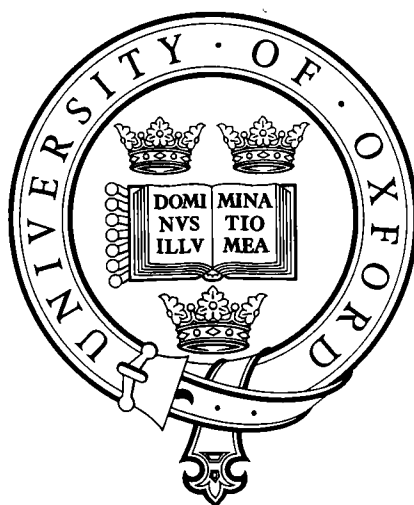


Titanium Imido Compounds with Pendant Arm Amidinate Ligands

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ABSTRACT

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This Thesis describes the synthesis and characterisation of titanium imido compounds supported by pendant arm functionalised amidinate ligands. Reactivity studies of cyclopentadienyl amidinate-imido compounds with CO₂ are presented.

Chapter 1 introduces transition metal imido chemistry, with a particular emphasis on imido complexes of titanium.

Chapter 2 describes recent developments in the chemistry of functionalised amidinate ligands. The synthesis and characterisation of new titanium imido compounds with pendant amine functionalised amidinate ligands is described. The preparation of an amidinate ligand with a pendant propyl arm is reported. Reactions of a selection of these complexes with small molecules are presented.

Chapter 3 reviews recent developments in the chemistry of cyclopentadienyl amidinate-imido compounds. The preparation of cyclopentadienyl-supported titanium imido compounds bearing pendant arm amidinate ligands is described and the reactions of these compounds with CO₂ are discussed. Kinetic and density functional theory studies of these reactions are presented.

Chapter 4 describes the synthesis and characterisation of alkyl and aryloxide titanium amidinate-imido compounds. The preparation of cationic derivatives is also described and reactions of these cationic derivatives with small molecules are discussed.

Chapter 5 presents full experimental procedures for all of the syntheses and reactivity studies outlined in Chapters 2 to 4.

Chapter 6 contains characterising data for all of the new compounds reported.

Appendices A - K contain tables of selected crystallographic data for all new crystallographically characterised complexes described in this Thesis.

Appendices L - O contain kinetics data relating to work discussed in Chapter 3.

The work described in this thesis was carried out in the Inorganic Chemistry Laboratory, South Parks Road, Oxford and the Chemistry Research Laboratory, Mansfield Road, Oxford from October 2001 to November 2004 under the supervision of Dr. Philip Mountford. All the work is my own unless stated to the contrary, and has not previously been submitted for any degree at this or any other university.

A handwritten signature in black ink, reading 'C. Boyd' in a cursive style.

Catherine Louise Boyd

November 2004

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Finally, my deepest thanks go to my family for their unwavering encouragement and belief in me throughout my years as a student.

Abbreviations

General

Å	Angstrom
Ar	aryl
atm	atmosphere(s)
^t Bu	<i>tert</i> -butyl
Bz	benzyl
°C	degrees Celsius
<i>ca.</i>	<i>circa</i> , about
Cp	cyclopentadienyl
Cy	cyclohexyl
d	day(s)
°	degrees
DFT	Density Functional Theory
EI	Electron Impact
Et	ethyl
g	gram(s)
h	hour(s)
Ind	indenyl
K	Kelvin
Me	methyl
MS	Mass Spectrometry
min	minute(s)
nacnac	ArNC(Me)CHC(Me)NAr
N ₂ N _{py}	MeC(2-C ₅ H ₄ N)(CH ₂ NSiMe ₃) ₂
OTf	CF ₃ SO ₃
Ph	phenyl
ⁱ Pr	<i>iso</i> -propyl
py	pyridine
pyr	pyridyl
pz	pyrazolyl
rt	room temperature

sec	second(s)
THF	tetrahydrofuran
Tol	4-C ₆ H ₄ Me
vs.	<i>versus</i>

Nuclear Magnetic Resonance spectroscopic data

app	apparent
ax	axial
br	broad
¹³ C-{ ¹ H}	proton-decoupled ¹³ C
COSY	CORrelation SpectroscopY
d	doublet
δ	chemical shift in ppm
DEPT	Distortionless Enhancement by Polarisation Transfer
eq	equatorial
HMBC	Heteronuclear Multiple Bond Connectivity
HMQC	Heteronuclear Multiple Quantum Coherence
Hz	Hertz
J	coupling constant
m	multiplet
MHz	Megahertz
NMR	Nuclear Magnetic Resonance
nOe	nuclear Overhauser effect
ROESY	Rotating-frame nuclear Overhauser Effect SpectroscopY
ppm	parts per million
s	singlet
sept	septet
t	triplet

Infrared Spectroscopic data

br	broad
cm ⁻¹	wavenumber
IR	Infrared

m	medium
v	frequency
s	strong
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 according to the Chapter in which they occur. The new compounds described in this Thesis are numbered 1 - 37.

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Chapter 1

Introduction

1.1 General introduction

This Thesis is concerned with titanium imido complexes supported by pendant arm functionalised amidinate ligands. The chemistry of transition metal complexes with metal-ligand multiple bonds has been an area of considerable interest for over thirty years.¹ The desire for a more complete understanding of the structure and reactivity of such complexes has resulted in rapid growth of the field. The applications of these complexes are wide-ranging and include organic synthesis,^{1,2} industrial catalysis³ and atom transfer reactions;⁴ they are also relevant to several biological systems.⁵ The reader is directed towards some reviews of the area for a more complete discussion.^{1,3,4,6-9}

A metal-ligand multiple bond is one in which the ligand binds to the metal through one σ - and one or more π -bonds. Donation of π -electrons to the metal in a complex by a heteroatom stabilises high oxidation states and this is commonly observed for the early transition metals. In some cases, *e.g.* alkylidene and alkylidyne ligands, the bond orders are fixed but in others, *e.g.* oxo and imido ligands, the bond order can vary depending upon the electronic and symmetry requirements of the metal centre, as well as the nature of the other ligands around the metal.¹⁰⁻¹⁶

This Chapter focuses on certain aspects of transition metal imido chemistry, with a particular emphasis on the chemistry of titanium imido compounds.

1.2 Aspects of transition metal imido chemistry

The first report of a transition metal imido complex was of $[\text{Os}(\text{N}^t\text{Bu})\text{O}_3]$ in 1956¹⁷ and much work has been carried out since then on the nature and reactivity of the metal-imido bond and of metal imido complexes in general. This Section will give a brief overview of some of the work that has been reported on transition metal imido complexes. For a more complete discussion the reader is directed towards some general^{1,6,18} and more specific reviews.^{9,19-26}

The imido ligand may behave either as a terminal or as a bridging fragment.¹⁴ A terminal imido ligand (NR , where R is typically an organic group) bonds to a single metal centre through one σ -bond and either one or two π interactions. This gives rise to three possible bonding arrangements in which the hybridisation of

nitrogen and bond order vary (Figure 1.1). The bonding in transition metal imido complexes has recently been reviewed.²⁰

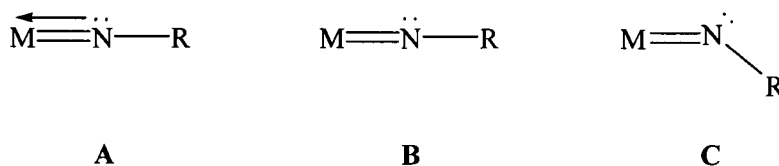


Figure 1.1 Bonding modes of the terminal imido ligand

The most common case (Figure 1.1, bonding mode **A**) involves an effectively linear linkage ($M=N-R$ angle in the range *ca.* $150^\circ - 180^\circ$) where the nitrogen is sp hybridised and donates four electrons to the metal centre. There is a triple bond composed of one σ and two π bonds to the metal. The metal-nitrogen bond is usually drawn as a formal double bond by convention, despite its variable bond order.

In the second case (bonding mode **B**), the nitrogen atom is sp hybridised and the linkage is also linear. However, the relevant acceptor orbitals on the metal are partially or entirely inaccessible to the lone pair due to symmetry restrictions or a severe disparity in energy. The nitrogen donates less than four electrons and only two in the limiting case; there will thus be significant electron density in a ligand-based non-bonding orbital. An example is Schrock's tris(imido) complex $[\text{Os}(\text{N}-2,6\text{-C}_6\text{H}_3\text{Pr}_2)_3]$ (**1.1**) where each imido ligand acts as a $3\frac{1}{3}$ electron donor due to symmetry restrictions.²⁷

In the case of bonding mode **C** there is a "bent" metal-imido linkage. There is a formal double bond to the metal composed of one σ - and one π -interaction and a lone pair of electrons localised in an sp^2 orbital on nitrogen. The nitrogen formally donates only two electrons to the metal centre. This type of coordination is rare, since it is now accepted that an imide with an $M-N-C$ angle as low as 150° is capable of behaving formally as a four electron donor. An example is $[\text{Mo}(\text{NPh})_2(\text{S}_2\text{CNEt}_2)_2]$ (**1.2**) where one $\text{Mo}-\text{N}-\text{C}$ angle is $139.4(4)^\circ$.^{28,29}

A molecular orbital energy diagram of a hypothetical six coordinate imido complex $[\text{M}(\text{NR})\text{L}_5]$ ($\text{L} = \sigma$ -donor ligand) is shown in Figure 1.2. The diagram illustrates the $\sigma^2\pi^4$ -triple bond and the fact that the imido group is formally a 2-

ligand. The metal-centred d_{π} -orbitals (d_{π} - p_{π} antibonding) are raised in energy, consistent with observations that transition metal imido complexes typically have d^0 , d^1 or d^2 electron configurations.

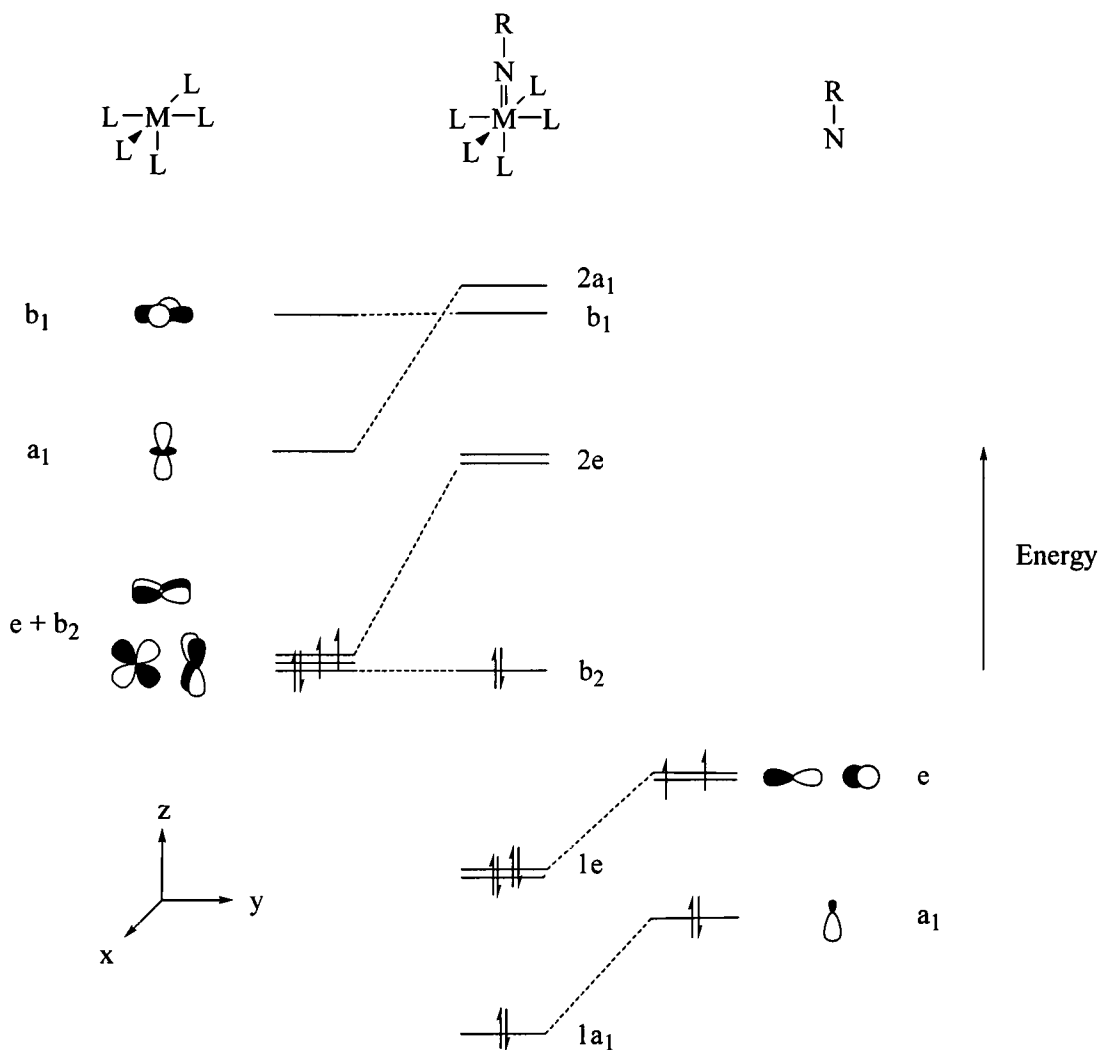
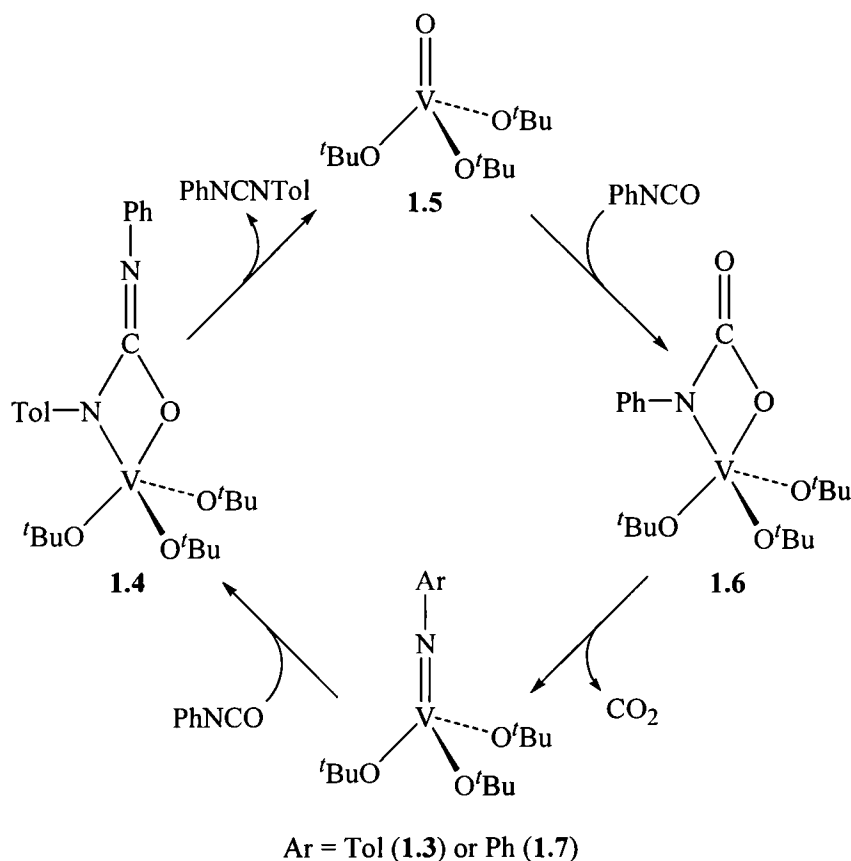


Figure 1.2 Molecular orbital diagram of $[M(NR)L_5]$ ($L = \sigma$ -donor ligand)

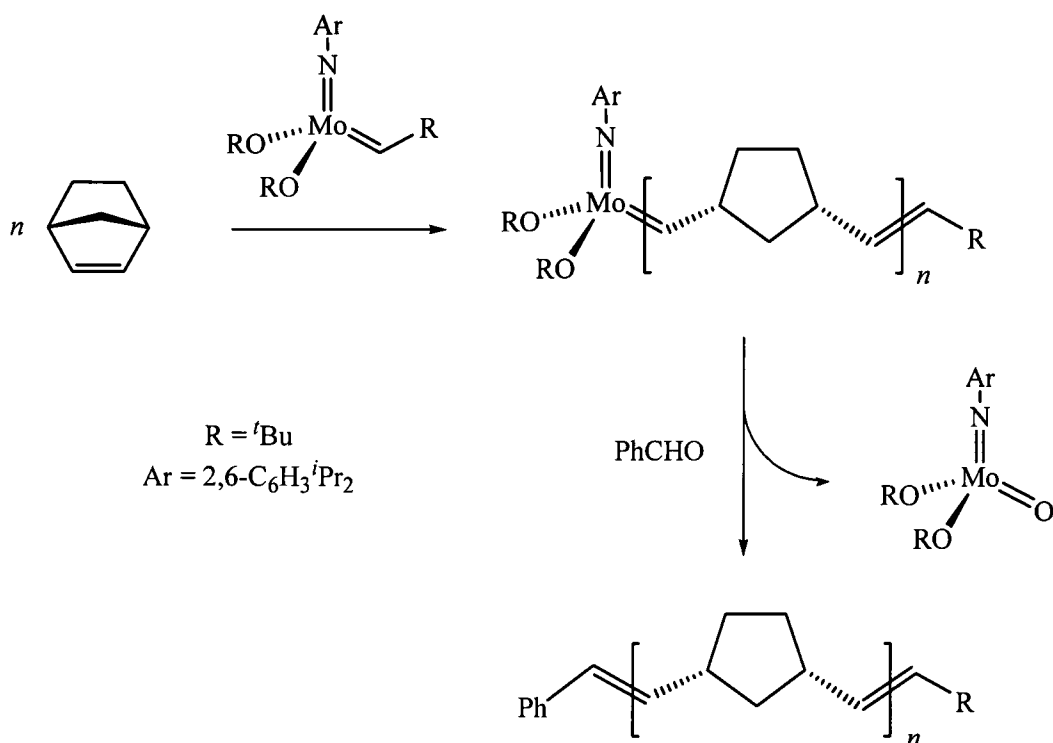
Apart from their potential use in materials chemistry as sources of the corresponding metal nitrides (*e.g. via* chemical vapour deposition),^{30,31} the main current interest in imido compounds is with regard to their stoichiometric or catalytic reactions. These reactions can be divided into two types: those where the $M=NR$ bond is the reactive site, and those in which the imido ligand behaves as a "spectator" or "supporting" ligand.

An example of an imido ligand functioning as a reactive site is provided by the complex $[\text{V}(\text{NTol})(\text{O}^t\text{Bu})_3]$ (**1.3**). Compound **1.3** converts aryl isocyanates into diarylcarbodiimides catalytically.³² The reaction between **1.3** and PhNCO has been studied using IR and NMR spectroscopies and the proposed catalytic cycle is shown in Scheme 1.1. Compound **1.3** reacts with PhNCO to form the metallacycle **1.4** which eliminates the corresponding carbodiimide and forms the oxo complex **1.5**. Complex **1.5** reacts with PhNCO to form the metallacycle **1.6**, which eliminates CO_2 to form the complex $[\text{V}(\text{NC}_6\text{H}_5)(\text{O}^t\text{Bu})_3]$ (**1.7**).



Scheme 1.1 Catalytic conversion of isocyanate into carbodiimide (Tol = 4- $\text{C}_6\text{H}_4\text{Me}$)

An example of an imido ligand functioning as a spectator ligand is provided by the compound $[\text{Mo}(\text{N}-2,6\text{-C}_3\text{H}_3^i\text{Pr}_2)(\text{CH}^i\text{Bu})(\text{O}^t\text{Bu})_2]$ (**1.8**).³ The compound **1.8** is a ROMP (ring opening metathesis polymerisation) initiator. The ROMP mechanism involves a [2+2] cycloaddition of a cyclic alkene and a metal alkylidene (Scheme 1.2). The reactive site is the alkylidene group and the imido ligand remains unchanged during the course of the reaction.



Scheme 1.2 The ROMP of norbornene by a general catalyst $[\text{M}(\text{N-2,6-C}_6\text{H}_3\text{ }i\text{Pr}_2)(\text{CH}^t\text{Bu})(\text{O}^t\text{Bu})_2]$ (1.8)

Although many examples of $\text{M}=\text{NR}$ group reactivity are known for other metals, the most reactive metal-imido linkages have been found for Group 4 compounds.^{19,21,33,34} The following Section will focus on the preparation and reactivity of titanium imido complexes, since these are of most relevance to this Thesis.

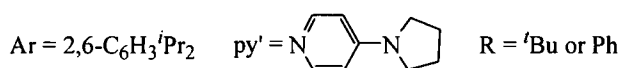
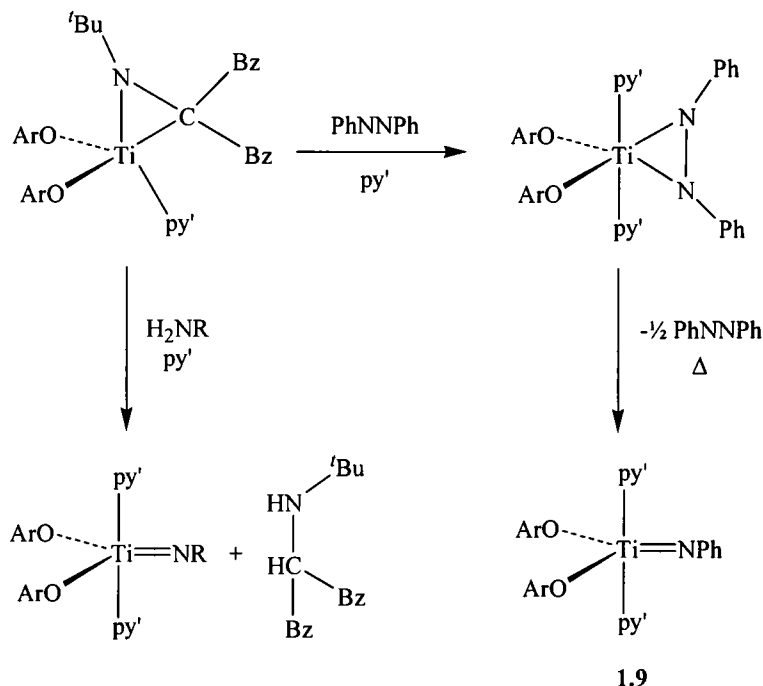
1.3 Preparation of titanium imido compounds

The first terminal titanium imido complex was reported by Buerger and Wannagat in 1963.³⁵ They proposed that $[\text{Ti}(\text{NSiMe}_3)\text{Cl}_2(\text{py})_3]$ was the product formed from $[\text{Ti}\{\text{N}(\text{SiMe}_3)_2\}\text{Cl}_3]$ upon its reaction with pyridine to eliminate trimethylsilylchloride.

Another early attempt to synthesise terminal titanium imido complexes was reported in 1963 by Bradley *et al.* Reaction of *tert*-butylamine with $[\text{Ti}(\text{NMe}_2)_4]$ yielded a mixture of dimeric bridging imido complexes $[\text{Ti}(\mu\text{-N}^t\text{Bu})(\text{NMe}_2)_2]_2$ and $[\text{Ti}(\mu\text{-N}^t\text{Bu})(\text{NH}^t\text{Bu})(\text{NMe}_2)_2]_2$.³⁶ In the early 1980s, Teuben and coworkers reported that reaction of $[\text{Ti}(\eta\text{-C}_5\text{H}_5)\text{Cl}_3]$ with Me_3SiNHR ($\text{R} = \text{Et}, ^t\text{Pr}, ^t\text{Bu}$ or Ph) yielded amido compounds of the type $[\text{Ti}(\eta\text{-C}_5\text{H}_5)(\text{NHR})\text{Cl}_2]$.³⁷ Subsequent

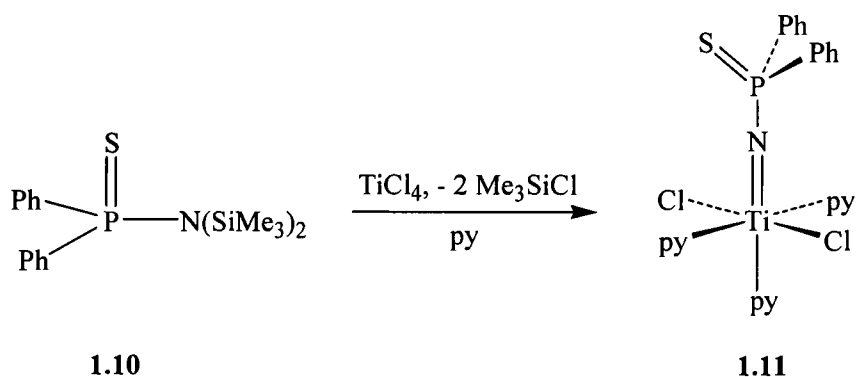
elimination of HCl lead to the dimeric imido complexes $[\text{Ti}_2(\eta\text{-C}_5\text{H}_5)_2(\mu\text{-NR})_2\text{Cl}_2]$.

The first structurally authenticated terminal titanium imido complexes were reported in 1990. Rothwell and coworkers prepared the 5-coordinate aryloxide supported titanium complex $[\text{Ti}(\text{NPh})(\text{O-2,6-C}_6\text{H}_3^i\text{Pr}_2)(\text{py}')_2]$ (**1.9**, $\text{py}' = 4\text{-pyrrolidinopyridine}$) by protonolysis of a η^2 -imine or by thermal decomposition of a η^2 -azobenzene complex (Scheme 1.3).³⁸



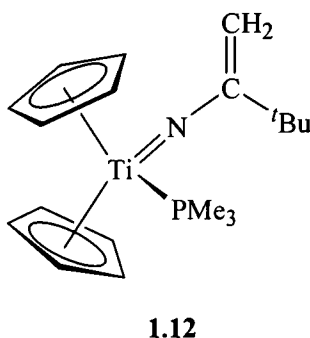
Scheme 1.3 Preparation of aryloxide-supported titanium imido complexes

At around the same time, Roesky *et al.* reported that reaction of phosphinamide **1.10** with TiCl_4 and subsequent addition of pyridine yielded the six-coordinate titanium arylimido complex $[\text{Ti}\{\text{NP}(\text{S})\text{Ph}_2\}\text{Cl}_2(\text{py})_3]$ (**1.11**, Equation 1.1).³⁹



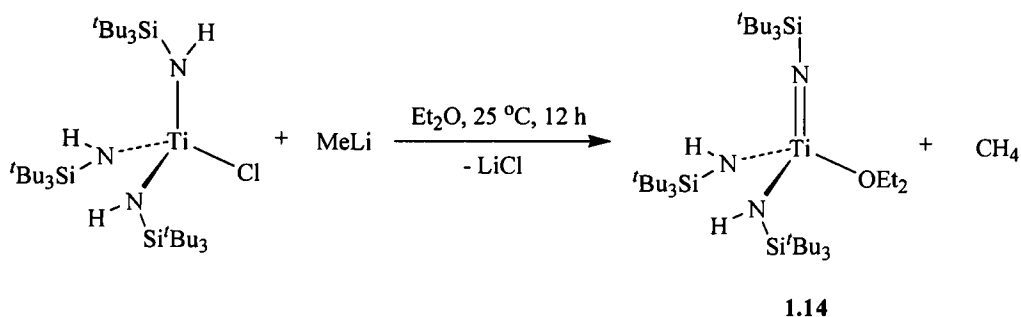
Equation 1.1

Also in 1990, Doxsee and coworkers reported that treatment of Tebbe's reagent $[\text{Ti}(\eta\text{-C}_5\text{H}_5)_2(\mu\text{-CH}_2)(\mu\text{-Cl})\text{AlMe}_2]$ with nitriles in the presence of PMe_3 produced the complex **1.12**.⁴⁰ Such complexes are also accessible from the reaction of titanacyclobutanes with nitriles and produce interesting [4+2] cycloaddition products with organic nitriles and carbonyls.

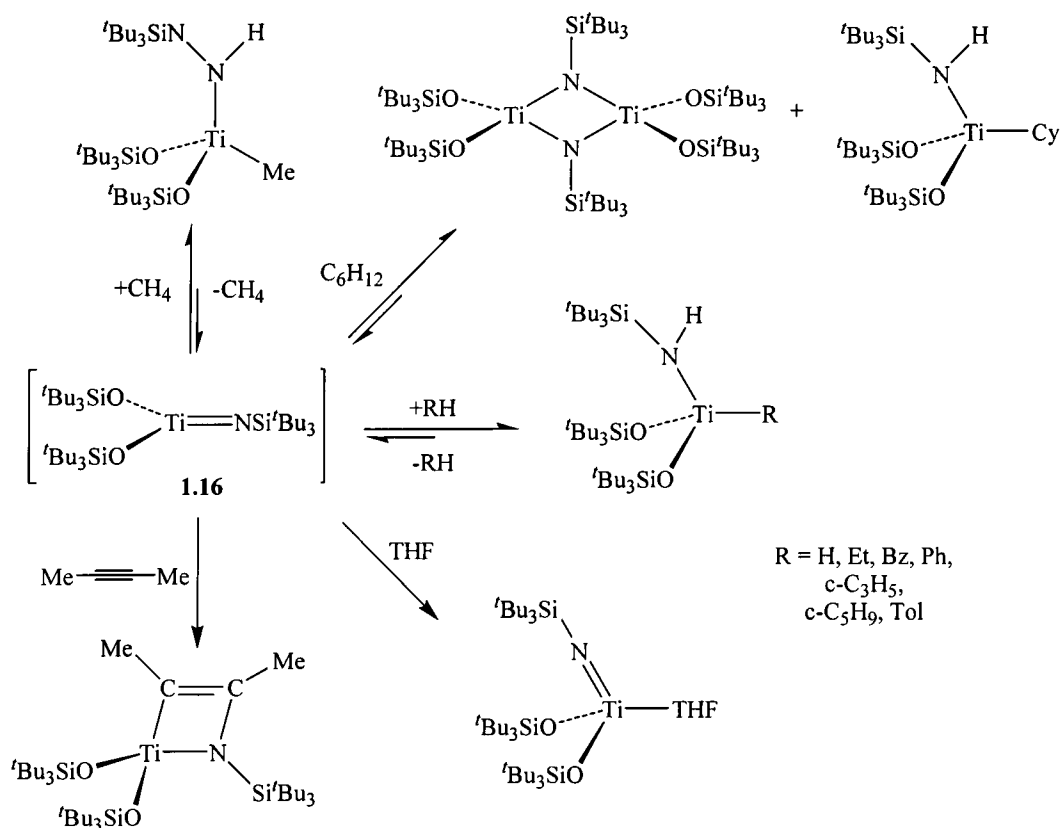


Winter *et al.* have conducted an investigation into the complex mixture of products arising from the reaction of TiCl_4 with primary amines. Their study was concerned with identifying the intermediates in the metal organic chemical vapour deposition (MOCVD) of titanium nitride from TiCl_4 and alkylamines.^{41,42} They found that reaction of TiCl_4 with *tert*-butylamine gave the trimer $[\text{Ti}(\mu\text{-N}^t\text{Bu})_2\text{Cl}_2(\text{NH}_2^t\text{Bu})]_3$. Reaction with three or more equivalents of $^t\text{BuNH}_2$ afforded the monomer $[\text{Ti}(\text{N}^t\text{Bu})\text{Cl}_2(\text{NH}_2^t\text{Bu})_3]$ (**1.13**).

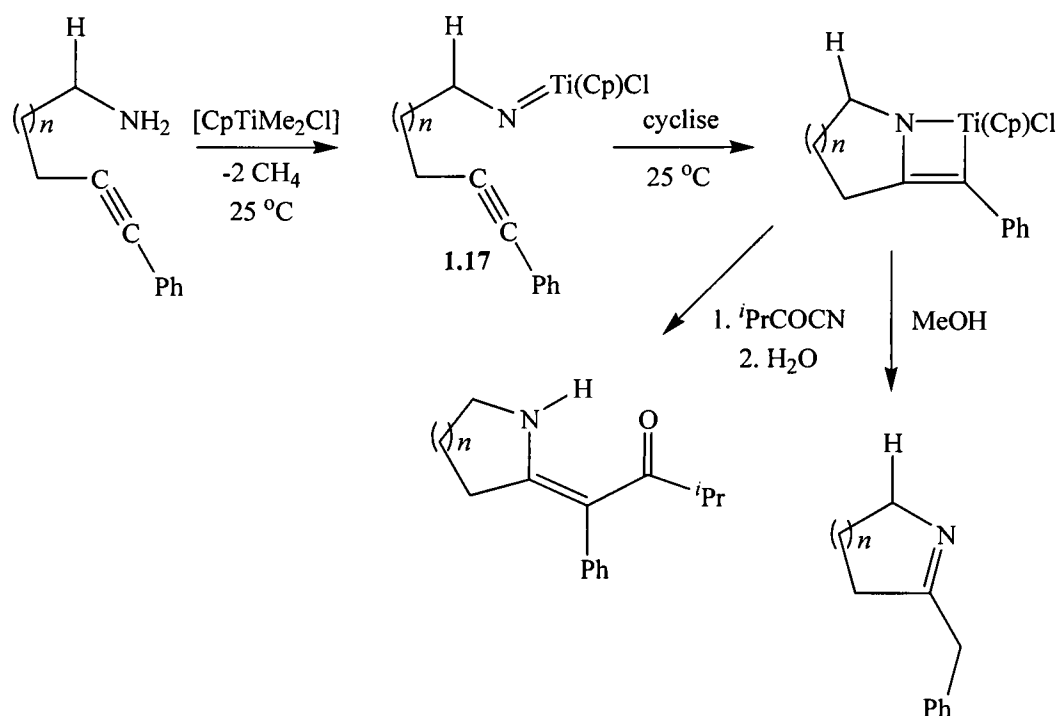
In 1991, Wolczanski and coworkers described the preparation of $[\text{Ti}(\text{NSi}^t\text{Bu}_3)(\text{NHSi}^t\text{Bu}_3)_2(\text{Et}_2\text{O})]$ (**1.14**) by treatment of $[\text{Ti}(\text{NHSi}^t\text{Bu}_3)_3\text{Cl}]$ with MeLi (Equation 1.2).⁴³ Thermolysis of **1.14** generates the reactive transient species $[\text{Ti}(\text{NSi}^t\text{Bu}_3)(\text{NHSi}^t\text{Bu}_3)_2]$ which activates the C-H bonds of benzene.

**Equation 1.2**

Thermolysis of $[\text{Ti}(\text{NHSi}^t\text{Bu})_3\text{Cl}]$ in THF yielded the closely related species $[\text{Ti}(\text{NSi}^t\text{Bu}_3)(\text{NHSi}^t\text{Bu}_3)_2(\text{THF})]$ (**1.15**), which could be alkylated with stoichiometric amounts of MeLi or $^t\text{BuLi}$.⁴³ When siloxane supporting ligands were used, the transient species $[\text{Ti}(\text{NSi}^t\text{Bu}_3)(\text{OSi}^t\text{Bu}_3)_2]$ (**1.16**) was generated by heating $[\text{Ti}(\text{NHSi}^t\text{Bu}_3)(\text{OSi}^t\text{Bu}_3)_2\text{Me}]$ with elimination of CH_4 .⁴⁴ Compound **1.16** activates alkyl, aryl and aromatic C-H bonds and reacts with alkynes to form metallacycles (Scheme 1.4).

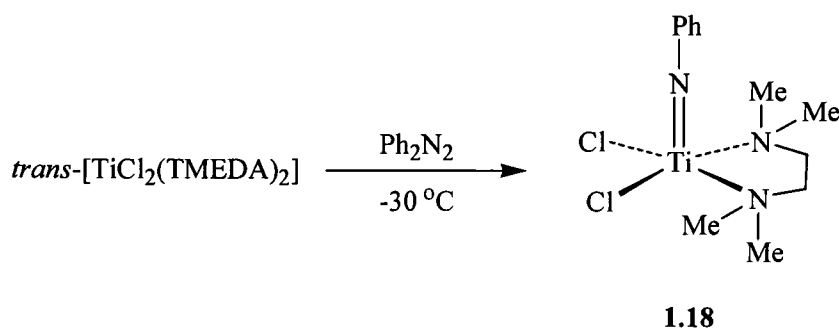
**Scheme 1.4** Reactions of the transient siloxane-supported titanium imide **1.16**

Other reactive transient titanium imido complexes were noted around this time by Livinghouse and coworkers in their studies of $[\text{Ti}(\eta\text{-C}_5\text{H}_5)\text{Me}_2\text{Cl}]$ and $[\text{Ti}(\eta\text{-C}_5\text{H}_5)\text{Cl}_3]$ as catalysts for heterocycle annulation.⁴⁵ They propose a mechanism in which reaction between the titanium complex and 1-amino-5-phenylpent-4-yne generates a transient titanium imido complex (**1.17**). This undergoes intramolecular cycloaddition with the alkene to generate a bicyclic species containing an azametallacycle, (Scheme 1.5). Neither the imido complex nor the metallacycle were isolated, but this methodology has been used to generate heterocycles by reaction of the metallacycles with alcohols or acylcyanides.⁴⁶ Use of this transformation has been reported in a total synthesis for the antifungal agent (+)-preussin.⁴⁷

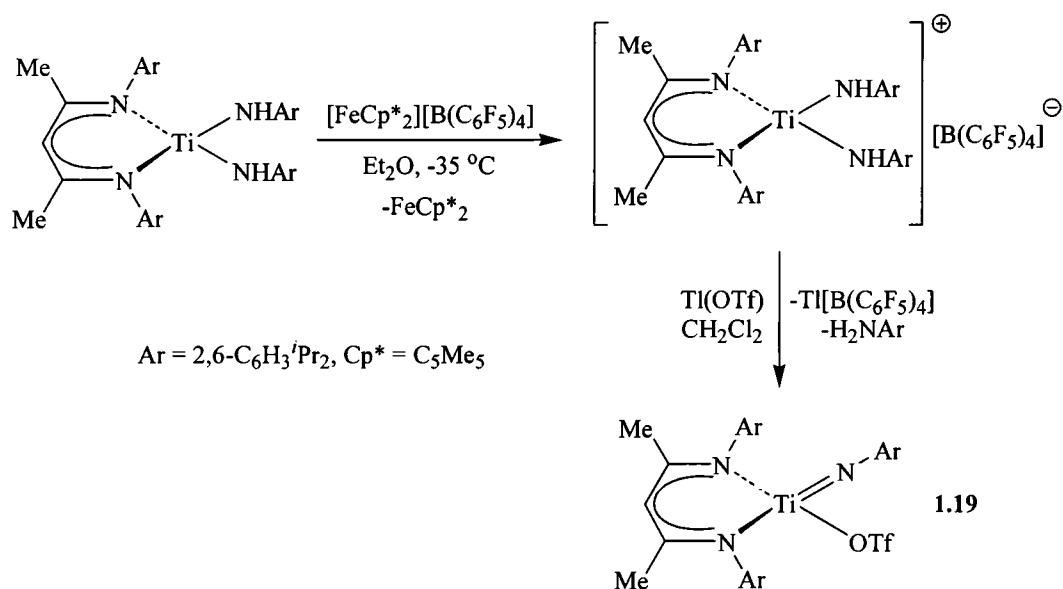


Scheme 1.5 A titanium imido compound as an intermediate in heterocycle annulation

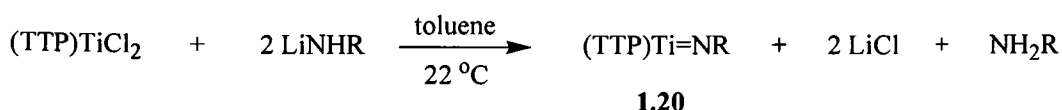
Several groups have used the oxidation of Ti^{II} to Ti^{IV} as a route to titanium imido complexes,^{38,47-49} one example being from Gambarotta's work on TMEDA complexes (TMEDA = N,N,N',N'-tetramethylethylenediamine).⁴⁹ Reaction of the Ti^{II} compound $\text{trans-}[\text{TiCl}_2(\text{TMEDA})_2]$ with azobenzene yielded the Ti^{IV} imido complex $[\text{Ti}(\text{NPh})\text{Cl}_2(\text{TMEDA})]$ (**1.18**, Equation 1.3).

**Equation 1.3**

Oxidation of a Ti^{III} precursor to Ti^{IV} has recently been used by Mindiola and coworkers to prepare the nacnac-supported imido complex **1.19** via an oxidatively induced α -hydrogen abstraction {nacnac = $ArNC(Me)CHC(Me)NAr$, $Ar = 2,6-C_6H_3^iPr_2$ } (Scheme 1.6).⁵⁰

**Scheme 1.6** Preparation of the nacnac-supported titanium imido complex **1.19**

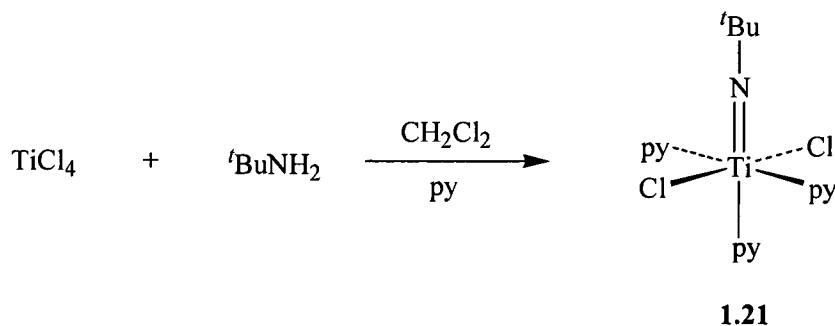
Woo *et al.* have prepared porphyrin-supported titanium imido complexes (**1.20**) from reaction of $LiNHR$ with the corresponding dichlorides (Equation 1.4).⁵¹ Treatment of the imido complexes with water leads to the formation of the oxo complex $[Ti(TTP)O]$.



R = Ph, Tol or C₆H₁₁; H₂TTP = tetratolylporphyrin

Equation 1.4

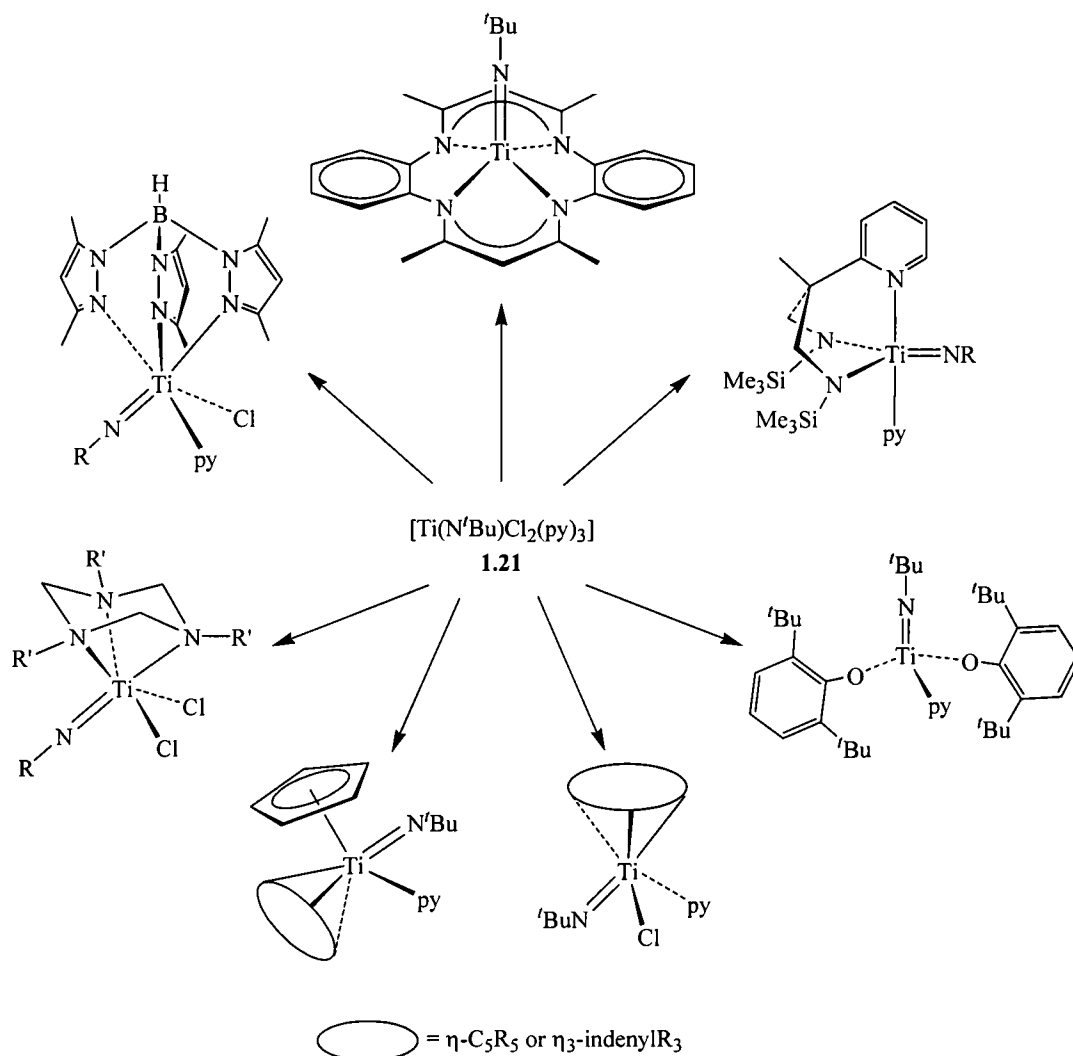
The syntheses of all of the complexes described above involve generation of the imido fragment after assembly of the supporting ligand set. A useful contribution to the development of titanium imido chemistry occurred in 1994, when, inspired by Winter's synthesis of [Ti(N^tBu)Cl₂(OPPh₃)₂],⁴¹ Mountford and coworkers prepared the compound [Ti(N^tBu)Cl₂(py)₃] (**1.21**).^{52,53} Compound **1.21** can be prepared from the reaction of TiCl₄ with ^tBuNH₂, followed by addition of pyridine, on a 40 g scale in near-quantitative yield (Equation 1.5).



Equation 1.5

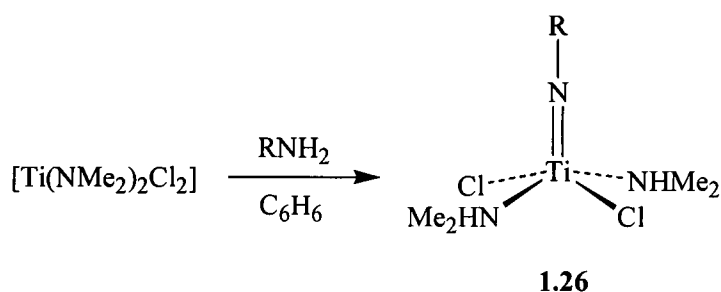
This is an especially convenient entry point into the synthesis of titanium imido compounds as **1.21** (and certain N-aryl substituted derivatives) have been shown to react successfully to yield derivatives with a wide range of ancillary ligands (Scheme 1.7).^{19,52} The π -donor properties of the imido ligand stabilise higher oxidation states, so the problem of titanium reduction during chloride metathesis reactions of this type of complex is avoided.

The reaction of TiCl₄ with ArNH₂ proved to be an unsuccessful route to the analogous arylimido compounds, but these complexes were successfully prepared by aniline/*tert*-butyl imide exchange reactions with **1.21**. Complexes prepared by this route include [Ti(NAr)Cl₂(py)₃] {Ar = 2,6-C₆H₃Me₂ (**1.22**), 2,6-C₆H₃^tPr₂ (**1.23**), C₆H₅ (**1.24**) and Tol (**1.25**)}.^{53,54}



Scheme 1.7 Compound **1.21** as a synthon for new titanium imido complexes

Motivated by the desire to apply semi-automated techniques to synthesise compound libraries containing a wider range of imido substituents, Mountford *et al.* have recently developed another route into imido chemistry. Reaction of $[Ti(NMe_2)_2Cl_2]$ with RNH_2 yielded compounds of the type $[Ti(NR)(NHMe_2)Cl_2]$ (**1.26**) (Equation 1.6).⁵⁵ This method is a versatile entry point into titanium imido chemistry and has been used to prepare imido complexes from over one hundred different commercially available amines.



Equation 1.6

1.4 Classes of titanium imido compounds

An enormous range of terminal titanium imido complexes has been prepared over the last fourteen years. This Section describes the synthesis and reactivity of some of the important classes.

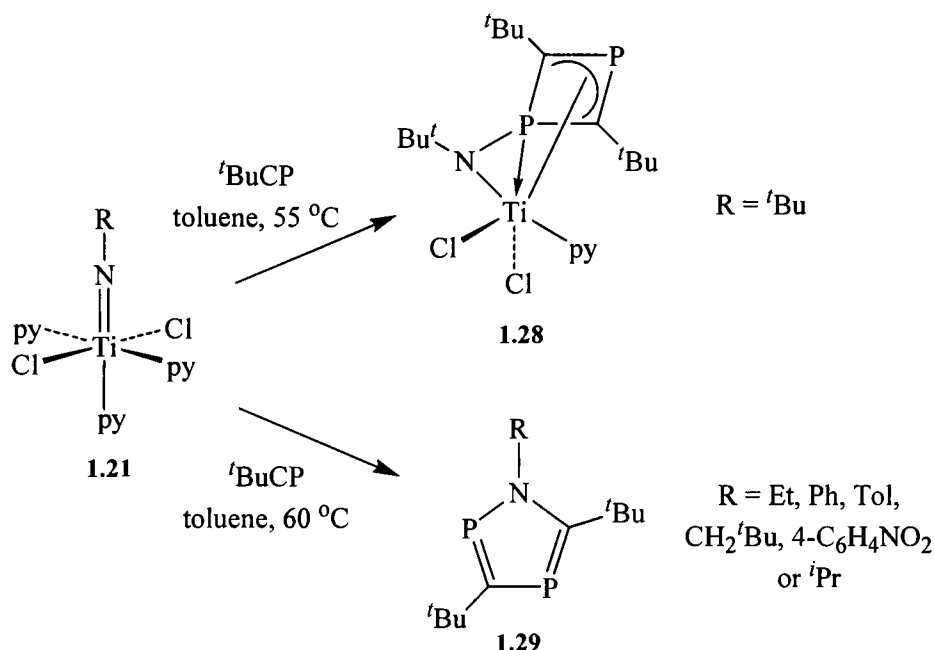
1.4.1 "Simple" coordination compounds of the type $[\text{Ti}(\text{NR})\text{Cl}_2(\text{L})_n]$

There are several examples of titanium imido complexes supported by monodentate donor ligands. Roesky's $[\text{Ti}\{\text{N}(\text{S})\text{PPh}_2\}\text{Cl}_2(\text{py})_3]$ (**1.11**) and the general entry point complexes $[\text{Ti}(\text{NR})\text{Cl}_2(\text{py})_3]$ (**1.21** - **1.25**) and $[\text{Ti}(\text{NR})(\text{NHMe}_2)_2\text{Cl}_2]$ (**1.26**) have already been discussed.^{39,53-55}

Compounds **1.21**, **1.22** and **1.23** react with α -diimines in a manner dependent upon both the imido N-substituent and the diimine N- and backbone C-substituents.⁵⁶ Reaction of $[\text{Ti}(\text{N}-2,6\text{-C}_6\text{H}_3\text{'Pr}_2)\text{Cl}_2(\text{py})_3]$ (**1.23**) with $\text{PhNC}(\text{Me})\text{C}(\text{Me})\text{NPh}$ gave the crystallographically characterised adduct $[\text{Ti}(\text{N}-2,6\text{-C}_6\text{H}_3\text{'Pr}_2)\{\kappa^2\text{-PhNC}(\text{Me})\text{C}(\text{Me})\text{NPh}\}\text{Cl}_2(\text{py})]$ (**1.27**) which possesses mutually *trans* chloride ligands and has one diimine nitrogen atom *cis* and one *trans* to the arylimido group. In contrast, reactions of $[\text{Ti}(\text{N}'\text{Bu})\text{Cl}_2(\text{py})_3]$ (**1.21**) with α -diimines of the type $\text{ArNC}(\text{H})\text{C}(\text{H})\text{NAr}$ ($\text{Ar} = \text{Tol}$ or $2,6\text{-C}_6\text{H}_3\text{Me}_2$) did not yield analogues of **1.27**. Instead, stoichiometric titanium imide/organic imine metathesis occurred to form $[\text{Ti}(\text{NAr})\text{Cl}_2(\text{py})_n]$ ($n = 2$ or 3) and $\text{'BuNC}(\text{H})\text{C}(\text{H})\text{N}'\text{Bu}$ and/or $\text{'BuNC}(\text{H})\text{C}(\text{H})\text{NAr}$.⁵⁶

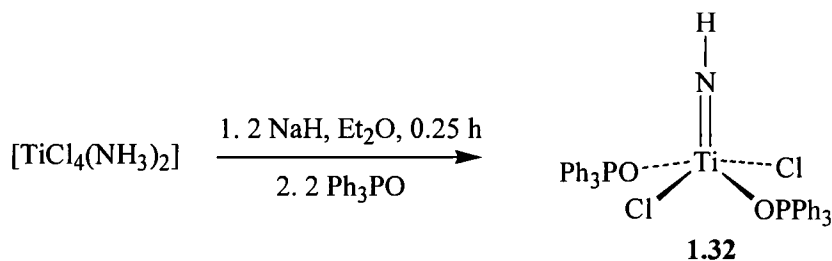
Reaction of $[\text{Ti}(\text{N}'\text{Bu})\text{Cl}_2(\text{py})_3]$ (**1.21**) with 'BuCP produced the compound $[\text{Ti}(\text{P}_2\text{C}_2\text{'Bu}_2\text{N}'\text{Bu})\text{Cl}_2(\text{py})]$ (**1.28**).⁵⁷ The reaction is proposed to proceed by sequential [2+2] cycloaddition reactions of 'BuCP to the $\text{Ti}=\text{N}$ double bond and then to the resulting $\text{P}=\text{C}$ double bond, although no reaction intermediates were

spectroscopically characterised. However, when complexes $[\text{Ti}(\text{NR})\text{Cl}_2(\text{py})_3]$ ($\text{R} = \text{Et, Ph, Tol, CH}^t\text{Bu, 4-C}_6\text{H}_4\text{NO}_2$ or ^iPr) were reacted with $^t\text{BuCP}$, the previously unknown azadiphospholes **1.29** were formed (Scheme 1.8).⁵⁸



Scheme 1.8 Reactions of $[\text{Ti}(\text{NR})\text{Cl}_2(\text{py})_3]$ with $^t\text{BuCP}$

Lorber and coworkers have recently prepared a complex of type **1.26**, namely $[\text{Ti}(\text{NPh})(\text{NHMe}_2)_2\text{Cl}_2]$ (**1.30**), by a one-pot method similar to that described in the previous Section. This and the related oligomeric complex $[\text{Ti}(\text{NPh})(\text{NHPh})_2]_n$ (**1.31**) are catalysts for the intermolecular hydroamination of various alkynes in the presence of amines. In the case of unsymmetrical alkynes the Markovnikov addition product is favoured.⁵⁹



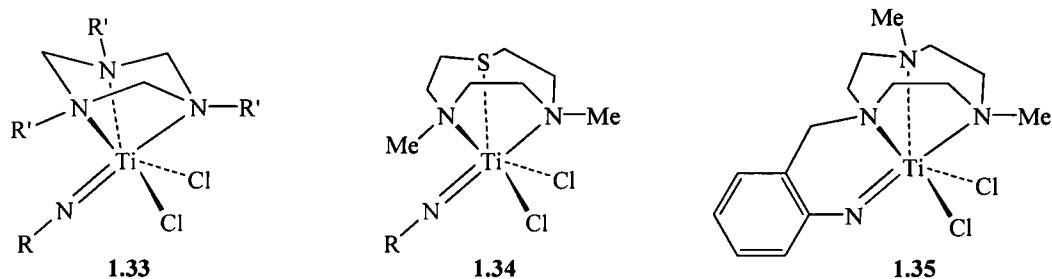
Equation 1.7

A further example is Winter's "parent" imido complex $[\text{Ti}(\text{NH})\text{Cl}_2(\text{OPPh}_3)_2]$ (**1.32**), prepared during their studies on the role of such species in the deposition

of metal nitride films (Equation 1.7).⁶⁰ In this case the imido nitrogen bears only a hydrogen substituent.

1.4.2 Neutral N₂ and N₃ donor and related ligands

In 1999, the groups of Baker⁶¹ and Mountford^{62,63} reported the preparation of a series of triazacyclohexane-supported titanium imido compounds. Interest in these compounds stemmed from the isolobal relationship of systems of the type $[M(NR)(fac-L_3)X_2]$ (*fac*-L₃ = facially capping tridentate ligand) with metallocenes $[M(\eta-C_5H_5)_2X_2]$, which form an important class of compounds in catalysis. The complexes were prepared by reaction of the synthons $[Ti(NR)Cl_2(py)_3]$ with the triazamacrocycle in benzene or CH₂Cl₂. Complexes of the type **1.33** (R = Me, Et or 'Bu) and their dialkyl derivatives were found to be very poor pre-catalysts for the polymerisation of ethylene.⁶⁴

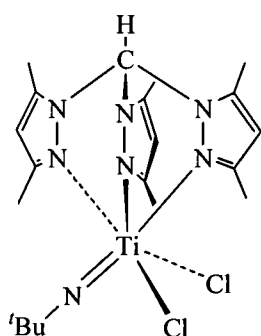
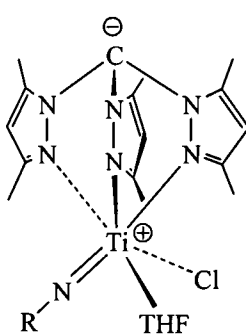
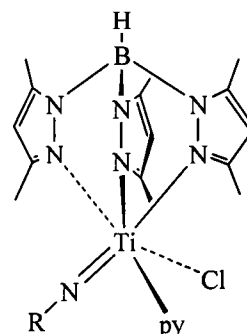


The chemistry of macrocycle-supported titanium imido systems has been extended to include triazacyclononane ligands. Thioether and mixed nitrogen-oxygen and nitrogen-sulphur macrocycles such as **1.34** have also been prepared.^{65,66} A series of *ansa*-linked macrocyclic-imides has also been synthesised (**1.35**) but these compounds so far show low activities for ethylene polymerisation.⁶⁷

More recently, a library of fifty triazacyclononane-supported titanium imido complexes has been prepared by semi-automated procedures and their activities for ethylene polymerisation examined using a high throughput screening method. These experiments were performed in order to examine the effect of the imido substituent on polymerisation. Complexes with bulky alkyl imido groups were found to have the most promising activities and are the first highly active Group 4 imido ethylene polymerisation catalysts to be reported.⁵⁵ Altogether, the library of triazacyclononane complexes contained seven highly active ethylene

polymerisation catalysts with activities in the range 3,400 - 10,340 kg(PE) mol⁻¹ h⁻¹ bar⁻¹.

A second type of neutral N₃-donor supporting ligand to be explored is the "scorpionate" type tris(pyrazolyl)methane ligand.⁶⁸ Compounds of this type were prepared from the synthons [Ti(NR)Cl₂(py)₃] and [Ti(NR)(NHMe₂)₂Cl₂]. A library of complexes of type **1.36** has been prepared using semi-automated synthesis, and initial screening suggests that it contains some highly active catalysts for ethylene polymerisation.⁶⁹ Reaction of the tris(3,5-dimethylpyrazolyl)methane complex [Ti(N^tBu){CH(Me₂pz)₃}Cl₂] (**1.36**) with MeLi or LiN^tPr₂ in THF gave the zwitterionic derivative [Ti(N^tBu){CH(Me₂pz)₃}Cl(THF)] (**1.37**).⁶⁸ This is the first example of a structurally authenticated naked *sp*³ hybridised carbanion. Complexes of the related monoanionic tris(pyrazolyl)hydroborate ligand have also been synthesised (**1.38**).^{70,71}

**1.36****1.37****1.38**

Flores *et al.* have recently reported the synthesis of the related tris(pyrazolyl)methane compound [Ti(N^tBu){Me₃SiOCH₂C(pz)₃}Cl₂] (**1.39**) as part of their studies on metallo-dendrimers.⁷²

A further neutral N-donor ligand that has been explored is TMEDA. Nielson and coworkers have demonstrated that [Ti(N-2-C₆H₄^tBu)(TMEDA)Cl₂] (**1.40**) is a moderately active catalyst for the polymerisation of ethylene and 1-hexene.⁷³

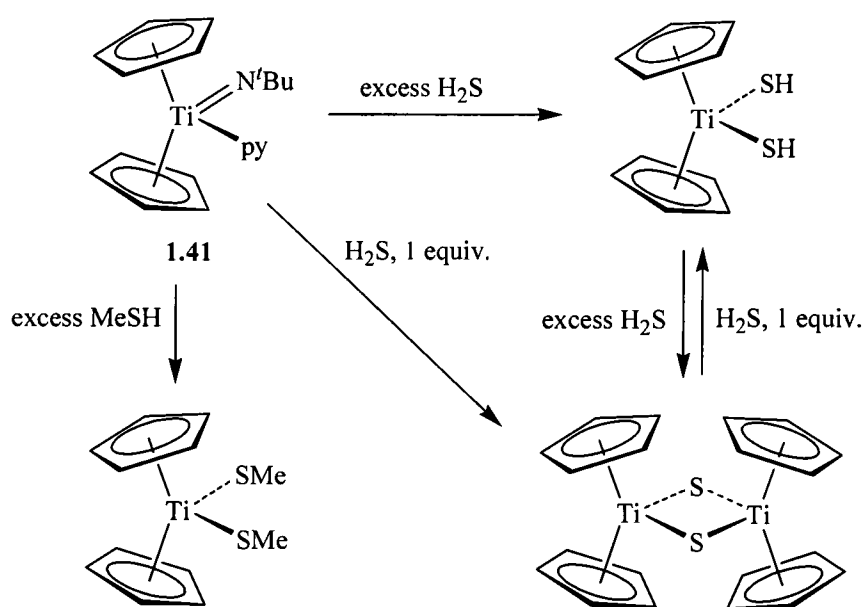
1.4.3 Complexes with monoanionic ligands

Titanium imido complexes supported by amido (**1.15**) and siloxane (**1.16**) ligands have already been described, and have been shown to be very reactive,

participating in C-H bond activation reactions.^{43,44} Another example already discussed is Rothwell's aryloxo derivative **1.9**.^{38,74} Mountford *et al.* have subsequently shown that mono- and bi-nuclear aryloxo derivatives can be prepared from the $[\text{Ti}(\text{N}^t\text{Bu})\text{Cl}_2(\text{py})_3]$ (**1.21**) and related arylimido synthons;⁷⁵ these complexes are discussed in Section 4.4.

1.4.3.1 Sandwich compounds

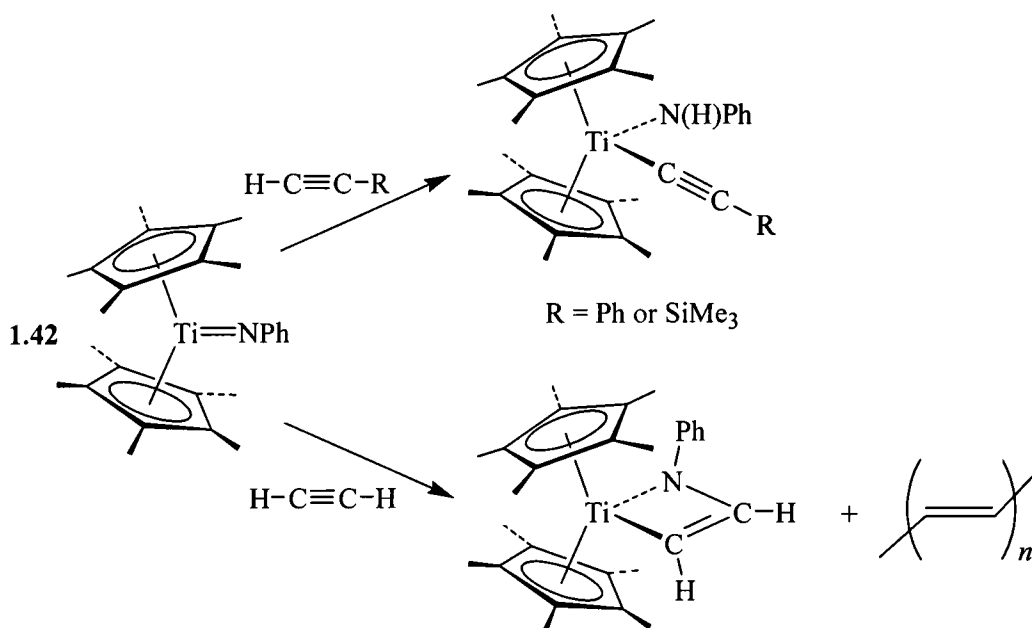
Reaction of two equivalents of sodium cyclopentadienide with **1.21** afforded the sandwich compound $[\text{Ti}(\eta\text{-C}_5\text{H}_5)_2(\text{N}^t\text{Bu})(\text{py})]$ (**1.41**).⁷⁶ Compound **1.41** undergoes reactions with MeSH to yield a bis(thiolate) complex and with H_2S to yield a bridging sulphide or thiol (Scheme 1.9).¹⁹ These reactions were the first reports of S-H bond activation by Group 4 imido complexes.



Scheme 1.9 Activation of S-H bonds by **1.41**

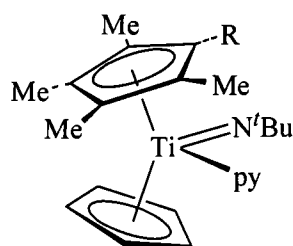
Attempts to synthesise bis(η^5 -pentamethylcyclopentadienyl) analogues of **1.41** via addition of a further equivalent of $\text{Li}[\text{C}_5\text{Me}_5]$ to a half-sandwich complex resulted in reduction of Ti^{IV} to Ti^{III} . However, Bergman and coworkers have found that reaction of $[\text{Ti}(\eta\text{-C}_5\text{Me}_5)_2(\eta^2\text{-C}_2\text{H}_4)]$ with PhN_3 affords $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)_2(\text{NPh})]$ (**1.42**).⁷⁷ Compound **1.42** activates the C-H bonds of phenyl- or trimethylsilylacetylene to yield anilido-acetylide complexes $[\text{Ti}(\eta\text{-C}_5\text{Me}_5)_2(\text{NHPH})(\text{C}\equiv\text{CR})]$ ($\text{R} = \text{Ph}$ or SiMe_3) and the metallacyclobutene products expected from $[2+2]$ cycloaddition to the imide are not observed. In contrast, **1.42**

reacts with acetylene to yield the azametallacycle $[\text{Ti}(\eta\text{-C}_5\text{Me}_5)\{\text{N}(\text{Ph})\text{C}(\text{H})=\text{CH}\}]$ *via* [2+2] cycloaddition. Reaction times greater than five minutes also lead to precipitation of polyacetylene. The preference for C-H activation over cycloaddition with bulkier substituents is probably related to steric interactions between imide and alkyl substituents (Scheme 1.10). Compound **1.42** also reacts with ethylene to generate a metallacycle *via* reversible [2+2] cycloaddition to the imide. The product was characterised at low temperature under an ethylene atmosphere.

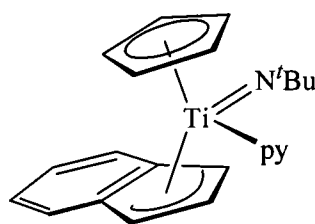


Scheme 1.10 Reactions of the sandwich compound **1.42** with alkynes

Mixed ring complexes of the type $[\text{Ti}(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_5\text{Me}_4\text{R})(\text{N}^t\text{Bu})(\text{py})]$ (**1.43**) have been formed from the reaction of $[\text{Ti}(\eta\text{-C}_5\text{Me}_4\text{R})(\text{N}^t\text{Bu})\text{Cl}(\text{py})]$ ($\text{R} = \text{Me}$ or Et) with sodium cyclopentadienide.⁷⁶ The η^5 -cyclopentadienyl, η^3 -indenyl mixed ring complex $[\text{Ti}(\eta^5\text{-C}_5\text{H}_5)(\eta^3\text{-C}_9\text{H}_7)(\text{N}^t\text{Bu})(\text{py})]$ (**1.44**) was prepared by an analogous route.⁷⁶

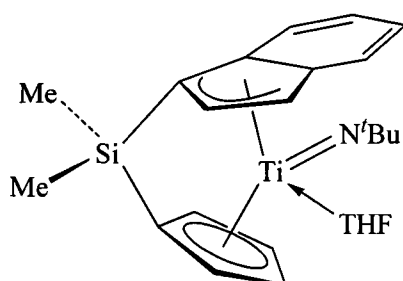


1.43

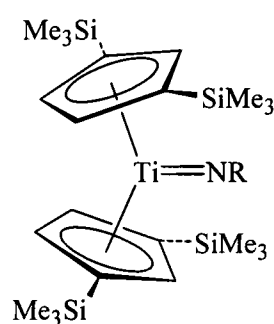


1.44

Recent studies by Chen and coworkers have shown that the chiral *ansa*-titanocene imido complex **1.45** is a catalyst for the syndiotactic polymerisation of methyl methacrylate in the presence of an aluminium activator.⁷⁸



1.45



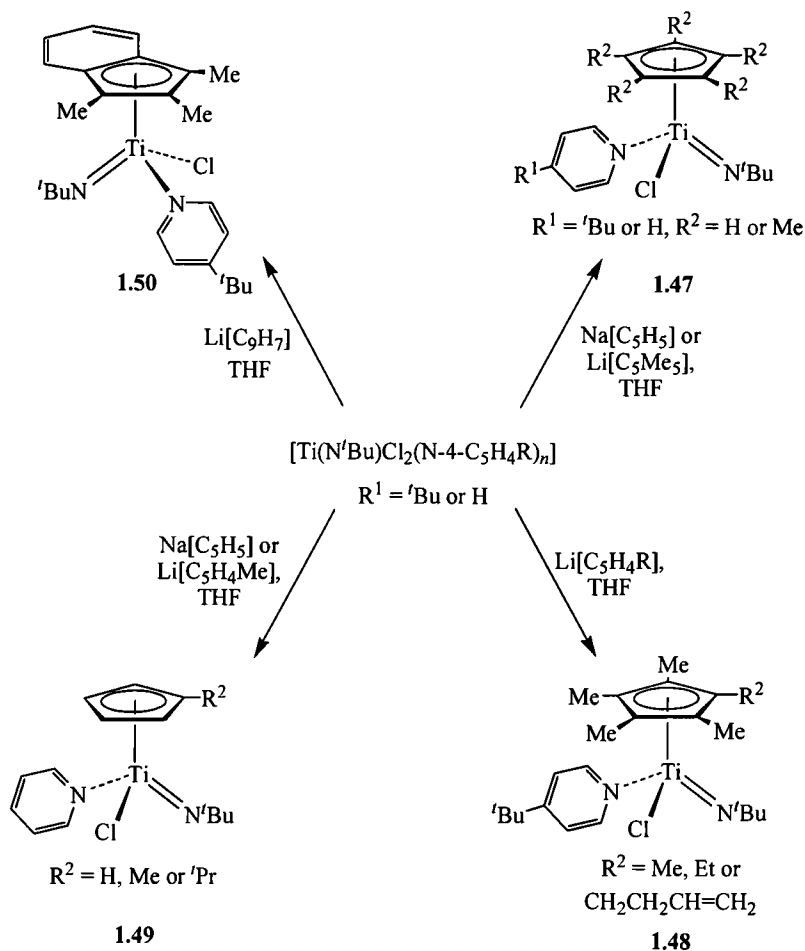
R = SiMe₃ (**1.46**) or
2,4,6-C₆H₂Me₃ (**1.47**)

Chirik and coworkers have prepared the sandwich titanium imido complex [Ti{ η -1,3-C₅H₃(SiMe₃)₂}₂(NR)] {R = SiMe₃ (**1.46**) or 2,4,6-C₆H₂Me₃ (**1.47**)} from reaction of a bridging dinitrogen compound of titanium with RN₃.⁷⁹ Exposure of **1.46** to 1 atm of CO afforded [Ti{ η -1,3-C₅H₃(SiMe₃)₂}₂(CO)₂] and Me₃SiNCO in near-quantitative yield. Nitrene group transfer to CO to yield isocyanate has been reported for complexes of iron, cobalt and nickel but this transformation was unknown for titanium. Complex **1.46** undergoes a [2+2] cycloaddition reaction with Me₃SiNCO to form an N,O-bound ureate complex.

1.4.3.2 Half sandwich compounds

Metathesis reactions of complexes of the type [Ti(N'Bu)Cl₂(4-N-C₅H₄R)_n] (*n* = 2 or 3) with sodium or lithium cyclopentadienides or indenides gave a range of half-sandwich cyclopentadienyl derivatives (Scheme 1.11).^{76,80} The indenyl derivative

$[\text{Ti}(\eta^5\text{-C}_9\text{H}_4\text{Me}_3)(\text{N}^t\text{Bu})\text{Cl}_2(\text{N-4-C}_5\text{H}_4^t\text{Bu})]$ (**1.50**) was also prepared by reaction of $[\text{Ti}(\text{N}^t\text{Bu})\text{Cl}_2(\text{N-4-C}_5\text{H}_4^t\text{Bu})_2]$ with lithium trimethylindenide.⁷⁶



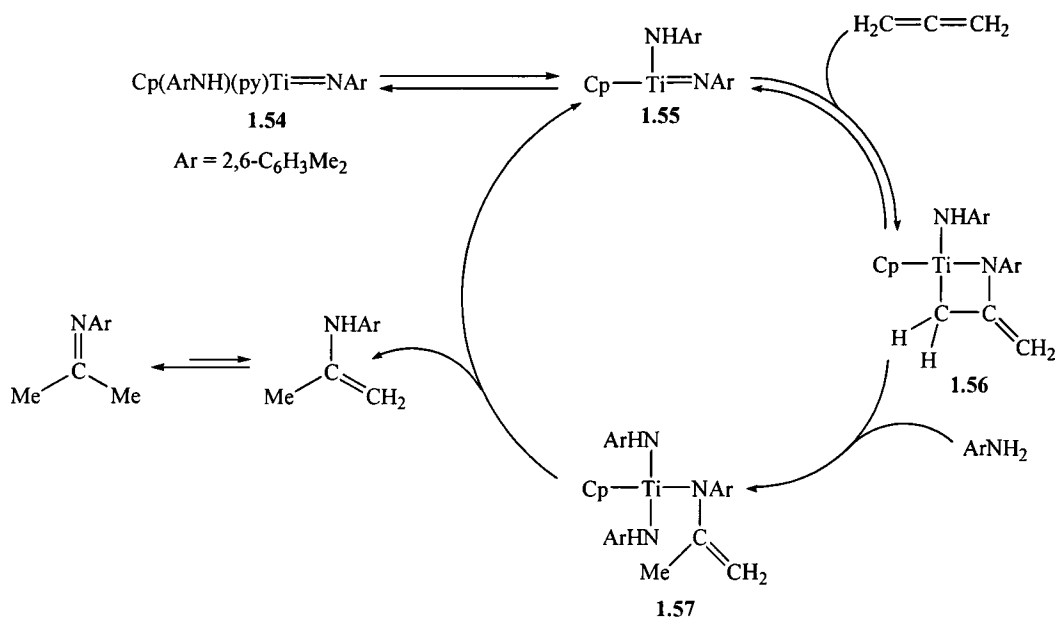
Scheme 1.11 Preparation of sandwich and half-sandwich titanium imido complexes

Jagirdar *et al.* have prepared the ionic half-sandwich complex $\text{Li}[\text{Ti}(\eta\text{-C}_5\text{Me}_5)(\text{N}^t\text{Bu})(\text{NH}^t\text{Bu})_2]$ (**1.51**) by reaction of $[\text{Ti}(\eta\text{-C}_5\text{Me}_5)\text{Cl}_3]$ with LiNH_2^tBu .⁸¹ Roesky and coworkers have prepared $[\text{Ti}(\eta\text{-C}_5\text{H}_4\text{Me})(\text{NPh})\text{Cl}(\text{py})]$ (**1.52**) by treatment of a bridging imido complex with trimethylstannyl fluoride in the presence of pyridine, although this compound was not isolated.⁸²

Both sandwich and half-sandwich titanium imido complexes have been proposed as important species in hydroamination catalysis with alkynes and allenes.^{83,84} Doye *et al.* have investigated the use of dimethyl titanocene (**1.53**) as a readily available catalyst for hydroamination.⁸³ Hydroamination of both symmetrical and

unsymmetrical alkynes has been accomplished, and for the unsymmetrical alkynes the regioselectivity of addition was particularly interesting, as it resulted in the anti-Markovnikov product.

Doye *et al.* suggested that **1.53** eliminates methane in the presence of an amine to generate the catalytically active titanium imido complex $[\text{Ti}(\eta\text{-C}_5\text{H}_5)_2(\text{NR})]$. However, mechanistic studies by Bergman and coworkers suggest that the active species arises from a cyclopentadienyl/amide ligand exchange reaction in the presence of an amine.⁸⁴ This transforms the bis(cyclopentadienyl) titanium precursors into mono(cyclopentadienyl) half-sandwich titanium(amido) complexes which can be trapped by pyridine (**1.54**). These amido complexes exhibit substantially higher reactivity than dimethyltitanocene. The proposed catalytic cycle for allene hydroamination is shown in Scheme 1.12.



Scheme 1.12 Proposed catalytic cycle for hydroamination of allene by $[\text{Cp}(\text{NHAr})\text{Ti}(\text{NAr})]$ (**1.55**)

Reversible pyridine dissociation from **1.54** generates the Lewis base-free complex **1.55**. Formal [2+2] cycloaddition with allene leads to an azametallacyclobutane (**1.56**) that is rapidly protonated by amine to generate tris(amido) titanium complex **1.57**. Elimination expels the enamine product (which tautomerises to the more thermodynamically stable imine) and regenerates the catalyst, **1.55**. Density Functional Theory studies have been performed by Bergman and Straub on the

mechanism of protonation of the titanacycle by the amine.⁸⁵ It has been shown that **1.54** can efficiently catalyse the regioselective hydroamination of substituted allenes and the reaction between 2,6-dimethylaniline and diphenylacetylene.⁸⁴

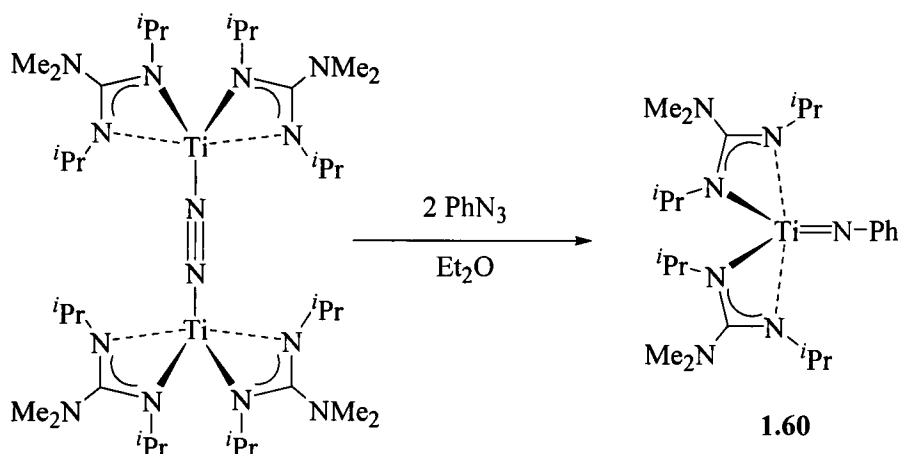
Regitz *et al.* have shown that $[\text{Ti}(\eta\text{-C}_5\text{H}_5)(\text{NR})\text{Cl}]_n$ (**1.58**, R = 'Bu, octyl, cyclopentyl, cyclohexyl, 1-adamantyl), formed from $[\text{Ti}(\eta\text{-C}_5\text{H}_5)\text{Cl}_3]$ in the presence of an amine, undergo cycloaddition reactions with phosphalkynes to yield azaphosphatitanacyclobutanes.⁸⁶ 1,2-Addition of an amine across the remaining C=P double bond followed, but selective cleavage of titanium from the heterocyclic system was not achieved. Cloke and Nixon have also published work in which a titanium imido complex is the proposed active species for phosphalkyne hydroamination.⁸⁷

1.4.3.3 Amidinate- and guanidinate-supported compounds

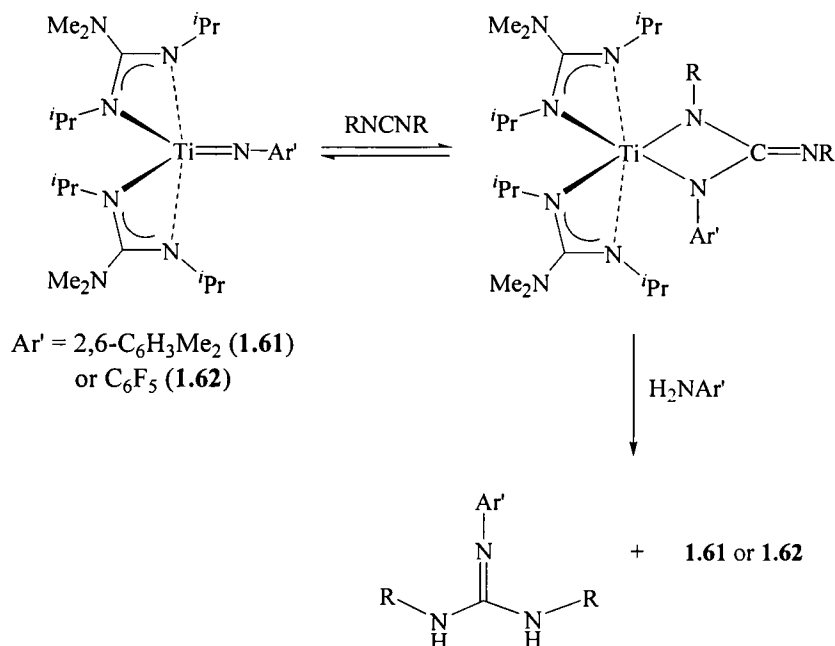
Compounds of the monoanionic N₂-donor amidinate and guanidinate ligands have been prepared. Amidinate-supported titanium imido complexes will be the main focus of this Thesis. An introduction to the amidinate ligand and work previously carried out in the Mountford group on Group 4 amidinate-imido compounds can be found in Section 2.2.5.⁸⁸⁻⁹⁰ Arnold and coworkers have also prepared the bis(amidinate)-supported titanium imido complex $[\text{Ti}(\text{N}^t\text{Bu})\{\text{PhC}(\text{NSiMe}_3)_2\}_2]$ (**1.59**) from the reaction of $[\text{Ti}\{\text{PhC}(\text{NSiMe}_3)_2\}_2\text{Me}_2]$ with *tert*-butylamine.⁹¹

Guanidinate ligands are closely related to amidinates, differing only in that they contain an amino (R₂N) substituent on the ligand's central carbon. It is proposed that use of guanidates results in complexes where the metal centre is more electron rich than for the corresponding amidinate. There is a contribution to bonding from a resonance structure where lone pair donation from the R₂N group places a formal negative charge on the metal.⁹² However, the electronic properties of the other metal-bound ligands may also influence the bonding structure of the guanidinate.

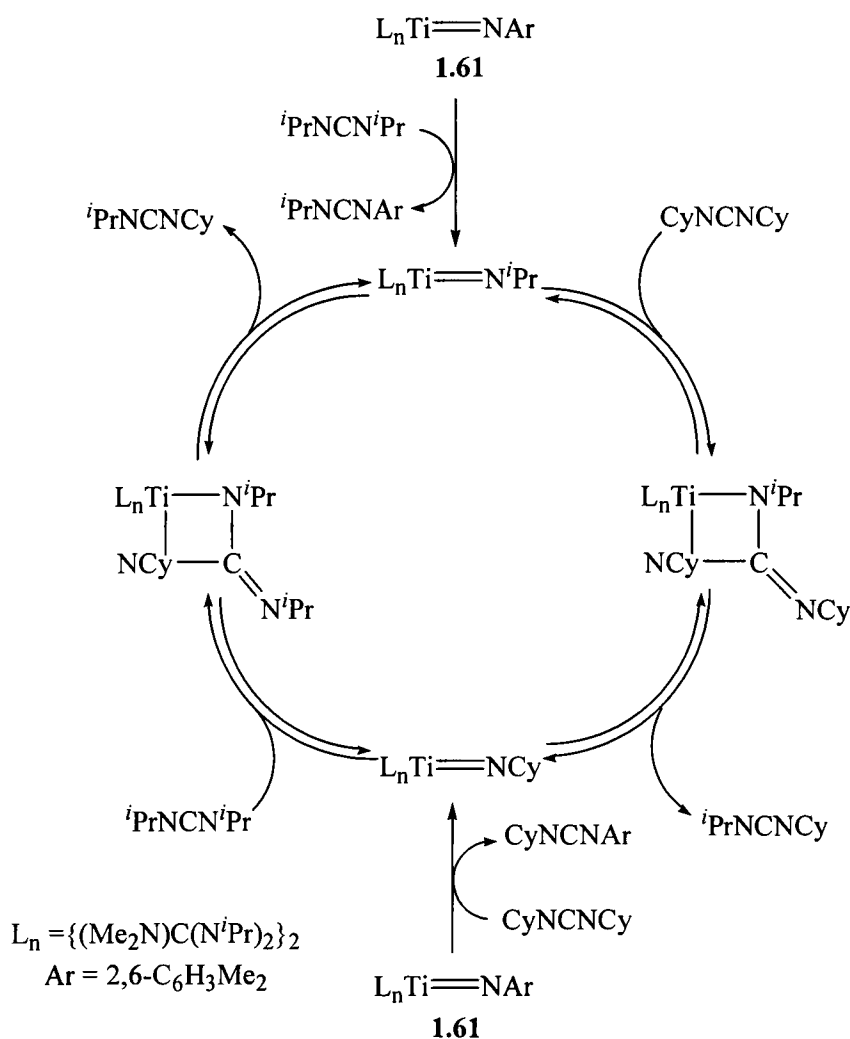
Bergman and Arnold *et al.* have prepared the guanidinate-supported titanium imido complex **1.60** by treatment of a dinitrogen complex with phenyl azide (Equation 1.8).⁹²

**Equation 1.8**

Richeson and coworkers have recently shown that the closely related compound $[\text{Ti}(\text{N}-2,6\text{-C}_6\text{H}_3\text{Me}_2)\{(\text{Me}_2\text{N})\text{C}(\text{N}^i\text{Pr}_2)\}_2]$ (**1.61**) is a catalyst for the hydroamination of alkynes in the presence of 2,6-dimethylphenylaniline, [2+2] cycloaddition of the alkyne to the $\text{Ti}=\text{NR}$ bond is the critical step in this type of catalysis.⁹³ The selectivity of hydroamination was found to depend on the choice of alkyne substrate, phenyl acetylene undergoes anti-Markovnikov addition, while 1-hexyne yields Markovnikov addition products.

**Scheme 1.13** Catalytic guanylation of amines with carbodiimide

Compound **1.61** and the corresponding perfluorophenylimido derivative **1.62** have also been used as catalysts for the first transition metal catalysed guanylation of amines with carbodiimides. Compounds **1.61** and **1.62** are also capable of facilitating a transamination reaction between guanidine and amines, leading to an "aryl-guanidine reconstruction".⁹⁴ A proposed mechanism for guanidine formation is shown in Scheme 1.13 and involves [2+2] cycloaddition of a carbodiimide to the Ti=NR bond. A proton transfer reaction between an aromatic amine and the metal-bound dianionic guanidate ligand releases guanidine and reforms the titanium imido bond.⁹⁴



Scheme 1.14 Catalytic carbodiimide metathesis by **1.61**

Compound **1.61** catalyses C=N bond metathesis reactions of carbodiimides *via* a similar mechanism (Scheme 1.14).⁹⁵ In the presence of a catalytic amount of **1.61**

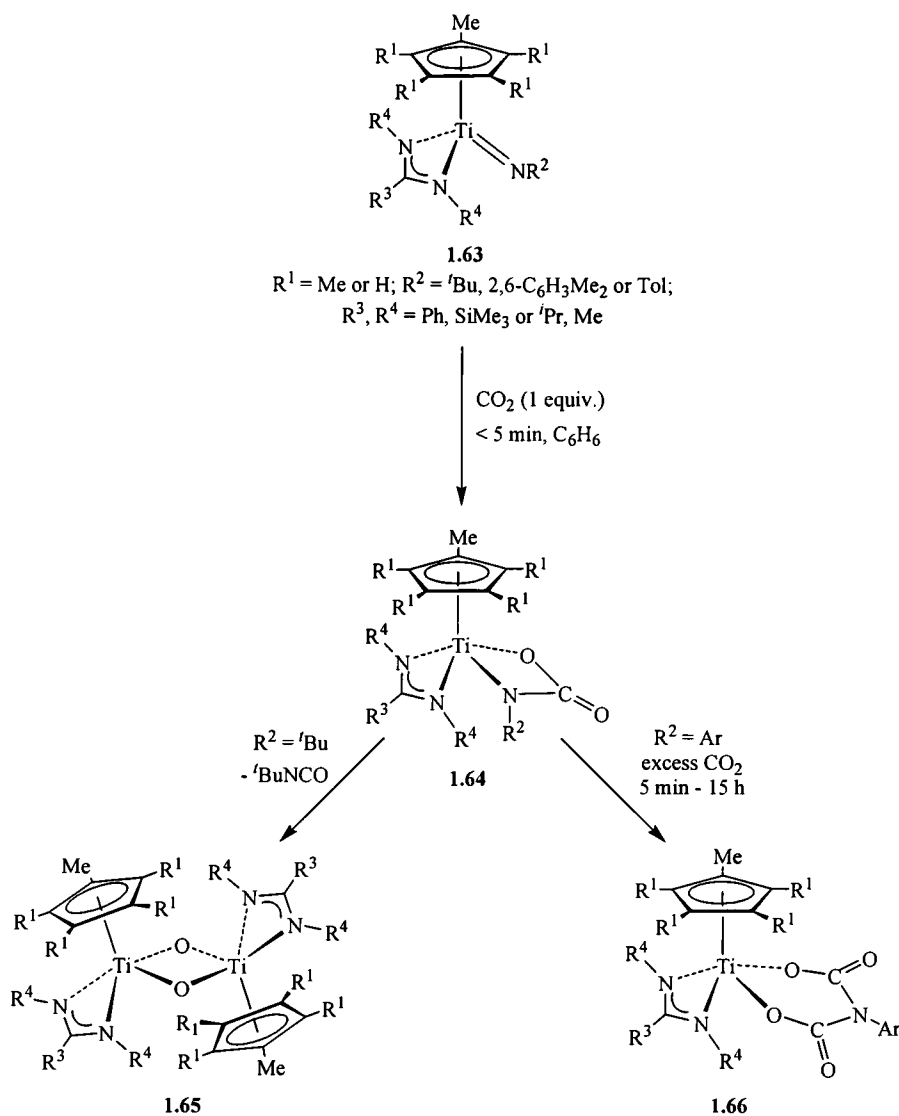
metathetical exchange occurs between $^i\text{PrNCN}^i\text{Pr}$ and CyNCNCy to yield $^i\text{PrNCNCy}$. The side products ArNCN^iPr and ArNCNCy ($\text{Ar} = 2,6\text{-C}_6\text{H}_3\text{Me}_2$) are also observed and arise from exchange of the carbodiimides with the imido group of the catalyst.

1.4.3.4 Cyclopentadienyl-amidinate compounds

Cyclopentadienyl ligands have been used in conjunction with amidinate ligands to support titanium imido complexes; the combined ligand set will be discussed in Section 3.2. The cyclopentadienyl-amidinate supporting environment provides a balance of steric protection and electron donation conducive to promoting reactivity at the $\text{Ti}=\text{NR}$ bond.⁹⁶ Cyclopentadienyl-amidinate complexes of the type $[\text{Ti}(\eta\text{-C}_5\text{R}^1_4\text{Me})(\text{NR}^2)\{\text{R}^3\text{C}(\text{NR}^4)_2\}]$ (**1.63**) display reactivity towards a range of polar substrates; the outcome of such reactions is often critically dependent upon the imido substituent with *tert*-butyl imides behaving differently from aryl imides.^{80,96} The reactivity of cyclopentadienyl complexes towards CO_2 will be discussed in more detail in Chapter 3 and is summarised in Scheme 1.15. CO_2 undergoes [2+2] cycloaddition to the $\text{Ti}=\text{NR}$ bond to yield carbamate species of the type **1.64**. Where $\text{R} = ^i\text{Bu}$ these species undergo retrocyclisation and loss of $^i\text{BuNCO}$ to yield bridging oxo dimers (**1.65**). Where $\text{R} = \text{Ar}$, the carbamate undergoes insertion of a second molecule of CO_2 to yield aryldicarboxylate complexes of the type **1.66**.

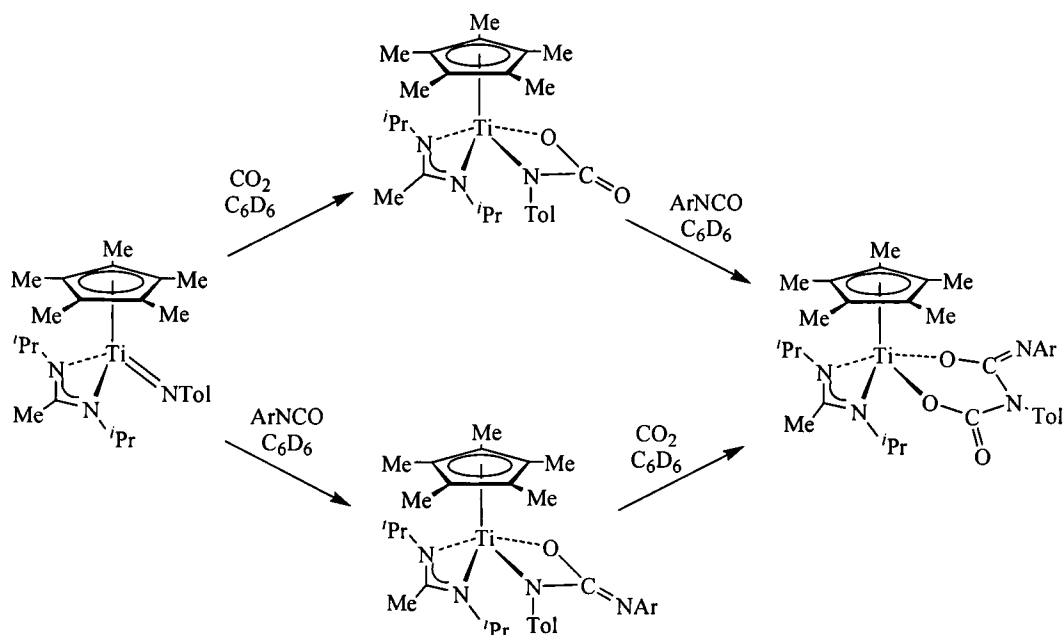
Cyclopentadienyl amidinate-imido complexes display parallel reactivity with isocyanates.⁸⁰ Reactions of $[\text{Ti}(\text{N}^i\text{Bu})(\eta\text{-C}_5\text{Me}_5)\{\text{MeC}(\text{N}^i\text{Pr})_2\}]$ with RNCO ($\text{R} = ^i\text{Bu}$ or aryl) take several days and give the dimeric oxo product $[\text{Ti}_2(\eta\text{-C}_5\text{Me}_5)\{\text{MeC}(\text{N}^i\text{Pr})_2\}_2(\mu\text{-O})_2]$ (**1.65**) with concomitant formation of the carbodiimides $^i\text{BuNCNR}$. NMR spectroscopic evidence supports a proposed mechanism for the reaction proceeding *via* N,O-bound ureate intermediates. In contrast, reaction of the aryl imido complexes $[\text{Ti}(\text{NAr})(\eta\text{-C}_5\text{Me}_5)\{\text{MeC}(\text{N}^i\text{Pr})_2\}]$ ($\text{R} = 2,6\text{-C}_6\text{H}_3\text{Me}_2$ or Tol) with ArNCO lead to formation of crystallographically characterised N,O-bound ureates $[\text{Ti}\{\text{N}(\text{Ar})\text{C}(\text{NAr}')\text{O}\}(\eta\text{-C}_5\text{Me}_5)\{\text{MeC}(\text{N}^i\text{Pr})_2\}]$ within hours. Addition of TolNCO to the ureates $[\text{Ti}\{\text{N}(\text{R})\text{C}(\text{NTol})\text{O}\}(\eta\text{-C}_5\text{Me}_5)\{\text{MeC}(\text{N}^i\text{Pr})_2\}]$ ($\text{R} = \text{Tol}$, $4\text{-C}_6\text{H}_4\text{NMe}_2$ or $4\text{-C}_6\text{H}_4\text{CF}_3$) yielded the products

$[\text{Ti}\{\text{OC}(\text{NTol})\text{N}(\text{R})\text{C}(\text{NTol})\text{O}\}\{\eta\text{-C}_5\text{Me}_5\}\{\text{MeC}(\text{N}^i\text{Pr})_2\}]$ *via* insertion of TolNCO into the Ti-NR bond of the N,O-bound ureate.



Scheme 1.15 Reactions of cyclopentadienyl amidinate-imido complexes with CO_2 .

It has been shown by NMR experiments that it is possible to perform cross-coupling reactions of CO_2 and isocyanates using the arylimido systems to yield mixed addition products (Scheme 1.16).⁸⁰



Scheme 1.16 Cross-coupling reactions of CO_2 and isocyanates with cyclopentadienyl-amidinate complexes

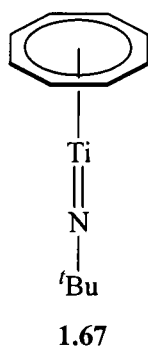
Other substrates that have been explored and undergo similar reactions include CS_2 , COS , and isothiocyanates.⁸⁰ Cyclopentadienyl-amidinate complexes also undergo cycloaddition reactions with mono-unsaturated substrates such as nitrosobenzene, benzophenone and benzaldehyde.⁸⁰

Other monoanionic N-donor ligands that have been used to support titanium imido compounds include nacnac⁹⁷ and pyrazolates.⁹⁸

1.4.4 Complexes with dianionic ligands

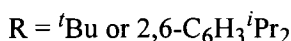
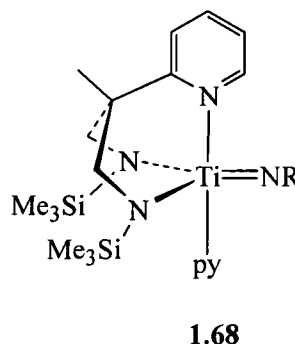
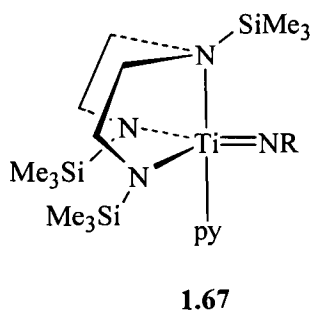
1.4.4.1 Cyclooctatetraene-supported compounds

An unusual 'one-legged piano stool' complex $[\text{Ti}(\text{N}^t\text{Bu})(\eta\text{-C}_8\text{H}_8)]$ (**1.67**) has been synthesised from the reaction of $[\text{Ti}(\text{N}^t\text{Bu})\text{Cl}_2(\text{py})_3]$ (**1.21**) with $\text{K}_2[\text{C}_8\text{H}_8]$,⁹⁹ this geometry is unique in early transition metal chemistry. Reactivity studies on this and related compounds are currently underway, preliminary results suggest that **1.67** undergoes stoichiometric coupling reactions with CO_2 , CS_2 , isocyanates and phosphalkynes.¹⁰⁰



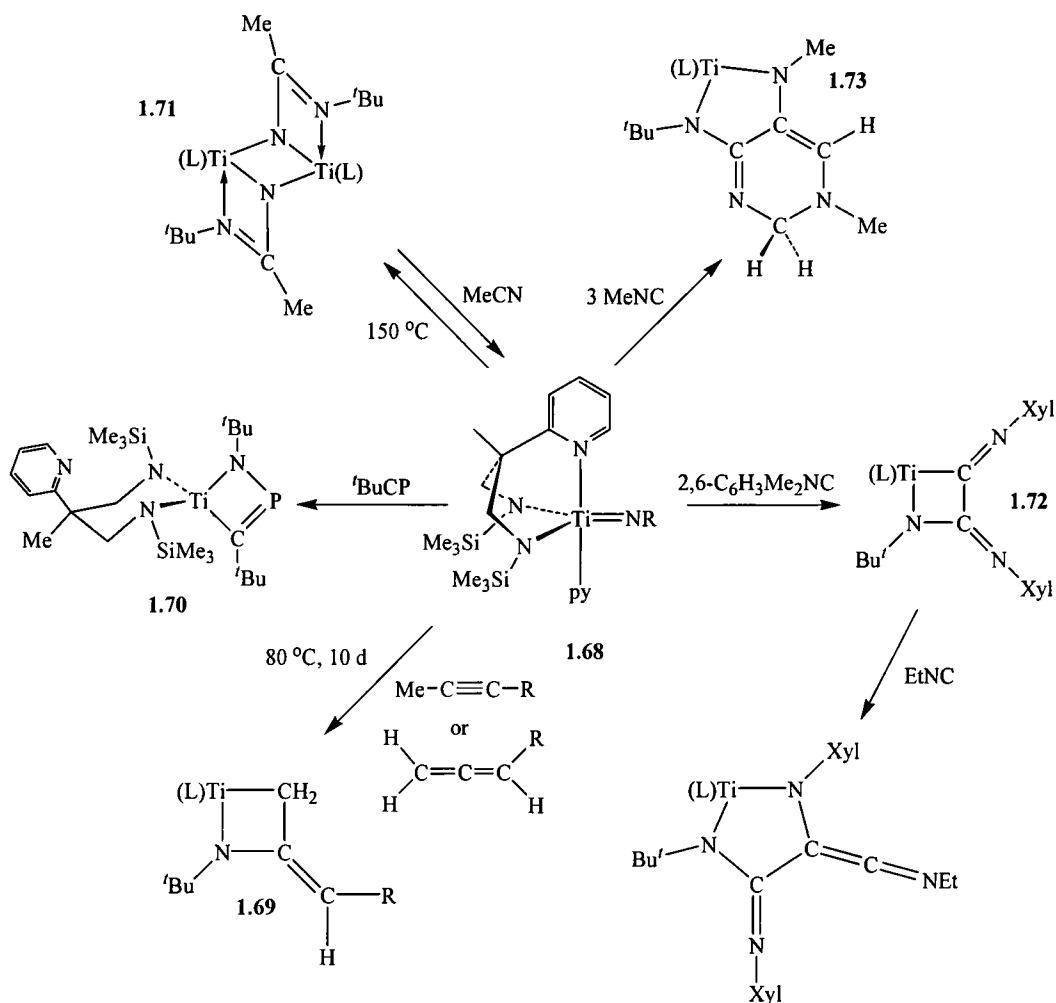
1.4.4.2 Compounds with N₂N donor ligands

Imido complexes supported by dianionic diamido ligands containing an additional neutral donor have been prepared during the collaborative work of Mountford *et al.* with Cloke¹⁰¹ and Gade.^{21,102} The resulting diamido amine (**1.67**) and diamido pyridine (**1.68**) complexes are shown below and were prepared by the reaction of [Ti(NR)Cl₂(py)₃] (**1.21**) with the corresponding lithiated diamido ligand.



Compound **1.68** undergoes reactions with a range of substrates at the Ti=NR bond (Scheme 1.17). Heating **1.68** in neat 2-butyne or 1-phenylpropyne at 80 °C led to complexes [Ti(N₂N_{py}){CH₂C(=CHR)N^{*t*}Bu}] [R = H or Ph, N₂N_{py} = {MeC(2-C₅H₄N)(CH₂NSiMe₃)₂}] (**1.69**).¹⁰³ Interestingly, reaction with 1-methylallene or 1-phenylallene yielded the same products. This suggests that reaction with alkynes proceeds *via* addition of the methyl group of the acetylene to the Ti=NR bond to generate an R(H)N-amido ligand and a Ti-alkyl unit. In the proposed second step, H-atom transfer to an acetylene carbon atom leads to the reformation of the imido unit and a η²-bonded allene ligand. These fragments couple to give the four-membered azatitanacycle present in **1.69**, which has been crystallographically characterised. These reactions are the first examples of such

reactions of imido complexes where activation of sp^3 C-H bonds occurs in apparent preference to forming the simple cyclisation products.

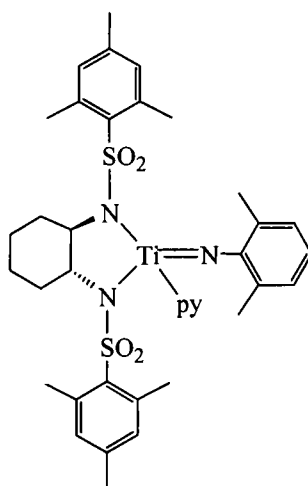


Scheme 1.17 Reactions of the diamido-pyridine-supported titanium-imido derivative **1.68** ($\text{L} = \text{N}_2\text{Npy}$, $\text{R} = \text{Me}$ or Ph)

Reaction with $^t\text{BuCP}$ yields $[\text{Ti}(\text{N}_2\text{Npy})\{\text{N}^t\text{BuPC}(\text{Me}_3\text{Si})_2\}]$ (**1.70**).¹⁰⁴ However, reaction with acetonitrile leads to the dimeric product $[\text{Ti}(\text{N}_2\text{Npy})(\mu\text{-NC}(\text{Me})\text{N}^t\text{Bu})_2]$ (**1.71**), the hemi-labile pyridyl "arm" of the ligand decoordinates from titanium to accommodate the additional bulky *tert*-butyl group. The differing polarity pattern of $\text{RC}\equiv\text{P}$ relative to the $\text{RC}\equiv\text{N}$ triple bond indicates a different regioselectivity of cycloaddition generating products containing NPC and NCN units respectively. Reactivity towards isocyanides was found to be dependent upon the steric demands of the substrate and also resulted in decoordination of the pyridyl arm.¹⁰³⁻¹⁰⁵ Reaction with 2,6-dimethylphenyl

isocyanide gives the product of clean addition across the Ti=NR bond, namely $[\text{Ti}(\text{N}_2\text{N}_{\text{py}})\{\text{N}(\text{tBu})\text{C}(\text{N}-2,6\text{-C}_6\text{H}_3\text{Me}_2)\}]$ (**1.72**).¹⁰⁶ While **1.72** does not react further with isocyanide, it is found to be reactive towards less sterically demanding isocyanides such as EtNC. With MeNC compound **1.67** reacts to give a metal-bound diaminodihydropyrimidine derivative (**1.73**).¹⁰⁶ Similar results were obtained with EtNC, *n*-BuNC and Ph₂CH₂NC. The diamido-amine complex **1.68** also reacts with phosphalkynes to yield [2+2] cycloaddition products.⁵⁷

Compound **1.68** and the related 2,6-di-*iso*-propylphenylimido derivative $[\text{Ti}(\text{N}-2,6\text{-C}_6\text{H}_3\text{tPr}_2)\{\text{MeC}(2\text{-C}_5\text{H}_4\text{N})(\text{CH}_2\text{NSiMe}_3)_2\}]$ react with phenylacetylene and tolylacetylene to give the products $[\text{Ti}\{\text{N}(\text{tBu})\text{CH}=\text{CR}\}(\text{N}_2\text{N}_{\text{py}})]$ and $[\text{Ti}\{\text{N}(2,6\text{-C}_6\text{H}_3\text{tPr}_2)\text{CH}=\text{CR}\}(\text{N}_2\text{N}_{\text{py}})]$ respectively (R = Ph or Tol).¹⁰⁷ The complex $[\text{Ti}\{\text{N}(2,6\text{-C}_6\text{H}_3\text{tPr}_2)\text{CH}=\text{C}(\text{Tol})\}\{\text{MeC}(2\text{-C}_5\text{H}_4\text{N})(\text{CH}_2\text{NSiMe}_3)_2\}]$ is the first example of a structurally characterised imido-acetylene [2+2] cycloaddition product that corresponds to the key intermediate in the anti-Markovnikov addition of a primary amine to a terminal acetylene. When $[\text{Ti}\{\text{N}(\text{tBu})\text{CH}=\text{CPh}\}(\text{N}_2\text{N}_{\text{py}})]$ (generated *in situ* by reaction of **1.68** with phenylacetylene) was reacted with *tert*-butylamine, complex **1.68** was regenerated and *trans*-cinnamyl(*tert*-butyl)amine was released. Reaction of *tert*-butylamine with phenylacetylene in the presence of 20 mol% of **1.68** lead to several reaction cycles of product formation.



