2004

SYNTHESIS, PROPERTIES, STRUCTURAL CHARACTERIZATION, AND REACTIVITY OF LOW-VALENT TITANIUM (BISDIIMINE) COMPLEXES

Marc Steven Maynor

University of Kentucky, maynor20@hotmail.com

ABSTRACT OF THESIS

SYNTHESIS, PROPERTIES, STRUCTURAL CHARACTERIZATION, AND REACTIVITY OF LOW-VALENT TITANIUM (BISDIIMINE) COMPLEXES

The synthesis, structure, and reactivity of titanium bis(diimine) complexes supported by 1,2-alternate dimethylsilyl-bridged p-tert-butylcalix[4]arene dianion and 2,2' methylene-bridged 4-methyl, 6-tertbutyl phenol ligands is reported. The molecular structure of [(DMSC)Ti(bpy)2] (**28**) and [(MBMP)Ti(bpy)2] (**55**) was characterized by X-ray crystallography. Complexes [(DMSC)Ti(bpy)2] (**28**), [(DMSC)Ti(dmbpy)2] (**29**), and [(DMSC)Ti(phen)2] (**30**) undergoes light-assisted reactions with two or more equivalents of (C6H5)2CO or (p-MeC6H4)2CO to give the corresponding 1-aza-5-oxa-titanacyclopentene complexes **37**-**42**. Similar reactivity was observed with [(MBMP)Ti(bpy)2] (**55**), [(MBMP)Ti(dmbpy)2] (**56**), and [(MBMP)Ti(phen)2] (**57**). The molecular structure of [(MBMP)Ti{kappa-3-OC(C6H5)2C10H7N2}{OCH(C6H5)2}] (**58**) was characterized by 1H and 13C NMR as well as X-Ray crystallography.

KEYWORDS: low-valent titanium, aromaticity, diimine complexes, X-ray crystallography, fluxionality

Marc Steven Maynor

July 28, 2004

SYNTHESIS, PROPERTIES, STRUCTURAL CHARACTERIZATION, AND REACTIVITY OF LOW-VALENT TITANIUM BIS (DIIMINE) COMPLEXES

By

Marc Steven Maynor

Folami T. Ladipo Ph.D.
Director of Thesis

Mark S.Meier, Ph.D.
Director of Graduate Studies

RULES FOR THE USE OF THESES

Unpublished theses submitted for the Master's degree and deposited at the University of Kentucky Library are as a rule open for inspection, but are to be used only with due regard to the rights of the authors. Bibliographical references may be note, but quotations or summaries of parts may be published only with the permission of the author, and with the usual scholarly acknowledgments. Extensive copying or publication of the thesis in whole or in part also requires the consent of the Dean of the Graduate School of the University of Kentucky.

THESIS

Marc Steven Maynor

The Graduate School

University of Kentucky

2004

SYNTHESIS, PROPERTIES, STRUCTURAL CHARACTERIZATION, AND REACTIVITY OF TITANIUM (BISDIIMINE) COMPLEXES

THESIS

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in the College of Arts and Sciences at the University of Kentucky

By

Marc Steven Maynor

Lexington, Kentucky

Director: Dr. Folami T. Ladipo, Associate Professor of Chemistry

Lexington, Kentucky

2004

This is dedicated to all of my family and friends

ACKNOWLEDGEMENTS

I would like to thank my advisor, Prof. Folami Ladipo, for his support throughout my stay here. There were many times that he pointed me towards the "truth" when I was running away from it. I appreciate his philosophical discussions about chemistry as well as topics outside of the discipline. I would like to thank Prof. Jack Selegue whose expert opinion and breadth of knowledge have often inspired me to learn more. I wish to thank Prof. Stephen Holmes who always helps me to remember the basics principles of chemistry (the answers always start with the basics). Crystallographic data within this thesis would not be possible without "super" crystallographer Dr. Sean Parkin. The NMR facility was my third home (behind the lab and my place of residence) and I would like to thank John Layton for the NMR training and for the thousands of questions I asked him about different NMR techniques. I would like to thank the staff in the stock room and in the chemistry and business office. They have always acted in a professional manner and their willingness to help is very much appreciated.

The members of the Ladipo group, David Owiny and Dr. J. Kingston, were truly a joy to work with. We have had several fruitful discussions about our respective research. Dr. Kingston was extremely helpful in helping me develop my lab techniques. Also his ability to beautifully wrap boxes for CHN analysis deserves special mention. David Owiny's hard work and dedication truly inspired me. His insightful opinions have helped me within chemistry as well as in life. I would like to thank Dr. David Eaton, Chad Snyder, Minh Truong, and Jeffrey Withers, past and current members of the Holmes and Selegue groups for helping create a friendly and stimulating environment in the otherwise "gloomy" basement.

I would like to thank my good friend Monica Rawlinson. Whenever the pressures of chemistry and research weighed heavy on me, your hard work and dedication to your craft has truly inspired me. Most of all, I would like to thank my parents, Mary and Alvin Maynor, my two sisters Sharon and Sharetta, and my brother Javon, for support (both mentally and financially) throughout my time in Kentucky.

I would like to thank Derrick Holeman and Rashada Alexander for all the good times we had inside and out of the department as well as the insightful conversations we had about life.

Okay, if I accidentally forgot to mention you please forgive me. In case I did, grab a pen. Special, special thanks to _____ for whatever he/she did to make that thing you helped me with happen. S/He was really an inspiration to me. Without him/her I wouldn't have made it this far.

TABLE OF CONTENTS

Acknowledgements……iii

List of Tables...…… .vii

List of Figures……..……viii

List of Schemes……ix

List of Files……..x

Chapter One: Introduction
1.1 Intent of Thesis……1

1.2 Background……...1

Chapter Two: Synthesis, structure, and reactivity of titanium bis(diimine) complexes supported by DMSC ligand

2.1 Introduction……...11

2.2 Synthesis and characterization of [(DMSC)Ti(bpy)$_2$], [(DMSC)Ti(dmbpy)$_2$], and [(DMSC)Ti(phen)$_2$] ..…….……..12

2.3 Reactivity of [(DMSC)Ti(L$_2$)$_2$] complexes]……..14

2.4 Experimental Section……..…26
2.4.1 General details……..26
2.4.2 Preparation of Ti(diimine) complexes……..26
2.4.3 NMR reactions of [(DMSC)Ti(L$_2$)$_2$] complexes **28**-**30**…….…. .28

Chapter Three: Synthesis, structure, and reactivity of titanium bis(diimine) complexes supported by MBMP ligand

3.1 Introduction……...29

3.2 Synthesis of [(MBMP)Ti(bpy)$_2$], [(MBMP)Ti(dmbpy)$_2$], and [(MBMP)Ti(phen)$_2$]……...……...30

3.3 Reactivity of [(MBMP)Ti(L$_2$)$_2$] complexes…….…..37

3.4 Experimental Section……..…44

3.4.1 General details……..44

3.4.2 Preparation of Ti (diimine) complexes…….44
3.4.3 Cyclotrimerization of Phenylisocyanate……..46
Chapter Four: Conclusion and future research……..…….47

Appendix……49

References..……...74

Vita…….77

LIST OF TABLES

Table 2.1 Selected ^{1}H NMR data for [(DMSC)Ti(L_2)$_2$] complexes……14

Table 2.2 Selected Bond distances and Angles of **28**……...16

Table 2.3 Selected Bond distances and Angles of **45**……..…….24

Table 3.1 Selected Bond distances and Angles of **55**……..…….34

Table 3.2 Selected Bond distances and Angles of **61**…..…….40

LIST OF FIGURES

Figure 2.1. Molecular Structure of **28** ……15

Figure 2.2. Molecular Structure of **40….**……20

Figure 2.3. Molecular Structure of **45**……...……...23

Figure 3.1. Molecular Structure of **55**…….…….……33

Figure 3.2 Variable Temperature ^{1}H NMR of **55**……35

Figure 3.3. Molecular Structure of **61…**……...……39

Figure 3.4. Molecular Structure of **64**……..……...……..42

LIST OF SCHEMES

Scheme 1.1 Examples of Well-Characterized [(η^5-$C_5R_5)_2$Ti(II)] Complexes…….3

Scheme 1.2 Reduction chemistry of [(BTBA)$TiCl_2$]……5

Scheme 1.3 Reactivity of $Ti(bpy)_3$...…….……7

Scheme 1.4 Reactivity of [(DMSC)Ti(1,2,4-$(Me_3Si)_3C_6H_3$)] …….……9

Scheme 2.1. Synthesis of [(DMSC)Ti$(L_2)_2$] Complexes …….……13

Scheme 2.2. Reactivity of [(DMSC)Ti$(L_2)_2$] Complexes with Ar_2CO……19

Scheme 2.3. Formation of **43-45**…….21

Scheme 2.4. Organic Products of **46-51** (detected by GC/MS)……...25

Scheme 3.1. Synthesis of [(MBMP-Ti$(L_2)_2$] Complexes (**55-57**)……31

Scheme 3.2 Possible Twist Mechanism……...…..…….…….32

Scheme 3.3 Cyclotrimerization of Phenylisocyanate…….……..42

List of files

MSMthes.pdf…….1.74 MB

Chapter One

Intoduction

1.1 Intent of Thesis

The intent of this research was to synthesize and structurally characterize low-valent titanium bis (diimine) complexes. The properties and reactivity of these complexes with organic substrates were investigated. Low-valent titanium (LVT) species have been shown to have a wide range of applications in organic syntheses, such as McMurry chemistry,[1-7] substitution of nitrobenzenes,[8] cyclodimerization of unsaturated ketones[9], coupling of chiral diimines,[10] oligomerization of olefins, acetylenes, and carbonyl derivatives,[11] and reduction of nitrobenzenes to amino arenes.[12,13] Commonly, LVT species used in organic synthesis are generated by reduction of titanium tetrachloride or titanium trichloride or Ti (IV) complexes of the type L_2TiX_2 (L = Cp, NR_2, and X = Cl, Br, or OR) with common electropositive reducing agents such as Na, Zn, Li, Mg, and K.

There are a few drawbacks to the "black box" approach in organic synthesis. The LVT species is usually generated *in situ* leading to ambiguity regarding (i) the oxidation state of the titanium, (ii) the reactive species in the reaction, as well as (iii) the mechanism of the reaction. Understanding the mechanism and the properties of the reactive titanium species is important in order to expand the use of LVT. Therefore, there is great interest in synthesis and reactivity of well-characterized LVT complexes.

1.2 Background

The commercially available $TiCl_2$ (**1**) and $TiCl_3$ (**2**) are two of the simplest examples of LVT species. Walton and coworkers have found that **1** will react with MeCN to form $[TiCl_2(MeCN)]$ (**3**). The reaction of **3** with various donor molecules results in compounds of the type $[TiCl_2L_2]$ or $[TiCl_2B]$, (L = mondentate ligand pyridine, tetrahydrofuran, or tetrahydropyran; B = bidentate ligand 2,2'-bipyridyl or 1,10-phenanthroline). In these cases the Ti was assigned a +2 oxidation state.[14] A series of TiE_2 (E = Cl, F, OBu^n, Opr^i and 0.5 NPh-CH_2-CH_2-NPh) compounds was prepared by Eisch and coworkers by the alkylative reduction of TiE_4 with two equivalents of *n*-butyllithium. [15] (eq. 1.1)

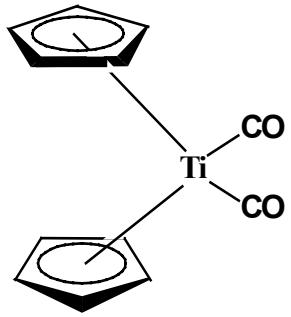
$$TiE_4 + 2BuLi \xrightarrow[-78\ C]{THF/Toluene} Ti(E)_2 + 2LiE \quad \text{(eq. 1.1)}$$

Without question, the use of metallocenes [$(\eta^5\text{-}C_5R_5)_2M$] has been a milestone in the development of organometallic chemistry. Scheme 1.1 depicts a few examples of stable, well-characterized Ti (II) complexes supported by cyclopentadienyl ligands. Bis(η^5-cyclopentadienyl)titanium (II) dicarbonyl (**4**) was prepared by Bercaw and coworkers[16] (Scheme 1.1). The authors found the compound to be diamagnetic. Hückel molecular orbital calculations were carried out for this complex showing that there is back-donation of electron density from the filled metal orbitals into the π^*-orbitals of the carbonyl ligands. These calculations indicated that this back-bonding is important for stabilizing the electron-rich Ti (II) center.[17] Reacting **4** with 2,2-bipyridyl led to the formation of bis(η^5-cyclopentadienyl)titanium 2,2'-bipyridyl **(5)**[18] (Scheme 1.1).

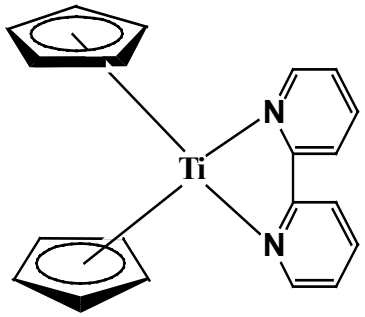
Calderazzo and coworkers were able to prepare **5** by reacting bis(η^5-cyclopentadienyl) titanium dichloride with the dilithium salt of 2,2-bipyridine dianion.[19] **5** was found to be weakly paramagnetic giving a room temperature EPR signal.[18,19] McPherson and coworkers conducted magnetic susceptibility and EPR studies on **5**. The results of this study suggest that the system is diamagnetic in the ground state but has a paramagnetic exited state that is thermally accessible. The authors concluded that one unpaired electron formally occupies a molecular orbital which is localized on bis(η^5-cyclopentadienyl) titanium while the second unpaired electron resides in the lowest energy anti-bonding orbital of the bipyridyl group.

Lawless and coworkers were able to isolate the bis[(η^5-(*tert*-butyldimethylsilyl)-tetramethylcyclopentadienyl)] titanium (II) complex (**6)** by the reduction of [{η^5-C_5Me_4 ($SiMe_2$-*t*-Bu)}$_2$TiCl] with sodium amalgam in toluene (Scheme 1.1). Following the discovery by Lawless, Mach and co workers were able to isolate and characterize the analogous {{η^5-$C_5Me_4(SiMe_3)$}$_2$$Ti^{II}$] (**7)** [20] (Scheme 1.1). Complex **7** was isolated by heating {{η^5-$C_5Me_4(SiMe_3)$}$_2$Ti-η^2-$Me_3SiC{\equiv}CSiMe_3$)] *in vacuo*. The paramagnetic species **6** and **7** were characterized by X-ray crystallography and revealed that the Cp-rings are parallel. The authors attributed the stability of **6** and **7** to the alignment and

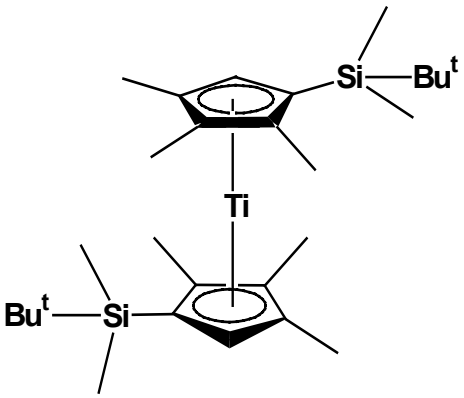
Scheme 1.1: Examples of Well-Characterized [(η^5-$C_5R_5)_2$Ti(II)] Complexes



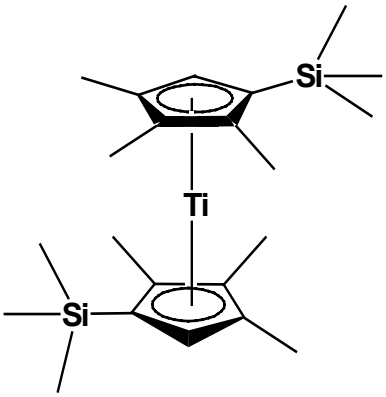
4



5



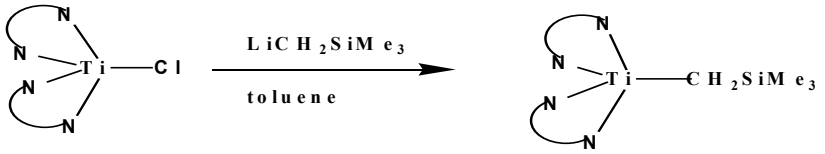
6



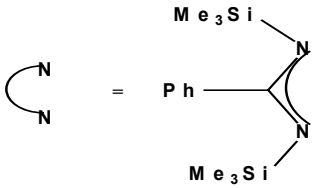
7

steric bulk of the Cp-rings.

The low cost, facile synthesis, high solubility and spectroscopic properties of the benzamidinate (BTBA) ligand were attractive to Arnold and coworkers. They were able to synthesize a series of titanium (II) and titanium (III) complexes supported by (BTBA) ligands.[21-22] The titanium (III) complex [$(BTBA)_2TiCl(THF)$](**8**) was synthesized from the reduction of [$(BTBA)_2TiCl_2$] with Na/Hg amalgam in THF (Scheme 1.2).[21] The paramagnetic species **8** was isolated as green crystals from recrystallization in hexanes in low yield (<30%). Solid-state magnetic susceptibility measurements were consistent with of a titanium (III) center. Further recrystallizations in hexanes provided paramagnetic solvent-free crystals of [$(TBA)_2TiCl$] (**9**) (Scheme 1.2). Magnetic susceptibility measurements were also consistent with a titanium (III) center. The X-ray structure was in contrast to the known titanocene derivative $[Cp_2TiCl]_2$ which is dimeric. Compound **9** was found to be a good starting material for the synthesis of Ti (III) alkyls (see equation 1.2 for example). Just as in the case of the precursors **8** and **9**, the complexes were found to be paramagnetic and monomeric species.



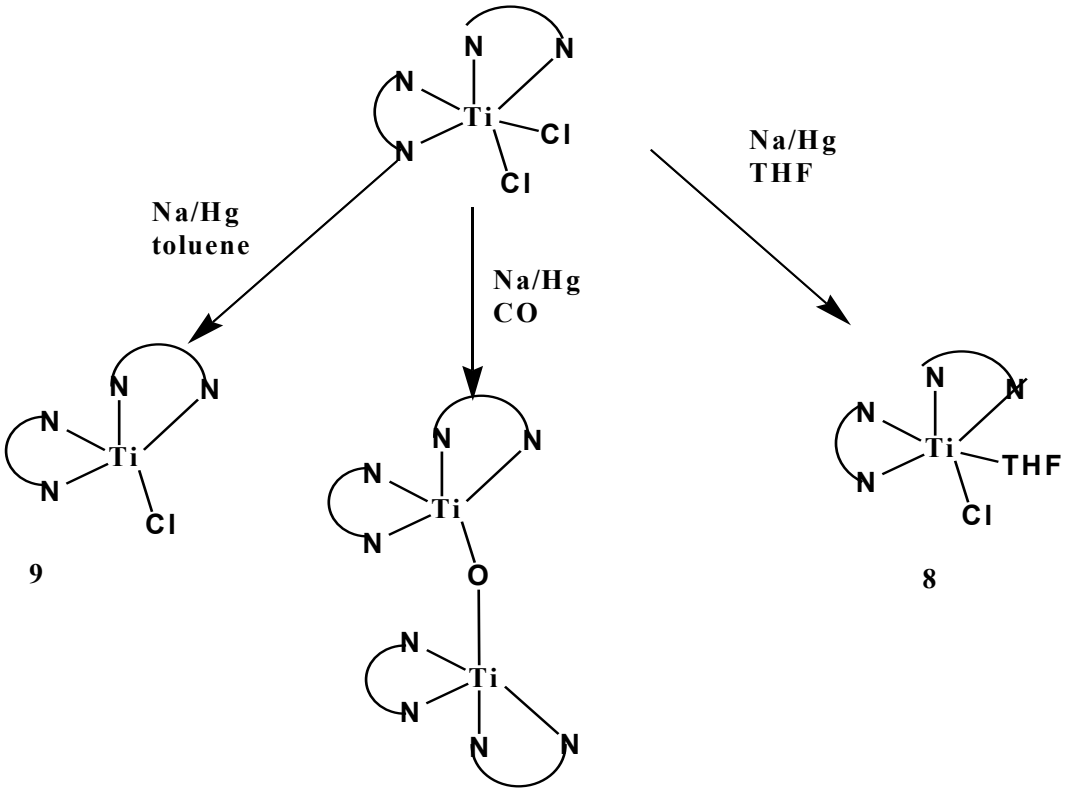
(eq. 1.2)

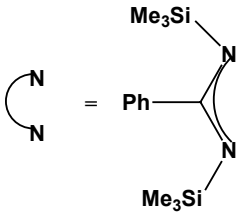


The reduction of [$(BTBATiCl_2)$] with Na/Hg in the presence of CO resulted in the formation of the paramagnetic Ti (III) bridging-oxo species [$(BTBA)_2Ti)_2(\mu$-O)] (**10**) complex (Scheme 1.2).[22] X-ray crystallography of the structure exhibits a linear Ti-O-Ti linkage. The short Ti-O bond lengths (1.821 Å) suggest partial double bond character. The magnetic susceptibility measurements were consistent with two essentially uncoupled d^1-Ti centers.[22]

The rich redox chemistry of divalent metalloporphyrin complexes led Woo and coworkers towards the synthesis of low-valent titanium porphyrin complexes.[23-24] The

Scheme 1.2: Reduction Chemistry of $[(BTBA)_2TiCl_2]$





group was able to synthesize and structurally characterize the first titanium (II) porphyrin complex.[23] The ligands used in this synthesis were octaethylporphyrinato (OEP) or *meso*-tetra-*p*-tolyl-porphyrinato (TTP). The titanium (II) complex was synthesized from the reduction of $[(OEP)TiCl_2]$ or $[(TTP)TiCl_2]$ with $LiAlH_4$ in the presence of diphenylacetylene in toluene. This produced the π-alkyne titanium (II) complexes $[(OEP)Ti(\eta^2\text{-}PhC{\equiv}CPh)]$ **(11)** and $[(TTP)Ti(\eta^2\text{-}PhC{\equiv}CPh)]$ (**12**) as purple microcrystals.

$$[(POR)TiCl_2] + PhC{\equiv}CPh \xrightarrow{LiAlH_4} [(POR)Ti(PhC{\equiv}CPh)] \quad (1.3)$$

POR = OEP (7)
TTP (8)

Complexes **11** and **12** are diamagnetic and exhibit sharp ^1H NMR signals. The X-ray structure of **11** revealed the geometry about the Ti center was square pyramidal with the pyrrole nitrogens forming the basal plane and the alkyne triple bond at the apical site. The C≡C stretching frequencies for the two complexes were consistent with a four-electron-donor acetylene. Woo and co-workers also synthesized a series of (TTP)Ti (II) η^2-alkyne complexes.[23] Facile synthesis of these complexes was later developed by the reduction of $[(OEP)TiCl_2]$ or $[(TTP)TiCl_2]$ with $NaBEt_3H$ in the presence of various alkynes.[24]

$[Ti(bpy)_3]$ (**13**), first prepared by Herzog and coworkers by the reduction of $TiCl_4$ in THF by lithium in the presence of 2-2'-bipyridyl, was isolated as a dark blue, air-and moisture-sensitive compound.[26] The ^1H NMR spectrum showed the coordinated bipyridyl of **13** as well as the analogous $Ti(dmbpy)_3$ (**14**) had an upfield shift of about 1.5 ppm relative to the free diimine.[27] The upfield shift of the coordinated diimines was attributed

$$TiCl_4 + 3\ bpy \xrightarrow[THF]{Li} [Ti(bpy)_3] \quad (1.4)$$

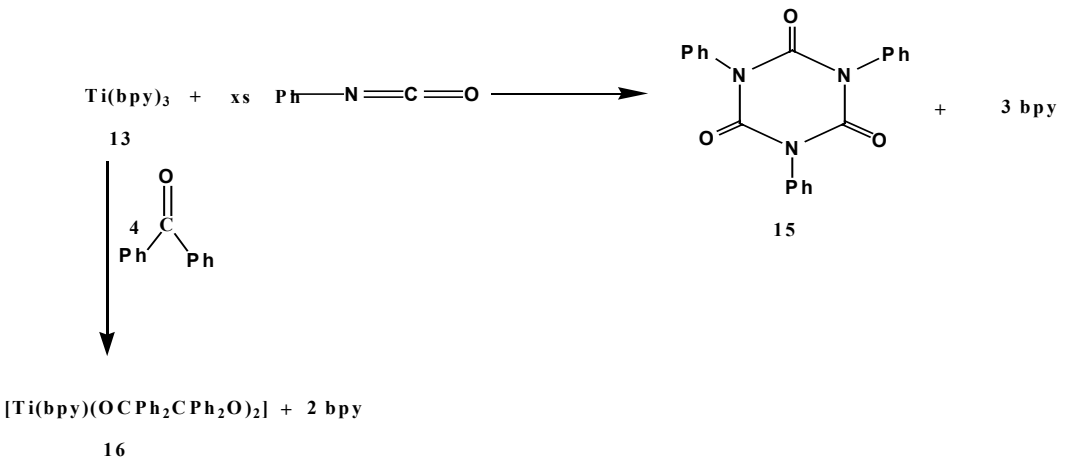
bpy = 2,2'-bipyridyl

to the presence of a considerable negative charge on the bonded ligand. Although this complex has been isolated and characterized, the exact oxidation state is not clear.

Assignments of the oxidation state of **13** and **14** have ranged from 0 to +4. Flamini and

coworkers have assigned the oxidation state of Ti for complexes **13** and **14** as +3. This suggests these complexes are best viewed as $[Ti^{3+}(bpy^{-1})_3]$ although formulation of the oxidation state of the metal center has not been fully defined.[28] The authors suggested complexes **13** and **14** have a singlet state far below the first excited triplet state that is not thermally accessible. An EPR signal was not given upon heating indicating a diamagnetic species. The reactivity of **13** was probed by Flamini and coworkers.[26,27] According to the authors, the reaction of **13** with 4 equivalents of benzophenone gave the Ti(IV) complex $[Ti(bpy)(OCPh_2CPh_2O)_2]$ (**15**) with 2 equivalents of free bipyridine as the by-product. The author mentioned the reactivity of **13** with benzophenone was consistent of a titanium (III) complex. The authors also discovered that the addition of excess phenylisocyanate to **15** led to the catalytic formation of triphenylisocyanurate (**16**).[27]

Scheme 1.3: Reactivity of $Ti(bpy)_3$



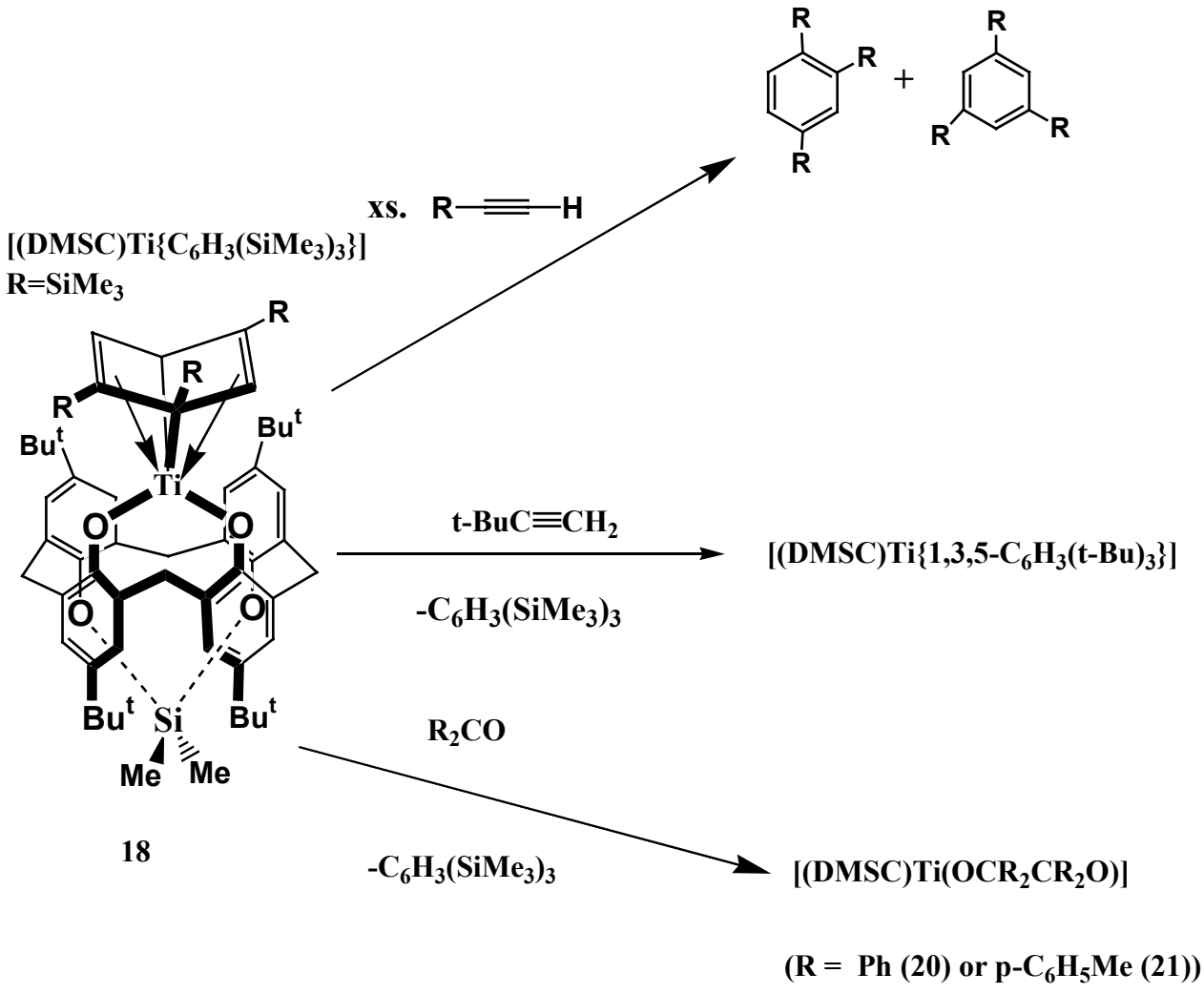
Recently, the synthesis of the titananorbornadiene (η^6-arene) complex [(DMSC)Ti(1,2,4-$(Me_3Si)_3C_6H_3$)] (**18**) (DMSC = 1,2-alternate dimethylsilyl-bridged *p-tert*-butylcalix[4]arene) was reported.[28] Complex **18** was prepared from the reduction of $[(DMSC)TiCl_2]$ with Mg* (activated magnesium) in the presence of excess $Me_3SiC{\equiv}CH$ and obtained as a yellow air-and moisture-sensitive diamagnetic solid in good yield. Compound **18** was characterized by ^1H and ^{13}C NMR and X-ray crystallography. The NMR data revealed **18** as being C_1-symmetric in solution. Three singlets were observed for the η^6-arene $SiMe_3$ group. The Bu^t groups of the calix[4]arene ligand are observed as four singlets. X-ray diffraction studies of **17** were consistent with 1,2 alternate conformation of the calix[4]arene ligand and showed that the $SiMe_3$ groups are 1,2,4-

substituted around the arene ring. Although **18** can be conceived as a Ti(II)-η^6-arene the complex has significant Ti (IV) character. The complex can be more precisely described as a 7-titananorbornadiene complex. Addition of excess $Bu^tC{\equiv}CH$ to **18** gave [(DMSC)Ti{η^6-1,3,5-$C_6H_3Bu^t_3$}] (**19**). Interestingly, **19** was found to be *Cs*-symmetric in solution by ^1H and ^{13}C NMR data. NMR data are consistent with the calixarene ligand of **19** being in the 1,2 alternate conformation.

