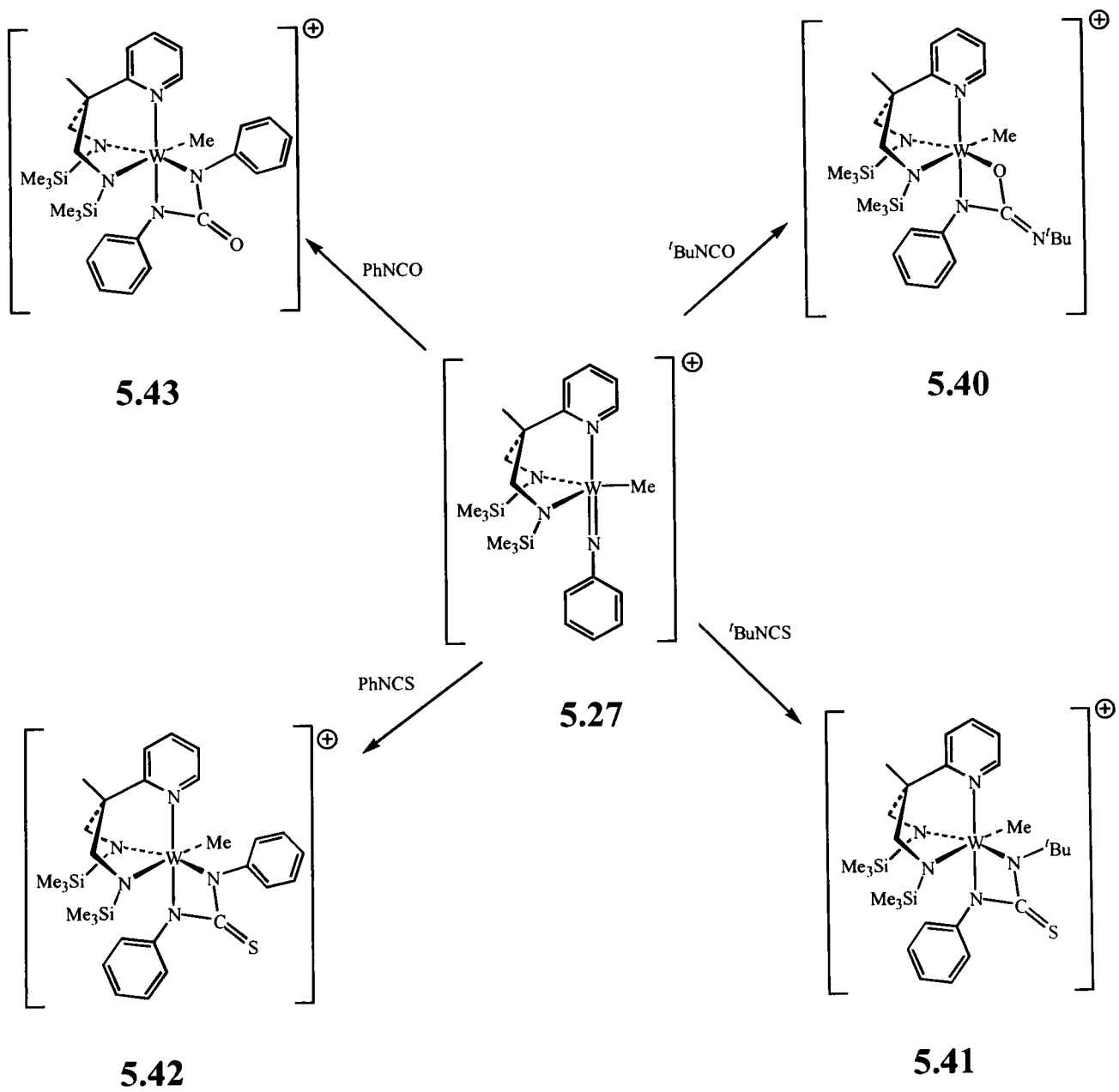
In 1994, Gibson reported the difference in behaviour between isocyanate and isothiocyanate insertion into alkoxo and imido bonds in a molybdenum complex.[24] The result is summarised in Scheme 5.3 below.



Scheme 5.3 – Reactions of Mo(N-2,6-C$_6$H$_3$^{i}Pr$_2$)$_2$(O^{t}Bu)$_2$ (**5.37**) with PhNCO and PhNCS

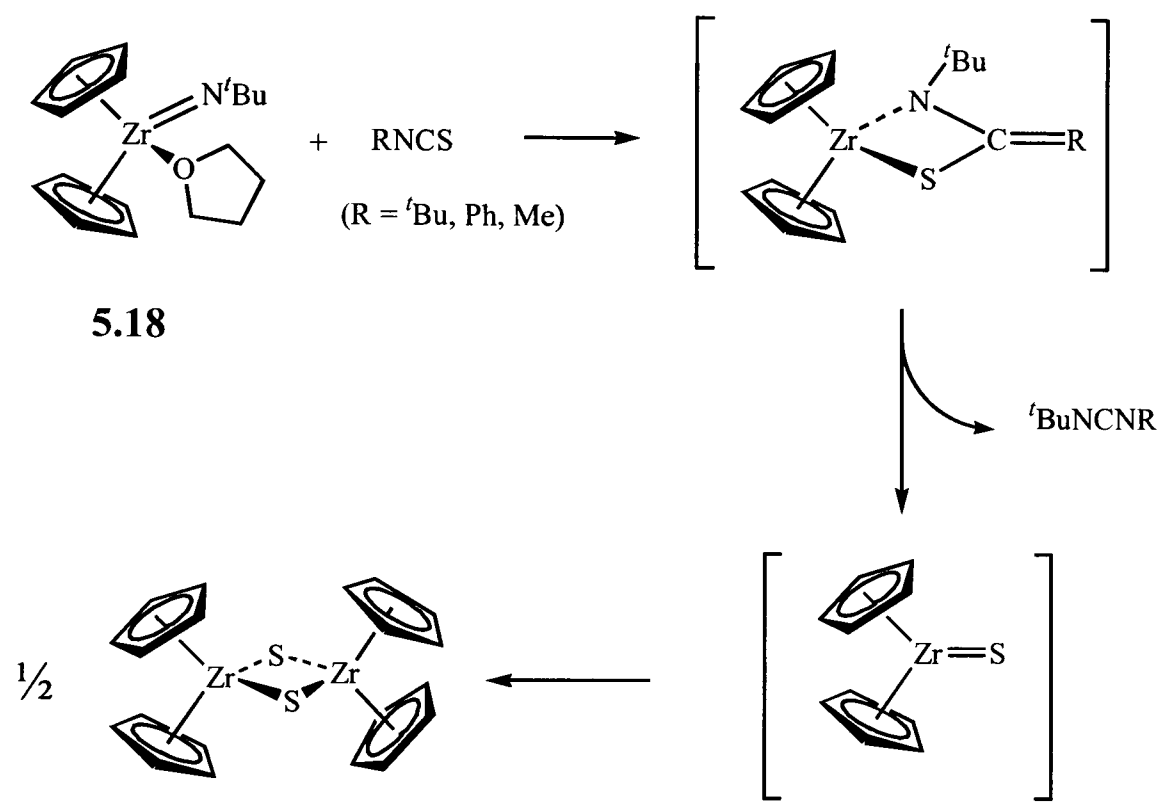
The isocyanate inserts selectively into the Mo–O bonds of the complex, whilst the isothiocyanate adds reversibly to one of the Mo–N bonds to give a N, N'-thioureate moiety. This work gave the first example of a structurally characterised N, N'- thioureate species, and also indicated that the imido ligand may be the kinetic site of attack by phenyl isocyanate.

Similar regioselectivity was found for the reactions of the cationic species $[W(N_2N_{py})(NPh)Me]^+$ **(5.27)** with *tert*-butyl isocyanate and *tert*-butyl isothiocyanate.[18] The product of reaction is also found to be dependent on the organic substituent of the heterocumulene (Scheme 5.4).



Scheme 5.4 – Reaction of $[W(N_2N_{py})(NPh)Me]^+$ **(5.27)** with isocyanates and isothiocyanates

In contrast to the N, N'- binding mode of the thioureate ligands in the above systems, some evidence has been found for the N, S- binding mode. Bergman[11] reported the reaction of the imidozirconocene complex $Zr(\eta\text{-}C_5H_5)_2(N^tBu)(THF)$ **(5.18)** with alkyl and aryl isothiocyanates to afford the dimeric sulfido-bridged complex $[Zr(\eta\text{-}C_5H_5)_2(\mu\text{-}S)]_2$ **(5.19)** and corresponding carbodiimide. The reaction was proposed to follow the same mechanistic pathway as that of CS_2, and is shown in Scheme 5.5.



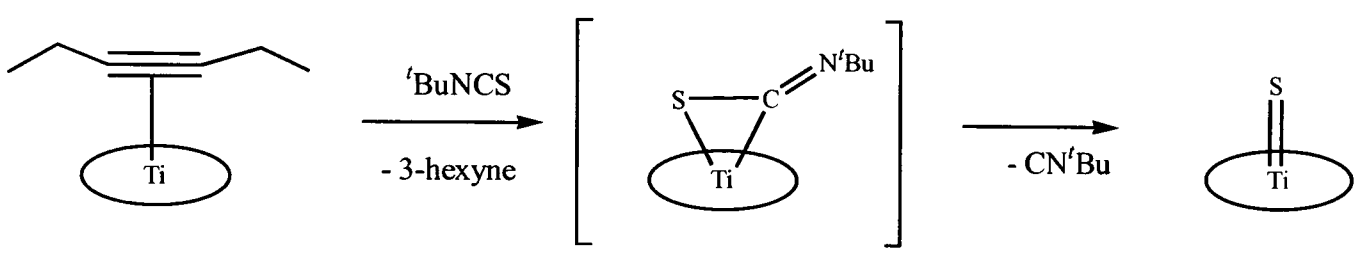
5.18 **5.19**

Scheme 5.5 – Reaction of $Zr(\eta\text{-}C_5H_5)_2(N^tBu)(THF)$ **(5.18)** with isothiocyanates

For the less sterically hindered methyl isothiocyanate, a second product was detected and tentatively identified as the N, N'- bound thioureate complex, but the complex was thermally unstable and could not be isolated.

Reaction of Ti(TTP)(η^2-3-hexyne) **(5.44)** with *tert*-butyl isothiocyanate was found to afford the sulfido complex Ti(TTP)(S) **(5.45)** and *tert*-butyl

isocyanide. This is in contrast to the reaction with *tert*-butyl isocyanate, which reacts to give the imido species Ti(TTP)(NR) (**5.46**) and CO.[10] Rather than [2 + 2] cycloadducts, the intermediates in these reactions are formulated as containing η^2-^{t}BuNCX (X = O, S) ligands, but with different binding modes, as shown in Scheme 5.6. The difference in reactivity is ascribed to the greater bond strength of C=O compared to that of C=S.

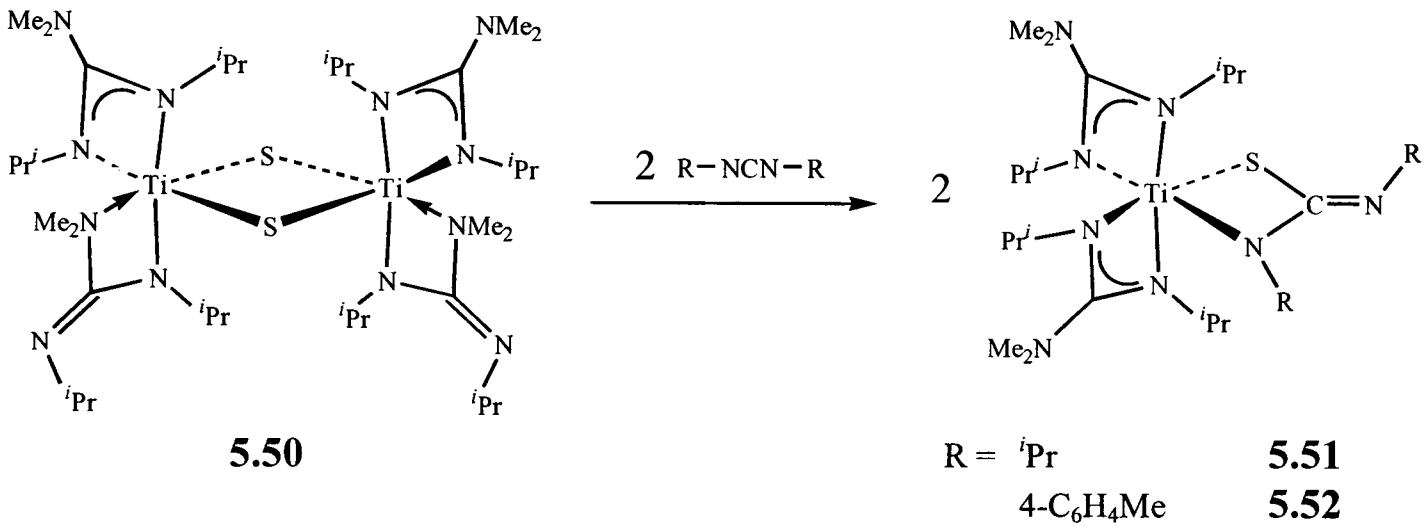


Scheme 5.6 – Reaction of Ti(TTP)(3-hexyne) with *tert*-butyl isocyanate and *tert*-butyl isothiocyanate

As in the case of CS_2, the complex Ti(N_2N_{py})(N^{t}Bu)(py) (**5.26**) was found to be unreactive towards isothiocyanates.[17] This is in marked contrast to the high reactivity of the species to isocyanates, which afford mixtures of products, except in the case of 2,6-di-*iso*-propylphenyl isocyanate, which affords the cycloaddition product Ti(N_2N_{py}){OC(N-2,6-$C_6H_3{}^iPr_2$)N(^{t}Bu)O}(py) (**5.47**).

The tetraazaannulene-supported titanium imido complex Ti(Me$_4$taa)(NPh) (**5.48**) was found to give a mixture of products on reaction with *tert*-butyl isothiocyanate, in contrast to the clean reaction with phenyl isocyanate to give the N, N'- bound ureate complex Ti(Me$_4$taa){N(Ph)C(O)N(Ph)} (**5.49**).[25]

Two examples of isolated and fully characterised N, S- thioureate complexes are the reaction products of a titanium sulfide with carbodiimides, reported by Bergman and Arnold.[26] The titanium centre is supported by a bis(guanidinate) ligand set. The reaction is shown in Equation 5.6.



Equation 5.6

5.3 REACTIONS OF TITANIUM CYCLOPENTADIENYL IMIDO AMIDINATE COMPLEXES WITH COS

This Section describes the reactivity of titanium cyclopentadienyl imido amidinate complexes with COS. The *tert*-butylimido complexes are addressed first, followed by the arylimido complexes.

5.3.1 REACTIONS OF *TERT*-BUTYLIMIDO COMPLEXES WITH COS

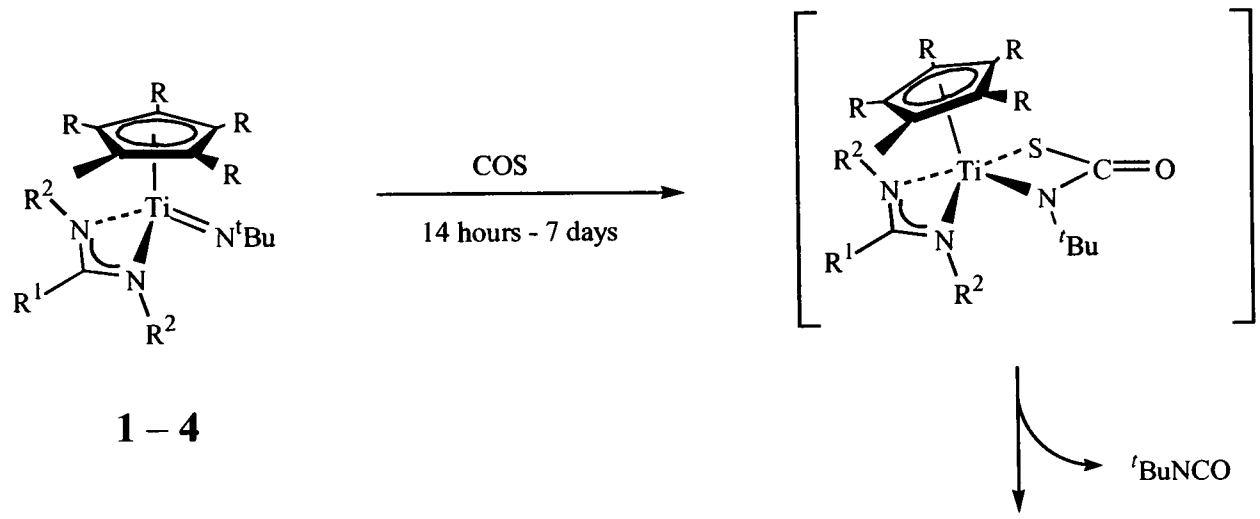
Samples of Ti(η-C_5Me_5)(N^{t}Bu){PhC(NSiMe$_3$)$_2$} (**1**), Ti(η-C_5Me_5)(N^{t}Bu){MeC(N^{i}Pr)$_2$} (**2**), Ti(η-C_5H_4Me)(N^{t}Bu){PhC(NSiMe$_3$)$_2$} (**3**) and Ti(η-C_5H_4Me)(N^{t}Bu){MeC(N^{i}Pr)$_2$} (**4**) were dissolved in benzene-d_6, degassed and exposed to COS at an absolute pressure of 500 mmHg. Reactions were monitored by ^{1}H NMR spectroscopy.

5.3.1.1 RESULTS AND DISCUSSION

The reactions were found to be slow, in contrast to those of CO_2, ranging from 7 days for **1** to less than 14 hours for **4**, as might be expected on steric grounds. The reactions were each found to afford a single clean product (complexes **58** – **61**), with no evidence for any intermediates being detected in the ^{1}H NMR spectra.

The products were isolated, and found to be the dimeric bridging-sulfido species [Ti(η-C_5Me_5)(μ-S){PhC(NSiMe$_3$)$_2$}]$_2$ (**58**), [Ti(η-C_5Me_5)(μ-S){MeC(N^{i}Pr)$_2$}]$_2$ (**59**), [Ti(η-C_5H_4Me)(μ-S){PhC(NSiMe$_3$)$_2$}]$_2$ (**60**) and [Ti(η-C_5H_4Me)(μ-S){MeC(N^{i}Pr)$_2$}]$_2$ (**61**). Apart from **58**, these were fully characterised by ^{1}H, and ^{13}C-{^{1}H} NMR and IR spectroscopies. **58** was found to be insoluble in all solvents tried, and so NMR data could not be obtained. The ^{1}H NMR spectra were consistent with the formation of a single product isomer, possessing C_{2h} symmetry. Unlike the analogous bridging-oxo species formed described in Chapter 3, no evidence was found for a cisoid C_{2v} isomer.

Satisfactory elemental analysis was obtained for all complexes except **61**. Parent ion peaks were detected in the EI mass spectra of **59** (*m/z* = 712, $[M]^+$), **60** (*m/z* = 844, $[M]^+$), and **61** (*m/z* = 600, $[M]^+$), with a daughter ion peak (*m/z* = 812, $[M\text{-}C_5Me_5]^+$) being the highest peak in the spectrum of **58**. Compounds **58** and **60** have been structurally characterised. Analysis of the crude reaction mixtures by GC-MS confirmed the presence of *tert*-butyl isocyanate. The proposed reaction scheme is shown in Scheme 5.7.



1 – 4

58 – 61

	R	R^1	R^2	
1	Me	Ph	$SiMe_3$	**58**
2	Me	Me	^{i}Pr	**59**
3	H	Ph	$SiMe_3$	**60**
4	H	Me	^{i}Pr	**61**

Scheme 5.7 – Reactions of $Ti(\eta\text{-}C_5R_4Me)(N^tBu)\{R^1C(NR^2)_2\}$ **(1 – 4)** with COS

The reaction is proposed to occur *via* a mechanism analogous to that which occurs between the imido complexes and CO_2. The more sluggish first step with COS prevents sufficient build up of the thiocarbamate species to be detected in the ^1H NMR spectra of the reaction mixtures.

It is interesting to note the preference for the Ti–S bond formation over the stronger Ti–O bond; a result which parallels that reported by Geoffroy[16] for the reaction of the Ti(Me_4taa)(O) system with COS. This preference can be explained by the greater energy needed to break the C=O bond compared to the C=S bond. The greater basicity of the lone pairs on sulfur would also lower the energy of the transition state involved in the formation of the [2 + 2] cycloadduct, compared to the other possible isomer.

It is also possible that the cycloadduct of the imido bond with the C=O linkage of COS does form, but that the retrocyclisation step prefers to regenerate the starting materials rather than give the oxo and isothiocyanate species. By this argument, the kinetically favoured process would be reaction with the carbonyl linkage, but reaction with the thiocarbonyl affords the thermodynamic product *via* an irreversible process. This suggestion has been made for other reactions, where competition between oxygen- and sulfur-containing substrates arises.[24]

5.3.1.2 X-RAY CRYSTAL STRUCTURE OF [Ti(η-C_5Me_5)(μ-S){PhC($NSiMe_3$)$_2$}]$_2$ (58)

A dark red block of **58** suitable for analysis by single crystal X-ray diffraction was grown from a saturated solution in pentane at -30 °C. The data were collected by the author, and the structure solved by Dr. P. Mountford. Table 5.1 summarises some important bond lengths and angles, and Figure 5.1 shows the molecular structure of the complex. Full details are provided in Appendix L.

Table 5.1 – Selected bond lengths (Å) and angles (°) for Ti(η-C_5Me_5)(μ-S){PhC($NSiMe_3$)$_2$}]$_2$ (**58**).

Ti(1) – $Cp_{(cent)}$	2.101	$Cp_{(cent)}$ – Ti(1) – S(1)	113.6
Ti(1) – S(1)	2.259(1)	$Cp_{(cent)}$ – Ti(1) – S(1B)	113.6*
Ti(1) – S(1B)	2.259(1)*	$Cp_{(cent)}$ – Ti(1) – N(1)	111.2
Ti(1) – N(1)	2.193 (3)	$Cp_{(cent)}$ – Ti(1) – N(1B)	111.2*
Ti(1) – N(1B)	2.193 (3)*	Ti(1) – S(1) – Ti(1C)	43.78 (3)
		S(1) – Ti(1) – S(1B)	87.56 (7)
		S(1) – Ti(1) – N(1)	132.67 (9)
		S(1B) – Ti(1) – N(1B)	132.67 (9)*
		N(1) – Ti(1) – N(1B)	61.6 (2)

* Value generated by appropriate symmetry operator

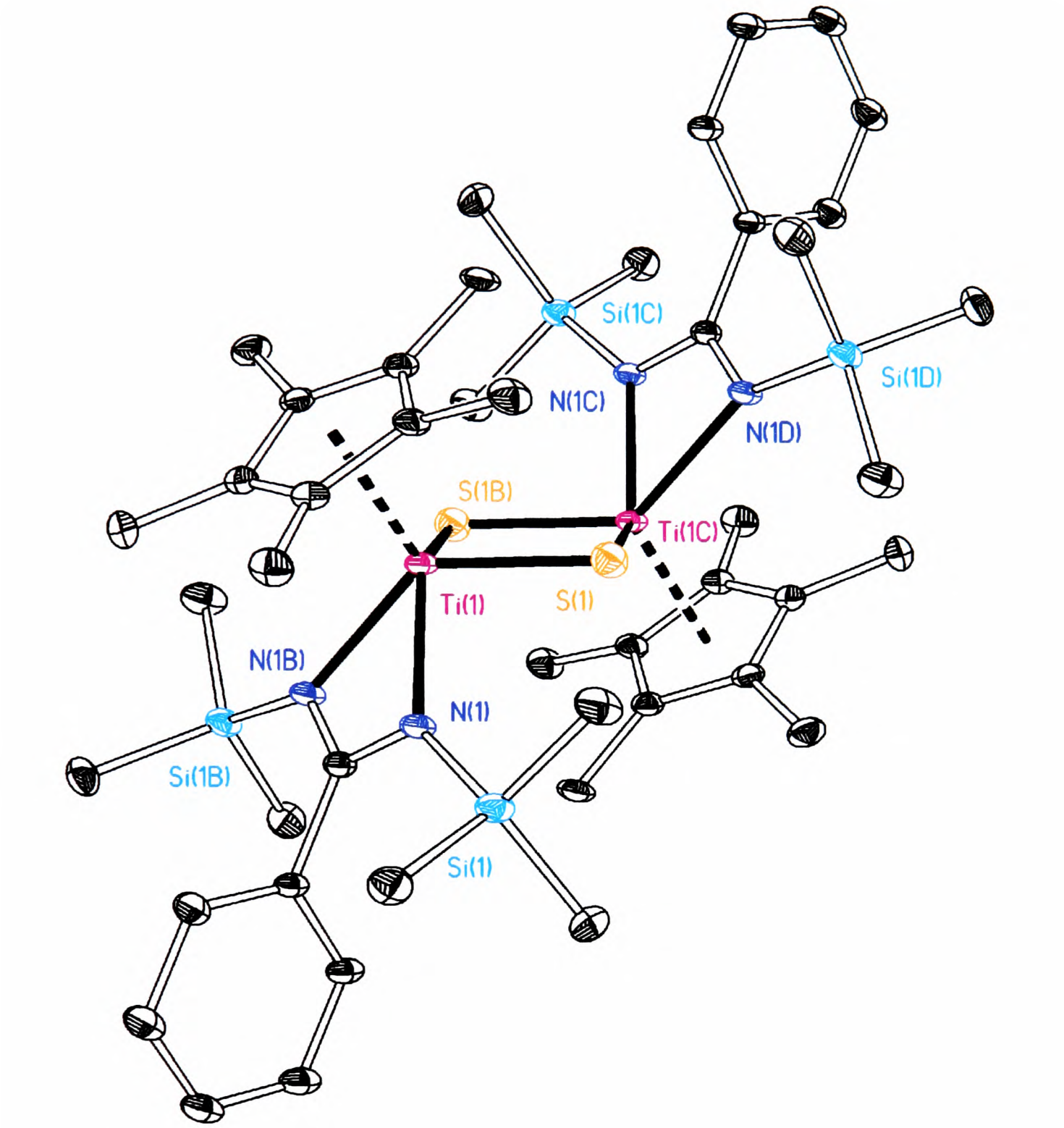


Figure 5.1 – Thermal ellipsoid plot (30 % probability) of [Ti(η-C_5Me_5)(μ-S){PhC($NSiMe_3$)$_2$}]$_2$ (**58**). H atoms omitted for clarity.

5.3.1.3 X-RAY CRYSTAL STRUCTURE OF [Ti(η-C_5H_4Me)(S){PhC($NSiMe_3$)$_2$}]$_2$ (60)

An orange block of **60** suitable for analysis by single crystal X-ray diffraction was grown from a saturated solution in benzene. The data were collected by

Dr. M. E. G. Skinner, and the structure solved by Dr. P. Mountford. Figure 5.2 shows the molecular structure, and Table 5.2 summarises some important bond lengths and angles. Full details are provided in Appendix M.

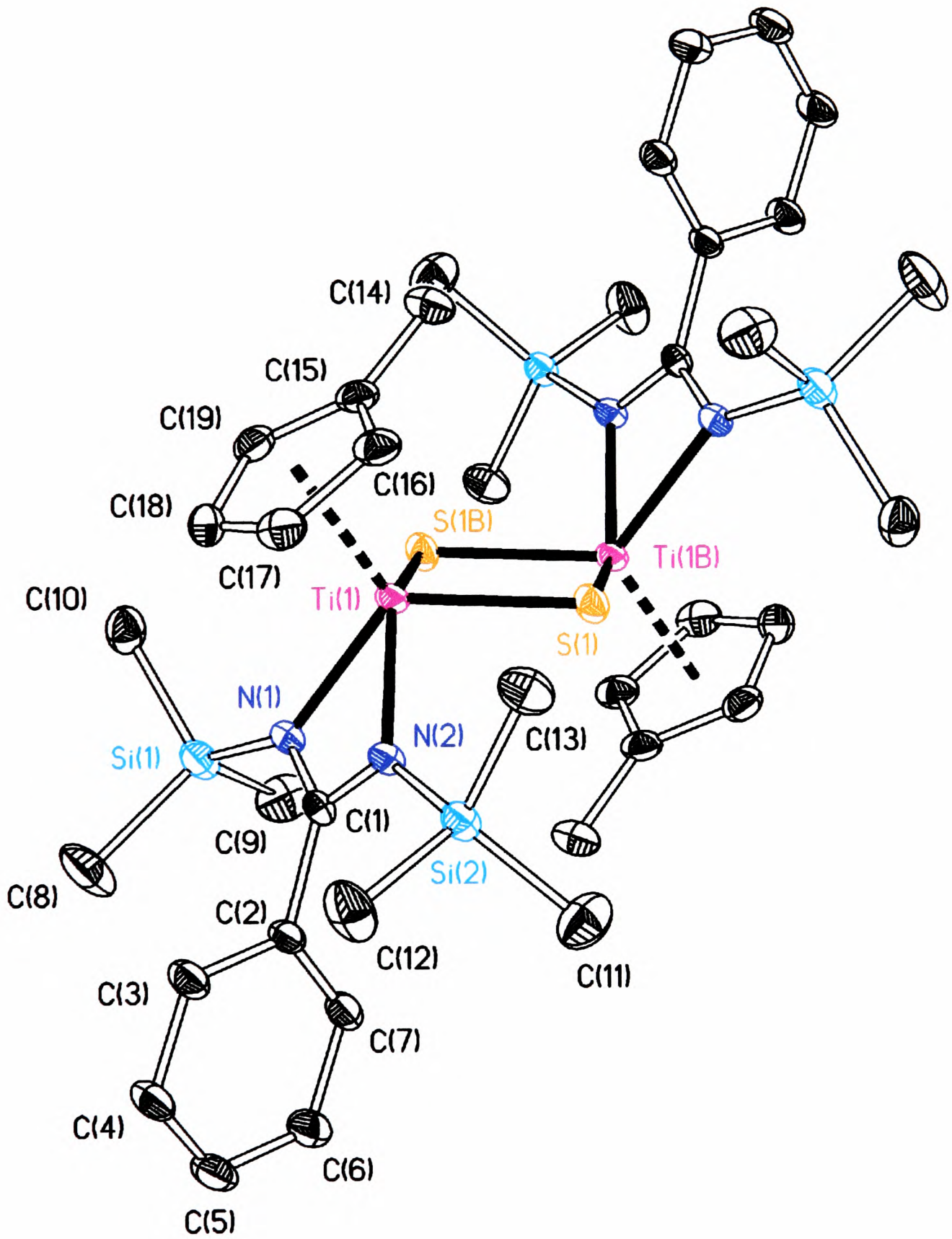


Figure 5.2 – Thermal ellipsoid plot (30 % probability) of $[Ti(\eta\text{-}C_5H_4Me)(\mu\text{-}S)\{PhC(NSiMe_3)_2\}]_2$ (**60**). H atoms omitted for clarity.

Table 5.2 – Selected bond lengths (Å) and angles (°) for [Ti(η-C_5H_4Me)(μ-S){$PhC(NSiMe_3)_2$}]$_2$ (**60**).

Ti(1) – $Cp_{(cent)}$	2.061	$Cp_{(cent)}$ – Ti(1) – S(1)	119.3
Ti(1) – S(1)	2.304(1)	$Cp_{(cent)}$ – Ti(1) – S(1B)	110.1
Ti(1) – S(1B)	2.363(1)	$Cp_{(cent)}$ – Ti(1) – N(1)	112.5
Ti(1) – N(1)	2.135(3)	$Cp_{(cent)}$ – Ti(1) – N(2)	108.2
Ti(1) – N(2)	2.197(3)	Ti(1) – S(1) – Ti(1B)	91.73(4)
		S(1) – Ti(1) – S(1B)	88.27(4)
		S(1) – Ti(1) – N(2)	86.39(8)
		S(1B) – Ti(1) – N(1)	88.89(8)
		N(1) – Ti(1) – N(2)	62.1(1)

5.3.1.4 Comparison of the structures of 58 and 60

Both complexes adopt a four-legged piano stool structure about the metal centres. The bonds between the metal centre and the amidinate ligand are longer than those of the imido complexes Ti(η-C_5H_4Me)(N^{t}Bu){$PhC(NSiMe_3)_2$} (**3**) and Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$){$PhC(NSiMe_3)_2$} (**14**) (Ti(1)–$N_{amidinate}$: 2.193(3) Å (**58**) cf. 2.107(2), 2.134(2) Å (**14**); 2.135(3) Å, 2.197(3) Å (**60**) cf. 2.098(2) Å, 2.111(2) Å (**3**)), reflecting the greater steric crowding present in the dimers. The bond between the titanium and the cyclopentadienyl ligand is longer in **58** than in **14** ($Cp_{(cent)}$–Ti(1): 2.101 Å (**58**) cf. 2.079 Å (**14**)) as expected, but the bond in **60** is shorter ($Cp_{(cent)}$–Ti(1): 2.061 Å (**60**) cf. 2.079 Å (**14**)). This may be due to the reorientation of the methyl group on the methylcyclopentadienyl ring, which is now directed away from the amidinate and over the bridging sulfur atoms. All bond lengths between titanium and the ancillary ligands are within the ranges reported for

other crystallographically determined Ti(IV) complexes ($Cp_{(cent)}$–Ti: 2.0 – 2.1 Å, Ti–$N_{amidinate}$: mean: 2.148 Å, range: 2.056 – 2.395 Å for 30 complexes).[27,28] The Ti(1)–S bonds are longer in **60** than in **58** (2.304(1), 2.363(1) Å cf. 2.259(1) Å), which may be due to unfavourable steric interactions between the sulfur atoms and the methyl group of the methylcyclopentadienyl ligand in **60**. The Ti(1)–S bonds fall within the range reported for other structurally characterised Ti(IV) sulfido complexes (mean: 2.352 Å, range: 2.254 – 2.427 Å for 9 compounds).[27,28]

5.3.1.5 Comparison of the structures of [Ti(η-C_5H_4Me)(μ-O){$PhC(NSiMe_3)_2$}]$_2$ (24) and [Ti(η-C_5H_4Me)(μ-S){$PhC(NSiMe_3)_2$}]$_2$ (60)

The sulfido species are structurally very similar to the congeneric dimeric oxo species. The only significant difference is the orientation of the methylcyclopentadienyl rings in **24** and **60**; the methyl group lies over the amidinate ligand in the oxo system as it does in the parent imido complex, while in the sulfido complex it lies over the sulfur ligands.

The bonds between titanium and the ancillary ligand set are shortened in the sulfido complex by 0.02 Å. This can be explained in terms of less crowding from the bridging ligands, with the Ti–S bonds being longer by *ca.* 0.5 Å than Ti–O. The arrangement of the four-membered metallacycle more closely resembles a square in **60** (angles: 91.73(4) ° and 88.27(4) °) than in **24**, in which the oxygen atoms lie closer together (angles: 97.01(4) ° and 82.99(4) ° respectively).

It is also interesting to note that while the oxo species forms two isomers (*cis* and *trans* with respect to the cyclopentadienyl ring orientation in the dimer), the sulfido species show no evidence of this. Comparison of the Ti ... Ti distances in the two systems reveals that the spacing between the metal centres is 3.350(4) Å in the sulfido and 2.7717(4) Å in the oxo. This would seem to suggest that isomerism would be more likely for the sulfido species than for the oxo.

The reason why isomerism is not observed for the bridging sulfido species is not obvious. The thermodynamic driving force to convert Ti=S into two Ti–S bonds is expected to be higher than that of Ti=O into two Ti–O bonds. This is due to the poorer π-overlap between Ti and S in Ti=S than between Ti and O in Ti=O, and the lower steric repulsion of a S–Ti–S bridge *versus* O–Ti–O. The cisoid dimer **24a** has already been shown to be a kinetic product, so a more rapid dimerisation of a transient terminal sulfido complex $Ti(\eta\text{-}C_5R_4Me)(S)\{R^1C(NR^2)_2\}$ would be expected to give a more equal mixture of *cis* and *trans* isomers.

To investigate the possibility of synthesising the mixed sulfido-oxo system $Ti_2(\eta\text{-}C_5H_4Me)_2(\mu\text{-}O)(\mu\text{-}S)\{PhC(NSiMe_3)_2\}_2$, a stoichiometric quantity of $[Ti(\eta\text{-}C_5H_4Me)(\mu\text{-}O)\{PhC(NSiMe_3)_2\}]_2$ **(24)** and $[Ti(\eta\text{-}C_5H_4Me)(\mu\text{-}S)\{PhC(NSiMe_3)_2\}]_2$ **(60)** were dissolved in benzene-d_6 and heated to 80 °C for 16 hours. No reaction was observed, and further heating gave only decomposition products.

5.3.2 REACTIONS OF ARYLIMIDO COMPLEXES WITH COS

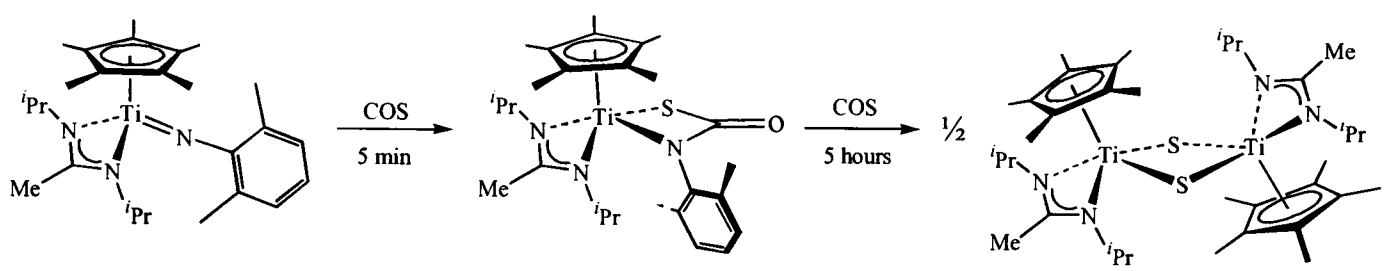
Samples of Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$){MeC(N^{i}Pr)$_2$} (**7**) and Ti(η-C_5Me_5)(N-4-C_6H_4Me){MeC(N^{i}Pr)$_2$} (**8**) were dissolved in benzene-d_6, degassed, and exposed to COS at an absolute pressure of 500 mmHg. The reactions were followed by ^{1}H NMR spectroscopy.

5.3.2.1 RESULTS AND DISCUSSION

In contrast to the reactions of an excess of COS with the *tert*-butylimido complexes, reaction with the aryl systems was found to be much more rapid. A colour change from green to brown was observed in both reactions in *ca.* 20 seconds, and the ^{1}H NMR spectra recorded after 5 minutes showed almost total consumption of imido starting material in both cases. Formation of new complexes which possessed no planes of symmetry were observed, which were found to decompose on standing in solution to give the sulfido species [Ti(η-C_5Me_5)(μ-S){MeC(N^{i}Pr)$_2$}]$_2$ (**59**), and 2,6-dimethylphenyl isocyanate or *p*-tolyl isocyanate respectively. The isocyanates were identified by comparison with ^{1}H NMR spectra of commercially obtained samples.