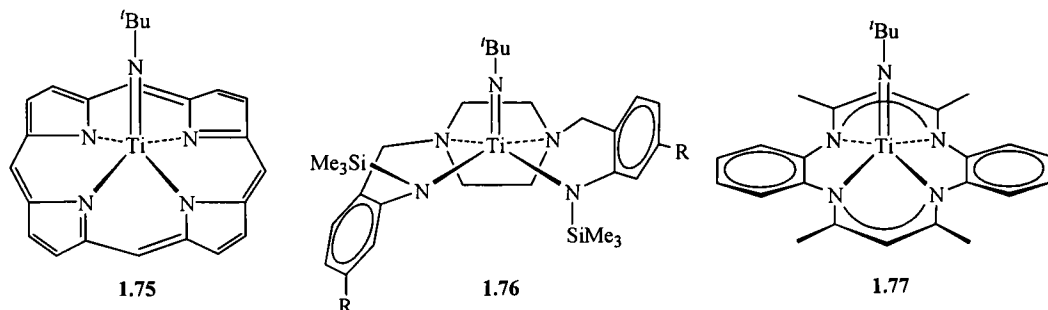
1.74

Bergman and coworkers have synthesised a bis(sulphonamido) supported titanium imido complex with a pyridine donor (**1.74**).¹⁰⁸ Compound **1.74** is a catalyst for

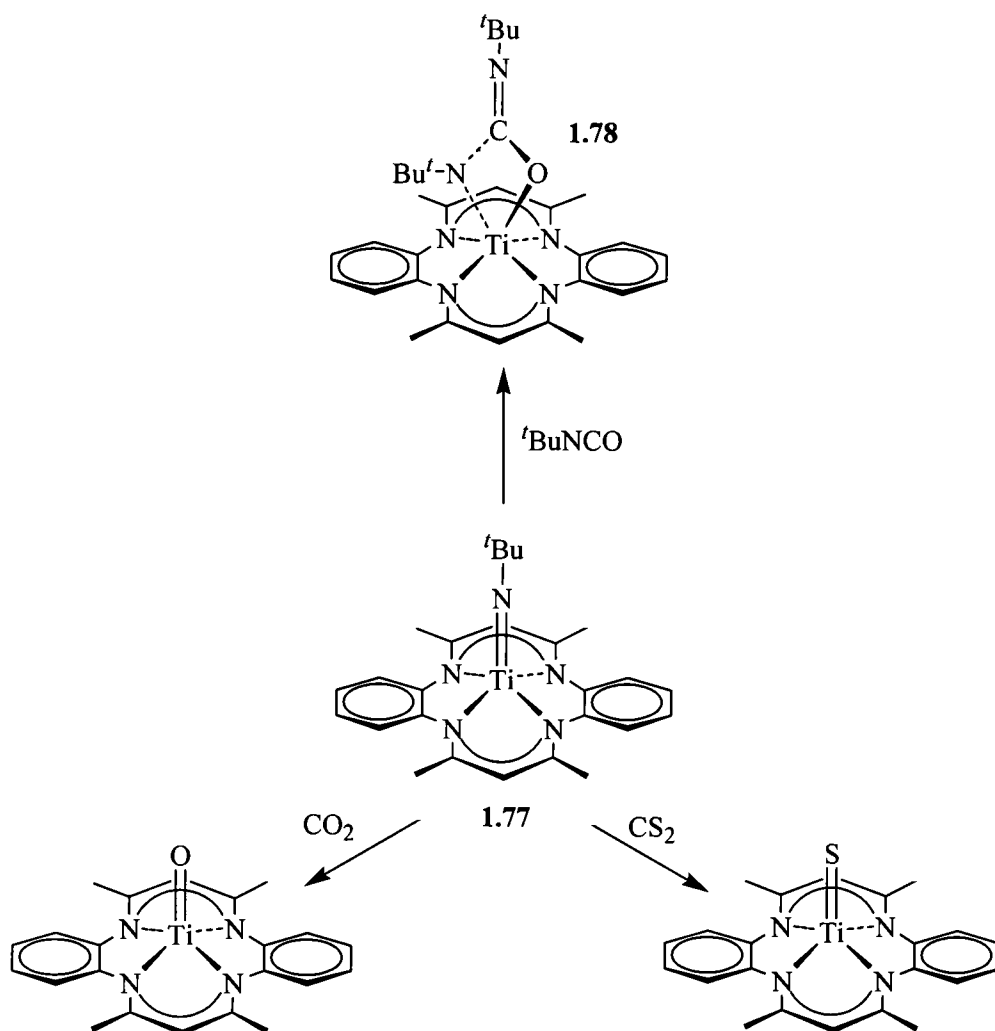
the intramolecular hydroamination of alkynes and can convert aminoallene into a cyclic imine.

1.4.4.3 Compounds with N₄ donor ligands

A range of titanium imido complexes with dianionic tetradentate nitrogen donor ligands has also been prepared. Woo *et al.* have synthesised imido complexes supported by tetratolylporphyrin ligands (**1.75**)⁵¹ and Mountford *et al.* have used piperazine-based diamido-diamine ligands (**1.76**).¹⁰⁹



Mountford and coworkers have also investigated dibenzotetraazaannulene-supported complexes of the type **1.77**. These were prepared by reactions of the dilithiated tetraazaannulene with [Ti(NR)Cl₂(py)₃] (Scheme 1.18).¹¹⁰ Reaction of **1.77** with ^tBuNCO led to formation of the N,O-bound ureate complex [Ti{N(^tBu)C(N^tBu)O}(Me₄taa)] (**1.78**, Me₄taa = tetramethyldibenzo tetraazaannulene). However, reaction of the corresponding aryl imides with RNCO gave the N,N-bound ureates [Ti{N(Ar)C(O)N(R)}(Me₄taa)] (**1.79**).¹¹¹ It has been shown that [Ti{N(Ph)C(O)N(Tol)}(Me₄taa)] reacts with an excess of PhNCO over 5 days to give near-quantitative conversion to the N,N-diphenylureato complex [Ti{N(Ph)C(O)N(Ph)}(Me₄taa)] with displacement of tolylisocyanate. NMR tube crossover experiments suggest that this reaction proceeds *via* an associative mechanism through a biuret-type complex. Reaction of **1.77** with CO₂ or H₂S resulted in terminal oxo or sulfido complexes.

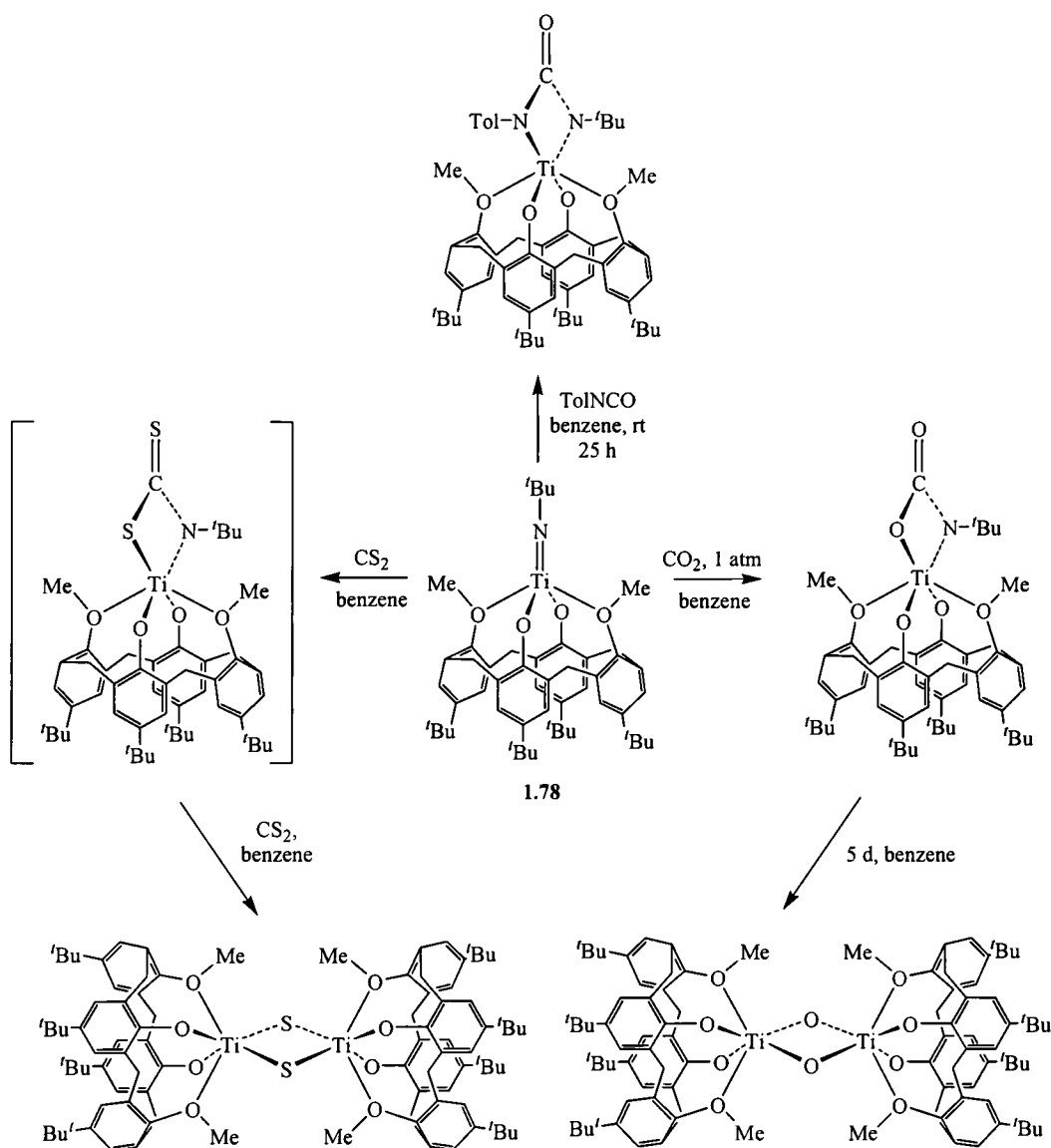


Scheme 1.18 Reactions of a dibenzotetraazamacrocyle-supported titanium imido complex

1.4.4.4 Compounds with O₄ donor ligands

The synthons $[\text{Ti}(\text{N}^t\text{Bu})\text{Cl}_2(\text{py})_3]$ (**1.21**) and $[\text{Ti}(\text{NR})(\text{NHMe}_2)_2\text{Cl}_2]$ (**1.26**) have been used to prepare calixarene-supported titanium imido complexes by reaction with the lithium or sodium salt of the calixarene in benzene.¹¹² Some reactions of the *tert*-butyl derivative $[\text{Ti}(\text{N}^t\text{Bu})(\text{Me}_2\text{calix})]$ (**1.78**) are shown in Scheme 1.19. The reaction of **1.78** with CO₂ led to the carbamate complex $[\text{Ti}\{\text{N}^t\text{BuC}(\text{O})\text{O}\}(\text{Me}_2\text{calix})]$, which undergoes extrusion of *tert*-butyl isocyanate to yield the dimeric oxo complex $[\text{Ti}_2(\mu\text{-O})_2(\text{Me}_2\text{calix})_2]$ (Scheme 1.19). The corresponding reaction of **1.78** with CS₂ was significantly slower and gave the bridging sulfido compound $[\text{Ti}_2(\mu\text{-S})_2(\text{Me}_2\text{calix})_2]$, it is proposed that this reaction proceeds *via* an intermediate thiocarbamate complex but this was not

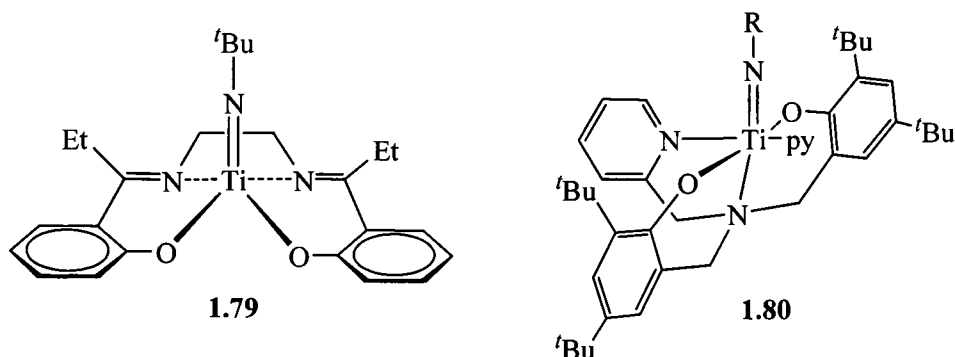
observed. Reaction with tolyl isocyanate gave a stable N,N-bound ureate derivative.



Scheme 1.19 Reactions of a calixarene-supported titanium imido complex

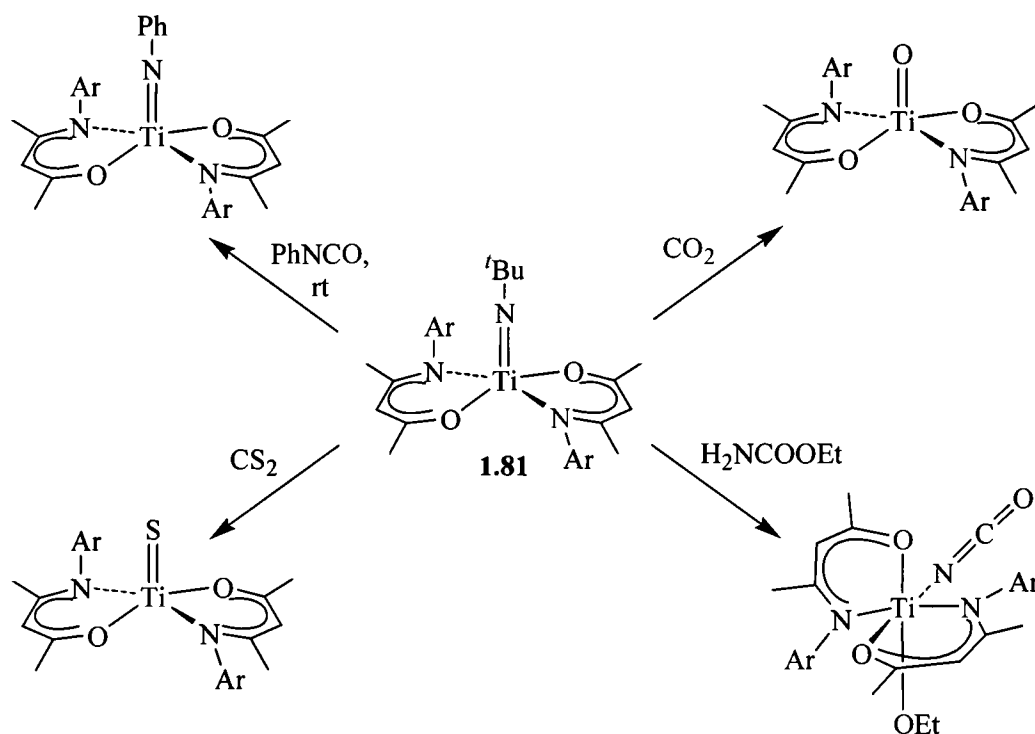
1.4.4.5 Compounds with N_2O_2 donor ligands

Related complexes containing tetradentate, dianionic Schiff base ligands have also been synthesised (**1.79**). In these complexes the oxygen donors are dianionic and the nitrogen donors are neutral.¹¹³



More recent work from the Mountford group has involved use of diaminobis(phenolate) supporting ligands to yield complexes of the type **1.80** ($R = t\text{Bu}$ or $2,6\text{-C}_6\text{H}_3\text{Me}_2$).¹¹⁴ Compound **1.80** reacts with CO_2 to form a bridging oxo complex with extrusion of the corresponding isocyanate.

Huang and coworkers have recently reported titanium imido compounds in which the N_2O_2 -supporting environment is comprised of two bidentate ketiminate ligands (**1.81**).¹¹⁵ Compound **1.81** undergoes imido ligand exchange with PhNCO to yield the phenyl imido derivative (Scheme 1.20).



Scheme 1.20 Reactions of the ketiminate-supported titanium imido compound **1.81**

The corresponding terminal oxo compound was obtained by heating **1.81** or by reaction with CO_2 . Reaction with CS_2 yielded the terminal sulphido compound.

Heating **1.81** with an equivalent of urethane produced a titanium isocyanate derivative.

1.5 Summary and objectives

It has been shown that titanium imido complexes undergo stoichiometric and catalytic coupling reactions with a range of small molecules. The aim of this Thesis is to further probe the synthesis and reactivity of titanium imido complexes using amidinate supporting ligands which will be introduced in the following Chapter.

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Chapter 2

Pendant Arm Functionalised Titanium Amidinate- Imido Chloride Compounds

2.1 Overview

Work previously carried out in the Mountford group has shown that amidinates are useful supporting ligands in the synthesis of new Group 4 imido compounds. This Chapter begins by introducing the amidinate ligand and examining recent developments in the chemistry of pendant arm functionalised amidinate complexes. The synthesis and characterisation of new titanium amidinate-imido compounds supported by pendant arm functionalised amidinate ligands is described. Some of this work has already been published.^{1,2}

2.2 Introduction

This Section briefly introduces the amidinate ligand and summarises its bonding properties. For a description of work on transition metal amidinate complexes up to 1994, the reader is directed towards some comprehensive reviews.^{3,4} The remainder of the Section will focus on work involving functionalised amidinates with a particular emphasis on recent work using pendant arm amidinate ligands. Some work previously carried out in the Mountford group on Group 4 imido complexes using amidinate supporting ligands is discussed.

2.2.1 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, ranging from early metals in high oxidation states to later metals in lower oxidation states. While the related allyl system often bonds to metals using its π -system, the amidine, like carboxylic acids, bonds through the heteroatom lone pairs. This gives rise to several coordination possibilities.

Amidines were first synthesised by Gerhardt⁵ in 1858 by the reaction of aniline with N-phenylbenzimidyl chloride, and are named after the acid or amide obtained by hydrolysis. Thus, when $R^1 = \text{Me}$, the compound is an acetamidine and when $R^1 = \text{C}_6\text{H}_5$ a benzamidine (Figure 2.1). Amidines act as monodentate, two-electron donors *via* the more basic and less sterically hindered imino lone pair, to form simple adducts such as $[\text{CoCl}_2(\text{AmH})_2]$ and $[\text{PdCl}_2(\text{AmH})_2]$, where $\text{AmH} =$ amidine.

If the R^4 group is displaced, the formally monoanionic amidinate group, $\{R^1C(NR^2)(NR^3)\}$, is formed. This is isoelectronic with the allyl and carboxylato ligands.

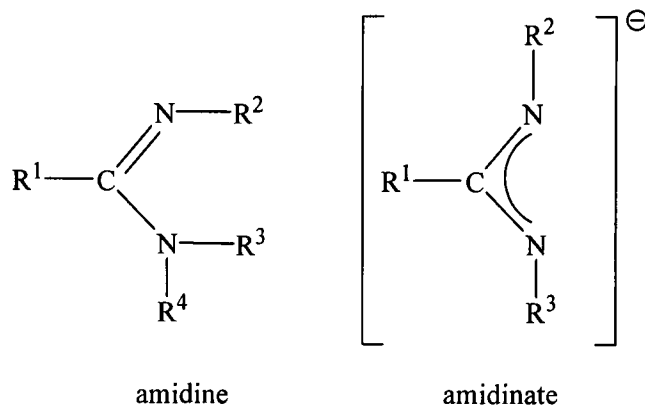


Figure 2.1 The amidine and amidinate ligands

Amidates are hard, three electron donors,⁶ and can support complexes with electron-deficient metal centres, allowing the isolation of cationic Lewis acidic compounds. In recent years, amidinate ligands have been the focus of much attention as alternatives to cyclopentadienyl ligands in the development of new "post-metallocene" catalysts.⁷⁻¹³ The steric and electronic characteristics of amidinate ligands may be tuned by the variation of the substituents R^1 , R^2 and R^3 .

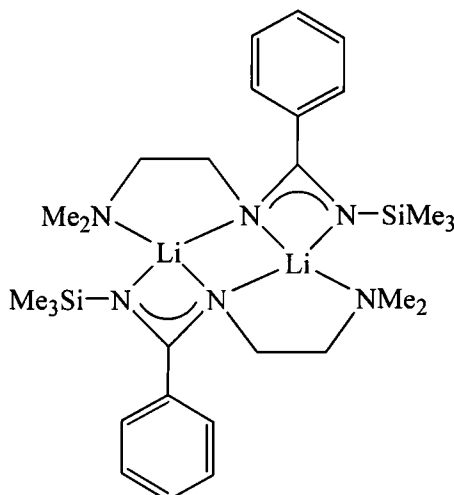
Amidinate ligands can adopt a wide variety of possible binding modes. They most commonly bind in a κ^2 (N,N-bidentate) manner, although bridging, allylic and cluster-capping binding modes have also been observed.³ The steric properties of the amidinate substituents can greatly influence the coordination mode.^{14,15}

2.2.2 Functionalised amidinate ligands

Much of the recent work in the development of transition metal amidinate chemistry has involved the use of new amidinato ligands designed to possess finely tuned steric and electronic properties. These include amidinates with bulky substituents,¹⁶⁻²² asymmetric and chiral substituents²³⁻²⁶ and tethered bis(amidinate) systems.²⁷⁻³¹ While a complete survey of this work lies outside the scope of this Thesis, the following Section highlights some recent advances in the chemistry of amidinates with pendant donor groups.

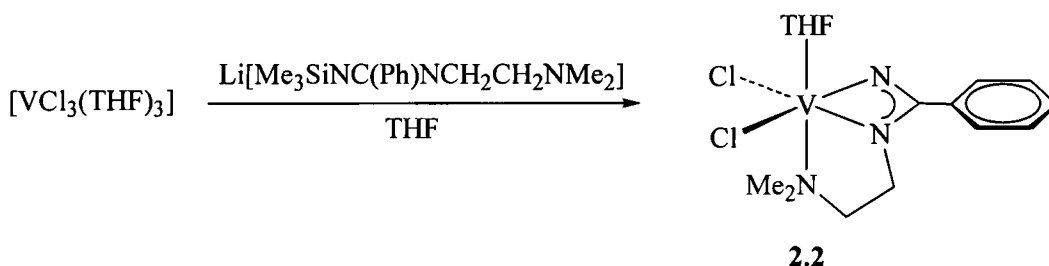
2.2.2.1 Pendant arm functionalised amidinate ligands

The first amidinate ligand with a pendant donor functionality, $\text{Me}_3\text{SiNC(Ph)NCH}_2\text{CH}_2\text{NMe}_2$, was prepared by Hessen and coworkers in 1998.³² The lithium salt of this ligand (**2.1**) has recently been crystallographically characterised and found to be dimeric.³³ The coordination around the lithium atoms is distorted tetrahedral, with each lithium bonding to two nitrogen atoms of an amidinate fragment in one ligand and to two nitrogen atoms of the other ligand.



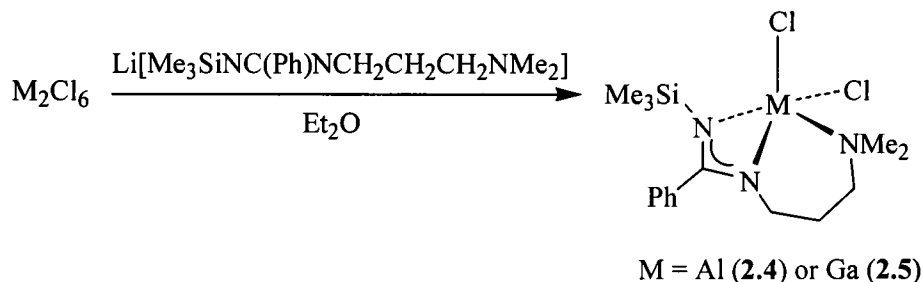
2.1

Reaction of **2.1** with $[\text{VCl}_3(\text{THF})_3]$ produces the V^{III} monoamidinate dichloride complex **2.2** (Equation 2.1). The pendant arm amidinate ligand adopts a facial coordination mode, with distorted octahedral coordination around vanadium. This is somewhat surprising, as it necessitates strong nonplanarity of the dimethylaminoethyl-substituted amidinate nitrogen. Compound **2.2** is an active catalyst for the polymerisation of ethylene in the presence of AlEt_2Cl as cocatalyst, and has been found to be significantly more active than the non-pendant arm amidinate catalyst $[\text{V}\{\text{PhC}(\text{NSiMe}_3)_2\}\text{Cl}_2(\text{THF})]_2$.³²



Equation 2.1

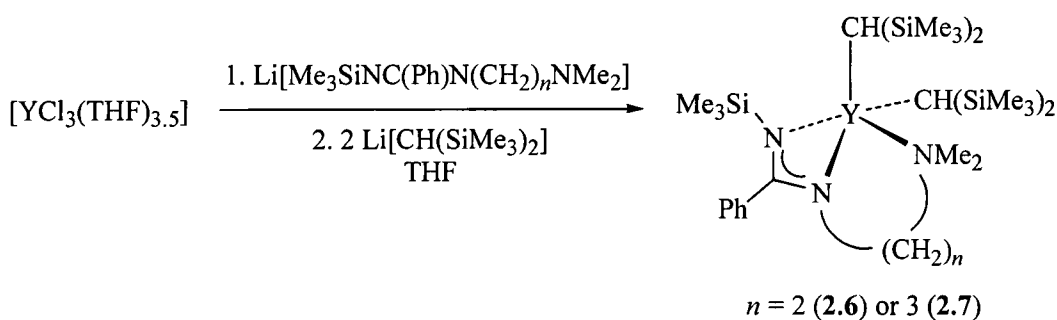
Lappert *et al.* have prepared the homologous pendant amidinate $\text{Me}_3\text{SiNC(Ph)NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2$, with an additional CH_2 linker in the pendant arm.³⁴ The lithium salt (**2.3**) is also dimeric, with the same structural motif as for the 2-carbon linker ligand **2.1**. Reaction of **2.3** with Al_2Cl_6 or Ga_2Cl_6 yielded the 5-coordinate square-based pyramidal monomers **2.4** and **2.5** (Equation 2.2). The crystal structures of these compounds showed that the amidinate ligand coordinates in a meridional fashion.



Equation 2.2

Reaction of **2.3** with LnCl_3 ($\text{Ln} = \text{La}$ or Ce) gives the chloride-bridged dimers $[\text{Ln}\{\text{Me}_3\text{SiNC(Ph)NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}_2(\mu\text{-Cl})_2]$. The cerium complex has been crystallographically characterised and this revealed that there is one bidentate and one tridentate amidinate ligand on each of the metal centres.

More recent work from the group of Hessen has involved preparation of highly electron deficient (10 electron) yttrium alkyl complexes of these ligands (Equation 2.3).³⁵

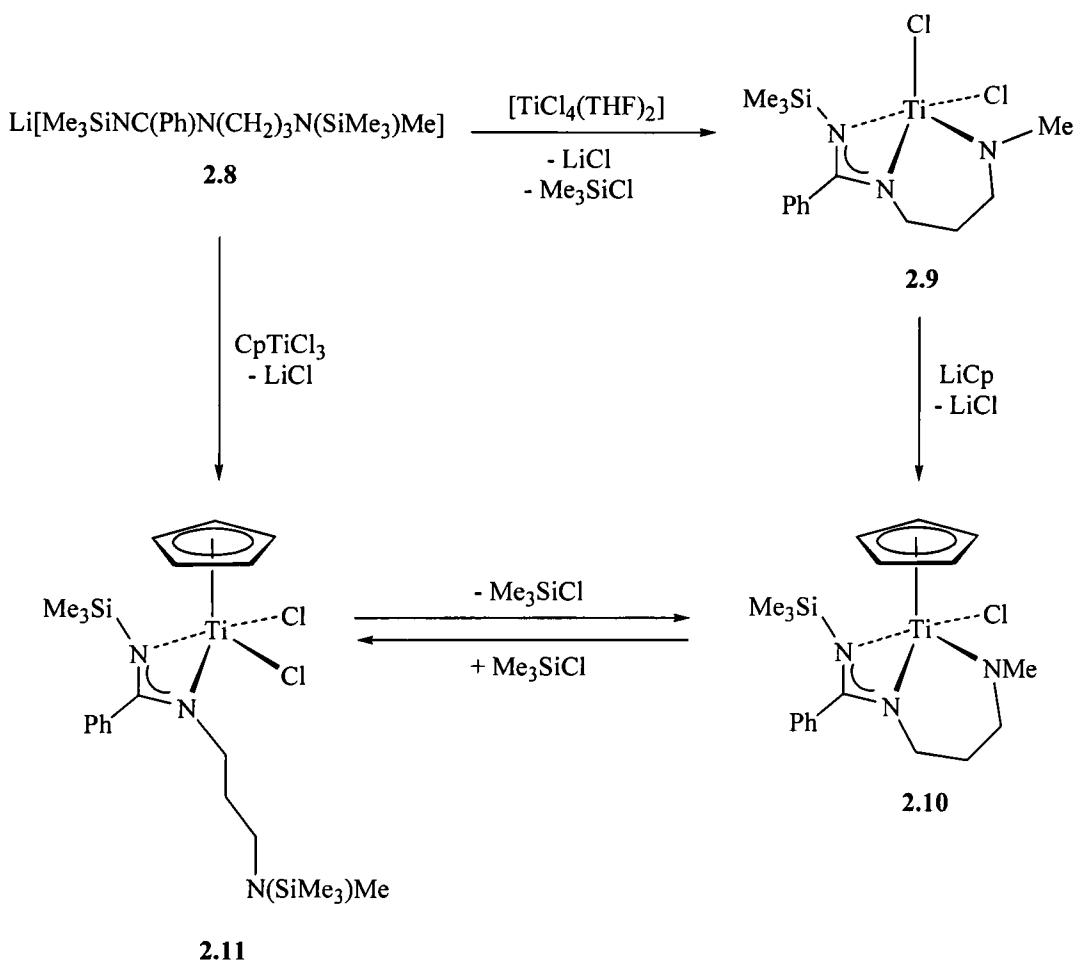


Equation 2.3

The compound **2.6** has been characterised by single crystal X-ray diffraction and the amino-amidinate is found to be tridentate, adopting an approximately meridional coordination mode. Attempts to reproduce this chemistry with a less bulky alkyl group yielded bis(amino-amidinate) yttrium "ate"-complexes of the

type $[\text{Li}\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{NMe}_2\}_2\text{Y}(\text{R})_2]$ ($\text{R} = \text{CH}_2\text{Ph}$, CH_2SiMe_3) with decoordination of the pendant amine from yttrium.

Hessen *et al.* have also synthesised a pendant alkyl(trimethylsilyl) amino-amidinate ligand precursor and used it in the preparation of titanium cyclopentadienyl-amidinate compounds (Scheme 2.1).³⁶ In this chemistry, elimination of Me_3SiCl led to the *in situ* formation of amido-amidinate ligands.

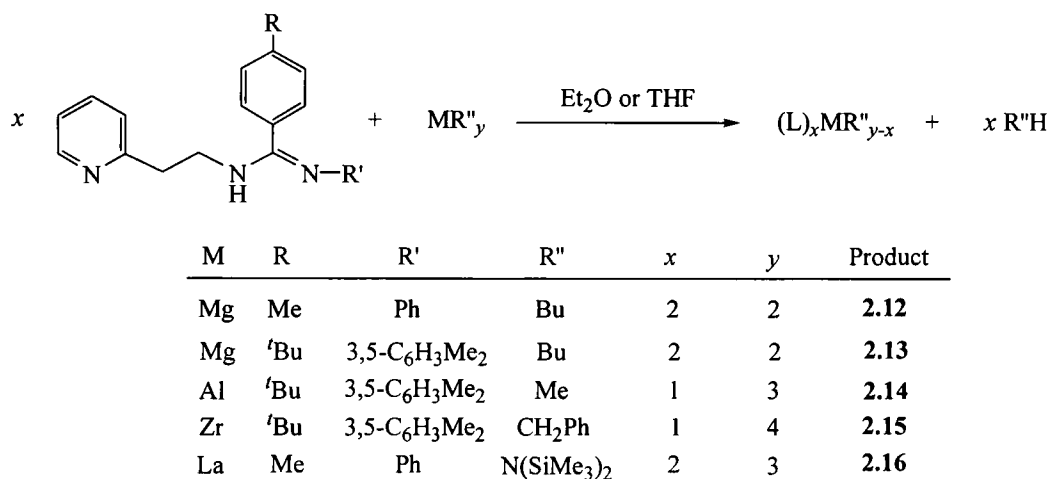


Scheme 2.1 Reactions of a pendant trimethylsilyl-amino amidinate ligand ($\text{Cp} = \text{C}_5\text{H}_5$)

The lithium salt of this amidinate ligand (**2.8**) was obtained as its THF solvate $[\text{Li}\{\text{Me}_3\text{SiNC}(\text{Ph})\text{N}(\text{CH}_2)_3\text{N}(\text{SiMe}_3)\text{Me}\}(\text{THF})]$, indicating that the pendant methyl(trimethylsilylmethyl)amine functionality is probably not coordinated to the lithium ion. This is in contrast to the THF-free lithium amidinate-amines **2.1** and **2.3** which adopt dimeric structures with a coordinated amine functionality. It was anticipated that alkyl derivatives of the chloride compound **2.9** might show

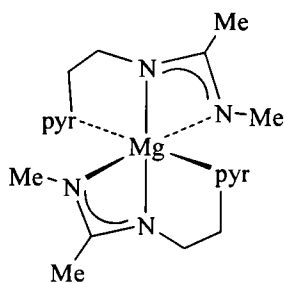
promise in catalytic olefin polymerisation. Dialkyl derivatives of **2.9** were readily prepared by reaction with alkyl lithium or Grignard reagents but were found to be thermally unstable and could not be converted into well-defined cationic alkyl compounds.

Concurrent with Hessen and Lappert's work on pendant arm amino-amidinate systems, Arnold *et al.* prepared a series of amidinate ligands with pendant pyridyl functionalities, of the type $\{R'NC(4-C_6H_4R)N(CH_2)_2(pyr)\}$.³⁷ These were reacted with a range of homoleptic metal alkyl and amide compounds to yield mono- or bisamidinate metal complexes (Equation 2.4).

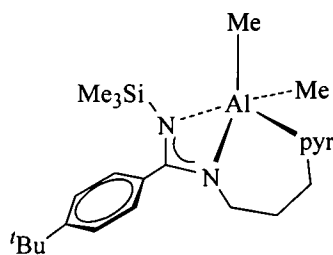


Equation 2.4

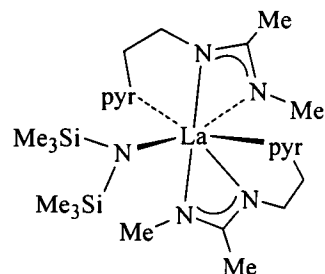
In compounds **2.12** - **2.15** the ligands coordinate meridionally. However, the crowded nature of the metal centre in the lanthanum derivative **2.16** forces coordination which is intermediate between meridional and facial.



2.12



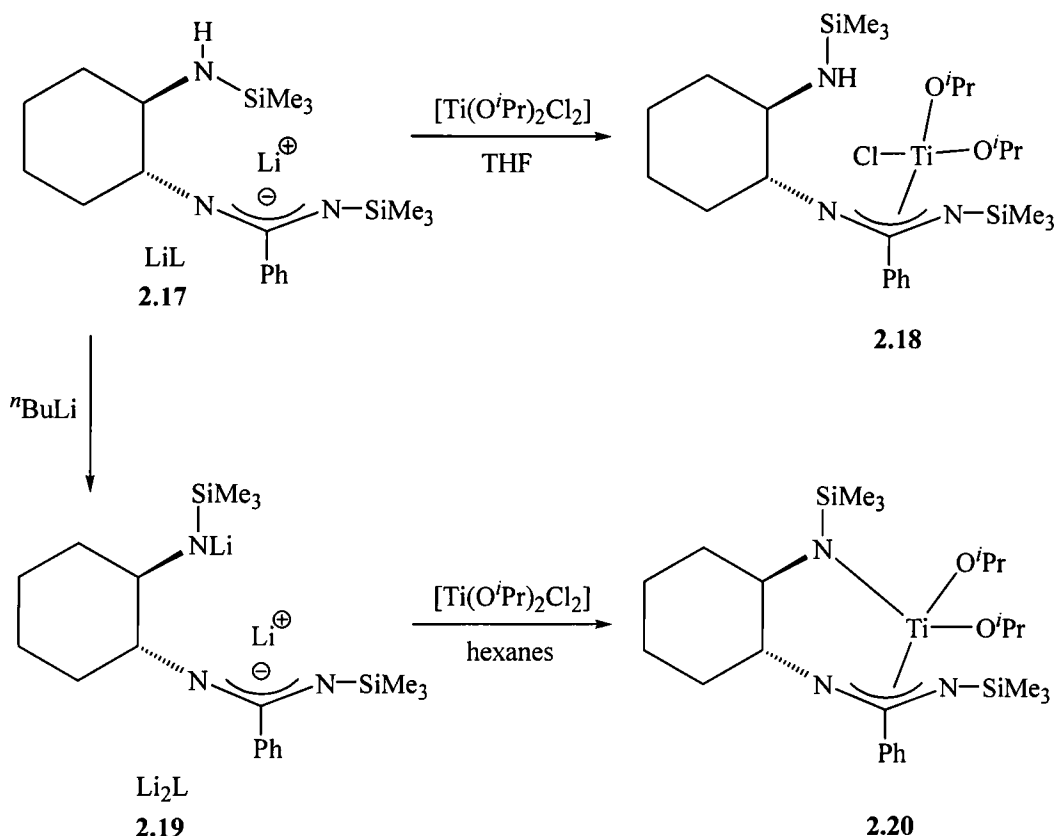
2.14



2.16

In addition to the pendant groups of these ligands binding to metals through a lone pair of electrons on the nitrogen atom of the donor group, another binding mode with both η^3 - π and σ -bonds to the metal is possible. This has been developed in

the groups of Huang and Liu during their work with chiral amidinate derivatives.³⁸ They have prepared chiral mono- and dianionic-tridentate amidinate ligands of the type $\text{Li}(\text{HL})$ and $\text{Li}_2(\text{L})$ $\{\text{H}_2\text{L} = (1R,2R\text{-})\text{-}1\text{-}[\text{N}(\text{H})\text{C}(\text{Ph})\text{NSiMe}_3]\text{-}2\text{-}[\text{N}(\text{H})\text{SiMe}_3]\text{C}_6\text{H}_{10}\}$ and have examined their reactions with a titanium alkoxide complex (Scheme 2.2). Compounds **2.17** - **2.20** have been crystallographically characterised.



Scheme 2.2 Reactions of a chiral amidinate ligand

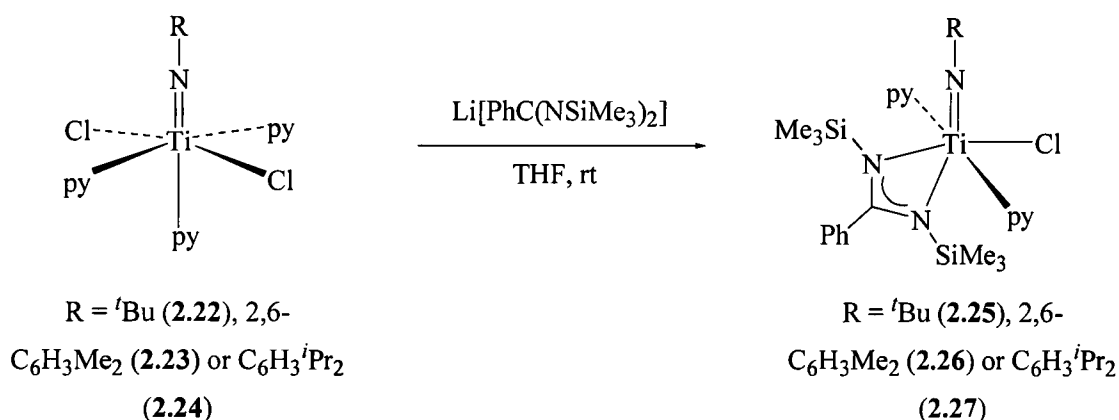
In summary, pendant arm functionalised amidinates have been introduced only recently and may display either meridional or facial coordination to metals in their complexes. In the majority of cases, these ligands bind to metals through both the amidinate and the pendant donor group (*i.e.* κ^3 -coordination). These ligands have so far not been used in the development of new metal imido chemistry.

2.2.3 Titanium benzamidinate and (cyclohexyl)acetamidinate imido complexes

Initial efforts to prepare Group 4 amidinate-imido compounds in the Mountford group focused on the $\text{N,N}'$ -bis(trimethylsilyl)benzamidinate $[\text{PhC}(\text{NSiMe}_3)_2]$ and

N,N'-bis(cyclohexyl)acetamidinate $[\text{MeC}(\text{NC}_6\text{H}_{11})_2]$ ligands, owing to the ease of preparation of their lithium salts^{39,40} and the stabilising properties that they generally impart to their metal complexes.

As discussed in Section 1.3, previous work in the Mountford group has shown that the complexes $[\text{Ti}(\text{NR})\text{Cl}_2(\text{py})_3]$ $\{\text{R} = \text{'Bu}$ (**2.21**), 2,6- $\text{C}_6\text{H}_3\text{Me}_2$ (**2.22**) or 2,6- $\text{C}_6\text{H}_3\text{'Pr}_2$ (**2.23**) $\}$ ⁴¹ are excellent synthons in the preparation of new titanium imido complexes supported by a wide range of ancillary ligands.⁴² The strategy chosen was therefore to react the complexes **2.21** - **2.23** with the lithium salt of the amidinate. Reactions with $\text{Li}[\text{PhC}(\text{NSiMe}_3)_2]$ (**2.21**) are shown in Equation 2.5 and resulted in the formation of mono(benzamidinato) titanium derivatives.⁴³

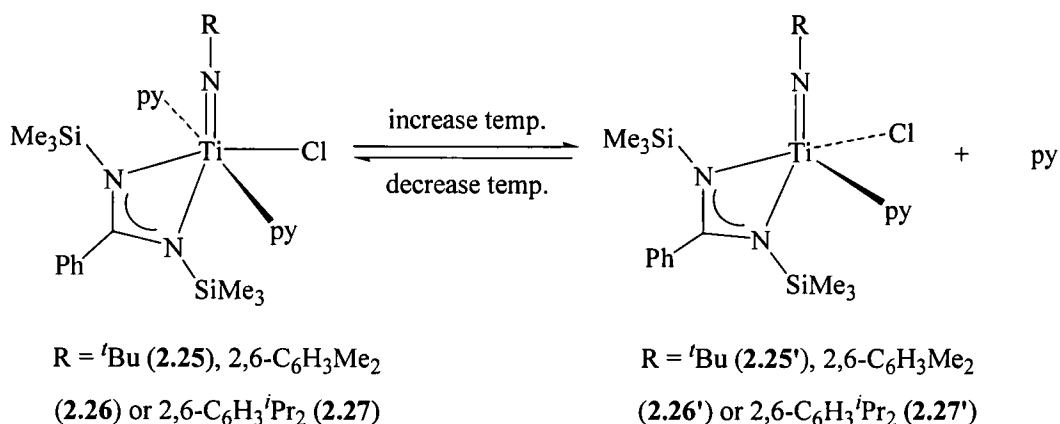


Equation 2.5

NMR scale *tert*-butyl imide/arylamine exchange reactions of **2.25** with H_2N -2,6- $\text{C}_6\text{H}_3\text{Me}_2$ or H_2N -2,6- $\text{C}_6\text{H}_3\text{'Pr}_2$ also gave the complexes **2.26** and **2.27** but these reactions proceeded slowly (*ca.* 6 days to go to completion), presumably due to the steric bulk of the benzamidinate ligand. The arylimido complex **2.26** has been crystallographically characterised.

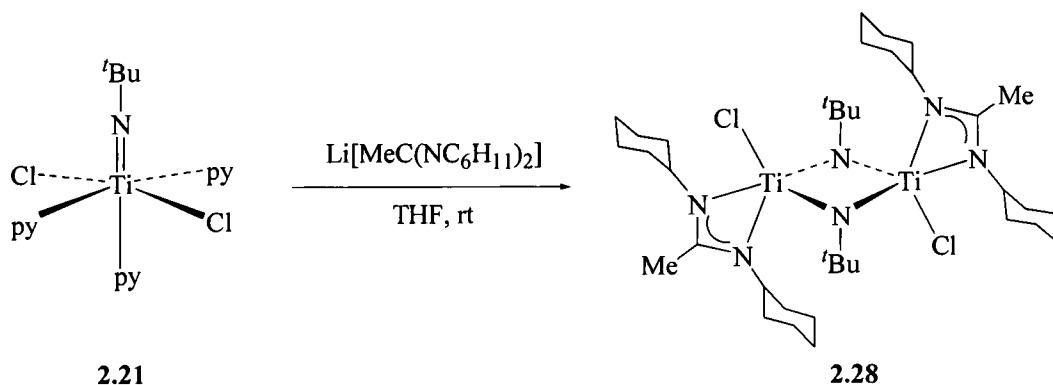
The room temperature ^1H NMR spectra of compounds **2.25** - **2.27** are broad, indicating that one or more fluxional processes take place in solution. Examination of the variable temperature NMR spectra in CDCl_3 showed the behaviour of all three complexes to be qualitatively the same, consistent with a temperature-dependent dynamic equilibrium between the six-coordinate species $[\text{Ti}(\text{NR})\{\text{PhC}(\text{NSiMe}_3)_2\}\text{Cl}(\text{py})_2]$ $\{\text{R} = \text{'Bu}$ (**2.25**), 2,6- $\text{C}_6\text{H}_3\text{Me}_2$ (**2.26**) or 2,6- $\text{C}_6\text{H}_3\text{'Pr}_2$ (**2.27**) $\}$ and the 5-coordinate mono-pyridine adducts

$[\text{Ti}(\text{NR})\{\text{PhC}(\text{NSiMe}_3)_2\}\text{Cl}(\text{py})]$ $\{\text{R} = \text{'Bu}$ (**2.25**'), 2,6- $\text{C}_6\text{H}_3\text{Me}_2$ (**2.26**') or 2,6- $\text{C}_6\text{H}_3\text{'Pr}_2$ (**2.27**') $\}$ as shown in Equation 2.6.



Equation 2.6

The resonances attributable to **2.25** - **2.27** increase in intensity relative to those of pyridine and **2.25'** - **2.27'** as the temperature is lowered. At intermediate temperatures, the relative concentrations of the two complexes in solution were found to change with the amount of added pyridine in a way consistent with the dissociative equilibrium illustrated. Integration of the resonances for the variable temperature NMR spectra afforded equilibrium constants (K_{eq}) at different temperatures and values of ΔS , ΔH and ΔG were extracted from plots of K_{eq} vs. $1/T$. This showed that all three equilibria are effectively thermochemically neutral, as the large positive ΔS (range 108 ± 5 - $172 \pm 5 \text{ JK}^{-1}\text{mol}^{-1}$, consistent with the dissociative equilibrium as written) nearly compensates for the endothermic ΔH term (range 38.7 ± 1.5 - $47.3 \pm 1.9 \text{ kJmol}^{-1}$) as the temperature is increased.



Equation 2.7

In order to investigate the effects of modifying the ligand substituents, a titanium N,N'-bis(cyclohexylamidinate) complex was also prepared by reaction of $\text{Li}[\text{MeC}(\text{NC}_6\text{H}_{11})_2]$ with $[\text{Ti}(\text{N}^t\text{Bu})\text{Cl}_2(\text{py})_3]$ in THF (Equation 2.7).

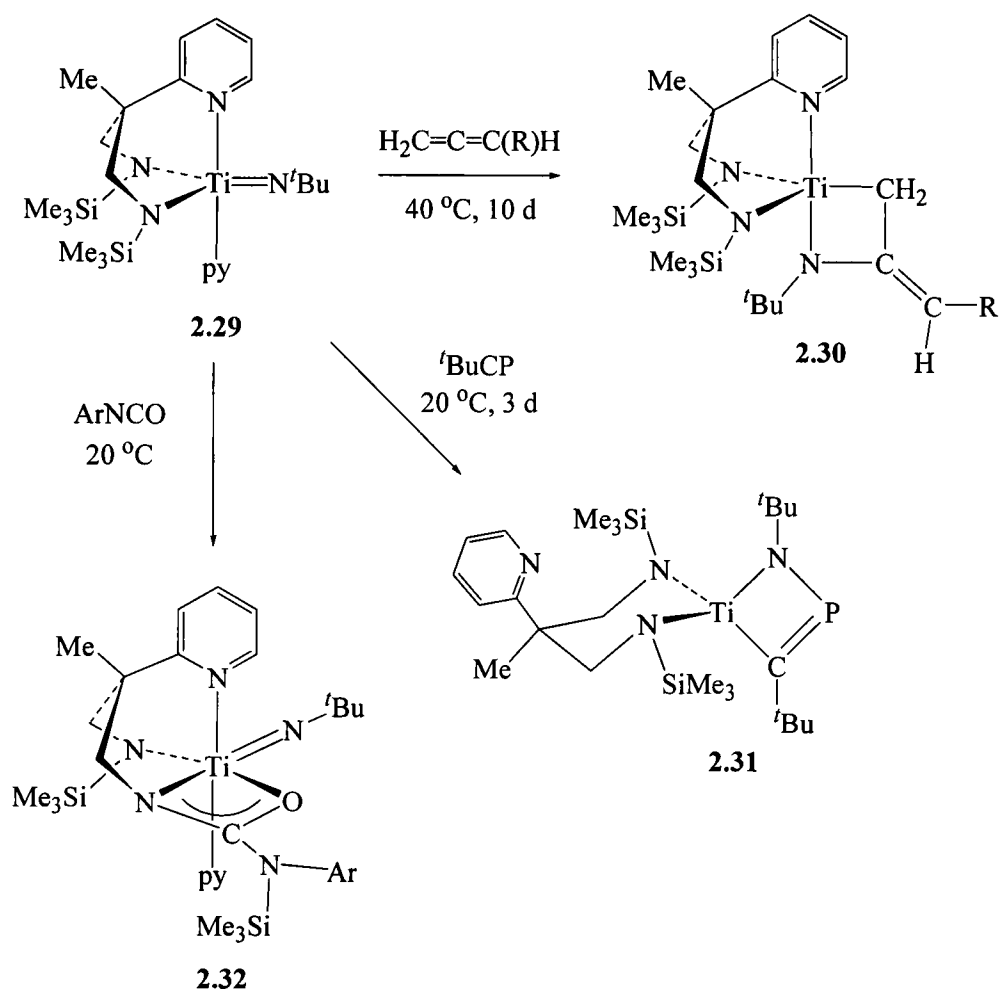
The product $[\text{Ti}_2(\mu\text{-N}^t\text{Bu})_2\{\text{MeC}(\text{NC}_6\text{H}_{11})_2\}_2\text{Cl}_2]$ (**2.28**) was found to be dimeric, with two 5-coordinate titanium centres. The different structures of **2.28** and **2.25** - **2.27** illustrate the importance of the amidinate N-substituents in these systems.

2.3 Synthesis of titanium imido complexes of pendant arm functionalised benzamidinate ligands

As demonstrated in the previous Section, benzamidinate-type ligands have been successfully used as supporting ligands in the preparation of new titanium imido complexes.^{43,44} The chloride derivatives so formed (Equation 2.5) undergo chloride metathesis reactions to yield a wide variety of derivatives (Section 4.2).⁴⁵ However, it is clear that partial (Equation 2.6) or complete (Equation 2.7) loss of pyridine from these complexes can be a complication in the formation of stable and/or well-defined reaction products.

Work carried out by Mountford, Gade *et al.* using diamido-pyridine supported titanium imido compounds has demonstrated how a hemi-labile donor can stabilise a reactive $\text{Ti}=\text{NR}$ complex but can decoordinate during the course of a reaction if required (Scheme 2.3).⁴⁶

Reaction of **2.29** with allene results in cycloaddition of allene to the $\text{Ti}=\text{N}$ bond without decoordination of the pendant arm from the metal. However, in the case of reaction with $^t\text{BuCP}$, the hemi-labile donor decoordinates from the metal in order to accommodate the bulky ^tBu group. A complication arises in reactions of complexes of this ligand with polar substrates, such as ArNCO . Instead of the desired cycloaddition to the imide, insertion into the metal amide bonds is observed to yield **2.32**. It was anticipated that the amidinate ligand, with its delocalised electrons, would be less likely to undergo undesirable insertion reactions of this type.



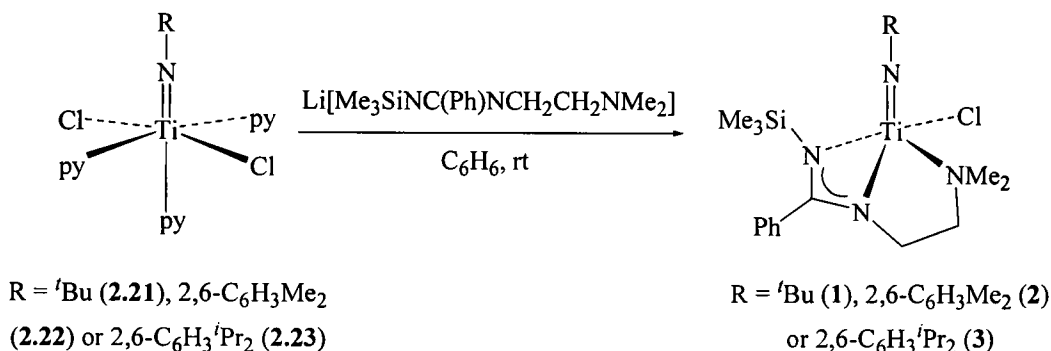
Scheme 2.3 Reactions of a titanium diamido-pyridine imido complex

It was decided to pursue the synthesis of titanium imido complexes with a hemilabile donor group using the two previously prepared dimethylamino-functionalised amidinate ligands Me₃SiNC(Ph)NCH₂CH₂NMe₂ (two carbon linker between the benzamidinate nitrogen and the NMe₂ group) and Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂ (three carbon linker).^{32,34} These ligands were selected for their ease of preparation and also because the Me groups of the pendant amine are a convenient NMR spectroscopic handle for examining coordination of the pendant arm to the metal centre in their complexes.

2.3.1 Synthesis of 2-carbon linker pendant arm derivatives

The titanium imido compounds [Ti(NR)Cl₂(py)₃] (R = ^tBu, 2,6-C₆H₃Me₂ or 2,6-C₆H₃^tPr₂)⁴¹ were reacted with one equivalent of the lithated amino-amidinate ligand **2.1**³² in benzene at room temperature. Removal of the volatiles, extraction into benzene and filtration yielded three new amidinate-imido compounds,

$[\text{Ti}(\text{NR})\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{NMe}_2\}\text{Cl}]$ $\{\text{R} = \text{'Bu}$ (**1**), 2,6- $\text{C}_6\text{H}_3\text{Me}_2$ (**2**) or 2,6- $\text{C}_6\text{H}_3\text{'Pr}_2$ (**3**) $\}$, as air- and moisture-sensitive solids in 69 - 85% yield (Equation 2.8).



Equation 2.8

The *tert*-butyl derivative **1** was recrystallised from cold pentane to yield diffraction-quality crystals from which the X-ray structure of **1** has been determined (Section 2.5.1) and which supports the proposed structures for **1** - **3**. The aryl imido analogues **2** and **3** did not easily crystallise, but were sublimed at high vacuum $\{1 \times 10^{-5}$ mbar; 150 - 160 °C (**2**), 100 - 110 °C (**3**) $\}$ in low yields ($< 20\%$) to yield analytically pure samples.

Compounds **1** - **3** have been characterised by NMR and IR spectroscopies, mass spectrometry and elemental analysis (Full details are given in Chapter 6). The high resolution E.I. mass spectra for **2** and **3** contained peaks attributable to the molecular ions of these compounds (Chapter 6).

The ^1H and $^{13}\text{C}\{-^1\text{H}\}$ NMR spectra for compounds **1** - **3** support the proposed structures. As they all contain similar features, discussion will be confined to the ^1H NMR spectrum of the 2,6-dimethylphenyl imido compound **2**, shown in Figure 2.1.

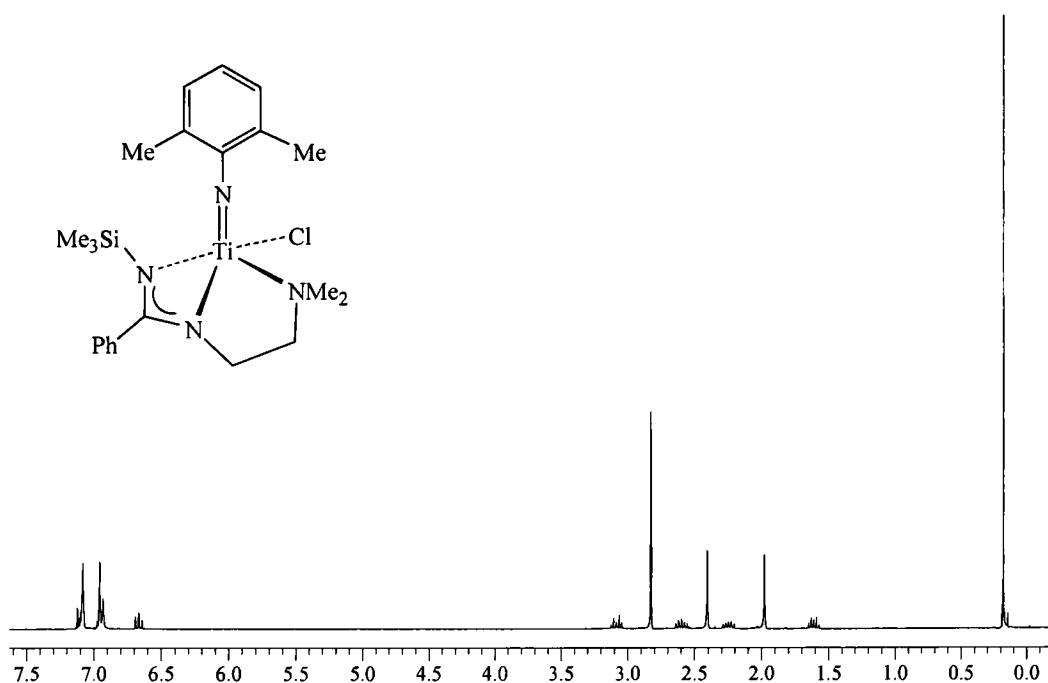


Figure 2.1 500.0 MHz ^1H NMR spectrum of $[\text{Ti}(\text{N}-2,6\text{-C}_6\text{H}_3\text{Me}_2)\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{NMe}_2\}\text{Cl}]$ (**2**) in C_6D_6

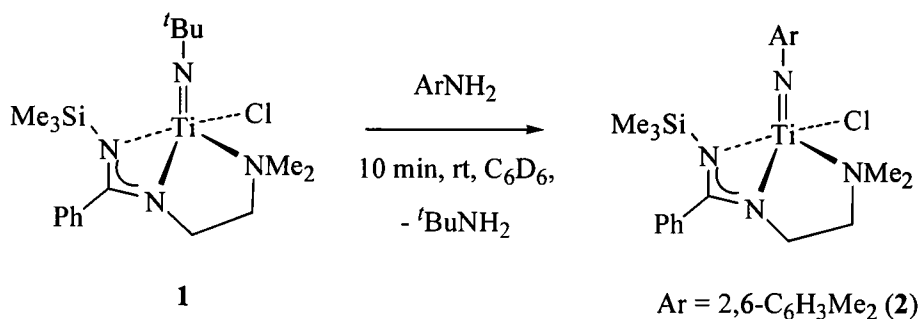
The SiMe_3 group of the amidinate ligand gives rise to a singlet at 0.18 ppm. Each of the four diastereotopic methylene hydrogens leads to an individual multiplet (1.63, 2.27, 2.63 and 3.10 ppm), and the two methyl groups appear as inequivalent sharp singlets in both the ^1H (2.00 and 2.43 ppm) and $^{13}\text{C}\{-^1\text{H}\}$ spectra. This confirms coordination of the pendant NMe_2 group to the metal centre. The imido N-substituents give rise to the expected resonances; the 6 H singlet (2.63 ppm) corresponding to the methyl groups of the aryl imide suggests that there is free rotation about the bond between the *ipso*-carbon and the nitrogen of the imide which renders these groups equivalent. The methyl groups of the aryl ring *isopropyl* substituents in **3** are inequivalent as required by the absence of a molecular mirror plane in these compounds.

The ^1H NMR spectrum of the *tert*-butyl derivative **1** in C_6D_6 at room temperature contains broad resonances for the CH_2 and NMe_2 protons at around 2.6 and 3.2 ppm. This may be due to rapid, reversible coordination of the pendant NMe_2 to the metal in this solvent at room temperature. However, upon changing the solvent to CD_2Cl_2 this region of the spectrum became well resolved, with two NMe singlets indicating firm coordination of the pendant arm to titanium.

2.3.2 Synthesis of **2** by imide/aniline exchange reactions

In several previous studies it has been found that aryl imido compounds $[\text{Ti}(\text{NAr})(\text{L}_n)]$ (L_n is a supporting ligand or ligand set) can be prepared from their *tert*-butyl analogues $[\text{Ti}(\text{N}^t\text{Bu})(\text{L}_n)]$ by reaction of the latter with the appropriate aniline, ArNH_2 .⁴¹

An NMR tube scale reaction between the *tert*-butyl imido compound **1** and one equivalent of $\text{H}_2\text{N}-2,6-\text{C}_6\text{H}_3\text{Me}_2$ showed quantitative formation of **2** and the expected *tert*-butyl amine side product (Equation 2.9).

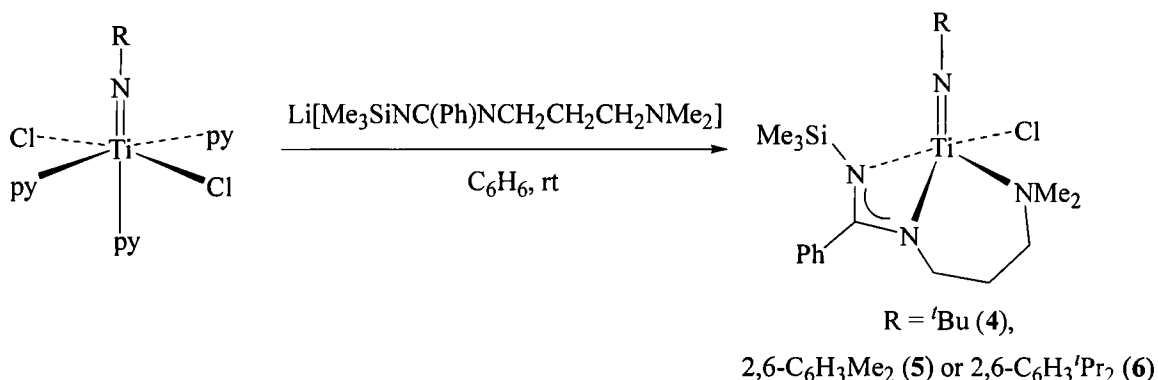


Equation 2.9

Attempts to scale up this reaction in C_6H_6 were hampered by the separation of the product **2** from residual amines. It seems likely that weak coordination of amines to the remaining vacant site in these 5-coordinate compounds is responsible.

2.4 Synthesis of 3-carbon linker pendant arm derivatives

The corresponding reactions of $[\text{Ti}(\text{NR})\text{Cl}_2(\text{py})_3]$ (**2.21** - **2.23**) with the lithiated 3-carbon linker amino-amidinate ligand **2.3** similarly afforded 5-coordinate complexes, namely $[\text{Ti}(\text{NR})\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}\text{Cl}]$ $\{\text{R} = ^t\text{Bu}$ (**4**), $2,6-\text{C}_6\text{H}_3\text{Me}_2$ (**5**) or $2,6-\text{C}_6\text{H}_3^i\text{Pr}_2$ (**6**)\} (Equation 2.10).



Equation 2.10

Compounds **4** - **6** were recrystallised from hexanes or CH_2Cl_2 /hexanes mixtures in good yields, diffraction-quality crystals of all three compounds were obtained and the crystal structures determined (Section 2.5.2).

The spectroscopic properties of compounds **4** - **6** are analogous to those of **1** - **3** (as confirmed by the X-ray structures). The NMR spectra suggest firm coordination of the NMe_2 fragment to titanium on the NMR timescale, with sharp resonances arising from each of the six inequivalent arm methylene protons and the two inequivalent NMe_2 groups. The ^1H NMR spectrum of the 2,6-dimethylphenylimido derivative **5** is shown in Figure 2.2 by way of example and is discussed below.

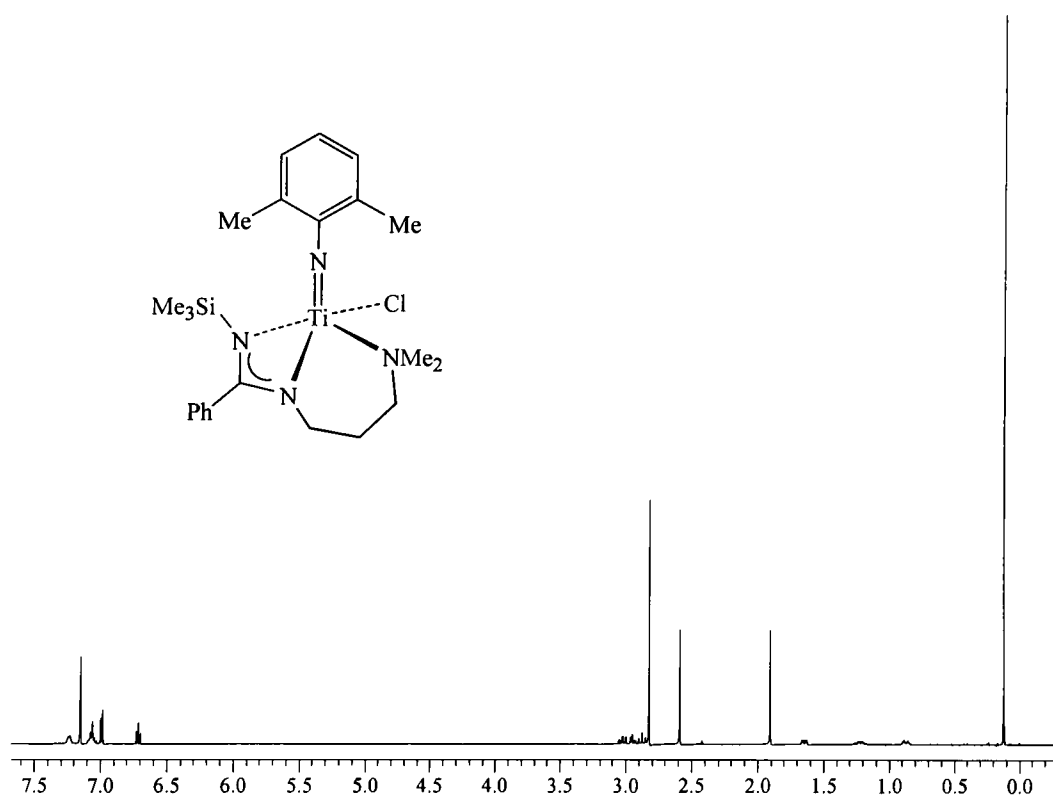


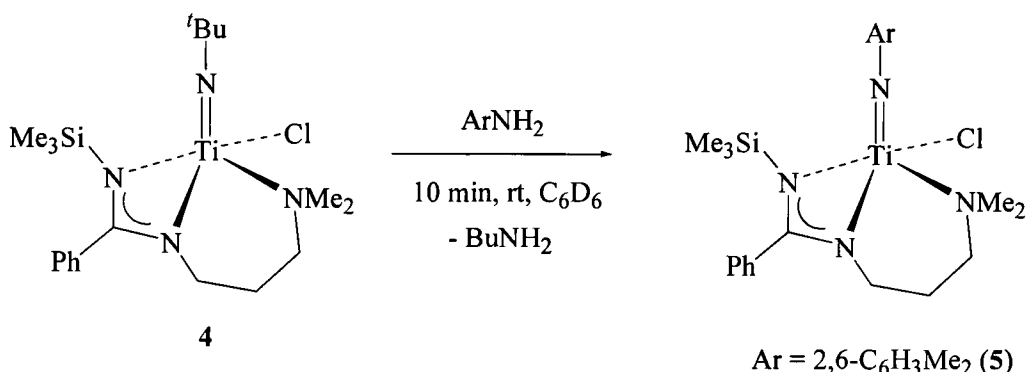
Figure 2.2 500.0 MHz ^1H NMR spectrum of $[\text{Ti}(\text{N}-2,6\text{-C}_6\text{H}_3\text{Me}_2)\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}\text{Cl}]$ (**5**) in C_6D_6

Full assignment of the ^1H NMR spectrum was possible from 2-dimensional ^1H - ^1H , ^1H - ^{13}C and ROESY NMR spectra. One reason for full assignment of the pendant arm resonances was the observation of a low field shifted multiplet (*ca.* 2.9 ppm) for one of the hydrogens of the methylene linkage next to the NMe_2 group in **5** and **6** (but not in **4** or the two-carbon arm complexes **1** - **3**); the other H atom of

this methylene group appears at *ca.* 1.6 ppm in **5** and **6** (Figure 2.2). This unusual shift is unambiguously assigned to the axial H atom (*i.e.* oriented "up", more or less parallel to the Ti=NAr bond) which apparently feels some anisotropic deshielding effects from the arylimido groups in **5** and **6** (details of the full assignment can be found in Chapter 6).

2.4.1 Synthesis of **5** by imide/aniline exchange reactions

As for the 2-carbon linker system **2**, the arylimido compound **5** may also be prepared from the *tert*-butyl complex **6** by an imide exchange reaction in C₆D₆ at room temperature, with quantitative elimination of *t*-BuNH₂ (Equation 2.11).



Equation 2.11

Attempts to scale up this reaction in benzene again resulted in difficulties in obtaining amine-free free product. Direct preparation of aryl imido complexes from reaction of the lithiated ligands **2.1** or **2.3** with the dichloride starting materials [Ti(NAr)Cl₂(py)₃] would appear to be the most convenient route to these compounds.

2.5 X-ray crystal structures of compounds **1** and **4** - **6**

X-ray diffraction data has been recorded for the 2-carbon linker complex **1** and the three carbon linker complexes **4** - **6**. The structures have been solved and will be discussed in the following Sections. The effect of the number of CH₂ linkers in the chelating donor arm and of the imido substituent on the crystal structures will be discussed.

2.5.1 X-ray crystal structures of *tert*-butyl complexes **1** and **4**

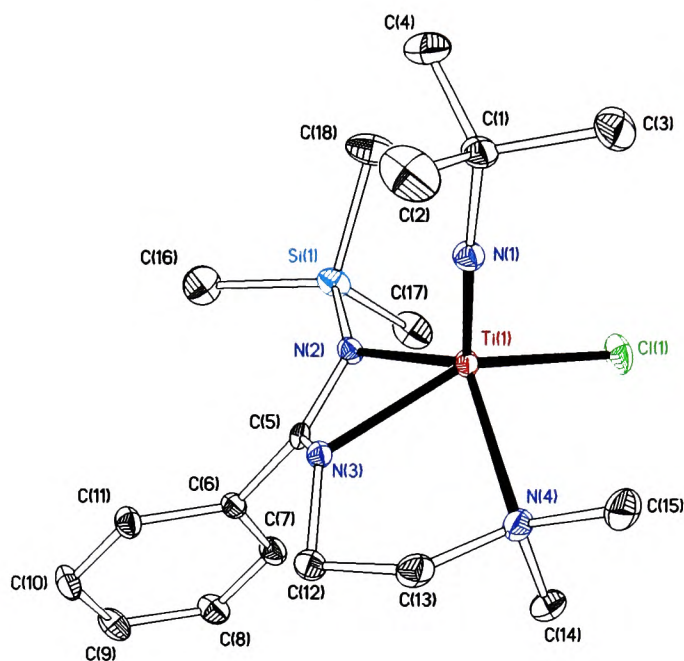
Diffraction-quality yellow crystals of [Ti(N^{*t*}Bu){Me₃SiNC(Ph)NCH₂CH₂NMe₂}Cl] (**1**) were grown from a solution in pentane at -80 °C. Data were collected at

150 K by Dr. S. Dubberley and the structure was solved by Dr. P. Mountford. Yellow crystals of the three carbon arm homologue $[\text{Ti}(\text{N}^i\text{Bu})\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}\text{Cl}]$ (**4**) were grown from a mixture of CH_2Cl_2 and hexanes at $-80\text{ }^\circ\text{C}$. Data were collected at 150 K and the structure was solved by Dr. A. Cowley. Figure 2.3 shows the molecular structures and Table 2.1 summarises important bond lengths and angles. Full details are provided in Appendices A and B.

Table 2.1 Selected bond lengths (Å) and angles (°) for $[\text{Ti}(\text{N}^i\text{Bu})\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{NMe}_2\}\text{Cl}]$ (**1**) and $[\text{Ti}(\text{N}^i\text{Bu})\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}\text{Cl}]$ (**4**)

	1	4
Ti(1)-N(1)	1.688(2)	1.6932(13)
Ti(1)-N(2)	2.126(2)	2.1479(13)
Ti(1)-N(3)	2.095(2)	2.0933(14)
Ti(1)-N(4)	2.248(2)	2.2391(14)
Ti(1)-Cl(1)	2.3231(6)	2.3429(5)
N(2)-Si(1)	1.7535(2)	1.7388(14)
N(2)-C(5)	1.339(3)	1.334(2)
N(3)-C(5)	1.325(3)	1.320(2)
Ti(1)-N(1)-C(1)	175.0(2)	173.35(11)
N(1)-Ti(1)-N(2)	116.07(8)	104.42(6)
N(1)-Ti(1)-N(3)	107.85(8)	110.56(6)
N(1)-Ti(1)-Cl(1)	109.42(6)	113.75(5)
N(1)-Ti(1)-N(4)	106.08(8)	99.04(6)
N(2)-Ti(1)-N(3)	63.14(6)	63.38(5)
Ti(1)-N(2)-C(5)	88.7(1)	88.45(9)
Si(1)-N(2)-C(5)	132.3(1)	129.51(11)
N(3)-Ti(1)-N(4)	73.89(6)	81.81(5)
N(2)-C(5)-N(3)	112.1(2)	114.18(14)
Ti(1)-N(2)-Si(1)	138.62(9)	136.23(8)
Ti(1)-N(3)-C(5)	90.4(1)	91.17(9)

(a)



(b)

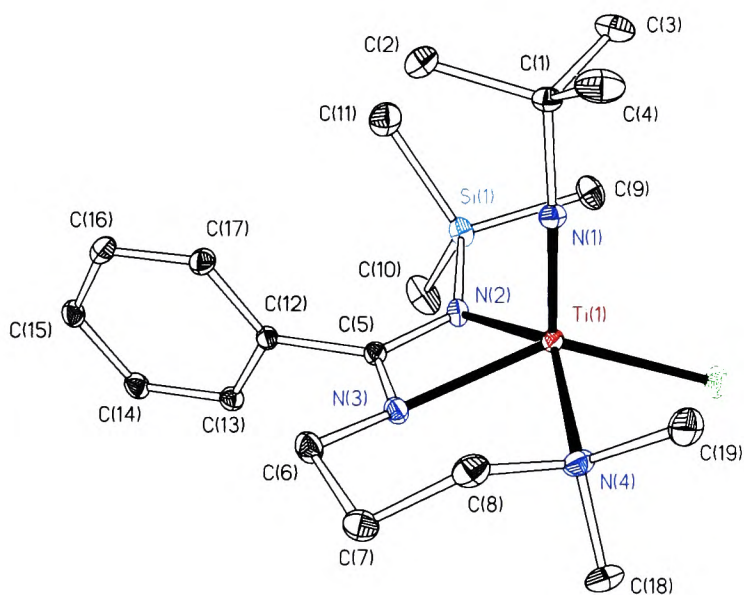


Figure 2.3 Thermal ellipsoid plots (20% probability) of (a) $[\text{Ti}(\text{N}^t\text{Bu})\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{NMe}_2\}\text{Cl}]$ (**1**) and (b) $[\text{Ti}(\text{N}^t\text{Bu})\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}\text{Cl}]$ (**4**). Hydrogen atoms omitted for clarity.

Molecules of **1** and **4** have square-based pyramidal geometries. In **1**, the atoms N(2), N(3), N(4) and Cl(1) form the square base with Ti(1) lying 0.75 Å out of the least squares best-fit plane containing these atoms. In **4**, the corresponding value is only 0.66 Å, suggesting that the three carbon ligand better accommodates the Ti=NR fragment. In the 2-carbon linker compound **1**, the N(1)-Ti(1)-L_{base} angles are in excess of 105° which is a feature of metal-ligand multiply bonded complexes of this kind.⁴⁷ However, in the 3-carbon linker compound **4** the N(1)-Ti(1)-N(4) angle is much smaller [99.04(6) Å], presumably to accommodate the extra CH₂ linker in the arm. The Ti=N_{imide} and Ti-Cl distances are at the short end of the range of values found for imidotitanium compounds,^{48,49} but consistent with the lower coordination number and lack of good electron-donating ligands. The Me₃SiNC(Ph)NCH₂CH₂NMe₂ and Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂ ligands adopt a κ^3 -coordination geometry with the pendant arm firmly coordinated in the solid state, consistent with the solution phase ¹H and ¹³C NMR data. Interestingly, the benzamidinate donors feature different degrees of planarity with N(3) being distinctly pyramidalised in **1**. This is apparent from visual inspection of the molecular structure, but is also quantified by the sums of the angles subtended at N(2) [359.3(12)°], (*i.e.* planar within error) and at N(3) [339.9(4)°]. The pyramidalisation of N(3) can be attributed to the distortions required to achieve coordination of the pendant NMe₂ group and is less marked in **4** [349.8(3)°]. Despite the pyramidalisation of N(3), the Ti(1)-N(2) distances are significantly longer than the Ti(1)-N(3) [differences = 0.031(3) Å (**1**), 0.055(3) Å (**4**)]. Factors contributing to this observation could be the additional binding through N(4) which would favour closer coordination of N(3). There is a small and marginally significant difference between the N(2)-C(5) (longer) and N(3)-C(5) bond lengths in **1** (difference = 0.014(4) Å) which is much less apparent in **4**. The longer chain pendant arm leads to an increased N(4)-Ti(1)-N(3) angle of 81.81(5)° in **4** compared to the more acute angle of 73.89(6)° in **1**.

2.5.2 X-ray crystal structures of aryl imido complexes **5** and **6**

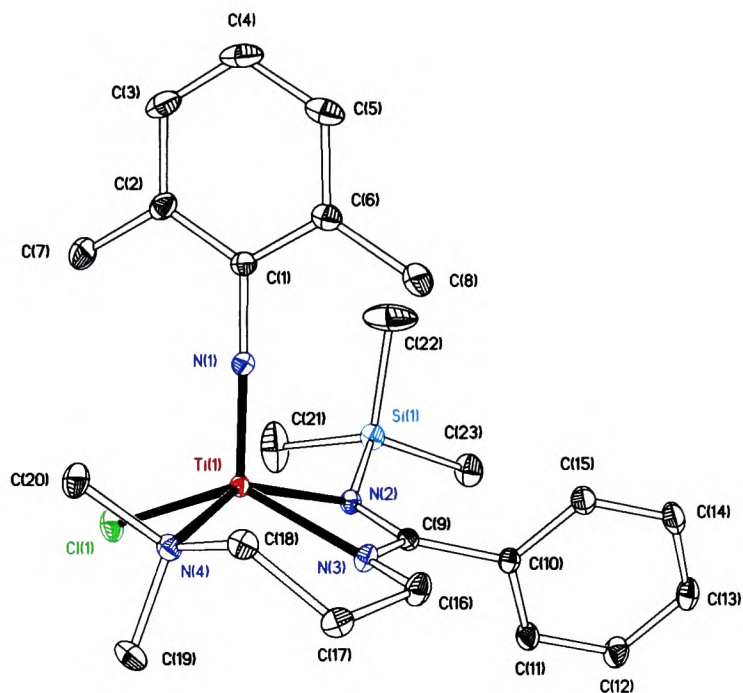
Red crystals of the 2,6-dimethylphenyl imido compound [Ti(N-C₆H₃Me₂){Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂}Cl] (**5**) suitable for X-ray diffraction analysis were grown from a mixture of CH₂Cl₂ and hexanes at room temperature. Data

were collected at 150 K and the X-ray structure was solved by Dr. S. Dubberley. Orange-red crystals of the 2,6-di-*iso*-propylimido homologue $[\text{Ti}(\text{N}-\text{C}_6\text{H}_3^i\text{Pr}_2)\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}\text{Cl}]$ (**6**) were grown by slow diffusion of a solution of **6** into paraffin oil. Data were collected at 150 K by Dr. B. Tyrrell and the X-ray structure was solved by Dr. P. Mountford. Figure 2.4 shows the molecular structures and Table 2.2 summarises important bond lengths and angles. Full details are provided in Appendices C and D.

Table 2.2 Selected bond lengths (Å) and angles (°) for $\text{Ti}(\text{N}-\text{C}_6\text{H}_3\text{Me}_2)\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}\text{Cl}$ (**5**) and $[\text{Ti}(\text{N}-\text{C}_6\text{H}_3^i\text{Pr}_2)\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}\text{Cl}]$ (**6**)

	5	6
Ti(1)-N(1)	1.713(1)	1.713(3)
Ti(1)-N(2)	2.124(1)	2.110(2)
Ti(1)-N(3)	2.080(1)	2.085(2)
Ti(1)-N(4)	2.223(1)	2.228(3)
Ti(1)-Cl(1)	2.3234(4)	2.3386(9)
N(2)-Si(1)	1.734(1)	1.735(3)
N(2)-CPh	1.337(2)	1.340(4)
N(3)-CPh	1.316(2)	1.317(4)
Ti(1)-N(1)-C(1)	178.58(9)	175.0(2)
N(1)-Ti(1)-N(2)	104.53(4)	109.03(12)
N(1)-Ti(1)-N(3)	110.09(5)	107.30(11)
N(1)-Ti(1)-N(4)	98.13(4)	102.19(11)
N(2)-Ti(1)-N(3)	63.71(4)	63.51(9)
N(3)-Ti(1)-N(4)	83.16(14)	82.7(1)
Ti(1)-N(2)-CPh	89.77(7)	91.2(2)
Ti(1)-N(2)-Si(1)	129.04(6)	133.83(13)
Si(1)-N(2)-CPh	131.58(8)	134.5(2)
Ti(1)-N(3)-CPh	92.26(7)	92.9(2)
Ti(1)-N(3)-CH ₂	138.75(8)	139.9(2)
PhC-N(3)-CH ₂	125.4(1)	126.9(2)

(a)



(b)

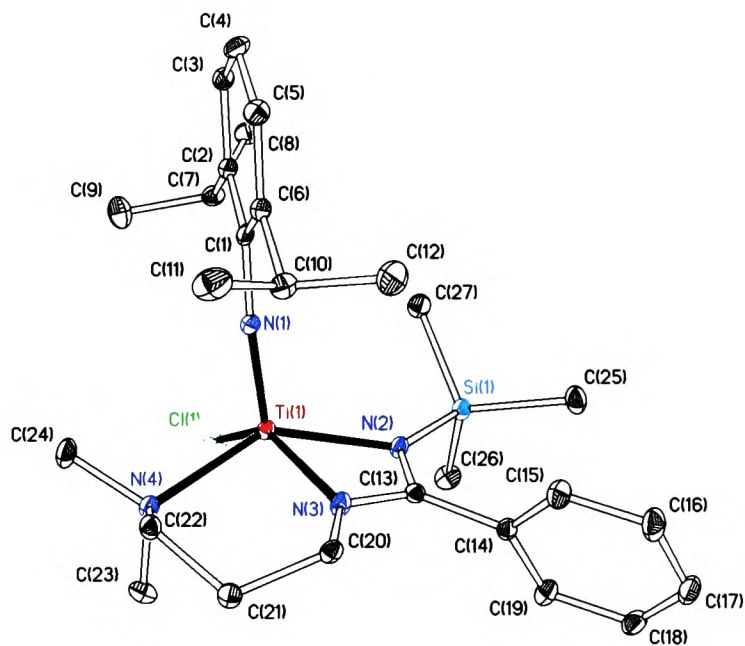


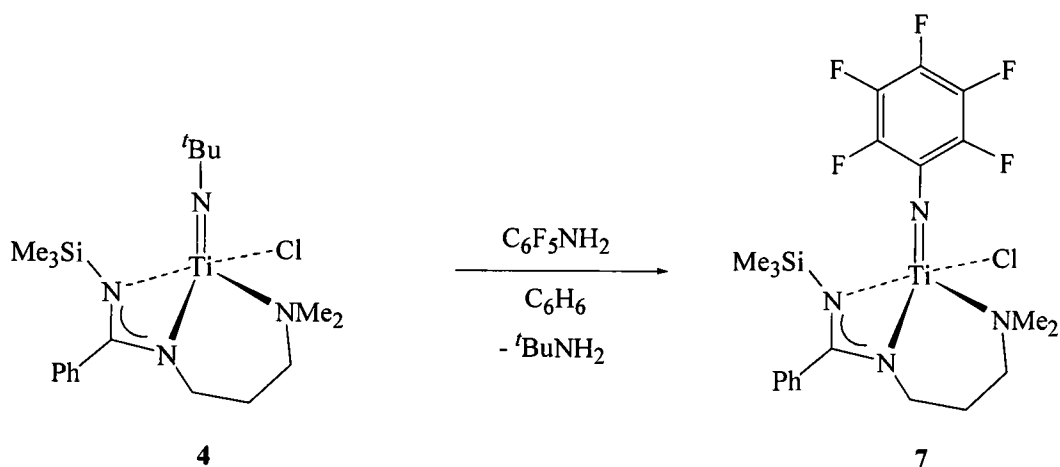
Figure 2.4 Thermal ellipsoid plots (20 and 25% probabilities respectively) of (a) $[\text{Ti}(\text{N}-\text{C}_6\text{H}_3\text{Me}_2)\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}\text{Cl}]$ (**5**) (b) $[\text{Ti}(\text{N}-\text{C}_6\text{H}_3'\text{Pr}_2)\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}\text{Cl}]$ (**6**). Hydrogen atoms omitted for clarity.

The structures of **5** and **6** are broadly analogous to those of **1** and **4**. The $\text{Ti}=\text{N}_{\text{imide}}$ distances are somewhat longer in the aryylimido systems, as is usually the case.^{41,47} The titanium atoms in **5** and **6** lie 0.64 and 0.67 Å out of the least squares plane of the {N(2),N(3),N(4),Cl(1)} donor set (corresponding value in **1** and **4** are 0.75 and 0.66 Å respectively). This again suggests that the three carbon arm ligand better accommodates the $\text{Ti}=\text{NR}$ fragment. The N(3) atoms in **5** and **6** are effectively planar, with the sums of the angles subtended at these atoms being 356.5(4) and 359.7(6)°, respectively. These values are closer to planarity than for their *tert*-butyl analogue **4**, where the sum of the N(3) angles is 349.78(34)°. The longer chain pendant arm again leads to increased N(4)-Ti(1)-N(3) angles of 83.16(14) and 82.7(1)° in **5** and **6** compared to the more acute angle of 73.89(6)° in **1**. As in compounds **1** and **4** the Ti(1)-N(2) distances in **5** and **6** are significantly longer than the Ti(1)-N(3) distances, presumably for the same reasons. As also in **1** and **4**, the N(2)-CPh distances are slightly longer than those for N(3)-CPh [differences 0.021(3) and 0.023(6) Å for **5** and **6**, respectively]. These small but persistent differences may be attributable (directly or indirectly) to steric factors associated with the SiMe_3 group.

2.6 Preparation of a perfluoroarylimido derivative

It was anticipated that a perfluoroimido analogues of compounds **4** - **6** would provide interesting structural and reactivity comparisons. It has recently been shown that perfluoroarylimido complexes can feature interesting π -stacked supramolecular solid state structures.⁵⁰

Numerous attempts to prepare the $[\text{Ti}(\text{NC}_6\text{F}_5)\text{Cl}_3(\text{py})_3]$ synthon required in sufficiently pure form for reaction with the lithiated ligand $\text{Li}[\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2]$ proved unsuccessful, so this was not a viable route to the target compound. Instead, the complex $[\text{Ti}(\text{NC}_6\text{F}_5)\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}\text{Cl}]$ (**7**) was prepared by a *tert*-butyl imide/perfluoroaniline exchange method (Equation 2.12).



Equation 2.12

The reaction proceeded in very good crude yields of over 90%. Unfortunately, while samples were >90% spectroscopically pure, they were always contaminated with residual amine. Pure samples were obtained in less than 5% yield by high vacuum tube sublimation and, disappointingly, it was not possible to obtain diffraction-quality crystals of **7**.

Compound **7** has been characterised by NMR and IR spectroscopies and mass spectrometry. The high resolution E.I. mass spectrum of **7** contained a peak at $m/z = 540$ attributable to the molecular ion. The ^1H NMR spectrum supports the proposed structure (Equation 2.12). As for the compounds **5** and **6**, very different chemical shifts (2.99 and 1.71 ppm) were observed for the two hydrogen atoms of the methylene group adjacent to NMe_2 . This is again attributed to anisotropic deshielding effects of the aryl imido group. The ^{19}F NMR spectrum contains 3 resonances for the three different fluorine environments of the aryl group (−154.90, −167.09 and −171.03 ppm for the *ortho*-, *meta*- and *para*-fluorines respectively).

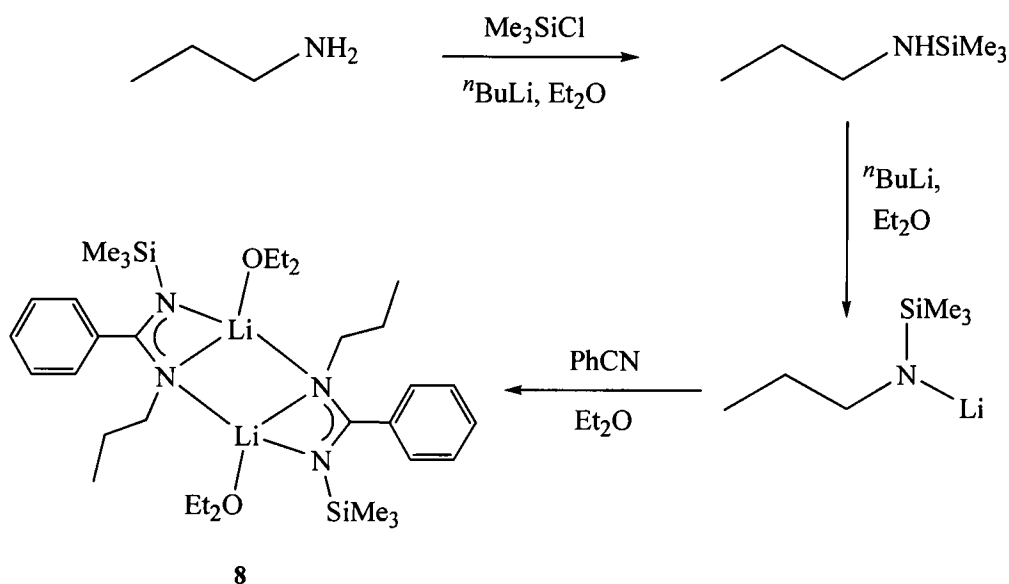
2.7 Synthesis of a pendant propyl "dummy" arm ligand derivative

As mentioned in Section 2.2.3, the benzamidinate-supported titanium imido complexes $[\text{Ti}(\text{NR})\{\text{PhC}(\text{NSiMe}_3)_2\}\text{Cl}(\text{py})_2]$ ($\text{R} = \textit{tert}$ -butyl or aryl) (**2.25** - **2.27**) exist in dynamic equilibrium with the 5-coordinate, monopyridine complexes (**2.25'** - **2.27'**). The compounds **1** - **6** clearly do not bind pyridine (present in the reaction mixtures) tightly, an observation that can be attributed to features of the $\text{Me}_3\text{SiNC}(\text{Ph})\text{N}(\text{CH}_2)_n\text{NMe}_2$ ($n = 2$ or 3) ligands' pendant arms, coupled with the

trans-labilising influence of the imido ligands themselves. To make a better comparison of the complexes **1** - **6** with the non-pendant arm species **2.25** - **2.27**, it was decided to prepare an isosteric benzamidinate compound without a pendant donor group.

2.7.1 Synthesis of $[\text{Li}_2\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{Me}\}_2(\text{Et}_2\text{O})_2]$

The necessary lithiated ligand was prepared by reaction of a pendant lithium amide with benzonitrile in a similar manner to the preparation of the lithium salts of the pendant amine-functionalised amidinates $\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{NMe}_2$ and $\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2$ (Scheme 2.4).^{32,34}



Scheme 2.4 Synthesis of $\text{Li}[\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{Me}]$ (**8**)

Crystallisation from Et_2O /hexanes at $-80\text{ }^\circ\text{C}$ afforded the diethyl ether adduct of the lithium salt of the ligand $[\text{Li}_2\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{Me}\}_2(\text{Et}_2\text{O})_2]$ (**8**) in 66% yield. The new compound was characterised by NMR and IR spectroscopies, mass spectrometry and elemental analysis. Full experimental details can be found in Chapter 5.

Diffraction-quality colourless crystals of **8** were grown from a mixture of Et_2O and hexanes at $-80\text{ }^\circ\text{C}$. Data were collected at 150 K by Dr. B. Tyrrell and the structure was solved by Dr. P. Mountford. Figure 2.8 shows the molecular structure and Table 2.3 summarises important bond lengths and angles. Full

details are provided in Appendix E.² The NMR data (Chapter 6) are consistent with the solid state structure.

Molecules of **8** adopt a dinuclear structure in the solid state, possessing crystallographically-imposed inversion symmetry. Each lithium atom, and each propyl-substituted benzamidinate nitrogen atom, is four-coordinate, with lithium deviating the most from an ideal tetrahedral geometry due to the restricted bite angle of the amidinate group. The central motif of the structure is a four-membered ring of alternating lithium and nitrogen atoms, which is planar by symmetry. To either end of this ring is fused another, slightly puckered, four-membered ring. This puckering sees atoms C(1) and Li(1) lying out of the [Li(1), N(1), C(1), N(2)] least-squares plane of the ring by *ca.* 0.19 and 0.07 Å, respectively. This creates a close Li(1)⋯C(1) contact of 2.334(3) Å, which is possibly electrostatic in nature. This distance is at the lower end of Li⋯CN₂ distances observed for other lithiated amidinates, which are in the range *ca.* 2.30 - 2.42 Å.^{48,49} The Li-N distances and N-Li-N angles in **8** span the typical ranges reported for lithiated amides.^{48,49}

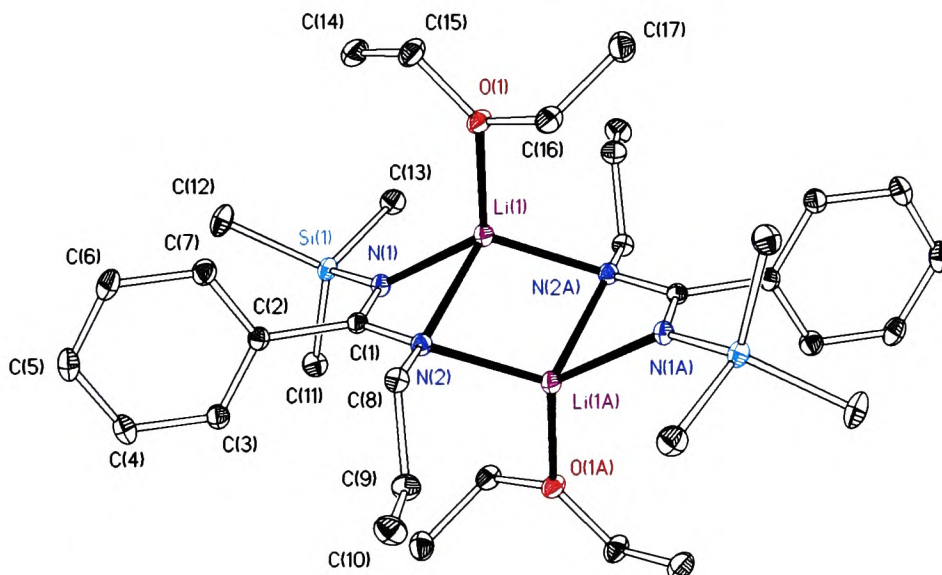


Figure 2.8 Thermal ellipsoid plot (25% probability) of [Li₂{Me₃SiNC(Ph)NCH₂CH₂Me}₂(Et₂O)₂] (**8**). Hydrogen atoms omitted for clarity.

Table 2.3 Selected bond lengths (Å) and angles (°) for $[\text{Li}_2\{\text{Me}_3\text{SiNC(Ph)NCH}_2\text{CH}_2\text{Me}\}_2(\text{Et}_2\text{O})_2]$ (**8**). Atoms carrying the suffix 'A' are related to their counterparts by the symmetry operator $[1-x, 1-y, 2-z]$.

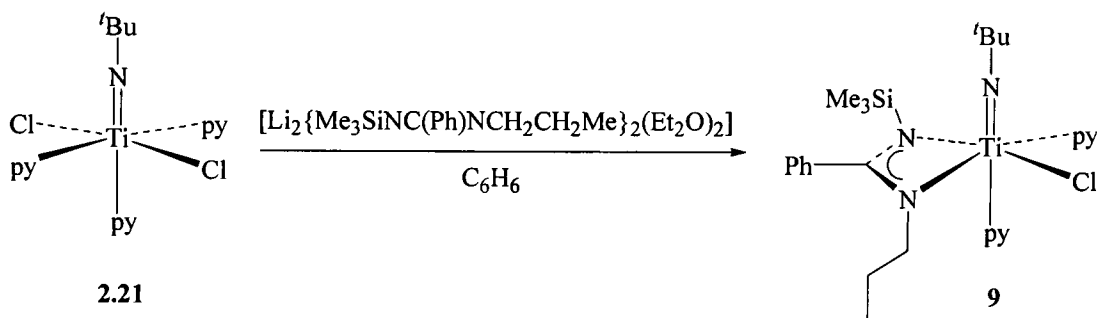
Li(1)-N(1)	2.023(3)	N(1)-Si(1)	1.7083(15)
Li(1)-N(2)	2.145(3)	N(1)-C(1)	1.330(2)
Li(1)-N(2A)	2.073(3)	N(2)-C(1)	1.332(2)
Li(1)-O(1)	1.965(3)	N(2)-C(8)	1.470(2)
Li(1)-C(1)	2.334(3)	C(1)-C(2)	1.512(2)
N(1)-Li(1)-N(2)	66.61(11)	Li(1A)-N(2)-C(1)	127.44(15)
N(1)-Li(1)-N(2A)	121.29(16)	Li(1)-N(2)-C(8)	141.30(14)
N(2)-Li(1)-N(2A)	107.22(14)	Li(1A)-N(2)-C(8)	108.94(14)
N(1)-Li(1)-O(1)	123.08(16)	C(1)-N(2)-C(8)	119.81(15)
N(2)-Li(1)-O(1)	111.49(16)	Li(1)-O(1)-C(15)	134.78(15)
N(2A)-Li(1)-O(1)	113.47(15)	Li(1)-O(1)-C(16)	109.67(14)
Li(1)-N(1)-Si(1)	140.05(12)	C(15)-O(1)-C(16)	112.43(15)
Li(1)-N(1)-C(1)	85.59(14)	N(1)-C(1)-N(2)	118.71(16)
Si(1)-N(1)-C(1)	131.63(13)	N(1)-C(1)-C(2)	119.68(15)
Li(1)-N(2)-Li(1A)	72.78(14)	N(2)-C(1)-C(2)	121.55 (15)
Li(1)-N(2)-C(1)	80.64(13)		

The structural motif in **8** is closely related to those of the Li salts of the pendant N-propylamine-substituted ligands, $\text{Li}_2[\text{Me}_3\text{SiNC(Ph)N(CH}_2)_n\text{NMe}_2]_2$ $\{n = 2$ (**2.1**) or 3 (**2.3**) $\}$.^{32,33} In both of these cases there is no Et_2O coordinated to lithium as this site is occupied by the chelating pendant amine N-donor. Hessen has also proposed a similar binuclear structure for the lithium salt of the pendant methyl(trimethylsilylmethyl)amine ligand $[\text{Li}_2\{\text{Me}_3\text{SiNC(Ph)N(CH}_2)_3\text{N(SiMe}_3\text{)Me}\}_2(\text{THF})_2]$ (**2.8**) in which THF occupies the remaining coordination site.³⁶

2.7.2 Synthesis of $[\text{Ti}(\text{N}^i\text{Bu})\{\text{Me}_3\text{SiNC(Ph)NCH}_2\text{CH}_2\text{Me}\}\text{Cl(py)}_2]$ (**9**)

The titanium imido complex $[\text{Ti}(\text{N}^i\text{Bu})\text{Cl}_2(\text{py})_3]$ (**2.21**) was reacted with one equivalent of the "dummy" arm ligand $[\text{Li}_2\{\text{Me}_3\text{SiNC(Ph)NCH}_2\text{CH}_2\text{Me}\}_2(\text{Et}_2\text{O})_2]$ (**8**) in benzene at room temperature (Equation 2.13). Removal of the volatiles, followed by extraction into benzene and filtration yielded the "dummy" arm

compound $[\text{Ti}(\text{N}^t\text{Bu})\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{Me}\}\text{Cl}(\text{py})_2]$ (**9**). This was recrystallised from a mixture of CH_2Cl_2 and hexanes at $-80\text{ }^\circ\text{C}$.



Equation 2.13

Compound **9** has been characterised by NMR and IR spectroscopies. The ^1H NMR spectrum of **9** is shown in Figure 2.9.

The NMR data are fully consistent with the structure proposed in Equation 2.13. Thus, in addition to the expected resonances for the N^tBu and $\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{Me}$ ligands, the ^1H NMR spectrum shows two very different pyridine ligand environments. The *ortho* hydrogen resonances for these two chemically distinct ligands appear at 9.55 and 8.7 ppm. All the ^1H resonances for the pyridine associated with the more downfield *ortho* resonances are sharp, whereas those for the other pyridine are rather broad. ROESY NMR spectra of **9** established that the two pyridines are in dynamic exchange on the NMR timescale, and a weak *nOe* between the SiMe_3 group of $\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{Me}$ and the sharp *ortho* hydrogen at 9.55 ppm suggested that these two groups are probably mutually *cis* to each other. The chemical shifts of the broad pyridine resonances suggest that this group lies opposite the very *trans*-labilising *tert*-butylimido group. With the N^tBu and two pyridine ligands thus lying in a meridional coordination mode, the remaining $\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{Me}$ and chloride ligands must adopt the relative coordination sites for **9** shown in Equation 2.13, with both of the N-donors of the benzamidinate being *cis* to the imido ligand.

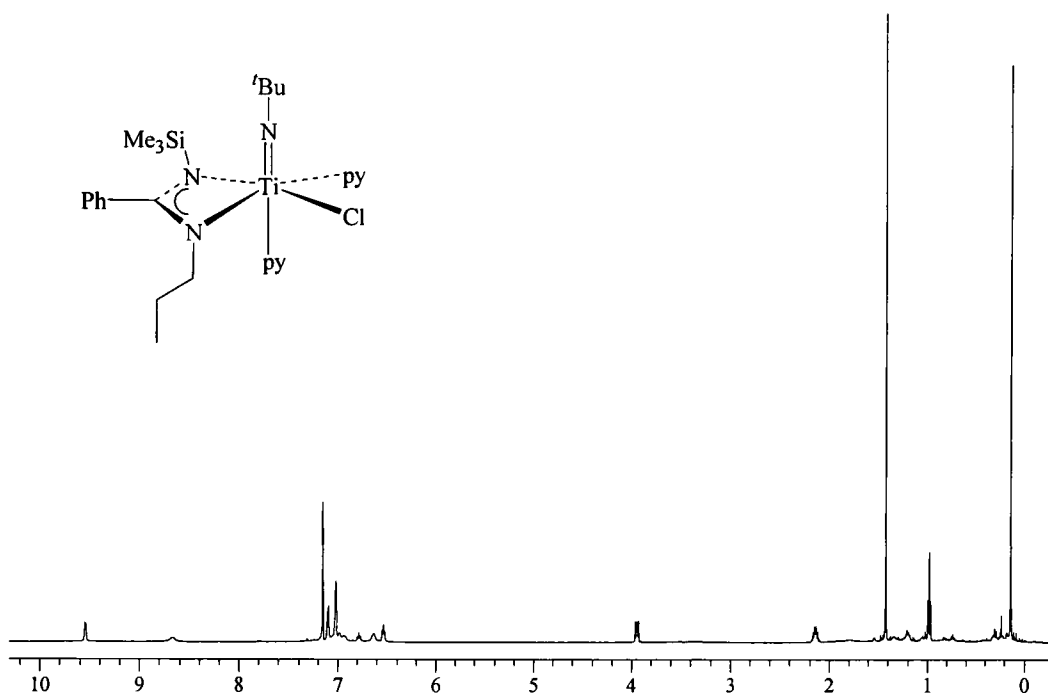


Figure 2.9 500.0 MHz ^1H NMR spectrum of
 $[\text{Ti}(\text{N}^t\text{Bu})\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{Me}\}\text{Cl}(\text{py})_2]$ (**9**) in C_6D_6

It was observed that **9** is not particularly stable in solution. Solutions of **9** in C_6D_6 in sealed tubes under N_2 show significant degradation after one or two hours at ambient temperature, and this thwarted attempts to obtain analytically pure samples. This instability provides further evidence for the importance of pendant arm coordination in the comparatively stable complexes **1** - **6**.

The structure of **9** is in contrast to the six-coordinate complexes $[\text{Ti}(\text{NR})\{\text{PhC}(\text{NSiMe}_3)_2\}\text{Cl}(\text{py})_2]$ ($\text{R} = \text{tert-butyl}$ or aryl) (**2.25** - **2.27**) in which the two chemically equivalent pyridine ligands are mutually *trans* (and *cis* to the imido group) (Equation 2.6). In these symmetrically substituted benzamidinate compounds, one of the benzamidinate nitrogens is *cis* to NR and one approximately *trans*, presumably to minimise the number of unfavourable $\text{N}^t\text{Bu}/\text{NSiMe}_3$ *cis*-interactions.

2.8 Product of trace hydrolysis of **2**

Perhaps unsurprisingly in the light of the somewhat strained structure discussed for **2**, all three 2-carbon arm compounds $[\text{Ti}(\text{NR})\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{NMe}_2\}\text{Cl}]$ (**1** - **3**) are significantly more sensitive to protonation-hydrolysis than their three-carbon arm homologues. An X-ray crystal structure of one such hydrolysis

product is included here. This shows interesting molecular features and demonstrates potential drawbacks of pendant arm amidinates with arms that are "too short". It also suggests possible uses of the parent amidine ligands $\text{Me}_3\text{SiN(H)C(Ph)=NCH}_2\text{CH}_2\text{NMe}_2$ in supramolecular chemistry.

An initial attempt to crystallise $[\text{Ti(N-2,6-C}_6\text{H}_3^i\text{Pr}_2)\{\text{Me}_3\text{SiNC(Ph)NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}\text{Cl}]$ (**2**) from hexanes yielded a small quantity of red crystals of $[\text{Ti}_2(\text{N-2,6-C}_6\text{H}_3\text{Me}_2)_2\text{Cl}_2(\mu\text{-O})\{\text{Me}_3\text{SiN(H)C(Ph)=NCH}_2\text{CH}_2\text{NMe}_2\})]$ (**10**) suitable for X-ray diffraction analysis. Data were collected at 150 K by Dr. B. Tyrrell and the X-ray structure was solved by Dr. P. Mountford. Figure 2.10 shows the molecular structures and Table 2.4 summarises important bond lengths and angles. Full details are provided in Appendix F.

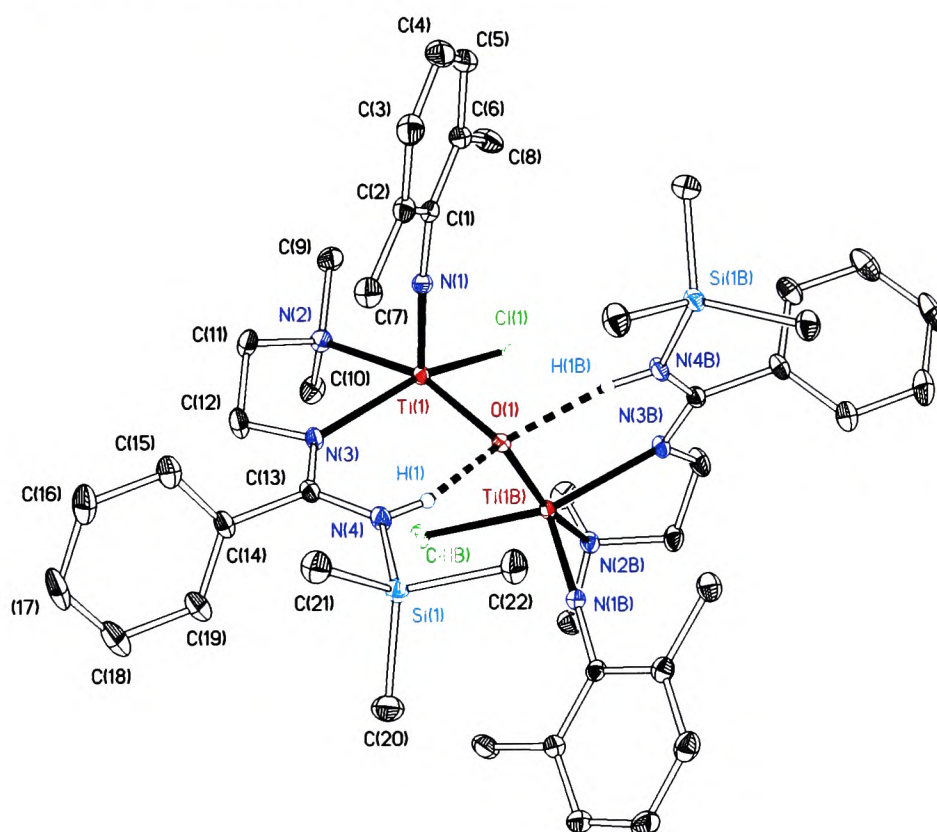


Figure 2.10 Thermal ellipsoid plot (30% probability) of $[\text{Ti}_2(\text{N-2,6-C}_6\text{H}_3\text{Me}_2)_2\text{Cl}_2(\mu\text{-O})\{\text{Me}_3\text{SiN(H)C(Ph)=NCH}_2\text{CH}_2\text{NMe}_2\})]$ (**10**). Hydrogen atoms omitted for clarity.