The isolation and characterization of **18** provided the authors an opportunity to gain an insight of the mechanism and scope of the [2 +2 +2] cycloaddition of terminal alkynes. The titananorbornadiene (η^6-arene) complexes **18** and **19** are highly efficient catalysts for [2 + 2 + 2] cycloaddition of terminal alkynes. 1,2,4-substituted benzenes were produced with excellent regioselectivity (due to the steric environment of the calix[4]arene) and in excellent yield. Compound **19** is generally less reactive toward alkynes than **18** for steric reasons. The authors found that the rate and regioselectivity of the cyclotrimerization was affected by the steric properties of the alkyne substituent. **18** and **19** were found to rarely cyclotrimerize internal alkynes. The authors noted that **18** cyclotrimerizes 65 equivalents of 2-butyne with 94% conversion. However, 93 h was required for this conversion. The potential of **18** as a (DMSC)Ti (II) synthon prompted authors to probe its reactivity with ketones and aldehydes.[29] Reactions of **18** with Ar_2CO (Ar = Ph or *p*-C_6H_5Me) gave 2,5-dioxatitanacyclopentane derivatives [(DMSC)Ti(OCR_2CR_2O)] (R = Ph (**20**) or *p*-C_6H_5Me (**21**)) in good yields. Compounds **20** and **21** were isolated as yellow thermally stable, air-and-moisture sensitive solids.[30]

While low-valent titanium complexes have been reported in the literature, the interest in the use of non-cyclopentadienyl ligands in LVT chemistry has grown in the past couple of decades due to the varying electronic and steric effects such ligands can impose on reactivity. This has led several groups to attempt to synthesize, isolate, and characterize LVT complexes supported by non-cyclopentadienyl complexes.[30-51] The overall goal of this research is to synthesize, characterize, and probe the reactivity of LVT complexes. The remainder of this thesis will examine the synthesis,

Scheme 1.4: Reactivity of [(DMSC)Ti(1,2,4-$(Me_3Si)_3C_6H_3$)]



characterization, and reactivity of low-valent titanium bis(diimine) complexes. The synthesis was investigated in order to find a facile method of producing these complexes in good yield. Characterization was carried out to confirm the composition of the LVT bis(diimine) complexes. The reactivity with various organic substrates was probed to define the scope of the chemistry of these complexes.

CHAPTER TWO

Synthesis, structure, and reactivity of low-valent titanium bis(diimine) complexes supported by DMSC ligand

2.1 Introduction

Low-valent titanium species are of great importance in reductive coupling processes. Over the past several years, research in our group has focused on developing well-characterized low-valent titanium complexes in an effort to understand the oxidation state, structure, mechanism, and transformations mediated by low-valent titanium. The synthesis of low-valent titanium bis(diimine) complexes [(DMSC)Ti(bpy)$_2$] (**28**, bpy = 2,2'-bipyridine) and [(DMSC)Ti(dmbpy)$_2$] (**29**, dmbpy = 44'-dimethyl-2,2'-dipyridyl) was recently reported by our group.[31] Rothwell reported the synthesis of the similar complex [(2,6-$Pr^i_2C_6H_3O)_2$Ti(bpy)$_2$] and cautiously assigned it as a Ti(II) complex based on preliminary electrochemical studies.[51] However, the properties and reactivity of these complexes have not been fully explored. In this chapter we would like to present our findings from our study of the properties and reactivity of **28**, **29**, and [(DMSC)Ti(phen)$_2$] (**30**, phen = 1,10 phenanthroline).

2.2 Synthesis and characterization of [(DMSC)Ti(bpy)$_2$], [(DMSC)Ti(dmbpy)$_2$], and [(DMSC)Ti(phen)$_2$]

Previous work in our group has shown [(DMSC)Ti(L_2)$_2$] (L_2 = aromatic diimine) complexes **28,** and **29** can be synthesized by several methods (Scheme 2.1).[30] The reaction of [(DMSC)TiPh$_2$] (**27**) with at least two equivalents of the appropriate aromatic diimine has been found to be the best and most convenient method to obtain these compounds in high yield. Ozerov found that using less than two equivalents of the appropriate diimine resulted in complexes **28** and **29** with the corresponding amount of **27** remaining. This suggests that the transformation of the putative [(DMSC)Ti(L_2)Ph$_2$] into [(DMSC)Ti(L_2)$_2$] complex is much faster that the initial coordination of the L_2 fragment to **27**.[30] Complexes **28** and **29** were found to be dark-blue, air-and moisture- sensitive solids. The compounds were found to be very soluble in aromatic hydrocarbon solvents, THF, moderately soluble in ether, and practically insoluble in pentane.

[(DMSC)Ti(phen)$_2$] (**30**) was similarly prepared to broaden the scope of the reactivity of the [(DMSC)Ti(L_2)$_2$] complexes. As with the previously prepared complexes, **30** was found to be air-and moisture sensitive. Interestingly, the color of **30** was found to be olive-green instead of dark-blue as in the cases of **28** and **29**. Complexes **28**-**30** were found to be stable in the solid state but are best stored for long periods of time at low temperatures under N_2 atmosphere. Complexes **28-30** were confirmed to be C_s-symmetric in solution at ca. 22 °C by ^{1}H and ^{13}C NMR data. Two of the six doublets integrate as two protons each and represent the methylene protons of the calix[4]arene ligand that are reflected by the mirror plane, which contains the remaining four methylene protons. The *tert*-butyl groups of the calixarene ligand are observed as two singlets each integrating as eighteen protons. In the case of **29**, the methyl protons of the dmbpy ligand were observed as two singlets (6H each). The high field shift of the *endo*-Me (located inside the calixarene cavity), compared to that of the *exo*-Me (located outside the calixarene cavity) of the bridging $SiMe_2$ group, gave evidence that the DMSC ligand exists in 1,2-alternate conformation (Table 2.1). The molecular structure of **28** in the solid state was determined by a single-crystal X-ray diffraction study. Selected bond angles and distances are summarized in Table 2.2.

The geometry about the Ti center is twisted away from trigonal prismatic towards

Scheme 2.1 Synthesis of [(DMSC)Ti(L_2)$_2$] Complexes

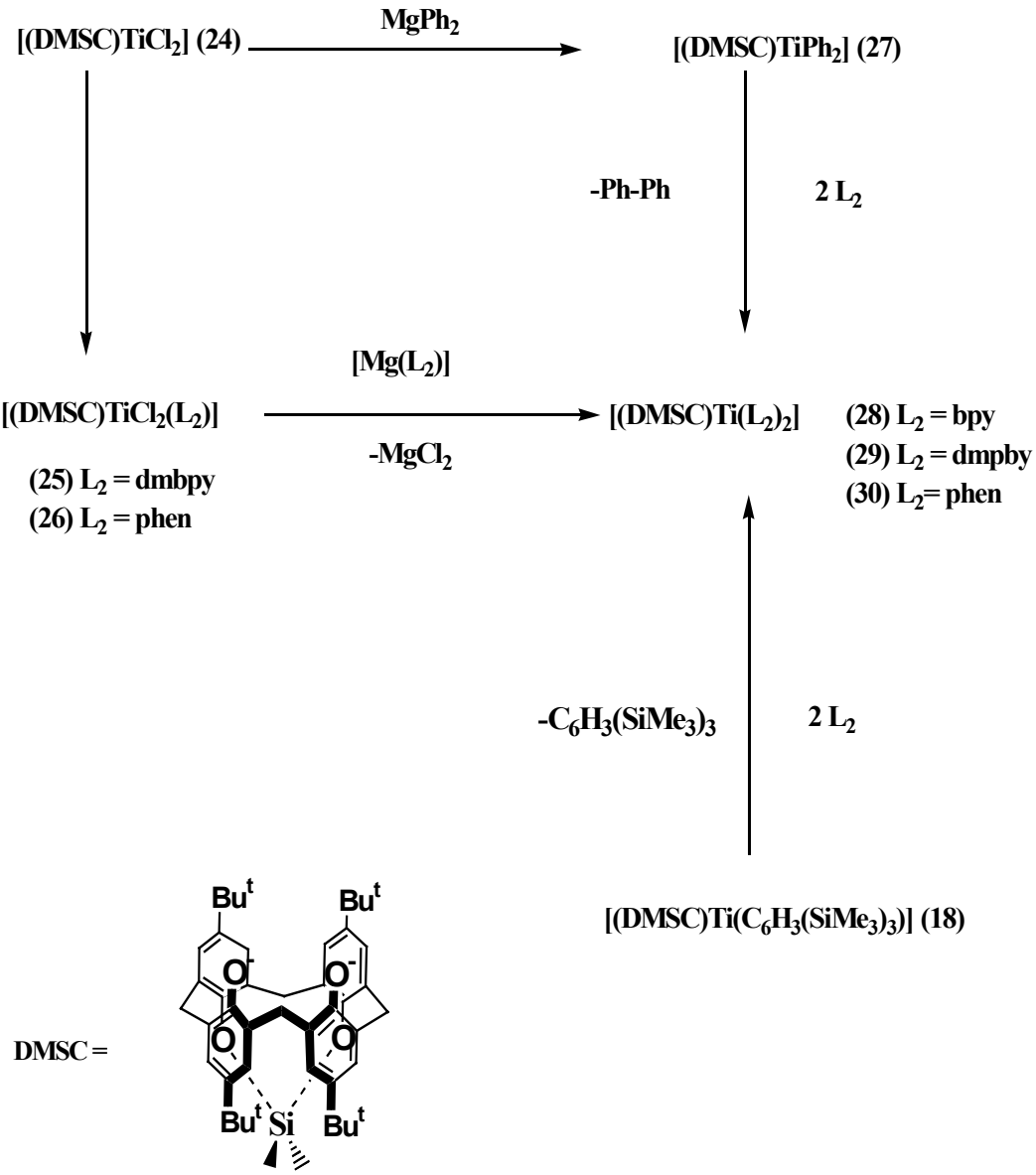


Table 2.1. Selected ^{1}H NMR data for [(DMSC)Ti(L_2)$_2$] complexes

Compound	*Endo*-SiMe δ ppm	*exo*-SiMe δ ppm
28	-0.85	0.29
29	-0.78	0.26
30	-0.74	0.34

octahedral by about 25°, which is most likely due to the acute bite angles of the bidentate bipyridyl ligands along with the demanding steric constraints imposed by the chelating DMSC ligand. The space group for **28** is P-1. The unit cell contains one independent unit of **28** and 1.5 molecules of non-coordinated 2,2'bipyridyl to give the empirical formula **28**•$(C_{10}H_8N_2)_{1.5}$. Rothwell and coworkers isolated and characterized a similar complex [(2,6-$Pr^i_2C_6H_3O)_2Ti(bpy)_2$)] (**31**).[51] The Ti-N and Ti-O bond distances of **28** are closely related to that of **31**. Unlike in free bipyridine, a small but systematic alternation of short and long C-C bond distances is observed within the bipyridyl ligands of **28**. The bridge C-C bonds of the bipyridyl ligands are intermediate between single and double bonds indicating disruption of aromaticity of each pyridine unit of the bipyridyl ligands. This suggests electron transfer into the LUMO of each bipyridyl ligand. Rothwell and coworkers reported similar occurrences for [(Mo(Opr^i)$_2$(bpy)$_2$].[52]

2.3 Reactivity of [(DMSC)Ti(L_2)$_2$] complexes

Photochemical and thermal substitution of an aromatic diimine ligand have been reported in the literature.[26-27, 53-54] This left us with a desire to see if we could observe similar activity with complexes **28-30**. We found reactions of complexes **28-30** with two or more equivalents of Ar_2CO (Ar = C_6H_5 or MeC_6H_4) led to formation of the orange-red 1-aza-5-oxa-titanacyclopentane complexes **37-42** (Scheme 2.2). Complexes **37-42** were previously synthesized in good yield by our research group from the facile reaction of one equivalent of the appropriate ketone with the titanium η^2-ketone complexes [(DMSC)Ti(η^2-$OCAr_2$)L_2)] **31-36.**[58] The transformation of complexes **31**-**36** to **37**-**42** in which C-H activation of the diimine ligand and subsequent hydride migration to a Ti-bound ketone to form an alkoxide group was

Figure 2.1 Molecular Structure of 28

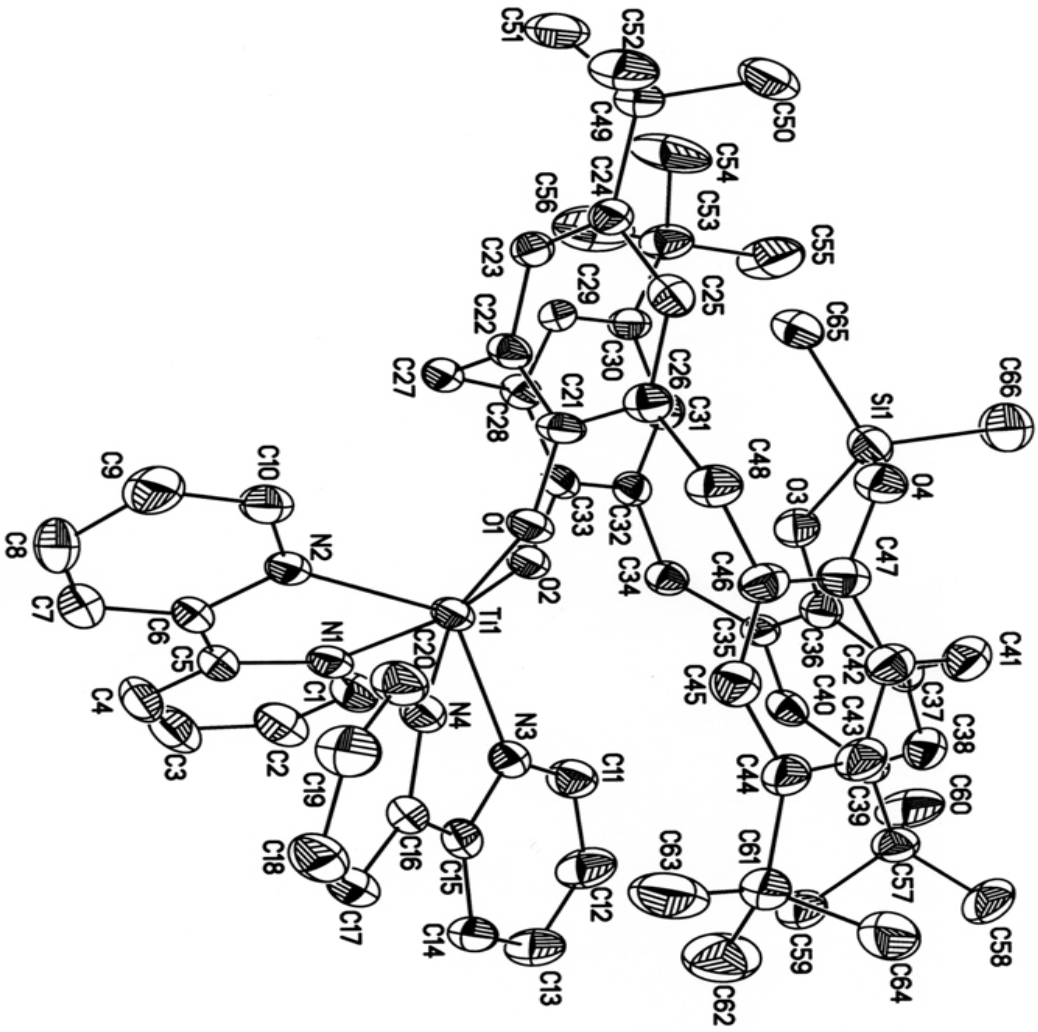
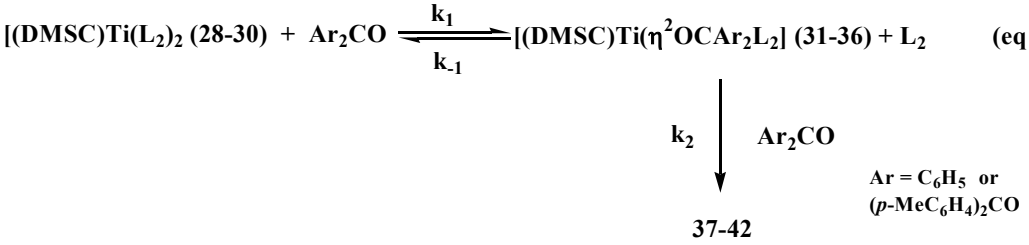


Table 2.2 Selected Bond Distances and Angles for 28

Ti-O(1)	1.880(2)
Ti-O(2)	1.926(2)
Ti-N(1)	2.156(3)
Ti-N(2)	2.129(3)
Ti-N(3)	2.156(3)
Ti-N(4)	2.178(3)
O(1)-Ti(1)-O(2)	91.83(10)
O(1)-Ti(1)-N(2)	91.49(11)
O(2)-Ti(1)-N(2)	126.36(12)
O(1)-Ti(1)-N(3)	124.26(11)
O(2)-Ti(1)-N(3)	91.55(11)
N(2)-Ti(1)-N(3)	128.48(11)
O(1)-Ti(1)-N(1)	158.06(12)
O(2)-Ti(1)-N(1)	86.45(11)
N(2)-Ti(1)-N(1)	72.30(12)
N(3)-Ti(1)-N(1)	77.67(11)
O(1)-Ti(1)-N(4)	86.51(11)
O(2)-Ti(1)-N(4)	157.69(11)
N(2)-Ti(1)-N(4)	75.94(12)
N(3)-Ti(1)-N(4)	71.36(11)
N(1)-Ti(1)-N(4)	103.13(11)

found to be photochemically assisted.[58]

Complexes **37-42** were characterized by ^{1}H and ^{13}C NMR spectroscopy and microanalysis data. The X-ray structure of **40** confirmed the structure assigned for complexes **37-42** by solution NMR spectroscopy. The η^2- ketone complexes [(DMSC)Ti(η^2-OCAr$_2$)L$_2$)] **31-36** were revealed as intermediates in the reaction by ^{1}H NMR data. The reactions of **28-30** with the appropriate ketone to produce the [(DMSC)Ti(η^2-OCAr$_2$)(L$_2$)] complexes **31-36** were found to be reversible. ^{1}H NMR indicated the reaction of [(DMSC)Ti{η^2-OC(*p*-MeC$_6$H$_4$)$_2$}(dmbpy)] (**34**) with one equivalent of dmbpy in C$_6$D$_6$ produced [(DMSC)Ti(dmbpy)$_2$] (**29**), **34**, and the corresponding 1-aza-5- oxa-titanacyclopentene derivative [(DMSC)Ti(κ^3-OC(*p*MeC$_6$H$_4$)$_2$C$_{10}$H$_5$Me$_2$N$_2$}{OCH(*p*-MeC$_6$H$_4$)$_2$}] (**40**) in ~3:22:1 ratio after two hours whereas the reaction of [(DMSC)Ti{η^2-OC(*p*-MeC$_6$H$_4$)$_2$}(bpy)] (**32**) with one equivalent of bpy in C$_6$D$_6$ produced [(DMSC)Ti(bpy)$_2$] (**28**), **32**, and [(DMSC)Ti(κ^3-OC(*p*-MeC$_6$H$_4$)$_2$C$_{10}$H$_7$N$_2$}{OCH(*p*-MeC$_6$H$_4$)$_2$}] (**38**) in ~2:2:1 ratio after two hours. The analogous reaction of [(DMSC)Ti{η^2-OC(*p*-MeC$_6$H$_4$)$_2$}(phen)] (**36**) and 1.4 equivalents of phen in C$_6$D$_6$ produced [(DMSC)Ti(phen)$_2$] (**30**) and [(DMSC)Ti(κ^3-OC(*p*-MeC$_6$H$_4$)$_2$C$_{12}$H$_7$N$_2$} {OCH(*p*-MeC$_6$H$_4$)$_2$}] (**42**) in a ~5:4 ratio in one hour. This indicates the equilibrium between [(DMSC)Ti(L$_2$)] (**28-30**) and [(DMSC)Ti{η^2-OC(*p*-MeC$_6$H$_4$)$_2$}(L$_2$)] (**31-36**) lies further away from **28-30** as the π-acidity of the L$_2$ ligand decreases. This also suggests that the reactions of **31-36** with aromatic diimines to form **28-30** occur at a faster rate than reactions of **31-36** with Ar$_2$CO to produce compounds by ^{1}H NMR.



The concentration of Ar$_2$CO also influences the rate of formation of **37-42** from **28-30**. ^{1}H NMR revealed that 5% of **28** was observed in solution after the reaction of **28** with two equivalents of (*p*-MeC$_6$H$_4$)$_2$CO in C$_6$D$_6$ for 21 hours. However, complete consumption of **28** was observed within ~10.5 hours in the reaction of three equivalents of (*p*-MeC$_6$H$_4$)$_2$CO with **28** in C$_6$D$_6$. The rate of formation of **37-42** from **28-30** was shown to increase in the following order: bpy<dmbpy<phen. This is in contrast to the reaction of [(DMSC)Ti{η^2-OC(*p*-MeC$_6$H$_4$)$_2$}(L$_2$)] and one equivalent of (*p*-MeC$_6$H$_4$)$_2$CO where the rate of reaction was shown to

increase in the following order: dmbpy<bpy<phen.[58] The equilibrium between [(DMSC)Ti(L_2)$_2$] and [(DMSC)Ti{η^2-OC(*p*-MeC_6H_4)$_2$}(L_2)] complexes lies much further toward the Ti-η^2-ketone complex when L_2 = dmbpy than when L_2 = bpy leading to greater conversion of [(DMSC)(dmbpy)$_2$] (**29**) into [(DMSC)Ti{κ^3-OC(*p*-MeC_6H_4)$_2$$C_{10}H_5Me_2N_2$)OCH(*p*-Me$C_6H_4$)$_2$}] (**40**) than more complete conversion of [(DMSC)Ti(bpy)$_2$] (**28**) into [(DMSC)Ti{κ^3-OC(*p*-MeC_6H_4)$_2$ $C_{10}H_7N_2$OCH (*p*-MeC_6H_4)$_2$}] (**38**). We found that the transformation of the [(DMSC)Ti(L_2)$_2$]complexes **28-30** into the 1-aza-5-oxa-titanacyclopentene compounds (**37-42**) is accelerated in the presence of light. For example, when three equivalents of (*p*-MeC_6H_4)$_2$CO was reacted with [(DMSC)Ti(dmbpy)$_2$] in the absence of light, the reaction was complete within ten hours whereas the reaction only took seven hours in ambient light.

Although the loss of a diimine from the titanium metal center is clearly involved in the reaction, the mechanistic details of the reaction of the [(DMSC)Ti(L_2)$_2$] complexes **28-30** with two or more equivalents of ketone to yield the titanium η^2-ketone complexes [(DMSC)Ti(η^2-OCAR_2)L_2)] **31-36** are still unclear. Two scenarios can be envisioned for the reaction: i) the reaction occurs through the dissociation of a diimine prior to coordinating with the incoming ketone or ii) the incoming ketone coordinates to the metal center to give a seven-coordinate species followed by subsequent loss of a diimine.

We were surprised to find that prolonged standings of C_6D_6 or THF solutions of **28-30** in ambient light leads to formation of Ti (IV) compounds **43-45** (Scheme 2.3). [(DMSC)H_2] was consistently noticed as a minor product in this transformation. This suggests that the conversion of the [(DMSC)Ti(L_2)$_2$] complexes **28-30** into **43-45** involves a small amount of adventitious water. To ascertain if this was the case, when a C_6D_6 solution of [(DMSC)Ti(phen)$_2$] (**30**) was exposed to air (atmospheric moisture present served as the water source), the solution immediately turned orange in color and the ^{1}H NMR indicated that **45** was present in solution along with [(DMSC)H_2][59] and other unidentified titanium species.

The conversion of complexes **28-30** into **43-45** appears to be photochemically assisted. When a C_6D_6 solution of [(DMSC)Ti(phen)$_2$] (**30**) along with a small amount of THF was irradiated by UV light, **45** along with minor amounts of [(DMSC)H_2]and unidentified titanium species in four hours. The analogous reaction in the absence of light results in no change.