The nature of the arylimido N-substituent was found to influence the stability of the intermediate product. In the reaction of COS with Ti(η-C_5Me_5)(N-4-C_6H_4Me){MeC(N^{i}Pr)$_2$} (**8**), decomposition of the intermediate complex to the sulfido was well advanced before all the imido starting material had completely reacted. Isolation of this complex was therefore not possible under these conditions. However, the more bulky imido complex Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$){MeC(N^{i}Pr)$_2$} (**7**) afforded a product which was clean by ^{1}H

NMR after 5 minutes reaction time, before detectable decomposition had occurred. This complex was isolated and identified as the cycloadduct $Ti(\eta\text{-}C_5Me_5)\{N(\text{-}2,6\text{-}C_6H_3Me_2)C(O)S\}\{MeC(N^iPr)_2\}$ (**62**). This is summarised in Scheme 5.8. Decomposition to the bridging sulfido species was also found to occur in solution in the absence of excess COS.



Scheme 5.8 – Reaction of $Ti(\eta\text{-}C_5Me_5)(N\text{-}2,6\text{-}C_6H_3Me_2)\{MeC(N^iPr)_2\}$ (**7**) with COS

The thiocarbamate species **62** was characterised by ^1H, and $^{13}C\text{-}\{^1H\}$ NMR, and IR spectroscopies, and elemental analysis. The N, S- binding mode of the thiocarbamate ligand was proposed on the basis of the final reaction products, and confirmed by the presence of a ν(C=O) stretching mode at 1672 cm^{-1} in the IR spectrum of the complex. The analogous stretching mode is observed in the carbamate complex $Ti(\eta\text{-}C_5Me_5)\{N(\text{-}2,6\text{-}C_6H_3Me_2)C(O)O\}\{MeC(N^iPr)_2\}$ (**27**) (ν = 1669 cm^{-1}), but is absent in the related dithiocarbamate complex (*vide infra*).

It is interesting to compare this reactivity with that displayed towards CO_2. Exposure of $Ti(\eta\text{-}C_5Me_5)(N\text{-}2,6\text{-}C_6H_3Me_2)\{MeC(N^iPr)_2\}$ (**7**) to CO_2 results in the immediate formation of the carbamate complex **27**, which undergoes

further reaction in the presence of excess CO_2 to give the arylimido dicarboxylate complex $Ti(\eta\text{-}C_5Me_5)\{OC(O)N(\text{-}2,6\text{-}C_6H_3Me_2)C(O)O\}\{MeC(N^iPr)_2\}$ (**31**). By contrast, **7** reacts with COS to afford the thiocarbamate complex **62**, but this complex is unreactive towards excess COS. Instead, $Ti(\eta\text{-}C_5Me_5)\{N(\text{-}2,6\text{-}C_6H_3Me_2)C(O)S\}\{MeC(N^iPr)_2\}$ (**62**) rapidly undergoes retrocyclisation to give the bridging sulfido complex $[Ti(\eta\text{-}C_5Me_5)(\mu\text{-}S)\{MeC(N^iPr)_2\}]_2$ (**59**) and 2,6-dimethylphenyl isocyanate. This process is even faster in the case of $Ti(\eta\text{-}C_5Me_5)(N\text{-}4\text{-}C_6H_4Me)\{MeC(N^iPr)_2\}$ (**7**); lower steric bulk in the *ortho* positions of the aryl ring presumably lowering the energy of the transition state for retrocyclisation.

It was noted in the previous Chapter that the 2,6-disubstituted aryl system did not insert a second molecule of substrate with the exception of reaction with CO_2. This was attributed to steric considerations, and explains why no such reactivity is observed for **62**. The adduct formed by the reaction of COS and $Ti(\eta\text{-}C_5Me_5)(N\text{-}4\text{-}C_6H_4Me)\{MeC(N^iPr)_2\}$ (**8**) might be expected to be more disposed to undergo subsequent further reaction; its instability however prevents such a reaction taking place before it undergoes retrocyclisation.

5.4 REACTIONS OF TITANIUM CYCLOPENTADIENYL IMIDO AMIDINATE COMPLEXES WITH CS_2

This Section describes the reactivity of titanium cyclopentadienyl imido amidinate complexes with CS_2. The *tert*-butylimido complexes are addressed first, followed by the arylimido complexes.

5.4.1 REACTIONS OF *TERT*-BUTYLIMIDO COMPLEXES WITH CS_2

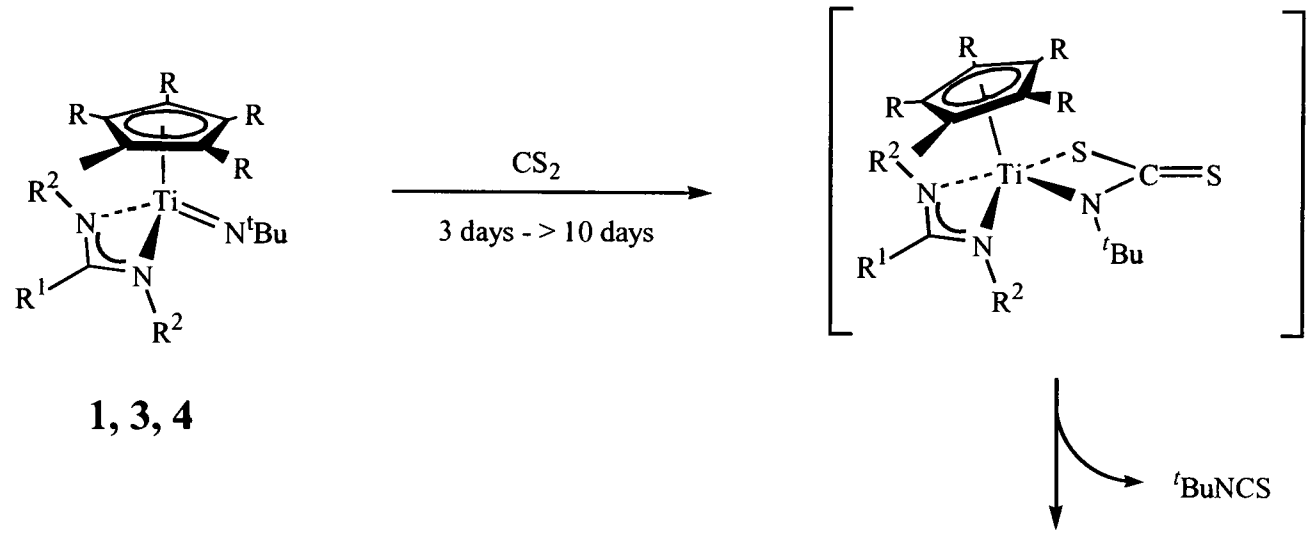
Samples of Ti(η-C_5Me_5)(N^{t}Bu){PhC(NSiMe$_3$)$_2$} (**1**), Ti(η-C_5Me_5)(N^{t}Bu){MeC(N^{i}Pr)$_2$} (**2**), Ti(η-C_5H_4Me)(N^{t}Bu){PhC(NSiMe$_3$)$_2$} (**3**) and Ti(η-C_5H_4Me)(N^{t}Bu){MeC(N^{i}Pr)$_2$} (**4**) were dissolved in benzene-d_6, and treated with an excess (over ten equivalents) of CS_2. Reactions were monitored using ^{1}H NMR spectroscopy.

5.4.1.1 RESULTS AND DISCUSSION

The reactions with CS_2 were found to be much slower than those with COS. Reaction times ranged from more than 10 days for Ti(η-C_5Me_5)(N^{t}Bu){PhC(NSiMe$_3$)$_2$} (**1**) to *ca.* 3 days for Ti(η-C_5H_4Me)(N^{t}Bu){MeC(N^{i}Pr)$_2$} (**4**). Heating the reaction mixtures of **1** and Ti(η-C_5Me_5)(N^{t}Bu){MeC(N^{i}Pr)$_2$} (**2**) to 80 °C for 2 days accelerated the rate, but caused decomposition to occur. Performing the reactions in the absence of light was not found to affect the products of reaction.

The reaction products of **1**, **3** and **4** were found to be the bridging sulfido species [Ti(η-C_5Me_5)(μ-S){PhC(NSiMe$_3$)$_2$}]$_2$ (**58**), [Ti(η-C_5H_4Me)(μ-S)

$\{PhC(NSiMe_3)_2\}]_2$ **(60)** and $[Ti(\eta\text{-}C_5H_4Me)(\mu\text{-}S)\{MeC(N^iPr)_2\}]_2$ **(61)** respectively, with concomitant formation of *tert*-butyl isothiocyanate. No intermediates were observed in the reactions, the parent imido complex being converted cleanly into the sulfido species. These reactions are analogous to those of COS, and are summarised in Scheme 5.9.



1, 3, 4

58, 60, 61

	R	R^1	R^2	
1	Me	Ph	$SiMe_3$	**58**
3	H	Ph	$SiMe_3$	**60**
4	H	Me	^iPr	**61**

Scheme 5.9 – Reaction of $Ti(\eta\text{-}C_5R_4Me)(N^tBu)\{R^1C(NR^2)_2\}$ **(1, 3, 4)** with CS_2

In contrast to this, it was found that $Ti(\eta\text{-}C_5Me_5)(N^tBu)\{MeC(N^iPr)_2\}$ **(2)** does not undergo the same reaction. The ^1H NMR spectrum showed the

formation of *tert*-butyl isothiocyanate, but the remaining peaks did not correspond to those of $[Ti(\eta\text{-}C_5Me_5)(\mu\text{-}S)\{MeC(N^iPr)_2\}]_2$ (**59**) (see Figure 5.3) Instead, a pair of septets was evident at 5.2 and 3.4 ppm, demonstrating that the product does not possess a plane of mirror symmetry.

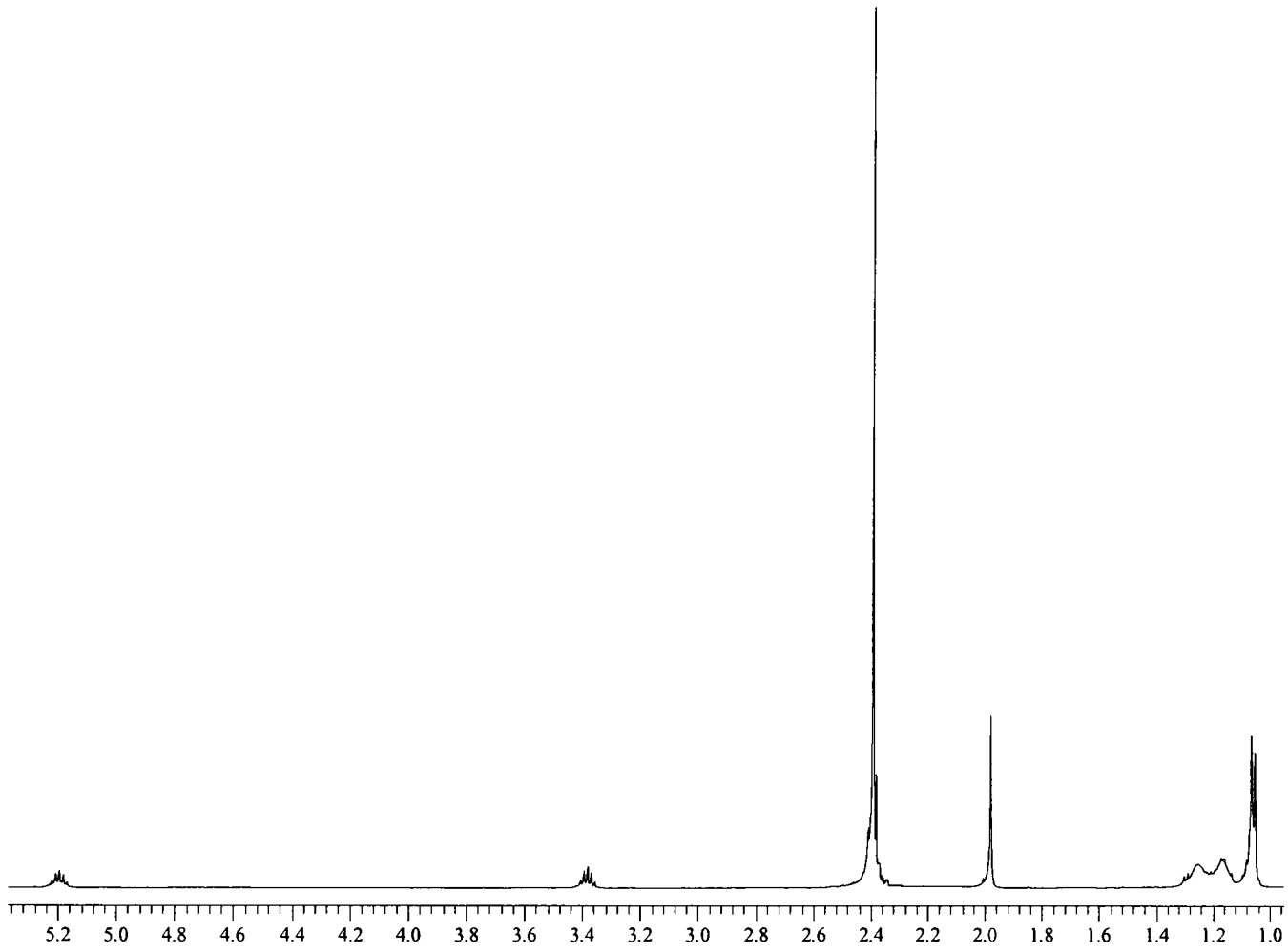


Figure 5.3 – 500.0 MHz ^1H NMR spectrum of $[Ti(\eta\text{-}C_5Me_5)(\mu\text{-}S)\{N(^iPr)C(Me)N(^iPr)C(S)S\}]_2$ (**63**) in benzene-d_6

The product was isolated and characterised as $[Ti(\eta\text{-}C_5Me_5)(\mu\text{-}S)\{N(^iPr)C(Me)N(^iPr)C(S)S\}]_2$ (**63**) by ^1H and $^{13}C\text{-}\{^1H\}$ NMR and IR spectroscopies. The virtual septet at 5.19 ppm is assigned as the methine proton of the *iso*-propyl group adjacent to the inserted CS_2 group, and the virtual septet at 3.38 ppm is assigned as the methine proton of the *iso*-propyl group adjacent to the titanium centre. Heating a sample in toluene-d_8 resulted

in coalescence of the peaks between 1.0 and 1.4 ppm into a pair of doublets, but cooling of the sample to -90 °C did not afford a clear decoalescence to four doublets. IR absorptions at 1398 cm^{-1} and 1357 cm^{-1} are within the range reported for a C=S stretch adjacent to a nitrogen atom. Satisfactory elemental analysis was obtained for the compound. Detection of a parent ion in the EI mass spectrum of the complex (*m/z* = 864, $[M]^+$) confirmed the proposed dimeric structure.

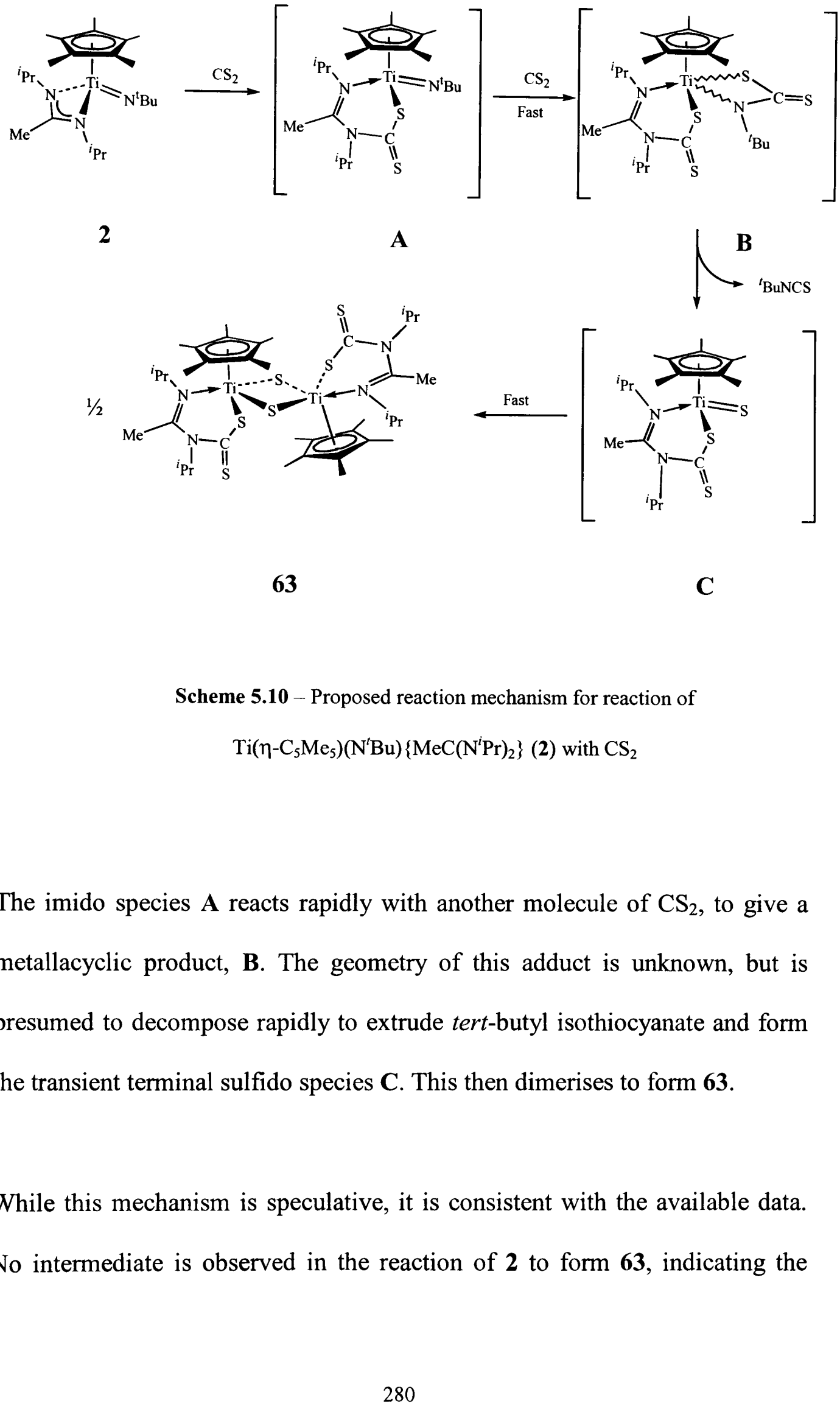
The product has been formed by attack of two molecules of CS_2 on the imido starting material. Further experiments were carried out in order to probe the mechanistic pathway of the reaction.

Treatment of the bridging sulfido complex $[Ti(\eta\text{-}C_5Me_5)(\mu\text{-}S)\{MeC(N^iPr)_2\}]_2$ **(59)** with CS_2 did not afford any reaction, with no evidence for **63** being observed in the ^1H NMR spectrum even after 3 weeks. Longer reaction times afforded only unidentified decomposition products.

Treatment of $Ti(\eta\text{-}C_5Me_5)(N^tBu)\{MeC(N^iPr)_2\}$ **(2)** with exactly one equivalent of CS_2 gave as the product of reaction a 2 : 1 : 2 ratio of **2**, **63**, and *tert*-butyl isothiocyanate respectively; *i.e.* **2** consumes two equivalents of CS_2 even when there is insufficient substrate for complete reaction.

These experiments are consistent with a mechanism in which the first CS_2 molecule inserts into the Ti–N bond of the amidinate ligand, to form a species

that is highly reactive towards further CS_2 attack at the imido function (**A**, see Scheme 5.10).



Scheme 5.10 – Proposed reaction mechanism for reaction of $Ti(\eta\text{-}C_5Me_5)(N^tBu)\{MeC(N^iPr)_2\}$ (**2**) with CS_2

The imido species **A** reacts rapidly with another molecule of CS_2, to give a metallacyclic product, **B**. The geometry of this adduct is unknown, but is presumed to decompose rapidly to extrude *tert*-butyl isothiocyanate and form the transient terminal sulfido species **C**. This then dimerises to form **63**.

While this mechanism is speculative, it is consistent with the available data. No intermediate is observed in the reaction of **2** to form **63**, indicating the

transient nature of all intermediates. Lack of reactivity of [Ti(η-C_5Me_5)(μ-S){$MeC(N^iPr)_2$}]$_2$ (**59**) with CS_2 indicates that the Ti–$N_{amidinate}$ bond is the first site of attack. The 2 : 1 ratio of starting material **2** to product **63** from the stoichiometric reaction of **2** with CS_2 demonstrates that the imido intermediate species **A** is more reactive towards CS_2 than **2**.

The reason why this reaction takes place rather than the expected [2 + 2] cycloaddition observed for the other three *tert*-butyl imides Ti(η-C_5Me_5)(N^tBu){$PhC(NSiMe_3)_2$} (**1**), Ti(η-C_5H_4Me)(N^tBu){$PhC(NSiMe_3)_2$} (**3**), and Ti(η-C_5H_4Me)(N^tBu){$MeC(N^iPr)_2$} (**4**) requires some explanation. Analysis of the Ti–$N_{amidinate}$ bond lengths in the crystal structures of Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$){$MeC(N^iPr)_2$} (**7**) and Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$){$PhC(NSiMe_3)_2$} (**14**) reveals that the $MeC(N^iPr)_2$ ligand is bonded more tightly to the metal centre than $PhC(NSiMe_3)_2$. This suggests that the nitrogens on the $PhC(NSiMe_3)_2$ ligand should be more prone to attack by the CS_2 than those of the $MeC(N^iPr)_2$. However, when the steric bulk of the group bound to the nitrogen is taken into consideration, it becomes more apparent why the amidinate ligands of **1** and **3** are not attacked by CS_2. The silyl groups act as an effective barrier to close approach of the CS_2 molecule, so only attack at the imide is observed.

The lack of insertion into the Ti–$N_{amidinate}$ bond of Ti(η-C_5H_4Me)(N^tBu){$MeC(N^iPr)_2$} (**4**) may be a kinetic result. The lower steric bulk of the C_5H_4Me ligand means that the approach to the imido group is less crowded, resulting in a faster rate of reaction at the imide than for Ti(η-C_5Me_5)

$(N^tBu)\{MeC(N^iPr)_2\}$ (**2**). This may mean that the preference for first attack is moved to the imido group in **4**, and once attack has occurred there no attack at the amidinate nitrogen is possible. The C_5Me_5 ligand is also more electron-releasing than C_5H_4Me, and so the amidinate nitrogens would be more basic in **2** than in **4**.

The question of why CO_2 and COS do not afford similar amidinate insertion products may be answered by the observations that (i) many systems reported in the literature undergo *reversible* insertion with oxo-bearing substrates, and *irreversible* insertion with sulfur-bearing substrates;[6,7,23,24,29] and (ii) some systems have been shown to undergo insertion reactions with CS_2 and not CO_2 or COS.[8] In the absence of evidence, it is impossible to state categorically whether insertion occurs with all three substrates but irreversibly only with CS_2, or insertion only occurs for CS_2. However, the sharpness of the lines in the ^1H NMR spectra of the reactions with CO_2 and COS suggest that if reversible insertion at the amidinate is occurring, it must be an extremely rapid process. On the basis of this, it seems more likely that the reaction is specific to CS_2, and only occurs with $Ti(\eta\text{-}C_5Me_5)(N^tBu)\{MeC(N^iPr)_2\}$ (**2**).

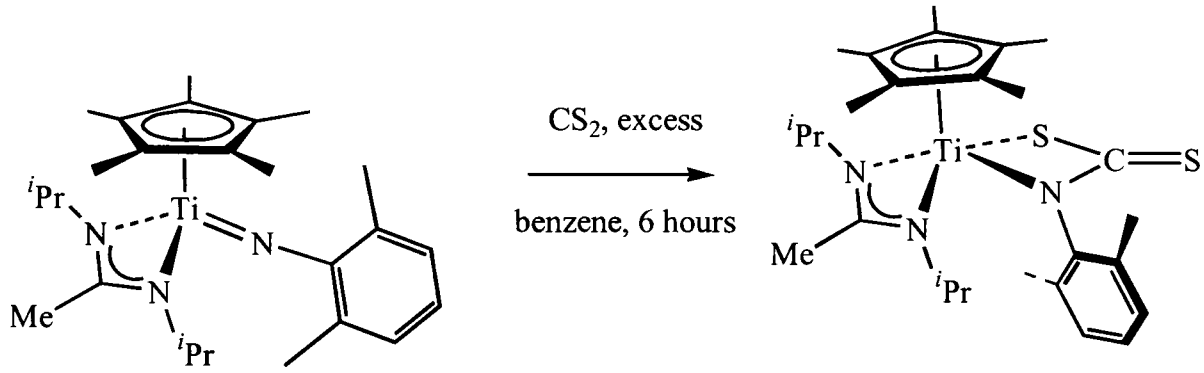
5.4.2 Reactions of Arylimido Complexes with CS_2

Samples of compounds $Ti(\eta\text{-}C_5Me_5)(N\text{-}2,6\text{-}C_6H_3Me_2)\{MeC(N^iPr)_2\}$ (**7**), $Ti(\eta\text{-}C_5Me_5)(N\text{-}4\text{-}C_6H_4Me)\{MeC(N^iPr)_2\}$ (**8**), and $Ti(\eta\text{-}C_5H_4Me)(N\text{-}2,6\text{-}C_6H_3Me_2)\{PhC(NSiMe_3)_2\}$ (**11**) were dissolved in aliquots of benzene-d_6 and treated with an excess (over ten equivalents) of CS_2. The reactions were monitored using ^1H NMR spectroscopy.

5.4.2.1 RESULTS AND DISCUSSION

The reactions of the arylimido complexes were much faster than those of the *tert*-butyl congeners. After 5 minutes, reaction was evident in all three cases, in contrast to the days required for Ti(η-C_5R_4Me)(N^tBu){$R^1C(NR^2)_2$} (**1 – 4**).

The reaction with Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$){$MeC(N^iPr)_2$} (**7**) showed evidence of formation of the expected dithiocarbamate within minutes of addition of CS_2. After 6 hours, all of the imido complex had been consumed to cleanly form a product which was isolated and identified as the dithiocarbamate complex Ti(η-C_5Me_5){N(-2,6-$C_6H_3Me_2$)C(S)S}{$MeC(N^iPr)_2$} (**64**) (Equation 5.7).



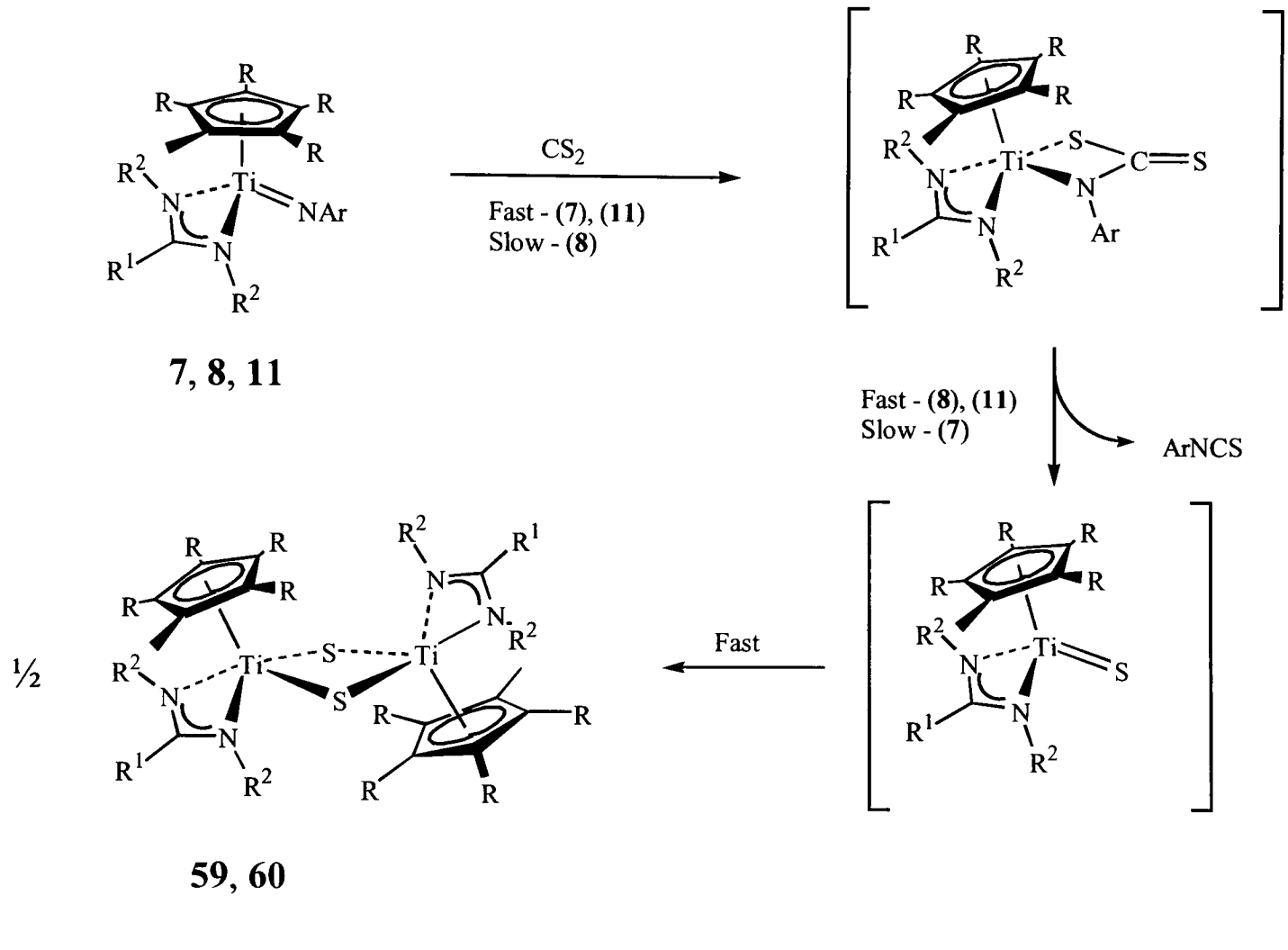
Equation 5.7

The dithiocarbamate complex was characterised by ^1H and ^{13}C-{^1H} NMR and IR spectroscopies, and satisfactory elemental analysis was obtained. The NMR data are closely related to those of the analogous carbamate Ti(η-C_5Me_5){N(-2,6-$C_6H_3Me_2$)C(O)O}{$MeC(N^iPr)_2$} (**27**) and thiocarbamate Ti(η-C_5Me_5){N(-2,6-$C_6H_3Me_2$)C(O)S}{$MeC(N^iPr)_2$} (**62**) discussed earlier. Ti(η-C_5Me_5){N(-2,6-$C_6H_3Me_2$)C(S)S}{$MeC(N^iPr)_2$} (**64**) was found to be

unstable in solution; decomposing to the sulfido complex $[Ti(\eta\text{-}C_5Me_5)(\mu\text{-}S)\{MeC(N^iPr)_2\}]_2$ (**59**) (1 : 1 ratio of **59** : **64** after 68 hours) with concomitant formation of the expected 2,6-dimethylphenyl isothiocyanate.

The reaction of $Ti(\eta\text{-}C_5H_4Me)(N\text{-}2,6\text{-}C_6H_3Me_2)\{PhC(NSiMe_3)_2\}$ (**11**) with CS_2 was found to be more rapid than that of **7**. The ^1H NMR spectrum recorded 5 minutes after CS_2 addition showed the complete consumption of the parent imido complex, and the formation of the dithiocarbamate product $Ti(\eta\text{-}C_5H_4Me)\{N(\text{-}2,6\text{-}C_6H_3Me_2)C(S)S\}\{PhC(NSiMe_3)_2\}$. This product was found to be fluxional in solution at room temperature, in a similar manner to the related carbamate complex $Ti(\eta\text{-}C_5H_4Me)\{N(\text{-}2,6\text{-}C_6H_3Me_2)C(O)O\}\{PhC(NSiMe_3)_2\}$ (**28**). However, after only 5 minutes, a considerable amount of decomposition to $[Ti(\eta\text{-}C_5H_4Me)(\mu\text{-}S)\{PhC(NSiMe_3)_2\}]_2$ (**60**) was observed, with formation of 2,6-dimethylphenyl isothiocyanate. Complete decomposition of the dithiocarbamate was observed after 2 hours, even in the absence of light. Isolation of this complex was therefore not possible under these conditions. $Ti(\eta\text{-}C_5Me_5)(N\text{-}4\text{-}C_6H_4Me)\{MeC(N^iPr)_2\}$ (**8**) was found to react with CS_2 to afford a similarly very unstable dithiocarbamate product. The ^1H NMR spectrum of the reaction recorded 5 minutes after addition of CS_2 revealed significant formation of $[Ti(\eta\text{-}C_5Me_5)(\mu\text{-}S)\{MeC(N^iPr)_2\}]_2$ (**59**) and *p*-tolyl isothiocyanate. After 10 minutes the ratio of **8** : **56** was about 1 : 1. Throughout the reaction, the dithiocarbamate intermediate was detectable only as a trace amount in the baseline of the ^1H NMR spectra recorded.

Thus, the reaction of the arylimides with CS_2 is found to follow the pattern of formal [2 + 2] cycloadduct formation, followed by decomposition to yield the final product, but the rates of the different processes vary considerably from case to case (see Scheme 5.11).



	R	R^1	R^2	Ar	
7	Me	Me	^{i}Pr	2,6-$C_6H_3Me_2$	**59**
8	Me	Me	^{i}Pr	4-C_6H_4Me	**59**
11	H	Ph	$SiMe_3$	2,6-$C_6H_3Me_2$	**60**

Scheme 5.11 – Reaction of $Ti(\eta\text{-}C_5R_4Me)(NAr)\{R^1C(NR^2)_2\}$ with CS_2

It is noteworthy that further reaction of a thiocarbamate with COS or dithiocarbamate with CS_2 was never observed. This is in marked contrast to the CO_2 chemistry of the arylimido complexes described in Chapter 3, in which the carbamate complexes cleanly react with a further molecule of CO_2 to afford arylimido dicarboxylate complexes.

In an attempt to see if a chalcogenido-bearing mixed arylimido carboxylate thiocarboxylate complex could be synthesised, a sample of the carbamate complex Ti(η-C_5Me_5){N(-2,6-$C_6H_3Me_2$)C(O)O}{MeC(N^{i}Pr)$_2$} (**27**) was treated with CS_2, and a sample of the dithiocarbamate complex Ti(η-C_5Me_5){N(-2,6-$C_6H_3Me_2$)C(S)S}{MeC(N^{i}Pr)$_2$} (**64**) was treated with CO_2. Neither showed any evidence for reaction to form a new product; **27** decomposed over 2 weeks to give unidentified products, and **64** decomposed over a period of 3 days to give the sulfido complex [Ti(η-C_5Me_5)(μ-S){MeC(N^{i}Pr)$_2$}]$_2$ (**59**). Reaction of the less hindered carbamate Ti(η-C_5Me_5){N(-4-C_6H_4Me)C(O)O}{MeC(N^{i}Pr)$_2$} (**34**) with CS_2 did, however, appear to give an insertion product (*vide infra*).

5.4.3 Conclusion

It has been shown that the reactions of both COS and CS_2 are much faster with the arylimido complexes of the form Ti(η-C_5R_4Me)(NAr){R^{1}C(NR^2)$_2$} than with the homologous *tert*-butyl imides Ti(η-C_5R_4Me)(N^{t}Bu){R^{1}C(NR^2)$_2$}, and that the preferential binding mode of COS is through sulfur rather than oxygen. Cycloaddition products of COS and CS_2 are generally unstable, the only isolable examples being those derived from the bulky 2,6-$C_6H_3Me_2$ imido species. Reaction of CS_2 with Ti(η-C_5Me_5)(N^{t}Bu){MeC(N^{i}Pr)$_2$} (**2**) deviates from the normal pattern, with a molecule of CS_2 inserting into the Ti–$N_{amidinate}$ bond of the MeC(N^{i}Pr)$_2$ ligand. Reaction of two molecules of COS or CS_2 at the imido linkage is not observed, in contrast to the chemistry shown with CO_2.

5.5 REACTIONS OF TITANIUM CYCLOPENTADIENYL IMIDO AMIDINATE COMPLEXES WITH H_2S

This Section describes the reactivity of titanium cyclopentadienyl imido amidinate complexes with H_2S. As with H_2O, the ability of H_2S to protonate the ancillary ligand set as well as reacting with the imido function added a potential complication to these reactivity studies. In spite of this, H_2S has been successfully used as a sulfido-transfer reagent in other Group 4 chemistry,[20,23] including imido chemistry.[19,22,30,31]

5.5.1 REACTIONS OF *TERT*-BUTYLIMIDO COMPLEXES WITH H_2S

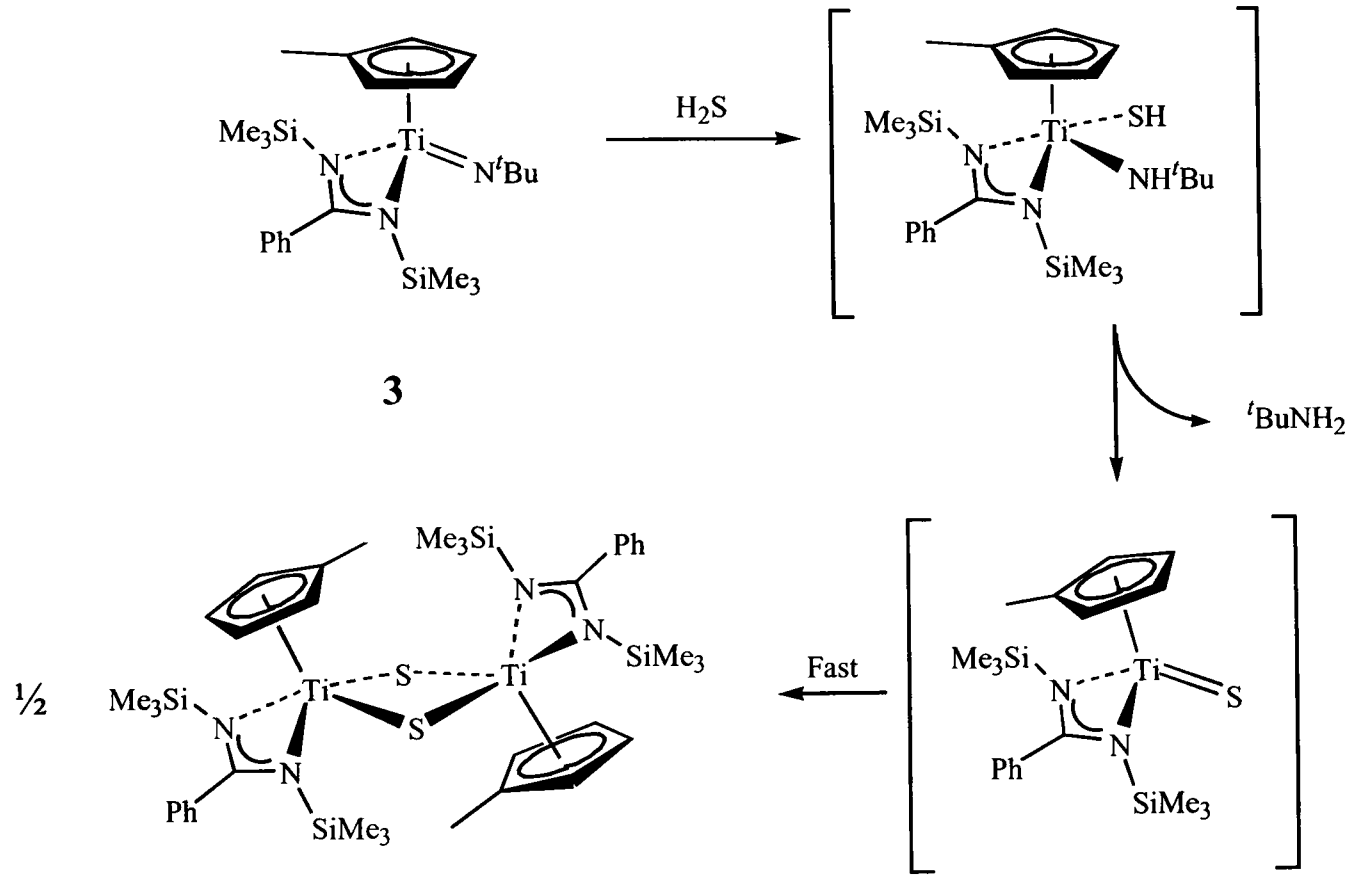
Samples of Ti(η-C_5Me_5)(N^{t}Bu){PhC(NSiMe$_3$)$_2$} (**1**), Ti(η-C_5Me_5)(N^{t}Bu){MeC(N^{i}Pr)$_2$} (**2**), Ti(η-C_5H_4Me)(N^{t}Bu){PhC(NSiMe$_3$)$_2$} (**3**), and Ti(η-C_5H_4Me)(N^{t}Bu){MeC(N^{i}Pr)$_2$} (**4**) were dissolved in aliquots of benzene-d_6 and degassed, before being exposed to H_2S at a pressure of 1 atm. Rapid colour changes from red to brown indicated reaction, and ^{1}H NMR spectroscopy was used to identify the products.