Table 2.4 Selected bond lengths (Å) and angles (°) for [Ti₂(N-2,6-C₆H₃Me₂)₂Cl₂(μ-O){Me₃SiN(H)C(Ph)=NCH₂CH₂NMe₂}] (**10**)

Ti(1)-N(1)	1.729(2)	N(3)-C(13)	1.308(3)
Ti(1)-N(2)	2.307(2)	N(4)-C(13)	1.352(3)
Ti(1)-N(3)	2.198(2)	N(4)-H(1)	0.88(3)
Ti(1)-Cl(1)	2.4103(6)	N(4)-Si(1)	1.767(2)
Ti(1)-O(1)	1.8808(1)	O(1)···H(1)	2.02(3)
Ti(1)-N(1)-C(1)	174.4(2)	Ti(1)-O(1)···H(1)	96(1)
N(1)-Ti(1)-N(2)	96.62(7)	Ti(1)-O(1)-H(1B)	116(1)
N(1)-Ti(1)-N(3)	101.45(7)	H(1)···O(1)···H(1B)	121(2)
Cl(1)-Ti(1)-N(1)	104.44(6)	C(13)-N(4)-H(1)	113(2)
O(1)-Ti(1)-N(1)	106.21(7)	Si(1)-N(4)-H(1)	116(2)
Ti(1)-O(1)-Ti(1)B	113.7(1)	C(13)-N(4)-Si(1)	131.64(14)
N(4)-H(1)···O(1)	161(3)		

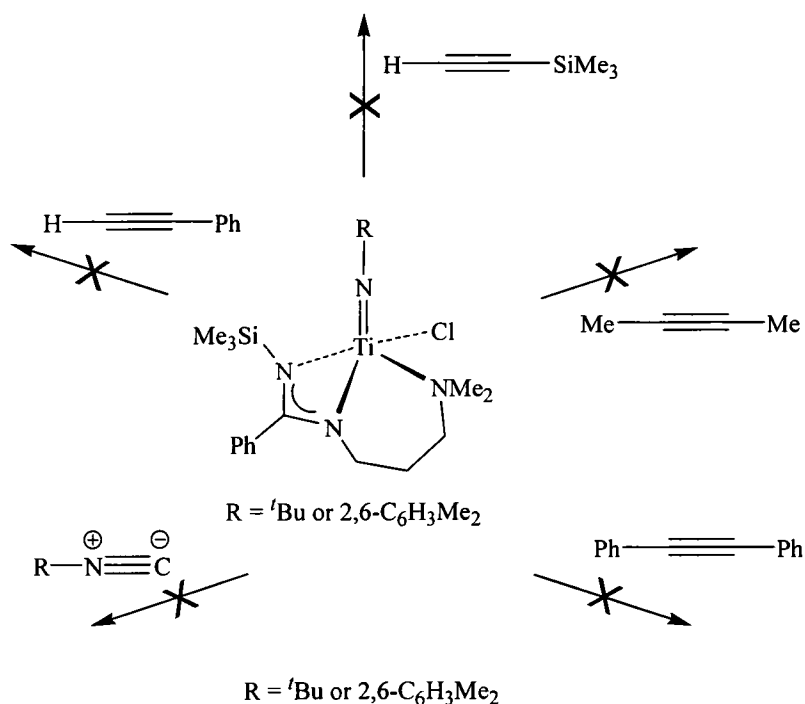
Molecules of **10** (which lie on crystallographic two-fold axes) apparently form from reaction of adventitious H₂O with two molecules of **2**, with the O-H bonds formally inserting into the Ti-NSiMe₃ bonds of **2**. The neutral Me₃SiN(H)C(Ph)=NCH₂CH₂NMe₂ amidine ligand shows shorter N(3)-C(13) [1.308(3) Å] distances, consistent with N(3) being an imino nitrogen and N(4) an amino nitrogen. The amidine acts as a Lewis base through the pendant NMe₂ and imino nitrogens, and as a hydrogen bond donor through the Me₃SiN-H group, this time to a bridging oxo ligand. The geometry at O(1) is close to tetrahedral and the N-H···O distances and angles are consistent with the formation of strong intramolecular hydrogen bonds.^{48,49} Very interestingly, the Ti(1)-O(1)-Ti(1B) angle has a highly acute angle of 113.7(1)°. Over 60 bridging mono-oxo complexes [(L_n)Ti(μ-O)Ti(L_n)] have been crystallographically characterised and the mean Ti-O-Ti angle is 171(7)° (range *ca.* 152-180°).^{48,49} This preference for linearity stems from a requirement to minimise steric interactions between the two titanium centres and to maximise O_{2π}→Ti_{3dπ} π interactions. It seems very likely that the two strong N-H···O interactions cause the highly bent Ti-O-Ti linkage in **10**.

The solution ^1H NMR spectrum of **10** is consistent with the solid state structure. There is a broad resonance at 10.6 ppm (integral 2 H per dimeric molecule) which is assigned to the $\text{NH}\cdots\text{O}$ hydrogen atoms.

2.9 Reaction of chloride derivatives with unsaturated substrates

Previous studies have shown that certain Group 4 imido complexes undergo interesting stoichiometric reactions with a variety of unsaturated substrates.⁵¹⁻⁵⁴ It was hoped that the 14-electron chloride derivatives **1** - **6** might react with substrates such as acetylenes, heterocumulenes and isocyanides.

The 3-carbon linker compounds **4** and **5** were initially selected for these screening reactions owing to their excellent stability in solution and towards heating. Stoichiometric amounts of acetylene, isocyanate or isocyanide were added to solutions of these compounds in C_6D_6 and their reactions were monitored over several days at room temperature and after heating to 80 °C. These reactions are summarised in Scheme 2.5.



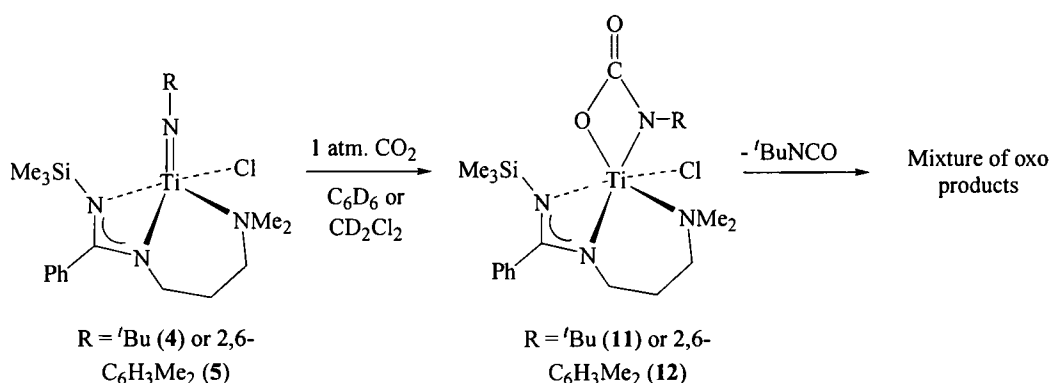
Scheme 2.5 Attempted reactions of **4** and **5** with unsaturated substrates

Disappointingly, the chloride compounds **4** and **5** proved to be unreactive towards most of the unsaturated substrates screened. However, they showed reactivity

towards CO₂ which mirrored that of the cyclopentadienyl amidinate-imido complexes to be discussed in Chapter 3.

2.9.1 Reactions of 4 and 5 with CO₂

A solution of **4** in C₆D₆ was exposed to *ca.* 1 atm CO₂ *via* a Schlenk line. The orange solutions immediately became cherry red in colour. The ¹H NMR spectrum of the reaction recorded after 4 minutes showed complete consumption of the starting material to form a new product presumed to be a carbamate complex formed by cycloaddition of CO₂ to the Ti=N^tBu bond. This began to decompose within 10 minutes and, after 1 hour, a complex mixture of products was formed, which included a resonance at 0.84 ppm attributed to ^tBuNCO by comparison with an authentic sample. This is consistent with decomposition to a mixture of oxo products with concomitant extrusion of isocyanate (Equation 2.14).



Equation 2.14

In order to examine these reactions more closely, solutions of **4** and **5** in CD₂Cl₂ at -78 °C were exposed to CO₂. Samples were immediately transferred to an NMR spectrometer with a probe maintained at the same temperature and full NMR data of the resulting carbamate complexes [Ti{N^tBuC(O)O}{Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂}Cl] (**11**) and [Ti{N(-2,6-C₆H₃Me₂)C(O)O}{Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂}Cl] (**12**) were recorded. The unstable nature of **11** and **12** in solution prevented these reactions being successfully scaled up, so only characterisation of these complexes by NMR spectroscopy was possible.

As the ¹H NMR spectra of compounds **11** and **12** contain very similar features, discussion will be confined to that of **11** shown in Figure 2.11.

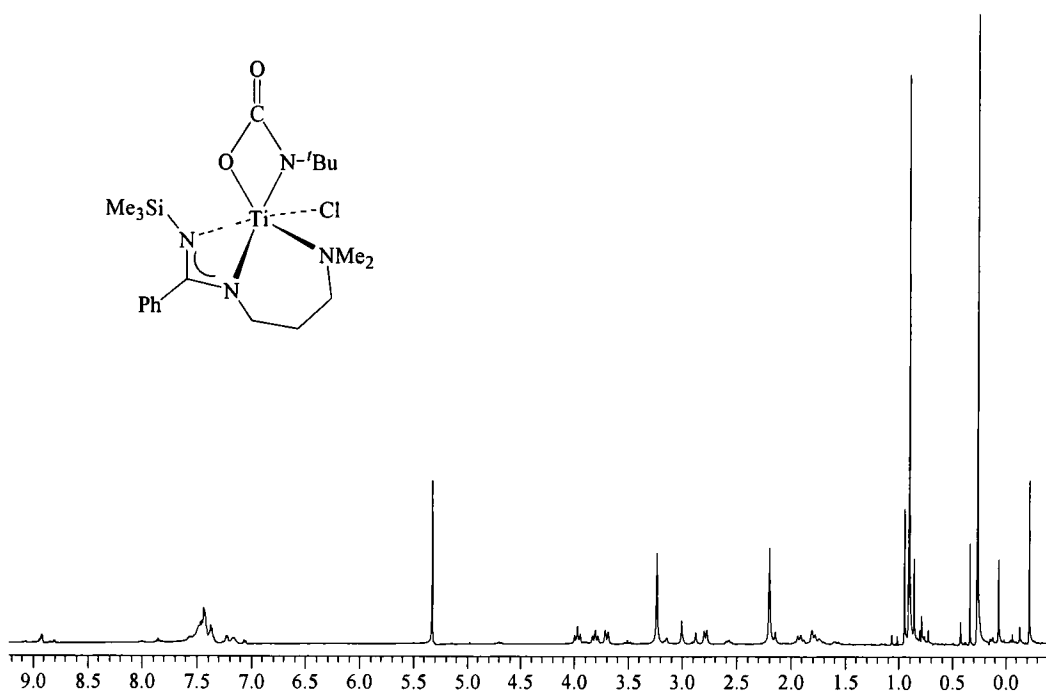


Figure 2.11 500.0 MHz ^1H NMR spectrum of
 $[\text{Ti}\{\text{N}'\text{BuC}(\text{O})\text{O}\}\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}\text{Cl}]$ (**11**)

As can clearly be seen from Figure 2.11, it was difficult to obtain a pure sample of **11** or **12** uncontaminated by either unreacted chloride **4** or **5** or by oxo decomposition products. The ^1H NMR spectra contain the expected resonances for a κ^3 -amidinate ligand and a *tert*-butyl group. The 3 H singlets (2.12 and 3.13 ppm) for the NMe groups of the pendant amine indicate firm coordination of the arm on the NMR timescale. The $^{13}\text{C}\{-^1\text{H}\}$ NMR spectra of **11** and **12** both contain a very deshielded resonance at *ca.* 175 ppm, attributed to the C=O carbon of the carbamate fragment.

2.10 Summary

This Chapter describes the synthesis and characterisation of a series of titanium amidinate-imido complexes with 2- and 3-carbon pendant arm functionalised amidinate ligands. Four of these compounds have been crystallographically characterised. A derivative has also been prepared with a pendant propyl "dummy" arm (**9**) in order to make a comparison with symmetrically substituted non-pendant arm amidinate compounds previously synthesised. The product of an adventitious protonation-hydrolysis reaction to form an intramolecularly hydrogen-bonded dimer **10** has been structurally characterised. The reactions of

some pendant arm functionalised amidinate-imido complexes with CO₂ have been described.

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Chapter 3

Cyclopentadienyl Amidinate-Imido Compounds: Synthesis and Reactions with CO₂

3.1 Overview

This Chapter describes the synthesis and characterisation of some pendant-arm functionalised cyclopentadienyl amidinate-imido complexes and examines their reactions with CO₂. It begins by introducing the cyclopentadienyl-amidinate ligand set, and work previously carried out in the Mountford group on the synthesis and reactivity of cyclopentadienyl-amidinate imido compounds is discussed (Sections 3.2 - 3.3). The remainder of the Chapter is divided into two parts. The first part discusses the synthesis and characterisation of new pendant arm functionalised amidinate-imido compounds and their reactions with CO₂, including kinetic and density functional theory studies (Sections 3.4 - 3.6). The second part focuses on some wider issues in the reactions of amidinate-imido compounds with CO₂ and addresses some questions raised by earlier work (Section 3.7).

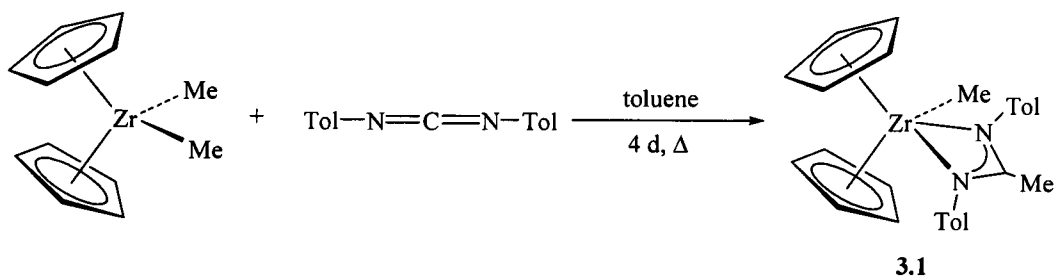
3.2 Introduction

This Section describes some recent work the chemistry of cyclopentadienyl-amidinate complexes, leading into a discussion of work previously carried out in the Mountford group using these ligands.

3.2.1 The cyclopentadienyl-amidinate ligand set

The possibility of combining amidinate ligands with cyclopentadienyl ligands to form a new supporting ligand environment has been investigated. The similarity with metallocene complexes (but with 2 fewer valence electrons) and the potential for Ziegler-Natta type polymerisation catalysts mean that the Group 4 complexes have been the most intensively studied.

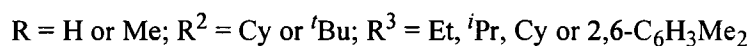
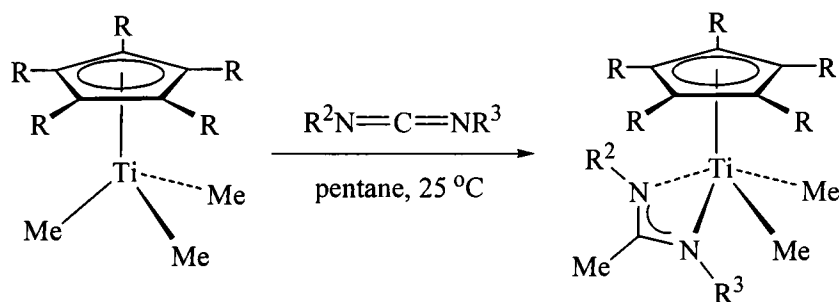
The first Group 4 cyclopentadienyl-amidinate titanium complex was synthesised in 1985 by Gambarotta and coworkers.¹ They found that *p*-tolylcarbodiimide inserted into a Zr-C bond of [Zr(η -C₅H₅)Me₂] to produce the acetamidinate derivative **3.1** as shown in Equation 3.1.



Equation 3.1

Another early example was the formation of $[\text{Ti}(\eta\text{-C}_5\text{Me}_5)\{(\text{4-C}_6\text{H}_4\text{OMe})\text{C}(\text{NSiMe}_3)_2\}\text{F}_2]$ by Roesky *et al.* by the reaction of $\text{Li}[(\text{4-C}_6\text{H}_4\text{OMe})\text{C}(\text{NSiMe}_3)_2]$ with $[\text{Ti}(\eta\text{-C}_5\text{Me}_5)\text{F}_3]$.²

The complexes $[\text{M}(\eta\text{-C}_5\text{R}_5)\{\text{PhC}(\text{NSiMe}_3)_2\}\text{Cl}_2]$ ($\text{R} = \text{H}$, $\text{M} = \text{Ti}$, Zr , Hf ; $\text{R} = \text{Me}$, $\text{M} = \text{Ti}$, Zr) were first prepared by Green *et al.* in 1993.³ A number of studies on these compounds have since been undertaken, mainly focusing on their potential for olefin polymerisation catalysis.⁴⁻⁶ More recently, Sita *et al.* have reported the facile synthesis of a varied library of complexes of the form $[\text{Ti}(\eta\text{-C}_5\text{R}_5)\{\text{MeC}(\text{NR}^2)(\text{NR}^3)\}\text{Me}_2]$ by reaction of $\text{Ti}(\eta\text{-C}_5\text{R}_5)\text{Me}_3$ with a range of carbodiimides (Equation 3.2).⁷ Sita has also synthesised and studied chiral complexes such as *meso*-(*R,S*)- and (*R,R*)- $[\text{Ti}(\eta\text{-C}_5\text{Me}_5)\{\text{MeC}(\text{N-1-phenylethyl})_2\}\text{Me}_2]$ $\{\text{R} = \text{H}$, (*R,S*) (*R,R*); $\text{R} = \text{Me}$, (*R,S*), (*R,R*) $\}$.⁸



Equation 3.2

In addition to these titanium systems, work has recently been published on zirconium cyclopentadienyl-amidinate dimethyl complexes. Structural characterisation⁹ and stability studies¹⁰ have been carried out, 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-hexene¹¹ and vinylcyclohexene,¹² and the cyclopolymerisation of nonconjugated dienes.¹³

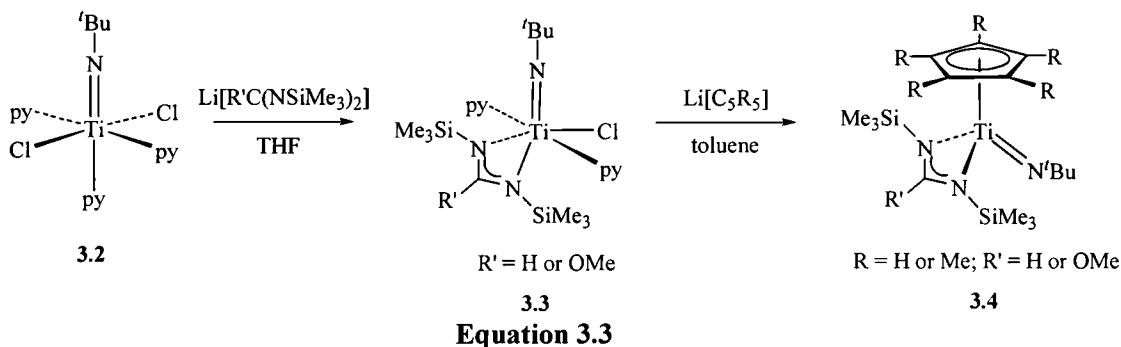
The cyclopentadienyl-amidinate ligand set has also been used to support complexes of vanadium,¹⁴ niobium,¹⁵ tantalum,^{15,16} ruthenium,^{17,18} and iridium.¹⁹ Transition metal imido complexes supported by the cyclopentadienyl-amidinate ligand set have only been reported in the case of titanium and will be discussed in the following Section.

3.3 Cyclopentadienyl amidinate-imido compounds

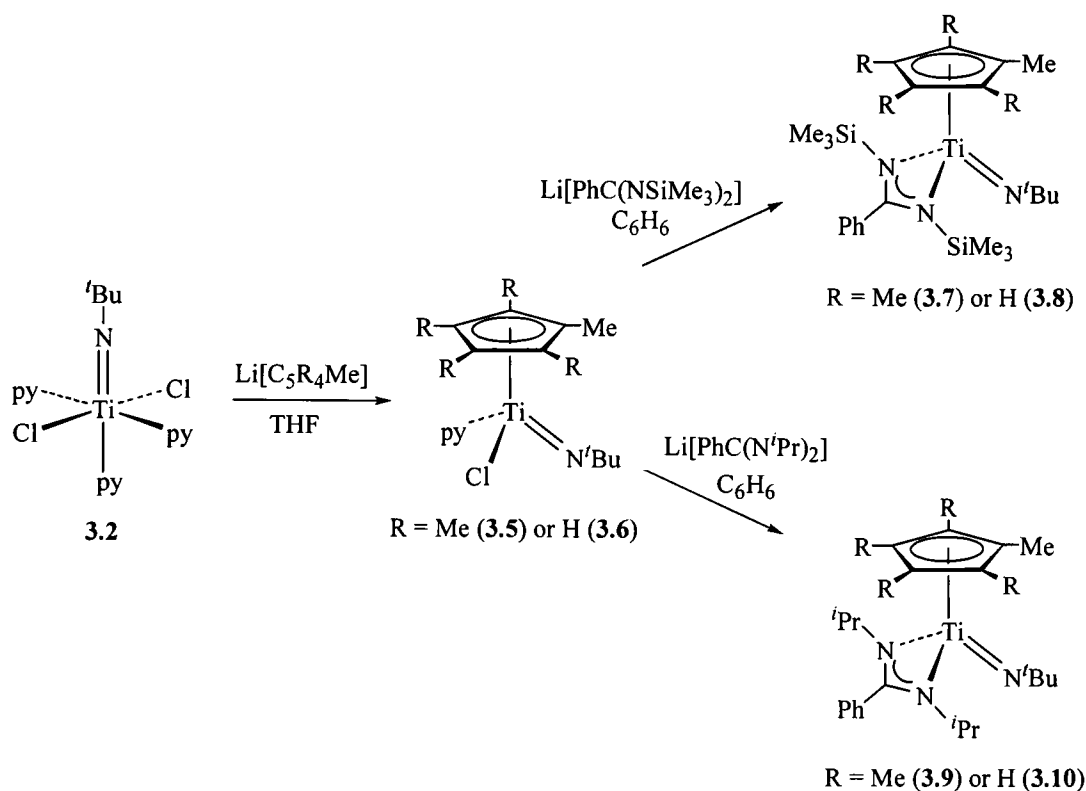
This Section will describe previous work on cyclopentadienyl-amidinate supported imido compounds and discuss the reactions of some of these compounds with CO₂.

3.3.1 Synthesis of cyclopentadienyl amidinate-imido compounds

The compound [Ti(N^{*t*}Bu)Cl₂(py)₃] (**3.2**), first synthesised by Mountford *et al.*,²⁰ has been found to be a versatile entry point into titanium imido chemistry. It was from this starting material that the first titanium imido complexes bearing a cyclopentadienyl-amidinate ancillary ligand set were synthesised, *via* metathesis of the starting complex with the lithium salt of the amidinate, followed by the introduction of the cyclopentadienyl ligand (Equation 3.3).²¹

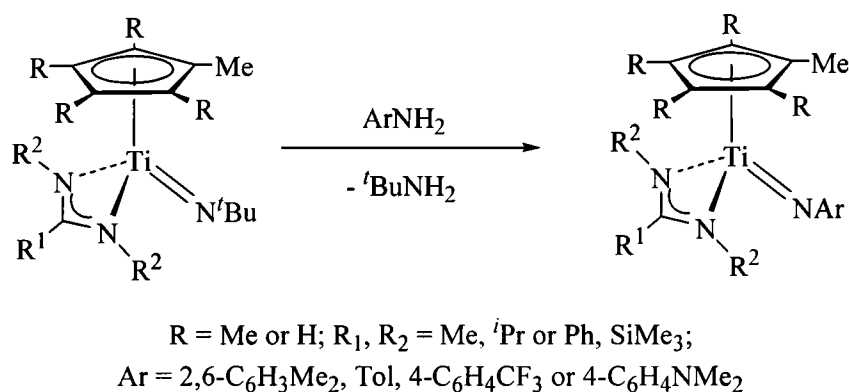


It was found that assembling the ancillary ligand set in the reverse order, by reacting the starting complex **3.2** with the appropriate lithium cyclopentadienide followed by the lithium amidinate, gave improved yields.²¹ A range of titanium *tert*-butyl imido complexes with cyclopentadienyl-amidinate supporting ligands have been prepared by this route (Scheme 3.1).²²



Scheme 3.1 Preparation of *tert*-butyl cyclopentadienyl amidinate-imido compounds

Reaction of these compounds with a range of anilines yielded arylimido cyclopentadienyl amidinate-imido compounds *via* amine-imido exchange reactions (Equation 3.4).²²



Equation 3.4

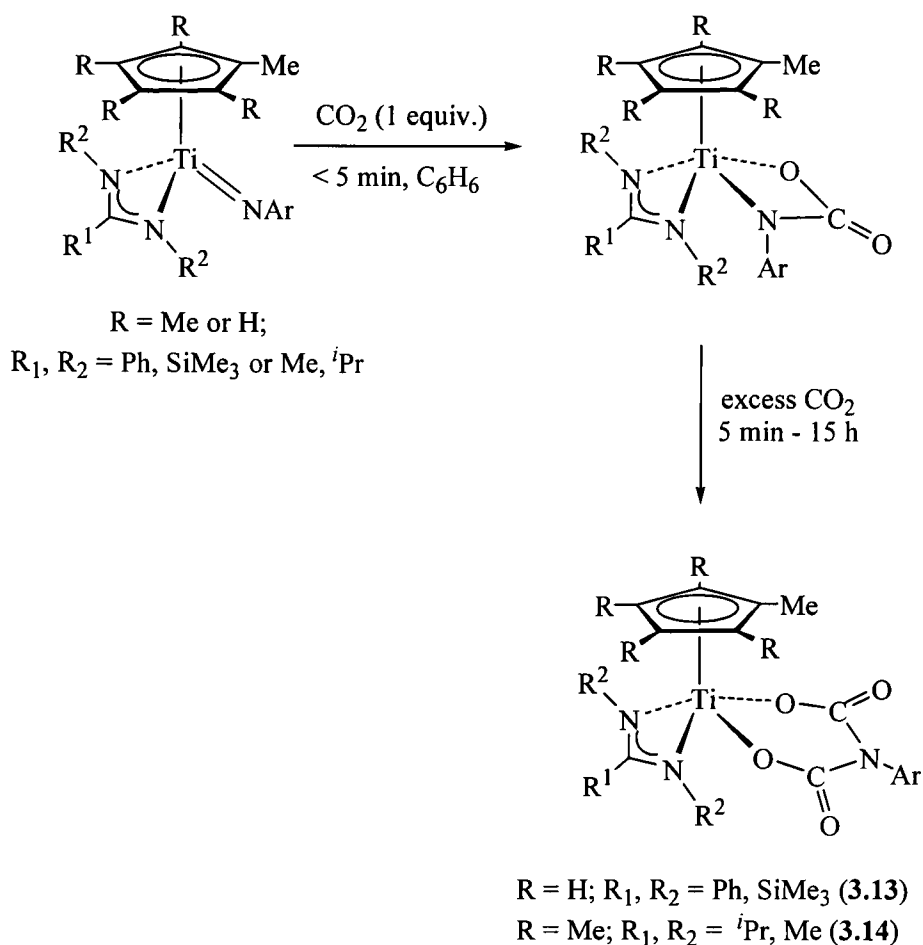
This method was generally the most successful synthesis of this type of compound, although the more crowded species $[\text{Ti}(\eta\text{-C}_5\text{Me}_5)(\text{N-2,6-C}_6\text{H}_3\text{Me}_2)\{\text{PhC}(\text{NSiMe}_3)_2\}]$ (3.11) was only obtained by assembling the

cyclopentadienyl-amidinate ligands around the first-formed arylimido starting complex $[\text{Ti}(\text{N}-2,6\text{-C}_6\text{H}_3\text{Me}_2)\text{Cl}_2(\text{py})_3]$ (**3.12**).²³

3.3.2 Reactions of cyclopentadienyl-amidinate imido compounds with CO_2

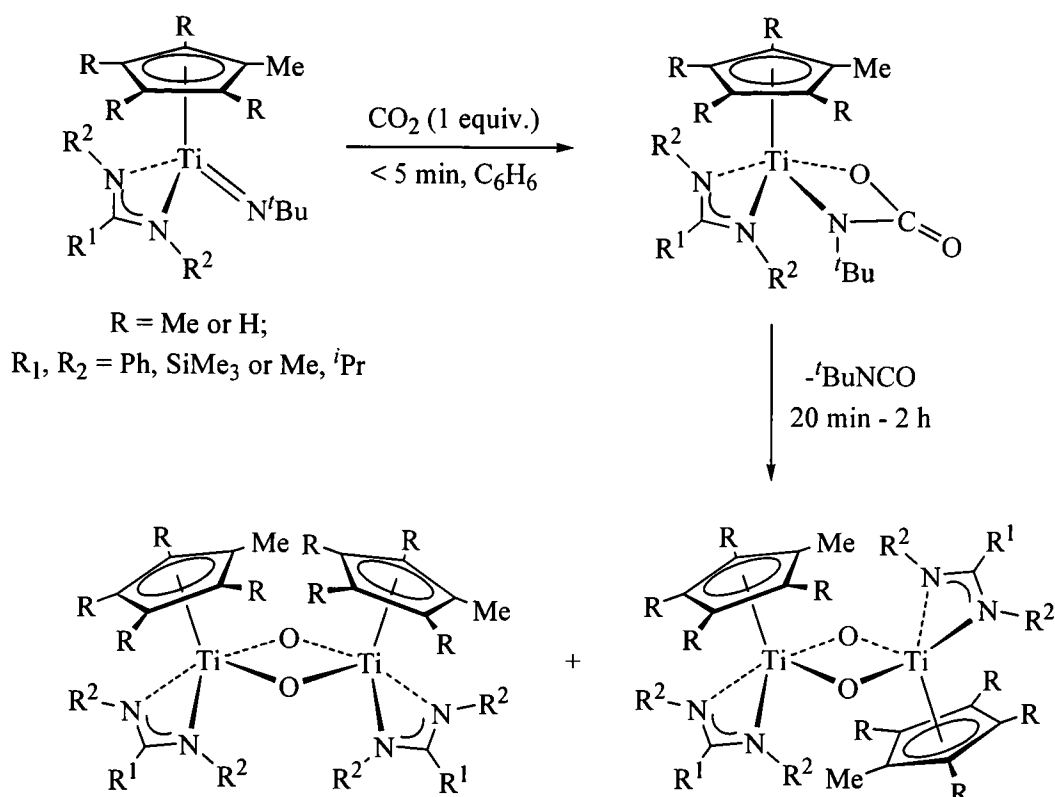
These cyclopentadienyl complexes were found to undergo reactions with a range of unsaturated substrates, including alkynes and the heteroallenes RNCO , CS_2 , RNCS , COS and CO_2 .^{22,23} The reactions with RNCO and CO_2 were especially interesting and novel. The CO_2 chemistry is most relevant to this Thesis and is described below.

The arylimido cyclopentadienyl-amidinate compounds (Equation 3.4) underwent reaction with one equivalent of CO_2 to form carbamate complexes *via* [2+2] cycloaddition to the $\text{Ti}=\text{NAr}$ bond (Scheme 3.2). This was accompanied by a loss of C_s symmetry of the starting compounds as evidenced by the ^1H and ^{13}C NMR spectra, and the appearance of a new absorption in the IR spectrum in the range $1667 - 1671\text{ cm}^{-1}$, indicative of a $\nu(\text{C}=\text{O})$ stretch. Upon standing in solution under a CO_2 atmosphere, these carbamates underwent further insertion of CO_2 to form dicarboxylate products. This was accompanied by regaining of C_s symmetry and observation of 2 new bands in the $\nu(\text{C}=\text{O})$ region of the IR spectrum. Two of these compounds, $[\text{Ti}(\eta\text{-C}_5\text{H}_4\text{Me})\{\text{OC}(\text{O})\text{N}(2,6\text{-C}_6\text{H}_3\text{Me}_2)\text{C}(\text{O})\text{O}\}\{\text{MeC}(\text{NSiMe}_3)_2\}]$ ²³ (**3.13**) and $[\text{Ti}(\eta\text{-C}_5\text{Me}_5)\{\text{OC}(\text{O})\text{N}(2,6\text{-C}_6\text{H}_3\text{Me}_2)\text{C}(\text{O})\text{O}\}\{\text{MeC}(\text{N}^i\text{Pr})_2\}]$ ²² (**3.14**) have been crystallographically characterised. This type of double substrate activation with complete cleavage of the metal-imide bond is highly unusual and has not been authenticated before for any allene or their heteroanalogues. The only related example is for the reaction of the late transition metal imide $[\text{Ir}(\eta\text{-C}_5\text{Me}_5)(\text{N}^i\text{Bu})]$ with certain alkynes.²⁴ The $\{\text{O}(\text{CO})\text{N}(\text{Ar})(\text{CO})\text{O}\}$ fragment (derived formally from the dianionic conjugate base of azamalononic acid) has not been structurally characterised previously and represents a new type of ligand. The rate at which the second molecule of CO_2 was incorporated into the molecule was found to be strongly dependent upon the ancillary ligand set, with the more bulky carbamates being more stable towards addition of a second molecule of CO_2 .



Scheme 3.2 Reactions of cyclopentadienyl-amidinate arylimido compounds with CO_2

In the case of the *tert*-butyl imido compounds, cycloaddition to form carbamate intermediates was also found to occur upon exposure to CO_2 (Scheme 3.3). However, these products were unstable and decomposed in solution (even under a CO_2 atmosphere) to form dimeric μ -bridged oxo compounds *via* extrusion of *tert*-butyl isocyanate. The rate of decomposition of carbamate was again dependent upon the bulk of the supporting ligands. In the case of the $\text{C}_5\text{H}_4\text{Me}$ -supported compounds, two isomeric μ -bridged oxo products were observed (*cis* and *trans* cyclopentadienyl ligands). It was proposed that carbamate decomposition proceeds *via* a transient terminal oxo compound which self-traps by dimerisation, although no evidence for such a species was observed in the NMR spectra during these reactions.



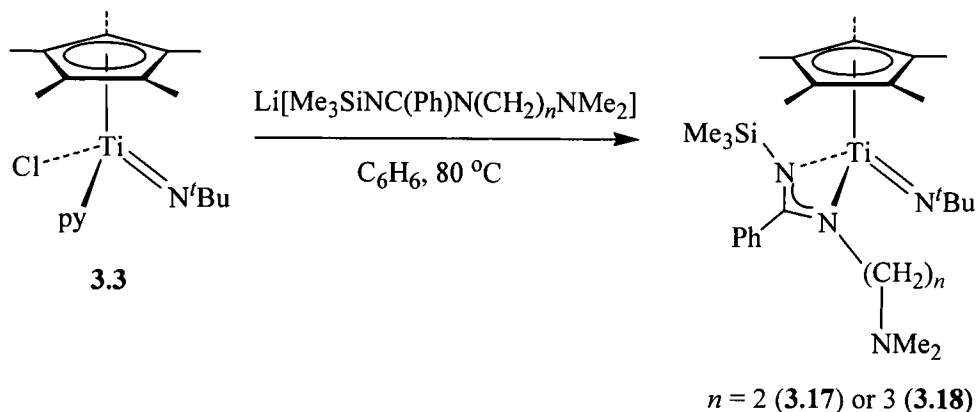
Scheme 3.3 Reactions of cyclopentadienyl-amidinate *tert*-butylimido compounds with CO_2

3.3.3 Cyclopentadienyl pendant arm functionalised-amidinate imido compounds

Motivated by the potential of cyclopentadienyl-amidinate titanium imido complexes to offer control of CO_2 reactivity, we set out to develop pendant-arm functionalised amidinate systems in order to probe the effects of an additional hemi-labile donor on the $\text{Ti}=\text{NR}/\text{CO}_2$ bond making and bond breaking reactions. In carrying this out, the two previously prepared dimethylamino-functionalised amidinate ligands $\text{Me}_3\text{SiNC(Ph)NCH}_2\text{CH}_2\text{NMe}_2$ (two carbon linker between the benzamidinate nitrogen and the NMe_2 group) and $\text{Me}_3\text{SiNC(Ph)NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2$ (three carbon linker), were used.^{25,26}

Reaction of $[\text{Ti}(\eta\text{-C}_5\text{Me}_5)(\text{N}^t\text{Bu})\text{Cl}(\text{py})]$ (**3.5**) with $\text{Li}[\text{Me}_3\text{SiNC(Ph)NCH}_2\text{CH}_2\text{NMe}_2]$ (**3.15**) or $\text{Li}[\text{Me}_3\text{SiNC(Ph)NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2]$ (**3.16**) in benzene at 80°C produced the compounds $[\text{Ti}(\eta\text{-C}_5\text{Me}_5)(\text{N}^t\text{Bu})$

$\{\text{Me}_3\text{SiNC(Ph)NCH}_2\text{CH}_2\text{NMe}_2\}$ (3.17) and $[\text{Ti}(\eta\text{-C}_5\text{Me}_5)(\text{N}^t\text{Bu})\{\text{Me}_3\text{SiNC(Ph)NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}]$ (3.18) in good yields. (Equation 3.5).²⁷

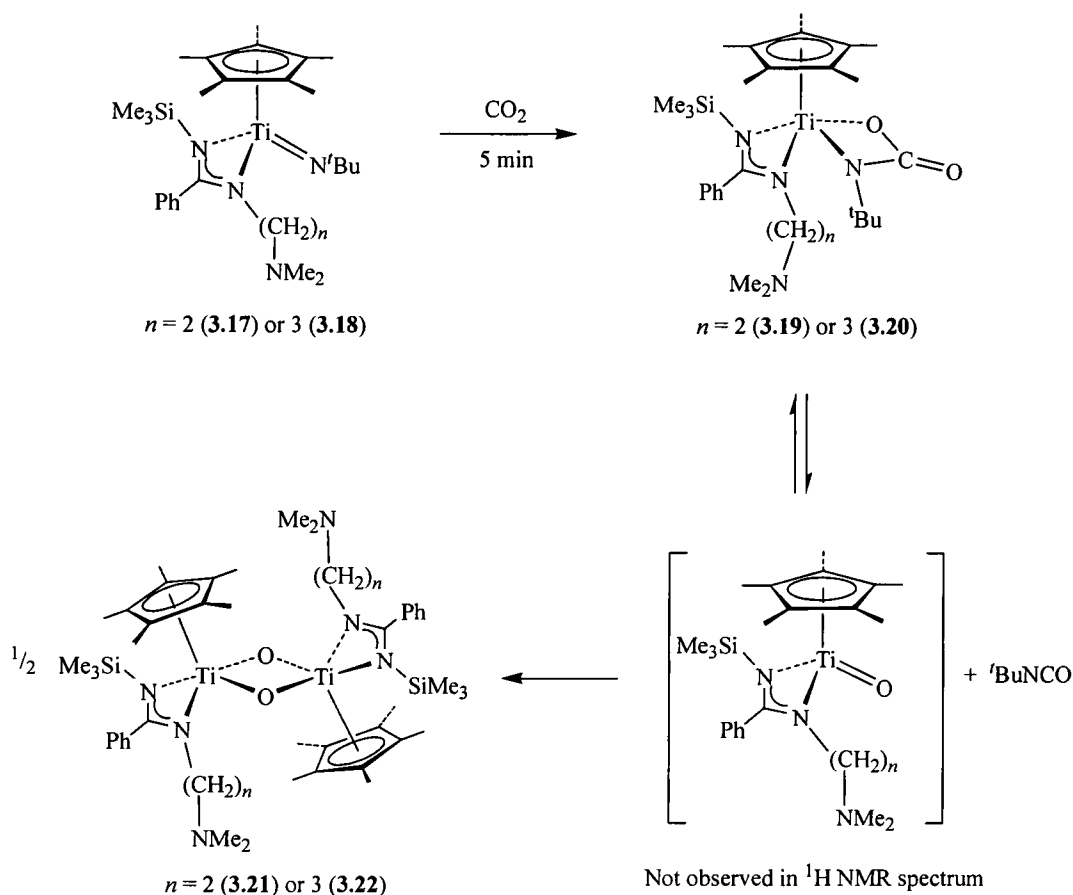


Equation 3.5

Room temperature ^1H NMR spectra for both compounds featured a singlet (6 H) for the NMe_2 protons, indicating either that the pendant arm is not coordinated to the metal centre or that methyl group exchange is fast on the NMR timescale at this temperature. Cooling NMR samples to $-90\text{ }^\circ\text{C}$ in CD_2Cl_2 (500.0 MHz ^1H resonance frequency) revealed some broadening of the NMe_2 resonances but did not result in splitting into two separate resonances. Therefore the pendant NMe_2 groups probably coordinate very weakly to the metal, but even at low temperatures easily dissociate. This was confirmed by the observation of only one resonance for the NMe_2 methyls in the $^{13}\text{C}\{-^1\text{H}\}$ NMR spectra at $-90\text{ }^\circ\text{C}$.

3.3.4 Reaction of cyclopentadienyl pendant arm functionalised amidinate imido compounds towards CO_2

Reaction of the compounds $[\text{Ti}(\eta\text{-C}_5\text{Me}_5)(\text{N}^t\text{Bu})\{\text{Me}_3\text{SiNC(Ph)N(CH}_2\text{)}_n\text{NMe}_2\}]$ [$n = 2$ (3.17) or 3 (3.18)] with CO_2 (1 atm) at room temperature for 5 minutes, followed by immediate isolation, yielded the cherry-red N,O-bound carbamates $[\text{Ti}(\eta\text{-C}_5\text{Me}_5)(\text{N}^t\text{BuC(O)O})\{\text{Me}_3\text{SiNC(Ph)N(CH}_2\text{)}_n\text{NMe}_2\}]$ [$n = 2$ (3.19) or 3 (3.20)] in 76 and 82% isolated yields respectively (Scheme 3.4)



Scheme 3.4 Reactions of pentamethylcyclopentadienyl pendant arm amidinate-imido compounds with CO_2

The 3-carbon linker carbamate **3.20** was crystallographically characterised (Figure 3.1). The carbamate products **3.19** and **3.20** were unstable in solution and decomposed over *ca.* 1 h with elimination of $^t\text{BuNCO}$, as identified by ^1H NMR spectroscopy, to form oxo compounds. The absence of terminal $\text{Ti}=\text{O}$ stretches²⁸⁻³¹ in the range $850 - 930\text{ cm}^{-1}$ in the IR spectra of these oxo products points to the dimeric μ -oxo bridged structures $[\text{Ti}_2(\eta\text{-C}_5\text{Me}_5)_2(\mu\text{-O})_2\{\text{Me}_3\text{SiNC(Ph)N(CH}_2)_n\text{NMe}_2\}_2]$ [$n = 2$ (**3.21**) or 3 (**3.22**)] and is supported by the non-pendant arm acetamidinate analogue $[\text{Ti}_2(\eta\text{-C}_5\text{Me}_5)_2(\mu\text{-O})_2\{\text{PhC(N}^t\text{Pr)}_2\}_2]$ (**3.23**) which has been shown to be dimeric by X-ray crystallography (Section 3.3.2).²² The dimeric μ -oxo compounds were found to be highly insoluble, so neither NMR data nor mass spectra could be obtained.

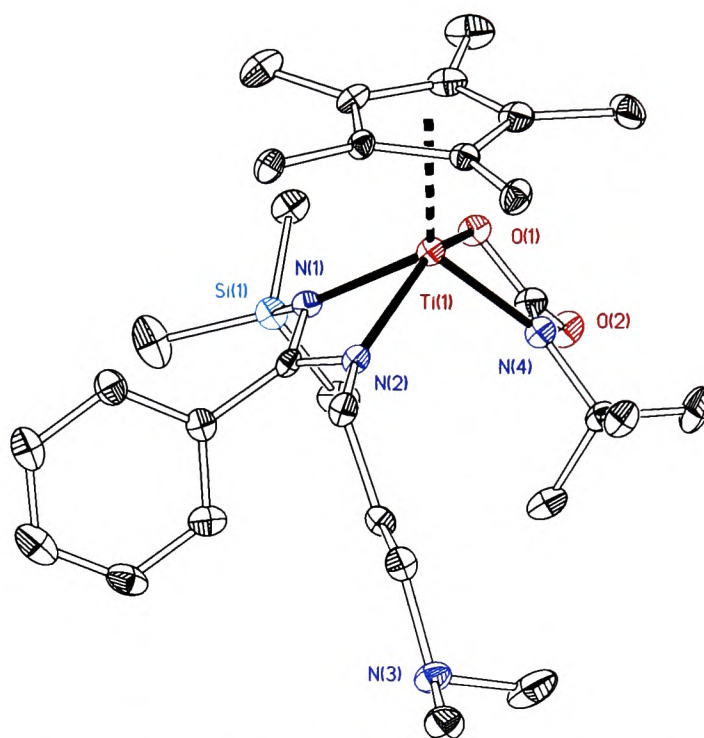


Figure 3.1 Thermal ellipsoid plot of [Ti(η -C₅Me₅)(NⁱBuC(O)O){Me₃SiNC(Ph)NCH₂CH₂NMe₂}] (**3.20**), 20%. Hydrogen atoms omitted for clarity.

The proposed mechanism for this process involves a retrocyclisation to initially form a terminal oxo complex (possibly with weak NMe₂ coordination). No evidence is observed for this species in the NMR tube scale reactions suggesting immediate back reaction with ^tBuNCO or self-trapping to give the corresponding oxo dimer occurs. Decomposition of the carbamates to form the oxo products was much faster in these pendant arm functionalised systems (*ca.* 1 hour) than for the previously reported acetamidinate system [Ti(η-C₅Me₅){N^tBuC(O)O}{MeCN(ⁱPr)₂}] and benzamidinate system [Ti(η-C₅Me₅){N^tBuC(O)O}{PhCN(SiMe₃)₂}] which take *ca.* 12 hours and 5 days respectively to completely decompose.²³ This possibly suggests that the pendant arm may play a role in the extrusion step (an anchimeric effect).³² Alternatively the difference in steric demands of the N-substituents of the two different amidinate ligands may be responsible, for example the C₅H₄Me-supported carbamate [Ti(η-C₅H₄Me){N^tBuC(O)O}{MeCN(NⁱPr)₂}] decomposes more rapidly than [Ti(η-C₅Me₅){N^tBuC(O)O}{MeCN(NⁱPr)₂}] .

3.3.5 Summary and objectives

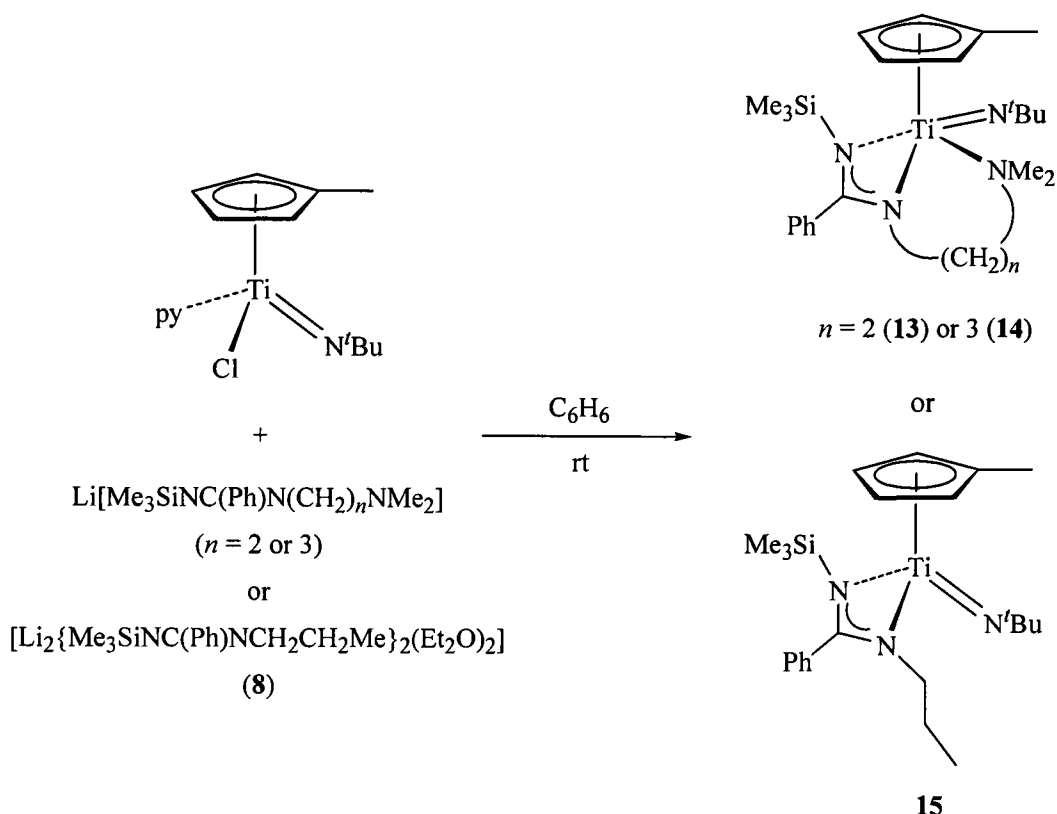
The reactions of the pendant arm functionalised amidinate complexes **3.17** and **3.18** demonstrate that these systems are convenient for more detailed studies of the reactions of cyclopentadienyl amidinate-imido complexes with CO₂. It was decided to synthesise the sterically less crowded methylcyclopentadienyl analogues and compare their reactivity, with the aim of gaining greater insight into the mechanisms of such reactions. This work is described in the following Sections.

3.4 Methyl cyclopentadienyl pendant arm functionalised benzamidinate *tert*-butyl imido compounds

The starting compound [Ti(η-C₅H₄Me)(N^tBu)Cl(py)] (**3.6**) was prepared as previously described by reaction of [Ti(N^tBu)Cl₂(py)₃] (**3.2**) with Li[C₅H₄Me].³³ The lithiated pendant arm amidinates Li[Me₃SiNC(Ph)NCH₂CH₂NMe₂] (**3.17**) and Li[Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂] (**3.18**) were prepared according to literature procedures.^{25,26}

Reaction of [Ti(η-C₅H₄Me)(N^tBu)Cl(py)] with **3.17** or **3.18** or with the "dummy arm" amidinate [Li₂{Me₃SiNC(Ph)NCH₂CH₂Me}₂(Et₂O)₂] (**8**) in benzene at room temperature afforded the compounds [Ti(η-C₅H₄Me)(N^tBu){Me₃SiNC(Ph)NCH₂CH₂NMe₂}] (**13**), [Ti(η-C₅H₄Me)(N^tBu){Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂}] (**14**) and [Ti(η-C₅H₄Me)(N^tBu){Me₃SiNC(Ph)NCH₂CH₂Me}] (**15**) in good crude yields (Equation 3.6).

The new compounds **13**, **14** and **15** are oils at room temperature but were purified by high vacuum sublimation (1 x 10⁻⁵ mbar, 120 - 130 °C) in 69 - 75% overall yields. They were characterised by NMR and IR spectroscopies, E.I. mass spectrometry and elemental analysis. In the case of the "dummy arm" compound **15** the molecular ion was observed in the high resolution E.I. mass spectrum. Full details are given in Chapter 6.

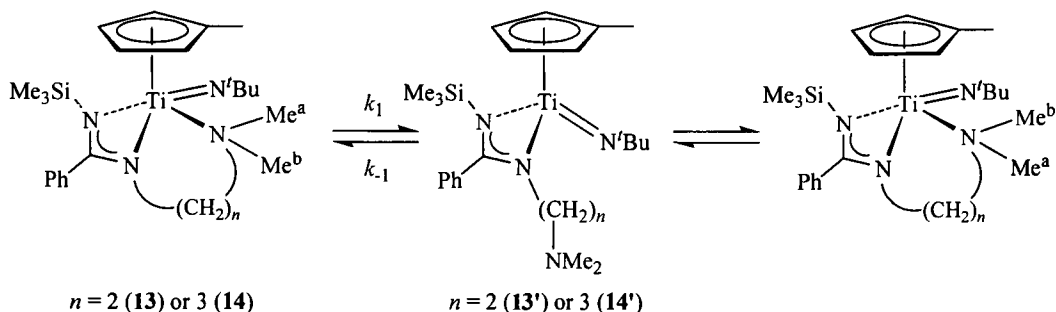


Equation 3.6

The ^1H NMR spectra of all three compounds are sharp and well resolved at room temperature, giving rise to the expected resonances. Without coordination of the pendant NMe_2 group to the metal, **13** and **14** are formally 16 valence electron complexes. Coordination of NMe_2 to titanium would form an 18 valence electron compound and also render the methyl groups of the NMe_2 fragment chemically inequivalent. The ^1H NMR spectra for both compounds at room temperature feature a 6 H singlet for the NMe_2 protons indicating either that the pendant arm is not coordinated to the metal centre or that methyl group exchange is fast on the NMR timescale at this temperature. However, it was thought likely that evidence of NMe_2 coordination might be found at lower temperatures. Therefore, a series of low and variable temperature NMR experiments was carried out.

Cooling NMR samples of **13** and **14** in CD_2Cl_2 revealed decoalescence points for the NMe_2 singlets at -36 °C and -65 °C respectively, below which two distinct NMe_2 resonances were observed. This indicates that the NMe_2 groups in **13** and **14** coordinate to titanium in the ground state, giving two chemically distinct Me

group environments (Equation 3.7, Figure 3.2), and was confirmed by the presence of two NMe resonances in the low temperature $^{13}\text{C}\{-^1\text{H}\}$ NMR spectra of these compounds. For compound **13** an nOe was observed at $-90\text{ }^{\circ}\text{C}$ between both of the NMe resonances and the $t\text{Bu}$ group of the imido ligand, confirming coordination of the NMe_2 group. Coordination of the pendant arm to titanium may be more favourable for the $\text{C}_5\text{H}_4\text{Me}$ systems than for the C_5Me_5 systems **3.17** and **3.18** (Section 3.3.3) since C_5Me_5 is both more sterically demanding and electron releasing.

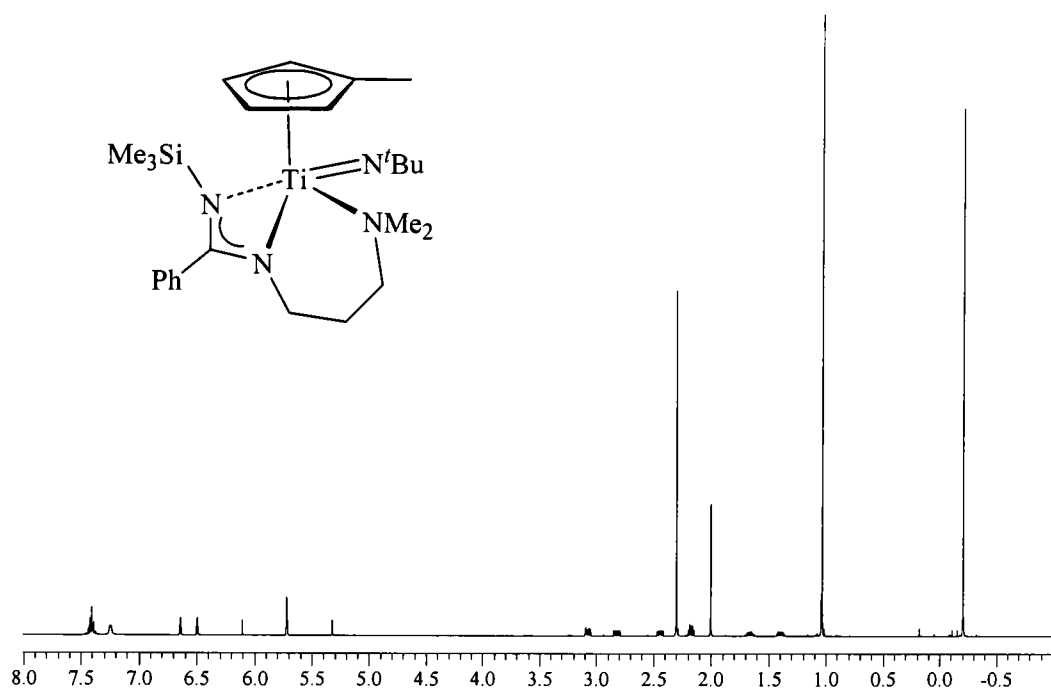


Equation 3.7

The ^1H NMR spectrum of **14** at $-90\text{ }^{\circ}\text{C}$ is shown in Figure 3.2(b). The singlet at 0.99 ppm corresponds to the *tert*-butyl group of the imido ligand and that at 1.89 ppm to the methyl group of the $\text{C}_5\text{H}_4\text{Me}$ ligand. The protons of the $\text{C}_5\text{H}_4\text{Me}$ ligand appear as four multiplets at 5.44, 5.48, 6.13 and 6.32 ppm. The benzamidinate ligand gives rise to a singlet at -0.31 ppm, which corresponds to the SiMe_3 group, and to three multiplets between 7.0 and 7.4 ppm corresponding to the phenyl group. There are two 3 H singlets at 2.43 and 2.57 ppm, attributed to the coordinated methyl groups of the NMe_2 fragment. The methylene protons of the pendant arm give rise to four 1 H multiplets at 1.23, 1.83, 2.07 and 2.57 ppm and one 2 H multiplet at 2.74 ppm.

Although it is likely that the NMe_2 methyls (arbitrarily labelled " Me^a " and " Me^b " in Equation 3.7) of **13** and **14** undergo mutual chemical exchange *via* the 16 valence electron isomers **13'** and **14'**, no evidence for significant equilibrium amounts of either of these compounds was indicated by any of the low temperature spectra. Therefore, assuming that ^1H NMR could detect a minimum of *ca.* 1% of **13'** or **14'** in the presence of a 99% relative amount of **13** or **14** (*i.e.*

(a)



(b)

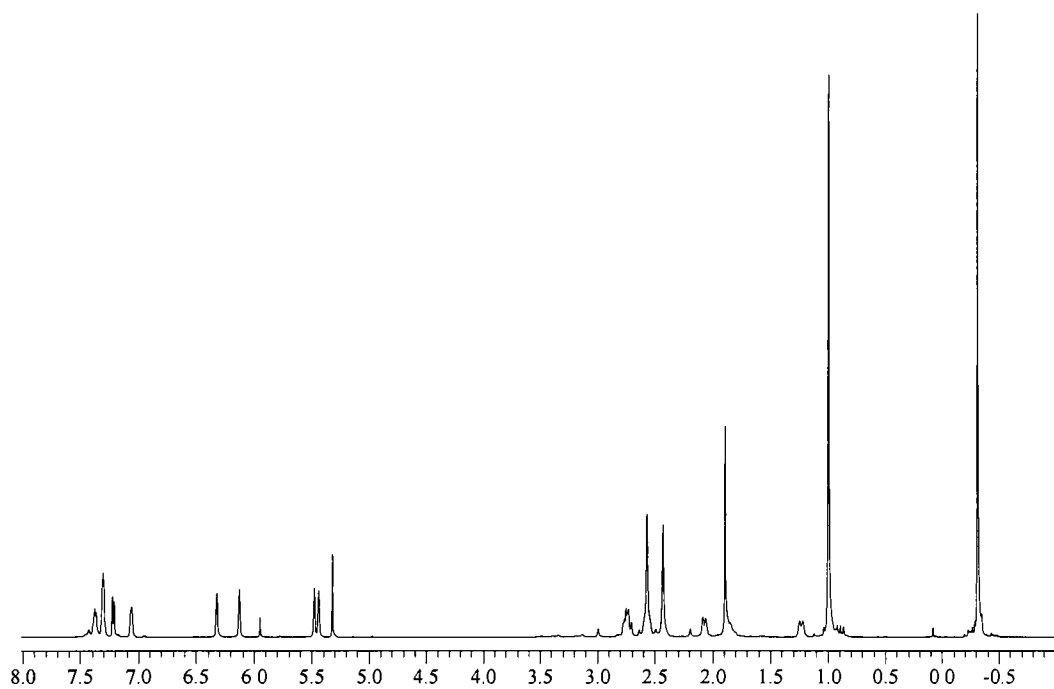


Figure 3.2 500.0 MHz ^1H NMR spectra of $[\text{Ti}(\eta\text{-C}_5\text{H}_4\text{Me})(\text{N}'\text{Bu})\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}]$ (**14**) in CD_2Cl_2 (a) at 25 °C; (b) at -90 °C

$K_{eq} = [13']/[13]$ or $[14']/[14] \leq 0.01$) then k_{-1} (Equation 3.7) must be at least two orders of magnitude greater than k_1 for both the **13/13'** and **14/14'** dynamic equilibria (since $K_{eq} = k_1/k_{-1}$).

3.4.1 Measurement of activation parameters for NMe₂ methyl group exchange in **13** and **14**

The values of $\Delta G^\ddagger_{T_c}$ (Gibbs free energy of activation at the coalescence temperature T_c) from coalescence measurements for the NMe₂ resonances of [Ti(η -C₅H₄Me)(N^tBu){Me₃SiNC(Ph)NCH₂CH₂NMe₂}] (**13**) and [Ti(η -C₅H₄Me)(N^tBu){Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂}] (**14**) in the ¹H NMR spectra at 237 ± 2 K and 208 ± 2 K respectively) were extracted using standard procedures³⁴ and are shown in Table 3.1. It is assumed that the $\Delta G^\ddagger_{T_c}$ values refer to the transition state for NMe₂ group dissociation on the way to the opening of the five-membered (for **13**) or six-membered (for **14**) chelate rings. The opening of a chelate ring leads to an increase in entropy, therefore $\Delta S^\ddagger$ for such processes is also expected to have a positive value.³⁵ $\Delta G^\ddagger_{T_c}$ values obtained at different T_c 's cannot be directly compared because of the $T\Delta S^\ddagger$ contribution, but since T_c (208 ± 2 K) for the 3-carbon linker compound **14** ($\Delta G^\ddagger_{208} = 41.6 \pm 0.4$ kJmol⁻¹) is *ca.* 30 K lower than that for the 2-carbon linker compound **13** ($\Delta G^\ddagger_{237} = 46.4 \pm 0.4$ kJmol⁻¹) the $\Delta G^\ddagger_{T_c}$ for **14** would be even lower than the value given in Table 3.1 at the T_c for **13**. Overall it seems very likely that the $\Delta G^\ddagger$ for NMe₂ dissociation is significantly lower for **14** than for **13**.

Table 3.1 Values of $\Delta G^\ddagger_{T_c}$ from coalescence measurements for [Ti(η -C₅H₄Me)(N^tBu){Me₃SiNC(Ph)NCH₂CH₂NMe₂}] (**13**) and [Ti(η -C₅H₄Me)(N^tBu){Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂}] (**14**)

Compound	T_c (K)	$\Delta G^\ddagger_{T_c}$ (kJmol ⁻¹)
13	237 ± 2	46.4 ± 0.4
14	208 ± 2	41.6 ± 0.4

In order to gain an additional insight into the activation parameters, an attempt was made to extract $\Delta H^\ddagger$ and $\Delta S^\ddagger$ (and hence $\Delta G^\ddagger$) values from ¹H NMR (500.0 MHz) NMe₂ linewidth measurements at temperatures below the coalescence

temperature for both compounds. Activation parameters for the exchange of the two NMe₂ groups in **13** and **14** (Equation 3.7) were obtained by ¹H NMR linewidth analysis of several measurements of the ¹H NMR spectrum at 3 K intervals at temperatures between 215 and 233 K (for **13**) and between 186 and 201 K (for **14**) in CD₂Cl₂. In each case, the linewidths at half height [$\nu_{1/2}(\text{obs})$] were corrected by subtracting the natural linewidths obtained from the low temperature limit ¹H NMR spectrum at 183 K. These corrected values [$\nu_{1/2}(\text{corr})$] were used to calculate the observed rate constants for the processes Me^a → Me^b [$k_{\text{obs}}(\text{a} \rightarrow \text{b})$] and Me^b → Me^a [$k_{\text{obs}}(\text{b} \rightarrow \text{a})$] according to $k = \pi \nu_{1/2}(\text{corr})^2$. The values of these rate constants are presented in Tables 3.2 and 3.3.

Table 3.2 Corrected linewidths (Hz) and rate constants (s⁻¹) for the exchange of the Me environments in [Ti(η-C₅H₄Me)(NⁱBu){Me₃SiNC(Ph)NCH₂CH₂NMe₂}] (**13**)

Temperature (K)	Me ^a → Me ^b		Me ^b → Me ^a	
	$\nu_{1/2}(\text{corr})$ (ab)	$k_{\text{obs}}(\text{a} \rightarrow \text{b})$	$\nu_{1/2}(\text{corr})$ (ba)	$k_{\text{obs}}(\text{b} \rightarrow \text{a})$
215	2.01	6.32		
218	2.63	8.26	1.19	3.73
221	4.12	12.96	2.25	7.08
224	7.45	23.40	5.12	16.09
237	12.89	40.52	10.30	32.28
230	23.00	72.30	18.73	58.86
233	36.78	36.78	33.46	105.15

Table 3.3 Corrected linewidths (Hz) and rate constants (s^{-1}) for the exchange of the Me environments in $[Ti(\eta-C_5H_4Me)(N^iBu)\{Me_3SiNC(Ph)NCH_2CH_2CH_2NMe_2\}]$ (**14**)

Temperature (K)	$Me^a \rightarrow Me^b$		$Me^b \rightarrow Me^a$	
	$\nu_{1/2}$ (corr) (ab)	k_{obs} (a $\rightarrow$ b)	$\nu_{1/2}$ (corr) (ba)	k_{obs} (b $\rightarrow$ a)
186			6.57	0.0043
189	7.60	5.04	6.71	0.45
192	7.87	5.89	7.10	1.69
195	9.54	11.13	7.89	4.17
198	13.71	24.23	11.81	16.50
201	18.67	39.83	22.24	49.25

These data have been used to construct Eyring plots using the Eyring equation in the form:

$$\ln\left(\frac{k_1}{T}\right) = \left\{ \ln\left(\frac{k_b}{h}\right) + \left(\frac{\Delta S^\ddagger}{R}\right) \right\} - \left(\frac{\Delta H^\ddagger}{RT}\right)$$

[k_1 = chemical exchange rate constant, T = absolute temperature, k_b = Boltzmann constant ($1.381 \times 10^{-23} \text{ JK}^{-1}$), h = Planck constant ($6.626 \times 10^{-34} \text{ Js}$), R = gas constant ($8.314 \text{ JK}^{-1}\text{mol}^{-1}$), $\Delta S^\ddagger$ = entropy of activation, $\Delta H^\ddagger$ = enthalpy of activation], where the chemical exchange rate constant k_1 (Equation 3.7) is equal to twice the observed rate constant k_{obs} since the conversion of methyl group environment "a" to "b" occurs at the same rate as the conversion from environment "b" to "a" (Figure 3.3).³⁶

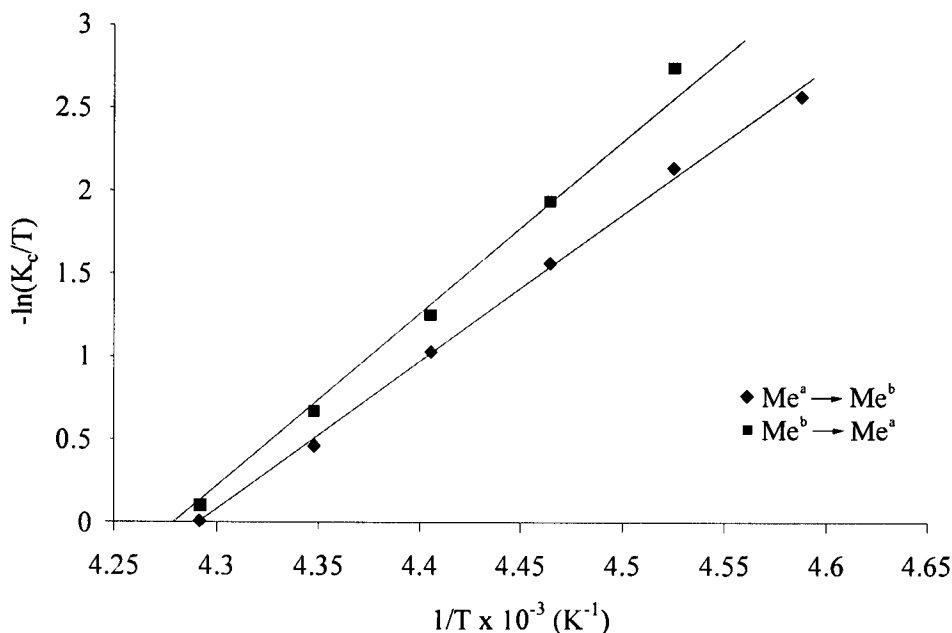


Figure 3.3 Eyring plot for NMe₂ methyl group exchange in **13**

From these Eyring plots, the values for $\Delta H^\ddagger$ and $\Delta S^\ddagger$ shown in Table 3.4 were extracted.

Table 3.4 Activation parameters for Me group exchange in [Ti(η -C₅H₄Me)(NⁱBu)
{Me₃SiNC(Ph)NCH₂CH₂NMe₂}] (**13**) and [Ti(η -C₅H₄Me)(NⁱBu)
{Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂}] (**14**)

	Data for 13		Data for 14	
	$\Delta H^\ddagger$ (kJmol ⁻¹)	$\Delta S^\ddagger$ (JK ⁻¹ mol ⁻¹)	$\Delta H^\ddagger$ (kJmol ⁻¹)	$\Delta S^\ddagger$ (JK ⁻¹ mol ⁻¹)
Me ^a → Me ^b	74.1	120.2	68.1	133
Me ^b → Me ^a	88.2	180.1	121.4	400
Averaged values	81.2 ± 7.1	150 ± 30	95 ± 27	267 ± 133

The errors on the activation paramaters displayed in Table 3.4 arise from the differences between the values calculated for $\text{Me}^a \rightarrow \text{Me}^b$ and $\text{Me}^b \rightarrow \text{Me}^a$. While a more in-depth form of error analysis could have been carried out, this is unlikely to affect the significance of the result. These errors arise from the difficulty in obtaining good quality spectra at the very low temperatures required, and are particularly large for the 3-carbon linker system **14**. Although one therefore

cannot make detailed comparisons of the $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values between the two compounds **13** and **14**, it is indisputable that the NMe₂ methyl group exchange processes are associated with significantly positive $\Delta S^\ddagger$ values. Likewise, the $\Delta H^\ddagger$ data are favourably comparable to those for related dissociative equilibria of amidinate-supported titanium imido complexes.³⁷

As a check on the internal consistency between the $\Delta G^\ddagger$ values obtained from coalescence and linewidth analyses, it is reassuring that $\Delta G^\ddagger$ values for **13** at 237 K (T_c) extracted from coalescence (46.4 ± 0.4 kJmol⁻¹) and the Eyring plots (45.6 ± 14.1 kJmol⁻¹) are in good agreement, despite the large errors on the activation parameters extracted from the linewidth data.

In order to make a comparison between $\Delta G^\ddagger$ for both systems at the same temperature, the more reliable activation parameters extracted for the 2-carbon linker system **13** have been used to calculate $\Delta G^\ddagger_{208}$ (208 K being T_c for the 3-carbon linker system **14**), which can be compared to $\Delta G^\ddagger_{208}$ for **14** calculated directly from the coalescence measurement (Table 3.5). The values thus obtained are $\Delta G^\ddagger_{208}$ of 50.0 ± 13.2 kJmol⁻¹ for **13** and 41.6 ± 0.4 kJmol⁻¹ for **14**. The magnitudes of these $\Delta G^\ddagger_{208}$ values are consistent with a larger barrier for dissociation of the three carbon linker arm, but the large error associated with the data for **13** does not allow a firm conclusion to be drawn from these measurements alone. While the data do not permit us to determine the origin of this effect with any certainty, it seems likely that it might be the result of a greater gain in entropy upon dissociation of a three carbon arm from the metal.³⁵

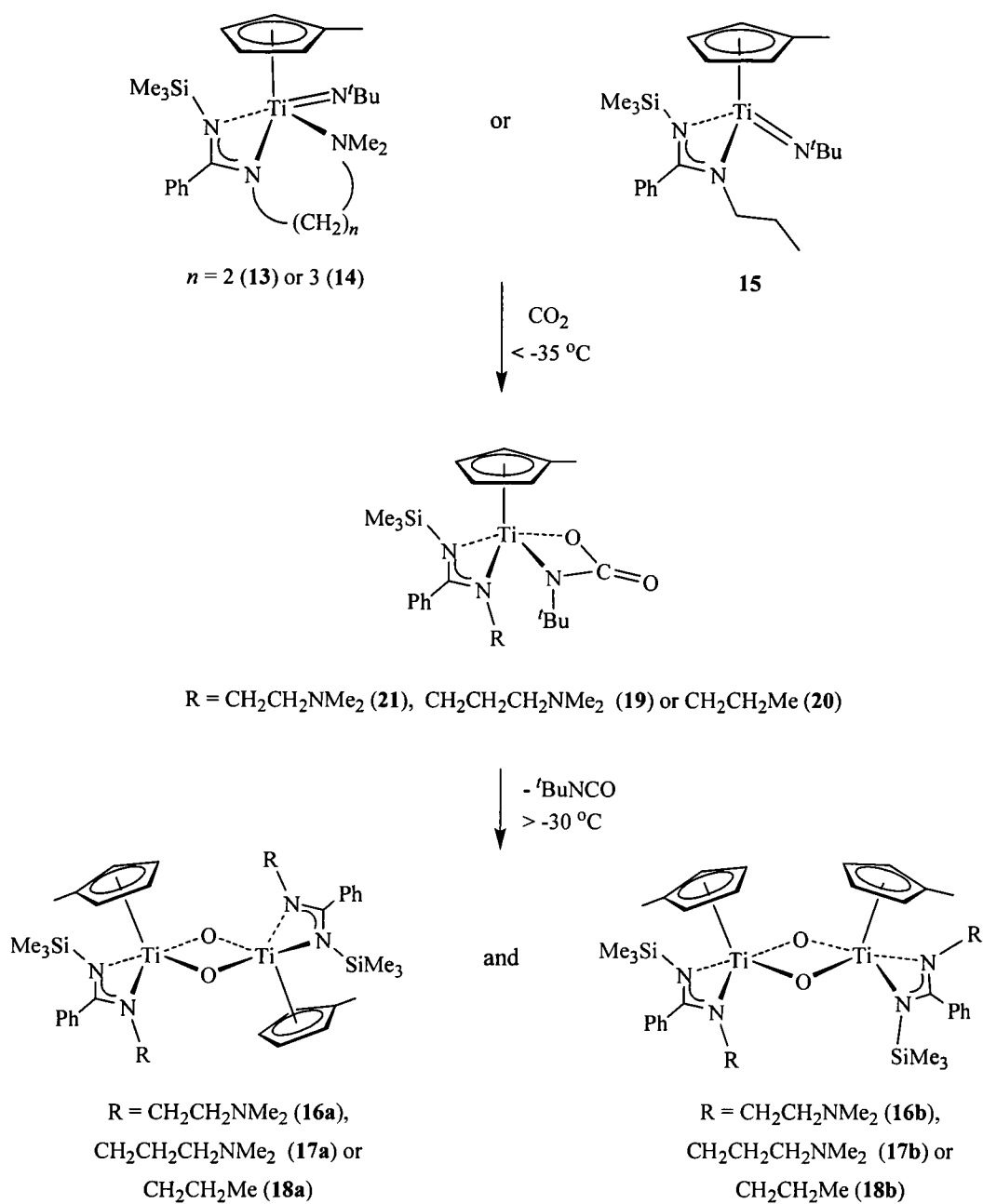
3.4.2 Reactions of the C₅H₄Me-supported compounds **13**, **14** and **15** with CO₂ at room temperature

Samples of [Ti(η -C₅H₄Me)(N^tBu){Me₃SiNC(Ph)N(CH₂)_nNMe₂}] { $n = 2$ (**13**) or 3 (**14**)} and [Ti(η -C₅H₄Me)(N^tBu){Me₃SiNC(Ph)NCH₂CH₂Me}] (**15**) were dissolved in C₆D₆ and exposed to CO₂ at a pressure of 1 atm *via* a Schlenk line. The behaviour of the C₅H₄Me systems, **13**, **14** and **15** upon exposure to CO₂ was found to differ from that of the C₅Me₅ systems previously described (Section

3.3.4). Scheme 3.5 summarises the overall sequence for the reactions of **13**, **14** and **15** with CO₂.

On reaction with CO₂, an immediate colour change to cherry red, consistent with formation a carbamate intermediate, was observed but the colour darkened to brown almost immediately, suggesting decomposition to the corresponding oxo compounds. When the reaction was followed at room temperature by ¹H NMR spectroscopy, spectra after 5 minutes contained resonances attributable to both the imido starting materials and the dimeric oxo products [Ti₂(η-C₅H₄Me)₂(μ-O)₂{Me₃SiNC(Ph)NR}₂] {R = CH₂CH₂NMe₂ (**16**), CH₂CH₂CH₂NMe₂ (**17**) or CH₂CH₂Me (**18**)}, together with ^tBuNCO (0.88 ppm), but not the predicted carbamate intermediates **19** - **21**. After 1 hour complete decomposition to the oxo products and ^tBuNCO was observed (Figure 3.4 shows the 3-carbon product ¹H NMR by way of example).

This is in contrast to the reactions of the C₅Me₅ systems, which display only resonances due to the intermediate carbamate after 5 minutes under the same reaction conditions. The immediate decomposition of the proposed carbamate intermediates **19** - **21** meant that characterisation was not possible at room temperature. The faster rate of their decomposition relative to the C₅Me₅ carbamates **3.19** and **3.20** is attributed to the decreased steric stabilisation towards dimerisation of a proposed transient monomeric oxo intermediate provided by C₅H₄Me compared to C₅Me₅ (evidence for such an intermediate is presented later in this Chapter).



Scheme 3.5 Reactions of $\text{C}_5\text{H}_4\text{Me}$ pendant arm amidinate-imido compounds with CO_2

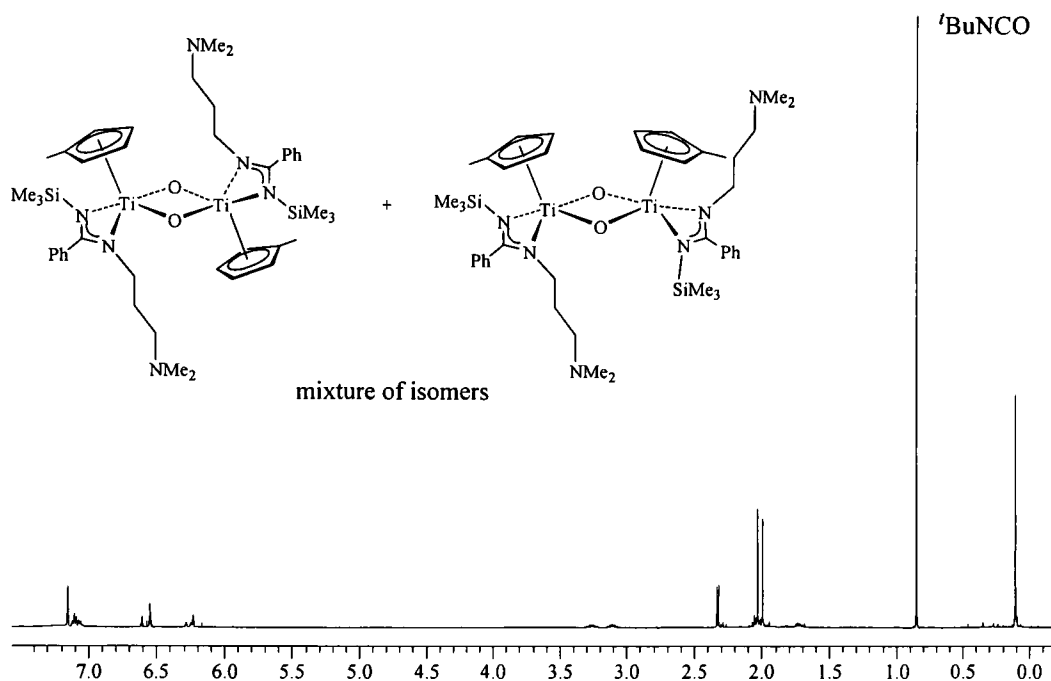


Figure 3.4 500.0 MHz ^1H NMR spectrum of reaction mixture formed from $[\text{Ti}(\eta\text{-C}_5\text{H}_4\text{Me})(\text{N}^t\text{Bu})\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}]$ (**14**) and CO_2 in C_6D_6 after 1 hour

The dimeric oxo products **16** - **18** have been isolated and characterised by NMR and IR spectroscopies and mass spectrometry. The NMR spectra were found to contain twice as many resonances as expected for single products and probably imply the formation of both *trans* and *cis* isomers **16a** - **18a** and **16b** - **18b** (Scheme 3.5). It was found that heating samples to 80 °C in C_6D_6 for several hours lead to a shift in the relative ratios of the two products in favour of the *trans* isomer. The *trans* isomers **16a** and **17a** have been crystallographically characterised as discussed below.

Diffraction quality crystals of the *trans* isomers **16a** and **17a** were grown by slow evaporation of pentane solutions at room temperature. Data were collected at 150 K by Dr. A Guiducci and the X-ray structures were solved by Dr. P. Mountford. Figure 3.5 shows the molecular structures and Tables 3.5 and 3.6 summarise important bond lengths and angles. Full details are provided in Appendices G and H.

Table 3.5 Selected bond lengths and angles for *trans*-[Ti₂(η-C₅H₄Me)₂(μ-O)₂{Me₃SiNC(Ph)NCH₂CH₂NMe₂}₂] (**16a**). Cp_(cent) refers to the computed C₅H₄Me ring centroid.

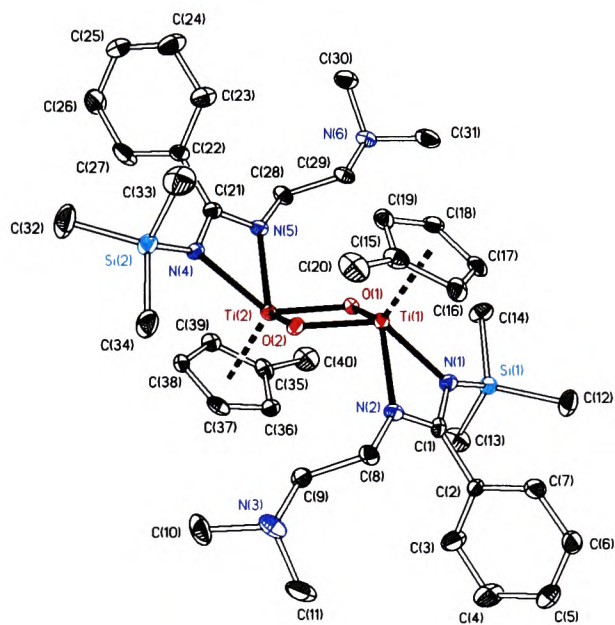
Cp _(cent) -Ti(1)-N(1)	108.5	Cp _(cent) -Ti(1)-O(1)	121.6
Cp _(cent) -Ti(1)-N(2)	110.9	Cp _(cent) -Ti(1)-O(2)	112.2
Ti(1)-N(1)	2.180(6)	Ti(1)-O(1)	1.813(5)
Ti(1)-N(2)	2.132(6)	Ti(1)-O(2)	1.892(5)
Ti(1)-Cp _(cent)	2.081		

Table 3.6 Selected bond lengths and angles for *trans*-[Ti₂(η-C₅H₄Me)₂(μ-O)₂{Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂}₂] (**17a**). Cp_(cent) refers to the computed C₅H₄Me ring centroid.

Cp _(cent) -Ti(1)-N(1)	109.6	Cp _(cent) -Ti(1)-O(1)	121.7
Cp _(cent) -Ti(1)-N(2)	115.6	Cp _(cent) -Ti(1)-O(1A)	111.3
Ti(1)-N(1)	2.203(1)	Ti(1)-O(1)	1.802(1)
Ti(1)-N(2)	2.096(1)	Ti(1)-O(2)	1.907(1)
Ti(1)-Cp _(cent)	2.086		

The structures of **16a** and **17a** confirm that they are μ-bridged oxo dimers and that the NMe₂ groups do not coordinate to the metal. Both compounds have a pseudo four-legged piano stool geometry about the titanium atoms. Compounds with Ti₂(μ-O)₂ cores are well established, and several have been crystallographically characterised.^{38,39} The bond lengths and angles are of comparable magnitudes for both compounds. Both compounds have slightly asymmetric Ti₂(μ-O)₂ cores in which the Ti-O bond *trans* to the SiMe₃-bearing nitrogen is slightly longer than the Ti-O bond *trans* to the pendant arm bearing nitrogen. This is reflected in the shorter Ti-NSiMe₃ bond lengths and may be attributed to the asymmetric ligand substitution, as the symmetric oxo dimer [Ti₂(η-C₅H₄Me)₂(μ-O)₂{PhC(NSiMe₃)₂}₂] has equal bond lengths for both Ti-O and Ti-N_{amidinate} bonds.

(a)



(b)

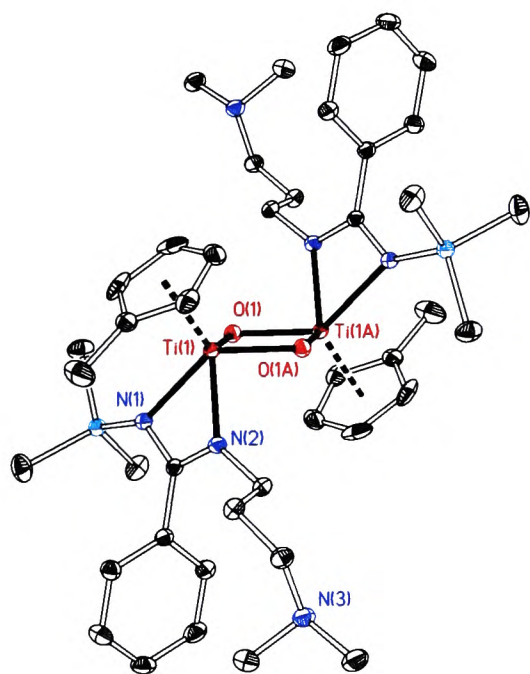


Figure 3.5 Thermal ellipsoid plots of *trans*-[Ti₂(η-C₅H₄Me)₂(μ-O)₂ {Me₃SiNC(Ph)NCH₂CH₂NMe₂}₂] (**16a**) and *trans*-[Ti₂(η-C₅H₄Me)₂(μ-O)₂ {Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂}₂] (**17a**), 25% and 30% probabilities respectively.

Hydrogen atoms omitted for clarity.

3.4.3 Reactions of the C₅H₄Me-supported compounds **13**, **14** and **15** with CO₂ at low temperature

Reactions between **13**, **14** and **15** and CO₂ at $-78\text{ }^{\circ}\text{C}$ revealed a difference between the 2-carbon and the 3-carbon pendant arm systems **13** and **14**. When an NMR tube sample of the 3 carbon linker compound **14** in CD₂Cl₂ was exposed to CO₂ (*ca.* 1 atm) the ¹H NMR spectrum ($-78\text{ }^{\circ}\text{C}$) recorded immediately afterwards contained only resonances attributable to the carbamate [Ti(η-C₅H₄Me){N^tBuC(O)O}{Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂}] (**19**) (Scheme 3.5, Figure 3.6). The ¹H NMR spectrum supports the proposed structure for **19** and contains one 6 H singlet (1.53 ppm) for the NMe₂ group, suggesting that the pendant arm is not coordinated to the metal.

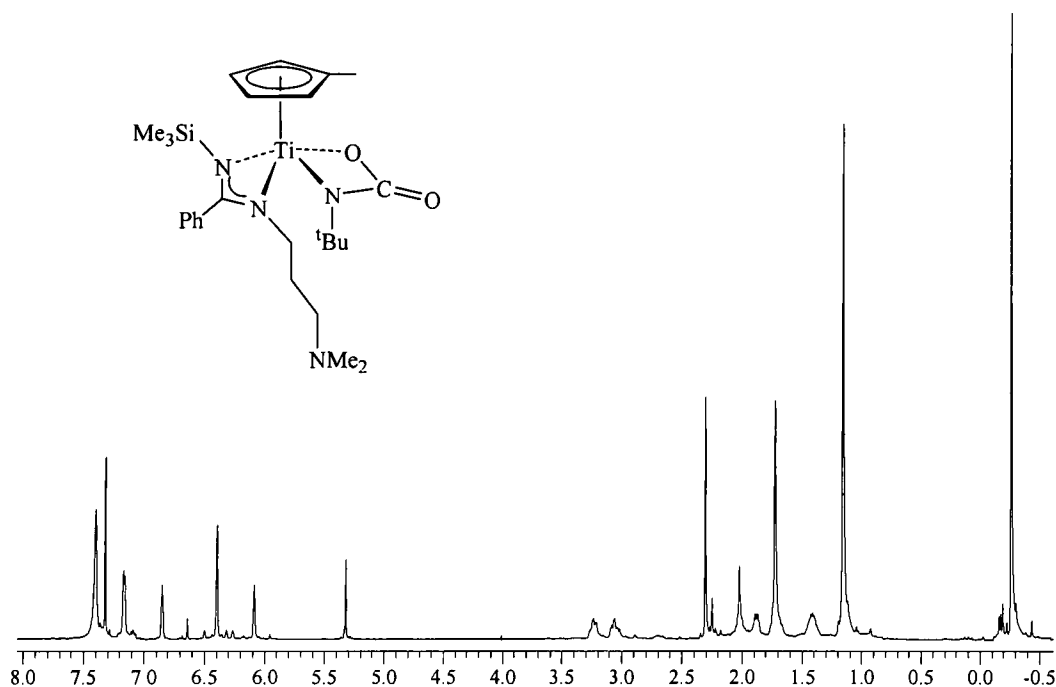


Figure 3.6 500.0 MHz ¹H NMR spectrum of [Ti(η-C₅H₄Me){N^tBuC(O)O}{Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂}] (**19**) in CD₂Cl₂ at $-78\text{ }^{\circ}\text{C}$

Subsequent warming of this solution to $-25\text{ }^{\circ}\text{C}$ lead to extrusion of ^tBuNCO and the *trans* and *cis* dimeric oxo compounds (**17a** and **17b**). This behaviour was mirrored by the dummy arm compound **15** which gave carbamate **20** immediately at $-78\text{ }^{\circ}\text{C}$ and then extrusion of isocyanate at $-25\text{ }^{\circ}\text{C}$ together with the oxo compounds **18a** and **18b**. However, when the two carbon pendant arm compound

13 was exposed to CO₂ at -78 °C, the ¹H NMR spectrum showed only resonances for **13**. Cycloaddition to form the carbamate [Ti(η-C₅H₄Me){N^tBuC(O)O}{Me₃SiNC(Ph)NCH₂CH₂NMe₂}] (**21**) did not occur at a significant rate until the solution was warmed to -35 °C. Further warming to -25 °C resulted in isocyanate extrusion to yield the dimeric oxo compounds **16a** and **16b**. This extrusion occurred at a rate which appeared qualitatively to be about twice as fast as for **19** and **20** at the same temperature. The lack of evidence for NMe₂ group coordination in the -78 °C NMR spectra of **19** and **21** suggests that these compounds are analogous to the C₅Me₅ homologues **3.19** and **3.20** (Scheme 3.4) in this regard and was supported by a ROESY NMR experiment on the 2-carbon linker system.

These observations suggested that the NMe₂ donor in the pendant arm systems could influence both the rate of cycloaddition of CO₂ to the Ti=N^tBu bond of **13** and also the extrusion of ^tBuNCO from the carbamate intermediates. Low temperature kinetic and mechanistic studies were therefore carried out to probe the role of the pendant donor group during the various stages of the reactions of **13**, **14** and **15** with CO₂.

3.4.4 Cycloaddition reaction of **13** with CO₂: mechanistic studies

Low temperature control of the cycloaddition of CO₂ to the Ti=N^tBu bond of **13** makes this reaction convenient for determining the rate law dependence on CO₂ in the reaction to form the carbamate **21**. These studies were carried out under pseudo-first order conditions whereby at least a 10-fold excess of CO₂ was present in the NMR tube at the lowest pressure studied [linear ln(I/I₀) plots showed no evidence for diffusion-control limitations in these experiments]. NMR samples of **13** in CD₂Cl₂ were exposed to known pressures of CO₂ at -78 °C *via* a calibrated gas manifold. Samples were transferred to a spectrometer with a probe maintained at the same temperature. The sample was warmed to -35 °C, at which temperature cycloaddition occurred at a significant rate and NMR spectra were recorded over at least three half-lives. The reaction was carried out at four pressures in the range 0.25 atm - 1.0 atm. The relative concentrations of the imido starting material **13** and the carbamate **21** were measured from each spectrum and

the results fitted to a first-order exponential relationship (Figures 3.7 and 3.8). The observed rate constants k_{obs} were extracted from plots of $\ln(I/I_0)$ vs. time for **13** and are summarised in Table 3.7; further details are given in the Appendix M.

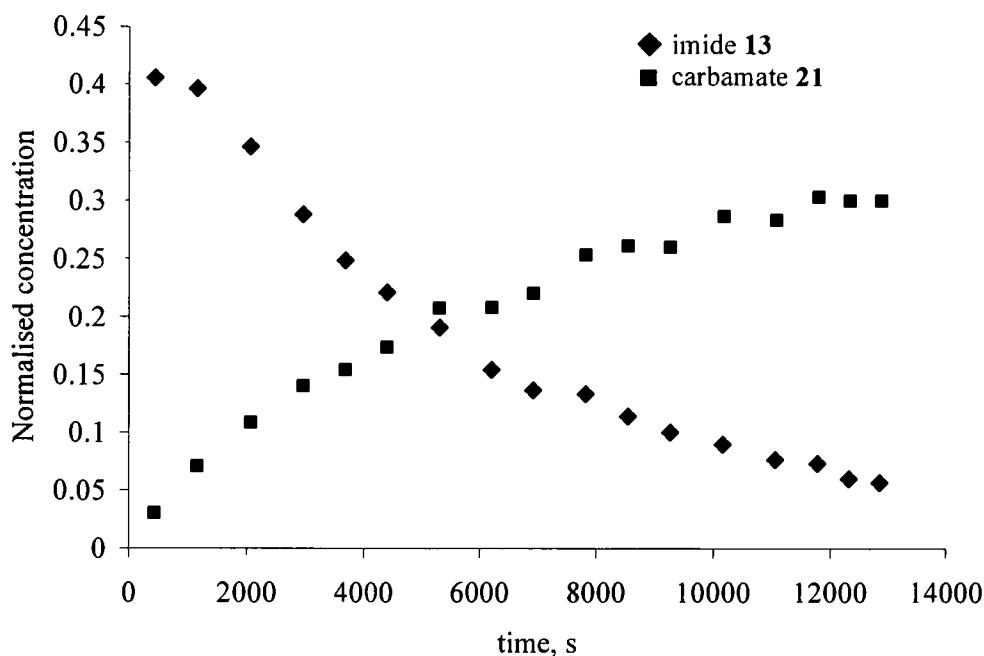


Figure 3.7 Plot of normalised concentrations against time for the cycloaddition reaction of **13** with CO_2 (0.5 atm). Values are given for starting imide (**13**) and product carbamate (**21**)

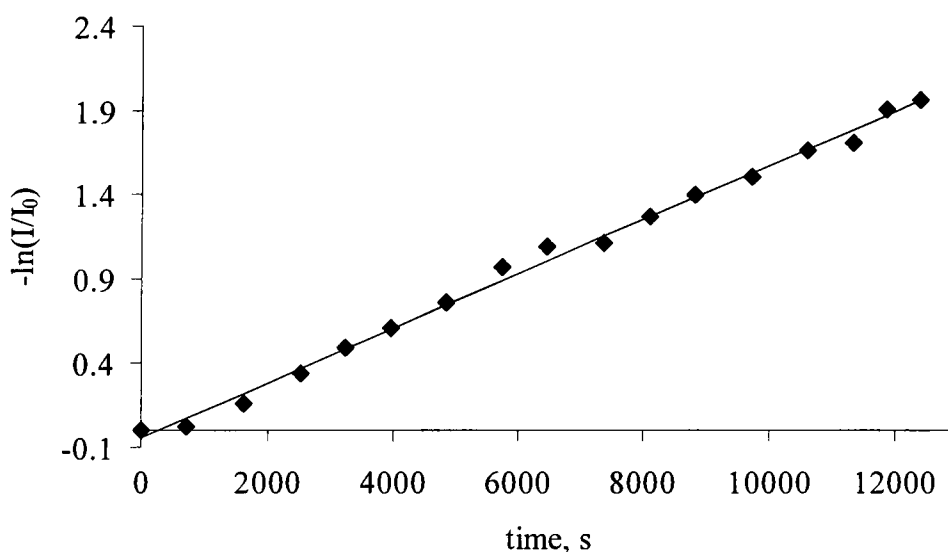


Figure 3.8 Plot of $\ln(I/I_0)$ vs. time for the reaction of $[\text{Ti}(\eta\text{-C}_5\text{H}_4\text{Me})(\text{N}'\text{Bu})\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{NMe}_2\}]$ (**13**) with CO_2 (0.5 atm)

Table 3.7 Observed rate constants k_{obs} for cycloaddition of CO_2 to $[\text{Ti}(\eta\text{-C}_5\text{H}_4\text{Me})(\text{N}^i\text{Bu})\{\text{Me}_3\text{SiNC(Ph)NCH}_2\text{CH}_2\text{NMe}_2\}]$ (**13**) at different CO_2 pressures

$p \text{ CO}_2 \text{ (atm)}$	$k_{\text{obs}} \times 10^4 \text{ (s}^{-1}\text{)}$
0.25	0.74 ± 0.02
0.5	1.6 ± 0.03
0.75	2.7 ± 0.03
1.0	3.7 ± 0.04

The exponential decay of starting material and evolution of carbamate indicate that the rate determining step is a bimolecular reaction which is first-order in CO_2 . This is confirmed by the linear dependence of k_{obs} on CO_2 pressure (Figure 3.9). Scheme 3.6 summarises the two likely mechanisms for addition of CO_2 to the pendant arm compounds **13** and **14**.

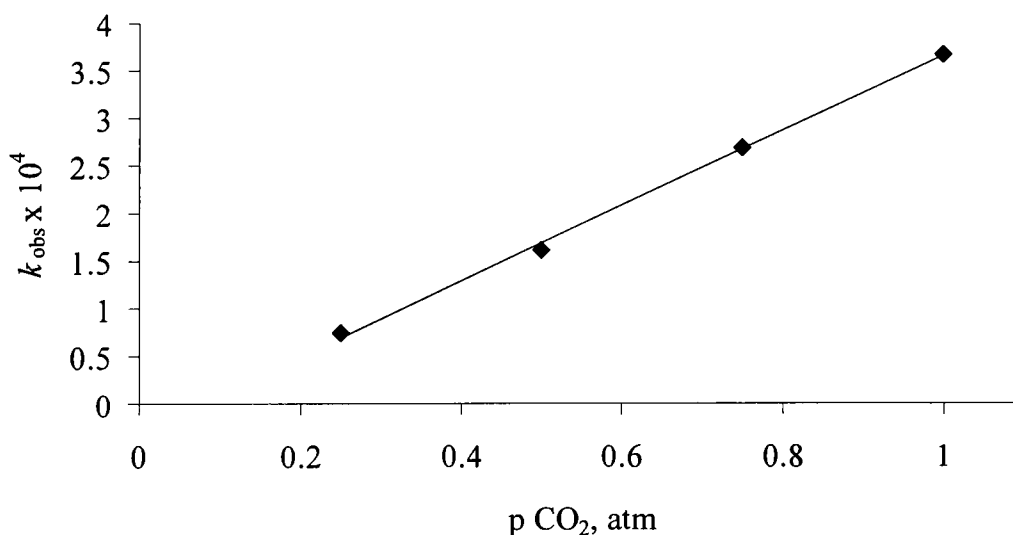
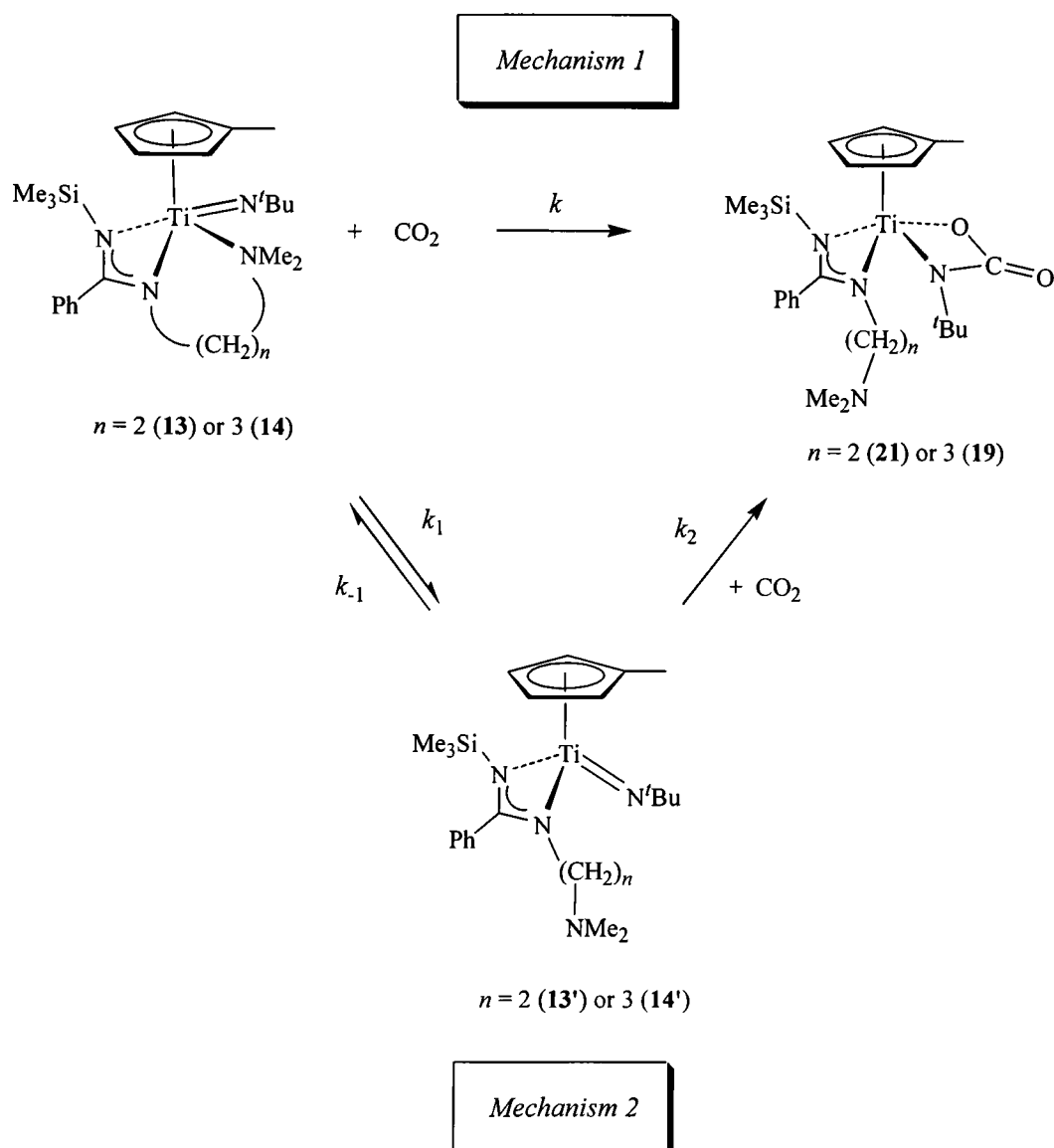


Figure 3.9 Plot of k_{obs} vs. CO_2 pressure for the reaction of $[\text{Ti}(\eta\text{-C}_5\text{H}_4\text{Me})(\text{N}^i\text{Bu})\{\text{Me}_3\text{SiNC(Ph)NCH}_2\text{CH}_2\text{NMe}_2\}]$ (**13**) with CO_2 at -35°C .



Scheme 3.6 Possible mechanisms for cycloaddition of CO₂ to **13** and **14**

In "Mechanism 1", cycloaddition of CO₂ to the Ti=N^tBu bond takes place without decoordination of the pendant arm from the metal. "Mechanism 2" involves a pre-equilibrium in which the pendant arm dissociates from the metal to generate an intermediate species (**13'** or **14'**) which then undergoes cycloaddition of CO₂. Note that for the "dummy" arm imide **15** a simple bimolecular process analogous to the second step of Mechanism 2 is the only possibility.

For Mechanism 1, the rate law is given by Equation 3.8 (where "imide" = **13** or **14**).

$$\text{Rate} = k[\text{imide}][\text{CO}_2] \quad (\text{Equation 3.8})$$

Under pseudo first order conditions (large and effectively constant $[\text{CO}_2]$ as in the experiments described above), this expression simplifies to Equation 3.9 where $k_{\text{obs}} = k[\text{CO}_2]$ and is linearly dependent upon $[\text{CO}_2]$.

$$\text{Rate} = k_{\text{obs}}[\text{imide}] \quad (\text{Equation 3.9})$$

The rate law for Mechanism 2 may be derived by applying the steady state approximation to the intermediates **13'** and **14'** such that the rate law in Equation 3.10 applies (with k_1 , k_{-1} , k_2 as defined in Equation 3.7 and Scheme 3.6).

$$\text{Rate} = \frac{k_1 k_2 [\text{imide}][\text{CO}_2]}{k_{-1} + k_2 [\text{CO}_2]} \quad (\text{Equation 3.10})$$

However, in the case where $k_{-1} \gg k_2 [\text{CO}_2]$, Equation 3.10 approximates to Equation 3.11 where $k'_{\text{obs}} = \frac{k_1 k_2}{k_{-1}} [\text{CO}_2]$ and again has a linear dependence on $[\text{CO}_2]$

$$\text{Rate} = k'_{\text{obs}}[\text{imide}] \quad (\text{Equation 3.11})$$

Therefore, the experimental data for the reaction of **13** with CO_2 fit either Mechanism 1 (Equation 3.9) or Mechanism 2 (Equation 3.11) provided that k_{-1} is larger than $k_2 [\text{CO}_2]$. This issue is further addressed using DFT calculations later in this Chapter (Section 3.5).

3.4.5 Extrusion of 'BuNCO: kinetic studies

Given the very different rates of cycloaddition of CO_2 to $\text{Ti}=\text{N}'\text{Bu}$ for the two carbon and three carbon arm NMe_2 donor systems **13** and **14**, it was of interest to quantify any anchimeric effect of the different arms on the rate of 'BuNCO extrusion.

Extrusion of 'BuNCO from all three carbamates **19** - **21** to form the bridging oxo products (Scheme 3.5) was monitored by low temperature NMR at the same concentrations. The isosteric "dummy" arm system **20** was used as a control to "benchmark" any effect of the pendant $(\text{CH}_2)_n\text{NMe}_2$ donors upon the rate of extrusion. All of the NMR studies were carried out on *in situ* generated carbamates (Section 3.4.3). Additional studies were made on the "dummy arm"

system (**20** $\rightarrow$ **18**) at three different concentrations, in order to probe the dependence of the rate of decomposition upon carbamate concentration (since compounds **19** - **21** are monomeric and the ultimate products **16** - **18** are dimeric, it is possible that the rate determining step could be bimolecular with respect to titanium). The experiments for **19** and **21** were carried out in duplicate.

NMR samples of *in situ* generated **19** - **21** were warmed to $-25\text{ }^{\circ}\text{C}$, at which point all of the imido starting materials had been consumed by reaction with CO_2 and only carbamate was present. In the case of the 2-carbon linker compound **13**, a small amount of imido starting material **13** was still present at $-25\text{ }^{\circ}\text{C}$ and the data obtained until all of this had been consumed were discarded. Extrusion of ${}^t\text{BuNCO}$ from the carbamates **19** - **21** to yield dimeric oxo compounds was followed over three half-lives of carbamate decomposition. The data fitted a first-order exponential relationship. The rate constants k extracted from plots of $\ln(I/I_0)$ vs. time are listed in Table 3.8 (Figures 3.10 and 3.11 show data for **19** by way of example).

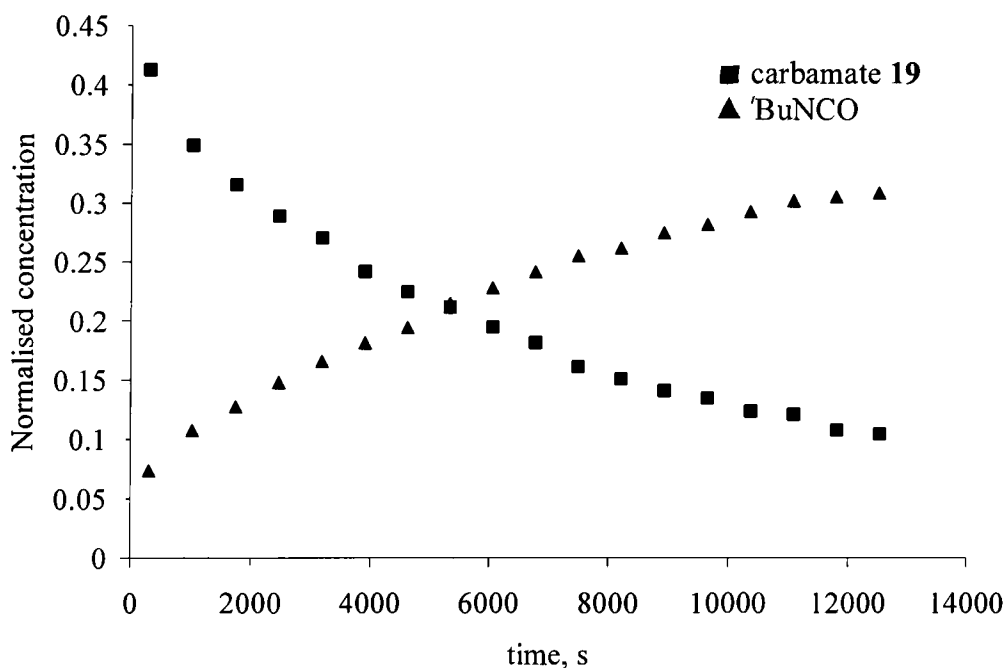


Figure 3.10 Plot of normalised concentrations for the ${}^t\text{BuNCO}$ extrusion reaction of $[\text{Ti}(\eta\text{-C}_3\text{H}_4\text{Me})\{\text{N}^t\text{BuC}(\text{O})\text{O}\}\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}]$ (**19**). Values are given for the carbamate **19** and ${}^t\text{BuNCO}$.