Scheme 2.2. Reactivity of [(DMSC)Ti(L_2)$_2$] Complexes with Ar_2CO

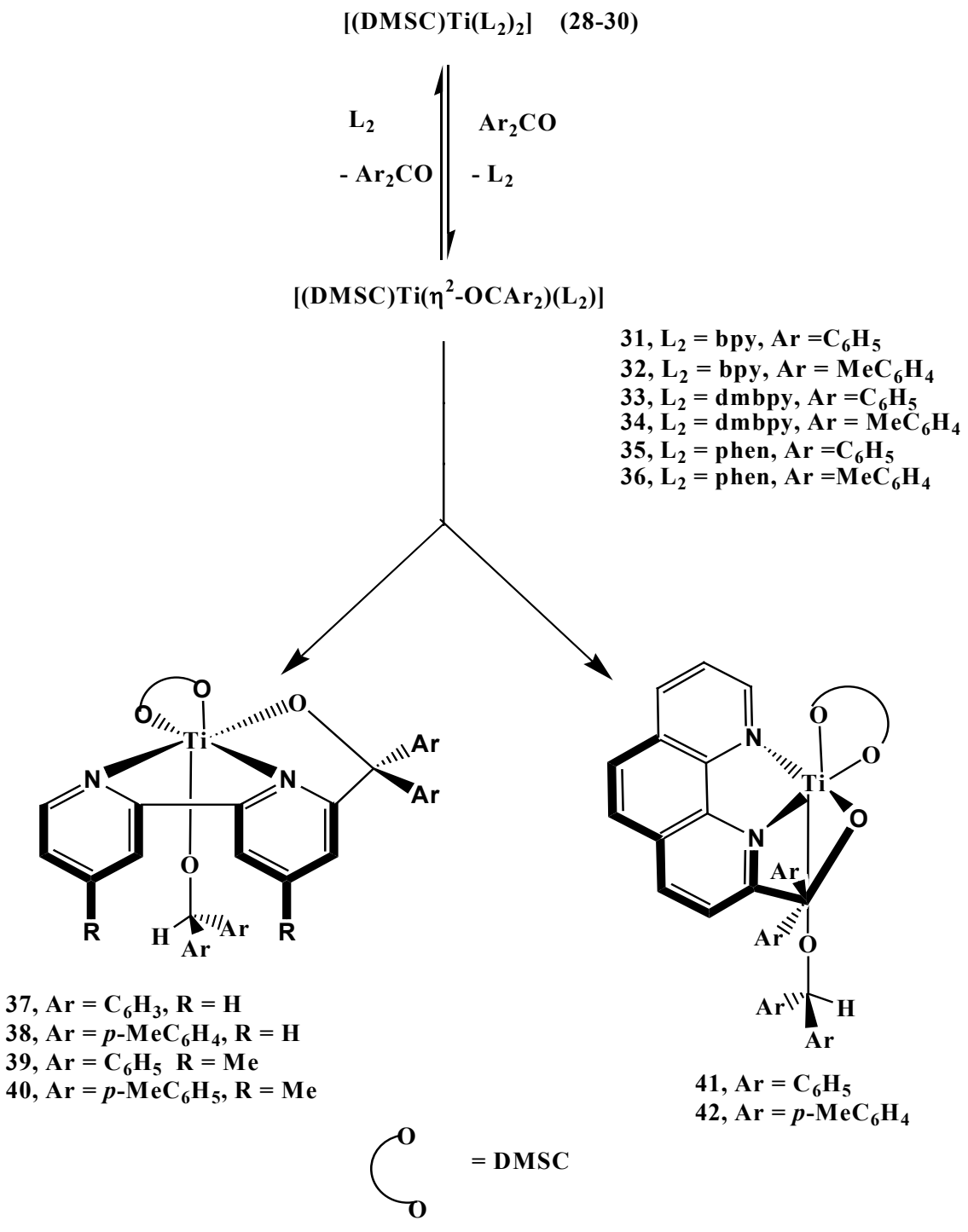
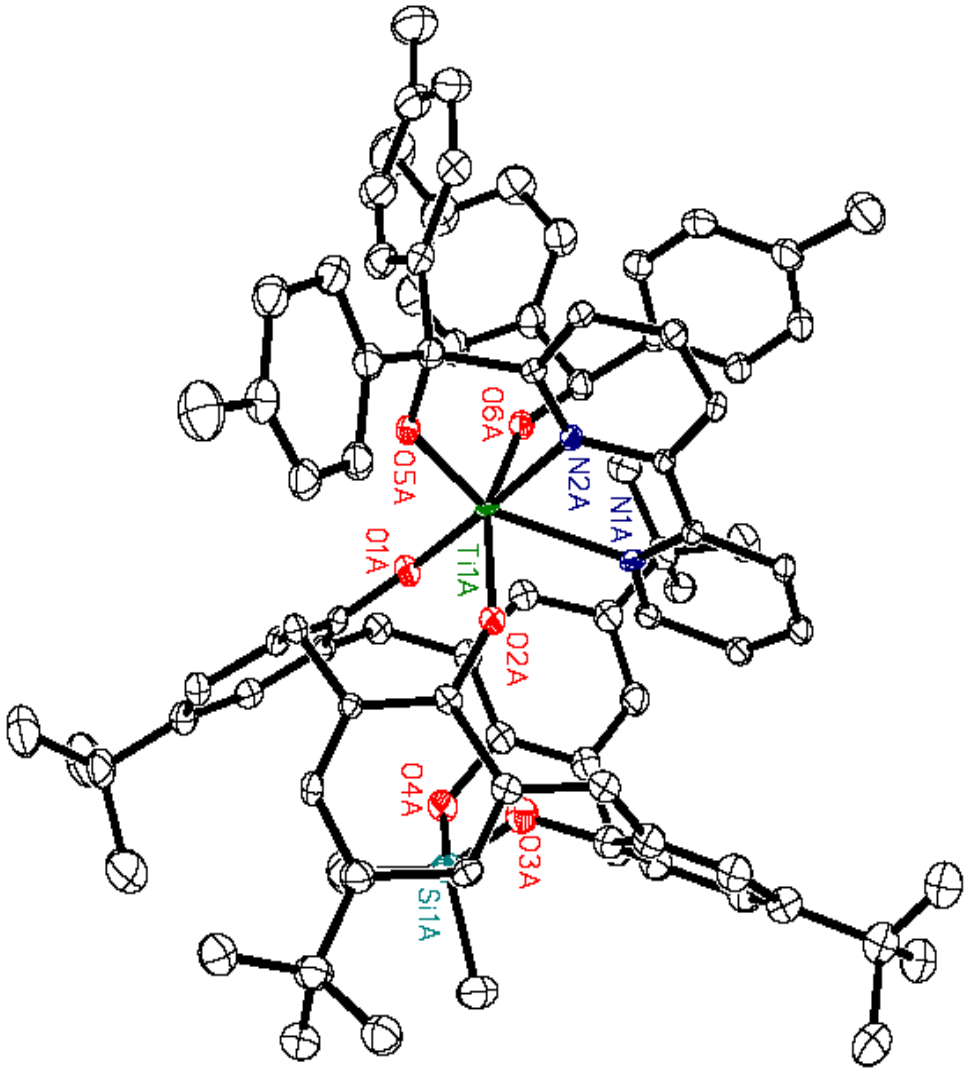
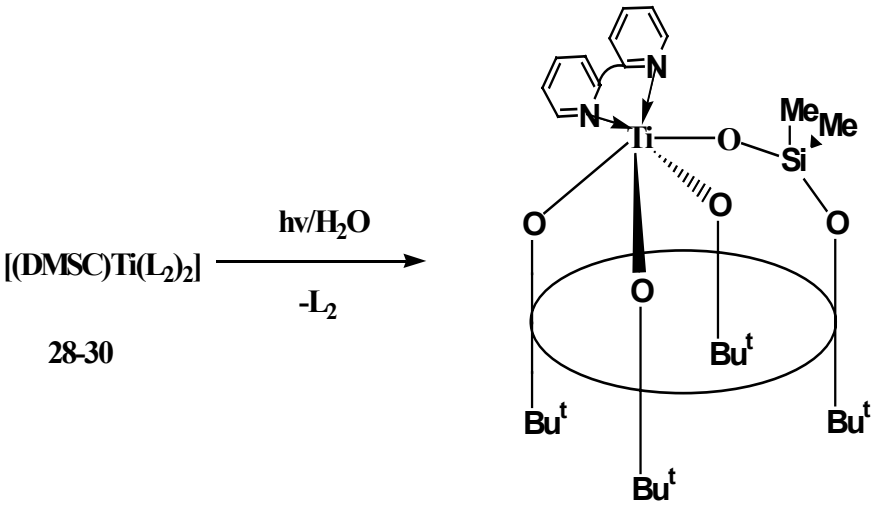
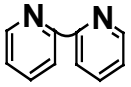


Figure 2.2 Molecular Structure of 40



Scheme 2.3 Formation of 43-45





= L_2 = 43, bpy
44, dmbpy
45, phen

Compounds **43**-**45** were characterized by ^{1}H NMR spectroscopy. The compounds were found to be C_s-symmetric in solution. We found the calix[4]arene ligand of complexes **43**-**45** adopts an approximately cone conformation and is no longer 1,2-alternate[29-31, 58-59] as in the case of the starting titanium bis(diimine) complexes **28**-**30**. The methylene protons of the calixarene ligand appear as four doublets. The Bu^t groups shows as three singlets integrating in a 2:1:1 ratio. The molecular structure of **45** was determined by X-ray crystallography (Figure 2.3). The structure was consistent with the ^{1}H NMR data. The titanium center adopts a distorted octahedral geometry. The X-ray structure confirms the calixarene ligand adopts a cone conformation with three of the aryloxide oxygens bound to the titanium center while the fourth is bound to the silicon atom of a $SiMe_2O$ unit that is bound to the titanium center through the oxygen. The Ti-N and Ti-O bond distances are within the expected lengths for six-coordinate Ti(IV) complexes[30,31] (Table 2.3).

Complexes **28**-**30** have a potential use in organic synthesis. The hydrolysis of 1-aza-5-oxa-titanacyclopentene compounds **37**-**42** produces 2,2'-bipyridinyl-6-yl-diphenylmethanol and 1,10-phenanthroline-6-yl-diphenylmethanol compounds[59] (Scheme 2.4). Similar types of compounds have been found to be useful in various applications such as asymmetric catalysis,[60] copper-catalyzed allylic oxidation of olefins, and asymetric diethylzinc addition to aldehydes.[61] The facile synthesis of $[(DMSC)Ti(L_2)_2]$ complexes **28**-**30** makes them attractive in synthesizing compounds similar to **46**-**51**. Complexes **28**-**30** can also be useful in understanding the role of low-valent titanium in reductive coupling of unsaturated organic substrates (i.e. ketones, aldehydes, alkynes, and imines). However, the widespread synthetic utilization of complexes **28**-**30** is hampered by the expense of the calix[4]arene ligand.

Figure 2.3 Molecular structure of 45

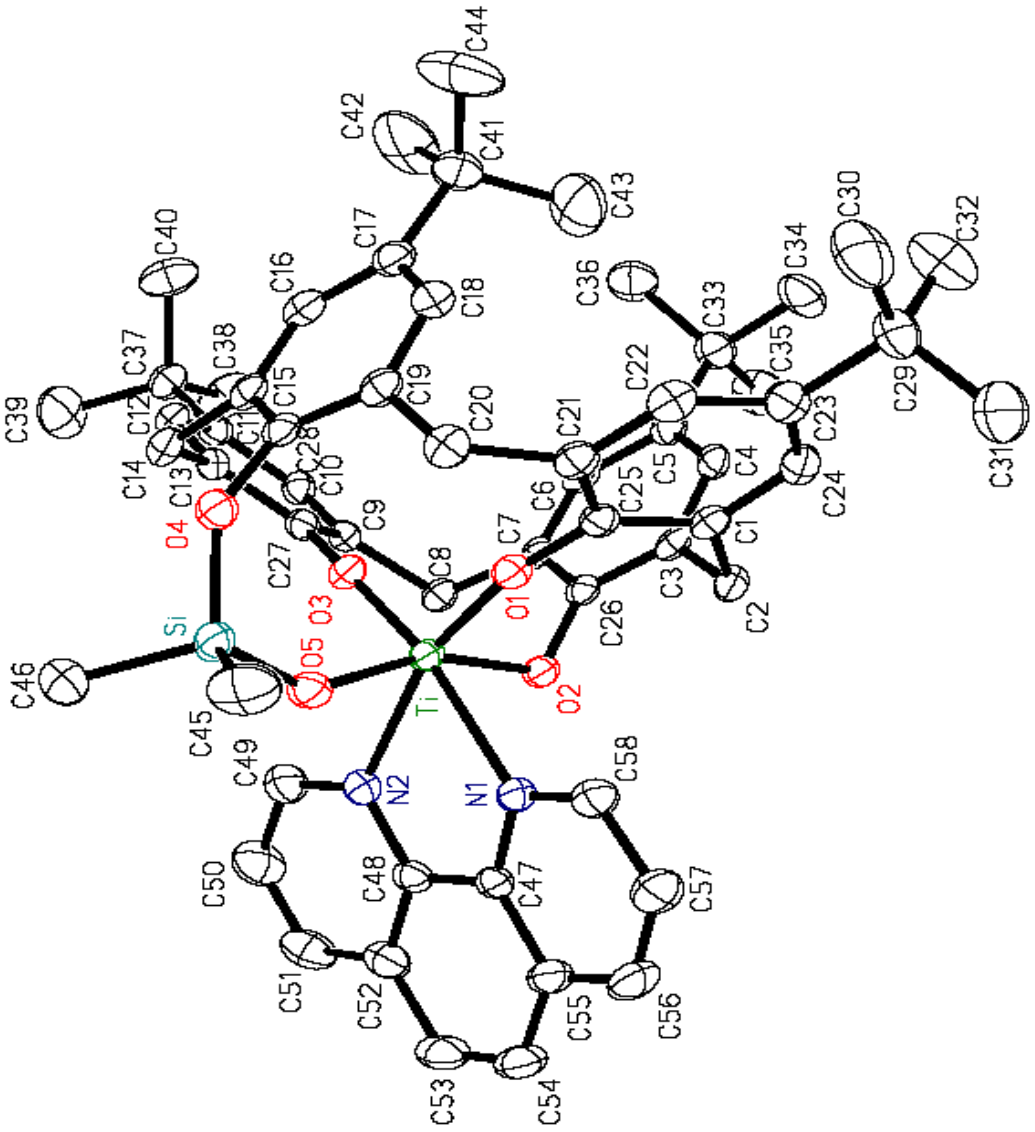
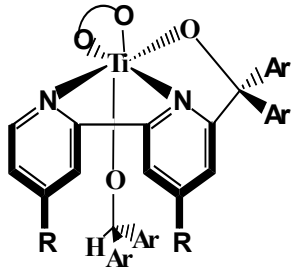


Table 2.3 Selected Bond Distances and Angles for 45

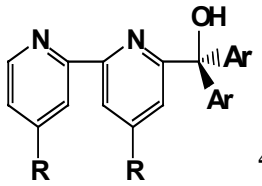
Ti(1)-O(1)	1.8350(15)
Ti(1)-O(2)	1.9404(14)
Ti(1)-O(3)	1.3177(14)
Ti(1)-N(1)	2.2475(18)
Ti(1)-N(2)	2.2540(18)
Si(1)-O(4)	1.6511(16)
Si(1)-O(5)	1.6035(16)
O(1)-Ti(1)-O(2)	94.81(6)
O(1)-Ti(1)-O(3)	105.88(6)
O(2)-Ti(1)-O(3)	94.08(6)
O(1)-Ti(1)-O(5)	97.78(7)
O(1)-Ti(1)-N(1)	89.82(7)
O(1)-Ti(1)-N(2)	162.52(7)
O(2)-Ti(1)-N(1)	79.54(6)
O(2)-Ti(1)-N(2)	80.13(6)
O(2)-Ti(1)-O(5)	159.64(6)
O(3)-Ti(1)-O(5)	97.77(7)
O(3)-Ti(1)-N(1)	163.57(7)
O(3)-Ti(1)-N(2)	91.22(7)
O(5)-Ti(1)-N(1)	84.54(6)
O(5)-Ti(1)-N(2)	83.11(7)
N(1)-Ti(1)-N(2)	72.85(7)
O(3)-Ti(1)-(O2)	94.08(6)
O(5)-Si(1)-O(4)	111.889(8)
Si(1)-O(5)-Ti(1)	143.55(9)

Scheme 2.4 Organic products 46-51 (detected by GC/MS)

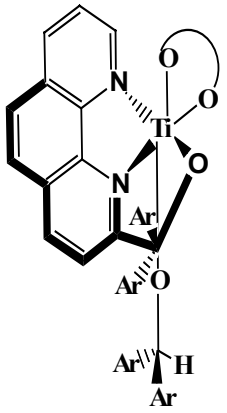


37, Ar = C_6H_5, R = H
38, Ar = *p*-MeC_6H_4, R = H
39, Ar = C_6H_5 R = Me
40, Ar = *p*-MeC_6H_5, R = Me

hydrolysis

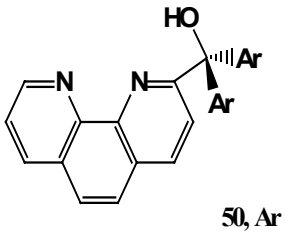


46, Ar = C_6H_5, R = H
47, Ar = *p*-MeC_6H_4, R = H
48, Ar = C_6H_5, R = Me
49, Ar = *p*-MeC_6H_4, R = Me



41, Ar = C_6H_5
42, Ar = *p*-MeC_6H_4

hydrolysis



50, Ar = C_6H_5
51, Ar = *p*-$Me_4C_6H_5$

2.4 Experimental section

2.4.1 General details.

All experiments were performed under dry nitrogen atmosphere using standard Schlenk techniques or in a Vacuum Atmospheres, Inc. glovebox. Toluene, tetrahydrofuran, ether, and toluene were distilled from sodium benzophenone ketyl. Pentane was distilled from sodium benzophenone ketyl with addition of 1ml of tetraethyleneglycol dimethyl ether as a solubilizing agent. Benzene-d_6 was distilled from calcium hydride. All solvents were stored in the glovebox over 4A molecular sieves, that were dried in a vacuum oven at least 48 hours prior to use. Benzophenone, 1,10-phenanthroline, 4,4'-dimethylbenzophenone, 2,2'-bipyridine, and 4,4'dimethyl, 2-2'bipyridine were purchased from Aldrich Chemical Co and sublimed before use. [(DMSC)$TiCl_2$] (**24**), [(DMSC)$Ti(Ph)_2$] (**27**), [(DMSC)$Ti(bpy)_2$] (**28**), and [(DMSC)$Ti(dmbpy)_2$] (**29**) were prepared as previously reported.[31] ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini-200 spectrometer or a Varian VXR-400 spectrometer at ca. 22ºC. ^1H and ^{13}C chemical shifts were referenced to residual solvent peaks. Elemental analyses were performed by Complete Analysis Laboratories, Inc., Parsippany, NJ.

2.4.2. Preparation of Ti(diimine) complexes

[(DMSC)Ti(phen)Cl_2] (**26**). 1,10-phenanthroline (54.9 mg, 0.304 mmol) was added into a 10 mL solution of [(DMSC)$TiCl_2$] (**24**) (0.250 g, 0.304 mmol) in diethyl ether. The solution was stirred at room temperature for one hour and the solvent was removed under reduced pressure to give an orange solid. The product was washed with pentane (3 x 3 mL) and dried under vacuum to give 0.266 g (87%) of product. ^1H NMR (C_6D_6) δ: 9.32 (dd, J = 4., 1.2 HZ, 2H, phen), 7.77 (d, J = 13.6 Hz, 1H, arom CH) 7.38 (d, 2H, arom CH), 7.34 (d, 2H, arom CH), 7.29 (d, J= 8.0 Hz, 2H, phen), 7.07 (d, 2H, arom CH), 6.95 (s, 2H, phen), 6.85 (dd, J = 8.0, 4.8 Hz, 2H, phen), 4.65 (d, J = 15.8 hz, 2H, calix-CH_2), 4.63 (d, 1H, calix-CH_2), 4.29 (d, J = 17.0 Hz, 2H, calix-CH_2), 3.56 (d, J = 14.0 Hz, 1H calix-CH_2), 3.38 (d, J = 15.0 Hz, 1H calix-CH_2), 1.42 (S, 18 H, t-Bu), 0.94 (s, 18H, t-Bu), 0.37 (s, 3H, *exo*-SiMe), -1.01 (s, 3H, *endo*-SiMe). ^{13}C NMR (C_6D_6) δ: 163.5, 151.4, 148.5, 145.0, 143.3, 142.1, 141.8, 137.3, 130.7, 129.8, 129.7, 129.6, 129.3, 127.2, 127.1, 126.8, 126.7, 124.5, 40.9 (calix-CH_2), 38.2 (calix-CH_2), 37.5 (calix-CH_2), 34.7 ($C(CH_3)_3$), 34.0 ($C(CH_3)_3$), 32.2 ($C(CH_3)_3$), 31.9 ($C(CH_3)_3$), 4.6 (*exo*-SiMe), -0.5

(*endo*-SiMe). Anal. Calcd. For $C_{58}H_{66}Cl_2N_2O_4SiTi$: C, 69.55; H, 6.59; N, 2.79. Found: C, 69.16; H, 6.38; N, 2.68.

[(DMSC)Ti(phen)$_2$] (**30**). 1,10-phenanthroline (0.617 g, 3.42 mmol) was added into a 15 mL solution of [(DMSC)TiPh$_2$] (**27**) (1.55 g, 1.71 mmol). The initially bright yellow solution immediately became dark olive-green in color. After stirring for two minutes, pentane (30 mL) was added to the solution and cooled at – 15 °C for 10 minutes. The olive-green solid was isolated by filtration and washed with pentane (3 x 5 mL) and dried under reduced pressure to give 1.44 g (77%) of product. ^{1}H NMR (C_6D_6) δ: 10.11 (d, J = 6.0 Hz, 2H, phen), 9.25 (d, J = 6.0 Hz, 2H, phen), 7.49 (d, 2H, arom CH), 7.46 (d, 2H, arom CH) 6.95(d, 2H, arom CH), 6.84 (s, 2H, phen), 6.70 (d, J = 7.2 Hz, 2H, phen), 6.75 (d, 2H, arom CH), 6.49 (s, 2H, phen), 6.13 (d, J = 7.2 Hz, 2H, phen), 6.05 (dd, J = 7.2, 5.6 Hz, 2H, phen), 5.75 (dd, J = 7.2, 5.6 Hz, 2H, phen), 4.82 (d, J = 16.0 Hz, 2H, calix-CH$_2$), 4.56 (d, J = 15.2 Hz, 1H, calix-CH$_2$) 4.35 (d, J = 16.0) Hz, 2H, calix-CH$_2$) 3.92 (d, J = 13.2 Hz, 1H, calix-CH$_2$), 1.51 (s, 18 H, t-Bu), 0.88 (s, 18H, t-Bu),) 0.32 (s, 3H, *exo*-SiMe), -0.74 (s, 3H, *endo*-SiMe). ^{13}C NMR (C_6D_6) δ: 163.6, 152.2, 150.7, 145.4, 142.8, 142.1, 140.2, 135.6, 132.1, 131.3, 130.1, 129.7, 127.6, 127.4, 127.0, 126.9, 126.5, 126.2, 125.9, 123.1, 115.8, 115.3, 41.2 (calix *C*H$_2$), 38.7 (calix *C*H$_2$), 38.5 (calix *C*H$_2$O, 34.5 (*C*(CH$_3$)$_3$, 33.8 (*C*(CH$_3$)$_3$), 32.6 (C(*C*H$_3$)$_3$), 31.6 (C(*C*H$_3$)$_3$), 2.0 (*exo*-SiMe), -1.09 (*endo*-SiMe). Anal. Calcd. For $C_{70}H_{74}N_4O_4SiTi$: C, 75.65; H, 6.71, N, 5.04. Found: C, 75.29; H, 6.57; and N, 4.95.

General Procedure for ^{1}H NMR Detection of Complexes 43-45

In a NMR tube, [(DMSC)Ti(phen)$_2$] (10.0mg) was placed in 0.800 mL of C_6D_6. 1 ul of THF was then added to the NMR tube. The NMR tube was placed under UV light and the transformation to **45** was monitored by ^{1}H NMR. Quantitative formation of **45** was formed within 36 hours along with minor amounts of [DMSC(H$_2$)].

44 ^{1}H NMR (C_6D_6) δ: 8.72 (d, 2H, dmbpy), 7.40 (d, 2H, arom CH), 7.37 (d, 2H, arom CH), 7.11 (s, 2H, arom CH), 6.80 (s, 2H, arom CH), 5.96 (d, 2H, dmbpy), 5.32 (d, J = 14.0 Hz, 2H, calix-CH$_2$), 4.64 (d, J = 12.4 Hz, 2H, calix-CH$_2$), 3.72 (d, J= 14.0 Hz, 2H, calix-CH$_2$), 3.30 (d, J = 12.4 Hz, 2H, calix-CH$_2$), 1.62 (s, 6H, dbpy), 1.47 (s, 18 H, t-Bu), 1.33 (s, 9H, t-Bu), 1.04 (s, 9H, t-Bu), 0.59 (s, 6H, SiMe$_2$)

45 ^{1}H NMR (C6D6) δ: 9.12 (br d, 2H, phen), 7.45 (br m 2H, phen), 7.44 (d, 2H, arom CH), 7.40 (d, 2H, arom CH), 7.12 (s, 2H, arom CH), 6.84 (s, 2H phen), 6.77 (br s, 2H, arom CH), 6.40

(dd, 2H, phen), 5.36 (d, J = 14.0 Hz, 2H, calix-CH_2), 4.73 (d, J 12.8 Hz, 2H, calix-CH_2), 3.74 (d, J = 14.0 Hz, 2H, calix-CH_2), 3.35 (d, J = 12.8 Hz, 2H, calix-CH_2), 1.49 (s, 18 H, t-Bu), 1.32 (s, 9H, t-Bu), 1.06 (s, 9H, t-Bu), o.48 (s, 6H, $SiMe_2$).

*2.4.3 NMR reactions of [(DMSC)Ti(L_2)$_2$] complexes **28-30***

Typical Procedure for NMR Study of the Reaction Between [(DMSC)Ti(L_2)$_2$] complexes 28-30 and 4,4'-Dimethylbenzophenone. 0.180 mL of a 0.100 M stock solution of (p-$MeC_6H_4)_2CO$ was added to a 0.094 mL of a 0.100 M stock solution of [(DMSC)Ti(bpy)$_2$] (**28**) in a screw-capped NMR tube followed by 0.518 ml of C_6D_6. This resulted in 0.800 mL of a 0.0117 M solution of **28** and a 0.0225 M solution of (p-$MeC_6H_4)_2CO$. The NMR tube was vigorously shaken and placed into the spectrometer at 22 °C. The reaction was monitored by recording ^{1}H NMR spectra immediately after inserting the sample in the spectrometer and every ten minutes thereafter. The dependence of the reaction on (p-$MeC_6H_4)_2CO$ was obtained by controlling the concentration of (p-$MeC_6H_4)_2CO$ while conducting each experiment at the same temperature using **28** as the control. The dependence of the nature of the diimine was obtained by conducting analogous reactions for **29** and **30**.

Chapter Three

Synthesis, structure, and reactivity of titanium bis(diimine) complexes supported by MBMP ligand

3.1 Introduction

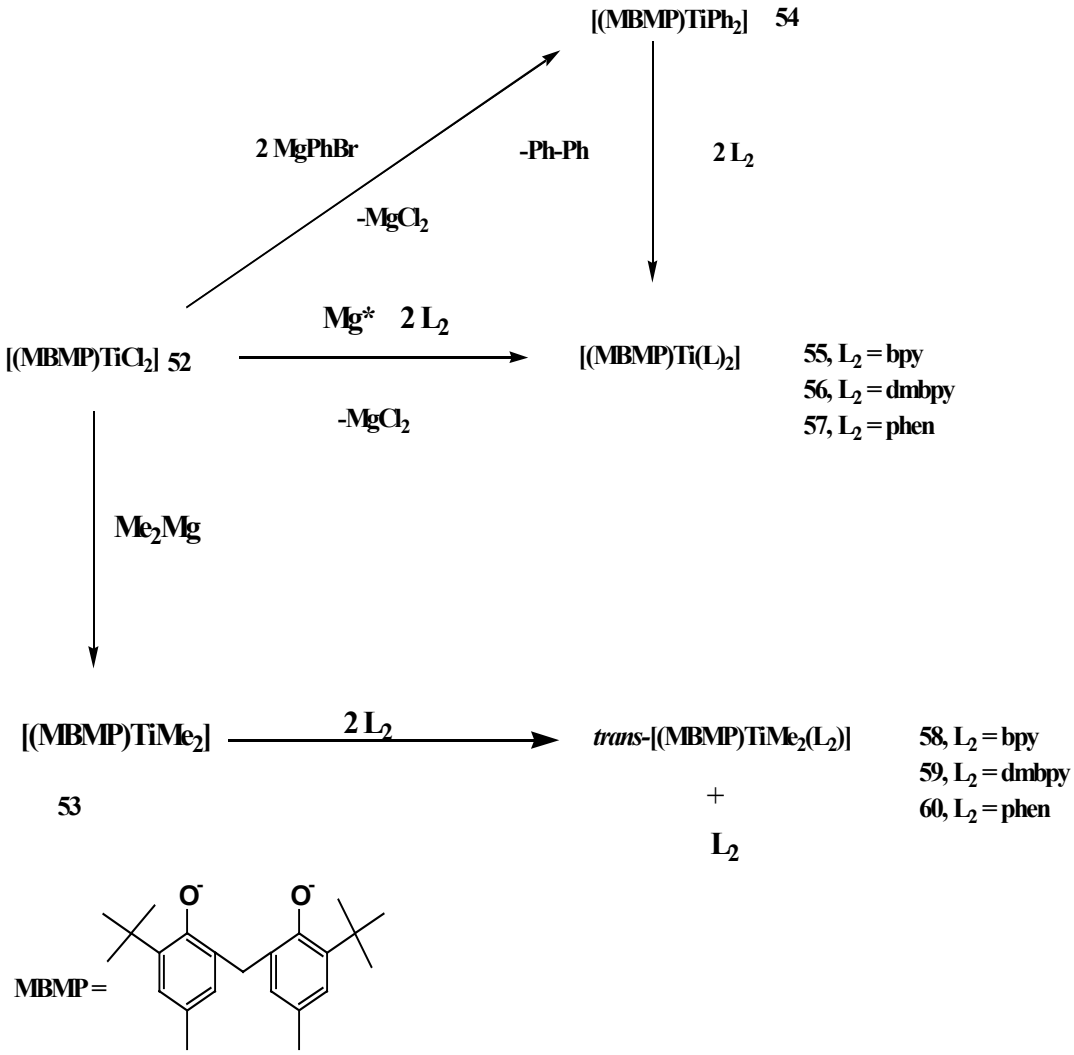
The interesting reactivity of the [(DMSC)Ti(L_2)$_2$] complexes **28-30** led us to wonder if we could synthesize and isolate similar complexes using a different ligand system. Stable and readily accessible complexes of this type could possibly be very useful in organic synthesis. We sought to find a ligand system that is i) relatively inexpensive, ii) commercially available, iii) structurally and electronically comparable to the DMSC ligand, and iv) able to form stable, monomeric titanium compounds. Our search for a ligand with the aforementioned characteristics led us to the 2,2'methylenebis(6-tert-butyl-4-methylphenaloto) (MBMP) ligand. Floriani and coworkers[63] reported the facile synthesis of the facile [(MBMP)$TiCl_2$] (**52**) from the reaction of $TiCl_4$ with $MBMPH_2$. Floriani and Okuda[64] reported the use of **52** to synthesize stable titanium alkyl compounds. In this chapter, we present the synthesis, characterization, and reactivity of low-valent titanium bis(diimine) complexes supported by 2,2' methylene-bridged 4-methyl, 6-tert-butyl phenol ligand.