5.5.1.1 RESULTS AND DISCUSSION

In the cases of Ti(η-C_5Me_5)(N^{t}Bu){PhC(NSiMe$_3$)$_2$} (**1**), Ti(η-C_5Me_5)(N^{t}Bu){MeC(N^{i}Pr)$_2$} (**2**), and Ti(η-C_5H_4Me)(N^{t}Bu){MeC(N^{i}Pr)$_2$} (**4**), the reaction afforded only a mixture of unidentified products. Peaks corresponding to free *tert*-butylamine were observed in the ^{1}H NMR spectra, and this could be removed from the reaction mixtures under reduced pressure, but the remaining material could neither be identified by ^{1}H NMR spectroscopy nor by EI mass

spectrometry. In contrast, reaction of Ti(η-C_5H_4Me)(N^{t}Bu){PhC(NSiMe_3)$_2$} (**3**) with excess H_2S afforded *tert*-butylamine and [Ti(η-C_5H_4Me)(μ-S){PhC(NSiMe_3)$_2$}]$_2$ (**60**) in a clean reaction.

It is proposed by analogy with the reaction of Ti(η-C_5H_5)$_2$(N^{t}Bu)(py) (**5.27**) with H_2S previously reported[19] that the reaction mechanism is as shown in Scheme 5.12.



Scheme 5.12 – Proposed mechanism for reaction of Ti(η-C_5H_4Me)(N^{t}Bu){PhC(NSiMe_3)$_2$} (**3**) with H_2S

No reaction was observed between a stoichiometric quantity of [Ti(η-C_5H_4Me)(μ-S){PhC(NSiMe_3)$_2$}]$_2$ (**60**) and Ti(η-C_5H_4Me)(N^{t}Bu){PhC(NSiMe_3)$_2$} (**3**) in benzene-d_6, as predicted on the basis of this mechanism.

The reasons why a clean reaction only occurs for **3** are not clear. From the CS_2 chemistry reported earlier in this Chapter, it would seem that the Ti–$N_{amidinate}$ bonds of the $MeC(N^iPr)_2$ ligand are more susceptible to attack than those of $PhC(NSiMe_3)_2$. This may explain why complexes $Ti(\eta\text{-}C_5Me_5)(N^tBu)\{MeC(N^iPr)_2\}$ (**2**) and $Ti(\eta\text{-}C_5H_4Me)(N^tBu)\{MeC(N^iPr)_2\}$ (**4**) are decomposed by H_2S. The sulfido species $[Ti(\eta\text{-}C_5Me_5)(\mu\text{-}S)\{PhC(NSiMe_3)_2\}]_2$ (**58**) has already been shown to have very poor solubility, and analysis of the ^1H NMR spectra from the reaction shows that the intensity of the solvent peak increases with reaction. In addition, a very fine precipitate can be seen in the NMR tube. It is likely therefore that the reaction of $Ti(\eta\text{-}C_5Me_5)(N^tBu)\{PhC(NSiMe_3)_2\}$ (**1**) with H_2S does yield the bridging sulfido species **58**, but that this species comes out of solution, so only impurities are detected.

5.6 REACTIONS OF TITANIUM CYCLOPENTADIENYL IMIDO AMIDINATE COMPLEXES WITH ISOTHIOCYANATES

This Section describes the reactivity of titanium cyclopentadienyl imido amidinate complexes with isothiocyanates. Three different isothiocyanates were employed in the reactivity studies: *tert*-butyl-, 2,6-dimethylphenyl- and *p*-tolyl- isothiocyanate. The reactions of each will be addressed separately.

5.6.1 REACTIONS OF TITANIUM CYCLOPENTADIENYL IMIDO AMIDINATE COMPLEXES WITH *TERT*-BUTYL ISOTHIOCYANATE

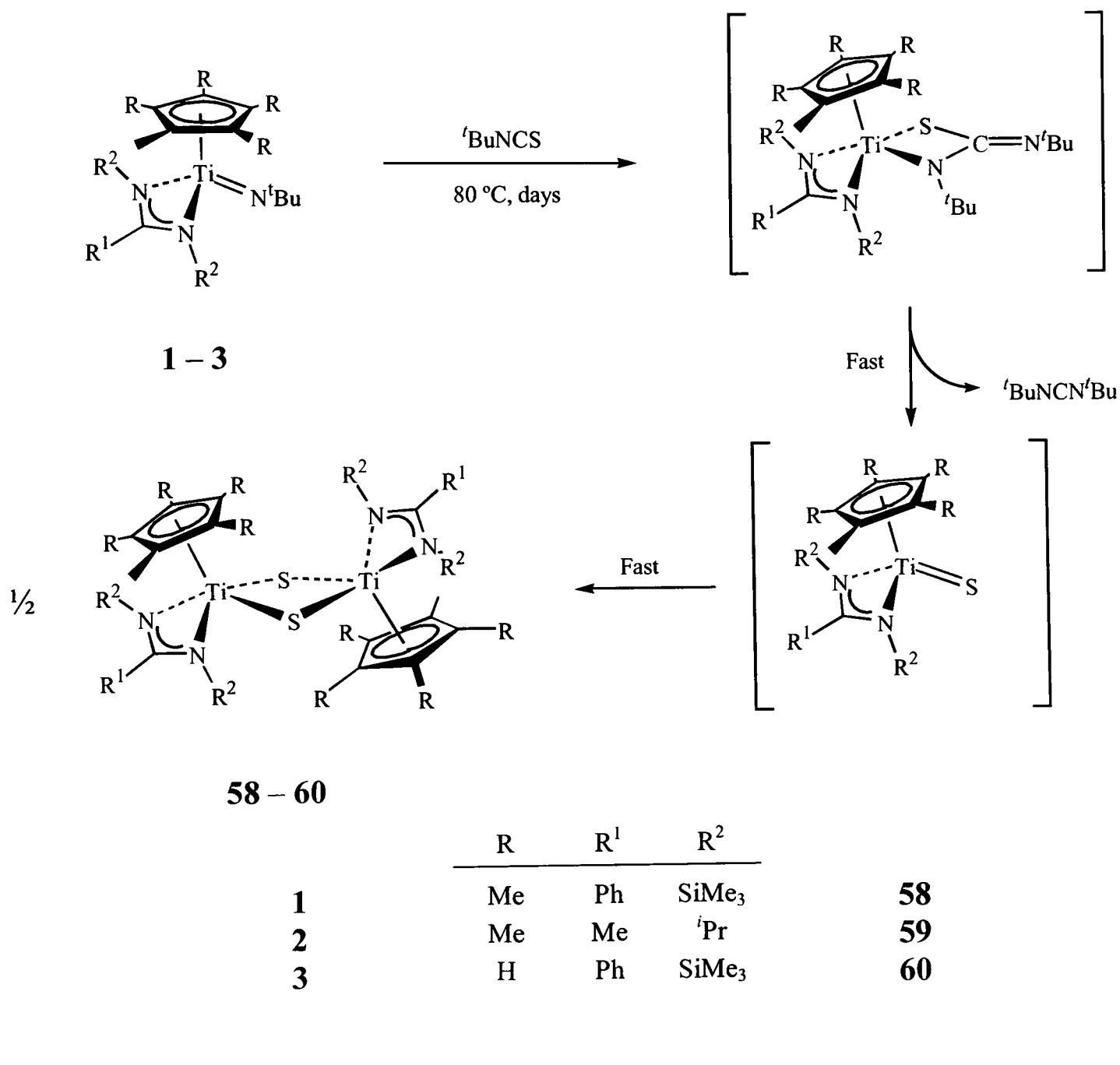
Samples of Ti(η-C_5Me_5)(N^{t}Bu){PhC(NSiMe$_3$)$_2$} (**1**), Ti(η-C_5Me_5)(N^{t}Bu){MeC(N^{i}Pr)$_2$} (**2**), and Ti(η-C_5H_4Me)(N^{t}Bu){PhC(NSiMe$_3$)$_2$} (**3**) were dissolved in aliquots of benzene-d_6 and treated with one equivalent of *tert*-butyl isothiocyanate. The reactions were monitored using ^{1}H NMR spectroscopy.

5.6.1.1 RESULTS AND DISCUSSION

The products of the three reactions were found to be the bridging sulfido species [Ti(η-C_5Me_5)(μ-S){PhC(NSiMe$_3$)$_2$}]$_2$ (**58**), [Ti(η-C_5Me_5)(μ-S){MeC(N^{i}Pr)$_2$}]$_2$ (**59**), and [Ti(η-C_5H_4Me)(μ-S){PhC(NSiMe$_3$)$_2$}]$_2$ (**60**) respectively, with concomitant formation of 1,3-di-*tert*-butylcarbodiimide. These reactions are analogous to those of **1** – **3** with *tert*-butyl isocyanate to give the oxo species [Ti(η-C_5R_4Me)(μ-O){R^{1}C(NR^2)$_2$}]$_2$ (**21** – **22, 24**), reported in Chapter 4.

No reaction was obtained for any of the samples at room temperature, even after several days in solution. Heating to 80 °C for a period of days was required to show any trace of products. As with the analogous isocyanate reactions, ^{1}H NMR spectra recorded during the reactions showed peaks which could be assigned to the sulfido species and carbodiimide, but none which would correspond to the thioureate intermediate. The nature of the products formed could, however, confirm that the isothiocyanate reacts *via* an

intermediate of the same geometry as that of the isocyanate reactions, rather than reacting *via* an N, N' - bound thioureate intermediate (Scheme 5.13).



	R	R^1	R^2	
1	Me	Ph	$SiMe_3$	**58**
2	Me	Me	^{i}Pr	**59**
3	H	Ph	$SiMe_3$	**60**

Scheme 5.13 – Proposed mechanism for reaction of $Ti(\eta\text{-}C_5R_4Me)(N^tBu)\{R^1C(NR^2)_2\}$ (**1** – **3**) with *tert*-butyl isothiocyanate

The reaction of *tert*-butyl isothiocyanate was found to be even slower than that of *tert*-butyl isocyanate. Thus, heating the reaction of $Ti(\eta\text{-}C_5Me_5)(N^tBu)\{MeC(N^iPr)_2\}$ (**2**) to 80 °C for 16 days only afforded a 1 : 3 ratio of product : starting materials. For the reaction of $Ti(\eta\text{-}C_5H_4Me)(N^tBu)\{PhC(NSiMe_3)_2\}$ (**3**), heating to 80 °C for 13 days

afforded only a 1 : 10 ratio. Further heating was found to increase the extent of reaction, but decomposition products were also detected.

5.6.2 REACTIONS OF TITANIUM CYCLOPENTADIENYL IMIDO AMIDINATE COMPLEXES WITH 2,6-DIMETHYLPHENYL ISOTHIOCYANATE

Samples of Ti(η-C_5Me_5)(N^{t}Bu){MeC(N^{i}Pr)$_2$} (**2**), Ti(η-C_5H_4Me)(N^{t}Bu){PhC(NSiMe$_3$)$_2$} (**3**), Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$){MeC(N^{i}Pr)$_2$} (**7**), and Ti(η-C_5H_4Me)(N-2,6-$C_6H_3Me_2$){PhC(NSiMe$_3$)$_2$} (**11**) were dissolved in aliquots of benzene-d_6 and treated with one equivalent of 2,6-dimethylphenyl isothiocyanate. The reactions were monitored using ^{1}H NMR spectroscopy.

5.6.2.1 RESULTS AND DISCUSSION

The reactions of the imido species with 2,6-dimethylphenyl isothiocyanate occurred more rapidly than those of *tert*-butyl isothiocyanate in all cases except for that of Ti(η-C_5Me_5)(N^{t}Bu){MeC(N^{i}Pr)$_2$} (**2**). No reaction was found between **2** and 2,6-dimethylphenyl isothiocyanate after 66 hrs. Heating the reaction to 80 °C for 4 days did not induce reaction.

After 48 hours at room temperature, new peaks were detected as a minor constituent in the reaction with Ti(η-C_5H_4Me)(N^{t}Bu){PhC(NSiMe$_3$)$_2$} (**3**). After 89 hours, all starting material had been consumed, but no single product could be identified from the ^{1}H NMR spectrum. However, analysis of a sample of the reaction mixture quenched in methanol using APCI mass spectrometry revealed a peak corresponding to the mixed

N-2,6-dimethylphenyl-*N'*-*tert*-butylcarbodiimide (*m/z* = 203, $[M+H]^+$). This indicated that reaction was taking place as expected; no carbodiimide peaks were observed in the ^1H NMR spectrum, suggesting the reaction product may contain the thioureate complex.

Reaction of $Ti(\eta\text{-}C_5Me_5)(N\text{-}2,6\text{-}C_6H_3Me_2)\{MeC(N^iPr)_2\}$ (**7**) did not afford any products after 66 hours at room temperature. Heating the reaction to 80 °C resulted in clean conversion of **7** to $[Ti(\eta\text{-}C_5Me_5)(\mu\text{-}S)\{MeC(N^iPr)_2\}]_2$ (**59**). After 24 hours at 80 °C, the ratio of **7** : **56** was found to be about 2 : 1 (i.e. 50 % conversion). No peaks corresponding to the thioureate intermediate could be detected.

$Ti(\eta\text{-}C_5H_4Me)(N\text{-}2,6\text{-}C_6H_3Me_2)\{PhC(NSiMe_3)_2\}$ (**11**) was found to react more quickly, and at lower temperature. Thus, some reaction could be detected 15 minutes after initiation, and after 42 hours at room temperature the ^1H NMR spectrum revealed peaks assignable as $[Ti(\eta\text{-}C_5H_4Me)(\mu\text{-}S)\{PhC(NSiMe_3)_2\}]_2$ (**60**) and 1,3-di-*N*-2,6-dimethylphenylcarbodiimide. The identity of the organic compound was confirmed by detection of a peak in the APCI mass spectrum of the reaction mixture corresponding to the parent ion (*m/z* = 251, $[M+H]^+$). After 17 hours of reaction, all the imido starting material had been consumed and broad features, which could be attributed to a fluxional thioureate intermediate, were visible. Fluxionality was also reported for the structurally related complex $Ti(\eta\text{-}C_5H_4Me)\{N(\text{-}2,6\text{-}C_6H_3Me_2)C(O)O\}\{PhC(NSiMe_3)_2\}$ (**28**), which like this intermediate has a

methylcyclopentadienyl in place of a pentamethylcyclopentadienyl ligand. The extra space around the metal centre is likely to be the cause.

5.6.3 REACTIONS OF TITANIUM CYCLOPENTADIENYL IMIDO AMIDINATE COMPLEXES WITH *p*-TOLYL ISOTHIOCYANATE

Samples of Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$){MeC(N^{i}Pr)$_2$} (**7**) and Ti(η-C_5Me_5)(N-4-C_6H_4Me){MeC(N^{i}Pr)$_2$} (**8**) were dissolved in aliquots of benzene-d_6 and treated with one equivalent of *p*-tolyl isothiocyanate. The reactions were monitored using ^{1}H NMR spectroscopy.

5.6.3.1 RESULTS AND DISCUSSION

No reaction between *p*-tolyl isothiocyanate and Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$){MeC(N^{i}Pr)$_2$} (**7**) was observed 1½ hours after the reaction had been initiated. After 18 hours at room temperature, the ^{1}H NMR spectrum of the reaction mixture showed evidence for a small quantity of thioureate product, but the sulfido species [Ti(η-C_5Me_5)(μ-S){MeC(N^{i}Pr)$_2$}]$_2$ (**59**) was already present. Unreacted starting materials were still the principal constituent of the reaction mixture, indicating that isolation of the thioureate adduct was not possible under these conditions.

Ti(η-C_5Me_5)(N-4-C_6H_4Me){MeC(N^{i}Pr)$_2$} (**8**) reacted much more quickly than **7**, reaction being evident after 5 minutes. After 20 minutes, the ratio of **7** : thioureate product was 1 : 1; after 30 minutes however peaks corresponding to the sulfido final product [Ti(η-C_5Me_5)(μ-S){MeC(N^{i}Pr)$_2$}]$_2$ (**59**) could be seen growing in. After 1.5 hours, the imido complex had been consumed, but

the ratio (thioureate : **59**) was 2 : 1 (50 % decomposition). Complete conversion to **59** and 1,3-di-*p*-tolylcarbodiimide was observed after 18 hours; the carbodiimide was identified by comparison with the ^{1}H NMR spectrum of a commercially obtained sample. Conversion to **59** occurred cleanly, with no peaks forming in the ^{1}H NMR spectrum that might correspond to a second insertion product such as that found for the reaction between **8** and *p*-tolyl isocyanate. Since decay of the thioureate to **59** occurred in the presence of excess *p*-tolyl isothiocyanate, it can be concluded that the insertion of a second molecule of substrate into the metallacyclic intermediate does not occur.

5.7 SULFUR-CONTAINING MIXED SECOND (INSERTION) COMPLEXES

The lack of reactivity of the sulfur-containing metallacycles towards insertion of a second molecule of substrate is in contrast with the oxygen containing systems reported in Chapters 3 and 4. Towards the end of this project, experiments were carried out to attempt the synthesis of a mixed oxygen-sulfur second (insertion) complex. Ti(η-C_5Me_5){N(-4-C_6H_4Me)C(O)O}{MeC(N^{i}Pr)$_2$} (**34**) was selected as the most reactive of the metallacycles synthesised in this work, owing to its lack of steric bulk and propensity to undergo further reaction with CO_2.

Samples of Ti(η-C_5Me_5){N(-4-C_6H_4Me)C(O)O}{MeC(N^{i}Pr)$_2$} (**34**) were dissolved in benzene-d_6 and treated with the sulfur heterocumulenes CS_2,

2,6-dimethylphenyl isothiocyanate, and *p*-tolyl isothiocyanate. The reactions were monitored using ^{1}H NMR spectroscopy.

5.7.1 RESULTS AND DISCUSSION

In all three cases, reaction of the carbamate Ti(η-C_5Me_5){N(-4-C_6H_4Me)C(O)O}{MeC(N^{i}Pr)$_2$} took place to afford new complexes. The reaction products were not the bridging oxo species [Ti(η-C_5Me_5)(μ-O){MeC(N^{i}Pr)$_2$}]$_2$ **(22)**, nor were they the bridging sulfido species [Ti(η-C_5Me_5)(μ-S){MeC(N^{i}Pr)$_2$}]$_2$ **(59)**.

No reaction was observed with CS_2 until *ca.* 6 hours had elapsed. Over a period of 4 days, the starting material was consumed to give a product lacking a mirror plane of symmetry. This compound appeared to decompose over the space of 1 month in solution to give unidentified products.

Reaction with 2,6-dimethylphenyl isothiocyanate was found to take *ca.* 4 days, after which the starting material had been consumed to give an unidentified product. The pattern of peaks in the ^{1}H NMR spectrum was consistent with isothiocyanate insertion into the carbamate, plus some other peaks due to impurities.

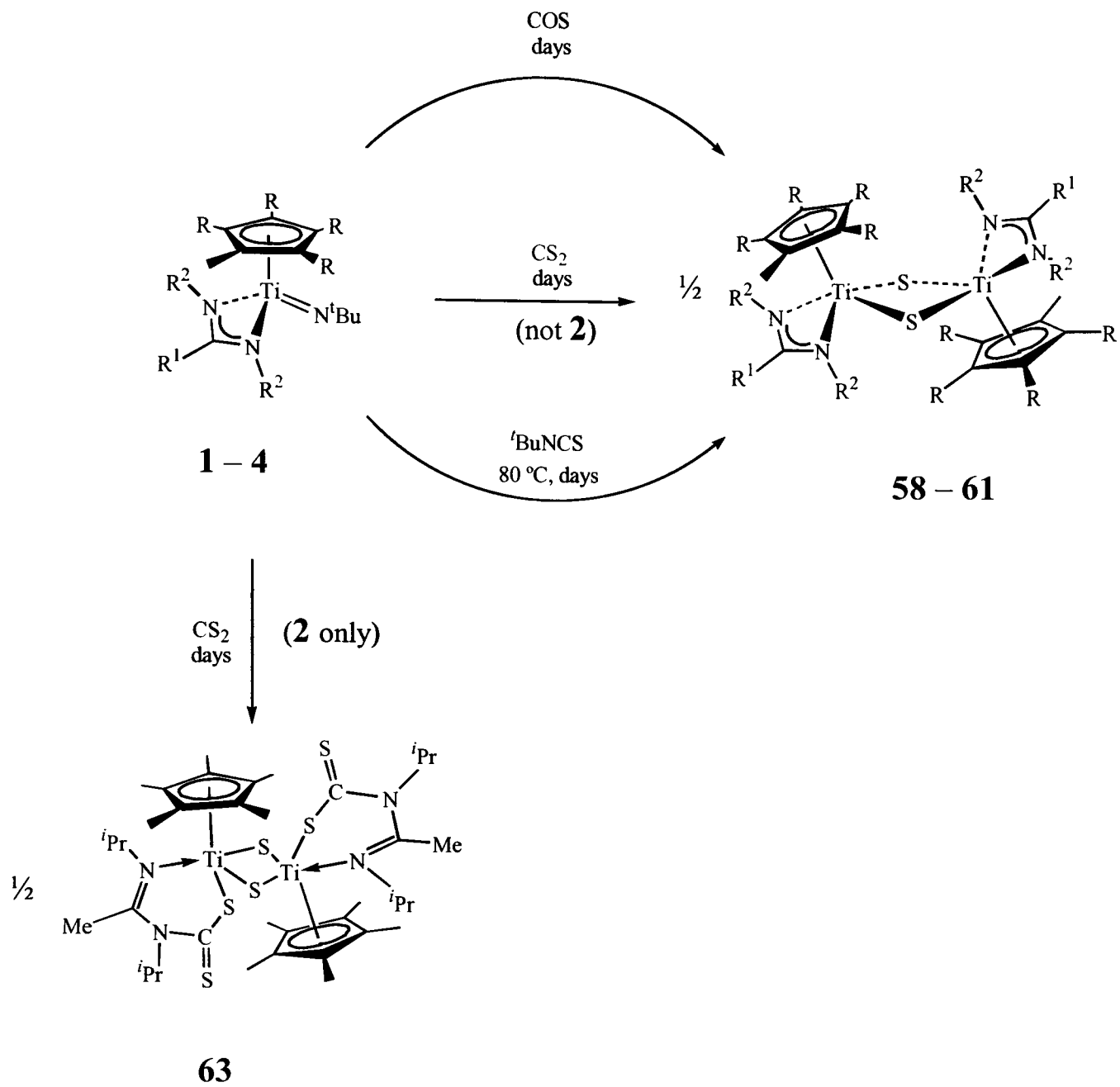
Reaction with *p*-tolyl isothiocyanate took about 2 days to go to completion. The product was also unidentified, but was consistent with the insertion of a molecule of isothiocyanate insertion into the carbamate. No parent ion was detected for such a species in the EI or FI mass spectra; however, the oxo-

based homologues of the proposed species are not found to give parent ions under similar conditions.

These experiments suggest that whereas the synthesis of complexes in which a sulfur-containing substrate inserts into a sulfur-containing metallacycle is not possible, it may be possible to form species in which a sulfur-containing substrate inserts into an oxygen-containing metallacycle. Further experiments are necessary to probe this chemistry, in order to confirm this prediction.

5.8 SUMMARY

The reactions of titanium cyclopentadienyl *tert*-butylimido amidinate complexes with sulfur-containing substrates have been shown to follow the same basic reaction pathways as those of their oxygen-based analogues, the exception being the reaction of $Ti(\eta\text{-}C_5Me_5)(N^tBu)\{MeC(N^iPr)_2\}$ with CS_2 giving a bridging sulfido complex in which insertion of CS_2 into the amidinate has also occurred (Scheme 5.14). The principal difference is in the rate of reaction; sulfur-containing species react considerably slower than do oxygen species. As a result, the unstable intermediate cycloaddition products are not observed. Of particular interest is the reaction of COS with the imido species; the reactive site is shown to be the C=S bond rather than C=O.

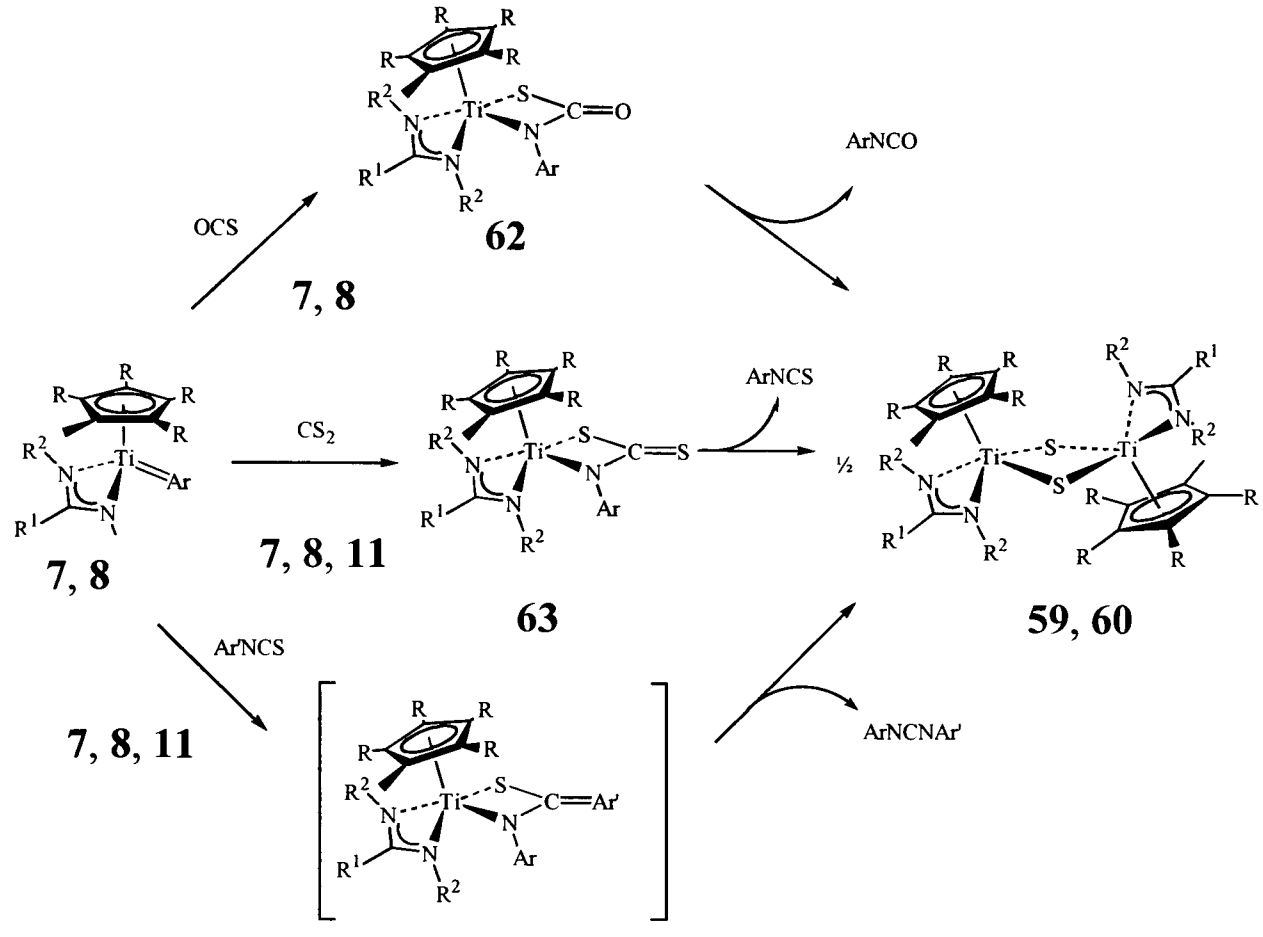


	R	R^1	R^2	
1	Me	Ph	$SiMe_3$	**58**
2	Me	Me	^{i}Pr	**59**
3	H	Ph	$SiMe_3$	**60**
4	H	Me	^{i}Pr	**61**

Scheme 5.14 – Summary of reactions of $Ti(\eta\text{-}C_5R_4Me)(N^tBu)\{R^1C(NR^2)_2\}$ with sulfur-containing heterocumulenes

The reactions of titanium cyclopentadienyl arylimido amidinate complexes with sulfur-containing heterocumulenes proceed much more rapidly than their *tert*-butyl homologues. Thiocarbamate and dithiocarbamate complexes have

been observed, and some have been successfully isolated and characterised Scheme 5.15).



	R	R^1	R^2	Ar	Adducts	Sulfido
7	Me	Me	^{i}Pr	2,6-$C_6H_3Me_2$	**62, 63**	**59**
8	Me	Me	^{i}Pr	4-C_6H_4Me		**59**
11	H	Ph	$SiMe_3$	2,6-$C_6H_3Me_2$		**60**

Scheme 5.15 – Summary of reactions of Ti(η-C_5R_4Me)(NAr){$R^1C(NR^2)_2$} with sulfur-containing heterocumulenes

Additionally, it has been shown that the thiocarbamate and dithiocarbamate complexes do not undergo the insertion process exhibited by the carbamates Ti(η-C_5R_4Me){N(Ar)C(O)O}{$R^1C(NR^2)_2$} (**27** – **29**, **34** – **36**) and ureates Ti(η-C_5Me_5){N(Ar)C(NAr')O}{$MeC(N^iPr)_2$} (**44** – **46**) with CO_2 or aryl isocyanate. Preliminary studies attempting the synthesis of complexes from insertion of sulfur-containing substrates into the carbamate complex

$Ti(\eta\text{-}C_5Me_5)\{N(N\text{-}4\text{-}C_6H_4Me)C(O)O\}\{MeC(N^iPr)_2\}$ **(34)** have proven inconclusive; further study into this area may yield an interesting new class of compounds.

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CHAPTER 6

Reactions with Mono-Unsaturated Substrates

6.1 OVERVIEW

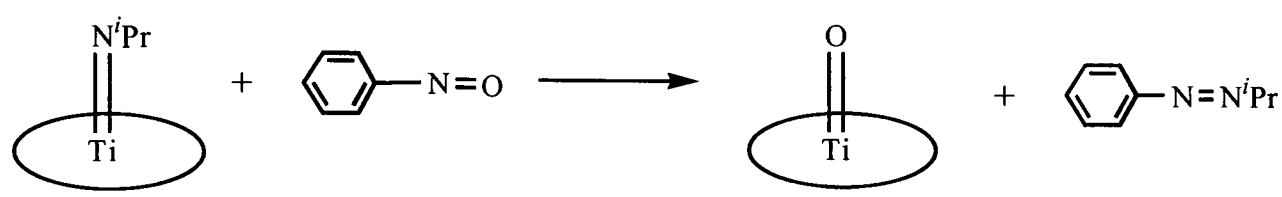
This Chapter focuses on the reactions between titanium cyclopentadienyl imido amidinate complexes and substrates with one unsaturated linkage. Section 6.2 describes the reactivity towards nitrosyl (RNO) compounds, Section 6.3 focuses on reactions with carbonyls (R_2CO and RHCO), Section 6.4 on reactions with imines (R_2CN), and Section 6.5 on alkynes (RC_2R). Owing to the diverse nature of the substrates studied, an introduction is provided at the beginning of each Section giving relevant background material.

6.2 REACTIONS OF TITANIUM CYCLOPENTADIENYL IMIDO AMIDINATE COMPLEXES WITH NITROSYLS

This Section describes the reactivity of titanium cyclopentadienyl imido amidinate complexes with nitrosobenzene. Section 6.2.1 provides an introduction to the reactivity of transition metal complexes with organic nitroso compounds. Section 6.2.2 describes the reactions of cyclopentadienyl *tert*-butylimido amidinate complexes with nitrosobenzene, followed by Section 6.2.3 which describes the reactions of cyclopentadienyl arylimido amidinate complexes with nitrosobenzene.

6.2.1 INTRODUCTION

Reaction of an imidotitanium complex with a nitrosyl compound (RNO) has been recently reported in the literature. Woo[1] has shown that the imido species Ti(TTP)(N^{i}Pr) (TTP = 5, 10, 15, 20- tetratolylporphyrin dianion) (**6.1**) reacts with nitrosobenzene to afford the terminal oxo complex Ti(TTP)(O) (**6.2**) and the azo compound ^{i}PrN=NPh, as shown in Equation 6.1.



6.1 **6.2**

Equation 6.1

It was proposed that the diazene product is formed from a monomeric intermediate in which the nitrosobenzene is bound to the titanium *cis* to the imido group. Woo has also reported the analogous reaction between nitrosobenzene and the complex Zr(TTP)(N-2,6-$C_6H_3{}^iPr_2$) (**6.3**) to give the bis(μ-oxo) complex $[Zr(TTP)(O)]_2$ (**6.4**) and corresponding diazene product.[2]

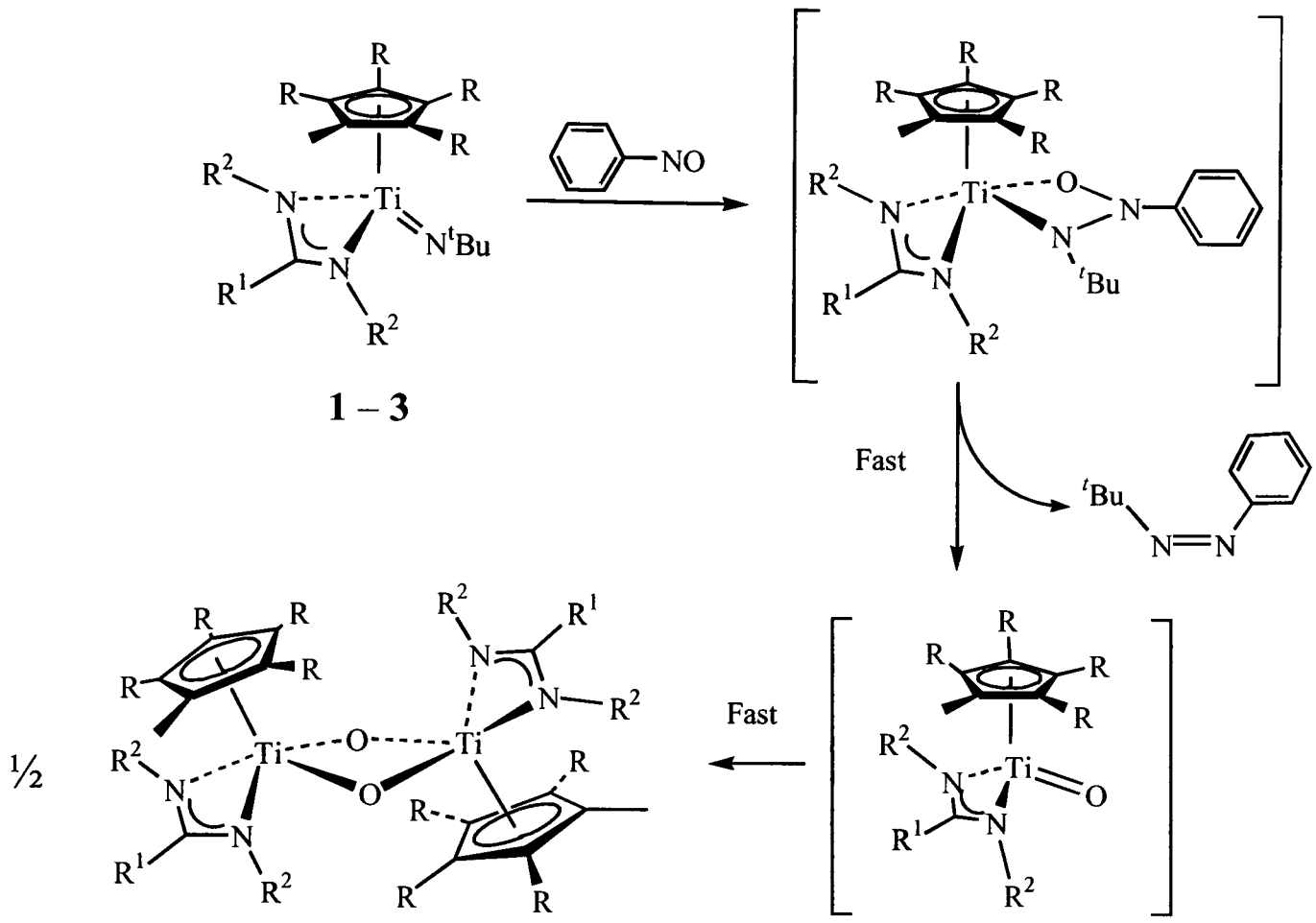
Although Woo has reported the synthesis of imidotitanium complexes from Ti(TTP)(η^2-RC_2R) (R = Et (**6.5**), Ph (**6.6**)) precursors reacting with azobenzene,[3,4] and azobenzene has been used previously in other imidotitanium synthesis,[5] there are no reports of reaction occurring between imidotitanium species and azobenzene.

6.2.2 REACTIONS OF CYCLOPENTADIENYL *TERT*-BUTYLIMIDO AMIDINATE COMPLEXES WITH NITROSOBENZENE

Samples of Ti(η-C_5Me_5)(N^{t}Bu){PhC(NSiMe$_3$)$_2$} (**1**) and Ti(η-C_5H_4Me)(N^{t}Bu){PhC(NSiMe$_3$)$_2$} (**3**) were dissolved in aliquots of benzene-d_6 and treated with one equivalent of nitrosobenzene. A sample of Ti(η-C_5Me_5)(N^{t}Bu){MeC(N^{i}Pr)$_2$} (**2**) was dissolved in benzene-d_6 and treated with two equivalents of nitrosobenzene. Reactions were monitored using ^{1}H NMR spectroscopy. Additionally, reactions between **3** and nitrosobenzene were carried out in chloroform-d and tetrachloromethane solvents.