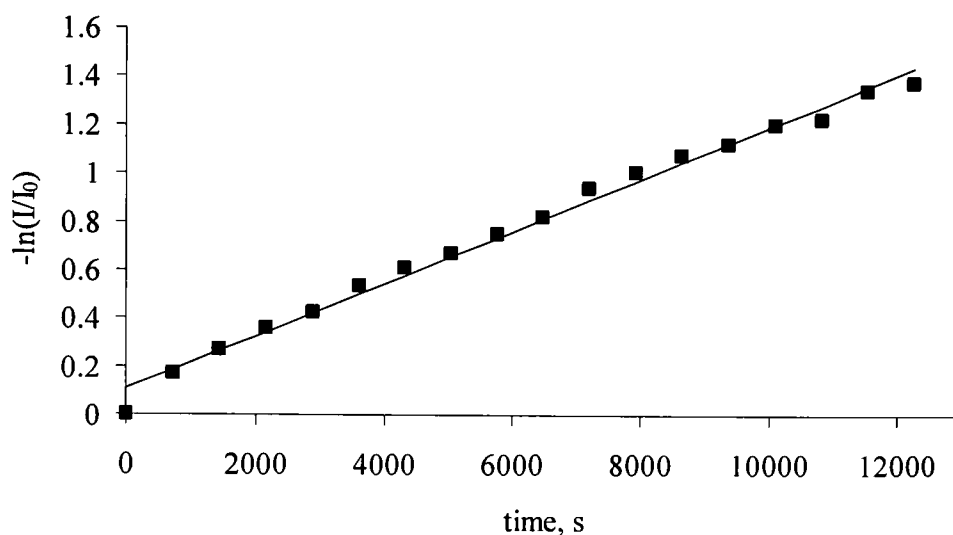


Figure 3.11 Plot of $\ln(I/I_0)$ vs. time for the 'BuNCO extrusion reaction of $[\text{Ti}(\eta\text{-C}_5\text{H}_4\text{Me})\{\text{N'BuC}(\text{O})\text{O}\}\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}]$ (**19**)

Table 3.8 First order rate constants k and associated half-lives ($t_{1/2}$) for extrusion of 'BuNCO from *in situ* generated carbamate complexes **19** - **21**. Values of initial concentration refer to the imido precursors **13** - **15**.

Carbamate	Initial concentration x 10^8 (mol dm $^{-3}$)	$k \times 10^4$ (s $^{-1}$)	$t_{1/2} \times 10^{-3}$ (s)
20	1.9	1.35 ± 0.03	5.63 ± 1.30
	2.9	1.24 ± 0.02	5.94 ± 0.99
	3.8	1.20 ± 0.03	6.16 ± 1.54
21	1.9	2.41 ± 0.03	2.93 ± 0.36
		2.10 ± 0.03	3.37 ± 0.48
19	1.9	1.09 ± 0.08	6.43 ± 0.55
		1.09 ± 0.02	6.30 ± 0.11

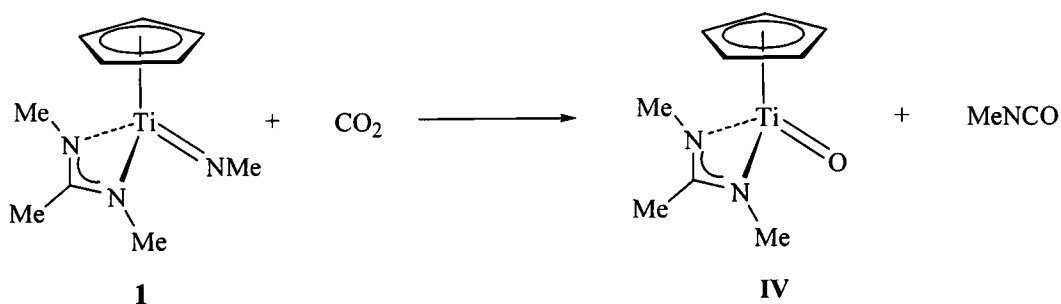
The data (Table 3.8) for isocyanate extrusion from **20** show that the reaction is independent of $[\text{20}]$ in the range studied, so a bimolecular rate limiting step is unlikely. A mechanism proceeding via a titanium terminal oxo compound seems likely given that a terminal titanium oxo species has been trapped using *p*-tolyl isocyanate for the non-pendant arm system $[\text{Ti}(\eta\text{-C}_5\text{Me}_5)(\text{N'Bu})\{\text{MeC}(\text{N'Pr})_2\}]$

(see Section 3.7.1). Examination of the rate constants for **19** and **21** reveals a small but persistent increase in the rate constant for extrusion with the two carbon arm system **21** compared with **19** and **20**. Energetically the effect is small (a 2-3 kJmol⁻¹ difference in $\Delta G^\ddagger$ for extrusion) but nonetheless it amounts to a quantitatively established doubling of the half life ($t_{1/2}$, Table 3.8) for extrusion on going from three carbon arm system **19** to the two carbon arm system **21**. This effect might arise from slight differences in steric effects between the two ligands, or from a small anchimeric effect of the ligand arm. The compounds **19** (three carbon arm) and **20** ("dummy" arm) have experimentally indistinguishable values for k , suggesting that the three carbon arm NMe₂ does not accelerate measurably the rate of 'BuNCO extrusion from the carbamate. This issue will be explored further *via* density functional theory calculations in the following Section (Section 3.5).

3.5 Density Functional Studies on reactions of pendant arm functionalised amidinate-imido systems with CO₂

Density Functional Theory calculations on these systems were carried out in collaboration with Dr. Eric Clot of the University of Montpellier, France. All calculations were performed using Gaussian 98 programs using hybrid DFT (B3PW91).^{40,41}

The reaction of the model compound [Ti(η -C₅H₅)(NMe){MeC(NMe)₂}] (**I**) with CO₂ was used as a reference. The global pathway for the reaction (Equation 3.12) is given in Figure 3.12 (energy values) and Figure 3.13 (free energy values).



Equation 3.12

Note that the final dimeric μ -oxo product $[\text{Ti}_2(\eta\text{-C}_5\text{H}_5)_2(\mu\text{-O})_2\{\text{MeC}(\text{NMe})_2\}_2]$ was not calculated by DFT since this would be very expensive in terms of CPU time; experimentally, the dimerisation of the terminal oxo products (as modelled by **IV**) is not the point of interest. These calculations do not take the presence of the solvent into account but, as the reactions are carried out in C_6D_6 , it seems unlikely that the solvent plays a role in the reaction mechanism.

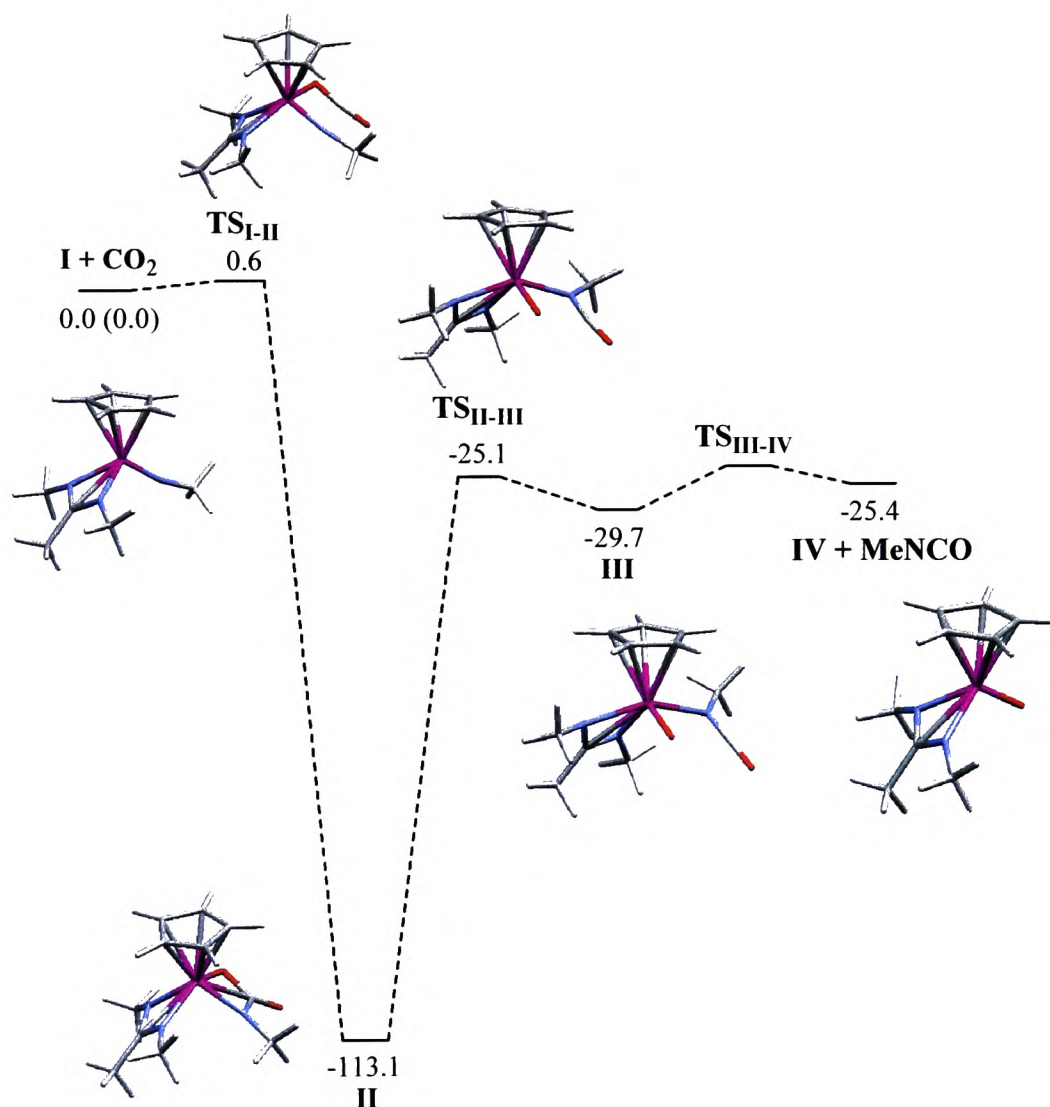


Figure 3.12 DFT computed pathway for the reaction of $[\text{Ti}(\eta\text{-C}_5\text{H}_5)(\text{NMe})\{\text{MeC}(\text{NMe})_2\}]$ (**I**) with CO_2 . Energies are given in kJ mol^{-1} . The connection shown between CN_2 and the metal centre arises due to their close proximity in space and should not be considered a bonding interaction.

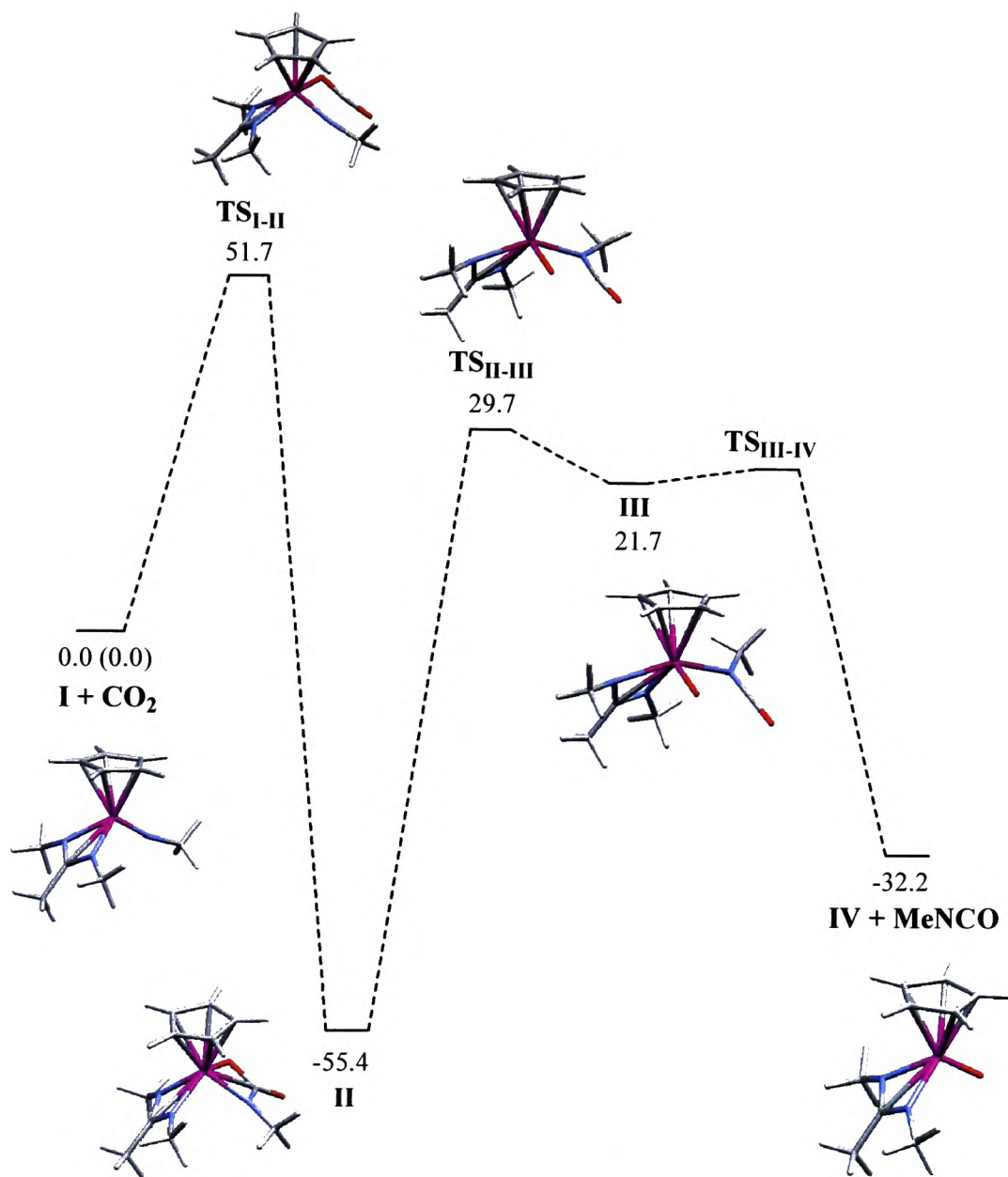


Figure 3.13 DFT computed pathway for the reaction of $[\text{Ti}(\eta\text{-C}_5\text{H}_5)(\text{NMe})\{\text{MeC}(\text{NMe})_2\}]$ (**I**) with CO_2 . Free energies at 298 K are given in kJ mol^{-1} . The connection shown between CN_2 and the metal centre arises due to their close proximity in space and should not be considered a bonding interaction.

The reaction leading to the titanium terminal oxo complex **IV** and MeNCO is exothermic by 25.4 kJ mol^{-1} ($\Delta G_{\text{I-IV}} = -32.2 \text{ kJ mol}^{-1}$). The first step in the reaction is the side-on cycloaddition of CO_2 to the $\text{Ti}=\text{NMe}$ bond. The geometry of the transition state (**TS_{I-II}**) is explained by the shape of the frontier orbitals of **I**

(Figure 3.14). The HOMO is one of the π -components of the Ti=N bond, resulting from the interaction of the titanium $3d_{yz}$ orbital with the nitrogen $2p_z$ orbital (see Figure 3.14 for definition of the axes) and the LUMO is essentially a $3d_{z^2}$ orbital. Consequently, the frontier orbitals of the imido group are ideally suited for efficient interaction with both the HOMO and the LUMO of CO₂, leading to a very low activation energy barrier for cycloaddition of 0.6 kJmol⁻¹ ($\Delta G^\ddagger_{\text{I-II}} = 51.7$ kJmol⁻¹ taking into account entropy effects). The reaction proceeds exothermically to form the very stable carbamate intermediate **II** at -113 kJmol⁻¹ ($\Delta G_{\text{I-II}} = -55.4$ kJmol⁻¹). The very low activation energy barrier and the relatively low energy of the carbamate are in agreement with the experimental results where cycloaddition of CO₂ to the imide to form the carbamate occurs readily, even at -78 °C for the 3-carbon and "dummy" arm systems **14** and **15**.

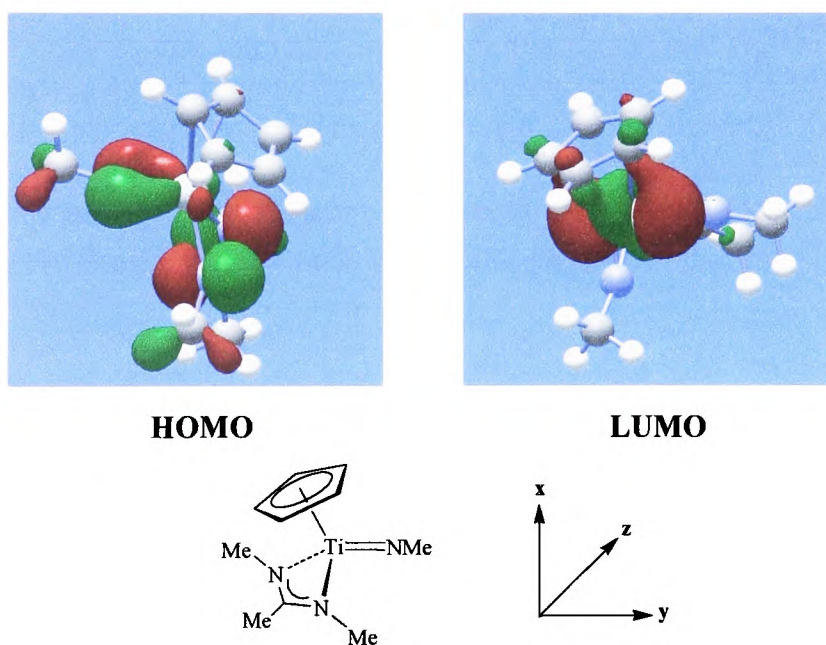


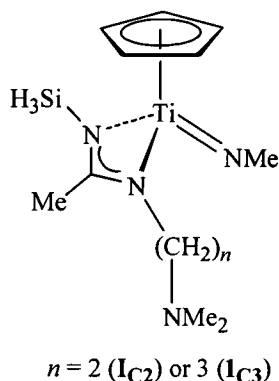
Figure 3.14 Representations of the HOMO and LUMO of the model complex **I**

Isocyanate extrusion is found to be a two-step process. The first step is the breaking of the C-O bond of carbamate **II** to yield the isocyanate adduct **III**. The activation energy barrier of 88 kJmol⁻¹ ($\Delta G^\ddagger_{\text{II-III}} = 85.1$ kJmol⁻¹) is associated with the concerted breaking of the C-O carbamate bond and formation of the Ti=O oxo bond [Ti-O = 1.945 Å, C-O = 1.346 Å (**II**), Ti-O = 1.666 Å, C-O = 2.222 Å (**TS_{II-III}**)]. The second step involves crossing **TS_{III-IV}**, which is essentially a transition

state corresponding to breaking the Ti-N bond. The transition state for this step has not yet been located but the activation barrier is likely to be no greater than *ca.* 10 kJmol⁻¹ ($\Delta G_{\text{III-IV}} = -53.9$ kJmol⁻¹).

3.5.1 Influence of the amidinate pendant arm substituent

In order to study the effect of a potentially coordinating amidinate pendant arm on the reaction, two model complexes **I_{C2}** and **I_{C3}** have been used in the calculations. These correspond to the real compounds **13** and **14**.



The reaction has been computed for both systems with the pendant NMe₂ not coordinated to titanium. The overall pathway is the same as that observed for **I**. However, in this case the cycloaddition of CO₂ can proceed either from the SiH₃-substituted side (SiMe₃ in the real compounds **13** and **14**), leading to the carbamate **II_{C2-Si}** or **II_{C3-Si}**, or from the pendant arm side, leading to **II_{C2-N}** and **II_{C3-N}** (Figure 3.15). The pathways for the two regiochemistries of addition have been computed and the energies of the various extrema are reported in Table 3.9.

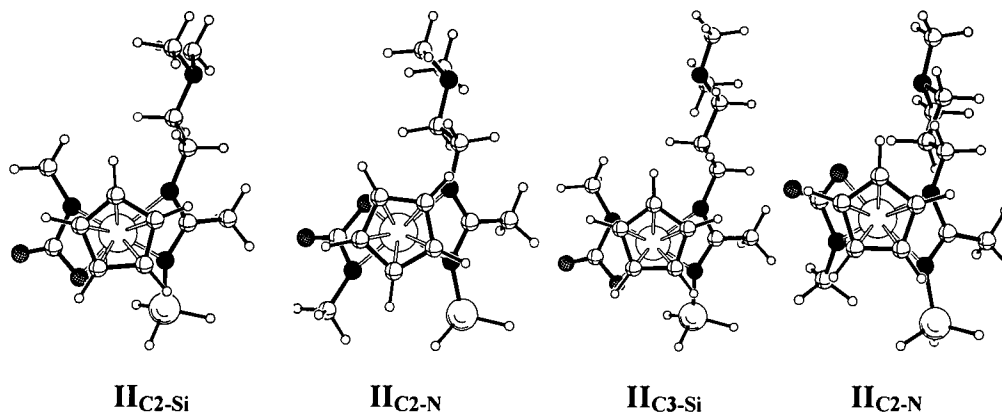


Figure 3.15 The various carbamate complexes formed from **I_{C2}** and **I_{C3}**

Table 3.9 Relative electronic energies (kJmol^{-1}) of extrema along the pathway for CO_2 cycloaddition/MeNCO extrusion on **I** and the two pendant arm functionalised titanium amidinate complexes (Free energy values at 298 K in parentheses). Energies are computed with respect to the separated imido-amidinate titanium complex and CO_2

Starting model:	I	I_{C2}		I_{C3}	
Side of CO_2 attack:	n/a	SiH ₃	C ₂ arm	SiH ₃	C ₃ arm
TS_{I-II}	0.6 (51.7)	3.5 (51.1)	4.5 (54.0)	3.0 (51.0)	4.6 (51.9)
II	-113.1 (-55.4)	-105.7 (-44.4)	-110.5 (-49.1)	-105.8 (-46.4)	-109.1 (-53.3)
TS_{II-III}	-25.1 (29.7)	-20.6 (31.6)	-25.2 (29.7)	-21.9 (29.2)	-23.7 (25.0)
III	-29.7 (21.7)	-23.7 (27.4)	-29.4 (25.3)	-25.0 (31.6)	-27.8 (22.3)
TS_{III-IV}	not located	-15.3 (30.5)	-21.4 (19.7)	-15.6 (27.1)	-20.4 (19.5)
IV + MeNCO	-25.4 (-32.2)	-24.6 (-33.1)		-23.7 (-33.0)	

In terms of the energies associated with the various pathways, it appears that the nature of the uncoordinated pendant arm substituent has no significant influence. There is, in each case, an almost barrierless cycloaddition of CO_2 to the imido group to form a stable η^2 -carbamate intermediate. In terms of the free energy values, 50 kJmol^{-1} is roughly the energy needed at 298 K to bring two reacting molecules together, so there is no extra energy needed to actually do the reaction. The reaction then proceeds in two steps by forming first an isocyanate adduct, then the oxo complex upon isocyanate dissociation. However, in all but one case, the isocyanate adduct is not stable enough to create a local minimum in the free energy surface (values in italics in Table 3.9) and so extrusion could equally well be considered to be a one step process. The difference in behaviour between the

energy and free energy surfaces for the extrusion could be explained by the influence of rotational energy contributions on dissociation. The energy of the transition state for extrusion is very low (below that of the entry channel in energy values, and below the cycloaddition transition state in free energy values) and this explains why the whole sequence (carbamate formation followed by isocyanate extrusion) occurs readily at room temperature.

The activation barriers for the cycloaddition and extrusion steps are summarised in Table 3.10.

Table 3.10 Relative electronic energies (kJmol^{-1}) of activation barriers along the pathway for CO_2 cycloaddition/MeNCO extrusion on pendant arm functionalised titanium amidinate complexes (Free energy values at 298 K in parentheses)

Starting material:	I_{C2}		I_{C3}	
Side of CO_2 attack:	SiH ₃	C ₂ arm	SiH ₃	C ₃ arm
I to TS_{I-II}	3.5 (51.1)	4.5 (54.0)	3.0 (51.0)	4.6 (51.9)
II to TS_{II-III}	85.1 (76.0)	85.3 (78.8)	83.9 (75.6)	85.4 (78.3)

In terms of the regiochemistry, the barriers for CO_2 cycloaddition and for isocyanate extrusion are very close in energy for all four cases. For both the C₂- and C₃-arm systems there is a small energetic preference for CO_2 attack from the SiH₃ side to form a carbamate intermediate where the imido NMe substituent and the SiH₃ group are on opposite sides. The dissociation of MeNCO from the pendant arm side that necessarily follows CO_2 addition from the SiH₃ direction is also slightly kinetically preferred (Table 3.10). While these differences are not significant within the accuracy of DFT calculations, it might be expected that the small energetic preference for this regiochemistry of addition and extrusion would be increased if the actual steric bulk were to be considered (*i.e.* SiMe₃ in place of SiH₃ and ^tBu in place of NMe). The crystallographically characterised carbamate complex **3.20** (Figure 3.1) formed from CO_2 and the real pentamethylcyclopentadienyl C₃-arm system **14** is consistent with CO_2 attack

from the SiMe_3 side. It is possible that this isomer could be the thermodynamic rather than the kinetic product but ^1H NMR spectra recorded during the reaction of **14** with CO_2 indicate the presence of only one carbamate isomer (although it is likely that the two carbamate isomers would give rise to extremely similar ^1H NMR spectra).

The calculations of the non-chelating model systems **I**_{C2} and **I**_{C3} imply that the reactions of the real complexes **13**, **14** and **15** would also be very similar if the pendant NMe_2 groups played no direct role. However, since the two carbon arm system **13** does not react with CO_2 at significant rates below $-35\text{ }^\circ\text{C}$ and the three carbon and "dummy arm" homologues react rapidly even at $-78\text{ }^\circ\text{C}$, it is clear that there must be an effect of the pendant NMe_2 that is different (or amplified) for the two-carbon system.

The extrusion step, however, occurs at the same temperature for all three of the real carbamate systems **19**, **20** and **21**, with rate constants that are very close in value. From the calculated values, the activation barrier for the isocyanate extrusion is *ca.* 85 kJmol^{-1} for both the two and three carbon arm model systems (energy difference between **II** and **TS_{II-III}** in Table 3.8). Although the experimental results indicate that the rate of extrusion is twice as fast for the two carbon pendant arm carbamate **21**, this translates into a $\Delta\Delta\text{G}$ value of less than 2 kJmol^{-1} which is also below the accuracy associated with these calculations.

3.5.2 Role of chelation of the pendant amine

Model imido-amidinate complexes with the pendant NMe_2 coordinated to titanium have been optimised and the resulting geometries are shown in Figure 3.16. The chelated isomer (**I**_{C2-chel} and **I**_{C3-chel}) is more stable than the non-chelated complex (**I**_{C2} and **I**_{C3}) in both cases by 25.4 and 23.3 kJmol^{-1} respectively. In **I**_{C3-chel}, the 6-membered ring is in a "chair" conformation. The alternative "boat" conformation has been optimised and lies 12.2 kJmol^{-1} higher in energy. When free energy values are considered at 298 K the chelated isomer **I**_{C2-chel} is still more stable than **I**_{C2}, but only by 6.2 kJmol^{-1} . For the C₃ system, however, the non-chelated isomer **I**_{C3-chel} is now only marginally more stable (0.4 kJmol^{-1}) than **I**_{C3}. The free energy differences between **I**_{C2} and **I**_{C2-chel} (and **I**_{C3}

and $\mathbf{I}_{\text{C3-chel}}$) are lower than the electronic ΔE values because the chelated form is entropically disfavoured. Since the C_3 chain has more rotational degrees of freedom the impact of the decoordination upon G is more pronounced. This is in agreement with the experimental observation that NMe_2 group methyl exchange occurs at a lower temperature for the real C_3 system **14**. Unfortunately, it was not possible to optimise a transition state for pendant arm dissociation for the model complexes $\mathbf{I}_{\text{C2-chel}}$ and $\mathbf{I}_{\text{C3-chel}}$.

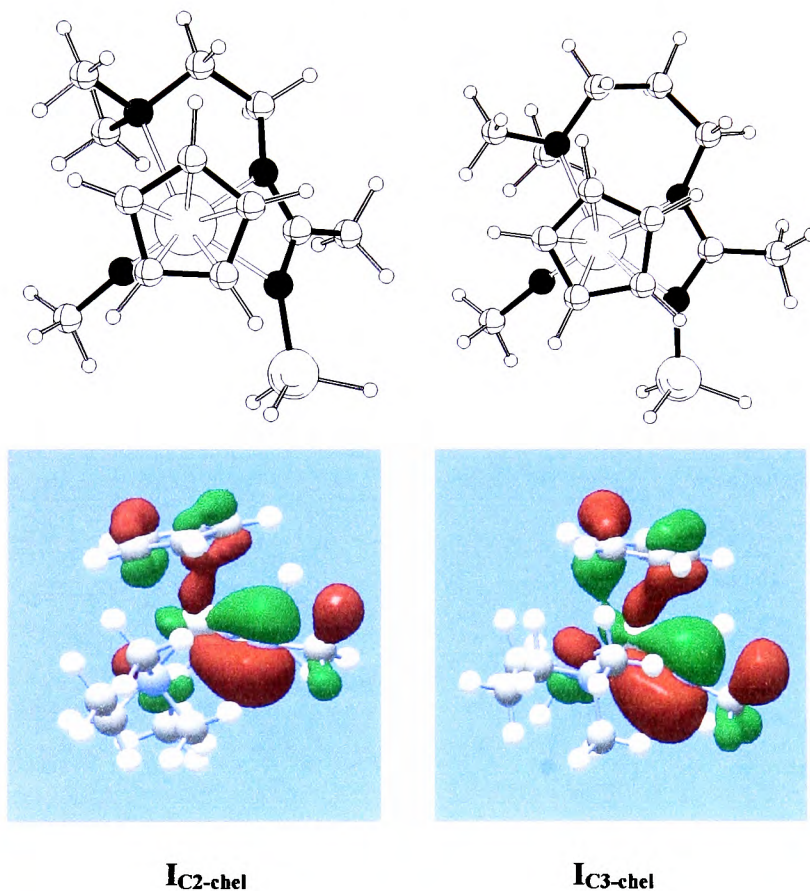


Figure 3.16 Geometry of the chelated imido-amidinate complexes $\mathbf{I}_{\text{C2-chel}}$ and $\mathbf{I}_{\text{C3-chel}}$ viewed along the $\text{Cp}_{(\text{cent})}\cdots\text{Ti}$ vectors. The HOMO of each complex is shown below viewed approximately perpendicular to these vectors

Interestingly, the HOMO for the chelated complexes (Figure 3.16) is not orientated in the same plane as for the non-chelated complexes (Figure 3.14). For the chelated complexes the frontier orbital preferred trajectory for CO_2 addition is from beneath, *trans* to the cyclopentadienyl ring. The corresponding transition

states ($\text{C2}_{\text{chel}}\text{TS}_{\text{I-II}}$ and $\text{C3}_{\text{chel}}\text{TS}_{\text{I-II}}$) are shown in Figure 3.17, the activation energy barriers corresponding to these transition states are 24.5 and 39.5 kJmol^{-1} respectively with respect to the isolated reactants.

The calculations show that, in terms of electronic energies, CO_2 attack on the chelated isomers $\text{I}_{\text{C2-chel}}$ and $\text{I}_{\text{C3-chel}}$ is disfavoured by some 20 - 35 kJmol^{-1} compared to the non-chelated isomers I_{C2} and I_{C3} . Furthermore, it is the chelated two carbon arm species that should, according to the calculations, react more readily with CO_2 which is in contrast to the experimental systems. Taken together, the experimental and computational data imply that preferred attack is thus *via* the non-chelated isomers, and that it is the activation barriers to accessing these that control the reactions.

As mentioned, it was not possible computationally to find a transition state for dissociation of NMe_2 in the model systems (*i.e.* $\text{I}_{\text{C2-chel}} \rightarrow \text{I}_{\text{C2}}$ or $\text{I}_{\text{C3-chel}} \rightarrow \text{I}_{\text{C3}}$). However the experimental values for NMe_2 methyl group exchange are available (*vide supra*) and it has therefore been possible to make a "hybrid" comparison of computational and experimental data for possibilities for CO_2 attack (Figure 3.18).

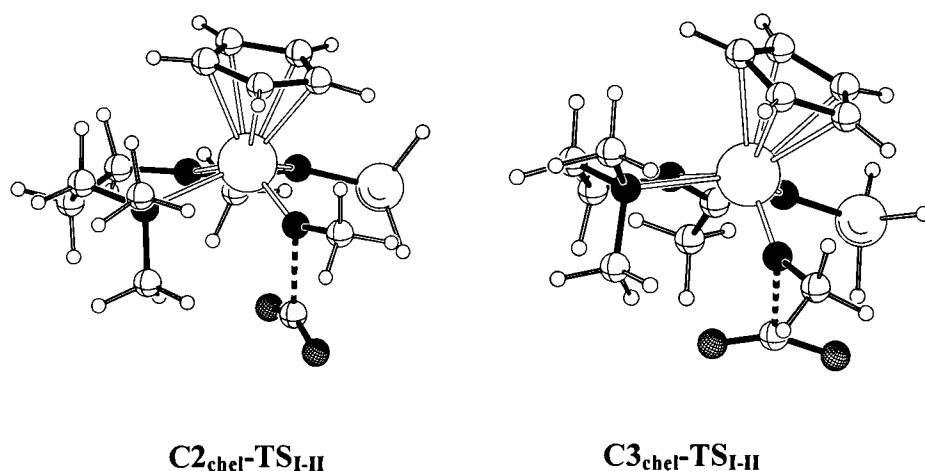


Figure 3.17 Geometries of the transition states for CO_2 cycloaddition to $\text{Ti}=\text{NMe}$ for the chelated amidinate-imido complexes $\text{I}_{\text{C2-chel}}$ and $\text{I}_{\text{C3-chel}}$

The free energies in Figure 3.18 were computed for 200 K, slightly above the temperature at which the real systems **14** (three carbon arm) and **15** ("dummy arm") react. All energies are from DFT calculations on the species or transition states indicated except for those for the transition state between $\text{I}_{\text{C2-chel}}$ and I_{C2}

(51.2 kJmol⁻¹) and $I_{C3\text{-chel}}$ and I_{C3} (41.2 kJmol⁻¹) which are taken from the experimental data for the real complexes **13** and **14** respectively.

Figure 3.18 unambiguously indicates that CO₂ attack would occur on the non-chelated isomers I_{C2} (real system **13**, Equation 3.7) and I_{C3} (real system **14**). Furthermore, this preference would be reinforced as the temperature is increased [**13** only reacts at a reasonable rate above -35 °C (238 K)] because attack by CO₂ is entropically disfavoured (thus the G for $C2_{\text{chel}} \rightarrow TS_{I-II}$ would be higher than shown in Figure 3.1.8) whereas (Table 3.3) $\Delta G^\ddagger$ for decooordination (leading to NMe₂ methyl exchange) is entropically favoured.

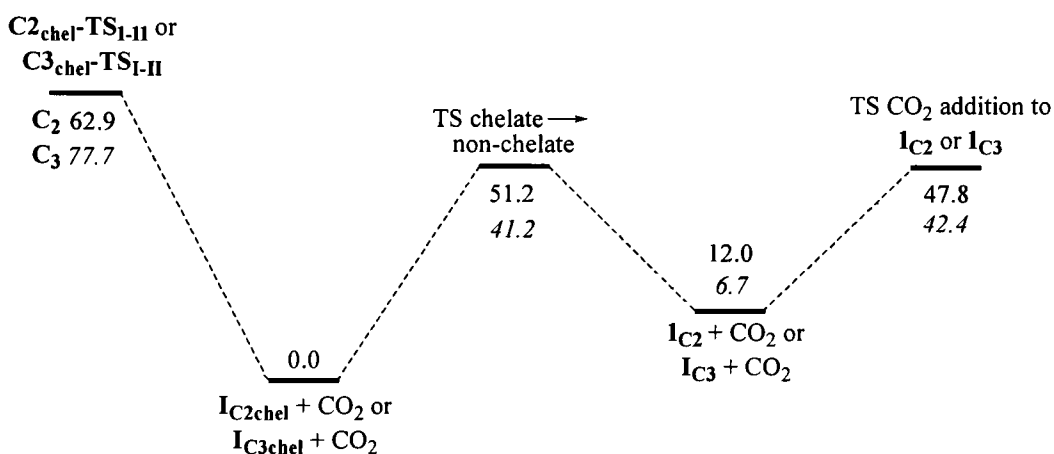


Figure 3.18 Schematic representation of the CO₂ addition mechanism for both the chelated and non-chelated systems as expressed by the free energy values at 200 K, relative to the respective chelated isomers. The upper values in each pair (italicised) are for the three carbon arm system and the lower values are for the two carbon arm systems (TS = transition state).

Although it is known experimentally (Section 3.4.3) that the real carbamate complexes **19** and **21** do not have a chelated NMe₂ group, attempts were made to elucidate computationally a mechanism for MeNCO extrusion from a carbamate complex with a chelating pendant arm. It was found that the κ^2 -carbamates formed from CO₂ cycloaddition to $I_{C2\text{chel}}$ or $I_{C3\text{chel}}$ have to be converted to κ^1 -carbamates before MeNCO extrusion could occur. However, it was not possible to find a transition state for this κ^2 to κ^1 interconversion which did not involve

dissociation of the NMe_2 group. Therefore, not only is CO_2 attack on the chelate isomer kinetically less favoured, but there is no exit channel from the κ_2 -carbamate so-formed leading to the observed products. This further militates against the likelihood of a pendant arm anchimeric effect on extrusion of isocyanate from the carbamate complexes.

3.5.3 Influence of steric bulk

ONIOM calculations (a form of hybrid QM/MM method) which take into account the influence of steric bulk have been performed. These indicate that the chelated isomer $\text{I}_{\text{C2-chel}}$ is more stable than the non-chelated isomer I_{C2} by 3.8 kJmol^{-1} for the C_2 system. In the case of the C_3 system, the non-chelated isomer I_{C3} is slightly more stable than the chelated isomer $\text{I}_{\text{C3-chel}}$ by 4.9 kJmol^{-1} . These values suggest that the equilibrium between the chelated and non-chelated isomers would lie in favour of the non-chelated isomer for the C_3 -system. This is in contrast to the clear evidence for chelation of the NMe_2 group in the low temperature NMR spectra of this compound. While these calculated energies do not entirely reflect the experimental behaviour of compound **14**, they do confirm that the stabilisation upon chelation is greater for the C_2 -system and that this trend is amplified when steric factors are considered. Again, the less favourable dissociation of the C_2 arm from titanium may account for the higher temperature required for CO_2 cycloaddition if the non-chelated isomer is the reactive species.

3.6 Discussion of combined kinetics and DFT studies

The kinetics studies on the cycloaddition of CO_2 to $\text{Ti}=\text{N}^t\text{Bu}$ for the C_2 -linker system (**13**) have established that the rate determining step is bimolecular with a first order dependence on CO_2 . In the case of the dummy arm system (**15**), cycloaddition necessarily occurs to a non-chelated pendant arm species. However, the CO_2 pressure-dependence in the case of the pendant amine functionalised compounds **13** and **14**, is consistent with both direct cycloaddition to the coordinated isomer and pendant arm dissociation followed by cycloaddition (Section 3.4). The DFT studies suggest that, for the C_3 -linker system, CO_2 cycloaddition occurs to the non-chelated isomer and is essentially barrierless. This is supported by the similar behaviour of the C_3 and dummy arm systems

which both undergo rapid cycloaddition of CO₂ even at -78 °C. For the C₂ system it is possible that CO₂ addition to the chelated isomer could be competitive, but comparison of the activation barriers for methyl group exchange (experimentally determined) and CO₂ cycloaddition (calculated) at 200 K suggest that decoordination of the pendant arm followed by CO₂ cycloaddition is energetically favoured. It was not possible to optimise a transition state for NMe₂ group dissociation by DFT so calculated values are not available for comparison with the experimentally determined activation parameters for methyl group exchange. The larger energy required to decoordinate the pendant amine from titanium for the C₂ system might explain the higher temperature needed before CO₂ cycloaddition occurs.

In the case of the extrusion step, kinetics experiments indicated a small but experimentally reproducible doubling in the rate of ^tBuNCO extrusion for the C₂-linker compound **13**. This might arise due either to slight steric differences between the ligand systems or from a slight anchimeric effect of the 2-carbon arm on the extrusion. The differences in the calculated activation barriers for isocyanate extrusion from the C₂ and C₃-carbamates without the pendant arms coordinated are too small to be significant. Low temperature ¹H NMR spectra of both carbamate intermediates (**19** and **21**) at -80 °C suggest that the pendant arms are not coordinated on the NMR timescale. The origin of the small increase in the rate of isocyanate extrusion for the C₂-arm systems is therefore still somewhat unclear.

The kinetic studies on the rate of isocyanate extrusion from the dummy arm system at different concentrations suggest a first order dependence on the carbamate in the rate determining step. This is consistent with extrusion to form a monomeric terminal oxo complex which then self-traps by dimerisation. No evidence is observed in the ¹H NMR spectra during these reactions for the presence of the calculated, loosely-bound isocyanate adduct that forms during extrusion. The flat nature of the energy profile between TS_{II-III} and the oxo compound **IV** suggests that there may be some reversibility in this part of the mechanism, whereby the transient terminal oxo complex can undergo

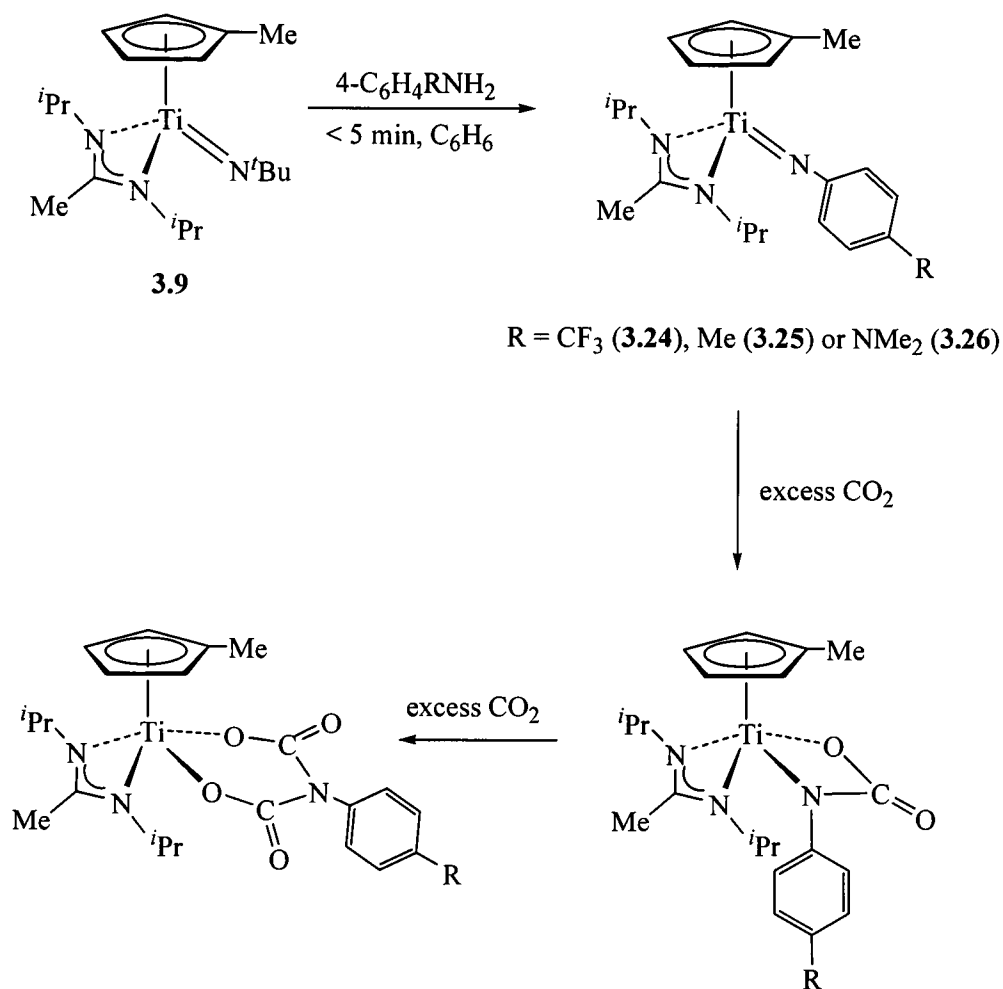
cycloaddition of $t\text{-BuNCO}$ to reform the carbamate intermediate unless it is trapped by dimerisation. Studies on the corresponding unfunctionalised amidinate-supported dimeric oxo complexes have confirmed that they are inert to reactions of this type.²³

3.7 Further studies on the mechanism of CO_2 reactions with imido compounds

The combined kinetic and DFT studies of the pendant arm functionalised *tert*-butyl amidinate-imido complexes (Sections 3.4 - 3.6) and the previous work on the reactivity of the unfunctionalised amidinate systems (Section 3.3) raised some additional questions that have been addressed by a further series of experiments.

It has been proposed that extrusion of isocyanate from *tert*-butyl carbamate compounds initially produces a titanium terminal oxo complex, although no evidence for any such species has been observed when these reactions have been monitored by ^1H NMR spectroscopy. The DFT calculated energy profile for isocyanate extrusion is rather flat, suggesting that there may be some reversibility in the mechanism, whereby the transient oxo complex could undergo $t\text{-BuNCO}$ cycloaddition to reform the carbamate until it is trapped by dimerisation and rendered inert. This has been probed by an NMR crossover reaction between $[\text{Ti}(\eta\text{-C}_5\text{Me}_5)(\text{N}^t\text{Bu})\{\text{MeC}(\text{N}^i\text{Pr})_2\}]$ (**3.23**) and CO_2 in the presence of excess $t\text{-BuNCO}$ or a toylisocyanate "trap" and will be discussed in Section 3.7.1.

Previous attempts have been made to probe the reasons for the stability of aryl-imido derived carbamate compounds relative to those derived from *tert*-butyl imides (resulting in the additional insertion of CO_2 into aryl-carbamates instead of decomposition and isocyanate extrusion). The electronic properties were varied by preparation of a series of arylimido complexes with different *para*-substituents, such that the steric properties of the compounds remained unchanged (Scheme 3.7). The electronic properties of the chosen substituents were assessed by means of their Hammett parameters, an empirically measured property of aryl substituents that gives a measure of their capacity to donate or withdraw electron density from the ring.⁴²



R = CF₃ (3.30), Me (3.31) or NMe₂ (3.32) R = CF₃ (3.27), Me (3.28) or NMe₂ (3.29)

Scheme 3.7 Preparation and reactivity of some para-substituted arylimido complexes

A series of pseudo-first order rate studies were carried out to determine rate constants for the second addition of CO₂ to the carbamate complexes derived from the reactions of **3.24** - **3.26** with CO₂. Studies were performed at room temperature in the presence of a constant > 10-fold excess of CO₂ (*ca.* 1.6 atm). Table 3.11 summarises Hammett parameters and rate constants for the different R-substituents.

Table 3.11 Comparison of Hammett parameters for the 4-substituted aryl groups and rate constants for conversion of carbamates **3.27** - **3.29** to aryldicarboxylate complexes **3.30** - **3.32**

R-substituent	$k_{\text{obs}} \times 10^4 \text{ (s}^{-1}\text{)}$	Hammett parameter, σ
<i>p</i> -CF ₃	9.1 ± 1.4	0.53
<i>p</i> -Me	9.0 ± 0.1	-0.14
<i>p</i> -NMe ₂	12.9 ± 1.4	-0.63

It can be seen that there is only a very small difference in rate between the *p*-CF₃ and *p*-Me substituted systems. However, the substitution with the *p*-NMe₂ group substantially increases the rate of reaction of the carbamate with CO₂. The lack of a retardation of the rate in the CF₃ system may be due to one of two reasons. Either two opposing factors affect the rate of the second insertion (*i.e.* the electron donating properties of the ring are balanced against the electron withdrawing properties of the metal centre) or the Hammett parameter for the CF₃ group does not reflect a true value in this organometallic system. However, it is also possible that the rate determining step for the mechanism of the second addition may involve rearrangement of the intermediate carbamate species and not feature CO₂. Section 3.7.2 of this Chapter describes a series of kinetics experiments designed to determine the CO₂-dependence of the second addition of CO₂ to *p*-tolyl carbamate **3.28**, and to allow further interpretation of the preliminary results outlined above.

The final question that will be addressed in the following Sections is the effect of a pendant donor arm on the reactivity of arylimido complexes towards CO₂. The synthesis of pendant arm functionalised amidinate-arylimido complexes will be described and the reactions of such complexes towards CO₂ will be examined (Section 3.7.3).

3.7.1 Crossover Reaction

In order to probe the possibility of reversibility in the extrusion of ^tBuNCO from cyclopentadienyl-amidinate supported carbamates and to further investigate the evidence for a transient titanium terminal oxo species, a series of NMR tube scale

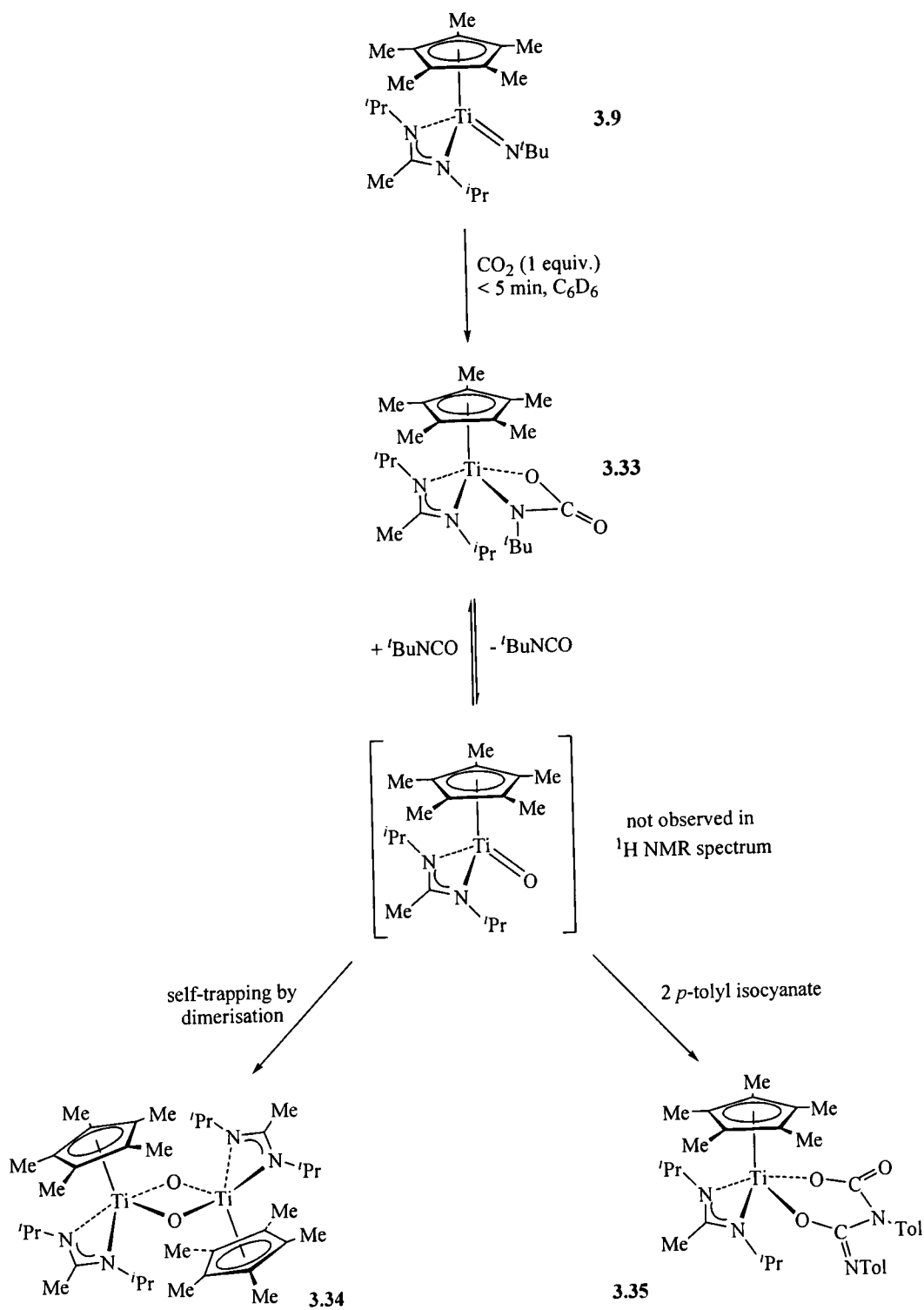
experiments were carried out. The aim of these experiments was to determine the effect upon the rate of isocyanate extrusion from the carbamate of the presence of a large excess of $t\text{-BuNCO}$ and also of the presence of a p -tolyl isocyanate "trap".

It was not possible to use the pendant arm functionalised amidinate-imido systems for these experiments because the imido compounds **13** and **14** were found to react with $t\text{-BuNCO}$ at rt. The compound $[\text{Ti}(\eta\text{-C}_5\text{Me}_5)(\text{N}^i\text{Bu})\{\text{MeC}(\text{N}^i\text{Pr})_2\}]$ (**3.9**) was selected instead, as work previously undertaken had shown it to react much more rapidly with CO_2 (complete reaction at room temperature in < 5 minutes) than with the p -tolyl isocyanate "trap" ($t_{1/2} = 2$ days).²³

Three parallel reactions in C_6D_6 were set up, each containing the same concentrations of $[\text{Ti}(\eta\text{-C}_5\text{Me}_5)(\text{N}^i\text{Bu})\{\text{MeC}(\text{N}^i\text{Pr})_2\}]$ (**3.9**) and of 1,4-dimethoxybenzene internal standard. One of these was used as a control reaction and the others had either 5 equivalents of $t\text{-BuNCO}$ or of p -tolyl isocyanate added (Scheme 3.8). Samples were exposed to *ca.* 1 atm CO_2 via a dual-manifold Schlenk line and the ^1H NMR spectra were monitored over 16 hours. The progress of the reaction was monitored by measuring extrusion of $t\text{-BuNCO}$ from the carbamate compound **3.33** relative to the internal standard. The progress of each reaction over time is shown in Table 3.12, errors have not been fully calculated for all cases but are likely to be less than $\pm 2\%$.

Table 3.12 Extrusion of $t\text{-BuNCO}$ from $[\text{Ti}(\eta\text{-C}_5\text{Me}_5)(\text{OC}(\text{O})\text{N}^i\text{Bu})\{\text{MeC}(\text{N}^i\text{Pr})_2\}]$ (**3.33**) with CO_2 in the presence of excess $t\text{-BuNCO}$ and in the presence of a p -tolyl isocyanate trap

Reaction	Percentage of carbamate 3.33 converted to oxo dimer 3.34		
	3 h	5 h	16 h
3.33 + dimethoxybenzene (control reaction)	30	38	72
control + 5 $t\text{-BuNCO}$	28	32	69
control + 5 p -tolyl isocyanate	47	57	89



Scheme 3.8 Interception of terminal oxo intermediate

Scheme 3.8 shows the proposed mechanism for the reaction, in which reversible extrusion of $t\text{-BuNCO}$ from the carbamate **3.33** forms a transient terminal oxo compound. This is not observed in the ^1H NMR spectrum which suggests that this undergoes immediate cycloaddition with $t\text{-BuNCO}$ to regenerate the carbamate or is trapped, either by dimerisation to yield the bridging oxo compound or by reaction with *p*-tolyl isocyanate.

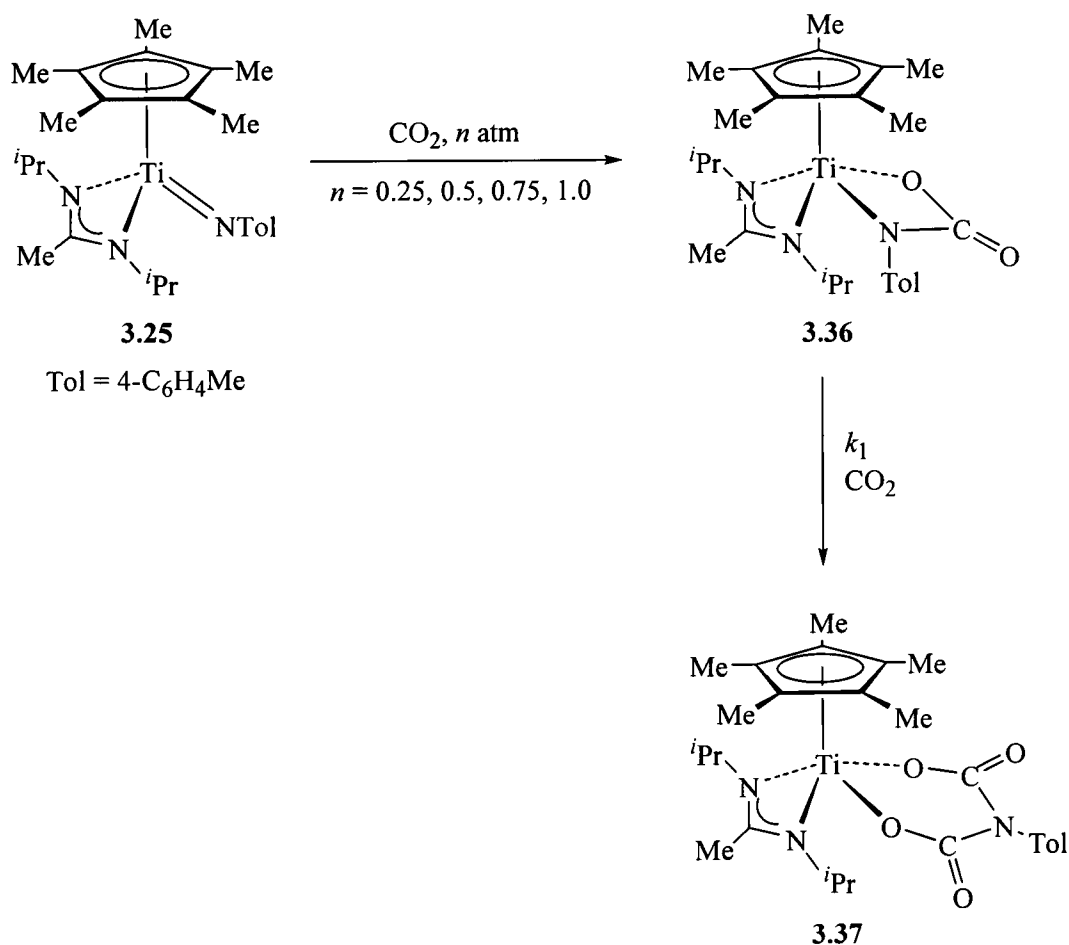
The "trapped" product of the *p*-tolyl isocyanate reaction was identified by ^1H NMR spectroscopy as the previously reported $[\text{Ti}(\eta\text{-C}_5\text{Me}_5)\{\text{OC}(\text{O})\text{N}(\text{Tol})\text{C}(\text{NTol})\text{O}\}\{\text{MeC}(\text{N}^i\text{Pr})_2\}]$ (**3.35**).²² This could only be formed by cycloaddition of *p*-tolyl isocyanate to the terminal oxo compound to yield the carbamate $[\text{Ti}(\eta\text{-C}_5\text{Me}_5)\{\text{OC}(\text{O})\text{NTol}\}\{\text{MeC}(\text{N}^i\text{Pr})_2\}]$, followed by insertion of a second molecule into the Ti-N bond. It therefore provides firm evidence for the presence of a titanium terminal oxo species in the reaction mixture. No evidence for the product of single addition of *p*-tolyl isocyanate to the titanium terminal oxo species was observed in the NMR spectra.

The data in Table 3.12 suggest that the presence of the *p*-tolyl isocyanate "trap" leads to faster decomposition of the carbamate **3.33** than for the control reaction, consistent with the equilibrium for $t\text{-BuNCO}$ extrusion being forced in favour of the terminal oxo species. There is corresponding evidence for a small retardation in the rate of carbamate consumption in the presence of excess $t\text{-BuNCO}$. These results are consistent with reversible extrusion of isocyanate from the carbamate intermediate to form a terminal oxo species. The DFT calculations on the model systems described in Section 3.5 support this possibility. The terminal oxo complex is calculated to be energetically less stable than the carbamate intermediate until it is trapped by dimerisation, so the addition of $t\text{-BuNCO}$ to reform the carbamate is favourable and involves crossing a relatively low energy barrier.

3.7.2 Second addition of CO₂ to arylimido-derived carbamate compounds: mechanistic studies

In order to gain a greater understanding of factors governing the rate of the second addition of CO₂ to arylimido-derived carbamate compounds, a kinetic study has been carried out to investigate the dependence on CO₂ pressure.

The rapid reaction of the carbamate complex [Ti(η-C₅Me₅){(NTol)C(O)O}{MeC(N^{*i*}Pr)₂}] (**3.36**) with CO₂ makes it convenient to study at room temperature using ¹H NMR spectroscopy. This system has been used to determine the rate law dependence of CO₂ in the reaction to form the insertion product **3.37** (Scheme 3.9).



Scheme 3.9 Mechanistic studies on second addition of CO₂ to aryl imido-derived carbamate compounds

These studies were carried out under pseudo-first order conditions (see Section 3.4.4) whereby at least a 10-fold excess of CO_2 was present in the NMR tube at the lowest pressure studied. NMR samples of **3.25** in C_6D_6 were exposed to known pressures of CO_2 *via* a calibrated gas manifold. Samples were transferred into the probe of an NMR spectrometer which was maintained at a temperature of 20°C . 1,4-Dimethoxybenzene was used as an internal standard to ensure the concentration of the reactant and product species in solution could be independently verified during the experiment. As expected, all of the imido complex **3.25** was consumed to form the carbamate complex **3.36** before any of the aryl imido dicarboxylate complex **3.37** was detected.

In each case, the reaction progress was monitored *via* ^1H NMR spectroscopy. The relative concentrations of carbamate **3.36** and arylimido dicarboxylate complexes **3.37** were measured from each spectrum, and the results fitted to a first-order exponential relationship (Figure 3.19). The rate constants k extracted from plots of $\ln(I/I_0)$ vs. time are listed in Table 3.13.

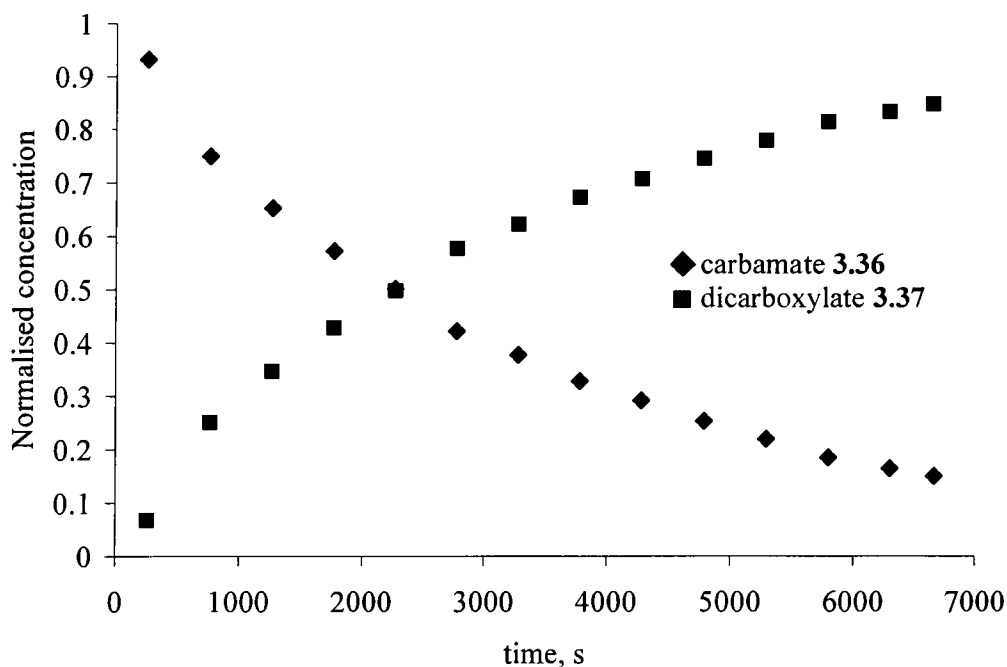


Figure 3.19 Plot of normalised concentrations against time for the insertion reaction of **3.37** with CO_2 (0.5 atm). Values are given for carbamate (**3.36**) and product dicarboxylate (**3.37**)

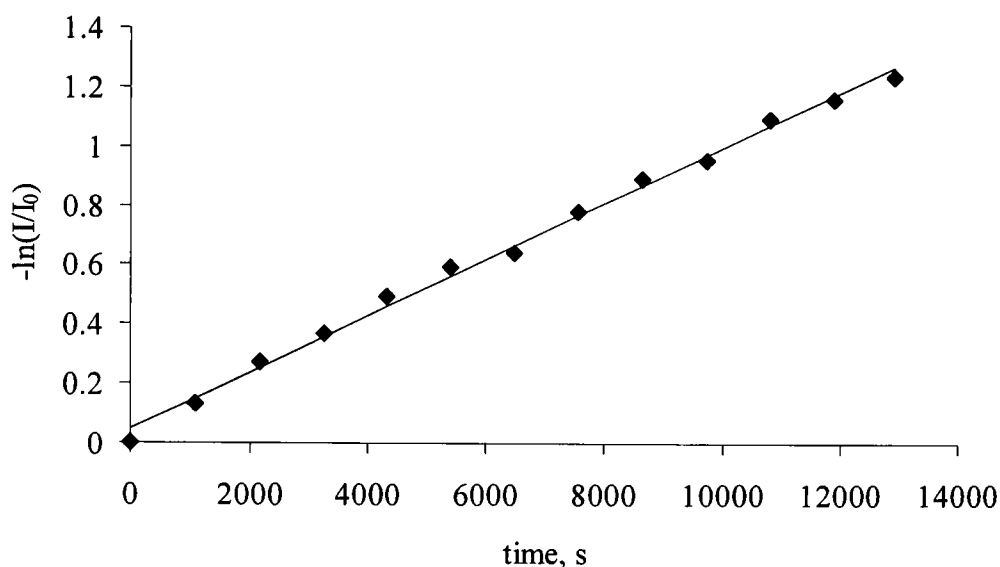


Figure 3.20 Plot of $\ln(I/I_0)$ vs. time for consumption of $[\text{Ti}(\eta\text{-C}_5\text{Me}_5)\{(\text{NTol})\text{C}(\text{O})\text{O}\}\{\text{MeC}(\text{N}^i\text{Pr})_2\}]$ (3.36)

Table 3.13 Observed rate constants k_{obs} for the insertion reaction of 3.36 with CO_2 at different CO_2 pressures.

p CO_2 (atm)	$k_{\text{obs}} \times 10^4 \text{ (s}^{-1}\text{)}$
0.25	0.95 ± 0.02
0.5	2.9 ± 0.03
0.75	4.1 ± 0.06
1.0	5.7 ± 0.09

The exponential decay of carbamate and evolution of the aryl imido dicarboxylate product indicate that the reaction is bimolecular and first order in CO_2 . This is confirmed by the linear dependence of k_{obs} on CO_2 pressure (Figure 3.21).

The dependence of the rate of this reaction on CO_2 pressure suggests that the lack of a direct correlation between Hammett parameter and reaction rate in the earlier study must be explained by factors other than exclusion of CO_2 from the rate determining step.

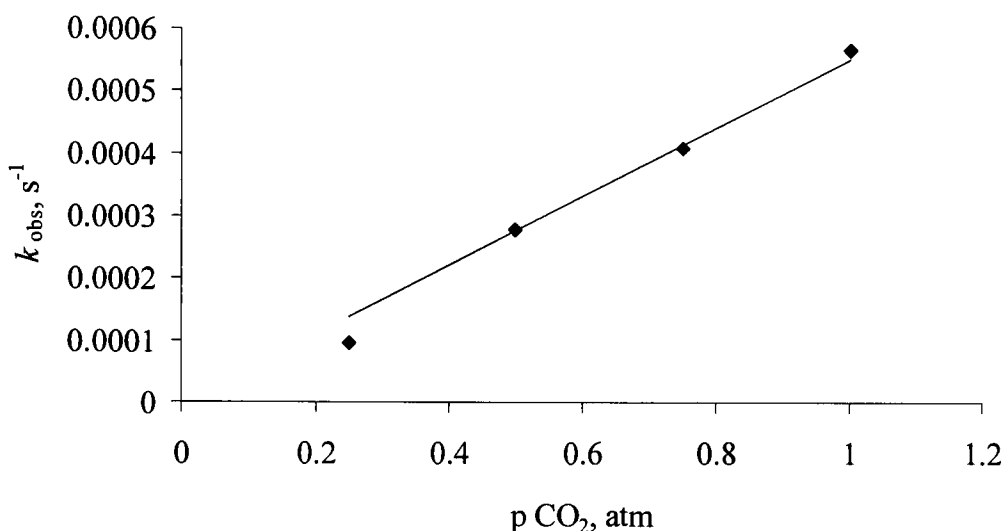


Figure 3.21 Plot of k_{obs} vs. CO_2 pressure for the reaction of $[\text{Ti}(\eta\text{-C}_5\text{Me}_5)\{\text{(NTol)C(O)O}\}\{\text{MeC(N}^i\text{Pr)}_2\}]$ (**3.44**) with CO_2

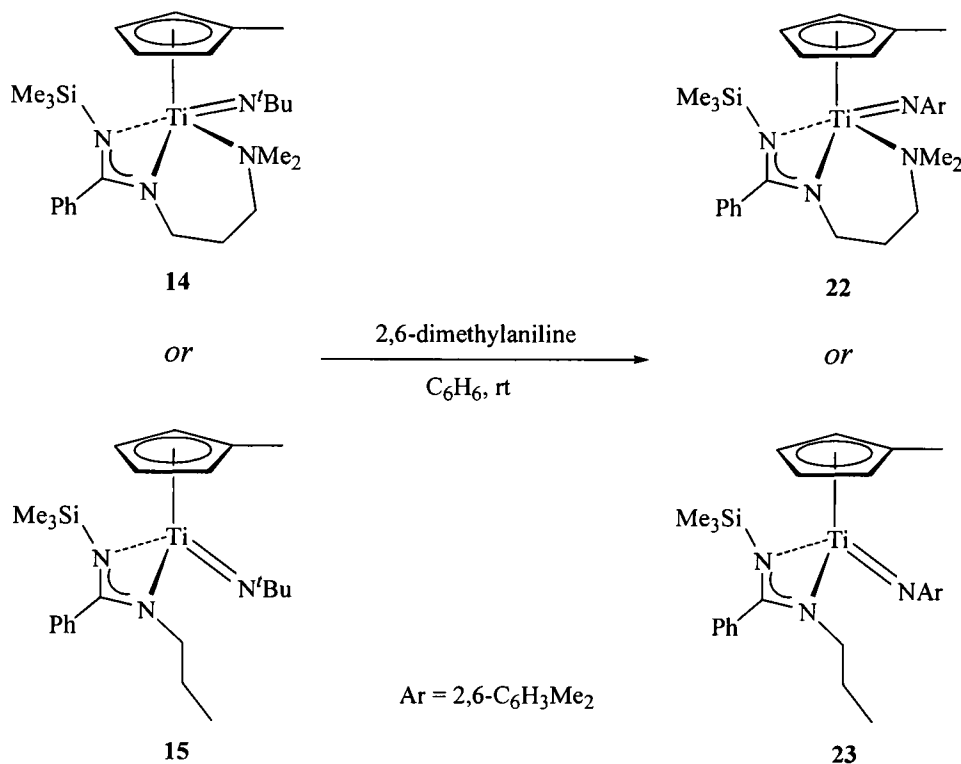
The Hammett parameter is empirically determined from measurements made on systems without a metal centre and may not hold for metal-containing compounds.⁴²⁻⁴⁴ However, it is also possible in this case that the rate determining step is dependent upon both the nucleophilicity of the lone pair on nitrogen and the electrophilicity of titanium. As the aryl ring becomes more electron-rich, the nucleophilicity of the nitrogen will increase. At some point this may cause an increase in electron density at titanium which may act to inhibit pre-coordination of CO_2 if this is involved in the insertion mechanism. However, no evidence for additional species resulting from pre-coordination of CO_2 was observed in the ^1H NMR spectra during the course of these reactions.

3.7.3 Methyl cyclopentadienyl pendant arm functionalised benzamidinate aryl imido compounds

Given the unprecedented reactivity of the non-pendant arm amidinate arylimido systems with CO_2 , it was decided to prepare some pendant arm functionalised arylimido derivatives, with the hope of evaluating the effect of the pendant donor on the second addition of CO_2 to aryl imides.

The compounds $[\text{Ti}(\eta\text{-C}_5\text{H}_4\text{Me})(\text{N}^i\text{Bu})\{\text{Me}_3\text{SiNC(Ph)NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}]$ (**14**) and $[\text{Ti}(\eta\text{-C}_5\text{H}_4\text{Me})(\text{N}^i\text{Bu})\{\text{Me}_3\text{SiNC(Ph)NCH}_2\text{CH}_2\text{Me}\}]$ (**15**) were reacted with

one equivalent of 2,6-dimethylaniline in benzene at room temperature to yield their arylimido homologues $[\text{Ti}(\eta\text{-C}_5\text{H}_4\text{Me})(\text{N}^t\text{Bu})\{\text{Me}_3\text{SiNC(Ph)NCH}_2\text{CH}_2\text{NMe}_2\}]$ (**22**) and $[\text{Ti}(\eta\text{-C}_5\text{H}_4\text{Me})(\text{N}^t\text{Bu})\{\text{Me}_3\text{SiNC(Ph)NCH}_2\text{CH}_2\text{Me}\}]$ (**23**) via an imide/aniline exchange process (Equation 3.13).



Equation 3.13

These new compounds are oils at room temperature but were purified by high vacuum sublimation (sublimed yields 15 and 47% respectively). NMR spectra of the compounds **22** and **23** confirm the proposed structures. There is a 6 H singlet for the NMe₂ protons of the pendant amine in **22** (2.10 ppm), suggesting that either the NMe₂ group is not coordinated to the metal centre or that methyl group exchange is fast on the NMR timescale at this temperature.

Attempts to record the low temperature ¹H NMR spectrum of **22** in order to examine the coordination of the pendant amine proved unsatisfactory. The resonances attributed to the pendant NMe₂ group and the methyl groups of the imido C₆H₃Me₂ substituent overlapped when CD₂Cl₂ was used as the solvent. Attempts to use toluene-d₈ as the solvent were unsuccessful due to overlap of the

residual solvent resonance at 2.09 ppm with the pendant NMe₂ singlet. It appears that there is a decoalescence of the NMe₂ singlet in both solvents between -40 and -45 °C but it was not possible to determine the coalescence temperature with sufficient precision to extract thermodynamic parameters for the exchange process.

3.7.4 Reaction of compound **22** with CO₂

A solution of the 3-carbon linker compound **22** in C₆D₆ was exposed to *ca.* 1 atm CO₂ *via* a Schlenk line. The ¹H NMR spectrum was monitored over several hours. The reaction yielded a mixture of products which appeared to decompose in solution. The NMR spectra of these products could not be assigned so these investigations were not pursued.

3.8 Summary

This Chapter has introduced the combined cyclopentadienyl-amidinate ligand set and discussed work previously carried out on cyclopentadienyl-amidinate imido complexes. The preparation of new cyclopentadienyl-supported titanium *tert*-butyl imido complexes with pendant arm functionalised amidinate ligands has been described. The reactions of these complexes to form bridging oxo compounds *via* isocyanate extrusion from carbamate intermediates have been discussed. Mechanistic studies have been performed to investigate the effects of the pendant arm substituent of the cycloaddition of CO₂ and the extrusion of isocyanate. Density Functional Theory studies to probe the mechanisms of these reactions more closely have been carried out. An NMR crossover study has investigated the reversible nature of the extrusion step. Further investigations into the reactions of arylimido complexes with CO₂ have established the CO₂ pressure-dependence of the second insertion of CO₂ in such systems. Pendant arm functionalised amidinate supported arylimido complexes have been synthesised and their reactions with CO₂ examined.

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Chapter 4

Alkyl, Aryloxy and Cationic Pendant Arm Functionalised Titanium Amidinate-Imido Compounds

4.1 Overview

Chapter 2 described the synthesis and properties of a series of new monomeric titanium imido complexes supported by pendant arm functionalised amidinate ligands. Previous work on benzamidinate-imido compounds has shown that this ligand set can support further substitution chemistry of such complexes.¹ It was therefore decided to investigate the synthesis and properties of these pendant arm functionalised amidinate-imido complexes where the chloride ligand is substituted by another monoanionic ligand. Part of this work has recently been published.²

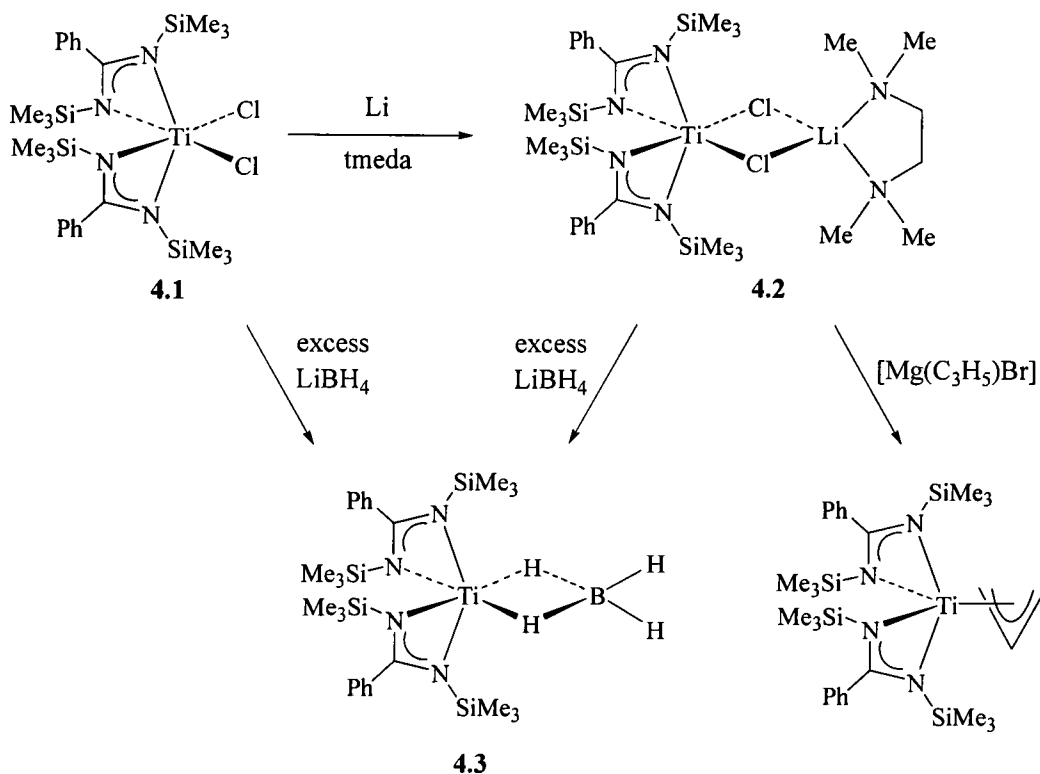
The reactions of complexes containing both potentially reactive $M=NR$ linkages and metal hydrocarbyl σ -bonds pose interesting questions of site selectivity. A recent example of this has been raised by the calculations of Jensen and Børve^{3,4} on Gibson's olefin polymerisation catalysts $[Cr(NR')_2R_2]$ ($R' = 'Bu$ or aryl; $R = Me$ or CH_2Ph).⁵ At first sight one would probably envisage that these would give rise to cationic active species $[Cr(NR')_2R]^+$ ($R =$ initiating group or growing polymer chain) with monomer enchainment proceeding through migratory insertion reactions of the $Cr-R$ bond. However, for chemically realistic model systems $[Cr(NR')_2R]^+$ it appears that ethylene cycloaddition to the $Cr=NR'$ bond can compete with insertion into the $Cr-R$ bond, in turn leading (after further modification) to a reduced $Cr(IV)$ species which may in fact be a resting state for this catalyst system. It was hoped that replacement of the chloride ligand in certain of the compounds $[Ti(NR)\{Me_3SiNC(Ph)N(CH_2)_nNMe_2\}Cl]$ ($R = 'Bu$, 2,6- $C_6H_3Me_2$ or 2,6- $C_6H_3^iPr_2$; $n = 2$ or 3) (**1** - **6**) would provide interesting and well-defined metal complexes for further studies with regard to site selectivity.

One particular feature of these compounds is the possibility of the pendant NMe_2 donor group of the amidinate ligand dissociating in solution during the course of a reaction to form a more reactive, lower coordination number metal centre. This approach has already been used with considerable success in other N-donor ligand supported imidotitanium systems (Scheme 2.3).⁶

This Section will describe some examples of chloride metathesis reactions of Group 4 amidinate complexes before focusing on those of some titanium amidinate-imido complexes already prepared in the Mountford group.

4.2 Introduction

Gambarotta and coworkers have prepared a number of bis(benzamidinate) titanium (III) complexes. Reduction of the titanium (IV) compound $[\text{Ti}\{\text{PhC}(\text{NSiMe}_3)_2\}_2\text{Cl}_2]$ (**4.1**) with a stoichiometric amount of metallic lithium in the presence of *N,N,N',N'*-tetramethylethylenediamine (tmeda) gave the paramagnetic compound $[\text{Ti}\{\text{PhC}(\text{NSiMe}_3)_2\}_2(\mu\text{-Cl})\text{Li}(\text{tmeda})]$ (**4.2**). Borohydride and allyl derivatives were formed by chloride metathesis reactions of **4.2** (Scheme 4.1).⁷ Compounds **4.1** - **4.3** have been crystallographically characterised.



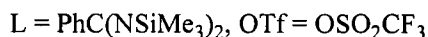
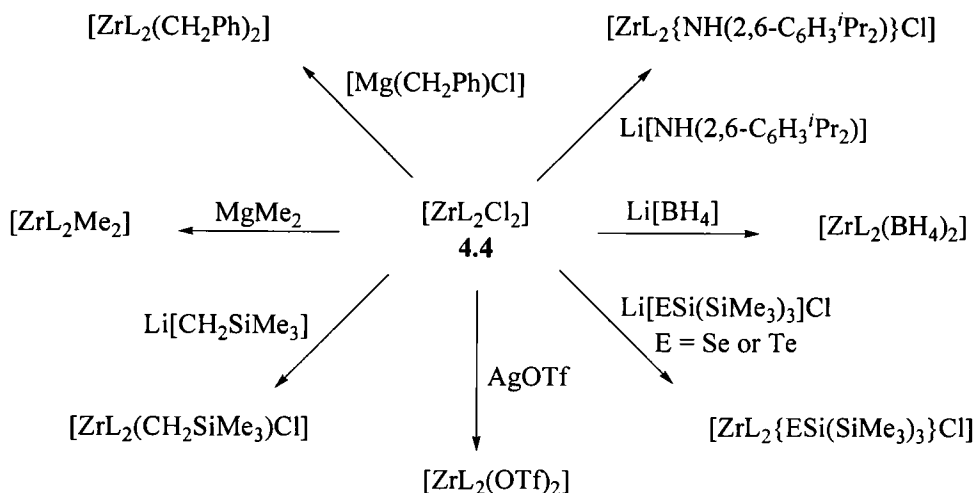
Scheme 4.1 Formation of bis(benzamidinate) titanium (III) complexes

The η^2 -borohydride derivative **4.3** was also accessible *via* reaction of LiBH_4 with the titanium (IV) complex $[\text{Ti}\{\text{PhC}(\text{NSiMe}_3)_2\}_2\text{Cl}_2]$, first reported by Roesky and coworkers.⁸

Arnold and coworkers have reported studies of bis(benzamidinate) titanium and zirconium systems.⁹⁻¹² Reaction of **4.3** with MgMe_2 gave the mixed alkyl chloride $[\text{Ti}\{\text{PhC}(\text{NSiMe}_3)_2\}_2(\text{Me})\text{Cl}]$. This was reduced using sodium amalgam to yield

the unusual titanium^{III} alkyl $[\text{Ti}\{\text{PhC}(\text{NSiMe}_3)_2\}\text{Me}]$, which was crystallographically characterised.⁹

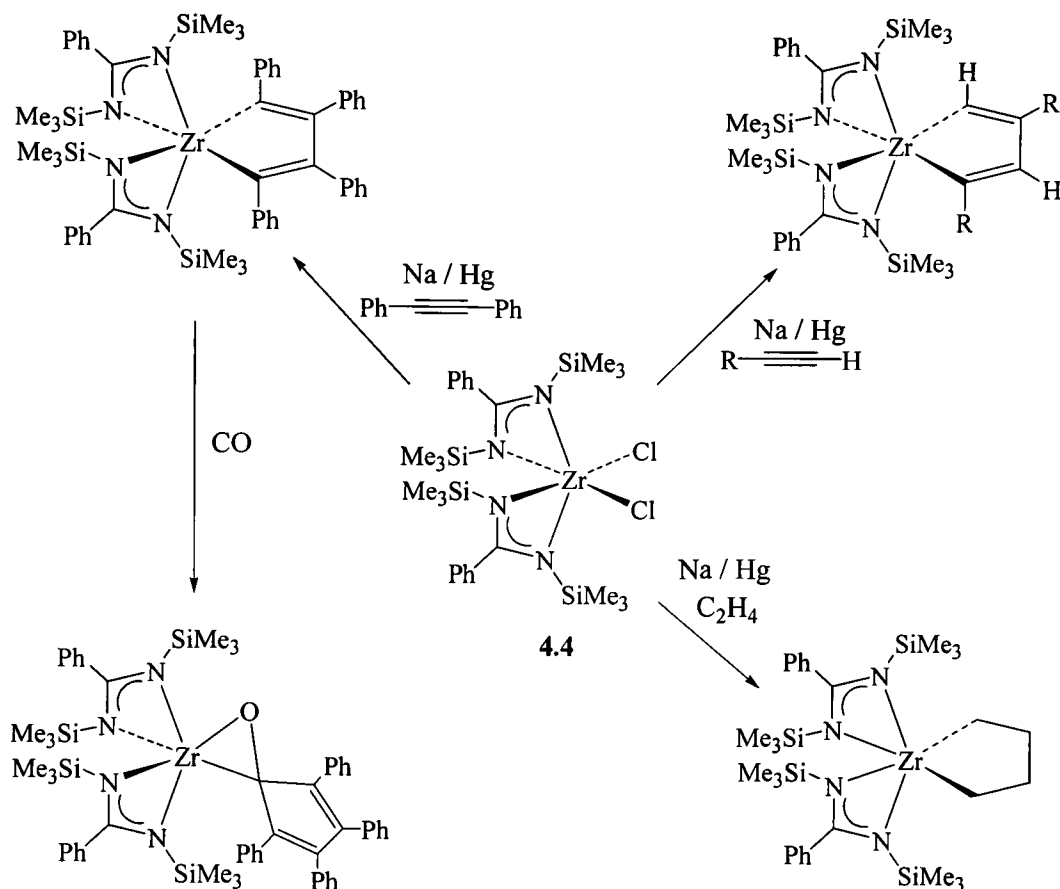
The reaction chemistry of $[\text{Zr}\{\text{PhC}(\text{NSiMe}_3)_2\}_2\text{Cl}_2]$ (**4.4**) has also been extensively probed.¹² Metathesis of the chloride ligands gave a wide variety of alkyl, triflate and borohydride derivatives (Scheme 4.2).



Scheme 4.2 Chloride metathesis reactions of $[\text{Zr}\{\text{PhC}(\text{NSiMe}_3)_2\}_2\text{Cl}_2]$ (**4.4**)

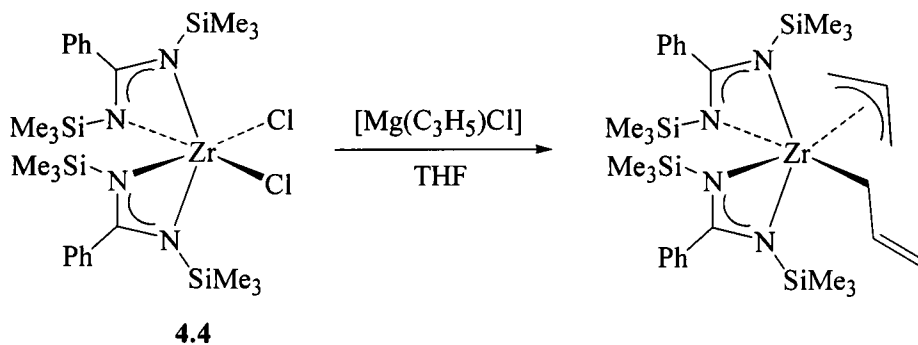
Under reducing conditions **4.4** has been shown to couple alkynes and ethylene to form metallacycles (Scheme 4.3) *via* Zr^{II} intermediates.

Walther *et al.* have also made contributions to the understanding of the bis(benzamidinate) zirconium system.¹³ They found that **4.4** would react cleanly with Grignard reagents to yield methyl, benzyl and allyl derivatives. They also formed the seven-coordinate tris(benzamidinate) complex $[\text{Zr}\{\text{PhC}(\text{NSiMe}_3)_2\}_3\text{Cl}]$ in good yield *via* addition of another equivalent of $\text{Li}[\text{PhC}(\text{NSiMe}_3)_2]$ to **4.4**.



Scheme 4.3 Oxidative coupling reactions of $[\text{Zr}\{\text{PhC}(\text{NSiMe}_3)_2\}_2\text{Cl}_2]$ (**4.4**)

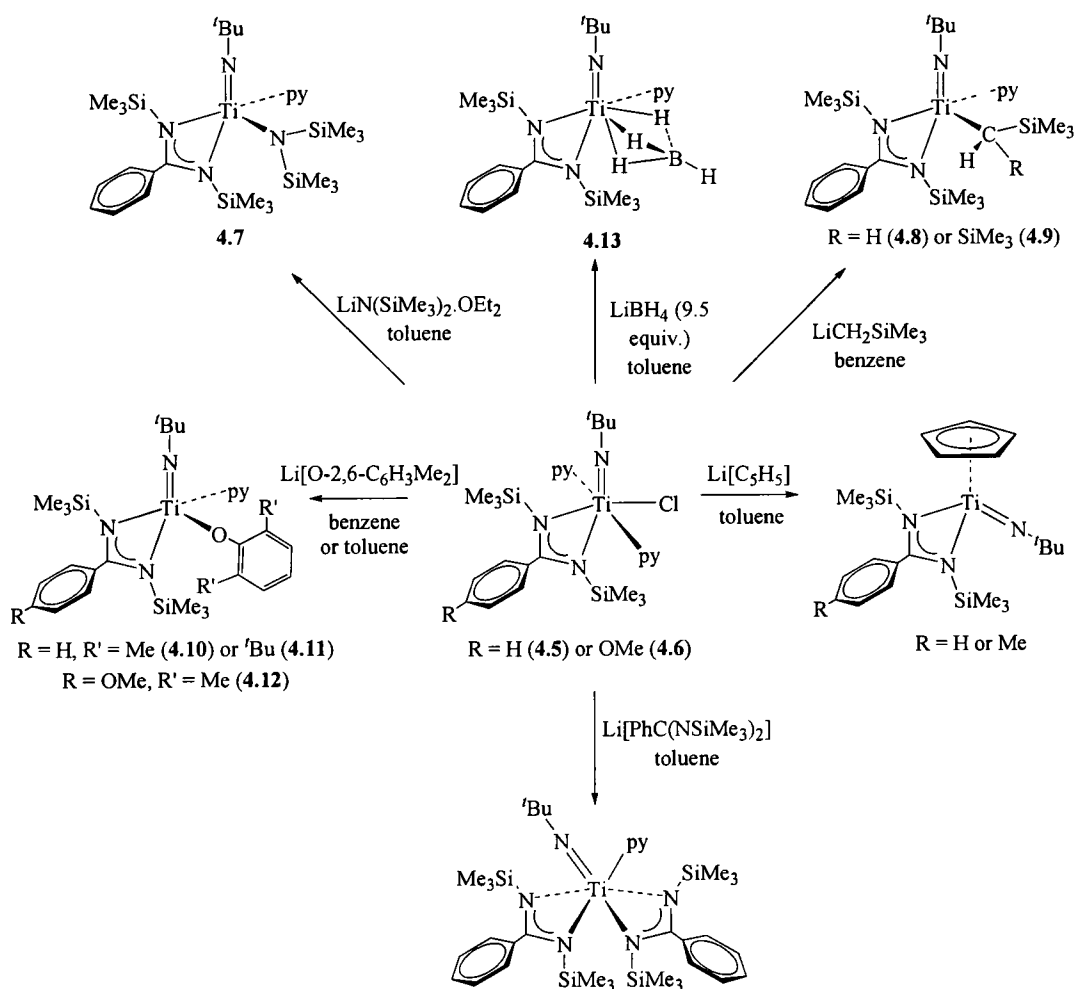
Further work from the group of Walther has investigated allyl derivatives of zirconium benzamidinate complexes.¹⁴ They found that in the solid state the allyl ligands of the complex $[\text{Zr}\{\text{PhC}(\text{NSiMe}_3)_2\}_2(\text{C}_3\text{H}_5)_2]$ adopt different coordination modes. One allyl ligand is η^3 -coordinated and the other is η^1 -coordinated, as shown in Equation 4.1.



Equation 4.1

In solution the two allyl ligands interconvert between the two coordination modes. Presumably, this is because the steric bulk of the bis(benzamidinate) ligand set is too great for both allyl ligands to simultaneously bind η^3 to the fourteen valence electron zirconium centre.

Previous work in the Mountford group has resulted in the synthesis of benzamidinate-imido compounds (Section 2.2.3). The compounds $[\text{Ti}(\text{N}^t\text{Bu})\{(4\text{-C}_6\text{H}_4\text{R})\text{C}(\text{NSiMe}_3)_2\}\text{Cl}(\text{py})_2]$ $\{\text{R} = \text{H}$ (**4.5**) or OMe (**4.6**) $\}$ were found to undergo chloride metathesis reactions to yield alkyl, borohydride, aryloxy and amide derivatives, in addition to the cyclopentadienyl amidinate-imido complexes already described (Section 3.3.1).¹ Scheme 4.4 summarises these reactions.



Scheme 4.4 Chloride metathesis reactions of benzamidinate-imido complexes

Complexes **4.7** - **4.9** are examples of Group 4 terminal imido alkyl derivatives and the first to be structurally characterised. Wolczanski was the first to report monomeric titanium imido alkyl complexes, namely $[\text{Ti}(\text{NSi}^i\text{Bu}_3)(\text{NHSi}^i\text{Bu}_3)(\text{R})(\text{THF})]$ ($\text{R} = \text{Me}$ or ^iBu), but these complexes were found to be quite thermally unstable.¹⁵ Transition metal imido complexes with alkyl ligands are well-established for the subsequent triads.¹⁶

Compounds **4.7** - **4.9** have formal 14 valence electron counts for titanium, which raise the possibility of stabilisation *via* Ti-H- C_α agostic interactions.¹⁷ Well-established examples of α - and β -agostic alkyltitanium compounds, namely $[\text{TiCl}_3\text{Me}(\text{dmpe})]$ (**4.14**) and $[\text{TiCl}_3\text{Et}(\text{dmpe})]$ (**4.15**, $\text{dmpe} = 1,2\text{-bis}(\text{dimethylphosphino})\text{ethane}$) respectively, were first reported by Green and coworkers.¹⁸ Comparison of the crystallographic data with that for **4.14** and examination of the $^1\text{J}_{\text{CH}}$ coupling constants for the alkyl α -carbons in **4.7** - **4.9** suggest that an agostic interaction is unlikely.

The aryloxide derivatives **4.10** - **4.12** are fluxional in solution on the NMR timescale. Low temperature NMR experiments on complex **4.11** suggest that the SiMe_3 and ^iBu groups are both undergoing exchange processes, and that these exchanges share a common transition state. This would probably involve some degree of Ti-N_{benzamidinate} bond cleavage to give a four-coordinate intermediate or transition state. In complexes **4.10** and **4.12** the SiMe_3 group exchange activation energy appears to be much lower than for the **4.11**, so a mechanism involving in-place benzamidinate rotation about the $\text{Ti}\cdots\text{CN}_2$ axis may be more probable, meaning that the SiMe_3 and aryloxide *ortho*-Me group exchange processes are not correlated.

Compound **4.13** is the first borohydride derivative of a Group 4 imido complex. The coordination mode of the BH_4 ligand can be inferred from the solid state I.R. spectrum, which contains three bands in the B-H stretching region. There is a strong absorption at 2464 cm^{-1} assigned to $\nu(\text{B-H}_{\text{terminal}})$ and two weaker bands at 2208 and 2145 cm^{-1} assigned to $\nu(\text{B-H})_{\text{bridging}}$. The solution state I.R. spectrum confirms these observations. This pattern of three absorptions indicates a tridentate coordination mode;¹⁹ the three bands may be designated as A_1

(terminal) and A_1 and E (bridging) respectively, if local C_{3v} symmetry for the $Ti(\mu-H)_3BH$ fragment is assumed.

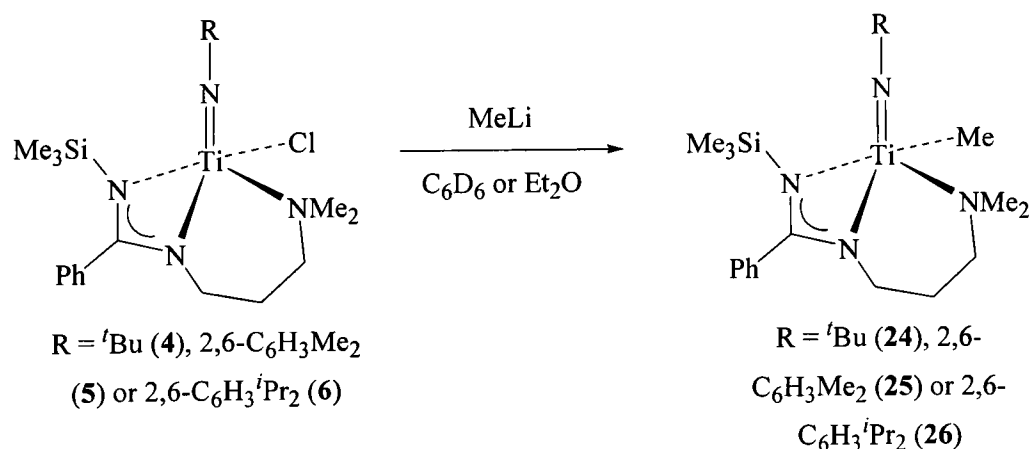
The versatile chloride metathesis reactivity of **4.5** and **4.6** suggested that the corresponding pendant arm functionalised amidinate-imido complexes **1** - **6** introduced in Chapter 2 might also undergo interesting chloride substitution reactions, and the results of this work will be described in the following Sections.

4.3 Alkyl derivatives

It was decided to focus initial efforts to synthesise alkyl derivatives on the three-carbon pendant arm complexes **4** - **6**, as earlier work had shown them to be more readily handled without decomposition in solution than their two-carbon arm analogues **1** - **3** (Section 2.3).

4.3.1 Synthesis of methyl derivatives

The NMR tube scale reaction of the *tert*-butyl derivative **4** with MeLi appeared to give clean conversion to the methyl derivative $[Ti(N^tBu)\{Me_3SiNC(Ph)NCH_2CH_2CH_2NMe_2\}Me]$ (**24**), as judged by ^1H NMR spectroscopy (Equation 4.2). In addition to the resonances for the *tert*-butyl group and the $Me_3SiNC(Ph)NCH_2CH_2CH_2NMe_2$ ligand a further singlet at 0.79 ppm (integral = 3 H) was reproducibly observed (full details in Chapter 6). Although the compound did not appear to be especially light- or temperature-sensitive in solution, attempts to reproduce the reaction on a preparative scale proved unsuccessful, yielding an intractable mixture of products.



Equation 4.2

Reaction of the arylimido derivatives **5** and **6** with MeLi in Et₂O at -78 °C followed by extraction into benzene yielded the compounds [Ti(N-C₆H₃R₂){Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂}Me] {R = Me (**25**) or *i*Pr (**26**)} in 50% and 52% yields respectively. The dimethylphenylimido derivative **25** is thermally sensitive both in solution and in the solid state, and decomposition in solution was observed within two to three hours and within days in a drybox at room temperature. Storing the compound at -35 °C appeared to prevent degradation. The di-*iso*-propylphenylimido derivative **26** is more stable, no decomposition was observed either in the solid state or after several hours in solution at room temperature. Attempts to recrystallise **25** and **26** from hexanes at low temperature resulted in decomposition. Both compounds have been characterised by NMR and IR spectroscopies. The E.I. mass spectrum of **26** contained a peak corresponding to the molecular ion.

As the ¹H NMR spectra of all three compounds **24** - **26** show the same basic features, discussion will be confined to the *iso*-propyl derivative **26**.

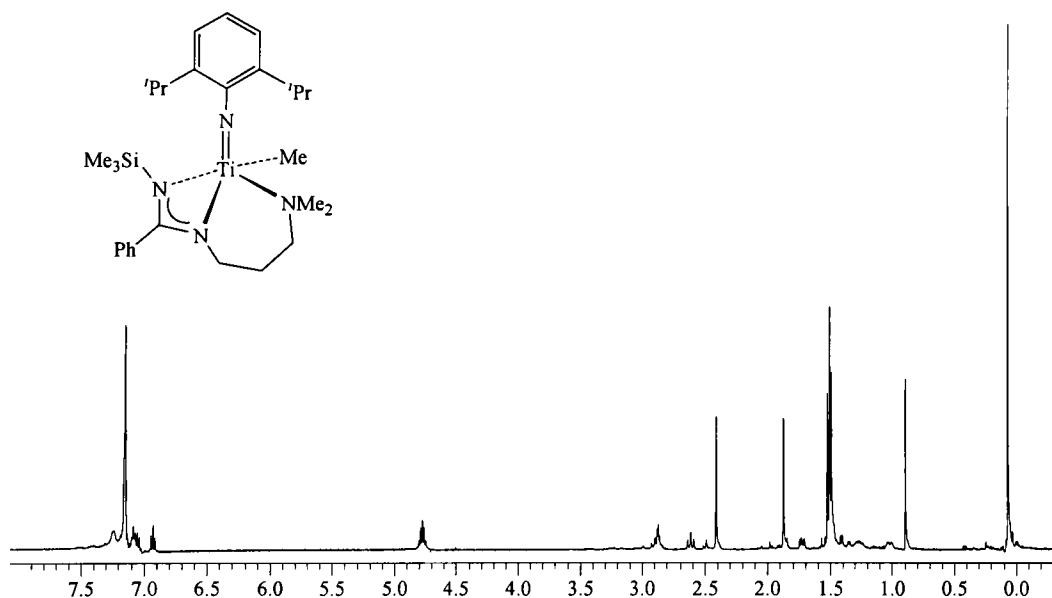


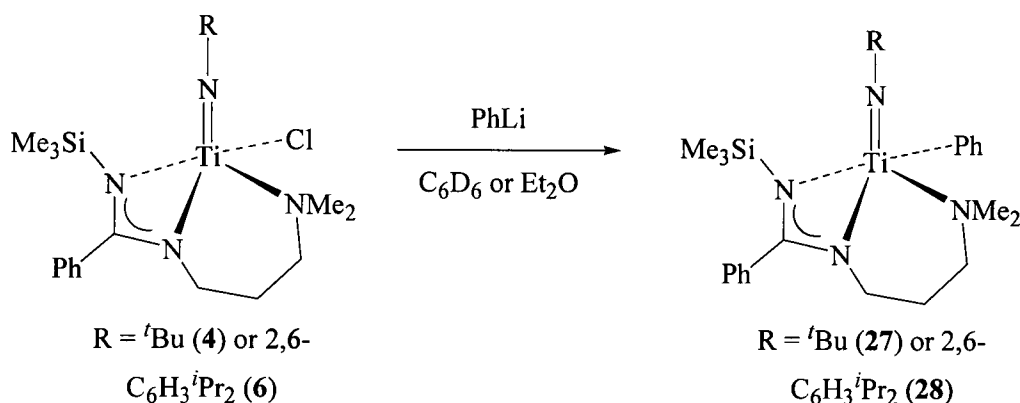
Figure 4.1 500.0 MHz ¹H NMR spectrum of [Ti(N-C₆H₃*i*Pr₂){Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂}Me] (**26**) in C₆D₆

The benzamido ligand gives rise to a 9 H singlet at 0.13 ppm corresponding to the SiMe₃ group. The pendant NMe₂ appears to be firmly coordinated to the metal on the NMR timescale at this temperature as there are two singlets for the

methyl groups at 1.90 and 2.44 ppm and six multiplets for the CH₂ protons of the pendant arm. As required by the absence of a molecular mirror plane in this complex, there are two (partly overlapping) doublets for the *iso*-propyl methyl groups and a septet at 4.72 ppm for the methine protons. The titanium bound methyl group gives rise to a 3 H singlet at 0.94 ppm, which is comparable to the corresponding shifts observed for the *tert*-butyl and 2,6-dimethylphenylimido derivatives **24** and **25** (0.79 and 0.95 ppm respectively).

4.3.2 Synthesis of phenyl derivatives

Synthesis of phenyl derivatives was attempted by reaction of the chloride compounds **4** - **6** with one equivalent of PhLi (Equation 4.3).



Equation 4.3

Reaction of [Ti(N^{*t*}Bu){Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂}Cl] (**4**) with PhLi at -80 °C in Et₂O gave a yellow solution which, on warming to room temperature, darkened markedly. Removal of the volatiles and extraction into benzene afforded the phenyl compound [Ti(N^{*t*}Bu){Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂}Ph] (**27**) as a brown/black solid in 50% yield. Solutions of **27** were very clean by NMR spectroscopy but clearly degraded over time in the dark (at room temperature) indicating the thermal sensitivity of the sample. Attempts to recrystallise **27** resulted in further degradation. Somewhat surprisingly, a parent molecular ion was observed in the high resolution E.I. mass spectrum confirming the elemental composition.

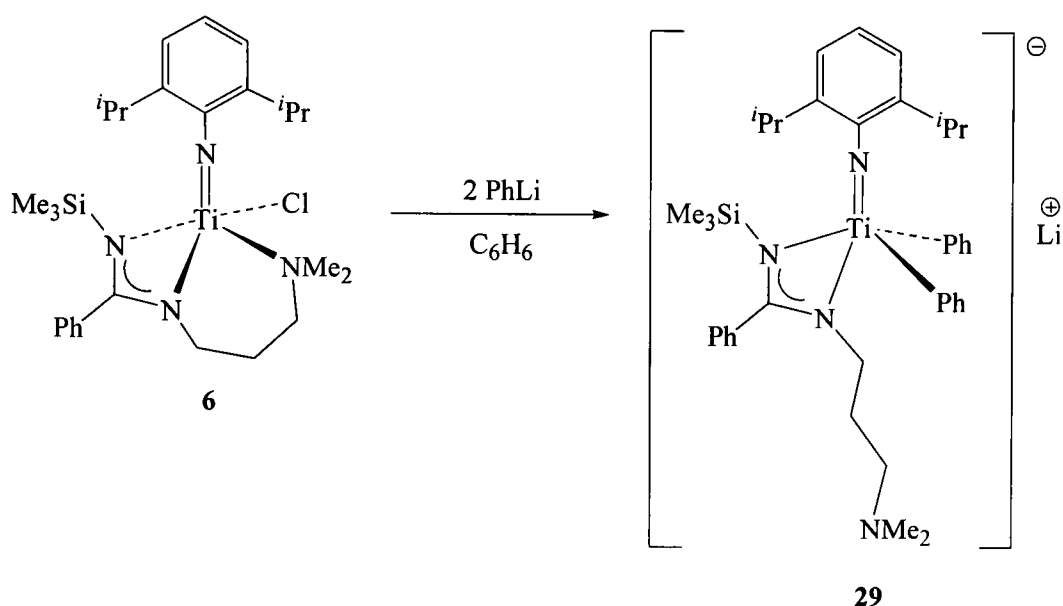
NMR tube scale reactions of the dimethylphenylimido derivative **5** with PhLi gave complex mixtures and so attempts to scale up the preparation of this

derivative were not pursued. Initial attempts at reaction with the *iso*-propyl derivative **6** also yielded mixtures of products. However, the phenyl compound **28** was successfully prepared by careful mixing of a solution of **6** with a solution of one equivalent of PhLi in benzene in a drybox. Rapid removal of the volatiles followed by extraction into benzene yielded spectroscopically pure $[\text{Ti}(\text{N-2,6-}\text{C}_6\text{H}_3^i\text{Pr}_2)\{\text{Me}_3\text{SiNC(Ph)NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}\text{Ph}]$ (**28**). Like the corresponding methyl derivative **26**, solutions of **28** also appeared to be more stable towards decomposition than their *tert*-butyl and 2,6-dimethylphenylimido analogues, although decomposition over time in solution still thwarted attempts at recrystallisation.

The NMR spectra of **27** and **28** are consistent with the structures proposed in Equation 4.3. The presence of the titanium-bound phenyl groups is established by doublet, triplet and multiplet resonances at *ca.* 8.3, 7.4 and 7.3 ppm in both compounds for the *ortho*, *para* and *meta*-protons respectively. Additional resonances characteristic of the imido substituents and a κ^3 -bound $\text{Me}_3\text{SiNC(Ph)NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2$ ligand were also observed.

4.3.3 Synthesis of an "ate"-complex of **28**

Examination of the ^1H NMR spectra of the products of initial attempts to synthesise **28** by dropwise addition of a solution of PhLi to a solution of the chloride compound **6** in Et_2O at -78°C , suggested that a mixture of the starting material **6** and a disubstituted product were present. Isolation of this product was attempted by reaction of **6** with two equivalents of PhLi in benzene at room temperature, extraction of the product into benzene yielded the "ate"-complex $\text{Li}[\text{Ti}(\text{N-2,6-}\text{C}_6\text{H}_3^i\text{Pr}_2)\{\text{Me}_3\text{SiNC(Ph)NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}\text{Ph}_2]$ (**29**) as a yellow powder in 42% yield (Equation 4.4).



Equation 4.4

The ^1H NMR spectrum of **29** is obviously different from that of the monosubstituted phenyl complex **28**, as the resonances no longer indicate a κ^3 -bound amidinate ligand. There is a 9 H singlet at -0.12 ppm for the SiMe_3 protons. The pendant arm is not coordinated to the metal on the NMR timescale at room temperature, as suggested by the equivalence of the two methyl groups of the pendant amine (6 H singlet at 1.28 ppm) and the three multiplets for the CH_2 groups of the arm (0.76, 1.50 and 2.44 ppm). The *iso*-propyl groups of the imide are equivalent and give rise to a doublet at 1.37 ppm and a septet at 4.82 ppm. The titanium-bound phenyl groups give rise to three resonances, those at 8.32 and 7.30 ppm correspond to the *ortho* and *meta*-protons, the *para*-protons being obscured by the solvent resonance. The equivalence of the two Ti-Ph groups suggests the presence of a molecular mirror plane in the compound on the NMR timescale.