3.2 Synthesis of [(MBMP)Ti(bpy)$_2$], [(MBMP)Ti(dmbpy)$_2$], and [(MBMP)Ti(phen)$_2$]

Ozerov has shown the methyl groups on the titanium center of [(DMSC)TiMe$_2$] undergo facile elimination. We were curious to see if the similar titanium complex [(MBMP)TiMe$_2$][63-64] (**53**) could be utilized to prepare the desired low-valent titanium complexes. The facile synthesis and high yield of **53** were attractive to us. However, we were surprised to find **53** does not undergo reductive elimination with two equivalents of the required aromatic diimine to produce the low-valent titanium bis(diimine) complexes [(MBMP)Ti(L_2)$_2$] (**55** L_2 = bpy, **56** L_2 = dmbpy, **57** L_2 = phen) (Scheme 3.1). Instead, ^{1}H NMR identified complexes **58**-**60** as the products in the reaction.

We believed that increasing the size of the alkyl groups on the titanium center would invoke reductive elimination. To support this argument, we set out to prepare [(MBMP)TiPh$_2$] (**54**) as reported in the literature.[63] The reaction reported by Floriani is hampered by tedious work-up and poor yields. We found that **54** could be easily isolated as a yellow solid in excellent yield (>90%) by the addition of PhMgBr at low temperatures to [(MBMP)TiCl$_2$] (**52**). The molecule is C*s*-symmetric in solution with the plane of symmetry bisecting the TiPh$_2$ and containing the -CH$_2$ group as indicated by ^{1}H NMR data. The *tert*-butyl groups of the MBMP ligand are observed as a singlet integrating as eighteen protons. The methyl protons of the MBMP ligand are observed as a singlet (six protons). The methylene protons appear as two doublets each integrating as one proton. The compound is extremely air-and moisture-sensitive but can be stored for long periods of time at ambient temperatures under N$_2$ atmosphere. We found that the addition of an aromatic diimine to **54** is the most efficient method to obtaining the [(MBMP)Ti(L_2)$_2$] complexes **55**-**57** in excellent yield. Compound **54** immediately turns deep dark blue upon addition of bpy or dmbpy whereas the addition of phen to **54** results in an immediate change of color to dark purple-brown. The reaction is extremely fast (complete within five minutes) and **55**-**57** can be easily isolated. The dark blue complexes [(MBMP)Ti(bpy)$_2$] (**55**), [(MBMP)Ti(dmbpy)$_2$] (**56**), and the dark brown-purple complex [(MBMP)Ti(phen)$_2$] (**57**) were found to be highly air-and moisture- sensitive solids. These complexes are less soluble than the [(DMSC)Ti(L_2)$_2$] complexes. Complexes **55** and **56** are highly soluble in THF, moderately soluble in aromatic hydrocarbon solvents and ether, and practically insoluble in pentane. Complex **57** is moderately soluble in THF, slightly soluble in aromatic solvents, and practically insoluble in ether and pentane.

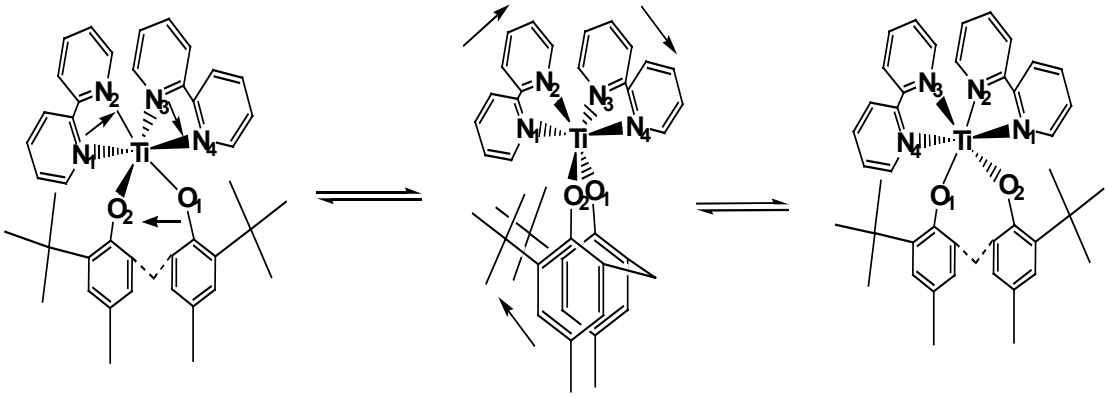
Scheme 3.1: Synthesis of [(MBMP-Ti(L_2)$_2$] Complexes (55-57)



The molecular structure of [(MBMP)Ti(bpy)$_2$] (**55**) was determined by single-crystal X-ray diffraction (figure 3.1). Selected bond angles and distances are summarized in Table 3.1. The geometry about the titanium center can be described as a distorted octahedral. The Ti-O and Ti-N bond distances are practically identical to those of the related complex [(2,6-$Pr^i_2C_6H_3O)_2$Ti(bpy)$_2$][51](**31**) and [(DMSC)Ti(bpy)$_2$] (**28**). We also noticed alternating short and long C-C bonds within each pyridine unit of the bipyridyl ligands as in the case of [(DMSC)Ti(bpy)$_2$] (**28).**

The [(MBMP)Ti(L_2)$_2$] complexes **55** and **56** have interesting ^{1}H NMR features. The ^{1}H NMR spectra show mostly broad peaks at ca. 22 °C. perhaps suggestive of a paramagnetic species. However, close examination of the spectra at room temperature revealed the methylene protons and the methyl groups of the MBMP ligand exhibit relatively sharp peaks. We then reasoned that the broad peaks within the ^{1}H NMR were due to a fluxional mechanism similar to that described in scheme 3.2. Scheme 3.2 shows an inversion of configuration by a trigonal twist via an idealized trigonal prismatic transition state. Although not as common, twist mechanisms of octahedral complexes have been reported.[53,54]

Scheme 3.2: Possible Twist Mechanism



We decided to conduct variable temperature (VT) experiments on **55** and **56**. The VT-NMR experiments confirmed that **55** and **56** are fluxional in solution. Figure 3.2 shows spectra from

Figure 3.1 Molecular structure of 55

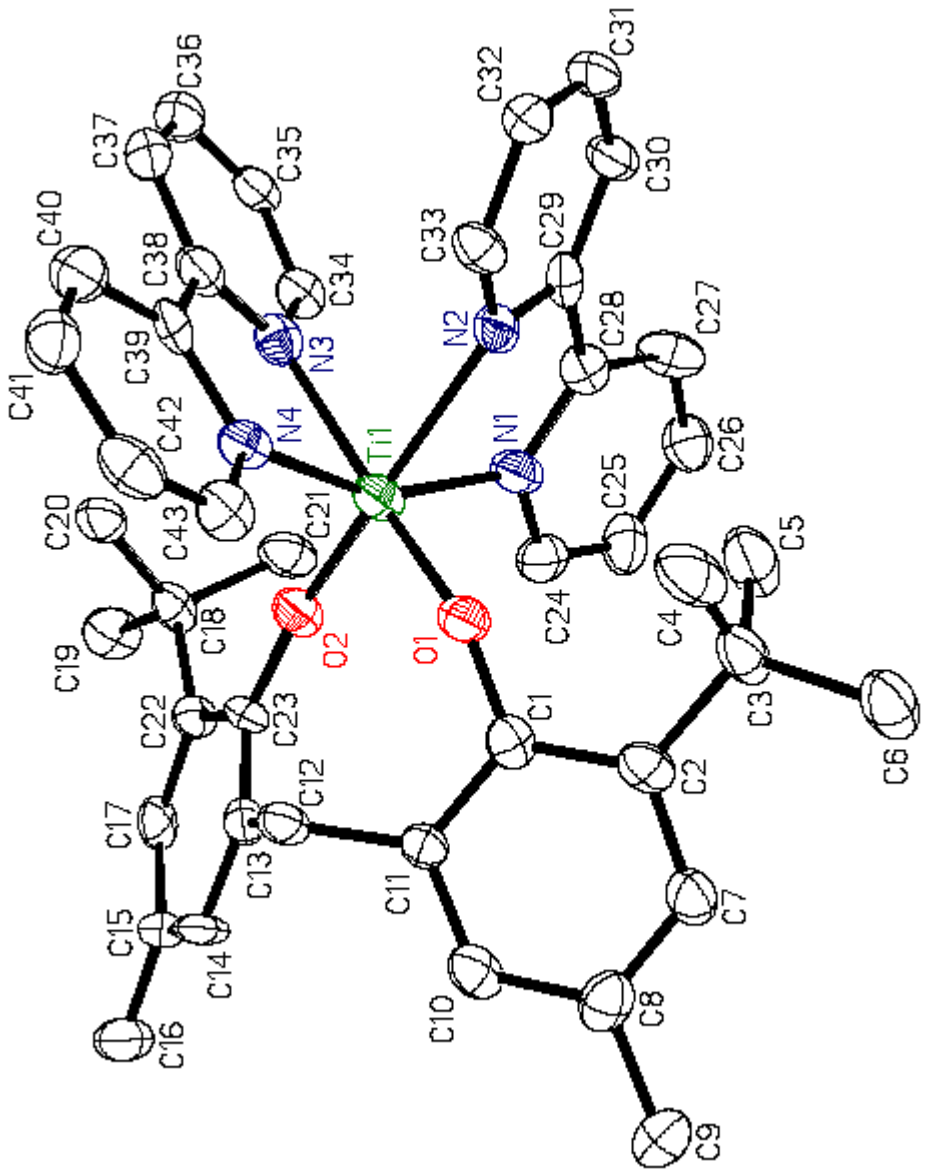
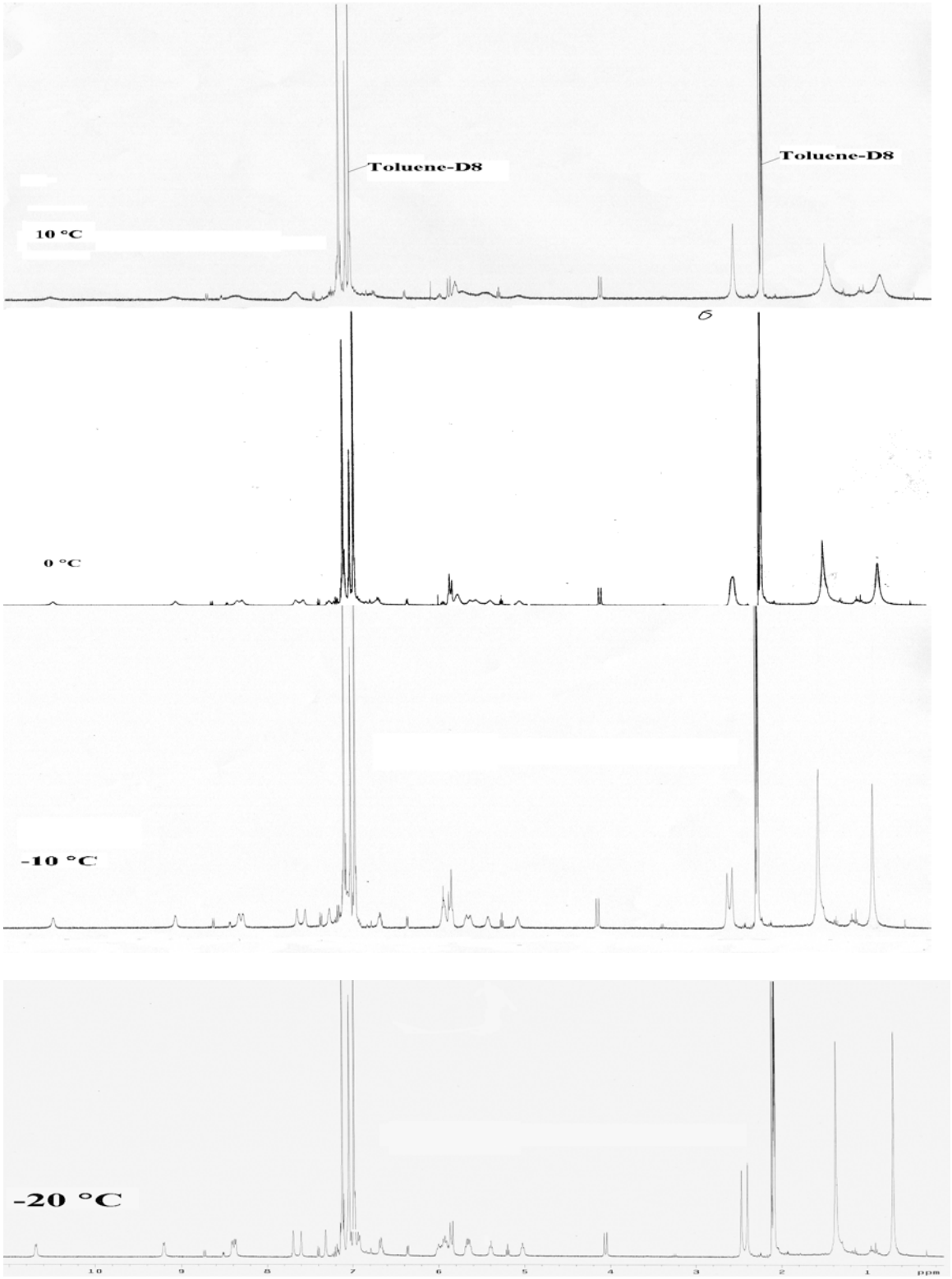


Table 3.1 Selected Bond Distances and Angles for 55

Ti(1)-O(1)	1.882(3)
Ti(1)-O(2)	1.908(3)
Ti(1)-N(1)	2.165(4)
Ti(1)-N(2)	2.216(4)
Ti(1)-N(3)	2.174(4)
Ti(1)-N(4)	2.070(4)
O(1)-Ti(1)-O(2)	97.27(14)
O(1)-Ti(1)-N(2)	95.78(14)
O(2)-Ti(1)-N(2)	158.86(15)
O(1)-Ti(1)-N(3)	165.66(16)
O(2)-Ti(1)-N(3)	159.86(15)
N(2)-Ti(1)-N(3)	76.24(14)
O(1)-Ti(1)-N(1)	91.64(15)
O(2)-Ti(1)-N(1)	90.18(15)
N(2)-Ti(1)-N(1)	72.52(16)
N(3)-Ti(1)-N(1)	89.41(16)
O(1)-Ti(1)-N(4)	92.63(16)
O(2)-Ti(1)-N(4)	106.90(14)
N(2)-Ti(1)-N(4)	87.71(16)
N(3)-Ti(1)-N(4)	75.36(17)
N(1)-Ti(1)-N(4)	157.57(17)

Figure 3.2 Variable Temperature ^{1}H NMR of 55



the VT experiments for complex **55** carried out between -20°C and 10°C in toluene-d_8 (the spectra between 22 °C and 10°C were essentially identical). As the temperature is lowered, the peaks sharpen . At 10°C the tert-butyl peaks of the MBMP ligand are observed as two broad singlets. As the temperature is lowered, the peaks for the tert-butyl groups begin to sharpen. MBMP appear as two sharp singlets at –20 °C whereas at 10 °C the methyl groups are observed as a singlet. The bipyridyl protons could also be observed at low temperatures allowing for complex **55** to be unambiguously characterized by ^{1}H NMR.

At -20°C the tert-butyl groups of the MBMP ligand are observed as two singlets integrating as nine protons each. The methyl protons of the MBMP ligand also appear as two singlets (three protons each). Four signals for the MBMP ring protons are also observed. Each proton of the bipyridine ligands is inequivalent in solution. The In addition, the methyl groups of the methlyene protons appear further upfield than typical Ti complexes supported by MBMP ligand[63-64] most likely from ring current effects of the bpy ligands. Although sharpening of peaks can be observed when solution [(MBMP)Ti(dmbpy)$_2$] (**56**) is lowered below room temperature , the peaks in the spectra are still somewhat broad, even at -80°C. However, we were able to easily assign the peaks for the complex at -80°C.

Although further experiments must be conducted to elucidate the mechanism of the fluxional process, the VT experiments help support the twist mechanism shown in scheme 3.2. Complex **55** is C_1-symmetric and if a fluxional process does not occur, the tert-butyl groups would be observed as two singlets. At room temperature, the tert-butyl groups are broad indicating fast conversion of the tert-butyl groups on the NMR timescale. As the temperature is lowered, the rate of conversion of the tert-butyl groups is slower on the NMR timescale and can be observed as two singlets.

The formation of complexes **55**-**57** from [(MBMP)TiPh$_2$] (**54**) appears to proceed in a similar fashion to that of the [(DMSC)Ti(L$_2$)$_2$] complexes **28**-**30** (See section 2.2.1). Addition of one equivalent of bpy or dmbpy to a C_6D_6 solution of **54** resulted in the formation of either **55** or **56** with the corresponding amount of **54** remaining. When one equivalent of phen was added to **54**, the solution immediately became dark purple in color and solids formed in the bottom of the tube. However, the ^{1}H NMR of the solution revealed the presence of **54**. This finding was significant because it indicates that two phen ligands coordinate to the titanium center. This, along with microanalysis data, helps confirm that **57** is formed in when two equivalents of phen

is added to **54**. Attempts to grow a single crystal of **57** for X-ray diffraction analysis have thus far been unsuccessful.

3.3 Reactivity of [(MBMP)Ti(L_2)$_2$] complexes

The [(DMSC)Ti(L_2)$_2$] complexes **28-30** demonstrates activity towards aromatic ketones to give 1-aza-5-oxa-titanacylcopentene compounds (see scheme 2.2). The [(MBMP)Ti(L_2)$_2$] complexes **55-57** exhibit similar behavior. Addition of two or more equivalents of benzophenone to a dark blue solution of [(MBMP)Ti(bpy)$_2$] (**55**) resulted in the formation of the orange 1-aza-5-oxa-titanacylcopentene derivative [(MBMP)Ti{κ^3-OC(C_6H_5)$_2$$C_{10}H_7N_2$}{OCH($C_6H_5$)$_2$}] (**61**) in good yield. Both ^{1}H and ^{13}C NMR data for **61** are consistent with the proposed formulation. In the ^{1}H NMR spectrum in CD_2Cl_2, two equally intense singlets are observed for the tert-butyl groups, and two equally intense singlets for the methyl groups of the MBMP ligand. Two doublets are observed for the methylene protons of the MBMP ligand. The difference of the chemical shift between the methylene protons are much greater than in previously reported titanium compounds bearing the MBMP ligand most likely due to steric and electronic reasons. The alkoxide group hydrogen (Ti-OCH(C_6H_5)$_2$) of **61** is observed as a singlet at ~δ 5.5 ppm. The ^{13}C NMR resonance for the alkoxide-carbon (Ti-O-CH(C_6H_5)$_2$) is observed at δ 86.8 range. This is similar to the compounds previously reported by our group.[58]

X-ray analysis of single crystals of **61** confirmed the structure assigned by spectroscopy (Figure 3.3). The space group for **61** was assigned P 2/c. Selected bond angles and lengths are summarized in Table 3.2. The compound adopts a slightly distorded octahedral structure. The slight distortion from the idealized octahedral geometry arises from acute bite angles of the tridentate bipyridyl-alkoxide ligand [ca. 74° for O(1)-Ti(1)-N(1) and 70° for N(1)-Ti(1)-N(2)] in addition to the steric constraint that the bidentate MBMP ligand imposes. The Ti-N and Ti-O bond lengths are essentially identical to the analagous 1-aza-5-oxa-titanacylcopentene derivative [(DMSC)Ti{κ^3-OC(*p*-Me C_6H_4)$_2$$C_{10}H_7N_2$}{OCH(*p*-Me$C_6H_4$)$_2$}] (**40**). The T-O bond distances for **61** are shorter than typical Ti-O σ-bond distances.[58] Kingston and coworkers explained the shorter Ti-O bond lengths for **40** might be reflective of a greater degree of partial Ti-O π-bonding.

The [(MBMP)Ti{κ^3-OC(C_6H_5)$_2$$C_{10}H_7N_2$}{OCH($C_6H_5$)$_2$}] (**61**) and the related 1-aza-5-oxa-titanacylcopentene derivatives supported by the MBMP ligand have very limited solubility. They are moderately soluble in methylene chloride, slightly soluble in chloroform, and

practically insoluble in ether, tetrahydrofuran, aromatic solvents, and pentane. However, since the reaction of [(MBMP)Ti(bpy)$_2$] (**55**) and two or more equivalents of benzophenone is carried out in ether, **61** crashes out of solution upon formation allowing for facile isolation. Furthermore, any impurities can be washed away with various solvents allowing for an easy work-up to get a clean compound (based on ^{1}H NMR data). Although the reaction can be carried out at room temperature, the rate of the reaction increases upon heating up to 65°C.

The reaction of [(MBMP)Ti(phen)$_2$] (**57**) with at least two equivalents of benzophenone does not readily go to the 1-aza-5-oxa-titanacylcopentene compound. Completion of the reaction took ~two weeks. Heating of the reaction while under high voltage UV lamp did not increase the rate of the reaction. The slow rate of the reaction is probably due to the high insolubility the titanium complex. The reaction between [(MBMP)Ti(L$_2$)$_2$] complexes (**55-57**) with excess phenylisocyanate gave us interesting results. Instead of producing the expected 1-aza-5-oxa-titanacyclopentene derivative, we found that complexes **(55-57**) readily leads to catalytic cyclotrimerization of phenylisocyanate in high yield (Scheme 3.3).[27, 66-71] For complexes **55** and **56** the reaction with twenty equivalents of phenylisocyanate to produce the cyclotrimerized product is typically complete within twenty minutes. However, the reaction with **57** takes ~3 hours, due the high insolubility of the complex. The formation of [PhNCO]$_3$ (**62**) was established by ^{1}H NMR and GC/MS and was essentially identical to those values reported in the literature. Flamini reported similar reactivity with [Ti(bpy)$_3$][27] (see Scheme 1.3). Initial attempts to cyclotrimerize tert-butylisocyanate have thus far failed most likely due to the steric and electronic effects the tert-butyl group of tertbutylisocyanate imposes.

In the presence of adventitious moisture or, in particular, upon exposure to air, complexes C_6D_6 solutions of **55-57** immediately turn orange. The ^{1}H NMR of these solutions reveals the presence the fairly air- and moisture-stable [(MBMP)$_2$Ti] (**63**). Okuda[63] reported a similar occurrence upon deliberate hydrolysis of [(MBMP)Ti(O*i*Pr)$_2$]. ^{1}H NMR showed that **63** could be formed from prolonged heating (>70ºC) of **55** under N_2 atmosphere. An X-ray crystal structure was obtained for the bipyridine adduct [(MBMP)$_2$Ti(bpy)] (**64**). Complexes **55-57** have been shown to have similar reactivity to the [(DMSC)Ti(L$_2$)$_2$] complexes **28-30**. We previously noted that DMSC 1-aza-5-oxa-titanacylcopentene compounds **37-42** have potential use in preparing produces 2,2'-bipyridinyl-6-yl-diphenylmethanol and 1,10-phenanthrolinine-6-yl-

Figure 3.3 Molecular Structure of 61

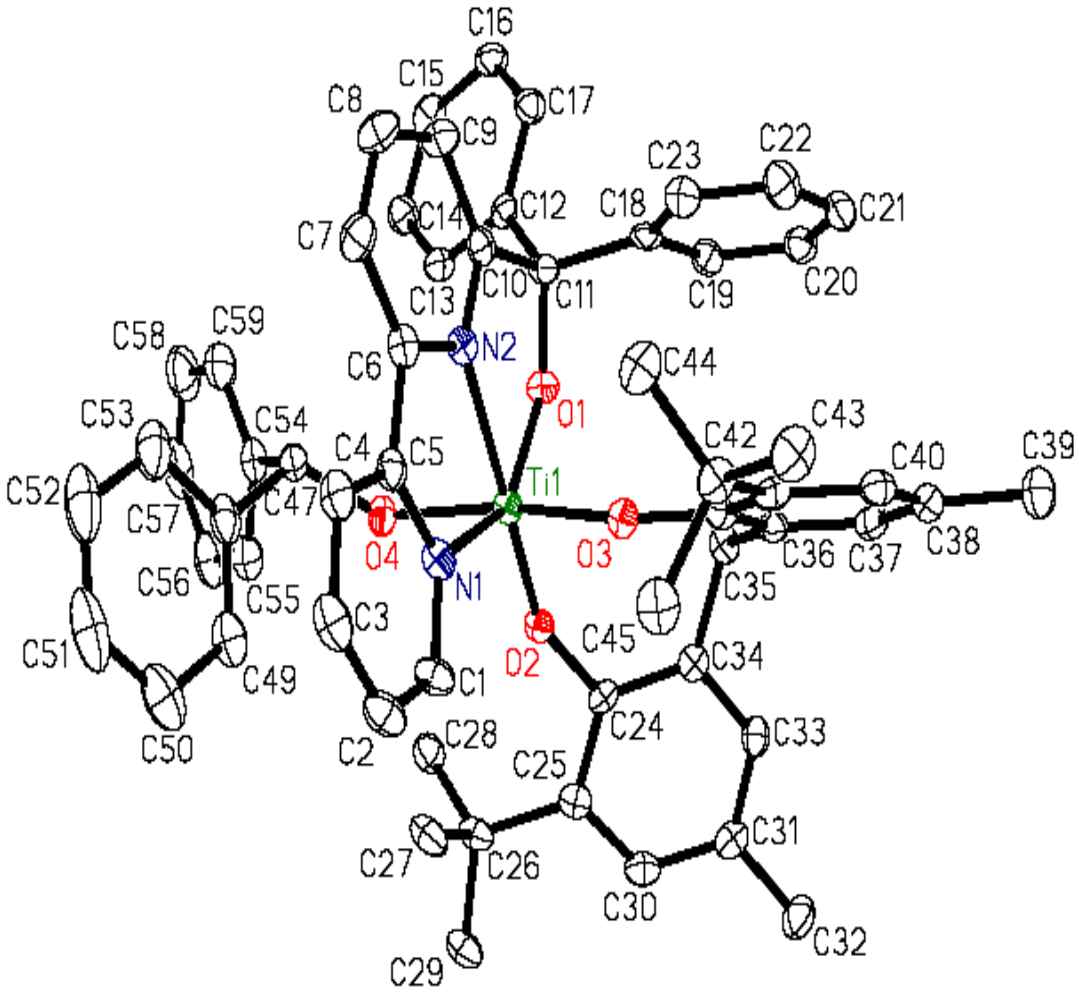
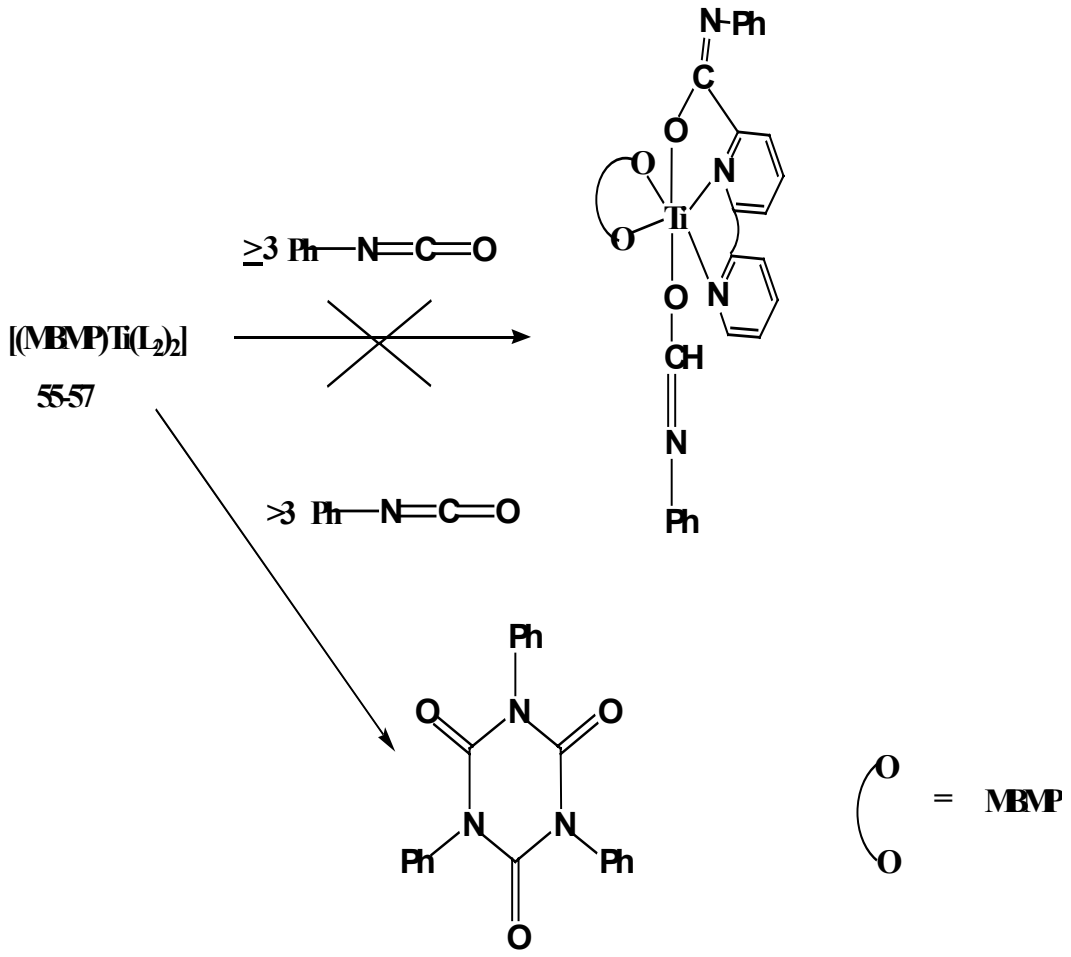