6.2.2.1 RESULTS AND DISCUSSION

A colour change from red to dark amber was observed for the reactions of Ti(η-C_5Me_5)(N^{t}Bu){PhC(NSiMe$_3$)$_2$} (**1**) and Ti(η-C_5H_4Me)(N^{t}Bu){PhC(NSiMe$_3$)$_2$} (**3**) with nitrosobenzene over *ca.* 5 minutes. Analysis of the samples using ^{1}H NMR spectroscopy confirmed that all the imido starting materials had been consumed, and that the products of reaction of **3** included the *cis*- and *trans*- oxo species [Ti(η-C_5H_4Me)(μ-O){PhC(NSiMe$_3$)$_2$}]$_2$ (**24** and **24a** respectively). A yellow precipitate was observed in the reaction vessel of **1**, suggesting the formation of the insoluble dimeric oxo species [Ti(η-C_5Me_5)(μ-O){PhC(NSiMe$_3$)$_2$}]$_2$ (**21**). The reaction was thus predicted to follow the pathway given in Scheme 6.1 below:



	R	R^1	R^2	
1	Me	Ph	$SiMe_3$	**21**
2	Me	Me	^iPr	**22 / 22a**
3	H	Ph	$SiMe_3$	**24 / 24a**

Scheme 6.1 – Reaction of $Ti(\eta\text{-}C_5R_4Me)(N^tBu)\{R^1C(NR^2)_2\}$ with nitrosobenzene

As indicated in Scheme 6.1, the organic by-product of the reaction was expected to be the azo compound 1-*tert*-butyl-2-phenyldiazene. The appearance of a new resonance at 1.05 ppm in the ^1H NMR spectrum of the product formed in benzene-d_6 solution after 20 minutes fitted this expectation. However, the ^1H NMR spectrum of the reaction underwent further change with time, as indicated in Figure 6.1 below:

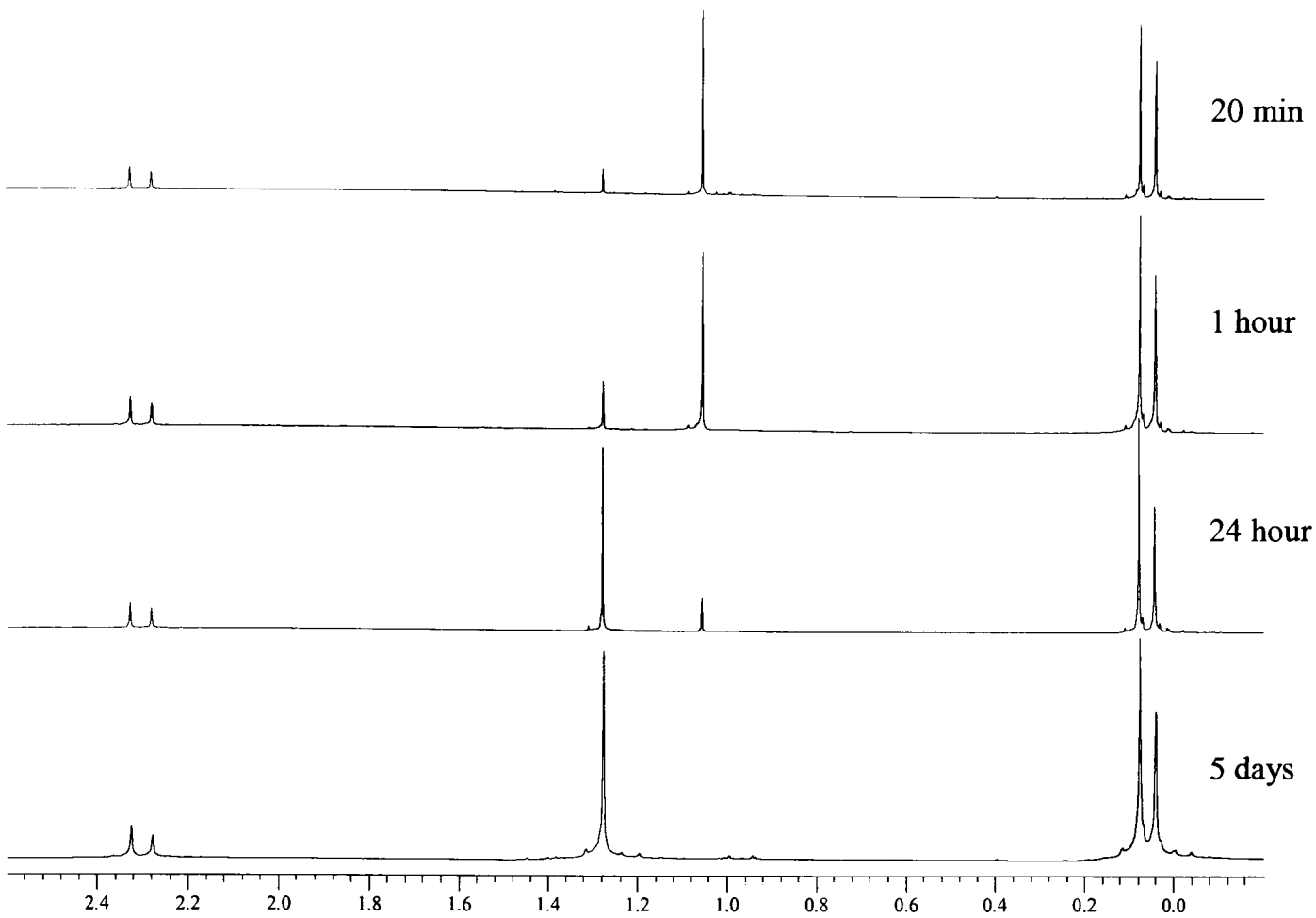


Figure 6.1 – 500.0 MHz ^{1}H NMR spectra of the reaction between Ti(η-C_5H_4Me)(N^{t}Bu){$PhC(NSiMe_3)_2$} (**3**) and nitrosobenzene in benzene-d_6 at time *t*

Decay of the ^{t}Bu-containing product to another compound was similarly observed when the reaction was carried out in chloroform-d. The first product formed was confirmed as *cis*-1-*tert*-butyl-2-phenyldiazene by comparison with ^{1}H NMR chemical shift values (chloroform-d) quoted in the literature.[6] Additionally, a sample of the reaction solution was analysed using APCI mass spectrometry, and a peak (*m/z* = 163, $[M+H]^+$) corresponding to protonated 1-*tert*-butyl-2-phenyldiazene was detected.

The conversion of the *cis*-1-*tert*-butyl-2-phenyldiazene to another compound was identified as isomerisation between the kinetically stable *cis*- isomer (formed in the decay of the four-membered metallacycle as shown in Scheme

6.1) and the thermodynamically favoured *trans*- isomer, by comparison with an account in the literature.[7] ^{1}H NMR measurements using tetrachloromethane as solvent gave values of 1.22 (s), 7.1 (m) and 6.6 (m) ppm for the *cis*-, and 1.33 (s), 7.3 (m), 7.6 (m) ppm for the *trans*- isomer, which were consistent with the values quoted by Sharp.[7]

It was noteworthy that the reaction of Ti(η-C_5H_4Me)(N^{t}Bu){PhC(NSiMe$_3$)$_2$} (**3**) with nitrosobenzene yielded the oxo species *trans*-[Ti(η-C_5H_4Me)(μ-O){PhC(NSiMe$_3$)$_2$}]$_2$ (**24**) and *cis*-[Ti(η-C_5H_4Me)(μ-O){PhC(NSiMe$_3$)$_2$}]$_2$ (**24a**) in a ratio much closer to 1 : 1 than was observed for the CO_2 synthetic route. The greater propensity for the formation of the less thermodynamically favoured *cis*- isomer will be addressed later in this Chapter.

The reaction of Ti(η-C_5Me_5)(N^{t}Bu){MeC(N^{i}Pr)$_2$} (**2**) was found to differ from that of the other two systems. The ^{1}H NMR spectrum recorded after 5 minutes confirmed that all the imido species had been consumed by the reaction. Peaks corresponding to *cis*-1-*tert*-butyl-2-phenyldiazene were present in the ^{1}H NMR spectrum of the reaction after 5 minutes. The remaining peaks could be assigned to two organometallic products. The oxo complex [Ti(η-C_5Me_5)(μ-O){MeC(N^{i}Pr)$_2$}]$_2$ (**22**) was identified as the minor product, along with a major product which showed a mirror plane on the NMR timescale. NMR studies showed that the unknown product decomposed to **22** with a half-life of *ca.* 15 minutes.

Initially, it was proposed that the intermediate complex was the cycloaddition product of **2** with nitrosobenzene. Due to its propensity to decompose to **22**, the complex could not be isolated and characterised.

However, the ^{1}H NMR spectrum of the intermediate is distinctive in comparison to all the other cycloadducts previously described in this Thesis, as the C_s symmetry of the imido species is retained in the product molecule. There are three possible explanations for this behaviour:

i) A rapid equilibrium exists between **2** and the cycloadduct, resulting in an averaging of ^{1}H NMR resonances at room temperature

ii) The metallacycle undergoes bond rupture of either Ti–O or Ti–N, followed by a 180 ° rotation of the group and reformation of the bond

iii) The plane of the metallacycle lies orthogonal to that of the cyclopentadienyl ring.

However, this interpretation of the data presented problems. The geometry for such a cycloadduct was surprising, although it could be rationalised by considering the crystal structures of $Ti(\eta\text{-}C_5Me_5)\{N(\text{-}2,6\text{-}C_6H_3Me_2)C(N\text{-}2,6\text{-}C_6H_3Me_2)\{MeC(N^iPr)_2\}$ (**41**) and $Ti(\eta\text{-}C_5Me_5)\{N(\text{-}2,6\text{-}C_6H_3Me_2)C(N\text{-}4\text{-}C_6H_4Me)O\}\{MeC(N^iPr)_2\}$ (**42**), both of which show distortion of the four-legged piano stool structure towards a more trigonal bipyramidal motif. Additionally, the resonance at 1.05 ppm did not change as the intermediate was converted into **22**. This was unexpected, and coincidental overlap seems unlikely in a process involving decoordination from a metal centre.

After experiments were carried out on arylimido species (*vide infra*), it was concluded that the unknown complex is in fact the hitherto unobserved cisoid isomer of the oxo complex $[Ti(\eta\text{-}C_5Me_5)(\mu\text{-}O)\{MeC(N^iPr)_2\}]_2$ (**22a**). This species was not observed during the synthesis of **22** from CO_2, isocyanates or H_2O.

Synthesis of the oxo species on a preparative scale using nitrosobenzene was found to be an effective method for $[Ti(\eta\text{-}C_5Me_5)(\mu\text{-}O)\{PhC(NSiMe_3)_2\}]_2$ (**21**), due to lack of solubility of the complex. This was not the case for the other oxo species $[Ti(\eta\text{-}C_5Me_5)(\mu\text{-}O)\{MeC(N^iPr)_2\}]_2$ (**22**) and $[Ti(\eta\text{-}C_5H_4Me)(\mu\text{-}O)\{PhC(NSiMe_3)_2\}]_2$ (**23**), as removal of the 1-*tert*-butyl-2-phenyldiazene by-product was complicated by their solubility.

6.2.3 Reactions of Titanium Cyclopentadienyl Arylimido Amidinate Complexes with Nitrosobenzene

Samples of $Ti(\eta\text{-}C_5Me_5)(N\text{-}2,6\text{-}C_6H_3Me_2)\{MeC(N^iPr)_2\}$ (**7**) and $Ti(\eta\text{-}C_5Me_5)(N\text{-}4\text{-}C_6H_4Me)\{MeC(N^iPr)_2\}$ (**8**) were dissolved in aliquots of benzene-d_6 and treated with one equivalent of nitrosobenzene. A sample of **7** was also treated with one equivalent of nitrosobenzene in toluene-d_8, to investigate the behaviour of the reaction at low temperature. A sample of **8** was also treated with a four-fold excess of nitrosobenzene. Reactions were monitored using ^1H NMR spectroscopy.

6.2.3.1 RESULTS AND DISCUSSION

Immediate colour changes from green to orange indicated reactions between the imido species and nitrosobenzene. The ^{1}H NMR spectrum of both reactions indicated complete consumption of both imides within 2 minutes. In both cases, the product after 2 minutes was found to be *ca.* 2 : 1 ratio of **22a** : **22**. Figure 6.2 shows the ^{1}H NMR spectrum of the reaction of **7** with nitrosobenzene after 5 minutes reaction time.

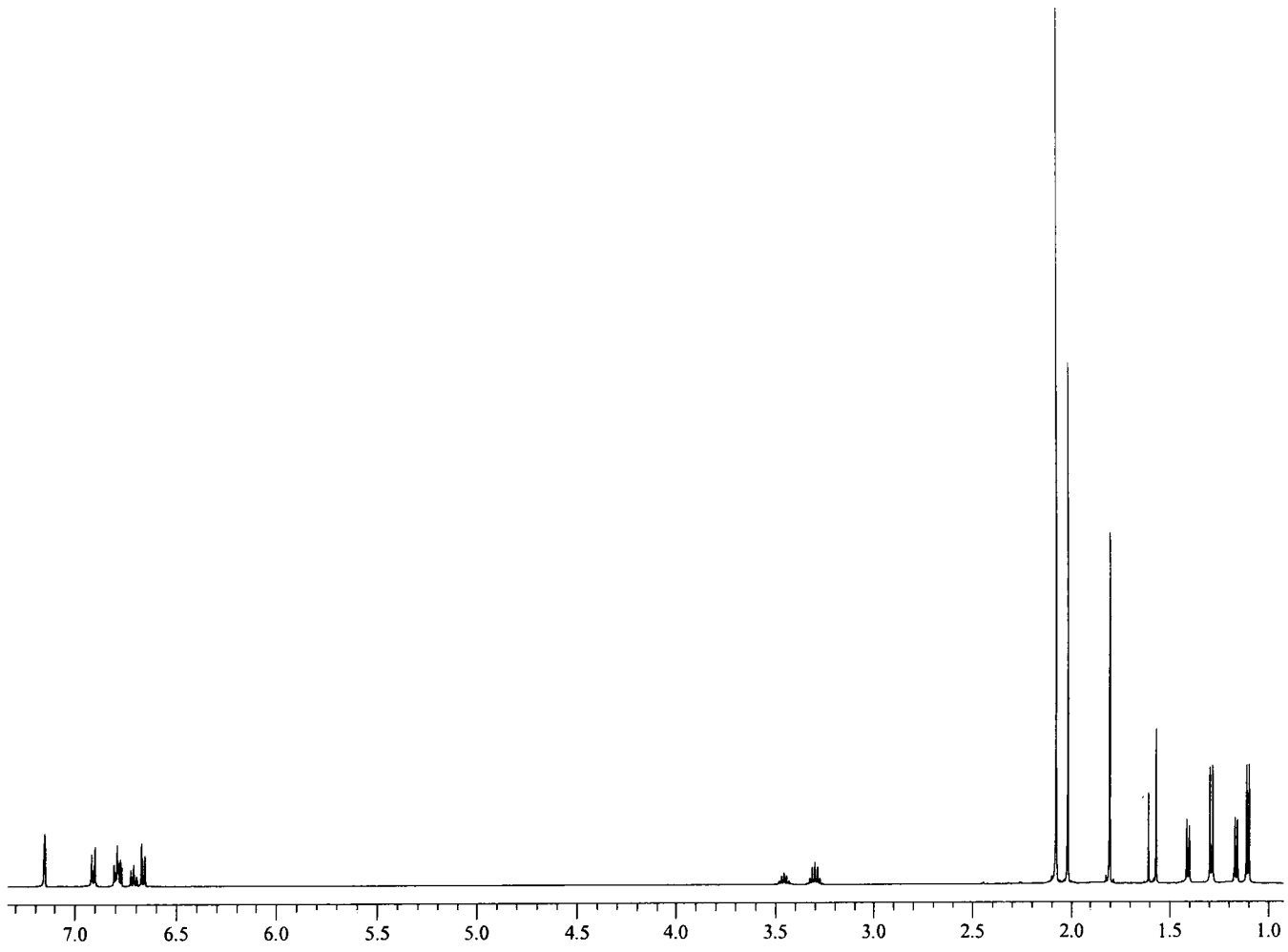


Figure 6.2 – 500.0 MHz ^{1}H NMR spectrum of the reaction of Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$){$MeC(N^iPr)_2$} (**7**) with nitrosobenzene in benzene-d_6 after 5 min.

Of particular note is the singlet at 1.80 ppm, assigned to the methyl groups in the *ortho-* positions on the aryl group, which indicates that the two methyl groups are magnetically equivalent. Furthermore, the peak does not shift as

the adduct is converted to the oxo complex. This is consistent with the methyl groups being on the organic by-product, *cis*-1-2,6-dimethylphenyl-2-phenyldiazene, and not part of a cycloaddition product.

Low temperature ^{1}H NMR experiments were carried out on the reaction mixture in an attempt to freeze out any fluxional processes occurring. It was predicted that if the intermediate were the cycloaddition product, the methyl resonances would be resolved into 2 distinct singlets. No significant broadening of the peaks was observed, even at -70 °C, supporting the suggestion that the aryl group is not part of the metal complex.

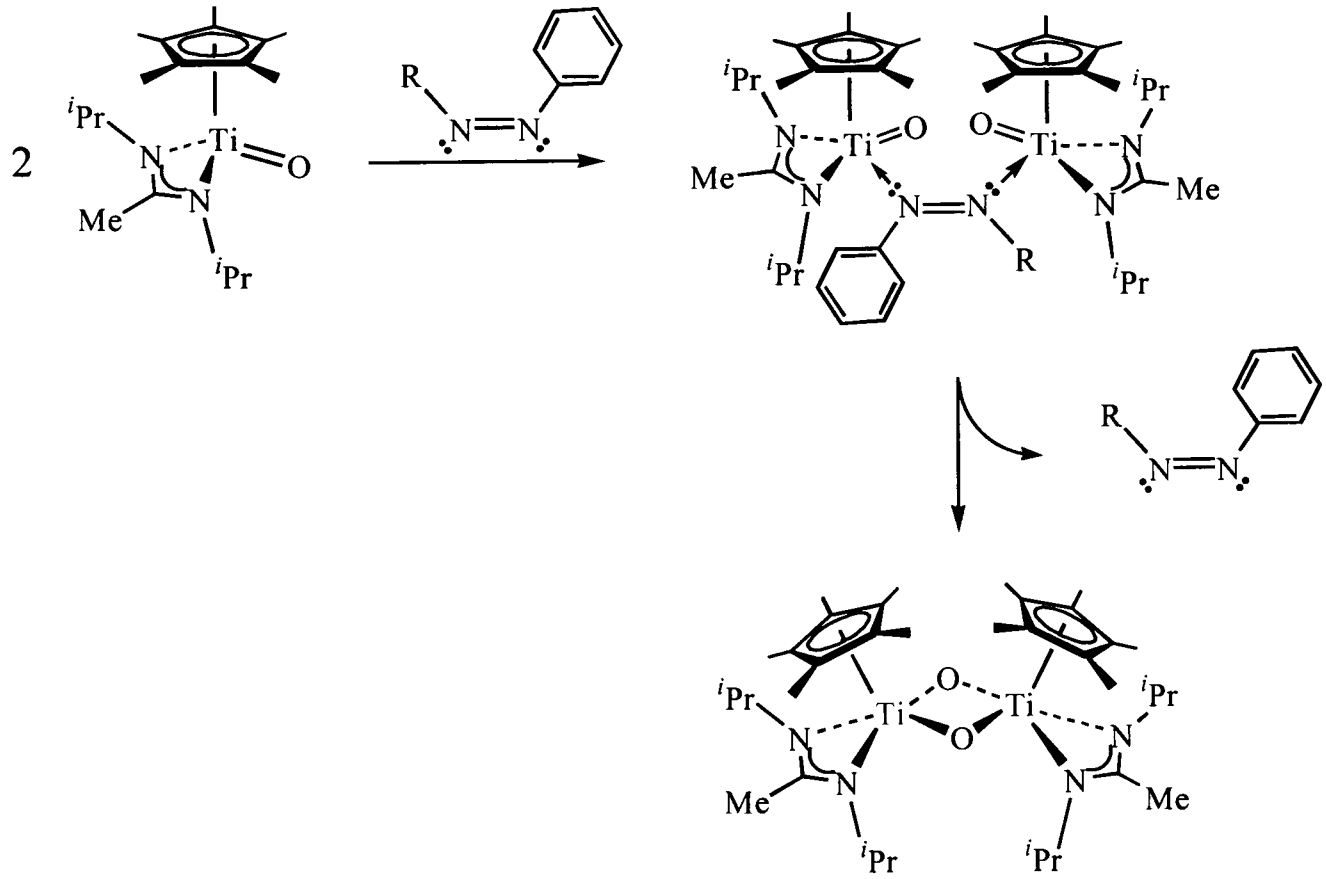
Furthermore, examination of the ^{1}H NMR spectra of the reactions of $Ti(\eta\text{-}C_5Me_5)(N^tBu)\{MeC(N^iPr)_2\}$ (**2**), $Ti(\eta\text{-}C_5Me_5)(N\text{-}2,6\text{-}C_6H_3Me_2)\{MeC(N^iPr)_2\}$ (**7**) and $Ti(\eta\text{-}C_5Me_5)(N\text{-}4\text{-}C_6H_4Me)\{MeC(N^iPr)_2\}$ (**8**) show the intermediate to be the same species in all three cases. It was therefore concluded that the *cis*- isomer of $[Ti(\eta\text{-}C_5Me_5)(\mu\text{-}O)\{MeC(N^iPr)_2\}]_2$ (**22a**) had been formed by the reaction of the imido complexes with nitrosobenzene.

Of interest is the fact that the reaction with nitrosobenzene preferentially forms the *cis* isomer **22a** over the *trans* isomer **22**. Conversion of **22a** to **22** occurs at room temperature over a period of *ca.* 1 hour, and is found to be independent of the identity of the diazo species present.

The diazo species formed in the reactions between $Ti(\eta\text{-}C_5Me_5)(N\text{-}2,6\text{-}C_6H_3Me_2)\{MeC(N^iPr)_2\}$ (**7**) and $Ti(\eta\text{-}C_5Me_5)(N\text{-}4\text{-}C_6H_4Me)$

{MeC(N^{i}Pr)$_2$} (**8**) were identified by both ^{1}H NMR spectroscopy (interconversion from *cis*- to *trans*- geometry about the diazo linkage was observed by ^{1}H NMR spectrsocopy over a period of hours) and detection of protonated parent ions using APCI mass spectrometry (*m/z* = 211, 197, $[M+H]^+$ respectively).

The reason why the *cis*- isomer forms preferentially may possibly be explained by the presence of the diazene by-product of the reaction. It is possible that the transient terminal oxo species Ti(η-C$_5$Me$_5$)(O){MeC(N^{i}Pr)$_2$} is stabilised by donation of a lone pair from the diazo species, and that the diazo species can donate simultaneously to two oxo monomers. Dimerisation may then occur, templated by the diazo species to give **22a** (see Scheme 6.2):



22a

Scheme 6.2 – Possible mechanism for the formation of *cis*- [Ti(η-C$_5$Me$_5$)(μ-O){MeC(N^{i}Pr)$_2$}]$_2$ (**22a**) *via* diazo templating

To investigate the possibility that the transient cycloaddition product may be able to insert a second molecule of nitrosobenzene and form a stable adduct (analogous to the reactions with CO_2 and *p*-tolyl isocyanate described in Chapters 3 and 4), Ti(η-C_5Me_5)(N-4-C_6H_4Me){$MeC(N^iPr)_2$} (**8**) was reacted with a four-fold excess of nitrosobenzene. No difference was observed in the ^1H NMR, indicating that the cycloadduct is not stable enough to undergo further reaction before it decomposes.

There was no evidence to suggest that the diazene by-product undergoes reaction with the parent imido complexes. Separate experiments carried out between the imido complexes Ti(η-C_5H_4Me)(N^tBu){$PhC(NSiMe_3)_2$} (**3**) and Ti(η-C_5Me_5)(N-4-C_6H_4Me){$MeC(N^iPr)_2$} (**8**) with azobenzene showed no reaction, even after heating to 80 °C for 4 days.

6.2.4 SUMMARY

Reaction with nitrosobenzene has been shown to rapidly afford bridging dimeric oxo products from imido complexes, with no intermediate species being observed. The rapidity of the reaction with Ti(η-C_5Me_5)(NR){$MeC(N^iPr)_2$} (R = ^{t}Bu (**2**), 4-C_6H_4Me (**7**) and 2,6-$C_6H_3Me_2$ (**8**) has led to the detection of a *cis*- isomer of [Ti(η-C_5Me_5)(μ-O){$MeC(N^iPr)_2$}]$_2$ (**22a**), which is not observed by the other oxo-forming routes described previously. The instability of this complex towards isomerisation has prevented its isolation and full characterisation. Its formation in preference to the thermodynamically more stable complex **22** suggests that templating by the diazo complex formed during the reaction may occur. The products formed from the trapping of the

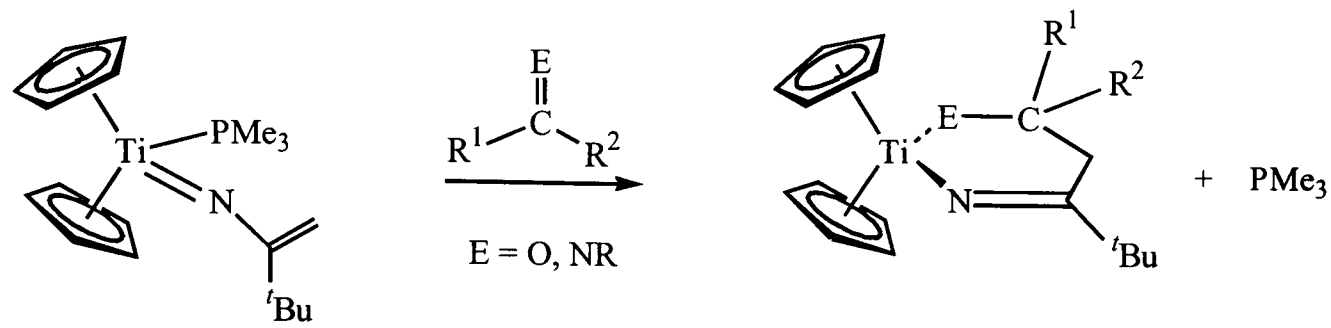
related transient species $Zr(\eta\text{-}C_5H_5)_2(O)$ have been shown to be reaction specific.[8]

6.3 Reactions of Titanium Cyclopentadienyl Imido Amidinate Complexes with Organic Carbonyls and Imines

6.3.1 Introduction

Since the 1980s it has been known that some organoimido species react with carbonyl species such as aldehydes to afford organic imines and metal oxo complexes.[9] This Section summarises the reactivity of imido species with carbonyls that has been reported in the literature, and also refers to some related reactivity such as that of imines with imido complexes.

Doxsee reported the first terminal vinylimido titanocene complex in 1990[10] and investigated its reactivity with acetone. In contrast to the previously observed reaction of metal imides with ketones to yield metal oxo complexes and organic imines,[11,12] the vinylimido titanocene complex afforded a metallacyclic product in which the imido fragment is retained. Further work by Doxsee showed similar reactivity with imines;[13] the complex undergoing a formal [4 + 2] reaction rather than the usual [2 + 2] metathesis. This reactivity is summarised in Equation 6.2:



6.7

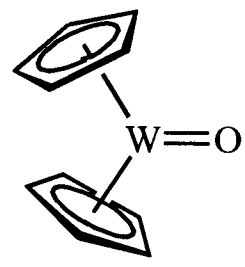
R^1	R^2	E	
Me	Me	O	**6.8**
Ph	H	NPh	**6.9**

Equation 6.2

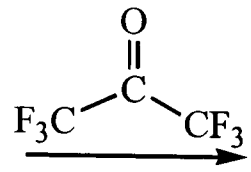
Subsequent reactivity with other early transition metal terminal imido species, including Ti(TTP)(N^{i}Pr) (**6.1**),[1] Cr(TPP)(N-4-C_6H_4Me) (**6.10**) (TPP = 5, 10, 15, 20- tetraphenylporphyrin dianion),[14] and Ta(η-C_5Me_5)(N^{t}Bu)Cl_2 (**6.11**)[15] all demonstrate imide / carbonyl metathesis chemistry with aldehydes and ketones, which were presumed to occur *via* a formal [2 + 2] cycloaddition followed by retrocyclisation. Reaction of Ta(η-C_5Me_5)(N^{t}Bu)Cl_2 with imines resulted in imido exchange, indicative of an analogous process.[15] No direct evidence for the cycloaddition products of the imido species with either carbonyls or imines was reported.

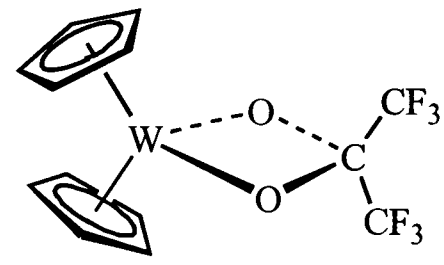
6.3.1.1 Carbonyl Reactions

Reactions with terminal oxo species have afforded cycloaddition products, which have been isolated and characterised. The first example was reported by Geoffroy *et al.* in 1990,[16] in which the tungstenocene oxo complex W(η-$C_5H_5)_2$(O) (**6.12**) reacts with the highly electrophilic ketone CF_3COCF_3 to form a [2 + 2] cycloaddition product, as shown in Equation 6.3.



6.12



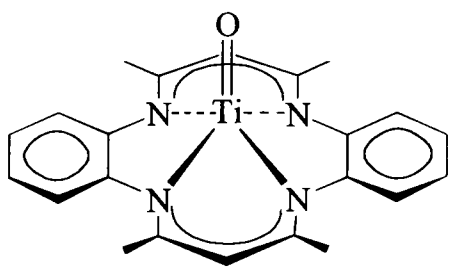


6.13

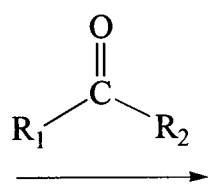
Equation 6.3

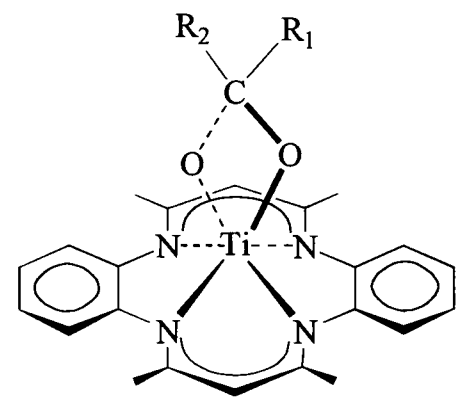
Other aldehydes and ketones failed to form detectable metallacycles of this sort, but labelling experiments using ^{17}O demonstrated that the label could be slowly transferred from the organometallic species to benzaldehyde and acetone. This scrambling of oxygen between $W(\eta\text{-}C_5H_5)_2(O)$ and the carbonyl suggests that they undergo reversible cycloaddition reactions.

One year later, Geoffroy demonstrated that the titanium macrocycle complex $Ti(Me_4taa)(O)$ (**6.14**) reacts with less electrophilic ketones such as $MeCOCH_2Cl$ to afford stable cycloaddition products (Equation 6.4).[17] Reaction is not observed with acetone or 3-pentanone. The reactions were found to afford clean products; the cycloadduct formed from CF_3COMe was isolated in 98 % yield and has been structurally characterised.



6.14





R_1	R_2	
CF_3	CF_3	**6.15**
CF_3	Me	**6.16**
CF_3	Ph	**6.17**
$CHCl_2$	Me	**6.18**
CH_2Cl	Me	**6.18**

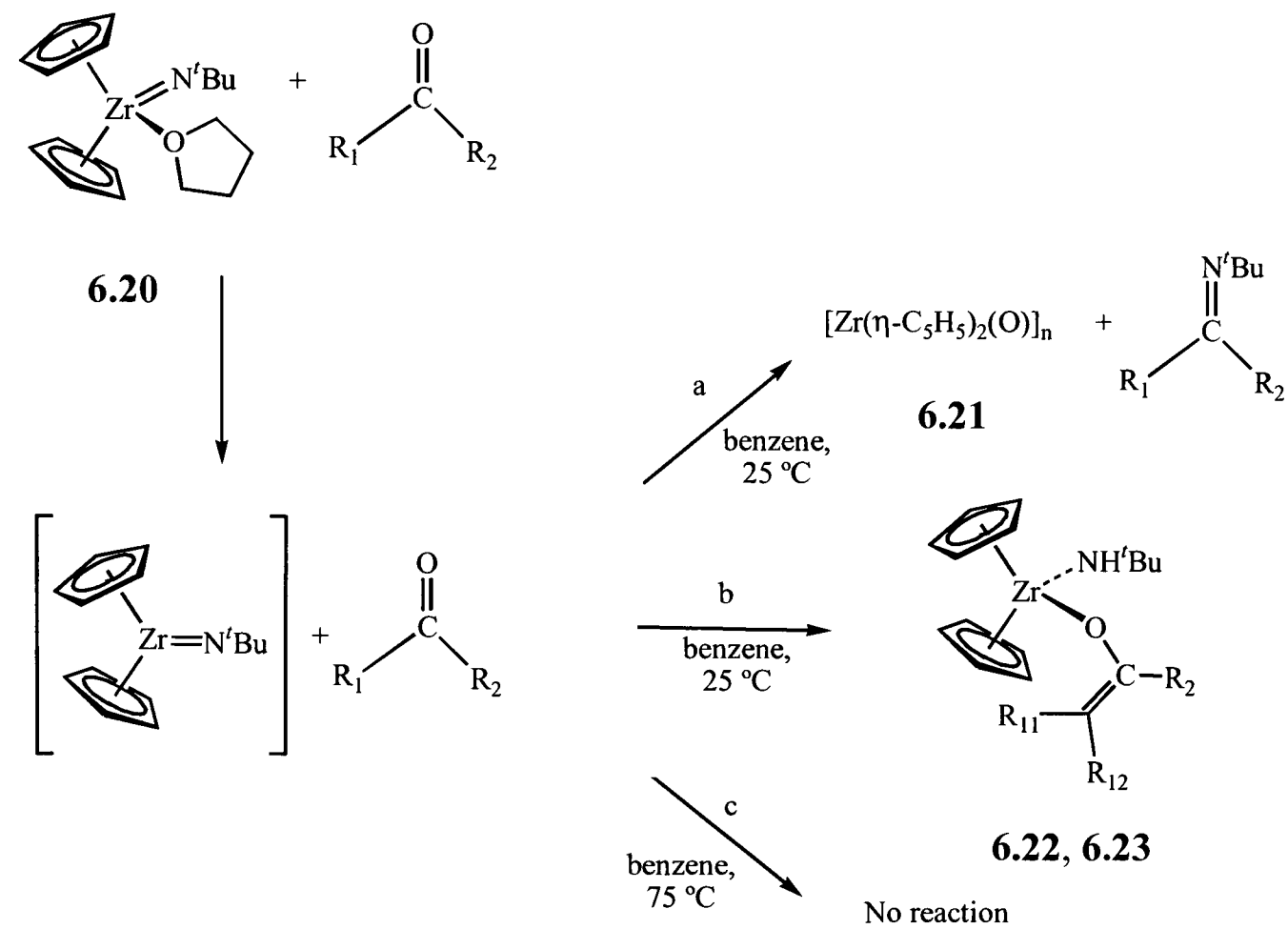
Equation 6.4

Though isolable, it was later reported that the complexes readily undergo ketone exchange; complex **6.16** was rapidly converted into **6.17** and released one equivalent of CF_3COMe upon addition of excess CF_3COPh. Similarly, **6.17** was rapidly converted into **6.16** upon treatment with excess CF_3COMe, liberating an equivalent of CF_3COPh.[18] This result points towards a reversible equilibrium existing between the cycloadduct and the dissociated oxo complex.

Geoffroy *et al.* also reported preliminary studies, in which the analogous sulfido species Ti(Me_4taa)(S) (**6.19**) was found to react with electron-deficient ketones in the same way. EI mass spectrometry showed ions due to Ti(Me_4taa)(O) (**6.14**) and CF_3CSCF_3 fragments, caused by retrocyclisation of the adduct by cleavage of Ti–S and C–O bonds.[18] The preparation of Ti(Me_4taa)(O) and thiocarbonyl species by this reaction was not reported, however.

Bergman has reported the imido / carbonyl exchange reaction between the zirconocene imido species $Zr(\eta\text{-}C_5H_5)_2(N^tBu)(THF)$ (**6.20**) and benzophenone to afford the oxozirconocene oligomer $[Zr(\eta\text{-}C_5H_5)_2O]_n$ (**6.21**) and the corresponding imine.[19] In further studies, it was found that the steric encumbrance of the carbonyl is critical in determining the product of reaction.[8] Thus aldehydes and simple ketones undergo rapid imido / carbonyl exchange to afford oligomeric zirconocene oxo complexes and organic imines, while more encumbered ketones possessing α-hydrogens give rise to zirconocene enolate complexes *via* α-hydrogen abstraction. Bulky ketones

lacking α-hydrogens demonstrate no reactivity. These observations are summarised in Scheme 6.3.