It was not possible to obtain a satisfactory elemental analysis or mass spectrometric data. It seems likely that there is coordination of Li^+ to the anionic amidinate-imido complex, but no evidence for the mode of this coordination is available.

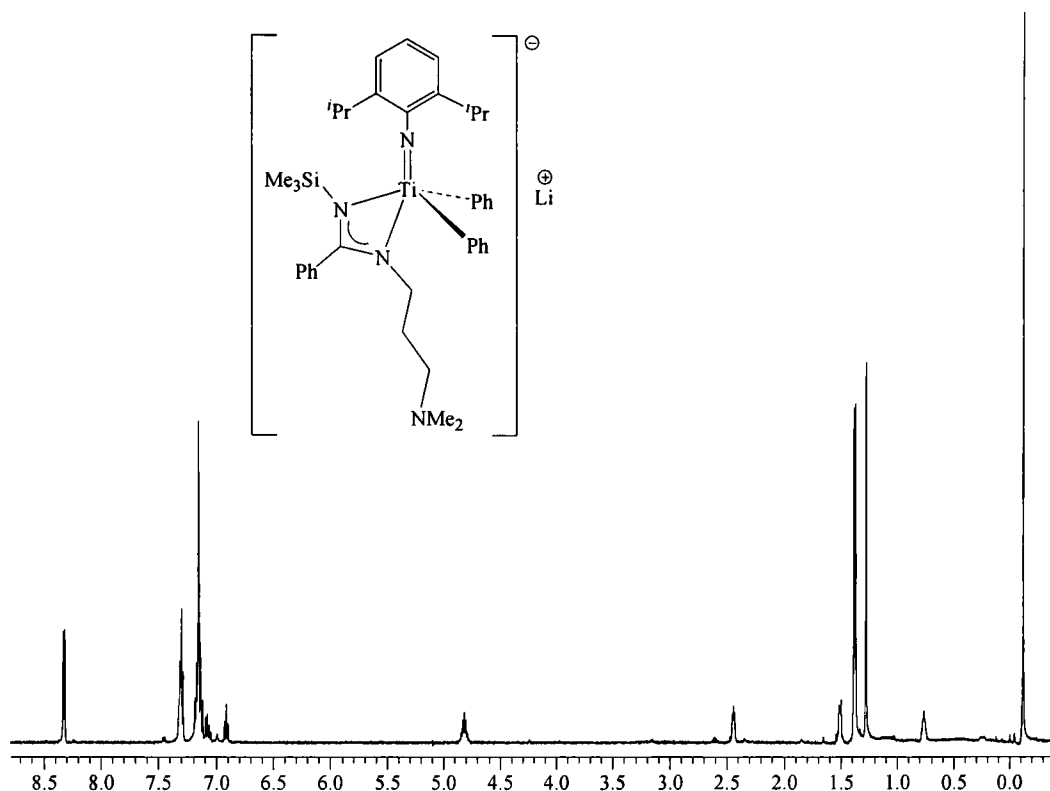


Figure 4.2 500.1 MHz ^1H NMR spectrum of $\text{Li}[\text{Ti}(\text{N}-2,6\text{-C}_6\text{H}_3'\text{Pr}_2)\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}\text{Ph}_2]$ (**29**) in C_6D_6

4.3.4 Attempted synthesis of alkyl derivatives with more sterically demanding alkyl ligands

It was anticipated that reactions of the chlorides **4** - **6** with a more bulky alkylating agent such as $\text{LiCH}_2\text{SiMe}_3$ would be less likely to result in the formation of "ate"-complexes. This reagent has been used successfully in a reaction with the unfunctionalised amidinate compound **4.5** to yield the corresponding alkyl compound $[\text{Ti}(\text{N}^t\text{Bu})\{\text{PhC}(\text{NSiMe}_3)_2\}\text{CH}_2\text{SiMe}_3(\text{py})]$ (**4.9**).¹

Reaction of **4** - **6** with one equivalent of $\text{LiCH}_2\text{SiMe}_3$ in C_6D_6 at room temperature resulted in complex mixtures which contained unreacted starting material and a mixture of products. Several attempts were made to synthesise these derivatives on a preparative scale by reaction of **4** - **6** with either one or two equivalents of $\text{LiCH}_2\text{SiMe}_3$ but intractable mixtures of products were obtained.

4.3.5 Attempted alkylation of two-carbon linker systems

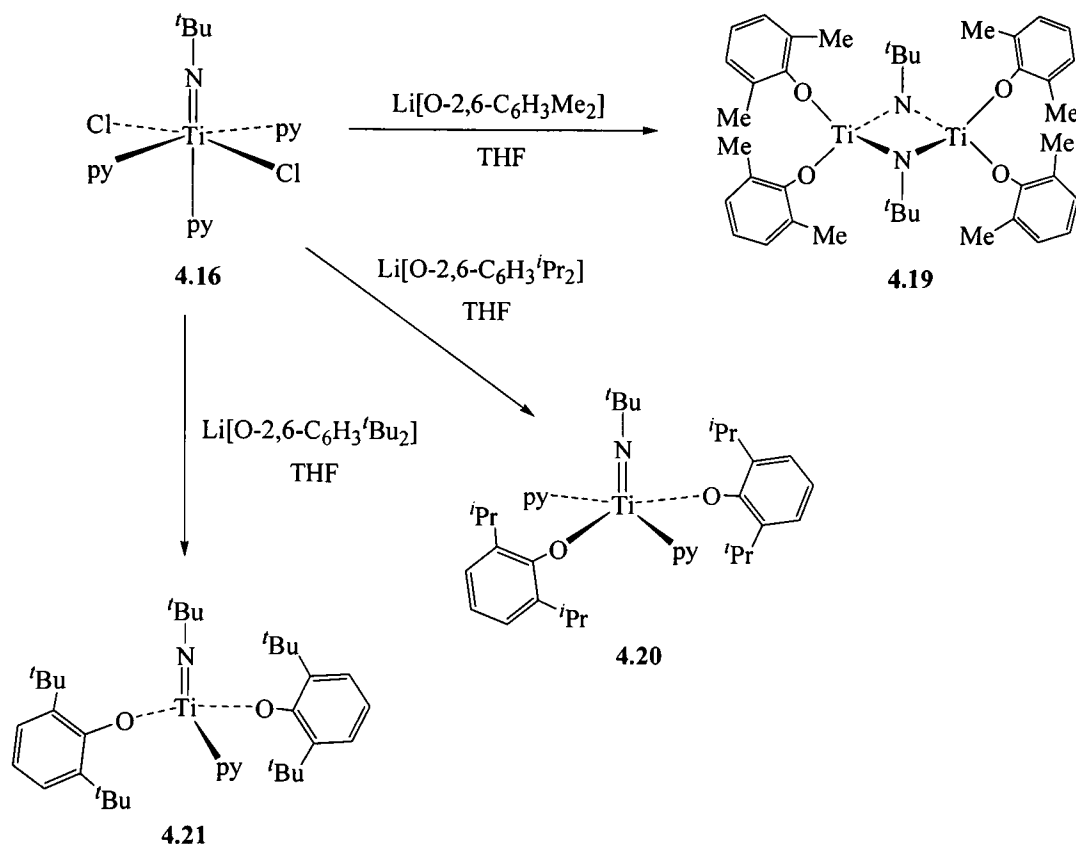
Given the successful alkylation reactions of **4** - **6** with MeLi and PhLi, attempts were made to prepare alkyl derivatives with shorter pendant arms for comparison. Although the NMR tube scale reaction of $[\text{Ti}(\text{N}^t\text{Bu})\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{NMe}_2\}\text{Cl}]$ (**1**) with MeLi initially looked promising, attempts to alkylate **1** on a preparative scale were unsuccessful and resulted in decomposition to intractable mixtures of products.

4.4 Aryloxide derivatives

Aryloxide derivatives (OAr where Ar = aryl group) are capable of donating up to five electrons to the metal if the M-O-C linkage is linear, forming a σ -bond and two π -bonds if the metal has available d_π -acceptor orbitals. Aryloxide and alkoxide ligands have been widely used in transition metal chemistry.²⁰⁻²³

Rothwell and coworkers have prepared a number of mononuclear, five coordinate, aryloxide-supported Group 4 imido derivatives.²⁴ The importance of the steric requirements of the aryloxide ligands in such complexes has also been thoroughly studied by Mountford and Collier.²⁵ They found that the reaction of two equivalents of lithium aryloxide with $[\text{Ti}(\text{N}^t\text{Bu})\text{Cl}_2(\text{py})_3]$ $\{\text{R} = ^t\text{Bu}$ (**4.16**), 2,6- $\text{C}_6\text{H}_3\text{Me}_2$ (**4.17**) or 2,6- $\text{C}_6\text{H}_3^i\text{Pr}_2$ (**4.18**) $\}$ lead to the formation of complexes whose structures show critical dependence on the *ortho* substituents of the aryloxide ligands. Where the imido substituent was *tert*-butyl, reaction with $\text{Li}[\text{O}-2,6-\text{C}_6\text{H}_3\text{Me}_2]$ lead to the dimeric species **4.19**, reaction with $\text{Li}[\text{O}-2,6-\text{C}_6\text{H}_3^i\text{Pr}_2]$ lead to the five coordinate derivative **4.20** and the reaction with $\text{Li}[\text{O}-2,6-\text{C}_6\text{H}_3^t\text{Bu}_2]$ lead to the four coordinate derivative **4.21**, as shown in Scheme 4.5.

Previous studies have shown both the *tert*-butyl and methyl substituted aryloxide derivatives of the symmetrically substituted amidinate derivative $[\text{Ti}(\text{N}^t\text{Bu})\{\text{PhC}(\text{NSiMe}_3)_2\}\text{Cl}(\text{py})_2]$ (**4.5**) to be four coordinate monomeric species (Scheme 4.4), although crystal structures of these compounds were not obtained.¹ It was therefore of interest to investigate the structures of aryloxides of some pendant arm functionalised amidinate imido complexes.

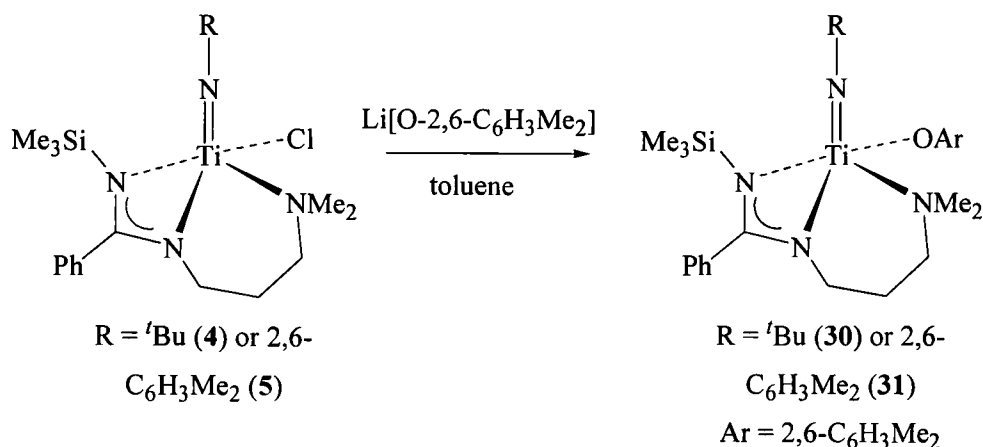


Scheme 4.5 Aryloxy derivatives of $[\text{Ti}(\text{N}^t\text{Bu})\text{Cl}_2(\text{py})_3]$ (**4.16**)

It was also hoped that the pendant arm functionalised amidinate aryloxy derivatives would prove more stable than the alkyl derivatives discussed in the previous Section in order that the geometries of some chloride-substitution products of compounds **1** - **6** could be structurally authenticated.

4.4.1 Synthesis of 3-carbon linker derivatives

Reaction of **4** or **5** with one equivalent of $\text{Li}[\text{O-2,6-C}_6\text{H}_3\text{Me}_2]$ in toluene at room temperature, followed by extraction into benzene or hexanes and recrystallisation from hexanes at -80°C , yielded crystalline aryloxy derivatives $[\text{Ti}(\text{NR})\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}(\text{O-2,6-C}_6\text{H}_3\text{Me}_2)]$ $\{\text{R} = ^t\text{Bu}$ (**30**) or $2,6\text{-C}_6\text{H}_3\text{Me}_2$ (**31**) $\}$, both in 63% yield (Equation 4.5). The X-ray structures of **30** and **31** have been determined and are discussed below.



Equation 4.5

The NMR data for the $[\text{Ti}(\text{N}'\text{Bu})\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}]$ fragment of **30** are analogous to those of their organometallic homologues **24** and **25**. Additional resonances are observed for a 2,6- $\text{C}_6\text{H}_3\text{Me}_2$ fragment. At room temperature, the methyl and *meta*-ring protons of this group are broad, but at low temperature they appear as four individual signals. This is evidence of restricted rotation about the Ti-OAr bond on the NMR timescale and indicates that the coordination environment around titanium in **30** is, in fact, quite crowded. The corresponding benzamidinate compound without a pendant arm, namely $[\text{Ti}(\text{N}'\text{Bu})\{\text{PhC}(\text{NSiMe}_3)_2\}(\text{O-2,6-C}_6\text{H}_3\text{Me}_2)(\text{py})]$ (**4.10**) did not exhibit evidence for restricted rotation about the Ti-OAr bond at room temperature, [although the 2,6-di-*tert*-butyl homologue $[\text{Ti}(\text{N}'\text{Bu})\{\text{PhC}(\text{NSiMe}_3)_2\}(\text{O-2,6-C}_6\text{H}_3\text{'Bu}_2)(\text{py})]$ (**4.11**) did].¹ In contrast to **30**, the ^1H NMR spectrum of **31** displays no evidence for restricted rotation about the Ti-OAr bond on the NMR scale at room temperature, the methyl groups of the aryloxide appearing as a 6 H singlet at 2.51 ppm.

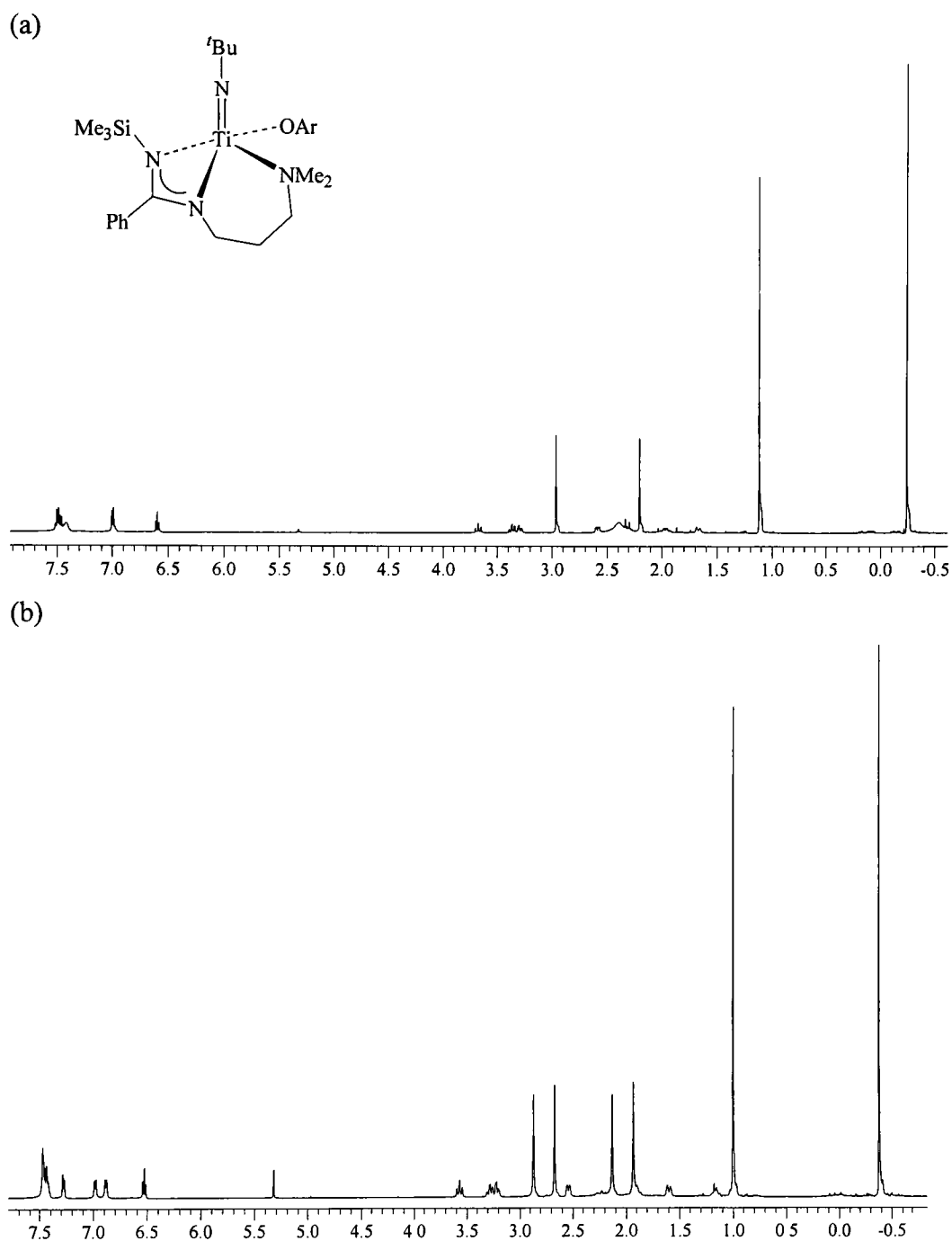
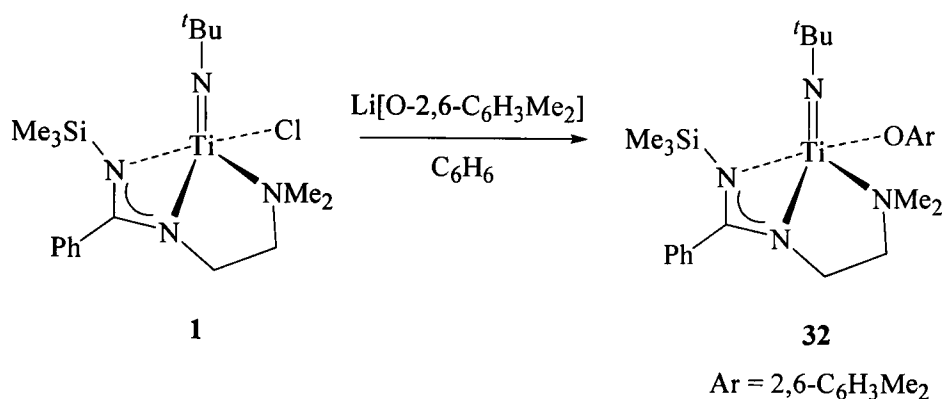


Figure 4.3 500.1 MHz ^1H NMR spectra of $[\text{Ti}(\text{N}^t\text{Bu})\{\text{Me}_3\text{SiNC}(\text{Ph})$

$\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}\text{(O-2,6-C}_6\text{H}_3\text{Me}_2)]$ (**30**) in CD_2Cl_2 (a) at 295 K; (b) at 223 K

For comparative purposes, the reaction of the 2-carbon linker chloride compound **1** with $\text{Li}[\text{O-2,6-C}_6\text{H}_3\text{Me}_2]$ was carried out; this afforded $[\text{Ti}(\text{N}^t\text{Bu})\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{NMe}_2\}\text{(O-2,6-C}_6\text{H}_3\text{Me}_2)]$ (**32**) as an orange solid in 63% yield (Equation 4.6).



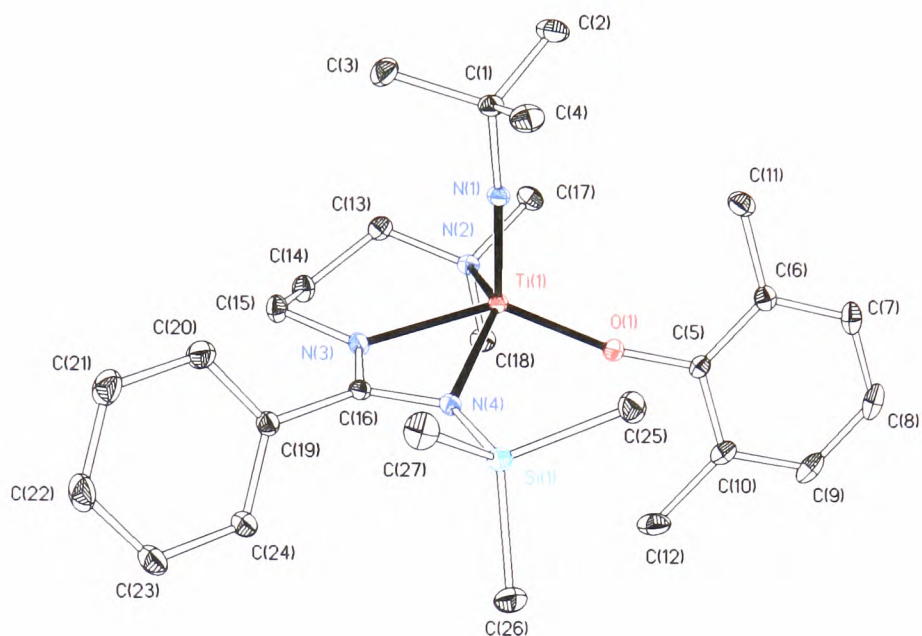
Equation 4.6

As for **31** (and in contrast to **30**) there is no evidence for restricted rotation about the Ti-O bond on the NMR timescale at room temperature.

Diffraction-quality yellow crystals of **30** and **31** were grown from solutions in hexanes at $-30\text{ }^{\circ}\text{C}$. Data were collected at 150 K and the crystal structures were solved by Dr. A. Cowley. Figure 4.4 shows the molecular structures and Table 4.1 summarises important bond lengths and angles. Full details are provided in Appendices I and J.

Molecules of **30** and **31** possess monomeric, five coordinate structures in the solid state. All three nitrogens of the $\text{Me}_3\text{SiNC(Ph)NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2$ ligands are firmly coordinated to titanium with similar Ti-N distances to those found previously in the chloride analogues $[\text{Ti}(\text{NR})\{\text{Me}_3\text{SiNC(Ph)NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}\text{Cl}]$ $\{\text{R} = \text{'Bu}$ (**4**), 2,6- $\text{C}_6\text{H}_3\text{Me}_2$ (**5**) or 2,6- $\text{C}_6\text{H}_3\text{Pr}_2$ (**6**) $\}$ (Chapter 2). The N(3) and N(4) atoms are approximately sp^2 hybridised as indicated by their approximately trigonal planar geometries [the sums of the angles subtended at the N(3) and N(4) atoms lie in the range $353.8(4) - 358.7(5)^\circ$]. The Ti-N distances to the amidinate ligand are significantly longer for **30** than for **31** as expected based on the better donor ability of *tert*-butylimido ligands compared to their arylimido homologues.²⁶⁻²⁹

(a)



(b)

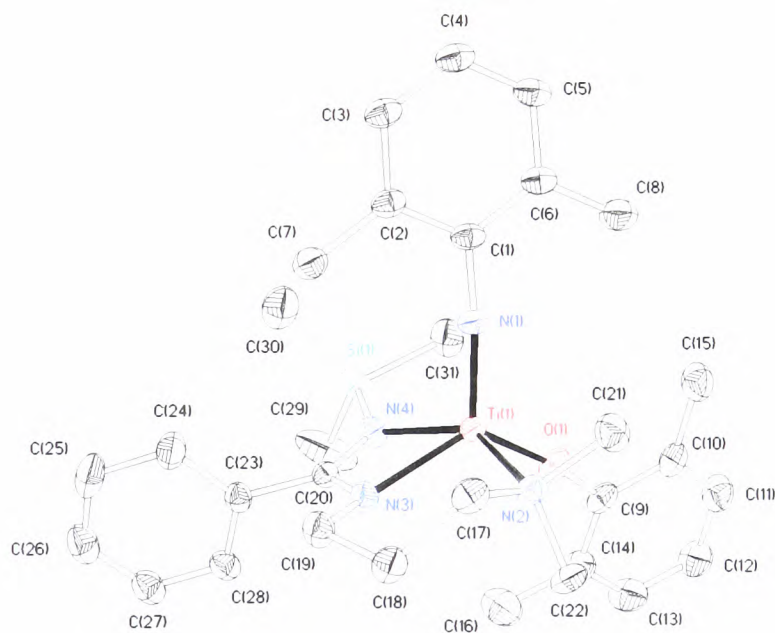


Figure 4.4 Displacement ellipsoid plots (20% probability) of (a) $[\text{Ti}(\text{N}^t\text{Bu})\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}(\text{O}-2,6\text{-C}_6\text{H}_3\text{Me}_2)]$ (**30**) and (b) $[\text{Ti}(\text{N}-2,6\text{-C}_6\text{H}_3\text{Me}_2)\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}(\text{O}-2,6\text{-C}_6\text{H}_3\text{Me}_2)]$ (**31**). H atoms omitted for clarity.

Table 4.1 Selected bond lengths (Å) and angles (°) for [Ti(N^tBu){Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂}(O-2,6-C₆H₃Me₂)] (**30**) and [Ti(N-2,6-C₆H₃Me₂){Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂}(O-2,6-C₆H₃Me₂)] (**31**)

	30	31
Ti(1)-N(1)	1.6991(15)	1.756(2)
Ti(1)-N(2)	2.2548(15)	2.235(2)
Ti(1)-N(3)	2.1081(15)	2.084(2)
Ti(1)-N(4)	2.1531(15)	2.119(2)
Ti(1)-O(4)	1.8887(13)	1.828(2)
N(4)-C(Ph)	1.336(2)	1.319(3)
N(1)-C(1)	1.446(2)	1.383(3)
O(1)-CAr	1.337(2)	1.352(3)
N(4)-Si(1)	1.7294(15)	1.730(2)
N(3) - CPh	1.320(2)	1.320(3)
N(1)-Ti(1)-O(1)	115.90(7)	118.75(12)
Ti(1)-O(1)-CAr	167.84(12)	170.3(2)
N(1)-Ti(1)-N(2)	100.81(7)	96.78(9)
Ti(1)-N(3)-CH2	136.65(12)	140.8(5)
N(1)-Ti(1)-N(3)	105.61(7)	113.99(11)
Ti(1)-N(3)-CPh	92.16(11)	92.88(16)
N(1)-Ti(1)-N(4)	105.36(7)	103.5(1)
CPh-N(3)-CH2	124.95(16)	124.3(2)
N(2)-Ti(1)-N(3)	81.55(6)	82.65(8)
Ti(1)-N(4)-CPh	89.8(1)	91.35(16)
N(2)-Ti(1)-N(4)	140.02(6)	144.82(8)
Ti(1)-N(4)-Si(1)	135.11(8)	134.03(12)
N(3)-Ti(1)-O(1)	138.45(6)	127.17(11)
Si(1)-N(4)-CAr	132.13(13)	133.3(2)
N(3)-Ti(1)-N(4)	62.69(6)	62.94(9)
N(4)-CPh-N(3)	113.22(15)	112.6(2)
Ti(1)-N(1)-C(1)	171.93(13)	174.5(2)

While the geometry at Ti(1) in **30** and **31** may be reasonably well described as distorted square base pyramidal (with N(1) occupying the axial position), that of **30** is somewhat closer to trigonal bipyramidal with N(1), O(1) and N(3) formally occupying the equatorial positions. Clearly both structures are constrained by the chelating amidinate ligand and inherently small bite angle of the N₂CPh fragment. Four five-coordinate, crystallographically characterised arylimidotitanium compounds containing two monodentate aryloxy ligands and two Lewis base donor atoms have been described previously.^{24,25,30} Two of these^{24,25} feature bidentate Lewis base donors and are thus somewhat constrained. The other two are of the type [Ti(NAr)(OAr')₂(L)₂] (Ar and Ar' = phenyl or 2,6-disubstituted phenyl; L = py or substituted py) and possess well-defined trigonal bipyramidal geometries with ArN=Ti-O angles of *ca.* 96 - 99 °. The compounds **30** and **31** are the first structurally characterised imidotitanium compounds featuring only one aryloxy ancillary ligand.

Turning now to the Ti=NR and Ti-OAr units, it is interesting to note the significant differences between the two Ti=NR distances for R = ^tBu [1.6991(15) Å] and R = 2,6-C₆H₃Me₂ [1.756(2) Å], and the two Ti-OAr distances [1.8887(13) Å for **30**; 1.828(2) Å for **31**]. The previously established ranges are as follows:^{26,27} for terminal Ti=N^tBu linkages the mean value is 1.725(16) Å with a range of 1.695(8) - 1.725(8) Å; for Ti-OAr linkages with two *ortho*-methyl (or sterically similar) substituents the mean value is 1.825(46) Å with a range of 1.735(7) - 1.952(4) Å. For the four arylimido titanium compounds containing monodentate aryloxy ligands and two Lewis base donor atoms mentioned above the average Ti=NAr distance is 1.721(4) Å [range 1.709(5) - 1.734(4) Å] and the average Ti-OAr distance is 1.882(9) Å [range 1.853(4) - 1.932(3) Å]. The angles subtended at N(1) and O(1) are approximately linear for these four compounds and for **30** and **31**, indicating that in all instances these atoms are effectively *sp* hybridised and the imido and aryloxy groups can, in principle, donate four or five electrons to titanium, subject to orbital availability.^{28,31} While the actual Ti=NR and Ti-OAr distances in **30** and **31** lie (within error) within the previously determined general ranges of values, there is an unexpectedly large difference between the Ti=NR and Ti-OAr distances between the two molecules.

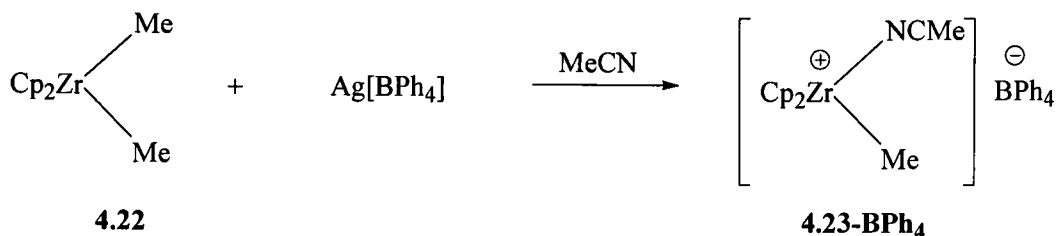
Furthermore, when specifically comparing data for **31** with those for the previous four arylimido titanium compounds containing two monodentate aryloxo ligands, the Ti=NAr distance appears to be surprisingly long and the Ti-OAr surprisingly short. Although, perhaps, it is not unreasonable that a longer Ti-O distance might be correlated with a shorter Ti-OAr (since both NR and OAr groups are π -donors and potentially in competition for d_{π} acceptor orbitals), it is not clear why the Ti=NAr distance is so comparatively long and the Ti-OAr so short in **31**, especially since most other features of **30** are comparable with those of **31** and of **5**. There appear to be no adverse intra- or inter-molecular contacts.

4.5 Preparation of cationic pendant arm functionalised amidinate-imido complexes

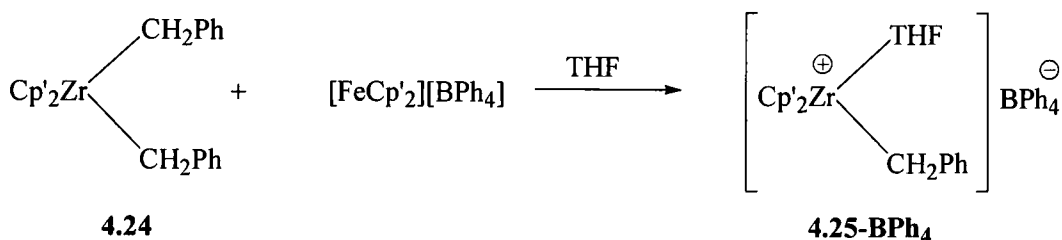
Given the generally unreactive nature of the chloride complexes **4** and **5** towards unsaturated substrates (Chapter 2), it was proposed that a cationic derivative of lower coordination number might display greater reactivity. The synthesis of cationic Group 4 organometallic compounds has been especially intensively studied due to their importance as active species in olefin polymerisation. This Section will give a brief introduction to some methods employed to generate metal cations, with a particular emphasis on Group 4 compounds. For a more complete discussion, the reader is directed towards some reviews of this area.^{32,33}

Generation of cationic catalytically active species can be achieved from metal alkyl complexes by the oxidative cleavage of M-R bonds, protonolysis of a metal-bound alkyl ligand or by abstraction of an alkyl ligand from a metal centre using tris(pentafluorophenyl)borane or trityl borate reagents.

Metal-alkyl bonds can be readily cleaved by one-electron oxidation with reagents such as $\text{Ag}[\text{BPh}_4]^{34,37}$ or $[\text{FeCp}'_2][\text{BPh}_4]$ ($\text{Cp}' = \text{C}_5\text{H}_4\text{Me}$)^{34,38} in the presence of a Lewis base. Two examples are illustrated in Equations **4.7** and **4.8**.^{35,38}



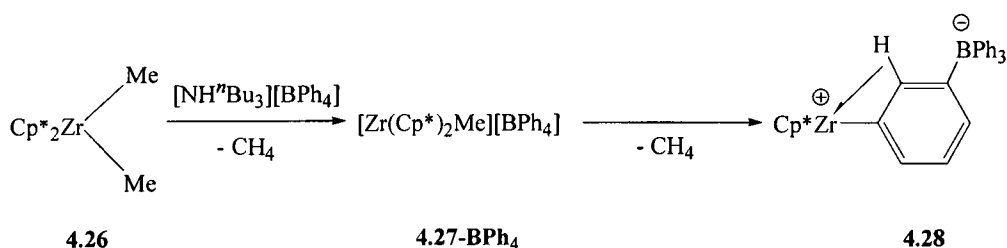
Equation 4.7



Equation 4.8

The choice of counterion in metal alkyl cationic systems is crucial. Relatively non-coordinating anions such as $[\text{BPh}_4]^-$ are frequently preferred since anions such as $[\text{BF}_4]^-$ or $[\text{CF}_3\text{SO}_3]^-$ coordinate strongly to the cation and render it unreactive.³⁹⁻⁴²

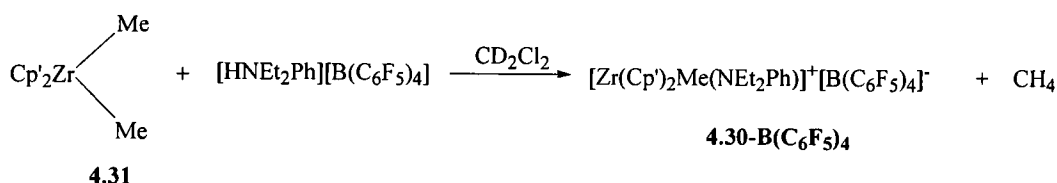
Another route to cations from metal alkyl compounds is *via* the protonolysis of an alkyl ligand, typically with an ammonium salt. In 1989, Hlatky and Turner reported that the reaction of $[\text{Zr}(\text{C}_5\text{Me}_5)_2\text{Me}_2]$ with $[\text{HN}^n\text{Bu}_3][\text{BPh}_4]$ in toluene yields the zwitterionic complex $[\text{Zr}^+(\text{C}_5\text{Me}_5)_2\text{C}_6\text{H}_4\text{BPh}_3^-]$ (**4.28**) *via* initial Zr-Me protonolysis, followed by BPh_4 -aryl C-H bond activation (Equation 4.9).⁴³



Equation 4.9

In a similar reaction, Bochmann and coworkers reported the synthesis of the cationic compound $[\text{Zr}(\text{C}_5\text{H}_5)_2\text{Me}][\text{BPh}_4]$ (**4.29-BPh₄**) by the protonolysis of $[\text{Zr}(\text{C}_5\text{H}_5)_2\text{Me}_2]$ (**4.22**) by $[\text{HNMe}_2\text{Ph}][\text{BPh}_4]$.⁴⁴ The cation **4.29⁺** is stabilised by strong ion pairing with the $[\text{BPh}_4]^-$ anion.

As illustrated in Equation 4.9, the $[\text{BPh}_4]^-$ anion is not always inert with respect to either coordination to or metallation of cationic compounds. In 1992 Bochmann reported on the use of the $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ anion, which is significantly more chemically inert and less coordinating than $[\text{BPh}_4]^-$.⁴⁵ An analogous protonolysis route to the cationic compound $[\text{Zr}(\text{C}_5\text{H}_4\text{Me})_2\text{Me}]^+$ (**4.30**⁺) can be achieved through the reaction of $[\text{Zr}(\text{C}_5\text{H}_4\text{Me})_2\text{Me}_2]$ (**4.31**) with $[\text{HNEt}_2\text{Ph}][\text{B}(\text{C}_6\text{F}_5)_4]$ (Equation 4.10).⁴⁶

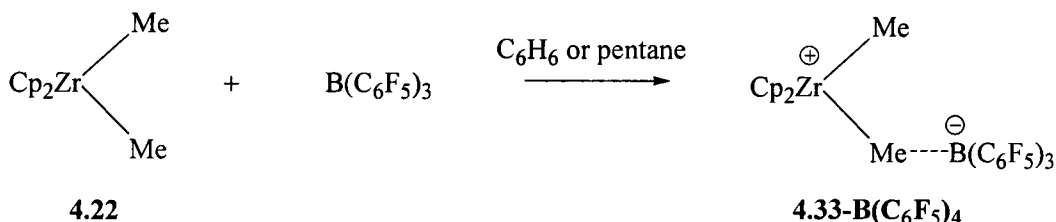


Equation 4.10

The other method of preparing cations from alkyl compounds to be discussed in this Section is by reaction with an alkyl abstracting agent. One example is the use of the trityl cation which abstracts R with the formation of Ph_3CR as the organic byproduct. Tilley *et al.* reported the use of $[\text{Ph}_3\text{C}][\text{BPh}_4]$ to abstract a methyl group from $[\text{Zr}(\text{C}_5\text{H}_5)_2\text{Me}_2]$ (**4.22**).⁴⁷ However, $[\text{Ph}_3\text{C}][\text{BPh}_4]$ is thermally and photolytically unstable, so the fluorinated derivative $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ often provides a more convenient alternative. This also has the advantage of minimising anion coordination and activation⁴⁵ and there have been several reported examples of its use.^{46,48,49} One potential drawback of the trityl cation is that it is also an oxidising agent; this can be a disadvantage where the metal systems to be studied are not d^0 . An example of this can be seen in the reaction of some tungsten alkyl complexes. Dimethyltungstenocene $[\text{W}(\text{C}_5\text{H}_5)_2\text{Me}_2]$ reacts with $[\text{CPh}_3]^+$ *via* a one electron oxidation pathway to give unstable d^1 $[\text{W}(\text{C}_5\text{H}_5)_2\text{Me}_2]^+$, and at room temperature loss of a hydrogen radical leads (ultimately) to the d^2 cationic olefin-hydride $[\text{W}(\text{C}_5\text{H}_5)_2\text{H}(\eta\text{-C}_2\text{H}_4)]^+$, most probably *via* the d^0 methyldiene $[\text{W}(\text{C}_5\text{H}_5)_2(\text{CH}_2)\text{Me}]^+$.⁵⁰ In contrast, Mountford and Ward found that the d^0 diamido-pyridine-supported alkyl complex $[\text{W}(\text{NPh})\{\text{MeC}(2\text{-C}_5\text{H}_4\text{N})(\text{CH}_2\text{NSiMe}_3)_2\}\text{Me}_2]$ (**4.32**) undergoes clean methyl abstraction with $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ to give the cationic complex $[\text{W}(\text{NPh})\{\text{MeC}(2\text{-C}_5\text{H}_4\text{N})(\text{CH}_2\text{NSiMe}_3)_2\}]^+$.

$\text{C}_5\text{H}_4\text{N}(\text{CH}_2\text{NSiMe}_3)_2\text{Me}]^+$.⁵¹ The W(VI) d^0 compound **4.32** does not have access to metal centered redox chemistry, which probably accounts for its simple behaviour with $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$.⁵²

Another commonly used abstracting agent is tris(pentafluorophenyl)borane, first reported by Massey and Park in 1964.^{53,54} Interest in $\text{B}(\text{C}_6\text{F}_5)_3$ waned until 1991, when Marks reported the reaction of **4.22** with $\text{B}(\text{C}_6\text{F}_5)_3$ to yield the zwitterionic compound $[\text{Zr}(\text{C}_5\text{H}_5)_2\text{Me}(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3]$ (**4.33-B(C₆F₅)₄**) (Equation 4.11).⁵⁵



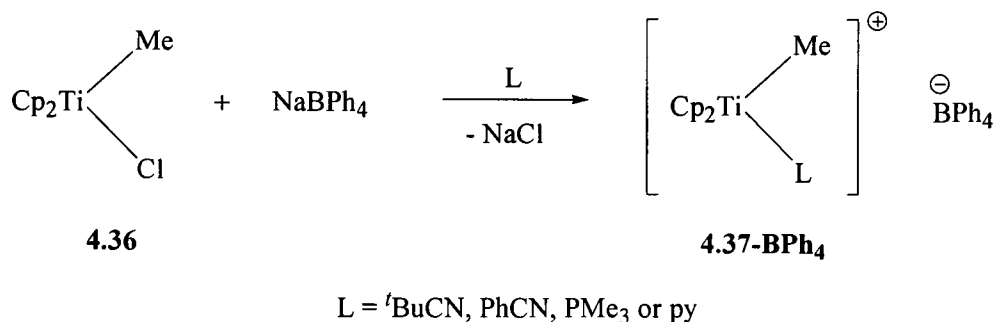
Equation 4.11

There have been other examples of reactions of alkyl compounds with $\text{B}(\text{C}_6\text{F}_5)_3$ yielding zwitterionic compounds containing a Zr-Me-B fragment.^{48,56-58} Britzinger has also reported that in cases where the $[\text{MeB}(\text{C}_6\text{F}_5)_4]^-$ anion is coordinated, it may easily be displaced by reaction with a Lewis base, such as PhNMe_2 , $\text{PhCH}_2\text{NMe}_2$ or $n\text{Bu}_2\text{O}$ to afford base stabilised cationic compounds.⁵⁹ Examples of non-coordination of the $[\text{MeB}(\text{C}_6\text{F}_5)_4]^-$ anion have also been reported; this occurs when there is another stabilising effect in the system. Green *et al.* have reported the benzyl ring-substituted zirconocene compound $[\text{Zr}(\text{C}_5\text{H}_4\text{CMe}_2\text{Ph})_2\text{Me}_2]$ (**4.34**) reacts with $\text{B}(\text{C}_6\text{F}_5)_3$ to afford the cationic compound $[\text{Zr}(\text{C}_5\text{H}_4\text{CMe}_2\text{Ph})_2\text{Me}]^+$ (**4.35⁺**) where the anion does not coordinate but intramolecular phenyl coordination stabilises the cationic metal centre.^{49,60}

The use of $\text{B}(\text{C}_6\text{F}_5)_3$ to abstract alkyl groups from less electron deficient metals has not been studied extensively although reports on its use with later transition metals have begun to appear.⁶¹ These include methyl abstraction from iron⁶² and platinum⁶³ alkyl complexes.

Other routes to cationic complexes have been reported where the cation is formed by displacement of halide from a complex. Bochmann and coworkers have found that displacement of chloride from $[\text{Ti}(\text{C}_5\text{H}_5)_2(\text{Me})\text{Cl}]$ and $[\text{Ti}(\text{Ind})_2(\text{Me})\text{Cl}]$ by

strong neutral donor ligands provides a general route to cationic $[\text{Ti}(\text{C}_5\text{H}_5)_2(\text{CH}_3)(\text{L})]^+$ complexes ($\text{L} = \text{'BuCN}$, PhCN , PMe_3 or py).⁶⁴ An example is shown in Equation 4.10. Halide displacement has so far been a less useful method for the preparation of zirconium cations.³²



Equation 4.12

Preparation of cationic pendant arm functionalised amidinate imido complexes directly from the chloride derivatives would be advantageous because it would eliminate the need to perform the alkylation step. It was proposed that reaction of chloride derivatives with NaBPh_4 or with silver reagents such as AgBPh_4 might be an entry point into this chemistry. The reactivity of the chloride derivatives towards silver reagents was tested by reaction of $[\text{Ti}(\text{N-2,6-C}_6\text{H}_3\text{'Pr}_2)\{\text{Me}_3\text{SiNC(Ph)NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}\text{Cl}]$ (**6**) with silver triflate.

4.6 Synthesis of a triflate derivative

Reaction of $[\text{Ti}(\text{N-2,6-C}_6\text{H}_3\text{'Pr}_2)\{\text{Me}_3\text{SiNC(Ph)NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}\text{Cl}]$ (**6**) with silver triflate in benzene at room temperature in the absence of light, followed by extraction into benzene and recrystallisation yielded $[\text{Ti}(\text{N-2,6-C}_6\text{H}_3\text{'Pr}_2)\{\text{Me}_3\text{SiNC(Ph)NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}\{\mu\text{-OSO}_2\text{CF}_3\}]_2$ (**33**) in 43% yield (Equation 4.13). The dimeric triflate complex **33** was characterised by NMR and IR spectroscopies and mass spectrometry. The ^1H NMR spectrum is shown in Figure 4.5.

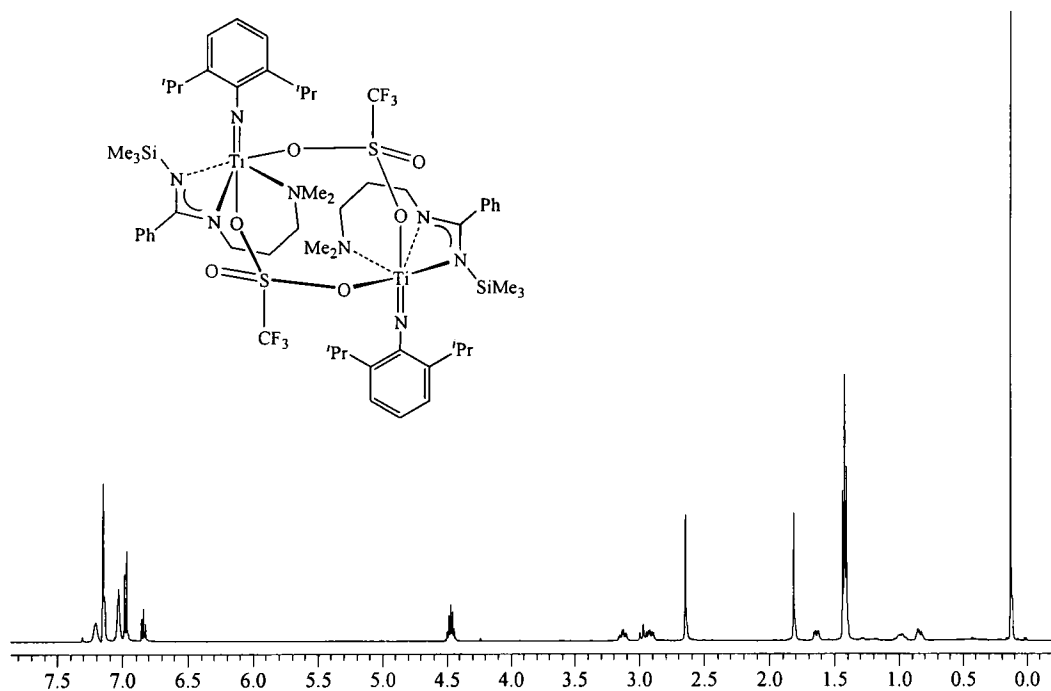
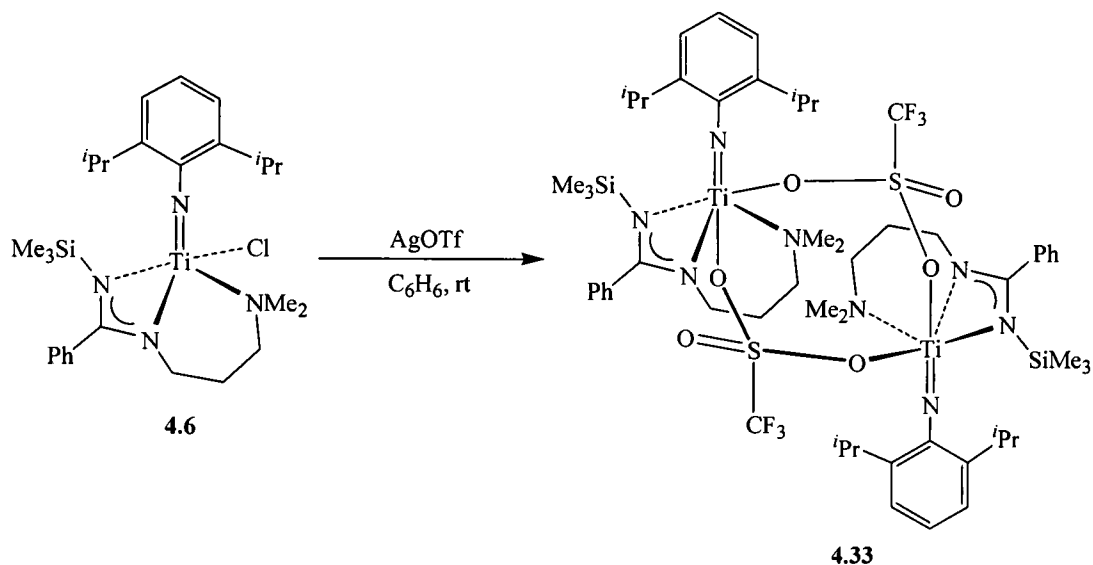


Figure 4.5 500.0 MHz ^1H NMR spectrum of $[\text{Ti}(\text{N}-2,6\text{-C}_6\text{H}_3\text{iPr}_2)]\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}\{\mu\text{-OSO}_2\text{CF}_3\}_2$ (**33**) in C_6D_6 .

The ^1H NMR spectrum contains the predicted resonances for a κ_3 -pendant arm amidinate. There are two sharp singlets at 2.67 and 1.83 ppm, consistent with firm coordination of the pendant amine to titanium on the NMR timescale at room temperature. The ^{19}F NMR spectrum contains a singlet at -58.5 ppm corresponding to the CF_3 group of the triflate.

The use of IR data to determine the bonding mode of the triflate anion is difficult, as is also the case for the closely related fluorosulfate anion, FSO_3^- . This is due to mixing of the CF_3 and SO_3 vibrational modes and accidental coincidences of these modes, arising particularly in the stretching region.⁶⁵ The IR data for **33** are consistent with those observed for other O,O'-bound bridging triflates; the bands at 1351, 1329, 1110, 1073, 975 and 959 cm^{-1} are all close in position to sulfur-oxygen stretching modes reported for related compounds of tin, chromium and copper.⁶⁶⁻⁶⁸ Other bands in this region may be assigned to CF_3 stretching modes.⁶⁹

Diffraction-quality red crystals of **33** were grown from a mixture of CH_2Cl_2 and hexanes at $-30\text{ }^\circ\text{C}$. Data were collected and the structure was solved by Dr. A. Cowley. The structure is shown in Figure 4.6 and selected bond lengths and angles are given in Table 4.2. Full details can be found in Appendix K.

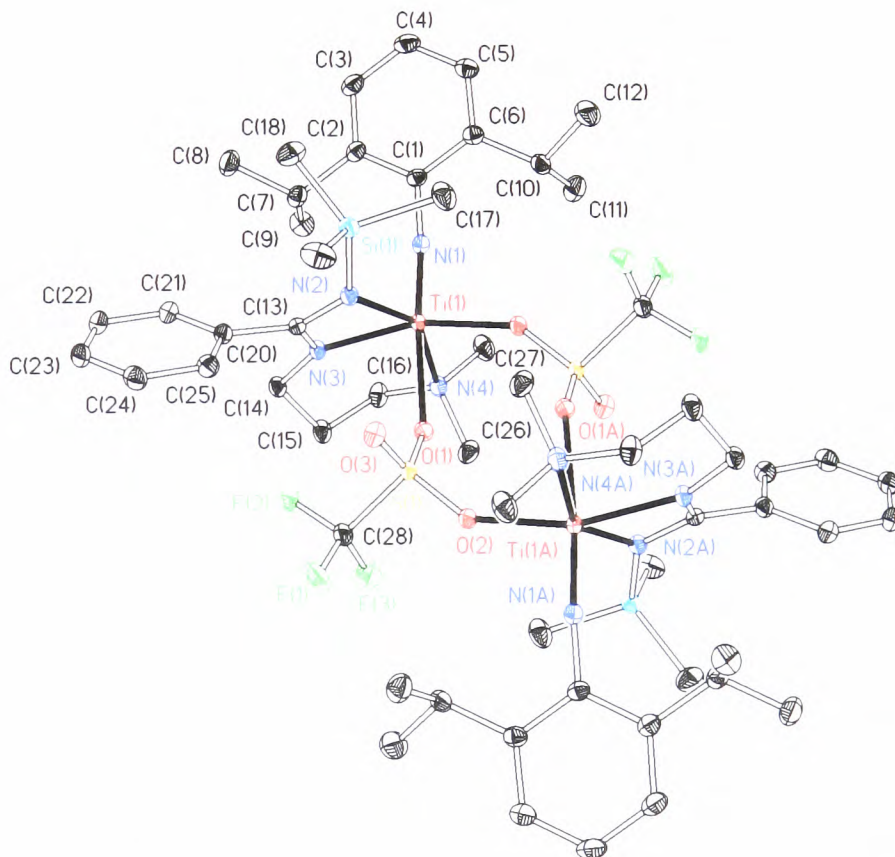


Figure 4.6 Thermal ellipsoid plot (30% probability) of $[\text{Ti}(\text{N}-2,6\text{-C}_6\text{H}_3'\text{Pr}_2)\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}\{\mu\text{-OSCF}_3(\text{O})\text{O}\}]_2$ (**33**). ^1H atoms omitted for clarity.

Table 4.6 Selected bond lengths (Å) and angles (°) for [Ti(N-2,6-C₆H₃Pr₂)
{Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂} {μ-OSCF₃(O)O}]₂ (**33**)

Ti(1)-N(1)	1.7192(16)	Ti(1)-N(2)	2.1169(16)
Ti(1)-N(3)	2.0785(15)	Ti(1)-N(4)	2.3140(16)
Ti(1)-O(1)	2.3869(13)	Ti(1)-O(1A)	2.0892(13)
N(1)-C(1)	1.3919(2)	N(2)-C(13)	1.345(2)
N(2)-Si(1)	1.7373(16)	C(13)-N(3)	1.320(2)
C(13)-N(3)	1.320(2)	C(13)-C(20)	1.493(3)
N(3)-C(14)	1.445(2)	C(14)-C(15)	1.524(3)
C(15)-C(16)	1.524(3)	C(16)-N(4)	1.499(2)
O(1)-S(1)	1.4441(14)	S(1)-O(2)	1.4693(13)
S(1)-O(3)	1.4229(15)	S(1)-C(28)	1.823(2)
N(1)-Ti(1)-N(2)	97.10(7)	N(1)-Ti(1)-N(3)	102.63(7)
N(2)-Ti(1)-N(3)	63.79(6)	N(1)-Ti(1)-N(4)	99.22(7)
N(2)-Ti(1)-N(4)	148.13(6)	N(3)-Ti(1)-N(4)	85.95(6)
N(1)-Ti(1)-O(1)	174.44(6)	N(2)-Ti(1)-O(1)	83.36(5)
N(3)-Ti(1)-O(1)	82.56(5)	N(4)-Ti(1)-O(1)	83.00(5)
N(1)-Ti(1)-O(1A)	98.46(6)	N(2)-Ti(1)-O(1A)	109.00(6)
N(3)-Ti(1)-O(1A)	158.37(6)	N(4)-Ti(1)-O(1A)	95.45(6)
O(1)-Ti(1)-O(1A)	76.21(5)	Ti(1)-N(1)-C(1)	167.18(14)
Ti(1)-O(1)-S(1)	144.99(8)	O(1)-S(1)-O(2)	113.27(8)
O(1)-S(1)-O(3)	117.74(9)	O(2)-S(1)-O(3)	113.97(9)
O(1)-S(1)-C(28)	102.84(9)	O(2)-S(1)-C(28)	101.82(9)
O(3)-S(1)-C(28)	104.7(1)	Ti(1A)-O(2)-S(1)	146.00(9)

Figure 4.6 shows that **33** possesses a dimeric structure in the solid state with the molecule lying across a crystallographic inversion centre. Each molecule contains two bridging triflate ligands which are O,O' bound. The structure confirms that the amino-amidinate ligands are κ^3 -bound with similar Ti-N distances to those found previously in the chloride and alkoxide analogues **4** - **6** and **30** - **31**. The N(3) and N(4) atoms are approximately sp^3 hybridised, the sums of the angles subtended at N(3) and N(4) are 354.36(33) and 359.54(39) ° respectively.

The geometry around titanium is slightly distorted from octahedral due to the chelating amidinate ligand and the small bite angle of the N₂CPh fragment. The only previous report of a Group 4 bridging triflate complex is the alkoxytitanium triflate [Ti(O^{*t*}Bu){μ-OSO₂CF₃}(^{*t*}BuOH)]₂ (**4.34**) prepared by Mikami and coworkers.⁷⁰ The Ti-O bond lengths in **33** [2.3869(13) Å and 2.0892(13) Å] are close in value to those for **4.34** [2.2225(4) and 2.059(4) Å]. The Ti-O distances in the related compound [Ti(η-C₅Me₅){μ-OSO₂(4-C₆H₄Me)}F]₂ (**4.35**) are also very close in value.⁷¹ The Ti(1)-N(1) bond length of 1.7192(16) is comparable to that for other titanium *tert*-butyl imides and the Ti(1)-N(1)-C(1) angle of 167.18(14) ° indicates that the imide is behaving as a four electron donor.^{26,27}

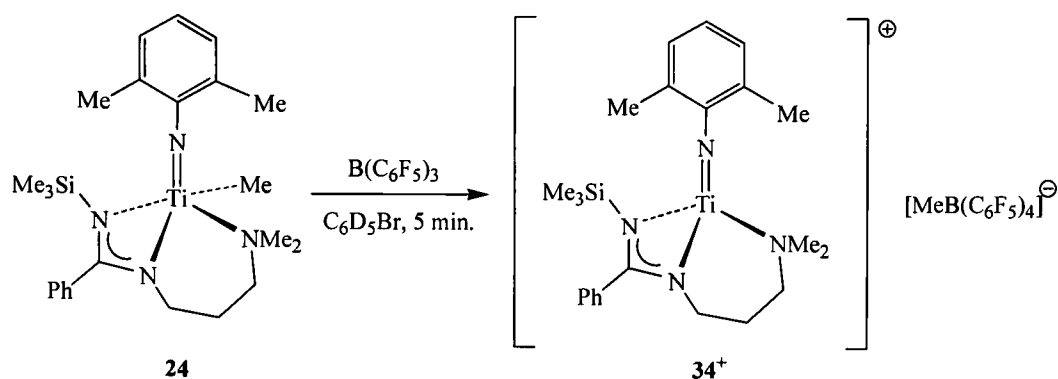
As the above reaction has shown, chloride metathesis by reaction with silver reagents is viable for these complexes. An attempt was therefore made to prepare a cationic compound by an analogous route but with a less strongly coordinating anion. Reaction of **6** with AgBPh₄ in THF or CD₃CN proved unsuccessful due to the extremely low solubility of AgBPh₄. Similarly, attempts to react **6** with NaBPh₄ in THF, CD₃CN or CD₂Cl₂ failed due to the poor solubility of NaBPh₄.

Since reactions to prepare cationic derivatives from the chloride starting materials were unpromising, the preparation of cationic derivatives from the alkyl compounds **25** and **26** was explored.

4.7 Cation formation from alkyl complexes **25** and **26**

Alkyl imido compounds to be used in the synthesis of cations were prepared using the appropriate chloride complexes as discussed in Section 4.3. The chloride complexes used in their preparation were sublimed under high vacuum before use in order to remove any impurities which might coordinate to the cation and quench its reactivity.

Initial efforts to generate a cationic amidinate-imido system focused on the arylimido methyl compound **25**, which was selected for its stability in solution. B(C₆F₅)₃ was chosen as the alkyl abstraction agent as no additional organic side product is formed by the reaction. Reaction of [Ti(N-2,6-C₆H₃Me₂) {Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂}Me] (**25**) with one equivalent of B(C₆F₅)₃ in C₆D₅Br at room temperature formed a very dark brown solution (Equation 4.14).



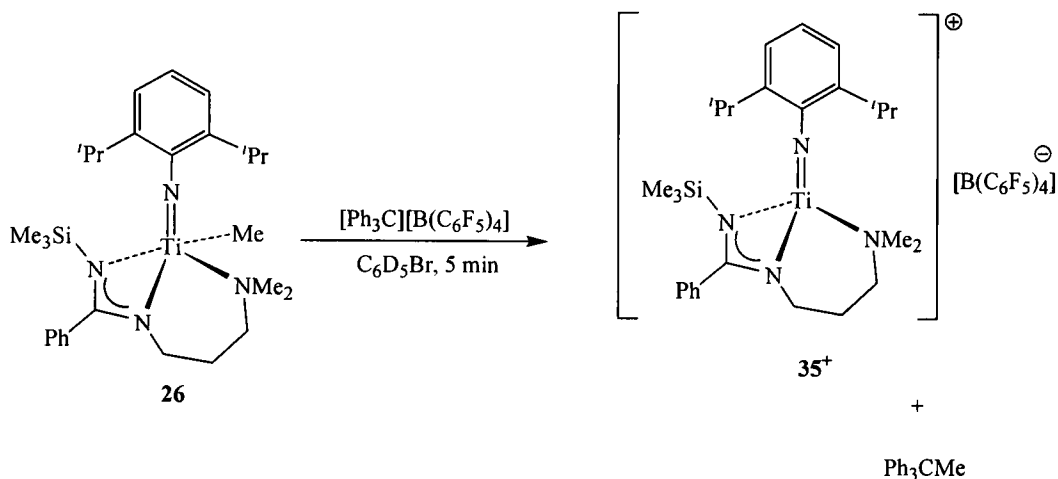
Equation 4.14

The ¹H NMR spectrum after 5 minutes showed complete consumption of **25** and formation of a new product, which no longer contained a resonance attributable to the titanium-bound methyl group ($\delta = ca.$ 0.6 ppm in C₆D₅Br). A broad 3 H singlet was observed at 1.27 ppm, consistent with the [MeB(C₆F₅)₃][⊖] anion and broadened due to the quadrupolar nature of boron (¹⁰B, $I = 3$, 19.9% natural abundance; ¹¹B, $I = 3/2$, 80.1 % natural abundance). A 6 H singlet at 2.49 ppm was assigned to the methyl groups of the arylimide. The resonances corresponding to the amidinate ligand were very broad, possibly suggesting competition between the anion and the hemi-labile pendant arm for coordination to titanium. The ¹⁹F NMR spectrum contained more than the predicted three resonances, possibly consistent with a more complex system than is indicated in Equation 4.14.

A reaction was carried out to screen the reactivity of the proposed cationic species, in which one equivalent of dimethylacetylene was added to *in situ* generated cation. The ¹H NMR spectrum after 10 minutes contained a complex mixture of several products. It was proposed that switching to the more bulky 2,6-di-*iso*-propylimido methyl compound **26** might yield a cation with more controlled reactivity towards unsaturated substrates.

Reaction of [Ti(N-C₆H₃^{*i*}Pr₂)NC(Ph)NCH₂CH₂CH₂NMe₂Me] (**26**) with one equivalent of B(C₆F₅)₃ in C₆D₅Br resulted in abstraction of Ti-Me and formation of the [MeB(C₆F₅)₃][⊖] anion as observed by ¹H NMR spectroscopy. The product again contained very broad resonances for the pendant arm protons and more ¹⁹F resonances than expected. In an attempt to improve matters, it was decided to change the alkyl abstraction agent to [Ph₃C][B(C₆F₅)₄], as this reagent has proved

more successful with other titanium imido-alkyl systems.⁷² Reaction of **26** with one equivalent of $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ in $\text{C}_6\text{D}_5\text{Br}$ resulted in a dark brown solution (Equation 4.15).



Equation 4.15

The ^1H NMR spectrum after 5 minutes showed complete consumption of the starting compound **26** and a 3 H singlet at 1.94 ppm, consistent with the expected organic side product, Ph_3CMe . When the reaction was repeated in CD_2Cl_2 , the cationic product **35⁺** was found to be stable in solution at room temperature without significant decomposition for 1 hour. The ^1H NMR spectrum of the product is shown in Figure 4.7.

The ^1H NMR spectrum contains a resonance at -0.02 ppm for the SiMe_3 group of the amidinate ligand. The resonances for the pendant arm are rather broad but two singlets at 2.46 and 3.34 ppm confirm coordination of the pendant amine to titanium on the NMR timescale. The sharp singlet at 2.16 ppm arises from the methyl group of the organic by-product Ph_3CMe and multiplet resonances for the phenyl protons of this species can be observed at 7.12, 7.22 and 7.28 ppm. Cooling the sample to -80 °C did not significantly alter the spectrum.

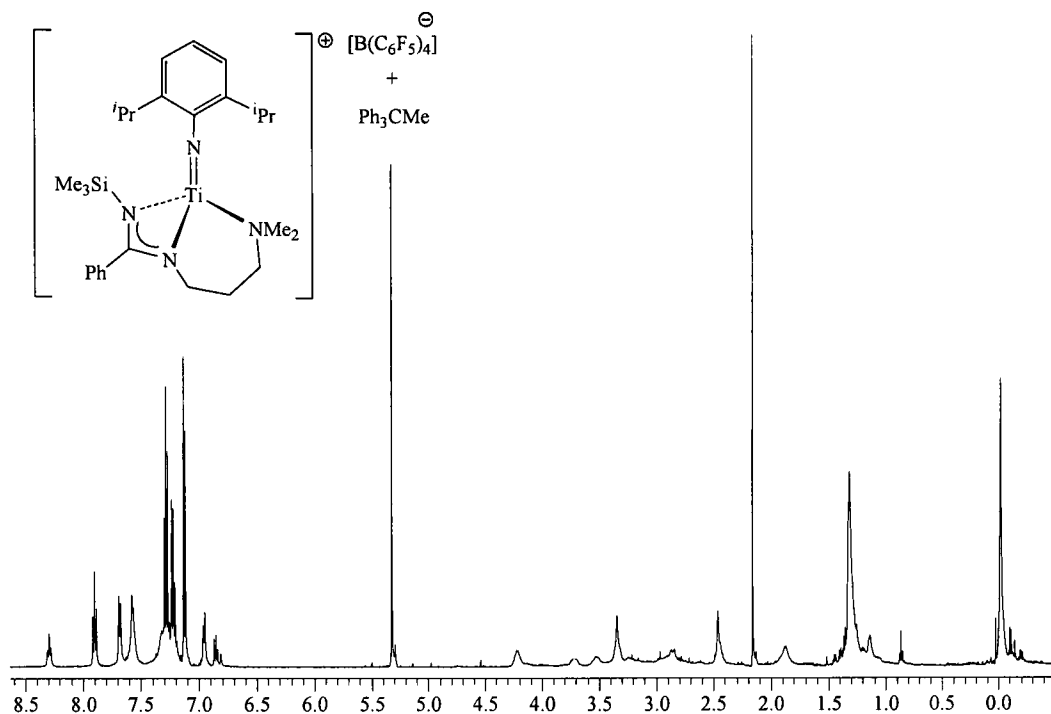


Figure 4.7 500.0 MHz ^1H NMR spectrum of a mixture of $[\text{Ti}(\text{N}-\text{C}_6\text{H}_3'\text{Pr}_2)\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}][\text{B}(\text{C}_6\text{F}_5)_4]$ (**35-B(C₆F₅)₄**) and Ph_3CMe in CD_2Cl_2

Attempts were made to isolate and characterise some Lewis base adducts of this cation. Generation of the cation in CD_2Cl_2 , followed by addition of one equivalent of THF yielded the adduct $[\text{Ti}(\text{N}-2,6-\text{C}_6\text{H}_3'\text{Pr}_2)\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}\text{THF}][\text{B}(\text{C}_6\text{F}_5)_4]$ (**36-B(C₆F₅)₄**). The 500.0 MHz ^1H NMR spectrum of **36-B(C₆F₅)₄** is shown in Figure 4.8.

Multiplet resonances at 2.34 ppm (obscured by NMe) and 4.55 and 4.63 ppm correspond to the coordinated THF. A spin saturation transfer experiment confirmed that the coordinated THF is undergoing exchange with the free THF present (broad singlets at *ca.* 1.9 and 3.7 ppm). The ^{19}F NMR contains three resonances at -133.15, -163.62 and -167.51 ppm which correspond to the *ortho*, *meta* and *para* protons of the anion respectively.

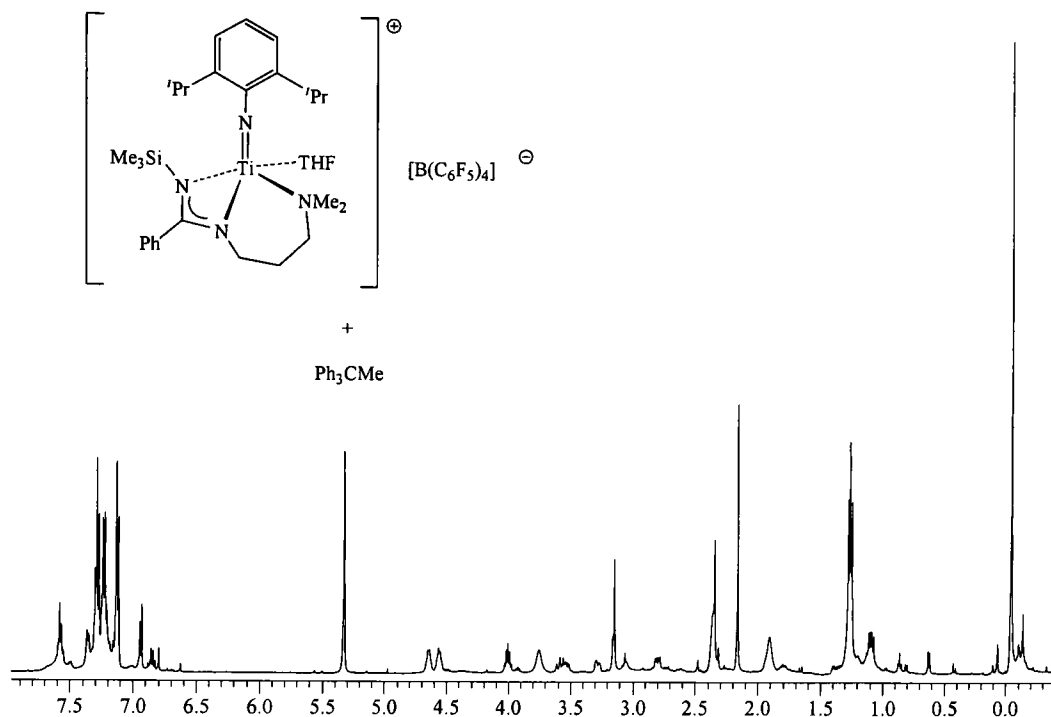


Figure 4.8 500.0 MHz ^1H NMR spectrum of a mixture of $[Ti(N-2,6-C_6H_3'Pr_2)\{Me_3SiNC(Ph)NCH_2CH_2CH_2NMe_2\}THF][B(C_6F_5)_4]$ (**36-B(C₆F₅)₄**) and Ph_3CMe in CD_2Cl_2

Attempts were made to isolate this adduct on a preparative scale by reaction of **26** with $[Ph_3C][B(C_6F_5)_4]$ in CH_2Cl_2 at $-78\text{ }^\circ C$, followed by addition of a stoichiometric amount of THF. Washing with pentane successfully removed the Ph_3CMe by-product and resulted in the formation of an oily clathrate product. While the ^1H NMR spectrum of the crude product showed formation of **36⁺** as the major product, it was not possible to crystallise the oil that formed or to obtain good elemental analysis data.

The corresponding NMR tube scale reaction of **26** with $[Ph_3C][B(C_6F_5)_4]$ in the presence of PPh_3 resulted in formation of the PPh_3 adduct $[Ti(N-2,6-C_6H_3'Pr_2)\{Me_3SiNC(Ph)NCH_2CH_2CH_2NMe_2\}(PPh_3)][B(C_6F_5)_4]$ (**37-B(C₆F₅)₄**). Again, attempts to isolate the product on a preparative scale were hampered by the oily nature of the product that was formed. The 500.0 MHz ^1H NMR spectrum of **37-B(C₆F₅)₄** is shown in Figure 4.9.

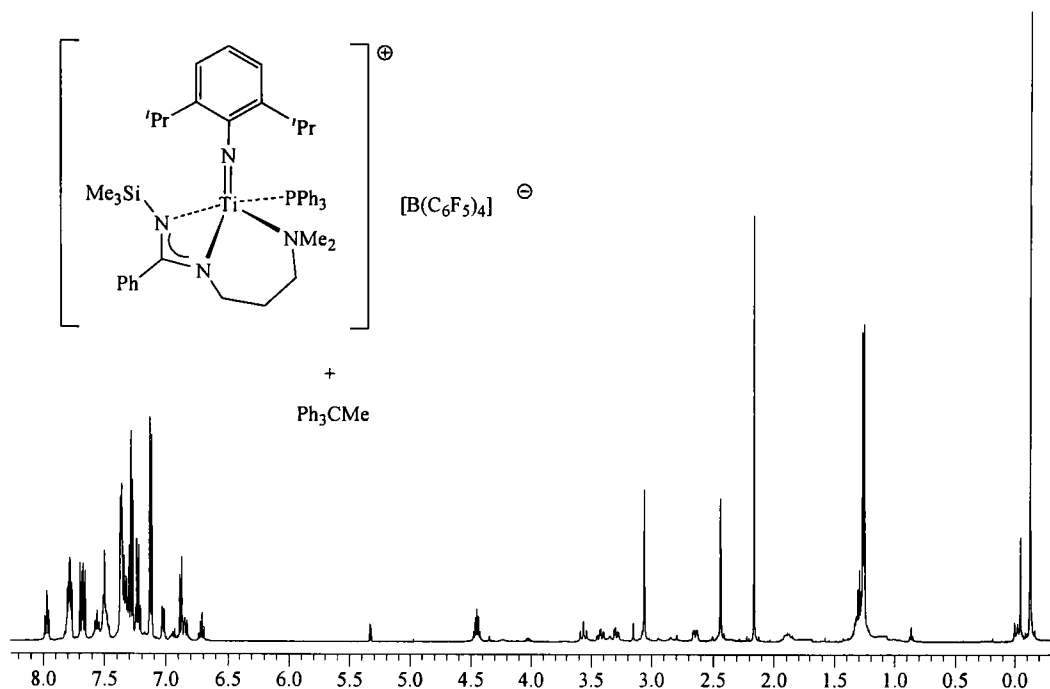
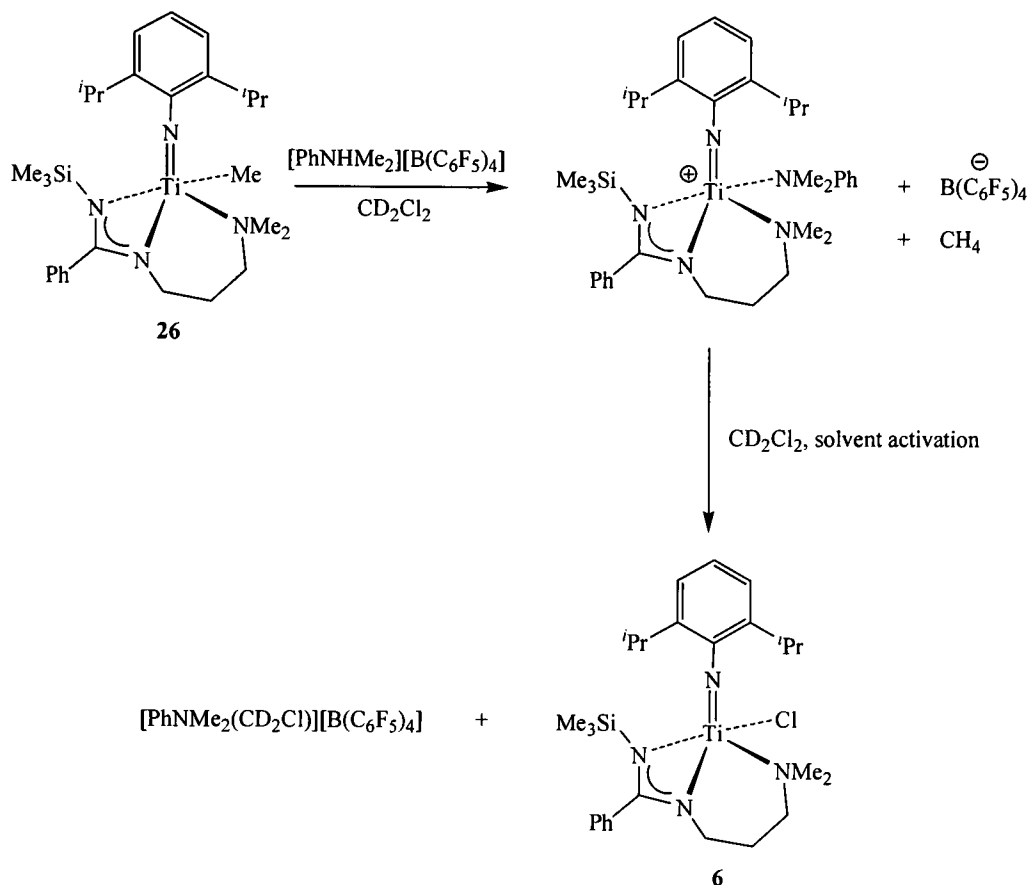


Figure 4.9 500.0 MHz ^1H NMR spectrum of a mixture of $[\text{Ti}(\text{N}-2,6\text{-C}_6\text{H}_3'\text{Pr}_2)\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}(\text{PPh}_3)][\text{B}(\text{C}_6\text{F}_5)_4]^-$ (**37-B(C₆F₅)₄**) and Ph_3CMe in CD_2Cl_2

An alternative route to the cation **35**⁺ was attempted *via* a Ti-Me protonolysis reaction with $[\text{HNMe}_2\text{Ph}][\text{B}(\text{C}_6\text{F}_5)_4]$ in CD_2Cl_2 . The ^1H NMR spectrum recorded after 10 minutes showed clean formation of the chloride derivative $[\text{Ti}(\text{N}-2,6\text{-C}_6\text{H}_3'\text{Pr}_2)\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}\text{Cl}]$ (**6**) which is likely to be formed *via* a solvent activation pathway (Scheme 4.6).

Choukroun *et al.* have reported an analogous reaction of $[\text{V}(\eta\text{-C}_5\text{H}_5)\text{Me}_2]$ with $[\text{HNMe}_2\text{Ph}][\text{BPh}_4]$.⁷³ A crystal structure for $[\text{PhNMe}_2(\text{CH}_2\text{Cl})][\text{BPh}_4]$ was obtained. Activation of CH_2Cl_2 is thought to occur by coordination of CH_2Cl_2 to the metal centre by a chlorine atom, followed by nucleophilic attack by PhNMe_2 at the now more electrophilic carbon atom of CH_2Cl_2 .⁷⁴ Analogous reactivity has also been reported for the reaction of the macrocycle-supported titanium imide $[\text{Ti}(\text{N}^t\text{Bu})(\text{Me}_3[9]\text{aneN}_3)(\text{CH}_2\text{SiMe}_3)_2]$ with $[\text{HNMe}_2\text{Ph}][\text{B}(\text{C}_6\text{F}_5)_4]$.⁷⁵



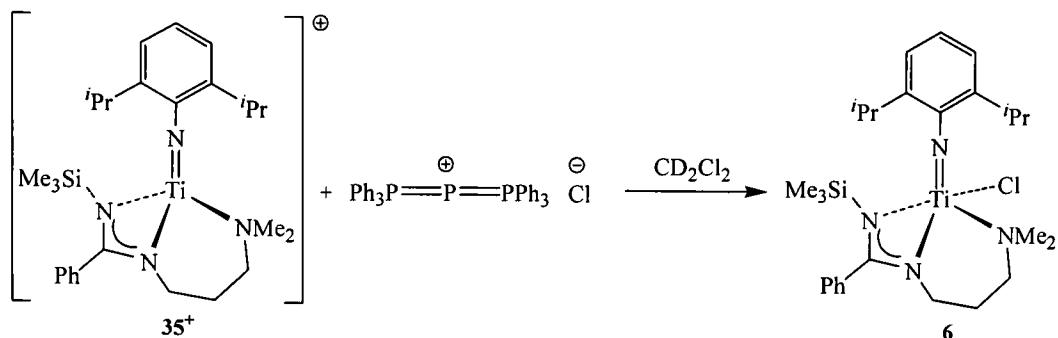
Scheme 4.6 Reaction of $[\text{Ti}(\text{N}-2,6\text{-C}_6\text{H}_3'\text{Pr}_2)\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}\text{Me}]$ (**2**) with $[\text{HNMe}_2\text{Ph}][\text{B}(\text{C}_6\text{F}_5)_4]$

4.8 Reactivity of cationic pendant arm functionalised amidinate-imido complexes

The 2,6-di-*iso*-propylphenyl imido cation **35**⁺ was chosen for reactivity studies as it was the most well-defined and stable in solution of the systems studied. Its reactivity towards a range of substrates was explored by NMR tube scale reactions.

4.8.1 Reaction with PPNCI

The cation **35**⁺ was generated by reaction of one equivalent of the methyl compound **26** with $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ in CD_2Cl_2 . To this was added one equivalent of bis(triphenylphosphorylidene)ammonium chloride (PPNCI) (Equation 4.16). The ¹H NMR spectrum after 10 minutes showed complete conversion to the chloride complex **6**.

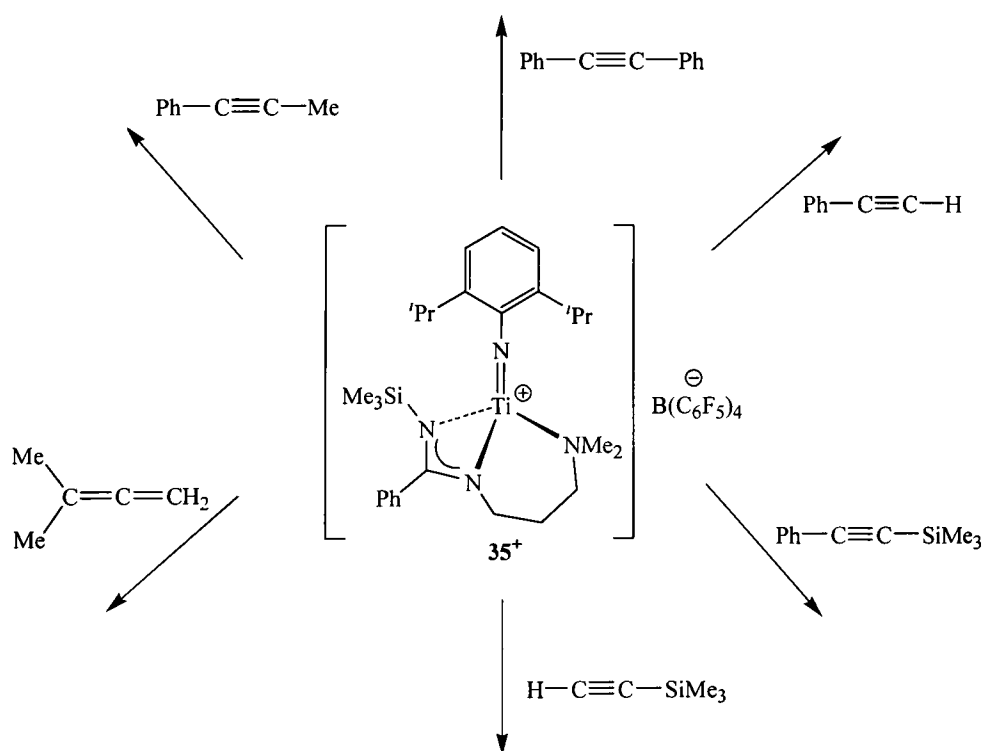


Equation 4.16

This reaction gives further support to the formation of the cationic complex 35^+ .

4.8.2 Reaction with unsaturated substrates

In recent years, there has been a great deal of interest in imido complexes as intermediates in the hydroamination of alkenes and allenes (Chapter 1).⁷⁶⁻⁸⁰ A crucial step in these reactions is the cycloaddition of an alkene or substituted allene to a metal imido bond.^{76,81} With these considerations in mind, the reactivity of the cationic complex 35^+ towards a range acetylenes and substituted allenes has been explored and the reactions monitored by ^1H NMR spectroscopy (Scheme 4.7).

Scheme 4.7 Attempted NMR scale reactions of 35^+ with alkenes/allenes

The cation 35^+ reacted with one equivalent of all of the substrates screened to give mixtures of products. Owing to the difficulties in purifying these cationic systems attempts to isolate stoichiometric cycloaddition products on a preparative scale were not pursued, but clearly systems of this type show promise for future development as hydroamination catalysts.

4.9 Summary

This Chapter describes the synthesis and characterisation of alkyl, aryloxy and triflate derivatives formed by metathesis reactions of the chloride complexes **1** - **6** described in Chapter 2. Three of these compounds have been crystallographically characterised. Methods used to generate Group 4 metal cations have been reviewed. The formation of cationic pendant arm functionalised amidinate-imido complexes has been described and the reactivity of these cationic derivatives towards unsaturated substrates has been assessed. The cationic complex 35^+ shows promise as a catalyst for the hydroamination of alkynes and allenes.

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Chapter 5

Experimental Details

5.1 General methods and instrumentation

All manipulations were carried out using standard Schlenk line or dry-box techniques under an atmosphere of argon or dinitrogen. Solvents were pre-dried over activated 4 Å molecular sieves and were refluxed over potassium (tetrahydrofuran, hexane, benzene), sodium/potassium alloy (pentane), sodium (diethyl ether), or calcium hydride (dichloromethane, acetonitrile) under a dinitrogen atmosphere and collected by distillation. For the latter part of the work they were degassed by sparging with dinitrogen and dried by passing through a column of activated alumina.^{1, 2} Deuterated solvents were dried over potassium (C₆D₆, toluene-d₈), P₂O₅ (CD₂Cl₂) or calcium hydride (CDCl₃), distilled under reduced pressure and stored under dinitrogen in Teflon valve ampoules. NMR samples were prepared under dinitrogen in 5 mm Wilmad 507-PP tubes fitted with J. Young Teflon valves.

¹H, ¹³C-{¹H} and ¹⁹F NMR spectra were recorded on Varian Mercury-VX 300 or Varian Unity Plus 500 spectrometers. ¹H and ¹³C assignments were confirmed where necessary with the use of DEPT-135, DEPT-90 and DEPT-45, and two dimensional ¹H-¹H and ¹³C-¹H NMR correlation experiments. ¹H and ¹³C-{¹H} spectra were referenced internally to residual protio-solvent (¹H) or solvent (¹³C) resonances, and are reported relative to tetramethylsilane (δ = 0 ppm). Chemical shifts are quoted in δ (ppm) and coupling constants in Hertz.

Infrared spectra were prepared as Nujol mulls or thin films between KBr or NaCl plates or as KBr pellets and were recorded on Perkin-Elmer 1600 and 1710 series FTIR spectrometers. Infrared data are quoted in wavenumbers (cm⁻¹).

Mass spectra were recorded by the mass spectrometry service of the University of Oxford Inorganic Chemistry Laboratory. Elemental analyses were carried out by the University of Oxford Inorganic Chemistry Laboratory and London Metropolitan University.

5.1.1 Literature Preparations

The compounds Li[Me₃SiNC(Ph)NCH₂CH₂NMe₂],³ Li[Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂],⁴ [Ti(NR)Cl₂(py)₃] (R = ^tBu, 2,6-C₆H₃Me₂ or 2,6-C₆H₃ⁱPr₂),⁵ [Ti(η-C₅H₄Me)Cl(py)],⁶ [Ti(η-C₅Me₅)(N^tBu){MeC(NⁱPr)₂}]⁷ and [Ti(η-C₅Me₅)

(NTol){MeC(NⁱPr)₂}}⁸ were prepared according to published procedures. The compounds PhLi,⁹ LiCH₂SiMe₃¹⁰ and AgBPh₄¹¹ were prepared according to literature methods. The compounds B(C₆F₅)₃, [HNMe₂Ph][B(C₆F₅)₄] and [Ph₃C][B(C₆F₅)₄] were generously provided by DSM Research. All other compounds and reagents were purchased from commercial suppliers and used without further purification.

5.2 Experimental details for Chapter 2

5.2.1 Preparation of [Ti(NⁱBu){Me₃SiNC(Ph)NCH₂CH₂NMe₂}Cl] (1)

To a stirred solution of [Ti(NⁱBu)Cl₂(py)₃] (1.01 g, 2.35 mmol) in benzene (40 ml) was added a solution of Li[Me₃SiNC(Ph)NCH₂CH₂NMe₂] (0.63 g, 2.35 mmol) in benzene (20 ml) dropwise over 15 min. The orange solution became orange-yellow in colour and a white precipitate formed. Volatiles were removed under reduced pressure and the orange oil was extracted into benzene (50 ml) and filtered. Volatiles were removed under reduced pressure and the waxy orange residue was recrystallised at -80 °C from pentane (20 ml), yielding **1** as an orange-yellow powder with some single diffraction-quality crystals. Yield: 0.68 g (69%).

5.2.2 Preparation of [Ti(N-2,6-C₆H₃Me₂){Me₃SiNC(Ph)NCH₂CH₂NMe₂}Cl] (2)

To a stirred solution of [Ti(N-2,6-C₆H₃Me₂)Cl₂(py)₃] (0.54 g, 1.14 mmol) in benzene (30 ml) was added a solution of Li[Me₃SiNC(Ph)NCH₂CH₂NMe₂] (0.31 g, 1.14 mmol) in benzene (15 ml) dropwise over 10 min. The solution remained brown in colour and a white precipitate formed. Volatiles were removed under reduced pressure and the brown residue was extracted into benzene (30 ml) and filtered. Volatiles were removed from the brown solution under reduced pressure and the brown residue was triturated with pentane (20 ml) to give **2** as a brown solid. Crude yield: 0.38 g (72 %). An analytically pure sample was obtained by sublimation (1 x 10⁻⁵ mbar, 150 - 160 °C) to yield **2** as a red-brown oil which hardened to a red-brown solid upon standing at rt. Yield: 59 mg (16%).

An attempt to crystallise $[\text{Ti}(\text{N}-2,6\text{-C}_6\text{H}_3\text{Me}_2)\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{NMe}_2\}\text{Cl}]$ (**2**) yielded a small quantity of crystals of $[\text{Ti}_2(\text{N}-2,6\text{-C}_6\text{H}_3\text{Me}_2)_2\text{Cl}_2(\mu\text{-O})\{\text{Me}_2\text{NCH}_2\text{CH}_2\text{N}=\text{C}(\text{Ph})\text{N}(\text{H})\text{SiMe}_3\}_2]$ (**10**).

5.2.3 Preparation of $[\text{Ti}(\text{N}-2,6\text{-C}_6\text{H}_3^i\text{Pr}_2)\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{NMe}_2\}\text{Cl}]$ (**3**)

To a stirred solution of $[\text{Ti}(\text{N}-2,6\text{-C}_6\text{H}_3^i\text{Pr}_2)\text{Cl}_2(\text{py})_3]$ (0.68 g, 1.29 mmol) in benzene (30 ml) was added a solution of $\text{Li}[\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{NMe}_2]$ (0.35 g, 1.29 mmol) in benzene (15 ml) dropwise over 10 min. The solution remained brown in colour and a white precipitate formed. Volatiles were removed under reduced pressure and the brown solid was extracted into benzene (20 ml) and filtered. Volatiles were removed under reduced pressure and the residue was triturated with pentane (30 ml) giving **3** as a brown solid. Crude yield: 0.51 g (85%). An analytically pure sample was obtained by sublimation (7×10^{-5} mbar, 100 - 100 °C) to yield **3** as a brown oil which hardened to a brown solid on standing at rt. Yield: 63 mg (19%).

5.2.4 NMR tube scale reaction of $[\text{Ti}(\text{N}^i\text{Bu})\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{NMe}_2\}\text{Cl}]$ (**1**) with 2,6-dimethylaniline

A solution of **1** (6.8 mg, 16.0 μmol) in C_6D_6 (0.5 ml) in a 5 mm Young's valve NMR tube was treated with *ca.* 1.0 equivalent of 2,6-dimethylaniline at room temperature. The ^1H NMR spectrum recorded after 10 min showed quantitative formation of **2**, together with new resonances attributable to $^i\text{BuNH}_2$.

5.2.5 Preparation of $[\text{Ti}(\text{N}^i\text{Bu})\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}\text{Cl}]$ (**4**)

To a stirred solution of $[\text{Ti}(\text{N}^i\text{Bu})\text{Cl}_2(\text{py})_3]$ (0.98 g, 2.30 mmol) in benzene (60 ml) was added a solution of $\text{Li}[\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2]$ (0.65 g, 2.30 mmol) in benzene (20 ml), dropwise over 10 min. The resulting orange-yellow solution was stirred for 3 days. Volatiles were removed under reduced pressure and the orange oil was extracted into benzene (40 ml) and filtered. Volatiles were removed under reduced pressure to yield an orange oil which was triturated with pentane (20 ml). Upon standing at rt the waxy orange solid **4** formed. Yield: 0.66 g (67%).

5.2.6 Preparation of [Ti(N-2,6-C₆H₃Me₂){Me₃SiNC(Ph)

NCH₂CH₂CH₂NMe₂}Cl] (5)

To a stirred solution of [Ti(N-2,6-C₆H₃Me₂)Cl₂(py)₃] (0.56 g, 1.18 mmol) in benzene (40 ml) was added a solution of Li[Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂] (0.33 g, 1.18 mmol) in benzene (20 ml) dropwise over 10 min. The brown solution became red-brown in colour and a white precipitate formed. Volatiles were removed under reduced pressure and the brown residue was extracted into benzene (30 ml). Volatiles were removed from the brown solution under reduced pressure and the resulting brown oil was recrystallised at rt from CH₂Cl₂ (5 ml) and hexanes (30 ml), yielding **5** as red-brown diffraction-quality crystals. Yield: 0.18 g (31%).

5.2.7 Preparation of [Ti(N-2,6-C₆H₃^{*i*}Pr₂){Me₃SiNC(Ph)

NCH₂CH₂CH₂NMe₂}Cl] (6)

To a stirred solution of [Ti(N-2,6-C₆H₃^{*i*}Pr₂)Cl₂(py)₃] (0.63 g, 1.18 mmol) in benzene (30 ml) was added a solution of Li[Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂] (0.34 g, 1.18 mmol) in benzene (30 ml) dropwise over 10 min. The solution remained brown in colour and a white precipitate formed. Volatiles were removed under reduced pressure and the brown solid was extracted into benzene (30 ml) and filtered. Volatiles were removed under reduced pressure and the brown oily residue was recrystallised at -30 °C from hexanes (40 ml), yielding **6** as a beige power. Yield: 0.44 g (69%). Diffraction-quality crystals of **6** were obtained by diffusion of a solution of **6** in hexanes into paraffin oil.

5.2.8 NMR tube scale reaction of [Ti(N^{*t*}Bu){Me₃SiNC(Ph)

NCH₂CH₂CH₂NMe₂}Cl] (4) with 2,6-dimethylaniline

A solution of **4** (7.0 mg, 16.0 μmol) in C₆D₆ (0.5 ml) in a 5 mm Young's valve NMR tube was treated with *ca.* 1.0 equivalent of 2,6-dimethylaniline at room temperature. The ¹H NMR spectrum recorded after 10 min showed quantitative formation of **5**, together with new resonances attributable to ^{*t*}BuNH₂.

5.2.9 Preparation of [Ti(NC₆F₅){Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂}Cl] (7)

To a stirred solution of [Ti(N^{*t*}Bu){Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂}Cl] (0.98 g, 2.27 mmol) in benzene (20 ml) was added a solution of pentafluoroaniline (0.42 g,

2.27 mmol) in benzene (20 ml), dropwise over 10 min. The orange solution darkened in colour. After stirring for 15 h, volatiles were removed under reduced pressure to yield **7** as an orange oil. Crude yield: 1.14 g (93 %). An analytically pure sample of **7** was obtained by sublimation at 3×10^{-5} mbar and 120 - 130 °C in poor yield.

5.2.10 Preparation of $[\text{Li}_2\{\text{CH}_3\text{CH}_2\text{CH}_2\text{NC}(\text{Ph})\text{NSiMe}_3\}(\text{Et}_2\text{O})_2]$ (**8**)

To a stirred solution of propylamine (4.31 g, 6 ml, 73 mmol) in Et_2O (150 ml) at -78 °C was added $n\text{BuLi}$ (1.6 M in hexanes, 45.6 ml, 73 mmol) dropwise over 20 min. A white precipitate formed and the mixture was stirred at rt for 15 h. The reaction mixture was cooled to -78 °C, trimethylsilylchloride (9.26 ml, 7.93 g, 73 mmol) added dropwise over 20 min and the mixture was stirred for a further 15 h at rt. The mixture was filtered and the white precipitate washed with Et_2O (3 x 20 ml). The combined filtrates were cooled to -78 °C and $n\text{BuLi}$ (1.6 M in hexanes, 45.6 ml, 73 mmol) was added over 30 min. The mixture was stirred at rt for 15 h, cooled to -78 °C and benzonitrile (7.45 ml, 7.53 g, 73 mmol) was added dropwise over 15 min. The resulting orange solution was stirred at rt for 15 h. Volatiles were removed under reduced pressure and the orange residue was extracted into hexanes (50 ml). The mixture was filtered and the white precipitate washed with hexanes (3 x 15 ml). The filtrates were combined, concentrated to 50 ml and Et_2O (15 ml) added. Crystallisation at -80 °C yielded **8** as a pale yellow powder. Yield: 15.0 g (66%).

5.2.11 Preparation of $[\text{Ti}(\text{N}^i\text{Bu})\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{Me}\}\text{Cl}(\text{py})_2]$ (**9**)

To a stirred solution of $[\text{Ti}(\text{N}^i\text{Bu})\text{Cl}_2(\text{py})_3]$ (0.46 g, 1.09 mmol) in benzene (30 ml) was added a solution of $[\text{Li}_2\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{Me}\}_2(\text{Et}_2\text{O})_2]$ (0.34 g, 1.09 mmol) in benzene (30 ml) dropwise over 10 min. The resulting orange mixture was stirred for 16 h. Volatiles were removed under reduced pressure and the resulting orange oil was extracted into benzene (20 ml) and filtered. The orange oily residue was triturated with pentane (20 ml) yielding **9** as an orange solid. The product was recrystallised at -80 °C from a mixture of hexanes (30 ml) and CH_2Cl_2 (20 ml). Yield: 0.17 g (34%).

5.2.12 NMR tube scale reactions to screen reactivity of **4** and **5** towards unsaturated substrates

The reactivity of $[\text{Ti}(\text{N}^i\text{Bu})\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}\text{Cl}]$ (**4**) and $[\text{Ti}(\text{N}-2,6\text{-C}_6\text{H}_3\text{Me}_2)\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}\text{Cl}]$ (**5**) towards a range of unsaturated substrates was examined by a series of stoichiometric reactions on the NMR tube scale. A representative example is outlined below.

A solution of **4** (10.6 mg, 24.6 μmol) in C_6D_6 (0.5 ml) in a Young's valve NMR tube was treated with *ca.* 1.0 equivalent of 2-butyne (1.9 μl , 1.3 mg, 24.6 μmol) at room temperature. The ^1H NMR spectrum was monitored over 3 d at room temperature and upon heating for 3 d at 80 $^\circ\text{C}$ but no change in the resonances present was observed.

The reactivity of **4** and **5** towards 2-butyne, 1,1-diphenylacetylene, phenylacetylene, trimethylsilylacetylene, 3-methyl-1,2-butadiene, RNC ($\text{R} = ^i\text{Bu}$ or 2,6- $\text{C}_6\text{H}_3\text{Me}_2$) and RNCO ($\text{R} = \text{R} = ^i\text{Bu}$, 2,6- $\text{C}_6\text{H}_3\text{Me}_2$ or Tol) was screened in this manner.

5.2.13 NMR tube scale synthesis of $[\text{Ti}\{\text{N}^i\text{Bu C}(\text{O})\text{O}\}\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}\text{Cl}]$ (**11**)

A solution of $[\text{Ti}(\text{N}^i\text{Bu})\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}\text{Cl}]$ (**11**) (12.3 mg, 0.029 mmol) in CD_2Cl_2 in a 5mm NMR tube was reacted with *ca.* 1.0 atm CO_2 via a dual-manifold Schlenk line. The ^1H NMR spectrum after 5 min showed quantitative formation of **11**. The sample was cooled to -78°C and maintained at this temperature while ^1H and $^{13}\text{C}\{-^1\text{H}\}$ NMR data were collected.

5.2.14 NMR tube scale synthesis of $[\text{Ti}\{\text{N}(2,6\text{-C}_6\text{H}_3\text{Me}_2)\text{C}(\text{O})\text{O}\}\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}\text{Cl}]$ (**12**)

A solution of $[\text{Ti}(\text{N}-2,6\text{-C}_6\text{H}_3\text{Me}_2)\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}\text{Cl}]$ (**12**) (14.4 mg, 30.0 μmol) in CD_2Cl_2 in a 5mm Young's valve NMR tube was reacted with *ca.* 1.0 atm CO_2 via a dual-manifold Schlenk line. The ^1H NMR spectrum after 5 min showed quantitative formation of **12**. The sample was cooled to -78°C and maintained at this temperature while ^1H and $^{13}\text{C}\{-^1\text{H}\}$ NMR data were collected.

5.3 Experimental details for Chapter 3

5.3.1 Preparation of $[\text{Ti}(\eta\text{-C}_5\text{H}_4\text{Me})(\text{N}^t\text{Bu})\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{NMe}_2\}]$ (13)

To a stirred solution of $[\text{Ti}(\eta\text{-C}_5\text{H}_4\text{Me})(\text{N}^t\text{Bu})\text{Cl}(\text{py})]$ (1.81 g, 5.78 mmol) in benzene (30 ml) was added a solution of $\text{Li}[\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{NMe}_2]$ in benzene (30 ml), dropwise over 15 min. Upon mixing, the dark brown solution became orange in colour and a white precipitate formed. The mixture was stirred for 15 h, volatiles were removed under reduced pressure and the resulting red-brown oil was extracted into benzene (40 ml). The brown solution was filtered and volatiles removed under reduced pressure to give a red-brown oil which was triturated with pentane (20 ml). Crude yield: 2.42 g (91%). The product was purified by sublimation (1×10^{-5} mbar, 120 - 130 °C) to yield **13** as a brown oil. Yield: 0.32 g (65%).

5.3.2 Preparation of $[\text{Ti}(\eta\text{-C}_5\text{H}_4\text{Me})(\text{N}^t\text{Bu})\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}]$ (14)

To a stirred solution of $[\text{Ti}(\eta\text{-C}_5\text{H}_4\text{Me})(\text{N}^t\text{Bu})\text{Cl}(\text{py})]$ (1.04 g, 3.33 mmol) in benzene (30 ml) was added a solution of $\text{Li}[\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2]$ (0.94 g, 3.33 mmol) in benzene (30 ml), dropwise over 15 min. The brown mixture was stirred for 15 h. Volatiles were removed under reduced pressure and the resulting brown oil was extracted into benzene (30 ml) and filtered. Volatiles were removed under reduced pressure and the solid brown residues were washed with benzene (2 x 20 ml). Volatiles were removed from the combined extracts under reduced pressure to give a dark brown oil. Crude yield: 1.33 g (84%). The product was sublimed under high vacuum (1×10^{-5} mbar, 120 - 130 °C) to yield **14** as a brown oil. Yield: 1.21 g (79%).

5.3.3 Preparation of $[\text{Ti}(\eta\text{-C}_5\text{H}_4\text{Me})(\text{N}^t\text{Bu})\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{Me}\}]$ (15)

To a stirred solution of $[\text{Ti}(\eta\text{-C}_5\text{H}_4\text{Me})(\text{N}^t\text{Bu})\text{Cl}(\text{py})]$ (1.53 g, 4.90 mmol) in benzene (30 ml) was added a solution of $[\text{Li}_2\{\text{Me}_3\text{NSiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{Me}\}_2(\text{Et}_2\text{O})_2]$ (1.54 g, 4.90 mmol) in benzene (30 ml). The deep red solution became slightly lighter in colour and was stirred for 15 h. Volatiles were removed under reduced pressure and the red oily residue extracted into benzene (30 ml), filtered

and volatiles removed under reduced pressure to yield **15** as a red oil. Yield: 1.96 g (94%).

5.3.4 Preparation of $[\text{Ti}_2(\eta\text{-C}_5\text{H}_4\text{Me})_2(\mu\text{-O})_2\{\text{Me}_3\text{SiNC(Ph)NCH}_2\text{CH}_2\text{NMe}_2\}_2]$ (**16**)

A solution of $[\text{Ti}(\eta\text{-C}_5\text{H}_4\text{Me})(\text{N}^i\text{Bu})\{\text{Me}_3\text{SiNC(Ph)NCH}_2\text{CH}_2\text{NMe}_2\}]$ (**13**) (0.40 g, 0.86 mmol) in benzene (15 ml) was exposed to *ca.* 1 atm CO_2 via a dual-manifold Schlenk line. The solution immediately changed colour from red-brown to cherry red, and after 24 h was brown in colour. Volatiles were removed under reduced pressure to give a brown oil which was triturated with pentane (20 ml) to give a waxy brown solid which was shown by NMR to be a mixture of two isomers, **16a** and **16b**. Yield: 0.19 g (56%). A sample of the crude product (0.16 g, 0.35 mmol) was recrystallised from a mixture of CH_2Cl_2 (10 ml) and hexanes (20 ml) to yield analytically pure product. Yield: 6.6 mg, (5%).

5.3.5 Preparation of $[\text{Ti}_2(\eta\text{-C}_5\text{H}_4\text{Me})_2(\mu\text{-O})_2\{\text{Me}_3\text{SiNC(Ph)NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}_2]$ (**17**)

A solution of $[\text{Ti}(\eta\text{-C}_5\text{H}_4\text{Me})(\text{N}^i\text{Bu})\{\text{Me}_3\text{SiNC(Ph)NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}]$ (**14**) (0.15 g, 0.32 mmol) in benzene (15 ml) was exposed to *ca.* 1 atm CO_2 via a dual-manifold Schlenk line. The solution was stirred and immediately changed colour from red-brown to cherry red and after five days was brown in colour. Benzene was removed under reduced pressure to give a red-brown solid which was shown by NMR to be a mixture of two isomers, **17a** and **17b**. Yield: 70 mg (50%). Attempts to recrystallise a portion of this product from a mixture of CH_2Cl_2 and hexanes failed to yield an analytically pure sample.

5.3.6 Preparation of $[\text{Ti}_2(\eta\text{-C}_5\text{H}_4\text{Me})_2(\mu\text{-O})_2\{\text{Me}_3\text{SiNC(Ph)NCH}_2\text{CH}_2\text{Me}\}_2]$ (**18**)

A solution of $[\text{Ti}(\eta\text{-C}_5\text{H}_4\text{Me})(\text{N}^i\text{Bu})\{\text{Me}_3\text{SiNC(Ph)NCH}_2\text{CH}_2\text{Me}\}]$ (**15**) (0.29 g, 0.67 mmol) in benzene (30 ml) was exposed to *ca.* 1 atm CO_2 via a dual-manifold Schlenk line. The solution was stirred and immediately changed colour from red-brown to cherry red and after 15 min was brown in colour. Volatiles were removed under reduced pressure to give a brown oil which was triturated with

pentane (20 ml) to give a brown waxy solid which was shown by NMR to be a mixture of two isomers, **18a** and **18b**. Yield: 0.14 g (37%).

5.3.7 NMR tube scale synthesis of $[\text{Ti}(\eta\text{-C}_5\text{H}_4\text{Me})\{\text{OC}(\text{O})\text{N}^i\text{Bu}\}\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}]$ (**19**)

A solution of $[\text{Ti}(\eta\text{-C}_5\text{H}_4\text{Me})(\text{N}^i\text{Bu})\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}]$ (**14**) (20 mg, 4.2 μmol) in CD_2Cl_2 (0.5 ml) at -78°C in a 5 mm Young's valve NMR tube was exposed to *ca.* 1 atm CO_2 via a dual-manifold Schlenk line. The brown solution immediately became cherry red in colour. The ^1H NMR spectrum recorded at -78°C after 5 min showed quantitative formation of **19**.

5.3.8 NMR tube scale synthesis of $[\text{Ti}(\eta\text{-C}_5\text{H}_4\text{Me})\{\text{OC}(\text{O})\text{N}^i\text{Bu}\}\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{Me}\}]$ (**20**)

A solution of $[\text{Ti}(\eta\text{-C}_5\text{H}_4\text{Me})(\text{N}^i\text{Bu})\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{Me}\}]$ (**15**) (23 mg, 5.3 μmol) in CD_2Cl_2 (0.5 ml) at -78°C in a 5 mm Young's valve NMR tube was exposed to *ca.* 1 atm CO_2 via a dual-manifold Schlenk line. The brown solution immediately became cherry red in colour. The ^1H NMR spectrum recorded at -78°C after 5 min showed quantitative formation of **20**.

5.3.9 NMR tube scale synthesis of $[\text{Ti}(\eta\text{-C}_5\text{H}_4\text{Me})\{\text{OC}(\text{O})\text{N}^i\text{Bu}\}\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{NMe}_2\}]$ (**21**)

A solution of $[\text{Ti}(\eta\text{-C}_5\text{H}_4\text{Me})(\text{N}^i\text{Bu})\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{NMe}_2\}]$ (**13**) (24 mg, 5.2 μmol) in CD_2Cl_2 (0.5 ml) at -78°C in a 5 mm Young's valve NMR tube was exposed to *ca.* 1 atm CO_2 via a dual-manifold Schlenk line. The sample was warmed to -35°C until the ^1H NMR spectrum showed quantitative formation of **21** (*ca.* 10 min) and then cooled back down to -78°C and maintained at this temperature while NMR data were collected.