Table 3.2 Selected Bond Distances and Angles for 61

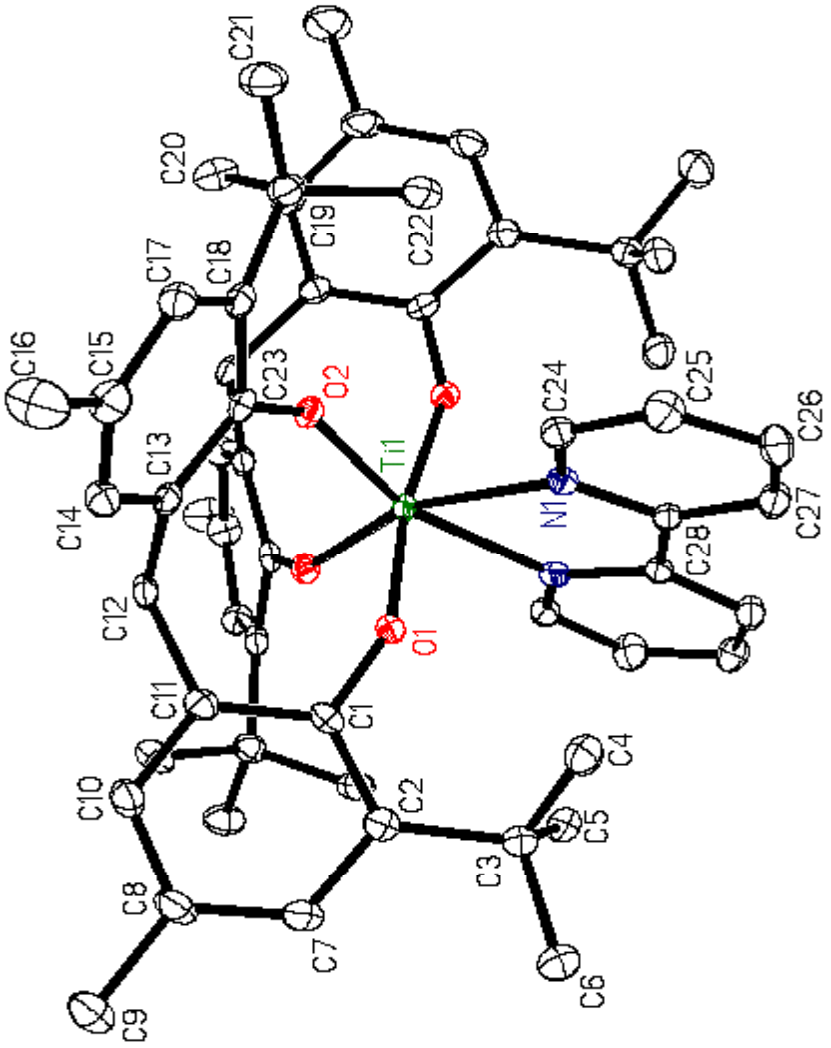
Ti(1)-O(1)	1.8651(17)	O(1)-Ti(1)-O(3)	98.66(7)
Ti(1)-O(2)	1.8502(17)	O(1)-Ti(1)-O(2)	99.09(7)
Ti(1)-O(3)	1.9075(17)	O(3)-Ti(1)-O(4)	161.86(7)
Ti(1)-O(4)	1.8850(17)	O(4)-Ti(1)-N(2)	85.26(8)
Ti(1)-N(1)	2.277(2)	O(1)-Ti(1)-N(2)	74.68(7)
Ti(1)-N(2)	2.185(2)	O(2)-Ti(1)-N(2)	172.25(8)
O(2)-Ti(1)-N(1)	115.73(8)	O(3)-Ti(1)-N(1)	80.56(7)
N(2)-Ti(1)-N(1)	70.54(8)	O(2)-Ti(1)-N(1)	115.73(8)
O(3)-Ti(1)-N(2)	91.55(7)	C(24)-O(2)-Ti(1)	148.95(16)
O(4)-Ti(1)-O(1)	97.71(8)	C(46)-O(3)-Ti(1)	151.84(16)
O(2)-Ti(1)-O(3)	94.00(7)	C(11)-O(1)-Ti(1)	127.42(11)
O(2)-Ti(1)-O(4)	91.09(7)	C(47)-O(4)-Ti(1)	143.2(6)

Scheme 3.3 Cyclotrimerization of Phenylisocyanate



62

Figure 3.4 Molecular Structure of 64



diphenylmethanol compounds **46-51.** The cost of the calix[4]arene ligand is not favorable for widespread synthesis. We have shown that [MBMP)Ti(L_2)$_2$] **55-57** can be used in preparing MBMP 1-aza-5-oxa-titanacylcopentene compounds. The facile preparation of complexes **55-57** and the low cost of the MBMP ligand are two attractive properties in the organic synthesis of produces 2,2'-bipyridinyl-6-yl-diphenylmethanol and 1,10-phenanthrolinine-6-yl-diphenylmethanol compounds. Preliminary results in our group have shown that compounds **46** and **47** can be obtained in good yield using **55**. O'Neal and coworkers have prepared similar phenanthroline compounds.[60] However, the synthesis of these compounds was limited to phenanthroline whereas we can potentially make similar bipyridine and phenanthroline compounds using **55-57**.

3.4 Experimental Section

3.4.1 General details

All experiments were performed under dry nitrogen atmosphere using standard Schlenk techniques or in a Vacuum Atmospheres, Inc. glovebox. Toluene, tetrahydrofuran, ether, and toluene were distilled from sodium benzophenone ketyl. Pentane was distilled from sodium benzophenone ketyl with addition of 1mL of tetraethyleneglycol dimethyl ether as a solubilizing agent. Benzene-d_6 was distilled from calcium hydride. All solvents were stored in the glovebox over 4A molecular sieves, that were dried in a vacuum oven at least 48 hours prior to use. Phenylisocyanate was purchased from Lancaster and stored over 4A molecular sieves for at least 24 hours prior to use. Benzophenone, 1,10-phenanthroline, 2,2'-bipyridine, and 4,4'dimethyl, 2-2'bipyridine were purchased from Aldrich Chemical Co and sublimed before use. 2,2' methylene-bridged 4-methyl, 6-tertbutyl phenol was purchased from Aldrich and dried under vacuum for 24 hours prior to use. [(MBMP)$TiCl_2$][63,64] was prepared according to published procedures. ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini-200 spectrometer or a Varian VXR-400 spectrometer at ca. 22ºC. ^1H and ^{13}C chemical shifts were referenced to residual solvent peaks. Elemental analyses were performed by Complete Analysis Laboratories, Inc., Parsippany, NJ.

3.4.2 Preparation of Ti (diimine) complexes.

[(MBMP)$TiPh_2$] (54) [(MBMP)$TiPh_2$] was prepared from a modification of a known procedure.[63] A 15 mL ether solution of [(MBMP)$TiCl_2$] (**52**) (1.5 g 0.0033 mol) (**52**) was treated with PhMgBr (2.136 ml, 0.0066 mol) at –78 °C. The reaction was then allowed to warm up slowly to room temperature and stir for one hour. The solvent was removed under reduced pressure and treated with toluene. The resulted suspension was then filtered and the volatiles were removed under reduced pressure. The solid was then washed with a small amount of pentane and dried *in vacuo* to give 1.7 g (96%) of the product as a yellow solid. ^1H NMR (C_6D_6) δ: 8.23-8.25 (m, 2H Ph), 8.13-8.15 (m, 2H, Ph), 7.12-7.07 (m, 6H, Ph) 7.03 (br s, 4H, MBMP-arom), 3.97 (d, J = 14.4 Hz, 1H, MBMP-CH_2) 3.41 (d, J = 14.4 Hz, MBMP-CH_2), 2.12 (s, 6H, Me), 1.605 (s, 18H, t-Bu).

Typical Procedure For the Preparation of [(MBMP)$Ti(L_2)_2$] Complexes 55-56 To a solution of [(MBMP)$TiPh_2$] (3.00 g, 0.0056 mol) in 15 mL of ether was added 2-2' bipyridine (1.74 g

0.0112 mol). The reaction mixture immediately turned dark-blue and was stirred for thirty minutes. The solvent was then removed under reduced pressure and washed with pentane (3 x 10 mL) to give 3.4 g (89.5 %) of the dark-blue product.

55 ^{1}H NMR at –20 °C (toluene-d_8) δ: 10.69 (d, J = 5.2 Hz, 1H bpy), 9.20 (d, J = 5.6 Hz 1H, bpy), 8.36-8.41 (m, 2H, bpy), 7.67 (s, 1H, MBMP-arom), 7.60 (s, 1H, MBMP-arom), 7.31 (s, 1H, MBMP arom), 7.02 (s, 1H, MBMP arom), 6.68 (d, J = 8Hz, 2H, bpy), 5.89-6.00 (m, 4H, bpy), 5.85 (d, J = 12.4 Hz, 1H, MBMP-CH_2), 5.64-5.69 (m, 2H, bpy), 5.39 (t, 1H, bpy), 5.02 (t, 1H, bpy), 4.06 (d, J= 12.4 Hz, 1H, MBMP-CH_2), 2.47 (s, 3H, Me), 2.40 (s, 3H, Me), 1.37 (s, 9H, t-Bu), 0.70 (s, 9H, t-Bu). Anal. Calcd. for $C_{43}H_{46}TiO_2N_4$: C, 73.91; H, 6.63; N, 8.01. Found: C, 73.79; H, 6.37; N, 7.92.

56 ^{1}H NMR at –80 °C (toluene-d_8) δ:10.74 (s, 1H, dmbpy), 9.22 (s, 1H, dmbpy), 8.67 (s, 1H, dmbpy), 8.52 (s, dmbpy), 7.53 (s, 1H, dmbpy), 7.28 (s, 1H, dmbpy), 7.16 (s, 1H MBMP), 7.01 (s, 1H, MBMP) 6.81 (s, 1H, MBMP), 6.60 (s, 1H, MBMP) 6.38 (s, 1H, dmbpy), 5.94 (s, CH_2, MBMP), 5.59 (s, 1H, dmbpy). 5.49 (s, 1H, dmbpy), (4.027, s, CH_2), 4.02 (s, 1H, CH_2), 2.34 (s, 3H, CH_3) .22 (s, 3H, CH_3), 1.46 (s, 9H, t-bu), 1.39 (s, 12H, dmbpy), 0.66 (s, 9H, t-bu).Anal. Calcd. for $C_{47}H_{64}TiO_2N_4$: C, 74.78; H, 7.2, N, 7.4. Found: C, 74.62; H, 7.25; N, 7.34.

57 Anal. Calcd. for $C_{47}H_{46}TiO_2N_4$: C, 75.6; H, 6.2; N, 7.50. Found: C, 74.94; H, 6.46; N, 7.32.

[(MBMP)Ti{κ^3-OC(C_6H_5)$_2$$C_{10}H_7N_2$}{OCH($C_6H_5$)$_2$}] (61). To [(MBMP)Ti(bpy)$_2$] (0.500 g, 0.00071 mol) in ether (10 mL) was added benzophenone (0.388 g, 0.0021 mol)

The reaction was heated at 65 °C for twelve hours. The solution was then filtered and the resulting orange solid was washed with THF (3 x 5mL) and toluene (3 x 5 mL) to give 452 mg (70.5%) of the product as an orange solid.

^{1}H NMR (CD_2Cl_2) δ: 8.68 (d, J = 6 Hz, 2H arom CH), 8.19 (d, J = 8.4 Hz, 1H arom CH), 7.89 (t, 2H, arom CH), 7.80 (t, 2H, arom CH), 7.69 (J = 7.6 Hz, 4H arom CH), 7.58 (t, 4H arom CH), 7.35 (t, 2H, arom CH), 7.16-7.62 (m, 10 H, arom CH), 6.65 (s, 2H, MBMP), 6.48 (s, 2H, MBMP), 5.92 (d, 1H, J = 13.2 Hz, CH_2), 5.57 (s, 1H, OC*H*Ph_2), 2.73 (d, 1H, d = 12.4 Hz, CH_2), 2.19 (s, 3H, Me), 2.10 (s, 3H, Me), 1.49 (s, 9H Bu^t), 1.49 (s, 9H Bu^t).

^{13}C NMR (CD_2Cl_2) δ: 170.42, 152.89, 151.32, 149.31, 148.64, 147.05, 146.60, 139.58, 138.47, 138.36, 137.29, 136.96, 135.29, 129.52, 129.42, 128.71, 128.53, 128.44, 128.20, 126.38, 126.31, 125.84, 125.71, 125.57, 125.41, 122.05, 121.89, 121.80, 119.71, 119.16, 99.54, 88.47, 86.84, 37.18, 35.54, 33.91, 31.34, 29.74, 21.70, 21.19, 20.94.

3.4.3 Cyclotrimerization of Phenylisocyanate

To [(MBMP)Ti(bpy)$_2$] (0.050 g), (0.071 mmol) in toluene was added phenylisocayante 4.27 g (35.9 mmol). The reaction became dark red-brown after five minutes. The reaction was allowed to stir for one hour and filtered. The solids were washed with pentane and toluene and dried *in vacuo* to give 4.10 g of product. ^{1}H NMR and GC/MS data are essentially identical to the reported literature values.[67-68]

Chapter Four

Conclusion and future research

In the course of this work, we have shown that titanium bis(diimine) complexes [(DMSC)Ti(bpy)$_2$] (**28**), [(DMSC)Ti(dmbpy)$_2$] (**29**), [(DMSC)Ti(phen)$_2$] (**30**). [(MBMP)Ti(bpy)$_2$] (**55**), [(MBMP)Ti(dmbpy)$_2$] (**56**), and [(MBMP)Ti(phen)$_2$] (**57**) can be easily prepared in good yield. The reactivity of the complexes was probed and we have shown that one of the diimine ligands of the titanium center can be readily displaced We have shown that the [(DMSC)Ti(L$_2$)$_2$] complexes **28-30** undergoes light assisted reactions with two or more equivalents of (*p*-MeC$_6$H$_4$)$_2$CO or (C$_6$H$_5$)CO to cleanly yield the corresponding 1-aza-5-oxa-titanacylcopentene compound complexes. We also established that there is an equilibrium between complexes **28-30** and the Ti-η^2-ketone complexes [(DMSC)Ti{η^2-OC(Ar)$_2$] (**31-36**). In addition, the amount of ketone present in the reaction was shown to affect the rate of the reaction.

The ligand about the titanium center also has an effect on the titanium bis(diimine) complexes. The [(DMSC)Ti(L$_2$)$_2$] complexes have been found to be much more soluble than the[(MBMP)Ti(L$_2$)$_2$] complexes. In addition, the ^{1}H NMR spectra of the [(DMSCTi(L$_2$)$_2$] complexes (**28-30)** display very sharp peaks and is shown to be C_s-symmetric in solution at room temperature whereas the ^{1}H NMR of the [(MBMP)Ti(L$_2$)$_2$] complexes **55** and **56** display broad peaks at room temperature and exhibit fluxional behavior.

The [(MBMP)Ti(L$_2$)$_2$] complexes **55** and **56** are attractive in their potential uses in organic synthesis. Research in our group has indicated that complexes **55** can be a useful starting material in preparing 2,2'-bipyridinyl-6-yl-diphenylmethanol and 1,10-phenanthroline-6-yl-diphenylmethanol compounds. Complex **57** is not favorable for this reaction due to its high insolubility. Further work needs to be conducted to find favorable conditions for the use of **57.** We have also shown that complexes **55-57** will readily cyclotrimerize phenylisocyanate in good yield. Cyclotrimerization of phenylisocyanate using complexes **55-57** is advantageous over other known procedures because of the ease of synthesis of the starting materials and favorable reaction conditions. Future investigation is necessary to gain a full understanding of the mechanism of the reaction. Possible isolation of the titanium species in the reaction is also of

great interest. Reactivity with other organic substrates is needed to widen the usefulness of these complexes. In addition, preparing more titanium bis(diimine) complexes with various ligands would be useful to further examine the effect the ancillary ligand will have on the titanium center.

The oxidation states of these complexes are difficult to assign. These complexes can be viewed as Ti (II) species bound to two neutral L_2 ligands, Ti (III) species bound to one radical anionic L_2^- ligand and one neutral L_2 ligand, or Ti (IV) species bound to two radical anionic L_2^- ligands. It may be possible for the excited electronic state to be thermally and photochemically accessible. Theoretical data has indicated of these complexes having titanium III oxidation state. Theoretical molecular orbital calculations have been carried out on [(MBMP)Ti(bpy)$_2$] (**55**) suggesting the singlet state is much higher in energy than the triplet state indicating the complex has two unpaired electrons. Evans[72] method using ^{1}H NMR was conducted on complex **55.** The diamagnetic contribution[73] was factored in and a magnetic moment of 1.68 was found for the complex, indicative of a titanium III species. However, further EPR studies as well as magnetic susceptibility analysis are still necessary to elucidate the oxidation state of these complexes.

APPENDIX

LIST OF TABLES

Table A1. Crystal data and structure refinement for [(DMSC)Ti(bpy)$_2$] (**28**) 57

Table A2. Bond lengths (Å) and angles (deg) for **28** 58

Table A3. Crystal data and structure refinement for (**45**) 61

Table A4. Bond lengths (Å) and angles (deg) for **45** 62

Table A5.. Crystal data and structure refinement for (**55**) 75

Table A6. Bond lengths (Å) and angles (deg) for **55** 76

Table A7. Crystal data and structure refinement for
[(MBMP)Ti{κ^3-OC(C_6H_5)$_2$$C_{10}H_7N_2$}{OCH($C_6H_5$)$_2$}] (**61**) 84

Table A8. Bond lengths (Å) and angles (deg) for **61** 85

Table A9. Crystal data and structure refinement for [(MBMP)$_2$Ti(bpy)] (**64**) 94

Table A10. Bond lengths (Å) and angles (deg) for **64** 95

Table A1. Crystal data and structure refinement for [(DMSC)Ti(bpy)$_2$] (28)

Compound	**28**
Empirical formula	C81H88N7O4SiTi
Formula weight	1299.57
Temperature	90.0(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 15.1753(13) A alpha = 99.096(2). b = 15.2345(13) beta = 113.247(2)deg. c = 17.0936(15) A gamma = 101.233(2).
Volume	3438.2(5)A^3
Z, Calculated density	2
Absorption coefficient	0.199 mm^{-1}
F(000)	1816
Crystal size	0.35 x 0.15 x 0.02 mm
Theta range for data collection	2.82 to 25.79 deg.
Limiting indices	-18<=h<=18, -18<=k<=18, -16<=l<=16
Reflections collected / unique	5846 / 6041 [R(int) = 0.0772]
Completeness to theta = 22.50	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9954 and 0.9232
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6041 / 7 / 568
Goodness-of-fit on F^2	1.123
Final R indices (2σ)	R1 = 0.0621, wR2 = 0.1156
R indices (all data)	R1 = 0.0991, wR2 = 0.1256
Absolute structure parameter	-0.01(4)
Extinction coefficient	0.0017(3)
Largest diff. peak and hole	0.350 and -0.253 e.A^-3

Atoms	Bond Distance	Atoms	Bond Distance
Si1 O3	1.640(2)	C24 C49	1.537(5)
Si1 O4	1.653(3)	C25 C26	1.395(5)
Si1 C65	1.820(4)	C26 C48	1.514(5)
Si1 C66	1.859(4)	C27 C28	1.515(5)
Ti1 O1	1.880(2)	C28 C29	1.387(5)
Ti1 O2	1.926(2)	C28 C33	1.405(5)
Ti1 N2	2.129(3)	C29 C30	1.384(5)
Ti1 N3	2.156(3)	C30 C31	1.382(5)
Ti1 N1	2.156(3)	C30 C53	1.542(5)
Ti1 N4	2.178(3)	C31 C32	1.393(5)
O1 C21	1.349(4)	C32 C33	1.407(5)
O2 C33	1.356(4)	C32 C34	1.494(5)
O3 C36	1.375(4)	C34 C35	1.517(5)
O4 C47	1.393(4)	C35 C36	1.393(5)
N1 C1	1.366(5)	C35 C40	1.404(5)
N1 C5	1.385(5)	C36 C37	1.393(5)
N2 C10	1.365(5)	C37 C38	1.397(5)
N2 C6	1.388(5)	C37 C41	1.518(5)
N3 C11	1.345(5)	C38 C39	1.385(5)
N3 C15	1.369(4)	C39 C40	1.376(5)
N4 C20	1.351(5)	C39 C57	1.530(5)
N4 C16	1.370(5)	C41 C42	1.504(5)
C1 C2	1.356(5)	C42 C43	1.381(5)
C2 C3	1.394(6)	C42 C47	1.400(5)
C3 C4	1.354(6)	C43 C44	1.392(5)
C4 C5	1.406(5)	C44 C45	1.386(5)
C5 C6	1.411(6)	C44 C61	1.534(5)
C6 C7	1.397(6)	C45 C46	1.401(5)
C7 C8	1.359(6)	C46 C47	1.378(5)
C8 C9	1.399(6)	C46 C48	1.515(5)
C9 C10	1 .371(5)	C49 C52	1.523(5)
C11 C12	1.370(5)	C49 C51	1.525(5)
C12 C13	1.390(6)	C49 C50	1.539(5)
C13 C14	1.366(5)	C53 C55	1.517(6)
C14 C15	1.393(5)	C53 C54	1.518(6)
C15 C16	1.445(5)	C53 C56	1.528(6)
C16 C17	1.389(5)	C57 C58	1.496(7)
C17 C18	1.378(6)	C57 C60A	1.528(5)
C18 C19	1.396(6)	C57 C58A	1.544(9)
C19 C2	1.361(5)	C57 C60	1.556(7)
C21 C26	1.400(5)	C57 C59	1.565(6)
C21 C22	1.405(5)	C57 C59A	1.619(1)
C22 C23	1.397(5)	C61 C63	1.517(6)
C22 C27	1.520(5)	C61 C64	1.522(6)
C23 C24	1.394(5)	C61 C62	1.522(5)
C67 C68	1.333(7)	C76 N6A	1.346(8)
C67 C72	1.402(8)	C76 N6A	1.346(8)
C67 C67	1.509(1)	C76 N6A	1.346(8)
C68 C69	1.290(7)	N6A C78	1.335(7)
C69 C70	1.364(8)	C78 C79	1.497(8)
C70 C71	1.377(9)	C79 C80	1.361(8)
C71 C72	1.322(8)	C79 N7A	1.379(7)
C73 C78	1.366(8)	C80 C81	1.373(9)
C73 C74	1.393(9)	C81 C82	1.347(1)

C74 C75	1.340(9)	C82 C83	1.366(8)
C75 C76	1.382(8)	C83 N7A	1.358(8)
C76 N6A	1.346(8)		

Table A3.. Crystal data and structure refinement for (45)

Compound	**45**
Empirical formula	C81 H90 N2 O5 Si Ti
Formula weight	1223.52
Temperature	150.0(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P 21/c
Unit cell dimensions	a = 13.34700(10) A alpha = 90 deg. b = 37.2230(3) A beta = 110.5650 (4) deg. c = 15.2170(2) A gamma = 90 deg.
Volume	7078.27(12) A^3
Z, Calculated density	4, 1.148 Mg/m^3
Absorption coefficient	0.189mm^{-1}
F(000)	2616
Crystal size	0.35 x 0.30 x 0.20 mm
Theta range for data collection	1.53 to 25.00 deg.
Limiting indices	-15<=h<=15, -44<=k<=44, -18<=l<=18
Reflections collected / unique	24621 /1254 [R(int) = 0.0389]
Completeness to theta = 22.50	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9633 and 0.9369
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	12454 /134 / 886
Goodness-of-fit on F^2	1.037
Final R indices (2σ)	R1 = 0.0474, wR2 = 0.1049
R indices (all data)	R1 = 0.0815, wR2 = 0.1165
Absolute structure parameter	-0.01(4)
Extinction coefficient	0.0017(3)
Largest diff. peak and hole	0.385 and -0.337 $e.A^3$

Atoms	Bond length	Atoms	Bond length
Ti-O(3)	1.8177(14)	C(17)-C(41)	1.532(3)
Ti-O(1)	1.8350(15)	C(18)-C(19)	1.388(3)
Ti-O(5)	1.8818(15)	C(18)-H(18)	0.9500
Ti-O(2)	1.9404(14)	C(19)-C(28)	1.394(3)
Ti-N(1)	2.2476(18)	C(19)-C(20)	1.523(3)
Ti-N(2)	2.2539(18)	C(20)-C(21)	1.513(3)
Si-O(5)	1.6034(16)	C(20)-H(20A)	0.9900
Si-O(4)	1.6511(1)	C(20)-H(20B)	0.9900
Si-C(46)	1.846(3)	C(21)-C(22)	1.393(3)
Si-C(45)	1.868(3)	C(21)-C(25)	1.403(3)
O(1)-C(25)	1.356(2)	C(22)-C(23)	1.397(3)
O(2)-C(26)	1.356(2)	C(22)-H(22)	0.9500
O(3)-C(27)	1.356(2)	C(23)-C(24)	1.395(3)
O(4)-C(28)	1.384(2)	C(23)-C(29)	1.539(3)
C(1)-C(24)	1.393(3)	C(24)-H(24)	0.9500
C(1)-C(25)	1.399(3)	C(29)-C(31)	1.523(4)
C(1)-C(2)	1.514(3)	C(29)-C(30)	1.528(3)
C(2)-C(3)	1.518(3)	C(29)-C(32)	1.533(4)
C(2)-H(2A)	0.9900	C(30)-H(30A)	0.9800
C(2)-H(2B)	0.9900	C(30)-H(30B)	0.9800
C(3)-C(4)	1.397(3)	C(30)-H(30C)	0.9800
C(3)-C(26)	1.398(3)	C(31)-H(31A)	0.9800
C(4)-C(5)	1.392(3)	C(31)-H(31B)	0.9800
C(4)-H(4)	0.9500	C(31)-H(31C)	0.9800
C(5)-C(6)	1.399(3)	C(32)-H(32A)	0.9800
C(5)-C(33)	1.536(3)	C(32)-H(32B)	0.9800
C(6)-C(7)	1.388(3)	C(32)-H(32C)	0.9800
C(6)-H(6)	0.9500	C(33)-C(34)	1.529(3)
C(7)-C(26)	1.408(3)	C(33)-C(35)	1.531(3)
C(7)-C(8)	1.511(3)	C(33)-C(36)	1.534(3
C(8)-C(9)	1.518(3)	C(34)-H(34A)	0.9800
C(8)-H(8A)	0.9900	C(34)-H(34B)	0.9800
C(8)-H(8B)	0.9900	C(34)-H(34C)	0.9800
C(9)-C(10)	1.397(3)	C(35)-H(35A)	0.9800
C(9)-C(27)	1.401(3)	C(35)-H(35B)	0.9800
C(10)-C(11)	1.392(3)	C(35)-H(35C)	0.9800
C(10)-H(10)	0.9500	C(36)-H(36A)	0.9800
C(11)-C(12)	1.398(3)	C(36)-H(36B)	0.9800
C(11)-C(37)	1.534(3)	C(36)-H(36C)	0.9800
C(12)-C(13)	1.383(3)	C(37)-C(39')	1.491(1)
C(12)-H(12)	0.9500	C(37)-C(38')	1.513(1)
C(13)-C(27)	1.406(3)	C(37)-C(39)	1.516(4)
C(13)-C(14)	1.508(3)	C(37)-C(38)	1.523(4)
C(14)-C(15)	1.519(3)	C(37)-C(40)	1.553(4)
C(14)-H(14A)	0.9900	C(37)-C(40')	1.588(1)
C(14)-H(14B)	0.9900	C(38)-H(38A)	0.9800
C(15)-C(28)	1.393(3)	C(38)-H(38B)	0.9800
C(15)-C(16)	1.396(3)	C(38)-H(38C)	0.9800
C(16)-C(17)	1.392(3)	C(39)-H(39A)	0.9800
C(16)-H(16)	0.9500	C(39)-H(39B)	0.9800
C(17)-C(18)	1.389(3)	C(39)-H(39C)	0.9800