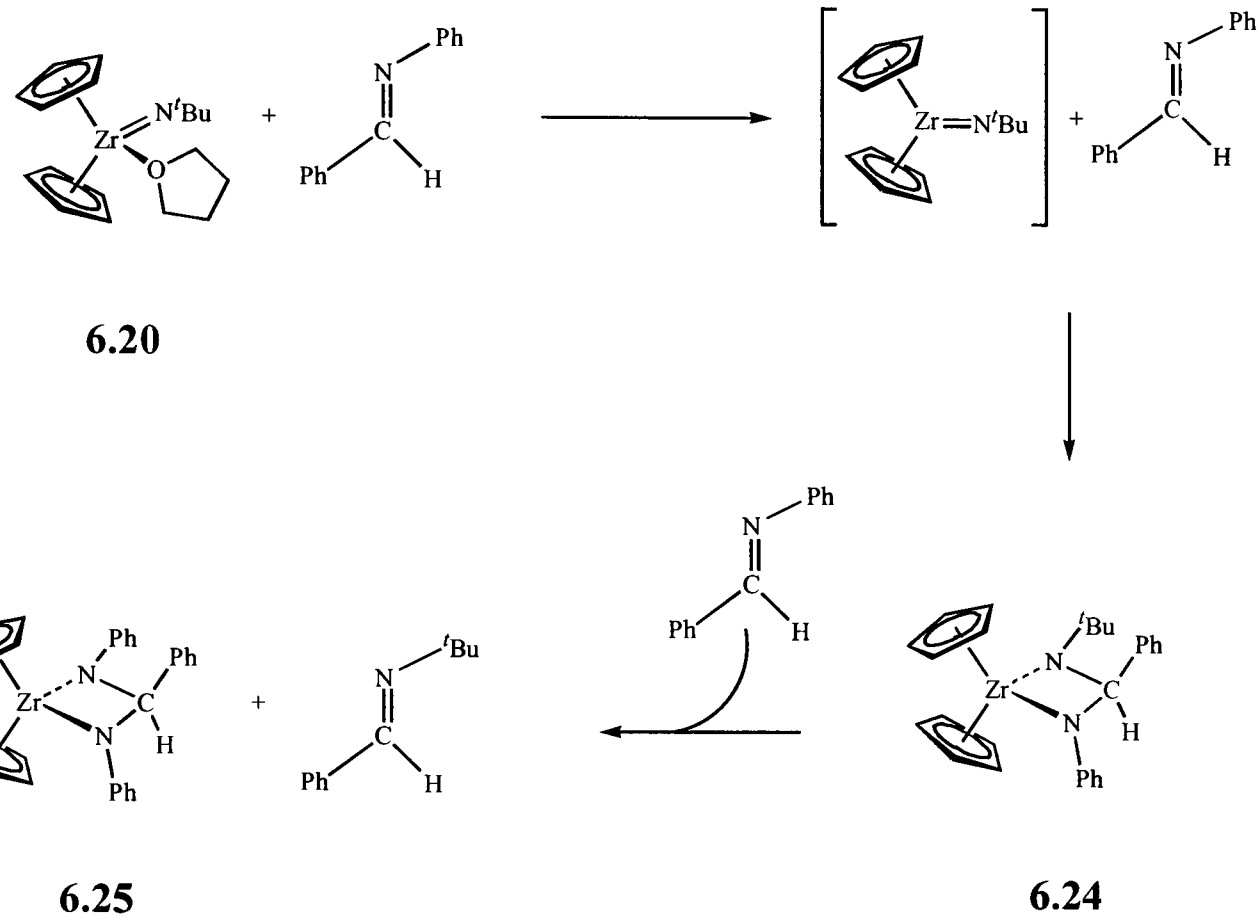
Reaction	R^1	R^2	(R^{11})	(R^{12})	
a)	Me	Me			**6.21**
	Ph	H			**6.21**
	^{i}Pr	H			**6.21**
b)	Me	^{t}Bu	H	H	**6.22**
	^{i}Pr	^{i}Pr	Me	Me	**6.23**
c)	^{t}Bu	^{t}Bu			

Scheme 6.3 – Reactions of Zr(η-C_5H_5)$_2$(N^{t}Bu)(THF) (**6.20**) with ketones

Low temperature NMR studies showed behaviour consistent with the imido / carbonyl exchange process proceeding *via* a transient [2 + 2] metallacyclic intermediate.

6.3.1.2 IMINE REACTIONS

Reaction of $Zr(\eta\text{-}C_5H_5)_2(N^tBu)(THF)$ (**6.20**) with organic imines has also been reported.[20] In contrast to the carbonyl chemistry of the imido complex, reaction of **6.20** with an imine affords a stable 2,4-diaza-1-zirconacyclobutane complex (**6.24**) as product. This compound has been shown to undergo imine metathesis in the presence of excess imines (Scheme 6.4)



6.20 **6.25** **6.24**

Scheme 6.4 – Reaction of $Zr(\eta\text{-}C_5H_5)_2(N^tBu)(THF)$ (**6.20**) with *N*-benzylideneaniline

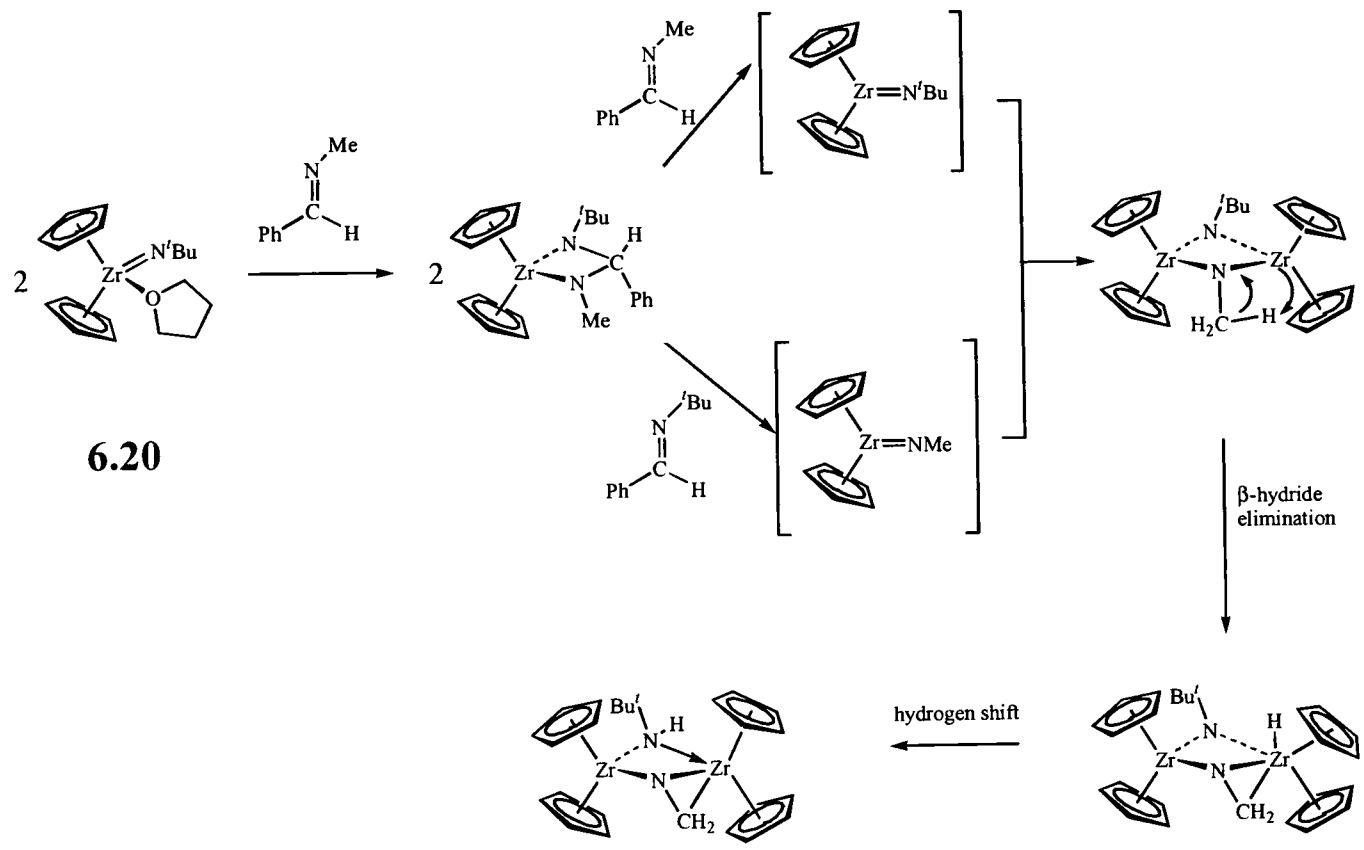
The 2,4-diaza-1-zirconacyclobutane complexes **6.24** and **6.25** are stable at 25 °C in the absence of excess imine, but undergo elimination of imine at elevated temperatures to afford the dimeric imido species $[Zr(\eta\text{-}C_5H_5)_2(\mu\text{-}NPh)]_2$ (**6.26**), which was found to be catalytically inactive. This observation, coupled with kinetic investigations, led to the proposal of a dissociative mechanism for the metathesis reaction, *via* a transient terminal

$[Zr(\eta\text{-}C_5H_5)_2(NPh)]$ species.[21] Subsequent work included replacing one of the cyclopentadienyl ligands with pentamethylcyclopentadienyl to reduce the propensity of the active monomeric species for dimerisation, and addition of diphenylacetylene to the reaction mixture to minimise the concentration of the free imido complex, by reversible formation of an azametallacyclobutene (*vide infra*).[22,23]

Whilst being effective agents in the metathetical exchange between different N-aryl imines, these zirconocene-based complexes were found to be completely unreactive towards metathesis with N-aryl aldimines.[23] Reaction with N-alkyl imines was found to be slow and erratic; stoichiometric reaction of $Zr(\eta\text{-}C_5H_5)_2(N^tBu)(THF)$ (**6.20**) and PhCH=NMe was found to yield the dimeric species $[Zr(\eta\text{-}C_5H_5)_2]_2(\mu\text{-}NH^tBu)(\mu\text{-}N{=}CH_2)$ (**6.27**). The crystal structure of this molecule revealed extreme asymmetry of the bridging methyleneamido group. The proposed mechanistic pathway for the formation of the product is shown in Scheme 6.5.[24]

Other transition metal imido complexes have been found to be effective reagents for imine metathesis reactions. Such species include the molybdenum complexes $Mo(N^tBu)_2Cl_2(dme)$ (**6.28**), $Mo(N\text{-}2,6\text{-}C_6H_3{}^iPr_2)_2Cl_2(dme)$ (**6.29**), and $Mo(N\text{-}2,6\text{-}C_6H_3{}^iPr_2)_2(O^tBu)_2$ (**6.30**),[25,26] and the titanium complex $Ti(N^tBu)Cl_2(py)_3$ (**6.31**).[27,28] Kinetics experiments carried out on this imidotitanium complex with organic imines have yielded some interesting results. It has been demonstrated that apparently straightforward transition metal imide / organic imine metathesis reactions do not necessarily involve

metal imide participation in the rate determining step.[28] Very recently, Meyer *et al.*[29] have reported imine metathesis studies of the complex $Ta(\eta\text{-}C_5H_5)(N^tBu)Cl_2$ (**6.32**). The mechanism of the reaction was found to be complex, involving both catalysis by adventitious amine (previously reported for $Ti(N^tBu)Cl_2(py)_3$),[27] and by the presence of trace HCl. It has been proposed that trace HCl may also act catalytically in some other imine metathesis processes.



6.20 **6.27**

Scheme 6.5 – Proposed mechanism for the reaction of $Zr(\eta\text{-}C_5H_5)_2(N^tBu)(THF)$ (**6.20**) with PhCHNMe

6.3.2 REACTIONS OF TITANIUM CYCLOPENTADIENYL IMIDO AMIDINATE COMPLEXES WITH ORGANIC CARBONYLS

The reactivity of a series of carbonyls (acetone, benzophenone, benzaldehyde and acetophenone) with titanium imido complexes supported by a cyclopentadienyl amidinate ligand set was explored, and the results given in the following Sections. Each of the carbonyls used will be dealt with separately.

6.3.2.1 REACTIONS OF TITANIUM CYCLOPENTADIENYL IMIDO AMIDINATE COMPLEXES WITH ACETONE

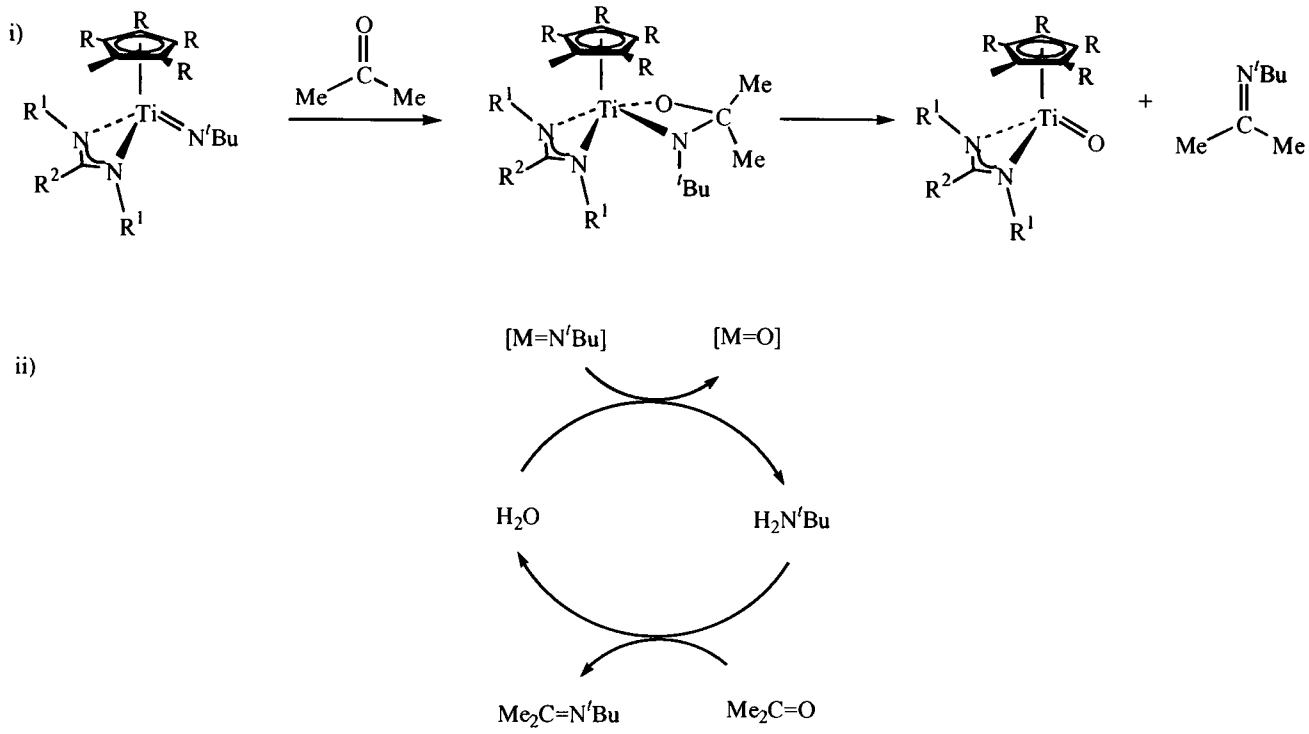
Samples of Ti(η-C_5Me_5)(N^{t}Bu){PhC(NSiMe$_3$)$_2$} (**1**), Ti(η-C_5Me_5)(N^{t}Bu){MeC(N^{i}Pr)$_2$} (**2**) and Ti(η-C_5H_4Me)(N^{t}Bu){MeC(N^{i}Pr)$_2$} (**3**) were dissolved in benzene-d_6, and treated with one equivalent of acetone. The reactions were followed using ^{1}H NMR spectroscopy.

6.3.2.1.1 RESULTS AND DISCUSSION

No reaction was observed after 30 minutes for any of the samples. Reaction was found to occur for Ti(η-C_5Me_5)(N^{t}Bu){MeC(N^{i}Pr)$_2$} (**2**) and Ti(η-C_5H_4Me)(N^{t}Bu){PhC(NSiMe$_3$)$_2$} (**3**) after 12 hours in solution, with the reaction of **3** proceeding more rapidly as expected on steric grounds. The reaction with Ti(η-C_5Me_5)(N^{t}Bu){PhC(NSiMe$_3$)$_2$} (**1**) required more forcing conditions (4 days at 80 °C). None of the reactions had reached completion after 4 days.

All three reactions gave a product which could be identified as *N-tert*-butyl-*iso*-propylideneamine from the ^{1}H NMR spectra. The organometallic products from the reactions of **1** and **2** with acetone could not be readily identified by ^{1}H NMR spectroscopy, but reaction of Ti(η-C_5H_4Me)(N^{t}Bu){PhC(NSiMe$_3$)$_2$} (**3**) with acetone gave the two isomeric bridging dimeric oxo products **24** and **24a**. No peaks corresponding to a formal [2 + 2] cycloadduct were observed in any of the reactions.

There are two possibilities to account for these observations. In agreement with the other examples of metal imido reactions with carbonyls cited above, the carbonyl could undergo cycloaddition with the imide to afford a metallacycle, which decomposes rapidly *via* retrocyclisation to yield the transient terminal oxo species and *N-tert*-butyl-*iso*-propylideneamine. Rapid dimerisation to form the dimeric oxo species would then occur. Alternatively, trace amounts of water or *tert*-butylamine present may effect catalytic conversion of the acetone to *N-tert*-butyl-*iso*-propylideneamine. Any water present would hydrolyse a small amount of the imido complex, to liberate *tert*-butylamine. The amine could then react with the carbonyl to yield an imine and water, which would continue the cycle catalytically (Scheme 6.6)



Scheme 6.6 – Possible mechanisms for reactions of Ti(η-C_5R_4Me)(N^{t}Bu){$R^1C(NR^2)_2$} with acetone

Since only a trace of water or amine would be necessary for the second mechanism to operate, it cannot be ruled out by analysis of the data collected. In addition, the keto-enol tautomerism that acetone readily undergoes may render it acidic enough to protonate the metal imido complexes, liberating *tert*-butylamine. As a result, work was discontinued with acetone, and attention turned to a carbonyl with no capacity for keto-enol tautomerism, namely benzophenone.

6.3.2.2 Reactions of titanium cyclopentadienyl imido amidinate complexes with benzophenone

Owing to its lack of α-hydrogens, benzophenone is unable to undergo keto-enol tautomerisation, precluding it from acting as an enol proton source. It was thus ideally suited for study with the imido complexes.

Samples of Ti(η-C_5Me_5)(N^{t}Bu){MeC(N^{i}Pr)$_2$} (**2**), Ti(η-C_5Me_5)(N-4-C_6H_4Me){MeC(N^{i}Pr)$_2$} (**8**), Ti(η-C_5Me_5)(N-4-C_6F_4H){MeC(N^{i}Pr)$_2$}, and Ti(η-C_5H_4Me)(N-2,6-$C_6H_3Me_2$){PhC(NSiMe$_3$)$_2$} (**11**) were dissolved in benzene-d_6, and treated with one equivalent of benzophenone. A sample of Ti(η-C_5H_4Me)(N-2,6-$C_6H_3Me_2$){MeC(N^{i}Pr)$_2$} (**12**) was dissolved in benzene-d_6, and treated with a three-fold excess of benzophenone. A sample of **8** was dissolved in toluene-d_8 for low temperature studies. Another sample of **8** was also dissolved in dichloromethane-d_2 with one equivalent of pyridine, and treated with one equivalent of benzophenone for low temperature studies. The reactions were all monitored using ^{1}H NMR spectroscopy.

6.3.2.2.1 RESULTS AND DISCUSSION OF REACTIONS OF Ti(η-C_5Me_5)(N^{t}Bu){MeC(N^{i}Pr)$_2$} (2) AND Ti(η-C_5Me_5)(N-4-C_6H_4Me){MeC(N^{i}Pr)$_2$} (8) WITH BENZOPHENONE

No reaction was observed between Ti(η-C_5Me_5)(N^{t}Bu){MeC(N^{i}Pr)$_2$} (**2**) and benzophenone after 16 hours in solution. The difference in reactivity can be explained by the larger steric bulk of benzophenone compared to acetone, and possibly by the lack of α-hydrogens precluding enol formation.

The ^{1}H NMR spectrum of the reaction of Ti(η-C_5Me_5)(N-4-C_6H_4Me){MeC(N^{i}Pr)$_2$} (**8**) with benzophenone after 10 minutes showed peaks corresponding to a new compound in addition to those of the starting materials (Figure 6.3).

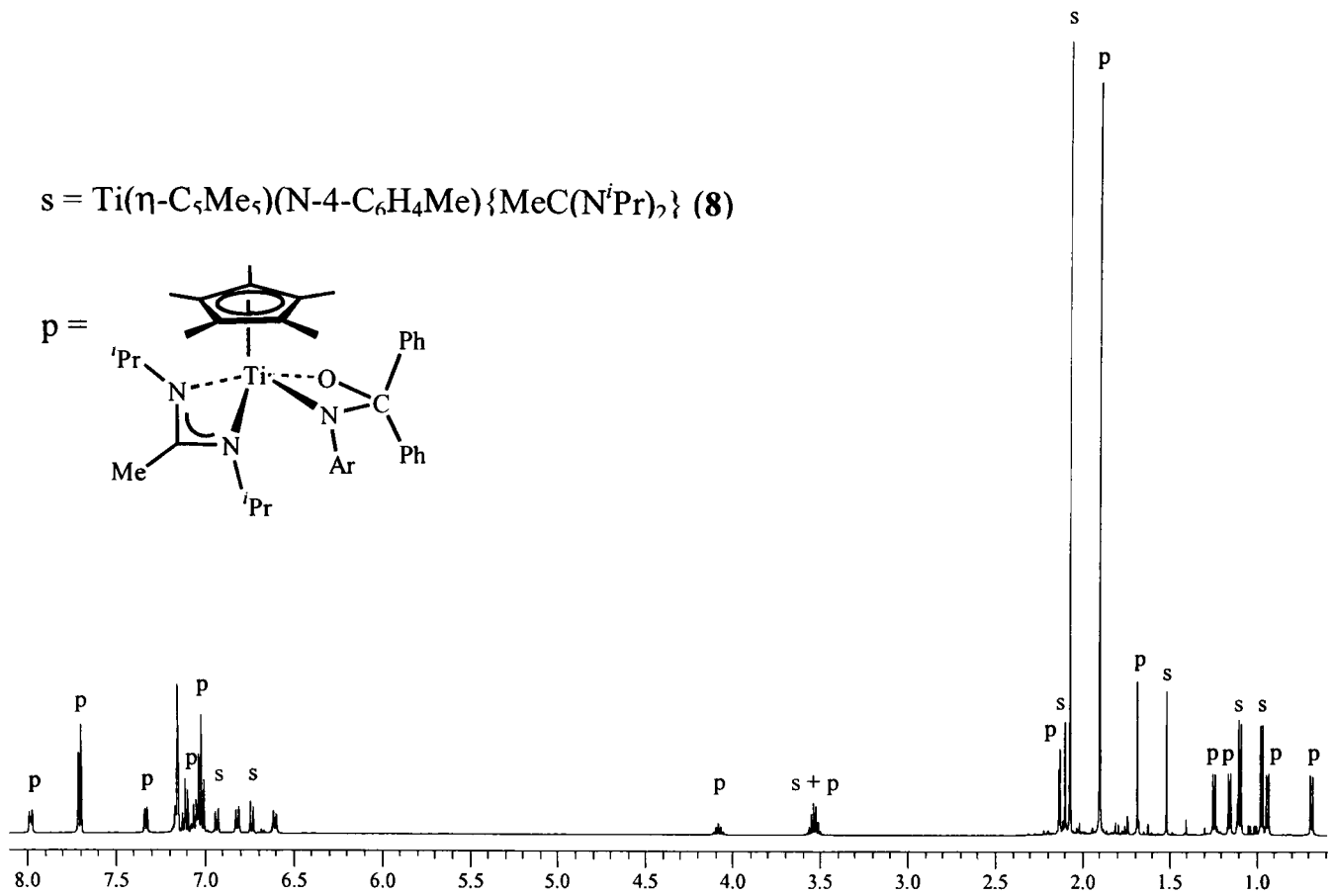


Figure 6.3 – 500.0 MHz ^{1}H NMR spectrum of reaction of Ti(η-C_5Me_5)(N-4-C_6H_4Me) {$MeC(N^iPr)_2$} (**8**) with benzophenone in benzene-d_6 after 10 min.

The ^{1}H NMR spectrum shows the formation of a new complex, in which the plane of symmetry has been removed. New peaks can be seen at 2.10 (3 H, 4-C_6H_4Me) and 1.90 (15 H, C_5Me_5) ppm, as well as singlets at 4.08, 3.54 (1 H) and 1.52 (3 H) ppm, and doublets at 1.24, 1.15, 0.94, and 0.68 ppm corresponding to the amidinate ligand in an unsymmetrical environment. This is consistent with the formation of the formal [2 + 2] cycloaddition product Ti(η-C_5Me_5){N(-4-C_6H_4Me)$C(Ph)_2O$}{$MeC(N^iPr)_2$} (**65**) from the imide **8** and benzophenone. No change was observed in the ^{1}H NMR spectra recorded over the following 3 hours, indicating that a stable equilibrium had been reached between the starting materials and the adduct. On heating the sample *in-situ* to 50 °C, the ^{1}H NMR spectrum showed decomposition of the adduct to starting materials, consistent with this view.

After 9 days, the majority of the peaks present in the ^{1}H NMR spectrum of the sample corresponded to the oxo complex **22,** along with other peaks due to an organic by-product. The organic was identified as *N*-benzhydrylidene-*p*-toluidine by detection of a protonated parent ion in the APCI mass spectrum (*m/z* = 272, $[M+H]^+$), and by comparison of the ^{1}H NMR spectrum in chloroform-d with literature values.[30]

The formation of **65** is the first example of a detected [2 + 2] cycloaddition product formed from an imidotitanium species and a ketone. It strongly supports the hypothesis that the imide / carbonyl metathesis process occurs *via* a metallacyclic pathway, and not by a trace hydrolysis mechanism. However, the possibility that carbonyls bearing α-hydrogens can react *via* another mechanism involving the enol tautomer, as found for the related $Zr(\eta\text{-}C_5H_5)_2(N^tBu)(THF)$ (**6.20**)[8] cannot be ruled out.

6.3.2.2.2 LOW TEMPERATURE ^{1}H NMR STUDIES OF THE REACTION BETWEEN $Ti(\eta\text{-}C_5Me_5)(N\text{-}4\text{-}C_6H_4Me)\{MeC(N^iPr)_2\}$ (8) AND BENZOPHENONE

To probe the thermodynamic stability of $Ti(\eta\text{-}C_5Me_5)\{N(\text{-}4\text{-}C_6H_4Me)C(Ph)_2O\}\{MeC(N^iPr)_2\}$ (**65**), 7.0 mg (0.016 mmol) of $Ti(\eta\text{-}C_5Me_5)(N\text{-}4\text{-}C_6H_4Me)\{MeC(N^iPr)_2\}$ (**8**) and 3.0 mg (0.016 mmol) of benzophenone were dissolved in 628 μl toluene-d_8. 1.9 mg (0.014 mmol) of 1,4-dimethoxybenzene was used as an internal standard. The ^{1}H NMR

spectrum of the reaction was measured over the temperature range +16 °C to -40 °C, as shown in Figure 6.4 below:

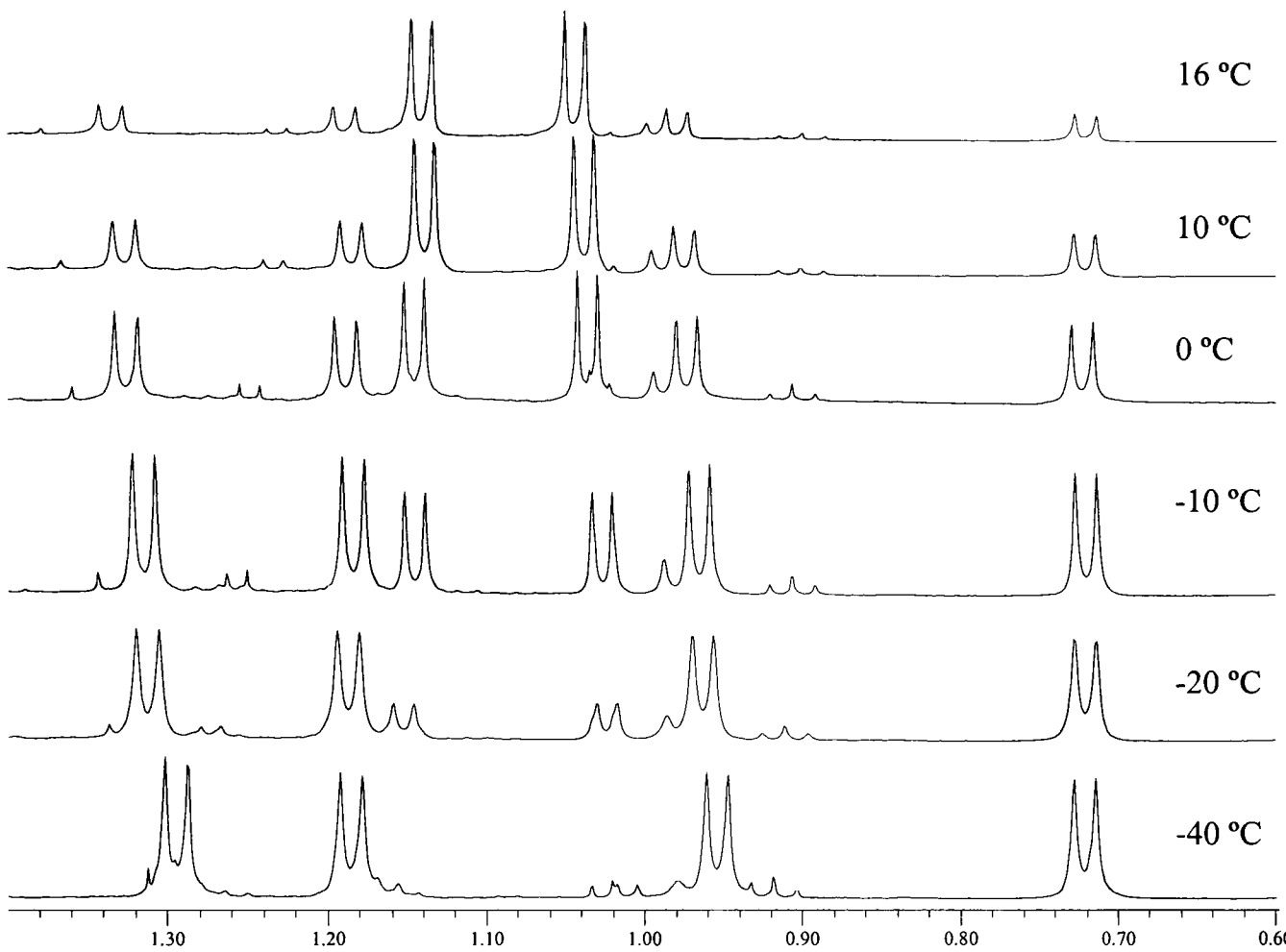
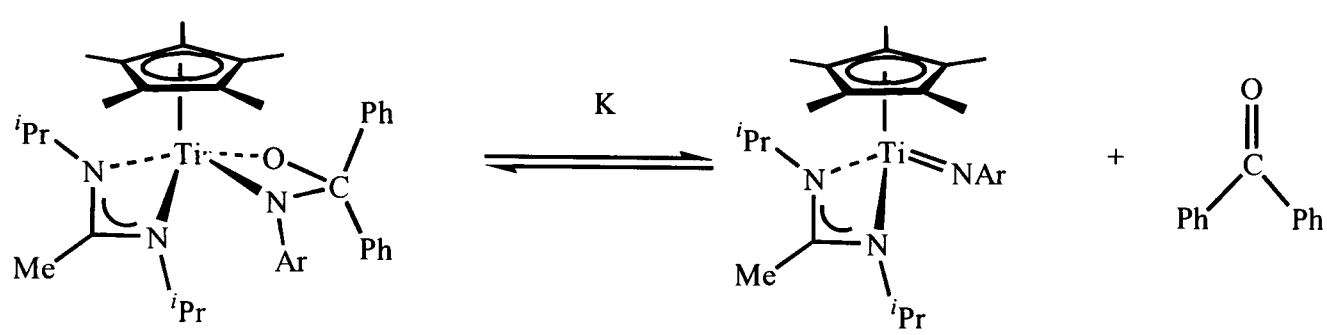


Figure 6.4 – 500.0 MHz ^{1}H NMR spectra of reaction between Ti(η-C_5Me_5)(N-4-C_6H_4Me) {$MeC(N^iPr)_2$} (**8**) and benzophenone in toluene-d_8 at temperatures indicated, showing the formation of Ti(η-C_5Me_5){N(-4-C_6H_4Me)$C(Ph)_2O$} {$MeC(N^iPr)_2$} (**65**) at low temperature

An additional series of low temperature ^{1}H NMR experiments were carried out on a sample of 13.9 mg (0.033 mmol) Ti(η-C_5Me_5)(N-4-C_6H_4Me) {$MeC(N^iPr)_2$} (**8**) in 810 μl dichloromethane-d_2. During the course of the experiments, 2.6 μl (0.033 mmol) pyridine and later 5.7 mg (0.033 mmol) benzophenone were added to the solution.

6.3.2.2.3 RESULTS AND DISCUSSION OF LOW TEMPERATURE EXPERIMENTS OF Ti(η-C_5Me_5)(N-4-C_6H_4Me){$MeC(N^iPr)_2$} (8) WITH BENZOPHENONE

The ^1H NMR resonances at each temperature are seen to be sharp, and show no evidence of broadening due to fluxional processes on the NMR timescale. It can therefore be stated that the equilibrium operates in the slow exchange regime of the ^1H NMR experiment throughout the temperature range studied. Equation 6.5 shows the equilibrium process being studied, and Table 6.1 details data extracted from the ^1H NMR measurements.



65 8

Equation 6.5

Table 6.1 – Concentration (mol dm^{-3}) of Ti(η-C_5Me_5)(N-4-C_6H_4Me){$MeC(N^iPr)_2$} (**8**) and Ti(η-C_5Me_5){N(-4-C_6H_4Me)$C(Ph)_2O$}{$MeC(N^iPr)_2$} (**65**) at various temperatures T

Temperature (K)	Adduct (65) (mol dm^{-3})	Parent imide (8) (mol dm^{-3})	K / mol dm^{-3}	ln K
233	0.025	non detected	-	-
243	0.024	1.4×10^{-3}	8.7×10^{-5}	-9.4
253	0.022	3.2×10^{-3}	4.6×10^{-4}	-7.7
263	0.020	5.8×10^{-3}	1.7×10^{-3}	-6.4
273	0.016	9.4×10^{-3}	5.5×10^{-3}	-5.2
283	0.012	0.014	0.017	-4.1

where:

$$K = \frac{[\text{concentration of } \mathbf{8}][\text{concentration of benzophenone}]}{[\text{concentration of } \mathbf{65}]}$$

Since:

$$\Delta G = - RT \ln K$$

and:

$$\Delta G = \Delta H - T\Delta S$$

then a plot of -ln K against 1/T enables the extraction of thermodynamic parameters, as shown in Figure 6.5.

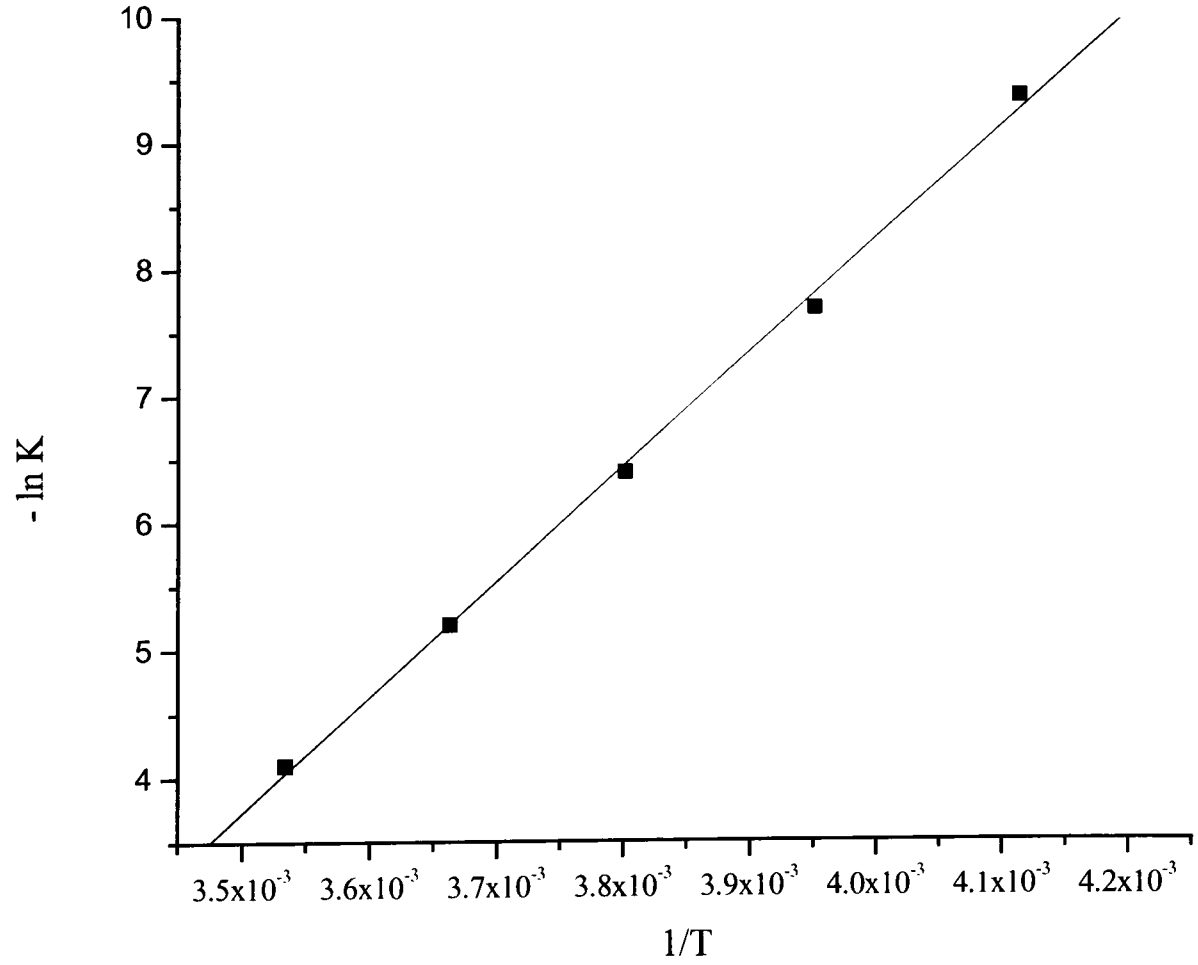


Figure 6.5 – Plot of -ln K against 1/T for the equilibrium of Ti(η-C_5Me_5){N(-4-C_6H_4Me)$C(Ph)_2O$}{$MeC(N^iPr)_2$} (**65**), Ti(η-C_5Me_5)(N-4-C_6H_4Me){$MeC(N^iPr)_2$} (**8**), and benzophenone

$$\Delta H = 75.1 \pm 1.9 \text{ kJ mol}^{-1}$$

$$\Delta S = 232 \pm 7 \text{ J K}^{-1} \text{ mol}^{-1}$$

These values are consistent with the dissociation of the adduct being an endothermic process, and resulting in an increase in entropy. The enthalpy of binding is found to be small (*c.f* ΔH_f(C–O) = 360 kJ mol^{-1}, ΔH_f(C–N) = 305 kJ mol^{-1}),[31] as expected from the reversible nature of binding of the compound in solution.

The ^{1}H NMR spectrum of the adduct at -40 °C in toluene-d_8 shows the characteristic four doublets (1.30, 1.19, 0.96, 0.72 ppm) and two virtual septets (4.14, 3.55 ppm) indicative of loss of symmetry of the amidinate group. Complete assignment of the ^{1}H NMR spectrum can be found in Chapter 8.