5.3.10 Cycloaddition reaction of **13** with CO_2 : kinetic studies

A standard solution of $[\text{Ti}(\eta\text{-C}_5\text{H}_4\text{Me})(\text{N}^i\text{Bu})\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{NMe}_2\}]$ (**13**) was prepared (11.5 mg, 25.0 μmol) with 1.5 equivalents of 1,4-dimethoxybenzene (5.4 mg, 37.0 μmol) in CD_2Cl_2 (4.8 ml). Aliquots (0.6 ml) of this solution were transferred to 5 mm NMR tubes equipped with J. Young Teflon valves. The solutions were freeze-pump-thawed three times and cooled to -78°C .

Samples were exposed to CO₂ at pressures of 0.25, 0.5, 0.75 and 1.0 atm (> 10-fold excess CO₂ at lowest pressure studied) *via* a calibrated gas manifold. Samples were transferred to an NMR spectrometer maintained at a probe temperature of -78 °C and then warmed to -35 °C. ¹H NMR spectra were recorded at 3 min intervals until >90% of **13** had been consumed (8 h for 0.25 atm CO₂, 2 h for 1 atm CO₂).

5.3.11 Extrusion of ^tBuNCO from carbamate compounds **19** - **21**: kinetic studies

Solutions of **13** - **15** at 1.98 moldm⁻³ concentration {5.2 mg (**13**), 5.4 mg (**14**), 4.9 mg (**15**), 11.4 μmol} with *ca.* 1.5 equiv. 1,4-dimethoxybenzene (2.3 mg, 16 μmol) in CD₂Cl₂ (0.6 ml) were prepared and transferred to 5 mm NMR tubes equipped with J. Young Teflon valves. The solution was freeze-pump-thawed three times and cooled to -78 °C. Samples were exposed to CO₂ at *ca.* 1.0 atm pressure (> 10-fold excess CO₂) *via* a dual-manifold Schlenk line. Samples were transferred to an NMR spectrometer maintained at -78 °C and warmed to -30 °C, at which point all of the imido starting materials **13** - **15** had been consumed and only the carbamate compounds **19**, **20** or **21** were present. ¹H NMR spectra were recorded at 3 min intervals until >90% of **19** - **21** had been consumed (*ca.* 4 h for **19** and **20**, *ca.* 2 h for **21**). Experiments were carried out in duplicate for **19** and **21** at the same concentration. The "dummy arm" system **20** was examined at 1.9 x 10⁻⁸, 2.9 x 10⁻⁸ and 3.8 x 10⁻⁸ moldm⁻³ concentrations {4.9 mg, 11.4 μmol; 7.4 mg, 17.4 μmol and 9.8 mg, 2.3 μmol} respectively in 0.6 ml CD₂Cl₂.

N.B. In the case of the 2-carbon linker system **19**, a small amount of imido starting material **13** was still present at -30 °C and the data obtained until this had been consumed were discarded.

5.3.12 Crossover reaction on [Ti(η-C₅Me₅)(NTol){MeC(N^tPr)₂}]

Three samples of [Ti(η-C₅Me₅)(NTol){MeC(N^tPr)₂}] (5.0 mg, 12.6 μmol) and *ca.* 1.5 equivalents of 1,4-dimethoxybenzene (2.7 mg, 19.0 μmol) in C₆D₆ (0.6 ml) were transferred to 5 mm NMR tubes equipped with J. Young Teflon valves. To one sample was added *ca.* 5.0 equivalents of ^tBuNCO (7.2 ml, 63 μmol) and to another was added *ca.* 5.0 equivalents of 4-tolylisocyanate (6.8 μl, 63 μmol). The

solutions were freeze-pump-thawed three times and exposed to CO₂ at *ca.* 1.0 atm pressure *via* a dual-manifold Schlenk line. Samples were transferred to an NMR spectrometer and ¹H NMR spectra were recorded after 3 h, 5 h and 16 h.

5.3.13 Second addition of CO₂ to an arylimido-derived carbamate compound: kinetic studies

A standard solution of [Ti(η-C₅Me₅)(NTol){MeCN(^{*i*}Pr)₂}] was prepared (7.7 mg, 18.0 μmol) with 1.5 equivalents of 1,4-dimethoxybenzene (6.6 mg, 11.6 μmol) in CD₂Cl₂ (4.2 ml). Aliquots (0.6 ml) of this solution were transferred to 5 mm NMR tubes equipped with J. Young Teflon valves. The solutions were freeze-pump-thawed three times and samples were exposed to CO₂ at pressures of 0.25, 0.5, 0.75 and 1.0 atm (>10-fold excess CO₂ at lowest pressure studied) *via* a calibrated gas manifold. Samples were transferred to an NMR spectrometer with a probe temperature maintained at 20 °C. All of the carbamate complex [Ti(η-C₅Me₅){N(Tol)C(O)O}{MeCN(^{*i*}Pr)₂}] was consumed before any of the aryldicarboxylate complex [Ti(η-C₅Me₅){OC(O)N(Tol)C(O)O}{MeCN(^{*i*}Pr)₂}] was detected. ¹H NMR spectra were recorded at 3 min intervals until >90% of [Ti(η-C₅Me₅){N(Tol)C(O)O}{MeCN(^{*i*}Pr)₂}] had been consumed (5 h for 0.25 atm CO₂, 45 min for 1 atm CO₂).

5.3.14 Preparation of [Ti(η-C₅H₄Me){Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂}(N-2,6-C₆H₃Me₂)] (22)

To a stirred solution of [Ti(η-C₅H₄Me)(N^{*i*}Bu){Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂}] (0.52 g, 1.09 mmol) in benzene (40 ml) was added 2,6-dimethylaniline (0.13 ml, 1.09 mmol). The red solution became slightly darker in colour and was stirred at room temperature for 15 h. Volatiles were removed under reduced pressure to yield the product as an orange oil. Crude yield: 0.50 g (88%). The product was purified by sublimation (1 × 10⁻⁵ mbar, 100 - 120 °C) to yield **22** as a red waxy solid. Yield: 86 mg (15%).

5.3.15 Preparation of [Ti(η-C₅H₄Me){Me₃SiNC(Ph)NCH₂CH₂CH₃}(N-2,6-C₆H₃Me₂)] (23)

To a stirred solution of [Ti(η-C₅H₄Me){Me₃SiNC(Ph)NCH₂CH₂CH₃}(N^{*i*}Bu)] (0.41 g, 0.95 mmol) in benzene (50 ml) was added 2,6-dimethylaniline (0.11 g,

0.95 mmol, 0.18 ml). The red solution became green-brown in colour and was stirred for 15 h. Volatiles were removed under reduced pressure to yield the product as a dark brown oil. Crude yield: 0.45 g (98%). The resulting oil was sublimed under high vacuum (1×10^{-5} mbar, 100 - 120 °C) to yield **23** as a red oil. Yield: 0.17 g (47%).

5.4 Experimental details for Chapter 4

5.4.1 NMR tube scale synthesis of

[Ti(NⁱBu){Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂}Me] (24)

A solution of [Ti(NⁱBu){Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂}Cl] (6.0 mg, 14.0 μmol) in C₆D₆ (0.5 ml) in a 5 mm Young's valve NMR tube was treated with *ca.* 1.0 equiv. of MeLi (1.6 M in Et₂O). The ¹H NMR spectrum showed formation of **24** as the dominant product.

5.4.2 Preparation of [Ti(N-2,6-

C₆H₃Me₂){Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂}Me] (25)

To a stirred solution of [Ti(N-2,6-C₆H₃Me₂){Me₃SiN(Ph)NCH₂CH₂CH₂NMe₂}Cl] (**5**) (0.36 g, 0.76 mmol) in Et₂O (40 ml) at -78 °C was added MeLi (1.6 M in Et₂O, 0.47 ml, 0.76 mmol) dropwise over 15 min. The resulting orange solution was stirred at -78 °C for 15 min before being warmed to rt over 20 min. Volatiles were removed under reduced pressure and the resulting brown solid was extracted into benzene (25 ml). The brown solution was filtered and volatiles removed under reduced pressure to yield a brown solid which was triturated with pentane (25 ml) to give **25** as a brown solid. Yield: 0.17 g (50%).

5.4.3 Preparation of [Ti(N-2,6-C₆H₃ⁱPr₂){Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂}Me] (26)

To a stirred solution of [Ti(N-2,6-C₆H₃ⁱPr₂){Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂}Cl] (**6**) (0.40 g, 0.75 mmol) in Et₂O (30 ml) at -78 °C was added MeLi (1.6 M in Et₂O, 0.47 ml, 0.75 mmol) dropwise over 10 min. The solution was warmed to rt for 30 min and volatiles were removed under reduced pressure to yield a brown solid which was extracted into benzene (30 ml) and filtered. Volatiles were removed from the resulting brown solution under reduced pressure to yield a

brown oil which was triturated with pentane (20 ml) to give **26** as a brown solid. Yield: 0.20 g (52%).

5.4.4 Preparation of [Ti(N^tBu){Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂}Ph] (**27**)

To a stirred solution of [Ti(N^tBu){Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂}Cl] (**4**) (0.41 g, 0.95 mmol) in Et₂O (15 ml) at -80 °C was added a solution of PhLi (0.10 g, 1.20 mmol) in Et₂O (15 ml) dropwise over 15 min. The yellow solution was stirred at rt for 30 min. Volatiles were removed under reduced pressure and the resulting black solid was extracted into benzene (20 ml) and filtered. Volatiles were removed from the dark brown solution under reduced pressure to give a brown-black product which was triturated with pentane (30 ml) to give **27**. Yield: 0.29 g, (68%).

5.4.5 Preparation of [Ti(N-2,6-C₆H₃ⁱPr₂){Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂}Ph] (**28**)

To a solution of [Ti(N-2,6-C₆H₃ⁱPr₂){Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂}Cl] (**6**) (0.59 g, 1.11 mmol) in benzene (20 ml) in a drybox was added a suspension of PhLi (93 mg, 1.11 mmol) in benzene (15 ml). The resulting brown mixture was transferred to a Schlenk tube and volatiles were removed under reduced pressure to yield a brown oil. This was redissolved in benzene (20 ml) and filtered to give a brown solution. Volatiles were removed under reduced pressure to yield **28** as a brown powder. Yield: 0.42 g (66%).

5.4.6 Preparation of Li[Ti(N-2,6-C₆H₃ⁱPr₂){Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂}Ph₂] (**29**)

To a stirred solution of [Ti(N-2,6-C₆H₃ⁱPr₂){Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂}Cl] (**6**) (0.96 g, 1.79 mmol) in benzene (30 ml) was added a solution of PhLi (0.30 g, 3.58 mmol) in benzene (30 ml). The brown solution became darker in colour and was stirred at rt for 15 h. Volatiles were removed under reduced pressure to yield a brown oil which was extracted into benzene (60 ml). The brown mixture was filtered and volatiles removed under reduced pressure to yield **29** as an orange powder. Yield: 0.50 g (42%).

5.4.7 NMR tube scale reactions of 4, 5 and 6 with $\text{LiCH}_2\text{SiMe}_3$

The reactions of the three carbon linker compounds 4, 5 and 6 with $\text{LiCH}_2\text{SiMe}_3$ have been examined on the NMR tube scale. A representative example is described below.

A solution of 6 (12.6 mg, 23.5 μmol) in C_6D_6 (0.5 ml) was used to dissolve *ca.* 1.0 equivalent of $\text{LiCH}_2\text{SiMe}_3$ (2.2 mg, 23.5 μmol) and the resulting mixture transferred to a 5 mm Young's valve NMR tube at room temperature. The ^1H NMR spectrum was monitored over 24 h and showed a complex mixture of products.

5.4.8 Attempted NMR tube scale alkylations of 1

A solution of 1 (10.3 mg, 22.1 μmol) in C_6D_6 (0.5 ml) was used to dissolve *ca.* 1.0 equivalent of PhLi (1.9 mg, 22.1 μmol) and the resulting mixture transferred to a 5 mm Young's valve NMR tube at room temperature. The ^1H NMR spectrum was monitored over 24 h and showed a complex mixture of products.

The corresponding reaction of 1 with MeLi was attempted and also yielded a complex mixture of products.

5.4.9 Preparation of $[\text{Ti}(\text{N}^i\text{Bu})\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}(\text{O}-2,6\text{-C}_6\text{H}_3\text{Me}_2)]$ (30)

To a stirred solution of $[\text{Ti}(\text{N}^i\text{Bu})\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}\text{Cl}]$ (4) (0.55 g, 1.29 mmol) in toluene (20 ml) was added a solution of $\text{LiO}-2,6\text{-C}_6\text{H}_3\text{Me}_2$ (0.16 g, 1.29 mmol) in toluene (40 ml) dropwise over 15 min. The yellow solution was stirred at rt for 2 h. Volatiles were removed under reduced pressure, and the resulting yellow solid was extracted into hexanes (50 ml) and filtered. Volatiles were removed under reduced pressure to give 30 as a yellow solid which was recrystallised from hexanes (20 ml) at -80°C and washed with cold hexanes (5 x 10 ml). Yield: 0.41 g (63%).

5.4.10 Preparation of $[\text{Ti}(\text{N}-2,6\text{-C}_6\text{H}_3\text{Me}_2)\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}(\text{O}-2,6\text{-C}_6\text{H}_3\text{Me}_2)]$ (31)

To a stirred solution of $[\text{Ti}(\text{N}-2,6\text{-C}_6\text{H}_3\text{Me}_2)\{\text{Me}_3\text{SiN}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}\text{Cl}]$ (5) (0.56 g, 1.17 mmol) in toluene (30 ml) was added a solution of $\text{LiO}-2,6\text{-C}_6\text{H}_3\text{Me}_2$ (0.15 g, 1.17 mmol) in toluene (30 ml) dropwise over 15 min. The red

brown solution became orange in colour and was stirred at rt for 16 h. Volatiles were removed under reduced pressure and the orange-brown solid was extracted into hexanes (50 ml). The orange solution was filtered and volatiles removed under reduced pressure to yield **31** as an orange solid which was recrystallised from pentane (15 ml) at $-80\text{ }^{\circ}\text{C}$ and washed with cold pentane (4 x 10 ml). Yield: 0.10g (63%).

5.4.11 Preparation of $[\text{Ti}(\text{N}^i\text{Bu})\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{NMe}_2\}(\text{O}-2,6\text{-C}_6\text{H}_3\text{Me}_2)]$ (**32**)

To a stirred solution of $[\text{Ti}(\text{N}^i\text{Bu})\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{NMe}_2\}\text{Cl}]$ (**1**) (0.41 g, 0.88 mmol) in toluene (15 ml) was added a solution of $\text{LiO}-2,6\text{-C}_6\text{H}_3\text{Me}_2$ (0.14 g, 0.88 mol) in toluene (30 ml) dropwise over 15 min. The yellow solution was stirred at rt for 16 h. Volatiles were removed under reduced pressure, and the resulting orange-brown solid was extracted into benzene (30 ml) and filtered. Volatiles were removed under reduced pressure to give **32** as a yellow solid which was recrystallised from hexanes (25 ml) at $-80\text{ }^{\circ}\text{C}$ and washed with cold hexanes (5 x 10 ml). Yield: 0.11g (25%).

5.4.12 $[\text{Ti}(\text{N}-2,6\text{-C}_6\text{H}_3^i\text{Pr}_2)\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}(\text{OTf})_2]$ (**33**)

To a stirred slurry of AgOTf (0.20 g, 0.77 mmol) in benzene (20 ml) was added a solution of $[\text{Ti}(\text{N}-2,6\text{-C}_6\text{H}_3^i\text{Pr}_2)\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}\text{Cl}]$ (**6**) (0.41 g, 0.77 mol) in benzene (30 ml). The resulting brown mixture was stirred in the dark for 15 h. Volatiles were removed under reduced pressure to yield a brown oil which was extracted into benzene (30 ml) and filtered. Volatiles were removed from the brown solution under reduced pressure to give a brown waxy solid which was recrystallised from CH_2Cl_2 (10 ml) and hexanes (15 ml) at $-30\text{ }^{\circ}\text{C}$ to yield **33** as a brown crystalline solid. Yield: 0.22 g (43%).

5.4.13 Attempted formation of cationic complexes of **6** by chloride abstraction (NMR tube scale)

Attempts were made to form a cationic derivative of **6** by reaction with AgBPh_4 or NaBPh_4 on the NMR tube scale. A representative example is described below.

A solution of **6** (8.0 mg, 15.0 μmol) in CD_3CN (0.5 ml) was mixed with AgBPh_4 (6.4 mg, 15.0 μmol). The resulting mixture was transferred to a 5 mm Young's

valve NMR tube. The ^1H NMR spectrum was monitored over 3 d and after heating to 70 °C for 24 h. No reaction was observed, probably due to the insoluble nature of AgBPh_4 .

The same reaction was attempted in THF but was also hampered by poor AgBPh_4 solubility. The corresponding reactions of **6** with NaBPh_4 in THF, CD_3CN and CD_2Cl_2 were also attempted.

5.4.14 NMR tube scale reaction of **25** with $\text{B}(\text{C}_6\text{F}_5)_3$

A solution of **25** (10.1 mg, 22.0 μmol) in $\text{C}_6\text{D}_5\text{Br}$ (0.5 ml) was used to dissolve $\text{B}(\text{C}_6\text{F}_5)_3$ (11.3 mg, 22.0 μmol) and the resulting dark brown solution transferred to a 5 mm Young's valve NMR tube. The ^1H NMR spectrum recorded after 10 min showed quantitative formation of 34^+ , together with a new resonance attributed to $\text{MeB}(\text{C}_6\text{F}_5)_3$.

5.4.15 NMR tube scale reaction of **26** with $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$

A solution of **26** (8.7 mg, 16.9 μmol) in CD_2Cl_2 (0.5 ml) was used to dissolve $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (15.6 mg, 16.9 μmol) and the resulting dark brown solution transferred to a 5 mm Young's valve NMR tube. The ^1H NMR spectrum recorded after 10 min showed quantitative formation of 35^+ , together with a new resonance attributed to Ph_3CMe .

5.4.16 NMR tube scale preparation of $[\text{Ti}(\text{N-2,6-}\text{C}_6\text{H}_3^i\text{Pr}_2)\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}\text{THF}][\text{B}(\text{C}_6\text{F}_5)_4]$ (**36-B**(C_6F_5)₄)

A solution of **26** (10.2 mg, 19.2 μmol) in CD_2Cl_2 (0.5 ml) was used to dissolve $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (18.3 mg, 19.2 μmol). To the resulting dark brown solution was added THF (1.6 μl , 1.4 mg, 19.2 μmol). The mixture was transferred to a 5 mm Young's valve NMR tube. The ^1H NMR spectrum recorded after 10 min showed quantitative formation of 36^+ , together with a new resonance attributed to Ph_3CMe .

5.4.17 Preparation of $[\text{Ti}(\text{N-2,6-}\text{C}_6\text{H}_3^i\text{Pr}_2)\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}(\text{THF})][\text{B}(\text{C}_6\text{F}_5)_4]$ (**36-B**(C_6F_5)₄)

To a stirred solution of $[\text{Ti}(\text{N-2,6-}\text{C}_6\text{H}_3^i\text{Pr}_2)\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}\text{Me}]$ (**26**) (0.41 g, 0.79 mmol) in CH_2Cl_2 (30 ml) at -78 °C was added a solution of

$[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (0.73 g, 0.79 mmol) in CH_2Cl_2 (20 ml) dropwise over 5 min. The light brown solution became very dark brown in colour and THF (57 mg, 64 μl , 0.79 mmol) was added. The mixture was warmed to rt for 30 min. Volatiles were removed under reduced pressure to give a brown oil which was dissolved in a mixture of CH_2Cl_2 (15 ml) and pentane (40 ml) to give a light brown suspension and a brown oil. The suspension was removed by decantation and the brown oil was washed with pentane (3 x 10 ml) and dried under vacuum to yield **36⁺** as a sticky brown solid. Yield: 0.56 g (57%).

5.4.18 NMR tube scale preparation of $[\text{Ti}(\text{N-2,6-}\text{C}_6\text{H}_3^i\text{Pr}_2)\{\text{Me}_3\text{SiNC(Ph)NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}(\text{PPh}_3)][\text{B}(\text{C}_6\text{F}_5)_4]$ (**37-B(C₆F₅)₄**)

A solution of **26** (9.3 mg, 18.1 μmol) in CD_2Cl_2 (0.5 ml) was used to dissolve $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (16.7 mg, 18.1 μmol) and PPh_3 (4.7 mg, 18.1 μmol). The resulting dark brown solution was transferred to a 5 mm Young's valve NMR tube. The ^1H NMR spectrum recorded after 10 min showed quantitative formation of **37⁺**, together with a new resonance attributed to Ph_3CMe .

5.4.19 Preparation of $[\text{Ti}(\text{N-2,6-}\text{C}_6\text{H}_3^i\text{Pr}_2)\{\text{Me}_3\text{SiNC(Ph)NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}(\text{PPh}_3)][\text{B}(\text{C}_6\text{F}_5)_4]$ (**37-B(C₆F₅)₄**)

To a stirred solution of $[\text{Ti}(\text{N-2,6-}\text{C}_6\text{H}_3^i\text{Pr}_2)\{\text{Me}_3\text{SiNC(Ph)NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}\text{Me}]$ (**26**) (0.21 g, 0.42 mmol) in CH_2Cl_2 (25 ml) at -78°C was added a solution of $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (0.38 g, 0.42 mmol) in CH_2Cl_2 (25 ml) dropwise over 5 min. The light brown solution became very dark brown in colour and a solution of PPh_3 (0.11 g, 0.42 mmol) in CH_2Cl_2 (20 ml) was added. The mixture was warmed to rt for 30 min and volatiles removed under reduced pressure to give a brown oil which was dissolved in a mixture of CH_2Cl_2 (10 ml) and pentane (40 ml) to give a brown oil and a light brown suspension. The suspension was removed by decantation and the brown oil washed with pentane (3 x 10 ml). The oil was dried under vacuum to give **37⁺** as a sticky brown solid. Yield: 0.21 g (35%).

5.4.20 NMR tube scale reaction of $[\text{Ti}(\text{N-2,6-}\text{C}_6\text{H}_3^i\text{Pr}_2)\{\text{Me}_3\text{SiNC(Ph)NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}\text{Me}]$ (**26**) with $[\text{HNMe}_2\text{Ph}][\text{B}(\text{C}_6\text{F}_5)_4]$

A solution of $[\text{Ti}(\text{N-2,6-}\text{C}_6\text{H}_3^i\text{Pr}_2)\{\text{Me}_3\text{SiNC(Ph)NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}\text{Me}]$ (**26**) (9.7 mg, 18.8 μmol) in CD_2Cl_2 in a 5mm Young's valve NMR tube was reacted

with $[\text{HNMe}_2\text{Ph}][\text{B}(\text{C}_6\text{F}_5)_4]$ (15.1 mg, 18.8 μmol). The ^1H NMR spectrum after 5 min showed quantitative formation of $[\text{Ti}(\text{N-2,6-C}_6\text{H}_3^i\text{Pr}_2)\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}\text{Cl}]$ (**6**).

5.4.21 NMR tube scale reaction of $[\text{Ti}(\text{N-2,6-C}_6\text{H}_3^i\text{Pr}_2)\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}][\text{B}(\text{C}_6\text{F}_5)_4]$ (**35-B**(C_6F_5)₄) with PPNCI

A solution of $[\text{Ti}(\text{N-2,6-C}_6\text{H}_3^i\text{Pr}_2)\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}\text{Me}]$ (**26**) (10.5 mg, 20.4 μmol) in CD_2Cl_2 in a 5mm Young's valve NMR tube was reacted with $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (18.8 mg, 20.4 μmol) to generate the cation **35**⁺. To this dark brown solution was added PPNCI (11.7 mg, 20.4 μmol). The ^1H NMR spectrum after 5 min showed quantitative formation of $[\text{Ti}(\text{N-2,6-C}_6\text{H}_3^i\text{Pr}_2)\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}\text{Cl}]$ (**6**).

5.4.22 NMR tube scale reactions to screen reactivity of **35**⁺ towards unsaturated substrates

The reactivity of the cation **35**⁺ towards a range of unsaturated substrates was examined by a series of stoichiometric reactions on the NMR tube scale. A representative example is outlined below.

A solution of **26** (13.3 mg, 25.8 μmol) in CD_2Cl_2 (0.5 ml) in a Young's valve NMR tube was used to dissolve $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (23.8 mg, 25.8 μmol) and *ca.* 1.0 equivalent of diphenylacetylene (4.6 mg, 25.8 μmol) at room temperature. The resulting dark brown solution was transferred to a Young's valve NMR tube. The ^1H NMR spectrum was monitored over 3 d at room temperature and displayed resonances due to a complex mixture of products. The reactivity of **35**⁺ towards 1,1-diphenylacetylene, phenylacetylene, trimethylsilylacetylene, 3-methyl-1,2-butadiene, 1-phenyl-2-(trimethylsilyl)acetylene and 1-phenyl-1-propyne was screened in this manner.

5.5 References for Chapter 5

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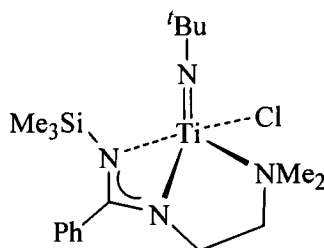
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Chapter 6

Characterising Data

6.1 Characterising data for Chapter 2

6.1.1 [Ti(N^tBu){Me₃SiNC(Ph)NCH₂CH₂NMe₂}Cl] (1)



¹H NMR data: (CD₂Cl₂, 500.0 MHz, 293 K)

7.50 - 7.35	5 H	m	C ₆ H ₅
3.75	1 H	m	CN ₂ CH ₂
3.31	1 H	m	<u>CH</u> ₂ NMe ₂
3.03	3 H	s	NMe
3.01	1 H	m	CN ₂ CH ₂
2.36	1 H	m	<u>CH</u> ₂ NMe ₂
2.16	3 H	s	NMe
1.02	9 H	s	CMe ₃
0.90	9 H	s	SiMe ₃

¹³C-{¹H} NMR data: (CD₂Cl₂, 75.5 MHz, 293 K)

173.74	CN ₂
134.25	<i>ipso</i> -C ₆ H ₅
130.41	C ₆ H ₅
128.50	C ₆ H ₅
127.86	C ₆ H ₅
123.80	C ₆ H ₅
123.60	C ₆ H ₅
70.31	<u>C</u> Me ₃
62.71	<u>CH</u> ₂ NMe ₂
50.18	NMe
46.12	CN ₂ <u>CH</u> ₂
46.12	NMe
32.10	<u>C</u> Me ₃
1.48	SiMe ₃

I.R. data: (KBr plates, Nujol mull, cm^{-1})

2727 (w), 1603 (w), 1578 (w), 1505 (w), 1349 (m), 1329 (w), 1245 (m), 1204 (m), 1176 (w), 1153 (w), 1134 (w), 1087 (w), 1073 (w), 1046 (w), 1023 (w), 950 (w), 933 (w), 869 (m), 836 (m), 793 (w), 776 (w), 757 (w), 723 (w), 702 (w), 627 (w), 594 (w), 563 (w), 515 (w), 500 (w), 442 (w).

Elemental analysis for $\text{C}_{18}\text{H}_{33}\text{N}_4\text{ClSiTi}$:

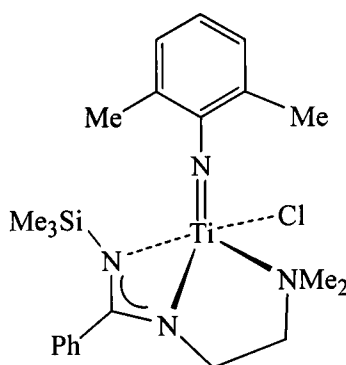
Found (calculated): C 51.7 (51.9), H 7.5 (8.0), N 13.4 (13.4) %

E.I. mass spectrum:

$m/z = 416 [\text{M}]^+$ (5%)

$m/z = 401 [\text{M} - \text{Me}]^+$ (100%)

6.1.2 $[\text{Ti}(\text{N}-2,6\text{-C}_6\text{H}_3\text{Me}_2)\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{NMe}_2\}\text{Cl}]$ (2)



^1H NMR data: (C_6D_6 , 500.0 MHz, 293 K)

7.17	2 H	dd	$^3\text{J} = 7.8$ $^4\text{J} = 1.5$	<i>o</i> - C_6H_5
6.98 – 7.03	5 H	m		<i>m</i> - C_6H_5 , <i>p</i> - C_6H_5 and <i>m</i> - $\text{C}_6\text{H}_3\text{Me}_2$
6.73	1 H	t	$^3\text{J} = 7.3$	<i>p</i> - $\text{C}_6\text{H}_3\text{Me}_2$
3.10	1 H	m		CN_2CH_2
2.86	6 H	s		$\text{C}_6\text{H}_3\text{Me}_2$
2.63	1 H	m		CN_2CH_2
2.43	3 H	s		NMe
2.27	1 H	m		CH_2NMe_2
2.00	3 H	s		NMe
1.63	1 H	m		CH_2NMe_2
0.18	9 H	s		SiMe_3

$^{13}\text{C}\{-^1\text{H}\}$ NMR data: (C_6D_6 , 75.5 MHz, 293 K)

174.43	CN_2
160.30	<i>ipso</i> - $\text{C}_6\text{H}_3\text{Me}_2$
134.67	<i>ipso</i> - C_6H_5
132.59	<i>o</i> - $\text{C}_6\text{H}_3\text{Me}_2$
130.53	<i>m</i> - or <i>p</i> - C_6H_5 or <i>m</i> - $\text{C}_6\text{H}_3\text{Me}_2$
128.65	<i>m</i> - or <i>p</i> - C_6H_5 or <i>m</i> - $\text{C}_6\text{H}_3\text{Me}_2$
127.87	<i>m</i> - or <i>p</i> - C_6H_5 or <i>m</i> - $\text{C}_6\text{H}_3\text{Me}_2$
120.68	<i>p</i> - $\text{C}_6\text{H}_3\text{Me}_2$
62.92	$\underline{\text{CH}_2}\text{NMe}_2$
49.45	NMe
47.78	NMe
45.97	$\text{CN}_2\underline{\text{CH}_2}$
20.17	$\text{C}_6\text{H}_3\underline{\text{Me}_2}$
2.22	SiMe_3

I.R. data: (KBr plates, Nujol mull, cm^{-1})

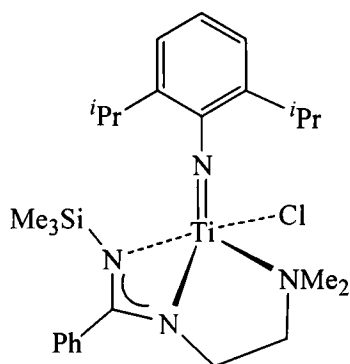
1892 (w, br), 1828 (w), 1770 (w), 1606 (w), 1582 (m), 1504 (w), 1404 (s), 1342 (m), 1312 (s), 1250 (m), 1198 (m), 1172 (w), 1158 (w), 1088 (m), 1076 (m), 1062 (w), 1050 (w), 1024 (w), 984 (w), 966 (w), 946 (m), 930 (w), 864 (s), 842 (s), 808 (w), 792 (w), 778 (w), 758 (m), 738 (m), 722 (w), 628 (w), 616 (w, br), 582 (w), 562 (w), 498 (w), 476 (w), 444 (w), 422 (w).

Elemental analysis for $\text{C}_{22}\text{H}_{33}\text{N}_4\text{ClSiTi}$:

Found (calculated): C 56.6 (56.8), H 7.3 (7.2), N 12.2 (12.1) %

High resolution E.I. mass spectrum for $[\text{Ti}(\text{N-2,6-}\text{C}_6\text{H}_3\text{Me}_2)_2\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{NMe}_2\}\text{Cl}]^+$:

Found (calculated for $\text{C}_{22}\text{H}_{33}\text{N}_4\text{ClSiTi}$): $m/z = 464.1630$ (464.1643)

6.1.3 [Ti(N-2,6-C₆H₃^{*i*}Pr₂){Me₃SiNC(Ph)NCH₂CH₂NMe₂}Cl] (3)¹H NMR data: (C₆D₆, 500.0 MHz, 293 K)

7.19 – 7.22	2 H	m, br		<i>o</i> -C ₆ H ₅
7.09	2 H	app d	app J = 7.3	<i>m</i> -C ₆ H ₃ ^{<i>i</i>} Pr ₂
7.00 – 7.05	3 H	m, br		<i>m</i> -C ₆ H ₅ and <i>p</i> -C ₆ H ₅
6.90	1 H	t	³ J = 7.3	<i>p</i> -C ₆ H ₃ ^{<i>i</i>} Pr ₂
4.71	2 H	sep	³ J = 6.8	CHMe ₂
3.16	1 H	m		CN ₂ CH ₂
2.60	1 H	m		CN ₂ CH ₂
2.49	3 H	s		NMe
2.37	1 H	m		CH ₂ NMe ₂
1.97	3 H	s		NMe
1.61	1 H	m		CH ₂ NMe ₂
1.54	6 H	d	³ J = 6.8	CHMe ₂
1.49	6 H	d	³ J = 6.8	CHMe ₂
0.19	9 H	s		SiMe ₃

¹³C-{¹H} NMR data: (C₆D₆, 75.5 MHz, 293 K)

176.36	CN ₂
157.73	<i>ipso</i> -C ₆ H ₃ ^{<i>i</i>} Pr ₂
143.18	<i>ipso</i> -C ₆ H ₅
134.78	<i>o</i> -C ₆ H ₃ ^{<i>i</i>} Pr ₂
130.55	<i>m</i> - or <i>p</i> -C ₆ H ₅
128.72	<i>m</i> - or <i>p</i> -C ₆ H ₅
127.85	<i>o</i> -C ₆ H ₅

122.25	$m\text{-C}_6\text{H}_3^i\text{Pr}_2$
121.58	$p\text{-C}_6\text{H}_3^i\text{Pr}_2$
62.92	$\underline{\text{C}}\text{H}_2\text{NMe}_2$
49.32	NMe
47.68	NMe
45.99	$\text{CN}_2\underline{\text{C}}\text{H}_2$
28.62	$\underline{\text{C}}\text{HMe}_2$
25.01	$\text{CH}\underline{\text{Me}}_2$
24.54	$\text{CH}\underline{\text{Me}}_2$
2.24	SiMe_3

I.R. data: (KBr plates, Nujol mull, cm^{-1})

1916 (w), 1582 (w), 1504 (m), 1328 (s), 1378 (s), 1290 (s), 1250 (s), 1200 (s),
1174 (w), 1158 (w), 1140 (w), 1088 (m), 1048 (m), 1022 (m), 982 (m), 948 (s, br),
848 (s), 790 (s), 758 (s), 704 (m), 692 (m), 632 (w), 562 (m), 408 (s, br)

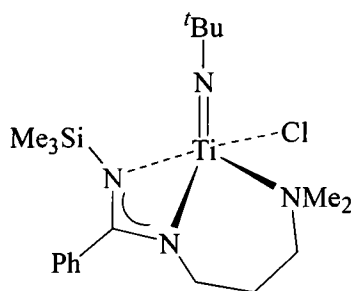
Elemental analysis for $\text{C}_{26}\text{H}_{41}\text{N}_4\text{ClSiTi}$:

Found (calculated): C 59.6 (59.9), H 7.7 (7.9), N 11.0 (10.8) %

High resolution E.I. mass spectrum for $[\text{Ti}(\text{N-2,6-}\text{C}_6\text{H}_3^i\text{Pr}_2)\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{NMe}_2\}\text{Cl}]^+$:

Found (calculated for $\text{C}_{26}\text{H}_{41}\text{N}_4\text{ClSiTi}$): $m/z = 520.2105$ (520.2083)

6.1.4 $[\text{Ti}(\text{N}^t\text{Bu})\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}\text{Cl}]$ (4)



^1H NMR data: (C_6D_6 , 500.0 MHz, 293 K)

7.38 - 7.02	5 H	m	C_6H_5
3.10	2 H	m	CN_2CH_2
2.83	3 H	s	NMe
2.04	1 H	m	$\underline{\text{C}}\text{H}_2\text{NMe}_{2(\text{ax})}$
1.87	3 H	s	NMe

1.82	1 H	m	$\text{CH}_2\text{NMe}_{2(\text{eq})}$
1.38	1 H	m	$\text{CH}_2\text{CH}_2\text{CH}_{2(\text{ax})}$
1.23	9 H	s	CMe_3
0.95	1 H	m	$\text{CH}_2\text{CH}_2\text{CH}_{2(\text{eq})}$
0.28	9 H	s	SiMe_3

$^{13}\text{C}\{-^1\text{H}\}$ NMR data: (C_6D_6 , 75.5 MHz, 293 K)

174.60	CN_2
136.04	<i>ipso</i> - C_6H_5
129.00	C_6H_5
128.60	C_6H_5
128.19	C_6H_5
127.80	C_6H_5
126.63	C_6H_5
70.77	CMe_3
62.95	CH_2NMe_2
53.25	NMe
47.49	CN_2CH_2
43.94	NMe
32.65	CMe_3
25.84	$\text{CH}_2\text{CH}_2\text{CH}_2$
2.42	SiMe_3

I.R. data (KBr plates, Nujol mull, cm^{-1}):

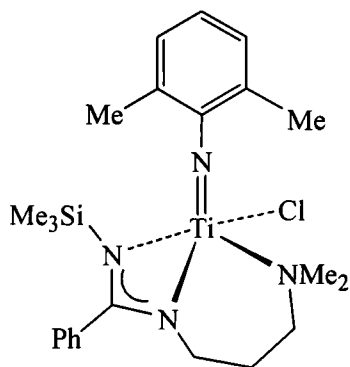
2724 (w), 1593 (w, br), 1466 (s, br), 1347 (m), 1302 (m), 1262 (w), 1244 (m), 1205 (s), 1154 (m), 1131 (w), 1109 (w), 1062 (w), 1016 (m), 978 (W), 946 (m), 923 (w), 897 (m), 857 (w), 841 (m), 818 (m), 786 (m), 764 (w), 721 (w), 707 (w), 629 (w), 597 (w), 547 (m), 510 (w), 455 (w), 435 (w).

Elemental analysis for $\text{C}_{19}\text{H}_{35}\text{N}_4\text{ClSiTi}$:

Found (calculated): C 53.0 (53.0), H 7.8 (8.2), N 12.8 (13.0) %

E.I. mass spectrum:

$m/z = 430 [\text{M}]^+$	(5 %)
$m/z = 415 [\text{M-Me}]^+$	(65 %)

6.1.5 [Ti(N-2,6-C₆H₃Me₂){Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂}Cl] (5)¹H NMR data: (C₆D₆, 500.0 MHz, 293 K)

7.26 – 7.20	2 H	d, br	³ J = 4.9	<i>o</i> -C ₆ H ₅
7.10 – 7.02	3 H	m, br		<i>m</i> -C ₆ H ₅ and <i>p</i> -C ₆ H ₅
6.99	2 H	app d	app J = 7.3	<i>m</i> -C ₆ H ₃ Me ₂
6.71	1 H	t	³ J = 7.8	<i>p</i> -C ₆ H ₃ Me ₂
3.02	1 H	m		CN ₂ CH _{2(ax)}
2.95	1 H	m		CN ₂ CH _{2(eq)}
2.87	1 H	app t	app J = 12.7	Me ₂ NCH _{2(ax)}
2.82	6 H	s		C ₆ H ₃ Me ₂
2.59	3 H	s		NMe _(eq)
1.90	3 H	s		NMe _(ax)
1.62	1 H	dd	² J = 12.7 ³ J = 5.4	Me ₂ NCH _{2(eq)}
1.21	1 H	m		CH ₂ CH ₂ CH _{2(ax)}
0.87	1 H	br d	³ J = 15.6	CH ₂ CH ₂ CH _{2(eq)}
0.12	9 H	s		SiMe ₃

¹³C-{¹H} NMR data: (C₆D₆, 75.5 MHz, 293 K)

174.95	CN ₂
160.30	<i>ipso</i> -C ₆ H ₃ Me ₂
134.97	<i>ipso</i> -C ₆ H ₅
132.58	<i>o</i> -C ₆ H ₃ Me ₂
129.24	<i>m</i> - or <i>p</i> -C ₆ H ₅
128.47	<i>m</i> - or <i>p</i> -C ₆ H ₅
127.70	<i>m</i> -C ₆ H ₃ Me ₂

127.28	<i>o</i> -C ₆ H ₅
120.65	<i>p</i> -C ₆ H ₃ Me ₂
62.18	<u>CH</u> ₂ NMe ₂
52.70	NMe _{eq}
45.90	CN ₂ <u>CH</u> ₂
45.87	NMe _{ax}
25.50	CH ₂ <u>CH</u> ₂ CH ₂
20.16	C ₆ H ₃ <u>Me</u> ₂
2.20	SiMe ₃

I.R. data: (KBr plates, Nujol mull, cm⁻¹)

2360 (w), 2338 (w), 1946 (w), 1894 (w), 1876 (w), 1830 (w), 1650 (w), 1604 (w), 1582 (w), 1506 (m), 1444 (s, br), 1412 (s, br), 1342 (s), 1316 (s), 1244 (s), 1204 (m), 1228 (m), 1176 (w), 1154 (w), 1128 (w), 1104 (m), 1058 (m), 1026 (w), 1008 (m), 978 (m), 946 (w), 916 (w), 892 (s), 838 (s), 818 (s), 780 (m), 734 (m), 698 (m), 628 (w), 554 (w), 514 (m), 494 (w), 436 (w), 412 (m)

Elemental analysis for C₂₃H₃₅N₄ClSiTi:

Found (calculated): C 57.6 (57.7), H 7.4 (7.4), N 11.5 (11.7) %

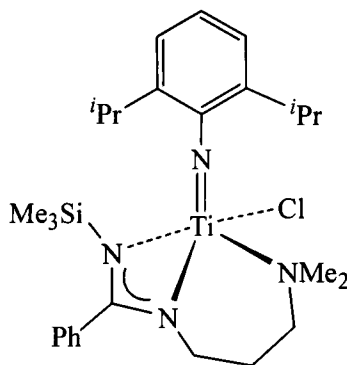
E.I. mass spectrum:

m/z = 478 [M]⁺ (50%)

m/z = 443 [M-Cl]⁺ (10%)

High resolution E.I. mass spectrum for [Ti(N-2,6-C₆H₃Me₂){Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂}Cl]⁺:

Found (calculated for C₂₃H₃₅N₄ClSiTi): *m/z* = 478.1816 (478.1799)

6.1.6 [Ti(N-2,6-C₆H^{*i*}Pr₂){Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂}Cl] (6)**¹H NMR data:** (C₆D₆, 500.0 MHz, 293 K)

7.20 - 7.32	2 H	m, br		<i>o</i> -C ₆ H ₅
7.10 - 7.03	3 H	m, br		<i>m</i> -C ₆ H ₅ and <i>p</i> -C ₆ H ₅
7.05	2 H	app d	app J = 7.8	<i>m</i> -C ₆ H ₃ ^{<i>i</i>} Pr ₂
6.88	1 H	t	³ J = 7.8	<i>p</i> -C ₆ H ₃ ^{<i>i</i>} Pr ₂
4.80	2 H	sept	³ J = 6.8	CHMe ₂
2.99 - 3.18	3 H	m		CN ₂ CH _{2ax} , CN ₂ CH _{2eq} and CH ₂ NMe _{2ax}
2.65	3 H	s		NMe _{eq}
1.90	3 H	s		NMe _{ax}
1.67	1 H	dd	² J = 4.9 ³ J = 12.7	CH ₂ NMe _{2eq}
1.48	12 H	app t	³ J = 6.8	CHMe ₂
1.19	1 H	m		CH ₂ CH ₂ CH _{2ax}
0.88	1 H	m		CH ₂ CH ₂ CH _{2eq}
0.15	9 H	s		SiMe ₃

¹³C-{¹H} NMR data: (C₆D₆, 125.7 MHz, 293 K)

175.17	CN ₂
157.57	<i>ipso</i> -C ₆ H ₃ ^{<i>i</i>} Pr ₂
143.48	<i>ipso</i> -C ₆ H ₅
135.05	<i>o</i> -C ₆ H ₃ ^{<i>i</i>} Pr ₂
129.47	<i>m</i> - or <i>p</i> -C ₆ H ₅ or <i>m</i> -C ₆ H ₃ ^{<i>i</i>} Pr ₂
128.18	<i>m</i> - or <i>p</i> -C ₆ H ₅ or <i>m</i> -C ₆ H ₃ ^{<i>i</i>} Pr ₂
127.85	<i>o</i> -C ₆ H ₅

122.34	<i>m</i> - or <i>p</i> -C ₆ H ₅ or <i>m</i> -C ₆ H ₃ ^{<i>i</i>} Pr ₂
121.87	<i>p</i> -C ₆ H ₃ ^{<i>i</i>} Pr ₂
62.17	<u>CH</u> ₂ NMe ₂
52.86	NMe _{eq}
46.24	NMe _{ax}
45.86	CN ₂ <u>CH</u> ₂
28.12	<u>CH</u> Me ₂
25.70	CH ₂ <u>CH</u> ₂ CH ₂
25.03	CH <u>Me</u> ₂
25.00	CH <u>Me</u> ₂
2.44	SiMe ₃

I.R. data: (KBr plates, Nujol mull, cm⁻¹)

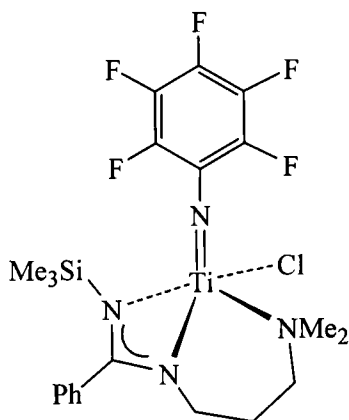
2722 (w), 2678 (w), 2624 (w), 1958 (w), 1894 (w), 1842 (w), 1606 (w), 1576 (w), 1514 (s), 1426 (s, br), 1336 (s), 1288 (s), 1244 (s), 1212 (s), 1174 (w), 1156 (s), 1110 (m), 1058 (m), 1012 (w), 980 (s), 942 (w), 918 (w), 898 (s), 842 (s), 818 (m), 786 (s), 750 (s), 720 (m), 702 (m), 672 (w), 632 (w), 594 (w), 632 (w), 516 (m), 496 (w), 446 (w).

Elemental analysis for C₂₇H₄₃N₄ClSiTi:

Found (calculated): C 60.1 (60.6); H 8.3 (8.1); N 10.4 (10.5) %

High resolution E.I. mass spectrum for [Ti(N-2,6-C₆H^{*i*}Pr₂) {Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂}Cl]⁺:

Found (calculated for C₂₇H₄₃N₄ClSiTi): 534.2433 (534.2425)

6.1.7 [Ti(NC₆F₅){Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂}Cl] (7)**¹H NMR data:** (C₆D₆, 500.0 MHz, 293 K)

7.01 – 7.06	5 H	m, br		C ₆ H ₅
2.99	1 H	app t	app ³ J=12.7	<u>CH</u> ₂ NMe ₂
2.91	2 H	app d, br	app ³ J=5.9	CN ₂ CH ₂
2.65	3 H	s		NMe
1.88	3 H	s		NMe
1.71	1 H	app d, br	app ³ J=11.7	<u>CH</u> ₂ NMe ₂
1.24	1 H	m		CH ₂ <u>CH</u> ₂ CH ₂
0.85	1 H	app d, br	app ³ J=15.6	CH ₂ CH ₂ <u>CH</u> ₂
0.16	9 H	s		SiMe ₃

¹³C-{¹H} NMR data: (C₆D₆, 75.5 MHz, 293 K)

177.19	CN ₂
152.43	C ₆ F ₅ or <i>ipso</i> -C ₆ H ₅
145.87	C ₆ F ₅ or <i>ipso</i> -C ₆ H ₅
142.72	C ₆ F ₅ or <i>ipso</i> -C ₆ H ₅
139.61	C ₆ F ₅ or <i>ipso</i> -C ₆ H ₅
137.35	C ₆ F ₅ or <i>ipso</i> -C ₆ H ₅
134.95	C ₆ F ₅ or <i>ipso</i> -C ₆ H ₅
133.78	C ₆ F ₅ or <i>ipso</i> -C ₆ H ₅
129.57	<i>p</i> -C ₆ H ₅
128.79	<i>o</i> - or <i>m</i> -C ₆ H ₅ , (2 overlapping)
126.50	<i>o</i> - or <i>m</i> -C ₆ H ₅ , (2 overlapping)
62.92	<u>CH</u> ₂ NMe ₂

53.17	NMe
47.78	CN ₂ CH ₂
45.72	NMe
26.28	CH ₂ CH ₂ CH ₂
2.24	SiMe ₃

¹⁹F NMR data: (C₆D₆, 282.2 MHz, 293 K)

-154.90	2 F	<i>o</i> -C ₆ F ₅
-167.09	2 F	<i>m</i> -C ₆ F ₅
-171.03	1 F	<i>p</i> -C ₆ F ₅

I.R. data: (KBr disc cm⁻¹)

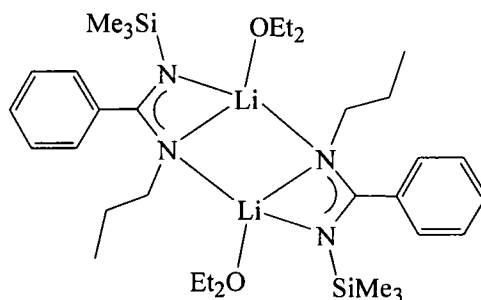
2956 (s), 2924 (s), 2362 (w), 2344 (w), 1670 (w), 1618 (m, br), 1580 (w), 1522 (s), 1504 (s), 1446 (m), 1404 (m), 1392 (m), 1344 (w), 1326 (w), 1304 (w), 1246 (m, br), 1198 (w), 1178 (w), 1158 (w), 1098 (w), 1042 (m), 1010 (s), 982 (s), 946 (m), 888 (m), 840 (s), 785 (m), 746 (m), 700 (s), 660 (m), 632 (w).

High resolution E.I. mass spectrum for

[Ti(NC₆F₅){Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂}Cl]⁺:

Found (calculated) for C₂₁H₂₆N₄ClF₅SiTi: 540.0989 (540.1015)

6.1.8 [Li₂{Me₃SiNC(Ph)NCH₂CH₂CH₃}₂(Et₂O)₂] (8)



¹H NMR data: (C₆D₆, 500.0 MHz, 293 K)

7.29	2 H	d, br		<i>o</i> -C ₆ H ₅
7.22	2 H	app t	app J = 7.8	<i>m</i> -C ₆ H ₅
7.08	1 H	t	³ J = 7.8	<i>p</i> -C ₆ H ₅
3.29	4 H	q	³ J = 7.3	OCH ₂ CH ₃
3.18	2 H	m, br		CN ₂ CH ₂
1.70	2 H	m, br		CH ₃ CH ₂

1.13	6 H	t	$^3J = 7.3$	OCH ₂ <u>C</u> H ₃
0.84	3 H	s, br		CH ₃
0.11	9 H	s, br		SiMe ₃

$^{13}\text{C}\{-^1\text{H}\}$ NMR data: (C₆D₆, 75.5 MHz, 293 K)

128.10	<i>m</i> -C ₆ H ₅
127.68	<i>p</i> -C ₆ H ₅
126.92	<i>o</i> -C ₆ H ₅
66.26	O <u>C</u> H ₂ CH ₃
52.92	NCH ₂
27.74	<u>C</u> H ₂ CH ₃
16.20	OCH ₂ <u>C</u> H ₃
12.98	<u>C</u> H ₂ CH ₃
4.14	SiMe ₃

I.R. data: (KBr plates, Nujol mull, cm⁻¹)

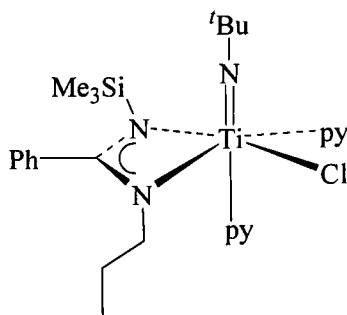
3584 (w), 3328 (w), 3058 (m), 3020 (m), 2730 (w), 2690 (w), 2632 (w), 2318 (w), 1946 (w), 1888 (w), 1808 (w), 1774 (w), 1622 (m), 1600 (m), 1578 (w), 1402 (s), 1138 (s), 1292 (m), 1246 (s), 1172 (m), 1148 (w), 1126 (w), 1102 (w), 1054 (s), 1018 (s), 928 (m), 876 (s), 830 (s), 782 (m), 754 (s), 678 (w), 630 (m), 410 (s).

Elemental analysis for C₁₃H₂₁N₂LiSi (Et₂O free):

Found (calculated): C 64.2 (65.0), H 8.7 (8.8), N 11.8 (11.6) %

E.I. mass spectrum:

A satisfactory mass spectrum could not be obtained for this compound.

6.1.9 [Ti(N^{*t*}Bu){Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂}Cl(py)₂] (9)¹H NMR data: (C₆D₆, 500.0 MHz, 293 K)

9.55	2 H	d, br	³ J = 4.9	<i>cis</i> - <i>o</i> -C ₅ H ₅ N
8.67	2 H	s, br		<i>trans</i> - <i>o</i> -C ₅ H ₅ N
7.09	2 H	m		<i>m</i> -C ₆ H ₅
7.02	3 H	m		<i>o</i> -C ₆ H ₅
				<i>p</i> -C ₆ H ₅
6.93	1 H	s, br		<i>trans</i> - <i>p</i> -C ₅ H ₅ N
6.78	1 H	t, br	³ J = 7.8	<i>cis</i> - <i>p</i> -C ₅ H ₅ N
6.63	2 H	s, br		<i>trans</i> - <i>m</i> -C ₅ H ₅ N
6.53	2 H	app t, br	app J = 6.8	<i>cis</i> - <i>m</i> -C ₅ H ₅ N
3.94	2 H	m		CN ₂ CH ₂
2.14	2 H	m		CH ₂ CH ₃
1.42	9 H	s		CMe ₃
0.98	3 H	t	³ J = 7.3	CH ₂ CH ₃
0.14	9 H	s		SiMe ₃

¹³C-{¹H} NMR data: (C₆D₆, 75.5 MHz, 293 K)

165.24	CN ₂
152.22	<i>cis</i> - <i>o</i> -C ₅ H ₅ N
137.92	<i>cis</i> - <i>p</i> -C ₅ H ₅ N
135.93	<i>ipso</i> -C ₆ H ₅
129.34	<i>o</i> -C ₆ H ₅ or <i>p</i> -C ₆ H ₅
128.55	<i>o</i> -C ₆ H ₅ or <i>p</i> -C ₆ H ₅
126.62	<i>m</i> -C ₆ H ₅
123.62	<i>cis</i> - <i>m</i> -C ₅ H ₅ N
67.46	CMe ₃

53.90	CN $\underline{2}$ CH $\underline{2}$
31.30	C <u>Me</u> $\underline{3}$
26.62	<u>CH</u> $\underline{2}$ CH $\underline{3}$
11.91	CH $\underline{2}$ C <u>H</u> $\underline{3}$
2.93	SiMe $\underline{3}$

**trans*-py not observed

I.R. data: (KBr plates, Nujol mull, cm $^{-1}$)

2610 (w), 1604 (w), 1510 (w), 1444 (s), 1400 (s), 1356 (m), 1296 (w), 1244 (m), 1194 (m), 1178 (w), 1158 (w), 1070 (m), 1042 (w), 1020 (m), 1002 (w), 918 (w), 902 (m), 868 (s), 842 (s), 780 (w), 764 (m), 702 (m), 636 (s), 412 (s).

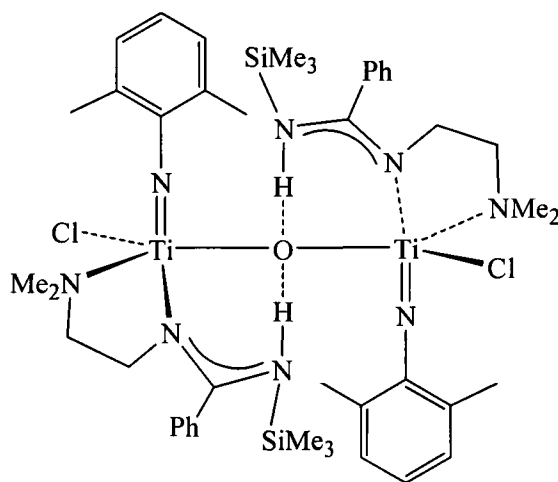
Elemental analysis for C $_{27}$ H $_{40}$ N $_5$ ClSiTi:

Satisfactory analysis could not be obtained for this compound

E.I. mass spectrum:

A satisfactory mass spectrum could not be obtained for this compound

6.1.10 [Ti(N-2,6-C $_6$ H $_3$ Me $_2$)Cl(μ -O){Me $_3$ SiN(H)C(Ph)NCH $_2$ CH $_2$ NMe $_2$ }] $_2$ (10)

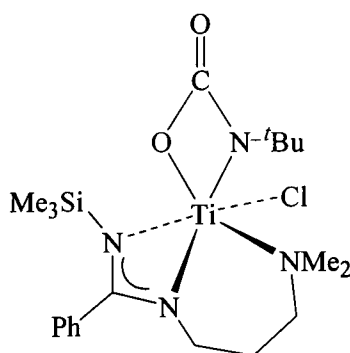


^{1} H NMR data: (C $_6$ D $_6$, 500.0 MHz, 293 K)

10.61	2 H	s		NH
7.48 – 7.57	6 H	m		<i>m</i> -C $_6$ H $_5$
				<i>p</i> -C $_6$ H $_5$
7.40	2 H	d	$^3J = 7.3$	<i>o</i> -C $_6$ H $_5$
7.27	2 H	d	$^3J = 7.3$	<i>o</i> -C $_6$ H $_5$
6.69	4 H	d		<i>m</i> -C $_6$ H $_3$ Me $_2$

6.33	2 H	t	<i>p</i> -C ₆ H ₃ Me ₂
3.51	2 H	m	CH of pendant arm
3.41	2 H	m	CH of pendant arm
3.20	2 H	m	CH of pendant arm
2.88	6 H	s	C ₆ H ₃ Me ₂
2.61	6 H	s	C ₆ H ₃ Me ₂
2.33 – 2.54	14 H	s, br and m, overlapping	NMe ₂ and CH of pendant arm
0.04	18 H	s	SiMe ₃

6.1.11 [Ti{N^{*t*}BuC(O)O}{Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂}Cl] (11)



Compound only prepared on the NMR tube scale

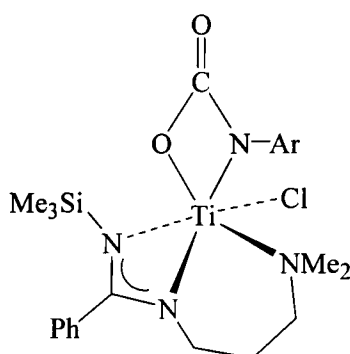
¹H NMR data: (CD₂Cl₂, 500.0 MHz, 195 K)

7.20 - 7.04	5 H	m	C ₆ H ₅
3.96	1 H	m	CN ₂ CH ₂
3.80	1 H	m	CN ₂ CH ₂
3.68	1 H	m	CH ₂ NMe ₂
3.23	3 H	s	NMe
2.80	1 H	m	CH ₂ NMe ₂
2.12	3 H	s	NMe
1.92	1 H	m	CH ₂ CH ₂ CH ₂
1.80	1 H	m	CH ₂ CH ₂ CH ₂
0.90	9 H	s	CMe ₃
0.26	9 H	s	SiMe ₃

^{13}C - $\{^1\text{H}\}$ NMR data: (C_6D_6 , 125.5 MHz, 195 K)

174.70	$\text{C}(\text{O})\text{O}$
160.93	CN_2
138.12	<i>ipso</i> - C_6H_5
128.67	C_6H_5 (2 overlapping)
124.11	C_6H_5 (2 overlapping)
123.52	C_6H_5
72.63	$\underline{\text{C}}\text{Me}_3$
64.24	$\underline{\text{CH}}_2\text{NMe}_2$
54.87	$\text{CN}_2\underline{\text{C}}\text{H}_2$
53.80	NMe (obscured by solvent)
43.65	NMe
30.66	$\underline{\text{C}}\text{Me}_3$
26.55	$\text{CH}_2\underline{\text{C}}\text{H}_2\text{CH}_2$
-0.72	SiMe_3

6.1.12 $[\text{Ti}\{\text{OC}(\text{O})\text{N}-2,6-\text{C}_6\text{H}_3\text{Me}_2\}\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}\text{Cl}]$ (12)



Compound only prepared on the NMR tube scale

^1H NMR data: (CD_2Cl_2 , 500.0 MHz, 195 K)

7.44	3 H	m		<i>o</i> - and <i>m</i> - C_6H_5
7.21	1 H	s, br		<i>p</i> - C_6H_5
6.72	2 H	d	$^3J = 7.4$	<i>m</i> - $\text{C}_6\text{H}_3\text{Me}_2$
6.51	1 H	t	$^3J = 7.4$	<i>p</i> - $\text{C}_6\text{H}_3\text{Me}_2$
4.00	1 H	m		CN_2CH_2
3.81	2 H	m		CN_2CH_2 and $\underline{\text{CH}}_2\text{NMe}_2$
2.81	1 H	m		$\underline{\text{CH}}_2\text{NMe}_2$

1.91	1 H	m	CH ₂ <u>CH</u> ₂ CH ₂
1.82	1 H	m	CH ₂ CH <u>2</u> CH ₂
3.32	3 H	s	NMe
2.33	6 H	s	C ₆ H ₃ <u>Me</u> ₂
2.26	3 H	s	NMe
0.28	9 H	s	SiMe ₃

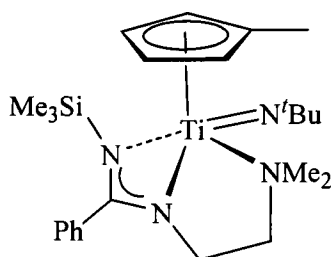
¹³C-{¹H} NMR data: (CD₂Cl₂, 125.7 MHz, 195 K)

174.67	C(O)O
160.57	CN ₂
159.42	<i>ipso</i> -C ₆ H ₃ Me ₂
137.92	<i>ipso</i> -C ₆ H ₅
131.42	<i>o</i> -C ₆ H ₃ Me ₂
128.62	<i>o</i> - and <i>m</i> -C ₆ H ₅ (2 overlapping)
126.48	<i>m</i> -C ₆ H ₃ Me ₂
125.22	<i>p</i> -C ₆ H ₅
121.12	<i>p</i> -C ₆ H ₃ Me ₂
64.14	<u>CH</u> ₂ NMe ₂
45.11	C ₆ H ₃ <u>Me</u> ₂
43.43	NMe
26.19	CH ₂ CH <u>2</u> CH ₂
0.71	SiMe ₃

*CN₂CH₂ and NMe obscured by solvent

6.2 Characterising data for Chapter 3

6.2.1 $[\text{Ti}(\eta\text{-C}_5\text{H}_4\text{Me})(\text{N}^t\text{Bu})\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{NMe}_2\}]\text{ (13)}$



^1H NMR data: (C_6D_6 , 300.1 MHz, 293 K)

7.00 - 7.12	5 H	m	C_6H_5
6.66	1 H	m	3- or 4- $\text{C}_5\text{H}_4\text{Me}$
6.21	1 H	m	4- or 3- $\text{C}_5\text{H}_4\text{Me}$
5.91	1 H	m	2- or 5- $\text{C}_5\text{H}_4\text{Me}$
5.52	1 H	m	5- or 2- $\text{C}_5\text{H}_4\text{Me}$
2.94	1 H	m	CN_2CH_2
2.89	1 H	m	CN_2CH_2
2.34	1 H	m	CH_2NMe_2
2.17	3 H	s	$\text{C}_5\text{H}_4\text{Me}$
2.07	6 H	s	NMe_2
1.80	1 H	m	CH_2NMe_2
1.22	9 H	s	CMe_3
0.15	9 H	s	SiMe_3

$^{13}\text{C}\{-^1\text{H}\}$ NMR data: (C_6D_6 , 75.5 MHz, 293 K)

172.91	CN_2
138.46	<i>ipso</i> - C_6H_5
128.34	C_6H_5
128.19	C_6H_5
127.99	C_6H_5
127.80	C_6H_5
127.28	C_6H_5
120.28	1- $\text{C}_5\text{H}_4\text{Me}$
112.27	2- or 5- $\text{C}_5\text{H}_4\text{Me}$
110.49	5- or 2- $\text{C}_5\text{H}_4\text{Me}$

105.30	3- or 4- <u>C</u> ₅ H ₄ Me
105.01	4- or 3- <u>C</u> ₅ H ₄ Me
67.01	<u>C</u> Me ₃
63.65	<u>CH</u> ₂ NMe ₂
49.68	NMe ₂
44.84	CN ₂ <u>CH</u> ₂
33.46	C <u>Me</u> ₃
15.17	C ₅ H ₄ <u>Me</u>
3.53	SiMe ₃

¹H NMR data: (CD₂Cl₂, 500.0 MHz, 193 K)

7.38	3 H	m	<i>o</i> - and <i>p</i> -C ₆ H ₅
7.28	2 H	m	<i>m</i> -C ₆ H ₅
6.34	1 H	s	3- or 4-C ₅ <u>H</u> ₄ Me
5.95	1 H	s	4- or 3-C ₅ <u>H</u> ₄ Me
5.68	1 H	s	2- or 5-C ₅ <u>H</u> ₄ Me
5.52	1 H	s	5- or 2-C ₅ <u>H</u> ₄ Me
3.16	1 H	m	CN ₂ CH ₂
3.09	1 H	m	CN ₂ CH ₂
2.63	3 H	s	NMe
2.35	3 H	s	NMe
2.21	2 H	m	<u>CH</u> ₂ NMe ₂
2.05	3 H	s	C ₅ H ₄ Me
0.99	9 H	s	CMe ₃
-0.19	9 H	s	SiMe ₃

¹³C-{¹H} NMR data: (CD₂Cl₂, 125.7 MHz, 193 K)

173.03	CN ₂
137.24	<i>ipso</i> -C ₆ H ₅
128.14	<i>p</i> -C ₆ H ₅
129.91	<i>m</i> -C ₆ H ₅
126.91	<i>o</i> -C ₆ H ₅
120.03	1- <u>C</u> ₅ H ₄ Me
110.68	2- or 5- <u>C</u> ₅ H ₄ Me

107.26	5- or 2- <u>C</u> ₅ H ₄ Me
104.15	3- and 4- <u>C</u> ₅ H ₄ Me, overlapping
66.67	<u>C</u> Me ₃
63.53	<u>CH</u> ₂ NMe ₂
51.48	NMe
48.25	NMe
44.45	CN ₂ <u>C</u> H ₂
32.50	<u>C</u> Me ₃
14.74	C ₅ H ₄ <u>M</u> e
2.64	SiMe ₃

I.R. data: (KBr plates, thin film, cm⁻¹)

3461 (m), 3060 (m), 2959 (s, br), 2785 (s, br), 2727 (s, br), 2648 (m), 2361(w), 2342 (w), 1952 (w), 1883 (w), 1812 (w), 1621 (w), 1602 (m), 1579 (s, br), 1402 (m), 1489 (s), 1362 (m), 1348 (m), 1331 (s), 1235 (s), 1205 (s), 1174 (w), 1159 (w), 1094 (m), 1052 (m), 1027 (s), 953 (m), 934 (w), 919 (m), 872 (s), 834 (s), 779 (s), 702 (m), 678 (m), 628 (m), 589 (w), 569 (m), 532 (w), 505 (w), 466 (w), 445 (w), 420 (w).

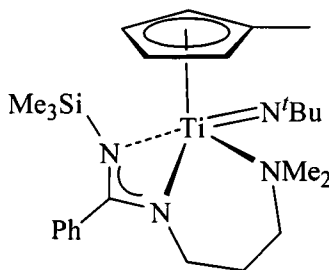
Elemental analysis for C₂₄H₄₀N₄SiTi:

Found (calculated): C 62.2 (62.6), H 8.7 (8.7), N 12.0 (12.2) %.

E.I. mass spectrum:

A satisfactory mass spectrum could not be obtained for this compound.

6.2.2 [Ti(C₅H₄Me)(N^tBu){Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂}] (14)



¹H NMR data: (C₆D₆, 500.0 MHz, 293 K)

7.13 - 7.00	5 H	m	C ₆ H ₅
6.81	1 H	m	3- or 4- <u>C</u> ₅ H ₄ Me
6.57	1 H	m	4- or 3- <u>C</u> ₅ H ₄ Me

5.87	1 H	m	2- or 5-C ₅ <u>H</u> ₄ Me
5.72	1 H	m	5- or 2-C ₅ <u>H</u> ₄ Me
3.20	1 H	m	CN ₂ CH ₂
2.81	1 H	m	CN ₂ CH ₂
2.29	1 H	m	CH ₂ NMe ₂
2.17	6 H	s	NMe ₂
2.04	3 H	s	C ₅ H ₄ <u>Me</u>
1.95	1 H	m	CH ₂ NMe ₂
1.60	1 H	m	CH ₂ CH ₂ CH ₂
1.28	9 H	s	CMe ₃
1.23	1 H	m	CH ₂ CH ₂ CH ₂
0.08	9 H	s	SiMe ₃

¹³C-{¹H} NMR data: (C₆D₆, 125.7 MHz, 293 K)

169.39	CN ₂
137.12	<i>ipso</i> -C ₆ H ₅
128.35	C ₆ H ₅
128.30	C ₆ H ₅
127.47	C ₆ H ₅ *
121.20	1-C ₅ <u>H</u> ₄ Me
113.27	2- or 5-C ₅ <u>H</u> ₄ Me
111.40	5- or 2-C ₅ <u>H</u> ₄ Me
106.53	3- or 4-C ₅ <u>H</u> ₄ Me
106.42	4- or 3-C ₅ <u>H</u> ₄ Me
67.38	<u>C</u> Me ₃
60.02	<u>CH</u> ₂ NMe ₂
48.96	NMe ₂
46.27	CN ₂ <u>CH</u> ₂
33.31	<u>C</u> Me ₃
28.26	CH ₂ <u>CH</u> ₂ CH ₂
14.84	C ₅ H ₄ <u>Me</u>
2.95	SiMe ₃

*other resonances obscured by solvent

^1H NMR data (CD_2Cl_2 , 500.0 MHz, 193 K):

7.38	1 H	m	<i>p</i> -C ₆ H ₅
7.31	2 H	m	<i>m</i> -C ₆ H ₅
7.21 - 7.06	2 H	m	<i>o</i> -C ₆ H ₅
6.32	1 H	m	3- or 4- C ₅ <u>H</u> ₄ Me
6.13	1 H	m	4- or 3- C ₅ <u>H</u> ₄ Me
5.48	1 H	m	2- or 5- C ₅ <u>H</u> ₄ Me
5.44	1 H	m	5- or 2-C ₅ <u>H</u> ₄ Me
2.74	1 H	m	CN ₂ CH ₂
2.74	1 H	m	<u>CH</u> ₂ NMe ₂
2.57	1 H	m	CN ₂ CH ₂
2.57	3 H	s	NMe
2.43	3 H	s	NMe
2.07	1 H	m	<u>CH</u> ₂ NMe ₂
1.89	3 H	s	C ₅ H ₄ <u>Me</u>
1.83	1 H	m	CH ₂ <u>CH</u> ₂ CH ₂
1.23	1 H	m	CH ₂ <u>CH</u> ₂ CH ₂
0.99	9H	s	CMe ₃
-0.31	9 H	s	SiMe ₃

 ^{13}C - $\{^1\text{H}\}$ NMR data (CD_2Cl_2 , 125.7 MHz, 193 K):

171.42	CN ₂
136.87	<i>ipso</i> -C ₆ H ₅
127.62	<i>p</i> -C ₆ H ₅
127.05	<i>m</i> -C ₆ H ₅
126.51	<i>o</i> -C ₆ H ₅
125.52	<i>o</i> -C ₆ H ₅
117.42	1- <u>C</u> ₅ H ₄ Me
113.16	2- or 5- <u>C</u> ₅ H ₄ Me
110.37	5- or 2- <u>C</u> ₅ H ₄ Me
102.34	3- or 4- <u>C</u> ₅ H ₄ Me
101.06	4- or 3- <u>C</u> ₅ H ₄ Me
66.84	<u>C</u> Me ₃

61.39	$\underline{\text{C}}\text{H}_2\text{NMe}_2$
53.57	NMe
53.36	NMe
44.00	$\text{CN}_2\underline{\text{C}}\text{H}_2$
32.29	$\text{C}\underline{\text{M}}\text{e}_3$
24.44	$\text{CH}_2\underline{\text{C}}\text{H}_2\text{CH}_2$
13.67	$\text{C}_5\text{H}_4\underline{\text{M}}\text{e}$
1.85	SiMe_3

I.R. data: (KBr plates, thin film, cm^{-1})

3050 (m), 2856 (s), 2824 (s, br), 2766 (s), 1422 (s, br), 1348 (s), 1298 (s), 1226 (s), 1200 (s), 1112 (m), 1098 (m), 1072 (m), 1018 (m), 980 (m), 944 (m), 898 (m, br), 836 (m, br), 782 (m), 758 (w), 700 (w), 678 (w), 626 (w), 548 (w), 530 (w), 508 (w).

Elemental analysis for $\text{C}_{25}\text{H}_{42}\text{N}_4\text{SiTi}$:

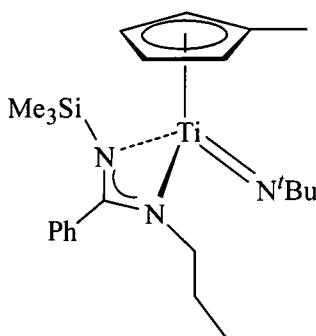
Found (calculated): C 62.7 (63.2), H 8.8 (8.9), N 11.4 (11.8) %.

E.I. mass spectrum:

$m/z = 279$ $[\text{Me}_3\text{SiNC(Ph)NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2]^+$ (13%)

$m/z = 58$ $[\text{CHMe}_3]^+$ (100%)

6.2.3 $[\text{Ti}(\eta\text{-C}_5\text{H}_4\text{Me})(\text{N}^t\text{Bu})\{\text{Me}_3\text{SiNC(Ph)NCH}_2\text{CH}_2\text{Me}\}]$ (15)



^1H NMR data: (C_6D_6 , 500.0 MHz, 293 K)

7.16	2 H	m	<i>o</i> - C_6H_5
7.05 – 7.10	3 H	m	<i>m</i> - and <i>p</i> - C_6H_5
6.83	2 H	m	3- and 4- $\text{C}_5\text{H}_4\text{Me}$
5.83	2 H	m	2- and 5- $\text{C}_5\text{H}_4\text{Me}$
3.12	1 H	m	CN_2CH_2

2.81	1 H	m	CN ₂ CH ₂
1.98	3 H	s	C ₅ H ₄ <u>Me</u>
1.33	2 H	m	<u>CH</u> ₂ CH ₃
1.19	9 H	s	CMe ₃
0.80	3 H	s	CH ₂ <u>CH</u> ₃
-0.05	9 H	s	SiMe ₃

¹³C-{¹H} NMR data: (C₆D₆, 125.5 MHz, 293 K)

165.24	CN ₂
135.94	<i>ipso</i> -C ₆ H ₅
128.68	<i>m</i> - or <i>p</i> -C ₆ H ₅
128.49	<i>m</i> - or <i>p</i> -C ₆ H ₅
127.78	<i>o</i> -C ₆ H ₅
123.11	1- <u>C</u> ₅ H ₄ Me
113.29	2- or 5- <u>C</u> ₅ H ₄ Me
112.19	5- or 2- <u>C</u> ₅ H ₄ Me
109.14	3- or 4- <u>C</u> ₅ H ₄ Me
108.98	4- or 3- <u>C</u> ₅ H ₄ Me
67.46	<u>C</u> Me ₃
51.72	CN ₂ <u>CH</u> ₂
33.51	C <u>Me</u> ₃
26.52	<u>CH</u> ₂ CH ₃
15.44	C ₅ H ₄ <u>Me</u>
13.13	CH ₂ <u>CH</u> ₃
3.24	SiMe ₃

¹H NMR data: (CD₂Cl₂, 500.1 MHz, 195 K)

7.29-7.45	3 H	m, br	<i>o</i> - and <i>m</i> -C ₆ H ₅
7.12	1 H	m	<i>p</i> -C ₆ H ₅
6.92	2 H	s	3- and 4-C ₅ H ₄ Me
5.59	1 H	s	5- or 2-C ₅ H ₄ Me
5.55	1 H	s	2- or 5-C ₅ H ₄ Me
3.02	1 H	m	CN ₂ CH ₂
2.77	1 H	m	CN ₂ CH ₂

1.81	3 H	s	$\text{C}_5\text{H}_4\text{Me}$
1.22	2 H	m	CH_2CH_3
0.89	9 H	s	CMe_3
0.77	3 H	m	CH_2CH_3
-0.35	9 H	s	SiMe_3

I.R. data: (KBr plates, Nujol mull, cm^{-1}) 3024 (m), 2932 (s), 2893 (s), 2854 (s), 1602 (w), 1578 (w), 1510 (s), 1480 (s), 1414(s), 1376 (m), 1348 (s), 1292 (m), 1244(s), 1206 (m), 1156 (w), 1120 (m), 1072 (s), 1016 (m), 922 (s), 878 (m), 836 (s), 804 (m), 782 (s), 758 (m), 686 (m), 632 (m), 594 (m), 426 (m), 412 (m).

Elemental analysis for $\text{C}_{23}\text{H}_{37}\text{N}_3\text{SiTi}$:

Found (calculated): C 62.9 (64.0), H 8.4 (8.6), N 9.8 (9.7) %

E.I. mass spectrum:

$m/z = 416 [\text{M}]^+$ (100 %)

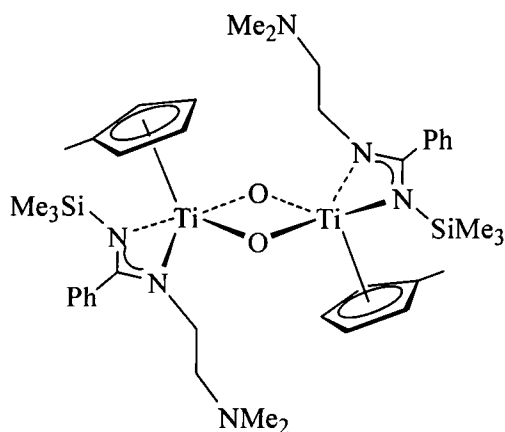
$m/z = 431 [\text{M} - \text{Me}]^+$ (60 %)

High resolution E.I. mass spectrum for $[\text{Ti}(\eta\text{-C}_5\text{H}_4\text{Me})(\text{N}^t\text{Bu})\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{Me}\}]^+$:

$\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{Me}\}^+$:

Found (calculated for $\text{C}_{23}\text{H}_{37}\text{N}_3\text{SiTi}$): $m/z = 431.2227$ (431.2236)

6.2.4 *trans*- $[\text{Ti}_2(\eta\text{-C}_5\text{H}_4\text{Me})_2(\mu\text{-O})_2\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{NMe}_2\}_2]$ (16a)



^1H NMR data: (C_6D_6 , 500.0 MHz, 293 K)

7.03 - 7.14	10 H	m	C_6H_5
6.63	2 H	m	3- or 4- $\text{C}_5\text{H}_4\text{Me}$
6.59	2 H	m	4- or 3- $\text{C}_5\text{H}_4\text{Me}$
6.30	2 H	m	2- or 5- $\text{C}_5\text{H}_4\text{Me}$

6.24	2 H	m	5- or 2-C ₅ <u>H</u> ₄ Me
3.34	2 H	m	CN ₂ CH ₂
3.17	2 H	m	CN ₂ CH ₂
2.65	2 H	m	CH ₂ NMe ₂
2.58	2 H	m	CH ₂ NMe ₂
2.33	6 H	s	NMe ₂
2.04	6 H	s	C ₅ H ₄ <u>Me</u>
0.11	18 H	s	SiMe ₃

¹³C-{¹H} NMR data: (C₆D₆, 125.7 MHz, 293 K)

173.93	CN ₂
136.54	<i>ipso</i> -C ₆ H ₅
128.68	C ₆ H ₅
128.42	C ₆ H ₅
128.29	C ₆ H ₅
127.00	C ₆ H ₅
126.96	C ₆ H ₅
114.25	2- or 5-C ₅ <u>C</u> H ₄ Me
113.0 - 113.1	3- and 4-C ₅ <u>C</u> H ₄ Me
112.18	5- or 2-C ₅ <u>C</u> H ₄ Me
60.90	<u>CH</u> ₂ NMe ₂
60.89	<u>C</u> Me ₃
47.00	CN ₂ <u>CH</u> ₂
45.89	C ₅ H ₄ <u>Me</u>
15.75	NMe ₂
2.84	SiMe ₃

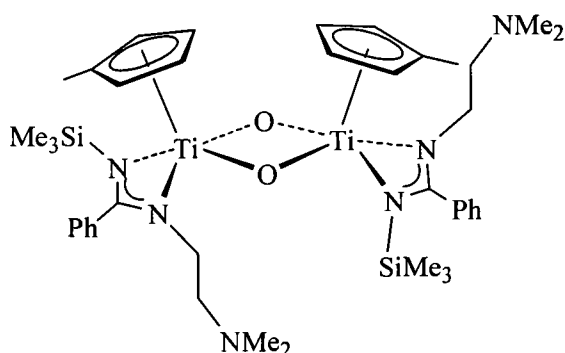
* 1-C₅CH₄Me not observed

¹H NMR data: (CD₂Cl₂, 500.0 MHz, 293 K)

7.48 - 7.39	10 H	m, br	C ₆ H ₅
6.30	2 H	m	3- or 4-C ₅ <u>H</u> ₄ Me
6.25	2 H	m	4- or 3-C ₅ <u>H</u> ₄ Me
6.04	2 H	m	2-or 5-C ₅ <u>H</u> ₄ Me
6.01	2 H	m	5- or 2-C ₅ <u>H</u> ₄ Me

3.14	2 H	m	CN ₂ CH ₂
3.00	2 H	m	CN ₂ CH ₂
2.43	2 H	m	CH ₂ NMe ₂
2.27	2 H	m	CH ₂ NMe ₂
2.21	6 H	s	C ₅ H ₄ Me
2.02	12 H	s	NMe ₂
-0.11	18 H	s	SiMe ₃

cis-[Ti₂(η-C₅H₄Me)₂(μ-O)₂(Me₃SiNC(Ph)NCH₂CH₂NMe₂)₂] (16b)



¹H NMR data: (C₆D₆, 500.0 MHz, 293 K)

7.03 - 7.14	10 H	m	C ₆ H ₅
6.63	2 H	m	3- or 4-C ₅ H ₄ Me
6.59	2 H	m	4- or 3-C ₅ H ₄ Me
6.30	2 H	m	2- or 5-C ₅ H ₄ Me
6.24	2 H	m	5- or 2-C ₅ H ₄ Me
3.34	2 H	m	CN ₂ CH ₂
3.17	2 H	m	CN ₂ CH ₂
2.65	2 H	m	CH ₂ NMe ₂
2.58	2 H	m	CH ₂ NMe ₂
2.33	6 H	s	NMe ₂
2.01	6 H	s	C ₅ H ₄ Me
0.88	18 H	s	SiMe ₃

¹³C-{¹H} NMR data: (C₆D₆, 125.7 MHz, 293 K)

173.82	CN ₂
136.45	<i>ipso</i> -C ₆ H ₅
128.64	C ₆ H ₅

128.44	C ₆ H ₅
127.91	C ₆ H ₅
127.00	C ₆ H ₅
126.84	C ₆ H ₅
114.12	2- or 5- <u>C</u> ₅ H ₄ Me
113.0 - 113.1	3- and 4- <u>C</u> ₅ H ₄ Me
112.50	5- or 2- <u>C</u> ₅ H ₄ Me
60.90	<u>CH</u> ₂ NMe ₂
60.89	<u>C</u> Me ₃
47.00	CN ₂ <u>CH</u> ₂
45.84	C ₅ H ₄ <u>Me</u>
15.75	NMe ₂
2.79	SiMe ₃

* 1-C₅H₄Me not observed

¹H NMR data (CD₂Cl₂, 500.0 MHz, 293 K):

7.48 - 7.39	10 H	m, br	C ₆ H ₅
6.30	2 H	m	3- or 4-C ₅ <u>H</u> ₄ Me
6.25	2 H	m	4- or 3-C ₅ <u>H</u> ₄ Me
6.04	2 H	m	2-or 5-C ₅ <u>H</u> ₄ Me
6.01	2 H	m	5- or 2-C ₅ <u>H</u> ₄ Me
3.14	2 H	m	CN ₂ CH ₂
3.00	2 H	m	CN ₂ CH ₂
2.43	2 H	m	<u>CH</u> ₂ NMe ₂
2.27	2 H	m	<u>CH</u> ₂ NMe ₂
2.23	6 H	s	C ₅ H ₄ <u>Me</u>
2.03	12 H	s	NMe ₂
-0.15	18 H	s	SiMe ₃

I.R. data (mixture of isomers): (KBr plates, Nujol mull, cm⁻¹)

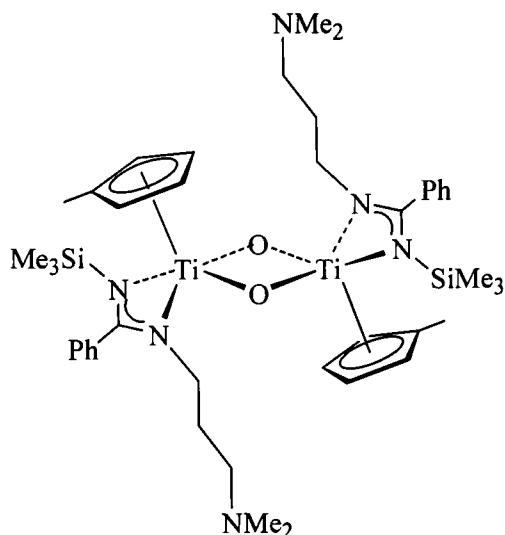
2726(w), 2670 (w), 1516 (w), 1488 (s), 1350 (m), 1304 (w, br), 1246 (m), 1204 (w), 1198 (w), 1154 (w), 1098 (w), 1024 (m), 938 (m), 918 (m), 900 (m, br), 862 (m), 836 (m), 796 (w), 722 (m, br), 700 (w), 680 (w).

Elemental analysis for $C_{40}H_{62}N_6O_2Si_2Ti_2$ (mixture of isomers):

Found (calculated): C 59.1 (59.2), H 7.6 (7.7), N 10.6 (10.4) %

E.I. mass spectrum:

A satisfactory mass spectrum could not be obtained for this compound.

6.2.5 *trans*-[$Ti_2(\eta-C_5H_4Me)_2(\mu-O)_2\{Me_3SiNC(Ph)CH_2CH_2CH_2NMe_2\}_2$] (17a) **^1H NMR data: (C_6D_6 , 500.0 MHz, 293 K)**

7.03 - 7.22	10 H	m	C_6H_5
6.61	2 H	m	3- or 4- C_5H_4Me
6.55	2 H	m	4- or 3- C_5H_4Me
6.28	2 H	m	2- or 5- C_5H_4Me
6.24	2 H	m	5- or 2- C_5H_4Me
3.25	2 H	m	CN_2CH_2
3.05	2 H	m	CN_2CH_2
2.36	6 H	s	C_5H_4Me
2.03	6 H	s	NMe_2
2.05	4 H	m	CH_2NMe_2
1.67	2 H	m	$CH_2CH_2CH_2$
1.42	2 H	m	$CH_2CH_2CH_2$
0.15	18 H	s	$SiMe_3$

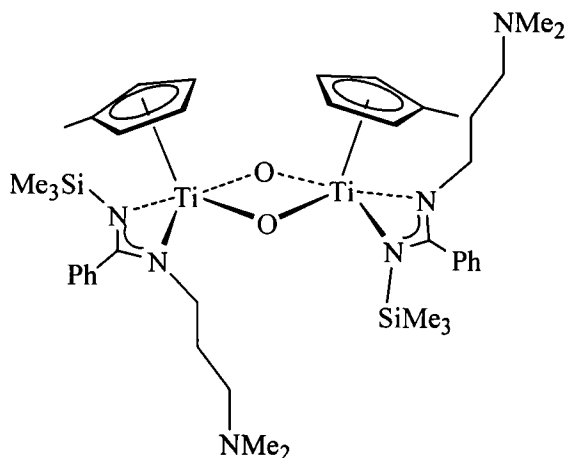
$^{13}\text{C}\{-^1\text{H}\}$ NMR data: (C_6D_6 , 125.7 MHz, 293 K)

173.54	CN_2
136.62	<i>ipso</i> - C_6H_5
128.48	C_6H_5
128.10	C_6H_5
127.91	C_6H_5
126.93	C_6H_5
126.91	C_6H_5
124.68	1- $\underline{\text{C}}_5\text{H}_4\text{Me}$
113.99	2- or 5- $\underline{\text{C}}_5\text{H}_4\text{Me}$
113.02	3- and 4- $\underline{\text{C}}_5\text{H}_4\text{Me}$
112.40	5- or 2- $\underline{\text{C}}_5\text{H}_4\text{Me}$
57.82	$\underline{\text{CH}}_2\text{NMe}_2$
55.12	$\underline{\text{C}}\text{Me}_3$
47.08	$\text{CN}_2\underline{\text{CH}}_2$
45.50	NMe_2
31.46	$\text{CH}_2\underline{\text{CH}}_2\text{CH}_2$
15.79	$\text{C}_5\text{H}_4\underline{\text{Me}}$
2.84	SiMe_3

 ^1H NMR data (CD_2Cl_2 , 500.0 MHz, 293 K):

7.12 - 7.50	10 H	m, br,	C_6H_5
6.28	2 H	m	3- or 4- $\text{C}_5\underline{\text{H}}_4\text{Me}$
6.21	2 H	m	4- or 3- $\text{C}_5\underline{\text{H}}_4\text{Me}$
6.04	4 H	m	2- and 5- $\text{C}_5\underline{\text{H}}_4\text{Me}$
2.7 - 3.2	4 H	m	CN_2CH_2
2.27	6 H	s	$\text{C}_5\text{H}_4\underline{\text{Me}}$
2.04	12 H	s	NMe_2
2.00	4 H	m	$\underline{\text{CH}}_2\text{NMe}_2$, overlapping
1.60	2 H	m	$\text{CH}_2\underline{\text{CH}}_2\text{CH}_2$
1.35	2 H	m	$\text{CH}_2\underline{\text{CH}}_2\text{CH}_2$
-0.10	18 H	s	SiMe_3

cis-[Ti₂(η-C₅H₄Me)₂(μ-O)₂{Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂}₂] (17b)



¹H NMR data: (C₆D₆, 500.0 MHz, 293 K)

7.03 - 7.22	10 H	m	C ₆ H ₅
6.61	2 H	m	3- or 4-C ₅ H ₄ Me
6.55	2 H	m	4- or 3-C ₅ H ₄ Me
6.28	2 H	m	2- or 5-C ₅ H ₄ Me
6.24	2 H	m	5- or 2-C ₅ H ₄ Me
3.25	2 H	m	CN ₂ CH ₂
3.05	2H	m	CN ₂ CH ₂
2.35	6 H	s	C ₅ H ₄ Me
2.06	6 H	s	NMe ₂
2.05	4 H	m	CH ₂ NMe ₂
1.67	2 H	m	CH ₂ CH ₂ CH ₂
1.42	2 H	m	CH ₂ CH ₂ CH ₂
0.12	18 H	s	SiMe ₃

¹³C-{¹H} NMR data: (C₆D₆, 125.7 MHz, 293 K)

173.62	CN ₂
136.62	<i>ipso</i> -C ₆ H ₅
128.61	C ₆ H ₅
128.10	C ₆ H ₅
127.91	C ₆ H ₅
126.87	C ₆ H ₅ *
124.68	1-C ₅ H ₄ Me

114.52	2- or 5- <u>C</u> ₅ H ₄ Me
113.02	3- and 4- <u>C</u> ₅ H ₄ Me
112.02	5- or 2- <u>C</u> ₆ H ₄ Me
57.82	<u>CH</u> ₂ NMe ₂
55.12	<u>C</u> Me ₃
47.08	CN ₂ <u>CH</u> ₂
45.49	NMe ₂
31.44	CH ₂ <u>CH</u> ₂ CH ₂
15.79	C ₅ H ₄ <u>Me</u>
2.79	SiMe ₃

*other C₆H₅ resonance obscured by solvent

¹H NMR data (CD₂Cl₂, 500.0 MHz, 293 K):

7.12 - 7.50	10 H	m, br,	C ₆ H ₅
6.45	2 H	m	3- or 4-C ₅ <u>H</u> ₄ Me
6.37	2 H	m	4- or 3-C ₅ <u>H</u> ₄ Me
6.04	4 H	m	2- and 5-C ₅ <u>H</u> ₄ Me
2.7 - 3.2	4 H	m	CN ₂ CH ₂
2.22	6 H	s	C ₅ H ₄ <u>Me</u>
2.01	12 H	s	NMe ₂
2.00	4 H	m	<u>CH</u> ₂ NMe ₂ , overlapping
1.60	2 H	m	CH ₂ <u>CH</u> ₂ CH ₂
1.35	2 H	m	CH ₂ <u>CH</u> ₂ CH ₂
-0.12	18 H	s	SiMe ₃

I.R. data (mixture of isomers): (KBr plates, Nujol mull, cm⁻¹)

1515 (s), 1309 (m), 1261 (s), 1203 (m), 1154 (w), 1090 (w), 1024 (w), 964 (m), 919 (m), 902 (m), 871 (w), 839 (s), 798 (s), 752 (w), 723 (m), 701 (m), 509 (m).

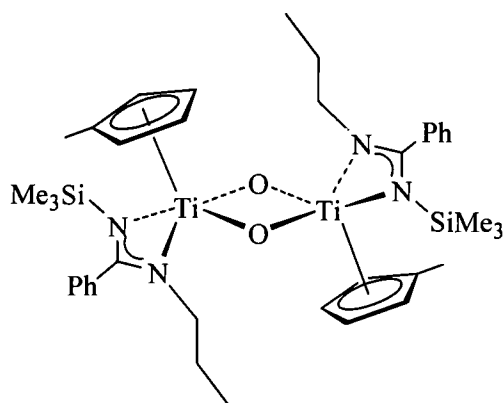
Elemental analysis for C₄₂H₆₆N₆O₂Si₂Ti₂ (mixture of isomers):

Found (calculated): C 58.9 (60.1), H 7.8 (7.9), N 10.1 (10.0) %

E.I. mass spectrum:

A satisfactory mass spectrum could not be obtained for this compound.

6.2.6 *trans*-[Ti₂(η-C₅H₄Me)₂(μ-O)₂{Me₃SiNC(Ph)NCH₂CH₂CH₃}₂] (18a)



¹H NMR data: (C₆D₆, 500.0 MHz, 293 K)

7.16 - 7.01	10 H	m		C ₆ H ₅
6.62	2 H	m		2- or 5-C ₅ H ₄ Me
6.53	2 H	m		5- or 2-C ₅ H ₄ Me
6.29	2 H	m		3- or 4-C ₅ H ₄ Me
6.23	2 H	m		4- or 3-C ₅ H ₄ Me
3.27	2 H	m		CN ₂ CH ₂
3.11	2 H	m		CN ₂ CH ₂
2.35	6 H	s		C ₅ H ₄ Me
1.60	4 H	m		CH ₂ CH ₃
0.65	4 H	t	³ J = 13.2	CH ₂ CH ₃
0.16	18 H	s		SiMe ₃

¹³C-{¹H} NMR data: (C₆D₆, 125.7 MHz, 293 K)

173.64	CN ₂
136.62	<i>ipso</i> -C ₆ H ₅
128.65	C ₆ H ₅
128.45	C ₆ H ₅
128.30	C ₆ H ₅
126.94	C ₆ H ₅ *
114.17	2- or 5-C ₅ H ₄ Me
113.01	3- or 4-C ₅ H ₄ Me
112.53	4- or 3-C ₅ H ₄ Me
112.06	5- or 2-C ₅ H ₄ Me

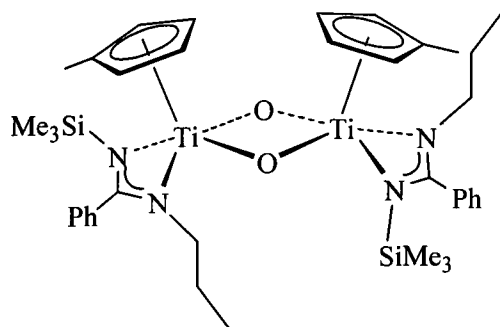
57.97	CN ₂ <u>C</u> H ₂
47.11	C ₅ H ₄ <u>M</u> e
29.84 or 29.66	<u>C</u> H ₂ CH ₃
15.79	CH ₂ <u>C</u> H ₃
2.85	SiMe ₃

*other resonance obscured by solvent, 1-C₅H₄Me not observed.

¹H NMR data: (CD₂Cl₂, 500.0 MHz, 293 K)

7.50 - 7.22	10 H	m		C ₆ H ₅
6.28	4 H	m		3- and 4-C ₅ <u>H</u> ₄ Me
6.03	4 H	s, br		2- and 5-C ₅ <u>H</u> ₄ Me
2.99	2 H	m		CN ₂ CH ₂
2.87	2 H	m		CN ₂ CH ₂
2.19	6 H	s		C ₅ H ₄ <u>M</u> e
1.43	4 H	m		<u>C</u> H ₂ CH ₃
0.71	6 H	t	³ J = 7.3	CH ₂ <u>C</u> H ₃
-0.16	18 H	s		SiMe ₃

cis-[Ti₂(η-C₅H₄Me)₂(μ-O)₂(Me₃SiNC(Ph)NCH₂CH₂CH₃)₂] (18b)



¹H NMR data: (C₆D₆, 500.0 MHz, 293 K)

7.0 - 7.2	6 H	m		C ₆ H ₅
6.62	2 H	m		2- or 5-C ₅ <u>H</u> ₄ Me
6.53	2 H	m		5- or 2-C ₅ <u>H</u> ₄ Me
6.29	2 H	m		3- or 4-C ₅ <u>H</u> ₄ Me
6.23	2 H	m		4- or 3-C ₅ <u>H</u> ₄ Me
3.27	2 H	m		CN ₂ CH ₂
3.11	2 H	m		CN ₂ CH ₂

2.34	6 H	s		$\text{C}_5\text{H}_4\text{Me}$
1.60	4 H	m		CH_2CH_3
0.78	6 H	t	$^3J = 7.3$	CH_2CH_3
0.15	18 H	s		SiMe_3

$^{13}\text{C}\{-^1\text{H}\}$ NMR data: (C_6D_6 , 125.7 MHz, 293 K)

173.58	CN_2
136.64	<i>ipso</i> - C_6H_5
128.62	C_6H_5
127.92	C_6H_5
127.34	C_6H_5
126.87	C_6H_5
126.82	C_6H_5
114.02	2- or 5- $\text{C}_5\text{H}_4\text{Me}$
113.26	3- or 4- $\text{C}_5\text{H}_4\text{Me}$
112.73	4- or 3- $\text{C}_5\text{H}_4\text{Me}$
112.44	5- or 2- $\text{C}_5\text{H}_4\text{Me}$
57.86	CN_2CH_2
45.53	$\text{C}_5\text{H}_4\text{Me}$
29.84 or 29.66	CH_2CH_3
15.79	CH_2CH_3
2.80	SiMe_3

*1- $\text{C}_5\text{H}_4\text{Me}$ not observed

^1H NMR data (CD_2Cl_2 , 500.0 MHz, 195 K):

7.4 - 7.5	10 H	m		C_6H_5
6.21	4 H	m		3- and 4- $\text{C}_5\text{H}_4\text{Me}$
6.03	4 H	s, br		2- and 5- $\text{C}_5\text{H}_4\text{Me}$
2.99	2 H	m		CN_2CH_2
2.87	2 H	m		CN_2CH_2
2.19	6 H	s		$\text{C}_5\text{H}_4\text{Me}$
1.43	4 H	m		CH_2CH_3
0.71	6 H	t	$^3J = 7.3$	CH_2CH_3
-0.13	18 H	s		SiMe_3

I.R. data (mixture of isomers): (KBr plates, Nujol mull, cm^{-1})

2816 (m), 2766 (m), 1514 (m), 1488 (s), 1436 (s), 1356 (m), 1246 (m), 1184 (w), 1154 (w), 1106 (m), 1096 (m), 1036 (m), 962 (m), 902 (s), 870 (m), 836 (s), 798 (m), 752 (m), 702 (s), 620 (w).

Elemental analysis for $\text{C}_{38}\text{H}_{56}\text{N}_6\text{O}_2\text{Si}_2\text{Ti}_2$ (mixture of isomers):

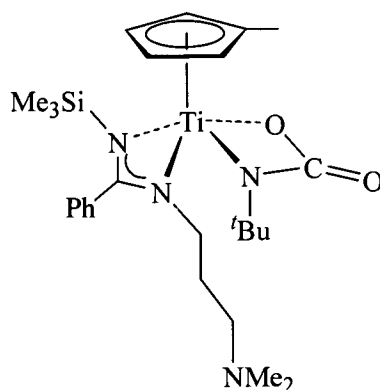
Found (calculated): C 60.6 (60.6), H 7.4 (7.5), N 7.3 (7.5) %.

E.I. mass spectrum:

$m/z = 673$ $[\text{M}-\text{C}_5\text{H}_4\text{Me}]^+$ (25%)

$m/z = 233$ $[\text{Me}_3\text{SiNC(Ph)NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3]^+$ (32%)

6.2.7 $[\text{Ti}(\eta\text{-C}_5\text{H}_4\text{Me})\{\text{OC(O)N}^t\text{Bu}\}\{\text{Me}_3\text{SiNC(Ph)NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}]$ (19)



Compound only prepared on the NMR tube scale.

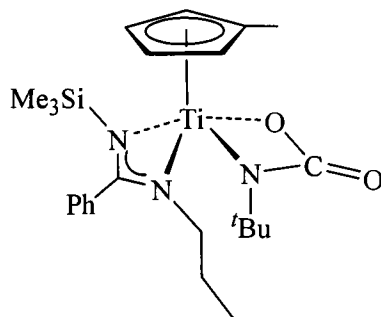
^1H NMR data: (CD_2Cl_2 , 500.0 MHz, 195 K)

7.40	2 H	app s, br		<i>o</i> - or <i>m</i> - C_6H_5
7.32	1 H	app s, br,		<i>p</i> - C_6H_5
7.16	2 H	app d	app $J = 5.5$	<i>o</i> - or <i>m</i> - C_6H_5
6.84	1 H	m		3- or 4- $\text{C}_5\text{H}_4\text{Me}$
6.39	2 H	m		2- or 5- and 4- or 3- $\text{C}_5\text{H}_4\text{Me}$
6.09	1 H	m		5- or 2- $\text{C}_5\text{H}_4\text{Me}$
3.23	1 H	m		CN_2CH_2
3.06	1 H	m		CN_2CH_2
2.30	3 H	s		$\text{C}_5\text{H}_4\text{Me}$
2.02	1 H	m		CH_2NMe_2
1.89	1 H	m		CH_2NMe_2
1.53	6 H	s		NMe_2

1.41	2 H	m	CH ₂ <u>CH</u> ₂ CH ₂
1.15	9 H	s	CMe ₃
-0.27	9 H	s	SiMe ₃

¹³C-{¹H} NMR data: (CD₂Cl₂, 75.5 MHz, 195 K)

171.96	NC(O)O
158.33	CN ₂
132.79	<i>ipso</i> -C ₆ H ₅ or 1- <u>C</u> ₅ H ₄ Me
131.99	1- <u>C</u> ₅ H ₄ Me or <i>ipso</i> -C ₆ H ₅
128.93	<i>o</i> - or <i>m</i> -C ₆ H ₅
128.34	<i>o</i> - or <i>m</i> -C ₆ H ₅
128.04	<i>p</i> -C ₆ H ₅
126.25	<i>o</i> - or <i>m</i> -C ₆ H ₅
125.64	<i>o</i> - or <i>m</i> -C ₆ H ₅
118.07	2- or 5- <u>C</u> ₅ H ₄ Me
117.48	5- or 2- or 3- or 4- <u>C</u> ₅ H ₄ Me
116.70	5- or 2- or 3- or 4- <u>C</u> ₅ H ₄ Me
116.04	4- or 3- <u>C</u> ₅ H ₄ Me
56.89	<u>CH</u> ₂ NMe ₂
56.45	<u>C</u> Me ₃
47.27	CN ₂ <u>CH</u> ₂
44.31	NMe ₂
29.32	<u>C</u> Me ₃
28.46	CH ₂ <u>CH</u> ₂ CH ₂
15.39	C ₅ H ₄ <u>Me</u>
0.76	SiMe ₃

6.2.8 [Ti(η -C₅H₄Me){OC(O)N^tBu}{Me₃SiNC(Ph)NCH₂CH₂Me}] (20)

Compound only prepared on the NMR tube scale.

¹H NMR data: (CD₂Cl₂, 500.0 MHz, 195 K)

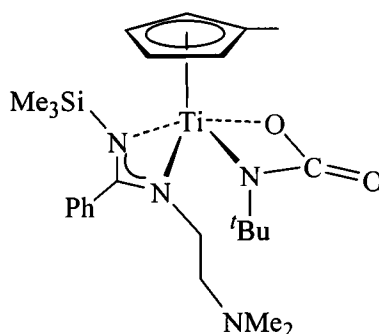
7.30 – 7.42	3 H	m		<i>o</i> - or <i>m</i> -C ₆ H ₅ and <i>p</i> -C ₆ H ₅
7.05 – 7.08	2 H	m		<i>o</i> - or <i>m</i> -C ₆ H ₅
6.85	1 H	m		3- or 4-C ₅ <u>H</u> ₄ Me
6.44	1 H	m		2- or 5- or 4- or 3-C ₅ <u>H</u> ₄ Me
6.41	1 H	m		2- or 5- or 4- or 3-C ₅ <u>H</u> ₄ Me
6.11	1 H	m		5- or 2-C ₅ <u>H</u> ₄ Me
3.09	1 H	m		CN ₂ CH ₂
2.94	1 H	m		CN ₂ CH ₂
2.30	3 H	s		C ₅ H ₄ <u>Me</u>
1.49	1 H	m		<u>CH</u> ₂ Me
1.34	1 H	m		<u>CH</u> ₂ Me
1.15	9 H	s		CMe ₃
0.60	3 H	t	³ J = 7.3	CH ₂ <u>CH</u> ₃
-0.29	9 H	s		SiMe ₃

¹³C-{¹H} NMR data: (C₆D₆, 75.5 MHz, 195 K)

172.15	NC(O)O
158.50	CN ₂
133.12	<i>ipso</i> -C ₆ H ₅ or 1-C ₅ <u>H</u> ₄ Me
132.30	1-C ₅ <u>H</u> ₄ Me or <i>ipso</i> -C ₆ H ₅
128.93	<i>o</i> -, <i>m</i> - or <i>p</i> -C ₆ H ₅
128.32	<i>o</i> -, <i>m</i> - or <i>p</i> -C ₆ H ₅
128.10	<i>o</i> -, <i>m</i> - or <i>p</i> -C ₆ H ₅
126.24	<i>o</i> - or <i>m</i> -C ₆ H ₅

125.77	<i>o</i> - or <i>m</i> -C ₆ H ₅
118.33	2- or 5-C ₅ H ₄ Me
117.53	5- or 2- or 3- or 4-C ₅ H ₄ Me
116.69	5- or 2- or 3- or 4-C ₅ H ₄ Me
116.22	4- or 3-C ₅ H ₄ Me
56.96	CMe ₃
51.47	CN ₂ CH ₂
29.42	CMe ₃
24.64	CH ₂ CH ₃
15.38	CH ₂ CH ₃
11.06	C ₅ H ₄ Me
0.73	SiMe ₃

6.2.9 [Ti(η-C₅H₄Me){OC(O)N^tBu}{Me₃SiNC(Ph)NCH₂CH₂NMe₂}] (21)



Compound only prepared on the NMR tube scale.