Atoms	Angles	Atoms	Angles
O(3)-Ti-O(1)	105.88(6)	C(9)-C(8)-H(8B)	109.3
O(3)-Ti-O(5)	97.77(7)	H(8A)-C(8)-H(8B)	107.9
O(1)-Ti-O(5)	97.78(7)	C(10)-C(9)-C(27)	118.28(1)
O(3)-Ti-O(2)	94.08(6)	C(10)-C(9)-C(8)	120.85(1)
O(1)-Ti-O(2)	94.81(6)	C(27)-C(9)-C(8)	120.79(1)
O(5)-Ti-O(2)	159.64(6)	C(11)-C(10)-C(9)	122.9(2)
O(3)-Ti-N(1)	163.57(7)	C(11)-C(10)-H(10)	118.6
O(1)-Ti-N(1)	89.82(6)	C(9)-C(10)-H(10)	118.6
O(5)-Ti-N(1)	84.54(6)	C(10)-C(11)-C(12)	116.7(2)
O(2)-Ti-N(1)	79.54(6)	C(10)-C(11)-C(37)	123.2(2)
O(3)-Ti-N(2)	91.22(7)	C(12)-C(11)-C(37)	120.10(1)
O(1)-Ti-N(2)	162.52(7)	C(13)-C(12)-C(11)	122.9(2)
O(5)-Ti-N(2)	83.11(7)	C(13)-C(12)-H(12)	118.5
O(2)-Ti-N(2)	80.13(6)	C(11)-C(12)-H(12)	118.5
N(1)-Ti-N(2)	72.85(7)	C(12)-C(13)-C(27)	118.6(2)
O(5)-Si-O(4)	111.89(8)	C(12)-C(13)-C(14)	121.17(1)
O(5)-Si-C(46)	112.08(1)	C(27)-C(13)-C(14)	120.18(1)
O(4)-Si-C(46)	106.53(1)	C(13)-C(14)-C(15)	111.05(1)
O(5)-Si-C(45)	109.77(1)	C(13)-C(14)-H(14A)	109.4
O(4)-Si-C(45)	107.92(1)	C(15)-C(14)-H(14A)	109.4
C(46)-Si-C(45)	108.48(1)	C(13)-C(14)-H(14B)	109.4
C(25)-O(1)-Ti	165.96(1)	C(15)-C(14)-H(14B)	109.4
C(26)-O(2)-Ti	117.58(1)	H(14A)-C(14)-H(14B)	108.0
C(27)-O(3)-Ti	166.53(1)	C(28)-C(15)-C(16)	118.6(2)
C(28)-O(4)-Si	139.70(1)	C(28)-C(15)-C(14)	122.1(2)
Si-O(5)-Ti	143.55(9)	C(16)-C(15)-C(14)	118.9(2)
C(24)-C(1)-C(25)	118.3(2)	C(17)-C(16)-C(15)	122.7(2)
C(24)-C(1)-C(2)	120.69(1)	C(17)-C(16)-H(16)	118.6
C(25)-C(1)-C(2)	120.98(1)	C(15)-C(16)-H(16)	118.6
C(1)-C(2)-C(3)	114.81(1)	C(18)-C(17)-C(16)	116.3(2)
C(1)-C(2)-H(2A)	108.6	C(18)-C(17)-C(41)	120.1(2)
C(3)-C(2)-H(2A)	108.6	C(16)-C(17)-C(41)	123.3(2)
C(1)-C(2)-H(2B)	108.6	C(19)-C(18)-C(17)	123.0(2)
C(3)-C(2)-H(2B)	108.6	C(19)-C(18)-H(18)	118.5
H(2A)-C(2)-H(2B)	107.5	C(17)-C(18)-H(18)	118.5
C(4)-C(3)-C(26)	119.3(2)	C(18)-C(19)-C(28)	118.7(2)
C(4)-C(3)-C(2)	120.17(1)	C(18)-C(19)-C(20)	118.4(2)
C(26)-C(3)-C(2)	120.51(1)	C(28)-C(19)-C(20)	122.3(2)
C(5)-C(4)-C(3)	122.6(2)	C(21)-C(20)-C(19)	108.57(1)
C(5)-C(4)-H(4)	118.7	C(21)-C(20)-H(20A)	110.0
C(3)-C(4)-H(4)	118.7	C(19)-C(20)-H(20A)	110.0
C(4)-C(5)-C(6)	116.6(2)	C(21)-C(20)-H(20B)	110.0
C(4)-C(5)-C(33)	123.3(2)	C(19)-C(20)-H(20B)	110.0
C(6)-C(5)-C(33)	120.0(2)	H(20A)-C(20)-H(20B)	108.4
C(7)-C(6)-C(5)	122.8(2)	C(22)-C(21)-C(25)	118.8(2)
C(7)-C(6)-H(6)	118.6	C(22)-C(21)-C(20)	121.0(2)
C(5)-C(6)-H(6)	118.6	C(25)-C(21)-C(20)	119.79(1)
C(6)-C(7)-C(26)	119.12(1)	C(21)-C(22)-C(23)	122.5(2)
C(6)-C(7)-C(8)	120.12(1)	C(21)-C(22)-H(22)	118.7
C(26)-C(7)-C(8)	120.72(1)	C(23)-C(22)-H(22)	118.7
C(7)-C(8)-C(9)	111.74(1)	C(24)-C(23)-C(22)	116.6(2)
C(7)-C(8)-H(8A)	109.3	C(24)-C(23)-C(29)	120.4(2)
C(9)-C(8)-H(8A)	109.3	C(22)-C(23)-C(29)	122.9(2)
C(7)-C(8)-H(8B)	109.3	C(1)-C(24)-C(23)	123.1(2)
C(23)-C(24)-H(24)	118.4	C(1)-C(24)-H(24)	118.4

O(1)-C(25)-C(1)	120.26(19)	H(36A)-C(36)-H(36B)	109.5
O(1)-C(25)-C(21)	119.17(19)	C(33)-C(36)-H(36C)	109.5
C(1)-C(25)-C(21)	120.56(19)	H(36A)-C(36)-H(36C)	109.5
O(2)-C(26)-C(3)	120.38(19)	H(36B)-C(36)-H(36C)	109.5
O(2)-C(26)-C(7)	120.12(19)	C(39')-C(37)-C(38')	112.3(13)
C(3)-C(26)-C(7)	119.50(19)	C(39')-C(37)-C(39)	140.7(9)
O(3)-C(27)-C(9)	120.37(19)	C(38')-C(37)-C(39)	53.1(9)
O(3)-C(27)-C(13)	119.06(19)	C(39')-C(37)-C(38)	48.8(10)
C(9)-C(27)-C(13)	120.57(19)	C(38')-C(37)-C(38)	132.5(8)
O(4)-C(28)-C(15)	120.03(19)	C(39)-C(37)-C(38)	109.9(2)
O(4)-C(28)-C(19)	119.87(19)	C(39')-C(37)-C(11)	109.5(8)
C(15)-C(28)-C(19)	120.1(2)	C(38')-C(37)-C(11)	114.4(8)
C(31)-C(29)-C(30)	108.7(2)	C(39)-C(37)-C(11)	109.5(2)
C(31)-C(29)-C(32)	109.5(2)	C(38)-C(37)-C(11)	113.1(2)
C(30)-C(29)-C(32)	107.3(2)	C(39')-C(37)-C(40)	61.4(10)
C(31)-C(29)-C(23)	109.4(2)	C(38')-C(37)-C(40)	57.1(10)
C(30)-C(29)-C(23)	112.2(2)	C(39)-C(37)-C(40)	109.0(2)
C(32)-C(29)-C(23)	109.7(2)	C(38)-C(37)-C(40)	106.3(2)
C(29)-C(30)-H(30A)	109.5	C(11)-C(37)-C(40)	108.89
C(29)-C(30)-H(30B)	109.5	C(39')-C(37)-C(40')	110.1(1)
H(30A)-C(30)-H(30B)	109.5	C(38')-C(37)-C(40')	106.2(2)
C(29)-C(30)-H(30C)	109.5	C(39)-C(37)-C(40')	55.5(8)
H(30A)-C(30)-H(30C)	109.5	C(38)-C(37)-C(40')	61.9(8)
H(30B)-C(30)-H(30C)	109.5	C(11)-C(37)-C(40')	103.9(8)
C(29)-C(31)-H(31A)	109.5	C(40)-C(37)-C(40')	147.1(8)
C(29)-C(31)-H(31B)	109.5	C(37)-C(38)-H(38A)	109.5
H(31A)-C(31)-H(31B)	109.5	C(37)-C(38)-H(38B)	109.5
C(29)-C(31)-H(31C)	109.5	C(37)-C(38)-H(38C)	109.5
H(31A)-C(31)-H(31C)	109.5	C(37)-C(39)-H(39A)	109.5
H(31B)-C(31)-H(31C)	109.5	C(37)-C(39)-H(39B)	109.5
C(29)-C(32)-H(32A)	109.5	C(37)-C(39)-H(39C)	109.5
C(29)-C(32)-H(32B)	109.5	C(37)-C(40)-H(40A)	109.5
H(32A)-C(32)-H(32B)	109.5	C(37)-C(40)-H(40B)	109.5
C(29)-C(32)-H(32C)	109.5	C(37)-C(40)-H(40C)	109.5
H(32A)-C(32)-H(32C)	109.5	C(37)-C(38')-H(38D)	109.5
H(32B)-C(32)-H(32C)	109.5	C(37)-C(38')-H(38E)	109.5
C(34)-C(33)-C(35)	108.7(2)	H(38D)-C(38')-H(38E)	109.5
C(34)-C(33)-C(36)	108.2(2)	C(37)-C(38')-H(38F)	109.5
C(35)-C(33)-C(36)	108.8(2)	H(38D)-C(38')-H(38F)	109.5
C(34)-C(33)-C(5)	111.88(19)	H(38E)-C(38')-H(38F)	109.5
C(35)-C(33)-C(5)	108.59(19)	C(37)-C(39')-H(39D)	109.5
C(36)-C(33)-C(5)	110.63(19)	C(37)-C(39')-H(39E)	109.5
C(33)-C(34)-H(34A)	109.5	H(39D)-C(39')-H(39E)	109.5
C(33)-C(34)-H(34B)	109.5	C(37)-C(39')-H(39F)	109.5
H(34A)-C(34)-H(34B)	109.5	H(39D)-C(39')-H(39F)	109.5
C(33)-C(34)-H(34C)	109.5	H(39E)-C(39')-H(39F)	109.5
H(34A)-C(34)-H(34C)	109.5	C(37)-C(40')-H(40D)	109.5
H(34B)-C(34)-H(34C)	109.5	C(37)-C(40')-H(40E)	109.5
C(33)-C(35)-H(35A)	109.5	H(40D)-C(40')-H(40E)	109.5
C(33)-C(35)-H(35B)	109.5	C(37)-C(40')-H(40F)	109.5
H(35A)-C(35)-H(35B)	109.5	H(40D)-C(40')-H(40F)	109.5
C(33)-C(35)-H(35C)	109.5	H(40E)-C(40')-H(40F)	109.5
H(35A)-C(35)-H(35C)	109.5	C(42)-C(41)-C(44)	109.1(3)
H(35B)-C(35)-H(35C)	109.5	C(42)-C(41)-C(17)	112.9(2)
C(33)-C(36)-H(36A)	109.5	C(44)-C(41)-C(17)	109.7(2)
C(33)-C(36)-H(36B)	109.5	C(42)-C(41)-C(43)	108.5(3)

C(44)-C(41)-C(43)	107.9(3)	C(6T2)-C(5T2)-H(5T2)	120.0
C(17)-C(41)-C(43)	108.7(2)	C(4T2)-C(5T2)-H(5T2)	120.0
C(41)-C(42)-H(42A)	109.5	C(5T2)-C(6T2)-C(1T2)	121.4(4)
C(41)-C(42)-H(42B)	109.5	C(5T2)-C(6T2)-H(6T2)	119.3
H(42A)-C(42)-H(42B)	109.5	C(1T2)-C(6T2)-H(6T2)	119.3
C(41)-C(42)-H(42C)	109.5	C(1T2)-C(7T2)-H(7T4)	109.5
H(42A)-C(42)-H(42C)	109.5	C(1T2)-C(7T2)-H(7T5)	109.5
H(42B)-C(42)-H(42C)	109.5	H(7T4)-C(7T2)-H(7T5)	109.5
C(41)-C(43)-H(43A)	109.5	C(1T2)-C(7T2)-H(7T6)	109.5
C(41)-C(43)-H(43B)	109.5	H(7T4)-C(7T2)-H(7T6)	109.5
H(43A)-C(43)-H(43B)	109.5	H(7T5)-C(7T2)-H(7T6)	109.5
C(41)-C(43)-H(43C)	109.5	C(6T3)-C(1T3)-C(2T3)	120.7(8)
H(43A)-C(43)-H(43C)	109.5	C(6T3)-C(1T3)-C(7T3)	120.0(7)
H(43B)-C(43)-H(43C)	109.5	C(2T3)-C(1T3)-C(7T3)	119.3(8)
C(41)-C(44)-H(44A)	109.5	C(3T3)-C(2T3)-C(1T3)	118.9(8)
C(41)-C(44)-H(44B)	109.5	C(3T3)-C(2T3)-H(2T3)	120.6
H(44A)-C(44)-H(44B)	109.5	C(1T3)-C(2T3)-H(2T3)	120.6
C(41)-C(44)-H(44C)	109.5	C(2T3)-C(3T3)-C(4T3)	120.7(10)
H(44A)-C(44)-H(44C)	109.5	C(2T3)-C(3T3)-H(3T3)	119.6
H(44B)-C(44)-H(44C)	109.5	C(4T3)-C(3T3)-H(3T3)	119.6
Si-C(45)-H(45A)	109.5	C(5T3)-C(4T3)-C(3T3)	120.0(11)
Si-C(45)-H(45B)	109.5	C(5T3)-C(4T3)-H(4T3)	120.0
H(45A)-C(45)-H(45B)	109.5	C(3T3)-C(4T3)-H(4T3)	120.0
Si-C(45)-H(45C)	109.5	C(4T3)-C(5T3)-C(6T3)	119.4(11)
H(45A)-C(45)-H(45C)	109.5	C(4T3)-C(5T3)-H(5T3)	120.3
H(45B)-C(45)-H(45C)	109.5	C(6T3)-C(5T3)-H(5T3)	120.3
Si-C(46)-H(46A)	109.5	C(1T3)-C(6T3)-C(5T3)	120.3(8)
Si-C(46)-H(46B)	109.5	C(1T3)-C(6T3)-H(6T3)	119.9
H(46A)-C(46)-H(46B)	109.5	C(5T3)-C(6T3)-H(6T3)	119.9
Si-C(46)-H(46C)	109.5	C(2T4)-C(1T4)-C(6T4)	119.9(7)
H(46A)-C(46)-H(46C)	109.5	C(2T4)-C(1T4)-C(7T4)	119.2(8)
H(46B)-C(46)-H(46C)	109.5	C(6T4)-C(1T4)-C(7T4)	120.9(7)
C(58)-N(1)-C(47)	118.04	C(3T4)-C(2T4)-C(1T4)	118.5(8)
C(58)-N(1)-Ti	125.71	C(3T4)-C(2T4)-H(2T4)	120.7
C(47)-N(1)-Ti	116.11	C(1T4)-C(2T4)-H(2T4)	120.7
C(49)-N(2)-C(48)	118.0(2)	C(2T4)-C(3T4)-C(4T4)	123.4(9)
C(49)-N(2)-Ti	125.84	C(2T4)-C(3T4)-H(3T4)	118.3
C(48)-N(2)-Ti	116.15	C(4T4)-C(3T4)-H(3T4)	118.3
N(1)-C(47)-C(55)	122.8(2)	C(3T4)-C(4T4)-C(5T4)	116.3(10)
N(1)-C(47)-C(48)	117.32	C(3T4)-C(4T4)-H(4T4)	121.8
C(55)-C(47)-C(48)	119.8(2)	C(5T4)-C(4T4)-H(4T4)	121.8
N(2)-C(48)-C(52)	123.2(2)	C(6T4)-C(5T4)-C(4T4)	121.7(10)
N(2)-C(48)-C(47)	116.90	C(6T4)-C(5T4)-H(5T4)	119.1
C(52)-C(48)-C(47)	119.9(2)	C(4T4)-C(5T4)-H(5T4)	119.1
N(2)-C(49)-C(50)	122.4(2)	C(1T4)-C(6T4)-C(5T4)	119.9(8)
N(2)-C(49)-H(49)	118.8	C(1T4)-C(6T4)-H(6T4)	120.0
C(50)-C(49)-H(49)	118.8	C(5T4)-C(6T4)-H(6T4)	120.0
C(51)-C(50)-C(49)	119.6(2)	C(1T4)-C(7T4)-H(7TX)	109.5
C(51)-C(50)-H(50)	120.2	C(1T4)-C(7T4)-H(7TY)	109.5
C(49)-C(50)-H(50)	120.2	H(7TX)-C(7T4)-H(7TY)	109.5
C(50)-C(51)-C(52)	119.7(2)	C(1T4)-C(7T4)-H(7TZ)	109.5
C(50)-C(51)-H(51)	120.1	H(7TX)-C(7T4)-H(7TZ)	109.5
C(52)-C(51)-H(51)	120.1	H(7TY)-C(7T4)-H(7TZ)	109.5
C(51)-C(52)-C(48)	117.2(2)	C(48)-C(52)-C(53)	118.9(2)
C(51)-C(52)-C(53)	124.0(2)	C(54)-C(53)-C(52)	121.2(2)
C(52)-C(53)-H(53)	119.4	C(54)-C(53)-H(53)	119.4

C(53)-C(54)-C(55)	121.1(2)	C(3T1)-C(4T1)-H(4T1)	120.9
C(53)-C(54)-H(54)	119.4	C(6T1)-C(5T1)-C(4T1)	120.9(5
C(55)-C(54)-H(54)	119.4	C(6T1)-C(5T1)-H(5T1)	119.6
C(56)-C(55)-C(47)	116.7(2)	C(4T1)-C(5T1)-H(5T1)	119.6
C(56)-C(55)-C(54)	124.2(2)	C(1T1)-C(6T1)-C(5T1)	120.1(4)
C(47)-C(55)-C(54)	119.1(2)	C(1T1)-C(6T1)-H(6T1)	119.9
C(57)-C(56)-C(55)	120.6(2)	C(5T1)-C(6T1)-H(6T1)	119.9
C(57)-C(56)-H(56)	119.7	C(1T1)-C(7T1)-H(7T1)	109.5
C(55)-C(56)-H(56)	119.7	C(1T1)-C(7T1)-H(7T2)	109.5
C(56)-C(57)-C(58)	118.8(2)	H(7T1)-C(7T1)-H(7T2)	109.5
C(56)-C(57)-H(57)	120.6	C(1T1)-C(7T1)-H(7T3)	109.5
C(58)-C(57)-H(57)	120.6	H(7T1)-C(7T1)-H(7T3)	109.5
N(1)-C(58)-C(57)	123.0(2)	H(7T2)-C(7T1)-H(7T3)	109.5
N(1)-C(58)-H(58)	118.5	C(6T2)-C(1T2)-C(2T2)	117.5(4)
C(57)-C(58)-H(58)	118.5	C(6T2)-C(1T2)-C(7T2)	120.2(4)
C(6T1)-C(1T1)-C(2T1)	120.2(4)	C(2T2)-C(1T2)-C(7T2)	122.3(4)
C(6T1)-C(1T1)-C(7T1)	119.1(4)	C(3T2)-C(2T2)-C(1T2)	121.9(4)
C(2T1)-C(1T1)-C(7T1)	120.7(3)	C(3T2)-C(2T2)-H(2T2)	119.1
C(3T1)-C(2T1)-C(1T1)	120.7(3)	C(1T2)-C(2T2)-H(2T2)	119.1
C(3T1)-C(2T1)-H(2T1)	119.6	C(4T2)-C(3T2)-C(2T2)	119.5(4)
C(1T1)-C(2T1)-H(2T1)	119.6	C(4T2)-C(3T2)-H(3T2)	120.2
C(2T1)-C(3T1)-C(4T1)	119.8(4)	C(2T2)-C(3T2)-H(3T2)	120.2
C(2T1)-C(3T1)-H(3T1)	120.1	C(3T2)-C(4T2)-C(5T2)	119.7(4)
C(4T1)-C(3T1)-H(3T1)	120.1	C(3T2)-C(4T2)-H(4T2)	120.2
C(5T1)-C(4T1)-C(3T1)	118.3(4)	C(5T2)-C(4T2)-H(4T2)	120.2
C(5T1)-C(4T1)-H(4T1)	120.9	C(6T2)-C(5T2)-C(4T2)	120.0(4)
O3 Si1 O4	106.31(13)	C32 C34 C35	122.9(3)
O3 Si1 C65	110.80(16)	C36 C35 C40	117.6(3)
O4 Si1 C65	107.43(16)	C36 C35 C34	125.8(3)
O3 Si1 C66	111.46(17)	C40 C35 C34	116.5(3)
O4 Si1 C66	113.04(18)	O3 C36 C35	118.3(3)
C65 Si1 C66	07.75(19)	O3 C36 C37	121.1(3)
O1 Ti1 O2	1.83(10)	C35 C36 C37	120.5(3)
O1 Ti1 N2	91.49(11)	C36 C37 C38	118.8(4)
O2 Ti1 N2	126.36(12)	C36 C37 C41	122.1(3)
O1 Ti1 N3	124.26(11)	C38 C37 C41	119.0(4)
O2 Ti1 N3	91.55(11)	C39 C38 C37	122.8(4)
N2 Ti1 N3	128.48(11)	C40 C39 C38	116.2(4)
O1 Ti1 N1	158.06(12)	C40 C39 C57	121.9(3)
O2 Ti1 N1	86.45(11)	C38 C39 C57	121.9(4)
N2 Ti1 N1	72.30(12)	C39 C40 C35	12
N3 Ti1 N1	77.67(11)		
O1 Ti1 N4	86.51(11)		
O2 Ti1 N4	157.69(11)		
N2 Ti1 N4	75.94(12)		
N3 Ti1 N4	71.36(11)		
N1 Ti1 N4	103.13(11)		
C21 O1 Ti1	147.1(2)		
C33 O2 Ti1	143.8(2)		
C36 O3 Si1	134.9(2)		
C47 O4 Si1	125.7(2)		
C1 N1 C5	116.8(3)		
C1 N1 Ti1	125.0(3)		
C5 N1 Ti1	118.2(3)		
C10 N2 C6	116.1(3)		
C10 N2 Ti1	124.9(3)		

Table A5. Crystal data and structure refinement for [(MBMP)Ti(bpy)$_2$] (55)

Compound	**55**
Empirical formula	C55 H58 N4 O2 Ti
Formula weight	854.95
Temperature	90.0(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, P 21 21 2
Unit cell dimensions	a = 16.9420(6) A alpha = 90 deg. b = 17.5720(7) A beta = 90.0000(17) deg. c = 15.4750(9) A gamma = 90 deg.
Volume	4607.0(4) A^3
Z, Calculated density	4, 1.233 Mg/m^3
Absorption coefficient	0.232 mm^{-1}
F(000)	1816
Crystal size	0.35 x 0.15 x 0.02 mm
Theta range for data collection	1.32 to 22.50 deg.
Limiting indices	-18<=h<=18, -18<=k<=18, -16<=l<=16
Reflections collected / unique	12042 / 6041 [R(int) = 0.0772]
Completeness to theta = 22.50	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9954 and 0.9232
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6041 / 7 / 568
Goodness-of-fit on F^2	1.123
Final R indices (2σ)	R1 = 0.0621, wR2 = 0.1156
R indices (all data)	R1 = 0.0991, wR2 = 0.1256
Absolute structure parameter	-0.01(4)
Extinction coefficient	0.0017(3)
Largest diff. peak and hole	0.350 and -0.253 e.A^-3

Table A6. Bond lengths (Å) and angles (deg) for 55

Atoms	Bond Lengths	Atoms	Bond Lengths
Ti(1)-O(1)	1.882(3)	C(13)-C(14)	1.391(6)
Ti(1)-O(2)	1.908(3)	C(13)-C(23)	1.402(7)
Ti(1)-N(4)	2.070(4)	C(14)-C(15)	1.373(7)
Ti(1)-N(1)	2.165(4)	C(14)-H(14)	0.9500
Ti(1)-N(3)	2.174(4)	C(15)-C(17)	1.401(7)
Ti(1)-N(2)	2.216(4)	C(15)-C(16)	1.500(7)
N(1)-C(24)	1.359(6)	C(16)-H(16A)	0.9800
N(1)-C(28)	1.361(6)	C(16)-H(16B)	0.9800
N(2)-C(33)	1.351(6)	C(16)-H(16C)	0.9800
N(2)-C(29)	1.374(6)	C(17)-C(22)	1.390(7)
N(3)-C(34)	1.348(6)	C(17)-H(17)	0.9500
N(3)-C(38)	1.369(6)	C(18)-C(20)	1.528(8)
N(4)-C(43)	1.363(6)	C(18)-C(22)	1.532(7)
N(4)-C(39)	1.407(6)	C(18)-C(21)	1.536(7)
O(1)-C(1)	1.350(6)	C(18)-C(19)	1.545(7)
C(1)-C(11)	1.410(7)	C(19)-H(19A)	0.9800
C(1)-C(2)	1.422(7)	C(19)-H(19B)	0.9800
C(2)-C(7)	1.390(7)	C(19)-H(19C)	0.9800
C(2)-C(3)	1.535(7)	C(20)-H(20A)	0.9800
C(3)-C(5)	1.538(8)	C(20)-H(20B)	0.9800
C(3)-C(6)	1.538(7)	C(20)-H(20C)	0.9800
C(3)-C(4)	1.551(8)	C(21)-H(21A)	0.9800
C(4)-H(4A)	0.9800	C(21)-H(21B)	0.9800
C(4)-H(4B)	0.9800	C(21)-H(21C)	0.9800
C(4)-H(4C)	0.9800	C(22)-C(23)	1.429(7)
C(5)-H(5A)	0.9800	C(23)-O(2)	1.343(5)
C(5)-H(5B)	0.9800	C(24)-C(25)	1.373(7)
C(5)-H(5C)	0.9800	C(24)-H(24)	0.9500
C(6)-H(6A)	0.9800	C(25)-C(26)	1.389(7)
C(6)-H(6B)	0.9800	C(25)-H(25)	0.9500
C(6)-H(6C)	0.9800	C(26)-C(27)	1.377(7)
C(7)-C(8)	1.410(7)	C(26)-H(26)	0.9500
C(7)-H(7)	0.9500	C(27)-C(28)	1.407(7)
C(8)-C(10)	1.383(7)	C(27)-H(27)	0.9500
C(8)-C(9)	1.526(7)	C(28)-C(29)	1.454(7)
C(9)-H(9A)	0.9800	C(29)-C(30)	1.386(7)
C(9)-H(9B)	0.9800	C(30)-C(31)	1.380(7)
C(9)-H(9C)	0.9800	C(30)-H(30)	0.9500
C(10)-C(11)	1.394(7)	C(31)-C(32)	1.376(7)
C(10)-H(10)	0.9500	C(31)-H(31)	0.9500
C(11)-C(12)	1.490(7)	C(32)-C(33)	1.363(7)
C(12)-C(13)	1.526(7)	C(32)-H(32)	0.9500
C(12)-H(12A)	0.9900	C(33)-H(33)	0.9500
C(12)-H(12B)	0.9900	C(34)-C(35)	1.353(7)
C(34)-H(34)	0.9500	C(3B)-C(4B)	1.379(8)
C(35)-C(36)	1.399(7)	C(3B)-H(3B)	0.9500
C(35)-H(35)	0.9500	C(4B)-C(5B)	1.359(8)
C(36)-C(37)	1.360(7)	C(4B)-H(4B1)	0.9500
C(36)-H(36)	0.9500	C(5B)-C(6B)	1.372(8)
C(37)-C(38)	1.415(7)	C(5B)-H(5B1)	0.9500
C(37)-H(37)	0.9500	C(6B)-H(6B1)	0.9500

C(38)-C(39)	1.426(7)	C(1C)-C(2C)	1.372(8)
C(39)-C(40)	1.408(7)	C(1C)-C(3C)#1	1.384(9)
C(40)-C(41)	1.369(7)	C(1C)-H(1C)	0.9500
C(40)-H(40)	0.9500	C(2C)-C(3C)	1.397(8)
C(41)-C(42)	1.404(7)	C(2C)-H(2C)	0.9500
C(41)-H(41)	0.9500	C(3C)-C(1C)#1	1.384(9)
C(42)-C(43)	1.355(7)	C(3C)-H(3C)	0.9500
C(42)-H(42)	0.9500	C(1D)-C(2D)	1.326(9)
C(43)-H(43)	0.9500	C(1D)-C(1D)#2	1.343(14)
C(1B)-C(2B)	1.354(7)	C(1D)-H(1D)	0.9500
C(1B)-C(6B)	1.385(8)	C(2D)-C(3D)	1.350(10)
C(1B)-H(1B)	0.9500	C(2D)-H(2D)	0.9500
C(2B)-C(3B)	1.374(8)	C(3D)-C(3D)#2	1.313(19)
C(2B)-H(2B)	0.9500	C(3D)-H(3D)	0.9500