In order to differentiate between a [2 + 2] cycloaddition complex and a simple Lewis base (σ) adduct, a second series of low temperature ^{1}H NMR experiments were carried out. 13.9 mg (0.03 mmol) of Ti(η-C_5Me_5)(N-4-C_6H_4Me){MeC(N^{i}Pr)$_2$} (**8**) was dissolved in 810 μl dichloromethane-d_2 and cooled to -90 °C. No change was evident in the ^{1}H NMR spectrum over this temperature range. To the sample was added 2.6 μl (0.03 mmol) pyridine, and the sample again cooled to -90 °C. No change was observed in the ^{1}H NMR spectrum of the imide, with no non-fluxional adduct being observed. Upon addition of 5.7 mg (0.03 mmol) benzophenone, small peaks corresponding to the product Ti(η-C_5Me_5)(N(-4-C_6H_4Me)C(Ph)$_2$O}

{MeC(N^{i}Pr)$_2$} (**65**) were observed. Lowering the temperature to -90 °C increased the amount of product present. The basicity of the lone pair on pyridine is much greater than those of the carbonyl oxygen of benzophenone. The lack of reactivity of Ti(η-C$_5$Me$_5$)(N-4-C$_6$H$_4$Me){MeC(N^{i}Pr)$_2$} (**8**) with pyridine, in contrast to the reaction with benzophenone, strongly supports the proposed metallacyclic nature of the product.

6.3.2.2.4 RESULTS AND DISCUSSION OF REACTIONS OF Ti(η-C$_5$Me$_5$)(N-4-C$_6$F$_4$H){MeC(N^{i}Pr)$_2$}, Ti(η-C$_5$H$_4$Me)(N-2,6-C$_6$H$_3$Me$_2$){PhC(NSiMe$_3$)$_2$} (11), AND Ti(η-C$_5$H$_4$Me)(N-2,6-C$_6$H$_3$Me$_2$){MeC(N^{i}Pr)$_2$} (12) WITH BENZOPHENONE

In an attempt to synthesise an isolable cycloadduct, Ti(η-C$_5$Me$_5$)(N-4-C$_6$F$_4$H){MeC(N^{i}Pr)$_2$} (**6.32**),[32] Ti(η-C$_5$H$_4$Me)(N-2,6-C$_6$H$_3$Me$_2$){PhC(NSiMe$_3$)$_2$} (**11**), and Ti(η-C$_5$H$_4$Me)(N-2,6-C$_6$H$_3$Me$_2$){MeC(N^{i}Pr)$_2$} (**12**) were reacted with benzophenone in benzene-d$_6$ solution, and the reaction products determined by ^{1}H NMR spectroscopy.

In all cases, the reactions failed to cleanly form a cycloaddition product. Ti(η-C$_5$Me$_5$)(N-C$_6$F$_4$H){MeC(N^{i}Pr)$_2$} (donated by T. Blundell of this research group[32]) was reacted with an equimolar amount of benzophenone to afford an equilibrium mixture of adduct : imide of *ca.* 1 : 18. Ti(η-C$_5$H$_4$Me)(N-2,6-C$_6$H$_3$Me$_2$){PhC(NSiMe$_3$)$_2$} (**11**) afforded no cycloaddition product on reaction with an equimolar amount of benzophenone, as determined by ^{1}H NMR spectroscopy. After 12 days, however, additional peaks were present in

the ^{1}H NMR spectrum. These were assigned to the two isomeric bridging oxo dimers $[Ti(\eta\text{-}C_5H_4Me)(\mu\text{-}O)\{PhC(NSiMe_3)_2\}]_2$ (**24** and **24a**), and another species presumed to be *N*-benzhydrylidene-2,6-dimethylphenylamine by analogy with the reaction of benzophenone with $Ti(\eta\text{-}C_5Me_5)(N\text{-}4\text{-}C_6H_4Me)\{MeC(N^iPr)_2\}$ (**8**). Similar behaviour was observed for the reaction $Ti(\eta\text{-}C_5H_4Me)(N\text{-}2,6\text{-}C_6H_3Me_2)\{MeC(N^iPr)_2\}$ (**12**) with benzophenone. No reaction was observed by ^{1}H NMR spectroscopy after 16 hours. After 3 days, trace amounts of the two isomeric oxo species $[Ti(\eta\text{-}C_5H_4Me)(\mu\text{-}O)\{MeC(N^iPr)_2\}]_2$ (**25** and **25a**), and *N*-benzhydrylidene-2,6-dimethylphenylamine were detected. No direct evidence for a cycloaddition product was observed.

6.3.2.2.5 SUMMARY

The reaction of benzophenone with $Ti(\eta\text{-}C_5Me_5)(N\text{-}4\text{-}C_6H_4Me)\{MeC(N^iPr)_2\}$ (**8**) has been shown to afford a cycloaddition product $Ti(\eta\text{-}C_5Me_5)\{N(\text{-}4\text{-}C_6H_4Me)C(Ph)_2O\}\{MeC(N^iPr)_2\}$ (**65**) in equilibrium with the starting materials; this is the first example of a [2 + 2] cycloaddition product between an imidotitanium species and a ketone. This product has been investigated and characterised by ^{1}H NMR spectroscopy at several temperatures, and thermodynamic parameters have been extracted. Retrocyclisation of the adduct occurs preferentially to regenerate the parent imide and benzophenone, but can also occur irreversibly to give the thermodynamic products $Ti(\eta\text{-}C_5Me_5)(\mu\text{-}O)\{MeC(N^iPr)_2\}$ (**22**) and *N*-benzhydrylidene-*p*-toluidine. Attempts to form a stable cycloaddition product with benzophenone by variation of the imido group and supporting ligands have proven unsuccessful.

6.3.2.3 REACTIONS OF TITANIUM CYCLOPENTADIENYL IMIDO AMIDINATE COMPLEXES WITH BENZALDEHYDE

Benzaldehyde was the next substrate selected for study. Structurally similar to benzophenone but with less steric bulk, benzaldehyde was predicted to afford a more stable cycloadduct.

Samples of Ti(η-C_5Me_5)(N^{t}Bu){MeC(N^{i}Pr)$_2$} (**2**), Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$){MeC(N^{i}Pr)$_2$} (**7**), and Ti(η-C_5Me_5)(N-4-C_6H_4Me){MeC(N^{i}Pr)$_2$} (**8**) were dissolved in aliquots of benzene-d_6, and treated with one equivalent of benzaldehyde. The reactions were monitored using ^{1}H NMR spectroscopy.

6.3.2.3.1 RESULTS AND DISCUSSION

^{1}H NMR spectroscopy showed that reaction of **2** with benzaldehyde occurred within 5 minutes to afford a cycloaddition product Ti(η-C_5Me_5){N(^{t}Bu)C(Ph)(H)O}{MeC(N^{i}Pr)$_2$} (**66**), with only traces of the imido starting material and benzaldehyde remaining (Figure 6.6). As indicated (*), peaks corresponding to the retrocyclisation product *N*-benzylidene-*tert*-butylamine were already forming after 5 minutes, and steady decomposition of the adduct with a half-life of *ca.* 30 minutes was observed by ^{1}H NMR spectroscopy. Not all peaks corresponding to *N*-benzylidene-*tert*-butylamine are shown, owing to overlaps with peaks assigned to other species present.

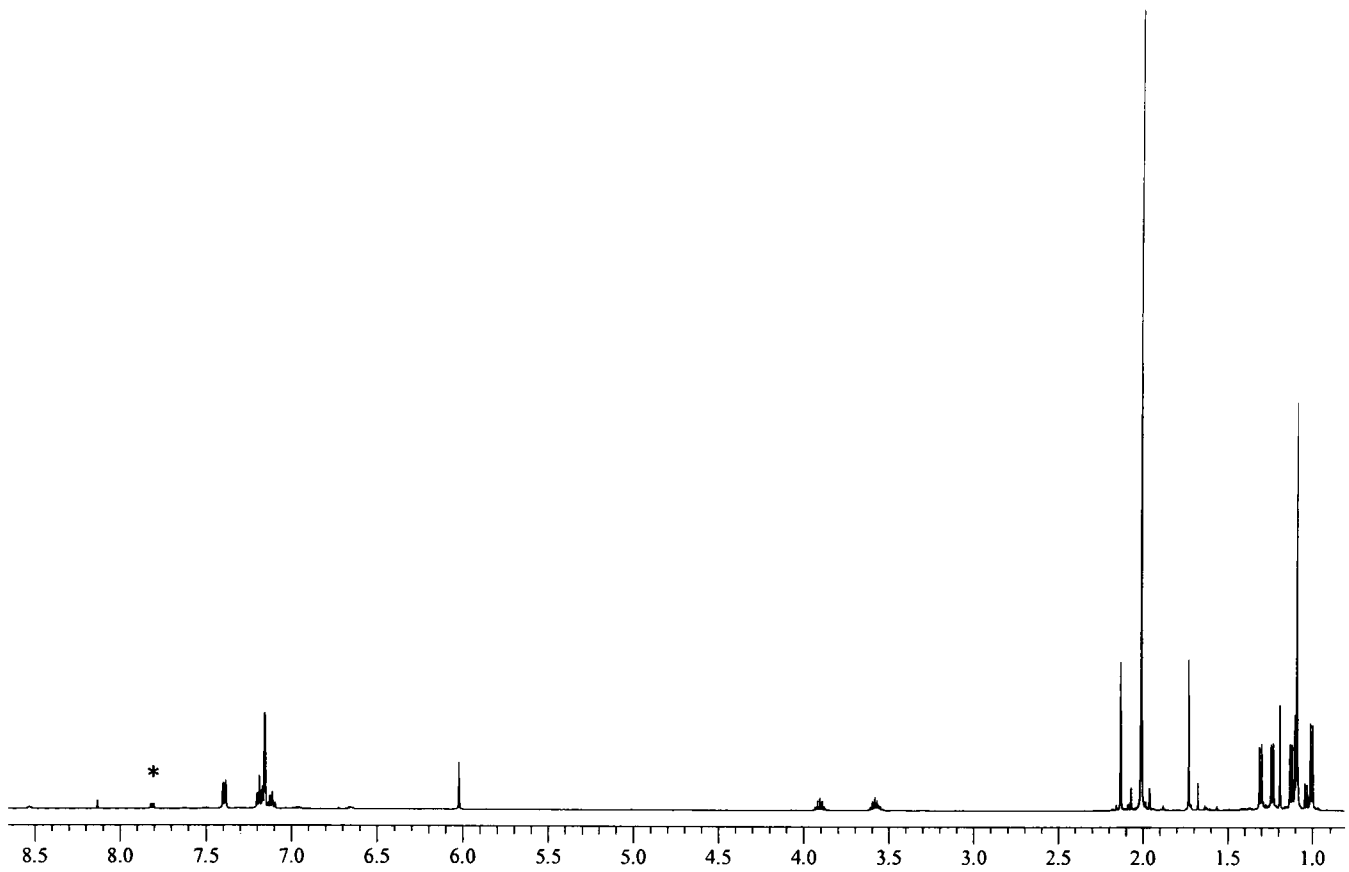


Figure 6.6 – 500.0 MHz ^{1}H NMR spectrum of reaction of Ti(η-C_5Me_5)(N^{t}Bu){MeC(N^{i}Pr)$_2$} (**2**) and benzaldehyde in benzene-d_6 after 5 min.

After 16 hours, the reaction had gone to completion, yielding the oxo compound [Ti(η-C_5Me_5)(μ-O){MeC(N^{i}Pr)$_2$}]$_2$ (**22**) and *N*-benzylidene-*tert*-butylamine. This product was identified by comparison of ^{1}H NMR spectroscopic data collected in chloroform-d with literature values[30] and by detection of a protonated parent ion peak in the APCI mass spectrum (*m/z* = 162, $[M+H]^+$).

The stereochemistry about the carbon atom of the four membered metallacycle in **66** cannot be stated with certainty. Two possible structures **A** and **B** exist; these are shown in Figure 6.7.

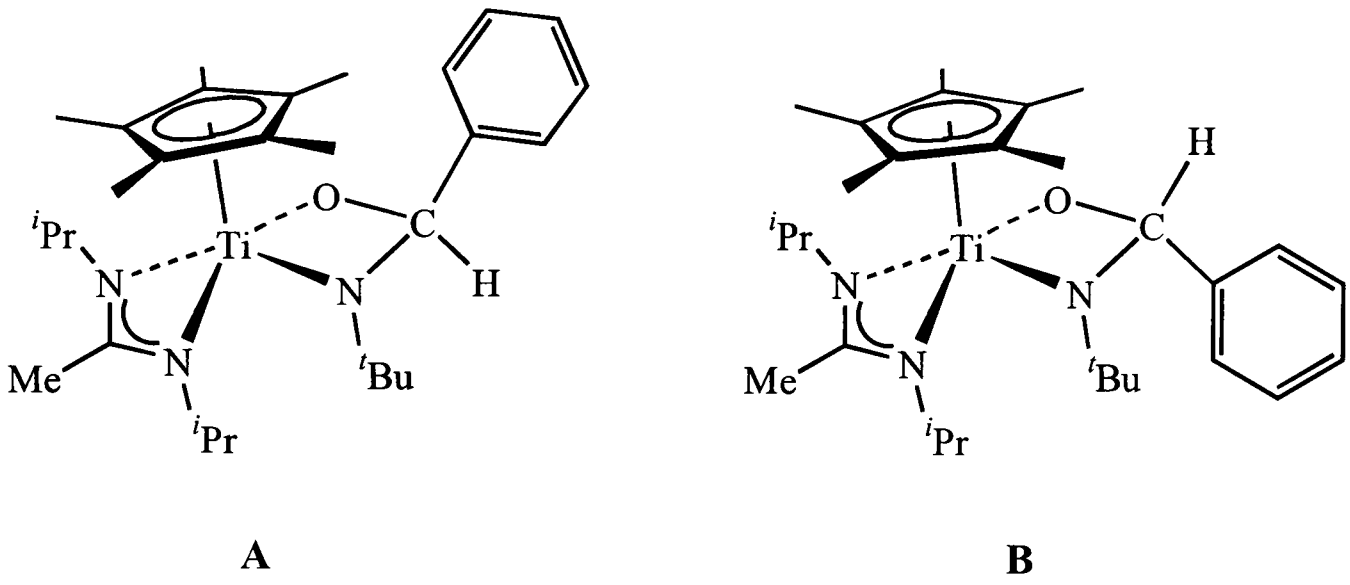


Figure 6.7 – Possible isomers of Ti(η-C_5Me_5){N(^{t}Bu)C(Ph)(H)O}{MeC(N^{i}Pr)$_2$} **(66)**

The instability of the complex precluded a more detailed study. However, steric considerations favour structure **B**, in which the repulsions between the methyl groups of the pentamethylcyclopentadienyl ring and the phenyl protons are minimised. This is also consistent with the observation that the phenyl ring is positioned away from the cyclopentadienyl ligand in the related complex Ti(η-C_5Me_5){N(4-C_6H_4Me)C(Ph)(Me)O}{MeC(N^{i}Pr)$_2$} **(68)** (*vide infra*).

7.5 mg (0.018 mmol) Ti(η-C_5Me_5)(N-4-C_6H_4Me){MeC(N^{i}Pr)$_2$}(**8**) and 1.8 μl (1.9 mg, 0.018 mmol) benzaldehyde were dissolved in benzene-d_6 and the extent of reaction was monitored using ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum of the reaction between Ti(η-C_5Me_5)(N-4-C_6H_4Me){MeC(N^{i}Pr)$_2$} (**8**) and benzaldehyde showed that reaction occurred within 5 minutes (Figure 6.8), with all the imido starting material being consumed. However, the ^{1}H NMR spectra of the reaction were found to be more complicated than in the reaction of Ti(η-C_5Me_5)(N^{t}Bu){MeC(N^{i}Pr)$_2$} (**2**) with benzaldehyde.

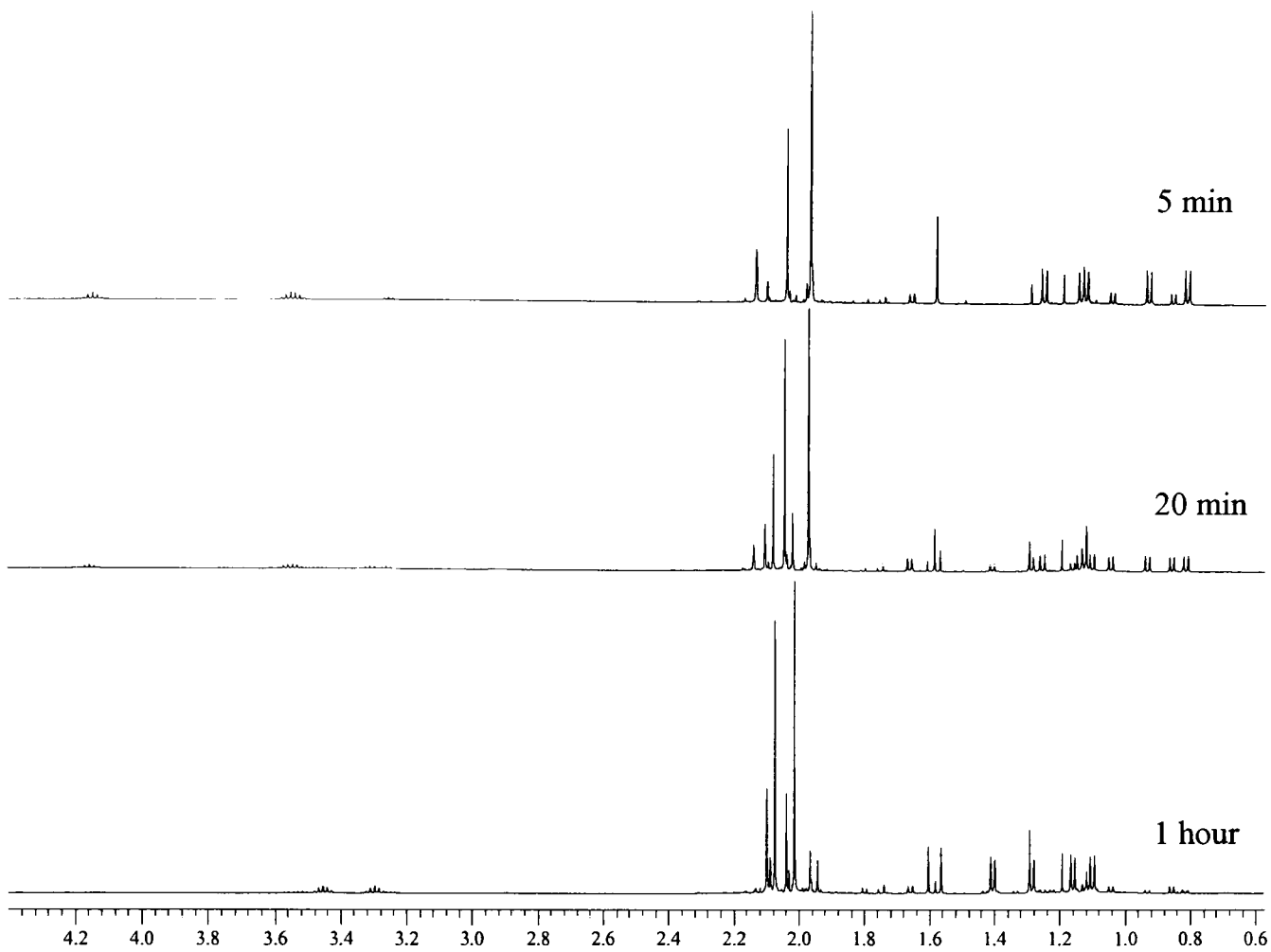
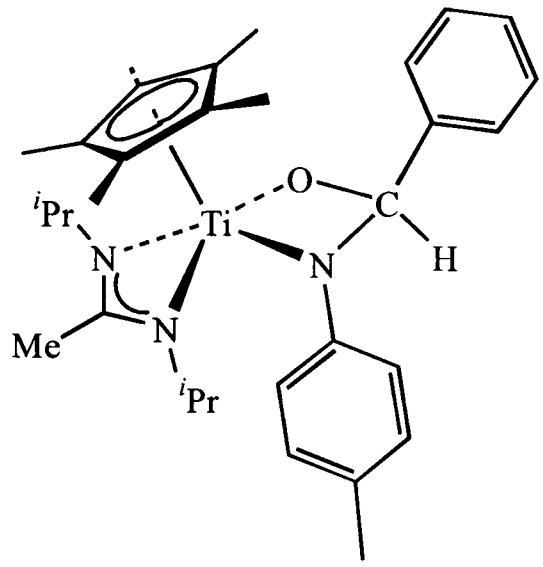


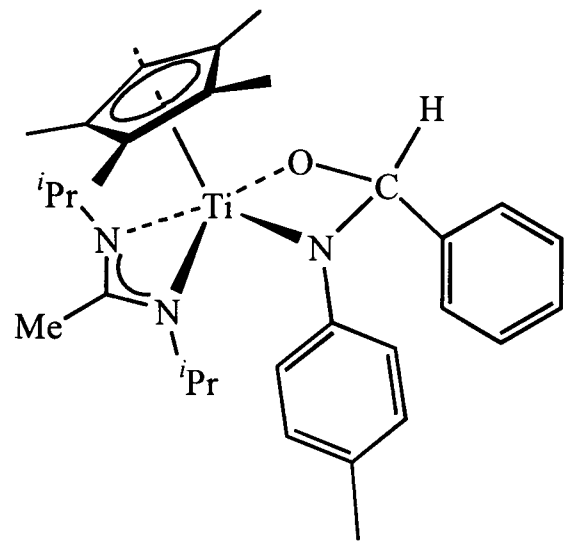
Figure 6.8 – 500.0 MHz ^{1}H NMR spectra of the reaction between Ti(η-C_5Me_5)(N-4-C_6H_4Me){$MeC(N^iPr)_2$} (**8**) and benzaldehyde in benzene-d_6 at time *t*

The reaction initially yields a product whose ^{1}H NMR spectrum is consistent with a cycloaddition product analogous to **66**. However, this product is found to interconvert to another species, also consistent with a cycloaddition product, before decomposing to give the final oxo complexes [Ti(η-C_5Me_5)(μ-O){$MeC(N^iPr)_2$}]$_2$ (**22** / **22a**) and *N*-benzylidene-*p*-toluidine. This latter species was identified by comparison with the ^{1}H NMR spectrum of a pure commercially obtained sample of *N*-benzylidene-*p*-toluidine.

As with the reaction of Ti(η-C_5Me_5)(N^tBu){$MeC(N^iPr)_2$} (**2**) with benzaldehyde, the stereochemistry about the carbon of the metallacycle allows two possible product molecules, **67A** and **67B**, as shown in Figure 6.9.



67A



67B

Figure 6.9 – Possible isomers of Ti(η-C_5Me_5){N(-4-C_6H_4Me)C(Ph)(H)O}{MeC(N^{i}Pr)$_2$} (**67**)

The data support the hypothesis that one of the isomers forms first as a kinetic product, and then interconverts to the other, more stable isomer, before decomposing to form the final oxo products and the imine. However, it is not clear why such a kinetic isomer should form preferentially, or why no analogous complex is observed in the reaction of Ti(η-C_5Me_5)(N^{t}Bu){MeC(N^{i}Pr)$_2$} (**2**) with benzaldehyde. **67B** would be expected to be the thermodynamically more stable isomer, owing to the lower steric interactions between the metallacycle and the methyl groups on the pentamethylcyclopentadienyl ligand. It is structurally related to **66**.

The reaction of Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$){MeC(N^{i}Pr)$_2$} (**7**) and benzaldehyde resulted in a colour change from green to red within 10 seconds, followed by a further colour change after *ca.* 5 minutes to give an orange solution. The ^{1}H NMR spectrum recorded after 10 minutes indicated complete conversion of **7** to the two isomeric oxo species [Ti(η-C_5Me_5)

$(\mu\text{-O})\{MeC(N^iPr)_2\}]_2$ (**22** / **22a**), with concomitant formation of *N*-benzylidene-2,6-dimethylphenylamine. The imine was identified by comparison of the ^1H NMR spectrum recorded in chloroform-d with literature values[30] and by detection of a protonated parent ion peak in the APCI mass spectrum ($m/z = 210$, $[M+H]^+$).

6.3.2.3.2 SUMMARY

It has been shown that the reaction between the titanium cyclopentadienyl imido amidinate complexes and benzaldehyde is extremely sensitive to the imido N-substituent. The differences in behaviour of the systems examined is not easily explained, although the greater steric crowding about the imido group of $Ti(\eta\text{-}C_5Me_5)(N\text{-}2,6\text{-}C_6H_3Me_2)\{MeC(N^iPr)_2\}$ (**7**) relative to $Ti(\eta\text{-}C_5Me_5)(N\text{-}4\text{-}C_6H_4Me)\{MeC(N^iPr)_2\}$ (**8**) may explain the greater ease of decomposition of the benzaldehyde adduct.

6.3.2.4 REACTIONS OF TITANIUM CYCLOPENTADIENYL IMIDO AMIDINATE COMPLEXES WITH ACETOPHENONE

The lower steric requirement of benzaldehyde was found to give reaction systems in which the initial equilibrium was shifted in favour of the cycloaddition product. Once formed, however, these adducts were found to be unstable and decomposed rapidly to the oxo species and organic imines. Acetophenone was selected as a substrate to investigate, as it has a lower steric bulk than benzophenone (promoting cycloaddition), but greater bulk than benzaldehyde (possibly stabilising the adduct). There could, however, be

complications from possible keto-enol tautomerisation of the α-hydrogens of the methyl groups.

Samples of Ti(η-C_5Me_5)(N^{t}Bu){MeC(N^{i}Pr)$_2$} (**2**), Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$){MeC(N^{i}Pr)$_2$} (**7**), and Ti(η-C_5Me_5)(N-4-C_6H_4Me){MeC(N^{i}Pr)$_2$} (**8**) were dissolved in aliquots of benzene-d_6, and the reactions monitored using ^{1}H NMR spectroscopy.

6.3.2.4.1. RESULTS AND DISCUSSION

No reaction was observed between either Ti(η-C_5Me_5)(N^{t}Bu){MeC(N^{i}Pr)$_2$} (**2**) or Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$){MeC(N^{i}Pr)$_2$} (**7**) and acetophenone after 16 hours in solution at room temperature. Heating the reactions to 80 °C for 24 hours began to decompose the compounds, with peaks assignable as the oxo species [Ti(η-C_5Me_5)(μ-O){MeC(N^{i}Pr)$_2$}]$_2$ (**22**) being noted in the ^{1}H NMR spectrum, along with unidentified decomposition products. No resonances for an intermediate cycloadduct were observed.

By contrast, the reaction of Ti(η-C_5Me_5)(N-4-C_6H_4Me){MeC(N^{i}Pr)$_2$} (**8**) with acetophenone gave an immediate colour change from dark green to brown. The ^{1}H NMR spectrum recorded after 10 minutes showed the clean formation of a product, with the characteristic ^{1}H NMR resonances of a cycloaddition product (Figure 6.10).

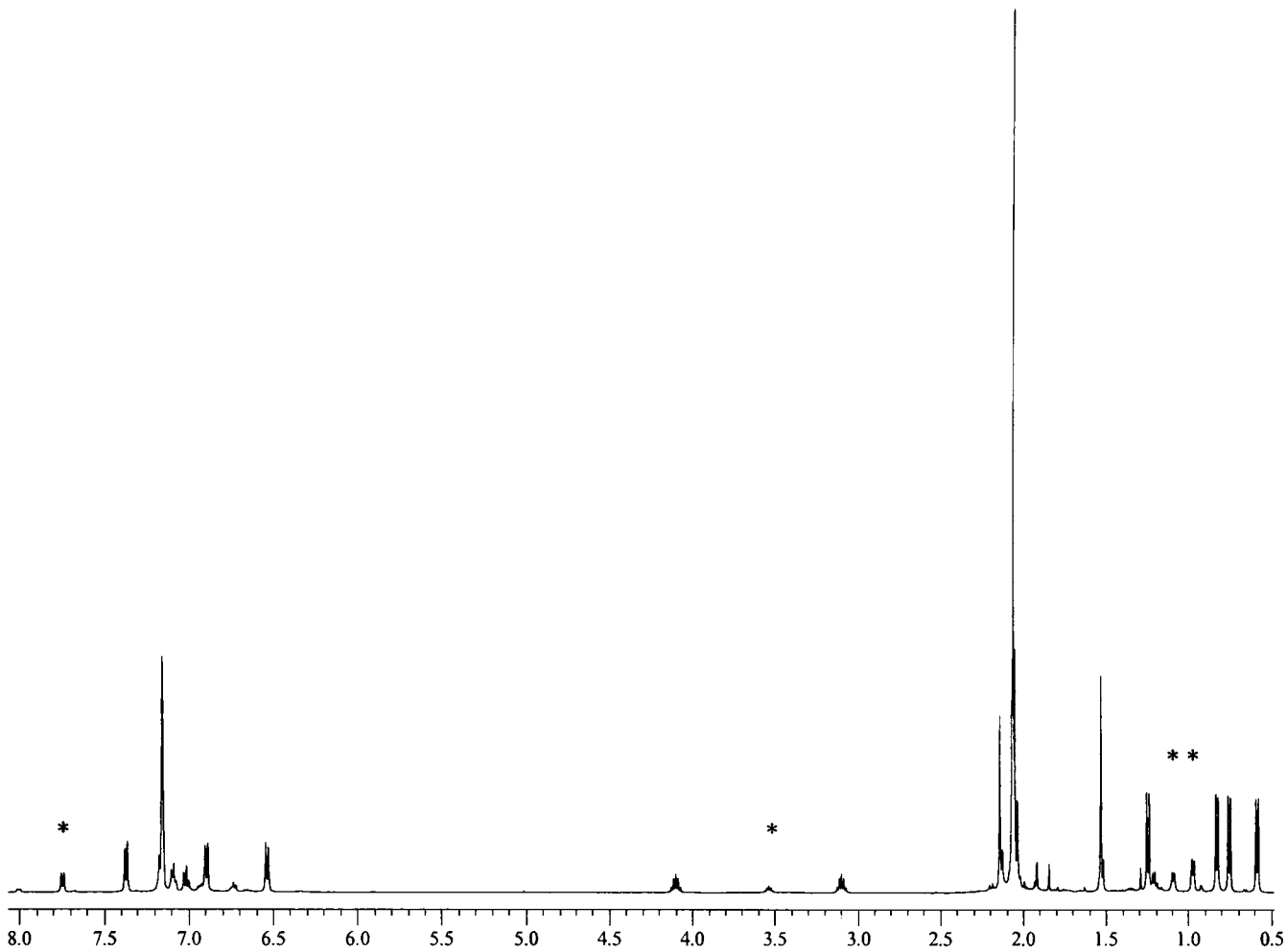


Figure 6.10 – 500.0 MHz ^{1}H NMR spectrum of reaction of Ti(η-C_5Me_5)(N-4-C_6H_4Me) {$MeC(N^iPr)_2$} (**8**) with acetophenone in benzene-d_6 after 10 min.

The compound was identified as Ti(η-C_5Me_5){N(-4-C_6H_4Me)C(Ph)(Me)O} {$MeC(N^iPr)_2$} (**68**). The presence of peaks corresponding to acetophenone and **8** (shown as (*) in Figure 6.10) reveal that the product is still formed in equilibrium with the starting materials, as with the benzophenone reaction. This was confirmed by recording the ^{1}H NMR spectrum of the reaction at 40 °C, and noting that the quantity of starting materials is greatly increased upon heating, as expected for such an equilibrium.

However, Ti(η-C_5Me_5){N(-4-C_6H_4Me)C(Ph)(Me)O}{$MeC(N^iPr)_2$} (**68**) forms in over 90 % yield at room temperature, compared to the 40 % yield at room temperature for the equilibrium of Ti(η-C_5Me_5){N(-4-C_6H_4Me) $C(Ph)_2O$}{$MeC(N^iPr)_2$} (**65**) under otherwise identical conditions.

Furthermore, no evidence of decomposition was observed in the ^{1}H NMR spectrum recorded after 75 minutes, suggesting that a more complete analysis of the compound could be carried out. The ^{1}H NMR spectrum recorded after 16 hours showed the formation of the oxo complex **22**, but as a minor constituent of the reaction mixture (*ca.* 25 %), the majority still being the cycloaddition complex **68**.

Further studies on the complex were carried out using freshly prepared reaction mixtures. The ^{13}C-{^{1}H} NMR spectrum of the complex was recorded, and the geometry of the metallacycle was determined by use of NOESY.

6.3.2.4.2 STRUCTURE OF Ti(η-C_5Me_5){N(-4-C_6H_4Me)C(Ph)(Me)O} {MeC(N^{i}Pr)$_2$} (68) DETERMINED FROM SOLUTION STUDIES

The geometry of Ti(η-C_5Me_5){N(-4-C_6H_4Me)C(Ph)(Me)O} {MeC(N^{i}Pr)$_2$} **(68)** was determined using the 2D NOESY technique. Figure 6.11 shows the geometry of the molecule, with the methyl group of the appended acetophenone pointing up towards the cyclopentadienyl ring, and the phenyl group pointing away from it.

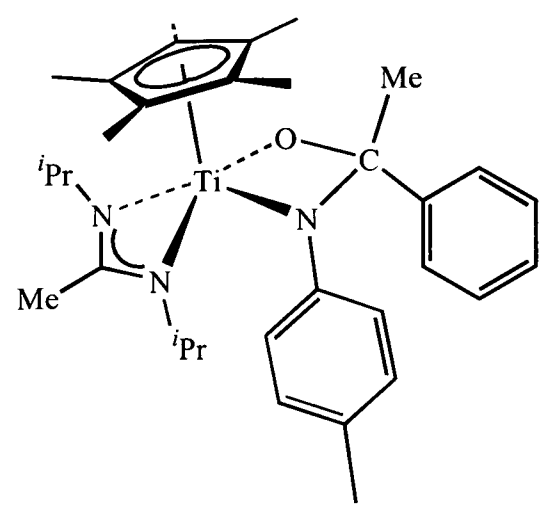


Figure 6.11 – Geometry of the Ti(η-C_5Me_5){N(-4-C_6H_4Me)C(Ph)(Me)O} {MeC(N^{i}Pr)$_2$} (**68**) molecule as determined by NOESY experiment

Analysis of the NOESY spectrum shows a correlation between the methyl groups on the cyclopentadienyl ring, and the methyl group of the acetophenone. The lack of any such correlation between the ortho protons on the phenyl ring with the methyl groups confirms this assignment (see Figure 6.12)

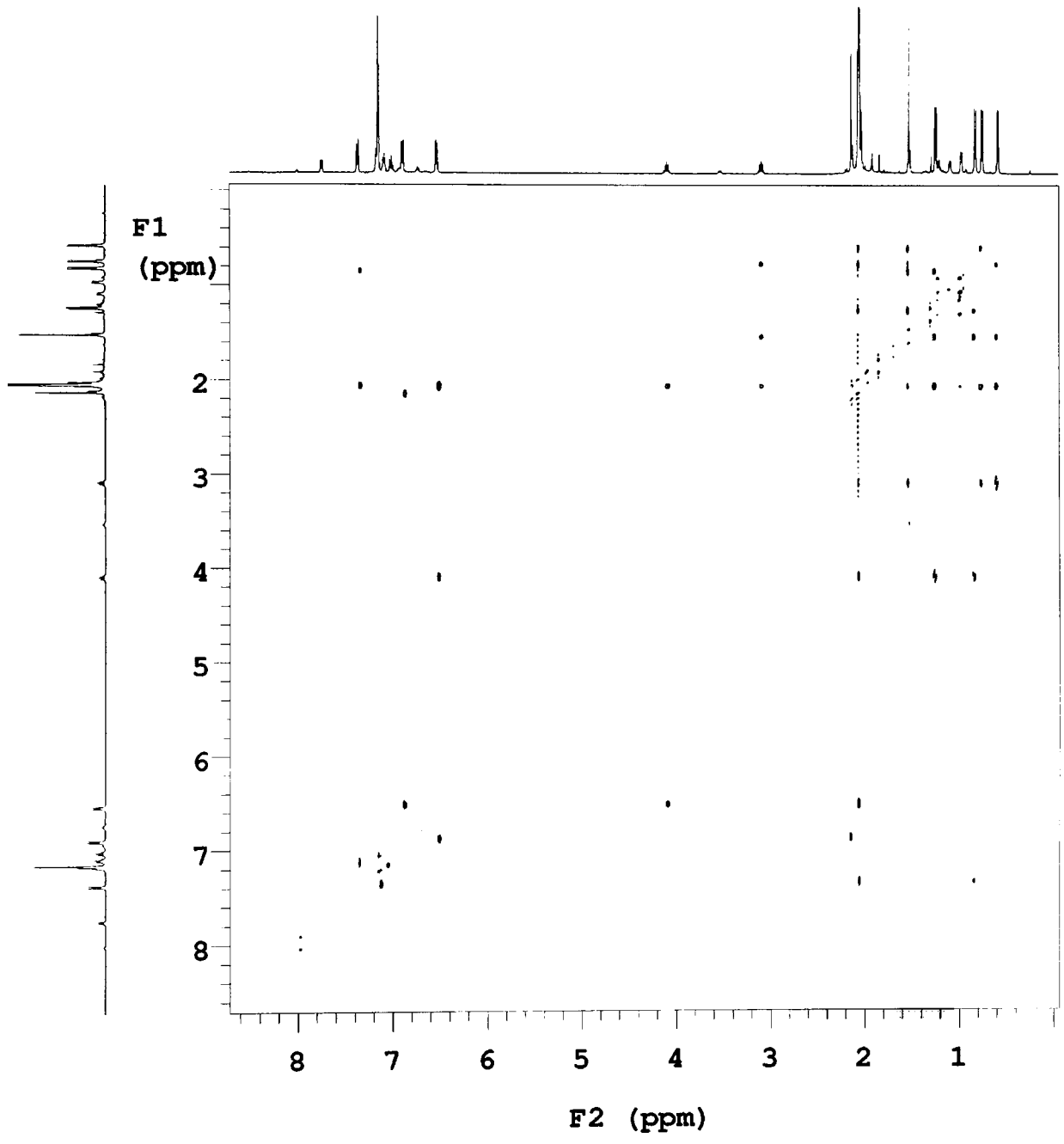


Figure 6.12 – 500.0 MHz ^{1}H NOESY NMR spectrum of Ti(η-C_5Me_5){N(-4-C_6H_4Me)C(Ph)(Me)O}{MeC(N^{i}Pr)$_2$} (**68**) in benzene-d_6

In addition to NMR studies, a sample of the complex was isolated as a sticky brown tar, and analysed by IR spectroscopy. Comparison with the IR

spectrum of pure acetophenone confirmed that the compound did not decompose to starting materials upon isolation; no evidence for a ν(C=O) stretch was observed. The compound was also analysed using EI and FI mass spectrometry, but no parent ion peak was detected.

6.3.2.4.3 SUMMARY

The compound Ti(η-C_5Me_5){N(-4-C_6H_4Me)C(Ph)(Me)O}{MeC(N^{i}Pr)$_2$} (**68**) represents the first example of an isolated and characterised product formed from reaction between an imidotitanium complex and an organic carbonyl. NMR spectroscopic studies have confirmed that the geometry of the compound is that which minimises steric repulsion between the metallacycle and the cyclopentadienyl ligand. The close proximity of the methyl group to the cyclopentadienyl ring is consistent with the complex being a [2 + 2] cycloadduct, rather than a σ-adduct.