¹H NMR data: (CD₂Cl₂, 500.0 MHz, 195 K)

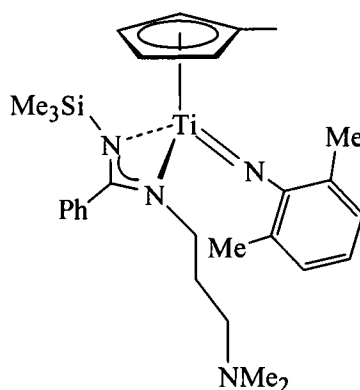
7.43	3 H	app s, br		<i>o</i> - or <i>m</i> -C ₆ H ₅ and <i>p</i> -C ₆ H ₅
7.16	2 H	app d	app ³ J = 21.5	<i>o</i> - or <i>m</i> -C ₆ H ₅
6.89	1 H	m		3- or 4-C ₅ H ₄ Me
6.44	2 H	m		2- or 5- and 4- or 3-C ₅ H ₄ Me
6.14	1 H	m		5- or 2-C ₅ H ₄ Me
3.22	1 H	m		CN ₂ CH ₂
3.16	1 H	m		CN ₂ CH ₂

2.30	3 H	s	$\text{C}_5\text{H}_4\text{Me}$
2.26	1 H	m	CH_2NMe_2
2.19	1 H	m	CH_2NMe_2
1.90	6 H	s	NMe_2
1.14	9 H	s	CMe_3
-0.30	9 H	s	SiMe_3

$^{13}\text{C}\{-^1\text{H}\}$ NMR data: (CD_2Cl_2 , 125.7 MHz, 195 K)

172.59	$\text{C}(\text{O})\text{O}$
158.37	CN_2
133.54	<i>ipso</i> - C_6H_5 or 1- $\text{C}_5\text{H}_4\text{Me}$
131.99	1- $\text{C}_5\text{H}_4\text{Me}$ or <i>ipso</i> - C_6H_5
129.01	C_6H_5
128.29	C_6H_5
128.04	C_6H_5
126.18	C_6H_5
125.99	C_6H_5
118.74	2- or 5- $\text{C}_5\text{H}_4\text{Me}$
117.27	3- or 4- $\text{C}_5\text{H}_4\text{Me}$
116.86	5- or 2- or 4- or 3- $\text{C}_5\text{H}_4\text{Me}$
116.68	5- or 2- or 4- or 3- $\text{C}_5\text{H}_4\text{Me}$
59.20	CMe_3
56.92	CH_2NMe_2
47.42	CN_2CH_2
45.05	NMe_2
29.56	CMe_3
15.38	$\text{C}_5\text{H}_4\text{Me}$
0.77	SiMe_3

6.2.10 [Ti(η -C₅H₄Me)(N-2,6-C₆H₃Me₂){Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂}]
(22)



¹H NMR data: (C₆D₆, 500.0 MHz, 293 K)

7.18 – 7.32	2 H,	d, br		<i>o</i> -C ₆ H ₅
7.10 – 7.16	3 H	m, br		<i>m</i> - and <i>p</i> -C ₆ H ₅
7.06	2 H	app d	app J = 7.3	<i>m</i> -C ₆ H ₃ Me ₂
6.87	1 H	m		3- or 4-C ₅ H ₄ Me
6.70	1 H	t	³ J = 7.8	<i>p</i> -C ₆ H ₃ Me ₂
6.23	2 H	m		2- or 5- and 3- or 4-C ₅ H ₄ Me
5.40	1 H	m		2- or 5-C ₅ H ₄ Me
3.04	1 H	m		CN ₂ CH ₂
2.71	6 H	s		2,6-C ₆ H ₃ Me ₂
2.43	1 H	m		CN ₂ CH ₂
2.19	1 H	m		CH ₂ NMe ₂
2.10	6 H	s		NMe ₂
2.00	3 H	s		C ₅ H ₄ Me
1.52	2 H	m		CH ₂ CH ₂ CH ₂ and CH ₂ NMe ₂
0.79	1 H	m		CH ₂ CH ₂ CH ₂
-0.01	9 H	s		SiMe ₃

¹³C-{¹H} NMR data: (C₆D₆, 75.5 MHz, 293 K)

172.24	CN ₂
158.23	<i>ipso</i> -2,6-C ₆ H ₃ Me ₂
137.19	<i>ipso</i> -C ₆ H ₅
131.89	1-C ₅ H ₄ Me
128.53	<i>m</i> -2,6-C ₆ H ₃ Me ₂

127.68	<i>o</i> -2,6-C ₆ H ₃ Me ₂ or <i>o</i> -, <i>m</i> - or <i>p</i> -C ₆ H ₅
127.88	<i>o</i> -2,6-C ₆ H ₃ Me ₂ or <i>o</i> -, <i>m</i> - or <i>p</i> -C ₆ H ₅
119.96	<i>o</i> -2,6-C ₆ H ₃ Me ₂ or <i>o</i> -, <i>m</i> - or <i>p</i> -C ₆ H ₅ *
119.29	<i>p</i> -2,6-C ₆ H ₃ Me ₂
115.65	3- or 4- or 2- or 5-C ₅ H ₄ Me
112.13	2- or 5-C ₅ H ₄ Me
106.08	3- or 4-C ₅ H ₄ Me
104.07	2- or 5- or 3- or 4-C ₅ H ₄ Me
62.85	<u>CH</u> ₂ NMe ₂
52.29	NMe ₂
45.38	CN ₂ <u>CH</u> ₂
26.28	CH ₂ CH ₂ CH ₂
20.21	2,6-C ₆ H ₃ <u>Me</u> ₂
14.92	C ₅ H ₄ <u>Me</u>
3.28	SiMe ₃

* other resonances obscured by solvent

I.R. data: (KBr plates, Nujol mull, cm⁻¹)

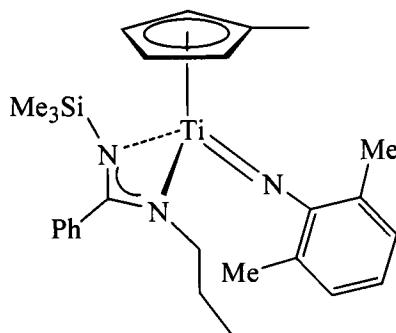
2852 (s, br), 2778 (m), 2362 (w), 2342 (w), 2202 (w), 1586 (w), 1504 (s), 1488 (s), 1404 (m), 1346 (s), 1312 (s), 1246 (m), 1226 (w), 1168 (w), 1150 (w), 1110 (m), 1096 (m), 1070 (w), 1058 (m), 1038 (w), 1026 (w), 1012 (m), 978 (m), 942 (s), 918 (s), 896 (s), 850 (s), 836 (s), 790 (s), 780 (m), 710 (w), 698 (m), 676 (w), 624 (m), 574 (m), 548 (s), 438 (s), 418 (s).

Elemental analysis for C₂₉H₄₂N₄SiTi:

Found (calculated): C 65.5 (66.6), H 7.9 (8.1), N 10.7 (10.7) %

E.I. mass spectrum:

$m/z = 522$ [M]⁺ (5%)

6.2.11 [Ti(η -C₅H₄Me)(N-2,6-C₆H₃Me₂){Me₃SiNC(Ph)NCH₂CH₂Me}] (23)¹H NMR data: (C₆D₆, 500.0 MHz, 293 K)

7.00 – 7.14	7 H	m, br		<i>m</i> -C ₆ H ₃ Me ₂ and C ₆ H ₅
6.73	1 H	t	³ J = 7.3	<i>p</i> -C ₆ H ₃ Me ₂
6.66	2 H	m, br		3- and 4-C ₅ H ₄ Me
5.89	2 H	app d, br	app J = 2.0	2- and 5-C ₅ H ₄ Me
3.13	1 H	m		CN ₂ CH ₂
2.92	1 H	m		CN ₂ CH ₂
2.52	6 H	s		C ₆ H ₃ Me ₂
2.08	3 H	s		C ₅ H ₄ Me
1.29	2 H	m		CH ₂ CH ₃
0.59	3 H	t	³ J = 7.3	CH ₂ CH ₃
-0.11	9 H	s		SiMe ₃

¹³C-{¹H} NMR data: (C₆D₆, 75.5 MHz, 293 K)

166.41	CN ₂
159.63	<i>ipso</i> -C ₆ H ₃ Me ₂
151.10	<i>ipso</i> -C ₆ H ₅
135.25	1-C ₅ H ₄ Me or <i>o</i> -C ₆ H ₃ Me ₂
132.18	<i>o</i> -C ₆ H ₃ Me ₂ or 1-C ₅ H ₄ Me
127.95	<i>m</i> -C ₆ H ₃ Me ₂ or C ₆ H ₅
127.56	<i>m</i> -C ₆ H ₃ Me ₂ or C ₆ H ₅
127.27	<i>m</i> -C ₆ H ₃ Me ₂ or C ₆ H ₅
126.60	<i>m</i> -C ₆ H ₃ Me ₂ or C ₆ H ₅ , 2 overlapping
126.48	<i>m</i> -C ₆ H ₃ Me ₂ or C ₆ H ₅
119.82	<i>p</i> -C ₆ H ₃ Me ₂

113.02	2- or 5- <u>C</u> ₅ H ₄ Me
112.78	5- or 2- <u>C</u> ₅ H ₄ Me
111.75	3- or 4- <u>C</u> ₅ H ₄ Me
111.62	4- or 3- <u>C</u> ₅ H ₄ Me
52.05	CN ₂ <u>C</u> H ₂
25.65	CH ₂ <u>C</u> H ₂ CH ₃
20.30	C ₆ H ₃ <u>M</u> e ₂
14.78	C ₅ H ₄ <u>M</u> e
11.89	CH ₂ <u>C</u> H ₃
1.37	SiMe ₃

I.R. data: (KBr plates, Nujol mull, cm⁻¹)

2920 (s), 2852 (s), 2636 (w), 1644 9w), 1588 (w), 1574 (w), 1504 (w), 1408 (m), 1356 (m), 1294 (m), 1246 (m), 1224 (w), 1194 (w), 1094 (m), 1070 (m), 1022 (m), 920 (m), 908 (m), 874 (s), 838 (s), 794 (s), 758 (m), 702 (m), 636 (m), 424 (s).

Elemental analysis for C₂₇H₃₇N₃SiTi:

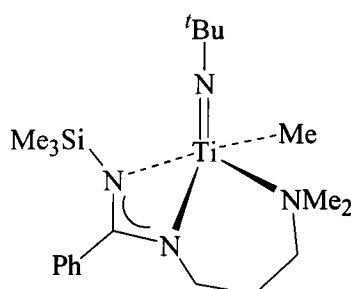
Found (calculated): C 64.3 (67.6), H 8.2 (7.8), N 8.5 (8.8) %

E.I. mass spectrum:

$m/z = 479$ [M⁺] (60%)

6.3 Characterising data for Chapter 4

6.3.1 [Ti(N^{*t*}Bu){Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂}Me] (24)



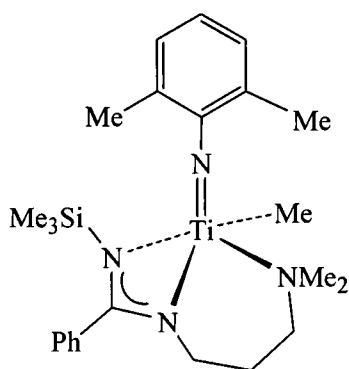
Compound only prepared on the NMR tube scale.

¹H NMR data: (C₆D₆, 300.2 MHz, 293 K)

7.21 - 7.02	5 H	m	C ₆ H ₅
3.03 - 2.80	3 H	m	2 x CN ₂ CH ₂ and <u>C</u> H ₂ NMe ₂
2.66	3 H	s	NMe

2.04 - 1.91	3 H	m	CH_2NMe_2 and 2 x $\text{CH}_2\text{CH}_2\text{CH}_2$
1.81	3 H	s	NMe
1.39	9 H	s	CMe_3
0.79	3 H	s	TiMe
0.22	9 H	s	SiMe_3

6.3.2 $[\text{Ti}(\text{N}-2,6\text{-C}_6\text{H}_3\text{Me}_2)\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}\text{Me}]$ (25)



^1H NMR data: (C_6D_6 , 300.0 MHz, 293 K)

7.21 - 7.06	7 H	m		$m\text{-C}_6\text{H}_3\text{Me}_2$ and C_6H_5
6.80	1 H	t	$^3J = 7.3$	$p\text{-C}_6\text{H}_3\text{Me}_2$
2.87	6 H	s		$\text{C}_6\text{H}_3\text{Me}_2$
2.85 - 2.73	2 H	m		CN_2CH_2
2.33	3 H	s		NMe
2.32	1 H	m		CH_2NMe_2
2.01	3 H	s		NMe
1.82	1 H	m		CH_2NMe_2
1.31 - 1.09	2 H	m		$\text{CH}_2\text{CH}_2\text{CH}_2$
0.95	3 H	s		TiMe
0.11	9 H	s		SiMe_3

$^{13}\text{C}\{-^1\text{H}\}$ NMR data: (C_6D_6 , 75.5 MHz, 293 K)

177.55	CN_2
159.66	$ipso\text{-C}_6\text{H}_3\text{Me}_2$
136.25	$ipso\text{-C}_6\text{H}_5$
132.09	$m\text{-C}_6\text{H}_3\text{Me}_2$
129.01	C_6H_5
128.63	C_6H_5

128.29	C ₆ H ₅
127.80	C ₆ H ₅ *
127.47	<i>o</i> -C ₆ H ₃ Me ₂
119.14	<i>p</i> -C ₆ H ₃ Me ₂
61.18	<u>CH</u> ₂ NMe ₂
50.54	NMe
46.88	NMe
45.76	CN ₂ <u>CH</u> ₂
38.20	Ti <u>Me</u>
20.20	C ₆ H ₃ <u>Me</u> ₂
1.96	SiMe ₃

*other resonances obscured by solvent

I.R. data: (NaCl plates, Nujol mull, cm⁻¹)

4330 (m), 4257 (m), 2726 (m), 1588 (m), 1505 (m), 1345 (m), 1316 (s), 1262 (m), 1247 (m), 1226 (w), 1205 (w), 1173 (m), 1153 (m), 1093 (s), 1063 (s), 1016 (m), 981 (w), 949 (w), 918 (m), 897 (s), 839 (m), 820 (s), 785 (m), 756 (s), 741 (w), 723 (m), 701 (m).

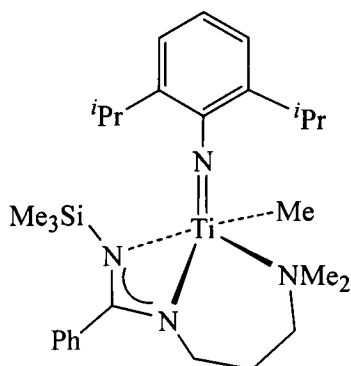
Elemental analysis for C₂₄H₃₈N₄TiSi:

Found (calculated): C 61.3 (62.8), H 8.9 (8.4), N 11.9 (12.2) %

E.I. mass spectrum:

A satisfactory mass spectrum could not be obtained for this compound.

6.3.3 [Ti(N-2,6-*i*Pr₂C₆H₃){Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂}Me] (26)



¹H NMR data: (C₆D₆, 500.0 MHz, 293 K)

7.02 - 7.28	7 H	m, br		C ₆ H ₅ and <i>m</i> -C ₆ H ₃ ^{<i>i</i>} Pr ₂
6.93	1 H	t	³ J = 7.3	<i>p</i> -C ₆ H ₃ ^{<i>i</i>} Pr ₂

4.72	2 H	sep		CH <u>Me</u> ₂
2.90	2 H	m		CN ₂ CH ₂
2.63	1 H	m		CH ₂ NMe ₂
2.44	3 H	s		NMe
1.90	3 H	s		NMe
1.75	1 H	m		CH ₂ NMe ₂
1.55	6 H	d	³ J = 7.1	CH <u>Me</u> ₂
1.53	6 H	d	³ J = 7.1	CH <u>Me</u> ₂
1.45	1 H	m		CH ₂ CH ₂ CH ₂
1.13	1 H	m		CH ₂ CH ₂ CH ₂
0.94	3 H	s		TiMe
0.11	9 H	s		SiMe ₃

¹³C-{¹H} NMR data: (C₆D₆, 75.5 MHz, 293 K)

177.23	CN ₂
156.93	<i>ipso</i> -C ₆ H ₃ ^{<i>i</i>} Pr ₂
142.61	<i>ipso</i> -C ₆ H ₅
129.10	<i>o</i> -C ₆ H ₃ ^{<i>i</i>} Pr ₂
128.63	C ₆ H ₅ or <i>m</i> -C ₆ H ₃ ^{<i>i</i>} Pr ₂
128.30	C ₆ H ₅ or <i>m</i> -C ₆ H ₃ ^{<i>i</i>} Pr ₂
128.10	C ₆ H ₅ or <i>m</i> -C ₆ H ₃ ^{<i>i</i>} Pr ₂
127.91	C ₆ H ₅ or <i>m</i> -C ₆ H ₃ ^{<i>i</i>} Pr ₂
126.54	C ₆ H ₅ or <i>m</i> -C ₆ H ₃ ^{<i>i</i>} Pr ₂
122.29	<i>p</i> -C ₆ H ₃ ^{<i>i</i>} Pr ₂
120.27	C ₆ H ₅ or <i>m</i> -C ₆ H ₃ ^{<i>i</i>} Pr ₂
61.42	<u>CH</u> ₂ NMe ₂
51.82	NMe
46.00	NMe
45.76	CN ₂ <u>CH</u> ₂
38.99	TiMe
28.01	<u>CH</u> Me ₂
25.56	CH ₂ <u>CH</u> ₂ CH ₂
24.64	CH <u>Me</u> ₂

24.59 CHMe_2 2.13 SiMe_3 **I.R. data:** (NaCl plates, Nujol mull, cm^{-1})

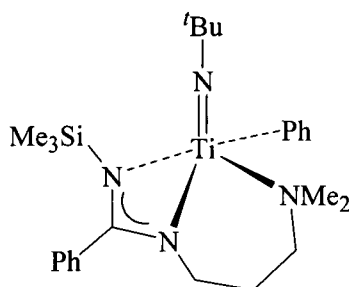
3044 (m), 2718 (m), 1947 (w), 1891 (w), 1838 (w), 1808 (w), 1693 (w), 1602 (w),
 1582 (m), 1503 (s), 1335 (s), 1279 (s), 1247 (s), 1202 (s), 1177 (m), 1154 (w),
 1142 (w), 1102 (s), 1073 (m), 1060 (m), 1044 (m), 1025 (m), 1013 (m), 995 (m),
 970 (m), 955 (m), 919 (s), 893 (s), 837 (s), 785 (s), 751 (s), 725 (m), 701 (s), 666
 (w), 629 (s), 594 (w).

Elemental analysis for $\text{C}_{28}\text{H}_{46}\text{N}_4\text{SiTi}$:

Found (calculated): C 62.7 (65.3), H 8.8 (9.0), N 10.5 (10.9) %

E.I. mass spectrum:

A satisfactory mass spectrum could not be obtained for this compound.

6.3.4 $[\text{Ti}(\text{N}^t\text{Bu})\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}\text{Ph}]$ (27) **^1H NMR data:** (C_6D_6 , 300.1 MHz, 293 K)

8.31	2 H	d	$^3J = 6.5$	<i>o</i> -TiPh
7.46	1 H	t	$^3J = 7.6$	<i>p</i> -TiPh
7.33	2 H	m		<i>m</i> -TiPh
7.42 - 7.06	5 H	m		C_6H_5
3.05 - 2.82	3 H	m		2 x CN_2CH_2 and CH_2NMe_2
2.65	3 H	s		NMe
1.82	1 H	m		CH_2NMe_2
1.68	3 H	s		NMe
1.41	9 H	s		CMe_3
1.34	1 H	m		$\text{CH}_2\text{CH}_2\text{CH}_2$
1.02	1 H	m		$\text{CH}_2\text{CH}_2\text{CH}_2$

-0.11	9 H	s	SiMe ₃
¹³C-{¹H} NMR data: (C ₆ D ₆ , 75.5 MHz, 293 K)			
187.10		CN ₂	
175.20		<i>ipso</i> -TiPh	
137.05		<i>o</i> -TiPh	
136.77		<i>ipso</i> -C ₆ H ₅	
128.59		TiPh or <u>C</u> ₆ H ₅ CN ₂	
128.50		TiPh or <u>C</u> ₆ H ₅ CN ₂	
128.43		TiPh or <u>C</u> ₆ H ₅ CN ₂	
127.76		TiPh or <u>C</u> ₆ H ₅ CN ₂	
126.91		TiPh or <u>C</u> ₆ H ₅ CN ₂	
126.53		TiPh or <u>C</u> ₆ H ₅ CN ₂	
126.31		TiPh or <u>C</u> ₆ H ₅ CN ₂ *	
69.23		<u>C</u> Me ₃	
61.79		<u>CH</u> ₂ NMe ₂	
52.04		NMe	
47.02		CN ₂ <u>CH</u> ₂	
43.71		NMe	
33.59		<u>C</u> Me ₃	
25.82		CH ₂ <u>CH</u> ₂ CH ₂	
2.21		SiMe ₃	

*other resonance obscured by solvent

I.R. data: (NaCl plates, Nujol mull, cm⁻¹)

2726 (w), 1944(w), 1578 (w), 1506 (w), 1344 (s), 1299 (m), 1248 (s), 1206 (m), 1153 (w), 1130 (w), 1104 (m), 1061 (m), 1017 (m), 979 (s), 946 (m), 918 (s), 898 (m), 857 (w), 838 (m), 820 (w), 783 (m), 766 (w), 722 (w), 702 (m), 648 (s).

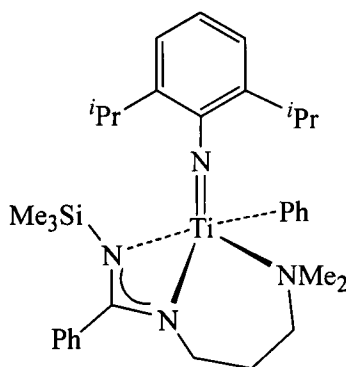
Elemental analysis for C₂₅H₄₀N₄TiSi:

Found (calculated): C 60.4 (63.5), H 9.1 (8.5), N 11.7 (11.9) %

High resolution E.I. mass spectrum for

[Ti(N'Bu){Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂}Ph]⁺:

Found (calculated for C₂₅H₄₀N₄TiSi): *m/z* = 472.2508 (472.2502)

6.3.5 [Ti(N-2,6-*i*-Pr₂C₆H₃){Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂}Ph] (28)¹H NMR data: (C₆D₆, 500.0 MHz, 293 K)

8.23	2 H	d	³ J = 6.4	<i>o</i> -TiPh
7.43	2 H	t	³ J = 7.1	<i>m</i> -TiPh
7.28	3 H	m		<i>p</i> -TiPh and <i>o</i> -C ₆ H ₅
7.02 - 7.16	5 H	m		<i>m</i> - and <i>p</i> -C ₆ H ₅ and <i>m</i> -C ₆ H ₃ <i>i</i> Pr ₂
6.92	1 H	t	³ J = 7.6	<i>p</i> -C ₆ H ₃ <i>i</i> Pr ₂
4.85	2 H	sep		CHMe ₂
3.00	1 H	m		CN ₂ CH ₂
2.82	1 H	m		CN ₂ CH ₂
2.46	4 H	s, m, overlapping		NMe, CH ₂ NMe ₂
1.84	1 H	m		CH ₂ NMe ₂
1.64	3 H	s		NMe
1.52	6 H	d	³ J = 6.8	CHMe ₂
1.50	6 H	d	³ J = 6.8	CHMe ₂
1.15	2 H	m		CH ₂ CH ₂ CH ₂
-0.13	9 H	s		SiMe ₃

¹³C-{¹H} NMR data: (C₆D₆, 75.5 MHz, 293 K)

188.89	CN ₂
178.12	<i>ipso</i> -TiPh
157.12	<i>ipso</i> -C ₆ H ₃ <i>i</i> Pr ₂
143.54	<i>ipso</i> -C ₆ H ₅ or <i>o</i> -C ₆ H ₃ <i>i</i> Pr ₂
142.31	<i>ipso</i> -C ₆ H ₅ or <i>o</i> -C ₆ H ₃ <i>i</i> Pr ₂
135.93	<i>o</i> -TiPh

133.56	<i>m</i> - C ₆ H ₃ ^{<i>i</i>} Pr ₂ or C ₆ H ₅
129.21	<i>m</i> - C ₆ H ₃ ^{<i>i</i>} Pr ₂ or C ₆ H ₅
128.53	<i>m</i> - C ₆ H ₃ ^{<i>i</i>} Pr ₂ or C ₆ H ₅
128.29	<i>m</i> - C ₆ H ₃ ^{<i>i</i>} Pr ₂ or C ₆ H ₅
127.90	<i>m</i> - C ₆ H ₃ ^{<i>i</i>} Pr ₂ or C ₆ H ₅
126.86	<i>m</i> -TiPh
126.58	<i>p</i> -TiPh
122.47	<i>m</i> - C ₆ H ₃ ^{<i>i</i>} Pr ₂ or C ₆ H ₅
120.64	<i>p</i> - C ₆ H ₃ ^{<i>i</i>} Pr ₂
61.43	<u>CH</u> ₂ NMe ₂
51.24	NMe
48.24	NMe
45.77	CN ₂ <u>C</u> H ₂
27.97	<u>CH</u> Me ₂
25.48	CH ₂ <u>CH</u> ₂ CH ₂
25.02	<u>CH</u> Me ₂
24.91	<u>CH</u> Me ₂
1.88	SiMe ₃

I.R. data: (NaCl plates, Nujol mull, cm⁻¹)

3053 (m), 3037 (m), 2854 (s), 1943 (w), 1898 (w), 1881 (w), 1860 (w), 1809 (w), 1699 (w), 1657 (w), 1621 (w), 1581 (w), 1417 (s), 1365 (s), 1357 (s), 1333 (s), 1300 (m), 1283 (s), 1260 (s), 1245 (s), 1225 (m), 1201 (s), 1181 (m), 1175 (m), 1151 (m), 1100 (s), 1083 (m), 1063 (s), 1047 (m), 1026 (w), 1013 (m), 992 (w), 977 (s), 970 (s), 950 (m), 934 (w), 917 (s), 894 (s), 841 (s), 821 (s), 797 (m), 782 (s), 769 (s), 753 (s), 731 (m), 719 (s), 701 (s), 679 (m), 666 (w), 652 (w), 628 (m), 596 (w), 547 (s), 509 (s).

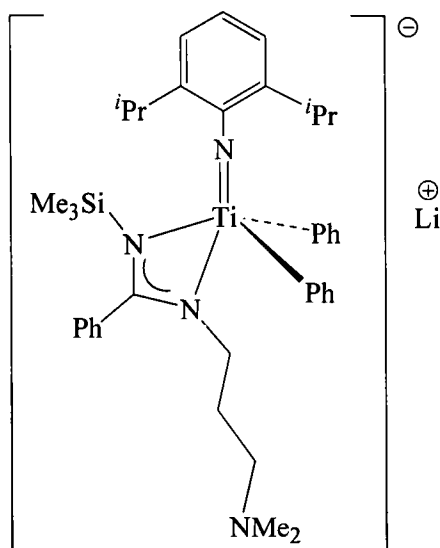
Elemental analysis for C₄₀H₄₆N₄SiTi:

Found (calculated): C 76.8 (68.7), H 9.6 (8.4), N 11.9 (9.7) %

E.I. mass spectrum:

A satisfactory mass spectrum could not be obtained for this compound

6.3.6 [Ti(N-2,6-*i*-Pr₂C₆H₃){Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂}Ph₂] (29)



¹H NMR data: (C₆D₆, 500.0 MHz, 293 K)

8.32	4 H	d	³ J = 7.6	<i>o</i> -TiPh
7.30	4 H	m		<i>m</i> -TiPh
7.02 - 7.19	9 H	m		<i>p</i> -TiPh, <i>m</i> -C ₆ H ₃ ^{<i>i</i>} Pr ₂ and C ₆ H ₅
6.91	2 H	t	³ J = 7.6	<i>p</i> -C ₆ H ₃ ^{<i>i</i>} Pr ₂
4.82	2 H	sep		<u>CH</u> Me ₂
2.44	2 H	m		CN ₂ <u>CH</u> ₂
1.50	2 H	m		<u>CH</u> ₂ NMe ₂
1.37	12 H	app d	app J = 6.3	<u>CH</u> Me ₂
1.28	6 H	s		NMe ₂
0.76	2 H	m		CH ₂ <u>CH</u> ₂ CH ₂
-0.12	9 H	s		SiMe ₃

¹³C-{¹H} NMR data: (C₆D₆, 125.5 MHz, 293 K)

191.68	CN ₂
142.69	<i>ipso</i> -C ₆ H ₅ or <i>o</i> - ^{<i>i</i>} Pr ₂ C ₆ H ₃
134.81	<i>o</i> -TiPh
128.63	<i>m</i> -TiPh
128.53	<i>p</i> -TiPh, <i>m</i> -C ₆ H ₃ ^{<i>i</i>} Pr ₂ or C ₆ H ₅
128.29	<i>p</i> -TiPh, <i>m</i> -C ₆ H ₃ ^{<i>i</i>} Pr ₂ or C ₆ H ₅

128.12	<i>p</i> -TiPh, <i>m</i> -C ₆ H ₃ ^{<i>i</i>} Pr ₂ or C ₆ H ₅
127.91	<i>p</i> -TiPh, <i>m</i> -C ₆ H ₃ ^{<i>i</i>} Pr ₂ or C ₆ H ₅
127.50	<i>p</i> -TiPh, <i>m</i> -C ₆ H ₃ ^{<i>i</i>} Pr ₂ or C ₆ H ₅
127.20	<i>p</i> -TiPh, <i>m</i> -C ₆ H ₃ ^{<i>i</i>} Pr ₂ or C ₆ H ₅
126.61	<i>p</i> -TiPh, <i>m</i> -C ₆ H ₃ ^{<i>i</i>} Pr ₂ or C ₆ H ₅
123.32	<i>p</i> -C ₆ H ₃ ^{<i>i</i>} Pr ₂
60.16	<u>CH</u> ₂ NMe ₂
50.60	CN ₂ <u>CH</u> ₂
44.89	NMe ₂
28.07	<u>CH</u> Me ₂
27.57	CH ₂ <u>CH</u> ₂ CH ₂
24.87	CH <u>Me</u> ₂
2.50	SiMe ₃

**ipso*-TiPh, *ipso*-C₆H₃^{*i*}Pr₂ and *o*-C₆H₃^{*i*}Pr₂ or *ipso*-C₆H₅ not observed

I.R. data: (NaCl plates, Nujol mull, cm⁻¹)

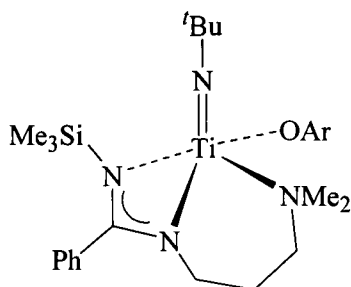
3091 (w), 3043 (m), 2927 (s), 1619 (w), 1599 (w), 1583 (w), 1564 (w), 1515 (m), 1484 (s), 1355 (m), 1325 (m), 1299 (m), 1270 (s), 1156 (w), 1141 (w), 1111 (m), 1100 (m), 1069 (m), 1054 (m), 1023 (m), 991 (m), 958 (m), 930 (s), 920 (m), 897 (w), 869 (m), 839 (m), 804 (s), 795 (s), 779 (m), 762 (m), 753 (m), 738 (m), 724 (w), 711 (w), 700 (w), 675 (w), 649 (m), 633 (m), 557 (m).

Elemental analysis for C₃₉H₁₇N₄LiSiTi:

Satisfactory analysis could not be obtained for this compound.

E.I. mass spectrum:

A satisfactory mass spectrum could not be obtained for this compound.

6.3.7[Ti(N^tBu){Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂}(O-2,6-C₆H₃Me₂)] (30)

¹H NMR data: (CD₂Cl₂, 500.0 MHz, 233 K)

7.50 - 7.29	5 H	m		C ₆ H ₅
7.03	1 H	d	³ J = 7.1	<i>m</i> -C ₆ H ₃ Me ₂
6.93	1 H	d	³ J = 6.5	<i>m</i> -C ₆ H ₃ Me ₂
6.57	1 H	m		<i>p</i> -C ₆ H ₃ Me ₂
3.63	1 H	m		CH ₂ NMe ₂
3.38 - 3.24	2 H	m		CN ₂ CH ₂
2.87	3 H	s		NMe
2.68	3 H	s		C ₆ H ₃ Me ₂
2.55	1 H	m		CH ₂ NMe ₂
2.13	3 H	s		C ₆ H ₃ Me ₂
1.94	3 H	s		NMe
1.89	1 H	m		CH ₂ CH ₂ CH ₂
1.59	1 H	m		CH ₂ CH ₂ CH ₂
1.00	9 H	s		CMe ₃
-0.38	9 H	s		SiMe ₃

¹³C-{¹H} NMR data: (CD₂Cl₂, 125.7 MHz, 233 K)

173.87	CN ₂
160.72	<i>ipso</i> -C ₆ H ₃ Me ₂
135.93	<i>ipso</i> -C ₆ H ₅
128.28	C ₆ H ₅ or C ₆ H ₃ Me ₂
128.19	C ₆ H ₅ or C ₆ H ₃ Me ₂
127.91	C ₆ H ₅ or C ₆ H ₃ Me ₂
127.81	C ₆ H ₅ or C ₆ H ₃ Me ₂
127.50	C ₆ H ₅ or C ₆ H ₃ Me ₂

127.08	C_6H_5 or $\text{C}_6\text{H}_3\text{Me}_2$
126.14	C_6H_5 or $\text{C}_6\text{H}_3\text{Me}_2$
126.08	C_6H_5 or $\text{C}_6\text{H}_3\text{Me}_2$
125.51	C_6H_5 or $\text{C}_6\text{H}_3\text{Me}_2^*$
116.43	$p\text{-C}_6\text{H}_3\text{Me}_2$
68.06	CMe_3
62.69	CH_2NMe_2
51.65	NMe
47.07	CN_2CH_2
43.74	NMe
32.59	CMe_3
25.49	$\text{CH}_2\text{CH}_2\text{CH}_2$
18.21	$\text{C}_6\text{H}_3\text{Me}_2$
17.09	$\text{C}_6\text{H}_3\text{Me}_2$
0.81	SiMe_3

*other resonance obscured by solvent

I.R. data: (NaCl plates, Nujol mull, cm^{-1})

2726 (m), 2684 (w), 2588 (w), 2360 (m), 2342 (m), 2250 (w), 2098 (w), 1942 (w), 1892 (w), 1832 (w), 1804 (w), 1590 (s), 1576 (m), 1506 (s), 1364 (m), 1348 (s), 1294 (s), 1250 (s), 1236 (s), 1208 (m), 1178 (w), 1150 (w), 1128 (w), 1110 (m), 1090 (m), 1062 (m), 1016 (m), 980 (m), 948 (m), 918 (m), 908 (s), 902 (s), 860 (m), 838 (s), 820 (m), 806 (w), 782 (m), 760 (s), 742 (w), 718 (m), 698 (s), 628 (w), 596 (w).

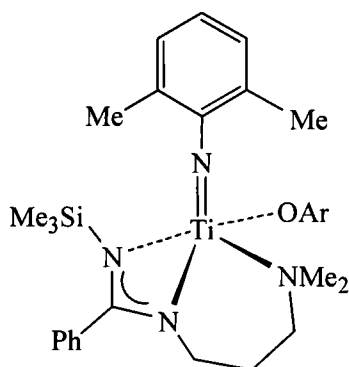
Elemental analysis for $\text{C}_{27}\text{H}_{44}\text{N}_4\text{OTiSi}$:

Found (calculated): C 62.1 (62.8), H 8.7 (8.6), N 10.4 (10.8) %

E.I. mass spectrum:

A satisfactory mass spectrum could not be obtained for this compound

6.3.8 [Ti(N-2,6-C₆H₃Me₂){Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂}(O-2,6-C₆H₃Me₂)] (31)



¹H NMR data: (C₆D₆, 500.0 MHz, 293 K)

7.26 - 7.05	9 H	m		<i>m</i> -N-2,6-C ₆ H ₃ Me ₂ , <i>m</i> -O-2,6-C ₆ H ₃ Me ₂ and C ₆ H ₅
6.86	1 H	t	³ J = 7.3	<i>p</i> -N-2,6-C ₆ H ₃ Me ₂
6.74	1 H	t	³ J = 7.3	<i>p</i> -O-2,6-C ₆ H ₃ Me ₂
3.12	1 H	m		CN ₂ <u>CH</u> ₂
2.95	1 H	m		CN ₂ <u>CH</u> ₂
2.86	1 H	m		<u>CH</u> ₂ NMe ₂
2.80	6 H	s		N-2,6-C ₆ H ₃ <u>Me</u> ₂
2.51	6 H	s		O-2,6-C ₆ H ₃ <u>Me</u> ₂
2.50	3 H	s		NMe
1.76	3 H	s		NMe
1.71	1 H	m		<u>CH</u> ₂ NMe ₂
1.25	1 H	m		CH ₂ <u>CH</u> ₂ CH ₂
1.04	1 H	m		CH ₂ <u>CH</u> ₂ CH ₂
-0.08	9 H	s		SiMe ₃

¹³C-{¹H} NMR data (C₆D₆, 125.7 MHz, 293 K):

175.93	CN ₂
162.37	<i>ipso</i> -N-2,6-C ₆ H ₃ <u>C</u> Me ₂
159.83	<i>ipso</i> -O-2,6-C ₆ H ₃ <u>C</u> Me ₂
135.96	<i>ipso</i> -C ₆ H ₅
132.24	<i>o</i> -O-2,6-C ₆ H ₃ Me ₂

129.10	<i>m</i> -O-2,6- <u>C</u> ₆ H ₃ Me ₂ , <i>m</i> -N-2,6- <u>C</u> ₆ H ₃ Me ₂ , <i>o</i> -N-2,6- <u>C</u> ₆ H ₃ Me ₂ or C ₆ H ₅
128.75	<i>m</i> -O-2,6- <u>C</u> ₆ H ₃ Me ₂ , <i>m</i> -N-2,6- <u>C</u> ₆ H ₃ Me ₂ , <i>o</i> -N-2,6- <u>C</u> ₆ H ₃ Me ₂ or C ₆ H ₅
128.61	<i>m</i> -O-2,6- <u>C</u> ₆ H ₃ Me ₂ , <i>m</i> -N-2,6- <u>C</u> ₆ H ₃ Me ₂ , <i>o</i> -N-2,6- <u>C</u> ₆ H ₃ Me ₂ or C ₆ H ₅
128.53	<i>m</i> -O-2,6- <u>C</u> ₆ H ₃ Me ₂ , <i>m</i> -N-2,6- <u>C</u> ₆ H ₃ Me ₂ , <i>o</i> -N-2,6- <u>C</u> ₆ H ₃ Me ₂ or C ₆ H ₅
127.48	<i>m</i> -O-2,6- <u>C</u> ₆ H ₃ Me ₂ , <i>m</i> -N-2,6- <u>C</u> ₆ H ₃ Me ₂ , <i>o</i> -N-2,6- <u>C</u> ₆ H ₃ Me ₂ or C ₆ H ₅
126.76	<i>m</i> -O-2,6- <u>C</u> ₆ H ₃ Me ₂ , <i>m</i> -N-2,6- <u>C</u> ₆ H ₃ Me ₂ , <i>o</i> -N-2,6- <u>C</u> ₆ H ₃ Me ₂ or C ₆ H ₅
126.41	<i>m</i> -O-2,6- <u>C</u> ₆ H ₃ Me ₂ , <i>m</i> -N-2,6- <u>C</u> ₆ H ₃ Me ₂ , <i>o</i> -N-2,6- <u>C</u> ₆ H ₃ Me ₂ or C ₆ H ₅ *
119.56	<i>p</i> -O-2,6-C ₆ H ₃ Me ₂
119.03	<i>p</i> -N-2,6-C ₆ H ₃ Me ₂
61.97	<u>C</u> H ₂ NMe ₂
52.06	NMe
45.89	<u>C</u> H ₂ CN ₂
45.74	NMe
25.40	CH ₂ <u>C</u> H ₂ CH ₂
20.44	N-2,6-C ₆ H ₃ <u>M</u> e ₂
18.13	O-2,6-C ₆ H ₃ <u>M</u> e ₂
1.68	SiMe ₃

*other resonances obscured by solvent

I.R. data: (NaCl plates, Nujol mull, cm⁻¹)

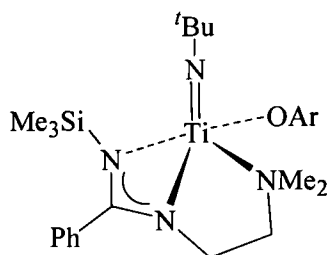
2722 (w), 2678 (w), 2356 (w), 2340 (w), 1888 (w), 1732 (w), 1590 (m), 1344 (m),
1312 (m), 1276 (s), 1236 (s), 1208 (m), 1178 (w), 1152 (w), 1110 (m), 1092 (s),
1060 (m), 1026 (w), 1012 (m), 980 (s), 948 (w), 896 (s), 854 (m), 838 (m), 818
(w), 784 (m), 756 (s), 740 (m), 722 (m), 626 (w), 566 (m).

Elemental analysis for C₃₁H₄₄N₄OSiTi:

Found (calculated): C 63.6 (65.9), H 8.2 (7.8), N 9.5 (9.9) %

E. I. mass spectrum:

A satisfactory mass spectrum could not be obtained for this compound.

6.3.9[Ti(N^tBu){Me₃SiNC(Ph)NCH₂CH₂NMe₂}(O-2,6-C₆H₃Me₂)] (32)**¹H NMR data:** (C₆D₆, 500.0 MHz, 293 K)

7.23 - 7.19	4 H	m		C ₆ H ₅ and <i>m</i> -C ₆ H ₃ Me ₂
7.04 - 7.03	3 H	m		C ₆ H ₅ and <i>m</i> -C ₆ H ₃ Me ₂
6.88	1 H	t	³ J = 7.3	<i>p</i> -C ₆ H ₃ Me ₂
3.25	1 H	m		CN ₂ CH ₂
2.70	1 H	m		CN ₂ CH ₂
2.62	3 H	s		NMe
2.61	6 H	s		C ₆ H ₃ Me ₂
2.12	1 H	m		CH ₂ NMe ₂
1.80	3 H	s		NMe
1.77	1 H	m		CH ₂ NMe ₂
1.32	9 H	s		CMe ₃
0.14	9 H	s		SiMe ₃

¹³C-{¹H} NMR data: (C₆D₆, 125.7 MHz, 293 K)

174.06	CN ₂
161.70	<i>ipso</i> -C ₆ H ₃ Me ₂
136.03	<i>ipso</i> -C ₆ H ₅
129.68	C ₆ H ₅ or <i>o</i> - or <i>m</i> -C ₆ H ₃ Me ₂
128.52	C ₆ H ₅ or <i>o</i> - or <i>m</i> -C ₆ H ₃ Me ₂
128.50	C ₆ H ₅ or <i>o</i> - or <i>m</i> -C ₆ H ₃ Me ₂
127.68	C ₆ H ₅ or <i>o</i> - or <i>m</i> -C ₆ H ₃ Me ₂
126.54	C ₆ H ₅ or <i>o</i> - or <i>m</i> -C ₆ H ₃ Me ₂ *
118.25	<i>para</i> -C ₆ H ₃ Me ₂
68.39	CMe ₃

63.11	CN ₂ CH ₂
49.49	NMe
46.88	CH ₂ NMe ₂
45.20	NMe
33.57	CMe ₃
18.50	C ₆ H ₃ Me ₂
2.32	SiMe ₃

*other resonances obscured by solvent

I.R. data: (NaCl plates, Nujol mull, cm⁻¹)

4331 (m), 4258 (m), 4065 (w), 2727 (m), 2361 (m), 2342 (w), 1950 (w), 1889 (w), 1828 (w), 1771 (w), 1592(m), 1505 (m) 1405 (m), 1349 (s), 1330(m), 1290 (m), 1262 (m), 1249 (s), 1232 (s), 1207 (m), 1159 (w), 1126(m), 1090 (s), 1063 (w), 1025 (s), 947 (m), 934 (m), 919 (m), 892 (s), 868 (s), 840 (s), 820 (m), 805 (m), 759 (s), 740 (w), 723 (m), 703 (m), 669 (w), 629 (w).

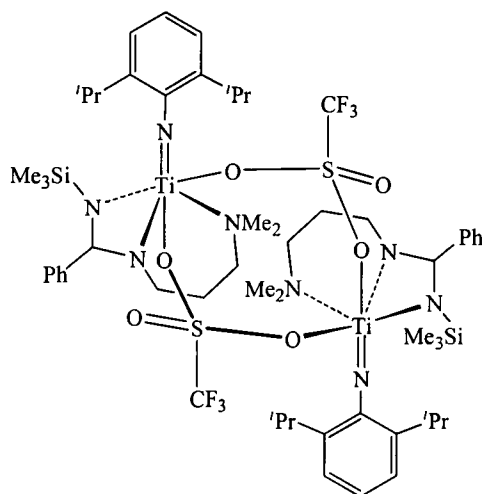
Elemental analysis for C₂₆H₄₅N₄TiOSi:

Found (calculated): C 58.2 (61.8), H 8.4 (9.0), N 9.6 (11.1) %

E.I. mass spectrum:

A satisfactory mass spectrum could not be obtained for this compound.

6.3.10 [Ti(N-2,6-*i*Pr₂C₆H₃){Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂}OTf]₂ (33)



¹H NMR data: (C₆D₆, 500.0 MHz, 293 K)

7.20	2 H	app s, br	<i>o</i> -C ₆ H ₅
7.03	3 H	m	<i>m</i> - and <i>p</i> -C ₆ H ₅

6.99	2 H	d	$^3J = 7.8$	<i>m</i> -C ₆ H ₃ ^{<i>i</i>} Pr ₂
6.83	1 H	t	$^3J = 7.8$	<i>p</i> -C ₆ H ₃ ^{<i>i</i>} Pr ₂
3.12	1 H	m		CN ₂ CH ₂
2.96	2 H	m		CH ₂ NMe ₂ and CN ₂ CH ₂
2.67	3 H	s		NMe
1.83	3 H	s		NMe
1.68	1 H	m		CH ₂ NMe ₂
1.43	12 H	app t	$^3J = 7.3$	CHMe ₂
0.97	1 H	m		CH ₂ CH ₂ CH ₂
0.89	1 H	m		CH ₂ CH ₂ CH ₂
0.17	9 H	s		SiMe ₃

¹³C-{¹H} NMR data: (C₆D₆, 75.5 MHz, 293 K)

176.31	CN ₂
158.12	<i>ipso</i> -C ₆ H ₃ ^{<i>i</i>} Pr ₂
143.60	<i>ipso</i> -C ₆ H ₅
134.02	<i>o</i> -C ₆ H ₃ ^{<i>i</i>} Pr ₂
130.10	C ₆ H ₅
127.14	C ₆ H ₅ *
123.00	<i>p</i> -C ₆ H ₃ ^{<i>i</i>} Pr ₂
122.48	<i>m</i> -C ₆ H ₃ ^{<i>i</i>} Pr ₂
62.18	CH ₂ NMe ₂
51.65	NMe
45.42	CN ₂ CH ₂
43.58	NMe
27.92	CH ₂ CH ₂ CH ₂
25.00	CHMe ₂
24.83	CHMe ₂
24.33	CHMe ₂
1.65	SiMe ₃

*other C₆H₅ resonances obscured by solvent

¹⁹F NMR data: (C₆D₆, 282.2 MHz, 293 K)

-58.46	CF ₃

I.R. data: (NaCl plates, Nujol mull, cm^{-1})

3051 (m), 2718 (m), 2408 (w), 2340 (w), 2197 (w), 1979 (w), 1962 (w), 1911 (w), 1900 (w), 1853 (w), 1822 (w), 1776 (w), 1697 (w), 1650 (w), 1600 (w), 1579 (w), 1512 (s), 1485 (s), 1423 (s), 1351 (s), 1329 (s), 1206 (s), 1110 (m), 1073 (m), 1057 (m), 1027 (s), 1006 (s), 975 (m), 959 (m), 950 (m), 928 (m), 895 (m), 666 (w), 568 (m), 593 (m).

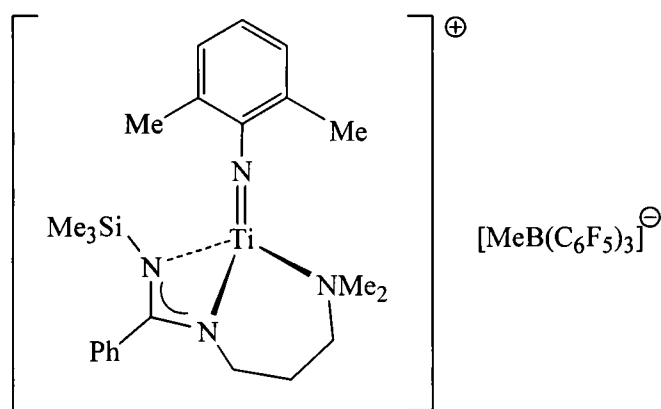
Elemental analysis for $\text{C}_{58}\text{H}_{86}\text{N}_8\text{F}_6\text{O}_6\text{S}_2\text{Si}_2\text{Ti}_2$:

Found (calculated): C 50.1 (52.7), H 6.7 (6.6), N 8.5 (8.5) %

E.I. mass spectrum:

A satisfactory mass spectrum could not be obtained for this compound

6.3.11 $[\text{Ti}(\text{N}-2,6\text{-C}_6\text{H}_3\text{Me}_2)\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}][\text{MeB}(\text{C}_6\text{F}_5)_3]$
(34- $\text{MeB}(\text{C}_6\text{F}_5)_4$)



Compound synthesised on the NMR scale only

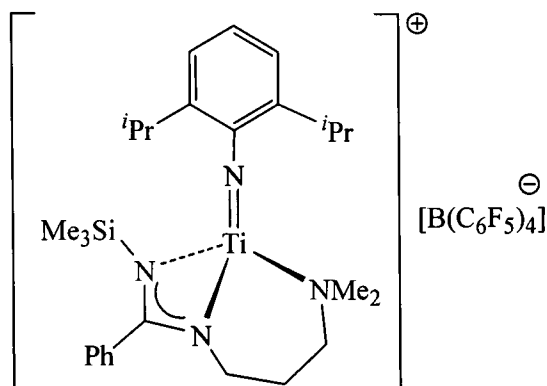
^1H NMR data: ($\text{C}_6\text{D}_5\text{Br}$, 300.0 MHz, 293 K)

7.2 - 7.0	5 H	m		C_6H_5
6.81	2 H	app d	app J = 7.1	<i>m</i> - $\text{C}_6\text{H}_3\text{Me}_2$
6.54	1 H	t	$^3\text{J} = 7.6$	<i>p</i> - $\text{C}_6\text{H}_3\text{Me}_2$
2.9 - 1.9	12 H	m, br		CH of pendant arm and NMe_2 , overlapping
2.28	6 H	s		$\text{C}_6\text{H}_3\text{Me}_2$
1.27	3 H	s, br		$\text{MeB}(\text{C}_6\text{F}_5)_3$
-0.27	9 H	s		SiMe_3

^{19}F NMR data: (C_6D_6 , 282.2 MHz, 293 K)

-131.01	6 F	app s	<i>o</i> - C_6F_5
-155.40	6 F	app s	<i>m</i> - C_6F_5
-162.10	3 F	app s	<i>p</i> - C_6F_5

6.3.12 $[\text{Ti}(\text{N}-2,6\text{-C}_6\text{H}_3^i\text{Pr}_2)\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}][\text{B}(\text{C}_6\text{F}_5)_4](35\text{-B}(\text{C}_6\text{F}_5)_4)$



Compound only synthesised on the NMR scale

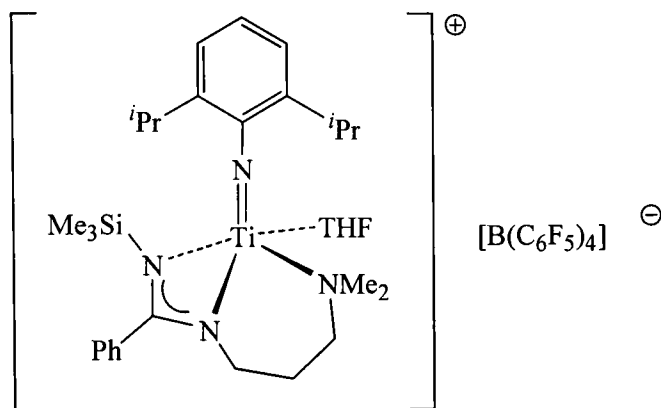
^1H NMR data: (CD_2Cl_2 , 500.0 MHz, 293 K)

7.10 - 7.40	5 H	m, br	C_6H_5
6.95	2 H	app d	<i>m</i> - $\text{C}_6\text{H}_3^i\text{Pr}_2$
6.86	1 H	t	<i>p</i> - $\text{C}_6\text{H}_3^i\text{Pr}_2$
		$^3J = 7.8$	
4.21	2 H	s, br	CHMe_2
3.72	1 H	s, br	CH of pendant arm
3.53	1 H	s, br	CH of pendant arm
3.34	3 H	s	NMe
3.21	1 H	s, br	CH of pendant arm
2.84	1 H	m, br	CH of pendant arm
2.46	3 H	s	NMe
1.88	1 H	s, br	CH of pendant arm
1.29	12 H	s, br	CHMe_2
1.13	1 H	s	CH of pendant arm
-0.02	9 H	s	SiMe_3

^{19}F NMR data: (C_6D_6 , 282.2 MHz, 293 K)

-133.36	8 F	app s	<i>o</i> - C_6F_5
-163.23	8 F	app s	<i>m</i> - C_6F_5
-167.19	4 F	app s	<i>p</i> - C_6F_5

6.3.13 $[\text{Ti}(\text{N}-2,6\text{-C}_6\text{H}_3^i\text{Pr}_2)\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}\text{THF}][\text{B}(\text{C}_6\text{F}_5)_4]$
(36-B(C_6F_5) $_4$)



^1H NMR data: (CD_2Cl_2 , 500.0 MHz, 293 K)

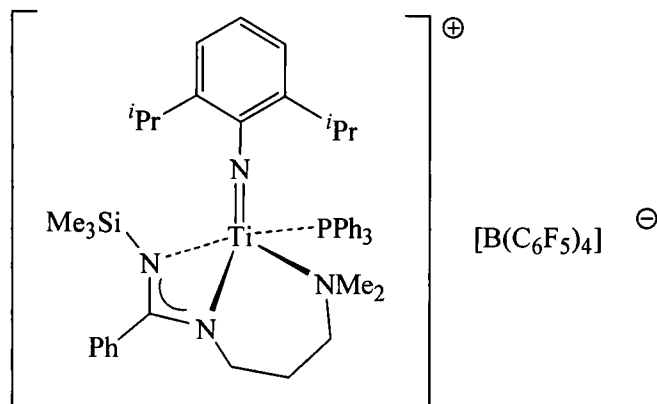
7.16 - 7.38	5 H	m, br		C_6H_5
6.92	2 H	app d	app J = 7.8	<i>m</i> - $\text{C}_6\text{H}_3^i\text{Pr}_2$
6.79	1 H	app s		<i>p</i> - $\text{C}_6\text{H}_3^i\text{Pr}_2$
4.63	1 H	m		OCH_2CH_2
4.55	1 H	m		OCH_2CH_2
3.99	2 H	sept	$^3\text{J} = 6.8$	CHMe_2
3.58	3 H	m		CH of pendant arm
3.27	1 H	m		CH of pendant arm
3.14	3 H	s		NMe
2.80	1 H	m		CH of pendant arm
2.34	5 H	s, br		NMe, OCH_2CH_2 overlapping
1.78	1 H	s, br		CH of pendant arm
1.26	12 H	app t	app J = 8.8	CHMe_2
-0.05	9 H	s		SiMe_3

^{19}F NMR data: (C_6D_6 , 282.2 MHz, 293 K)

-133.15	8 F	app s	<i>o</i> - C_6F_5

-163.62	8 F	app s	<i>m</i> -C ₆ F ₅
-167.51	4 F	app s	<i>p</i> -C ₆ F ₅

6.3.14 [Ti(N-2,6-C₆H₃^{*i*}Pr₂){Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂}PPh₃][B(C₆F₅)₄] (37-B(C₆F₅)₄)



Data reported for compound synthesised on the NMR scale.

¹H NMR data: (CD₂Cl₂, 500.0 MHz, 293 K)

6.6 - 8.0	33 H	several resonances	PPh ₃ , Ph ₃ CMe, C ₆ H ₅ and C ₆ H ₃ Me ₂
4.46	2 H	sept ³ J = 6.8	CHMe ₂
3.56	1 H	m	CH of pendant arm
3.43	1 H	m	CH of pendant arm
3.27	1 H	m	CH of pendant arm
3.10	3 H	s	NMe
2.66	1 H	m	CH of pendant arm
2.43	3 H	s	NMe
1.91	1 H	m	CH of pendant arm
1.73	1 H	m	CH of pendant arm
1.26	12 H	app d app J = 7.3	CHMe ₂
-0.13	9 H	s	SiMe ₃

¹⁹F NMR data: (CD₂Cl₂, 282.2 MHz, 293 K)

-133.16	8 F	app s	<i>o</i> -C ₆ F ₅
-163.50	8 F	app s	<i>m</i> -C ₆ F ₅
-167.38	4 F	app s	<i>p</i> -C ₆ F ₅

^{31}P NMR data: (CD_2Cl_2 , 121.5 MHz, 293 K)

96.0

PPh_3

Appendices

[Ti(N^tBu){Me₃SiNC(Ph)NCH₂CH₂NMe₂}Cl] (1)

A1. Crystal data and structure refinement

Empirical formula	C ₁₈ H ₃₃ ClN ₄ SiTi
Formula weight	416.93
Crystal description	yellow block
Crystal size	0.40 x 0.30 x 0.10 mm
Temperature	150 K
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
Unit cell dimensions	<i>a</i> = 11.7460(3) Å α = 90 ° <i>b</i> = 9.9836(3) Å β = 90.265(1) ° <i>c</i> = 20.1557(7) Å γ = 90 °
Reflections for cell refinement	3916
Range in θ	2.910 to 26.022 °
Volume, <i>Z</i>	2363.6 Å ³ , 4
Density (calculated)	1.17 Mg/m ³
Absorption coefficient	0.53 mm ⁻¹
<i>F</i> (000)	888
Diffractometer type	Nonius Kappa CCD
Wavelength	0.71073 Å
Scan type	ω -2 θ
θ range for data collection	3.03 to 26.01 °
Index ranges	-13 ≤ <i>h</i> ≤ 14, -10 ≤ <i>k</i> ≤ 12, -24 ≤ <i>l</i> ≤ 24
Reflections collected	7790
Independent reflections	4570 [<i>R</i> _{merge} = 0.02]
Observed reflections	3204 [<i>I</i> > 3 σ (<i>I</i>)]
Absorption correction	Multi-scan (<i>T</i> _{min} = 0.853, <i>T</i> _{max} = 0.948)
Structure solution by	direct methods and Fourier difference maps
Hydrogen atom location	geometric

Hydrogen atom treatment	riding model
Refinement method	Full-matrix least-squares on F
Weighting scheme	Chebychev polynomial
Data / restraints / parameters	3204 / 0 / 227
Goodness-of-fit on F	1.0513
Final R indices [$I > 3\sigma(I)$]	$R_1 = 0.0329$, $R_w = 0.0366$
Extinction coefficient	251(35)
Final maximum δ/σ	0.0065
Largest diff. peak and hole	0.22 and -0.27 e.Å ⁻³

A2. Bond lengths (Å) and angles (°)

Ti(1)-N(1)	1.688(2)	Ti(1)-N(2)	2.126(2)
Ti(1)-N(3)	2.095(2)	Ti(1)-N(4)	2.248(2)
Ti(1)-Cl(1)	2.3231(6)	Ti(1)-C(5)	2.486(2)
N(1)-C(1)	1.454(3)	N(2)-Si(1)	1.735(2)
N(2)-C(5)	1.339(3)	N(3)-C(5)	1.325(3)
N(3)-C(12)	1.450(3)	N(4)-C(13)	1.486(3)
N(4)-C(14)	1.480(3)	N(4)-C(15)	1.485(3)
Si(1)-C(16)	1.863(3)	Si(1)-C(17)	1.861(3)
Si(1)-C(18)	1.854(3)	C(1)-C(2)	1.520(4)
C(1)-C(3)	1.532(3)	C(1)-C(4)	1.523(4)
C(5)-C(6)	1.490(3)	C(6)-C(7)	1.390(3)
C(6)-C(11)	1.391(3)	C(7)-C(8)	1.382(3)
C(8)-C(9)	1.383(3)	C(9)-C(10)	1.383(3)
C(10)-C(11)	1.386(3)	C(12)-C(13)	1.528(3)
N(1)-Ti(1)-N(2)	116.07(8)	N(1)-Ti(1)-N(3)	107.85(8)
N(2)-Ti(1)-N(3)	63.14(6)	N(1)-Ti(1)-N(4)	106.08(8)
N(2)-Ti(1)-N(4)	126.47(7)	N(3)-Ti(1)-N(4)	73.89(6)
N(1)-Ti(1)-Cl(1)	109.42(6)	N(2)-Ti(1)-Cl(1)	99.56(5)
N(3)-Ti(1)-Cl(1)	142.73(5)	N(4)-Ti(1)-Cl(1)	95.79(5)
N(1)-Ti(1)-C(5)	123.53(8)	N(2)-Ti(1)-C(5)	32.59(6)
N(3)-Ti(1)-C(5)	32.20(6)	N(4)-Ti(1)-C(5)	96.42(7)

Cl(1)-Ti(1)-C(5)	119.08(5)	Ti(1)-N(1)-C(1)	175.0(2)
Ti(1)-N(2)-Si(1)	138.62(9)	Ti(1)-N(2)-C(5)	88.7(1)
Si(1)-N(2)-C(5)	132.3(1)	Ti(1)-N(3)-C(5)	90.4(1)
Ti(1)-N(3)-C(12)	123.8(1)	C(5)-N(3)-C(12)	125.7(2)
Ti(1)-N(4)-C(13)	107.9(1)	Ti(1)-N(4)-C(14)	108.8(1)
C(13)-N(4)-C(14)	109.8(2)	Ti(1)-N(4)-C(15)	111.4(1)
C(13)-N(4)-C(15)	109.9(2)	C(14)-N(4)-C(15)	108.9(2)
N(2)-Si(1)-C(16)	110.1(1)	N(2)-Si(1)-C(17)	111.7(1)
C(16)-Si(1)-C(17)	110.8(1)	N(2)-Si(1)-C(18)	105.5(1)
C(16)-Si(1)-C(18)	109.7(1)	C(17)-Si(1)-C(18)	108.9(1)
N(1)-C(1)-C(2)	108.7(2)	N(1)-C(1)-C(3)	108.1(2)
C(2)-C(1)-C(3)	111.0(2)	N(1)-C(1)-C(4)	109.3(2)
C(2)-C(1)-C(4)	110.3(2)	C(3)-C(1)-C(4)	109.4(2)
Ti(1)-C(5)-N(2)	58.8(1)	Ti(1)-C(5)-N(3)	57.4(1)
N(2)-C(5)-N(3)	112.1(2)	Ti(1)-C(5)-C(6)	159.6(1)
N(2)-C(5)-C(6)	125.3(2)	N(3)-C(5)-C(6)	122.6(2)
C(5)-C(6)-C(7)	121.5(2)	C(5)-C(6)-C(11)	118.8(2)
C(7)-C(6)-C(11)	119.6(2)	C(6)-C(7)-C(8)	120.1(2)
C(7)-C(8)-C(9)	119.8(2)	C(8)-C(9)-C(10)	120.6(2)
C(9)-C(10)-C(11)	119.6(2)	C(6)-C(11)-C(10)	120.2(2)
N(3)-C(12)-C(13)	103.8(2)	N(4)-C(13)-C(12)	110.2(2)

[Ti(N^tBu){Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂}Cl] (4)**B1. Crystal data and refinement details**

Empirical formula	C ₁₉ H ₃₅ N ₄ ClSiTi
Formula weight	430.96
Crystal description:	Yellow fragment
Crystal size:	0.18 x 0.34 x 0.42 mm
Temperature (K)	150
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P \bar{1}$
Unit cell dimensions	$a = 8.5998(2) \text{ \AA}$ $\alpha = 75.3970(10)^\circ$ $b = 10.9442(2) \text{ \AA}$ $\beta = 76.4740(8)^\circ$ $c = 13.8813(3) \text{ \AA}$ $\gamma = 73.0526(9)^\circ$
Volume, Z	1191.08(4) Å ³ , 2
Calculated density	1.202 Mg/m ³
Absorption coefficient	0.532 mm ⁻¹
F000	460
Absorption correction	Semi-empirical from equivalent reflections
Transmission coefficients	0.80, 0.91(min,max)
θ range for data collection	$5.0 \leq \theta \leq 27.5^\circ$
Index ranges	$-10 \leq h \leq 11$, $-13 \leq k \leq 14$, $0 \leq l \leq 18$
Reflections measured	15717
Unique reflections	5403
R _{int}	0.029
Observed reflections [$I > 3\sigma(I)$]	4112
Refinement method	Full-matrix least-squares on F
Parameters refined	235
Weighting scheme	Chebychev 3-term polynomial
Goodness of fit	1.0752
R ₁	0.0321

R_w	0.0372
Residual electron density	-0.34, 0.30 eÅ ⁻³

2. Bond lengths and angles

Ti(1)-Cl(1)	2.3429(5)	C(6)-C(7)	1.522(2)
Ti(1)-N(1)	1.6932(13)	C(7)-C(8)	1.521(3)
Ti(1)-N(2)	2.1479(13)	C(8)-N(4)	1.500(2)
Ti(1)-N(3)	2.0933(14)	N(4)-C(18)	1.481(2)
Ti(1)-N(4)	2.2391(14)	N(4)-C(19)	1.484(2)
N(1)-C(1)	1.449(2)	Si(1)-C(9)	1.863(2)
C(1)-C(2)	1.528(3)	Si(1)-C(10)	1.869(2)
C(1)-C(3)	1.523(2)	Si(1)-C(11)	1.870(2)
C(1)-C(4)	1.527(2)	C(12)-C(13)	1.390(2)
N(2)-C(5)	1.334(2)	C(12)-C(17)	1.390(2)
N(2)-Si(1)	1.7388(14)	C(13)-C(14)	1.394(2)
C(5)-N(3)	1.320(2)	C(14)-C(15)	1.387(3)
C(5)-C(12)	1.502(2)	C(15)-C(16)	1.382(3)
N(3)-C(6)	1.457(2)	C(16)-C(17)	1.390(2)
Cl(1)-Ti(1)-N(1)	113.75(5)	C(5)-N(3)-C(6)	122.46(14)
Cl(1)-Ti(1)-N(2)	101.83(4)	N(3)-C(6)-C(7)	109.34(14)
N(1)-Ti(1)-N(2)	104.42(6)	C(6)-C(7)-C(8)	114.11(15)
Cl(1)-Ti(1)-N(3)	135.58(4)	C(7)-C(8)-N(4)	116.62(15)
N(1)-Ti(1)-N(3)	110.56(6)	Ti(1)-N(4)-C(8)	112.68(10)
N(2)-Ti(1)-N(3)	63.38(5)	Ti(1)-N(4)-C(18)	109.58(11)
Cl(1)-Ti(1)-N(4)	94.21(4)	C(8)-N(4)-C(18)	110.28(14)
N(1)-Ti(1)-N(4)	99.04(6)	Ti(1)-N(4)-C(19)	109.46(11)
N(2)-Ti(1)-N(4)	143.00(5)	C(8)-N(4)-C(19)	107.09(14)
N(3)-Ti(1)-N(4)	81.81(5)	C(18)-N(4)-C(19)	107.60(14)
Ti(1)-N(1)-C(1)	173.35(11)	N(2)-Si(1)-C(9)	105.70(8)
N(1)-C(1)-C(2)	108.47(14)	N(2)-Si(1)-C(10)	110.35(9)
N(1)-C(1)-C(3)	108.78(13)	C(9)-Si(1)-C(10)	110.74(10)
C(2)-C(1)-C(3)	109.94(16)	N(2)-Si(1)-C(11)	113.21(8)
N(1)-C(1)-C(4)	109.99(14)	C(9)-Si(1)-C(11)	107.53(11)

C(2)-C(1)-C(4)	109.86(17)	C(10)-Si(1)-C(11)	109.24(12)
C(3)-C(1)-C(4)	109.78(16)	C(5)-C(12)-C(13)	120.33(14)
Ti(1)-N(2)-C(5)	88.45(9)	C(5)-C(12)-C(17)	119.91(14)
Ti(1)-N(2)-Si(1)	136.23(8)	C(13)-C(12)-C(17)	119.70(15)
C(5)-N(2)-Si(1)	129.51(11)	C(12)-C(13)-C(14)	119.95(15)
N(2)-C(5)-N(3)	114.18(14)	C(13)-C(14)-C(15)	119.91(15)
N(2)-C(5)-C(12)	124.27(14)	C(14)-C(15)-C(16)	120.22(15)
N(3)-C(5)-C(12)	121.51(14)	C(15)-C(16)-C(17)	120.03(16)
Ti(1)-N(3)-C(5)	91.17(9)	C(12)-C(17)-C(16)	120.18(16)
Ti(1)-N(3)-C(6)	136.15(11)		

[Ti(N-2,6-C₆H₃Me₂){Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂}Cl] (5)**C1. Crystal data and structure refinement**

Empirical formula	C ₂₃ H ₃₅ N ₄ ClSiTi
Formula weight	479.00
Crystal description	red block
Crystal size	0.50 x 0.40 x 0.40 mm
Temperature	150 K
Crystal system	Triclinic
Space group	$P \bar{1}$
Unit cell dimensions	$a = 8.8806(1) \text{ \AA}$ $\alpha = 70.6889(7)^\circ$ $b = 11.2263(1) \text{ \AA}$ $\beta = 88.3802(5)^\circ$ $c = 15.0212(2) \text{ \AA}$ $\gamma = 66.8105(5)^\circ$
Reflections for cell refinement	5532
Range in θ	2.910 to 27.485 °
Volume, Z	1290.11(3) Å ³ , 2
Density (calculated)	1.23 Mg/m ³
Absorption coefficient	0.50 mm ⁻¹
F(000)	508.94
Diffractometer type	Nonius Kappa CCD
Wavelength	0.71073 Å
Scan type	CCD
θ range for data collection	2.91 to 27.45 °
Index ranges	$-11 \leq h \leq 11$, $-13 \leq k \leq 14$, $0 \leq l \leq 19$
Reflections collected	11005
Independent reflections	5879 [$R_{\text{merge}} = 0.01$]
Observed reflections	4948 [$I > 3\sigma(I)$]
Absorption correction	Multi-scan ($T_{\text{min}}=0.819$, $T_{\text{max}}=0.819$)
Structure solution by	direct methods and Fourier difference maps
Hydrogen atom location	geometric
Hydrogen atom treatment	riding model

Refinement method	Full-matrix least-squares on F
Weighting scheme	calc
Data / restraints / parameters	4948 / 0/ 272
Goodness-of-fit on F	1.0209
Final R indices [$I > 3\sigma(I)$]	$R_1 = 0.0308$, $R_w = 0.0318$
Extinction coefficient	185(40)
Final maximum δ / σ	0.0008
Largest diff. peak and hole	0.31 and -0.34 e. $\text{\AA}^{-3}$

C2. Selected bond lengths ($\text{\AA}$) and angles ($^\circ$)

Ti(1)-Cl(1)	2.3234(4)	Ti(1)-N(1)	1.713(1)
Ti(1)-N(2)	2.124(1)	Ti(1)-N(3)	2.080(1)
Ti(1)-N(4)	2.223(1)	N(1)-C(1)	1.377(2)
N(2)-Si(1)	1.734(1)	N(2)-C(9)	1.337(2)
N(3)-C(9)	1.316(2)	N(3)-C(16)	1.455(2)
N(4)-C(18)	1.499(2)	N(4)-C(19)	1.487(2)
N(4)-C(20)	1.487(2)	Si(1)-C(21)	1.859(2)
Si(1)-C(22)	1.863(2)	Si(1)-C(23)	1.868(2)
C(1)-C(2)	1.416(2)	C(1)-C(6)	1.413(2)
C(2)-C(3)	1.394(2)	C(2)-C(7)	1.500(2)
C(3)-C(4)	1.377(3)	C(4)-C(5)	1.383(3)
C(5)-C(6)	1.393(2)	C(6)-C(8)	1.503(2)
C(9)-C(10)	1.498(2)	C(10)-C(11)	1.388(2)
C(10)-C(15)	1.389(2)	C(11)-C(12)	1.390(2)
C(12)-C(13)	1.383(2)	C(13)-C(14)	1.380(2)
C(14)-C(15)	1.390(2)	C(16)-C(17)	1.525(2)
C(17)-C(18)	1.525(2)		
Cl(1)-Ti(1)-N(1)	113.67(4)	Cl(1)-Ti(1)-N(2)	101.07(3)
N(1)-Ti(1)-N(2)	104.53(4)	Cl(1)-Ti(1)-N(3)	136.08(3)
N(1)-Ti(1)-N(3)	110.09(5)	N(2)-Ti(1)-N(3)	63.71(4)
Cl(1)-Ti(1)-N(4)	94.13(3)	N(1)-Ti(1)-N(4)	98.13(4)
N(2)-Ti(1)-N(4)	144.58(4)	N(3)-Ti(1)-N(4)	83.16(4)

Ti(1)-N(1)-C(1)	178.58(9)	Ti(1)-N(2)-Si(1)	129.04(6)
Ti(1)-N(2)-C(9)	89.77(7)	Si(1)-N(2)-C(9)	131.58(8)
Ti(1)-N(3)-C(9)	92.26(7)	Ti(1)-N(3)-C(16)	138.75(8)
C(9)-N(3)-C(16)	125.4(1)	Ti(1)-N(4)-C(18)	112.12(7)
Ti(1)-N(4)-C(19)	111.76(8)	C(18)-N(4)-C(19)	110.0(1)
Ti(1)-N(4)-C(20)	107.41(8)	C(18)-N(4)-C(20)	107.4(1)
C(19)-N(4)-C(20)	108.0(1)	N(2)-Si(1)-C(21)	105.60(7)
N(2)-Si(1)-C(22)	108.60(7)	C(21)-Si(1)-C(22)	111.01(13)
N(2)-Si(1)-C(23)	115.37(6)	C(21)-Si(1)-C(23)	109.33(9)
C(22)-Si(1)-C(23)	106.97(9)	N(1)-C(1)-C(2)	119.68(12)
N(1)-C(1)-C(6)	120.35(11)	C(2)-C(1)-C(6)	119.97(12)
C(1)-C(2)-C(3)	118.63(14)	C(1)-C(2)-C(7)	120.19(12)
C(3)-C(2)-C(7)	121.18(13)	C(2)-C(3)-C(4)	121.41(14)
C(3)-C(4)-C(5)	119.93(13)	C(4)-C(5)-C(6)	121.1(2)
C(1)-C(6)-C(5)	118.92(13)	C(1)-C(6)-C(8)	120.30(12)
C(5)-C(6)-C(8)	120.78(13)	Ti(1)-C(9)-N(2)	57.98(6)
Ti(1)-C(9)-N(3)	56.07(6)	N(2)-C(9)-N(3)	113.5(1)
Ti(1)-C(9)-C(10)	174.07(8)	N(2)-C(9)-C(10)	122.1(1)
N(3)-C(9)-C(10)	124.35(11)	C(9)-C(10)-C(11)	118.97(11)
C(9)-C(10)-C(15)	121.27(11)	C(11)-C(10)-C(15)	119.65(12)
C(10)-C(11)-C(12)	120.16(13)	C(11)-C(12)-C(13)	119.95(13)
C(12)-C(13)-C(14)	120.02(12)	C(13)-C(14)-C(15)	120.37(13)
C(10)-C(15)-C(14)	119.82(13)	N(3)-C(16)-C(17)	110.0(1)
C(16)-C(17)-C(18)	114.57(11)	N(4)-C(18)-C(17)	115.8(1)

[Ti(N-2,6-C₆H₃ⁱPr₂)(Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂)Cl] (6)

D1. Crystal data and structure refinement

Empirical formula	C ₂₇ H ₄₃ ClN ₄ SiTi
Formula weight	535.10
Crystal description	red-orange block
Crystal size	0.21 x 0.19 x 0.13 mm
Temperature	150 K
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
Unit cell dimensions	<i>a</i> = 16.0613(5) Å α = 90 ° <i>b</i> = 11.3483(4) Å β = 112.749(2) ° <i>c</i> = 17.5211(6) Å γ = 90 °
Reflections for cell refinement	5532
Range in θ	5.097 to 27.485 °
Volume, <i>Z</i>	2945.1(2) Å ³ , 4
Density (calculated)	1.207 Mg/m ³
Absorption coefficient	0.443 mm ⁻¹
<i>F</i> (000)	1146.13
Diffractometer type	Nonius Kappa CCD
Wavelength	0.71073 Å
Scan type	CCD
θ range for data collection	2.9 to 27.5 °
Index ranges	-20 ≤ <i>h</i> ≤ 19, 0 ≤ <i>k</i> ≤ 14, 0 ≤ <i>l</i> ≤ 22
Reflections collected	10992
Independent reflections	6629 [<i>R</i> _{merge} = 0.03]
Observed reflections	3325 [<i>I</i> > 3σ(<i>I</i>)]
Absorption correction	Multi-scan (<i>T</i> _{min} = 0.919, <i>T</i> _{max} = 0.944)
Structure solution by	direct methods and Fourier difference maps
Hydrogen atom location	geometric

Hydrogen atom treatment	riding model
Refinement method	Full-matrix least-squares on F
Weighting scheme	calc
Data / restraints / parameters	3325 / 0 / 308
Goodness-of-fit on F	1.1162
Final R indices [$I > 3\sigma(I)$]	$R_1 = 0.0411$, $R_w = 0.0254$
Extinction coefficient	0 (none required)
Final maximum δ / σ	0.006
Largest diff. peak and hole	0.35 and -0.32 e.Å ⁻³

D2. Bond lengths (Å) and angles (°).

Ti(1)-Cl(1)	2.3386(9)	Ti(1)-N(1)	1.713(3)
Ti(1)-N(2)	2.110(2)	Ti(1)-N(3)	2.085(2)
Ti(1)-N(4)	2.228(3)	Ti(1)-C(1)	2.522(3)
N(1)-C(1)	1.392(4)	N(2)-Si(1)	1.735(3)
N(2)-C(13)	1.340(4)	N(3)-C(13)	1.317(4)
N(3)-C(20)	1.451(3)	N(4)-C(22)	1.503(4)
N(4)-C(23)	1.486(4)	N(4)-C(24)	1.485(4)
Si(1)-C(25)	1.863(4)	Si(1)-C(26)	1.859(3)
Si(1)-C(27)	1.867(3)	C(1)-C(2)	1.420(4)
C(1)-C(6)	1.422(4)	C(2)-C(3)	1.387(5)
C(2)-C(7)	1.520(4)	C(3)-C(4)	1.387(4)
C(4)-C(5)	1.385(5)	C(5)-C(6)	1.387(5)
C(6)-C(10)	1.510(4)	C(7)-C(8)	1.538(4)
C(7)-C(9)	1.522(5)	C(10)-C(11)	1.524(5)
C(10)-C(12)	1.524(5)	C(13)-C(14)	1.490(4)
C(14)-C(15)	1.389(5)	C(14)-C(19)	1.393(5)
C(15)-C(16)	1.395(5)	C(16)-C(17)	1.372(5)
C(17)-C(18)	1.376(5)	C(18)-C(19)	1.384(5)
C(20)-C(21)	1.526(4)	C(21)-C(22)	1.526(4)
Cl(1)-Ti(1)-N(1)	111.32(9)	Cl(1)-Ti(1)-N(2)	98.93(7)
N(1)-Ti(1)-N(2)	109.03(12)	Cl(1)-Ti(1)-N(3)	141.11(8)

N(1)-Ti(1)-N(3)	107.30(11)	N(2)-Ti(1)-N(3)	63.51(9)
Cl(1)-Ti(1)-N(4)	93.38(7)	N(1)-Ti(1)-N(4)	102.19(11)
N(2)-Ti(1)-N(4)	139.2(1)	N(3)-Ti(1)-N(4)	82.7(1)
Cl(1)-Ti(1)-C(13)	123.97(7)	N(1)-Ti(1)-C(13)	110.87(12)
N(2)-Ti(1)-C(13)	32.09(9)	N(3)-Ti(1)-C(13)	31.44(9)
N(4)-Ti(1)-C(13)	111.7(1)	Ti(1)-N(1)-C(1)	175.0(2)
Ti(1)-N(2)-Si(1)	133.83(13)	Ti(1)-N(2)-C(13)	91.2(2)
Si(1)-N(2)-C(13)	134.5(2)	Ti(1)-N(3)-C(13)	92.9(2)
Ti(1)-N(3)-C(20)	139.9(2)	C(13)-N(3)-C(20)	126.9(2)
Ti(1)-N(4)-C(22)	114.2(2)	Ti(1)-N(4)-C(23)	108.6(2)
C(22)-N(4)-C(23)	110.2(2)	Ti(1)-N(4)-C(24)	107.9(2)
C(22)-N(4)-C(24)	107.0(2)	C(23)-N(4)-C(24)	108.8(3)
N(2)-Si(1)-C(25)	113.91(14)	N(2)-Si(1)-C(26)	109.2(2)
C(25)-Si(1)-C(26)	109.4(2)	N(2)-Si(1)-C(27)	105.73(14)
C(25)-Si(1)-C(27)	109.1(2)	C(26)-Si(1)-C(27)	109.3(2)
N(1)-C(1)-C(2)	120.2(3)	N(1)-C(1)-C(6)	119.6(3)
C(2)-C(1)-C(6)	120.2(3)	C(1)-C(2)-C(3)	118.6(3)
C(1)-C(2)-C(7)	120.0(3)	C(3)-C(2)-C(7)	121.3(3)
C(2)-C(3)-C(4)	121.4(3)	C(3)-C(4)-C(5)	119.7(3)
C(4)-C(5)-C(6)	121.7(3)	C(1)-C(6)-C(5)	118.4(3)
C(1)-C(6)-C(10)	121.0(3)	C(5)-C(6)-C(10)	120.7(3)
C(2)-C(7)-C(8)	112.8(3)	C(2)-C(7)-C(9)	110.4(3)
C(8)-C(7)-C(9)	111.3(3)	C(6)-C(10)-C(11)	112.7(3)
C(6)-C(10)-C(12)	110.3(3)	C(11)-C(10)-C(12)	110.9(3)
Ti(1)-C(13)-N(2)	56.7(2)	Ti(1)-C(13)-N(3)	55.6(2)
N(2)-C(13)-N(3)	112.4(3)	Ti(1)-C(13)-C(14)	178.1(2)
N(2)-C(13)-C(14)	123.1(3)	N(3)-C(13)-C(14)	124.6(3)
C(13)-C(14)-C(15)	120.4(3)	C(13)-C(14)-C(19)	120.5(3)
C(15)-C(14)-C(19)	119.0(3)	C(14)-C(15)-C(16)	120.1(3)
C(15)-C(16)-C(17)	120.0(4)	C(16)-C(17)-C(18)	120.4(3)
C(17)-C(18)-C(19)	120.1(4)	C(14)-C(19)-C(18)	120.3(3)
N(3)-C(20)-C(21)	109.4(3)	C(20)-C(21)-C(22)	114.8(3)

N(4)-C(22)-C(21) 116.2(3)

[Li₂{Me₃SiNC(Ph)NCH₂CH₂CH₃}₂(OEt₂)₂] (8)**E1. Crystal data and structure refinement**

Empirical formula	C ₃₄ H ₆₂ Li ₂ N ₄ O ₂ Si ₂
Formula weight	628.94
Crystal description	Colourless block
Crystal size	0.32 x 0.28 x 0.28 mm
Temperature	150 K
Crystal system	Triclinic
Space group	$P \bar{1}$
Unit cell dimensions	$a = 8.411(2) \text{ \AA}$ $\alpha = 106.59(3)^\circ$ $b = 10.486(2) \text{ \AA}$ $\beta = 96.05(3)^\circ$ $c = 11.774(2) \text{ \AA}$ $\gamma = 99.38(3)^\circ$
Reflections for cell refinement	3991
Range in θ	5 to 27°
Volume, Z	$969.2(4) \text{ \AA}^3$, 1
Density (calculated)	1.078 Mg/m^3
Absorption coefficient	0.124 mm^{-1}
F(000)	344.000
Diffractometer type	Nonius Kappa CCD
Wavelength	$0.71073 \text{ \AA}$
Scan type	ψ and ω scans
Index ranges	$-10 \leq h \leq 10$, $-13 \leq k \leq 13$, $0 \leq l \leq 15$
Reflections collected	7923
Independent reflections	4372 [$R_{\text{merge}} = 0.02$]
Observed reflections	2907 [$I > 2\sigma(I)$]
Absorption correction	Multi-scan ($T_{\text{min}} = 0.97$, $T_{\text{max}} = 0.97$)
Structure solution by	direct methods and Fourier difference maps
Hydrogen atom location	geometric
Hydrogen atom treatment	riding model
Refinement method	Full-matrix least-squares on F

Weighting scheme	Chebychev
Data / restraints / parameters	4117 / 0 / 199
Goodness-of-fit on F	1.0541 ($I > 0$)
Final R indices	$R_1 = 0.0463$ ($I > 2\sigma(I)$)
	$R_w = 0.0424$ ($I > 0$)
Final maximum δ/σ	0.0003
Largest diff. peak and hole	0.39 and -0.47 e.Å ⁻³

E2. Bond lengths (Å) and angles (°)

Li(1)-N(1)	2.023(3)	Li(1)-N(2)	2.145(3)
Li(1)-N(2A)	2.073(3)	Li(1)-O(1)	1.965(3)
N(1)-Si(1)	1.708(2)	N(1)-C(1)	1.330(2)
N(2)-C(1)	1.332(2)	N(2)-C(8)	1.470(2)
O(1)-C(15)	1.421(2)	O(1)-C(16)	1.444(2)
Si(1)-C(11)	1.871(2)	Si(1)-C(12)	1.872(2)
Si(1)-C(13)	1.870(2)	C(1)-C(2)	1.512(2)
C(2)-C(3)	1.395(3)	C(2)-C(7)	1.393(3)
C(3)-C(4)	1.386(3)	C(4)-C(5)	1.384(3)
C(5)-C(6)	1.384(3)	C(6)-C(7)	1.387(3)
C(8)-C(9)	1.516(3)	C(9)-C(10)	1.525(3)
C(14)-C(15)	1.494(3)	C(16)-C(17)	1.507(3)
N(1)-Li(1)-N(2)	66.61(11)	N(1)-Li(1)-N(2A)	121.3(2)
N(2)-Li(1)-N(2A)	107.22(14)	N(1)-Li(1)-O(1)	123.1(2)
N(2)-Li(1)-O(1)	111.5(2)	N(2A)-Li(1)-O(1)	113.5(2)
Li(1)-N(1)-Si(1)	140.05(12)	Li(1)-N(1)-C(1)	85.59(14)
Si(1)-N(1)-C(1)	131.63(13)	Li(1)-N(2)-Li(1A)	72.78(14)
Li(1)-N(2)-C(1)	80.64(13)	Li(1A)-N(2)-C(1)	127.4(2)
Li(1)-N(2)-C(8)	141.30(14)	Li(1A)-N(2)-C(8)	108.94(14)
C(1)-N(2)-C(8)	119.8(2)	Li(1)-O(1)-C(15)	134.8(2)
Li(1)-O(1)-C(16)	109.67(14)	C(15)-O(1)-C(16)	112.4(2)
N(1)-Si(1)-C(11)	111.66(9)	N(1)-Si(1)-C(12)	117.17(9)
C(11)-Si(1)-C(12)	106.78(11)	N(1)-Si(1)-C(13)	105.94(9)

C(11)-Si(1)-C(13)	107.1(1)	C(12)-Si(1)-C(13)	107.7(1)
N(1)-C(1)-N(2)	118.7(2)	N(1)-C(1)-C(2)	119.7(2)
N(2)-C(1)-C(2)	121.6(2)	C(1)-C(2)-C(3)	120.3(2)
C(1)-C(2)-C(7)	120.8(2)	C(3)-C(2)-C(7)	118.9(2)
C(2)-C(3)-C(4)	120.1(2)	C(3)-C(4)-C(5)	120.6(2)
C(4)-C(5)-C(6)	119.6(2)	C(5)-C(6)-C(7)	120.2(2)
C(2)-C(7)-C(6)	120.58(9)	N(2)-C(8)-C(9)	113.2(2)
C(8)-C(9)-C(10)	112.4(2)	O(1)-C(15)-C(14)	109.8(2)
O(1)-C(16)-C(17)	112.2(2)		

Comment: Symmetry transformations used to generate equivalent atoms
 carrying the suffix 'A': -x+1,-y+1,-z+2

[Ti₂(N-2,6-C₆H₃Me₂)Cl₂(μ-O){Me₃SiNC(Ph)=NCH₂CH₂CH₂NMe₂}₂] (10)

F1. Crystal data and structure refinement

Empirical formula	C ₄₆ H ₆₈ N ₈ Cl ₂ OSi ₂ Ti ₂
Formula weight	931.96
Crystal description	Red block
Crystal size	0.3 x 0.3 x 0.4 mm
Temperature	150 K
Crystal system	Monoclinic
Space group	<i>P</i> 2/ <i>n</i>
Unit cell dimensions	<i>a</i> = 13.9462(2) Å α = 90 ° <i>b</i> = 10.0038(2) Å β = 96.337(1) ° <i>c</i> = 17.9894(3) Å γ = 90 °
Reflections for cell refinement	5531
Range in theta	2.910 to 27.485 °
Volume, <i>Z</i>	2494.45(7) Å ³ , 2
Density (calculated)	1.24 Mg/m ³
Absorption coefficient	0.51 mm ⁻¹
<i>F</i> (000)	1005.88
Diffractometer type	Nonius Kappa CCD
Wavelength	0.71073 Å
Scan type	CCD
θ range for data collection	2.91 to 27.49 °
Index ranges	-18 ≤ <i>h</i> ≤ 18, 0 ≤ <i>k</i> ≤ 12, 0 ≤ <i>l</i> ≤ 23
Reflections collected	9895
Independent reflections	5676 [R(merge) = 0.02]
Observed reflections	3931 [I > 3σ(<i>I</i>)]
Absorption correction	Multi-scan (<i>T</i> _{min} = <i>T</i> _{max} = 0.858)
Structure solution by	direct methods and Fourier difference maps
Hydrogen atom location	mixed
Hydrogen atom treatment	mixed

Refinement method	Full-matrix least-squares on F
Weighting scheme	calc
Data / restraints / parameters	3931 / 0/ 278
Goodness-of-fit on F	1.0420
Final R indices [I > 3σ(I)]	R ₁ = 0.0351, R _w = 0.0399
Extinction coefficient	117(29)
Final maximum δ / σ	0.003
Largest diff. peak and hole	0.37 and -0.36 e.Å ⁻³

F2. Bond lengths (Å) and angles (°)

Ti(1)-O(1)	1.8808(11)	Ti(1)-Cl(1)	2.4103(6)
Ti(1)-N(1)	1.729(2)	Ti(1)-N(2)	2.307(2)
Ti(1)-N(3)	2.198(2)	O(1)-H(1)	2.02(3)
O(1)-H(1A)	2.02(3)	N(1)-C(1)	1.373(3)
N(2)-C(9)	1.484(3)	N(2)-C(10)	1.475(3)
N(2)-C(11)	1.486(3)	N(3)-C(12)	1.476(3)
N(3)-C(13)	1.308(3)	N(4)-Si(1)	1.767(2)
N(4)-C(13)	1.352(3)	N(4)-H(1)	0.88(3)
Si(1)-C(20)	1.860(2)	Si(1)-C(21)	1.862(2)
Si(1)-C(22)	1.858(2)	C(1)-C(2)	1.421(3)
C(1)-C(6)	1.418(3)	C(2)-C(3)	1.389(3)
C(2)-C(7)	1.502(3)	C(3)-C(4)	1.385(4)
C(4)-C(5)	1.385(4)	C(5)-C(6)	1.393(3)
C(6)-C(8)	1.507(3)	C(11)-C(12)	1.502(3)
C(13)-C(14)	1.502(3)	C(14)-C(15)	1.393(3)
C(14)-C(19)	1.389(3)	C(15)-C(16)	1.393(3)
C(16)-C(17)	1.385(4)	C(17)-C(18)	1.380(4)
C(18)-C(19)	1.395(3)		
O(1)-Ti(1)-Cl(1)	89.68(4)	O(1)-Ti(1)-N(1)	106.21(7)
Cl(1)-Ti(1)-N(1)	104.44(6)	O(1)-Ti(1)-N(2)	157.15(6)
Cl(1)-Ti(1)-N(2)	85.51(5)	N(1)-Ti(1)-N(2)	96.62(7)
O(1)-Ti(1)-N(3)	96.59(5)	Cl(1)-Ti(1)-N(3)	150.45(5)

N(1)-Ti(1)-N(3)	101.45(7)	N(2)-Ti(1)-N(3)	77.55(6)
Ti(1)-O(1)-Ti(1A)	113.7(1)	Ti(1)-O(1)-H(1)	95.9(8)
Ti(1)-O(1)-H(1A)	116.0(8)	H(1)-O(1)-H(1A)	121(2)
Ti(1)-N(1)-C(1)	174.4(2)	Ti(1)-N(2)-C(9)	111.31(14)
Ti(1)-N(2)-C(10)	117.08(13)	C(9)-N(2)-C(10)	107.5(2)
Ti(1)-N(2)-C(11)	102.95(13)	C(9)-N(2)-C(11)	107.2(2)
C(10)-N(2)-C(11)	110.4(2)	Ti(1)-N(3)-C(12)	113.61(13)
Ti(1)-N(3)-C(13)	128.33(14)	C(12)-N(3)-C(13)	118.0(2)
Si(1)-N(4)-C(13)	131.64(14)	Si(1)-N(4)-H(1)	116(2)
C(13)-N(4)-H(1)	113(2)	N(4)-Si(1)-C(20)	111.47(11)
N(4)-Si(1)-C(21)	111.6(1)	C(20)-Si(1)-C(21)	110.72(11)
N(4)-Si(1)-C(22)	103.2(1)	C(20)-Si(1)-C(22)	109.28(12)
C(21)-Si(1)-C(22)	110.29(11)	N(1)-C(1)-C(2)	119.6(2)
N(1)-C(1)-C(6)	121.3(2)	C(2)-C(1)-C(6)	119.1(2)
C(1)-C(2)-C(3)	119.4(2)	C(1)-C(2)-C(7)	119.1(2)
C(3)-C(2)-C(7)	121.5(2)	C(2)-C(3)-C(4)	121.4(2)
C(3)-C(4)-C(5)	119.3(2)	C(4)-C(5)-C(6)	121.6(2)
C(1)-C(6)-C(5)	119.1(2)	C(1)-C(6)-C(8)	120.3(2)
C(5)-C(6)-C(8)	120.6(2)	N(2)-C(11)-C(12)	111.1(2)
N(3)-C(12)-C(11)	109.3(2)	N(3)-C(13)-N(4)	121.8(2)
N(3)-C(13)-C(14)	121.2(2)	N(4)-C(13)-C(14)	117.1(2)
C(13)-C(14)-C(15)	120.3(2)	C(13)-C(14)-C(19)	119.7(2)
C(15)-C(14)-C(19)	120.1(2)	C(14)-C(15)-C(16)	119.6(2)
C(15)-C(16)-C(17)	120.2(3)	C(16)-C(17)-C(18)	120.2(2)
C(17)-C(18)-C(19)	120.2(2)	C(14)-C(19)-C(18)	119.8(2)

Comment: Symmetry transformations used to generate equivalent atoms carrying the suffix 'A': $-x+1/2, y, -z+5/2$

trans*-[Ti₂(η -C₅H₄Me)₂(μ -O)₂{Me₃SiNC(Ph)NCH₂CH₂NMe₂}]₂] (16a)*G1. Crystal data and structure refinement**

Empirical formula	C ₄₀ H ₆₂ N ₆ O ₂ Si ₂ Ti ₂
Formula weight	810.95
Crystal description	pale yellow block
Crystal size	0.20 x 0.10 x 0.10 mm
Temperature	150 K
Crystal system	Triclinic
Space group	$P \bar{1}$
Unit cell dimensions	$a = 12.7045(4) \text{ \AA}$ $\alpha = 108.200(1)^\circ$ $b = 16.1774(4) \text{ \AA}$ $\beta = 94.168(1)^\circ$ $c = 22.8120(8) \text{ \AA}$ $\gamma = 90.162(2)^\circ$
Reflections for cell refinement	13497
Range in θ	2.910 to 24.108 $^\circ$
Volume, Z	4440.5 $\text{\AA}^3$, 4
Density (calculated)	1.21 Mg/m ³
Absorption coefficient	0.45 mm ⁻¹
F(000)	1728
Diffractometer type	Nonius Kappa CCD
Wavelength	0.71073 $\text{\AA}$
Scan type	$\omega \setminus (2\theta)$
θ range for data collection	2.91 to 24.11 $^\circ$
Index ranges	$-14 \leq h \leq 14$, $-18 \leq k \leq 17$, $0 \leq l \leq 26$
Reflections collected	26452
Independent reflections	13969 [$R_{\text{merge}} = 0.037$]
Observed reflections	6099 [$I > 2\sigma(I)$]
Absorption correction	Multi-scan ($T_{\text{min}} = T_{\text{max}} = 0.980$)
Structure solution by	direct methods and Fourier difference
Hydrogen atom location	geometric
Hydrogen atom treatment	riding model
Refinement method	Blocked least-squares on F

Weighting scheme	unit weights
Data / restraints / parameters	6099 / 0 / 939
Goodness-of-fit on F	0.2534
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0522$, $R_w = 0.0575$
Extinction coefficient	52(7)
Final maximum δ/σ	0.0025
Largest diff. peak and hole	0.34 and -0.34 e. $\text{\AA}^{-3}$

Comments: There are two independent dimers in the asymmetric unit.

The atoms for the second molecule are related to those of the first by adding 100 to the atom serial number [eg Ti(1), Ti(101)].