Atoms	**Angle**	**Atoms**	**Angle**
O(1)-Ti(1)-O(2)	97.27(14)	C(34)-N(3)-C(38)	117.6(5)
O(1)-Ti(1)-N(4)	92.63(16)	C(34)-N(3)-Ti(1)	126.1(4)
O(2)-Ti(1)-N(4)	106.90(14)	C(38)-N(3)-Ti(1)	115.3(3)
O(1)-Ti(1)-N(1)	99.64(15)	C(43)-N(4)-C(39)	116.9(4)
O(2)-Ti(1)-N(1)	90.18(15)	C(43)-N(4)-Ti(1)	124.6(3)
N(4)-Ti(1)-N(1)	157.57(16)	C(39)-N(4)-Ti(1)	118.2(3)
O(1)-Ti(1)-N(3)	165.66(16)	C(1)-O(1)-Ti(1)	147.6(3)
O(2)-Ti(1)-N(3)	93.77(15)	O(1)-C(1)-C(11)	118.5(5)
N(4)-Ti(1)-N(3)	75.36(17)	O(1)-C(1)-C(2)	120.9(4)
N(1)-Ti(1)-N(3)	89.41(16)	C(11)-C(1)-C(2)	120.5(5)
O(1)-Ti(1)-N(2)	95.78(14)	C(7)-C(2)-C(1)	118.1(5)
O(2)-Ti(1)-N(2)	159.86(15)	C(7)-C(2)-C(3)	120.3(5)
N(4)-Ti(1)-N(2)	87.71(16)	C(1)-C(2)-C(3)	121.6(5)
N(1)-Ti(1)-N(2)	72.52(16)	C(2)-C(3)-C(5)	109.5(4)
N(3)-Ti(1)-N(2)	76.24(14)	C(2)-C(3)-C(6)	113.4(5)
C(24)-N(1)-C(28)	118.7(4)	C(5)-C(3)-C(6)	107.5(5)
C(24)-N(1)-Ti(1)	122.2(3)	C(2)-C(3)-C(4)	109.1(5)
C(28)-N(1)-Ti(1)	118.8(3)	C(5)-C(3)-C(4)	110.1(5)
C(33)-N(2)-C(29)	116.5(4)	C(6)-C(3)-C(4)	107.2(5)
C(33)-N(2)-Ti(1)	124.9(3)	C(3)-C(4)-H( )	109.5
C(38)-N(3)-Ti(1)	115.3(3)	C(3)-C(4)-H(4B)	109.5

H(4A)-C(4)-H(4B)	109.5	C(17)-C(15)-C(16)	120.6(5)
C(3)-C(4)-H(4C)	109.5	C(15)-C(16)-H(16A)	109.5
H(4A)-C(4)-H(4C)	109.5	C(15)-C(16)-H(16B)	109.5
H(4B)-C(4)-H(4C)	109.5	H(16A)-C(16)-H(16B)	109.5
C(3)-C(5)-H(5A)	109.5	C(15)-C(16)-H(16C)	109.5
C(3)-C(5)-H(5B)	109.5	H(16A)-C(16)-H(16C)	109.5
H(5A)-C(5)-H(5B)	109.5	H(16B)-C(16)-H(16C)	109.5
C(3)-C(5)-H(5C)	109.5	C(22)-C(17)-C(15)	123.9(5)
H(5A)-C(5)-H(5C)	109.5	C(22)-C(17)-H(17)	118.1
H(5B)-C(5)-H(5C)	109.5	C(15)-C(17)-H(17)	118.1
C(3)-C(6)-H(6A)	109.5	C(20)-C(18)-C(22)	109.4(4)
C(3)-C(6)-H(6B)	109.5	C(20)-C(18)-C(21)	110.3(4)
H(6A)-C(6)-H(6B)	109.5	(22)-C(18)-C(21)	110.2(4)
C(3)-C(6)-H(6C)	109.5	C(20)-C(18)-C(19)	107.9(4)
H(6A)-C(6)-H(6C)	109.5	C(22)-C(18)-C(19)	112.2(4)
H(6B)-C(6)-H(6C)	109.5	C(21)-C(18)-C(19)	106.8(4)
		C(18)-C(19)-H(19A)	109.5

C(2)-C(7)-C(8)	122.3(5)	C(18)-C(19)-H(19B)	109.5
C(2)-C(7)-H(7)	118.8	H(19A)-C(19)-H(19B)	109.5
C(8)-C(7)-H(7)	118.8	C(18)-C(19)-H(19C)	109.5
C(10)-C(8)-C(7)	117.5(5)	H(19A)-C(19)-H(19C)	109.5
C(10)-C(8)-C(9)	122.2(5)	H(19B)-C(19)-H(19C)	109.5
C(7)-C(8)-C(9)	120.3(5)	C(18)-C(20)-H(20A)	109.5
C(8)-C(9)-H(9A)	109.5	C(18)-C(20)-H(20B)	109.5
C(8)-C(9)-H(9B)	109.5	H(20A)-C(20)-H(20B)	109.5
H(9A)-C(9)-H(9B)	109.5	C(18)-C(20)-H(20C)	109.5
C(8)-C(9)-H(9C)	109.5	H(20A)-C(20)-H(20C)	109.5
H(9A)-C(9)-H(9C)	109.5	H(20B)-C(20)-H(20C)	109.5
H(9B)-C(9)-H(9C)	109.5	C(18)-C(21)-H(21A)	109.5
C(8)-C(10)-C(11)	123.1(5)	C(18)-C(21)-H(21B)	109.5
C(8)-C(10)-H(10)	118.4	H(21A)-C(21)-H(21B)	109.5
C(11)-C(10)-H(10)	118.4	C(18)-C(21)-H(21C)	109.5
C(10)-C(11)-C(1)	118.1(5)	H(21A)-C(21)-H(21C)	109.5
C(10)-C(11)-C(12)	120.1(5)	H(21B)-C(21)-H(21C)	109.5
C(1)-C(11)-C(12)	121.8(5)	C(17)-C(22)-C(23)	117.0(4)
C(11)-C(12)-C(13)	117.1(4)	C(17)-C(22)-C(18)	121.1(4)
C(11)-C(12)-H(12A)	108.0	C(23)-C(22)-C(18)	121.8(4)
C(13)-C(12)-H(12A)	108.0	O(2)-C(23)-C(13)	119.0(5)
C(11)-C(12)-H(12B)	108.0	O(2)-C(23)-C(22)	121.6(5)
C(13)-C(12)-H(12B)	108.0	C(13)-C(23)-C(22)	119.3(4)
H(12A)-C(12)-H(12B)	107.3	N(1)-C(24)-C(25)	122.7(5)
C(14)-C(13)-C(23)	120.0(5)	N(1)-C(24)-H(24)	118.7
C(14)-C(13)-C(12)	118.4(5)	C(25)-C(24)-H(24)	118.7
C(23)-C(13)-C(12)	121.5(4)	C(24)-C(25)-C(26)	118.7(5)
C(15)-C(14)-C(13)	122.1(5)	C(24)-C(25)-H(25)	120.6
C(15)-C(14)-H(14)	118.9	C(26)-C(25)-H(25)	120.6
C(13)-C(14)-H(14)	118.9	C(27)-C(26)-C(25)	119.9(5)
C(14)-C(15)-C(17)	117.0(4)	C(27)-C(26)-H(26)	120.0
C(14)-C(15)-C(16)	122.3(5)	C(41)-C(40)-H(40)	119.7
(25)-C(26)-H(26)	120.0	C(39)-C(40)-H(40)	119.7
C(26)-C(27)-C(28)	1191(5)	C(40)-C(41)-C(42)	118.6(5)
C(26)-C(27)-H(27)	120.4	C(40)-C(41)-H(41)	120.7
C(28)-C(27)-H(27)	120.4	C(42)-C(41)-H(41)	120.7
N(1)-C(28)-C(27)	120.8(5)	C(43)-C(42)-C(41)	119.7(5)
N(1)-C(28)-C(29)	115.2(5)	C(43)-C(42)-H(42)	120.1
C(27)-C(28)-C(29)	123.8(5)	C(41)-C(42)-H(42)	120.1
N(2)-C(29)-C(30)	122.1(5)	C(42)-C(43)-N(4)	124.0(5)
N(2)-C(29)-C(28)	113.2(4)	C(42)-C(43)-H(43)	118.0
C(30)-C(29)-C(28)	124.6(5)	N(4)-C(43)-H(43)	118.0
C(31)-C(30)-C(29)	118.7(5)	C(23)-O(2)-Ti(1)	159.5(3)
C(31)-C(30)-H(30)	120.6	C(2B)-C(1B)-C(6B)	119.2(6)
C(29)-C(30)-H(30)	120.6	C(2B)-C(1B)-H(1B)	120.4
C(32)-C(31)-C(30)	119.9(5)	C(6B)-C(1B)-H(1B)	120.4
C(32)-C(31)-H(31)	120.1	C(1B)-C(2B)-C(3B)	121.9(6)
C(30)-C(31)-H(31)	120.1	C(1B)-C(2B)-H(2B)	119.0
C(33)-C(32)-C(31)	118.5(5)	C(3B)-C(2B)-H(2B)	119.0
C(33)-C(32)-H(32)	120.8	C(2B)-C(3B)-C(4B)	119.1(6)
C(31)-C(32)-H(32)	120.8	C(2B)-C(3B)-H(3B)	120.4
N(2)-C(33)-C(32)	124.2(5)	C(4B)-C(3B)-H(3B)	120.4
N(2)-C(33)-H(33)	117.9	C(5B)-C(4B)-C(3B)	118.8(6)
C(32)-C(33)-H(33)	117.9	C(5B)-C(4B)-H(4B1)	120.6
N(3)-C(34)-C(35)	124.3(5)	C(3B)-C(4B)-H(4B1)	120.6

N(3)-C(34)-H(34)	117.8	C(4B)-C(5B)-C(6B)	122.3(6)
C(35)-C(34)-H(34)	117.8	C(4B)-C(5B)-H(5B1)	118.9
C(34)-C(35)-C(36)	118.9(5)	C(6B)-C(5B)-H(5B1)	118.9
C(34)-C(35)-H(35)	120.6	C(5B)-C(6B)-C(1B)	118.7(6)
C(36)-C(35)-H(35)	120.6	C(5B)-C(6B)-H(6B1)	120.7
C(37)-C(36)-C(35)	118.7(5)	C(1B)-C(6B)-H(6B1)	120.7
C(37)-C(36)-H(36)	120.6	C(2C)-C(1C)-C(3C)#1	121.5(7)
C(35)-C(36)-H(36)	120.6	C(2C)-C(1C)-H(1C)	119.2
C(36)-C(37)-C(38)	120.2(5)	C(3C)#1-C(1C)-H(1C)	119.2
C(36)-C(37)-H(37)	119.9	C(1C)-C(2C)-C(3C)	119.9(7)
C(38)-C(37)-H(37)	119.9	C(1C)-C(2C)-H(2C)	120.0
N(3)-C(38)-C(37)	120.3(5)	C(3C)-C(2C)-H(2C)	120.0
N(3)-C(38)-C(39)	115.3(5)	C(1C)#1-C(3C)-C(2C)	118.5(7)
C(37)-C(38)-C(39)	124.4(5)	C(1C)#1-C(3C)-H(3C)	120.7
N(4)-C(39)-C(40)	120.1(5)	C(2C)-C(3C)-H(3C)	120.7
N(4)-C(39)-C(38)	114.4(4)	C(2D)-C(1D)-C(1D)#2	121.1(5)
C(40)-C(39)-C(38)	125.5(5)	C(2D)-C(1D)-H(1D)	119.5
C(41)-C(40)-C(39)	120.7(5)	C(3D)#2-C(3D)-C(2D)	121.1(5)
C(1D)#2-C(1D)-H(1D)	119.5	C(3D)#2-C(3D)-H(3D)	119.4
C(1D)-C(2D)-C(3D)	117.5(8)	C(2D)-C(3D)-H(3D)	119.4
C(1D)-C(2D)-H(2D)	121.2	C(3D)-C(2D)-H(2D)	121.2

Table A5. Crystal data and structure refinement for [(MBMP)Ti{κ^3-OC(C_6H_5)$_2$$C_{10}H_7N_2$}{OCH($C_6H_5$)$_2$}] (61)

Compound	**61**
Empirical formula	C65 H64 N2 O4 Ti
Formula weight	985.08
Temperature	90.0(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, P 21/c
Unit cell dimensions	a = 9.54100(10) A alpha = 90 deg. b = 26.3230(3) A beta = 95.9410(5) deg. c = 20.9570(3) A gamma = 90 deg.
Volume	5235.03(11) A^3
Z, Calculated density	4, 1.250 Mg/m^3
Absorption coefficient	0.215 mm^{-1}
F(000)	2088
Crystal size	0.22 x 0.20 x 0.15 mm
Theta range for data collection	1.55 to 25.00 deg.
Limiting indices	-11<=h<=11, -31<=k<=31, -24<=l<=24
Reflections collected / unique	17990 / 9226 [R(int) = 0.0594]
Completeness to theta = 22.50	100.0 %
Absorption correction	Multi-scan
Max. and min. transmission	0.9684 and 0.9542
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9226 /189 / 679
Goodness-of-fit on F^2	1.022
Final R indices (2σ)	R1 = 0.0508, wR2 = 0.1068
R indices (all data)	R1 = 0.0958, wR2 = 0.1224
Absolute structure parameter	-0.01(4)
Extinction coefficient	0.0017(3)
Largest diff. peak and hole	0.408 and -0.436 $e.A^{-3}$

Atoms	Bond Lengths	Atoms	Bond Lengths
Ti(1)-O(2)	1.8502(17)	C(21)-H(21)	0.9500
Ti(1)-O(1)	1.8651(17)	C(22)-C(23)	1.387(4)
Ti(1)-O(4)	1.8850(17)	C(22)-H(22)	0.9500
Ti(1)-O(3)	1.9075(17)	C(23)-H(23)	0.9500
Ti(1)-N(2)	2.185(2)	C(24)-C(34)	1.396(3)
Ti(1)-N(1)	2.277(2)	C(24)-C(25)	1.417(3)
N(1)-C(1)	1.347(3)	C(25)-C(30)	1.395(3)
N(1)-C(5)	1.357(3)	C(25)-C(26)	1.535(4)
N(2)-C(10)	1.341(3)	C(26)-C(27)	1.534(4)
N(2)-C(6)	1.350(3)	C(26)-C(28)	1.536(4)
O(1)-C(11)	1.417(3)	C(26)-C(29)	1.537(3)
O(2)-C(24)	1.362(3)	C(27)-H(27A)	0.9800
O(3)-C(46)	1.351(3)	C(27)-H(27B)	0.9800
O(4)-C(47)	1.406(5)	C(27)-H(27C)	0.9800
O(4)-C(47')	1.415(16)	C(28)-H(28A)	0.9800
C(1)-C(2)	1.380(4)	C(28)-H(28B)	0.9800
C(1)-H(1)	0.9500	C(28)-H(28C)	0.9800
C(2)-C(3)	1.370(4)	C(29)-H(29A)	0.9800
C(2)-H(2)	0.9500	C(29)-H(29B)	0.9800
C(3)-C(4)	1.379(4)	C(29)-H(29C)	0.9800
C(3)-H(3)	0.9500	C(30)-C(31)	1.392(4)
C(4)-C(5)	1.387(4)	C(30)-H(30)	0.9500
C(4)-H(4)	0.9500	C(31)-C(33)	1.383(4)
C(5)-C(6)	1.473(4)	C(31)-C(32)	1.513(3)
C(6)-C(7)	1.381(4)	C(32)-H(32A)	0.9800
C(7)-C(8)	1.385(4)	C(32)-H(32B)	0.9800
C(7)-H(7)	0.9500	C(32)-H(32C)	0.9800
C(8)-C(9)	1.379(4)	C(33)-C(34)	1.394(3)
C(8)-H(8)	0.9500	C(33)-H(33)	0.9500
C(9)-C(10)	1.384(3)	C(34)-C(35)	1.523(3)
C(9)-H(9)	0.9500	C(35)-C(36)	1.510(3)
C(10)-C(11)	1.528(3)	C(35)-H(35A)	0.9900
C(11)-C(12)	1.529(3)	C(35)-H(35B)	0.9900
C(11)-C(18)	1.540(4)	C(36)-C(37)	1.383(3)
C(12)-C(17)	1.388(3)	C(36)-C(46)	1.407(3)
C(12)-C(13)	1.388(4)	C(37)-C(38)	1.391(4)
C(13)-C(14)	1.385(4)	C(37)-H(37)	0.9500
C(13)-H(13)	0.9500	C(38)-C(40)	1.389(4)
C(14)-C(15)	1.387(4)	C(38)-C(39)	1.507(4)
C(14)-H(14)	0.9500	C(39)-H(39A)	0.9800
C(15)-C(16)	1.381(4)	C(39)-H(39B)	0.9800
C(15)-H(15)	0.9500	C(39)-H(39C)	0.9800
C(16)-C(17)	1.385(3)	C(40)-C(41)	1.400(4)
C(16)-H(16)	0.9500	C(40)-H(40)	0.9500
C(17)-H(17)	0.9500	C(41)-C(46)	1.420(3)
C(18)-C(23)	1.383(4)	C(41)-C(42)	1.541(4)
C(18)-C(19)	1.392(3)	C(42)-C(43)	1.531(4)
C(19)-C(20)	1.376(4)	C(42)-C(45)	1.532(4)
C(19)-H(19)	0.9500	C(42)-C(44)	1.532(4)
C(20)-C(21)	1.384(4)	C(43)-H(43A)	0.9800
C(20)-H(20)	0.9500	C(43)-H(43B)	0.9800
C(21)-C(22)	1.376(4)	C(43)-H(43C)	0.9800

C(49)-H(49)	0.9500	C(54)-C(55)	1.386(4)
C(50)-C(51)	1.370(6)	C(55)-C(56)	1.376(4)
C(50)-H(50)	0.9500	C(55)-H(55)	0.9500
C(51)-C(52)	1.387(7)	C(56)-C(57)	1.379(4)
C(51)-H(51)	0.9500	C(56)-H(56)	0.9500
C(52)-C(53)	1.397(7)	C(57)-C(58)	1.365(5)
C(52)-H(52)	0.9500	C(57)-H(57)	0.9500
C(53)-H(53)	0.9500	C(58)-C(59)	1.399(5)
C(47')-C(48')	1.51(3)	C(58)-H(58)	0.9500
C(47')-C(54)	1.52(5)	C(59)-H(59)	0.9500
C(47')-H(47')	1.0000	C(1B)-C(2B)	1.368(4)
C(48')-C(49')	1.373(1)	C(1B)-C(6B)	1.373(4)
C(48')-C(53')	1.401(1)	C(1B)-H(1B)	0.9500
C(49')-C(50')	1.402(1)	C(2B)-C(3B)	1.357(4)
C(49')-H(49')	0.9500	C(2B)-H(2B)	0.9500
C(50')-C(51')	1.361(1)	C(3B)-C(4B)	1.373(4)
C(50')-H(50')	0.9500	C(3B)-H(3B)	0.9500
C(51')-C(52')	1.398(1)	C(4B)-C(5B)	1.371(5)
C(51')-H(51')	0.9500	C(4B)-H(4B)	0.9500
C(52')-C(53')	1.401(1)	C(5B)-C(6B)	1.357(5)
C(52')-H(52')	0.9500	C(5B)-H(5B)	0.9500
C(53')-H(53')	0.9500	C(6B)-H(6B)	0.9500
C(54)-C(59)	1.383(4)		

Atoms	**Angles**	**Atoms**	**Angles**
O(2)-Ti(1)-O(1)	99.09(7)	C(47)-O(4)-C(47')	11.1(16)
O(2)-Ti(1)-O(4)	91.09(7)	C(47)-O(4)-Ti(1)	143.2(6)
O(1)-Ti(1)-O(4)	97.71(8)	C(47')-O(4)-Ti(1)	136(2)
O(2)-Ti(1)-O(3)	94.00(7)	N(1)-C(1)-C(2)	123.2(2)
O(1)-Ti(1)-O(3)	98.66(7)	N(1)-C(1)-H(1)	118.4
O(4)-Ti(1)-O(3)	161.86(8)	C(2)-C(1)-H(1)	118.4
O(2)-Ti(1)-N(2)	172.25(8)	C(3)-C(2)-C(1)	118.9(3)
O(1)-Ti(1)-N(2)	74.68(7)	C(3)-C(2)-H(2)	120.6
O(4)-Ti(1)-N(2)	85.26(8)	C(1)-C(2)-H(2)	120.6
O(3)-Ti(1)-N(2)	91.55(7)	C(2)-C(3)-C(4)	119.1(3)
O(2)-Ti(1)-N(1)	115.73(8)	C(2)-C(3)-H(3)	120.4
O(1)-Ti(1)-N(1)	145.16(8)	C(4)-C(3)-H(3)	120.4
O(4)-Ti(1)-N(1)	81.55(7)	C(3)-C(4)-C(5)	119.5(3)
O(3)-Ti(1)-N(1)	80.56(7)	C(3)-C(4)-H(4)	120.2
N(2)-Ti(1)-N(1)	70.54(8)	C(5)-C(4)-H(4)	120.2
C(1)-N(1)-C(5)	117.5(2)	N(1)-C(5)-C(4)	121.7(2)
C(1)-N(1)-Ti(1)	124.26(17)	N(1)-C(5)-C(6)	114.4(2)
C(5)-N(1)-Ti(1)	118.18(17)	C(4)-C(5)-C(6)	123.8(2)
C(10)-N(2)-C(6)	121.1(2)	N(2)-C(6)-C(7)	120.6(2)
C(10)-N(2)-Ti(1)	116.36(16)	N(2)-C(6)-C(5)	113.7(2)
C(6)-N(2)-Ti(1)	121.85(17)	C(7)-C(6)-C(5)	125.8(2)
C(11)-O(1)-Ti(1)	127.42(14)	C(6)-C(7)-C(8)	118.5(3)
C(24)-O(2)-Ti(1)	148.95(16)	C(6)-C(7)-H(7)	120.7
C(46)-O(3)-Ti(1)	151.84(16)	C(8)-C(7)-H(7)	120.7

C(9)-C(8)-H(8)	119.8	C(27)-C(26)-C(25)	110.8(2)
C(7)-C(8)-H(8)	119.8	C(27)-C(26)-C(28)	109.6(2)
C(8)-C(9)-C(10)	118.7(2)	C(25)-C(26)-C(28)	109.1(2)
C(8)-C(9)-H(9)	120.7	C(27)-C(26)-C(29)	107.3(2)
C(10)-C(9)-H(9)	120.7	C(25)-C(26)-C(29)	112.1(2)
N(2)-C(10)-C(9)	120.7(2)	C(28)-C(26)-C(29)	107.8(2)
N(2)-C(10)-C(11)	112.0(2)	C(26)-C(27)-H(27A)	109.5
C(9)-C(10)-C(11)	127.3(2)	C(26)-C(27)-H(27B)	109.5
O(1)-C(11)-C(10)	106.79(1)	H(27A)-C(27)-H(27B)	109.5
O(1)-C(11)-C(12)	108.35(1)	C(26)-C(27)-H(27C)	109.5
C(10)-C(11)-C(12)	109.6(2)	H(27A)-C(27)-H(27C)	109.5
O(1)-C(11)-C(18)	106.80(1)	H(27B)-C(27)-H(27C)	109.5
C(10)-C(11)-C(18)	111.6(2)	C(26)-C(28)-H(28A)	109.5
C(12)-C(11)-C(18)	113.3(2)	C(26)-C(28)-H(28B)	109.5
C(17)-C(12)-C(13)	119.1(2)	H(28A)-C(28)-H(28B)	109.5
C(17)-C(12)-C(11)	121.8(2)	C(26)-C(28)-H(28C)	109.5
C(13)-C(12)-C(11)	119.0(2)	H(28A)-C(28)-H(28C)	109.5
C(14)-C(13)-C(12)	120.6(2)	H(28B)-C(28)-H(28C)	109.5
C(14)-C(13)-H(13)	119.7	C(26)-C(29)-H(29A)	109.5
C(12)-C(13)-H(13)	119.7	C(26)-C(29)-H(29B)	109.5
C(13)-C(14)-C(15)	119.9(3)	H(29A)-C(29)-H(29B)	109.5
C(13)-C(14)-H(14)	120.1	C(26)-C(29)-H(29C)	109.5
C(15)-C(14)-H(14)	120.1	H(29A)-C(29)-H(29C)	109.5
C(16)-C(15)-C(14)	119.9(3)	H(29B)-C(29)-H(29C)	109.5
C(16)-C(15)-H(15)	120.1	C(31)-C(30)-C(25)	123.4(2)
C(14)-C(15)-H(15)	120.1	C(31)-C(30)-H(30)	118.3
C(15)-C(16)-C(17)	120.1(3)	C(25)-C(30)-H(30)	118.3
C(15)-C(16)-H(16)	119.9	C(33)-C(31)-C(30)	117.6(2)
C(17)-C(16)-H(16)	119.9	C(33)-C(31)-C(32)	121.8(2)
C(16)-C(17)-C(12)	120.4(3)	C(30)-C(31)-C(32)	120.6(2)
C(16)-C(17)-H(17)	119.8	C(31)-C(32)-H(32A)	109.5
C(12)-C(17)-H(17)	119.8	C(31)-C(32)-H(32B)	109.5
C(23)-C(18)-C(19)	118.5(2)	H(32A)-C(32)-H(32B)	109.5
C(23)-C(18)-C(11)	123.3(2)	C(31)-C(32)-H(32C)	109.5
C(19)-C(18)-C(11)	117.8(2)	H(32A)-C(32)-H(32C)	109.5
C(20)-C(19)-C(18)	120.7(3)	H(32B)-C(32)-H(32C)	109.5
C(20)-C(19)-H(19)	119.7	C(31)-C(33)-C(34)	122.1(3)
C(18)-C(19)-H(19)	119.7	C(31)-C(33)-H(33)	118.9
C(19)-C(20)-C(21)	120.3(3)	C(34)-C(33)-H(33)	118.9
C(19)-C(20)-H(20)	119.9	C(33)-C(34)-C(24)	118.8(2)
C(21)-C(20)-H(20)	119.9	C(33)-C(34)-C(35)	119.0(2)
C(22)-C(21)-C(20)	119.7(3)	C(24)-C(34)-C(35)	122.2(2)
C(22)-C(21)-H(21)	120.2	C(36)-C(35)-C(34)	115.8(2)
C(20)-C(21)-H(21)	120.2	C(36)-C(35)-H(35A)	108.3
C(21)-C(22)-C(23)	120.1(3)	C(34)-C(35)-H(35A)	108.3
C(21)-C(22)-H(22)	120.0	C(36)-C(35)-H(35B)	108.3
C(23)-C(22)-H(22)	120.0	C(34)-C(35)-H(35B)	108.3
C(18)-C(23)-C(22)	120.8(3)	H(35A)-C(35)-H(35B)	107.4
C(18)-C(23)-H(23)	119.6	C(37)-C(36)-C(46)	120.1(2)
C(22)-C(23)-H(23)	119.6	C(37)-C(36)-C(35)	118.9(2)
O(2)-C(24)-C(34)	119.7(2)	C(46)-C(36)-C(35)	121.0(2)
O(2)-C(24)-C(25)	119.2(2)	C(36)-C(37)-C(38)	122.4(2)
C(34)-C(24)-C(25)	121.1(2)	C(36)-C(37)-H(37)	118.8
C(30)-C(25)-C(24)	116.8(2)	C(38)-C(37)-H(37)	118.8
C(30)-C(25)-C(26)	121.5(2)	C(40)-C(38)-C(37)	116.9(2)
C(24)-C(25)-C(26)	121.7(2)	C(40)-C(38)-C(39)	121.1(2)