6.3.3 REACTIONS OF TITANIUM CYCLOPENTADIENYL IMIDO AMIDINATE COMPLEXES WITH IMINES

As discussed earlier in this Chapter, stable cycloaddition complexes have been synthesised by reaction of transition metal imido complexes with imines.[20,21] Other organometallic species have been shown to be effective in imine metathesis reactions, but the mechanism in these cases is somewhat less certain.[25,26,28,29]

This Section describes the reactivity of Ti(η-C_5Me_5)(N^{t}Bu){MeC(N^{i}Pr)$_2$} (**2**), Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$){MeC(N^{i}Pr)$_2$} (**7**), Ti(η-C_5Me_5)(N-4-C_6H_4Me)

{MeC(N^{i}Pr)$_2$} (**8**) and Ti(η-C$_5$Me$_5$)(N-4-C$_6$H$_4$NMe$_2$){MeC(N^{i}Pr)$_2$} (**10**) with *N*-benzylidene-*p*-toluidine, PhC(N-4-C$_6$H$_4$Me)H. This imine was used due to its low steric requirements, and thus among the most likely to undergo reaction. Samples of each of these complexes were dissolved in aliquots of benzene-d$_6$, and treated with one equivalent of *N*-benzylidene-*p*-toluidine. Reactions were monitored using ^{1}H NMR spectroscopy.

6.3.3.1 RESULTS AND DISCUSSION

The samples of Ti(η-C$_5$Me$_5$)(N^{t}Bu){MeC(N^{i}Pr)$_2$} (**2**) and Ti(η-C$_5$Me$_5$)(N-2,6-C$_6$H$_3$Me$_2$){MeC(N^{i}Pr)$_2$} (**7**) with *N*-benzylidene-*p*-toluidine gave no reaction after 2 hours. Heating these to 80 °C for 5 days afforded no change in the ^{1}H NMR spectra of the two systems. Similarly, Ti(η-C$_5$Me$_5$)(N-4-C$_6$H$_4$Me){MeC(N^{i}Pr)$_2$} (**8**) showed no reaction after heating for 24 hours at 80 °C.

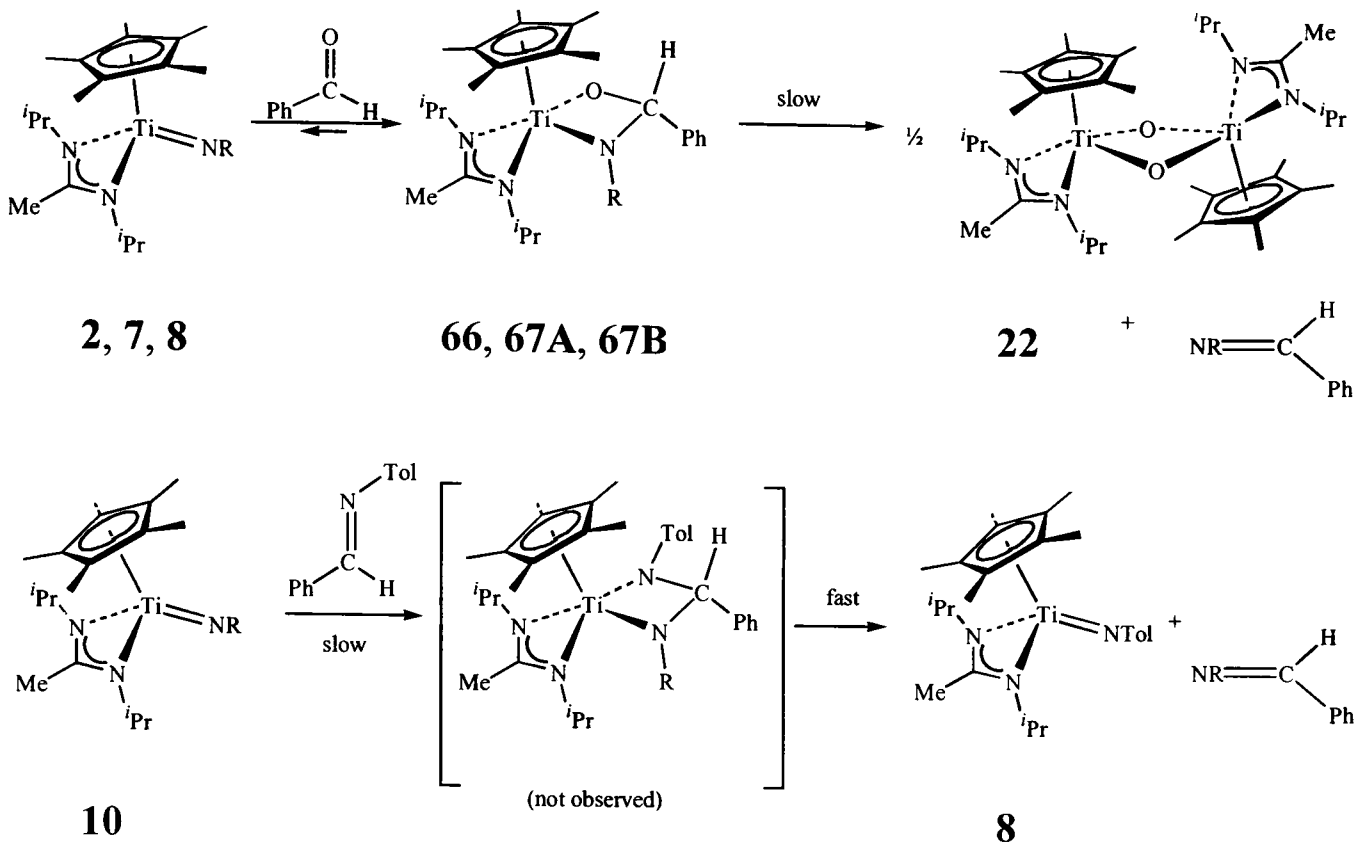
Upon heating the reaction of Ti(η-C$_5$Me$_5$)(N-4-C$_6$H$_4$NMe$_2$){MeC(N^{i}Pr)$_2$} (**10**) to 80 °C for 3 hours, new resonances were detected in the ^{1}H NMR spectrum, correponding to the formation of the imido species Ti(η-C$_5$Me$_5$)(N-4-C$_6$H$_4$Me){MeC(N^{i}Pr)$_2$} (**8**). Further heating of the sample to 80 °C for a total of 19 hours produced a 60 : 40 mixture of **8** : **10**. Additionally, peaks attributed to the formation of metathesis product *N*-benzylidene-*N'*,*N'*-dimethyl-1,4-phenylenediamine were detected in the ^{1}H NMR spectrum. The identity of this species was further corroborated by the detection of a protonated parent ion peak in the APCI mass spectrum (*m/z* = 225, [M+H]$^+$).

No evidence for the presence of cycloaddition products was found in any of the ^{1}H NMR spectra recorded for these four reaction systems.

There is considerable difference between the reactions of benzaldehyde and *N*-benzylidene-*p*-toluidine. While the titanium imido complexes all reacted rapidly at room temperature with benzaldehyde, the reaction with *N*-benzylidene-*p*-toluidine was found to require much more forcing conditions. In the cases of Ti(η-C_5Me_5)(N^{t}Bu){MeC(N^{i}Pr)$_2$} (**2**) and Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$){MeC(N^{i}Pr)$_2$} (**7**), no reaction was observed even after extensive heating.

The products of reaction between benzaldehyde and the imido species were cycloadducts, which decomposed to give the final metathesis products. By contrast, no evidence for a cycloadduct intermediate was directly observed for the reaction of Ti(η-C_5Me_5)(N-4-$C_6H_4NMe_2$){MeC(N^{i}Pr)$_2$} (**10**) with *N*-benzylidene-*p*-toluidine. These differences are summarised in Scheme 6.7.

This difference in reactivity is most likely due to the differing degrees of steric crowding at the heteroatom of the organic substrates. However, the reactions between Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$){MeC(N^{i}Pr)$_2$} (**7**) and Ti(η-C_5Me_5)(N-4-C_6H_4Me){MeC(N^{i}Pr)$_2$} (**8**) with di-*p*-tolylcarbodiimide reported in Chapter 4 were found to give the stable cycloaddition products Ti(η-C_5Me_5){N(-2,6-$C_6H_3Me_2$)C(N-4-C_6H_4Me)N(-4-C_6H_4Me){MeC(N^{i}Pr)$_2$} (**57**) and Ti(η-C_5Me_5){N(-4-C_6H_4Me)C(N-4-C_6H_4Me)N(-4-C_6H_4Me) {MeC(N^{i}Pr)$_2$} (**56**) respectively, in which the steric crowding around the



Scheme 6.7 – Comparison of the reactivity of Ti(η-C_5Me_5)(NR){$MeC(N^iPr)_2$} with benzaldehyde and with *N*-benzylidene-*p*-toluidine

metal centre would be very similar to the imine reaction product. The difference in hybridisation at the carbon atom may be the significant factor. In the carbodiimide cycloaddition product, the hybridisation is sp^2, which would allow delocalisation of the π-electrons across the triazatrimethylene methane ligand, stabilising the complex. No such delocalisation can occur in the imine cycloaddition intermediate, as the carbon is formally sp^3 hybridised.

6.3.3.2 SUMMARY

The previously reported metathesis reactions of metal imido species with carbonyls and imines have been explored using titanium cyclopentadienyl imido amidinate complexes.

The carbonyl metathesis reaction occurs to give bridging oxo species and an organic imine. It has been found to occur *via* a formal [2 + 2] cycloaddition intermediate, the stability of which is strongly dependant on the imido N-substituent, and the steric bulk of the substrate. The adduct exists in an equilibrium with the starting materials in solution, the extent of which is strongly dependant on the identity of the carbonyl substrate. A number of these adducts have been characterised by ^{1}H NMR spectroscopy.

The imine metathesis reaction was found to be less facile than the carbonyl metathesis, requiring much more forcing conditions. No evidence for a cycloaddition complex was detected.

6.4 Reactions of Titanium Cyclopentadienyl Imido Amidinate Complexes with Alkynes

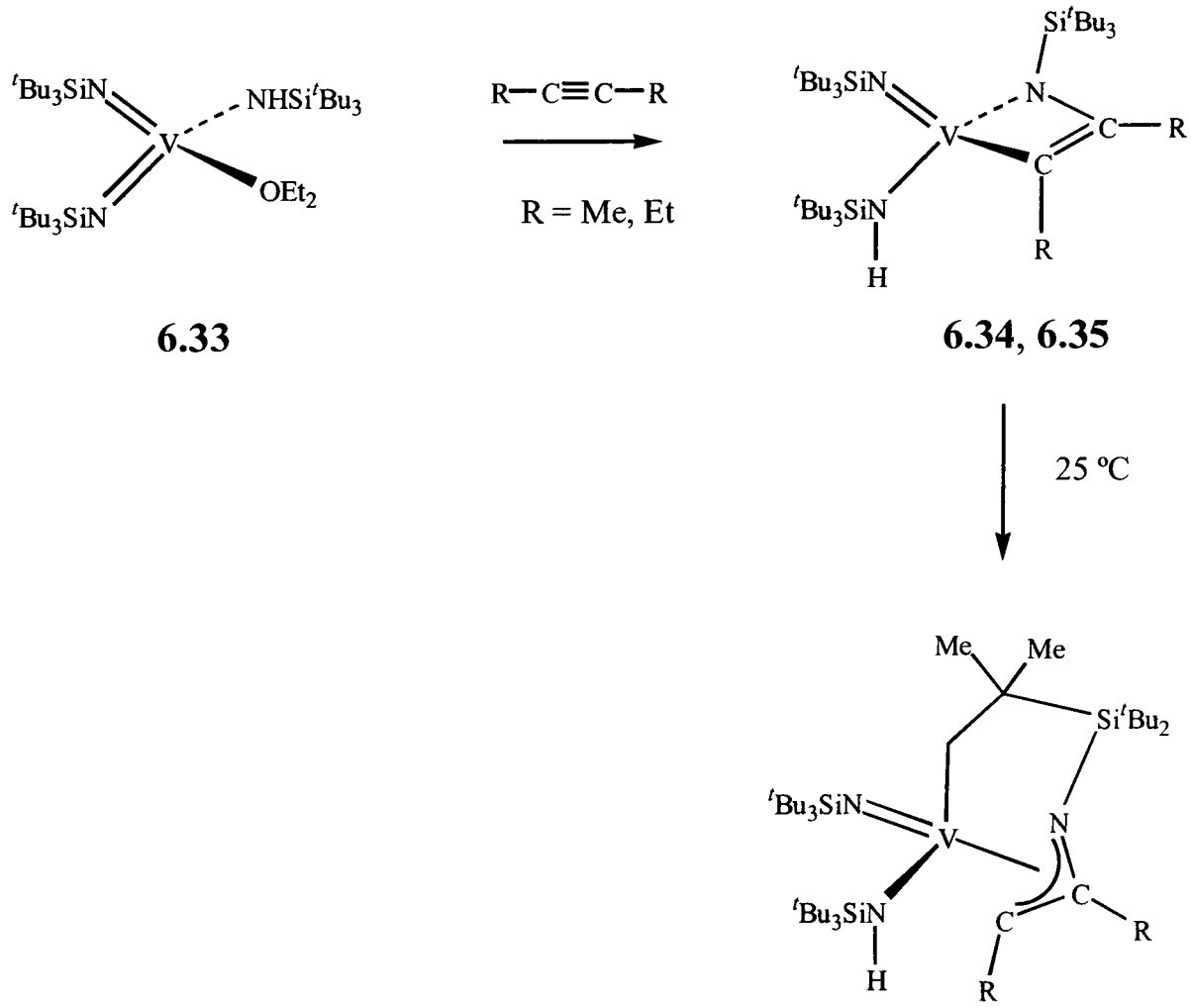
The reactivity of transition metal imido complexes with substrates bearing unsaturated carbon-carbon linkages has been a subject of interest for the past decade or so, and has been focussed mainly on acetylinic substrates. This Section starts by reviewing relevant work that has been published in this area, beginning with alkyne reactivity towards some metal imido species, and concludes with reactivity studies conducted on titanium cyclopentadienyl imido amidinate complexes.

6.4.1 INTRODUCTION

Although some work has been reported for Group 5 and 6 metal imido complexes, the majority of studies have focussed on Group 4 systems. This Introduction will begin by reviewing the Group 5 and 6 chemistry, before moving on to relate that of the Group 4 complexes.

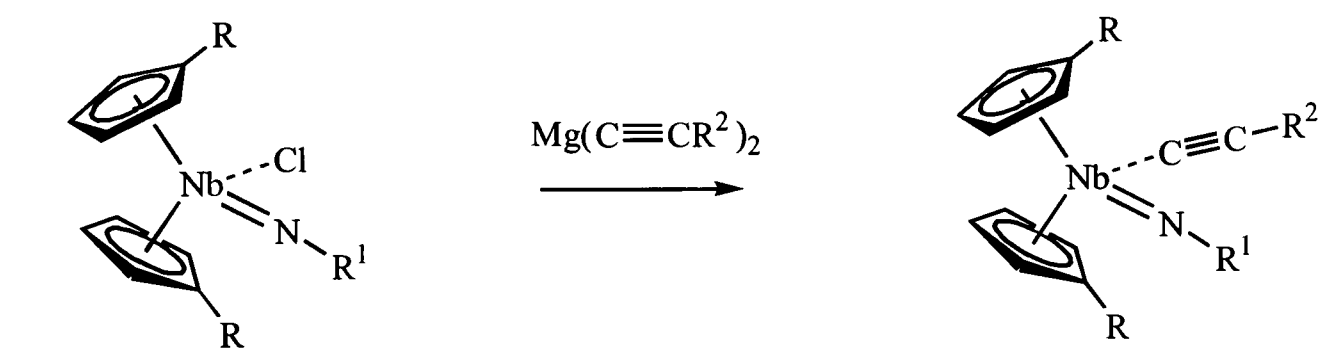
6.4.1.1 REACTIONS OF GROUP 5 COMPLEXES WITH ALKYNES AND ALKYNYLS

Horton reported[33] the reaction of the imidovanadium species $V(NSi^tBu_3)_2(NHSi^tBu_3)(OEt_2)$ (**6.33**) with 2-butyne and 3-hexyne to afford formal [2 + 2] cycloaddition products (**6.34**, **6.35**), which decomposed to give the first reported examples of η^3-1-azaallyl d^0 transition metal complexes as final products (**6.36**, **6.37**) (Equation 6.6).

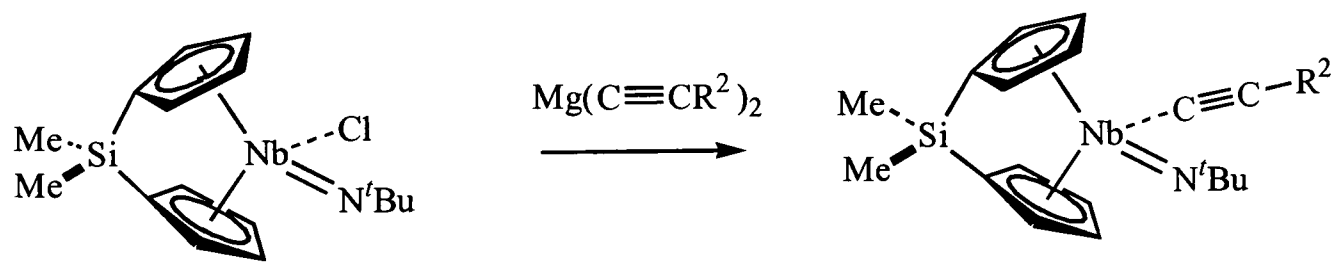


Equation 6.6

Otero has reported the synthesis of both niobocene and *ansa*-niobocene complexes bearing an imido and an η^1-alkynyl group by reaction of the niobocene imido chloride precursors with 0.5 equivalents of magnesium bis(alkynyl) compounds[34] (Scheme 6.8).



6.38 – 6.43 **6.46 – 6.51**



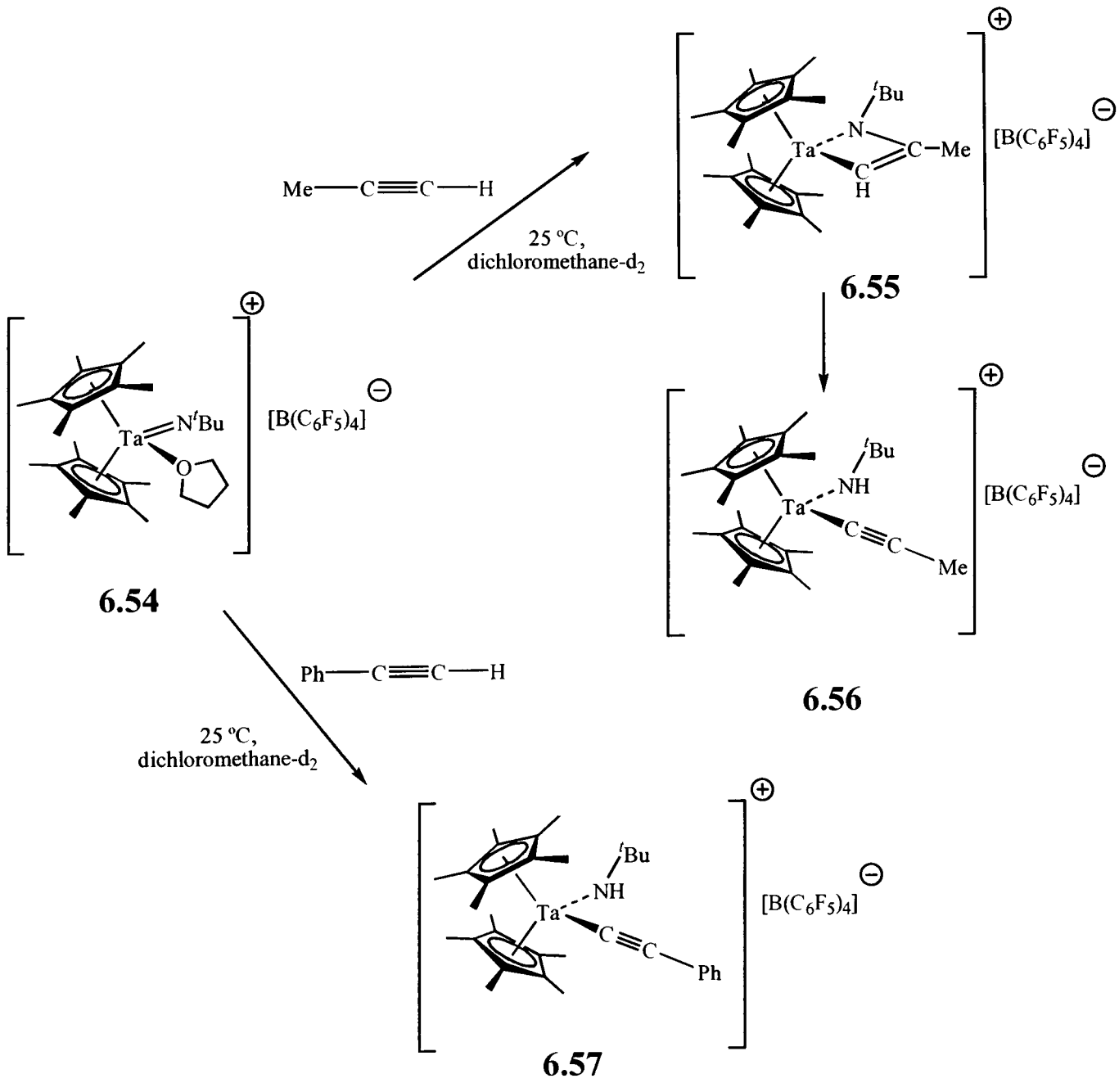
6.44, 6.45 **6.52, 6.53**

	R	R^1	R^2	
6.38	H	^{t}Bu	^{t}Bu	**6.46**
6.39	H	4-C_6H_4Me	^{t}Bu	**6.47**
6.40	$SiMe_3$	^{t}Bu	^{t}Bu	**6.48**
6.41	$SiMe_3$	^{t}Bu	Ph	**6.49**
6.42	$SiMe_3$	Ph	Ph	**6.50**
6.43	$SiMe_3$	4-C_6H_4Me	^{t}Bu	**6.51**
6.44			^{t}Bu	**6.52**
6.45			$SiMe_3$	**6.53**

Scheme 6.8 – Reaction of niobocene complexes Nb(η-C_5H_4R)(NR')Cl (**6.38 – 6.43**) and Nb{(η-C_5H_4)$_2$(μ-$SiMe_2$)}(N^{t}Bu)Cl (**6.44, 6.45**) with alkynyls

Compounds **6.46** – **6.53** were characterised spectroscopically, and bands in the IR spectra of these complexes at 2050 – 2110 cm^{-1} were assigned to the ν(C C) stretch of the alkynyl ligand. Compound **6.50** was structurally characterised, and no evidence was found for any interaction between the alkynyl and imido groups.

The cationic tantalocene complex $[Ta(\eta\text{-}C_5Me_5)_2(N^tBu)(THF)]^+[B(C_6F_5)_4]^-$ (**6.54**) was found to react with acetylenes, as shown in Scheme 6.9. The reaction was found to proceed *via* a formal [2 + 2] cycloadduct, which then underwent proton transfer to afford the final product.[35]

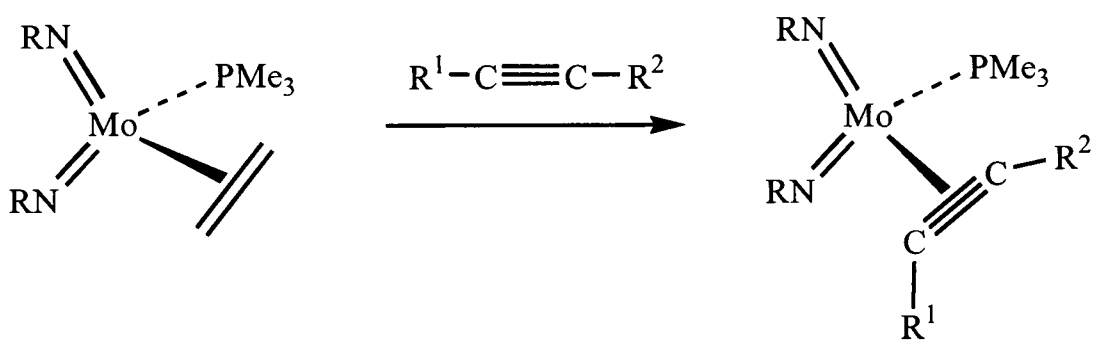


Scheme 6.9 – Reaction of $[Ta(\eta\text{-}C_5Me_5)_2(N^tBu)(THF)]^+[B(C_6F_5)_4]^-$ (**6.54**) with alkynes

The structure of **6.57** was confirmed by single crystal X-ray diffraction, whilst the structure of the metallacyclic intermediate was tentatively proposed on the basis of the ^{1}H NMR spectrum.

6.4.1.2 Reactions of Group 6 complexes with alkynes

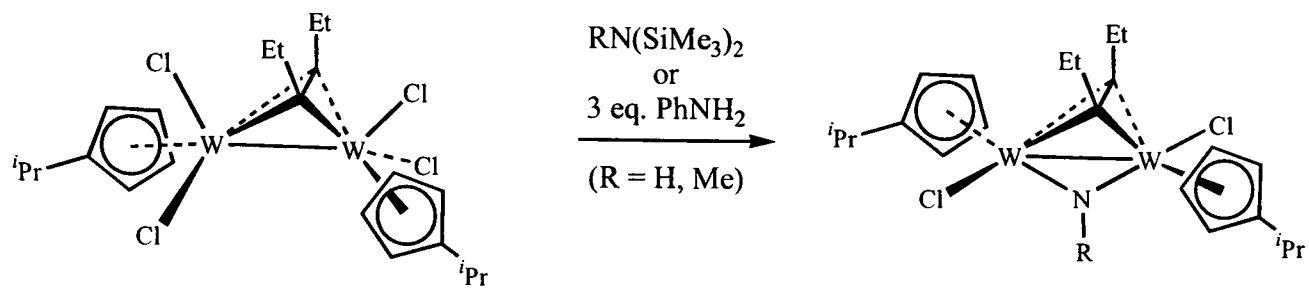
Treatment of the molybdenum species $Mo(NR)_2(PMe_3)(\eta^2\text{-}C_2H_4)$ (**6.58**) with alkynes caused the displacement of the ethene ligand with the coordination of the alkyne in an η^2 mode, as shown in Equation 6.7. No reaction was observed between the alkynes and the imido ligands.[36]



	R	R^1	R^2	
6.58	^{t}Bu	Ph	Ph	**6.61**
6.59	^{t}Bu	Ph	H	**6.62**
6.60	adamantyl	Ph	Ph	**6.63**

Equation 6.7

The bridging alkyne dimer complex $[W(\eta\text{-}C_5H_4{}^iPr)Cl_2]_2(\mu\text{-}C_2Et_2)$ (**6.64**) was found to react with hexa- or hepta- methyldisilazane, or excess aniline, to afford a μ-alkyne μ-imido complex, as shown in Equation 6.8.[37]



6.64

R	
H	**6.65**
Me	**6.66**
Ph	**6.67**

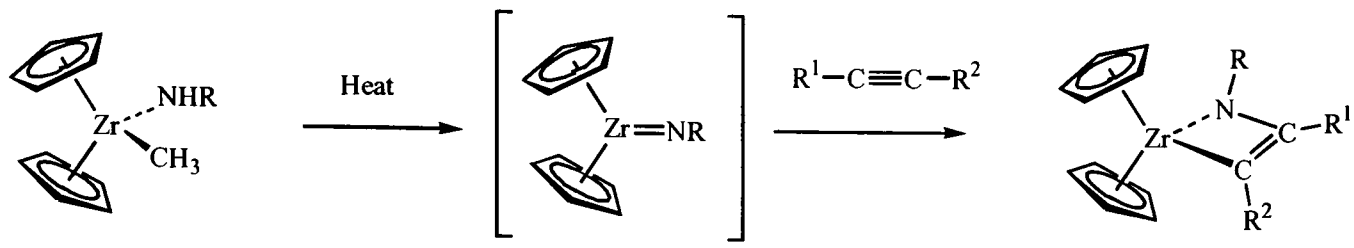
Equation 6.8

6.4.1.3 REACTIONS OF GROUP 4 COMPLEXES WITH ALKYNES

By far the most studied have been the imido complexes of Group 4 transition metals. In contrast to the complexes of Groups 5 and 6, in which the imido group often acts as an ancillary ligand, the imido bonds of Group 4 complexes are typically the reactive sites.

Bergman reported the trapping of the first monomeric imidozirconocene complexes $Zr(\eta\text{-}C_5H_5)_2(NR)$ (R = ^{t}Bu (**6.68**), 2,6-$C_6H_3Me_2$ (**6.69**), 4-$C_6H_4{}^t$Bu (**6.70**)) with internal alkynes to give intensely coloured azametallacyclobutene complexes, as shown in Equation 6.9.[38]

Subsequent studies involving the thermolysis of the bis(amide) complexes $Zr(\eta\text{-}C_5H_5)_2(NHR)_2$ (R = 2,6-$C_6H_3Me_2$ (**6.80**), 2-C_6H_4Me (**6.81**), 4-$C_6H_4{}^t$Bu (**6.82**)) in the presence of internal alkynes also gave azametallacyclobutene products. X-ray diffraction studies carried out on a single crystal of $Zr(\eta\text{-}C_5H_5)_2\{N(\text{-}2,6\text{-}C_6H_3Me_2)C(Ph)C(Ph)\}$ (**6.76**) confirmed its azametallacyclic



6.68 – 6.70 **6.71 – 6.79**

	R	R^1	R^2	
6.68	^{t}Bu	Me	Me	**6.71**
	^{t}Bu	Me	Ph	**6.72**
	^{t}Bu	Ph	Ph	**6.73**
6.69	2,6-$C_6H_3Me_2$	Me	Me	**6.74**
	2,6-$C_6H_3Me_2$	Me	Ph	**6.75**
	2,6-$C_6H_3Me_2$	Ph	Ph	**6.76**
6.70	4-C_6H_4Me	Me	Me	**6.77**
	4-C_6H_4Me	Me	Ph	**6.78**
	4-C_6H_4Me	Ph	Ph	**6.79**

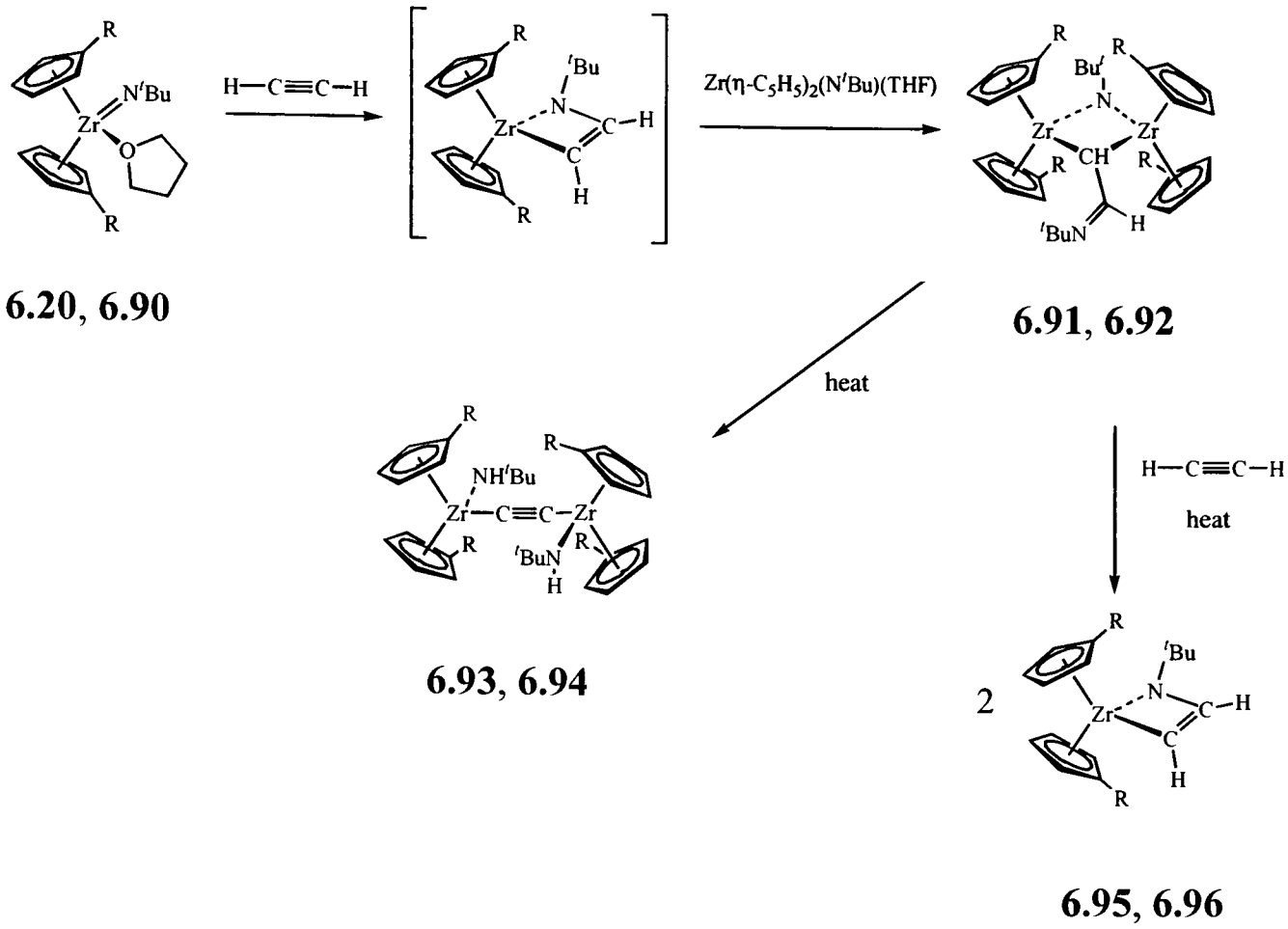
Equation 6.9

structure.[38,39] Trapping of the terminal imidozirconocene formed from thermolysis of 2,4-diazametallacyclobutane complexes (formed by cycloaddition of $Zr(\eta\text{-}C_5H_5)_2(N^tBu)(THF)$ with imines) with alkynes was also demonstrated.[20] Kinetic studies have been carried out on this class of compounds, which have corroborated the mechanistic pathway proposed, and shown that the rates of formation of the metallacycles are affected only slightly by the electronic character of the alkyne. The reaction occurs with excellent regioselectivity, yielding azametallabutenes in which the largest substituent is in the R^2 position (α to zirconium).[40]

This reaction has been used to reduce the concentration of the free imido species $Zr(\eta\text{-}C_5H_5)_2(NR)$ (**6.68** – **6.70**) in catalytic imine metathesis, improving the longevity of the active species by reducing irreversible self-trapping to give the unreactive $[Zr(\eta\text{-}C_5H_5)_2(\mu\text{-}NR)]_2$ (R = ^{t}Bu (**6.83**), 2,6-$C_6H_3Me_2$ (**6.84**), 4-C_6H_4Me (**6.85**)) dimer.[22] This has also confirmed the reversible nature of the azametallacyclobutene formation.

Treatment of the diazametallacycles of the form $Zr(\eta\text{-}C_5H_5)_2\{N(R)C(NR^1)N(R^1)\}$ (R, R^1 = ^{t}Bu, $SiMe_3$ (**6.86**); ^{t}Bu, ^{t}Bu (**6.87**); 2,6-$C_6H_3Me_2$, $SiMe_3$ (**6.88**); 2,6-$C_6H_3Me_2$, ^{t}Bu (**6.89**)) (formed by cycloaddition of $Zr(\eta\text{-}C_5H_5)_2(NR)(THF)$ with carbodiimides) with diphenylacetylene afforded the corresponding azametallacyclobutene product and carbodiimide in high yield.[41] Kinetic investigations again supported the proposed retrocycloaddition / cycloaddition pathway.

More recent studies on $Zr(\eta\text{-}C_5H_4R)_2(N^tBu)(THF)$ (R = H (**6.20**), Me (**6.90**)) using acetylene instead of internal alkynes has demonstrated an unusual reactivity, in which the azametallacyclobutene can react with an equivalent of imido starting material, as shown in Scheme 6.10.[42]



6.20, 6.90

6.91, 6.92

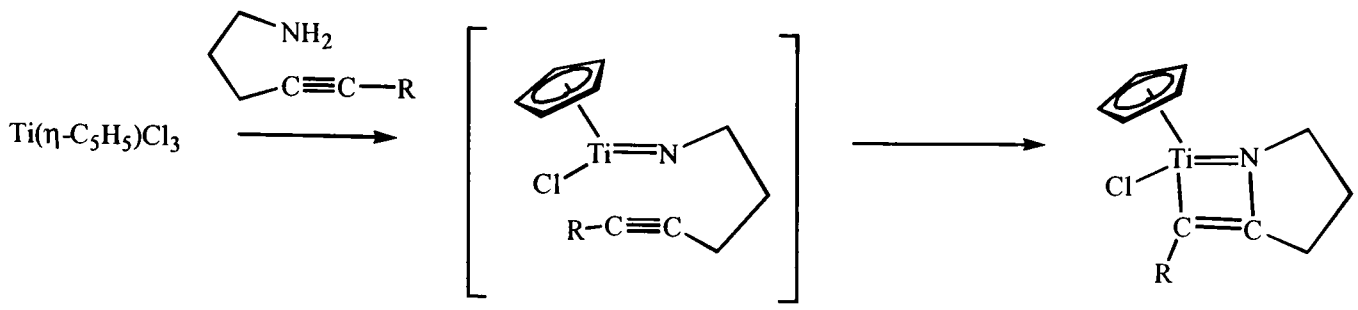
6.93, 6.94

6.95, 6.96

Scheme 6.10 – Reaction of $Zr(\eta\text{-}C_5H_4R)_2(N^tBu)(THF)$ (R = H (**6.20**), Me (**6.90**) with acetylene

In addition to trapping transient imido species, alkynes have been used in the trapping of the transient oxo[43-45] and sulfido[44,45] species $Zr(\eta\text{-}C_5H_5)_2(O)$ and $Zr(\eta\text{-}C_5H_5)_2(S)$ to give analogous metallacyclic products.