G2. Bond lengths ($\text{\AA}$) and angles ($^\circ$)

Ti(1)...Ti(2)	2.775(2)	Ti(1)-N(1)	2.180(6)
Ti(1)-N(2)	2.123(6)	Ti(1)-O(1)	1.813(5)
Ti(1)-O(2)	1.892(5)	Ti(1)-C(15)	2.441(8)
Ti(1)-C(16)	2.472(8)	Ti(1)-C(17)	2.410(7)
Ti(1)-C(18)	2.364(8)	Ti(1)-C(19)	2.350(8)
Ti(2)-N(4)	2.202(6)	Ti(2)-N(5)	2.116(7)
Ti(2)-O(1)	1.897(5)	Ti(2)-O(2)	1.813(5)
Ti(2)-C(35)	2.428(7)	Ti(2)-C(36)	2.349(7)
Ti(2)-C(37)	2.374(8)	Ti(2)-C(38)	2.399(7)
Ti(2)-C(39)	2.439(7)	N(1)-Si(1)	1.720(6)
N(1)-C(1)	1.34(1)	N(2)-C(1)	1.317(9)
N(2)-C(8)	1.460(9)	N(3)-C(9)	1.44(1)
N(3)-C(10)	1.478(11)	N(3)-C(11)	1.450(11)
N(4)-Si(2)	1.717(6)	N(4)-C(21)	1.33(1)
N(5)-C(21)	1.327(9)	N(5)-C(28)	1.45(1)
N(6)-C(29)	1.46(1)	N(6)-C(30)	1.47(1)
N(6)-C(31)	1.448(11)	Si(1)-C(12)	1.854(8)
Si(1)-C(13)	1.864(9)	Si(1)-C(14)	1.869(8)
Si(2)-C(32)	1.85(1)	Si(2)-C(33)	1.87(1)
Si(2)-C(34)	1.83(1)	C(1)-C(2)	1.50(1)

C(2)-C(3)	1.373(11)	C(2)-C(7)	1.383(11)
C(3)-C(4)	1.386(13)	C(4)-C(5)	1.395(12)
C(5)-C(6)	1.375(12)	C(6)-C(7)	1.347(12)
C(8)-C(9)	1.53(1)	C(15)-C(16)	1.419(11)
C(15)-C(19)	1.414(12)	C(15)-C(20)	1.481(11)
C(16)-C(17)	1.433(12)	C(17)-C(18)	1.385(11)
C(18)-C(19)	1.393(11)	C(21)-C(22)	1.495(11)
C(22)-C(23)	1.380(11)	C(22)-C(27)	1.382(11)
C(23)-C(24)	1.395(12)	C(24)-C(25)	1.337(13)
C(25)-C(26)	1.353(13)	C(26)-C(27)	1.395(13)
C(28)-C(29)	1.53(1)	C(35)-C(36)	1.414(12)
C(35)-C(39)	1.390(11)	C(35)-C(40)	1.512(11)
C(36)-C(37)	1.400(11)	C(37)-C(38)	1.403(11)
C(38)-C(39)	1.410(11)		
Ti(101)...Ti(102)	2.765(2)	Ti(101)-N(101)	2.207(6)
Ti(101)-N(102)	2.086(7)	Ti(101)-O(101)	1.784(5)
Ti(101)-O(102)	1.910(5)	Ti(101)-C(115)	2.440(8)
Ti(101)-C(116)	2.436(8)	Ti(101)-C(117)	2.395(8)
Ti(101)-C(118)	2.375(8)	Ti(101)-C(119)	2.383(8)
Ti(102)-N(104)	2.211(6)	Ti(102)-N(105)	2.091(7)
Ti(102)-O(101)	1.916(5)	Ti(102)-O(102)	1.787(5)
Ti(102)-C(135)	2.419(8)	Ti(102)-C(136)	2.354(8)
Ti(102)-C(137)	2.377(9)	Ti(102)-C(138)	2.400(8)
Ti(102)-C(139)	2.435(8)	N(101)-Si(101)	1.737(6)
N(101)-C(101)	1.32(1)	N(102)-C(101)	1.332(9)
N(102)-C(108)	1.46(1)	N(103)-C(109)	1.46(1)
N(103)-C(110)	1.426(11)	N(103)-C(111)	1.432(12)
N(104)-Si(102)	1.730(6)	N(104)-C(121)	1.34(1)
N(105)-C(121)	1.349(9)	N(105)-C(128)	1.46(1)
N(106)-C(129)	1.45(1)	N(106)-C(130)	1.412(11)
N(106)-C(131)	1.458(11)	Si(101)-C(112)	1.881(9)
Si(101)-C(113)	1.879(9)	Si(101)-C(114)	1.865(8)

Si(102)-C(132)	1.849(8)	Si(102)-C(133)	1.85(1)
Si(102)-C(134)	1.863(8)	C(101)-C(102)	1.501(11)
C(102)-C(103)	1.40(1)	C(102)-C(107)	1.38(1)
C(103)-C(104)	1.367(11)	C(104)-C(105)	1.395(11)
C(105)-C(106)	1.404(12)	C(106)-C(107)	1.379(12)
C(108)-C(109)	1.475(11)	C(115)-C(116)	1.401(12)
C(115)-C(119)	1.392(12)	C(115)-C(120)	1.481(11)
C(116)-C(117)	1.404(12)	C(117)-C(118)	1.401(13)
C(118)-C(119)	1.394(12)	C(121)-C(122)	1.466(11)
C(122)-C(123)	1.39(1)	C(122)-C(127)	1.39(1)
C(123)-C(124)	1.381(11)	C(124)-C(125)	1.370(12)
C(125)-C(126)	1.370(12)	C(126)-C(127)	1.365(11)
C(128)-C(129)	1.496(11)	C(135)-C(136)	1.401(12)
C(135)-C(139)	1.386(12)	C(135)-C(140)	1.526(11)
C(136)-C(137)	1.401(12)	C(137)-C(138)	1.383(13)
C(138)-C(139)	1.395(12)		
Ti(2)...Ti(1)-N(1)	118.9(2)	Ti(2)...Ti(1)-N(2)	110.5(2)
N(1)-Ti(1)-N(2)	61.7(2)	Ti(2)...Ti(1)-O(1)	42.75(14)
N(1)-Ti(1)-O(1)	90.1(2)	N(2)-Ti(1)-O(1)	126.2(2)
Ti(2)...Ti(1)-O(2)	40.4(2)	N(1)-Ti(1)-O(2)	135.8(2)
N(2)-Ti(1)-O(2)	87.8(2)	O(1)-Ti(1)-O(2)	83.2(2)
Ti(2)...Ti(1)-C(15)	115.6(2)	N(1)-Ti(1)-C(15)	125.4(3)
N(2)-Ti(1)-C(15)	96.3(3)	O(1)-Ti(1)-C(15)	135.5(3)
O(2)-Ti(1)-C(15)	86.5(2)	Ti(2)...Ti(1)-C(16)	149.2(2)
N(1)-Ti(1)-C(16)	91.9(3)	N(2)-Ti(1)-C(16)	81.8(3)
O(1)-Ti(1)-C(16)	148.2(3)	O(2)-Ti(1)-C(16)	116.0(2)
Ti(2)...Ti(1)-C(17)	145.6(2)	N(1)-Ti(1)-C(17)	79.9(3)
N(2)-Ti(1)-C(17)	103.7(3)	O(1)-Ti(1)-C(17)	115.7(3)
O(2)-Ti(1)-C(17)	141.6(2)	Ti(2)...Ti(1)-C(18)	112.0(2)
N(1)-Ti(1)-C(18)	103.7(3)	N(2)-Ti(1)-C(18)	136.5(3)
O(1)-Ti(1)-C(18)	92.0(3)	O(2)-Ti(1)-C(18)	120.1(3)
Ti(2)...Ti(1)-C(19)	97.4(2)	N(1)-Ti(1)-C(19)	135.5(3)

N(2)-Ti(1)-C(19)	130.5(3)	O(1)-Ti(1)-C(19)	102.1(3)
O(2)-Ti(1)-C(19)	88.4(2)	C(15)-Ti(1)-C(16)	33.6(3)
C(15)-Ti(1)-C(17)	56.2(3)	C(16)-Ti(1)-C(17)	34.1(3)
C(15)-Ti(1)-C(18)	57.0(3)	C(16)-Ti(1)-C(18)	56.7(3)
C(17)-Ti(1)-C(18)	33.7(3)	C(15)-Ti(1)-C(19)	34.3(3)
C(16)-Ti(1)-C(19)	56.3(3)	C(17)-Ti(1)-C(19)	56.1(3)
C(18)-Ti(1)-C(19)	34.4(3)	Ti(1)...Ti(2)-N(4)	120.7(2)
Ti(1)...Ti(2)-N(5)	110.5(2)	N(4)-Ti(2)-N(5)	61.7(2)
Ti(1)...Ti(2)-O(1)	40.4(2)	N(4)-Ti(2)-O(1)	136.7(2)
N(5)-Ti(2)-O(1)	87.3(2)	Ti(1)-Ti(2)-O(2)	42.6(2)
N(4)-Ti(2)-O(2)	90.5(2)	N(5)-Ti(2)-O(2)	124.8(2)
O(1)-Ti(2)-O(2)	83.0(2)	Ti(1)...Ti(2)-C(35)	113.6(2)
N(4)-Ti(2)-C(35)	125.7(3)	N(5)-Ti(2)-C(35)	98.0(3)
O(1)-Ti(2)-C(35)	85.6(2)	O(2)-Ti(2)-C(35)	134.8(3)
Ti(1)...Ti(2)-C(36)	96.0(2)	N(4)-Ti(2)-C(36)	134.5(3)
N(5)-Ti(2)-C(36)	132.4(3)	O(1)-Ti(2)-C(36)	88.6(2)
O(2)-Ti(2)-C(36)	101.6(3)	Ti(1)...Ti(2)-C(37)	112.2(2)
N(4)-Ti(2)-C(37)	102.0(3)	N(5)-Ti(2)-C(37)	136.5(3)
O(1)-Ti(2)-C(37)	121.0(3)	O(2)-Ti(2)-C(37)	93.2(3)
Ti(1)...Ti(2)-C(38)	146.4(2)	N(4)-Ti(2)-C(38)	78.7(2)
N(5)-Ti(2)-C(38)	102.9(3)	O(1)-Ti(2)-C(38)	141.3(2)
O(2)-Ti(2)-C(38)	118.0(3)	Ti(1)...Ti(2)-C(39)	146.7(2)
N(4)-Ti(2)-C(39)	92.6(3)	N(5)-Ti(2)-C(39)	82.9(3)
O(1)-Ti(2)-C(39)	114.1(2)	O(2)-Ti(2)-C(39)	149.3(3)
C(35)-Ti(2)-C(36)	34.4(3)	C(35)-Ti(2)-C(37)	56.9(3)
C(36)-Ti(2)-C(37)	34.5(3)	C(35)-Ti(2)-C(38)	56.2(3)
C(36)-Ti(2)-C(38)	56.8(3)	C(37)-Ti(2)-C(38)	34.2(3)
C(35)-Ti(2)-C(39)	33.2(3)	C(36)-Ti(2)-C(39)	56.2(3)
C(37)-Ti(2)-C(39)	56.4(3)	C(38)-Ti(2)-C(39)	33.9(3)
Ti(1)-N(1)-Si(1)	138.3(4)	Ti(1)-N(1)-C(1)	91.4(4)
Si(1)-N(1)-C(1)	129.7(5)	Ti(1)-N(2)-C(1)	94.7(5)
Ti(1)-N(2)-C(8)	140.9(5)	C(1)-N(2)-C(8)	124.4(7)

C(9)-N(3)-C(10)	110.6(7)	C(9)-N(3)-C(11)	110.2(7)
C(10)-N(3)-C(11)	108.9(7)	Ti(2)-N(4)-Si(2)	135.4(4)
Ti(2)-N(4)-C(21)	90.6(4)	Si(2)-N(4)-C(21)	131.1(5)
Ti(2)-N(5)-C(21)	94.5(5)	Ti(2)-N(5)-C(28)	140.8(5)
C(21)-N(5)-C(28)	124.6(7)	C(29)-N(6)-C(30)	111.4(7)
C(29)-N(6)-C(31)	111.0(7)	C(30)-N(6)-C(31)	108.4(7)
Ti(1)-O(1)-Ti(2)	96.8(2)	Ti(1)-O(2)-Ti(2)	97.0(2)
N(1)-Si(1)-C(12)	113.1(4)	N(1)-Si(1)-C(13)	110.5(4)
C(12)-Si(1)-C(13)	108.5(5)	N(1)-Si(1)-C(14)	106.8(3)
C(12)-Si(1)-C(14)	108.9(4)	C(13)-Si(1)-C(14)	109.0(5)
N(4)-Si(2)-C(32)	113.7(4)	N(4)-Si(2)-C(33)	110.3(4)
C(32)-Si(2)-C(33)	107.0(5)	N(4)-Si(2)-C(34)	107.2(4)
C(32)-Si(2)-C(34)	109.4(5)	C(33)-Si(2)-C(34)	109.2(5)
N(1)-C(1)-N(2)	112.1(7)	N(1)-C(1)-C(2)	124.7(6)
N(2)-C(1)-C(2)	123.1(7)	C(1)-C(2)-C(3)	121.5(7)
C(1)-C(2)-C(7)	119.5(7)	C(3)-C(2)-C(7)	119.0(8)
C(2)-C(3)-C(4)	121.1(9)	C(3)-C(4)-C(5)	118.0(9)
C(4)-C(5)-C(6)	120.6(9)	C(5)-C(6)-C(7)	120.1(9)
C(2)-C(7)-C(6)	121.1(8)	N(2)-C(8)-C(9)	109.6(6)
N(3)-C(9)-C(8)	113.3(7)	Ti(1)-C(15)-C(16)	74.4(4)
Ti(1)-C(15)-C(19)	69.3(4)	C(16)-C(15)-C(19)	107.0(7)
Ti(1)-C(15)-C(20)	122.2(6)	C(16)-C(15)-C(20)	125.2(9)
C(19)-C(15)-C(20)	127.8(9)	Ti(1)-C(16)-C(15)	72.0(4)
Ti(1)-C(16)-C(17)	70.6(4)	C(15)-C(16)-C(17)	106.5(8)
Ti(1)-C(17)-C(16)	75.3(4)	Ti(1)-C(17)-C(18)	71.3(4)
C(16)-C(17)-C(18)	109.3(8)	Ti(1)-C(18)-C(17)	75.0(5)
Ti(1)-C(18)-C(19)	72.3(5)	C(17)-C(18)-C(19)	107.5(8)
Ti(1)-C(19)-C(15)	76.4(5)	Ti(1)-C(19)-C(18)	73.4(4)
C(15)-C(19)-C(18)	109.7(8)	N(4)-C(21)-N(5)	113.1(7)
N(4)-C(21)-C(22)	124.3(7)	N(5)-C(21)-C(22)	122.5(7)
C(21)-C(22)-C(23)	121.1(7)	C(21)-C(22)-C(27)	120.7(7)
C(23)-C(22)-C(27)	118.2(8)	C(22)-C(23)-C(24)	119.9(8)

C(23)-C(24)-C(25)	121.2(10)	C(24)-C(25)-C(26)	119.9(9)
C(25)-C(26)-C(27)	120.5(9)	C(22)-C(27)-C(26)	120.2(9)
N(5)-C(28)-C(29)	109.3(6)	N(6)-C(29)-C(28)	111.7(7)
Ti(2)-C(35)-C(36)	69.8(4)	Ti(2)-C(35)-C(39)	73.8(4)
C(36)-C(35)-C(39)	107.1(7)	Ti(2)-C(35)-C(40)	120.6(5)
C(36)-C(35)-C(40)	126.8(8)	C(39)-C(35)-C(40)	126.0(9)
Ti(2)-C(36)-C(35)	75.9(4)	Ti(2)-C(36)-C(37)	73.7(4)
C(35)-C(36)-C(37)	108.8(7)	Ti(2)-C(37)-C(36)	71.8(4)
Ti(2)-C(37)-C(38)	73.9(4)	C(36)-C(37)-C(38)	107.4(8)
Ti(2)-C(38)-C(37)	71.9(4)	Ti(2)-C(38)-C(39)	74.6(4)
C(37)-C(38)-C(39)	107.9(7)	Ti(2)-C(39)-C(35)	73.0(4)
Ti(2)-C(39)-C(38)	71.5(4)	C(35)-C(39)-C(38)	108.7(8)
Ti(102)...Ti(101)-N(101)	122.2(2)		
Ti(102)...Ti(101)-N(102)	104.7(2)		
N(101)-Ti(101)-N(102)	61.4(2)		
Ti(102)...Ti(101)-O(101)	43.5(2)		
N(101)-Ti(101)-O(101)	91.7(2)		
N(102)-Ti(101)-O(101)	119.5(2)		
Ti(102)...Ti(101)-O(102)	39.9(2)		
N(101)-Ti(101)-O(102)	138.6(2)		
N(102)-Ti(101)-O(102)	85.5(2)		
O(101)-Ti(101)-O(102)	83.4(2)		
Ti(102)...Ti(101)-C(115)	98.6(2)		
N(101)-Ti(101)-C(115)	137.7(3)		
N(102)-Ti(101)-C(115)	122.1(3)		
O(101)-Ti(101)-C(115)	114.0(3)		
O(102)-Ti(101)-C(115)	79.8(2)		
Ti(102)...Ti(101)-C(116)	126.9(2)		
N(101)-Ti(101)-C(116)	110.6(3)		
N(102)-Ti(101)-C(116)	94.2(3)		
O(101)-Ti(101)-C(116)	145.9(3)		
O(102)-Ti(101)-C(116)	94.9(3)		

Ti(102)...Ti(101)-C(117)	154.2(2)
N(101)-Ti(101)-C(117)	81.6(3)
N(102)-Ti(101)-C(117)	95.5(3)
O(101)-Ti(101)-C(117)	135.7(3)
O(102)-Ti(101)-C(117)	128.7(3)
Ti(102)...Ti(101)-C(118)	129.0(3)
N(101)-Ti(101)-C(118)	86.6(3)
N(102)-Ti(101)-C(118)	126.3(3)
O(101)-Ti(101)-C(118)	102.1(3)
O(102)-Ti(101)-C(118)	134.6(3)
Ti(102)...Ti(101)-C(119)	99.7(2)
N(101)-Ti(101)-C(119)	119.5(3)
N(102)-Ti(101)-C(119)	148.8(3)
O(101)-Ti(101)-C(119)	91.6(3)
O(102)-Ti(101)-C(119)	101.7(3)
C(115)-Ti(101)-C(116)	33.4(3)
C(115)-Ti(101)-C(117)	56.4(3)
C(116)-Ti(101)-C(117)	33.8(3)
C(115)-Ti(101)-C(118)	56.5(3)
C(116)-Ti(101)-C(118)	56.0(3)
C(117)-Ti(101)-C(118)	34.2(3)
C(115)-Ti(101)-C(119)	33.5(3)
C(116)-Ti(101)-C(119)	55.2(3)
C(117)-Ti(101)-C(119)	56.2(3)
C(118)-Ti(101)-C(119)	34.1(3)
Ti(101)...Ti(102)-N(104)	122.5(2)
Ti(101)..Ti(102)-N(105)	104.4(2)
N(104)-Ti(102)-N(105)	61.8(2)
Ti(101)-Ti(102)-O(101)	39.8(2)
N(104)-Ti(102)-O(101)	138.1(2)
N(105)-Ti(102)-O(101)	84.5(2)
Ti(101)...Ti(102)-O(102)	43.3(2)

N(104)-Ti(102)-O(102)	91.4(2)
N(105)-Ti(102)-O(102)	118.3(2)
O(101)-Ti(102)-O(102)	83.2(2)
Ti(101)...Ti(102)-C(135)	100.4(2)
N(104)-Ti(102)-C(135)	136.1(3)
N(105)-Ti(102)-C(135)	119.8(3)
O(101)-Ti(102)-C(135)	81.0(2)
O(102)-Ti(102)-C(135)	117.4(3)
Ti(101)...Ti(102)-C(136)	98.4(2)
N(104)-Ti(102)-C(136)	121.1(3)
N(105)-Ti(102)-C(136)	149.2(3)
O(101)-Ti(102)-C(136)	100.7(3)
O(102)-Ti(102)-C(136)	92.5(3)
Ti(101)...Ti(102)-C(137)	127.1(3)
N(104)-Ti(102)-C(137)	87.3(3)
N(105)-Ti(102)-C(137)	128.5(3)
O(101)-Ti(102)-C(137)	134.5(3)
O(102)-Ti(102)-C(137)	101.3(3)
Ti(101)...Ti(102)-C(138)	153.6(2)
N(104)-Ti(102)-C(138)	80.8(3)
N(105)-Ti(102)-C(138)	97.6(3)
O(101)-Ti(102)-C(138)	130.8(3)
O(102)-Ti(102)-C(138)	134.1(3)
Ti(101)...Ti(102)-C(139)	129.3(2)
N(104)-Ti(102)-C(139)	107.8(3)
N(105)-Ti(102)-C(139)	93.1(3)
O(101)-Ti(102)-C(139)	97.4(3)
O(102)-Ti(102)-C(139)	148.5(3)
C(135)-Ti(102)-C(136)	34.1(3)
C(135)-Ti(102)-C(137)	56.5(3)
C(136)-Ti(102)-C(137)	34.5(3)
C(135)-Ti(102)-C(138)	55.3(3)

C(136)-Ti(102)-C(138)	56.1(3)
C(137)-Ti(102)-C(138)	33.7(3)
C(135)-Ti(102)-C(139)	33.2(3)
C(136)-Ti(102)-C(139)	56.3(3)
C(137)-Ti(102)-C(139)	56.4(3)
C(138)-Ti(102)-C(139)	33.5(3)
Ti(101)-N(101)-Si(101)	137.3(4)
Ti(101)-N(101)-C(101)	90.8(4)
Si(101)-N(101)-C(101)	131.8(5)
Ti(101)-N(102)-C(101)	95.8(5)
Ti(101)-N(102)-C(108)	138.5(5)
C(101)-N(102)-C(108)	125.2(7)
C(109)-N(103)-C(110)	111.5(7)
C(109)-N(103)-C(111)	112.3(8)
C(110)-N(103)-C(111)	108.2(8)
Ti(102)-N(104)-Si(102)	137.6(4)
Ti(102)-N(104)-C(121)	91.2(4)
Si(102)-N(104)-C(121)	131.0(5)
Ti(102)-N(105)-C(121)	96.2(5)
Ti(102)-N(105)-C(128)	139.3(5)
C(121)-N(105)-C(128)	124.3(7)
C(129)-N(106)-C(130)	112.4(8)
C(129)-N(106)-C(131)	110.1(7)
C(130)-N(106)-C(131)	108.8(7)
Ti(101)-O(101)-Ti(102)	96.7(2)
Ti(101)-O(102)-Ti(102)	96.8(2)
N(101)-Si(101)-C(112)	113.8(4)
N(101)-Si(101)-C(113)	109.5(4)
C(112)-Si(101)-C(113)	110.2(5)
N(101)-Si(101)-C(114)	107.1(3)
C(112)-Si(101)-C(114)	107.7(4)
C(113)-Si(101)-C(114)	108.4(5)

N(104)-Si(102)-C(132)	114.8(4)
N(104)-Si(102)-C(133)	107.7(4)
C(132)-Si(102)-C(133)	107.6(4)
N(104)-Si(102)-C(134)	109.6(4)
C(132)-Si(102)-C(134)	108.4(4)
C(133)-Si(102)-C(134)	108.7(5)
N(101)-C(101)-N(102)	111.9(7)
N(101)-C(101)-C(102)	124.2(7)
N(102)-C(101)-C(102)	123.9(7)
C(101)-C(102)-C(103)	120.8(7)
C(101)-C(102)-C(107)	118.9(7)
C(103)-C(102)-C(107)	120.3(7)
C(102)-C(103)-C(104)	119.6(8)
C(103)-C(104)-C(105)	120.7(8)
C(104)-C(105)-C(106)	119.4(8)
C(105)-C(106)-C(107)	119.3(8)
C(102)-C(107)-C(106)	120.6(8)
N(102)-C(108)-C(109)	111.8(7)
N(103)-C(109)-C(108)	113.1(7)
Ti(101)-C(115)-C(116)	73.1(5)
Ti(101)-C(115)-C(119)	71.0(4)
C(116)-C(115)-C(119)	106.3(8)
Ti(101)-C(115)-C(120)	121.6(5)
C(116)-C(115)-C(120)	125.3(9)
C(119)-C(115)-C(120)	128.5(9)
Ti(101)-C(116)-C(115)	73.5(5)
Ti(101)-C(116)-C(117)	71.5(5)
C(115)-C(116)-C(117)	109.2(8)
Ti(101)-C(117)-C(116)	74.7(5)
Ti(101)-C(117)-C(118)	72.2(5)
C(116)-C(117)-C(118)	107.4(8)
Ti(101)-C(118)-C(117)	73.7(5)

Ti(101)-C(118)-C(119)	73.3(5)
C(117)-C(118)-C(119)	107.3(8)
Ti(101)-C(119)-C(115)	75.5(5)
Ti(101)-C(119)-C(118)	72.7(5)
C(115)-C(119)-C(118)	109.9(8)
N(104)-C(121)-N(105)	110.7(7)
N(104)-C(121)-C(122)	125.1(7)
N(105)-C(121)-C(122)	124.1(7)
C(121)-C(122)-C(123)	122.6(7)
C(121)-C(122)-C(127)	120.1(7)
C(123)-C(122)-C(127)	117.1(7)
C(122)-C(123)-C(124)	120.6(7)
C(123)-C(124)-C(125)	120.8(8)
C(124)-C(125)-C(126)	119.4(8)
C(125)-C(126)-C(127)	120.2(8)
C(122)-C(127)-C(126)	121.8(8)
N(105)-C(128)-C(129)	112.4(6)
N(106)-C(129)-C(128)	111.9(6)
Ti(102)-C(135)-C(136)	70.4(5)
Ti(102)-C(135)-C(139)	74.1(5)
C(136)-C(135)-C(139)	108.3(8)
Ti(102)-C(135)-C(140)	121.1(5)
C(136)-C(135)-C(140)	124.9(9)
C(139)-C(135)-C(140)	126.8(9)
Ti(102)-C(136)-C(135)	75.5(5)
Ti(102)-C(136)-C(137)	73.7(5)
C(135)-C(136)-C(137)	108.1(9)
Ti(102)-C(137)-C(136)	71.9(5)
Ti(102)-C(137)-C(138)	74.1(5)
C(136)-C(137)-C(138)	106.7(8)
Ti(102)-C(138)-C(137)	72.3(5)
Ti(102)-C(138)-C(139)	74.6(5)

C(137)-C(138)-C(139)	109.8(8)
Ti(102)-C(139)-C(135)	72.8(5)
Ti(102)-C(139)-C(138)	71.8(5)
C(135)-C(139)-C(138)	107.0(9)

trans*-[Ti₂(η -C₅H₄Me)₂(μ -O)₂{Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂}₂] (17a)*H1. Crystal data and structure refinement**

Empirical formula	C ₄₂ H ₆₂ N ₆ O ₂ Si ₂ Ti ₂
Formula weight	838.99
Crystal description	orange plate
Crystal size	0.45 x 0.30 x 0.20 mm
Temperature	150 K
Crystal system	Triclinic
Space group	$P \bar{1}$
Unit cell dimensions	$a = 9.3597(2) \text{ \AA}$ $\alpha = 72.8419(8)^\circ$ $b = 10.7886(2) \text{ \AA}$ $\beta = 76.2046(8)^\circ$ $c = 12.1749(3) \text{ \AA}$ $\gamma = 72.8192(9)^\circ$
Reflections for cell refinement	4378
Range in θ	2.910 to 27.485 $^\circ$
Volume, Z	1106.74(4) $\text{\AA}^3$, 1
Density (calculated)	1.26 Mg/m ³
Absorption coefficient	0.45 mm ⁻¹
F(000)	448
Diffractometer type	Nonius Kappa CCD
Wavelength	0.71073 $\text{\AA}$
Scan type	$\omega - 2\theta$
θ range for data collection	3.01 to 27.49 $^\circ$
Index ranges	$-12 \leq h \leq 12$, $-12 \leq k \leq 13$, $-15 \leq l \leq 15$
Reflections collected	9040
Independent reflections	4955 [$R_{\text{merge}} = 0.02$]
Observed reflections	3814 [$I > 3\sigma(I)$]
Absorption correction	Multi-scan ($T_{\text{min}} = 0.874$, $T_{\text{max}} = 0.914$)
Structure solution by	direct methods and Fourier difference maps

Hydrogen atom location	geometric
Hydrogen atom treatment	riding model
Refinement method	Full-matrix least-squares on F
Weighting scheme	Chebychev polynomial
Data / restraints / parameters	3814 / 0 / 245
Goodness-of-fit on F	1.076
Final R indices [$I > 3\sigma(I)$]	$R_1 = 0.0367$, $R_w = 0.0387$
Extinction coefficient	127(35)
Final maximum δ / σ	0.0025
Largest diff. peak and hole	0.31 and -0.31 e.Å ⁻³

H2. Selected bond lengths (Å) and angles (°)

Ti(1)...Ti(1B)	2.7709(6)	Ti(1)-N(1)	2.203(1)
Ti(1)-N(2)	2.096(1)	Ti(1)-O(1)	1.802(1)
Ti(1)-O(1B)	1.907(1)	Ti(1)-C(16)	2.461(2)
Ti(1)-C(17)	2.417(2)	Ti(1)-C(18)	2.359(2)
Ti(1)-C(19)	2.349(2)	Ti(1)-C(20)	2.402(2)
N(1)-Si(1)	1.737(2)	N(1)-C(1)	1.333(2)
N(2)-C(1)	1.315(2)	N(2)-C(8)	1.460(2)
N(3)-C(10)	1.461(2)	N(3)-C(11)	1.457(3)
N(3)-C(12)	1.454(3)	Si(1)-C(13)	1.868(2)
Si(1)-C(14)	1.857(2)	Si(1)-C(15)	1.870(2)
C(1)-C(2)	1.498(2)	C(2)-C(3)	1.391(3)
C(2)-C(7)	1.392(3)	C(3)-C(4)	1.387(3)
C(4)-C(5)	1.376(3)	C(5)-C(6)	1.385(3)
C(6)-C(7)	1.388(3)	C(8)-C(9)	1.519(3)
C(9)-C(10)	1.529(3)	C(16)-C(17)	1.386(3)
C(16)-C(20)	1.413(3)	C(16)-C(21)	1.489(3)
C(17)-C(18)	1.379(3)	C(18)-C(19)	1.367(4)
C(19)-C(20)	1.408(4)		
Ti(1B) ...Ti(1)-N(1)	119.31(4)	Ti(1B) ...Ti(1)-N(2)	106.40(4)
N(1)-Ti(1)-N(2)	61.86(6)	Ti(1B) ...Ti(1)-O(1)	43.14(4)

N(1)-Ti(1)-O(1)	89.88(6)	N(2)-Ti(1)-O(1)	121.90(6)
Ti(1B) ...Ti(1)-O(1B)	40.23(4)	N(1)-Ti(1)-O(1B)	135.49(5)
N(2)-Ti(1)-O(1B)	84.89(5)	O(1)-Ti(1)-O(1B)	83.37(5)
Ti(1B) ...Ti(1)-C(16)	154.47(5)	N(1)-Ti(1)-C(16)	85.51(6)
N(2)-Ti(1)-C(16)	90.08(6)	O(1)-Ti(1)-C(16)	140.37(7)
O(1B) -Ti(1)-C(16)	125.68(7)	Ti(1B) ...Ti(1)-C(17)	124.53(6)
N(1)-Ti(1)-C(17)	115.70(7)	N(2)-Ti(1)-C(17)	92.84(7)
O(1)-Ti(1)-C(17)	144.41(7)	O(1B) -Ti(1)-C(17)	93.17(6)
Ti(1B) ...Ti(1)-C(18)	98.47(6)	N(1)-Ti(1)-C(18)	139.58(7)
N(2)-Ti(1)-C(18)	123.21(8)	O(1)-Ti(1)-C(18)	111.26(8)
O(1B) -Ti(1)-C(18)	82.61(7)	Ti(1B) ...Ti(1)-C(19)	103.16(6)
N(1)-Ti(1)-C(19)	116.48(9)	N(2)-Ti(1)-C(19)	145.74(7)
O(1)-Ti(1)-C(19)	91.64(7)	O(1B) -Ti(1)-C(19)	107.68(8)
Ti(1B) ...Ti(1)-C(20)	134.80(7)	N(1)-Ti(1)-C(20)	85.22(7)
N(2)-Ti(1)-C(20)	118.79(8)	O(1)-Ti(1)-C(20)	106.67(7)
O(1B) -Ti(1)-C(20)	138.82(7)	C(16)-Ti(1)-C(17)	33.01(7)
C(16)-Ti(1)-C(18)	56.00(7)	C(17)-Ti(1)-C(18)	33.55(8)
C(16)-Ti(1)-C(19)	56.46(8)	C(17)-Ti(1)-C(19)	55.61(8)
C(18)-Ti(1)-C(19)	33.77(9)	C(16)-Ti(1)-C(20)	33.75(8)
C(17)-Ti(1)-C(20)	55.31(7)	C(18)-Ti(1)-C(20)	56.36(8)
C(19)-Ti(1)-C(20)	34.46(9)	Ti(1)-N(1)-Si(1)	136.15(8)
Ti(1)-N(1)-C(1)	89.1(1)	Si(1)-N(1)-C(1)	129.4(1)
Ti(1)-N(2)-C(1)	94.3(1)	Ti(1)-N(2)-C(8)	139.0(1)
C(1)-N(2)-C(8)	124.1(1)	C(10)-N(3)-C(11)	109.7(2)
C(10)-N(3)-C(12)	111.8(2)	C(11)-N(3)-C(12)	109.4(2)
Ti(1)-O(1)-Ti(1B)	96.63(5)	N(1)-Si(1)-C(13)	111.82(9)
N(1)-Si(1)-C(14)	107.46(8)	C(13)-Si(1)-C(14)	108.3(1)
N(1)-Si(1)-C(15)	111.35(9)	C(13)-Si(1)-C(15)	108.9(1)
C(14)-Si(1)-C(15)	108.9(1)	N(1)-C(1)-N(2)	113.2(1)
N(1)-C(1)-C(2)	123.6(2)	N(2)-C(1)-C(2)	123.2(2)
C(1)-C(2)-C(3)	120.0(2)	C(1)-C(2)-C(7)	120.8(2)

C(3)-C(2)-C(7)	119.2(2)	C(2)-C(3)-C(4)	120.0(2)
C(3)-C(4)-C(5)	120.4(2)	C(4)-C(5)-C(6)	120.2(2)
C(5)-C(6)-C(7)	119.8(2)	C(2)-C(7)-C(6)	120.3(2)
N(2)-C(8)-C(9)	112.1(1)	C(8)-C(9)-C(10)	113.4(2)
N(3)-C(10)-C(9)	113.8(2)	Ti(1)-C(16)-C(17)	71.7(1)
Ti(1)-C(16)-C(20)	70.8(1)	C(17)-C(16)-C(20)	106.1(2)
Ti(1)-C(16)-C(21)	121.7(1)	C(17)-C(16)-C(21)	127.1(3)
C(20)-C(16)-C(21)	126.8(3)	Ti(1)-C(17)-C(16)	75.2(1)
Ti(1)-C(17)-C(18)	70.9(1)	C(16)-C(17)-C(18)	109.9(2)
Ti(1)-C(18)-C(17)	75.5(1)	Ti(1)-C(18)-C(19)	72.7(1)
C(17)-C(18)-C(19)	108.1(2)	Ti(1)-C(19)-C(18)	73.5(1)
Ti(1)-C(19)-C(20)	74.8(1)	C(18)-C(19)-C(20)	108.2(2)
Ti(1)-C(20)-C(16)	75.4(1)	Ti(1)-C(20)-C(19)	70.7(1)
C(16)-C(20)-C(19)	107.7(2)		

Comment: Symmetry transformations used to generate equivalent atoms carrying the suffix 'B': 1-x, -y+1, -z+1.

[Ti(N^tBu){Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂}(O-2,6-C₆H₃Me₂)] (30)

II. Crystal data and structural refinement

Chemical formula	C ₂₇ H ₄₄ N ₄ OSiTi
Formula weight	516.66
Crystal description	Pale-yellow block
Crystal size	0.20 x 0.28 x 0.32 mm
Temperature	150 K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
Unit cell dimensions	<i>a</i> = 10.4590(2) Å α = 90° <i>b</i> = 15.8439(3) Å β = 97.3378(7) ° <i>c</i> = 18.0981(4) Å γ = 90°
Cell volume, <i>Z</i>	2974.5 Å ³ , 4
Calculated density	1.154 Mg/m ³
Absorption coefficient	0.352 mm ⁻¹
<i>F</i> (000)	1113.390
Absorption correction	Semi-empirical from equivalent reflections
Transmission coefficients	0.89, 0.93 (min,max)
θ range for data collection (°)	5.0 ≤ θ ≤ 27.5
Index ranges	-13 ≤ <i>h</i> ≤ 13, 0 ≤ <i>k</i> ≤ 20, 0 ≤ <i>l</i> ≤ 23
Reflections measured	26442
Unique reflections	7024
<i>R</i> _{int}	0.048
Observed reflections [<i>I</i> > 3σ(<i>I</i>)]	4606
Refinement method	Full-matrix least-squares on <i>F</i>
Parameters refined	307
Weighting scheme	Chebychev 3-term polynomial
Goodness of fit	1.0631
<i>R</i> ₁	0.0364

R_w	0.0407
Residual electron density	-0.27, 0.31 e.Å ⁻³

I2. Selected bond lengths (Å) and angles (°)

Ti(1)-N(1)	1.6991(15)	Ti(1)-O(1)	1.8887(13)
Ti(1)-N(2)	2.2548(15)	Ti(1)-N(3)	2.1081(15)
Ti(1)-C(16)	2.5288(17)	Ti(1)-N(4)	2.1531(15)
N(1)-C(1)	1.446(2)	C(1)-C(2)	1.531(3)
C(1)-C(3)	1.529(3)	C(1)-C(4)	1.527(3)
O(1)-C(5)	1.337(2)	C(5)-C(6)	1.409(3)
C(5)-C(10)	1.404(3)	C(6)-C(7)	1.391(3)
C(6)-C(11)	1.502(3)	C(7)-C(8)	1.375(4)
C(8)-C(9)	1.388(4)	C(9)-C(10)	1.395(3)
C(10)-C(12)	1.502(3)	N(2)-C(13)	1.497(2)
N(2)-C(17)	1.485(2)	N(2)-C(18)	1.482(2)
C(13)-C(14)	1.522(3)	C(14)-C(15)	1.521(3)
C(15)-N(3)	1.454(2)	N(3)-C(16)	1.320(2)
C(16)-N(4)	1.336(2)	C(16)-C(19)	1.497(2)
N(4)-Si(1)	1.7294(15)	C(19)-C(20)	1.390(3)
C(19)-C(24)	1.390(3)	C(20)-C(21)	1.392(3)
C(21)-C(22)	1.381(4)	C(22)-C(23)	1.382(4)
C(23)-C(24)	1.389(3)	Si(1)-C(25)	1.864(2)
Si(1)-C(26)	1.868(2)	Si(1)-C(27)	1.867(2)
N(1)-Ti(1)-O(1)	115.90(7)	Ti(1)-N(2)-C(13)	114.93(11)
N(1)-Ti(1)-N(2)	100.81(7)	Ti(1)-N(2)-C(17)	108.42(11)
O(1)-Ti(1)-N(2)	92.09(6)	C(13)-N(2)-C(17)	106.80(15)
N(1)-Ti(1)-N(3)	105.61(7)	Ti(1)-N(2)-C(18)	108.33(11)
O(1)-Ti(1)-N(3)	138.45(6)	C(13)-N(2)-C(18)	110.35(15)
N(2)-Ti(1)-N(3)	81.55(6)	C(17)-N(2)-C(18)	107.78(15)
N(1)-Ti(1)-C(16)	103.55(7)	N(2)-C(13)-C(14)	116.65(15)
O(1)-Ti(1)-C(16)	128.33(6)	C(13)-C(14)-C(15)	113.85(16)
N(2)-Ti(1)-C(16)	112.54(6)	C(14)-C(15)-N(3)	108.02(16)
N(3)-Ti(1)-C(16)	31.43(6)	Ti(1)-N(3)-C(15)	136.65(12)

N(1)-Ti(1)-N(4)	105.36(7)	Ti(1)-N(3)-C(16)	92.16(11)
O(1)-Ti(1)-N(4)	102.75(6)	C(15)-N(3)-C(16)	124.95(16)
N(2)-Ti(1)-N(4)	140.02(6)	Ti(1)-C(16)-N(3)	56.41(9)
N(3)-Ti(1)-N(4)	62.69(6)	Ti(1)-C(16)-N(4)	58.37(9)
C(16)-Ti(1)-N(4)	31.88(6)	N(3)-C(16)-N(4)	113.22(15)
Ti(1)-N(1)-C(1)	171.93(13)	Ti(1)-C(16)-C(19)	167.51(13)
N(1)-C(1)-C(2)	109.86(16)	N(3)-C(16)-C(19)	122.65(16)
N(1)-C(1)-C(3)	108.12(16)	N(4)-C(16)-C(19)	124.13(16)
C(2)-C(1)-C(3)	109.35(18)	Ti(1)-N(4)-C(16)	89.8(1)
N(1)-C(1)-C(4)	109.47(15)	Ti(1)-N(4)-Si(1)	135.11(8)
C(2)-C(1)-C(4)	109.77(17)	C(16)-N(4)-Si(1)	132.13(13)
C(3)-C(1)-C(4)	110.26(17)	C(16)-C(19)-C(20)	120.55(17)
Ti(1)-O(1)-C(5)	167.84(12)	C(16)-C(19)-C(24)	120.08(17)
O(1)-C(5)-C(6)	121.03(16)	C(20)-C(19)-C(24)	119.37(18)
O(1)-C(5)-C(10)	118.69(17)	C(19)-C(20)-C(21)	120.0(2)
C(6)-C(5)-C(10)	120.29(17)	C(20)-C(21)-C(22)	120.4(2)
C(5)-C(6)-C(7)	118.65(19)	C(21)-C(22)-C(23)	119.6(2)
C(5)-C(6)-C(11)	120.10(17)	C(22)-C(23)-C(24)	120.4(2)
C(7)-C(6)-C(11)	121.24(19)	C(19)-C(24)-C(23)	120.1(2)
C(6)-C(7)-C(8)	121.7(2)	N(4)-Si(1)-C(25)	105.98(9)
C(7)-C(8)-C(9)	119.4(2)	N(4)-Si(1)-C(26)	110.3(1)
C(8)-C(9)-C(10)	121.1(2)	C(25)-Si(1)-C(26)	107.70(11)
C(5)-C(10)-C(9)	118.8(2)	N(4)-Si(1)-C(27)	113.06(9)
C(5)-C(10)-C(12)	119.16(18)	C(25)-Si(1)-C(27)	109.66(11)
C(9)-C(10)-C(12)	122.0(2)	C(26)-Si(1)-C(27)	109.92(11)

[Ti(N- 2,6-C₆H₃Me₂){Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂}(O-2,6-C₆H₃Me₂)]
(31)

J1. Crystal data and structure refinement

Empirical formula	C ₃₄ H ₅₁ N ₄ OSiTi
Formula weight	607.80
Crystal description	Orange fragment
Crystal size	0.06 x 0.12 x 0.34 mm
Temperature	150 K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
Unit cell dimensions	<i>a</i> = 12.7710(2) Å α = 90 ° <i>b</i> = 19.5990(3) Å β = 99.2435(7) ° <i>c</i> = 14.4818(3) Å γ = 90 °
Cell volume, <i>Z</i>	3577.7 Å ³ , 4
Calculated density	1.128 Mg/m ³
Absorption coefficient	0.302 mm ⁻¹
<i>F</i> (000)	1309.422
Absorption correction	Semi-empirical from equivalent reflections
Transmission coefficients	0.90, 0.98 (min,max)
θ range for data collection	5.0 ≤ θ ≤ 27.5 °
Index ranges	-16 ≤ <i>h</i> ≤ 16, 0 ≤ <i>k</i> ≤ 25, 0 ≤ <i>l</i> ≤ 18
Reflections measured	41144
Unique reflections	8147
<i>R</i> _{int}	0.043
Observed reflections [<i>I</i> > 3σ(<i>I</i>)]	4733
Refinement method	Full-matrix least-squares on <i>F</i>
Parameters refined	388
Weighting scheme	Chebyshev 3-term polynomial

Goodness of fit	0.9628
R_1	0.0507
R_w	0.0645
Residual electron density	-0.30, 0.43 e.Å ⁻³

J2. Bond lengths (Å) and angles (°)

Ti(1)-N(1)	1.756(2)	Ti(1)-O(1)	1.828(2)
Ti(1)-N(2)	2.235(2)	Ti(1)-N(3)	2.084(2)
Ti(1)-N(4)	2.119(2)	N(1)-C(1)	1.383(3)
C(1)-C(2)	1.410(4)	C(1)-C(6)	1.408(4)
C(2)-C(3)	1.392(4)	C(2)-C(7)	1.497(4)
C(3)-C(4)	1.369(5)	C(4)-C(5)	1.370(5)
C(5)-C(6)	1.391(4)	C(6)-C(8)	1.494(5)
O(1)-C(9)	1.352(3)	C(9)-C(10)	1.403(5)
C(9)-C(14)	1.398(5)	C(10)-C(11)	1.378(4)
C(10)-C(15)	1.500(6)	C(11)-C(12)	1.363(6)
C(12)-C(13)	1.384(6)	C(13)-C(14)	1.403(5)
C(14)-C(16)	1.501(6)	N(2)-C(17)*	1.476(4)
N(2)-C(117)*	1.552(8)	N(2)-C(21)*	1.505(4)
N(2)-C(22)*	1.481(4)	N(2)-C(121)*	1.475(9)
N(2)-C(122)*	1.482(9)	C(17)-C(18)*	1.541(5)
C(18)-C(19)*	1.528(5)	C(19)-N(3)*	1.486(4)
C(117)-C(118)*	1.496(19)	C(118)-C(119)*	1.512(9)
C(119)-N(3)*	1.489(8)	N(3)-C(20)	1.320(3)
C(20)-N(4)	1.319(3)	C(20)-C(23)	1.495(4)
N(4)-Si(1)	1.730(2)	C(23)-C(24)	1.378(4)
C(23)-C(28)	1.391(4)	C(24)-C(25)	1.413(6)
C(25)-C(26)	1.378(7)	C(26)-C(27)	1.351(6)
C(27)-C(28)	1.374(5)	Si(1)-C(29)	1.830(4)
Si(1)-C(30)	1.855(5)	Si(1)-C(31)	1.851(4)
C(32)-C(33)*	1.465(15)	C(33)-C(34)*	1.474(15)
C(34)-C(35)*	1.418(15)	C(35)-C(36)*	1.445(17)
C(36)-C(37)*	1.418(16)		

N(1)-Ti(1)-O(1)	118.75(12)	C(17)-N(2)-C(21)*	106.8(3)
N(1)-Ti(1)-N(2)	96.78(9)	Ti(1)-N(2)-C(22)*	110.6(2)
O(1)-Ti(1)-N(2)	93.90(9)	C(17)-N(2)-C(22)*	111.2(3)
N(1)-Ti(1)-N(3)	113.99(11)	C(21)-N(2)-C(22)*	105.7(3)
O(1)-Ti(1)-N(3)	127.17(11)	Ti(1)-N(2)-C(121)*	110.0(5)
N(2)-Ti(1)-N(3)	82.65(8)	C(117)-N(2)-C(121)*	108.6(6)
N(1)-Ti(1)-N(4)	103.5(1)	Ti(1)-N(2)-C(122)*	106.7(5)
O(1)-Ti(1)-N(4)	100.9(1)	C(117)-N(2)-C(122)*	106.3(6)
N(2)-Ti(1)-N(4)	144.82(8)	C(121)-N(2)-C(122)*	112.0(9)
N(3)-Ti(1)-N(4)	62.94(9)	N(2)-C(17)-C(18)*	114.6(3)
Ti(1)-N(1)-C(1)	174.5(2)	C(17)-C(18)-C(19)*	114.3(3)
N(1)-C(1)-C(2)	120.2(3)	C(18)-C(19)-N(3)*	109.2(3)
N(1)-C(1)-C(6)	120.4(3)	N(2)-C(117)-C(118)*	122.0(7)
C(2)-C(1)-C(6)	119.5(2)	C(117)-C(118)-C(119)*	114.6(8)
C(1)-C(2)-C(3)	118.7(3)	Ti(1)-N(3)-C(19)*	137.3(2)
C(1)-C(2)-C(7)	119.9(2)	Ti(1)-N(3)-C(119)*	140.8(5)
C(3)-C(2)-C(7)	121.5(3)	Ti(1)-N(3)-C(20)*	92.88(16)
C(2)-C(3)-C(4)	121.6(3)	C(19)-N(3)-C(20)*	124.3(2)
C(3)-C(4)-C(5)	120.0(3)	C(119)-N(3)-C(20)*	115.4(5)
C(4)-C(5)-C(6)	121.0(3)	N(3)-C(20)-N(4)	112.6(2)
C(1)-C(6)-C(5)	119.3(3)	N(3)-C(20)-C(23)	123.6(2)
C(1)-C(6)-C(8)	119.5(3)	N(4)-C(20)-C(23)	123.9(2)
C(5)-C(6)-C(8)	121.1(3)	Ti(1)-N(4)-C(20)	91.35(16)
Ti(1)-O(1)-C(9)	170.3(2)	Ti(1)-N(4)-Si(1)	134.03(12)
O(1)-C(9)-C(10)	119.0(3)	C(20)-N(4)-Si(1)	133.3(2)
O(1)-C(9)-C(14)	119.7(3)	C(20)-C(23)-C(24)	121.1(3)
C(10)-C(9)-C(14)	121.3(3)	C(20)-C(23)-C(28)	119.2(3)
C(9)-C(10)-C(11)	118.9(3)	C(24)-C(23)-C(28)	119.7(3)
C(9)-C(10)-C(15)	119.8(3)	C(23)-C(24)-C(25)	119.0(4)
C(11)-C(10)-C(15)	121.3(3)	C(24)-C(25)-C(26)	119.0(4)
C(10)-C(11)-C(12)	121.0(4)	C(25)-C(26)-C(27)	122.1(3)

C(11)-C(12)-C(13)	120.3(3)	C(26)-C(27)-C(28)	119.1(4)
C(12)-C(13)-C(14)	121.0(4)	C(23)-C(28)-C(27)	121.1(3)
C(9)-C(14)-C(13)	117.4(3)	N(4)-Si(1)-C(29)	111.7(2)
C(9)-C(14)-C(16)	121.0(3)	N(4)-Si(1)-C(30)	111.66(18)
C(13)-C(14)-C(16)	121.6(4)	C(29)-Si(1)-C(30)	108.4(3)
Ti(1)-N(2)-C(17)*	114.38(18)	N(4)-Si(1)-C(31)	105.08(15)
Ti(1)-N(2)-C(117)*	113.2(4)	C(29)-Si(1)-C(31)	111.1(3)
Ti(1)-N(2)-C(21)*	107.61(19)	C(30)-Si(1)-C(31)	108.8(2)
C(32)-C(33)-C(34)*	106.6(8)	C(34)-C(35)-C(36)*	110.0(9)
C(33)-C(34)-C(35)*	114.3(8)	C(35)-C(36)-C(37)*	110.8(9)

*bond angle included in geometric restraint

[Ti(N-2,6-C₆H₃ⁱPr₂){Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂}(OTf)]₂ (33)

K1. Crystal data and refinement details

Empirical formula	C ₅₈ H ₈₆ N ₈ F ₆ O ₆ S ₂ Si ₂ Ti ₂
Formula weight	1297.44
Crystal description	Brown tablet
Crystal size	0.06 x 0.18 x 0.26 mm
Temperature	150 K
Crystal system	Triclinic
Space group	<i>P</i> $\bar{1}$
Unit cell dimensions	<i>a</i> = 11.2172(3) Å α = 84.3494(10) ° <i>b</i> = 11.7127(3) Å β = 80.1191(11) ° <i>c</i> = 13.0977(4) Å γ = 74.8903(11) °
Cell volume, <i>Z</i> (Å ³)	1634.08(8) Å ³ , 1
Calculated density	1.318 Mg/m ³
Absorption coefficient	0.414 mm ⁻¹
<i>F</i> (000)	684
Absorption correction	Semi-empirical from equivalent reflections
Transmission coefficients (min,max)	0.90, 0.98
θ range for data collection	5.0 ≤ θ ≤ 27.5 °
Index ranges	-14 ≤ <i>h</i> ≤ 14, -15 ≤ <i>k</i> ≤ 15, 0 ≤ <i>l</i> ≤ 17
Reflections measured	27879
Unique reflections	7453
<i>R</i> _{int}	0.043
Observed reflections [<i>I</i> > 3σ(<i>I</i>)]	5162
Refinement method	Full-matrix least-squares on <i>F</i>
Parameters refined	370
Weighting scheme	Chebychev 3-term polynomial
Goodness of fit	1.1021
<i>R</i> ₁	0.0345
<i>R</i> _w	0.0391

Residual electron density	-0.39, 0.30 e.Å ⁻³
Wavelength (Å)	0.71073

K2. Selected bond lengths and angles

Ti(1)-N(1)	1.7192(16)	N(3)-C(14)	1.445(2)
Ti(1)-N(2)	2.1169(16)	C(14)-C(15)	1.524(3)
Ti(1)-N(3)	2.0785(15)	C(15)-C(16)	1.524(3)
Ti(1)-N(4)	2.3140(16)	C(16)-N(4)	1.499(2)
Ti(1)-O(1)	2.3869(13)	N(4)-C(26)	1.488(3)
Ti(1)-O(2)*	2.0892(13)	N(4)-C(27)	1.485(3)
N(1)-C(1)	1.391(2)	Si(1)-C(17)	1.864(2)
C(1)-C(2)	1.423(3)	Si(1)-C(18)	1.863(2)
C(1)-C(6)	1.423(3)	Si(1)-C(19)	1.866(2)
C(2)-C(3)	1.387(3)	C(20)-C(21)	1.397(3)
C(2)-C(7)	1.521(3)	C(20)-C(25)	1.390(3)
C(3)-C(4)	1.391(3)	C(21)-C(22)	1.393(3)
C(4)-C(5)	1.388(3)	C(22)-C(23)	1.385(3)
C(5)-C(6)	1.389(3)	C(23)-C(24)	1.385(3)
C(6)-C(10)	1.521(3)	C(24)-C(25)	1.394(3)
C(7)-C(8)	1.529(3)	O(1)-S(1)	1.4441(14)
C(7)-C(9)	1.536(3)	S(1)-O(2)	1.4693(13)
C(10)-C(11)	1.532(3)	S(1)-O(3)	1.4229(15)
C(10)-C(12)	1.529(3)	S(1)-C(28)	1.823(2)
N(2)-C(13)	1.345(2)	C(28)-F(1)	1.327(3)
N(2)-Si(1)	1.7373(16)	C(28)-F(2)	1.328(2)
C(13)-N(3)	1.320(2)	C(28)-F(3)	1.325(3)
C(13)-C(20)	1.493(3)		
N(1)-Ti(1)-N(2)	97.10(7)	Ti(1)-N(3)-C(13)	92.99(11)
N(1)-Ti(1)-N(3)	102.63(7)	Ti(1)-N(3)-C(14)	140.03(12)
N(2)-Ti(1)-N(3)	63.79(6)	C(13)-N(3)-C(14)	126.52(16)
N(1)-Ti(1)-N(4)	99.22(7)	N(3)-C(14)-C(15)	109.24(15)
N(2)-Ti(1)-N(4)	148.13(6)	C(14)-C(15)-C(16)	112.81(17)
N(3)-Ti(1)-N(4)	85.95(6)	C(15)-C(16)-N(4)	115.35(17)

N(1)-Ti(1)-O(1)	174.44(6)	Ti(1)-N(4)-C(16)	111.69(11)
N(2)-Ti(1)-O(1)	83.36(5)	Ti(1)-N(4)-C(26)	116.76(13)
N(3)-Ti(1)-O(1)	82.56(5)	C(16)-N(4)-C(26)	108.22(16)
N(4)-Ti(1)-O(1)	83.00(5)	Ti(1)-N(4)-C(27)	105.77(12)
N(1)-Ti(1)-O(2)*	98.46(6)	C(16)-N(4)-C(27)	107.30(16)
N(2)-Ti(1)-O(2)*	109.00(6)	C(26)-N(4)-C(27)	106.58(17)
N(3)-Ti(1)-O(2)*	158.37(6)	N(2)-Si(1)-C(17)	105.96(9)
N(4)-Ti(1)-O(2)*	95.45(6)	N(2)-Si(1)-C(18)	109.64(9)
O(1)-Ti(1)-O(2)*	76.21(5)	C(17)-Si(1)-C(18)	109.91(12)
Ti(1)-N(1)-C(1)	167.18(14)	N(2)-Si(1)-C(19)	114.19(9)
N(1)-C(1)-C(2)	120.12(17)	C(17)-Si(1)-C(19)	107.46(12)
N(1)-C(1)-C(6)	120.31(17)	C(18)-Si(1)-C(19)	109.57(12)
C(2)-C(1)-C(6)	119.55(17)	C(13)-C(20)-C(21)	120.53(18)
C(1)-C(2)-C(3)	119.12(19)	C(13)-C(20)-C(25)	119.72(17)
C(1)-C(2)-C(7)	120.55(17)	C(21)-C(20)-C(25)	119.70(18)
C(3)-C(2)-C(7)	120.28(18)	C(20)-C(21)-C(22)	119.9(2)
C(2)-C(3)-C(4)	121.20(19)	C(21)-C(22)-C(23)	119.9(2)
C(3)-C(4)-C(5)	119.82(19)	C(22)-C(23)-C(24)	120.63(19)
C(4)-C(5)-C(6)	121.3(2)	C(23)-C(24)-C(25)	119.7(2)
C(1)-C(6)-C(5)	119.01(18)	C(20)-C(25)-C(24)	120.23(19)
C(1)-C(6)-C(10)	119.95(17)	Ti(1)-O(1)-S(1)	144.99(8)
C(5)-C(6)-C(10)	120.98(18)	O(1)-S(1)-O(2)	113.27(8)
C(2)-C(7)-C(8)	114.46(18)	O(1)-S(1)-O(3)	117.74(9)
C(2)-C(7)-C(9)	109.37(17)	O(2)-S(1)-O(3)	113.97(9)
C(8)-C(7)-C(9)	109.64(18)	O(1)-S(1)-C(28)	102.84(9)
C(6)-C(10)-C(11)	109.44(17)	O(2)-S(1)-C(28)	101.82(9)
C(6)-C(10)-C(12)	113.45(18)	O(3)-S(1)-C(28)	104.7(1)
C(11)-C(10)-C(12)	110.15(19)	Ti(1)*-O(2)-S(1)	146.00(9)
Ti(1)-N(2)-C(13)	90.58(11)	S(1)-C(28)-F(1)	111.37(15)
Ti(1)-N(2)-Si(1)	132.96(9)	S(1)-C(28)-F(2)	108.80(14)
C(13)-N(2)-Si(1)	130.82(13)	F(1)-C(28)-F(2)	107.97(17)
N(2)-C(13)-N(3)	112.57(16)	S(1)-C(28)-F(3)	112.06(14)

N(2)-C(13)-C(20)	124.74(17)	F(1)-C(28)-F(3)	108.46(18)

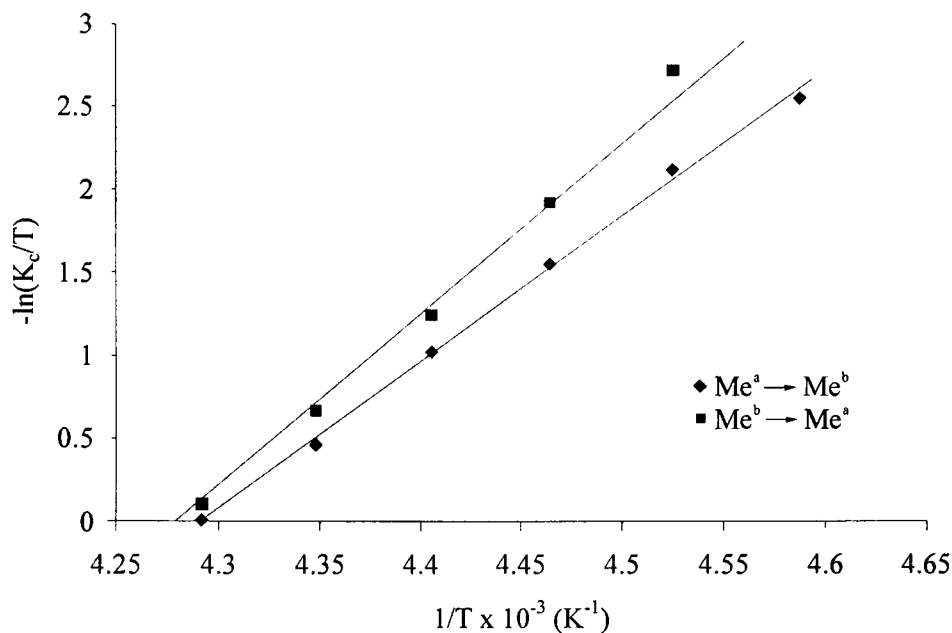
N(3)-C(13)-C(20)	122.68(16)	F(2)-C(28)-F(3)	108.05(18)

*related to asymmetric unit by crystallographic inversion by the symmetry

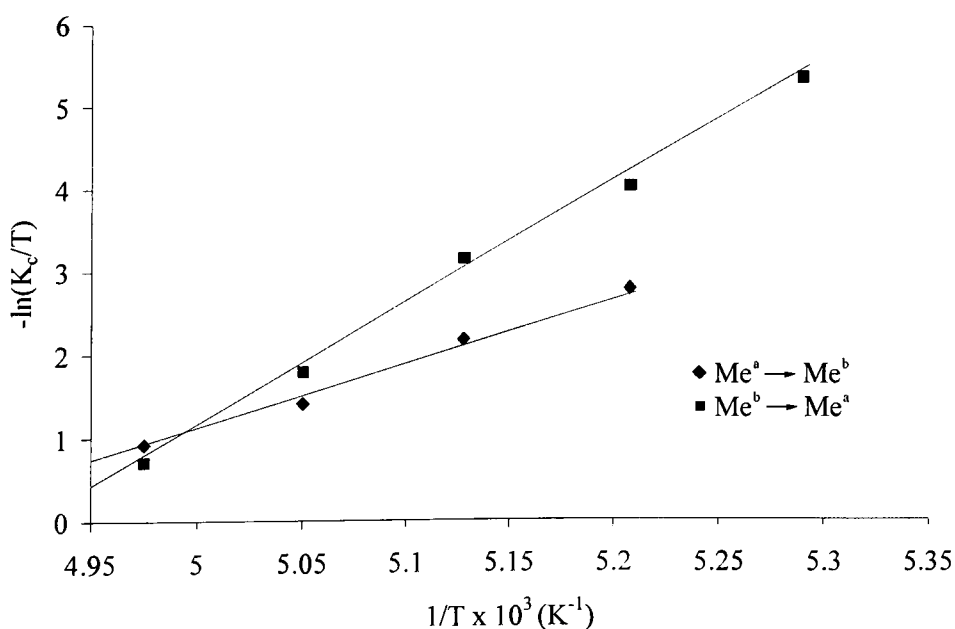
operator 1-x, -y, 1-z

Eyring plots for NMe₂ methyl group exchange data in 13 and 14

(i) Eyring plot for NMe₂ methyl group exchange in [Ti(η-C₅H₄Me)(N^tBu){Me₃SiNC(Ph)NCH₂CH₂NMe₂}] (13)



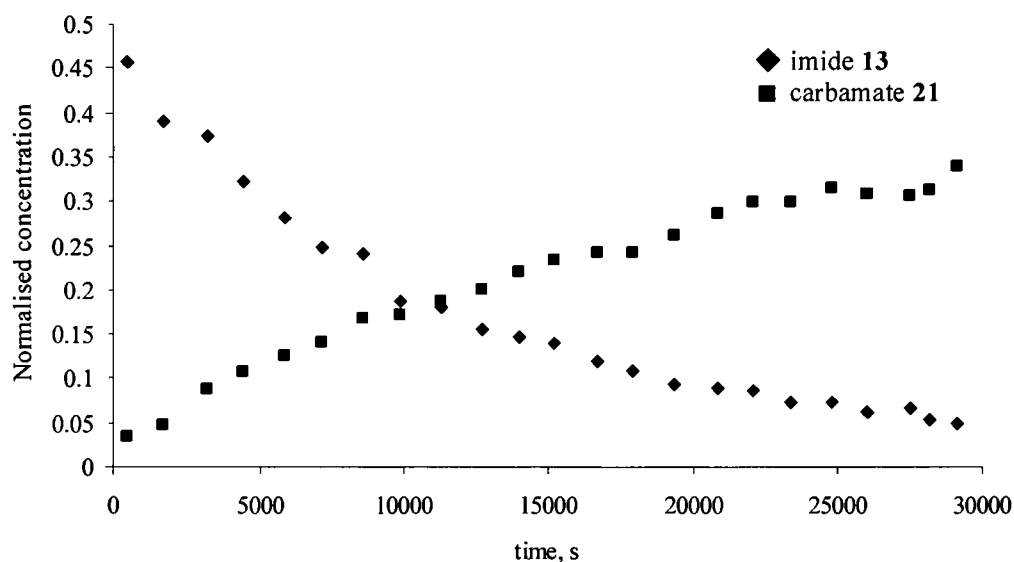
(ii) Eyring plot for NMe₂ methyl group exchange in [Ti(η-C₅H₄Me)(N^tBu){Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂}] (14)



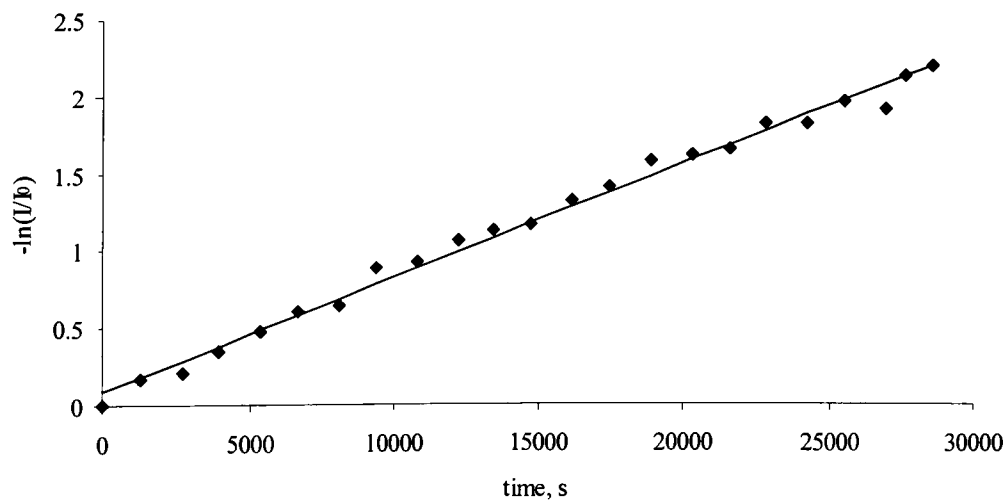
Cycloaddition reaction of $[\text{Ti}(\eta\text{-C}_5\text{H}_4\text{Me})(\text{N}^t\text{Bu})$

$\{\text{Me}_3\text{SiNC(Ph)NCH}_2\text{CH}_2\text{NMe}_2\}$ (**13**) with CO_2 : kinetic studies

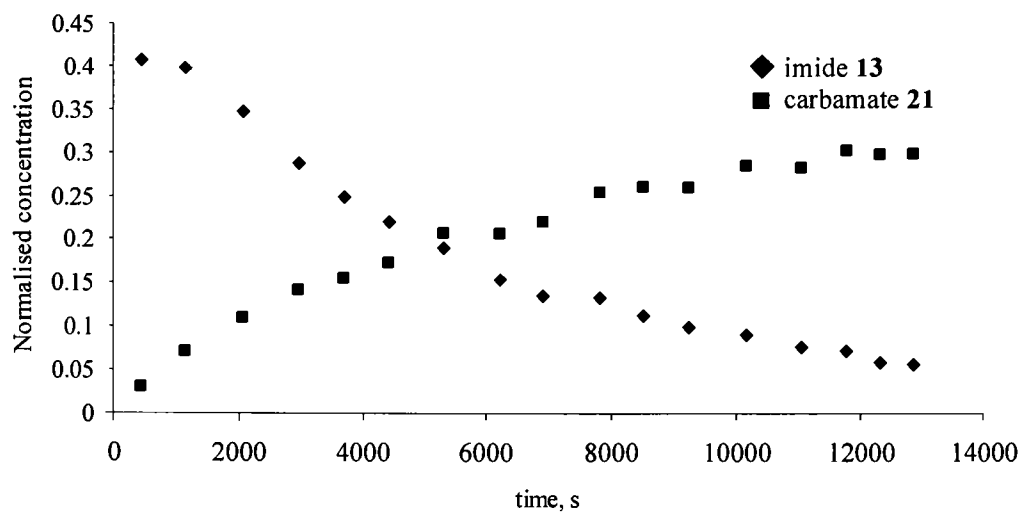
(i) Plot of normalised concentrations against time for the cycloaddition reaction of **13** with CO_2 (0.25 atm). Values are given for starting imide **13** and product carbamate **21**



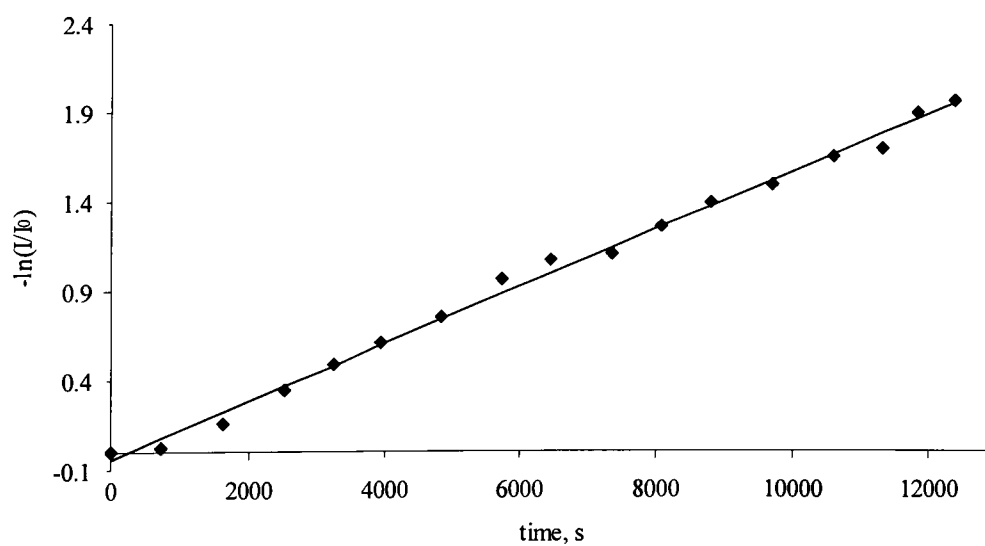
(ii) Plot of $\ln(I/I_0)$ vs. time for the reaction of **13** with CO_2 (0.25 atm)



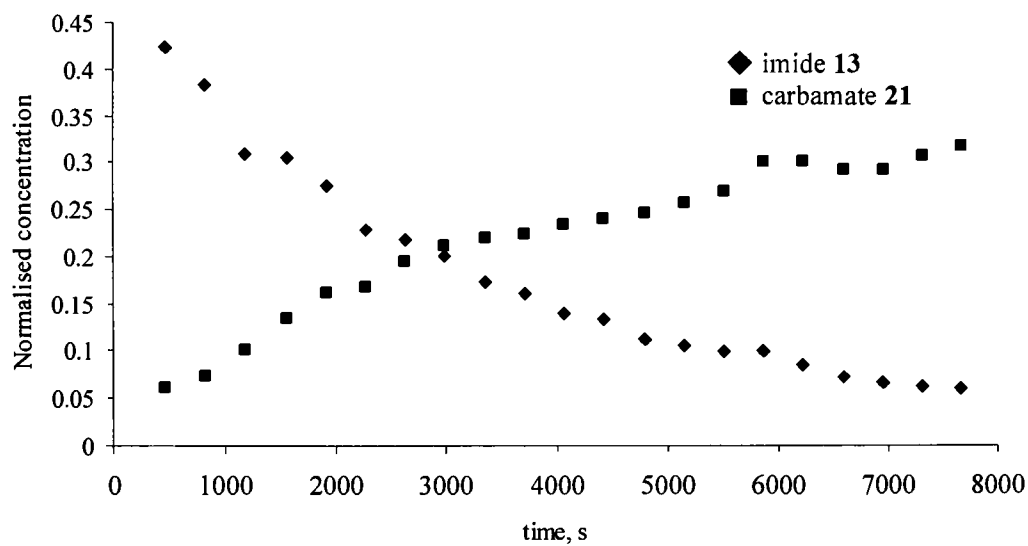
(iii) Plot of normalised concentrations against time for the cycloaddition reaction of **13** with CO₂ (0.5 atm). Values are given for starting imide **13** and product carbamate **21**



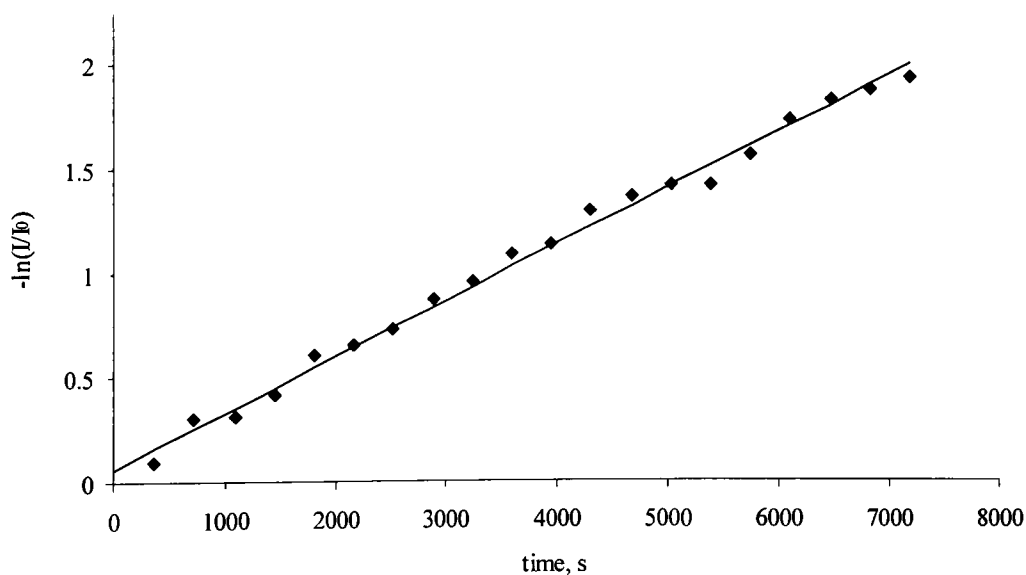
(iv) Plot of $\ln(I/I_0)$ vs. time for the reaction of **13** with CO₂ (0.5 atm)



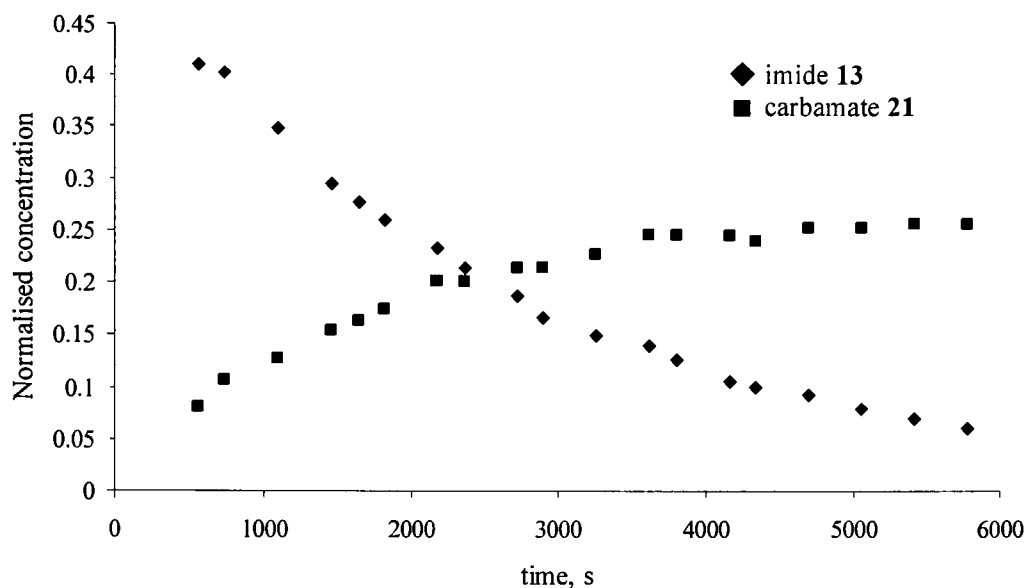
(v) Plot of normalised concentrations against time for the cycloaddition reaction of **13** with CO₂ (0.75 atm). Values are given for starting imide **13** and product carbamate **21**



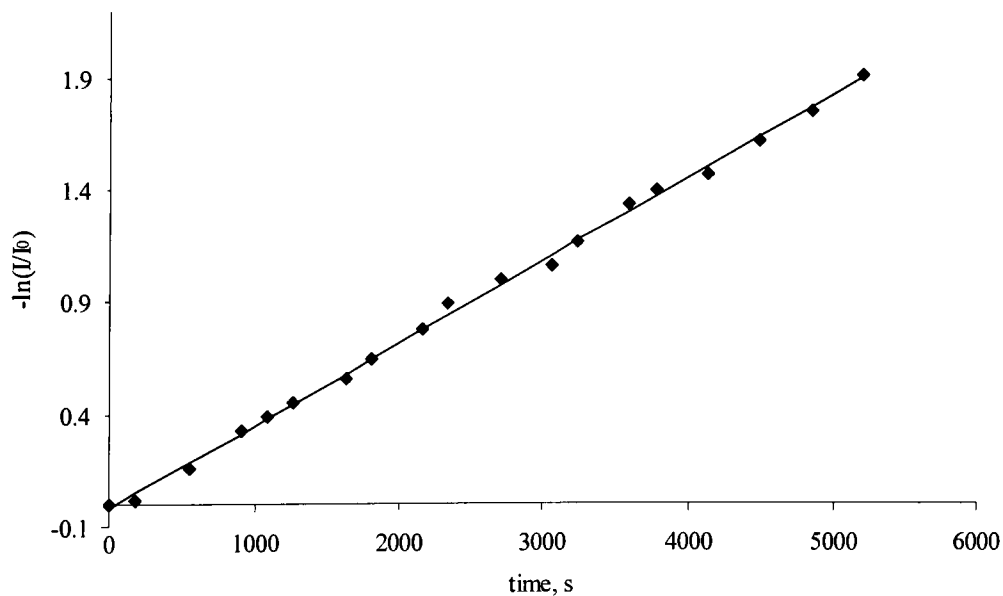
(vi) Plot of $\ln(I/I_0)$ vs. time for the reaction of **13** with CO₂ (0.75 atm)



(vii) Plot of normalised concentrations against time for the cycloaddition reaction of **13** with CO₂ (1.0 atm). Values are given for starting imide **13** and product carbamate **21**

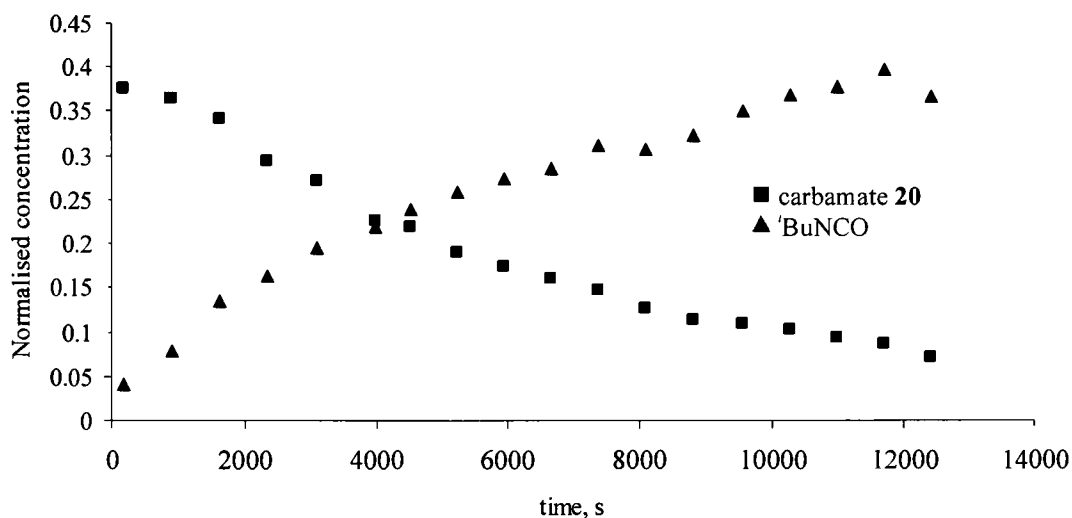


(viii) Plot of $\ln(I/I_0)$ vs. time for the reaction of **13** with CO₂ (1.0 atm)

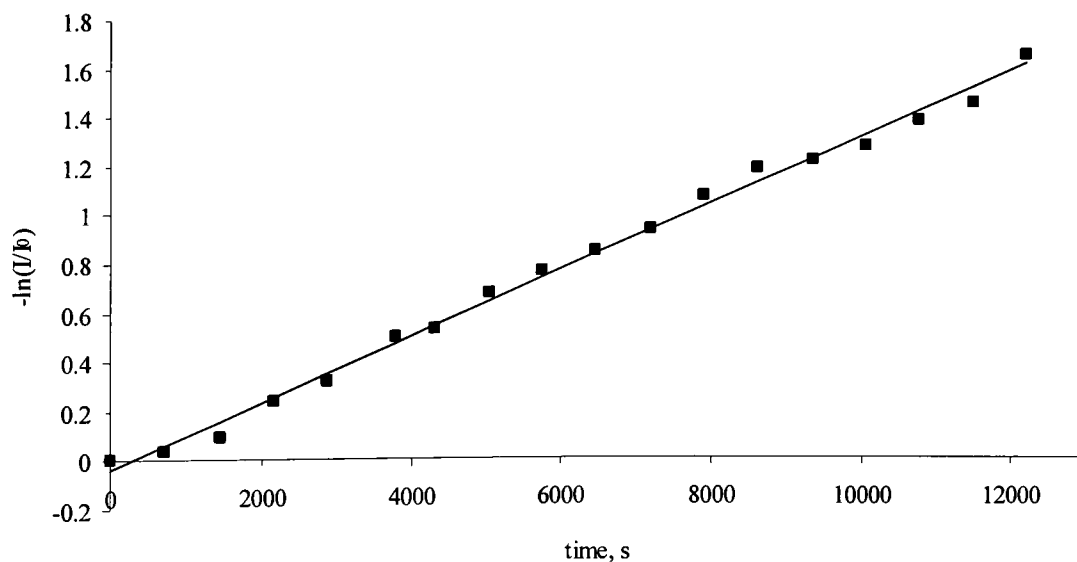


Extrusion of t BuNCO from carbamate intermediates **19**, **20** and **21**: kinetic studies

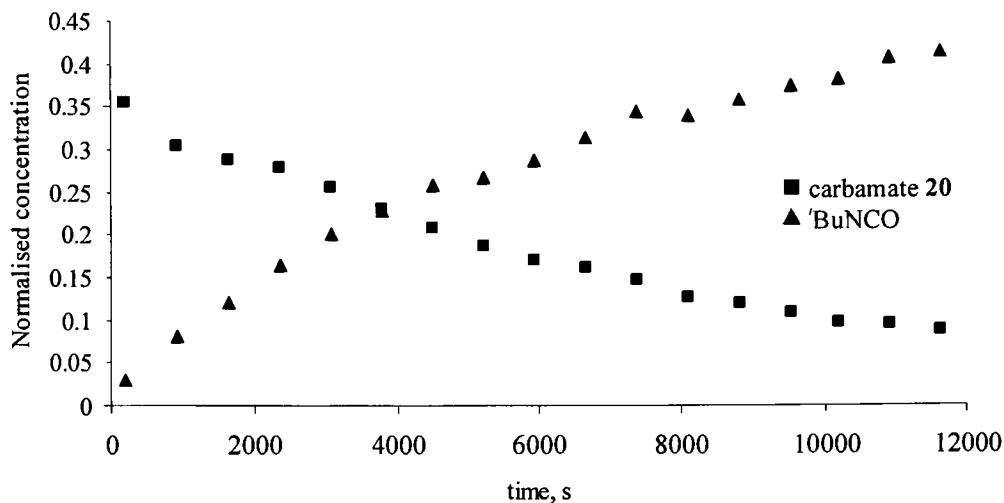
(i) Plot of normalised concentrations for the t BuNCO extrusion reaction of $[\text{Ti}(\eta\text{-C}_5\text{H}_4\text{Me})\{\text{N}'\text{BuC}(\text{O})\text{O}\}\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{Me}\}]$ (**20**) at $1.9 \times 10^8 \text{ mol dm}^{-3}$. Values are given for the carbamate **20** and t BuNCO.



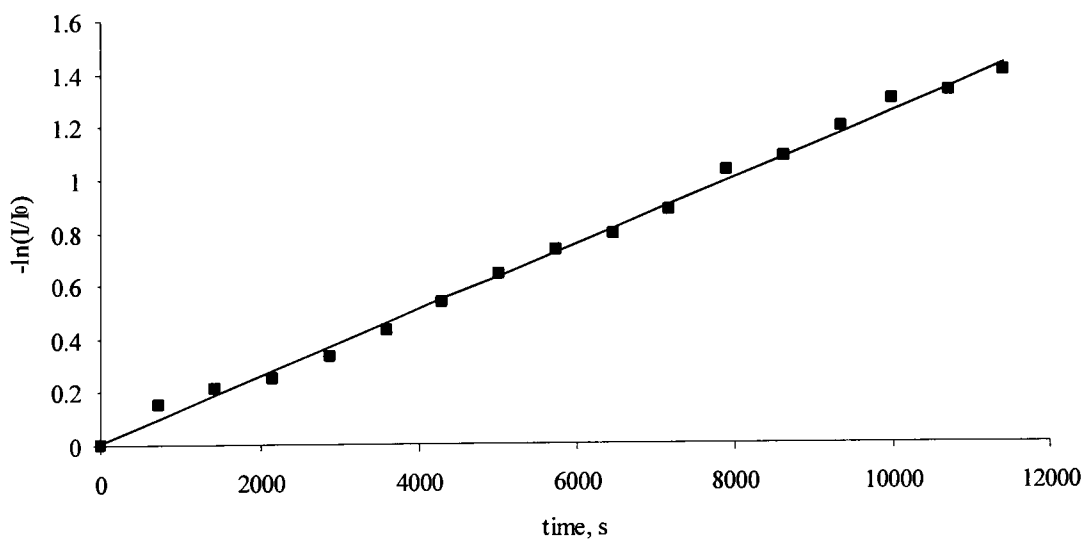
(ii) Plot of $\ln(I/I_0)$ vs. time for the t BuNCO extrusion reaction of $[\text{Ti}(\eta\text{-C}_5\text{H}_4\text{Me})\{\text{N}'\text{BuC}(\text{O})\text{O}\}\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{Me}\}]$ (**20**) at $1.9 \times 10^8 \text{ mol dm}^{-3}$.



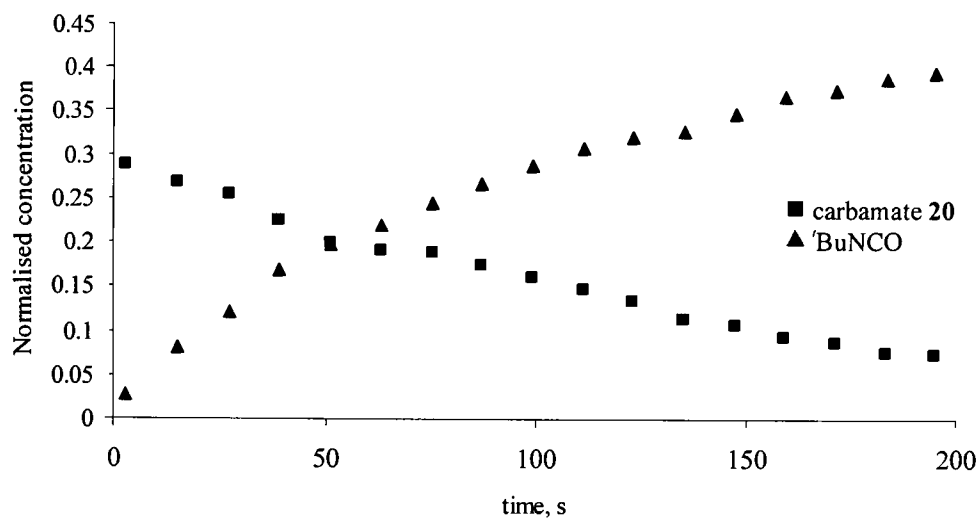
(iii) Plot of normalised concentrations for the ^tBuNCO extrusion reaction of [Ti(η-C₅H₄Me){N^tBuC(O)O}{Me₃SiNC(Ph)NCH₂CH₂Me} (**20**) at 2.9 × 10⁸ mol dm⁻³. Values are given for the carbamate **20** and ^tBuNCO.



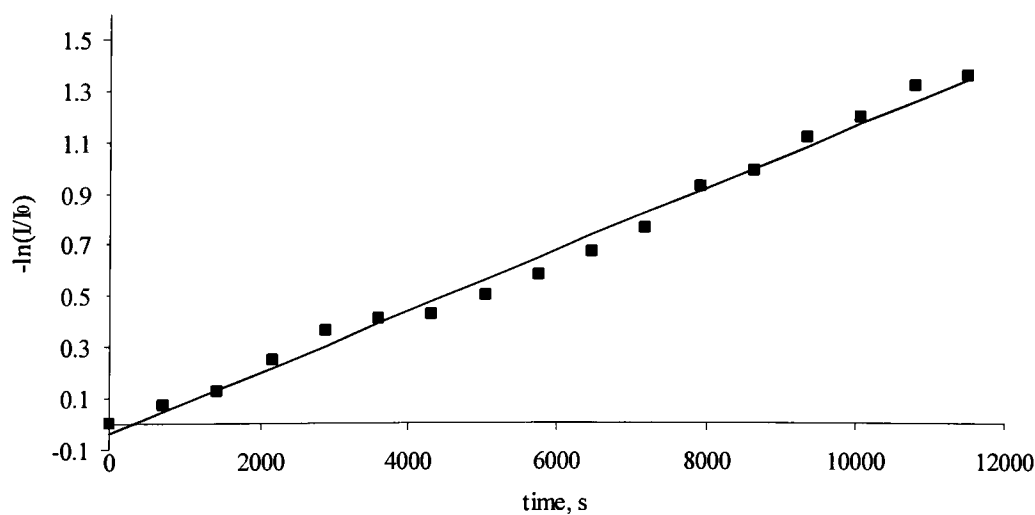
(iv) Plot of $\ln(I/I_0)$ vs. time for the ^tBuNCO extrusion reaction of [Ti(η-C₅H₄Me){N^tBuC(O)O}{Me₃SiNC(Ph)NCH₂CH₂Me} (**20**) at 2.9 × 10⁸ mol dm⁻³.



(v) Plot of normalised concentrations for the 'BuNCO extrusion reaction of $[\text{Ti}(\eta\text{-C}_5\text{H}_4\text{Me})\{\text{N'BuC(O)O}\}\{\text{Me}_3\text{SiNC(Ph)NCH}_2\text{CH}_2\text{Me}\}]$ (**20**) at $3.8 \times 10^8 \text{ mol dm}^{-3}$. Values are given for the carbamate **20** and 'BuNCO .

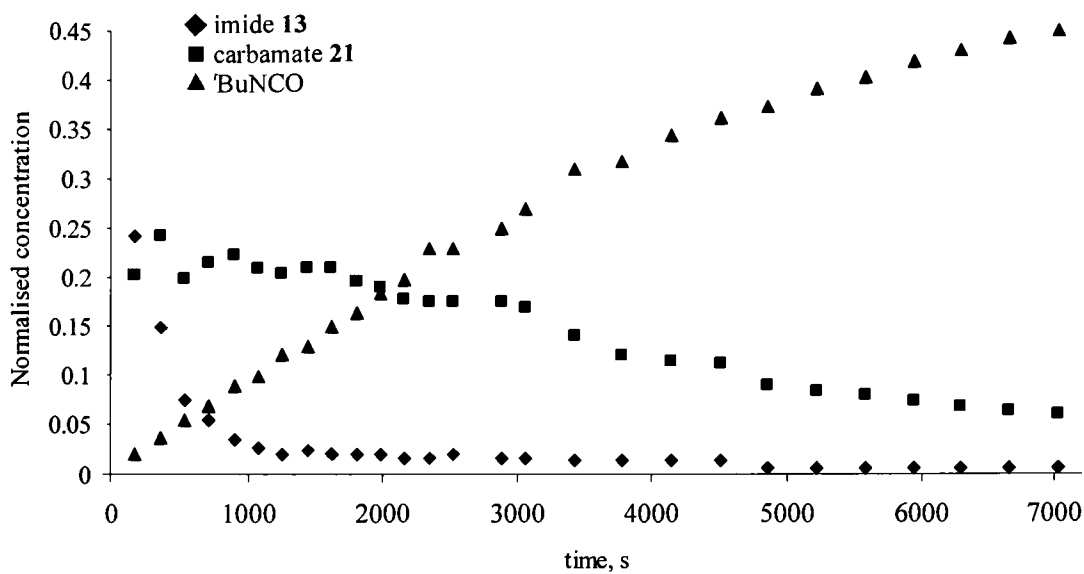


(vi) Plot of $\ln(I/I_0)$ vs. time for the 'BuNCO extrusion reaction of $[\text{Ti}(\eta\text{-C}_5\text{H}_4\text{Me})\{\text{N'BuC(O)O}\}\{\text{Me}_3\text{SiNC(Ph)NCH}_2\text{CH}_2\text{Me}\}]$ (**20**) at $3.8 \times 10^8 \text{ mol dm}^{-3}$.

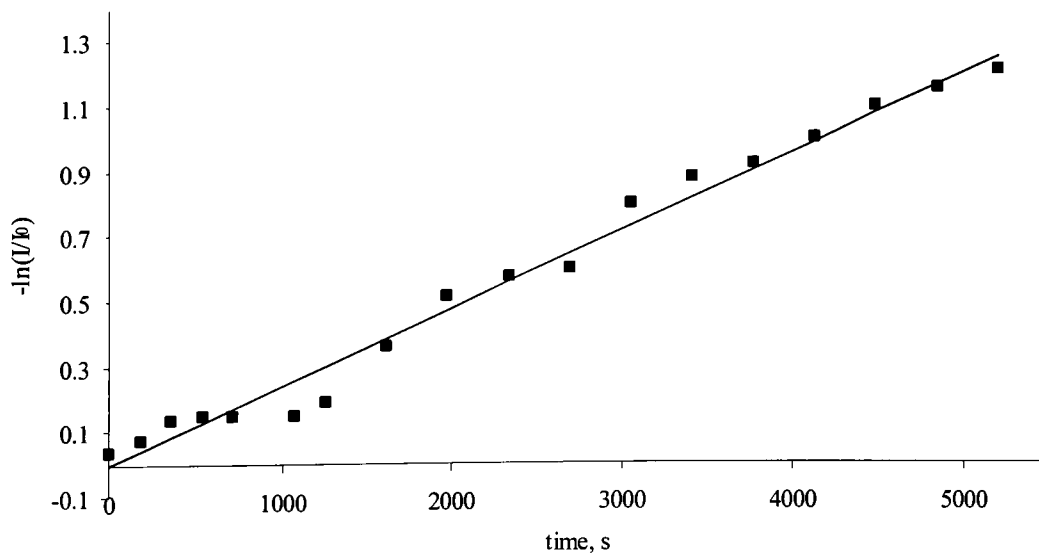


(vii) Plot of normalised concentrations for the 'BuNCO extrusion reaction of $[\text{Ti}(\eta\text{-C}_5\text{H}_4\text{Me})\{\text{N}'\text{BuC}(\text{O})\text{O}\}\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{NMe}_2\}]$ (**21**) at $1.9 \times 10^8 \text{ mol dm}^{-3}$.

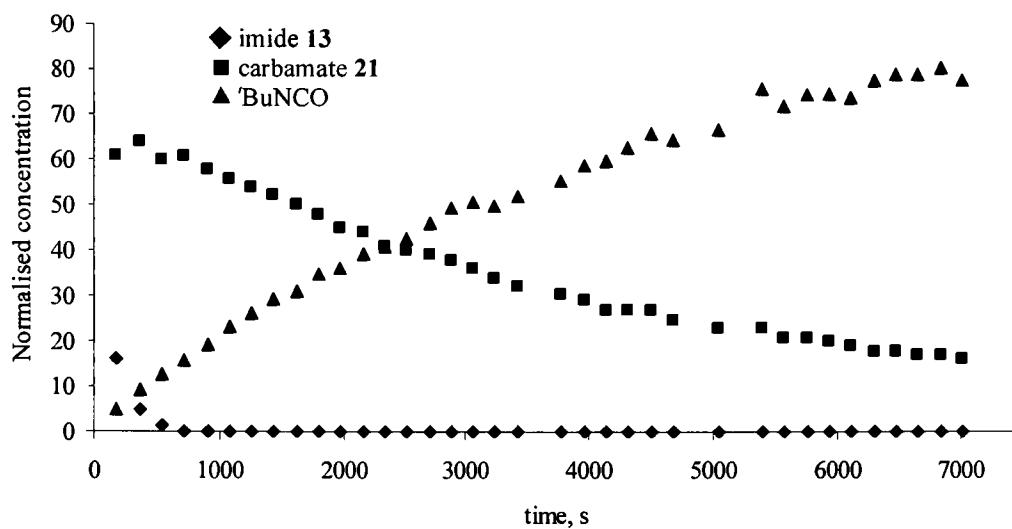
Values are given for the carbamate **21** and 'BuNCO.



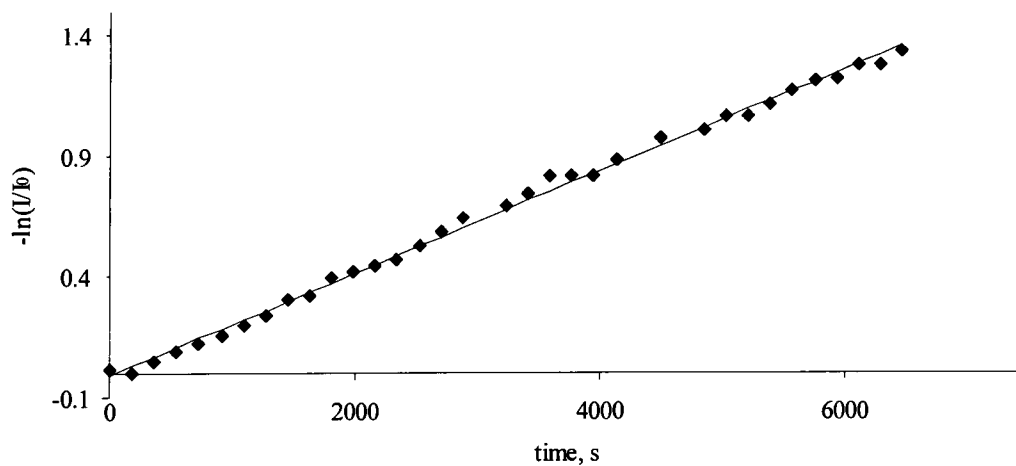
(viii) Plot of $\ln(I/I_0)$ vs. time for the 'BuNCO extrusion reaction of $[\text{Ti}(\eta\text{-C}_5\text{H}_4\text{Me})\{\text{N}'\text{BuC}(\text{O})\text{O}\}\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{NMe}_2\}]$ (**21**) at $1.9 \times 10^8 \text{ mol dm}^{-3}$.



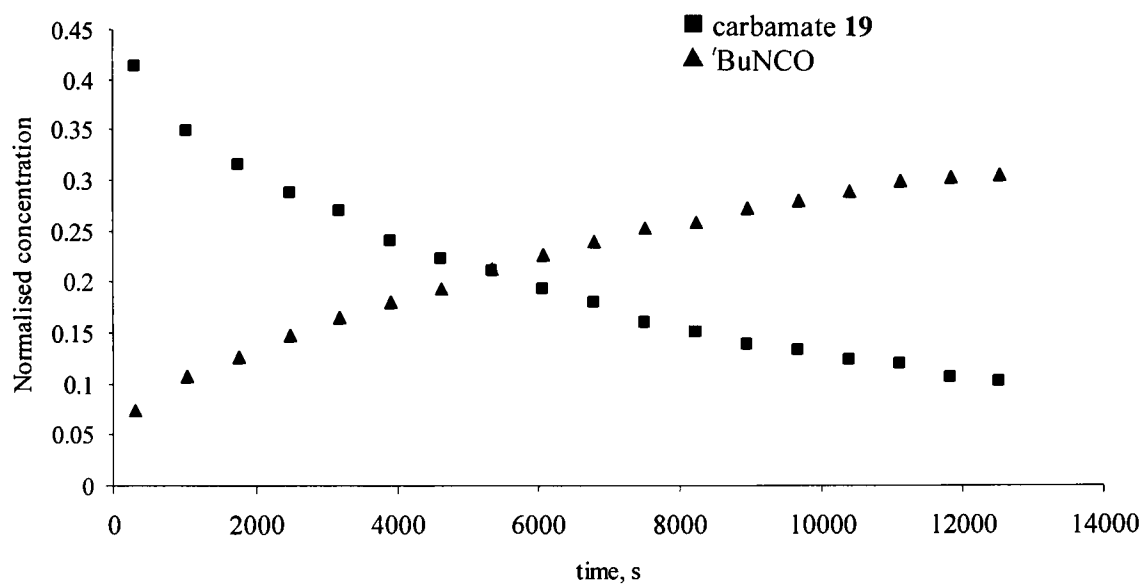
(ix) Plot of normalised concentrations for the 'BuNCO extrusion reaction of $[\text{Ti}(\eta\text{-C}_5\text{H}_4\text{Me})\{\text{N}'\text{BuC}(\text{O})\text{O}\}\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{NMe}_2\}]$ (**21**) at $1.9 \times 10^8 \text{ mol dm}^{-3}$ (duplicate run). Values are given for the carbamate **21** and 'BuNCO.



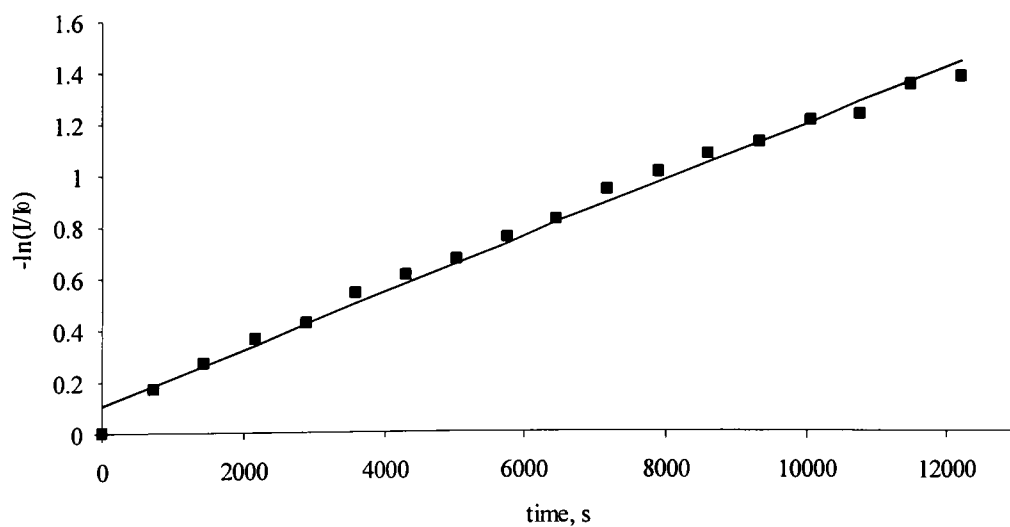
(x) Plot of $\ln(I/I_0)$ vs. time for the 'BuNCO extrusion reaction of $[\text{Ti}(\eta\text{-C}_5\text{H}_4\text{Me})\{\text{N}'\text{BuC}(\text{O})\text{O}\}\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{NMe}_2\}]$ (**21**) at $1.9 \times 10^8 \text{ mol dm}^{-3}$ (duplicate run).



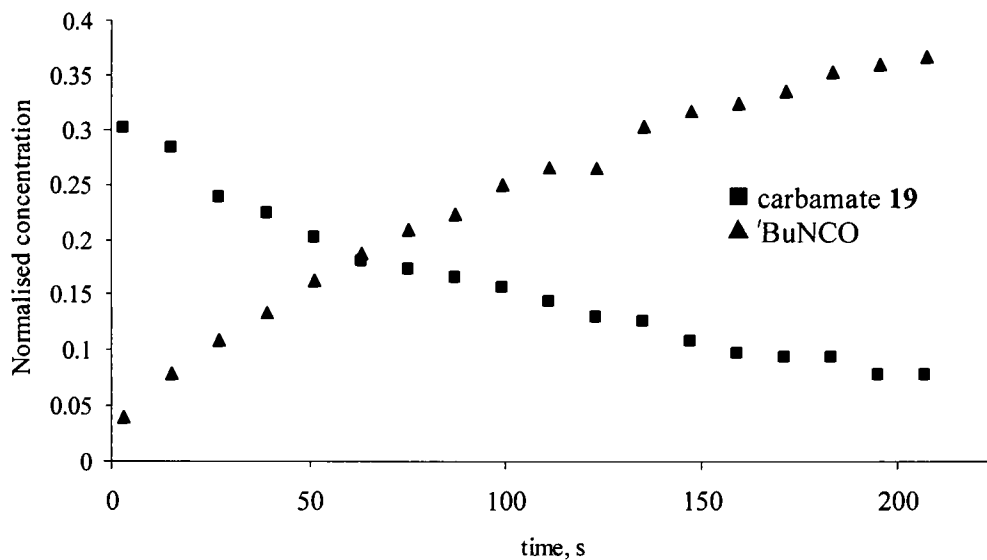
(xi) Plot of normalised concentrations for the ^tBuNCO extrusion reaction of [Ti(η-C₅H₄Me){N^tBuC(O)O}{Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂} (19) at 1.9 × 10⁸ mol dm⁻³. Values are given for the carbamate 19 and ^tBuNCO.



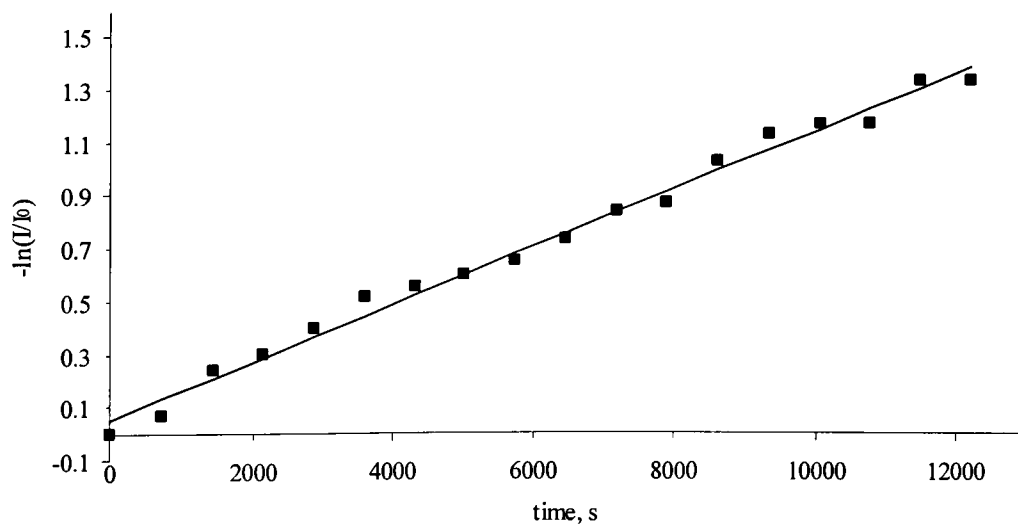
(xii) Plot of ln(I/I₀) vs. time for the ^tBuNCO extrusion reaction of [Ti(η-C₅H₄Me){N^tBuC(O)O}{Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂} (19) at 1.9 × 10⁸ mol dm⁻³.



(xiii) Plot of normalised concentrations for the 'BuNCO extrusion reaction of $[\text{Ti}(\eta\text{-C}_5\text{H}_4\text{Me})\{\text{N}'\text{BuC}(\text{O})\text{O}\}\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}]$ (**19**) at $1.9 \times 10^8 \text{ mol dm}^{-3}$ (duplicate run). Values are given for the carbamate **19** and 'BuNCO



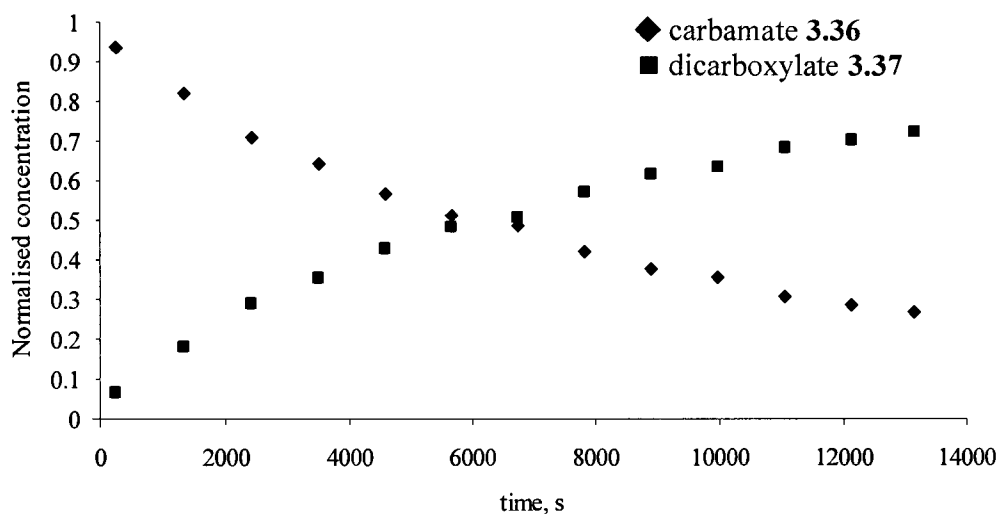
(xiv) Plot of $\ln(I/I_0)$ vs. time for the 'BuNCO extrusion reaction of $[\text{Ti}(\eta\text{-C}_5\text{H}_4\text{Me})\{\text{N}'\text{BuC}(\text{O})\text{O}\}\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}]$ (**19**) at $1.9 \times 10^8 \text{ mol dm}^{-3}$ (duplicate run).



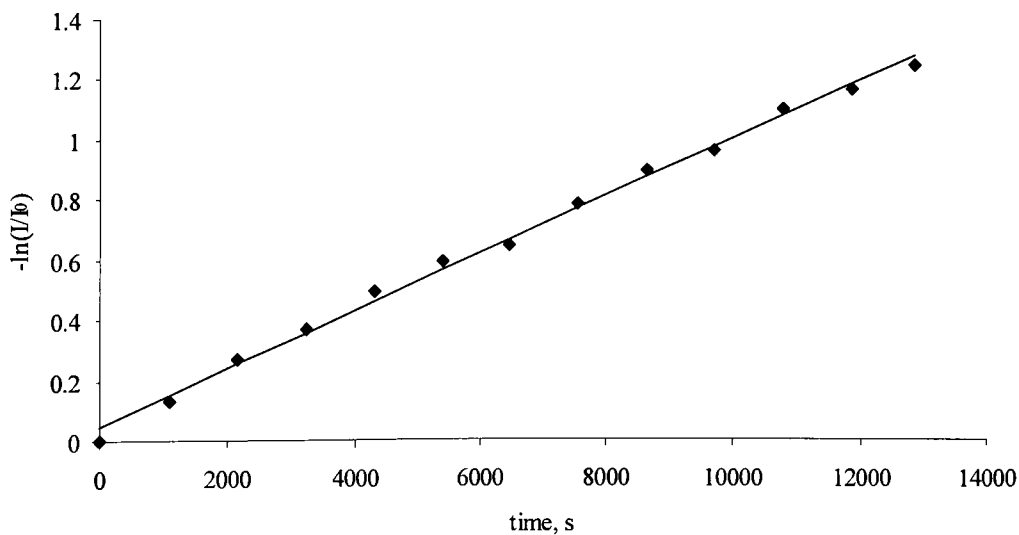
Second addition of CO₂ to [Ti(η -C₅Me₅){N-4-C₆H₄Me}C(O)O]{MeC(N^{*i*}Pr)₂}]

(3.36): kinetic studies

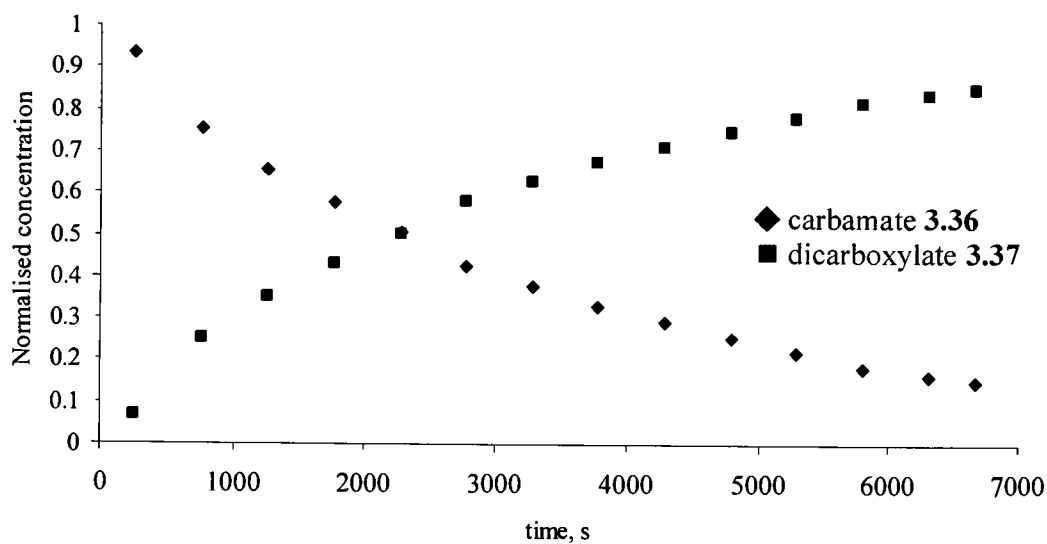
(i) Plot of normalised concentrations against time for the insertion reaction of **3.36** with CO₂ (0.25 atm). Values are given for starting carbamate **3.36** and product dicarboxylate **3.37**.



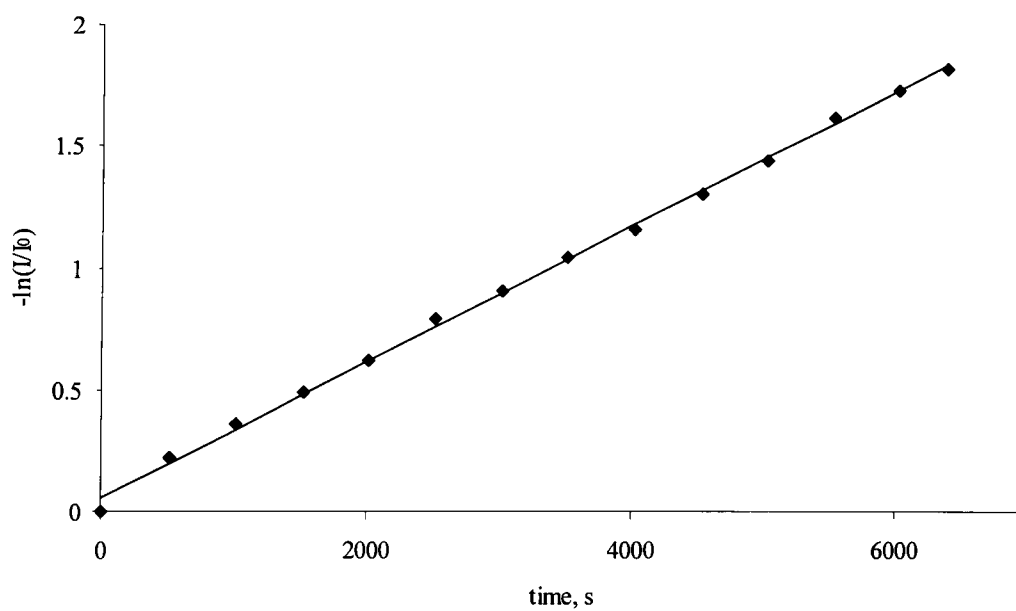
(ii) Plot of $\ln(I/I_0)$ vs. time for the consumption of **3.36** (0.25 atm CO₂)



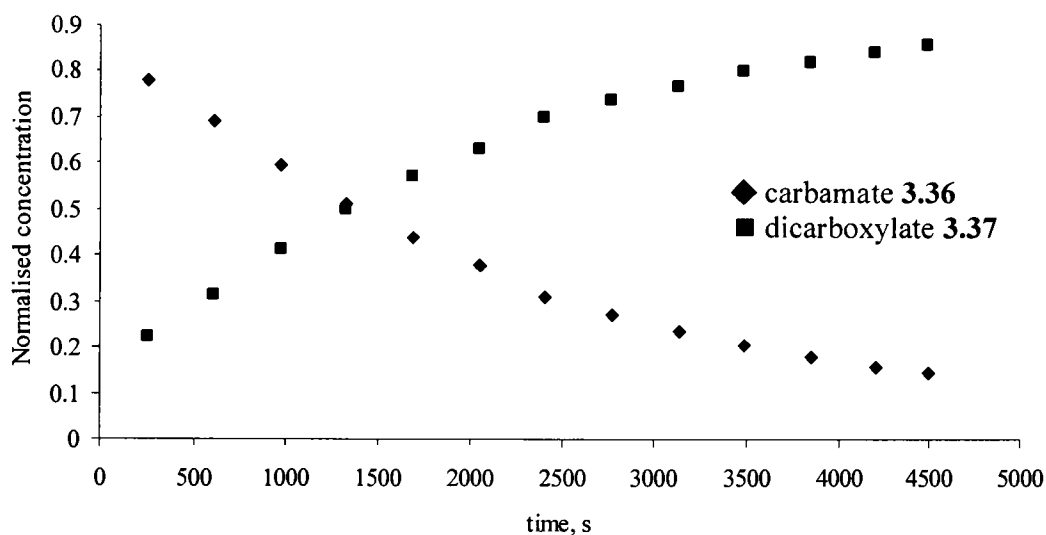
(iii) Plot of normalised concentrations against time for the insertion reaction of **3.36** with CO₂ (0.5 atm). Values are given for starting carbamate **3.36** and product dicarboxylate **3.37**.



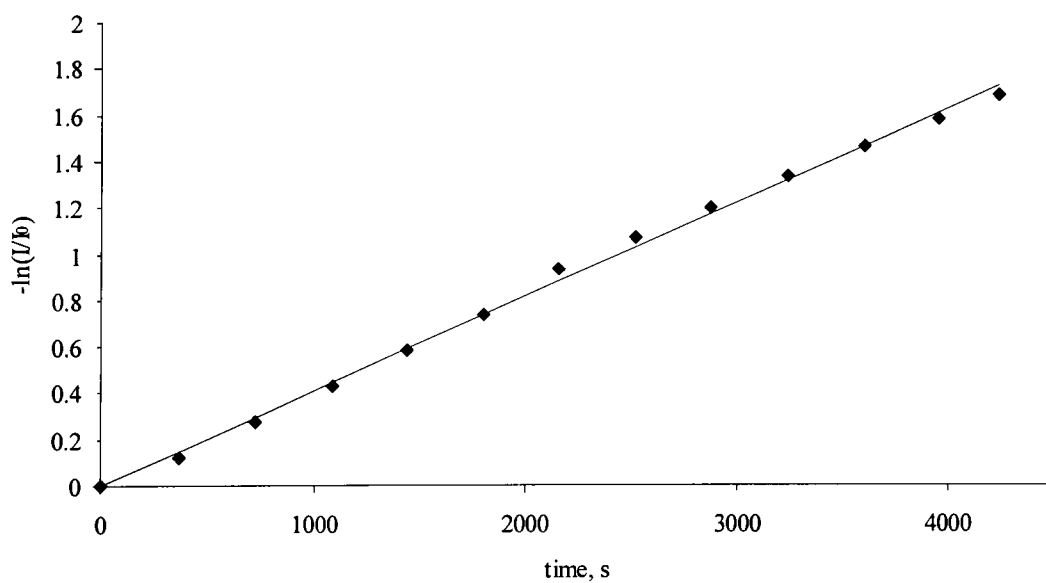
(iv) Plot of $\ln(I/I_0)$ vs. time for the consumption of **3.36** (0.5 atm CO₂)



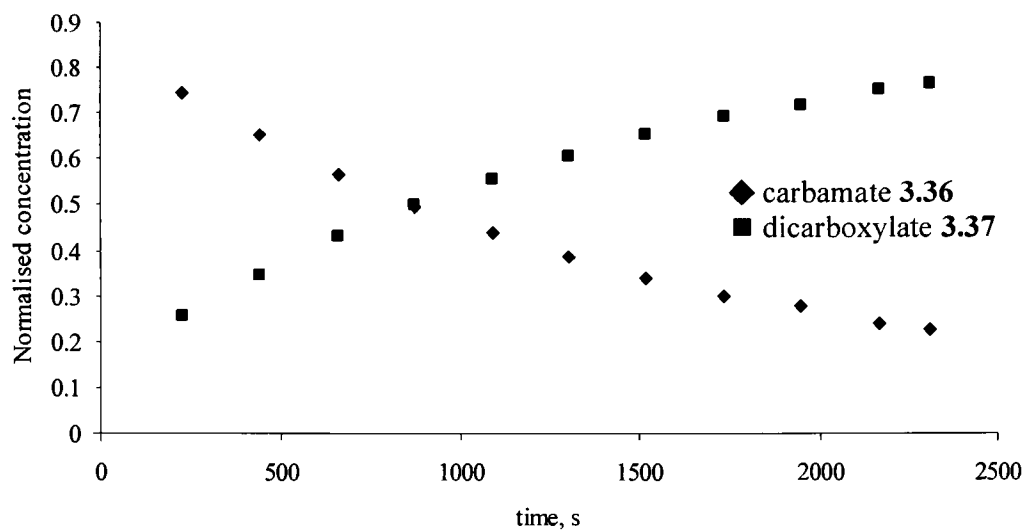
(v) Plot of normalised concentrations against time for the insertion reaction of **3.36** with CO₂ (0.75 atm). Values are given for starting carbamate **3.36** and product dicarboxylate **3.37**.



(vi) Plot of $\ln(I/I_0)$ vs. time for the consumption of **3.36** (0.75 atm CO₂)



(vii) Plot of normalised concentrations against time for the insertion reaction of **3.36** with CO₂ (1.0 atm). Values are given for starting carbamate **3.36** and product dicarboxylate **3.37**.



(viii) Plot of $\ln(I/I_0)$ vs. time for the consumption of **3.36** (1.0 atm CO₂)