C(37)-C(38)-C(39)	122.0(2)	C(50)-C(51)-H(51)	119.7
C(38)-C(39)-H(39A)	109.5	C(52)-C(51)-H(51)	119.7
C(38)-C(39)-H(39B)	109.5	C(51)-C(52)-C(53)	119.3(4)
H(39A)-C(39)-H(39B)	109.5	C(51)-C(52)-H(52)	120.3
C(38)-C(39)-H(39C)	109.5	C(53)-C(52)-H(52)	120.3
H(39A)-C(39)-H(39C)	109.5	C(48)-C(53)-C(52)	120.2(4)
H(39B)-C(39)-H(39C)	109.5	C(48)-C(53)-H(53)	119.9
C(38)-C(40)-C(41)	123.5(2)	C(52)-C(53)-H(53)	119.9
C(38)-C(40)-H(40)	118.3	O(4)-C(47')-C(48')	111.7(19)
C(41)-C(40)-H(40)	118.3	O(4)-C(47')-C(54)	110(3)
C(40)-C(41)-C(46)	118.0(2)	C(48')-C(47')-C(54)	100(3)
C(40)-C(41)-C(42)	119.8(2)	O(4)-C(47')-H(47')	111.4
C(46)-C(41)-C(42)	122.1(2)	C(48')-C(47')-H(47')	111.4
C(43)-C(42)-C(45)	107.6(2)	C(54)-C(47')-H(47')	111.4
C(43)-C(42)-C(44)	106.5(2)	C(49')-C(48')-C(53')	120.4(15)
C(45)-C(42)-C(44)	110.9(2)	C(49')-C(48')-C(47')	119.7(17)
C(43)-C(42)-C(41)	112.6(2)	C(53')-C(48')-C(47')	119.7(16)
C(45)-C(42)-C(41)	108.9(2)	C(48')-C(49')-C(50')	121.3(15)
C(44)-C(42)-C(41)	110.5(2)	C(48')-C(49')-H(49')	119.3
C(42)-C(43)-H(43A)	109.5	C(50')-C(49')-H(49')	119.3
C(42)-C(43)-H(43B)	109.5	C(51')-C(50')-C(49')	118.4(15)
H(43A)-C(43)-H(43B)	109.5	C(51')-C(50')-H(50')	120.8
C(42)-C(43)-H(43C)	109.5	C(49')-C(50')-H(50')	120.8
H(43A)-C(43)-H(43C)	109.5	C(50')-C(51')-C(52')	120.9(15)
H(43B)-C(43)-H(43C)	109.5	C(50')-C(51')-H(51')	119.5
C(42)-C(44)-H(44A)	109.5	C(52')-C(51')-H(51')	119.5
C(42)-C(44)-H(44B)	109.5	C(51')-C(52')-C(53')	120.9(15)
H(44A)-C(44)-H(44B)	109.5	C(51')-C(52')-H(52')	119.5
C(42)-C(44)-H(44C)	109.5	C(53')-C(52')-H(52')	119.5
H(44A)-C(44)-H(44C)	109.5	C(52')-C(53')-C(48')	117.5(14)
H(44B)-C(44)-H(44C)	109.5	C(52')-C(53')-H(53')	121.3
C(42)-C(45)-H(45A)	109.5	C(48')-C(53')-H(53')	121.3
C(42)-C(45)-H(45B)	109.5	C(59)-C(54)-C(55)	118.5(3)
H(45A)-C(45)-H(45B)	109.5	C(59)-C(54)-C(47')	115.6(12)
C(42)-C(45)-H(45C)	109.5	C(55)-C(54)-C(47')	125.9(12)
H(45A)-C(45)-H(45C)	109.5	C(59)-C(54)-C(47)	122.8(4)
H(45B)-C(45)-H(45C)	109.5	C(55)-C(54)-C(47)	118.6(4)
O(3)-C(46)-C(36)	119.8(2)	C(47')-C(54)-C(47)	10.2(15)
O(3)-C(46)-C(41)	121.1(2)	C(56)-C(55)-C(54)	121.1(3)
C(36)-C(46)-C(41)	119.1(2)	C(56)-C(55)-H(55)	119.4
O(4)-C(47)-C(54)	109.8(7)	C(54)-C(55)-H(55)	119.4
O(4)-C(47)-C(48)	111.6(5)	C(55)-C(56)-C(57)	120.0(3)
C(54)-C(47)-C(48)	112.6(7)	C(55)-C(56)-H(56)	120.0
O(4)-C(47)-H(47)	107.5	C(57)-C(56)-H(56)	120.0
C(54)-C(47)-H(47)	107.5	C(58)-C(57)-C(56)	119.9(3)
C(48)-C(47)-H(47)	107.5	C(58)-C(57)-H(57)	120.1
C(49)-C(48)-C(53)	119.1(4)	C(56)-C(57)-H(57)	120.1
C(49)-C(48)-C(47)	121.3(4)	C(57)-C(58)-C(59)	120.3(3)
C(53)-C(48)-C(47)	119.6(4)	C(57)-C(58)-H(58)	119.9
C(48)-C(49)-C(50)	121.0(4)	C(59)-C(58)-H(58)	119.9
C(48)-C(49)-H(49)	119.5	C(54)-C(59)-C(58)	120.2(3)
C(50)-C(49)-H(49)	119.5	C(54)-C(59)-H(59)	119.9
C(51)-C(50)-C(49)	119.7(4)	C(58)-C(59)-H(59)	119.9
C(51)-C(50)-H(50)	120.1	C(2B)-C(1B)-C(6B)	120.2(3)
C(49)-C(50)-H(50)	120.1	C(2B)-C(1B)-H(1B)	119.9
C(50)-C(51)-C(52)	120.7(4)	C(6B)-C(1B)-H(1B)	119.9

C(3B)-C(2B)-C(1B)	120.0(3)	C(3B)-C(4B)-H(4B)	119.8
C(3B)-C(2B)-H(2B)	120.0	C(6B)-C(5B)-C(4B)	119.6(3)
C(1B)-C(2B)-H(2B)	120.0	C(6B)-C(5B)-H(5B)	120.2
C(2B)-C(3B)-C(4B)	119.8(3)	C(4B)-C(5B)-H(5B)	120.2
C(2B)-C(3B)-H(3B)	120.1	C(5B)-C(6B)-C(1B)	120.0(3)
C(4B)-C(3B)-H(3B)	120.1	C(5B)-C(6B)-H(6B)	120.0
C(5B)-C(4B)-C(3B)	120.4(3)	C(1B)-C(6B)-H(6B)	120.0
C(5B)-C(4B)-H(4B)	119.8		

Table A9. Crystal data and structure refinement for [$(MBMP)_2Ti(bpy)$] (64)

Compound	**64**
Empirical formula	C34 H40 N O2 Ti 0.50
Formula weight	518.62
Temperature	90.0(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P 2/n
Unit cell dimensions	a = 14.2780(2) A alpha = 90 deg. b = 9.51900(10) A beta = 90.9800(5) deg. c = 21.1200(3) A gamma = 90 deg.
Volume	2870.05(6) A^3
Z, Calculated density	4, 1.200 Mg/m^3
Absorption coefficient	0.199 mm^{-1}
F(000)	1112
Crystal size	0.32 x 0.08 x 0.03 mm
Theta range for data collection	1.71 to 27.46 deg.
Limiting indices	-18<=h<=18, -12<=k<=12, -27<=l<=27
Reflections collected / unique	12692 / 6577 [R(int) = 0.0506]
Completeness to theta = 22.50	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9940 and 0.9389
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6577 /0 / 347
Goodness-of-fit on F^2	1.014
Final R indices (2σ)	R1 = 0.0492, wR2 = 0.11109
R indices (all data)	R1 = 0.0848, wR2 = 0.1245
Absolute structure parameter	-0.01(4)
Extinction coefficient	0.0017(3)
Largest diff. peak and hole	0.486 and -0.438 $e.A^{-3}$

Table A10. Bond lengths (Å) and angles (deg) for 64

Atoms	Bond Lengths	Atoms	Bond Lengths
Ti(1)-O(2)	1.8801(12)	C(15)-C(16)	1.516(3)
Ti(1)-O(2)#1	1.8802(12)	C(16)-H(16A)	0.9800
Ti(1)-O(1)#1	1.8870(12)	C(16)-H(16B)	0.9800
Ti(1)-O(1)	1.8871(12)	C(16)-H(16C)	0.9800
Ti(1)-N(1)	2.2366(16)	C(17)-C(18)	1.397(3)
Ti(1)-N(1)#1	2.2367(16)	C(17)-H(17)	0.9500
N(1)-C(24)	1.339(2)	C(18)-C(23)	1.422(3)
N(1)-C(28)	1.354(2)	C(18)-C(19)	1.539(3)
O(1)-C(1)	1.357(2)	C(19)-C(21)	1.532(3)
O(2)-C(23)	1.356(2)	C(19)-C(22)	1.538(3)
C(1)-C(11)	1.412(3)	C(19)-C(20)	1.539(3)
C(1)-C(2)	1.420(3)	C(20)-H(20A)	0.9800
C(2)-C(7)	1.397(3)	C(20)-H(20B)	0.9800
C(2)-C(3)	1.541(3)	C(20)-H(20C)	0.9800
C(3)-C(6)	1.533(3)	C(21)-H(21A)	0.9800
C(3)-C(5)	1.533(3)	C(21)-H(21B)	0.9800
C(3)-C(4)	1.536(3)	C(21)-H(21C)	0.9800
C(4)-H(4A)	0.9800	C(22)-H(22A)	0.9800
C(4)-H(4B)	0.9800	C(22)-H(22B)	0.9800
C(4)-H(4C)	0.9800	C(22)-H(22C)	0.9800
C(5)-H(5A)	0.9800	C(24)-C(25)	1.382(3)
C(5)-H(5B)	0.9800	C(24)-H(24)	0.9500
C(5)-H(5C)	0.9800	C(25)-C(26)	1.381(3)
C(6)-H(6A)	0.9800	C(25)-H(25)	0.9500
C(6)-H(6B)	0.9800	C(26)-C(27)	1.384(3)
C(6)-H(6C)	0.9800	C(26)-H(26)	0.9500
C(7)-C(8)	1.389(3)	C(27)-C(28)	1.385(3)
C(7)-H(7)	0.9500	C(27)-H(27)	0.9500
C(8)-C(10)	1.385(3)	C(28)-C(28)#1	1.480(4)
C(8)-C(9)	1.510(3)	C(1B1)-C(2B1)	1.362(4)
C(9)-H(9A)	0.9800	C(1B1)-C(1B1)#2	1.383(7)
C(9)-H(9B)	0.9800	C(1B1)-H(1B1)	0.9500
C(9)-H(9C)	0.9800	C(2B1)-C(3B1)	1.373(6)
C(10)-C(11)	1.385(3)	C(2B1)-H(2B1)	0.9500
C(10)-H(10)	0.9500	C(3B1)-C(3B1)#2	1.370(12)
C(11)-C(12)	1.510(3)	C(3B1)-H(3B1)	0.9500
C(12)-C(13)	1.516(2)	C(1B2)-C(3B2)#3	1.371(3)
C(12)-H(12A)	0.9900	C(1B2)-C(2B2)	1.378(3)
C(12)-H(12B)	0.9900	C(1B2)-H(1B2)	0.9500
C(13)-C(14)	1.389(3)	C(2B2)-C(3B2)	1.381(3)
C(13)-C(23)	1.409(3)	C(2B2)-H(2B2)	0.9500
C(14)-C(15)	1.391(3)	C(3B2)-C(1B2)#3	1.371(3)
C(14)-H(14)	0.9500	C(3B2)-H(3B2)	0.9500
C(15)-C(17)	1.390(3)		

Atoms	Angle	Atoms	Angle
(2)-Ti(1)-O(2)#1	103.74(8)	O(2)#1-Ti(1)-O(1)#1	95.95(5)
O(2)-Ti(1)-O(1)#1	90.20(5)	O(2)-Ti(1)-O(1)	95.95(5)
O(2)#1-Ti(1)-O(1)#1	95.95(5)	H(9A)-C(9)-H(9B)	109.5
O(2)-Ti(1)-O(1)	95.95(5)	C(8)-C(9)-H(9C)	109.5
O(2)#1-Ti(1)-O(1)	90.20(5)	H(9A)-C(9)-H(9C)	109.5
O(1)#1-Ti(1)-O(1)	170.04(8)	H(9B)-C(9)-H(9C)	109.5
O(2)-Ti(1)-N(1)	93.27(5)	C(8)-C(10)-C(11)	121.61(19)

O(2)#1-Ti(1)-N(1)	161.02(6)	C(8)-C(10)-H(10)	119.2
O(1)#1-Ti(1)-N(1)	92.29(5)	C(11)-C(10)-H(10)	119.2
O(1)-Ti(1)-N(1)	79.58(5)	C(10)-C(11)-C(1)	119.82(18)
O(2)-Ti(1)-N(1)#1	161.03(6)	C(10)-C(11)-C(12)	119.71(17)
O(2)#1-Ti(1)-N(1)#1	93.26(5)	C(1)-C(11)-C(12)	120.45(16)
O(1)#1-Ti(1)-N(1)#1	79.58(5)	C(11)-C(12)-C(13)	115.98(15)
O(1)-Ti(1)-N(1)#1	92.29(5)	C(11)-C(12)-H(12A)	108.3
N(1)-Ti(1)-N(1)#1	71.43(8)	C(13)-C(12)-H(12A)	108.3
C(24)-N(1)-C(28)	118.39(16)	C(11)-C(12)-H(12B)	108.3
C(24)-N(1)-Ti(1)	121.96(12)	C(13)-C(12)-H(12B)	108.3
C(28)-N(1)-Ti(1)	119.57(12)	H(12A)-C(12)-H(12B)	107.4
C(1)-O(1)-Ti(1)	151.50(12)	C(14)-C(13)-C(23)	119.09(17)
C(23)-O(2)-Ti(1)	141.04(11)	C(14)-C(13)-C(12)	119.81(16)
O(1)-C(1)-C(11)	117.61(16)	C(23)-C(13)-C(12)	120.86(16)
O(1)-C(1)-C(2)	122.48(17)	C(13)-C(14)-C(15)	121.73(18)
C(11)-C(1)-C(2)	119.90(17)	C(13)-C(14)-H(14)	119.1
C(7)-C(2)-C(1)	116.44(18)	C(15)-C(14)-H(14)	119.1
C(7)-C(2)-C(3)	120.72(17)	C(17)-C(15)-C(14)	117.51(17)
C(1)-C(2)-C(3)	122.84(17)	C(17)-C(15)-C(16)	121.58(18)
C(6)-C(3)-C(5)	107.07(17)	C(14)-C(15)-C(16)	120.87(18)
C(6)-C(3)-C(4)	107.00(17)	C(15)-C(16)-H(16A)	109.5
C(5)-C(3)-C(4)	110.81(16)	C(15)-C(16)-H(16B)	109.5
C(6)-C(3)-C(2)	112.14(16)	H(16A)-C(16)-H(16B)	109.5
C(5)-C(3)-C(2)	109.88(16)	C(15)-C(16)-H(16C)	109.5
C(4)-C(3)-C(2)	109.89(16)	H(16A)-C(16)-H(16C)	109.5
C(3)-C(4)-H(4A)	109.5	H(16B)-C(16)-H(16C)	109.5
C(3)-C(4)-H(4B)	109.5	C(15)-C(17)-C(18)	123.68(18)
H(4A)-C(4)-H(4B)	109.5	C(15)-C(17)-H(17)	118.2
C(3)-C(4)-H(4C)	109.5	C(18)-C(17)-H(17)	118.2
H(4A)-C(4)-H(4C)	109.5	C(17)-C(18)-C(23)	116.50(17)
H(4B)-C(4)-H(4C)	109.5	C(17)-C(18)-C(19)	121.79(17)
C(3)-C(5)-H(5A)	109.5	C(23)-C(18)-C(19)	121.29(16)
C(3)-C(5)-H(5B)	109.5	C(21)-C(19)-C(22)	107.19(16)
H(5A)-C(5)-H(5B)	109.5	C(21)-C(19)-C(20)	107.05(16)
C(3)-C(5)-H(5C)	109.5	C(22)-C(19)-C(20)	108.78(16)
H(5A)-C(5)-H(5C)	109.5	C(21)-C(19)-C(18)	111.70(16)
H(5B)-C(5)-H(5C)	109.5	C(22)-C(19)-C(18)	113.51(16)
C(3)-C(6)-H(6A)	109.5	C(20)-C(19)-C(18)	108.39(16)
C(3)-C(6)-H(6B)	109.5	C(19)-C(20)-H(20A)	109.5
H(6A)-C(6)-H(6B)	109.5	C(19)-C(20)-H(20B)	109.5
C(3)-C(6)-H(6C)	109.5	H(20A)-C(20)-H(20B)	109.5
H(6A)-C(6)-H(6C)	109.5	C(19)-C(20)-H(20C)	109.5
H(6B)-C(6)-H(6C)	109.5	H(20A)-C(20)-H(20C)	109.5
C(8)-C(7)-C(2)	124.17(19)	H(20B)-C(20)-H(20C)	109.5
C(8)-C(7)-H(7)	117.9	C(19)-C(21)-H(21A)	109.5
C(2)-C(7)-H(7)	117.9	C(19)-C(21)-H(21B)	109.5
C(10)-C(8)-C(7)	117.42(18)	H(21A)-C(21)-H(21B)	109.5
C(10)-C(8)-C(9)	120.4(2)	C(19)-C(21)-H(21C)	109.5
C(7)-C(8)-C(9)	122.12(19)	H(21A)-C(21)-H(21C)	109.5
C(8)-C(9)-H(9A)	109.5	H(21B)-C(21)-H(21C)	109.5
C(8)-C(9)-H(9B)	109.5	C(19)-C(22)-H(22A)	109.5
C(19)-C(22)-H(22B)	109.5	N(1)-C(28)-C(28)#1	114.70(10)
H(22A)-C(22)-H(22B)	109.5	C(27)-C(28)-C(28)#1	123.62(11)
C(19)-C(22)-H(22C)	109.5	C(2B1)-C(1B1)-C(1B1)#2	120.3(3)
H(22A)-C(22)-H(22C)	109.5	C(2B1)-C(1B1)-H(1B1)	119.9

H(22B)-C(22)-H(22C)	109.5	C(1B1)#2-C(1B1)-H(1B1)	119.9
O(2)-C(23)-C(13)	119.81(16)	C(1B1)-C(2B1)-C(3B1)	119.4(4)
O(2)-C(23)-C(18)	119.87(16)	C(1B1)-C(2B1)-H(2B1)	120.3
C(13)-C(23)-C(18)	120.23(17)	C(3B1)-C(2B1)-H(2B1)	120.3
N(1)-C(24)-C(25)	122.62(18)	C(3B1)#2-C(3B1)-C(2B1)	120.3(3)
N(1)-C(24)-H(24)	118.7	C(3B1)#2-C(3B1)-H(3B1)	119.9
C(25)-C(24)-H(24)	118.7	C(2B1)-C(3B1)-H(3B1)	119.9
C(26)-C(25)-C(24)	118.97(19)	C(3B2)#3-C(1B2)-C(2B2)	119.7(2)
C(26)-C(25)-H(25)	120.5	C(3B2)#3-C(1B2)-H(1B2)	120.2
C(24)-C(25)-H(25)	120.5	C(2B2)-C(1B2)-H(1B2)	120.2
C(25)-C(26)-C(27)	118.87(18)	C(1B2)-C(2B2)-C(3B2)	120.4(2)
C(25)-C(26)-H(26)	120.6	C(1B2)-C(2B2)-H(2B2)	119.8
C(27)-C(26)-H(26)	120.6	C(3B2)-C(2B2)-H(2B2)	119.8
C(26)-C(27)-C(28)	119.30(18)	C(1B2)#3-C(3B2)-C(2B2)	119.9(2)
C(26)-C(27)-H(27)	120.4	C(1B2)#3-C(3B2)-H(3B2)	120.0
C(28)-C(27)-H(27)	120.4	C(2B2)-C(3B2)-H(3B2)	120.0
N(1)-C(28)-C(27)	121.68(17)		

References

1. McMurry, J. *Acc. Chem. Res*. **1983,** *16*, 405.
2. McMurry, J. *J. Org. Chem*. **1976,** *41*, 3929.
3. Balu, N;. Nayak, S.K.; Banerji, A. *J. Am. Chem. Soc*. **1996**, *118*, 5932-5937.
4. Furnstner, A.; Seidel, G., Gabor; B., Kopiske, C.; Kruger,C.; and R. Mynott. *Tetrahedron*. **1995**, *51*, 8875.
5. Furstner, A; and Seidel, G. *Synthesis*. **1995**, 63.
6. McMurry, J.E; Kee, K.L. *J. Org. Chem.* **1977**, 42, 2655.
7. Hashimoto, Y.; Mizuno, U.; Matsuoka, H.; Miyahara T., Takakura; M., Yoshimoto; Oshima D.; Matsubara, S. *J. Am Chem. Soc*. **2001**, *123*. 1503-1504.
8. Wang, J.; Xing, Z.; Zhang; M.; Hu, Y. *J. Chem. Res. Synop*. **1988**, 182-183.
9. Zhou, L.; Shi, D, Gao; Y., Shen; W., Dai, G.; Chen, W. *Tetrahedron Letters* **1997**, *15*, 2729-2732.
10. Periasomy, J. *Tetrahedron Letters*. **2001**, *42*. 7123-7125.
11. Eisch, J.; Gitua, J.; Otieno P.; and Shi, X. *J. Organomet. Chem*. **2001**, *624*. 229-238.
12. Knecht, E; Hibbert, E. *Chem. Ber.*, **1903**, *36*, 166.
13. Knecht, E; Hibbert, E. *Chem. Ber.*, **1907**, *40*, 3819.
14. Fowles, G.; Lester, T; Walton, R. *Inorg. Chim. Acta* **1969**, 1081-1085.
15. Eisch, J.; Shi, X.; Owuor, F. *Organometallics*. **1998**, *17*. 5219
16. Sanner, R.; Duggan, D.; McKenzie, T.; Marsh, R.; Bercaw, J. *J. Am. Chem. Soc*. **1975**, *94*, C4.
17. Lauher, J.; Hoffman C., *J. Am. Chem. Soc*. **1976**, *98*, 1729.
18. Anderson, J.; Gregory, T; McAndrews, C.; and Kool, L. *Organometallics*. **1990,** *9*, 1702-1703.
19. Calderazzo, F.; Salzmann J.; Mosimann, P. *Inorganic Chim. Acta*. **1967**, *1*, 65.
20. Hitchcock, P; Kerton, F.M.; Lawless, G.A. *J. Am. Chem. Soc*. **1998** *39*, 10265-10265.
21. Hagadorn, J.; Arnold, J. *Organometallics*. **1998**, *17*, 1355-1368.
22. Hagadorn, J.; Arnold, J. *J. Am. Chem. Soc*. **1996**, *118*, 893-894.
23. Woo, K; Hays, J.; Jacobosn, R.; Day, C. *Organometallics*. **1991**, *10*. 2102-2104.
24. Wang, X.; Gray S.; Chen, J.; Woo K. *Inorg. Chem*. **1998**, *37*. 5-9
25. Herzog, S.; Taube, R.; *Z. Anorg. Allg. Chem* **1960**, *306*. 159.
26. Flamini, A.; Giuliani M. *Inorg. Chim. Acta*. **1986**, *112*. L7-L9
27. Flamini, A.; Giuliani, A.; Poli, N. *Tetrahedron Lett.* **1987** *19*, 2169-2170.
28. Nikiforov, G; Roesky, H,; Noltemeyer, M; Schmidt, H. *Polyhedron* **2004,** *23,* 561-566.
29. Ozerov, O.V.; Patrick, B.P.; Ladipo, F.T. *J. Am. Chem. Soc*. **2000**, *122*, 6423-6431
30. Ozerov, O.V.; Parkin, S.; Brock, C.P.; Ladipo, F.T. *Organometallics*. **2000**, *19,* 4187-4190.
31. Ozerov, O.V.; Brock, C.P.; Carr, S.D; Ladipo, F.T. *Organometallics*. **2000**, *19* 5019.
31. Mokuolu, Q.F.; Duckmonton, P.A.; Blake, A.J.; Wilson C.; Love, J.B. *Organometallics* **2003**. 4381-4389
32. Love, J.B.; Clark, H.C.; Cloke, F.G.; Green, J.C.; Hitchock, P.B.; *J. Am. Chem. Soc*. **1999** 121, 6843
33. Mokuolu, Q.F.; Duckmonton, P.A.; Blake, A.J.; Wilson C.; Love, J.B. *J. Chem. Soc. Dalton Trans.* **2001** 2551
34. Rosa, P.; Mezailles, N.; Ricard, L.; Mathey, F.; Flock, P. *Angew. Chem. Int. Ed.* **2000**, *39*. 1823-1826.

35. Wolczanski, P. T. *Polyhedron* **1995**, *14*, 3335.
36. Covert, K. J.; Mayol, A.-R.; Wolczanski, P. T. *Inorg. Chim. Acta* **1997**, *263*, 263.
37. Hagadorn, J. R.; Arnold, J. *Angew. Chem., Int. Ed.* **1998**, *37*, 1729.
39. Hagadorn, J. R.; Arnold, J. *J. Chem. Soc., Dalton Trans*. **1997**, 3087.
40. Steinhuebel, D. P.; Lippard, S. J. *J. Am. Chem. Soc.* **1999**, *121*, 11762.
41. Woo, L. K.; Hays, J. A.; Young, V. G.; Day, C. L.; Caron, C.; D'Souza, F.; Kadish, K. M. *Inorg. Chem*. **1993**, *32*, 4186.
42. Waratuke, S. A.; Johnson, E. S.; Thorn, M. G.; Fanwick, P. E.;
43. Rothwell, A. P.; Rothwell, I. P. *J. Am. Chem. Soc.* **1999**, *121*, 9111.
44. Thorn, M. G.; Hill, J. E.; Waratuke, S. A.; Johnson, E. S.; Fanwick, P. E.; Rothwell, I. P. *J. Am. Chem. Soc.* **1997**, *119*, 8630.
45. Johnson, E. S.; Balaich, G. J.; Rothwell, I. P. *J. Am. Chem. Soc.* **1997**, *119*, 7685.
46. Hill, J. E.; Balaich, G. J.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1993**, *12*, 2911.
47. Balaich, G. J.; Rothwell, I. P. *J. Am. Chem. Soc.* **1993**, *115*, 1581.
48. Hill, J. E.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1992**, *11*, 1771.
49. Hill, J. E.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1990**, *9*, 2211.
50. Rothwell, I. P. *Acc. Chem. Res.* **1988**, *21*, 153.
51. Durfee, L.D.; Fanwick, P.E.; and Rothwell, I.P. *J. Am. Chem. Soc*. **1987**, *109*, 4720-4722.
52. Chisolm, M.H.; Huffman, J.D.; Rothwell, I.P.; Bradley, P.G.; Kress, N; Woodruff, W.H. *J. Am. Chem. Soc.*, **1981**, *103*, 4945.
53. Orrell, K; Osbourne, A; Sik, U.; Dasiva, M.; *Polyhedron*, *14*. **2000** 2793-2802
54. Rikkou, M; Manos, M; Tolis, E; Sigalas, M; Kabaros, T; Keramidas, A. *Inorg. Chem.* **2003**, *42* 4640-4649.
55. Connor, J.A.; James, E.J.; Overton, C.; Walshe, M.A.; Head, R.A. *J. Chem. Soc. Dalt. Trans*. **1986**, 513.
56. Baranoff, E.; Collin J.P.; Furusho, J.; Furusho, Y.; Laemmel A.; Sauvage, J. *Inorg. Chem.*, **2002**, *41*, 1215-1222.
57. Riesgo, E.; Hu, Y.; and Thummel, R.P. *Inorg. Chem.*, **2002**, *40*, 2541-2546.
58. Kingston, J.V.; Sarveswaran, V; Parkin, S.; Ladipo, F.T. *Organometallics*, **2003**, *22*, 136-144.
59. Fan, M.; Zhang, H.; Lattman, M. *Organometallics*, **1996**, *15*, 5216-5219.
60. O'Neill, D.J.; Helquist, P. *Org. Lett.* **1999**, *10*, 1659-1662.
61. Lee, W.; Kwong, H.; Chan, H.; Choig, W.; Nu, L. *Tetrahedron: Assembly* **2001**, *12,* 1007-1013.
62. Kwong, H.; Lee, W. *Tetrahedron: Assembly* **1999**, *10*, 3791-3801.
63. Floriani C.; Corazzo F.; Lesueur, W.; Chiesi-Villa, A.; Guastini, C. *Agnew. Chem.* **1989,** *101,* 93.
64. Okuda, J.; Fokken, S.; Kang, H; Massa W.; *Chem. Ber.* **1995**, *128* 221-227.
65. Fukuda, H.; Oda, M.; Endo, T; *J. Polym. Sci. Part A. Polym. Chem.* **1999**, *37* 699
66. Foley, S.R.; Zhou, Y; Yap, G; Richeson, D.S. *Inorg. Chem.* **2000,** *39,* 924-929
67. Foley, S.R.; Yap, G; Richeson, D.S. *Organometallics* **1999,** *18,* 4700-4705
68. Wong, W; Zhang, L; Wong, W; Xue, F; Mak, T. *J. Chem. Soc*., *Dalton Trans*.,

1999, 615–622
70. Spirkova, M.; Kubin, M.; Spacek, P.; Krakovsky, I.; Dusek, K. **1994** *J. Appl. Polym. Sci. 52*. 895-904
71. Muller, A.; Das, S.K.; Fedin, Vladimir P.; Krickemeyer, E; E; Beugholt, C.; Bogge, H.; Schmidtmann, M.; Hauptfleisch,B. *Z. Anorg. Allg. Chem.* **1999**, 625(7), 1187-1192
72. Evans, D.F. *J. Chem. Soc.* **1995**, 2003.
73. Cotton, F.A.; Duraj, A.A.; and Roth W. *J. Am. Chem. Soc.* **1984**, *106*, 3527-3531.

Vita

Author's Name Marc S. Maynor

Bithplace Detroit, Michigan

Birth Date May 7, 1978

Education

Bachelor of Science in Chemistry

Claflin University

May 2000

Research Experience

University of Kentucky

Lexington, Ky

8/00-8/03

Lymon T. Johnson Fellow/Graduate Research Assistant

Presentations

"Synthesis, Characterization, and Reactivity of $[(DMSC)Ti(bpy)_2]$ and $[(DMSC)Ti(phen)_2]$"

National Meeting of the American Chemical Society, Boston, Ma, August 2002

Society Memberships

American Chemical Society

National Organization of Black Chemist and Engineers