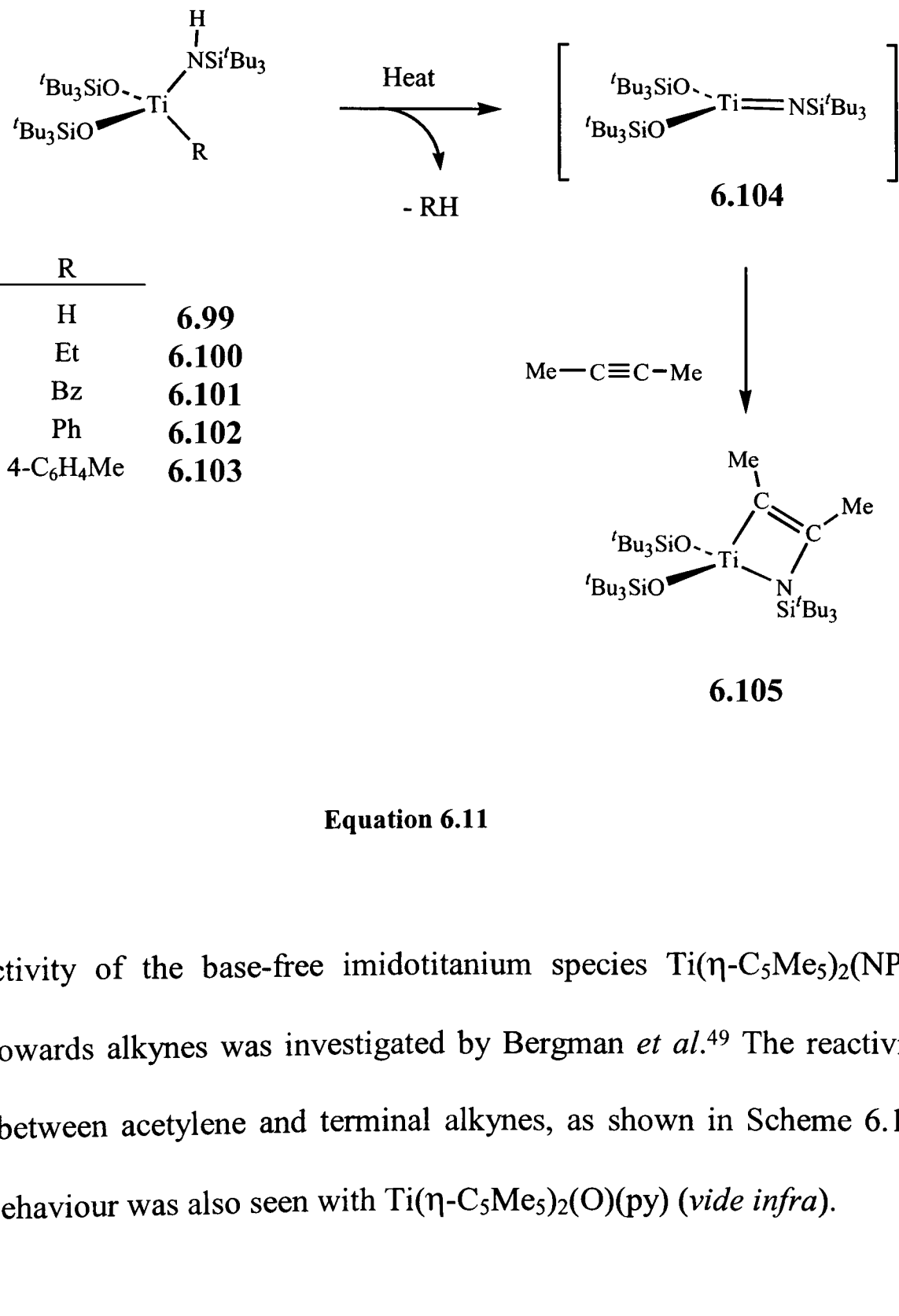
Titanium complexes have also shown reactivity towards alkynes. Similar to Bergman's work in synthesis and intermolecular trapping of transient imidozirconocene complexes (*vide supra*), Livinghouse reported the synthesis and intramolecular trapping of imidotitanium species using alkynes.[46] The reaction, summarised in Equation 6.10, has found use synthetically for the stereochemically controlled synthesis of the antifungal agent (+)-Preussin.[47]



R = Ph **6.97**
^{n}Bu **6.98**

Equation 6.10

Wolczanski reported the trapping of the transient imidotitanium species $Ti(NSi^tBu_3)(OSi^tBu_3)_2$ (**6.104**) using 2-butyne, as shown in Equation 6.11.[48]



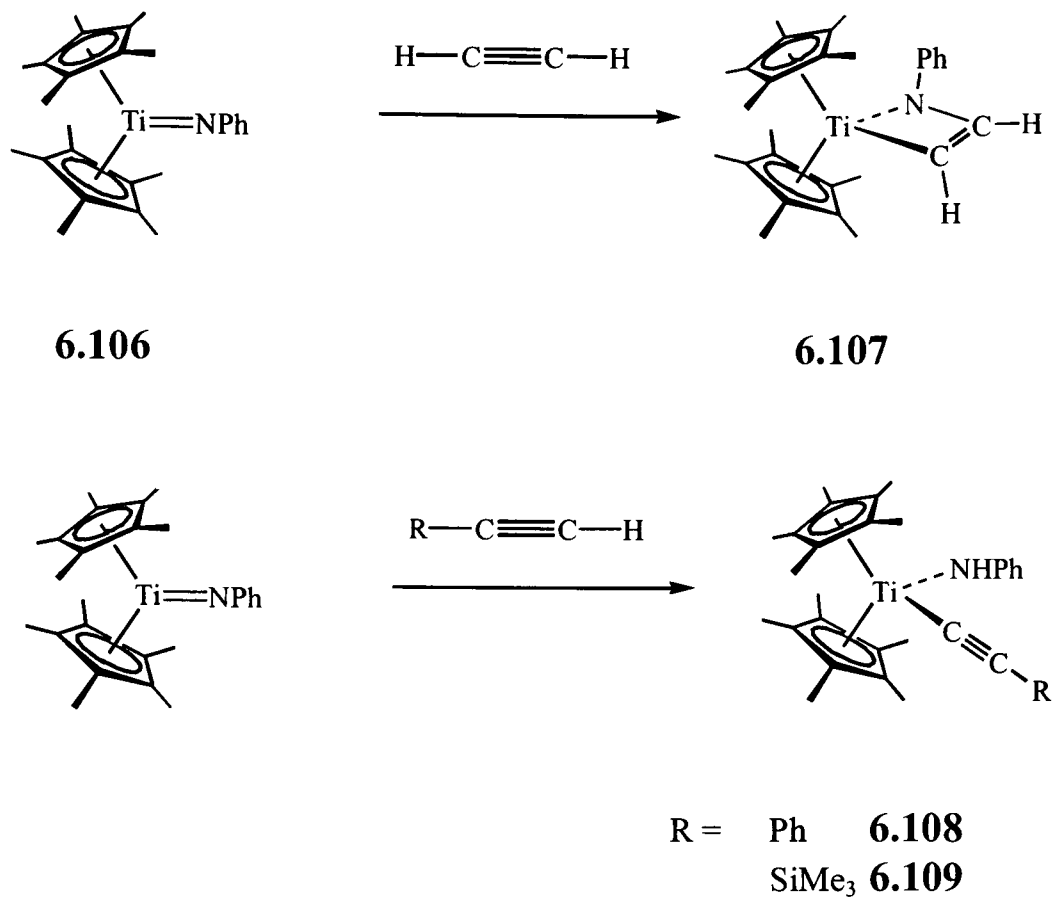
R	
H	**6.99**
Et	**6.100**
Bz	**6.101**
Ph	**6.102**
4-C_6H_4Me	**6.103**

6.104

6.105

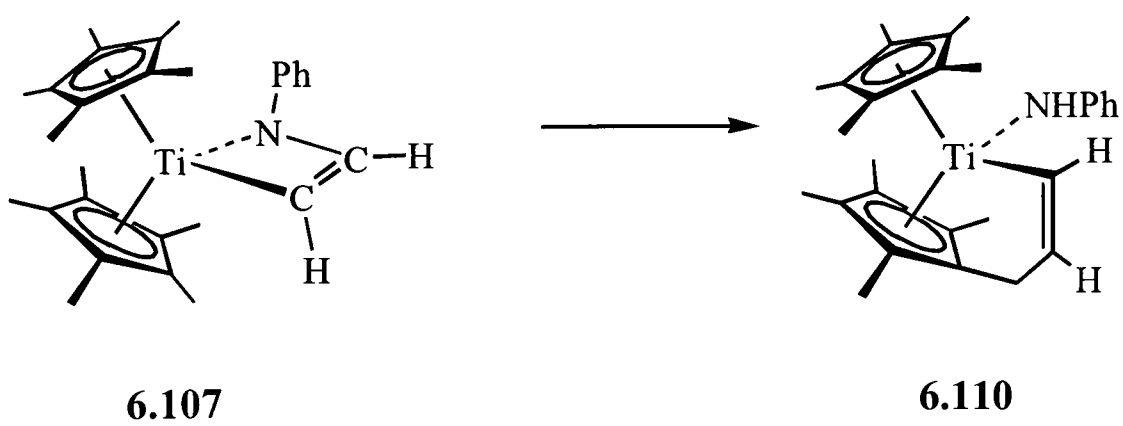
Equation 6.11

The reactivity of the base-free imidotitanium species $Ti(\eta\text{-}C_5Me_5)_2(NPh)$ (**6.106**) towards alkynes was investigated by Bergman *et al.*[49] The reactivity differed between acetylene and terminal alkynes, as shown in Scheme 6.11. Similar behaviour was also seen with $Ti(\eta\text{-}C_5Me_5)_2(O)(py)$ (*vide infra*).



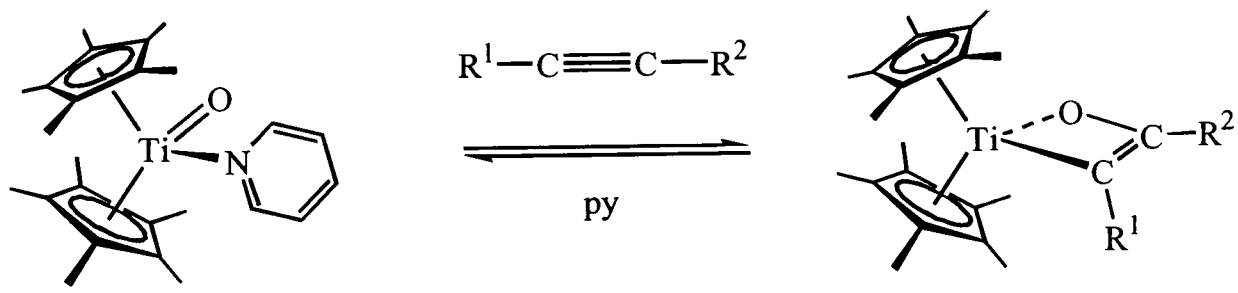
Scheme 6.11 – Reactions of Ti(η-C_5Me_5)$_2$(NPh) (**6.106**) with alkynes

In contrast to other Group 4 aza- and oxa- metallacyclobutenes,[19,43-45,50] the reaction of Ti(η-C_5Me_5)$_2$(NPh) (**6.106**) with acetylene is irreversible; isotopic labelling experiments gave no evidence for alkyne exchange. Heating **6.107** did not lead to the expected anilido-acetylide product, but instead gave a new fulvene complex **6.110** (Equation 6.12).



Equation 6.12

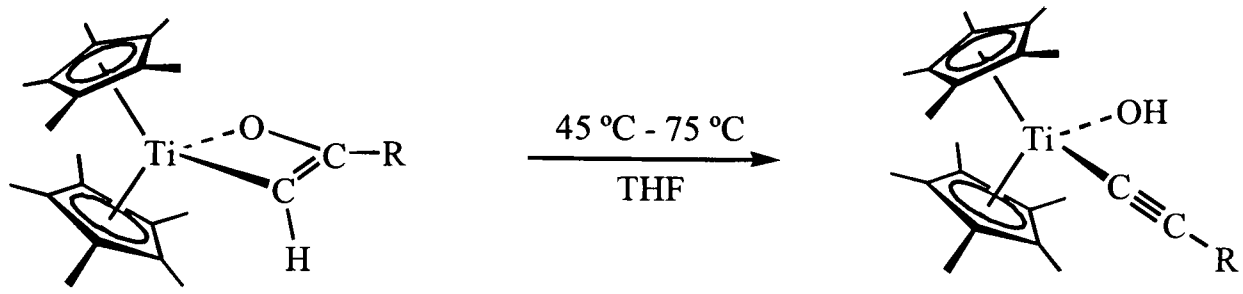
The reaction between alkynes and the terminal oxo complex $Ti(\eta\text{-}C_5Me_5)_2(O)(py)$ (**6.111**) has also been investigated.[50] In contrast with the zirconocene imido and oxo systems cited earlier, $Ti(\eta\text{-}C_5Me_5)_2(O)(py)$ reacts preferentially with terminal, rather than internal alkynes. In addition, the regioselectivity of the cycloaddition is the opposite of that found with zirconocene systems; the more bulky group of the alkyne lying at the β-position in the titanium metallacycle (Equation 6.13). This is attributed to the greater degree of steric crowding in the $Ti(\eta\text{-}C_5Me_5)_2$ fragment compared with $Zr(\eta\text{-}C_5Me_5)_2$.



R^1	R^2	
Ph	Ph	**6.112**
H	Ph	**6.113**
H	4-C_6H_4Me	**6.114**
H	^{t}Bu	**6.115**
H	Me	**6.116**

Equation 6.13

Finally, thermolysis of the oxametallacyclobutenes formed from terminal alkynes gave rise to hydroxoacetylide complexes (Equation 6.14).[50]



R	
Ph	**6.117**
4-C_6H_4Me	**6.118**
^{t}Bu	**6.119**
Me	**6.120**

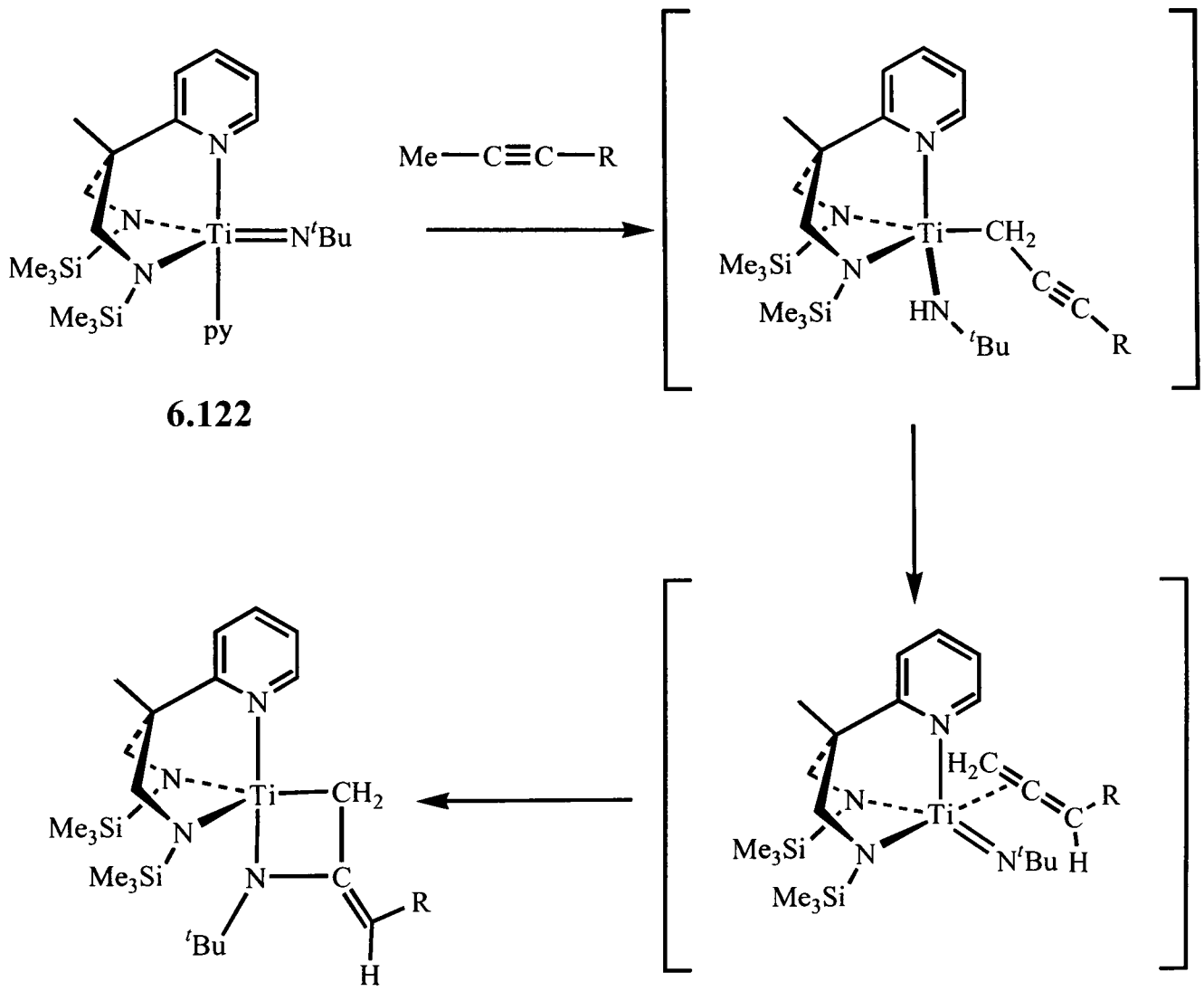
Equation 6.14

No rate acceleration was observed when the thermolysis is run in THF rather than benzene, indicating that no ion pair is formed in the interconversion of the oxametallacyclobutene to the hydroxoacetylide. The group postulate a retrocyclisation to give a transient terminal oxo species and alkyne, which then undergoes proton transfer and Ti–C bond formation in an essentially concerted fashion.[50]

The analogous sulfido complex, Ti(η-C_5Me_5)$_2$(S)(py) (**6.121**), has also been studied.[51] It reacts with terminal alkynes to give thiometallacyclobutenes, in which the bulkier substituent lies in the β-position analogous to the stereoselectivity of the oxametallacyclobutene formation from Ti(η-C_5Me_5)$_2$(O)(py) with alkynes. Unlike the oxygen-containing congener, no reaction is observed with internal alkynes such as diphenylacetylene, and the thiometallacyclobutenes are stable with respect to rearrangement upon heating, unlike the oxametallacyclobutenes which rearrange to give

hydroxoacetylides. This is attributed to the greater thermodynamic driving force for the formation of an O–H bond, compared to S–H.

The less sterically hindered imidotitanium complex Ti(N_2N_{py})(N^tBu) (**6.122**) was also found to react with alkynes to give azatitanatetracycles.[52] The mechanism proposed for the reaction is shown in Scheme 6.12.



6.122

R = Ph **6.123**
Me **6.124**

Scheme 6.12 – Reaction of Ti(N_2N_{py})(N^tBu) (**6.122**) with methylacetylenes

Further evidence for this mechanism was provided by the observation that Ti(N_2N_{py})(N^tBu) reacted with 1-methylallene and 1-phenylallene to afford identical products. Both compounds have been structurally characterised.[53]

6.4.2 REACTIONS OF TITANIUM CYCLOPENTADIENYL IMIDO AMIDINATE COMPLEXES WITH ALKYNES

The reactivity of both the internal alkyne 2-butyne, and the terminal alkynes trimethylsilylacetylene, phenylacetylene, and *p*-tolylacetylene towards titanium cyclopentadienyl imido amidinate complexes were investigated.

6.4.2.1 REACTIONS WITH 2-BUTYNE

Samples of Ti(η-C_5H_4Me)(N^{t}Bu){PhC(NSiMe$_3$)$_2$} (**3**) and Ti(η-C_5Me_5)(N-4-C_6H_4Me){MeC(N^{i}Pr)$_2$} (**8**) were dissolved in aliquots of benzene-d_6, loaded into 5 mm Wilmad NMR tubes fitted with Teflon valves, and treated with an excess of 2-butyne. Reactions were monitored using ^{1}H NMR spectroscopy. No reactions were observed after 16 hours, nor after heating to 80 °C for 1 week.

6.4.2.2 REACTIONS WITH TRIMETHYLSILYLACETYLENE

Reactions with Ti(η-C_5Me_5)(N^{t}Bu){PhC(NSiMe$_3$)$_2$} (**1**), Ti(η-C_5Me_5)(N^{t}Bu){MeC(N^{i}Pr)$_2$} (**2**), and Ti(η-C_5H_4Me)(N^{t}Bu){PhC(NSiMe$_3$)$_2$} (**3**) were investigated. Three sets of experiments were attempted, using one equivalent, ten equivalents, and finally neat trimethylsilylacetylene.

6.4.2.2.1 RESULTS AND DISCUSSION OF REACTIONS OF $Ti(\eta\text{-}C_5Me_5)(N^tBu)\{PhC(NSiMe_3)_2\}$ (1) WITH TRIMETHYLSILYLACETYLENE

The reaction with one equivalent of alkyne was found to proceed slowly, taking *ca.* 24 hours to reach an equilibrium between the starting materials (86 %) and a product (14 %) in which the plane of symmetry had been removed. No further change was observed after 3 days in solution. Upon heating to 80 °C for 1 hour, the product was found to decompose to give starting materials. Prolonged heating caused the peaks in the ^1H NMR spectrum corresponding to trimethylsilylacetylene to decrease in intensity relative to those of **1**; this was attributed to polyacetylene formation at elevated temperature. The reaction with ten equivalents of alkyne showed formation of a greater amount of adduct (**1** : product ratio was *ca.* 1 : 1), as expected for an equilibrium. Attempts to grow crystals of the product by dissolving **1** in neat trimethylsilylacetylene were unsuccessful.

6.4.2.2.2 RESULTS AND DISCUSSION OF REACTIONS WITH $Ti(\eta\text{-}C_5Me_5)(N^tBu)\{MeC(N^iPr)_2\}$ (2) WITH TRIMETHYLSILYLACETYLENE

The reaction with one equivalent of alkyne was found to proceed slowly, taking *ca.* 24 hours to reach an equilibrium between the starting materials (85 %) and a product (15 %) in which the plane of symmetry had been removed. No further change was observed after 3 days in solution. Upon heating to 80 °C for 24 hours, the product was found to decompose to give starting materials. Prolonged heating caused the peaks corresponding to

trimethylsilylacetylene to decrease in intensity relative to those of **2**; this was attributed to polyacetylene formation at elevated temperature. The reaction with ten equivalents of alkyne showed formation of a greater amount of adduct (**1** : product ratio was *ca.* 1 : 5), as expected for an equilibrium. Attempts to grow crystals of the product by dissolving **2** in neat trimethylsilylacetylene were unsuccessful.

6.4.2.2.3 RESULTS AND DISCUSSION OF REACTIONS OF Ti(η-C_5H_4Me)(N^{t}Bu){PhC(NSiMe_3)$_2$} (3) WITH TRIMETHYLSILYLACETYLENE

The reaction with one equivalent of alkyne was found to proceed slowly, taking *ca.* 24 hours to reach an equilibrium between the starting materials and a product in which the plane of symmetry had been removed. Only a trace of product (*ca.* 2 %) was observed. No further change was observed after 3 days in solution. Upon heating to 80 °C for 1 hour, the product was found to decompose to give starting materials. Prolonged heating caused the peaks in the ^{1}H NMR spectrum corresponding to trimethylsilylacetylene to decrease in intensity relative to those of **3**; this was attributed to polyacetylene formation at elevated temperature. The reaction with ten equivalents of alkyne showed formation of a greater amount of adduct (**1** : product ratio was *ca.* 1 : 5), as expected for an equilibrium. Attempts to grow crystals of the product by dissolving **1** in neat trimethylsilylacetylene were unsuccessful.

6.4.2.2.4 SUMMARY

The *tert*-butylimido species Ti(η-C_5Me_5)(N^{t}Bu){PhC(NSiMe$_3$)$_2$} (**1**), Ti(η-C_5Me_5)(N^{t}Bu){MeC(N^{i}Pr)$_2$} (**2**), and Ti(η-C_5H_4Me)(N^{t}Bu){PhC(NSiMe$_3$)$_2$} (**3**) react slowly with trimethylacetylene to give an equilibrium mixture of the starting materials and an adduct. The adduct has been shown to be unstable at elevated temperature, decomposing to regenerate the parent imido complex. Attempts to isolate the product have been unsuccessful.

6.4.2.3 REACTIONS WITH PHENYLACETYLENE

A possible reason for the instability of the trimethylsilylacetylene adducts is the steric bulk of the substrate. Thus, phenylacetylene was selected as a suitable alkyne for investigation.

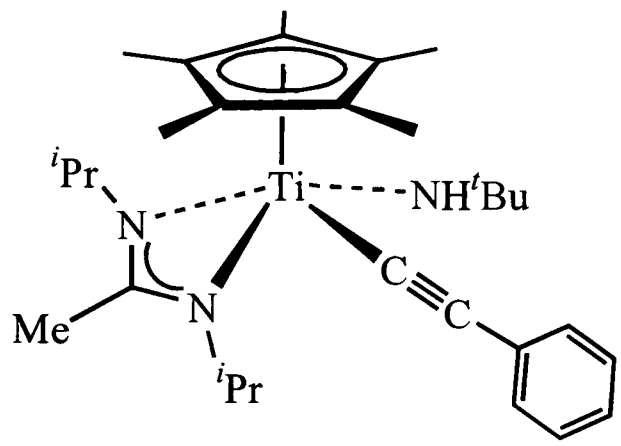
Samples of Ti(η-C_5Me_5)(N^{t}Bu){PhC(NSiMe$_3$)$_2$} (**1**), Ti(η-C_5Me_5)(N^{t}Bu){MeC(N^{i}Pr)$_2$} (**2**), Ti(η-C_5H_4Me)(N^{t}Bu){PhC(NSiMe$_3$)$_2$} (**3**), Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$){MeC(N^{i}Pr)$_2$} (**7**), and Ti(η-C_5Me_5)(N-4-C_6H_3Me){MeC(N^{i}Pr)$_2$} (**8**) were dissolved in aliquots of benzene-d_6. They were then loaded into 5 mm Wilmad NMR tubes fitted with Teflon valves, and treated with one equivalent of phenylacetylene. Reactions were monitored using ^{1}H NMR spectroscopy.

6.4.2.3.1 RESULTS AND DISCUSSION OF REACTIONS WITH PHENYLACETYLENE

The reactions followed the same pattern as those with trimethylsilylacetylene, with equilibrium mixtures of the imido starting materials, phenylacetylene, and products forming in all cases. The arylimido complexes Ti(η-C_5Me_5)(N-2,6-$C_6H_3Me_2$){$MeC(N^iPr)_2$} (**7**) and Ti(η-C_5Me_5)(N-4-C_6H_4Me){$MeC(N^iPr)_2$} (**8**) were found to form only trace amounts of product at room temperature.

In contrast to the reaction with trimethylsilylacetylene, however, the product of reaction of Ti(η-C_5Me_5)(N^tBu){$MeC(N^iPr)_2$} (**2**) with phenylacetylene formed in much higher yield (50 %) under a 1 : 1 starting material ratio. Adding a further two equivalents of phenylacetylene increased the yield to 88 % (based on titanium). Attempts to grow crystals of the product proved unsuccessful; however, the compound was fully characterised by ^1H and ^{13}C-{^1H} NMR spectroscopy.

The complex was identified as the amide-alkynyl complex Ti(η-C_5Me_5)(NH^tBu)(η^1-C_2Ph){$MeC(N^iPr)_2$} (**69**). Reaction of the phenylacetylene with the imido group results in proton transfer, and an η^1-coordination mode of the alkynyl fragment (Figure 6.13). The binding mode, and geometry of the adduct, were determined by analogy to the complex Ti(η-C_5Me_5)(NH^tBu)(η^1-C_2-4-C_6H_4Me){$MeC(N^iPr)_2$} (**70**), which was structurally assigned in solution using a NOESY experiment (*vide infra*).



69

Figure 6.13 – Geometry of the Ti(η-C_5Me_5)(NH^{t}Bu)(η^1-C_2-C_6H_5){MeC(N^{i}Pr)$_2$} (**69**) molecule

The broad singlet at 7.93 ppm in the ^{1}H NMR spectrum is assigned as the amido N–H proton. The two virtual septets (4.13, 3.18 ppm) and four doublets (1.51, 1.27, 1.19, 1.05 ppm) are typical of the acetamidinate ligand in an asymmetrical environment.

The differences in reaction between trimethylsilylacetylene and phenylacetylene may be due to the greater acidity of phenylacetylene. However, it may also be that that the mechanism of reaction involves the η^2-coordination of HC_2R prior to proton transfer. This is very possible, and would be strongly affected by the steric bulk of the R substituent, despite the fact that steric differences are likely to be unimportant in the final products, owing to the distance of the $SiMe_3$ or Ph groups from the metal centre. The greater reactivity of Ti(η-C_5Me_5)(N^{t}Bu){MeC(N^{i}Pr)$_2$} (**2**) compared to its arylimido congeners is attributed to the greater basicity of the lone pair of electrons on the *tert*-butylimido group, relative to the arylimido lone pairs.

6.4.2.4 REACTIONS WITH *p*-TOLYLACETYLENE

In order to more easily characterise the products of reaction between the titanium cyclopentadienyl imido amidinate complexes and phenylacetylene, reactions were carried out using *p*-tolylacetylene. The methyl group on the aryl ring affords a useful NMR handle which facilitiates NMR assignments.

Samples of Ti(η-C_5Me_5)(N^{t}Bu){PhC(NSiMe$_3$)$_2$} (**1**), Ti(η-C_5Me_5)(N^{t}Bu){MeC(N^{i}Pr)$_2$} (**2**), Ti(η-C_5H_4Me)(N^{t}Bu){PhC(NSiMe$_3$)$_2$} (**3**) and Ti(η-C_5Me_5)(N-4-C_6H_4Me){MeC(N^{i}Pr)$_2$} (**8**) were dissovled in benzene-d_6, and loaded into 5 mm Wilmad NMR tubes fitted with Teflon valves. To these was added one equivalent of *p*-tolylacetylene. The reactions were monitored using ^{1}H NMR spectroscopy.

6.4.2.4.1 RESULTS AND DISCUSISON OF REACTIONS WITH *p*-TOLYLACETYLENE

The reactions again followed the pattern found for the reactions with the preceeding terminal alkyne reactions. Equilibrium mixtures of starting materials and products were obtained, with by far the greatest formation of products being found for the reaction of Ti(η-C_5Me_5)(N^{t}Bu){MeC(N^{i}Pr)$_2$} (**2**) with *p*-tolylacetylene. However, the equilibrium did not afford as much product as the reaction of (**2**) with phenylacetylene. This difference was attributed to the greater acidity of phenylacetylene compared to that of *p*-tolylacetylene.

The product Ti(η-C_5Me_5)(NH^{t}Bu)(η^1-C_2-4-C_6H_4Me){MeC(N^{i}Pr)$_2$} (**70**) was characterised by ^{1}H and ^{13}C-{^{1}H} NMR spectroscopy. In addition, a 2D NOESY experiment was performed on the compound (Figure 6.14).

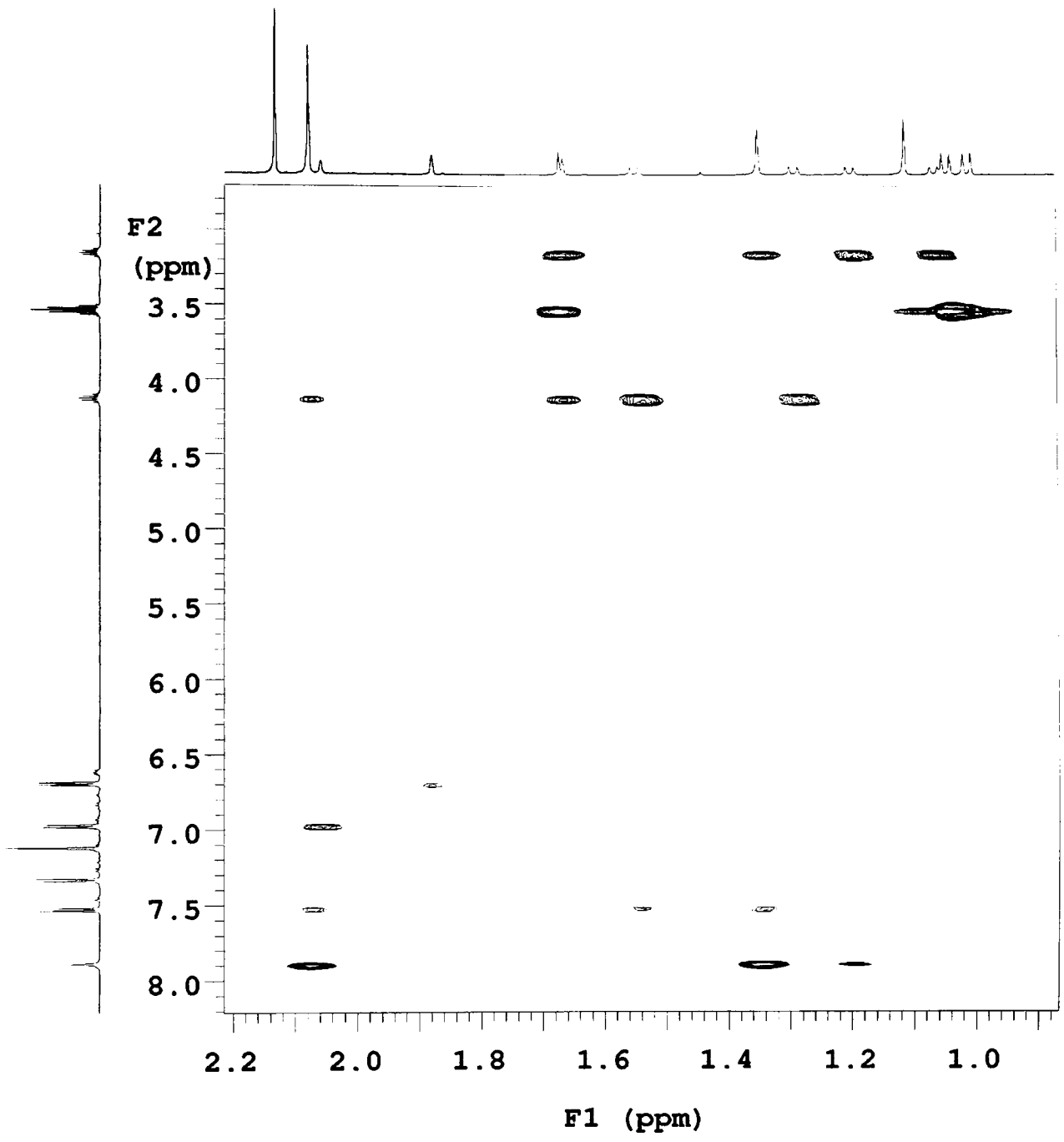


Figure 6.14 – 500.0 MHz ^{1}H NOESY NMR spectrum of Ti(η-C_5Me_5)(NH^{t}Bu)(η^1-C_2-4-C_6H_4Me){MeC(N^{i}Pr)$_2$} (**70**) in benzene-d_6

Analysis of this spectrum revealed that of the three possible binding modes (a total of five possible molecules) of the complex, the structure of **70** was correct (Figure 6.15).

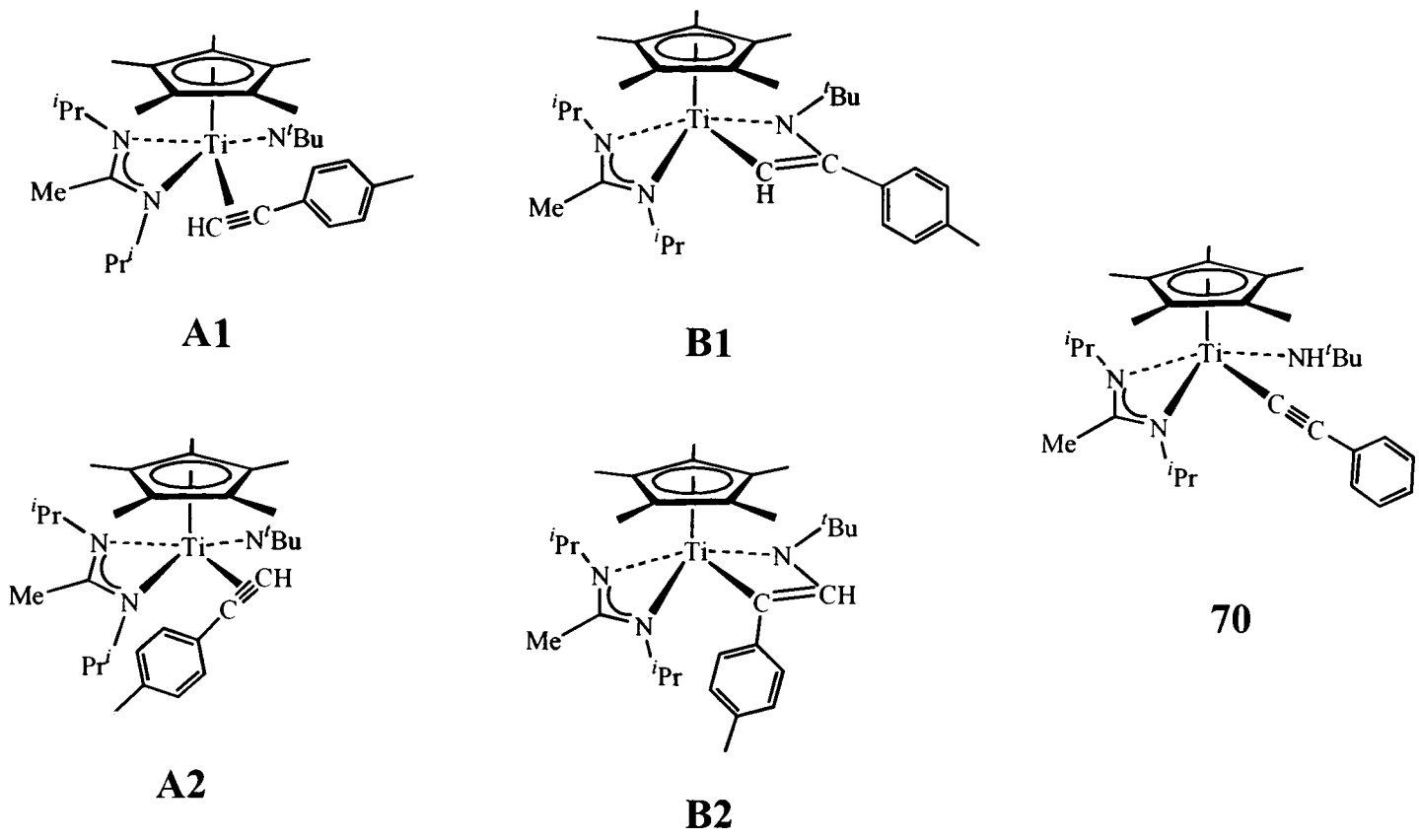


Figure 6.15 – Possible structures of product formed in reaction of $Ti(\eta\text{-}C_5Me_5)(N^tBu)\{MeC(N^iPr)_2\}$ (**2**) and *p*-tolylacetylene

The cross-peak between the amido (7.93 ppm) and *tert*-butyl (1.35 ppm) resonances indicates spatial proximity, eliminating structures **A1** and **B1**. Similarly, **A2** and **B2** are eliminated by analysis of the ^1H-^{13}C correlation spectrum, in which no C–H correlation is observed for the peak at 7.92 ppm, confirming the assignment as an amido proton. The four-legged piano stool structure is proposed on the basis of crystallographic evidence that such geometry is favoured in the solid state for titanium cyclopentadienyl amidinate complexes (as demonstrated in previous Chapters).

6.4.2.5 SUMMARY OF REACTIONS OF TITANIUM CYCLOPENTADIENYL IMIDO AMIDINATE COMPLEXES WITH ALKYNES

In contrast to the wealth of reactivity found for other Group 4 imido species with internal alkynes, the titanium cyclopentadienyl imido amidinate complexes show a complete lack of reactivity towards 2-butyne. The reactions with terminal acetylenes afford equilibrium mixtures of starting materials and adducts which are consistent with amido-η^1-alkynyl species. The equilibria are found to depend strongly on the basicity of the imido nitrogen, and probably on the sterics and acidity of the acetylene. Two such complexes are formed in sufficient quantity to enable partial characterisation, using NMR techniques.

6.5 REFERENCES FOR CHAPTER 6

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